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Synthesis, Characterization, and X-Ray Structure of Confacial-Bioctahedral Iron(II)- and Cobalt(II)-Hydrido Complexes with Tridentate Tripod Ligands Containing Phosphorus and Arsenic as the Donor Atoms

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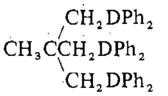
Received August 14, 1974		AIC405774

The dimeric hydrido complexes of iron(II) and cobalt(II) having the formula $[M_2H_3L_2]X$, where L is 1,1,1-tris(diphenylphosphinomethyl)ethane (p_3) or 1,1,1-tris(diphenylarsinomethyl)ethane (as_3) and X is PF_6 or BPh_4, have been prepared and characterized. The iron complexes are diamagnetic whereas the cobalt complexes have a magnetic moment corresponding to two unpaired electrons per molecule. The structures of the complexes $[Fe_2H_3(p_3)_2]PF_6\cdot1.5CH_2Cl_2$ and $[Co_2H_3(as_3)_2]BPh_4$ were determined by X-ray analyses using diffractometer data. Both cations have the structure $[LMH_3ML]^+$ (L = p_3, as_3; M = Fe, Co) with confacial-bioctahedral geometry. The shared face of the two octahedrons consists of three hydrogen atoms which bridge the gap between the two metal atoms. Each metal is bound to the three phosphorus or arsenic atoms of the ligand. The short Fe–Fe [2.332 (3) Å] and Co–Co [2.377 (8) Å] distances suggest that multiple metal–metal bonds may be present.

Introduction

The tripod ligands 1,1,1-tris(diphenylphosphinomethyl)ethane (p_3) and 1,1,1-tris(diphenylarsinomethyl)ethane (as_3)



$$CH_3C(CH_2DPh_2)_3$$

p_3: D = P
as_3: D = As

(the latter first synthetized in this laboratory) have been used to prepare complexes with 3d metals in oxidation states from 0 to +2.[1-11] The ligand p_3 has been found to function as bidentate or tridentate, and complexes with iron, cobalt, and nickel have been described, the metal having four-, five-, or six-coordinate stereochemistry.

The p_3 ligand reacts with cobalt(II) or nickel(II) halides in the presence of $NaBH_4$ to form the monovalent complexes $M(p_3)X$ (X = Cl or Br).[9] The $M(p_3)I$ complexes are obtained simply by the reaction of p_3 with the nickel(II) and cobalt(II) iodides. Possibly the reducing agent is the ligand p_3 which may form an iodide of pentavalent phosphorus. An X-ray structural analysis of $Ni(p_3)I$ derivative has shown this complex to have a distorted tetrahedral geometry.[12] The related four-coordinated complexes $Ni(as_3)X$ (X = Br or I) have also been previously described.[10]

When iron(II) or cobalt(II) salts react with p_3 in the presence of $NaBH_4$ and bulky anions such as BPh_4^- or PF_6^-, hydrides of the formula $[M_2H_3(p_3)_2]Y$ (M = Fe, Co; Y = BPh_4, PF_6), containing the metal in the formal oxidation state +2, are obtained. With the ligand as_3 only the cobalt(II) hydride $[Co_2H_3(as_3)_2]BPh_4$ could be prepared.

The complexes have been characterized by their electronic, infrared, and nmr spectra and by magnetic measurements. Complete X-ray structural analyses have been carried out for the compounds $[Fe_2H_3(p_3)_2]PF_6\cdot1.5CH_2Cl_2$ and $[Co_2H_3(as_3)_2]BPh_4$.

A preliminary account of part of this work has already been published.[13]

Results and Discussion of the Chemistry

When a solution of p_3 and an iron salt (halides, tetrafluoroborate, perchlorate) in methylene chloride–alcohol, at room temperature, is allowed to react with sodium tetrahydroborate, an intense blue coloration is obtained. Upon addition of $NaBPh_4$ [or $((n\text{-}Bu)_4N)PF_6$] dark blue crystals of the composition $[Fe_2H_3(p_3)_2]Y\cdot x$(solvent) are precipitated. If the same reaction is carried out with the corresponding cobalt(II) halides, the monovalent metal complexes $Co(p_3)X$ are formed.[9] However when cobalt(II) salts of poorly coordinating anions, such as BF_4^-, are used and the reaction is carried out in alcohol–ethyl ether (or alcohol–tetrahydrofuran) at 0°, a cherry red solution is obtained from which the dark red complex $[Co_2H_3(p_3)_2]BPh_4\cdot x$(solvent) may be precipitated.

Table I. Analytical Data for the Complexes

Compd	% calcd				% found			
	C	H	M	P (As)	C	H	M	P (As)
$[Fe_2H_3(p_3)_2]PF_6 \cdot 1.5CH_2Cl_2$[a]	61.27	5.18	6.83	13.26	60.42	5.59	6.44	13.06
$[Fe_2H_3(p_3)_2]BPh_4 \cdot 2C_4H_8O$	75.24	6.49	6.14	10.22	75.40	6.80	6.15	10.20
$[Co_2H_3(p_3)_2]BPh_4 \cdot 2C_4H_8O$	74.99	6.46	6.46	10.18	75.27	6.57	6.45	9.67
$[Co_2H_3(as_3)_2]BPh_4$	65.18	5.21	6.03	23.02	64.72	5.48	5.80	22.60
$[Co(p_3)(CO)_2]BPh_4$	75.99	5.62	5.56	8.96	76.01	5.85	5.65	8.86
$[Co(as_3)(CO)_2]BPh_4$	67.60	5.00	4.95	18.88	67.70	5.02	4.90	18.71

[a] Cl: calcd, 6.50; found, 7.09.

Table II. Physical Properties of the Complexes

Compd	Color	μ_{eff},[a] BM	Λ_M, Ω cm^2 mol^{-1}		Absorption max, kK (ϵ_M for soln)
			b	*c*	
$[Fe_2H_3(p_3)_2]PF_6 \cdot 1.5CH_2Cl_2$	Dark blue	0		78	*c*: 12.4 (1700), 16.5 (990) *d*: 12,4, 16.5
$[Co_2H_3(p_3)_2]BPh_4 \cdot 2C_4H_8O$	Dark red	3.29	24		*b*: 8.7 (500), 15.4 sh, 20.0 (7210), 26.7 sh *d*: 9.1, 16.5 sh, 20.2, 26.7 sh
$[Co_2H_3(as_3)_2]BPh_4$	Mauve	3.17	25	44	*b*: 7.6 (343), 14.3 sh, 18.4 sh, 19.4 (7800), 286 sh *d*: 7.8, 13.9 sh, 19.6, 26.7 sh
$[Co(P_3)(CO)_2]BPh_4$	Orange	0	26	46	*c*: 23.5 sh *d*: 23.5 sh
$[Co(as_3)(CO)_2]BPh_4$	Red-orange	0	26	48	*c*: 23.5 sh *d*: 23.5 sh

[a] Measured at 293 K. [b] 1,2-Dichloroethane solution ($\Lambda_M = 21$ for Bu_4NBPh_4). [c] Nitroethane solution ($\Lambda_M = 90$ for Bu_4NPF_6; $\Lambda_M = 51$ for Bu_4NBPh_4). [d] Solid.

Table III. Volumetric Titration of H_2 Evolved by the Reaction $[M_2H_3L_2]Y$ + HCl(excess) at 60° in THF

Compd	Amt, μmol		H_2:2M ratio
	Compd	H_2 evolved	
$[Fe_2H_3(p_3)_2]BPh_4 \cdot 2C_4H_8O$	4.8	16.2	3.37
	8.6	23.2	2.71
$[Co_2H_3(p_3)_2]BPh_4 \cdot 2C_4H_8O$	4.6	13.7	2.97
	4.1	11.5	2.83
$[Co_2H_3(as_3)_2]BPh_4$	6.85	21.2	3.09
	7.1	21.4	3.01

No corresponding iron complex with as3 could be isolated, while with cobalt(II) salts (halides, tetrafluoroborate, perchlorate) the mauve compound $[Co_2H_3(as_3)_2]BPh_4$ is obtained.

