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Preparation and Structure Studies of Monomeric and Dimeric [Bis(diphenylphosphino)pentane]tricarbonyliron(0)

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The $(CH_3)_3NO$ oxidative decarbonylation of (maleic acid)$Fe(CO)_4$, followed by precipitation of trimethylammonium maleate in the presence of $Ph_2P(CH_2)_5PPh_2$ results in dimeric $[(Ph_2P(CH_2)_5PPh_2)Fe(CO)_3]_2$ (**1**). The low-temperature quenching of (*cis*-cyclooctene)$_2$Fe(CO)$_3$ with $Ph_2P(CH_2)_5PPh_2$ yields monomeric $(Ph_2P(CH_2)_5PPh_2)Fe(CO)_3$ (**2**). Both monomeric and dimeric forms have been studied by spectroscopic methods and X-ray diffraction. X-ray crystallographic data for the title compounds are as follows: **1**, monoclinic space group *C*2/*c*, $a = 27.170$ (8) Å, $b = 14.458$ (2) Å, $c = 8.255$ (3) Å, $\beta = 102.88$ (2)°, $V = 6991$ (3) Å^3, $Z = 4$, 2443 data with $I_0 > 2.5\sigma(I_0)$ refined to $R = 0.054$ and $R_w = 0.061$; **2**, monoclinic, space group *Cc*, $a = 19.094$ (1) Å, $b = 10.455$ (1) Å, $c = 15.786$ (3) Å, $\beta = 114.89$ (3)°, $V = 2858$ (2) Å^3, $Z = 4$, 1723 data with $I_0 > 2.5\sigma(I_0)$ refined to $R = 0.044$ and $R_w = 0.051$. Monomeric **2** has a trigonal bipyramidal Fe(0) center with the chelating diphosphine occupying one axial and one equatorial site, corresponding to a cis form. The structure of **1** reveals that the two trigonal bipyramidal Fe(0) centers are bridged by two $Ph_2P(CH_2)_5PPh_2$ ligands and each Fe(0) center has two P donors diaxially coordinated, corresponding to a trans form.

Introduction

The established methods of synthesizing (diphosphine)$Fe(CO)_3$ derivatives generally involve the direct reaction of a diphosphine with iron carbonyls under various conditions.[1–13] The treatment of iron carbonyls with diphosphines such as dppm, dppe, or dppp at elevated temperatures or under UV irradiation leads to the formation of both $(P{\sim}P)Fe(CO)_3$ and $(OC)_4Fe(\mu\text{-}P{\sim}P)Fe(CO)_4$ ($P{\sim}P$ = dppm, dppe, dppp). The yields are variable, and generally the separation of diphosphine, chelated and bridging products is tedious.

Increasing the chain length of a diphosphine inevitably changes the chelate ring size of the corresponding $(P{\sim}P)Fe(CO)_3$ derivatives. For $P{\sim}P$ = dppm and dppe,[14,15] the bonding geometry of $(P{\sim}P)Fe(CO)_3$ conforms to a distorted square pyramid with the two P donors being dibasal and cis. For $P{\sim}P$ = dppp and dppf,[16,17] the coordination geometry of $(P{\sim}P)Fe(CO)_3$ can be described as trigonal bipyramidal with one of the P donors being in the axial position and the other equatorial. For $P{\sim}P$ = $Ph_2P(CH_2)_5PPh_2$, abbreviated as dppt, we report here the successful synthesis of both dimeric $[(dppt)Fe(CO)_3]_2$ (**1**) and monomeric (dppt)$Fe(CO)_3$ (**2**) in very good yields via routes not previously reported. We also present the X-ray structure determinations of **1** and **2**.

Experimental Section

All manipulations were performed under an atmosphere of prepurified nitrogen with standard Schlenk techniques, and all solvents were distilled from an appropriate drying agent.[18] Infrared spectra were recorded in CH_2Cl_2 using CaF_2 optics on a Perkin-Elmer 882 spectrophotometer. The $^{31}P\{^1H\}$ NMR spectra were obtained on a Bruker MSL 200 spectrometer using 85% H_3PO_4 as an external standard. (MA-)$Fe(CO)_4$, MA = maleic acid, and $(COE)_2Fe(CO)_3$, COE = *cis*-cyclooctene, were prepared according to the literature procedures.[19,20] Other reagents were obtained from commercial sources, e.g. Aldrich and Merck, and used without further purification.

