pentadienyl-substituted organogermylenes represent a promising class of compounds in the chemistry of low-valent germanium.

Experimental Section

All reactions and preparations were performed in an atmosphere of dried, oxygen-free argon by using Schlenk-type flasks. Solvents and reagents were appropriately dried and purified.

Melting points were determined with a Büchi 510 capillary melting point apparatus. ^{1}H NMR spectra were recorded on a Bruker AM 300 (300-MHz) spectrometer; ^{13}C NMR spectra (75-MHz, ^{1}H-decoupled) were also recorded on the Bruker AM 300 spectrometer. Mass spectra were obtained from a Varian 311 A spectrometer (70 eV, 300-μA emission); only characteristic fragments are listed. Elemental analyses were carried out by "Mikroanalytisches Laboratorium Beller" (Göttingen, Germany). (Pentamethylcyclopentadienyl)germanium chloride (1),[7] (tris(trimethylsilyl)methyl)lithium,[16] and (2,4,6-tri-*tert*-butylphenyl)lithium[17] were prepared as previously described.

(Pentamethylcyclopentadienyl)(tris(trimethylsilyl)methyl)germylene (3). A solution of (tris(trimethylsilyl)methyl)lithium-2-tetrahydrofuran (54.3 mL, 10.25 mmol) in diethyl ether was added to a solution of Me_5C_5GeCl (1) (2.50 g, 10.25 mmol) in 75 mL of toluene at −80 °C. The solution, which turned immediately orange-red, was allowed to warm up to room temperature within 5 h. After evaporation of the solvent in vacuo, the red residue was extracted with hexane. Concentrating the solution and cooling to −55 °C yielded 2.79 g (62%) of red-orange crystals: mp 87 °C; ^{1}H NMR (C_6D_6) δ 1.95 (s, 15 H), 0.36 (s, 27 H); ^{13}C NMR (C_6D_6) δ 120, 43 (Me_5C_5), 10.97 (Me_5C_5), 6.31 (Me_5Si); MS (m/z (relative intensity)) 305 ($[Me_3Si]_3CGe^+$, 4), 209 ($Me_5C_5Ge^+$, 100), 73 (Me_3Si^+, 33). Anal. Calcd for $C_{20}H_{42}Si_3Ge$ (Mn = 439.40): C, 54.67; H, 9.64. Found: C, 55.60; H, 9.79.

(Pentamethylcyclopentadienyl)(2,4,6-tri-*tert*-butylphenyl)germylene (4). A solution of 1 (7.31 g, 30.10 mmol) in 100 mL of toluene was added to freshly prepared (2,4,6-tri-*tert*-butylphenyl)lithium (7.58 g, 30.10 mmol) in 200 mL of THF/hexane (10:1) within 2 h at −80 °C. The reaction mixture was allowed to warm to room temperature very slowly, giving a orange-red suspension. Evaporation of the solvents and extraction of the residue with hexane (60 mL) were followed by concentrating the solution. Cooling to −25 °C yielded 8.07 g (59%) of orange crystals: mp 103 °C; ^{1}H NMR (C_6D_6) δ 7.43 (s, 2 H, $C_6\mathit{H}_2{}^t\mathrm{Bu}_3$), 1.76 (s, 15 H, Me_5C_5), 1.50 (s, 18 H, 2,6-^{t}Bu), 1.35 (s, 9 H, 4-^{t}Bu); ^{13}C NMR ($CDCl_3$) δ 164.70, 156.01, 148.35, 120.89, (4 s, $\mathit{C}_6H_2{}^t\mathrm{Bu}_3$), 120.78 (s, $Me_5\mathit{C}_5$), 40.38, 34.54 (2 s, $\mathit{C}Me_3$), 34.92, 31.38 (2 s, $C\mathit{Me}_3$), 11.00 (s, Me_5C_5); MS (m/z (relative intensity)) 319 ($M^+ - Me_5C_5$, 2), 245 ($C_6H_2{}^tBu_3{}^+$, 6), 231 ($C_6H_2{}^tBu_3 - Me^+$, 100), 209 ($Me_5C_5Ge^+$, 24), 57 (Me_3C^+, 53). Anal. Calcd for $C_{28}H_{44}Ge$ (Mr = 453.25): C, 74.20; H, 9.78. Found: C, 74.13; H, 9.85.

Registry No. 1, 85085-98-9; **3**, 136630-26-7; **4**, 136630-27-8; (tris(trimethylsilyl)methyl)lithium, 28830-22-0; (2,4,6-tri-*tert*-butylphenyl)lithium, 35383-91-6.

Supplementary Material Available: Listings of crystal data and structure determination and refinement details, atomic coordinates and isotropic thermal parameters, bond lengths and angles, and anisotropic thermal parameters for compounds 3 and 4 (9 pages); listings of observed and calculated structure factors (28 pages). Ordering information is given on any current masthead page.

Bis(acetylide) Complexes of Iron

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Received April 29, 1991

The synthesis and spectroscopic characterization of six bis(acetylido)(phosphino)iron(II) complexes is reported. NMR spectroscopy has been used to determine the geometry of the compounds to be trans with respect to the acetylide ligands. The crystal structures of three iron bis(acetylides) are reported. Crystals of $Fe(C{\equiv}CCH_3)_2(DMPE)_2$ (**3a**) are tetragonal, space group $P\bar{4}n2$, with a = 9.1599 (5) Å, c = 14.234 (2) Å, Z = 2, and R = 0.040 (877 F). Crystals of $Fe(C{\equiv}CPh)_2(DEPE)_2$ (**4b**) are monoclinic, space group $P2_1/c$, with a = 9.783 (2) Å, b = 10.675 (2) Å, c = 17.855 (3) Å, β = 94.35 (2)°, Z = 2, and R = 0.040 (2195 F). Crystals of $Fe(C{\equiv}CC_6H_4C{\equiv}CH)_2(DMPE)_2$ (**5a**) are monoclinic, space group $C2/c$, a = 22.017 (5) Å, b = 12.366 (2) Å, c = 16.952 (4) Å, β = 135.16 (2)°, Z = 4, and R = 0.034 (2026 F).

