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Improved Synthesis, Chemistry, and X-ray and Neutron Diffraction Studies of $[(\text{Ph}_3\text{P})_2\text{N}]^+_2[\text{H}_2\text{W}_2(\text{CO})_8]^{2-}$

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The compound $[(\text{Ph}_3\text{P})_2\text{N}]^+_2[\text{H}_2\text{W}_2(\text{CO})_8]^{2-}$ has been synthesized in 65% yield from the reaction of $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{BH}_4]^-$ with $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{W}(\text{CO})_5(\text{I})]^-$ in refluxing THF. The dianion reacts with $\text{BH}_3\cdot\text{THF}$ in THF to produce $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{W}(\text{CO})_4(\text{BH}_4)]^-$ in 60% yield. The structure of $[(\text{Ph}_3\text{P})_2\text{N}]^+_2[\text{H}_2\text{W}_2(\text{CO})_8]^{2-}$ has been studied with X-ray and neutron diffraction techniques at room temperature and 28 K, respectively. The $[\text{H}_2\text{W}_2(\text{CO})_8]^{2-}$ anion has approximately D_{2h} symmetry with a planar $\text{W}(\mu\text{-H})_2\text{W}$ bridge, confirming the earlier X-ray results by Churchill and co-workers on $[\text{Et}_4\text{N}]^+_2[\text{H}_2\text{W}_2(\text{CO})_8]^{2-}$. In the $[(\text{Ph}_3\text{P})_2\text{N}]^+$ salt, the anions are situated on crystallographic inversion centers, and distances and angles in the $\text{W}(\mu\text{-H})_2\text{W}$ core are as follows: $\text{W-H} = 1.920$ (3) and 1.933 (2) Å, $\text{W}\cdots\text{W} = 3.010$ (2) Å, $\text{H}\cdots\text{H} = 2.405$ (3) Å, $\text{W-H-W} = 102.7$ (1)°, $\text{H-W-H} = 77.3$ (1)°, and $\text{H-W-W} = 38.78$ (6) and 38.48 (6)°. The two bridging H atoms are displaced slightly from the intersections of the trans CO-metal vectors in the direction of the metal-metal axis. The $[(\text{Ph}_3\text{P})_2\text{N}]^+$ cation has the usual bent P-N-P configuration, but the phenyl rings are in an uncommon staggered conformation. Crystal data from the neutron diffraction analysis of $[(\text{Ph}_3\text{P})_2\text{N}]^+_2[\text{H}_2\text{W}_2(\text{CO})_8]^{2-}$ at 28 K: space group $P\bar{1}$; $a = 12.949$ (1), $b = 13.871$ (2), $c = 11.000$ (1) Å; $\alpha = 110.828$ (8), $\beta = 105.788$ (9), $\gamma = 69.334$ (8)°; $V = 1703.4$ (4) Å³; $Z = 1$. Final agreement factors were $R(F) = 0.027$ for 5206 neutron reflections with $I \geq \sigma(I)$ and $R(F) = 0.040$ for 4238 X-ray reflections with $I \geq 3\sigma(I)$.

Introduction

In an attempt to produce the tungsten analogue of $[\text{Mo}(\text{CO})_4(\text{BH}_4)]^{2-}$, the known dianion $[\text{H}_2\text{W}_2(\text{CO})_8]^{2-}$,^{3,4} inadvertently was synthesized in good yield. The existence of an inexpensive, easily prepared bonding analogue of the highly interesting and reactive $\text{H}_2\text{Os}_3(\text{CO})_{10}$ ⁵ prompted an investigation of the chemistry of $[\text{H}_2\text{W}_2(\text{CO})_8]^{2-}$.

The structural analysis of $[\text{H}_2\text{W}_2(\text{CO})_8]^{2-}$ represents a continuation of our work on transition-metal hydrides. For the past decade, we have been employing neutron diffraction techniques to study a series of binuclear transition-metal carbonyl complexes containing bridging hydride ligands.⁶ In our work to date, we have characterized a series of complexes having a single hydrogen bridge, $\text{M}(\mu\text{-H})\text{M}$,⁷ and also examples of compounds having three $[\text{M}(\mu\text{-H})_3\text{M}]$ and four $[\text{M}(\mu\text{-H})_4\text{M}]$ bridging H atoms.⁸ In the present paper we complete the series by describing the X-ray and neutron diffraction analysis of a compound having two hydrogen bridges, $[\text{M}(\mu\text{-H})_2\text{M}]$.

The title anion was first analyzed crystallographically as the $[\text{Et}_4\text{N}]^+$ salt by Churchill and Chang using X-ray methods.⁴ In order to get more precise metal-hydrogen distances and angles, we embarked upon a neutron diffraction analysis, this time using the $[(\text{Ph}_3\text{P})_2\text{N}]^+$ salt, which forms larger crystals and, unlike $[\text{Et}_4\text{N}]^+_2[\text{H}_2\text{W}_2(\text{CO})_8]^{2-}$, has an ordered structure. The neutron results turn out to be remarkably

similar to those of the earlier X-ray analysis of $[\text{Et}_4\text{N}]^+_2[\text{H}_2\text{W}_2(\text{CO})_8]^{2-}$.

Experimental Section

All operations were carried out in a prepurified nitrogen atmosphere with Schlenk techniques. Solvents were dried, deaerated, and stored over activated Linde 3A molecular sieves, except for THF and diethyl ether, which were distilled from sodium-benzophenone ketyl. $\text{W}(\text{CO})_6$ was purchased from Pressure Chemical Co. and used without further purification. The 1 M solution of $\text{BH}_3\cdot\text{THF}$ was purchased from Aldrich Chemical Co.; $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{Cl}]^-$ was prepared with published methods.⁹ Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer and calibrated against polystyrene. Solution spectra were recorded with the use of CaF_2 cells with a 0.5-mm spacer, and solid spectra were recorded as Nujol mulls between NaCl plates. The room-temperature ¹H NMR spectra were recorded on a Varian A-60A spectrometer in $\text{Me}_2\text{SO}-d_6$ with Me_4Si as an internal standard. Melting points were determined in sealed capillaries under nitrogen and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Synthesis of $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{W}(\text{CO})_5(\text{I})]^-$. A solution composed of $\text{W}(\text{CO})_6$ (2.6 g, 7.4 mmol), $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{I}]^{2-}$ (5.0 g, 7.5 mmol), and 100 mL of THF was refluxed for 30 h to produce a bright yellow solution and a small amount of white precipitate. The precipitate was removed by filtration and the filtrate volume reduced by 70%. Absolute ethanol (75 mL) was added and the solution cooled and held at -10°C overnight, during which time yellow needlelike crystals formed. A second crop of crystals was obtained in a similar manner to give a combined yield of $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{W}(\text{CO})_5(\text{I})]^-$ of 6.6 g (90%): IR (THF) ν_{max} (2100–1650-cm⁻¹ region) 2056 w ($\nu(\text{CO})$), 1916 vs ($\nu(\text{CO})$), 1851 s ($\nu(\text{CO})$) cm⁻¹, identical with those of $[\text{Et}_4\text{N}]^+[\text{W}(\text{CO})_5(\text{I})]^-$.¹⁰

Reaction of $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{W}(\text{CO})_5(\text{I})]^-$ and NaBH_4 . A solution composed of $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{W}(\text{CO})_5(\text{I})]^-$ (3.44 g, 3.48 mmol), NaBH_4 (0.24 g, 6.34 mmol), and 125 mL of THF was refluxed for 50 h to produce a bright orange solution and a small amount of precipitate. IR of the solution showed carbonyl region absorptions due to the two anions $[\text{HW}_2(\text{CO})_{10}]^{11}$ and $[\text{W}(\text{CO})_4(\text{BH}_4)]^-$ (vide infra).

Synthesis of $[(\text{Ph}_3\text{P})_2\text{N}]^+_2[\text{H}_2\text{W}_2(\text{CO})_8]^{2-}$. A solution of $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{W}(\text{CO})_5(\text{I})]^-$ (3.0 g, 3.0 mmol), $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{BH}_4]^{2-}$ (3.0 g, 5.4 mmol), and 150 mL of THF was refluxed for 50 h to produce a bright orange solution and a large amount of orange precipitate. IR of the solution showed carbonyl region absorptions due to $[\text{HW}_2(\text{CO})_{10}]^{11}$, $[\text{W}(\text{CO})_4(\text{BH}_4)]^-$ (vide infra), and in some runs $[\text{W}(\text{CO})_5(\text{I})]^-$. IR of the orange precipitate showed carbonyl

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- (7) (a) Olsen, J. P.; Koetzle, T. F.; Kirtley, S. W.; Andrews, M.; Tipton, D. L.; Bau, R. *J. Am. Chem. Soc.* **1974**, *96*, 6621. (b) Love, R. A.; Chin, H. B.; Koetzle, T. F.; Kirtley, S. W.; Whittlesey, B. R.; Bau, R. *Ibid.* **1976**, *98*, 4491.
- (8) (a) $\text{M}(\mu\text{-H})_3\text{M}$ system: $[\text{H}_3\text{Ir}_2(\text{C}_3\text{Me}_3)_2]^+[\text{BF}_4]^-$ (Bau, R.; Carroll, W. E.; Hart, D. W.; Teller, R. G.; Koetzle, T. F. *Adv. Chem. Ser.* **1978**, No. 167, 73. (b) $\text{M}(\mu\text{-H})_4\text{M}$ system: $\text{H}_3\text{Re}_2(\text{PEt}_2\text{Ph})_4$ (Bau, R.; Carroll, W. E.; Teller, R. G.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 3872).

