full resolution of all Tb(III) crystal field components is possible, the luminescence data can be used to deduce the actual solution-phase structure of the complex. In the absence of such resolution (which is probably the most likely situation workers will encounter), one can draw distinctions between monomer and dimer complexation modes. This information would be of great use in beginning a quantitative interpretation of NMR data, and correlation of luminescence and NMR investigations could provide the most powerful approach to the study of compound structures in fluid solutions.

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Registry No. Tb(MeCp)$_3$(THF), 87184-39-2; Tb(MeCp)$_2$(Cl)(THF), 97210-70-3; Tb(MeCp)$_2$(CH$_3$)(THF), 97210-71-4; [Tb(MeCp)$_2$(Cl)]$_2$, 97210-72-5; [Tb(MeCp)$_2$(CH$_3$)]$_2$, 97234-21-4; Na(MeCp), 55562-83-9; TbCl$_3$, 10042-88-3; THF, 109-99-9; PhMe, 108-88-3.

A Neutron Diffraction Study of $[Ph_4P]^+[HW_2(CO)_{10}]^-$

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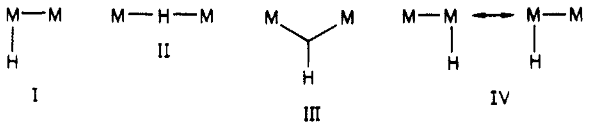
The structure of $[Ph_4P]^+[HW_2(CO)_{10}]^-$ has been analyzed at low temperature with single-crystal neutron diffraction techniques. The W–H–W linkage in the $[HW_2(CO)_{10}]^-$ anion is bent and symmetric, with W–H and W–W distances of 1.897 (5) Å and 3.340 (5) Å, respectively, and a W–H–W angle of 123.4 (5)°. The anion has a structure almost identical with that of the isoelectronic $HW_2(CO)_9(NO)$, including a non-hydrogen skeleton which is bent and staggered. These results support our earlier conclusion that the M–H–M bond is inherently bent. Crystallographic details: crystals of $[Ph_4P]^+[HW_2(CO)_{10}]^-$ are tetragonal, space group $P\bar{4}$, $a = b = 15.529$ (2) Å, $c = 6.680$ (1) Å, $V = 1611$ Å^3, $Z = 4$. The final R value is 0.050 for 2279 neutron reflections measured at 40 K.

Introduction

Few metal carbonyl complexes have attracted as much interest during the past two decades as the hydridometal carbonyl anions $[HM_2(CO)_{10}]^-$ (M = Cr, Mo, W). First prepared by Behrens and co-workers in 1957,[2] the anions have been extensively studied because of speculation that they might contain a single unsupported M–H–M three-center/two-electron (3c–2e) bond, a suspicion which was later essentially confirmed by an X-ray analysis of $[Et_4N]^+[HCr_2(CO)_{10}]^-$.[3] Unsupported[4] 3c–2e bonds are extremely rare: The $[HM_2(CO)_{10}]^-$ family, and close analogues such as $HW_2(CO)_9(NO)$, are among the very few transition-metal complexes known to contain such bonds. For compounds of the main-group elements, unsupported 3c–2e bonds are known to exist in $[B_2H_7]^-$ and related species.[5] In addition, the hybrid M–H–B system, as found in $(Ph_2MeP)_3$ Cu(BH$_4$), recently has also been accurately characterized.[6]

In 1966, Hayter reported an improved preparation of $[HM_2(CO)_{10}]^-$ and the mixed derivatives $[HMM'(CO)_{10}]^-$ (M, M′ = Cr, Mo, W) involving the NaBH$_4$ reduction of the parent hexacarbonyls M(CO)$_6$ in refluxing THF.[7] At that time, Hayter also described the IR and NMR spectra of the anions, the latter of which were analyzed further by Whitesides and Maglio.[8] Both groups of investigators concluded that the ^{1}H NMR spectrum of $[HW_2(CO)_{10}]^-$ is inconsistent with a static terminal structure (I), but were unable to distinguish between a linear bridged (II), a bent bridged (III), or a rapidly equilibrating pair of terminal structures (IV).



