Syntheses, molecular structures, and thermal decomposition of cyclopentadienyldicarbonylmanganese chalcogenide derivatives*

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Transmetallation of the dichalcogenide complexes $[CpMn(CO)_2]_2(\mu-X_2)$ (X = S or Se) with $M(CO)_5(thf)$ (M = Cr or W) afforded new heterometallic complexes $CpMn(CO)_2(\mu-Se_2)Cr(CO)_5$, $CpMn(CO)_2(\mu-Se_2)[Cr(CO)_5]_2$, $CpMn(CO)_2(\mu-X_2)[W(CO)_5]_2$ (X = S or Se), and $CpMn(CO)_2(\mu-Se_2)[Cr(CO)_5][W(CO)_5]$. According to the X-ray diffraction data, their molecular structures contain the cyclic MnX_2 fragments coordinated by one or two $M(CO)_5$ groups *via* the X atoms. Study of thermal decomposition of the manganese complexes with different Mn : M : X ratios (M = Cr, W; X = S, Se, Te) by differential scanning calorimetry (DSC) and thermogravimetry demonstrated that this process took place at rather low temperatures (100–400 °C) and was accompanied by complete elimination of the CO groups followed by elimination of the Cp groups. At any metal to chalcogen ratio, the resulting inorganic chalcogenides contained no impurities of metal oxides and carbides.

Key words: synthesis, X-ray diffraction analysis, thermal decomposition, cyclopentadienyl complexes, metal carbonyls, metal chalcogenides, manganese, chromium, tungsten.

The step-by-step building-up of a cluster core using mono- and binuclear dichalcogenide complexes as ligands for other metal complexes has wide application in the cluster design of heterometallic chalcogenide clusters. In particular, the reactions of the binuclear complexes $[(CO)_3Fe]_2(\mu-X_2)$ (X = S, Se, or Te) with Mo(CO)₅(thf) or Mo(CO)₃(MeCN)₃ were used for modeling the active site of the MoFeS cofactor of nitrogenase.¹

The binuclear complexes $[CpMn(CO)_2]_2(\mu-X_2)$ (X = S (1) or Se (2)) were first synthesized by the reactions of photochemically generated CpMn(CO)_2(thf) with COS or COSe, respectively.² Recently, these complexes were synthesized using a new method (Scheme 1) through the anionic carbene complex CpMn(CO)_2C(Ph)(O)⁻ (paramagnetic complexes CpMn(CO)_2XC(=O)Ph were generated as intermediates; the molecular structure of the complex with X = S was established by X-ray diffraction analysis³).

In molecules **1** and **2**, the X–X bond was readily cleaved by reduction with sodium borohydride in ethanol or with sodium in tetrahydrofuran. The further reactions with iodomethane afforded new CpMn(CO)₂XMe₂ or [CpMn(CO)₂]₂XMe₂ (X = S or Se) complexes.³ We ex-





X = S(1), Se(2)

pected that, by analogy with the known reactions of $[(CO)_3Fe]_2(\mu-X_2)$,⁴ the M(CO)₅ fragments (M = Cr or W) would be inserted into the X-X bond of molecules 1 and 2.

Results and Discussion

The reaction of complex **2** with $Cr(CO)_5$ (thf) unexpectedly gave rise to the mono- and dichromium transmetallation products as dark-lilac-colored crystals of $[CpMn(CO)_2](\mu-Se_2)[Cr(CO)_5]$ (**3**) and dark-green crystals of $([CpMn(CO)_2](\mu-Se_2)[Cr(CO)_5]_2$ (**4**), respectively (Scheme 2).

Each step of this reaction is reversible. The synthesis of complex **3** from **4** in THF in the presence of CO proved to be a more convenient procedure compared to the di-

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rect synthesis of complex **3** from **2**. Analogously, darkgreen crystals of the CpMn(CO)₂(μ -S₂)[Cr(CO)₅]₂ complex (**5**) were prepared starting from complex **1** and Cr(CO)₅(thf).

In the reactions of complexes **1** and **2** with $W(CO)_5(thf)$, only the trinuclear complexes $CpMn(CO)_2(\mu-S_2)[W(CO)_5]_2$ (6) and $CpMn(CO)_2(\mu-Se_2)[W(CO)_5]_2$ (7), respectively, were isolated (Scheme 3).

Finally, the reaction of complex **3** with $W(CO)_5(thf)$ gave a new complex containing three different metals, *viz.*, $[CpMn(CO)_2](\mu-Se_2)[Cr(CO)_5][W(CO)_5]$ (8) (Scheme 4).

Complexes **3–8** were characterized by IR spectroscopy, elemental analysis, and/or DSC. The molecular structures of compounds **3**, **4**, **6**, and **8** were established by X-ray diffraction analysis (Figs. 1–4, Tables 1–3).

All these complexes contain the triangular MnX_2 fragment with the single Mn-X and X-X bonds. This fragment is coordinated by one or two $M(CO)_5$ groups *via* the substantially shortened M-X bonds (in **3**, Se(1)-Cr(1), 2.503(2) Å; in **4**, Se-Cr (aver.), 2.497(1) Å; in **6**, W(1)-S(1) (aver.), 2.538(3) Å; in **8**, the Cr-Se and W-Se distances (2.548(1)-2.567(2) Å) are averaged due to disorder). These groups deviate from the MnX_2 plane. In complexes **4**, **6**, and **8**, these groups are in the *anti* conformation. The CpMn(CO)₂ and M(CO)₅ groups have a typical two-legged piano-stool and tetragonal-pyramidal geometry, respectively.