Preparation of $[(dppt)Fe(CO)_3]_2$ (1). (MA)$Fe(CO)_4$ (284 mg, 1 mmol) and dppt (440 mg, 1 mmol) were dissolved in THF (50 mL), and the solutions were stirred for 30 min at 0 °C. $(CH_3)_3NO{\cdot}2H_2O$ (167 mg, 1.5 mmol) in CH_3OH (1 mL)/THF (15 mL) was added dropwise to the solution during a period of 2 h. The color of the solution changed from yellow to dark-brown. The solution was then refluxed at 70 °C for 2 h before filtration and evaporation to dryness under vacuum. The resulting yellow crystals were purified by chromatography (Al_2O_3, eluting with CH_2Cl_2/*n*-hexane) and recrystallization (CH_2Cl_2/*n*-hexane) to give **1** (527 mg, 45.4%) as a yellowish compound. Crystals suitable for X-ray diffraction were grown from CH_2Cl_2/*n*-hexane by a slow evaporation method: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 75.53 (s); IR (CH_2Cl_2) ν_{CO} 1877 cm^{-1}; mp 208–210 °C dec; MS (*m*/*z*) for $C_{64}H_{60}Fe_2O_6P_4$, 1415 (M^+, parent ion). Anal. Calcd for $C_{67}H_{66}Cl_6Fe_2O_6P_4$: C, 56.82; H, 4.66. Found: C, 57.67; H, 5.03.

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(1) King, R. B.; Eggers, C. A. *Inorg. Chim. Acta* **1968**, *2*, 33.

(2) Cullen, W. R.; Harbourn, D. A. *Can. J. Chem.* **1969**, *47*, 3371.

(3) Collman, J. P.; Komoto, R. G.; Siegl, W. O. *J. Am. Chem. Soc.* **1972**, *95*, 2389.

(4) Carroll, W. E.; Deeney, F. A.; Delaney, J. A.; Lalor, F. J. *J. Chem. Soc., Dalton Trans.* **1973**, 718.

(5) Fenske, D. *Chem. Ber.* **1979**, *112*, 363.

(6) Manuel, T. A. *Inorg. Chem.* **1963**, *2*, 854.

(7) Akhtar, M.; Ellis, P. D.; Macdiarmid, A. G.; Odom, J. D. *Inorg. Chem.* **1972**, *11*, 2917.

(8) Allison, D. A.; Clardy, J.; Verkade, J. G. *Inorg. Chem.* **1972**, *11*, 2804.

(9) Langford, G. R.; Akhtar, M.; Ellis, P. D.; Macdiarmid, A. G.; Odom, J. D. *Inorg. Chem.* **1975**, *14*, 2937.

(10) Alper, H.; Partis, R. A. *J. Organomet. Chem.* **1972**, *44*, 371.

(11) Claucas, J. A.; Dawson, R. H.; Dolby, P. A.; Harding, M. M.; Peason, K.; Smith, A. K. *J. Organomet. Chem.* **1986**, *311*, 153.

(12) Brunet, J. J.; Kindela, F. B.; Neibecker, D. *J. Organomet. Chem.* **1989**, *368*, 209.

(13) Hor, T. S. A.; Phang, L. T. *J. Organomet. Chem.* **1990**, *381*, 121.

(14) Cotton, F. A.; Hardcastle, K. I.; Rusholme, G. A. *J. Coord. Chem.* **1973**, *2*, 217.

(15) Battaglia, L. P.; Nardelli, M.; Delledonne, D.; Pelizzi, C.; Predieri, G.; Chiusoli, G. P. *J. Organomet. Chem.* **1987**, *330*, 101.

(16) Luh, L.-S. Masters Thesis, Department of Chemistry, National Chung-Hsing University, Taichung, Taiwan, 1990.

(17) Liu, L.-K.; Yeh, S. K.; Lin, C. C. *Bull. Inst. Chem. Acad. Sin.* **1988**, *35*, 45.

(18) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon Press: Oxford, England, 1981.

(19) Weiss, E.; Stark, K.; Lancaster, J. E.; Murdoch, H. D. *Helv. Chem. Acta* **1963**, *46*, 288.

(20) Fleckner, H.; Grevels, F.-W.; Hess, D. *J. Am. Chem. Soc.* **1984**, *106*, 2027.

