rangement $\Pi^x{}_{\xi\xi}$ and $\Pi^x{}_{\eta\eta}$ are expected to be the dominant terms because $\xi_a(\eta_a)$ and $\xi_b(\eta_b)$ can overlap with the same oxygen p orbital leading to a strong interaction.[3] This is in good agreement with the observed high intensities of the two bands at 14 652 and 14 812 cm^{-1}.

We therefore conclude that the polarized absorption spectrum of the dinuclear chromium(III) complex $[(NH_3)_5Cr(OH)Cr(NH_3)_5]^{5+}$ in the region of single pair excitations $^4A_{2g}{}^4A_{2g} \rightarrow {}^4A_{2g}{}^2E_g$, $^4A_{2g}{}^2T_{1g}$ offers clear evidence for the presence of at least two intensity-gaining mechanisms. The determination of the crystal structure was necessary to obtain this information.

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Registry No. $[(NH_3)_5Cr(OH)Cr(NH_3)_5]Cl_5 \cdot 2H_2O$, 62521-11-3.

Supplementary Material Available: Listings of structure factor amplitudes and anisotropic temperature factors (11 pages). Ordering information is given on any current masthead page.

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Synthesis and Spectroscopic Characterization of Binuclear, Phosphido-Bridged σ–π-Acetylido Complexes of Iron. X-Ray Structure of a Triphenylphosphine Derivative

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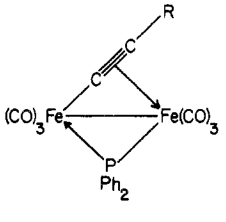
The syntheses of a range of binuclear σ–π-acetylide complexes of iron $Fe_2(CO)_6(C_2R)(PR'R'')$ (R = R′ = R″ = Ph; R = R′ = Ph, R″ = C_2Ph; R = Ph, R′ = Bu^t, R″ = C_2Ph; R = Bu^t, R′ = R″ = Ph; R = Pr^i, R′ = R″ = Ph; R = Cy, R′ = R″ = Ph) from phosphinoacetylenes $RC{\equiv}CPR'R''$ and diiron enneacarbonyl are described. These compounds and the corresponding PPh_3 substitution products $Fe_2(CO)_5(C_2R)(PR'R'')(PPh_3)$ have been characterized by microanalysis and infrared, mass, and Mössbauer spectroscopy. Single crystals of $Fe_2(CO)_5(C_2Ph)(PPh_2)(PPh_3) \cdot C_6H_{12}$ are triclinic, space group $P\bar{1}$, with cell dimensions $a = 17.975$ (8), $b = 10.143$ (6), $c = 13.181$ (8) Å; $\alpha = 95.10$ (7), $\beta = 112.30$ (4), $\gamma = 97.54$ (4)°. There are two molecules in the unit cell. The structure was solved by a combination of Patterson and Fourier techniques using 3973 independent observed reflections ($I > 3\sigma(I)$) measured on a GE-XRD6 diffractometer. Refinement by full-matrix least-squares methods gave values of R and R_w of 0.038 and 0.045, respectively. In the binuclear molecule the two iron atoms (Fe(1)–Fe(2) = 2.648 (1) Å) are bridged by a diphenylphosphido group and an acetylide σ-bonded to Fe(1) and π-bonded to Fe(2). The σ–π-acetylide has a C(6)–C(7) acetylenic bond length of 1.225 (6) Å and has a trans bent configuration. The triphenylphosphine molecule occupies a terminal position on Fe(1) (Fe(1)–P(2) = 2.274 (1) Å) trans to the phosphorus atom of the phosphide bridge. The mode of formation of these σ–π-acetylides and structural similarities to σ–π-vinyl complexes are discussed.

Introduction

Recognition of the enhancement and modification of reactivity afforded by π coordination of acetylenes has led to the discovery of synthetic routes to numerous important organometallic and organic compounds.[1-5] For metals in low oxidation states, it is generally accepted that π-coordinated acetylenes are susceptible to electrophilic attack although mechanisms have been firmly established in relatively few cases.[6] Dimerization and oligomerization of acetylenes by low-valent metal complexes are special cases.[1-3] Acetylene π complexes are accepted intermediates but the oligomerization may proceed via concerted multicentered or ionic mechanisms. Cyclobutadiene,[7] metallocyclic,[8] and σ-acetylide[9] complexes have been frequently postulated intermediaries. During the course of studies designed to trap various π-acetylene intermediates using phosphinoacetylenes we investigated the reactions of $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ with ligands of the type $R_2PC{\equiv}CR$. A common feature of these reactions is the facile cleavage of a $P–C_{sp}$ bond which occurs in the formation of trinuclear ferracyclopentadiene[10] and ferracyclobutene[11] complexes from $Fe_3(CO)_{12}$ as well as σ–π-acetylide[12] and phosphoniacyclopentadiene[13] complexes from $Fe_2(CO)_9$. The possible role of acetylido complexes in these reactions and in other oligomerization sequences prompted a more detailed investigation of the synthesis, characterization, and reactions of σ–π-acetylide complexes of type I. This paper describes a general route to these derivatives from $Fe_2(CO)_9$. Since the initial characterization



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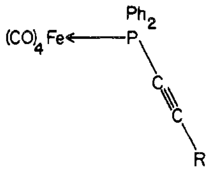

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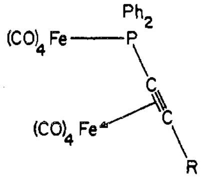

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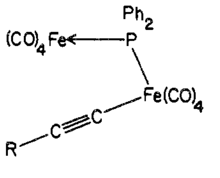

IV

of I (R = R′ = R″ = Ph) several other σ–π-acetylide complexes, other than the copper, silver, and gold alkynyls and phosphine derivatives,[14] have been described. Thus, reactions of group 1B acetylides with η^5-$C_5H_5Fe(CO)_2X$ (X = Cl,Br), η^5-$C_5H_5Ru(Cl)(PPh_3)_2$, $RhCl(PPh_3)_3$, and *trans*-$Ir(CO)Cl(PPh_3)_2$ have afforded the compounds $[\eta^5$-$C_5H_5Fe(CO)_2(C_2Ph)CuCl]_2$,[15] $[\eta^5$-$C_5H_5Ru(PPh_3)_2(C_2R)CuCl]$,[16] $Rh(PPh_3)_3(C_2C_6F_5)_5Ag_2$,[17] and $Cu_4Ir_2(PPh_3)_2(C_2Ph)_8$[18] which contain acetylides σ-bonded to one metal and π-bonded to a second metal atom. There are strong indications from recent studies on the reactivity of the σ–π-acetylide in $Fe_2(CO)_6(C_2R)(PPh_2)$[19] that the chemistry of the triple bond in these derivatives is uniquely different from but equally as rich as that in π-acetylene[5,6] or σ-acetylide complexes.[20]

Experimental Section

Acetylenes were obtained from Farchan Research Laboratories, Willoughby, Ohio, or from Aldrich Chemical Co. Ltd.

Synthesis of Ligands. The ligands Ph_2PC_2Ph, $Ph_2PC_2Bu^t$, and $Ph_2PC_2Pr^i$ were synthesized according to literature methods.[21]

$PhP(C_2Ph)_2$. This compound was prepared in 85% yield from $PhPCl_2$ and the lithium salt of PhC_2H as described for Ph_2PC_2Ph.[20] The white crystalline material had mp 53–55 °C with $\nu(C{\equiv}C)$ at 2160 cm^{-1} in a Nujol mull and a parent ion peak at *m/e* 310 in the mass spectrum. The unit cell and space group have been briefly reported but no other physical characteristics were given.[22]

Ph_2PC_2Cy. *n*-Butyllithium (58 mL of 15%) in ether was added over 1 h to cyclohexylacetylene (10.8 g) in diethyl ether (75 mL) at −78 °C in a three-necked 500-mL flask. The mixture was stirred for 1 h; then diphenylchlorophosphine (22.0 g) in diethyl ether (50 mL) was added over a period of 1 h. After the addition, the reaction mixture was allowed to warm up to room temperature. The precipitate of LiCl was filtered off in vacuo and solvent removed under reduced pressure. The residual oil was dissolved in anhydrous ether, ethanol added, and the solution cooled overnight at −10 °C. Colorless crystals of the product, mp 56–58 °C (yield 56%), were obtained. Anal. Calcd: C, 82.19; H, 7.19; P, 10.62. Found: C, 82.06; H, 7.23; P, 10.55. IR (cm^{-1}; Nujol): 2172 (s) 2140 (w) ($\nu(C{\equiv}C)$). Mass spectrum: *m/e* 292 (100) M$^+$, 277 (4), 263 (10), 251 (6), 237 (9), 224 (9), 210 (16).