It can be assumed that the first step of this reaction involves coordination of the $M(CO)_5$ fragment to one of the chalcogen atoms in the Mn-X-X-Mn chain, like in the known $[CpFe(CO)_2]_2S_2W(CO)_5$ complex⁵ (W–S, 2.582 Å) (Scheme 5).



Fig. 1. Molecular structure of complex 3.







Fig. 2. Molecular structure of complex 4.





Fig. 3. Molecular structure of complex 6.











Parameter	3	4	6	8
Molecular formula	C ₁₂ H ₅ CrMnO ₇ Se ₂	$C_{17}H_5Cr_2MnO_{12}Se_2$	C ₁₇ H ₅ MnO ₁₂ S ₂ W ₂	C ₁₇ H ₅ CrMnO ₁₂ Se ₂ W
Molecular weight	526.02	718.07	887.97	849.92
Color of crystals	Dark-lilac	Dark-green	Dark-green	Dark-green
Diffractometer	«Bruker Smart	«Siemens P3»	«Siemens P3»	«Bruker Smart
	1000CDD»			1000CDD»
Temperature/K	110(2)	293(2)	293(2)	110(2)
Space group	$\overline{P}1$	P2(1)/n	P2(1)/n	P2(1)/n
<i>a</i> /Å	7.020(3)	11.851(2)	11.935(2)	11.862(8)
b/Å	9.944(5)	13.591(3)	13.597(3)	13.364(9)
c/Å	11.718(5)	14.317(3)	14.420(3)	14.077(10)
α/deg	87.381(9)	90	90	90
β/deg	85.720(9)	92.85(3)	93.55(3)	92.98(1)
γ/deg	78.548(9)	90	90	90
$V/Å^3$	799.1(6)	2303.1(8)	2335.5(8)	2228(3)
Ζ	2	4	4	4
<i>F</i> (000)	500	1376	1632	1576
$\rho_{calc}/g \ cm^{-3}$	2.186	2.071	2.525	2.533
Radiation,	0.71073	0.71073	0.71073	0.71073
λ(Mo-Kα)/Å				
Linear	6.054	4.687	10.597	9.515
absorption, μ/mm^{-1}				
Absorption correction	Semiempirically	Psi scan	Psi scan	Semiempirically
	based on equivalent			based on equivalent
	reflections			reflections
Scan mode	ω	$\theta/2\theta$	$\theta/2\theta$	ω
$2\theta_{\rm max}/{\rm deg}$	56.14	50.06	52.02	54.38
Number of measured	6629	3691	4741	26937
Number of independent reflections	3720 ($R_{\rm int} = 0.0593$)	3432 ($R_{\rm int} = 0.0542$)	4518 ($R_{\rm int} = 0.0487$)	4857 ($R_{\rm int} = 0.0642$)
Number of reflections	2632	2946	3326	2936
with $I > 2\sigma(I)$	• • • •	2 0 7		• • • •
Number of parameters	208	297	307	308
R_1	0.0650	0.0639	0.0530	0.0537
wK ₂	0.1585	0.1865	0.1321	0.1182
GOF	0.971	0.949	1.115	1.062
$(\rho_{\text{max}}/eA^{-3})/(\rho_{\text{min}}/eA^{-3})$	1.036/-0.747	1.226/-1.328	1.608 / -0.823	2.859/-1.422

 Table 1. Crystallographic data for complexes 3, 4, 6, and 8

Such a coordination of the $M(CO)_5$ group by the lone electron pair at the chalcogen atom decreases the degree of its involvement in additional binding to the manganese atom observed in complexes 1 and 2³ and facilitates disproportionation accompanied by the transformation of two Mn^{II} ions into the Mn^{III} ion in complexes 3–8 as well as into the Mn^{I} ion, which is, presumably, removed as CpMn(CO)₂(thf).

Apparently, the energy difference between the chain and triangular structures is not-too-large, and the transformation of the former into the latter occurs already upon the replacement of one $CpMn(CO)_2$ group in diselenide 2 by the isoelectronic $Cr(CO)_5$ group giving rise to complex 3. However, the triangular structure is again transformed into the chain structure in the reverse reaction. In addition to the above-mentioned $[CpFe(CO)_2]_2S_2W(CO)_5$ complex,⁵ these chains have also been observed earlier in electronically saturated ditellurides, *viz.*, the dianionic chromium complex $(CO)_5Cr-Te-Te-Cr(CO)_5^{2-}$ (Te-Te, 2.736 Å; Cr-Te, 2.743 Å)⁶ and the uncharged manganese complex $(PEt_3)_2(CO)_3Mn-Te-Te-Mn(PEt_3)(CO)_3$ (Te-Te, 2.763 Å; Mn-Te, 2.718 Å).⁷

