

a small amount of benzene after 2 h.

¹H NMR spectra were measured on a JEOL PS-100 spectrometer operating at 100 MHz.

Registry No. erythro-1a-d, 75276-79-8; threo-1a-d, 75276-80-1; (E)-1c, 80515-36-2; (Z)-1c, 80515-37-3; 1d, 55073-66-0; 1e, 20425-82-5;

2a-d, 80515-38-4; (E,E)-2c, 80515-39-5; (Z,Z)-2c, 80515-40-8; 2d, 50795-46-5; diphenylthallium(III)⁺, 16785-98-1; Tl(PhCH(OMe)-CH₂)₂⁺, 80533-28-4; (E)-PhCH=CH, 6783-05-7; (Z)-PhCH=CH-B(OAc)₃, 60806-02-2; (Z)-PhCH=CHBr, 588-73-8; Tl(OAc)₃, 2570-63-0; B(OAc)₃, 121-43-7; P(OMe)₃, 121-45-9; NaSPh, 930-69-8; NaCH(OMe)₂, 1543-71-9.

Regiochemistry of Nucleophilic Addition to MeC≡CCO₂Et π Coordinated to Iron. Synthesis and Structural Characterization of (η⁵-C₅H₅)Fe(CO)(PPh₃)(σ-C(CO₂Et)=CMe₂)

D. L. Reger,* P. J. McElligott, N. G. Charles, E. A. H. Griffith, and E. L. Amma*

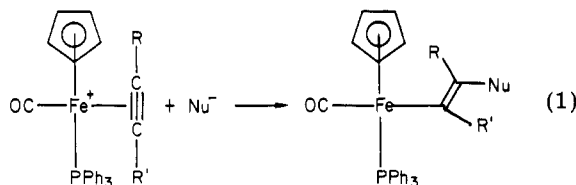
Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208

Received October 5, 1981

The reaction of LiMe₂Cu and [(η⁵-C₅H₅)Fe(CO)(PPh₃)(η²-MeC≡CCO₂Et)]BF₄ yields (η⁵-C₅H₅)Fe(CO)(PPh₃)(σ-C(CO₂Et)=CMe₂) as proven by an X-ray structural determination. The structure is made up of isolated molecules separated by ordinary van der Waals distances. The Fe atom is four coordinate with CO, PPh₃, Cp, and the fourth coordination site made up of an Fe-C σ bond to the *gem*-dimethyl alkene. The Fe-C distance of 2.030 (2) Å is indicative of a single bond, a result expected from the orientation of the alkene relative to the rest of the iron substituents. The Fe-C(CO) distance is 1.724 (4) Å, and the Fe-P distance is 2.224 (1) Å. The molecule is very compact and the orientation of the ester group is largely determined by the triphenylphosphine moiety. The regiochemistry of the addition reaction seems to be dominated by the electronic influence of the ester group although the overall geometry of the entire complex may also be important. Crystal data: triclinic, *P*1̄, *a* = 10.333 (4) Å, *b* = 17.750 (3) Å, *c* = 8.334 (7) Å, α = 96.66 (3)°, β = 109.05 (6)°, γ = 104.81 (2)°, ρ_{obsd} = 1.27 g/cm³, ρ_{calcd} = 1.31 g/cm³, *Z* = 2, λ = 0.710 73 Å, NO = 6501, NV = 325, *R*_{final} = 0.057. Structure refined by full-matrix least squares including anisotropic temperature factors and anomalous dispersion corrections.

Introduction

The addition of nucleophiles to alkenes π coordinated to a transition metal is a well-developed method for the synthesis of alkylmetal complexes.¹ Only recently has this approach been extended to the synthesis of alkenylmetal complexes starting from π-alkyne derivatives.² An example is shown in eq 1 for an iron system developed by



some of us.^{2a,c} A very important question that needs to be answered is what factors will determine the regiochemistry of the addition reaction for unsymmetrical alkynes (*R* ≠ *R'*). This problem has been partially addressed for π-alkene complexes³ and is the subject of a recent theoretical paper.⁴ Trends for alkene and alkyne

complexes should be similar for cases in which the alkyne is viewed as a two-electron donor. In fact, alkynes offer a simplification of the problem because, assuming free rotation about the alkyne single bonds, the π-metal complexes would have a local mirror plane containing the metal, the C≡C atoms, and at least the adjacent carbon atoms. In contrast, (π-alkene)metal complexes would have such a local mirror plane only with *geminal* substitution. We present here the synthesis and definitive characterization by X-ray crystallography of the product obtained in the reaction of LiMe₂Cu and [(η⁵-C₅H₅)Fe(CO)(PPh₃)(η²-MeC≡CCO₂Et)]BF₄. The results establish the regiochemistry of the addition reaction for the interesting case of an alkyne containing an electron-withdrawing substituent. This is a particularly informative case because these results can be compared to the same addition reaction with the free alkyne.⁵

Experimental Section

Preparation of (η⁵-C₅H₅)Fe(CO)(PPh₃)[C(CO₂Et)C(Me)₂]. All of the following procedures were carried out under an inert atmosphere using solvents that were dried and degassed. CH₂Cl₂ (30 mL) was added to a flask containing (η⁵-C₅H₅)Fe(CO)(PPh₃)I (1.0 g, 1.8 mmol), AgBF₄ (0.36 g, 1.9 mmol), and MeC≡CCO₂Et (0.25 g, 2.2 mmol). The solution was stirred at room temperature until a deep red color appeared and immediately cooled to -78 °C. The solution was filtered cold (-78 °C) through filter-aid on a medium glass frit, and the solvent was evaporated below 0 °C. Tetrahydrofuran (THF, 30 mL) chilled to -78 °C was added by cannula tubing to the prechilled residue. A chilled solution of freshly prepared LiCuMe₂ (0.18 g, 1.8 mmol) in THF (20 mL) was

(1) (a) Nicholas, K. M.; Rosan, A. M. *J. Organomet. Chem.* 1975, 84, 351. (b) Sanders, A.; Magatti, C. V.; Giering, W. P. *J. Am. Chem. Soc.* 1974, 96, 1610. (c) Wong, P. K.; Madhavarao, M.; Marten, D. F.; Rosenblum, M. *Ibid.* 1977, 99, 2823. (d) Reger, D. L. *Inorg. Chem.* 1975, 14, 660.