$Bu^tP(C_2Ph)_2$. *tert*-Butyldichlorophosphine was prepared as described elsewhere.[23] The synthesis of $Bu^tP(C_2Ph)_2$ from 2 mol of PhC_2Li and Bu^tPCl_2 followed the procedure established for Ph_2PC_2Ph. White needles of the product were obtained in 50% yield and had mp 87–88 °C. Anal. Calcd: C, 82.74; H, 6.60. Found: C, 82.78; H, 6.66. IR (cm^{-1}; Nujol): 2155 ($\nu(C{\equiv}C)$). Mass spectrum: *m/e* 290 (15) M$^+$, 233 (100), 206 (9), 202 (11), 150 (9), 132 (29).

Synthesis of Iron Carbonyl Complexes. General Procedures. All reactions, chromatography, and subsequent workup were carried out under nitrogen using standard double-manifold techniques and solvents dried and deoxygenated over $LiAlH_4$. Alumina and Florisil were Fisher A540 and Baker reagents, respectively, and were used after degassing in vacuo. Reactions were monitored by infrared spectroscopy in the ν(CO) region with 2.5× abscissa expansion. Samples were removed by a syringe through a serum cap, solvent was evaporated in vacuo, and residue was dissolved in cyclohexane.

$Fe_2(CO)_6(C_2Ph)(PPh_2)$. Diiron enneacarbonyl (5.5 g, 0.015 mmol) and Ph_2PC_2Ph (2.86 g, 0.01 mmol) were stirred in benzene (150 mL) for 5 days. The solution was filtered, reduced to low volume, and chromatographed on a Florisil column made up in petroleum ether. The first band, eluted with petroleum ether, is composed mainly of $Fe_2(CO)_6(C{\equiv}CPh)(PPh_2)$ mixed with the smaller quantities of the phosphine complex $Fe(CO)_4(Ph_2PC{\equiv}CPh)$. [These two compounds have very similar R_f values and cannot be completely separated. However, on fractional crystallization of the eluate from the first band, $Fe_2(CO)_6(C_2Ph)(PPh_2)$ crystallized preferentially leaving mother liquor rich in $Fe(CO)_4(Ph_2PC{\equiv}CPh)$.] The volume of solution was then reduced to ca. 20 mL and cooled to −20 °C affording large prisms of pure $Fe_2(CO)_6(C{\equiv}CPh)(PPh_2)$; yield 20% based on phosphine; mp 108–110 °C dec. Anal. Calcd for $Fe_2(CO)_6(C_2Ph)(PPh_2)$: C, 55.17; H, 2.67; P, 5.47. Found: C, 55.07; H, 2.56; P, 5.35. Mass spectrum: *m/e* 566 (3) M$^+$, 538 (4), 510 (19), 482 (8), 454 (6), 426 (50), 398 (100), 362 (18), 320 (16), 296 (9).

$Fe(CO)_4(Ph_2PC_2Ph)$. This compound was obtained as an oil (15%) from the mother liquors after removal of $Fe_2(CO)_6(C_2Ph)(PPh_2)$ as above. The compound is better obtained via the reaction of equimolar quantities of $Fe_2(CO)_9$ and Ph_2PC_2Ph in tetrahydrofuran under carbon monoxide followed by chromatography on alumina. The bright yellow complex was eluted with petroleum ether. The complex is an oil at 25 °C. Anal. Calcd for $Fe(CO)_4(Ph_2PC_2Ph){\cdot}0.5C_6H_6$: C, 65.74; H, 3.68; P, 6.28. Found: C, 66.33; H, 5.12; P, 6.63. Mass spectrum: *m/e* 454 (4) M$^+$, 426 (4), 398 (13), 370 (47), 342 (100). IR (cm^{-1}; C_6H_{12}): 2052 (s), 1980 (s), 1953 (vs), 1942 (vs).

$Fe_2(CO)_6(C_2Ph)[PPh(C_2Ph)]$. This complex was obtained in a fashion identical with that above using the ligand $PhP(C_2Ph)_2$. Red-brown prisms were crystallized from petroleum ether; mp 132 °C. Anal. Calcd for $Fe_2(CO)_6(C_2Ph)PhP(C_2Ph)$: C, 56.98; H, 2.56; P, 5.25. Found: C, 56.75; H, 2.39; P, 5.29. Mass spectrum: *m/e* 590 (9) M$^+$, 562 (12), 534 (12), 506 (24), 478 (14), 450 (40), 422 (100). IR (cm^{-1}; C_6H_{12}): 2180 (w) ($\nu(C{\equiv}C)$ (uncoordinated)).

$Fe_2(CO)_6(C_2Bu^t)(PPh_2)$. Diiron enneacarbonyl (3.6 g, 0.01 mol) and $Ph_2PC_2Bu^t$ (2.7 g, 0.01 mol) were stirred together in benzene (150 mL) for 2 days at room temperature. Infrared spectra of the reaction mixture indicated that the major product was the phosphorus-coordinated complex $Fe(CO)_4(Ph_2PC_2Bu^t)$ together with much smaller quantities of *trans*-$Fe(CO)_3(Ph_2PC_2Bu^t)_2$ and the required complex $Fe_2(CO)_6(C_2Bu^t)(PPh_2)$. A further 0.01 mol of $Fe_2(CO)_9$ was added and the mixture stirred for a further 2 days. At this stage approximately equal quantities of $Fe(CO)_4(Ph_2PC_2Bu^t)$ and $Fe_2(CO)_6(C_2Bu^t)(PPh_2)$ were present. Precipitation of unwanted side products was accomplished by addition of *n*-heptane and the mixture was filtered with a filter stick. The clear red solution was evaporated to a few milliliters and chromatographed on a Florisil column made up in petroleum ether. Fast-traveling bands due to $Fe(CO)_4(Ph_2PC_2Bu^t)$ and $Fe_2(CO)_6(C_2Bu^t)(PPh_2)$ had almost the same R_f values and only small amounts of these components could be separated on elution with petroleum ether. Fractions rich in $Fe_2(CO)_6(C_2Bu^t)(PPh_2)$ yielded bright red prisms of the binuclear complex on standing at 0 °C overnight. Eventually yellow needles of $Fe(CO)_4(Ph_2PC_2Bu^t)$ crystallized on prolonged standing (~20%); mp 80–81 °C. Anal. Calcd for $Fe(CO)_4(Ph_2PC_2Bu^t)$: C, 51.17; H, 2.25. Found: C, 51.27; H. 2.09. Mass spectrum: *m/e* 434 (2) M$^+$, 406 (1), 378 (7), 350 (22), 322 (100). IR (cm^{-1}; C_6H_{12}): ν(CO) 2053 (s), 1979 (s), 1951 (vs), 1942 (vs); $\nu(C{\equiv}C)$ (uncoordinated) 2169 (w).

Yields of $Fe_2(CO)_6(C_2Bu^t)(PPh_2)$ were in the range 15–25%. Some improvement in yield (5–10%) occurred when excess $Fe_2(CO)_9$ was used; mp 95–97 °C. Anal. Calcd for $Fe_2(CO)_6(C_2Bu^t)(PPh_2)$: C, 52.79; H, 3.64; P, 5.49. Found: C, 52.92; H, 3.51; P, 5.67. Mass spectrum: *m/e* 546 (3) M$^+$, 518 (6), 490 (16), 460 (6), 434 (3), 406 (43), 378 (100), 322 (5), 296 (3). Similar yields of the same compound were formed on photolysis of *trans*-$Fe(CO)_3(Ph_2PC_2Bu^t)_2$ and $Fe_2(CO)_9$ in benzene. Another product eluted from the column was $Fe_2(CO)_5(C_2Bu^t)(PPh_2)(Ph_2PC_2Bu^t)$, bright red crystals, mp 168–172 °C (second band; 1:1 benzene–petroleum ether, yield <5%). Anal. Calcd: C, 62.77; H, 4.88; P, 7.90. Found: C, 62.67; H, 4.97; P, 7.70. IR (cm^{-1}; C_6H_{12}): 2035 (s), 1993 (vs), 1969 (s), 1956 (s), 1937 (w), (ν(CO)); 2194 (w), 2154 (w) ($\nu(C{\equiv}C)$(uncoordinated)). *trans*-

$Fe(CO)_3(Ph_2PC_2Bu^t)_2$ was also eluted from the column (third band, 100% benzene, yield <5%).[24]

$Fe_2(CO)_6(C_2Ph)[P(Bu^t)(C_2Ph)]$. This compound was prepared similarly to $Fe_2(CO)_6(C_2Bu^t)(PPh_2)$. Large red-brown clusters crystallized out from mixtures of $Fe(CO)_4[Ph(Bu^t)PC_2Ph]$ and $Fe_2(CO)_6(C_2Ph)[P(Bu^t)C_2Ph]$ rich in the latter; mp 118–120 °C; yield 25–30%. Anal. Calcd for $Fe_2(CO)_6(C_2Ph)[P(Bu^t)(C_2Ph)]$: C, 54.78; H, 3.34; P, 5.43. Found: C, 54.84; H, 3.45; P, 5.25. Mass spectrum: *m/e* 570 (1) M^+, 542 (1), 526 (8), 514 (3), 506 (4), 486 (12), 458 (10), 430 (12), 402 (36), 346 (100), 304 (11), 244 (27), 233 (51). IR (cm^{-1}; C_6H_{12}): 2156 (w) (ν(C≡C)(uncoordinated)).