The coordination mode in dirhenium ditelluride $CpRe(CO)_2(\mu_3-Te_2)[CpRe(CO)_2]$ (9) is analogous to that observed in complex 3. The structures of types 4, 6, and 8 were found in dimanganese rhenium ditelluride $Cp*Re(CO)_2(\mu_3-Te_2)[CpMn(CO)_2]_2$ (10), which was prepared by the reaction of the $CpMn(CO)_2$ (thf) complex with $Cp*Re(CO)_2H(TeH)$ and contains the single Te—Te

Bond	d∕Å	Angle	ω/deg
3		3	
Se(1)-Se(2)	2.307(1)	Se(2) - Se(1) - Cr(1)	114.16(4)
Se(1)-Cr(1)	2.503(2)	Se(2)-Se(1)-Mn(1)	62.16(4)
Se(1)-Mn(1)	2.510(1)	Cr(1)- $Se(1)$ - $Mn(1)$	123.45(4)
Mn(1)-Se(2)	2.493(1)	Se(2)-Mn(1)-Se(1)	54.92(3)
		Se(1) - Se(2) - Mn(1)	62.92(3)
4		4	
Se(1)-Se(2)	2.3160(9)	Se(2) - Se(1) - Cr(1)	108.50(4)
Se(1)-Cr(1)	2.506(1)	Se(2)-Se(1)-Mn(1)	63.20(3)
Se(1)-Mn(1)	2.516(1)	Cr(1)-Se(1)-Mn(1)	121.53(5)
Mn(1)-Se(2)	2.538(1)	Se(1)-Mn(1)-Se(2)	54.55(3)
Se(2)-Cr(2)	2.488(1)	Se(1) - Se(2) - Cr(2)	111.85(4)
		Se(1)-Se(2)-Mn(1)	62.25(3)
		Cr(2)-Se(2)-Mn(1)	122.82(4)
6		6	
S(1) - S(2)	2.068(4)	S(2) - S(1) - W(1)	109.3(1)
W(1) - S(1)	2.538(3)	S(1) - S(2) - W(2)	113.5(1)
Mn(1) - S(1)	2.389(3)	S(2) - S(1) - Mn(1)	64.9(1)
Mn(1) - S(2)	2.407(3)	S(1) - S(2) - Mn(1)	64.0(1)
W(2) - S(2)	2.503(3)	S(1) - Mn(1) - S(2)	51.1(1)
		Mn(1) - S(2) - W(2)	124.4(1)
		Mn(1) - S(1) - W(1)	122.75(11)

Table 2. Bond lengths (*d*) and bond angles (ω) in the structures of **3**, **4**, and **6**

Table 3. Bond lengths (*d*) and bond angles (ω) in the structure of **8**

Bond	d∕Å	Angle	ω/deg
W/Cr(1)—Se(1)	2.548(1)	Se(1)— $Se(2)$ — $Mn(1)$	62.91(5)
W/Cr(2)-Se(2)	2.567(2)	Se(1) - Se(2) - W(2)	107.46(4)
Se(2)-Se(1)	2.305(1)	Mn(1) - Se(2) - W(2)	121.17(4)
Se(2)-Mn(1)	2.507(2)	Se(1) - Se(2) - Cr(2)	107.46(4)
Mn(1)-Se(1)	2.517(2)	Mn(1)-Se(2)-Cr(2)	121.17(4)
		Se(2)-Se(1)-Mn(1)	62.48(5)
		Se(2)-Se(1)-Cr(1)	110.37(5)
		Mn(1)-Se(1)-Cr(1)	122.52(5)
		Se(2) - Se(1) - W(1)	110.37(5)
		Mn(1)-Se(1)-W(1)	122.52(5)

(2.732 Å) and Te-Re (2.827 and 2.807 Å) bonds (Te-Mn bonds are substantially shortened and are, on the average, 2.525 Å).⁸

Thermolysis of complexes 3–8 and other cyclopentadienyldicarbonylmanganese chalcogenides. Thermolysis of complexes 3–8 under argon in the temperature range of 20-400 °C was studied in comparison with pyrolysis of the starting complexes 1 and 2 as well as of other cyclopentadienylcarbonylmanganese chalcogenides studied by us earlier.³

Chalcogen-containing complexes of some metals were used in the pyrolytic synthesis of chalcogenide materials.⁹ The characteristic features of thermal decomposition of metal carbonyls and Cp₂M-type cene compounds were



analyzed in detail in the monograph.¹⁰ Recently, we studied pyrolysis of homo- and heterometallic carbonyl chalcogenides¹¹ and established the important dependence of the composition of inorganic compounds obtained after pyrolysis on the M : X ratio in the complexes. If this value is larger than unity, pyrolysis affords impurities of metal oxides and carbides due to partial decomposition of the CO groups. If this ratio is equal to or smaller than unity, the CO ligands are completely removed. It was noted¹¹ that the organic groups and CO were completely eliminated in the presence of the methylcyclopentadienyl ligands irrespective of the transition metal : chalcogen ratio. This was attributed to the fact that fulvene $C_5H_4=CH_2$ was readily detached from the manganese atom to form the Mn—H bond.

In the present study, we found that thermal decomposition of cyclopentadienylcarbonylmanganese chalcogenide complexes, which cannot produce fulvene, giving rise to manganese-containing chalcogenides was also not accompanied by the formation of metal oxides and carbides regardless of the metal : chalcogen ratio.

