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X-Ray and Neutron Diffraction Studies on $HW_2(CO)_8(NO)(P(OCH_3)_3)$. A Compound with a Slightly Asymmetric Hydrogen Bridge Bond[1]

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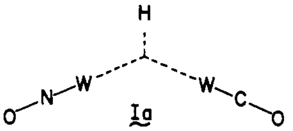
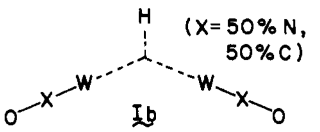
Abstract: The molecular structure of $HW_2(CO)_8(NO)(P(OCH_3)_3)$, prepared by treating $HW_2(CO)_9(NO)$ with trimethyl phosphite, was studied with x-ray and neutron diffraction techniques. The presence of the bulky $P(OCH_3)_3$ ligand eliminated the packing disorder problems which occurred in the earlier neutron diffraction analysis of $HW_2(CO)_9(NO)$, and allowed the detailed geometry of the WHW region to be examined closely for possible asymmetric features. The structure of $HW_2(CO)_8(NO)(P(OCH_3)_3)$ consists of $W(CO)_5$ and $W(CO)_3(NO)(P(OCH_3)_3)$ fragments joined by a single WHW three-center bond. The nitrosyl ligand was located at an axial position, thereby confirming earlier results on $HW_2(CO)_9(NO)$. In the present neutron diffraction study the WHW bond was found to be slightly asymmetric, the difference between the two W-H distances being 0.035 (10) Å. The hydrogen atom is closer to the $W(CO)_5$ group than to the $W(CO)_3(NO)(P(OCH_3)_3)$ group, as expected since the $W(CO)_5$ unit is the more electron-deficient half of the molecule. The rest of the structure is very similar to that of $HW_2(CO)_9(NO)$: the molecule has a bent backbone with staggered equatorial ligands, and the hydrogen atom is significantly removed from the point of intersection of the axial W-C and W-N vectors. Other details of the WHW region: W-H = 1.859 (6) and 1.894 (6) Å, W⋯W = 3.381 (2) Å, W-H-W = 129.4 (3)°, H-W-W = 25.5 (2)° and 25.0 (2)°. Crystallographic details for $HW_2(CO)_8(NO)(P(OCH_3)_3)$: unit cell $P\bar{1}$; $a = 10.012\ (7)$, $b = 11.261\ (8)$, $c = 9.062\ (6)$ Å; $\alpha = 90.84\ (5)$, $\beta = 90.52\ (6)$, $\gamma = 76.35\ (4)°$; $V = 992.7$ Å^3, $Z = 2$. Final agreement factors for data with $I > 3\sigma$: $R = 0.050$ for 2481 x-ray reflections and $R = 0.089$ for 2385 neutron reflections. In comparing compounds having bent W-H-W bonds (such as $HW_2(CO)_9(NO)$, $HW_2(CO)_8(NO)(P(OCH_3)_3)$, $[(Ph_3P)_2N]^+[HW_2(CO)_{10}]^-$) with those having linear W-H-W bonds (such as $[Et_4N]^+[HW_2(CO)_{10}]^-$), it is found that the W-W overlap distance remains constant rather than the W-W or W-H bond distances.

Our recent neutron diffraction analysis of $HW_2(CO)_9(NO)$[4] indicated the presence in this compound of a central three-center W-H-W bond in which the hydrogen atom is displaced off the extrapolated intersection of the lines through the axial ligands (Ia). Since the two tungsten atoms are situated in different environments, we were hopeful of finding a noticeable degree of asymmetry in the W-H-W bond. However, a 50-50% nitrosyl-carbonyl packing disorder (Ib) gave rise to a hydrogen position symmetrically disposed about the normal to the W⋯W bond. It was not possible to decide if this observed symmetry was intrinsic to the $HW_2(CO)_9(NO)$ molecule or if the symmetry was a consequence of the packing disorder.



Ia



Ib

The isoelectronic molecule $HW_2(CO)_8(NO)(P(OCH_3)_3)$ was therefore prepared with the expectation that the axial carbonyl-nitrosyl disorder would be prevented by the presence of the bulky $P(OCH_3)_3$ ligand on one of the tungsten atoms. The structural results for this compound would then allow an improved assessment of the bonding for a bridging hydrogen atom in an asymmetric environment.

Experimental Section

Preparation of $HW_2(CO)_8(NO)(P(OCH_3)_3)$. All manipulations were performed under nitrogen and all solvents were thoroughly purged with nitrogen before use. $HW_2(CO)_9NO$ (1.497 g, 2.3 mmol), prepared by published methods,[4,5] was dissolved in 300 ml of hexane and $P(OCH_3)_3$ (0.35 ml, 2.8 mmol) was added. This solution was stirred under nitrogen for 40 h and the solvent removed under vacuum; the resultant orange-yellow powder was dissolved in a minimum volume of 5% CH_2Cl_2–95% C_6H_{14} mixture and chromatographed on a 5 × 22 cm column of silica gel packed in hexane. Three bands were developed: first a small light yellow band, then a long dark yellow band, and finally a short bright orange band. The solvent was removed from the fractions and the dark yellow band recrystallized from hexane to give $HW_2(CO)_8(NO)(P(OCH_3)_3)$ (40% yield). Anal. Calcd for $HW_2(CO)_8(NO)(P(OCH_3)_3)$: C, 17.69; H, 1.34; N, 1.87. Found: C, 17.70; H, 1.53; N, 1.86.

Table I. Crystal Data for $HW_2(CO)_8(NO)(P(OCH_3)_3)$

Space group $P\bar{1}$	X-Ray	Neutron
$Z = 2$	$a = 10.012$ (7) Å	$a = 10.012$ (5) Å
Mol wt = 746.9 g/mol	$b = 11.261$ (8) Å	$b = 11.249$ (5) Å
ρ(obsd)[a] = 2.49 g/cm^3	$c = 9.062$ (6) Å	$c = 9.046$ (5) Å
	$\alpha = 90.84$ (5)°	$\alpha = 90.96$ (4)°
	$\beta = 90.52$ (6)°	$\beta = 90.53$ (4)°
	$\gamma = 76.35$ (4)°	$\gamma = 76.24$ (4)°
	$V = 992.7$ Å^3	$V = 1000.2$ Å^3
	$\mu = 124$ cm^{-1} (for Mo Kα radiation)	$\mu = 0.846$ cm^{-1} (for λ 1.0 Å neutrons)
	ρ(calcd) = 2.50 g/cm^3	ρ(calcd) = 2.48 g/cm^3

[a] Obtained via flotation from an aqueous zinc iodide solution.

The ^{1}H NMR spectrum[6] in $DCCl_3$ showed a split doublet at τ 22.50 (J(HP) = 27.0 Hz; J(H^{183}W) = 39.5 Hz) due to the metal hydrogen and a doublet at τ 6.22 (J(HP) = 11.5 Hz) due to the trimethyl phosphite hydrogens. The infrared spectrum[7] of the carbonyl region shows the following absorptions (cyclohexane solution): 2095 (w), 2060 (w), 2017 (m), 2003 (s), 1966 (w), and 1915 (vs, br) cm^{-1}. The nitrosyl stretching band is found at 1693 cm^{-1} (m, br; in KBr pellet). The compound is indefinitely stable in air in the solid form, but solutions in common organic solvents are somewhat air-sensitive.

