

X-Ray and Neutron Diffraction Studies on μ -Hydrido-nonacarbonyl(nitrosyl)ditungsten $[\text{HW}_2(\text{CO})_9(\text{NO})]$. Evidence for a Closed Three-Center Metal-Hydrogen-Metal Bond¹

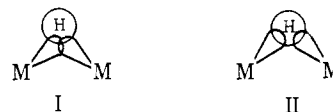
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Abstract: X-Ray and neutron diffraction studies on the complex $\text{HW}_2(\text{CO})_9(\text{NO})$ have been carried out. $\text{HW}_2(\text{CO})_9(\text{NO})$, prepared by the treatment of $[\text{HW}_2(\text{CO})_{10}]^-$ with $\text{NaNO}_2\text{-CH}_3\text{COOH}$, crystallizes in two different modifications: a triclinic form (α - $\text{HW}_2(\text{CO})_9(\text{NO})$; space group $P\bar{1}$, $a = 12.284(14) \text{ \AA}$, $b = 9.621(5) \text{ \AA}$, $c = 6.921(4) \text{ \AA}$, $\alpha = 112.84(2)^\circ$, $\beta = 91.31(5)^\circ$, $\gamma = 97.34(4)^\circ$, $Z = 2$) and a monoclinic form (β - $\text{HW}_2(\text{CO})_9(\text{NO})$; space group $C2/c$, $a = 14.582(8) \text{ \AA}$, $b = 6.771(4) \text{ \AA}$, $c = 15.627(9) \text{ \AA}$, $\beta = 102.336(6)^\circ$, $Z = 4$). X-Ray studies of the α -crystals first revealed the unexpected bent nature of the molecule, but did not locate the position of the hydrogen atom. This was accomplished in the subsequent neutron diffraction analyses of both crystalline forms, which showed essentially the same structure: a molecule held together by a single bent W-H-W linkage, with W-H = 1.873 \AA , W...W = 3.329 \AA , W-H-W = 125.5° , H-W-W = 27.3° . A particularly significant finding is the fact that the axial ligand-metal vector does not point directly at the hydrogen atom but approximately bisects the H-W-W angle. This strongly suggests the presence of a closed, three-center two-electron W-H-W bridge bond in which appreciable W-W overlap exists. Refinement of the neutron scattering lengths of the light atoms showed that the nitrosyl group is disordered over the two axial positions. The position of the hydrogen atom in the W-H-W bond appears to be symmetric, but it was not possible to tell if this effect is real or merely an artifact caused by the 50-50% nitrosyl-carbonyl packing disorder. Final agreement factors were based on strong reflections ($I > 3\sigma$): α - $\text{HW}_2(\text{CO})_9(\text{NO})$ (X-ray data) $R = 6.1\%$ for 1932 reflections; α - $\text{HW}_2(\text{CO})_9(\text{NO})$ (neutron data) $R = 6.0\%$ for 2518 reflections; β - $\text{HW}_2(\text{CO})_9(\text{NO})$ (neutron data) $R = 6.6\%$ for 919 reflections.

Among the various types of bonds known to exist, the metal-hydrogen-metal bond is perhaps the most poorly characterized and least understood. Although several recent X-ray studies⁴⁻¹² have succeeded in locating, and in a few cases refining, hydrogen atom positions, it is clear that such studies are on the whole unable to generate hydrogen positions with the precision necessary to answer some of the more fundamental questions about the M-H-M bond. One such question has to do with symmetry. Are M-H-M bonds inherently asymmetric or can they be symmetric in certain cases?^{13,19} Another question

has to do with the nature of overlap. Are the three-center two-electron M-H-M bonds of the closed variety (I) with some M-M overlap or are they open (II) with no M-M interaction?



In this paper, we report X-ray and neutron diffraction analysis on two crystalline forms of $\text{HW}_2(\text{CO})_9(\text{NO})$.²⁰ This work, together with the recently completed studies on $\text{HMo}_2\text{Cp}_2(\text{CO})_3(\text{PMe})$,¹⁹ is the first single-crystal neutron diffraction characterization of the M-H-M bond.²¹ There were several reasons which made $\text{HW}_2(\text{CO})_9(\text{NO})$ particularly suitable for such an analysis: (a) it readily forms large crystals

ambiguity in the interpretation of the $[\text{HF}_2]^-$ anion diffraction data (ref 14-18).

(14) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N. Y., 1968, p 108-124.

(15) S. W. Peterson and H. A. Levy, *J. Chem. Phys.*, **20**, 704 (1952).

(16) B. L. McGaw and J. A. Ibers, *J. Chem. Phys.*, **39**, 2677 (1963).

(17) J. A. Ibers, *J. Chem. Phys.*, **40**, 402 (1964).

(18) J. M. Williams and L. F. Schneemeyer, *J. Amer. Chem. Soc.*, **95**, 5780 (1973).

(19) Since the completion of our work, it has come to our attention that neutron studies on $\text{HMo}_2\text{Cp}_2(\text{CO})_3(\text{PMe}_2)$ have recently been completed [J. L. Petersen, L. F. Dahl, and J. M. Williams, *J. Amer. Chem. Soc.*, **96**, 6610 (1974)]. In that compound, a symmetric, bent Mo-H-Mo bond was found.

(20) M. Andrews, D. L. Tipton, S. W. Kirtley, and R. Bau, *J. Chem. Soc., Chem. Commun.*, 181 (1973).

(21) It should be pointed out that neutral diffraction studies on a powdered sample of HNb_6I_7 have been reported. In this study, the hydrogen atom was located in the center of a metal octahedron: A. Simon, *Z. Anorg. Allg. Chem.*, **355**, 311 (1967).

(1) This work, performed under the auspices of the Atomic Energy Commission, was presented on March 28, 1974, at the Spring Meeting of the American Crystallographic Association, held at Berkeley, Calif.

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

(3) Research Fellow of the Alfred P. Sloan Foundation, 1974-1976.

(4) For pre-1973 X-ray structure determinations of M-H-M bonds, see Table XVI in ref 6. Also see section E of ref 5 for more detailed descriptions.

(5) B. A. Frenz and J. A. Ibers in "Transition Metal Hydrides," E. L. Muetterties, Ed., Marcel Dekker, New York, N. Y., 1971.

(6) H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, **72**, 231 (1972).

(7) S. W. Kirtley, J. P. Olsen, and R. Bau, *J. Amer. Chem. Soc.*, **95**, 4532 (1973).

(8) A. J. P. Domingos, B. F. G. Johnson, J. Lewis, and G. M. Sheldrick, *J. Chem. Soc., Chem. Commun.*, 912 (1973).

(9) L. J. Guggenberger and F. N. Tebbe, *J. Amer. Chem. Soc.*, **95**, 7870 (1973).

(10) M. R. Churchill and S. W. Y. Ni Chang, *J. Amer. Chem. Soc.*, **95**, 2150 (1973).

(11) M. R. Churchill, S. W. Y. Ni Chang, M. L. Berch, and A. Davison, *J. Chem. Soc., Chem. Commun.*, 691 (1973).

(12) R. Bau, B. Don, R. A. Love, R. D. Wilson, R. Greatrex, and R. J. Haines, manuscript in preparation.