For example, pyrolysis of complexes 1, 2, and $[CpMn(CO)_2]_2S(11)$ (11 contains the monosulfide bridge between the manganese atoms¹²) proceeded according to

Scheme 6

$$[CpMn(CO)_{2}]_{2}S_{2} \xrightarrow{120-155 \circ C} -4 CO, -0.5 Cp} 1$$

$$(Cp)_{1.5}Mn_{2}S_{2} \xrightarrow{240-450 \circ C} MnS$$

Schemes 6-8, respectively, and was accompanied by an exothermic peak in the thermograms (Fig. 5, a).



Study of thermolysis of the binuclear complexes $[CpMn(CO)_2]_2SMe_2$ (12) and $[CpMn(CO)_2]_2SeMe_2$ (13) containing the dimethylsulfide and dimethylselenide



Fig. 5. Schematic representation of the thermograms for decomposition of complexes 1, 2, 11 (*a*), 12, 13 (*b*), and 14 (*c*).

bridges, respectively,³ demonstrated that complex 12 melts virtually without decomposition (m.p. = $131 \pm 1 \circ C$, $\Delta_m H =$ $37674\pm800 \text{ J mol}^{-1}$), whereas complex **13** melts with decomposition, and subsequent pyrolysis of the complexes occurs according to Schemes 9 and 10, respectively.

Scheme 9

ſ

CpMn(CO)₂]₂SMe₂
$$\xrightarrow{135-145 \circ C}$$

12
→ Cp₂Mn₂SMe₂ $\xrightarrow{145-190 \circ C}$
→ Cp_{0.5}Mn₂SMe₂ $\xrightarrow{145-190 \circ C}$
→ Mn₂SMe₂ $\xrightarrow{190-270 \circ C}$ Mn₂SMe₂ Mn₂ Mn₂SMe₂ Mn₂ Mn₂SMe₂ Mn₂ M

Scheme 10

-0.5 Cp, -2 Me

$$[CpMn(CO)_2]_2SeMe_2 \xrightarrow{110-135 \circ C} -4 CO$$
13
$$\longrightarrow Cp_2Mn_2SeMe_2 \xrightarrow{135-210 \circ C} -1.5 Cp$$

$$\longrightarrow Cp_{0.5}Mn_2SeMe_2 \xrightarrow{210-250 \circ C} -0.5 Cp, -2 Me$$

The total effect of each process is exothermic. However, the exothermic peaks in the thermograms of complexes 12 and 13, unlike those observed in thermolysis of compounds 1, 2, and 11, have a complex shape (Fig. 5, b).

Solid products of thermolysis of complexes 2, 12, and 13 were studied by powder X-ray diffraction analysis (Tables 4-6), which showed that the reaction products

Table 4. Data of powder X-ray diffraction analysis of the decomposition product of [CpMn(CO)₂]₂Se₂ (2)

Decomposition product		MnSe					
		Ι	*	I	II**		
d/Å	I (%)	<i>d</i> /Å <i>I</i> (%)		d∕Å	I (%)		
3.115	20	3.100	5	3.141	10		
2.731	100	2.770	_	2.720	100		
2.580	20	2.590	20	_	_		
2.153	20	2.160	25	_	_		
1.933	60	_	_	1.923	60		
1.857	80	1.810	80	_	_		
1.702	10	1.690	5	_	_		
1.578	30	1.520	10	1.570	20		

* Hexagonal modification.

** Cubic modification.

473

500

Decomposition product		MnS		Mn	
d∕Å	I (%)	d∕Å	I (%)	d∕Å	I (%)
3.994	60	_	_	4.030	100
3.086	30	3.025	20	3.130	10
2.861	10	_	_	2.844	20
2.651	100	2.620	100	_	_
2.470	60	_	_	2.472	60
2.031	20	_	_	2.022	50
1.945	10	_	_	1.935	10
1.860	50	1.853	60	_	_
1.641	20	_	_	1.610	20
1.497	10	_	_	1.493	10

Table 5. Data of powder X-ray diffraction analysis of the decomposition product of [CpMn(CO)₂]₂SMe₂ (**12**)

Table 6. Data of powder X-ray diffraction analysis of the decomposition product of [CpMn(CO)₂]₂SeMe₂ (13)

Decomposition product		MnSe		Mn	
d∕Å	I (%)	d∕Å	I (%)	d∕Å	I (%)
3.995	70	_	_	4.030	100
2.852	10	_	_	2.844	20
2.740	100	2.720	100	_	_
2.452	40	_	_	2.472	60
2.052	60	_	_	2.022	50
1.915	50	1.923	60	1.935	10
1.615	10	_	_	1.610	20
1.560	15	1.570	20	_	_
1.497	10	_	—	1.493	10

contained manganese monochalcogenides. In addition, thermolysis of complexes **12** and **13** afforded also manganese metal.

To correctly determine the composition of the solid pyrolysis product of compound **2**, we studied the temperature dependence of the thermal capacity of the thermolysis product in the temperature range of 27-227 °C. According to the powder X-ray diffraction data, this product is a nonequilibrium mixture of two modifications of manganese selenide. Therefore, we carried out homogenizing annealing at 800 °C in an inert atmosphere for 8 h. A comparison of the results of measurements of thermal capacity and the published data on manganese selenide¹³ demonstrated that they are in satisfactory agreement within the experimental error (Table 7).

