(6) P. M. Boymel, J. R. Chang, D. L. DuBois, D. J. Greenslade, G. R. Eaton, and S. S. Eaton, *J. Am. Chem. Soc.*, **99**, 5500 (1977).
(7) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958); H. St. Rade, *J. Phys. Chem.*, **77**, 424 (1973); D. B. Brown, V. H. Crawford, J. W. Hall, and W. E. Hatfield, *ibid.*, **81**, 1303 (1977).
(8) N. F. Curtis, *J. Chem. Soc.*, 3147 (1961).
(9) A. Earnshaw, "Introduction to Magnetochemistry", Academic Press, New York, 1968: (a) pp 5–7; (b) pp 34–36, 58.
(10) E. A. Boudreaux and L. N. Mulay, Eds., "Theory and Applications of Molecular Paramagnetism", Wiley, New York, 1976; B. N. Figgis and C. M. Harris, *J. Chem. Soc.*, 855 (1959); R. L. Martin and H. Waterman, *ibid.*, 2960 (1959).
(11) C. H. Klopfenstein, P. Jost, and O. H. Griffith, *Comput. Chem. Biochem. Res.*, **1**, 176 (1972).
(12) P. N. Howells, J. W. Kenney, J. H. Nelson, and R. A. Henry, *Inorg. Chem.*, **15**, 124 (1976).
(13) S. S. Eaton, D. L. DuBois, and G. R. Eaton, *J. Magn. Reson.*, **32**, 251 (1978).
(14) H. McConnell, *J. Chem. Phys.*, **25**, 709 (1956); D. Kivelson, *ibid.*, **33**, 1094 (1960).
(15) B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, **5**, 143 (1970); R. Barbucci, P. Paoletti, and M. J. M. Campbell, *Inorg. Chim. Acta*, **10**, 69 (1974).
(16) R. L. Lancione, H. C. Allen, Jr., and D. R. Sydor, *J. Coord. Chem.*, **4**, 153 (1975).
(17) T. Ogata, T. Fujisawa, N. Tanake, and H. Yokoi, *Bull. Chem. Soc. Jpn.*, **49**, 2759 (1976).
(18) E. K. Metzner, L. J. Libertini, and M. Calvin, *J. Am. Chem. Soc.*, **96**, 6516 (1974).
(19) K. More, G. R. Eaton, and S. S. Eaton, to be published.

# Metal Complexes of Fluorophosphines. 9. Structure of a Novel Complex from Benzalacetonetricarbonyliron and Methylaminobis(difluorophosphine)[1,2]

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**Abstract:** Reaction of $(C_6H_5CH{=}CHCOCH_3)Fe(CO)_3$ with $CH_3N(PF_2)_2$ in boiling hexane gives yellow $[C_6H_5CH{=}CHC(CH_3){=}C(POF_2)N(CH_3)PF_2]Fe(CO)(PF_2)_2NCH_3$. X-ray diffraction analysis of this complex indicates an unexpected structure containing a novel chelating ligand bonding to iron through both tetrahapto-1,3-diene and aminodifluorophosphine units. The formation of this complex can be rationalized by a scheme involving an intramolecular Wittig-type reaction as a key step.

