Synthesis and Properties of the Open Clusters $(L_nM)_3\mu_3$-E (L_nM = η^5-CpMo/W$(CO)_3$, $Mn(CO)_5$; E = P, As, Sb, Bi and V)

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Abstract

The open clusters $[Cp(CO)_3M]_{3-n}ECl_n$ (M = Mo, W; E = P: n = 0–2; E = V: n = 0) and $[(CO)_5Mn]_{3-n}E_n$ (E = As: n = 0, 2; E = Sb, Bi: n = 0) have been prepared by salt metathesis from ECl_3 and the carbonylmetalate precursors. The complexes $[Cp(CO)_3M]_3\mu_3$-P react with phosphines PR_3 [PPh_3, $CH_2(PPh_2)_2$, Ph_2P–PPh_2] to form $[Cp(CO)_2R_3PM]_2(\mu_3\text{-E})M(CO)_2Cp$. Thermolabile $[(CO)_5Mn]_3\mu_3$-As is converted into $[(CO)_5Mn]_2(\mu_3\text{-As})Mn(CO)_4$. The compounds have been characterized by IR, ^{31}P and ^{55}Mn NMR. For $[(CO)_5Mn]_3\mu_3$-E, the normal polarizability dependence of $\delta(^{55}Mn)$ (an increase of shielding in the order E = As, Sb, Bi) has been established.

Introduction

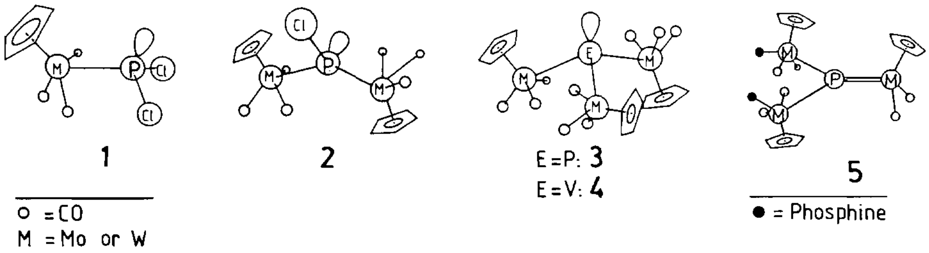
The isolobal analogy between the methyl radical $\cdot CH_3$ and metal carbonyl fragments ML_n such as CpMo/W$(CO)_3$ (d^5) or $Mn(CO)_5$ (d^7) suggests an analogy of the chemistry of $E^{15}(CH_3)_3$ and $E^{15}(L_nM)_3$, where E^{15} is a group 15 element. We shall refer to this type of compound as *open clusters* to indicate that there is no bonding interaction between the transition metals. While a large number of closed clusters of composition $E^{15}(L_mM')_3$ exists [1], the number of open clusters with single bonds between transition metal and a bare main group element is scarce [2]. The reason for this lack is (i) the consistently close contact between the electron clouds of the metals, favouring metal–metal interaction [3] and (ii) the tendency of vacant metal orbitals to interact with the lone pair on phosphorus, arsenic etc. This latter behaviour is being documented by the existence of many oligonuclear complexes between carbonyl transition metal fragments and sp^2 hybridized phosphorus or arsenic [4–6]. Among the few known open clusters are the bismuth compounds [7] $[(CO)_4Co]_3\mu_3$-Bi [3], $[(CO)_5Mn]_3\mu_3$-Bi [8] and $[Cp(CO)_2Fe]_3\mu_3$-Bi [9], while the planar indium and thallium complexes $(L_nM)_3\mu_3\text{-}E^{13}$ [10] differ from the group 15 derivatives in that they lack the lone pair.

Based on preliminary work on $[Cp(CO)_3Mo]_3\mu_3$-P [11], we wish now to report on a systematic study into this family of complexes. We have complemented our study by including a few investigations with vanadium as the E element. Vanadium exhibits a chemical similarity to phosphorus in several aspects.

Results and Discussion

$[Cp(CO)_3M]_{3-n}ECl_n$

Salt metathesis between $K[M(CO)_3Cp]$ and PCl_3 at dry-ice temperature yields, depending on the molar ratio of the reactants, the complexes $Cp(CO)_3MPCl_2$ (M = Mo: 1a, M = W: 1b), $[Cp(CO)_3M]_2\mu$-PCl (2a, 2b) and $[Cp(CO)_3M]_3\mu_3$-P (3a, 3b), Scheme 1. The



Scheme 1.

