The compound undergoes rapid decarbonylation even at temperatures <0 °C, in contrast with $[CuCO(O\text{-}t\text{-}Bu)]_4$, which survives vacuum sublimation.[18] The resistance of the latter compound to decarbonylation has been attributed to its kinetic stability, i.e. the unfavorable pyramidal cooordination geometry for copper(I), which would result from the initial decarbonylation product.[18] Similar reasoning has also been exploited to account for the formation of a copper(I) carbonyl complex stabilized by a trischelating oxygen ligand.[21] Such a model[18] would also be applicable to the lability of Cu(CO)Cl(s), in that the tetrahedral coordination of copper(I) would not be hindered on decarbonylation, owing to the proximity of chloride ligands to an initially pyramidal decarbonylated copper(I) center. Indeed, the decarbonylated product is CuCl(s).

The Cu–Cl distances are normal, and the ligand tetrahedron is distorted such that the Cl–Cu–Cl angles all assume values somewhat less than the ideal tetrahedral values, indicating a slight displacement of copper(I) toward the carbonyl ligand (Cu lies 1.0 Å from the plane through the three chloride ligands). The Cu···Cu separations are 3.672 (1) Å (the *a* axis repeat distance) and $Cu\cdots Cu^{ii}$ = 3.837 (2) Å (symmetry code: (ii) $^1/_2 - x, -y, ^1/_2 + z$).

Acknowledgment. Financial support from the Swedish Natural Science Research Council is gratefully acknowledged.

Supplementary Material Available: Table SI, listing anisotropic thermal parameters (1 page); a table of calculated and observed structure factors (3 pages). Ordering information is given on any current masthead page.

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Contribution from the Laboratoire de Synthèse
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Hydrido Phosphido Derivatives of Bis(cyclopentadienyl)molybdenum and -tungsten and the Structure of $[(\eta^5\text{-}Cp)_2Mo(H)(\mu\text{-}PPh_2)Mn(CO)_2(\eta^5\text{-}Cp)]$

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Binuclear transition-metal complexes represent an important group of compounds interesting with respect to their structure, bonding, and potential catalytic activity.[1] Phosphido-bridged complexes, although known for a long time,[2] have received a good deal of attention only in the last decade.

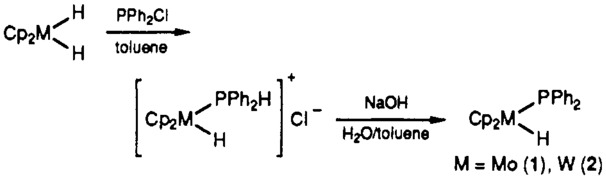
In the course of our studies on the chemistry of metallocene derivatives of the group 5 and 6 transition metals we decided to make a new family of phosphido-bridged di- or polymetallic compounds. The simplest potential precursors for such polymetallics may be of the type $Cp_2M(PR_2)_2$, $Cp_2M(L)PR_2$, or $Cp_2M(H \text{ or } X)PR_2$. Some examples of diphosphido complexes are known in the chemistry of group 4 metals (Zr, Hf).[3-5] Monophosphido complexes of Nb and Ta have been prepared from monohydrides Cp_2MHL (L = CO, PMe_2Ph) and PPh_2Cl, the resulting salts being further converted to the neutral species by treatment with NaOH.[6] The similar salts of Mo and W $[Cp_2M(H)(PPh_2H)]Cl$ have been obtained from the corresponding dihydrides Cp_2MH_2 and PPh_2Cl.[7] We report here the synthesis and characterization of the first molecules of molybdenum and tungsten containing both a terminal hydride and a phosphide ligand. Related complexes of hafnium $Cp^*_2Hf(H)PRR'$ have been reported during the preparation of this note.[8]