0020-1669/92/1331-3434$03.00/0

Table I. Crystallographic Data and Refinement Details for $[(dppt)Fe(CO)_3]_2 \cdot 3CH_2Cl_2$ (**1**) and $(dppt)Fe(CO)_3$ (**2**)

	1	**2**
empirical formula	$C_{67}H_{66}Cl_6Fe_2O_6P_4$	$C_{32}H_{30}FeO_3P_2$
fw	1415.56	580.38
space group	*C*2/*c*	*Cc*
a, Å	27.170 (8)	19.094 (1)
b, Å	14.458 (2)	10.455 (1)
c, Å	8.255 (3)	15.786 (3)
β, deg	102.88 (2)	114.89 (3)
V, Å^3	6991 (3)	2858 (2)
Z	4	4
T, K	298	298
λ(Mo Kα), Å	0.7093	0.7093
D_{calc}, g cm^{-3}	1.345	1.349
μ, mm^{-1}	0.78	0.67
abs corr	yes	yes
transm factors	0.948–1.000	0.889–1.000
$R(F_o)^a$	0.054	0.044
$R_w(F_o)^a$	0.061	0.051

[a] $R(F_o) = \sum(F_o - F_c)/\sum F_o$; $R_w(F_o) = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$.

Structure Analysis of $[(dppt)Fe(CO)_3]_2 \cdot 3CH_2Cl_2$ (1). A single crystal of ca. 0.47 × 0.31 × 0.34 mm was used for the data collection. Intensity measurements were performed on a Nonius CAD-4 automated diffractometer using graphite-monochromated Mo Kα radiation. A total of 25 high-angle reflections, $18.98 \leq 2\theta \leq 36.54°$, were used in a least-squares fit to obtain accurate cell constants. Diffraction intensities were measured up to $2\theta \leq 45°$ using the $\theta/2\theta$ scan technique, with background counts made for half the total scan time on each side of the peak. Three standard reflections, remeasured every 1 h, showed no significant decrease in intensity during data collection. Of the 4568 unique reflections measured, 2443 were classed as observed $[I_0 > 2.5\sigma(I_0)]$ and were used for solution and structure refinement. Data were corrected for Lorentz–polarization factors. An empirical absorption correction based on a series of ψ scans was applied to the data. The structure was solved by direct methods[21] and refined by a full-matrix least-squares routine[22] with anisotropic thermal parameters for all non-hydrogen atoms (weight = $1/[\sigma(F_o)^2 + 0.0001(F_o)^2]$, $\sigma(F_o)$ from counting statistics). All of the hydrogen atoms were placed isotropically at their calculated positions (C–H = 1.00 Å) and fixed in the calculations. Atomic scattering factor curves f_0, $\Delta f'$, and $\Delta f''$ of Fe, P, O, and C and f_0 of H were taken from ref 23. Final refinement converged to $R = 0.054$ and $R_w = 0.061$. For a summary of crystal data and refinement details, see Table I. Selected bond distances and angles are given in the caption of Figure 1, and final atomic fractional coordinates, in Table II.

Preparation of $(dppt)Fe(CO)_3$ (2). A solution of $(COE)_2Fe(CO)_3$ (360 mg, 1 mmol) in THF (30 mL) was stirred for 10 min at −60 °C before adding dropwise dppt (440 mg, 1 mmol) in THF (15 mL). After the temperature was kept at −60 °C for an additional 2 h, the solution was allowed to warm to room temperature. The solution was then filtered, and the filtrate was evaporated to dryness under vacuum giving a yellow solid. The solid was washed with *n*-hexane (3 × 30 mL) to give **2** (541 mg, 93.1%) as a yellow powder. Crystals suitable for X-ray diffraction were grown by slow evaporation from CH_2Cl_2/*n*-hexane: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 55.48 (s); IR (CH_2Cl_2) ν_{CO} 1983 (s), 1912 (s), 1883 (vs) cm^{-1}; mp 155–158 °C; MS (*m*/*z*) for $C_{32}H_{30}FeO_3P_2$, 580 (M^+, parent ion). Anal. Calcd for $C_{32}H_{30}FeO_3P_2$: C, 66.22; H, 5.21. Found: C, 66.20; H, 4.86.

Structure Analysis of $(dppt)Fe(CO)_3$ (2). A crystal of ca. 0.44 × 0.36 × 0.22 mm was used for the data collection. Intensity data were collected in a fashion similar to that for **1**. Of 1957 unique reflections measured, 1723 were classed as observed $[I_0 > 2.5\sigma(I_0)]$ and were used for solution and structure refinement. The structure was solved by direct methods. Final refinement converged to $R = 0.044$ and $R_w = 0.051$. For a summary of crystal data and refinement details, see Table I. Selected bond distances and angles are given in the caption of Figure 2, and final fractional atomic coordinates, in Table III.