(13) The detection of asymmetry in hydrogen bonding is a difficult problem, even with the best neutron diffraction data as evidenced by the

and is completely air-stable in the solid form; (b) it contains the highly unusual feature of a molecule held together solely by a bent M–H–M bond;²² (c) there was the possibility of detecting an asymmetric W–H–W linkage, since the two halves of the molecule, $W(CO)_5$ and $W(CO)_5(NO)$, are different; (d) the presence of a clearly defined axial ligand in an octahedral environment would serve as a convenient "pointer" to identify the direction of the metal orbital used in the three-center overlap.

Experimental Section

Preparation of $HW_2(CO)_9(NO)$. All manipulations were performed under nitrogen and all solvents degassed before use. $[Na^-][HW_2(CO)_{10}^-]$, prepared from $W(CO)_6$ (2.51 g, 7.14 mmol) using published methods,²³ was dissolved in 200 ml of water, and sodium nitrite (2.02 g, 29.3 mmol) was added. Dropwise addition of acetic acid (3.5 ml, 6 M) to the stirred solution caused vigorous gas evolution and the formation of a brownish yellow precipitate which, after overnight stirring, was filtered, washed, and dried. Recrystallization from dichloromethane gave orange crystals of $HW_2(CO)_9NO$ in 40% yield based on $W(CO)_6$.²⁴ The solid is stable in air (mp 128–129.5°) but solutions of $HW_2(CO)_9(NO)$ in common organic solvents are somewhat air-sensitive. *Anal.* Calcd for $HW_2(CO)_9(NO)$: C, 16.60; H, 0.15; N, 2.15. Found: C, 16.34; H, 0.27; N, 2.28.

The mass spectrum²⁵ showed a parent multiplet in agreement with the formula $HW_2(CO)_9(NO)$. Additional multiplets were observed corresponding to progressive loss of four CO groups, the NO group, four additional CO groups, and the hydrogen with the final CO group. The retention of the isotope pattern during the entire sequence indicates that the hydrogen is almost always lost with the last CO group.

The ¹H nmr of $HW_2(CO)_9(NO)$ showed a single resonance at τ 21.77 in acetone and τ 21.71 in tetrahydrofuran (TMS internal standard). No ¹⁸³W satellites were observed because of the limited solubility of the compound. The infrared spectrum of the carbonyl and nitrosyl regions showed the following absorptions²⁶ in cyclohexane solution: 2069 (m), 2045 (s), 2011 (w), 1989 (w), 1953 (sh), 1944 (s), 1735 (m, br), 1717 (sh) cm^{-1} . The Raman spectrum of a powdered sample in the same region showed the following absorptions:²⁷ 2132 (s), 2068 (vs), 2051 (m), 2023 (m), 1986 (s), 1941 (sh), 1923 (m), 1896 (m), 1725 (m), 1715 (sh) cm^{-1} . Absorptions in the 800–1200- cm^{-1} region of the Raman spectrum were also observed: 1205 (w, br), 1115 (m, br), 1045 (m, br), 965 (m, br), 900 (w, br), 790 (w, br) cm^{-1} .

Crystallographic Section²⁸

$HW_2(CO)_9(NO)$ crystallizes from acetone in two forms in approximately equal amounts: a triclinic form (hereafter referred to as the

(22) In most compounds with M–H–M bonds, the hydride bridge is either part of a structured metal cluster framework or exists in conjunction with other bridging ligands such as CO, PR₃, or SR groups.

(23) (a) U. Anders and W. A. G. Graham, *Chem. Commun.*, 499 (1965); (b) R. G. Hayter, *J. Amer. Chem. Soc.*, 88, 4376 (1966); (c) W. C. Kaska, *ibid.*, 90, 6340 (1968); 91, 2411 (1969).

(24) The VIB analogs, $HCr_2(CO)_9NO$ and $HMo_2(CO)_9NO$, have also been prepared. They are considerably less stable, and during preparation the overnight stirring step is omitted. The chromium compound is quite unstable, and only small yields have been produced. The molybdenum analog, purified by sublimation at 50° (1–2 hr) affords yields of above 20%, although the material is slightly contaminated by $Mo(CO)_6$. *Anal.* Calcd for $HMo_2(CO)_9(NO)$: C, 22.76; H, 0.21; N, 2.95. Found: C, 22.80; H, 0.32; N, 2.96.

(25) A. E. I. Model MS-9 mass spectrometer, inlet probe 110°, ionizing current 70 eV.

(26) Perkin-Elmer 457 spectrophotometer. ϵ (cm^{-1}) of $HCr_2(CO)_9NO$: 2049 (s), 2025 (m), 1987 (m), 1944 (s), 1763 (m), 1746 (w). $HMo_2(CO)_9NO$: 2069 (m), 2057 (s), 2023 (w), 1951 (s), 1946 (sh), 1738 (m), 1726 (sh). Cyclohexane solutions.

(27) Cary Model 81 laser Raman spectrophotometer.

(28) 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 CDC6600 computers 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).

α form) and a monoclinic β form. X-Ray data were collected on α - $HW_2(CO)_9(NO)$ and neutron data on both forms. Each of these will be described in turn.

X-Ray Diffraction on α - $HW_2(CO)_9(NO)$. This work was reported earlier by us in a preliminary communication.²⁰ α - $HW_2(CO)_9(NO)$ crystallizes as bright red-orange parallelepipeds with well-formed faces. A specimen of dimensions $0.06 \times 0.09 \times 0.22$ mm was mounted in a capillary tube along its long axis. Weissenberg and precession photographs indicated a triclinic crystal system. The unit cell parameters, obtained by measuring the setting angles of 44 reflections on a Nonius CAD-3 automated diffractometer, are given together with other relevant crystal data in Table I.

Table I. Crystal Data

	(A) α - $HW_2(CO)_9(NO)$	
	X-Ray	Neutron
Triclinic unit cell	$a = 12.228(4) \text{ \AA}$	$a = 12.284(14) \text{ \AA}$
Space group $P\bar{1}$	$b = 9.634(4) \text{ \AA}$	$b = 9.621(5) \text{ \AA}$
$Z = 2$	$c = 6.925(3) \text{ \AA}$	$c = 6.921(4) \text{ \AA}$
Mol wt = 650.8	$\alpha = 112.83(3)^\circ$	$\alpha = 112.84(2)^\circ$
$\rho(\text{obsd})^a = 2.89 \text{ g cm}^{-3}$	$\beta = 91.28(3)^\circ$	$\beta = 91.31(5)^\circ$
	$\gamma = 97.38(3)^\circ$	$\gamma = 97.34(4)^\circ$
	$V = 745.29 \text{ \AA}^3$	$V = 747.34 \text{ \AA}^3$
	$\mu = 164 \text{ cm}^{-1}$	$\mu = 0.165 \text{ cm}^{-1}$
	(Mo K α)	
	$\rho(\text{calcd}) = 2.899 \text{ g cm}^{-3}$	$\rho(\text{calcd}) = 2.892 \text{ g cm}^{-3}$
	(B) β - $HW_2(CO)_9(NO)$	
	Neutron	
Monoclinic unit cell	$a = 14.582(8) \text{ \AA}$	
Space group $C2/c$	$b = 6.771(4) \text{ \AA}$	
$Z = 4$	$c = 15.627(9) \text{ \AA}$	
$\rho(\text{obsd})^a = 2.89 \text{ g cm}^{-3}$	$\beta = 102.336(6)^\circ$	
$\rho(\text{calcd}) = 2.868 \text{ g cm}^{-3}$	$V = 1507.30 \text{ \AA}^3$	

^a Measured by flotation from a $CHBr_3$ – CH_2I_2 mixture.

