$R = 0.044$. Successive Fourier synthesis calculated with reflections having $\sin \theta/\lambda < 0.5$ Å^{-1} showed 19 of the 27 H atoms, the remainder being geometrically placed. The final refinement cycles, with the H atoms held invariant, yielded a final R value of 0.038 ($R_W = 0.044$). Unit weights were used, and no trend in ΔF vs. F_o or $\sin \theta/\lambda$ was observed.

Compound 3b. A yellow-orange, block-shaped crystal was used, and 4163 unique reflections were measured in a quadrant within the θ range $0 \leqslant \theta \leqslant 25$, of which 3493 were considered observed $[F_o^2 \geqslant 3\sigma(F_o^2)]$ after data reduction (Lorentz and polarization but no absorptions corrections were made) and used in the subsequent calculations. The Patterson map permitted the location of the Mo atom, and successive F_{obsd} Fourier synthesis provided the coordinates of the remaining non-H atoms. The refinement was carried out by full-matrix least-squares procedures (isotropic for the isopropyl group and phosphine carbon atoms; anisotropic for the rest) using unit weights as no bias on ΔF was appreciated. The final R value was 0.076 ($R_W = 0.080$).

Compound 3e. A yellow irregular-shaped crystal was studied, and 4044 unique reflections from it were measured up to $\theta = 28°$. Due to radiation damage, a progressive decrease in intensity occurred as revealed for the three periodically checked standard reflections. To minimize the effect, a time limit of 45 s was adopted for the final scan of a reflecting position. The data were scaled from the standard intensities variations (ca. 30% at the end of the collecting process) and corrected for Lorentz, polarization, and absorption[41] effects; 1907 reflections were considered observed ($I > 3\sigma(I)$) and used for structure solution and refinement. Three-dimensional Patterson and Fourier syntheses allowed location for all non-H atoms, and subsequent full-matrix least-squares refinement, using F's and unit weights, keeping the methyl carbon atoms isotropic, led to $R = 0.096$. The H atoms were included in the refinement with fixed contributions at their calculated positions.

In order to prevent bias on ΔF vs. F_o or $\sin \theta/\lambda$, the last steps of the refinement were carried out with weights[42] $w = 1/(a + b|F_o|)^2$, where $a = 5.91$, $b = -0.09$, if $|F_o| < 32$, and $a = 1.31$, $\beta = 0.06$, if $|F_o| \geqslant 32$. The final R values were $R = 0.093$ and $R_W = 0.093$.

Acknowledgment. We are very grateful to the Comisión Asesora de Investigación Científica y Técnica for continuous support of this work (to E.C. and E.G.-P.). R.A. acknowledges a research grant to the Ministerio de Educación y Ciencia.

Registry No. 1, 89711-40-0; **1**-$^{13}C_2$, 100790-42-9; **2**, 100790-43-0; **3a**, 94985-87-2; **3b**, 94985-86-1; **3c**, 94985-88-3; **3d**, 100790-44-1; **3e**, 100790-45-2; *cis*-$Mo(N_2)_2(PMe_3)_4$, 82044-78-8; $MoI_2(PMe_3)_4$, 82456-13-1; *cis*-$Mo(CO)_2(PMe_3)_4$, 30513-06-5; *cis*-$Mo(N_2)_2(PMe_2Ph)_4$, 32457-67-3; $[Mo(CO_3)(CO)(PMePh)_3]_2$, 55913-76-3.

Supplementary Material Available: Thermal parameters and observed and calculated structure factor amplitudes for Mo(S_2CO)$(CO)_2(PMe_3)_3$, $Mo(CO_2)_2$(CN-*i*-Pr)$(PMe_3)_3$, and Mo-$(CO_2)_2(CNCH_2Ph)(PMe_3)_3$ (Tables A–F) (75 pages). Ordering information is given on any current masthead page.

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Molecular Hydrogen Complexes of the Transition Metals. 3.[1] Preparation, Structure, and Reactivity of $W(CO)_3(PCy_3)_2$ and $W(CO)_3(P(i\text{-}Pr)_3)_2$, η^2-H_2 Complex Precursors Exhibiting M···H—C Interaction

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Abstract: The synthesis, reactivity, and molecular structures of coordinatively and electronically unsaturated complexes $M(CO)_3(PR_3)_2$ [M = Mo, W; R = Cy, *i*-Pr] are described. Ligands that bind reversibly to $W(CO)_3(PCy_3)_2$ include H_2, N_2, C_2H_4, H_2O, ROH, and thiophene; irreversibly bound ligands are MeCN, pyridine, NH_3, $CyNH_2$, and PR_3. The structures of $W(CO)_3(PCy_3)_2$ and $W(CO)_3(P(i\text{-}Pr)_3)_2$ involve incipient intramolecular oxidative addition of a distal phosphine C–H bond to the metal. The three-center M···H—C interaction in $W(CO)_3(PCy_3)_2$ has W–H(11a)–C(11) = 127.6°, W–C(11) = 2.945 (6) Å, and W–H(11a) ≅ 2.27 Å. Crystal data for $W(CO)_3(PCy_3)_2$ are the following: space group $P\bar{1}$, $a = 10.300$ (1) Å, $b = 12.675$ (2) Å, $c = 15.473$ (1) Å, $\alpha = 91.44$ (1)°, $\beta = 90.37$ (1)°, $\gamma = 103.99$ (1)°, $Z = 2$, ρ(calcd) = 1.34 g cm^{-3}, $R = 0.025$, 6211 reflections. Crystal data for $W(CO)_3(P\text{-}i\text{-}Pr_3)_2$ are the following: $P2_1/m$, $a = 8.425$ (1) Å, $b = 13.375$ (2) Å, $c = 12.039$ (2) Å, $\beta = 109.58$ (1)°, $Z = 2$, ρ(calcd) = 1.53 g cm^{-3}, $R = 0.034$, 2212 reflections. Since these molecules add dihydrogen to form stable η^2-H_2 complexes, they afford an unprecedented opportunity to observe both H–H and C–H bond activation at a single metal center.

Recently we reported the preparation and complete characterization of complexes in which a dihydrogen *molecule* is present as an η^2-bound ligand.[1] These species, of composition M-$(CO)_3(PR_3)_2(\eta^2\text{-}H_2)$ [M = Mo, W; R = cyclohexyl, isopropyl], were prepared at room temperature by addition of H_2 to solutions containing the formally five-coordinate, 16-electron complexes, $M(CO)_3(PR_3)_2$. The synthesis of the latter compounds from available reagents was reported in preliminary form several years ago.[2] We now report in full the properties and reactions of these unusual formally coordinatively and electronically unsaturated complexes, including full three-dimensional single-crystal X-ray diffraction analyses of $W(CO)_3(PCy_3)_2$ and $W(CO)_3(P(i\text{-}Pr)_3)_2$. The results of these investigations show that the stable form of these compounds involves incipient intramolecular oxidative addition of a distal phosphine C–H bond to the metal. The complexes thus join a rapidly expanding class of molecules possessing three-center M···H—C ("agostic") interactions,[3] although they present rare examples in which this type of interaction occurs in

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[1] (a) Part I: Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451. (b) Part II: Kubas, G. J.; Ryan, R. R.; Wrobleski, D. *J. Am. Chem. Soc.*, in press. (c) Part III: submitted to *J. Am. Chem. Soc.* (d) Kubas, G. J.; Ryan, R. R. *Polyhedron*, in press.

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Table I. Infrared Frequencies for $M(CO)_3(PR_3)_2$[a]

compound	$\nu(CO)$[b]	$\nu(CH)$
$Mo(CO)_3(PCy_3)_2$	1951, 1843, 1801	2710
$W(CO)_3(PCy_3)_2$[c]	1946, 1832, 1797	2670
$W(CO)_3(PCy_3)_2$[d]	1946, 1832, 1811	2542
$W(CO)_3[P(C_6D_{11})_3]_2$[d]	1948, 1832, 1810	
$Mo(CO)_3(PCy_2\text{-}i\text{-}Pr)_2$	1952, 1840, 1811	2613
$W(CO)_3(PCy_2\text{-}i\text{-}Pr)_2$	1946, 1829, 1803	2540
$Mo(CO)_3(P(i\text{-}Pr)_3)_2$	1952, 1850, 1823	2694
$W(CO)_3(P(i\text{-}Pr)_3)_2$	1945, 1831, 1801	2673

[a] Nujol mulls prepared in an argon-filled glovebag. [b] Bands of varying intensity were also observed at 1860–1870 cm^{-1} due to minor amounts of $M(CO)_4(PR_3)_2$ which display intense absorptions in this region. [c] Blue-purple form. [d] Violet form.

an *alkyl*phosphine ligand.[4] Furthermore, the complexes are the only ones of which we are aware, in which both H–H and C–H bond activation occurs.

