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Mössbauer and X-Ray Diffraction Studies on $HFe_3(CO)_9(SR)$ (R = i-C_3H_7 and t-C_4H_9). Example of Noncorrelation of M–M Distance with M–H–M Bonding

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The structure of $HFe_3(CO)_9(SR)$ (R = i-C_3H_7 or t-C_4H_9) has been solved by a combination of Mössbauer spectroscopy and single-crystal X-ray diffraction studies. The Mössbauer spectra of the two compounds contain two quadrupole-split doublets of relative intensity 2:1 consistent with the equivalence of two of the three iron atoms. The diffraction study on $HFe_3(CO)_9(S$-i-$C_3H_7)$ revealed a structure in which the iron atoms occupy the vertices of a near-equilateral triangle. The sulfido group bridges all three iron atoms with the symmetry of the $Fe_3(CO)_9S$ fragment being essentially C_{3v}. The hydrogen atom has been located using a special set of low-angle data. It is situated on the opposite side of the triiron plane to the sulfur and symmetrically bridges two of the iron atoms in such a way that it lies essentially on the plane defined by these two irons and the sulfur atom. The bonding influence of the triply bridging SR group causes the equilateral symmetry of the iron triangle to be virtually unaltered by the presence of the M–H–M bridge.

Introduction

A wide range of di-, tri-, and polynuclear transition metal hydride complexes in which a hydrido group bridges two metal atoms is now known.[3,4] In most cases the position of the hydrogen atom has been inferred, either from spectroscopic evidence or more commonly from crystallographic data. Although recent X-ray diffraction studies have succeeded in locating the positions of bridging hydrogens in several compounds,[5–11] success is not always guaranteed when this is attempted, especially when the heavier transition metals are involved. Neutron diffraction, of course, provides more reliable hydrogen positions[12–14] but this technique is not routinely accessible. In cases where hydrogen positions are not directly observed from an X-ray analysis, one frequently has to resort to indirect methods, such as inferring hydrogen atom locations from molecular distortions in the rest of the molecule. One commonly used approach is to attribute unusually long metal–metal distances to the presence of M–H–M bridges. This was done in the structure determinations of $[HCr_2(CO)_{10}]^-$,[15] $HCrRe(CO)_{10}$,[16] $HRe_2Mn(CO)_{14}$,[17,18] $HRe_3(CO)_{14}$,[19] $[H_2Re_3(CO)_{12}]^-$,[20] $[HRe_3(CO)_{12}]^{2-}$,[21] $[H_6Re_4(CO)_{12}]^{2-}$,[22] and many other compounds. Essentially the same argument was used to justify the assignment of triply bridging hydrogens in $H_6Cu_6(PPh_3)_6$[23] and $H_2Ru_6(CO)_{18}$.[24] In all of the above cases the M–H–M linkage is not bridged by other groups. In this paper we examine the situation when another bridging group *is* present.

The reaction of triruthenium and triosmium dodecacarbonyl with mercaptans in benzene under reflux gives trinuclear derivatives of the type $HM_3(CO)_{10}(SR)$ (M = Ru or Os; R = alkyl or aryl group)[25] in which both the sulfido and hydrido groups are doubly bridging.[26] In contrast, the corresponding reactions involving triiron dodecacarbonyl and *sec*- or *tert*-alkyl mercaptans afford nonacarbonyl derivatives of stoichiometry $HFe_3(CO)_9(SR)$ (R = i-C_3H_7, s-C_4H_9, or t-C_4H_9).[27] Assuming these compounds obey the effective atomic number rule, the sulfido group must of necessity bridge all three iron atoms. With a view of establishing whether the hydrogen is similarly triply bridging, Mössbauer and X-ray crystallographic studies have been carried out on these products.

Experimental Section

Materials. $HFe_3(CO)_9(S$-i-$C_3H_7)$ and $HFe_3(CO)_9(S$-t-$C_4H_9)$ were obtained as reported previously[27] and were crystallized from benzene–petroleum ether.

Mössbauer Measurements. The Mössbauer spectra were obtained at 77°K by use of apparatus described previously.[28] The radioactive source, which was kept at room temperature, was a nominal 10 mCi of ^{57}Co in palladium, supplied by the Radiochemical Centre, Amersham. The data were analyzed by a least-squares curve-fitting procedure, with the aid of programs developed by Dr. T. C. Gibb.

X-Ray Data Collection and Structure Determination. Crystals of $HFe_3(CO)_9(S$-i-$C_3H_7)$ were mounted in 0.2-mm diameter glass capillaries in an inert-atmosphere chamber. Preliminary precession photographs indicated the monoclinic space group $P2_1/c$. Unit cell parameters, obtained by centering 42 reflections on a Nonius CAD-3 diffractometer, are $a = 9.59$ (1) Å, $b = 9.88$ (1) Å, $c = 19.59$ (2) Å, $\beta = 96.11$ (7)°, and $V = 1845.6$ Å^3; ρ(calcd) = 1.78 g cm^{-3} for $Z = 4$. Two quadrants of data were collected by the θ–2θ scan technique [$((\sin\theta)/\lambda)_{max} = 0.53$ Å^{-1}] using Zr-filtered Mo Kα radiation in a manner described in an earlier publication.[7] Standard deviations were estimated for each intensity reading using a standard expression.[29] An absorption correction was not applied because of the low absorption coefficient ($\mu = 14.20$ cm^{-1} for molybdenum Kα radiation) and the observation that an axial reflection at $\chi = 90°$ showed no significant intensity variation with spindle angle ϕ. After data reduction in which Lorentz and polarization corrections were applied, 1227 reflections with intensities greater than 3σ were retained and used in the subsequent structure analysis.