X-Ray Data Collection and Structure Analysis. An irregularly shaped crystal of $HW_2(CO)_8(NO)(P(OCH_3)_3)$ was mounted in a 0.2-mm glass capillary. Preliminary precession photographs indicated that the crystals belonged to the triclinic class. The unit cell parameters, which are given in Table I together with other crystallographic details, were obtained by carefully measuring the setting angles of 23 reflections on a Nonius CAD-3 automated diffractometer.

One hemisphere of data was collected by the $\theta/2\theta$ scan technique with Zr-filtered Mo Kα radiation up to a 2θ limit of 50°. A scan speed of 10°/min was used, with the scan defined as $\Delta\theta = (1.2 + 0.15 \tan \theta)°$ Each reflection was scanned between two and ten times, depending on its intensity. Background counts were taken at the beginning and the end of each scan. Zirconium foil attenuators were automatically inserted to prevent the counting rate from exceeding 2500 counts/s. The take-off angle used was 4° and the lower and upper level discriminators of the pulse height analyzer were set to obtain a 90% window centered on the Mo Kα peak. As a check on the stability of the diffractometer and the crystal, the $(5,3,\bar{3})$, $(0,\bar{7},0)$, and $(4,0,\bar{4})$ reflections were measured at 40-reflection intervals during data collection. No significant variation in these monitor intensities was observed. Data reduction yielded intensities greater than three standard deviations for a total of 2481 reflections. The standard deviation of each intensity reading, $\sigma(F_o^2)$, was estimated using the expression[8]

$$\sigma(F_o^2) = [(\text{peak} + \text{background counts}) + (0.04 \text{ net intensity})^2]^{1/2}$$

Values of F_o^2 were corrected for Lorentz and polarization effects. An empirical absorption correction[9] was applied, with transmission coefficients varying between 0.58 and 1.39 (normalized to an average of unity).

The structure was solved with conventional heavy-atom methods: the coordinates of the two tungsten atoms were obtained from a Patterson map, and the other non-hydrogen atoms were located from a series of difference-Fourier maps.[10] This trial structure was refined by several cycles of full-matrix least-squares refinement with anisotropic temperature factors included for all atoms. The final agreement factors[11] are: $R_F = 0.050$ and $R_{wF} = 0.055$. In the x-ray analysis all diatomic ligands were treated as carbonyl groups; no attempt was made to distinguish between carbon and nitrogen atoms.

Neutron Data Collection and Structure Analysis. A crystal of $HW_2(CO)_8(NO)(P(OCH_3)_3)$ with a volume of 6.5 mm^3 (approximate dimensions 2.9 × 2.3 × 1.0 mm^3) was grown from a concentrated acetone solution at −20 °C. Neutron diffraction data were collected on a four-circle diffractometer at the Brookhaven National Laboratory high flux beam reactor[13] with a $\theta/2\theta$ step-scan technique and a neutron beam of wavelength 1.021 Å. Unit cell parameters, obtained from setting angles observed on the neutron diffractometer, agree well with the x-ray values (Table I). These latter values were used throughout the present work to compute bond distances and angles. Intensities were measured to a d^* limit of 1.25 Å^{-1} in two stages: low angle data ($0.0 < d^* < 0.5$) were collected with a scan formula $\Delta 2\theta = 3.76(1 - 1.9 \tan \theta)°$ and high angle data ($0.5 < d^* < 1.25$) with $\Delta 2\theta = 1.20(1 + 5.3 \tan \theta)°$. Each reflection was scanned from high to low 2θ in approximately 40 steps. Intensities of 4881 reflections were measured, including two standard intensities monitored every 30 reflections. After averaging, intensities were obtained for 4070 unique reflections in space group $P\bar{1}$.

Background corrections were made with a method[14] which divides the reflection profile in such a way that $\sigma(I)/I$ is minimized. The observed intensities were corrected for Lorentz effects. An absorption correction was applied by numerical integration over a Gaussian grid of 64 sampling points. The crystal was approximated by 12 rational crystal boundary planes. Values for the calculated transmission coefficients range from 0.850 to 0.913.[15]

Of the 4070 unique reflections, 2385 had intensities above 3σ and these were used in the initial Fourier and least-squares refinements. All refinements were performed on F_o^2, with reflections for which $F_o^2 < 0$ included in the final cycles, as had been suggested by several authors.[16] The function minimized was $\Sigma w(F_o^2 - |F_c|^2)^2$, where $w = [\sigma^2_{\text{count}} + 0.02 F_o^2]^{-1}$, and σ^2_{count} is based on counting statistics. The neutron scattering lengths ($b \times 10^{-12}$ cm) used in the refinements were: $b_H = -0.3723$, $b_C = 0.6626$, $b_N = 0.940$, $b_O = 0.575$, $b_P = 0.51$, $b_W = 0.477$.[17]

Refinement was initiated with values of the positional parameters for all non-hydrogen atoms taken from the x-ray structure determination. The bridging hydrogen position was readily located in an initial difference-Fourier synthesis. However, the peaks due to the methyl group hydrogen atoms in the trimethyl phosphite ligand were not immediately resolvable. These atoms were located in difference-Fourier maps after several cycles of refinement in which all positional parameters were varied, along with anisotropic thermal parameters for the oxygen and carbon atoms of the methoxy groups.[10]

The Nitrogen Position. Since the one nitrosyl ligand had not been identified from the x-ray structure, its location was sought early in the refinement. Initially, all diatomic ligands (i.e., carbonyl and/or nitrosyl) were treated as carbonyl groups. However, it was noted early in the refinement (Table II) that the isotropic temperature factor of the axial "carbon" atom on the phosphite-substituted tungsten had

Table II. Summary of Isotropic B Values for all Carbonyl Carbons and Unlocated Nitrosyl Nitrogen in $HW_2(CO)_8(NO)(P(OCH_3)_3)$

Atom	B (Å^2)	Atom	B (Å^2)
C_1	3.16	C_6	3.04
C_2	2.56	C_7	3.56
C_3	3.07	C_8	3.76
C_4	3.53	N[a]	0.72
C_5	3.66	C (av)	3.30

[a] When N was originally assigned a scattering length equal to carbon, its temperature factor refined to the very small value shown here. Later, when this atom was reassigned as nitrogen, its temperature factor refined to a more reasonable 3.84 Å^2.

Table III. Summary of Scattering Amplitudes, b, for Each Carbonyl Carbon and the Nitrosyl Nitrogen during Two Cycles of Anisotropic Refinement in Which the Coordinates and Scattering Lengths Were Allowed to Vary

Atom	Starting scattering lengths[a] b (×10^{-12} cm)	Δ	Final scattering lengths b' (×10^{-12} cm)
C_1	0.663	0.008	0.671 (6)
C_2	0.663	0.008	0.671 (5)
C_3	0.663	0.008	0.671 (6)
C_4	0.663	0.001	0.664 (6)
C_5	0.663	0.007	0.670 (6)
C_6	0.663	0.013	0.676 (6)
C_7	0.663	0.009	0.672 (6)
C_8	0.663	0.008	0.671 (6)
N	0.940	−0.001	0.939 (6)

[a] The starting scattering lengths are standard values for carbon and nitrogen. The fact that they do not vary appreciably during refinement, as shown in this table, indicates that this particular elemental assignment is correct.

