Synthesis and Characterisation of Novel Complexes Containing Group 15 Elements and Their Potential Use as Molecular Precursors for the Formation of Transition Metal Pnictides

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Dedicated to Prof. Dr. M. Veith on the occasion of his 60th birthday

The reaction of $[\{W(CO)_5\}_2PCl]$ with $K[Co(CO)_4]$ yields the novel compounds $[\{W(CO)_4Co_2(CO)_6\}\{\mu_3\text{-}PW(CO)_5\}_2]$ (**3**) and $[\{(CO)_4WCo_3(CO)_6\}\{\mu_3\text{-}PW(CO)_5\}_3]$ (**4**) along with known derivatives $[Co_2(CO)_6\{\mu,\eta^2\text{-}PW(CO)_5\}_2]$ (**1**) and $[Co_3(CO)_9\{\mu_3\text{-}PW(CO)_5\}]$ (**2**). The complex $[\{W_2(CO)_8(\mu\text{-}CO)\}\{\mu,\eta^2{:}\eta^1{:}\eta^1\text{-}PW(CO)_5\}_2)]$ (**5**) was synthesised by treating $Na_2[W_2(CO)_{10}]$ with PBr_3. Reaction of $K[Mn(CO)_5]$ with $SbCl_3$ affords $[Sb\{Mn(CO)_5\}_3]$ (**6**) in high yields. The spectroscopic and structural characterisation of the novel products is discussed, as well as the thermolytic behaviour of **2**, **3** and **6** for the potential formation of novel phases of transition metal pnictides.

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Introduction

One of our research interests is focused on the synthesis of P_n ligand complexes[1] starting from P_1-containing compounds. The use of $[(CO)_5CrPCl_3]$ or L_nMPCl_2 in the reaction with transition-metal metalates leads to novel as well as known P_n ligand ($n \geq 2$) complexes under special conditions in low-temperature reactions.[2] However, the use of complexes of the type $[(L_nM)_2PX]$ $[L_nM = M(CO)_5; M = Cr, W]$ in these reactions gives the formation of only P_2-ligand complexes that are probably formed via an intermediate of the composition $[L_nM{\equiv}P{\rightarrow}M(CO)_5]$.[3]

In continuation of these investigations we have focussed our interests particularly on products containing, besides the transition metal and the group 15 element ligand, only CO. The general interest in this type of complex is the challenge of their use as molecular precursors for the generation of novel, metastable phases[4] of transition metal pnictides by eliminating CO ligands quantitatively at moderate temperatures and ending up with a solid of a given non-metal/metal composition. Transition metal pnictides were usually obtained by high-temperature routes.[5] This idea was supported by a previous report by Gladfelter et al. on the use of $[\{Co(CO)_3\}_2(\mu,\eta^2\text{-}E_2)]$ (E = P, As) as molecular precursors for the generation of CoE layers by CVD techniques.[6]

We describe here the synthesis of novel E_1 ligand complexes starting from different E_1 sources and the first investigations of the thermolysis behaviour of selected products under high vacuum as well as inert gas atmosphere conditions with MS control.

Results and Discussion

Looking into the details of existing Co/P complexes one example for these potential precursor compounds is $[Co_2(CO)_6(\mu,\eta^2\text{-}P_2\{W(CO)_5\}_2)]$ (**1**), which was described by Huttner et al. as a product of the reaction between the chlorophosphinidene complex $[\{W(CO)_5\}_2PCl]$ and $K[Co(CO)_4]$.[7] They observed **1** as the only product if the reaction is carried out at room temperature. In agreement with our general reaction methodology we found that, by carrying out this reaction at low temperature, it is possible to isolate three further products.

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Reaction between the chlorophosphinidene complex [{W(CO)$_5$}$_2$PCl] and K[Co(CO)$_4$] in THF at −78 °C yields the novel products **3** and **4** as well as the previously described complexes **1**[7] and **2** [Equation (1)].[8] Vahrenkamp has obtained the latter product from the reaction of [(CO)$_5$WPH$_3$] with Co$_2$(CO)$_8$.[8] Complexes **1** and **2** can also be obtained by the reaction of [Cl$_3$PW(CO)$_5$] with K[Co(CO)$_4$] in THF at −78 °C [Equation (2)]. Column chromatographic workup was necessary for the separation of the products, leading to reduced yields.

