much more hindered. It is assumed here that a bimolecular nucleophilic displacement mechanism applies[4] and that the path of approach lies along a line approximately normal to the iridium complex molecular plane. Another feature which may be operative in the present case is partial steric blockage by the ortho hydrogens on the phenyl rings. This effect is known to occur in a number of other complexes and in several cases[29-31] has been used as a rationalization for the lowered reactivity observed for those complexes. For $(\eta^5\text{-}C_5H_5)IrP(C_6H_5)_3(CO)$ there appears to be some blocking by H(26) (Ir-H(26) = 3.2 (1) Å) and a possibility of interference form H(16) (Ir-H(16) = 3.6 (1) Å). H(26) is illustrated in Figure 1. It should also be noted here that the observed reactivities of $(\eta^5\text{-}C_5H_5)IrP(C_6H_5)_3(CO)$ toward various alkyl halides[3,4] do not preclude the inductive electronic properties of the alkyl substituents from being an important factor in these reactions. Although both electronic and steric factors seem to be operative in the reactions of this complex, further studies are required to assess the relative importance of these.

An inspection of the closest intermolecular contacts shows that none of these is significantly less than the distance predicted from the sum of van der Waals radii.

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Registry No. $(\eta^5\text{-}C_5H_5)IrP(C_6H_5)_3(CO)$, 32612-68-3.

Supplementary Material Available. A listing of structure factor amplitudes 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 INORG-74-2408.

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X-Ray Crystallographic Determination of the Molecular Structure of Bis(tetraethylammonium) Di-μ-hydrido-octacarbonylditungstate(2−), $[Et_4N^+]_2[H_2W_2(CO)_8{}^{2-}]$. A Unique Example of the Successful Location and Refinement of Hydride Ligands in Positions Bridging Third-Row Transition Metal Atoms

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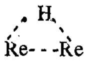
The species bis(tetraethylammonium) di-μ-hydrido-octacarbonylditungstate(2−), $[Et_4N^+]_2[H_2W_2(CO)_8{}^{2-}]$, crystallizes in the centrosymmetric monoclinic space group $C2/m$ [$C_{2h}{}^3$; No. 12] with $a = 15.863$ (4) Å, $b = 12.129$ (3) Å, $c = 8.145$ (2) Å, $\beta = 105.28$ (2)°, $V = 1511.7$ Å^3, and $Z = 2$. Observed and calculated densities are 1.86 (1) and 1.877 g cm^{-3}, respectively. All atoms, including hydrogen atoms, have been located from a single-crystal X-ray structural analysis based on counter data collected with a Picker FACS-1 automated diffractometer. Final discrepancy indices are $R_F = 3.34\%$ and $R_{wF} = 3.18\%$ for 1051 independent reflections representing data complete to $2\theta = 45°$ (Mo Kα radiation). The $[H_2W_2(CO)_8{}^{2-}]$ dianion has crystallographically dictated C_{2h} symmetry with a planar $W(\mu\text{-}H)_2W$ bridge in which W–H = 1.857 (60) Å, W–H–W′ = 108.6 (52)°, and H–W–H′ = 71.4 (52)°. The tungsten–tungsten distance of 3.0162 (11) Å is shorter than the W–W single-bond distance of 3.222 (1) Å in $(\eta^5\text{-}C_5H_5)_2W_2(CO)_6$ and is described (using the Mason–Mingos formalism) as approaching a W=W double bond. The $[Et_4N^+]$ cation is disordered about a crystallographic mirror plane; however its hydrogen atoms (each of occupancy $^1/_2$) have been located unambiguously and their parameters refined (with limited success).

Introduction

For some years we have been interested in the structural characterization of polynuclear transition metal complexes containing bridging hydride ligands. A series of X-ray crystallographic investigations on the hydridorhenium species $HRe_2Mn(CO)_{14}$,[1] $[H_2Re_3(CO)_{12}{}^-]$,[2] $[HRe_3(CO)_{12}{}^{2-}]$,[3] and $[H_6Re_4(CO)_{12}{}^{2-}]$[4] failed to reveal directly the positions of the μ_2-bridging hydride ligand(s) but did show a pattern of molecular distortions indicating that these positions could be determined *indirectly* by considering (i) metal-metal distances and (ii) "holes" in the distribution of ligands around the metal atom cluster, as indicated (for example) by abnormally large M–M–(CO) angles. The net result of these studies was some quantitative information on rhenium-rhenium distances: (1) a normal rhenium-rhenium single bond (in rhenium carbonyl species) is ~3.0 Å; (2) a singly (μ_2-) hydrido bridged rhenium-rhenium distance in a triangulated rhenium-carbonyl species is ~3.16 Å; (3) a linear Re–H–Re system has a rhenium· · ·rhenium distance ≥3.40 Å.

We note at this time that cases (2) and (3), which may be represented formally by I and II (respectively), are examples



$$\overset{H}{Re\cdots Re}$$

I

Re- - -H- - -Re

II

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of two-electron, three-center bonds and that a steady gradation from I to II is possible (depending upon the Re-H-Re angle).

Recently, Bennett, *et al.*,[5] have reported a structural study of $H_2Re_2(CO)_8$ and found a rhenium-rhenium distance of 2.896 (3) Å—*i.e.*, considerably shorter than a normal *non-bridged* rhenium-rhenium single-bond distance. Thus, while the presence of one μ_2-bridging hydride ligand causes a net *increase* of $\geqslant$0.15 Å in a rhenium-rhenium bond, the presence of two μ_2-bridging hydride ligands causes a *decrease* of ~0.1 Å. While the correlation between bond length and bond order is tenuous for the metal-metal vector in ligand-bridged dimetallic species, it seems possible that the presence of two μ_2-hydrido ligands may cause a metal-metal bond order to become greater than unity.

The recent synthesis of the anion $[H_2W_2(CO)_8{}^{2-}]$ by Davison, *et al.*,[6] has prompted our present X-ray diffraction study of the species $[Et_4N^+]_2[H_2W_2(CO)_8{}^{2-}]$. Our results are reported below.

Collection and Treatment of the X-Ray Diffraction Data

Red crystals of $[Et_4N^+]_2[H_2W_2(CO)_8{}^{2-}]$ were supplied by Professor A. Davison of the Massachusetts Institute of Technology.

