Regularities of thermal decay of carbonyl chalcogenide metal clusters

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The thermal decay of 19 individual carbonyl homo- and heterochalcogenide clusters with different M/X ratios (M = Fe, Mn, Pt, Cr, W, Mo, Re, Ru; X = S, Se, Te) was studied by differential scanning calorimetry and thermogravimetry. The process is stepwise and occurs at relatively low temperatures (100–350 °C). The general fact of incomplete removal of carbon monoxide (due to the formation of carbide and oxide impurities) during thermolysis of carbonyl chalcogenide clusters with the M : X ratio greater than 1 was elucidated. Conversely, when M : X \leq 1 (or at any M/X ratio for clusters containing methylcyclopentadienyl groups), pure metal chalcogenides are formed.

Key words: thermal decay, carbonyl chalcogenides, heterometallic clusters.

The synthesis of inorganic chalcogenides of a specified complex composition is a problem of modern material science. Chalcogenide complexes of some transition metals are used to prepare solid-state chalcogenide materials for electronic engineering.^{1,2} Heterometallic chalcogenide clusters appear to be quite promising precursors in the synthesis of polymetallic chalcogenides; however, there are no examples describing the use of these compounds, as these clusters are difficult to prepare.

This work outlines the results of a study of thermal decomposition of 19 carbonyl chalcogenide clusters of transition metals including heterometallic and hetero-chalcogenide clusters, whose structures have been determined by X-ray diffraction analysis.

Results and Discussion

Heating of all of the clusters studied leads to stepwise elimination of the carbonyl groups and organic fragments; the presence of carbides or oxides in the final product of thermal decay depends on the metal/chalcogen ratio in the cluster.* In the case of starting iron chalcogenide carbonyls $Fe_3E_2(CO)_9$, where E = S, Se, Te (1–3, respectively),^{3,4} prepared by a known procedure,⁵ the Fe : E ratio is 3 : 2 and decomposition proceeds stepwise by reactions (1)–(3).

Thermolysis is accompanied by energy absorption. The formation of a mixture of inorganic chalcogenides, oxides, and carbides upon decomposition of iron carbonyl selenide and carbonyl telluride was demonstrated in our

* The metal : chalcogen ratio is indicated in parentheses at each reaction equation.

Fe(CO)₃ E = S (1), Se (2), Te (3) e(CO) 1-3 Bond d/Å 2 3 13 34 Fe(2)-Fe(3) 2.590 2.645 2.740Fe(1)-Fe(3)2.595 2.657 2.754

previous study⁶ using powder X-ray diffraction analysis of the decomposition products.

$$\begin{array}{ccc} \operatorname{Fe}_{3}S_{2}(\operatorname{CO})_{9} & \xrightarrow{110-138^{\circ}} & \operatorname{Fe}_{3}S_{2}(\operatorname{CO})_{3} & \xrightarrow{150-215^{\circ}} \\ (3:2) & & & \\ & & \\ & & & \\$$

$$Fe_{3}Se_{2}(CO)_{9} \xrightarrow{90-150^{\circ}} Fe_{3}Se_{2}(CO)_{2} \xrightarrow{180-250^{\circ}} (3:2) \xrightarrow{} Fe_{3}Se_{2}(C)(O), \qquad (2)$$

$$Fe_{3}Te_{2}(CO)_{9} \xrightarrow{110-160^{\circ}} Fe_{3}Te_{2}(CO)_{4} \xrightarrow{170-210^{\circ}} (3:2) \xrightarrow{} Fe_{3}Te_{2}(CO)_{4} \xrightarrow{170-210^{\circ}} (3)$$

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Com- pound	Bond	d/Å	Ref.
4	Fe—Fe Se—Mn(CO) ₅ Se—Mn(CO) ₃ Fe→Mn(CO) ₃	2.623(3) 2.516 2.394 2.709	7
5	Mo—Fe Se—Mo	2.793, 2.823 2.544	7
6	Fe—Fe Fe—Ru Se—Ru	2.672 2.720 2.422—2.435	8
7*	W-Fe(1) W-Fe(2) W-Te(1) W-Te(2) Fe(1)-Te	2.925 2.898 2.736 2.736 2.537—2.549	9
8	Sn—Se Fe—Fe	2.539—2.549 2.544, 2.521	7

* Fe–W–Fe angle 80.9°.

