



## Review

## Recent progress in the chemistry of anionic groups 6–8 carbonyl chalcogenide clusters

Minghuey Shieh\*, Chia-Yeh Miu, Yen-Yi Chu, Chien-Nan Lin

Department of Chemistry, National Taiwan Normal University, Taipei 116, Taiwan, ROC

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\* Corresponding author. Tel.: +886 2 77346118; fax: +886 2 29309081.  
E-mail address: [mshieh@ntnu.edu.tw](mailto:mshieh@ntnu.edu.tw) (M. Shieh).

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## ABSTRACT

Main-group element-bridged transition metal carbonyl complexes represent an important field in contemporary chemistry. This review will focus on the recent development of groups 6–8 carbonyl chalcogenide clusters, in particular on the anionic clusters which have been proven to exhibit versatile reactivity. This paper presents a review and discussion, from our group and others, of the rational synthetic methodologies, structural features, cluster-growth and transformations, and novel reactivities of these anionic clusters, as well as their special electrochemical, magnetic, and semiconducting properties. The description of the clusters in this review is arranged group-by-group based on the formation of both metal–chalcogen and metal–metal bonds. The literature survey is current through January 2011, and the review covers the chemistry of anionic groups 6–8 carbonyl chalcogenide clusters in this area of research and should significantly contribute to future research.

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## 1. Introduction

Although metal carbonyl complexes have been known for more than 100 years, it was not until the 1950s that German chemist Walter Hieber systematically investigated main-group-incorporated transition metal carbonyl complexes [1]. Hieber reported a synthetic methodology that employed iron carbonyl in basic methanol solutions with main-group salts to generate a series of interesting mixed main-group iron carbonyl complexes [1]. This so-called “Hieber’s synthesis” was applied to the iron carbonyl system; however, the resultant products were only characterized by conventional spectroscopic methods and elemental analysis [1]. After years of research in this area, the chemistry of main-group transition metal carbonyl complexes has flourished and some representative reviews have been published [2–7]. However, most studies in this area were aimed at neutral complexes, which are easier to isolate by column chromatography, but are usually more difficult to chemically activate. However, anionic main-group transition metal complexes have attracted special attention because of their synergistic capability to act as both electrophiles and nucleophiles [2a,3a,5e,5f,6,7c–e].

The introduction of main-group elements into the transitional metal carbonyl complexes can help stabilize reactive metal fragments, which results in versatile structures, and provides novel reactivities [2–7]. Among these complexes, chalcogenide derivatives of metal carbonyls characteristically exist as clusters, and this field has matured over the past few decades [4–7]. Although the structures of these clusters, as well as their redox and substituted derivatives, have been well documented and surveyed in the past, the chemistry of the anionic metal carbonyl clusters remained relatively scarce [4,6,8]. These anionic metal clusters are known to be very reactive, and most of them can be isolated as solids after metathesis with appropriate non-redox cationic salts. Some anionic metal carbonyl clusters are noted to have enhanced electrical or magnetic properties by the introduction of redox-active counteractions, which has been less explored in chalcogenide-incorporated metal carbonyl anions [9]. Recently, these anionic metal clusters have been used as synthetic synthons and building blocks for further cluster-expansion reactions. As a consequence, the physical properties of different-sized clusters can be modulated and

fine-tuned, mainly owing to the narrow-spaced electronic states at higher nuclearities [10].

Due to the intensive studies on the sulfur-incorporated system [4,6,11], this review surveys recent progress in the heavier chalcogen-incorporated (E = Se, Te) anionic groups 6–8 carbonyl clusters. Metal clusters will be restricted to molecular complexes with metal–metal bonds that form triangular or larger structures. In addition, the main focus will be on anionic metal carbonyl clusters involving the first row groups 6–8 transition metals (Cr, Mn, Fe) and Ru, because the second and the third rows of transition metal carbonyl complexes have been thoroughly reported and reviewed [2a–c,3,5a–1,6]. This survey was performed based on the search of the Cambridge Structural Database (CSD) through January 2011. Selected important structural parameters of these anionic and related neutral carbonyl clusters are given and summarized in Table 1. This review introduces synthetic strategies in Section 2. Also, the syntheses, reactivities, and their structural features for groups 6–8 carbonyl anionic clusters are covered in Sections 3–6. Sections 7 and 8 then describe the recent exploration of the electrochemical and special properties of groups 6–8 carbonyl chalcogenide clusters and polymers. Computational methods such as Density Functional Theory (DFT) have recently been extensively employed to examine, support, and verify experimental results.

This review is not comprehensive, but is an attempt to summarize the representative examples of anionic metal carbonyl clusters on the basis of their synthetic methodologies and reactivities, focusing particularly on their cluster transformations and stepwise cluster-growth processes, as well as their electrochemical, magnetic, and semiconducting properties, which have rarely been systematically surveyed. Some related metal complexes or neutral metal carbonyl clusters will also be included for comparison.

## 2. Synthesis strategy

Several approaches have been developed for the synthesis of anionic chalcogen-incorporated metal carbonyl clusters. In the following subsections, we will introduce the characteristics of several typical methodologies for the production of chalcogen-containing groups 6–8 carbonyl anions, with some representative examples.

**Table 1**  
Selected complexes with E–M, E–M', M–M, M–M', and E–E bonds.

Complex	E–M	E–M'	M–M	M–M'	E–E	Ref.
[S <sub>2</sub> Fe <sub>2</sub> (CO) <sub>6</sub> ] <b>1a</b> (M = Fe)	2.228(2)		2.552(2)		2.007(5)	[94a]
[Se <sub>2</sub> Fe <sub>2</sub> (CO) <sub>6</sub> ] <b>1b</b> (M = Fe)	2.36(1)		2.575(2)		2.293(2)	[94c]
[Te <sub>2</sub> Fe <sub>2</sub> (CO) <sub>6</sub> ] <b>1c</b> (M = Fe)	2.54(2)		2.645(3)		2.71(1)	[94e]
[S <sub>2</sub> Fe <sub>3</sub> (CO) <sub>9</sub> ] <b>2a</b> (M = Fe)	2.229(4)		2.60(2)			[94b]
[Se <sub>2</sub> Fe <sub>3</sub> (CO) <sub>9</sub> ] <b>2b</b> (M = Fe)	2.35(1)		2.65(1)			[94d]
[Te <sub>2</sub> Fe <sub>3</sub> (CO) <sub>9</sub> ] <b>2c</b> (M = Fe)	2.54(1)		2.75(1)			[94f]
[PPN] <sub>2</sub> [SFe <sub>3</sub> (CO) <sub>9</sub> ] <b>3a</b> (M = Fe)	2.201(6)		2.596(9)			[111a]
[PPh <sub>4</sub> ] <sub>2</sub> [SeFe <sub>3</sub> (CO) <sub>9</sub> ] <b>3b</b> (M = Fe)	2.317(2)		2.6203(6)			[19]
[Et <sub>4</sub> N] <sub>2</sub> [TeFe <sub>3</sub> (CO) <sub>9</sub> ] <b>3c</b> (M = Fe)	2.486(9)		2.631(7)			[13b]
[Et <sub>4</sub> N] <sub>2</sub> [Se <sub>2</sub> Cr <sub>3</sub> (CO) <sub>10</sub> ] <b>4b</b> (M = Cr)	2.5(1)		2.89(5)			[14]
[Et <sub>4</sub> N] <sub>2</sub> [Te <sub>2</sub> Cr <sub>3</sub> (CO) <sub>10</sub> ] <b>4c</b> (M = Cr)	2.6(1)		2.95(7)			[50]
[Et <sub>4</sub> N] <sub>2</sub> [Te{Cr(CO) <sub>5</sub> } <sub>2</sub> ] <b>5</b> (M = Cr)	2.783(2)					[15]
[Et <sub>4</sub> N] <sub>2</sub> [Te{Cr(CO) <sub>5</sub> } <sub>3</sub> ] <b>6</b> (M = Cr)	2.788(3)					[15]
[PPh <sub>3</sub> Me][S <sub>2</sub> Mn <sub>3</sub> (CO) <sub>9</sub> ] <b>7a</b> (M = Mn)	2.25(2)		2.78(1)			[65]
[Et <sub>4</sub> N][Se <sub>2</sub> Mn <sub>3</sub> (CO) <sub>9</sub> ] <b>7b</b> (M = Mn)	2.36(2)		2.83(2)			[16]
[PPN][Te <sub>2</sub> Mn <sub>3</sub> (CO) <sub>9</sub> ] <b>7c</b> (M = Mn)	2.54(2)		2.92(2)			[85]
[TMBA] <sub>2</sub> [Te <sub>6</sub> Fe <sub>3</sub> (CO) <sub>24</sub> ] <b>8</b> (M = Fe)	2.59(4)		2.60(3)			[95]
[Et <sub>4</sub> N] <sub>2</sub> [Se <sub>2</sub> Cr <sub>2</sub> Mo(CO) <sub>10</sub> ] <b>9</b> (M = Cr, M' = Mo)	2.416(4)	2.6744(7)	2.948(1)	2.951(1)		[25]
[Et <sub>4</sub> N] <sub>2</sub> [Se <sub>2</sub> Mo <sub>3</sub> (CO) <sub>10</sub> ] <b>10</b> (M = Mo)	2.6(2)		3.017(4)			[25]
[Et <sub>4</sub> N][Se <sub>2</sub> Fe <sub>2</sub> Mn(CO) <sub>9</sub> ] <b>11</b>						[26]
[PPh <sub>3</sub> Me][(S <sub>2</sub> ) <sub>2</sub> Mn <sub>3</sub> (CO) <sub>10</sub> ] <b>12a</b> (M = Mn)	2.36(2)				2.078(4)	[28]
[Et <sub>4</sub> N][Se <sub>4</sub> Mn <sub>3</sub> (CO) <sub>10</sub> ] <b>12b</b> (M = Mn)	2.48(2)				2.3588(5)	[66]
[TMBA][Te <sub>4</sub> Mn <sub>3</sub> (CO) <sub>10</sub> ] <b>12c</b> (M = Mn)	2.65(1)				2.727(9)	[85]
[AsPh <sub>4</sub> ] <sub>2</sub> [MoS <sub>6</sub> Fe <sub>6</sub> (CO) <sub>16</sub> ] <b>13</b> (M = Fe, M' = Mo)	2.3(1)	2.43(4)	2.6(1)	2.79(1)		[31]
[Et <sub>4</sub> N] <sub>2</sub> [Se <sub>2</sub> Mn <sub>3</sub> (CO) <sub>10</sub> {Cr(CO) <sub>5</sub> } <sub>2</sub> ] <b>14</b> (M = Cr, M' = Mn)	2.541(1)	2.43(3)				[32]
[Et <sub>4</sub> N] <sub>2</sub> [SFe <sub>2</sub> Ru <sub>3</sub> (CO) <sub>14</sub> ] <b>15a</b>						[33]
[Et <sub>4</sub> N] <sub>2</sub> [SeFe <sub>2</sub> Ru <sub>3</sub> (CO) <sub>14</sub> ] <b>15b</b>						[113c]
[BzEt <sub>2</sub> MeN] <sub>2</sub> [S <sub>6</sub> Fe <sub>6</sub> (CO) <sub>12</sub> ] <b>16a</b> (M = Fe)	2.29(6)		2.6(1)			[99a]
[TMBA] <sub>2</sub> [Se <sub>6</sub> Fe <sub>6</sub> (CO) <sub>12</sub> ] <b>16b</b> (M = Fe)	2.42(1)		2.7(1)			[34a]
[PPh <sub>4</sub> ] <sub>2</sub> [Te <sub>4</sub> Fe <sub>5</sub> (CO) <sub>14</sub> ] <b>17</b> (M = Fe)	2.61(5)		2.592(4)			[103]
[PPN] <sub>2</sub> [Se <sub>2</sub> Mn <sub>4</sub> (CO) <sub>12</sub> ] <b>18b</b> (M = Mn)	2.475(2)		2.703(8)			[16]
[PPN] <sub>2</sub> [Te <sub>2</sub> Mn <sub>4</sub> (CO) <sub>12</sub> ] <b>18c</b> (M = Mn)	2.641(6)		2.81(2)			[85]
[Et <sub>4</sub> N] <sub>4</sub> [Se <sub>6</sub> Mn <sub>6</sub> (CO) <sub>18</sub> ] <b>19</b> (M = Mn)	2.49(2)		2.695(2)		2.394(1)	[35]
[SeCr <sub>2</sub> Cp <sub>2</sub> (CO) <sub>4</sub> ] <b>20</b> (M = Cr)	2.210(2)					[38]
[CoCp <sub>2</sub> ][SeCr <sub>3</sub> Cp <sub>3</sub> (CO) <sub>6</sub> ] <b>21</b> (M = Cr)	2.32(4)		3.088(3)			[41]
[K(2,2,2-crypt)][(η <sup>2</sup> -Se <sub>2</sub> )CrCp(CO) <sub>2</sub> ] <b>22</b> (M = Cr)	2.530(1)				2.290(2)	[40]
[PPh <sub>4</sub> ] <sub>2</sub> [Te <sub>2</sub> Cr <sub>4</sub> (CO) <sub>18</sub> ] <b>23</b> (M = Cr)	2.72(5)		3.052(2)			[44]
[PPh <sub>4</sub> ] <sub>2</sub> [Te <sub>2</sub> Cr <sub>4</sub> (CO) <sub>20</sub> ] <b>24</b> (M = Cr)	2.748(2)				2.785(3)	[44]
[PPh <sub>4</sub> ] <sub>2</sub> [Te <sub>3</sub> Cr <sub>4</sub> (CO) <sub>20</sub> ] <b>25</b> (M = Cr)	2.74(1)				2.69(2)	[44]
[K(2,2,2-crypt)] <sub>2</sub> [Te <sub>3</sub> Cr(CO) <sub>5</sub> ] <b>26</b> (M = Cr)	2.754(5)				2.71(3)	[45]
[K(2,2,2-crypt)] <sub>2</sub> [Te <sub>2</sub> {Cr(CO) <sub>5</sub> } <sub>2</sub> ] <b>27</b> (M = Cr)	2.74(2)				2.737(3)	[45]
[PPh <sub>4</sub> ] <sub>2</sub> [Te <sub>4</sub> Cr(CO) <sub>4</sub> ] <b>28</b> (M = Cr)	2.73(4)				2.72(2)	[43]
[Et <sub>4</sub> N] <sub>2</sub> [Se <sub>2</sub> Cr <sub>2</sub> W(CO) <sub>10</sub> ] <b>29</b> (M = Cr, M' = W)	2.418(2)	2.676(2)	2.955(3)	2.971(2)		[25]
[Cp(CO) <sub>3</sub> W(μ-SeCH <sub>2</sub> Ph)Cr(CO) <sub>5</sub> ] <b>30</b> (M = Cr, M' = W)	2.60(1)	2.673(1)				[46]
[Et <sub>4</sub> N] <sub>2</sub> [Se <sub>2</sub> W <sub>3</sub> (CO) <sub>10</sub> ] <b>31</b> (M = W)	2.6(1)		3.06(1)			[25]
[Et <sub>4</sub> N] <sub>2</sub> [Se <sub>2</sub> W <sub>4</sub> (CO) <sub>18</sub> ] <b>32</b> (M = W)	2.65(5)		3.0196(5)			[25]
[Et <sub>4</sub> N][Me <sub>2</sub> CSe <sub>2</sub> Mn(CO) <sub>4</sub> {Cr(CO) <sub>5</sub> } <sub>2</sub> ] <b>33</b> (M = Cr, M' = Mn)	2.586(3)	2.5044(8)				[32]
[CpMn(CO) <sub>2</sub> (μ-Se <sub>2</sub> )Cr(CO) <sub>5</sub> ] <b>34</b> (M = Cr, M' = Mn)	2.503(2)	2.50(1)			2.307(1)	[48a]
[CpMn(CO) <sub>2</sub> (μ <sub>3</sub> -Se <sub>2</sub> )Cr(CO) <sub>5</sub> ] <b>35</b> (M = Cr, M' = Mn)	2.50(1)	2.53(2)			2.3159(9)	[48a]
[Et <sub>4</sub> N][MeTe{Cr(CO) <sub>5</sub> } <sub>2</sub> ] <b>36</b> (M = Cr)	2.7415(7)					[15]
[Me <sub>4</sub> N][MeTe{Cr(CO) <sub>5</sub> } <sub>3</sub> ] <b>38</b> (M = Cr)	2.724(9)					[49]
[Me <sub>2</sub> Te{Cr(CO) <sub>5</sub> } <sub>2</sub> ] <b>39</b> (M = Cr)	2.643(5)					[49]
[Et <sub>4</sub> N][ClH <sub>2</sub> CTe{Cr(CO) <sub>5</sub> } <sub>2</sub> ] <b>40</b> (M = Cr)	2.72(1)					[49]
[Et <sub>4</sub> N] <sub>2</sub> [H <sub>2</sub> CTe <sub>2</sub> {Cr(CO) <sub>5</sub> } <sub>4</sub> ] <b>41</b> (M = Cr)	2.75(1)					[15]
[PPN][ClH <sub>2</sub> CTe{Cr(CO) <sub>5</sub> } <sub>3</sub> ] <b>42</b> (M = Cr)	2.72(1)					[49]
[Et <sub>4</sub> N] <sub>2</sub> [H <sub>2</sub> C(C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> CH <sub>2</sub> Te <sub>2</sub> {Cr(CO) <sub>5</sub> } <sub>4</sub> ] <b>44</b> (M = Cr)	2.725(2)					[49]
[Me <sub>4</sub> N] <sub>2</sub> [H <sub>2</sub> C(C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> CH <sub>2</sub> Te <sub>2</sub> {Cr(CO) <sub>5</sub> } <sub>6</sub> ] <b>45</b> (M = Cr)	2.74(1)					[49]
[Et <sub>4</sub> N] <sub>2</sub> [HgTe <sub>2</sub> {Cr(CO) <sub>5</sub> } <sub>4</sub> ] <b>46</b> (M = Cr, M' = Hg)	2.75(2)	2.6397(2)				[49]
[Et <sub>4</sub> N] <sub>2</sub> [HgTe <sub>2</sub> {Cr(CO) <sub>5</sub> } <sub>6</sub> ] <b>47</b> (M = Cr, M' = Hg)	2.732(8)	2.6955(4)				[49]
[Et <sub>4</sub> N] <sub>2</sub> [OTe <sub>2</sub> {Cr(CO) <sub>5</sub> } <sub>4</sub> ] <b>48</b> (M = Cr)	2.74(1)					[49]
[Bu <sub>4</sub> N] <sub>2</sub> [Te <sub>2</sub> Cr <sub>2</sub> Mo <sub>2</sub> (CO) <sub>18</sub> ] <b>49</b> (M = Cr, M' = Mo)	2.953(2)	2.9(2)	3.229(2)			[50]
[Bu <sub>4</sub> N] <sub>2</sub> [Te <sub>2</sub> Cr <sub>2</sub> W <sub>2</sub> (CO) <sub>18</sub> ] <b>50</b> (M = Cr, M' = W)	2.753(2)	2.782(4)	3.1159(7)			[50]
[Et <sub>4</sub> N] <sub>2</sub> [Te <sub>2</sub> CrMo <sub>2</sub> (CO) <sub>10</sub> ] <b>51</b>						[50]
[Et <sub>4</sub> N] <sub>2</sub> [Te <sub>2</sub> CrW <sub>2</sub> (CO) <sub>10</sub> ] <b>52</b>						[50]
[(CO) <sub>5</sub> W(TePh) <sub>2</sub> Cr(CO) <sub>5</sub> ] <b>53</b> (M = Cr, M' = W)					2.828(1)	[51]
[PPN] <sub>2</sub> [Se <sub>2</sub> Cr <sub>2</sub> Fe(CO) <sub>10</sub> ] <b>54b</b> (M = Cr, M' = Fe)	2.50(1)	2.35(4)	2.725(1)	2.913(1)		[52]
[PPN] <sub>2</sub> [Te <sub>2</sub> Cr <sub>2</sub> Fe(CO) <sub>10</sub> ] <b>54c</b> (M = Cr, M' = Fe)	2.67(2)	2.524(3)	2.776(2)	2.99(2)		[52]
[(Se <sub>2</sub> ) <sub>2</sub> CrFe <sub>2</sub> (CO) <sub>10</sub> ] <b>55</b> (M = Cr, M' = Fe)	2.42(1)	2.43(1)				[53]
[(μ-Se <sub>2</sub> )Cp <sub>2</sub> CrFe(CO) <sub>4</sub> ] <b>56</b> (M = Cr, M' = Fe)	2.53(4)	2.389(2)			2.298(2)	[54]
[(μ <sub>3</sub> -S) <sub>2</sub> FeCp <sub>2</sub> Cr <sub>2</sub> (μ-S'Bu) <sub>2</sub> (μ-Se) <sub>2</sub> ] <b>57</b> (E = Se, M = Cr, M' = Fe)		2.31(1)	2.680(4)	2.84(3)		[55]
[(Cp' <sup>2</sup> NbH)(Te) <sub>2</sub> Fe <sub>2</sub> (CO) <sub>6</sub> ]Cr(CO) <sub>5</sub> <b>58</b> (Cp' = tBuC <sub>5</sub> H <sub>4</sub> ) (M = Cr, M' = Fe)	2.706(2)	2.566(9)			3.157(2)	[57]
[PPh <sub>4</sub> ] <sub>2</sub> [(Se <sub>2</sub> ) <sub>2</sub> Mn <sub>2</sub> (CO) <sub>6</sub> ] <b>59</b> (M = Mn)	2.49(3)				2.327(3)	[61]
[PPh <sub>4</sub> ] <sub>2</sub> [(Se <sub>4</sub> ) <sub>2</sub> Mn <sub>2</sub> (CO) <sub>6</sub> ] <b>60</b> (M = Mn)	2.51(2)				2.36(4)	[61]
[PPh <sub>4</sub> ] <sub>2</sub> [Se <sub>2</sub> Mn <sub>3</sub> (CO) <sub>9</sub> ] <b>61b</b> (M = Mn)	2.43(2)		2.76(6)			[62]
[PPN] <sub>2</sub> [Te <sub>2</sub> Mn <sub>3</sub> (CO) <sub>9</sub> ] <b>61c</b> (M = Mn)	2.617(8)		2.80(1)			[85]
[(S <sub>2</sub> )Mn <sub>2</sub> (CO) <sub>7</sub> ] <b>62</b> (M = Mn)	2.287(2)		2.6745(5)		2.047(1)	[63]





Table 1 (Continued)

Complex	E–M	E–M'	M–M	M–M'	E–E	Ref.
$\{[Fe_2(CO)_6](\mu_3-Se_3P)\{CpCr(CO)_2\}\} (M = Cr, M' = Fe)$	2.685(1)	2.3934(7)				[216c]
$\{[FcSe(CH_2)_3Se]Cr(CO)_4\} (M = Cr, M' = Fe)$	2.545(2)					[216d]
$\{[FcTe(CH_2)_3TeFc]Cr(CO)_4\} (M = Cr, M' = Fe)$	2.661(8)					[216e]
$\{[(^tBuC_5H_4)_2Nb(CO)_3Co_9(CO)_8Te_6\{Cr(CO)_5\}_3]\} (M = Co, M' = Cr)$	2.7(2)	2.638(5)	2.5(2)			[91]
<b>E–Mn, Re complexes</b>						
$[Et_4N][\{S_2CH\}Mn_2(CO)_6] (M = Mn)$	2.31(3)		2.674(2)			[20]
$[S_4Mn_3(CO)_{10}\{CpFe(CO)_2\}] (M = Mn, M' = Fe)$	2.34(3)	2.2773			2.080(7)	[28]
$[S_2Mn_2(CO)_6\{SMn(CO)_4AsMe_2Ph\}_2] (M = Mn)$	2.38(3)				2.070(2)	[63]
$[(S_2)(S)_2Mn_4(CO)_{14}(NiCp)_2] (M = Mn, M' = Ni)$	2.31(6)	2.18(2)		2.53(1)	2.257(1)	[72]
$\{[HTe]HRe(CO)_2Cp^+\} (M = Re)$	2.743(1)					[78]
$\{[Te_2]\{Re(CO)_2Cp^+\}_2\} (M = Re)$	2.800(9)				2.703(1)	[78]
$\{[Te]\{Re(CO)_2Cp^+\}_2\} (M = Re)$	2.679(1)		3.140(1)			[78]
$[Te_2\{Mn(CO)_2Cp\}_2\{Re(CO)_2Cp^+\}] (M = Mn, M' = Re)$	2.525(7)	2.82(1)			2.732(1)	[78]
$[TeFe_2Mn(CO)_8Cp^+] (M = Fe, M' = Mn)$	2.474(3)	2.518(1)	2.677(2)	2.740(5)		[80]
<b>E–Fe, Ru, Os complexes</b>						
$[H_2SRu_3(CO)_9] (M = Ru)$	2.84(7)		2.363(9)			[217]
$[(K-crypt)_2][\{Te\}Te_2Fe_2(CO)_6] (M = Fe)$	2.57(1)		2.614(4)		2.705(3)	[18]
$[Bu_4N]_2[S_2Fe_5(CO)_{14}] (M = Fe)$	2.18(2)		2.60(3)			[19]
$[PPh_4]_2[Se_2Fe_5(CO)_{14}] (M = Fe)$	2.31(2)		2.65(4)			[19]
$[PPh_4]_2[Ni\{S_2Fe_2(CO)_6\}_2] (M = Fe, M' = Ni)$	2.283(8)	2.19(1)	2.503(3)			[19]
$[^tPr_2NH_2][^tBuSFe_3(CO)_9]$	2.120(2)		2.64(1)			[218]
$[PPh_4]_2[\{Te_2\}_7Fe_6(CO)_{12}] (M = Fe)$	2.62(3)				2.76(2)	[23a]
$[Me_4N]_2[\{TeMe\}_2(Te)_2(Te)_2Fe_4(CO)_8] (M = Fe)$	2.61(4)				2.818(1)	[23b]
$[PPh_4]_2[\{TeEt\}_2(Te)_2(Te)_2Fe_4(CO)_8] (M = Fe)$	2.61(3)				2.817(2)	[23a]
$[Na][Et_4N]_2[\{TeMe\}Te_8Fe_3W_2(CO)_{12}] (M = Fe, M' = W)$	2.59(3)	2.75(2)			2.78(4)	[24]
$[Te_2Fe_4(CO)_{11}] (M = Fe)$	2.58(3)		2.7(1)			[27]
$[PPN][SFe_3Mn(CO)_{12}] (M = Fe, M' = Mn)$	2.24(3)	2.274(1)	2.58(2)	2.590(3)		[29]
$[(Se)_2Fe_3(CO)_{10}][SbF_6]_2 (M = Fe)$	2.41(2)				2.318(6)	[75]
$[(S_2)\{EtSFe_2(CO)_6\}_2] (M = Fe)$	2.254(5)		2.5311(7)			[98b]
$[(Te_2)\{PhTeFe_2(CO)_6\}_2] (M = Fe)$	2.54(2)		2.61(1)		2.826(5)	[98c]
$[(S_2)\{SFe_2(CO)_6\}_2\{CH_2(CH_2OCH_2)_2CH_2\}] (M = Fe)$	2.26(2)		2.52(1)		2.118(2)	[98d]
$[(S_2)\{SFe_2(CO)_6\}_2\{Re_2(CO)_8(\mu-PCy_2)_2\}] (M = Fe, M' = Re)$	2.28(3)	2.56(2)	2.51(1)		2.127(5)	[89d]
$[(Se)_2\{SeFe_2(CO)_6\}_2\{Re_2(CO)_8(\mu-PCy_2)_2\}] (M = Fe, M' = Re)$	2.38(3)	2.648(7)	2.595(1)		2.438(1)	[89d]
$[(Te_2)\{TeFe_2(CO)_6\}_2\{Re_2(CO)_8(\mu-PCy_2)_2\}] (M = Fe, M' = Re)$	2.534(9)	2.77(1)	2.656(3)		2.808(2)	[89d]
$[Et_4N]_2[Mn\{S_2Fe_2(CO)_6\}_2] (M = Fe, M' = Mn)$	2.299(8)	2.37(1)	2.49(1)			[101]
$[Me_2Te_2Fe_2(CO)_6] (M = Fe)$	2.550(2)		2.634(5)			[102a]
$[PPh_4]_2[\{Fe(CO)_4\}_2Te_2Fe_2(CO)_6] (M = Fe)$	2.60(3)		2.641(5)			[102b]
$\{[Re(CO)_5]_2Te_2Fe_2(CO)_6\} (M = Fe, M' = Re)$	2.59(2)	2.831(6)	2.622(2)			[102c]
$\{[Fe(CO)_2Cp]_2Se_2Fe_2(CO)_6\} (M = Fe)$	2.40(3)		2.563(1)			[102d]
$[S_4Fe_4(CO)_{12}] (M = Fe)$	2.327(2)					[104a]
$[Se_4Fe_4(CO)_{12}] (M = Fe)$	2.446(6)					[104a]
$[SFeCo_2(CO)_9]$	*	*	*	*		[109c]
$[SeFeCo_2(CO)_9]$	*	*	*	*		[109d]
$[TeFeCo_2(CO)_9]$	*	*	*	*		[109d]
$[Te_2Fe_2(CO)_6\{Fe(CO)_3PPh_3\}] (M = Fe)$	2.60(5)		2.585(1)			[108d]
$[PPh_4][Te_2Fe_2(CO)_6\{Fe(CO)_3\}] (M = Fe)$	2.59(3)		2.606(1)			[110]
$[Te_2Fe(CO)_3\{Mo(CO)_2Cp\}_2] (M = Fe, M' = Mo)$	2.583(1)	2.80(2)				[108a]
$[S_2FeMnMoCp(CO)_8] (M = Fe, M' = Mn, Mo)$	2.229(1)	2.277(1)		2.641(1)		[73a]
		(M' = Mn)				
		2.449(1)				
		(M' = Mo)				
$[PPN][HSFe_3(CO)_9] (M = Fe)$	2.20(2)		2.61(4)			[112a]
$[PPN][HSeFe_3(CO)_9] (M = Fe)$	2.32(2)		2.64(4)			[113a]
$[PPN][HTeFe_3(CO)_9] (M = Fe)$	2.491(3)		2.67(5)			[113a]
$[(H)_2SFe_3(CO)_9] (M = Fe)$	2.20(1)		2.64(3)			[112a]
$[(H)_2SeFe_3(CO)_9] (M = Fe)$	2.32(2)		2.66(5)			[113a]
$[(H)_2TeFe_3(CO)_9] (M = Fe)$	2.505(4)		2.693(3)			[113a]
$[PPN][MeSFe_3(CO)_9] (M = Fe)$	2.130(4)		2.636(3)			[112a]
$[PPN][MeSeFe_3(CO)_9] (M = Fe)$	2.30(5)		2.61(8)			[112a]
$[PPN][Fe_3(CO)_9\{\mu_3-SFeCp(CO)_2\}] (M = Fe)$	2.18(5)		2.628(8)			[112b]
$[PPh_4][TeFe_3(CO)_9(AuPPh_3)] (M = Fe, M' = Au)$	2.49(3)		2.7(1)	2.67(2)		[110]
$[Au_6S_2(PPh_3)_6][SFe_3(CO)_9(\mu-AuPPh_3)]_2 (M = Fe, M' = Au)$	2.183(5)		2.64(7)	2.67(3)		[113d]
$[(\mu_4-Se)Fe_3(CO)_9RhCp^+] (M = Fe, M' = Rh)$	2.353(8)	2.521(1)	2.59(3)	2.588(6)		[114a]
$[(\mu_4-Te)Fe_3(CO)_9IrCp^+] (M = Fe, M' = Ir)$	2.53(2)	2.6893(7)	2.60(2)	2.58(7)		[114a]
$[(\mu_3-Te)Fe_2(CO)_7IrCp^+] (M = Fe, M' = Ir)$	2.47(1)	2.568(1)	2.659(1)	2.704(6)		[114a]
$[SFe_3(CO)_9(\mu_3-AuPPh_3)_2] (M = Fe, M' = Au)$	2.201(9)		2.8(1)	2.72(3)		[114b]
$[(SbFp')SeFe_3(CO)_9] (M = Fe; Fp' = \eta^5-C_5H_4^tBuFe(CO)_2)$	2.36(2)		2.732(1)			[114d]
$[(SbMes)SeFe_3(CO)_9] (M = Fe)$	2.38(2)		2.75(3)			[114e]
$[(BiFp')SeFe_3(CO)_9] (M = Fe)$	2.37(3)		2.72(1)			[114d]
$[(SbCp')TeFe_3(CO)_9] (M = Fe)$	2.54(2)		2.78(2)			[114d]
$[(SbFp')TeFe_3(CO)_9] (M = Fe)$	2.55(3)		2.76(1)			[114d]
$[(SbMes)TeFe_3(CO)_9] (M = Fe)$	2.54(2)		2.79(5)			[114e]
$[(\mu_3-\eta^2:\eta^1-SeSbMes)(\mu_3-SbMes)Fe_3(CO)_{10}] (M = Fe)$	2.37(2)		2.6478(8)			[114e]
$[PPh_4][\{Se_2Fe_4Rh_3(CO)_{16}\}] (M = Fe, M' = Rh)$	2.41(4)	2.50(3)	2.64(6)	2.66(5)		[89e]
$[PPh_4]_2[Te_2Fe_3Rh_4(CO)_{15}] (M = Fe, M' = Rh)$	2.551(3)	2.66(6)	2.703(2)	2.72(8)		[89e]
$\{[W(CO)_4(PPh_3)](\mu_5-S)Os_5(CO)_{15}\} (M = Os, M' = W)$	2.47(4)	2.52(2)	2.84(2)			[116a]
$\{[W(CO)_4PMe_2Ph](\mu_5-S)(\mu_4-S)Ru_4(CO)_9(PMe_2Ph)_2\} (M = Ru, M' = W)$	2.47(4)	2.486(2)	2.76(4)			[116b]

Table 1 (Continued)

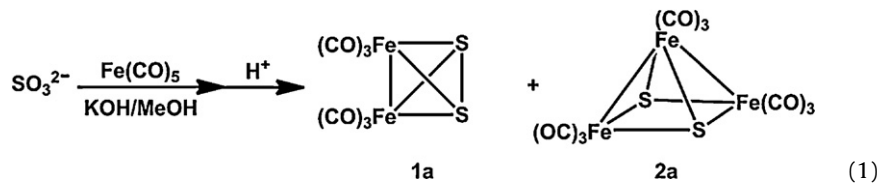
Complex	E–M	E–M'	M–M	M–M'	E–E	Ref.
[W(CO) <sub>5</sub> (μ <sub>4</sub> -S)(μ <sub>5</sub> -S)Ru <sub>4</sub> (CO) <sub>10</sub> {C(Ph)NMe <sub>2</sub> }] (M = Ru, M' = W)	2.5(1)	2.533(2)	2.78(5)			[116c]
[{μ-TeCHCl <sub>2</sub> }] <sub>2</sub> Fe <sub>2</sub> (CO) <sub>6</sub> (M = Fe)	2.53(1)		2.656(5)			[22]
[{μ-Te(CH <sub>2</sub> )Te}] <sub>2</sub> Fe <sub>2</sub> (CO) <sub>6</sub> (M = Fe)	2.546(4)		2.587(2)			[108e]
[{μ-Te(CH <sub>2</sub> ) <sub>2</sub> Te}] <sub>2</sub> Fe <sub>2</sub> (CO) <sub>6</sub> (M = Fe)	2.526(5)		2.626(2)			[117]
[{μ-Te(CH <sub>2</sub> ) <sub>3</sub> Te}] <sub>2</sub> Fe <sub>2</sub> (CO) <sub>6</sub> (M = Fe)	2.535(4)		2.633(1)			[117]
[{μ-TeCHPhTe}] <sub>2</sub> Fe <sub>2</sub> (CO) <sub>6</sub> (M = Fe)	2.547(9)		2.585(6)			[22]
[Et <sub>4</sub> N][BrTe <sub>2</sub> Fe <sub>2</sub> (CO) <sub>6</sub> ] (M = Fe)	2.54(2)		2.629(3)		2.732(2)	[117]
[BrTe <sub>2</sub> FeMo(CO) <sub>5</sub> Cp] (M = Fe, M' = Mo)	2.54(4)	2.75(4)		2.876(2)	2.807(1)	[118]
[PPh <sub>4</sub> ] <sub>2</sub> [{(CO) <sub>5</sub> MoTe]Te <sub>2</sub> Fe <sub>2</sub> (CO) <sub>6</sub> ] (M = Fe, M' = Mo)	2.56(3)	2.839(4)	2.628(5)		2.769(3)	[24]
[(μ-Me <sub>3</sub> CS)(μ-η <sup>2</sup> -CH=C=CH <sub>2</sub> )Fe <sub>2</sub> (CO) <sub>6</sub> ] (M = Fe)	2.27(2)		2.550(1)			[123a]
[Te <sub>2</sub> Fe <sub>2</sub> Ru <sub>3</sub> (CO) <sub>17</sub> ] (M = Fe, M' = Ru)	2.54(6)	2.7(1)	2.650(2)			[89a]
[Te <sub>2</sub> Fe <sub>2</sub> Ru <sub>2</sub> (CO) <sub>11</sub> ] (M = Fe, M' = Ru)	2.606(2)	2.737(2)	2.872(4)	2.794(2)		[89c]
[SeTeFe <sub>2</sub> Ru <sub>3</sub> (CO) <sub>17</sub> ]	2.334(1)	2.46(3)	2.605(2)			[134a]
(M = Fe, M' = Ru)	(E = Se) 2.591(2)	(E = Se) 2.7957(9)				
	(E = Te)	(E = Te)				
[Se <sub>2</sub> Fe <sub>3</sub> Ru(CO) <sub>11</sub> ]						[107d]
[Te <sub>2</sub> Ru <sub>4</sub> (CO) <sub>10</sub> (PPh <sub>3</sub> )] (M = Ru)	2.73(4)		2.9(1)			[88a]
[Te <sub>2</sub> Ru <sub>3</sub> (CO) <sub>6</sub> (PPh <sub>3</sub> ) <sub>3</sub> ] (M = Ru)	2.68(2)		2.96(1)			[88c]
[H <sub>2</sub> TeRu <sub>3</sub> (CO) <sub>7</sub> (dppm)] (M = Ru)	2.68(2)		2.9(1)			[88c]
[Te <sub>2</sub> Ru <sub>3</sub> (CO) <sub>7</sub> (dppm)] (M = Ru)	2.66(2)		2.91(5)			[88c]
[(μ <sub>3</sub> -S)Cu <sub>2</sub> Ru <sub>3</sub> (CO) <sub>9</sub> (μ-PPh <sub>2</sub> CH <sub>2</sub> PPh <sub>2</sub> )] (M = Ru, M' = Cu)	2.35(1)		2.84(2)	2.7(1)		[131a]
[(μ <sub>3</sub> -S)CuFe <sub>2</sub> Co(CO) <sub>8</sub> (PPh <sub>3</sub> ) <sub>2</sub> ] (M = Fe, M' = Cu)	2.1911(4)		2.6236(2)	2.582(1)		[139b]
[Et <sub>4</sub> N][{(μ <sub>4</sub> -S) <sub>6</sub> Cu <sub>5</sub> Fe <sub>6</sub> (CO) <sub>18</sub> (PPh <sub>3</sub> ) <sub>2</sub> ] (M = Fe, M' = Cu)	2.32(3)	2.4(1)	2.525(8)	2.71(2)		[139a]
[PPN] <sub>2</sub> [Ru <sub>3</sub> Cu(CO) <sub>9</sub> (CCO)] (E = C, M = Ru, M' = Cu)	2.1484(1)		2.78(1)	2.67753(6)		[151]
[PPN] <sub>2</sub> [{Ru <sub>4</sub> H(CO) <sub>12</sub> }] <sub>2</sub> (Cu <sub>7</sub> Cl <sub>3</sub> ) (M = Ru, M' = Cu)			2.88(7)	2.66(5)		[149c]
[PPN] <sub>2</sub> [{Ru <sub>6</sub> H(CO) <sub>17</sub> }] <sub>2</sub> (Cu <sub>6</sub> Cl <sub>2</sub> ) (M = Ru, M' = Cu)			2.90(7)	2.66(5)		[149c]
[Bu <sub>4</sub> N] <sub>4</sub> [{Ru <sub>10</sub> H <sub>2</sub> (CO) <sub>24</sub> }] <sub>2</sub> (Cu <sub>6</sub> Cl <sub>2</sub> ) (M = Ru, M' = Cu)			2.87(9)	2.66(5)		[149d]
[Ph <sub>4</sub> As] <sub>2</sub> [{Ru <sub>5</sub> C(CO) <sub>14</sub> }] <sub>2</sub> Ag <sub>3</sub> Cl (E = C, M = Ru, M' = Ag)	2.9(1)		2.9(1)	2.92(9)		[158]
[PPh <sub>4</sub> ] <sub>2</sub> [{Ru <sub>6</sub> C(CO) <sub>16</sub> }] <sub>2</sub> Cu <sub>2</sub> Ag <sub>2</sub> Cl <sub>2</sub> (M = Ru, M' = Cu)	2.06(2)		2.9(1)	2.74(4)		[155]
[PPh <sub>4</sub> ] <sub>2</sub> [{Ru <sub>6</sub> C(CO) <sub>15</sub> }] <sub>2</sub> (Cu <sub>4</sub> Cl <sub>2</sub> )(Cu <sub>3</sub> Cl) (M = Ru, M' = Cu)	2.06(2)		2.91(7)	2.71(6)		[155]
[(μ-Hg){Fe(CO) <sub>3</sub> {Si(OMe) <sub>3</sub> (dppm-S)} <sub>2</sub> ] (M = Fe, M' = Hg)				2.581(1)		[164a]
cis-[(μ <sub>3</sub> -Hg) <sub>2</sub> Ru(CO) <sub>4</sub> {Ru <sub>3</sub> (CO) <sub>9</sub> (μ-η <sup>3</sup> -SC <sub>5</sub> H <sub>4</sub> N)} <sub>2</sub> ] (M = Ru, M' = Hg)	2.372(8)		2.83(7)	2.75(7)		[164b]
[Ru <sub>3</sub> (μ <sub>3</sub> -C <sub>2</sub> <sup>t</sup> Bu)(CO) <sub>9</sub> (HgBr)] (M = Ru, M' = Hg)			2.84(5)	2.736(4)		[168]
[(μ <sub>4</sub> -Hg){Fe <sub>2</sub> Co(μ <sub>3</sub> -COMe)(CO) <sub>7</sub> Cp}] <sub>2</sub> (M = Fe, M' = Hg)			2.688(4)	2.729(4)		[169a]
[(μ <sub>4</sub> -Hg){Fe <sub>2</sub> Rh(μ <sub>3</sub> -COMe)(CO) <sub>7</sub> Cp}] <sub>2</sub> (M = Fe, M' = Hg)			2.609(3)	2.775(3)		[169a]
[Et <sub>4</sub> N] <sub>2</sub> [(μ <sub>4</sub> -Hg){Fe <sub>5</sub> C(CO) <sub>14</sub> }] <sub>2</sub> (E = C, M = Fe, M' = Hg)	1.9(5)		2.6(1)	2.73(2)		[169b]
[(μ <sub>4</sub> -Hg){(μ-CH <sub>3</sub> OCH <sub>2</sub> CH=C)(μ- <sup>t</sup> BuS)Fe <sub>2</sub> (CO) <sub>6</sub> }] <sub>2</sub> (M = Fe, M' = Hg)	2.260(5)		2.646(1)	2.771(7)		[122b]
[PPN] <sub>2</sub> [(μ <sub>4</sub> -Hg){Ru <sub>6</sub> C(CO) <sub>16</sub> }] <sub>2</sub> (M = Ru, M' = Hg)	2.05(3)		2.89(8)	2.84(5)		[169c]
[PPh <sub>4</sub> ] <sub>2</sub> [(μ <sub>4</sub> -Cd){Fe <sub>2</sub> (CO) <sub>6</sub> (μ-CO) <sub>2</sub> }] <sub>2</sub> (M = Fe, M' = Cd)			2.616(4)	2.724(4)		[169d]
[PPN] <sub>2</sub> [(μ <sub>4</sub> -Cd)Fe <sub>6</sub> (CO) <sub>20</sub> (μ-CO) <sub>2</sub> ] (M = Fe, M' = Cd)			2.67(1)	2.743(7)		[169e]
[Hg <sub>7</sub> {Fe(CO) <sub>4</sub> }] <sub>5</sub> (S <sup>t</sup> Bu) <sub>3</sub> Cl (M = Fe, M' = Hg)		2.5(2)		2.57(5)		[172]
[Hg <sub>14</sub> Fe <sub>12</sub> {Fe(CO) <sub>4</sub> }] <sub>6</sub> S <sub>6</sub> (S <sup>t</sup> Bu) <sub>8</sub> Br <sub>18</sub> (M = Fe, M' = Hg)	2.37(2)	2.42(3)		2.523(9)		[172]
[Hg <sub>39</sub> Fe <sub>8</sub> {Fe(CO) <sub>4</sub> }] <sub>18</sub> S <sub>8</sub> (S <sup>t</sup> Bu) <sub>14</sub> Br <sub>28</sub> (M = Fe, M' = Hg)	2.32(1)	2.5(1)		2.53(1)		[172]

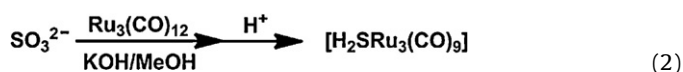
\* M atoms were disordered.

### 2.1. Chalcogen oxides or powders with metal carbonyl anions

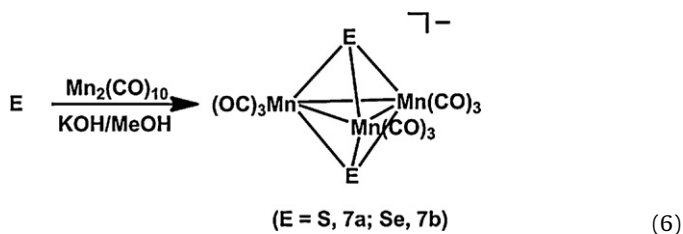
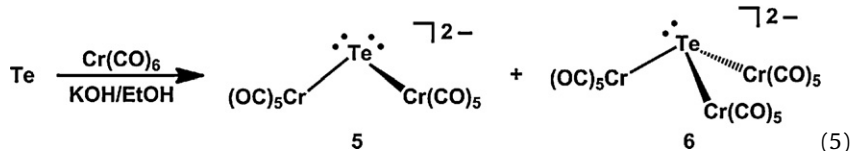
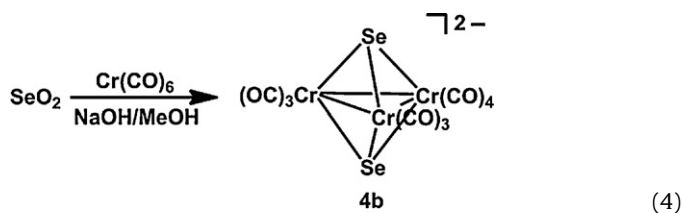
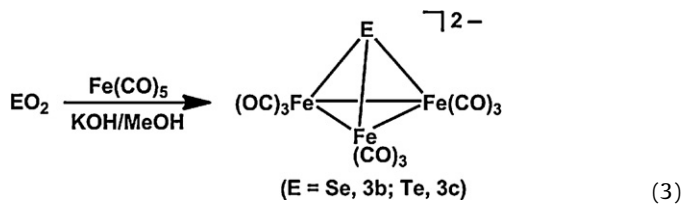
The deoxygenation process of main-group oxides by metal carbonyl anions is one useful approach to introduce main-group atoms into metal carbonyl clusters. Such reactions involve the reduction of the main-group oxides by metal carbonyl anions, derived from the attack of the hydroxide ion on the carbon atom of the carbonyls on the metal, followed by the transfer of oxygen atom and the liberation of gaseous CO<sub>2</sub>, to form main-group–metal bonds [1,5e,5j]. Hieber et al. discovered this facile method to obtain useful

dinuclear tetrahedral complexes [E<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>] (E = S, **1a**; Se, **1b**) and square-pyramidal triiron clusters [E<sub>2</sub>Fe<sub>3</sub>(CO)<sub>9</sub>] (E = S, **2a**; Se, **2b**; Te, **2c**) by utilizing the reactions of EO<sub>3</sub><sup>2-</sup> (E = S, Se, Te) with Fe(CO)<sub>5</sub> in basic methanol solutions, followed by acidification (Eq. (1)) [1a]. Although the anionic species initially produced from these reactions were not fully characterized, this strategy is available for the production of many groups 15- and 16-containing metal carbonyl complexes [5b,5f]. For example, the tetrahedral complex [H<sub>2</sub>SRu<sub>3</sub>(CO)<sub>9</sub>] was reported to be synthesized from the reaction of SO<sub>3</sub><sup>2-</sup> with Ru<sub>3</sub>(CO)<sub>12</sub> in KOH/MeOH solutions followed by acidification (Eq. (2)) [12].