An initial examination of the diffraction patterns from several crystals suggested that the crystals belonged to the orthorhombic system. However, a careful examination of an $h0l$ precession photograph revealed a slight unevenness in the separation of spots in the a^* direction. Further study indicated that the diffraction pattern was actually that of a twinned monoclinic crystal with a false mirror plane perpendicular to a^* (*i.e.*, in the real bc plane), such that the $00l$ reflections of one net superimpose the $\bar{1}0l$ reflections of another for $l = 2n$ and produce an apparent halving of a^* for $l = 2n + 1$. [This mode of twinning was common to all crystals examined.]

Finally, a small fragment was cleaved from an apparently untwinned (as viewed in a polarizing microscope) section of a large (macroscopically twinned) crystal. This fragment proved, indeed, to be a single crystal. Dimensions were $(001)\rightarrow(00\bar{1}) = 0.7$ mm, $(110)\rightarrow(\bar{1}\bar{1}0) = 0.3$ mm, and $(\bar{1}10)\rightarrow(1\bar{1}0) = 0.4$ mm.

Precession and cone-axis photographs yielded the approximate cell dimensions, indicated C_{2h} $(2/m)$ Laue symmetry, and exhibited the absences hkl for $h + k = 2n + 1$. Possible space groups are $C2$ [$C_2{}^3$; No. 5], Cm [$C_s{}^3$; No. 8], and $C2/m$ [$C_{2h}{}^3$; No. 12]. The successful solution of the structure proved this last, centrosymmetric, space group to be the true one.

The crystal was transferred to a Picker FACS-1 computer-controlled diffractometer,[7] was accurately centered, and was orientated with its c^* axis precisely coincident with the instrumental ϕ axis. The 2θ, ω, and χ settings of the resolved Mo Kα_1 peaks of 12 high-angle ($2\theta \approx 40°$) reflections were determined automatically.[8] These values were used in a least-squares refinement of cell parameters and orientation parameters. Using λ(Mo Kα_1) 0.70926 Å, the derived cell dimensions (at 24°) and their estimated standard deviations are $a = 15.8625$ (40) Å, $b = 12.1292$ (29) Å, $c = 8.1449$ (17) Å, and $\cos\beta = -0.2635$ (3), which corresponds to $\beta = 105.28$ (2)°. The unit cell volume is $V = 1511.7$ Å^3. The observed density ($\rho_{\text{obsd}} = 1.86$ (1) g cm^{-3}, by neutral buoyancy in CCl_4-*sym*-$C_2H_4Br_2$) is in good agreement with that calculated for mol wt 854.31 and $Z = 2$ ($\rho_{\text{calcd}} = 1.877$ g cm^{-3}).

Using a 3.0° takeoff angle and a Nb β filter (~47% transmission of Mo Kα radiation) at the detector (6 mm × 6 mm aperture, 330 mm from the crystal), intensity data were collected by executing a coupled θ(crystal)-2θ(counter) scan from 0.8° in 2θ below the Mo Kα_1 peak to 0.8° in 2θ above the Mo Kα_2 peak, the scan rate being 2°/min. Stationary-crystal, stationary-counter background counts, each of 40-sec duration, were recorded at the two extremes of the scan.

Before collecting the data set, the 002 reflection was measured (by a θ-2θ scan) at $\chi = 90°$ and at 10° intervals of ϕ, from $\phi = 0°$ to $\phi = 350°$. The observed variation in intensity (±9% from the mean) with ϕ was eliminated upon application of an absorption correction, thereby confirming the validity of the absorption correction.

A unique data set having $0° < 2\theta \leqslant 45°$ was collected (reflections hkl and $\bar{h}\bar{k}l$). Three "standard reflections" in approximately orthogonal directions in reciprocal space were monitored after each batch of 48 reflections. The net intensity of each of the standards decreased steadily throughout the course of data collection (400 by 39%, 040 by 35%, and 002 by 28%). A careful check at the termination of data collection showed that the crystal was still accurately centered and aligned. Application of an *anisotropic* linear decay correction[9] to the entire data set reduced the root-mean-square deviations in the standard reflections to 0.76, 1.55, and 1.43%, respectively.

The raw intensity data were assigned estimated standard deviations (assuming an "ignorance factor" of $p = 0.04$) and were reduced to values of $|F_o|$ and $\sigma(|F_o|)$ in the customary manner.[9] Any reflection having a net negative count was assigned an intensity of zero and retained. No data were rejected on the basis of being "not significantly above background."

All data were corrected for absorption.[10] With μ(Mo Kα) = 79.75 cm^{-1}, maximum and minimum transmission factors were 0.676 and 0.507, respectively. Finally, equivalent pairs of $hk0$ and $\bar{h}k0$ reflections were averaged, and their intensities replaced by the σ^{-2}-weighted average, with appropriately modified standard deviations. The final data set consisted of 1051 symmetry-independent reflections.

Solution and Refinement of the Structure

Scattering factors for neutral tungsten, oxygen, nitrogen, and carbon were taken from the compilation of Cromer and Waber;[11] both the real and the imaginary components of anomalous dispersion were included in the calculation of structure factor amplitudes, using the values of Cromer and Liberman.[12] For hydrogen, the "best floated spherical H atom" values of Stewart, *et al.*,[13] were used. The function minimized during least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$, where $w(hkl) = \sigma^{-2}(hkl)$. Discrepancy indices used in the text are defined as

$$R_F = \frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|} \times 100\ (\%)$$

$$R_{wF} = \left[\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w|F_o|^2}\right]^{1/2} \times 100\ (\%)$$

Programs used during the course of the analysis included FORDAP (Fourier synthesis, by A. Zalkin), LSHF (full-matrix least-squares refinement, derived from C. T. Prewitt's SFLS5 by B. G. DeBoer), STAN1 (distances, angles, and their esd's, by B. G. DeBoer), and ORTEP (thermal ellipsoid drawings, by C. K. Johnson).

The structure was solved by assuming the centrosymmetric space group $C2/m$ and recognizing that the intensities of reflections were very strong for $k = 4n$ and very weak for $k = 4n + 2$. The trigonometric equation for the structure factor for space group $C2/m$ is[14]

$$A = 8 \cos 2\pi(hx + lz) \cos 2\pi ky$$

It follows, therefore, that the dominant scatterers (*i.e.*, the tungsten atoms) must lie at $\pm(0, \sim{}^1/_8, 0)$, suggesting a W-W bond of length $b/4$ or ~3.03 Å.