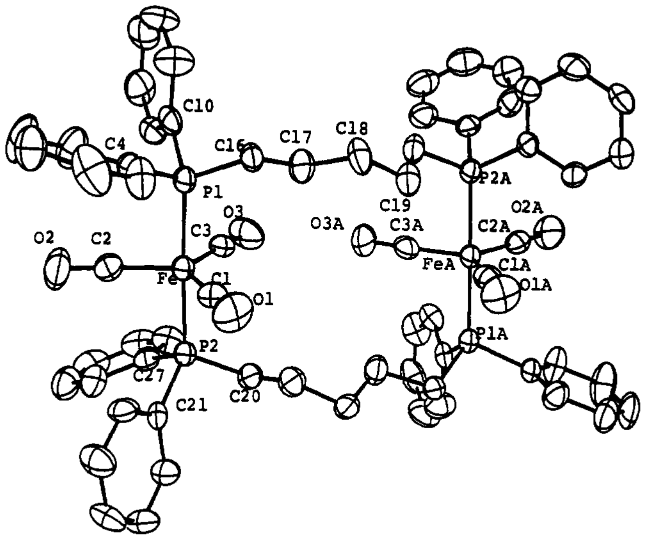

Figure 1. ORTEP diagram with atom-numbering scheme for **1** with thermal ellipsoids scaled to enclose 50% of the electron density. The H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe–P(1) = 2.206 (2), Fe–P(2) = 2.216 (2), Fe–C(1) = 1.769 (9), Fe–C(2) = 1.762 (9), Fe–C(3) = 1.763 (9); P(1)–Fe–P(2) = 177.78 (9), P(1)–Fe–C(1) = 90.8 (3), P(1)–Fe–C(2) = 87.6 (3), P(1)–Fe–C(3) = 90.3 (3), P(2)–Fe–C(1) = 87.6 (3), P(2)–Fe–C(2) = 91.9 (3), P(2)–Fe–C(3) = 91.8 (3), C(1)–Fe–C(2) = 122.5 (4), C(1)–Fe–C(3) = 117.9 (4), C(2)–Fe–C(3) = 119.6 (4).

Monitoring of Changes of 2 under Heating. Compound **2** was dissolved in THF (50 mL) and refluxed under nitrogen for 2 days. The IR ν_{CO} pattern was monitored every 4 h, revealing no significant changes throughout the period. The $^{31}P\{^1H\}$ NMR spectra of reaction mixtures after 2 days exhibited the presence of paramagnetic species but not **1**.

Results and Discussion

Synthesis. Two different routes have been employed for the dppt ligation onto a $Fe(CO)_3$ moiety (Scheme I). The first proceeds by an oxidative decarbonylation of $(MA)Fe(CO)_4$ by Me_3NO followed by precipitation of trimethylammonium maleate in the presence of $Ph_2P(CH_2)_5PPh_2$, dppt. The initial stage is the O atom transfer from Me_3NO to a CO ligand producing gaseous CO_2 and NMe_3 with NMe_3 temporarily occupying the vacated site. Then during the dppt chelation stage in refluxing THF, the leaving ligand MA reacts with NMe_3 to form a salt $(HNMe_3)^+MA^-$. The second is a low-temperature reaction of $(COE)_2Fe(CO)_3$ with dppt. The oxidative decarbonylation method requires a much higher temperature than the ligand substitution of $(COE)_2Fe(CO)_3$. The two methods result in different products. The high-temperature route produces **1** in a 45.4% yield whereas the low-temperature route gives **2** in a virtually quantitative yield.

Spectroscopy. Both **1** and **2** have been characterized with $^{31}P\{^1H\}$ NMR, IR, mp, EA, MS, and X-ray structure analysis. **1** exhibits only one ν_{CO} absorption and **2** exhibits three ν_{CO} absorptions in the IR spectra. This suggests that there are completely different coordination arrangements around Fe(0) in **1** and **2**. With one ν_{CO} band, **1** is expected to have two P atoms coordinated diaxially at trans positions around a tbp Fe(0) center, whereas, with three ν_{CO} bands, **2** is expected to have one P atom axial and the other P atom equatorial.[24] In d^8 complexes, π-accepting ligands will prefer the equatorial position. As a less

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(21) Main, P. In *Crystallographic Computing 3: Data Collection, Structure Determination, Proteins and Databases*; Sheldrick, G. M., Krueger, C., Goddard, R., Eds.; Clarendon Press: Oxford, England, 1985; pp 206–215.