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complexes **3**, also prepared by reacting **2** with K[M(CO)$_3$Cp], can be isolated and are stable at room temperature, i.e. they are not subject to CO elimination, aggregation, or formation of a metal–phosphorus double bond as described, *inter alia*, for Cp(CO)$_3$Mo–PMe$_2$ [12]. Isolation of the partially metalated compounds in the pure form is not possible, owing to equilibration reactions of the kind described by eqns. (1) and (2).

$$\underset{\mathbf{1}}{2\mathrm{Cp(CO)_3M\text{-}PCl_2}} \rightleftarrows \underset{\mathbf{2}}{[\mathrm{Cp(CO)_3M}]_2\mu\text{-}\mathrm{PCl}} + \mathrm{PCl_3} \qquad (1)$$

$$\underset{\mathbf{2}}{2[\mathrm{Cp(CO)_3M}]_3\mu_3\text{-}\mathrm{P}} + \mathrm{PCl_3} \rightleftarrows \underset{\mathbf{3}}{3[\mathrm{Cp(CO)_3M}]_2\mu\text{-}\mathrm{PCl}} \qquad (2)$$

Spectroscopic data are collected in Table 1. The corresponding reaction with the anionic chromium compound [Cr(CO)$_3$Cp]$^-$ quantitatively yields the oxidation product [CpCr(CO)$_3$]$_2$. The dimeric, neutral complexes [CpM(CO)$_3$]$_2$ (M = Mo, W) are obtained as K[M(CO)$_3$Cp] when reacted with AsCl$_3$, SbCl$_3$ or BiCl$_3$. Hence, [Cp(CO)$_3$Mo]$_2\mu$-BiCl and [Cp(CO)$_3$Mo]$_3\mu_3$-Bi, which have been mentioned in the literature [7, 13], cannot be obtained along this route. VCl$_3$ on the other hand yields the open metal clusters [Cp(CO)$_3$M]$_3\mu_3$-V (**4a**, **4b**) with IR characteristics in the ν(CO) region similar to those of the phosphorus analogues (Table 1).

The ^{31}P NMR spectra show an increase of ^{31}P shielding in the order PCl$_3$, **1**, **2**, **3**, i.e. with increasing metalation of phosphorus. This pattern is very much reminiscent of the increase of shielding observed with increasing alkylation. This analogy in the behaviour of ^{31}P shielding needs some comment. The L$_n$M fragment is a very large substituent which should give rise to a large deshielding contribution due to steric effects, similar to those observed with bulky alkyl substituents on phosphorus [PCy$_3$, P(iBu)$_3$] [14]. In the metalaphosphines, this sterically induced deshielding effect is, however, largely overbalanced by an electronic shielding effect, namely the ability of the metal centre to act as a π donating source for phosphorus–d orbitals. The $\delta(^{31}\mathrm{P})$ values of **3**, along with the IR and ^{1}H NMR patterns (singlets at 5.86 (**3a**) and 5.82 (**3b**) ppm, are strong evidence for the trigonal pyramidal structure (sp^3 hybridized P) shown in Scheme 1. In P–M clusters containing sp^2 phosphorus, the ^{31}P nucleus is substantially deshielded (compare, for example, [Cr(CO)$_5$]$_2$(μ_3-P)W(CO)$_2$Cp: $\delta(^{31}\mathrm{P}) = +945$ ppm [6]).

The complexes **3** do not undergo temperature- or light-induced CO-elimination. However, in the presence of phosphines (PPh$_3$, P$_2$Ph$_4$, Ph$_2$PCH$_2$PPh$_2$ (dppm)) and at room temperature, CO is partially replaced and the complexes [Cp(CO)$_2$PR$_3$M]$_2\mu_3$-P=M(CO)$_2$Cp (M = Mo: **5a**, M = W: **5b**; Scheme 1; data in Table 1) are formed. In the case of PR$_3$ = PPh$_3$ and dppm, two signals (dppm: two sets of signals corresponding to coordinated and uncoordinated P) are observed which may reflect geometrical isomers. CO substitution beyond that represented by the complexes **5** cannot be achieved.