Initial calculations were performed using data which had yet to be corrected for absorption. The first structure factor calculation, phased only by a tungsten atom (at 0, $^1/_8$, 0) had discrepancy indices of $R_F = 17.4\%$ and $R_{wF} = 23.1\%$. A series of difference-Fourier synthesis, each being phased by a greater number of atoms than the previous one, led to the location of all nonhydrogen atoms. Refinement of positional and isotropic thermal parameters for these atoms converged with $R_F = 7.4\%$ and $R_{wF} = 8.4\%$. The use of anisotropic thermal parameters for tungsten led to $R_F = 4.7\%$ and $R_{wF} = 4.8\%$;

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(10) Using the program DRAB by B. G. DeBoer.

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Table I. Final Positional and Isotropic Thermal Parameters[a] for $[Et_4N^+]_2[H_2W_2(CO)_8{}^{2-}]$, with Esd's[b]

Atom	Occupancy[c]	x	y	z	B, Å^2
(A) Atoms in the Asymmetric Unit of the $[H_2W_2(CO)_8{}^{2-}]$ Anion					
W	$^1/_2$	0	0.124338 (34)	0	4.12
O(1)	1	−0.01050 (38)	0.31044 (45)	0.25646 (77)	6.88
O(2)	1	0.20450 (37)	0.15066 (60)	0.12401 (85)	7.85
C(1)	1	−0.00586 (47)	0.24031 (55)	0.16251 (97)	4.69
C(2)	1	0.12985 (46)	0.13631 (65)	0.07813 (90)	5.17
H	$^1/_2$	−0.0113 (64)	0	0.1254 (134)	6.8 (25)
(B) Atoms in the Asymmetric Unit of the $[Et_4N^+]$ Cation					
N	$^1/_2$	0.24411 (44)	$^1/_2$	0.35728 (99)	4.13
C(11)	$^1/_2$	0.1868 (9)	0.5658 (13)	0.4472 (25)	5.25
C(21)	$^1/_2$	0.1886 (10)	0.4366 (14)	0.2080 (21)	5.34
C(31)	$^1/_2$	0.2974 (12)	0.4198 (17)	0.4841 (22)	5.71
C(41)	$^1/_2$	0.3022 (11)	0.5786 (17)	0.2922 (21)	6.36
C(12)	$^1/_2$	0.1248 (9)	$^1/_2$	0.5161 (22)	6.93
C(22)	$^1/_2$	0.1277 (11)	$^1/_2$	0.0768 (22)	7.64
C(32)	1	0.3669 (8)	0.3580 (12)	0.4253 (17)	8.13
H(11A)	$^1/_2$	0.158 (13)	0.630 (16)	0.340 (28)	8.5 (51)
H(11B)	$^1/_2$	0.244 (14)	0.644 (16)	0.531 (26)	9.1 (49)
H(21A)	$^1/_2$	0.135 (12)	0.394 (15)	0.273 (26)	8.2 (24)
H(21B)	$^1/_2$	0.220 (9)	0.401 (11)	0.141 (18)	5.2 (27)
H(31A)	$^1/_2$	0.319 (11)	0.478 (17)	0.569 (23)	10.3 (56)
H(31B)	$^1/_2$	0.224 (8)	0.402 (11)	0.542 (16)	4.4 (23)
H(41A)	$^1/_2$	0.320 (10)	0.527 (16)	0.214 (23)	9.9 (53)
H(41B)	$^1/_2$	0.263 (5)	0.639 (6)	0.197 (10)	3.5 (13)
H(12A)	$^1/_2$	0.088 (15)	0.555 (22)	0.524 (36)	12.6 (77)
H(12B)	$^1/_2$	0.140 (11)	0.459 (14)	0.629 (22)	7.6 (90)
H(12C)	$^1/_2$	0.077 (7)	0.460 (8)	0.383 (14)	4.1 (15)
H(22A)	$^1/_2$	0.158 (14)	0.526 (20)	−0.017 (29)	12.0 (73)
H(22B)	$^1/_2$	0.151 (20)	0.585 (25)	0.098 (40)	13.2 (73)
H(22C)	$^1/_2$	0.095 (11)	0.465 (13)	0.017 (22)	7.5 (45)
H(32A)	$^1/_2$	0.423 (12)	0.425 (15)	0.460 (23)	7.7 (43)
H(32B)	$^1/_2$	0.340 (17)	0.319 (25)	0.349 (37)	12.8 (42)
H(32C)	$^1/_2$	0.413 (19)	0.304 (27)	0.505 (39)	14.1 (47)
H(42A)	$^1/_2$	0.355 (18)	0.606 (22)	0.472 (36)	11.2 (76)
H(42B)	$^1/_2$	0.419 (17)	0.667 (23)	0.364 (38)	12.9 (32)
H(42C)	$^1/_2$	0.354 (12)	0.695 (19)	0.500 (28)	8.5 (32)

[a] "Equivalent isotropic thermal parameters" are given for the nonhydrogen atoms. These correspond to the average mean-square displacement along the three principal axes of the vibration ellipsoid. [b] Estimated standard deviations, shown in parentheses, are right-adjusted to the least significant digit of the preceding number. They are derived from the inverse of the final least-squares matrix. [c] The occupancy is the multiplier for the atom's contribution to $F_c(hkl)$ using the general expression for the space group $C2/m$, which has eight equipoints.

incorporation of anisotropic thermal parameters for all nonhydrogen atoms yielded $R_F = 4.3\%$ and $R_{wF} = 4.3\%$.

At this stage the absorption-corrected data were introduced, leading to convergence with $R_F = 3.8\%$ and $R_{wF} = 3.7\%$. A difference-Fourier synthesis now showed, as its highest feature, the bridging hydride ligand (H), with a peak height of 0.87 e Å^{-3} and a position of $x \simeq 0.00, y = 0, z = 0.12$. Inclusion and refinement of this atom led to the reduced discrepancy indices, $R_F = 3.6\%$ and $R_{wF} = 3.5\%$.