Meanwhile, we and other groups have investigated[9-18]

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[1] (a) University of Southern California. (b) Present address: Shell Development Co., P.O. Box 481, Houston, TX 77001. (c) Brookhaven National Laboratory.

[2] (a) Behrens, H.; Klek, W. *Z. Anorg. Allg. Chem.* **1957,** *292,* 151. (b) Behrens, H.; Haag, W. *Chem. Ber.* **1961,** *94,* 312. (c) Behrens, H.; Vogl, J. *Chem. Ber.* **1963,** *96,* 2220.

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[4] We define a molecule having an *unsupported* 3c–2e bond as one in which the two halves of the molecule are held together solely by one 3c–2e bond, without other bridging groups. Thus, molecules such as B_2H_6 or $H_2Re_2(CO)_8$, which have two X–H–X brdiges, are not included by this definition.

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[13] Harris, D. C.; Gray, H. B. *J. Am. Chem. Soc.* **1975,** *97,* 3073.

[14] For an illustration of the $[HW_2(CO)_{10}]^-$ anion in $[Et_4N]^+[HW_2(CO)_{10}]^-$, see Figure 4 in: Bau, R.; Teller, R. G.; Kirtley, S. W.; Koetzle, T. F. *Acc. Chem. Res.* **1979,** *12,* 176. The anion in this salt has a *non-hydrogen framework* which is eclipsed and almost linear (or very slightly bent). However, *the W–H–W bond* is found to be markedly bent and surprisingly asymmetric, with W–H distances of 1.718 (12) and 2.070 (12) Å, a W–W distance of 3.528 (2) Å, and a W–H–W angle of 137.1 (10)°. The H atom is disordered and is displaced by 0.71 (1) Å from the center of the W–W bond. Disorder is also found in the $W_2(CO)_{10}$ framework, where it is minor, and in the $[Et_4N]^+$ cation, where it is extensive.

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Table I. Summary of Crystal Data, Data Collection Conditions, and Refinement Results of $[Ph_4P]^+[HW_2(CO)_{10}]^-$

	X-ray	neutron
	Crystal Data	
space group	$P\bar{4}$	$P\bar{4}$
$a = b$, Å	15.614 (5)	15.529 (2)
c, Å	6.887 (2)	6.680 (1)
V, Å^3	1682	1611
ρ(obsd), g/cm^3	2.10	...
ρ(calcd), g/cm^3	1.94	2.02
no. of reflctns used to determine unit cell	54	58
μ, cm^{-1}	37.5 (calcd)	0.87 (calcd)[a]
variatn of transmissn coeff	0.73–1.23[b]	0.79–0.83
cryst faces	{100}, {010}, {001}, {011}	{100}, {010}, {001}
cryst dimens, mm	0.25 × 0.25 × 0.25	2.75 × 2.90 × 3.80
	Data Collection Conditions	
radiation wavelength, Å	0.7107 (Mo Kα)	1.0386
monochromator	none	Be(002)
temperature	room temp	40 K
2θ(max), deg	55.0	90.0
scan range ($\Delta 2\theta$), deg	2.9	3.0–3.6
no. of observns	4144	2610
no. of unique reflctns	1931	2279
no. of reflctns used in refinement	1500	2279
	Refinement Results[c]	
quant minimized	F	F^2
$R(F)$	0.051	0.050
$R(wF)$	0.061	...
$R(F^2)$	0.080	0.068
$R(wF^2)$	...	0.095
S	1.80[d]	2.39[e]
extinction parameter 10^4g	...	0.19 (3)
n(obsd)/n(var)	14.3	7.3

[a] Calculated assuming the absorption cross-section due to incoherent scattering of hydrogen to be 69 barn. [b] Normalized to an average of unity. [c] $R(F) = \sum|F_o - k|F_c||/\sum F_o$; $R(wF) = [\sum w(F_o - k|F_c|)^2/\sum wF_o^2]^{1/2}$; $R(F^2) = \sum|F_o^2 - k^2F_c^2|/\sum F_o^2$; $R(wF^2) = [\sum w(F_o^2 - k^2F_o^2)^2/\sum wF_o^4]^{1/2}$. [d] $S = \{\sum w(F_o - k|F_c|)^2/[n(\text{obsd}) - n(\text{var})]\}^{1/2}$. [e] $S = \{\sum w(F_o^2 - k^2F_c^2)^2/[n(\text{obsd}) - n(\text{var})]\}^{1/2}$.