(2) (a) Reger, D. L.; McElligott, P. J. *J. Am. Chem. Soc.* 1980, 102, 5923. (b) Reger, D. L.; Coleman, C. J. *Inorg. Chem.* 1979, 18, 3155. (c) Reger, D. L.; Coleman, C. J.; McElligott, P. J. *J. Organomet. Chem.* 1979, 171, 73. (d) Bottrill, M.; Green, M. *J. Am. Chem. Soc.* 1977, 99, 5795.

(3) (a) Chang, T. C. T.; Rosenblum, M.; Samuels, S. B. *J. Am. Chem. Soc.* 1980, 102, 5930. (b) Lennon, P.; Rosan, A. M.; Rosenblum, M. *Ibid.* 1977, 99, 8426. (c) Chang, T. C. T.; Foxman, B. M.; Rosenblum, M.; Stockman, C. *Ibid.* 1981, 103, 7361.

(4) Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* 1981, 103, 4308. (5) Normant, J. F. *Synthesis* 1972, 63.

Table I. Cell Data, Data Collection, and Refinement Parameters

Cell Data	
$a = 10.333 (4) \text{ \AA}$	$\rho_{\text{obsd}} = 1.27 \text{ g/cm}^3$
$b = 17.750 (3) \text{ \AA}$	$\rho_{\text{calcd}} = 1.31 \text{ g/cm}^3$
$c = 8.334 (7) \text{ \AA}$	$V = 1363.2$
$\alpha = 96.66 (3)^\circ$	$fw = 538.3$
$\beta = 109.05 (6)^\circ$	$Z = 2$
$\gamma = 104.81 (2)^\circ$	

Data Collection	
wavelength, Mo $K\alpha$ 0.710 73 \AA	
graphite monochromator used, $2\theta = 6.1^\circ$	
space group $P\bar{1}$	
size of crystal = 0.58 \times 0.53 \times 0.56 mm	
no systematic absences	
$\mu = 6.59 \text{ cm}^{-1}$	
faces of the form $\{100\}\{010\}\{001\}\{101\}\{110\}$	
absorption corrections made and max-min transmission factor found were 0.817–0.705 ⁷	
P factor = 0.030 in $\sigma(F_o^2) = [\sigma(I_{\text{raw}})^2 + (PI_{\text{raw}})^2]^{1/2}/LP$	
and $w = 1/\sigma(F_o^2)$	
data considered nonzero if $F^2 > 4\sigma(F^2)$, 11944 independent hkl 's measured in ω - 2θ mode to $2\theta = 70^\circ$	
6501 reflections used to solve and refine structure	
variable scan speed with preliminary scan speed of $4^\circ/(\text{min } 2\theta)$	
25 reflections used in orientation matrix (checked every 24 h)	
3 std reflections monitored every 100 reflections, decay less than 2% I	
room temp $\approx 18^\circ\text{C}$	
structure refined by full-matrix least squares, including anisotropic temperature factors and anomalous dispersion corrections with weights based upon intensity statistics ⁷	
final least squares performed on Amdahl V6 with weights as above ⁸	
largest shift at end of refinement = 0.04 σ	
no. of variables = 325	
final $R = 0.057$, weighted $R = 0.082$	
error of obsd of unit weight = 2.19	

added. After being stirred cold (-78°C) for 1 h, the solution was warmed to ambient temperature, concentrated to 10 mL, and placed on an alumina column. Elution with a mixture of CH_2Cl_2 -hexane (1:2) resulted in one red band which was collected and the solvent evaporated (0.70 g, 72%). The crystal used in the X-ray study was formed from a mixture of hexane-pentane (1:1) over a 21-day period in a cold room at -17°C (mp 119 – 120°C): $^1\text{H NMR}$ spectrum (δ in CDCl_3) 7.2 (15, m, PPh_3), 4.34 (5, d, $J = 1.0 \text{ Hz}$, $\eta^5\text{-C}_5\text{H}_5$); 3.6 (2, br m, CH_2), 1.83, 1.66 (3, 3, s, s, $=\text{CMe}_2$), 0.76 (3, t, $J = 7.0 \text{ Hz}$, CH_2CH_3); IR spectrum (cm^{-1} in CH_2Cl_2) $\nu(\text{CO})$ 1925, $\nu(\text{CO}_2\text{Et})$ 1678.

X-ray Data. Single crystals were placed in thin walled glass capillaries and mounted on a Enraf-Nonius CAD-4 diffractometer interfaced to a PDP-11/40. The crystal was aligned by standard methods.⁶ Unit cell data and data collection parameters are summarized in Table I. The structure was solved by standard heavy-atom methods⁷ and final complete matrix least squares with anomalous dispersion corrections was performed on the Amdahl V6-470⁸ to a final conventional R of 0.057. For the final refinement the scattering factors were from Vol. IV of ref 9. A listing of structure factors is available as supplementary material. Table II contains the atomic positional and thermal parameters. Interatomic distances and angles are in Table III, and relevant

(6) Enraf-Nonius CAD-4 Data Collection Package, Revised for PDP 8A-11 operation April 1980. Input parameters: fastest scan speed $4^\circ/\text{min}$, base width 0.8° , θ - 2θ scan, nonequal test, $\sigma(I)/I = 3$, max scan time = 90 s, bisecting mode, intensity control—3 ref every 2 h, update of 25 orienting reflections every 24 h.

(7) Frenz, B. A. "Enraf-Nonius Structure Determination Package", Version 17, 1980, modified locally for the PDP-11/40.

(8) Stewart, J. M. Technical Report TR-446. An update of the X-ray System, University of Maryland, 1979.

(9) Ibers, J. A., Hamilton, W. C., Eds., "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, 71–95, 148–150.