Introduction

Transition-metal σ-acetylide complexes have been formed by a variety of different methods, including displacement of existing ligands by acetylides,[1] by oxidative addition of a coordinatively unsaturated metal center to a terminal acetylene,[2] or by deprotonation of vinylidene species.[3] More recently, successful synthesis of the bond between a metal and an sp-hybridized carbon has been achieved by displacement of a neutral diatomic ligand (dihydrogen or dinitrogen) by an acetylide anion.[4]

Iron(II) dihydrides of the type $FeH_2(PP)_2$ (PP = $R_2PCH_2CH_2PR_2$; R = CH_3 (**1a**), $-CH_2CH_3$ (**1b**)) are protonated by weak acids to form a cationic complex containing an η^2-bound molecule of dihydrogen, $[FeH(H_2)$-

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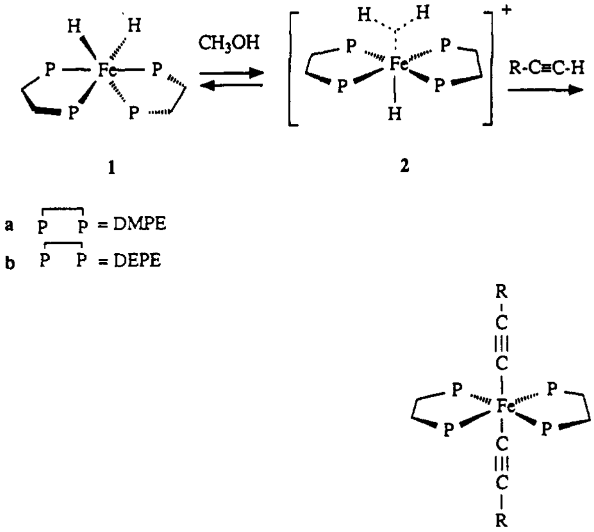
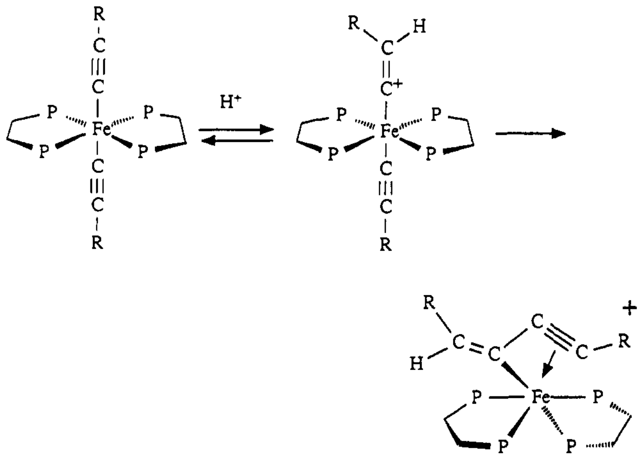
Scheme I



3 R = CH_3-
4 R = C_6H_5-
5 R = 4-(HC≡C)-C_6H_4-
6 R = 3,5-$(HC{\equiv}C)_2C_6H_3$-
7 R = $(CH_3)_3C$-

Scheme II



$(PP)_2]^+$ (2).[5] In these complexes, molecular hydrogen is only weakly coordinated and may be displaced by a variety of neutral ligands (e.g. dinitrogen, nitriles, tertiary phosphines, or ethylene)[6] or anions (e.g. halides, thiolates, cyanide, or acetylides).[7] If the conjugate base (B^-) of the protonating acid (B–H) is itself a good ligand, protonation followed by H_2 displacement results effectively in the substitution of a hydride ligand by B^- (Scheme I).

Terminal acetylenes are sufficiently acidic to protonate $FeH_2(DMPE)_2$ (**1a**; DMPE = 1,2-bis(dimethylphosphino)ethane) to form the molecular hydrogen complex **2a**, which reacts rapidly to give an (acetylido)metal hydride complex and eventually the metal bis(acetylide) complex. In a previous communication[4] we reported the facile formation of $Fe(C{\equiv}CPh)_2(DMPE)_2$ (**4a**) using this method. We report here the synthesis and characterization of a selection of iron bis(acetylide) phosphine complexes together with the X-ray crystal structures of the bis(acetylide) complexes $Fe(C{\equiv}CCH_3)_2(DMPE)_2$ (**3a**) and $Fe(C{\equiv}CC_6H_4C{\equiv}CH)_2(DMPE)_2$ (**5a**) derived from reaction of propyne and 1,4-diethynylbenzene (respectively) with $FeH_2(DMPE)_2$ (**1a**) and of the bis(acetylide) complex $Fe(C{\equiv}CPh)_2(DEPE)_2$ (**4b**; DEPE = 1,2-bis(diethylphosphino)ethane), derived from reaction of phenylacetylene and $FeH_2(DEPE)_2$ (**1b**).

Results and Discussion

Reaction of $FeH_2(DMPE)_2$ with Terminal Acetylenes. The iron dihydride complex **1a** is almost completely protonated in protic solvents such as methanol to form the molecular hydrogen complex **2a**. The reaction between $FeH_2(DMPE)_2$ (**1a**) and excess phenylacetylene in methanol is rapid and cleanly gives quantitative conversion of the molecular hydrogen complex to the *trans*-bis(phenylacetylide) complex **4a**. In methanol solvent, the bis(acetylide) **4a** crystallizes directly from the reaction mixture over the space of a few minutes following the addition of phenylacetylene. In an exactly analogous sequence, **1a** reacts with the di- and trifunctional arylacetylenes 1,4-diethynylbenzene[8] and 1,3,5-triethynylbenzene[9] in methanol solution to give the corresponding iron bis(acetylides) **5a** and **6a**. In aprotic solvents a mixture of acetylide hydride and bis(acetylide) complexes are formed in solution; however, in methanol solvent, the bis(acetylides) precipitate cleanly.

tert-Butylacetylene reacts with $[FeH(H_2)(DMPE)_2]^+$ (**2a**), generated from **1a**, to produce the corresponding *trans*-bis(acetylide) complex $Fe(C{\equiv}CC(CH_3)_3)_2(DMPE)_2$ (**7a**) as a pale yellow crystalline solid. In a similar fashion, treatment of **1a** with a solution of propyne and sodium methoxide in methanol forms $Fe(C{\equiv}CCH_3)_2(DMPE)_2$ (**3a**).

All of the *trans*-bis(acetylido)iron complexes were obtained as yellow solids that were essentially insoluble in methanol, slightly soluble in benzene, and soluble in THF and dichloromethane. The complexes are moderately air stable and may be kept indefinitely as dry solids under an argon atmosphere. The bis(acetylide) complexes are acid sensitive and are protonated even by weak acids to form vinylidene complexes[3] which rearrange slowly to the red cationic complexes **8** containing an η^3-bound 1,4-disubstituted but-1-en-3-yn-2-yl ligand (Scheme II).[10] The bis(methylacetylide) complex was significantly more acid sensitive than the bis(arylacetylide) complexes, and unless the synthesis was performed in the presence of a base such as methoxide, **3a** rearranged spontaneously in the methanol solvent to **8a**.