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region absorptions due to [H₂W₂(CO)₈]²⁻ (vide infra). The supernatant was removed by syringe, and the precipitate was dried and extracted with two 150-mL portions of acetonitrile. The orange extracts were combined and reduced by roughly 75% in volume until cloudiness appeared. The solution was cooled to -10 °C and held overnight to yield bright orange-red to deep red crystals. The crystals were washed with ethanol and dried to give [(Ph₃P)₂N]⁺₂[H₂W₂(CO)₈]²⁻ (1.7 g) (65%): mp 147–148 °C; IR (CH₃CN) ν_{\max} (2100–1650-cm⁻¹ region) 1970 m (ν (CO)), 1878 vs (ν (CO)), 1824 s (ν (CO)), 1797 s (ν (CO)) cm⁻¹, identical with those of [Et₄N]⁺₂[H₂W₂(CO)₈]²⁻; IR (mull) ν_{\max} (4000–400-cm⁻¹ region) (excluding [(Ph₃P)₂N]⁺ and mull absorptions) 1955 s (ν (CO)), 1848 s (ν (CO)), 1819 s (ν (CO)), 1795 s (ν (CO)), 1261 s (ν (WHW?)), 620 sh, 581 sh cm⁻¹; ¹H NMR δ -4.72 (t, μ -H, $J(^{133}\text{W}-\text{H}) = 32$ Hz), 7.72 (m, [(Ph₃P)₂N]⁺). The crystals are stable in air for a few weeks and are somewhat soluble in CH₃CN, acetone, and Me₂SO but insoluble in THF, diethyl ether, and nonpolar organic solvents; solutions are moderately air sensitive.

Synthesis of [(Ph₃P)₂N]⁺[W(CO)₄(BH₄)]⁻. BH₃·THF (2 mL of 1 M in THF, 2 mmol) was added to a suspension of [(Ph₃P)₂N]⁺₂[H₂W₂(CO)₈]²⁻ (0.41 g, 0.24 mmol) in 125 mL of THF, and the combination was stirred for 18 h to produce a light orange supernatant with a precipitate of unreacted [(Ph₃P)₂N]⁺₂[H₂W₂(CO)₈]²⁻. The supernatant was transferred by syringe to another flask and the solvent removed under vacuum to produce a dark orange tar. The tar was extracted with 100 mL of diethyl ether to give a light orange solution and a small amount of white residue. The solution was filtered, reduced in volume until cloudiness appeared, and cooled to -10 °C overnight. The resultant orange microcrystals were dried under vacuum to obtain [(Ph₃P)₂N]⁺[W(CO)₄(BH₄)]⁻ (0.25 g) (61%): IR (THF) ν_{\max} (2500–1650-cm⁻¹ region) 2420 sh (ν (RH₂)), 239 m (ν (BH₂)), 2351 sh, 2294 w, 2011 m (ν (CO)), 1883 vs (ν (CO)), 1868 s, sh (ν (CO)), 1837 s (ν (CO)); IR (mull) ν_{\max} (4000–400-cm⁻¹ region) (excluding [(Ph₃P)₂N]⁺ and mull absorptions): 2433 w (ν (BH₂)), 2407 m (ν (BH₂)), 2372 sh, 2307 w, 2010 m (ν (CO)), 1878 s (ν (CO)), 1868 s (ν (CO)), 1835 s (ν (CO)), 1317 s (BHW bridge expansion), 1301 s (BHW bridge expansion), 1159 m (ν (BH₂)), 621 sh, 594 sh, 575 sh cm⁻¹. The crystals darken and clump at 76 °C and melt at 101–102 °C. The solid is soluble in THF, somewhat soluble in diethyl ether, insoluble in nonpolar organic solvents, and reacts with Me₂SO. The compound is extremely air sensitive as a solid and in solution.

Reaction of [(Ph₃P)₂N]⁺₂[H₂W₂(CO)₈]²⁻ with CO. The dianion [(Ph₃P)₂N]⁺₂[H₂W₂(CO)₈]²⁻ (0.4 g, 0.24 mmol) was dissolved in 100 mL of acetonitrile, and carbon monoxide gas was bubbled through the orange solution for 15 min. The reaction flask was closed and stirred under a nitrogen atmosphere for 24 h at room temperature to produce a slightly pale orange solution. The solution was again bubbled with carbon monoxide for 15 min and stirred for an additional 24 h under an atmosphere of carbon monoxide to produce a yellow solution and no precipitate. The solvent was removed to leave a yellow tar, which was extracted with THF. The IR spectrum of the THF extract in the carbonyl region showed only absorptions due to [H₂W₂(CO)₁₀]²⁻.¹¹

Crystallization of [(Ph₃P)₂N]⁺₂[H₂W₂(CO)₈]²⁻ for Neutron Analysis. A saturated solution of [(Ph₃P)₂N]⁺₂[H₂W₂(CO)₈]²⁻ in acetonitrile was prepared and a 15 × 75 mm test tube half-filled with the solution. The test tube was placed in a 200-mL Schlenk flask, and THF was added to the flask until the THF level was below the mouth of the test tube. The system was allowed to stand at room temperature under nitrogen for 1–3 weeks. The slow diffusion of THF vapor into the acetonitrile solution produced one or two large crystals of [(Ph₃P)₂N]⁺₂[H₂W₂(CO)₈]²⁻ which grew at the bottom of the test tube. The crystals were washed with THF and dried under vacuum. Typical crystal dimensions were 3 × 2 × 2 mm (ca. 10 mm³).

X-ray Diffraction. A crystal of dimensions 0.35 × 0.22 × 0.23 mm was cut from a larger specimen and mounted in air on a glass fiber. Data were collected on a Syntex P2₁ automated diffractometer with graphite-monochromatized Mo K α radiation. A total of 15 reflections (11° < 2 θ < 24°) were centered to obtain cell constants and an orientation matrix. A least-squares fit of these reflections produced a body-centered triclinic cell which was later reindexed to give a primitive reduced triclinic cell (Table I). One hemisphere of data up to a 2 θ limit of 45° was collected by the $\theta/2\theta$ scan technique. A variable-scan mode was employed, with a scan range from [2 θ (Mo K α_1) - 1.0]° to [2 θ (Mo K α_2) + 1.0]°. Three monitor reflections, measured at 50-reflection intervals, showed no significant changes

Table I. Summary of Crystal Data and Refinement Results for [(Ph₃P)₂N]⁺₂[H₂W₂(CO)₈]²⁻

space group Z	$\bar{P}1$ 1	mol wt ρ (obsd) ^a	1670.9 1.56 g cm ⁻³	
			X-ray (298 K)	neutron (28 K)
a, Å		13.199 (4)	12.949 (1)	
b, Å		14.096 (3)	13.871 (2)	
c, Å		11.075 (4)	11.000 (1)	
α , deg		110.59 (2)	110.828 (8)	
β , deg		105.44 (3)	105.788 (9)	
γ , deg		68.03 (2)	69.334 (8)	
V, Å ³		1767 (1)	1703.4 (4)	
ρ (calcd), g cm ⁻³		1.57	1.629	
cryst dims, mm		0.35 × 0.22 × 0.23	4.0 × 2.2 × 1.3	
wavelength, Å		0.710 69 (Mo K α)	1.1604 (1)	
abs coeff (μ), cm ⁻¹		35.9	1.567	
(sin θ)/ λ limit, Å ⁻¹		0.538 (2 θ = 45°)	0.513 (2 θ = 73°) ^b	
total no. of reflctns measd		4768	5855	
no. of independent reflctns		4564	5469	
no. of reflctns used in structural analysis (n_o)		4238 [$I > 3\sigma(I)$]	5206 [$I > \sigma(I)$]	
no. of variable parameters (n_v)		213	714	
final agreement factors ^c				
R(F)		0.040	0.027	
R(wF)		0.059	0.016	
R(F ²)			0.030	
R(wF ²)			0.032	

^a Obtained at room temperature via flotation in a solution of carbon tetrachloride and heptane. ^b Selected strong reflections were sampled out to 2 θ = 105°. ^c $R(F) = \sum |F_o - |F_c|| / \sum F_o$. $R(wF) = [\sum w(F_o - |F_c|)^2 / \sum wF_o^2]^{1/2}$. $R(F^2) = \sum |F_o^2 - |F_c|^2| / \sum F_o^2$. $R(wF^2) = [\sum w(F_o^2 - |F_c|^2)^2 / \sum wF_o^4]^{1/2}$.

in intensity. The standard deviation of each intensity reading was estimated from the expression¹² $\sigma(I) = [(peak + background counts) + (0.04 (net I))^2]^{1/2}$. The raw data were reduced to yield integrated intensities of 4238 independent reflections satisfying the criterion $I > 3\sigma(I)$. The intensities were collected for Lorentz, polarization, and absorption effects.

The coordinates of the unique W atom were obtained from a Patterson map, and the other nonhydrogen atoms were located from successive difference-Fourier maps.¹³ For the subsequent least-squares refinement, the parameters were blocked into two matrices. One block contained the scale factor, anion coordinates, and thermal parameters; the other, the cation coordinates and thermal parameters. The W, P, and N atoms were refined anisotropically while the C and O atoms were refined isotropically. After several cycles of least-squares refinement, the agreement factors were $R(F) = 0.043$ and $R(wF) = 0.062$. The positions of phenyl group H atoms were then calculated and temperature factors were assigned values equal to one plus the temperature factors of the corresponding C atoms. The H atoms were not refined but when added to the model reduced the agreement factors to $R(F) = 0.040$ and $R(wF) = 0.059$.

The hydride ligand was located successfully by using the low-angle data method.¹⁴ High-angle data (2 θ > 33.0°) were removed, leaving 1734 reflections in the calculation of a new difference-Fourier map. The peak due to the H atom became apparent in the map at this point, but its position could not be refined successfully.

Neutron Diffraction. A crystal with approximate dimensions 4.0 × 2.2 × 1.3 mm was mounted on an aluminum pin oriented ap-

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(13) For the X-ray portion of this work, major computations were performed on the USC IBM 370-158 computer using CRYM, an amalgamated set of crystallographic programs developed by Dr. Richard Marsh's group at the California Institute of Technology. Also used in the least-squares refinement was UCIGLS, a version of W. R. Busing and H. A. Levy's ORFLS, modified by J. A. Ibers and R. J. Doedens. For the neutron diffraction analysis, calculations were performed on CDC 6600 and 7600 computers using programs described by: Berman, H. M.; Bernstein, F. C.; Bernstein, H. J.; Koetzle, T. F.; Williams, G. J. P. *Informal Report 21714*; Brookhaven National Laboratory: Upton, NY, 1976, or modifications thereof.

