Nucleophilic Attack at Carbon in σ,π-Acetylides. Bridging One Carbon and Two Carbon Iminium Ion Complexes via Addition of Cyclohexylamine to [Fe₂(CO)₆(C₂Ph)(PPh₂)]. X-Ray Structures of [Fe₂(CO)₆{CHC(NHC₆H₁₁-c)(Ph)}PPh₂] and [Fe₂(CO)₆{C(NHC₆H₁₁-c)CHPh}(PPh₂)]·0.5C₆H₆

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Abstract: The synthesis of two zwitterionic complexes, [Fe₂(CO)₆{CHC(NHC₆H₁₁-c)(Ph)}(PPh₂)] (IV) and [Fe₂(CO)₆-{C(NHC₆H₁₁-c)CHPh}(PPh₂)]·0.5C₆H₆ (V), via addition of cyclohexylamine across the acetylenic carbon atoms of the σ,π-acetylide in [Fe₂(CO)₆(C≡CPh)(PPh₂)] is described. The complexes IV and V have been characterized by microanalysis, mass spectroscopy, ^{1}H and ^{31}P NMR spectroscopy, Mössbauer measurements, and full single-crystal x-ray structure analysis. Red crystals of IV are triclinic, space group P1̄ with a = 14.185 (8), b = 11.602 (4), c = 10.985 (4) Å; α = 64.98 (3), β = 101.15 (2), γ = 100.76 (2)°. With Z = 2 the calculated density of 1.423 g cm^{-3} agrees with the value of 1.41 g cm^{-3} measured by flotation. For V, yellow crystals are monoclinic, space group P2₁/c with a = 9.987 (3), b = 17.206 (5), c = 20.518 (6) Å, β = 102.93 (2)°, and Z = 4. Calculated and measured densities are 1.361 and 1.37 g cm^{-3}, respectively. Both structures were solved using heavy-atom techniques and refined by full matrix least-squares methods with anisotropic temperature factors for nonhydrogen atoms and isotropic coefficients for hydrogen atoms to R and R_w values of 0.025 and 0.028 for IV and 0.043 and 0.049 for V. In IV the dipolar ligand is coordinated as a one-carbon, three-electron donor and in V as a two-carbon, three-electron ligand. In both complexes the nitrogen atoms have planar stereochemistry with the bond lengths between nitrogen atoms and the original acetylenic carbon atoms (N–C(8) of 1.312 (3) Å in IV and N–C(7) of 1.340 (9) Å in V) typical of >N⁺=C< double bonds. The coordinated carbon atoms are thus formally carbanionic but infrared ν(CO) frequencies indicate substantial charge transfer onto the iron tricarbonyl groups. The unusual single bridging carbon atom in IV gives rise to a very acute Fe(1)–C(7)–Fe(2) angle of 77.4 (0)°, one of the smallest yet noted for a single carbon bridge. Mössbauer spectra do not distinguish the structurally nonequivalent iron sites in either IV or V. The mode of formation of dipolar iminium ion derivatives via nucleophilic attack by amines on the α and β carbon atoms of σ,π-acetylides is discussed. These reactions offer a useful method of elaborating σ,π-acetylides.

Introduction

There is now a considerable body of evidence to suggest that ligands with 1,2-dipolar character, for example, the phosphorus[1] or sulfur[2] ylides, form remarkably stable transition metal complexes. Delocalization of charge from the ylidic carbanion onto the metal in these complexes undoubtedly modifies the 1,2-dipolar character of the "free" ylides and is of major importance in stabilizing the metal–carbon (ylide) bond. In contrast, relatively few organometallic complexes of 1,3-dipoles have been synthesized and it has even been suggested[3] that trapping of reactive 1,3-dipoles via a transition metal fragment is unpromising. Recent work has shown, however, that zwitterionic complexes containing ligands with formally 1,3-dipolar character can be generated via nucleophilic attack by phosphorus[4] or nitrogen[5] bases at the carbon atoms of binuclear σ,π-acetylides. Thus I and II can be synthesized quantitatively from the σ,π-acetylide III and triethylphosphite[4] or diethylamine.[5] In I the dipolar phosphonium ligand behaves as a two-carbon, three-electron bridging ligand whereas in II the iminium ion functions as a one-carbon, three-electron ligand. While the ligands in I and II are expected to exhibit significant 1,3-dipolar character, charge transfer from the formally carbanionic carbon atoms into the diiron framework is evident from the lowered ν(CO) frequencies in I and II compared to III. Since these initial reports appeared, Shapley, Churchill and co-workers,[6] and Deeming et al.[7] have described attack by phosphorus nucleophiles at carbon in σ,π-vinyl,[6,7] σ,π-phenylacetylide,[7] and σ,π-acetylene[7] triosmium clusters generating complexes related to I and II. When consideration is given to the fact that nucleophilic attack at
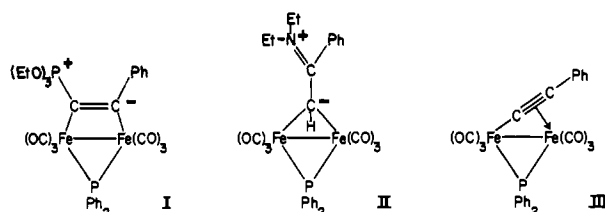
carbon by group 5 donors is generally restricted to cationic complexes[8] it is evident that the simultaneous σ,π coordination of a hydrocarbon moiety exemplified by III creates a uniquely activated C–C multiple bond. We are currently exploiting this reactivity and we describe herein the complete structural characterization of two compounds produced via addition of cyclohexylamine to the triple bond of III. The first of these, [Fe₂(CO)₆{CHC(NHC₆H₁₁-c)Ph}(PPh₂)] (IV), is structurally similar to II, whereas the other compound, [Fe₂(CO)₆-{C(NHC₆H₁₁-c)C(H)Ph}(PPh₂)]·0.5C₆H₆ (V), contains a new type of dipolar two-carbon three-electron ligand. The synthesis, infrared, Mössbauer, ^{1}H, and ^{31}P NMR spectra, and single-crystal x-ray structural analyses of IV and V are described in detail.

Experimental Section

Synthesis. The preparation of the σ,π-acetylide Fe₂(CO)₆-(C₂Ph)(PPh₂) has been described in detail elsewhere.[9] Cyclohexylamine (0.12 g) (a slight excess) was added to a solution of Fe₂-(CO)₆(C₂Ph)(PPh₂)(0.5 g) in benzene (30 mL) under an N₂ atmosphere. The reaction mixture was stirred for ~2 h at 50 °C and the progress of the reaction monitored by solution infrared spectroscopy

Table I. Crystal Data for [Fe₂(CO)₆{CHC(NHC₆H₁₁-c)(Ph)}(PPh₂)] (IV) and [Fe₂(CO)₆{C(NHC₆H₁₁-c)CH(Ph)}(PPh₂)]·0.5C₆H₆ (V)

	IV	V
Space group	$P\bar{1}$	$P2_1/c$
Cell dimensions	$a = 14.185\,(8)$, $b = 11.602\,(4)$, $c = 10.985\,(4)$ Å;	$a = 9.987\,(3)$, $b = 17.206\,(5)$,
	$\alpha = 64.98\,(3)$, $\beta = 101.15\,(2)$, $\gamma = 100.76\,(20°)$	$c = 20.518\,(6)$ Å; $\beta = 102.93\,(3)°$
Mol wt	665.24	704.30
Volume, Å³	1552.7	3436.3
Z	2	4
ρ calcd, g cm⁻³	1.423	1.361
ρ meas, g cm⁻³	1.41	1.37
μ (Mo Kα), cm⁻¹	10.56	9.37
F (000)	684	1452
Crystal size, mm³	0.38 × 0.40 × 0.35	0.30 × 0.30 × 0.30
Cell refinement	32 reflections	30 reflections
Reflections measd $(2\theta < 45°)$	4175	4495
Reflections obsd $(I \geqslant 3\sigma(I))$	3454	2665

and thin layer chromatography. At the end of this period, it was evident that all of the starting material, readily identified by its highest frequency (2072 cm⁻¹) ν(CO) band,[9] had been consumed. The solvent was removed in vacuo and the mixture chromatographed under nitrogen by column chromatography using Florisil absorbant. The first yellow band was eluted with petroleum ether (100 mL). On concentration in vacuo and cooling at −10 °C overnight, yellow plates of [Fe₂(CO)₆{C(NHC₆H₁₁-c)CH(Ph)}(PPh₂)]·0.5C₆H₆ were obtained in 40% yield, mp 150 °C. Anal. Calcd: C, 59.69; H, 4.42; Found: C, 59.96; H, 4.74. IR (C₆H₁₂) 2055 s, 2012 vs, 1984 m, 1965 m, 1948 m cm⁻¹; mass spectrum (70 eV) m/e (rel intensity) 665 (2.8) (M⁺), 637 (1.4), 609 (13.4), 581 (12.7), 553 (12.7), 525 (14.1), 497 (100) (Fe₂L⁺); NMR (¹H, 60 MHz) (C₆D₆) δ 7.7–6.8 m (C₆H₅), 3.0 m (N–H), 1.67 s (C–H), 1.1 m (C₆H₁₁). (³¹P, 24.29 MHz) (C₆H₆, 85% H₃PO₄ external standard) 154.0 ppm s (PPh₂). A slow-moving red band was then eluted using benzene (100 mL). Concentration of the solution in vacuo followed by addition of a few milliliters of *n*-hexane effected crystallization of red prisms of [Fe₂(CO)₆-{CHC(NHC₆H₁₁-c)(Ph)}(PPh₂)] in 40% yield, mp 140 °C. Anal. Calcd: C, 56.78; H, 4.42; P, 4.66. Found: C, 57.61; H, 4.25; P, 4.50. IR (C₆H₁₂) 2033 m, 1999 vs, 1956 s, 1913 m cm⁻¹; mass spectrum (70 eV) m/e (rel intensity) 665 (4.8) (M⁺), 637 (3.2), 609 (9.5), 581 (12.7), 553 (12.7), 525 (12.7), 497 (100) (Fe₂L⁺); NMR (¹H, 60 MHz) (C₆D₆) δ 7.8–6.9 m (C₆H₅), 4.35 m (N–H), 3.1 d (C–H), $^3J_{\text{P-CH}} = 12$ Hz, 2.07 m (C₆H₁₁). (³¹P, 23.46 MHz) (C₆D₆, 85% H₃PO₄ external standard) 183.5 ppm s (PPh₂).