Hydrogenation. The reaction of $FeH_2(DMPE)_2$ (**1a**) with a terminal acetylene to form a bis(acetylide) complex, $Fe(C{\equiv}CR)_2(DMPE)_2$, results formally in the liberation of 2 equiv of dihydrogen. Alkenes are formed as byproducts of the reaction, and careful analysis of the products formed

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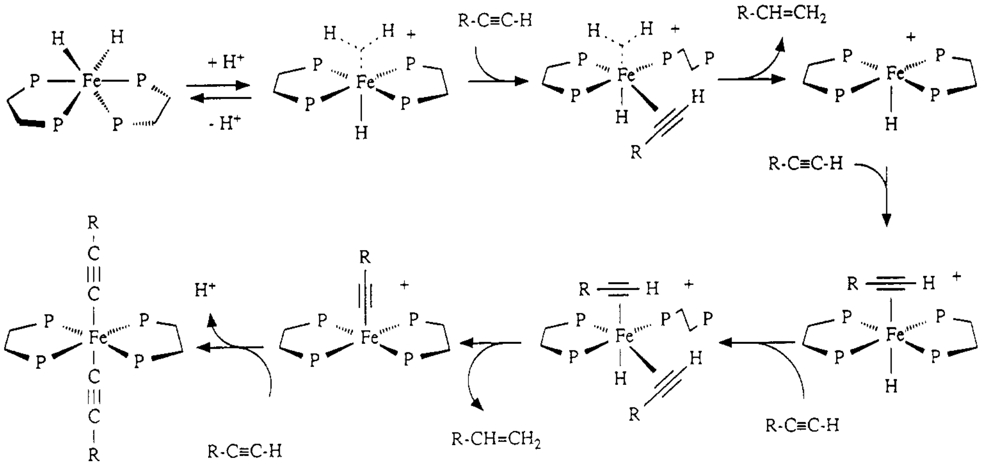
(10) A full study of η^3-butenynyl complexes will be reported elsewhere.

Scheme III



when phenylacetylene reacted with **1a** indicated that 2 equiv of styrene was formed in the reaction sequence. This suggests the iron complex of molecular hydrogen (**2a**) may also serve as a hydrogenation agent. Metal hydride complexes have been shown to undergo insertion of a carbon–carbon triple bond into the metal–hydride bond to form a vinyl complex when a stoichiometric amount of alkyne is employed,[11] while in the presence of an excess of the alkyne, elimination of the corresponding alkene results[12] and a metal acetylide is the isolated end product.[13] Under an atmosphere of hydrogen, the hydrogenation is catalytic in the case of $OsHCl(\eta^2\text{-}H_2)CO(PR_3)_2$, though vinylosmium compounds have also been isolated.[14] In the absence of an excess of the alkyne, hydrogenation of the alkenyl complex to form an alkane is observed.[12,14] Reaction of the iron complex $FeH(\eta^2\text{-}H_2)(P(CH_2CH_2PPh_2)_3$ with phenylacetylene is reported to give a five-coordinate acetylide complex, $Fe(C{\equiv}CPh)(P(CH_2CH_2PPh_2)_3)$, and 1 equiv of styrene with no σ-alkenyl complex being detected.[15]

A possible route to hydrogenation of the alkynes is illustrated in Scheme III and involves partial loss of one bisphosphine ligand, allowing the coordination of the acetylene, hydrogenative rearrangement, and loss of an alkene to form a five-coordinate cationic intermediate, $FeH(DMPE)_2^+$. Reversible loss of a ligand to allow coordination of an acetylene prior to hydrogenation has been proposed as a mechanism for alkyne reduction by an analogous ruthenium complex.[13] The coordinatively unsaturated intermediate reacts with 2 equiv of the alkyne, and elimination of a second equivalent of alkene forms the intermediate $Fe(C{\equiv}CR)(DMPE)_2^+$, which may react with acetylide in solution to yield the observed bis(acetylido)iron complex.

In order to maximize the yield of bis(acetylido)iron complex, an excess of terminal acetylene was employed in the syntheses. In the reaction of **1a** with 2 equiv of 1,4-diethynylbenzene, the partially reduced complex $Fe(C{\equiv}CC_6H_4C{\equiv}CH)(C{\equiv}CC_6H_4CH{=}CH_2)(DMPE)_2$ was isolated as one of the products.

Table I. Crystal Data for 3a, 4b, and 5a

	3a	**4b**	**5a**
space group	$P\bar{4}n2$	$P2_1/c$	$C2/c$
a, Å	9.1599 (5)	9.783 (2)	22.017 (5)
b, Å		10.675 (2)	12.366 (2)
c, Å	14.234 (2)	17.855 (3)	16.952 (4)
β, deg		94.35 (2)	135.16 (2)
V, $Å^3$	1194.3 (2)	1859.3 (5)	3254.8 (9)
fw	434.25	670.59	606.42
D_{calcd}, g cm^{-3}	1.207	1.198	1.238
empirical formula	$C_{18}H_{38}FeP_4$	$C_{36}H_{58}FeP_4$	$C_{32}H_{42}FeP_4$
Z	2	2	4
abs coeff, cm^{-1}	8.56	5.59	6.38
transmissn coeffs	0.840–0.695	0.825–0.701	0.888–0.804
temp, °C		21	
λ, Å		0.71069	
$R(F_o)$	0.040	0.040	0.034
R_w	0.046	0.047	0.040
2θ range, deg	1.0–50.0	1.0–50.0	1.0–50.0
no. of rflns measd	1235	3315	3103

Table II. Positional Parameters (×10^4) for $Fe(C{\equiv}CCH_3)_2(DMPE)_2$ (3a)

	x	y	z
Fe(1)	0	4999 (1)	2500
P(1)	8869 (4)	3824 (3)	1382 (1)
C(1)	11082 (4)	-1081 (4)	2500
C(2)	-3037 (6)	13038 (6)	2500
C(3)	-4816 (6)	14817 (6)	2500
C(4)	8881 (22)	1918 (13)	1299 (17)
C(5)	6860 (15)	4189 (15)	1132 (14)
C(6)	9259 (21)	4530 (26)	291 (4)

Crystallography and Structural Characterization of Iron Bis(acetylides). Crystals of $Fe(C{\equiv}CCH_3)_2(DMPE)_2$ (**3a**), $Fe(C{\equiv}CPh)_2(DEPE)_2$ (**4b**), and $Fe(C{\equiv}CC_6H_4C{\equiv}CH)_2(DMPE)_2$ (**5a**) suitable for X-ray analysis were grown by slow evaporation of the benzene solutions of the complexes **4b** and **5a** or an ethanol solution of **3a**. The crystal structures of $Fe(C{\equiv}CPh)_2(DMPE)_2$ (**4a**)[4] and $FeCl(C{\equiv}CPh)(DMPE)_2$ (**9a**)[16] have been reported previously. The structure of **4a** showed that the seven atoms of the C—C≡C—Fe—C≡C—C grouping are collinear with the bond lengths indicatig a strong Fe—C bond, an unusually short C≡C bond (1.209 Å), and a significant amount of delocalization into the C—C(Ph) bond (1.438 Å). The crystallographic data for **3a**, **4b**, and **5a** are summarized in Table I, and non-hydrogen atom coordinates are listed in Tables II–IV. The atomic nomenclatures are defined in Figure 1.[17]