(with crystallographic and spectroscopic techniques) a series of M–H–M bridged complexes, which show this linkage to be not only bent but "off-axis".[10] In this paper we report the results of a low-temperature neutron diffraction study of $[Ph_4P]^+[HW_2(CO)_{10}]^-$. These results provide additional evidence that the favored geometry of the metal–hydrogen linkage in the $[HM_2(CO)_{10}]^-$ anions, at least in the solid state, is that of the bent M–H–M bond (III).

Experimental Section

The $[HW_2(CO)_{10}]^-$ ion was made by the reaction of $NaBH_4$ with $W(CO)_6$ following the procedure given by Hayter.[7] The desired salt was isolated by the addition of $[Ph_4P]^+Br^-$ to the sodium salt of the anion.

The neutron diffraction analysis was preceded by X-ray diffraction work in order to locate the non-hydrogen atoms and to ensure that the compound was suitable for further study. The results of the X-ray investigation are briefly summarized in Tables I and III.

Large, transparent, light yellow crystals were grown by slowly cooling a saturated 5:1 EtOH/toluene solution of $[Ph_4P]^+$-$[HW_2(CO)_{10}]^-$ from room temperature to −20 °C. Neutron diffraction data were measured on an automated four-circle diffractometer[19] at the Brookhaven High Flux Beam Reactor. The sample was mounted on a hollow aluminum pin and placed inside a specially adapted closed-cycle helium refrigerator.[20] Unit-cell constants, determined from the observed 2θ values for 58 centered reflections, together with other experimental details, are given in Table I. Intensities of Bragg reflections were measured by using $\theta/2\theta$ step scans, with data being accumulated at each point for a predetermined monitor count of the incident neutron beam. The time per step was approximately 3 s. Scan ranges are indicated in Table I; the step was adjusted to give approximately 70 steps in each scan. The background count was derived from seven points at the end of each scan. Squared observed structure factors were obtained as $F_o^2 = (I)\sin 2\theta$ and corrected for absorption by means of numerical integration over a Gaussian grid.[21]

Initial positions of the non-hydrogen atoms were obtained from the X-ray analysis, and the H atoms were then located from difference-Fourier maps. Least-squares computations were carried out with a local modification of the program described by Busing, Martin, and Levy.[22] Weights were taken to be equal to $1/\sigma^2$, where $\sigma^2(F_o^2) = \sigma^2_{\text{count}}(F_o^2) + 0.0004F_o^2$. Toward the end of the refinement, an extinction correction of the type introduced by Zachariasen[23] was included in the calculations.

Final atomic coordinates for the neutron analysis are given in Table II. Distances and angles of the $[HW_2(CO)_{10}]^-$ anion, together with esd's calculated from variance–covariance matrices,[24] are listed in Table III. Other details of the structural analyses, and a compilation of the observed and calculated structure factors for the neutron study, are available as supplementary material.[25]

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(23) Zachariasen, W. H. *Acta Crystallogr.* **1967**, *23*, 558.

(24) The variance–covariance matrices were prepared in final refinement cycles in which all positional parameters were varied (thermal parameters were held fixed). [Busing, W. R.; Levy, H. A., A Crystallographic Function and Error Program (ORXFE), Report ORNL 59-12-3; Oak Ridge National Laboratory: Oak Ridge, TN, 1959.]

