Structures of Transition-Metal Hydride Complexes

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One of the more difficult problems for a structural chemist is to properly characterize a transition-metal hydride complex. This is so because of the small X-ray scattering cross section of the H atom, which tends to be "swamped out" by the transition metal to which it is bonded. Since the scattering of X-rays is roughly proportional in amplitude to the number of electrons in an atom, it is clear that this problem becomes worse as the metal becomes heavier and as the number of transition metals bonded to the H atom increases. Consequently, it is difficult to get accurate coordinates of H atoms bonded to heavy atoms, and often it is not possible to find them at all. It is understandable, then, that transition-metal hydride complexes have for a long time been considered a rather mysterious class of compounds in the organometallic literature. The early history of this area is well covered by a number of review articles,[1-3] one of which comprehensively summarizes all structural work carried out up to 1970.[2b]

A number of key structure determinations in the 1960s laid the foundation toward our understanding of the geometry of M–H bonds. A few X-ray investigations[4-6] showed hydrogen to be a stereochemically active ligand occupying a distinct coordination position, and two important neutron diffraction studies[7,8] established that the M–H bond length is on the order of 1.6–1.7 Å. Thus, by the early 1970s, terminal M–H bonds were beginning to be fairly well understood. Many other types of metal–hydrogen bonding, however, such as the bridging (M–H–M) and

triply bridging (HM_3) modes, remained poorly characterized. The present review article is largely concerned with the efforts, of our group and others (particularly the work of Dahl, Williams, Petersen, and co-workers), to gather structural information on hydrogen bridge bonds with neutron diffraction data.

Location of H Atoms Using X-ray Diffraction

Before we begin a discussion of neutron diffraction results, it would be helpful to briefly review the status of X-ray diffraction as applied to metal hydride complexes. Early attempts to locate H atoms with X-ray data were indirect: the "missing" hydrogen positions were deduced by examining the geometry of the rest of the molecule. X-ray analyses of $HPtBr(PEt_3)_2$ and $HMn(CO)_5$ by Owston,[4] Ibers,[5] and their co-workers revealed distorted T-shaped and square-pyramidal geometries, respectively, indicating square-planar and octahedral coordinations with one "vacant" site presumably occupied by a H atom. The first bridging system examined using this approach was the Cr–H–Cr linkage in the salt $[Et_4N]^+[HCr_2(CO)_{10}]^-$.[9] This structure analysis, carried out by Dahl et al., shows the nonhydrogen portion of the anion to have D_{4h} symmetry, with a linear backbone and eclipsed equatorial carbonyl groups (Figure 1). The high symmetry of the anion, taken together with an unusually long Cr–Cr separation (3.41 (1) Å, compared with 2.97 (1) Å in $[Cr_2(CO)_{10}]^{2-}$), led to the reasonable hypothesis that the bridging H atom is nestled midway between the Cr atoms to produce a linear, symmetric Cr–H–Cr bond.[9] We later used much the same argument to postulate a

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(2) (a) J. A. Ibers, *Annu. Rev. Phys. Chem.*, 16, 375 (1965); (b) B. A. Frenz and J. A. Ibers, in "Transition Metal Hydrides", E. L. Muetterties, Ed., Marcel Dekker, Inc., New York, 1971, p 33.
(3) H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, 72, 231 (1972).
(4) P. G. Owston, J. M. Partridge, and J. M. Rowe, *Acta Crystallogr.*, 13, 246 (1960).
(5) S. J. LaPlaca, W. C. Hamilton, and J. A. Ibers, *Inorg. Chem.*, 3, 1491 (1964).
(6) (a) S. J. LaPlaca and J. A. Ibers, *J. Am. Chem. Soc.*, 85, 3501 (1963); (b) S. J. LaPlaca and J. A. Ibers, *Acta Crystallogr.*, 18, 511 (1965).
(7) S. C. Abrahams, A. P. Ginsberg, and K. Knox, *Inorg. Chem.*, 3, 558 (1964).
(8) S. J. LaPlaca, W. C. Hamilton, J. A. Ibers, and A. Davison, *Inorg. Chem.*, 8, 1928 (1969).
(9) (a) L. B. Handy, P. M. Treichel, L. F. Dahl, and R. G. Hayter, *J. Am. Chem. Soc.*, 88, 366 (1966); (b) L. B. Handy, J. K. Ruff, and L. F. Dahl, *ibid.*, 92, 7312 (1970).
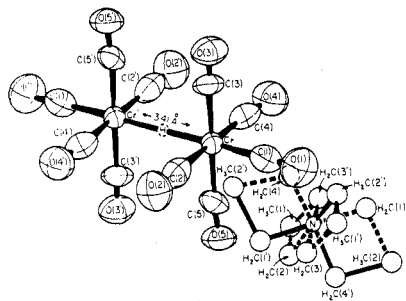
Figure 1. The structure of $[Et_4N]^+[HCr_2(CO)_{10}]^-$ as determined by Dahl and co-workers by X-ray diffraction in 1966.[9] The H position is inferred.

linear Re–H–Re bridge in $HRe_2Mn(CO)_{14}$.[10] Actually, the situation in $[HCr_2(CO)_{10}]^-$ turns out to be much more complicated than originally believed, as will be seen later.