(22) (a) Gabe, E. J.; Le Page, Y.; White, P. S.; Lee, F. L. *Acta Crystallogr.* **1987**, *43A*, S294. (b) Gabe, E. J.; Le Page, Y.; Lee, F. L. In *Crystallographic Computing 3: Data Collection, Structure Determination, Proteins and Databases*; Sheldrick, G. M., Krueger, C., Goddard, R., Eds.; Clarendon Press: Oxford, England, 1985; pp 167–174.

(23) Ibers, J. A.; Hamilton, W. C. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974 (current distributor D. Reidel, Dordrecht, The Netherlands); Vol. IV, Tables 2.2A, 2.3.1D.

(24) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley; CA, 1980; pp 81–89.

Table II. Final Atomic Fractional Coordinates and Equivalent Isotropic Displacement Coefficients (Å^2) for $[(dppt)Fe(CO)_3]_2 \cdot 3CH_2Cl_2$ (**1**)

atom	*x*	*y*	*z*	B_{iso}[a]
Fe	0.12367 (4)	0.25753 (8)	0.18543 (6)	2.73 (5)
P(1)	0.15924 (7)	0.26594 (14)	0.30632 (12)	2.78 (10)
P(2)	0.08566 (7)	0.24550 (15)	0.06507 (11)	2.78 (10)
Cl(1)	0.6180 (3)	0.2874 (6)	0.1272 (5)	23.55 (69)
Cl(2)	0.5964 (3)	0.1720 (7)	0.2271 (5)	29.95 (82)
Cl(3)	0.4777 (4)	0.3980 (5)	0.1779 (4)	28.38 (81)
O(1)	0.1103 (3)	0.0574 (4)	0.1955 (4)	6.1 (4)
O(2)	0.0493 (2)	0.3904 (5)	0.2153 (4)	5.8 (4)
O(3)	0.2177 (2)	0.3228 (5)	0.1502 (4)	6.2 (4)
C(1)	0.1158 (3)	0.1366 (6)	0.1925 (5)	3.8 (5)
C(2)	0.0785 (3)	0.3376 (6)	0.2020 (4)	3.6 (4)
C(3)	0.1797 (3)	0.2979 (6)	0.1630 (5)	3.6 (4)
C(4)	0.2091 (3)	0.1818 (5)	0.3438 (4)	2.7 (4)
C(5)	0.2312 (3)	0.1279 (6)	0.2968 (4)	3.5 (4)
C(6)	0.2698 (3)	0.0671 (6)	0.3259 (5)	4.7 (5)
C(7)	0.2873 (3)	0.0596 (6)	0.4023 (5)	4.3 (4)
C(8)	0.2661 (3)	0.1103 (6)	0.4496 (5)	4.2 (5)
C(9)	0.2280 (3)	0.1717 (5)	0.4219 (5)	3.5 (4)
C(10)	0.1909 (3)	0.3763 (5)	0.3361 (4)	3.2 (4)
C(11)	0.1635 (3)	0.4529 (6)	0.3492 (5)	4.3 (4)
C(12)	0.1874 (4)	0.5362 (6)	0.3713 (5)	5.3 (6)
C(13)	0.2385 (4)	0.5437 (7)	0.3798 (6)	5.6 (6)
C(14)	0.2661 (4)	0.4696 (7)	0.3653 (6)	5.0 (5)
C(15)	0.2427 (3)	0.3875 (6)	0.3443 (5)	4.0 (4)
C(16)	0.1159 (3)	0.2539 (6)	0.3694 (4)	3.4 (4)
C(17)	0.0881 (3)	0.1608 (6)	0.3606 (5)	3.9 (4)
C(18)	0.0559 (3)	0.1454 (6)	0.4186 (5)	4.1 (4)
C(19)	−0.0119 (3)	0.2106 (5)	0.0898 (5)	3.8 (4)
C(20)	0.0272 (3)	0.1765 (5)	0.0456 (4)	3.2 (4)
C(21)	0.1241 (3)	0.1881 (5)	0.0081 (4)	3.0 (4)
C(22)	0.1562 (3)	0.2399 (6)	−0.0234 (5)	4.9 (5)
C(23)	0.1876 (4)	0.1970 (7)	−0.0644 (6)	6.4 (6)
C(24)	0.1864 (4)	0.1045 (8)	−0.0741 (6)	5.5 (6)
C(25)	0.1556 (4)	0.0520 (7)	−0.0404 (6)	6.0 (6)
C(26)	0.1243 (3)	0.0932 (6)	0.0000 (5)	4.5 (5)
C(27)	0.0674 (3)	0.3515 (5)	0.0113 (5)	3.3 (4)
C(28)	0.0406 (4)	0.3460 (6)	−0.0638 (6)	5.1 (5)
C(29)	0.0295 (4)	0.4273 (8)	−0.1049 (5)	5.7 (6)
C(30)	0.0434 (4)	0.5102 (7)	−0.0749 (7)	5.4 (6)
C(31)	0.0696 (4)	0.5172 (6)	−0.0019 (6)	5.1 (6)
C(32)	0.0816 (3)	0.4383 (6)	0.0408 (5)	3.9 (4)
C(33)	0.6362 (7)	0.2817 (24)	0.2189 (10)	22.9 (26)
C(34)	0.5000	0.4623 (19)	0.2500	19.2 (27)