Collection and Reduction of X-Ray Data. While red crystals of IV were indefinitely stable in air, yellow crystals of V were coated with epoxy to prevent solvent loss during data collection. Weissenberg and precession photographs of the zero, first, and second levels were obtained for both crystals. Systematic absences 0*k*0, *k* = 2*n*, and *h*0*l*, *l* = 2*n*, established that V crystallized in the monoclinic space group $P2_1/c$. There were no systematic absences for IV suggesting space groups $P1$ or $P\bar{1}$; the latter was proven to be correct by refinement of the structure. The crystals were accurately aligned on a GE-XRD-6 Datex automated diffractometer and cell constants refined using the local program DIFSET by least-squares refinement of 2θ values for 32 reflections in the case of IV and 30 reflections for V. Crystal data are gathered in Table I.

Intensity data were collected at room temperature using zirconium filtered Mo Kα radiation ($\lambda = 0.710\,69$ Å) at a takeoff angle of 4°. Crystals of IV were mounted on the a^* axis and V on the b axis. Integrated intensities were measured with a scintillation counter and pulse height analyzer set for 100% of the Mo Kα peak. The diffracted beam passed through a collimator of 1-mm diameter placed 5 cm from the crystal and thence to the counter via an aperture of 1-cm diameter, 18 cm from the crystal. For both crystals, a θ–2θ scan mode with a scan width determined by the equation $\Delta\theta = \pm(0.9 + 0.43\tan\theta)$ was employed. The scan rate in each case was 2° min⁻¹. Stationary counter stationary crystal background counts of 10 s were taken before and after each scan. Three standard reflections, monitored after every 100 reflections measured, showed that no noticeable deterioration of the crystals occurred during data collection. Standard deviations were estimated from counting statistics. Lorentz and polarization correc-

tions were applied as usual to the derivation of structure amplitudes.

Solution and Refinement of Structures. The positions of the two independent iron atoms in each molecule were located in three-dimensional unsharpened Patterson maps. Structure factor calculations based on the iron atom coordinates gave R values [$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$] of 0.48 and 0.46 for IV and V, respectively. Fourier and difference Fourier syntheses subsequently revealed positions for all of the remaining nonhydrogen atoms in each molecule including the half molecule of benzene of crystallization in V. Full-matrix least-squares refinement using isotropic thermal parameters for all nonhydrogen atoms located yielded R values of 0.079 and 0.118, respectively, for IV and V. Refinement was continued with anisotropic thermal parameters included for the nonhydrogen atoms. After three cycles of refinement R values of 0.046 for IV and 0.060 for V were obtained. At this stage difference Fourier syntheses were calculated in attempts to locate hydrogen atoms. This was accomplished readily for IV and with some difficulty for V. In subsequent least-squares refinement of both molecules, hydrogen atom positions and isotropic temperature coefficients were allowed to vary. Introduction of weighting schemes of the form $w^{-1} = 0.8184 - 0.0274|F| + 0.0007|F|^2$ for IV and $w^{-1} = 25.0 - 0.15|F| + 0.0025|F|^2$ for V followed by a final refinement cycle gave R and R_w values [$R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$] of 0.025 and 0.028 for IV and 0.043 and 0.049 for V. Final difference maps showed residual electron density up to 0.5 e Å⁻³ in IV and 0.8 e Å⁻³ in V.

Scattering factors used in calculations (including corrections for anomalous dispersion for iron) were those of ref 10 with the exception of hydrogen atom values, when the data of Stewart et al.[11] were employed. Computer programs used are listed in ref 12.

Tables of structure factors are available.[13] Atomic positions and hydrogen atom thermal parameters for IV are listed in Table II with anisotropic thermal parameters in Table III. Corresponding data for V are to be found in Tables V and VI.

Results and Discussion

The Molecular Structures of [Fe₂(CO)₆{CHC(NHC₆H₁₁-c)(Ph)}(PPh₂)] (IV) and [Fe₂(CO)₆{C(NHC₆H₁₁-c)CH(Ph)}-(PPh₂)]·0.5C₆H₆ (V). Interatomic distances and angles for IV are listed in Table IV and those for V are shown in Table VII. Distances and angles for phenyl rings in IV and V are deposited in supplementary tables SI and S2. A compilation of relevant least-squares planes for the two compounds is given in Table VIII. ORTEP II plots are illustrated in Figures 1 and 2.

The crystal structures of both molecules consist of discrete monomeric units separated by normal van der Waals distances. There are no short intermolecular contacts of chemical significance. The asymmetric unit of V contains half a molecule of benzene of crystallization situated on the center at 0, 0, 0.5. It is convenient to discuss structural features of the skeletal framework and the synthesized (de novo) ligands separately.

Table II. Atomic Positions[a] and Hydrogen Atom Thermal Parameters for $[Fe_2(CO)_6\{CHC(NHC_6H_{11}\text{-}c)(Ph)\}(PPh_2)]$ (IV)

	x	y	z	β_{iso}
Fe(1)	3370.4 (2)	1010.0 (3)	3904.1 (3)	
Fe(2)	1582.3 (2)	1225.0 (3)	3823.3 (3)	
P	2751.7 (4)	2848.2 (6)	3322.1 (7)	
O(1)	4587 (1)	1240 (2)	6290 (2)	
O(2)	4928 (2)	1773 (2)	2209 (2)	
O(3)	3385 (1)	−1798 (2)	5248 (2)	
O(4)	790 (2)	1932 (2)	5658 (2)	
O(5)	−129 (1)	1670 (3)	1787 (2)	
O(6)	1370 (1)	−1415 (2)	5920 (2)	
N	1367 (1)	−1087 (2)	2641 (2)	
C(1)	4094 (2)	1162 (2)	5352 (3)	
C(2)	4315 (2)	1479 (2)	2869 (3)	
C(3)	3364 (2)	−708 (2)	4699 (2)	
C(4)	1138 (2)	1679 (2)	4940 (3)	
C(5)	542 (2)	1518 (3)	2592 (3)	
C(6)	1459 (2)	−409 (2)	5055 (2)	
C(7)	2208 (2)	975 (2)	2439 (2)	
C(8)	2013 (2)	−120 (2)	2092 (2)	
C(11)	1100 (2)	−2301 (2)	2446 (3)	
C(12)	97 (2)	−2297 (3)	1648 (3)	
C(13)	−214 (3)	−3566 (3)	1466 (3)	
C(14)	−160 (3)	−4706 (3)	2837 (3)	
C(15)	832 (3)	−4697 (3)	3643 (3)	
C(16)	1144 (2)	−3436 (2)	3829 (3)	
C(21)	2522 (2)	−211 (2)	1067 (2)	
C(22)	3370 (2)	−746 (4)	1440 (3)	
C(23)	3809 (3)	−921 (4)	514 (4)	
C(24)	3398 (3)	−557 (4)	−792 (4)	
C(25)	2534 (4)	−31 (4)	−1203 (4)	
C(26)	2093 (3)	148 (4)	−268 (3)	
C(31)	3160 (2)	3799 (2)	4337 (3)	
C(32)	3545 (2)	5092 (3)	3780 (4)	
C(33)	3859 (3)	5765 (4)	4595 (5)	
C(34)	3795 (3)	5203 (4)	5950 (5)	
C(35)	3412 (3)	3931 (4)	6526 (4)	
C(36)	3103 (2)	3233 (3)	5724 (3)	
C(41)	2762 (2)	4079 (2)	1581 (3)	
C(42)	3576 (3)	4461 (4)	937 (4)	
C(43)	3587 (4)	5467 (4)	−335 (5)	
C(44)	2797 (3)	6099 (3)	−971 (4)	
C(45)	1983 (3)	5740 (3)	−358 (4)	
C(46)	1958 (2)	4719 (3)	916 (3)	
H(7)	237 (1)	171 (2)	165 (2)	3.1 (5)
H(N)	105 (2)	−97 (2)	319 (2)	3.6 (6)
H(11)	156 (2)	−232 (2)	187 (2)	4.0 (5)
H(12A)	8 (2)	−157 (3)	76 (3)	5.0 (7)
H(12B)	−34 (2)	−215 (2)	213 (3)	4.5 (6)
H(13A)	28 (2)	−362 (3)	89 (3)	7.1 (8)
H(13B)	−87 (3)	−350 (3)	95 (3)	7.7 (8)
H(14A)	−66 (2)	−466 (3)	334 (3)	5.3 (7)
H(14B)	−28 (2)	−547 (3)	270 (3)	6.8 (8)
H(15A)	134 (2)	−481 (3)	314 (3)	6.3 (8)
H(15B)	84 (2)	−543 (3)	453 (3)	5.5 (7)
H(16A)	67 (2)	−333 (2)	438 (3)	4.7 (6)
H(16B)	182 (2)	−342 (3)	433 (3)	4.8 (7)
H(22)	366 (3)	−100 (4)	236 (4)	8.5 (11)
H(23)	446 (3)	−138 (4)	87 (4)	9.8 (10)
H(24)	369 (3)	−71 (3)	−145 (4)	9.0 (10)
H(25)	220 (3)	22 (4)	−212 (5)	11.7 (14)
H(26)	152 (3)	54 (3)	−45 (4)	8.2 (10)
H(32)	366 (2)	549 (3)	280 (3)	6.2 (8)
H(33)	413 (3)	668 (4)	418 (4)	9.6 (13)
H(34)	405 (3)	571 (4)	658 (4)	10.9 (11)
H(35)	337 (3)	348 (4)	743 (4)	8.2 (11)
H(36)	287 (2)	242 (3)	609 (3)	5.1 (7)
H(42)	417 (3)	405 (4)	145 (4)	11.1 (13)
H(43)	416 (4)	566 (5)	−76 (5)	12.6 (15)
H(44)	273 (3)	683 (4)	−193 (4)	11.1 (13)
H(45)	136 (3)	612 (3)	−73 (3)	7.4 (10)
H(46)	137 (2)	444 (3)	132 (3)	5.9 (8)