[(CO)$_5$Mn]$_3\mu_3$-E

Reaction between K[Mn(CO)$_5$] and PCl$_3$ does not lead to defined products. With AsCl$_3$, SbCl$_3$ and

TABLE 1. IR and ^{31}P NMR data of [Cp(CO)$_3$M]$_{3-n}$ECl$_n$ and related complexes[a]

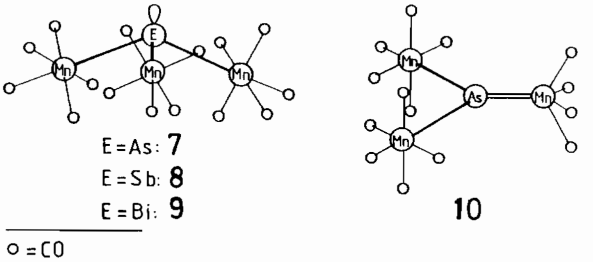
Complex	ν(CO) [b] (cm^{-1})			$\delta(^{31}\mathrm{P})/J(\mathrm{PX})$ (ppm)/(Hz)
Cp(CO)$_3$MoPCl$_2$ (**1a**)	2035	1960	1945	+132
Cp(CO)$_3$WPCl$_2$ (**1b**)	2030	1950	1927	+134.2/284[c]
[Cp(CO)$_3$Mo]$_2\mu$-PCl (**2a**)	2050	1965		+60.4
[Cp(CO)$_3$W]$_2\mu$-PCl (**2b**)	2039	1950		+62.2/294[c]
[Cp(CO)$_3$Mo]$_3\mu_3$-P (**3a**)	2055	1965		−40.2
[Cp(CO)$_3$W]$_3\mu_3$-P (**3b**)	2045	1949		−38.0/300[c]
[Cp(CO)$_3$Mo]$_3\mu_3$-V (**4a**)	2030	1950		
[Cp(CO)$_3$W]$_3\mu_3$-V (**4b**)	2027	1945		
[Cp(CO)$_2$PR$_3$M]$_2$(μ-P)M(CO)$_2$Cp (**5**)	1960	1878[d]		
M = Mo, PR$_3$ = PPh$_3$ (**5a**)				+57.8
				+49.8
(Ph$_2$P)$_2$CH$_2$				+40.6, −26.7/65[e]
				+25.6, −28.1/45[e]
Ph$_2$P-PPh$_2$				+64.1, −9.5/87[e]

[a] In THF. [b] Band intensities: **1**: s, sh, vs; **2**, **3**: m, vs(br); **4**: s, vs(br). [c] $J(^{31}\mathrm{P}-^{183}\mathrm{W})$. [d] There are no significant differences in the band positions for M = Mo and W, and for variation of the phosphine ligand. Both bands are rather broad; intensities: vs and s. [e] $J(^{31}\mathrm{P}-^{31}\mathrm{P})$, all signals are doublets. The negative values correspond to the uncoordinated phosphorus.

$BiCl_3$, green solutions of the permetalated complexes $[(CO)_5Mn]_3\mu_3$-E (E = As: **7**, Sb: **8**, Bi: **9**) are obtained at dry-ice temperature. **9**, which is stable at room temperature, has been structurally characterized earlier [8]; for **7** and **8**, which exhibit IR patterns in the ν(CO) region very similar to **9** (Table 2), we assume the same (trigonal pyramidal) structure (Scheme 2). Solutions of **7** and **8** are stable only at low temperature (*vide infra*). Applying a large excess of $AsCl_3$, the monometalated species $(CO)_5MnAsCl_2$ (**6**) can also be identified; the dimetalated complex $[(CO)_5Mn]_2\mu$-AsCl apparently undergoes rapid dismutation to **6** and **7** (eqn. (3)).

$$2[(CO)_5Mn]_2\mu\text{-AsCl} \longrightarrow \underset{\mathbf{7}}{[(CO)_5Mn]_3\mu_3\text{-As}} + \underset{\mathbf{6}}{(CO)_5MnAsCl_2} \qquad (3)$$

The ^{55}Mn NMR spectra of **6**–**9** (Table 2) show resonances typical of the $Mn(CO)_5$ moiety attached to a metal or metalloid fragment (compare the $\delta(^{55}Mn)$ values for $(CO)_5MnE^{14}Z_3$: −1910 to −2530 ppm [15–17]). The increase of shielding in the series **7**, **8**, **9** is in accord with the normal polarizability dependence of metal shielding generally observed for the metals in their low oxidation states (d^n configurations), as the polarizability of the ligand function increases (the electronegativity decreases) [17]. The signals are broad as expected for a nucleus belonging to the medium quadrupole category (nuclear spin 5/2, quadrupole moment = 0.33×10^{-28} m^2) in a non-cubic environment, where relaxation is dominated by the quadrupole mechanism.



Scheme 2.