$Fe_2(CO)_6(C_2Pr^i)(PPh_2)$. The method used was basically similar to that outlined above for $Fe_2(CO)_6(C_2Bu^t)(PPh_2)$. However, no crystals were obtained after storage at −20 °C for 1 week. Repeated treatment of the $Fe(CO)_4(Ph_2PC_2Pr^i)/Fe_2(CO)_6(C_2Pr^i)(PPh_2)$, mixture with $Fe_2(CO)_9$ failed to completely convert $Fe(CO)_4(Ph_2PC_2Pr^i)$ to the σ–π-acetylide. The mixture of these two compounds was therefore photolyzed in benzene using a 150-W air-cooled Hanovia medium-pressure mercury lamp placed 5 cm from the Pyrex reaction vessel. From earlier work it was known that on photolysis the compounds $Fe(CO)_4(Ph_2PC_2R)$ (R = Bu^t Pr^i, Ph) are converted to the derivatives $Fe_2(CO)_5(C_2R)(PPh_2)(Ph_2PC_2R)$, which are phosphine substitution products of $Fe_2(CO)_6(C_2R)(PPh_2)$. The substitution products can be readily separated from $Fe_2(CO)_6(C_2R)(PPh_2)$ on a Florisil column. A photolysis time of 30 min gave a quantitative conversion of $Fe(CO)_4(Ph_2PC_2Pr^i)$. The σ–π-acetylide $Fe_2(CO)_6(C_2Pr^i)(PPh_2)$ eluted with petroleum ether was obtained as an oil which could not be crystallized. The compound was shown to be spectroscopically pure by infrared spectroscopy and was converted to the triphenylphosphine substitution product (vide infra).

$Fe_2(CO)_6(C_2Cy)(PPh_2)$. This complex was prepared from $Fe_2(CO)_9$ and Ph_2PC_2Cy as for the isopropyl derivative above. The purified complex which would not crystallize was identified by infrared spectroscopy and converted to the triphenylphosphine derivative (vide infra).

$Fe_2(CO)_5(C_2R)(PPh_2)(PPh_3)$ (R = Ph, Bu^t, Pr^i, Cy). All of these substitution products were synthesized from the $Fe_2(CO)_6(C_2R)(PPh_2)$ precursors by refluxing with a slight excess of triphenylphosphine in benzene for 30 min followed by chromatography on Florisil and elution with a 50:50 benzene–petroleum ether mixture. Recrystallization from *n*-heptane afforded in all cases dark red crystals. Yields were in the range 80–90%. Anal. Calcd for R = Ph: C, 67.46; H, 4.85; P, 7.10. Found: C, 66.81; H, 4.50; P, 6.92. Calcd for R = Bu^t: C, 63.11; H, 4.39; P, 7.94. Found: C, 63.22; H, 4.45; P, 7.81. Calcd for R = Pr^i: C, 62.69; H, 4.21; P, 8.08. Found: C, 62.69; H, 4.24; P, 7.93. Calcd for R = Cy: C, 64.05; H, 4.57; P, 7.68. Found: C, 63.18; H, 4.47; P, 7.75.

Physical Measurements. Infrared spectra were measured on a Perkin-Elmer 180 spectrometer using 0.5-mm matched sodium chloride cells. The Mössbauer drive and associated electronics have been previously described.[25] The source was 10 mCi of ^{57}Co in a palladium matrix. The source was maintained at room temperature and absorbers were kept at liquid nitrogen temperature. Compounds were examined as thick mulls. The velocity scale was calibrated against the quadrupole splitting of a nitroprusside absorber. The accuracy of the Mössbauer parameters is estimated to be ±0.02 mm s^{-1}. Spectra were fitted to Lorenztian line shapes by a least-squares fitting program LFIT which allows variation of positions, line widths, and intensities separately or sequentially for each component in a spectrum. Goodness of fit was assessed by the magnitude of the estimated standard deviation for the fitted spectrum. Mass spectra were obtained from an AEI MS30 spectrometer, operating at 70 eV.

X-Ray Crystal Structure Analysis of $Fe_2(CO)_5(C_2Ph)(PPh_2)(PPh_3)\cdot C_6H_{12}$. Space Group and Lattice Parameters. On the basis of Weissenberg and precession photography, the crystals were assigned to the triclinic system. Least-squares refinement of 2θ values for 26 reflections measured using Mo Kα radiation (λ 0.7107 Å) on a General Electric XRD-6 Datex automated diffractometer yielded the following unit cell dimensions: $a = 17.975$ (8), $b = 10.143$ (6), $c = 13.181$ (8) Å; $\alpha = 95.10$ (7), $\beta = 112.30$ (4), $\gamma = 97.54$ (4)°. The experimental density of 1.34 g cm^{-3} measured by flotation is in agreement with the value of 1.348 g cm^{-3} calculated on the basis of two formula units of $Fe_2(CO)_5(C_2Ph)(PPh_2)(PPh_3)\cdot C_6H_{12}$ of mol wt 884.52/unit cell. With $Z = 2$ and no systematic absences the choice of space groups was $P1$ or $P\bar{1}$ of which the latter proved to be correct by the successful refinement of the structure.

Table I. Atomic Positions (Fractional × 10^4) for Selected Atoms of $Fe_2(CO)_5(C_2Ph)(PPh_2)(PPh_3)\cdot C_6H_{12}$

	x	*y*	*z*
Fe(1)	2480.0 (4)	1474.9 (6)	250.3 (5)
Fe(2)	3722.6 (4)	178.8 (6)	985.8 (5)
P(1)	3656.5 (7)	2231 (1)	1676.0 (9)
P(2)	1517.6 (7)	108 (1)	−1268.1 (9)
O(1)	5161 (2)	−237 (4)	2850 (3)
O(2)	4510 (2)	1245 (4)	−407 (3)
O(3)	3309 (3)	−2448 (4)	−439 (4)
O(4)	1378 (2)	2892 (4)	865 (3)
O(5)	2839 (2)	3415 (4)	−1085 (3)
C(1)	4596 (3)	−94 (5)	2126 (4)
C(2)	4200 (3)	866 (5)	153 (4)
C(3)	3447 (3)	−1441 (5)	109 (4)
C(4)	1801 (3)	2325 (5)	602 (4)
C(5)	2706 (3)	2646 (5)	−566 (4)
C(6)	2579 (2)	69 (4)	1117 (3)
C(7)	2871 (2)	−692 (4)	1773 (4)
C(11)	3005 (3)	−1636 (4)	2570 (4)
C(12)	3424 (4)	−1157 (6)	3697 (4)
C(13)	3530 (4)	−2052 (7)	4454 (5)
C(14)	3230 (4)	−3388 (7)	4092 (6)
C(15)	2821 (4)	−3879 (6)	2992 (6)
C(16)	2698 (3)	−2998 (5)	2215 (5)

Collection and Reduction of Intensity Data. A prism of dimensions ~0.33 mm^3 was mounted on a glass fiber and aligned with a^* parallel to the ϕ axis of the diffractometer. The intensity data were collected at room temperature (298 K) using Zr-filtered Mo Kα radiation (λ 0.7107 Å) and a takeoff angle of 4°. The integrated intensities were measured with a scintillation counter employing a pulse height analyzer. The diffracted x-ray beam passed through a collimator of 1-mm diameter placed 5 cm from the crystal and then to the counter via an aperture of 1-cm diameter, 18 cm from the crystal. Data were collected in the θ–2θ scan mode with the scan width determined by the equation $\Delta\theta = \pm(0.9 + 0.43 \tan \theta)°$ and the scan rate 2°/min. Stationary-counter, stationary-crystal background counts of 10 s were taken before and after each scan. Three standard reflections ($20\bar{3}$, 030, 003) were monitored after every 100 reflections measured. These varied in intensity by ±2% over the course of data collection and were used to scale the data to a common level. Standard deviations were estimated from counting statistics. Of 5683 independent reflections measured ($2\theta \leq 45°$), 3973 with intensities $I > 3\sigma(I)$ were considered observed and used in the analysis. Lorentz and polarization corrections were applied to the derivation of structure amplitudes. The value of μ for these atoms using Mo Kα radiation was 8.05 cm^{-1}. The maximum error introduced by neglect of absorption effects was estimated as ±4% in *F*.