Analyses and some physical data for the complexes are shown in Tables I and II. All the complexes are soluble in methylene chloride, 1,2-dichloroethane, acetone, nitroethane, and tetrahydrofuran. All the hydride compounds are stable in the solid state; in solution the iron compounds remain unchanged for many days while the cobalt complexes decompose appreciably even in inert-gas atmospheres.

All the compounds behave as 1:1 electrolytes in nitroethane and 1,2-dichloroethane solutions (Table II). The diffuse-reflectance spectra of the compounds are in all cases similar to the solution spectra (Table II) showing the hydride complexes remain unchanged in solutions. The spectra of the cobalt complexes $[Co_2H_3(p_3)_2]Y$ and $[Co_2H_3(as_3)_2]Y$ are similar to each other but show the expected spectrochemical shifts when substituting arsenic for phosphorus (Table II).

On treating the hydride compounds with an excess of concentrated hydrochloric acid, at 60° in THF solution, 3 mol of hydrogen is evolved per mole of complex (Table III), according to the reaction

$$[M_2H_3L_2]^+ + 3H^+ \rightarrow 2M^{2+} + 3H_2 + 2L$$

The presence of metal(II) species was confirmed by spectroscopic measurements of the final solution.

The salts of the cation $[Fe_2H_3(p_3)_2]^+$ are diamagnetic while the cobalt hydrides $[Co_2H_3(p_3)_2]BPh_4 \cdot 2THF$ and $[Co_2H_3(as_3)_2]BPh_4$ are paramagnetic with μ_{eff} values of 3.29 and 3.17 BM, respectively, for each dimeric entity, at room temperature. The dependence of $1/\chi$ on temperature is linear in the range 88–293 K for the $[Co_2H_3(as_3)_2]BPh_4$ complex, with a θ value of 0 K.

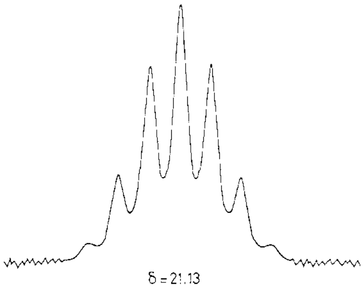


Figure 1. Hydride absorption in the nmr spectrum of $[Fe_2H_3(p_3)_2]BPh_4 \cdot 2THF$ complex (CD_2Cl_2 solution), at room temperature.

None of the hydride complexes show absorption bands in the 1700–2200-cm^{-1} region thereby indicating the absence of terminally bonded hydrogens. The infrared spectrum of $[Fe_2H_3(p_3)_2]PF_6 \cdot 1.5CH_2Cl_2$ shows an absorption band at 1048 cm^{-1} which shifts to 790 cm^{-1} in the deuterated compound. This band is assigned to the metal–hydride groups in which hydrogen is acting as a bridging ligand.[14]

The ^1H nmr spectra of the complexes $[Fe_2H_3(p_3)_2]Y$ in CD_2Cl_2, at room temperature, display a septet at δ +21.1 ppm (relative to TMS) with J_{PH} = 8.0 Hz (Figure 1). This septet band must be assigned to the hydrogen bound to the iron atom. At room temperature, the ^{31}P nmr spectra of the same compounds show a quartet band at δ +50.1 ppm (relative to H_3PO_4) with the same splitting as the proton septet. These data are in agreement with the presence of three magnetically equivalent hydridic hydrogens and six equivalent phosphorus atoms. Because the cobalt complexes are paramagnetic, their nmr spectra do not show any resonance which may be reasonably assigned to a hydrogen bound to the metal.

The two cobalt complexes react with carbon monoxide in hot methylene chloride solution to form carbonyl derivatives of the formula $[Co(CO)_2L]BPh_4$ (L = p3, as3). These two carbonyls are diamagnetic and 1:1 electrolytes in nitroethane. Their infrared spectra in CH_2Cl_2 solution show two very strong bands at 2030 and 1972 cm^{-1} for $[Co(CO)_2(p_3)]BPh_4$ and at

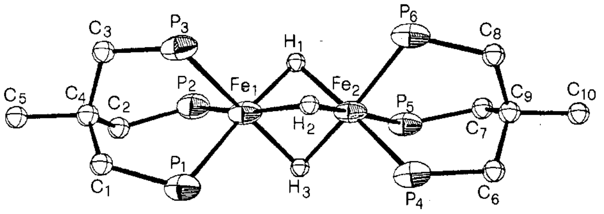


Figure 2. A perspective view of the skeleton of the $[Fe_2H_3(p_3)_2]^+$ cation (ORTEP diagram, showing 30% probability ellipsoids). (Isotropic *B* temperature factors of 2 and 1.5 Å^2 were assigned to carbon and hydrogen atoms, respectively, in the present and in the following diagrams.)

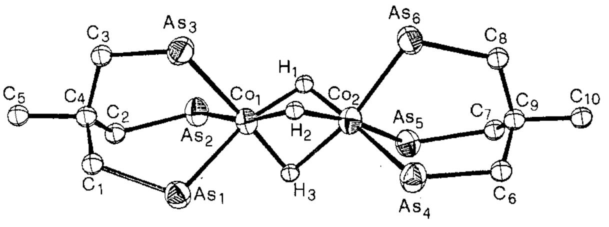


Figure 3. A perspective view of the skelton of the $[Co_2H_3(as_3)_2]^+$ cation.

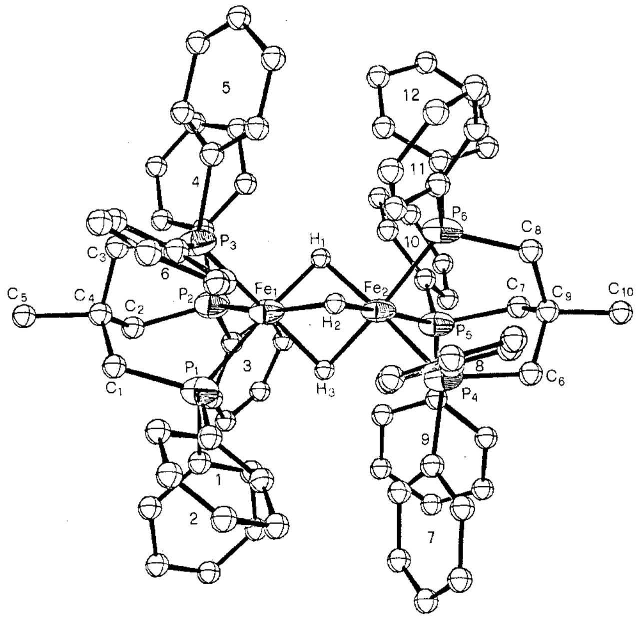


Figure 4. A perspective view of the $[Fe_2H_3(p_3)_2]^+$ cation. (Nonhydridic hydrogen atoms have been omitted in the present and in the following diagram.)

2020 and 1972 cm^{-1} for $[Co(CO)_2(as_3)]BPh_4$ and are consistent with two carbonyls cis coordinated to the cobalt. A similar coordination mode has been reported for the compound $[Ir(CO)_2(p_3)]BPh_4$ (ν_{CO} 2045, 1970 cm^{-1}).[15] The hydride complexes $[Fe_2H_3(p_3)_2]Y$ do not react with carbon monoxide in hot methylene chloride or 1,2-dichloroethane solutions.

Description and Discussion of the Structures

The structure of the iron complex consists of $[Fe_2H_3(p_3)_2]^+$ cations, PF_6^- anions, and interposed CH_2Cl_2 solvent molecules; the structure of the cobalt complex consists of $[Co_2H_3(as_3)_2]^+$ and BPh_4^- ions. The chromophores of both structures can be best described by two octahedra sharing a face having the three hydrogen atoms at the edges (Figures 2 and 3). Figures 4 and 5 show ORTEP diagrams of the two complex cations. Selected distances and angles of the two complexes are reported in Tables IV and V.

