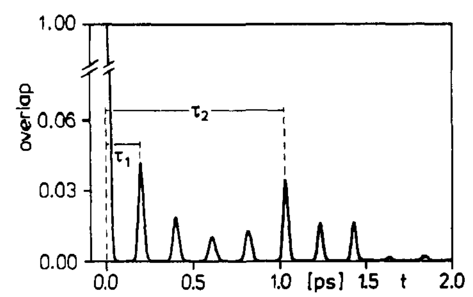

Figure 7. Time dependence of the magnitude of the overlap used in the calculation of the emission spectrum. Note the two distinct times τ_1 (0.2 ps) and τ_2 (1 ps) which respectively correspond to the 162-cm^{-1} separation between the most prominent bands and the 26-cm^{-1} separation for the smaller sidebands.

All of the parameters in Table II were left unchanged with the exception of one vibrational frequency, that of the 162-cm^{-1} mode, and E_0. The vibrational frequency in the excited electronic state was decreased to 150 cm^{-1}, the value obtained from the absorption spectrum. E_0 was 14520 cm^{-1}.

The experimental and calculated absorption spectra are compared in the insert to Figure 6. The agreement in the low-energy region is good. These findings support the assignments of the two lowest electronic excited states made in the preceding section; both ${}^3B_{3g}$ (the emitting state) and ${}^1B_{3g}$ derive from the same orbital configuration and therefore are expected to have similar potential energy surfaces and show similar fine structure in the electronic spectra as is observed. The overall bandwidth is poorly reproduced, suggesting that more than one excited state is involved in the absorption band. Thus, the calculations of the vibronic structure provide insight into both the fine structure and the assignments of the lowest energy excited states.

Analysis of the Small Repetitive Spacings. The small energy differences between many of the vibronic features in the emission spectrum are exactly equal to the frequency differences between higher energy molecular vibrational modes. The time-dependent theoretical point of view provides a simple interpretation of the small spacings.[21] The new insight arises from interpreting the system in the time domain. In the time domain, the overlap $\langle \phi_k | \phi_k(t) \rangle$ as a function of time for a given mode oscillates. The separation between the recurrences is a vibrational period. The total overlap is the product of the overlaps of each of the individual normal modes. Because each contributing mode has a different vibrational period, the product will be modulated and contain "beats". An analogue is found in sound waves. When the difference in frequencies between two sound waves is small compared to the sum of the two, the oscillation is rapid, but its "envelope" undergoes slow periodic variations, known as "beats". For two waves, the beat frequency is the difference between the frequencies of the waves.

The modulation of the overlap in the time domain can be clearly seen in Figure 7. This plot shows the overlap that gives the spectrum in Figure 6. The modulation that gives rise to the 26-cm^{-1} separation will be emphasized in this discussion. At $t = 0$ the total overlap is 1. The plot of the overlap versus time shows the initial falloff and subsequent recurrence at time $\tau_1 = 0.2$ ps. The 162-cm^{-1} spacing in the frequency domain is equal to $2\pi/\tau_1$. Most importantly, the magnitude of the overlap on successive recurrences rises and falls; i.e., the overlap is modulated. In Figure 7, the first maximum of the modulation occurs at the fifth recurrence, i.e., at $t = 1$ ps, labeled τ_2. The 26-cm^{-1} spacing in the emission spectrum of Figure 4 corresponds to $2\pi/\tau_2$ in the time domain and is the difference in the frequencies of the 162- and 188-cm^{-1} modes. In this case, the separation between the bands within a cluster is the difference in wavenumbers between the two most highly distorted modes in the excited electronic state.

The time domain picture used above provides a clear explanation of the features in the luminescence spectrum. Time-dependent theory is equivalent to the traditional Franck–Condon picture, which can also be used to interpret the vibronic spacings. For example, the peak at 12320 cm^{-1} (Figure 6) arises from two quanta of the 162-cm^{-1} mode, and the lower energy sidebands on this peak arise from the combinations of two quanta of the 162-cm^{-1} mode and one quantum of the 52-cm^{-1} mode, the 93-cm^{-1} mode, or the 126-cm^{-1} mode, respectively.