A further difference-Fourier synthesis now led to the approximate location of all 20 independent hydrogen atoms of the disordered Et_4N^+ ion. [The mode of disorder of this cation, *i.e.*, reflection about the plane $y = {}^1/_2$, leads to each of these hydrogen atoms having an occupancy of $^1/_2$.] Positional and anisotropic thermal parameters for all nonhydrogen atoms (and positional and isotropic thermal parameters for H) were now refined, with all hydrogen atoms of the Et_4N^+ cation included in calculated positions with isotropic thermal parameters of $B = 6.0$ Å^2. Following convergence $[(\Delta/\sigma)_{max} < 0.1]$, we decided to attempt to refine the positional and isotropic thermal parameters of the "half-hydrogen" atoms. The difficulties inherent in successfully performing this cannot be underestimated. We were attempting to refine disordered hydrogen atoms (effective $Z = {}^1/_2$) in the presence of tungsten atoms ($Z = 74$). The experiment was not an unqualified success but, in our estimation, was worthwhile. After several cycles of refinement, a state of "semiconvergence" was reached in which parameters of the "half-hydrogen" atoms were varying by no more than 0.5σ. Refinement was terminated at this point since it was clear that some of the positional parameters of the "half-hydrogen" atoms were oscillating with successive cycles of refinement. The final discrepancy indices are $R_F = 3.34\%$ and $R_{wF} = 3.18\%$. The standard deviation in an observation of unit weight, defined by $[\Sigma w(|F_o| - |F_c|)^2/(m-n)]^{1/2}$, was 0.88, where the number of observations (m) was 1051 and the total number of variables (n) was 189 ($m/n = 5.6$). The function $\Sigma w(|F_o| - |F_c|)^2$ showed no appreciable dependence either upon $(\sin\theta)/\lambda$ or upon $|F_o|$, thereby indicating a correctly chosen weighting scheme. A final difference Fourier synthesis showed no feature greater than 0.3 e Å^{-3} except in the immediate vicinity of the tungsten atom, where there were peaks up to 0.68 e Å^{-3} in height.

A list of observed and calculated structure factor amplitudes is available.[15] Positional parameters are collected in Table I, while thermal parameters are shown in Table II.

The Molecular Structure

Interatomic distances and their estimated standard deviations (esd's) are shown in Table III; bond angles, with their esd's, are given in Table IV. The crystal consists of discrete $[Et_4N^+]$ cations and $[H_2W_2(CO)_8{}^{2-}]$ anions which are mutually separated by normal van der Waals distances. There are no abnormally close contacts. The packing of these ions within the unit cell is shown in Figure 1.

Description of the $[H_2W_2(CO)_8{}^{2-}]$ Anion. The $[H_2W_2(CO)_8{}^{2-}]$ anions are centered on the positions 0, 0, 0 and $^1/_2, {}^1/_2, 0$ corresponding to Wyckoff notation a and point group symmetry C_{2h} ($2/m$).[16] The ion, in fact, is only slightly distorted from idealized D_{2h} symmetry (see Figure 2). The labeling of atoms is such that atom X is at x, y, z; atom X′ is at $-x, y, -z$; atom X″ is at $x, -y, z$; and atom X‴ is at $-x, -y, -z$.

The two bridging hydride ligands are crystallographically equivalent and lie on the plane $y = 0$. [We emphasize that,

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

(16) See ref 14, p 95.

Table II. Anisotropic Thermal Parameters[a] with Esd's[b] for $[Et_4N^+]_2[H_2W_2(CO)_8]$

Atoms	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	$\langle U \rangle$[c]
(A) Atoms in the $[H_2W_2(CO)_8{}^{2-}]$ Anion							
W	4.39 (2)	4.22 (2)	3.63 (2)	0	0.88 (1)	0	0.21, 0.23, 0.23
O(1)	7.5 (3)	6.1 (3)	7.2 (4)	−0.8 (3)	2.3 (3)	−1.9 (3)	0.24, 0.30, 0.33
O(2)	5.6 (6)	10.2 (5)	7.5 (4)	−0.9 (2)	1.2 (3)	0.0 (3)	0.26, 0.31, 0.36
C(1)	4.7 (4)	4.5 (4)	4.7 (4)	−0.5 (3)	0.9 (3)	0.0 (1)	0.22, 0.24, 0.26
C(2)	4.9 (4)	6.0 (5)	4.6 (4)	−0.6 (5)	1.3 (3)	0.1 (3)	0.23, 0.24, 0.28
(B) Atoms in the $[Et_4N^+]$ Cation							
N	3.7 (3)	3.9 (4)	4.7 (5)	0	1.0 (3)	0	0.21, 0.22, 0.24
C(11)	4.1 (7)	5.4 (9)	6.6 (9)	−0.7 (5)	2.1 (6)	−1.8 (7)	0.21, 0.22, 0.31
C(21)	5.0 (8)	5.5 (9)	5.1 (8)	−0.9 (7)	0.5 (8)	−1.8 (9)	0.19, 0.27, 0.30
C(31)	5.5 (8)	6.9 (10)	5.2 (8)	2.0 (7)	2.1 (8)	2.7 (6)	0.20, 0.23, 0.34
C(41)	6.6 (10)	7.5 (11)	5.0 (8)	−2.9 (8)	1.4 (4)	1.3 (4)	0.20, 0.25, 0.36
C(12)	6.0 (7)	7.8 (4)	8.0 (8)	0	3.7 (7)	0	0.23, 0.31, 0.33
C(22)	6.2 (6)	9.5 (10)	5.8 (7)	0	−1.0 (5)	0	0.22, 0.34, 0.34
C(32)	7.2 (5)	9.1 (7)	8.2 (7)	3.6 (5)	2.3 (5)	1.3 (5)	0.23, 0.31, 0.38

[a] These anisotropic thermal parameters are in the usual form of the *isotropic* thermal parameter and have units of Å². They enter the equation for the structure factor in the form $\exp[-\frac{1}{4}(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$. [b] See footnote *b* to Table I. [c] These values correspond to the root-mean-square amplitudes of vibration (in Å) along the minor, median, and major axes of the atomic vibration ellipsoid. For relative orientations, see the figures.