7 and **8** are thermolabile. The green solutions of these complexes in THF turn to cherry red at temperatures >210 K (**7**) and >240 K (**8**), and 1 CO per molecule is released. The conversion of the green to the red complexes, as monitored by IR, is illustrated in Fig. 1 for the arsenic compound. The typical pattern for the $Mn(CO)_5$ unit is retained; two new ν(CO) bands at lower wave numbers are indicative of the newly arising carbonylmanganese moiety, likely $Mn(CO)_4$ in a complex of composition $[(CO)_5Mn]_2\mu_3$-As=$Mn(CO)_4$ (**10**, Scheme 2). This view is supported by the ^{55}Mn NMR spectrum, which shows a broad band at −2090 ppm (i.e. close to $\delta(^{55}Mn)$ of

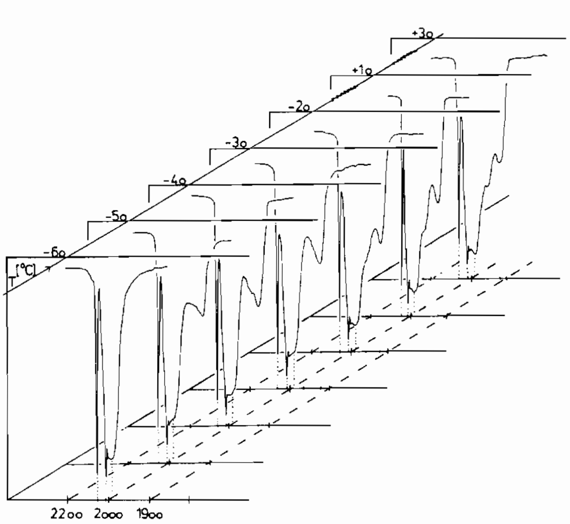


Fig. 1. The conversion of $[(CO)_5Mn]_3\mu_3$-As (**7**) to $[(CO)_5Mn]_2(\mu_3\text{-As})Mn(CO)_4$ (**10**) with increasing temperature, monitored by IR. The spectrum at the lower left corresponds to **7** (punctuated elongations), that at the upper right to **10**.

TABLE 2. IR and ^{55}Mn NMR data of $[(CO)_5Mn]_3\mu_3$-E and related complexes[a]

Complex	ν(CO) [b] (cm^{-1})			$\delta(^{55}Mn)/W_{1/2}$ [c] (ppm)/(Hz)
$(CO)_5MnAsCl_2$ (**6**)	2140	2090	2030	−1940/3200
$[(CO)_5Mn]_3\mu_3$-As (**7**)	2082	2024	1995	−2020/3500
$[(CO)_5Mn]_3\mu_3$-Sb (**8**)	2078	2020	1993	−2230/7700
$[(CO)_5Mn]_3\mu_3$-Bi (**9**)	2070	2015	1990	−2320/1300
$[(CO)_5Mn]_2(\mu\text{-As})Mn(CO)_4$ (**10**)	2070	2015	1990	−2090/2500
		1947	1925	−1976/500

[a] In THF at 195 K (**6**, **7**, **8**) or room temperature (**9** and **10**). [b] Band intensities: s, s, vs(vbr); compare also Fig. 1. [c] Relative to $[MnO_4]^-$. The temperature gradient is c. 0.4 ppm/deg (decrease of shielding with increasing temp.). $W_{1/2}$ is the width of the resonance signal at half-height. The $W_{1/2}$ values are not directly comparable, since linewidths drastically increase with decreasing temperature.

7) and a comparatively sharp resonance at −1976 ppm, in the intensity ratio 2:1. A downfield shift of the manganese resonance is commonly observed on going from the pentacarbonyl to the tetracarbonyl complex [17, 18]. Efforts to isolate the complex have been unsuccessful.

Experimental

General

All operations were carried out in highly purified, absolute solvents under inert gas. Starting materials (ECl_3, $M(CO)_6$, $Mn_2(CO)_{10}$ and phosphines) were obtained from commercial sources, distilled or recrystallized and stored under nitrogen. The following compounds were prepared according to literature procedures: $[Cp(CO)_3M]_2$ [19], $K[CpM(CO)_3]$ and $K[Mn(CO)_5]$ [20]. Silica gel (Merck, 70-230 mesh ASTM) was evacuated for 6 h in high vacuum and pretreated with N_2. Column dimensions: 8 × 12 cm.