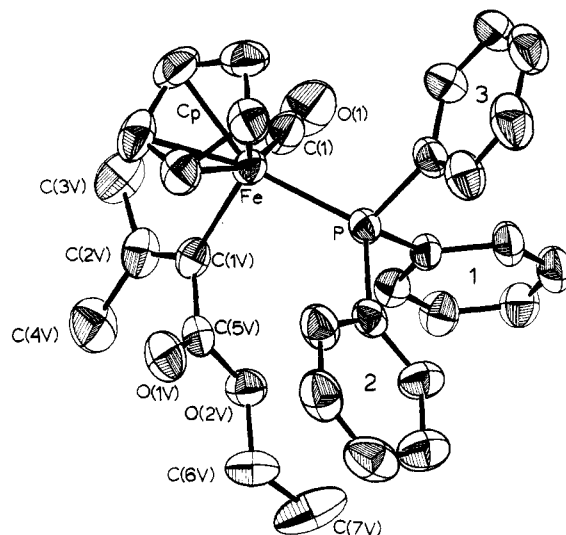


Figure 1. An ORTEP¹⁰ drawing of an isolated $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)[\text{C}(\text{CO}_2\text{Et})\text{CMe}_2]$ molecule. The notation is consistent with the tables except for the rings which have been denoted as rings 1, 2, and 3 for simplicity. The notation for the phenyl rings of the triphenylphosphine moiety is e.g., C(3P2), carbon 3 of ring 2. C(1Pn) is bound to phosphorous, n = ring number, for each ring and the number increases C(2Pn), C(3Pn), etc. in a counterclockwise fashion around the ring. The notation for the Cp ring is such that C(4C) C for Cp is above C(3v) and increases C(5C) then to C(1C), etc. in a counterclockwise fashion around the ring. The ellipsoids are drawn at the 50% probability level.

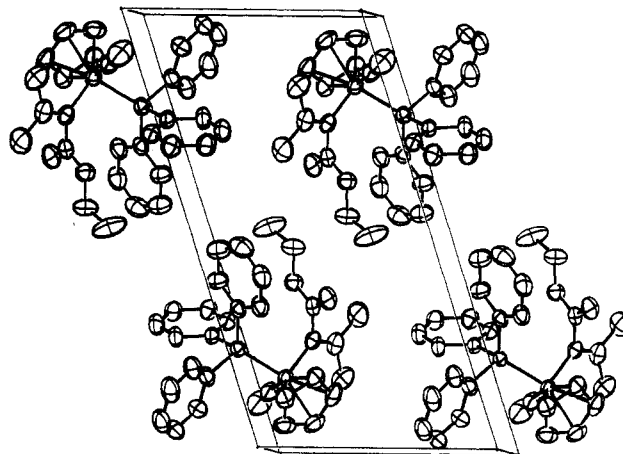
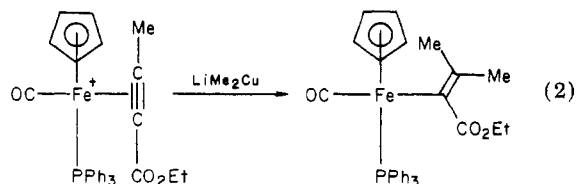


Figure 2. An ORTEP¹⁰ drawing of the contents of the unit cell of the above. The origin is at the front lower left hand corner with a horizontal, b back into the paper, and c vertical.

dihedral angles and nonbonded distances are in Table IV. An ORTEP¹⁰ drawing of an individual molecule is shown in Figure 1. Figure 2 shows an ORTEP drawing of the unit cell contents.

Results

The reaction of LiMe_2Cu and $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(\eta^2\text{-MeC}\equiv\text{CCO}_2\text{Et})]\text{BF}_4$ produces the alkenyl isomer shown in eq 2. The iron starting material for this



(10) Johnson, C. A. ORTEP II, "A Fortran Thermal-Ellipsoid Plot Program For Crystal Structure Illustrations", ORNL-3974, 1970.

Table II. Positional Parameters and Their Estimated Standard Deviations

atom	x	y	z	atom	x	y	z
P	0.01819 (6)	0.22805 (3)	0.30169 (8)	C(1P3)	-0.1299 (3)	0.1610 (2)	0.1071 (4)
Fe	0.17169 (3)	0.16434 (1)	0.42233 (4)	C(2P3)	-0.1644 (3)	0.1787 (2)	-0.0588 (4)
C(6P1)	-0.2282 (3)	0.2543 (2)	0.3433 (4)	C(1C)	0.1631 (3)	0.1155 (2)	0.1721 (4)
C(1P1)	-0.0829 (2)	0.2590 (1)	0.4250 (3)	C(2C)	0.1194 (4)	0.0536 (2)	0.2521 (4)
C(2P1)	-0.0141 (3)	0.2945 (2)	0.6022 (4)	C(3C)	0.2339 (4)	0.0606 (2)	0.4052 (5)
C(3P1)	-0.0877 (3)	0.3240 (2)	0.6960 (4)	C(4C)	0.3501 (4)	0.1265 (2)	0.4267 (4)
C(4P1)	-0.2291 (3)	0.3192 (2)	0.6132 (4)	C(5C)	0.3097 (3)	0.1632 (2)	0.2812 (4)
C(5P1)	0.3003 (3)	0.2837 (2)	0.4360 (4)	C(1)	0.0738 (3)	0.1337 (2)	0.5485 (4)
C(1P2)	0.0789 (3)	0.3183 (1)	0.2232 (3)	O(1)	0.0093 (3)	0.1117 (2)	0.6324 (4)
C(2P2)	0.1805 (3)	0.3235 (2)	0.1450 (4)	C(1V)	0.3181 (3)	0.2539 (2)	0.6235 (3)
C(3P2)	0.2304 (3)	0.3904 (2)	0.0845 (4)	C(2V)	0.3935 (3)	0.2481 (2)	0.7856 (4)
C(4P2)	0.1830 (4)	0.4568 (2)	0.1101 (5)	C(3V)	0.3725 (4)	0.1722 (2)	0.8516 (4)
C(5P2)	0.0781 (4)	0.4520 (2)	0.1856 (5)	C(4V)	0.5155 (4)	0.3184 (2)	0.9183 (4)
C(6P2)	0.0289 (3)	0.3833 (2)	0.2426 (4)	C(5V)	0.3658 (3)	0.3309 (2)	0.5794 (3)
C(3P3)	-0.2738 (4)	0.1260 (2)	-0.1998 (4)	O(1V)	0.4450 (2)	0.3480 (1)	0.4984 (3)
C(4P3)	-0.3542 (4)	0.0549 (2)	-0.1829 (5)	O(2V)	0.3111 (2)	0.3855 (1)	0.6371 (3)
C(5P3)	-0.3224 (3)	0.0365 (2)	-0.0167 (6)	C(6V)	0.3581 (4)	0.4655 (2)	0.6067 (4)
C(6P3)	-0.2109 (3)	0.0878 (2)	0.1238 (5)	C(7V)	0.2781 (7)	0.5116 (2)	0.6834 (7)