Table IV. Final Atomic Parameters for $HW_2(CO)_8(NO)(P(OCH_3)_3)^a$

Atom	x	y	z
W_1	0.04695 (33)	0.19120 (30)	0.31060 (34)
	0.04739 (6)	0.19104 (5)	0.31051 (6)
W_2	0.33169 (33)	0.20579 (27)	0.11802 (33)
	0.33102 (6)	0.20557 (5)	0.11874 (6)
P	0.3816 (3)	0.3815 (3)	0.2589 (4)
	0.3808 (4)	0.3812 (3)	0.2588 (5)
C_1	0.8671 (3)	0.1641 (3)	0.3709 (3)
	0.8696 (17)	0.1619 (14)	0.3745 (19)
C_2	0.1104 (3)	0.1807 (2)	0.5269 (3)
	0.1124 (15)	0.1801 (14)	0.5243 (20)
C_3	0.9766 (3)	0.3756 (2)	0.3365 (3)
	0.9784 (16)	0.3733 (14)	0.3368 (18)
C_4	0.9695 (3)	0.2065 (3)	0.1019 (3)
	0.9712 (19)	0.2042 (19)	0.1022 (22)
C_5	0.1221 (3)	0.0068 (2)	0.2873 (3)
	0.1242 (20)	0.0020 (19)	0.2883 (19)
C_6	0.4559 (3)	0.0764 (2)	0.2511 (3)
	0.4556 (17)	0.0773 (14)	0.2477 (21)
C_7	0.2648 (3)	0.0711 (2)	0.0033 (3)
	0.2652 (16)	0.0709 (14)	0.0003 (17)
C_8	0.1916 (3)	0.3361 (2)	0.0019 (3)
	0.1913 (18)	0.3373 (15)	0.0045 (20)
C_9	0.2448 (4)	0.6092 (3)	0.3162 (5)
	0.2448 (21)	0.6127 (13)	0.3230 (28)
C_{10}	0.4142 (4)	0.3065 (4)	0.5349 (4)
	0.4097 (27)	0.3075 (22)	0.5370 (24)
C_{11}	0.6218 (4)	0.4021 (4)	0.1587 (5)
	0.6250 (20)	0.3977 (21)	0.1600 (25)
N	0.4650 (2)	0.2046 (2)	0.9826 (2)
	0.4638 (11)	0.2043 (9)	0.9846 (13)
O_1	0.7619 (4)	0.1490 (4)	0.4024 (4)
	0.7631 (12)	0.1480 (12)	0.4040 (15)
O_2	0.1406 (4)	0.1775 (4)	0.6480 (4)
	0.1414 (15)	0.1734 (13)	0.6458 (15)
O_3	0.9335 (4)	0.4774 (3)	0.3530 (4)
	0.9326 (13)	0.4778 (11)	0.3541 (15)
O_4	0.9177 (5)	0.2179 (5)	0.9892 (4)
	0.9197 (16)	0.2170 (17)	0.9924 (18)
O_5	0.1640 (5)	0.9035 (3)	0.2772 (4)
	0.1650 (17)	0.9013 (11)	0.2776 (16)
O_6	0.5217 (4)	0.0045 (3)	0.3212 (4)
	0.5213 (15)	0.0053 (12)	0.3203 (17)
O_7	0.2321 (4)	0.9990 (3)	0.9339 (4)
	0.2340 (13)	0.9999 (11)	0.9348 (15)
O_8	0.1195 (4)	0.4069 (4)	0.9356 (5)
	0.1184 (16)	0.4043 (12)	0.9364 (17)
O_9	0.5492 (4)	0.2064 (4)	0.8940 (4)
	0.5520 (15)	0.2040 (13)	0.8938 (17)
O_{10}	0.2526 (4)	0.4897 (3)	0.2567 (4)
	0.2519 (11)	0.4879 (9)	0.2565 (16)
O_{11}	0.4480 (6)	0.3718 (4)	0.4132 (6)
	0.4490 (19)	0.3708 (13)	0.4088 (21)
O_{12}	0.4873 (5)	0.4489 (4)	0.1783 (6)
	0.4867 (15)	0.4490 (12)	0.1794 (22)
H_1	0.2189 (6)	0.2240 (6)	0.2877 (6)
H_2	0.2888 (12)	0.6587 (7)	0.2518 (11)
H_3	0.1450 (10)	0.6502 (8)	0.3276 (14)
H_4	0.2907 (13)	0.6058 (8)	0.4205 (12)
H_5	0.3400 (24)	0.3542 (16)	0.5913 (20)
H_6	0.3999 (15)	0.2250 (10)	0.5052 (10)
H_7	0.4851 (15)	0.2923 (17)	0.5987 (16)
H_8	0.6837 (9)	0.4219 (13)	0.2358 (16)
H_9	0.6480 (9)	0.3109 (10)	0.1454 (15)
H_{10}	0.6399 (16)	0.4379 (15)	0.0778 (18)

[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.

refined to an unusually small value of 0.72 Å^2 (compared to an average for the remaining carbonyl carbons of 3.30 Å^2). This observation, together with a significantly smaller W–"C" bond distance of that axial group relative to other W–C distances, was sufficient indication that this ligand was a nitrosyl rather than a carbonyl group. The scattering length for this atom was then changed to the appropriate value for nitrogen and the refinements continued. The temperature factor for the nitrogen subsequently became normal (B = 3.84 Å^2). In a later refinement the scattering lengths of all carbonyl carbons and the nitrosyl nitrogen were allowed to vary together with their temperature factors. No significant changes in scattering lengths of any of these atoms were observed[18] (Table III).

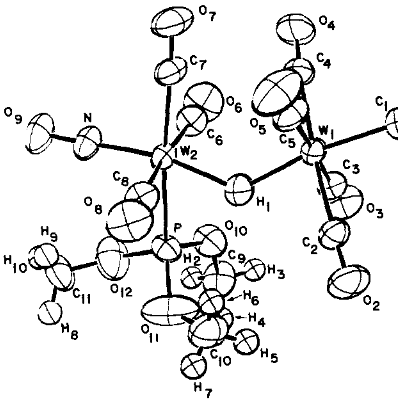


Figure 1. Molecular plot of $HW_2(CO)_8(NO)(P(OCH)_3)$ projected normal to the WHW plane. The refined anisotropic thermal parameters are represented by 60% probability ellipsoids, except the methyl hydrogen atoms which have been arbitrarily assigned isotropic B values of 2.0 Å^2 for clarity. (Refer to Figure 3 for an actual representation of the thermal ellipsoids for these hydrogen atoms.)