Table I. Crystallographic Data for $Cp_2Mo(H)(\mu\text{-}PPh_2)Mn(CO)_2Cp$ (**3**)

formula $C_{29}H_{26}MnMoO_2P$	fw 588.38
a = 13.753 (2) Å	space group $P2_1/n$ (No. 14)
b = 16.756 (7) Å	d_{calc} = 1.628 g cm^{-3}
c = 10.426 (2) Å	λ = 0.71073 Å
β = 92.39 (1)°	μ(Mo Kα) = 11.055 cm^{-1}
V = 2400.5 Å^3	$R(F)$ = 0.032
Z = 4	$R_w(F)$ = 0.035
T = 20 °C	GOF = 1.288

Results

Molecular complexes $[Cp_2M(H)PPh_2]$ (M = Mo (**1**), W (**2**)) have been prepared according to reaction 1 in high yields. A phosphine-type behavior of metallophosphanes **1** and **2** was checked by their reactions with $Cp(CO)_2(THF)Mn$, which gave the expected binuclear phosphido-bridged complexes $Cp_2M(H)(\mu\text{-}PPh_2)Mn(CO)_2Cp$ (M = Mo (**3**), W (**4**)). All new complexes were characterized by their ^1H and ^{31}P NMR spectra, IR spectra, and elemental analyses. The X-ray structure determination of **3** is the first one carried out on a singly bridged μ-phosphido binuclear complex without a metal–metal bond.



(1)

Discussion

The metallophosphanes **1** and **2** belong to the family of bent metallocenes. Some ionic and molecular biscyclopentadienides with molybdenum–phosphorus bonds are known, and they generally contain tertiary or secondary phosphines.[9-11] ^1H resonances of C_5H_5 ligands in **1** and **2** are recorded in the very high fields with respect to the other known Cp_2MX_2 (M = Mo, W) complexes[12,13] and are close to those reported for the d^4 Mo(II) complex $Cp_2Mo–PMe_3$.[11] This suggests an electron-rich Cp_2M fragment and probably a highly covalent nature of the metal–phosphide bond in **1** and **2**. The ^{31}P NMR resonance in **2** (W) is shifted upfield by 36 ppm with respect to the molybdenum complex **1**. This shift is the same as in the precursor $[Cp_2M(H)PPh_2H]^+$ salts[7] but higher than that observed in monocyclopentadienides $Cp(CO)_2(PMe_3)M–PPh_2$ (metal(II), d^4), where it is equal to 24 ppm.[14] This indicates that the phosphorus nuclei

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Table II. Selected Interatomic Distances (Å) and Angles (deg) for $Cp_2Mo(H)(\mu\text{-}PPh_2)Mn(CO)_2Cp$ (3)[a]

Mo⋯Mn	4.391 (1)	Mn–P	2.359 (2)
Mo–P	2.602 (2)	Mn–C1	1.753 (7)
Mo–H1	1.71 (9)	Mn–C2	1.743 (7)
Mo–G2	1.961	Mn–G1	1.791
Mo–G3	1.964	P–C21	1.845 (7)
		P–C27	1.861 (6)
Mo–P–Mn	124.47 (7)	P–Mn–C1	89.9 (2)
P–Mo–H1	82 (3)	P–Mn–C2	99.2 (2)
P–Mo–G2	107.8	P–Mn–G1	121.0
P–Mo–G3	107.8	C1–Mn–C2	90.1 (3)
H1–Mo–G2	99	C1–Mn–G1	124.0
H1–Mo–G3	103	C2–Mn–G1	123.9
G2–Mo–G3	139.8	Mn–P–C21	98.8 (2)
Mo–P–C21	113.5 (2)	Mn–P–C27	111.8 (2)
Mo–P–C27	104.2 (2)	C21–P–C27	102.1 (3)

[a] The G symbols represent the gravity centers of cyclopentadienyl rings: G1, C3–C7; G2, C11–C15; G3, C16–C20.

are more sensitive to the metal changes in biscyclopentadienides (metal(IV), d^2) than in monocyclopentadienides and so that there may be a difference in the nature and in the strength of the metal–phosphide bonding in these two classes of compounds.