Thermolysis of the trinuclear telluride complex $[CpMn(CO)_2]_3Te_2$ (14) containing the cyclic MnTe₂ group in which each Te atom is additionally coordinated by the CpMn(CO)₂ group¹⁴ proceeded stepwise according to Scheme 11 with considerable energy release. The exothermic peak has a complex shape (Fig. 5, *c*).

<i>T</i> /K	C _p /J	K mol ⁻¹
	Lit. data ¹³	Present study
300	51.05	51.2
333	51.31	51.5
373	51.61	51.9
403	51.85	52.1
443	52.15	51.4

52.38

52.59

 Table 7. Temperature dependence of the thermal capacity of manganese selenide (MnSe)

Scheme 11

52.6

53.0



Powder X-ray diffraction analysis of the decomposition products of complex **14** (Table 8) showed that the resulting mixture contained manganese metal as well as manganese mono- and ditellurides.

Table 8. Data of powder X-ray diffraction analysis of the decomposition product of $[CpMn(CO)_2]_3Te_2$ (14)

Decor produ	nposition ct	Mn	Те	MnTe ₂		Mn	
d∕Å	I (%)	$d/{ m \AA}$	I (%)	$d/{ m \AA}$	I (%)	$d/{ m \AA}$	I (%)
3.985	50	_	_	_	_	4.030	100
3.209	100	3.170	100	_	_	_	_
3.107	100	_	_	3.110	100	_	_
2.837	50	_	_	2.836	95	2.844	20
2.492	30	_	_	_	_	2.472	60
2.452	90	2.458	95	_	_	_	_
2.080	90	2.079	80	2.097	50	2.022	50
1.929	50	1.903	35	1.926	50	1.935	10
1.860	50	_	_	1.858	65	1.871	10
1.780	10	1.769	15	_	_	_	_
1.630	20	1.680	20	_	_	1.610	20
1.548	20	1.589	20	_	_	1.529	10
1.477	5	_	_	_	_	1.493	10
1.399	10	1.405	15	—	—	_	_

Thermolysis of heterometallic cyclopentadienylcarbonyl chalcogenide complexes 3-8 containing manganese in combination with Group VI metals (Cr or W), which were synthesized in the present study, proceeded analogously.

Thermal decomposition of compound **3** proceeded according to Scheme 12.

Scheme 12

$$CpMn(CO)_{2}Se_{2}Cr(CO)_{5} \xrightarrow{110-116 \circ C} -2 CO$$
3
$$\longrightarrow CpMnSe_{2}Cr(CO)_{5} \xrightarrow{116-141 \circ C} -5 CO, -0.5 Cp$$

$$\longrightarrow Cp_{0.5}MnCrSe_{2} \xrightarrow{260-350 \circ C} CrMnSe_{2}$$

Elimination of the first two CO groups was accompanied by energy absorption. A further rise in temperature led to elimination of the remaining CO groups and onehalf of the Cp groups with considerable energy release. In the final step of decomposition accompanied by weak energy absorption, the Cp groups were completely removed (Fig. 6, a). The total effect of the process is exothermic. Powder X-ray diffraction analysis of the solid product of thermal destruction of complex **3** (Table 9) revealed the presence of the MnSe and CrSe phases.

Thermal decomposition of isostructural complexes 4-7, in which the metallocycle MnX₂ is additionally coordinated by two M(CO)₅ groups, proceeded according to Schemes 13–16, respectively.

The energy changes in the course of thermal decomposition of compounds **4** and **5** (see Schemes 13 and 14) are similar in character. The decomposition process starts with partial elimination of the CO molecules and energy

Table 9. Data of powder X-ray diffraction analysis of the decomposition product of $CpMn(CO)_2Se_2Cr(CO)_5$ (3)

Decomposition product		MnSe		CrSe	
d∕Å	I (%)	d∕Å	I (%)	d∕Å	I (%)
5.754	10	_	_	5.750	20
3.178	5	3.141	11	_	_
2.870	30	_	_	2.880	40
2.730	100	2.720	100	2.740	100
2.035	80	_	_	2.110	100
1.934	40	1.923	60	_	_
1.756	60	_	_	1.800	100
1.640	40	_	_	1.640	50
1.566	20	1.570	20	1.568	10
1.523	20	_	_	1.535	50
1.386	10	1.366	11	_	_



Fig. 6. Schematic representation of the thermograms for decomposition of complexes 3(a), 4, 5(b), and 6, 7(c).

Scheme 13

CpMn(CO)₂Se₂[Cr(CO)₅]₂
$$\frac{100-117 \circ C}{-2 \circ CO}$$

4
→ CpMnSe₂Cr₂(CO)₁₀ $\frac{117-136 \circ C}{-10 \circ CO}$ →

→ CpMnCr₂Se₂
$$\xrightarrow{140-250 \circ C}$$
 MnCr₂Se₂

Scheme 14

CpMn(CO)₂S₂[Cr₂(CO)₅]₂
$$\xrightarrow{100-110 \circ C}$$

5
→ CpMnS₂Cr₂(CO)₁₀ $\xrightarrow{110-140 \circ C}$
→ CpMnCr₂S₂ $\xrightarrow{140-270 \circ C}$ MnCr₂S₂



release. Then, the majority of CO groups are removed with considerable energy absorption. Finally, the Cp ligand is eliminated with energy release (Fig. 6, b). In the thermogram, the above process corresponds to the onset of the exothermic effect, which is then superimposed with the endothermic effect and completed with the exothermic effect. The total effect of thermal decomposition is endothermic.

