0.1, respectively, provide the remaining four water molecules per cell. Each of the water molecules forms two to four hydrogen bonds, mostly among themselves but also to the equatorial OH and H_2O groups of the cluster molecule. The O···O distances range from 2.56 to 2.92 Å. A complete tabulation of hydrogen bonds is available as supplementary material.

The metal cluster unit deviates slightly but significantly from threefold symmetry. We believe that these deviations can be understood in the following way. O(5) represents an equatorial OH group. The Mo(1)–O(5) distance, 1.979 (7) Å, is appreciably shorter than the Mo–OH_2 distances previously reported,[11] which run from 2.083 [10] to 2.144 [4] Å. Evidently, OH^- is a significantly stronger donor in this context than H_2O. The Mo(2)–O(7) and Mo(2)′–O(7)′ bond lengths are each considered to represent an equal-weighted average of Mo–OH and Mo–OH_2 bonds, and the observed bond distance, 2.049 (5) Å compares favorably with the average of ca. 1.98 and ca. 2.11 Å, the typical Mo–OH and Mo–OH_2 distances.

If we then make the reasonable assumption that the stronger the Mo–O (equatorial) bond the weaker will be the adjacent Mo–Mo bonds, we can account for the observed pattern of Mo–Mo bond lengths. The Mo(1)–Mo(2) and Mo(1)–Mo(2)′ bonds, which always have OH^- at one end and have OH^- at the other end half the time, are longer, 2.796 (1) Å, than the Mo(2)–Mo(2)′ bond, which is always of the HO–Mo–Mo–OH_2 type (though disordered) and is shorter at 2.773 (1) Å. In cases containing only axial Mo–OH_2 bonds, the Mo–Mo bond lengths are shorter than either of the above, running from 2.752 [2] Å to 2.766 (2) Å.[10]

The effect of replacing Mo–OH_2 by Mo–OH in lengthening adjacent Mo–Mo bonds (by an amount that can be estimated to be about 0.040–0.050 Å on going from all Mo–OH_2 to all Mo–OH) is not surprising, since the Mo–OH bonds are evidently appreciably stronger than Mo–OH_2 bonds. It is, however, important to be cognizant that such a change in Mo–Mo distances can occur even when the nominal bond order (i.e., number of electrons formally available in the cluster for Mo–Mo bonding) is not changed.

The Mo–(μ_3-O) bond lengths average 1.998 [3] Å, which is not different from values found in other bi-oxo-capped Mo_3 cluster species, where they are in the range[11] 1.984 [4]–2.004 [6] Å.

Acknowledgment. We thank the U.S. National Science Foundation and the U.S.-Israeli Binational Science Foundation for financial support.

Registry No. $[Mo_3O_2(O_2CCH_3)_6(H_2O)(OH)_2]\cdot xH_2O$, 86709-53-7; $Na[Mo_3O_2(O_2CCH_3)_9]$, 86695-77-4; Na_2MoO_4, 7631-95-0.

Supplementary Material Available: Tables of structure factors, thermal parameters, and bond angles and nonbonded contacts less than 3.0 Å (19 pages). Ordering information is given on any current masthead page.

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Chemistry of Multisite-Bound Ligands. Addition of Amines to μ-η^2-Acetylides: Dipolar, Electron-Rich μ-η^1- and μ-η^2-Alkylidene and μ-η^1-Vinylidene Diiron Hexacarbonyl Complexes

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As part of a major effort to explore and establish patterns of reactivity for multisite-bound unsaturated ligands, the reactions of the μ-η^2-acetylides $Fe_2(CO)_6(C_2R)[P(C_6H_5)_2]$ (**1**) (R = C_6H_5, *p*-$MeOC_6H_4$, *p*-BrC_6H_4, C_6H_{11}, $C(CH_3)_3$) toward primary, secondary, and tertiary amines have been investigated. Three types of addition products have been isolated and characterized by microanalysis and infrared, ^1H and ^{31}P NMR, and Mössbauer spectroscopy. Solid-state structures by X-ray crystallography are available for several of the adducts. Attack at the β-carbon of the acetylide affords zwitterionic μ-vinylidene compounds $Fe_2(CO)_6[C{=}C\{NHR^1R^2\}R][P(C_6H_5)_2]$ (**4**); attack at the β-carbon atom by primary or secondary amines with hydrogen transfer yields dipolar μ-alkylidene derivatives $Fe_2(CO)_6[CHC\{NR^1R^2\}R][P(C_6H_5)_2]$ (**3**) with a single carbon atom bridge between iron atoms. Attack at the α-carbon atom of the μ-η^2-acetylide with hydrogen migration gives the μ-η^2-alkylidene derivatives $Fe_2(CO)_6[C\{NR^1R^2\}CR][P(C_6H_5)_2]$ (**2**) where a two-carbon three-electron ligand is present. ^{31}P NMR and Mössbauer studies permit facile differentiation of the three structural types; in particular $\delta(^{31}P)$ shifts show a systematic variation with M–P–M angle and M- - -M bond length, with larger, downfield shifts corresponding to greater Fe–P–Fe angles. Factors affecting the electrophilicity of the multisite-bound acetylides in **1** and the regiospecificity of nucleophilic attack have been probed via ^{13}C NMR studies of the precursors and variable-temperature ^{31}P studies of reactions of **1** with a variety of nucleophiles. Multisite coordination confers enhanced reactivity toward nucleophilic attack with the site of attachment of the nitrogen nucleophile determined principally by polarization in the μ triple bond, the steric bulk of the substituent R in **1**, and the incoming nucleophile.

Introduction

There is now abundant evidence that multisite coordination of unsaturated molecules to two or more metals in polynuclear transition-metal clusters frequently leads to ligand activation and novel types of chemical reactivity.[1] Particular attention has recently focused on the reactivity of highly coordinated carbon monoxide[2] and carbidic carbon atoms[3] in carbonyl clusters and on the chemistry of certain proposed model intermediates[4] such as μ-methylidyne, μ-methylene, μ-vinylidene, and formyl and hydroxymethyl complexes possibly implicated

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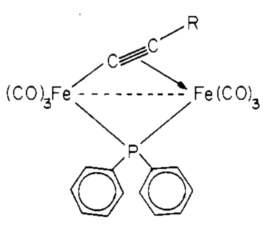
in catalytic carbon monoxide reduction. Although a great many novel transformations of cluster-bound unsaturated ligands have been discovered,[5] often serendipitously, few systematic studies of reactivity patterns for multisite coordinated ligands have been reported. For binuclear complexes the reactivity of μ-alkylidene,[6] μ-alkylidyne,[7] and μ-vinylidene[8] ligands has recently come under intense scrutiny, with particular emphasis on reactions involving protonation, insertion, and carbon-chain growth. In an effort to shed light on the fundamental reactivity patterns associated with μ-bound unsaturated ligands, we set out several years ago to investigate the behavior of μ-bound acetylides toward simple nucleophilic and electrophilic reagents. From a chemical standpoint binuclear or cluster-bound acetylides offer a number of attractive features: (a) a variety of multisite-bound bonding modes (e.g., *sym*-μ, μ-η^2, μ_3-η^2, μ_4-η^2)[9] is accessible for comparative studies; (b) the polarity of the unsaturated linkage can be varied by changing the electronic characteristics of the group R in C≡CR; (c) the problem of ligand mobility, and hence the difficulty of associating a particular reactivity with bonding mode, is much less severe for acetylides than for their isoelectronic counterpart CO. Initial studies on $Fe_2(CO)_6(\mu$-η^2-$C{\equiv}CC_6H_5)[P(C_6H_5)_2]$ (**1**)[10] indicated a remarkable susceptibility to nucleophilic attack at the acetylidic carbon by a wide variety of nitrogen,[11] phosphorus,[12] and carbon nucleophiles.[13] These μ-η^2-acetylides also undergo facile carbon–carbon bond-forming reactions with electrophilic acetylenes.[14] In an earlier paper[12b] we described the products of nucleophilic attack on $Fe_2(CO)_6(\mu$-η^2-$C{\equiv}CC_6H_5)[P(C_6H_5)_2]$ by cyclohexylamine. We have now investigated in detail the addition of a wide variety of primary and secondary amines across the μ-η^2-acetylide in $Fe_2(CO)_6(C{\equiv}CR)[P(C_6H_5)_2]$ (**1**, R = C_6H_5, p-$MeOC_6H_4$, p-BrC_6H_4, $C(CH_3)_3$, C_6H_{11}). These reactions generate novel dipolar μ-η^1- and μ-η^2-alkylidene and μ-η^1-vinylidene complexes via nucleophilic attack at carbon and hydrogen transfer, with the regiospecificity of nucleophilic attachment appearing to depend on the electronic and steric properties of the group R as well as on the steric bulk of the amine. The products of these reactions have been fully characterized by analytical, spectroscopic (IR, ^1H and ^{31}P NMR, Mössbauer), and where appropriate X-ray structural methods. We have discovered that the ^{31}P NMR chemical shift of the phosphide bridge and the Mössbauer quadrupole splittings in these systems are sensitive probes not only to provide insight into the progress of nucleophilic attack on the sideways-bound ligand but also to structurally differentiate η^1- and η^2-bonding modes for the products.



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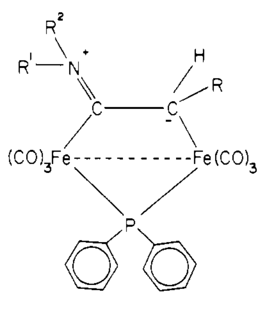

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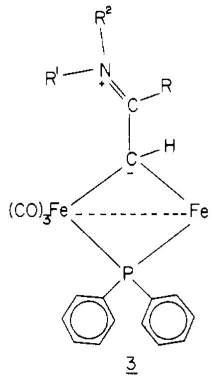

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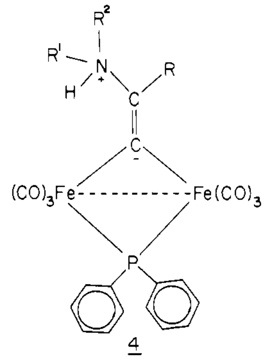

4

Experimental Section

All preparations, reactions, and chromatography procedures were carried out under a nitrogen atmosphere by using standard Schlenk-tube techniques. Solvents were dried and degassed by refluxing over lithium aluminum hydride or sodium benzophenone under a nitrogen atmosphere. ^1H and ^{31}P NMR spectra were recorded on a Bruker WP-60 spectrometer, the latter at a spectrometer frequency of 24.29 MHz. ^{13}C NMR spectra were recorded on a Bruker WP-80 spectrometer at 20.1 MHz in solutions containing 1 mg/mL of $Cr(acac)_3$ as relaxation agent. Mössbauer spectra were recorded at liquid-nitrogen temperature on an Austin Science Associates Inc. drive equipped with a Kicksort pulse height analyzer. Spectra were fitted to Lorentzian line shapes by using the local program MOSS as previously described.[15] The standard absorber was sodium nitroprusside, and the accuracy of the Mössbauer parameters is ±0.01 mm s^{-1}.

Synthesis. The acetylides $Fe_2(CO)_6(C_2R)[P(C_6H_5)_2]$ (R = C_6H_5, $C(CH_3)_3$, C_6H_{11}) were prepared by the general procedures outlined elsewhere.[10] Amines were used as received.

Preparation of p-$BrC_6H_4C_2[P(C_6H_5)_2]$. p-Bromophenylacetylene was prepared in 47% yield from p-bromoacetophenone by the method of Jacobs.[16] The ligand was then synthesized by a modification of the method used for $C_6H_5C_2P(C_6H_5)_2$ using n-butyllithium and then chlorodiphenylphosphine in ether.[10] Recrystallization under nitrogen from ethanol gave the pure material: 45% mp 88 °C; IR (CCl_4) $\nu(C{\equiv}C)$ 2165 cm^{-1}; accurate mass of $[(p\text{-}^{79}BrC_6H_4C_2P(C_6H_5)_2]^+$ calcd 364.0016; found 364.0017; ^1H NMR ($CDCl_3$) δ 7.47 (m) (C_6H_5, C_6H_4). Anal. Calcd: C, 65.8; H, 3.9; P, 8.5; Br, 21.9. Found: C, 64.5; H, 3.9; P, 8.3; Br, 22.2.