A three-dimensional Patterson map[30] was found to be consistent with a near-equilateral triangular array of iron atoms. All other nonhydrogen atoms were then found without difficulty from a series of difference Fourier maps. Anisotropic least-squares refinement of these atoms resulted in the agreement factors $R = 5.5\%$ and $R_w = 5.9\%$.[31]

Results and Discussion

The ^{57}Fe Mössbauer spectra of $HFe_3(CO)_9(S$-i-$C_3H_7)$ and $HFe_3(CO)_9(S$-t-$C_4H_9)$, both measured at 77 K, are almost identical and can be curve-fitted very satisfactorily, without any constraints, in terms of four partially overlapping lorentzian lines. The spectrum of the *tert*-butyl derivative is shown in Figure 1. For both spectra the fitted peaks have normal half-widths. The intensities of the peaks are in the approximate ratio 2:1:1:2, consistent with the presence of one unique and two equivalent iron atoms. The two equivalent iron atoms clearly give rise to the outer, more intense doublet A, whereas the unique iron atom generates the weaker doublet B. Although the results at once rule out a symmetrical structure in which both the sulfido and hydrido groups bridge all three iron atoms, they do not indicate immediately the precise disposition of the hydrido group. However, on the tentative assumption that the compounds obey the EAN rule and that the sulfido group is therefore triply bridging, the evidence strongly suggests that the hydrido group is in fact doubly bridging between the two equivalent iron atoms as suggested earlier.[27]

This suggestion also receives some support from a consideration of the Mössbauer parameters, full details of which are summarized in Table I, together with previous data on a number of closely related trimeric iron compounds with which the present data can be compared. The chemical isomer shift

Table I. Mössbauer Data at 77 K for $HFe_3(CO)_9(SR)$ (R = i-C_3H_7, t-C_4H_9) and Related Compounds

Compd	Line assignment	Chem isomer shift,[a,b] δ/mm sec^{-1}	Quadrupole splitting,[b] Δ/mm sec^{-1}	Full width at half-height, Γ/mm sec^{-1}	Rel intens	χ^2/degrees of freedom
$HFe_3(CO)_9(S$-i-$C_3H_7)$	A(1,4)	0.04	1.06	0.25, 0.27	1.8, 2.0	186.2/187
	B(2,3)	0.06	0.67	0.28, 0.27	1.1, 1.0	
$HFe_3(CO)_9(S$-t-$C_4H_9)$	A(1,4)	0.05	1.03	0.27, 0.29	1.8, 1.9	266.7/162
	B(2,3)	0.06	0.63	0.29, 0.26	1.0, 1.0	
$Fe_3(CO)_{12}$[c]	A(1,4)	0.11	1.13			
	B(2,3)	0.05	0.13			
$Fe_3(CO)_9[P(CH_3)_2(C_6H_5)]_3$[d]	A(1,4)	0.09	1.15			
	B(2,3)	0.02	0.57			
$HFe_3(CO)_{10}[CN(CH_3)_2]$[e]	A(1,4)	−0.04	0.94			
	B(2,3)	0.04	0.16			

[a] Relative to metallic iron at 295 K. [b] For the compounds $HFe_3(CO)_9(SR)$ the errors associated with δ and Δ are ca. ±0.02 mm sec^{-1}; these are due mainly to uncertainties which arise in curve fitting overlapping lines and are reflected in the standard deviations; errors due to instrumental factors are negligible by comparison. [c] Reference 32. [d] Reference 34. [e] Reference 35.

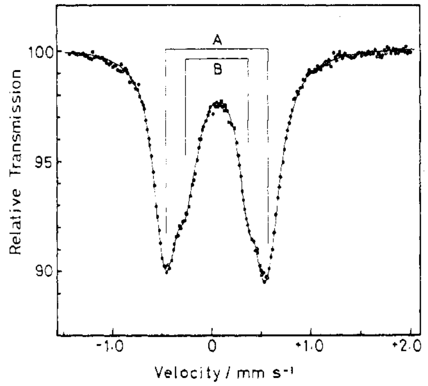

Figure 1. Mössbauer spectrum at 77 K of $HFe_3(CO)_9(S$-t-$C_4H_9)$, showing the computed line positions and intensities of the component doublets A and B referred to in Table I. The total number of counts per channel at the base line is ca. 840,000 and the velocity scale is relative to metallic iron at 295 K.