One hemisphere of data was collected by the $\theta/2\theta$ scan technique with Zr-filtered Mo K α radiation up to a 2θ limit of 50°. A scan speed of 10°/min was used, with the scan range defined as $\Delta\theta = 1.2 + 0.15 \tan \theta$. Each reflection was scanned between two and six 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/sec. The takeoff 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 K α peak. As a check on the stability of the diffractometer and the crystal, the (800), (050), and (004) reflections were measured at 20-reflection intervals during data collection. No significant variation in the monitor intensities was noted.

The standard deviation of each intensity reading, $\sigma(I)$, was estimated using the expression²⁹

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

Out of the total of 2492 collected reflections, 1932 had intensities greater than 3σ ; these were retained for the subsequent structure analysis. The intensities were further corrected for Lorentz, polarization, and absorption effects; transmission coefficients varied between 0.15 and 0.37.³⁰

The coordinates of the two tungsten atoms were obtained from a Patterson map, and the other nonhydrogen atoms were readily located from a difference Fourier. Several cycles of isotropic least-squares refinement³¹ were then performed in which each ligand was

(29) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 6, 197 (1967).

(30) For $HW_2(CO)_9(NO)$, X-ray absorption effects ($\mu = 164 \text{ cm}^{-1}$ for Mo K α) are 1000 times more severe than they are for neutron radiation ($\mu = 0.165 \text{ cm}^{-1}$). This is one of the chief reasons why we regard the results of the neutron diffraction analysis as being more definitive, particularly the final thermal parameters.

(31) Scattering factors were taken from the "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, 1968.

treated as a carbonyl group. This was followed by several cycles of full-matrix anisotropic refinement, resulting in final agreement factors of $R = 6.1\%$ and $R_w = 8.1\%$.³²

Neutron Diffraction on α -HW₂(CO)₆(NO). A crystal of α -HW₂(CO)₆(NO) 3.6 mm³ in volume was grown by slow recrystallization from hot acetone. Neutron diffraction data were collected at room temperature on an automatic four-circle diffractometer at the Brookhaven high flux beam reactor under the multiple spectrometer control system,³³ using a crystal-monochromated neutron beam of wavelength λ 1.021 Å. The cell dimensions, refined by least-squares techniques from 30 well-centered reflections evenly distributed in reciprocal space, are given in Table I. Intensities were measured for 4791 reflections having $d^* < 1.36 \text{ \AA}^{-1}$, with a $\theta/2\theta$ step-scan technique. The scan range was varied according to the formula $\Delta 2\theta = 1.0^\circ(1 + 8 \tan \theta)$ for the high angle data ($0.5 < d^* < 1.36 \text{ \AA}^{-1}$) and $\Delta 2\theta = 4.0^\circ(1 - 1.2 \tan \theta)$ for the low angle data (195 reflections), and the step size was varied to give approximately 40 readings for each scan.

Background corrections were made using a method which divides the reflection profile in such a way that $\sigma(I)/I$ is minimized.³⁴ I is the integrated intensity and $\sigma(I)$ its estimated standard deviation based on counting statistics. The observed intensities were corrected for absorption by numerical integration over a Gaussian grid (96 sampling points); calculated transmission coefficients range from 0.974 to 0.989.³⁵ Squared observed structure factors were obtained as $F_o^2 = I \sin 2\theta$ and were averaged for symmetry-related reflections. The agreement factor is $R_o = [\sum |F_o^2 - \bar{F}_o^2|] / \sum F_o^2 = 4.0\%$, where \bar{F}_o^2 is the mean value for the symmetry-related reflections. All 3954 unique reflections measured were included in the subsequent least-squares refinements. Contrary to common practice, 463 weak reflections with negative F_o^2 values were retained in order to avoid biasing the results. Schomaker³⁶ has argued along statistical lines for the inclusion of negative F_o^2 values in least-squares refinements, and more recently the same approach has been advocated by Rabinovich and Hirschfeld³⁷ and by Moore.³⁸

The starting parameters for the refinement were the final coordinates from the X-ray analysis. The location of the hydrogen atom was determined from a Fourier synthesis. The structure was refined by full-matrix least-squares techniques, using anisotropic temperature factors for all atoms and an isotropic extinction correction factor.³⁹ Also refined were the "C" scattering lengths of the ten "carbon" atoms, a technique used to locate the nitrogen atom position(s), as will be seen in the following discussion. Neutron scattering lengths used were $b_W = 0.466$, $b_O = 0.575$, $b_N = 0.920$, $b_C = 0.6626$, and $b_H = -0.3723$ ($\times 10^{-12}$ cm). The quantity minimized by the refinement was $\sum w |F_o^2 - |F_c|^2|^2$; weights were chosen as $w = 1/\sigma^2(F_o^2)$, with

$$\sigma^2(F_o^2) = \sigma^2_{\text{count}}(F_o^2) + (0.02F_o^2)^2$$

and with σ_{count} based on counting statistics. The results of this refinement (Table IIA) were extremely revealing. Of the ten refined "C" scattering lengths, eight stayed very close to values expected for true carbons, while two (the axial atoms) adopted values midway between C and N. This conclusively shows that the nitrogen atom is disordered approximately equally between the two axial positions.

For the final cycles of least-squares refinement, the scattering lengths of the equatorial carbons were fixed at $b_C = 0.6626 \times 10^{-12}$ cm, while those of the axial hybrids were allowed to vary, since there

(32) $R = (\sum |F_o^2 - |F_c|^2|) / (\sum |F_o^2|)$; $R_w = [\sum w(|F_o^2 - |F_c|^2|)^2 / \sum w F_o^2]^{1/2}$.

(33) D. R. Beaucage, M. A. Kelley, D. Ophir, S. Rankowitz, R. J. Spinrad, and R. Van Norton, *Nucl. Instrum. Methods*, **40**, 26 (1966).

(34) M. S. Lehmann, W. C. Hamilton, and F. K. Larsen, Abstract No. 09, American Crystallographic Association Meeting, Albuquerque, N. M., 1972. Submitted for publication in *Acta Crystallogr.*

(35) The neutron absorption coefficient was calculated to be 0.165 cm⁻¹ assuming the incoherent scattering cross section for hydrogen to be 40 barn and using the values of (μ_i/ρ) for W, C, N, and O tabulated in ref 31, p 197.

(36) V. Shoemaker, private communication to W. C. Hamilton during the 1969 Seattle American Crystallographic Association meeting.

(37) D. Rabinovich and F. L. Hirschfeld, *Acta Crystallogr., Sect. A*, **29**, 510 (1973).

(38) F. H. Moore, *Acta Crystallogr., Sect. A*, **28**, S256 (1972) (Abstract XXV-15 from the Ninth International Congress of Crystallography, Kyoto, Japan, 1972).

(39) The extinction correction is discussed in W. H. Zachariasen, *Acta Crystallogr.*, **23**, 558 (1967), and the extinction correction factor used here, E , is defined in T. F. Koetzle, M. S. Lehmann, and W. C. Hamilton, *Acta Crystallogr., Sect. B*, **29**, 231 (1973).