The three hydrogen atoms in the iron complex are not geometrically equivalent with respect to the six phosphorus atoms because each hydrogen has four phosphorus atoms in

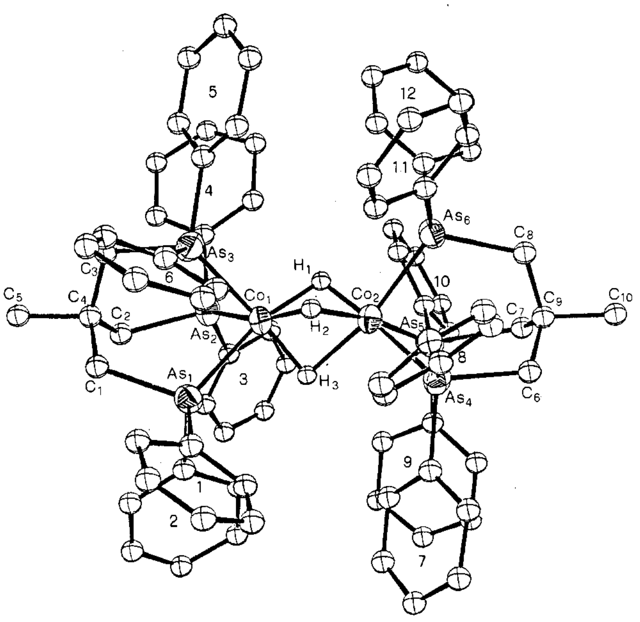


Figure 5. A perspective view of the $[Co_2H_3(as_3)_2]^+$ cation.

Table IV. Selected Distances (Å) and Angles (deg) in $[Fe_2H_3(p_3)_2]PF_6 \cdot 1.5CH_2Cl_2$

Distances			
Fe_1-Fe_2	2.332 (3)	Fe_2-H_3	1.83
Fe_1-P_1	2.218 (4)	C_1-C_4	1.58 (3)
Fe_1-P_2	2.212 (5)	C_2-C_4	1.54 (3)
Fe_1-P_3	2.207 (5)	C_3-C_4	1.56 (3)
Fe_2-P_4	2.232 (5)	C_4-C_5	1.46 (3)
Fe_2-P_5	2.235 (5)	C_6-C_9	1.57 (3)
Fe_2-P_6	2.220 (5)	C_7-C_9	1.53 (3)
Fe_1-H_1	1.87[a]	C_8-C_9	1.51 (3)
Fe_1-H_2	1.79	C_9-C_{10}	1.53 (3)
Fe_1-H_3	1.82	$P-C_{aliph}$(av)	1.80 (2)
Fe_2-H_1	1.94	$P-PhC_1$(av)	1.83 (2)
Fe_2-H_2	1.73	P-F(av)	1.49 (2)

Angles			
$P_1-Fe_1-P_2$	89.4 (2)	$P-Fe-H_{cis}$(av)	93.9
$P_1-Fe_1-P_3$	89.1 (2)	H-Fe-H(av)	83.6
$P_2-Fe_1-P_3$	88.0 (2)	$Fe-P-C_{aliph}$(av)	113.4 (7)
$P_4-Fe_2-P_5$	89.1 (2)	$Fe-P-PhC_1$(av)	120.1 (7)
$P_4-Fe_2-P_6$	88.9 (2)	$C-C-C_{aliph}$(av)	109.5 (16)
$P_5-Fe_2-P_6$	87.2 (2)	Fe-H-Fe(av)	79.3
$P-Fe-H_{trans}$(av)	173.1		

[a] Hydrogens from Δ*F* Fourier.

Table V. Selected Distances (Å) and Angles (deg) in $[Co_2H_3(as_3)_2]BPh_4$

Distances			
Co_1-Co_2	2.377 (8)	Co_2-H_3	1.78
Co_1-As_1	2.321 (7)	C_1-C_4	1.45 (5)
Co_1-As_2	2.338 (7)	C_2-C_4	1.55 (6)
Co_1-As_3	2.337 (6)	C_3-C_4	1.54 (5)
Co_2-As_4	2.338 (6)	C_4-C_5	1.57 (5)
Co_2-As_5	2.365 (7)	C_6-C_9	1.56 (6)
Co_2-As_6	2.369 (6)	C_7-C_9	1.53 (6)
Co_1-H_1	1.70[a]	C_8-C_9	1.51 (5)
Co_1-H_2	1.74	C_9-C_{10}	1.57 (5)
Co_1-H_3	1.58	$As-C_{aliph}$(av)	2.03 (4)
Co_2-H_1	1.57	$As-PhC_1$(av)	1.94 (3)
Co_2-H_2	1.84	$B-PhC_1$(av)	1.68 (6)

Angles			
$As_1-Co_1-As_2$	91.2 (2)	$As-Co-H_{cis}$(av)	97.2
$As_1-Co_1-As_3$	90.0 (2)	H-Co-H(av)	76.6
$As_2-Co_1-As_3$	88.5 (2)	$Co-As-C_{aliph}$(av)	111.8 (11)
$As_4-Co_2-As_5$	88.7 (2)	$Co-As-PhC_1$(av)	119.8 (10)
$As_4-Co_2-As_6$	89.3 (2)	$C-C-C_{aliph}$(av)	109.2 (30)
$As_5-Co_2-As_6$	87.2 (2)	Co-H-Co(av)	88.7
$As-Co-H_{trans}$(av)	168.1		

[a] Hydrogens from Δ*F* Fourier.

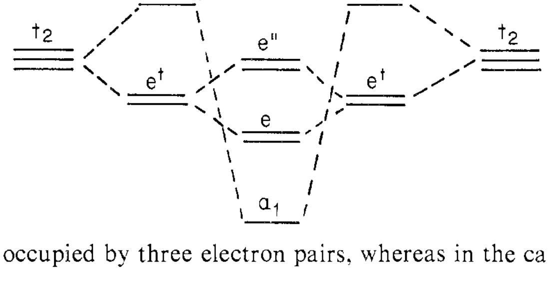
cis and two in trans positions. However the nmr spectra may be explained by an intramolecular rearrangement in solution which, at room temperature, is fast enough to make the hydrogen atoms appear equivalent. Such a result is analogous to that found in the other metal–hydrido complex μ-hydridobis[1,3-trimethylenebis(dicyclohexylphosphane)-nickel].[16,17]

The values of the cis angles P–Fe–H and As–Co–H are close to 90°, the trans angles P–Fe–H and As–Co–H are close to 180°, and the angles P–Fe–P and As–Co–As are close to 90°, all as expected for a confacial-bioctahedral geometry. The Fe–H distances are in the range 1.7–1.9 Å while the Co–H distances are in the range 1.6–1.8 Å. These values are in good agreement with those already reported in the literature for 3d metal-bridging hydrogen distances.[18]

Until now no structure of a complex with the ligand as$_3$ has been reported, whereas three structures of metal complexes with tripod triphosphines (p$_3$ and tep, where tep is 1,1,1-tris(diethylphosphinomethyl)ethane) have been determined, two of nickel(0),[8,11] and one of nickel(I).[12] These three complexes all have distorted tetrahedral geometries. For these complexes of nickel(0), [Ni(tep)NO]BF$_4$ and Ni(p$_3$)C$_2$F$_4$, and nickel(I), Ni(p$_3$)I, bond angles P–Ni–P from 92 to 97° and bond distances Ni–P from 2.21 to 2.28 Å have been found. The Fe–P distances and the P–Fe–P angles in the complex [Fe$_2$H$_3$(p$_3$)$_2$]PF$_6$·1.5CH$_2$Cl$_2$ are close to those found in the three tetrahedral complexes described above. However, although the inflexibility of the p$_3$ ligand does not allow much variation of the P–M–P angles, it appears significant that the angles found in the confacial-bioctahedral arrangement show a certain straightening of the ligand molecule with respect to the tetrahedral geometry (the average P–Fe–P angle is 88.6°). A similar value for the average As–Co–As angle (89.1°) has been found in [Co$_2$H$_3$(as$_3$)$_2$]BPh$_4$.