Preparation of p-$MeOC_6H_4C_2[P(C_6H_5)_2]$. p-Methoxyphenylacetylene was prepared in 46% yield from p-methoxycinnamic acid by the method of Allen and Cook.[17] The ligand was then synthesized as for other $RC_2P(C_6H_5)_2$ complexes[18,19] by using ethylmagnesium

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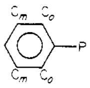
Table I. ^{13}C and ^{31}P NMR Data for the Complexes $Fe_2(CO)_6[C_\alpha{\equiv}C_\beta R][P(C_6H_5)_2]$

R	$\delta(^{31}P)$	$\delta(^{13}C)^{a,c,d}$
$C(CH_3)_3$	148.4 (s)^a	211.1 (s) (CO); 139.2 (d) (C_o, $^1J_{P-C_o}$ = 25 Hz); 134.8 (d), 133.3 (d) (C_m, $^2J_{P-C_m}$ = 9 Hz); 128.0 (m) (C_6H_5); 107.0 (d) (C_β, $^2J_{P-C_\beta}$ = 9 Hz); 98.4 (d) (C_α, $^2J_{P-C_\alpha}$ = 54 Hz); 31.3 (s) (C(*t*-Bu)); 30.7 (s) (CH_3)
c-C_6H_{11}	150.1 (s)^b	210.9 (s) (CO); 139.2 (d) (C_o, $^1J_{P-C_o}$ = 23 Hz); 134.3 (d), 133.1 (d) (C_m, $^2J_{P-C_m}$ = 8 Hz); 127.9 (m) (C_6H_5); 99.7 (d) (C_β, $^2J_{P-C_\beta}$ = 7 Hz). 99.3 (d) (C_α, $^2J_{P-C_\alpha}$ = 53 Hz); 34.8 (s), 33.3 (s), 25.8 (s), 25.1 (s) (c-C_6H_{11})
p-$CH_3OC_6H_4$	148.0 (s)^a	210.3 (s) (CO); 159.8 (s) (COMe); 138.4 (d) (C_o, $^1J_{P-C_o}$ = 24 Hz); 133.0 (m), 127.7 (m) (C_6H_5, C_6H_4); 113.6 (s) ($C(C_6H_5)$); 106.1 (d) (C_α, $^2J_{P-C_\alpha}$ = 53 Hz); 93.3 (d) (C_β, $^2J_{P-C_\beta}$ = 7 Hz); 54.0 (s) (OCH_3)^e
C_6H_5	148.3 (s)^a	210.1 (s) (CO); 138.3 (d) (C_o, $^1J_{P-C_o}$ = 24 Hz); 133.8 (d), 132.7 (d) (C_m, $^2J_{P-C_m}$ = 8 Hz); 110.4 (d) (C_α, $^2J_{P-C_\alpha}$ = 53 Hz); 92.1 (d) (C_β, $^2J_{P-C_\beta}$ = 7 Hz)
p-BrC_6H_4	148.4 (s)^a	209.9 (s) (CO); 138.0 (d) (C_o, $^1J_{P-C_o}$ = 24 Hz); 133.5 (m), 127.7 (m) (C_6H_5, C_6H_4); 113.1 (d) (C_α, $^2J_{P-C_\alpha}$ = 53 Hz); 90.7 (d) (C_β, $^2J_{P-C_\beta}$ = 8 Hz)

^{a} C_6D_6 solvent. ^{b} C_7D_8 solvent. ^{c} 20.1-MHz spectrum. ^{d} Phenyl-ring notation



^{e} At −80 °C, 62.8-MHz spectrum (CD_2Cl_2 δ 210.9 (s), 210.6 (s), 209.9 (s), 209.7 (s), 208.1 (s), 207.4 (s) (CO); 158.2 (s) (COMe); 131.9 (m), 127.3 (m) (C_6H_5, C_6H_4); 112.4 (s) ($C(C_6H_5)$); 105.0 (d) (C_α, $^2J_{P-C_\alpha}$ = 54 Hz); 92.0 (d) (C_β, $^2J_{P-C_\beta}$ = 9 Hz); 54.2 (s) (OCH_3).

bromide and chlorodiphenylphosphine. After chromatography on Florisil using pentane as eluant the pure product was obtained as a colorless oil (47%) that on cooling to −20 °C slowly solidified: mp ca. −5 °C; IR (CCl_4) ν(C≡C) 2161 cm^{-1}; accurate mass of [*p*-$CH_3OC_6H_4C_2P(C_6H_5)_2$]$^+$ calcd 316.0017, found 316.0037; ^{1}H NMR ($CDCl_3$) δ 7.45 (m) (C_6H_5, C_6H_4), 3.80 (s) (OCH_3). Anal. Calcd: C, 79.7; H, 5.4; P, 9.8. Found: C, 81.4; H, 5.4; P, 8.9.

Preparation of $Fe_2(CO)_6$(*p*-$MeOC_6H_4C_2$)[$P(C_6H_5)_2$]. This complex was prepared from $Fe_2(CO)_9$ and *p*-$CH_3OC_6H_4C_2P(C_6H_5)_2$ as previously described for the phenyl and *tert*-butyl analogues.[10] The purified complex crystallized from heptane, forming bright red prisms: 31%; mp 111 °C; ^{1}H NMR (C_6D_6) δ 7.60 (m), 6.90 (m) (C_6H_5, C_6H_4), 3.10 (s) (OCH_3); IR (C_6H_{12}) ν(CO) 2070 (s), 2033 (vs), 2007 (s), 1988 (s), 1971 (w) cm^{-1}. Anal. Calcd: C, 54.4; H, 2.9; P, 5.2. Found: C, 53.7; H, 3.0; P, 5.1.

Preparation of $Fe_2(CO)_6$(*p*-$BrC_6H_4C_2$)[$P(C_6H_5)_2$]. Prepared in an analogous fashion to the cyclohexyl derivative,[10] the purified product did not crystallize. Removal of solvent under reduced pressure (10^{-2} mm), over several days, resulted in formation of a glassy dark red solid: 25%; mp 60 °C; ^{1}H NMR (C_6D_6) δ 7.60–7.00 (m) (C_6H_5, C_6H_4); IR (C_6H_{12}) ν(CO) 2073 (s), 2035 (vs), 2010 (s), 1991 (s), 1974 (w) cm^{-1}. Anal. Calcd: C, 50.8; H, 2.3; P, 5.0; Br, 13.0. Found: C, 49.4; H, 2.6; P, 4.8; Br, 12.4. ^{31}P and ^{13}C NMR data for the compounds $Fe_2(CO)_6(C_2R)[P(C_6H_5)_2]$ are presented in Table I.

Reaction of $Fe_2(CO)_6(C_2R)[P(C_6H_5)_2]$ with Amines. 1. Primary Amines. Optimum yields of products were obtained by using a large (≥4-fold) excess of amine to drive reactions to completion as rapidly as possible. Either one or two products, namely $Fe_2(CO)_6$[C{NHR^1}CH{R}][$P(C_6H_5)_2$] (2) (R^2 = H) (yellow or yellow-orange) and $Fe_2(CO)_6$[CHC{NHR^1}R][$P(C_6H_5)_2$] (3) (R^2 = H) (red), were formed. The following procedures are typical.

Reaction of $Fe_2(CO)_6(C_2C_6H_5)[P(C_6H_5)_2]$ with CH_3NH_2. A 20-mL quantity of a 40% solution of methylamine in water was shaken with 20 mL of diethyl ether. The organic layer was separated and added to 1 g of $Fe_2(CO)_6(C_2C_6H_5)[P(C_6H_5)_2]$ dissolved in 20 mL of diethyl ether at room temperature. The solution was stirred for 10 min until the solution IR spectra (C_6H_{12}) of small aliquots taken from the reaction mixture indicated the complete disappearance of starting material by loss of its highest ν(CO) stretching frequency at 2072 cm^{-1}. Two products were separated and crystallized as indicated below.

Reaction of $Fe_2(CO)_6(C_2R)[P(C_6H_5)_2]$ with R^1NH_2 (R = C_6H_5, R^1 = C_2H_5, C_4H_9, $CH(CH_3)(C_2H_5)$, $C(CH_3)_3$, $CH(CH_3)_2$, $CH_2CH_2NH_2$, $CH_2CH_2N(CH_3)_2$; R = *p*-BrC_6H_4, R^1 = $CH(CH_3)_2$, C_4H_9, $C(CH_3)_3$; R = *p*-$OCH_3C_6H_4$, R^1 = $CH(CH_3)_2$, C_4H_9). Typically, $Fe_2(CO)_6(C_2R)[P(C_6H_5)_2]$ (0.3 g, ca. 0.5 mmol) was dissolved in 30 mL of benzene. A large excess of (>4 mmol) amine was added and the reaction mixture stirred at room temperature until the solution IR spectra of small aliquots indicated that all of the starting material had reacted. The two isomers were isolated as described below. When R = C_6H_5 and R^1 = $C(CH_3)_3$ and when R = *p*-BrC_6H_4 and R^1 = $C(CH_3)_3$, only the red complexes $Fe_2(CO)_6$[CHC{$NHC(CH_3)_3$}{R}][$P(C_6H_5)_2$] were obtained.

Reaction of $Fe_2(CO)_6(C_2R)[P(C_6H_5)_2]$ with R^1NH_2 (R = C_6H_5, R^1 = C_6H_5, c-C_6H_{11}; R = *p*-BrC_6H_4, R^1 = c-C_6H_{11}). These reactions were carried out in refluxing benzene again until all $Fe_2(CO)_6(C_2R)[P(C_6H_5)_2]$ had reacted, generally 1–2 h. Two isomers were obtained except for the case where R = C_6H_5 and R^1 = C_6H_5, when only the red complex $Fe_2(CO)_6$[CHC{NHC_6H_5}(C_6H_5)][$P(C_6H_5)_2$] was formed.

Methods of Separation and Crystallization. Two methods of separation were used: (i) The reaction mixture was reduced to a few milliliters and chromatographed on a Florisil column made up in heptane. Since the complexes of types 2 and 3 have similar R_f values, complete separation takes up to 2 h. Elution with heptane/benzene (70:30) afforded yellow 2, and heptane/benzene (50:50) eluted red 3. Both products crystallized from saturated heptane at −70 °C. (ii) The reaction mixture was chromatographed on Florisil made up in benzene. Elution with benzene removed both products as one band. Fractional crystallization from heptane afforded red 3 preferentially, leaving mother liquor rich in 2. Yields of yellow 2 were greater by using method i. Yields of red 3 were superior by using method ii since these compounds partially isomerize on Florisil, resulting in reduced yields. Analytical data are listed in Table II; optimum yields are recorded.

2. Secondary Amines. Reaction of $Fe_2(CO)_6(C_2C_6H_5)[P(C_6H_5)_2]$ with $(CH_3)_2NH$. Isolation of Simple Adducts. A 20-mL portion of a 40% solution of dimethylamine in water was shaken with 20 mL of diethyl ether. The organic layer was separated and added to a filtered solution of $Fe_2(CO)_6(C_2C_6H_5)[P(C_6H_5)_2]$ (0.3 g, ca. 0.5 mmol) in diethyl ether (20 mL) at 0 °C. The reaction mixture was stirred for a few minutes, resulting in the formation of a heavy yellow precipitate. Diethyl ether was removed by syringe and the product, $Fe_2(CO)_6$[CC{$NH(CH_3)_2$}{C_6H_5}][$P(C_6H_5)_2$], washed with cold heptane (3 × 20 mL), dried in vacuo at 0 °C, and stored under nitrogen at −10 °C.

Reaction of $Fe_2(CO)_6(C_2R)[P(C_6H_5)_2]$ with $(C_2H_5)_2NH$ (R = C_6H_5, *p*-$CH_3OC_6H_4$). Isolation of Simple Adducts. A heptane (30 mL) solution of $Fe_2(CO)_6(C_2R)[P(C_6H_5)_2]$ (0.3 g, 0.5 mmol) was filtered and cooled to 0 °C. Excess diethylamine (0.2 g, ca. 3 mmol) was added to the stirred solution, affording an immediate yellow precipitate of $Fe_2(CO)_6$[CC{$NH(C_2H_5)_2$}{R}][$P(C_6H_5)_2$]. Heptane was removed and the product washed several times with cold heptane and dried in vacuo at 0 °C.

The above complexes are thermally unstable and decompose on dissolution in any solvent at room temperature. Analytical data are given in Table II.

Conversion of $Fe_2(CO)_6$[CC{$NH(R^1)_2$}{R}][$P(C_5H_5)_2$] to $Fe_2(CO)_6$[CHC{$N(R^1)_2$}{R}][$P(C_6H_5)_2$] (R = C_6H_5, R^1 = CH_3, C_2H_5; R = *p*-$CH_3OC_6H_4$, R^1 = C_2H_5). The yellow powders obtained in the

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(19) Charrier, C.; Chodkiewicz, W.; Cadiot, P. *Bull. Soc. Chim. Fr.* **1966**, 1002.