IR spectra (Perkin-Elmer 325) were obtained in THF solution in 0.1 mm KBr cuvettes. For low-temperature measurements, a low-temperature cuvette (VLT-2 RIIC, Beckmann, Munich) fitted with Irtran (ZnS) windows was employed; temperature measurements were carried out with a thermocouple. NMR spectra: ^1H: Bruker WP-80, 5 mm diameter vials, THF-d_8. ^{31}P: Bruker WP-80 (32.4 MHz), 10 mm diameter vials, THF/THF-d_8 2/1, standard 85% H_3PO_4. ^{55}Mn: Bruker SWL 3-100 (16 MHz, central magnetic field 1.52 T) equipped with an adapted Varian 4230B (8-16 MHz) probe head, 14 mm diameter tubes, THF; typical measuring parameters: sweep width 10 mT, modulation amplitude 0.1 mT, scan time 2 min, time constant 0.5 s, scan number 250, r.f. field strength 10 μT; standard: saturated aqueous $K[MnO_4]$. Low-temperature ^{55}Mn: Bruker AM 360 (89.3 MHz), THF solutions in 7.5 mm diameter vials fitted into 10 mm tubes containing acetone-d_6 as external lock. $Mn_2(CO)_{10}$ was used as internal standard ($\delta = -2326$ ppm relative to $[MnO_4]^-$). Typical measuring parameters: sweep width 125 kHz, time domaine 1025 K, pulse width 10 μs, relaxation delay 0.5 s, scan number 5000.

Preparation of Complexes

(cf. Tables 1 and 2 for allocation of the numbers.)

1 and **2**: 360 μl (4 mmol) of PCl_3 dissolved in 5 ml of THF were cooled to 195 K and treated with a solution of 1 mmol $K[M(CO)_3Cp]$ in 30 ml of THF. After stirring for 1 h at 195 K, the solution was allowed to warm up to room temperature (r.t.) and the complexes **1** were obtained as yellow (**1a**) or orange (**1b**) powdery products. Dropwise addition (dry-ice temperature) of 20 ml of a THF solution containing 1 mmol $K[M(CO)_3Cp]$ to **1** yielded orange–red solutions of the complexes **2**, which were stored at 195 K and directly used for IR and NMR measurements.

3 and **4**: A solution of 1.02 mmol $K[Cp(CO)_3M]$ in 5 ml of THF, pre-cooled to 195 K and kept in brown Duran glassware, was treated with 30 μl (0.33 mmol) of PCl_3 dissolved in 1 ml of THF. After stirring for 30 min, the dark red solution was warmed up to r.t. and stirred again for half an hour. The THF was then removed *in vacuo*, the residue redissolved in 2 ml of THF and chromatographed on silica gel with THF/pentane 1/1 to yield spectroscopically pure **3**.

4 was prepared accordingly from $K[M(CO)_3Cp]$ and 52.5 mg (0.33 mmol) VCl_3 at 273 K. After evaporation of the THF, the residue was treated with 5 ml of benzene and filtered to give red solutions of spectroscopically pure **4a** and **4b**.

5: 0.33 mmol freshly prepared **1** were dissolved in 30 ml of THF, treated with 2 mmol phosphine (PPh_3, P_2Ph_4 or dppm) and stirred for 2 days at r.t. The solutions were evaporated to dryness, washed with two 20 ml portions of pentane, redissolved in 5 ml of THF and chromatographed on silica gel (elutant: THF/pentane 1/1) to yield the pure complexes.

6 was prepared as described for **1** from 1 mmol $K[Mn(CO)_5]$ and 360 μl (4 mmol) of $AsCl_3$. The solution was kept at 195 K.

7, **8** and **9**: 1.1 mmol $K[Mn(CO)_5]$ dissolved in 2 ml of THF was treated (at 195 K: **7**, **8**; at 240 K: **9**) with 0.36 mmol ECl_3 to yield greenish solutions. These were stirred for half an hour and kept, in the case of thermolabile **7** and **8**, at 195 K. In the case of **9**, the solution was brought to r.t., the THF evaporated *in vacuo*, the residue washed with three 15 ml portions of diethyl ether (these washings were discarded) and finally redissolved in 5 ml of THF. Column chromatography on silica gel with THF/pentane as elutant yielded a green–brown fraction of **9**, which, after evaporation to dryness, was recrystallized from CH_2Cl_2/ether at 245 K. Spectroscopic data were identical to those of an authentic sample of **9** [8].

A cherry red solution of **10** forms as a solution of **7** in THF is allowed to warm up to r.t.

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