Results

Synthesis, Properties, and Reactions of $M(CO)_3(PR_3)_2$. The formally 16-electron complexes[2] $M(CO)_3(PCy_3)_2$ (M = Mo, W; M ≠ Cr) are readily prepared in good yield from $M(CO)_3$(cycloheptatriene):

$$fac\text{-}M(CO)_3(\text{cycloheptatriene}) + 2PCy_3 \xrightarrow[\text{argon}]{Et_2O} mer,trans\text{-}M(CO)_3(PCy_3)_2 + C_7H_8 \quad (1)$$

For M = Mo, an intermediate rust-colored precipitate forms, elemental analysis of which did not correspond to a rational stoichiometry. The PCy_2-*i*-Pr analogues are prepared in hexane in similar fashion. The $P(i\text{-}Pr)_3$ complexes are not directly isolable by eq 1 and are best synthesized by removal of H_2 from $W(CO)_3(P(i\text{-}Pr)_3)_2(H_2)$[1] or N_2 from $[Mo(CO)_3(P(i\text{-}Pr)_3)_2]_2(N_2)$. The nature of the phosphine is absolutely critical to the success of the preparations. Smaller phosphines, such as PPh_3 and PPh_2Cy, give $M(CO)_3(PR_3)_3$.[5a] The reaction of $Mo(CO)_3(C_7H_8)$ with $P(NMe_2)_3$ in 1:3 ratio has been reported to give an off-white precipitate, from which was isolated a low yield of $Mo(CO)_4[P(NMe_2)_3]_2$.[5b] For PR_3 with R = *sec*-Bu, *t*-Bu, Bz, *o*-tolyl, and $SiMe_3$, as well as for PCy_2Ph, $P(t\text{-}Bu)_2Ph$, $P(OCy)_3$, and $(neo\text{-}C_5H_{12})_2PCH_2CH_2P(neo\text{-}C_5H_{12})$, the reactions do not proceed according to eq 1. Also $Cr(CO)_3$(benzene), $W(CO)_3$(mesitylene), or $W(CO)_3(NCMe)_3$ do not react with PCy_3 according to eq 1 although $M(CO)_3$(diglyme) does yield $Mo(CO)_3(PCy_3)_2(N_2)$ if N_2 is present. $Mo(CO)_3$(toluene) gives a rust-colored precipitate within 2 h, but conversion to $Mo(CO)_3(PCy_3)_2$ is incomplete even after a week.

The $M(CO)_3(PR_3)_2$ complexes are intensely colored, nearly black in the solid state and deep purple in solution. Their air-sensitivity varies with M (Mo > W) and R ($P(i\text{-}Pr)_3$ > PCy_2-*i*-Pr > PCy_3). The solids are indefinitely stable, but solutions slowly (weeks) decompose by disproportionation to the very stable $M(CO)_4(PR_3)_2$ at room temperature. Disproportionation occurs more rapidly in refluxing aromatic solvents. This explains why Moers and Reuvers[6] obtained $Mo(CO)_4(PCy_3)_2$ when they carried out reaction 1 at 60 °C in benzene (under *nitrogen*, presumably[6]).

Three ν(CO) bands (Table I) are observed for $M(CO)_3(PR_3)_2$ in accord with their meridional CO configuration. Most importantly, ν(CH) infrared absorptions assignable to the novel agostic C–H group[3] are observed at 2540–2710 cm^{-1} and are confirmed by the spectrum of $W(CO)_3[P(C_6D_{11})_3]_2$, which does not show a band in this region. IR also indicates that two forms of solid $W(CO)_3(PCy_3)_2$ can be prepared: a thermally unstable blue-purple form isolated from eq 1 with ν(C–H) = 2670 cm^{-1} and a violet form with ν = 2542 cm^{-1} obtained by heating the blue form. Solution electronic spectra (Figure 1) and ^1H NMR spectra of the two forms are identical, however.

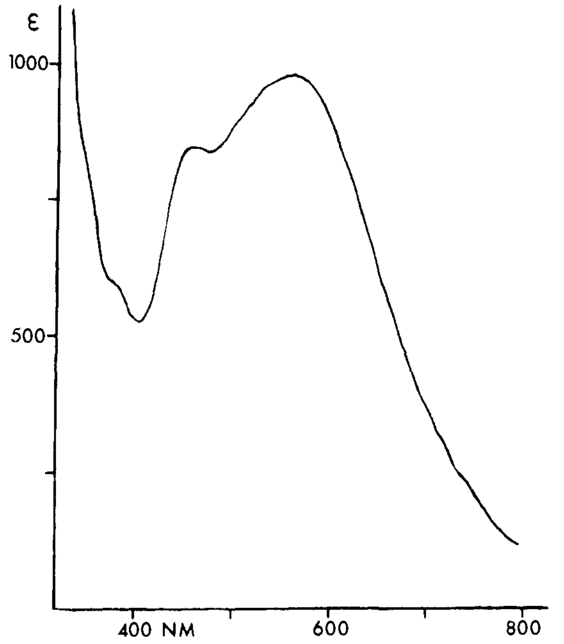

Figure 1. Electronic spectrum of 0.093 M $W(CO)_3(PCy_3)_2$ in toluene (λ = 566 (ϵ = 980) and 465 (ϵ = 850) nm).

^{13}C and ^1H NMR spectra of $W(CO)_3(P(i\text{-}Pr)_3)_2$ in toluene-d_8 suggest that the C—H···M bonding is fluctional at room temperature since neither low values for $J(^{13}C\text{-}H)$ nor high field chemical shifts for the agostic hydrogen are observed.[3] Furthermore, ^{31}P NMR shows only one signal, indicating that the alkyl groups on both phosphines interact with the metal in on–off fashion, so that chemically equivalent phosphines result. The protons on the alkylphosphine groups do not undergo exchange with the deuteria of benzene-d_6 or toluene-d_8 solvent, even at 80 °C, in contrast with $ReH_7(PCy_3)_2$[4a] and $RuH_4(PR_3)_3$.[4c]

$M(CO)_3(PR_3)_2$ readily "add" donor ligands, either reversibly or irreversibly, to give *mer,trans*-$M(CO)_3(PR_3)_2L$ (Table II). Crystal structure analyses have been reported for $Mo(CO)_3(P(i\text{-}Pr)_3)_2(SO_2)$[7] and $W(CO)_3(P(i\text{-}Pr)_3)_2(H_2)$.[1] A dinuclear formulation for the N_2 adduct with R = *i*-Pr is supported by infrared (ν(N≡N) absent) and Raman spectral evidence (Table II). The structure of a μ-N_2 complex containing $P(i\text{-}Pr)_3$ ligands, $[RhH(P(i\text{-}Pr)_3)_2]_2(\mu\text{-}N_2)$, has been reported.[8]

As with other unsaturated complexes, the ability to bind additional ligands is strongly influenced by steric factors. However, exhaustive studies of these effects for the group VIB metals are rare. The only other example of which we are aware is for $Mo(diphos)_2(CO)$;[9] the menu of ligands which this complex will add is also listed in Table II. Clearly, the steric requirements for $Mo(diphos)_2(CO)$ and $Mo(CO)_3(PR_3)_2$ are similar. For example, both complexes coordinate primary but not secondary or tertiary amines. Other ligands which fail to form isolable adducts with our complexes include propylene, cyclohexene, butadiene, C_2F_4, and furan. THF appears to form a very weakly bound rose-pink adduct, but a pure product could not be isolated because of the high lability of the THF. Certain strong ligands, such as phosphines and phosphites, will form adducts despite their relative bulkiness: other workers have even provided evidence for equilibrium amounts of $Mo(CO)_3(PCy_3)_3$ in the presence of excess PCy_3.[10] Also, in spite of the strong Lewis acidity of the metal

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(4) For other examples of C–H activation (e.g., H–D exchange) see, for instance: (a) Kelle Zeiher, E. H.; DeWit, D. G.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 7006. (b) Otsuka, S.; Yoshida, T.; Matsumoto, M.; Nakatsu, K. *J. Am. Chem. Soc.* **1976**, *98*, 5850. (c) Chaudret, B.; Poilblanc, R. *Organometallics* **1985**, *4*, 1722.