[a] Positions are fractional $\times 10^4$ for nonhydrogen atoms and $\times 10^3$ for hydrogen atoms.

Table III. Anisotropic Thermal Parameters for $[Fe_2(CO)_6\{CHC(NHC_6H_{11}\text{-}c)(Ph)\}PPh_2]$ (IV)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe(1)	39.4 (2)	63.9 (4)	98.5 (4)	5.6 (2)	8.0 (2)	−29.4 (3)
Fe(2)	40.1 (2)	68.1 (4)	88.8 (4)	3.7 (2)	12.2 (2)	−30.6 (3)
P	41.0 (4)	58.0 (6)	105.6 (8)	4.0 (4)	8.6 (4)	−29.2 (6)
O(1)	69 (1)	137 (2)	146 (3)	18 (1)	−24 (2)	−69 (2)
O(2)	75 (2)	156 (3)	196 (3)	11 (2)	66 (2)	−30 (2)
O(3)	89 (2)	67 (2)	162 (3)	17 (1)	6 (2)	−29 (2)
O(4)	90 (2)	155 (3)	164 (3)	18 (2)	40 (2)	−91 (2)
O(5)	59 (1)	263 (4)	121 (3)	28 (2)	−13 (2)	−61 (3)
O(6)	91 (2)	91 (2)	123 (2)	6 (1)	41 (2)	−8 (2)
N	55 (1)	82 (2)	105 (3)	−6 (1)	27 (1)	−47 (2)
C(1)	48 (2)	70 (2)	121 (3)	10 (2)	6 (2)	−34 (2)
C(2)	50 (2)	83 (3)	133 (4)	9 (2)	15 (2)	−31 (3)
C(3)	47 (2)	81 (3)	106 (3)	10 (2)	3 (2)	−43 (2)
C(4)	57 (2)	80 (3)	113 (3)	7 (2)	14 (2)	−40 (2)
C(5)	50 (2)	117 (3)	98 (3)	10 (2)	19 (2)	−33 (3)
C(6)	54 (2)	83 (3)	98 (3)	3 (2)	23 (2)	−38 (2)
C(7)	41 (1)	63 (2)	84 (3)	2 (1)	12 (2)	−20 (2)
C(8)	39 (1)	72 (2)	77 (3)	7 (1)	4 (1)	−26 (2)
C(11)	57 (2)	75 (2)	104 (3)	−9 (2)	28 (2)	−46 (2)
C(12)	77 (2)	92 (3)	89 (3)	2 (2)	7 (2)	−37 (3)
C(13)	98 (3)	109 (3)	121 (4)	−18 (2)	6 (3)	−54 (3)
C(14)	109 (3)	85 (3)	142 (4)	−27 (2)	26 (3)	−49 (3)
C(15)	96 (2)	77 (3)	129 (4)	7 (2)	18 (2)	−35 (3)
C(16)	60 (2)	81 (3)	107 (3)	4 (2)	9 (2)	−32 (2)
C(21)	49 (1)	72 (2)	85 (3)	0 (1)	18 (2)	−31 (2)
C(22)	61 (2)	206 (5)	138 (4)	37 (2)	8 (2)	−92 (4)
C(23)	76 (2)	220 (6)	209 (6)	28 (3)	37 (3)	−114 (5)
C(24)	115 (3)	182 (5)	186 (6)	−2 (3)	86 (4)	−85 (4)
C(25)	145 (4)	225 (6)	96 (4)	39 (4)	41 (3)	−45 (4)
C(26)	99 (3)	175 (5)	97 (4)	52 (3)	15 (3)	−29 (3)
C(31)	48 (2)	82 (3)	162 (4)	14 (2)	−2 (2)	−59 (3)
C(32)	67 (2)	81 (3)	219 (6)	5 (2)	−4 (3)	−73 (3)
C(33)	94 (3)	108 (4)	298 (8)	11 (3)	−24 (4)	−120 (5)
C(34)	104 (3)	166 (5)	310 (8)	39 (3)	−47 (4)	−172 (6)
C(35)	115 (3)	184 (5)	198 (6)	32 (3)	−15 (3)	−128 (5)
C(36)	81 (2)	117 (4)	165 (5)	9 (2)	−0 (3)	−84 (4)
C(41)	60 (2)	62 (2)	121 (3)	3 (2)	22 (2)	−22 (2)
C(42)	97 (3)	131 (4)	249 (7)	35 (3)	88 (4)	52 (4)
C(43)	143 (4)	172 (6)	300 (9)	44 (4)	138 (5)	74 (6)
C(44)	151 (4)	108 (4)	155 (5)	14 (3)	52 (4)	2 (4)
C(45)	99 (3)	110 (4)	124 (4)	19 (2)	−15 (3)	−36 (3)
C(46)	69 (2)	92 (3)	108 (3)	7 (2)	3 (2)	−34 (3)

The Binuclear Framework. In both IV and V the phosphido bridged binuclear framework of $Fe_2(CO)_6(C\equiv CPh)(PPh_2)$[14] is retained but the hydrocarbon moiety is coordinated as a bridging monohapto ligand in IV and as a bridging dihapto group in V (Figures 1 and 2). The Fe(1)–Fe(2) distances of 2.576 (1) Å in IV and 2.628 (1) Å in V both differ significantly from the intermediate value of 2.597 (2) Å in the parent molecule $Fe_2(CO)_6(C\equiv CPh)(PPh_2)$. The Fe(1)–P–Fe(2) angle of 71.6 (1)° in $Fe_2(CO)_6(C\equiv CPh)(PPh_2)$ is also intermediate between the corresponding values for IV (70.5 (0)°) and V (72.5 (0)°). These differences are a direct consequence of the type of hydrocarbon bridge present, with the single carbon bridge in IV associated with the shortest iron–iron bond and most acute Fe–P–Fe angle. In both molecules the phosphido bridge is slightly asymmetric with Fe(1)–P bond lengths (2.249 (1) Å in IV and 2.232 (2) Å in V longer than Fe(2)–P (2.216 (1) Å in IV and 2.214 (2) Å in V) distances. The coordination geometry of the iron atoms is of interest because Mössbauer spectra (vide infra) indicate stereochemical and electronic equivalence of the two iron sites in each molecule. By analogy with phosphido[15] and sulfido[16] bridged binuclear iron carbonyls, the stereochemistry of the iron sites in IV might be related to two tetragonal pyramids sharing a common (C(7)—P) edge. For V the two pyramids, with apical atoms C(1), C(2), C(3), C(7), P and C(4), C(5), C(6), C(8), P, share
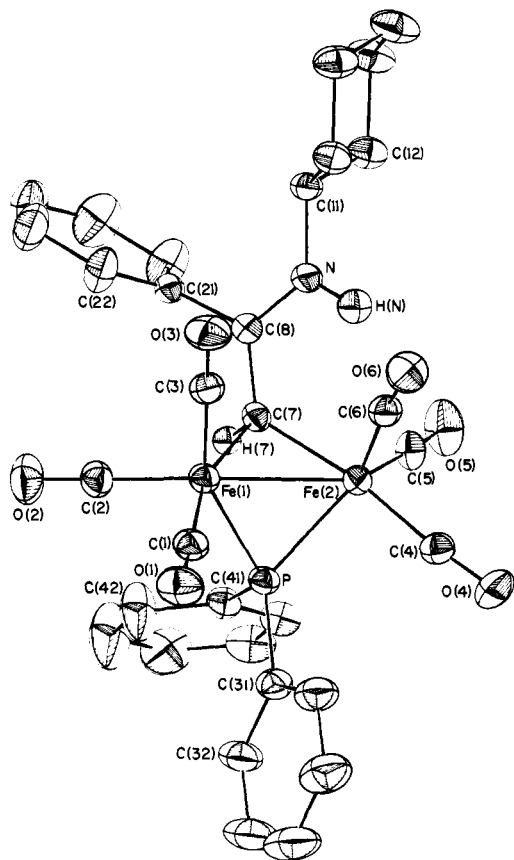
Figure 1. The molecular structure of [Fe₂(CO)₆{CHC(NHC₆H₁₁-c)-(Ph)}PPh₂] (IV) showing the atomic numbering scheme used. Ellipsoids represent 30% of the electron density.
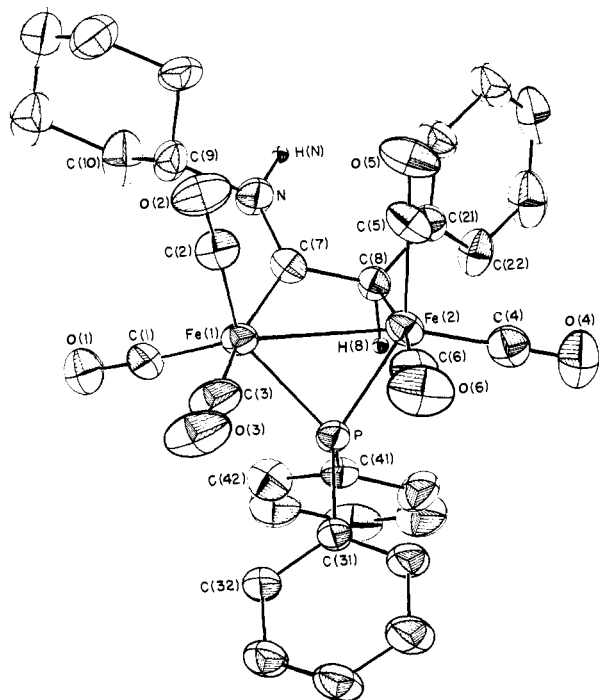
Figure 2. The molecular structure of [Fe₂(CO)₆{C(NHC₆H₁₁-c)-CHPh}(PPh₂)]·0.5C₆H₆. Ellipsoids are drawn at the 30% level.