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The thermal decay* of the iron manganese selenide carbonyl $Fe_2Mn_2Se_2(CO)_{14}$ (4), prepared by a previ-

ously described procedure,⁷ follows an almost identical route, and the thermal effect of the reaction has the same sign:

$$\begin{array}{c} \operatorname{Fe_2Mn_2Se_2(CO)_{14}} \xrightarrow{40-100^{\circ}} \operatorname{Fe_2Mn_2Se_2(CO)_{12}} \xrightarrow{} \\ (4:2) \end{array}$$

$$\xrightarrow{110-160^{\circ}} \operatorname{Fe}_{2}\operatorname{Mn}_{2}\operatorname{Se}_{2}(\operatorname{CO})_{4} \xrightarrow{170-220^{\circ}} -2 \operatorname{CO}^{\circ}$$

$$\longrightarrow \operatorname{Fe}_{2}\operatorname{Mn}_{2}\operatorname{Se}_{2}\{\operatorname{CO}\}_{2}. \tag{4}$$

Thermolysis of homoselenide carbonyl clusters, namely, iron ruthenium $RuFe_2Se_2(CO)_9$ (5) and iron molybdenum-containing $Fe_2MoSe_2(CO)_{10}$ (6) clusters, and of the homotelluride iron tungsten-containing carbonyl cluster $Fe_2WTe_2(CO)_{10}$ (7), which were prepared previously,⁷ is also stepwise and is described by the reactions (5)–(7):

$$\operatorname{RuFe_2Se_2(CO)_9} \xrightarrow{90-130^{\circ}} \operatorname{RuFe_2Se_2(CO)_6} \longrightarrow$$
(3:2)
$$\xrightarrow{130-250^{\circ}} \operatorname{RuFe_2Se_2(CO)_6} \xrightarrow{(5)}$$

$$Fe_{2}MoSe_{2}(CO)_{10} \xrightarrow[-7 CO]{} Fe_{2}MoSe_{2}(CO)_{3} \longrightarrow$$
(3 : 2)
$$\xrightarrow{200-300^{\circ}}{} Fe_{2}MoSe_{2}\{CO\}, \qquad (6)$$

$$Fe_{2}WTe_{2}(CO)_{10} \xrightarrow{100-130^{\circ}} Fe_{2}WTe_{2}(CO)_{8} \longrightarrow$$

$$(3:2)$$

$$\xrightarrow{135-150^{\circ}} Fe_{2}WTe_{2}(CO)_{6} \xrightarrow{170-230^{\circ}} -2CO \longrightarrow$$

$$Fe_{2}WTe_{2}\{CO\}_{4}.$$

$$(7)$$

However, in this case, the thermal effects of the processes are different: the onset of the decay is accompanied by a substantial heat evolution but this amount of energy is insufficient to make up for the energy spent for elimination of the carbonyl groups in the second step; therefore, the thermograms display endothermic dips on exothermic peaks.

Similar thermal effects are observed in the case of the pentanuclear tin-containing iron selenium carbonyl cluster $Fe_4Se_4(CO)_{12}Sn(8)$ prepared by a previously described procedure;⁷ however, the transition metal to chalcogen ratio in this cluster is equal to unity and carbon monoxide

^{*} Apparently, in this case and in other examples, mixtures of metal chalcogenides, carbides, and oxides are also formed at the final stage; however, this was not confirmed experimentally. Therefore, the number of CO molecules not evolved during the decay is shown in braces.