Table II. Final Atomic Coordinates for $HFe_3(CO)_9(S$-i-$C_3H_7)$

Atom	x	y	z
Fe_1	0.31722 (17)	0.17738 (17)	0.92713 (8)
Fe_2	0.05038 (16)	0.20944 (15)	0.87866 (8)
Fe_3	0.21498 (16)	0.42444 (16)	0.90961 (8)
S	0.23497 (27)	0.27253 (29)	0.83351 (13)
C_1	0.5035 (16)	0.2831 (15)	0.4382 (7)
C_2	0.2869 (14)	0.3424 (13)	0.5154 (7)
C_3	0.3366 (14)	0.4962 (14)	0.4064 (6)
C_4	0.9693 (13)	0.9559 (14)	0.1540 (6)
C_5	0.0214 (13)	0.8246 (12)	0.0426 (6)
C_6	0.1042 (14)	0.7281 (14)	0.1716 (6)
C_7	0.8826 (14)	0.4402 (14)	0.1352 (6)
C_8	0.8106 (12)	0.5449 (12)	0.0026 (6)
C_9	0.6166 (15)	0.4916 (14)	0.0865 (6)
C_{10}	0.7121 (12)	0.7247 (12)	0.2547 (6)
C_{11}	0.6890 (19)	0.8744 (18)	0.2769 (8)
C_{12}	0.4094 (20)	0.1289 (20)	0.2474 (9)
O_1	0.3790 (10)	0.7621 (16)	0.0539 (6)
O_2	0.2657 (11)	0.3590 (12)	0.5717 (4)
O_3	0.3464 (12)	0.6065 (10)	0.3943 (5)
O_4	0.9839 (12)	0.0606 (10)	0.1778 (5)
O_5	0.0654 (10)	0.8442 (11)	0.9903 (5)
O_6	0.2039 (11)	0.6920 (11)	0.2037 (6)
O_7	0.9471 (13)	0.3601 (12)	0.1640 (6)
O_8	0.1718 (10)	0.4782 (10)	0.0530 (4)
O_9	0.5133 (10)	0.4365 (11)	0.0842 (4)
H	0.053 (13)	0.358 (14)	0.934 (6)

for the unique iron atom B (0.06 ± 0.02 mm sec^{-1}) is the same, within experimental error, as that of the unique iron atom in $Fe_3(CO)_{12}$ (0.05 ± 0.01 mm sec^{-1}),[32] consistent with the direct replacement of a terminal carbonyl group by another two-electron donor bond,[33] which in this instance is from the triply bridging sulfido ligand. The accompanying increase in quadrupole splitting (from 0.13 to 0.63 mm sec^{-1}) reflects the reduction in symmetry at this iron atom and is entirely consistent with the proposed substitution. A similar increase in quadrupole splitting is observed when a single carbonyl group on this iron atom is replaced by the two-electron donor ligand $P(CH_3)_2(C_6H_5)$ as in $Fe_3(CO)_9[P(CH_3)_2(C_6H_5)]_3$.[34] For comparison, the effect of leaving the unique iron atom in $Fe_3(CO)_{12}$ unchanged is seen in the spectrum of $HFe_3(CO)_{10}[CN(CH_3)_2]$ for which both δ (0.04 ± 0.01 mm sec^{-1}) and Δ (0.16 ± 0.01 mm sec^{-1}) are almost identical with those in the parent carbonyl.[35] The chemical isomer shifts for the equivalent iron atoms in $HFe_3(CO)_9(SR)$ are much smaller than those for the equivalent iron atoms in $Fe_3(CO)_{12}$, indicating enhanced s-electron density at these nuclei. The trend is similar to that observed in $HFe_3(CO)_{10}[CN(CH_3)_2]$[35] and in other systems[32] for replacement of a bridging carbonyl group by a hydride group and is again consistent with the structure proposed[27] in which the hydride is doubly bridging.

The X-ray analysis of $HFe_3(CO)_9(S$-i-$C_3H_7)$ revealed basically a C_{3v} arrangement for the $Fe_3(CO)_9S$ moiety, with the irons forming a near-equilateral triangle capped by a triply bridging sulfur atom. The threefold symmetry of this fragment strongly suggested that the unique hydrogen was triply bridging on the triangular face opposite the SR group. Because this conclusion was at variance with the Mössbauer results, it was decided to make a careful search for the missing hydrogen atom. Its position was located by application of a method outlined in an earlier publication,[7] in which low-angle data were preferentially used to enhance hydrogen positions in difference Fourier maps. Accordingly, the low-angle data (708 reflections) were carefully recollected for this purpose: each reflection was scanned twice as long as in the original data collection. These new reflections were then used to calculate a series of difference Fourier maps with decreasing $(\sin\theta)/\lambda$ limits (0.33, 0.25, 0.17 Å^{-1}). These maps, on inspection, clearly revealed the presence of a symmetric doubly bridging hydrogen below the basal plane of the three iron atoms. Subsequent cycles of full-matrix least-squares refinement resulted in the successful convergence of the coordinates and isotropic temperature factor of the hydrogen atom. The final agreement factors are R = 3.5% and R_w = 4.2% for the low-angle data set and R = 5.3% and R_w = 5.7% for the full data set.[36]

The final molecular geometry of $HFe_3(CO)_9(S$-i-$C_3H_7)$ is shown in Figures 2–4. The final atomic parameters are listed in Tables II and III, and distances and angles are given in Tables IV and V, respectively.