(20) Mott, G. N. Ph.D. Thesis, University of Waterloo, Waterloo, Ontario, Canada, 1980.

previous reactions were dissolved in benzene (20 mL), and the solutions were heated at 40–50 °C for 1 h. The resulting dark red solutions were reduced in volume and introduced onto a Florisil column made up in heptane. Elution with heptane removed $Fe_2(CO)_6(C_2R)[P(C_6H_5)_2]$ (ca. 10%), identified by its solution IR carbonyl spectrum, and then benzene removed a dark red band, which on crystallization from cold (−10 °C) heptane afforded light red crystals of $Fe_2(CO)_6[CHC\{N(R^1)_2\}\{R\}][P(C_6H_5)_2]$ in 70–80% yield.

Synthesis of $Fe_2(CO)_6[CHC\{\overline{NCH_2(CH_2)_3C}H_2\}\{C_6H_5\}][P(C_6H_5)_2]$, $Fe_2(CO)_6[CHC\{\overline{NCH_2CH_2OCH_2C}H_2\}\{C_6H_5\}][P(C_6H_5)_2]$, and $Fe_2(CO)_6[CHC\{N(R^1)_2\}\{R\}][P(C_6H_5)_2]$ ($R = C_6H_5$, $R^1 = C_3H_7$; $R =$ c-C_6H_{11}, $R^1 = C_2H_5$; $R = p$-BrC_6H_4, $R^1 = C_2H_5$). These compounds were obtained by heating benzene solutions of $Fe_2(CO)_6(C_2R)[P(C_6H_5)_2]$ and a 2–3-fold excess of the appropriate amines at 40 °C for periods between 30 min and 1 h. Removal of any remaining starting material, isolation, and crystallization of the red products were essentially the same as those described above. There was no reaction between $Fe_2(CO)_6(C_2C_6H_5)[P(C_6H_5)_2]$ and either diisopropylamine or dicyclohexylamine.

Tertiary Amines. Reaction of triethylamine and trimethylamine with $Fe_2(CO)_6(C_2C_6H_5)[P(C_6H_5)_2]$ at temperatures between −78 and +50 °C in heptane, benzene, or ether failed to produce any indication, either by color change or precipitation, of the adducts $Fe_2(CO)_6[CC\{amine\}(C_6H_5)][P(C_6H_5)_2]$ or $Fe_2(CO)_6[C\{amine\}C(C_6H_5)][P(C_6H_5)_2]$.

Miscellaneous Amine Reactions. There was no reaction between $Fe_2(CO)_6(C_2C(CH_3)_3)[P(C_6H_5)_2]$ and an excess of $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$, pyridine, or morpholine, either at low temperatures or even after refluxing in benzene for several days. However, reaction of $Fe_2(CO)_6(C_2C(CH_3)_3)[P(C_6H_5)_2]$ (0.3 g, ca. 0.5 mmol) and a large excess of piperidine (2 g, ca. 25 mmol) in 50 mL of benzene at 50 °C for 2 days afforded, from a cold (−10 °C) heptane solution after chromatography on Florisil (benzene eluant), red crystals of a complex identified as $Fe_2(CO)_5[P\{\overline{NCH_2(CH_2)_3C}H_2\}\{(C_6H_5)_2\}](C_2C(CH_3)_3)[P(C_6H_5)_2]$, mp 140–142 °C, analogous to the phosphine monosubstituted products described previously:[10] yield ca. 5%; IR (C_6H_{12}) (a) ν(CO) 2032 (s), 1986 (vs), 1968 (s), 1956 (s), 1929 (m) cm^{-1}, (b) $\nu(C{\equiv}C)$ 1899 (vw) cm^{-1}; mol wt (mass spectra) calcd 787, found 787. Anal. Calcd: C, 61.0; H, 5.0; N, 1.8. Found: C, 61.3; H, 5.2; N, 1.5. This complex was completely characterized by an X-ray crystallographic study.

^{31}P NMR Studies. In an effort to follow the progress of the reactions described above, variable-temperature ^{31}P NMR spectra of reaction mixtures were measured as follows: (a) A 0.1-g sample (ca. 0.2 mmol) of $Fe_2(CO)_6(C_2C_6H_5)[P(C_6H_5)_2]$ was dissolved in 2 mL of degassed $C_6D_5CD_3$ and transferred to a cooled (−76 °C) 5-mm NMR tube under a stream of dry nitrogen. A 0.6-g sample (ca. 0.6 mmol) of cyclohexylamine was added on top of the frozen solution. The tube was then sealed under vacuum and placed in the ^{31}P NMR probe, initially at −80 °C. The mixture was slowly warmed (rapid spinning ensured efficient mixing), and spectra were run at 10 °C intervals up to +50 °C. (b) The procedure was the same as (a) except that an excess (3-fold) of dipropylamine was used as nucleophile. (c) The procedure was the same as (a) except that 0.1 g (ca. 0.2 mmol) of $Fe_2(CO)_6(C_2C_6H_{11})[P(C_6H_5)_2]$ and an excess (0.06 g, ca. 0.6 mmol) of cyclohexylamine were used as reactants.

In order to assess *exact* ratios of reaction products derived from attack of primary amines at the α- and β-carbon atoms in $Fe_2(CO)_6(C_\alpha{\equiv}C_\beta R)[P(C_6H_5)_2]$, the following spectra were recorded at ambient temperature: for $Fe_2(CO)_6(C_2C_6H_5)[P(C_6H_5)_2]$, the addition of $C_6H_{11}NH_2$, $C_4H_9NH_2$, $CH_3(C_2H_5)CHNH_2$, and $(CH_3)_2CHNH_2$; for $Fe_2(CO)_6[C_2C_6H_4CH_3O$-$p][P(C_6H_5)_2]$, the addition of $C_4H_9NH_2$ and $(CH_3)_2CHNH_2$; for $Fe_2(CO)_6[C_2C_6H_4Br$-$p][P(C_6H_5)_2]$, the addition of $C_4H_9NH_2$ and $(CH_3)_2CHNH_2$.

In each case 0.1 g (ca. 0.2 mmol) of complex was dissolved in 2 mL of C_6D_6 and ca. 0.05 g (>0.5 mmol) of amine was added. The mixture was spun rapidly at probe temperature for 5 min (except for the c-$C_6H_{11}NH_2$ mixture, which required ca. 30 min), at which time reaction was shown to be complete by the disappearance of the signal ($\delta(P(C_6H_5)_2)$ +148) due to the starting material. Spectra were then recorded, and ratios of the two adducts formed were assessed by integration of the appropriate signals. Test samples were run, in each case with different ratios of pure isolated adducts dissolved in C_6D_6. Integration of signals confirmed that errors were no greater than ±3%.

The results of these experiments are presented in Table III.

In addition to Tables I–III mentioned above, Table IV contains a selection of pertinent infrared, NMR, and Mössbauer data for the complexes prepared. Complete tables of ν(CO), ν(N—H), and $\nu(C{\equiv}N)$ stretching frequencies (Tables S1–S3) and ^1H and ^{31}P NMR and Mössbauer parameters (Tables S4–S6) are available as supplementary data.

Results and Discussion

The μ-η^2-sideways-bound acetylide in $Fe_2(CO)_6(C_2R)[P(C_6H_5)_2]$ (**1**) undergoes facile nucleophile attack at carbon by primary and secondary amines. The end products of these reactions are unusual binuclear complexes with phosphido bridges and zwitterionic μ-η^1-alkylidene (**3**) or μ-η^2-alkylidene (**2**) ligands formed via formal addition of an N-H group across the acetylide. The structural features of these derivatives have been adequately established by single-crystal X-ray diffraction.[11,12b] The nature and scope of these reactions have now been examined in greater detail.

In order to shed some light on the electronic and steric factors influencing the outcome of these nucleophilic additions, we synthesized the new ligands p-$BrC_6H_4C_2[P(C_6H_5)_2]$ and p-$MeOC_6H_4C_2[p(C_6H_5)_2]$ and the new complexes **1** ($R = p$-BrC_6H_4, p-$MeOC_6H_4$) derived therefrom. The ^{13}C NMR spectra of **1** ($R = C_6H_5$, p-BrC_6H_4, p-$MeOC_6H_4$) were examined in particular detail in an attempt to correlate changes in acetylide electronic structure with the regiospecificity of amine additions. Crucial structural information on key intermediates has been obtained from Mössbauer studies of isolated solids and variable-temperature ^{31}P NMR solution work.

Synthesis. Several features of the amine additions are noteworthy. Amines of small or moderate steric bulk (e.g., $C_6H_{11}NH_2$) with **1** ($R = C_6H_5$) afforded good yields of both **2** and **3** ($R^1 = C_6H_{11}$, $R^2 = H$). In contrast, bulkier primary amines (e.g., $(CH_3)_3CNH_2$) yielded only the product of nucleophilic addition at the β-carbon (**3**, $R = C_6H_5$, $R^1 = C(CH_3)_3$, $R^2 = H$). Similarly, at ~40 °C reaction with small secondary amines (e.g., $(CH_3)_2NH$ and $(C_2H_5)_2NH$) resulted in formation of **3** ($R = C_6H_5$, $R^1 = R^2 = CH_3$, C_2H_5) as the sole product. However, addition of $(CH_3)_2NH$ or $(C_2H_5)_2NH$ at 0 °C to **1** ($R = C_6H_5$) gave yellow 1:1 amine: acetylide adducts in >90% yields, which underwent smooth isomerization in benzene, forming **3** ($R = C_6H_5$, $R^1 = R^2 = CH_3$, C_2H_5). In contrast, **2**, also a yellow product, is thermally stable in solution and does not isomerize. There was no observable reaction between $Fe_2(CO)_6(C_2R)[P(C_6H_5)_2]$ and bulky secondary amines, e.g. $((CH_3)_2CH)_2NH$ and $(C_6H_{11})_2NH$, or tertiary amines. In addition, a change in the group R of **1** from C_6H_5 to $C(CH_3)_3$ and for C_6H_{11} produced a dramatic change in the reactivity of the acetylide moiety. Thus, reaction of primary amines with **1** ($R = C_6H_{11}$) gave only **3**, and the acetylide moiety in **1** ($R = C(CH_3)_3$) is unreactive toward primary, secondary, or tertiary amines.

Mössbauer Data: The Nature of the Simple 1:1 Adducts. The Mössbauer spectra of the phosphite,[12a] phosphine,[12b] carbene,[13a] and amine addition products of $Fe_2(CO)_6(C_2R)[P(C_6H_5)_2]$ all consist of resolved doublets, indicating equivalence of the iron environments. While X-ray structural studies[11-13] show that the two metal sites are chemically inequivalent, it is easy to appreciate that in reality the stereochemical and electronic environments of the two iron atoms in each of the μ-η^1-alkylidene (**3**), μ-η^2-alkylidene (**2**), or μ-η^1-vinylidene (**4**) complexes are quite similar. In practice, the Mössbauer experiment is insufficiently sensitive to differentiate between them. Our parallel investigation of Mössbauer spectra and molecular structures of the addition products have, however, established that the nature of the ligand present may be determined unambiguously from an examination of the quadrupole splittings. Table V correlates

