CO substitution reactions of metal carbonyls containing chelating phosphines (*e.g.*, diphos) will depend on both steric and *electronic* effects.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-2902.

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Crystal and Molecular Structure of μ-Hydroxo-μ-di(*p*-tolyl)phosphido-hexacarbonyldiiron, $Fe_2(CO)_6[P(p\text{-}C_6H_4CH_3)_2]OH$

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An X-ray crystal structure determination has shown that the compound previously characterized as $Fe_2(CO)_6[P(p\text{-}C_6H_4\text{-}CH_3)_2]H$, and as containing a bridging hydride ligand, is in fact $Fe_2(CO)_6[P(p\text{-}C_6H_4CH_3)_2]OH$, having a bridging hydroxide ligand. The compound crystallizes in the monoclinic space group $C2/c$ with eight molecules in a unit cell with dimensions $a = 10.534$ (6) Å, $b = 17.231$ (8) Å, $c = 23.810$ (15) Å, and $\beta = 100.72$ (5)°. Full-matrix isotropic–anisotropic least-squares refinement of 1219 independent counter data yielded a final unweighted R factor of 4.6%. The molecular configuration of approximate C_s-m symmetry consists of two $Fe(CO)_3$ units linked by bridging bis(*p*-tolyl)phosphido and hydroxide groups and by an iron–iron bond. The properties and structural features of this molecule are discussed and compared with those of other related complexes.

Introduction

Studies of reactions of various secondary phosphines with metal carbonyls have recently been reported[1-4] by several groups including ours. With some variation in chosen reaction conditions a number of different products have been isolated. For example, the room temperature reaction of several phosphines PR_2H ($R = CH_3, C_2H_5, C_6H_5, p\text{-}C_6H_4CH_3$) and $Fe_2(CO)_9$ gave three complexes: yellow solid or liquid $Fe(CO)_4PR_2H$, always the primary product under these conditions, and two solid yellow to orange complexes in yields generally under 10%. The first of these latter species belonged to the well-known group of complexes having the general formula $Fe_2(CO)_6(PR_2)_2$[1,2,4,5] and as such were not of particular interest. The second complex was initially characterized by analyses as having the formula $Fe_2(CO)_6(PR_2)H$. Infrared data (ν_{CO}) suggested that the overall geometry of these species was similar to the $Fe_2(CO)_6(PR_2)_2$ complexes, and the pmr spectrum showed a high-field peak in the range τ 12.20-12.60 which was consistent with the bridging hydride formulation, although this value was a little lower than might have been expected.

Many metal carbonyl complexes containing bridging hydrides are known, of course, so another compound with this functionality would not be considered unusual. However, this particular type of complex was of significance from another point of view, namely that it could have provided unique information with respect to an interesting controversy concerning the bonding in these species.[6] The question has been posed as to whether one should view a metal-hydrogen-metal linkage as having only a three-center two-electron bridging bond, or whether it has such a linkage in addition to a formal metal-metal bond. A satisfactory answer to the question of which bonding representation best fits these systems has not been obtained unequivocally from bond length data alone.

Whereas earlier examples of complexes with bridging hydride ligands were of such a nature that the M-H-M unit and the M-M bond (if present) were required to lie in one plane, this would not necessarily have been the case with a complex $Fe_2(CO)_6(PR_2)H$. If the structure of such a species conformed to the structures of other $Fe_2(CO)_6X_2$ species (wherein X represents a bridging group such as PR_2[7]) then the planes for the Fe-H-Fe unit and for a *bent* Fe-Fe bond would not be coincident. By virtue of this fact, there would be present unambiguous evidence for the existence of both Fe-H-Fe and Fe-Fe bonds. This would in turn allow assessment of the structural parameters (bond lengths and bond angles) for the Fe-H-Fe unit in this structure which need not be qualified for lack of the knowledge of the correct bonding representation.

If, on the other hand, there was no Fe–Fe bond (a postulate which seemed unlikely considering the electron count), then

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[7] The crystal structures of $Fe_2(CO)_6[PRR']_2$ (with $R = C_6H_5$, $R' = CH_3$, H, and C_6H_5; $R = CH_3$, $R' = H$) have been determined at Wisconsin by L. F. Dahl and J. J. Huntsman and will be published shortly. The general structure is analogous to the known structure[8] of $Fe_2(CO)_6(SC_2H_5)_2$, with the PRR′ groups replacing the SC_2H_5 groups in the latter structure.

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a planar $Fe_2(PR_2)H$ unit would be required, analogous to the geometry observed for $[C_5H_5NiP(C_6H_5)_2]_2$.[9]

As noted above, the infrared spectra (ν_{CO}) of these compounds seemed to indicate a bent Fe_2X_2 framework. In order to obtain definite proof of this, and to investigate the stereochemical consequences of the bonding implied by a bent structure, an X-ray crystal structure determination was initiated on one of the compounds. The compound $Fe_2(CO)_6[P(p\text{-}C_6H_4CH_3)_2]H$ was chosen since it was one of the most stable members of the series and since it yielded well-formed crystals. During the course of this investigation, however, it was discovered that the compound contained a bridging *hydroxide* rather than a bridging hydride ligand as had been thought and that the compound was properly formulated as $Fe_2(CO)_6[P(p\text{-}C_6H_4CH_3)_2]OH$.

Experimental Section

All reactions were carried out under a nitrogen atmosphere. Tetrahydrofuran was distilled from $LiAlH_4$ before use; other solvents were used as obtained. The preparation of $Fe(CO)_4[P(p\text{-}C_6H_4\text{-}CH_3)_2H]$ has been described previously.[1] Diiron enneacarbonyl was prepared as described in the literature.[10] Commercial *n*-butyllithium in hexane was standardized by the usual method.[11]

The carbonyl-stretching frequencies in the infrared spectrum were recorded in heptane solution using a Perkin-Elmer 421 high-resolution spectrophotometer; other regions of the spectrum were recorded as Nujol or Fluorolube mulls on a Beckman IR-10 spectrophotometer. Proton nmr data were recorded on a Varian A-60 A spectrometer. The molecular weight was determined using a Mechrolab vapor pressure osmometer. Analyses were performed by the Galbraith Laboratories, Knoxville, Tenn., and by Meade Microanalytical Laboratory, Amherst, Mass.