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Table II. Properties and Infrared Spectra of $M(CO)_3(PR_3)_2L$[a]

L	M	color	ν(CO)	ν(other)
		A. Complexes with Reversibly Bound L for R = Cy		
N_2	Mo	yellow	1956, 1841	2159[b]
N_2	W	yellow	1952, 1835	2120[b]
C_2H_4	Mo	yellow	1961, 1838	1240[c]
C_2H_4	W	yellow	1962, 1834	1208[c]
H_2O	Mo	yellow	1933, 1806, 1710	3660, 3515, 3420, 3305, 1674[d]
H_2O	W	yellow	1928, 1798, 1705	3668, 3640, 3500, 3290, 1674[d]
D_2O	Mo	yellow	1933, 1806, 1702	2718, 2583, 2510, 2439[e]
D_2O	W	yellow	1928, 1796, 1695	2715, 2700, 2570, 2425[e]
$H_2{}^{18}O$	W	yellow	1928, 1798, 1705	3650, 3624, 3500, 3385, 3285, 1674[d]
MeOH	W	red	1950, 1931, 1821, 1721	3415, 3170, 1013[f]
EtOH	W	red-orange	1941, 1806, 1744	3450, 3185, 1046[f]
acetone	Mo	lt. orange	1923, 1808, 1793, 1777	1658[g]
acetone	W	yellow-orange	1930, 1817, 1803, 1776	1673[g]
acetaldehyde	W	deep red	1931, 1812, 1798, 1774	1671[g]
Et_2S	Mo	yellow-orange	1946, 1813	
Et_2S	W	orange	1939, 1820	
thiophene	W	yellow-orange	1950, 1831, 1820	
		B. Complexes with Irreversibly Bound L for R = Cy		
MeCN	Mo	lt. yellow	1940, 1836, 1820, 1786	2293, 2260[h]
MeCN	W	yellow	1935, 1822, 1810, 1786	2294, 2260[h]
pyridine	Mo	yellow-orange	1933, 1801, 1761	
pyridine	W	red-orange	1925, 1791, 1757	
NH_3	Mo	orange	1937, 1815, 1787	
NH_2-*n*-Bu	Mo	lt. orange	1943, 1816	
NH_2-*n*-Bu	W	salmon pink	1936, 1811, 1788	
NH_2Cy	W	salmon pink	1932, 1804, 1796	
DMF	W	lt. orange	1925, 1801, 1775	1665[g]
py-O	Mo	red	1928, 1795, 1762	1221[i]
$P(OMe)_3$	W	lt. yellow	1945, 1827	
$P(OPh)_3$	W	yellow	1950, 1327	
PPh_2Me	W	yellow	1928, 1825, 1803	
P-*n*-Bu_3	W	yellow	1931, 1816, 1806	

C. Complexes for R = *i*-Pr

compound	color	ν(CO)	ν(other)
$[Mo(CO)_3(P(i\text{-}Pr)_3)_2]_2N_2$	yellow-orange	1953, 1863, 1849	
$[W(CO)_3(P(i\text{-}Pr)_3)_2]_2N_2$	orange	1948, 1872, 1836	1996, 1939, 472[j]
$Mo(CO)_3(P(i\text{-}Pr)_3)_2(H_2O)$	yellow	1936, 1822, 1807, 1725	3390, 1621[d]
$W(CO)_3(P(i\text{-}Pr)_3)_2(H_2O)$	yellow-orange	1925, 1800, 1717	3360, 3300, 3220, 1620[d]
$W(CO)_4(P(i\text{-}Pr)_3)_2$	light yellow	1870 (vs), 1920	

D. Ligands That Add to $Mo(diphos)_2(CO)$[k]

CO
nitriles
NH_3
4-aminopyridine
N_2
imidazoles
amides
amines
pyridine
ethylene

[a] Nujol mulls. [b] ν(NN). [c] ν(CC). [d] Bands due to H_2O. [e] Bands due to D_2O. [f] Bands due to ROH. [g] ν(CO) of L. [h] ν(CN). [i] ν(NO). [j] Raman bands for solid sample. The 1996- and 1939-cm^{-1} bands are very intense and *both* shift [to 1978 (*much weaker*) and 1896 cm^{-1}] on ^{15}N substitution, indicating strong coupling between ν(NN) and a carbonyl mode. [k] In approximate order of binding strengths, reading down.

atom in $M(CO)_3(PR_3)_2$ (i.e., stable adducts formed with H_2), it has been shown that CO_2 does not add, even in liquid CO_2.[11] A hydrido bicarbonate complex, $W(CO)_3(PCy_3)_2(H)(HCO_3)$, has been suggested as the result of reaction with "wet" CO_2.[11]

The yellow-orange thiophene complex, $W(CO)_3(PCy_3)_2(C_4H_4S)$, apparently represents one of the few examples[12] of coordination of this molecule via the sulfur atom; π-coordination is prohibited for steric reasons. The thiophene is very labile, and the complex is highly dissociated in solution (the Mo analogue could not be isolated). Less well defined adducts are obtained for some of the oxygen–donor ligands. Reaction of toluene solutions of $W(CO)_3(PCy_3)_2$ with aqueous formaldehyde gives an orange precipitate with a new IR band at 967 cm^{-1}. This is about 50 cm^{-1} lower than those reported for η^2-CH_2O complexes.[13] The insolubility of the complex in nonreactive solvents precludes further characterization. The use of THF as solvent or use of paraformaldehyde instead of aqueous CH_2O leads to other products. Infrared data indicate that the H_2O complex, $W(CO)_3(PCy_3)_2(H_2O)$, does not contain ordinary oxygen-bound H_2O,[11,14] and indeed it has been claimed[11] that oxidative addition to give a hydrido hydroxo species takes place. A band near 3660 cm^{-1} characteristic of a hydroxo ligand is present for $M(CO)_3(PCy_3)_2(H_2O)$ but is not seen for the P-*i*-Pr_3 analogue (Table II). The reaction of $M(CO)_3(PR_3)_2$ with O_2 leads to decomposition as does reaction with NO, N_2O, and CS_2. Treatment with HPF_6 in THF leads to disproportionation to $Mo(CO)_4(PCy_3)_2$.

Crystal Structure of $W(CO)_3(PCy_3)_2$. Crystals of the violet form of this compound are composed of discrete molecular units separated by van der Waals distances. The geometry of the molecule and atomic numbering scheme are depicted in Figure 2. Important interatomic distances and angles are collected in Table III.

Clearly from inspection of the distances and angles for this formally five-coordinate species, there appears to be a nearly *octahedral* distribution of ligands about the tungsten atom. The

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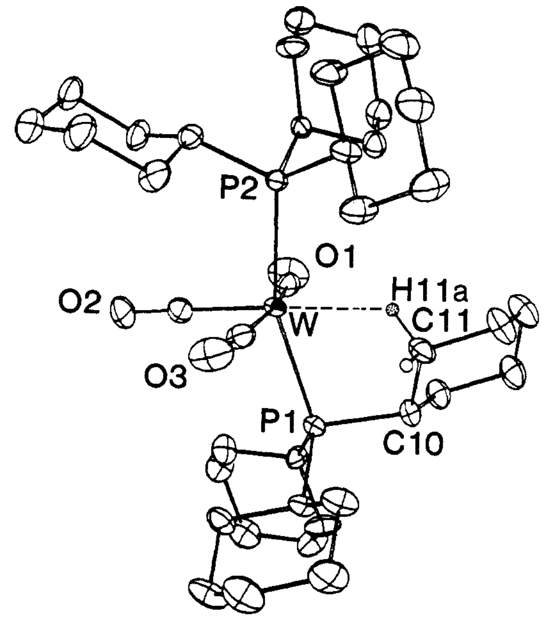

Figure 2. Ortep drawing of $W(CO)_3(PCy_3)_2$ (30% thermal ellipsoids).

Table III. Selected Interatomic Distances (Å) with esd's, $W(CO)_3(PCy_3)_2$

A. Distances from the Tungsten Atom			
W—P(1)	2.463 (1)	W—C(3)	2.006 (6)
W—P(2)	2.494 (1)	W···C(11)	2.945 (6)
W—C(1)	1.998 (6)	W—H(11a)[a]	2.27
W—C(2)	1.902 (6)		
B. Phosphorus–Carbon Distances			
P(1)—C(4)	1.867 (5)	P(2)—C(22)	1.854 (5)
P(1)—C(10)	1.865 (5)	P(2)—C(28)	1.881 (6)
P(1)—C(16)	1.856 (5)	P(2)—C(34)	1.873 (5)
C. Carbon–Oxygen Distances			
C(1)—O(1)	1.172 (7)	C(3)—O(3)	1.155 (7)
C(2)—O(2)	1.180 (7)		
D. "Cis" Angles about Tungsten			
P(1)—W—C(1)	88.5 (2)	P(2)—W—C(3)	90.3 (2)
P(1)—W—C(2)	102.4 (2)	P(2)—W···H(11a)	89.9
P(1)—W—C(3)	92.0 (2)	C(1)—W—C(2)	83.9 (2)
P(1)—W···H(11a)	71.0	C(1)—W···H(11a)	88.4
P(2)—W—C(1)	92.6 (2)	C(2)—W—C(3)	85.7 (3)
P(2)—W—C(2)	96.6 (2)	C(3)—W···H(11a)	101.8
E. "Trans" Angles about Tungsten			
P(1)—W—P(2)	160.94 (4)	C(2)—W···H(11a)	170.2
C(1)—W—C(3)	169.4 (2)		
F. Tungsten–Phosphorus–Carbon Angles			
W—P(1)—C(4)	122.0 (2)	W—P(2)—C(22)	117.3 (2)
W—P(1)—C(10)	99.0 (2)	W—P(2)—C(28)	115.9 (2)
W—P(1)—C(16)	119.8 (2)	W—P(2)—C(34)	112.4 (2)
G. Carbon–Phosphorus–Carbon Angles			
C(4)—P(1)—C(10)	103.3 (2)	C(22)—P(2)—C(28)	104.1 (3)
C(4)—P(1)—C(16)	104.4 (2)	C(22)—P(2)—C(34)	102.0 (2)
C(10)—P(1)—C(16)	105.7 (2)	C(28)—P(2)—C(34)	103.1 (2)
H. Angles Involving the W···H—C System[a]			
C(11)—W···H(11a)	14.7	W···H(11a)—C(11)	127.6
W···C(11)—H(11a)	37.7		
I. Tungsten–Carbon–Oxygen Angles			
W—C(1)—O(1)	171.4 (5)	W—C(3)—O(3)	171.5 (6)
W—C(2)—O(2)	178.2 (5)		
J. Phosphorus–Carbon–Carbon Angles			
P(1)—C(4)—C(5)	110.8 (4)	P(2)—C(22)—C(23)	111.6 (4)
P(1)—C(4)—C(9)	114.1 (4)	P(2)—C(22)—C(33)	113.5 (4)
P(1)—C(10)—C(11)	104.7 (4)	P(2)—C(28)—C(29)	115.5 (4)
P(1)—C(10)—C(15)	115.3 (4)	P(2)—C(28)—C(39)	114.0 (4)
P(1)—C(16)—C(17)	113.8 (4)	P(2)—C(34)—C(27)	111.8 (3)
P(1)—C(16)—C(21)	114.2 (3)	P(2)—C(34)—C(35)	119.5 (4)