Table II. Analytical Data

complex	% yield	mp °C	anal.,[a] %				
			C	H	N	P	Br
$Fe_2(CO)_6[C\{NHCH_3\}CH\{C_6H_5\}][P(C_6H_5)_2]$	27	150	54.4 54.3	3.5 3.4	2.3 2.3		
$Fe_2(CO)_6[CHC\{NHCH_3\}\{C_6H_5\}][P(C_6H_5)_2]$	48	138	54.2 54.3	3.4 3.4		5.2 5.2	
$Fe_2(CO)_6[C\{NHC_2H_5\}CH\{C_6H_5\}][P(C_6H_5)_2]$	30	152	54.7 55.0	3.7 3.6	2.3 2.3		
$Fe_2(CO)_6[CHC\{NHC_2H_5\}\{C_6H_5\}][P(C_6H_5)_2]$	53	141	54.8 55.0	3.7 3.6	2.2 2.3		
$Fe_2(CO)_6[CHC\{NHC_2H_5\}\{c\text{-}C_6H_{11}\}][P(C_6H_5)_2]$	74	128	54.4 54.5	4.7 4.6	2.1 2.2	5.1 5.0	
$Fe_2(CO)_6[C\{NHC_4H_9\}CH\{C_6H_5\}][P(C_6H_5)_2]$	33	147–149	56.1 56.4	4.2 4.1	2.0 2.2		
$Fe_2(CO)_6[CHC\{NHC_4H_9\}\{C_6H_5\}][P(C_6H_5)_2]$	47	132–134	56.2 56.4	4.2 4.1	2.1 2.2		
$Fe_2(CO)_6[C\{NHC_4H_9\}CH\{C_6H_4Br\text{-}o\}][P(C_6H_5)_2]$	33	147	49.9 50.2	3.4 3.5	1.9 1.9		
$Fe_2(CO)_6[CHC\{NHC_4H_9\}\{C_6H_4Br\text{-}p\}][P(C_6H_5)_2]$	35	138–141	49.6 50.2	3.4 3.5	1.9 1.9		
$Fe_2(CO)_6[C\{NHC_4H_9\}CH\{C_6H_4OCH_3\text{-}p\}][P(C_6H_5)_2]$	5	141	55.9 55.6	4.3 4.2			
$Fe_2(CO)_6[CHC\{NHC_4H_9\}\{C_6H_4OCH_3\text{-}p\}][P(C_6H_5)_2]$	73	128	55.8 55.6	4.3 4.2	2.1 2.1	4.6 4.6	
$Fe_2(CO)_6[CHC\{NHC_6H_5\}\{C_6H_5\}][P(C_6H_5)_2]$	47	125	58.6 58.4	3.5 3.4	2.0 2.1		
$Fe_2(CO)_6[CHC\{NHC_6H_5\}\{c\text{-}C_6H_{11}\}][P(C_6H_5)_2]$	43	127–129	57.6 57.8	4.3 4.2	2.2 2.1	4.7 4.7	
$Fe_2(CO)_6[C\{NHCH_2CH_2NH_2\}CH\{C_6H_5\}][P(C_6H_5)_2]$	23	157	53.9 53.7	3.9 3.7	4.4 4.5		
$Fe_2(CO)_6[CHC\{NHCH_2CH_2NH_2\}\{C_6H_5\}][P(C_6H_5)_2]$	41	130	54.9 53.7	3.8 3.7	4.4 4.5		
$Fe_2(CO)_6[C\{NHCH_2CH_2N(CH_3)_2\}CH\{C_6H_5\}][P(C_6H_5)_2]$	26	125	55.0 55.1	4.2 4.2	4.0 4.3		
$Fe_2(CO)_6[CHC\{NHCH_2CH_2N(CH_3)_2\}\{C_6H_5\}][P(C_6H_5)_2]$	43	114	55.0 55.1	4.3 4.2	4.2 4.3	4.6 4.7	
$Fe_2(CO)_6[C\{NHC_6H_{11}\text{-}c\}CH\{C_6H_5\}][P(C_6H_5)_2]$	22	150	60.0 59.7	4.4 4.7[b]			
$Fe_2(CO)_6[CHC\{NHC_6H_{11}\text{-}c\}\{C_6H_5\}][P(C_6H_5)_2]$	48	140	57.6 56.8	4.3 4.4		4.5 4.7	
$Fe_2(CO)_6[C\{NHC_6H_{11}\text{-}c\}CH\{C_6H_4Br\text{-}p\}][P(C_6H_5)_2]$	43	145–147 dec	51.8 51.7	3.8 3.6		4.0 4.2	10.5 10.7
$Fe_2(CO)_6[CHC\{NHC_6H_{11}\text{-}c\}\{C_6H_4Br\text{-}p\}][P(C_6H_5)_2]$	34	123–125	51.5 51.7	3.9 3.6	1.8 1.9		10.5 10.7
$Fe_2(CO)_6[CHC\{NHC_6H_{11}\text{-}c\}\{c\text{-}C_6H_{11}\}][P(C_6H_5)_2]$	69	124	57.5 57.3	5.2 5.1	2.1 2.1	4.7 4.6	
$Fe_2(CO)_6[C\{NHCH(CH_3)_2\}CH\{C_6H_5\}][P(C_6H_5)_2]$	21	150–151	55.4 55.7	4.0 3.9	2.1 2.2		
$Fe_2(CO)_6[CHC\{NHCH(CH_3)_2\}\{C_6H_5\}][P(C_6H_5)_2]$	61	130–131	55.5 55.7	3.9 3.9	2.2 2.2		
$Fe_2(CO)_6[C\{NHCH(CH_3)_2\}CH\{C_6H_4OCH_3\text{-}p\}][P(C_6H_5)_2]$	5	140–141	55.0 55.0	4.3 4.0	2.0 2.1	4.6 4.7	
$Fe_2(CO)_6[CHC\{NHCH(CH_3)_2\}\{C_6H_4OCH_3\text{-}p\}][P(C_6H_5)_2]$	77	124	55.0 55.0	4.1 4.0	2.2 2.1	4.5 4.7	
$Fe_2(CO)_6[C\{NHCH(CH_3)_2\}CH\{C_6H_4Br\text{-}p\}][P(C_6H_5)_2]$	22	154–155 dec	50.0 49.5	3.5 3.3	1.8 2.0		11.2 11.4
$Fe_2(CO)_6[CHC\{NHCH(CH_3)_2\}\{C_6H_4Br\text{-}p\}][P(C_6H_5)_2]$	45	136 dec	49.9 49.5	3.4 3.3	2.0 2.0		11.3 11.4
$Fe_2(CO)_6[CHC\{NHCH(CH_3)_2\}\{c\text{-}C_6H_{11}\}][P(C_6H_5)_2]$	79	124–127 dec	55.2 55.2	4.9 4.8	2.2 2.2	5.1 4.9	
$Fe_2(CO)_6[C\{NHCH(CH_3)(C_2H_5)\}CH\{C_6H_5\}][P(C_6H_5)_2]$	18	152 dec	58.7 58.3	4.5 4.3	2.0 2.1[b]		
$Fe_2(CO)_6[CHC\{NHCH(CH_3)(C_2H_5)\}\{C_6H_5\}][P(C_6H_5)_2]$	43	121	56.7 56.4	4.1 4.1	2.1 2.2		
$Fe_2(CO)_6[CHC\{NHC(CH_3)_3\}\{C_6H_5\}][P(C_6H_5)_2]$	72	120–122	56.2 56.4	4.3 4.1	2.1 2.2		
$Fe_2(CO)_6[CHC\{NHC(CH_3)_3\}\{C_6H_4Br\text{-}p\}][P(C_6H_5)_2]$	81	137	50.3 50.2	3.6 3.5	1.9 2.0		
$Fe_2(CO)_6[CC\{NH(CH_3)_2\}\{C_6H_5\}][P(C_6H_5)_2]$	85	70–72 dec	55.0 55.0	3.6 3.6			
$Fe_2(CO)_6[CC\{NH(C_2H_5)_2\}\{C_6H_5\}][P(C_6H_5)_2]$	82	76–78 dec	56.1 55.3	4.0 4.1		4.7 4.9	
$Fe_2(CO)_6[CC\{NH(C_2H_5)_2\}\{C_6H_4OCH_3\text{-}p\}][P(C_6H_5)_2]$	85	88–90 dec	55.7 55.6	4.3 4.2	1.9 2.1	4.7 4.6	
$Fe_2(CO)_6[CHC\{N(CH_3)_2\}\{C_6H_5\}][P(C_6H_5)_2]$	80	148	54.9 55.0	3.7 3.6	2.2 2.3		

Table II (*Continued*)

complex	% yield	mp °C	anal.,[a] % C	H	N	P	Br
$Fe_2(CO)_6[CHC\{N(C_2H_5)_2\}\{C_6H_5\}][P(C_6H_5)_2]$	72	145	56.5 56.3	4.1 4.1		4.7 4.9	
$Fe_2(CO)_6[CHC\{N(C_2H_5)_2\}\{C_6H_4Br\text{-}p\}][P(C_6H_5)_2]$	71	144-147	52.3 52.4	4.1 3.7	1.8 1.8[b]		
$Fe_2(CO)_6[CHC\{N(C_2H_5)_2\}\{C_6H_4OCH_3\text{-}p\}][P(C_6H_5)_2]$	74	138	56.0 55.6	4.3 4.2	2.0 2.1		
$Fe_2(CO)_6[CHC\{N(C_2H_5)_2\}\{c\text{-}C_6H_{11}\}][P(C_6H_5)_2]$	72	128	55.7 55.8	5.0 5.0	4.8 4.8		
$Fe_2(CO)_6[CHC\{N(C_3H_7)_2\}\{C_6H_5\}][P(C_6H_5)_2]$	74	126	57.7 57.6	4.4 4.5	2.1 2.1		
$Fe_2(CO)_6[CHC\{NCH_2(CH_2)_3CH_2\}\{C_6H_5\}][P(C_6H_5)_2]$	68	154-156 dec	57.0 57.2	4.1 4.0		4.6 4.8	
$Fe_2(CO)_6[CHC\{NCH_2CH_2OCH_2CH_2\}\{C_6H_5\}][P(C_6H_5)_2]$	64	140 dec	55.2 55.2	3.9 3.7	2.1 2.1		

[a] Upper value found; lower value calculated. [b] Includes 0.5 mol of C_6H_6.

Table III. Ratios[a-c] of the Products Formed by the Additions of Primary Amines across the Triple Bond of $Fe_2(CO)_6(C_2R)[P(C_6H_5)_2]$

amine	R = *p*-$CH_3OC_6H_4$ ratio 3:2	R = C_6H_5 ratio 3:2	R = *p*-BrC_6H_4 ratio 3:2
$(CH_3)_2CHNH_2$	21.0:1	3.7:1	1.5:1
$C_4H_9NH_2$	10.7:1	2.2:1	1.4:1
c-$C_6H_{11}NH_2$		3.2:1	
$(C_2H_5)(CH_3)CHNH_2$		4.2:1	

[a] By ^{31}P NMR. [b] Reaction of $Fe_2(CO)_6[(C_2C_6H_{11})][P(C_6H_5)_2]$ with primary amines gives only products of type **3**. [c] The complexes **2** and **3** are formed via amine addition to the α- or β-carbon atoms, respectively, of the acetylide.

the available structural data for these and related complexes with Mössbauer quadrupole splittings Δ. It is readily apparent that, when a μ-η^2-alkylidene ligand is present, the quadrupole splitting, Δ, is significantly lower than that for a μ-η^1-alkylidene or μ-η^1-vinylidene derivative. Table V also indicates the average angular deviation from octahedral geometry at the iron atoms of structurally characterized dimers based on each iron having three carbonyl carbon atoms, a phosphido bridge phosphorus atom, either C_α or C_β of the hydrocarbyl ligand, and the center of a bent Fe–Fe bond at the apices of a distorted octahedron.[21] There is ample justification on structural and theoretical grounds for such a description.[22] Clearly, there is less distortion from octahedral geometry at the iron sites in the μ-η^2-alkylidene derivatives (**2**) than for compounds of types **3** or **4**, and this is reflected in the lower Δ values of the former. From this information, the remaining structural type studied in this present work was readily classified. Thus, the complexes initially produced on addition of secondary amines to $Fe_2(CO)_6(C_2R)[P(C_6H_5)_2]$ at 0 °C are yellow precipitates, known to be 1:1 adducts from analytical data. Attempts to crystallization of these precipitates proved impossible as reconversion to the σ,π-acetylide occurs on dissolution in organic solvents. Inspection of the Mössbauer spectra of these latter complexes, however, revealed a resolved doublet with a quadrupole splitting of ca. 0.6 mm s^{-1}, characteristic of complexes containing μ-η^1 ligands. A μ-η^1-vinylidene structure (**4**) can be confidently assigned to these complexes. This formulation is analogous to that shown by X-ray crystallography for the dicyclohexylphosphine adduct $Fe_2(CO)_6\{\mu$-η^1-$CCPh[P(C_6H_{11})_2H]\}[P(C_6H_5)_2]$.[12b] Infrared spectroscopic data (Table III) confirm the μ-η^1-vinylidene structure proposed for the amine adducts. Thus the appearance of a ν(N—H) frequency (3100–3200 cm^{-1}) and the absence of a ν(N=C) band between 1490 and 1550 cm^{-1} (cf. type **3** complexes, Table III) effectively eliminate an iminium ion ($>N^+=C<$) structure. Moreover, the frequency of the highest ν(CO) band is entirely characteristic of a one-carbon dipolar ligand (vide infra; Table IV).

There is no clear distinction between the isomer shifts, δ, for the two types of addition products (δ(av) for the μ-η^1-alkylidenes and μ-η^1-vinylidenes 0.16 mm s^{-1}; for the μ-η^2-alkylidenes δ(av) 0.18 mm s^{-1}), although the infrared ν(CO) frequencies suggest a greater delocalization of charge onto the metal framework for the μ-η^1 ligands than for the μ-η^2 ligands. Evidently "s" electron densities are approximately the same at the iron atoms in both of these types of complexes presumably because the net $\sigma + \pi$ effects of both ligand types are similar.

