Organometallics **1988,** *7,* 189–193

in other similar structures.[3,9a,16] The C(3)–C(4)(alkenyl) bond length is normal at 1.329 (4) Å and is not conjugated to either the acyl (O(2)C(2)–C(3)C(4) torsion angle = –70.9 (5)°) or the phenyl (C(3)C(4)–C(41)C(42) torsion angle = 45.0 (5)°) group.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this project and the NSF (CHE 84-11172) and NIH (RR-02435) for funds supporting NMR instrumentation.

Registry No. 1, 111237-17-3; **2**, 111237-18-4; **3**, 111237-19-5; **4**, 111237-20-8; **5**, 111237-21-9; **6**, 111237-22-0; **7**, 111237-23-1; **8**, 111237-24-2; **9**, 111237-25-3; **10**, 111266-86-5; **11**, 111237-26-4; **12**, 111237-27-5; **13**, 111290-83-6; **14**, 111266-87-6; $[CpFeCO[P(OPh)_3](\eta^2\text{–}MeC{\equiv}CCH_iOMe)]BF_4$, 111237-29-7; $Me_iCuCNLi_2$, 80473-70-7; $Ph_2CuCNLi_2$, 80473-66-1; *p*–$NaSC_6H_4Me$, 10486-08-5; $[Cp_2Fe]BF_4$, 1282-37-7; (*E*)–$MeO_2CC(CH_2OMe){=}C(Me)Ph$, 111209-36-0; (*E*)–$MeO_2CC(CH_2OMe){=}C(Me)S$–*p*–$C_6H_4Me$, 111209-37-1; $EtO_2CC(CH_2OMe){=}CMe_2$, 102674-24-8; $EtO_2CCnCMe_iOEt){=}CH_2$, 111209-38-2; $[CpFeCO[P(OPh)_3](\eta^2\text{–}MeC{\equiv}CCHMe_2)]BF_4$, 111237-31-1; NaSPh, 930-69-8; (*Z*)–$CpFeCO[P(OPh)_3][\eta'\text{–}COC(Me){=}CCHMe_2)Me]$, 111237-32-2; (*E*)–$CPFeCO[P(OPh)_3][\eta'\text{-}COC(Me){=}C(CHMe_2)Me]$, 111320-43-5.

Supplementary Material Available: Tables of bond distances and angles for the phenyl rings, positional parameters of H atoms, and anisotropic thermal parameters (8 pages); a listing of structure factor amplitudes (24 pages). Ordering information is given on current masthead page.

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Iron η^2-Alkyne Complexes. Crystal and Molecular Structures of $[CpFeCO[P(OPh)_3](\eta^2\text{-}MeC{\equiv}CPh)]SbF_6$ and $[CpFeCO[P(OPh)_3](\eta^2\text{-}MeC{\equiv}CMe)]SbF_6$

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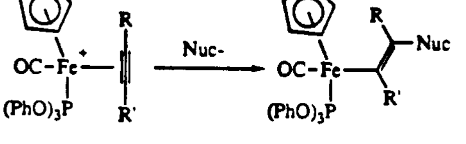
The complexes $[CpFeCO[P(OPh)_3](\eta^2\text{-}MeC{\equiv}CMe)]SbF_6$ (**1**) and $[CpFeCO[P(OPh)_3](\eta^2\text{-}MeC{\equiv}CPh)]SbF_6$ have been crystallized and their solid-state structures determined by X-ray crystallography. Crystals of **1** are monoclinic of space group $P2_1/n$ with $Z = 4$, $a = 18.995$ (3) Å, $b = 16.711$ (3) Å, $c = 9.434$ (1) Å, and $\beta = 101.17$ (1)°. Crystals of **2** are monoclinic of space group $P2_1/c$ with $Z = 4$, $a = 9.108$ (2) Å, $b = 20.658$ (3) Å, $c = 17.510$ Å, and $\beta = 94.57$ (1)°. The unsymmetrical alkyne in **2** is symmetrically bonded to iron with carbon–iron bond distances of 2.14 (1) and 2.146 (9) Å. For **1**, a slight distortion in these bond distances is observed (2.165 (7) and 2.114 (6) Å). The alkyne is oriented orthogonal to the Fe–center Cp vector. For **1**, the center Cp–Fe–center alkyne–alkyne carbon torsion angles are both 90° whereas in **2** they are –85.3 and 94.6°. Bonding to the iron does not greatly purturb the alkyne. The C≡C bond lengths are the same (1.19 (1) Å for **1**, 1.21 (1) Å for **2**) as in the free alkynes and C≡C—R bend back angles range from 155 (2) to 159 (1)°. Complex **1** is fluxional in solution. The alkyne rotates about the Fe–alkyne bond with a barrier to rotation of 12.5 kcal/mol at 241 K. The NMR spectra of **2** are invariant from 210 to 330 K, but the cation $[CpFeCO[P(OPh)_3](\eta^2\text{-}MeC{\equiv}CCO_2Me)]^+$ shows two rotamers in a 1/1.7 ratio at low temperature that interconvert with a barrier of 11.3 kcal/mol at 204 K.