Table III. Interatomic Distances (in Å) for $[Et_4N^+]_2[H_2W_2(CO)_8{}^{2-}]$

Atoms	Dist	Atoms	Dist
(A) Distances within the $[H_2W_2(CO)_8{}^{2-}]$ Anion			
W-W′	3.0162 (11)		
W-H	1.857 (60)	W-H′	1.857 (60)
W-C(1)	1.950 (7)	W· · ·O(1)	3.110 (5)
W-C(2)	1.995 (7)	W· · ·O(2)	3.149 (6)
C(1)-O(1)	1.159 (8)	C(2)-O(2)	1.157 (9)
C(1)· · ·C(1′)	2.702 (15)	O(1)· · ·O(1′)	4.278 (12)
C(1)· · ·C(2)	2.735 (10)	O(1)· · ·O(2)	4.300 (9)
C(2)· · ·C(1′)	2.696 (10)	O(2)· · ·O(1′)	4.219 (9)
(B) Distances within the $[Et_4N^+]$ Cation			
N-C(11)	1.534 (15)	C(11)-C(12)	1.486 (18)
N-C(21)	1.510 (15)	C(21)-C(22)	1.457 (23)
N-C(31)	1.506 (16)	C(31)-C(32)	1.512 (21)
N-C(41)	1.516 (16)	C(41)-C(32′)	1.495 (21)
(C) Distances Involving Hydrogen Atoms of CH_2 Groups			
C(11)-H(11A)	1.17 (21)	C(31)-H(31A)	0.98 (20)
C(11)-H(11B)	1.36 (19)	C(31)-H(31B)	1.38 (12)
C(21)-H(21A)	1.22 (19)	C(41)-H(41A)	0.98 (17)
C(21)-H(21B)	0.93 (13)	C(41)-H(41B)	1.13 (7)
(D) Distances in CH_3 Groups			
C(12)-H(12A)	0.90 (25)	C(32)-H(32A)	1.18 (17)
C(12)-H(12B)	1.01 (18)	C(32)-H(32B)	0.80 (28)
C(12)-H(12C)	1.25 (11)	C(32)-H(32C)	1.07 (30)
C(22)-H(22A)	1.05 (24)	C(32′)-H(42A)	0.63 (31)
C(22)-H(22B)	1.09 (27)	C(32′)-H(42B)	1.11 (25)
C(22)-H(22C)	0.75 (18)	C(32′)-H(42C)	0.95 (22)

Table IV. Interatomic Angles (in deg) for $[Et_4N^+]_2[H_2W_2(CO)_8{}^{2-}]$

Atoms	Angle	Atoms	Angle
(A) Angles Involving the Tungsten Atom			
W′-W-C(1)	136.15 (20)	H-W-H′	71.4 (52)
W′-W-C(2)	94.17 (23)	W′-W· · ·O(1)	136.54 (11)
W′-W-H	35.7 (27)	W′-W· · ·O(2)	95.82 (13)
C(1)-W-C(1′)	87.69 (41)	O(1)· · ·W· · ·O(1′)	86.91 (22)
C(1)-W-C(2)	87.76 (30)	O(1)· · ·W· · ·O(2)	86.79 (17)
C(1)-W-C(2′)	86.22 (30)	O(1)· · ·W· · ·O(2′)	84.77 (17)
C(1′)-W-C(2)	86.22 (30)	O(1′)· · ·W· · ·O(2)	84.77 (17)
C(2)-W-C(2′)	171.65 (47)	O(2)· · ·W· · ·O(2′)	168.36 (27)
H-W-C(1)	100.6 (26)	H-W· · ·O(1)	101.0 (26)
H-W-C(1′)	171.1 (34)	H-W· · ·O(1′)	171.6 (35)
H-W-C(2)	97.2 (31)	H-W· · ·O(2)	98.4 (31)
H-W-C(2′)	89.6 (31)	H-W· · ·O(2′)	91.1 (31)
(B) Angle Involving the Hydride Ligands			
W-H-W′	108.6 (52)		
(C) Angles within the Carbonyl Groups			
W-C(1)-O(2)	178.6 (11)	W-C(2)-O(2)	175.5 (8)
(D) Angles within the $[Et_4N^+]$ Cation			
C(11)-N-C(21)	110.9 (10)	C(21)-N-C(31)	109.0 (11)
C(11)-N-C(31)	107.8 (12)	C(21)-N-C(41)	108.5 (11)
C(11)-N-C(41)	109.4 (10)	C(31)-N-C(41)	111.3 (11)
N-C(11)-C(12)	115.8 (11)	N-C(31)-C(32)	115.3 (12)
N-C(21)-C(22)	117.1 (12)	N-C(41)-C(32′)	115.7 (12)

as discussed in our report on the structure of $[\pi\text{-}C_5(CH_3)_5\text{-}RhCl]_2(\mu\text{-}H)(\mu\text{-}Cl)$,[17] we cannot truly distinguish between a single-minimum or double-minimum potential well for the M-H-M systems. However, the essentially isotropic appearance of this peak on difference-Fourier maps, along with its sensible thermal parameter of $B = 6.8\ (25)$ Å², leads us to favor the single-minimum (*i.e.*, symmetric M-H-M) possibility.]

The four W-H bonds are crystallographically equivalent, the interatomic distance being 1.857 (60) Å. Angles within the strictly planar $W(\mu\text{-}H)_2W$ system are W-H-W′ = W-H′-W′ = 108.6 (52)° and H-W-H′ = H-W′-H′ = 71.4 (52)°. The angles W-W′-H and W-W′-H′ are each 35.7 (27)°.

The two crystallographically independent tungsten-carbonyl linkages are W-C(1) = 1.950 (7) Å and W-C(2) = 1.995 (7) Å; the difference of 0.045 Å corresponds to ~4.6σ [using σ^2(diff) = $\sigma_1{}^2 + \sigma_2{}^2$] and is statistically significant. Similarly, the tungsten· · ·oxygen distances are W· · ·O(1) = 3.110 (5) Å and W· · ·O(2) = 3.149 (6) Å, the difference of 0.039 Å representing ~5.0σ. The different metal-carbonyl distances presumably reflect the different trans-lengthening influence of bridging hydride and carbonyl ligands [H′ is trans to C(1), with H′-W-C(1) = 171.1 (34)°, while C(2′)-O(2′) is trans to C(2), with C(2′)-W-C(2) = 171.65 (47)°]. This result may be compared to that obtained from a neutron diffraction study on β-pentacarbonylmanganese hydride,[18] in which Mn-CO(axial) = 1.822 (12) Å (axial = trans to H) and Mn-CO(equatorial) = 1.853 (12) Å (equatorial = cis to H and trans to CO). This pattern of distances, *i.e.*, M-CO(trans to H) < M-CO(trans to CO), is also reflected in X-ray studies of α-$HMn(CO)_5$ [Mn-CO(trans to H) = 1.821 (9) Å, Mn-CO(trans to CO) = 1.840 (5) Å][19] and β-$HMn(CO)_5$ [Mn-CO(trans to H) = 1.824 (17) Å, Mn-CO(trans to CO) = 1.853

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

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

(19) S. J. LaPlaca, W. C. Hamilton, and J. A. Ibers, *Inorg. Chem.*, **3**, 1491 (1964).