is totally evolved; the final product does not contain carbide or oxide impurities:

$$Fe_4Se_4(CO)_{12}Sn \xrightarrow{60-160^{\circ}} Fe_4Se_4(CO)_8Sn \longrightarrow$$
(4:4)
$$\xrightarrow{320-470^{\circ}} Fe_4Se_4Sn. \qquad (8)$$

Thermal decay of the pentanuclear iron molybdenum selenide telluride cluster $Fe_4MoTe_2Se_2(CO)_{14}$ (9), synthesized by a known procedure,⁷ is similar, regarding the pattern of energy changes, to the decay of the abovenoted trinuclear iron molybdenum and iron tungsten chalcogen carbonyls and proceeds by reaction (9).

$$Fe_{4}MoTe_{2}Se_{2}(CO)_{14} \xrightarrow{60-130^{\circ}}_{-CO}$$

$$(5:4)$$

$$\longrightarrow Fe_{4}MoTe_{2}Se_{2}(CO)_{13} \xrightarrow{165-180^{\circ}}_{-7 CO}$$

$$\longrightarrow Fe_{4}MoTe_{2}Se_{2}(CO)_{6} \xrightarrow{200-220^{\circ}}_{-2 CO}$$

$$\longrightarrow Fe_{4}MoTe_{2}Se_{2}\{CO\}_{4}.$$

$$(9)$$

The thermal transformations of the binuclear phenyltellurylcarbonylmolybdenum $[Mo(PhTe)(CO)_4]_2$ (10), obtained by a known procedure,¹⁰ resemble in the pattern of energy changes the thermal decay of chalcogenide iron molybdenum carbonyls. However, in this case, the molybdenum to tellurium ratio is equal to unity and the pyrolysis is accompanied by complete elimination of all carbonyl groups and organic ligands, giving rise to pure molybdenum telluride (MoTe).

A similar pattern of energy changes, but with a more clearly defined transition of the exotherm in the beginning of the decay into an endotherm in the middle of the temperature range of thermolysis was noted for the platinum carbonyl telluride $Pt_2Te_2(CO)_4$ (11) synthesized by a known procedure.⁷

In this case, the Pt : Te ratio is also equal to unity and CO molecules are completely split off; the platinum telluride thus formed contains no carbide or oxide impurities.

$$\begin{array}{ccc} \mathsf{Pt}_{2}\mathsf{Te}_{2}(\mathsf{CO})_{4} & \frac{130-150^{\circ}}{-3 \ \mathsf{CO}} \\ (2:2) & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & &$$

This outcome differs from that observed in thermolysis of the carbonyl clusters $(C_8H_{12})PtFe_2E_2(CO)_6$ (E = S (12), Se (13), Te (14)) synthesized by a previously described procedure.¹¹ Although the energy patterns that accompany the decay of these complexes and the platinum carbonyl telluride are qualitatively the same, the transition metal to chalcogen ratio is 3 : 2; therefore, these three compounds undergo successive elimination of the organic ligands and only four of the six carbonyl groups (reactions (12)–(14)):

$$(C_{8}H_{12})PtFe_{2}S_{2}(CO)_{6} \xrightarrow{110-140^{\circ}}_{-C_{8}H_{12}}$$

$$(3:2)$$

$$\longrightarrow PtFe_{2}S_{2}(CO)_{6} \xrightarrow{140-175^{\circ}}_{-3 CO}$$

$$\longrightarrow PtFe_{2}S_{2}(CO)_{3} \xrightarrow{180-300^{\circ}}_{-CO}$$

$$\longrightarrow PtFe_{2}S_{2}\{CO\}_{2}, \qquad (12)$$

$$(C_{8}H_{12})PtFe_{2}Se_{2}(CO)_{6} \xrightarrow{110-160^{\circ}}_{-C_{8}H_{12}}$$

$$(3:2)$$

$$\longrightarrow PtFe_{2}Se_{2}(CO)_{6} \xrightarrow{165-185^{\circ}}_{-3 CO}$$

$$\longrightarrow PtFe_{2}Se_{2}(CO)_{3} \xrightarrow{200-330^{\circ}}_{-CO}$$

$$\longrightarrow PtFe_{2}Se_{2}\{CO\}_{2}, \quad (13)$$

Note that the replacement of cyclooctadiene (C_8H_{12}) π -coordinated to platinum by dicyclopentadiene ($C_{10}H_{12}$)^{7,12} (compounds **15**, **16**) barely changes the route of the decay (reactions (15), (16)).