Table II. Fractional Atomic Coordinates from the Neutron Diffraction Study of $[Ph_4P]^+[HW_2(CO)_{10}]^-$ at 40 K

atom	10^4x	10^4y	10^4z
W	0527 (2)	4062 (2)	0297 (4)
H(1)[a]	0[b]	5000[b]	1643 (12)
C(11)	1120 (1)	2999 (1)	-581 (3)
C(12)	1511 (1)	4790 (1)	-796 (3)
C(13)	1128 (1)	3993 (1)	3014 (3)
C(14)	-490 (1)	3408 (1)	1527 (3)
C(15)	-81 (1)	4057 (1)	-2406 (3)
O(11)	1463 (2)	2383 (2)	-1154 (4)
O(12)	2074 (2)	5191 (2)	-1405 (4)
O(13)	1473 (2)	3917 (2)	4516 (4)
O(14)	-1052 (2)	3040 (2)	2242 (4)
O(15)	-426 (2)	4020 (2)	-3922 (4)
P(1)[a]	0[b]	0[b]	0[b]
C(31)	638 (1)	687 (1)	1576 (3)
C(32)	203 (1)	1235 (1)	2907 (3)
C(33)	679 (1)	1784 (1)	4131 (4)
C(34)	1571 (1)	1779 (1)	4046 (4)
C(35)	2000 (1)	1227 (1)	2743 (3)
C(36)	1532 (1)	679 (1)	1500 (4)
H(321)	-492 (3)	1234 (4)	2985 (9)
H(331)	341 (3)	2213 (3)	5144 (9)
H(341)	1929 (3)	2205 (3)	5007 (9)
H(351)	2690 (3)	1222 (4)	2675 (9)
H(361)	1871 (3)	246 (3)	496 (9)
P(2)[a]	5000[b]	5000[b]	0[b]
C(41)	4612 (1)	4141 (1)	8449 (3)
C(42)	3809 (1)	3771 (1)	8731 (3)
C(43)	3561 (1)	3072 (1)	7548 (4)
C(44)	4115 (1)	2750 (1)	6095 (3)
C(45)	4915 (1)	3137 (1)	5792 (4)
C(46)	5171 (1)	3830 (1)	6952 (3)
H(421)	3372 (3)	4008 (3)	9845 (9)
H(431)	2945 (4)	2774 (4)	7792 (9)
H(441)	3927 (4)	2200 (3)	5213 (9)
H(451)	5338 (4)	2886 (3)	4645 (8)
H(461)	5786 (3)	4128 (3)	6710 (9)

[a] Atom H(1) has an occupancy factor of 0.5, and atoms P(1) and P(2) have occupancies of 0.25. [b] Coordinates fixed by symmetry.

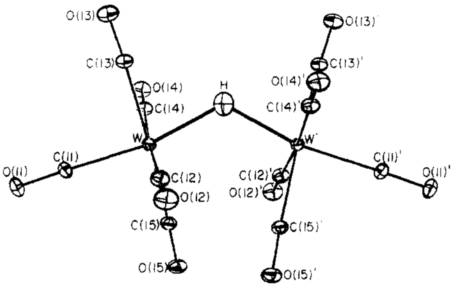

Figure 1. A molecular plot of the $[HW_2(CO)_{10}]^-$ anion in $[Ph_4P]^+[HW_2(CO)_{10}]^-$, based on neutron diffraction data collected at 40 K. A crystallographic twofold axis passes throgh the bridging H atom, bisecting the W-H-W angle. The bridging H atom is again found in a bent position, with W-H = 1.897 (5) Å, W-W = 3.340 (5) Å, and W-H-W = 123.4 (5)°. Because of the C_2 axis, the W-H-W bond in $[Ph_4P]^+[HW_2(CO)_{10}]^-$ is required to be symmetric. The structure is essentially identical with that of the isoelectronic $HW_2(CO)_9(NO)$.[10] As in $HW_2(CO)_9(NO)$, the axial O-C-W vector in $[Ph_4P]^+[HW_2(CO)_{10}]^-$ is not collinear with the bridging H atom but is directed approximately toward the center of the WHW triangle. This is interpreted as evidence that the nature of the overlap in MHM bonds is "closed" (see III in the text).

