Table VII. Some Magnetic and Structural Features

complex	Cu-Cu, Å	ϕ(Cu–O–Cu), deg	τ, deg	$2J$, cm^{-1} [b]
$[Cu(5\text{-}Cl\text{-}salpn)]_2$ [a,c]	2.92	103.7	13.7	$\geq$800
$[Cu(3\text{-}NO_2\text{-}salpn)]_2$ [a,c]	3.01	103.5	9.6	$\geq$800
$[Cu(5,6\text{-}benzo\text{-}salpn)]_2$ [a,c]	3.04	104.0	10.4	$\geq$800
$[Cu(5\text{-}NO_2\text{-}salpn)]_2$ [a,c]	2.96	106.0	4.0	$\geq$1000
2 [e]	3.00	103.2	6.8	$\geq$600
3 [e]	3.01	104.1	1.0	$\geq$600

[a] salpn = salicylaldehyde 3-aminopropanol Schiff base. [b] Because of the very low observed paramagnetism (no maximum in the magnetic susceptibility vs. temperature curve at accessible temperatures), the values of $2J$ cannot be estimated accurately, though lower limits are clearly implied. [c] Reference 23. [d] Reference 24. [e] Reference 8 and this work.

in the alkoxy chelate series is probably due to the different strain effects produced by the wide variety of multidentate chelates employed in the comparison.

Table VII compares the various parameters of the complexes **1** and **2** with some other Cu(II) complexes of tridentate alkoxy ligands. There is obviously a general correlation between Cu–Cu distances, ϕ, τ, and $2J$ values, but no direct linear relationship is observed.

The effect of changing the chelate ring size from six to seven members on going from **2** to **1** is a barely significant decrease in the magnetic moment (from 0.57 to 0.38 μ_B at 300 K), consistent with the small changes in geometry around Cu^{2+}. In the absence of data on any other complex containing a 7-membered chelate ring in this position, it is difficult to suggest why compound **1** is not completely diamagnetic, since it appears to contain the ideal geometry ($\tau \approx 0°$) for complete coupling.

The dramatic decrease in magnetic moment as the chelate ring containing the bridging oxygen atom increases from five to six members is consistent with previous observations[19] and is associated with structural effects discussed above. As the bridging oxygen becomes trigonal, rather than tetrahedral, spin pairing between Cu^{2+} ions is facilitated because of more favorable orbital overlap.[25] Interactions between Cu^{2+} ions in complexes containing 5-membered chelate rings, where association into tetranuclear units may occur, are small but detectable, and we are currently undertaking a study on a group of such compounds in an attempt to elucidate further the relationship between structure and magnetic properties.

Acknowledgment. This work was supported by Grant No. A-259 from the Robert A. Welch Foundation (A.E.M.) and by the National Research Council of Canada (C.J.W.).

Supplementary Material Available: Tables of calculated and observed structure factors for complex **1** (Table A) and complex **2** (Table B) (17 pages). Ordering information is given on any current masthead page.

---

(24) Lemay, H. D.; Hodgson, D. J.; Pruettiangkura, P.; Theriot, L. J. *J. Chem. Soc., Dalton Trans.* **1979**, 781.

(25) Muto, Y.; Kato, M.; Jonassen, H. B.; Ramaswamy, H. M. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1535.

(26) Johnson, C. K. Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, Tenn., 1965.

Contribution from the Departments of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Y6, and Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

Crystal and Molecular Structure of Two Isomeric Iron Carbonyl Derivatives Which Contain an Extensively Rearranged Bis(tertiary phosphine)

ROGER E. COBBLEDICK, WILLIAM R. CULLEN,* FREDERICK W. B. EINSTEIN,*
and MANGAYARKARASY WILLIAMS

Received June 13, 1980

The bis(tertiary phosphines) $(C_6H_{11})_2PC{=}CP(C_6H_{11})_2(CF_2)_n$ [A (n = 2), B (n = 3)] and $(C_6H_5)_2PC{=}C(CF_2)_2C{=}CP(C_6H_5)_2(CF_2)_2$ (C) react with iron carbonyls to give a number of products of known structure, namely, $(L–L)Fe(CO)_3$ [(L–L) = A or B], $(L–L)Fe_2(CO)_6$ [(L–L) = A], and $(L–L)Fe_2(CO)_8$ [(L–L) = C]. In addition two isomers of formula $(L–L)Fe_2(CO)_6$ (V and VI) can be isolated from the reactions of C, and the structures of these were determined by conventional X-ray crystallographic techniques. The cell constants for V are a = 15.348 (6) Å, b = 9.231 (5) Å, c = 26.839 (12) Å, and β = 104.90 (3)°; the space group is $P2_1/c$. The cell constants for VI are a = 12.45 (2) Å, b = 17.21 (5) Å, c = 18.86 (3) Å, and β = 97.67 (9)°; the space group is $P2_1/c$. The structures of V and VI were refined by full-matrix least-squares techniques to conventional R indices of 0.055 and 0.072, respectively. In IV the basic structure consists of two $Fe(CO)_3$ moieties bridged by two different phosphido groups. One of those groups is a $-\ddot{P}(C_6H_5)_2$ unit which has been cleaved from the ligand and the other is a $-\ddot{P}(C_6H_5)C{=}C(CF_2)_2C{=}C(C_6H_5)(CF_2)_2$ group formed by extensive rearrangement of the remainder of the ligand. The phenyl group migrates from the phosphorus to the end of the conjugated fluorocarbon chain. In VI, again two bridged $Fe(CO)_3$ fragments are present. One of these is a cleaved $-\ddot{P}(C_6H_5)_2$ group but the other is the intact remaining portion of the ligand which forms a metal–carbon σ bond to one iron atom and coordinates to the second iron with the remaining phosphorus atom. These unusual ligand fragmentation reactions are discussed in the light of related examples.

Introduction

The reactions of bis(tertiary phosphines and arsines) with metal carbonyls usually result in simple substitution of carbonyl groups.[1] In our laboratories we are currently interested in the properties of the fluorocarbon-bridged ligands A, B, and C, which belong to a class of compounds which have unsaturated bridging groups. In principle they could use the unsaturated bridge in bonding,[2-7] but in practice ligands related

---

* To whom correspondence should be addressed: W.R.C., University of British Columbia; F.W.B.E., Simon Fraser University.

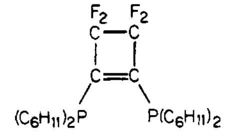
(1) McAuliffe, C. A.; Levason, W. "Phosphine, Arsine and Stibine Complexes of the Transition Elements"; Elsevier: New York, 1979.

0020-1669/81/1320-0186$01.00/0

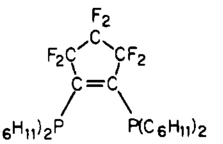
Table I. Preparative Data for New Complexes

L-L	iron carbonyl	reacn time, h	eluant diethyl ether:pet. ether	product	yield, %
A (0.28 g, 0.54 mmol)	$Fe(CO)_5$ (1.0 g, 5.4 mmol)	66	8:92	$(L\text{-}L)Fe(CO)_3$ (I)	45
			12:88	$(L\text{-}L)Fe_2(CO)_6$ (II)	2
A (0.50 g, 0.98 mmol)	$Fe_3(CO)_{12}$ (1.0 g, 1.98 mmol)	8.5	0:100	$(L\text{-}L)Fe(CO)_3$ (I)	33
			1:99	$(L\text{-}L)Fe_2(CO)_6$ (II)	11
B (0.26 g, 0.45 mmol)	$Fe(CO)_5$ (0.95 g, 4.84 mmol)	66	1:99	$(L\text{-}L)Fe(CO)_3$ (III)	40
C (0.36 g, 0.57 mmol)	$Fe(CO)_5$ (1.11 g, 5.7 mmol)	49	0:100	$(L\text{-}L)Fe_2(CO)_8$ (IV)	trace
			15:85	$(L\text{-}L)Fe_2(CO)_6$ (V)	1.9
			50:50	$(L\text{-}L)Fe_2(CO)_6$ (VI)	4.2
C (0.61 g, 0.099 mmol)	$Fe_3(CO)_{12}$ (1.07 g, 2.12 mmol)	6.5	0:100	$(L\text{-}L)Fe_2(CO)_8$ (IV)	trace
			8:92	$(L\text{-}L)Fe_2(CO)_6$ (V)	1.5
			15:83	$(L\text{-}L)Fe_2(CO)_6$ (VI)	12.4

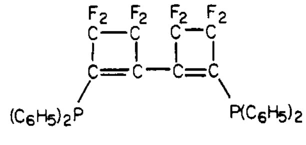
to A and B bind in a tridentate manner only in complexes of structure D ($n = 2$–4; $R_2E = (C_6H_5)_2P$ and/or $(CH_3)_2As$; M = Fe, Ru, Os).[8–10]



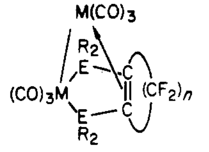
A



B

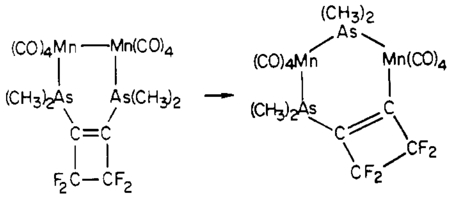


C



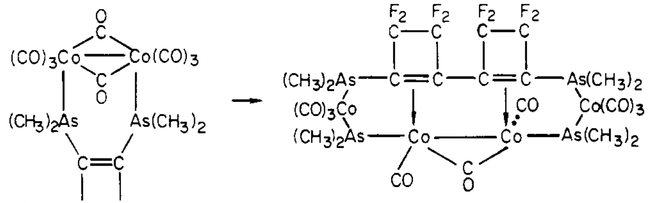
D

Some bis(tertiary arsines) such as $(CH_3)_2As\overline{C{=}CAs(CH_3)_2(C}F_2)_2$ show a remarkable ability to afford derivatives of metal carbonyl clusters, and here the mode of binding is invariably biligate bimetallic. This same ligand also forms complexes in which one $As(CH_3)_2$ moiety is cleaved from the ligand, a process which results in (a) the formation of a metal–cyclobutene σ bond with the cleaved group being accommodated elsewhere in the molecule (eq 1).[9b,11–14]



(1)

The alternative process (b) affords a complexed bicyclobuten-1-yl, through a coupling reaction, with the incorporation of the cleaved groups elsewhere in the molecule (eq 2).[15–18]



(2)

The work described in the present paper was initiated as part of a program designed to establish if bulky groups such as $(C_6H_{11})_2P$ would have any effect on the properties of the fluorocarbon-bridged bis(tertiary phosphines) (ligands A and B). In the case of C, which is itself of interest because it is photochromic,[21] we wished to establish if complexes like D could be obtained.