$$(C_{10}H_{12})PtFe_{2}S_{2}(CO)_{6} \xrightarrow{100-135^{\circ}} -C_{10}H_{12}$$

$$(3:2)$$

$$\longrightarrow PtFe_{2}S_{2}(CO)_{6} \xrightarrow{135-160^{\circ}} -CO$$

$$\longrightarrow PtFe_{2}S_{2}(CO)_{5} \xrightarrow{205-380^{\circ}} -3CO$$

$$\longrightarrow PtFe_{2}S_{2}(CO)_{2}, \quad (15)$$







Com- pound	Bond	$d/{ m \AA}$	Ref.
10	Mo—Mo Mo—Te	3.116 2.751—2.761	10
17	Cr–Mn	3.0239	13

E = S (12), Se (13), Te (14)

Bond	$d/\text{\AA}$				
	12 ¹¹	13 ¹¹	14 ¹¹	15 ¹²	16 ⁷
Fe—Fe	2.506	2.537	2.612(2)	2.515	2.543
Fe-E	2.285	2.393	2.559(1)	2.276	2.373
	2.295	2.395	2.590(1)	2.309	2.427
Pt—E	2.288	2.398	2.572(1)	2.299	2.413
	2.291	2.403	2.582(1)	2.303	2.454
Pt-Fe(1)	—	—	_	3.028	3.169

* The geometry of the metal—chalcogen core was determined by X-ray diffraction analysis, but due to the disorder of the chalcogen positions, the M—M and M—X distances were not determined.⁷

$$(C_{10}H_{12})PtFe_{2}Se_{2}(CO)_{6} \xrightarrow{110-123^{\circ}}_{-C_{10}H_{12}}$$

$$(3:2) \qquad \longrightarrow PtFe_{2}Se_{2}(CO)_{6} \xrightarrow{130-140^{\circ}}_{-CO}$$

$$\longrightarrow PtFe_{2}Se_{2}(CO)_{5} \xrightarrow{155-180^{\circ}}_{-3 CO}$$

$$\longrightarrow PtFe_{2}Se_{2}(CO)_{2}. \qquad (16)$$

Chalcogenide carbonyl clusters 17-19, containing methylcyclopentadienyl groups, decompose with complete loss of all the carbon-containing fragments and CO groups at any M : X ratio.

$$(C_{5}H_{4}Me)CrMn(SPh)_{3}(CO)_{3} \xrightarrow{130-205^{\circ}}_{-3 CO}$$

$$(2:3)$$

$$(C_{5}H_{4}Me)CrMn(SPh)_{3} \xrightarrow{205-360^{\circ}}_{-3 Ph}$$

$$(C_{5}H_{4}Me)CrMnS_{3} \xrightarrow{360-440^{\circ}}_{-(C_{5}H_{4}CH_{3})}$$

$$\longrightarrow CrMnS_{3}, \qquad (17)^{13}$$

** Assumed based on the data of IR spectra and analogy with the structure of $(PPh_3)_4Pt_2Te_2$ ¹⁴ The structure of complex 11 was not determined by X-ray diffraction.⁷

$$(C_{5}H_{4}Me)_{2}Cr_{2}Fe_{3}(SPh)_{2}Se_{3}(CO)_{8} \xrightarrow{50-120^{\circ}} (5:5)$$