^{31}P Chemical Shifts: Correlation with Ligand Type. We have recently amassed a large body of X-ray data for binuclear iron carbonyl complexes of the $Fe_2(CO)_6(X)[P(C_6H_5)_2]$ type where X represents a three-electron ligand. The ^{31}P chemical shifts for a selection of structurally related complexes including several reported here are listed in Table VI. Data for other selected amine derivatives are given in Table IV, and a complete listing of ^{31}P shifts for all of the complexes prepared in this study can be found in supplementary Table S4. Two features of Tables IV and VI are noteworthy: (i) The ^{31}P chemical shifts for these phosphide bridges across strong ($\sim$2.55–2.71 Å) Fe–Fe bonds lie within the range 100–200 ppm downfield of 85% H_3PO_4. In these compounds the angle at the phosphide bridge is acute ($\sim$69–76°). (ii) Although the correlation of Fe–P–Fe angle with $\delta(^{31}P)$ is by no means perfect, there is a rough but unmistakable increase in δ (i.e., a downfield shift) as the Fe–P–Fe angle increases. While the variation in angles ($\sim$6 °C) is small, the range of ^{31}P shifts ($\sim$120–200 ppm) is impressive.

As pointed out elsewhere for di- and polynuclear phosphide-bridged iron, ruthenium, and osmium compounds, there

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(21) The angles of the "top" half of the octahedron shown in Table V are used as determinants.

(22) For a discussion of the merits of this description for bridged $Fe_2(CO)_6(X)_2$ systems see: (a) Teo, B. K.; Hall, M. B.; Fenske, R. F.; Dahl, L. F. *Inorg. Chem.* **1975**, *14*, 3103. (b) Burdett, J. K. *J. Chem. Soc., Dalton Trans.* **1977**, 423.

(23) (a) Mott, G. N.; Carty, A. J. *Inorg. Chem.* **1979**, *18*, 2926. (b) Taylor, N. J.; Mott, G. N.; Carty, A. J. *Ibid.* **1980**, *19*, 560.

(24) Carty, A. J.; Mott, G. N.; Taylor, N. J. *J. Am. Chem. Soc.* **1979**, *101*, 3131.

(25) Carty, A. J.; Mott, G. N.; Taylor, N. J. *J. Organomet. Chem.* **1979**, *182*, C69.

(26) Smith, W. F.; Mott, G. N.; Taylor, N. J.; Carty, A. J., unpublished results.

(27) Huntsman, J. R.; Dahl, L. F., unpublished results quoted by: Clegg, W. *Inorg. Chem.* **1976**, *15*, 1609.

Table IV. Selected Spectroscopic Data

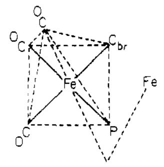
	ν(CO),^{a} cm^{-1}	ν(N–H),^{b} cm^{-1}	ν(C=N),^{b} cm^{-1}	^{31}P NMR δ^c	δ, mm s^{-1}	Δ, mm s^{-1}	Γ, mm s^{-1}
$Fe_2(CO)_6[C(NHCH_3)CH(C_6H_5)][P(C_6H_5)_2]$	2052 (s), 2014 (vs), 1981 (s), 1964 (s), 1948 (m)	3302 (w)	1537 (m)	183.1	0.18	0.29	0.34
$Fe_2(CO)_6[C(NH\text{-}c\text{-}C_6H_{11})CH(C_6H_5)][P(C_6H_5)_2]$	2055 (s), 2012 (vs), 1984 (s), 1965 (s), 1948 (m)	3280 (w)	1521 (m)	183.5	0.17	0.36	0.28
$Fe_2(CO)_6[CHC(NHCH_3)(C_6H_5)][P(C_6H_5)_2]$	2038 (m), 2034 (m), 2000 (vs), 1957 (s), 1953 (s), 1914 (w)	3379 (w)	1537 (m)	153.7	0.20	0.69	0.34
$Fe_2(CO)_6[CHC(NH\text{-}c\text{-}C_6H_{11})(C_6H_5)][P(C_6H_5)_2]$	2033 (m), 1999 (vs), 1956 (s, br), 1913 (w)	3280 (w)	1547 (m)	154.0	0.16	0.66	0.26
$Fe_2(CO)_6[CC(NH(C_2H_5)_2)(C_6H_{11})][P(C_6H_5)_2]$	2032 (s), 1975 (s, br), 1950 (s, br), 1920 (s, br)	3102 (w)		129.4^{d,e}	0.15	0.62	0.29
$Fe_2(CO)_6[CC(NH(C_2H_5)_2)(C_6H_4OCH_3\text{-}p)][P(C_6H_5)_2]$	2033 (s), 1975 (s, br), 1950 (s, br), 1920 (s, br)	3120 (vw) 3160 (vw)		*f*	0.12	0.65	0.20
$Fe_2(CO)_6[CHC(N(C_2H_5)_2)(C_6H_5)][P(C_6H_5)_2]$	2036 (s), 1997 (vs), 1966 (s), 1944 (s), 1934 (m)		1520	153.9	0.19	0.63	0.24
$Fe_2(CO)_6[CHC(N(C_3H_7)_2)(C_6H_5)][P(C_6H_5)_2]$	2037 (s), 1997 (vs), 1966 (s), 1944 (s), 1934 (m)		1522	155.2	0.19	0.69	0.32

[a] C_6H_{12} solvent. [b] Nujol mull. [c] C_6D_6 solvent. [d] Identified at −30 °C in $C_6D_5CD_3$. [e] $C_6D_5CD_3$. [f] Decomposes on dissolution.

Table V. Comparison between the Deviations from an Idealized Octahedral Geometry[a] at the Two Iron Atoms and Mössbauer Parameters for the Complexes $Fe_2(CO)_6[L][P(C_6H_5)_2]$

L	av dev from 90°, deg	δ, mm s^{-1}	Δ, mm s^{-1}	ref
$[C\{P(OC_2H_5)_3\}C\{C_6H_5\}]^b$	6.9	0.21	0.28	12a
$[C\{CNC(CH_3)_3\}C\{C_6H_5\}]^b$	7.4	0.20	0.28	13b
$[C\{CN(CH_3)CH_2CH_2N(CH_3)\}C\{C_6H_5\}]^b$	6.6	0.19	0.21	13a
$[C\{NH\text{-}c\text{-}C_6H_{11}\}CH\{C_6H_5\}]^b$	6.2	0.17	0.36	11b
$[CHC\{NH\text{-}c\text{-}C_6H_{11}\}\{C_6H_5\}]^c$	8.9	0.16	0.66	11b
$[CC\{PH(c\text{-}C_6H_{11})_2\}\{C_6H_5\}]^c$	9.2	0.14	0.76	12b
$[CHC\{N(C_2H_5)_2\}\{C_6H_5\}]^c$	8.8	0.19	0.63	11a

[a] Notation:



[b] Contains a two-carbon, three-electron bridging ligand.
[c] Contains a one-carbon, three-electron bridging ligand.

are strong indications that $\delta(^{31}P)$ values for $P(C_6H_5)_2$ groups bridging noninteracting metals[28] lie at considerably higher field than the corresponding shifts for PPh_2 groups bridging two metals where the M- - -M distance is indicative of a strong metal–metal bond. Recent studies with other metals confirm that the ^{31}P ($P(C_6H_5)_2$) shift may indeed be a useful spectroscopic criterion for determining the presence or absence of M- - -M interactions provided that the comparison is made within structurally related series.[29] An important point to note here is that for the low-field shifts $\delta(^{31}P)$ increases with M–P–M angle whereas for $P(C_6H_5)_2$ groups bridging nonbonded metals $\delta(^{31}P)$ becomes more negative (moves upfield) with an increase in M–P–M angle.[28] Thus, it is tempting to suggest that there may be a continuous curve, passing through a minimum, relating δ and M–P–M angle for a given metal. Gorenstein has shown that such a relationship exists for $\delta(^{31}P)$ vs. ∠O–P–O in phosphate esters.[30]

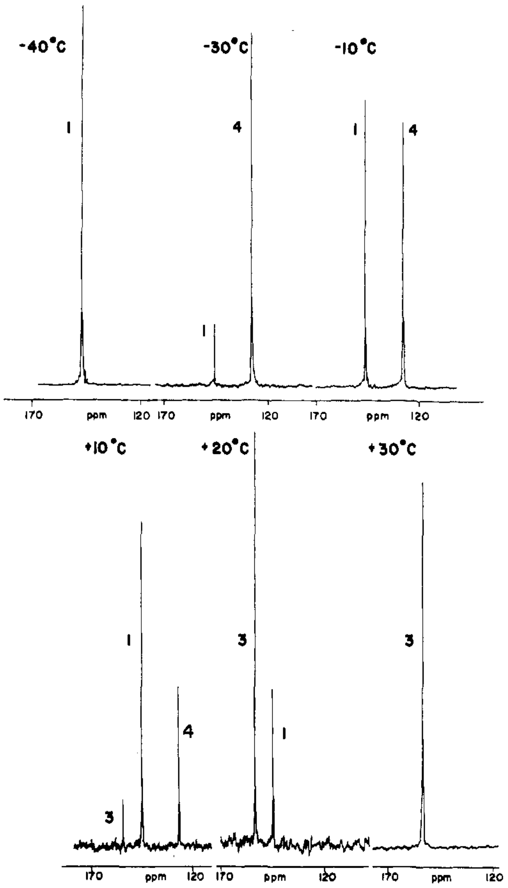


Figure 1. Variable-temperature ^{31}P NMR spectra for the reaction of $Fe_2(CO)_6(C_2C_6H_5)[P(C_6H_5)_2]$ (1) with dipropylamine. Peaks labeled 3 and 4 are $Fe_2(CO)_6[CHC\{N(C_3H_7)_2\}(C_6H_5)][P(C_6H_5)_2]$ and $Fe_2(CO)_6[CC\{NH(C_3H_7)_2\}(C_6H_5)][P(C_6H_5)_2]$, respectively.

As the structural data in Table VI imply, $\delta(^{31}P)$ should be a rather sensitive probe for differentiating η^1- and η^2-alkylidene bonding modes and hence establishing the site of nucleophilic attack by the amine. This is indeed the case. Thus, the entire set of μ-η^1-alkylidene compounds $Fe_2(CO)_6[CHC\{NHR^1\}R][P(C_6H_5)_2]$ (3) have $\delta(^{31}P)$ within the narrow range 153.0–160.8 while the μ-η^2 species $Fe_2(CO)_6[C\{NHR^1\}CHR][P(C_6H_5)_3]$ have $\delta(^{31}P)$ between 183.1 and 185.3. In

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[28] Carty, A. J. *Adv. Chem. Ser.* **1982**, *No. 196*, 163.

[29] See for example: (a) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229. (b) Pez, G. P.; Grey, R. A.; Corsi, J. *J. Am. Chem. Soc.* **1981**, *103*, 7528. (c) Petersen, J. L.; Stewart, R. P., Jr. *Inorg. Chem.* **1980**, *19*, 186. (d) Meek, D. W.; Kreter, P. *Ibid.* **1983**, *22*, 319. (e) Geoffroy, G. L.; Novotnak, G. C.; Roberts, D. A.; Shulman, P. M.; Steinmetz, G. R. *Organometallics* **1982**, *1*, 1008. (f) Rheingold, A. L.; Mazanec, P.; Meek, D. W. *Inorg. Chem.* **1983**, *22*, 860.

[30] Gorenstein, D. G. *J. Am. Chem. Soc.* **1975**, *97*, 898.