Introduction

Over the past several years, a series of papers has been published[1] describing the preparation and reactivity of $[CpFeCO(L)(\eta^2\text{-alkyne})]^+$ (L = CO, PPh_3, $P(OPh)_3$) complexes. Coordination to iron activates the alkyne toward nucleophilic addition reactions yielding an extensive series (studied most completely for L = $P(OPh)_3$) of alkenyliron complexes (eq 1).



(1)

Nuc = Me, Ph, $CH(CO_2Et)_2$, $CH{=}CH_2$, $C{\equiv}CMe$, CN, SPh
R = R' = Me; R = Me, R' = CO_2Me or CH_2OMe; R = Ph or i-Pr, R' = Me

To support these synthetic studies, it was desired to determine crystallographically the solid-state structures of representative examples of the η^2-alkyne starting materials. Two main features are important. Studying analogous η^2-alkene complexes, Hoffmann and co-workers[2]

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0276-7333/88/2307-0189$01.50/0

Table I. Crystallographic Data for the Structural Analyses

	1	2
formula	$C_{28}H_{26}F_6FeO_4PSb$	$C_{33}H_{28}F_6FeO_4PSb$
cryst system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a, Å	18.995 (3)	9.108 (2)
b, Å	16.711 (3)	20.658 (3)
c, Å	9.434 (1)	17.510 (3)
β, deg	101.17 (1)	94.57 (1)
V, Å^3	2940	3284
Z	4	4
D_{calcd}, g cm^{-3}	1.692	1.640
cryst size, mm	0.3 × 0.2 × 0.1	0.2 × 0.2 × 0.1
monochromator	graphite	graphite
radiatn	Mo K_α (0.71073 Å)	Mo K_α (0.71073 Å)
temp, °C	ambient	ambient
2θ range, deg	4–50	4–50
no. of reflctns. measd	6297	10793
data used after sym averaging	5359	5673
linear absorp coeff, cm^{-1}	15.4	13.8
absorptn correctns	analytical	ref 11
transmissn factors		
max	0.822	1.101
min	0.730	0.671
av	0.793	0.975
cryst decay correctn	1.9% over 145 h	1.5% over 245 h
av	1.005	1.004
max	1.010	1.008
R_{int}	3.2%	4.4%
R_F	0.045	0.039
R_{wF}	0.047	0.046

Table II. Atomic Positional Parameters for 1 with Estimated Standard Deviations in Parentheses

	x/a	y/b	z/c	B, A^2
Fe(1)	0.2338 (1)	0.0597 (1)	0.4294 (1)	3.61
C(1)	0.2544 (4)	−0.0384 (5)	0.3713 (8)	4.49
O(1)	0.2653 (3)	−0.1014 (3)	0.3426 (6)	6.69
C(2)	0.3265 (4)	0.2206 (5)	0.3734 (9)	5.69
C(3)	0.3242 (4)	0.1374 (4)	0.4222 (8)	4.23
C(4)	0.3463 (4)	0.0757 (5)	0.4775 (9)	5.14
C(5)	0.3995 (5)	0.0157 (7)	0.5504 (12)	8.51
P(1)	0.1991 (1)	0.0978 (1)	0.2088 (2)	3.26
O(2)	0.2565 (2)	0.0974 (3)	0.1051 (5)	3.96
O(3)	0.1359 (2)	0.0512 (3)	0.1070 (4)	3.88
O(4)	0.1754 (2)	0.1891 (2)	0.1989 (5)	3.74
C(12)	0.3664 (3)	0.0251 (3)	0.1275 (6)	6.16
C(13)	0.4045 (3)	−0.0423 (3)	0.0986 (6)	8.05
C(14)	0.3689 (3)	−0.1051 (3)	0.0175 (6)	8.36
C(15)	0.2951 (3)	−0.1006 (3)	−0.0346 (6)	7.37
C(16)	0.2569 (3)	−0.0332 (3)	−0.0056 (6)	5.12
C(11)	0.2926 (3)	0.0297 (3)	0.0754 (6)	4.39
C(22)	0.0869 (2)	−0.0723 (3)	0.1689 (5)	4.72
C(23)	0.0313 (2)	−0.1149 (3)	0.2115 (5)	5.76
C(24)	−0.0293 (2)	−0.0747 (3)	0.2374 (5)	5.84
C(25)	−0.0343 (2)	0.0081 (3)	0.2207 (5)	5.46
C(26)	0.0212 (2)	0.0507 (3)	0.1781 (5)	4.22
C(33)	0.0352 (2)	0.3068 (3)	−0.0277 (5)	6.39
C(34)	0.0617 (2)	0.3137 (3)	−0.1552 (5)	7.06
C(35)	0.1269 (2)	0.2781 (3)	−0.1658 (5)	7.14
C(36)	0.1656 (2)	0.2357 (3)	−0.0490 (5)	5.37
C(31)	0.1391 (2)	0.2288 (3)	0.0784 (5)	3.51
C(41)	0.2021 (3)	0.1418 (3)	0.5745 (6)	6.08
C(42)	0.2395 (3)	0.0774 (3)	0.6537 (6)	6.15
C(43)	0.2013 (3)	0.0058 (3)	0.6094 (6)	5.63
C(44)	0.1403 (3)	0.0259 (3)	0.5028 (6)	5.25
C(45)	0.1408 (3)	0.1100 (3)	0.4813 (6)	4.84
SB(1)	0.9077 (0)	0.2494 (0)	0.3801 (1)	4.69
F(1)	0.9082 (4)	0.2110 (4)	0.2006 (4)	18.99
F(2)	1.0025 (2)	0.2269 (4)	0.4309 (6)	16.74
F(3)	0.8864 (3)	0.1513 (2)	0.4374 (6)	17.44
F(4)	0.8139 (2)	0.2727 (4)	0.3264 (6)	19.51
F(5)	0.9085 (4)	0.2879 (4)	0.5582 (4)	19.50
F(6)	0.9299 (3)	0.3478 (3)	0.3205 (7)	17.68
C(21)	0.0818 (2)	0.0105 (3)	0.1522 (5)	3.53
C(32)	0.0739 (2)	0.2643 (3)	0.0891 (5)	4.81