The bridging hydrogen atom is situated 1.0 Å below the basal plane of the iron triangle and is coplanar with the sulfur and the two hydrido-bridged iron atoms (Fe_2 and Fe_3) to within 0.04 Å. The iron–hydrogen bonding distances are essentially equal [1.82 (13) and 1.79 (13) Å]. These bond

Table III. Final Thermal Parameters[a] for $HFe_3(CO)_9(S\text{-}i\text{-}C_3H_7)$

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Fe_1	92 (2)	115 (2)	24 (1)	12 (4)	12 (2)	12 (2)
Fe_2	86 (2)	81 (2)	25 (1)	−7 (3)	22 (2)	5 (2)
Fe_3	103 (2)	88 (2)	25 (1)	−27 (4)	23 (2)	−10 (2)
S	93 (4)	104 (4)	24 (1)	−1 (6)	22 (3)	−1 (3)
C_1	130 (25)	237 (25)	50 (6)	−6 (41)	−22 (19)	−40 (17)
C_3	152 (22)	172 (20)	37 (5)	−38 (34)	36 (14)	−7 (16)
C_4	131 (21)	142 (21)	46 (5)	−38 (34)	32 (14)	−12 (16)
C_5	107 (22)	190 (18)	37 (5)	15 (32)	34 (14)	17 (16)
C_6	128 (20)	189 (20)	39 (5)	11 (34)	35 (15)	30 (15)
C_7	172 (21)	141 (21)	35 (5)	5 (32)	18 (14)	0 (15)
C_8	133 (19)	152 (17)	29 (4)	−6 (28)	29 (14)	−15 (14)
C_9	188 (23)	136 (20)	38 (5)	−12 (32)	45 (16)	−26 (15)
C_{10}	148 (18)	167 (18)	22 (4)	−31 (29)	45 (13)	−4 (14)
C_{11}	429 (32)	204 (29)	34 (7)	205 (48)	112 (21)	−51 (22)
C_{12}	290 (39)	427 (32)	41 (8)	442 (58)	161 (25)	29 (26)
O_1	101 (14)	420 (24)	89 (6)	−67 (36)	−15 (15)	96 (19)
O_2	295 (22)	356 (22)	31 (3)	6 (35)	30 (12)	−63 (15)
O_3	315 (22)	133 (13)	73 (5)	−134 (29)	78 (14)	3 (13)
O_4	291 (22)	120 (14)	79 (5)	−93 (28)	31 (15)	−69 (13)
O_5	196 (18)	306 (20)	47 (4)	8 (29)	88 (12)	76 (14)
O_6	164 (17)	302 (24)	68 (5)	95 (30)	−7 (13)	98 (16)
O_7	307 (25)	202 (17)	72 (5)	163 (32)	−29 (16)	56 (15)
O_8	235 (18)	243 (16)	36 (3)	18 (27)	65 (11)	−51 (12)
O_9	169 (18)	281 (20)	65 (4)	−274 (29)	70 (12)	−50 (15)
H	9.3 (36)[b]					

[a] The anisotropic thermal parameters are expressed in the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] The thermal parameter for hydrogen is isotropic, in units of Å^2.

Table IV. Bond Distances in $HFe_3(CO)_9(S\text{-}i\text{-}C_3H_7)$

Atoms	Dist, Å	Atoms	Dist, Å
	(a) Metal-Hydrogen Distances		
Fe_2-H	1.82 (13)	Fe_3-H	1.79 (13)
	(b) Metal-Metal Distances		
Fe_1-Fe_2	2.653 (2)	Fe_1-Fe_3	2.640 (2)
Fe_2-Fe_3	2.678 (2)		
	(c) Metal-Sulfur Distances		
Fe_1-S	2.136 (2)	Fe_2-S	2.154 (2)
Fe_3-S	2.139 (3)		
	(d) Metal-Carbon Distances		
Fe_1-C_1	1.82 (1)	Fe_1-C_2	1.80 (1)
Fe_1-C_3	1.78 (1)	Fe_2-C_4	1.76 (1)
Fe_2-C_5	1.79 (1)	Fe_2-C_6	1.80 (1)
Fe_3-C_7	1.81 (1)	Fe_3-C_8	1.79 (1)
Fe_3-C_9	1.81 (1)		
	(e) Carbonyl Distances		
C_1-O_1	1.14 (1)	C_2-O_2	1.15 (1)
C_3-O_3	1.12 (1)	C_4-O_4	1.14 (1)
C_5-O_5	1.16 (1)	C_6-O_6	1.14 (1)
C_7-O_7	1.12 (1)	C_8-O_8	1.14 (1)
C_9-O_9	1.13 (1)		
	(f) Thiol Group Distances		
S-C_{10}	1.85 (1)	C_{10}-C_{11}	1.56 (2)
C_{10}-C_{12}	1.50 (2)		

lengths are, expectedly, significantly longer than the terminal Fe–H distances in $[HFe(CO)_4]^-$ [1.57 (12) Å]^{37} and $H_2Fe(PPh(OEt)_2)_4$ [1.51 (9) Å]^{38} but agree quite well with those found in other bridging hydrides: Mn–H = 1.72 (3) Å in $H_3Mn_3(CO)_{12}$,^{7} Ru–H = 1.75 Å in $HRu_2(CO)_6(C_{10}H_9O)$,^{8} Ti–H = 1.80 Å in $H[Ti(C_5H_5)]_2(H_2AlEt_2)(C_{10}H_8)$,^{9} Rh–H = 1.85 (5) Å in $H[Rh(C_5Me_5)Cl]_2Cl$,^{10} W–H = 1.85 (7) Å in $[NEt_4]_2[H_2W_2(CO)_8]$,^{11} Mn–H = 1.86 (6) Å in $HMn_2(CO)_8(PPh_2)$,^{6} Mo–H = 1.860 (4) Å in $HMo_2(CO)_4(C_5H_5)_2(PMe_2)$,^{12} and W–H = 1.873 (3) Å in $HW_2(CO)_9(NO)$.^{13} The last two values are accurately known parameters derived from recent neutron diffraction analyses.