(1)
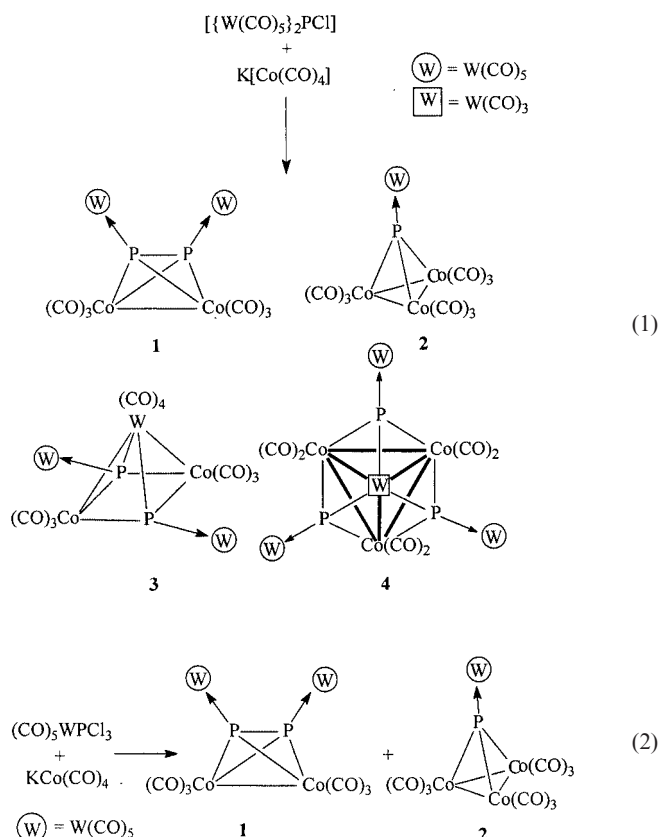
Other P$_1$ starting materials are the non-coordinated phosphorus trihalides. We recently found that the reaction of PCl$_3$ with Na$_2$[W$_2$(CO)$_{10}$] at ambient temperature leads to the formation of [{W(CO)$_5$}$_2$PCl], [W(CO)$_5$PCl$_3$] and [(CO)$_5$W(μ,η^2:η^1:η^1-P$_2$Cl$_2${W(CO)$_5$}$_2$)], the latter complex containing a novel ClP=PCl ligand.[9] We have found that with a different stoichiometric ratio (1:1.5) the reaction of PBr$_3$ with Na$_2$[W$_2$(CO)$_{10}$] in toluene results in the formation of **5** [Equation (3)]. Complex **5** is the first homoleptic complex of phosphorus and carbonyltungsten.

(3)
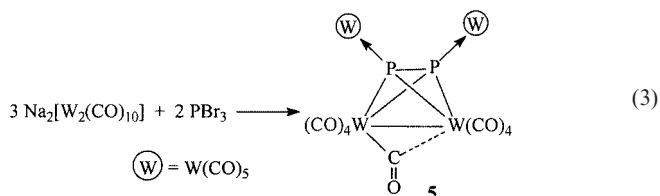
Furthermore, the reaction of SbCl$_3$ with K[Mn(CO)$_5$] in THF at low temperatures leads to the homoleptic metallo-stibane **6** [Equation (4)], which was obtained in 52% yield. Complex **6** has been described previously in the literature, but the authors only characterised it at low temperature and found that the compound decomposes at room temperature.[10] However, by performing the workup of the reaction mixture very rapidly at room temperature, we were able to isolate **6** in high yields as a crystalline solid that can be stored under inert gas for months at room temperature without decomposition.

(4)
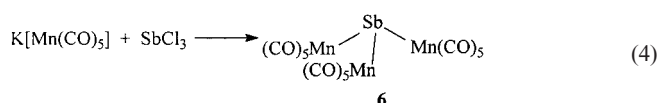
All compounds were characterised by IR, and ^{31}P NMR spectroscopy and mass spectrometry. The data for **1** and **2** were found to be identical with the values described in the literature. An X-ray structure analysis was carried out for **2**, which, due to a lower measurement temperature, resulted in slightly better *R* values than the previously described measurement[8] and is therefore included in this paper.

Complex **3** forms red crystals and compound **4** forms black crystals that are slightly soluble in hexane and readily soluble in toluene and CH$_2$Cl$_2$. The black crystals of **5** are only slightly soluble in toluene and CH$_2$Cl$_2$. The black, crystalline complex **6** is soluble in hydrocarbons and other organic solvents, but solutions must be kept at low temperature to avoid decomposition. The IR spectra of the products show various absorptions in the region of terminal carbonyl ligands. In the mass spectra of **3**, **4** and **5** only fragments were observed, whereas for **6** the appropriate molecular-ion peak and peaks for subsequent loss of all CO ligands were detected.

The ^{31}P NMR spectrum of **3** shows a broad signal at $\delta = -40$ ppm which is probably due to the quadrupole moment of the ^{59}Co nuclei. Compound **4** reveals a singlet at $\delta = -135$ ppm in the ^{31}P NMR spectrum, which shows two tungsten satellites ($J_{P,W} = 87.2$ and 131.2 Hz). The larger coupling constant can be assigned to the coordinative bonding to the [W(CO)$_5$] moiety, while the smaller one reflects the coupling to the central cluster atom W4 (see below). This assignment is supported by the intensity ratio of the satellites, which is almost 3:1. The ^{31}P NMR spectrum of **5** shows a singlet at $\delta = -123$ ppm, which exhibits only one pair of tungsten satellites ($^1J_{P,W} = 116$ Hz), which can be assigned to the coupling to the coordinatively bound [W(CO)$_5$] moieties. The expected second pair of satellites should possess a smaller coupling constant and therefore seems to be hidden in the broadening of the signal.