Synthesis of $Fe_2(CO)_6[P(p\text{-}C_6H_4CH_3)_2]OH$. Solid $Fe(CO)_4[P\text{-}(p\text{-}C_6H_4CH_3)_2H]$ (5.40 g, 14.15 mmol) was dissolved in 250 ml of tetrahydrofuran and deprotonated with 10.50 ml of 1.355 *M* *n*-butyllithium at 0°. Then 5.15 g of $Fe_2(CO)_9$ (14.15 mmol) was added and the mixture was stirred overnight while being allowed to warm slowly to room temperature. The solvent was then removed and the residue dissolved in hexane and chromatographed over an alumina column. Hexane eluted a small yellow band of $Fe(CO)_4[P(p\text{-}C_6H_4\text{-}CH_3)_2H]$; 1:1 hexane–chloroform eluted a bright orange band of $Fe_2(CO)_6[P(p\text{-}C_6H_4CH_3)_2]OH$, which was obtained as orange-red crystals from dichloromethane: mp 142–143°; yield 4.20 g (60%); infrared data ν_{CO} (heptane) 2081 (s), 2074 (sh), 2030 (s), 1993 (sh), 1987 cm^{-1} (s); ir ν_{OH} 3552 cm^{-1} (w); other bands at 1600 (w), 1500 (w), 1450 (w), 1400 (w), 1384 (vw), 1340 (vw), 1305 (w), 1187 (vw), 1000 (w), 1014 (vw), 844 (w), 810 (m), 720 (m), 630 (sh), 610 cm^{-1} (m); nmr ($CDCl_3$) τ 2.74 (multiplet, C_6H_4), 7.67 (singlet, CH_3), 12.86 (doublet, J_{P-OH} = 11.2 Hz, OH). *Anal.* Calcd for $C_{20}H_{15}O_7PFe_2$: C, 47.2; H, 2.94; P, 6.09; O, 22.0; mol wt, 510. Found: C, 48.1; H, 2.93; P, 6.33; O, 22.0; mol wt, 499.

Single Crystal X-Ray Data. Satisfactory crystals of $Fe_2(CO)_6\text{-}[P(p\text{-}C_6H_4CH_3)_2]OH$ were obtained by slowly chilling a dichloromethane solution of the compound to −20°. A single crystal with dimensions (each defined by the perpendicular distance between the opposite pair of crystal faces) 0.45 ($\bar{2}21$) × 0.22 ($22\bar{1}$) × 0.12 mm (001) was attached to a glass fiber with Canadian balsam. Although preliminary oscillation, Weissenberg, and precession photographs indicated the crystal symmetry to be triclinic $P\bar{1}$, it was later determined[12] by successful least-squares refinement that the actual space group was the monoclinic $C2/c$. The crystal was placed on a Syntex $P\bar{1}$ four-circle, computer-controlled diffractometer equipped with a graphite monochromator, and after careful optical crystal and X-ray tube alignment, 15 diffraction maxima were automatically centered in 2θ, χ, and ω. Mo $K\bar{\alpha}$ radiation (λ = 0.7107 Å) was used throughout the alignment and data-collection procedures. After being assigned correct indices the reflections were used in a least-squares procedure to give lattice and orientation parameters.[13]

Intensity data were collected by the θ–2θ scan technique with stationary crystal–stationary counter background counts taken at the beginning and end of each scan. In the Syntex procedure, variable scan rates and scan ranges are determined according to the intensity and width of the peak being measured. The total time spent in taking the background counts was set equal to the total scan times.[13] A total of 8221 reflections were measured, distributed through the four octants hkl, $h\bar{k}l$, $h\bar{k}\bar{l}$, and $\bar{h}kl$, and for which $5° \leqslant 2\theta \leqslant 40°$.

Two standard reflections were monitored every 50 reflections in order to check electronic and crystal stability. During the entire data collection process, the intensity of the standard reflections varied by only ±2%; hence, no corrections for crystal decay were made. The data were corrected in the usual fashion for Lorentz–polarization effects with the polarization term including a correction for the graphite monochromator.[14]

A given reflection was considered statistically unobserved if the net intensity (I) was less than twice the standard deviation of the intensity $[\sigma(I)]$. An instrument stability constant of $0.003(I^2)$ was introduced into $\sigma(I)$ to avoid overweighting the strong reflections in least-squares refinement. Transmission factors based on the linear absorption coefficient[15] for Mo Kα radiation of 15.20 cm^{-1} varied from 0.73 to 0.85, causing a fluctuation of ±4% in the observed structure amplitudes; accordingly, the appropriate absorption corrections were made.[16]

After merging the data[17] and then limiting the data to $10° < 2\theta < 38°$ (for reasons of cost effectiveness) a total of 1219 independent observed reflections were obtained, all of which were used in the structural determination and least-squares refinement, giving a final data to parameter ratio of approximately 7:1.

Unit Cell and Space Group. The measured lattice constants (~23°) with estimated standard deviations for the monoclinic unit cell of $Fe_2(CO)_6[P(p\text{-}C_6H_4CH_3)_2]OH$ are a = 10.534 (6) Å, b = 17.231 (8) Å, c = 23.810 (15) Å, and β = 100.72 (5)°; the volume of the unit cell is 4246.5 Å^3. The density of 1.590 g cm^{-3}, measured by flotation in a mixture of carbon tetrabromide and heptane, agrees well with the value of 1.595 g cm^{-3} calculated on the basis of eight of the above species per unit cell. The total number of electrons per unit cell, F(000), is 2064. The general positions of the space group $C2/c$ are $\pm(x, y, z; x, -y, \frac{1}{2} + z) + (0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0)$. It should be noted that the calculated structure amplitudes listed in Table I[18] are based on the inclusion of only those symmetry elements which are not related by the C centering and hence are scaled to 0.5 times the true values.