only a phosphorus atom. The planes (3, 4, 10, 11) in Table VIII show that this description is at best a poor one for IV and V, with the basal planes of the pyramids very distorted. The alternate description, with a bent Fe–Fe bond and distorted oc-

Table IV. Bond Lengths (Å) and Angles (deg) for [Fe₂(CO)₆{CHC(NHC₆H₁₁-c)(Ph)}PPh₂] (IV)ᵃ

Fe(1)-Fe(2)	2.576 (1)	Fe(2)-Fe(1)-P	54.2 (0)
Fe(1)-P	2.249 (1)	Fe(2)-Fe(1)-C(1)	111.9 (0)
Fe(1)-C(1)	1.776 (3)	Fe(2)-Fe(1)-C(2)	142.5 (0)
Fe(1)-C(2)	1.783 (3)	Fe(2)-Fe(1)-C(3)	101.2 (0)
Fe(1)-C(3)	1.806 (3)	Fe(2)-Fe(1)-C(7)	50.7 (0)
Fe(1)-C(7)	2.077 (2)	P-Fe(1)-C(1)	92.0 (0)
Fe(2)-P	2.216 (1)	P-Fe(1)-C(2)	103.5 (0)
Fe(2)-C(4)	1.775 (3)	P-Fe(1)-C(3)	154.1 (0)
Fe(2)-C(5)	1.775 (3)	P-Fe(1)-C(7)	76.1 (0)
Fe(2)-C(6)	1.804 (3)	C(1)-Fe(1)-C(2)	97.1 (1)
Fe(2)-C(7)	2.044 (2)	C(1)-Fe(1)-C(3)	90.7 (1)
P-C(31)	1.829 (3)	C(1)-Fe(1)-C(7)	162.5 (1)
P-C(41)	1.842 (3)	C(2)-Fe(1)-C(3)	101.8 (1)
C(1)-O(1)	1.155 (3)	C(2)-Fe(1)-C(7)	98.1 (1)
C(2)-O(2)	1.150 (4)	C(3)-Fe(1)-C(7)	94.7 (1)
C(3)-O(3)	1.151 (3)	Fe(1)-Fe(2)-P	55.4 (0)
C(4)-O(4)	1.162 (4)	Fe(1)-Fe(2)-C(4)	124.7 (0)
C(5)-O(5)	1.150 (3)	Fe(1)-Fe(2)-C(5)	136.8 (0)
C(6)-O(6)	1.155 (3)	Fe(1)-Fe(2)-C(6)	88.0 (0)
C(7)-C(8)	1.440 (4)	Fe(1)-Fe(2)-C(7)	51.9 (0)
C(7)-H(7)	0.95 (2)	P-Fe(2)-C(4)	94.0 (0)
C(8)-N	1.312 (3)	P-Fe(2)-C(5)	112.9 (0)
C(8)-C(21)	1.498 (3)	P-Fe(2)-C(6)	136.3 (0)
N-C(11)	1.482 (4)	P-Fe(2)-C(7)	77.5 (0)
N-H(N)	0.88 (2)	C(4)-Fe(2)-C(5)	95.6 (1)
C(11)-C(12)	1.519 (4)	C(4)-Fe(2)-C(6)	88.4 (1)
C(12)-C(13)	1.541 (5)	C(4)-Fe(2)-C(7)	171.3 (1)
C(13)-C(14)	1.528 (5)	C(5)-Fe(2)-C(6)	110.3 (1)
C(14)-C(15)	1.511 (5)	C(5)-Fe(2)-C(7)	85.9 (1)
C(15)-C(16)	1.534 (5)	C(6)-Fe(2)-C(7)	99.2 (1)
C(16)-C(11)	1.533 (4)	Fe(1)-P-Fe(2)	70.5 (0)
Fe(1)-P-C(31)	119.9 (0)	Fe(2)-C(7)-H(7)	118 (1)
Fe(1)-P-C(41)	119.6 (0)	C(8)-C(7)-H(7)	108 (1)
Fe(2)-P-C(31)	123.1 (0)	C(7)-C(8)-N	121.8 (1)
Fe(2)-P-C(41)	120.6 (0)	C(7)-C(8)-C(21)	122.0 (1)
C(31)-P-C(41)	102.2 (1)	N-C(8)-C(21)	116.1 (1)
Fe(1)-C(1)-O(1)	177.7 (1)	C(8)-N-C(11)	129.1 (1)
Fe(1)-C(2)-O(2)	179.5 (1)	C(8)-N-H(N)	113 (2)
Fe(1)-C(3)-O(3)	177.2 (1)	C(11)-N-H(N)	118 (2)
Fe(2)-C(4)-O(4)	175.5 (1)	N-C(11)-C(12)	109.3 (1)
Fe(2)-C(5)-O(5)	177.5 (1)	N-C(11)-C(16)	109.5 (1)
Fe(2)-C(6)-O(6)	174.2 (1)	C(16)-C(11)-C(12)	111.5 (1)
Fe(1)-C(7)-Fe(2)	77.4 (0)	C(11)-C(12)-C(13)	110.5 (1)
Fe(1)-C(7)-C(8)	117.7 (0)	C(12)-C(13)-C(14)	110.6 (1)
Fe(1)-C(7)-H(7)	104 (1)	C(13)-C(14)-C(15)	111.9 (1)
Fe(2)-C(7)-C(8)	126.4 (0)	C(14)-C(15)-C(16)	111.5 (1)
		C(15)-C(16)-C(11)	110.0 (1)

ᵃ Excluding phenyl ring parameters.

tahedral stereochemistry at each iron atom, appears to be more useful, especially in view of the very small quadrupole splittings observed in the Mössbauer spectra. An analysis of angles and distances within the Fe(CO)₃ units of each complex provided evidence for the essential similarity of the two iron environments in IV and also in V. For example, the average OC–Fe(1)–CO and OC–Fe(2)–CO angles are 96.5 and 97.7° in IV and 96.3 and 97.5° in V while the Fe(1)–CO (av 1.788 Å in IV and 1.780 Å in V) and Fe(2)–CO (av 1.785 Å in IV and 1.793 Å in V) distances are statistically indistinguishable. The major differences in the iron coordination polyhedra of IV and V are due to the modes of bonding of the bridging hydrocarbon moieties. Thus for IV the angles C(7)–Fe(1)–P (76.1 (0)°) and Fe(2)–Fe(1)–C(7) (50.7 (0)°) are much smaller than the corresponding angles (89.6 (1) and 67.2 (1)°) in V where a two-carbon bridging unit is present. Similar angular differences (C(7)–Fe(2)–P 77.5 (0)° in IV vs. C(8)–Fe(2)–P (82.3 (1)°) in V and Fe(1)–Fe(2)–C(7) 51.9 (0)° in IV vs. Fe(1)–Fe(2)–C(8) (75.1 (1)°) in V are evident at Fe(2). These differences rather than inequalities in bond lengths are probably