We were unable to prepare such a derivative. However, we describe below two products from C which involves cleavage of $(C_6H_5)_2P$ groups from the ligand. This had not been observed previously in our studies on ligands like A and B although in recent years a number of instances of cleavage of $(C_6H_5)_2P$ groups from $(C_6H_5)_3P$ and $(C_6H_5)_2PC{\equiv}CR$ have been noted.[22,23] In most instances the separated fragments are retained in the final product.

---

(2) Cullen, W. R. *Adv. Inorg. Chem. Radiochem.* **1972**, *15*, 323.
(3) Cullen, W. R.; Hou, F. L. *Can. J. Chem.* **1975**, *53*, 1735.
(4) Cullen, W. R.; Mihichuk, L. M. *Can. J. Chem.* **1976**, *54*, 2548.
(5) Cullen, W. R.; Davis, A. R.; Einstein, F. W. B.; Hazlett, J. D.; Wu, A. W. *Can. J. Chem.* **1976**, *54*, 2871.
(6) Cullen, W. R.; Williams, M.; Einstein, F. W. B.; Huang, C.-H. *J. Fluorine Chem.* **1978**, *11*, 365.
(7) Cullen, W. R.; Williams, M. *J. Fluorine Chem.* **1979**, *14*, 85.
(8) Einstein, F. W. B.; Trotter, J. *J. Chem. Soc. A* **1967**, 824.
(9) (a) Cullen, W. R.; Harborne, D. A.; Liengme, B. V.; Sams, J. R. *Inorg. Chem.* **1969**, *8*, 1464. (b) Chia, L. S.; Cullen, W. R.; Harborne, D. A. *Can. J. Chem.* **1972**, *50*, 2182. (c) Cullen, W. R.; Harborne, D. A. *Inorg. Chem.* **1970**, *9*, 1839. (d) Crow, J. P.; Cullen, W. R. *Ibid.* **1971**, *10*, 1529.
(10) Not all combinations symbolized in D have been prepared.
(11) (a) Chan, L. Y. Y.; Einstein, F. W. B. *J. Chem. Soc., Dalton Trans.* **1973**, 111. (b) Cullen, W. R.; Hou, F. L. *Can. J. Chem.* **1975**, *53*, 1735.
(12) (a) Crow, J. P.; Cullen, W. R.; Hou, F. L. *Inorg. Chem.* **1972**, *11*, 2125. (b) Einstein, F. W. B.; MacGregor, A. C. *J. Chem. Soc., Dalton Trans.* **1974**, 783.
(13) Cullen, W. R.; Harborne, D. A.; Liengme, B. V.; Sams, J. R. *Inorg. Chem.* **1970**, *9*, 702.
(14) (a) Roberts, P. J.; Penfold, B. R.; Trotter, J. *Inorg. Chem.* **1970**, *9*, 2137. (b) Einstein, F. W. B.; Pilotti, A. M.; Restivo, R. *Ibid.* **1971**, *10*, 1947. (c) Einstein, F. W. B.; Jones, R. D. G. *J. Chem. Soc., Dalton Trans.* **1972**, 2563.
(15) Crow, J. P.; Cullen, W. R. *Inorg. Chem.* **1971**, *10*, 2165.
(16) (a) Harrison, W.; Trotter, J. *J. Chem. Soc. A* **1971**, 1607. (b) Einstein, F. W. B.; Jones, R. D. G. *J. Chem. Soc., Dalton Trans.* **1972**, 2568.
(17) Electron counting for the product of eq 2 suggests that it is a dihydride.
(18) *cis*-$(CH_3)_2AsC(CF_3){=}C(CF_3)As(CH_3)_2$ can lose $As(CH_3)_2$ *and* F^- when heated with $Mn_2(CO)_{10}$. The resulting product has a bridging $-As(CH_3)_2$ group and an η^3-allyl group.[19] Bound η^3-allyl groups are also obtained when tertiary phosphines such as $(C_6H_{11})_2P\overline{C{=}CCl(C}F_2)_3$ are reacted with iron carbonyls.[20]
(19) Cullen, W. R.; Mihichuk, L.; Einstein, F. W. B.; Field, J. *J. Organomet. Chem.* **1974**, *73*, C53.
(20) (a) Cullen, W. R.; Williams, M. *Can. J. Chem.* **1980**, *58*, 143. (b) Cullen, W. R.; William, M.; Einstein, F. W. B.; Willis, A. C. *J. Organomet. Chem.* **1978**, *155*, 259.
(21) Cullen, W. R.; Williams, M. *J. Fluorine Chem.* **1979**, *13*, 85.
(22) See, for example: (a) Bruce, M. I.; Shaw, G.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1972**, 2094. (b) Lambert, R. F. *Chem. Ind. (London)* **1961**, 830. (c) Blickensderfer, J. R.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 2686. (d) Taylor, N. J.; Chieh, P. C.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1975**, 448. (e) Fahey, D. R.; Mahan, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 4499. (f) Mason, R.; Sotofte, L.; Robinson, S. D.; Uttley, M. F. *J. Organomet. Chem.* **1972**, *46*, C61. (g) Bradford, C. W.; Nyholm, R. S. *J. Chem. Soc., Dalton Trans.* **1973**, 529. (h) Gainsford, G. J.; Guss, R. M.; Ireland, P. R.; Mason, R. S.; Bradford, C. W.; Nyholm, R. S. *J. Organomet. Chem.* **1972**, *40*, C70.
(23) (a) Patel, H. A.; Fischer, R. G.; Carty, A. J.; Naik, D. V.; Palenik, G. J. *J. Organomet. Chem.* **1973**, *60*, C49. (b) O'Connor, T.; Carty, A. J.; Mathew, M.; Palenik, G. J. *Ibid.* **1972**, *38*, C15.

Table II. Analytical and Spectroscopic Data for New Complexes

			% C		% H		ν(CO), cm^{-1}				
compd[a,b]	color	mp, °C	calcd	found	calcd	found					
I	red	210	50.5	56.4	6.70	2.77	2000 (s)	1921 (s)	1910 (vs)		
II	orange	182	51.1	51.3	5.55	5.54	2050 (s) 1940 (m)	2022 (vs)	1980 (s)	1990 (s)	1955 (w)
III	red	212	55.2	55.3	6.26	6.30	1988 (s)	1917 (m)	1899 (s)		
IV	yellow						2062 (s)	1994 (s)	1964 (s, sh)	1954 (vs)	
V[c,d]	yellow	176	51.4	51.4	2.69	2.48	2063 (s) 1970 (m)	2025 (vs)	2005 (s)	1999 (sh)	1980 (s)
VI[c,d]	red	168	51.4	51.7	2.69	2.52	2062 (vw) 1970 (sh)	2030 (s)	2000 (s)	1990 (m)	1980 (m)

[a] See Table I for compound identification. [b] ^{19}F spectra (all multiplets): I, 108.3; II, 90.1, 92.3, 106.9, 109.3 (equal area); III, 108.8 (area 2), 126.8 (area 1); V, 107.6, 109.5, 111.2, 113.9 (equal area); VI, 107.4 (area 1), 110.5 (area 2), 113.4 (area 1). [c] Analytical data are for (L-L)$Fe_2(CO)_6 \cdot 0.5Et_2O$. [d] ^{31}P NMR (all multiplets): V, −136.1, −132.8 (total area 1), −92.69, −89.35 (total area 1); VI, −130.3, −129.5 (total area 1), −35.97, −35.11 (total area 1).

Experimental Section

The ligands A, B, and C were prepared as described in the literature.[6,7] Solution infrared spectra were recorded on a Perkin-Elmer 457 instrument. The solvent was cyclohexane. ^{19}F and ^{31}P NMR spectra were run on a Varian XL-100 spectrometer. The solvent was $CDCl_3$, and chemical shifts are given in ppm upfield from internal $CFCl_3$ (^{19}F) and upfield from external 85% H_3PO_4 (^{31}P). Mass spectra were measured with an AEI MS-9 instrument. Melting points were determined in open capillaries with use of a Gallenkamp apparatus and are uncorrected. Microanalyses were performed by Mr. Peter Borda, Chemistry Department, University of British Columbia.

Reaction of Bis(tertiary phosphines) A, B, and C with Iron Carbonyls. The following general procedure was used, and the details applying to specific complexes are listed in Table I.

A benzene solution (~8 mL) containing a 1:10 mole ratio of ligand to $Fe(CO)_5$ (or 1:2 mole ratio in the case of $Fe_3(CO)_{12}$) was heated in a Carius tube at 150 °C for 8.5–66 h. Removal of solvent gave a solid residue which was dissolved in dichloromethane or benzene and chromatographed on a Florisil column. The colored bands were eluted with mixtures of diethyl ether and petroleum ether (bp 40–60 °C). Removal of solvent gave the crude products which were usually recrystallized from hexane. Analytical and spectroscopic data for products are presented in Table II.

X-ray Diffraction Studies. Complex V. Crystals of V were grown from hexane as yellow plates. The space group and approximate unit cell parameters were determined from Weissenberg and precession photographs taken with use of Cu Kα radiation. Systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$ were consistent with the space group $P2_1/c$. A crystal of approximate dimensions 0.25 × 0.30 × 0.25 mm, mounted with b offset from the diffractometer ϕ axis, was used for the determination of accurate unit cell parameters and collection of intensity data. Accurate unit cell parameters were obtained by least-squares refinement of the setting angles of 12 reflections, having $2\theta > 25°$, measured on a Picker FACS-1 computer-controlled, four-circle diffractometer using Mo Kα radiation. The compound has a formula weight of 898.2 and crystallizes in the space group $P2_1/c$ with cell dimensions $a = 15.348$ (6) Å, $b = 9.231$ (5) Å, $c = 26.839$ (12) Å, $\beta = 104.90$ (3)°, and $V = 3674.6$ Å^3. $d_{\text{exptl}} = 1.60$ (flotation) and $d_{\text{calcd}} = 1.62$ g cm^{-3}, $Z = 4$, λ(Mo Kα_1) = 0.709 26 Å, μ(Mo Kα) = 9.89 cm^{-1}, and $T = 22$ (1) °C.