Description of the Structure

Table III. Geometry of the $[HW_2(CO)_{10}]^-$ Anion[a]

	X-ray (room temp)	neutron (40 K)
W-W′	3.343 (2)	3.340 (5)
W-H		1.897 (5)
W-H-W′		123.4 (5)
H-W′-W		28.3 (5)
W-C(11)	1.98 (2)	1.979 (4)
W-C(12)	1.98 (2)	2.037 (3)
W-C(13)	2.05 (3)	2.044 (4)
W-C(14)	2.05 (2)	2.049 (3)
W-C(15)	2.08 (3)	2.038 (4)
C(11)-O(11)	1.23 (3)	1.160 (3)
C(12)-O(12)	1.18 (3)	1.148 (3)
C(13)-O(13)	1.18 (4)	1.143 (4)
C(14)-O(14)	1.17 (3)	1.147 (3)
C(15)-O(15)	1.09 (3)	1.147 (4)
H-W-C(11)		168.9 (3)
H-W-C(12)		93.9 (2)
H-W-C(13)		79.4 (2)
H-W-C(14)		81.9 (1)
H-W-C(15)		102.9 (2)
W-C(11)-O(11)	176 (2)	178.0 (2)
W-C(12)-O(12)	174 (2)	179.0 (2)
W-C(13)-O(13)	168 (2)	177.0 (2)
W-C(14)-O(14)	173 (2)	178.9 (2)
W-C(15)-O(15)	173 (2)	177.3 (2)
W-W′-C(11)	163.0 (6)°	162.4 (6)
W-W′-C(12)	83.6 (7)	83.4 (7)
W-W′-C(13)	101.5 (8)	106.1 (6)
W-W′-C(14)	93.7 (5)	93.0 (8)
W-W′-C(15)	77.3 (7)	77.4 (6)
C(11)-W-C(12)	90.0 (10)°	90.4 (1)
C(11)-W-C(13)	94.3 (10)	90.4 (1)
C(11)-W-C(14)	92.6 (9)	93.7 (1)
C(11)-W-C(15)	87.0 (9)	87.1 (1)
C(12)-W-C(13)	90.8 (11)	90.3 (1)
C(12)-W-C(14)	177.3 (9)	175.7 (2)
C(12)-W-C(15)	90.2 (10)	91.8 (1)
C(13)-W-C(14)	89.8 (10)	88.3 (1)
C(13)-W-C(15)	178.3 (11)	176.8 (2)
C(14)-W-C(15)	89.2 (8)	89.8 (1)

[a] Bond distances in angstroms and bond angles in degrees.

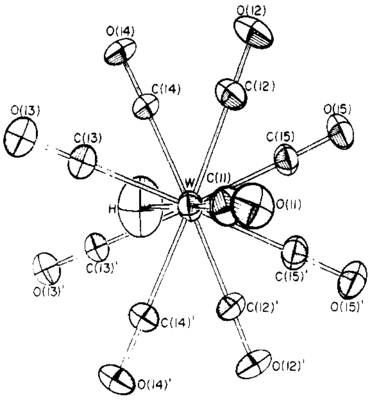

Figure 2. An end-on view of the same anion, showing the 45° staggering of the equatorial carbonyl groups. Note the planarity of the OC(ax)-W-H-W-CO(ax) fragment, which is staggered at 22.5° relative to the equatorial carbonyls.

The $[HW_2(CO)_{10}]^-$ anion (Figures 1 and 2) is situated on a crystallographic twofold (C_2) axis which is perpendicular to the W-W vector, and the $[Ph_4P]^+$ cation is located on a site of $\bar{4}$ (S_4) symmetry. The anion has the familiar bent geometry found in the isoelectronic $HW_2(CO)_9(NO)$[10] and $HW_2(CO)_8(NO)[P(OMe)_3]$[11] and presumed to occur in $[(Ph_3P)_2N]^+[HW_2(CO)_{10}]^-$.[12] The W-H-W angle is 123.4 (5)°, and the W-H and W-W distances are 1.897 (5) and 3.340 (5), respectively. In contrast to $[Et_4N]^+[HW_2(CO)_{10}]^-$,[14] the W-H-W bond in $[Ph_4P]^+$-$[HW_2(CO)_{10}]^-$ is symmetric, probably reflecting the most stable configuration of the $[HW_2(CO)_{10}]^-$ anion in the solid state. The hydride ligand is located on a twofold axis that relates the two $W(CO)_5$ units. As a result of the hydrogen

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(25) See paragraph at the end of paper for details of supplementary material.