Table VI. Comparison of Fe–Fe Bond Lengths and Fe–P–Fe Angles with $\delta(P(C_6H_5)_2)$ for a Variety of Iron Carbonyl Complexes

complex	Fe–Fe bond, Å	Fe–P–Fe, deg	$\delta(P(C_6H_5)_2)$	ref
$Fe_2(CO)_6[Cl][P(C_6H_5)_2]$	2.5607 (5)	69.8 (0)	142.7	23
$Fe_2(CO)_6[CHC\{N(C_2H_5)_2\}\{C_6H_5\}][P(C_6H_5)_2]$	2.548 (1)	70.1 (0)	153.9	11a
$Fe_2(CO)_6[CHC\{NHC_6H_{11}\text{-}c\}\{C_6H_5\}][P(C_6H_5)_2]$	2.576 (1)	70.5 (0)	154.0	11b
$Fe_2(CO)_6[C\{P(OC_2H_5)_3\}C\{C_6H_5\}][P(C_6H_5)_2]$	2.671 (2)	74.0 (0)	194.5	12a
$Fe_2(CO)_6[CC\{PH(c\text{-}C_6H_{11})_2\}\{C_6H_5\}][P(C_6H_5)_2]$	2.550 (2)	70.7 (1)	123.0	12b
$Fe_2(CO)_6[C_2C_6H_5][P(C_6H_5)_2]$	2.597 (2)	71.64 (7)	148.4	10
$Fe_2(CO)_6[C\{NHC_6H_{11}\text{-}c\}CH\{C_6H_5\}][P(C_6H_5)_2]$	2.628 (1)	72.5 (0)	183.5	11b
$Fe_2(CO)_6[C\{CN(CH_3)CH_2CH_2N(CH_3)\}C\{C_6H_5\}][P(C_6H_5)_2]$	2.644 (2)	73.4 (0)	190.3	13a
$Fe_2Ag(CO)_6[CHC\{NHCH_3\}\{C_6H_5\}][P(C_6H_5)_2]^+ClO_4^-$	2.682 (1)	74.1 (0)	173.4	24
$Fe_2(CO)_6[C\{CNC(CH_3)_3\}C\{C_6H_5\}][P(C_6H_5)_2]$	2.671 (2)	74.1 (0)	194.2	13b
$Fe_2(CO)_6[CCHC\{C_6H_5\}NH\{C_6H_5\}O][P(C_6H_5)_2]$	2.60	71	179.0	20
$Fe_2(CO)_6[CH_2C\{C_6H_5\}NCH_3][P(C_6H_5)_2]$	2.707 (1)	75.6 (0)	198.5	25
$Fe_2(CO)_4[CNC(CH_3)_3]_2[C_2C(CH_3)_3][P(C_6H_5)_2]$	2.5946 (7)	71.5 (0)	145.3	13b
$Fe_2(CO)_6[C_2C(CH_3)_3][P(C_6H_5)_2]$	2.5959 (6)	71.7 (0)	148.3	26
$Fe_2(CO)_6[P(C_6H_5)_2]_2$	2.623 (3)	72.0 (1)	142.8	27
$Fe_2(CO)_5[P(C_6H_5)_3][C_2C_6H_5][P(C_6H_5)_2]$	2.648 (1)	73.1 (0)	153.0	10

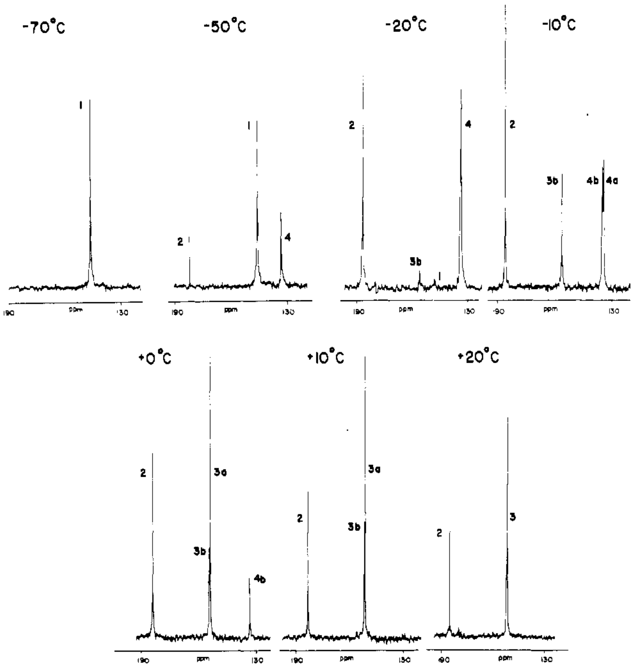


Figure 2. Variable-temperature ^{31}P NMR spectra of the reaction between $Fe_2(CO)_6(C_2C_6H_5)[P(C_6H_5)_2]$ (**1**) and cyclohexylamine. Peaks labeled 2 are due to $Fe_2(CO)_6[C\{NHC_6H_{11}\}CHC_6H_5][P(C_6H_5)_2]$, those labeled 3a and 3b are isomers of $Fe_2(CO)_6[CHC\{NHC_6H_{11}\}(C_6H_5)][P(C_6H_5)_2]$, and 4 is $Fe_2(CO)_6[CC\{NH_2C_6H_{11}\}(C_6H_5)][P(C_6H_5)_2]$. Peaks 4a and 4b are thought to be due to isomeric μ-η^2-enamines (see text).

addition, the simple adduct obtained from **1** and diethylamine at 0 °C was identified as a μ-η^1-vinylidene complex by the similarity of its low-temperature ^{31}P shift (129.4 ppm) to that of $Fe_2(CO)_6[C\{P(C_6H_{11})_2H\}CC_6H_5]P(C_6H_5)_2$ (123.0 ppm).

Variable-Temperature ^{31}P NMR Studies. 1 (R = C_6H_5) and Dipropylamine. ^{31}P NMR spectra over the range −40 to +30 °C are illustrated in Figure 1. Reaction began at $\sim$−35 °C with the conversion of **1** to **4** (R = C_6H_5, $R^1 = R^2 = n\text{-}C_3H_7$). As the temperature increased, **4** reverted to **1** until at +10 °C **3** (R = C_6H_5, $R^1 = (C_3H_7)_2NH$) was formed at the expense of **1**. Reconversion of **4** to **1** and the absence of a second intermediate were confirmed by observing the decomposition of **4** and the subsequent generation of **3** in an IR cell (C_6H_{12}) when acetylide **1** was readily identified. No additional unassigned bands could be detected in this experiment. The conversion of **4** → **1** → **3** was complete at $\sim$+25 °C. Complex **3** was identified by comparison with an authentic sample. Complex **4** ($\delta(^{31}P) = 129$) was identified as a μ-η^1-vinylidene complex by its ^{31}P shift (vide supra). An entirely analogous reaction sequence was apparent for diethylamine.

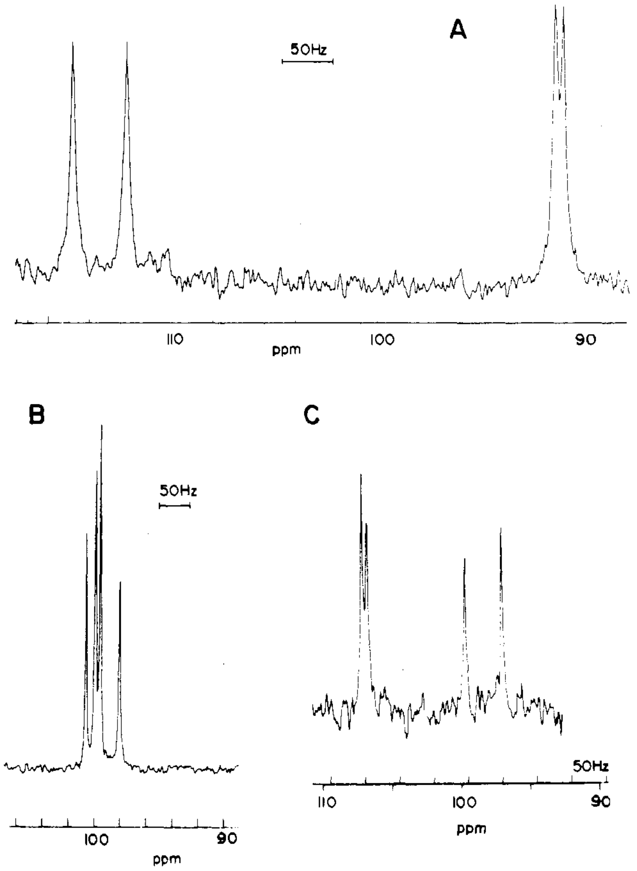
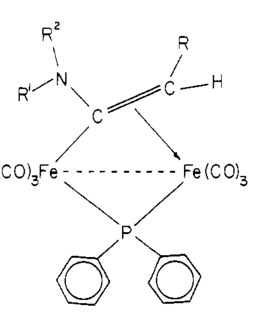


Figure 3. Comparison between the ^{13}C NMR spectra of $Fe_2(CO)_6[C_2C_6H_4Br\text{-}p][P(C_6H_5)_2]$ (A), $Fe_2(CO)_6[C_2C_6H_{11}][P(C_6H_5)_2]$ (B), and $Fe_2(CO)_6[C_2C(CH_3)_3][P(C_6H_5)_2]$ (C) showing resonances due to acetylenic carbon atoms C_α and C_β only.

1 (R = C_6H_5) and Cyclohexylamine. As shown in Figure 2, reaction began at $\sim$−50 °C with the simultaneous formation of **4** (R = C_6H_5, R^1 = H, $R^2 = C_6H_{11}$) and **2** (R = C_6H_5, R^1 = H, $R^2 = C_6H_{11}$). The concentration of these increased at the expense of **1** until at $\sim$−20 °C a new signal appeared (**3b** in Figure 2) at the expense of **4**. As the temperature increased, the signal due to complex **4** resolved, giving signals 4a and 4b. Signal 3b was then formed at the expense of signal 4b and signal 3a at the expense of signal 4a. The latter conversion was considerably more rapid than the former. Complete conversion had occurred by +10 °C, and an average signal 3 of signals 3a and 3b was observed at +30 °C. Signals 3 and 2 were identified as due to $Fe_2(CO)_6[CHC\{NHC_6H_{11}\}Ph]$-

$[P(C_6H_5)_2]$ and $Fe_2(CO)_6[C\{NHC_6H_{11}\}CHPh][P(C_6H_5)_2]$ by comparison of shifts with authentic samples. The ratio of products **3**:**2** on completion of reaction was ca. 3:1. We believe that the appearance of a single signal due to **3** at +30 °C, which is resolved into two separate ^{31}P resonances at lower temperatures, indicates the presence of two isomeric species differing only in the cis or trans orientation of the cyclohexyl group and the adjacent metal atom, across the formal >N=C< bond of the complex. At or above +20 °C interconversion of the two stereoisomers becomes fast on the NMR time scale, resulting in coalescence of the two ^{31}P resonances. The single resonance due to **4** ($\delta = 134$) observable at −50 °C is consistent with a μ-η^1-vinylidene structure analogous to those identified in the case of dipropylamine above. The origin of the two resonances labeled 4a and 4b in Figure 2, their average chemical shift coincident with **4**, is more difficult to establish. In an earlier paper, we drew an analogy between the reactivity of the μ-η^2-acetylide in **1** and a highly activated acetylene such as dimethyl acetylenedicarboxylate.[11b] The latter undergoes rapid reactions with secondary amines, generating enamines.[31] In contrast, the σ,π-acetylides yield not the σ,π-enamines **5** and **6** but their valence isomers, the metallo iminium zwitterions **2** and **3**. We tend to believe that the intermediates 4a and 4b (Figure 2) may well be the two isomeric μ-η^2-enamine complexes **6** and **7**. In support of this, an average $\delta(^{31}P)$ of 134 is midway between the values observed for $Fe_2(CO)_6[\mu$-η^2-$C{\equiv}CPh][P(C_6H_5)_2]$ (+148) and $Fe_2(CO)_6[\mu$-η^1-$C\{PCy_2H\}CPh][P(C_6H_5)_2]$ (+123), as might be expected for **6** or **7**. In contrast to the evidence for μ-η^1vinylidene and μ-η^2-enamine species along the reaction path to **3**, no intermediates were detected in the formation of **2** via nucleophilic attack at the α-carbon atom of **1**, even at temperatures as low as −50 °C. Thus, the generation of the μ-η^2-alkylidene complexes **2** may be a facile one-step process.