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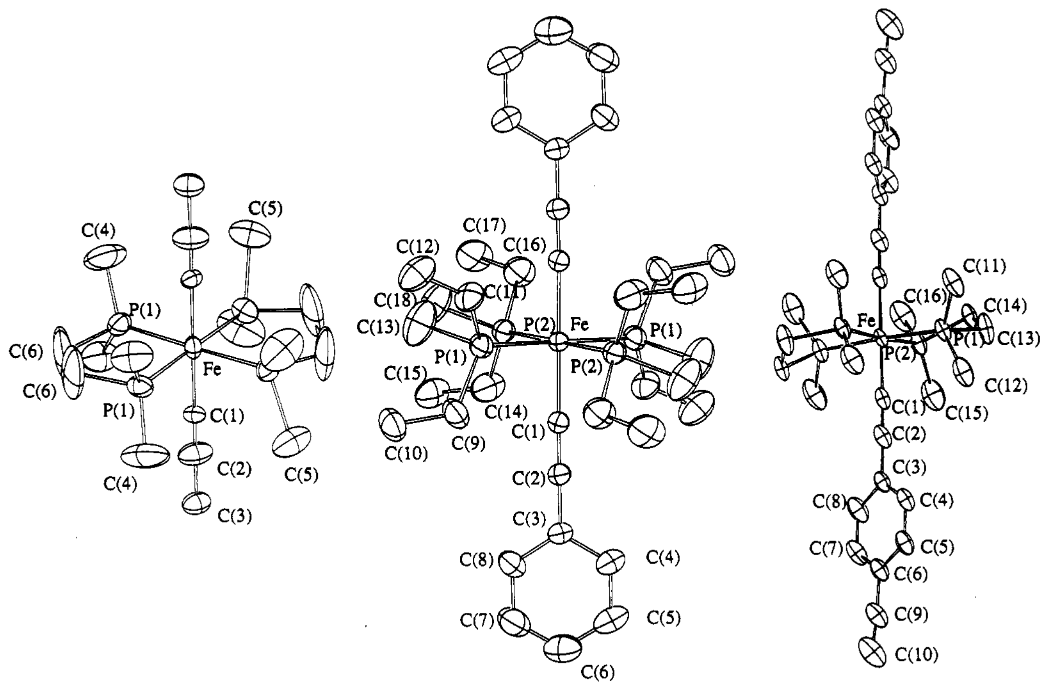

Figure 1. ORTEP plots (left to right) of complexes **3a**, **4b**, and **5b** giving the crystallographic atom numbering (30% probability ellipsoids are shown).

Table III. Positional Parameters (×10^4) for Fe(C≡CPh)$_2$(DEPE)$_2$ (4b)[a]

	x	*y*	*z*
Fe(1)	0	0	0
P(1)	-1480 (1)	1579 (1)	-5 (1)
P(2)	687 (1)	682 (1)	-1090 (1)
C(1)	1401 (3)	965 (3)	544 (2)
C(2)	2311 (3)	1560 (3)	892 (2)
C(3)	3406 (3)	2252 (3)	1279 (2)
C(4)	4373 (4)	1679 (5)	1769 (2)
C(5)	5432 (5)	2348 (7)	2134 (3)
C(6)	5550 (6)	3578 (7)	2017 (4)
C(7)	4645 (7)	4152 (5)	1546 (4)
C(8)	3570 (5)	3499 (4)	1170 (3)
C(9)	-1151 (18)	2937 (13)	607 (9)
C(10)	-1775 (11)	4242 (12)	434 (8)
C(11)	-3287 (7)	1341 (9)	30 (6)
C(12)	-4367 (14)	2046 (18)	-320 (9)
C(13)	-1456 (13)	2305 (14)	-1015 (6)
C(14)	2222 (15)	1566 (16)	-1139 (7)
C(15)	2397 (16)	2597 (16)	-1724 (6)
C(16)	741 (15)	-454 (12)	-1875 (5)
C(17)	812 (17)	70 (13)	-2652 (7)
C(18)	-756 (12)	1681 (15)	-1512 (8)
C(9′)	-822 (22)	3170 (19)	253 (13)
C(10′)	-1560 (50)	4014 (21)	448 (21)
C(11′)	-2753 (16)	1864 (14)	-728 (9)
C(12′)	-4071 (27)	2271 (39)	-693 (12)
C(13′)	2576 (23)	-1202 (18)	-792 (15)
C(14′)	1462 (15)	2283 (12)	-1085 (7)
C(15′)	2199 (31)	2721 (18)	-1539 (21)
C(16′)	-316 (17)	605 (22)	-1946 (6)
C(17′)	-78 (42)	410 (41)	-2636 (18)
C(18′)	2294 (18)	-212 (12)	-1283 (10)

[a] Primes indicate minor sites of disordered atoms. Occupancies: C(9)–C(18), 0.54 (1); C(9′)–C(18′), 0.46 (1).

Table IV. Positional Parameters (×10^4) for Fe(C≡CC$_6$H$_4$C≡CH)$_2$(DMPE)$_2$ (5a)[a]

	x	*y*	*z*
Fe(1)	0	799 (1)	2500
P(1)	686 (1)	2017 (1)	3856 (1)
P(2)	753 (1)	-412 (1)	3858 (1)
C(1)	939 (2)	801 (2)	2616 (2)
C(2)	1530 (2)	790 (2)	2712 (3)
C(3)	2248 (2)	802 (2)	2837 (2)
C(4)	2413 (2)	1684 (2)	2494 (2)
C(5)	3118 (2)	1698 (3)	2643 (3)
C(6)	3689 (2)	829 (2)	3149 (2)
C(7)	3524 (2)	-57 (3)	3477 (3)
C(8)	2822 (2)	-69 (3)	3328 (3)
C(9)	4442 (2)	851 (3)	3346 (3)
C(10)	5081 (3)	842 (3)	3562 (4)
C(11)	1308 (3)	3076 (4)	3957 (4)
C(12)	109 (3)	2790 (4)	4073 (4)
C(13)	1493 (3)	1311 (4)	5230 (3)
C(14)	1738 (3)	256 (4)	5121 (3)
C(14′)	1331 (14)	425 (17)	5214 (16)
C(15)	297 (3)	-1078 (4)	4297 (4)
C(16)	1251 (3)	-1568 (4)	3812 (4)

[a] A prime indicates the minor site of the disordered atom. Occupancies: C(14), 0.81 (1); C(14′), 0.19 (1).