For compounds **6** and **7** (see Schemes 15 and 16, respectively), the onset of thermal decomposition is accompanied by energy absorption. Then the process is strongly exothermic with a weak endothermic dip (Fig. 6, c). The total effect of thermolysis of compounds **6** and **7** is exothermic.

Apparently, the above-described differences as well as a substantial difference in the temperature at which thermal decomposition was completed ($250-270 \degree C$ for compounds **4** and **5**, $320-440 \degree C$ for compounds **6** and **7**) are attributed to a superposition of the endothermic effect associated with the cleavage of the M–CO bonds and the

Scheme 17





Fig. 7. Schematic representation of the thermogram for decomposition of complex 8.

exothermic effect upon the formation of new M–X and M–M bonds, including the multiple metal–chalcogen and metal–metal bonds.¹⁵ In particular, at the beginning of decarbonylation of heterometallic complexes **4**–7, the partially multiple M–X bonds that appear should be stronger in the case of M = Cr than in the case of M = W, whereas the multiple M–M bonds are more stronger in the case of M = W.¹⁵

These effects are particularly difficult to take into account for mixed Cr,W-containing complex 8 (Scheme 17).

Initially, the character of energy changes in the course of thermal decomposition is analogous to that observed for compounds 6 and 7. Then an increase of the temperature leads to considerable energy release without a change in the weight. The Cp ligand is eliminated with energy absorption only in the last step (Fig. 7). The total effect of decomposition is exothermic.

Therefore, complete decarbonylation is typical of this class of cyclopentadienylcarbonyl chalcogenide complexes independently of the M : X ratio, whereas thermal destruction of metal carbonyl chalcogenides with the M : X ratio larger than unity gives rise to inorganic chalcogenides with impurities of metal oxides and carbides.¹¹ Apparently, this is associated with the characteristic features of compensation of the electron deficiency, which appears upon partial decarbonylation of complexes 1-8 and 11-14, compared to the carbonyl chalcogenide complexes considered in the study.¹¹ In the latter complexes, structures with σ,π -coordinated CO groups, which donate a larger number of electrons to the metal core compared to the terminal CO group, should be generated as intermediates (for example, in the Cp₂Nb(μ -CO)(σ , π -CO)Mo(CO)Cp¹⁶ (type A) or $Cp_3Nb_3(CO)_7^{17}$ (type **B**) clusters, in which the CO groups are readily disrupted to form carbides and oxides due to weakening of the C=O bonds).

In the presence of the methylcyclopentadienyl ligands, the electron deficiency, which appears upon elimination of the carbonyl groups, can be compensated by the transformation of the rings into the coordinated six-elec-



tron donor fulvene ligand $C_5H_4CH_2$ and the M-H bond (Scheme 18).

Scheme 18



Therefore, even at M : X > 1, there is no need for the formation of σ -, π -bridging CO ligands until CO groups are completely eliminated.

The unsubstituted Cp ligands in complexes 1–8 and 11–14 considered in the presence study can, apparently, compensate the electron deficiency through the σ -, π -bridging coordination of the Cp ligand with the additional formation of the M–H bond, like in the structure of dimeric niobocene¹⁸ (C), as well as through the formation of stacked structures of the Cp₃Ni₂⁺ type in which the π -electron system of the central Cp ligand is involved in coordination to two metal atoms¹⁹ (D).



The methylcyclopentadienyl ligand also can compensate the electron deficiency in this way. However, the above-mentioned assumption (fulvene scheme) adequately explains a sharp decrease in the temperature of complete thermal decomposition of the methylcyclopentadienyl complexes compared to the analogous cyclopentadienyl complexes, as we have observed earlier, for example, in the $[RC_5H_4Fe(CO)_2]_2Sn(TePh)_2$ complexes, where R = H (for Cp) or Me (for Cp*)²⁰ (Scheme 19).

Scheme 19

$$[CpFe(CO)_{2}]_{2}Sn(TePh)_{2} \xrightarrow{84-165 \circ C} -4 CO$$

$$\longrightarrow [CpFe]_{2}Sn(TePh)_{2} \xrightarrow{182 \circ C} -2 Ph$$

$$\longrightarrow [CpFe]_{2}SnTe_{2} \xrightarrow{350-450 \circ C} -2 Cp \qquad Fe_{2}SnTe_{2}$$

$$[Cp^{*}Fe(CO)_{2}]_{2}Sn(TePh)_{2} \xrightarrow{80-151 \circ C} -4 CO$$

$$\longrightarrow [Cp^{*}Fe]_{2}Sn(TePh)_{2} \xrightarrow{185 \circ C} -4 CO$$

$$\longrightarrow [Cp^{*}Fe]_{2}SnTe_{2} \xrightarrow{217 \circ C} -2 Ph \qquad Fe_{2}SnTe_{2}$$

Therefore, the use of the Cp and Cp* ligands in carbonyl chalcogenide complexes allows one to prevent the formation of impurities of oxides and carbides in inorganic metal chalcogenides generated by pyrolysis at all metal : chalcogen ratios in the complexes. It should be noted that inorganic composites formed at relatively low temperatures (below 450 °C) already consist of crystalline phases of binary metal chalcogenides and individual metals.