$$(5:5) \xrightarrow{(C_{5}H_{4}Me)_{2}Cr_{2}Fe_{3}(SPh)_{2}Se_{3}(CO)_{6} \xrightarrow{120-150^{\circ}} (C_{5}H_{4}Me)_{2}Cr_{2}Fe_{3}(SPh)_{2}Se_{3} \xrightarrow{230-360^{\circ}} (C_{5}H_{4}CH_{3})_{2}Cr_{2}Fe_{3}(SPh)_{2}Se_{3} \xrightarrow{230-360^{\circ}} (C_{5}H_{4}Me)_{2}Cr_{2}Fe_{3}S_{2}Se_{3} \xrightarrow{360-414^{\circ}} (C_{5}H_{4}Me)_{2}Cr_{2}Fe_{3}S_{2}Se_{3} \xrightarrow{360-414^{\circ}} (C_{5}H_{4}Me)_{2}Cr_{2}Fe_{3}S_{2}Se_{3}, \qquad (18)^{7}$$

$$(C_{5}H_{4}Me)ReFe_{2}Se_{2}(CO)_{8} \xrightarrow{140-150^{\circ}}_{-8 CO}$$

$$(3:2)$$

$$(C_{5}H_{4}Me)ReFe_{2}Se_{2} \xrightarrow{154-200^{\circ}}_{-(C_{5}H_{4}Me)}$$

$$\longrightarrow ReFe_{2}Se_{2}. \qquad (19)^{7}$$

For processes that follow reactions (17)-(19), the first step of the decay is accompanied by appreciable en-



ergy absorption; on further heating, the thermograms display exotherms with endothermic dips.

2.515

Fe-Fe

We found that thermolysis of the clusters we studied takes place at relatively low temperatures, 100-350 °C. Four types of energy patterns of the decay (*i.e.*, the schemes of energy evolution and absorption during heating) can be clearly distinguished for these compounds:

(*i*) only endotherms appear on thermograms during the elimination of carbonyl groups (Fig. 1, a) (reactions (1)-(4)) for clusters of 3d elements;

(*ii*) thermal decay is accompanied by a complex exotherm (Fig. 1, *b*), which can be interpreted as an exotherm with endothermic dips; this type of decay is typical of 4d- and 5d-metal carbonyl chalcogenides (reactions (5)–(10));

(*iii*) thermolysis starts with pronounced heat evolution, but before it ends, a substantial endotherm appears, and only after that, the exothermic effect is completed (Fig. 1, c), reactions (11)—(16); this pattern is characteristic of Pt-containing clusters;

(iv) combination of the first two cases (Fig. 1, d), in particular, the primary loss of carbonyl groups is accom-

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Fig. 1. Averaged patterns of the temperature dependence of the heat flux (Q) during the thermal decay of 3d-metal (a), 4d- and 5d-metal (b), Pt-containing (c), and methylcyclopentadienyl-containing (d) carbonyl chalcogenide clusters.

panied by heat absorption, while further decomposition gives rise to a complex exotherm (reactions (17)-(19)).

The energy patterns *i* and *ii* can be interpreted resorting to the views on the parameters and types of M-Mbonds in carbonyls. It appears probable that during stepwise decarbonylation, additional M-M, M-X, M-O, and M-C bonds are formed.

For 3*d*-metal clusters, the M—M bonds are much weaker than for 4*d*- and 5*d*-metal clusters; in addition, in the latter case, multiple Mo—Mo and W—W bonds are readily formed. Therefore, for the first-group clusters, the energy spent for decarbonylation is not made up for by the energy evolved due to formation of new M—M bonds, whereas for second-group clusters, such a compensation is quite probable.

The pattern *iii* of energy loss can be explained by assuming that elimination of the diene ligand (C_8H_{12} or $C_{10}H_{12}$) from the platinum atom is followed by the formation of new Pt—Pt and Pt—X bonds; however, the concomitant amount of energy does not make for the energy spent for further elimination of CO molecules; therefore, energy absorption starts to predominate.

Of particular interest is the clear-cut dependence of the final product of thermolysis of carbonyl chalcogenide clusters on the transition metal to chalcogen atomic ratio (M : X).