have predicted that slippage of the alkene toward η^1-coordination during the nucleophilic addition reaction is the reason for the metal activation. Given the reactivity and regioselectivity of the reactions in eq 1, it is of interest to determine if slippage of this type would be observed in the ground-state structures for these η^2-alkyne complexes.

Second, the overall geometry of the alkyne ligand and its orientation with respect to the other ligands in these highly asymmetric complexes is of interest. Calculations, again by Hoffmann,[3,4] have shown that back-bonding to the alkyne should be maximized in particular orientations. The geometry and orientation of the alkyne would yield information on its bonding and reactivity. The importance of the orientation of unsaturated ligands to the chemistry of $[CpReNO(PPh_3)L]^+$ (L = CHR, η^2-RCH=O) complexes has been elegantly demonstrated by Gladysz[5] and by a variety of workers[6] in the $[CpFeCO(PPh_3)L]^+$ and $CpFeCO(PPh_3)(\eta^1\text{-COR})$ systems.

Reported here are the results of X-ray structural analyses of $[CpFeCO[P(OPh)_3](\eta^2\text{-alkyne})]SbF_6$ (alkyne = MeC≡CMe (1), MeC≡CPh (2)). Unfortunately, suitable crystals of the alkyne = $MeC{\equiv}CCO_2Me$ complex, 3, have not been obtained. In addition to the structural analyses, variable-temperature NMR data on these complexes are presented that probe dynamic processes for 1 and 3.

Experimental Section

General Procedure. Complexes 1–3 were prepared as described previously,[1f] with $AgSbF_6$ being substituted for $AgBF_4$. The reported ^1H NMR spectra were obtained at 80 or 90 MHz, and the ^{13}C NMR spectra were obtained at 20 MHz. Chemical shifts are reported as δ vs Me_4Si, and coupling constants are reported in Hertz. The rotational barriers were determined by the method of initial line broadening of the static, low-temperature NMR spectra.[7] This method has been used previously on very similar π-alkyne complexes, and the procedure is discussed more fully in that report.[8] The line broadening measurements for both complexes 1 and 3 were taken from the methyl resonances in low-temperature ^1H NMR spectra. The complexes were dissolved in degassed CD_2Cl_2 and sealed under vacuum immediately prior to the measurements. A static, low-temperature spectrum and a partially broadened spectrum were then obtained. The change in line width was then related to the rotational barrier at the temperature of the broadened spectrum. The broadened line widths in both studies were approximately double the original line widths.