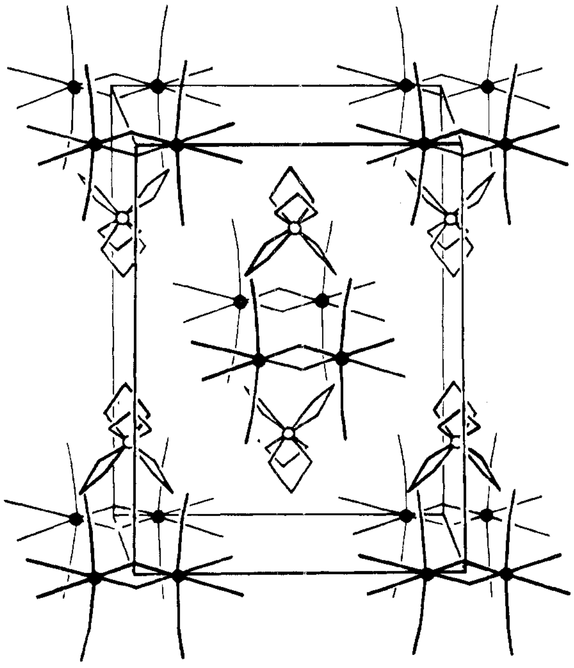

Figure 1. Packing of ions within the unit cell of $[\mathrm{Et_4N^+}]_2[\mathrm{H_2W_2}$-$(\mathrm{CO_8}{}^{2-}]$. The *b* axis is horizontal and the *a* axis is vertical.

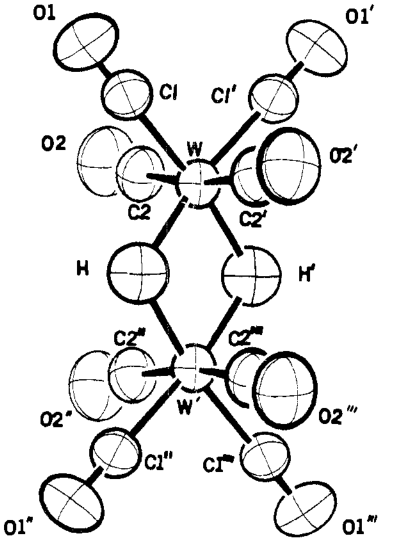

Figure 2. Geometry of the $[\mathrm{H_2W_2(CO)_8}{}^{2-}]$ anion (ORTEP drawing, 50% vibration ellipsoids).

(7) Å].[18] We conclude, therefore, that the trans influence of a μ_2-bridging hydride ligand is not substantially different from that of a terminal hydride ligand.

Angles between adjacent carbonyl ligands are C(1)-W-C(1') = 87.69 (41)°, C(1)-W-C(2) = 87.76 (30)°, C(1)-W-C(2') = 86.22 (30)°, C(1')-W-C(2) = 86.22 (30)°, and C(1')-W-C(2') = 87.76 (30)°. The nonequivalence of C(1)-W-C(2) and C(1)-W-C(2') [difference is 1.54° or $\sim 3.6\sigma$] destroys the possible perfect D_{2h} symmetry of the ion.

Angles within the terminal carbonyl ligands are W-C(1)-O(1) = 178.6 (11)° and W-C(2)-O(2) = 175.5 (8)°, while carbon-oxygen distances are C(1)-O(1) = 1.159 (8) Å and C(2)-O(2) = 1.157 (9) Å.

The angles W'-W-C(1) = 136.15 (20)° and W'-W-C(2) = 94.17 (23)° reflect the bisoctahedral geometry of the $[\mathrm{H_2W_2(CO)_8}{}^{2-}]$ anion.

Finally we should note that the W-W' distance of 3.0162 (11) Å is appreciably shorter than the tungsten-tungsten single-bond distance of 3.222 (1) Å in $[(\pi\text{-C}_5\mathrm{H}_5)\mathrm{W(CO)_3}]_2$[20] and the tungsten-tungsten separation of 3.181 (1) Å in $\mathrm{W_2(CO)_8H_2(SiEt_2)_2}$.[21,22]

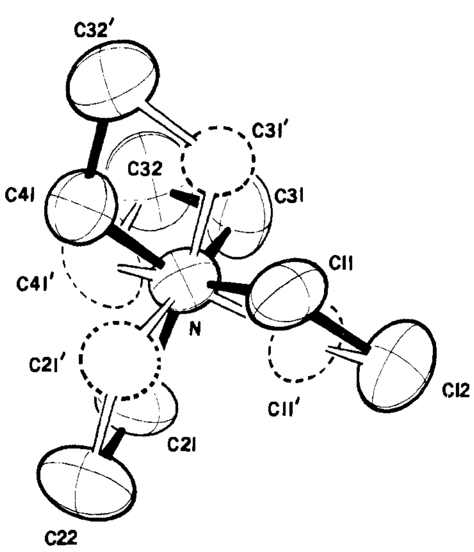

Figure 3. Disorder of the ethyl groups in the $[\mathrm{Et_4N^+}]$ cation.

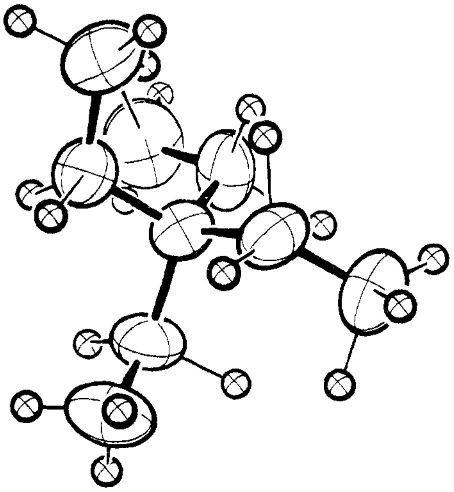

Figure 4. Stereochemistry of one of the $[\mathrm{Et_4N^+}]$ ions (including hydrogens). [This diagram has the same orientation as Figure 3.]