Determination of the Structure. The solution of the structure, which required the location of one molecule as the independent unit, was accomplished by heavy-atom techniques. A Fourier synthesis,[19] phased on the location of the two iron atoms obtained from the interpretation of a three-dimensional Patterson map,[20] yielded initial coordinates for the phosphorus atom and for three carbon and three oxygen atoms. Two preliminary least-squares refinement cycles were performed on these atoms; the discrepancy factors at this stage were $R_1 = [\Sigma ||F_o| - |F_c|| / \Sigma |F_o|] \times 100 = 34.0\%$ and $R_2 = [\Sigma w_i ||F_o| - |F_c||^2 / \Sigma w_i |F_o|^2]^{1/2} \times 100 = 38.2\%$, using individual weights $w_i = 1/\sigma(F_o)^2$. All remaining nonhydrogen atoms were located by successive Fourier syntheses. The discrepancy factors at this stage were $R_1 = 20.4\%$ and $R_2 = 27.0\%$. It was at this time that the unexpected oxygen atom of the bridging hydroxide ligand was identified, on the basis of its intensity on the Fourier map, which was comparable to the intensities of the carbonyl oxygen atoms. The identity of this oxygen atom was subsequently further confirmed by the well-behaved nature of its temperature factor throughout the least-squares refinement, as well as by an oxygen analysis of the compound. The observ-

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ed infrared and nmr spectra could be interpreted equally well in terms of a bridging hydride or a bridging hydroxide ligand.

After all of the atoms had been located, the program MIRAGE[21] was used to calculate rigid-body parameters constraining the two six-carbon rings of the tolyl groups to an idealized D_{6h} geometry which was maintained throughout the subsequent least-squares refinement.[22] The rigid aryl groups also included ideal coordinates for the four hydrogen atoms. The methyl carbon atoms of the tolyl groups were allowed to refine independently. After three isotropic least-squares refinement cycles the discrepancy factors were $R_1 = 6.7\%$ and $R_2 = 8.1\%$. Three more cycles were performed with anisotropic thermal parameters for all iron, phosphorus, oxygen, and carbonyl carbon atoms. The tolyl carbon atoms were allowed to vary only isotropically, and the hydrogen atom thermal parameters were fixed at 6.0 Å^2. The discrepancy factors following the last cycle were $R_1 = 4.6\%$ and $R_2 = 5.4\%$; no parameter shifted by more than 0.12σ. A three-dimensional Fourier difference map at this stage revealed the location of the individual hydrogen atoms for both tolyl methyl groups. Three clearly defined peaks could be seen tetrahedrally disposed about atom C(20); however, four peaks were seen near C(13), among which no clear geometrical choice of the best three could be made. It is assumed that the hydrogens of this methyl group are approximately twofold disordered. A peak was also located corresponding to the hydrogen atom of the bridging hydroxide group, H(7), which lies very near the calculated "ideal" position for this hydrogen atom.[21]

All least-squares refinements were based on the minimization of $\Sigma w_i ||F_o| - |F_c||^2$. The atomic scattering factors used for all nonhydrogen atoms were those compiled by Hanson, *et al.*,[23] while those used for the hydrogen atoms were from Stewart, *et al.*[24] No corrections for anomalous dispersion were made.

The calculated and observed structure amplitudes obtained from the last cycle of the anisotropic–isotropic least-squares refinement are presented in Table I.[18] The positional and thermal parameters for all atoms are given in Table II. Interatomic distances and bond angles with estimated standard deviations, calculated with the Busing–Martin–Levy function and error program[25] from the full inverse matrix (with inclusion of the estimated uncertainties in the lattice parameters), are presented in Table III. Equations of least-squares planes along with distances of selected atoms from these planes and dihedral angles are listed in Table IV.[26]

Results

Description of the Molecular Structure. The compound $Fe_2(CO)_6[P(p\text{-}C_6H_4CH_3)_2]OH$ has the molecular structure depicted in Figure 1.[27] This overall geometry is typical of compounds of the general stoichiometry $Fe_2(CO)_6X_2$, where X is a bridging group; other structures of analogous compounds that have been defined by X-ray crystallographic studies include $Fe_2(CO)_6[P(C_6H_5)(CH_3)]_2$,[1,7] $Fe_2(CO)_6(SC_2H_5)_2$,[8] $[Fe_2(CO)_6SCH_3]_2S$,[28] $Fe_2(CO)_6[(C_6H_5N)_2CO]$,[29] $Fe_2(CO)_6(SCC_6H_5)_2$,[30] $Fe_2(CO)_6[HNC_6H_4NC_6H_5]$,[31] $Fe_2(CO)_6[NHN{=}C(p\text{-}C_6H_4CH_3)_2]_2$,[32] $Fe_2(CO)_6[N{=}C(p\text{-}C_6H_4CH_3)_2]_2$,[33] $Fe_2(CO)_6[(CH_3N)_2CO]$,[34] $Fe_2(CO)_6(NH_2)_2$,[35,36] and $Fe_2(CO)_6(AsCH_3)_4$.[37] The present compound differs from others whose structures have been determined in that two different bridging atoms are involved. The $Fe_2(CO)_6(PR_2)OH$ species are not the first reported examples of such compounds, however; the compound $Fe_2(CO)_6[P(C_6H_5)_2]SC_6H_5$ was reported in 1966.[38]

Like other molecules of this type, the $Fe_2(CO)_6[P(p\text{-}C_6H_4CH_3)_2]OH$ molecule may be regarded as being composed of two tetragonal pyramids which are joined along one basal edge. In this case, the four basal positions of each tetragonal pyramid are occupied by a phosphorus and an oxygen atom (along the edge which joins the two pyramids) and by two carbonyl groups; each apical position is occupied by a third carbonyl group. The dihedral angle between the plane defined by Fe(1), P, and O(7) and that defined by Fe(2), P, O(7) is 75.8° and is smaller than the corresponding angles reported for other $Fe_2(CO)_6X_2$ species, which range from 78.1 to 95.2°.[35] The two iron atoms are displaced above the mean plane of the basal oxygen, phosphorus, and carbonyl carbon atoms by a 0.35 [Fe(1)] and 0.34 Å [Fe(2)]. These values may be compared with average displacements of 0.34 Å in $Fe_2(CO)_6(NH_2)_2$,[35] 0.36 Å in $[Fe_2(CO)_6SCH_3]_2S$,[28] and 0.38 Å in $Fe_2(CO)_6(SC_2H_5)_2$.[8] These pyramidal deformations have been attributed to nonbonding intramolecular repulsions between the apical and equatorial ligands which bend the equatorial ligands downward.[28]