Solution and Refinement of the Structure. The coordinates of the iron atoms were determined from a three-dimensional Patterson synthesis. A subsequent Fourier map phased by the iron atoms revealed the majority of nonhydrogen atoms present. The remaining nonhydrogen atoms including the solvent (cyclohexane) were located from a further Fourier map. With all atoms having isotropic temperature parameters, the structure was refined by full-matrix least-squares methods to an agreement value $R = \sum||F_o| - |F_c||/\sum|F_o|$ of 0.069. Refinement with anisotropic temperature factors reduced *R* to 0.051. A difference Fourier at this stage showed the positions of all phenyl ring hydrogen atoms. These were included in the refinement together with a weighting scheme of the type $w^{-1} = 1.1910 - 0.0371|F| + 0.0007|F|^2$ with coefficients derived from the program Ranger. The refinement converged at $R = 0.038$ with a weighted residual $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ of 0.045. In the final cycle, no nonhydrogen atom parameters were observed to shift by more than one-fourth of their standard deviations. A final difference Fourier revealed no peaks greater than 0.29 e $Å^{-3}$. In all least-squares cycles the function minimized was $\sum w(|F_o| - |F_c|)^2$. Scattering factors used including anomalous scattering corrections for iron were taken from ref 26. Atomic positional parameters for heavy atoms excluding phosphorus phenyl ring carbon atoms are listed in Table I. Corresponding thermal parameters are shown in Table II. The atomic positional and thermal parameters for the 30 carbon atoms of phenyl rings attached to phosphorus and the six carbon atoms of the molecule of cyclohexane of crystallization are listed in supplementary Tables S1 and S2, respectively. Hydrogen atom positions and isotropic

Table II. Anisotropic Thermal Parameters for Selected Atoms of $Fe_2(CO)_5(C_2Ph)(PPh_2)(PPh_3)\cdot C_6H_{12}$[a]

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe(1)	26.7 (3)	77.4 (7)	56.2 (5)	5.8 (3)	14.8 (3)	10.7 (4)
Fe(2)	29.7 (3)	86.9 (7)	65.2 (5)	10.5 (3)	18.7 (3)	11.0 (5)
P(1)	28.5 (5)	86 (1)	62.8 (9)	5.4 (6)	15.6 (5)	8.0 (8)
P(2)	32.8 (5)	88 (1)	57.3 (9)	5.0 (6)	19.0 (5)	7.5 (8)
O(1)	47 (2)	213 (6)	112 (4)	41 (3)	4 (2)	35 (4)
O(2)	58 (2)	173 (5)	112 (4)	20 (2)	54 (2)	39 (3)
O(3)	72 (2)	140 (5)	138 (4)	30 (3)	23 (3)	−44 (4)
O(4)	56 (2)	214 (6)	115 (4)	59 (3)	35 (2)	2 (4)
O(5)	62 (2)	175 (6)	106 (4)	−8 (3)	27 (2)	75 (4)
C(1)	38 (2)	108 (6)	90 (5)	17 (3)	24 (3)	13 (4)
C(2)	39 (2)	107 (6)	89 (5)	19 (3)	26 (3)	6 (4)
C(3)	40 (2)	124 (6)	88 (5)	21 (3)	24 (3)	12 (4)
C(4)	35 (2)	108 (6)	64 (4)	17 (3)	16 (2)	14 (4)
C(5)	33 (2)	120 (6)	71 (4)	4 (3)	11 (2)	16 (4)
C(6)	21 (2)	81 (5)	61 (3)	5 (2)	13 (2)	4 (3)
C(7)	26 (2)	94 (5)	73 (4)	8 (2)	18 (2)	10 (4)
C(11)	31 (2)	112 (6)	80 (4)	18 (3)	24 (2)	39 (4)
C(12)	61 (3)	147 (7)	80 (5)	22 (4)	19 (3)	37 (5)
C(13)	80 (4)	210 (10)	87 (5)	42 (5)	26 (4)	63 (6)
C(14)	75 (4)	199 (10)	141 (7)	58 (5)	56 (4)	113 (7)
C(15)	74 (3)	112 (7)	154 (7)	16 (4)	51 (4)	47 (6)
C(16)	56 (3)	97 (6)	112 (5)	12 (3)	40 (3)	39 (4)

[a] The form of the anisotropic thermal parameter used throughout is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table III. Important Bond Lengths and Angles for $Fe_2(CO)_5(C_2Ph)(PPh_2)(PPh_3)\cdot C_6H_{12}$

Lengths, Å			
Fe(1)–Fe(2)	2.648 (1)	P(1)–C(21)	1.816 (5)
Fe(1)–P(1)	2.212 (1)	P(1)–C(31)	1.824 (5)
Fe(1)–P(2)	2.274 (1)	P(2)–C(41)	1.828 (5)
Fe(1)–C(4)	1.756 (5)	P(2)–C(51)	1.823 (4)
Fe(1)–C(5)	1.778 (5)	P(2)–C(61)	1.842 (5)
Fe(1)–C(6)	1.890 (4)	C(1)–O(1)	1.136 (7)
Fe(2)–P(1)	2.233 (1)	C(2)–O(2)	1.145 (7)
Fe(2)–C(1)	1.788 (5)	C(3)–O(3)	1.138 (7)
Fe(2)–C(2)	1.767 (5)	C(4)–O(4)	1.143 (7)
Fe(2)–C(3)	1.815 (5)	C(5)–O(5)	1.143 (6)
Fe(2)–C(6)	2.116 (4)	C(6)–C(7)	1.225 (6)
Fe(2)–C(7)	2.284 (5)	C(7)–C(11)	1.458 (6)
Angles, deg			
Fe(2)–Fe(1)–P(1)	53.8 (0)	C(2)–Fe(2)–C(3)	89.8 (2)
Fe(2)–Fe(1)–P(2)	106.0 (0)	C(2)–Fe(2)–C(6)	137.7 (2)
Fe(2)–Fe(1)–C(4)	145.6 (1)	C(2)–Fe(2)–C(7)	168.6 (2)
Fe(2)–Fe(1)–C(5)	107.8 (1)	C(3)–Fe(2)–C(6)	94.5 (2)
Fe(2)–Fe(1)–C(6)	52.4 (1)	C(3)–Fe(2)–C(7)	87.1 (2)
P(1)–Fe(1)–P(2)	159.7 (0)	C(6)–Fe(2)–C(7)	32.0 (2)
P(1)–Fe(1)–C(4)	102.5 (1)	Fe(1)–P(1)–Fe(2)	73.1 (0)
P(1)–Fe(1)–C(5)	92.5 (1)	Fe(1)–P(1)–C(21)	120.6 (1)
P(1)–Fe(1)–C(6)	77.2 (1)	Fe(1)–P(1)–C(31)	122.2 (1)
P(2)–Fe(1)–C(4)	96.5 (1)	Fe(2)–P(1)–C(21)	118.6 (1)
P(2)–Fe(1)–C(5)	92.4 (1)	Fe(2)–P(1)–C(31)	119.4 (1)
P(2)–Fe(1)–C(6)	91.8 (1)	C(21)–P(1)–C(31)	102.3 (2)
C(4)–Fe(1)–C(5)	96.7 (2)	Fe(1)–P(2)–C(41)	118.0 (1)
C(4)–Fe(1)–C(6)	102.1 (2)	Fe(1)–P(2)–C(51)	115.6 (1)
C(5)–Fe(1)–C(6)	160.1 (2)	Fe(1)–P(2)–C(61)	113.0 (1)
Fe(1)–Fe(2)–P(1)	53.1 (0)	C(41)–P(2)–C(51)	103.8 (2)
Fe(1)–Fe(2)–C(1)	148.3 (1)	C(41)–P(2)–C(61)	100.8 (1)
Fe(1)–Fe(2)–C(2)	93.8 (1)	C(51)–P(2)–C(61)	103.7 (1)
Fe(1)–Fe(2)–C(3)	108.1 (1)	Fe(1)–C(4)–O(4)	178.3 (2)
Fe(1)–Fe(2)–C(6)	45.0 (1)	Fe(1)–C(5)–O(5)	176.5 (2)
Fe(1)–Fe(2)–C(7)	76.8 (1)	Fe(2)–C(1)–O(1)	176.9 (2)
P(1)–Fe(2)–C(1)	98.0 (1)	Fe(2)–C(2)–O(2)	177.8 (2)
P(1)–Fe(2)–C(2)	91.0 (1)	Fe(2)–C(3)–O(3)	178.5 (2)
P(1)–Fe(2)–C(3)	161.2 (1)	Fe(1)–C(6)–Fe(2)	82.5 (0)
P(1)–Fe(2)–C(6)	72.5 (1)	Fe(1)–C(6)–C(7)	162.0 (2)
P(1)–Fe(2)–C(7)	88.4 (1)	Fe(2)–C(6)–C(7)	81.6 (2)
C(1)–Fe(2)–C(2)	100.2 (2)	Fe(2)–C(7)–C(6)	66.4 (2)
C(1)–Fe(2)–C(3)	100.3 (2)	Fe(2)–C(7)–C(11)	128.8 (1)
C(1)–Fe(2)–C(6)	120.2 (2)	C(6)–C(7)–C(11)	164.7 (2)
C(1)–Fe(2)–C(7)	91.1 (2)		

temperature coefficients are included in supplementary Table S3. Important bond lengths and angles are included in Table III.