The last cycles of the refinement included all of the observed data. The final agreement factors[11] based on F are: for all reflections with $F_o^2 > 0$, $R_F = 0.131$ and $R_{wF} = 0.115$; for data with $F_o^2 > 3\sigma$, $R_F = 0.089$ and $R_{wF} = 0.107$. The agreement factors based on F^2 are: for all reflections, $R_{F^2} = 0.147$ and $R_{wF^2} = 0.171$;[19] for data with $F_o^2 > 3\sigma$, $R_{F^2} = 0.136$ and $R_{wF^2} = 0.163$.

An extinction parameter, g, as defined by Zachariasen,[20] was included in the final cycles of refinement. Here

$$E_{hkl} = \left[1 + \frac{2\bar{T}|F_c|^2 g}{V \sin 2\theta}\right]^{-1/4}$$

where: E_{hkl} is the extinction correction which divides F_o for reflection hkl, F_c is the calculated structure factor, $\bar{T}$ is the average beam path length in the crystal for reflection hkl, appropriately modified for absorption, $V = (V_c^2/\lambda^3)$, V_c is the volume of the unit cell, λ 1.021 Å, the wavelength of neutrons employed, 2θ is the Bragg diffraction angle. The final value for g is $3.1(5) \times 10^3$ and corresponds to a mosaic spread of approximately 19 s of arc.

Description of the Structure

The final atomic and thermal parameters for $HW_2(CO)_8(NO)[P(OCH_3)_3]$ are given in Tables IV and V, respectively, and bond distances and angles in the molecule listed in Tables VI and VII. In these tables the results of the x-ray and neutron diffraction analyses are compared wherever possible. Because of the large absorption effects associated with x-ray data, the thermal parameters from the neutron data set are more reliable than the corresponding x-ray values. Structure factor tables for both data sets are available.[12] Various drawings which show different views of the molecule are given in Figures 1-4. The large thermal ellipsoids associated with the methoxy groups are clearly evident in Figure 3. The thermal parameters of the hydrogen atoms in these groups are particularly large, and probably indicate a combination of hindered rotational motion and packing disorder.

The W-H-W linkage is bent with the equatorial ligands of the two tungsten atoms in a staggered conformation. A consequence of the bent configuration is that the bulky phosphite ligand assumes an exo configuration that minimizes steric interactions with the rest of the molecule. The WHW plane bisects the $PW_1W_2C_2$ dihedral angle, as shown in Figure 2.

The bond lengths and angles are similar to those found in a previous neutron diffraction analysis of $HW_2(CO)_9(NO)^4$ (Figure 5), though the W-W separation and the W-H-W angle are slightly increased in the present structure.

As in $HW_2(CO)_9(NO)$, the hydrogen atom is displaced

Table V. Final Anisotropic Temperature Factors[a] for $HW_2(CO)_8(NO)(P(OCH_3)_3)$[b]

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
W_1	97 (4)	81 (3)	90 (4)	−36 (3)	14 (3)	−6 (3)
	103 (1)	74 (1)	94 (1)	−20 (1)	6 (1)	4 (1)
W_2	101 (4)	58 (3)	87 (4)	−20 (3)	17 (3)	−3 (3)
	100 (1)	53 (1)	93 (1)	−1 (1)	12 (1)	7 (1)
P	105 (4)	64 (3)	166 (6)	−20 (3)	−15 (4)	−11 (3)
	115 (5)	63 (3)	154 (7)	−9 (3)	−8 (5)	−1 (4)
C_1	112 (4)	118 (3)	129 (4)	−49 (3)	12 (3)	−1 (3)
	142 (22)	107 (16)	144 (26)	−50 (16)	21 (19)	−4 (16)
C_2	121 (4)	96 (3)	100 (4)	−29 (3)	1 (3)	8 (3)
	117 (19)	92 (15)	132 (26)	−11 (13)	5 (18)	11 (15)
C_3	118 (4)	80 (3)	123 (4)	−16 (3)	−6 (3)	3 (3)
	144 (21)	87 (15)	130 (24)	−15 (15)	−14 (18)	33 (15)
C_4	131 (4)	159 (4)	104 (4)	−69 (3)	−10 (3)	−1 (3)
	144 (24)	179 (24)	128 (28)	−74 (20)	−18 (21)	−24 (21)
C_5	186 (5)	78 (3)	126 (4)	−46 (3)	29 (3)	−13 (3)
	192 (27)	143 (23)	114 (25)	−47 (21)	26 (21)	22 (19)
C_6	137 (4)	63 (2)	128 (4)	−7 (2)	−3 (3)	9 (3)
	149 (22)	73 (14)	175 (29)	−10 (15)	−25 (21)	20 (17)
C_7	149 (4)	80 (3)	107 (4)	−38 (3)	14 (3)	−16 (2)
	158 (21)	86 (14)	83 (21)	−11 (15)	−2 (17)	−6 (14)
C_8	134 (4)	89 (3)	132 (4)	−11 (3)	−14 (3)	24 (3)
	155 (23)	92 (16)	134 (26)	−4 (16)	13 (20)	9 (17)
C_9	198 (7)	68 (3)	258 (9)	−25 (4)	43 (6)	−29 (5)
	229 (30)	40 (13)	322 (46)	−4 (16)	26 (31)	−18 (20)
C_{10}	247 (9)	191 (7)	149 (7)	−116 (7)	8 (6)	8 (6)
	364 (48)	210 (32)	138 (33)	−158 (34)	−8 (31)	38 (26)
C_{11}	113 (6)	233 (8)	253 (9)	−81 (6)	9 (6)	12 (7)
	135 (25)	225 (30)	199 (38)	−50 (23)	12 (25)	44 (27)
N	133 (3)	88 (2)	125 (3)	−27 (2)	41 (2)	0 (2)
	139 (13)	77 (9)	141 (17)	3 (9)	46 (12)	4 (10)
O_1	133 (5)	192 (6)	212 (7)	−77 (4)	24 (5)	17 (5)
	132 (16)	170 (16)	221 (25)	−51 (13)	19 (16)	16 (16)
O_2	220 (7)	173 (5)	112 (6)	−49 (5)	−26 (5)	21 (4)
	242 (22)	185 (18)	115 (20)	−22 (16)	−37 (17)	32 (15)
O_3	207 (6)	83 (4)	206 (7)	2 (4)	−15 (5)	−4 (4)
	213 (20)	105 (13)	194 (23)	−4 (14)	−12 (17)	18 (14)
O_4	205 (7)	304 (8)	131 (6)	−111 (6)	−52 (5)	4 (6)
	208 (23)	296 (27)	166 (26)	−78 (20)	−45 (20)	19 (21)
O_5	345 (10)	76 (7)	202 (7)	−50 (5)	61 (6)	−16 (4)
	358 (29)	68 (11)	211 (26)	−36 (15)	57 (22)	−8 (13)
O_6	214 (7)	103 (4)	201 (7)	−6 (4)	−32 (5)	36 (4)
	240 (24)	125 (14)	224 (27)	15 (15)	−59 (21)	42 (17)
O_7	244 (7)	124 (4)	146 (6)	−79 (5)	12 (5)	−42 (4)
	219 (21)	134 (14)	157 (21)	−69 (14)	−24 (16)	−19 (14)
O_8	211 (7)	145 (5)	215 (7)	13 (5)	−48 (6)	70 (5)
	227 (21)	135 (14)	212 (26)	48 (15)	−53 (20)	65 (16)
O_9	182 (6)	154 (5)	183 (6)	−54 (4)	87 (5)	0 (4)
	231 (23)	203 (18)	234 (28)	−92 (17)	99 (21)	−4 (18)
O_{10}	137 (5)	70 (3)	247 (7)	−6 (3)	−8 (5)	−34 (4)
	146 (15)	59 (9)	297 (27)	13 (10)	−2 (17)	−11 (13)
O_{11}	396 (12)	136 (5)	254 (9)	−59 (6)	−141 (8)	−21 (6)
	395 (34)	108 (14)	308 (36)	−32 (18)	−127 (29)	−33 (19)
O_{12}	192 (7)	132 (5)	374 (11)	−75 (5)	66 (7)	−29 (6)
	191 (21)	142 (16)	420 (42)	−45 (15)	37 (25)	24 (21)
H_1	154 (8)	188 (8)	151 (9)	−94 (7)	42 (7)	−35 (7)
H_2	504 (29)	121 (10)	375 (23)	−109 (14)	154 (20)	−275 (11)
H_3	240 (16)	149 (11)	712 (42)	−8 (11)	80 (22)	−159 (17)
H_4	595 (36)	151 (11)	349 (23)	−75 (15)	−92 (23)	−100 (14)
H_5	1008 (71)	407 (33)	546 (51)	−19 (37)	558 (56)	−32 (28)
H_6	691 (43)	225 (16)	260 (20)	−181 (23)	35 (23)	17 (14)
H_7	492 (40)	625 (49)	487 (38)	−304 (37)	−337 (37)	319 (36)
H_8	147 (14)	484 (30)	677 (42)	−91 (16)	−111 (20)	−171 (28)
H_9	151 (14)	248 (17)	706 (44)	−14 (14)	115 (18)	−96 (24)
H_{10}	499 (36)	518 (38)	577 (47)	−146 (26)	−75 (32)	374 (37)