In the last decade, the increased accuracy obtainable with automated diffractometers has in many instances made possible the direct location of H atoms. However, one of the oldest and best-known examples of direct determination of H atom positions occurred in the days of visually estimated X-ray film data: the structure of $HRh(CO)(PPh_3)_3$ as reported by LaPlaca and Ibers.[6] In that structure determination, it was shown that one could enhance H atom peak positions in difference-Fourier maps by eliminating high-angle data. We subsequently applied this technique successfully to $H_3Mn_3(CO)_{12}$[11] and several other compounds. In the case of $H_4Re_4(CO)_{12}$ we introduced a "symmetry averaging" method to show that composite difference-Fourier sections can be used to locate H atoms in molecules of high symmetry, even when individual electron density map sections are hopelessly "noisy".[12]

Currently, investigators are increasingly extending the limits of X-ray diffraction analysis not only to locate, but also to refine, the positions of metal-bonded H atoms. Notable among these are the work of M. R. Churchill on bridged systems such as Rh–H–Rh, W–H–W, Os–H–Os and Ir–H–Ir,[13] and the work of Ibers[14] and Guggenberger[15] on various terminal M–H systems.

Neutron Diffraction

X-ray diffraction has served to establish the stereochemical role of hydride ligands and in some instances to delineate the complete geometries of transition-metal complexes. However, even when direct location of H atoms is possible, their positions are of fairly low precision. Moreover, M–H distances measured by X-ray methods are often 0.1–0.2 Å shorter than their true values, because the hydrogen electron density is somewhat perturbed from the H nucleus toward the M–H σ bond. To improve accuracy it is necessary to turn to neutron diffraction. Although the

techniques and theory of the two scattering experiments are very similar, the pertinent difference (for this discussion) is that H atoms scatter neutrons with about the same efficiency as do most other elements. The two major drawbacks to neutron diffraction are the necessity of using large single crystals (approximately 10 mm^3 in volume) and the lack of numerous facilities, since a nuclear reactor or a high-energy accelerator is required for the neutron source. While neutron diffraction is undoubtedly the best technique for locating H atoms, it is by no means routine.

Terminal M–H Bonds

The first hydride complexes to be investigated by the neutron diffraction technique were compounds containing the terminal M–H linkage. The classic investigations of K_2ReH_9 by Abrahams, Ginsberg, and Knox[7] and $HMn(CO)_5$ by LaPlaca, Hamilton, Ibers, and Davison[8] established unequivocally that the length of a M–H single bond is in the range 1.6–1.7 Å, consistent with what is expected for a normal covalent linkage. These results also settled the long-standing controversy concerning whether a M–H bond is "long" (~ 1.6 Å) or "short" (1.2–1.4 Å).[1-3]

Because of space limitations of this article, we are unable to give a detailed description of all terminally bonded hydride species that have been investigated by neutron diffraction. A listing of these is given in Table I, and a more comprehensive review is in preparation.[16] However, we do wish to mention that among the compounds that have been so characterized are the "bent sandwich" complexes H_2MoCp_2[17] and H_3TaCp_2,[18] the former of which was the subject of some controversy in earlier days regarding the placement of the hydride ligands.[19] Also analyzed recently are the polyhydride complexes $H_4Os(PMe_2Ph)_3$[20] and $H_8Re_2(PEt_2Ph)_4$,[21] the latter of which will be discussed later in connection with M–H–M bridged species. For more details on the structures of polyhydride/phosphine complexes (e.g., compounds of the type H_3IrL_3, H_4OsL_3, H_5ReL_3, H_7ReL_2, etc., where L is a tertiary phosphine), the reader is referred to a recent article in which we have summarized this work.[22]

M–H–M Bridged Systems

The M–H–M bridge bond is particularly interesting to study because it is a member of a select family of bonds: electron-deficient three-center–two-electron bonds, of which the B–H–B bridge bond is perhaps the best-known example. Boron hydrides are difficult to study by neutron diffraction[23] because of the high neutron absorption cross section of ^{10}B, but compounds

(10) (a) H. D. Kaesz, R. Bau, and M. R. Churchill, *J. Am. Chem. Soc.*, **89**, 2775 (1967); (b) M. R. Churchill and R. Bau, *Inorg. Chem.*, **6**, 2086 (1967).

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

(12) R. D. Wilson and R. Bau, *J. Am. Chem. Soc.*, **98**, 4689 (1976).

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(14) Summarized in J. A. Ibers, *Adv. Chem. Ser.*, **No. 167**, 26 (1978).

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(17) A. J. Schultz, K. L. Stearley, J. M. Williams, R. Mink, and G. D. Stucky, *Inorg. Chem.*, **16**, 3303 (1977).

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(20) D. W. Hart, R. Bau, and T. F. Koetzle, *J. Am. Chem. Soc.*, **99**, 7557 (1977).

(21) R. Bau, W. E. Carroll, R. G. Teller, and T. F. Koetzle, *J. Am. Chem. Soc.*, **99**, 3872 (1977).

(22) R. Bau, W. E. Carroll, D. W. Hart, R. G. Teller, and T. F. Koetzle, *Adv. Chem. Ser.*, **No. 167**, 73 (1978).

(23) An exception is the neutron diffraction analysis of $B_{10}H_{14}$, which was carried out on a ^{11}B-enriched sample: A. Tippe and W. C. Hamilton, *Inorg. Chem.*, **8**, 464 (1969).

Table I
Compilation of M-H Bond Lengths Determined by Single-Crystal Neutron Diffraction