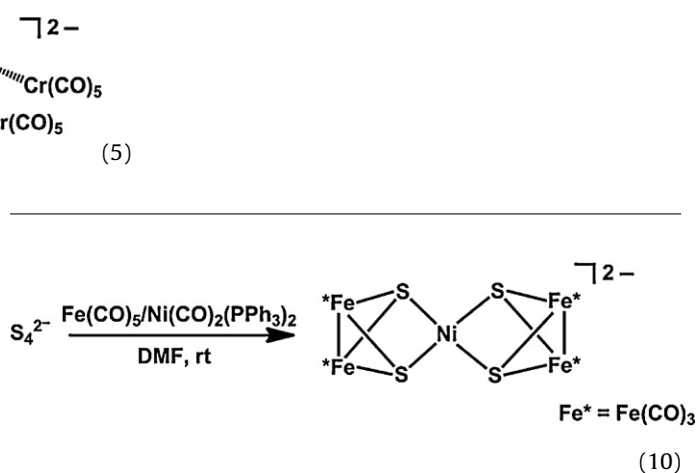
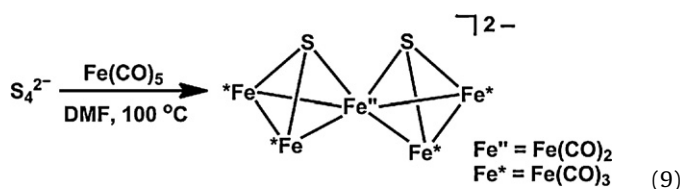
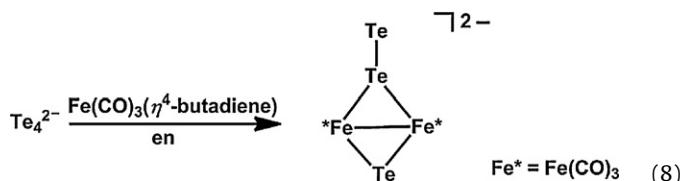
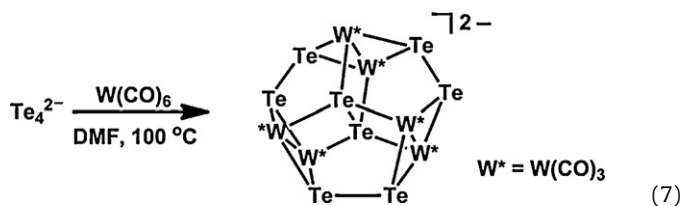
Hieber's method, modified by using  $\text{EO}_2$  or E powder as the chalcogen source, has also been found in the production of anionic group 16-transition metal carbonyl clusters. In the iron system, in addition to  $\text{K}_2\text{EO}_3$ ,  $\text{EO}_2$  (E=Se, Te) was also found to react with iron carbonyl in basic solutions to form tetrahedral clusters  $[\text{EFe}_3(\text{CO})_9]^{2-}$  (E=Se, **3b**; Te, **3c**) (Eq. (3)) [13]. In the Cr system,  $\text{SeO}_2$  or Te powder could react with  $\text{Cr}(\text{CO})_6$  in basic solutions under appropriate reaction conditions to form the trigonal-bipyramidal cluster  $[\text{Se}_2\text{Cr}_3(\text{CO})_{10}]^{2-}$  (**4b**) (Eq. (4)) or the open structures  $[\text{Te}\{\text{Cr}(\text{CO})_5\}_2]^{2-}$  (**5**) and  $[\text{Te}\{\text{Cr}(\text{CO})_5\}_3]^{2-}$  (**6**), respectively (Eq. (5)) [14,15]. However, in the Mn system, E powder (E=S, Se) was used as a convenient chalcogen source to react with  $\text{Mn}_2(\text{CO})_{10}$  in basic solutions to form trigonal-bipyramidal clusters  $[\text{E}_2\text{Mn}_3(\text{CO})_9]^-$  (E=S, **7a**; Se, **7b**) (Eq. (6)) [16].



## 2.2. Polychalcogenide anions (Zintl ions) with metal carbonyls

Another useful method for the preparation of chalcogen-containing metal anions is the utilization of soluble polychalcogenides (Zintl ions) with metal carbonyls. This type of reaction occurs via the reductive attack of polychalcogenides on the zero-valent metal atom, followed by oxidative decarbonylation, which has led to the formation of numerous interesting high-nuclearity carbonyl clusters. The polytungsten telluride dianion  $[(\text{Te}_2)_4\text{W}_6(\text{CO})_{18}]^{2-}$  was reported to result from the reaction of  $\text{Te}_4^{2-}$  with  $\text{W}(\text{CO})_6$  in DMF solutions at  $100^\circ\text{C}$  (Eq. (7)) [17]. A similar method was also applied for the synthesis of group 8 carbonyl chalcogenide clusters. It was reported that when  $\text{Te}_4^{2-}$  was treated with the labile iron carbonyl derivative  $[\text{Fe}(\text{CO})_3(\eta^4\text{-butadiene})]$ , the butterfly  $[(\text{Te})\text{Te}_2\text{Fe}_2(\text{CO})_6]^{2-}$  was obtained (Eq. (8)) [18]. Furthermore, the reaction of  $\text{S}_4^{2-}$  with  $\text{Fe}(\text{CO})_5$  in DMF at  $100^\circ\text{C}$  formed the two vertex-fused bis-tetrahedral cluster  $[\text{S}_2\text{Fe}_5(\text{CO})_{14}]^{2-}$  (Eq. (9)). The mixed Fe–Ni carbonyl sulfide cluster

$[\text{Ni}\{\text{S}_2\text{Fe}_2(\text{CO})_6\}_2]^{2-}$  was also synthesized using a similar methodology (Eq. (10)) [19].

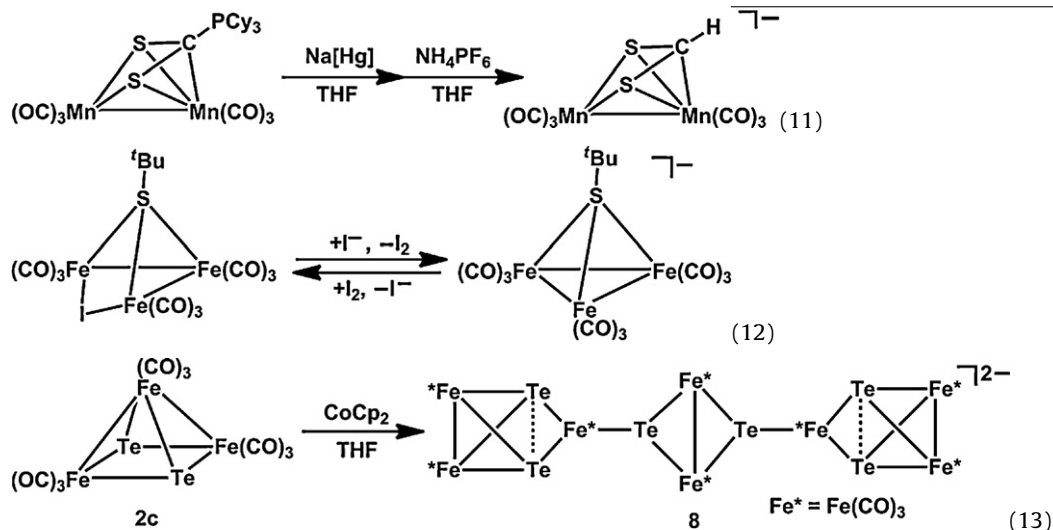


## 2.3. Reduction of neutral metal carbonyl complexes or clusters

The reduction of neutral metal carbonyl complexes or clusters by suitable reducing agents such as Na and  $\text{CoCp}_2$  is a straightforward approach for the preparation of anionic metal carbonyl complexes or clusters. This strategy has long been employed to produce negatively charged metal carbonyl clusters; however, these reduction reactions usually involve complicated isolation and purification processes.  $[(\text{S}_2\text{CPCy}_3)\text{Mn}_2(\text{CO})_6]$  was reported to be reduced with  $\text{Na}[\text{Hg}]$  in THF solutions followed by treatment with  $\text{NH}_4\text{PF}_6$  to produce the dithioformate complex  $[(\text{S}_2\text{CH})\text{Mn}_2(\text{CO})_6]^-$  (Eq. (11)) [20]. In addition, by treatment with iodide, the 1-bridged butterfly cluster  $[\text{tBuSFe}_3(\text{CO})_9(\mu\text{-I})]$  underwent reductive elimination to form the anionic tetrahedral *closo*-cluster  $[\text{tBuSFe}_3(\text{CO})_9]^-$  which



was reconverted back to the neutral complex upon the oxidative addition of  $I_2$  (Eq. (12)) [21]. Moreover, the reduction of neutral carbonyl complexes often occurs via the cleavage of E–M and/or M–M bonds and/or loss of COs, accompanied by condensation, to form higher-nuclearity anionic metal carbonyl clusters. For instance, the reduction of the triiron telluride cluster  $[Te_2Fe_3(CO)_9]$  (**2c**) with 2 equiv of  $CoCp_2$  led to the formation of the large  $Te_2Fe_2^{2-}$ -linked di- $Te_2Fe_3$  cluster  $[Te_6Fe_8(CO)_{24}]^{2-}$  (**8**) (Eq. (13)) [22].

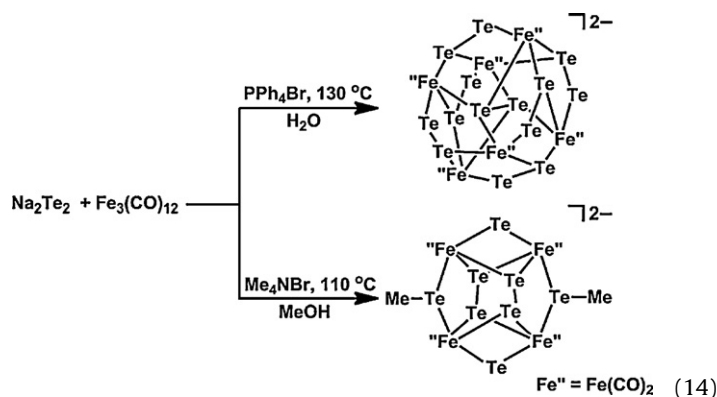


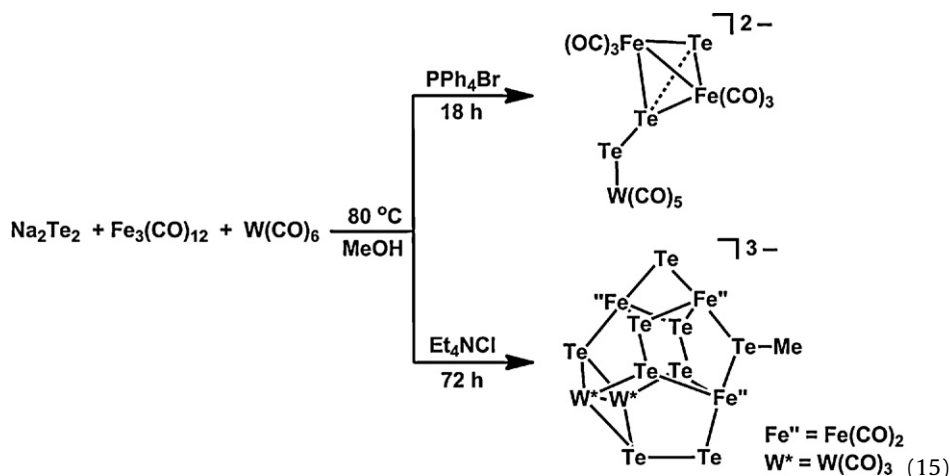
#### 2.4. Hydro(solvo)thermal reactions

Hydro(solvo)thermal reactions also provide an efficient methodology for the synthesis of polychalcogenido metal carbonyl clusters. This methodology has great potential to produce

structurally interesting anionic clusters, in which alkali-metal polychalcogenido salts and metal carbonyl complexes, along with organic solvents, are sealed in a Pyrex tube and heated at a suitable temperature. For example, the oxidative decarbonylation of  $Fe_3(CO)_{12}$  with  $Na_2Te_2$  in water at  $130^\circ C$  or MeOH at  $110^\circ C$  produced the poly-ditelluride-stabilized iron clusters  $[(Te_2)_7Fe_6(CO)_{12}]^{2-}$  and  $[(TeMe)_2(Te)_2(Te_2)_2Fe_4(CO)_8]^{2-}$ , respectively (Eq. (14)) [23]. Besides, the solvothermal reaction of

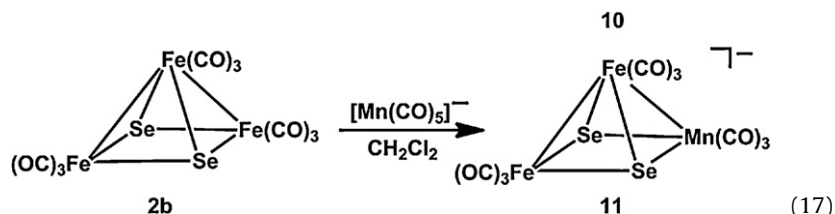
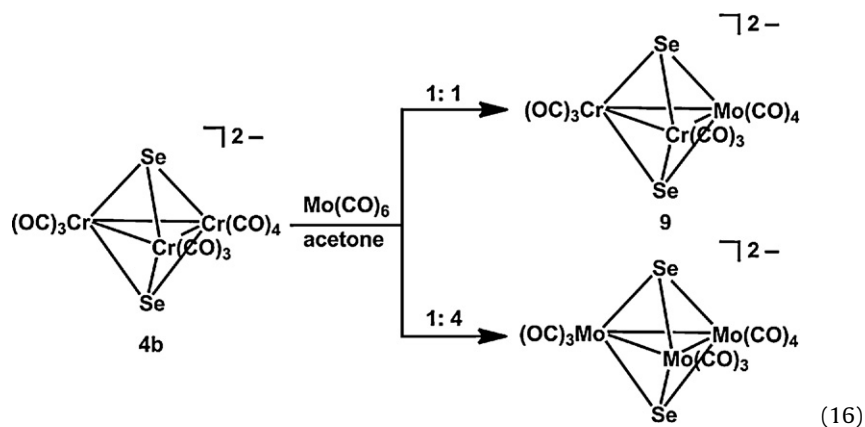
$CoRe(CO)_3$  with  $Na_2Te_2$  in MeOH could afford a novel cluster,  $[Re_4(Te_2)_3(TeCH_3)(CO)_{12}]^{3-}$  [5d], where the methylation of the monotelluride took place. Mixed-metal carbonyl telluride anions,  $[Te_3Fe_2W(CO)_{11}]^{2-}$  and  $[(TeMe)Te_8Fe_3W_2(CO)_{12}]^{3-}$ , were also reported to have been synthesized methanothermally from the reaction of  $Na_2Te_2$ ,  $Fe_3(CO)_{12}$ , and  $W(CO)_6$  in the presence of  $PPh_4Br$  or  $Et_4NCl$  with different molar ratios and reaction times (Eq. (15)) [24].





### 2.5. Metal-exchange reactions

Substitution of the metal fragments of metal clusters by their isolobal analogy is also an available method for the generation

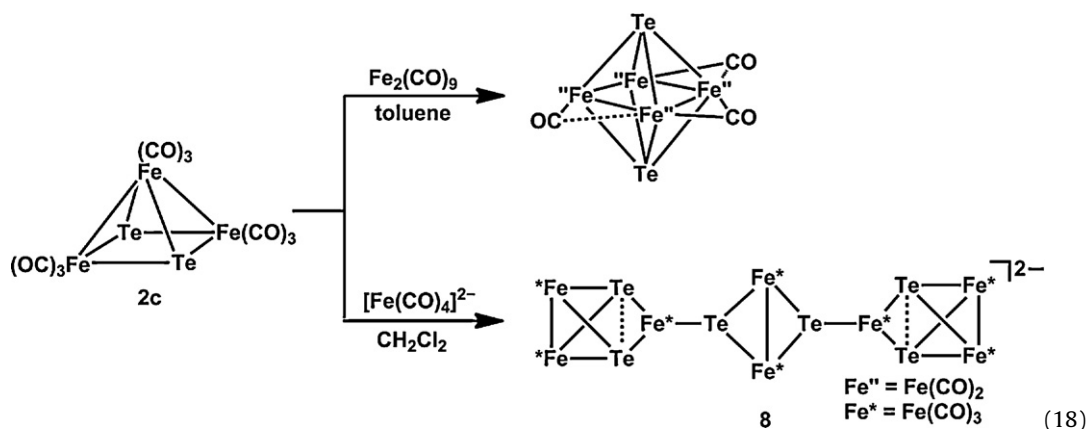


of mixed-metal carbonyl clusters. We utilized this concept to synthesize a series of heterometallic chalcogenide anions. For example, when the selenium-capped trichromium cluster  $[\text{Se}_2\text{Cr}_3(\text{CO})_{10}]^{2-}$  (**4b**) was treated with 1 equiv of  $\text{Mo}(\text{CO})_6$  in refluxing acetone solutions, the mono-molybdenum-substituted cluster  $[\text{Se}_2\text{Cr}_2\text{Mo}(\text{CO})_{10}]^{2-}$  (**9**) was obtained in good yield. Moreover, the tri-molybdenum cluster  $[\text{Se}_2\text{Mo}_3(\text{CO})_{10}]^{2-}$  (**10**) could be obtained if the ratio was increased to 1:4 (Eq. (16)) [25]. The square-pyramidal cluster  $[\text{Se}_2\text{Fe}_3(\text{CO})_9]$  (**2b**), produced via Hieber's synthesis [1], was found to undergo a metal-exchange reaction with  $[\text{Mn}(\text{CO})_5]^-$  to afford the anionic cluster  $[\text{Se}_2\text{Fe}_2\text{Mn}(\text{CO})_9]^-$  (**11**), in which the  $\text{Fe}(\text{CO})_3$  fragment was replaced by the  $[\text{Mn}(\text{CO})_3]^-$  moiety (Eq. (17)) [26].

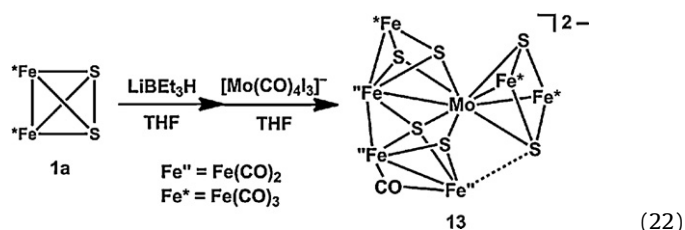
### 2.6. Cluster-growth reactions

Cluster-growth reactions have been developed as an effective methodology for the construction of extended metal frameworks. These reactions usually involve complicated redox processes, of which the most common and well-known type is the coupling reaction of neutral metal carbonyl complexes. For instance,  $[\text{Te}_2\text{Fe}_3(\text{CO})_9]$  (**2c**) was reported to react with  $\text{Fe}_2(\text{CO})_9$  in toluene to produce a higher-nuclearity octahedral cluster  $[\text{Te}_2\text{Fe}_4(\text{CO})_{11}]$  [27]. The neutral metal carbonyl clusters also reacted readily with the negatively charged metal carbonyl species to give larger anionic clusters. The neutral complex **2c** reacted with the Collman's reagent

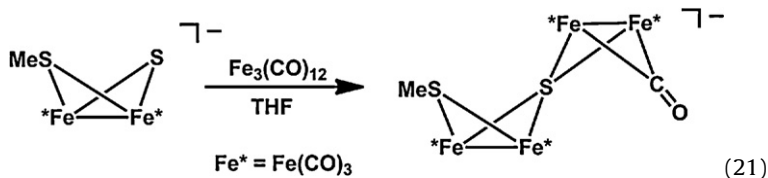
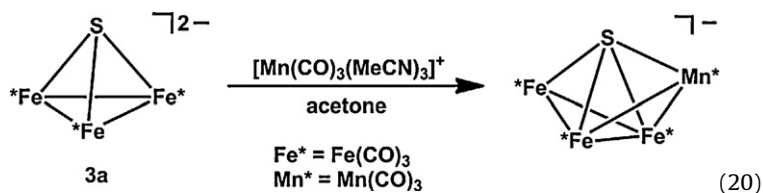
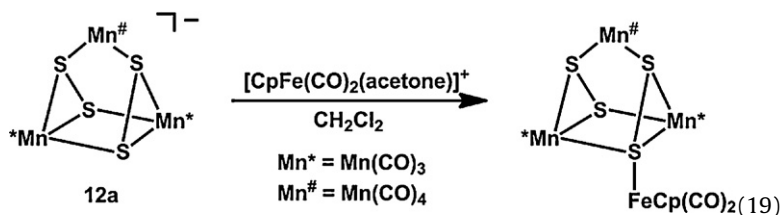
$[\text{Fe}(\text{CO})_4]^{2-}$  in  $\text{CH}_2\text{Cl}_2$  to produce a polynuclear iron telluride carbonylate  $[\text{Te}_6\text{Fe}_8(\text{CO})_{24}]^{2-}$  (**8**) (Eq. (18)) [26].



Anionic carbonyl clusters have been known to react efficiently with cationic metal carbonyl complexes to form larger neutral clusters. For instance, the trimanganese disulfide anionic cluster  $[\text{S}_4\text{Mn}_3(\text{CO})_{10}]^-$  (**12a**) underwent nucleophilic attack on the cationic complex  $[\text{CpFe}(\text{CO})_2(\text{acetone})]^+$  to produce the neutral mixed-metal carbonyl cluster  $[\text{S}_4\text{Mn}_3(\text{CO})_{10}\{\text{CpFe}(\text{CO})_2\}]$  (Eq. (19)) [28]. It should be mentioned that such condensation reactions have also been found to be useful for the preparation of high-nuclearity anionic clusters if the ratios of the reactants and/or reaction conditions are carefully controlled. For example, the tetrahedral cluster  $[\text{SFe}_3(\text{CO})_9]^{2-}$  (**3a**) was reported to react with 1 equiv of  $[\text{Mn}(\text{CO})_3(\text{MeCN})_3]^+$  in acetone solutions, forming the mixed Fe–Mn cluster  $[\text{SFe}_3\text{Mn}(\text{CO})_{12}]^-$  (Eq. (20)) [29]. Anionic clusters also undergo redox-condensation reactions, with or without the addition of other metal fragments, to give rise to larger anionic clusters. For instance, the single-butterfly complex  $[\text{S}(\text{SMe})\text{Fe}_2(\text{CO})_6]^-$  reacted with  $\text{Fe}_3(\text{CO})_{12}$  to produce the double-butterfly cluster  $[\text{S}(\text{SMe})\text{Fe}_4(\text{CO})_{13}]^-$  (Eq. (21)), which further reacted with various electrophiles to give an array of neutral compounds [30]. When the disulfur diiron  $[\text{S}_2\text{Fe}_2(\text{CO})_6]$  (**1a**) was reduced with 2 equiv of  $\text{LiEt}_3\text{H}$  in THF, followed by the addition of  $[\text{Mo}(\text{CO})_4\text{I}_3]^-$  at  $-78^\circ\text{C}$ , the molybdenum-linked tri- $\text{S}_2\text{Fe}_2$ -cluster  $[\text{MoS}_6\text{Fe}_6(\text{CO})_{16}]^{2-}$  (**13**) was obtained (Eq. (22)) [31].



This concept was adapted by using low-nuclearity anionic metal carbonyl clusters as starting materials to react with cationic, neutral, or anionic species, under appropriate conditions, to afford high-nuclearity clusters. For example,  $[\text{Se}_2\text{Cr}_3(\text{CO})_{10}]^{2-}$  (**4b**) reacted with  $\text{Mn}(\text{CO})_5\text{Br}$  under controlled conditions to afford a novel cluster-expansion product  $[\text{Se}_2\text{Mn}_3(\text{CO})_{10}\{\text{Cr}(\text{CO})_5\}_2]^{2-}$  (**14**) (Eq. (23)) [32]. Similarly,  $[\text{SFe}_3(\text{CO})_9]^{2-}$  (**3a**) underwent cluster-expansion to form the heterometallic octahedral cluster  $[\text{SFe}_2\text{Ru}_3(\text{CO})_{14}]^{2-}$  (**15a**) upon treatment with  $\text{Ru}_3(\text{CO})_{12}$  in

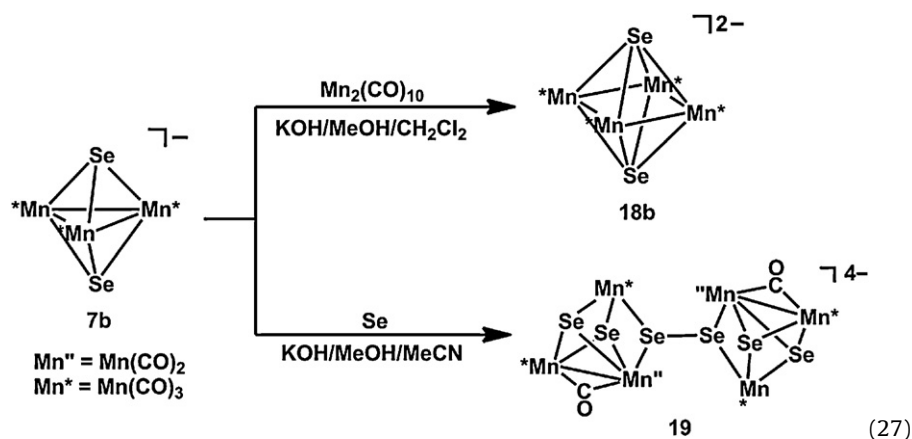
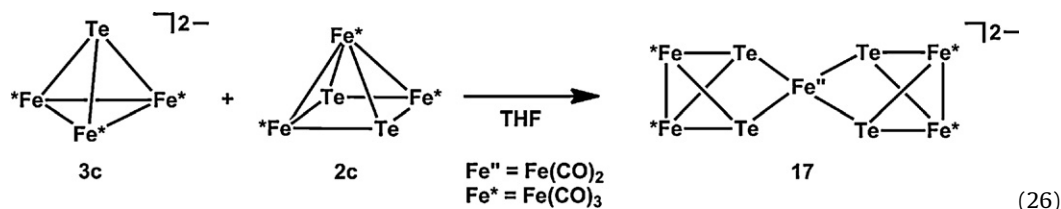
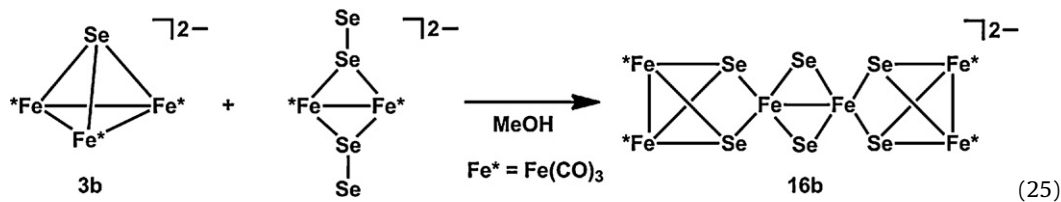
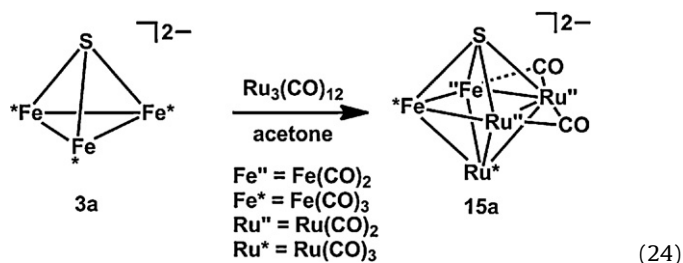
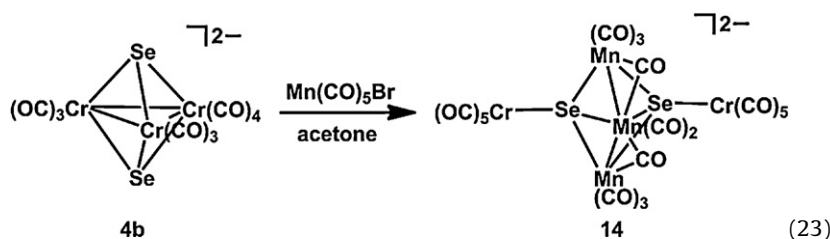


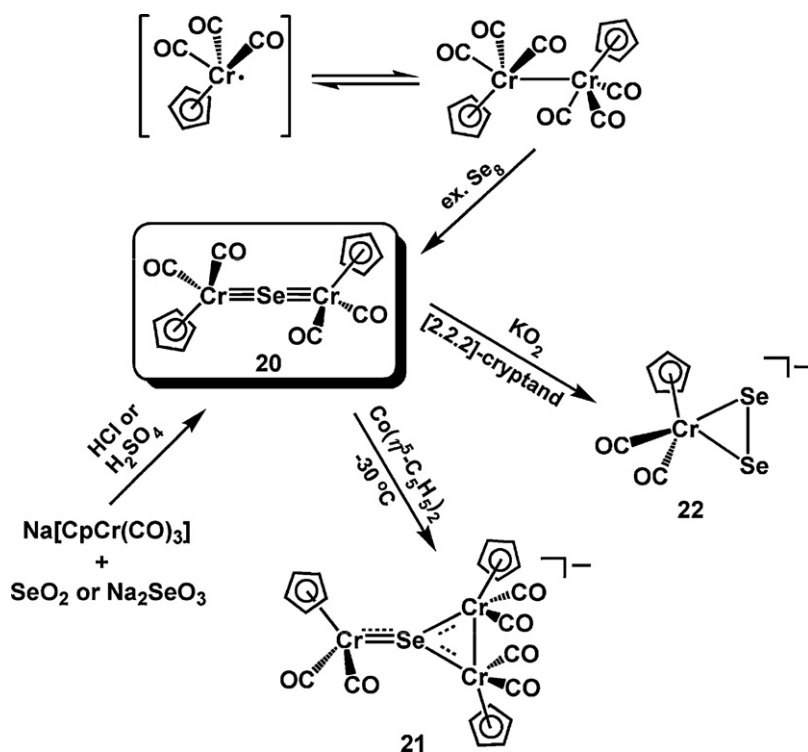
refluxing acetone (Eq. (24)) [33]. In addition, the tetrahedral clusters  $[\text{EFe}_3(\text{CO})_9]^{2-}$  ( $\text{E} = \text{Se}$ , **3b**;  $\text{Te}$ , **3c**) have been used as useful building blocks to react with some iron carbonyl complexes to form higher-nuclearity clusters  $[\text{Se}_6\text{Fe}_6(\text{CO})_{12}]^{2-}$  (**16b**) and  $[\text{Te}_4\text{Fe}_5(\text{CO})_{14}]^{2-}$  (**17**) (Eqs. (25 and 26)) [34]. It is interesting that in the Mn system, the reaction of the trigonal-bipyramidal cluster  $[\text{Se}_2\text{Mn}_3(\text{CO})_9]^-$  (**7b**) with  $\text{Mn}_2(\text{CO})_{10}$  in  $\sim 1 \text{ M KOH/MeOH/CH}_2\text{Cl}_2$  solutions produced the cluster-expansion octahedral cluster  $[\text{Se}_2\text{Mn}_4(\text{CO})_{12}]^{2-}$  (**18b**) [16], whereas the treatment of **7b** with Se powder in concentrated  $\text{KOH/MeOH/MeCN}$  solutions produced the Se-inserted hexamanganese carbonyl cluster  $[\text{Se}_6\text{Mn}_6(\text{CO})_{18}]^{4-}$  (**19**) (Eq. (27)) (*vide infra*) [35].

### 3. Group 6 (Cr) carbonyl clusters

#### 3.1. E-Cr clusters ( $\text{E} = \text{Se}, \text{Te}$ )

The utilization of the sulfur atom as the ligand to bridge group 6, chromium, carbonyl fragments has been well studied [5n,36]. However, the heavier congeners, selenium- and tellurium-chromium carbonyl complexes, have not been explored as thoroughly. According to a search of the CSD, a variety of carbonylchromium selenide and telluride complexes were neutral species; however, few anionic complexes were reported, due to the lack of practical synthetic methodologies (*vide infra*).





Scheme 1. Reactivities of **20** toward some nucleophiles.

The neutral dimer  $[\text{CpCr}(\text{CO})_3]_2$ , featuring an unusually long Cr–Cr bond (3.281(1) Å) [37], is reportedly easily dissociated into the 17-electron radical species  $[\text{CpCr}(\text{CO})_3\cdot]$  and shows high reactivities toward group 16 or mixed group 15/16 elements [4d,5n]. As shown in Scheme 1, the Se-incorporated dichromium linear complex  $[\text{SeCr}_2\text{Cp}_2(\text{CO})_4]$  (**20**) was shown to be reactive toward some nucleophiles. Complex **20** was obtained by two methods: (i) the treatment of  $[\text{CpCr}(\text{CO})_3]_2$  with more molar equivalents of selenium powder [38], and (ii) the reaction of  $\text{Na}[\text{CpCr}(\text{CO})_3]$  with a selenium oxide such as  $\text{SeO}_2$  and  $\text{Na}_2\text{SeO}_3$  under HCl or  $\text{H}_2\text{SO}_4$  acidic conditions [39]. In addition, complex **20** exhibited two one-electron reversible reductions, at  $E_{1/2} = -0.72$  V ( $\Delta E = 65$  mV) and  $-1.40$  V ( $\Delta E = 70$  mV), suggesting that **20** could be reduced by two electrons [40]. Herrmann and co-workers successfully discovered the selective reduction of **20** with cobaltocene in THF/ether solutions at  $-30$  °C or  $\text{KO}_2$ , followed by the addition of a [2.2.2]-cryptand to produce novel anionic complexes  $[\text{SeCr}_3\text{Cp}_3(\text{CO})_6]^-$  (**21**) and  $[(\eta^2\text{-Se}_2)\text{CrCp}(\text{CO})_2]^-$  (**22**), respectively (see Scheme 1) [40,41]. X-ray analysis of complex **21** revealed that the  $\text{SeCr}_3$  unit was strictly planar and the Se–Cr bonds showed significant multiple-bond characteristics (2.32(4) Å) (Fig. 1). However, in complex **22**, the Se–Cr distance (2.530(1) Å) of the  $\text{Se}_2\text{Cr}$  unit corresponded to a single bond (see Table 1).

In the anionic Te–Cr–CO system (see Scheme 2), the protonated chalcogenide ( $\text{TeH}^-$ )-incorporated anionic chromium complex  $[(\text{TeH})\text{Cr}(\text{CO})_5]^-$  was obtained from the decarbonylation complex,  $[\text{Cr}(\text{CO})_5\text{THF}]$ , produced by photochemical reaction, with  $\text{Na}_2\text{Te}$  in methanol, and the analogous  $[(\text{SeH})\text{Cr}(\text{CO})_5]^-$  was also obtained.  $[(\text{TeH})\text{Cr}(\text{CO})_5]^-$  could further react with the labile  $[\text{Cr}(\text{CO})_5\text{THF}]$  to form the  $\text{TeH}^-$ -bridged anionic dinuclear chromium complex  $[(\text{CO})_5\text{Cr}(\mu\text{-TeH})\text{Cr}(\text{CO})_5]^-$  [42]. These two kinds of mono- and dinuclear Te–Cr–CO anionic complexes have been studied by spectroscopic methods, but have not been characterized by X-ray analysis. A variety of novel carbonyltelluride chromium anionic cluster complexes **23–28** were afforded by varying the stoichiometry of  $\text{Cr}(\text{CO})_6$  and polytellurides under

different reaction conditions, which are summarized in Scheme 2 [43–45]. X-ray analysis showed that complex  $[\text{Te}_2\text{Cr}_4(\text{CO})_{18}]^{2-}$  (**23**) contained two  $\text{Cr}(\text{CO})_4$  fragments bridged by two tellurides generating a four-membered ring with a Cr–Cr bond and two tellurium atoms externally bonded to two  $\text{Cr}(\text{CO})_5$  groups. Complexes  $[\text{Te}_2\text{Cr}_4(\text{CO})_{20}]^{2-}$  (**24**) and  $[\text{Te}_3\text{Cr}_4(\text{CO})_{20}]^{2-}$  (**25**) were chain complexes consisting of four  $\text{Cr}(\text{CO})_5$  fragments bound to a di- and tri-telluride chain, respectively. Compared with the structure of **25**, complex  $[\text{Te}_3\text{Cr}(\text{CO})_5]^{2-}$  (**26**) also contained a  $\text{Te}_3^{2-}$  ligand but it was coordinated to one  $\text{Cr}(\text{CO})_5$  fragment in an end-on fashion. In complex  $[\text{Te}_2\{\text{Cr}(\text{CO})_5\}_2]^{2-}$  (**27**), the two  $\text{Cr}(\text{CO})_5$  fragments were

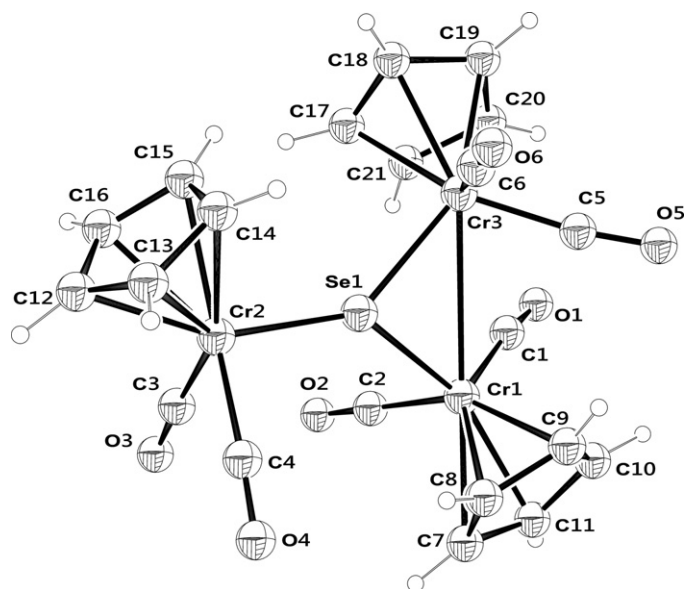
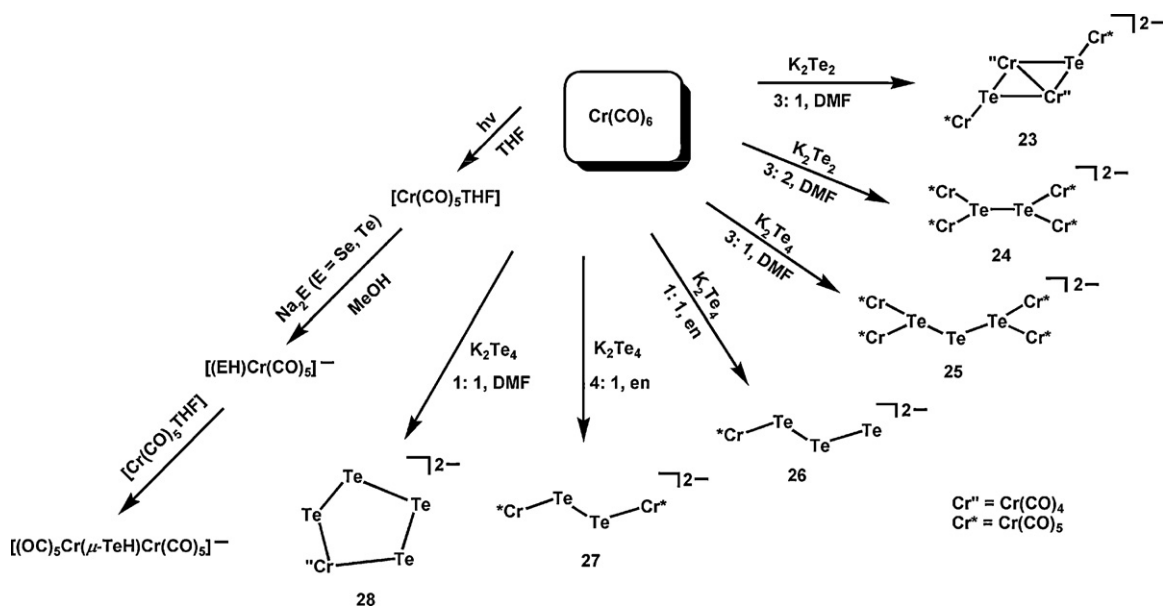


Fig. 1. ORTEP diagram of anion **21**.

Adapted from ref. [40].



Scheme 2. Using “Zintl ions” to form chromium carbonyl chalcogenide complexes.

bridged by a  $\text{Te}_2^{2-}$  ligand. In contrast with the chain complex **26**, complex  $[\text{Te}_4\text{Cr}(\text{CO})_4]^{2-}$  (**28**) exhibited a five-membered ring with the  $\text{Te}_4^{2-}$  chain coordinated to a  $\text{Cr}(\text{CO})_4$  fragment with a different reaction solvent.

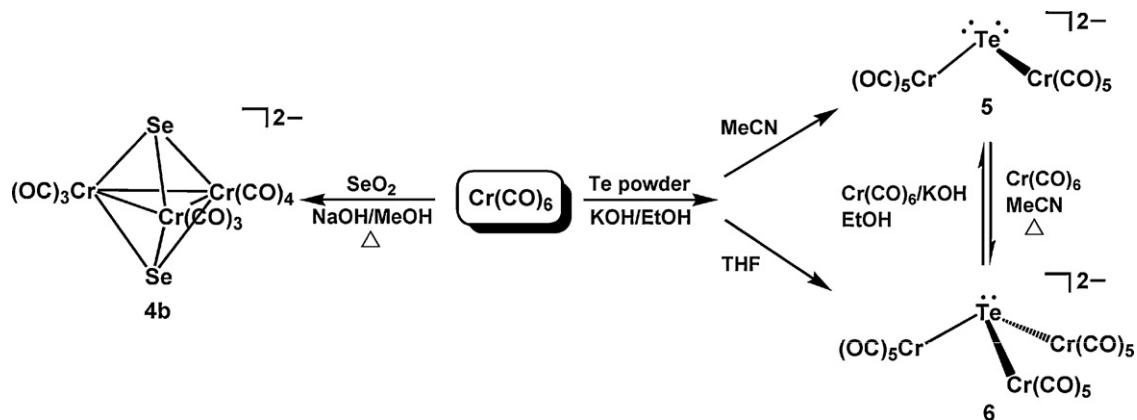
As mentioned above, some interesting carbonylchromium selenide and telluride anionic clusters have been reported [40–45]. However, the rational methodologies for anionic carbonylchromium chalcogenides have not been explored as thoroughly. We started our studies of the chemistry of anionic chromium carbonyl chalcogenide clusters by using the modified “Hieber’s synthesis” (Scheme 3). In 2001, we prepared the first example of the selenium-capping trichromium carbonyl anionic cluster  $[\text{Se}_2\text{Cr}_3(\text{CO})_{10}]^{2-}$  (**4b**), with three rare Cr–Cr bonds, from the reaction of  $\text{SeO}_2$  with  $\text{Cr}(\text{CO})_6$  in basic  $\text{NaOH}/\text{MeOH}$  solutions [14]. It was noted that **4b** was isolated only from the  $\text{NaOH}$ – $\text{MeOH}$  solutions, and not from the  $\text{KOH}$ – $\text{MeOH}$  solutions, due to the alkali-metal cation effect on the stabilization of the cluster anion **4b**. In the heavier telluride system, although several approaches to carbonylchromium polytelluride complexes using “Zintl” tellurides to react with  $\text{Cr}(\text{CO})_6$  in various organic solvents were reported, there were no feasible routes for the direct isolation of the chromium carbonyl monotelluride intermediates. We found that when  $\text{Te}$  powder was treated with 3 equiv of  $\text{Cr}(\text{CO})_6$  in a concentrated  $\text{KOH}/\text{EtOH}$  solution, the monotelluride complexes

$[\text{Te}\{\text{Cr}(\text{CO})_5\}_2]^{2-}$  (**5**) and  $[\text{Te}\{\text{Cr}(\text{CO})_5\}_3]^{2-}$  (**6**) were isolated on the basis of their different solubilities in THF and MeCN [15]. Complex **6** could transform to **5** in the presence of a  $\text{Cr}(\text{CO})_6/\text{KOH}/\text{EtOH}$  solution. Conversely, **5** could convert back to **6** upon reaction with  $\text{Cr}(\text{CO})_6$  in MeCN. Complexes **4b**, **5**, and **6** were shown to be very effective starting materials for further cluster-expansion reactions.

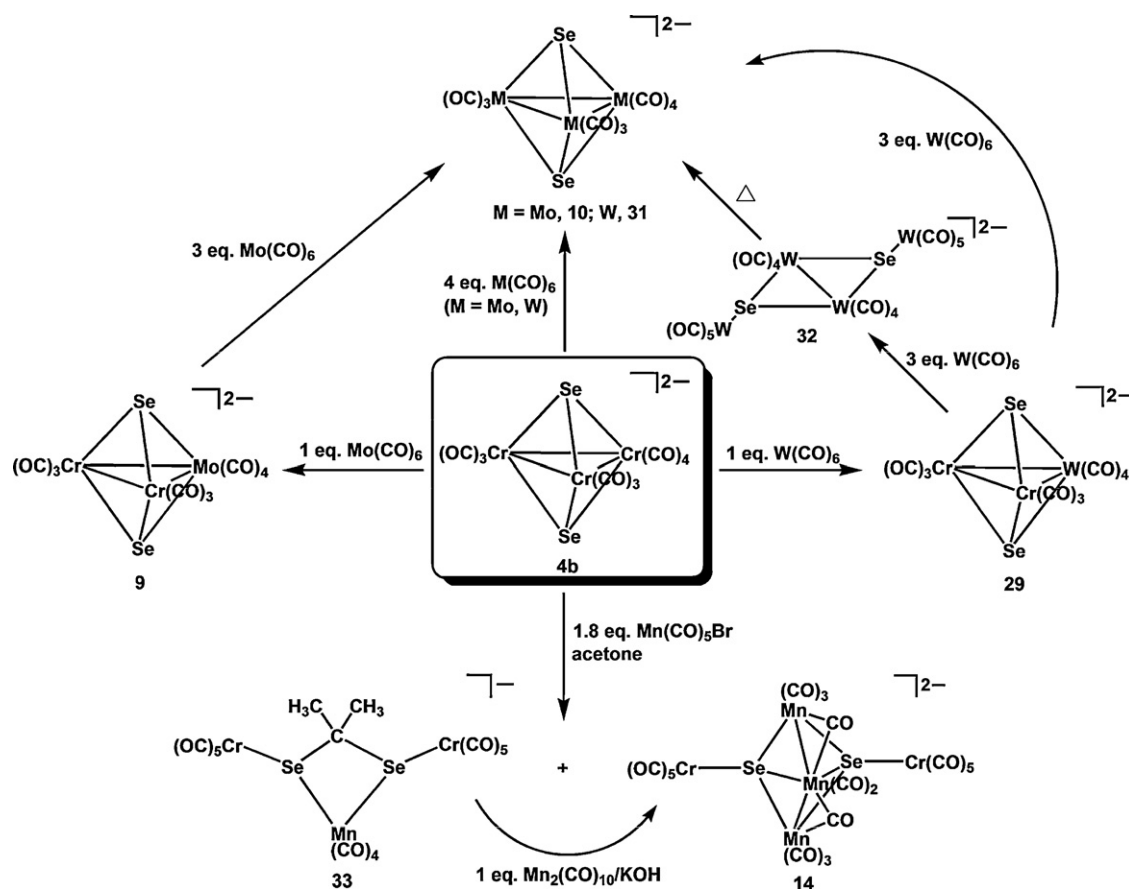
### 3.2. Reactivity

#### 3.2.1. Se–Cr clusters with metal carbonyls (Mo, W, Mn)

As determined by X-ray analysis, cluster **4b** possessed the  $\text{Cr}_3$  ring capped above and below by two  $\mu_3$ -Se atoms, with two chromium atoms coordinated with three COs and one chromium atom with four COs. It was noted that the average  $\text{Se}-\text{Cr}(\text{CO})_4$  distance (2.575(2) Å) was greater than the  $\text{Se}-\text{Cr}(\text{CO})_3$  distance (2.387(1) Å) [14], indicating the ease with which the  $\text{Cr}(\text{CO})_4$  group was replaced by other metal fragments. In addition, the electron-precise, trigonal-bipyramidal *closo*-cluster **4b** obeyed electron-counting rules, but was found to exhibit novel paramagnetic properties. The SQUID measurement showed that **4b** had the effective magnetic moment  $\mu_{\text{eff}} = 3.05\mu_{\text{B}}$  at 300 K, predicted for an  $S=1$  species. As shown in Scheme 4, cluster **4b** showed contrasting reactivity toward group 6 (Mo and W) and group 7



Scheme 3. Syntheses of chromium carbonyl chalcogenide complexes.



Scheme 4. Reactivities of **4b** toward group 6 and group 7 metal carbonyls.

(Mn) metal carbonyls, to afford a new series of group 6-containing selenide clusters [25,32].

Metal–metal-exchange reactions of complex **4b** with group 6 (Mo and W) in various ratios were carried out due to their differences in reactivity (see Scheme 4). Cluster **4b** reacted with 1 equiv of  $M(\text{CO})_6$  ( $M = \text{Mo}, \text{W}$ ) and produced mono-metal-substituted clusters  $[\text{Se}_2\text{Cr}_2\text{M}(\text{CO})_{10}]^{2-}$  ( $M = \text{Mo}, \mathbf{9}; \text{W}, \mathbf{29}$ ), respectively [25]. The trigonal–bipyramidal clusters **9** and **29** each exhibited a mixed-metal  $\text{Cr}_2\text{M}$  ring with the two chromium atoms each coordinated with three carbonyls and one hetero-metal ( $M = \text{Mo}, \text{W}$ ) with four carbonyls. The only Se–Cr–W complex reported in the literature,  $[\text{Cp}(\text{CO})_3\text{W}(\mu\text{-SeCH}_2\text{Ph})\text{Cr}(\text{CO})_5]$  (**30**), prepared from the reaction of  $[\text{Cp}(\text{CO})_3\text{WSeCH}_2\text{Ph}]$  with  $[\text{Cr}(\text{CO})_5(\text{THF})]$ , was a neutral complex in which the  $[\text{Cp}(\text{CO})_3\text{W}]$  fragment and the  $\text{Cr}(\text{CO})_5$  fragment were bridged by a  $\text{SeCH}_2\text{Ph}$  ligand [46]. In addition, when **4b** was treated with 4 equiv of  $M(\text{CO})_6$ , tri-metal-substituted clusters  $[\text{Se}_2\text{M}_3(\text{CO})_{10}]^{2-}$  ( $M = \text{Mo}, \mathbf{10}; \text{W}, \mathbf{31}$ ) were produced [25]. The isostructural **10** and **31** each possessed a homo- $\text{M}_3$  ring ( $M = \text{Mo}, \text{W}$ ), and they were the first examples of di-selenium-capped  $\text{Mo}_3$  and  $\text{W}_3$  carbonyl clusters. Complexes **10** and **31** were also obtained by the addition of 3 equiv of  $M(\text{CO})_6$  to complexes **9** and **29** via stepwise substitution. In contrast with the Cr–Mo system, the *arachno*-complex  $[\text{Se}_2\text{W}_4(\text{CO})_{18}]^{2-}$  (**32**) was isolated as an intermediate of the substitution reaction of *closo*-complex **4b** to *closo*-complex **31**, due to the lower reactivity of  $\text{W}(\text{CO})_6$  versus  $\text{Mo}(\text{CO})_6$  [25]. Complex **32** was similar to the Te-containing ring complex **23**, but was the first reported example of selenium-group 6  $\text{E}_2\text{M}_2$  ring clusters.

The formation of complexes **9**, **10**, **29**, and **31** could be related to the lower singly occupied molecular orbital (SOMO) of **4b** [47].

The calculation results showed that the lower-energy SOMO of **4b** had a significant contribution from the d orbitals of the Cr atom coordinated by four carbonyls, with some contribution from the d orbitals of the other two Cr atoms, and each was bound with three carbonyls (Fig. 2). Therefore, the  $\text{Cr}(\text{CO})_4$  fragment of **4b** would initially be a reactive site for the metal–metal-exchange reactions, which underwent complicated ring opening and re-forming to give the metal-substituted products **9**, **10**, **29**, and **31**.