[a] $B_{iso} = 8\pi^2/3(U_{11} + U_{22} + U_{33})$.

π-accepting ligand than CO, a phosphine is generally found to preferentially occupy the axial position.[25] Accordingly, one phosphine moiety of dppt coordinates to the axial site of a tbp Fe(0). Chelation then brings the second phosphine moiety cis to the first one, forming a chelate structure **2**. However, there is also the possibility of dppt coordinating in bridging or unidentate modes for which the two phosphine moieties from two different dppt's would coordinate to a $Fe(CO)_3$ unit diaxially. Such species would exhibit only one ν_{CO} infrared stretching frequency.

The ^{31}P NMR spectrum also suggests that **1** contains two axial P donors whereas **2** contains two cis P donors since *diaxial*-$P_2Fe(CO)_3$ (P = a phosphine ligand) generally exhibits a lower field chemical shift than *cis*-$P_2Fe(CO)_3$, e.g. $(Ph_2PMe)_2Fe(CO)_3$ at δ 64.7 (in $CDCl_3$)[26] and (dppb)$Fe(CO)_3$ at δ 61.7 (in acetone-d_6), which would be correlated to a peak at ca. δ 57 in $CDCl_3$.[16] For **1** the resonance of the P donor atoms appears at δ 75.53, as compared to the higher field resonance of **2** at δ 55.48. It is reasonable to conclude that **1** is likely in a diaxial form and **2** is likely in a cis form.

Although the two cis P donor atoms in **2** have different environments, the $^{31}P\{^1H\}$ NMR spectrum of **2** exhibits only one single peak at 298 K at an apparently fluxional average on the NMR time scale, similar to other *cis*-$P_2Fe(CO)_3$ complexes whose ^{13}C NMR spectra were reported to display only one resonance down to e.g. −70 °C for $(Me_2PCF_2CH_2PMe_2)Fe(CO)_3$, −80 °C for dpppFe$(CO)_3$, and −140 °C for $[o\text{-}C_6H_4(AsMe_2)_2]Fe(CO)_3$.[7,9] The low-temperature ^{13}C or $^{31}P\{^1H\}$ NMR data of **2** were not measured.

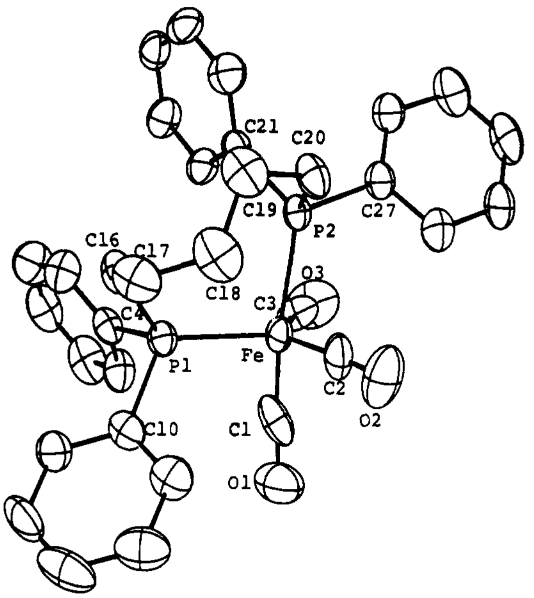

Figure 2. ORTEP diagram with atom-numbering scheme for **2** with thermal ellipsoids scaled to enclose 50% of the electron density. The H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe–P(1) = 2.250 (3), Fe–P(2) = 2.256 (3), Fe–C(1) = 1.657 (14), Fe–C(2) = 1.727 (11), Fe–C(3) = 1.763 (12); P(1)–Fe–P(2) = 97.05 (12), P(1)–Fe–C(1) = 90.8 (4), P(1)–Fe–C(2) = 114.6 (4), P(1)–Fe–C(3) = 117.0 (4), P(2)–Fe–C(1) = 171.8 (4), P(2)–Fe–C(2) = 87.9 (4), P(2)–Fe–C(3) = 87.5 (4), C(1)–Fe–C(2) = 90.9 (6), C(1)–Fe–C(3) = 86.9 (5), C(2)–Fe–C(3) = 128.4 (5).