Complexes **1** and **2** react with $Cp(CO)_2Mn(THF)$ to give **3** and **4**, respectively. These are the rare examples of stable bimetallic *mono*phosphido-bridged terminal hydrido compounds. A few *di*phosphido-bridged terminal hydrido heterobimetallics has been reported.[1,15–21] The known complexes containing a single phosphido bridge without metal–metal interactions are $Cp_2Hf(PEt_2)(\mu\text{-}PEt_2)Fe(CO)_4$[22] and $(CO)_5M(\mu\text{-}PPh_2)Pt(H)(PPh_3)_2$ (M = Cr, Mo, W).[23] No byproduct with a metal–metal bond or with a hydride bridge was detected in the reactions of **1** and **2** with $Cp(CO)_2(THF)Mn$, thus suggesting that neither the metal (Mo(IV), W(IV); d^2) lone pair nor the hydride is able to displace one carbonyl ligand from the $Cp(CO)_2Mn$ unit. Rather large low-field coordination shifts ($\Delta = \delta_{(complex)} - \delta_{(freeligand)}$) of ^{31}P resonances[24] were observed for **3** (Δ = +67 ppm) and **4** (Δ = +54 ppm) with respect to the starting complexes **1** and **2**, respectively. As shown by X-ray structure determination of **3**, there is neither a metal–metal interaction nor a cycle involving phosphorus. A similar coordination shift (Δ = +52 ppm) was observed upon coordination of the terminal phosphide of $Cp(CO)_2FePPh_2$ ($\delta(^{31}P)$ = +54.3 ppm) by manganese in $Cp(CO)Fe(\mu\text{-}C(O)Me)(\mu\text{-}PPh_2)Mn(CO)_4$ ($\delta(^{31}P)$ = +106.3 ppm).[25] The authors suggested that the downfield position of the $\mu\text{-}PPh_2$ resonance does agree with the Garrou's[26] "ring effect". Perhaps it is related to a simple coordination effect, showing that the interpretation of ^{31}P resonances needs more theoretical studies.

Crystal structure determination of **3** (Table I, Figure 1) showed two outstanding features: the very long (2.602 (2) Å) Mo–P bond and the largely opened (124.5 (1)°) Mo–P–Mn angle (Table II). The Mo⋯Mn separation of 4.271 (1) Å is clearly nonbonding. The single Mo–Mn bond lengths were observed in the range 2.680 (1)–3.092 (1) Å.[27,28] The Mo–P bond lengths in phosphido-bridged monocyclopentadienyl complexes of molybdenum fall in the range 2.329–2.481 Å,[27–30] and in the biscyclopentadienyl cation $[Cp_2MoCH(CF_3)CH(CF_3)PPh_2]^+$ it is also much shorter (2.487 (1) Å)[7] than in **3**. The only one μ-phosphido compound of a group 6 metal with a metal–phosphorus bond as long as in **3** is the dibridged electron-rich dianion $[(CO)_4W(\mu\text{-}PPh_2)_2W(CO)_4]^{2-}$, in which the W–P distances are 2.610 (1) and 2.588 (1) Å.[31] However, the W–P–W angles in this dibridged bimetallic are relatively small (104.20 (5)°) although the long W⋯W separation of 4.1019 (8) Å was found therein. The M–P–M angle as large as in **3** was observed in the tungstaphosphirene $Cp(CO)_2W{=}C(Ph)P(Ph)W(CO)_5$ (127.52 (8)°).[32] The Mo–P–Mn angle found in **3** (sp^3-hybridized phosphorus) approaches the values observed in "open" bimetallic phosphinidenes (128.2–134.0°),[33,34] where the phosphorus atom is formally sp^2-hybridized. The above observations indicate that, for the sp^3-hybridized phosphorus in phosphido-bridged complexes, the large M–P–M angles are to be expected in the absence of the metal–metal interactions and in the absence of the other bridges. Unusual geometrical parameters observed for **3** may result from steric repulsions of Cp_2MoH and $Cp(CO)_2Mn$ fragments, but the electronic structure of this new class of compounds, especially in that which concerns the nature of the metal–phosphorus bond, remains uncertain. Chemical, theoretical, and structural studies on terminal hydrido–phosphido complexes are currently in progress.