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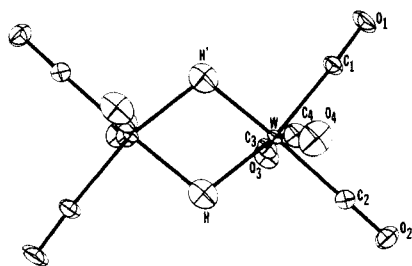


Figure 1. $[\text{H}_2\text{W}_2(\text{CO})_8]^{2-}$ anion viewed normal to the equatorial $\text{W}(\mu\text{-H})_2\text{W}$ plane. A crystallographic inversion center is situated at the middle of the anion. Note that the axial carbonyl groups C_3O_3 and C_4O_4 are slightly tilted. In this and subsequent plots, atoms are drawn as 85% probability ellipsoids.⁴⁷

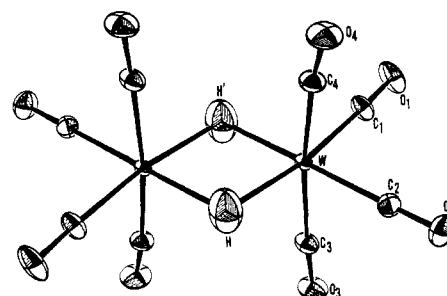


Figure 2. Alternative view of the $[\text{H}_2\text{W}_2(\text{CO})_8]^{2-}$ anion, rotated approximately 45° about the horizontal axis from that shown in Figure 1.

proximately along the b^* direction and placed in a closed-cycle helium refrigerator.¹⁵ Neutron diffraction data were collected at 28 K on an automated four-circle diffractometer¹⁶ at the Brookhaven High Flux Beam Reactor using a $\text{Ge}(220)$ -monochromated neutron beam of wavelength $1.1604(1) \text{ \AA}$ (calibrated with an Al_2O_3 powder sample, hexagonal, $a = 4.7580 \text{ \AA}$, $c = 12.991 \text{ \AA}$). In the course of the measurement of the low-angle reflections ($2\theta < 73^\circ$), a water supply failure caused a temperature rise in the cryostat. During the recooling process the crystal dropped from the pin and a small piece was chipped off. The sample (by now reduced in volume from 11.4 to 11.0 mm^3) was remounted along the same direction, recentered, and again cooled to 28 K. The collection of low-angle data then was completed followed by measurement of 1766 selected strong high-angle reflections ($73^\circ < 2\theta < 105^\circ$). Intensities were measured in the $\theta/2\theta$ step-scan mode with variable scan widths ranging from a $\Delta(2\theta)$ of 2.6° for $2\theta < 55^\circ$ to 6.0° for $2\theta > 105^\circ$. Counts were accumulated for approximately 0.8 s/step , with the exact time interval determined by monitoring the incident neutron flux, and the step size was adjusted to give about 65 steps in each scan. Two intense reflections [$(\bar{1}54)$ and (720)] were monitored at 100-reflection intervals, and no significant variations in their intensities were observed, except at the point when the crystal became chipped. The data later were normalized to account for this discontinuity and placed on a single scale.

The cell constants (Table I) were determined from a least-squares fit to the averaged centered 2θ angles of 16 Friedel pairs. The raw intensities were integrated and background corrections applied based on the counts of approximately five steps on either end of each scan. The squared observed structure factor (F_o^2) and the standard deviation (σ_c) for each reflection were obtained upon applying Lorentz and absorption corrections. The latter were calculated by numerical integration over a Gaussian grid of 480 sampling points (the crystal was approximated by 13 boundary faces). Values for the transmission coefficients ranged from 0.676 to 0.804. The validity of the absorption correction was confirmed by comparison with ψ -scan intensity data. Averaging Friedel pairs yielded data for 5206 independent reflections with $F_o^2 > \sigma_c(F_o^2)$; the agreement factor was 0.03.

The starting point for the structure refinement was a model which included all nonhydrogen atoms and the unique hydride ligand. Initial least-squares refinement of this model was undertaken with the low-angle data ($0^\circ < 2\theta < 73^\circ$). The phenyl H atoms were then included and the entire structure refined to give $R(F) = 0.070$. At this point the high-angle data were added, and a few cycles of differential synthesis followed by block-matrix least-squares refinement^{17a} were carried out with anisotropic thermal parameters for all atoms. The quantity minimized in this least squares was $\sum w(F_o^2 - F_c^2)^2$, where weights w were taken as being inversely proportional to the variances

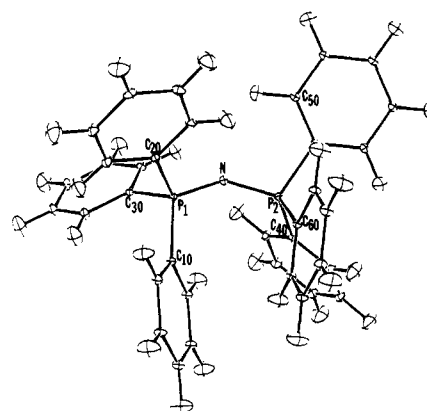


Figure 3. Molecular plot of the $[(\text{Ph}_3\text{P})_2\text{N}]^+$ cation viewed approximately normal to the $\text{N-P}(2)$ bond.

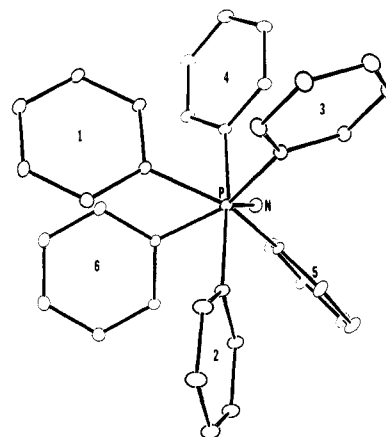


Figure 4. Drawing of the $[(\text{Ph}_3\text{P})_2\text{N}]^+$ cation projected along the P-N axis to depict the staggered conformation. Phenyl H atoms have been removed for clarity.

$\sigma^2(F_o^2) = \sigma_c^2(F_o^2) + (0.01F_o^2)^2 + (8.80/F_o^2)^2$. The factors 0.01 and 8.80 represent estimates of the non-Poisson contributions to the error. Neutron scattering lengths were taken from the compilation by Koester.^{17b} The data were only modestly affected by extinction,^{17c} with the most significant correction (on F^2) amounting to 11% for reflection (230). The final refinement resulted in $R(F^2) = 0.030$, $R(wF^2) = 0.032$, $R(F) = 0.027$, $R(wF) = 0.016$, and goodness-of-fit $S = [\sum w(F_o^2 - F_c^2)^2 / (n_o - n_v)]^{1/2} = 1.037$.

Results and Discussion

The final positional and thermal parameters for $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{H}_2\text{W}_2(\text{CO})_8]^{2-}$ are given in Tables II and III, respectively, and bond distances and angles are listed in Tables IV and V. In these tables the results of the X-ray and neutron diffraction analyses are compared wherever possible, but in the following discussion the results of the more accurate neutron analysis are described. Drawings of the $[\text{H}_2\text{W}_2(\text{CO})_8]^{2-}$ anion and the $[(\text{Ph}_3\text{P})_2\text{N}]^+$ cation are given in Fig-

(15) Air Products and Chemicals, Inc., Displex Model CS-202.

(16) (a) Dimmler, D. G.; Greenlaw, N.; Kelley, M. A.; Potter, D. W.; Rankowitz, S.; Stubblefield, F. W. *IEEE Trans. Nucl. Sci.* **1976**, *NS-23*, 398. (b) McMullan, R. K.; Andrews, L. C.; Koetzle, T. F.; Reidinger, F.; Thomas, R.; Williams, G. J. B., "NEXDAS, Neutron and X-ray Data Acquisition System", unpublished work, 1976.

(17) (a) The scale factor, overall temperature factor, and isotropic extinction parameters were put in one block (3×3), while the atomic positional and anisotropic thermal parameters were distributed into 14 additional blocks. Refinement was continued until the largest parameter shift was less than 0.5σ . (b) Koester, L. In "Neutron Physics"; Springer-Verlag: New York, 1977; p 36. (c) Becker, P.; Coppens, P. *Acta Crystallogr., Sect. A* **1975**, *A31*, 417. An isotropic type I extinction model with Lorentzian mosaic was employed.