Experimental

All operations associated with the synthesis and isolation of the complexes were carried out under pure argon and in anhydrous solvents. Commercial CO, $W(CO)_6$, and $Cr(CO)_6$ were used without preliminary purification. Complexes 1 and 2 were synthesized according to a procedure published earlier.³

Thermal decomposition of compounds **1–8** and **11–14** was studied by DSC and thermogravimetry on DSC-20 and TG-50 units of a TA-3000 thermoanalyzer (Mettler). In all experiments, samples were heated under dry argon at a constant rate (5 K min⁻¹). Three—four DSC experiments and three—five TGA experiments were carried out for each compound. The weight loss upon thermal destruction was determined directly on a TG-50 unit; the accuracy of the weighing device was $\pm 2 \cdot 10^{-3}$ mg. Thermal destruction was studied by DSC in steps, the temperature range of investigation being divided into intervals. The width and number of these intervals were determined based on the preliminary general information on the changes in the weight and energy in the course of decomposition. This method of performing the experiment made it possible to determine the weight loss in each temperature interval and compare the results obtained by DSC and TGA. The anomalous points and thermal effects in the thermograms were determined with an accuracy of $\pm 1^{\circ}$ and $\pm 0.5\%$, respectively.

The IR spectra were recorded on a Specord IR-75 spectrophotometer in KBr pellets.

(Cyclopentadienyldicarbonylmanganese)(µ-diselenide)(pentacarbonylchromium), [CpMn(CO)₂](µ-Se₂)[Cr(CO)₅] (3). A solution of Cr(CO)₆ (0.34 g, 1.5 mmol) in THF (30 mL) was UV irradiated in a water-cooled quartz Schlenk vessel for 1.5 h. The resulting orange solution was added dropwise to a green solution of [CpMn(CO)₂]₂(µ-Se₂) (0.4 g, 0.78 mmol) in THF (20 mL) at 0 °C for 1.5 h. The gray-green reaction mixture was stirred for 1 h and concentrated to dryness in vacuo. The green residue was washed with hexane (40 mL) and extracted with CH_2Cl_2 (30 mL). The green extract was concentrated to dryness *in vacuo* and the green residue was extracted with THF (30 mL). Gaseous CO was bubbled through the resulting violet solution (1 bubble per second) with stirring for 5 h. The solvent was removed in vacuo. The residue was recrystallized from a CH₂Cl₂-hexane mixture after storage of the solution at -18 °C for 72 h. Compound 3 was obtained in a yield of 0.24 g (58%) as needle-like violet crystals suitable for X-ray diffraction analysis. Found (%): CO, 37.5*; C₅H₅; 12.3* (solid residue corresponds to MnCrSe₂). C₁₂H₅MnO₇Se₂. Calculated (%): CO, 37.3; C₅H₅, 12.3. IR, v/cm⁻¹: 2040 m, 1990 s, 1960 s, 1920 v.s, 1885 v.s, 1415 w, 1020 w, 1005 w, 845 m, 630 s, 555 m.

(Cyclopentadienyldicarbonylmanganese)(µ-diselenide)bis(pentacarbonylchromium), $[CpMn(CO)_2](\mu$ -Se₂)[Cr(CO)₅]₂ (4). A solution of Cr(CO)₆ (0.25 g, 1.13 mmol) in THF (20 mL) was irradiated with UV light in a water-cooled quartz Schlenk vessel for 1.5 h. A green solution of 2 (0.3 g, 0.58 mmol) in THF (20 mL) was added to the resulting orange solution. After stirring for 1 h, the color of the solution changed to gray-green. The solution was concentrated to dryness in vacuo. The green residue was washed with hexane (40 mL) and extracted with diethyl ether (50 mL). The green extract was concentrated to 1/3 of the initial volume. Then hexane (5 mL) was added and the solution was kept at -18 °C. The residue was extracted with CH₂Cl₂ (30 mL), the extract was concentrated to 1/2 of the initial volume, and hexane (4 mL) was added. Storage of both solutions (which are identical according to the results of IR spectroscopy and TLC) at -18 °C for 24 h afforded a darkgreen crystalline precipitate. Rhombic-like prismatic crystals were filtered off and washed with hexane. The total vield of compound 4 was 0.15 g (35.7%) (single crystals). Found (%): C, 28.5; H, 0.2; CO, 46.0*; C₅H₅, 8.0*. C₁₇H₅Cr₂MnO₁₂Se₂. Calculated (%): C, 28.4; H, 0.7; CO, 46.0; C₅H₅, 9.0. IR, v/cm⁻¹: 2068 m, 2048 s, 2032 m, 1940 s, 1912 s, 849 w, 640 s, 560 w, 448 w.