Intensity data for one quadrant were collected with the use of a scintillation counter with pulse-height analysis and graphite-monochromatized Mo Kα radiation. The θ–2θ scan technique was used, and data were collected in two sets. For reflections with $2\theta \leq 30°$ a scan of 1.4° base width was used with background counts for 10 s at both scan limits. Reflections having $30° < 2\theta \leq 40°$ were measured with a base width of 1.1° with 20-s background counts at the scan limits. For both sets the scan was extended to allow for spectral dispersion, and the scan rate was 2° min^{-1} in 2θ. Two standard reflections were measured every 60 reflections, and the maximum variation was ±3% during the data collection. A total of 3435 reflection intensities with $4° \leq 2\theta \leq 40°$ were measured, of which those 2612 with a net count $>2.3\sigma(I)$ were considered observed, where $\sigma_I = [S + (t_s/t_b)^2(B_1 + B_2) + (kI)^2]^{1/2}$, where S is the total scan count, B_1 and B_2 are the background counts, t_s is the scan time, t_b is the total background time, k is a constant set at 0.03, and the net count $I = S - (t_s/t_b)(B_1 + B_2)$. The intensities were corrected for Lorentz and polarization effects. No correction was made for absorption.

The positions of the iron atoms in V were obtained from a three-dimensional Patterson function. A cycle of least-squares refinement followed by a difference Fourier revealed the remaining nonhydrogen atoms. Refinement continued with isotropic thermal parameters and later anisotropic parameters for the iron, phosphorus, fluorine, and carbonyl atoms. A difference Fourier synthesis based on reflections having $(\sin \theta)/\lambda < 0.34$ revealed the positions of most of the hydrogen atoms. Positions of the hydrogen atoms were calculated by using a C–H bond length of 1.00 Å and assigned isotropic temperature factors of the carbon atom to which they were attached. Further refinement in which the hydrogen atom parameters were not varied converged with final R factors $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.055$ and $R_2 = [\sum w(|F_o - F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.059$ for the observed reflections. The largest peaks on the final difference map (0.46 ± 0.12 e Å^{-3}) occurred near the iron atoms. In the early stages of refinement unit weights were used while in the later stages weights $w = 1/\sigma_{F_o}{}^2$ where $\sigma_{F_o} = \sigma_I/(2(Lp)F_o)$. An analysis of $\sum w(|F_o| - |F_c|)^2$ as a function of $|F_o|$, $(\sin \theta)/\lambda$, and Miller indices showed no unusual trends. Atomic scattering factors, including anomalous dispersion corrections for the iron atoms, were taken from the literature.[24] A list of observed structure amplitudes and calculated structure factors and calculated fractional atomic coordinates for the hydrogen atoms are available as supplementary material. Computer programs used in the structure determination and refinement have been described elsewhere.[25]

Complex VI. Very small, red crystals were obtained from diethyl ether. There was insufficient material to attempt a recrystallization, and the largest crystal available (0.15 × 0.18 × 0.20 mm) was used for data collection. Unit cell dimensions were obtained from a least-squares fit of the setting angles of 11 reflections ($2\theta > 20°$) measured on the automatic diffractometer. The compound has a formula weight of 972.3 and crystallizes in the space group $P2_1/c$ with cell dimensions $a = 12.45$ (2) Å, $b = 17.21$ (5) Å, $c = 18.86$ (3) Å, $\beta = 97.67$ (9)°, and $V = 4005$ Å^3. $d_{\text{exptl}} = 1.56$ (flotation) and $d_{\text{calcd}} = 1.61$ g cm^{-3}, $Z = 4$, λ(Mo Kα_1) = 0.709 26 Å, μ(Mo Kα) = 9.17 cm^{-1}, and $T = 22$ (1) °C.

Intensity data out to $2\theta = 30°$ were collected with a scan base width of 1.3° with background counts of 40 s at the scan limits and a reduced scan rate of 1° min^{-1} in 2θ. Measurements of 1623 unique reflection intensities were made, of which only the 934 with $I > 2.3\sigma_I$ were considered observed and used in structural refinement. Lorentz and polarization corrections were applied but no correction was made for absorption.

A Patterson synthesis located the two iron atoms, and subsequent Fourier syntheses gave the positions of the remaining nonhydrogen atoms of the molecule. Full-matrix least-squares refinement followed by a difference synthesis indicated the presence of solvent of crystallization. Although the crystals were crystallized from diethyl ether only, three solvent peaks were located on the difference map. These peaks were assigned as carbon atoms with site occupancies of 1.0 and included in the refinement. The site occupancies were not refined. Anisotropic thermal parameters for the iron and fluorine atoms were

---

(24) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1962; Vol. 3, p 273.

(25) Einstein, F. W. B.; Jones, R. D. G. *Inorg. Chem.* **1972**, *11*, 395.

allowed to refine, and hydrogen atoms in calculated positions (C–H = 1.00 Å) were included as fixed contributions. The discrepancy factors after the last cycle were $R_1 = 0.072$ and $R_2 = 0.066$. The largest peak ($\sim 3\sigma$) on the final difference map was near the iron atoms. In the least-squares refinement $\sum w||F_o| - |F_c||^2$ was minimized where $x = 1/\sigma_{F_o}{}^2$. Anomalous dispersion corrections were made for the iron atoms.

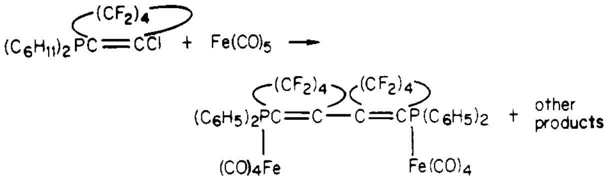
Final positional and thermal parameters for both isomers V and VI are listed in Table III. Interatomic distances and angles with estimated standard deviations are given in Table IV. Relevant least-squares plane data for selected atomic groups are listed in Table V.

Results and Discussion

The reaction of the fluorocarbon-bridged bis(tertiary phosphines) $(C_6H_5)_2P\overline{C{=}CP(C_6H_5)_2(C}F_2)_n$ (n = 2–4) with iron carbonyls gives the chelate complexes (L–L)Fe$(CO)_3$ in addition to compounds of structure D.[2] We now find that chelate derivatives I and II are also obtained from A and B.

The ^{19}F NMR spectra of I and II are very similar to those of the free ligand. However, this must be due to stereochemical nonrigidity since the crystal structure of I shows that the phosphorus atoms are situated in the axial and equatorial positions of a distorted trigonal bipyramid.[26,27] In spite of the presence of the bulky $(C_6H_{11})_2P$ groups, the Fe–P bond lengths are not significantly elongated. In contrast the bis(dicyclohexyl)phosphino analogue of C forms the chelate complex (L–L)Mo$(CO)_4$, among others, in which the Mo–P bonds are longer than usual.[6]

Similar $M(CO)_4$ chelate derivatives are formed by C;[5] thus the failure of C to give a (L–L)Fe$(CO)_3$ complex is at first sight surprising. It seems that the bite of the ligand is too large to chelate to iron. An identical situation prevails in the reactions of $(CH_3)_2As\overline{C{=}CAs(CH_3)_2(CF_2}{})_2$[9a] with iron carbonyls. The bis monoligate derivative (L–L)$Fe_2(CO)_8$ is isolated and a complex of this formula, IV, appears to be formed by C although not enough was obtained for complete characterization. The mass spectrum of IV shows the molecular peak at m/e 954 and other peaks associated with the loss of up to eight carbonyl groups. The ν(CO) bands (Table II) are similar in energy and pattern to well-characterized related compounds obtained by the coupling reaction shown in eq 3.[28]



(3)

Only one of the new ligands gave a (L–L)$Fe_2(CO)_6$ complex of structure D. This compound, II, is obtained in very low yield (2%) in spite of the use of reaction conditions reported to be the best for the preparation of such complexes.[29] The yield is increased slightly when $Fe_3(CO)_{12}$ is used.

The pattern of the infrared spectrum of II is very similar to that of other molecules of this known structure.[8] The band frequencies are lower than those of the bis(diphenylphosphino) analogue.[9] The failure of B to give a derivative, (L–L)Fe$(CO)_3$, may be due to steric hindrance caused by bulky groups and a decrease in the bite of the ligand.[30]

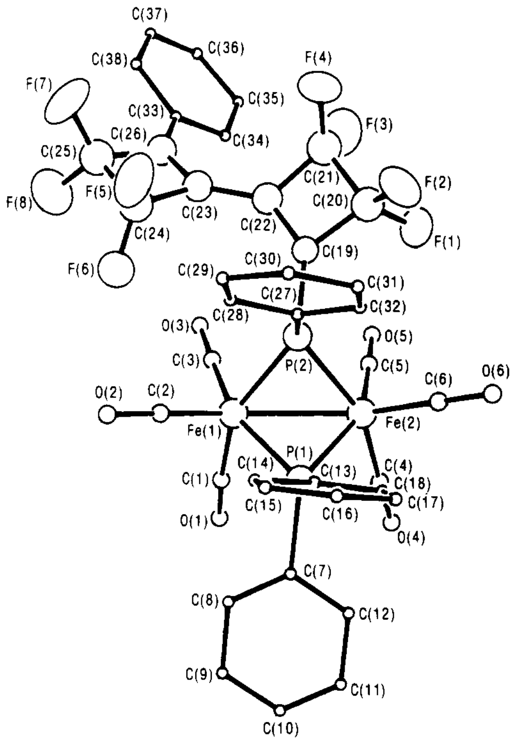


Figure 1. View of the structure of V showing the atomic numbering scheme.

Apparently C does not form a (L–L)$Fe_2(CO)_6$ derivative of structure D because the double bond in the necessarily puckered seven-membered chelate ring would be too far away from the second iron atom to bind to it.[5] However, as can be seen in Table I, two molecules of formula (L–L)$Fe_2(CO)_6$, V and VI, can be isolated from the reaction of C with iron carbonyls. The mass spectra of both isomers show a molecular ion followed by loss of six CO groups. However, no peak corresponding to the free ligand (m/e 618) is present, so some ligand fragmentation has taken place.

Crystal Structure of V. A perspective view of the molecule is shown in Figure 1. The most striking features in the formation of this complex are the cleavage of one diphenylphosphino group and the fragmentation of the other. The cleaved group bridges the two iron atoms with distances Fe(1)–P(1) = 2.239 (3) and Fe(2)–P(1) = 2.219 (3) Å. Fragmentation of the remaining diphenylphosphino group occurs by cleavage of a phenyl ring from P(2) and attachment of the phenyl ring to the cyclobutene ring by a carbon–carbon bond at the point of cleavage of P(1). As a result of this fragmentation, a modified phosphido group is formed which also bridges both the iron atoms. This bridge is not symmetrical since Fe(1)–P(2) is 2.197 (2) Å and Fe(2)–P(2) is 2.241 (2) Å.