Table V. Comparison of Bond Lengths (Å) for Iron(II) Acetylide Complexes

complex	Fe—C	Fe—P	C≡C	C—C
Fe(C≡CCH$_3$)$_2$-(DMPE)$_2$ (**3a**)	1.968 (6)	2.183 (1)	1.152 (9)	1.465 (11)
Fe(C≡CPh)$_2$-(DMPE)$_2$[a] (**4a**)	1.925 (6)	2.191 (3) 2.180 (5)	1.209 (9)	1.438 (9)
Fe(C≡CPh)$_2$-(DEPE)$_2$ (**4b**)	1.918 (3)	2.222 (1) 2.231 (1)	1.222 (4)	1.435 (4)
Fe(C≡CC$_6$H$_4$C≡CH)$_2$-(DMPE)$_2$ (**5a**)	1.933 (3)	2.216 (1) 2.209 (1)	1.193 (4)	1.438 (4)
FeCl(C≡CPh)-(DMPE)$_2$[a] (**9a**)	1.880 (5)	2.216 (2) 2.216 (2) 2.213 (2) 2.217 (2)	1.216 (8)	1.421 (8)

[a] Crystallographic data for **4a**[4] and **9a**[16] have previously been reported.

The structures of **3a**, **4b**, and **5a** consist of Fe(II) atoms coordinated in the equatorial plane by two bidentate phosphine ligands and in the axial positions by acetylide ligands. There was disorder in the structures of **4b** and

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(17) Figures were drawn with ORTEP (Johnson, C. K. "ORTEP, A Thermal Ellipsoid Plotting Program"; Oak Ridge National Laboratory: Oak Ridge, TN, 1965).

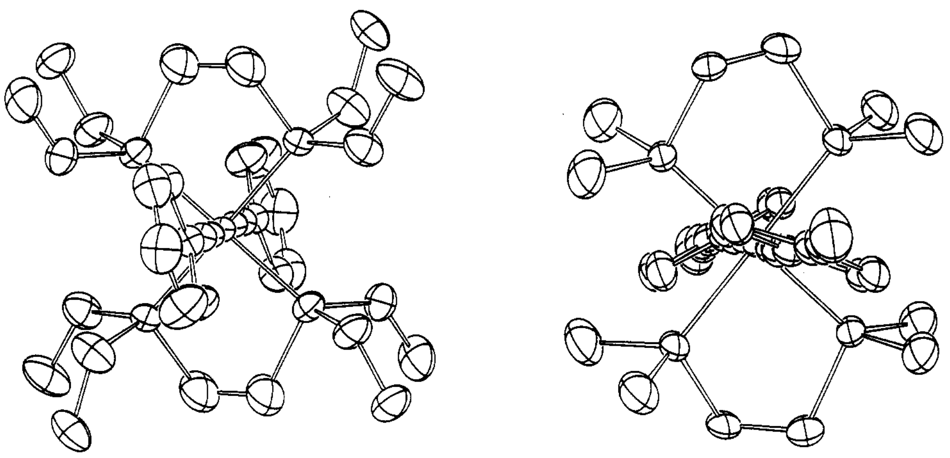

Figure 2. ORTEP plots (left to right) of complexes **4b** and **5a** viewed down the principal axis.

Table VI. Infrared Data for Terminal Acetylenes and Iron Acetylides[a]

acetylene/complex	compd no.	ν(C≡CH), cm^{-1}	ν(C≡CFe), cm^{-1}	$\Delta\nu$,[b] cm^{-1}
phenylacetylene		2110		
1,4-diethynylbenzene		2099		
1,3,5-triethynylbenzene		2105		
tert-butylacetylene		2107		
$Fe(C{\equiv}CCH_3)_2(DMPE)_2$	**3a**		2075	
$Fe(C{\equiv}CPh)_2(DMPE)_2$	**4a**		2037	73
$Fe(C{\equiv}CPh)_2(DEPE)_2$	**4b**		2035	75
$Fe(C{\equiv}CC_6H_4C{\equiv}CH)_2$-$(DMPE)_2$	**5a**	2037	2016	83
$Fe(C{\equiv}CC_6H_3(C{\equiv}CH)_2)_2$-$(DMPE)_2$	**6a**	2033	2033	72
$Fe(C{\equiv}CC(CH_3)_3)_2$-$(DMPE)_2$	**7a**		2059	48
$FeCl(C{\equiv}CPh)(DMPE)_2$	**9a**		2044	66

[a] Nujol mull. [b] $\Delta\nu$ = ν(C≡C in unbound ligand) − ν(C≡C of complexed acetylide).

5a, which limits the accuracy of these structures. The Fe—C and Fe—P bond lengths show significant variation, and there was a smaller, and possibly correlated, variation in the C≡C and (C≡)C—C bond lengths (Table V). Thus, the longest Fe—C bond was found in the methylacetylide structure, and it has the shortest C≡C and Fe—P bond lengths and the longest C—C bond length. Conversely, the two shortest Fe—C bond lengths were associated with the longest Fe—P and C≡C bond lengths (**4b** and **9a**[16]) and the shortest (C≡)C—C bond lengths (**4b**). However, all these variations are at a marginal level of significance, and therefore, firm conclusions cannot be reached.

A relatively short Fe—C bond and long C≡C bond in **9a** suggests a greater degree of M→π* bonding in the case of the acetylide chloride complex than in the bis(acetylides). The increase in the Fe—P distance in **4b** compared to that in **4a** is consistent with the increased steric requirements of the bulkier ligand substituents.

In the three phenylacetylide complexes, different orientations of the phenyl groups with respect to each other (**4a** and **4b**) and with respect to the phosphine ligands (**4a**, **4b**, and **9a**) were observed. Disorder of the phosphine ligands was observed in all three complexes, yet no disorder was imparted to the phenyl groups. This strongly suggests that there are no directional steric or electronic interactions between the phosphine and phenylacetylide ligands.

Infrared Spectroscopy. On complexation of the terminal acetylene to the metal, the C≡C bond stretch in the infrared spectrum shifts to lower frequency (Table VI). This suggests a weakening of the C≡C bond, which is consistent with a conjugative interaction with the metal (M→π*). In complexes containing polyacetylenic ligands, **5a** and **6a**, the frequency of the noncoordinated C≡C is also shifted to lower energy and this provides evidence for some delocalization through the aromatic π system to the metal bound C≡C. The shift in stretching frequency of the C≡C bond of the bis(*tert*-butylacetylide) complex **7a** ($\Delta\nu$ = 48 cm^{-1}) is significantly less than in the arylmetal complexes.