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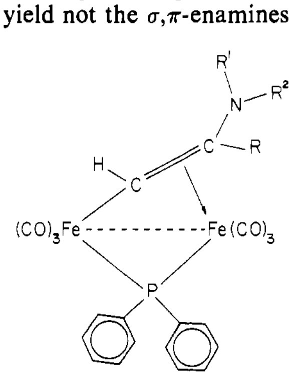

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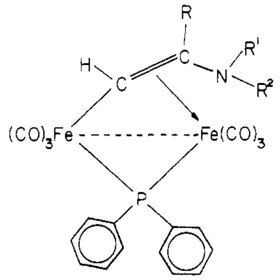

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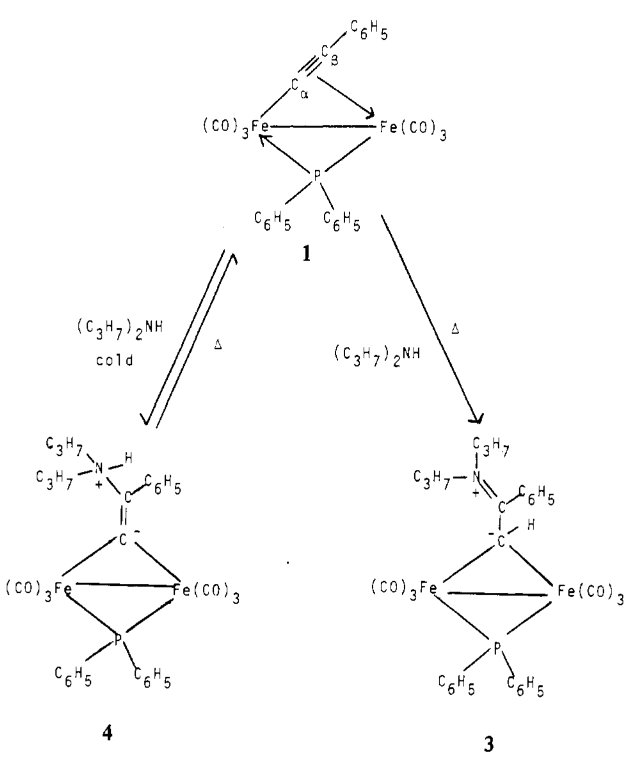
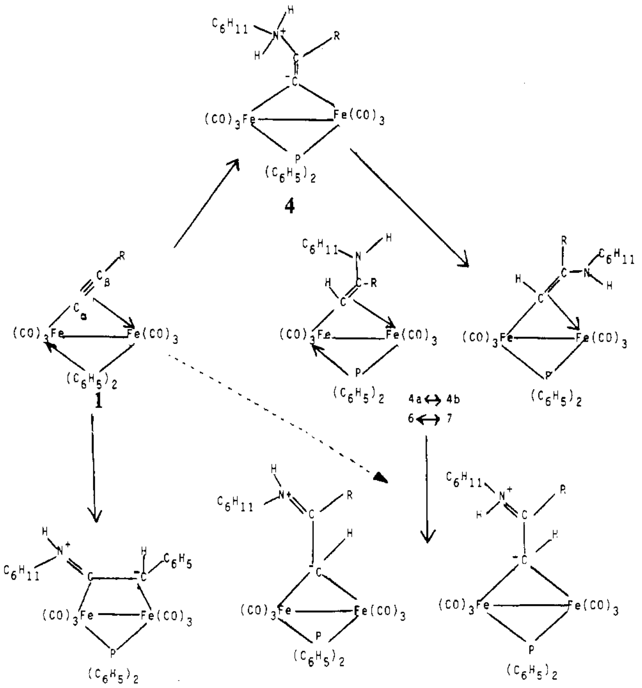
1 (R = C_6H_{11}) and Cyclohexylamine. This reaction was similar to that immediately above, but a higher temperature was needed for initial reaction at the β-carbon atom of **1**.

Scheme I. Suggested Pathways for the Reaction of $Fe_2(CO)_6[C_2C_6H_5][P(C_6H_5)_2]$ (1) with Dipropylamine



Scheme II. Suggested Pathways for the Reaction of $Fe_2(CO)_6[C_2C_6H_5][P(C_6H_5)_2]$ (1) with Cyclohexylamine



None of α-addition product **2** (R = C_6H_{11}, R^1 = H, R^2 = C_6H_{11}) was formed. The ^{31}P resonance at ~135 ppm attributed to the isomeric enamine intermediates was observed *only* as a doublet up to the point of disappearance of these species. At 30 °C twin resonances at ~155 ppm indicated the presence of two isomers of the μ-η^1-alkylidene complex **3** (R = C_6H_{11}, R^1 = H, R^2 = C_6H_{11}).

Reaction Pathways. In the light of the ^{31}P NMR data, appropriate reaction pathways for the reactions of **1** (R = C_6H_5) with dipropylamine and cyclohexylamine are shown in Schemes I and II. Note the following important points: (i)

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(31) (a) Huisgen, R.; Geise, B.; Huber, H. *Tetrahedron Lett.* **1967**, 1883. (b) Huisgen, R.; Herbig, K.; Siegl, A.; Huber, H. *Chem. Ber.* **1966**, *99*, 2526.

Table VII. Products and Differences of the Chemical Shifts $\delta(C_\alpha)$ and $\delta(C_\beta)$ for the Complexes $Fe_2(CO)_6(C_2R)[P(C_6H_5)_2]$

R	$\delta(C_\alpha) + \delta(C_\beta)$	$\delta(C_\alpha) - \delta(C_\beta)$	R	$\delta(C_\alpha) + \delta(C_\beta)$	$\delta(C_\alpha) - \delta(C_\beta)$
$C(CH_3)_3$	205.4	−8.6	C_6H_5	202.5	+18.3
c-C_6H_{11}	199.0	−0.4	*p*-BrC_6H_4	203.8	+22.4
p-$CH_3OC_6H_4$	199.4	+12.8			

below 0 °C the reaction of dipropylamine with **1** ($R = C_6H_5$) involves a simple thermal equilibrium between **1** and **4** ($R = C_6H_5$, $R^1 = R^2 = C_3H_7$). Above 0 °C the amine adds across the triple bond in a single nonreversible step. No complexed enamine intermediate was observed although at 0 °C the lifetime of such a species might be short. There was no direct evidence for direct conversion of **4** to **3** ($R = C_6H_5$, $R^1 = R^2 = C_3H_7$) via a simple proton transfer. Thus, concerted addition of R_2NH across the triple bond seems likely. (ii) In contrast to (i) above, conversion of the 1:1 adduct **4** ($R = C_6H_5$, C_6H_{11}, $R^1 = H$, $R^2 = C_6H_{11}$) seems to involve a simple proton transfer from nitrogen to carbon and subsequent valence isomerization of the enamines. This is confirmed by the absence of **1** ($R = C_6H_5$) as complexes **3** are formed. Furthermore, the concentration of **2** remains constant during the conversion **4** → **3**. The direct conversion of **1** to **3** (implied by the dotted line in Scheme II) at elevated temperatures cannot of course be ruled out since it is unlikely that either **4** or the enamine intermediates would be detectable under these conditions. (iii) There is no isomerization **3** ⇌ **2** under these conditions.

Factors Influencing the Regiospecificity of Amine Additions: ^{31}C NMR Studies. In general, metal hydrocarbon π-complexes are susceptible to nucleophilic attack by neutral group 5 nucleophiles only when the complex carries a positive charge.[32] Exceptions to this rule are certain platinum(II) olefin complexes that are attacked by amines, generating organometallic zwitterions.[33] Clearly, μ-η^2-coordination of an acetylide as in **1** renders the unsaturated ligand unusually electrophilic. Indeed, the chemistry of the μ-η^2-acetylide rather closely resembles that of electrophilic, coordinated carbenes.[34] To examine the influence of electronic effects on acetylide reactivity, in particular the regiospecificity of nucleophilic additions, we measured the ^{13}C NMR spectra of the parent molecules **1** ($R = C_6H_5$, *p*-BrC_6H_4, *p*-$MeOC_6H_4$, C_6H_{11}, $C(CH_3)_3$). Typical spectra in the acetylenic carbon region are shown in Figure 3; complete data are in supplementary Table S3. In each case C_α and C_β appear as doublets due to coupling to ^{31}P. We assign the resonance with the largest J_{P-C} value (~53 Hz) to C_α and the other doublet to C_β (J_{P-C} = ~8 Hz). The C_α shifts lie between 98.4 and 113.1 ppm downfield of Me_4Si. These shifts are at considerably higher field than the carbene carbon resonances in carbene complexes (200–350 ppm).[35] Note the fact that the C_α resonance is at high field for $R = C(CH_3)_3$, almost coincidental with C_β for R = c-C_6H_{11}, and downfield of C_β in the case of R = *p*-BrC_6H_4. These variations in shift are indicative of changes in polarization of the triple bond. If it is assumed, as others have done,[36] that a change in $\delta(^{13}C)$ is mainly associated with a change in charge on the carbon atom, then $\delta(C_\alpha) + \delta(C_\beta)$ gives an idea of total charge change in the triple bond while $\delta(C_\alpha) - \delta(C_\beta)$ is a measure of polarization in the bond. Table VII contains sums and differences of shifts for the acetylides. For these complexes $\delta(C_\alpha) + \delta(C_\beta)$ is relatively constant for all R groups. Values of $\delta(C_\alpha) - \delta(C_\beta)$ however suggest a marked change in polarization within the triple bond as R is changed from $C(CH_3)_3$ to *p*-BrC_6H_4. In the phenyl and *p*-bromophenyl compounds the acetylidic triple bond is more polarized, with the greater positive charge on C_α; for the *p*-methoxyphenyl and particularly the *tert*-butyl compounds the polarity of the triple bond is in the opposite sense. The values of $\delta(^{13}C)$ confirm that both carbon atoms are electrophilic. To test whether the changes in acetylide polarization were reflected in reactivity patterns, the ratios of α- to β-addition products were measured under equilibrium conditions for several amines with **1** ($R = C_6H_5$, *p*-BrC_6H_5, *p*-$MeOC_6H_5$) (Table III). In the case of isopropylamine the ratio of products formed by addition to the β- and α-carbon atoms changed from 21:1 for R = *p*-$CH_3OC_6H_4$ to only 1.5:1 for the more electron-withdrawing *p*-BrC_6H_4 group. In the latter case the electrophilicity of C_α is increased by the electron-withdrawing *p*-BrC_6H_4 group.[37] The ^{13}C NMR studies also suggest that for R = *t*-Bu, polarization in the triple bond places greater positive charge on C_β. Simplistically, nucleophilic attack at C_β might be favored. In practice, phosphines,[12b] phosphites,[12a] amines,[11] and isocyanides[13b] fail to add to **1** ($R = C(CH_3)_3$), in marked contrast to the facile reactions of **1** ($R = C_6H_5$). We attribute this to the fact that C_α is less electrophilic than for $R = C_6H_5$ and addition at C_β, while electronically favored, is hindered by the steric bulk of the *tert*-butyl group.[38]

The regiospecificity of nucleophilic attack also shows a dependence on the incoming nucleophile and may reflect a subtle balance of steric and electronic effects. Thus for **1** ($R = C_6H_5$), primary amines generally produce *both* addition products. Exceptions are aniline and *tert*-butylamine, when only complexes **3** are formed. Secondary amines add solely to the β-carbon atom, giving **3**, while tertiary amines do not react at all. Table III shows that there are small differences in product ratios between straight-chain (e.g., $C_4H_9NH_2$) and branched-chain (e.g., $(CH_3)_2CHNH_2$ and $(C_2H_5)(CH_3)CHNH_2$) primary amines with the bulkier nucleophile favoring β-attack. This probably reflects the fact that in **2** there may be an unfavorable steric interaction between the $Fe(CO)_3$ group and an amine substituent cis to the metal attached to the >N═C< bond. Even when C_α is made more electrophilic (**1**, R = *p*-BrC_6H_4), *tert*-butylamine will not add to C_α. The slightly larger steric bulk of the secondary amines may also account for the preference for C_β attack. Clearly however there is a steric limit; diisopropylamine and dicyclohexylamine do not react with **1** even under forcing conditions.

The effectiveness of amines as nucleophiles is notoriously difficult to assess as base strengths and solvation both influence nucleophilicity. It is notable that the inductive effect of alkyl groups increases in the series $C_4H_9 < CH(CH_3)_2 \approx CH(CH_3)(C_2H_5) < C(CH_3)_3$, a fact reflected in the ratios of **3**:**2** (Table III) although the overall range of values is not large.

Finally, it is worth noting that the products **2** and **3** contain highly dipolar organic ligands, with the center of positive charge on nitrogen and the negative charge, formally on carbon, but delocalized somewhat into the binuclear framework. Herrmann[39] has recently suggested that in certain μ-methylene compounds the bridging carbon carries an excess of electron density. By comparison the substituted μ-methylenes of type **3** must be exceedingly electron rich. This is borne out by the susceptibility of these dipolar compounds to elec-

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(32) See for example: (a) John, G. R. Kane-Maguire, L. A. P. *J. Organomet. Chem.* **1976**, *120*, C45. (b) Salzer, A. *Inorg. Chim. Acta* **1976**, *18*, L31. (c) Hackett, P.; Jaouen, G. *Ibid.* **1975**, *12*, L19.

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(38) A complete single-crystal X-ray study of **1** ($R = C(CH_3)_3$ shows the expected steric hindrance around C_β as a result of the *tert*-butyl substituent. See ref 9 and 26.

(39) Herrmann, W. A.; Plank, J.; Ziegler, M. L.; Weidenhammer, K.; Guggoltz, E.; Balbach, B. *J. Am. Chem. Soc.* **1980**, *103*, 63.

trophilic attack by both protons[25] and metal electrophiles.[24] These reactions are the subject of a forthcoming publication.