Table IV. Summary of Configurations of MHM-Bridged Species Derived from Neutron Diffraction Data on $[HM_2(CO)_{10}]^-$ Ions and Related Complexes

compound	conformatn[a]	M–H, Å	M–H–M, deg	M–M, Å	displacement,[b] Å	ref
$[HCr_2(CO)_{10}]^-[Et_4N]^+$	eclipsed	1.707 (21) 1.737 (19)	158.9 (6)	3.386 (6)	0.3	15
$[HCr_2(CO)_{10}]^-[(Ph_3P)_2N]^+$[c]	eclipsed	1.675	(180?)[c]	3.349 (13)	(0?)[c]	16
$[DCr_2(CO)_{10}]^-[(Ph_3P)_2N]^+$[d]	eclipsed	1.718 (9) 1.729 (11) 1.737 (9) 1.750 (8)	157.6 (7) 153.9 (10)	3.390 (3)	0.3[d]	17
$[HCr_2(CO)_{10}]^-[K(crypt\text{-}222)]^+$	intermediate	1.723 (5) 1.734 (5)	145.2 (3)	3.300 (4)	0.52	30
$[HMo_2(CO)_{10}]^-[(Ph_3P)_2N]^+$[e]	staggered	1.76 (5) 1.93 (5)	136 (3)	3.422 (1)	0.69	31
$[HMo_2(CO)_{10}]^-[K(crypt\text{-}222)]^+$[e]	staggered	1.89 (4) 1.91 (4)	127 (2)	3.406 (1)	0.85	31
$[HMo_2(CO)_9(PPh_3)]^-[Et_4N]^+$[e]	staggered	1.68 (5) 2.19 (6)	127 (3)	3.474 (1)	0.85	32
$[HMo_2(CO)_8(PPh_2Me)_2]^-[Et_4N]^+$[e]	staggered	...	...	3.443 (1) 3.442 (1)	...	33
$[HW_2(CO)_{10}]^-[Et_4N]^+$	eclipsed	1.718 (12) 2.070 (12)	137.0 (10)	3.528 (2)	0.71 (1)	14
$[HW_2(CO)_{10}]^-[Ph_4P]^+$	staggered	1.897 (5)	123.4 (5)	3.340 (5)	0.899 (5)	this work
$[HW_2(CO)_{10}]^-[(Ph_3P)_2N]^+$[e]	staggered	...	...	3.391 (1)	...	12
α-$HW_2(CO)_9(NO)$	staggered	1.875 (4) 1.876 (4)	125.0 (2)	3.328 (3)	0.866 (4)	10
β-$HW_2(CO)_9(NO)$	staggered	1.870 (4)	125.9 (4)	3.330 (3)	0.850 (4)	10
$HW_2(CO)_8(NO)[P(OMe)_3]$	staggered	1.859 (6) 1.894 (6)	129.4 (3)	3.393 (4)	0.803 (6)	11

[a] Conformation of equatorial carbonyl groups. [b] Distance from H atom to center of M–M bond. [c] Although the Cr–H–Cr bond in $[(Ph_3P)_2N]^+[HCr_2(CO)_{10}]^-$ appears to be linear, the large root-mean-square amplitudes of thermal displacement normal to the Cr–Cr vector [0.42 (4) and 0.53 (3) Å] strongly suggest a radially disordered bridging H atom. Thus, it was not possible to differentiate a truly linear bond from a composite of slightly bent structures (see ref 16b). [d] Model with fourfold disordered D atom. [e] Results from X-ray diffraction analysis.

being at a special position, the two W–H bond lengths are necessarily the same [1.897(5) Å]. If any asymmetry (as was observed in $[Et_4N]^+[HW_2(CO)_{10}]^-)$[14] did exist, it would be expected to appear in the thermal parameters of the H atom as an elongation of the ellipsoid toward the metal atoms. Such an elongation was not observed (Figure 1). Moreover, a limited set of data collected at 10 K, the lowest stable temperature that is readily maintained in our apparatus for the prolonged periods of time necessary for data collection,[26] were essentially indistinguishable from those obtained at 40 K, and we therefore conclude that the W–H–W bridge is symmetric down to temperatures as low as 10 K.