Table II. Final Positional Parameters^a for [(Ph₃P)₂N]⁺₂[HW₂(CO)₈]²⁻

atom	x	y	z	atom	x	y	z
(A) [H ₂ W ₂ (CO) ₈] ²⁻ Anion							
H	0.5536 (2)	0.0014 (1)	0.1084 (2)	O(2)	0.59184 (8)	0.29291 (8)	0.24823 (9)
	0.529	0.015	0.120		0.5900 (6)	0.2836 (6)	0.2338 (7)
W	0.50460 (9)	0.11190 (8)	0.02161 (10)	C(3)	0.65447 (7)	0.05513 (7)	-0.03985 (8)
	0.50319 (2)	0.10890 (2)	0.01610 (3)		0.6473 (7)	0.0516 (7)	-0.0452 (8)
C(1)	0.44670 (7)	0.19983 (7)	-0.10167 (8)	O(3)	0.74187 (8)	0.02874 (6)	-0.06919 (10)
	0.4454 (8)	0.1915 (8)	-0.1053 (9)		0.7357 (7)	0.0274 (6)	-0.0726 (7)
O(1)	0.41143 (9)	0.24745 (8)	-0.17988 (10)	C(4)	0.36547 (7)	0.18457 (7)	0.10711 (8)
	0.4112 (7)	0.2423 (7)	-0.1832 (8)		0.3677 (8)	0.1820 (8)	0.0975 (9)
C(2)	0.56105 (7)	0.22509 (6)	0.16247 (8)	O(4)	0.29121 (8)	0.23408 (8)	0.1635 (1)
	0.5582 (8)	0.2176 (8)	0.1513 (9)		0.2916 (8)	0.2328 (8)	0.1525 (9)
(B) [(Ph ₃ P) ₂ N] ⁺ Cation							
N	0.76994 (5)	0.30893 (5)	0.56743 (6)	C(35)	0.65246 (7)	0.13546 (6)	0.47210 (8)
	0.7761 (5)	0.3120 (5)	0.5710 (6)		0.6558 (6)	0.1496 (6)	0.4758 (7)
P(1)	0.78861 (8)	0.24665 (8)	0.67118 (10)	C(40)	0.91394 (6)	0.27742 (6)	0.39843 (8)
	0.79176 (15)	0.25001 (14)	0.67148 (17)		0.9139 (6)	0.2769 (6)	0.3971 (7)
P(2)	0.83880 (8)	0.36652 (8)	0.53088 (10)	C(41)	0.87219 (7)	0.19279 (6)	0.31015 (8)
	0.84167 (15)	0.36729 (15)	0.53156 (18)		0.8745 (7)	0.1956 (7)	0.3147 (8)
C(10)	0.93391 (6)	0.18455 (6)	0.72605 (8)	C(42)	0.92548 (7)	0.12423 (7)	0.20344 (8)
	0.9354 (5)	0.1857 (5)	0.7274 (7)		0.9255 (9)	0.1268 (9)	0.2067 (10)
C(11)	0.99821 (6)	0.11858 (6)	0.62672 (8)	C(43)	1.02002 (7)	0.13963 (7)	0.18430 (8)
	0.9982 (6)	0.1172 (6)	0.6326 (7)		1.0164 (9)	0.1411 (9)	0.1850 (11)
C(12)	1.11299 (7)	0.07452 (7)	0.65952 (8)	C(44)	1.06123 (7)	0.22432 (7)	0.27157 (8)
	1.1126 (7)	0.0722 (7)	0.6661 (8)		1.0587 (10)	0.2183 (10)	0.2672 (11)
C(13)	1.16459 (7)	0.09433 (7)	0.79146 (8)	C(45)	1.00832 (7)	0.29353 (7)	0.37830 (8)
	1.1602 (8)	0.0960 (7)	0.7960 (9)		1.0075 (9)	0.2905 (9)	0.3752 (10)
C(14)	1.10026 (7)	0.15756 (7)	0.89037 (8)	C(50)	0.74212 (6)	0.47944 (6)	0.47853 (8)
	1.0951 (8)	0.1631 (8)	0.8912 (10)		0.7448 (6)	0.4798 (6)	0.4798 (7)
C(15)	0.98508 (7)	0.20336 (6)	0.85828 (8)	C(51)	0.77833 (7)	0.53352 (7)	0.41947 (8)
	0.9819 (7)	0.2103 (7)	0.8567 (8)		0.7794 (9)	0.5367 (9)	0.4302 (10)
C(20)	0.72613 (6)	0.33483 (6)	0.81387 (8)	C(52)	0.70632 (7)	0.62751 (7)	0.39169 (8)
	0.7272 (6)	0.3365 (6)	0.8120 (7)		0.7029 (10)	0.6277 (9)	0.3962 (11)
C(21)	0.68502 (7)	0.44516 (6)	0.82696 (8)	C(53)	0.59817 (7)	0.66786 (7)	0.42137 (8)
	0.6888 (8)	0.4454 (7)	0.8275 (9)		0.5963 (9)	0.6564 (9)	0.4053 (10)
C(22)	0.63943 (7)	0.51657 (7)	0.93821 (8)	C(54)	0.56224 (7)	0.61383 (7)	0.47949 (9)
	0.6431 (9)	0.5161 (9)	0.9410 (11)		0.5595 (12)	0.5948 (11)	0.4420 (14)
C(23)	0.63646 (7)	0.47813 (7)	1.03762 (8)	C(55)	0.63377 (7)	0.51939 (7)	0.50753 (8)
	0.6347 (9)	0.4765 (9)	1.0289 (11)		0.6360 (11)	0.5086 (10)	0.4879 (12)
C(24)	0.67635 (7)	0.36802 (7)	1.02506 (8)	C(60)	0.93611 (6)	0.42184 (6)	0.66692 (8)
	0.6726 (10)	0.3702 (9)	1.0182 (11)		0.9379 (6)	0.4198 (6)	0.6625 (7)
C(25)	0.72017 (7)	0.29592 (7)	0.91272 (8)	C(61)	0.89599 (7)	0.52688 (6)	0.74633 (8)
	0.7170 (8)	0.2962 (8)	0.9024 (10)		0.8994 (8)	0.5204 (8)	0.7410 (9)
C(30)	0.72558 (6)	0.13819 (6)	0.59249 (8)	C(62)	0.96469 (7)	0.56948 (7)	0.85984 (8)
	0.7275 (6)	0.1465 (6)	0.5924 (7)		0.9681 (10)	0.5617 (10)	0.8528 (12)
C(31)	0.75095 (7)	0.05573 (6)	0.65070 (8)	C(63)	1.07327 (7)	0.50811 (7)	0.89473 (8)
	0.7528 (7)	0.0628 (7)	0.6447 (9)		1.0759 (9)	0.4983 (9)	0.8827 (11)
C(32)	0.70213 (7)	-0.02834 (7)	0.58918 (8)	C(64)	1.11338 (7)	0.40332 (7)	0.81642 (8)
	0.7034 (9)	-0.0163 (8)	0.5846 (10)		1.1128 (9)	0.3976 (8)	0.8052 (10)
C(33)	0.62909 (7)	-0.03082 (7)	0.46915 (8)	C(65)	1.04533 (7)	0.35996 (6)	0.70258 (8)
	0.6299 (9)	-0.0118 (8)	0.4689 (10)		1.0462 (8)	0.3548 (8)	0.6940 (9)
C(34)	0.60452 (7)	0.05075 (6)	0.41089 (8)				
	0.6049 (8)	0.0701 (8)	0.4136 (9)				
H(11)	0.9590 (2)	0.1038 (2)	0.5237 (2)	H(41)	0.7989 (2)	0.1810 (2)	0.3257 (2)
H(12)	1.1627 (1)	0.0258 (2)	0.5820 (2)	H(42)	0.8932 (2)	0.0587 (2)	0.1352 (2)
H(13)	1.2545 (1)	0.0603 (2)	0.8177 (2)	H(43)	1.0624 (2)	0.0854 (2)	0.1025 (2)
H(14)	1.1401 (2)	0.1717 (2)	0.9932 (2)	H(44)	1.1355 (2)	0.2362 (2)	0.2572 (2)
H(15)	0.9364 (1)	0.2536 (1)	0.9360 (2)	H(45)	1.0415 (2)	0.3592 (1)	0.4461 (2)
H(21)	0.6882 (2)	0.4754 (1)	0.7502 (2)	H(51)	0.8618 (2)	0.5018 (2)	0.3937 (2)
H(22)	0.6064 (2)	0.6017 (2)	0.9463 (2)	H(52)	0.7331 (2)	0.6690 (2)	0.3440 (2)
H(23)	0.6019 (2)	0.5340 (2)	1.1247 (2)	H(53)	0.5422 (2)	0.7405 (2)	0.3980 (2)
H(24)	0.6722 (2)	0.3381 (2)	1.1022 (2)	H(54)	0.4789 (2)	0.6452 (2)	0.5049 (2)
H(25)	0.7497 (2)	0.2105 (1)	0.9038 (2)	H(55)	0.6060 (2)	0.4770 (2)	0.5525 (2)
H(31)	0.8096 (2)	0.0555 (2)	0.7424 (2)	H(61)	0.8120 (2)	0.5764 (1)	0.7200 (2)
H(32)	0.7220 (2)	-0.0919 (2)	0.6344 (2)	H(62)	0.9320 (2)	0.6504 (1)	0.9207 (2)
H(33)	0.5925 (2)	-0.0972 (2)	0.4198 (2)	H(63)	1.1266 (2)	0.5414 (2)	0.9835 (2)
H(34)	0.5495 (2)	0.0477 (2)	0.3159 (2)	H(64)	1.1981 (1)	0.3553 (2)	0.8439 (2)
H(35)	0.6354 (2)	0.1975 (1)	0.4251 (2)	H(65)	1.0775 (2)	0.2785 (1)	0.6427 (2)

^a For each atom, the neutron diffraction result is given on the first line and the X-ray diffraction result, if available, on the second line. Numbering scheme for the [(Ph₃P)₂N]⁺ cation: C(10)–C(15) = phenyl 1, C(20)–C(25) = phenyl 2, etc., with phenyl 1–phenyl 3 attached to P(1) and phenyl 4–phenyl 6 attached to P(2). H(11) is attached to C(11), H(12) is attached to C(12), etc.

ures 1–4. A listing of the observed and calculated F^2 values for the neutron structure determination is available (see paragraph at the end of the paper for details).

The anions are situated on crystallographic inversion centers, surrounded by cations at normal van der Waals contact distances (See Figure 5). The two crystallographically equivalent