[a] Distances involving H(11a) are based upon idealized coordinates for this atom.

sixth coordination site of the distorted octahedron is occupied by a hydrogen atom of one cyclohexyl group, H(11a). This hydrogen atom is almost directly opposite carbonyl group C(2)–O(2), the "trans" angle about the tungsten atom being 170.2°. Of the remaining carbonyl groups, one, C(1)–O(1), is oriented nearly perpendicular to the tungsten–H(11a) bond, with C(1)–W–H(11a) = 88.4°, while the other is directed away from the activated cyclohexyl group, with C(3)–W–H(11a) = 101.8°. This enlarged angle occurs in order to minimize repulsion between C(3)–O(3) and the other hydrogen atom [H(11b)] associated with the carbon atom in the active site. As a result, the *trans*-carbonyl groups are separated by an angle of 169.4 (2)°. The three carbonyl carbon atoms and the coordinated hydrogen atom form a least-squares plane, from which the deviation of these four atoms ranges from only −0.03 to +0.03 Å. The tungsten atom lies only −0.069 Å from this plane.

The smallest "cis" angle about the tungsten atom, 71.0°, is subtended by H(11a) and atom P(1). This angle represents what is essentially the "bite" angle of a five-membered chelate ring, which includes the tungsten atom, P(1), two cyclohexyl carbon atoms, and H(11a). Within the chelate tungsten ring the tungsten–phosphorus–carbon (ipso) angle is severely contracted relative to (a) other W–P–C angles within the same phosphine ligand and (b) W–P–C angles in the other, nonchelating phosphine. The two noncoordinated cyclohexyl groups attached to phosphine(1) have larger than normal angles, with W–P(1)–(C4) = 122.0 (2)° and W–P(1)–C(16) = 119.8(2)°, while the chelating group has W–P–C(10) = 99.0 (2)°. The highly distorted geometry about P(1) is evidence that the tungsten atom is exerting a strong *attractive* force upon the H(11a) atom. Note that this is in distinct contrast with several other coordinatively unsaturated complexes in which hydrogen atoms from coordinated phosphine groups are located near the open site about the metal. For example, the triphenylphosphine ligands in both $RhHCl(SiCl_3)(PPh_3)_2$[15] and $RuCl_2(PPh_3)_3$[16] have normal, undistorted geometries. Ibers et al.[16] attribute the particular location of ring hydrogen atoms near the metal in these complexes to geometric effects, rather than any true metal–hydrogen bonding interactions. The same is apparently true in the case of the $Mo(CO)(diphos)_2$ molecule.[17]

Attempts at refinement of H(11a) in the structure of $W(CO)_3(PCy_3)_2$ were unsuccessful. The position in which the activated hydrogen atom was included is based upon idealized tetrahedral geometry about the carbon atom to which it is attached and $d(C–H) = 0.95$ Å. This distance provides the best discription of the electron density distribution[18] but typical internuclear C–H distances are about 1.08 Å, and activated C–H distances have been found to be as long as 1.16 Å.[19] The tungsten-H(11a) distance thus obtained is 2.27 Å. Although this distance is outside the range that neutron diffraction studies have indicated for both metal–metal bridging and terminal tungsten–hydride bonds,[20] it still must represent a substantial interaction. An interesting comparison may be made with $[Et_2B(pz)_2][\eta^3\text{-}CH_2C(Ph)CH_2](CO)_2Mo$[21] (pz = 1-pyrazolyl) since appropriate bonding radii for tungsten and molybdenum are nearly the same. In that structure the Mo···H distance is ~2.27 Å (with $d(C–H) = 0.97$ Å). A more reasonable C–H distance (1.10 Å), it was noted, brought the Mo–H separation to ~2.15 Å. In $W(CO)_3(PCy_3)_2$

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Table IV. Selected Interatomic Distances and Angles in the $W(CO)_3(P(i\text{-}Pr)_3)_2$ Molecule

A. Distances from the Tungsten Atom			
W—P(1)	2.493 (2)	W—C(2)	1.899 (10)
W—P(2)	2.458 (2)	W···C(12)	3.027 (10)
W—C(1)	1.998 (8)		
B. Phosphorus–Carbon Distances			
P(1)—C(3)	1.857 (9)	P(2)—C(8)	1.873 (11)
P(1)—C(4)	1.860 (7)	P(2)—C(9)	1.863 (2)
C. Carbon–Oxygen Distances and Tungsten–Carbon–Oxygen Angles			
C(1)—O(1)	1.155 (10)	C(2)—O(2)	1.174 (12)
W—C(1)—O(1)	172.6 (8)	W—C(2)—O(2)	177.5 (9)
D. "Cis" Angles about Tungsten			
P(1)—W—C(1)	87.0 (2)	P(2)—W—C(2)	99.6 (3)
P(1)—W—C(2)	97.6 (3)	C(1)—W—C(2)	85.1 (2)
P(2)—W—C(1)	94.4 (2)		
E. "Trans" Angles about Tungsten			
P(1)—W—P(2)	162.78 (7)	C(2)—W···C(12)	157.3 (3)
C(1)—W—C(1′)	167.8 (4)		
F. Tungsten–Phosphorus–Carbon and Carbon–Phosphorus–Carbon Angles			
W—P(1)—C(3)	115.0 (3)	W—P(2)—C(8)	122.6 (4)
W—P(1)—C(4)	113.4 (2)	W—P(2)—C(9)	99.4 (4)
C(3)—P(1)—C(4)	101.9 (3)	C(8)—P(2)—C(9)	118.1 (4)
C(4)—P(1)—C(4′)	110.0 (4)	C(8)—P(2)—C(8′)	97.3 (5)

extension of d(C–H) to 1.08 Å brings the tungsten–H(11a) distance to 2.20 Å. Metal–carbon distances are also of relevance: in the Mo complex this distance is 3.06 Å while in $W(CO)_3(PCy_3)_2$ the W–C(11) separation is significantly shorter, at 2.945 (6) Å.[22] The overall geometry of the M···H—C fragment in these systems is similar, with M-H-C angles of 136 (6)° for M = Mo and M-H-C = 127.6° for M = W. This geometry contrasts with that observed for the activated alkyl C-H bond in $[Fe(P(OMe)_3)_3(\eta^3\text{-}C_8H_{13})][BF_4]$,[19] for which neutron diffraction studies have shown Fe-H-C = 99.4 (2)°. A neutron analysis of $Mo(CO)_3(PCy_3)_2$ is currently underway at the Los Alamos Pulsed Spallation Neutron Facility (WNR/PSR).

Another interesting feature of the structure arising from the presence of a M···H—C interaction is the difference in tungsten–phosphorus bond lengths: that for W–P(1) (2.463 (1) Å) is shorter than that for the noninteracting group, for which W–P(2) = 2.494 (1) Å.

Crystal Structure of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2$. Distances and angles are listed in Table IV. The molecule resides on a crystallographic mirror plane of symmetry, which contains atoms labeled W, P(1), P(2), C(1), O(1), C(3), C(12), and C(13) (see Figure 3). Carbon atom C(9) is located approximately 0.48 Å from and is disordered across the plane. Additionally, several other atoms associated with phosphine group 2 display excessively large thermal motion, indicating disorder, although resolution of disordered components was not possible. Phosphine group P(1) is not disordered; in fact all eleven unique hydrogen atoms associated with this ligand were located. Generally speaking, the low R factor and small bond length σ's attest to a relatively high level of precision for the structure. Although the disorder hampers precise description of the crucial activated portion of the molecule, several important structural features of the complex are readily discernable. We note the following:

(1) The overall geometry about the tungsten atom is similar to that in $W(CO)_3(PCy_3)_2$, being best described as a distorted octahedron. Within the framework of this description, "cis" angles about the tungsten atom subtended from the nonactivated phosphine ligand to the carbonyl ligands are in the range 85.1 (2)–97.6 (3)°. The carbonyl ligands again encroach upon one another, being separated by the angles C(1)–W–O(1) = C(1′)–W–O(1′) = 85.1 (2)° and C(1)–W–C(1′) = 167.8 (4)°. The P–W–P angle is 162.8 (1)°.

