and C(10) to Ru(2) and Ru(3) with corresponding bond lengths for $HRu_3(CO)_9(C{\equiv}C$-*t*-Bu) reveals Δ(Ru–C) values of only 0.002 and 0.019 Å for C(9) and 0.025 and 0.019 Å for C(10). Thus the substitution of a carbonyl group by PPh_2OEt has an almost negligible effect on the acetylide–metal interactions. It is thus apparent that phosphine substitution, in this cluster system at least, affects predominantly the metallic skeleton.

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Registry No. $HRu_3(CO)_8(C_2$-*t*-Bu)(P(OEt)Ph_2), 79272-81-4.

Supplementary Material Available: A listing of observed and calculated structure factors, Table S1 containing hydrogen atom coordinates, and Table S2 listing additional bond lengths and angles (21 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
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Length of a Tungsten–Phosphine Bond Free of Excessive Steric Interactions: Crystal Structure of $W(CO)_5P(CH_3)_3$

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Although interest in the relationship between structure and reactivity of octahedral complexes containing a mixture of CO and phosphine ligands has led to the determination of a number of crystal structures, the available structural data are still far from complete or comprehensive. Many of the known structures are for polyphosphine species such as *fac*-$Cr(CO)_3(PEt_3)_3$,[1] *cis*-$Cr(CO)_2(PH_3)_4$,[2] and *cis*-{$Mn(CO)_2[P(OMe)_2Ph]_4$}PF_6,[3] in which there are geometrical irregularities caused by steric crowding. We have recently undertaken some systematic studies[4] of the relationship between the chemical properties of some *cis*-$Mo(CO)_4L_2$ (L = PR_3 or PAr_3) compounds and their structures, including steric interactions. These studies, which have revealed several correlations between structure and reactivity, were facilitated by the ready availability of the compounds in useful crystalline form.

However, in trying to analyze the geometry changes forced upon these complexes by multiple carbonyl substitutions, we find there is a limited base of information available on the structures of monosubstituted derivatives of the type $M(CO)_5L$ (M = Cr, Mo, W; L = a phosphine). This is inherently due to the low melting points of most of these derivatives, which make them unsuitable for X-ray study under normal conditions. Some results have been reported for bulkier phosphine such as PPh_3 and $P(OPh)_3$ since these give complexes with acceptable physical properties. The majority of these reports deal with chromium compounds such as $Cr(CO)_5(PPh_3)$,[5] $Cr(CO)_5[P(OPh)_3]$,[6] and $Cr(CO)_5[P(CH_3)_2SH]$.[6] The structures of complexes of molybdenum with L = PPh_3 and $P(CH_2CH_2CN)_3$ have also been published.[7] The only structural report of a tungsten compound deals with $W(CO)_5[P(t\text{-}Bu)_3]$.[8] These derivatives also exhibit some steric interaction between the bulky phosphine ligand and the cis carbonyl groups. This is particularly the case in the structure of $W(CO)_5[P(t\text{-}Bu)_3]$, where these forces are so large that no reliable estimate of a "normal" W–PR_3 bond length can be obtained.

Table I. Crystallographic Data and Enraf-Nonius CAD-4 Data Collection Parameters

formula	$WPO_5C_8H_9$	c, Å	15.479 (2)
mol wt	400.0	β, deg	103.11 (1)
space group	$P2_1/n$	V, Å^3	1278.0 (5)
a, Å	7.134 (1)	Z	4
b, Å	11.882 (2)	d_{calcd}, g/cm^3	2.08

μ(Mo Kα), cm^{-1}	96.99
radiation	graphite-monochromated Mo Kα (λ = 0.710 73 Å)
scan type	ω-2θ
scan width ($\Delta\omega$), deg	0.75 + 0.35 tan θ
maximum counting time, s	30
collection range	$+h,+k,\pm l$
no. of unique data	2228
no. of data, $I > 3\sigma(I)$	1689
P	0.05
no. of variables	136
R_1[a]	0.043
R_2[a]	0.053
esd	1.62
largest shift[b]	0.01
largest peak[c]	0.59

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. [b] Largest parameter shift in final refinement cycle. [c] Largest peak in a final difference Fourier, e/Å^3.