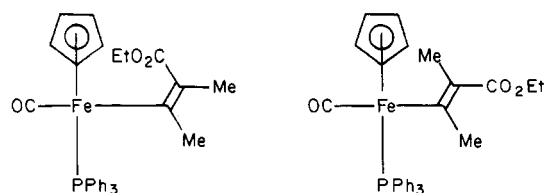
Thermal Parameters and Their Estimated Standard Deviations [$U(I,J)$]^a

atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
P	0.0298 (3)	0.0356 (3)	0.0380 (3)	0.0092 (2)	0.0134 (3)	0.0091 (2)
Fe	0.0363 (2)	0.0359 (2)	0.0451 (2)	0.0145 (1)	0.0202 (2)	0.0120 (2)
C(6P1)	0.031 (1)	0.058 (2)	0.057 (2)	0.015 (1)	0.012 (1)	0.010 (1)
C(1P1)	0.030 (1)	0.038 (1)	0.046 (1)	0.0118 (9)	0.014 (1)	0.014 (1)
C(2P1)	0.042 (1)	0.044 (1)	0.043 (1)	0.016 (1)	0.018 (1)	0.014 (1)
C(3P1)	0.050 (2)	0.060 (2)	0.052 (2)	0.021 (1)	0.025 (1)	0.015 (1)
C(4P1)	0.050 (2)	0.058 (2)	0.071 (2)	0.022 (1)	0.033 (2)	0.013 (2)
C(5P1)	0.037 (1)	0.063 (2)	0.068 (2)	0.016 (1)	0.020 (1)	0.010 (2)
C(1P2)	0.034 (1)	0.042 (1)	0.032 (1)	0.007 (1)	0.004 (1)	0.009 (1)
C(2P2)	0.040 (1)	0.059 (2)	0.056 (2)	0.010 (1)	0.017 (1)	0.023 (1)
C(3P2)	0.047 (2)	0.074 (2)	0.063 (2)	0.012 (1)	0.021 (1)	0.033 (2)
C(4P2)	0.076 (2)	0.059 (2)	0.056 (2)	-0.000 (2)	0.014 (2)	0.023 (2)
C(5P2)	0.084 (2)	0.048 (2)	0.063 (2)	0.020 (2)	0.027 (2)	0.020 (1)
C(6P2)	0.065 (2)	0.040 (1)	0.049 (2)	0.015 (1)	0.019 (1)	0.014 (1)
C(3P3)	0.054 (2)	0.088 (2)	0.053 (2)	0.021 (2)	0.008 (2)	-0.006 (2)
C(4P3)	0.044 (2)	0.070 (2)	0.079 (3)	0.014 (2)	0.007 (2)	-0.023 (2)
C(5P3)	0.041 (2)	0.047 (2)	0.105 (3)	0.005 (1)	0.018 (2)	-0.002 (2)
C(6P3)	0.048 (2)	0.046 (1)	0.077 (2)	0.008 (1)	0.021 (2)	0.010 (1)
C(1P3)	0.032 (1)	0.046 (1)	0.050 (2)	0.008 (1)	0.015 (1)	0.003 (1)
C(2P3)	0.047 (2)	0.068 (2)	0.044 (2)	0.014 (1)	0.009 (1)	0.006 (1)
C(1C)	0.050 (2)	0.060 (2)	0.052 (2)	0.019 (1)	0.022 (1)	-0.003 (1)
C(2C)	0.069 (2)	0.038 (1)	0.071 (2)	0.014 (1)	0.031 (2)	0.002 (1)
C(3C)	0.074 (2)	0.048 (2)	0.085 (2)	0.037 (2)	0.039 (2)	0.019 (2)
C(4C)	0.061 (2)	0.074 (2)	0.059 (2)	0.045 (2)	0.021 (2)	0.006 (2)
C(5C)	0.047 (2)	0.060 (2)	0.060 (2)	0.020 (1)	0.029 (1)	0.002 (1)
C(1)	0.050 (2)	0.054 (2)	0.079 (2)	0.025 (1)	0.038 (2)	0.037 (2)
O(1)	0.100 (2)	0.094 (2)	0.136 (3)	0.045 (2)	0.085 (2)	0.072 (2)
C(1V)	0.041 (1)	0.047 (1)	0.040 (1)	0.021 (1)	0.020 (1)	0.012 (1)
C(2V)	0.053 (2)	0.072 (2)	0.037 (1)	0.030 (1)	0.015 (1)	0.010 (1)
C(3V)	0.093 (3)	0.079 (2)	0.051 (2)	0.045 (2)	0.032 (2)	0.031 (2)
C(4V)	0.073 (2)	0.087 (3)	0.047 (2)	0.025 (2)	0.002 (2)	0.003 (2)
C(5V)	0.030 (1)	0.048 (1)	0.040 (1)	0.011 (1)	0.011 (1)	0.007 (1)
O(1V)	0.044 (1)	0.073 (1)	0.072 (2)	0.015 (1)	0.035 (1)	0.018 (1)
O(2V)	0.049 (1)	0.0401 (9)	0.055 (1)	0.0118 (8)	0.0262 (9)	0.0078 (8)
C(6V)	0.081 (2)	0.036 (1)	0.064 (2)	0.008 (1)	0.032 (2)	0.011 (1)
C(7V)	0.183 (5)	0.060 (2)	0.098 (3)	0.064 (3)	0.073 (3)	0.020 (2)