As extended to the mixed group 6 (Cr) and 7 (Mn) system, **4b** reacted with 1.8 equiv of  $\text{Mn}(\text{CO})_5\text{Br}$  in acetone to produce two novel mixed-metal Cr–Mn selenide carbonyl clusters  $[\text{Me}_2\text{CSe}_2\text{Mn}(\text{CO})_4\{\text{Cr}(\text{CO})_5\}_2]^-$  (**33**) and  $[\text{Se}_2\text{Mn}_3(\text{CO})_{10}\{\text{Cr}(\text{CO})_5\}_2]^{2-}$  (**14**) [32]. The X-ray analysis showed that complex **33** consisted of two  $\text{SeCr}(\text{CO})_5$  fragments bridged by an isopropylene group and one  $\text{Mn}(\text{CO})_4$  fragment to generate a strained four-membered  $\text{Se}_2\text{Cr}_2\text{Mn}$  ring, in which the two  $\text{Cr}(\text{CO})_5$  moieties occupied the *syn* orientation because of the steric hindrance of the  $\text{Mn}(\text{CO})_4$  fragment, indicating **33** was a product that resulted from a novel C=O activation of acetone (Fig. 3a). Complex **14** was a cluster-expansion species containing a distorted  $\text{Se}_2\text{Mn}_3$  square-pyramidal core with each basal Se atom bound to one  $\text{Cr}(\text{CO})_5$  fragment (Fig. 3b). There have only been seven Se–Cr–Mn complexes reported in the literature to date [48]. Related examples include neutral complexes  $[\text{CpMn}(\text{CO})_2(\mu\text{-Se}_2)\text{Cr}(\text{CO})_5]$  (**34**) and  $[\text{CpMn}(\text{CO})_2(\mu_3\text{-Se}_2)\{\text{Cr}(\text{CO})_5\}_2]$  (**35**) [48a], consisting of one  $[\text{CpMn}(\text{CO})_2]$  and one or two  $\text{Cr}(\text{CO})_5$  fragments bridged by a  $\text{Se}_2$  ligand, which were obtained from the transmetalation of  $[\{\text{CpMn}(\text{CO})_2\}_2(\mu\text{-Se}_2)]$  with  $[\text{Cr}(\text{CO})_5\text{THF}]$ . Other interesting hetero-chalcogen Cr–Mn complexes  $[\{\text{Cp}^*\text{Cr}(\mu\text{-SPh})\}_2(\mu_3\text{-Se})\text{Mn}_2(\text{CO})_9]$  and  $[\{\text{Cp}^*\text{Cr}(\mu\text{-SPh})\}_2(\mu_4\text{-Se})\text{Mn}_2(\text{CO})_8]$

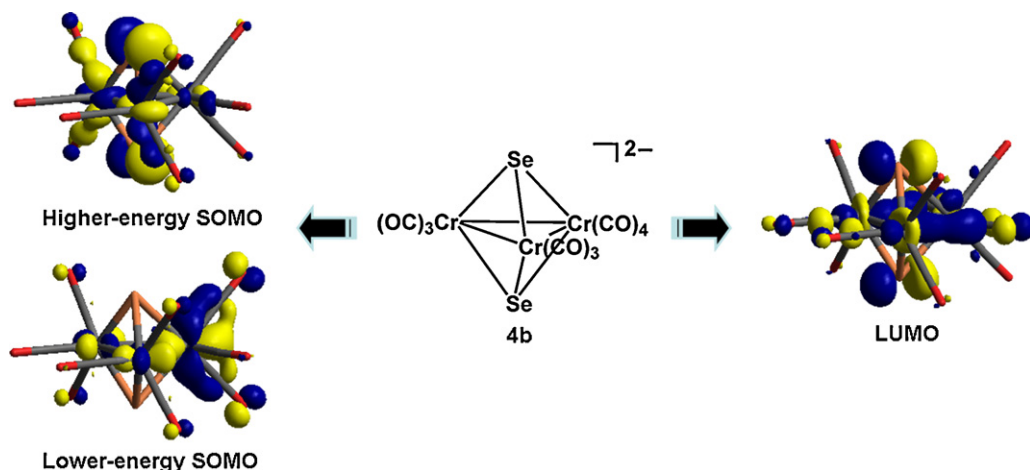


Fig. 2. Spatial plots of the selected frontier orbitals of **4b**.

Adapted from ref. [47].

(Cp' =  $\eta^5$ -CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>), with the bridging Se atom further coordinated to one or two Mn atoms of the Mn<sub>2</sub>(CO)<sub>x</sub> fragment, were formed by the photochemical reaction of [{Cp'Cr( $\mu$ -SPh)}<sub>2</sub>( $\mu$ -Se)] with Mn<sub>2</sub>(CO)<sub>10</sub> [48b].

While the formation of **9**, **10**, **29**, and **31** was controlled by the lower-energy singly occupied molecular orbital (SOMO) of **4b**, the selective formation of **33** and **14** was related to the higher-energy SOMO of **4b** (Fig. 1) [32]. The calculation results showed that the higher-energy SOMO of **4b** received a major contribution from the d orbitals of Cr atoms, each bound with three carbonyls, and the p orbitals of Se atoms. Thus, it was proposed that the less hindered "Se" sites of **4b** might undergo nucleophilic attack on the carbon center of acetone and/or the incoming [Mn(CO)<sub>5</sub>]<sup>+</sup> fragment, accompanied by complicated Se–Cr and Cr–Cr bond breakage and Se–C and Se–Mn or Mn–Mn formation, to give rise to **33** or **14**.

### 3.2.2. Te–Cr complexes with organic and inorganic electrophiles

As mentioned above, there are two or one lone pairs on the Te atom of **5** and **6**, and, therefore, the basicity of the Te atom toward a series of organic and inorganic electrophiles was investigated (see Scheme 5) [15,49]. When **5** was treated with a NaOH/MeOH solution, the dimeric ring complex **23** was formed presumably via further elimination of carbonyls from the open dimeric cluster **24** and subsequent bond re-formation under basic conditions. Surprisingly, when **6** was treated with NaOH/MeOH solution at 70 °C, the Te-methylated complex [MeTe{Cr(CO)<sub>5</sub>}<sub>2</sub>]<sup>−</sup> (**36**) was produced presumably via C–O activation of MeOH. The cleavage of the C–O bond of alcohol was further confirmed by the fact that the corresponding Et-substituted complex [EtTe{Cr(CO)<sub>5</sub>}<sub>2</sub>]<sup>−</sup> was obtained

from similar reaction conditions with the use of EtOH as the solvent. The acidification and methylation of complexes **5** and **6** were also investigated and compared (see Scheme 5), and the monohydrido complex [HTe{Cr(CO)<sub>5</sub>}<sub>2</sub>]<sup>−</sup> (**37**), **24**, **36**, and [MeTe{Cr(CO)<sub>5</sub>}<sub>3</sub>]<sup>−</sup> (**38**) as well as the dimethylated product [Me<sub>2</sub>Te{Cr(CO)<sub>5</sub>}<sub>2</sub>] (**39**) were formed under appropriate conditions.

Further reactions with dihaloalkanes were also studied. Complex **5** was found to be unstable in CH<sub>2</sub>Cl<sub>2</sub> and could react readily with CH<sub>2</sub>Cl<sub>2</sub> at 0 °C to give the Cl-functionalized product [ClH<sub>2</sub>CTe{Cr(CO)<sub>5</sub>}<sub>2</sub>]<sup>−</sup> (**40**). Complex **40** could then act as an electrophile, to react with **5** to give the CH<sub>2</sub>-bridged dimeric complex [H<sub>2</sub>CTe<sub>2</sub>{Cr(CO)<sub>5</sub>}<sub>4</sub>]<sup>2−</sup> (**41**), which could also be obtained directly by stirring **5** in CH<sub>2</sub>Cl<sub>2</sub> at room temperature. Similarly, the reaction of complex **6** with CH<sub>2</sub>Cl<sub>2</sub> at 0 °C formed the Cl-functionalized product [ClH<sub>2</sub>CTe{Cr(CO)<sub>5</sub>}<sub>3</sub>]<sup>−</sup> (**42**), while the same reaction at room temperature produced the CH<sub>2</sub>-bridged dimeric complex [H<sub>2</sub>CTe<sub>2</sub>{Cr(CO)<sub>5</sub>}<sub>6</sub>]<sup>2−</sup> (**43**). Like complex **40**, complex **42** could be easily transformed into complex **43** upon treatment with complex **6**. It was noted that the <sup>1</sup>H and <sup>13</sup>C NMR resonances of **42** and **40** or of **43** and **41** were close, indicating the comparable effect of the lone pair and the Cr(CO)<sub>5</sub> fragment.

As was the case with CH<sub>2</sub>Cl<sub>2</sub>, the reaction of complexes **5** and **6** with the bisbenzyl-dichloride ClH<sub>2</sub>C(C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CH<sub>2</sub>Cl formed corresponding bisbenzyl-bridged dimeric complexes [H<sub>2</sub>C(C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CH<sub>2</sub>Te<sub>2</sub>{Cr(CO)<sub>5</sub>}<sub>4</sub>]<sup>2−</sup> (**44**) and [H<sub>2</sub>C(C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CH<sub>2</sub>Te<sub>2</sub>{Cr(CO)<sub>5</sub>}<sub>6</sub>]<sup>2−</sup> (**45**). For further comparison, the Hg-bridged dimeric complexes [HgTe<sub>2</sub>{Cr(CO)<sub>5</sub>}<sub>4</sub>]<sup>2−</sup> (**46**) and [HgTe<sub>2</sub>{Cr(CO)<sub>5</sub>}<sub>6</sub>]<sup>2−</sup> (**47**) were also obtained from the reaction of **5** and **6** with ~0.5 equiv of HgCl<sub>2</sub>. It is interesting that

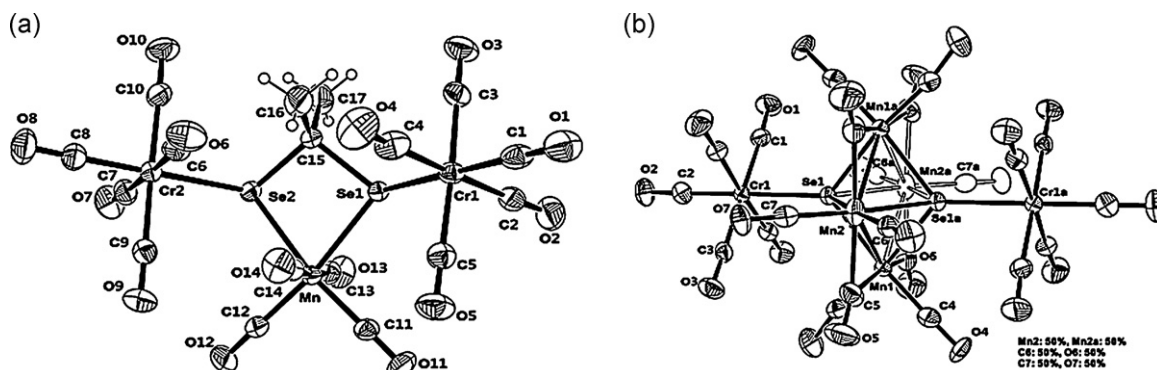
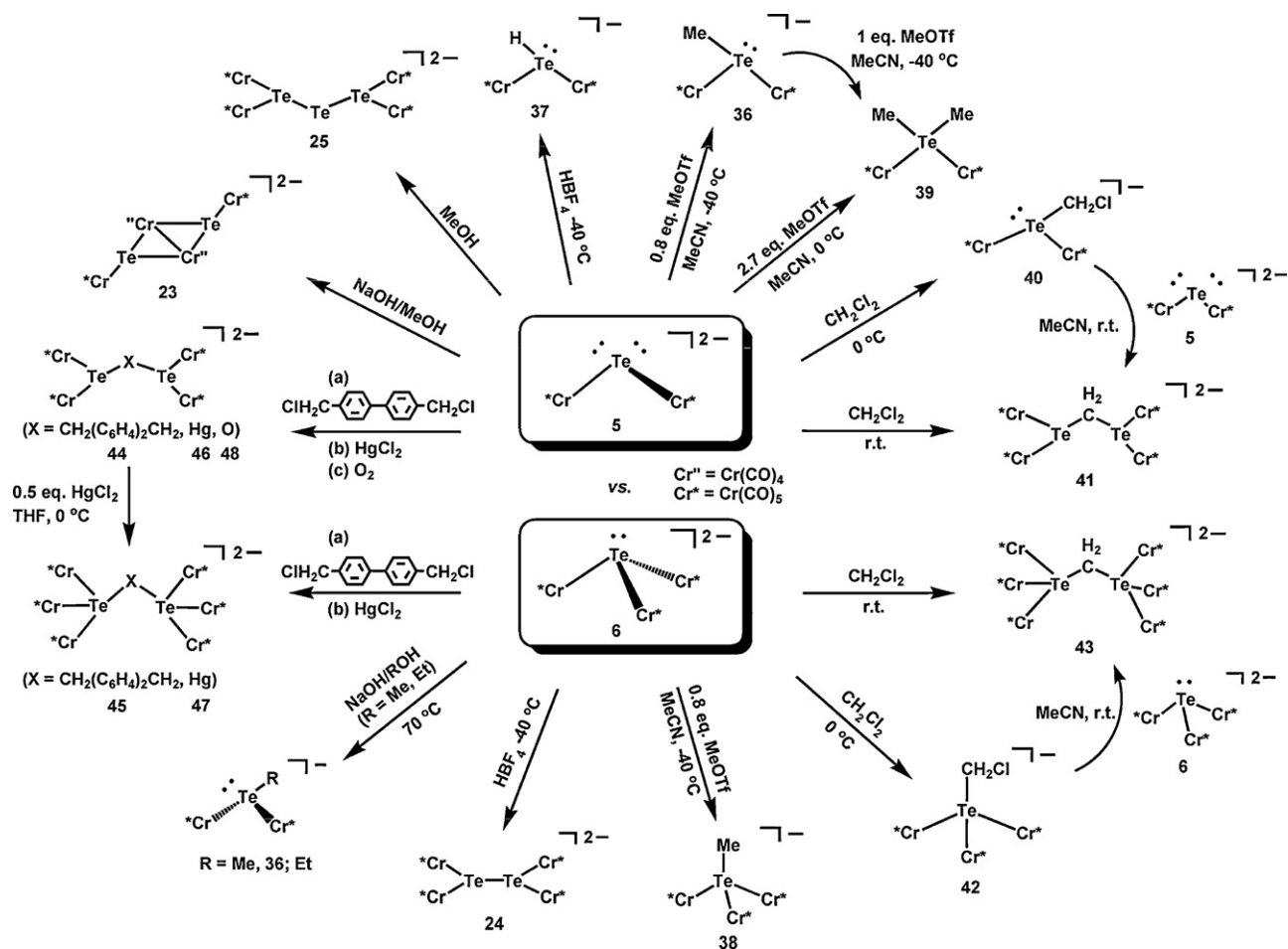
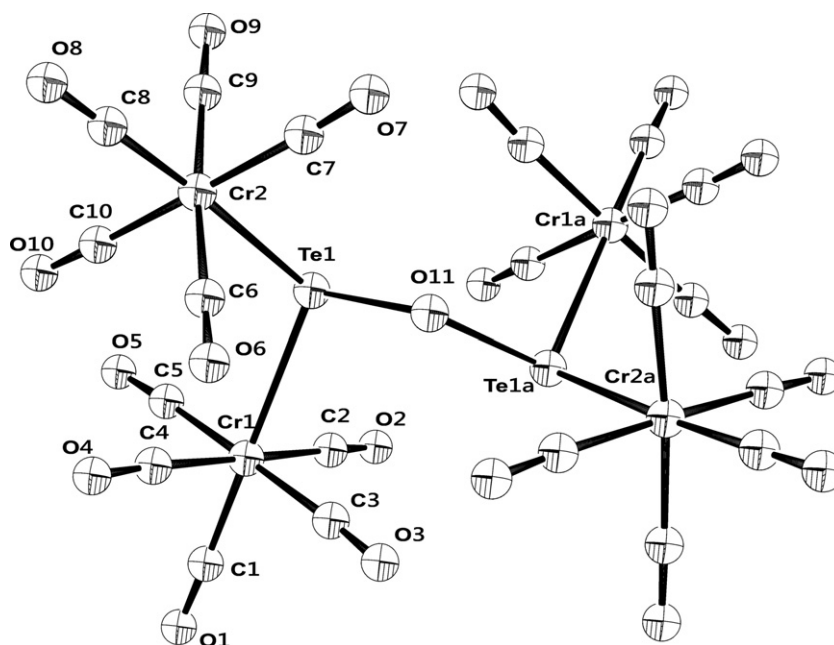


Fig. 3. (a) ORTEP diagram of anion **33** (b) ORTEP diagram of anion **14**.

Adapted from ref. [32].



Scheme 5. Reactivities of **5** or **6** toward a series of organic and inorganic electrophiles.Fig. 4. ORTEP diagram of anion **48**.

the novel O-bridged dimeric complex  $[\text{OTe}_2\{\text{Cr}(\text{CO})_5\}_4]^{2-}$  (**48**) was obtained from the reaction of **5** with  $\text{O}_2$ . This was a rare example of  $\text{O}_2$  activation by the Te–Te bond. The Te–O–Te bond angle of **48** was  $108.2(3)^\circ$  (Fig. 4), which was indicative of the tetrahedral geometry around the O center that was significantly larger than the Te–Te–Te angle ( $98.4(1)^\circ$ ) in the related  $\text{Te}_3$ -bridged complex **25**. This can be attributed to the diminished s-character of the atomic orbital of the central Te atom, caused by the larger size of Te versus O.

In summary, complexes **5** and **6** showed good affinity toward organic and inorganic electrophiles, to afford a large family of the  $\text{TeCr}_2$ - and  $\text{TeCr}_3$ -based monomeric and dimeric complexes (see Scheme 5) because of the existence of two or one lone pairs of the tellurium atom [15,49]. These interesting reactivities were related to the HOMOs of complexes **5** and **6**, each of which had a significant contribution (48% and 34%, respectively) from the p orbital of the central Te atom, and the slightly anti-bonding character between the p orbital of the Te atom and d orbitals of the Cr atom (Fig. 5) [49].

### 3.3. The homo- and hetero- $\text{E}_2\text{M}_3$ trigonal-bipyramidal clusters

As mentioned above, a series of selenium-containing group 6 homonuclear complexes **10** and **31** and heteronuclear complexes **9** and **29** were conveniently prepared from the trigonal-bipyramidal complex **4b** via metal–metal-exchanged reactions. A similar synthetic methodology was not applicable to the Te–Cr system. However, in the Te–Cr system, the open-structural complex **5** was used as a precursor for the construction of mixed-metal Cr–Mo and Cr–W telluride cluster complexes. As shown in Scheme 6 [50], the reaction of complex **5** with  $\text{M}(\text{CO})_6$  ( $\text{M} = \text{Mo}$ ,  $\text{W}$ ) in MeCN at  $65^\circ\text{C}$  yielded the mixed Cr–M ring complexes  $[\text{Te}_2\text{Cr}_2\text{Mo}_2(\text{CO})_{18}]^{2-}$  (**49**) and  $[\text{Te}_2\text{Cr}_2\text{W}_2(\text{CO})_{18}]^{2-}$  (**50**). Most significantly, the highly strained trigonal-bipyramidal complexes  $[\text{Te}_2\text{CrM}_2(\text{CO})_{10}]^{2-}$  ( $\text{M} = \text{Cr}$ , **4c**;  $\text{Mo}$ , **51**;  $\text{W}$ , **52**) could be produced, respectively, from the ring-closure reactions of **23**, **49**, and **50** in refluxing acetone solutions [50]. Complexes **4c**, **51**, and **52** represent the first examples of the di-tellurium-capped group 6 trimetallic carbonyl *closo*-clusters. Only a few examples of Te–Cr–W(Mo) complexes had been reported in the literature before the present study, and  $[(\text{CO})_5\text{W}(\text{TePh})_2\text{Cr}(\text{CO})_5]$  (**53**) was the only structurally characterized Te–Cr–W complex that displayed an open structure with the  $\text{W}(\text{CO})_5$  and the  $\text{Cr}(\text{CO})_5$  fragments bridged by a  $\text{Te}_2\text{Ph}_2$  ligand [51] (Scheme 6).

To summarize, there are two different synthetic routes to form a new family of homo- and hetero-nuclear group 6 trigonal-bipyramidal clusters **4b**, **4c**, **9**, **10**, **29**, **31**, **51**, and **52** (Chart 1). The  $(\text{Se})_2$ -capped mixed group 6 clusters were synthesized from the metal-exchange reaction of the  $\text{Se}_2\text{Cr}_3$ -cluster **4b** with appropriate amounts of  $\text{M}(\text{CO})_6$  ( $\text{M} = \text{Mo}$ ,  $\text{W}$ ) [25]. However,  $(\text{Te})_2$ -capped mixed group 6 clusters were only formed from the ring-closure reaction of the  $\text{Te}_2\text{M}_2$ -based ring complexes [50]. The difference between the Se and Te systems was probably due to the stronger Se–Cr versus Te–Cr bond, which made **4b** more susceptible to the metal substitution. Surprisingly complex **4b** exhibited paramagnetism, which could be responsible for its different reactivities toward groups 6 and 7 carbonyl fragments. It would be of interest to further investigate the reactivity, electronic, and magnetic as well as electrochemical properties of these  $\text{M}_3$ -tuned *closo*-clusters ( $\text{M}$ : group 6 metals). Moreover, rationally designed preparative routes will be systematically exploited by using such trigonal-bipyramidal  $\text{E}_2\text{M}_3$  clusters as starting materials with other transition metal fragments to form cluster-expanded structures.

Apart from the stepwise routes applied for the mixed Cr–M ( $\text{M} = \text{Mo}$ ,  $\text{W}$ ,  $\text{Mn}$ ) systems, direct synthesis, also called a “one-pot

reaction”, was also developed in the mixed Cr–Fe system, in which two unusual electron-rich mixed-metal carbonyl chalcogenide clusters  $[\text{E}_2\text{Cr}_2\text{Fe}(\text{CO})_{10}]^{2-}$  ( $\text{E} = \text{Se}$ , **54b**;  $\text{Te}$ , **54c**) were formed from the reaction of chalcogen powder with a mixture of  $\text{Cr}(\text{CO})_6$  and  $\text{Fe}(\text{CO})_5$  in concentrated  $\text{KOH}/\text{MeOH}$  solutions at  $35\text{--}40^\circ\text{C}$  (Scheme 7) [52]. Complexes **54b** and **54c** each displayed a trigonal-bipyramidal  $\text{E}_2\text{Cr}_2\text{Fe}$  core with a  $\text{Cr}_2\text{Fe}$  ring capped by two  $\mu_3$ -E atoms, and represented the first examples of the *closo*-trigonal-bipyramidal Cr–Fe chalcogenide clusters. A limited number of other Cr–Fe selenide and telluride complexes were also reported in the literature. The neutral complex  $[(\text{Se}_2)_2\text{CrFe}_2(\text{CO})_{10}]$  (**55**), produced from  $[\text{Se}_2\text{Fe}_2(\text{CO})_6]$  (**1b**) with  $[\text{Cr}(\text{CO})_5(\text{THF})]$ , was shown to consist of two  $\text{Fe}(\text{CO})_3$  and one  $\text{Cr}(\text{CO})_4$  fragments linked by two  $\mu_3$ - $\text{Se}_2$  moieties [53]. Furthermore, the reaction of  $[\text{Cp}_2\text{CrFe}(\text{CO})_5]$  with selenium powder [54] was reported to produce the  $\text{Se}_2$ -inserted neutral complex  $[(\mu\text{-Se}_2)\text{Cp}_2\text{CrFe}(\text{CO})_4]$  (**56**). Another interesting hetero-chalcogen Cr–Fe cluster,  $[\{(\mu_3\text{-S})_2\text{FeCp}_2\text{Cr}_2(\mu\text{-S}^t\text{Bu})_2(\mu\text{-Se})_2\}]$  (**57**), was synthesized from  $[\{(\mu_3\text{-S})_2\text{Fe}(\text{CO})_3\text{Cp}_2\text{Cr}_2(\mu\text{-S}^t\text{Bu})\}]$  [55] with an excess amount of selenium powder [56], in which **57** consisted of two  $\text{S}_2\text{Cr}_2\text{Fe}$ -based trigonal-pyramidal clusters connected via the Fe–Fe bond and two selenium atoms. At last, the Te-containing Cr–Fe–Nb complex,  $[\{\text{Cp}'_2\text{NbH}(\text{Te})_2\text{Fe}_2(\text{CO})_6\}[\text{Cr}(\text{CO})_5]$  ( $\text{Cp}' = {}^t\text{BuC}_5\text{H}_4$ ) (**58**) was an adduct from  $[\{\text{Cp}'_2\text{NbH}(\text{Te})_2\}\text{Fe}_2(\text{CO})_6]$  with  $[\text{Cr}(\text{CO})_5(\text{THF})]$  [57].

## 4. Group 7 (Mn) carbonyl clusters

### 4.1. E–Mn clusters ( $\text{E} = \text{S}$ , $\text{Se}$ )

Although neutral manganese carbonyl chalcogenide or organochalcogenide complexes have been widely investigated [4b,5c,58–60], the chemistry of anionic manganese carbonyl chalcogenide complexes is comparatively scarce [5a,5d,5j]. In 1990, the chair-like manganese selenide complexes  $[(\text{Se}_2)_2\text{Mn}_2(\text{CO})_6]^{2-}$  (**59**) and  $[(\text{Se}_4)_2\text{Mn}_2(\text{CO})_6]^{2-}$  (**60**) were synthesized from the reactions of soluble “Zintl” polyselenides and  $\text{Mn}_2(\text{CO})_{10}$  in DMF [61]. The paramagnetic square-pyramidal cluster  $[\text{Se}_2\text{Mn}_3(\text{CO})_9]^{2-}$  (**61b**) was also reported to be synthesized from the reaction of  $\text{Se}^{2-}$  with  $\text{Mn}_2(\text{CO})_{10}$  in THF [62]. On the other hand, the useful starting material  $[(\text{S}_2)\text{Mn}_2(\text{CO})_7]$  (**62**) [63] was produced from the reaction of thiirane with  $\text{Mn}_2(\text{CO})_9(\text{MeCN})$  involving the transfer of the sulfur atom to manganese carbonyl. Complex **62** could be further reduced by sodium amalgam to give  $[(\text{S}_2)_2\text{Mn}_3(\text{CO})_{10}]^-$  (**12a**) which was shown to have two  $\text{Mn}(\text{CO})_3$  moieties doubly bridged by two  $\text{S}_2$  fragments that were further bonded to a  $\text{Mn}(\text{CO})_4$  group [28]. In addition, manganese sulfide anionic complexes  $[(\text{SH})_3\text{Mn}_2(\text{CO})_6]^-$  (**63**) and  $[(\text{S}_2)_2(\text{SH})\text{Mn}_3(\text{CO})_9]^{2-}$  (**64**) were obtained from ethanothral synthesis, while the trimanganese dichalcogenide clusters  $[(\text{E}_2)_2\text{Mn}_3(\text{EMe})(\text{CO})_9]^{2-}$  ( $\text{E} = \text{S}$ ,  $\text{Se}$ ,  $\text{Te}$ ) were produced methanothermally [64,5d]. In addition, the trimanganese anionic cluster  $[\text{S}_2\text{Mn}_3(\text{CO})_9]^-$  (**7a**) was synthesized from the reaction of 5-phenyl-1,3,4-oxathiazol-2-one with  $[\text{Mn}(\text{CO})_5]^-$  (Scheme 8) [65].

In this E–Mn system ( $\text{E} = \text{S}$  or  $\text{Se}$ ), several facile routes were successfully developed to a series of sulfur- and selenium–manganese carbonylates from the modified “Hieber’s synthesis” (Scheme 9). As shown in Scheme 9, the reactions of  $\text{Mn}_2(\text{CO})_{10}$  and sulfur or selenium in various ratios in  $\sim 1\text{ M}$   $\text{KOH}/\text{MeOH}$  produced a family of manganese carbonyl chalcogenide anions, trigonal-bipyramidal clusters  $[\text{E}_2\text{Mn}_3(\text{CO})_9]^-$  ( $\text{E} = \text{S}$ , **7a**;  $\text{Se}$ , **7b**), chair-like complexes  $[\text{C}_2\text{E}_8\text{Mn}_2(\text{CO})_6]^{2-}$  ( $\text{E} = \text{S}$ , **65a**;  $\text{Se}$ , **65b**), and octahedral clusters  $[\text{E}_2\text{Mn}_4(\text{CO})_{12}]^{2-}$  ( $\text{E} = \text{S}$ , **18a**;  $\text{Se}$ , **18b**) [16]. However, recently, when Se was treated with  $\text{Mn}_2(\text{CO})_{10}$  in a 4:3 molar ratio in 4 M  $\text{KOH}/\text{MeOH}$ , the paramagnetic square-pyramidal cluster **61b** was obtained [66]. More interestingly, if the molar ratio was changed

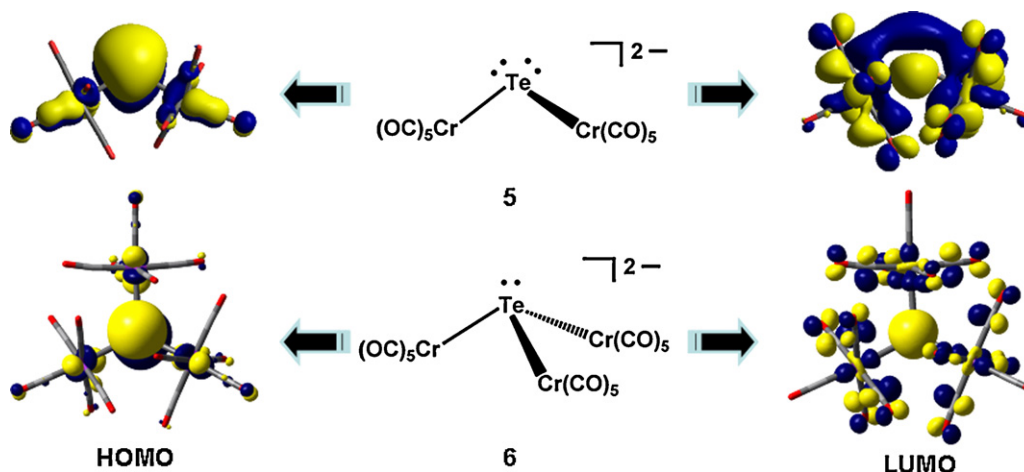
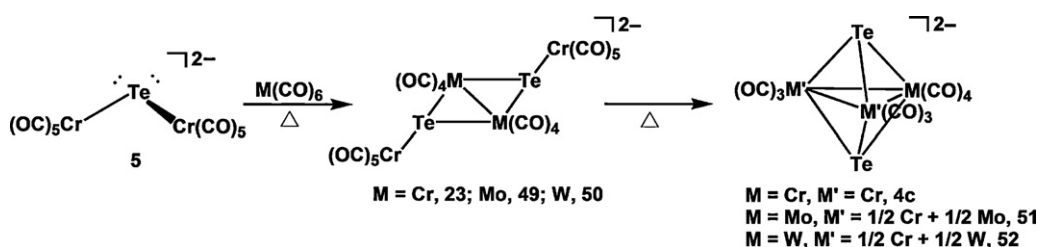


Fig. 5. Spatial plots of the selected frontier orbitals of 5 and 6.

Adapted from ref. [49].

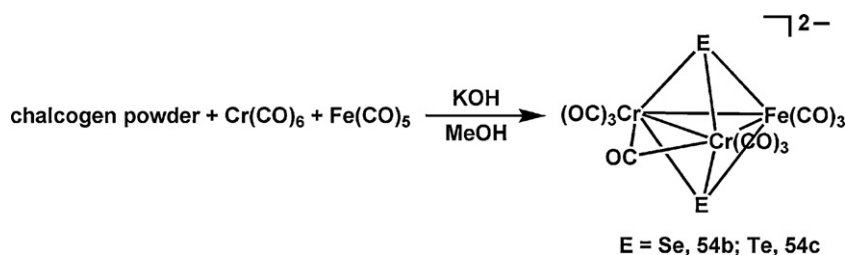


Scheme 6. The stepwise construction of homo- and hetero-nuclear group 6 carbonyl telluride complexes.

to 10:3, a novel electron-precise paramagnetic hexamanganese carbonyl selenide cluster  $[\text{Se}_6\text{Mn}_6(\text{CO})_{18}]^{4-}$  (**19**) was produced (Scheme 9) [35]. These results indicate that both the molar ratio and the concentration of the base play key roles in determining the resultant clusters. The chair-like complex  $[\text{C}_2\text{S}_8\text{Mn}_2(\text{CO})_6]^{2-}$  (**65a**) was also reported by Alper et al. from the treatment of  $[\text{Mn}_2(\text{CO})_9\text{Br}]^-$  with sulfur [67]. Complexes **65a** and **65b** were shown to consist of two  $\text{Mn}(\text{CO})_3$  moieties bridged by two  $\mu\text{-}\eta^2\text{-C}(\text{E})_2(\text{E}_2)$  fragments, which should arise from deoxygenation of the manganese carbonyl, and which might be somewhat related to the reduction of CO to carbide atoms in the iron clusters [68]. There are rare examples of  $\text{C}(\text{E})_2(\text{E}_2)^{2-}$  ( $\text{E}=\text{S}, \text{Se}$ ) fragments as ligands in metal complexes. Complexes **65a** and **65b** represented the first examples of the  $\text{C}(\text{E})_2(\text{E}_2)^{2-}$  fragment incorporated into metal carbonyls. Another  $\text{E}_2\text{Mn}_2$ -chair-like structure was seen in  $[\text{S}_2\text{Mn}_2(\text{CO})_6\{\text{SMn}(\text{CO})_4\text{AsMe}_2\text{Ph}\}_2]$  [63]. Besides, the high-nuclearity cluster **19** was composed of two  $\text{Se}_2\text{Mn}_3(\text{CO})_9$  units linked by a  $\mu_4\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-Se}_2^{2-}$  ligand in which one of the three Mn atoms was octahedrally coordinated and the other two Mn atoms were seven-coordinated with a direct Mn–Mn interaction (Fig. 6). The average Mn–Mn distance of **19** (2.695(2) Å) was slightly shorter than that found in **7b** (2.83(2) Å) but close to those in

**61b** (2.76(6) Å) and **18b** (2.703(8) Å),  $[\text{Se}_2\text{Mn}_2(\text{CO})_5(\text{PPh}_3)_2]$  (**66**) (2.702(2) Å) [58f], and  $[(\text{SePh})_2\text{Mn}_2(\text{CO})_5(\text{PPh}_3)_2]$  (**67**) (2.6952(7) Å) [60e]. The Se–Se distance of **19** (2.394(1) Å), which was similar to that of a Se–Se single bond (2.34 Å) but longer than that of a Se=Se double bond (2.19 Å), was slightly longer than those in the related compounds **59** (2.327(3) Å), **60** (2.36(4) Å), **65b** (2.357(2) Å), and  $[(\text{Se}_2)\text{MnMo}(\text{CO})_5\text{Cp}]$  (**68b**) (2.3144(6) Å) [69a], indicating a weaker Se–Se bonding in complex **19**.

Controlled cluster transformations of E–Mn clusters (E=S, Se) mentioned above were accomplished to elucidate their structural relationships (Scheme 10). When the concentration of the base was low ( $\sim 1$  M), the trigonal-bipyramidal cluster **7a(7b)** would react with chalcogen powder in the appropriate ratio to convert to the chair-like complex **65a(65b)**, which was further transformed into the octahedral complex **18a(18b)** by treatment with  $\text{Mn}_2(\text{CO})_{10}/\text{KOH}$  in MeOH/ $\text{CH}_2\text{Cl}_2$  solutions. Complex **65a(65b)** was therefore proposed as an intermediate for the transformation of cluster **7a(7b)** to **18a(18b)**. In addition, cluster **7b** was able to transform into the square-pyramidal cluster **61b** upon treatment with 4M KOH/MeOH/MeCN solutions. Cluster **61b** was a 49-electron species that fell one-electron short of the value required by the electron-counting rule for a species possessing three metals



Scheme 7. One-pot reaction for mixed Cr–Fe carbonyl chalcogenide clusters.

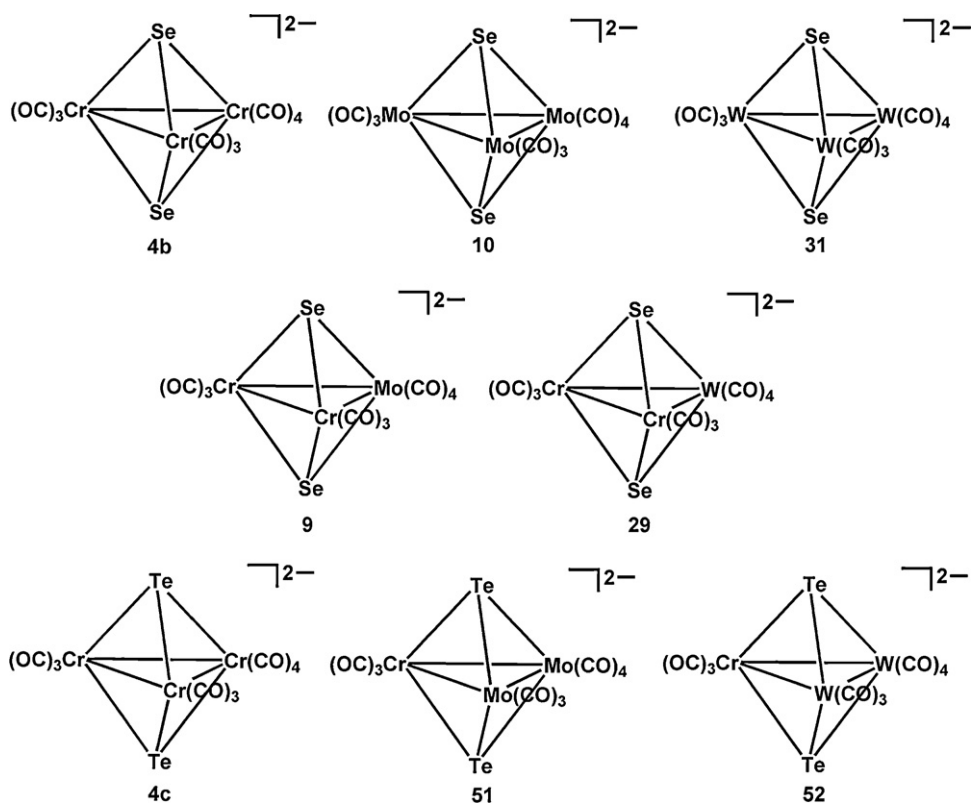
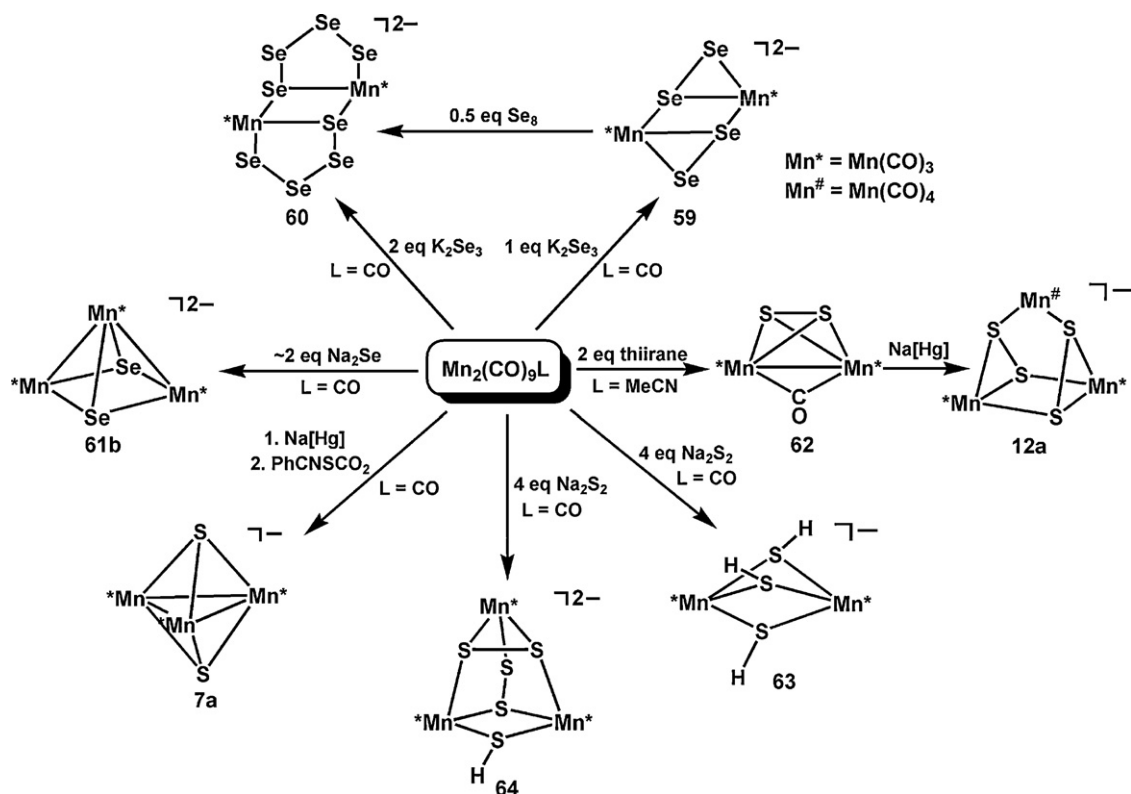
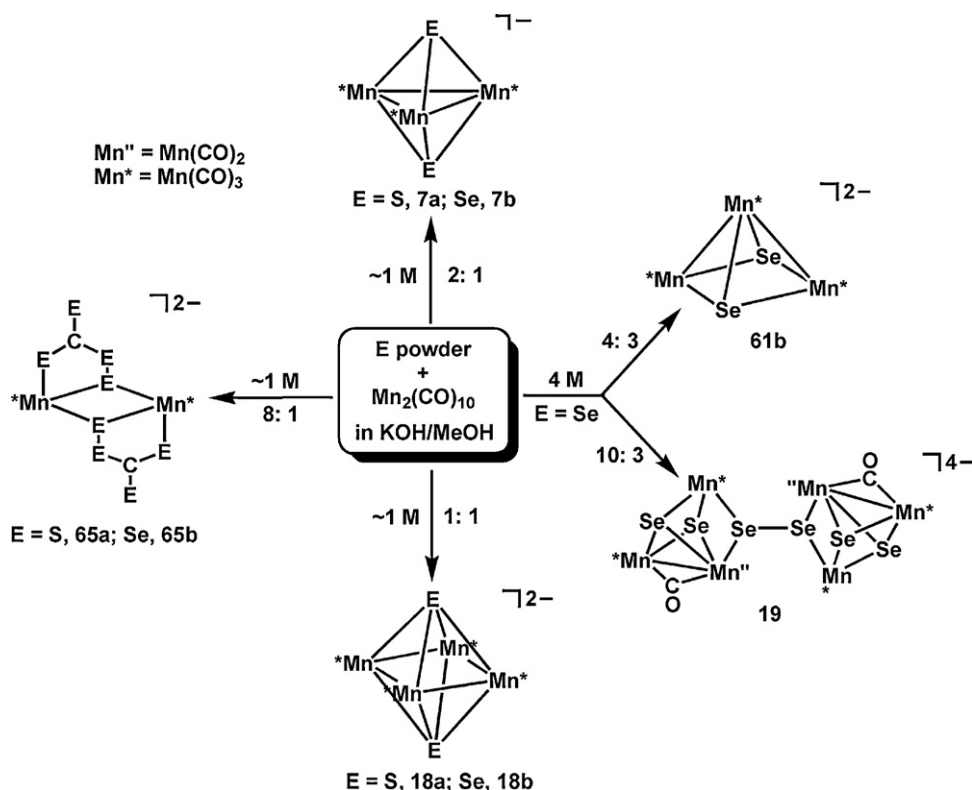


Chart 1. A family of homo- and hetero-nuclear group 6 trigonal-bipyramidal chalcogenide clusters.



Scheme 8. Using different chalcogen sources to form manganese carbonyl chalcogenide complexes.



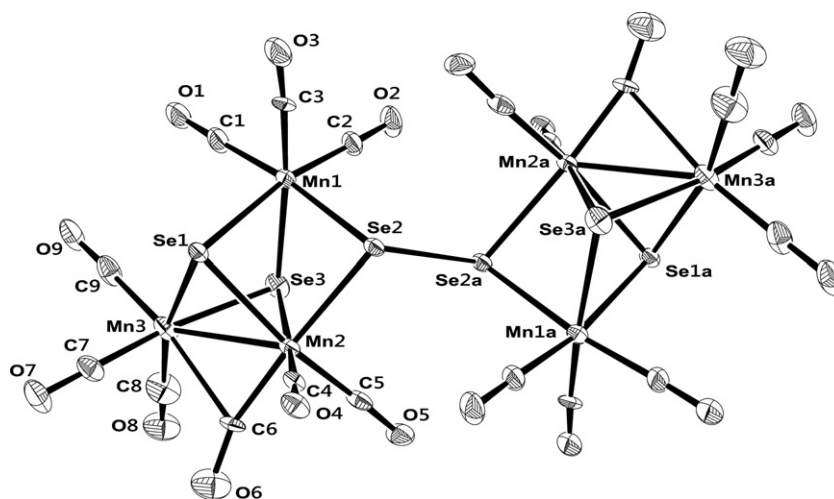
**Scheme 9.** Using the modified “Hieber’s synthesis” to form manganese carbonyl chalcogenide complexes.

with two metal–metal bonds. Hence, cluster **61b** could be oxidized with 1 equiv of  $[\text{Cu}(\text{MeCN})_4][\text{BF}_4]$  in MeCN to afford the trigonal-bipyramidal cluster **7b**. However, **7b** could undergo further cluster expansion with 1 equiv of Se powder in concentrated KOH/MeOH/MeCN solutions to form the Se-inserted larger cluster **19**. Conversely, cluster **19** was reconverted to **7b** or **61b** upon treatment with  $[\text{Cu}(\text{MeCN})_4][\text{BF}_4]$  or  $\text{Mn}_2(\text{CO})_{10}/\text{KOH}$ , respectively [16,66].

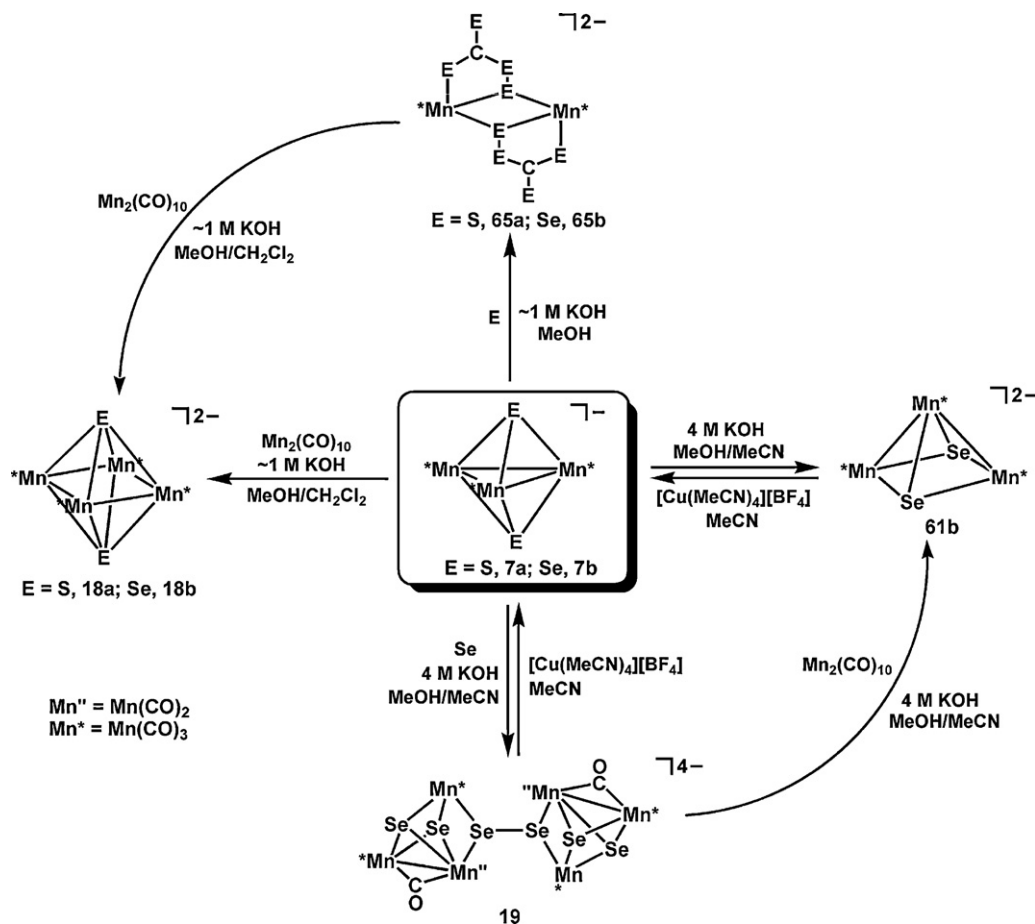
#### 4.2. Reactivity of Se–Mn clusters

The dichalcogenide-manganese carbonyl complexes are known to have a high affinity toward small molecules or metal fragments [4b,5c,5f]. The dimanganese disulfide complex  $[(\text{S}_2)\text{Mn}_2(\text{CO})_7]$  (**62**)

reportedly transformed into two higher-nuclearity complexes,  $[(\text{S}_2)_2\text{Mn}_4(\text{CO})_{15}]$  (**69**) and  $[(\text{S}_2)_2\text{Mn}_4(\text{CO})_{14}(\text{MeCN})]$  (**70**), upon the addition of CO or MeCN, respectively [70]. Complex **69** was also produced from the reaction of  $[(\text{SSnMe}_3)_2\text{Mn}_2(\text{CO})_8]$  with iodine via cleavage of the  $\text{SnMe}_3$  groups [58a]. Complex **62** added Co-, Rh-, and Pt-fragment moieties across the S–S bond to form a series of metal-incorporated  $\text{S}_2\text{Mn}_2$ -based complexes [71]. In addition, while complex **62** reacted with  $[\text{CpNi}(\text{CO})_2]$  to form the paramagnetic complex  $[(\text{S}_2)\text{Mn}(\text{CO})_3(\text{NiCp})_2]$  (**71a**) and the hexanuclear metal complex  $[(\text{S}_2)(\text{S}_2)\text{Mn}_4(\text{CO})_{14}(\text{NiCp})_2]$  [72], its reaction with  $[\text{CpMo}(\text{CO})_3]_2$  yielded the metal-exchange product  $[(\text{S}_2)\text{MnMo}(\text{CO})_5\text{Cp}]$  (**68a**) [69b]. Complex **68a** and its Se analogue  $[(\text{Se}_2)\text{MnMo}(\text{CO})_5\text{Cp}]$  (**68b**) can also react with small organic molecules or transition metal complexes via



**Fig. 6.** ORTEP diagram of anion **19**.



**Scheme 10.** Controlled cluster transformations of manganese carbonyl chalcogenide complexes.

the oxidative addition across the E–E bond (Scheme 11) [69,73].