## Introduction

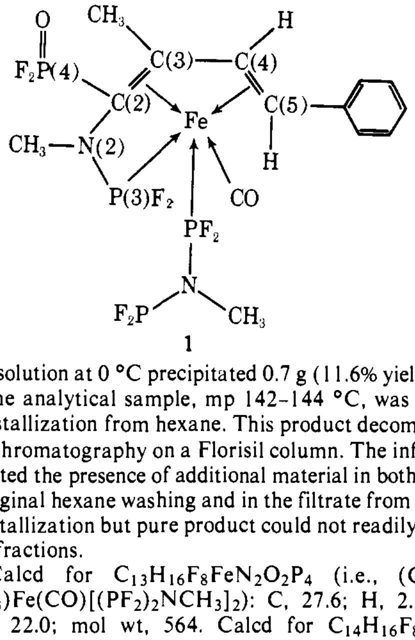
Previous papers from this laboratory have described a variety of iron carbonyl complexes of the potentially bidentate ligand $CH_3N(PF_2)_2$ including $CH_3N(PF_2)_2[Fe(CO)_4]_2$,[3,4] $CH_3N(PF_2)_2Fe_2(CO)_7$,[3,4] $[CH_3N(PF_2)_2Fe(CO)_3]_2$,[3,4] $[CH_3N(PF_2)_2]_2Fe_2(CO)_5$,[3,4] $[CH_3N(PF_2)_2]_2FeCO$,[4] and $[CH_3N(PF_2)_2]_4Fe_2CO$.[5] An obvious gap in this chemistry is the mononuclear complex $CH_3N(PF_2)_2Fe(CO)_3$ derived from $Fe(CO)_5$ by substitution of a single pair of its CO groups with the bidentate $CH_3N(PF_2)_2$ ligand. In an attempt to fill this gap the reaction of benzalacetonetricarbonyliron with $CH_3N(PF_2)_2$ was investigated hoping to effect the following reaction:

$$\begin{aligned}&(C_6H_5CH{=}CHCOCH_3)Fe(CO)_3 + CH_3N(PF_2)_2\\&\quad\rightarrow CH_3N(PF_2)_2Fe(CO)_3 + C_6H_5CH{=}CHCOCH_3 \qquad (1)\end{aligned}$$

However, preliminary investigation of the resulting product indicated retention of the benzalacetone ligand and suggested the unexpected formulation $(C_6H_5CH{=}CHCOCH_3)Fe(CO)[(PF_2)_2NCH_3]_2$. An X-ray crystal structure of this complex, however, revealed that this suggested structure was incorrect and instead indicated structure I containing a chelating ligand with both tetrahapto-1,3-diene and aminodifluorophosphine as donor units. This paper describes the details of this work.

## Experimental Section

**Reaction of Benzalacetonetricarbonyliron with $CH_3N(PF_2)_2$.** A mixture of 3.0 g (10.5 mmol) of $(C_6H_5CH{=}CHCOCH_3)Fe(CO)_3$,[6,7] 5.0 g (30 mmol) of $CH_3N(PF_2)_2$,[4,8] and 150 mL of hexane was boiled for 3 h under reflux in a nitrogen atmosphere. The reaction mixture turned yellow and a yellow powder precipitated. The hot reaction mixture was filtered and the precipitate washed with hexane. Cooling the hexane solution at 0 °C precipitated 0.7 g (11.6% yield) of yellow crystals. The analytical sample, mp 142–144 °C, was purified by further crystallization from hexane. This product decomposed upon attempted chromatography on a Florisil column. The infrared spectrum suggested the presence of additional material in both the residue from the original hexane washing and in the filtrate from the original hexane crystallization but pure product could not readily be isolated from these fractions.



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Anal. Calcd for $C_{13}H_{16}F_8FeN_2O_2P_4$ (i.e., $(C_6H_5CH{=}CHCOCH_3)Fe(CO)[(PF_2)_2NCH_3]_2$): C, 27.6; H, 2.8; F, 27.0; N, 5.0; P, 22.0; mol wt, 564. Calcd for $C_{14}H_{16}F_8FeN_2O_2P_4$ (i.e., $[C_6H_5CH{=}CHC(CH_3){=}C[P(O)F_2]N(CH_3)PF_2]Fe(CO)(PF_2)_2NCH_3$): C, 29.2; H, 2.8; F, 26.4; N, 4.9; P, 21.5; mol wt, 576. Found: C, 28.8; H, 2.9; F, 24.9; N, 4.9; P, 20.4; mol wt, 600 in benzene.