compound	M	M-H, Å	M-H-M, deg	M-M, Å	ref
A. Terminal (M-H) Bonds					
$HMn(CO)_5$	Mn	1.601 (16)	–	–	8
$[HZnN(Me)C_2H_4NMe_2]_2$	Zn	1.60	–	–	49
H_2MoCp_2	Mo	1.685 (3)	–	–	17
H_3TaCp_2	Ta	1.774 (3)^a	–	–	18
$[H_9Re]K_2$	Re	1.68 (1)^a	–	–	7
$H_8Re_2(PEt_2Ph)_4$	Re	1.669 (7)^a	–	–	21
$H_4Os(PMe_2Ph)_3$	Os	1.659 (3)^a	–	–	20
$H_4Th_2(C_5Me_5)_4$	Th	2.03 (1)^a	–	–	51
B. Bridging (M-H-M) Bonds					
$[HCr_2(CO)_{10}]^-[Et_4N]^+$	Cr	1.737 (19)	158.9 (6)	3.386 (6)	31
		1.707 (21)			
$[HCr_2(CO)_{10}]^-[(Ph_3P)_2N]^+$	Cr	1.675	(180?)^b	3.349 (13)	32
$HMo_2(C_5H_5)_2(CO)_4(PMe_2)$	Mo	1.851 (4)	122.9 (2)	3.267 (2)	52
		1.869 (4)			
$HRu_3(CO)_9(C{\equiv}CCMe_3)$	Ru	1.789 (5)	102.3 (2)	2.792 (3)	53
		1.796 (5)			
α-$HW_2(CO)_9(NO)$	W	1.875 (4)	125.0 (2)	3.328 (3)	25
		1.876 (4)			
β-$HW_2(CO)_9(NO)$	W	1.870 (4)	125.9 (4)	3.330 (3)	25
$HW_2(CO)_8(NO)(P(OMe)_3)$	W	1.859 (6)	129.4 (3)	3.393 (4)	29
		1.894 (6)			
$[HW_2(CO)_{10}]^-[Et_4N]^+$	W	1.718 (12)	137.1 (10)	3.528 (2)	33
		2.070 (12)			
$[HW_2(CO)_{10}]^-[Ph_4P]^+$	W	1.897 (5)	123.4 (5)	3.340 (5)	33
$H_2Os_3(CO)_{10}$	Os	1.850 (5)^a	92.9 (2)^a	2.680 (2)	54
$H_2Os_3(CO)_{10}$	Os	1.845 (3)^a	94 (1)^a	2.683 (1)	55
$HOs_3(CO)_{10}(C_2H_3)$	Os	1.813 (4)^c	101.6 (2)^c	2.845 (2)^c	54, 56
		1.857 (4)^c			
$H_2Os_3(CO)_{10}(CH_2)$	Os	1.808 (10)^d	111.7 (5)^d	2.824 (3)^d	57
		1.834 (11)^d			
		1.754 (8)	114.1 (5)	3.053 (3)	
		1.883 (9)			
$HDOs_3(CO)_{10}(CHD)$	Os	1.7 (1)	112	3.066 (6)	58
		2.0 (1)			
$H_2Os_3(CO)_9S$	Os	1.819 (3)^a	106.5 (1)^a	2.915 (1)^a	59
$H_8Re_2(PEt_2Ph)_4$	Re	1.878 (7)^a	85.0 (3)^a	2.538 (4)	21
$[H_3Ir_2(C_5Me_5)_2]^+BF_4^-$	Ir	1.75 (1)^a	89.5 (8)^a	2.458 (6)	22
$H_4Th_2(C_5Me_5)_4$	Th	2.29 (3)^a	122 (4)^a	4.007 (8)	51

	M	M-H, Å	M-H-B, deg	M-B, Å	ref
C. M-H-B Bonds					
$U(BH_4)_4$	U	2.34 (1)^e	83 (1)^e	2.52 (1)^e	50
		2.40 (3)^f	98 (1)^f	2.86 (2)^f	
$Hf(BH_4)_4$	Hf	2.06 (2)	83 (1)	2.25 (3)	60
$Hf(C_5H_4Me)_2(BH_4)_2$	Hf	2.09 (3)^a	96.8 (5)^a	2.553 (6)	61

	M	M-H, Å	M-H-C, deg	M-C, Å	C-H, Å	ref
D. M-H-C Interactions						
${Fe[P(OMe)_3]_3(C_8H_{13})}^+[BF_4]^-$	Fe	1.879 (9)	100.6 (6)	2.368 (10)	1.137 (10)	62
$[Ta({\equiv}CHCMe_3)(PMe_3)Cl_3]_2$	Ta	2.119 (4)	63.1 (2)	1.898 (2)	1.131 (3)	63

|	M	M-H, Å	M-H-M, deg	M-M, Å	H-M$_3$, Å^g	ref
E. Triply bridging (M$_3$H) Bonds						
$HFeCo_3(CO)_9(P(OMe)_3)_3$	Co	1.734 (4)^a	91.8 (2)^a	2.489 (7)^a	0.978 (3)^a	37
$H_3Ni_4Cp_4$	Ni	1.691 (8)^a	93.9 (3)^a	2.469 (6)^a	0.907 (6)^a	38
F. "Interstitial" Hydrides						
$[HCo_6(CO)_{15}]^-[(Ph_3P)_2N]^+$	Co	1.824 (13)^a	90.0 (6)^a	2.579 (15)^a	1.054 (14)^a	44
$[H_2Ni_{12}(CO)_{21}]^{2-}[(Ph_3P)_2N]^+_2$	Ni	1.84^h	92.5^h	2.659^h	1.04^h	48
		(2.00)^i	(75.1)^i	(2.439)^i	(1.40)^i	
$[H_2Ni_{12}(CO)_{21}]^{2-}[(Ph_3P)_2N]^+_3$	Ni	1.72^h	102.5^h	2.682^h	0.73^h	48
		(2.22)^i	(66.2)^i	(2.425)^i	(1.69)^i	