In structures of the general type $Fe_2(CO)_6(\mu\text{-}X)_2$, each of the iron atoms can be considered to be in a distorted octahedral environment consisting of three carbonyl groups, two bridging atoms, and an Fe–Fe bond. The bond lengths and angles and dihedral angles for the central four-membered ring differ markedly with the type of bridging atom. For phosphorus bridging atoms, apart from the structure of $Fe_2(CO)_6[\mu\text{-}P(CF_3)_2]_2$, distances and angles lie within the ranges Fe–Fe = 2.619–2.665 Å, Fe–P = 2.203–2.233 Å, Fe–P–Fe = 72.0–74.3°, and flap angles (angle between the FeP_2 planes) = 100–107.3°.[31] In the structure of $Fe_2(CO)_6[\mu\text{-}P(CF_3)_2]_2$

---

[26] Einstein, F. W. B.; Huang, C.-H. *Acta Crystallogr., Sect. B* **1978**, *B34*, 1486.

[27] Similar nonrigid (L–L)Fe$(CO)_3$ derivatives of known crystal structure have been described:[9a] (a) Brown, D. S.; Bushnell, G. W. *Acta Crystallogr.* **1967**, *22*, 292. (b) Cotton, F. A.; Hardcastle, K. I.; Rusholme, G. A. *J. Coord. Chem.* **1973**, *2*, 217.

[28] The coupled ligand shown in eq 3 has not been prepared by more conventional means.[5,6]

[29] Chia, L. S.; Cullen, W. R.; Sams, J. R.; Scott, J. C. *Can. J. Chem.* **1975**, *53*, 2232.

[30] Cullen, W. R.; Mihichuk, L. *Can. J. Chem.* **1973**, *51*, 936.

Table III

(a) Fractional Atomic Coordinates ($\times 10^5$ for Fe and P; $\times 10^4$ for F, O, and C) and Isotropic Temperature Parameters ($\times 10^3$ Å^2) for V

	x	*y*	*z*	*U*		*x*	*y*	*z*	*U*
Fe(1)	65190 (7)	26837 (12)	4980 (4)		C(11)	5514 (5)	4513 (9)	2353 (3)	56 (2)
Fe(2)	70029 (7)	7817 (12)	12337 (4)		C(12)	6048 (5)	3669 (9)	2111 (3)	47 (2)
P(1)	69527 (13)	31601 (22)	13437 (7)		C(13)	7961 (5)	4124 (8)	1691 (3)	32 (2)
P(2)	78286 (13)	15722 (22)	7109 (7)		C(14)	8230 (5)	5403 (8)	1505 (3)	47 (2)
F(1)	8394 (4)	−2128 (5)	736 (2)		C(15)	8974 (6)	6168 (9)	1788 (3)	58 (3)
F(2)	9590 (3)	−859 (5)	811 (2)		C(16)	9441 (5)	5654 (9)	2264 (3)	57 (2)
F(3)	8343 (4)	−2671 (5)	−237 (2)		C(17)	9177 (5)	4392 (9)	2454 (3)	52 (2)
F(4)	9529 (3)	−1385 (5)	−181 (2)		C(18)	8451 (5)	3631 (8)	2171 (3)	45 (2)
F(5)	8768 (4)	2902 (5)	−631 (2)		C(19)	8195 (5)	221 (8)	316 (3)	37 (2)
F(6)	7375 (4)	3201 (5)	−654 (2)		C(20)	8768 (6)	−1090 (9)	504 (3)	51 (2)
F(7)	8303 (4)	2108 (6)	−1620 (2)		C(21)	8737 (6)	−1406 (10)	−64 (3)	55 (2)
F(8)	6897 (4)	2420 (6)	−1644 (2)		C(22)	8178 (5)	−56 (8)	−182 (3)	40 (2)
O(1)	4644 (4)	2898 (9)	552 (3)		C(23)	7896 (5)	716 (8)	−664 (3)	42 (2)
O(2)	6886 (5)	5441 (7)	56 (3)		C(24)	7949 (6)	2299 (9)	−790 (3)	53 (2)
O(3)	5913 (4)	923 (8)	−430 (3)		C(25)	7682 (6)	1827 (10)	−1364 (3)	61 (3)
O(4)	5410 (5)	392 (7)	1628 (3)		C(26)	7623 (5)	319 (8)	−1172 (3)	41 (2)
O(5)	6395 (5)	−1800 (8)	600 (3)		C(27)	8890 (5)	2536 (8)	910 (3)	35 (2)
O(6)	8385 (5)	−343 (7)	2101 (3)		C(28)	9057 (5)	3685 (8)	605 (3)	45 (2)
C(1)	5358 (6)	2850 (11)	528 (3)		C(29)	9872 (6)	4424 (9)	743 (3)	60 (3)
C(2)	6732 (6)	4359 (11)	227 (3)		C(30)	10504 (6)	4041 (10)	1174 (3)	65 (3)
C(3)	6156 (6)	1621 (10)	−69 (3)		C(31)	10364 (6)	2909 (10)	1479 (3)	63 (3)
C(4)	6028 (6)	567 (10)	1478 (3)		C(32)	9555 (5)	2143 (9)	1348 (3)	50 (2)
C(5)	6672 (6)	−814 (11)	851 (3)		C(33)	7350 (5)	−1010 (8)	−1461 (3)	46 (2)
C(6)	7843 (6)	108 (9)	1766 (4)		C(34)	6987 (6)	−2145 (10)	−1254 (3)	64 (3)
C(7)	6153 (5)	4112 (8)	1634 (3)	40 (2)	C(35)	6754 (7)	−3424 (12)	−1530 (4)	89 (3)
C(8)	5738 (5)	5336 (9)	1404 (3)	55 (2)	C(36)	6897 (7)	−3470 (11)	−2020 (4)	85 (3)
C(9)	5208 (6)	6161 (10)	1656 (3)	65 (3)	C(37)	7233 (6)	−2378 (10)	−2229 (3)	67 (3)
C(10)	5121 (6)	5717 (10)	2120 (3)	62 (3)	C(38)	7466 (5)	−1118 (9)	−1965 (3)	54 (2)

(b) Final Anisotropic Parameters (Å^2 × 10^4 for Fe; Å^2 × 10^3 for P, F, O, and C) for V^a

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}		U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe(1)	366 (8)	495 (9)	355 (8)	45 (6)	80 (5)	−13 (6)	O(1)	33 (4)	193 (8)	93 (5)	17 (5)	10 (4)	−24 (6)
Fe(2)	428 (8)	404 (8)	379 (8)	−42 (6)	162 (6)	−1 (6)	O(2)	109 (6)	62 (5)	83 (5)	11 (4)	31 (4)	19 (4)
P(1)	39 (1)	38 (1)	33 (1)	2 (1)	11 (1)	−2 (1)	O(3)	69 (5)	111 (6)	72 (5)	−13 (4)	2 (4)	−39 (5)
P(2)	37 (1)	38 (1)	32 (1)	3 (1)	12 (1)	2 (1)	O(4)	82 (5)	102 (6)	111 (6)	−24 (4)	67 (5)	−8 (5)
F(1)	121 (4)	61 (4)	78 (4)	29 (3)	54 (3)	29 (3)	O(5)	113 (6)	75 (5)	91 (6)	−25 (5)	34 (5)	−35 (5)
F(2)	69 (4)	87 (4)	73 (4)	36 (3)	4 (3)	−7 (3)	O(6)	76 (5)	87 (6)	84 (5)	4 (4)	−4 (4)	39 (4)
F(3)	108 (4)	50 (3)	72 (4)	−2 (3)	23 (3)	−12 (3)	C(1)	34 (6)	113 (9)	58 (6)	24 (6)	3 (5)	−15 (6)
F(4)	74 (4)	85 (4)	83 (4)	23 (3)	43 (4)	1 (3)	C(2)	55 (6)	70 (7)	38 (5)	6 (6)	17 (5)	−3 (5)
F(5)	100 (4)	63 (4)	69 (4)	−28 (3)	20 (3)	3 (3)	C(3)	47 (6)	59 (7)	51 (6)	−1 (5)	8 (5)	−2 (5)
F(6)	123 (4)	58 (3)	60 (3)	25 (3)	41 (3)	5 (3)	C(4)	72 (7)	64 (7)	60 (6)	−12 (6)	33 (6)	5 (5)
F(7)	135 (5)	86 (4)	69 (4)	−17 (4)	64 (4)	5 (3)	C(5)	76 (7)	56 (7)	47 (6)	2 (6)	29 (5)	−6 (5)
F(8)	117 (5)	88 (4)	60 (3)	34 (4)	1 (3)	9 (3)	C(6)	66 (7)	35 (6)	68 (7)	4 (5)	28 (6)	15 (5)

(c) Fractional Atomic Coordinates ($\times 10^4$ for Fe, P, F, and O; $\times 10^3$ for C) and Isotropic Temperature Parameters (Å^2 × 10^3) for VI

	x	*y*	*z*	*U*		*x*	*y*	*z*	*U*
Fe(1)	1820 (3)	2814 (2)	2933 (2)		C(13)	336 (2)	232 (2)	465 (1)	42 (9)
Fe(2)	744 (3)	1936 (2)	3865 (2)		C(14)	359 (3)	171 (2)	510 (2)	113 (13)
F(1)	−3528 (12)	2232 (12)	2519 (8)		C(15)	408 (3)	189 (2)	583 (2)	124 (15)
F(2)	−2620 (14)	1195 (11)	2369 (9)		C(16)	433 (3)	260 (3)	593 (2)	129 (15)
F(3)	−2878 (13)	2812 (12)	1314 (9)		C(17)	427 (3)	318 (3)	543 (3)	158 (17)
F(4)	−1994 (12)	1776 (10)	1157 (8)		C(18)	373 (3)	302 (2)	468 (2)	125 (14)
F(5)	−494 (11)	3190 (10)	644 (9)		C(19)	−152 (2)	233 (2)	273 (2)	49 (10)
F(6)	−1024 (12)	4185 (10)	1205 (9)		C(20)	−259 (3)	196 (3)	231 (2)	84 (13)
F(7)	1616 (12)	3512 (11)	1173 (8)		C(21)	−227 (3)	229 (3)	171 (3)	110 (16)
F(8)	1035 (13)	4473 (11)	1742 (8)		C(22)	−127 (2)	260 (2)	218 (2)	61 (10)
P(1)	2490 (6)	2000 (5)	3775 (4)	47 (3)	C(23)	−39 (2)	306 (2)	188 (1)	40 (9)
P(2)	−993 (6)	2376 (4)	3671 (4)	40 (3)	C(24)	−32 (3)	358 (2)	129 (2)	65 (12)
O(1)	1319 (14)	4154 (12)	3775 (11)	81 (8)	C(25)	89 (3)	375 (2)	153 (2)	43 (11)
O(2)	3764 (18)	3566 (13)	2572 (12)	119 (9)	C(26)	66 (2)	322 (2)	217 (1)	57 (10)
O(3)	1985 (14)	1663 (12)	1799 (11)	83 (8)	C(27)	−128 (2)	337 (1)	390 (1)	25 (8)
O(4)	1154 (13)	3014 (11)	5094 (10)	70 (7)	C(28)	−113 (2)	358 (2)	459 (2)	62 (10)
O(5)	754 (14)	591 (13)	4851 (10)	75 (7)	C(29)	−129 (2)	436 (2)	482 (2)	99 (13)
O(6)	284 (12)	918 (10)	2636 (10)	58 (6)	C(30)	−146 (2)	489 (2)	431 (2)	97 (13)
C(1)	149 (2)	360 (2)	348 (10)	28 (9)	C(31)	−164 (3)	472 (2)	365 (2)	117 (14)
C(2)	297 (3)	329 (2)	271 (2)	70 (11)	C(32)	−151 (2)	395 (2)	339 (2)	83 (11)
C(3)	189 (2)	207 (2)	226 (2)	43 (9)	C(33)	−203 (2)	182 (2)	405 (1)	22 (8)
C(4)	100 (2)	256 (2)	463 (2)	41 (9)	C(34)	−193 (2)	105 (2)	403 (1)	26 (8)
C(5)	68 (2)	108 (2)	451 (2)	51 (10)	C(35)	−269 (2)	56 (2)	430 (1)	58 (10)
C(6)	48 (2)	135 (2)	316 (2)	34 (9)	C(36)	−350 (2)	94 (2)	461 (1)	67 (10)
C(7)	321 (2)	117 (1)	350 (1)	34 (9)	C(37)	−362 (2)	173 (2)	459 (2)	82 (11)
C(8)	414 (2)	127 (2)	315 (2)	72 (11)	C(38)	−285 (2)	216 (1)	426 (1)	50 (9)
C(9)	473 (2)	68 (2)	291 (2)	91 (12)	C(39)	593 (11)	434 (9)	361 (8)	440 (90)