The metal–metal distances found in the two complexes [Fe$_2$H$_3$(p$_3$)$_2$]PF$_6$·1.5CH$_2$Cl$_2$ and [Co$_2$H$_3$(as$_3$)$_2$]BPh$_4$ (Fe–Fe = 2.332 (3) Å, Co–Co = 2.377 (8) Å) are among the shortest so far found in polynuclear complexes of iron and cobalt and indicate a marked metal–metal interaction.[19]

Room-temperature magnetic susceptibility measurements indicate that in the iron complex all electrons are paired whereas in the cobalt compound there are two unpaired electrons. This situation may be rationalized using the MO scheme previously proposed for the other confacial-bioctahedral complexes Fe$_2$(CO)$_9$ and Co$_2$(CO)$_8$.[19b] With the formation of M–P and M–H bonds the iron and cobalt atoms must have six and eight electrons, respectively, and each metal atom has three valence-shell orbitals remaining. The three valence-shell orbitals remaining on each metal atom correspond to triply degenerate t$_2$ orbitals of octahedral groups which are then split into e and a$_1$ orbitals under the trigonal field along the molecular axis. The assumption that the e^t and a$_1^t$ orbitals of one metal atom interact with those from the second metal atom gives three bonding and three antibonding orbitals as shown. In the case of [Fe$_2$H$_3$(p$_3$)$_2$]$^+$ the three bonding orbitals are occupied by three electron pairs, whereas in the case of the [Co$_2$H$_3$L$_2$]$^+$ complexes the two extra electrons occupy the degenerate antibonding e'' orbitals. This scheme gives an estimate of the metal–metal bond order of 3 for the iron compounds and of 2 for the cobalt compounds. However these bond orders seem in contrast to the actual metal–metal distances which are very similar for the cobalt and iron complexes. At this point it is useful to remember that (as previously pointed out by Cotton[20]) the metal–metal approach in metal atom clusters is more strongly influenced by the steric requirements of the ligand molecules than by the intrinsic character of the metal–metal bonding.



Experimental Section

The ligands p$_3$ and as$_3$ were prepared as described previously.[10,22] Reagent grade solvents were used throughout. All reactions were carried out under a nitrogen atmosphere except where stated otherwise.

Preparation of the Complexes. Fe$_2$H$_3$(p$_3$)$_2$Y·x(solvent) (Y = BPh$_4$, PF$_6$; solvent = CH$_2$Cl$_2$, C$_4$H$_8$O). A solution of NaBH$_4$ (1.5 mmol in 10 ml of ethanol) was added dropwise, with stirring, at room temperature, to the solution obtained by mixing p$_3$ in methylene chloride (1 mmol in 15 ml) and FeCl$_2$·6H$_2$O in 1-butanol (1 mmol in 10 ml). Solid NaBPh$_4$ (0.5 mmol) [or ((*n*-Bu)$_4$N)PF$_6$] was then added to the resultant blue solution. After stirring for an additional 10 min, the sodium halide was filtered off and a brisk stream of nitrogen passed through the solution at room temperature until sufficient methylene chloride had evaporated and crystallization initiated. The crystalline product was filtered into a glass sinter, washed with absolute ethanol, water, absolute ethanol, and light petroleum ether, and finally dried under a stream of nitrogen. The compound can be recrystallized from methylene chloride–1-butanol or THF–ligroin mixtures.

[Co$_2$H$_3$(p$_3$)$_2$]BPh$_4$·x(solvent) (solvent = THF). p$_3$ (1 mmol in 30 ml of ethyl ether) was added to a solution of Co(BF$_4$)$_2$·6H$_2$O (1 mmol in 10 ml of 1-butanol) and the resultant mixture cooled to 0°. NaBH$_4$ (1.5 mmol in 10 ml of absolute ethanol) was then added dropwise, with continuous stirring. A dark red cherry color developed immediately. Solid NaBPh$_4$ (0.5 mmol) was added to the solution and crystallization initiated as before. The crude compound was collected as for the previous iron complex and recrystallized from THF and ligroin.

[Co$_2$H$_3$(as$_3$)$_2$]BPh$_4$. The compound was obtained when CoCl$_2$·6H$_2$O, as$_3$, and NaBH$_4$ were allowed to react by the method used to prepare the [Fe$_2$H$_3$(p$_3$)$_2$]BPh$_4$·x(solvent) complex.

Deuterated Iron Derivatives. The compounds were prepared by the method used to prepare the corresponding hydrido derivatives, using FeCl$_2$·6D$_2$O and NaBD$_4$ as reagents and C$_2$H$_5$OD, CH$_2$Cl$_2$, and C$_4$H$_8$O as solvents.

[Co(CO)$_2$L]BPh$_4$ (L = p$_3$, as$_3$). A stream of CO was passed through a solution of [Co$_2$H$_3$L$_2$]BPh$_4$ (0.5 mmol in 50 ml of CH$_2$Cl$_2$), the color changing from cherry red to orange (30 min). To the filtered solution was added butyl ether (20 ml) and CH$_2$Cl$_2$ was evaporated at room temperature under a stream of N$_2$. The red-orange crystals which precipitated were filtered off, washed with petroleum ether, and dried under a stream of N$_2$.

Physical Measurements. Infrared and electronic spectra, conductivity measurements, and magnetic susceptibilities were all recorded by previously described methods.[21] The ^{1}H nmr spectra were recorded on a Varian DA-60, and the ^{31}P nmr spectra on a Varian 100.

Collection of X-Ray Data. [Fe$_2$H$_3$(p$_3$)$_2$]·1.5CH$_2$Cl$_2$. The crystals used for the X-ray determination were obtained by recrystallizing the compound from 1-butanol and methylene chloride in the cold. These crystals have a parallelepiped shape; particularly the crystal used for the data collection has approximate dimensions of 0.2 × 0.2 × 0.1 mm. The unit cell of the [Fe$_2$H$_3$(p$_3$)$_2$]PF$_6$·1.5CH$_2$Cl$_2$ complex in monoclinic, space group $P2/c$, with a = 22.669 (2) Å, b = 17.839 (2) Å, c = 20.106 (2) Å, β = 95.57 (1)°, V = 8092.3 Å^3, d_m = 1.33 g cm^{-3}, Z = 4, mol wt 1636.4, and d_c = 1.343 g cm^{-3}. Cell parameters were determined by least-squares refinement of 20 2θ values measured on a four-circle Hilger diffractometer with Mo Kα radiation (λ 0.7107 Å). The intensity data were collected using a θ–ω scan technique. Scans of 70 sec, with steps of 0.01° and a count of 1 sec for each step, were taken across the peaks; background was counted for 35 sec on each side of the peak. The intensities were calculated according to the expression $I = P - 0.5(T_p/T_b)(B_1 + B_2)$, where P is the peak count, B_1 and B_2 are the background counts, and T_p and T_b are the count

Table VI. Final Least-Squares Parameters[a]