Table III. Final Thermal Parameters^a for [(Ph₃P)₂N]⁺₂[H₂W₂(CO)₈]²⁻

atom	<i>B</i> , Å ²	10 ⁴ <i>U</i> ₁₁	10 ⁴ <i>U</i> ₂₂	10 ⁴ <i>U</i> ₃₃	10 ⁴ <i>U</i> ₁₂	10 ⁴ <i>U</i> ₁₃	10 ⁴ <i>U</i> ₂₃
(A) [H ₂ W ₂ (CO) ₈] ²⁻ Anion							
H		340 (10)	207 (9)	195 (9)	-112 (8)	-26 (7)	95 (7)
W		41 (5)	46 (5)	40 (5)	-5 (4)	10 (4)	21 (4)
		403 (2)	407 (2)	355 (2)	-69 (2)	26 (1)	159 (1)
C(1)	4.9 (2)	110 (4)	76 (4)	68 (4)	-4 (3)	13 (3)	36 (3)
O(1)	7.6 (2)	198 (5)	104 (5)	95 (4)	-4 (4)	0 (4)	71 (4)
C(2)	4.8 (2)	81 (4)	81 (4)	75 (4)	-25 (3)	6 (3)	23 (3)
O(2)	6.3 (2)	139 (5)	110 (5)	93 (4)	-61 (4)	6 (4)	9 (4)
C(3)	4.0 (2)	71 (4)	88 (4)	97 (4)	-1 (3)	28 (3)	38 (3)
O(3)	6.8 (2)	78 (4)	154 (5)	155 (5)	1 (4)	53 (4)	67 (4)
C(4)	4.6 (2)	62 (4)	84 (4)	96 (4)	-5 (3)	25 (3)	19 (3)
O(4)	8.6 (2)	84 (4)	143 (5)	165 (5)	0 (4)	66 (4)	-1 (4)
(B) [(Ph ₃ P) ₂ N] ⁺ Cation							
N		70 (2)	73 (3)	79 (2)	-18 (2)	14 (2)	35 (2)
		348 (3)	422 (3)	457 (4)	-131 (30)	50 (3)	202 (3)
P(1)		54 (4)	48 (4)	58 (4)	-9 (3)	16 (3)	17 (4)
		304 (1)	319 (1)	319 (1)	-77 (1)	69 (1)	78 (1)
P(2)		45 (4)	50 (4)	60 (4)	-12 (4)	9 (3)	12 (4)
		319 (1)	351 (1)	393 (1)	-77 (1)	63 (1)	143 (1)
C(10)	2.6 (3)	52 (3)	64 (3)	65 (3)	-4 (3)	9 (3)	21 (3)
C(11)	3.3 (1)	61 (3)	76 (4)	68 (4)	2 (3)	12 (3)	16 (3)
C(12)	4.2 (2)	58 (3)	83 (4)	85 (4)	4 (3)	14 (3)	19 (3)
C(13)	4.5 (2)	64 (4)	94 (4)	103 (4)	-4 (3)	6 (3)	29 (3)
C(14)	5.1 (2)	61 (3)	105 (4)	82 (4)	-11 (3)	-11 (3)	30 (3)
C(15)	3.9 (2)	78 (4)	85 (4)	59 (3)	-13 (3)	9 (3)	23 (3)
C(20)	3.0 (1)	66 (3)	63 (3)	66 (3)	-10 (3)	26 (3)	16 (3)
C(21)	4.5 (2)	88 (4)	66 (4)	80 (4)	2 (3)	28 (3)	16 (3)
C(22)	5.8 (2)	103 (4)	83 (4)	93 (4)	-2 (3)	30 (3)	6 (3)
C(23)	6.0 (2)	96 (4)	104 (4)	98 (4)	-18 (3)	46 (3)	-1 (3)
C(24)	6.3 (2)	130 (4)	110 (4)	94 (4)	-31 (3)	60 (3)	10 (3)
C(25)	5.3 (2)	123 (4)	83 (4)	81 (4)	-21 (3)	49 (3)	17 (3)
C(30)	2.8 (1)	62 (3)	63 (3)	65 (3)	-20 (3)	10 (3)	23 (3)
C(31)	4.3 (2)	102 (4)	75 (4)	79 (4)	-41 (3)	-1 (3)	32 (3)
C(32)	5.6 (2)	115 (4)	80 (4)	106 (4)	-47 (3)	-5 (3)	39 (3)
C(33)	5.4 (2)	113 (4)	86 (4)	101 (4)	-46 (3)	14 (3)	21 (3)
C(34)	4.8 (2)	85 (4)	88 (4)	84 (4)	-32 (3)	5 (3)	21 (3)
C(35)	3.4 (1)	72 (3)	75 (4)	72 (3)	-15 (3)	3 (3)	30 (3)
C(40)	3.4 (1)	68 (3)	56 (4)	79 (4)	-13 (3)	25 (3)	15 (3)
C(41)	4.3 (2)	80 (4)	82 (4)	84 (4)	-22 (3)	30 (3)	13 (3)
C(42)	5.7 (2)	112 (4)	87 (4)	86 (4)	-23 (3)	43 (3)	-1 (3)
C(43)	6.1 (2)	112 (4)	100 (4)	105 (4)	-9 (3)	56 (3)	23 (3)
C(44)	6.9 (3)	101 (4)	97 (4)	116 (4)	-18 (3)	59 (3)	26 (3)
C(45)	5.9 (2)	78 (4)	87 (4)	106 (4)	-19 (3)	44 (3)	17 (3)
C(50)	2.8 (1)	52 (3)	63 (4)	74 (4)	0 (3)	13 (3)	35 (3)
C(51)	6.0 (2)	77 (4)	101 (4)	126 (4)	-6 (3)	23 (3)	74 (3)
C(52)	6.3 (2)	76 (4)	107 (4)	146 (4)	7 (3)	30 (3)	85 (3)
C(53)	5.7 (2)	78 (4)	93 (4)	140 (4)	5 (3)	22 (3)	69 (3)
C(54)	8.0 (3)	79 (4)	88 (4)	172 (4)	10 (3)	42 (3)	71 (3)
C(55)	7.2 (3)	70 (4)	87 (4)	159 (4)	-1 (3)	27 (3)	69 (3)
C(60)	3.2 (1)	56 (3)	59 (3)	65 (3)	-7 (3)	6 (3)	24 (3)
C(61)	4.8 (2)	72 (4)	63 (4)	81 (4)	-6 (3)	7 (3)	8 (3)
C(62)	7.1 (3)	94 (4)	82 (4)	93 (4)	-19 (3)	-1 (3)	8 (3)
C(63)	6.2 (2)	87 (4)	110 (4)	87 (4)	-31 (3)	-6 (3)	29 (3)
C(64)	5.6 (2)	66 (4)	95 (4)	94 (4)	-9 (3)	-2 (3)	40 (3)
C(65)	4.6 (2)	64 (3)	74 (4)	97 (4)	-10 (3)	8 (3)	38 (3)
H(11)		207 (8)	299 (10)	128 (8)	-36 (7)	6 (7)	42 (7)
H(12)		186 (9)	281 (10)	186 (8)	1 (7)	76 (7)	12 (7)
H(13)		129 (8)	289 (10)	257 (9)	15 (7)	18 (7)	61 (8)
H(14)		198 (9)	334 (10)	134 (8)	-38 (8)	-27 (7)	47 (7)
H(15)		189 (8)	255 (9)	159 (8)	-9 (7)	62 (7)	7 (7)
H(21)		340 (10)	192 (9)	224 (9)	-22 (7)	99 (8)	94 (7)
H(22)		342 (10)	174 (9)	291 (10)	14 (8)	135 (8)	57 (7)
H(23)		317 (10)	229 (9)	211 (9)	-42 (8)	129 (8)	-24 (7)
H(24)		414 (10)	283 (10)	228 (9)	-101 (9)	143 (8)	77 (8)
H(25)		389 (10)	152 (8)	293 (10)	-21 (8)	143 (8)	87 (7)
H(31)		272 (9)	267 (10)	194 (9)	-134 (8)	-79 (7)	118 (7)
H(32)		379 (10)	229 (9)	274 (10)	-136 (8)	-27 (8)	150 (8)
H(33)		315 (10)	208 (9)	268 (10)	-160 (8)	-16 (8)	38 (7)
H(34)		258 (9)	300 (10)	179 (8)	-131 (8)	-73 (7)	92 (7)
H(35)		262 (9)	183 (8)	207 (9)	-56 (7)	-4 (7)	115 (7)
H(41)		210 (9)	284 (10)	255 (9)	-125 (8)	91 (7)	16 (8)
H(42)		325 (10)	246 (10)	218 (9)	-150 (8)	90 (8)	-61 (7)
H(43)		288 (10)	263 (10)	252 (10)	-63 (8)	166 (8)	-22 (8)
H(44)		196 (9)	286 (10)	315 (10)	-78 (7)	132 (8)	50 (8)

Table III (Continued)

atom	$B, \text{\AA}^2$	$10^4 U_{11}$	$10^4 U_{22}$	$10^4 U_{33}$	$10^4 U_{12}$	$10^4 U_{13}$	$10^4 U_{23}$
H(45)		254 (9)	224 (9)	256 (9)	-138 (8)	84 (7)	-22 (7)
H(51)		193 (9)	273 (10)	420 (10)	26 (7)	134 (8)	201 (9)
H(52)		241 (9)	323 (10)	442 (10)	-18 (8)	110 (9)	267 (9)
H(53)		214 (9)	212 (9)	387 (10)	23 (7)	82 (8)	177 (8)
H(54)		186 (9)	288 (10)	499 (10)	25 (8)	155 (8)	192 (9)
H(55)		207 (9)	266 (10)	409 (10)	-24 (7)	113 (8)	205 (9)
H(61)		179 (8)	198 (9)	270 (9)	2 (7)	-4 (7)	49 (7)
H(62)		264 (10)	158 (9)	248 (9)	-6 (7)	0 (8)	-29 (7)
H(63)		213 (9)	280 (10)	209 (9)	-87 (7)	-53 (7)	27 (7)
H(64)		144 (8)	249 (9)	266 (9)	2 (7)	-23 (7)	78 (8)
H(65)		187 (8)	158 (8)	263 (9)	0 (7)	18 (7)	7 (7)

^a For anisotropic temperature factors, the neutron result is given on the first line, and the X-ray result, if available, on the second line. The isotropic temperature factors are derived from X-ray data. Anisotropic thermal parameters are of the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$.

Table IV. Bond Distances (Å) and Angles (Deg) in the $[\text{H}_2\text{W}_2(\text{CO})_8]^{2-}$ Anion

	neutron	X-ray		neutron	X-ray
W-W'	3.010 (2)	2.9945 (5)	W-C(4)	2.028 (1)	1.975 (10)
W-H	1.920 (3)	1.93 ^a	C(1)-O(1)	1.167 (2)	1.202 (14)
W-H'	1.933 (2)	1.96 ^a	C(2)-O(2)	1.167 (1)	1.170 (13)
W-C(1)	1.966 (2)	1.907 (11)	C(3)-O(3)	1.158 (1)	1.178 (12)
W-C(2)	1.966 (1)	1.938 (11)	C(4)-O(4)	1.156 (1)	1.172 (14)
W-C(3)	2.025 (1)	1.971 (9)			

	neutron	X-ray		neutron	X-ray
W-H-W'	102.7 (1)	101 ^a	H-W-C(1)	167.42 (8)	166 ^a
H-W-H'	77.3 (1)	79 ^a	H-W-C(2)	99.96 (8)	98 ^a
W'-W-H'	38.48 (7)	39 ^a	H-W-C(3)	88.85 (8)	99 ^a
W'-W-H	38.78 (6)	40 ^a	H-W-C(4)	91.68 (9)	82 ^a
C(1)-W-C(2)	92.44 (6)	93.6 (5)	H'-W-C(1)	90.44 (8)	91 ^a
C(1)-W-C(3)	89.47 (7)	89.7 (4)	H'-W-C(2)	176.35 (11)	171 ^a
C(1)-W-C(4)	91.89 (5)	90.9 (4)	H'-W-C(3)	94.20 (8)	85 ^a
C(2)-W-C(3)	88.07 (6)	87.6 (4)	H'-W-C(4)	94.54 (9)	104 ^a
C(2)-W-C(4)	83.13 (5)	84.0 (4)	W-C(1)-O(1)	176.57 (8)	178.4 (9)
C(3)-W-C(4)	171.14 (6)	171.6 (4)	W-C(2)-O(2)	177.80 (10)	179.2 (8)
			W-C(3)-O(3)	175.47 (8)	172.7 (9)
			W-C(4)-O(4)	173.08 (9)	173.8 (10)

^a The H atom position was not refined in the X-ray work.