Ph Te-Te Ph 20, 21 M = Cr (20), W (21)		Ph (CO) ₅ M′	Te-Te ^{Mi} Ph	(CO) ₅
		22, 23, 24 M = M' = Cr (22), W (24) M = Cr, M' = W (23)		
20 ¹⁵	21 ¹⁵	22 ¹⁶	23 ¹⁶	24 ¹⁶
2.679 2.718	 2.810 2.737	2.656 2.812	2.720* 2.720* 2.828(2)	 2.779 2.808
	$-T_{e}^{M(C)}$ Ph 30, 21 (20), W (2) $-T_{e}^{M(C)}$ 30, 21 31, 21 31, 21	$M(CO)_{5}$ Ph	$-T_{e} = Ph \qquad (CO)_{5} = Ph \qquad (CO)_{5}M'$ $r(20), 21 \qquad 22$ $r(20), W(21) \qquad M = M' \qquad M = M' \qquad M = Cr, \qquad M$	$ \begin{array}{c} \begin{array}{c} Ph \\ CO_{5} \\ Ph \\ CO_{5} \\ M' \\ \mathbf{Ph} \\ \mathbf$

* Disordered.





Bond	$d/\text{\AA}$		
	25 ¹⁷	26 ¹⁷	
Co—Co Co—Te TeTe	2.664(5), 2.674, 2.544 2.516(4)—2.618 —	2.590—2.622 	

Previously, we observed this dependence in the study of the thermal decay of mono-15 and binuclear¹⁶ diphenyl telluride complexes with chromium and tungsten pentacarbonyls 20-24 (reactions (20)-(24), respectively) and a trinuclear cobalt phenyltelluride carbonyl cluster (25) and tetranuclear cobalt bis-telluride carbonyl¹⁷ (26) (reactions (25) and (26), respectively):

$$\begin{array}{c} \operatorname{CrPh}_{2}\operatorname{Te}_{2}(\operatorname{CO})_{5} & \xrightarrow{90-170^{\circ}} & \operatorname{CrPh}_{2}\operatorname{Te}_{2} & \xrightarrow{170-200^{\circ}} \\ (1:2) & & \\ & \longrightarrow & \operatorname{CrTe}_{2} & \xrightarrow{220-270^{\circ}} & \operatorname{CrTe}, \end{array}$$
(20)

$$WPh_{2}Te_{2}(CO)_{5} \xrightarrow[-5]{100-160^{\circ}} WPh_{2}Te_{2} \xrightarrow[-2]{160-190^{\circ}} (1:2) \longrightarrow WTe_{2} \xrightarrow[-Te]{200-250^{\circ}} WTe, \qquad (21)$$

$$\begin{array}{ccc} \operatorname{Cr}_{2}\operatorname{Ph}_{2}\operatorname{Te}_{2}(\operatorname{CO})_{10} & \xrightarrow{130-170^{\circ}} & \operatorname{Cr}_{2}\operatorname{Ph}_{2}\operatorname{Te}_{2} & \xrightarrow{170-200^{\circ}} \\ (2:2) & & & \\ & & & & \\ & & & \\ & & &$$

CrWPh₂Te₂(CO)₁₀
$$\xrightarrow{140-170^{\circ}}$$
 CrWPh₂Te₂ $\xrightarrow{160-180^{\circ}}$
(2 : 2) 200-250°

$$\longrightarrow$$
 CrWPhTe₂ $\xrightarrow{200-250^\circ}$ CrWTe₂, (23)

$$W_{2}Ph_{2}Te_{2}(CO)_{2} \xrightarrow{140-170^{\circ}} W_{2}Ph_{2}Te_{2} \xrightarrow{170-200^{\circ}} (2:2) \longrightarrow W_{2}PhTe_{2} \xrightarrow{200-240^{\circ}} WTe, \quad (24)$$