[a] For the expression: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] For each atom, the neutron diffraction result is given on the first line and the x-ray diffraction result, if available, on the second.

from the extrapolated intersection point of the two opposite axial ligands. If the hydrogen atom were to be located at this intersection, the W-H-W angle would be 153°, whereas the observed value is 129.4°. Thus any prediction of the location of a bridging hydrogen atom based on idealized octahedral geometry may lead to an overestimation of the M-H-M bond angle and an underestimation of the M-H bond lengths.

As mentioned earlier, the disorder of the axial nitrosyl and carbonyl ligands in $HW_2(CO)_9(NO)$ prevented an assessment of the degree of asymmetry in the two W-H bonds. The present results for $HW_2(CO)_8(NO)(P(OCH_3)_3)$ show the hydrogen atom to be slightly displaced toward the $W(CO)_5$ half of the molecule (1.859 (6) Å vs. 1.894 (6) Å).

The present structure determination unambiguously locates

Table VI. Bond Distances (in Å) in $HW_2(CO)_8(NO)(P(OCH_3)_3)$

	Neutron	X Ray		Neutron	X Ray
(a) Distances Involving Tungsten					
W_1–W_2	3.393 (4)	3.381 (2)			
W_1–H_1	1.859 (7)	. . .	W_2–H_1	1.894 (6)	. . .
W_1–C_1	1.980 (4)	1.98 (2)	W_2–C_6	2.070 (4)	2.04 (2)
W_1–C_2	2.048 (4)	2.03 (2)	W_2–C_7	2.058 (4)	2.07 (2)
W_1–C_3	2.036 (4)	2.02 (2)	W_2–C_8	2.065 (4)	2.07 (2)
W_1–C_4	2.028 (4)	2.02 (2)	W_2–N	1.818 (4)	1.81 (1)
W_1–C_5	2.039 (4)	2.09 (2)	W_2–P	2.481 (5)	2.480 (4)
(b) Carbonyl and Nitrosyl Distances					
C_1–O_1	1.145 (5)	1.15 (2)	C_6–O_6	1.117 (5)	1.13 (2)
C_2–O_2	1.133 (4)	1.13 (2)	C_7–O_7	1.124 (5)	1.09 (2)
C_3–O_3	1.132 (5)	1.17 (2)	C_8–O_8	1.118 (5)	1.10 (2)
C_4–O_4	1.135 (5)	1.11 (2)	N–O_9	1.172 (4)	1.21 (2)
C_5–O_5	1.140 (5)	1.11 (2)			
(c) Distances within the Phosphite Ligand					
P–O_{10}	1.550 (5)	1.54 (1)	C_9–H_4	1.04 (1)	
P–O_{11}	1.534 (6)	1.51 (2)	C_{10}–H_5	0.95 (1)	
P–O_{12}	1.625 (6)	1.62 (2)	C_{10}–H_6	0.99 (1)	
O_{10}–C_9	1.424 (5)	1.51 (2)	C_{10}–H_7	0.90 (1)	
O_{11}–C_{10}	1.420 (6)	1.48 (3)	C_{11}–H_8	0.98 (1)	
O_{12}–C_{11}	1.337 (6)	1.38 (2)	C_{11}–H_9	1.00 (1)	
C_9–H_2	0.98 (1)		C_{11}–H_{10}	0.88 (1)	
C_9–H_3	1.00 (1)				

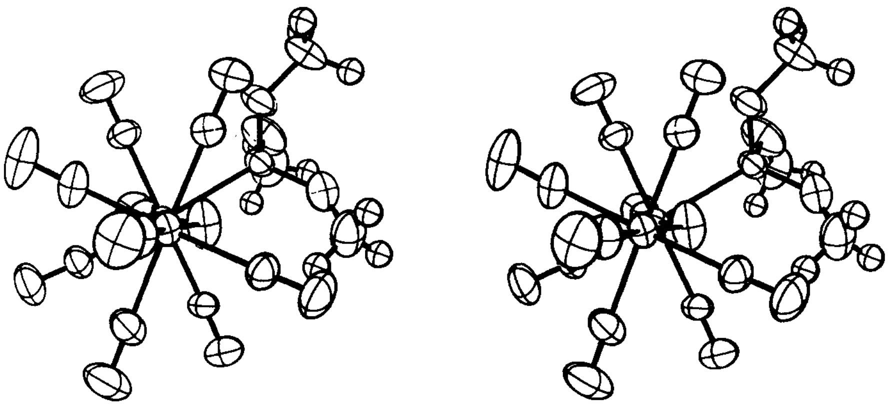


Figure 2. A stereoscopic view of $HW_2(CO)_8(NO)(P(OCH_3)_3)$ projected down the W_1–W_2 axis. This shows the staggered conformation of the equatorial ligands.

the nitrogen atom in an axial position (See Experimental Section and Tables II and III) and thus substantiates the conclusions reached in the $HW_2(CO)_9(NO)$ analysis.[4] It is interesting to note that the average W-(axial ligand) bond length (1.899 Å) in the present structure is very close to the W-X (X = hybrid C and N atoms) bond in $HW_2(CO)_9(NO)$ (1.915 (6) Å). As has been noted by other workers (Tables 3 and 4 in ref 21), the carbonyl ligand trans to the bridging hydrogen atom, i.e., C_1–O_1, has a significantly shorter metal-carbon bond length (1.984 (4) Å) than the average of the remaining carbonyls (2.049 (4) Å).