In the $[HW_2(CO)_{10}]^-$ anion, the bonding of the axial carbonyl groups is significantly different than that of the equatorial carbonyls (Table III). The axial W–C distance is 1.979 (4) Å while the average equatorial W–C bond length is 2.042 (3) Å. The corresponding C–O distances are 1.160 (3) Å for the axial groups and 1.146 (1) Å for the equatorial carbonyls. This effect demonstrates the influence that the bridging hydride ligand has on the carbonyl trans to it. Carbonyl groups opposite a poor π-acceptor (such as a hydride) do not have to compete with the trans ligand for available metal π-electron density, thus leading to a higher M–C bond order and a shorter M–C bond length. On the other hand, carbonyl groups opposite a good π-acceptor (such as another CO group) are expected to have correspondingly longer M–C distances.[27]

The geometry of the cation is not particularly unusual but is worthy of some mention. $[Ph_4P]^+[HW_2(CO)_{10}]^-$ contains two unique P atoms in each unit cell. The four phenyl rings on each P atom are related to one other by the $\bar{4}$ site symmetry. They appear to be quite normal and are essentially planar.

Discussion

In $[Ph_4P]^+[HW_2(CO)_{10}]^-$, the geometry adopted by the anion is the standard bent/staggered one (with a symmetric W–H–W bond), first discovered in $HW_2(CO)_9(NO)$.[10] This configuration is also believed to occur in $[(Ph_3P)_2N]^+[HW_2(CO)_{10}]^-$,[12] although the H atom was not located in that X-ray study. It is likely that the bent/staggered configuation (Figures 1 and 2) represents the preferred geometry of the $[HW_2(CO)_{10}]^-$ anion in the solid state and that the configuration in $[Et_4N]^+[HW_2(CO)_{10}]^-$[14] is an anomaly created by crystal-packing effects. We have gathered all available structural information on M–H–M systems in Table IV.

The solid-state vibrational spectra of $[HM_2(CO)_{10}]^-$ have been analyzed by various groups: by Kirtley and Kaesz,[28] Harris and Gray,[13] Shriver et al.,[18] and Kettle et al.[29] A comprehensive and detailed analysis of the whole situation is given by Shriver et al.,[18] who independently deduced, from low-temperature Raman data, that the solid-state geometry of the M–H–M linkage in $[HM_2(CO)_{10}]^-$ salts is bent. They recommended the following assignment for the

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(26) The limited quantity of data collected at 10 K (562 reflections) prohibited refining the entire structure with this data set. The atomic coordinates were initially set at their values from the 40 K data set. An overall temperature factor was refined, and then the positional parameters of the atoms in the anion and the anisotropic thermal parameters of the hydride atom were varied. The final agreement factors for the 10 K data are $R(F) = 0.081$, $R(wF) = 0.086$, and $R(F^2) = 0.143$.

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M–H–M bonds in these compounds: ~1700 cm^{-1} for the asymmetric stretch (IR active), ~850 cm^{-1} for the out-of-plane deformation modes (Raman active), and <150 cm^{-1} for the symmetric stretch (Raman active). The first and third assignments are basically in agreement with those of Harris and Gray.[13] The bent configuration provides a partial explanation for the puzzling phenomenon, first noticed by Kirtley,[28] that most $[HW_2(CO)_{10}]^-$ ions seem to exhibit more bands assignable to hydrogen motion than expected on the basis of a linear M–H–M model.

In solution it is generally agreed that all $[HM_2(CO)_{10}]^-$ ions adopt a common geometry of high symmetry: The simple three-band infrared pattern[7] in the carbonyl stretching region may be interpreted on the basis of a structure having a linear *non-hydrogen* skeleton, in which the two $M(CO)_5$ moieties are freely rotating about each other. Whether the M–H–M core itself remains bent in *solution* is not clear. It is our guess that it should be, but there are insufficient vibrational data to settle this point.

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Registry No. $[Ph_4P]^+[HW_2(CO)_{10}]^-$, 97012-34-5.