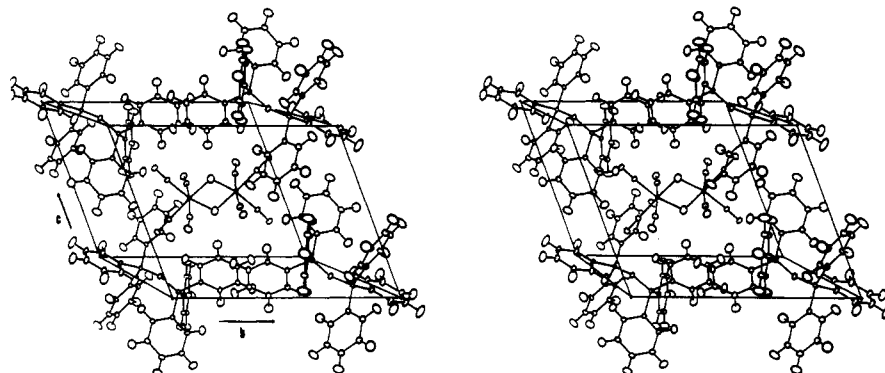
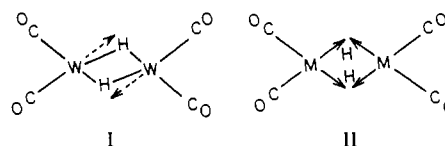


Figure 5. Stereoscopic view of the contents of the unit cell.

H atoms bridge the W-W bond in a slightly asymmetric manner, with the two W-H distances [1.920 (3) and 1.933 (2) Å] differing by 3.6σ . The interatomic distances and angles within the strictly planar $\text{W}(\mu\text{-H})_2\text{W}$ core are $\text{W}\cdots\text{W}' = 3.010$ (2) Å, $\text{H}\cdots\text{H}' = 2.405$ (3) Å, $\text{W-H-W}' = \text{W-H'-W}' = 102.7$ (1)°, $\text{H-W-H}' = \text{H-W'-H}' = 77.3$ (1)°, $\text{W'-W-H} = 38.78$ (6)°, and $\text{W'-W-H}' = 38.48$ (6)°. These values agree to within experimental uncertainty with the results obtained from the room-temperature X-ray diffraction analysis of $[\text{Et}_4\text{N}]^+_2[\text{H}_2\text{W}_2(\text{CO})_8]^{2-}$.⁴ The coordination about each W atom is, as expected, approximately octahedral. However, in the present structure the anion is slightly but significantly distorted from ideal D_{2h} symmetry. The most noticeable feature of this distortion is that, while the two axial ligands [C(3)O(3) and C(4)O(4)] are coplanar with H' and C(2)O(2),

they are not coplanar with H and C(1)O(1) (see Figure 1). In other words, the H-W-C(1) angle [167.4 (1)°] is substantially more bent than the H'-W-C(2) angle [176.4 (1)°]. We have no ready explanation for this distortion, which is schematically depicted in I. Another feature worth pointing

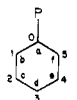


out is the fact that, as noted by Churchill and Chang,⁴ the H atoms are situated somewhat "inside" the intersection of the trans OC-M vectors, as shown in II. If the H atoms were

Table V. Bond Distances (Å) and Angles (Deg) in the $[(\text{Ph}_3\text{P})_2\text{N}]^+$ Cation^a

	neutron		X-ray		neutron		X-ray	
N-P(1)	1.585 (2)		1.572 (7)		P(2)-C(40)	1.800 (1)		1.806 (8)
N-P(2)	1.588 (2)		1.578 (7)		P(2)-C(50)	1.794 (1)		1.791 (8)
P(1)-C(10)	1.804 (1)		1.812 (7)		P(2)-C(60)	1.804 (1)		1.798 (8)
P(1)-C(20)	1.800 (1)		1.796 (8)		P(1)-N-P(2)	136.84 (6)		139.4 (4)
P(1)-C(30)	1.799 (1)		1.801 (9)					
	Ph(1)		Ph(2)		Ph(3)			
C-C dist	neutron	X-ray	neutron	X-ray	neutron	X-ray		
0-1	1.404 (1)	1.368 (10)	1.399 (1)	1.387 (14)	1.403 (1)	1.387 (14)		
1-2	1.392 (1)	1.404 (12)	1.395 (1)	1.417 (14)	1.394 (1)	1.380 (16)		
2-3	1.395 (1)	1.383 (12)	1.391 (2)	1.327 (18)	1.396 (1)	1.392 (15)		
3-4	1.395 (1)	1.385 (14)	1.397 (1)	1.361 (20)	1.394 (1)	1.387 (17)		
4-5	1.399 (1)	1.397 (13)	1.397 (1)	1.441 (16)	1.394 (1)	1.398 (14)		
5-0	1.397 (1)	1.374 (11)	1.404 (2)	1.369 (14)	1.400 (1)	1.387 (10)		
	Ph(1)		Ph(2)		Ph(3)			
C-C-C angles	neutron	X-ray	neutron	X-ray	neutron	X-ray		
a	119.70 (7)	121.2 (7)	119.67 (7)	120.6 (8)	120.10 (8)	120.5 (8)		
b	120.21 (7)	120.2 (7)	120.33 (9)	119.7 (10)	119.86 (7)	120.6 (8)		
c	120.19 (7)	119.2 (8)	119.86 (8)	119.2 (12)	119.93 (9)	118.6 (11)		
d	119.61 (7)	120.0 (9)	120.29 (8)	122.8 (11)	120.18 (8)	121.7 (11)		
e	120.59 (7)	120.4 (9)	120.08 (10)	119.2 (11)	120.28 (7)	118.8 (9)		
f	119.65 (7)	119.0 (8)	119.73 (8)	118.2 (11)	119.64 (9)	119.7 (9)		
	Ph(4)		Ph(5)		Ph(6)			
C-C dist	neutron	X-ray	neutron	X-ray	neutron	X-ray		
0-1	1.402 (1)	1.369 (14)	1.402 (2)	1.368 (16)	1.401 (1)	1.362 (14)		
1-2	1.394 (1)	1.397 (14)	1.390 (1)	1.405 (19)	1.393 (1)	1.408 (16)		
2-3	1.395 (2)	1.381 (17)	1.395 (1)	1.332 (16)	1.394 (1)	1.392 (18)		
3-4	1.396 (1)	1.345 (19)	1.391 (2)	1.352 (21)	1.395 (1)	1.356 (18)		
4-5	1.393 (1)	1.408 (17)	1.395 (1)	1.413 (22)	1.394 (1)	1.396 (14)		
5-0	1.403 (1)	1.412 (15)	1.395 (1)	1.357 (15)	1.404 (1)	1.408 (13)		
	Ph(4)		Ph(5)		Ph(6)			
C-C-C angles	neutron	X-ray	neutron	X-ray	neutron	X-ray		
a	119.96 (7)	120.4 (8)	119.90 (8)	119.3 (10)	119.72 (7)	120.3 (8)		
b	119.77 (9)	120.0 (9)	119.68 (8)	119.4 (10)	119.90 (7)	120.5 (10)		
c	120.22 (8)	119.3 (11)	120.45 (10)	121.2 (13)	120.30 (7)	119.3 (12)		
d	120.08 (8)	121.5 (11)	119.78 (8)	119.8 (13)	120.03 (7)	119.8 (11)		
e	120.13 (9)	120.5 (12)	120.21 (8)	119.8 (13)	120.13 (7)	122.0 (10)		
f	119.83 (8)	118.2 (11)	119.98 (10)	119.9 (13)	119.93 (6)	118.2 (9)		
	Ph(1)		Ph(2)		Ph(3)		Ph(4)	
C-H dist								
1-H	1.086 (2)	1.084 (3)	1.086 (2)	1.084 (3)	1.088 (2)	1.087 (2)		
2-H	1.086 (2)	1.084 (2)	1.083 (3)	1.085 (2)	1.087 (3)	1.082 (3)		
3-H	1.090 (2)	1.086 (2)	1.086 (2)	1.083 (2)	1.084 (2)	1.087 (2)		
4-H	1.086 (2)	1.089 (3)	1.089 (2)	1.091 (3)	1.086 (2)	1.089 (2)		
5-H	1.083 (2)	1.085 (2)	1.085 (3)	1.090 (2)	1.082 (3)	1.083 (2)		

^a Distances and angles are defined as in



located at the intersections of the trans ligand-metal vectors, the calculated W-H-W angle would be 87.6° (as opposed to the observed 102.7°). Configuration II was also observed in the $\text{M}(\mu\text{-H})_2\text{M}$ portion of the structure of $\text{H}_2\text{Os}_3(\text{CO})_{10}$.¹⁸ By contrast, the single-bridged W-H-W systems have the H atom situated "outside" the intersection of the trans ligand-M vectors.⁷

The present structure determination allows the first accurate comparison between $\text{M}(\mu\text{-H})\text{M}$ and $\text{M}(\mu\text{-H})_2\text{M}$ linkages involving the same metal atom. We note that the average W-H distance in $[\text{H}_2\text{W}_2(\text{CO})_8]^{2-}$ [1.926 (2) Å] is significantly longer than the average W-H distance [1.882 (5) Å] measured in several single-bridged W-H-W systems (see Table VI). Perhaps this is an indication that the M-H bond order is, for

some reason, lower in $\text{M}(\mu\text{-H})_2\text{M}$ linkages than in $\text{M}(\mu\text{-H})\text{M}$ linkages.