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Notes

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Preparation and Structural Characterization of Cu(CO)Cl

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That solutions of copper(I) chloride in hydrochloric acid absorb carbon monoxide, yielding a white solid that readily loses CO, has been known for well for over a century.[1,2] The process has been recognized as the most satisfactory for reversible fixation of carbon monoxide under mild conditions, aromatic solvents containing, e.g., $[CuAlCl_4]$ as the active component being employed industrially.[2,3] Various stoichiometries have been proposed for the solid precipitated from solutions of CuCl in hydrochloric acid, i.e. Cu(CO)Cl, $Cu(CO)Cl\cdot 2H_2O$, and $2CuCl\cdot CO\cdot 2H_2O$,[1] investigation of the CuCl/CO molar ratio in the precipitate by manometric methods indicating it to be anhydrous with the formula Cu(CO)Cl.[4] The solid-state structure of the compound formed when carbon monoxide is absorbed by solutions of chlorocuprates(I) has been reported to be a halogen-bridged $(CuClCO)_2$ dimer,[5] whereas the gold(I) analogue has been shown to be a linear monomer.[6] Infrared spectroscopic investigation of the white solid denoted "Cu(CO)Cl", precipitating on passage of carbon monoxide through suspensions or solutions of copper(I) chloride in several different organic solvents, have shown that, whereas the CO band in solution varies slightly from solvent to solvent lying in the range 2070–2085 cm^{-1}, the solid exhibits a band at 2120 cm^{-1} despite its origin.[7] The higher frequency for the CO stretching vibration in the solid was interpreted as suggesting that copper(I) may have a coordination number lower than 4.[7]

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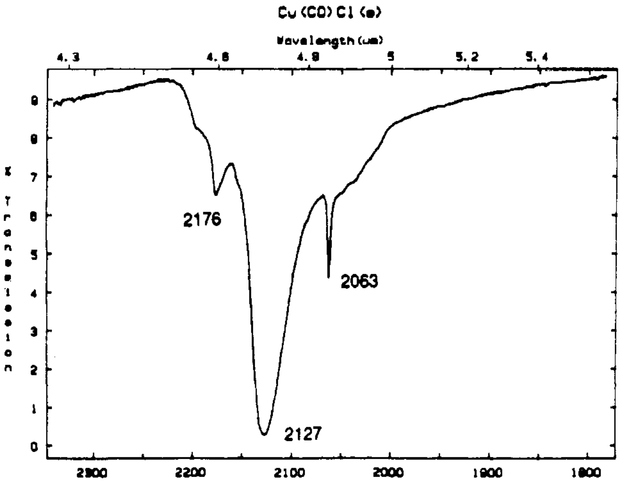

Figure 1. High-frequency infrared spectrum of Cu(CO)Cl(s), prepared by using ethyl vinyl ketone as solvent.

Cu(CO)Cl prepared in organic solvents has been considered to be a useful precursor for the synthesis of organometallic and coordination complexes of copper(I), i.e. a source of $[Cu(CO)]^{+}$[7] or of copper(I).[7,8] In a halogen-bridged $(CuClCO)_2$ dimer, copper(I) might be expected to exhibit trigonal-planar coordination as in the dimeric $[Cu_2X_4]^{2-}$ anions (X = Cl, Br, I)[9] and thus be coordinately unsaturated. Apart from inherent synthetic applications,[7,8] Cu(CO)Cl might therefore prove to be a valuable precursor in the preparation of structural models for intermediates occurring in copper(I)-promoted carbonylation reactions, part of an ongoing project directed toward various copper(I)-promoted reactions, e.g. conjugate addition to α,β-unsaturated carbonyl compounds.[10] In this context it was of interest to investigate the solid-state structure of Cu(CO)Cl. We have therefore devised a new method for the preparation of Cu(CO)Cl and have determined its crystal structure.

Experimental Section

All operations were carried out under nitrogen or argon, using Schlenk techniques, or under carbon monoxide, using vacuum line techniques, the carbon monoxide pressure being monitored with a u-type mercury manometer. 1-Penten-3-one, methanol, tetrahydrofuran, and benzene were dried with 3- or 4-Å molecular sieves, distilled, and deoxygenated. Copper(I) chloride was purified as described in ref 11 and dried under reduced pressure. Carbon monoxide (99.998%) was used without further purification. Infrared spectra were recorded on a Mattson Polaris FTIR spectrometer.