Table VII. ^{31}P and ^{13}C NMR Data for Terminal Acetylenes and Iron Acetylides

acetylene/complex	compd no.	^{31}P[a] Fe–*P*	^{13}C[b] Z—*C*≡CR (Z = H, Fe)	Z—C≡*C*R (Z = H, Fe)	$^2J_{PC\equiv}$
phenylacetylene			78.5[c]	84.6	
1,4-diethynylbenzene			80.0[d]	84.2	
1,3,5-triethynylbenzene			80.9[d]	82.9	
tert-butylacetylene			69.3	94.3	
$Fe(C{\equiv}CCH_3)_2(DMPE)_2$	**3a**	69.5	112.8	104.7	
$Fe(C{\equiv}CPh)_2(DMPE)_2$	**4a**	64.7[c]	140.0	133.1	32
$Fe(C{\equiv}CC_6H_4C{\equiv}CH)_2$-$(DMPE)_2$	**5a**	67.9[c]	147.2	133.3	41
$Fe(C{\equiv}CC_6H_3$-$(C{\equiv}CH)_2)_2(DMPE)_2$	**6a**	66.5	146.9	133.0	26
$Fe(C{\equiv}CC(CH_3)_3)_2$-$(DMPE)_2$	**7a**	69.4	121.9	111.9	30

[a] Spectra recorded at 162 MHz at 300 K in THF-d_8 solutions. Chemical shifts (δ) are in ppm relative to external, neat trimethyl phosphite, taken as δ 140.85 ppm. [b] Spectra recorded at 100 MHz at 300 K in THF-d_8 solutions. Chemical shifts (δ) are in ppm and referenced to tetrahydrofuran-d_8 (δ 26.7 and 68.6). Coupling constants are in Hz, and signs of coupling constants are not implied. [c] In benzene-d_6. [d] In chloroform-*d*.

NMR Spectroscopy. The $Fe(C{\equiv}CR)_2(PP)_2$ complexes are all diamagnetic and the $^{31}P\{^1H\}$ NMR spectra (Table VII) contain a single sharp resonance, typically in the range δ 64–70 ppm. This confirms that all of the complexes adopt an exclusively trans configuration in solution.

In the ^{13}C NMR spectrum, the terminal sp-hybridized carbon of the free acetylene experiences a downfield shift of approximately 60 ppm on complexation to the metal center (Table VII). In all of the iron acetylide complexes the iron-bound sp-hybridized carbon exhibits a quintet splitting (ca. 30 Hz) due to coupling to four ^{31}P nuclei of the ligands.

UV–Visible Spectroscopy. In the complexes described in this work it would be expected that absorptions associated with M-L charge transfer and π → π* transitions would be observed in the UV–visible spectrum. The absorptions in the range 220–280 nm are associated with the π → π* transitions in the ligand. Transitions at longer wavelengths (350–410 nm) are due to M-L charge transfer (Table VIII). The small shift in the π → π* transition of the complexed ligand indicates that extended conjuga-

Table VIII. UV–Visible Data for Terminal Acetylenes and Iron Acetylides[a]

acetylene/complex	compd no.	λ_{max}, nm (log ϵ)
phenylacetylene		247 (4.14), 237 (4.21)
1,4-diethynylbenzene		274 (3.55), 261 (3.52)
1,3,5-triethynylbenzene		252 (3.60), 240 (3.74)
tert-butylacetylene		214 (1.08)
$Fe(C{\equiv}CCH_3)_2(DMPE)_2$	**3a**	400, 232
$Fe(C{\equiv}CPh)_2(DMPE)_2$	**4a**	364 (4.26), 259 (4.05)
$Fe(C{\equiv}CPh)_2(DEPE)_2$	**4b**	375 (4.54), 258 (4.52)
$Fe(C{\equiv}CC_6H_4C{\equiv}CH)_2(DMPE)_2$	**5a**	413 (4.17), 284 (4.17), 222 (3.95)
$Fe(C{\equiv}CC_6H_3(C{\equiv}CH)_2)_2(DMPE)_2$	**6a**	405 (3.72), 250 (4.10)
$Fe(C{\equiv}CC(CH_3)_3)_2(DMPE)_2$	**7a**	350 (3.91)
$FeCl(C{\equiv}CPh)(DMPE)_2$	**9a**	466 (1.52), 358 (3.18), 247 (3.20)

[a] Samples dissolved in THF at room temperature.

tion is present to some extent in these molecules.

Conclusions

Iron hydride complexes may be employed in the synthesis of *trans*-bis(acetylido)iron complexes in reasonable yield. There is some evidence of conjugative interaction between the organic fragment and the metal center and there is potential to extend the linear framework to incorporate additional metal centers.[18]

Experimental Section

General Data. All reactions and manipulations were performed under nitrogen or argon, in a drybox or in Schlenk apparatus. Tetrahydrofuran (THF), benzene, and light petroleum ether (bp 60–70 °C) were distilled from benzophenone ketyl under nitrogen prior to use. Methanol (500 mL) was dried over magnesium by adding absolute methanol (75 mL) to a mixture of clean, dry magnesium turnings (5 g) and iodine crystals (0.5 g). The mixture was warmed until the color of the iodine disappeared and all the magnesium had reacted. The remainder of the methanol (425 mL) was added to the solution, which was refluxed for a further 30 min before distillation. Deuterated solvents were obtained from Merck and Aldrich and used as received. $FeCl_2(DMPE)_2$, $FeH_2(DMPE)_2$, and $FeH_2(DEPE)_2$ were prepared according to literature procedures.[19] Similarly 1,4-diethynylbenzene[8] and 1,3,5-triethynylbenzene[9] were synthesized with use of known methodology. ^1H (400.1 MHz), ^{31}P (162.0 MHz), and ^{13}C (100.6 MHz) NMR spectra were recorded on a Bruker AMX-400 spectrometer, in the solvents indicated. UV–visible spectra were recorded on a Hitachi 150-20 spectrometer with THF as the solvent. Infrared spectra were recorded on a Bio-Rad FTS 20/60 spectrometer with the sample in a Nujol mull. Electron impact mass spectra were obtained with an AEI MS30 mass spectrometer. Microanalyses were performed by National Analytical Laboratories (NAL). All solvents were degassed by three to five freeze–pump–thaw cycles prior to use. Nitrogen (>99.5%) and propyne (>96.0%) were obtained from Commonwealth Industrial Gases (CIG) and used as received.