Although all the atoms of the $Fe_2(CO)_6[P(p\text{-}C_6H_4CH_3)_2]OH$ molecule lie in general positions, the molecule possesses approximate C_s symmetry, with the mirror plane defined as perpendicular to the iron–iron axis and passing nearly through the bridging phosphorus and oxygen atoms. This mirror plane is nearly parallel with the plane of one tolyl group [C(14)→C(19)] and perpendicular to the plane of the other tolyl group [C(7)→C(12)]. The dihedral angles between the approximate C_s plane and these groups are 2.1 and 89.2°, respectively; the dihedral angle between the planes of the two tolyl groups is 90.5°.

The Fe–Fe bond distance of 2.511 (2) Å is of about average length, compared to Fe–Fe bond distances found in other $Fe_2(CO)_6X_2$ type complexes, which range from 2.40 to 2.664 Å.[8,28–37] The experimentally equivalent Fe–P bond distances of 2.236 (3) and 2.239 (3) Å are also of average length, compared to the Fe–P bond lengths found in a variety of other phosphine- and phosphide-iron carbonyl complexes, which range from 2.215 to 2.303 Å.[39–43] No Fe–O bond distances have been reported for low-valent iron complexes, but the experimentally equivalent Fe–O distances of 1.974 (6) and 1.969 (6) Å observed in $Fe_2(CO)_6[P(p\text{-}C_6H_4CH_3)_2]OH$ are within the range of the Fe–O distances reported for three iron(III) complexes (1.95–2.04 Å).[44–46] The fact that the

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Table II

Final Atomic Parameters[a]

	x	*y*	*z*	*B*, Å^2
Fe(1)	−0.0697 (1)	0.0650 (1)	0.6119 (1)	*b*
Fe(2)	0.1678 (1)	0.0626 (1)	0.6100 (1)	*b*
P	0.0357 (2)	0.1608 (2)	0.5768 (1)	*b*
O(1)	−0.3313 (8)	0.0751 (5)	0.5436 (3)	*b*
O(2)	−0.0887 (8)	−0.0707 (6)	0.6860 (4)	*b*
O(3)	−0.1328 (8)	0.1583 (6)	0.7042 (4)	*b*
O(4)	0.3670 (9)	0.0704 (6)	0.5381 (4)	*b*
O(5)	0.2481 (9)	−0.0743 (5)	0.6819 (4)	*b*
O(6)	0.3228 (8)	0.1502 (5)	0.7020 (4)	*b*
O(7)	0.0250 (5)	0.0073 (4)	0.5611 (2)	*b*
C(1)	−0.2285 (12)	0.0697 (6)	0.5696 (4)	*b*
C(2)	−0.0802 (10)	−0.0209 (8)	0.6555 (5)	*b*
C(3)	−0.1076 (10)	0.1224 (7)	0.6670 (5)	*b*
C(4)	0.2885 (11)	0.0661 (6)	0.5641 (5)	*b*
C(5)	0.2148 (10)	−0.0241 (7)	0.6524 (5)	*b*
C(6)	0.2605 (10)	0.1178 (7)	0.6652 (5)	*b*
C(7)[c]	0.0010	0.1770	0.4998	3.6 (2)
C(8)[c]	−0.1265	0.1874	0.4714	4.2 (2)
C(9)[c]	−0.1521	0.2077	0.4136	4.9 (2)
C(10)[c]	−0.0503	0.2176	0.3841	4.9 (2)
C(11)[c]	0.0772	0.2073	0.4124	4.9 (2)
C(12)[c]	0.1029	0.1869	0.4703	4.4 (2)
C(13)	−0.0798 (10)	0.2419 (6)	0.3193 (5)	6.1 (3)
C(14)[c]	0.0507	0.2580	0.6060	3.7 (2)
C(15)[c]	0.0309	0.3223	0.5696	4.0 (2)
C(16)[c]	0.0409	0.3973	0.5924	4.7 (2)
C(17)[c]	0.0707	0.4080	0.6516	4.8 (2)
C(18)[c]	0.0905	0.3437	0.6880	4.7 (2)
C(19)[c]	0.0805	0.2687	0.6652	4.1 (2)
C(20)	0.0793 (10)	0.4919 (6)	0.6766 (4)	5.5 (2)
H(8)[c]	−0.2055	0.1796	0.4943	
H(9)[c]	−0.2510	0.2157	0.3916	
H(11)[c]	0.1562	0.2150	0.3896	
H(12)[c]	0.2017	0.1789	0.4923	
H(15)[c]	0.0077	0.3140	0.5237	
H(16)[c]	0.0255	0.4471	0.5642	
H(18)[c]	0.1136	0.3520	0.7339	
H(19)[c]	0.0959	0.2189	0.6934	
H(7)[d]	0.0417	0.0188	0.5375	
H(13-1)[d]	−0.0917	0.1941	0.3022	
H(13-2)[d]	−0.0543	0.2935	0.3233	
H(13-3)[d]	−0.0009	0.2337	0.3071	
H(13-4)[d]	−0.1750	0.2313	0.3098	
H(20-1)[d]	0.1083	0.5264	0.6520	
H(20-2)[d]	−0.0083	0.5091	0.6891	
H(20-3)[d]	0.1722	0.4938	0.7011	

Anisotropic Temperature Factors[b]