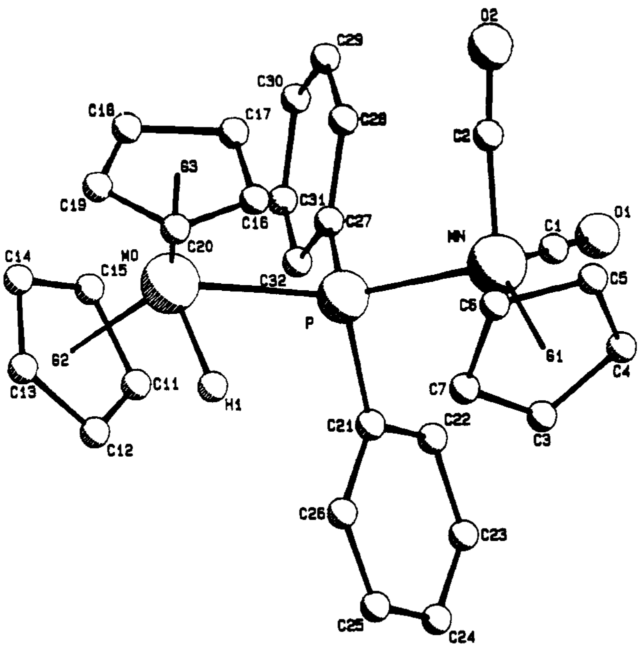

Figure 1. Molecular structure of 3.

Experimental Section

Manipulations were conducted under an atmosphere of argon by using Schlenk techniques. Degassed solvents were employed throughout. Cp_2MH_2,[35] $[Cp_2M(H)PPh_2H]Cl$,[7] and $Cp(CO)_2(THF)Mn$[36] were pre-

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Table III. Positional Parameters and Equivalent Isotropic Thermal Parameters for $Cp_2Mo(H)(\mu\text{-}PPh_2)Mn(CO)_2Cp$ (**3**)