Table V. Atomic Positions[a] and Hydrogen Atom Thermal Parameters for $[Fe_2(CO)_6\{C(NHC_6H_{11}\text{-}c)CH(Ph)\}(PPh_2)]\cdot0.5C_6H_6$

	x	y	z		x	y	z
Fe(1)	3826 (1)	384.3 (5)	1082.9 (5)	C(43)	6420 (11)	−2 (6)	3551 (5)
Fe(2)	1570 (1)	624.0 (6)	1512.1 (5)	C(44)	5786 (12)	56 (5)	4073 (5)
P	3198 (2)	−229 (1)	1926.0 (9)	C(45)	4428 (12)	22 (6)	3961 (4)
O(1)	6808 (6)	273 (4)	1297 (4)	C(46)	3593 (10)	−88 (5)	3319 (4)
O(2)	3004 (7)	1206 (3)	−186 (3)	CS(1)[b]	334 (15)	−89 (18)	4444 (10)
O(3)	3166 (9)	−1028 (3)	278 (3)	CS(2)[b]	700 (15)	942 (14)	4509 (12)
O(4)	−103 (7)	726 (4)	2501 (4)	CS(3)[b]	163 (17)	667 (13)	5185 (14)
O(5)	473 (7)	1854 (3)	535 (3)				
O(6)	−115 (7)	−529 (4)	644 (3)				

	x	y	z	β_{iso}
H(N)	444 (11)	251 (6)	177 (5)	11 (3)
H(8)	335 (7)	102 (4)	249 (4)	7 (2)
H(9)	537 (6)	165 (3)	67 (3)	4 (1)
H(10A)	718 (7)	205 (4)	168 (3)	5 (2)
H(10B)	654 (9)	299 (5)	163 (4)	12 (2)
H(11A)	835 (10)	239 (6)	127 (5)	9 (3)
H(11B)	816 (16)	214 (9)	65 (8)	21 (5)
H(12A)	677 (13)	372 (7)	46 (6)	15 (4)
H(12B)	786 (11)	323 (6)	−4 (5)	14 (3)
H(13A)	552 (10)	241 (6)	−36 (5)	10 (3)
H(13B)	493 (12)	341 (7)	−58 (6)	16 (4)
H(14A)	332 (14)	247 (8)	7 (7)	19 (5)
H(14B)	452 (8)	329 (5)	72 (4)	7 (2)
H(22)	482 (10)	−161 (5)	170 (5)	9 (3)
H(23)	443 (9)	−301 (5)	175 (4)	7 (2)
H(24)	211 (14)	−352 (8)	179 (7)	19 (5)
H(25)	34 (11)	−256 (7)	202 (5)	12 (3)
H(26)	73 (12)	−102 (7)	193 (6)	16 (4)
H(32)	596 (9)	−12 (5)	248 (4)	8 (2)
H(33)	755 (13)	5 (7)	360 (6)	16 (4)
H(34)	662 (10)	11 (5)	457 (5)	11 (3)
H(35)	392 (9)	7 (5)	432 (4)	7 (2)
H(36)	257 (13)	1 (7)	324 (6)	16 (4)
H(42)	293 (11)	169 (6)	329 (5)	10 (3)
H(43)	232 (10)	284 (5)	392 (5)	11 (3)
H(44)	169 (12)	404 (7)	326 (6)	14 (4)
H(45)	117 (13)	404 (8)	187 (6)	18 (4)
H(46)	202 (9)	284 (5)	140 (4)	7 (2)

(continuation of left column data)

	x	y	z
N	4424 (6)	2057 (3)	1435 (3)
C(1)	5647 (9)	296 (4)	1218 (4)
C(2)	3323 (8)	904 (4)	324 (4)
C(3)	3430 (10)	−491 (5)	608 (4)
C(4)	565 (8)	689 (4)	2106 (4)
C(5)	897 (8)	1388 (5)	921 (4)
C(6)	552 (8)	−107 (5)	981 (4)
C(7)	3855 (7)	1389 (4)	1574 (3)
C(8)	3030 (7)	1421 (4)	1064 (3)
C(9)	5279 (8)	2214 (4)	948 (4)
C(10)	6678 (10)	2485 (6)	1317 (5)
C(11)	7596 (11)	2665 (7)	796 (6)
C(12)	6862 (14)	3206 (7)	275 (7)
C(13)	5430 (13)	2977 (6)	−64 (6)
C(14)	4553 (10)	2818 (4)	435 (5)
C(21)	2604 (7)	2170 (4)	2342 (4)
C(22)	2715 (8)	2213 (5)	3027 (4)
C(23)	2373 (10)	2891 (6)	3331 (5)
C(24)	1892 (9)	3532 (5)	2927 (6)
C(25)	1733 (9)	3507 (5)	2256 (5)
C(26)	2096 (9)	2814 (4)	1955 (5)
C(31)	2865 (7)	−1282 (4)	1882 (3)
C(32)	3903 (8)	−1806 (4)	1805 (4)
C(33)	3633 (9)	−2610 (4)	1782 (5)
C(34)	2383 (9)	−2886 (5)	1842 (5)
C(35)	1379 (9)	−2374 (5)	1936 (5)
C(36)	1633 (8)	−1558 (4)	1968 (5)
C(41)	4228 (8)	−141 (4)	2774 (4)
C(42)	5614 (9)	−99 (5)	2904 (4)

[a] Positions are fractional $\times10^4$ for nonhydrogen atoms and $\times10^3$ for hydrogen atoms. [b] Atoms of solvent of crystallization.

responsible for the larger quadrupole splitting in IV.

The single bridging carbon atom in IV structurally resembles the carbon atom of a bridging carbonyl group, with an acute Fe(1)-C(7)-Fe(2) angle similar to that in $Fe_2(CO)_9$ (77.6°).[17] The iron-carbon distances (av 2.061 Å) to C(7) are also comparable with the Fe-CO$_{br}$ bond lengths (2.016 Å) in $Fe_2(CO)_9$[17] if allowance is made for the difference in covalent radii (0.04 Å) between $C_{(sp^2)}$ and $C_{(sp^3)}$. In contrast Fe-C distances in π-hydrocarbon complexes such as $(C_{12}H_8)$-$Fe(CO)_4$ (av 2.151 Å),[18] $(PhCH=CHCH=NPh)Fe(CO)_3$ (av 2.090 Å),[19] and $[(C_5N_2H_7)Fe(CO)_3](CF_3CO_2)$[20] (av 2.104 Å) are somewhat larger. For V the discrepancy between the Fe(1)-C(7) (1.999 (7) Å) and Fe(2)-C(8) (2.133 (7) Å) distances reflects the sp^2 and sp^3 character of C(7) and C(8) as well as the asymmetry of the bridging two-carbon ligand.

The Bridging One-Carbon and Two-Carbon Ligands. It is instructive to compare the molecular geometries of the hydrocarbon moieties in IV and V. The nitrogen atoms in IV and V are attached to the β- and α-carbon atoms, respectively, of the original σ,π-acetylide; the stereochemistry of both heteroatoms, C(8) in IV and C(7) in V, is planar while carbon atoms C(7) in IV and C(8) in V are tetrahedral. Hydrogen atoms on C(7) of IV and C(8) of V were located and refined isotropically; neither hydrogen atom is within bonding distance of a metal atom. The C-N distances (C(8)-N of 1.312 (3) and C(7)-N of 1.340 (9) Å) indicate extensive double bond character in these bonds as expected from the planarity of both nitrogen atoms. These distances correspond closely with C=N

bond lengths in iminium and imonium salts.[21,22] Thus for N,N-dimethylisopropylideniminium perchlorate the C=N distance is 1.30 (2) Å and in the 2,6-dihydroxypyridinium cation the C-N bond distances are 1.346 (3) and 1.355 (3) Å.[22] Nevertheless some delocalization over the N-C(8)-C(7) and N-C(7)-C(8) moieties is evident from the C(8)-C(7) bond lengths (1.440 (4) and 1.436 (10) Å in IV and V, respectively) which are shorter than expected when compared with the normal $C_{(sp^2)}$-$C_{(sp^3)}$ bond distance (1.53 (1) Å).[23] This is further borne out by the internal comparison in V of the C(7)-C(8) and C(8)-C(21) (1.509 (9) Å) bond lengths. Thus, although the structural results imply considerable iminium ion character, as represented by formulas IV and V, it is apparent that there is some delocalization of negative charge from the carbanionic carbon atoms in structures IV and V onto the $Fe_2(CO)_6$ fragments. This charge transfer will presumably modify the formal 1,3-dipolar character of these ligands represented by IV and V and be of some relevance to the chemistry of these zwitterions.

Comparison with Related Molecules. The structural similarity between the bridging one-carbon ligand in IV and a bridging carbonyl group pointed out earlier can obviously be extended to include μ-bound isocyanide,[24] alkylidene,[25] phenylvinylidene,[26] and dicyanovinylidene[27] ligands in binuclear complexes. All of these compounds have characteristically acute M-C-M bond angles. However, these ligands are two-electron donors and a closer analogy is with other one-carbon three-electron ligands. A number of complexes con-

Table VI. Anisotropic Thermal Parameters for [Fe₂(CO)₆{C(NHC₆H₁₁-c)CH(Ph)}(PPh₂)]·0.5C₆H₆