The novel products were also characterized by single-crystal X-ray diffraction. The molecular structure of **3** (Figure 1) reveals a *cyclo*-Co$_2$P$_2$ moiety — the torsion angle Co−P−P−Co is 16.52(7)° — that is capped by a W(CO)$_4$ group. This *nido* structure is expected for this 14-skeletal -
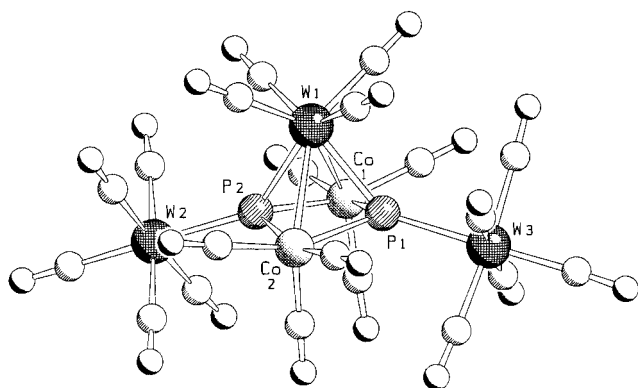
Figure 1. Molecular structure of **3** in the crystal; selected bond lengths [Å] and angles [°]: W1−P1 2.471(3), W2−P1 2.430(3), W2−P2 2.439(3), W2−Co1 2.787(2), W2−Co1 2.807(2), W3−P2 2.471(3), Co1−P1 2.271(3), Co1−P2 2.266(3), Co2−P1 2.261(3), Co2−P2 2.263(3); P1−W2−P2 73.19(9), P1−W2−Co1 51.06(7), P2−W2−Co1 50.86(7), P1−W2−Co2 50.54(7), P2−W2−Co2 50.53(7), Co1−W2−Co2 75.98(5), P1−Co1−P2 79.53(11), P1−Co1−W2 56.31(7), P2−Co1−W2 56.59(7), P1−Co2−P2 79.81(11), P1−Co2−W2 56.07(7), P2−Co2−W2 56.29(7), Co1−P1−Co2 98.87(12), Co1−P1−W2 72.63(8), Co2−P1−W2 73.40(9), Co1−P2−Co2 98.96(12), Co1−P2−W2 72.55(9), Co2−P1−W2 73.19(8)

Figure 2. Molecular structure of **4** in the crystal; selected bond lengths [Å] and angles [°]: W1−P1 2.406(6), W2−P2 2.407(7), W3−P3 2.412(7), W4−P1 2.496(6), W4−P2 2.467(7), W4−P3 2.442(6), W4−Co1 2.638(3), W4−Co2 2.695(3), W4−Co3 2.652(3), Co1−P1 2.229(7), Co1−P3 2.197(7), Co2−P1 2.189(7), Co2−P2 2.186(7), Co3−P2 2.264(7), Co3−P3 2.200(7), Co1−Co2 2.549(5), Co1−Co3 2.580(5), Co2−Co3 2.545(5); Co1−W4−Co2 57.10(10), Co1−W4−Co3 58.38(10), Co2−W4−Co3 56.85(10), Co2−Co1−Co3 59.49(13), Co2−Co1−W4 62.56(10), Co3−Co1−W4 61.07(10), Co1−Co2−Co3 60.86(13), Co1−Co2−W4 60.34(10), Co3−Co2−W4 60.73(10), Co1−Co3−Co2 59.65(13), Co1−Co3−W4 60.55(10), Co2−Co3−W4 62.42(10)

electron compound. The lone pair of each phosphorus atom is further coordinated to a [W(CO)$_5$] fragment. The carbonyl ligands of the atom W1 are in eclipsed positions to the ring atoms resulting in a quadratic antiprismatic coordination pattern around the atom W1, which is unusual for tungsten. The same structural arrangement has been found for the capping Cr atom in the isostructural complex [(CO)$_4$CrCo$_2$(CO)$_6${μ$_3$-AsCr(CO)$_5$}$_2$].[11] The average Co−P bond length (2.265 Å) is within the usual range. The bond lengths from phosphorus to the capping tungsten atom are 2.430(3) and 2.439(3) Å, respectively. They are surprisingly short in comparison to [W(CO)$_4${η^4-P$_4$⟨W(CO)$_5$⟩$_4$}],[12] where the average W−P distance within the cluster core is found to be 2.604 Å. In contrast, the Co−W bond lengths with [2.807(2) and 2.787(2) Å] are unusually long compared, for example, with the bond lengths in the cluster [{Co(CO)$_2$(μ-CO)}$_3$W(CO)$_2$Cp] [2.715 Å (av)].[13]