atom	*x*	*y*	*z*	B_{eq}, Å^2
Mo	0.71420 (4)	0.14391 (4)	0.53022 (6)	2.282 (9)
Mn	0.87163 (7)	0.36964 (6)	0.48668 (9)	2.23 (2)
P	0.7300 (1)	0.2914 (1)	0.4559 (2)	1.92 (3)
H1	0.795 (6)	0.128 (6)	0.413 (9)	5.0^a
G1	0.9795	0.3475	0.4029	
G2	0.5970	0.0990	0.4441	
G3	0.7936	0.1312	0.6899	
O1	0.7614 (4)	0.5173 (3)	0.4500 (6)	4.3 (1)
O2	0.8718 (4)	0.3986 (4)	0.7615 (5)	4.4 (1)
C1	0.8020 (5)	0.4564 (4)	0.4625 (7)	2.8 (1)
C2	0.8695 (5)	0.3833 (4)	0.6522 (7)	2.9 (1)
C3	0.9341 (5)	0.3567 (6)	0.3033 (7)	3.7 (2)
C4	0.9845 (5)	0.4166 (5)	0.3755 (8)	3.9 (2)
C5	1.0275 (5)	0.3810 (5)	0.4852 (8)	4.3 (2)
C6	1.0041 (5)	0.2990 (5)	0.4810 (8)	3.9 (2)
C7	0.9474 (5)	0.2846 (5)	0.3698 (8)	3.6 (2)
C11	0.5886 (5)	0.1557 (5)	0.3760 (7)	3.5 (2)
C12	0.6396 (6)	0.0864 (5)	0.3491 (8)	4.3 (2)
C13	0.6335 (6)	0.0340 (5)	0.4523 (8)	4.3 (2)
C14	0.5761 (5)	0.0711 (5)	0.5453 (7)	3.4 (2)
C15	0.5473 (5)	0.1480 (5)	0.4981 (7)	3.3 (1)
C16	0.8494 (7)	0.1706 (6)	0.6491 (8)	6.0 (2)
C17	0.7769 (9)	0.1968 (6)	0.7178 (8)	6.9 (3)
C18	0.7216 (7)	0.127 (1)	0.7447 (8)	9.8 (5)
C19	0.7723 (8)	0.0666 (5)	0.698 (1)	10.4 (3)
C20	0.8479 (8)	0.0950 (6)	0.640 (1)	7.9 (3)
C21	0.7102 (5)	0.3048 (4)	0.2811 (6)	2.3 (1)
C22	0.6730 (5)	0.3763 (4)	0.2300 (7)	3.3 (2)
C23	0.6716 (6)	0.3895 (5)	0.0988 (8)	4.6 (2)
C24	0.7078 (6)	0.3347 (5)	0.0165 (7)	4.3 (2)
C25	0.7431 (6)	0.2647 (5)	0.0660 (7)	4.4 (2)
C26	0.7436 (6)	0.2492 (5)	0.1939 (7)	3.3 (2)
C27	0.6213 (4)	0.3416 (4)	0.5194 (6)	2.1 (1)
C28	0.6265 (5)	0.3688 (5)	0.6442 (7)	3.2 (2)
C29	0.5447 (6)	0.4008 (5)	0.6997 (8)	3.9 (2)
C30	0.4577 (5)	0.4080 (5)	0.6323 (9)	4.0 (2)
C31	0.4525 (5)	0.3821 (5)	0.5076 (8)	4.1 (2)
C32	0.5322 (5)	0.3480 (5)	0.4504 (7)	3.1 (1)

^{a} *B* value is for an atom that was refined isotropically. The G symbols represent the gravity centers of cyclopentadienyl rings: G1, C3–C7; G2, C11–C15; G3, C16–C20.

pared by the literature procedures. ^1H and ^{31}P NMR spectra were recorded on JEOL-FX100 and Bruker WM400 spectrometers. Chemical shifts are relative to external TMS and H_3PO_4. IR spectra were recorded on a Perkin-Elmer 580B spectrophotometer.

$Cp_2Mo(H)PPh_2$ (1). In a typical operation a solution of NaOH (0.04 g, 1 mmol) in water (10 mL) was added to a suspension of $[Cp_2Mo(H)PPh_2H]Cl$ (0.4 g, 0.9 mmol) in 15 mL of toluene and the mixture was stirred for 45 min at room temperature. During this time the solution turned deep orange. This solution was filtered and evaporated, yielding after extraction with toluene and evaporation 0.35 g (95% yield) of **1**. Anal. Calcd (found) for $C_{22}H_{21}MoP$: C, 64.09 (63.2); H, 5.13 (5.3); P, 7.51 (7.3). NMR, δ (ppm): ^1H ($(CD_3)_2CO$), 7.53–6.87 (Ph, m), 4.69 (Cp, d, J_{PH} = 1.5 Hz), −7.65 (Mo–H, d, J_{PH} = 31.5 Hz); ^1H (C_6D_6), 7.79–6.94 (Ph, m), 4.17 (Cp, d, J_{PH} = 1.5 Hz), −7.41 (Mo–H, d, J_{PH} = 32.6 Hz); ^{31}P ($(CD_3)_2CO$), −10.3 (d).