The $[\mathrm{Et_4N^+}]$ Cation. The four tetraethylammonium cations lie at $y = 0$ and $y = {}^1/_2$ in Wyckoff position i with point symmetry C_s (m).[16] The result of the crystallographically imposed C_s symmetry is that the tetraethylammonium cations are disordered within the crystal. The positions of carbon and nitrogen atoms within the disordered cation are shown in Figure 3. As can seen from this diagram, the crystallographic mirror plane contains atoms N, C(12), and C(22). All the other atoms except the symmetry-related C(32) and C(32') are disordered; the cation thus appears on an electron density map as one central nitrogen atom, eight "half-carbon" atoms in the α positions, and four carbon atoms in the β positions. The hydrogen atoms are, likewise, disordered; the net observed cation contains 40 "half-hydrogen" atoms. One of the two (mirror-related) configurations of the $[\mathrm{Et_4N^+}]$ cation is depicted in Figure 4.

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(20) R. D. Adams, D. M. Collins, and F. A. Cotton, *Inorg. Chem.*, 13, 1086 (1974).

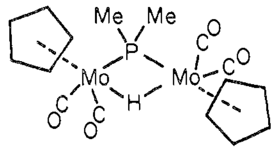
(21) M. J. Bennett and K. A. Simpson, *J. Amer. Chem. Soc.*, 93, 7156 (1971).

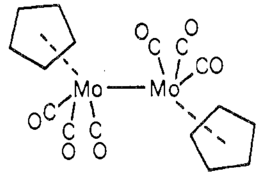
(22) Note that the hydride ligands in this species do not directly bridge the two tungsten atoms. Rather, they are postulated to be involved in W-H-Si bridges.

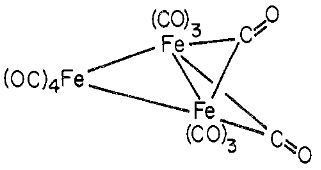
The four independent nitrogen-carbon distances range from 1.506 (16) to 1.534 (15) Å, averaging 1.517 ± 0.012 Å.[23] The C(α)-C(β) distances range from 1.457 (23) to 1.512 (21) Å, averaging 1.488 ± 0.023 Å.[23] Carbon-hydrogen distances do vary widely (as expected!), with maximum and minimum values of 1.38 (12) Å for C(31)-H(31B) and 0.63 (31) Å for C(32′)-H(42A); the mean of the 20 independent values is 1.05 ± 0.19 Å.[23] While we must admit that these distances are of low precision, the positions of hydrogen atoms are essentially sensible (*cf.* Figure 4) and the attempt to refine "half-hydrogen" atoms in the presence of tungsten atoms is (at least) an interesting exercise.

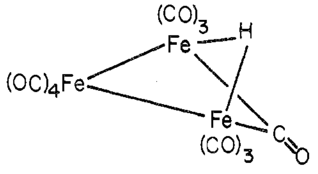
Discussion

It has always seemed strange that the molecule $[\pi\text{-}C_5H_5(CO)_2Mo]_2(H)(PMe_2)$ [in which the Mo· · ·Mo distance is 3.26 Å[24]] is customarily drawn without a direct molybdenum· · ·molybdenum bond (*i.e.*, III), whereas a metal-metal bond *is* required for $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ [Mo-Mo = 3.235 (1) Å[25]]—see IV. A similar disparity occurs for $Fe_3(CO)_{12}$ (in which the bridged Fe-Fe distance is 2.560 (6) Å[26]) and $HFe_3(CO)_{11}^-$ (in which the bridged Fe· · ·Fe distance is 2.577 (3) Å).[27] These two molecules are customarily depicted as in V and VI.

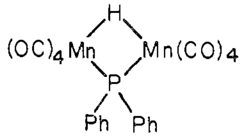

III


IV


V


VI

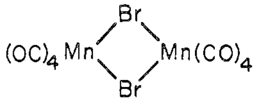
A further example of this phenomenon occurs with $Mn_2(CO)_8(H)(PPh_2)$, VII, in which the hydride-bridged Mn· · · Mn distance of 2.937 (5) Å[28] is not appreciably different from the value of 2.923 Å found for the *bonding* Mn-Mn distance in $Mn_2(CO)_{10}$[29] (VIII).


VII

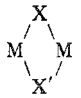
$(OC)_5Mn{-}Mn(CO)_5$

VIII

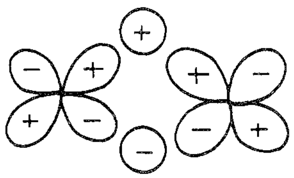
For the sake of comparison we may note that the (clearly nonbonding) Mn· · ·Mn distance in $Mn_2(CO)_8Br_2$ (IX) is 3.743 (8) Å.[30]

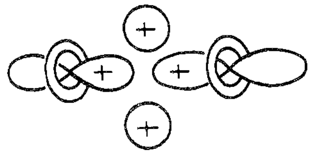

IX

Mason and Mingos have recently published an interesting paper[31,32] in which were discussed binuclear and polynuclear complexes of transition and main group metals bearing such bridging groups as Cl, Br, I, OR, SR, NR_2, PR_2, H, and R (alkyl or aryl). The authors pointed out, *inter alia,* that for a

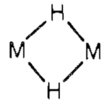


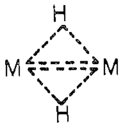
bridge, the two lowest lying molecular orbitals may be regarded as derived in the manner shown in X and XI.


X


XI

If the ligands X and X′ each have only one orbital available for bond formation (*i.e.*, are H or Me etc.), then orbitals X and XI give the complete bonding picture (*i.e.*, two three-center, two-electron bonds) which customarily has been depicted as in XII. The symmetry of the metal orbitals represents a situation in which *direct* metal-metal interaction is possible, so (in our opinion) a better diagram is that shown in XIII. [A determination of the degree of direct metal-metal interaction is possible only by the calculation of overlap integrals for the orbitals involved.]


XII


XIII

When the ligands X and X′ *do* have other available electron pairs (*i.e.*, X = Cl, Br, I, OR, SR, NR_2, PR_2 etc.), then two further orbitals must be considered, each of which is *antibonding* with respect to the metal· · ·metal vector (see XIV and XV).[32c]

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(23) Esd's on mean bond lengths etc. are preceded by "±" and are calculated by the scatter formula $\sigma = [\Sigma(\chi_i - \bar{\chi})^2/(N-1)]^{1/2}$, where the sum is over N independent values, χ_i is the ith value, and $\bar{\chi}$ is the average value.

(24) R. J. Doedens and L. F. Dahl, *J. Amer. Chem. Soc.*, **87**, 2576 (1965).

(25) This value comes from ref 20. A previous study gave a value of 3.222 Å—see F. C. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, **27**, 809 (1957).