A slight disordering of the trimethyl phosphite group and the large thermal parameters of the methyl hydrogens may be the cause of the poor agreement between the observed methyl parameters and those expected on the basis of idealized tetrahedral geometry. The final difference-Fourier map shows residual density in the phosphite region (less than 12% of a nitrogen atom) that was not accounted for in the refinement. An analysis of variance shows that values of $|F_o^2 - F_c^2|/\sigma(F_o^2)$ decrease with increasing d^*, as is to be expected for a structure with partial disorder. Mean values of $F_o^2 - F_c^2/\sigma(F_o^2)$ approach zero for $d^* > 1.2$, but are significantly positive for lower ranges of d^*. This result is a direct consequence of the residual density in the phosphite region.

Discussion

It is seen from this structure determination that M-H-M bonds can exhibit a slight amount of asymmetry. The difference in M-H bond lengths observed here, 0.035 (10) Å, corresponds to three and a half standard deviations and hence can be considered significant. Nevertheless, it is a very small difference, suggesting that perhaps the two-electron/three-center M-H-M linkage cannot be grossly distorted from a symmetric configuration. This was suspected in our earlier neutron diffraction analysis of $HW_2(CO)_9(NO)$, which showed the thermal ellipsoid of the bridging hydrogen atom to have its longest axis perpendicular to the WHW plane, indicating that the WHW bond in that compound is either symmetric or very slightly asymmetric. If the W-H-W bond in $HW_2(CO)_9(NO)$ had been more asymmetric we would have seen a greater elongation of the anisotropic thermal ellipsoid in the W-W direction.

The direction of asymmetry in $HW_2(CO)_8(NO)(P(OCH_3)_3)$ is consistent with EAN (effective atomic number rule) considerations. W_1, with ten electrons from its five carbonyl ligands, can be considered more electron-deficient than W_2, which is formally receiving 11 electrons from its ligands. The electron pair that comprises the three-center W-H-W

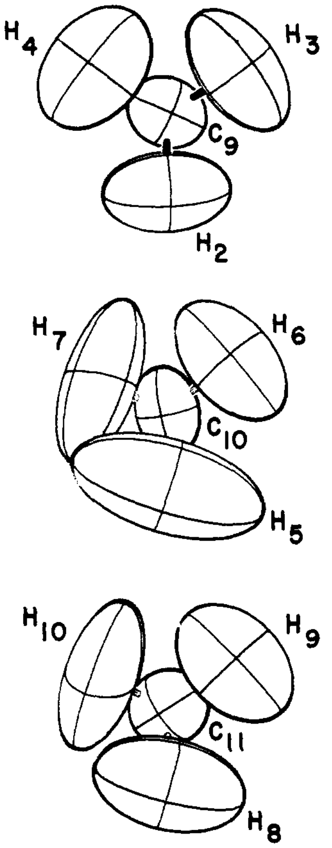


Figure 3. ORTEP plot of the methoxy groups in $HW_2(CO)_8(NO)(P(OCH_3)_3)$. The view for each group is down the C–O bonds.

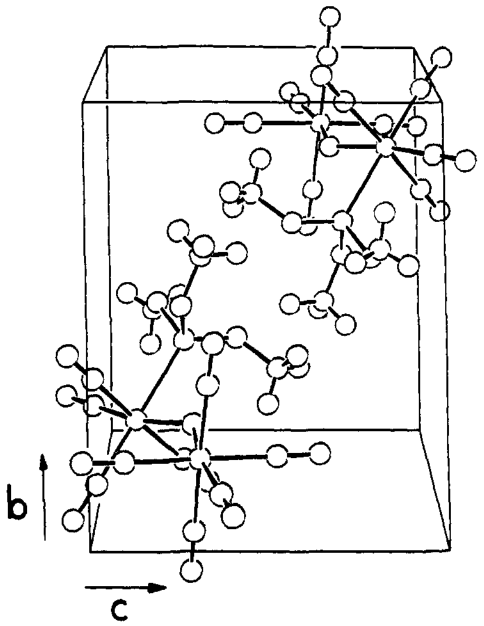


Figure 4. An ORTEP plot of the unit cell for $HW_2(CO)_8(NO)(P(OCH_3)_3)$.

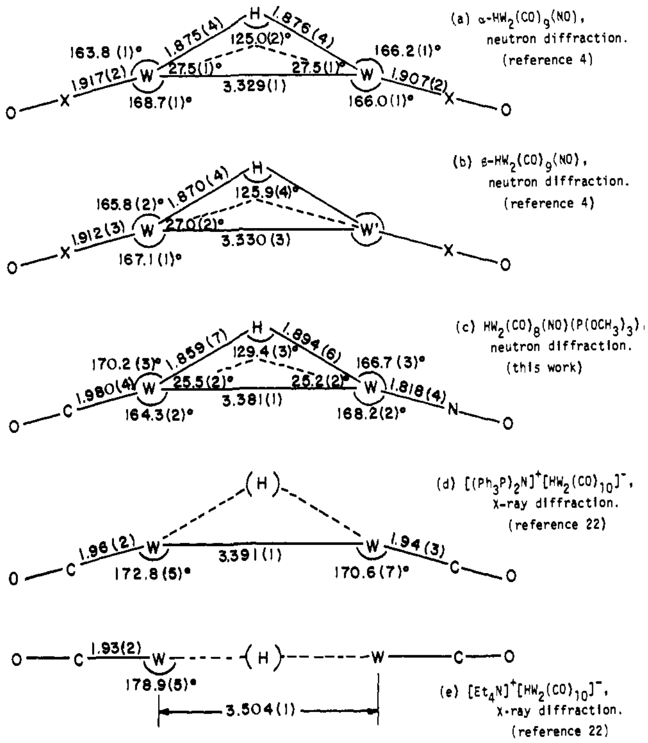
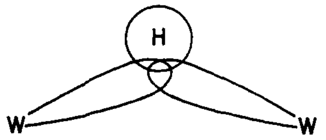


Figure 5. A comparison of the inner coordination geometries in several W–H–W bonded molecules. The symbols "X" in (a) and (b) refer to 50–50% carbon/nitrogen hybrid atoms, generated by packing disorder. The hydrogen atoms in (d) and (e) have not actually been located; their positions are inferred from the geometry of the rest of the molecule.

bond would thus be expected to be preferentially drawn towards W_1.

In replacing one of the carbonyl groups of $HW_2(CO)_9(NO)$ by trimethyl phosphite it is quite possible that the original asymmetry of the W–H–W bond may have been modified by the new substituent. One could presumably assess this effect by studying the structure of a different isomer of $HW_2(CO)_8(NO)(P(OCH_3)_3)$, one with the phosphite on the nonnitrosylated tungsten, and comparing the W–H–W regions of the two isomers. Actually, the discovery of the equatorial position of the phosphite ligand in the present compound came as a mild surprise. Because of the trans-directing influence of the hydrogen ligand (which presumably caused the axial nitrosyl incorporation in the $[HW_2(CO)_{10}]^- \rightarrow HW_2(CO)_9(NO)$ reaction in the first place (ref 4)), it was expected that the incoming phosphite ligand would replace the remaining axial carbonyl on the non-nitrosylated tungsten. Instead, it selected an equatorial position on the nitrosylated tungsten. There could, however, be other monosubstituted phosphite derivatives among the other products of the $HW_2(CO)_9(NO) + P(OCH_3)_3$ reaction mixture.