Crystallography. Cell constants were determined by least-squares fits to the setting parameters of 25 independent reflections, measured and refined on an Enraf-Nonius CAD4-F diffractometer with a graphite monochromator. Data were reduced and Lorentz, polarization, and absorption corrections were applied with use of the Enraf-Nonius structure determination package (SDP).[20] The structures were solved by direct methods with SHELXS-86[21] or heavy-atom methods with SHELX-76[22] and were refined by full-matrix (**3a** and **5a**) or blocked-matrix (**4b**) least-squares analysis with SHELX-76. In **4b** the complex was rotationally disordered; the phenylacetylide groups and the P atoms did not move, but two sites were observed for each of the C atoms of the phosphine ligands, each set of sites bridging a different pair of P atoms. In **5a** one of the bridging C atoms was disordered over two sites 1.03 Å apart. Hydrogen atoms in **3a** and **4b** were included at calculated sites (C–H = 0.97 Å) with individual isotropic thermal parameters, and those in **5a** were refined, also with individual isotropic thermal parameters. All other atoms except minor contributors to disordered groups were refined anisotropically. Scattering factors and anomalous dispersion corrections for Fe were taken from ref 23 and for all others the values supplied in SHELX-76 were used. Listings of H atom coordinates, anisotropic thermal parameters, close intermolecular contacts, torsion angles, and observed and calculated structure factor amplitudes have been deposited as supplementary material.

***trans*-$Fe(C{\equiv}CPh)_2(DMPE)_2$ (4a).** A solution of $FeH_2(DMPE)_2$ (**1a**; 20 mg, 56 μmol) in methanol (3 mL) was added to a solution of phenylacetylene (420 mg, 4.1 mmol) in methanol (3 mL) with vigorous stirring. The crude product precipitated from solution over a period of 30 min. The solution was filtered and the residue washed with methanol and recrystallized from benzene to afford $Fe(C{\equiv}CPh)_2(DMPE)_2$ (**4a**) as a yellow crystalline solid (20 mg, 43%): decomposed without melting at $T >$ 300 °C; $^{31}P\{^1H\}$ NMR (C_6D_6) δ 64.7; ^1H NMR (C_6D_6) δ 1.61 (bs, 24 H, CH_3), 1.72 (bs, 8 H, CH_2), 7.18 (m, 2 H, CH), 7.38 (m, 4 H, CH), 7.54 (m, 4 H, CH); $^{13}C\{^1H,^{31}P\}$ NMR (THF-d_8) δ 17.6 (CH_3), 32.7 (CH_2), 117.1 ($C{\equiv}CC$), 123.9 (CH), 129.4 (CH), 131.7 (CH), 133.1 ($FeC{\equiv}C$), 140.0 ($FeC{\equiv}C$); λ_{max} (THF; log ϵ) 215 (3.63), 260 (4.05), 365 (4.26) nm; $\nu_{C{\equiv}C}$ (Nujol) 2037 cm^{-1}; m/e = 558 (M^+), 408, 356, 206, 202, 135, 122, 107, 61. Anal. Calcd for $FeC_{28}H_{42}P_4$: C, 60.23; H, 7.58. Found: C, 60.3; H, 7.6.

***trans*-$Fe(C{\equiv}CC_6H_4C{\equiv}CH)_2(DMPE)_2$ (5a).** A solution of $FeH_2(DMPE)_2$ (**1a**) (40 mg, 0.11 mmol) in methanol (3 mL) was added to a solution of 1,4-diethynylbenzene (800 mg, 6.34 mmol) in methanol (3 mL) with vigorous stirring. The crude product precipitated from solution over a period of 30 min. The solution was filtered and the residue washed with methanol and recrystallized from benzene to afford $Fe(C{\equiv}CC_6H_4C{\equiv}CH)_2(DMPE)_2$ (**5a**) as a dark yellow crystalline solid (44 mg, 65%): decomposed without melting at $T >$ 300 °C; $^{31}P\{^1H\}$ NMR (C_6D_6) δ 67.9; ^1H NMR (C_6D_6) δ 1.54 (bs, 24 H, CH_3), 1.67 (bs, 8 H, CH_2), 3.38 (s, 2 H, $C{\equiv}CH$), 7.25 (m, 4 H, CH), 7.57 (m, 4 H, CH); $^{13}C\{^1H,^{31}P\}$ NMR (THF-d_8) δ 17.4 (CH_3), 32.5 (CH_2), 79.1 ($C{\equiv}CH$), 86.6 ($C{\equiv}CH$), 117.7 ($FeC{\equiv}CC$), 117.9 ($CC{\equiv}CH$), 130.8 (CH), 133.3 ($FeC{\equiv}C$), 134.2 (CH), 147.2 ($FeC{\equiv}C$); λ_{max} (THF, log ϵ) 222 (3.95), 284 (4.17), 413 (4.17) nm; $\nu_{C{\equiv}C}$ (Nujol) 2037, 2016 cm^{-1}; m/e = 606 (M^+), 456, 356, 250, 135, 122, 107, 62.

***trans*-$Fe(C{\equiv}CC_6H_3(C{\equiv}CH)_2)_2(DMPE)_2$ (6a).** A solution of $FeH_2(DMPE)_2$ (**1a**) (30 mg, 84 μmol) in methanol (3 mL) was added to a solution of 1,3,5-triethynylbenzene (600 mg, 4.00 mmol) in methanol (3 mL) with vigorous stirring. The crude product precipitated from solution over a period of 30 min. The solution was filtered, and the residue was washed with methanol and recrystallized from benzene to give $Fe(C{\equiv}CC_6H_3(C{\equiv}CH)_2)_2(DMPE)_2$ (**6a**) as a pale yellow solid (40 mg, 73%): decomposed without melting at $T >$ 300 °C. $^{31}P\{^1H\}$ NMR (THF-d_8) δ 66.5; ^1H NMR (THF-d_8) δ 1.62 (bs, 24 H, CH_3), 1.89 (bs, 8 H, CH_2), 3.51 (s, 4 H, $C{\equiv}CH$), 7.08 (m, 4 H, CH), 7.38 (m, 2 H, CH); $^{13}C\{^1H,^{31}P\}$ NMR (THF-d_8) δ 17.4 (CH_3), 32.5 (CH_2), 79.5 ($C{\equiv}CH$),

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85.1 ($C\equiv CH$), 115.7 ($FeC\equiv CC$), 124.5 ($CC\equiv CH$), 130.7 (CH), 133.0 ($FeC\equiv C$), 135.4 (CH), 146.9 ($FeC\equiv C$); λ_{max} (THF, log ϵ) 250 (4.10), 405 (3.72) nm; $\nu_{C\equiv C}$ (Nujol) 2033 cm^{-1}. Anal. Calcd for $FeC_{36}H_{42}P_4$: C, 66.06; H, 6.42. Found: C, 66.5; H, 6.7.