^{a} Average values. ^{b} Although at 22 °C the Cr-H-Cr bond in $[(Ph_3P)_2N]^+[HCr_2(CO)_{10}]^-$ appears 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 the possibility of a fourfold or radially disordered bridging H atom.^{32a,b} In a very recent study of $[(Ph_3P)_2N]^+[DCr_2(CO)_{10}]^-$ at 17 K,^{32c} a fourfold disordered model was refined, leading to Cr-D-Cr angles of approximately 155°, although it was not possible to resolve the disordered D atom positions in a difference-Fourier map. ^{c} Joint X-ray/neutron refinement. ^{d} Distances and angles associated with a methylene-bridged metal-metal bond $[Os(\mu\text{-}H)(\mu\text{-}CH_2)Os]$. ^{e} Distances and angles associated with terminal BH_4 groups [i.e., $M(\mu\text{-}H)_3BH$]. ^{f} Distances and angles associated with bridging BH_4 groups [i.e., $M(\mu\text{-}H)_2B$-$(\mu\text{-}H)_2M'$]. ^{g} Displacement of the H atom from a triangular M_3 face. ^{h} Distances and angles associated with Ni atoms 5, 7, 9 (see Figure 11). ^{i} Distances and angles associated with Ni atoms 1, 2, 3 or 10, 11, 12 (see Figure 11).

with M–H–M bonds generally pose no special difficulties as far as neutron scattering is concerned. Moreover, the characteristic octahedral coordination of many metal complexes serves as a convenient internal coordinate system to pinpoint the direction of the orbital used by the metal atom to achieve M–H–M overlap, as will be evident in the following discussion.

The classic M–H–M bridged system is the [H-$Cr_2(CO)_{10}$]$^-$ anion,[9] with a D_{4h} structure (linear, eclipsed) which has been described above (Figure 1). The other members of the series, [HMo$_2$(CO)$_{10}$]$^-$ and [HW$_2$-(CO)$_{10}$]$^-$, have been widely assumed to have similar geometries. We were interested to see what effect the isoelectronic replacement of a (CO)$^-$ group by a neutral NO group would have on the geometry of [HW$_2$(CO)$_{10}$]$^-$, and so in 1973 we investigated the structure of HW$_2$(CO)$_9$(NO) using X-ray techniques.[24] Surprisingly, the overall structure of the molecule turned out to be bent, rather than linear, with the carbonyl groups staggered instead of eclipsed. From the bending angle of the main axis, assuming the "invisible" H atom to lie at the intersection of the two axial ligand–metal vectors (I), we predicted a W–H–W angle of 159°.

I: predicted WHW
angle = 159°

II: observed WHW
angle = 125°
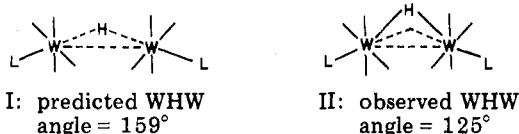
However, from the subsequent neutron diffraction experiment,[25] we found that the H atom was not at the predicted position (Figure 2). The axial ligand–metal vectors point, not at the bridging H atom (I), but at the center of the WHW triangle (II). This unexpected result strongly suggests that the nature of M–H–M overlap is such that all three orbitals come together in a common region of space (III). In other words, we


III   IV   V   VI
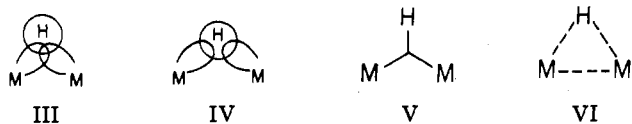
think that our result provides experimental evidence that there is a substantial amount of metal–metal overlap in a M–H–M bridge bond. If M–M overlap were unimportant (as in IV), then structure I would have been expected. In analogy with the terminology used in the boron hydride literature, we suggested symbolism V (a "closed" MHM bond[26]) to represent III.

(24) M. A. Andrews, D. L. Tipton, S. W. Kirtley, and R. Bau, *J. Chem. Soc., Chem. Commun.*, 181 (1973).
(25) J. P. Olsen, T. F. Koetzle, S. W. Kirtley, M. A. Andrews, D. L. Tipton, and R. Bau, *J. Am. Chem. Soc.*, 96, 6621 (1974).
(26) The use of the words "closed" and "open" to describe structures III and IV, respectively, is not completely analogous to the usage of these terms in boron hydride chemistry, as can be seen in the following sketches:

closed   open   "closed"   "open"
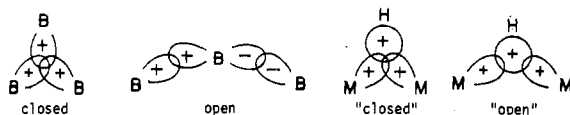
For M–H–M bonds, the difference between the terms "closed" and "open" is somewhat qualitative: in both cases all three orbitals should have the same sign of the wavefunction, and in both there would be expected to be a nonzero amount of M–M bonding. The difference is mainly a matter of degree: in a "closed" M–H–M bond there should be substantial M–M bonding and one predominant region of overlap, while an "open" M–H–M bond would imply very little M–M bonding and two predominant regions of overlap.
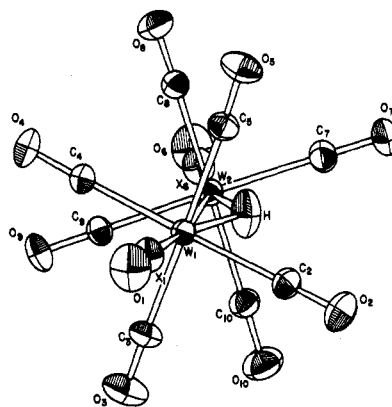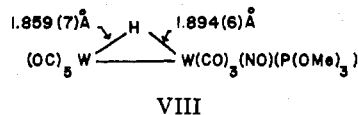

Figure 2. The structure of HW$_2$(CO)$_9$(NO) as determined by neutron diffraction (ref 25). Note that the axial ligand–metal vectors do not point at the bridging H atom, but rather at the center of the W–H–W triangle.