Table IV. Some Relevant Least-Squares Planes and Deviations of Atoms Therefrom[a] (Å)

Plane 1		Plane 4	
Fe(2)*	0	Fe(1)*	−0.1742
C(6)*	0	Fe(2)*	0.2237
C(7)*	0	C(4)*	0.2466
C(11)	−0.0188	C(5)*	−0.0801
Fe(1)	0.2750	C(6)*	−0.2161
Plane 2		**Plane 5**	
Fe(1)*	0	Fe(2)*	−0.0673
C(6)*	0	C(1)*	0.1049
C(7)*	0	C(2)*	−0.0443
C(11)	0.1636	C(6)*	0.1891
		C(7)*	−0.1824
Plane 3			
C(6)*	0		
C(7)*	0		
C(11)*	0		
Fe(1)	0.2493		

Equations

Plane 1: $0.0132X + 0.6682Y + 0.7439Z - 0.9642 = 0$

Plane 2: $-0.4458X + 0.5084Y + 0.7368Z + 0.8910 = 0$

Plane 3: $-0.0348X + 0.6586Y + 0.7514Z - 0.7802 = 0$

Plane 4: $0.2341X + 0.5493Y + 0.8022Z - 0.1943 = 0$

Plane 5: $-0.1362X + 0.8408Y + 0.5239Z + 0.1525 = 0$

[a] Only atoms with asterisks are included in the calculation of the plane.

Supplementary Table S4 gives a compilation of bond lengths and angles for phenyl rings and the molecule of solvent. Relevant least-squares planes are tabulated in Table IV.

Results and Discussion

Synthesis and Characterization. The reaction of $Fe_2(CO)_9$ with Ph_2PC_2Ph was originally carried out in the hope of stabilizing simple acetylene π complexes of Fe(0). When excess ligand is used, a phosphinoacetylene π complex $Fe_2(CO)_6(Ph_2PC_2Ph)_2$ can indeed be isolated as a major product.[24] However, from reaction mixtures containing an excess of $Fe_2(CO)_9$, a red crystalline product of stoichiometry $Fe_2(CO)_6(C_2Ph)(PPh_2)$ and a yellow complex $Fe(CO)_4(Ph_2PC_2Ph)$ were isolated. The ν(CO) infrared spectrum of the latter complex is characteristic of a phosphine complex $Fe(CO)_4(PR_3)$ (cf. $Fe(CO)_4(PPh_2H)$: ν(CO) (cm^{-1}; C_6H_{14}) 2056 (s), 2024 (w), 1984 (w), 1953 (s), 1946 (s)),[27] and $\nu(C{\equiv}C)$ of the uncoordinated triple bond appears at 2156 cm^{-1}. An analogous complex $Fe(CO)_4(Ph_2PC_2Bu^t)$ was obtained from the reaction of $Fe_2(CO)_9$ with $Ph_2PC_2Bu^t$. Other $Fe(CO)_4(R'R''PC_2R)$ compounds were identified spectroscopically in reaction mixtures but further characterization was not attempted. The conversion of these phosphorus-coordinated derivatives into new, red, binuclear complexes $Fe_2(CO)_6(C_2R)(PR'R'')$ can be accomplished by stirring with excess $Fe_2(CO)_9$ over an extended period. The binuclear complexes $Fe_2(CO)_6(C_2R)(PR'R'')$ (I: R = Ph, R′ = R″ = Ph; R = R′ = Ph, R″ = C_2Ph; R = Ph, R′ = Bu^t, R″ = C_2Ph; R = Bu^t, R′ = R″ = Ph) showed parent ions in their respective mass spectra and the consecutive loss of six carbonyl groups to give the carbonyl-free ions $[Fe_2(C_2R)(PR'R'')]^+$. An x-ray crystal structure analysis finally revealed the exact nature of this skeleton.[12] The two iron atoms are bridged by a diphenylphosphido group and a σ–π-acetylide as shown in I. The solution infrared spectra of these complexes in cyclohexane (Table V) are virtually identical with four strong and one weak absorption bands in the $\nu(CO)_t$ region. For $Fe_2(CO)_6(C_2Ph)[PBu^t(C_2Ph)]$ the band near 1990 cm^{-1} is split into a closely spaced doublet. Absorption bands at ca. 2200 cm^{-1} due to $\nu(C{\equiv}C)$ of the free ligands are absent. There is an interesting comparison of ν(CO) frequencies for

Table V. Mössbauer Parameters (mm s^{-1}) and Infrared Spectra (cm^{-1}) for σ–π-Acetylides

Compd		δ	Δ	Γ[a]	ν(CO)[b]
$Fe_2(CO)_6(C_2Ph)(PPh_2)$	Fe(1)	0.14	0.36		2072 s, 2035 vs, 2009 s, 1989 s, 1973 w
	Fe(2)	0.22	1.09		
$Fe_2(CO)_6(C_2Bu^t)(PPh_2)$	Fe(1)	0.13	0.38	0.25	2072 s, 2032 vs, 2007 s, 1986 s, 1984 s, 1969 w
	Fe(2)	0.23	0.99	0.24	
$Fe_2(CO)_6(C_2Ph)[PPh(C_2Ph)]$	Fe(1)	0.14	0.38	0.31	2074 s, 2038 vs, 2010 s, 1996 s, 1980 w
	Fe(2)	0.24	1.07	0.32	
$Fe_2(CO)_6(C_2Ph)[PBu^t(C_2Ph)]$	Fe(1)	0.15	0.33	0.24	2073 s, 2035 vs, 2009 s, 1992 s, 1990 s, 1979 m
	Fe(2)	0.27	1.08	0.23	
$Fe_2(CO)_6(C_2Pr^i)(PPh_2)$	Fe(1)	0.13	0.35	0.26	2072 s, 2033 vs, 2008 s, 1986 s, 1969 w
	Fe(2)	0.24	1.09	0.36	
$Fe_2(CO)_6(C_2Cy)(PPh_2)$					2072 s, 2033 vs, 2007 s, 1985 s, 1969 w
$Fe_2(CO)_5(C_2Ph)(PPh_2)(PPh_3)$	Fe(1)	0.16	0.51	0.23	2036 s, 1991 vs, 1973 s, 1954 s, 1932 m
	Fe(2)	0.23	0.93	0.28	
$Fe_2(CO)_5(C_2Bu^t)(PPh_2)(PPh_3)$	Fe(1)	0.16	0.64	0.24	2035 s, 1992 vs, 1969 s, 1953 s, 1933 m
	Fe(2)	0.22	0.95	0.22	
$Fe_2(CO)_5(C_2Pr^i)(PPh_2)(PPh_3)$	Fe(1)	0.21	0.61	0.22	2033 s, 1990 vs, 1967 vs, 1950 vs, 1927 m
	Fe(2)	0.25	0.88	0.22	
$Fe_2(CO)_5(C_2Cy)(PPh_2)(PPh_3)$	Fe(1)	0.16	0.65	0.26	2035 s, 1993 vs, 1970 s, 1955 s, 1932 m
	Fe(2)	0.21	0.99	0.21	

[a] An average line width for the fitted components of the quadrupole doublet. [b] In cyclohexane solution.

$Fe_2(CO)_6(C_2R)(PR'R'')$ with those for $Fe_2(CO)_6(CH{=}CHX)X'$ (X = halogen),[28] with ν(CO) values for the latter being ca. 20 cm^{-1} higher than those for the σ–π-acetylides. This undoubtedly results in large part from the superior σ-donor properties of a bridging phosphido group as compared to a bridging halogen. For the structurally related sulfido-bridged derivatives $Fe_2(CO)_6(HC{=}CH_2)(SR)$,[29] the frequencies and intensity pattern for ν(CO) bands are closely similar to those for $Fe_2(CO)_6(C_2R)(PR'R'')$.