Synthesis of Cu(CO)Cl. Copper(I) chloride (0.20 g) was dissolved in 10 mL of ethyl vinyl ketone at 20 °C, and carbon monoxide was allowed to diffuse slowly into the solution by maintaining an atmosphere of CO above the solution in the Schlenk tube overnight. This procedure yielded very thin plates of Cu(CO)Cl at the solution–vapor interface. A few of these plates were allowed to grow at the bottom of the Schlenk tube by slow evaporation of the solution under carbon monoxide, over a period of several days.

Passage of carbon monoxide through the solution led to immediate precipitation of Cu(CO)Cl as a white powder (**1**). Cu(CO)Cl was also precipitated as a white solid from a suspensions of copper(I) chloride in methanol (**2**) and in tetrahydrofuran (**3**), and from solutions of copper(I) chloride in hydrochloric acid (**4**) and in anhydrous aluminium chloride dissolved in benzene (**5**). IR (Nujol mull, CaF_2 windows, cm^{-1}) ν_{CO} stretch: (**1**) 2176 w, 2127 s, 2063 w; (**2**) 2177 w, 2127 s, 2063 w; (**3**) 2177 w, 2127 s, 2063 w; (**4**) 2176 w, 2127 s, 2063 w; (**5**) 2120 s. Corresponding measurements for the solutions (CaF_2 cell, solvent bands excluded, cm^{-1}) ν_{CO} stretch: (**1**) 2108 s; (**2**) 2095 m; (**3**) 2095 m; (**4**) 2104 s, 1950 s; (**5**) 2180 s, 2157 s, 2107 w. The high-frequency spectrum of Cu(CO)Cl precipitated from ethyl vinyl ketone is depicted in Figure 1.

Table I. Crystallographic Data for Cu(CO)Cl

chem formula	CClCuO	T, °C	−144
fw	127.0	λ(Mo Kα)	0.71069
a, Å	3.672 (1)	ρ_{calcd}, g cm^{-3}	2.83
b, Å	8.197 (2)	μ, cm^{-1}	79.7
c, Å	4.947 (2)	transm coeff	0.25–1.00
V, $Å^3$	148.9 (1)	no. obs reflns	277
space group	$Pmn2_1$ (No. 31)	R	0.054
Z	2	R_w	0.060

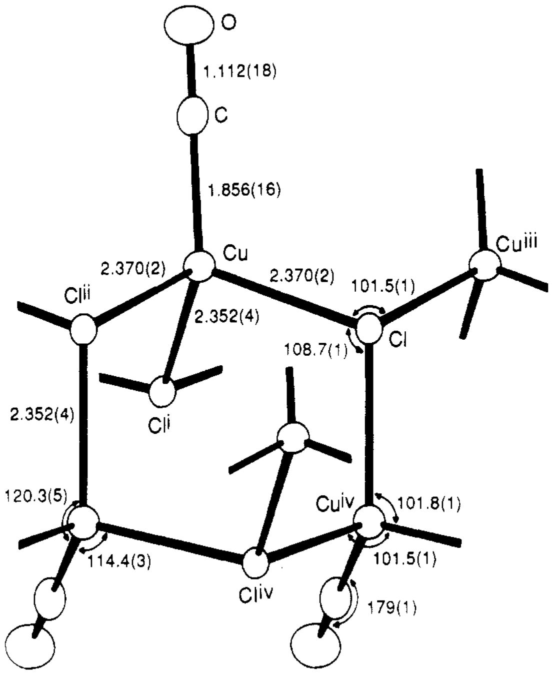

Figure 2. Part of a layer in Cu(CO)Cl(s). Bond lengths are given in Å and angles in deg. Thermal ellipsoids enclose 50% probability.[15] Symmetry code: (i) $^1/_2 - x, -y, z - {}^1/_2$; (ii) $x - 1, y, z$; (iii) $1 + x, y, z$; (iv) $^1/_2 - x, -y, {}^1/_2 + z$.