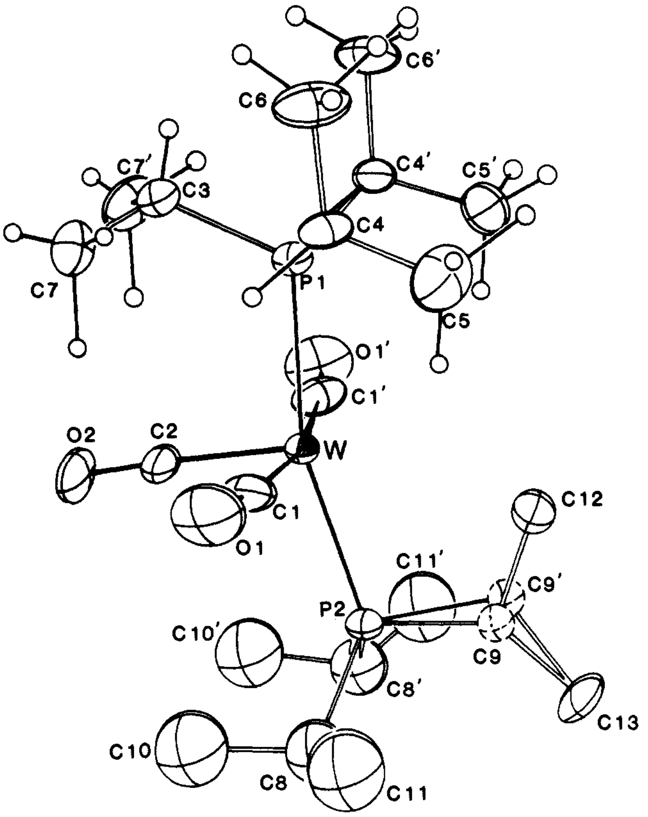

Figure 3. Ortep drawing of $W(CO)_3(P(i\text{-}Pr)_3)_2$ (30% thermal ellipsoids).

(2) As in $W(CO)_3(PCy_3)_2$, the tungsten–phosphorus bond length to the activated phosphine is shorter, with W–P(2) = 2.458 (2) Å as compared with W–P(1) = 2.493 (2) Å.

(3) Distortion within the activated alkyl group occurs, as in $W(CO)_3(PCy_3)_2$. The W–P(2)–C(9) angle is only 99.4 (4)° whereas the same type of angles about atom P(1) range from 113.4 (2) to 115.0 (3)°. The carbon atom involved in the M···H—C interaction, C(12), is located 3.03 (1) Å from the tungsten atom (cf. 2.94 Å in $W(CO)_3(PCy_3)_2$; vide supra).

Discussion

The synthetic route to and the stability of the formally coordinatively unsaturated complexes, $M(CO)_3(PR_3)_2$, is largely a result of the well-known steric demands imposed by bulky phosphine ligands. Nevertheless, coordinatively and electronically unsaturated complexes of zero-valent molybdenum and tungsten are rare. In fact, only one other example of such a species exists for tungsten, $W(CO)_3(P(Me_2pz)_2Ph)$.[22a] In all such complexes, except for $Mo[Ph_2B(pz)_2](CO)_2(\eta^3\text{-}CH_2CH(CH_3)CH_2)_2$,[22b] the metal gains additional electron density through intramolecular interaction with a distal ligand C–H or C–C bond. The strength of this interaction, indeed the reason it does not occur at all in $Mo[Ph_2B(pz)_2](CO)_2(\eta^3\text{-}CH_2CH(CH_3)CH_2)$, is dependent upon conformational barriers within the ligand. The five-coordinate complex most similar to the species reported herein is Mo(diphos)$_2$(CO), the only other complex in which only carbonyl and phosphine ligands are present.[9,17] As noted above, the chemistry of Mo(diphos)$_2$(CO) is quite similar to that of $W(CO)_3(PCy_3)_2$ and $W(CO)_3(P(i\text{-}Pr)_3)_2$. The chemistry of the Mo-pyrazolylphosphine complexes is, however, different. For example, $PhP(Me_2pz)_2M(CO)_3$ reacts *reversibly* with CO and not at all with N_2, H_2, or C_2H_4.[23]

The most remarkable feature of the chemistry of the complexes reported herein results from their reaction with H_2. Thus, the

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(22) Similar or shorter M–C distances also have been reported in other group 6 16-electron complexes, but CH···M bonding is not involved: (a) Cobbledick, R. E.; Dowdell, L. R. J.; Einstein, F. W. B.; Hoyano, J. K.; Peterson, L. K. *Can J. Chem.* **1979**, *57*, 2285. (b) Cotton, F. A.; Frenz, B. A.; Murrillo, C. A. *J. Am. Chem. Soc.* **1975**, *97*, 2118.

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$M(CO)_3(PR_3)_2$ complexes represent unique formally five-coordinate species which show *both* C–H bond activation *and* the ability to add molecular hydrogen forming stable η^2-H_2 complexes. As such, they make an unprecedented experimental comment on the relative competitive binding ability for these two types of ligands. Furthermore, one can conclude that complexes displaying agostic interactions will be excellent candidates for molecular hydrogen coordination.

A recent theoretical analysis of C–H and H–H bond activation in transition-metal complexes, by Saillard and Hoffman,[24] has focused on the relative ligand binding strengths of H_2 vs. C–H (C–H in the form of methane). The extended-Hückel calculations seem to indicate that η^2-H_2 is a better ligand than CH_4 toward a prototype $Cr(CO)_5$ fragment, based upon total energy and overlap populations. Furthermore, it was noted that a "perpendicular" approach of CH_4 (binding as a η^1 ligand through hydrogen) is a more stable geometry than one with the M–H–CH_3 angle less than 180°. The present study supports the view that H_2 can displace R–H–M interactions; note, however, that the W–H(11a)–C(11) angle is only 126.5°. Many metal surfaces are known on which both C–H and H–H activation occur. The present work will provide a valuable benchmark for future efforts to understand these important processes.

An interesting question is whether η^2-H_2 bonding will occur upon addition of hydrogen to other complexes similar in structure to $W(CO)_3(PCy_3)_2$, such as $RuCl_2(PPh_3)_3$, $RhHCl(SiCl_3)(PPh_3)_2$ and, especially, $Mo(diphos)_2(CO)$.

Experimental Section

All syntheses were carried out with use of Schlenk-line techniques and argon atmospheres. $Mo(CO)_3$(cycloheptatriene), $W(CO)_6$, and most phosphines were obtained from Strem Chemicals, Inc., Newburyport, MA, and used as received ($Mo(CO)_3(C_7H_8)$ was resublimed). PCy_2-*i*-Pr,[1c] $W(CO)_3$(cycloheptatriene),[25] and $Mo(CO)_3$(diglyme)[26] were prepared according to literature methods, and $P(C_6D_{11})_3$ was custom-synthesized by MSD Isotopes, Montreal, Canada. Infrared spectra were recorded as Nujol mulls on a Perkin Elmer 683, NMR spectra were measured on Varian EM-390 and Bruker WM-300 instruments, and elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Preparation of $M(CO)_3(PR_3)_2$ (M = Mo, W; R_3 = Cy_3, Cy_2-*i*-Pr). A mixture of 1.876 g (6.89 mmol) of $Mo(CO)_3(C_7H_8)$, 3.96 g (14.12 mmol) of PCy_3, and 30 mL of argon-saturated Et_2O was stirred vigorously under argon. After a few minutes a bulky red-orange precipitate[27] formed and the suspension was stirred overnight or until all of the orange material was converted to a microcrystalline deep purple-brown solid. The latter was then collected on a frit, washed thoroughly with 1:1 ether–heptane, and dried in vacuo. The yield of $Mo(CO)_3(PCy_3)_2$ was 3.76 g (74%).

Preparation of $W(CO)_3(PCy_3)_2$ is analogous except that an intermediate precipitate does not form and the reaction is complete within 1.5 h to give a 77% yield. The reaction can also be carried out in 4:1 hexane–toluene. The product, which is blue-purple in color when finely ground, thermally isomerizes (55 °C, toluene solution, 0.5 h, or on long-term storage) to a violet form with a different IR spectrum (Table I). The preparations for R_3 = Cy_2-*i*-Pr were carried out in hexane (20 mL) overnight with 2.5 mL of PCy_2-*i*-Pr and 4.15 mmol of $M(CO)_3(C_7H_8)$. The complexes are moderately air-sensitive in the solid state and very air-sensitive in solution. They are moderately soluble in benzene and toluene, giving intense purple coloration, slightly soluble in alkanes, and react with most nonhydrocarbon solvents to give adducts or decomposition. IR spectra (Table I) show the presence of small amounts of $M(CO)_4(PR_3)_2$ produced by disproportionation and/or minor oxidation. ^1H NMR (benzene-d_6, 90 MHz) of $W(CO)_3(PCy_3)_2$, δ 2.26 (6 H), 1.85 (12 H), 1.4 (48 H); $Mo(CO)_3(PCy_2$-*i*-Pr), δ 2.10, 1.77, 1.55, 1.18 (d of d, J = 6.5 Hz, $J(^1H-^{31}P)$ = 13 Hz).