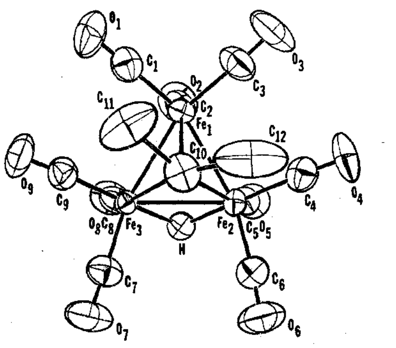

Figure 2. Geometry of $HFe_3(CO)_9(S\text{-}i\text{-}C_3H_7)$, projected onto the triiron plane. *The triply bridging sulfur atom is obscured by the central carbon of the isopropyl group.* The slight distortion of the axial carbonyl groups away from the hydrogen atom is apparent by rotating the figure 120° in a counterclockwise manner.

Table V. Bond Angles in $HFe_3(CO)_9(S\text{-}i\text{-}C_3H_7)$

Atom	Angle, deg	Atom	Angle, deg
	(a) Angle around Hydride		
Fe_2-H-Fe_3	96 (6)		
	(b) Angles around Fe_1		
Fe_2-Fe_1-Fe_3	60.79 (5)	C_1-Fe_1-C_3	96.3 (5)
C_1-Fe_1-C_2	99.6 (5)	C_1-Fe_1-S	106.0 (4)
C_1-Fe_1-Fe_2	156.2 (4)	C_2-Fe_1-C_3	98.5 (5)
C_1-Fe_1-Fe_3	99.4 (4)	C_2-Fe_1-S	142.4 (4)
C_2-Fe_1-Fe_2	96.3 (4)	C_3-Fe_1-Fe_2	98.8 (3)
C_2-Fe_1-Fe_3	97.5 (4)	C_3-Fe_1-Fe_3	155.4 (3)
C_3-Fe_1-S	105.4 (3)	S-Fe_1-Fe_3	51.91 (7)
Fe_2-Fe_1-S	52.11 (7)		
	(c) Angles around Fe_2		
Fe_1-Fe_2-Fe_3	59.36 (5)	H-Fe_2-Fe_3	42 (4)
H-Fe_2-Fe_1	86 (4)	H-Fe_2-C_5	68 (4)
H-Fe_2-C_4	164 (4)	H-Fe_2-S	93 (4)
H-Fe_2-C_6	90 (4)	C_4-Fe_2-C_6	94.0 (5)
C_4-Fe_2-C_5	95.9 (5)	C_4-Fe_2-S	100.4 (3)
C_4-Fe_2-Fe_3	149.1 (3)	C_5-Fe_2-C_6	99.6 (5)
C_4-Fe_2-Fe_1	94.7 (3)	C_5-Fe_2-S	144.9 (3)
C_5-Fe_2-Fe_3	103.1 (3)	C_6-Fe_2-Fe_3	106.5 (4)
C_5-Fe_2-Fe_1	96.6 (3)	C_6-Fe_2-Fe_1	160.8 (4)
C_6-Fe_2-S	110.0 (4)	S-Fe_2-Fe_1	51.50 (7)
Fe_3-Fe_2-S	51.15 (4)		
	(d) Angles around Fe_3		
Fe_1-Fe_3-Fe_2	59.85 (5)	H-Fe_3-Fe_2	42 (4)
H-Fe_3-Fe_1	87 (4)	H-Fe_3-C_8	66 (3)
H-Fe_3-C_7	89 (4)	H-Fe_3-S	94 (4)
H-Fe_3-C_9	162 (4)	C_7-Fe_3-C_9	95.5 (5)
C_7-Fe_3-C_8	103.0 (5)	C_7-Fe_3-S	105.1 (3)
C_7-Fe_3-Fe_1	156.1 (3)	C_8-Fe_3-C_9	95.5 (4)
C_7-Fe_3-Fe_2	102.4 (3)	C_8-Fe_3-S	145.2 (3)
C_8-Fe_3-Fe_1	96.8 (3)	C_9-Fe_3-Fe_1	95.8 (4)
C_8-Fe_3-Fe_2	102.4 (3)	C_9-Fe_3-Fe_2	151.1 (4)
C_9-Fe_3-S	101.8 (3)	S-Fe_3-Fe_2	51.67 (7)
Fe_1-Fe_3-S	51.83 (7)		
	(e) M-C-O Angles		
Fe_1-C_1-O_1	178 (1)	Fe_1-C_2-O_2	178 (1)
Fe_1-C_3-O_3	178 (1)	Fe_2-C_4-O_4	178 (1)
Fe_2-C_5-O_5	178 (1)	Fe_2-C_6-O_6	178 (1)
Fe_3-C_7-O_7	177 (1)	Fe_3-C_8-O_8	178 (1)
Fe_3-C_9-O_9	178 (1)		
	(f) Angles around Sulfur Atom		
Fe_1-S-Fe_2	76.39 (9)	Fe_1-S-Fe_3	76.26 (9)
Fe_2-S-Fe_3	77.18 (9)	Fe_1-S-C_{10}	134.0 (3)
Fe_2-S-C_{10}	134.9 (3)	Fe_3-S-C_{10}	133.9 (3)
	(g) Thiol Group Angles		
S-C_{10}-C_{11}	107.8 (7)	S-C_{10}-C_{12}	105.8 (7)
C_{11}-C_{10}-C_{12}	118 (1)		