(a) $[Fe_2H_3(p_3)_2]PF_6 \cdot 1.5CH_2Cl_2$

Atom	x	y	z	U_{11}[b] or U (Å^2)	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe_1	2869 (1)[c]	2566 (1)	4214 (1)	45 (2)	28 (1)	37 (2)	−3 (1)	−19 (1)	3 (1)
Fe_2	2317 (1)	2578 (1)	5134 (1)	45 (2)	30 (2)	42 (2)	−4 (2)	−19 (1)	0 (1)
P_1	2503 (2)	2767 (2)	3166 (2)	48 (3)	30 (3)	44 (3)	−3 (3)	−21 (3)	2 (2)
P_2	3382 (2)	1609 (3)	3872 (2)	50 (3)	32 (3)	44 (3)	−1 (3)	−19 (3)	4 (3)
P_3	3628 (2)	3293 (3)	4046 (2)	46 (3)	32 (3)	45 (3)	−3 (3)	−28 (3)	7 (3)
P_4	1403 (2)	3042 (3)	5140 (2)	47 (3)	45 (3)	53 (3)	−6 (3)	−15 (3)	−4 (3)
P_5	2038 (2)	1580 (3)	5698 (2)	58 (4)	38 (3)	48 (3)	−6 (3)	−18 (3)	4 (3)
P_6	2556 (2)	3120 (3)	6117 (2)	59 (4)	33 (3)	45 (3)	−3 (3)	−18 (3)	2 (3)
C_1	3047 (8)	2871 (10)	2594 (9)	47 (6)					
C_2	3628 (8)	1728 (10)	3035 (9)	48 (6)					
C_3	4029 (9)	3030 (11)	3333 (10)	57 (6)					
C_4	3689 (8)	2539 (11)	2781 (9)	47 (5)					
C_5	4029 (8)	2515 (12)	2198 (10)	58 (6)					
C_6	1049 (9)	2736 (12)	5843 (10)	67 (7)					
C_7	1757 (9)	1829 (12)	6459 (10)	60 (6)					
C_8	1930 (9)	3215 (12)	6584 (10)	59 (6)					
C_9	1470 (9)	2599 (12)	6500 (10)	60 (6)					
C_{10}	1079 (11)	2623 (14)	7078 (12)	99 (8)					
P_7	5000	170 (5)	2500	49 (6)	51 (5)	61 (5)	0	−9 (5)	0
P_8	0	722 (6)	7500	67 (6)	44 (5)	118 (5)	0	−23 (5)	0
F_1	4722 (10)	148 (15)	1820 (9)	230 (13)	419 (12)	87 (12)	51 (12)	−78 (12)	−56 (12)
F_2	4388 (8)	173 (9)	2739 (11)	106 (10)	153 (10)	276 (10)	−2 (10)	89 (10)	5 (10)
F_3	5000	−665 (14)	2500	209 (13)	61 (13)	432 (13)	0	87 (13)	0
F_4	5000	1012 (12)	2500	181 (12)	55 (11)	335 (11)	0	103 (11)	0
F_5	−29 (8)	72 (10)	7029 (9)	129 (11)	262 (10)	330 (10)	53 (10)	−74 (10)	−167 (10)
F_6	−44 (9)	1400 (11)	7083 (9)	125 (12)	333 (11)	505 (11)	−107 (11)	−107 (11)	282 (11)
F_7	676 (7)	717 (8)	7648 (10)	70 (10)	119 (9)	359 (9)	−14 (9)	−18 (9)	−12 (9)
Cl_1[d]	5000	4697 (7)	2500	117 (9)	157 (11)	157 (11)	0	−22 (8)	0
Cl_2[d]	4750 (6)	6255 (10)	2512 (12)	119 (11)	200 (12)	150 (12)	4 (12)	12 (10)	−47 (11)
Cl_3[d]	3355 (9)	2400 (10)	43 (11)	198 (11)	150 (12)	282 (12)	14 (12)	−6 (10)	95 (11)
Cl_4[d]	2342 (10)	2742 (12)	641 (7)	318 (12)	225 (12)	81 (11)	58 (11)	−19 (10)	5 (11)
Cl_5[d]	1693 (8)	2764 (12)	8849 (7)	193 (11)	314 (11)	96 (11)	−33 (10)	−17 (10)	−41 (11)
Cl_6[e]	698 (12)	2301 (15)	9503 (16)	153 (15)	109 (14)	177 (15)	−85 (14)	61 (15)	−54 (14)
Cl_7[e]	539 (11)	3533 (19)	8615 (14)	112 (18)	324 (20)	140 (19)	−103 (19)	91 (18)	−138 (19)
C_{83}[d]	2732 (27)	2278 (35)	282 (32)	137 (24)					
H_1[f]	315[g]	235	510	63					
H_2[f]	250	330	462	63					
H_3[f]	220	205	435	63					
H_1[h]	310 (6)	235 (8)	500 (7)	102 (23)					
H_2[h]	255 (6)	325 (8)	470 (7)	93 (21)					
H_3[h]	215 (6)	200 (8)	440 (7)	95 (22)					

(b) $[Co_2H_3(as_3)_2]BPh_4$

Atom	x	y	z	U_{11}[b] or U (Å^2)	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co_1	−3607 (4)	1927 (3)	3782 (1)	31 (3)	28 (3)	40 (4)	1 (3)	−1 (3)	6 (3)
Co_2	−3336 (4)	3207 (3)	3739 (1)	39 (3)	22 (3)	34 (4)	1 (3)	1 (3)	−1 (3)
As_1	−5108 (3)	1332 (2)	3639 (1)	36 (3)	31 (3)	42 (3)	−1 (2)	−2 (2)	−3 (2)
As_2	−2756 (3)	1038 (2)	3487 (1)	40 (3)	30 (3)	47 (3)	−1 (2)	5 (2)	−3 (2)
As_3	−3341 (3)	1223 (2)	4295 (1)	53 (3)	32 (3)	34 (3)	0 (2)	−4 (2)	6 (2)
As_4	−4344 (3)	3980 (2)	3370 (1)	44 (3)	28 (3)	41 (3)	−1 (2)	−4 (2)	2 (2)
As_5	−1919 (3)	3787 (2)	3539 (1)	44 (3)	37 (3)	39 (3)	−8 (2)	6 (2)	1 (2)
As_6	−3287 (3)	4108 (2)	4188 (1)	44 (3)	31 (3)	36 (3)	−3 (2)	0 (2)	−4 (2)
C_1	−495 (3)[g]	21 (2)	367 (1)	65 (14)					
C_2	−312 (3)	2 (2)	363 (1)	56 (12)					
C_3	−384 (3)	18 (2)	424 (1)	52 (13)					
C_4	−402 (3)	−5 (2)	385 (1)	38 (12)					
C_5	−417 (3)	−90 (2)	386 (1)	52 (12)					
C_6	−406 (3)	504 (2)	350 (1)	35 (14)					
C_7	−220 (3)	482 (2)	341 (1)	53 (12)					
C_8	−269 (3)	508 (2)	402 (1)	61 (14)					
C_9	−295 (3)	519 (2)	363 (1)	58 (14)					
C_{10}	−287 (3)	604 (2)	359 (1)	50 (13)					
B	52 (4)	270 (3)	131 (1)	47 (17)					
H_1[f]	−270	255	390	63					
H_2[f]	−425	265	395	63					
H_3[f]	−360	245	345	63					
H_1[h]	−289 (10)	246 (9)	378 (5)	122 (32)					
H_2[h]	−433 (10)	278 (9)	401 (5)	114 (29)					
H_3[h]	−347 (11)	241 (9)	355 (6)	126 (34)					

[a] The coordinates are multiplied by 10^4; the U values, by 10^3. [b] Form of the anisotropic thermal parameters is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2 \cdot b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* \cos\gamma^* + 2U_{13}hla^*c^* \cos\beta^* + 2U_{23}klb^*c^* \cos\alpha^*)]$. [c] Numbers in parentheses are the estimated standard deviations. [d] Multiplicity factor of 0.5. [e] Multiplicity factor of 0.25. [f] Positions derived from the ΔF map. [g] The coordinates of H atoms of both structures and of C_1–C_{10} and B atoms of $[Co_2H_3(as_3)_2]BPh_4$ are multiplied by 10^3. [h] Parameters from least-squares refinement.