The molecular structure of **4** (Figure 2) shows a distorted tetrahedral WCo$_3$ cluster core (angles between 58° and 62°), in which each of the Co$_2$W faces is bridged by one phosphorus atom. The lone pairs of these three P atoms are additionally coordinated to [W(CO)$_5$] fragments. This structure is in agreement with the EAN rule,[14] which predicts a tetrahedral geometry for a 60-valence-electron cluster. A comparison of the average Co−Co bond lengths of **4** with those of the compound [Co$_4$(μ$_3$-PPh)$_4$(PPh$_3$)$_4$],[15] which also possesses phosphorus-capped Co$_3$ faces, shows similar values (2.558 Å vs. 2.578 Å). However, the Co−W bond lengths of **4** [2.662 Å (av)] are slightly shorter than in [{Co(CO)$_2$(μ-CO)}$_3$W(CO)$_2$Cp][13] [2.715 Å (av)], which has a similar cluster core. This longer Co−W bond length is attributed to the absence of capping P atoms in the latter compound.
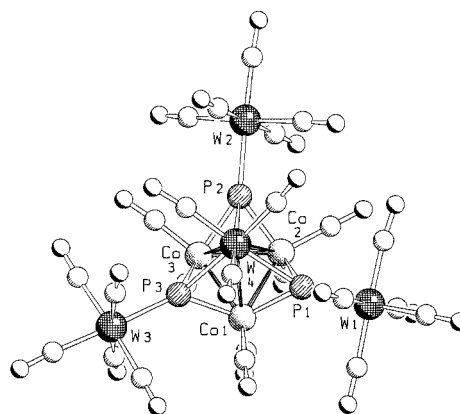
The central structural feature of the molecular structure of **5** (Figure 3) is a distorted tetrahedral W$_2$P$_2$ core, where the lone pairs of each phosphorus atom coordinate to a [W(CO)$_5$] moiety. The two phosphorus atoms are shifted significantly towards the atom W2 [W1−P1 2.610(2), W1−P2 2.636(2), W2−P1 2.500(2), W2−P2 2.514(2) Å]. This asymmetry is electronically compensated for by the semibridging CO ligand between the two W atoms (W1−C5 2.086(6) Å, W2···C5 2.750 Å). The P1−P2 distance [2.062(2) Å] is slightly shorter than in the tetrahedral complexes [{Cp(CO)$_2$W}$_2$(μ,η^2-P$_2$)] [2.104(4) Å][16] and
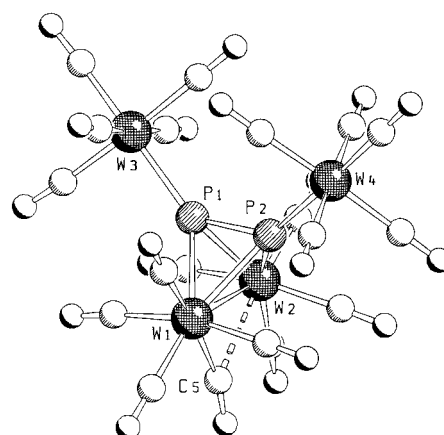
Figure 3. Molecular structure of **5** in the crystal; selected bond lengths [Å] and angles [°]: W1−W1 3.0819(6), W1−P1 2.610(2), W1−P2 2.636(2), W2−P1 2.500(2), W2−P2 2.514(2), W3−P1 2.484(2), W4−P2 2.477(2), P1−P2 2.062(2), W1−C5 2.086(6), W2···C5 2.750; P1−W1−P2 46.29(5), P1−W1−W2 51.29(4), P2−W1−W2 51.45(4), P1−W2−P2 48.58(5), P1−W2−W1 54.57(4), P2−W2−W1 55.08(4), P2−P1−W1 67.50(7), P2−P1−W2 66.07(7), P2−P1−W3 137.00(9), P1−P2−W1 66.20(6), P1−P2−W2 65.36(7), P1−P2−W4 133.70(9)

[{Cp*(CO)$_2$W}$_2$(μ,η^2:η^1-P$_2$){W(CO)$_5$}] [2.092(4) Å].[17] The W1−W2 bond length [3.082(1) Å] is similar to that in the latter complex [3.092(1) Å].