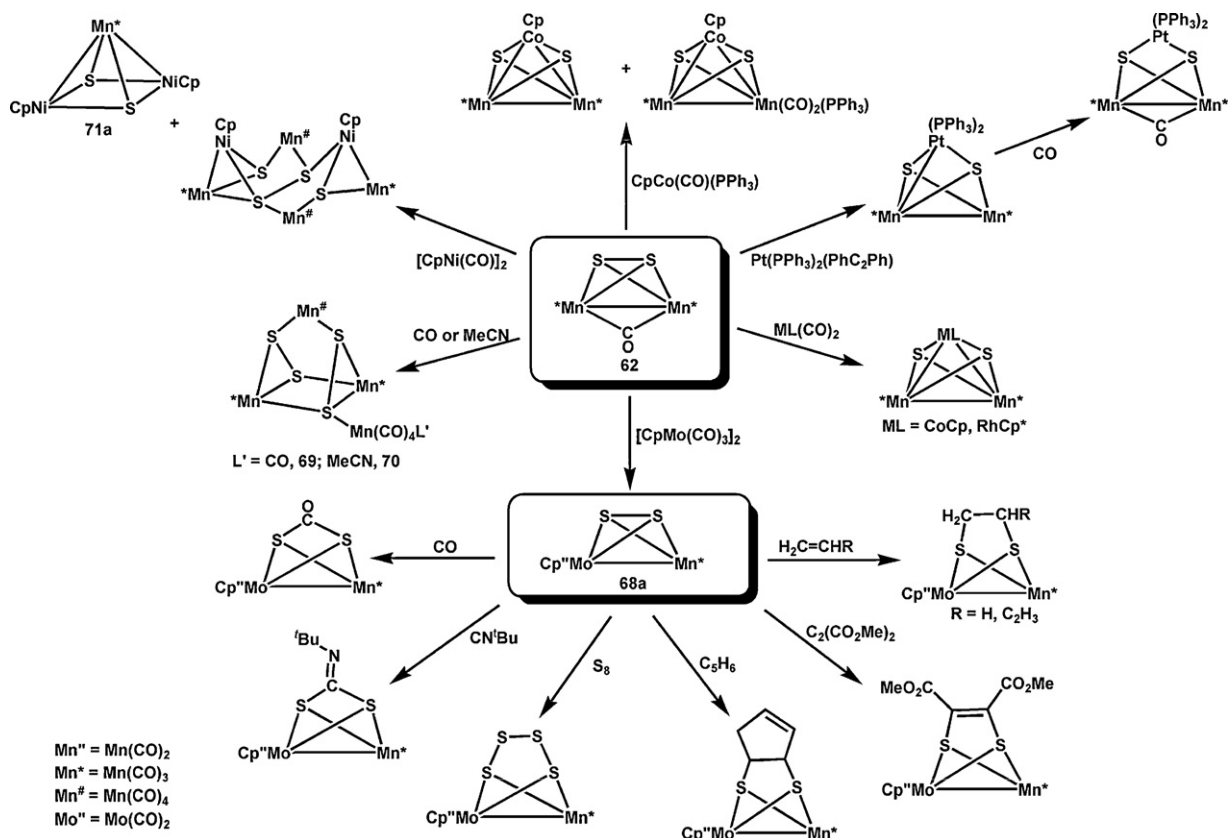
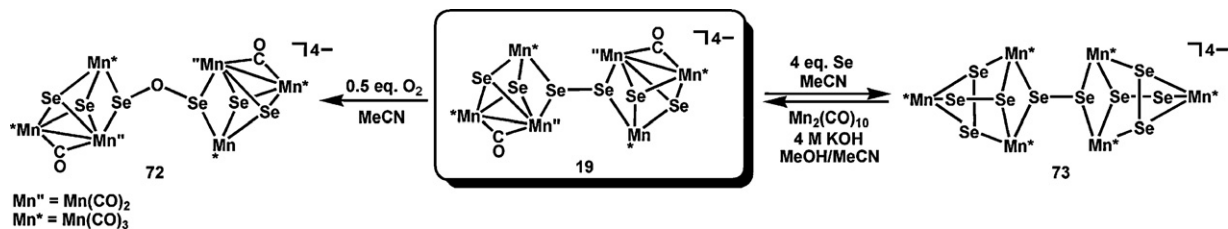
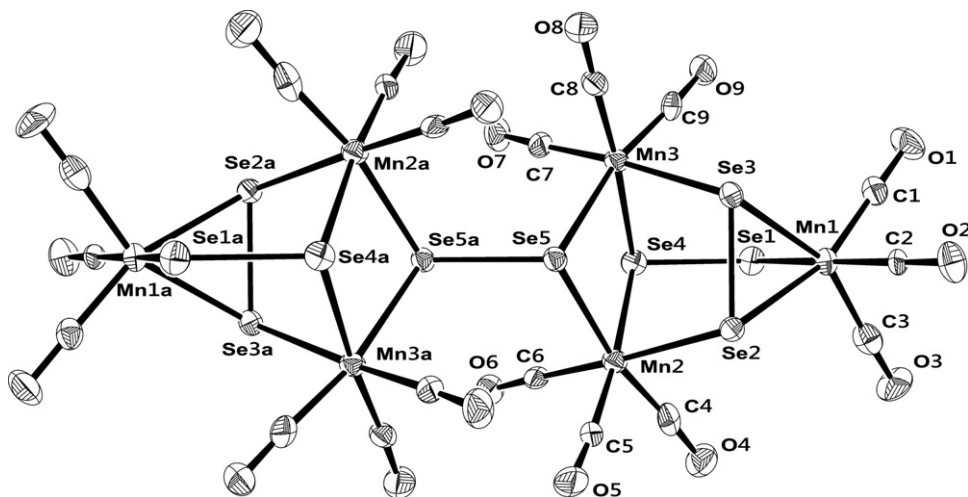
Although the E–E bond of many iron and manganese carbonyl dichalcogenide complexes can activate small molecules or metal fragments [4b,5c,69], the reactivity of the Se–Se bond of the paramagnetic hexamanganese cluster **19** toward O<sub>2</sub> is worthy of mention. Very recently, the novel complex **19** exhibited contrasting reactivity toward O<sub>2</sub> and selenium [35] (Scheme 12). Cluster **19** could add 0.5 equiv of O<sub>2</sub> across the Se–Se bond to form the O-inserted cluster [Se<sub>6</sub>Mn<sub>6</sub>(CO)<sub>18</sub>(O)]<sup>4-</sup> (**72**), whereas cluster **19** reacted with 4 equiv of selenium to form the Se-rich, dumbbell-like product [Se<sub>10</sub>Mn<sub>6</sub>(CO)<sub>18</sub>]<sup>4-</sup> (**73**). The formation of cluster **73** can be regarded as the insertion of Se atoms into the Se–Mn and Mn–Mn bonds of cluster **19**, accompanied by the Se–Se bond formation. Cluster **73** was reconverted back to **19** by treatment with Mn<sub>2</sub>(CO)<sub>10</sub> in 4 M KOH/MeOH/MeCN solutions. Besides cluster **19**, the O- and Se-inserted clusters **72** and **73** are all electron-precise species and have exhibited surprising paramagnetic properties, which will be discussed later (Section 7.2).

X-ray analysis showed that complex **72** was composed of two Se<sub>2</sub>Mn<sub>3</sub>(CO)<sub>9</sub> units bridged by an η<sup>2</sup>-Se<sub>2</sub>O fragment with the O atom inserted between two Se atoms. The isomeric η<sup>2</sup>-Se<sub>2</sub>O was also observed in [Ir(Se<sub>2</sub>O)(dppe)<sub>2</sub>]<sup>+</sup> produced from [Ir(Se<sub>2</sub>)(dppe)<sub>2</sub>]<sup>+</sup> with peracetic acid [74]. It was noted that the sum of the covalent bond radii for selenium and oxygen is 1.90 Å, and, therefore, the average Se–O bond in cluster **72** (1.99(1) Å) could be considered a normal single bond. In addition, the Se–O–Se bond angle was 106.2(3)°, indicating tetrahedral geometry around the O center. The dumbbell-like cluster **73** was composed of two (μ<sub>3</sub>-Se<sub>2</sub>)<sub>2</sub>Mn<sub>3</sub>(CO)<sub>9</sub> moieties bridged by a Se<sub>2</sub><sup>2-</sup> linkage, and the six Mn

atoms in **73** were nonbonded (Mn...Mn, 3.665(3) to 4.244(3) Å), and were held together by five Se<sub>2</sub><sup>2-</sup> units to generate three different bonding modes: μ<sub>4</sub>-η<sup>1</sup>:η<sup>1</sup>:η<sup>1</sup>:η<sup>1</sup>-, μ<sub>3</sub>-η<sup>1</sup>:η<sup>1</sup>:η<sup>1</sup>-, and μ<sub>3</sub>-η<sup>1</sup>:η<sup>1</sup>:η<sup>2</sup>-Se<sub>2</sub><sup>2-</sup> (Fig. 7).

The contrasting reactivities of cluster **19** toward O<sub>2</sub> and selenium were also examined using DFT calculations. As shown in Fig. 8, the higher-energy SOMO of **19** was mainly composed of the anti-bonding interaction of the *p*-orbitals of the Se<sub>2</sub>-linkage, which interacted with the π\* orbital of the incoming O<sub>2</sub> molecule followed by the insertion of the *p*-like orbital of one of two oxygen atoms into the Se–Se bond to form the O-bridged cluster **72**. Instead of forming the analogue Se of **72**, the treatment of **19** with selenium to give cluster **73** was related to the lower-energy SOMO of cluster **19**. This orbital had major contributions from the *s* and *d* orbitals of the Mn atoms and *p* orbitals of the Se atoms of the two Se<sub>2</sub>Mn<sub>3</sub>(CO)<sub>9</sub> units, in which the overlaps between the terminal Mn atoms and the two nearby Se or Mn atoms were not significant. Thus, it is reasonable to propose that this orbital might be a reactive site for the reaction of cluster **19** with Se to produce the Se-rich cluster **73** [35].

Further reactivities of clusters **19** and **73** with different electrophiles such as [Cu(MeCN)<sub>4</sub>][BF<sub>4</sub>] or Mn(CO)<sub>5</sub>Br were also investigated [66]. Basically, these reactions of **19** and **73** with Mn(CO)<sub>5</sub>Br led to the formation of [Se<sub>5</sub>Mn<sub>4</sub>(CO)<sub>12</sub>]<sup>2-</sup> (**74**) and [Se<sub>4</sub>Mn<sub>3</sub>(CO)<sub>10</sub>]<sup>-</sup> (**12b**). However, the reaction of **73** with [Cu(MeCN)<sub>4</sub>][BF<sub>4</sub>] formed **74** and **12b**, while a similar reaction of **19** produced the trigonal-bipyramidal Se<sub>2</sub>Mn<sub>3</sub>-cluster **7b** (Scheme 13). Cluster **74** consisted of four Mn(CO)<sub>x</sub> fragments bridged by two Se<sub>2</sub> and one Se ligand. Cluster **12b** was isostructural to **12a** and structurally similar to the organic quadricyclane, [(Se<sub>2</sub>)<sub>2</sub>CrFe<sub>2</sub>(CO)<sub>10</sub>] (**55**), and [(Se<sub>2</sub>)<sub>2</sub>Fe<sub>3</sub>(CO)<sub>10</sub>]<sup>2+</sup> [53,75]. These

Scheme 11. Reactivities of **62** or **68a** toward small molecules or metal fragments.Scheme 12. Selective reactivity of **19** toward  $\text{O}_2$  and selenium.Fig. 7. ORTEP diagram of anion **73**.

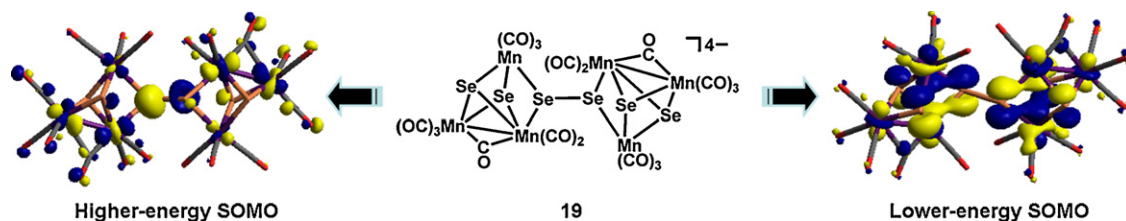


Fig. 8. Spatial plots of the selected frontier orbitals of cluster **19**.

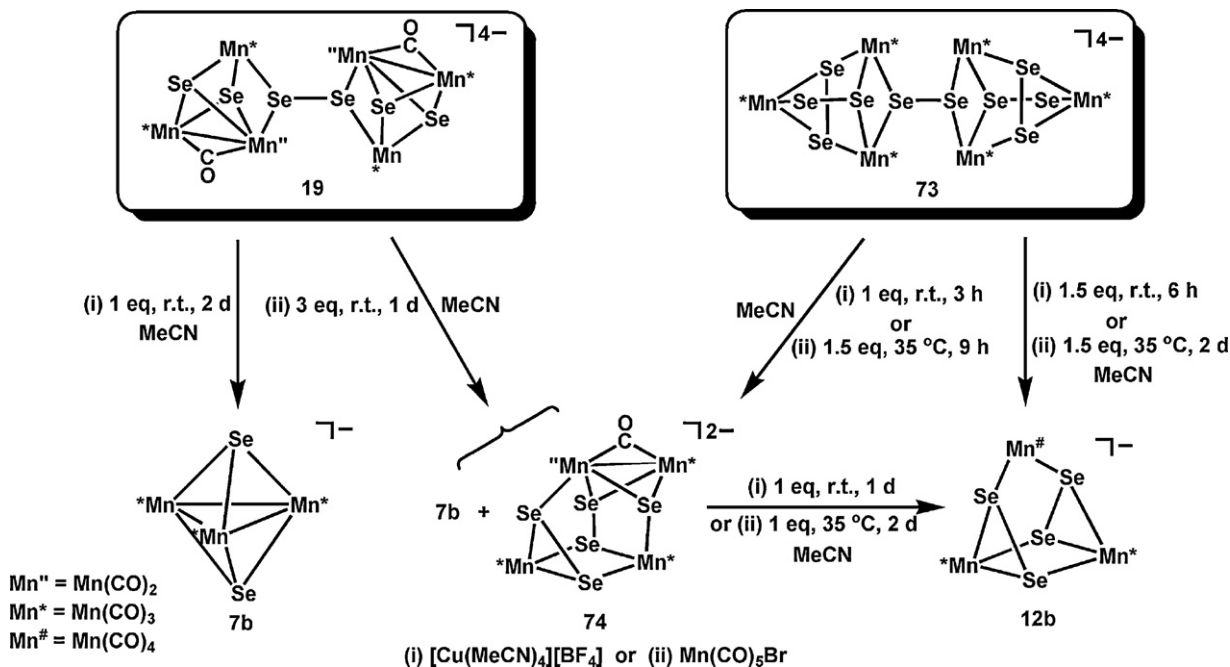
Adapted from ref. [35].

results indicated that the Se<sub>2</sub> ligand of cluster **19** was more easily cleaved upon oxidation, compared to the case of cluster **73**. The average Se–Se bonds of the Se<sub>2</sub> ligand in clusters **19**, **73**, **74**, and **12b** were similar and in the range of 2.36–2.39 Å. The Mn–Mn bond in **74** (2.714(2) Å) was slightly shorter than those found in Se<sub>2</sub>Mn<sub>3</sub>-based complexes **61b** (2.76(6) Å) and **7b** (2.83(2) Å), but close to those found in complexes **19**, **66**, **67**, and **72** (2.70(1) Å).

#### 4.3. Te–Mn clusters

In contrast to the sulfur and selenium systems, the chemistry of the tellurium–manganese carbonyl complexes has been explored much less, due to the lack of rational synthetic routes. In the 1980s, the interesting bent complex [Te{Mn(CO)<sub>2</sub>Cp\*}<sub>2</sub>] (**75**) and the planar compound [Te{Mn(CO)<sub>2</sub>Cp\*}<sub>3</sub>] (**76**) were reported to result from the reaction of Al<sub>2</sub>Te<sub>3</sub>/HCl with THF-stabilized [LMn(CO)<sub>2</sub>(THF)] (L = Cp\*, Cp), respectively [76]. X-ray analysis showed that the average of the Te–Mn bonds in clusters **75** (2.459(2) Å) and **76** (2.49(2) Å) was shorter than the sum of the covalent single bond radii (Te, 1.37 Å; Mn, 1.33 Å), an indication of multiple bonding character [77]. A similar synthetic methodology was also applied to the Re system, where a series of Te–Re complexes [(HTe)HRe(CO)<sub>2</sub>Cp\*], [(Te<sub>2</sub>)<sub>2</sub>{Re(CO)<sub>2</sub>Cp\*}<sub>2</sub>], and [Te{Re(CO)<sub>2</sub>Cp\*}<sub>2</sub>] were synthesized, in which the mononuclear complex [(HTe)HRe(CO)<sub>2</sub>Cp\*] could further react with [CpMn(CO)<sub>2</sub>(THF)] to give the mixed Mn–Re complex [Te<sub>2</sub>{Mn(CO)<sub>2</sub>Cp\*}<sub>2</sub>{Re(CO)<sub>2</sub>Cp\*}] [78]. Another neutral

tellurium–manganese complex, [TeMn(CO)<sub>3</sub>(PEt<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (**77**), was obtained from the Te transfer agent Te = PEt<sub>3</sub> with Mn<sub>2</sub>(CO)<sub>10</sub> in refluxing toluene [79]. Complex **77** consisted of two octahedral Mn(CO)<sub>4</sub>(PEt<sub>3</sub>)<sub>2</sub> bridged by a ditelluride unit, in which the two PEt<sub>3</sub> ligands were in *trans* positions. The mixed Mn–Fe tetrahedral complex [TeFe<sub>2</sub>Mn(CO)<sub>8</sub>Cp\*] could be synthesized from the reaction of complex **75** and Fe<sub>2</sub>(CO)<sub>9</sub> [80]. In addition, mixed-metal complexes [TeM(CO)<sub>5</sub>{Mn(CO)<sub>2</sub>Cp\*}<sub>2</sub>] (M = Cr, **78**; W, **79**) were obtained from reaction of M(CO)<sub>5</sub>THF with the reactive intermediate [Te{Mn(CO)<sub>2</sub>Cp\*}<sub>2</sub>]<sup>2-</sup>, which was derived from the reaction of [CpMn(CO)<sub>2</sub>PhC(O)]<sup>-</sup> with Te powder in THF [81]. Nevertheless, there have been very few anionic metal carbonyl clusters reported in the literature. For example, the tetrahedral complex [MeTe{CpMn(CO)<sub>2</sub>}]<sup>-</sup> (**80**), reported by Herrmann et al., was produced from the methylation of cluster **76** with methyl lithium, while the bent anion [PhTe{Mn(CO)<sub>2</sub>Cp\*}<sub>2</sub>]<sup>-</sup> (**81**), reported by Huttner et al., was obtained from the reduction of [PhTeMn(CO)<sub>2</sub>Cp\*]<sub>2</sub> with NaBH<sub>4</sub> [82,83]. Furthermore, Huang et al. employed the ethanothetical synthesis of Na<sub>2</sub>Te<sub>2</sub> with Mn<sub>2</sub>(CO)<sub>10</sub> at 85 °C to give the dianionic cluster [(Te<sub>2</sub>)<sub>3</sub>Mn<sub>4</sub>(CO)<sub>13</sub>]<sup>2-</sup> (**82**). Cluster **82** exhibited three Mn(CO)<sub>3</sub> and one Mn(CO)<sub>4</sub> fragments bridged by three Te<sub>2</sub><sup>2-</sup> ligands [64]. In addition, the propeller-like dinuclear anion [(MeTe)<sub>3</sub>Mn<sub>2</sub>(CO)<sub>6</sub>]<sup>-</sup> (**83**) was obtained by Liaw et al. from the reaction of [Mn(CO)<sub>5</sub>]<sup>-</sup> and Me<sub>2</sub>Te<sub>2</sub> in THF at ambient temperature, whereas the similar benzenetellurolate-bridged complex [(PhTe)<sub>3</sub>Mn<sub>2</sub>(CO)<sub>6</sub>]<sup>-</sup> (**84**) was produced



Scheme 13. Reactivities of **19** and **73** toward different electrophiles.



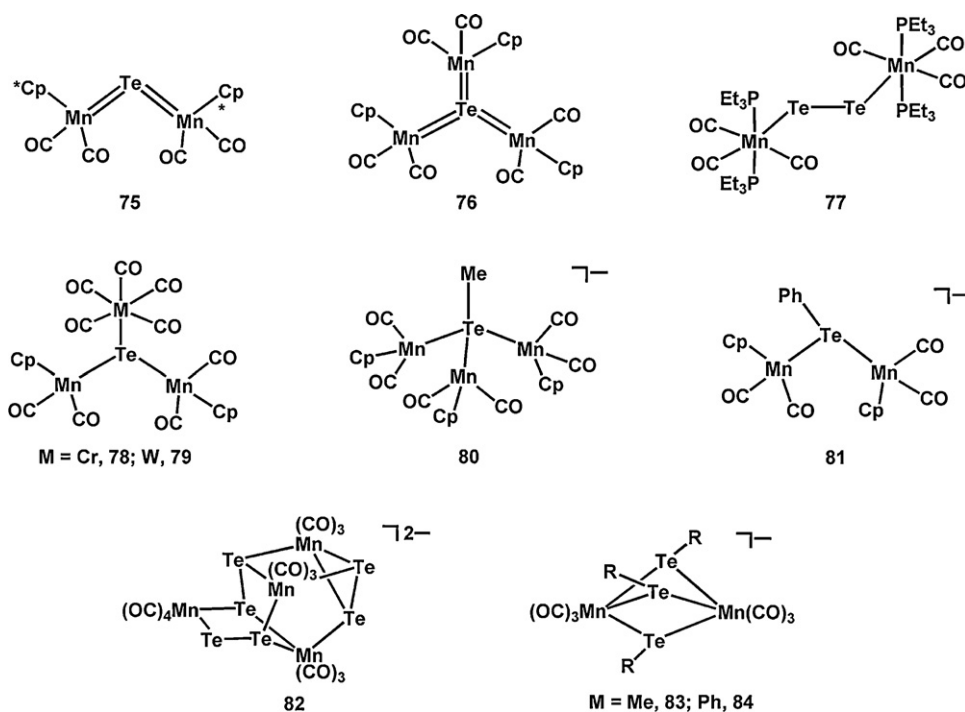


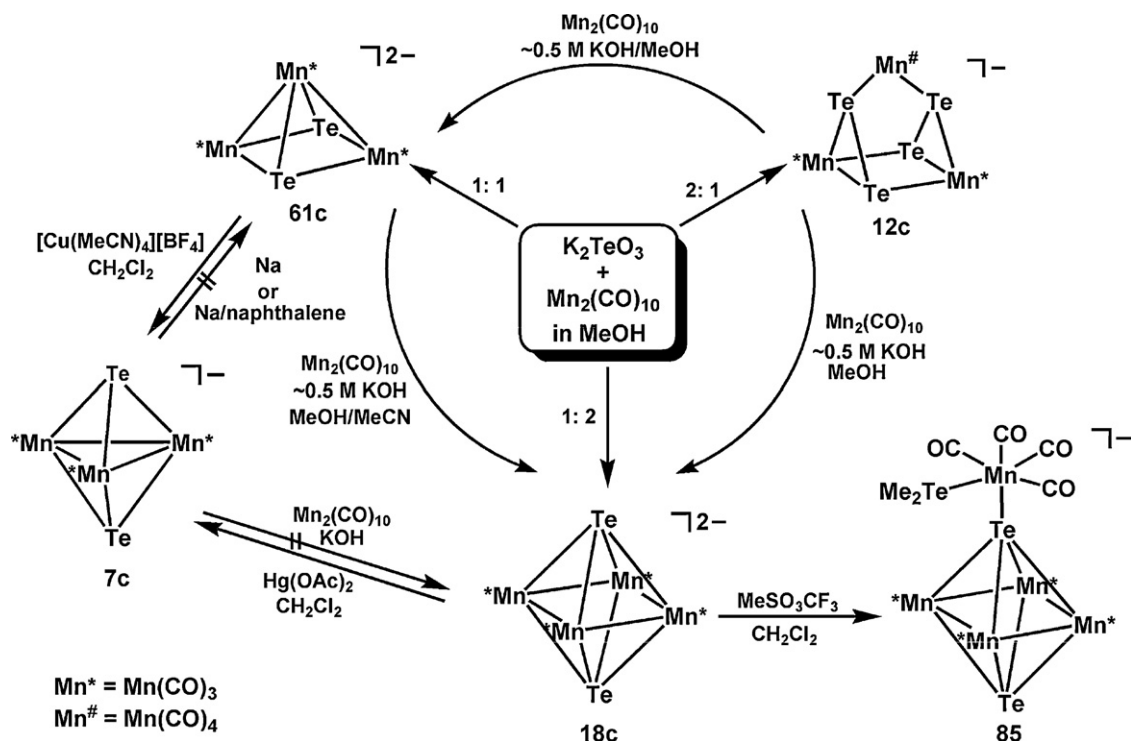
Chart 2. Structures of manganese carbonyl telluride complexes.

from the thermolytic conversion of *cis*-[(TePh)<sub>2</sub>Mn(CO)<sub>4</sub>] in refluxing THF [84]. [(RTe)<sub>3</sub>Mn<sub>2</sub>(CO)<sub>6</sub>]<sup>−</sup> (R = Me, **83**; Ph, **84**) were structurally similar to the dimanganese sulfide complex [(SH)<sub>3</sub>Mn<sub>2</sub>(CO)<sub>6</sub>]<sup>−</sup> (**63**) but with different organo groups [64] (Chart 2).

In this Te–Mn system, a direct and efficient route was discovered to a series of novel tellurium-bridged manganese carbonylates that involved the direct thermal reactions of K<sub>2</sub>TeO<sub>3</sub> with Mn<sub>2</sub>(CO)<sub>10</sub> in superheated MeOH solutions. The driving force for this methodology was the liberation of CO<sub>2</sub> at elevated temperature, which led to the generation of [Te<sub>4</sub>Mn<sub>3</sub>(CO)<sub>10</sub>]<sup>−</sup> (**12c**), [Te<sub>2</sub>Mn<sub>3</sub>(CO)<sub>9</sub>]<sup>2−</sup> (**61c**), and [Te<sub>2</sub>Mn<sub>4</sub>(CO)<sub>12</sub>]<sup>2−</sup> (**18c**), depending on the ratio of K<sub>2</sub>TeO<sub>3</sub> to Mn<sub>2</sub>(CO)<sub>10</sub> (Scheme 14) [85]. Cluster **12c** was structurally similar to clusters **12a** and **12b**, and clusters **61c** and **18c** were also each structurally similar to their S and/or Se analogues mentioned above.

Since the ratio of K<sub>2</sub>TeO<sub>3</sub> to Mn<sub>2</sub>(CO)<sub>10</sub> affects the outcome of these reactions, structural transformations of these tellurium–manganese carbonylates were also accomplished (Scheme 14). By adjusting the appropriate amounts of Mn<sub>2</sub>(CO)<sub>10</sub> in KOH/MeOH, stepwise cluster-expansion processes were observed from **12c** to **61c**, and then to **18c**. These results suggest that cluster **61c** represented an intermediate state for the transformation of **12c** to **18c**. Just like cluster **61b**, cluster **61c** is a 49-electron species, and is very sensitive to the air due to its electron deficiency. When cluster **61c** was carefully oxidized with 1 equiv of [Cu(MeCN)<sub>4</sub>][BF<sub>4</sub>], the 48e, trigonal-bipyramidal cluster [Te<sub>2</sub>Mn<sub>3</sub>(CO)<sub>9</sub>]<sup>−</sup> (**7c**) was obtained (Scheme 14). Note that cluster **7c** could not be obtained directly from the thermal reaction of K<sub>2</sub>TeO<sub>3</sub> with Mn<sub>2</sub>(CO)<sub>10</sub>. Unlike the high reactivity of **7b**, **7c** remained intact upon treatment with Na/naphthalene or even with Na, which was indicative of a high degree of inertness. However, the paramagnetic square-pyramidal cluster **61c** showed its reactivity toward Mn<sub>2</sub>(CO)<sub>10</sub>/KOH to give the octahedral cluster **18c**, presumably via radical processes.

It is interesting that the Te-metallated cluster [(CO)<sub>4</sub>Mn(TeMe<sub>2</sub>)(μ<sub>5</sub>-Te)(μ<sub>4</sub>-Te)Mn<sub>4</sub>(CO)<sub>12</sub>]<sup>−</sup> (**85**) was obtained from the reaction of the octahedral cluster **18c** with MeSO<sub>3</sub>CF<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> (Scheme 14). Cluster **85** was shown by X-ray analysis to consist of an octahedral Te<sub>2</sub>Mn<sub>4</sub>(CO)<sub>12</sub> core with one Te atom externally bonded to a Mn(CO)<sub>4</sub>TeMe<sub>2</sub> fragment to demonstrate the novel μ<sub>5</sub>-Te bonding mode (Fig. 9), presumably by the formation of a Te → Mn donor–acceptor bond [86]. Although μ<sub>4</sub>-Te ligands had been observed in several metal carbonyl clusters [87–90], the reactivity and basicity of the long pair of μ<sub>4</sub>-Te atoms were much less explored in transition metal carbonyl complexes. Wachter et al. also reported the Cr(CO)<sub>5</sub>-adduct cluster [(<sup>t</sup>BuC<sub>5</sub>H<sub>4</sub>)<sub>2</sub>Nb(CO)<sub>3</sub>Co<sub>9</sub>(CO)<sub>8</sub>Te<sub>6</sub>{Cr(CO)<sub>5</sub>}<sub>3</sub>] with μ<sub>5</sub>-Te atoms each capping the face of the Co<sub>9</sub>-based body-centered cube [91]. The increased basicity of Te in the Te–Mn–CO case, to give the μ<sub>5</sub>-Te bonding mode, might be due to the more electropositive character of the Mn involved. Note that the μ<sub>4</sub>-Te atom in [Te<sub>2</sub>Mn<sub>4</sub>(CO)<sub>12</sub>]<sup>2−</sup> (**18c**) could not be metallated upon the addition of Mn(CO)<sub>5</sub>Br. A detailed study by IR spectroscopy showed that the mononuclear cationic species [Mn(CO)<sub>4</sub>(TeMe<sub>2</sub>)]<sup>+</sup> was produced in the course of this reaction [92], which explained the formation of **85**. There are several interesting features in **85**. First, the geometry of the μ<sub>5</sub>-Te ligand was almost square-pyramidal, but slight differences in the Te–Mn distances and the Mn–μ<sub>5</sub>-Te–Mn angles of **85** caused a deviation from perfect C<sub>4v</sub> symmetry. The bulky Te<sub>2</sub>Mn<sub>4</sub>(CO)<sub>12</sub> group and the TeMe<sub>2</sub> moiety were *cis* rather than *trans* to each other. This was explained in terms of the *trans* influence of the Te<sub>2</sub>Mn<sub>4</sub>(CO)<sub>12</sub> moiety. Since Te<sub>2</sub>Mn<sub>4</sub>(CO)<sub>12</sub> was not a strong σ-bonding ligand, a strong σ-bonding CO ligand was preferred to a TeMe<sub>2</sub> group in the position *trans* to the Te<sub>2</sub>Mn<sub>4</sub>(CO)<sub>12</sub> ligand. The (μ<sub>4</sub>-Te)–Mn bond lengths of the Te-metallated octahedral cluster **85** and the octahedral cluster **18c** were almost equal (2.632–2.648 Å). The (μ<sub>5</sub>-Te)–Mn bonds of **85** were expected to be significantly longer, but the opposite effect was observed: these bonds were unusually short (2.577–2.602 Å) (Fig. 9).



## 5. Group 8 (Fe, Ru) carbonyl clusters

The chemistry of chalcogen-containing iron carbonyl clusters has been widely investigated and well documented, due to their

unique structures and unusual reactivities [2a,5d–f,6,7a–d,93]. We will mainly focus on some representative examples of anionic iron carbonyl clusters in this section, due to the large numbers of neutral complexes, which have been studied and reviewed

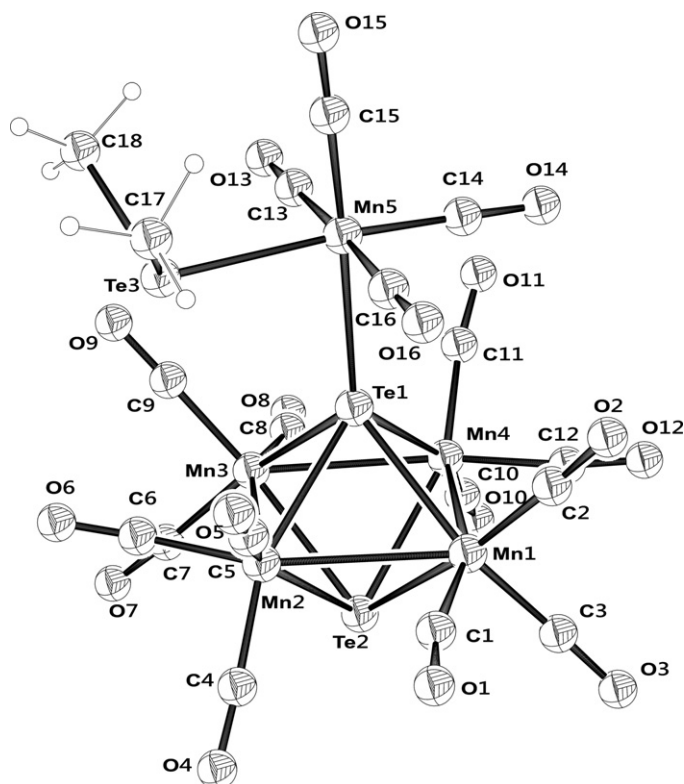


Fig. 9. ORTEP diagram of anion 85.

in the past [2a,5d,5f,93b–e]. Compared to the iron system, relatively few ruthenium carbonyl chalcogenide clusters have been identified probably due to the lower reactivity of Ru versus Fe. However, they often display versatile structural features and exhibit special properties, which will be discussed in Section 5.3.

Hieber et al. discovered the first chalcogen–iron carbonyl complexes, dinuclear tetrahedral compounds  $[E_2Fe_2(CO)_6]$  ( $E = S$ , **1a**;  $Se$ , **1b**) and square-pyramidal triiron clusters  $[E_2Fe_3(CO)_9]$  ( $E = S$ , **2a**;  $Se$ , **2b**;  $Te$ , **2c**), utilizing the reactions of  $EO_3^{2-}$  with  $Fe(CO)_5$  in basic methanol solutions followed by acidification [1a,94a–e]. Subsequently, complex  $[Te_2Fe_2(CO)_6]$  (**1c**) was isolated by Lesch and Rauchfuss [94f] (Scheme 15). Although some mechanistic information for the formation of the cluster **1a–c** and **2a–c** was proposed, the anionic intermediate species in these reactions remained rare, which plagued the understanding of the chemical transformations of this system [34a,95]. The following section reviews rational synthesis of anionic chalcogen-containing iron carbonyl clusters derived from the “Hieber’s synthesis”. Cluster-growth and transformations, as well as reactivities of the resultant anionic clusters, also are systematically described.

### 5.1. Cluster-growth processes of anionic E–Fe clusters ( $E = S, Se, Te$ )

#### 5.1.1. S–Fe–CO system

An important anionic complex in the S–Fe system,  $[S_2Fe_2(CO)_6]^{2-}$  (**86a**), was synthesized by Seyferth et al. from the reaction of **1a** with 2 equiv of  $LiEt_3BH$  in THF at  $-78^\circ C$  [96]. The formation of **86a** involved a nucleophilic attack on the S–S bond by 1 equiv of hydride to form the intermediate monoanionic cluster  $[HS_2Fe_2(CO)_6]^-$  followed by deprotonation by another equiv of hydride. The related study with the derivatives of **86a**, to mimic the biological enzymes, has been well documented and surveyed [4a,11,93a–d]. Averill et al. isolated a disulfide-bridged dimeric cluster  $[(S_2)\{SFe_2(CO)_6\}_2]^{2-}$  (**87a**) from the reaction of **1a** with 1 equiv of  $LiEt_3BH$  in THF, which was further reduced by 1 equiv of reductant  $LiEt_3BH$  to form the dianion **86a** [97]. Complex **87a** contained two “ $S_2Fe_2(CO)_6$ ” butterfly units connected by a S–S bond. Until now, geometry consisting of  $\mu_4-E_2$ -bridged di- $EFe_2(CO)_6$  was rare and found only in the Se-analogue  $[(Se_2)\{SeFe_2(CO)_6\}_2]^{2-}$  (**87b**), chalcogen-bound clusters  $[(E_2)\{REFe_2(CO)_6\}_2]$  ( $E = S, Te$ ;  $R = Et, Ph$ ),  $[(S_2)\{SFe_2(CO)_6\}_2\{CH_2(CH_2OCH_2)_2CH_2\}]$ , and  $[(E_2)\{EFe_2(CO)_6\}_2\{Re_2(CO)_8(\mu-PCy_2)_2\}]$  ( $E = S, Se, Te$ ) [98,89d]. The butterfly complex **86a** had high reactivity toward various organic and inorganic reagents, which has been extensively studied and reviewed [5e,11d,93b,93c,96]. If the unstable complex **86a** was treated with 0.5 equiv of  $FeBr_2$ , the iron-bridged cluster  $[Fe\{S_2Fe_2(CO)_6\}_2]^{2-}$  (**88**) was produced. When cluster **88** was bubbled with gaseous  $O_2$  in MeCN, a larger dianionic cluster  $[S_6Fe_6(CO)_{12}]^{2-}$  (**16a**) was formed [99]. Cluster **16a** was also produced directly from the reaction of **1a** with equimolar **87a** in MeCN at room temperature. X-ray analysis showed that cluster **16a** consisted of two  $[S_2Fe_2(CO)_6]^{2-}$  fragments linked by a  $[S_2Fe_2]^{2+}$  moiety. Recently, it was reported that the reduction of **1a** with  $[LnCp^*(THF)_2]$  in toluene produced wheel-shaped sulfur–iron–lanthanide clusters  $[S_6Fe_6(CO)_{12}(LnCp^*)_2]$  ( $Ln = Sm, 89; Yb, 90$ ) which were composed of two  $LnCp^*$  fragments bound to the central  $[S_6Fe_6(CO)_{12}]^{2-}$  unit [100]. Besides, the cationic metal ions were found to link two **86a** to give mixed-metal clusters  $[V\{S_2Fe_2(CO)_6\}_2]$  (**91**) and  $[M\{S_2Fe_2(CO)_6\}_2]^{2-}$  ( $M = Cr, Mn, Ni, Pd$ ) [19,101]. In addition, **86a** reacted with  $Mo(CO)_4I_3$  to form a Mo-bridged tri- $S_2Fe_2$  cluster  $[MoS_6Fe_6(CO)_{16}]^{2-}$  (**13**) [31]. As shown in Scheme 16, a series of cluster-growth reactions were established via the oxidation or reduction reactions.

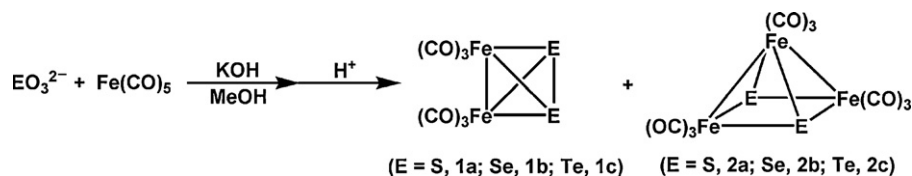
#### 5.1.2. Se–Fe–CO system

In the Se–Fe system, interesting cluster transformations were also observed by carefully controlling Hieber’s synthesis. The iron-selenide carbonyl dianionic cluster  $[Se_6Fe_6(CO)_{12}]^{2-}$  (**16b**) was successfully isolated by the reaction of an aqueous  $K_2SeO_3$  solution with 1 equiv of  $Fe(CO)_5$  in  $KOH/MeOH$  [34a]. Cluster **16b** was isostructural with its S-analogue **16a** (Fig. 10). If the molar ratio of  $K_2SeO_3$  with  $Fe(CO)_5$  in  $KOH/MeOH$  was increased to 1:3, the tetrahedral cluster  $[SeFe_3(CO)_9]^{2-}$  (**3b**) was formed (Scheme 17). To probe the transformations of these anionic species in this Se–Fe system, we carried out a reaction that employed solid  $K_2SeO_3$  and 1 equiv of  $Fe(CO)_5/KOH$  in a methanol solution. The low solubility of  $K_2SeO_3$  in MeOH allowed for a gradual increase in  $SeO_3^{2-}$  concentration, and the observation of other anionic species in this system was therefore feasible. The reaction showed that this reaction mixture first formed the open-cluster  $[Se\{Fe(CO)_4\}_3]^{2-}$ , which was confirmed by its IR spectrum [34a,13b]. Continued stirring of the reaction mixture produced the tetrahedral complex  $[SeFe_3(CO)_9]^{2-}$  (**3b**) and a reactive anionic species proposed to be  $[(Se_2)_2Fe_2(CO)_6]^{2-}$  based on an IR absorption pattern, similar to that of its Te counterpart  $[(Te_2)_2Fe_2(CO)_6]^{2-}$  [34a,102a]. After prolonged stirring,  $Fe(CO)_5$  consumed a total amount of 1 equiv of  $K_2SeO_3$ , which led to the formation of the dianion **16b** as the ultimate anionic product. Cluster **16b** was an intermediate in Hieber’s synthesis, which transformed further to the neutral complex **1b** by acidification. However, when **16b** was oxidized with  $[Cu(CH_3CN)_4][BF_4]$ , the neutral complex **2b** was obtained instead. The acidification of the dianionic  $SeFe_3$ -cluster **3b** gave the trinuclear complex **2b** as well. These results clearly demonstrated that the ratio of the oxidant  $SeO_3^{2-}$  to the reductant  $Fe(CO)_5/KOH$  was a controlling factor in determining which intermediate anion was formed in Hieber’s synthesis and  $[Se_2Fe_2(CO)_6]$  (**1b**) and  $[Se_2Fe_3(CO)_9]$  (**2b**) were the acidification products of these dianionic intermediates. These transformations also demonstrated the controlled stepwise cluster-growth processes from smaller diiron and triiron clusters to the hexa-iron cluster, which also provided useful insights into the formation of Hieber’s products **1b** and **2b** (Scheme 17).

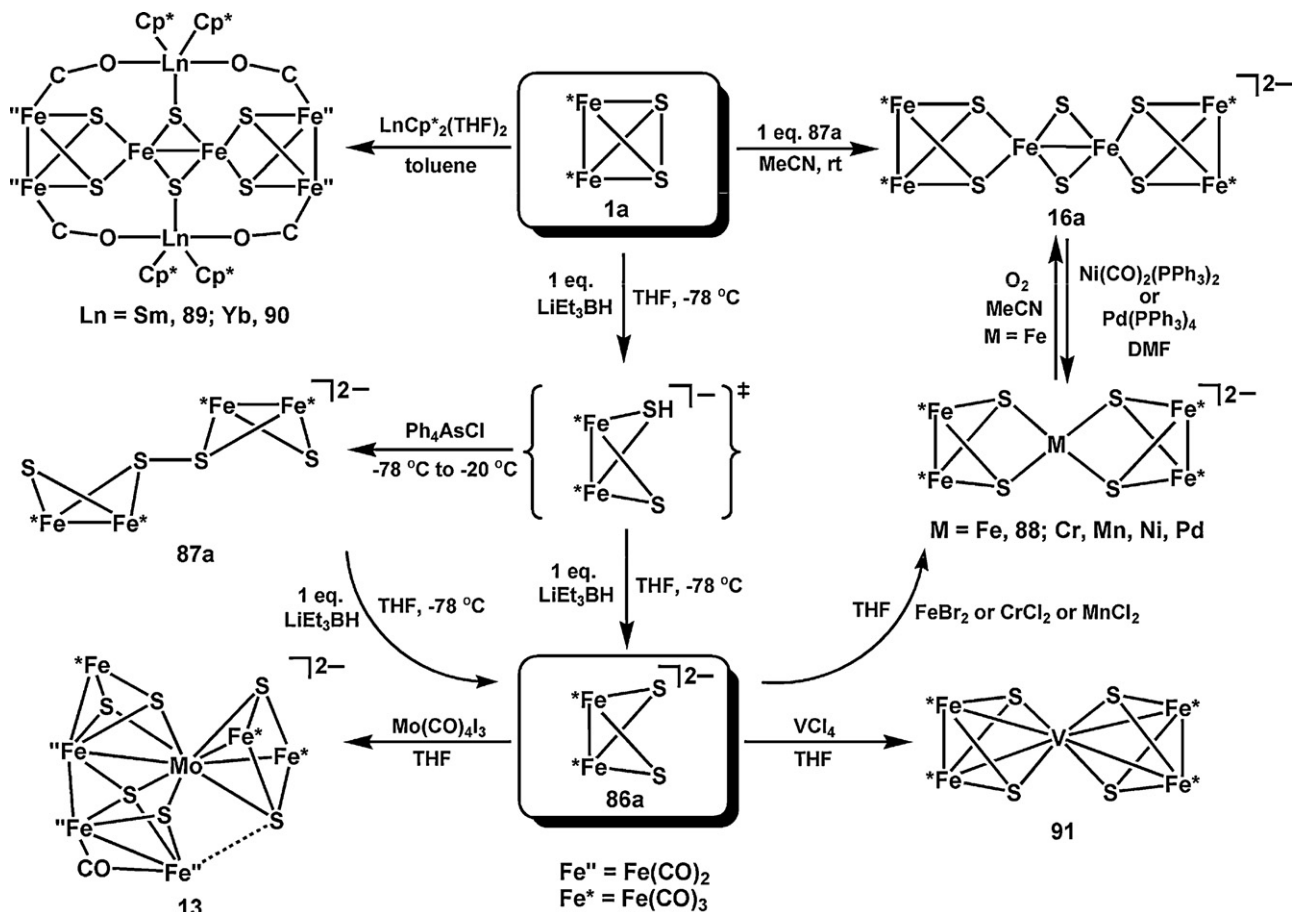
#### 5.1.3. Te–Fe–CO system

The details of Hieber’s synthesis in the Te–Fe system were also investigated. When  $K_2TeO_3$  was treated with 1 equiv of  $Fe(CO)_5$  in  $KOH/MeOH$  solutions, the first tellurium–iron carbonyl anionic cluster  $[Te_6Fe_6(CO)_{24}]^{2-}$  (**8**) was obtained [22,95]. The dianion **8** can be viewed as two  $Te_2Fe_3(CO)_9$  (**2c**) clusters, each asymmetrically attached to the two Te atoms of the butterfly anion  $[Te_2Fe_2(CO)_6]^{2-}$  (**86c**) (Fig. 11). Similar E-bound  $E_2Fe_2(CO)_6$ -bridged clusters were also found in  $[Me_2Te_2Fe_2(CO)_6]$  [102a],  $[(ML)_2Te_2Fe_2(CO)_6]$  ( $ML = Fe(CO)_4$  or  $Re(CO)_5$ ) [102b,102c], and  $[\{Fe(CO)_2Cp\}_2Se_2Fe_2(CO)_6]$  [102d]. Furthermore, cluster **8** could react with dilute HCl or  $[Cu(MeCN)_4][BF_4]$  to form complex **2c** as the major product, indicating that cluster **8** was an important anionic intermediate species in Hieber’s synthesis. Cluster **2c** could be reconverted back to the dianion **8** upon reduction with 2 equiv of  $CoCp_2$  [22] (Scheme 18). If  $K_2TeO_3$  reacted with  $Fe(CO)_5/KOH$  in a 1:3 molar ratio, the open-cluster  $[TeFe_3(CO)_{12}]^{2-}$  was obtained, which further formed the tetrahedral complex  $[TeFe_3(CO)_9]^{2-}$  (**3c**) via decarbonylation [34b]. These results indicated that different stoichiometries and subtle changes in the reaction conditions could give rise to different anionic intermediates in Hieber’s synthesis.

The cluster-growth processes of anionic Te–Fe clusters were also investigated, and are summarized in Scheme 18. When the tetrahedral cluster **3c** was treated with  $[Te_2Fe_3(CO)_9]$  (**2c**), the medium-sized cluster  $[Te_4Fe_5(CO)_{14}]^{2-}$  (**17**) was obtained [34b]. Cluster **17** was also prepared by Kolis et al. from the reaction of the “Zintl” ion  $Te_4^{2-}$  with  $Fe(CO)_5$  in DMF at  $85^\circ C$  [103].



Scheme 15. Synthesis of chalcogen-iron carbonyl complexes by the "Hieber's method".



Scheme 16. Cluster-growth reactions of iron carbonyl sulfide complexes.

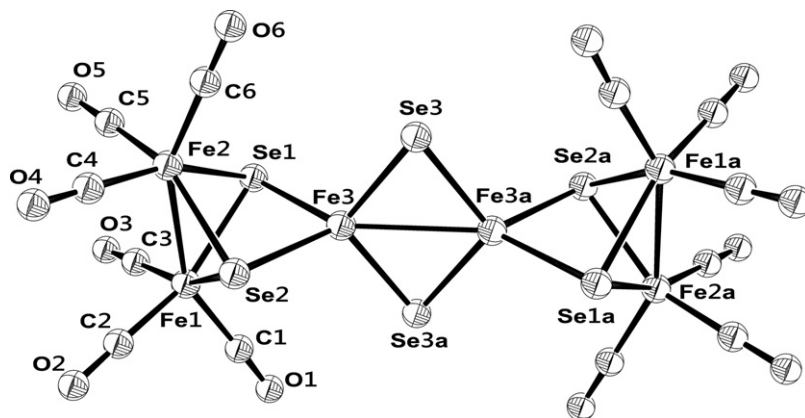
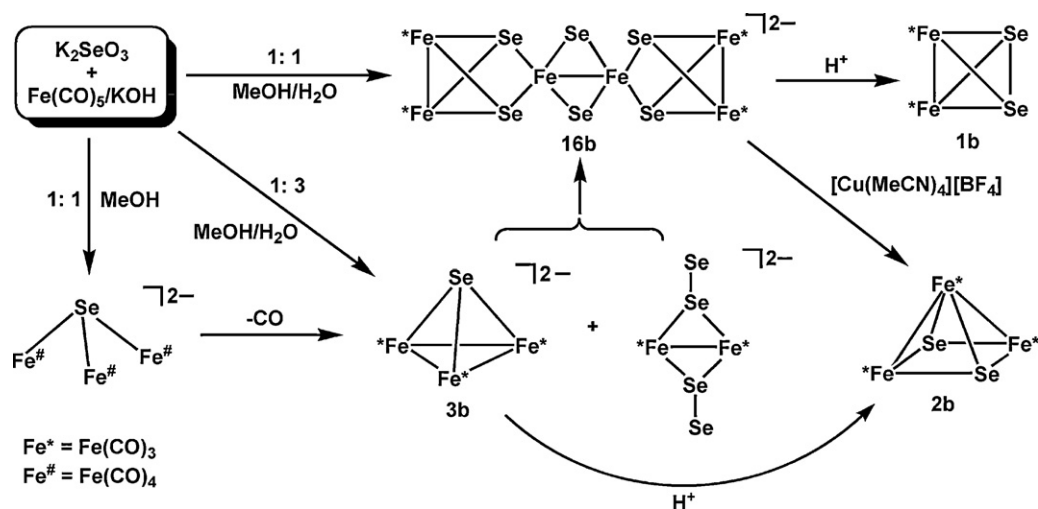


Fig. 10. ORTEP diagram of anion 16b.