An alternative, equivalent designation VI has been suggested by Churchill.[27] In contrast, for a halide bridge (a situation corresponding to two localized M–X σ bonds), the bridging atom *is* collinear with the axial ligands (as in [Cr$_2$(CO)$_{10}$I]$^-$).[28]

Originally, we had hoped to find an asymmetric M–H–M bond in HW$_2$(CO)$_9$(NO), a reasonable expectation since the two halves of the molecule, W(CO)$_5$ and W(CO)$_4$(NO), have different electronic requirements. However, a 50%–50% packing disorder involving the axial NO and CO groups generated the appearance of a symmetric W–H–W bond (VII):

VII
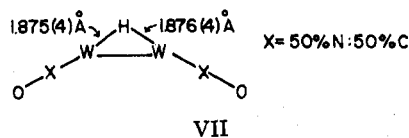
In order to circumvent this problem, we carried out a reaction in which an equatorial carbonyl group was replaced by a trimethyl phosphite molecule. The bulky nature of the phosphite ligand prevents disorder from taking place, and the resulting structure, as found by neutron diffraction,[29] does show some asymmetry in the WHW core (VIII). The extent of asymmetry, however, is very small.


VIII

After completion of the structure determinations of HW$_2$(CO)$_9$(NO) and HW$_2$(CO)$_8$(NO)(P(OMe)$_3$), attention shifted to their precursor, the [HW$_2$(CO)$_{10}$]$^-$ ion. Would it adopt the bent/staggered arrangement of the isoelectronic HW$_2$(CO)$_9$(NO) (Figure 2) or the linear/eclipsed configuration of the analogous [HCr$_2$(CO)$_{10}$]$^-$ (Figure 1), as had been assumed all along? The answer is that it can assume both geometries. In two X-ray structure determinations that revealed the nonhydrogen skeletons of the anions,[30] we showed that in the salt

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(29) R. A. Love, H. B. Chin, T. F. Koetzle, S. W. Kirtley, B. R. Whittlesey, and R. Bau, *J. Am. Chem. Soc.*, 98, 4491 (1976).
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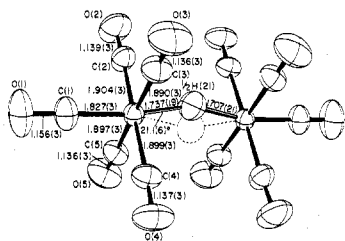
Figure 3. The structure of the $[HCr_2(CO)_{10}]^-$ anion in $[Et_4N]^+[HCr_2(CO)_{10}]^-$, based on neutron diffraction data measured at room temperature by Dahl, Petersen, Williams, and co-workers.[31] A crystallographic center of inversion is situated between the Cr atoms. In contrast to an earlier conclusion (Figure 1), the H atom is seen to be off-axis (0.3 Å from the center of the Cr–Cr bond), giving rise to a bent Cr–H–Cr linkage [158.9 (6)°].

$[(Ph_3P)_2N]^+[HW_2(CO)_{10}]^-$ the anion adopts a bent/staggered geometry, while in $[Et_4N]^+[HW_2(CO)_{10}]^-$ the $M_2(CO)_{10}$ skeleton is, as in $[Et_4N]^+[HCr_2(CO)_{10}]^-$, eclipsed and ostensibly linear. This difference was subsequently confirmed by neutron diffraction analyses of $[Ph_4P]^+[HW_2(CO)_{10}]^-$ and $[Et_4N]^+[HW_2(CO)_{10}]^-$ (vide infra).

During the past 2 years the true picture of the structure of the $[HM_2(CO)_{10}]^-$ ions has begun to emerge, and it is turning out to be more complicated than originally thought. Recently, Dahl, Williams, and their colleagues have reinvestigated the structure of $[Et_4N]^+[HCr_2(CO)_{10}]^-$, this time with neutrons.[31] They found that, contrary to earlier assumptions, the bridging H atom is in an off-axis position, situated about 0.3 Å from the center of the Cr–Cr bond (Figure 3). Because of the presence of a crystallographic center of inversion in the middle of the anion, what is actually observed is a disordered superposition of two bent Cr–H–Cr bonds [158.9 (6)°] in a 1:1 ratio. A later study of $[(Ph_3)_2N]^+[HCr_2(CO)_{10}]^-$ by the same group[32] also suggests a bent Cr–H–Cr bond. Although in this case the disorder of the bridging H atom could not be resolved, the unusual disk-shaped appearance of the hydrogen thermal ellipsoid suggests that it, too, is off-axis, probably in a fourfold or radially disordered fashion.

We have recently completed the neutron diffraction analysis, at very low temperature (14 K), of $[Et_4N]^+[HW_2(CO)_{10}]^-$.[33] The off-axis location of the bridging H atom is confirmed, and the carbonyl groups are also seen to be disordered (Figure 4). The H atom is displaced further from the M–M axis [0.71 (1) Å] than in $[Et_4N]^+[HCr_2(CO)_{10}]^-$, and its disposition is found to be, surprisingly, quite asymmetric [W–H distances are 1.718 (12) and 2.070 (12) Å]. In fact, the asymmetry of the W–H–W bond in $[Et_4N]^+[HW_2(CO)_{10}]^-$ is so pronounced that the anion can be crudely viewed as a donor–acceptor complex, in which the electrons of the W–H bond of $[HW(CO)_5]^-$ (an 18-electron species) are donated to the empty orbital of an electron-deficient $W(CO)_5$ moiety. Due to the low temperature at which the experiment was carried out, four of the ten sets of disordered carbonyl groups in $[Et_4N]^+[HW_2(CO)_{10}]^-$
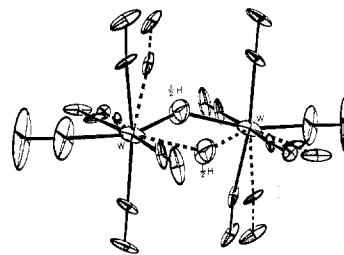
Figure 4. The disordered structure of the $[HW_2(CO)_{10}]^-$ anion in $[Et_4N]^+[HW_2(CO)_{10}]^-$, based on neutron diffraction data measured at a temperature of 14 K.[33] The H atom is situated in a very asymmetric position [W–H = 1.72 (1), 2.07 (1) Å]. Note that the carbonyl groups are also disordered.
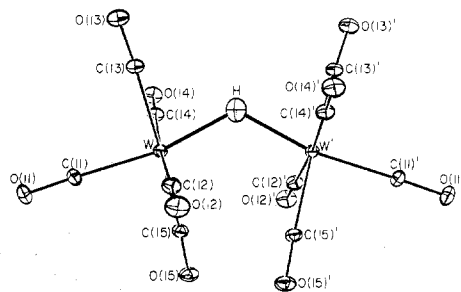
Figure 5. The ordered structure of the $[HW_2(CO)_{10}]^-$ anion in $[Ph_4P]^+[HW_2(CO)_{10}]^-$ (ref 33), which is markedly different from that in $[Et_4N]^+[HW_2(CO)_{10}]^-$ (Figure 4). The structure shown strongly resembles that of the isoelectronic $HW_2(CO)_9(NO)$ (Figure 2) and probably represents the most stable configuration of the $[HW_2(CO)_{10}]^-$ anion in the solid state.