Crystallographic Analyses. Brown crystals of 1 were grown from toluene/CH_2Cl_2 (ca. 4/1) at −20 °C. Red crystals of 2 were grown from hexane/CH_2Cl_2 (ca. 2/1) at −20 °C. The data crystals

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Table III. Atomic Positional Parameters for 2 with Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*	*B*, Å^2
Sb(1)	0.15294 (9)	0.10974 (4)	0.22575 (5)	5.95 (2)
Fe(1)	0.7712 (1)	0.28247 (7)	0.41608 (7)	3.29 (3)
P(1)	0.5613 (2)	0.3299 (1)	0.3912 (1)	3.26 (5)
F(1)	0.3221 (7)	0.1070 (4)	0.1746 (4)	9.1 (2)
F(2)	0.0528 (8)	0.1358 (4)	0.1368 (5)	10.1 (2)
F(3)	0.1928 (7)	0.1953 (3)	0.2525 (4)	7.4 (2)
F(4)	0.1162 (8)	0.0240 (3)	0.2018 (4)	8.5 (2)
F(5)	0.269 (1)	0.0813 (4)	0.3124 (5)	11.8 (3)
F(6)	−0.007 (1)	0.1120 (4)	0.2799 (5)	16.3 (3)
O(1)	0.7249 (7)	0.2602 (4)	0.5761 (4)	6.1 (2)
O(2)	0.5168 (6)	0.3894 (3)	0.4417 (3)	4.0 (1)
O(3)	0.4130 (5)	0.2887 (3)	0.3935 (3)	3.5 (1)
O(4)	0.5423 (6)	0.3546 (3)	0.3065 (3)	4.0 (1)
C(1)	0.738 (1)	0.2682 (5)	0.5137 (6)	4.6 (2)
C(2)	0.608 (1)	0.2037 (6)	0.2680 (6)	6.1 (3)
C(3)	0.6752(9)	0.2048 (5)	0.3486 (5)	4.2 (2)
C(4)	0.7264 (9)	0.1807 (5)	0.4077 (5)	4.0 (2)
C(11)	0.6168 (8)	0.4304 (4)	0.4839 (5)	3.4 (2)
C(12)	0.649 (1)	0.4183 (5)	0.5610 (5)	4.5 (2)
C(13)	0.675 (1)	0.4825 (4)	0.4479 (5)	4.1 (2)
C(14)	0.770 (1)	0.5224 (5)	0.4898 (6)	5.3 (3)
C(15)	0.809 (1)	0.5122 (5)	0.5651 (6)	5.5 (3)
C(16)	0.746 (1)	0.4599 (5)	0.6005 (6)	5.1 (3)
C(21)	0.3737 (8)	0.2516 (4)	0.4551 (5)	3.1 (2)
C(22)	0.343 (1)	0.1883 (5)	0.4409 (6)	4.8 (2)
C(23)	0.295 (1)	0.1497 (5)	0.4995 (7)	6.4 (3)
C(24)	0.287 (1)	0.1749 (6)	0.5705 (7)	6.3 (3)
C(25)	0.316 (1)	0.2376 (6)	0.5835 (6)	5.9 (3)
C(26)	0.3628 (9)	0.2797 (5)	0.5269 (5)	4.6 (2)
C(31)	0.4328 (9)	0.3981 (5)	0.2738 (5)	4.0 (2)
C(32)	0.286 (1)	0.3846 (6)	0.2728 (6)	5.3 (3)
C(33)	0.191 (1)	0.4298 (7)	0.2370 (6)	6.4 (3)
C(34)	0.241 (1)	0.4833 (6)	0.2017 (6)	6.4 (3)
C(35)	0.385 (1)	0.4943 (6)	0.2041 (7)	7.4 (3)
C(36)	0.485 (1)	0.4515 (6e	0.2407 (6)	5.6 (3)
C(41)	0.998 (1)	0.2917 (6)	0.4486 (7)	5.9 (3)
C(42)	0.9313 (9)	0.3517 (5)	0.4446 (6)	5.3 (3)
C(43)	0.8746 (9)	0.3618 (5)	0.3677 (6)	4.4 (2)
C(44)	0.904 (1)	0.3065 (5)	0.3274 (6)	5.5 (3)
C(45)	0.981 (1)	0.2626 (5)	0.3772 (7)	5.9 (3)
C(51)	0.762 (1)	0.1313 (5)	0.4646 (6)	4.6 (2)
C(52)	0.660 (1)	0.0946 (7)	0.494 (1)	11.6 (5)
C(53)	0.702 (2)	0.0479 (7)	0.552 (1)	13.7 (5)
C(54)	0.836 (2)	0.0366 (7)	0.5759 (8)	9.8 (4)
C(55)	0.933 (2)	0.0720 (8)	0.544 (1)	15.8 (5)
C(56)	0.898 (1)	0.1181 (7)	0.491 (1)	13.3 (5)

were mounted on a CAD-4 diffractometer in thin-walled capillaries. The unit cells were determined and refined from 25 general reflections. Crystal data, data collection parameters, and results of the analysis are listed in Table I. The structures were solved by the heavy-atom method. Refinement calculations were carried out by using SHELX 76[9] for 1 and SDP[10] for 2. Hydrogen atoms were placed in calculated positions and not refined except for the methyl hydrogen atoms that were placed in positions found in the difference Fourier map. Full-matrix least-squares refinements were carried out with $w = (\sigma^2(F) + 0.0004F_2)^{-1}$ for reflections with $I > 3\sigma(I)$. The SbF_6 anions are partially disordered in both structures. Table II shows atomic positional parameters for 1 and Table III atomic positional parameters for 2.