Table III (*Continued*)

	x	y	z	U		x	y	z	U
C(10)	439 (3)	−6 (2)	299 (2)	91 (11)	C(40)	547 (10)	452 (7)	435 (7)	275 (58)
C(11)	349 (3)	−25 (2)	335 (2)	103 (12)	C(41)	449 (8)	505 (6)	446 (5)	210 (43)
C(12)	290 (2)	39 (2)	360 (2)	78 (11)					

(d) Anisotropic Temperature Parameters ($Å^2 \times 10^2$) for VI[a]

	U_{11}	U_{22}	U_{32}	U_{12}	U_{13}	U_{23}		U_{11}	U_{22}	U_{32}	U_{12}	U_{13}	U_{23}
Fe(1)	50 (4)	53 (4)	51 (4)	−10 (3)	7 (3)	3 (3)	F(4)	114 (15)	112 (17)	30 (13)	−28 (13)	22 (12)	−6 (12)
Fe(2)	38 (3)	54 (4)	36 (4)	−5 (3)	6 (3)	−4 (3)	F(5)	70 (12)	112 (17)	46 (13)	−9 (11)	8 (10)	3 (12)
F(1)	46 (13)	207 (24)	56 (13)	−1 (14)	8 (11)	7 (13)	F(6)	51 (12)	91 (16)	118 (17)	20 (12)	14 (12)	40 (13)
F(2)	146 (19)	75 (17)	116 (18)	−61 (15)	−33 (13)	12 (13)	F(7)	55 (13)	174 (21)	41 (14)	18 (12)	31 (11)	10 (11)
F(3)	78 (14)	158 (21)	116 (17)	−54 (15)	−52 (13)	66 (17)	F(8)	129 (16)	63 (15)	82 (15)	−21 (14)	−17 (13)	12 (12)

[a] The parameters are in the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12} + \ldots)]$.

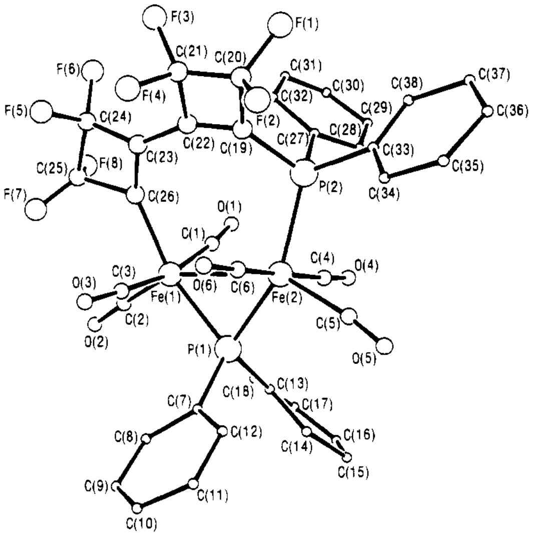


Figure 2. View of the structure of VI showing the atomic numbering scheme.

the values are quite different with Fe–Fe = 2.819 (1) Å, Fe–P = 2.193 (1) Å, Fe–P–Fe = 80.0 (1)°, and flap angle = 118.9°.[31] The differences are attributed to the effects of the electron-withdrawing CF_3 groups on the phosphorus atom. In V the Fe–Fe bond of 2.604 (2) Å lies slightly outside the range observed above. The P–Fe–P angles lie within the range, but the Fe–P–Fe angles are on the low side, giving a slightly lower flap angle between the FeP_2 planes (98.7°) than for the other reported phosphorus bridging compounds.[31] As a consequence the Fe–Fe bond is slightly shorter. The dihedral angle between the two Fe_2P planes is 103.4° and the P---P contact is 2.831 Å, which may indicate an attractive interaction between the phosphorus atoms. Molecular orbital calculations on the $[Fe_2(CO)_6(\mu\text{-}PF_2)_2]$ series indicate positive overlap populations.[32] In the modified ligands, the cyclobutene rings are joined by a short C–C bond of 1.44 (1) Å. Similar short connecting bonds are observed in related compounds in the series. The cyclobutene C═C bond distances are 1.35 (1) and 1.371 (1) Å.

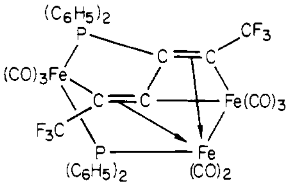
The ^{19}F NMR spectrum of V shows the expected four sets of multiplets (CF_2 groups), and the ^{31}P spectrum consists of two doublets ($J(P,P)$ = 135.1 Hz).

Crystal Structure of VI. A perspective view is given in Figure 2. Again a diphenylphosphino group has been cleaved from the starting ligand C and bridges the two iron atoms. However, in this case the remaining fragment bridges the iron atoms in such a way that the phosphorus atom is coordinated to one iron atom and the residual cyclobutene group is σ bonded to the other. The iron–iron bond of 2.791 (6) Å is longer than that found in the isomer V. The bridging diphenylphosphino group is symmetrically bound with Fe(1)–P(1) = 2.197 (9) and Fe(2)–P(1) = 2.206 (8) Å, which is slightly shorter than that found in V. The Fe(2)–P(2) distance is longer at 2.274 (8) Å. Carbonyl groups on both iron atoms are in a *mer* arrangement in contrast to the *fac* distribution in V. This accounts for the marked difference in the infrared spectra of V and VI.

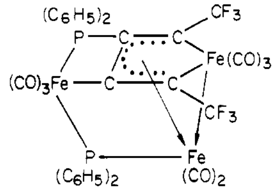
The C–C bond joining the cyclobutene rings in VI is 1.50 (3) Å compared with 1.44 (1) Å in V, and the C═C bond distances are 1.38 (3) and 1.22 (3) Å, respectively. The last distance is unusually short, but the precision in the lengths is not great because of the poor quality of the data. This probably accounts for the unreasonably short C(20)–C(21) single-bond length of 1.37 (4) Å.

The spectroscopic data reported in Table II are in accord with the structure of VI.

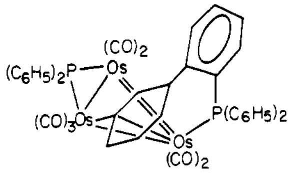
As mentioned in the Introduction there are a number of instances of cleavage of a $(C_6H_5)_2P$ moiety from $(C_6H_5)_2PR$, where R = C_6H_5, upon complex formations. Less well-known are compounds in which $(C_6H_5)_2P$ groups are cleaved from phosphines, $(C_6H_5)_2PR$, in which R is an alkyl or aryl group. Carty and co-workers[23] have reported a compound similar to VI from the reaction of $(C_6H_5)_2PC{\equiv}CC_6H_5$ with $Fe_2(CO)_9$ under mild conditions. The product has the structure $(CO)_3FeP(C_6H_5)_2Fe(CO)_3C{\equiv}CCF_3$ so that the displaced fluorocarbon group is σ bonded to one iron atom and η^2 bonded to the other. A related phosphinoacetylene $(C_6H_5)_2PC{\equiv}CCF_3$ reacts with iron carbonyls to give products in which the $(C_6H_5)_2P$ group from one ligand is cleaved and acts in a bridging capacity. The cleaved fluorocarbon group then combines with an intact $(C_6H_5)_2PC{\equiv}CCF_3$ ligand to afford complexes E and F. This type of reaction is also seen in G,



E



F



G

---

(31) Clegg, W. *Inorg. Chem.* **1976**, *15*, 1609 and references quoted therein.

(32) Burdett, J. K. *J. Chem. Soc., Dalton Trans.* **1977**, 423.