have been resolved completely, while the other six, though not resolved, have unusually elongated ellipsoids consistent with the presence of packing disorder. Thus, what at room temperature appears to be a linear, eclipsed $[HW_2(CO)_{10}]^-$ ion, at low temperature turns out to be a disordered superposition of two bent, approximately eclipsed anions (Figure 4). In contrast, the structure of $[Ph_4P]^+[HW_2(CO)_{10}]^-$ (Figure 5) is not disordered,[33] and the anion in this latter salt is almost identical in geometry with that of $HW_2(CO)_9(NO)$. The results of low-temperature Raman studies on the $[HM_2(CO)_{10}]^-$ anions by Shriver and co-workers are also completely consistent with the bent M–H–M model.[34]

The evidence accumulated thus far strongly suggests that the M–H–M bond is inherently bent, at least for transition metals. A qualitative molecular orbital argument can be put forward regarding this point. Figure 6 compares the linear $[F–H–F]^-$ bond (3c, 4e⁻) with the bent M–H–M bond (3c, 2e⁻). If one accepts the fact that there is significant M–M overlap in an M–H–M bond, one can appreciate that the mid-energy orbital, which is nonbonding (β) in the $[F–H–F]^-$ case, is antibonding (β') in the M–H–M case. One can then argue that the M–H–M system would prefer to remain bent, and not place an additional two electrons into this energetically unfavorable (β') orbital. If forced to do so, the M–H–M system would revert into a linear (3c, 4e⁻) configuration which is most likely unstable with respect to dissociation into (M–H + M) fragments. The crux of the argument is that, as long as there is significant M–M overlap, the 2e⁻ bond will bend, allowing closer M–M approach. It has been pointed out to us[35]

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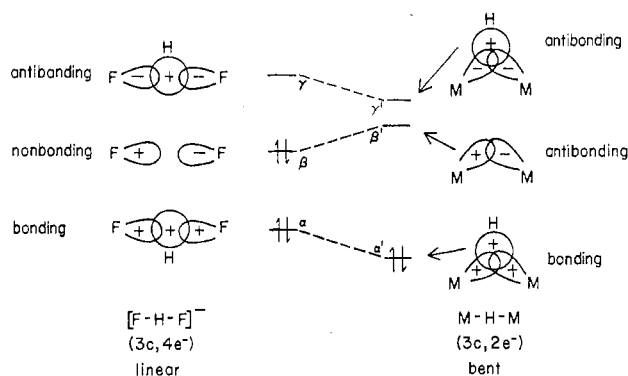
Figure 6. A schematic comparison between the orbitals of linear (3c, 4e⁻) and bent (3c, 2e⁻) X–H–X systems.

Figure 7. The $H_8Re_2P_4$ core of the $H_8Re_2(PEt_2Ph)_4$ molecule, as determined by neutron diffraction, showing the unprecedented feature of a metal–metal bond bridged by four H atoms.[21]

that the situation represented by Figure 6 is not unlike the H_3 system, which in the two-electron case (H_3^+) is calculated to exist as a stable equilateral triangle, but in the four-electron case (H_3^-) is not bound with respect to ($H_2 + H^-$). The H_3^- system, although unstable, prefers a linear geometry to a bent one, for all interatomic distances.

The structure of one other M–H–M bridged compound is worthy of comment. Mild pyrolysis of $H_7Re(PEt_2Ph)_2$ yields $H_8Re_2(PEt_2Ph)_4$, a rare example of a dimeric hydride/phosphine complex. Originally synthesized by Coffey and Chatt in 1969,[36] the exact nature of this dimer was unknown until our recent neutron diffraction analysis.[21] In this molecule is found the first example of a metal–metal bond bridged by four H atoms (Figure 7). The core of the molecule consists of a planar, ethylene-like Re_2P_4 skeleton surrounded by four terminal and four bridging hydride ligands at average Re–H distances of 1.669 (7) and 1.878 (7) Å respectively. The bridging H atoms are arranged in a rectangle around the M–M bond, with H⋯H distances of 1.870 (8) and 2.042 (8) Å. From this structure determination, the difference between bridging and terminal M–H bonds (0.21 Å) can be accurately compared within the same molecule for the first time. The existence of the M(μ-H)$_4$M linkage in $H_8Re_2(PEt_2Ph)_4$ raises the interesting question of whether a molecule having a M–M bond bridged by a quintet of H atoms can be synthesized.