The bridging hydrogen does not exert a profound influence on the geometry of the rest of the molecule, the only discernible feature being a slight perturbation of the carbonyl groups away from the protonated side of the iron triangle: the four C–Fe–Fe angles associated with the Fe_2–Fe_3 bond (102.4, 102.4, 103.1, 106.5°) are all consistently larger than the eight

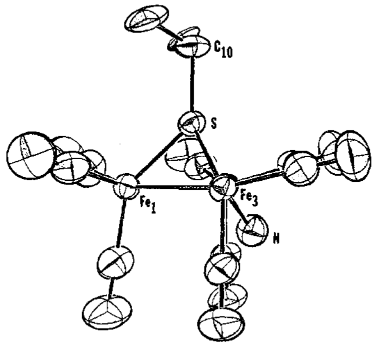

Figure 3. Projection of the $HFe_3(CO)_9(S\text{-}i\text{-}C_3H_7)$ molecule along the Fe_3–Fe_2 axis, showing the planarity of the SFe_2Fe_3H fragment and the eclipsing of the carbonyl groups. Fe_2 is hidden behind Fe_3. One of the equatorial carbonyl groups on Fe_3 has been removed for clarity. Note the approximate staggering of the Fe_2–H–Fe_3 plane relative to the carbonyls.

C–Fe–Fe angles associated with the other two iron–iron bonds (94.7, 95.8, 96.3, 96.6, 96.8, 97.5, 98.8, 99.4°). As mentioned earlier, the triangle of iron atoms is essentially equilateral: the protonated bond [Fe_2–Fe_3 = 2.678 (2) Å] is only slightly longer than the other two [Fe_1–Fe_2 = 2.653 (2) Å; Fe_1–Fe_3 = 2.640 (2) Å].

The triply bridging sulfur atom is 1.50 Å above the plane of the three iron atoms and is essentially equidistant from the three irons. The S–Fe bonding distances are significantly shorter than those found for several bridging sulfido structures elucidated by Dahl and coworkers: 2.259 Å in $[C_2H_5SFe(CO)_3]_2$,[39] 2.23 Å in $[Fe(CO)_3S]_2$,[40] and 2.540 Å in $[Fe_2(CO)_6(SCH_3)]_2S$.[41] The entire cluster satisfies the effective atomic number rule if the sulfido ligand is considered to be a five-electron donor to the cluster as a whole.

Projections down the Fe–Fe bonds show that each Fe–C–O group eclipses a corresponding Fe'–C'–O' group on the neighboring iron. Each of these eclipsed configurations (i.e., the six-atom groups OCFeFe'C'O') is coplanar within ±0.03 Å. The Fe_2–H–Fe_3 plane is roughly staggered with respect to two of the eclipsed carbonyl planes, as shown in Figure 3.

Despite the fact that the stereochemical influence of the hydrogen atom is low, its presence certainly affects the infrared spectrum of the molecule,[27] causing it to be much more complex than what would have been expected for a near-C_{3v} arrangement of carbonyl groups. The observed eight-band carbonyl pattern in solution was in fact the original evidence for a doubly bridging hydride structure for the molecule. A triply bridging hydride model (C_{3v} symmetry) would have predicted five carbonyl stretches (2 A_1 + 3 E); $Co_3(CO)_9S$, which belongs to this particular point group, gives four CO stretching modes in its infrared spectrum.[42]

The minimal stereochemical influence of the bridging hydride in $HFe_3(CO)_9(S\text{-}i\text{-}C_3H_7)$ contrasts dramatically with its role in most other M–H–M-bridged compounds such as $HW_2(CO)_9(NO)$,[13] in which it occupies a distinct coordination site and causes a more conspicuous lengthening of the M–M distance. The geometrical constraints placed on the molecular architecture by the triply bridging sulfido ligand and the eclipsing carbonyl groups (necessarily eclipsed to preserve an octahedral basis set of orbitals around each iron atom) offer little opportunity for the hydride to exert any large influence on the rest of the molecular structure. As discussed earlier, there is only a slight perturbation of the cis carbonyl ligands attached to the hydrido-bridged iron–iron bond. The hydride ligand itself adjusts and achieves a minimum in steric repulsions by interleaving between the eclipsing carbonyl planes.

Our result clearly shows that arguments involving the lengthening of M–M bonds as evidence for the presence of hydrogen bridging[15-22] cannot be applied to cases where another bridging group [as the SR moiety in this case and in $Os_3(CO)_{10}(H)(SEt)$[26]] imposes stereochemical constraints on the molecule. Other investigators have noted that a pair of bridging hydrides {as in $[Et_4N]^+{}_2[H_2W_2(CO)_8]^{2-}$}[11] or a trio of bridging hydrides {as in $[P_3FeH_3FeP_3]^+PF_6^-$; P_3 = $CH_3C(CH_2PPh_2)_3$}[43] gives rise to a shorter-than-normal M–M distance.

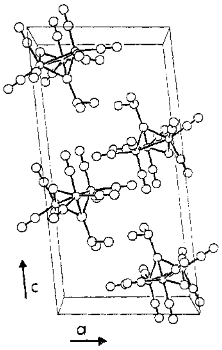

Figure 4. Projection of the unit cell down the *b* axis.

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Registry No. $HFe_3(CO)_9(S\text{-}i\text{-}C_3H_7)$, 56421-56-8; $HFe_3(CO)_9(S\text{-}t\text{-}C_4H_9)$, 56421-55-7.

Supplementary Material Available. Listings of the final observed and calculated structure factors 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 Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number AIC50276+-12-75.