Preparation of $W(CO)_3(PCy_3)_2$ from $W(CO)_3(PCy_3)_2(H_2)$. A 50-mL flask containing a slurry of $W(CO)_3(PCy_3)_2(H_2)$[1,2] (2 g) in toluene (15 mL) under argon was connected to a vacuum line via a reflux condenser. The argon pressure was adjusted to ca. 100 torr and the slurry was heated to reflux (ca. 55 °C), driving off H_2 from the complex. The argon atmosphere was periodically replaced until all the H_2 was removed, resulting in the formation of an intense purple solution. The $W(CO)_3(PCy_3)_2$ was isolated as for the $P(i\text{-}Pr)_3$ congener, and IR showed it was the violet isomer.

Table V. Experimental Data for the X-ray Diffraction Analyses of $W(CO)_3(PCy_3)_2$ and $W(CO)_3(P(i\text{-}Pr)_3)_2$

(A) Crystal Parameters

compd	$W(CO)_3(PCy_3)_2$	$W(CO)_3(P(i\text{-}Pr)_3)_2$
crystal system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/m$
a, Å	10.300 (1)	8.4250 (7)
b, Å	12.675 (2)	13.375 (2)
c, Å	15.473 (1)	12.039 (2)
α, deg	91.44 (1)	
β, deg	90.37 (1)	109.58 (1)
γ, deg	103.99 (1)	
V, Å^3	1959.4	1278.1
Z	2	2
mol wt	828.7	587.9
ρ(calcd), g cm^{-3}	1.34	1.53
abs coeff, cm^{-1}	31.2	47.5
no. of refl, $I \geq 2\sigma(I)$	6211	2212
extinction parameter, mm	$1.1 (3) \times 10^{-6}$	$1.14 (8) \times 10^{-5}$

(B) Measurement of Data

diffractometer	Enraf-Nonius CAD4	
radiation	Mo $K\alpha$ (λ = 0.7093 Å)	
monochromator	highly oriented graphite	
reflections measd	$\pm h, +k, l$	$\pm h, k, l$
2θ range, deg	2.0–50.0	
scan type	coupled θ (crystal)–2θ (detector)	
scan range, deg	1.0 + 0.35 tan θ	
scan speed, deg min	variable, 2–6	

Preparation of $W(CO)_3(P(i\text{-}Pr)_3)_2$. A solution of $W(CO)_3(P(i\text{-}Pr)_3)_2(H_2)$[1] in nonane or decane (ca. 1 g/10 mL) was filtered under hydrogen and pumped in vacuo at 30–40 °C. The reversibly coordinated H_2 was removed, and $W(CO)_3(P(i\text{-}Pr)_3)_2$ precipitated in nearly quantitative yield as nearly black microcrystals. The latter were collected on a frit and dried in vacuo.

$W(CO)_3(P(i\text{-}Pr)_3)_2$ is very air-sensitive, nearly insoluble in hexane, and soluble in aromatic hydrocarbons. ^1H NMR (toluene-d_8, 90 MHz) δ 2.40 (sept, J = 6.7 Hz), 1.13 (d of d, J = 6.7 Hz, $J(^1H-^{31}P)$ = 13 Hz). $^{31}P\{^1H\}$ NMR (toluene-d_8, 121.5 MHz, H_3PO_4 reference) δ 45.6 (s), 45.6 (d), $J(^{31}P-^{183}W)$ = 305 Hz). ^{13}C NMR (toluene-d_8, 75.5 MHz) δ 223.5 (s, CO), 216.5 (t, $J(^{31}P-^{13}C)$ = 6.3 Hz, 2 CO), 29.6 (d, $J(^{13}C-^1H)$ = 126 Hz, CH_3CHCH_3), 19.0 (q, $J(^{13}C-^1H)$ = 126 Hz, CH_3). $^{13}C\{^1H\}$ NMR (toluene-d_8, 75.5 MHz) δ 223.5 (s, CO), 216.5 (t, $J(^{31}P-^{13}C)$ = 6.3 Hz, 2 CO), 29.6 (t, $J(^{31}P-^{13}C)$ = 9.4 Hz, CH_3CHCH_3), 19.0 (s, CH_3). The $^{31}P\{^1H\}$ spectrum also displayed a peak at 25.9 ppm [J(PW) = 262 Hz] presumably due to $W(CO)_4(P(i\text{-}Pr)_3)_2$. Integration showed that the area of this peak was ca. 8% of the total area.

Preparation of $[M(CO)_3(P(i\text{-}Pr)_3)_2]_2(\mu\text{-}N_2)$ (M = Mo, W). A mixture of $M(CO)_3(C_7H_8)$ (6 mmol), $P(i\text{-}Pr)_3$ (2.5 mL), and toluene (8 mL) was stirred for 5 h under N_2. Heptane (15 mL) was added and stirring was continued for 30 min to complete precipitation. The solid was collected, washed with 10:1 heptane–toluene, and dried in a stream of N_2. Yields were ca. 60%.

Evidence for the dinuclear formulation includes elemental analysis (Table Is), the absence of ν(NN) bands in the IR spectra, and the presence of strong Raman bands assignable to bridging N_2 (Table II).

Preparation of $Mo(CO)_3(P(i\text{-}Pr)_3)_2$. A slurry of $[Mo(CO)_3(P(i\text{-}Pr)_3)_2]_2(\mu\text{-}N_2)$ (0.434 g) in 10 mL of 1:1 toluene–nonane was evacuated at room temperature. A deep purple solution resulted, followed by crystallization of deep red-purple $Mo(CO)_3(P(i\text{-}Pr)_3)_2$. This was collected on a frit and dried in vacuo. The tungsten analogue could not be prepared by this route.

Preparation of $M(CO)_3(PCy_3)_2L$ (M = Mo, W; L = N_2, C_2H_4). A mixture of $M(CO)_3(C_7H_8)$ (1 mmol), PCy_3 (2.05 mmol), and toluene (4 mL) was stirred under an atmosphere of L for 3 h in the case of M = Mo and for 30 min for M = W (for larger scales, these times are quadrupled). A yellow precipitate of $M(CO)_3(PCy_3)_2L$ formed, and precipitation was completed by addition of heptane (10 mL) and further stirring for ca. 45 min in the presence of L. The product was collected, washed with 3:1 heptane–toluene, and dried in a stream of L (yield 65–80%). The complexes were stored and handled at all times under an atmosphere of L.

The complexes were also prepared by addition of L to toluene solutions of $M(CO)_3(PCy_3)_2$. Solid $M(CO)_3(PCy_3)_2L$ slowly decomposes in air

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(27) Anal. Found: C, 62.3; H, 8.9; P, 8.5; Mo, 9.6. The P/Mo ratio was 2.7. IR showed seven carbonyl bands in the range 1790–2010 cm^{-1} (Nujol mull), indicating the presence of more than one species.

Table VI. Fractional Coordinates and Equivalent Isotropic Thermal Parameters for $W(CO)_3(PCy_3)_2$