$Cp_2W(H)PPh_2$ (2). The procedure was the same as for **1**, with a 90% yield. Anal. Calcd (found) for $C_{22}H_{21}PW$: C, 52.82 (52.2); H, 4.23 (4.4); P, 6.19 (5.6). NMR, δ (ppm): ^1H ($(CD_3)_2CO$), 7.57–6.81 (Ph, m), 4.65 (Cp, d, J_{PH} = 1.5 Hz), −11.26 (W–H, dt, J_{PH} = 24 Hz, J_{WH} = 79 Hz); ^1H (C_6D_6), 7.80–6.90 (Ph, m), 4.11 (Cp, d, J_{PH} = 0.8 Hz), −11.01 (W–H, dt, J_{PH} = 25 Hz, J_{WH} = 79 Hz); ^{31}P ($(CD_3)_2CO$), −46.3 (br).

$Cp_2Mo(H)(\mu\text{-}PPh_2)Mn(CO)_2Cp$ (3). A 2-fold excess of freshly prepared $Cp(CO)_2(THF)Mn$ in THF was added at room temperature to a solution of **1** in THF, and the mixture was stirred overnight. After evaporation of the solvent, the solid was washed with pentane (to eliminate the nonreacted $Cp(CO)_3Mn$) and extracted with toluene. Crystallization gave deep orange crystals of **3** in 40% yield. Anal. Calcd (found) for $C_{29}H_{26}MnMoO_2P$: C, 59.20 (57.3); H, 4.45 (4.3). NMR, δ (ppm): ^1H (C_6D_6), 7.94–6.92 (Ph, m), 4.14 (Cp_{Mo}, d, J_{PH} = 1.5 Hz), 3.93 (Cp_{Mn}, d, J_{PH} = 1.5 Hz), −7.50 (Mo–H, d, J_{PH} = 34 Hz); ^{31}P ($(CD_3)_2CO$), +57.0 (d). IR, cm^{-1}, THF: 1909, 1841 (ν_{CO}).

$Cp_2W(H)(\mu\text{-}PPh_2)Mn(CO)_2Cp$ (4) was prepared in the same manner as **3**, with a 30% yield. Anal. Calcd (found) for $C_{29}H_{26}MnO_2PW$: C, 51.50 (49.7); H, 3.87 (3.8). NMR, δ (ppm) (CD_2Cl_2): ^1H, 7.80–6.97 (Ph, m), 4.66 (Cp_W, d, J_{PH} = 1.5 Hz), 3.91 (Cp_{Mn}, d, J_{PH} = 1.5 Hz), −11.18 (W–H, d, J_{PH} = 27.5 Hz); ^{31}P, +8.0 (br). IR, cm^{-1}, THF: 1909, 1841 (ν_{CO}).

Crystallographic Studies. An orange irregularly shaped crystal having approximate dimensions of 0.20 × 0.15 × 0.15 mm was mounted on an Enraf-Nonius CAD4 diffractometer. The unit cell was determined and refined from 25 randomly selected reflections (CAD4 routines). Intensities were measured with filtered Mo radiation, λ = 0.71073 Å, ω–2θ scan, $2° < \theta < 25°$. A total of 2008 unique reflections with $I > 3\sigma(I)$ were used in structure determination and refinement. Crystal data and refinement residuals are given in Table I. All calculations were carried out by using the Enraf-Nonius SDP library[37] with neutral-atom scattering factors. No absorption correction was made. The structure was solved and refined by conventional Patterson, difference Fourier, and full-matrix least-squares methods. The position of the hydride ligand was found from a difference Fourier map and refined with a fixed B_{iso} = 5.0 Å^2; other hydrogen atoms placed in calculated positions were ridden on the carbon atoms bearing them and included in the final refinements with B_{iso} = 5.0 Å^2. The final atomic coordinates of non-hydrogen atoms refined with anisotropic temperature factors and of the hydride are given in Table III.

Supplementary Material Available: Tables of hydrogen atom positions, anisotropic temperature factors, bond distances, bond angles, least-squares planes, and crystallographic data (8 pages); a listing of calculated and observed structure factors (11 pages). Ordering information is given on any current masthead page.

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