Table VII. Derived Group Atom Positional and Thermal Parameters ($\times 10^3$)

Atom	Cobalt				Iron			
	x	*y*	*z*	U, Å^2	*x*	*y*	*z*	U, Å^2
Ph_1-C_1	−615 (2)	148 (2)	395 (1)	42 (12)	199 (1)	207 (1)	278 (1)	46 (6)
C_2	−642 (2)	100 (2)	421 (1)	53 (12)	144 (1)	199 (1)	302 (1)	47 (6)
C_3	−714 (2)	119 (1)	443 (1)	72 (12)	104 (1)	146 (1)	274 (1)	60 (6)
C_4	−761 (2)	187 (2)	439 (1)	70 (12)	119 (1)	101 (1)	221 (1)	72 (6)
C_5	−735 (2)	235 (2)	413 (1)	73 (12)	174 (1)	109 (1)	197 (1)	76 (6)
C_6	−662 (2)	216 (1)	391 (1)	41 (12)	214 (1)	162 (1)	225 (1)	56 (6)
Ph_2-C_1	−589 (2)	138 (1)	319 (1)	49 (12)	211 (1)	−359 (1)	782 (1)	89 (6)
C_2	−689 (2)	119 (2)	315 (1)	80 (12)	207 (1)	−424 (1)	836 (1)	76 (6)
C_3	−744 (2)	124 (2)	283 (1)	86 (12)	171 (1)	−486 (1)	819 (1)	81 (6)
C_4	−699 (2)	149 (1)	253 (1)	83 (12)	140 (1)	−489 (1)	755 (1)	81 (6)
C_5	−599 (2)	169 (2)	257 (1)	104 (12)	143 (1)	−425 (1)	715 (1)	95 (6)
C_6	−544 (2)	163 (2)	289 (1)	49 (13)	179 (1)	−364 (1)	726 (1)	68 (6)
Ph_3-C_1	−131 (2)	100 (2)	357 (1)	48 (12)	307 (1)	66 (1)	379 (1)	38 (7)
C_2	−83 (2)	154 (2)	378 (1)	62 (13)	346 (1)	63 (2)	377 (1)	62 (7)
C_3	20 (2)	152 (1)	385 (1)	67 (13)	324 (1)	−65 (1)	362 (1)	85 (7)
C_4	75 (2)	96 (2)	371 (1)	86 (12)	263 (1)	−77 (1)	349 (1)	74 (7)
C_5	26 (2)	42 (2)	350 (1)	88 (13)	224 (1)	−17 (2)	351 (1)	74 (7)
C_6	−77 (2)	43 (1)	343 (1)	71 (13)	246 (1)	55 (1)	366 (1)	57 (7)
Ph_4-C_1	−287 (2)	103 (2)	298 (1)	42 (12)	407 (1)	138 (1)	439 (1)	34 (7)
C_2	−234 (3)	154 (2)	280 (1)	65 (13)	399 (1)	111 (1)	502 (1)	61 (7)
C_3	−236 (2)	150 (2)	243 (1)	74 (13)	448 (1)	89 (2)	545 (1)	69 (7)
C_4	−290 (2)	96 (2)	224 (1)	69 (12)	505 (1)	95 (2)	525 (1)	72 (7)
C_5	−343 (3)	45 (2)	242 (1)	57 (13)	512 (1)	123 (1)	461 (1)	74 (7)
C_6	−342 (2)	49 (2)	279 (1)	55 (13)	464 (1)	144 (2)	418 (1)	59 (7)
Ph_5-C_1	−197 (2)	110 (2)	451 (1)	48 (12)	428 (1)	338 (1)	466 (1)	46 (6)
C_2	−160 (2)	168 (2)	472 (1)	71 (13)	435 (1)	294 (1)	523 (1)	50 (6)
C_3	−63 (2)	167 (2)	488 (1)	80 (13)	484 (1)	302 (2)	569 (1)	54 (6)
C_4	−3 (2)	107 (2)	483 (1)	76 (12)	527 (1)	355 (1)	558 (1)	74 (6)
C_5	−39 (2)	48 (2)	462 (1)	91 (13)	521 (1)	399 (1)	501 (1)	73 (7)
C_6	−136 (2)	50 (2)	446 (1)	64 (13)	472 (1)	390 (2)	454 (1)	72 (7)
Ph_6-C_1	−401 (2)	148 (2)	470 (1)	60 (13)	345 (1)	429 (1)	391 (1)	36 (6)
C_2	−378 (2)	111 (2)	502 (1)	91 (12)	329 (1)	468 (2)	446 (1)	49 (6)
C_3	−425 (2)	130 (2)	532 (1)	92 (12)	315 (1)	544 (1)	440 (1)	56 (6)
C_4	−496 (2)	186 (2)	530 (1)	86 (12)	317 (1)	580 (1)	379 (1)	64 (6)
C_5	−520 (2)	222 (2)	498 (1)	65 (12)	333 (1)	540 (2)	324 (1)	59 (6)
C_6	−472 (2)	203 (2)	468 (1)	51 (12)	347 (1)	465 (1)	330 (1)	67 (6)
Ph_7-C_1	−412 (2)	395 (2)	288 (1)	50 (13)	133 (1)	408 (1)	519 (1)	40 (6)
C_2	−394 (2)	326 (1)	273 (2)	69 (13)	83 (1)	439 (2)	537 (1)	61 (7)
C_3	−386 (3)	319 (2)	237 (1)	89 (12)	74 (1)	516 (1)	541 (1)	73 (6)
C_4	−394 (2)	380 (2)	215 (1)	70 (12)	119 (1)	559 (1)	520 (1)	79 (6)
C_5	−412 (2)	449 (1)	230 (2)	73 (13)	170 (1)	531 (2)	502 (1)	69 (7)
C_6	−421 (3)	456 (2)	266 (1)	67 (12)	176 (1)	452 (1)	502 (1)	59 (7)
Ph_8-C_1	−579 (2)	392 (2)	334 (1)	65 (12)	82 (1)	293 (1)	445 (1)	45 (7)
C_2	−632 (2)	437 (2)	355 (1)	59 (13)	42 (1)	234 (1)	446 (1)	87 (7)
C_3	−735 (2)	432 (2)	353 (1)	63 (12)	−4 (1)	226 (1)	396 (1)	88 (7)
C_4	−785 (2)	384 (2)	329 (1)	63 (12)	−10 (1)	278 (1)	343 (1)	76 (7)
C_5	−732 (2)	339 (2)	308 (1)	83 (13)	30 (1)	337 (1)	342 (1)	80 (7)
C_6	−629 (2)	344 (2)	310 (1)	69 (13)	76 (1)	344 (1)	392 (1)	64 (7)
Ph_9-C_1	−122 (2)	349 (2)	315 (1)	49 (13)	146 (1)	99 (1)	529 (1)	49 (7)
C_2	−50 (3)	295 (2)	320 (1)	70 (13)	120 (1)	44 (1)	566 (1)	63 (7)
C_3	7 (2)	271 (2)	292 (2)	80 (13)	82 (1)	−9 (2)	534 (1)	84 (7)
C_4	−21 (2)	301 (2)	259 (1)	78 (12)	70 (1)	−8 (1)	465 (1)	96 (7)
C_5	−94 (3)	355 (2)	253 (1)	82 (13)	96 (1)	46 (1)	428 (1)	80 (7)
C_6	−144 (2)	379 (2)	281 (2)	86 (12)	134 (1)	99 (2)	460 (1)	54 (7)
Ph_{10}-C_1	−79 (2)	389 (2)	390 (1)	33 (12)	254 (1)	80 (1)	596 (1)	46 (7)
C_2	−70 (2)	336 (2)	416 (1)	62 (13)	277 (1)	68 (2)	662 (1)	54 (7)
C_3	10 (2)	338 (2)	442 (2)	56 (13)	314 (1)	7 (1)	678 (1)	69 (7)
C_4	81 (2)	394 (2)	441 (1)	50 (12)	329 (1)	−41 (1)	627 (1)	66 (7)
C_5	71 (2)	447 (2)	415 (1)	59 (13)	307 (1)	−28 (2)	561 (1)	89 (7)
C_6	−9 (2)	444 (2)	389 (2)	58 (13)	270 (1)	33 (1)	546 (1)	65 (7)
Ph_{11}-C_1	−456 (2)	441 (2)	435 (1)	44 (12)	291 (1)	404 (1)	620 (1)	38 (7)
C_2	−473 (2)	511 (1)	448 (1)	77 (13)	261 (1)	470 (2)	634 (1)	64 (7)
C_3	−563 (2)	528 (2)	460 (1)	87 (13)	291 (1)	538 (1)	639 (1)	72 (7)
C_4	−638 (2)	475 (2)	460 (1)	78 (12)	352 (1)	540 (1)	631 (1)	80 (7)
C_5	−622 (2)	406 (1)	447 (1)	67 (13)	381 (1)	474 (2)	617 (1)	75 (7)
C_6	−531 (2)	388 (2)	435 (1)	74 (13)	351 (1)	406 (1)	612 (1)	56 (7)
Ph_{12}-C_1	−252 (2)	401 (2)	465 (1)	26 (12)	311 (1)	263 (1)	669 (1)	30 (6)
C_2	−286 (2)	347 (2)	486 (1)	56 (13)	312 (1)	278 (1)	737 (1)	58 (7)
C_3	−235 (2)	333 (2)	519 (1)	77 (12)	357 (1)	247 (1)	782 (1)	75 (6)
C_4	−151 (2)	372 (2)	531 (1)	75 (12)	399 (1)	200 (1)	757 (1)	69 (6)
C_5	−117 (2)	427 (2)	509 (1)	78 (13)	397 (1)	185 (1)	689 (1)	61 (7)
C_6	−167 (2)	441 (2)	476 (1)	70 (13)	353 (1)	217 (1)	645 (1)	50 (7)