Table IV

(a) Bond Distances (Å) for V

Fe(1)–Fe(2)	2.604 (2)	C(6)–O(6)	1.135 (9)	C(17)–C(18)	1.37 (1)	C(20)–F(1)	1.349 (9)
Fe(1)–P(1)	2.239 (3)	P(1)–C(7)	1.837 (7)	C(27)–C(28)	1.40 (1)	C(20)–F(2)	1.334 (9)
Fe(1)–P(2)	2.197 (2)	P(1)–C(13)	1.821 (7)	C(27)–C(32)	1.39 (1)	C(21)–F(3)	1.341 (9)
Fe(2)–P(1)	2.219 (3)	P(2)–C(19)	1.817 (7)	C(28)–C(29)	1.39 (1)	C(21)–F(4)	1.333 (9)
Fe(2)–P(2)	2.241 (2)	P(2)–C(27)	1.812 (7)	C(29)–C(30)	1.35 (1)	C(24)–F(5)	1.340 (9)
Fe(1)–C(1)	1.811 (9)	C(7)–C(8)	1.36 (1)	C(30)–C(31)	1.38 (1)	C(24)–F(6)	1.329 (9)
Fe(1)–C(2)	1.78 (1)	C(7)–C(12)	1.39 (1)	C(31)–C(32)	1.39 (1)	C(25)–F(7)	1.337 (9)
Fe(1)–C(3)	1.78 (1)	C(8)–C(9)	1.41 (1)	C(19)–C(20)	1.50 (1)	C(25)–F(8)	1.359 (9)
Fe(2)–C(4)	1.79 (1)	C(9)–C(10)	1.35 (1)	C(19)–C(22)	1.35 (1)	C(26)–C(33)	1.46 (1)
Fe(2)–C(5)	1.79 (1)	C(10)–C(11)	1.34 (1)	C(20)–C(21)	1.54 (1)	C(33)–C(34)	1.37 (1)
Fe(2)–C(6)	1.77 (1)	C(11)–C(12)	1.40 (1)	C(21)–C(22)	1.50 (1)	C(33)–C(38)	1.41 (1)
C(1)–O(1)	1.115 (9)	C(13)–C(14)	1.39 (1)	C(22)–C(23)	1.44 (1)	C(34)–C(35)	1.39 (1)
C(2)–O(2)	1.148 (9)	C(13)–C(18)	1.39 (1)	C(23)–C(24)	1.51 (1)	C(35)–C(36)	1.39 (1)
C(3)–O(3)	1.143 (9)	C(14)–C(15)	1.39 (1)	C(23)–C(26)	1.37 (1)	C(36)–C(34)	1.32 (1)
C(4)–O(4)	1.133 (9)	C(15)–C(16)	1.38 (1)	C(24)–C(25)	1.55 (1)	C(37)–C(38)	1.36 (1)
C(5)–O(5)	1.148 (9)	C(16)–C(17)	1.37 (1)	C(25)–C(16)	1.50 (1)	C(37)–C(38)	1.36 (1)

(b) Bond Angles (Deg) for V

Fe(2)–Fe(1)–P(1)	53.92 (7)	C(5)–Fe(2)–C(6)	102.3 (4)	C(14)–C(14)–C(18)	118.2 (7)	C(19)–C(22)–C(21)	94.8 (6)
Fe(2)–Fe(1)–P(2)	54.86 (6)	Fe(1)–C(1)–O(1)	177 (1)	C(13)–C(14)–C(15)	121.0 (7)	C(19)–C(22)–C(23)	135.8 (7)
Fe(2)–Fe(1)–C(1)	96.6 (3)	Fe(1)–C(2)–O(2)	178.7 (9)	C(14)–C(15)–C(16)	119.3 (8)	C(21)–C(22)–C(23)	128.5 (7)
Fe(2)–Fe(1)–C(2)	148.4 (3)	Fe(1)–C(3)–O(3)	179 (1)	C(15)–C(16)–C(17)	120.3 (8)	C(22)–C(23)–C(24)	131.3 (7)
Fe(2)–Fe(1)–C(3)	103.1 (3)	Fe(2)–C(4)–O(4)	178 (1)	C(16)–C(17)–C(18)	120.2 (7)	C(22)–C(23)–C(26)	134.8 (7)
P(1)–Fe(1)–P(2)	79.31 (8)	Fe(2)–C(5)–O(5)	174.8 (9)	C(13)–C(18)–C(17)	121.0 (7)	C(24)–C(23)–C(26)	93.3 (6)
P(1)–Fe(1)–C(1)	88.7 (3)	Fe(2)–C(6)–O(6)	179 (1)	P(2)–C(27)–C(28)	119.0 (5)	C(23)–C(24)–C(25)	86.2 (6)
P(1)–Fe(1)–C(2)	101.9 (3)	Fe(1)–P(1)–Fe(2)	71.47 (7)	P(2)–C(27)–C(32)	121.9 (6)	C(23)–C(24)–F(5)	115.6 (7)
P(1)–Fe(1)–C(3)	157.5 (3)	Fe(1)–P(2)–Fe(2)	71.83 (8)	C(28)–C(27)–C(32)	119.1 (7)	C(23)–C(24)–F(6)	117.9 (7)
P(2)–Fe(1)–C(1)	150.8 (3)	Fe(1)–P(1)–C(7)	117.8 (2)	C(27)–C(28)–C(29)	120.1 (7)	C(25)–C(24)–F(5)	114.8 (7)
P(2)–Fe(1)–C(2)	105.1 (3)	Fe(1)–P(1)–C(13)	127.4 (2)	C(28)–C(29)–C(30)	120.0 (8)	C(25)–C(24)–F(6)	115.1 (7)
P(2)–Fe(1)–C(3)	91.7 (3)	Fe(2)–P(1)–C(7)	125.4 (3)	C(29)–C(30)–C(31)	121.2 (9)	F(5)–C(24)–F(6)	106.7 (7)
C(1)–Fe(1)–C(2)	103.4 (4)	Fe(2)–P(1)–C(13)	119.9 (2)	C(30)–C(31)–C(32)	120.1 (8)	C(24)–C(25)–C(26)	86.7 (6)
C(1)–Fe(1)–C(3)	89.4 (4)	Fe(1)–P(2)–C(19)	124.6 (2)	C(27)–C(32)–C(31)	119.5 (7)	C(24)–C(25)–F(7)	114.5 (7)
C(2)–Fe(1)–C(3)	100.4 (4)	Fe(1)–P(2)–C(27)	122.7 (2)	P(2)–C(19)–C(20)	126.7 (5)	C(24)–C(25)–F(8)	113.9 (7)
Fe(1)–Fe(2)–P(1)	54.61 (7)	Fe(2)–P(2)–C(19)	116.9 (2)	P(2)–C(19)–C(22)	140.8 (6)	C(26)–C(25)–F(7)	118.2 (7)
Fe(1)–Fe(2)–P(2)	53.31 (6)	Fe(2)–P(2)–C(27)	125.9 (2)	C(20)–C(19)–C(22)	92.4 (6)	C(26)–C(25)–F(8)	116.2 (7)
Fe(1)–Fe(2)–C(4)	104.5 (3)	C(7)–P(1)–C(13)	97.0 (3)	C(19)–C(20)–C(21)	87.3 (6)	F(7)–C(25)–F(8)	106.6 (7)
Fe(1)–Fe(2)–C(5)	97.8 (3)	C(19)–P(2)–C(27)	96.8 (3)	C(19)–C(20)–F(1)	116.4 (7)	C(23)–C(2)–C(25)	93.7 (6)
Fe(1)–Fe(2)–C(6)	148.7 (3)	P(1)–C(7)–C(8)	119.3 (6)	C(19)–C(20)–F(2)	117.2 (7)	C(23)–C(26)–C(33)	136.9 (7)
P(1)–Fe(2)–P(2)	78.80 (8)	P(1)–C(7)–C(12)	119.8 (6)	C(21)–C(20)–F(1)	114.4 (7)	C(25)–C(26)–C(33)	129.4 (7)
P(1)–Fe(2)–C(4)	90.0 (3)	C(8)–C(7)–C(12)	120.6 (7)	C(21)–C(20)–F(2)	115.1 (7)	C(26)–C(33)–C(34)	121.2 (7)
P(1)–Fe(2)–C(5)	151.0 (3)	C(7)–C(8)–C(9)	119.4 (7)	F(1)–C(20)–F(2)	106.1 (7)	C(26)–C(33)–C(38)	118.8 (7)
P(1)–Fe(2)–C(6)	106.4 (3)	C(8)–C(9)–C(10)	119.0 (8)	C(20)–C(21)–C(22)	85.5 (6)	C(34)–C(33)–C(38)	120.0 (8)
P(2)–Fe(2)–C(4)	157.6 (3)	C(9)–C(10)–C(11)	122.7 (9)	C(20)–C(21)–F(3)	113.8 (7)	C(33)–C(34)–C(35)	120.5 (8)
P(2)–Fe(2)–C(5)	91.8 (3)	C(10)–C(11)–C(12)	119.6 (8)	C(20)–C(21)–F(4)	115.7 (7)	C(34)–C(35)–C(36)	117 (1)
P(2)–Fe(2)–C(6)	102.0 (3)	C(7)–C(12)–C(11)	118.7 (7)	C(22)–C(21)–F(3)	117.9 (7)	C(35)–C(36)–C(37)	124 (1)
C(4)–Fe(2)–C(5)	88.8 (4)	P(1)–C(13)–C(14)	121.7 (5)	C(22)–C(21)–F(4)	116.4 (7)	C(36)–C(37)–C(38)	120.6 (9)
C(4)–Fe(2)–C(6)	99.7 (4)	P(1)–C(13)–C(18)	120.0 (6)	F(3)–C(21)–F(4)	106.8 (7)	C(33)–C(38)–C(37)	118.6 (8)

(c) Bond Distances (Å) for VI

Fe(1)–Fe(2)	2.791 (6)	P(1)–C(7)	1.79 (2)	C(17)–C(18)	1.52 (4)	C(21)–C(22)	1.55 (4)
Fe(1)–P(1)	2.197 (9)	P(1)–C(13)	1.92 (3)	C(27)–C(28)	1.34 (3)	C(22)–C(23)	1.50 (3)
Fe(1)–C(1)	1.78 (3)	P(2)–C(19)	1.81 (3)	C(27)–C(32)	1.39 (3)	C(23)–C(24)	1.44 (3)
Fe(1)–C(2)	1.75 (4)	P(2)–C(27)	1.81 (2)	C(28)–C(29)	1.43 (4)	C(23)–C(26)	1.38 (3)
Fe(1)–C(3)	1.81 (3)	P(2)–C(33)	1.82 (2)	C(29)–C(30)	1.32 (4)	C(24)–C(25)	1.54 (3)
Fe(1)–C(26)	2.02 (3)	C(7)–C(8)	1.41 (3)	C(30)–C(31)	1.27 (4)	C(25)–C(26)	1.57 (3)
Fe(2)–P(1)	2.206 (8)	C(7)–C(12)	1.42 (3)	C(31)–C(32)	1.42 (4)	C(20)–F(1)	1.36 (4)
Fe(2)–P(2)	2.274 (8)	C(8)–C(9)	1.37 (3)	C(33)–C(34)	1.33 (3)	C(26)–F(2)	1.32 (4)
Fe(2)–C(4)	1.79 (3)	C(9)–C(10)	1.37 (4)	C(33)–C(38)	1.29 (3)	C(21)–F(3)	1.35 (4)
Fe(2)–C(5)	1.92 (3)	C(10)–C(11)	1.43 (4)	C(34)–C(35)	1.42 (3)	C(21)–F(4)	1.44 (4)
Fe(2)–C(6)	1.67 (3)	C(11)–C(12)	1.44 (4)	C(35)–C(36)	1.39 (3)	C(24)–F(5)	1.38 (3)
C(1)–O(1)	1.14 (2)	C(13)–C(14)	1.36 (4)	C(36)–C(37)	1.37 (3)	C(24)–F(6)	1.35 (3)
C(2)–O(2)	1.16 (3)	C(13)–C(18)	1.28 (4)	C(37)–C(28)	1.43 (3)	C(25)–F(7)	1.26 (3)
C(3)–O(3)	1.13 (3)	C(14)–C(15)	1.46 (4)	C(19)–C(20)	1.59 (4)	C(15)–F(8)	1.32 (3)
C(4)–O(4)	1.17 (3)	C(15)–C(16)	1.27 (4)	C(19)–C(22)	1.22 (3)	C(39)–C(40)	1.60 (16)
C(5)–O(5)	1.06 (3)	C(16)–D(17)	1.36 (5)	C(20)–C(21)	1.37 (4)	C(40)–C(41)	1.57 (3)
C(6)–O(6)	1.23 (3)						