The X-ray structure analysis of **6** reveals two independent molecules in the unit cell with similar bond lengths and angles (Figure 4 shows molecule A). The central antimony atom is surrounded by three Mn(CO)$_5$ moieties and adopts a trigonal pyramidal geometry with Mn−Sb−Mn angles ranging from 107.91(2)° to 111.00(2)°. The average Mn−Sb bond length [2.808(1) Å] is significantly longer than in other complexes with a similar bonding situation (cf. [(F$_3$C)$_2$SbMn(CO)$_5$] 2.663(1) Å[18]); these long bonds reflect the steric crowding of the antimony atom by the bulky pentacarbonylmanganese groups, which themselves show a slightly distorted octahedral coordination.
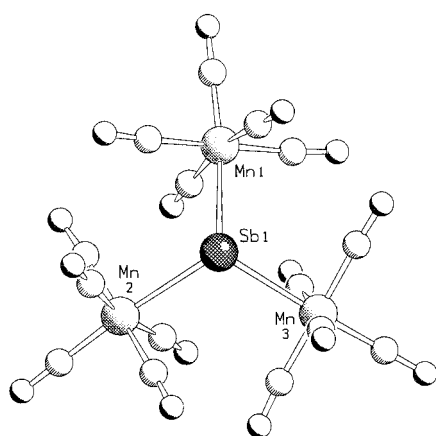

Figure 4. Molecular structure of **6** in the crystal (molecule A); selected bond lengths [Å] and angles [°]: Sb1−Mn1 2.8135(8), Sb1−Mn2 2.8027(7), Sb1−Mn3 2.7928(8); Mn1−Sb1−Mn2 110.02(2), Mn1−Sb1−Mn3 108.22(2), Mn2−Sb1−Mn3 109.71(2)

Thermogravimetric measurements were carried out on the clusters **2**, **3** and **6** under high vacuum as well as on **3** and **6** under inert gas flow conditions, and were combined with MS control of the volatile products in the temperature range up to 1000 °C. Thermogravimetric analysis of **3** under vacuum conditions shows that it decomposes in two steps: between 90 and 130 °C with a mass loss of about 39%, and between 540 and 640 °C with a further mass loss of about 11%, both of which are accompanied by W(CO)$_6$ elimination.[19] The second step also occurs with elimination of Co- and P-containing moieties.

The thermogravimetric analysis of **2** in high vacuum shows a two-step decomposition in the temperature range of 65 to 165 °C (first step 65−134 °C, second step 134−165 °C), with a mass loss of about 62% due to the elimination of CO and W(CO)$_6$,(Figure 5)[19] that leaves a CO-containing sample with the formal composition Co$_3$P(CO)$_3$.[20] In contrast, complex **6** decomposes by Mn(CO)$_n$ elimination in two steps (between 65−120 °C and 120−180 °C) with an overall mass loss of about 67% that leaves a nearly C-free sample with the composition Mn$_2$Sb.[21] However, if the thermogravimetric experiments are carried out under a flow

of an inert gas (Ar or He) there is a significant change in the decomposition behaviour, which is characterised mainly by CO elimination. For **2** the only detectable volatile material is CO, leading to a mass loss of about 50% in the temperature range 120−180 °C (Figure 5). For **6**, CO and Mn(CO)$_n$ fragments are eliminated in two steps between 100 °C and 200 °C, and this is accompanied by a weight loss of 56%. The remaining amorphous solids have the compositions Co$_3$WP and SbMn$_{2.6}$, respectively,[22] and are very sensitive to oxygen.
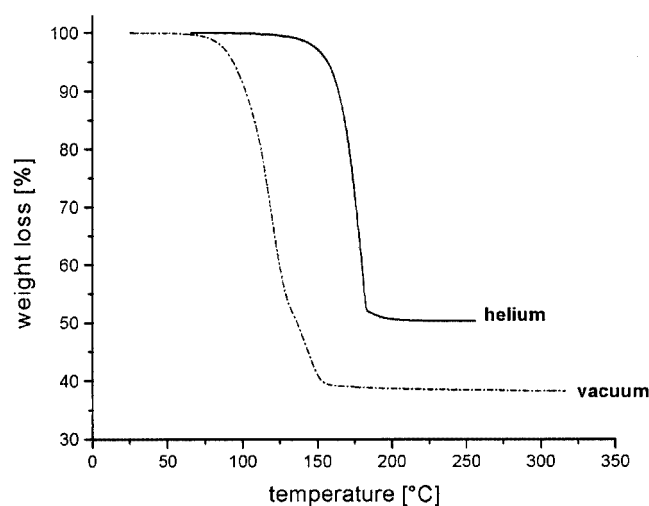

Figure 5. Thermogravimetric analysis of **2** in helium gas (solid line) and in vacuo (dashed line)

Initial attempts to obtain crystalline materials suitable for powder XRD characterisation were carried out by heating the remaining solids at 550 °C for 500 h. While no novel phase could be observed for the compound generated from **2**, reflections of a hexagonal phase could be indexed for the solid originating from **6**, with $a = b = 5.139$, $c = 13.017$ Å; and $V = 297.7$ Å^3.[23]