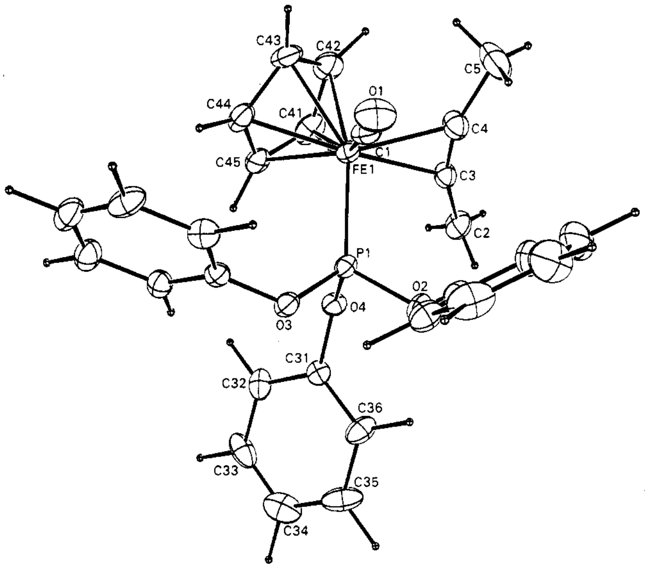

Figure 1. ORTEP drawing of $[CpFeCO[P(OPh)_3](\eta^2\text{-}MeC{\equiv}CMe)]SbF_6$ (1).

Table IV. Selected Bond Distances (Å) for Complexes 1 and 2 with Estimated Standard Deviations in Parentheses

bond	1	2
Fe(1)–C(1)	1.796 (8)	1.78 (1)
Fe(1)–C(3)	2.165 (7)	2.14 (1)
Fe(1)–C(4)	2.114 (6)	2.146 (9)
Fe(1)–P(1)	2.155 (2)	2.162 (2)
Fe(1)–C(41)	2.107 (5)	2.105 (9)
C(1)–O(1)	1.12 (1)	1.12 (2)
C(2)–C(3)	1.47 (1)	1.49 (1)
C(3)–C(4)	1.19 (1)	1.21 (1)
C(4)–C(5) or (51)	1.49 (1)	1.44 (1)
Sb(1)–F(av)	1.805 (4)	1.840 (7)

Table V. Selected Bond Angles (deg) for Complexes 1 and 2 with Estimated Standard Deviations in Parentheses

angle	1	2
C(1)–Fe(1)–C(3)	108.5 (3)	108.2 (4)
C(1)–Fe(1)–C(4)	84.8 (3)	81.9 (4)
C(1)–Fe(1)–Cp[a,b]	121.1	120.4
C(1)–Fe(1)–P(1)	91.1 (2)	93.0 (3)
C(1)–Fe(1)–C3,4[b,c]	96.9	95.1
C(3)–Fe(1)–C(4)	32.4 (3)	32.8 (4)
C3,4–Fe(1)–P(1)[b]	94.8	95.5
C3,4–Fe(1)–Cp[b]	120.9	121.9
P(1)–Fe(1)–Cp[b]	124.6	123.7
Fe(1)–C(1)–O(1)	175.3 (7)	175.9 (8)
C(2)–C(3)–C(4)	157.7 (7)	155 (2)
C(3)–C(4)–C(5) or (51)	158.4 (8)	159 (1)

[a] Cp = center of cyclopentadienyl ring. [b] Standard deviations not calculated for this composite angle. [c] C3,4 = center of C≡C bond.

$[CpFeCO[P(OPh)_3](\eta^2\text{-}MeC{\equiv}CMe)]SbF_6$ (1): ^1H NMR (δ in CD_2Cl_2 at −62 °C) 7.2 (15, m, $P(OPh)_3$), 4.91 (5, s, Cp), 2.53, 1.99 (3, 3, s, s, Me's); ^1H NMR (δ in CD_2Cl_2 at 25 °C) 7.2 (15, m, $P(OPh)_3$), 4.85 (5, s, Cp), 2.36 (6, s, Me's); IR (cm^{-1} in CH_2Cl_2) ν(CO) 2018; ^{13}C NMR (δ in CD_2Cl_2 at −62 °C) 212.9 (d, J = 42, CO), 149.3, 130.2, 126.3, 120.6 (d, s, s, d, J = 9, 4, $P(OPh)_3$), 86.7 (s, Cp), 46.2, 44.3 (s, d, J = 9, C≡C), 11.0, 10.4 (d, s, J = 4, Me's); ^{13}C NMR (δ in CD_2Cl_2 at 30 °C) 214.3 (d, J = 41, CO), 150.6, 130.9, 127.0, 121.2 (d, s, s, d, J = 11, 5, $P(OPh)_3$), 87.3 (d, J = 1, Cp), 46.4 (d, J = 4, C≡C), 11.0 (d, J = 2, Me's).