atom	*x*	*y*	*z*	*B*
W(1)	0.18496 (2)	0.20612 (2)	0.21462 (1)	2.75[a]
P(2)	0.3075 (1)	0.1900 (1)	0.3513 (1)	2.81[a]
O(2)	0.0942 (5)	−0.0393 (4)	0.1701 (3)	6.99[a]
C(1)	0.0089 (6)	0.1800 (4)	0.2740 (3)	3.81[a]
C(3)	0.3492 (6)	0.2043 (5)	0.1462 (4)	4.42[a]
C(5)	0.1718 (6)	0.2021 (5)	−0.0576 (4)	4.49[a]
C(7)	0.3699 (7)	0.2976 (7)	−0.1445 (4)	7.21[a]
C(9)	0.3073 (6)	0.3870 (5)	−0.0085 (4)	4.79[a]
C(11)	0.2254 (6)	0.4434 (5)	0.2033 (4)	4.35[a]
C(13)	0.1303 (8)	0.5664 (6)	0.3009 (4)	6.63[a]
C(15)	−0.0169 (6)	0.4453 (5)	0.1906 (4)	4.70[a]
C(17)	−0.1408 (6)	0.1116 (5)	0.0580 (4)	4.42[a]
C(19)	−0.3415 (6)	0.1338 (6)	−0.0280 (4)	6.05[a]
C(21)	−0.1431 (6)	0.2914 (6)	−0.0087 (4)	5.32[a]
C(23)	0.4712 (7)	0.0574 (6)	0.2873 (4)	6.36[a]
C(25)	0.4286 (9)	−0.1436 (6)	0.3145 (5)	8.67[a]
C(27)	0.1479 (6)	0.2871 (4)	0.4624 (3)	4.29[a]
C(29)	0.5546 (7)	0.2824 (5)	0.4457 (4)	5.51[a]
C(31)	0.7326 (7)	0.4394 (5)	0.3945 (4)	5.72[a]
C(33)	0.2658 (6)	−0.0390 (4)	0.3686 (4)	4.67[a]
C(35)	0.2495 (7)	0.1521 (5)	0.5357 (4)	5.24[a]
C(37)	0.0793 (7)	0.2285 (5)	0.6141 (4)	5.26[a]
C(39)	0.5278 (6)	0.3608 (5)	0.3024 (4)	5.22[a]
P(1)	0.0854 (1)	0.2859 (1)	0.0951 (1)	2.82[a]
O(1)	−0.0973 (5)	0.1514 (5)	0.3045 (3)	7.64[a]
O(3)	0.4367 (5)	0.1897 (5)	0.1050 (3)	8.38[a]
C(2)	0.1312 (6)	0.0546 (4)	0.1869 (4)	4.19[a]
C(4)	0.1678 (5)	0.3099 (4)	−0.0122 (3)	3.47[a]
C(6)	0.2327 (7)	0.2213 (7)	−0.1474 (4)	6.67[a]
C(8)	0.3651 (7)	0.4034 (7)	−0.0994 (4)	6.63[a]
C(10)	0.1047 (5)	0.4260 (4)	0.1419 (3)	3.38[a]
C(12)	0.2563 (7)	0.5538 (5)	0.2545 (4)	5.82[a]
C(14)	0.0153 (7)	0.5561 (5)	0.2383 (4)	6.02[a]
C(16)	−0.0952 (5)	0.2354 (4)	0.0683 (3)	3.06[a]
C(18)	−0.2935 (6)	0.0761 (5)	0.0469 (4)	5.23[a]
C(20)	−0.2960 (6)	0.2544 (5)	−0.0187 (4)	5.67[a]
C(22)	0.3752 (5)	0.0680 (5)	0.3620 (3)	3.93[a]
C(24)	0.5350 (8)	−0.0381 (6)	0.3020 (5)	7.58[a]
C(26)	0.3302 (8)	−0.1332 (5)	0.3851 (5)	6.20[a]
C(28)	0.4538 (6)	0.3069 (5)	0.3797 (3)	4.19[a]
C(30)	0.6611 (7)	0.3856 (6)	0.4719 (4)	6.39[a]
C(32)	0.6345 (7)	0.4634 (6)	0.3302 (5)	6.56[a]
C(34)	0.1987 (5)	0.1822 (4)	0.4486 (3)	2.99[a]
C(36)	0.1345 (7)	0.1265 (5)	0.6012 (4)	5.59[a]
C(38)	0.0326 (7)	0.2618 (5)	0.5293 (4)	5.20[a]
H(11A)[b]	0.2118 (0)	0.3869 (0)	0.2433 (0)	5.00 (0)

[a] Anisotropic temperature factors are listed in supplementary data. [b] Calculated coordinates for hydrogen atom H(11A); see text.

and reversibly loses L in vacuo (at room temperature dinitrogen loss is very slow). The sparingly soluble adducts are reactive toward most nonhydrocarbon solvents. The dinitrogen complexes retain ca. 0.25 mol of lattice solvent.

Preparation of $M(CO)_3(PCy_3)_2L$ (M = Mo, W; L = Nitrogen, Phosphorus, Oxygen, and Sulfur Donor Ligands). Toluene solutions of $M(CO)_3(PCy_3)_2$ (ca. 0.1 M) under argon were treated with a small excess of donor ligand. After about 15 min of stirring, the resulting precipitates were collected by filtration, washed with 1:1 toluene–heptane, and dried briefly in vacuo. In the case of L = H_2O or ROH, the wash solvent contained a small amount of L, and the complexes were dried in a stream of argon containing L. Yields ranged from 80 to 95%; properties of the complexes are given in Table II and elemental analysis in Table Is (the H_2O complexes appeared to contain H_2O of solvation).

Although the great majority of the adducts were sparingly soluble, the tungsten complexes with L = P donor, NH_2-*n*-Bu, thiophene, and Et_2S were relatively soluble in toluene, and their isolation required partial solvent removal and/or heptane addition. For solubility reasons also, $W(CO)_3(PCy_3)_2$(acetone) and $Mo(CO)_3(PCy_3)_2(Et_2S)$ were prepared from suspensions of $M(CO)_3(PCy_3)_2$ in Et_2O. ^1H NMR of $W(CO)_3(PCy_3)_2$(thiophene) in benzene-d_6 showed a high degree of dissociation: the thiophene and PCy_3 signals were nearly identical with those for free thiophene and $W(CO)_3(PCy_3)_2$. Integration showed a ratio of Cy: thiophene = 6.3 (theory 6.0).

The reaction of $W(CO)_3(PCy_3)_2$ with aqueous formaldehyde in toluene rapidly gave an insoluble orange precipitate (ν(CO) = 1975, 1878, and 1845 cm^{-1}) which did not reconvert to $W(CO)_3(PCy_3)_2$ in vacuo.

Table VII. Fractional Coordinates and Thermal Parameters for $W(CO)_3(P\text{-}i\text{-}Pr_3)_2$

atom	*x*	*y*	*z*	*B*
W(1)	0.11304 (4)	0.25000 (0)	0.30136 (2)	3.34[a]
P(2)	0.2077 (3)	0.2500 (0)	0.5181 (2)	3.89[a]
O(2)	0.4554 (10)	0.2500 (0)	0.2667 (8)	12.74[a]
C(2)	0.3218 (12)	0.2500 (0)	0.2771 (8)	6.75[a]
C(4)	−0.2052 (9)	0.1360 (5)	0.0462 (5)	4.98[a]
C(6)	−0.3126 (12)	0.1250 (0)	−0.0848 (6)	7.60[a]
C(12)	−0.1368 (12)	0.2500 (0)	0.4349 (8)	6.32[a]
C(8)	0.3331 (14)	0.1449 (8)	0.6085 (10)	7.98 (24)
C(10)	0.4882 (22)	0.1272 (13)	0.5756 (15)	12.90 (47)
H(1)	−0.0397 (0)	0.2500 (0)	−0.0859 (0)	5.00 (0)
H(3)	−0.3658 (0)	0.0713 (0)	−0.0911 (0)	5.00 (0)
H(5)	−0.4195 (0)	0.1771 (0)	−0.1150 (0)	5.00 (0)
H(7)	−0.3660 (0)	0.0661 (0)	0.0978 (0)	5.00 (0)
H(9)	−0.1198 (0)	0.0859 (0)	0.0607 (0)	5.00 (0)
H(11)	0.2324 (0)	0.1537 (0)	0.0706 (0)	5.00 (0)
P(1)	−0.07221 (3)	0.2500 (0)	0.0901 (2)	3.41[a]
O(1)	0.1386 (0)	0.0174 (5)	0.2727 (6)	9.73[a]
C(1)	0.1217 (9)	0.1014 (6)	0.2881 (5)	5.39[a]
C(3)	0.0426 (2)	0.2500 (0)	−0.0174 (7)	4.95[a]
C(5)	−0.3129 (12)	0.1150 (8)	0.1215 (8)	9.38[a]
C(7)	0.1480 (10)	0.1562 (7)	−0.0058 (7)	7.66[a]
C(13)	−0.0098 (16)	0.2500 (0)	0.6625 (10)	10.29[a]
C(9)	0.0078 (16)	0.2134 (9)	0.5414 (11)	4.13 (25)
C(11)	0.2328 (21)	0.0515 (13)	0.5958 (14)	12.45 (44)
H(2)	−0.2248 (0)	0.1207 (0)	0.2118 (0)	5.00 (0)
N(4)	0.0508 (0)	0.0902 (0)	−0.0192 (0)	5.00 (0)
H(6)	−0.2618 (0)	0.1426 (0)	−0.1497 (0)	5.00 (0)
H(8)	−0.4011 (0)	0.1606 (0)	0.1204 (0)	5.00 (0)
H(10)	0.2013 (0)	0.1556 (0)	−0.0639 (0)	5.00 (0)

[a] $(U_{11} + U_{22} + U_{33})/3$. Anisotropic thermal parameters are published as supplementary data.

Attempts to dissolve it in CH_2Cl_2 and $CHCl_3$ led to decomposition. Reaction with L(CH_3CN, $P(OR)_3$) in benzene yielded $W(CO)_3(PCy_3)_2L$. Reactions of $W(CO)_3(PCy_3)_2$ with paraformaldehyde in toluene were slow (6 h) and produced primarily $W(CO)_4(PCy_3)_2$.

Reaction of $Mo(CO)_3$(diglyme) with $2PCy_3$; Formation of $Mo(CO)_3(PCy_3)_2(N_2)$. A mixture of 0.83 g (2.64 mmol) of $Mo(CO)_3$(diglyme), 1.52 g (5.42 mmol) of PCy_3, and 10 mL of Et_2O was stirred under agon. Within ca. 10 min a copious, bright red-orange precipitate formed, and further stirring overnight resulted in no further apparent reaction. Toluene (12 mL) was added, and Et_2O was removed in vacuo. The resulting suspension was heated to 85 °C in an argon atmosphere, whereupon the red solid dissolved to yield a solution, which, upon being cooled to room temperature, did not deposit any solids. Addition of nitrogen resulted in precipitation of $Mo(CO)_3(PCy_3)_2(N_2)$ (1.30 g; 62% yield). Overnight stirring of $Mo(CO)_3$(diglyme) (0.203 g, 0.646 mmol), PCy_3 (0.37 g, 1.32 mmol), and toluene (5 mL) in a nitrogen atmosphere directly yielded 0.20 g (39%) of the N_2 complex.