It is interesting to note that the ¹H NMR hydride resonance for $[\text{H}_2\text{W}_2(\text{CO})_8]^{2-}$ (δ -4.72) is considerably deshielded relative to the hydride resonance for $[\text{HW}_2(\text{CO})_{10}]^-$ (δ -12.6).¹¹ Perhaps this is due to a lower bond order in the $\text{M}(\mu\text{-H})_2\text{M}$ system. Alternatively, the longer W-H distance might cause the same effect. Other hydrides bridging "unsaturated" or electron-deficient metal systems also show similar deshielding: $[\text{H}_2\text{Re}_2(\text{CO})_8]$, δ -9.04;¹⁹ $[\text{H}_4\text{Re}_4(\text{CO})_{12}]$, δ -5.08;²⁰ $[\text{H}_3\text{Re}_3(\text{CO})_{10}]^{2-}$, δ -6.4.²¹ For $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$, the Os($\mu\text{-H})_2\text{Os}$ resonance is at δ -11.36,⁵ close to the terminal Os-H

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Table VI. Comparison of Molecular Parameters for Various M-H-M and M-H-B Linkages^a (Values Derived from Neutron Data)

(A) M-H-M Compounds						
	M-M, Å	M-H, Å	H···H, Å	M-H-M, deg	H-M-H, deg	ref
		M(μ-H)M				
$[\text{HCr}_2(\text{CO})_{10}]^-[\text{Et}_4\text{N}]^+$	3.386 (6)	1.722 (20)		158.9 (6)		31
$[\text{DCr}_2(\text{CO})_{10}]^-[(\text{Ph}_3\text{P})_2\text{N}]^+$	3.390 (3)	1.734 (9)		155.7 (9)		32
$[\text{HW}_2(\text{CO})_{10}]^-[\text{Et}_4\text{N}]^+$	3.528 (2)	1.894 (12)		137.1 (10)		6b, 33
$[\text{HW}_2(\text{CO})_{10}]^-[\text{Ph}_4\text{P}]^+$	3.340 (5)	1.897 (5)		123.4 (5)		6b, 33
$[\text{HW}_2(\text{CO})_8(\text{NO})\text{P}(\text{OMe})_3]$	3.393 (4)	1.876 (6)		129.4 (3)		7b
$[\text{HW}_2(\text{CO})_8(\text{NO})]$ (monoclinic form)	3.330 (3)	1.870 (4)		125.9 (4)		7a
$[\text{HW}_2(\text{CO})_8(\text{NO})]$ (triclinic form)	3.328 (3)	1.875 (4)		125.0 (2)		7a
		M(μ-H) ₂ M				
$\text{H}_4\text{Th}_2(\text{C}_5\text{Me}_5)_4$	4.007 (8)	2.29 (3)	2.22 (1)	122 (4)	58 (1)	26
$[\text{H}_2\text{W}_2(\text{CO})_8]^{2-}[(\text{Ph}_3\text{P})_2\text{N}]^+_2$	3.010 (2)	1.926 (2)	2.405 (3)	102.7 (1)	77.3 (1)	this work
$\text{H}_2\text{Os}_3(\text{CO})_{10}^b$	2.683 (1)	1.845 (3)	2.376 (3)	94.3 (1)	80.2 (1)	18
$\text{H}_2\text{Rh}_2[\text{P}(\text{O}-i\text{-Pr})_3]_4$	2.647 (13)	1.808 (14)	2.465 (14)	94.1 (4)	85.9 (5)	34
		M(μ-H) ₃ M				
$[\text{H}_3\text{Ir}_2(\text{C}_5\text{Me}_5)_2]^+[\text{BF}_4]^-$	2.458 (6)	1.75 (3)	2.14 (4)	89.5 (8)	75.8 (9)	8a, 35
		M(μ-H) ₄ M				
$\text{H}_8\text{Re}_2(\text{PEt}_2\text{Ph})_4$	2.538 (4)	1.878 (7)	1.956 (8)	85.0 (3)	62.6 (3)	8b
(B) M-H-B Compounds						
	M-B, Å	M-H, Å	H···H, Å	M-H-B, deg	H-M-H, deg	ref
		M(μ-H)B				
$\text{Cu}(\text{BH}_4)(\text{PMePh}_2)_3$	2.518 (3)	1.697 (5)		121.7 (4)		36
		M(μ-H) ₂ B				
$\text{U}(\text{BH}_4)_4$	2.86 (4)	2.41 (3)	2.09 (2)	98 (1)	51 (2)	37
$\text{Hf}(\text{C}_5\text{H}_4\text{Me})_2(\text{BH}_4)_2$	2.553 (6)	2.095 (7)	2.27 (1)	96.8 (5)	57.0 (3)	38
$\text{Co}(\text{terpy})(\text{BH}_4)^c$	2.15 (1)	1.724 (12)	2.06 (1)	90.0 (6)	73.5 (6)	39
		M(μ-H) ₃ B				
$\text{U}(\text{BH}_4)_4$	2.52 (1)	2.34 (2)	1.97 (5)	83 (1)	50 (2)	37
$\text{Hf}(\text{BH}_4)_4$	2.28 (1)	2.13 (1)	1.97 (2)	80.6 (6)	55.1 (4)	40

^a Compounds sorted in order of decreasing M-H-M and M-H-B angles. ^b In $\text{H}_2\text{Os}_3(\text{CO})_{10}$, the M(μ-H)₂M unit is embedded as part of the cluster structure. ^c terpy = terpyridine.

Table VII. Structural Results on Compounds Containing M(μ-H)₂M Bonds

	M-M, Å	M-H, Å	H···H, Å	M-H-M, deg	H-M-H, deg	method ^a	ref
(A) Binuclear Complexes							
$\text{H}_4\text{Mo}_2(\text{PMe}_3)_6$	2.194 (3)	1.52 (3)	2.11	92	88	X	41
$[\text{H}_2\text{W}_2(\text{CO})_8]^{2-}[\text{NEt}_4]^+_2$	3.016 (1)	1.86 (6)	2.17	109 (5)	71 (5)	X	4
$[\text{H}_2\text{W}_2(\text{CO})_8]^{2-}[(\text{Ph}_3\text{P})_2\text{N}]^+_2$	3.010 (2)	1.926 (2)	2.405 (3)	102.7 (1)	77.3 (1)	N	this work
$[\text{H}_2\text{W}(\text{C}_5\text{H}_5)_2\text{Rh}(\text{PPh}_3)_2]^+[\text{PF}_6]^-$	2.721 (8)					X	42
$\text{H}_2\text{Re}_2(\text{CO})_8$	2.896 (3)					X	19
$\text{H}_4\text{Ru}_2(\text{PMe}_3)_4$	2.811 (4)	1.95 (7)	2.70	92	88	X	43
$\text{H}_2\text{Rh}_2[\text{P}(\text{O}-i\text{-Pr})_3]_4$	2.647 (13)	1.808 (14)	2.465 (14)	94.1 (4)	85.9 (5)	N	34
$\text{H}_2\text{Ni}_2[\text{Cy}_2\text{P}(\text{CH}_2)_3\text{PCy}_2]_2$	2.441 (1)	1.58 (4)	2.03	100 (2)	80 (2)	X	24
$\text{H}_2\text{Pt}_2(\text{SiEt}_3)_2(\text{PCy}_3)_2$	2.692 (3)					X	23
$\text{H}_4\text{Th}_2(\text{C}_5\text{Me}_5)_4$	4.007 (8)	2.29 (3)	2.22 (1)	122 (4)	58 (1)	N	26
(B) Trinuclear Complexes ^b							
$[\text{H}_4\text{Re}_3(\text{CO})_{10}]^-[\text{NEt}_4]^+$	2.821 (7)					X	44
$[\text{H}_3\text{Re}_3(\text{CO})_{10}]^{2-}[\text{NEt}_4]^+_2$	2.797 (4)					X	21
$\text{H}_2\text{Os}_3(\text{CO})_{10}$	2.683 (1)	1.845 (3)	2.376 (3)	94.3 (1)	80.2 (1)	N	18
$\text{H}_2\text{Os}_3(\text{CO})_9(\text{PPh}_3)$	2.683 (2)					X	45
$\text{H}_2\text{Os}_3(\text{CO})_9(\text{CN}-t\text{-Bu})$	2.690 (1)					X	46

^a X = X-ray diffraction; N = neutron diffraction. ^b For trinuclear complexes, the M(μ-H)₂M unit is located on one edge of the triangular cluster.

resonance in $\text{H}_2\text{Os}_3(\text{CO})_{10}\text{L}$ species (δ -10.25 to -10.50) and considerably deshielded from the Os(μ-H)Os resonance of $\text{H}_2\text{Os}_3(\text{CO})_{10}\text{L}$ species (δ -19.75 to -20.45).²²

Although the equatorial $\text{L}_2\text{M}(\mu\text{-H})_2\text{ML}_2$ fragment in $[\text{H}_2\text{W}_2(\text{CO})_8]^{2-}$ is essentially planar, it is known from the structures of other compounds that this unit can be distorted easily, especially when bulky L ligands are present. In $\text{H}_2\text{Pt}_2(\text{SiEt}_3)_2(\text{PCy}_3)_2$, for example, the dihedral angle (twist angle) between the two PtL_2 planes is 21°,²³ while in

$\text{H}_2\text{Ni}_2[\text{Cy}_2\text{P}(\text{CH}_2)_3\text{PCy}_2]_2$ it is 63°. ²⁴ In the latter case, the central Ni(μ-H)₂Ni plane was found to bisect the angle between the two NiP₂ planes, and it was shown (by using extended Hückel calculations) that this twisting deformation is a facile process. In $\text{H}_2\text{Os}_3(\text{CO})_{10}$, the M(μ-H)₂M core itself is buckled to form a butterfly-shaped fragment, but this

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molecule represents a special case since the $M(\mu-H)_2M$ unit is actually part of a cluster skeleton. A listing of structural results on $M(\mu-H)_2M$ systems known to us at present is given in Table VII. Qualitative descriptions of the bonding in $M(\mu-H)_2M$ systems, and other $M(\mu-X)_2M$ linkages, have been given by Churchill and Chang³ (and earlier by Mason and Mingos²⁵) and will not be repeated here.

A sufficient number of $M(\mu-H)_nM$ bonds ($n = 1-4$) have now been characterized accurately to allow one to search for meaningful structural trends. The available neutron results are summarized in Table VI. Perhaps the most striking feature is the fact that the $M-H-M$ angles show a steady decrease along the series $M(\mu-H)_nM$ ($n = 1-4$). If the results on $H_4Th_2(C_5Me_5)_4$ ²⁶ are discounted, since this compound represents somewhat of an anomaly,²⁷ it can be seen that there is an especially sharp drop in $M-H-M$ angles from $M(\mu-H)M$ -type compounds to $M(\mu-H)_2M$ -type compounds. The same trend is also seen along the sequence $M(\mu-H)_nB$ ($n = 1-3$) (Table VIB). The decrease in $M-H-M$ angle can be correlated with an increase in formal $M-M$ bond order: it can be seen that $M-M$ distances (which should be adjusted to account for differences in covalent radii) decrease more-or-less regularly along the sequence $M(\mu-H)_nM$ ($n = 1-4$).