Structure. Figure 1 shows the X-ray structure of **1**, in which the dimeric trigonal-bipyramidal Fe(0) centers have two dppt bridges and the two P atoms coordinated to the same Fe(0) center are trans. The six atoms constituting of Fe, P(1), P(2), Fe(a), P(1a), and P(2a) are nearly coplanar within ±0.164 (3) Å. A crystallographically required 2-fold axis passes through the center of gravity and is perpendicular to this plane. With $Z = 4$ in the space group *C*2/*c*, only half of the dimeric **1** is crystallographically independent. As three CH_2Cl_2 solvate molecules are associated with one dimeric **1**, one and one-half CH_2Cl_2 molecules are independent. The crystallographically independent half CH_2Cl_2 has its C atom located along the above-mentioned 2-fold axis about 2.97 Å from the six-atom plane. The Fe–P distances are approximately equal (2.206 (2) and 2.216 (2) Å) and the angle P(1)–Fe–P(2) is 177.78 (9)°. Other structural parameters for the ligands are in the expected range for distances and angles involving P or C atoms.

The X-ray structure of **2** as shown in Figure 2 reveals a trigonal-bipyramidal Fe(0) complex with the chelating diphosphine occupying one axial and one equatorial sites, corresponding to a cis form. Because of the five carbon chain between two phosphine moieties, **2** has an eight-membered chelate ring and a distorted trigonal-bipyramidal geometry around the Fe(0) center. The P(1)–Fe–P(2) angle is 97.1 (1)°, which is larger than the corresponding angles in (dppm)$Fe(CO)_3$, 73.5 (1)°,[14] (dppe)$Fe(CO)_3$, 84.1 (1)°,[15] (dppp)$Fe(CO)_3$, 91.5 (7)°,[16] and (dppb)$Fe(CO)_3$, 92.4 (1)°,[16] corresponding to the increase in the carbon chain length of the diphosphine. The axis of the tbp is along P(2)–Fe–C(1) with an angle of 171.8 (4)°. The bond distances and angles about P and C are similar to those in similar (diphosphine)$Fe(CO)_3$ structures. The axial Fe–C(1) length, 1.657 (14) Å, is much shorter than other Fe–C lengths ranging 1.74–1.78

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(25) (a) Huheey, J. E. *Inorganic Chemistry*; Harper & Row Publishers: New York, 1983; pp 471–484. (b) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365.

(26) Albers, M. O.; Colville, N. J.; Ashworth, T. V.; Singleton, E. *J. Organomet. Chem.* **1981**, *217*, 385.

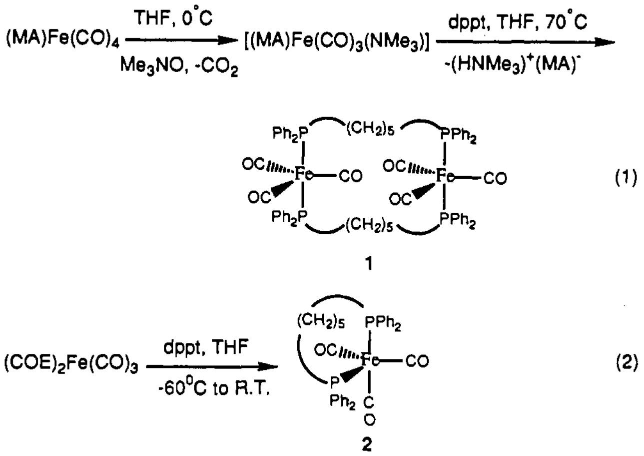
Table III. Final Atomic Fractional Coordinates and Equivalent Isotropic Displacement Coefficients (Å^2) for (dppt)Fe(CO)$_3$ (**2**)