Reactions of $Fe_2(CO)_6(C_2R)(PR'R'')$ with triphenylphosphine were carried out for several reasons. First, it was felt that Mössbauer spectra of the substitution products would facilitate an assignment for the parents. Second, it was known that both phosphines and phosphites preferentially attack the α-carbon atom of the acetylene at room temperature but that a rearrangement of the initially formed betaine complexes occurs on heating.[19a] A conclusive structure determination for one of these red complexes was sought since infrared spectra were remarkably similar to spectra of red 1,3-dipolar species $Fe_2(CO)_6(CHC(R)(NR_2)(PPh_2))$ formed from secondary amines.[19b] Third, there has been considerable recent interest in mechanisms of substitution reactions for nitrogen-, phosphorus-, and sulfur-bridged binuclear complexes.[30] The availability of $Fe_2(CO)_6(C_2R)(PR'R'')$ offered the opportunity to compare positions of substitution for symmetrical and unsymmetrical dibridged species. In boiling benzene, reactions of $Fe_2(CO)_6(C_2R)(PR'R'')$ with PPh_3 were not complicated by attack on the alkyne. Thin-layer chromatography and infrared monitoring showed formation of only one type of product with the position of substitution, as confirmed by x-ray analysis, on the iron atom σ-bonded to the acetylide and trans to the bridging phosphido group. There was no evidence, either infrared or chromatographic, for the isomers with substitution trans to the Fe–Fe bond. Comparison of the infrared spectra of $Fe_2(CO)_6(C_2Ph)(PPh_2)$ and $Fe_2(CO)_5(C_2Ph)(PPh_2)(PPh_3)$ shows that three bands (at 2035, 1989, and 1973 cm^{-1}) remain essentially unchanged in frequency on substitution. These can be attributed to the three CO groups on Fe(2) (Figure 1). If bands at 1954 and 1932 cm^{-1} in $Fe_2(CO)_5(C_2Ph)(PPh_2)(PPh_3)$ are reasonably assigned to ν(CO) of the two CO groups on Fe(1), the band at 1899 cm^{-1} can be assigned to ν(C≡C). This assignment immediately suggests that a very weak but quite reproducible band near 1930 cm^{-1} in the parent σ–π-acetylides is due to ν(C≡C). The lowering of 30 cm^{-1} in ν(C≡C) from $Fe_2(CO)_6(C_2R)(PR'R'')$ to $Fe_2(CO)_5(C_2R)(PR'R'')(PPh_3)$ parallels the somewhat shorter Fe(2)–acetylenic carbon bond lengths and slightly stronger Fe(2)–alkyne π interaction (vide infra) in the substitution product. The value of ν(C≡C)(coordinated) is entirely reasonable when viewed in the light of the relatively weak Fe(2)–acetylene π interaction and the normal frequencies[31] (near 2100 cm^{-1}) for ν(C≡C) in metal acetylides.

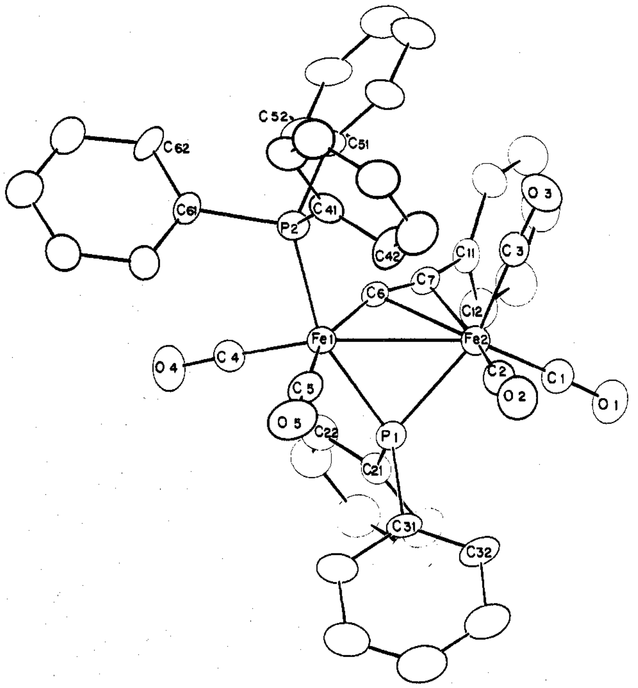

Figure 1. A perspective view of the molecular structure of $Fe_2(CO)_5(C_2Ph)(PPh_2)(PPh_3)\cdot C_6H_{12}$ showing the atomic numbering scheme used. The cyclohexane of crystallization is not shown.

Crystal and Molecular Structure of $Fe_2(CO)_5(C_2Ph)(PPh_2)PPh_3\cdot C_6H_{12}$. A view of the binuclear molecule illustrating the atomic numbering scheme used is shown in Figure 1. The molecule is derived from the original σ–π-acetylide $Fe_2(CO)_6(C_2Ph)(PPh_2)$ by substitution of one carbonyl ligand on Fe(1) by a terminal triphenylphosphine molecule. The iron atom Fe(1) is bonded to two carbonyl groups, the phosphorus atom of a bridging phosphido group, the α carbon of the acetylide, the second iron atom, and the tripenylphosphine ligand. The stereochemistry at Fe(1) is distorted octahedral with the two phosphorus ligands approximately trans to one another; the P(1)–Fe(1)–P(2) angle is 159.7 (0)°. The Fe(1)–P(2) distance of 2.274 (1) Å appears quite normal when compared with Fe–P bond lengths of 2.190 (4) Å in trans-$P(OCH_2)_3PFe(CO)_3P(OCH_2)_3P$[32] and 2.37 (2) Å in $Fe(CO)_4(PPh_2H)$.[33] An electron count indicates that if both iron atoms obey the 18-electron rule, the phosphorus atom of the phosphido bridge behaves formally as a two-electron donor to Fe(1) and a one-electron donor to Fe(2). The expected asymmetry in this bridge is apparent with the Fe(1)–P(1) distance (2.212 (1) Å) somewhat shorter than the Fe(2)–P(1) (2.233 (1) Å) bond length. The stereochemistry of Fe(2), which is essentially similar to that in $Fe_2(CO)_6(C_2Ph)(PPh_2)$,[12] is severely distorted from that of a regular polyhedron whether the acetylene is considered to occupy only one coordination site or two. Comparison of x-ray data for $Fe_2(CO)_6(C_2Ph)(PPh_2)$ and $Fe_2(CO)_5(C_2Ph)(PPh_2)(PPh_3)$ reveals that substitution of a CO group on Fe(1) has a small but perceptible effect on the Fe(2)–acetylene interaction. Thus the Fe(2)–C(6) (2.116 (4) Å) and Fe(2)–C(7) (2.284 (5) Å) bond lengths, which compare with corresponding distances of 2.125 (8) and 2.304 (7) Å in $Fe_2(CO)_6(C_2Ph)(PPh_2)$, suggest a slight increase in the strength of the metal–acetylene π interaction. An alternative measure of the perturbation of an acetylene which occurs on coordination is the magnitude of the bend-back angles, with larger values generally consistent with a greater departure from linearity and a stronger interaction. In the present case, the decrease in Fe–C(acetylene) distances is not paralleled by an increase in bend-back angles. Indeed the acetylene in $Fe_2(CO)_5(C_2Ph)(PPh_2)(PPh_3)$ is closer to linearity than in $Fe_2(CO)_6(C_2Ph)(PPh_2)$ with increases of 1.7 and 2.4°, respectively, in the angles Fe(1)–C(6)–C(7) and C(6)–C(7)–C(11) compared to their counterparts in the parent complex. The two carbon–carbon triple-bond lengths (1.232 (10) Å in $Fe_2(CO)_6(C_2Ph)(PPh_2)$ and 1.225 (6) Å in $Fe_2(CO)_5(C_2Ph)(PPh_2)(PPh_3)$) are not significantly different although both values are larger than the accepted distance (1.204 (2) Å) for –C≡C– in uncoordinated acetylene[34] or the –C≡C– bond length of 1.18 (2) Å in the σ-acetylide *trans*-$Ni(C{\equiv}CPh)_2(PEt_3)_2$.[35] Perhaps the most notable feature of the Fe(2)–acetylene interaction is the trans bent configuration of the alkyne. This contrasts with the cis bent configuration invariably found for nonbridging acetylenes as in $M(PR_3)_2(RC{\equiv}CR')$ (M = Ni, Pd, Pt)[36] or bridging acetylenes as in $Co_2(CO)_6(RC{\equiv}CR')$.[37] Plane 1 of Table IV shows that C(11) of the phenyl substituent on the alkyne lies almost in the plane defined by Fe(2), C(6), and C(7) whereas Fe(1) deviates more and in the opposite sense. The dihedral angle between planes 2 and 3 (Table IV) is 25.30°. It seems clear that for both $Fe_2(CO)_6(C_2Ph)(PPh_2)$ and $Fe_2(CO)_5(C_2Ph)(PPh_2)(PPh_3)$ the metal–acetylene π interaction is a compromise between the unfavorable geometry of the acetylide for η^2 bonding and the attempt of Fe(2) to achieve an 18-e configuration. It is doubtful therefore whether the observed trans stereochemistry of the coordinated acetylene has a meaningful electronic origin. However, it does appear from recent work that the trans bent geometry may be a common feature of σ–π-acetylide structures.[17b]