Infrared spectrum in KBr: 1975 (s), 1932 (w), 1490 (w), 1447 (w), 1381 (vw), 1316 (m), 1244 (w), 1192 (w), 1071 (s), 1048 (vw), 1033 (vw), 997 (vw), 974 (m), 910 (s), 882 (s), 858 (s), 835 (s), 822 (s), 808 (s), 778 (s), 760 (m), 697 (m), 682 (m), 642 (m), 595 (m), 556 (s), 533 (m), 510 (m), 485 (m) cm$^{-1}$.

$^1$H NMR spectrum in $CDCl_3$: $\tau$ 2.69 (singlet, 5 H, $C_6H_5$), 4.15 (broad triplet, $J \approx 9$ Hz, 1 H, CH), 5.6 (broad, 1 H, CH), 7.15 (doublet, $J = 11$ Hz, 3 H, $CH_3$), and 7.43 (singlet, 6 H, 2 $CH_3$).

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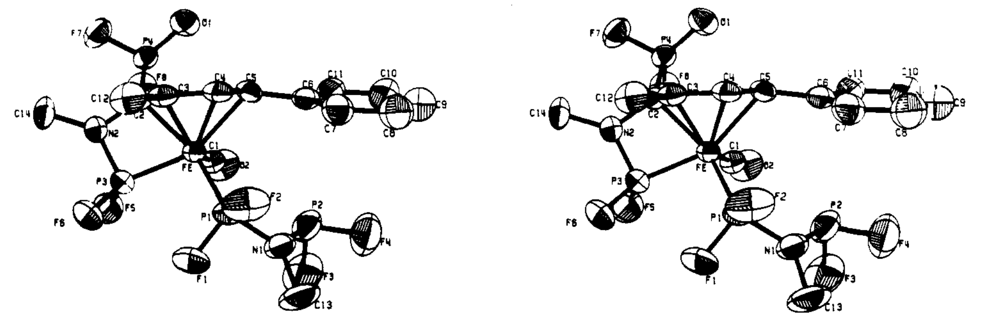

**Figure 1.** ORTEP stereoplot of a molecular unit showing the numbering scheme used in the X-ray analysis.

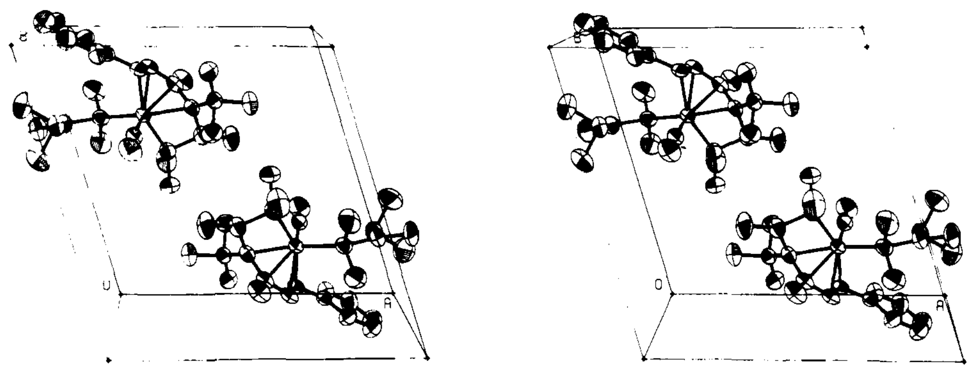

**Figure 2.** ORTEP stereoplot of unit cell contents.

**Table I.** Summary of Crystallographic Data for $[C_6H_5CH{=}CHC(CH_3){=}C(POF_2)N(CH_3)PF_2]Fe(CO)[(PF_2)_2NCH_3]$

| | |
|---|---|
| molecular formula | $FeC_{14}H_{16}N_2O_2P_4F_8$ |
| mol wt | 576.02 |
| linear absorption coefficient: | 10.82 cm$^{-1}$ |
| density (calcd for $Z$ = 2) | 1.741 g/cm$^3$ |
| space group | $P1$ or $P\bar{1}$ ($P\bar{1}$ determined by structure analysis) |
| cell dimensions | $a$ = 12.347 (2) Å<br>$b$ = 12.682 (2) Å<br>$c$ = 7.557 (1) Å<br>$\alpha$ = 102.57 (2)°<br>$\beta$ = 91.34 (1)°<br>$\gamma$ = 107.16 (2)°<br>$V$ = 1098.6 Å$^3$ |
| no. of reflections | 3856 measured<br>2451 obsd |
| final $R$ 0.035<br>$R_w$ 0.036 | |