**Scheme 17.** Syntheses and transformations of iron carbonyl selenide complexes.

Cluster **17** can be viewed as composed of **2c** and  $[\text{Te}_2\text{Fe}_2(\text{CO})_6]^{2-}$  (**86c**) with the loss of one CO. More interestingly, cluster **17** underwent a cluster-growth reaction with **2c** to produce the larger cluster  $[\text{Te}_6\text{Fe}_8(\text{CO})_{24}]^{2-}$  (**8**), which could further afford the high-nuclearity double-cubic cluster  $[\text{Te}_{10}\text{Fe}_8(\text{CO})_{20}]^{2-}$  (**92**) upon the addition of 4 equiv of Te [**34b**]. Cluster **92** was composed of two  $[\text{Te}_4\text{Fe}_4(\text{CO})_{10}]^{2-}$  cubanes bridged by the  $\eta^2\text{-Te}_2^{2-}$  moiety between the opposite corners of one face of each cube. Cluster **92** reportedly also was obtained from  $\text{Te}_4^{2-}$  and  $\text{Fe}(\text{CO})_5$  in DMF [**103**]. Other structurally interesting  $\text{Te}_2$ -bridged Te–Fe anionic clusters,  $[(\text{Te}_2)_7\text{Fe}_6(\text{CO})_{12}]^{2-}$ ,  $[(\text{TeR})_2(\text{Te})_2(\text{Te}_2)_2\text{Fe}_4(\text{CO})_8]^{2-}$  (R = Me, Et), and  $[(\text{TeMe})(\text{Te})_2(\text{Te}_2)_3\text{Fe}_3\text{W}_2(\text{CO})_{12}]^{3-}$ , were also produced from the hydro(solvo)thermal synthesis [**23,24**]. On the other hand, when **92** was treated with  $[\text{Cu}_2(\text{dppm})_2(\text{MeCN})_4][\text{BF}_4]_2$ , the dppm-bridged cubic complex  $[\text{Te}_4\text{Fe}_4(\text{CO})_{10}(\text{dppm})]$  (**93**) was produced. Cluster **93** consisted of a  $\text{Te}_4\text{Fe}_4$  cubic core geometry, in which the two Fe atoms of one  $\text{Te}_2\text{Fe}_2$  face were bridged by a dppm ligand [**34b**]. This structural feature was similar to the  $\text{Te}_2\text{Fe}_2(\text{CO})_6$ -bridged cubic cluster  $[\text{Te}_4\text{Fe}_4(\text{CO})_{10}\{\text{Te}_2\text{Fe}_2(\text{CO})_6\}]^{2-}$  (**94**), obtained from the reaction of  $\text{Te}_3^{2-}$  and  $\text{Fe}(\text{CO})_5$  [**5j**]. Other  $\text{E}_4\text{Fe}_4$ -based cubane-like geometries were also found in clusters  $[\text{E}_4\text{Fe}_4(\text{CO})_{12}]$  (E = S, Se, Te) [**104a,104b**]. Another interesting neutral cubane-like cluster  $[(\mu_3\text{-CTeBr}_4)\text{Te}_4\text{Fe}_3(\text{CO})_9]$  was synthesized from cluster **2c** with  $\text{CBr}_4$ , where one iron vertex of the  $\text{Te}_4\text{Fe}_4$  core was replaced by the carbide fragment [**104c**]. As shown in **Scheme 18**, the controlled

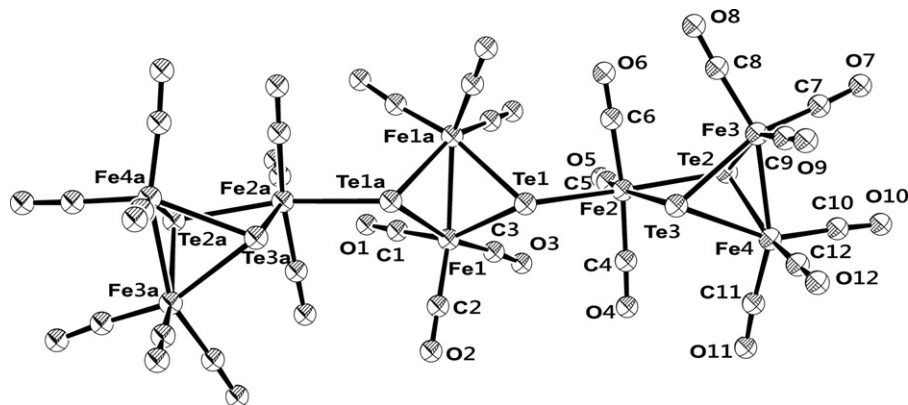
stepwise cluster-expansion processes from the small cluster  $[\text{TeFe}_3(\text{CO})_9]^{2-}$  (**3c**) to the large-size cluster  $[\text{Te}_{10}\text{Fe}_8(\text{CO})_{20}]^{2-}$  (**92**) have been established, providing some useful information on nano-sized cluster-growth processes. Compared to the clusters in sulfur and selenium systems, the clusters in the Te–Fe system are often found to possess larger metal skeletons with a higher coordination of the chalcogen atom, due to the greater size of the Te atom versus Se and S.

## 5.2. Reactivities of E–Fe clusters

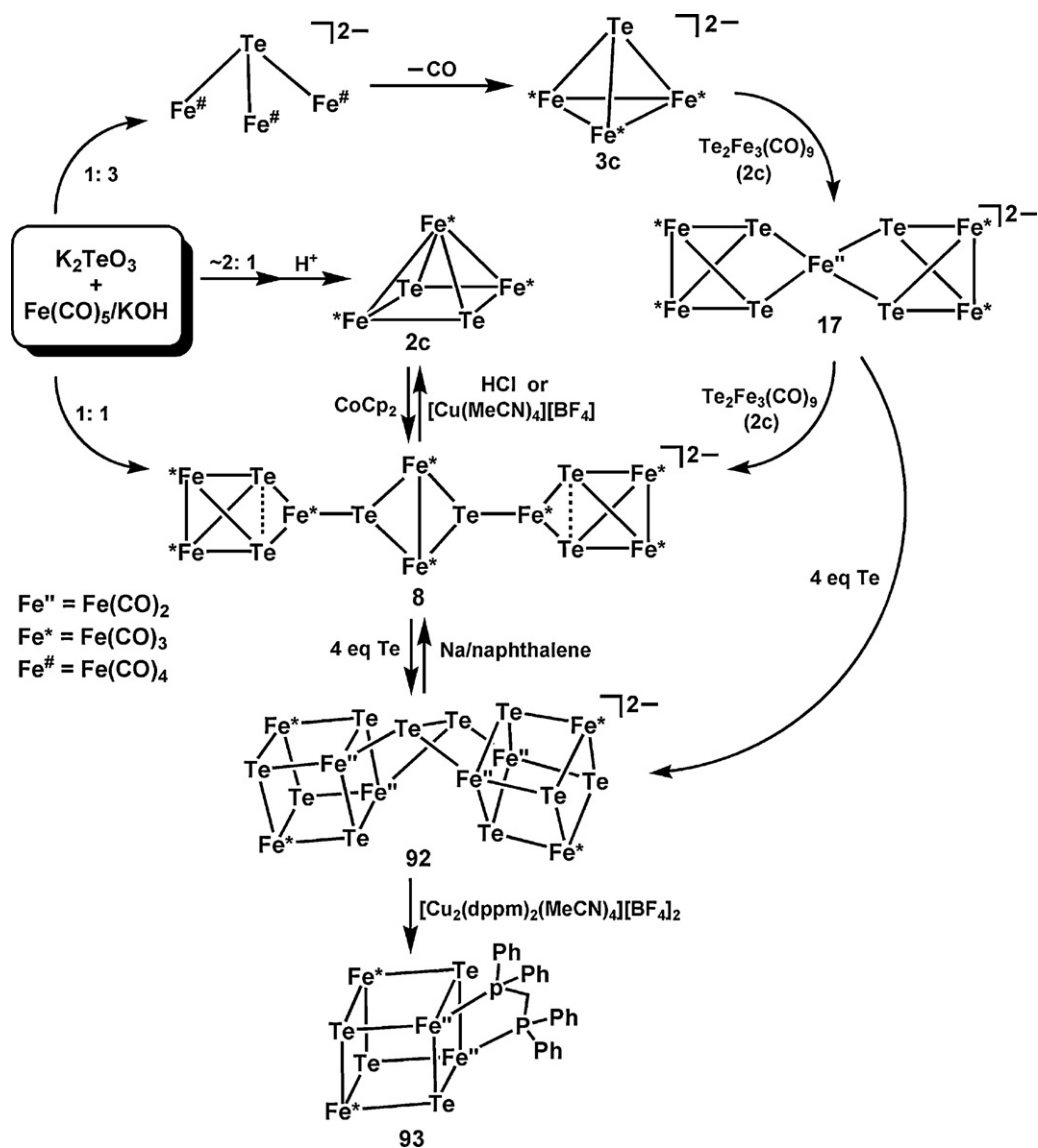
### 5.2.1. $[\text{E}_2\text{Fe}_3(\text{CO})_9]$ (E = Se, Te) with metal carbonyl fragments

The previous study showed that the E–E bond of the tetrahedral  $\text{E}_2\text{Fe}_2$ -based clusters **1a–c** were susceptible to many electron-deficient metal moieties, giving rise to numerous cluster-expansion products [**5e–j,105–107**].  $\text{E}_2\text{Fe}_3$ -based clusters **2a–c** were also found to act in a manner similar to **1a–c**, as the  $\text{Fe}(\text{CO})_3$  fragment could easily be lost upon the addition of electrophiles [**2a,5f–j,108**]. The focus of those publications was to study the rational synthesis of anionic iron carbonyl chalcogenide clusters to probe the effects of the chalcogen elements on the resultant anionic clusters. Hence, a series of parallel reactions of the neutral triiron carbonyl clusters **2b** and **2c** with different anionic metal carbonyls were examined (**Scheme 19**).

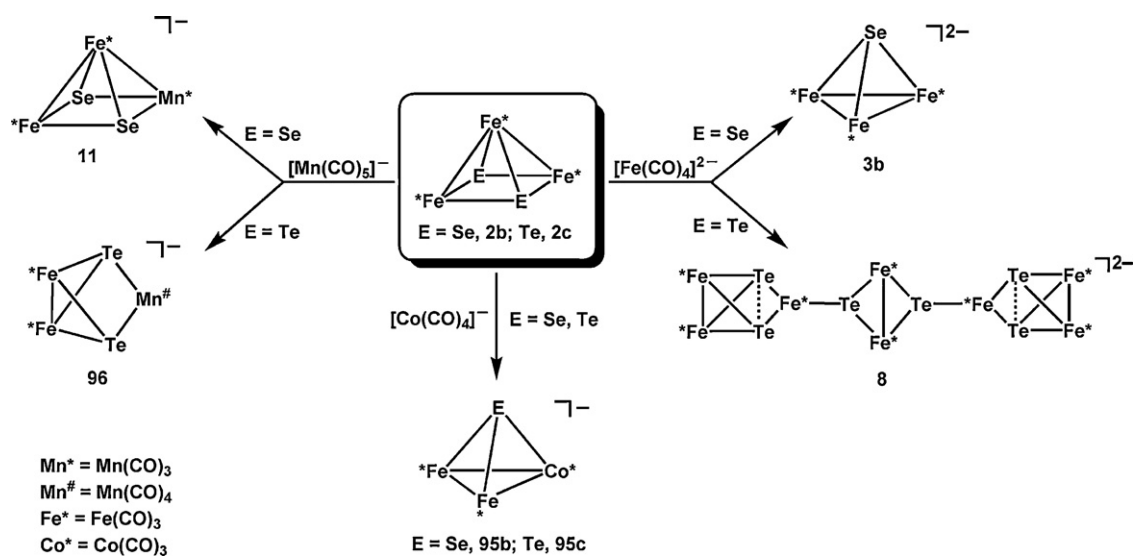
As shown in **Scheme 19**, clusters **2b** and **2c** reacted with  $[\text{Co}(\text{CO})_4]^-$  to produce anionic tetrahedral *closo*-clusters



**Fig. 11.** ORTEP diagram of anion **8**.



Scheme 18. Stepwise cluster-expansion reactions of iron carbonyl telluride clusters.



Scheme 19. Reactivities of 2b and 2c toward some anionic metal carbonyls.

[EFe<sub>2</sub>Co(CO)<sub>9</sub>]<sup>−</sup> (E = Se, **95b**; Te, **95c**), respectively [26]. If cluster **2c** was treated with Co<sub>2</sub>(CO)<sub>8</sub>, the neutral tetrahedral *closo*-cluster [TeFeCo<sub>2</sub>(CO)<sub>9</sub>] was formed [104b]. Clusters **95b** and **95c**, composed of an EFe<sub>2</sub>Co tetrahedral (E = Se, Te) core, were isostructural and isoelectronic with the related clusters [SFe<sub>2</sub>Co(CO)<sub>9</sub>]<sup>−</sup> (**95a**) and [EFeCo<sub>2</sub>(CO)<sub>9</sub>] (E = S, Se, Te) [109]. Transition metals similar in sizes (Fe, Co) were proposed to facilitate the metal–metal bond formation, giving rise to the *closo*-clusters **95b–c** regardless of the different sizes of Se and Te. On the contrary, when the selenium-iron cluster **2b** was treated with [Mn(CO)<sub>5</sub>]<sup>−</sup>, the square-pyramidal *nido*-cluster [Se<sub>2</sub>Fe<sub>2</sub>Mn(CO)<sub>9</sub>]<sup>−</sup> (**11**) was formed by the replacement of one Fe(CO)<sub>3</sub> fragment with a Mn(CO)<sub>3</sub><sup>−</sup> moiety, and the *arachno*-cluster [Te<sub>2</sub>Fe<sub>2</sub>Mn(CO)<sub>10</sub>]<sup>−</sup> (**96**) was produced from the reaction of cluster **2c** with [Mn(CO)<sub>5</sub>]<sup>−</sup>. The differing sizes of the chalcogen atoms seemed to affect the outcomes of these reactions. In the case of Se, the smaller size of Se made a shorter Se–Mn distance, which favored the Mn–Fe bond formation to give the more closed *nido*-structure **11**, while in the case of Te, the longer Te–Mn length kept the Mn atom far from the Fe atoms, resulting in the *arachno*-cluster **96**. Cluster **96** was isostructural to cluster [Te<sub>2</sub>Fe<sub>3</sub>(CO)<sub>10</sub>] (**97**) with an [Fe(CO)<sub>4</sub>] moiety replaced by the [Mn(CO)<sub>4</sub>]<sup>−</sup> fragment [94g]. Similar *arachno*-clusters [Te<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>{Fe(CO)<sub>3</sub>I}]<sup>−</sup> [110], [Te<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>{Fe(CO)<sub>3</sub>PPh<sub>3</sub>}] [108d], [Te<sub>2</sub>Fe(CO)<sub>3</sub>{Mo(CO)<sub>2</sub>Cp}]<sub>2</sub> [108a], [Te<sub>2</sub>Fe<sub>2</sub>(CO)<sub>7</sub>MCp] (M = Co, Rh) [104b,108c], and [Te<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>M(PPh<sub>3</sub>)<sub>2</sub>] (M = Pd, Pt) [107c] are known. To probe the charge effect, the reactions of **2b** and **2c** with the dianion [Fe(CO)<sub>4</sub>]<sup>2−</sup> were investigated. Unexpectedly, the reaction of [Fe(CO)<sub>4</sub>]<sup>2−</sup> with cluster **2b** produced the tetrahedral dianionic cluster [SeFe<sub>3</sub>(CO)<sub>9</sub>]<sup>2−</sup> (**3b**), while the reaction with **2c** formed the previously mentioned cluster [Te<sub>6</sub>Fe<sub>8</sub>(CO)<sub>24</sub>]<sup>2−</sup> (**8**) [26]. As suggested by the observation of hypervalent bonding modes in some related tellurium complexes, the hypervalency of tellurium may play a key role in the formation of cluster **8**. Schmid suggested that the ease of formation of bonds between the transition metals in transition metal-main-group clusters was related to the size of the main-group and transition elements [111a]. These different outcomes tended to agree with Schmid's statement in terms of the greater size of tellurium (1.35 Å) and similar sizes of the selenium (1.17 Å) and iron (1.25 Å) [111b]. However, this argument was not supported in the cases of the E<sub>2</sub>M<sub>4</sub>-octahedral clusters (E = Se, Te; M = Fe, Ru) derived from **2b** and **2c** [27,107d,108b].

### 5.2.2. [EFe<sub>3</sub>(CO)<sub>9</sub>]<sup>2−</sup> (E = S, Se, Te) with organic reagents or metal fragments

In addition to the reactions with neutral E<sub>2</sub>Fe<sub>3</sub>-based clusters **2b–c**, the reactions of the *closo*-tetrahedral clusters [EFe<sub>3</sub>(CO)<sub>9</sub>]<sup>2−</sup> (E = S, **3a**; Se, **3b**; Te, **3c**) with a series of organic and inorganic electrophiles were also studied and reviewed [5f,5h–k,7c,7d]. As illustrated in Chart 3, there are several representative bonding modes of M(R)-EFe<sub>3</sub>-based clusters reported in the literature. In contrast to the sulfur-bound cluster [MeSFe<sub>3</sub>(CO)<sub>9</sub>]<sup>−</sup> (type **A**) observed in the methylation of cluster **3a**, a similar reaction of cluster **3b** and **3c** occurred at one of the iron atoms to give type **B**-clusters [112a]. Other S-metallated clusters (type **C**), [Fe<sub>3</sub>(CO)<sub>9</sub>{μ<sub>3</sub>-SFeCp(CO)<sub>2</sub>}]<sup>−</sup> and [Fe<sub>3</sub>(CO)<sub>9</sub>{μ<sub>3</sub>-SM(CO)<sub>5</sub>}]<sup>2−</sup> (M = Cr, W), were produced from the reaction of **3a** with [CpFe(CO)<sub>2</sub>THF] or [M(CO)<sub>5</sub>(THF)] [112b,112c]. Clusters **3a–c** could also react with various Lewis acids such as CuX (X = Cl, Br, I), HgI<sub>2</sub>, PhHgOAc, PPh<sub>3</sub>AuCl, and Me<sub>2</sub>SnBr<sub>2</sub> to form Fe–Fe bridged mixed-metal clusters (type **D**) [90c,110,113]. Similar Fe–Fe bridged hydrido-clusters [(H)EFe<sub>3</sub>(CO)<sub>9</sub>]<sup>−</sup> and [(H)<sub>2</sub>EFe<sub>3</sub>(CO)<sub>9</sub>] (E = S, Se, Te) were also reported [112a,113a]. In contrast, the μ<sub>4</sub>-M bridged clusters [(μ<sub>4</sub>-M){SeFe<sub>3</sub>(CO)<sub>9</sub>}]<sup>2−</sup> (M = Cd, **98**; Hg, **99**) (type **E**) were produced from the reaction of cluster **3b** with M(OAc)<sub>2</sub> [13a]. In addition, the reaction of clusters **3a–c** with the cationic

agent [Cp<sup>+</sup>Rh(MeCN)<sub>3</sub>]<sup>2+</sup>, [Mn(CO)<sub>3</sub>(MeCN)<sub>3</sub>]<sup>+</sup>, or [Re(CO)<sub>5</sub>]<sup>+</sup> led to the formation of vertex-expanded butterfly clusters (type **F**), in which the incorporated metal fragment capped the EFe<sub>2</sub> plane, giving the μ<sub>4</sub>-E bonding mode [114a,29]. Similar reactions of **3b** and **3c** with [Cp<sup>+</sup>Ir(MeCN)<sub>3</sub>]<sup>2+</sup> formed type **F**-clusters [(μ<sub>4</sub>-E)Fe<sub>3</sub>(CO)<sub>9</sub>IrCp<sup>+</sup>] along with the metal-substituted derivatives [(μ<sub>3</sub>-E)Fe<sub>2</sub>(CO)<sub>7</sub>IrCp<sup>+</sup>] as minor products (E = Se, Te) [114a]. The incoming metal fragment, such as [PPh<sub>3</sub>Au]<sup>+</sup>, [Cu(MeCN)<sub>4</sub>]<sup>+</sup>, or CuX (X = Cl, Br), was found to cap and bridge the Fe<sub>3</sub> plane, forming pentanuclear clusters (type **G**, *vide infra*) [114b,114c,113b]. Clusters **3b** and **3c** were electrophilically attacked by the RQ<sup>2+</sup> (R = Me, Mes, Cp<sup>+</sup>, (η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>tBu)Fe(CO)<sub>2</sub>; Q = P, As, Sb, Bi) fragments, accompanied by the cleavage of one Fe–Fe bond, to form square-pyramidal *nido*-clusters (type **H**) [114d–f]. It is interesting that the reaction of **3b** with MesSb<sup>2+</sup> occurred via metathesis and redox processes to form the open-cluster [(μ<sub>3</sub>-η<sup>2</sup>:η<sup>1</sup>-SeSbMes)(μ<sub>3</sub>-SbMes)Fe<sub>3</sub>(CO)<sub>10</sub>] (type **I**) [114e].

Other than these, complicated cluster-expansion reactions were also reported (Scheme 20). It was found when cluster **3a** was treated with AgBF<sub>4</sub>, the bis-tetrahedral anionic cluster [S<sub>2</sub>Fe<sub>5</sub>(CO)<sub>14</sub>]<sup>2−</sup> was formed via the oxidative condensation [115]. [S<sub>2</sub>Fe<sub>5</sub>(CO)<sub>14</sub>]<sup>2−</sup> and its Se-analogue were also reported to have been synthesized from the reactions of polychalcogenides and Fe(CO)<sub>5</sub> [19]. Besides, clusters **3b** and **3c** could react, respectively, with Rh<sub>2</sub>(CO)<sub>4</sub>Cl<sub>2</sub> to give rise to the bis-octahedral mixed-metal clusters [Se<sub>2</sub>Fe<sub>4</sub>Rh<sub>3</sub>(CO)<sub>16</sub>]<sup>−</sup> and [Te<sub>2</sub>Fe<sub>3</sub>Rh<sub>4</sub>(CO)<sub>15</sub>]<sup>2−</sup> [89e]. Clusters **3a–c** were also found to react with Ru<sub>3</sub>(CO)<sub>12</sub> in refluxing acetone to undergo skeletal expansion, forming octahedral clusters [EFe<sub>2</sub>Ru<sub>3</sub>(CO)<sub>14</sub>]<sup>2−</sup> (E = S, **15a**; Se, **15b**; Te, **15c**), respectively [33,113c]. In order to test the basicity of the chalcogen atoms of clusters **15a–c**, the methylation reactions of clusters **15a–c** with MeSO<sub>3</sub>CF<sub>3</sub> were also examined. Only in the S case, did the reaction produce the sulfur-methylated octahedral cluster [Me(μ<sub>5</sub>-S)Fe<sub>2</sub>Ru<sub>3</sub>(CO)<sub>14</sub>]<sup>−</sup> (**100**) [33], in which the sulfur atom is pentacoordinated to one methyl group, two Ru and two Fe atoms, indicative of the greater basicity of the μ<sub>4</sub>-S atom versus μ<sub>4</sub>-Se and μ<sub>4</sub>-Te. The capability of the μ<sub>4</sub>-S atom to serve as a Lewis donor was rare. Reported examples included only [{W(CO)<sub>4</sub>(PPh<sub>3</sub>)}(μ<sub>5</sub>-S)Os<sub>5</sub>(CO)<sub>15</sub>], [{W(CO)<sub>4</sub>PMe<sub>2</sub>Ph}(μ<sub>5</sub>-S)(μ<sub>4</sub>-S)Ru<sub>4</sub>(CO)<sub>9</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>], and [W(CO)<sub>5</sub>(μ<sub>4</sub>-S)(μ<sub>5</sub>-S)Ru<sub>4</sub>(CO)<sub>10</sub>{C(Ph)NMe<sub>2</sub>}] [116].

### 5.2.3. [Te<sub>6</sub>Fe<sub>8</sub>(CO)<sub>24</sub>]<sup>2−</sup> with organic dihalides

As described, although the nucleophilicity of *closo*-tetrahedral clusters [EFe<sub>3</sub>(CO)<sub>9</sub>]<sup>2−</sup> (E = S, **3a**; Se, **3b**; Te, **3c**) has been studied, the reactions of the larger anionic clusters with organic reagents in this system were extremely rare. Since [Te<sub>6</sub>Fe<sub>8</sub>(CO)<sub>24</sub>]<sup>2−</sup> (**8**) contained a [Te<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>]<sup>2−</sup> anion attached to two Te<sub>2</sub>Fe<sub>3</sub>(CO)<sub>9</sub> fragments, the capability of **8** serving as a source of [Te<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>]<sup>2−</sup> was investigated. As Scheme 21 shows, cluster **8** readily reacted with a series of organic halides or dihalides to give Te<sub>2</sub>Fe<sub>2</sub>-based complexes [(μ-TeCHCl<sub>2</sub>)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>], [{μ-Te(CH<sub>2</sub>)<sub>n</sub>Te}Fe<sub>2</sub>(CO)<sub>6</sub>] (n = 1–3), and [{μ-TeCHPhTe}Fe<sub>2</sub>(CO)<sub>6</sub>], in which the two Te atoms were bridged or bound by the organic fragments [22,117]. It was noted that the CH<sub>2</sub>-bridged Te<sub>2</sub>Fe<sub>2</sub> complex was also obtained by Mathur et al. from the reaction of cluster **2c** with CH<sub>2</sub>N<sub>2</sub> [108e,108f]. In contrast, the reaction with Br(CH<sub>2</sub>)<sub>2</sub>Br formed the anionic tetrahedral complex [BrTe<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>]<sup>−</sup> due to the stronger oxidizing ability of Br(CH<sub>2</sub>)<sub>2</sub>Br [117]. The distance between the Te atoms of [BrTe<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>]<sup>−</sup> was close enough to form a single bond (2.732(2) Å), which was comparable to that in **1c** (2.71(1) Å) and [BrTe<sub>2</sub>FeMo(CO)<sub>5</sub>Cp] (2.807(1) Å) [94e,118], but shorter than those in the Te<sub>2</sub>Fe<sub>2</sub>-based butterfly complexes [(Te)Te<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>]<sup>2−</sup> (3.215(3) Å) and [{(CO)<sub>5</sub>MoTe}Te<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>]<sup>2−</sup> (3.157(3) Å) [18,24].

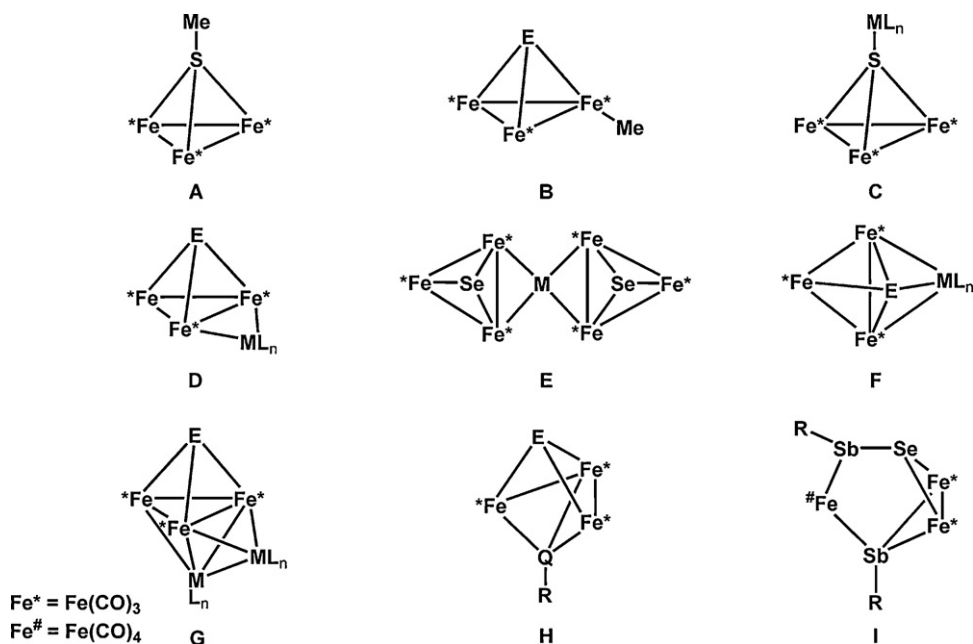
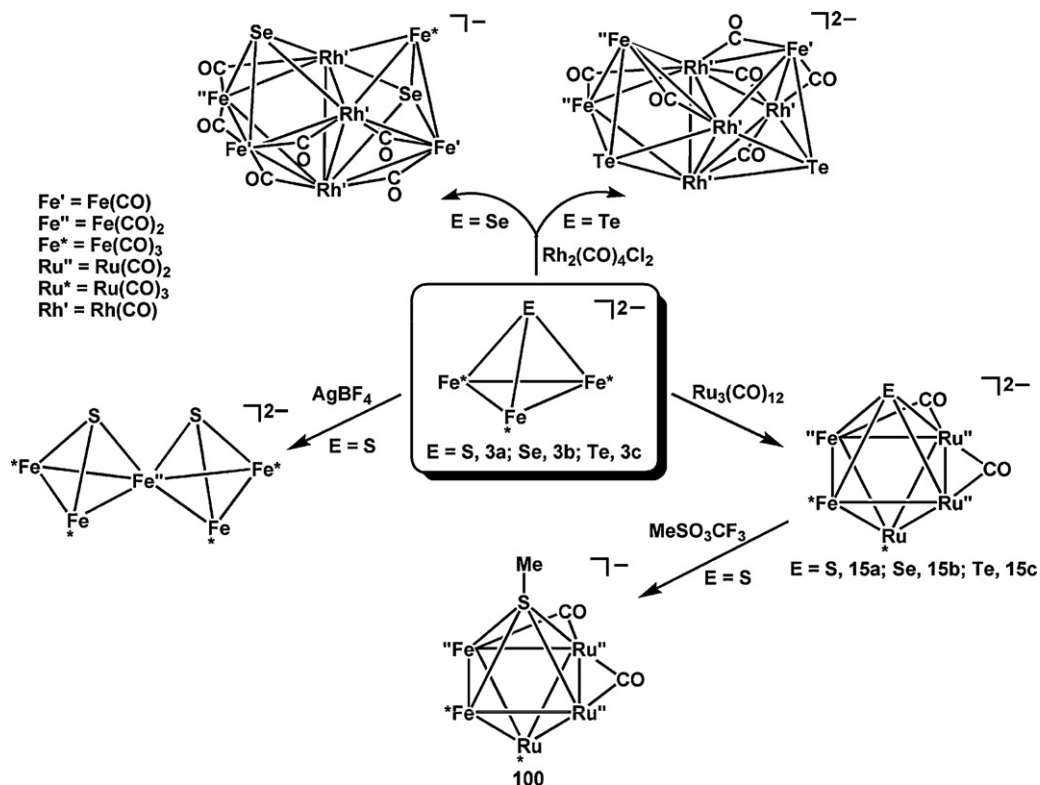


Chart 3. Different structural types (A–I) of  $EFe_3$ -based carbonyl clusters ( $E = S, Se, Te$ ).

#### 5.2.4. $[EFe_3(CO)_9]^{2-}$ ( $E = S, Se, Te$ ) with propargyl bromide

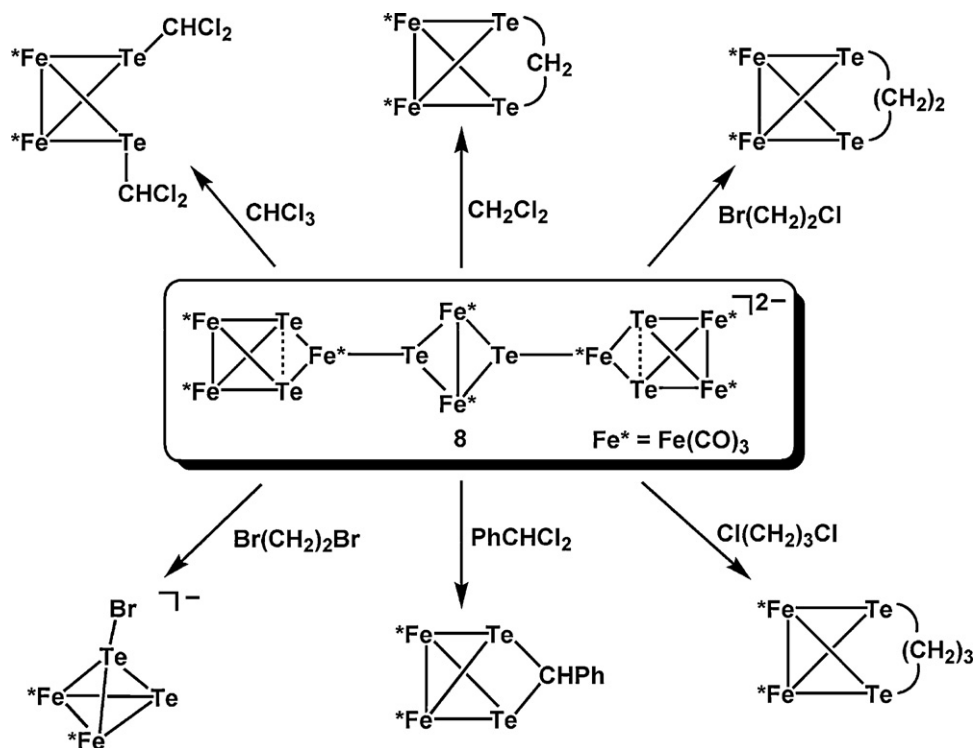
Although transition metal–alkyne complexes have attracted much attention due to their versatile bonding modes and intriguing structural transformations [119], in which metal–propargyl and its tautomeric allenyl species exhibited various structural types and reactivities owing to their diverse electronic characters [120,121], reactions of metal carbonyl anionic clusters with propargyl halides are rare [119e,122,123]. In the iron system, Mathur et al. reported that dianionic clusters  $[E_2Fe_2(CO)_6]^{2-}$  ( $E = S, 86a$ ;  $Se, 86b$ ;  $Te, 86c$ ) exhibited contrasting reactivities with propargyl

bromide. While the reactions with complexes **86a–b** produced propargyl-complexes  $[E_2Fe_2(CO)_6(CH_2C\equiv CH)_2]$  ( $E = S, 101a$ ;  $Se, 101b$ ), the reaction with the  $Te$ -complex **86c** formed the mixed propargyl–allenyl complex  $[Te_2Fe_2(CO)_6(CH_2C\equiv CH)(CH=C=CH_2)]$  (**102**) [119e]. Seyferth et al. reported that the butterfly anionic complex  $[(\mu-Me_3CS)(\mu-CO)Fe_2(CO)_6]^-$  was electrophilically attacked by propargyl bromide to form the allenyl complex  $[(\mu-Me_3CS)(\mu,\eta^2-CH=C=CH_2)Fe_2(CO)_6]$  [123a]. Furthermore, Wojcicki et al. reported the syntheses and reactivities of many dinuclear and polynuclear transition metal–propargyl and/or –allenyl carbonyl



Scheme 20. Cluster-expansion reactions of **3** with metal reagents.





Scheme 21. Syntheses of  $\text{Te}_2\text{Fe}_2$ -based complexes from **8** with organic halides.

complexes [121,124]. The reactions of  $[\text{EFe}_3(\text{CO})_9]^{2-}$  ( $\text{E} = \text{S}$ , **3a**;  $\text{Se}$ , **3b**;  $\text{Te}$ , **3c**) with bifunctional organic reagent-propargyl bromide were studied with great interest in our laboratory, and a detailed discussion of the  $\text{Se}$  and  $\text{Te}$  systems has been reported in our previous reviews [7d,93f], so, these complexes will be briefly described in this section in comparison with the sulfur analogue.

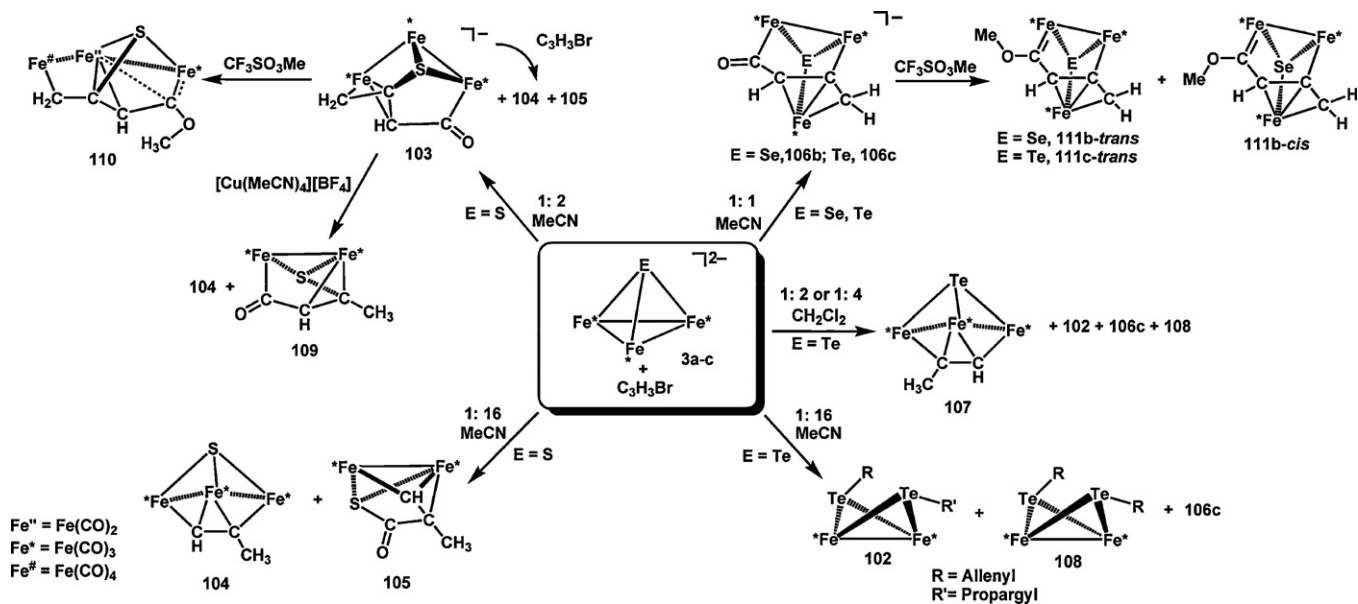
In the  $\text{S}$ - $\text{Fe}$  system, the reaction of cluster **3a** with 2 equiv of propargyl bromide in  $\text{MeCN}$  at room temperature produced the major acyl product  $[\text{Fe}_3(\text{CO})_9(\mu_3-\eta^3:\eta^1:\eta^2-\text{CH}_2\text{C}(\text{S})\text{CHC}(\text{O}))]^-$  (**103**) and two minor products  $[(\mu_3-\text{S})\text{Fe}_3(\text{CO})_9(\mu_3-\eta^1:\eta^2:\eta^1-\text{CH}=\text{C}(\text{Me}))]$  (**104**) and  $[\text{Fe}_2(\text{CO})_6(\mu_2-\eta^2:\eta^3-\text{SC}(\text{O})\text{C}(\text{Me})\text{CH})]$  (**105**). When the reaction was carried out with excess propargyl bromide in  $\text{MeCN}$ , only the neutral products **104** and **105** were obtained [125] (Scheme 22). X-ray analysis showed that the tri-iron atoms of cluster **103** were bridged by an unprecedented sulfur-substituted allylcarbonyl ligand  $\text{CH}_2=\text{C}(\text{S})\text{CHC}(\text{O})$  as a  $7e$  donor in the  $\mu_3-\eta^3:\eta^1:\eta^2$  bonding mode, whereas those of complex **104** were capped by a  $\text{S}$  atom and a  $4e$  donating propyne ligand,  $\text{HC}\equiv\text{CMe}$ , in the  $\mu_3-\eta^1:\eta^2:\eta^1$  fashion. On the other hand, complex **105** comprised an  $\text{Fe}_2(\text{CO})_6$  unit coordinated with a  $\text{SC}(\text{O})\text{C}(\text{Me})=\text{CH}$  fragment as a  $6e$  donor in the  $\mu_2-\eta^2:\eta^3$  fashion. The formation of anion **103** could be viewed as a result of the nucleophilic attack of **3a** onto the propargyl bromide, accompanied by one  $\text{Fe}-\text{Fe}$  and one  $\text{S}-\text{Fe}$  bond breakage, followed by a series of bond formations and a  $\text{CO}$  insertion. Furthermore, the propargyl bromide could act as the oxidizing agent to convert anion **103** to neutral complexes **104** and **105**.

In contrast to the sulfur system,  $[\text{EFe}_3(\text{CO})_9]^{2-}$  ( $\text{E} = \text{Se}$ , **3b**;  $\text{Te}$ , **3c**) behaved very differently with propargyl bromide. When clusters **3b** and **3c** were treated with 1 equiv of propargyl bromide in  $\text{MeCN}$ , the acyl complexes  $[(\mu_3-\text{E})\text{Fe}_3(\text{CO})_9(\mu_3-\eta^1:\eta^1:\eta^3-\text{C}(\text{O})\text{C}(\text{H})\text{CCH}_2)]^-$  ( $\text{E} = \text{Se}$ , **106b**;  $\text{Te}$ , **106c**), respectively, were produced. Clusters **106b** and **106c** each exhibited an  $\text{EFe}_3$  core capped by an allylcarbonyl ligand in the  $\mu_3-\eta^1:\eta^1:\eta^3$  fashion [126,127]. When anion **3c** reacted with excess propargyl bromide in  $\text{CH}_2\text{Cl}_2$  or  $\text{MeCN}$ , the oxidation product  $[(\mu_3-\text{Te})\text{Fe}_3(\text{CO})_9(\mu_3-\eta^1:\eta^2:\eta^1-\text{C}(\text{Me})=\text{CH})]$  (**107**), anion **106c**, and butterfly clusters  $[\text{Te}_2\text{Fe}_2(\text{CO})_6(\text{CH}_2\text{C}\equiv\text{CH})(\text{CH}=\text{C}=\text{CH}_2)]$

(**102**) and  $[\text{Te}_2\text{Fe}_2(\text{CO})_6(\text{CH}=\text{C}=\text{CH}_2)_2]$  (**108**) were formed [127]. Cluster **107** consisted of a  $\text{TeFe}_3$  core with a propyne ligand  $\text{C}(\text{Me})\equiv\text{CH}$  in a  $\mu_3-\eta^1:\eta^2:\eta^1$  bonding mode, which was similar to the sulfur-containing cluster **104** but with a different arrangement of the propyne ligand.

To further explore the reactivities of the acyl  $\text{S}$ -cluster **103**, reactions of **103** with  $[\text{Cu}(\text{MeCN})_4][\text{BF}_4]$  and  $\text{MeSO}_3\text{CF}_3$  were performed. When **103** was treated with 1.1 equiv of  $[\text{Cu}(\text{MeCN})_4][\text{BF}_4]$  in  $\text{CH}_2\text{Cl}_2$ , the diiron complex  $[\text{Fe}_2(\text{CO})_6(\mu_2-\eta^2:\eta^3-\text{C}(\text{O})\text{CHC}(\text{S})(\text{Me}))]$  (**109**) was yielded, with a small amount of **104**. Complex **109** was composed of an  $\text{Fe}_2(\text{CO})_6$  moiety linked by the  $\text{C}(\text{O})\text{CH}=\text{C}(\text{S})(\text{Me})$  ligand in a  $\mu-\eta^2:\eta^3$  fashion, which was an isomer of complex **105** but with a different arrangement of the methylvinylcarbonyl moiety. On the other hand, when cluster **103** was carefully treated with  $\text{MeSO}_3\text{CF}_3$  in  $\text{CH}_2\text{Cl}_2$ , the novel Fischer-type  $\text{Fe}_3$  carbene complex  $[\text{Fe}_3(\text{CO})_9(\mu_3-\eta^1:\eta^4:\eta^2-\text{CH}_2\text{C}(\text{S})\text{CHC}(\text{OMe}))]$  (**110**) was obtained. Complex **110** consisted of an  $\text{Fe}_3$  core bridged by the  $\text{CH}_2=\text{C}(\text{S})\text{CHC}(\text{OMe})$  ligand as an unprecedented  $8e$  donor in the  $\mu_3-\eta^1:\eta^4:\eta^2$ -fashion, which was structurally related to anion **103** but with a distinct bonding mode of the organic fragment to the  $\text{Fe}_3$  framework (Fig. 12). It was noted that complex **110** was isolated as a *trans*-form in the solid state but the *cis*-isomer was not yielded. The calculations showed that the total energies of cluster **110** (*trans*-form) and the proposed *cis*-form were 121.09 and 143.25 kcal/mol, respectively, in agreement with the fact that the *cis*-form was not isolated under our reaction conditions [125]. For comparison, only the *trans*-form of the tellurium-iron Fischer-type carbene complex  $[(\mu_3-\text{Te})\text{Fe}_3(\text{CO})_9(\mu_3-\eta^1:\eta^1:\eta^3-\text{C}(\text{OMe})\text{CHCCH}_2)]$  (**111c-trans**) was isolated from the methylation of cluster **106c** [127]. However, in the selenium system, both **111b-trans** and **111b-cis** were isolated due to the higher rotation energy of the  $\text{O}-\text{C}_{\text{carbene}}$  bond, which contrasted with the cases of many mononuclear iron carbene complexes, mainly due to the resonance effect of the iron cluster core [126].

In general, these reactions of  $[\text{EFe}_3(\text{CO})_9]^{2-}$  ( $\text{E} = \text{S}$ , **3a**;  $\text{Se}$ , **3b**;  $\text{Te}$ , **3c**) with bifunctional propargyl bromide were complicated and

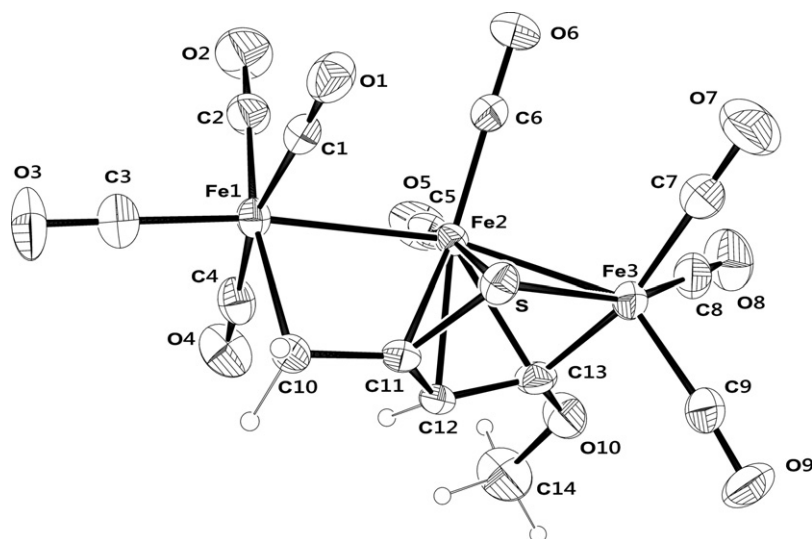
Scheme 22. Reactivities of **3** toward propargyl bromide.

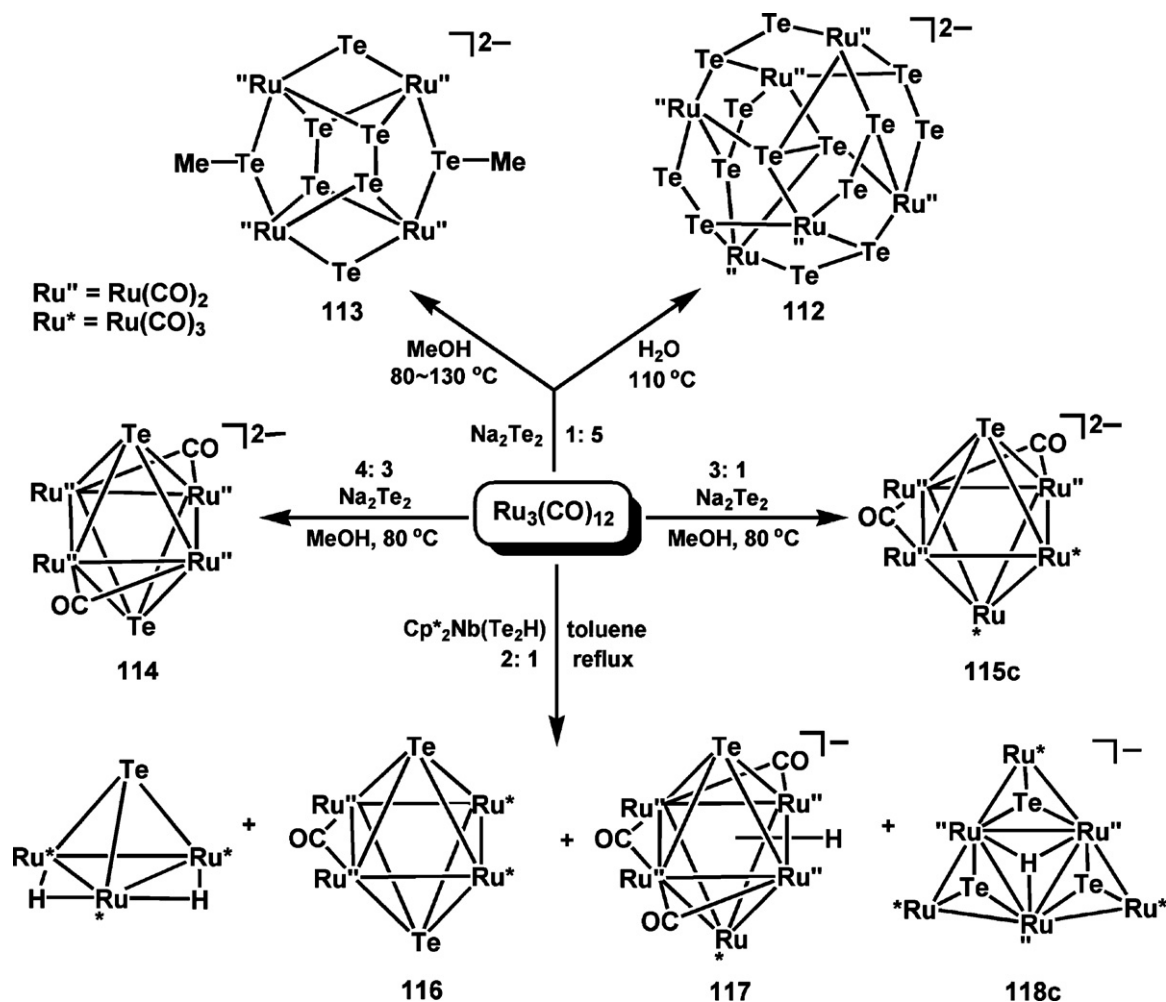
required careful treatments. The outcomes showed that similar results were observed in the Se and Te systems, but not the S system. This can probably be attributed to the larger electronegativity of S versus Se or Te, which made S show more affinity toward the propargyl group and led to the S–propargyl interaction. However, detailed study indicated that some complex factors, such as the size of chalcogen elements, the reaction temperature, and the solvents, were also involved in controlling the results.