$$\begin{array}{ccc} \text{Co}_{3}(\text{PhTe})_{5}(\text{CO})_{4} & \frac{120-170^{\circ}}{-4 \text{ CO}} & \text{Co}_{3}(\text{PhTe})_{5} & \frac{200-270^{\circ}}{-5 \text{ Ph}} \\ (3:5) & & \\ & & & & \\ & & & \\ & & & &$$

$$\begin{array}{ccc} \operatorname{Co}_{4}\operatorname{Te}_{2}(\operatorname{CO})_{11} & \xrightarrow{70-90^{\circ}} & \operatorname{Co}_{4}\operatorname{Te}_{2}(\operatorname{CO})_{8} & \xrightarrow{90-130^{\circ}} \\ (4:2) & & & \\ & \longrightarrow & \operatorname{Co}_{4}\operatorname{Te}_{2}(\operatorname{CO})_{6} & \xrightarrow{150-180^{\circ}} & \operatorname{Co}_{4}\operatorname{Te}_{2}\{\operatorname{CO}\}_{4}. \end{array}$$
(26)

For any of the carbonyl chalcogenide clusters studied, complete decarbonylation does not take place if the M : X ratio is greater than unity (reactions (1)-(7), (9), (12)–(16), (26)). In the case where $M: X \leq 1$ (reactions (8), (10), (11), (17), (18), (20)–(25)), the carbonyl groups split off completely, irrespective of the nature of the chalcogen atom. When the cluster contains methylcyclopentadienyl ligands, pure chalcogenides are formed even with M : X > 1.

These regularities can be explained in terms of the tendency of transition metal atoms to compensate the electron deficiency in each step of thermal decay with ligand elimination. When the ratio M: X > 1, the electronic deficiency is compensated by the formation of σ -, π -bonded CO bridges of type A, $Cp_2Nb(\mu-CO)(\sigma,\pi-CO)Mo(CO)Cp$,¹⁸ or of type B, $Cp_3Nb_3(CO)_7$,¹⁹ in which weakening of the C–O bond results in easy cleavage of carbon oxide to give carbides and oxides.



When the ratio $M : X \leq 1$, the electron deficiency is

made up for by additional π -bonding \ddot{X} —M through the lone electron pairs of the chalcogen atoms without the formation of σ -, π -CO bridges. Finally, in the presence of 5-electron-donating methylcyclopentadienyl ligands, the electron deficiency arising due to the elimination of carbonyl groups may be compensated by transformation of the rings into coordinated 6-electron-donating fulvene C₅H₄CH₂ and formation of M—H bonds



Therefore, even with M: X > 1, there is no need for the formation of σ -, π -CO bridges until the carbonyl groups have completely split off.

This unusual but a rather general regularity of incomplete elimination of CO groups in the thermolysis of transition metal carbonyl chalcogenide clusters with M : X > 1 and formation of pure metal chalcogenides from clusters with $M : X \le 1$ can prove quite useful for controlling the formation of oxide and carbide impurities in the inorganic chalcogenides formed upon the pyrolysis of such clusters.

Experimental

The main experimental methods used in the study were differential scanning calorimetry (DSC) and thermogravimetry (TG). Measurements were carried out on a Mettler TA-3000 thermal analyzer using DSC-20 and TG-50 modules, which were described in previous publications.^{20,21} Experiments were carried out with a constant heating rate of 5 K min⁻¹ in a dry argon atmosphere. Samples were heated either in aluminum containers (DSC) or in alundum crucibles (TG). The sample weight did not exceed 10 mg. The variation of the weight during heating was monitored directly with the TG-50 module with an accuracy of $\pm 2 \boldsymbol{\cdot} 10^{-3}~\text{mg}$ and in DSC studies of the stepwise decomposition of the compounds over fixed temperature ranges. The accuracy of temperature measurement at the anomalous points in the thermograms was $\pm 0.5^{\circ}$. At least four experiments by each of the procedures was carried out for every compound. The final results were obtained by statistical processing of the experimental data.

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