$^{13}C$ NMR spectrum in $CDCl_3$ (proton-decoupled; multiplicities obtained from off-resonance decoupling): $\delta$ 239.6 (broad singlet, CO), 139.0, 129.1, 127.3, 126.6 ($C_6H_5$ pattern), 98.2 (doublet, $J$ = 31 Hz, in either the fully decoupled or the off-resonance decoupled spectrum, diene C), 92.8 (doublet, $J$ = 43 Hz, in either the fully decoupled or the off-resonance decoupled spectrum, diene C), 91.1 (doublet only in the off-resonance decoupled spectrum, diene C), 58.1 (doublet, $J$ = 8 Hz, splitting into an additional doublet in the off-resonance decoupled spectrum, diene C), 35.7 (quartet, $CH_3$), 24.9 (quartet, $CH_3$), 19.3 (quartet, $CH_3$).

Mass spectrum (Perkin-Elmer Hitachi RMU-6, 70 eV): major high $m/e$ ions at $m/e$ (rel intensity) 576 (3) (molecular ion for $[C_6H_5CH{=}CHC(CH_3){=}C[P(O)F_2]N(CH_3)PF_2]Fe(CO)(PF_2)_2NCH_3$), 548 (47) (molecular ion − CO), 400 (3) (molecular ion − $CH_3NP_2F_3$), 381 (100) (molecular ion − CO − $CH_3N(PF_2)_2$), 296 (13) (molecular ion − CO − $CH_3N(PF_2)_2$ − $POF_2$), and 287 (32) (molecular ion − CO − $CH_3N(PF_2)_2$ − $FeF_2$).

**Determination of the Structure of $[C_6H_5CH{=}CHC(CH_3){=}C[P(O)F_2]N(CH_3)PF_2]Fe(CO)(PF_2)_2NCH_3$.** A crystal of the complex was mounted on an Enraf-Nonius CAD-4 diffractometer using Mo K$\bar{\alpha}$ X-radiation with a graphite monochromator throughout the measurements. The cell dimensions and crystal system were determined from 15 accurately centered reflections. A summary of pertinent crystallographic data is provided in Table I.

The diffraction data were collected using the $\omega$–2$\theta$ scan technique and were corrected for Lorentz and polarization effects but not for absorption. In all, 2451 unique observable ($I > 3\sigma_I$) reflections were used in the structural analysis. The structure was solved using phases produced by program MULTAN.[9] The $E$ map using these phases led to starting coordinates for the iron atom and two of the four phosphorus atoms. Successive isotropic least-squares refinements and Fourier electron density maps revealed positions for all nonhydrogen atoms. Hydrogen atom positions were not determined. Full-matrix least-squares refinement for all atoms produced a final $R$ = 0.035 ($R_w$ = 0.036). Final coordinates and anisotropic temperature factors are listed in Table II. ORTEP plots of the molecular structure and unit cell contents are shown in Figures 1 and 2, respectively. Table III lists bond lengths and Table IV lists bond angles derived from final positional coordinates.