Determination of the Crystal Structure of Cu(CO)Cl. Colorless, irregular-shaped plates of Cu(CO)Cl were obtained as described above. Owing to rapid loss of carbon monoxide from the compound, the crystals were transferred to a Dewar vessel adapted for mounting crystals in glass capillaries at low temperature and in an inert atmosphere. A single crystal, with the approximate dimensions 0.30 × 0.30 × 0.10 mm, was thus sealed in a glass capillary at approximately −150 °C and transferred, at the same temperature, to a Rigaku AFC6R diffractometer. Intensity data were measured at −144 ± 1 °C for $3.5 < 2\theta < 60°$, by using graphite-monochromated Mo Kα radiation from a RU200 rotating anode source operated at 9 kW (50 kV; 180 mA). The $\omega/2\theta$ scan mode was employed with an ω scan rate of 32° min^{-1} and a scan width of $(1.70 + 0.30 \tan \theta)°$; weak reflections ($I < 10\sigma(I)$) were rescanned up to three times and counts accumulated to improve counting statistics. Stationary background counts were recorded on each side of the reflection, the ratio of peak counting time vs background counting time being 2:1. A total of 513 reflections were measured and intensities corrected empirically for absorption based on azimuthal scans for several reflections (min, max transmission factors: 0.25, 1.00). On merging, a unique set of 301 reflections ($R_{int} = 0.013$), 285 excluding those reflections systematically absent was obtained. Of these, 277 were considered to be observed ($I > 3\sigma(I)$). Cell constants were obtained by least-squares refinement using the setting angles for 25 reflections in the range $48.9 < 2\theta < 49.7°$.

The structure was solved by direct methods (MITHRIL),[12] all the atoms being located in the mirror plane of $Pmn2_1$, i.e. in site $2a$. Since intensity

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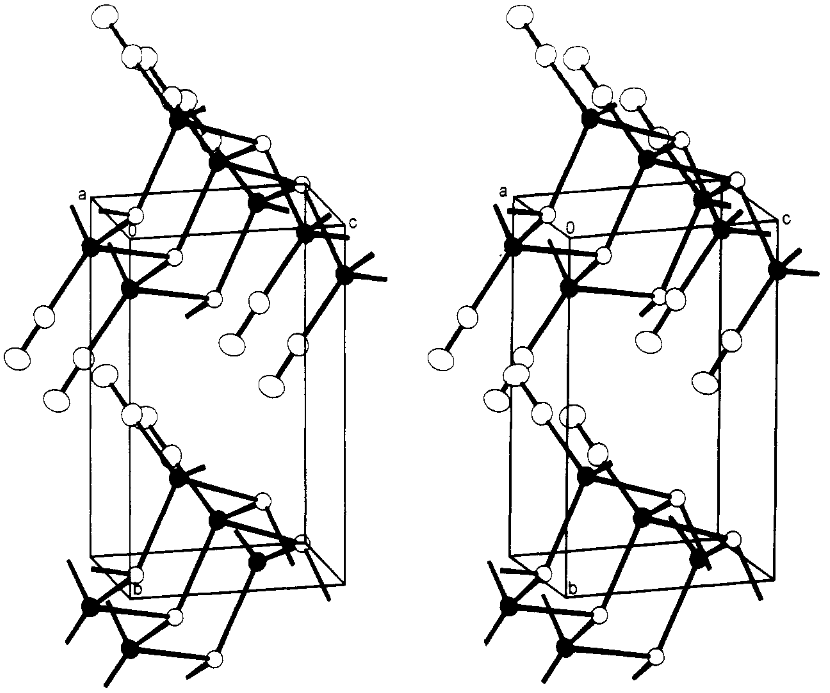

Figure 3. Stereoscopic view of the structure showing the interleaving of terminal carbonyl groups in adjacent layers. Copper(I) centers are depicted as filled ellipsoids.

Table II. Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) for Cu(CO)Cl

	x	y	z	B(eq)[a]
Cu	0	0.1396 (2)	0	1.31 (6)
Cl	$^1/_2$	0.1213 (4)	0.3016 (8)	1.1 (1)
C	0	0.325 (2)	−0.216 (3)	1.7 (6)
O	0	0.438 (1)	−0.341 (3)	2.7 (5)

[a] B(eq) is defined as $(8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j$.

statistics clearly indicated acentricity and the centric counterpart, *Pmmm*, would not be compatible with an ordered structural model, assignment of the structure to space group $Pmn2_1$ was considered unambiguous. Full-matrix least-squares refinement of positional and anisotropic thermal parameters gave a final R value of 0.054 (R_w = 0.060; weighting scheme $w = [\sigma^2(F_o)]^{-1}$) for 24 parameters and 277 reflections, the maximum Δ/σ in the final cycle being 0.0007 and the maximum residual electron density 1.38 e Å^{-3}. Atomic scattering factors and anomalous dispersion corrections were taken from ref 13; the enantiomorph refined to R = 0.057. All calculations were performed by using the TEXSAN[14] software package, and structural illustrations were drawn with ORTEP.[15]

Crystal data are summarized in Table I; atomic coordinates and equivalent isotropic thermal parameters are given in Table II.