***trans*-Fe(C≡CC(CH$_3$)$_3$)$_2$(DMPE)$_2$ (7a).** A solution of $FeH_2(DMPE)_2$ (**1a**) (40 mg, 0.11 mmol) in methanol (3 mL) was added to a solution of *tert*-butylacetylene (91 mg, 1.11 mmol) in methanol (3 mL) with vigorous stirring. The crude product precipitated from solution over a period of 30 min. The solution was filtered, and the residue was washed with methanol and recrystallized from benzene to afford $Fe(C\equiv CC(CH_3)_3)_2(DMPE)_2$ (**7a**) as a pale yellow crystalline solid (41 mg, 71%): decomposed without melting at $T > 300$ °C. $^{31}P\{^1H\}$ NMR (THF-d_8) δ 69.4; ^1H NMR (THF-d_8) δ 1.12 (s, 18 H, CCH_3), 1.58 (bs, 24 H, PCH_3), 1.84 (bs, 8 H, CH_2); $^{13}C\{^1H,^{31}P\}$ NMR (THF-d_8) δ 17.7 (PCH_3), 31.7 (CCH_3), 32.9 (CH_2), 35.0 (CCH_3), 111.9 ($FeC\equiv C$), 121.9 ($FeC\equiv C$); λ_{max} (THF, log ϵ) 350 (3.91); $\nu_{C\equiv C}$ (Nujol) 2059 cm^{-1}. Anal. Calcd for $FeC_{24}H_{50}P_4$: C, 55.60; H, 9.65. Found: C, 56.0; H, 10.0.

***trans*-Fe(C≡CCH$_3$)$_2$(DMPE)$_2$ (3a).** A solution of $FeH_2(DMPE)_2$ (**1a**) (20 mg, 56 μmol) in methanol (3 mL) was added, with vigorous stirring, to a methanol solution of propyne (2 mL, 0.22 M) in which sodium (5 mg) had been dissolved. The crude product precipitated from solution over a period of 30 min. The solution was filtered, and the residue was washed with pentane and recrystallized from pentane to afford $Fe(C\equiv CCH_3)_2(DMPE)_2$ (**3a**) as a pale yellow crystalline solid (14 mg, 57%): decomposed without melting at $T > 300$ °C; $^{31}P\{^1H\}$ NMR (THF-d_8) δ 69.5; ^1H NMR (THF-d_8) δ 1.30 (bs, 24 H, PCH_3), 1.53 (s, 6 H, CCH_3), 1.57 (bs, 8 H, CH_2); $^{13}C\{^1H,^{31}P\}$ NMR (THF-d_8) δ 8.0 (CH_3), 17.7 (PCH_3), 32.8 (CH_2), 104.7 ($FeC\equiv C$), 112.8 ($FeC\equiv C$); λ_{max} (THF) 232, 400 nm; $\nu_{C\equiv C}$ (Nujol) 2075 cm^{-1}. Anal. Calcd for $FeC_{18}H_{38}P_4$: C, 49.77; H, 8.76. Found: C, 50.0; H, 8.9.

***trans*-Fe(C≡CPh)$_2$(DEPE)$_2$ (4b).** A solution of $FeH_2(DEPE)_2$ (**1b**) (5 mg, 10 μmol) in methanol (3 mL) was added, with vigorous stirring, to a solution of phenylacetylene (500 mg, 5 mmol) in methanol. The crude product precipitated from solution over a period of 30 min. The solution was filtered, and the residue was washed with methanol and recrystallized from benzene to afford $Fe(C\equiv CPh)_2(DEPE)_2$ (**4b**) as an orange-yellow crystalline solid: decomposed at $T > 250$ °C; $^{31}P\{^1H\}$ NMR (THF-d_8) δ 76.0; ^1H NMR (THF-d_8) δ 1.20 (bs, 24 H, CH_3), 1.61 (bs, 16 H, CH_2), 2.39 (bs, 8 H, CH_2), 6.75 (m, 2 H, CH), 6.87 (m, 4 H, CH), 6.94 (m, 4 H, CH); $^{13}C\{^1H,^{31}P\}$ NMR (dichloromethane-d_2) δ 10.2 (CH_3), 21.8 (CH_2CH_3), 30.5 (CH_2), 117.8 ($C\equiv CC$), 122.6 (CH), 128.5 (CH), 130.4 (CH), 131.7 ($FeC\equiv C$), 142.0 ($FeC\equiv C$); λ_{max} (THF, log ϵ) 258 (4.52), 374 (4.54) nm; $\nu_{C\equiv C}$ (Nujol) 2035 cm^{-1}. Anal. Calcd for $FeC_{36}H_{58}P_4$: C, 64.49; H, 8.66. Found: C, 64.2; H, 8.6.

Acknowledgment. We gratefully acknowledge financial support from the Australian Research Grants Scheme.

Supplementary Material Available: Tables of crystal data, bond lengths and angles, thermal parameters, and hydrogen atom positional and thermal parameters for **3a**, **4b**, and **5a** and tables of least-squares calculations for **4b** and **5a** (11 pages); tables of observed and calculated structure factors for **3a**, **4b**, and **5a** (30 pages). Ordering information is given on any current masthead page.

EPR Characterization of the Photolysis and Thermolysis Products of Alkylcobaloximes with Symmetric Phosphines and Phosphites. Factors That Stabilize the Cobalt Homolysis Fragments

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Received January 2, 1991

The products of anaerobic photolysis of several alkylcobaloximes with symmetric phosphines and phosphites were studied by electron paramagnetic resonance spectroscopy in nonaqueous solutions and at several temperatures. Evidence is provided for photochemically induced homolytic cleavage of the cobalt–carbon bond and for the formation of stable cobalt(II) five-coordinated species and of organic radicals as homolysis products. The resulting cobalt(II) species are independent of the alkyl group of the cobaloxime, as the EPR spectra of the different alkylcobaloximes with the same phosphorus ligand are identical. A rationale for the lack of reactivity of the cobalt(II) five-coordinated species is provided by an analysis of the EPR parameters and the use of extended Hückel calculations that show the cobalt atom to lie well above the equatorial coordination plane defined by the glyoximes, thus rendering the sixth position not easily available for coordination.

Introduction

The recognition that homolysis of the Co–C bond in coenzyme B_{12} (5′-deoxyadenosylcobalamin) dependent rearrangements is the only role identified thus far for this cofactor has spurred a new interest in the aspects that promote cleavage of this bond.[1-3] Conformational changes in both coenzyme B_{12} and the protein upon addition of the substrate to the holoenzyme have been widely accepted to be responsible for enzyme-accelerated Co–C bond cleavage. An enzyme-induced distortion of the corrin ring toward the adenosyl moiety reminiscent of the butterfly conformation observed in the corrin,[2-5] a lengthening of

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