## Results

The unusual structure I is indicated by the X-ray structural data on this complex. A noteworthy feature of this structure is the presence of a chelating ligand functioning as a six-electron donor with four electrons coming from a tetrahapto-1,3-diene unit and the remaining two electrons from a difluorophosphine unit. The coordination of both the 1,3-diene portion and the difluorophosphine unit of this ligand was found to produce rather severe twisting around the $C_2$–$C_3$ bond of the butadiene. The angle between the best plane through $C_2$–$C_3$–$C_4$–$C_5$ and through $P_4$–$C_2$–$N_2$ is 47.9°. The $C_2$–$N_2$–$P_3$ plane is 91.0° from the butadiene best plane. The four metal-carbon bond distances in the tetrahapto-1,3-diene unit (Fe–$C_2$, Fe–$C_3$, Fe–$C_4$, and Fe–$C_5$) are 2.067 (4), 2.051 (4), 2.092 (3), and 2.175 (3) Å, respectively. These four iron-carbon bond distances span a wider range than comparable iron-carbon bond distances in other 1,2,3,4-tetrahapto-1,3-diene iron tricarbonyl complexes[10] except for 1,2,3,4-tetrahapto vinylketene derivatives.[11] This is a consequence of the extreme asymmetry of the 1,3-diene ligand in I. This asymmetry in the bonding of the tetrahapto-1,3-diene ligand is not

**Table II.** Positional Coordinates and Temperature Factors for $[C_6H_5CH{=}CHC(CH_3){=}C(POF_2)N(CH_3)PF_2]Fe(CO)[(PF_2)_2NCH_3]$