References and Notes

(1) (a) University of Southern California. (b) The University of Leeds. (c) University of Cape Town.
(2) Alfred P. Sloan Fellow, 1974–1976.
(3) H. D. Kaesz, *Chem. Br.*, **9**, 344 (1973).
(4) H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, **72**, 231 (1972).
(5) H. D. Kaesz, W. Fellmann, G. Wilkes, and L. F. Dahl, *J. Am. Chem. Soc.*, **87**, 2853 (1965).
(6) R. J. Doedens, W. T. Robinson, and J. A. Ibers, *J. Am. Chem. Soc.*, **89**, 4323 (1967).
(7) S. W. Kirtley, J. P. Olsen, and R. Bau, *J. Am. Chem. Soc.*, **95**, 4532 (1973).
(8) A. J. P. Domingos, B. F. G. Johnson, J. Lewis, and G. M. Sheldrick, *J. Chem. Soc., Chem. Commun.*, 912 (1973).
(9) L. J. Guggenberger and F. N. Tebbe, *J. Am. Chem. Soc.*, **95**, 7870 (1973).
(10) M. R. Churchill and S. W. Y. Ni Chang, *J. Am. Chem. Soc.*, **95**, 2150 (1973).
(11) (a) M. R. Churchill, S. W. Y. Ni Chang, M. L. Berch, and A. Davison, *J. Chem. Soc., Chem. Commun.*, 691 (1973); (b) M. R. Churchill and S. W. Y. Chang, *Inorg. Chem.*, **13**, 2413 (1974).
(12) J. L. Peterson, L. F. Dahl, and J. M. Williams, *J. Am. Chem. Soc.*, **96**, 6610 (1974).
(13) J. P. Olsen, T. F. Koetzle, S. W. Kirtley, M. Andrews, D. L. Tipton, and R. Bau, *J. Am. Chem. Soc.*, **96**, 6621 (1974).
(14) R. A. Love, H. B. Chin, B. R. Whittlesey, S. W. Kirtley, T. F. Koetzle, and R. Bau, in preparation.
(15) L. B. Handy, J. K. Ruff, and L. F. Dahl, *J. Am. Chem. Soc.*, **92**, 7312 (1970).
(16) A. S. Foust, W. A. G. Graham, and R. P. Stewart, *J. Organomet. Chem.*, **54**, C22 (1973).
(17) H. D. Kaesz, R. Bau, and M. R. Churchill, *J. Am. Chem. Soc.*, **89**, 2775 (1967).
(18) M. R. Churchill and R. Bau, *Inorg. Chem.*, **6**, 2086 (1967).
(19) R. P. White, Jr., T. E. Block, and L. F. Dahl, private communication.

(20) M. R. Churchill, P. H. Bird, H. D. Kaesz, R. Bau, and B. Fontal, *J. Am. Chem. Soc.*, **90**, 7135 (1968).
(21) S. W. Kirtley, Ph.D. Dissertation, University of California at Los Angeles, 1972.
(22) H. D. Kaesz, B. Fontal, R. Bau, S. W. Kirtley, and M. R. Churchill, *J. Am. Chem. Soc.*, **91**, 1021 (1969).
(23) M. R. Churchill, S. A. Bezman, J. A. Osborn, and J. Wormald, *Inorg. Chem.*, **11**, 1818 (1972).
(24) (a) M. R. Churchill, J. Wormald, J. Knight, and M. J. Mays, *Chem. Commun.*, 458 (1970); (b) M. R. Churchill and J. Wormald, *J. Am. Chem. Soc.*, **93**, 5670 (1971).
(25) G. R. Crooks, B. F. G. Johnson, J. Lewis, and I. G. Williams, *J. Chem. Soc. A*, 797 (1969).
(26) R. Mason, lecture presented at the 23rd International Congress of Pure and Applied Chemistry, Boston, Mass., July 1971; *Pure Appl. Chem.*, **6**, 31 (1971).
(27) J. A. de Beer and R. J. Haines, *J. Organomet. Chem.*, **24**, 757 (1970).
(28) J. A. de Beer, R. J. Haines, R. Greatrex, and J. A. van Wyk, *J. Chem. Soc., Dalton Trans.*, 2341 (1973).
(29) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967). The expression used was $\sigma(I) = [(\text{peak count}) + (\text{background count}) + 0.04(\text{net intensity})^2]^{1/2}$.
(30) All the major computations in this work were performed using CRYM, an amalgamated set of crystallographic programs developed by Dr. R. E. Marsh's group at the California Institute of Technology.
(31) $R = (\sum||F_o| - |F_c||)/(\sum|F_o|)$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.
(32) K. Farmery, M. Kilner, R. Greatrex, and N. N. Greenwood, *J. Chem. Soc. A*, 2339 (1969).
(33) R. H. Herber, R. B. King, and G. K. Wertheim, *Inorg. Chem.*, **3**, 101 (1964).
(34) W. S. McDonald, J. R. Moss, G. Raper, B. L. Shaw, R. Greatrex, and N. N. Greenwood, *Chem. Commun.*, 1295 (1969).
(35) R. Greatrex, N. N. Greenwood, I. Rhee, M. Ryang, and S. Tsutsumi, *Chem. Commun.*, 1193 (1970).
(36) Supplementary material.
(37) M. B. Smith and R. Bau, *J. Am. Chem. Soc.*, **95**, 2388 (1973).
(38) L. J. Guggenberger, D. D. Titus, M. T. Flood, R. E. Marsh, A. A. Orio, and H. B. Gray, *J. Am. Chem. Soc.*, **94**, 1135 (1972).
(39) L. F. Dahl and C. H. Wei, *Inorg. Chem.*, **2**, 328 (1963).
(40) C. H. Wei and L. F. Dahl, *Inorg. Chem.*, **4**, 1 (1965).
(41) J. M. Coleman, A. Wojcicki, P. J. Pollick, and L. F. Dahl, *Inorg. Chem.*, **6**, 1236 (1967).
(42) L. Marko, G. Bor, E. Klumpp, B. Marko, and G. Almasy, *Chem. Ber.*, **96**, 955 (1963).
(43) P. Dapporto, G. Fallani, S. Midollini, and L. Sacconi, *J. Am. Chem. Soc.*, **95**, 2021 (1973).