Comparisons with Other W–H–W System. It is appropriate at this point to compare the structural results obtained recently from several W–H–W systems. Figure 5 summarizes the results from the neutron diffraction analyses of α- and β-$HW_2(CO)_9(NO)$, $HW_2(CO)_8(NO)(P(OCH_3)_3)$, and the x-ray diffraction analyses of the linear and bent forms of the $[HW_2(CO)_{10}]^-$ anion.[22] The neutron diffraction studies of the bent species all show that the (axial ligand)-tungsten vectors point at the centroid of the WHW triangle (dotted lines in Figures 5a–c) and not at the bridging hydrogen atom. From this it can be deduced that there is a common overlap region at the center of the WHW triangle where all three orbitals interact; this also implies that there is a significant amount of metal–metal interaction in a bent M–H–M bond:



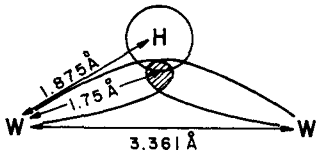
The central region of the bent $[HW_2(CO)_{10}]^-$ anion in $[(Ph_3P)_2N]^+[HW_2(CO)_{10}]^-$ is shown in Figure 5d. Although the hydrogen atom was not located in that x-ray study, it is almost certain that the WHW region in the bent form of

Table VII. Bond Angles (in deg) in $HW_2(CO)_8(NO)(P(OCH_3)_3)$

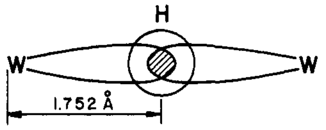
	Neutron	X Ray		Neutron	X Ray
(a) Angles within the W–H–W Triangle					
W_1–H_1–W_2	129.4 (3)				
H_1–W_1–W_2	25.5 (2)				
H_1–W_2–W_1	25.0 (2)				
(b) Angles around W_1					
W_2–W_1–C_1	164.3 (2)	165.0 (5)	C_1–W_1–C_2	89.9 (2)	89.4 (6)
W_2–W_1–C_2	104.4 (1)	103.8 (4)	C_1–W_1–C_3	91.2 (2)	91.8 (6)
W_2–W_1–C_3	95.4 (1)	95.5 (5)	C_1–W_1–C_4	86.3 (2)	87.5 (7)
W_2–W_1–C_4	79.6 (1)	79.4 (5)	C_1–W_1–C_5	89.9 (2)	89.2 (7)
W_2–W_1–C_5	83.8 (1)	83.9 (5)	C_2–W_1–C_3	89.4 (2)	89.4 (6)
H_1–W_1–C_1	170.2 (3)		C_2–W_1–C_4	175.7 (2)	176.6 (7)
H_1–W_1–C_2	80.8 (2)		C_2–W_1–C_5	89.6 (2)	89.0 (6)
H_1–W_1–C_3	88.6 (3)		C_3–W_1–C_4	88.6 (2)	89.5 (8)
H_1–W_1–C_4	102.9 (2)		C_3–W_1–C_5	178.5 (2)	178.1 (7)
H_1–W_1–C_5	93.2 (3)		C_4–W_1–C_5	92.5 (2)	92.1 (8)
(c) Angles around W_2					
W_1–W_2–C_6	91.7 (1)	92.5 (5)	C_6–W_2–C_7	90.9 (2)	91.1 (6)
W_1–W_2–C_7	78.2 (1)	79.2 (4)	C_6–W_2–C_8	173.9 (2)	174.5 (7)
W_1–W_2–C_8	82.3 (1)	82.2 (5)	C_6–W_2–N	94.4 (2)	93.5 (6)
W_1–W_2–N	168.2 (2)	168.3 (4)	C_6–W_2–P	93.8 (2)	94.1 (5)
W_1–W_2–P	96.2 (1)	96.2 (1)	C_7–W_2–C_8	89.2 (2)	89.5 (6)
H_1–W_2–C_6	80.8 (2)		C_7–W_2–N	91.6 (2)	90.7 (6)
H_1–W_2–C_7	100.8 (2)		C_7–W_2–P	172.9 (2)	173.1 (4)
H_1–W_2–C_8	93.2 (2)		C_8–W_2–N	91.6 (2)	92.0 (6)
H_1–W_2–N	166.7 (3)		C_8–W_2–P	85.5 (2)	84.8 (5)
H_1–W_2–P	74.7 (2)		N–W_2–P	93.4 (2)	93.4 (4)
(d) Carbonyl and Nitrosyl Angles					
W_1–C_1–O_1	178.3 (3)	176 (1)	W_2–C_6–O_6	178.4 (3)	178 (2)
W_1–C_2–O_2	177.4 (3)	176 (1)	W_2–C_7–O_7	176.1 (3)	178 (1)
W_1–C_3–O_3	177.7 (3)	177 (1)	W_2–C_8–O_8	174.5 (3)	176 (2)
W_1–C_4–O_4	175.4 (3)	174 (2)	W_2–N–O_9	178.4 (3)	179 (1)
W_1–C_5–O_5	178.6 (3)	179 (2)			
(e) Angles within the Phosphite Ligand					
W_2–P–O_{10}	109.2 (2)	108.9 (5)	O_{11}–P–O_{12}	97.7 (3)	96 (1)
W_2–P–O_{11}	124.1 (2)	123.9 (6)	P–O_{10}–C_9	125.6 (3)	124 (1)
W_2–P–O_{12}	114.7 (2)	115.1 (7)	P–O_{11}–C_{10}	126.6 (4)	126 (2)
O_{10}–P–O_{11}	109.8 (3)	110.9 (9)	P–O_{12}–C_{11}	125.8 (4)	124 (1)
O_{10}–P–O_{12}	98.0 (3)	98.3 (7)	O_{10}–C_9–H_2	113 (1)	
H_5–C_{10}–H_6	113 (1)		O_{10}–C_9–H_3	107 (1)	
H_5–C_{10}–H_7	104 (1)		O_{10}–C_9–H_4	112 (1)	
H_6–C_{10}–H_7	106 (1)		H_3–C_9–H_4	109 (1)	
O_{12}–C_{11}–H_8	116 (1)		H_3–C_9–H_5	108 (1)	
O_{12}–C_{11}–H_9	114 (1)		H_4–C_9–H_5	108 (1)	
O_{12}–C_{11}–H_{10}	103 (1)		O_{11}–C_{10}–H_5	112 (1)	
H_8–C_{11}–H_9	106 (1)		O_{11}–C_{10}–H_6	112 (1)	
H_8–C_{11}–H_{10}	106 (1)		O_{11}–C_{10}–H_7	109 (1)	
H_9–C_{11}–H_{10}	110 (1)				

$[HW_2(CO)_{10}]^-$ is essentially the same as that in $HW_2(CO)_9(NO)$, since the rest of its geometry is so similar. The linear form of $[HW_2(CO)_{10}]^-$ (found in $[Et_4N]^+[HW_2(CO)_{10}]^-$),[22,32] however, represents an intriguing counter-example (Figure 5e). Although the W-W distance here is longer than that in the bent compounds, it is not as long as expected. From the three neutron diffraction analyses of bent W-H-W systems it has been found that the W-H bridging distance remains fairly constant at a value of 1.875 (6) Å. The W···W distance in linear $[HW_2(CO)_{10}]^-$ would be expected to have twice this value, or 3.750 Å. Instead, it turns out to be almost a quarter of an Ångstrom shorter (3.504 (1) Å).[23]

One possible explanation for this discrepancy would be to suppose that it is not the W-H bond length but the *W-W overlap distance* which remains fairly constant: this distance can be estimated as the distance from tungsten to the centroid of the WHW triangle in bent WHW bonds.