(d) Bond Angles (Deg) for VI

Fe(2)–Fe(1)–P(1)	50.8 (2)	Fe(1)–C(1)–O(1)	172 (2)	C(13)–C(14)–C(15)	117 (4)	C(19)–C(22)–C(23)	145 (3)
Fe(2)–Fe(1)–C(1)	82.9 (8)	Fe(1)–C(2)–O(2)	176 (3)	C(14)–C(15)–C(16)	114 (4)	C(21)–C(22)–C(23)	122 (3)
Fe(2)–Fe(1)–C(2)	151.6 (9)	Fe(1)–C(3)–O(3)	174 (3)	C(15)–C(16)–C(17)	128 (4)	C(22)–C(23)–C(24)	139 (3)
Fe(2)–Fe(1)–C(3)	97.9 (8)	Fe(2)–C(4)–O(4)	175 (2)	C(16)–C(17)–C(18)	119 (4)	C(22)–C(23)–C(26)	129 (3)
Fe(2)–Fe(1)–C(26)	106.1 (8)	Fe(2)–C(5)–O(5)	172 (3)	C(13)–C(18)–C(17)	109 (3)	C(24)–C(23)–C(26)	92 (3)
P(1)–Fe(1)–C(1)	98.9 (8)	Fe(2)–C(6)–O(6)	179 (3)	P(2)–C(27)–C(25)	119 (2)	C(23)–C(24)–C(25)	93 (3)
P(1)–Fe(1)–C(2)	102.9 (9)	Fe(1)–P(1)–Fe(2)	78.7 (3)	P(2)–C(27)–C(32)	123 (2)	C(23)–C(24)–F(5)	111 (3)
P(1)–Fe(1)–C(3)	90.6 (8)	Fe(1)–P(1)–C(1)	117.0 (9)	C(25)–C(27)–C(32)	117 (3)	C(23)–C(24)–F(6)	117 (3)
P(1)–Fe(1)–C(26)	154.2 (8)	Fe(1)–P(1)–C(13)	123 (1)	C(27)–C(25)–C(29)	123 (3)	C(25)–C(24)–F(5)	113 (3)
C(1)–Fe(1)–C(2)	92 (1)	Fe(2)–P(1)–C(7)	121.2 (9)	C(25)–C(29)–C(30)	116 (3)	C(25)–C(24)–F(6)	119 (3)

Table IV (*Continued*)

C(1)-Fe(1)-C(3)	168 (1)	Fe(2)-P(1)-C(13)	113.2 (8)	C(29)-C(30)-C(31)	122 (4)	F(5)-C(24)-F(6)	104 (3)
C(1)-Fe(1)-C(26)	88 (1)	C(7)-P(1)-C(13)	103 (1)	C(30)-C(31)-C(32)	123 (4)	C(24)-C(25)-C(26)	81 (3)
C(2)-Fe(1)-C(3)	92 (1)	Fe(2)-P(2)-C(19)	111.0 (9)	C(27)-C(32)-C(31)	117 (3)	C(24)-C(25)-F(7)	121 (3)
C(2)-Fe(1)-C(26)	102 (1)	Fe(2)-P(2)-C(27)	119.4 (8)	P(2)-C(19)-C(20)	133 (3)	C(24)-C(25)-F(8)	110 (3)
C(3)-Fe(1)-C(26)	81 (1)	Fe(2)-P(2)-C(33)	118.0 (9)	P(2)-C(19)-C(22)	134 (3)	C(26)-C(25)-F(7)	116 (3)
Fe(1)-Fe(2)-1(1)	50.5 (2)	C(19)-P(2)-C(27)	102 (1)	C(20)-C(19)-C(22)	93 (3)	C(26)-C(25)-F(8)	111 (3)
Fe(1)-Fe(2)-P(2)	104.1 (2)	C(19)-P(2)-C(33)	100 (1)	C(19)-C(20)-C(21)	86 (3)	F(7)-C(25)-F(8)	113 (3)
Fe(1)-Fe(2)-C(4)	97.6 (8)	C(27)-P(2)-C(33)	103 (1)	C(19)-C(20)-F(1)	114 (3)	C(23)-C(2)-C(25)	94 (3)
Fe(1)-Fe(2)-C(5)	151.6 (8)	P(1)-C(7)-C(8)	121 (2)	C(19)-C(20)-F(2)	113 (3)	Fe(1)-C(26)-C(23)	140 (2)
Fe(1)-Fe(2)-C(6)	83.4 (9)	P(1)-C(7)-C(12)	124 (2)	C(21)-C(20)-F(1)	117 (4)	Fe(1)-C(26)-C(25)	124 (2)
P(1)-Fe(2)-P(2)	153.7 (3)	C(8)-C(7)-C(12)	115 (2)	C(21)-C(20)-F(2)	120 (4)	P(2)-C(33)-C(34)	116 (2)
P(1)-Fe(2)-C(4)	87.7 (8)	C(7)-C(8)-C(9)	126 (3)	F(1)-C(20)-F(2)	107 (4)	P(2)-C(33)-C(38)	121 (2)
P(1)-Fe(2)-C(5)	102.2 (8)	C(8)-C(9)-C(10)	118 (3)	C(20)-C(21)-C(22)	89 (4)	C(34)-C(33)-C(38)	122 (2)
P(1)-Fe(2)-C(6)	93.3 (8)	C(9)-C(10)-C(11)	123 (3)	C(20)-C(21)-F(3)	122 (4)	C(33)-C(34)-C(35)	121 (2)
P(2)-Fe(2)-C(4)	89.6 (8)	C(10)-C(11)-C(12)	117 (3)	C(20)-C(21)-F(4)	118 (4)	C(34)-C(35)-C(36)	115 (3)
P(2)-Fe(2)-C(5)	103.8 (8)	C(7)-C(12)-C(11)	122 (3)	C(22)-C(21)-F(3)	117 (3)	C(35)-C(36)-C(37)	123 (3)
C(2)-Fe(2)-C(6)	89.7 (8)	P(1)-C(13)-C(14)	111 (3)	C(22)-C(21)-F(4)	112 (3)	C(36)-C(37)-C(38)	117 (3)
C(4)-Fe(2)-C(5)	88 (1)	P(1)-C(13)-C(18)	118 (3)	F(3)-C(21)-F(4)	100 (4)	C(33)-C(38)-C(37)	121 (3)
C(4)-Fe(2)-C(6)	179 (1)	C(14)-C(13)-C(15)	130 (3)	C(19)-C(22)-C(21)	92 (3)	C(39)-C(40)-C(41)	127 (13)
C(5)-Fe(2)-C(6)	91 (1)						

Table V

(a) Selected Weighted Least-Squares Planes for V[a]

Plane 1: $-0.7116x - 0.5355y - 0.4548z = -9.874$

C(7)	−0.003 (7)	C(10)	−0.004 (9)	P(1)[b]	−0.206
C(8)	0.003 (8)	C(11)	0.002 (8)		
C(9)	0.001 (9)	C(12)	0.001 (8)		

Plane 2: $0.7352x - 0.5192y - 0.4358z = 4.236$

C(13)	0.000 (7)	C(16)	0.001 (9)	P(1)[b]	−0.106
C(14)	−0.004 (8)	C(17)	−0.005 (8)		
C(15)	0.005 (9)	C(18)	0.004 (8)		

Plane 3: $0.5475x - 0.6385y - 0.5410z = 4.360$

C(27)	−0.004 (7)	C(30)	−0.006 (9)	P(2)[b]	0.025
C(28)	0.001 (8)	C(31)	0.000 (9)		
C(29)	0.004 (9)	C(32)	0.005 (8)		

Plane 4: $-0.8521x + 0.3585y - 0.3813z = -9.352$

C(33)	−0.009 (8)	C(36)	−0.006 (10)	C(26)[b]	−0.041
C(34)	0.008 (8)	C(37)	0.001 (9)		
C(35)	0.000 (11)	C(38)	0.006 (8)		

Plane 5: $-0.8324x - 0.5465y - 0.0917z = -10.48$

C(19)	0.003 (7)	C(22)	−0.003 (8)
C(20)	−0.004 (9)	P(2)[b]	−0.077
C(21)	0.004 (9)	C(23)[b]	−0.195

Plane 6: $-0.9910x + 0.1338y - 0.0058z = -12.35$

C(23)	−0.014 (8)	C(26)	0.014 (8)
C(24)	0.017 (9)	C(22)[b]	−0.215
C(25)	−0.019 (9)	C(33)[b]	0.070

Dihedral Angles between Planes

plane	plane	angle, deg	plane	plane	angle, deg
1	2	42.7	3	4	119.3
1	3	78.6	3	5	93.3
1	4	54.0	3	6	128.7
1	5	22.1	4	5	56.7
1	6	50.5	4	6	26.5
2	3	14.1	5	6	41.2
2	4	130.3	Fe(1),Fe(2),P(1)	Fe(1),Fe(2),P(2)	103.4
2	5	106.8	Fe(1),P(1),P(2)	Fe(2),P(1),P(2)	98.7
2	6	142.7			

[a] Equations are referred to orthogonal axes with x along a, z along c^*, and y in the ab plane. [b] Atom not included in the plane.