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Structure and Bonding in $\Delta^{1,4}$-Bicyclo[2.2.0]hexenebis(triphenylphosphine)platinum, $Pt[C_6H_8][P(C_6H_5)_3]_2$

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$\Delta^{1,4}$-Bicyclo[2.2.0]hexene displaces ethylene from the complex $Pt[C_2H_4][P(C_6H_5)_3]_2$. The crystal and molecular structure of the resulting bicyclic olefin complex, $Pt[C_6H_8][P(C_6H_5)_3]_2$, has been determined from three-dimensional X-ray diffraction data. $Pt[C_6H_8][P(C_6H_5)_3]_2$ crystallizes in space group $P2_12_12_1$ of the orthorhombic system with four molecules in a unit cell of dimensions $a = 17.726$ (3), $b = 9.748$ (2), $c = 19.724$ (3) Å. The structural parameters were refined by least-squares techniques and the absolute configuration was deduced by comparison of the R factors, after refinement of the two possible configurations. The final R factor on F was 4.0% for the 3510 independent reflections (measured using a four-circle diffractometer) classed as observed and for which $2\theta \leq 55°$. No symmetry is crystallographically imposed upon the molecules. The six carbon atoms in the coordinated olefin form two squares having a common edge with a dihedral angle of 56 (1)° between the two four-membered rings. The olefinic carbon atoms form the common edge and are separated by 1.52 (2) Å, a greater separation than observed in several analogous complexes formed by acyclic olefins. The other six C–C bond lengths within the olefin moiety are, as expected, not significantly different from that typical of carbon atoms linked by a single σ bond. Coordination around platinum is not quite planar, the dihedral angle between the PtP_2 and PtC_2 planes being 3.2 (5)°. The olefinic carbon atoms are not exactly equidistant from platinum with Pt–C distances of 2.067 (14) and 2.138 (16) Å. This asymmetry may be due to minimization of intramolecular contacts since, even with this structure, there appear to be several short contacts between hydrogen atoms in one of the triphenylphosphine ligands and hydrogen atoms on the olefin. The Pt–P bond lengths are 2.289 (3) and 2.278 (3) Å, the slight difference possibly due to a trans effect since the longer Pt–P separation is trans to the shorter Pt–C separation. The binding energy of the Pt $4f_{7/2}$ electrons in $Pt[C_6H_8][P(C_6H_5)_3]_2$ is closer to that in Pt(0) compounds than in Pt(II) compounds. Thus transfer of electrons from the metal to the olefin is not the major component in the olefin–metal bonding, and redistribution of the olefin electrons through the intermediacy of the metal must be important. That the redistribution of the olefin electrons is considerable is shown by the large deviation from coplanarity of the two four-membered rings in the olefin and the relatively large separation of the olefinic carbon atoms.

Introduction

The compounds of general formula $PtL[P(C_6H_5)_3]_2$, where L is an olefin, have been chosen for a systematic investigation of the way in which different olefins are affected by interaction with a given metal system. Earlier reports from this laboratory[1,2] described studies of the complexes where L is 4,4'-dinitro-*trans*-stilbene and octafluoro-*trans*-but-2-ene. Surprising, perhaps, was the observation that the separation of the olefinic carbon atoms was the same (1.42 Å) in both of these complexes in spite of the widely differing electronic characteristics of the olefin substituents. One of the objectives of this investigation was to see if the olefinic C–C separation can be increased to an unusual degree by interaction with a metal system, since unusual reactivities might be induced thereby. This objective has not been achieved with the acyclic olefins examined so far and alternative approaches were sought.

Ring strain increases the coordinative ability of an olefin: 1,2-dimethylcyclopropene displaces ethylene from $Pt[C_2H_4][P(C_6H_5)_3]_2$.[3] The structure of the resulting complex has been reported[4] and the separation of the olefinic carbon atoms is 1.50 (2) Å, significantly longer than in the acyclic olefin complexes discussed above. Work by Wiberg et al.[5] resulted in the synthesis of $\Delta^{1,4}$-bicyclo[2.2.0]hexene as a mixture with 1,2-dimethylenecyclobutane. This paper reports the structure and properties of the platinum complex formed by $\Delta^{1,4}$-bicyclo[2.2.0]hexene; a preliminary communication of this work has appeared.[6]

Preparation of $Pt[C_6H_8][P(C_6H_5)_3]_2$

All solvents were distilled from EDTA and dried prior to use. All reactions were performed under vacuum or dry nitrogen. The synthesis of $\Delta^{1,4}$-bicyclo[2.2.0]hexene has been reported earlier.[5] Freshly

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