Table VII (*Continued*)

	Cobalt			
Atom	x	y	z	U, Å^2
Ph_{13}-C_1	18 (2)	197 (2)	148 (1)	67 (13)
C_2	66 (2)	169 (2)	180 (1)	61 (12)
C_3	27 (2)	109 (1)	196 (1)	66 (12)
C_4	−60 (2)	76 (2)	181 (1)	71 (13)
C_5	−108 (2)	104 (2)	149 (1)	80 (12)
C_6	−68 (2)	165 (1)	133 (1)	73 (12)
Ph_{14}-C_1	103 (2)	256 (2)	93 (1)	42 (12)
C_2	156 (2)	312 (2)	78 (1)	48 (12)
C_3	201 (2)	299 (2)	47 (1)	75 (12)
C_4	193 (2)	230 (2)	31 (1)	76 (12)
C_5	141 (2)	175 (2)	46 (1)	74 (12)
C_6	96 (2)	187 (2)	77 (1)	66 (12)
Ph_{15}-C_1	−49 (2)	328 (1)	122 (1)	52 (12)
C_2	−111 (2)	338 (2)	149 (1)	47 (13)
C_3	−194 (2)	383 (2)	143 (2)	71 (12)
C_4	−214 (2)	418 (1)	111 (1)	90 (12)
C_5	−152 (2)	408 (2)	84 (1)	95 (12)
C_6	−69 (2)	363 (2)	90 (2)	70 (12)
Ph_{16}-C_1	141 (2)	316 (2)	159 (1)	41 (12)
C_2	120 (2)	364 (2)	186 (1)	53 (12)
C_3	194 (2)	382 (2)	212 (1)	73 (12)
C_4	289 (2)	353 (2)	212 (1)	52 (12)
C_5	310 (2)	305 (2)	185 (1)	69 (12)
C_6	236 (2)	286 (2)	159 (1)	43 (13)

times on the peak and background, respectively. The standard deviations on the intensities were calculated by use of the expression $\sigma = [P - 0.25(B_1 + B_2)(T_p/T_b) + (0.02I)^2]^{1/2}$.[23]

The 4038 reflections having $I \geq 3\sigma(I)$, in the range $0° < 2\theta \leq 40°$, were considered observed and were used in the structure analysis. These reflections were corrected for Lorentz and polarization effects. No correction was made for absorption because the linear absorption coefficient was rather low (μ = 6.77 cm^{-1}) and also because the crystal used was small. Atomic scattering factors were taken from ref 24 for iron, chlorine, phosphorus, fluorine, and carbon atoms and from ref 25 for hydrogen atoms.

[$Co_2H_3(as_3)_2$]BPh_4. The crystals of [$Co_2H_3(as_3)_2$]BPh_4 were recrystallized from 1-butanol and acetone. The crystal used for the data collection has a parallelepiped shape with dimensions 0.3 × 0.3 × 0.1 mm. The unit cell of this complex is monoclinic, space group $P2_1/c$, with a = 13.515 (3) Å, b = 18.286 (4) Å, c = 38.036 (8) Å, β = 95.40 (2)°, V = 9358.4 Å^3, and d_m = 1.38 g cm^{-3}. Cell parameters were determined as for [$Fe_2H_3(p_3)$]PF_6·$1.5CH_2Cl_2$. The crystal used for the X-ray collection was protected by a coating of paraffin. The intensity data were collected on a four-circle Philips diffractometer with a θ–ω scan technique (scans of 1° in 14 sec). In the range $0° < 2\theta \leq 40°$ were taken 3327 observed reflections [$I \geq 3\sigma(I)$]. An absorption correction (μ = 25.65 cm^{-1}) was applied by numerical methods.[26] The intensities were then corrected for Lorentz and polarization effects. Scattering factors for nonhydrogen atoms were taken from ref 24 and those for hydrogen atoms from ref 25.

Solution and Refinement of the Structures

[$Fe_2H_3(p_3)_2$]PF_6·$1.5CH_2Cl_2$. The structures was solved by direct methods. Signs for 534 normalized structure factors were obtained by the symbolic addition procedure[27] for centrosymmetric crystals, using Ahmed's program SAP.[28] An E-map calculation showed the positions of iron and phosphorus atoms. Two subsequent Fourier syntheses, followed by a ΔF Fourier synthesis, were carried out to find the other nonhydrogen atoms. These calculations were made with an IBM 1130 computer with the programs of the ref 29. The ΔF Fourier synthesis showed the presence of solvent CH_2Cl_2 molecules. One molecule lies near the axis of symmetry (the atom Cl_1 has been found on the axis) and so the occupancy factor of its atoms (Cl_1 and Cl_2) is at most 0.5. The carbon atom of this molecule has not been located. A second molecule is in a general position but an occupancy factor of 0.5 will be assigned also to its atoms (Cl_3, Cl_4, and C_{83}) during the refinement. A third molecule of CH_2Cl_2 is also found near a symmetry axis. Besides, one of the chlorine atoms of this molecule has a disordered array, since the ΔF Fourier synthesis shows two peaks about of the same height for this atom. Therefore an occupancy factor of 0.5 is assigned to the chlorine atom (Cl_5) which does not appear disordered and a factor of 0.25 is assigned to two disordered atoms (Cl_6 and Cl_7). Also for this molecule the carbon atom has not been located. Refinement was then undertaken by use of the full-matrix least-squares program of Busing and Levy, adapted by Stewart.[30] The F values were weighted according the expression $w = 1/\sigma^2(F_o)$. The hydrogen atoms linked to the carbon atoms were introduced in calculated positions (C–H distance of 0.9 Å) with an overall B temperature factor of 5 Å^2 and were not refined. Several cycles were carried out with anisotropic temperature factors for iron, phosphorus, fluorine, and chlorine atoms and isotropic for the carbon atoms. The carbon atoms of the phenyl groups were refined as rigid groups with individual isotropic temperature factors for each atom. Occupancy factors were also refined for the chlorine and carbon atoms of the solvent molecule. The results of this refinement gave values close to 0.5 for the atoms Cl_1, Cl_2, Cl_3, Cl_4, Cl_5, and C_{83} and 0.25 for the atoms Cl_6 and Cl_7. In the final stage of refinement these values were left fixed at 0.5 and 0.25. The temperature factors for these atoms are rather high. Using these values of the occupancy factors for the chlorine atoms of the solvent, it is deduced that there are 1.5 solvent molecules for each complex unit, and therefore the complete formula is [$Fe_2H_3(p_3)_2$]PF_6·$1.5CH_2Cl_2$. The elemental analyses of these crystals are in good accordance with the latter formulation (Table I). During the refinement high thermal parameters for some fluorine atoms of PF_6^- were also noted. Probably there is disorder in the PF_6^- ions but it has not been possible to treat this disorder in any satisfactory mode because of the complexity demonstrated by the ΔF map in the zones occupied by these ions.