Conclusion

Our results have shown that novel cluster complexes of naked group-15 elements can be obtained by reacting pnicogen halide complexes with transition metal metalates at low temperature. These cluster compounds with naked group-15 elements and CO as the only ligands can be used as potential precursors for the generation of novel solids. Their decomposition occurs at relatively low temperatures of up to 200 °C, and the composition of the remaining amorphous solids is partially controlled by the composition of the metals of the employed cluster core. Whereas the thermolysis under high-vacuum conditions leads partially to the elimination of CO and metalcarbonyl fragments, the better way to obtain non-metal/metal materials from single-source precursors is to carry out the thermal decomposition under a flow of inert gas. There are some indications that the presence of bonds between the transition metals in the

molecular precursor compound is one precondition for the exclusive elimination of CO. Thus, for cluster **2** only CO elimination occurs under the latter conditions, whereas the Sb-linked complex **6**, which possesses only Sb−Mn bonds loses $Mn(CO)_n$ units. Furthermore, the stability and the vapour pressure of the eliminated moieties also influence the decomposition behaviour.

The preliminary results presented in this paper show that the use of CO-containing molecular precursors for the preparation of novel transition metal pnictides seems to be of substantial potential. Nevertheless, further research is necessary to obtain more information about the structure and the properties of these novel compounds.

Experimental Section

General Remarks: All manipulations were performed under dry nitrogen using standard glove-box and Schlenk techniques. All solvents were freshly distilled from appropriate drying reagents immediately prior to use. IR spectra were obtained with a Bruker IFS280 spectrometer, and ^{31}P NMR spectra were recorded at room temperature with a Bruker AMX 300 spectrometer (^{31}P: 121.49 MHz) using 85% H_3PO_4 as an external standard; mass spectra were recorded with a Varian MAT-711 spectrometer. [{W(CO)$_5$}$_2$PCl],[7] [Cl$_3$PW(CO)$_5$][24] and K[Co(CO)$_4$][25] were synthesised according to literature procedures.

Reaction of [{W(CO)$_5$}$_2$PCl] with K[Co(CO)$_4$]: K[Co(CO)$_4$] (0.33 g, 1.55 mmol) was added to a solution of [{W(CO)$_5$}$_2$PCl] (1.11 g, 1.55 mmol) in 20 mL of THF at −78 °C. After stirring for 30 min, the mixture was allowed to reach room temperature within 1 h and was stirred for an additional 1 h. The reaction mixture was filtered through Celite, 5 mL of silica gel was added and all solvents were removed in vacuo. Products **1**, **2**, **3** and **4** were separated by column chromatography on silica gel.

[Co$_2$(CO)$_6$(μ,η²-P$_2${W(CO)$_5$}$_2$)] (1): After elution of a purple fraction with hexane/toluene (10:1) crystals of **1** were obtained by recrystallisation from CH_2Cl_2 (0.11 g, 15% based on P). The analytical data agreed with the literature values.[7]

[Co$_3$(CO)$_9${μ$_3$-P{W(CO)$_5$}}] (2): This compound was eluted with hexane as a yellowish-brown fraction and obtained as brown platelets after recrystallisation from CH_2Cl_2 (0.036 g, 3% based on P). $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 41.0 ppm (s, br). The analytical data agreed with the literature values.[8]

[(CO)$_4$WCo$_2$(CO)$_6${μ$_3$-PW(CO)$_5$}$_2$] (3): Elution of a brown fraction with hexane/toluene (5:1) and recrystallisation from CH_2Cl_2 yielded **3** as black, metallic crystals (0.07 g, 7% based on P). IR (KBr): ν(CO) = 2090 (sh), 2064 (s, br), 2046 (sh), 2014 (w), 2007 (w), 1991 (sh), 1960 (sh), 1947 (vs, br), 1932 (sh) cm^{-1}. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −40.0 (s, $w_{1/2}$ = 500 Hz) ppm. EI-MS: m/z (%) = 821.3 (0.6) [(CO)$_{13}$PCoW$_2$]$^+$, 457.5 (3.6) [PCoW$_2$]$^+$. $C_{20}Co_2O_{20}P_2W_3$ (1291.57): calcd. C 18.60; found C 18.09.

[WCo$_3$(CO)$_{12}${μ$_3$-PW(CO)$_5$}$_3$] (4): A brown fraction eluted with hexane/toluene (2:1) yielded a small amount of **4** after recrystallisation from CH_2Cl_2 (0.015 g, 2% based on P). IR (KBr): ν(CO) = 2076 (s), 2070 (sh), 2017 (sh), 2003 (sh), 1984 (sh), 1943 (vs, br), 1919 (sh), 1891 (sh) cm^{-1}. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −135.3 ppm (s, $J_{P,W}$ = 87.2, 131.2 Hz) cm^{-1}. $C_{24}Co_3O_{24}P_3W_3$ (1493.52): calcd. C 19.30; found C 19.01.