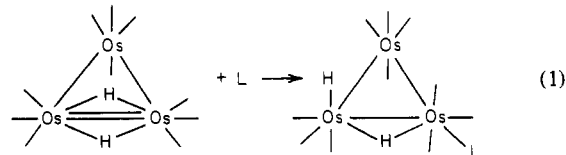
Another interesting correlation concerns the intramolecular $H\cdots H$ nonbonding contact distances. From the limited data available so far, it is clear that $H\cdots H$ distances decrease along the series $M(\mu-H)_nM$ ($n = 2-4$) (Table VIA). This is expected, of course, since the overall arrangement becomes more crowded as more H atoms are packed around a $M-M$ bond. For an $(H)_n$ ring of radius 1.2 Å surrounding the $M-M$ bond, one would predict $H\cdots H$ distances of ~ 2.4 Å (2×1.2 Å) for $M(\mu-H)_2M$ and ~ 2.1 Å ($3^{1/2} \times 1.2$ Å) for $M(\mu-H)_3M$, as observed. However, for an $(H)_4$ ring, a radius of 1.2 Å would correspond to an $H\cdots H$ distance of 1.7 Å ($2^{1/2} \times 1.2$ Å), significantly less than the experimental value of 1.96 Å found in $H_8Re_2(PEt_2Ph)_4$.^{8b} Thus, it appears that at the $M(\mu-H)_4M$ stage, $H\cdots H$ steric interactions become important. From various neutron diffraction measurements on polyhydrido-metal complexes, the minimum $H\cdots H$ contact distances appears to be around 1.8–1.9 Å.^{6b} Using 1.85 Å as a value for $H\cdots H$, one can estimate that minimum radii of $(H)_4$ and hypothetical $(H)_5$ rings would be $1.85/2^{1/2} = 1.3$ Å and $1.85/(2 \sin 36^\circ) = 1.6$ Å, respectively.

The $[(Ph_3P)_2N]^+$ cation in $[(Ph_3P)_2N]^+[H_2W_2(CO)_8]^{2-}$ has the common²⁸ bent configuration (Figure 3), but the phenyl rings have an unusual staggered conformation (Figure 4) (first found in $[(Ph_3P)_2N]^+[Fe(CO)_4(n-Pr)]^-$).²⁹ Normally, the phenyl rings in $[(Ph_3P)_2N]^+$ are eclipsed, with one pair of rings oriented in a parallel π -stacked fashion. In the present structure, the rings are very regular, with mean C–C and C–H distances of 1.397 (1) and 1.086 (1) Å, respectively.

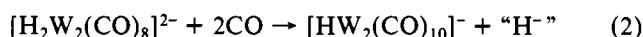
Discussion of the Chemistry of $[H_2W_2(CO)_8]^{2-}$ and Related Species. The high-yield synthesis of the inexpensive $[H_2W_2(CO)_8]^{2-}$ should facilitate the continued exploration of the reaction chemistry of the $M(\mu-H)_2M$ system III. Many



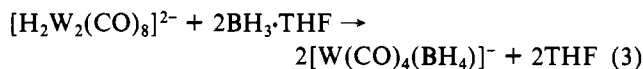
complexes that include $[H_2Os_3(CO)_{10}]$,²² $[H_2Re_2(CO)_8]$,¹⁹ $[H_3Re_3(CO)_{10}]^{2-}$,²¹ and $[H_2W_2(CO)_8]^{2-}$ share a high reactivity as well as the formal bonding system III. Most reactions remove the "unsaturation" of the metal-metal bond, as with reactions of CO, phosphines, nitriles, etc. with $[H_2Os_3(CO)_{10}]$ (eq 1).^{22,30}



In a similar manner, $[H_2W_2(CO)_8]^{2-}$ reacts smoothly with carbon monoxide at atmospheric pressure and room temperature (eq 2). Reactions with phosphines and phosphites also



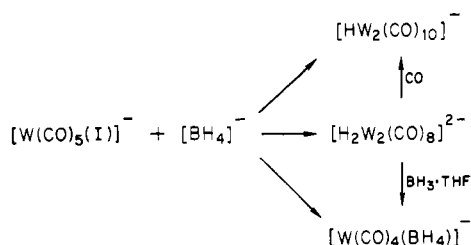
proceed smoothly at room temperature, as do reactions with hydrogen gas, but the products remain uncharacterized. It is ironic that the original goal of this investigation, the synthesis of $[W(CO)_4(BH_4)]^-$, can be achieved starting from the dianion by means of reaction 3. The molybdenum analogue $[Mo(CO)_4(BH_4)]^-$, is known to exhibit interesting fluxional behavior in solution.² It would be interesting to see if $[W(CO)_4(BH_4)]^-$ behaves likewise.



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Previous work^{3,11} had shown that both $[\text{HW}_2(\text{CO})_{10}]^-$ and $[\text{H}_2\text{W}_2(\text{CO})_8]^{2-}$ can also be produced from the direct reaction of $\text{W}(\text{CO})_6$ and $[\text{BH}_4]^-$, but yields of $[\text{H}_2\text{W}_2(\text{CO})_8]^{2-}$ were small. In the reaction of $[\text{W}(\text{CO})_5(\text{I})]^-$ with $[\text{BH}_4]^-$, the role of the cation is crucial in determining the relative yields of the three anions: When the $[(\text{Ph}_3\text{P})_2\text{N}]^+$ cation is used exclusively, a large amount of $[\text{H}_2\text{W}_2(\text{CO})_8]^{2-}$ is produced, but when a mixed $[(\text{Ph}_3\text{P})_2\text{N}]^+/\text{Na}^+$ system is used, little or no $[\text{H}_2\text{W}_2(\text{CO})_8]^{2-}$ is isolated. Apparently, it is the precipitation of the insoluble $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{H}_2\text{W}_2(\text{CO})_8]^{2-}$ from THF that

provides the driving force of the reaction.

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Registry No. $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{H}_2\text{W}_2(\text{CO})_8]^{2-}$, 81293-88-1; $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{W}(\text{CO})_5(\text{I})]^-$, 81315-55-1; $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{W}(\text{CO})_4(\text{BH}_4)]^-$, 81293-90-5; $\text{W}(\text{CO})_6$, 14040-11-0; $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{BH}_4]^-$, 65013-26-5; $\text{BH}_3\cdot\text{THF}$, 14044-65-6.

Supplementary Material Available: A listing of the squared structure factor amplitudes for the neutron diffraction analysis (28 pages). Ordering information is given on any current masthead page.

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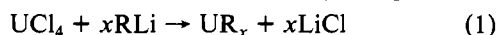
Reinvestigation of the Reaction of *tert*-Butyllithium with Uranium Tetrachloride: Formation of Catalytically Active Uranium(III) Hydride Complexes

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The reaction of UCl_4 with $t\text{-C}_4\text{H}_9\text{Li}$ in alkane solvents has been reinvestigated in detail by quantitative collection and identification of gaseous products and by spectral, analytical, and chemical characterization of the solid uranium products. Treatment of UCl_4 with 4 equiv of $t\text{-C}_4\text{H}_9\text{Li}$ generates 1.5–1.8 equiv of 2-methylpropane and 2-methylpropene in a 2.5–3 to 1 ratio and a solid U(III) hydride product which readily dissolves in tetrahydrofuran (THF). As much as 1.7 equiv of the starting alkyllithium reagent can be recovered unreacted in this reaction, and hence the primary features of the reaction can be reproduced by using only 2 equiv of $t\text{-C}_4\text{H}_9\text{Li}$. Reaction of 1 equiv of $t\text{-C}_4\text{H}_9\text{Li}$ with UCl_4 forms a U(III) product free of hydride. The reaction of $n\text{-C}_4\text{H}_9\text{Li}$ with UCl_4 is similar. Detailed analysis of alkane/alkene ratios of gaseous products suggests that these systems abstract hydrogen from the alkane solvent possibly through a low-valent uranium center. The U(III) hydride product of these reactions is catalytically active in alkyne and alkene hydrogenation reactions conducted under mild conditions.

One of the more controversial reactions in organoactinide chemistry is the reaction of alkyllithium reagents with uranium tetrachloride (reaction 1). Since binary alkyl complexes are

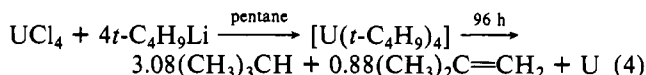
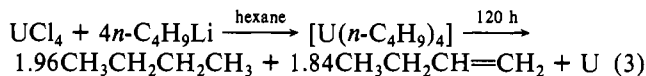


of central importance to the organometallic chemistry of any metal, and since for uranium there was the additional interest of utilizing such species in gaseous diffusion processes for isotope separation, it is not surprising that research on this synthetic approach to uranium alkyls dates back to efforts in the 1940s by Gilman and co-workers.³ Neither those attempts nor others subsequently reported^{4,5} were successful in providing a stable, characterizable homoleptic uranium alkyl.

In 1974, Marks and Seyam⁶ described the reaction of alkyllithium reagents with uranium tetrachloride according to eq 2, where R = isopropyl, *n*-butyl, *tert*-butyl, methyl, 2-*cis*-



2-butenyl, 2-*trans*-2-butenyl, and neopentyl. For R = isopropyl, *n*-butyl, and *tert*-butyl, the "products" of reaction 2 were found to be the alkane and alkene appropriate for β -hydrogen elimination as exemplified for R = *n*-butyl in eq 3 and R = *t*-Bu in eq 4. The yield of butane plus butene was



reported to be 95% for the *n*-butyl reaction and 99% for the *tert*-butyl reaction based upon the amount of lithium reagent used (4 equiv). These results were taken as evidence that coordinatively unsaturated U(IV) alkyls readily decompose via β -hydrogen elimination. Although it was acknowledged in the original paper⁶ that the excess of alkane over alkene in eq 4 suggested that another mechanism may be operative, in subsequent discussions only β -hydrogen elimination was mentioned.⁷⁻¹⁴ For example, in a discussion⁷ of uranium

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