Table II. Refined Neutron Scattering Lengths for Carbon-Nitrogen Atoms (in units of 10^{-12} cm)

(A) α -HW ₂ (CO) ₆ (NO)		(B) β -HW ₂ (CO) ₆ (NO)	
Axial			
X ₁	0.786 (4)	X ₁	0.790 (6)
X ₆	0.785 (4)		
Equatorial			
C ₂	0.657 (3)	C ₂	0.659 (6)
C ₇	0.661 (3)		
C ₃	0.657 (3)	C ₃	0.657 (5)
C ₈	0.653 (3)		
C ₄	0.651 (3)	C ₄	0.664 (6)
C ₉	0.663 (3)		
C ₅	0.666 (3)	C ₅	0.659 (5)
C ₁₀	0.660 (4)		
Normal Scattering Lengths			
Carbon: 0.6626×10^{-12} cm			
Nitrogen: 0.920×10^{-12} cm			

is no symmetry-imposed requirement of a 50-50% disorder. In the final cycle none of the 211 parameters shifted by more than 0.1 σ . The final agreement factors are: for all nonzero data (3954 reflections), $R = 9.2\%$ and $R_w = 17.0\%$; for "significant" data ($> 3\sigma$) (2518 reflections), $R = 6.0\%$ and $R_w = 13.3\%$.⁴⁰ The final scattering lengths for the axial hybrids are both $0.785(4) \times 10^{-12}$ cm, indicating a true 50-50% disorder within experimental error. Extinction effects were generally small, with only eight reflections having values of $E^2 < 0.97$.³⁹ The final refined value of the extinction parameter $g = 1523$ corresponds to a mosaic spread parameter of 38 sec or a domain size of 0.1 μ .

In a series of tests conducted by Dr. S. C. Abrahams of Bell Laboratories, no piezoelectric response was detected from the crystals; tests for the presence of second harmonics⁴¹ were also negative. These results are in agreement with the assignment of $P\bar{1}$ as the space group.

Neutron Diffraction on β -HW₂(CO)₆(NO). From an initial analysis using X-ray precession photographs, the space group of the monoclinic form could be assigned as either Cc or $C2/c$, with systematic extinctions of the form hkl , $h + k \neq 2n$, and $h0l$, $l \neq 2n$. The unit cell parameters, first measured from these photographs and eventually refined on the neutron diffractometer (32 centered reflections), are given together with other crystal data in Table IB.

It was possible, from an analysis of the fringes on the X-ray photographs, to deduce a W-W vector of 3.35 Å making an angle of 18° 25' with the c^* axis.⁴² The absolute position of the W atom (in $C2/c$) was obtained by visually estimating, on a 1-4 scale, the intensities of 302 X-ray reflections from six Polaroid films (0; 1; $2kl$ and $hk0$; 1; 2). Analysis of the Patterson map calculated with these data allowed the W atom to be placed at (0.560, 0.291, 0.354). A crystal of β -HW₂(CO)₆(NO) 1.6 mm³ in volume was grown from acetone. Neutron diffraction data collection was similar to that for the α form. Intensities were measured for 4834 reflections. The scan formula was $\Delta 2\theta = 1.0^\circ(1 + 8 \tan \theta)$ for the high angle data ($0.5 < d^* < 1.36$) and $\Delta 2\theta = 4.5^\circ(1 - 1.3 \tan \theta)$ for the low angle data (210 reflections). The same background and absorption corrections were made. The calculated transmission coefficients ranged from 0.979 to 0.987. This data set was considerably weaker than that for the α form, with approximately half of the reflections having intensities less than 3σ . Thus, the agreement factor for data merging was much higher, $R_o = 9.9\%$. All 1992 unique reflections measured were used in subsequent least-squares refinements, including 342 with negative F_o^2 values.

Since the W atom position was known from the earlier analysis of the rough X-ray intensities, it was possible to deduce from the neutron Patterson map the position of the axial "carbonyl" group and the hydrogen atom. This was done as follows: the axial O-O and "C-C" vectors could be identified easily from the neutron Patterson, since they were collinear with the known W-W vector and with the origin, and since their lengths were known. Extrapolation

(40) Additionally, agreement factors based on F^2 may be quoted. For the α form, $R_2 = 8.3\%$ and $R_{w2} = 9.0\%$ (all data).

(41) S. C. Abrahams, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **125**, 48 (1967).

(42) The results of this crude analysis agree incredibly well with the final values of 3.33 Å and 18° 34'.

Table III. Final Atomic Parameters for α -HW₂(CO)₉(NO)