^a The form of the anisotropic thermal parameter is $\exp(-2(PI)^2(U(1,1)h^2a^2 + U(2,2)h^2b^2 + U(3,3)l^2c^2 + 2U(1,2)hka b \cos(\gamma) + 2U(1,3)hla c \cos(\beta) + 2U(2,3)kib c \cos(\alpha)))$.

reaction is prepared in CH₂Cl₂ by mixing (η^5 -C₅H₅)Fe(CO)(PPh₃)I, AgBF₄, and MeC≡CCO₂Et.^{2c} Although the π complex is not very stable, its formation is readily monitored visually because the solution turns from green to red. In order to avoid displacement of the alkyne in reaction 2 by THF or iodide ions present in the LiMe₂Cu solution, both the THF solvent and the solution of LiMe₂Cu are prechilled to -78 °C prior to addition to the cooled reaction flask containing the π -alkyne complex. Failure to follow these precautions can lead to the formation of (η^5 -C₅H₅)FeCO(PPh₃)I as a byproduct. Once formed, the σ -alkenyl complex is thermally stable and only slowly decomposes in air. Note that none of the other two

isomers, as pictured below, that could have formed in the reaction were observed.



Description of the Structure

Of the three possible alkene product isomers that could

Table III. Bonded Distances (Å) and Angles (Deg) with Esd's in Parentheses

Fe-P	2.2236 (8)	C(2V)-C(4V)	1.529 (4)	C(5P3)-C(6P3)	1.365 (4)
Fe-C(1)	1.724 (4)	C(5V)-O(1V)	1.225 (4)	C(6P3)-C(1P3)	1.403 (4)
Fe-C(1V)	2.030 (2)	C(5V)-O(2V)	1.357 (4)	C(1P1)-C(2P1)	1.398 (4)
Fe-C(1C)	2.128 (4)	O(2V)-C(6V)	1.458 (4)	C(2P1)-C(3P1)	1.400 (5)
Fe-C(2C)	2.116 (3)	C(6V)-C(7V)	1.526 (8)	C(3P1)-C(4P1)	1.373 (4)
Fe-C(3C)	2.104 (4)	C(1)-O(1)	1.149 (6)	C(4P1)-C(5P1)	1.400 (5)
Fe-C(4C)	2.108 (4)	C(1C)-C(2C)	1.403 (5)	C(5P1)-C(6P1)	1.380 (5)
Fe-C(5C)	2.127 (4)	C(2C)-C(3C)	1.395 (5)	C(6P1)-C(1P1)	1.407 (4)
Fe-Center* ^a	1.745 (4)	C(3C)-C(4C)	1.391 (5)	C(1P2)-C(2P2)	1.396 (5)
P-C(1P3)	1.841 (2)	C(4C)-C(5C)	1.435 (5)	C(2P2)-C(3P2)	1.389 (5)
P-C(1P1)	1.820 (3)	C(5C)-C(1C)	1.451 (4)	C(3P2)-C(4P2)	1.407 (6)
P-C(1P2)	1.840 (3)	C(1P3)-C(2P3)	1.405 (5)	C(4P2)-C(5P2)	1.410 (7)
C(1V)-C(2V)	1.352 (4)	C(2P3)-C(3P3)	1.367 (4)	C(5P2)-C(6P2)	1.395 (5)
C(1V)-C(5V)	1.462 (4)	C(3P3)-C(4P3)	1.374 (6)	C(6P2)-C(1P2)	1.392 (5)
C(2V)-C(3V)	1.504 (5)	C(4P3)-C(5P3)	1.412 (7)		
P-Fe-C(1)	89.8 (1)	C(1V)-C(5V)-O(1V)	126.7 (3)	C(5P3)-C(6P3)-C(1P3)	120.7 (4)
P-Fe-C(1V)	99.59 (9)	C(1V)-C(5V)-O(2V)	112.7 (3)	P-C(1P1)-C(2P1)	120.4 (2)
P-Fe-Center*	124.7 (1)	O(1V)-C(5V)-O(2V)	120.6 (3)	P-C(1P1)-C(6P1)	121.5 (2)
C(1)-Fe-C(1V)	91.1 (1)	C(5V)-O(2V)-C(6V)	116.8 (3)	C(6P1)-C(1P1)-C(2P1)	117.9 (3)
C(1)-Fe-Center*	125.4 (2)	O(2V)-C(6V)-C(7V)	104.2 (3)	C(1P1)-C(2P1)-C(3P1)	121.1 (3)
C(1V)-Fe-Center*	118.2 (2)	Fe-C(1)-O(1)	178.6 (4)	C(2P1)-C(3P1)-C(4P1)	119.9 (3)
Fe-P-C(1P3)	110.04 (9)	C(5C)-C(1C)-C(2C)	108.0 (3)	C(3P1)-C(4P1)-C(5P1)	120.0 (4)
Fe-P-C(1P1)	117.81 (9)	C(1C)-C(2C)-C(3C)	108.2 (3)	C(4P1)-C(5P1)-C(6P1)	120.2 (3)
Fe-P-C(1P2)	120.62 (9)	C(2C)-C(3C)-C(4C)	109.8 (3)	C(5P1)-C(6P1)-C(1P1)	120.9 (3)
C(1P3)-P-C(1P1)	100.7 (1)	C(3C)-C(4C)-C(5C)	108.1 (3)	P-C(1P2)-C(2P2)	119.7 (2)
C(1P3)-P-C(1P2)	103.2 (1)	C(4C)-C(5C)-C(1C)	105.9 (3)	P-C(1P2)-C(6P2)	122.1 (2)
C(1P1)-P-C(1P2)	101.9 (1)	P-C(1P3)-C(2P3)	123.2 (2)	C(6P2)-C(1P2)-C(2P2)	118.3 (3)
Fe-C(1V)-C(2V)	127.8 (2)	P-C(1P3)-C(6P3)	118.7 (2)	C(1P2)-C(2P2)-C(3P2)	121.9 (3)
Fe-C(1V)-C(4V)	115.7 (2)	C(6P3)-C(1P3)-C(2P3)	118.1 (2)	C(2P2)-C(3P2)-C(4P2)	119.3 (4)
C(2V)-C(1V)-C(5V)	115.6 (2)	C(1P3)-C(2P3)-C(3P3)	120.8 (3)	C(3P2)-C(4P2)-C(5P2)	119.4 (3)
C(1V)-C(2V)-C(3V)	124.4 (2)	C(2P3)-C(3P3)-C(4P3)	121.0 (4)	C(4P2)-C(5P2)-C(6P2)	119.6 (4)
C(1V)-C(2V)-C(4V)	122.5 (3)	C(3P3)-C(4P3)-C(5P3)	118.9 (3)	C(5P2)-C(6P2)-C(1P2)	121.4 (4)
C(3V)-C(2V)-C(4V)	113.0 (3)	C(4P3)-C(5P3)-C(6P3)	120.4 (3)		