### 5.3. Te–Ru clusters

Ruthenium-containing clusters have attracted great attention due to their interesting structural features, optoelectronics, and catalytic applications [2a,3h,5d–f,6,128,129]. Although chalcogen-containing iron or osmium clusters have been widely studied [5e,5f,6,7c,130], ruthenium carbonyl chalcogenide complexes have been comparatively rare. Furthermore, tellurium–ruthenium complexes have been explored even less than sulfur-

selenium–ruthenium clusters [5e,5f,128b,131–134], due to a lack of applicable synthetic routes. In this section, we will describe the recent development of anionic Te–Ru carbonyl clusters. Kanatzidis and Das utilized the hydrothermal or methanothermal synthesis by using  $\text{Na}_2\text{Te}_2$  and  $\text{Ru}_3(\text{CO})_{12}$  to produce various tellurium–ruthenium anionic carbonyl clusters [( $\text{Te}_2$ ) $_7\text{Ru}_6(\text{CO})_{12}$ ] $^{2-}$  (**112**) [135], [( $\text{TeMe}$ ) $_2(\text{Te})_2(\text{Te}_2)_2\text{Ru}_4(\text{CO})_8$ ] $^{2-}$  (**113**) [23b], [ $\text{Te}_2\text{Ru}_4(\text{CO})_{10}$ ] $^{2-}$  (**114**), and [ $\text{TeRu}_5(\text{CO})_{14}$ ] $^{2-}$  (**115c**) [88b] (Scheme 23). The centrosymmetric cluster **112** contained an octahedral  $\text{Ru}_6$  metal core held by a central ditelluride  $\text{Te}_2^{2-}$  with the ruthenium atoms further bridged by six  $\text{Te}_2^{2-}$  units on the periphery. Cluster **113** was composed of a  $\text{Ru}_4$  rectangular plane in which each of the shorter edges was bridged by a  $\mu_2\text{-Te}_2^{2-}$  moiety, while the longer ones were linked by  $\mu_2\text{-TeMe}^-$  fragments. It was noted that the Te–Fe clusters, structurally similar to clusters **112** and **113**, were also synthesized hydro(solvo)thermally (*vide supra*). The octahedral cluster **114** exhibited a  $\text{Ru}_4$  rectangular plane capped by two  $\mu_4\text{-Te}$  atoms

Fig. 12. ORTEP diagram of anion **110**.



Scheme 23. Syntheses of poly ruthenium carbonyl telluride complexes.

on both faces, whereas cluster **115c** consisted of a  $\text{Ru}_5$  square-pyramidal framework capped by a  $\mu_4$ -Te atom. Moreover, Wachter et al. also reported a series of tellurium-bridged ruthenium clusters  $[\text{H}_2\text{TeRu}_3(\text{CO})_9]$ ,  $[\text{Te}_2\text{Ru}_4(\text{CO})_{11}]$  (**116**),  $[\text{HTeRu}_5(\text{CO})_{14}]^-$  (**117**), and  $[\text{HTe}_3\text{Ru}_6(\text{CO})_{15}]^-$  (**118c**) from the reaction of  $\text{Ru}_3(\text{CO})_{12}$  and  $[\text{Cp}^*_2\text{Nb}(\text{Te}_2\text{H})]$  in boiling toluene [88c]. X-ray analysis showed that cluster **118c** was composed of three corner-shared  $\text{TeRu}_3$  tetrahedra and displayed an inner and an outer  $\text{Ru}_3$  triangles. After numerous attempts to synthesize Te–Ru–CO clusters under milder conditions, a facile method for the synthesis of cluster **115c** in good yields (~80%) was discovered from the reaction of  $\text{K}_2\text{TeO}_3$  and  $\text{Ru}_3(\text{CO})_{12}$  in MeOH at 80 °C, followed by the metathesis with  $\text{PPh}_4\text{Cl}$  [90b]. As shown in Table 1, the average Te–Ru (2.71(4) Å) and Ru–Ru (2.86(3) Å) bonds of cluster **115c** were within the range of those in the related Te–Ru complexes. Cluster **115c** has been developed into a useful building block for the further reaction with  $\text{CuX}$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ) in different ratios, which will be discussed in the following section.

## 6. Groups 6–8 (Cr, Mo, Fe, Ru) carbonyl clusters with Cu(I), Cd(II), or Hg(II) salts

### 6.1. E–M ( $E = \text{Se}, \text{Te}; M = \text{Mo}, \text{Fe}, \text{Ru}$ ) clusters with $\text{CuX}$ ( $X = \text{Cl}, \text{Br}, \text{I}$ )

Mixed-metal–copper complexes have attracted attention, due to the synergistic effects of two different types of metal atoms and their important roles in molecular catalysis for some

industrially important processes [129b,136]. Although Cu(II) and Cu(I) salts have been widely used in synthetic chemistry, Cu(I) salts have played a role in constructing mixed-metal frameworks with transition metal complexes, due to the softness of the Cu(I) ion and its filled  $d^{10}$  configuration [3k,137]. According to a search of the CSD, the number of heavier chalcogen-incorporated groups 6–8–copper carbonyl clusters was few, mainly group 8 (Fe, Ru) clusters. It was noted that there were no examples of group 6 (Cr) or 7 (Mn)–copper complexes reported. The other coinage metal ions as Ag(I) and Au(I), mostly stabilized with mono- or diphosphine ligands, were also found to bind to groups 6–8 carbonyl chalcogenide clusters, particularly in the sulfide cases [58c,110,113e,114b,131a,138].

In these Cu-incorporated clusters, the Cu(I)-phosphine or Cu-solvent linkers have been found. They included the limited sulfur-containing clusters,  $[(\mu_3\text{-S})\text{Ru}_3(\text{CO})_9\text{Cu}_2(\mu\text{-PPh}_2\text{CH}_2\text{PPh}_2)]$ ,  $[(\mu_3\text{-S})\text{Fe}_2(\text{CoPPh}_3)(\text{CuPPh}_3)(\text{CO})_8]$ , and  $[(\mu_4\text{-S})_6\text{Cu}_3\text{Fe}_6(\text{CO})_{18}(\text{CuPPh}_3)_2]^-$  which were synthesized from  $[\text{SRu}_3(\text{CO})_9]^{2-}$  (**119**),  $[\text{SFe}_2\text{Co}(\text{CO})_9]^-$  (**95a**), and  $[\text{S}_2\text{Fe}_2(\text{CO})_6]^{2-}$  (**86a**) with different Cu(I) sources,  $[\text{Cu}_2(\mu\text{-PPh}_2\text{CH}_2\text{PPh}_2)\text{Cl}_2]$ ,  $[(\text{PPh}_3)_2\text{Cu}(\text{NO})]$ , and  $[\text{Et}_4\text{N}][\text{CuCl}_2\text{PPh}_3]$ , respectively [131a,139a,139b]. Besides, heavier chalcogen-clusters  $[\text{Cu}\{\text{CpFe}(\text{CO})_2\text{P}(\text{Se})(\text{O}^n\text{Pr})_2\}_3]^+$  (**120**) and  $[\text{TeFe}_3(\text{CO})_9\text{Cu}_2(\text{MeCN})_2]$  (**121**) were reported from the reactions of  $[\text{CpFe}(\text{CO})_2\text{P}(\text{Se})(\text{O}^n\text{Pr})_2]$  (**122-Pr**) and  $[\text{TeFe}_3(\text{CO})_9]^{2-}$  (**3c**) with  $[\text{Cu}(\text{MeCN})_4]^+$ , respectively [138d,114c].

It was noted that most of Cu-incorporated clusters were further stabilized with halides, in the forms of  $\text{Cu}_m\text{X}_n$ . Chart 4 depicted the useful anionic and neutral group 6 (Mo) or group 8 (Fe, Ru) metal carbonyl complexes used as building blocks toward  $[\text{Cu}(\text{MeCN})_4]^+$  in the presence of  $[\text{PPN}]\text{X}$  or copper halides to construct a variety of copper halide-incorporated metal frameworks. For comparison, some groups 13–15-incorporated metal carbonyl clusters and Ru-clusters linked by  $\text{Cu}_m\text{X}_n$  were also included. These building blocks basically exhibited a more closed geometry, which included  $[\text{Ru}_4\text{H}(\text{CO})_{12}\text{BH}]^-$  (**123**) [140],  $[\text{Ru}_6\text{H}(\text{CO})_{18}]^-$  (**124**) [141],  $[\text{Ru}_{10}(\text{H})_2(\text{CO})_{25}]^{2-}$  (**125**) [142],  $[\text{Fe}_3(\text{CO})_9(\text{CCO})]^{2-}$  (**126**) [143],  $[\text{Cp}^*\text{Mo}(\text{CO})_2(\eta^3\text{-As}_3)]$  (**127**) [144],  $[\{\text{CpMo}(\text{CO})_2\}_2(\mu\text{-}\eta^2\text{-Sb}_2)]$  (**128**) [145a],  $[\text{CpFe}(\text{CO})_2\text{P}(\text{Se})(\text{O}^i\text{Pr})_2]$  (**122-<sup>i</sup>Pr**) [146],  $[\text{M}_6\text{C}(\text{CO})_{16}]^{2-}$  (M = Fe, **129**; Ru, **130**) [147,148],  $[\text{EFe}_3(\text{CO})_9]^{2-}$  (E = Se, **3b**; Te, **3c**) [13], and  $[\text{TeRu}_5(\text{CO})_{14}]^{2-}$  (**115c**) [90b].

It is worthwhile, first, to mention several  $\text{Cu}_m\text{X}_n$ -stabilized high-nuclearity Ru-clusters, in which the  $\text{Cu}_m\text{X}_n$  occupied in the center of the metal frameworks and linked anionic clusters together [149]. The first example  $[\{\text{Ru}_4(\text{CO})_{12}\text{BH}\}_2\{\text{Cu}_4(\mu\text{-Cl})\}]$  (**131**), was published by Rheingold and Housecroft, which was synthesized from complex **123** with  $[\text{Cu}(\text{MeCN})_4][\text{BF}_4]$  in the presence of  $[\text{PPN}]\text{Cl}$  [149a,149b]. Other interesting  $\text{Cu}_7\text{Cl}_3$ - and  $\text{Cu}_6\text{Cl}_2$ -linked Ru-clusters,  $[\{\text{Ru}_4\text{H}(\text{CO})_{12}\}_2(\text{Cu}_7\text{Cl}_3)]^{2-}$ ,  $[\{\text{Ru}_6\text{H}(\text{CO})_{17}\}_2(\text{Cu}_6\text{Cl}_2)]^{2-}$ , and  $[\{\text{Ru}_{10}\text{H}_2(\text{CO})_{24}\}_2(\text{Cu}_6\text{Cl}_2)]^{4-}$ , were constructed from complex **124** or **125**, respectively, via a similar methodology [149c,149d]. In addition, the low-nuclearity cluster  $[\text{Fe}_3\text{Cu}(\text{CO})_9(\mu_4\text{-CCO})]^{2-}$  (**132**) was obtained from cluster **126** with  $[\text{Cu}(\text{MeCN})_4][\text{PF}_6]$  in the presence of  $[\text{PPN}]\text{I}$  [150], and the Ru-analogue  $[\text{Ru}_3\text{Cu}(\text{CO})_9(\mu_3\text{-CCO})]^{2-}$  was also reported and synthesized similarly [151]. All these Cu-bridged clusters demonstrated the importance of the presence of the halide which was apparently required to stabilize the resultant copper-transition metal clusters [152].

Scheer et al. also developed a synthetic route by treating the neutral starting complex **127** with copper halides  $\text{CuX}$  (X = Cl, Br, I) to give  $\text{Cu}_2\text{X}_2$ -bridged dimeric complexes  $[\text{Cu}(\mu\text{-X})\{\text{Cp}^*\text{Mo}(\text{CO})_2(\mu\text{-}\eta^3\text{-}\eta^2\text{-As}_3)\}_2]$  (X = Cl, **133-Cl**, Br, **133-Br**, I, **133-I**) [153]. Dimeric  $\text{Cu}_2\text{X}_2$ -bridged complexes  $[\text{Cu}(\mu\text{-X})\{\text{CpMo}(\text{CO})_2\}_2(\mu\text{-}\eta^2\text{-Sb}_2)]_2$  (X = Cl, **134-Cl**; Br, **134-Br**) and  $[\text{Cu}(\mu\text{-X})\{\text{CpFe}(\text{CO})_2\text{P}(\text{Se})(\text{O}^i\text{Pr})_2\}_2]$  (X = Cl, **135-Cl**; Br, **135-Br**) were obtained by using the neutral complex **128** or **122-<sup>i</sup>Pr** with copper halides [145b,138d]. On the other hand, the *closo*-octahedral complexes **129** and **130** were utilized as anionic building blocks to construct heteronuclear metal clusters. The iron-cluster **129** with copper(I) chloride in the presence of  $[\text{PPh}_4]\text{Br}$  was reported to produce an octahedral complex  $[\text{Fe}_5\text{C}(\text{CO})_{14}\text{CuBr}]^{2-}$  (**136**), with the CuBr occupying one vertex [154]. In contrast, the similar Ru-cluster **130** with copper(I) chloride produced an octahedral-based cluster  $[\text{Ru}_6\text{C}(\text{CO})_{16}\text{CuCl}]^{2-}$  (**137**) with the CuCl capping one of the triangular faces [155].

In the group 8 (Fe, Ru) system, three anionic clusters,  $[\text{EFe}_3(\text{CO})_9]^{2-}$  (E = Se, **3b**; Te, **3c**) and  $[\text{TeRu}_5(\text{CO})_{14}]^{2-}$  (**115c**), were successfully utilized as building units toward copper halides, which resulted in different types of mixed group 8 (Fe, Ru)–copper halide clusters [90b,90c,113b]. The anionic building blocks **3b** and **3c** were found to react readily with  $\text{CuX}$  (X = Cl, Br, I), or, following by the addition of  $[\text{Cu}(\text{MeCN})_4][\text{BF}_4]$ , to produce a series of  $\text{CuX}$ -,  $\text{Cu}_2\text{X}_2$ -,  $\text{Cu}_3\text{X}$ -,  $\text{Cu}_4\text{X}_2$ -, or  $\text{Cu}_4\text{X}_4$ -incorporated mono or di- $\text{EFe}_3$  (E = Se, Te) carbonyl clusters under appropriate conditions [90c,113b]. By controlling the ratio of the reactant to copper halides and the reaction temperature, the rational synthesis, stepwise cluster expansion, and cluster transformation of these E–Fe–CuX (E = Se, Te) clusters were successfully achieved, as shown in Scheme 24. As shown, clusters **3b** and **3c** reacted with  $\text{CuX}$  (X = Cl, Br, I) in molar ratios of 1:1, 1:2, and 1:3 or 1:4 in THF to produce mono- $\text{CuX}$ -incorporated  $\text{EFe}_3$ -based clusters  $[\text{EFe}_3(\text{CO})_9\text{CuX}]^{2-}$  (E = Se, **138b**; Te **138c**),  $\text{Cu}_2\text{X}_2$ -incorporated clusters  $[\text{EFe}_3(\text{CO})_9\text{Cu}_2\text{X}_2]^{2-}$  (E = Se, **139b**, X = Cl, Br; Te, **139c**),  $\text{Cu}_4\text{X}_2$ -linked di- $\text{EFe}_3$  clusters

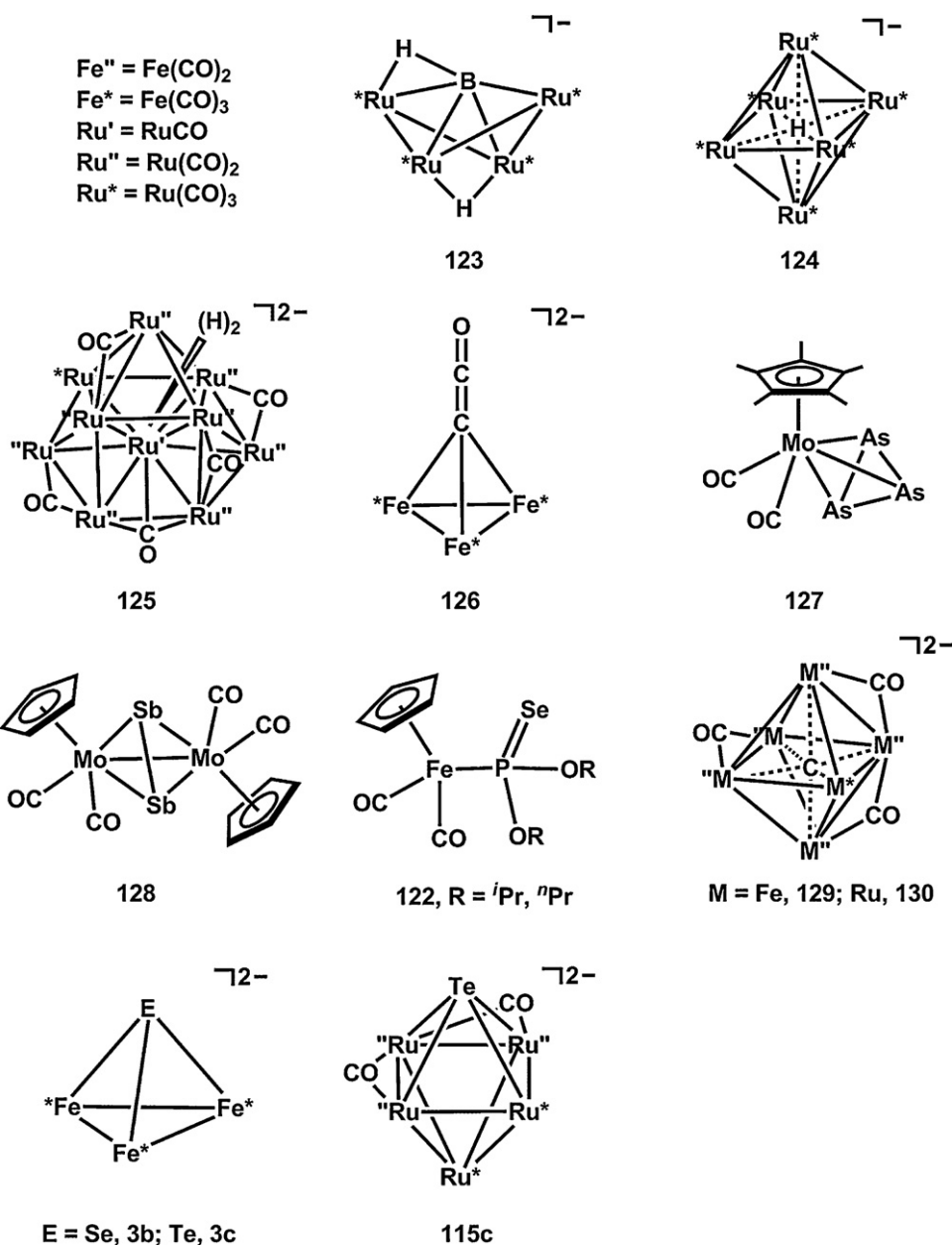
$[\{\text{EFe}_3(\text{CO})_9\}_2\text{Cu}_4\text{X}_2]^{2-}$  (E = Se, **140b**, X = Cl, Br; Te, **140c**, X = Cl, Br), and  $\text{Cu}_4\text{X}_4$ -linked di- $\text{EFe}_3$  cluster  $[\{\text{SeFe}_3(\text{CO})_9(\text{CuCl})_2\}_2]^{4-}$  (**141**). Complex **141** is a thermodynamic dimeric product from the coupling reaction of the  $\text{Cu}_2\text{Cl}_2$ -bridged cluster **139b-Cl**. Furthermore, by controlling the amounts of copper halides or  $[\text{Cu}(\text{MeCN})_4][\text{BF}_4]$ ,  $\text{CuX}$ -bridging clusters **138b** and **138c** could be converted into  $\text{Cu}_2\text{X}_2$ -bridging **139b** and **139c** or  $\text{Cu}_3\text{X}$ -bridging **142** via cluster-expansion processes. Similarly, clusters **139b**, **139c**, and **142** could transform into  $\text{Cu}_4\text{X}_2$ -bridging clusters **140b** and **140c**.

Controllable stepwise cluster-growth processes were also observed in the Te–Ru–CuX system (Scheme 25), in which cluster **115c** was employed as a useful building block to react with  $\text{CuX}$  (X = Cl, Br, I) at different ratios [90b]. With the ratio of 1:1 or 1:2, mono- $\text{CuX}$ – $\text{TeRu}_5$  clusters  $[\text{TeRu}_5(\text{CO})_{14}(\text{CuX})]^{2-}$  (**143**), bis- $\text{CuX}$ – $\text{TeRu}_5$  clusters  $[\text{TeRu}_5(\text{CO})_{14}\text{Cu}_2\text{X}_2]^{2-}$  (**144**, X = Cl, Br),  $\text{Cu}_4\text{X}_2$ -linked di- $\text{TeRu}_5$  clusters  $[\{\text{TeRu}_5(\text{CO})_{14}\}_2\text{Cu}_4\text{X}_2]^{2-}$  (**145**, X = Cl, Br), and bis- $\text{CuX}$ – $\text{Te}_2\text{Ru}_4$  clusters  $[\text{Te}_2\text{Ru}_4(\text{CO})_{10}\text{Cu}_2\text{X}_2]^{2-}$  (**146**) were obtained under appropriate conditions. It was noted that bis- $\text{CuX}$ – $\text{TeRu}_5$  clusters  $[\text{TeRu}_5(\text{CO})_{14}\text{Cu}_2\text{X}_2]^{2-}$  (**144**, X = Cl, Br) were isolated as intermediate complexes, which were stable only in MeCN at temperatures ranging from –35 to 0 °C. However, in THF at room temperature, clusters **144** underwent a coupling reaction to form  $\text{Cu}_4\text{X}_2$ -linked di- $\text{TeRu}_5$  complexes  $[\{\text{TeRu}_5(\text{CO})_{14}\}_2\text{Cu}_4\text{X}_2]^{2-}$  (**145**, X = Cl, Br). In addition, complexes **144** readily transformed into bis- $\text{CuX}$ – $\text{Te}_2\text{Ru}_4$  clusters  $[\text{Te}_2\text{Ru}_4(\text{CO})_{10}\text{Cu}_2\text{X}_2]^{2-}$  (**146**, X = Cl, Br) in MeCN at room temperature. Furthermore,  $\text{CuX}$ -incorporated clusters **143** with 1 equiv of  $\text{CuX}$  (X = Cl, Br, I) in THF at room temperature or 0 °C formed corresponding  $\text{Cu}_4\text{X}_2$ -linked di- $\text{TeRu}_5$  clusters **145**. However, complex **143-I** with 1 equiv CuI at room temperature led to the formation of the  $\text{Te}_2\text{Ru}_4$ -based **146-I**.

It would be of more interest to sort these copper halide-incorporated structures by bonding modes. For comparison, groups 14 (C), 15 (As, Sb), and 16 (Se, Te)-containing group 6 (Mo) or group 8 (Fe, Ru) metal–copper halide carbonyl clusters were included. Please noted that  $\text{Cu}_m\text{X}_n$ -linked coordination polymers were not included in this section, and will be mentioned in Section 8.2. These  $\text{Cu}_m\text{X}_n$ -incorporated structures were categorized according to  $\text{CuX}$ -,  $\text{Cu}_2\text{X}_2$ -,  $\text{Cu}_3\text{X}$ -,  $\text{Cu}_4\text{X}_2$ -, and  $\text{Cu}_4\text{X}_4$  bonding modes, which are shown in Chart 5. The arrows in Chart 5 indicate the existence of the available coordination sites, which showed a tolerance of the coordination numbers with either main-group elements (E) or transition metals (M) bound to the copper atom.

### 6.1.1. $\text{CuX}$ -bridged clusters

Bonding mode **1a** involved the  $\text{CuX}$  (X = Cl, Br, I) fragment incorporated into anionic metal units (M) or main-group elements (E) accompanied with the formation of the Cu–M or Cu–E bond (Chart 5). Complexes  $[\text{SeFe}_3(\text{CO})_9\text{CuX}]^{2-}$  (X = Cl, **138b-Cl**; Br, **138b-Br**; I, **138b-I**) [113b] and  $[\text{TeFe}_3(\text{CO})_9\text{CuX}]^{2-}$  (X = Cl, **138c-Cl**; Br, **138c-Br**; I, **138c-I**) [113a,90c] each displayed an  $\text{EFe}_3$  tetrahedral geometry with one Fe–Fe bond bridged by one  $\text{CuX}$  (mode **1a**), which have been mentioned in Section 5.2.2. In addition, clusters  $[\text{TeRu}_5(\text{CO})_{14}\text{CuX}]^{2-}$  (X = Cl, **143-Cl**; Br, **143-Br**; I, **143-I**) each possessed a  $\text{TeRu}_5$  octahedral geometry with one  $\text{Ru}_3$  triangle capped by one  $\text{CuX}$  [90b]. A similar example was found with octahedral-based cluster  $[\text{Ru}_6\text{C}(\text{CO})_{16}\text{CuCl}]^{2-}$  (**137**), where CuCl capped one of the trigonal faces of the  $\text{Ru}_6$  core to form three Ru–Cu bonds [155]. Complex  $[\text{Fe}_3\text{Cu}(\text{CO})_9(\mu_4\text{-CCO})]^{2-}$  (**132**) [150] displayed a tetrahedral  $\text{Fe}_3(\mu_3\text{-CCO})$  core in which the  $\text{Fe}_2\text{CCO}$  triangle was capped by a CuI fragment while complex  $[\text{Fe}_5\text{C}(\text{CO})_{14}\text{CuBr}]^{2-}$  (**136**) [154] was composed of an octahedral  $\text{Fe}_5\text{Cu}$  core, in which one vertex of the octahedron was occupied by the CuBr.

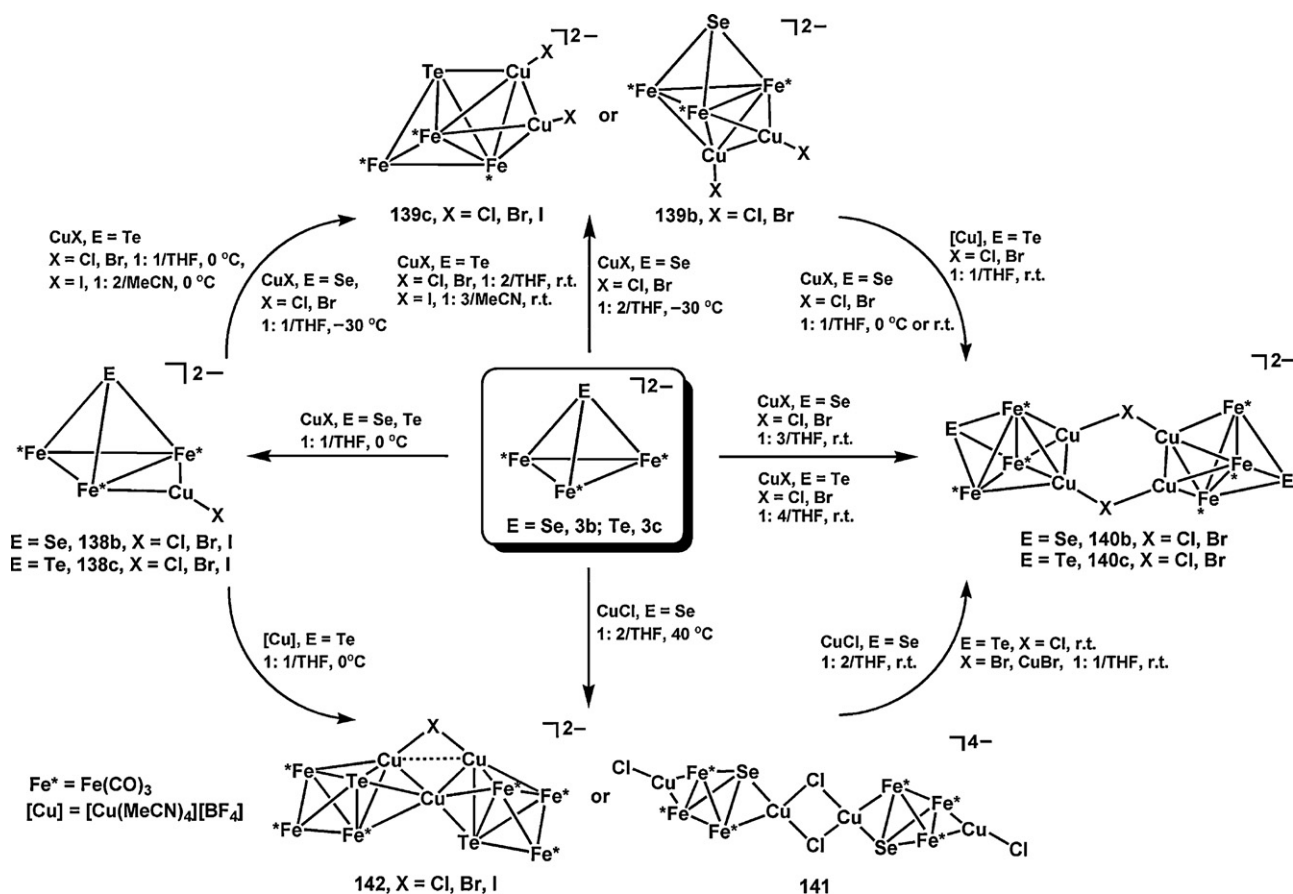


**Chart 4.** Useful building blocks of group 6 or group 8 carbonyl complexes for the construction of copper halide-incorporated metal frameworks.

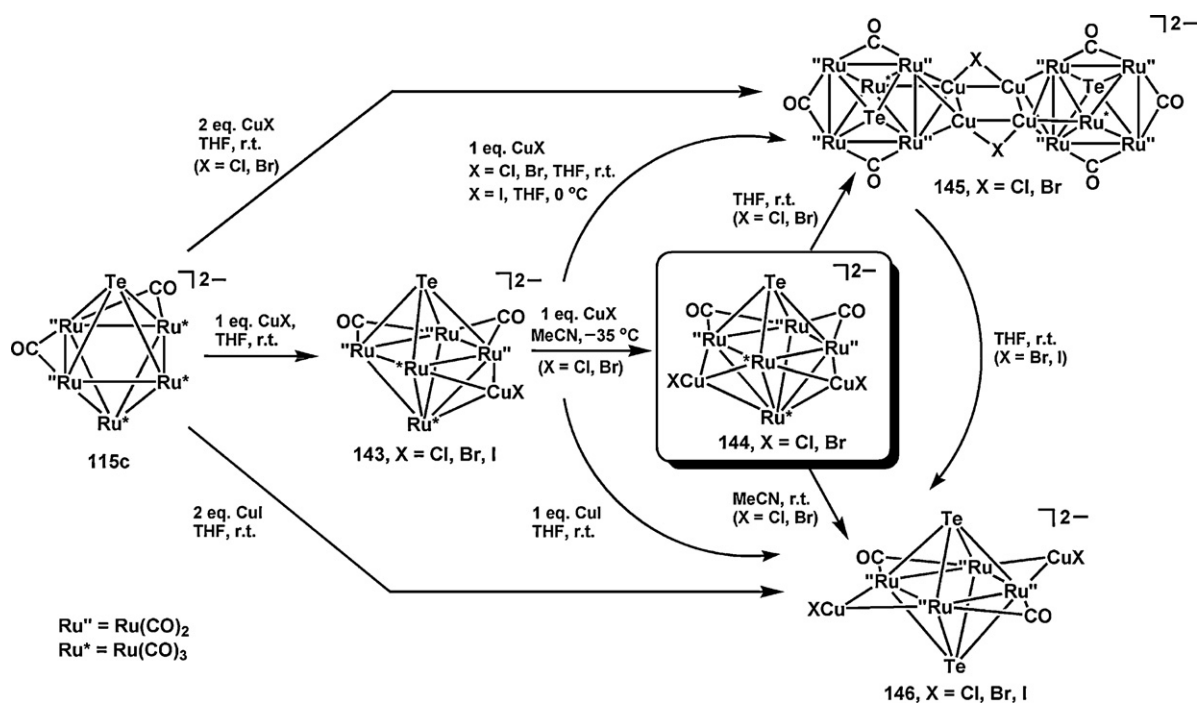
### 6.1.2. $\text{Cu}_2\text{X}_2$ - and $\text{Cu}_3\text{X}$ -bridged clusters

Bonding modes **1b–1e** were involved in the  $\text{Cu}_2\text{X}_2$ -bridged clusters, in which the two Cu atoms could form the Cu–Cu bonding or be bridged by X (X = Cl, Br, I) or metal clusters. It was noted that the bridged halide across the Cu atoms usually weakened the Cu–Cu bond. Complexes  $[\text{SeFe}_3(\text{CO})_9\text{Cu}_2\text{X}_2]^{2-}$  (X = Cl, **139b-Cl**; Br, **139b-Br**) represented an example of bonding mode **1b**, in which the  $\text{Fe}_3$  ring of the  $\text{SeFe}_3$  core was asymmetrically bridged by one  $\mu$ - $\text{CuX}$  (X = Cl, Br) and capped by another  $\mu_3$ - $\text{CuX}$  (X = Cl, Br) with two Cu atoms bonded [**113b**], which was structurally related to the previously reported  $[\text{SFe}_3(\text{CO})_9(\text{AuPPh}_3)_2]$  [**114b**]. However, its Te-analogue  $[\text{TeFe}_3(\text{CO})_9\text{Cu}_2\text{Cl}_2]^{2-}$  (**139c-Cl**) also displayed mode **1b**, but with one of the two CuCl bonded to the Te atom, where one triangular  $\text{TeFe}_2$  plane of the tetrahedral  $\text{TeFe}_3$  core was asymmetrically bridged and capped by two bonded Cu atoms [**90c**]. Complex  $[\text{Fe}_4\text{C}(\text{CO})_{12}\text{Cu}_2\text{Cl}_2]^{2-}$  (**147**) was an octahedral structure composed of an  $\text{Fe}_4\text{Cu}_2$  metal core with two CuCl occupying two adjacent sites of the octahedra (mode **1b**), in which each copper atom was bound

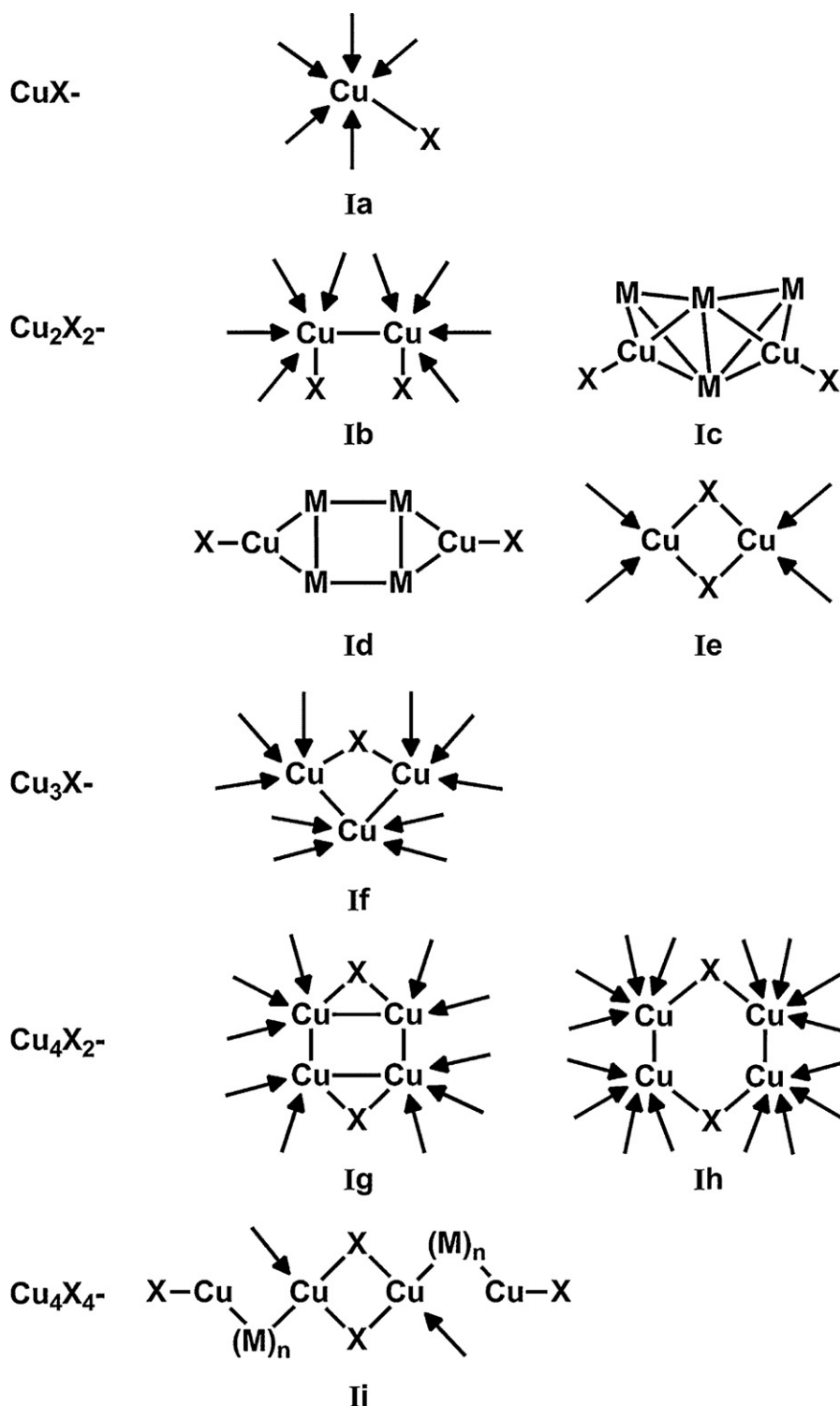
to three Fe atoms and the interstitial C atom [**154**]. The bonding mode **1c**, where the  $\text{M}_4$  butterfly fragment was capped by two copper halides, was observed in  $[\text{TeRu}_5(\text{CO})_{14}\text{Cu}_2\text{Br}_2]^{2-}$  (**144-Br**), which displayed a  $\text{TeRu}_5$  octahedral geometry with two neighboring  $\text{Ru}_3$  planes, each capped by a CuBr fragment [**90b**]. For the bonding mode **1d**, complexes  $[\text{Te}_2\text{Ru}_4(\text{CO})_{10}\text{Cu}_2\text{X}_2]^{2-}$  (X = Cl, **146-Cl**; Br, **146-Br**; I, **146-I**) each had an octahedral  $\text{Te}_2\text{Ru}_4$  cluster core with a rectangular  $\text{Ru}_4$  plane, of which the two opposite edges each was bridged by a  $\text{CuX}$  (X = Cl, Br, I) [**90a,90b**]. The bonding mode **1e** was found in dimeric complexes  $[\text{Cu}(\mu\text{-X})\{\text{CpFe}(\text{CO})_2\text{P}(\text{Se})(\text{O}^i\text{Pr})_2\}]_2$  (X = Cl, **135-Cl**; Br, **135-Br**), in which both Cu atoms are trigonally coordinated with one Se atom and two bridging Cl atoms to give a  $\text{Cu}_2\text{Cl}_2$  parallelogram core [**138d**]. Other examples are  $[\text{Cu}(\mu\text{-X})\{\text{Cp}^*\text{Mo}(\text{CO})_2(\mu\text{-}\eta^3\text{-}\eta^2\text{-As}_3)\}]_2$  (X = Cl, **133-Cl**; Br, **133-Br**; I, **133-I**), each of which consisted of a planar four-membered  $\text{Cu}_2\text{X}_2$  ring, and each Cu(I) atom was side-on coordinated by an As–As edge of the *cyclo*- $\text{As}_3$  moiety [**153**]. Similar bonding features of  $[\text{Cu}(\mu\text{-X})\{\text{CpMo}(\text{CO})_2\}_2(\mu\text{-}\eta^2\text{-Sb}_2)]_2$  (X = Cl, **134-Cl**; Br, **134-Br**) were also



Scheme 24. Stepwise cluster transformations of E-Fe-CuX carbonyl clusters (E = Se, Te; X = Cl, Br, I).



Scheme 25. Stepwise cluster-expansion reactions of Te-Ru-CuX carbonyl clusters (X = Cl, Br, I).



**Chart 5.** Bonding modes (**Ia–Ii**) of  $Cu_mX_n$ -linked metal carbonyl complexes ( $X = Cl, Br, I$ ).

observed, where each copper atom was coordinated by two bridging X atoms and also by the  $Sb_2$  bond of the  $[CpMo(CO)_2]_2Sb_2$  moiety, achieving a distorted tetrahedral coordination environment [145b].

The bonding mode **If** was seen in complexes  $[\{TeFe_3(CO)_9\}_2Cu_3X]^{2-}$  ( $X = Br$ , **142-Br**; **I**, **142-I**), which represented the first examples of  $Cu_3X$  as a bridging unit to coordinate to both the main-group element (E) and the transition-metal atom

(M) (Fig. 13) [90c].  $Cu_3X$ -incorporated di- $TeFe_3$  clusters **142-Br** and **142-I** were isostructural species, and each consisted of two  $TeFe_3(CO)_9$  units linked by three Cu atoms in a triangular arrangement where the Cu–Cu bond was externally bridged by one X ( $X = Br, I$ ) atom. A close look showed that clusters **142-Br** and **142-I** possessed two  $TeFe_3$  cores, each with one  $TeFe_2$  face capped by a Cu atom, to give a  $TeFe_3Cu$  trigonal bipyramidal geometry, two of which were further linked by a  $\mu_6$ -Cu atom and an X atom ( $X = Br,$

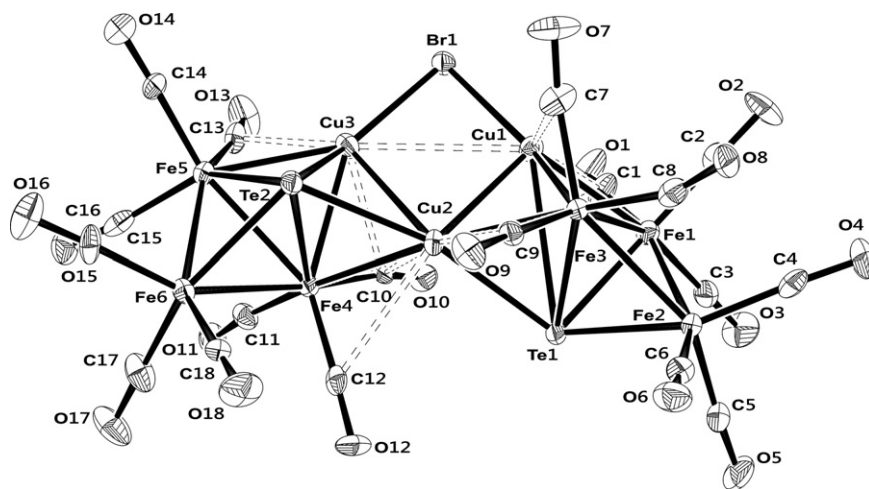


Fig. 13. ORTEP diagram of anion **142-Br**.

Adapted from ref. [90c].

l). Noteworthy in **142-Br** and **142-I**, each Te atom was coordinated to three Fe and two Cu atoms in a  $\mu_5$ -Te fashion that is rarely seen in the literature [8b,86,91,156]. Although  $\text{Cu}_3$  triangle-bridged metal carbonyl complexes have been reported [3k,137c,157], the planar  $\text{M}_3\text{X}$  was only found in  $[\{\text{Ru}_5\text{C}(\text{CO})_{14}\}_2\text{Ag}_3\text{Cl}]^{2-}$  [158].

### 6.1.3. $\text{Cu}_4\text{X}_2$ - and $\text{Cu}_4\text{X}_4$ -bridged clusters

The bonding mode **lg** was involved in a structure, in which the four Cu atoms were covalently bonded to form a  $\text{Cu}_4$  parallelogram with two opposite Cu–Cu edges each bridged by a halide. This mode was found in complex  $[\{\text{TeRu}_5(\text{CO})_{14}\}_2\text{Cu}_4\text{X}_2]^{2-}$  (X = Cl, **145-Cl**; Br, **145-Br**) [90a,90b], each of which contained two  $\text{TeRu}_5$ -clusters bridged by a  $\text{Cu}_4\text{X}_2$  unit. The four Cu atoms were covalently bonded, with two lengthening halide-bridged Cu–Cu bonds (ranging 2.773(2)–2.779(1) Å). The similar bonding mode in the mixed-coinage  $\text{Cu}_2\text{Ag}_2\text{Cl}_2$ -bridged di- $\text{Ru}_6\text{C}$  cluster  $[\{\text{Ru}_6\text{C}(\text{CO})_{16}\}_2\text{Cu}_2\text{Ag}_2\text{Cl}_2]^{2-}$  was also observed [155]. Furthermore, a similar bonding mode **lg** was found in the case of a special anionic cluster  $[\text{Pd}_2\{\text{Ru}_6\text{C}(\text{CO})_{16}\}_2\text{Cu}_4\text{Cl}_2]^{2-}$  (**148**) which had a crystallographic center of symmetry at the center of the molecule (the mid-point between Pd–Pd<sup>+</sup>), where the Pd atoms sat in the center of the  $\text{Cu}_4\text{X}_2$  ring to make the unbridged Cu–Cu bonds nonbonding and each Cu atom was bound with one or two Pd atoms and two or three Ru atoms. The entire structure could be viewed as the linear edge-condensation of four octahedra, two  $[\text{Ru}_6\text{C}]$  and two  $[\text{Ru}_2\text{Pd}_2\text{Cu}_2]$ , if some long metal–metal distances were taken as edges [155]. Another interesting cluster  $[\{\text{Ru}_6\text{C}(\text{CO})_{15}\}_2(\text{Cu}_4\text{Cl}_2)(\text{Cu}_3\text{Cl})]^{2-}$  could be described to display a mixed type of modes **lg** and **lf** [155].

The bonding mode **lh** was found in  $[\{\text{SeFe}_3(\text{CO})_9\}_2\text{Cu}_4\text{X}_2]^{2-}$  (X = Cl, **140b-Cl**; Br, **140b-Br**) [113b] and  $[\{\text{TeFe}_3(\text{CO})_9\}_2\text{Cu}_4\text{Cl}_2]^{2-}$  (**140c-Cl**) [90c], where the four Cu atoms and two halides formed a six-membered ring, similar to the bonding mode **lg**. It was found that the X-bridged Cu...Cu distances are long (3.503(2) Å, **140b-Cl**; 3.8246(6) Å, **140b-Br**; 3.849(2) Å, **140c-Cl**), and are considered to be nonbonding. In addition, the  $\text{Cu}_4\text{X}_2$ -linked clusters  $[\{\text{Ru}_6\text{C}(\text{CO})_{16}\}_2\text{Cu}_4\text{Cl}_2]^{2-}$  (**149**) [152a] and  $[\{\text{Fe}_4\text{C}(\text{CO})_{12}\}_2\text{Cu}_4\text{Cl}_2]^{2-}$  (**150**) [154] also demonstrated the bonding mode **lh**, with the X-bridged Cu...Cu distances of 3.011(4) and 3.1322(2) Å, respectively.

The bonding mode **li** was seen in complex  $[\{\text{SeFe}_3(\text{CO})_9(\text{CuCl})_2\}_2]^{4-}$  (**141**), in which two asymmetric  $\text{SeFe}_3\text{CuCl}$  clusters were linked by a central  $\text{Cu}_2\text{Cl}_2$  ring, and the Fe–Fe and Se–Fe edges of the  $\text{SeFe}_3$  core were each bridged

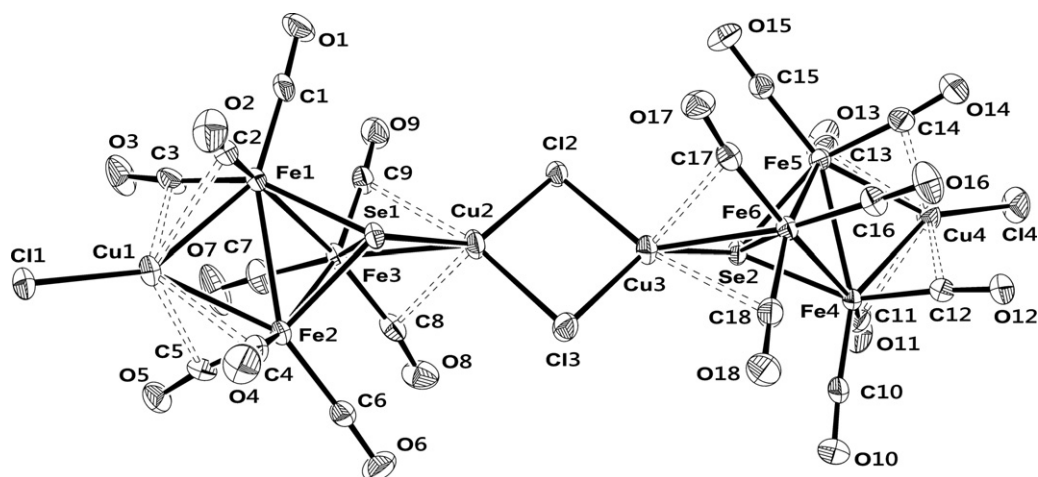
by one  $\text{CuCl}$  in the *trans* position [113b]. It was noted that the central  $\mu$ - $\text{Cu}_2\text{X}_2$  bridging unit was bound to two Se and two Fe centers (Fig. 14). According to the CSD search, this bonding mode represented a rare example of the  $\text{Cu}_2\text{Cl}_2$  unit coordinated to both main-group elements (E) and transition metal atoms (M).