(b) Selected Weighted Least-Squares Planes for VI

Plane 1: $-0.4747x + 0.0329y - 0.8795z = -7.174$

C(7)	0.01 (2)	C(10)	0.02 (3)	P(1)[b]	0.062
C(8)	0.00 (3)	C(11)	−0.01 (3)		
C(9)	−0.01 (3)	C(12)	−0.01 (3)		

Plane 2: $0.9272x - 0.2261y - 0.2985z = -0.6400$

C(13)	−0.07 (3)	C(16)	−0.06 (4)	P(1)[b]	−0.251
C(14)	0.08 (3)	C(17)	0.03 (4)		
C(15)	0.00 (4)	C(18)	0.07 (4)		

Plane 3: $0.9882x + 0.1507y - 0.0285z = -1.867$

C(27)	−0.01 (2)	C(30)	0.04 (3)	P(2)[b]	0.154
C(28)	0.02 (3)	C(31)	−0.03 (3)		
C(29)	−0.04 (3)	C(32)	0.01 (3)		

Plane 4: $-0.4408x - 0.0488y - 0.8963z = -5.333$

C(33)	−0.04 (2)	C(36)	−0.03 (3)	P(2)[b]	−0.062
C(34)	0.00 (2)	C(37)	−0.01 (3)		
C(35)	0.03 (3)	C(38)	0.05 (3)		

Plane 5: $0.5179x - 0.8431y - 0.1443z = -5.451$

C(19)	−0.01 (3)	C(22)	0.01 (3)
C(20)	0.01 (4)	C(23)[b]	0.00
C(21)	−0.02 (4)	P(2)[b]	−0.107

Plane 6: $0.3595x - 0.7837y - 0.5065z = -6.276$

C(23)	0.02 (3)	C(26)	−0.02 (3)
C(24)	−0.04 (4)	C(22)[b]	−0.05
C(25)	0.03 (3)	Fe(1)[b]	0.252

Plane 7: $-0.1089x - 0.7108y - 0.6949z = -7.399$

Fe(1)	−0.019 (4)	C(19)[b]	1.29
Fe(2)	0.016 (4)	C(22)[b]	1.61
P(2)	−0.040 (8)	C(23)[b]	1.32
C(26)	0.61 (3)	P(1)[b]	−0.184

Dihedral Angles between Planes

plane	plane	angle, deg	plane	plane	angle, deg
1	2	101	3	4	115
1	3	116	3	5	67
1	4	5	3	6	75
1	5	98	3	7	101
1	6	76	4	5	93
1	7	50	4	6	71
2	3	27	4	7	45
2	4	97	5	6	23
2	5	44	5	7	50
2	6	49	6	7	30
2	7	74	7	Fe(1),Fe(2),P(1)	6

[a] Equations are referred to orthogonal axes with x along a, z along c^*, and y in the ab plane. [b] Atom not included in the plane.

where a phenyl group from one $(C_6H_5)_3P$ ligand couples with a bound $(C_6H_5)_3P$. There appear to be no other examples where the displaced group undergoes a rearrangement of the type seen in V to allow it to bridge two metal atoms.

Acknowledgment. This work was supported by the National Science and Engineering Research Council of Canada in the form of operating grants to W.R.C. and F.W.B.E.

Registry No. I, 67124-61-2; II, 75010-83-2; III, 72765-07-2; IV, 75010-84-3; V, 75024-08-7; VI, 75010-86-5; $Fe(CO)_5$, 13463-40-6; $Fe_3(CO)_{12}$, 17685-52-8.

Supplementary Material Available: Tables of the observed and calculated structure factors for both isomers (29 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
University of Minnesota, Minneapolis, Minnesota 55455

Photochemical Properties and X-ray Structural Characterization of a Tetranuclear Bimetallic Complex: $[Rh_2(TM4\text{-}bridge)_4Mn_2(CO)_{10}](PF_6)_2 \cdot 2(CH_3)_2CO$ (TM4-bridge = 2,5-Dimethyl-2,5-diisocyanohexane)

DAVID A. BOHLING, THOMAS P. GILL, and KENT R. MANN*

Received June 18, 1980

The sunlight irradiation of $Mn_2(CO)_{10}$ in the presence of $Rh_2(TM4\text{-}bridge)_4PF_6$ (TM4-bridge = 2,5-dimethyl-2,5-diisocyanohexane) in acetone solution yields the mixed-metal tetranuclear compound $[Rh_2(TM4\text{-}bridge)_4Mn_2(CO)_{10}](PF_6)_2 \cdot 2(CH_3)_2CO$. The dark green crystals obtained from acetone/hexane crystallize in the space group *Pna*2 (No. 33) (a = 18.265 (11), b = 23.185 (7), c = 17.836 (4) Å; Z = 4, ρ(calcd) = 1.391 (1), ρ(obsd) = 1.41 (2) g/cm^3). The structure is composed of tetranuclear $[(CO)_5MnRh_2(TM4\text{-}bridge)_4Mn(CO)_5]^{2+}$ cations having approximate D_{2d} symmetry, PF_6^- anions, and two acetone molecules of crystallization per formula unit. The geometry about each Mn and Rh atom is approximately pseudooctahedral. The RhRh bond length is 2.922 (2) Å while the two RhMn bonds are 2.905 (5) and 2.883 (4) Å. The quantum yields for the formation of $[Rh_2(TM4\text{-}bridge)Mn_2(CO)_{10}]^{2+}$ in acetone solution (2.6×10^{-3} M in $Mn_2(CO)_{10}$ and 1.2×10^{-3} M in $Rh_2(TM4\text{-}bridge)_4^{2+}$) were measured by irradiation with 405- and 546-nm light. At 405 nm, the quantum yield for the formation of $[Rh_2(TM4\text{-}bridge)_4Mn_2(CO)_{10}]^{2+}$ (a wavelength corresponding to absorbance by $Mn_2(CO)_{10}$) was ϕ = 0.20 (1). At 546 nm, where greater than 99% of the light is absorbed by $Rh_2(TM4\text{-}bridge)_4^{2+}$, the quantum yield was found to be $\phi \approx 3\ (1) \times 10^{-4}$, almost 3 orders of magnitude smaller than at 405 nm. These data are tentatively interpreted in terms of the generation of $Mn(CO)_5$ radicals which are efficiently collected by the $Rh_2(TM4\text{-}bridge)_4^{2+}$ ion present in solution. The $[Rh_2(TM4\text{-}bridge)_4Mn_2(CO)_{10}]^{2+}$ ion was found to be relatively stable in degassed acetone solution under photolysis with a 4-mW HeNe laser ($\phi_{\text{decomposition}} \approx 5\ (2) \times 10^{-5}$). In the presence of oxygen, however, irradiation of the complex regenerates $Rh_2(TM4\text{-}bridge)_4^{2+}$ ($\phi_{\text{decomposition}} \approx 2\ (1) \times 10^{-2}$) and an undetermined Mn complex. These properties are discussed in terms of simple molecular orbital theory.

There has been much recent interest[1] in the synthesis and properties of metal cluster compounds as candidates for catalyzing potentially useful reactions. Of interest to us has been the synthesis of mixed-metal cluster compounds which incorporate the potential to serve as photoassistance agents utilizing visible radiation for the initiation of the photoassistance cycle. As our visible-light-absorbing chromophore, we have chosen to investigate compounds which contain $\sigma \rightarrow \sigma^*$ transitions due to the metal–metal bonds contained in the molecule. Our hope was to extend the metal–metal interaction to multiple metal centers, so as to move the $\sigma \rightarrow \sigma^*$ transitions from the near-ultraviolet[2] into the visible spectral region. Second, we hope that similar photochemical reactions as found in binuclear systems (i.e., metal–metal bond cleavage[3]) could be induced, photogenerating reactive intermediates which could be used as the catalytic agents in the photoassistance cycle.

We now wish to report the synthesis, X-ray structure determination, and a preliminary photochemical investigation of a linear tetranuclear cluster containing Rh and Mn, which represents our initial attempt at producing a cluster with the properties which we feel will be useful in visible-light photoassistance schemes.

Experimental Section

General Information. The synthesis of the starting material $Rh_2(TM4\text{-}bridge)_4(PF_6)_2$ (TM4-bridge = 2,5-dimethyl-2,5-diisocyanohexane) has been reported previously.[4] $Mn_2(CO)_{10}$ was purchased from ROC/RIC. The solvents used were of spectroscopic quality. IR, NMR, and UV-vis spectra were obtained by using a Perkin-Elmer 283, a Varian Associates CFT 20 equipped with a 79.5-MHz proton accessory, and a Cary 17D spectrophotometer, respectively. The elemental analyses were performed at Galbraith Laboratories, Knoxville, Tenn.

Preparation of $[Rh_2(TM4\text{-}bridge)_4Mn_2(CO)_{10}](PF_6)_2 \cdot 2(CH_3)_2CO$. A sample of 81.1 mg of $Rh_2(TM4\text{-}bridge)_4(PF_6)_2$ (0.0707 mmol) and 84.7 mg of $Mn_2(CO)_{10}$ (0.271 mmol) in 20 mL of acetone were placed along with a stir bar in a Pyrex test tube sealed with a serum stopper and degassed by a N_2 purge for 20 min. The resulting bright red solution was then stirred in bright Minneapolis sunshine at ambient temperature. Immediately, on exposure to sunlight, the solution turned a dark royal blue color and was stirred for an additional 1.5 h. The solution was evaporated to dryness on a rotary evaporator and washed several times with hexane to remove the remaining excess $Mn_2(CO)_{10}$. Recrystallization of the residue from acetone/hexane afforded 93.4 mg (0.0565 mmol) of $[Rh_2(TM4\text{-}bridge)_4Mn_2(CO)_{10}](PF_6)_2 \cdot 2(CH_3)_2CO$, an 80% yield (based on the Rh complex). Anal. Calcd for $Rh_2Mn_2C_{56}H_{70}N_8O_{12}P_2F_{12}$: C, 40.69; H, 4.27; N, 6.78. Found: C, 40.40; H, 4.41; N, 6.81. Mp: 175 °C dec (sealed capillary). NMR spectrum (acetone-d_6): CH_3, acetone of crystallization, τ 7.92; CH_3, TM4-bridge, τ 8.37 (br, s); CH_2, TM4-bridge, τ 8.25 (br, s). IR spectrum (acetone solution): $\bar{\nu}$(CN) 2178 cm^{-1} (vs), $\bar{\nu}$(CO) 2038 cm^{-1}

---

[1] (a) Moskovits, M. *Acc. Chem. Res.* **1979**, *12*, 229–236. (b) Muetterities, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91–138. (c) Muetterties, E. L. *Ibid.* **1978**, *78*, 639–658 and references contained therein.

[2] Levenson, R. A.; Gray, H. B. *J. Am. Chem. Soc.* **1975**, *97*, 6042–6047.

[3] (a) Wrighton, M. S. *Top. Curr. Chem.* **1976**, *37*, 69–78. (b) Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photohemistry"; Academic Press: New York, 1979; pp 136–141 and references therein.

[4] (a) Mann, K. R.; Thich, J. A.; Bell, R. A.; Coyle, C. L.; Gray, H. B. *Inorg. Chem.*, in press. (b) Mann, K. R.; Gray, H. B. *Adv. Chem. Ser.* **1979**, *No. 173*, 225–235.