	$10^5\beta_{11}$	$10^5\beta_{22}$	$10^5\beta_{33}$	$10^5\beta_{12}$	$10^5\beta_{13}$	$10^5\beta_{23}$
Fe(1)	941 (18)	407 (7)	120 (3)	−47 (9)	50 (6)	16 (4)
Fe(2)	921 (18)	380 (7)	120 (3)	42 (9)	54 (6)	11 (4)
P	931 (31)	395 (12)	97 (5)	2 (16)	40 (10)	9 (7)
O(1)	1386 (102)	893 (56)	308 (23)	−242 (66)	−131 (41)	135 (27)
O(2)	2364 (137)	684 (49)	359 (25)	59 (68)	375 (47)	216 (28)
O(3)	1796 (111)	911 (52)	264 (22)	−22 (60)	276 (40)	−176 (28)
O(4)	1883 (112)	965 (58)	338 (23)	377 (70)	500 (46)	169 (29)
O(5)	2206 (129)	547 (44)	346 (24)	−47 (61)	−164 (43)	194 (26)
O(6)	1604 (109)	716 (47)	271 (21)	−144 (54)	−69 (39)	−142 (25)
O(7)	1082 (82)	463 (32)	156 (14)	−48 (40)	59 (26)	−38 (17)
C(1)	1464 (158)	492 (54)	167 (25)	−220 (87)	43 (53)	48 (31)
C(2)	1151 (144)	584 (64)	212 (29)	20 (76)	122 (50)	23 (35)
C(3)	1282 (141)	472 (53)	168 (25)	−94 (70)	106 (49)	24 (32)
C(4)	1273 (139)	452 (52)	189 (26)	96 (80)	1 (52)	62 (31)
C(5)	1103 (138)	475 (58)	205 (27)	−41 (72)	10 (49)	−5 (32)
C(6)	1189 (136)	457 (53)	166 (25)	110 (72)	91 (48)	22 (31)

[a] The estimated standard deviation in the last digit is given in parentheses in this and the following tables. [b] Of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$, used for these atoms; the resulting thermal coefficients were given with estimated standard deviations. [c] These individual atomic parameters are based on the refined rigid-body crystallographic coordinates for both tolyl rings which were based on the following model. Each ring was presumed to have D_{6h} symmetry with a C–C bond length of 1.398 Å and a C–H bond length of 1.085 Å. The origin of each ring was chosen at the center of the ring. An isotropic temperature factor was varied for each ring carbon atom, while for each ring hydrogen atom the isotropic temperature factor was fixed at 6.0 Å^2. The methyl atom of each tolyl group [C(13) and C(20)] was allowed to refine independently. H(8) is attached to C(8), H(9) to C(9), etc. [d] These hydrogen atoms were located on a three-dimensional Fourier difference map. H(7) is attached to O(7), H(13-1)–H(13-4) are attached to C(13), and H(20-1)–H(20-3) are attached to C(20). H(13-1), H(13-2), H(13-3), and H(13-4) represent those peaks which were resolved in this disordered methyl group.

Table III. Interatomic Distances and Bond Angles

A. Intramolecular Distances (Å)

Fe(1)-Fe(2)	2.511 (2)	O(5)-C(5)	1.128 (11)
Fe(1)-P	2.236 (3)	O(6)-C(6)	1.139 (11)
Fe(2)-P	2.239 (3)	P-C(7)	1.823
Fe(1)-O(7)	1.974 (6)	P-C(14)	1.810
Fe(2)-O(7)	1.969 (6)	C(10)-C(13)	1.572
Fe(1)-C(1)	1.787 (13)	C(17)-C(20)	1.559
Fe(1)-C(2)	1.824 (14)	O(7)-H(7)	0.837
Fe(1)-C(3)	1.749 (13)	C(13)-H(13-1)	0.918
Fe(2)-C(4)	1.826 (14)	C(13)-H(13-2)	0.929
Fe(2)-C(5)	1.819 (13)	C(13)-H(13-3)	0.942
Fe(2)-C(6)	1.763 (13)	C(13)-H(13-4)	1.003
O(1)-C(1)	1.147 (11)	C(20)-H(20-1)	0.927
O(2)-C(2)	1.137 (12)	C(20)-H(20-2)	1.063
O(3)-C(3)	1.149 (11)	C(20)-H(20-3)	1.042
O(4)-C(4)	1.124 (11)	O(7)· · ·P	2.670

B. Intermolecular Distances Less than 3.5 Å (Å)

O(7)-O(7)^{a}	2.868 (11)	O(5)-C(13)^{a}	3.386 (14)
O(1)-O(4)^{a}	3.152 (14)	O(6)-C(13)^{d}	3.400 (14)
O(1)-O(4)^{b}	3.158 (13)	O(5)-C(10)^{a}	3.419
O(3)-O(3)^{c}	3.213 (17)	O(3)-C(13)^{f}	3.436 (14)
O(5)-C(9)^{a}	3.258	O(2)-C(13)^{a}	3.457 (14)
O(2)-O(2)^{c}	3.267 (19)	O(4)-C(16)^{e}	3.469
O(3)-O(6)^{c}	3.269 (12)	O(4)-C(15)^{e}	3.491
O(6)-C(13)^{e}	3.353 (14)	H(7)-O(7)^{a}	2.427