[$Co_2H_3(as_3)_2$]BPh_4. This structure was also solved by direct methods as for [$Fe_2H_3(p_3)_2$]PF_6·$1.5CH_2Cl_2$. An E-map calculation showed clearly the positions of the cobalt and arsenic atoms. Two subsequent Fourier syntheses showed all nonhydrogen atoms. The refinement was then continued as for [$Fe_2H_3(p_3)_2$]PF_6·$1.5CH_2Cl_2$ with the weighting scheme $w = 1/\sigma^2(F_o)$. The hydrogen atoms of the ligand molecule were introduced in calculated position, as described for [$Fe_2H_3(p_3)_2$]PF_6·$1.5CH_2Cl_2$. Several cycles were carried out with anisotropic temperature factors for cobalt and arsenic atoms and isotropic for the other atoms. The carbon atoms of the phenyl groups were refined as rigid groups with individual isotropic temperature factors for each atom.

Localization of Bridging Hydrogen Atoms. The nmr spectra, gas chromatographic analysis, and infrared spectra of the iron complex indicate the presence of three hydrogen atoms for every formula unit of complex. Considering the coordination geometry given by the iron and phosphorus atoms at this point of refinement, it was deduced that the hydrogen atoms were between the two iron atoms of the dimeric cation, because only hydrogen atoms bridging the iron atoms could in some way explain the phosphorus and hydrogen nmr spectra (six magnetically equivalent phosphorus and three magnetically equivalent hydrogen atoms). Therefore at this point of refinement (R factor equal to 9.8%) a ΔF Fourier synthesis was calculated and examined in particular in the region of the iron atoms. This examination revealed the presence of three peaks of height 0.4–0.5 e/Å^3 between the iron atoms and these peaks were hypothesized to be due to the three hydridic hydrogen atoms. A second ΔF Fourier synthesis executed limiting the reflections to those having $(\sin \theta)/\lambda \leq 0.30$ Å^{-1} again shows the existence of these peaks about in the same positions and this fact confirms that they are hydrogen atoms.[31] Also the positions of the three peaks confirm this hypothesis because they are all approximately equidistant from the two iron atoms at distances expected for bridging Fe–H bonds and are disposed symmetrically about the axis which joins the two iron atoms. Besides, the positioning of the hydrogen atoms completes a confacial-bioctahedral coordination polyhedron (Figure 2).

A least-squares refinement executed on the positional and thermal parameters of the three hydrogen atoms has given values of the positional parameters not much different from those obtained from the ΔF map. The refined thermal parameters are reasonable enough even though rather high. The calculation of the final structure factors was nevertheless executed using the positions obtained from the ΔF synthesis and using temperature factors B = 5 Å^2, since the positions from the ΔF map appeared more realistic, giving a more regular coordination polyhedron geometry. The final R factor was 9.8%. Final positional and thermal parameters of the atoms of the complex are given in Tables VI and VII. Also reported in Table VI are the refined parameters of the hydridic hydrogen atoms.

The gas chromatographic analysis of the hydrogen gas evolved upon the addition of hydrochloric acid to the cobalt complex, [Co_2H_3-

$(as_3)_2]BPh_4$, has also shown the presence of three hydridic hydrogen atoms and a similar molecular geometry to the iron compound is suggested. Furthermore the strict geometrical similarity of the cobalt and arsenic atoms in this structure (Figure 3) to the iron and phosphorus atoms in the preceding structure suggests that in the cobalt compound there are also three bridging hydridic hydrogen atoms to complete a confacial-bioctahedral geometry. Also for this structure at this point of refinement ($R = 8.2\%$) a ΔF Fourier synthesis was calculated. This map revealed three maxima with intensity of about 0.5 e/Å^3 in the expected positions. A ΔF Fourier, limited to the reflections having $(\sin \theta)/\lambda \leq 0.30$ Å^{-1}, confirmed the presence of these three peaks which then were considered hydrogen atoms. A least-squares refinement of these atoms resulted in a certain shift in their positions and furthermore yielded temperature factors rather high. However there was not any divergence during this refinement. Also in this case the positions obtained from the ΔF Fourier synthesis showed a more regular geometry and appeared more realistic. For this reason in the final structure factor calculation the three hydrogen atoms were introduced into the positions obtained from the ΔF Fourier and assigned an overall isotropic temperature factor, B, equal to 5 Å^2. The final R factor is 8.2%. Tables VI and VII give the final positional and thermal parameters of the atoms of the complex. Table VI also includes the refined parameters of the bridging hydrogen atoms.

Acknowledgment. Thanks are expressed to Professor L. M. Venanzi for the ^{31}P nmr measurements, Mr. F. Cecconi and Mr. D. Masi for technical assistance, Mr. G. Vignozzi and Mr. F. Nuzzi for microanalyses.

Registry No. $[Fe_2H_3(p_3)_2]PF_6\cdot 1.5CH_2Cl_2$, 54003-33-7; $[Fe_2H_3(p_3)_2]BPh_4$, 41517-54-8; $[Co_2H_3(p_3)_2]BPh_4$, 54003-35-9; $[Co_2H_3(as_3)_2]BPh_4$, 54036-76-9; $[Co(p_3)(CO)_2]BPh_4$, 54003-37-1; $[Co(as_3)(CO)_2]BPh_4$, 54003-39-3.

Supplementary Material Available. Listings of structure factor amplitudes for $[Fe_2H_3(p_3)_2]PF_6\cdot 1.5CH_2Cl_2$ and $[Co_2H_3(as_3)_2]BPh_4$ will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC405774.

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Crystal and Molecular Structure of Dichloronitrosylbis(triphenylphosphine)rhodium, $RhCl_2(NO)(P(C_6H_5)_3)_2$

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Received November 6, 1974 AIC40769Z

The structure of dichloronitrosylbis(triphenylphosphine)rhodium, $RhCl_2(NO)(P(C_6H_5)_3)_2$, has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in the monoclinic space group $I2/c$ with four molecules in a unit cell of dimensions $a = 22.019$ (4) Å, $b = 9.604$ (2) Å, $c = 15.854$ (2) Å, $\beta = 104.57$ (1)°. Least-squares refinement of the structure converged to values of 0.0514 and 0.0569 for the unweighted and weighted discrepancy indices. The structure consists of discrete monomeric units. The molecular geometry is that of a distorted square pyramid with a bent nitrosyl in the apical position. A crystallographically imposed twofold axis passes through the molecule and requires a disorder of the nitrosyl ligand. In treating the disorder the N–O distance is constrained to be 1.15 Å. Other important distances are Rh–N = 1.912 (10) Å, Rh–Cl = 2.3439 (14) Å, and Rh–P = 2.3672 (13) Å. The Rh–N–O angle is 124.8 (16)° and the direction of the bend is such that the planes defined by Rh, N, O and P, Rh, P' form a dihedral angle of 10.3 (29)°.

Introduction

In the course of our studies[1] on the metal-catalyzed reduction of NO by CO it became clear that the isolation and identification of catalytically active intermediates would be exceedingly useful in elucidating the manner in which this reaction proceeds. With this aim in mind, we isolated a red-orange material via the addition of triphenylphosphine to the green catalytically active solution obtained when an ethanolic solution of $Rh(CO)_2Cl_2^-$ is exposed to an atmosphere of CO and NO for a period of several hours.[1]

The infrared spectrum of the material, both before and after