| atom | $x$ | $y$ | $z$ | $\beta_{11} \times 10^5$ | $\beta_{22} \times 10^5$ | $\beta_{33} \times 10^5$ | $\beta_{12} \times 10^5$ | $\beta_{13} \times 10^5$ | $\beta_{23} \times 10^5$ |
|---|---|---|---|---|---|---|---|---|---|
| Fe | 0.306 68 (6) | 0.719 36 (6) | 0.447 11 (9) | 523 (6) | 509 (6) | 1254 (14) | 132 (9) | 108 (14) | 340 (13) |
| P1 | 0.147 76 (12) | 0.691 64 (12) | 0.300 14 (20) | 675 (12) | 656 (12) | 1916 (33) | 108 (19) | −412 (31) | 473 (31) |
| P2 | 0.020 03 (15) | 0.700 83 (17) | 0.612 28 (29) | 724 (15) | 1152 (19) | 3917 (57) | 564 (26) | 1197 (45) | 1452 (51) |
| P3 | 0.346 30 (13) | 0.575 47 (13) | 0.300 71 (21) | 718 (13) | 672 (12) | 2096 (34) | 308 (20) | 256 (32) | −190 (32) |
| P4 | 0.569 18 (12) | 0.790 41 (12) | 0.650 51 (19) | 603 (11) | 732 (12) | 1538 (29) | 301 (19) | 72 (28) | 555 (30) |
| F1 | 0.109 20 (30) | 0.582 37 (30) | 0.140 63 (47) | 1092 (35) | 1155 (36) | 2712 (87) | 247 (57) | −1129 (86) | −780 (88) |
| F2 | 0.143 82 (32) | 0.776 18 (32) | 0.178 88 (51) | 1215 (37) | 1315 (38) | 3248 (95) | 215 (60) | −1091 (94) | 2191 (101) |
| F3 | −0.072 39 (38) | 0.585 72 (40) | 0.616 92 (78) | 1332 (46) | 1550 (49) | 7472 (197) | 455 (76) | 2728 (155) | 3552 (164) |
| F4 | −0.066 50 (37) | 0.770 71 (40) | 0.638 77 (69) | 1338 (46) | 1701 (52) | 5831 (160) | 1626 (81) | 2062 (137) | 1395 (144) |
| F5 | 0.320 64 (32) | 0.462 87 (28) | 0.364 41 (62) | 1149 (37) | 687 (29) | 5768 (143) | 590 (53) | 1018 (113) | 1051 (104) |
| F6 | 0.320 96 (32) | 0.515 81 (35) | 0.093 03 (49) | 1151 (37) | 1506 (43) | 2663 (90) | 602 (64) | −220 (88) | −1913 (96) |
| F7 | 0.684 46 (25) | 0.775 40 (31) | 0.599 77 (45) | 648 (27) | 1394 (38) | 2700 (84) | 628 (51) | 201 (73) | 710 (89) |
| F8 | 0.531 32 (28) | 0.691 89 (27) | 0.743 59 (42) | 1101 (32) | 981 (31) | 2339 (75) | 581 (51) | 271 (77) | 1373 (78) |
| O1 | 0.581 53 (31) | 0.900 11 (31) | 0.770 24 (48) | 906 (36) | 877 (34) | 1962 (83) | 481 (56) | −800 (85) | 85 (85) |
| O2 | 0.252 21 (37) | 0.640 06 (39) | 0.776 80 (58) | 1211 (45) | 1429 (50) | 2274 (100) | 473 (74) | 715 (105) | 2063 (119) |
| N1 | 0.024 53 (36) | 0.680 86 (39) | 0.387 16 (69) | 597 (38) | 848 (43) | 3208 (135) | 235 (65) | −210 (111) | 698 (120) |
| N2 | 0.482 73 (37) | 0.634 94 (38) | 0.334 96 (59) | 715 (38) | 872 (41) | 1928 (100) | 428 (64) | 480 (98) | −124 (100) |
| C1 | 0.269 36 (43) | 0.669 73 (44) | 0.645 43 (74) | 642 (45) | 697 (45) | 1922 (124) | 249 (71) | 183 (117) | 637 (122) |
| C2 | 0.480 06 (40) | 0.746 04 (42) | 0.445 51 (64) | 564 (41) | 685 (43) | 1441 (103) | 157 (66) | 295 (100) | 180 (105) |
| C3 | 0.442 95 (41) | 0.817 59 (43) | 0.345 81 (64) | 616 (42) | 710 (44) | 1357 (102) | −93 (69) | 64 (104) | 510 (108) |
| C4 | 0.379 00 (42) | 0.887 47 (41) | 0.428 29 (68) | 655 (43) | 548 (40) | 1689 (112) | −139 (68) | 109 (109) | 369 (106) |
| C5 | 0.348 06 (42) | 0.892 26 (38) | 0.610 85 (66) | 695 (43) | 452 (37) | 1678 (110) | 84 (64) | 195 (107) | 205 (99) |
| C6 | 0.262 50 (42) | 0.948 27 (40) | 0.679 65 (69) | 623 (42) | 538 (40) | 1906 (120) | 147 (67) | −236 (110) | 294 (109) |
| C7 | 0.201 04 (52) | 0.992 70 (50) | 0.573 51 (87) | 957 (58) | 781 (51) | 2964 (160) | 657 (89) | −189 (150) | 770 (145) |
| C8 | 0.127 16 (60) | 1.051 46 (58) | 0.654 70 (118) | 1090 (68) | 957 (64) | 4376 (238) | 861 (108) | −203 (205) | 1060 (199) |
| C9 | 0.112 14 (61) | 1.064 84 (61) | 0.839 93 (117) | 1095 (70) | 1112 (70) | 3756 (220) | 787 (113) | 311 (199) | 517 (199) |
| C10 | 0.172 76 (56) | 1.019 02 (61) | 0.944 18 (97) | 900 (62) | 1242 (71) | 3213 (185) | 772 (109) | 432 (170) | 186 (183) |
| C11 | 0.246 49 (47) | 0.962 22 (50) | 0.864 94 (76) | 763 (51) | 961 (55) | 1906 (128) | 441 (86) | 203 (125) | 51 (130) |
| C12 | 0.468 57 (51) | 0.814 92 (54) | 0.148 91 (70) | 1022 (58) | 1248 (63) | 1258 (111) | 133 (97) | 536 (125) | 903 (134) |
| C13 | −0.084 62 (54) | 0.646 33 (65) | 0.262 47 (117) | 690 (58) | 1395 (80) | 5342 (264) | 330 (109) | −1926 (197) | 666 (226) |
| C14 | 0.579 94 (54) | 0.611 27 (62) | 0.242 29 (92) | 851 (58) | 1530 (80) | 3018 (175) | 1011 (112) | 960 (160) | −789 (184) |