(A) Atomic Positions ^a				(B) Thermal Parameters ^{a,c,d}													
Atom	x	y	z	Atom	10 ⁴ β_{11}	10 ⁴ β_{22}	10 ⁴ β_{33}	10 ⁴ β_{12}	10 ⁴ β_{13}	10 ⁴ β_{23}	Atom	10 ⁴ β_{11}	10 ⁴ β_{22}	10 ⁴ β_{33}	10 ⁴ β_{12}	10 ⁴ β_{13}	10 ⁴ β_{23}
W ₁	0.23428 (14)	0.97704 (19)	0.72677 (26)	C ₁₀	49 (1)	90 (2)	165 (4)	1 (1)	4 (2)	54 (3)	C ₁₀	51 (1)	157 (2)	278 (4)	15 (1)	3 (2)	101 (3)
	0.23423 (6)	0.97708 (9)	0.72722 (10)		51 (1)	77 (1)	180 (2)	-3 (1)	-4 (1)	54 (1)		55 (15)	130 (36)	349 (63)	12 (18)	12 (24)	122 (39)
W ₂	0.27169 (14)	0.61296 (19)	0.53978 (26)	O ₁	47 (1)	97 (2)	177 (4)	9 (1)	13 (2)	64 (3)	O ₁	152 (3)	90 (3)	453 (8)	42 (2)	85 (4)	40 (4)
	0.27155 (6)	0.61329 (9)	0.54035 (10)		49 (1)	87 (1)	189 (2)	8 (1)	7 (1)	64 (1)		149 (20)	74 (26)	497 (60)	24 (18)	87 (27)	64 (31)
X ₁ ^b	0.1935 (1)	1.1754 (1)	0.8694 (2)	O ₂	87 (1)	77 (2)	256 (4)	15 (1)	31 (2)	36 (2)	O ₂	77 (2)	217 (4)	478 (8)	-34 (2)	32 (3)	153 (5)
	0.1936 (16)	1.1763 (18)	0.8674 (26)		85 (16)	72 (24)	259 (49)	36 (16)	31 (22)	32 (27)		78 (14)	219 (36)	496 (60)	-35 (18)	22 (22)	148 (38)
C ₂	0.3769 (1)	1.0825 (2)	0.6591 (2)	O ₃	61 (1)	121 (2)	269 (4)	-10 (11)	11 (2)	75 (2)	O ₃	129 (2)	207 (4)	231 (5)	17 (2)	-56 (3)	83 (4)
	0.3734 (18)	1.0836 (26)	0.6569 (29)		82 (19)	149 (40)	234 (55)	-7 (22)	-4 (24)	69 (37)		128 (17)	168 (31)	316 (46)	22 (18)	-64 (22)	95 (30)
C ₃	0.3147 (1)	0.9788 (2)	0.9925 (2)	C ₃	77 (1)	128 (2)	191 (4)	7 (1)	-15 (2)	57 (2)	C ₃	60 (1)	170 (3)	407 (7)	17 (2)	60 (2)	131 (4)
	0.3144 (17)	0.9778 (23)	0.9914 (30)		76 (17)	96 (33)	293 (59)	4 (19)	-16 (15)	70 (35)		68 (12)	163 (29)	392 (47)	15 (15)	37 (19)	133 (30)
C ₄	0.0883 (1)	0.8797 (1)	0.7922 (2)	C ₄	54 (1)	104 (2)	236 (4)	15 (1)	23 (2)	72 (2)	C ₄	116 (2)	211 (4)	255 (5)	31 (2)	-40 (3)	107 (4)
	0.0902 (17)	0.8798 (21)	0.7924 (26)		84 (18)	74 (29)	204 (48)	26 (18)	3 (22)	50 (30)		127 (16)	161 (29)	267 (41)	11 (17)	-72 (20)	92 (28)
C ₅	0.1534 (1)	0.9552 (2)	0.4512 (2)	C ₅	69 (1)	112 (2)	204 (4)	17 (1)	-2 (2)	69 (2)	C ₅	162 (3)	93 (3)	535 (9)	36 (2)	61 (4)	114 (4)
	0.1529 (15)	0.9534 (21)	0.4518 (28)		55 (14)	66 (29)	298 (58)	-9 (16)	6 (22)	46 (31)		171 (23)	145 (33)	553 (68)	44 (22)	87 (31)	156 (38)
X ₆ ^b	0.2637 (1)	0.3997 (1)	0.4720 (2)	X ₆ ^b	91 (1)	80 (2)	291 (4)	20 (1)	38 (2)	73 (2)	X ₆ ^b	90 (2)	248 (4)	244 (5)	28 (2)	57 (2)	108 (4)
	0.2633 (17)	0.4036 (21)	0.4740 (28)		96 (18)	76 (31)	291 (57)	37 (9)	70 (25)	113 (35)		102 (15)	301 (33)	276 (42)	26 (17)	46 (19)	97 (30)
C ₇	0.3441 (1)	0.5846 (2)	0.2628 (2)	C ₇	64 (1)	133 (2)	211 (4)	14 (1)	27 (2)	77 (2)	C ₇	60 (1)	242 (4)	368 (7)	-14 (2)	-31 (2)	130 (4)
	0.3458 (15)	0.5852 (23)	0.2669 (27)		52 (14)	131 (34)	227 (51)	14 (17)	17 (20)	84 (33)		72 (13)	234 (36)	389 (50)	-36 (17)	-33 (20)	133 (33)
C ₈	0.1176 (1)	0.5809 (2)	0.3912 (2)	C ₈	56 (1)	128 (2)	227 (4)	-6 (1)	0 (2)	77 (2)	C ₈	101 (2)	171 (3)	223 (5)	24 (2)	45 (2)	112 (3)
	0.1202 (16)	0.5808 (22)	0.3920 (26)		71 (16)	104 (32)	195 (48)	-21 (18)	6 (21)	41 (30)		88 (13)	140 (26)	257 (39)	9 (14)	32 (17)	109 (26)
C ₉	0.2042 (1)	0.6349 (1)	0.8173 (2)	C ₉	62 (1)	108 (2)	186 (3)	15 (1)	14 (1)	72 (2)	C ₉	60 (1)	282 (5)	486 (8)	13 (2)	-33 (3)	186 (5)
	0.2018 (15)	0.6355 (21)	0.8168 (26)		59 (14)	76 (28)	216 (48)	18 (16)	-5 (20)	56 (29)		51 (12)	298 (43)	496 (59)	14 (17)	-34 (20)	208 (41)
				H							H	120 (3)	129 (4)	433 (11)	31 (3)	100 (5)	111 (6)

^a For each atom, the neutron result is given on the first line and the X-ray result on the second. Numbers in parentheses here and in subsequent tables are estimated standard deviations in the least significant figures. ^b Atoms designated X are hybrid atoms (50% C, 50% N). ^c The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. ^d The anisotropic thermal parameters from the neutron data are more reliable, because of the severe absorption effects associated with the X-ray data. See footnote 30.

olation along the O-C-W direction then produced a reasonably good estimate of the hydrogen position, which was situated on the twofold axis. Phasing by these four atoms was sufficient to reveal the rest of the structure from subsequent Fourier maps.

The question of the nitrogen position was treated, as in the α form, by refining the "C" scattering lengths, and again the indication of the nitrogen being axial was evident (Table IIB). In the final cycles of anisotropic least-squares refinement, the axial hybrid atom was given intermediate scattering lengths $b_X = (b_C + b_N)/2$, since now symmetry dictates an exact 50-50% disorder. In the last cycle none of the 106 parameters shifted by more than 0.5 σ . The final agreement factors are: for all nonzero data (1650 reflections), $R = 13.1\%$ and $R_w = 16.6\%$; for "significant" data (>3 σ) (919 reflections), $R = 6.6\%$ and $R_w = 11.8\%$.⁴³ Extinction effects were even smaller than in α -HW₂(CO)₉(NO), and the refined value of the extinction parameter is $g = 956$.

(43) For the β form, agreement factors based on F^2 are $R_2 = 11.9\%$ and $R_{w2} = 12.2\%$ (all data).

As with α -HW₂(CO)₉(NO), piezoelectric, pyroelectric, and second harmonics tests were conducted to distinguish between $C2/c$ and Cc . The absence of these effects confirms the $C2/c$ space group assignment.

Discussion of the Structure

The final atomic parameters for α -HW₂(CO)₉(NO), both X-ray and neutron results, are given in Table III; those for the β form are given in Table IV. Bond lengths and bond angles are collectively listed in Tables V and VI, respectively. Figures 1 and 2 show the molecular geometries of the α and β forms; they are essentially identical. Structure factor tables for all three structure determinations are available.⁴⁴

(44) See paragraph at end of paper regarding supplementary material.

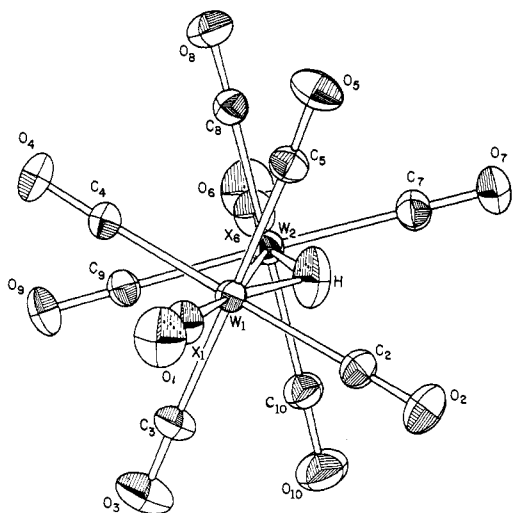


Figure 1. The molecular geometry of the α form of $\text{HW}_2(\text{CO})_9(\text{NO})$. The equatorial carbonyl groups are roughly staggered, with a dihedral angle $\text{C}_2\text{-W}_1\text{-W}_2\text{-C}_7$ of $39.7(1)^\circ$; the HWW plane approximately bisects this angle. Note that the axial ligands do not point at the H atom but at the center of the HWW triangle.