^a Center of cyclopentadiene ring. Esd's are approximate.

have formed in the reaction, the crystal structure (Figure 1) clearly shows that the major product is the *gem*-dimethyl isomer. This decision could not be made by ¹H or ¹³C NMR spectroscopy. The structure may be described as isolated molecules separated by normal van der Waals distances. In space group *P* $\bar{1}$ with two molecules per unit cell, the two optical enantiomers of the chiral complex are related by a center of symmetry. The environment of the iron atom, assuming one coordination site for the center of the cyclopentadienyl (Cp) ring, is distorted tetrahedral. As expected (see Table III), the angles involving the center of the Cp ring (Center*): (Center*)-Fe-P, (Center*)-Fe-C(1), Center*-Fe-C(1V), are all $\sim 120^\circ$ whereas the other three angles about Fe are $\sim 90^\circ$, indicating the steric effect of the Cp ring. The P-C distances are normal and within less than one standard deviation of the average, 1.840 Å. However, the Fe-P-C angles are not so regular, varying from 110 to 120° (vide infra). The Fe-P bond length of 2.224 (1) Å is normal compared to other Fe-P bonds in similar systems.¹¹ The Cp C-C distances and the Fe-C(Cp) distances are normal for this type of organometallic structure, as are the Fe-C(1) and C≡O and C-C phenyl ring distances.

An examination of the dihedral angles between normals to planes shows that Fe,C(1V),C(2V),C(3V),C(4V) are all essentially coplanar. This coupled with the Fe-C(1V) distance of 2.030 (2) Å clearly specifies this as an Fe-C single bond in which the carbon atom is sp² hybridized. This distance is significantly longer than that found by Churchill and Wormald^{12a} in Cp(CO)₂FeC=CC=CFe-

(CO)₂Cp at 1.987 (5) Å.^{12b} The potential for multiple bonding is apparently reduced by the facts that the dihedral angle between the normals to the planes: Center*-Fe-C(1V) and Fe-C(1V)-C(2V) etc. is 82.8 (2)° and the angle between the Fe-CO line and the normal to the Fe-C(1V)-C(2V) etc. plane is 40.4 (1)°. The former angle delineates the π* orbital of the alkene as 7.2 (1)° from the Center*-Fe-C(1V) plane, and the latter describes the orientation of this orbital relative to the Fe-CO line. In order to obtain efficient overlap with the metal HOMO as calculated by Hoffmann et al.,¹³ the alkene would have to be oriented along the Fe-CO line.

The orientation of the alkene relative to the ester group is of some interest. One might expect the carbonyl of the ester to be coplanar with the alkene. However, the plane of the carbonyl (Table IV) is almost orthogonal to the alkene (planes 1-2) at 78.5 (1)°. This orientation is determined (Table IV) primarily by nonbonding interactions with phenyl ring 2 of the triphenylphosphine moiety. Neglecting hydrogen atoms, the entire ester group is planar within 8°. This geometry is probably also a result of the interactions with ring 2. These same interactions are no doubt responsible for the more open Fe-P-C(1P2) angle of 120.62 (9)°. The observed molecular conformation in the solid is very compact, and although Figure 1 makes it appear that there exists a large cavity between the Cp and the phenyl rings, that is not the case. For example: C-

(12) (a) Churchill, M. R.; Wormald, J. *Inorg. Chem.* 1969, 8, 1936. (b) For a discussion on Fe-C sp² bond lengths see also: Rybin, L. V.; Petrovskaya, E. A.; Batsanov, A. S.; Struchkov, Y. T.; Rybinskaya, M. I., *J. Organomet. Chem.* 1981, 212, 95. Lenhart, P. G.; Lukehart, C. M.; Warfield, L. T. *Inorg. Chem.* 1980, 19, 2343.

(13) Schilling, B. E. R.; Hoffmann, R.; Faller, J. W. *J. Am. Chem. Soc.* 1979, 101, 592.

(11) Miles, S. L.; Miles, D. L.; Bau, R.; Flood, T. C. *J. Am. Chem. Soc.* 1978, 100, 7278.

Table IV. Selected Nonbonded Distances (Å) and Dihedral Angles (Deg) between Plane Normals

C(1P2)-O(1V)	3.590 (3)	C(1)-C(1P1)	3.149 (4)
C(1P2)-C(5V)	3.378 (3)	C(1)-C(2P1)	3.237 (5)
C(1P2)-O(2V)	3.355 (3)	C(1)-C(6P3)	3.627 (4)
C(2P2)-C(1C)	3.686 (5)	C(1)-C(1P3)	3.753 (4)
C(2P2)-C(5C)	3.586 (5)	C(1C)-C(1P3)	3.224 (5)
C(2P2)-C(5V)	3.476 (4)	C(1C)-C(2P3)	3.822 (5)
C(2P2)-O(1V)	3.189 (3)	C(1C)-C(6P3)	3.648 (5)
C(2P2)-O(2V)	3.799 (4)	C(3V)-C(3C)	3.630 (5)
C(2P2)-C(6V)	3.864 (4)	C(3V)-C(4C)	3.458 (6)
C(3P2)-O(1V)	3.721 (4)	C(3V)-C(1)	3.131 (5)
C(4P2)-C(6V)	3.905 (5)	C(1V)-C(4C)	2.790 (5)
C(5P2)-C(6V)	3.684 (5)	C(1V)-C(5C)	3.072 (5)
C(5P2)-C(7V)	3.856 (6)	C(1V)-C(1)	2.688 (4)
C(6P2)-O(2V)	3.601 (4)		
C(6P2)-C(6V)	3.550 (4)		
C(6P2)-C(7V)	3.768 (5)		