C. Bond Angles (deg)

Fe(1)-P-Fe(2)	68.3 (1)	P-Fe(2)-O(7)	78.5 (2)
Fe(1)-O(7)-Fe(2)	79.1 (2)	P-Fe(2)-C(4)	102.7 (3)
Fe(2)-Fe(1)-P	55.9 (1)	P-Fe(2)-C(5)	154.6 (3)
Fe(2)-Fe(1)-O(7)	50.4 (2)	P-Fe(2)-C(6)	94.5 (3)
Fe(2)-Fe(1)-C(1)	145.3 (3)	O(7)-Fe(2)-C(4)	102.6 (4)
Fe(2)-Fe(1)-C(2)	99.4 (3)	O(7)-Fe(2)-C(5)	91.7 (4)
Fe(2)-Fe(1)-C(3)	113.0 (3)	O(7)-Fe(2)-C(6)	163.5 (4)
P-Fe(1)-O(7)	78.4 (2)	C(4)-Fe(2)-C(5)	102.2 (5)
P-Fe(1)-C(1)	103.5 (3)	C(4)-Fe(2)-C(6)	94.5 (5)
P-Fe(1)-C(2)	154.0 (3)	C(5)-Fe(2)-C(6)	88.5 (5)
P-Fe(1)-C(3)	93.6 (3)	Fe(2)-C(4)-O(4)	176.2 (10)
O(7)-Fe(1)-C(1)	101.8 (4)	Fe(2)-C(5)-O(5)	174.8 (10)
O(7)-Fe(1)-C(2)	91.8 (4)	Fe(2)-C(6)-O(6)	176.7 (10)
O(7)-Fe(1)-C(3)	163.2 (4)	P-C(7)-C(8)	120.0
C(1)-Fe(1)-C(2)	102.0 (5)	P-C(7)-C(12)	119.7
C(1)-Fe(1)-C(3)	94.4 (5)	P-C(14)-C(15)	120.2
C(2)-Fe(1)-C(3)	89.1 (5)	P-C(14)-C(19)	119.8
Fe(1)-C(1)-O(1)	177.4 (11)	C(7)-P-C(14)	103.4
Fe(1)-C(2)-O(2)	174.7 (11)	C(7)-P-Fe(1)	118.0
Fe(1)-C(3)-O(3)	178.1 (10)	C(7)-P-Fe(2)	123.6
Fe(1)-Fe(2)-P	55.8 (1)	C(14)-P-Fe(1)	117.8
Fe(1)-Fe(2)-O(7)	50.5 (2)	C(14)-P-Fe(2)	124.0
Fe(1)-Fe(2)-C(4)	144.8 (3)	C(9)-C(10)-C(13)	119.6
Fe(1)-Fe(2)-C(5)	99.9 (3)	C(11)-C(10)-C(13)	120.4
Fe(1)-Fe(2)-C(6)	113.2 (3)	C(16)-C(17)-C(20)	119.6
		C(18)-C(17)-C(20)	120.4

$^{a-f}$ The distances are given from the indicated atoms in one molecule to those in another molecule related by the following symmetry transformations: ^{a} $-x, -y, 1-z$; ^{b} $-1+x, y, z$; ^{c} $-x, y, 3/2-z$; ^{d} $1/2+x, 1/2-y, 1/2+z$; ^{e} $1/2-x, 1/2-y, 1-z$; ^{f} $-1/2-x, 1/2-y, 1-z$.

bridging phosphorus and oxygen atoms are nearly equidistant from both iron atoms is a manifestation of the near-C_s symmetry of the molecule. The angle between the Fe(1)-Fe(2) axis and the P-O(7) axis is 89.8°.

The Fe-C bond lengths, varying from 1.749 to 1.825 Å, are typical of the values previously observed in iron carbonyl complexes, which range from 1.61 to 1.873 Å.[8,28-43] Interestingly, the Fe-C distances reflect significant trans influence in that the Fe-carbonyl distances trans to the bridging hydroxide ligand [av 1.756 (13) Å] are much shorter than the other Fe-C distances [av 1.814 (14) Å]. A similar effect was noted by us in another system.[47] The C-O bond lengths range from 1.124 (11) to 1.149 (11) Å and are typical of the values observed in metal carbonyl complexes. The Fe-CO systems are all essentially linear, with the Fe-C-O angles ranging from 174.7 (11) to 178.1 (10)°.

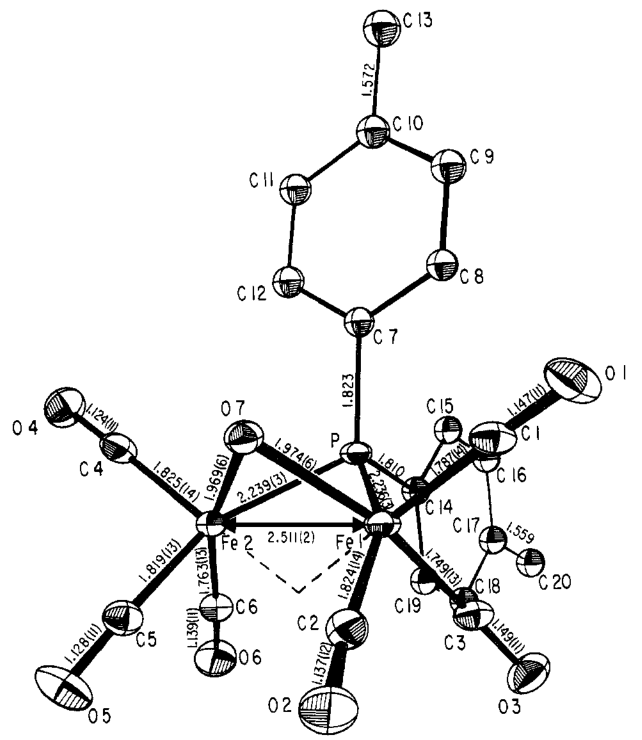

Figure 1. Molecular configuration of $Fe_2(CO)_6[P(p\text{-}C_6H_4CH_3)_2]OH$.

The ligand-iron-ligand bond angles about the iron atoms range from 78.5 (2) to 103.5 (3)°. The acute P-Fe-O(7) bond angles [78.5 (2)°] seem to be typical of such angles in bridged systems containing a metal-metal bond and may be compared with (bridging ligand)-(metal)-(bridging ligand) angles ranging from 65 to 80.9° in other $Fe_2(CO)_6X_2$ complexes.[8,28-37]

The Fe(1)-P-Fe(2) angle [68.3 (1)°] and the Fe(1)-O(7)-Fe(2) angle [79.1 (2)°] are both much smaller than the tetrahedral angle of 109.5°; this distortion from the tetrahedral angle is a result of geometrical constraints imposed by the iron-iron bond. Corresponding (metal)-(bridging ligand)-(metal) angles range from 67.4 to 80.5° in other $Fe_2(CO)_6X_2$ complexes.[8,28-37] The fact that the Fe(1)-O(7)-Fe(2) bond angle is greater than the Fe(1)-P-Fe(2) bond angle is a natural consequence of the shorter Fe-O bond distance, given the constant iron-iron distance. The distortions imposed by the small Fe(1)-P-Fe(2) bond angle are further reflected in the other bond angles about the phosphorus. Although the C(7)-P-C(14) angle of 103.4° is slightly smaller than the tetrahedral angle, the Fe-P-C bond angles range from 117.8 to 124.0° with a mean value of 120.8°, somewhat larger than the tetrahedral angle. The P-C bond lengths of 1.823 and 1.810 Å are normal.