Reaction of [Cl$_3$PW(CO)$_5$] with K[Co(CO)$_4$]: A solution of K[Co(CO)$_4$] (1.26 g, 6.00 mmol) in 40 mL of THF was added dropwise to a solution of [Cl$_3$PW(CO)$_5$] (0.922 g, 2.00 mmol) in 40 mL of THF at −78 °C. After 30 min, the reaction mixture was allowed to warm to room temperature and stirred for an additional 14 h. All volatiles were removed in vacuo and [W(CO)$_6$] was removed by sublimation under high vacuum at 50 °C. The residue was dissolved in CH_2Cl_2, 5 mL of silica gel was added, and the solution was reduced to dryness. Compounds **1** and **2** were separated by column chromatography. Compound **1** was eluted with hexane (yellow-brown fraction) and obtained by recrystallisation from CH_2Cl_2 (0.12 g, 12% based on P). Elution with hexane/toluene (10:1) yielded a purple fraction from which **2** could be isolated after recrystallisation from CH_2Cl_2 (0.16 g, 10.2% based on P).

[W$_2$(CO)$_9$(μ,η²:η¹:η¹-P$_2${W(CO)$_5$}$_2$] (5): Solid Na$_2$[W$_2$(CO)$_{10}$] (0.768 g, 1.11 mmol) was added at room temperature to a solution of PBr$_3$ (0.2 g, 0.74 mmol) in 50 mL of toluene, which immediately became purple. The solution was stirred for 3 hours and the solvent removed in vacuo. Extraction of the remaining solid twice with 10 mL of CH_2Cl_2 and reduction of the solvent volume to about 10 mL yielded black crystals of **5** after one day at 4 °C (0.15 g, 30%). Further reduction of the solvent volume gave more product. The ^{31}P NMR spectrum of the crude reaction mixture in [D$_8$]THF shows singlets at δ = 103.5 and −90.8 ppm besides the major singlet at δ = −122.7 ppm for **5**. IR (CH_2Cl_2): ν(CO) = 2051 (vs), 2035 (s), 1999 (m), 1956 (s, br) cm^{-1}. $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ = −122.6 (s, $^1J_{P,W}$ = 116 Hz) cm^{-1}. $C_{19}O_{19}P_2W_4$ (1329.55): calcd. C 17.16; found C 17.23.

[{(CO)$_5$Mn}$_3$Sb] (6): A solution of K[Mn(CO)$_5$] (2.20 g, 9.40 mmol) in 50 mL of THF was added to a solution of SbCl$_3$ (715 mg, 3.13 mmol) in 50 mL of THF at −78 °C over a period of 1 h. The reaction mixture was stirred at low temperature for an additional 1 h before the cold bath was removed and the solution warmed to room temperature. All solvents were evaporated in vacuo and the remaining residue was extracted with pentane. Filtration through Celite and storage at −30 °C yielded **6** as black needles (1.16 g, 52%). *Note:* Care has to be taken that the operations carried out at room temperature are performed as quickly as possible to avoid decomposition. IR (KBr): ν(CO) = 2105 (m), 2071 (s), 1980 (vs, br) cm^{-1}. EI-MS: m/z (%) = 706.7 (20) [M$^+$], 678.7 (22) [M$^+$ − CO], 594.7 (2) [M$^+$ − 4 CO], 566.7 (7) [M$^+$ − 5 CO], 538.7 (20) [M$^+$ − 6 CO], 510.7 (43) [M$^+$ − 7 CO], 482.6 (3) [M$^+$ − 8 CO], 454.6 (9) [M$^+$ − 9 CO], 426.6 (21) [M$^+$ − 10 CO], 398.6 (19) [M$^+$ − 11 CO], 370.6 (17) [M$^+$ −12 CO], 342.6 (9) [M$^+$ − 13 CO], 314.6 (8) [M$^+$ − 14 CO], 286.6 (27) [M$^+$ − 15 CO]. $C_{15}Mn_3O_{15}Sb$ (706.72): calcd. C 25.49; found C 25.34.

Thermogravimetric Analysis: Thermogravimetric analyses were carried out with a thermobalance STA 409 from Netzsch either in vacuo or with a dynamic helium gas flow (70 mL/min) at a heating rate of 5 K/min. The balance was coupled to a quadrupole mass spectrometer QMG 422 (Balzers) that includes a skimmer system for measurements under normal pressure.