plane	largest deviation
1, [Fe, C(1V), C(2V), C(3V), C(4V), C(5V)]	0.08 (1)
2, [C(1V), C(5V), O(1V), O(2V)]	0.01 (1)
3, [O(2V), C(6V), C(7V)]	
4, ring 1	0.01 (1)
5, ring 2	0.02 (1)
6, ring 3	0.01 (1)
7, [C(1V)-Fe-center*]	
8, [C(1)-Fe-center*]	
9, [Fe-C(1V)-C(2V)]	
10, [C(1V)-Fe-P]	
11, [C(1V)-C(2V)-C(4V)]	
12, [C(1C), C(2C), C(3C), C(4C), C(5C)]	0.01 (1)
13, Fe-C(1)	

Angles between Plane Normals

plane 1-plane 2	78.5 (1)	plane 7-plane 8	66.0 (1)
plane 1-plane 7	82.8 (2)	plane 7-plane 9	77.6 (1)
plane 1-plane 12	25.6 (1)	plane 7-plane 10	41.8 (1)
plane 1-line 13	40.4 (1)	plane 8-plane 10	89.1 (1)
plane 2-plane 3	3.5 (1)	plane 9-plane 11	8.5 (1)
plane 2-plane 5	7.3 (1)	plane 12-line 13	54.5 (1)
plane 3-plane 5	7.3 (1)		

(2P2)-C(1C) = 3.686 (5) Å, C(2P2)-C(5C) = 3.586 (5) Å, C(2P2)-C(5V) = 3.467 (4) Å. The environment of the alkene group is very crowded. Counterclockwise rotation about the Fe-C(IV) bond (when viewing down the C(I-V)-Fe bond) is restricted by the interaction between the ester group and phenyl ring 2 and the fact that the C(3V) to C(1) distance is 3.131 (5) Å. Clockwise rotation about this bond is restricted by the fact that the C(3V)-C(4C) distance is already close at 3.458 (6) Å.

Discussion

The observed regiochemistry of the addition reaction reported here is the same as that observed for the analogous reaction carried out on the free alkyne.^{5,14} A recent theoretical paper⁴ has considered both the basis for activation of alkenes bonded to $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^+$ and the effect of donor atom alkene substituents on the regio-

chemistry of the addition reaction. These arguments should be readily applicable to η^2 -alkyne complexes acting as two-electron donors.¹⁵ In this work, it was suggested that the origin of the activation of the alkene in the addition reaction is slippage of the metal along the π bond to an intermediate resembling η^1 coordination. Experimental work with vinyl ether π complexes has shown that nucleophiles add specifically to the carbon bearing the donor group.^{3a} It was argued that the donor substituent should favor slippage away from the substituent (this slippage in the ground state has very recently been verified crystallographically^{3c}), thus leading to the proper intermediate for the observed regiochemistry. The effect of an electron acceptor substituent was not as clear and "further theoretical and experimental study" was called for. The results reported here demonstrate that the addition occurred at the alkyne carbon away from the acceptor substituent. Note that this result is *opposite* to that which would be expected on a purely steric grounds where one would expect that the metal would slip to the side away from the larger ester substituent. Thus, the regiochemistry of the reaction appears to be dominated by electronic effects. In a reaction that is probably quite similar to that reported here, methoxide was shown to also add away from the electron-withdrawing CF_3 group in an $(\eta^2\text{-CF}_3\text{C}\equiv\text{CH})\text{Pt}^{\text{II}}$ complex.¹⁶ A very recent paper¹⁷ has shown similarly that nucleophilic addition to CH_2CHCN and $\text{CH}_2\text{CHCO}_2\text{Me}$ π coordinated to Pt(II) takes place at the carbon not bearing the acceptor substituent.

We note that although the regiochemistry of the reaction reported here seems to be controlled by the electronic characteristics of the alkyne substituents, certainly the steric and electronic requirements of the whole molecule really need to be taken into account. This is particularly true in this case because the other ligands coordinated to the iron each have quite different electronic and steric characteristics. Thus, the regiochemistry could also be influenced or controlled by a preferred orientation of the alkyne dictated mainly by the other ligands. It has been shown that both the location of nucleophilic addition reactions¹⁸ and the preferred orientation of π -back-bonding ligands can be controlled by the other ligands of the π complex.¹³ Moreover, the steric requirements of the product of these reactions could be very important. The molecule discussed here is quite crowded, particularly in the region of phenyl ring 2, the C(5C) atom, and the ester group. The special planar arrangement of the ester group observed in this structure allows it to fit even though this forces a loss of conjugation between the carbon-carbon and carbon-oxygen double bonds. A larger substituent would have difficulty fitting into this space, and this fact could also control the regiochemistry of the reaction. Additional substituents are being tested at present and attempts are underway to crystallize the unstable π complex starting

(14) A reviewer suggested that the product could be formed by the cuprate first reacting with free alkyne followed by reaction with iron. Although this seemed unlikely to us in view of the variety of nucleophiles and alkynes (most of which, like 2-butyne, are not activated toward nucleophilic addition) that have been shown to be successful in this reaction,² taken in the context of this paper, it was a reasonable possibility. Accordingly, $[\text{CpFeCO}(\text{PPh}_3)(\text{THF})]^+$ was prepared in THF and cooled to -78°C . In a separate flask, LiMe_2Cu was added to a solution of $\text{MeC}\equiv\text{CCO}_2\text{Et}$ in THF at -78°C . After 1 h, the two solutions were mixed. Workup as in the Experimental Section for the complex studied here did not yield any of this complex.