### 6.2. E–M (E = S, Se, Te; M = Cr, Fe, Ru) clusters with Cd(II) or Hg(II) salts

As mentioned above, metals with the  $d^{10}$  electron configuration, like the Cu(I) ion, can back-donate electrons from filled d orbitals to unoccupied d orbitals of chalcogen elements or specific transition metals, to form  $\pi$  bonds. Soft Lewis acids, such as zinc(II), cadmium(II), or mercury(II) salts, with the same  $d^{10}$  configuration, could also be employed as a useful linker for the construction of high-nuclearity clusters. Excellent reviews of group 12-incorporated transition metal clusters have been reported [159]. The structures of group 12-incorporated groups 6–8 carbonyl chalcogenide (S, Se, Te) clusters will be reviewed, based on a search of CSD. There were no examples of group 7-containing carbonyl clusters, so as a result we focused only on group 6 (Cr) and group 8 (Fe, Ru) carbonyl chalcogenide clusters. A number of neutral or anionic group 6 (Cr) and group 8 (Fe) carbonyl chalcogenide complexes have been reported to be used as starting materials toward zinc(II), cadmium(II), or mercury(II) salts for cluster expansion. These starting materials are summarized in Chart 6, and include  $[\text{S}_2\text{Fe}_2(\text{CO})_6]^{2-}$  (**86a**) [96],  $[\text{Te}\{\text{Cr}(\text{CO})_5\}_2]^{2-}$  (**5**) [15],  $[\text{Te}\{\text{Cr}(\text{CO})_5\}_3]^{2-}$  (**6**) [15], *fac*- $[\text{Fe}(\text{CO})_3(\text{SePh})_3]^-$  (**151**) [160],  $[\text{Cp}(\text{CO})\text{FeC}(\text{S})\text{SC}(\text{Fp})\text{S}]$  (Fp = CpFe(CO)<sub>2</sub>) (**152**) [161],  $[\text{CpFe}(\text{CO})_2\text{P}(\text{Se})(\text{O}^i\text{Pr})_2]$  (**122-<sup>i</sup>Pr**) [146], *trans*- $[\text{Fe}(\text{CO})_3(\text{Ph}_2\text{PNS})_2]$  (Ph<sub>2</sub>PNS = 2-(diphenylphosphino)thiazole) (**153**) [162],  $[\text{SeFe}_3(\text{CO})_9]^{2-}$  (**3b**) [13a], and  $[\text{SFe}_2\text{Co}(\text{CO})_9]^-$  (**95a**) [109a]. The bonding modes of these products were further categorized into M-bridged or MX-bridged (M = Zn, Cd, Hg; X = Cl, Br, I) types and sorted in Chart 7 (modes **IIa–IIg**). It was noted that only very limited Zn-bridged complexes were reported. The arrows in Chart 7 indicate the available coordination sites for the M metals (M = Zn, Hg, Cd) showing a tolerance of the coordinating main-group elements (E = N, O, S, Se, Te) or group 8 metals (Fe, Ru). The bonding modes **IIc** and **IIf** were similar to mode **Ie** for the  $\text{Cu}_2\text{X}_2$ -bridge cases (**Chart 5**).

Seyferth et al. reported alkylmercurithio-bridged  $\text{Fe}_2(\text{CO})_6$  complexes  $[(\mu\text{-SHgR})(\mu\text{-SR})\text{Fe}_2(\text{CO})_6]$  (R = CH<sub>3</sub>, **154**; C<sub>2</sub>H<sub>5</sub>, **155**) [163a] and  $[(\mu\text{-SHgCH}_3)_2\text{Fe}_2(\text{CO})_6]$  (**156**) [163b] (mode **IIa**), which



Fig. 14. ORTEP diagram of anion **141**.

Adapted from ref. [113b].

resulted from a nucleophilic attack of the sulfur atom of complex **86a** at the methyl- or ethylmercuric(II) chloride. In addition, Te–Cr complexes **5** and **6** reacted with HgCl<sub>2</sub>, via the formation of the Te–Hg bond, to give their corresponding Hg-bridged clusters [HgTe<sub>2</sub>{Cr(CO)<sub>5</sub>}<sub>n</sub>]<sup>2-</sup> (*n*=4, **46**; 6, **47**) (mode **IIb**) [49]. Examples of  $\mu$ -Hg and  $\mu_3$ -Hg atoms (mode **IIb**) were found in the Fe/Ru–Hg carbonyl sulfide clusters [( $\mu$ -Hg){Fe(CO)<sub>3</sub>[Si(OMe)<sub>3</sub>](dppm-S)}<sub>2</sub>] [164a] and *cis*-[( $\mu_3$ -Hg)<sub>2</sub>Ru(CO)<sub>4</sub>{Ru<sub>3</sub>(CO)<sub>9</sub>( $\mu$ - $\eta^3$ -SC<sub>5</sub>H<sub>4</sub>N)}<sub>2</sub>] [164b]. The highest coordination number (6) of mode **IIb** was reported in complexes [Fe(CO)<sub>3</sub>( $\mu$ -SePh)<sub>3</sub>M( $\mu$ -SePh)<sub>3</sub>Fe(CO)<sub>3</sub>] (M=Zn, **157**; Cd, **158**), which were obtained from the reaction of the starting complex **151** with Zn(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O and

Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, respectively [165]. On the other hand, the M<sub>2</sub>X<sub>4</sub>-linked complex [Cp(CO)FeC(SHgBr<sub>2</sub>)SC(Fp)S]<sub>2</sub> (Fp=CpFe(CO)<sub>2</sub>) (**159**) (mode **IIb**) was synthesized from complex **152** with HgBr<sub>2</sub> [166]. Liu et al. used building block **122-<sup>i</sup>Pr**, which contained a secondary selenophosphito [(<sup>i</sup>PrO)<sub>2</sub>PSe]<sup>-</sup> moiety with coordination properties at the Se atom, toward cadmium(II) and mercury(II) salts, forming iron–mercury/cadmium carbonyl complexes [146,167]. By controlling the ratio of complex **122-<sup>i</sup>Pr** to M(ClO<sub>4</sub>)<sub>2</sub> or MX<sub>2</sub> (M=Cd, Hg), a series of **122-<sup>i</sup>Pr**-based complexes were afforded: [Hg{CpFe(CO)<sub>2</sub>P(Se)(O<sup>i</sup>Pr)<sub>2</sub>}<sub>2</sub>]<sup>2+</sup> (**160**) (mode **IIb**), [Hg{CpFe(CO)<sub>2</sub>P(Se)(O<sup>i</sup>Pr)<sub>2</sub>}<sub>3</sub>]<sup>2+</sup> (**161**) (mode **IIb**), [Cd{CpFe(CO)<sub>2</sub>P(Se)(O<sup>i</sup>Pr)<sub>2</sub>}<sub>3</sub>(H<sub>2</sub>O)]<sup>2+</sup> (**162**)

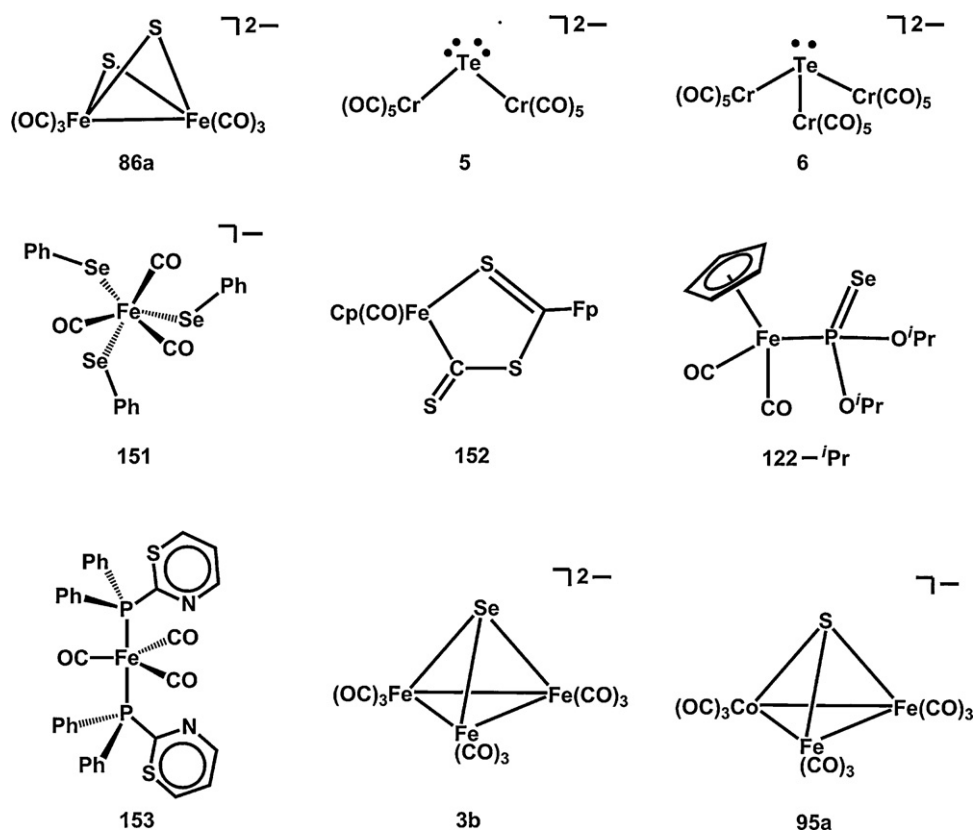


Chart 6. Useful building blocks of group 6 or group 8 carbonyl complexes for the construction of group 12-incorporated metal frameworks.

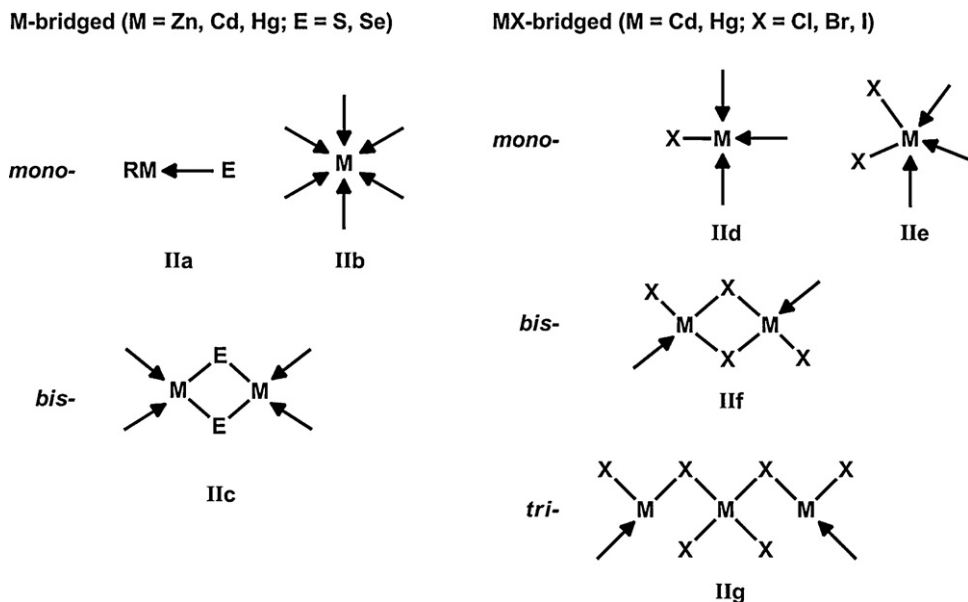


Chart 7. Bonding modes (IIa–IIg) of group 12-bridged group 6 or group 8 carbonyl complexes.

(mode **IIb**),  $[\text{HgI}_2\{\text{CpFe}(\text{CO})_2\text{P}(\text{Se})(\text{O}^i\text{Pr})_2\}_2]$  (**163**) (mode **IIe**),  $[\text{Hg}_3\text{I}_4(\mu\text{-I})_2\{\text{CpFe}(\text{CO})_2\text{P}(\text{Se})(\text{O}^i\text{Pr})_2\}_2]$  (**164**) (mode **IIg**),  $[\text{HgX}(\mu\text{-X})\{\text{CpFe}(\text{CO})_2\text{P}(\text{Se})(\text{O}^i\text{Pr})_2\}_2]$  (**165**, X = Cl, Br, I) (mode **IIIf**), and  $[\text{CdX}(\mu\text{-X})\{\text{CpFe}(\text{CO})_2\text{P}(\text{Se})(\text{O}^i\text{Pr})_2\}_2]$  (**166**, X = Cl, Br, I) (mode **IIIf**).

Mak et al. used complex **153** toward  $\text{CdI}_2$  to produce Fe–Cd bonded complexes  $[\text{Fe}(\text{CO})_3(\mu\text{-Ph}_2\text{PNS})_2\text{CdI}_2]$  (**167**) (mode **IIe**), which were supported and stabilized by the polydentate ligand of **153** [162]. However, this type of donor–accepter metal–metal bonding is usually weak, and in most cases bridging ligands or anionic building units were necessary to stabilize the metal–metal framework. Without any support from the bridging ligands, complexes  $[\text{SeFe}_3(\text{CO})_9(\mu\text{-HgI})]^-$  (**168**) (mode **IIId**) and  $[(\mu_4\text{-M})\{\text{SeFe}_3(\text{CO})_9\}_2]^{2-}$  (M = Cd, **98**; Hg, **99**) (mode **IIb**) were obtained in our laboratory by using the anionic complex **3b** toward  $\text{HgI}_2$  and  $\text{M}(\text{OAc})_2$  (M = Cd, Hg) salts, respectively [13a,113c]. Clusters **98**, **99**, and **168** represented the first examples of anionic cadmium– or mercury–iron carbonyl chalcogenide clusters. A  $\text{HgX}$  fragment occupying an edge-bridging position was first reported in clusters  $[\text{Ru}_3(\mu_3\text{-C}_2^t\text{Bu})(\text{CO})_9(\text{HgX})]$  (X = Br, I) [168]. The formation of the  $\mu\text{-HgI}$  bridged cluster **168** was attributed to the stronger Hg–I bond of  $\text{HgI}_2$  due to the better soft–soft interaction. A study of the dianion **3b** toward  $\text{HgI}_2$  and  $\text{M}(\text{OAc})_2$  (M = Cd, Hg) revealed a lack of reactivity at the exposed selenium atom, which may be attributed to the lower basicity of the Se atom. Other complexes with the same  $\mu_4$ -fashion were also found in complexes  $[(\mu_4\text{-Hg})\{\text{Fe}_2\text{M}(\mu_3\text{-COMe})(\text{CO})_7\text{Cp}\}_2]$  (M = Co, Rh),  $[(\mu_4\text{-Hg})\{\text{Fe}_5\text{C}(\text{CO})_{14}\}_2]^{2-}$ ,  $[(\mu_4\text{-Hg})\{(\mu\text{-CH}_3\text{OCH}_2\text{CH}=\text{C})(\mu\text{-}^t\text{BuS})\text{Fe}_2(\text{CO})_6\}_2]$ ,  $[(\mu_4\text{-Hg})\{\text{Ru}_6\text{C}(\text{CO})_{16}\}_2]^{2-}$ ,  $[(\mu_4\text{-Cd})\{\text{Fe}_2(\text{CO})_6(\mu\text{-CO})_2\}_2]^{2-}$ , and  $[(\mu_4\text{-Cd})\{\text{Fe}_6(\text{CO})_{20}(\mu\text{-CO})_2\}_2]^{2-}$  [169,122b]. The mixed-metal tetrahedral cluster  $[\text{SFe}_2\text{Co}(\text{CO})_9]^-$  (**95a**) could react with  $\text{HgCl}_2$  to produce the dimeric complex  $[(\mu_4\text{-S}_2\text{Hg}_2)\{\text{Fe}_2\text{Co}(\text{CO})_9(\mu_3\text{-Cl})\}_2]$  (**169**) (mode **IIc**), in which the central  $\mu_4\text{-S}_2\text{Hg}_2$  ring bridged two  $\text{Fe}_2\text{Co}$  carbonyl moieties via complicated bond breakage and formation processes [170]. Furthermore, in addition to the  $\mu_4\text{-Hg}$  bonding mode,  $\mu_6\text{-Hg}$  metal carbonyl complexes also have been reported [171]. Finally, Fenske and Bettenhausen reported three high-nuclearity iron–mercury sulfide carbonyl clusters,  $[\text{Hg}_7\{\text{Fe}(\text{CO})_4\}_5(\text{S}^t\text{Bu})_3\text{Cl}]$ ,  $[\text{Hg}_{14}\text{Fe}_{12}\{\text{Fe}(\text{CO})_4\}_6\text{S}_6(\text{S}^t\text{Bu})_8\text{Br}_{18}]$ ,

and  $[\text{Hg}_{39}\text{Fe}_8\{\text{Fe}(\text{CO})_4\}_{18}\text{S}_8(\text{S}^t\text{Bu})_{14}\text{Br}_{28}]$ , which were obtained from  $[\text{Fe}(\text{CO})_4(\text{HgX})_2]$  (X = Cl, Br) with  $^t\text{BuSSiMe}_3$  and displayed modes **IIb**, **IIId**, and **IIe** [172].

## 7. Electrochemical and magnetic properties

### 7.1. Electrochemistry

The tendency of metal carbonyl clusters with a *closo*-geometry to possess rich redox properties has been reported [6,8a,8b,173,174]. There have been relatively few such studies, in comparison with those of high-valent organometallic complexes [6b,8a,175–179]. In general, the electronic properties of metal carbonyl clusters can be modulated by the introduction of main-group elements and/or metal fragments, which was shown by pronounced redox potential shifts in their electrochemistry [6,8d,19,180,181]. The electrochemistry of the neutral sulfur-containing metal carbonyl complexes, specifically for the iron system, was comprehensively discussed and reviewed [4c,11,105e,182,183]. Nevertheless, related investigations of selenium- or tellurium-containing metal clusters have seldom been explored [88c,133e], particularly for the anionic metal clusters [8a,19,87b,115]. This section is focused on a discussion of the recent study of the reversible or quasi-reversible redox properties of some representative anionic groups 8 (Fe, Ru) and 7 (Mn) chalcogenide clusters from the perspective of the cooperative properties of chalcogen elements and metals.

#### 7.1.1. Copper halide-incorporated E–M clusters (E = Se, Te; M = Fe, Ru)

The redox properties of iron anionic carbonyl clusters containing different chalcogen atoms have been examined. For example, the electrochemistry of  $\text{S}_2\text{Fe}_2$ -linked bisbutterfly clusters  $[\text{Se}_6\text{Fe}_6(\text{CO})_{12}]^{2-}$  (**16b**) was reported by Kolis et al. to display one reduction couple, which was similar to the corresponding S-cluster  $[\text{S}_6\text{Fe}_6(\text{CO})_{12}]^{2-}$  (**16a**) but with an anodic shift of approximately

**Table 2**  
Electrochemical data.

Complex	Oxidation process		Reduction process		Natural charge (metal cores)	Ref
	$E_p^{ox}/V^a$	$E_p^{red}/V^b$	$E_p^{ox}/V^a$	$E_p^{red}/V^b$		
	( $W_{1/2}/mV^c$ )	( $W_{1/2}/mV^c$ )	( $W_{1/2}/mV^c$ )	( $W_{1/2}/mV^c$ )		
[Et <sub>4</sub> N] <sub>2</sub> [SeFe <sub>3</sub> (CO) <sub>9</sub> ] <b>3b</b>				–0.233 <sup>d,e</sup> –0.521 <sup>d,f</sup>	–2.00	[113b]
[Et <sub>4</sub> N] <sub>2</sub> [TeFe <sub>3</sub> (CO) <sub>9</sub> ] <b>3c</b>		0.135 <sup>d,e</sup>		–0.270 <sup>d,e</sup> –0.523 <sup>d,f</sup>	–2.00	[90c]
[Et <sub>4</sub> N] <sub>2</sub> [SeFe <sub>3</sub> (CO) <sub>9</sub> CuCl] <b>138b-Cl</b>		0.282 <sup>d,e</sup>		–0.142 <sup>d,e</sup> –0.518 <sup>d,f</sup>	–1.90	[113b]
[Et <sub>4</sub> N] <sub>2</sub> [SeFe <sub>3</sub> (CO) <sub>9</sub> CuBr] <b>138b-Br</b>		0.242 <sup>d,e</sup>		–0.343 <sup>f,g</sup> –0.150 <sup>d,e</sup> –0.522 <sup>d,f</sup>	–1.87	[113b]
[Et <sub>4</sub> N] <sub>2</sub> [SeFe <sub>3</sub> (CO) <sub>9</sub> CuI] <b>138b-I</b>		0.222 <sup>d,e</sup>		–0.369 <sup>f,g</sup> –0.150 <sup>d,e</sup> –0.514 <sup>d,f</sup>	–1.86	[113b]
[Et <sub>4</sub> N] <sub>2</sub> [TeFe <sub>3</sub> (CO) <sub>9</sub> CuCl] <b>138c-Cl</b>		0.294 <sup>d,e</sup>		–0.289 <sup>f,g</sup> –0.146 <sup>d,e</sup> –0.654 <sup>d,f</sup>	–1.90	[90c]
[Et <sub>4</sub> N] <sub>2</sub> [TeFe <sub>3</sub> (CO) <sub>9</sub> CuBr] <b>138c-Br</b>		0.256 <sup>d,e</sup>		–0.333 <sup>f,g</sup> –0.144 <sup>d,e</sup> –0.620 <sup>d,f</sup>	–1.87	[90c]
[Et <sub>4</sub> N] <sub>2</sub> [TeFe <sub>3</sub> (CO) <sub>9</sub> CuI] <b>138c-I</b>		0.338 <sup>d,e</sup>		–0.349 <sup>f,g</sup> –0.162 <sup>d,e</sup> –0.618 <sup>d,f</sup>	–1.87	[90c]
[Et <sub>4</sub> N] <sub>2</sub> [SeFe <sub>3</sub> (CO) <sub>9</sub> Cu <sub>2</sub> Br <sub>2</sub> ] <b>139b-Br</b>		0.229 <sup>d,e</sup>		–0.321 <sup>f,g</sup> –0.131 <sup>d,e</sup> –0.511 <sup>d,f</sup> –0.623 <sup>d,f</sup>	–1.70	[113b]
[Et <sub>4</sub> N] <sub>2</sub> [TeFe <sub>3</sub> (CO) <sub>9</sub> Cu <sub>2</sub> Br <sub>2</sub> ] <b>139c-Br</b>		0.236 <sup>d,e</sup>		–0.259 <sup>f,g</sup> –0.124 <sup>d,e</sup> –0.484 <sup>d,f</sup>	–1.78	[90c]
[Et <sub>4</sub> N] <sub>2</sub> [{TeFe <sub>3</sub> (CO) <sub>9</sub> ] <sub>2</sub> Cu <sub>3</sub> Br] <b>142-Br</b>		0.292 <sup>d,e</sup>		–0.219 <sup>f,g</sup> –0.116 <sup>d,e</sup> –0.516 <sup>d,f</sup>	–3.27	[90c]
[Et <sub>4</sub> N] <sub>2</sub> [{SeFe <sub>3</sub> (CO) <sub>9</sub> ] <sub>2</sub> Cu <sub>4</sub> Br <sub>2</sub> ] <b>140b-Br</b>		0.247 <sup>d,e</sup>		–0.280 <sup>f,g</sup> –0.117 <sup>d,e</sup> –0.525 <sup>d,f</sup> –0.597 <sup>d,f</sup>	–3.06	[113b]
[Et <sub>4</sub> N] <sub>2</sub> [{TeFe <sub>3</sub> (CO) <sub>9</sub> ] <sub>2</sub> Cu <sub>4</sub> Br <sub>2</sub> ] <b>140c-Br</b>		0.262 <sup>d,e</sup>		–0.209 <sup>f,g</sup> –0.130 <sup>d,e</sup> –0.486 <sup>d,f</sup>	–3.24	[90c]
[PPh <sub>4</sub> ] <sub>2</sub> [TeRu <sub>5</sub> (CO) <sub>14</sub> ] <b>115c</b>		0.090 <sup>d,e</sup>		–1.178 <sup>d,e</sup> –1.474 <sup>d,e</sup> –1.798 <sup>d,e</sup>	–2.00	[90b]
[PPh <sub>4</sub> ] <sub>2</sub> [TeRu <sub>5</sub> (CO) <sub>14</sub> CuCl] <b>143-Cl</b>		0.134 <sup>d,e</sup>		–0.291 <sup>f,g</sup> –1.086 <sup>d,e</sup> –1.326 <sup>d,e</sup> –1.770 <sup>d,e</sup>	–1.92	[90b]
[PPh <sub>4</sub> ] <sub>2</sub> [TeRu <sub>5</sub> (CO) <sub>14</sub> CuBr] <b>143-Br</b>		0.139 <sup>d,e</sup>		–0.230 <sup>f,g</sup> –1.141 <sup>d,e</sup> –1.405 <sup>d,e</sup> –1.781 <sup>d,e</sup>	–1.83	[90b]
[PPh <sub>4</sub> ] <sub>2</sub> [TeRu <sub>5</sub> (CO) <sub>14</sub> CuI] <b>143-I</b>		0.132 <sup>d,e</sup>		–0.246 <sup>f,g</sup> –1.184 <sup>d,e</sup> –1.428 <sup>d,e</sup> –1.824 <sup>d,e</sup>	–1.80	[90b]
[PPh <sub>4</sub> ] <sub>2</sub> [{TeRu <sub>5</sub> (CO) <sub>14</sub> ] <sub>2</sub> Cu <sub>4</sub> Cl <sub>2</sub> ] <b>145-Cl</b>		0.180 <sup>d,e</sup>		–0.129 <sup>f,g</sup> –1.124 <sup>d,e</sup> –1.396 <sup>d,e</sup> –1.776 <sup>d,e</sup>	–2.89	[90b]
[PPh <sub>4</sub> ] <sub>2</sub> [{TeRu <sub>5</sub> (CO) <sub>14</sub> ] <sub>2</sub> Cu <sub>4</sub> Br <sub>2</sub> ] <b>145-Br</b>		0.202 <sup>d,e</sup>		–0.179 <sup>f,g</sup> –1.134 <sup>d,e</sup> –1.394 <sup>d,e</sup> –1.778 <sup>d,e</sup>	–2.88	[90b]

Table 2 (Continued)

Complex	Oxidation process		Reduction process		Natural charge (metal cores)	Ref
	$E_p^{ox}/V^a$	$E_p^{red}/V^b$	$E_p^{ox}/V^a$	$E_p^{red}/V^b$		
	( $W_{1/2}/mV^c$ )	( $W_{1/2}/mV^c$ )	( $W_{1/2}/mV^c$ )	( $W_{1/2}/mV^c$ )		
[PPh <sub>4</sub> ] <sub>2</sub> [Te <sub>2</sub> Ru <sub>4</sub> (CO) <sub>10</sub> Cu <sub>2</sub> Cl <sub>2</sub> ] <b>146-Cl</b>		0.200 <sup>d,e</sup>	–0.255 <sup>f,g</sup>	–1.146 <sup>d,e</sup> –1.426 <sup>d,e</sup> –1.770 <sup>d,e</sup>	–1.64	[90b]
[PPh <sub>4</sub> ] <sub>2</sub> [Te <sub>2</sub> Ru <sub>4</sub> (CO) <sub>10</sub> Cu <sub>2</sub> Br <sub>2</sub> ] <b>146-Br</b>		0.166 <sup>d,e</sup>	–0.303 <sup>f,g</sup>	–1.222 <sup>d,e</sup> –1.458 <sup>d,e</sup> –1.826 <sup>d,e</sup>	–1.63	[90b]
[PPh <sub>4</sub> ] <sub>2</sub> [Te <sub>2</sub> Ru <sub>4</sub> (CO) <sub>10</sub> Cu <sub>2</sub> I <sub>2</sub> ] <b>146-I</b>		0.162 <sup>d,e</sup>	–0.279 <sup>f,g</sup>	–1.116 <sup>d,e</sup> –1.356 <sup>d,e</sup> –1.748 <sup>d,e</sup>	–1.60	[90b]
[Et <sub>4</sub> N] <sub>2</sub> [Se <sub>2</sub> Cr <sub>3</sub> (CO) <sub>10</sub> ] <b>4b</b>	0.367 <sup>d,e</sup> 0.067 <sup>d,e</sup>	0.371 <sup>d,e</sup> 0.067 <sup>d,e</sup>	–0.029 <sup>d,e</sup> –0.201 <sup>d,e</sup>	–0.037 <sup>d,e</sup> –0.189 <sup>d,e</sup>	–2.00	[32]
[PPN][Se <sub>2</sub> Mn <sub>3</sub> (CO) <sub>9</sub> ] <b>7b</b>	0.554 (110) <sup>d,e</sup>	0.601 (118) <sup>d,e</sup>			–1.00	[66]
[PPN] <sub>2</sub> [Se <sub>2</sub> Mn <sub>3</sub> (CO) <sub>9</sub> ] <b>61b</b>	0.515 (112) <sup>d,e</sup>	0.579 (106) (br) <sup>d,e</sup>	–0.104 (105) <sup>d,e</sup> –0.260 (114) <sup>d,e</sup>	–0.100 (111) <sup>d,e</sup> –0.272 (103) <sup>d,e</sup>	–2.00	[66]
[Et <sub>4</sub> N] <sub>4</sub> [Se <sub>6</sub> Mn <sub>6</sub> (CO) <sub>18</sub> ] <b>19</b>	0.398 (212) <sup>d,e</sup>	0.398 <sup>(h)</sup>	–0.347 (98) (br) <sup>d,e</sup> –0.550 (99) <sup>d,e</sup> –1.102 (114) <sup>d,e</sup>	–0.356 (99) <sup>d,e</sup> –0.540 (109) <sup>d,e</sup> –1.142 (117) <sup>d,e</sup>	–4.00	[66]
[Et <sub>4</sub> N] <sub>4</sub> [Se <sub>10</sub> Mn <sub>6</sub> (CO) <sub>18</sub> ] <b>73</b>	0.334 (172) <sup>d,e</sup>	0.344 (175) <sup>d,e</sup>	–0.028 (102) (br) <sup>d,e</sup> –0.200 (115) <sup>d,e</sup> –0.400 (111) <sup>d,e</sup>	0.000 (119) <sup>d,e</sup> –0.176 (97) <sup>d,e</sup> –0.392 (117) <sup>d,e</sup>	–4.00	[66]
[Et <sub>4</sub> N] <sub>2</sub> [Se <sub>2</sub> Mn <sub>3</sub> (CO) <sub>10</sub> {Cr(CO) <sub>5</sub> } <sub>2</sub> ] <b>14</b>	0.428 <sup>d,e</sup> 0.340 <sup>d,e</sup> 0.132 <sup>d,e</sup>	0.464 <sup>d,e</sup> 0.368 <sup>d,e</sup> 0.160 <sup>d,e</sup>			–1.00	[32]

<sup>a</sup>  $E_p^{ox}$  = The oxidative peak potential.

<sup>b</sup>  $E_p^{red}$  = The reductive peak potential.

<sup>c</sup>  $W_{1/2}$  = The width at half-height.

<sup>d</sup> From differential pulse voltammetry.

<sup>e</sup> Quasi-reversible peak.

<sup>f</sup> Irreversible peak.

<sup>g</sup> The desorption of Cu atom.

<sup>h</sup> Difficult to determine.

70 mV. Moreover, the bistetrahedral cluster [S<sub>2</sub>Fe<sub>5</sub>(CO)<sub>14</sub>]<sup>2-</sup> displayed two quasi-reversible reductions, whereas its Se analogue [Se<sub>2</sub>Fe<sub>5</sub>(CO)<sub>14</sub>]<sup>2-</sup> exhibited only one reduction couple at a more positive potential. These trends suggested that the selenide clusters are more easily reduced than the sulfide analogues [19]. In addition, the incorporated metal halides might affect the electronic properties of metal carbonyl cores. The electrochemistry of Cd<sub>2</sub>Cl<sub>3</sub>-bridged bis-trigonal prismatic cluster [{Ni<sub>6</sub>(CO)<sub>12</sub>}<sub>2</sub>Cd<sub>2</sub>Cl<sub>3</sub>]<sup>3-</sup> showed that the two Ni<sub>6</sub>-cores were electronically independent, compared to the electrochemical behavior of its parent antiprismatic nickel carbonyl anionic cluster [Ni<sub>6</sub>(CO)<sub>12</sub>]<sup>2-</sup> [181c]. Furthermore, the effect of the incorporation of CuX into metal carbonyl chalcogenide has been systematically studied by electrochemistry [90b,90c,113b]. Most redox peaks of metal carbonyl clusters were found to be broad, due to the coupling effect of metal atoms [8a]. Differential pulse voltammetry (DPV) has been effectively utilized for unambiguous assignments. We will describe here some representative examples and, their electrochemical data are summarized in Table 2.

Since a series of CuX-incorporated EFe<sub>3</sub>(CO)<sub>9</sub>-based clusters (E = Se, Te) (Chart 8) have been synthesized, their redox properties were explored to elucidate the effect of CuX on the resultant clusters. The parent clusters [SeFe<sub>3</sub>(CO)<sub>9</sub>]<sup>2-</sup> (**3b**) and [TeFe<sub>3</sub>(CO)<sub>9</sub>]<sup>2-</sup> (**3c**) exhibited one quasi-reversible redox couple similar to its S-analogue [SFe<sub>3</sub>(CO)<sub>9</sub>]<sup>2-</sup> (**3a**) [19,90c,113b]. However, one additional quasi-reversible oxidation was found for **3c**, indicative of the ease of oxidation due to the lower electronegativity of

the Te atom versus the Se and S atoms. The DFT calculations indicated that their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) came from the Fe<sub>3</sub> ring, indicating the quasi-reversible redox processes occurred on the Fe<sub>3</sub> ring [90c,113b]. Besides the desorption peak of Cu around –0.28 to –0.37 V [184–186], the electrochemistry of the CuX-, Cu<sub>2</sub>Br<sub>2</sub>-, Cu<sub>3</sub>Br-, and Cu<sub>4</sub>Br<sub>2</sub>-incorporated mono- or di-EFe<sub>3</sub>-based clusters [EFe<sub>3</sub>(CO)<sub>9</sub>CuX]<sup>2-</sup> (E = Se, **138b**; Te, **138c**, X = Cl, Br, I), [EFe<sub>3</sub>(CO)<sub>9</sub>Cu<sub>2</sub>Br<sub>2</sub>]<sup>2-</sup> (E = Se, **139b-Br**; Te, **139c-Br**), [{TeFe<sub>3</sub>(CO)<sub>9</sub>}<sub>2</sub>Cu<sub>3</sub>Br]<sup>2-</sup> (**142-Br**), and [EFe<sub>3</sub>(CO)<sub>9</sub>]<sub>2</sub>Cu<sub>4</sub>Br<sub>2</sub>]<sup>4-</sup> (E = Se, **140b-Br**; Te, **140c-Br**) displayed a redox pattern similar to that of the parent clusters. Compared to the parent complexes, the first quasi-reversible reduction of these copper halide-incorporated clusters revealed a more anodic shift as the number of introduced CuX or Cu(I) increased (Table 2). The DFT calculations were employed for the interpretation. They showed that the natural charges of each EFe<sub>3</sub>(CO)<sub>9</sub> core of these clusters were decreased with the decreasing negative values compared with clusters **3b** and **3c**, which was consistent with the anodic shifts due to the electron-withdrawing effect of copper halides. The decreasing negative reduction potential was also explained by their calculated electron affinity and the LUMO energy level [90c,113b].

In the Te–Ru system, the parent complex [TeRu<sub>5</sub>(CO)<sub>14</sub>]<sup>2-</sup> (**115c**) showed four quasi-reversible couples. The DPV studies showed that mono-CuX–TeRu<sub>5</sub> clusters [TeRu<sub>5</sub>(CO)<sub>14</sub>CuX]<sup>2-</sup> (**143**, X = Cl, Br, I) and Cu<sub>4</sub>Br<sub>2</sub>-linked di-TeRu<sub>5</sub> clusters [{TeRu<sub>5</sub>(CO)<sub>14</sub>}<sub>2</sub>Cu<sub>4</sub>X<sub>2</sub>]<sup>2-</sup> (**145**, X = Cl, Br) each revealed a

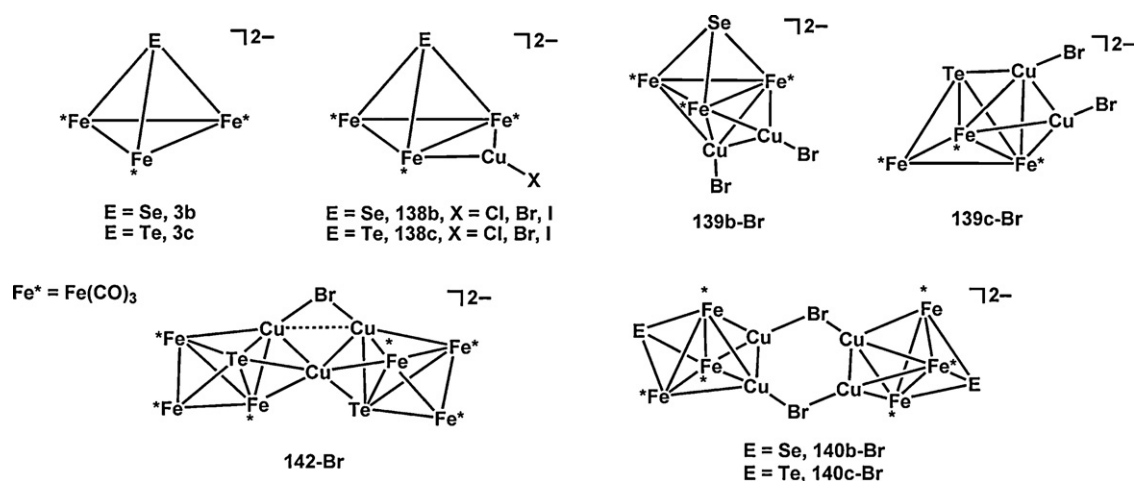


Chart 8. CuX-incorporated  $EF_3$ -based carbonyl clusters (E = Se, Te).

similar but shifted redox pattern, due to the introduction of CuX in different ratios. It was noted that the first quasi-reversible oxidation of these CuX-incorporated  $TeRu_5$ -based clusters also exhibited a more anodic shift as the number of CuX increased. This result was also supported by DFT calculations in terms of the natural charges of each  $TeRu_5$  core. It was worth mentioning that  $Cu_4X_2$ -linked di- $TeRu_5$  clusters **145-Cl/Br** consisted of two  $TeRu_5(CO)_{14}$  cores, but displayed only four redox couples like mono- $TeRu_5$ -clusters **115c** and **143-Cl/Br/I**, suggesting a well-delocalized electron density over the two  $TeRu_5(CO)_{14}$  cores and the  $Cu_4X_2$  linkers (X = Cl, Br). This phenomenon was also supported by the similar electron density distribution of the two  $TeRu_5$  cores of the HOMO and LUMO in clusters **145-Cl/Br** (Fig. 15) [90b]. Moreover, bis-CuX-incorporated  $Te_2Ru_4$ -based clusters  $[Te_2Ru_4(CO)_{10}Cu_2X_2]^{2-}$  (**146**, X = Cl, Br, I) displayed a redox pattern similar to that of  $TeRu_5$ -based clusters, which could be attributed to the fact that their HOMOs and LUMOs have major contributions from the *p* and *d* orbitals of the Ru atoms, suggesting that both reduction and oxidation occur in the ruthenium centers [90b].

### 7.1.2. Se–Cr/Mn clusters

Apart from diamagnetic clusters, paramagnetic chalcogen-containing carbonyl clusters are known to exhibit diverse electrochemical behaviors, and some of these clusters had electron-sponge properties [8a]. The high-nuclearity pentagonal prismatic cluster  $[Te_5Co_{11}(CO)_{15}]^-$  and the paramagnetic cobalt-centered cubic cluster  $[Te_6Co_9(CO)_8]^-$  were reported to possess rich redox properties, and each displayed four reversible redox couples in the reduction process [8b,87b]. Moreover, the mixed-metal square-pyramidal sulfide cluster  $[S_2Mn(CO)_3(NiCp)_2]$  (**71a**) was an odd-electron species with  $S = 1/2$  that displayed two quasi-reversible

redox couples, due to the addition to or removal from the SOMO orbital of one-electron [72]. To further investigate the magnetic effect of the clusters on their electrochemical properties, we also examined a series of paramagnetic homo- or heteronuclear chromium and manganese carbonyl selenide clusters. The isoelectronic clusters  $[Se_2Cr_3(CO)_{10}]^{2-}$  (**4b**) and  $[Se_2Mn_3(CO)_9]^-$  (**7b**) both had a trigonal-bipyramidal geometry, but the former exhibited more redox waves than the latter, probably due to a high-spin state for **4b** ( $S = 1$ ) at room temperature. As a result, complex **4b** exhibited four quasi-reversible redox couples (0.371, 0.067,  $-0.037$ ,  $-0.189$  V) (seen in Table 2). The DFT calculations showed that the SOMOs of **4b** received a significant contribution from the *d* orbitals of  $Cr_3$  atoms, indicating that the rich redox reactions mainly occurred in the  $Cr_3$  ring [32]. However, cluster **7b** displayed only one quasi-reversible oxidation at 0.554 V [66].

In order to further understand the effect of paramagnetism and the different metal cores, redox behaviors of the paramagnetic clusters  $[Se_2Mn_3(CO)_9]^{2-}$  (**61b**),  $[Se_6Mn_6(CO)_{18}]^{4-}$  (**19**), and  $[Se_{10}Mn_6(CO)_{18}]^{4-}$  (**73**) were also examined. In addition to quasi-reversible oxidation, the one-electron-reduced  $Se_2Mn_3$ -cluster **61b** exhibited two additional one-electron quasi-reversible reductions compared with  $Se_2Mn_3$ -cluster **7b**. Furthermore, clusters **61b**, **19**, and **73** showed decreased quasi-reversible oxidation compared to **7b**, due to the increasingly negative charge, i.e., **7b** ( $-1$ ) to **61b** ( $-2$ ) to **19** ( $-4$ ) and **73** ( $-4$ ). Moreover, clusters **19** and **73** (both  $S = 1$ ) exhibited three one-electron redox couples in the reduction and two redox in the oxidation, indicating an electron-sponge behavior, which was intriguing because of their paramagnetism [66].

To study the mixed-metal effect, we also extended the study to some Cr–Mn selenide clusters. The  $Se_2Mn_3$ -cluster **61b** and its di-Cr(CO)<sub>5</sub>-incorporated derivative  $[Se_2Mn_3(CO)_{10}\{Cr(CO)_5\}_2]^{2-}$  (**14**) are both paramagnetic species with  $S = 1/2$  and  $3/2$  at room

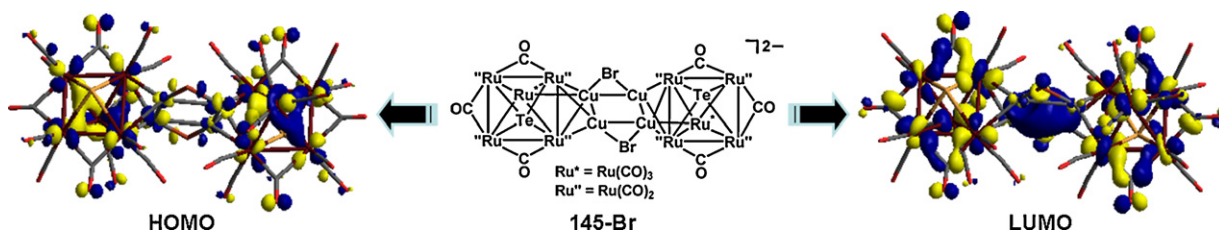


Fig. 15. Spatial graphs (isovalue = 0.03 ~ 0.04) of the selected frontier molecular orbitals of **145-Br**.

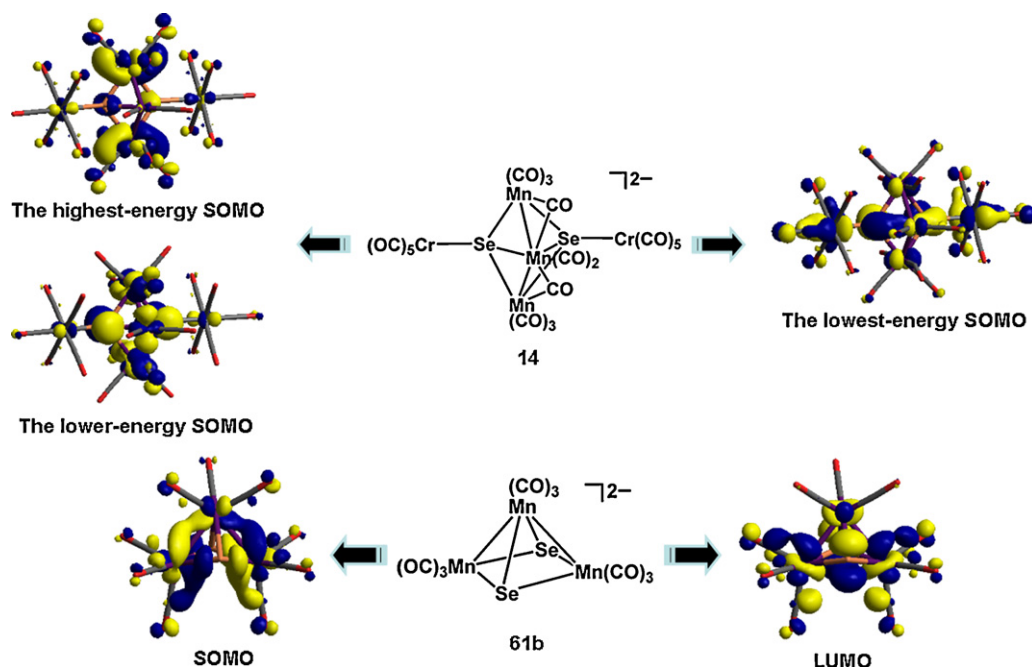


Fig. 16. Spatial graphs (isovalue = 0.03 ~ 0.04) of the selected frontier molecular orbitals of **14** and **61b**.

Adapted from ref. [32].

temperature, respectively (*vide infra*). DPV studies showed that cluster **14** exhibited a similar redox pattern similar to that of cluster **61b**, which was supported by evidence that the SOMOs of **14** and the LUMO and SOMO of **61b** each received a significant contribution from the d orbitals of Mn<sub>3</sub> atoms (Fig. 16), indicating the redox reactions mainly occurred in the Mn<sub>3</sub> atoms. The three quasi-reversible redox couples of **14** (0.160, 0.368, 0.464 V) were, in general, shifted to more positive potentials than those of **61b** (0.579, -0.100, -0.272 V), which indicated that **14** was more easily reduced, but oxidized with more difficulty because of the electron-withdrawing effect of the attached Cr(CO)<sub>5</sub> fragments [32].

Although the previous studies showed that most metal carbonyl clusters, particularly neutral clusters, tended to be reduced due to the electron-withdrawing effect of the vacant frontier orbitals of carbonyl ligands [4c], recent studies have clearly indicated that the redox properties could be modulated by the incorporation of main-group elements and other metal fragments, or by increasing the negative charges of the clusters. Anionic transition metal carbonyl chalcogenide clusters have demonstrated rich reduction and oxidation capability, mainly due to their symmetrical and more closed geometries, highly negative charges, and/or magnetic properties.

## 7.2. Magnetic properties

Anionic odd-electron metal carbonyl clusters are rare due to their instability and reactive nature, and they are expected to be paramagnetic [62,85,181a,188]. In contrast to the odd-electron clusters, the paramagnetic properties of the even-electron clusters have rarely been investigated, because it was believed that even-electron metal carbonyl clusters were diamagnetic species due to the existence of carbonyl ligands [35,52,87b,174b,187,189]. Herein, some novel examples of odd-electron and even-electron clusters with surprising magnetic properties will be discussed, which also provides informative insights into the metal–metal interaction.

### 7.2.1. Odd-electron species in E–Mn/Cr complexes (E = Se, Te)

The square-pyramidal clusters, [E<sub>2</sub>Mn<sub>3</sub>(CO)<sub>9</sub>]<sup>2-</sup> (E = Se, **61b**; Te, **61c**) are 49-electron species. As expected, the Superconducting

Quantum Interference Device (SQUID) magnetometry showed that cluster **61b** had an effective magnetic moment  $\mu_{\text{eff}} = 2.11\mu_{\text{B}}$  at 300 K [66], as observed in the case of [PPh<sub>4</sub>]<sub>2</sub>[Se<sub>2</sub>Mn<sub>3</sub>(CO)<sub>9</sub>] (**61b**) reported by Henkel et al. [62]. The paramagnetism of its Te-analogue **61c** was confirmed by the powder electron paramagnetic resonance (EPR) spectrum at room temperature, in which  $g = 2.49$  [85]. The paramagnetic properties were also observed in mixed Ni–Mn clusters [E<sub>2</sub>Mn(CO)<sub>3</sub>(NiCp)<sub>2</sub>] (E = S, **71a**; Se, **71b**), in which the unpaired electron was delocalized over the metal skeleton [72]. In addition, the heterochalcogen-bridged mixed-chromium and manganese complex [ $\{\text{Cp}'\text{Cr}(\mu\text{-SPh})\}_2(\mu_4\text{-Se})\text{Mn}_2(\text{CO})_8$ ] was an antiferromagnetic species, while the S-bridged complex [Cp'Cr(μ-SPh)<sub>3</sub>Mn(CO)<sub>3</sub>], with a weak Cr–Mn bond, displayed paramagnetic properties [48b]. It is interesting that, although the di-Cr(CO)<sub>5</sub>-attached Se<sub>2</sub>Mn<sub>3</sub>-cluster [Se<sub>2</sub>Mn<sub>3</sub>(CO)<sub>10</sub>{Cr(CO)<sub>5</sub>}<sub>2</sub>]<sup>2-</sup> (**14**) possessed one more electron than expected for a square-pyramidal cluster having three metals with two metal–metal bonds, SQUID showed that cluster **14** had an effective magnetic moment  $\mu_{\text{eff}} = 3.56\mu_{\text{B}}$  at 300 K. This value was close to the spin-only value ( $\mu_{\text{eff}} = 3.87\mu_{\text{B}}$ ) predicted for a simple  $S = 3/2$  species. However, at low temperature, complex **14** gave the  $\mu_{\text{eff}} = 1.59\mu_{\text{B}}$  at 2 K, which corresponded to an  $S = 1/2$  species. The DFT calculations showed that cluster **14**, with one unpaired electron ( $S = 1/2$ ), was more stable than the configuration with three unpaired electrons by  $\Delta G = -26.26$  and  $\Delta E = -28.35$  kcal/mol, indicating that cluster **14**, with a low-spin state ( $S = 1/2$ ) at low temperature, was more stable and could convert into its high-spin state ( $S = 3/2$ ) by thermal excitation of the paired electrons into the unpaired ones at 300 K [32]. In addition, the three SOMOs of cluster **14** had major contributions from the d and p orbitals of the Mn atoms where the proportions were increased. The small energy gaps and the increasing contribution of Mn atoms for the two nearby highest SOMO orbitals might suggest spin-pairing for complex **14** at low temperature. Moreover, the energy difference between LUMO and the highest SOMO of the di-Cr(CO)<sub>5</sub>-attached Se<sub>2</sub>Mn<sub>3</sub>-based cluster **14** was about 0.84 eV, while the energy gap for the Se<sub>2</sub>Mn<sub>3</sub>-complex **61b** was calculated to be 1.40 eV, indicating narrow-spaced frontier orbitals as the size of the cluster increased.