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe(1)	145 (1)	27.5 (3)	23.9 (3)	−0.7 (5)	16.5 (4)	−2.5 (2)
Fe(2)	122 (1)	31.5 (4)	32.2 (3)	1.7 (5)	8.4 (5)	4.7 (3)
P	115 (2)	27.7 (6)	26.1 (5)	−3.1 (9)	16.0 (8)	1.4 (4)
O(1)	156 (8)	83 (3)	77 (3)	29 (4)	48 (4)	21 (2)
O(2)	270 (10)	65 (3)	33 (2)	−28 (4)	7 (3)	11 (2)
O(3)	513 (18)	43 (2)	46 (2)	−40 (5)	58 (5)	17 (2)
O(4)	214 (10)	98 (4)	61 (2)	−12 (5)	58 (4)	12 (2)
O(5)	247 (10)	54 (3)	54 (2)	40 (4)	16 (4)	7 (2)
O(6)	258 (11)	60 (3)	60 (2)	−41 (4)	29 (4)	17 (2)
N	162 (9)	33 (2)	40 (2)	−15 (3)	32 (3)	7 (2)
C(1)	178 (12)	41 (3)	41 (3)	21 (5)	39 (5)	4 (2)
C(2)	165 (11)	42 (3)	27 (2)	−9 (5)	7 (4)	5 (2)
C(3)	309 (17)	39 (3)	34 (2)	−23 (6)	38 (5)	6 (2)
C(4)	153 (11)	43 (3)	45 (3)	−10 (5)	18 (4)	9 (2)
C(5)	145 (11)	45 (3)	41 (3)	24 (5)	4 (4)	7 (2)
C(6)	146 (11)	47 (3)	42 (3)	−5 (5)	5 (4)	2 (2)
C(7)	115 (8)	33 (2)	24 (2)	2 (4)	4 (3)	6 (2)
C(8)	123 (9)	28 (2)	26 (2)	−5 (4)	18 (3)	8 (2)
C(9)	161 (11)	39 (3)	39 (3)	−19 (4)	39 (4)	10 (2)
C(10)	197 (13)	71 (5)	56 (4)	−44 (7)	43 (6)	27 (4)
C(11)	225 (17)	89 (6)	64 (5)	−12 (8)	61 (8)	17 (4)
C(12)	319 (25)	81 (6)	95 (7)	−49 (10)	110 (11)	29 (5)
C(13)	341 (21)	60 (4)	62 (4)	−14 (8)	80 (8)	5 (4)
C(14)	291 (16)	30 (3)	57 (3)	−1 (5)	67 (6)	5 (3)
C(21)	113 (9)	31 (3)	40 (2)	−6 (4)	22 (4)	−7 (2)
C(22)	158 (11)	52 (4)	31 (2)	−20 (5)	28 (4)	−17 (2)
C(23)	181 (13)	73 (5)	55 (4)	−27 (6)	44 (5)	−34 (3)
C(24)	132 (11)	53 (4)	86 (5)	−27 (5)	54 (6)	−39 (4)
C(25)	176 (13)	36 (3)	75 (4)	1 (5)	44 (6)	−16 (3)
C(26)	172 (11)	36 (3)	49 (3)	11 (4)	30 (5)	−5 (2)
C(31)	116 (9)	27 (2)	35 (2)	−4 (4)	19 (3)	−1 (2)
C(32)	143 (10)	36 (3)	40 (3)	−1 (4)	26 (4)	3 (2)
C(33)	180 (12)	32 (3)	56 (3)	5 (5)	29 (5)	−1 (2)
C(34)	152 (12)	32 (3)	73 (4)	−1 (5)	11 (6)	−2 (3)
C(35)	142 (11)	37 (3)	84 (5)	−17 (5)	24 (6)	7 (3)
C(36)	138 (11)	32 (3)	59 (3)	−9 (4)	25 (5)	7 (2)
C(41)	133 (10)	30 (2)	35 (2)	−1 (4)	20 (4)	2 (2)
C(42)	180 (12)	59 (4)	29 (2)	9 (5)	7 (4)	−3 (2)
C(43)	214 (16)	67 (4)	42 (3)	4 (6)	6 (5)	1 (3)
C(44)	281 (18)	50 (4)	42 (3)	5 (7)	−6 (7)	5 (3)
C(45)	326 (19)	69 (4)	24 (2)	14 (7)	31 (6)	2 (2)
C(46)	235 (15)	58 (4)	31 (2)	−1 (6)	39 (5)	5 (2)
Solvent						
CS(1)	191 (20)	281 (22)	134 (10)	102 (18)	−33 (12)	−52 (14)
CS(2)	256 (24)	256 (18)	128 (10)	85 (17)	−41 (11)	1 (12)
CS(3)	201 (23)	229 (17)	165 (13)	79 (17)	−55 (14)	−13 (13)

Table VII. Bond Lengths (Å) and Angles (deg) for [Fe₂(CO)₆{C(NHC₆H₁₁c)CH(Ph)}PPh₂]·0.5C₆H₆ (V) [a]

Fe(1)–Fe(2)	2.628 (1)	Fe(2)–Fe(1)–P	53.4 (0)
Fe(1)–P	2.233 (2)	Fe(2)–Fe(1)–C(1)	151.9 (2)
Fe(1)–C(1)	1.784 (9)	Fe(2)–Fe(1)–C(2)	96.9 (2)
Fe(1)–C(2)	1.767 (7)	Fe(2)–Fe(1)–C(3)	102.3 (2)
Fe(1)–C(3)	1.790 (8)	Fe(2)–FE(1)–C(7)	67.2 (1)
Fe(1)–C(7)	1.999 (7)	P–Fe(1)–C(1)	107.0 (2)
Fe(2)–P	2.214 (2)	P–Fe(1)–C(2)	148.0 (2)
Fe(2)–C(4)	1.748 (8)	P–Fe(1)–C(3)	87.6 (2)
Fe(2)–C(5)	1.813 (8)	P–Fe(1)–C(7)	89.6 (1)
Fe(2)–C(6)	1.819 (8)	C(1)–Fe(1)–C(2)	105.0 (3)
Fe(2)–C(8)	2.133 (7)	C(1)–Pe(1)–C(3)	96.1 (3)
P–C(31)	1.840 (7)	C(1)–Fe(1)–C(7)	95.5 (3)
P–C(41)	1.818 (8)	C(2)–Fe(1)–C(3)	87.8 (3)
C(1)–O(1)	1.135 (11)	C(2)–Fe(1)–C(7)	88.6 (3)
C(2)–O(2)	1.147 (9)	C(3)–Fe(1)–C(7)	168.4 (3)
C(3)–O(3)	1.141 (10)	Fe(1)–Fe(2)–P	54.1 (0)
C(4)–O(4)	1.161 (11)	Fe(1)–Fe(2)–C(4)	155.9 (2)
C(5)–O(5)	1.140 (10)	Fe(1)–Fe(2)–C(5)	96.2 (2)
C(6)–O(6)	1.115 (11)	Fe(1)–Fe(2)–C(6)	95.6 (2)
C(7)–C(8)	1.436 (10)	Fe(1)–Fe(2)–C(8)	75.1 (1)
C(7)–N	1.340 (9)	P–Fe(2)–C(4)	105.2 (2)
C(8)–C(21)	1.509 (9)	P–Fe(2)–C(5)	150.2 (2)
N–C(9)	1.476 (10)	P–Fe(2)–C(6)	92.0 (2)
C(9)–C(10)	1.506 (13)	P–Fe(2)–C(8)	82.3 (1)
C(10)–C(11)	1.586 (15)	C(4)–Fe(2)–C(5)	103.6 (3)
C(11)–C(12)	1.482 (18)	C(4)–Fe(2)–C(6)	97.5 (3)
C(12)–C(13)	1.497 (19)	C(4)–Fe(2)–C(8)	91.1 (3)
C(13)–C(14)	1.513 (16)	C(5)–Fe(2)–C(6)	91.5 (3)
C(14)–C(9)	1.541 (12)	C(5)–Fe(2)–C(8)	89.8 (3)
		C(6)–Fe(2)–C(8)	170.7 (3)
		Fe(1)–P–Fe(2)	72.5 (0)
Fe(1)–P–C(31)	120.5 (2)	Fe(2)–C(8)–C(21)	122.2 (2)
Fe(1)–P–C(41)	120.3 (2)	Fe(2)–C(8)–H(8)	93 (4)
Fe(2)–P–C(31)	121.6 (2)	C(7)–C(8)–C(21)	123.5 (3)
Fe(2)–P–C(41)	121.4 (2)	C(7)–C(8)–H(8)	115 (4)
C(31)–P–C(41)	100.7 (3)	C(21)–C(8)–H(8)	107 (4)
Fe(1)–C(1)–O(1)	176.9 (3)	C(7)–N–C(9)	129.7 (4)
Fe(1)–C(2)–O(2)	176.4 (3)	C(7)–N–H(N)	116 (6)
Fe(1)–C(3)–O(3)	176.7 (3)	C(9)–N–H(N)	113 (6)
Fe(2)–C(4)–O(4)	179.5 (3)	N–C(9)–C(10)	109.3 (4)
Fe(2)–C(5)–O(5)	178.0 (3)	N–C(9)–C(14)	109.3 (4)
Fe(2)–C(6)–O(6)	176.7 (3)	C(14)–C(9)–C(10)	112.1 (5)
Fe(1)–C(7)–C(8)	116.1 (2)	C(9)–C(10)–C(11)	109.5 (5)
Fe(1)–C(7)–N	126.3 (2)	C(10)–C(11)–C(12)	109.9 (6)
C(8)–C(7)–N	117.0 (3)	C(11)–C(12)–C(12)	115.9 (6)
Fe(2)–C(8)–C(7)	92.0 (2)	C(12)–C(13)–C(14)	111.7 (6)
		C(13)–C(14)–C(9)	109.2 (5)

[a] Excluding phenyl ring and solvent parameters.

taining tetrahedral three-electron donor one-carbon ligands have recently been synthesized via attack by nitrogen[5] or phosphorus[4,6,7] nucleophiles on binuclear σ,π-acetylides[4,5] or trinuclear σ,π-acetylide[7] and σ,π-vinyl compounds.[6,7] Two complexes, namely, [HOs₃(CO)₁₀(CHCH₂PMe₂Ph)][6] and [Fe₂(CO)₆{CHC(Ph)NEt₂}(PPh₂)],[5] have been structurally characterized. The Os(1)–C(1)–Os(2) angle to the bridging ligand in the former is 80.8 (3)°, which compares with Fe(1)–C(7)–Fe(2) angles of 77.4 (0)° in IV and 76.2 (0)° in [Fe₂(CO)₆{(CHC(Ph)NEt₂}(PPh₂)]. The recently reported complex ReW(CO)₉{C(Ph)PMe₃}[28] prepared via treatment of the carbyne complex [(CO)₅Re(CO)₄WCPh] with PMe₃ appears to be yet another example of a three-electron bridging one-carbon ligand but lack of structural details precludes further discussion of this molecule.