Crystal Packing and Intermolecular Forces. A [010] projection of the monoclinic cell of $Fe_2(CO)_6[P(p\text{-}C_6H_4CH_3)_2]$-OH is shown in Figure 2.[27] An examination of the intermolecular distances (which are included in Table III) shows that the crystal packing is determined primarily by van der Waals and hydrogen-bonding interactions. It is noteworthy that the distance between the bridging oxygen atoms of adjacent, centrosymmetrically related molecules is 2.868 (11) Å, indicative of a substantial, hydrogen-bonding interaction between the bridging hydroxide ligands. The O(7)-H(7)-O(7)′ angle is 113.7°. It may also be noted that several of the carbonyl oxygen atoms are closely approached by tolyl group carbon

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Table IV. Equations of Best Least-Squares Planes, Distances of Selected Atoms from These Planes, and Dihedral Angles between These Planes[a,b]

A. Equations of Planes and Distances (Å) of Selected Atoms from These Planes

(a) Plane through Fe(1), Fe(2), P $0.023X + 0.432Y + 0.902Z - 13.313 = 0$

(b) Plane through Fe(1), Fe(2), O(7) $0.001X + 0.768Y - 0.640Z + 8.312 = 0$

(c) Plane through Fe(1), Fe(2), C(1), O(1), C(4), O(4) $0.013X + 0.996Y + 0.091Z - 2.355 = 0$

Fe(1)	−0.01	O(1)	−0.01
Fe(2)	−0.00	C(4)	−0.02
C(1)	0.02	O(4)	−0.01

(d) Plane through Fe(1), Fe(2), C(2), O(2), C(5), O(5) $0.029X + 0.585Y + 0.81Z - 12.149 = 0$

Fe(1)	−0.01	O(2)	−0.03
Fe(2)	−0.02	C(5)	0.04
C(2)	0.04	O(5)	−0.02

(e) Plane through Fe(1), Fe(2), C(3), O(3), C(6), O(6) $0.013X + 0.809Y - 0.587Z + 7.527 = 0$

Fe(1)	−0.02	O(3)	0.00
Fe(2)	0.00	C(6)	0.02
C(3)	0.01	O(6)	−0.02

(f) Plane through C(7), C(8), C(9), C(10), C(11), C(12) $0.006X + 0.968Y + 0.250Z - 5.868 = 0$

P	−0.18	C(13)	−0.03

(g) Plane through C(14), C(15), C(16), C(17), C(18), C(19) $0.999X + 0.013Y - 0.039Z + 2.648 = 0$

P	−0.02	C(20)	−0.02

(h) Plane through P, O(7), C(2), C(3) $0.785X - 0.033Y + 0.618Z - 6.453 = 0$

P	−0.08	C(2)	−0.09
O(7)	0.09	C(3)	0.09
Fe(1)	0.35		

(i) Plane through P, O(7), C(5), C(6) $0.763X + 0.017Y - 0.646Z + 10.256 = 0$

P	−0.08	C(5)	−0.09
O(7)	0.08	C(6)	0.08
Fe(2)	0.34		

(j) Plane Perpendicular to and Bisecting the Fe(1)–Fe(2) Axis[c] $1.000X - 0.017Y - 0.018Z + 2.458 = 0$

Fe(1)	−1.255	Fe(2)	1.255
O(7)	−0.003	P	0.004
C(1)	−2.725	C(4)	2.747
C(2)	−1.552	C(5)	1.570
C(3)	−1.938	C(6)	1.948
O(1)	−3.683	O(4)	3.699
O(2)	−1.775	O(5)	1.792
O(3)	−2.393	O(6)	2.418
C(7)	−0.001	C(14)	−0.014
C(8)	−1.209	C(15)	−0.065
C(9)	−1.205	C(16)	−0.092
C(10)	0.008	C(17)	−0.016
C(11)	1.216	C(18)	−0.016
C(12)	1.212	C(19)	−0.011
C(13)	0.003	C(20)	−0.121

B. Dihedral Angles (deg) between Normals to Planes

a and b	75.8	c and e	138.8	b and c	135.0	f and g	90.5
a and c	59.2	c and j	89.7	b and d	86.0	f and j	89.2
a and d	10.2	d and e	89.9	b and e	3.9	h and j	2.1
a and e	79.6	d and j	90.3	b and j	90.0	h and i	101.5
a and j	90.0	e and j	89.4	c and d	49.0		

C. Dihedral Angles (deg) between Selected Interatomic Vectors and Selected Planes

Fe(1)–C(1) and plane h	85.4	Fe(2)–C(4) and plane i	85.7

[a] The equations of the planes are given in an orthogonal angstrom coordinate system (X, Y, Z) which is related to the fractional coordinates (x, y, z) of the monoclinic unit cell by the transformation $X = ax + cz \cos\beta$, $Y = by$, $Z = cz \sin\beta$. [b] Unit weights were used for all atoms in the application of the Smith least-squares planes program. [c] This is the approximate C_s mirror plane of the $Fe_2(CO)_6[P(p\text{-}C_6H_4CH_3)_2]OH$ molecule.