Supplementary Material Available: Listings of the final atomic positions and thermal parameters from the X-ray analysis (Table A), the geometry of the $[Ph_4P]^+$ cation (Table B), final thermal parameters from the neutron analysis (Table C), and the observed and calculated squared structure factor amplitudes (Table D) from the neutron analysis (7 pages). Ordering information is given on any current masthead page.

Synthesis, Structure, and Redox Properties of $[(\eta\text{-}C_5H_5)Fe\{\mu\text{-}\sigma:\eta^4\text{-}NiC_4R_4(\eta\text{-}C_5H_5)\}]$. A Ferrocene Analogue with a Nickelapentadiene Ring

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The reaction of $[Fe_2(CO)(\mu\text{-}CO)\{\mu\text{-}\sigma:\eta^3\text{-}(CO)C_2RR'\}(\eta\text{-}C_5H_5)_2]$ (R = Ph or H; R′ = Ph) with nickelocene or $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with nickelocene and alkyne gave the brown heterodinuclear $[\eta\text{-}C_5H_5Fe\{\mu\text{-}\sigma:\eta^4\text{-}NiC_4R_2R_2'(\eta\text{-}C_5H_5)\}]$ (R = H, R′ = Ph (**1**); R = R′ = Ph (**2**)), the first examples of compounds with a nickelapentadiene ring. Compound **2**, as a benzene solvate, crystallizes in space group $C2/m$ with $Z = 4$ and lattice constants of $a = 22.153$ (8) Å, $b = 18.850$ (7) Å, $c = 9.816$ (4) Å, and $\beta = 116.06$ (3)°. The structure consists of an iron atom sandwiched between approximately coplanar $\eta\text{-}C_5H_5$ and $\sigma:\eta^4\text{-}NiC_4Ph_4$ rings. The Fe atom is slightly displaced toward the nickel atom of the nickelapentadiene ring with Ni–Fe = 2.419 (2) Å. Compound **2** has a reversible one-electron oxidation at $E_{1/2} = 0.67$ V vs. Ag/AgCl, and green salts of $\mathbf{2}^+$ have been prepared by chemical and electrochemical oxidation. An acid-mediated oxidation by O_2 is described. The ^1H NMR and electronic spectra of **1**, **2**, and $\mathbf{2}^+$ are analyzed, and options for assignments of the near-infrared band in $\mathbf{2}^+$ at 1110 nm are given. Photolysis of $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with PhC_2H gives a differracyclopentadiene, $[Fe_2(CO)(\mu\text{-}C_4Ph_2H_2)(\eta\text{-}C_5H_5)_2]$, a possible intermediate in the above synthesis.

Homonuclear low-valent metal clusters can function as oxidizable or reducible centers depending on the type of peripheral group bound to the metal atoms.[1] In general the redox properties of reducible heteronuclear clusters (where the peripheral group is CO) are less attractive and electron transfer usually results in fragmentation of the cluster;[2] an exception is $(\eta\text{-}C_5H_{5-n}Me_n)CONi_2(\mu_3\text{-}CO)_2(\eta\text{-}C_5H_5)_2$ (n = 1–5).[3] Whether this is true for oxidizable heteronuclear clusters (where the peripheral group is probably cyclopentadienyl) is not known. This paper describes the products obtained in an attempt to prepare heteronuclear analogues of the bis(carbyne) cluster[4] $Co_3(\mu\text{-}CR)_2(\eta\text{-}C_5H_5)_3$ which can be[1] reversibly oxidized to $[Co_3(\mu\text{-}CR)_2(\eta\text{-}C_5H_5)_3]^+$. Key components in the syntheses of heteronuclear bis(carbyne) clusters would be heterometallic μ-alkyne complexes which have labile CO groups—complexes similar to the intermediate $Co_2(\mu\text{-}C_2R_2)(CO)(\eta\text{-}C_5H_5)_2$ in the synthesis of $Co_3(\mu\text{-}CR)_2(\eta\text{-}C_5H_5)_3$[5]—where scission of the μ-alkyne bond in the presence of another $M(CO)_x(\eta\text{-}C_5H_5)_y$ species would give the desired cluster.[6] These heterometallic μ-alkyne complexes could be prepared via a dimetallacyclopentadiene or dimetallacyclopentadienone complex as these complexes

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