(Cyclopentadienyldicarbonylmanganese)(μ -disulfide)bis(pentacarbonylchromium), [CpMn(CO)₂](μ -S₂)[Cr(CO)₅]₂ (5). The synthesis was carried out as described above for complex 4 starting from a solution of Cr(CO)₆ (0.31 g, 1.44 mmol) in THF (20 mL) and a solution of compound 1 (0.2 g, 0.48 mmol) in THF (20 mL). Dark-green crystals were prepared by recrystallization from a diethyl ether—hexane mixture. Compound 5 was obtained in a yield of 0.08 g (18%). Found (%): CO, 52.0*; C_5H_5 , 11.5*. $C_{17}H_5Cr_2MnO_{12}S_2$. Calculated (%): CO, 53.8; C_5H_5 , 10.4. IR, v/cm⁻¹: 2035 s, 1940 v.s, 1910 v.s, 835 m, 630 s, 555 w, 430 w.

(Cyclopentadienyldicarbonylmanganese)(µ-disulfide)bis(pentacarbonyltungsten), $[CpMn(CO)_2](\mu - S_2)[W(CO)_5]_2$ (6). A solution of W(CO)₆ (0.5 g, 1.42 mmol) in THF (30 mL) was irradiated with UV light in a water-cooled quartz Schlenk vessel for 1.5 h. The resulting orange solution was added dropwise to a green solution of $[CpMn(CO)_2]_2(\mu-S_2)$ (0.3 g, 0.72 mmol) in THF (20 mL) at 15 °C for 1.5 h. The reaction mixture was stirred for 1 h and the solvent was removed in vacuo. The green residue was washed with hexane (40 mL) and extracted with CH_2Cl_2 (20 mL). The extract was concentrated to 1/3 of the initial volume, hexane (5 mL) was added, and the solution was kept at -18 °C to obtain rhombic green crystals. The yield of compound 6 was 0.06 g (10%). Found (%): C, 23.56; S, 6.53; CO*, 37.5; $C_5H_5^*$, 8.0. $C_{17}H_5MnO_{12}S_2W_2$. Calculated (%): C, 23.0; S, 7.2; CO, 37.8; C₅H₅, 7.3. IR, v/cm⁻¹: 2055 s, 2040 m, 1930 s, 1900 v.s, 830 w, 665 w.

(Cyclopentadienyldicarbonylmanganese) (μ -diselenide)bis(pentacarbonyltungsten), [CpMn(CO)₂](μ -Se₂)[W(CO)₅]₂ (7). The synthesis was carried out analogously to that described above for complex **6** starting from a solution of W(CO)₆ (0.41 g, 1.17 mmol) in THF (30 mL) and a solution of compound **2** (0.3 g, 0.58 mmol) in THF (20 mL). Rhombic-like dark-green crystals were prepared by recrystallization from a dichloromethane—hexane mixture. The yield of compound **7** was 0.07 g (15%). Found (%): C, 21.69; (CO + C₅H₅)*, 40.3. C₁₇H₅MnO₁₂Se₂W₂. Calculated (%): C, 20.8; (CO + C₅H₅) 40.8. IR, v/cm⁻¹: 2005 s, 1980 s, 1880 v.s, 1855 v.s, 1370 w, 1000 w, 880 w, 820 w, 785 m, 510 s.

(Cyclopentadienyldicarbonylmanganese)(µ-diselenide)(pentacarbonylchromium)(pentacarbonyltungsten), $[CpMn(CO)_2](\mu-Se_2)[Cr(CO)_5][W(CO)_5]$ (8). A solution of W(CO)₆ (0.2 g, 0.57 mmol) in THF 30 mL was irradiated with UV light in a quartz Schlenk vessel for 3 h. The resulting yellowbrown solution was added dropwise to a lilac-colored solution of compound 3 (0.24 g, 0.45 mmol) in THF (20 mL) with cooling in an ice bath at 0 °C for 2 h. The dark-yellow-brown reaction mixture was stirred for 1 h and then concentrated to dryness in vacuo. The dark-green residue was washed with hexane (30 mL) and extracted with CH₂Cl₂ (30 mL). The vellowish-green extract was filtered through a SiO₂ layer and concentrated to 1/3 of the initial volume. Then hexane (18 mL) was added and the solution was kept at -18 °C for 24 h. The rhombic-like darkgreen crystals that precipitated were used for X-ray diffraction analysis. The yield of compound 8 was 0.11 g (23%). Found (%): C, 24.07; CO, 39.5*; C₅H₅, 7.6*. C₁₇H₅Se₂CrMnO₁₂W. Calculated (%): C, 24.02; CO, 39.5; C₅H₅, 7.6. IR, v/cm⁻¹: 2040 s, 2015 s, 1930 v.s, 1905 v.s, 1610 w, 820 w, 580 s, 500 m.

X-ray diffraction analysis. The crystallographic data, details of X-ray diffraction study, and characteristics of the structure refinement of compounds **3**, **4**, **6**, and **8** are given in Table 1. The structures were solved by direct methods and refined by the fullmatrix least-square method with anisotropic and isotropic thermal parameters for nonhydrogen and H atoms, respectively. All calculations were carried out with the use of the SHELXTL PLUS 5 program package.²¹ The principal geometric parameters for the structures of **3**, **4**, **6**, and **8** are given in Tables 2 and 3. The atomic coordinates and thermal parameters were deposited with the Cambridge Structural Database: CCDC

^{*} Hereinafter, the DSC data are marked with asterisks.

215210 (**3**), CCDC 215211 (**4**), CCDC 215212 (**6**), and CCDC 215213 (**8**).

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