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Registry No. $Fe_2(CO)_6[C\{NHCH_3\}CH\{C_6H_5\}][P(C_6H_5)_2]$, 73970-08-8; $Fe_2(CO)_6[CHC\{NHCH_3\}\{C_6H_5\}][P(C_6H_5)_2]$, 70657-55-5; $Fe_2(CO)_6[C\{NHC_2H_5\}CH\{C_6H_5\}][P(C_6H_5)_2]$, 73979-53-0; $Fe_2(CO)_6[CHC\{NHC_2H_5\}\{C_6H_5\}][P(C_6H_5)_2]$, 70657-57-7; $Fe_2(CO)_6[CHC\{NHC_2H_5\}\{c\text{-}C_6H_{11}\}][P(C_6H_5)_2]$, 86196-56-7; $Fe_2(CO)_6[C\{NHC_4H_9\}CH\{C_6H_5\}][P(C_6H_5)_2]$, 82647-72-1; $Fe_2(CO)_6[CHC\{NHC_4H_9\}\{C_6H_5\}][P(C_6H_5)_2]$, 82647-70-9; $Fe_2(CO)_6[C\{NHC_4H_9\}CH\{C_6H_4Br\text{-}o\}][P(C_6H_5)_2]$, 82647-76-5; $Fe_2(CO)_6[CHC\{NHC_4H_9\}\{C_6H_4Br\text{-}p\}][P(C_6H_5)_2]$, 82647-74-3; $Fe_2(CO)_6[C\{NHC_4H_9\}CH\{C_6H_4OCH_3\text{-}p\}][P(C_6H_5)_2]$, 82647-68-5; $Fe_2(CO)_6[CHC\{NHC_4H_9\}\{C_6H_4OCH_3\text{-}p\}][P(C_6H_5)_2]$, 82647-66-3; $Fe_2(CO)_6[CHC\{NHC_6H_5\}\{C_6H_5\}][P(C_6H_5)_2]$, 86196-57-8; $Fe_2(CO)_6[CHC\{NHC_6H_5\}\{c\text{-}C_6H_{11}\}][P(C_6H_5)_2]$, 86196-58-9; $Fe_2(CO)_6[C\{NHCH_2CH_2NH_2\}CH\{C_6H_5\}][P(C_6H_5)_2]$, 86196-59-0; $Fe_2(CO)_6[CHC\{NHCH_2CH_2NH_2\}\{C_6H_5\}][P(C_6H_5)_2]$, 86217-11-0; $Fe_2(CO)_6[C\{NHCH_2CH_2N(CH_3)_2\}CH\{C_6H_5\}][P(C_6H_5)_2]$, 86196-60-3; $Fe_2(CO)_6[CHC\{NHCH_2CH_2N(CH_3)_2\}\{C_6H_5\}][P(C_6H_5)_2]$, 86196-61-4; $Fe_2(CO)_6[C\{NHC_6H_{11}\text{-}c\}CH\{C_6H_5\}][P(C_6H_5)_2]$, 67168-86-9; $Fe_2(CO)_6[CHC\{NHC_6H_{11}\text{-}c\}\{C_6H_5\}][P(C_6H_5)_2]$, 67168-85-8; $Fe_2(CO)_6[C\{NHC_6H_{11}\text{-}c\}CH\{C_6H_4Br\text{-}p\}][P(C_6H_5)_2]$, 86196-62-5; $Fe_2(CO)_6[CHC\{NHC_6H_{11}\text{-}c\}\{C_6H_4Br\text{-}p\}][P(C_6H_5)_2]$, 86196-63-6; $Fe_2(CO)_6[CHC\{NHC_6H_{11}\text{-}c\}\{c\text{-}C_6H_{11}\}][P(C_6H_5)_2]$, 86196-64-7; $Fe_2(CO)_6[C\{NHCH(CH_3)_2\}CH\{C_6H_5\}][P(C_6H_5)_2]$, 82647-71-0; $Fe_2(CO)_6[CHC\{NHCH(CH_3)_2\}\{C_6H_5\}][P(C_6H_5)_2]$, 82647-69-6; $Fe_2(CO)_6[C\{NHCH(CH_3)_2\}CH\{C_6H_4OCH_3\text{-}p\}][P(C_6H_5)_2]$, 82647-67-4; $Fe_2(CO)_6[CHC\{NHCH(CH_3)_2\}\{C_6H_4OCH_3\text{-}p\}][P(C_6H_5)_2]$, 82647-65-2; $Fe_2(CO)_6[C\{NHCH(CH_3)_2\}CH\{C_6H_4Br\text{-}p\}][P(C_6H_5)_2]$, 82647-75-4; $Fe_2(CO)_6[CHC\{NHCH(CH_3)_2\}\{C_6H_4Br\text{-}p\}][P(C_6H_5)_2]$, 82647-73-2; $Fe_2(CO)_6[CHC\{NHCH(CH_3)_2\}\{c\text{-}C_6H_{11}\}][P(C_6H_5)_2]$, 86196-65-8; $Fe_2(CO)_6[C\{NHCH(CH_3)(C_2H_5)\}CH\{C_6H_5\}][P(C_6H_5)_2]$, 86196-66-9; $Fe_2(CO)_6[CHC\{NHCH(CH_3)(C_2H_5)\}\{C_6H_5\}][P(C_6H_5)_2]$, 86196-67-0; $Fe_2(CO)_6[CHC\{NHC(CH_3)_3\}\{C_6H_5\}][P(C_6H_5)_2]$, 86196-68-1; $Fe_2(CO)_6[CHC\{NHC(CH_3)_3\}\{C_6H_4Br\text{-}p\}][P(C_6H_5)_2]$, 86196-69-2; $Fe_2(CO)_6[CC\{NH(CH_3)_2\}\{C_6H_5\}][P(C_6H_5)_2]$, 86196-70-5; $Fe_2(CO)_6[CC\{NH(C_2H_5)_2\}\{C_6H_5\}][P(C_6H_5)_2]$, 86196-71-6; $Fe_2(CO)_6[CC\{NH(C_2H_5)_2\}\{C_6H_4OCH_3\text{-}p\}][P(C_6H_5)_2]$, 86196-72-7; $Fe_2(CO)_6[CHC\{N(CH_3)_2\}\{C_6H_5\}][P(C_6H_5)_2]$, 86196-73-8; $Fe_2(CO)_6[CHC\{N(C_2H_5)_2\}\{C_6H_5\}][P(C_6H_5)_2]$, 59584-64-4; $Fe_2(CO)_6[CHC\{N(C_2H_5)_2\}\{C_6H_4Br\text{-}p\}][P(C_6H_5)_2]$, 86196-74-9; $Fe_2(CO)_6[CHC\{N(C_2H_5)_2\}\{C_6H_4OCH_3\text{-}p\}][P(C_6H_5)_2]$, 86196-75-0; $Fe_2(CO)_6[CHC\{N(C_2H_5)_2\}\{c\text{-}C_6H_{11}\}][P(C_6H_5)_2]$, 59584-65-5; $Fe_2(CO)_6[CHC\{N(C_3H_7)_2\}\{C_6H_5\}][P(C_6H_5)_2]$, 70657-56-6; $Fe_2(CO)_6[CHC\{\overline{NCH_2(CH_2)_3C}H_2\}\{C_6H_5\}][P(C_6H_5)_2]$, 70657-58-8; $Fe_2(CO)_6[CHC\{\overline{NCH_2CH_2OCH_2C}H_2\}\{C_6H_5\}][P(C_6H_5)_2]$, 86196-76-1; $Fe_2(CO)_6[CC\{NH(C_2H_5)_2\}\{C_6H_{11}\text{-}c\}][P(C_6H_5)_2]$, 86196-77-2; $Fe_2(CO)_6[CC\{C(CH_3)_3\}][P(C_6H_5)_2]$, 59584-68-8; $Fe_2(CO)_6[CC\{C_6H_{11}\text{-}c\}][P(C_6H_5)_2]$, 59584-69-9; $Fe_2(CO)_6[CC\{C_6H_4OCH_3\text{-}p\}][P(C_6H_5)_2]$, 86196-78-3; $Fe_2(CO)_6[CC\{C_6H_5\}][P(C_6H_5)_2]$, 52970-25-9; $Fe_2(CO)_6[CC\{C_6H_4Br\text{-}p\}][P(C_6H_5)_2]$, 86196-79-4; *p*-$BrC_6H_4C_2[P(C_6H_5)_2]$, 86196-80-7; *p*-$MeOC_6H_4C_2[P(C_6H_5)_2]$, 86196-81-8; $Fe_2(CO)_5[P\{\overline{NCH_2(CH_2)_3C}H_2\}\{C_6H_5\}_2\}](C_2C(CH_3)_3)[P(C_6H_5)_2]$, 86196-82-9; Fe, 7439-89-6; chlorodiphenylphosphine, 1079-66-9; *p*-bromophenylacetylene, 766-96-1; *p*-methoxyphenylacetylene, 768-60-5.

Supplementary Material Available: Tables S1–S3, showing IR stretching frequencies for the complexes $Fe_2(CO)_6[C\{NHR^1\}CHR][P(C_6H_5)_2]$, $Fe_2(CO)_6[CHC\{NHR^1\}R][P(C_6H_5)_2]$, $Fe_2(CO)_6[CC\{NH(R^1)_2\}R][P(C_6H_5)_2]$, $Fe_2(CO)_6[CHC\{N(R^1)_2\}R][P(C_6H_5)_2]$, and $Fe_2(CO)_6[CHC\{\overline{NR}^1\}R][P(C_6H_5)_2]$, and Tables S4–S6, showing ^1H and ^{31}P NMR data and Mössbauer parameters for the complexes $Fe_2(CO)_6[C(NHR^1)CHR][P(C_6H_5)_2]$, $Fe_2(CO)_6[CHC\{NHR^1\}R][P(C_6H_5)_2]$, $Fe_2(CO)_6[CC\{NH(R^1)_2\}R][P(C_6H_5)_2]$, $Fe_2(CO)_6[CHC\{N(R^1)_2\}R][P(C_6H_5)_2]$ and $Fe_2(CO)_6[CHC\{\overline{\underline{NR}}^1\}R][P(C_6H_5)_2]$ (10 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, Absolute Configuration, and Magnetic Studies of Some Copper(II) Complexes of Chiral Bidentate and Tridentate Fluorinated Aminoalkoxy Ligands[1]

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Template condensation of 5,5,5-trifluoro-4-(trifluoromethyl)-4-hydroxy-2-pentanone, $CH_3COCH_2C(CF_3)_2OH$, with primary amines RNH_2 in the presence of Cu^{2+} leads to Cu^{2+} complexes of bidentate iminoalkoxy ligands. Hydrogenation of these gives the amino alcohols, $RNHCH(CH_3)CH_2C(CF_3)_2OH$, in which a new chiral center is present; these also act as bidentate ligands toward Cu^{2+}, giving stable, neutral complexes. A complete structural determination for the latter with R = menthyl has been carried out. The complex, of molecular formula $C_{32}H_{52}CuF_{12}N_2O_2$, crystallizes in the orthorhombic space group $P2_12_12_1$ with four formula units per unit cell. The unit cell dimensions are $a = 16.225$ (5) Å, $b = 18.021$ (5) Å, and $c = 13.248$ (5) Å. Knowledge of the absolute configuration of the chiral substituent enables that of the new center in the ring to be assigned. Through the use of CD spectra, assignments of configuration are then made to complexes where other R groups are present. Tridentate iminoalkoxy ligands are formed by similar template condensation reactions using chiral-substituted amino alcohols, $NH_2CH(R')CH_2OH$. Hydrogenation of their Cu^{2+} complexes leads to amino diols, $HOCH_2CH(R')NHCH(CH_3)C(CF_3)_2OH$, where two chiral centers are now present. By formation of Cu^{2+} complexes and comparison of CD spectra with those of bidentate ligands, assignments of absolute configuration are made. The amino diol Cu^{2+} complexes are dinuclear, and magnetic studies show antiferromagnetic interactions between Cu^{2+} ions; the degree of interaction is related to the bulk of the substituent R′ group.

Introduction

The correlation between magnetic properties and structural parameters in multinuclear copper(II) complexes has received considerable attention recently. Apart from the intrinsic interest of the magnetic exchange interaction, such complexes may serve as models for the copper(II) sites ("type III blue copper") in biological systems.

Previous work here[3-5] has shown that template condensation of 5,5,5-trifluoro-4-(trifluoromethyl)-4-hydroxy-2-pentanone

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