Other significant skeletal changes accompany substitution of triphenylphosphine for a carbonyl group on Fe(1). Thus the Fe(1)–Fe(2) bond length (2.597 (2) Å in $Fe_2(CO)_6(C_2Ph)(PPh_2)$) lengthens to 2.648 (1) Å in the substitution product. As a consequence of the larger Fe–Fe bond, the Fe(1)–P(1)–Fe(2) angle opens up to 73.1 (0)° from 71.64 (7)°. Phosphido bridges are known to be extremely flexible, being capable of accommodating both strongly bonding and nonbonding Fe–Fe distances.[38,39] Despite the above structural modifications the Fe(1)–C(6) bond length (1.891 (6) Å in $Fe_2(CO)_6(C_2Ph)(PPh_2)$ vs. 1.890 (4) Å in $Fe_2(CO)_5(C_2Ph)(PPh_2)(PPh_3)$) remains unaltered on substitution and the average Fe–CO distance (1.78 Å) is identical in both complexes. Thus the electronic effects of CO substitution by PPh_3 are manifest principally as changes in the internuclear framework of the complex.

The position of substitution is not trans to the Fe–Fe bond of $Fe_2(CO)_6(C_2Ph)(PPh_2)$ and is thus in direct contrast with observations for a range of nitrogen-, phosphorus-, sulfur-, and butatriene-bridged species.[30] In the present case, the dominant factor influencing the position of substitution is steric in origin. The incoming nucleophile occupies the least hindered apex of the distorted octahedron of ligands surrounding Fe(1), being remote from the bulky bridging diphenylphosphido group and adjacent to the sterically less demanding σ-acetylide group. The mechanism of substitution is not however simple since at 0 °C the phosphine initially attacks the α carbon of the acetylide affording a pale yellow 1,3-dipolar complex analogous to $Fe_2(CO)_6(CP(OEt)_3CPh)(PPh_2)$.[19] Subsequent carbonyl substitution is effected by refluxing in benzene.

Mössbauer Spectra. Mössbauer parameters for the $Fe_2(CO)_6(C_2R)(PR'R'')$ and $Fe_2(CO)_5(C_2R)(PR'R'')(PPh_3)$ compounds are listed in Table V. The parent σ–π-acetylides all give four-line Mössbauer spectra. With the exception of the compounds $Fe_2(CO)_6(C_2Ph)[PPh(C_2Ph)]$ and $Fe_2(CO)_6(C_2Pr^i)(PPh_2)$ for which lower quality spectra were obtained owing to the small quantities of material available, the line widths are narrow and the lines are well resolved. For a four-line Mössbauer spectrum, with two nonidentical, noncubic iron sites, there are three ways in which the spectral lines numbered 1–4 from right to left can be assigned. If we designate a quadrupole doublet by E_{ij}, then the possible pairs are E_{12}, E_{34}; E_{13}, E_{24}; and E_{14}, E_{23}. Each pair must then be assigned to one or the other iron atom in the binuclear molecule. A number of features simplify this analysis considerably. First, the assignment E_{12}, E_{34} can be eliminated since this gives isomer shifts of 0.54 and −0.19 mm s^{-1}, both values of which are outside the range −0.05 to +0.4 mm s^{-1} normally encountered for low-spin iron complexes.[40] This assignment would also imply, from values for the quadrupole splittings (0.45 and 0.28 mm s^{-1} for E_{12} and E_{34}, respectively), very little distortion from octahedral symmetry. The x-ray data clearly indentify a very much greater asymmetry for the iron atom π-bonded to the acetylide. Of the two remaining assignments the pairs of quadrupole doublets E_{13} and E_{24} give δ values of 0.36 and −0.01 mm s^{-1} and Δ values of 0.81 and 0.64 mm s^{-1}. This assignment seems unlikely due to the large difference in field gradients at the two iron sites implied by the x-ray analysis. The isomer shift difference between the two iron atoms would also be excessively large in this case. There are several reasons for favoring the third assignment E_{14}, E_{23} with the larger isomer shift and quadrupole splitting associated with Fe(2) in Figure 1. First, this assignment, in accord with the x-ray data, suggests a substantial difference in stereochemistry between the two iron atoms. The isomer shifts are in the normal range for low-spin Fe(0) complexes and can be compared with δ values of 0.245 and 0.22 mm s^{-1} for the phosphido-bridged complexes $Fe_2(CO)_6(PR_2)_2$ (R = Ph, Me).[41] The magnitudes of δ and Δ for Fe(2) are qualitatively similar to what one would predict on the basis of simple bonding and stereochemical arguments. Thus, the x-ray data for $Fe_2(CO)_6(C_2Ph)(PPh_2)$[12] show a relatively weak Fe(2)–acetylene interaction. Since acetylenes are poor σ donors, Fe(2) is electron deficient. A lower s-electron density at Fe(2) than at Fe(1) and a higher isomer shift for Fe(2) is indicated, as is observed. The magnitude of Δ for Fe(2) is typical of a severely distorted octahedral environment or a seven-coordinate stereochemistry.[40]

Meaningful comparisons are difficult to make due to the unusual environment of Fe(2) and a lack of Mössbauer data for acetylene complexes of Fe(0). Olefin π complexes, for example, $(\eta^2\text{-}C_4H_2O_3)Fe(CO)_4$ ($\delta = 0.27$, $\Delta = 1.41$ mm s^{-1}),[42] have slightly higher Δ values while the π-bonded iron atoms in tricarbonylferrole complexes yield very similar quadrupole splittings.[43]

Finally, the Mössbauer data for the $Fe_2(CO)_5(C_2R)(PR'R'')(PPh_3)$ derivatives provide confirmatory evidence for the assignment E_{14} to (Fe(2)) and E_{23} to (Fe(1)). These spectra consist of three lines with the broad line twice the intensity of the others. Spectra fitted well to four independent Lorentzian line shapes. The assignment (Table V) for these compounds follows directly from that for $Fe_2(CO)_6(C_2R)(PR'R'')$ above and from the result predicted on the basis of a comparison of the x-ray structure for $Fe_2(CO)_6(C_2Ph)(PPh_2)$ and $Fe_2(CO)_5(C_2Ph)(PPh_2)(PPh_3)$. Substitution of a terminal CO ligand by triphenylphosphine changes the parameters for Fe(2) very little, while Fe(1) suffers a substantial increase in Δ and δ moves to more positive velocities. These results exactly parallel the observations of Greenwood, Haines, and coworkers for a series of binuclear sulfido-bridged compounds.[44] Moreover, these workers surmised that substitution of a CO group by a phosphine led to a sizable increase in Δ for the substituted iron *only* when the position of substitution was other than trans to the Fe–Fe bond. Our x-ray analysis of $Fe_2(CO)_5(C_2Ph)(PPh_2)(PPh_3)$ and corresponding Mössbauer parameters establish the correctness of this assumption.

Comments on the Mode of Formation of σ–π-Acetylides. A possible intermediate in the formation of $Fe_2(CO)_6(C_2R)(PR'R'')$ from $Fe(CO)_4(R'R''PC_2R)$ (II) is the π-phosphinoacetylene complex $Fe_2(CO)_8(R'R''PC_2R)$ (III). Careful infrared monitoring of the reactions of $Fe(CO)_4(Ph_2PC_2R)$ with $Fe_2(CO)_9$ revealed the decay of bands due to the phosphine complexes II, the growth of $Fe_2(CO)_6(C_2R)PPh_2$ (R = Ph, Bu^t,), and the presence of $Fe(CO)_5$. However, we were unable to positively identify $\nu(CO)_t$ bands due to the intermediates III (R = Ph, Bu^t; R′ = R″ = Ph). This may be due in part to the similarity, also apparent in the $\nu(CO)_t$ spectrum of $Fe_2(CO)_6(Ph_2PC_2Ph)_2$,[24] of the spectra of the intermediates and $Fe(CO)_4(Ph_2PC_2R)$ (R = Ph, Bu^t). Evidence favoring the intermediacy of III was the presence of a medium weak band at 1803 cm^{-1} in these reaction mixtures. This band attributable to $\nu(C{\equiv}C)$ of the coordinated acetylene appears at a very similar frequency in $Fe_2(CO)_6(Ph_2PC_2Ph)_2$, known from x-ray studies[24] to contain π-bonded phosphinoacetylene ligands. Furthermore, photolysis of $Fe(CO)_4(Ph_2PC_2Bu^t)$ was also shown to provide a route to the derivative $Fe_2(CO)_5(C_2Bu^t)(PPh_2)(Ph_2PC_2Bu^t)$, presumably via a π-acetylene intermediate. The latter observation was useful since it allowed the removal of $Fe(CO)_4(Ph_2PC_2Bu^t)$ from mixtures with $Fe_2(CO)_6(C_2Bu^t)(PPh_2)$ via conversion to $Fe_2(CO)_5(C_2Bu^t)(PPh_2)(Ph_2PC_2Bu^t)$. The transformation of III to I requires the cleavage of a P–C$_{sp}$ bond and the formation of an Fe–Fe bond. The process can be envisaged as an insertion of $[Fe(CO)_4]$ into the P–C bond generating IV, followed by intramolecular π coordination of the σ-acetylide and CO elimination. This sequence resembles the mode of formation of σ–π-vinyl halide complexes from 1,2-dihalogenoethylenes via initial π complexation and insertion into a carbon–halogen bond proposed by Von Gustorf et al.[28] There is now considerable evidence that cleavage of P–C$_{sp}$ bonds is a common feature of reactions involving phosphinoacetylenes and metal carbonyls.[10,11,39] Moreover, the activation of phosphinoacetylenes afforded by phosphorus coordination has been exploited in the synthesis of numerous inorganic derivatives via reactions which involve P–C bond fission.[45]