Triply Bridging Hydride Systems [(μ_3-H)M$_3$ Bonds]

An H atom covalently bound to three other atoms simultaneously is rarely found. To our knowledge, in molecular species this type of linkage has been definitively characterized only in metal cluster complexes. The structures of two tetrahedral clusters, $HFeCo_3$-$(CO)_9(P(OMe)_3)_3$ and $H_3Ni_4Cp_4$, have been studied by our group.[37,38] The iron–cobalt cluster complex, first synthesized by Chini and co-workers,[39] had been the subject of considerable debate over the placement of the hydride ligand. Originally thought to be inside the
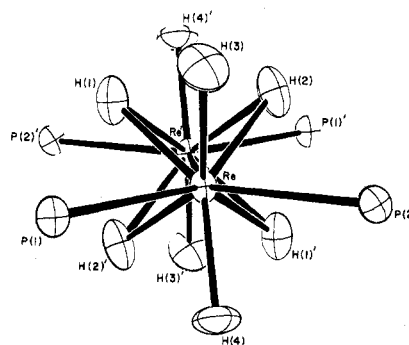
metal "cage",[40] a low-temperature X-ray analysis definitively located it outside the cluster, capping the Co_3 face.[41] In order to gain more accurate coordinates for the H atom, we undertook the neutron diffraction analysis of this compound (Figure 8).[37] The triply bridging location of the H atom is confirmed, at a position displaced 0.978 (3) Å from the Co_3 face. Average M–H and M–H–M values are 1.734 (4) Å and 91.8 (2)°, respectively.

An X-ray investigation of $H_3Ni_4Cp_4$ was conducted by Müller, Huttner, and co-workers in 1973.[42] Although the H atoms were not located directly, the authors were able to assign them to face-bridging positions, based on the observation that three of the cyclopentadienyl rings seemed to be tilted away from the fourth. Curiously enough, no distortion of the Ni_4 cluster itself was observed. A neutron diffraction analysis confirms this picture,[38] and reveals a H_3Ni_4 core which resembles a cube with a missing corner (Figure 9). The average Ni–H distance is 1.691 (8) Å, and the H atoms are displaced 0.907 (6) Å from the faces of the tetrahedron.

It has occurred to us that the arrangement of H atoms in a metal cluster complex might serve as a good model for studying the structure of chemisorbed hydrogen. In both $HFeCo_3(CO)_9(P(OMe)_3)_3$ and $H_3Ni_4Cp_4$ we found that the M–M distances associated with the H-capped faces are very similar to those in the metals themselves. Thus, one can postulate that the dimensions of the (μ_3-H)Co_3 and (μ_3-H)Ni_3 fragments of these covalent molecules might be good representations of H atoms attached to a surface consisting of a triangular array of metal atoms (such as the {111} surface of a cubic close-packed metal or the {001} face of a hexagonal close-packed metal). In an analysis of the metal orbitals associated with the {111} faces of cubic metals, Bond[43] pointed out that there are no metallic orbitals oriented normal to the surface. Rather, the orbitals are directed at points situated over the M_3 triangles and are inclined to the surface at angles of 30 and 36.3°. Interestingly, in $HFeCo_3(CO)_9(P(OMe)_3)_3$ and $H_3Ni_4Cp_4$ the corresponding angles associated with the triply bridging H atoms are 34.3 and 32.2°, respectively.[37,38]

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(43) G. C. Bond, *Discuss. Faraday Soc.*, 200 (1966).
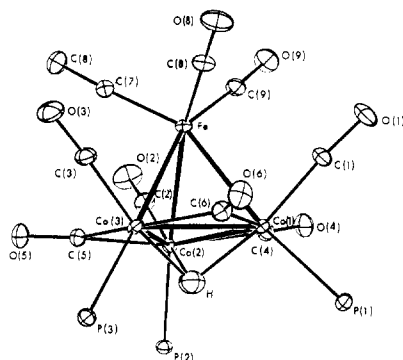
Figure 8. The molecular structure of HFeCo$_3$(CO)$_9$(P(OMe)$_3$)$_3$, with methoxy groups removed for clarity.[37]
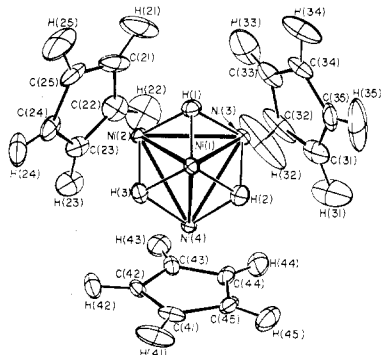
**Figure 9.** The molecular structural of H$_3$Ni$_4$Cp$_4$,[38] with one of the cyclopentadienyl rings removed for clarity.

"Interstitial" H Atoms

We have very recently completed the neutron diffraction analysis of the interesting complex [(Ph$_3$P)$_2$N]$^+$[HCo$_6$(CO)$_{15}$]$^-$,[44] which was kindly provided to us by Paolo Chini of the University of Milan. We were attracted to this anion because of its unusual ^{1}H NMR chemical shift (τ –13.2 ppm),[45] which suggested that the H atom might be attached to the CO ligands either as part of a formyl group or perhaps even oxygen bonded. An X-ray analysis of this salt carried out at 177 K revealed that one of the Co–Co distances in the Co$_6$ octahedron [2.662 (2) Å] is significantly longer than the others [average 2.550 (2) Å], and that the carbonyl groups surrounding the long bond seemed to be "splayed out" from that bond, suggesting that the H atom in [HCo$_6$(CO)$_{15}$]$^-$ is edge-bridging. A subsequent low-temperature (80 K) neutron diffraction analysis, however, revealed the unexpected result shown in Figure 10: the H atom is right in the middle of the cluster! The six-coordinate H atom (an example of an "interstitial"[45] hydride ligand) is situated within one standard deviation of the geometric center of the octahedron, resulting in an average Co–H distance of 1.824 (13) Å. The reason for the unusual τ value of –13.2 ppm for this H atom is not yet clear: whether it remains in the cluster, or comes out onto the carbonyl ligands in solution, is still being investigated. It is worth pointing out that [HRu$_6$(CO)$_{18}$]$^-$, in which X-ray evidence strongly suggests an "interstitial" H atom, also has an anomalously low-field NMR signal (τ –6.4).[46]