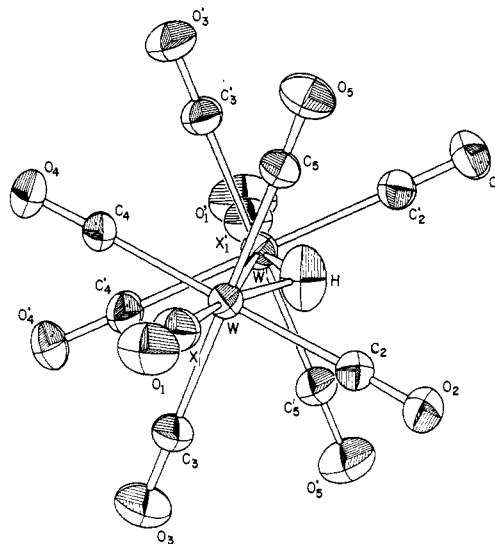


Figure 2. The molecular geometry of the β form of $\text{HW}_2(\text{CO})_9(\text{NO})$, showing a structure essentially identical with that of the α form. The main difference is that the dihedral angle $(\text{C}_2\text{-W-W}'\text{-C}_2')$ in this compound is larger ($48.3(2)^\circ$).

Table IV. Final Atomic Parameters for $\beta\text{-HW}_2(\text{CO})_9(\text{NO})$

Atom	(A) Atomic Positions		
	<i>x</i>	<i>y</i>	<i>z</i>
W	0.5601 (2)	0.2892 (4)	0.3534 (2)
X ₁ ^a	0.6288 (1)	0.3521 (3)	0.4686 (1)
C ₂	0.6254 (1)	0.0147 (3)	0.3620 (1)
C ₃	0.6672 (1)	0.4030 (3)	0.3005 (1)
C ₄	0.4955 (1)	0.5591 (3)	0.3461 (1)
C ₅	0.4511 (1)	0.1740 (3)	0.4032 (1)
O ₁	0.6718 (2)	0.3863 (5)	0.5386 (2)
O ₂	0.6622 (2)	-0.1327 (4)	0.3684 (2)
O ₃	0.7272 (2)	0.4653 (4)	0.2737 (2)
O ₄	0.4614 (2)	0.7099 (4)	0.3446 (2)
O ₅	0.3927 (2)	0.1137 (4)	0.4323 (2)
H	0.5000 ^b	0.1636 (9)	0.2500 ^b

Atom	(B) Thermal Parameters ^c					
	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
W	43 (1)	181 (6)	41 (1)	4 (2)	13 (1)	6 (2)
X ₁ ^a	58 (1)	335 (6)	49 (1)	23 (2)	11 (1)	42 (2)
C ₂	50 (1)	215 (5)	54 (1)	2 (2)	11 (1)	12 (2)
C ₃	55 (1)	250 (6)	65 (1)	16 (2)	27 (1)	15 (2)
C ₄	64 (1)	191 (5)	70 (1)	16 (2)	31 (1)	24 (2)
C ₅	55 (1)	251 (6)	54 (1)	10 (2)	20 (1)	-6 (2)
O ₁	81 (2)	630 (13)	55 (1)	43 (4)	4 (1)	76 (4)
O ₂	68 (2)	232 (7)	97 (2)	-18 (3)	16 (1)	12 (3)
O ₃	74 (2)	415 (10)	104 (2)	33 (3)	49 (2)	-1 (4)
O ₄	94 (2)	194 (7)	120 (2)	-9 (3)	49 (2)	30 (3)
O ₅	78 (2)	412 (9)	93 (2)	28 (3)	44 (1)	-18 (4)
H	128 (5)	295 (18)	53 (3)	0 ^b	-11 (3)	0 ^b

^a Atoms designated X are hybrid atoms (50% C, 50% N).
^b Values fixed by symmetry. ^c The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

The agreement between the X-ray and neutron results of $\alpha\text{-HW}_2(\text{CO})_9(\text{NO})$ is quite good as far as atomic positions are concerned; most agree within a standard deviation and all agree within 2σ . The standard deviations for the light atom positions are an order of magnitude greater for the X-ray data than for the neutron data, an effect due to the dominating influence of the tungsten atoms in the X-ray scattering process. The agreement between the thermal parameters is not as good as that between the positional parameters, an expected result because of the severe

Table V. Bond Distances (\AA)

	$\alpha\text{-HW}_2(\text{CO})_9(\text{NO})$		$\beta\text{-HW}_2(\text{CO})_9(\text{NO})$	
	Neutron	X-Ray		Neutron
W ₁ -W ₂	3.328 (3)	3.3292 (12)	W-W'	3.330 (3)
W ₁ -H	1.875 (4)		W-H	1.870 (4)
W ₂ -H	1.876 (4)			
W ₁ -X ₁	1.917 (2)	1.922 (19)	W-X ₁	1.912 (3)
W ₂ -X ₆	1.907 (2)	1.878 (22)		
W ₁ -C ₂	2.066 (3)	2.040 (23)	W-C ₂	2.080 (3)
W ₂ -C ₇	2.068 (2)	2.056 (17)		
W ₁ -C ₃	2.061 (3)	2.054 (20)	W-C ₃	2.066 (3)
W ₂ -C ₈	2.062 (3)	2.024 (19)		
W ₁ -C ₄	2.058 (3)	2.030 (20)	W-C ₄	2.048 (3)
W ₂ -C ₉	2.055 (2)	2.060 (17)		
W ₁ -C ₅	2.054 (3)	2.049 (18)	W-C ₅	2.065 (3)
W ₂ -C ₁₀	2.055 (3)	2.045 (20)		
X ₁ -O ₁	1.144 (2)	1.103 (26)	X ₁ -O ₁	1.162 (3)
X ₆ -O ₆	1.151 (2)	1.168 (31)		
C ₂ -O ₂	1.124 (2)	1.141 (29)	C ₂ -O ₂	1.128 (3)
C ₇ -O ₇	1.128 (2)	1.124 (23)		
C ₃ -O ₃	1.129 (2)	1.136 (26)	C ₃ -O ₃	1.129 (3)
C ₈ -O ₈	1.132 (2)	1.153 (25)		
C ₄ -O ₄	1.134 (2)	1.147 (25)	C ₄ -O ₄	1.134 (3)
C ₉ -O ₉	1.130 (2)	1.139 (21)		
C ₅ -O ₅	1.128 (2)	1.125 (24)	C ₅ -O ₅	1.125 (3)
C ₁₀ -O ₁₀	1.130 (2)	1.121 (25)		

absorption effects associated with the X-ray data.³⁰ All in all, this structure analysis is comparable to a similar X-ray-neutron double determination on $\text{HMn}(\text{CO})_5$.⁴⁵ The agreement between the X-ray-derived and neutron-derived atomic positions in $\text{HW}_2(\text{CO})_9(\text{NO})$ is slightly better than in $\text{HMn}(\text{CO})_5$, but the agreement between temperature factors is slightly worse.