$[CpFeCO[P(OPh)_3](\eta^2\text{-}MeC{\equiv}CPh)]SbF_6$ (2): ^1H NMR (δ in CD_2Cl_2 at 25 °C) 7.2 (20, m, $P(OPh)_3$ and CPh), 4.88 (5, s, Cp), 2.65 (3, s, Me); IR (cm^{-1} in CH_2Cl_2) ν(CO) 2008; ^{13}C NMR (δ in CD_2Cl_2 at −62 °C), 211.8 (d, J = 41, CO), 149.3, 130.3, 126.4, 120.6 (d, s, s, s, J = 9, $P(OPh)_3$), 131.8, 129.2, 127.8, 123.7 (all s, C*Ph*), 87.2 (s, Cp), 57.8, 51.5 (d, s, J = 8, C≡C), 12.6 (d, J = 3, Me).

$[CpFeCO[P(OPh)_3](\eta^2\text{-}MeC{\equiv}CCO_2Me)]SbF_6$ (3): ^1H NMR (δ in CD_2Cl_2 at −87 °C) 7.2 (15, m, $P(OPh)_3$), 5.01, 4.88 (total of 5, s, s, Cp), 3.91, 3.83 (total of 3, s, s, OMe), 2.93, 2.39 (total of 3, s, s, CMe); ^1H NMR (δ in CD_2Cl_2 at 25 °C) 7.2 (15, m, $P(OPh)_3$), 5.09 (5, s, Cp), 3.89 (3, s, OMe), 2.62 (3, s, CMe); IR (cm^{-1} in CH_2Cl_2) ν(CO) 2005; ^{13}C NMR (δ in CD_2Cl_2 at −82 °C) 210.9, 209.6 (d, d, J = 41, 41, C≡O), 160.3, 158.0 (d, s, J = 7, C=O), 149.2, 130.3, 126.6, 120.5 (d, s, s, s, J = 10, $P(OPh)_3$), 88.1, 87.9 (s, s, Cp),

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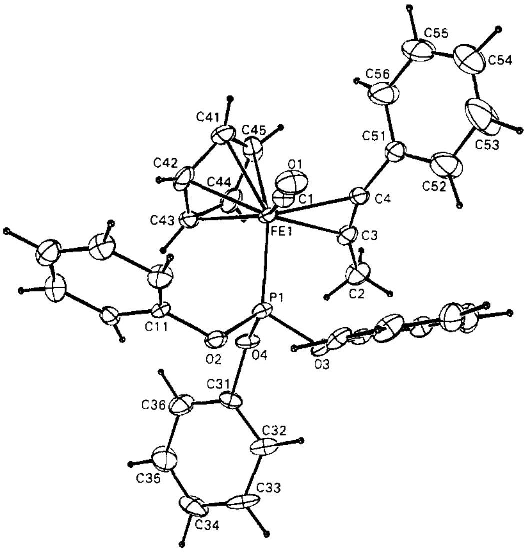


Figure 2. ORTEP drawing of $[CpFeCO[P(OPh)_3](\eta^2\text{-}MeC{\equiv}CPh)]SbF_6$ (**2**).

82.7, 76.1, 74.6 (m, d, s, $J = 12$, C≡C), 43.3, 42.4 (s, s, OMe), 12.9, 11.6 (d, s, $J = 2$, C*Me*).

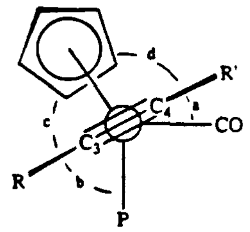
Description of Structures

An ORTEP drawing with numbering scheme for $[CpFeCO[P(OPh)_3](\eta^2\text{-}MeC{\equiv}CMe)]SbF_6$ (**1**) is shown in Figure 1 and for $[CpFeCO[P(OPh)_3](\eta^2\text{-}MeC{\equiv}CPh)]SbF_6$ (**2**) in Figure 2. Table IV gives selected bond distances and Table V selected bond angles for both structures. The numbering schemes are similar for both structures. The quality of the crystal was better for **1** than **2** leading to a slightly more precisely determined structure. Estimated standard deviations are not given for bond and torsion angles involving the composite positions center of cyclopentadienyl ligand (Cp) and middle of the C≡C bond (C3,4).