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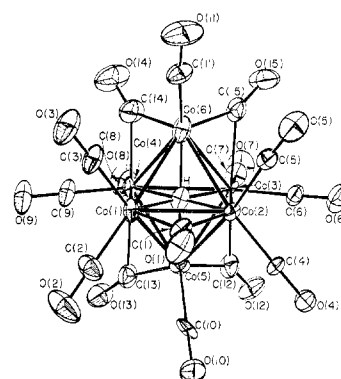
Figure 10. The [HCo$_6$(CO)$_{15}$]$^-$ anion in [(Ph$_3$P)$_2$N]$^+$[HCo$_6$-(CO)$_{15}$]$^-$.[44] Within experimental error, the H atom is situated at the center of the metal octahedron.
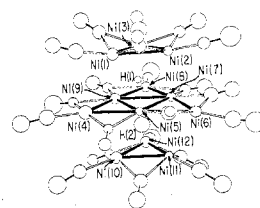
Figure 11. The structure of the [H$_2$Ni$_{12}$(CO)$_{21}$]$^{2-}$ ion, showing the two interstitial H atoms in octahedral cavities. The H atoms are slightly displaced toward the central Ni(5,7,9) triangle of the cluster.[48]

The structure determination of [HCo$_6$(CO)$_{15}$]$^-$ represents the first time that an "interstitial" H atom in a hexanuclear metal cluster has been accurately characterized by single-crystal neutron diffraction techniques. Earlier, powder neutron diffraction work by Simon had shown the existence of this type of structure in polymeric HNb$_6$I$_{11}$.[47] More recently, single-crystal neutron diffraction studies by Chini, Dahl, Williams, and their colleagues[48] on the [HNi$_{12}$(CO)$_{21}$]$^{3-}$ and [H$_2$Ni$_{12}$(CO)$_{21}$]$^{2-}$ anions (Figure 11) have definitively shown the existence of H atoms inside the octahedral holes of these Ni$_{12}$ clusters. In contrast to the exact centering of the H atom in [HCo$_6$(CO)$_{15}$]$^-$, the H atoms in [HNi$_{12}$(CO)$_{21}$]$^{3-}$ and [H$_2$Ni$_{12}$(CO)$_{21}$]$^{2-}$ were found to be displaced toward the face of the octahedral holes formed by the central layer of metal atoms. In a sense, then, the H atoms in the Ni$_{12}$ clusters can be considered somewhat triply bridging, capping a face of an octahedron from within. The H-capped face, moreover, is found to be slightly expanded relative to the others, and the average dimension of the octahedral hole is expanded by about 2–3% when the H atom is inserted.[48] So it is seen that there is more than enough room within a M$_6$ octahedron to accommodate a H atom, with sufficient clearance for the hydrogen to "rattle around" in its metal cage. A tetrahedral metal cluster has of course much less room in its interior, and it is not clear at this point if a H atom could be accommodated within such a cluster without causing appreciable "swelling" of the M$_4$ framework. A large metal cluster ($\geq$12 atoms), however, might provide the necessary stability for this arrangement, and thus the existence of 4-coordinate or 5-coordinate H atoms in such clusters is an intriguing possibility.

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Summary

When we began our neutron diffraction work in early 1974, only four metal hydride complexes had been investigated by this technique.[7,8,49,50] Four years later,

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through the efforts of several different groups, the situation has changed dramatically: there are now over two dozen metal hydride complexes whose structures have been accurately analyzed by single-crystal neutron diffraction, as summarized in Table I. It seems clear that neutron diffraction will continue to be extensively used to analyze such compounds. At the rate new results are appearing, it may not take long before most of the major types of metal–hydrogen linkages are explored.

Coordination Chemistry and Microbial Iron Transport

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Iron is an essential element for all living things.[1-3] This is a consequence of the extremely large number of enzymes and proteins in which iron plays an essential part. The ubiquitous role of metal ions in biochemistry has in fact generated the whole area of "bioinorganic chemistry", which has been almost synonymous with studies of how metal ions interact with biological molecules. Our interest has been from another perspective—how the biological systems acquire the metal ion for incorporation into macromolecules.

Kenneth N. Raymond was born in Astoria, Oregon, in 1942. He completed his B.A. degree at Reed College and his Ph.D. at Northwestern University and joined the faculty at the University of California, Berkeley, in 1968. His research interests are in coordination chemistry and include microbial iron metabolism, specific sequestering agents for toxic metal ions, and the structure and bonding of transition-metal and organometallic complexes.

Carl Carrano was born in New York, in 1950. He received his B.S. degree from the University of California, Santa Barbara, and his Ph.D. from Texas A&M University while working with Minoru Tsutsui. He is at present a postdoctoral fellow in the laboratory of Professor Raymond, and will be joining the faculty at the University of Vermont in the Fall.

Specifically, we have been concerned with the coordination chemistry of low-molecular-weight chelating agents called siderophores: molecules which are manufactured by microbes to obtain the iron they need to grow.[4]

Since the evolution of an oxidizing atmosphere on this planet, the availability of iron to aerobic organisms in an aqueous environment has been limited by the extreme insolubility of ferric hydroxide ($K_{sp} \approx 10^{-38}$).[5] With the equilibrium concentration of ferric ion at pH 7 about 10^{-18} M, even diffusion limited transport would

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