Structure of $W(CO)_3(PCy_3)_2$. Crystals were obtained by slowly cooling to −20 °C a solution of $W(CO)_3(PCy_3)_2$ in toluene–heptane–ether obtained from H_2 removal from $W(CO)_3(PCy_3)_2(H_2)$. A large irregularly shaped crystal with an average dimension of ca. 0.3 mm was jam-fit into a thin-wall glass capillary under inert atmospheric conditions (argon). Intensity data were collected as described in detail in another publication.[28] Conditions pertinent to the current investigation appear in Table V.

An absorption correction by an empirical method was applied by using a ϕ scan about a reflection near $\chi = 90°$.

A Patterson synthesis was used to determine the tungsten atom coordinates; difference Fourier calculations provided the location of all other non-hydrogen atoms. Subsequent ΔF and low angle-biased ΔF maps yielded some but not all hydrogen atom positions. All hydrogen atoms were thus included fixed in calculated positions [d(C–H) = 0.95 Å] with $B_{iso} = 5.0$ Å^2. The final residuals for the 407 parameter model (including isotropic mosaic block size refinement to account for secondary extinction[29]) were $R_F = 2.5\%$ and $R_{wF} = 4.2\%$. Final positional parameters for non-hydrogen atoms are listed in Table VI; anisotropic thermal parameters are given in Table IIs.

Structure of $W(CO)_3(P(i\text{-}Pr)_3)_2$. Data were collected with use of a crystal of approximate dimensions 0.3 × 0.3 × 0.2 mm, which had been

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mounted in a glass capillary under argon. Experimental details may be found in Table V.

Systematic absences observed, $0k0$, $k = 2n + 1$, are consistent with space groups $P2_1$ (No. 4) or $P2_1/m$ (No. 11). A Patterson synthesis allowed location of the tungsten atom; difference Fourier calculations allowed location of other atoms. The molecule is disordered in $P2_1/m$ in one-half of the molecule. Phosphine group P(1) is ordered and all carbon atoms in this ligand were located and refined anisotropically. Most hydrogen atoms were located from ΔF maps and were fixed in positions thus obtained; others were calculated. However, the data did not allow resolution of individual components of each disordered carbon atom, except in the case of atom C(9), which lies ~0.5 Å from the mirror plane at $y = {}^1/_4$, and was included with an "occupancy" factor of ${}^1/_2$. Electron density in the remaining "half-atoms" is described by artificially large thermal ellipsoids.

Since the disorder in $P2_1/m$ affected only a few atoms, we carried out final refinement in this space group. The model consisted of 119 parameters with 2212 data and resulted in $R_F = 0.033$ and $R_{wF} = 0.046$. The refined value of the mosaic block size (secondary extinction) parameter[29] was 1.14 (8) × 10^{-5} mm. Final positional parameters are listed in Table VII; thermal parameters may be found in Table IIIs.

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Supplementary Material Available: Lists of analytical data (Table Is), anisotropic thermal parameters (Tables IIs and IIIs), and structure factor amplitudes (Table IVs and Vs) (28 pages). Ordering information is given on any current masthead page.

Formation and Cleavage of N-H Bonds on Nitrido Metal Carbonyl Clusters

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Abstract: A study of the protonation of three tetranuclear nitrido clusters having the butterfly geometry is reported. While the final product of each of these reactions is a hydrido-nitrido cluster, the intermediates contain the imido (NH) ligand which can be trapped by CO. For $[FeRu_3N(CO)_{12}]^{1-}$, the products of protonation in a CO atmosphere are $FeRu_2(NH)(CO)_{10}$, $[FeRu_4N(CO)_{14}]^{1-}$, and small amounts of $HFeRu_3N(CO)_{12}$ and $Ru_3(CO)_{12}$. With $[Ru_4N(CO)_{12}]^{1-}$, this reaction generates $Ru_3(NH)(CO)_{10}$, $[Ru_5N(CO)_{14}]^{1-}$, $HRu_4N(CO)_{12}$, and small quantities of $Ru_3(CO)_{12}$. The new NH-containing clusters $FeRu_2(NH)(CO)_{10}$ and $Ru_3(NH)(CO)_{10}$ contain a triply bridging N-H ligand and a triply bridging carbon monoxide. The substituted cluster $\{FeRu_3N(CO)_{10}[P(OCH_3)_3]_2\}^{1-}$ was shown by X-ray crystallography [crystal system = orthorhombic, space group = $Pnn2$, a = 11.603 (3) Å, b = 18.521 (6) Å, c = 8.908 (4) Å, Z = 2] to contain the two $Ru(CO)_2[P(OCH_3)_3]$ fragments in the wing-tip positions. Protonation leads to a green intermediate that reacts with CO to give $FeRu_2(NH)(CO)_9[P(OCH_3)_3]$, which was structurally characterized [crystal system = monoclinic, space group = $P2_1/m$, a = 8.596 (2) Å, b = 15.576 (3) Å, c = 7.870 (4) Å, β = 100.37 (3)°, Z = 2]. The structure contains both a triply bridging CO and NH ligand, and the phosphite is bound to a ruthenium and oriented trans to the NH group. ^1H and ^{15}N NMR spectroscopies were used to identify the intermediate imido cluster $FeRu_3(NH)(CO)_{10}[P(OCH_3)_3]_2$.

The formation and cleavage of N-H bonds on metal surfaces is an integral part of several important heterogeneously catalyzed reactions such as the Haber process[3] and the oxidation of ammonia.[4] In some of these reactions, surface-coordinated nitrogen atoms are key intermediates. Much of the interest in metal carbonyl clusters containing a nitrido ligand stems from the comparison of their reactivity to those of nitrogen atoms bound to metal surfaces. We report in this paper the results of our studies of the protonation of several nitrido clusters in which the initially formed imido (NH) cluster undergoes a facile N-H bond cleaving reaction, yielding a hydrido-nitrido cluster.

Experimental Section

$PPN[Ru_4N(CO)_{12}]$,[5] $PPN[Ru_4{}^{15}N(CO)_{12}]$,[5] $PPN[FeRu_3N(CO)_{12}]$,[6] $PPN[FeRu_3{}^{15}N(CO)_{12}]$,[6] and $PPN\{FeRu_3N(CO)_{10}[P(OCH_3)_3]_2\}$[7] were prepared according to published procedures. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone ketyl under nitrogen. Hexane was dried by distillation from sodium metal under nitrogen. Methylene chloride was distilled from P_2O_5 immediately prior to use. All reactions were carried out under a nitrogen atmosphere, and chromatography was conducted on silica gel. Infrared spectra were recorded on a Beckman Model 4250 spectrophotometer or Mattson Cygnus 25 FTIR spectrophotometer equipped with a HgCdTe detector. NMR data were recorded on a Nicolet NTCFT-1130 300-MHz spectrophotometer. Each ^{15}N NMR experiment was conducted with CH_2Cl_2 as the solvent (3.0 mL) in a 12-mm tube with $Cr(acac)_3$ (53 mg) as the shiftless relaxation reagent. Nitromethane was used as an external reference, set at 379.60 ppm downfield from NH_3(liquid, 25 °C).[8] A summary of the spectroscopic data is shown in Table I.

$PPN[FeRu_3N(CO)_{12}] + CF_3SO_3H$. CH_2Cl_2 (10 mL) was distilled into a Schlenk tube containing 202.0 mg (0.162 mmol) of $PPN[FeRu_3N(CO)_{12}]$. CF_3SO_3H (16.5 μL, 0.165 mmol) was added by syringe, causing a deep-red color that lasted for several minutes. The solution was stirred for 10 min. After the solvent was removed, the product was extracted into 2 × 50 mL of hexane. The hexane was evaporated, leaving 109 mg (0.152 mmol, 95%) of amber crystalline $HFeRu_3N(CO)_{12}$. The product can be recrystallized by slowly cooling a saturated hexane solution. Anal. Calcd for $C_{12}HFeNO_{12}Ru_3$: C, 20.09; H, 0.14; N, 1.97. Found: C, 20.32; H, 0.15; N, 1.97.

$PPN[FeRu_3N(CO)_{12}] + CF_3SO_3H$ under CO. $PPN[FeRu_3N(CO)_{12}]$ (200 mg, 0.160 mmol) was dissolved in 10 mL of CH_2Cl_2, and the resulting solution was saturated with CO. Immediately following the addition of 14.3 μL of CF_3SO_3H (0.160 mmol), a dark-red color was observed for several seconds, after which a stable orange solution was formed. The volume of CH_2Cl_2 was reduced to ~1 mL and was extracted with 4 × 10 mL of hexane. After filtration of the yellow-orange hexane solution, the products were separated by column chromatography. When hexane was used as the eluent, four bands were observed. The first band to elute contained trace amounts of $Ru_3(CO)_{12}$ and was closely

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