To obtain structural information for a nondistorted tungsten complex that will provide equilibrium distances mainly determined by electronic factors, we have undertaken an X-ray structural investigation of $W(CO)_5(PMe_3)$. We report here the results of this determination and contrast the observed features with those determined for the tri-*tert*-butylphosphine derivative.

Experimental Section

Preparation of $W(CO)_5(PMe_3)$. A procedure similar to that described[9] for other $M(CO)_5L$ complexes was employed. A methylene chloride solution (30 mL) containing 0.90 g (1.0 mmol) of PPN[$W(CO)_5Cl$] and 0.10 mL (0.80 g; 1.1 mmol) of PMe_3 was treated with 10 mL methanol. The mixture was stirred at ambient temperature under nitrogen for 12 h and then filtered through Celite, and volatile materials were removed under reduced pressure. The white residue was then sublimed (45 °C; 10^{-2} torr) to produce crystals of $W(CO)_5(PMe_3)$ deemed suitable for X-ray work.

The infrared spectrum in hexane solution has three ν_{CO} bands (each ±1 cm^{-1}) at 2073, 1952, and 1942 cm^{-1}, corresponding to the $A_1^{(2)}$, $A_1^{(1)}$, and E modes, respectively, of the $W(CO)_5$ moiety under C_{4v} symmetry.

X-ray Crystallography. A crystal of dimensions 0.20 × 0.25 × 0.30 mm was fixed in a 0.2-mm thin-walled capillary with epoxy cement. The crystal was then mounted on an Enraf-Nonius CAD-4 automated diffractometer where alignment and determination of lattice parameters were performed by using standard routines. The observed cell constants (Table I) and the systematic absences in $h0l$ for $h + l \neq 2n$ and in $0k0$ for $k \neq 2n$ uniquely determined the space group $P2_1/n$.

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Table II. Positional Parameters for $W(CO)_5PMe_3$ [a]

atom	x	y	z
W	0.02094 (6)	0.14322 (3)	0.29480 (2)
P	0.1507 (4)	0.2773 (2)	0.4199 (2)
O(1)	0.369 (1)	0.2100 (10)	0.2091 (6)
O(2)	0.269 (2)	−0.0565 (8)	0.3957 (7)
O(3)	−0.325 (1)	0.0774 (9)	0.3826 (7)
O(4)	−0.230 (2)	0.3427 (7)	0.1918 (8)
O(5)	−0.149 (1)	−0.0185 (8)	0.1353 (6)
C(1)	0.242 (2)	0.1869 (10)	0.2416 (8)
C(2)	0.179 (2)	0.0148 (9)	0.3600 (8)
C(3)	−0.198 (2)	0.1025 (10)	0.3477 (8)
C(4)	−0.143 (2)	0.2711 (9)	0.2319 (7)
C(5)	−0.085 (2)	0.0379 (10)	0.1952 (7)
C(6)	0.009 (2)	0.2944 (12)	0.5038 (8)
C(7)	0.162 (2)	0.4266 (11)	0.3840 (9)
C(8)	0.397 (2)	0.2484 (13)	0.4848 (10)

[a] Estimated standard deviations in the least significant figure are shown in parentheses.