reflected in any anomalies in the carbon–carbon bond distances $C_2$–$C_3$, $C_3$–$C_4$, and $C_4$–$C_5$, which are 1.459 (5), 1.412 (5), and 1.433 (7) Å, respectively, corresponding to a typical $\Delta_2$ parameter (difference between the "inner" C–C distance and the average values of the "outer" C–C distances)[10] of 0.034 Å for 1,2,3,4-tetrahaptodiene-iron tricarbonyl derivatives. The bond angles around $C_3$, $C_4$, and $C_5$ clearly indicate $sp^2$ hybridization. However, bond angles involving $C_2$ show an unusual variation suggesting distortion from the twisting necessary to form the chelate "ring": $P_4$–$C_2$–$C_3$ is 127.3 (3)° whereas $P_4$–$C_2$–$N_2$ [112.5 (3)°] and $N_2$–$C_2$–$C_3$ [115.7 (4)°] are much less than ideal $sp^2$ angles. However, the sum of these three angles is 355.5°, which is close to the 360° required for planar $sp^2$-hybridized carbon. The phenyl ring plane is tilted only 14.4° from the butadiene best plane. The interaction between the hydrogen atoms on $C_4$ and $C_7$ owing to the near coplanarity causes the $C_5$–$C_6$–$C_7$ angle to expand to 124.3 (5)°. Other distances and angles are in agreement with values observed in related structures.

**Table III.** Bond Lengths for $[C_6H_5CH{=}CHC(CH_3){=}C(POF_2)N(CH_3)PF_2]Fe(CO)[(PF_2)_2NCH_3]$

| atoms | distance, Å[a] | atoms | distance, Å[a] |
|---|---|---|---|
| Fe–$P_1$ | 2.128 (1) | $P_4$–$C_2$ | 1.762 (5) |
| Fe–$P_3$ | 2.113 (1) | $O_2$–$C_1$ | 1.139 (6) |
| Fe–$C_1$ | 1.768 (5) | $N_1$–$C_{13}$ | 1.519 (8) |
| Fe–$C_2$ | 2.067 (4) | $N_2$–$C_2$ | 1.483 (5) |
| Fe–$C_3$ | 2.051 (4) | $N_2$–$C_{14}$ | 1.477 (7) |
| Fe–$C_4$ | 2.092 (3) | $C_2$–$C_3$ | 1.459 (5) |
| Fe–$C_5$ | 2.175 (3) | $C_3$–$C_4$ | 1.412 (5) |
| $P_1$–$F_1$ | 1.567 (3) | $C_3$–$C_{12}$ | 1.524 (7) |
| $P_1$–$F_2$ | 1.564 (3) | $C_4$–$C_5$ | 1.433 (7) |
| $P_1$–$N_1$ | 1.652 (4) | $C_5$–$C_6$ | 1.483 (6) |
| $P_2$–$F_3$ | 1.573 (3) | $C_6$–$C_7$ | 1.399 (6) |
| $P_2$–$F_4$ | 1.568 (3) | $C_6$–$C_{11}$ | 1.399 (8) |
| $P_2$–$N_1$ | 1.669 (6) | $C_7$–$C_8$ | 1.411 (8) |
| $P_3$–$F_5$ | 1.553 (2) | $C_8$–$C_9$ | 1.396 (12) |
| $P_3$–$F_6$ | 1.567 (4) | $C_9$–$C_{10}$ | 1.395 (8) |
| $P_3$–$N_2$ | 1.618 (4) | $C_{10}$–$C_{11}$ | 1.390 (7) |
| $P_4$–$F_7$ | 1.537 (3) | | |
| $P_4$–$F_8$ | 1.526 (2) | | |
| $P_4$–$O_1$ | 1.448 (3) | | |

[a] Bond distances have not been corrected for thermal motion. The estimated standard deviations do not contain cell constant errors.