Structural and Chemical Similarities of σ–π-Acetylides and σ–π-Vinyl Complexes. There is now considerable evidence that metal acetylides can function as two-electron or even four-electron ligands[14–18,46,47] in analogous fashion to disubstituted acetylenes. Indeed a convincing argument could be made that in some instances, metal acetylides form more stable π complexes than corresponding organo-substituted alkynes,[48] although their utility in this regard is virtually unexplored. More importantly, however, we wish not only to emphasize the structural similarity of the σ–π-acetylides $Fe_2(CO)_6(C_2R)(PR'R'')$ to several vinyl complexes in the literature but also to show that in terms of unusual chemical reactivity these compounds are closely related. The simple vinyl analogue $Fe_2(CO)_6(CH{=}CH_2)(PPh_2)$ of I has not been prepared (although it might be accessible from $Ph_2PCH{=}CH_2$ and $Fe_2(CO)_9$) but the sulfido-bridged species $Fe_2(CO)_6(HC{=}CH_2)(SR)$ have been characterized.[29] To our knowledge no chemistry has been explored. By contrast, there has been much recent interest in the cluster compound $HOs_3(CO)_{10}(CHCH_2)$ formed in the reaction of $H_2Os_3(CO)_{10}$ with ethylene[49] or acetylene.[47,50] A variety of closely related derivatives $HOs_3(CO)_{10}(CR{=}CHR')$ with bridging vinyl groups have been synthesized from acetylenes.[47,50] These trinuclear osmium compounds are susceptible to hydrogen-transfer reactions on heating. Thus $HOs_3(CO)_{10}(CH{=}CH_2)$ is converted to $H_2Os_3(CO)_9(CCH_2)$ in *n*-octane.[47] The complex $HOs_3(CO)_{10}(CH{=}CH_2)$ reacts with acetylene in refluxing hexane to give $Os_3(CO)_{10}(CH{=}CH)$ in which acetylene is formally σ-bonded to two osmium atoms and π-bonded to a third.[47] It will be interesting to see if the mobility of hydrogen atoms and the facile cleavage of C–H bonds occurring in these systems also apply to the much simpler binuclear iron complexes. Shapley, Churchill, and co-workers[51] have very recently reported that reaction of $HOs_3(CO)_{10}(CH{=}CH_2)$ with phosphines and phosphites results in nucleophilic attack on the β carbon of the σ–π-vinyl group. This is identical with the behavior of $Fe_2(CO)_6(C_2R)(PR'R'')$ with phosphorus nucleophiles[19] and suggests a similar type of activation of the unsaturated moiety in the two types of compound. Presumably, the novel reactions of $Fe_2(CO)_6(C_2Ph)(PPh_2)$ with group 5 donors[19] will be repeated with the complex $HOs_3(CO)_{10}(C_2Ph)$ prepared by Deeming et al.[47]

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Registry No. $Fe_2(CO)_6(C_2Ph)(PPh_2)$, 52970-25-9; $Fe_2(CO)_6(C_2Bu^t)(PPh_2)$, 59584-68-8; $Fe_2(CO)_6(C_2Ph)[PPh(C_2Ph)]$, 62475-92-7; $Fe_2(CO)_6(C_2Ph)[PBu^t(C_2Ph)]$, 62475-93-8; $Fe_2(CO)_6(C_2Pr^i)(PPh_2)$, 62475-91-6; $Fe_2(CO)_6(C_2Cy)(PPh_2)$, 59584-69-9; $Fe_2(CO)_5(C_2Ph)(PPh_2)(PPh_3)$, 62475-90-5; $Fe_2(CO)_5(C_2Bu^t)(PPh_2)(PPh_3)$, 62475-88-1; $Fe_2(CO)_5(C_2Pr^i)(PPh_2)(PPh_3)$, 62475-87-0; $Fe_2(CO)_5(C_2Cy)(PPh_2)(PPh_3)$, 62475-86-9; $Fe(CO)_4(Ph_2PC_2Ph)$, 62415-28-5; $Fe(CO)_4(Ph_2PC_2Bu^t)$, 62415-19-4; $Fe_2(CO)_5(C_2Bu^t)(PPh_2)(Ph_2PC_2Bu^t)$, 62475-85-8; *trans*-$Fe(CO)_3(Ph_2PC_2Bu^t)_2$, 62415-20-7; $PhP(C_2Ph)_2$, 27258-73-7; Ph_2PC_2Cy, 21543-67-9; $Bu^tP(C_2Ph)_2$, 39768-05-3; $Fe_2(CO)_9$, 15321-51-4; cyclohexylacetylene, 931-48-6; diphenylchlorophosphine, 1079-66-9.

Supplementary Material Available: Tables S1–S5, giving atomic positional and thermal parameters for the carbon atoms of the phenyl rings attached to phosphorus and the carbon atoms of the cyclohexane of crystallization, hydrogen atom positions and isotropic temperature coefficients, bond lengths and angles for phenyl rings and the solvent molecule, and structure factor amplitudes (28 pages). Ordering information is given on any current masthead page.

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A Ferromagnetically Coupled Chromium(III) Dimer: Synthesis, Structure, and Magnetic Properties of Sodium Di-μ-hydroxo-bis[bis(malonato)chromate(III)] Pentahydrate

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The dimeric chromium(III) complex sodium di-μ-hydroxo-bis[bis(malonato)chromate(III)] pentahydrate, $Na_4[Cr(C_3H_2O_4)_2OH]_2{\cdot}5H_2O$ or $Na_4[Cr(mal)_2OH]_2{\cdot}5H_2O$, has been synthesized and its magnetic and structural properties have been examined. The complex crystallizes in the triclinic space group $P\bar{1}$ with one dimeric formula unit in a cell of dimensions $a = 8.937$ (6), $b = 10.279$ (7), $c = 8.310$ (6) Å; $\alpha = 75.20$ (3), $\beta = 76.01$ (3), $\gamma = 112.07$ (3)°. The structure has been refined by a full-matrix least-squares method to a conventional R factor (on F) of 0.039 using 2902 independent single-crystal counter data. The structure is comprised of dimeric $[Cr(mal)_2OH]_2^{4-}$ anions which interact with sodium cations and water molecules in the cell. The geometry around each chromium(III) center is six-coordinate, approximately octahedral. The bridging Cr_2O_2 unit is strictly planar, as required by the crystallographic symmetry. The Cr–O–Cr′ bridging angle is 99.34 (7)° and the Cr–Cr′ separation is 3.031 (2) Å. The malonato ligands are bidentate, each coordinating through two oxygen atoms; the uncoordinated oxygen atoms are involved in extensive hydrogen bonding in the crystal. The magnetic susceptibility of the complex has been examined in the range 2–50 K, and the data have been analyzed by application of the magnetization expression for coupled pairs of $S = {}^3/_2$ ions. The exchange interaction is small, but J is clearly positive (i.e., the coupling is ferromagnetic), the best fit to the data giving $g = 1.988$ (3), $J = +1.08$ (2) cm^{-1}, and $\gamma = -0.106$. This complex, therefore, represents the first documented example of a ferromagnetically coupled chromium(III) dimer.

Introduction

Recent experimental studies of the structural and magnetic properties of a variety of dihydroxo-bridged complexes of copper(II) have demonstrated that the singlet–triplet splitting, $2J$, is dependent upon the Cu–O–Cu bridging angle, ϕ.[1-12] The functional form of this correlation is nearly linear, at least over the range of ϕ's observed to date. The theoretical basis for this correlation can be understood in terms of the Good-