Results and Discussion

From the infrared spectra of the white solid precipitated on passage of carbon monoxide through solutions or suspensions of copper(I) chloride in ethyl vinyl ketone, methanol, tetrahydrofuran, hydrochloric acid, and anhydrous aluminium chloride dissolved in benzene, it would seem that, in accordance with the findings of Pasquali et al.,[7] the solids are identical, despite their origin, whereas the spectra of the solutions vary somewhat from solvent to solvent. The broad band at 1950 cm^{-1} exhibited by the solution containing copper(I) chloride dissolved in hydrochloric acid, saturated with carbon monoxide, suggests the presence of a bridging carbonyl group, frequencies of 1925 and 1926 cm^{-1}, having been found for μ-CO bridging copper(I) in the solid state.[1,16,17]

As mentioned above, Cu(CO)Cl has been considered to be a valuable precursor for the synthesis of organometallic and coordination compounds of copper(I) (cf. refs 6 and 7). Use of ethyl vinyl ketone as a solvent during preparation, as described above, affords a rapid method of obtaining high-purity Cu(CO)Cl(s), since copper(I) chloride is readily soluble in ethyl vinyl ketone, due to complexation,[10c] and the resulting solution is much less sensitive to oxygen than are, e.g., suspensions of copper(I) chloride in methanol or tetrahydrofuran.

The solid Cu(CO)Cl has now been shown to contain chloride-bridged layers in which copper(I) is approximately tetrahedrally coordinated (Figure 2). As is seen from Figure 3, layer formation is effected through fusion of six-membered copper(I) chloride rings in the chair conformation. Terminal carbonyl groups in adjacent layers are interleaved such that these groups are inclined at 112°, the closest nonbonding distance between layers being O···O^{i} = 3.246 (8) Å (symmetry code: (i) $^1/_2 - x$, $1 - y$, $^1/_2 + z$).

The Cu–C distance, 1.86 (2) Å (cf. Figure 2), appears to lie in the upper region for such bonds determined for terminal carbonyl groups[2] and approaches the value of 1.88 Å predicted as the lower limit for the Cu(I)–CO single bond.[18] The C–O bond, 1.11 (2) Å, is correspondingly short, although by no means exceptionally so, in accordance with the high ν(CO) of 2127 cm^{-1}. This frequency is reduced to 2120 cm^{-1} during decomposition of the compound, while the band at 2175 cm^{-1} disappears. A detailed vibrational analysis of Cu(CO)Cl(s) will be presented elsewhere.[19] The relatively long Cu–C, short C–O, and high ν(CO) in Cu(CO)Cl suggest a low d_π–p_{π^*} contribution to the metal–carbonyl bond. Those most comparable values of Cu–C, C–O, and ν(CO) would appear to be for carbonyl[glyoxal bis(2,4-dimethylpentyl-3-imine)](trifuoromethanesulfonato)copper(I),[20] viz. Cu–C, C–O, and ν(CO) are 1.820 (6), 1.11 (1) Å, and 2108 cm^{-1}, respectively.[20]

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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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Received February 27, 1990

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.

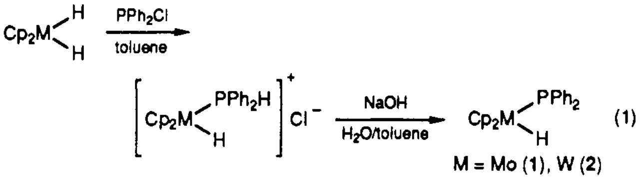
In the course of our studies on the chemistry of metallocene derivatives of the group 5 and 6 transition metals we decided to make a new family of phosphido-bridged di- or polymetallic compounds. The simplest potential precursors for such polymetallics may be of the type $Cp_2M(PR_2)_2$, $Cp_2M(L)PR_2$, or $Cp_2M(H$ 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.



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 $Cp_2Mo\text{–}PMe_3$.[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 $Cp(CO)_2(PMe_3)M\text{–}PPh_2$ (metal(II), d^4), where it is equal to 24 ppm.[14] This indicates that the phosphorus nuclei

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