When the bridging carbon atom of the three-electron donor ligand is sp² hybridized somewhat larger M–C–M angles are observed. For example, in the recently characterized 1,3-dipolar complex Fe₂(CO)₆{C₂(Ph)(PCy₂H)}(PPh₂)[29] where the nucleophile, dicyclohexylphosphine, is attached to the β carbon of the acetylide in Fe₂(CO)₆(C₂Ph)(PPh₂) the Fe(1)–C(7)–Fe(2) angle is 81.0 (2)° and in [HRu₃(CO)₁₀(C=NMe₂)][30]

containing a 1,2-dipolar iminium ion the Ru(21)–C(2)–Ru(22) angle is 87.98 (17)°. In the complexes HOs₃-{CNMe(R)}(CO)₁₀ (R = Me, CH₂Ph) prepared from Os₃(CO)₁₂ and NMe₃ or NMe₂CH₂Ph[31] a single sp² hybridized bridging three-electron donor carbon atom is also present but no structural data are available.

Two-carbon three-electron ligands analogous to that in V are rare. Tertiary phosphines and phosphites give 1:1 adducts with Fe₂(CO)₆(C₂Ph)(PPh₂).[4] Structurally, these zwitterions resemble V but there is relatively little multiple bonding between phosphorus and the α carbon of the olefin. Adducts of HOs₃(CH=CH₂)(CO)₁₀, HOs₃(CO)₁₀(C≡CPh), and Os₃(CH≡CH)(CO)₁₀ with phosphines have also been described.[6,7] These complexes are zwitterionic and contain three-electron donors which may be one- or two-carbon ligands. A rather different type of two-carbon ligand has been found in the complex (η-C₅H₅)W(CO)(PMe₃)-(CH₃C₆H₄C₂O) where a p-totylketenyl group is coordinated to a single tungsten atom as a three-electron donor.[32] The coordinated olefinic bond length (1.32 Å) in (η-C₅H₅)-W(CO)(PMe₃)(CH₃C₆H₄C₂O) closely resembles the corre-

Table VIII. Selected Least-Squares Planes and Atomic Displacements (Å)[a]

$[Fe_2(CO)_6\{CHC(NHC_6H_{11}\text{-}c)(Ph)\}(PPh_2)]$ (IV)

Plane 1	N	−0.0153	Plane 3		P	−0.0915
Equation: $0.6531X − 0.1500Y$	C(7)	0.0123	Equation: $0.7979X + 0.0772Y$		C(1)	0.0959
$+ 0.7422Z + 3.0190 = 0$	C(8)	−0.0101	$− 0.5979Z + 0.5518 = 0$		C(3)	−0.0975
	C(11)	0.0131			C(7)	0.0930
	C(22)*	−0.0523				
	H(N)*	−0.0551				
Plane 2	C(21)	0.0051	Plane 4		P	0.3467
Equation: $0.3844X + 0.8949Y$	C(22)	−0.0030	Equation: $0.7496X − 0.0066Y$		C(4)	−0.3758
$− 0.2268Z + 1.2595 = 0$	C(23)	−0.0031	$+ 0.6619Z + 3.7280 = 0$		C(6)	0.3766
	C(24)	0.0069			C(7)	−0.3475
	C(25)	−0.0046				
	C(26)	−0.0013				

$[Fe_2(CO)_6\{C(NHC_6H_{11}\text{-}c)CH(Ph)\}(PPh_2)]\cdot0.5C_6H_6$ (V)

|						
Plane 5	Fe(1)	0.1249	Plane 9		C(21)	0.0120
Equation: $0.2534X − 0.06064Y$	Fe(2)	−0.0992	Equation: $0.9354X + 0.3377Y$		C(22)	−0.0093
$+ 0.7537Z + 1.9486 = 0$	C(7)	−0.2325	$+ 0.1054Z + 3.1690 = 0$		C(23)	−0.0013
	C(8)	0.2068			C(24)	0.0093
					C(25)	−0.0064
					C(26)	−0.0043
Plane 6	Fe(1)	0.1978				
Equation: $0.4312X − 0.4480Y$	Fe(2)	−0.3710				
$+ 0.7832Z + 2.6350 = 0$	N	−0.3526	Plane 10		P	−0.1522
	C(7)	0.1084	Equation: $0.9720X − 0.1216Y$		C(2)	−0.1968
	C(8)	0.3987	$+ 0.2009Z + 3.2191 = 0$		C(3)	0.1864
					C(7)	0.1626
Plane 7	N	0.0210				
Equation: $0.6325X − 0.1068Y$	C(7)	−0.0416	Plane 11		P	0.2011
$+ 0.7672Z + 4.1799 = 0$	C(8)	0.0405	Equation: $−0.4521X + 0.3552Y$		C(5)	0.3751
	C(21)	−0.0199	$+ 0.8182Z + 1.7663 = 0$		C(6)	−0.2722
	C(9)*	−0.0724			C(8)	−0.3040
	H(N)*	0.3611				
Plane 8	N	−0.0584				
Equation: $0.7145 − 0.3084Y$	C(7)	0.0197				
$+ 0.6280Z + 3.4551 = 0$	C(9)	0.0174				
	H(N)	0.0214				

[a] Only atoms without asterisks were used in calculating planes.

sponding value of 1.34 (2) Å in $Fe_2(CO)_6\{CP(OEt)_3\text{-}CPh\}(PPh_2)$.[4]

Finally, in the context of the iminium ion character of coordinated ligands in IV and V, it is pertinent to note that reactions of iminium ions with transition metal organometallics have provided several series of complexes in which the $>C=N<$ multiple bond is coordinated in π fashion. Examples are $Mn(CO)_4(CH_2NR_2)$,[33] $[Mo(CO)_3(bpy)(CH_2NMe_2)]I$,[34] $Ni\{OC_6H_4CHNMe\}\{HOC_6H_4CHNHMe\}$,[35] a derivative of the ferrocenylmethylmethyleniminium ion,[36] and $[(R_3P)\text{-}Ni(X)L]$ (X = Cl, Br, I; L = $CH_2NMe_2^+$, ch_2NMeEt^+).[37] Coordination in η^1 fashion is also known as in $(\eta\text{-}C_5H_5)\text{-}Mo(CO)_3(CH_2NMe_2)$,[34] $\eta\text{-}C_5H_5Ni(CH_2NMe_2)PPh_3$,[37] and $[(\eta\text{-}C_5H_5)_2Mo(Cl)(CCF_3NH_2)]Cl$.[38]

Comments on the Reaction of $Fe_2(CO)_6(C_2Ph)(PPh_2)$ with Cyclohexylamine. The addition of cyclohexylamine across the triple bond of $Fe_2(CO)_6(C_2Ph)PPh_2$ proceeds readily at or slightly above room temperature giving the complexes IV and V in good overall yields. This reaction is unusual in organometallic chemistry since it involves attack by a neutral nucleophile at carbon in a neutral complex. A comparison might be made with the complexes of electrophilic carbenes, which form ylide complexes with certain phosphorus[39] and nitrogen nucleophiles.[40] Such a comparison emphasizes the electron-deficient nature of the α- and β-carbon atoms in $Fe_2(CO)_6\text{-}(C_2Ph)(PPh_2)$. In terms of acetylide reactivity in $Fe_2(CO)_6\text{-}(C_2Ph)(PPh_2)$ there is also a rather close analogy with highly activated acetylenes such as dimethyl acetylenedicarboxylate which undergo rapid reactions with secondary amines to

generate enamines.[41] However, in contrast to activated acetylenes, the products of amine addition to the σ,π-acetylide are not the σ,π-enamines VI and VII but their valence isomers, the metalloiminium zwitterions. Mechanistically, the enamines VI and VII may well be implicated in these reactions since an attractive sequence of events involves initial attack at either the α- or β-carbon atom of the acetylide followed by hydrogen transfer and isomerization of the resulting enamine.[42] Such a mechanism is strongly supported by the characterization of insoluble adducts (cf. VIII) from addition of secondary amines to $Fe_2(CO)_6(C_2Ph)(PPh_2)$ at low temperature which convert smoothly to iminium ion complexes analogous to IV above room temperature[43] and by the structural characterization via x-ray crystallography of a
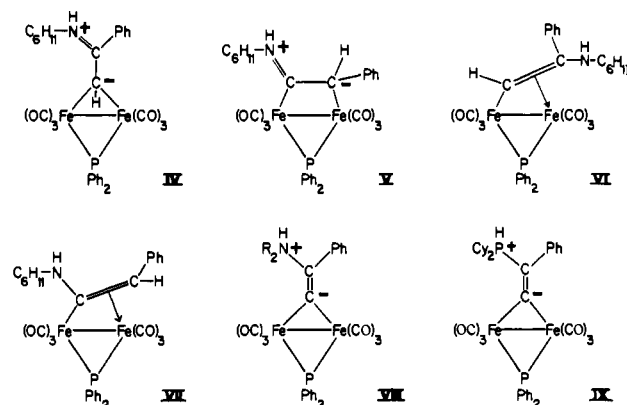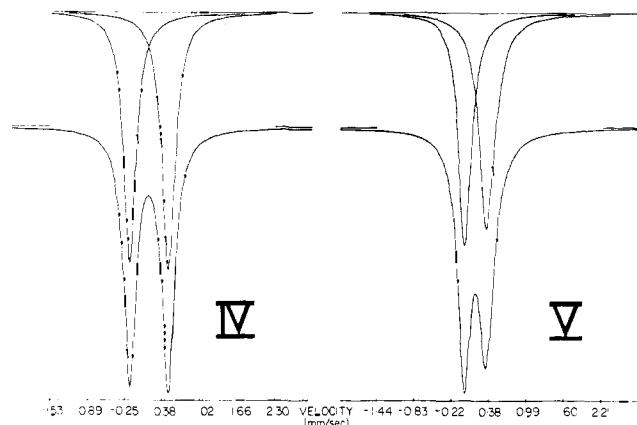
Figure 3. Mössbauer spectra of [Fe₂(CO)₆{CHC(NHC₆H₁₁-c)}Ph(PPh₂)] (IV) and [Fe₂(CO)₆{C(NHC₆H₁₁-c)CHPh}(PPh₂)]·0.5C₆H₆ (V). Upper lines represent Lorentzian components and lower lines the fitted spectra.