Table III. Bond Distances (A) and Bond Angles (Deg)

Distances

W-P	2.516 (2)	C(1)-O(1)	1.17 (1)
W-C(1)	2.00 (1)	C(2)-O(2)	1.13 (1)
W-C(2)	2.02 (1)	C(3)-O(3)	1.19 (1)
W-C(3)	1.98 (1)	C(4)-O(4)	1.15 (1)
W-C(4)	2.03 (1)	C(5)-O(5)	1.15 (1)
W-C(5)	2.00 (1)	P-C(7)	1.87 (1)
P-C(6)	1.83 (1)	P-C(8)	1.85 (1)

Angles

P-W-C(1)	88.1 (3)	C(3)-W-C(4)	87.7 (5)
-C(2)	91.6 (3)	-C(5)	88.3 (4)
-C(3)	91.3 (3)	C(4)-W-C(5)	91.3 (4)
-C(4)	88.1 (3)	W-C(1)-O(1)	178 (1)
-C(5)	179.3 (3)	W-C(2)-O(2)	179 (1)
C(1)-W-C(2)	90.0 (5)	W-C(3)-O(3)	178 (1)
-C(3)	179.1 (4)	W-C(4)-O(4)	179 (1)
-C(4)	91.7 (5)	W-C(5)-O(5)	176.8 (9)
-C(5)	92.3 (4)	C(6)-P-C(7)	100.0 (6)
C(2)-W-C(3)	90.6 (5)	-C(8)	104.1 (6)
-C(4)	178.2 (4)	C(7)-P-C(8)	103.9 (6)
-C(5)	89.0 (5)	W-P-C(8)	116.0 (4)
W-P-C(6)	116.8 (4)		
-C(7)	113.9 (4)		

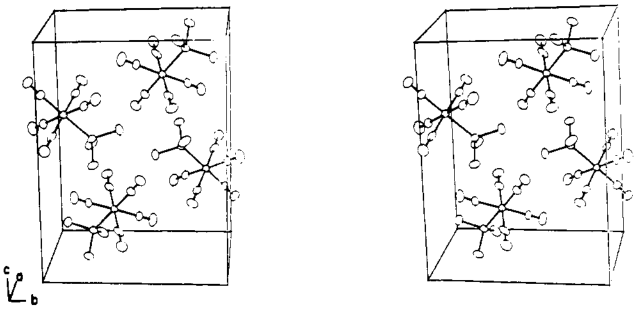

Figure 1. Stereoscopic view of the unit cell approximately down the *b* axis.

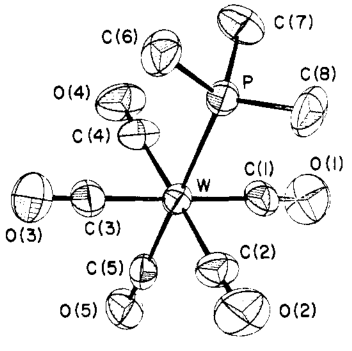

Figure 2. Molecular structure of $W(CO)_5(PMe_3)$ (ORTEP, 40% thermal ellipsoids).

Data were collected at 22 ± 1 °C in the range $2\theta \leq 50°$ with use of previously reported methods.[10] (Details appear in Table I.) The data were corrected[11] for Lorentz and polarization effects, as well as for absorption. The latter correction was performed by an empirical method based on ψ scans, which exhibited a minimum transmission of 62.3%, a maximum transmission of 99.9%, and an average transmission of 84.2%. Also, during data collection, a linear isotropic decay (2.8%/h) in the intensities of three standard reflections (measured every 100 reflections) was observed, and an appropriate correction was made. Of a total of 2228 unique intensities measured, 1689 had $I > 3\sigma(I)$ and were used in subsequent solution and refinement of the structure.

The structure was solved and refined by standard heavy-atom methods and full-matrix least-squares calculation. In this instance, a difference Fourier map phased on the tungsten atom position (obtained from a three-dimensional Patterson synthesis) yielded positions for all nonhydrogen atoms. The model was refined to convergence by using anisotropic thermal parameters for the 15 atoms. A difference Fourier map failed to reveal the positions of any hydrogen atoms, and because of the large thermal motion exhibited by the methyl carbons, none were included in the model at calculated positions. During the final refinement, the 002 reflection with $|F_o| = 196$ and $|F_c| = 271$ was omitted from the calculation. A secondary extinction coefficient, *g*, equal to 1.70×10^{-7} was included, and convergence produced the final parameters listed in Table I. A final difference Fourier map exhibited peaks as high as 0.59 e/Å^3 in the region of the W atom.