X-ray Structure Determination and Details of Refinement: Data were collected with a STOE STADI4 four-cycle diffractometer for complexes **2**, **3** and **4** and for complexes **5** and **6** on an IPDS area-detector diffractometer using Mo-K_α (λ = 0.71069 Å) radiation. Machine parameters, crystal data and data collection parameters are summarised in Table 1. The structures were solved by direct methods using SHELXS-86,[26a] with full-matrix least-squares refinement on F^2 in SHELXL-93[26b] with anisotropic displacement for non-H atoms. Hydrogen atoms were placed in idealised posi-

Table 1. Crystallographic data for **2−6**

	2	**3**	**4**	**5**	**6**
Empirical formula	$C_{14}Co_3O_{14}PW$	$C_{20}Co_2O_{20}P_2W_3$	$C_{24}Co_3O_{24}P_3W_4$	$C_{19}O_{19}P_2W_4$	$C_{15}Mn_3O_{15}Sb$
M_r	783.75	1291.55	1677.34	1329.53	706.72
T [K]	200(2)	200(2)	200(2)	210(2)	200(1)
Crystal size	$0.95 \times 0.38 \times 0.24$	$0.38 \times 0.23 \times 0.02$	$0.15 \times 0.08 \times 0.04$	$0.22 \times 0.08 \times 0.04$	$0.30 \times 0.15 \times 0.02$
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
Crystal system	triclinic	triclinic	triclinic	monoclinic	triclinic
a [Å]	8.746(2)	8.959(2)	9.735(2)	11.944(2)	6.744(1)
b [Å]	9.052(2)	9.202(2)	10.060(2)	12.786(2)	16.208(3)
c [Å]	14.989(3)	21.800(4)	20.688(4)	19.717(4)	20.389(4)
α [°]	73.22(3)	79.07(3)	100.40(3)	90	90.31(2)
β [°]	83.97(3)	81.50(3)	93.07(3)	101.17(3)	99.55(2)
γ [°]	71.01(3)	61.52(3)	98.91(3)	90	90.07(2)
V [Å^{-3}]	1074.2(4)	1547.6(5)	1961.8(7)	2954.0(10)	2086.7(7)
Z	2	2	2	4	4
D_c [g cm^{-3}]	2.423	2.722	2.840	2.989	2.136
μ_c [mm^{-1}]	7.755	12.244	13.122	15.715	2.974
2θ range [°]	$4.92 \leq 2\theta \leq 55.00$	$3.82 \leq 2\theta \leq 50.00$	$1.00 \leq 2\theta \leq 48.02$	$3.48 \leq 2\theta \leq 51.76$	$4.06 \leq 2\theta \leq 51.70$
hkl range	$-11 \leq h \leq 10$	$-10 \leq h \leq 10$	$-11 \leq h \leq 11$	$-14 \leq h \leq 14$	$-7 \leq h \leq 7$
	$-11 \leq k \leq 11$	$-10 \leq k \leq 10$	$-11 \leq k \leq 11$	$-15 \leq k \leq 15$	$-19 \leq k \leq 19$
	$-0 \leq l \leq 19$	$0 \leq l \leq 25$	$-0 \leq l \leq 23$	$-22 \leq l \leq 22$	$-24 \leq l \leq 24$
Data/restraints/parameters	4874/0/298	5401/0/424	6136/0/283	5343/0/397	7877/0/613
No. of unique data	4876 (R_{int} = 0.0000)[a]	5422 (R_{int} = 0.0000)[a]	6168 (R_{int} = 0.0000)[a]	5343 (R_{int} = 0.1232)	7877 (R_{int} = 0.0480)
Reflections collected	4876	5422	6168	20649	15901
Independent reflections [$I > 2\sigma(I)$]	4759	4562	4579	4772	6978
Goodness-of fit on F^2	1.139	1.112	1.570	1.071	0.990
R_1,[b] wR_2[c] [$I > 2\sigma(I)$]	0.0224, 0.0586	0.0405, 0.1006	0.0630, 0.1427	0.0277, 0.0758	0.0282, 0.0695
R_1,[b] wR_2[c] (all data)	0.0232, 0.0596	0.0540, 0.1203	0.1001, 0.1635	0.0319, 0.0807	0.0318, 0.0709
Largest diff. peak/hole [e·Å^{-3}]	1.699, -1.605	1.453, -2.823	2.335, -2.992	1.491, -1.014	0.898, -0.816

[a] Four-circle diffractometer. [b] $R = |F_o| - |F_c||/|F_o|$. [c] $wR_2 = [\omega(F_o^2 - F_c^2)^2]/[(F_o^2)^2]^{1/2}$.

tions and refined isotropically according to the riding model. Due to the low crystal quality of **4**, only the heavy atoms W, Co and P were anisotropically refined, leaving a relatively large residual electron density. The two independent molecules of the molecular structure of **6** were tested to be identical, but this resulted in noteworthy differences in angles and bond lengths. Attempts to refine the data set of **6** in the higher monoclinic space group resulted in a R_{int} value greater than 0.50. Thus, it can be concluded that the two molecules are independent in the triclinic unit cell. CCDC-245196 to -245200 (**2−6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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