secondary phosphine model, structure IX[29] for VIII. Although this mechanism is entirely reasonable, it might be argued that the appearance of products in approximately equal quantities derived from the parent by nucleophilic attack at *both* acetylenic carbon atoms is unexpected. Certainly the very unsymmetrical σ,π mode of bonding of the acetylide in Fe₂(CO)₆-(C₂Ph)(PPh₂) shown by the x-ray analysis[14] implies a definite polarization in the multiple bond and the α-carbon atom appears to be less sterically hindered than the β atom which bears a phenyl substituent. It is apparent, however, from other experiments with a variety of group 5 bases that the site of attack cannot be rationalized on the basis of steric bulk of the incoming nucleophile alone. Thus the secondary amines NR₂H (R = Me, Et, *n*-Pr)[5,43] give quantitative yields of products from β-attack while phosphites P(OR)₃ (R = Me, Et, *n*-Bu) attack the α carbon[4,43] and secondary phosphines PR₂H (R = Ph, Cy-c) give, quantitatively, products from β-carbon attack.[29,43] Low-temperature ³¹P and ¹³C NMR experiments, the latter utilizing specific ¹³C enrichment of the α-carbon position, are currently in progress to elucidate factors influencing the path of these reactions.[43] In particular the possibility of phenyl group migration, analogous to the "phenonium ion" concept in organic chemistry,[44] accounting for different product distributions is being investigated.

The dipolar character of the ligands in IV and V render both complexes highly susceptible to attack by both electrophiles and nucleophiles as well as dipolar acetylenes and olefins. These reactions will be the subject of a forthcoming publication.

Spectroscopic Properties. The solution infrared spectra of IV exhibit five bands in the carbonyl region while spectra of V are characterized by only four bands, one of which (1956 cm⁻¹) is very broad. Compared to the parent Fe₂(CO)₆-(C₂Ph)(PPh₂), the ν(CO) bands of IV and V appear at significantly lower frequencies indicating charge delocalization from the ligands to the Fe(CO)₃ moieties. From the ν(CO) frequencies, greater ligand to metal charge transfer occurs with the one-carbon ligand in IV. Indeed from studies with both nitrogen and phosphorus nucleophiles it is apparent that the frequency of the highest ν(CO) band can be used as a diagnostic criterion for the site of nucleophilic attack, with higher ν(CO) values invariably associated with the two-carbon three-electron ligands.

Despite the structural similarities between the phosphido bridges in IV and V there is a difference of almost 30 ppm in ³¹P chemical shifts for IV and V. The origin of this difference may well be related to the charge transfer capabilities of the ligands. Whether ³¹P shifts for phosphido bridges in general

are sensitive to electronic structure in binuclear complexes remains to be seen.

Mössbauer spectra of IV and V are shown in Figure 3. The most significant features of these spectra are the appearance of only one quadrupole doublet in each case (IV, δ 0.16, Δ 0.65; V, δ 0.17, Δ 0.39 mm s⁻¹) indicating that the Mössbauer experiment is incapable of distinguishing the two iron environments in each of IV and V, the presence of small quadrupole splittings typical of distorted octahedral stereochemistry of the iron sites and the larger Δ value in IV. These Δ values are characteristic for one- and two-electron ligands derived from Fe₂(CO)₆(C₂Ph)(PPh₂) via attack by group 5 nucleophiles. Isomer shifts for IV and V are in the range normally associated with low-spin Fe(0) complexes.

Supplementary Material Available: Tables of phenyl ring distances and angles and carbon–hydrogen distances for IV and V and structure factor tables for IV and V (35 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of Trimethyl Phosphite Derivatives $HFeCo_3(CO)_{12-x}[P(OCH_3)_3]_x$, $x = 1, 2, 3, 4$. Crystal and Molecular Structure of $HFeCo_3(CO)_9[P(OCH_3)_3]_3$ at -139 °C[1]

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Abstract: The series of derivatives $HFeCo_3(CO)_{12-x}[P(OCH_3)_3]_x$, $x = 1, 2, 3, 4$, has been synthesized from $HFeCo_3(CO)_{12}$ and $P(OCH_3)_3$ under a variety of conditions. Infrared and Mössbauer spectral data were obtained; ^1H NMR gives satisfactory signals for hydrogen of methyl groups on the ligand but no signals were observed for hydrogen on the metal cluster. The structure of $HFeCo_3(CO)_9[P(OCH_3)_3]_3$ has been determined from data collected at -139 °C on an automated diffractometer with monochromatized Mo Kα radiation. The compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 16.336 (3)$ Å, $b = 10.896 (2)$ Å, $c = 18.583 (2)$ Å, $\beta = 97.26 (1)°$, and $V = 3281 (1)$ Å³ at 25 °C. The density at 25 °C of 1.737 g cm⁻³ calculated on the basis of four molecules per unit cell agrees with the flotation value of 1.72 g cm⁻³. At -139 °C the cell parameters are $a = 15.992 (6)$ Å, $b = 10.638 (3)$ Å, $c = 18.403 (4)$ Å, $\beta = 98.575 (25)°$, $V = 3093 (3)$ Å³, and $d_{calcd} = 1.843$ g cm⁻³. The structure was solved by use of direct methods and Fourier summations and the full-matrix, least-squares refinement, based on 6057 independent observed reflections measured at -139 °C, converged to a conventional R index of 0.061. The four metal atoms are at the corners of a tetrahedron. Six of the nine carbonyl groups are terminally bound, three to Fe with an average Fe–C distance of 1.798 Å and one to each Co with an average Co–C distance of 1.755 Å. The other three carbonyl groups form symmetric Co–C–Co bridges with an average Co–C distance of 1.954 Å. The molecule has Fe–Co distances averaging 2.560 Å and Co–Co distances averaging 2.488 Å. All three trimethyl phosphite ligands are trans to Fe; the average Fe–Co–P angle is 174°. The hydrogen atom is located outside the cluster on the threefold axis in a face-bridging position 0.75 Å from the Co₃ plane; the average Co–H distance is 1.63 (15) Å. The molecular threefold axis lies approximately parallel to the c axis in the crystal.

Introduction

The tetranuclear mixed metal carbonyl hydride $HFeCo_3(CO)_{12}$ was first synthesized and characterized by Chini et al. in 1960.[2] A comparison of carbonyl IR spectra and x-ray powder patterns indicated that this compound is isostructural with $Co_4(CO)_{12}$ and thus has C_{3v} symmetry.[3] Mays[4,5] and coworkers have carried out IR and mass spectra on this compound and kinetic isotope studies on the protonation of the anion $FeCo_3(CO)_{12}^-$, and proposed on the basis of this evidence that the hydrogen atom might be located in the center of the cluster.

White and Wright[6] confirmed the C_{3v} symmetry of the molecule through inelastic neutron scattering spectroscopy, and on the basis of the magnitude of bonding force constants also concluded that the hydrogen atom must be located in the center of the cluster and not outside of the tetrahedron. Following earlier success in our laboratory in the characterization and elucidation of the intramolecular tautomerism of hydrogen through ^1H NMR studies of $P(OCH_3)_3$-substituted hy-

drido-metal cluster complexes,[7] we were prompted to synthesize the series of complexes described in the title. A parallel but independent effort by Cooke and Mays on a more extensive but nonoverlapping series of complexes with a variety of phosphorus donor ligands has recently been described in the literature.[8] The infrared and Mössbauer data obtained in both studies yielded some useful information about stereochemistry; however, this could not lead to a conclusive assignment for the position of hydrogen on the cluster. Significantly, in every case, no ^1H NMR signal for this hydrogen atom could be obtained. We then turned to a low-temperature x-ray study on the tris(trimethyl phosphite) derivative in an attempt to locate the hydrogen atom. The full account of this work is contained in the present article. A complementary and independent neutron diffraction study of $HFeCo_3(CO)_9[P(OCH_3)_3]_3$ appears in a companion paper.[9]

Experimental Section

Reagents. $Co_2(CO)_8$ was purchased from Ventron Chemical Co., $Fe(CO)_5$ from Strem Chemical Co., and $P(OCH_3)_3$ from Matheson