Final positional parameters are given in Table II. Tables listing observed and calculated structure factors and the anisotropic thermal parameters are available as supplementary material.

Discussion

The solid-state structure of $W(CO)_5(PMe_3)$ has been determined at room temperature and provides for the first time the equilibrium bond distances in an unstrained tungsten pentacarbonyl phosphine. The inherent difficulty in determining structures such as these lies in the low melting points of the complexes. The problems created are high thermal motion of the molecule within the crystal and rapid loss of crystallinity even at −10 °C. However, in choosing the small trimethylphosphine, we obtained compounds with more suitable properties,[12] although by no means ideal, as indicated by the slow loss of crystallinity and therefore the decrease in intensity during data collection at 25 or even at 3 °C. Only the tungsten compound was tractable at around room temperature. Before discussing the results of the tungsten study, we note that although crystals of the Cr and Mo compounds were not sufficiently stable even at 3 °C to obtain a detailed structural analysis, the three compounds are isomorphous. In the case of molybdenum, a partial data set indicates in a conclusive way that the Mo and W compounds are isostructural.

The crystal structure of $W(CO)_5(PMe_3)$ is depicted in Figure 1 as a stereoscopic view of the unit cell. The molecule resides on a general position within the unit cell and is found in a relatively open environment. All of the intermolecular contacts are greater than the sum of van der Waals radii. A view of the molecular structure is presented in Figure 2, where

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(11) All crystallographic computing was performed at the Molecular Structure Corp., College Station, TX, using the Enraf-Nonius Structure Determination Package.

(12) The melting points of the $M(CO)_5P(CH_3)_3$ compounds are 38–40 (Cr), 44–45 (Mo), and 55–57 °C (W). Earlier attempts, in collaboration with Dr. M. Fredrich, to collect data on the Cr and Mo compounds at ca. 3 °C gave results that were entirely unsatisfactory for the Cr compound and of doubtful quality for the Mo compound. We hope to return to these substances in the future using a cryostat.

the atomic numbering scheme is defined as well. The arrangement of the ligands around the central tungsten atom closely defines a regular octahedron. The longest coordination sphere bond, W–P, has a length of 2.516 (2) Å while the average W–C bond distance is 2.01 [2] Å.[13] There are no significant differences among any of the W–C bond lengths, and, in particular, none between the axial one, 2.00 (1) Å, and the average of the four equatorial ones, 2.01 [2] Å. Considering the results obtained for some other $M(CO)_5L$ structures,[7] a difference of 0.02–0.05 Å might have been expected. Such a difference is, in fact, permitted within the uncertainties. The average C–O bond length is 1.16 [2] Å, and the W–C–O moieties are linear.

The trimethylphosphine ligand has normal bond distances and angles. The average P–C distance and C–P–C angle are 1.85 [1] Å and 102.7 [2.7]°, respectively, and are statistically identical with the dimensions observed for this ligand in *cis*-$Mo(CO)_4(PMe_3)_2$.[14] The refinement of this ligand indicated fairly high thermal activity, but it is reasonably well-behaved and there is no indication of rotational disorder.