### 7.2.2. Even-electron species: electron-rich E–Cr/Fe clusters (E = Se, Te) and electron-precise Se–Cr and Se–Mn clusters

The cobalt-centered pentagonal prismatic telluride carbonyl  $[\text{Te}_7\text{Co}_{11}(\text{CO})_{10}]^-$  was an even-electron anionic cluster, but had a paramagnetic property with the effective magnetic moment  $\mu_{\text{eff}} = 2.65\mu_{\text{B}}$ , corresponding to the  $S = 1$  species at room temperature [8b]. In addition, the hexacapped cubic cobalt cluster  $[\text{Te}_6\text{Co}_9(\text{CO})_8]^-$  possessed paramagnetic properties with a quintuplet state ( $\mu_{\text{eff}} = 4.65\mu_{\text{B}}$ ), which exhibited a triplet ground state at low temperature via antiferromagnetic intermolecular interactions in a 1D space [87b]. Furthermore, isostructural mixed-metal clusters  $[\text{N}_2\text{Co}_{10}\text{Rh}_2(\text{CO})_{24}]^{2-}$ ,  $[\text{N}_2\text{Fe}_6\text{Ni}_6(\text{CO})_{24}]^{2-}$ ,  $[\text{C}_2\text{Co}_7\text{Pt}_5(\text{CO})_{24}]^-$ , and  $[\text{C}_2\text{Co}_8\text{Pt}_4(\text{CO})_{24}]^{2-}$  were also paramagnetic species with an  $S = 1$  ground state, in which  $[\text{C}_2\text{Co}_8\text{Pt}_4(\text{CO})_{24}]^{2-}$  could further be oxidized to give the odd-electron cluster  $[\text{C}_2\text{Co}_8\text{Pt}_4(\text{CO})_{24}]^-$  [174b]. In the iron–manganese carbonyl system, Whittlesey et al. has reported a paramagnetic xenophilic Mn–Fe carbonyl cluster  $\{[\mu\text{-Mn}(\text{THF})_2]_2\text{Fe}_2(\text{CO})_8\}$  that possesses effective magnetic moments  $\mu_{\text{eff}} = 5.0(1)\mu_{\text{B}}$ , close to the spin-only value ( $\mu_{\text{eff}} = 4.90\mu_{\text{B}}$ ) for four unpaired electrons, due to the interaction between Mn and Fe/Mn atoms [189e].

Mixed Cr–Fe carbonyl chalcogenide clusters  $[\text{E}_2\text{Cr}_2\text{Fe}(\text{CO})_{10}]^{2-}$  (E = Se, **54b**; Te, **54c**) had two more electrons than expected for the trigonal bipyramidal geometry in terms of Wade's rules. SQUID showed that clusters **54b** and **54c** had effective magnetic moments  $\mu_{\text{eff}} = 4.80$  and  $5.38\mu_{\text{B}}$  at 300 K, respectively, which were closed to the spin-only value ( $\mu_{\text{eff}} = 4.90\mu_{\text{B}}$ ) predicted for a simple  $S = 2$  species. However, at low temperature, cluster **54b** possessed the  $\mu_{\text{eff}} = 2.83\mu_{\text{B}}$  at 20 K, while **54c** gave the value of  $2.98\mu_{\text{B}}$  at 5 K, which corresponded to the  $S = 1$  species [52]. The reasons for their high paramagnetism may be related to the metal–metal interaction, which results in narrow-spaced frontier orbitals to induce the novel paramagnetism.

Another interesting example was seen in the electron-precise trigonal-bipyramidal cluster  $[\text{Se}_2\text{Cr}_3(\text{CO})_{10}]^{2-}$  (**4b**) which exhibited paramagnetic properties with  $S = 1$  [32]. It was noted that cluster **4b** could be expanded to its di-Cr(CO)<sub>5</sub>-sandwiched  $\text{Se}_2\text{Mn}_3$ -cluster **14** with  $S = 3/2$ , indicating the switch of the spin states accompanied by a structural transformation. The high-nuclearity hexamanganese carbonyl selenide cluster  $[\text{Se}_6\text{Mn}_6(\text{CO})_{18}]^{2-}$  (**19**) was a 104-electron species and obeyed the 18-electron rule. SQUID showed that cluster **19** had an effective magnetic moment  $\mu_{\text{eff}} = 2.98\mu_{\text{B}}$  at 300 K, close to an  $S = 1$  species [35]. Cluster **19** represented the first of the electron-precise paramagnetic main-group transition metal carbonyl complexes. Its magnetism was demonstrated in selective reactivities toward  $\text{O}_2$  and selenium, which resulted in the O-inserted cluster  $[\text{Se}_6\text{Mn}_6(\text{CO})_{18}(\text{O})]^{4-}$  (**72**) and the Se-inserted  $[\text{Se}_{10}\text{Mn}_6(\text{CO})_{18}]^{4-}$  (**73**) (*vide supra*). Both **72** and **73** were also electron-precise species with 104 and 108 electrons, respectively, but had effective magnetic moments  $\mu_{\text{eff}} = 2.47$  and  $2.79\mu_{\text{B}}$  at 300 K [35], corresponding to an  $S = 1$  species with two unpaired electrons. In summary, these results suggest that a progressive tightening of the frontier energy levels as a function of metal cluster size could trigger magnetism in the complexes [187], in which selective reactivities were observed to be induced by the differing nature of the narrowly spaced frontier orbitals.

## 8. Metal cluster-based coordination polymers

During the past few decades, coordination polymers, which are built from metal ions linked by ligands to form one-, two-, and three-dimensional (1D, 2D, and 3D) frameworks, have been extensively studied [190,191]. Much attention has been directed to 1D coordination polymers due to their interesting magnetic,

electrical, and optical properties [192–195]. In this section, we will describe the recent progress in the synthesis, structural features, and special properties of some representative examples of groups 6–8 metal cluster-based 1D coordination polymers, formed via the metal–metal and metal–ligand (pyridyl-based multidentate bridging ligands) interactions as well as hydrogen bonding. A special type, metal carbonyl cluster-based polymers, will be discussed in detail due to their potential uses as semiconducting materials.

### 8.1. Metal cluster-based 1D coordination polymers

In the field of metal–organic frameworks (MOFs), Yaghi and co-workers demonstrated the use of transition metal clusters as good secondary building units (SBUs) for the construction of many useful porous structures, which provided an effective synthetic methodology for the construction of coordination frameworks [196]. Other than these, the introduction of bulky ligands bound to metal centers and/or symmetry-directing linkers can lead to the formation of low-dimensional or even 1D coordination frameworks.

In the group 6 system (Mo, W), cyano-coordinated octahedral clusters  $[\text{S}_8\text{W}_6(\text{CN})_6]^{6-}$  and  $[\text{Se}_8\text{Mo}_6(\text{CN})_6]^{n-}$  ( $n = 6$  or  $7$ ) [197] have reportedly been used as building blocks with transition metal cations  $\text{M}^{2+}$  ( $\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{Zn}$ ) or N-donor ligands as linking units to construct high-dimensional frameworks [198]. In the E/M/Cu/L (E = S, Se; M = Mo, W; L = N-donor ligands) system, most of the frameworks were two- or three-dimensional coordination polymers [199]. Nevertheless, 1D coordination polymers were much less [200], for example, Lang and co-workers explored the reactions of the open-cluster  $[\text{Cp}^*\text{MoS}_3(\text{CuX})_3]^-$  ( $\text{X} = \text{Br}$  or  $\text{NCS}$ ;  $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) with low symmetrical ligands, 1,2-bis(4-pyridyl)ethane (bpe) and 1,3-bis(4-pyridyl)propane (bpp), to afford the 1D “Great Wall”-like chain,  $[(\text{Cp}^*\text{MoS}_3\text{Cu}_3)_2(\mu\text{-bpe}_{3,5}\text{Br}_4)]_n$  (**170**), the 1D zigzag chain  $[(\text{Cp}^*\text{MoS}_3\text{Cu}_3)_2(\mu\text{-bpe}_3\text{Br}_4)]_n$  (**171**), 1D double-stranded chain  $[(\text{Cp}^*\text{MoS}_3\text{Cu}_3)_2(\mu\text{-bpe})_3(\text{bpe})\text{Br}_4]_n$  (**172**), 1D zigzag chain  $[(\text{Cp}^*\text{MoS}_3\text{Cu}_3)_2(\mu\text{-bpe})_2(\mu\text{-Br})(\mu_3\text{-Br})\text{Br}_2]_n$  (**173**), 1D helical chain  $[\text{Cp}^*\text{MoS}_3\text{Cu}_3(\mu\text{-bpp})(\mu\text{-Br})\text{Br}]_n$  (**174**), and 1D quadruple chain  $\{[(\text{Cp}^*\text{MoS}_3\text{Cu}_3)_2(\mu\text{-bpp})_3(\mu\text{-NCS})_2(\text{NCS})](\text{NCS})\}_n$  (**175**). In addition, complex  $[\text{Cp}^*\text{MoS}_3(\text{CuBr})_3]^-$  and polymers **170–175** showed good third-order NLO properties as reflected in their optical indexes ( $\alpha_2$ : ranging from  $4.80 \times 10^{-11}$  to  $7.08 \times 10^{-11} \text{ mW}^{-1}$ ;  $\chi^{-3}$ : ranging from  $1.94 \times 10^{-12}$  to  $2.86 \times 10^{-12} \text{ esu}$ ;  $\gamma$ : ranging from  $2.98 \times 10^{-29}$  to  $5.85 \times 10^{-29} \text{ esu}$ ) [200a]. These 1D self-assembly structures from  $[\text{Cp}^*\text{MoS}_3(\text{CuX})_3]^-$  precursors indicated that low-symmetry N-donor ligands (bpe and bpp) could induce the  $[\text{Cp}^*\text{MoS}_3(\text{CuX})_3]^-$  core to function as irregular connecting nodes to form less-symmetrical frameworks. To our surprise, Cr-cluster-based 1D coordination polymers have remained unknown, probably due to the electropositivity of the Cr atom and the weak Cr–Cr bond.

In the group 7 system (Re), cyano-hexarhenium clusters  $[\text{E}_8\text{Re}_6(\text{CN})_6]^{4-}$  (E = S, Se, Te) have been used as molecular building blocks to form a variety of high-dimensional coordination polymers in crystal engineering [201]. However, Zheng and co-workers synthesized the site-differentiated 1D cluster complexes  $[\text{Se}_8\text{Re}_6(\text{PET}_3)_4(\text{isonicotinamide})_2]^{2+}$  (**176**, *trans*-; **177**, *cis*-) that were yielded from the reaction of  $[\text{Se}_8\text{Re}_6(\text{PET}_3)_4(\text{MeCN})_2]^{2+}$  (*trans*- or *cis*-) with isonicotinaamide in a molar ratio of 1:1 [202]. These amide-functionalized clusters **176** (Fig. 17) and **177** displayed the 1D linear or 1D zigzag chain via the amide–amide hydrogen-bonding interaction.

Zheng and co-workers also synthesized *cis*- $[\text{Se}_8\text{Re}_6(\text{PPh}_3)_4(4,4'\text{-dipyridyl})_2]^{2+}$  as a useful building unit, prepared from the reaction of *cis*- $[\text{Se}_8\text{Re}_6(\text{PPh}_3)_4(\text{MeCN})_2]^{2+}$  with 4,4'-dipyridyl [203]. Vapor diffusion of diethyl ether into a  $\text{MeOH}/\text{CH}_2\text{Cl}_2$  solution of  $\text{Cd}(\text{NO}_3)_2$  and  $[\text{Se}_8\text{Re}_6(\text{PPh}_3)_4(4,4'\text{-dipyridyl})_2]^{2+}$  formed the 1D chain polymer  $\{[\text{Se}_8\text{Re}_6(\text{PPh}_3)_4(4,4'\text{-dipyridyl})_2]_2\text{Cd}(\text{NO}_3)_2\}^{4+}_n$  (**178**)

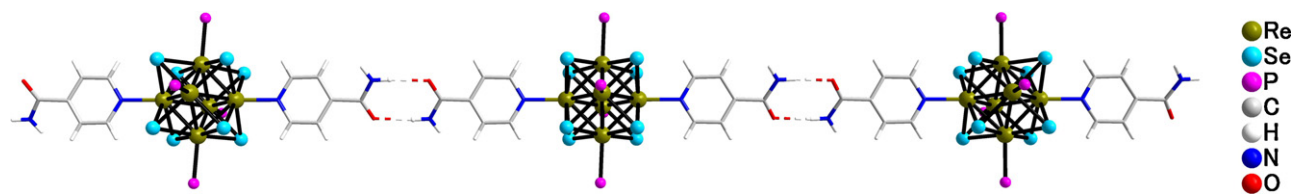


Fig. 17. Portion of amide-functionalized cluster **176**. Only the framework structure is shown.

Adapted from ref. [203].

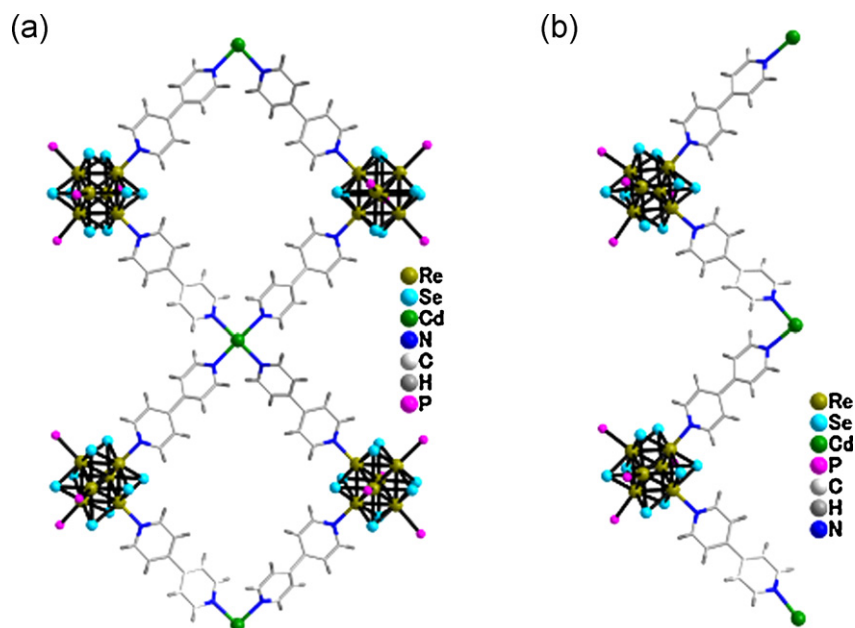


Fig. 18. (a) Portion of polymer **178** (b) portion of polymer **179**. Only the framework structure is shown.

Adapted from ref. [204].

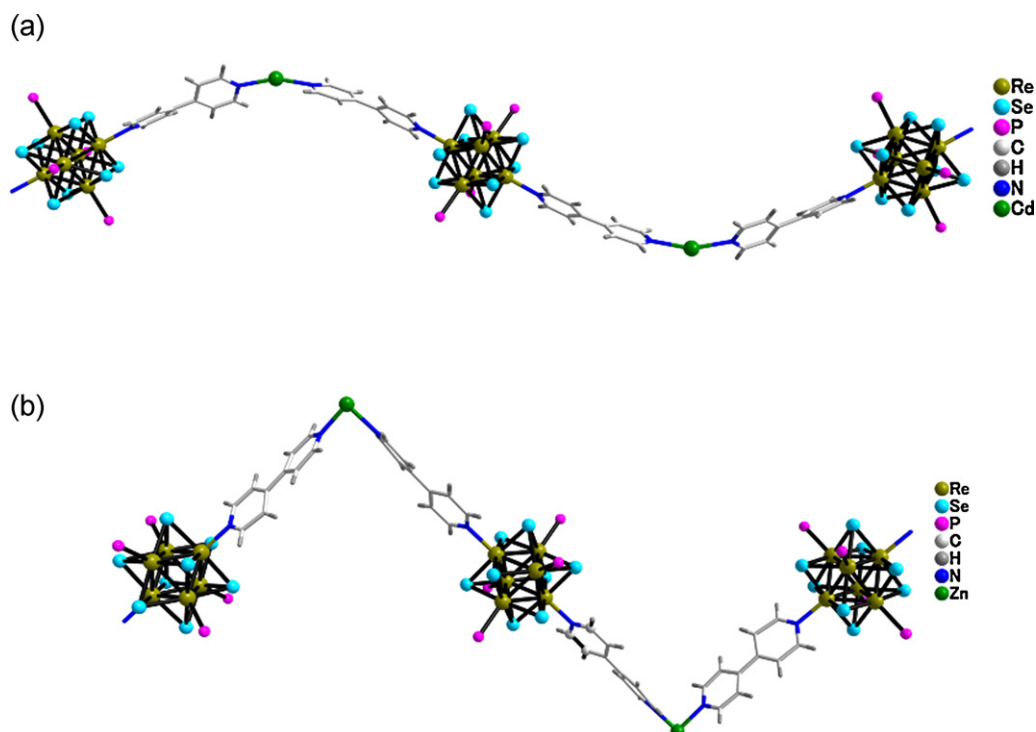


Fig. 19. (a) Portion of polymer **181** (b) Portion of polymer **183**. Only the framework structure is shown.

Adapted from ref. [205].



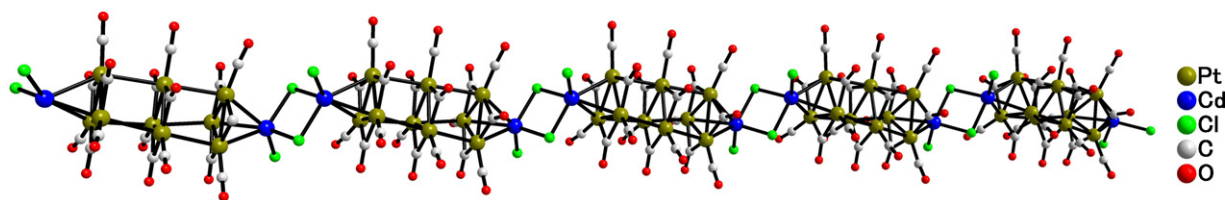


Fig. 20. Portion of polymer 185.

Adapted from ref. [209].

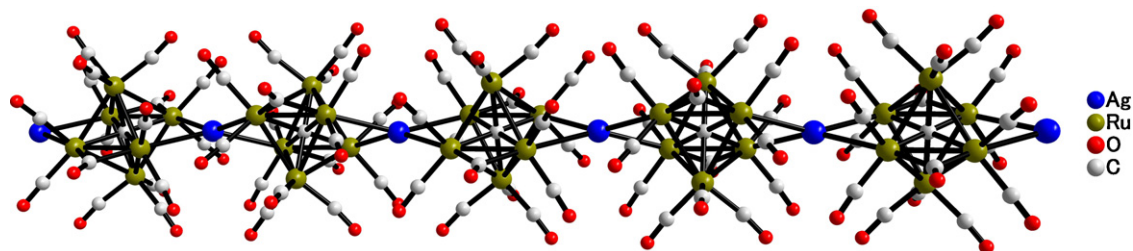
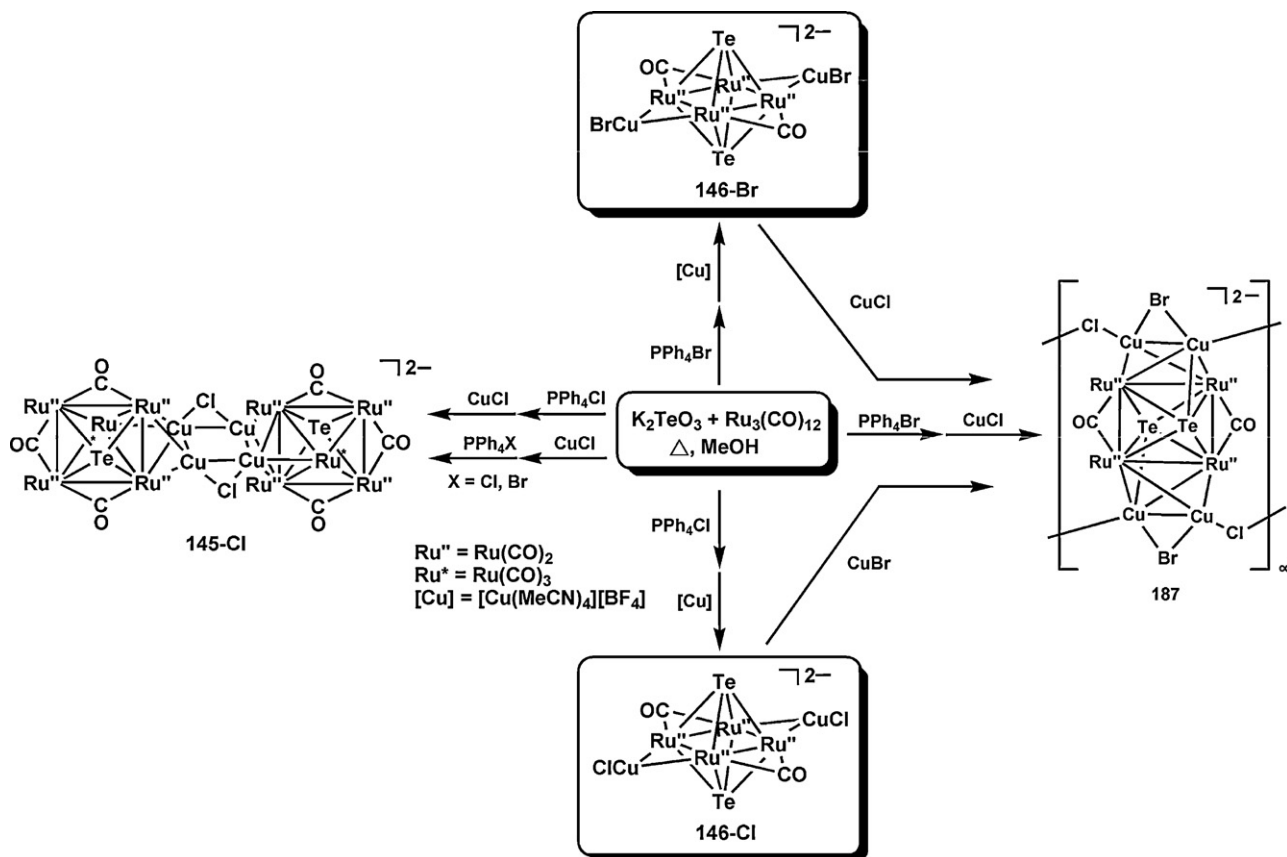


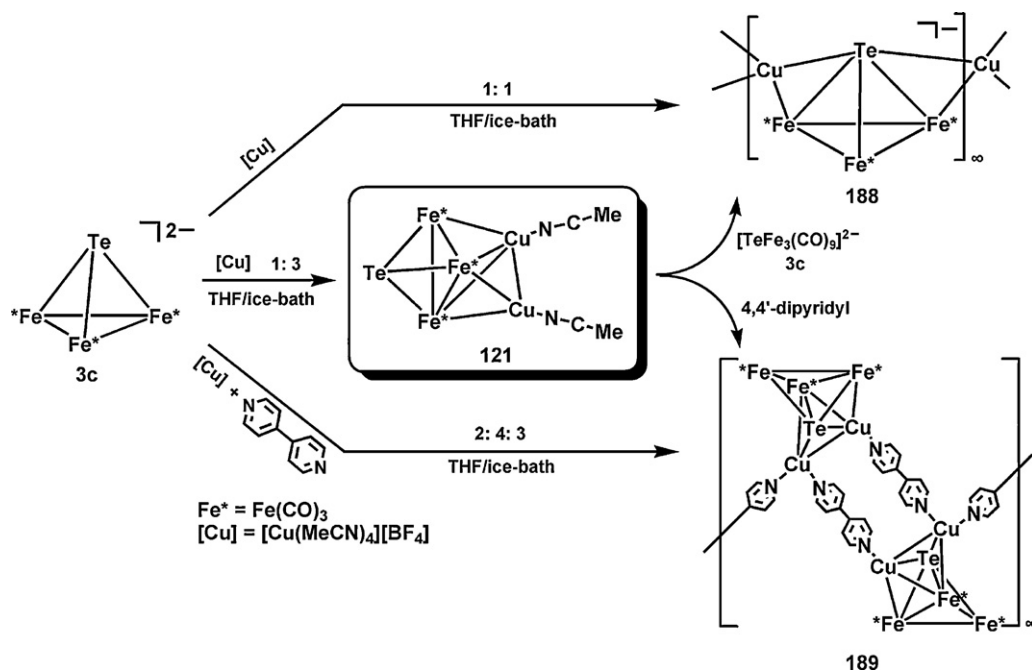
Fig. 21. Portion of polymer 186.

Adapted from ref. [210].

[203]. As shown in Fig. 18a, the chain polymer **178** contained squares, of which the four vertices were occupied by two  $\text{Cd}^{2+}$  metal ions and two  $[\text{Se}_8\text{Re}_6]^{2+}$  clusters. The  $\text{Cd}^{2+}$  ion was coordinated by four equatorial pyridyls and two axial  $\eta^1\text{-NO}_3^-$  ligands to give an octahedral geometry. When complex  $[\text{Se}_8\text{Re}_6(\text{PPh}_3)_4(4,4'\text{-dipyridyl})_2]^{2+}$  was treated with a large excess of  $\text{Cd}(\text{NO}_3)_2$ , the 1D zigzag chain  $[\{\text{Se}_8\text{Re}_6(\text{PPh}_3)_4(4,4'\text{-dipyridyl})_2\text{Cd}(\text{NO}_3)_3\}^+]_n$  (**179**) was afforded [203]. For chain **179**, each  $\text{Cd}^{2+}$  ion displayed

a distorted trigonal-bipyramidal geometry and was coordinated by one equatorial and axial pyridyls and three  $\eta^2\text{-NO}_3^-$  ligands. In addition, polymer **178** was transformed into polymer **179** upon ether vapor diffusion into the MeOH solution of **178** (Fig. 18b) and  $\text{Cd}(\text{NO}_3)_2$ . Another site-differentiated cluster complex,  $\text{trans-}[\text{Se}_8\text{Re}_6(\text{PEt}_3)_4(4,4'\text{-dipyridyl})_2]^{2+}$ , reacted with transition metal ions ( $\text{M} = \text{Cd}^{2+}, \text{Co}^{2+}, \text{Zn}^{2+}$ ) to form 1D multi-cluster-based polymers **180–183** [204]. These polymers were all prepared

Scheme 26. Reactions of  $\text{K}_2\text{TeO}_3$  with  $\text{Ru}_3(\text{CO})_{12}$  and  $\text{PPh}_4\text{X}/\text{CuX}$  ( $\text{X} = \text{Br}, \text{Cl}$ ).



Scheme 27. Two different synthetic routes to 1-D zigzag polymers **188** and **189**.

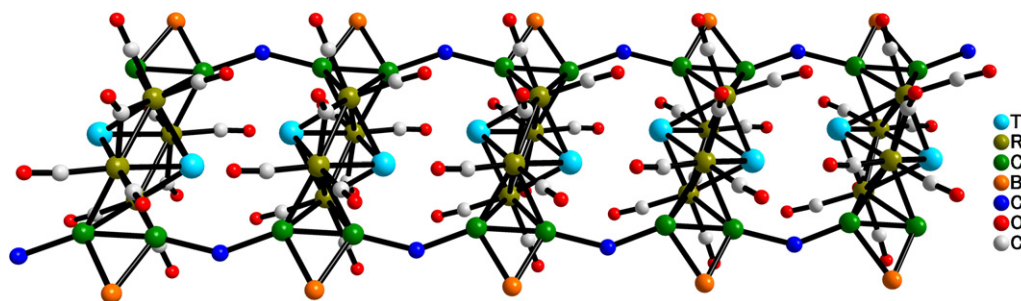


Fig. 22. Portion of polymer **187**.

Adapted from ref. [90a].

from the vapor diffusion of diethyl ether into a mixture of *trans*- $[\text{Se}_8\text{Re}_6(\text{PET}_3)_4(4,4'\text{-dipyridyl})_2]^{2+}$  in  $\text{CH}_2\text{Cl}_2$  and  $\text{M}(\text{NO}_3)_2$  in MeOH ( $\text{M} = \text{Cd}^{2+}, \text{Co}^{2+}, \text{Zn}^{2+}$ ). The two polymorphous polymers **180** and **181**, formulated as  $[\{\text{Se}_8\text{Re}_6(\text{PET}_3)_4(4,4'\text{-dipyridyl})_2\text{M}(\text{NO}_3)_3\}^+]_n$ , have been structurally characterized, and **180** displayed a highly porous 1D framework, whereas **181** exhibited a wavy 1D framework (Fig. 19a). The cobalt polymer,  $[\{\text{Se}_8\text{Re}_6(\text{PET}_3)_4(4,4'\text{-dipyridyl})_2\text{Co}(\text{NO}_3)_3\}^+]_n$

(**182**), was structurally similar to the porous structure of **180** and the zinc polymer,  $[\{\text{Se}_8\text{Re}_6(\text{PET}_3)_4(4,4'\text{-dipyridyl})_2\text{Zn}(\text{NO}_3)_3\}^+]_n$  (**183**), exhibited a 1D zigzag chain (Fig. 19b).

## 8.2. Metal carbonyl cluster-based 1D coordination polymers

In the field of metal carbonyl chemistry, rational syntheses of 1D coordination polymers using metal carbonyl clusters as

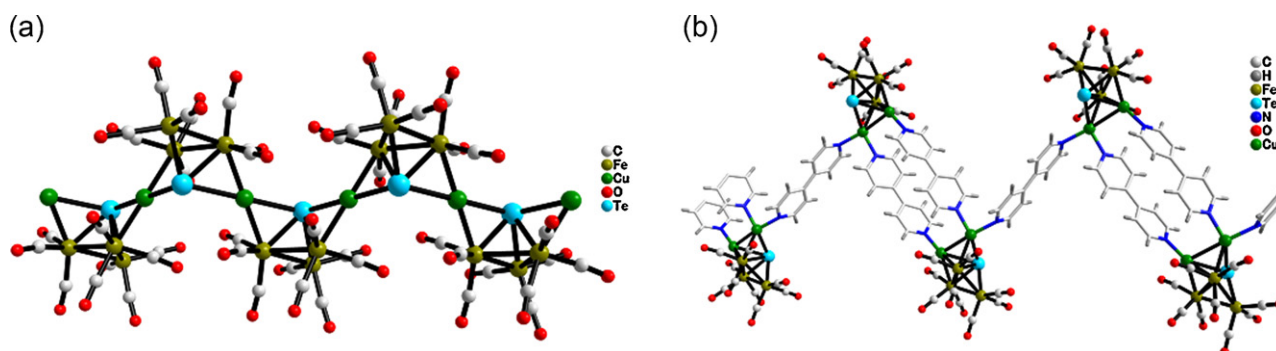
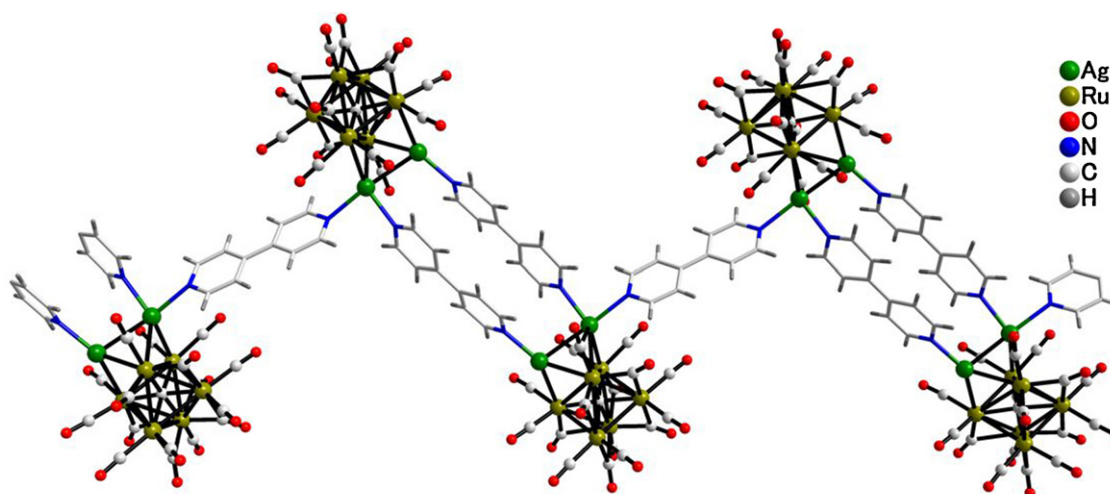


Fig. 23. (a) Portion of polymer **188** (b) portion of polymer **189**.

Adapted from ref. [114c].

Fig. 24. Portion of polymer **190**.

Adapted from ref. [211].

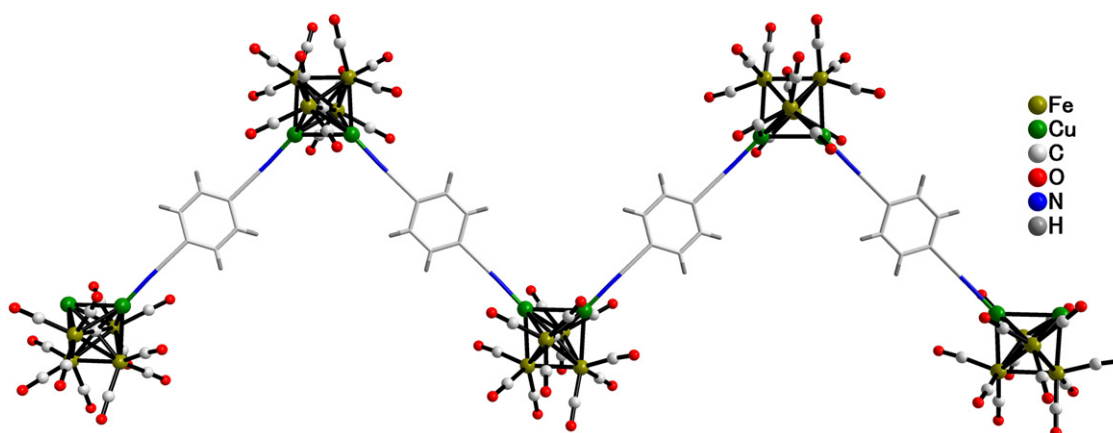
building blocks have attracted attention in recent years. It was believed that carbonyl groups [205] of metal carbonyl clusters can effectively block the coordination sites, and the well-protected cluster core was thought to be beneficial for the construction of 1D frameworks. Besides, metal carbonyl clusters provided good models for better understanding of metal nanoparticles in nanotechnology [206]. Therefore, one of the great advances in metal carbonyl clusters was to construct low-dimensional coordination polymers by the use of metal carbonyl clusters as building blocks.

Longoni and co-workers synthesized a series of  $\text{Pt}_3(\text{CO})_6$ -based 1D chains. For example,  $[\text{Pt}_{24}(\text{CO})_{48}]^{2-}$  (**184**) was isolated as the  $[\text{Bu}_4\text{N}]^+$  salt by the oxidation of  $[\text{Pt}_6(\text{CO})_{12}]^{2-}$  [207]. The mixed-metal 1D coordination polymer  $[\{\text{Pt}_9(\text{CO})_{18}(\mu_3\text{-CdCl}_2)_2\}^{2-}]_n$  (**185**) was prepared from the reaction of  $[\text{Pt}_9(\text{CO})_{18}]^{2-}$  with  $\text{CdCl}_2$  [208]. Complex **185** was shown by X-ray analysis to contain a  $\{\text{Pt}_3(\text{CO})_6\}_3$  core, in which the top and bottom  $\text{Pt}_3$  planes were each capped by a  $\mu_3\text{-CdCl}_2$  fragment and the three stacked  $\{\text{Pt}_3(\text{CO})_6\}$  units were slightly twisted. The anionic  $\{\text{Pt}_9(\text{CO})_{18}\}$  units were further held together by the chloride atoms to form a 1D chain polymer (Fig. 20). Moreover, electrical resistivity measurement on a series of discontinuous, semi-continuous, and continuous  $\text{Pt}_3(\text{CO})_6$ -based anionic clusters was also performed (ranging from  $10^2$  to  $>10^8 \Omega \text{ cm}$ ) [207,209].

In the group 8 (Ru) system, Wakatsuki and co-workers reported a novel 1D metal wire,  $[\{\text{AgRu}_6\text{C}(\text{CO})_{16}\}^-]_n$  (**186**), which was produced from the reaction of  $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$  (**130**) with 1 equiv of  $\text{AgNO}_3$  in the presence of  $[\text{PPN}]^+$  salt [210]. Complex **186** possessed the octahedral  $\{\text{Ru}_6\text{C}(\text{CO})_{16}\}$  repeating unit with a  $\text{Ru}_4$  plane, with two opposite edges that were each bridged by the Ag ion (Fig. 21).

In 2007, our group reported a series of tellurium-containing ruthenium–copper complexes, which are summarized in Scheme 26 [90a]. The tendency of the reactions of  $\text{K}_2\text{TeO}_3$  and  $\text{Ru}_3(\text{CO})_{12}$  with  $\text{PPh}_4\text{X}$  and  $\text{CuX}$  ( $\text{X}=\text{Br}, \text{Cl}$ ) with subtle differences to produce bis- $\text{CuX-Te}_2\text{Ru}_4$  clusters (**146**,  $\text{X}=\text{Cl}, \text{Br}$ ), the  $\text{Cu}_4\text{Cl}_2$ -linked di- $\text{TeRu}_5$  cluster (**145-Cl**), and the 1D chain polymer  $[\{\text{Te}_2\text{Ru}_4(\text{CO})_{10}\text{Cu}_4\text{Br}_2\text{Cl}_2\}^{2-}]_n$  (**187**) was surprising and intriguing (Scheme 26).

It was noted that chain polymer **187** could be prepared by two methods: (i) the reaction of complex **146-Cl** or **146-Br** with 2 equiv of  $\text{CuX}$ , and (ii) the reaction of  $\text{K}_2\text{TeO}_3$  and  $\text{Ru}_3(\text{CO})_{12}$  with  $\text{PPh}_4\text{Br}$  followed by the addition of  $\text{CuCl}$  (Scheme 26). The anionic unit **187** has an octahedral  $\text{Te}_2\text{Ru}_4$  cluster core in which two opposite edges of the rectangular  $\text{Ru}_4$  plane are bridged by carbonyl ligands and the other two edges are each linked by a  $\text{Cu}_2$  unit that is further bridged by one Br atom and externally bonded to one Cl atom. The bis- $\text{CuBrCuCl}$ -incorporated 1D chain polymer **187** provided a novel bonding mode for  $\text{Cu}_2\text{X}_2$  and modes **la–li** were not

Fig. 25. Portion of polymer **192**.

Adapted from ref. [212].

seen (Section 6.1, Chart 5). As shown in Fig. 22, the anionic units are held together by chloride ions to form infinite metal cluster chains. Besides, chain polymer **187** was the first example of the ternary Te–Ru–Cu 1D coordination polymer and exhibited semi-conducting behavior ( $(1-5) \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$ ) with a small energy gap,  $\sim 0.37$  eV. Furthermore, when the semiconducting properties of **187** were examined by DFT, calculations showed a drastically decreasing energy gap as the number of the chain units increased.

In 2008, our group discovered two novel Cu- and Cu-dipyridyl-linked Te–Fe carbonyl cluster-based 1D zigzag polymers, namely  $\{[\text{TeFe}_3(\text{CO})_9\text{Cu}]^-\}_n$  (**188**) and  $\{[\text{TeFe}_3(\text{CO})_9\text{Cu}_2](\mu\text{-}4,4'\text{-dipyridyl})_{1,5}\}_n$  (**189**) [114c], by using complex **3c** as a starting material with  $[\text{Cu}(\text{MeCN})_4][\text{BF}_4]/4,4'\text{-dipyridyl}$  in the appropriate molar ratio (Scheme 27). These two polymers were also obtained from the neutral cluster  $[\text{TeFe}_3(\text{CO})_9(\text{CuMeCN})_2]$  (**121**) with **3c** or  $4,4'\text{-dipyridyl}$  under suitable conditions.

The anionic polymer **188** can be viewed as consisting of two cross-linked metal chains composed of the zigzag  $\cdots\text{Te}-\text{Cu}\cdots$  and  $\cdots\text{Fe}-\text{Fe}-\text{Cu}\cdots$  wires that intersect at the Cu centers (see Fig. 23a). The neutral polymer **189** consisted of  $\{\text{TeFe}_3(\text{CO})_9\text{Cu}_2\}$  units alternately linked by single and double  $4,4'\text{-dipyridyl}$  ligands to form a one-dimensional, zigzag-like framework (see Fig. 23b). These two complexes, **188** and **189**, were the first examples of ternary Te–Fe–Cu polymers and exhibited surprising semiconducting behavior ( $2 \times 10^{-2}$  and  $5 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$ ) with small energy gaps,  $\sim 0.59$  and  $0.41$  eV, respectively. Their interesting optical properties were also supported by DFT calculations, which showed a decreasing energy gap as the number of repeating units increased. Of great interest, calculations further showed the HOMO–LUMO energy gap of the anionic polymer **188** was greatly increased if  $[\text{Et}_4\text{N}]^+$  cations were included, which explained a conductivity that was lower than expected for a metal–metal wire. Moreover, the almost parallel  $4,4'\text{-dipyridyl}$  linker pairs played an important role in the enhanced conductivity of the neutral polymer **189**.

Della Pergola et al. reported the 1D zigzag chain polymer,  $\{[\text{Ru}_6\text{C}(\text{CO})_{16}\text{Ag}_2](4,4'\text{-dipyridyl})_{1,5}\}_n$  (**190**), which was self-assembled from the carbide cluster **130**,  $\text{AgBF}_4$ , and  $4,4'\text{-dipyridyl}$  ligand [211]. Similar to the single and double dipyridyl linkers in cluster **189**, complex **190** possessed the octahedral  $\{\text{Ru}_6\text{C}(\text{CO})_{16}\}$  moiety, of which the triangular  $\text{Ru}_3$  plane was bridged by the  $\mu_3:\eta^2\text{-Ag}_2$  fragment with the  $\{\text{Ru}_6\text{C}(\text{CO})_{16}\text{Ag}_2\}$  units alternately linked by single and double  $4,4'\text{-dipyridyl}$  ligands to form a one-dimensional zigzag-like framework (Fig. 24).

Other interesting 1D Fe–Cu carbonyl polymers were reported by Femoni et al. by using the neutral carbonyl cluster  $[\text{Fe}_4\text{Cu}_2(\mu_6\text{-C})(\text{CO})_{12}(\text{MeCN})_2]$  as the precursor to react with bidentate N-donor ligands such as pyrazine (pyz), *p*-dicyanobenzene (*p*-DCB), and  $4,4'\text{-dipyridyl}$  (dpy), in which three neutral polymers were obtained, namely  $[\text{Fe}_4\text{Cu}_2(\mu_6\text{-C})(\text{CO})_{12}(\text{L})]_n$  (L = pyz, **191**; *p*-DCB, **192**; dpy, **193**) [212]. Polymers **191–193** each consisted of  $\{\text{Fe}_4\text{Cu}_2(\mu_6\text{-C})(\text{CO})_{12}\}$  units alternately linked by a single L ligand to form one-dimensional zigzag frameworks (Fig. 25).

Finally, for comparison, N-donor ligands were also established as a preparative tool to form extended frameworks. Scheer and co-workers used the  $P_n$  ligand  $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu\text{-}\eta^2\text{-P}_2)]$  as the starting material to react with  $\text{AgNO}_3$  and  $\text{CuX}$  (X = Cl, Br, I) in MeCN solution at room temperature, to afford a series of 1D chain polymers, namely  $[\text{Ag}_2\{\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu\text{-}\eta^2:\eta^1:\eta^1\text{-P}_2)\}_3(\mu\text{-}\eta^1:\eta^1\text{-NO}_3^+)]_n$  (**194**) and  $[\text{Cu}(\mu\text{-X})\{\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu\text{-}\eta^2:\eta^1:\eta^1\text{-P}_2)\}]_n$  (**195**, X = Cl, Br, I) [213,214], respectively. The 1D wave polymer **194** was formed by alternating six-membered  $\text{Ag}_2\text{P}_2\text{P}_2$  rings and seven-membered  $\text{Ag}_2\text{P}_2\text{NO}_2$  rings. However,  $\text{CuX}$ -incorporated complexes **195-Cl**, **195-Br**, and **195-I** were 1D linear chains, composed of alternating six-membered  $\text{Cu}_2\text{P}_2\text{P}_2$  rings and orthogonally oriented four-membered  $\text{Cu}_2\text{X}_2$  rings. The P atoms of the  $\{\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu\text{-}\eta^2\text{-P}_2)\}$  moiety were coordinated to the Cu atoms

of the  $\text{Cu}_2\text{X}_2$  ring with bonding mode **1e** (Section 6.1, Chart 5).

## 9. Conclusions and remarks

This review represents a survey of the recent progress in anionic groups 6–8 carbonyl chalcogenide complexes in terms of their synthetic methodologies and structural features, as well as versatile reactivities and special properties. In this account, the modified “Hieber’s synthesis” has been extensively developed for the synthesis of many anionic transition metal (groups 6–8) chalcogenide clusters, from small to medium to large clusters. Subsequent reactions of the resultant clusters toward a series of organic or inorganic reagents were explored to give rise to a large collection of metal-cluster-based derivatives, which include organic or inorganic functionalized metal clusters, cluster-aggregation products, high-nuclearity magnetic metal clusters, and metal carbonyl cluster-based semiconducting polymers. Their formation and bonding properties were further summarized as follows.

- (I) The molar ratios of reactants, the reaction temperature, solvents, cation salts, and particularly the sources and sizes of the chalcogen elements, as well as bases with different concentrations are important factors in determining the formation of a variety of anionic E–M–CO clusters (E = Se, Te; M = Cr, Mn, Fe, Ru).
- (II) Contrasting synthetic routes and reactivities were discovered in the group 6 (Cr), group 7 (Mn), and group 8 (Fe, Ru) systems due to the coupling effect of the chalcogen elements and the nature of the metals, which offered better understanding and control of the design of tailored anionic clusters.
- (III) A large family of homo- and heteronuclear *closo*-trigonal-bipyramidal  $\text{E}_2\text{M}_3$  anionic clusters (M = Cr, Mo, W, Mn, Fe) can be rationally synthesized from a variety of methodologies, such as the modified Hieber method, metal-exchange reaction, ring-closure process, or one-pot reaction.
- (IV) Stepwise cluster-expansion reactions from low-nuclearity to high-nuclearity anionic E–M–CO clusters (M = groups 6–8) have been accomplished by the incorporation of inorganic reagents (metal carbonyls and cationic metal ions), organic reagents, or chalcogen sources (such as chalcogen powder) via oxidative or reductive condensations. The controlled transformations of metal clusters of different sizes provided insightful information into cluster-growth in nanotechnology.
- (V) The activation of small molecules, such as  $\text{MeOH}$  (C–O), acetone (C=O),  $\text{CH}_2\text{Cl}_2$  (C–Cl), and  $\text{O}_2$  or selenium (formation of Te–O, Se–O, or Se–Se bond), has been observed in anionic group 6 or 7 chalcogenide complexes. In addition, the stability of the *cis*- and *trans*-forms of the first iron cluster-based carbene chalcogenide complexes, versus mononuclear iron carbene complexes, has been studied and compared in terms of the effects of the electronic resonances and chalcogen elements.

In addition, recent studies of the electrochemical and magnetic properties of these anionic clusters were rapidly developed to probe the complicated bonding properties of the metal–metal bonds. The most important issues can be summarized as follows.

- (I) The *closo*-type of anionic metal carbonyl chalcogenide clusters possessed rich reversible/quasi-reversible redox couples, which made them behave as electron sponges for potential use as molecular capacitors (see Table 2).
- (II) The effect of the incorporation of metal fragments (such as  $\text{CuX}$  or  $\text{Cr}(\text{CO})_5$ ) into *closo*-clusters (such as  $[\text{EFe}_3(\text{CO})_9]^{2-}$  (**3**),  $[\text{TeRu}_5(\text{CO})_{14}]^{2-}$  (**115c**), and  $[\text{Se}_2\text{Mn}_3(\text{CO})_9]^{2-}$  (**61b**)) could

be probed by pronounced redox potential shifts relative to their parent metal cores, which offered evidence of the electronic effect of the incorporated metal fragments on the resultant clusters. Furthermore, the effect of negative charges and the size of the metal cores (such as  $[\text{Se}_2\text{Mn}_3(\text{CO})_9]^-$  (**7b**),  $[\text{Se}_2\text{Mn}_3(\text{CO})_9]^{2-}$  (**61b**),  $[\text{Se}_6\text{Mn}_6(\text{CO})_{18}]^{4-}$  (**19**), and  $[\text{Se}_{10}\text{Mn}_6(\text{CO})_{18}]^{4-}$  (**73**)) could also be examined by DPV measurement.

(III) The odd- to even-electrons, as well as the lower- to higher-nuclearity carbonyl anionic clusters, displayed surprising paramagnetic behaviors, which were induced by the manifold metal–metal interaction and narrowly spaced frontier orbitals due to the increasing number of metals.

(IV) DFT calculations were extensively employed to elucidate experimental findings as well as their special properties (such as rodod and novel magnetic properties) in recent years.

Finally, and more importantly, these anionic chalcogen-containing group 8 (Fe and Ru) carbonyl clusters can be used as different types of the synthons for the development of 1D coordination networks via metal–metal and metal–ligand (such as bifunctional pyridyl-based ligands) interactions. There are several special observations. First, these metal carbonyl cluster-based 1D coordination polymers can be prepared using a convenient one-pot reaction. Secondly, the ease of the formation of metal carbonyl cluster-based 1D coordination polymers was ascribed to the structural features of metal carbonyl clusters, in which COs can block some coordination sites and protect the metal core. Moreover, metal carbonyl cluster-based neutral or anionic 1D coordination polymers have exhibited surprising semiconducting behaviors, with tunable energy gaps affected by metals, cations (cation–anion interaction), and organic  $\pi$ -system linkers ( $\pi$ – $\pi$  interaction), which were further elucidated by DFT calculations. Future studies on the design and synthesis of such metal carbonyl cluster-based polymers with different inorganic and organic linkers will be of great interest and should provide more insightful information. It is believed that this review can offer a convenient platform for the understanding of the fundamental chemistry of anionic chalcogen-containing groups 6–8 carbonyl clusters, as well as their potential future uses in optoelectronics and nanotechnology.

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