(26) C. H. Wei and L. F. Dahl, *J. Amer. Chem. Soc.*, **91**, 1351 (1969).

(27) L. F. Dahl and J. F. Blount, *Inorg. Chem.*, **4**, 1373 (1965).

(28) R. J. Doedens, W. T. Robinson, and J. A. Ibers, *J. Amer. Chem. Soc.*, **89**, 4323 (1967).

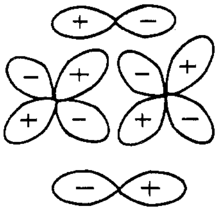
(29) L. F. Dahl and R. E. Rundle, *Acta Crystallogr.*, **16**, 419 (1963).

(30) L. F. Dahl and C. H. Wei, *Acta Crystallogr.*, **16**, 611 (1963).

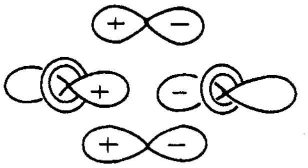
(31) R. Mason and D. M. P. Mingos, *J. Organometal. Chem.*, **50**, 53 (1973).

(32) Structural features of $M(\mu\text{-}X)_2M$ systems have also been considered by Professor L. F. Dahl and his coworkers: (a) L. F. Dahl, E. Rodulfo de Gil, and R. D. Feltham, *J. Amer. Chem. Soc.*, **91**, 1653 (1969) (see, especially, Table VI on p 1659); (b) G. L. Simon and L. F. Dahl, *ibid.*, **95**, 783 (1973).

(32c) Note Added in Proof. Recent theoretical calculations [B. K. Teo, M. B. Hall, R. F. Fenske, and L. F. Dahl, *J. Organometal. Chem.*, **70**, 413 (1974)] suggest that these additional electrons occupy an in-plane antibonding σ* type dimetal orbital. These results do not invalidate our basic argument concerning metal-metal bond order.



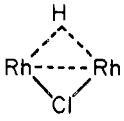
XIV



XV

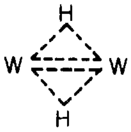
Thus, if we consider the sequence $X = X' = H$; $X = H$, $X' = Cl$; $X = X' = Cl$, the maximum possible order of the metal-metal bond changes, sequentially, from 2 to 1 to 0.

We have previously published an account of the crystal structure of $[\pi\text{-}C_5(CH_3)_5RhCl]_2(\mu\text{-}H)(\mu\text{-}Cl)$[17] and have shown that the rhodium-rhodium distance in this molecule is 2.9064 (10) Å, which seems compatible with a *bonding* rhodium-rhodium interaction, particularly since the angle Rh-Cl-Rh′ is acute, with a value of 73.20 (6)°. [To our knowledge, there is no known Rh^{III}-Rh^{III} bond distance with which to compare the above value; however the Rh^{II}-Rh^{II} bond length in $[Ph_3P(dmg)_2Rh]_2$ is 2.936 Å.[33]] We regard the core of the $[\pi\text{-}C_5(CH_3)_5RhCl]_2(\mu\text{-}H)(\mu\text{-}Cl)$ molecule as best written as in XVI.

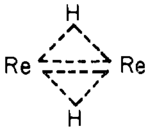


XVI

The present structural analysis of the $[H_2W_2(CO)_8^{2-}]$ ion and the study by Bennett, *et al.*, of $H_2Re_2(CO)_8$[5] each show metal-metal distances substantially below that accepted for single-bond lengths. The representation of the cores of these species by XVII and XVIII both illustrates the bridging nature of the hydride ligands and indicates pictorially that the metal-metal bond order may be greater than unity.



XVII



XVIII

Extension of this picture is both desirable and possible. Thus, both the species $[Re_2(CO)_6(\mu\text{-}H)_3^-]$ and $[Re_2(CO)_6(\mu\text{-}OEt)_3^-]$ are known.[34] A rather imprecise crystallographic study of $[Ph_4As^+][Re_2(CO)_6(OEt)_3^-]$[35] shows a (nonbonding) rhenium· · ·rhenium distance of ~3.17 Å. While no data are yet available, we would expect the rhenium-rhenium distance in the $[Re_2(CO)_6(\mu\text{-}H)_3^-]$ anion to be substantially shorter (perhaps as low as ~2.7-2.8 Å), since the maximum possible rhenium-rhenium bond order here is 3.

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Registry No. $[Et_4N^+]_2[H_2W_2(CO)_8^{2-}]$, 52032-34-5.

Supplementary Material Available. A listing of structure factor amplitudes 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 $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-2413.

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A Metalloborane Zwitterion. Synthesis and X-Ray Crystal Structure of $8\text{-}[(C_2H_5)_3N(CH_2)_4O]\text{-}6\text{-}(CO)_3\text{-}6\text{-}MnB_9H_{12}$

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Reaction of $2\text{-}THF\text{-}6\text{-}(CO)_3\text{-}6\text{-}MnB_9H_{12}$ with Et_3N produces the title compound by a complex mechanism involving ether cleavage and an unusual internal rearrangement of the metalloborane cage. Its stereochemistry was determined from an X-ray analysis on crystals having the triclinic space group $P\bar{1}$ with cell parameters of $a = 10.018$ (2), $b = 12.843$ (3), $c = 9.305$ (2) Å; $\alpha = 99.661$ (15), $\beta = 94.545$ (14), $\gamma = 96.918$ (15)°; $Z = 2$; $\rho_{calcd} = 1.201$, $\rho_{exptl} = 1.207$ g cm^{-3}. Intensity data for 1803 independent reflections having $I > 2\sigma(I)$ were recorded at room temperature using monochromated Cu Kα radiation and a Syntex $P\bar{1}$ autodiffractometer. The structure was solved using conventional heavy-atom techniques and refined to $R_1 = 0.056$ and $R_2 = 0.061$. The structure is similar to that of $B_{10}H_{14}$, but with B(6) replaced by the Mn of the $Mn(CO)_3$ group. The coordination about the Mn is nearly octahedral, and the $\text{-}O(CH_2)_4N(Et)_3$ side chain is attached to the metalloborane cage at B(8) or B(10).

We recently reported[1] the existence of a new class of metalloboranes in which the borane ligands $B_9H_{13}^{2-}$ or $B_9H_{12}L^-$ (L = ethers) are bound to manganese or rhenium by a σ-bonding interaction and two equivalent MHB bridge hydrogen bonds. This combination of bonding interactions from the tridentate borane ligands is probably responsible

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