The overall geometry of the two molecules is very similar. Both structures are best described as octahedral with the cyclopentadienyl ligand occupying three sites. Defining the middle of the C≡C bond as the location in the octahedron of the alkyne (justified by nearly equal Fe—C (alkyne) bond distances, vide infra) yields bond angles through iron for this center point (C3,4),P(1), and C(1)-(carbonyl) ranging from 91.1 (2)° to 96.9°. Angles through iron from the center of the cyclopentadienyl ligand to the other three ligands range from 120.4° to 124.6°. Bond distances and angles for the Cp, CO, and $P(OPh)_3$ ligands are normal.

The acetylenic triple-bond lengths are statistically equivalent at 1.19 (1) Å for **1** and 1.21 (1) Å for **2**. The C≡C—Me bend back angles in **1** are 157.7 (7)° and 158.4 (8)°. For **2**, the C≡C—Me angle is 155 (2)° and the C≡C—Ph angle is 159 (1)°. The Fe-C(alkyne) bond distances are similar at 2.165 (7) Å to C(3) and 2.114 (6) Å to C(4) for **1** and 2.14 (1) Å to C(3) and 2.146 (9) Å to C(4) for **2**.

The orientation of the alkyne with respect to the other ligands is also fairly similar in the two structures. Drawing A shows a Newman type projection of the molecules looking down the center of alkyne (C3,4)-Fe axis. The C(1)-Fe-C3,4-C(4) torsion angle (a) is -42.7° for **1** and -36.1° for **2**. The P(1)-Fe-C3,4-C(3) torsion angle (b) is 45.6° for **1** and 50.4° for **2**. The alkyne ligand is symmetrically rotated from the Cp ligand in **1** with the center Cp-Fe-C3,4-C(3) torsion angle (c) and center Cp-Fe-C3,4-C(4) torsion angle (d) both equal at 90.0°. For **2**, the alkyne is rotated somewhat from this symmetrical orientation with angle $c = -85.3°$ and $d = 94.6°$.



A

Discussion

A feature of considerable interest in the two structures is the symmetry of the bonding of the alkyne carbon atoms with respect to iron. Studying alkene activation by metals to nucleophilic addition, Hoffmann[2] has pointed out that symmetrical coordination of the alkene should actually deactivate it to addition. The LUMO, the antibonding combination of the π^* on the alkene with the filled π-back-bonding orbital on the metal, would be higher in energy and less localized than the free alkene. To explain the known activation, they have proposed that the alkene can slip toward η^1-coordination during the nucleophilic addition lowering the activation energy for the reaction. This idea is strongly supported by the reactivity and solid-state structure[12] of $[CpFe(CO)_2(\eta^2\text{-}CH_2{=}CHOMe)]^+$. This molecule shows a ground-state slippage of the alkene with an Fe–CH_2 distance of 2.09 (2) Å (a disorder problem in the structural analysis may have reduced this value somewhat) and an Fe–CHOMe distance of 2.32 (2) Å. The complex is more reactive with nucleophiles than the analogous $\eta^2\text{-}C_2H_4$ complex, and the reactions are completely regioselective with the nucleophile adding to the substituted alkene carbon atom.

These ideas, as noted previously,[13] should also apply to the nucleophilic addition chemistry with η^2-alkyne complexes shown in eq 1. The additional π orbital ($\pi\perp$) of the alkyne should not significantly change the bonding because no empty metal orbital of appropriate symmetry and energy is available to form a bond with this $\pi\perp$ orbital.[3] The chemistry of complex **2** fits the theory (eq 1). The phenyl substituent for **2** controls the regiochemistry of the addition reaction so that the nucleophile adds exclusively to the alkyne carbon atom bearing the phenyl group. Surprisingly, in the solid-state structure of **2** there is no slippage of the alkyne, the two Fe–C(alkyne) bond lengths are statistically equivalent. Thus, although the nucleophilic addition reactions of **2** takes place readily and are regioselective, there is no indication of a ground-state distortion in the alkyne to iron bonding. A similar symmetrical structure is found in $CpFeCO(SnPh_3)(\eta^2\text{-}PhC{\equiv}CPh)$[14] (large esd's in this paper limit the usefulness of the comparison) and $(PPh_3)_2Pt(\eta^2\text{-}MeC{\equiv}CPh)$.[15] Of interest is the slight slippage of the symmetrical alkyne in complex **1**. The average M–C(alkyne) distance is the same as that observed with **2**, but the two bond distances differ by 0.051 (9) Å.