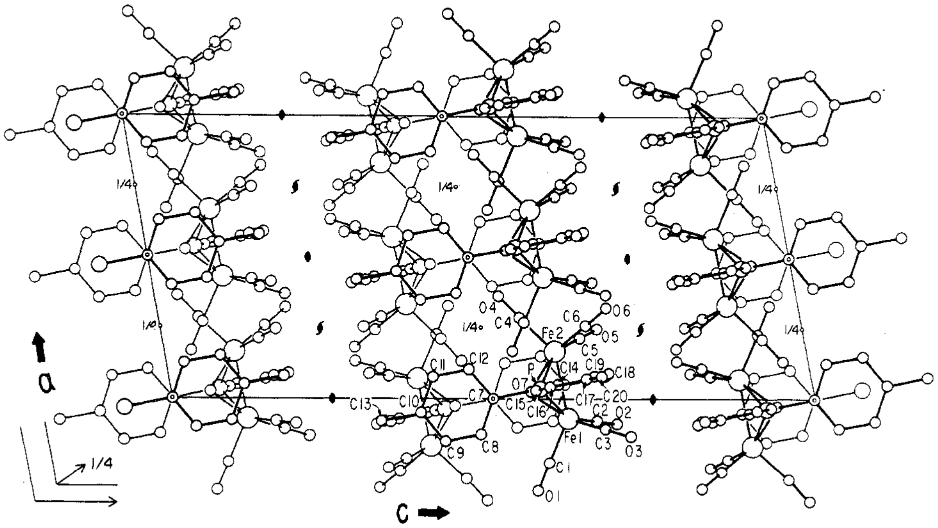

Figure 2. [010] projection showing the eight $Fe_2(CO)_6[P(p\text{-}C_6H_4CH_3)_2]OH$ molecules in the monoclinic unit cell of symmetry $C2/c$.

atoms, indicating the possibility of interactions between the aromatic or methyl hydrogen atoms and the oxygen atoms of the carbonyl groups.

As can be seen in Figure 2, the effect of the hydrogen bonding between the bridging hydroxide ligands on the packing of $Fe_2(CO)_6[P(p\text{-}C_6H_4CH_3)_2]OH$ is to arrange the molecules in closely spaced, centrosymmetrically related pairs, which are in turn arrayed on end in the *ab* plane (due to the *c* centering imposed by the space group) to form "sheets" of molecules.

Discussion

The characterization of this compound as $Fe_2(CO)_6[P(p\text{-}C_6H_4CH_3)_2]OH$, rather than as the bridging hydrido complex as originally suggested,[1] was a disappointment, in that it denied us the possibility of evaluating the bonding in bridging hydrides. Nonetheless, the structure itself proved interesting in a number of ways.

Following the preliminary crystallographic evidence for the bridging oxygen atom, we were able to verify its presence through an oxygen analysis. The presence of an OH group was also suggested by infrared evidence; a weak peak (easily overlooked) at 3552 cm^{-1} was assigned to ν_{OH}. The pmr spectrum, which originally had appeared as primary evidence for a hydridic group, could be interpreted only by the reassignment of the peak at quite high field, τ 12.86 in the title compound, to the proton bonded to oxygen. Whether this assignment is reasonable or not is unknown since, remarkably, no proton resonance associated with a hydroxide group bridging metal carbonyl groups has been recorded. The N-H proton resonances have been identified in several complexes with nitrogen bridging groups;[32] these appear at positions which are not out of the ordinary, falling between τ 3.3 and 5.5.

The origin of a hydroxide-bridged complex in this reaction system remains obscure in that the source of the oxygen atom is not known. We are inclined to favor the mechanism postulated by us earlier[1] for the initial steps in this reaction, that is, deprotonation of the secondary phosphine complexes, followed by its reaction with $Fe_2(CO)_9$ to give $Li[(CO)_4FePR_2Fe(CO)_4]$. The next step, incorporation of the oxygen, might well arise from molecular oxygen although standard procedures for reaction under nitrogen were employed; alternatively, the source of the oxygen could be a carbonyl group. Such a proposal has some precedent.[48]

A large number of transition-metal hydroxide complexes have been reported, and their properties, and the properties of hydroxide ion as a ligand, have been reviewed.[49] However, comparatively few hydroxide complexes of metal carbonyl compounds and other low-valent metal complexes are known. These include the following reported species: $M_2(CO)_6(OH)_3{}^{3-}$ and related protonated species (M = Cr,[50,51] Mo,[52] W[53]), $W_3(CO)_9(OH)_2(H_2O)H_4$,[52] $W_2(CO)_6(OH)_2(CH_3OH)_2{}^{4-}$,[51] $W_3(CO)_9(OH)(OCH_3)(CH_3OH)^{3-}$,[54] $Re_2(CO)_8(O)(OH)^-$,[51,55] and $RuH(OH)(CO)[p\text{-}CNC_6H_4CH_3][P(C_6H_5)_3]_2$.[56] In addition, X-ray crystal structure studies have been reported for the compounds $K_3[W_2(CO)_6(OH)_3]\cdot H_2O$,[57] $[Mo(OH)(CO)_2NO]_4\cdot 4OP(C_6H_5)_3$,[58] and $[(C_5H_5)_2Co_2[P(C_6H_5)_2]_2OH]PF_6$.[59] The compounds $Fe_2(CO)_6[PR_2]OH$[1] are the first iron carbonyl complexes containing a hydroxide ligand to be reported.

An abundance of low-valent complexes with various sulfur, phosphorus, and chlorine ligands, and with ligands derived from the lower congeners in these groups, is known. Species utilizing the second period elements nitrogen, oxygen, and fluorine in analogous ligand groups are, nonetheless, quite rare although recent efforts have made the differences somewhat less striking. As one can see no obvious reason for nonexistence or instability of such species, it is reasonable to assume that further work will narrow this distinction still further.

It seems likely that the scarcity of metal carbonyl complexes containing bridging nitrogen and oxygen ligands stems, at least in part, from the fact that effective general methods for synthesizing them have not been discovered. For instance, sulfur-bridged complexes can be made by reacting metal carbonyls with complexes containing S-S bonds; however, peroxides are powerful oxidizing agents and destroy metal carbonyl complexes. Phosphorus-bridged complexes can arise in some instances from the interaction of metal carbonyl anions with compounds containing phosphorus-halogen bonds; however, compounds containing nitrogen or oxygen bonded to a halogen are not commonly available as reagents. Finally, a hydroxide ion, in the presence of a metal carbonyl complex, will probably attack the electrophilic site of the carbonyl carbon atom, rather than coordinate to the metal. Thus, low-valent metal complexes with nitrogen- or oxygen-bridging ligands must often be made by less direct methods.

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Registry No. $Fe_2(CO)_6[P(p\text{-}C_6H_4CH_3)_2]OH$, 41735-99-3; $Fe(CO)_4[P(p\text{-}C_6H_4CH_3)_2H]$, 41699-87-0.

Supplementary Material Available. Table I, a listing of structure amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-2908.

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