atom	*x*	*y*	*z*	B_{iso}[a]
Fe	0.03934	0.23257 (12)	0.33927	2.85 (7)
P(1)	0.04078 (17)	0.34159 (25)	0.21715 (25)	2.84 (13)
P(2)	−0.07657 (16)	0.30304 (24)	0.32643 (25)	2.75 (12)
O(1)	0.1904 (6)	0.1239 (10)	0.3858 (6)	7.1 (6)
O(2)	−0.0227 (6)	−0.0246 (8)	0.2979 (7)	6.6 (6)
O(3)	0.1098 (6)	0.3484 (9)	0.5241 (6)	7.0 (6)
C(1)	0.1265 (7)	0.1743 (13)	0.3639 (8)	4.8 (7)
C(2)	−0.0004 (7)	0.0814 (10)	0.3125 (8)	4.1 (6)
C(3)	0.0806 (6)	0.3084 (10)	0.4492 (9)	4.2 (6)
C(4)	0.0942 (5)	0.4947 (10)	0.2527 (7)	3.2 (5)
C(5)	0.1695 (7)	0.4908 (11)	0.3180 (8)	4.3 (6)
C(6)	0.2103 (7)	0.6033 (14)	0.3523 (8)	5.3 (7)
C(7)	0.1756 (8)	0.7185 (12)	0.3183 (10)	5.2 (8)
C(8)	0.1008 (7)	0.7225 (11)	0.2550 (10)	5.1 (7)
C(9)	0.0609 (6)	0.6110 (11)	0.2205 (8)	4.5 (6)
C(10)	0.0889 (6)	0.2609 (11)	0.1516 (7)	3.4 (5)
C(11)	0.0877 (6)	0.1301 (11)	0.1446 (8)	4.3 (6)
C(12)	0.1166 (8)	0.0682 (13)	0.0878 (9)	5.5 (7)
C(13)	0.1480 (7)	0.1391 (17)	0.0390 (9)	6.1 (8)
C(14)	0.1495 (7)	0.2717 (15)	0.0463 (9)	5.4 (8)
C(15)	0.1208 (7)	0.3321 (12)	0.1021 (8)	4.4 (6)
C(16)	−0.0481 (6)	0.3927 (10)	0.1186 (7)	3.6 (5)
C(17)	−0.0983 (6)	0.2874 (12)	0.0559 (8)	4.7 (6)
C(18)	−0.1402 (7)	0.2011 (12)	0.0930 (9)	5.2 (7)
C(19)	−0.1901 (6)	0.2639 (12)	0.1343 (8)	4.6 (6)
C(20)	−0.1661 (6)	0.2313 (11)	0.2381 (7)	3.8 (5)
C(21)	−0.0973 (6)	0.4759 (9)	0.3146 (7)	2.9 (5)
C(22)	−0.0356 (6)	0.5613 (10)	0.3532 (7)	3.7 (5)
C(23)	−0.0508 (7)	0.6907 (10)	0.3524 (8)	3.9 (6)
C(24)	−0.1250 (7)	0.7356 (10)	0.3132 (8)	4.0 (6)
C(25)	−0.1866 (7)	0.6533 (11)	0.2723 (8)	4.2 (6)
C(26)	−0.1734 (6)	0.5233 (11)	0.2723 (7)	4.1 (6)
C(27)	−0.0926 (6)	0.2661 (10)	0.4310 (7)	3.1 (5)
C(28)	−0.0611 (7)	0.1501 (11)	0.4791 (9)	4.9 (7)
C(29)	−0.0768 (7)	0.1175 (12)	0.5542 (8)	5.1 (7)
C(30)	−0.1192 (7)	0.1934 (13)	0.5846 (8)	4.9 (7)
C(31)	−0.1482 (7)	0.3072 (12)	0.5404 (8)	4.8 (7)
C(32)	−0.1339 (6)	0.3432 (10)	0.4639 (7)	3.5 (5)

[a] $B_{iso} = 8\pi^2/3(U_{11} + U_{22} + U_{33})$.

Å. The reason for the shortening may be due to a steric effect derived from elongating the carbon chain of the diphosphine.

Scheme I



The major difference between the two synthetic routes is the difference in temperature. Since dimeric **1** is produced at a much higher temperature than monomeric **2**, **1** is likely the thermodynamically more stable form whereas **2** may simply be a kinetic product. To test whether **2** converts to **1** at high temperature, the THF solution of **2** was heated at reflux and monitored periodically with IR spectroscopy. The IR ν_{CO} single-band pattern of dimeric **1** is totally different from the three-band pattern of monomeric **2**. Yet the THF solution has not shown any significant change in IR ν_{CO} band pattern over 2 days. Final mixtures have been worked-up, too, and subjected to $^{31}P\{^1H\}$ NMR studies, which exhibit some paramagnetic species but not dimeric **1**. Apparently, monomeric **2** in refluxing THF proceeds with reaction pathways other than transformation to **1**.

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Supplementary Material Available: For the structures of **1** and **2**, listings of crystallographic data, positional and anisotropic thermal parameters, and bond distances and angles (11 pages). Ordering information is given on any current masthead page.