As best observed in the Newman type drawing A, the orientation of the alkyne with respect to the other ligands

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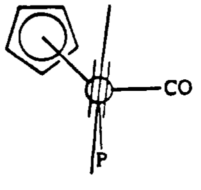
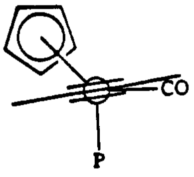
places it orthogonal to the center Cp–iron vector. For 1 the torsion angles *c* and *d* are equivalent; for 2 they differ by 9.3° with $d > c$. This orientation is the same as observed for $CpRe(CO)_2(\eta^2\text{-}PhC{\equiv}CPh)$.[16] Calculations, again by Hoffmann and co-workers, have shown that back-bonding to the alkyne should be maximized in certain orientations. For 16-electron (CpMCOL) fragments, two filled π-symmetry orbitals are available for back-bonding to ligands in the remaining octahedral site. For L = CO, these orbitals are parallel and perpendicular to the Cp ring[3] and calculations predict the structure as observed for $CpRe(CO)_2(\eta^2\text{-}PhC{\equiv}CPh)$. For $L = PR_3$, the orientation of these orbitals is along the Fe–P and Fe–CO vectors.[4] The HOMO orbital is best suited to overlap with the high energy π^* orbital on an alkyne and is located along the Fe–P vector. A structure like B would maximize back-bonding with this HOMO orbital whereas structure C would be a second choice. For $CpMoCO(NO)(\eta^2\text{-}HC{\equiv}CH)$, the d^6 molecule for which calculations were carried out, the most stable conformation had the alkyne twisted 20° from the Fe–CO axis (CO is the weaker back-bonding ligand in this case and is analogous to $P(OPh)_3$ in 1 and 2).



B



C

While favored by electronic factors, a structure close to B has an alkyne substituent pointing directly at the bulky phosphite ligand. Related conformational studies by Seeman and Davies[6d] on $CpFeCO(PPh_3)R$ ($R = CH_2CH_3$, $CHMe_2$, Ph, etc.) complexes have shown that substituents on the α-carbon interact unfavorably with the PPh_3 group if they dip more than 10° below the Fe–(CO)–C_α plane and the lowest energy rotamer for R groups with a single C_α substituent places this group between the Cp and CO ligands. As applied to the η^2-alkyne complexes, the orientation A such as found for 1 and 2 should be favored on steric grounds. For 2, the larger phenyl group should locate between the CO and Cp ligand as observed. Note one difference between the structures is that the alkyne is rotated in 2 such as to move the alkyne phenyl group away from the bulky Cp ligand.

In an orientation like A, back-bonding should be minimized. The amount of back-bonding in metal–η^2-alkyne structures is generally inferred from the lengthening of the C≡C bond and the extent of deformation of the C≡C—R angles.[17] The C≡C bond distance in 1 and 2 are the same as observed in noncoordinated alkynes, 1.21 Å.[15,18] The C≡C—R deformation angles in 1 and 2 are 21 (1)–25 (2)°. These are some of the smallest deformation angles yet reported. Angles observed for a number of η^2-PhC≡CPh complexes (see Table II in ref 16) range from 27 to 42°. The deformation angles observed for 1 and 2 are similar to those observed in the weakly back-bonding Cu(I) complex $[CuC_2Ph_2(PhCO_2)]_2$[19] and are slightly larger than those reported for $[Me(\eta^2\text{-}MeC{\equiv}CMe)Pt(PMe_2Ph)_2]PF_6$.[20] In the recently reported structure of $(\eta^5\text{-}Me_5C_5)_2Yb(\eta^2\text{-}MeC{\equiv}CMe)$,[21] where back-bonding is not possible, the deformation angle is only 2.6° with a C≡C bond distance of 1.154 (6) Å. Thus, the structures of 1 and 2 show limited back-bonding to the alkyne ligand.

Solution Structure of 1, 2, and 3. Low-temperature NMR spectra of 1 show two inequivalent methyl resonances that collapse to a single resonance upon warming. We have proposed earlier that rotation of the alkyne about the Fe–alkyne bond is responsible for this observed signal averaging.[8] The rotational barrier for 1 has been measured as 12.5 kcal/mol at 241 K. The observation of P–C coupling in the averaged high-temperature ^{13}C spectrum indicates that the dynamic process being observed is intramolecular. Complex 3, with the unsymmetrical alkyne $MeC{\equiv}CCO_2Me$, shows two rotamers in a 1/1.7 ratio in low-temperature ^1H NMR spectra. Signal averaging is also seen for this complex upon warming, and the rotational barrier has been measured as 11.3 kcal/mol at 204 K. The NMR spectra of 2 is invariant from 210 to 330 K.

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Registry No. 1, 111237-15-1; 2, 111320-42-4; 3, 111237-16-2.

Supplementary Material Available: Tables of positional parameters of H atoms and anisotropic thermal parameters (9 pages); listings of structure factor amplitudes (43 pages). Ordering information is given on any current masthead page.

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