(15) This assumes that the nucleophile does not react with the non-coordinated π orbital perpendicular to the Fe-alkyne axis. The well-known activation of alkenes bonded to this cationic iron moiety should also occur with the π orbital of the alkyne bonded to the metal. Also, we have reported similar addition reactions at low temperatures to π complexes of 2-butyne. In these reactions, the perpendicular π bond is not activated by an ester functional group and should not be very reactive toward nucleophiles. Thus in this case, and presumably the case reported here, the π orbital bonded to the metal should be the site of nucleophilic addition.

(16) Chisholm, M. H.; Clark, H. C.; Manger, L. E. *Inorg. Chem.* 1972, 11, 1269.

(17) Green, M.; Sarhan, J. K. K.; Al-Najjar, I. M. *J. Chem. Soc., Dalton, Trans.* 1981, 1565.

(18) Faller, J. W.; Rosan, A. M. *Ann. N.Y. Acad. Sci.* 1977, 295, 186.

material for an X-ray structural investigation.

Acknowledgment is made to the National Science Foundation for its support of this research through Grant CHE8019513 (D.L.R.). We also thank the University of South Carolina for funds used to purchase the diffractometer.

Registry No. ($\eta^6\text{-C}_6\text{H}_6$)Fe(CO)(PPh₃)[C(CO₂Et)C(Me)₂], 80485-08-1; ($\eta^6\text{-C}_6\text{H}_6$)Fe(CO)(PPh₃)I, 12099-18-2; MeC≡CCO₂Et, 4341-76-8; [$(\eta^6\text{-C}_6\text{H}_6)$ Fe(CO)(PPh₃)($\eta^2\text{-MeC}\equiv\text{CCO}_2\text{Et}$)]BF₄, 80501-96-8.

Supplementary Material Available: Listings of structural factors (28 pages). Ordering information is given on any current masthead page.

Crystal and Molecular Structure of Dicarbonyl(hexaethylbenzene)(triethylphosphine)chromium (0). A Novel Example of Conformational Variability in Hexaethylbenzene π Complexes

Geoffrey Hunter,^{*1a} John F. Blount,^{1b} James R. Damewood, Jr.,^{1c} Daniel J. Iverson,^{1c} and Kurt Mislow^{*1c}

Department of Chemistry, The University, Dundee DD1 4HN, Scotland, Chemical Research Department, Hoffmann-La Roche, Inc., Nutley, New Jersey 07110, and Department of Chemistry, Princeton University, Princeton, New Jersey 08544

Received October 8, 1981

The crystal and molecular structure of the title compound, (HEB)Cr(CO)₂PEt₃ (1), has been determined: space group $P2_1/c$, $a = 9.729$ (4) Å, $b = 18.353$ (6) Å, $c = 29.869$ (12) Å, $\beta = 98.26$ (2)°, and $Z = 8$, with two different conformations (1A and 1B) present in equal population. In 1A one terminal methyl (C(31)) projects toward the complexed (proximal) side of the ring while the other five project toward the uncomplexed (distal) side. The molecule is in an eclipsed conformation, with the PEt₃ ligand anti to C(31); the resulting structure has near C_6 symmetry. Conformation 1A is unprecedented among HEB transition-metal complexes. In 1B all six methyls are distal and the molecule adopts a staggered arrangement. The resulting conformation closely resembles that of the previously reported (HEB)Cr(CO)₂PPh₃ (2), and a detailed comparison of these structures has served to clarify the origin of the steric effect responsible for this conformational preference. Arguments are advanced that four diastereomeric HEB π complexes are energetically favored and that the range of stabilities spanned by these four is less than the calculated range spanned by the corresponding uncomplexed HEB conformers. Structures corresponding to three of these four isomers have been experimentally realized in this and a previous study.

Special interest in hexaethylbenzene (HEB) derives from its role as a simple representative of a class of hexaalkylbenzenes and hexaalkylbenzene analogues in which the alkyl groups point alternately up and down around the ring perimeter; such alternation is found in HEB itself and in its tricarbonylchromium and -molybdenum π complexes.² In a previous study² we had found that replacement of one carbonyl group in tricarbonyl(hexaethylbenzene)chromium(0) by triphenylphosphine leads to a striking change in the conformation of the arene moiety: whereas the conformation of the tricarbonyl complex is eclipsed, with the terminal methyl groups alternately projecting toward the complexed (proximal) and uncomplexed (distal) side of the ring, in the dicarbonyl triphenylphosphine complex the conformation is staggered and all six methyls are distal. This conformational change was found to persist in solution and was ascribed to steric effects of the triphenylphosphine group. The present work was initiated in the hope that a study of conformational preferences in dicarbonyl(hexaethylbenzene)(triethyl-

Table I. Selected Bond Lengths for 1A and 1B^a

atoms ^b	1A	1B
C(11)-C(12)	1.412	1.423
C(12)-C(13)	1.428	1.425
C(13)-C(14)	1.432	1.413
C(14)-C(15)	1.414	1.426
C(15)-C(16)	1.432	1.412
C(16)-C(11)	1.412	1.426
Cr-C(11)	2.224	2.184
Cr-C(12)	2.201	2.196
Cr-C(13)	2.250	2.231
Cr-C(14)	2.263	2.272
Cr-C(15)	2.232	2.256
Cr-C(16)	2.209	2.232
Cr-C(1)	1.809	1.812
Cr-C(2)	1.790	1.817
Cr-P	2.308	2.324
C(1)-O(1)	1.164	1.175
C(2)-O(2)	1.174	1.168

^a In angstrom units. Estimated standard deviations for bond lengths are 0.002-0.009 and 0.001-0.009 Å for 1A and 1B, respectively. ^b Numbering as in Figures 1, 2, and 4.

phosphine)chromium(0) (1) might serve to clarify the origin of this remarkable steric effect in the previously studied dicarbonyl(hexaethylbenzene)(triphenyl-

(1) (a) University of Dundee. (b) Hoffmann-La Roche, Inc. (c) Princeton University.

(2) (a) Hunter, G.; Iverson, D. J.; Mislow, K.; Blount, J. F. *J. Am. Chem. Soc.* 1980, 102, 5942. (b) Iverson, D. J.; Hunter, G.; Blount, J. F.; Damewood, J. R., Jr.; Mislow, K. *Ibid.* 1981, 103, 6073.