The angles around the tungsten atom approximate closely to the expected octahedral angles of 90° and 180°. The P–W–C(5) angle is 179.3 (3)°, and the P–W–C(5) vector is essentially perpendicular to the equatorial carbonyl plane. The small observed deviation from a right angle is caused by the orientation of the PMe_3 ligand with respect to the cis CO groups. The C(7) methyl group points out over the C(1)–W–C(4) quadrant, slightly opening this angle to 91.7 (5)°. The two remaining methyl groups are located directly over carbonyl groups CO(2) and CO(3). The interaction produces P–W–C(2) and P–W–C(3) angles of 91.6 (3) and 91.3 (3)°, respectively. Conversely, the ligand groups CO(1) and CO(4) shift up toward methyl group C(7), giving a P–W–C(1) angle of 88.1 (3)° and a P–W–C (2) angle of 88.1 (3)°. The overall effect is to keep the W(1),C(1),C(2),C(3),C(4) unit totally planar but also to tilt this plane very slightly, thus reducing intramolecular contacts. These interactions are minor and we would not expect them to lengthen significantly the W–P bond distance. This type of interaction is also observable in the structures of the $M(CO)_5L$ (M = Mo, Cr; L = PPh_3, $P(CH_2CH_2CN)_3$) complexes.[7] The ligands in those complexes are also oriented in such a way as to yield two P–M–C angles greater than 90° and two that are slightly acute; as a whole, the equatorial unit is planar. However, in the $Mo(CO)_5(PPh_3)$ compound these deviations are much larger (P–M–C angles average 95 [1]° and 87.5 [2]° for the two sets) and may well imply a lengthening and weakening of the Mo–P bond as compared to a sterically unstressed bond.

There can be no doubt that such a steric factor causes the long W–P bond distance of 2.686 (4) Å in the structure of the $W(CO)_5[P(t\text{-}Bu)_3]$ complex. This $W\text{–}P(t\text{-}Bu)_3$ bond is 0.170 (6) Å longer than the $W\text{–}P(CH_3)_3$ bond. The steric crowding of the *tert*-butyl groups is also reflected in the large P–W–C angles, which average 96.6 [1.8]° for those three CO ligands most closely contacting the phosphine ligand. The similarities in the basicities of PMe_3 and $P(t\text{-}Bu)_3$ and the reported similarities in their (nonsteric) binding properties[15,16] would lead us to expect similar W–P bond lengths. Presumably, the large increase in the W–P bond length has decreased significantly the W–P bond strength, and we would predict, therefore, a greater lability of the phosphine ligand in $W(CO)_5[P(t\text{-}Bu)_3]$ than in $W(CO)_5(PMe_3)$.

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Registry No. $W(CO)_5(PMe_3)$, 26555-11-3; PPN[$W(CO)_5Cl$], 39048-34-5.

Supplementary Material Available: Listings of observed and calculated structure factors and anisotropic thermal parameters (9 pages). Ordering information is given on any current masthead page.

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[13] Square brackets enclose average standard deviations. See: Churchhill, M. R.; Amoh, K. N.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 1609.

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Probable Fluxional Behavior in B_5H_{11}. A Theoretical Study Which Supports C_1 Symmetry

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Although the early X-ray diffraction study[1] assigned C_s symmetry to B_5H_{11} (Figure 1), the precision was insufficient to detect small distortions to C_1 (identity only) symmetry. Nor do the NMR results distinguish between C_s symmetry and two equivalent rapidly interconverting C_1 structures.[2] While a recent, much more precise, X-ray study shows C_1 symmetry, the question remains as to whether molecular crystal packing has induced this distortion.[3]

The most recent theoretical study[4] indicated that the C_s structure is the more stable, although the unique (endo) hydrogen on the apex boron could be displaced by as much as 10° at the cost of no more than about 1 kcal/mol. Inasmuch as this distortion converts a terminal, but weakly doubly bridged, hydrogen to a singly bridged hydrogen, correlation corrections, omitted from this earlier study, might be expected to favor the C_1 structure. This is indeed the case, as we now describe.

Recent work in this laboratory[5,6] has shown that geometry optimization at the double-ζ level followed by fixed geometry calculations including polarization or correlation can be combined to predict relative energies within a few kilocalories per mol. In the present study, we used the 3-21G basis to optimize the C_s and C_1 geometries of B_5H_{11}. The small number of Gaussian functions in this basis allows computational efficiency in calculating derivatives. All geometries were completely optimized within the assigned molecular symmetry.

The structure constrained to C_s symmetry was subjected[8] to 20 cycles of optimization, beginning with the symmetry-averaged structure of the X-ray diffraction study.[1] During the last four cycles of optimization the energy changed by only 0.3 kcal/mol.

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