A comparison between the molecular structures of the α and β forms (see Tables V and VI, and Figures 1 and 2) shows that the two forms are essentially identical. There are no significant differences worth mentioning, except perhaps the subtle observation that in the α form the thermal ellipsoids of the axial atoms

(45) S. J. LaPlaca, W. C. Hamilton, J. A. Ibers, and A. Davison, *Inorg. Chem.*, **8**, 1928 (1969).

Table VI. Bond Angles (deg)

	α -HW ₂ (CO) ₉ (NO)		β -HW ₂ (CO) ₉ (NO)	
	Neutron	X-Ray		Neutron
W ₁ -H-W ₂	125.0 (2)		W-H-W'	125.9 (4)
H-W ₁ -W ₂	27.5 (1)		H-W-W'	27.0 (2)
H-W ₂ -W ₁	27.5 (1)			
H-W ₁ -X ₁	163.8 (1)		H-W-X ₁	165.8 (2)
H-W ₂ -X ₆	166.2 (1)			
H-W ₁ -C ₂	77.1 (1)		H-W-C ₂	76.9 (2)
H-W ₂ -C ₇	76.8 (1)			
H-W ₁ -C ₃	92.3 (1)		H-W-C ₃	94.5 (1)
H-W ₂ -C ₈	90.6 (1)			
H-W ₁ -C ₄	104.9 (1)		H-W-C ₄	103.5 (2)
H-W ₂ -C ₉	105.0 (1)			
H-W ₁ -C ₅	83.6 (1)		H-W-C ₅	84.1 (1)
H-W ₂ -C ₁₀	84.8 (1)			
W ₂ -W ₁ -X ₁	168.7 (1)	169.3 (6)	W'-W-X ₁	167.1 (1)
W ₁ -W ₂ -X ₆	166.0 (1)	165.9 (6)		
W ₂ -W ₁ -C ₂	102.5 (1)	103.4 (7)	W'-W-C ₂	101.6 (1)
W ₁ -W ₂ -C ₇	103.1 (1)	103.3 (6)		
W ₂ -W ₁ -C ₃	81.8 (1)	81.6 (6)	W'-W-C ₃	84.2 (1)
W ₁ -W ₂ -C ₈	82.6 (1)	82.9 (6)		
W ₂ -W ₁ -C ₄	79.8 (1)	79.4 (6)	W'-W-C ₄	78.8 (1)
W ₁ -W ₂ -C ₉	78.9 (1)	78.7 (6)		
W ₂ -W ₁ -C ₅	93.3 (1)	92.8 (6)	W'-W-C ₅	94.4 (1)
W ₁ -W ₂ -C ₁₀	92.6 (1)	92.5 (7)		
X ₁ -W ₁ -C ₂	87.9 (1)	86.6 (9)	X ₁ -W-C ₂	89.8 (1)
X ₆ -W ₂ -C ₇	89.6 (1)	89.6 (9)		
X ₁ -W ₁ -C ₃	93.8 (1)	94.5 (8)	X ₁ -W-C ₃	90.3 (1)
X ₆ -W ₂ -C ₈	91.4 (1)	91.1 (9)		
X ₁ -W ₁ -C ₄	89.9 (1)	90.8 (8)	X ₁ -W-C ₄	89.8 (1)
X ₆ -W ₂ -C ₉	88.6 (1)	88.7 (8)		
X ₁ -W ₁ -C ₅	90.9 (1)	90.8 (8)	X ₁ -W-C ₅	91.2 (1)
X ₆ -W ₂ -C ₁₀	93.4 (1)	93.3 (9)		
C ₂ -W ₁ -C ₃	90.4 (1)	91.8 (8)	C ₂ -W-C ₃	89.1 (1)
C ₇ -W ₂ -C ₈	90.8 (1)	91.0 (7)		
C ₂ -W ₁ -C ₄	177.3 (1)	176.4 (9)	C ₂ -W-C ₄	179.4 (1)
C ₇ -W ₂ -C ₉	177.4 (1)	177.5 (8)		
C ₂ -W ₁ -C ₅	91.4 (1)	90.5 (8)	C ₂ -W-C ₅	91.0 (1)
C ₇ -W ₂ -C ₁₀	89.9 (1)	90.0 (7)		
C ₃ -W ₁ -C ₄	91.4 (1)	90.8 (8)	C ₃ -W-C ₄	91.3 (1)
C ₈ -W ₂ -C ₉	91.0 (1)	90.8 (7)		
C ₃ -W ₁ -C ₅	175.0 (1)	174.3 (9)	C ₃ -W-C ₅	178.6 (2)
C ₈ -W ₂ -C ₁₀	175.2 (1)	175.5 (9)		
C ₄ -W ₁ -C ₅	87.0 (1)	87.1 (7)	C ₄ -W-C ₅	88.6 (1)
C ₉ -W ₂ -C ₁₀	88.5 (1)	88.3 (7)		
W ₁ -X ₁ -O ₁	177.0 (2)	179.0 (18)	W-X ₁ -O ₁	178.4 (2)
W ₂ -X ₆ -O ₆	178.8 (2)	178.1 (18)		
W ₁ -C ₂ -O ₂	176.5 (2)	176.6 (17)	W-C ₂ -O ₂	178.3 (2)
W ₂ -C ₇ -O ₇	176.9 (2)	176.3 (19)		
W ₁ -C ₃ -O ₃	178.4 (2)	178.1 (20)	W-C ₃ -O ₃	178.2 (2)
W ₂ -C ₈ -O ₈	179.1 (2)	178.1 (17)		
W ₁ -C ₄ -O ₄	177.1 (2)	176.7 (18)	W-C ₄ -O ₄	177.9 (2)
W ₂ -C ₉ -O ₉	176.6 (2)	175.2 (18)		
W ₁ -C ₅ -O ₅	177.2 (2)	178.0 (17)	W-C ₅ -O ₅	176.0 (2)
W ₂ -C ₁₀ -O ₁₀	179.5 (2)	179.5 (18)		

are slightly elongated in a direction perpendicular to the WHW plane, whereas in the β form the elongation direction is parallel to that plane. The chief features of the molecular geometry will now be discussed.

The Hydrogen Atom. The original X-ray diffraction study²⁰ showed a bent molecule with a W...W separation of 3.329 (1) Å. The position of the H atom, which of course was not found in that work, was estimated to be at the intersection of the two axial lines. Based on this assumption, a W-H-W angle of 159° was estimated.⁴⁶ The neutron diffraction work, how-

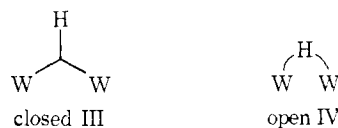
(46) The W-H-W angle could be estimated either by computing the angle between two equatorial planes (this gave an angle of 151°) or by defining the H position as the intersection of the two axial ligand-tungsten vectors (this gave an angle of 159°). These results compared reasonably well with Kirtley and Kaesz's method⁴⁷ of correlating the W-H-W angle with the Raman hydrogen stretching frequency. They

ever, shows an average W-H-W angle of 125.5°, coupled with a W-H distance of 1.873 Å and a W...W separation of 3.329 Å. The bridging W-H distance found here is 0.10 Å longer than the estimated⁴⁸ W-H distance of 1.77 Å for a terminal hydride. This lengthening of the M-H distance in going from a terminal to a bridging mode has been noticed by us before in H₃Mn₃(CO)₁₂⁷ and can be ascribed to a formal lowering of the bond order.