The distance one gets by this procedure (1.75 Å) is consistent with half the observed W···W separation (1.752 Å) in linear $[HW_2(CO)_{10}]^-$[32].



As has been pointed out earlier,[22] the very existence of two forms of $[HW_2(CO)_{10}]^-$ in the solid state shows that the W-H-W linkage is an easily deformable entity.

The neutron diffraction analysis of $HW_2(CO)_8(NO)(P(OCH_3)_3)$ described here brings the total number of bent M-H-M systems analyzed by this method to four. The compounds examined so far (Table VIIIa) exhibit a remarkable consistency of molecular parameters . . . it may be reasonable to estimate at this point that most bent M-H-M bonds involving second- and third-row transition metals will contain M-H distances in the range 1.8–1.9 Å and M-H-M angles in

Table VIII. A Summary of Recent Structural Results on Bent M–H–M Bonds

Compound	M	M–H (Å)	M–H–M (deg)	M–M (Å)	Ref
		(a) Neutron Diffraction			
α-$HW_2(CO)_9(NO)$	W	1.875 (4) 1.876 (4)	125.0 (2)	3.328 (3)	4
β-$HW_2(CO)_9(NO)$	W	1.870 (4)	125.9 (4)	3.330 (3)	4
$Mo_2(\pi Cp)_2(CO)_4(H)(P(CH_3)_2)$	Mo	1.851 (4) 1.869 (4)	122.9 (2)	3.267 (2)	24
$HW_2(CO)_8(NO)(P(OCH_3)_3)$	W	1.859 (6) 1.894 (6)	129.4 (3)	3.393 (4)	(This work)
		(b) X-Ray Diffraction			
$[(\pi Cp)Ti]_2(H)(H_2AlEt_2)(C_{10}H_8)$	Ti	1.80	138	3.374	25
$[H_2W_2(CO)_8][Et_4N]_2$	W	1.85 (7)	110 (6)	2.017 (1)	26
$H_3Mn_3(CO)_{12}$	Mn	1.72 (3)	131 (7)	3.111 (2)	27
$Mn_2(CO)_8(H)(P(C_6H_5)_2)$	Mn	1.86 (6)	104 (5)	2.937 (5)	28
$HFe_3(CO)_9(S\text{-}i\text{-}C_3H_7)$	Fe	1.80 (13)	96 (6)	2.678 (2)	29
$H(C_{10}H_9O)Ru_3(CO)_6$	Ru	1.85 (12) 1.64 (11)	110 (6)	2.862 (3)	30
$[\pi C_5(CH_3)_5RhCl]_2 \cdot HCl$	Rh	1.85 (5)	104 (4)	2.906 (1)	31

the range 115–135°. Terminal M–H bonds will generally be about 0.1–0.2 Å shorter, as will M–H bridging distances involving first-row transition elements. Measurements of M–H–M parameters by x-ray diffraction methods show a larger spread os values (Table VIIIb), which is undoubtedly a consequence of the lower sensitivity of the x-ray method to hydrogen positions.

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Supplementary Material Available: A listing of structure factor amplitudes for both x-ray and neutron data sets (Tables IX and X, respectively) (17 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Research performed under the auspices of the U.S. Energy Research and Development Administration.

(2) (a) University of Southern California; (b) Brookhaven National Laboratory; (c) New College.

(3) Alfred P. Sloan Fellow, 1974–1976. NIH Research Career Development Awardee, 1975–1980.

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(6) Varian A-60 NMR spectrometer.

(7) Perkin-Elmer Model 457 spectrometer, CaF_2 cells.

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(10) For the x-ray portion of this work, the major computations were performed on the USC IBM 370-155 computer using CRYM, an amalgamated set of crystallographic programs developed by Dr. Richard Marsh's group at the California Institute of Technology. For the neutron diffraction work, the calculations have been performed on the CDC 7600 of the Brookhaven Central Scientific Computing Facility using programs from the Brookhaven Crystallographic Computing Library which have been described briefly in E. O. Schlemper, W. C. Hamilton, and S. J. LaPlaca, *J. Chem. Phys.*, **54**, 3990 (1971).

(11) $R_F = \Sigma \big| F_o - |F_c| \big| / \Sigma F_o$; $R_{wF} = \{\Sigma w \big| F_o - |F_c| \big|^2 / \Sigma w F_o^2\}^{1/2}$; $R_{F^2} = \Sigma \big| F_o^2 - |F_c|^2 \big| / \Sigma F_o^2$; $R_{wF^2} = \{\Sigma w \big| F_o^2 - |F_c|^2 \big|^2 / \Sigma w F_o^4\}^{1/2}$.

(12) See paragraph at the end of this paper for details.

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(15) The linear absorption coefficient, μ, was calculated to be 0.846 cm^{-1} with the incoherent scattering cross section for hydrogen taken to be 40 barn and with the cross section for true absorption σ_a (barn) for C, N, O, P, and W taken from the "International Tables for X-Ray Crystallography", Vol. 3, the Kynoch Press, Birmingham, England, 1967, pp 197–198.

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(18) This technique was used successfully in our previous structure determination of $HW_2(CO)_9(NO)$ where the nitrosyl was found to be 50% disordered with a carbonyl between two axial coordination positions. In that study the scattering lengths of the equivalent axial groups refined to a value midway between the carbon and nitrogen scattering lengths (ref 4).

(19) For this refinement, the standard deviation of an observation of unit weight was found to be 2.47.

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(32) A recent neutron diffraction investigation of the isostructural compound $[Et_4N]^+[HCr_2(CO)_{10}]^-$ indicates a disordered structure with two hydrogen sites each of 50% occupancy, *displaced approximately 0.6 Å from the Cr–Cr axis*, and equidistant from the two Cr atoms (J. M. Williams, private communication. Based upon results of J. Roziere, J. M. Williams, R. P. Stewart, L. F. Dahl, and J. L. Petersen, to be submitted for publication. This result indicates that the linear WHW overlap diagram as drawn in the text should be modified to accomodate an off-axis location for the H atom. It does not, however, alter the essential argument given in this paper, namely, that it is the metal–metal overlap distance which appears to be controlling the M···M separation.