The Nitrogen Atom. The location of the nitrogen atom has also been a vexing problem. In the original X-ray study, it was not possible to locate the nitrogen atom unambiguously, but unusually short W-C(ax) bonds strongly suggested that the nitrogen atoms were disordered in the axial positions.⁵² Later, however, we convinced ourselves that the only conceivable cause for the bending of the molecule had to be an equatorial nitrogen.⁵³

Now it appears that our original assignment was in fact correct. The neutron diffraction study conclusively shows that the nitrosyl is axial. As mentioned earlier in the Experimental Section, refinement of the scattering lengths of all the "carbon" atoms resulted in the equatorial atoms converging to normal carbon values, while the axial atoms converged to values precisely midway between C and N (Table II).

Evidence for a Closed Three-Center Bond. A very significant feature in the structure of HW₂(CO)₉(NO) is the fact that the axial ligands do not point directly at the hydrogen atom, preferring instead to make an angle of 165.3° with it. This strongly suggests the presence of a three-center, two-electron bond of the type I, in which appreciable metal-metal overlap exists. Adopting a formalism used in boron hydride chemistry, such a bond could be written as III, in



postulate that within the bridging hydrogen range (800-1400 cm⁻¹), the lower the frequency, the larger the bridge angle. Using this correlation, a W-H-W angle of ~140° is estimated, corresponding to a ν [HW₂(CO)₉(NO)] stretch at 1045 cm⁻¹.

(47) S. W. Kirtley, Ph.D. Thesis, UCLA, 1969.

(48) The known⁴⁹ distance for a Re-H terminal bond is 1.68 (1) Å. The difference between the covalent radii for Re and W, as estimated from an average W-C(eq) distance of 2.060 (2) Å found in HW₂(CO)₉(NO) (this work) and an average Re-C(eq) distance of 1.97 (2) Å found in HRe₃Mn(CO)₁₄⁵⁰ and HRe₃(CO)₁₄⁵¹ is 0.09 Å. Thus, the terminal W-H distance is estimated to be 1.77 Å.

(49) S. C. Abraham, A. P. Ginsberg, and K. Klux, *Inorg. Chem.*, **3**, 558 (1964).

(50) M. R. Churchill and R. Bau, *Inorg. Chem.*, **6**, 2086 (1967).

(51) R. P. White, T. E. Block, and L. F. Dahl, private communication.

(52) The average axial metal-ligand distance (1.90 Å) found in HW₂(CO)₉NO is 0.15 Å shorter than the average equatorial metal-ligand distance (2.05 Å). A comparison of metal-carbon and metal-nitrogen bond distances in mixed carbonyl-nitrosyl complexes⁵³ indicates that the M-N bond distance is generally about 0.07 Å shorter than the M-C distance. Although M-C bond lengths opposite hydrogen atoms are usually shorter than M-C bond lengths opposite carbonyl groups,⁵⁴ such differences are typically only of the order of 0.10 Å or less. To explain as large a difference as 0.15 Å, the effect of the nitrogen atom had to be taken into account.

(53) B. A. Frenz, J. H. Enemark, and J. A. Ibers, *Inorg. Chem.*, **8**, 1288 (1969).

(54) In most octahedral compounds of the type M(CO)₅X, where X is a poorer charge acceptor than the carbonyl groups, the axial M-C distances have been observed to be shorter than the equatorial by ~0.10 Å. See ref 7 and references therein.

(55) R. Bau, S. W. Kirtley, T. N. Sorrell, and S. Winarko, *J. Amer. Chem. Soc.*, **96**, 988 (1974).

contrast to the open three-center bond, which would then be written as IV.

It would seem reasonable to assume that most, if not all, bent M–H–M bonds overlap in this manner. If that is the case, arguments about whether bent M–H–M linkages should be written with or without M–M bonds (V and VI, respectively) would be rendered



pointless, for the preferred designation III would indicate partial M–M character.

Comparison between $[\text{HW}_2(\text{CO})_{10}]^-$ and $[\text{HCr}_2(\text{CO})_{10}]^-$. The previous discussion could provide a clue as to why $\text{HW}_2(\text{CO})_9(\text{NO})$ and the isoelectronic $[\text{HW}_2(\text{CO})_{10}]^-$ are bent,⁵⁶ while $[\text{HCr}_2(\text{CO})_{10}]^-$ and $\text{HCrRe}(\text{CO})_{10}$ are linear.⁵⁷ The smaller size of the Cr orbitals would probably make overlaps of type I rather difficult in $[\text{HCr}_2(\text{CO})_{10}]^-$, unless some way could be found to make the Cr–H–Cr angle more acute; but this is prevented by the steric contacts between equatorial carbonyl groups. Even in the tungsten case, these contacts are already rather severe ($\text{C}_4 \cdots \text{C}_9 = 2.92 \text{ \AA}$ in $\alpha\text{-HW}_2(\text{CO})_9(\text{NO})$ and $\text{C}_4 \cdots \text{C}_4' = 3.04 \text{ \AA}$ in $\beta\text{-HW}_2(\text{CO})_9(\text{NO})$]; this could be the prime reason why the W–H–W angle in $\text{HW}_2(\text{CO})_9(\text{NO})$ is not observed to be more bent.

The Symmetric vs. Asymmetric Question. We were originally hoping to find an asymmetric W–H–W bond in this molecule, a reasonable expectation in view of the fact that the electronic requirements of the two halves of the molecule are different. The 50–50%

(56) Preliminary X-ray results on $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{HW}_2(\text{CO})_{10}]^-$ indicate that the geometry of the anion is bent, much as in $\text{HW}_2(\text{CO})_9(\text{NO})$: S. Graham and R. Bau, manuscript in preparation.

(57) (a) L. B. Handy, J. K. Ruff, and L. F. Dahl, *J. Amer. Chem. Soc.*, **92**, 7312 (1970); (b) A. S. Foust, W. A. G. Graham, and R. P. Stewart, *J. Organometal. Chem.*, **54**, C22 (1973).

nitrosyl–carbonyl packing disorder has unfortunately masked this effect and has generated the appearance of a symmetric W–H–W bond. It is therefore unclear at this point whether the observed symmetry of the W–H–W bond is real or an artifact of packing disorder.

Even under the best conditions, the characterization of a truly symmetric hydrogen bond is an agonizing problem.¹³ It has been shown that it is virtually impossible to distinguish a truly symmetric condition from a superposition of a disordered, slightly asymmetric pair.¹⁴ At present we are attempting to break the disorder by the replacement of a carbonyl group by a bulky ligand. The derivative $\text{HW}_2(\text{CO})_8(\text{NO})\text{-}[\text{P}(\text{OMe})_3]$ has been prepared and crystallized. We are presently collecting X-ray and neutron diffraction data on it, and hope to present these results in the near future.

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Supplementary Material Available. A listing of structure factor amplitudes (Table A, $\alpha\text{-HW}_2(\text{CO})_9(\text{NO})$, X-ray; Table B, $\alpha\text{-HW}_2(\text{CO})_9(\text{NO})$, neutron; Table C, $\beta\text{-HW}_2(\text{CO})_9(\text{NO})$, neutron) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-6621.