The spectroscopic properties of this new iron complex are in accord with structure I. A predominant feature in the infrared spectrum is the expected strong $\nu$(CO) frequency at 1975 $cm^{-1}$ for the single carbonyl group; the weak band at 1932 $cm^{-1}$ can be assigned to the corresponding $\nu(^{13}CO)$ frequency. The $\nu$(PF) region around 800-900 $cm^{-1}$ is rather complex owing to the low symmetry and large number of nonequivalent P–F bonds in the system. The $^1H$ NMR spectrum exhibits in addition to the expected phenyl and methyl resonances olefinic proton resonances at $\tau$ 4.15 and 5.6 as compared with olefinic proton resonances at $\tau$ 3.91 and 6.88 for $(C_6H_5CH{=}CHCOCH_3)Fe(CO)_3$.

The $^{13}C$ NMR spectrum is particularly useful since each of the individual carbon atoms can be located. The carbonyl and phenyl resonances occur in typical regions. The expected three methyl resonances are observed. Comparison with the methyl resonance in $(C_6H_5CH{=}CHCOCH_3)Fe(CO)_3$ ($\delta$ 20.9) and in a typical monoligate monometallic $CH_3N(PF_2)_2$ complex[12] such as $C_5H_5Mo(CO)(NO)(PF_2)_2NCH_3$ ($\delta$ 26.0) suggests that in the $^{13}C$ NMR spectrum of I the resonance at $\delta$ 19.3 can be assigned to the *C*-methyl group and the resonance at $\delta$ 24.9 to the *N*-methyl group of the monoligate monometallic $CH_3N(PF_2)_2$ ligand leaving the $\delta$ 35.7 resonance for the *N*-methyl group in the chelating 1,3-diene-difluorophosphine ligand. The four carbon atoms of the 1,3-diene ligand appear at $\delta$ 98.2, 92.8, 91.1, and 58.1. All are doublets in the fully proton-decoupled $^{13}C$ NMR spectrum except for the singlet at $\delta$ 91.1, thus indicating that the other three resonances are

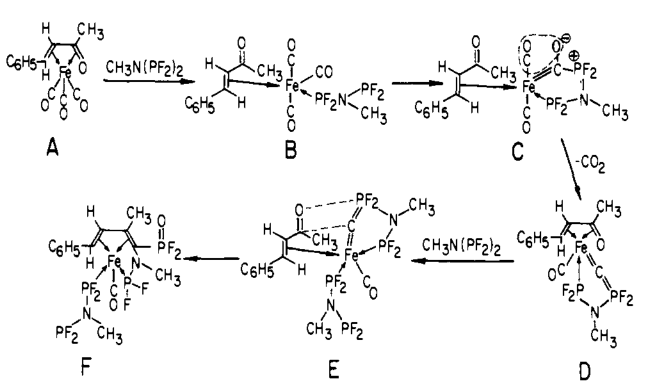

**Figure 3.** Proposed scheme for the reaction of benzalacetonetricarbonyliron with $CH_3N(PF_2)_2$.

split by phosphorus-31 coupling and therefore suggesting that they correspond to the three carbon atoms which are within three bonds of the phosphorus of the $P(O)F_2$ substituent on $C_2$. Accordingly, the resonance at $\delta$ 91.1 must be assigned to $C_5$, which is the only 1,3-diene carbon more than three bonds from the $P(O)F_2$ phosphorus. Off-resonance decoupling shows further doublet splitting of the $\delta$ 58.1 resonance, indicating that this resonance must be assigned to $C_4$ bearing a single hydrogen. This leaves the doublets centered at $\delta$ 98.2 and 92.8 for $C_2$ and $C_3$, which are coupled with the $P(O)F_2$ phosphorus but which have no directly bonded hydrogen.

An attempt was made to obtain a $^{31}P$ NMR spectrum of I. However, the pattern was so complex because of the four nonequivalent phosphorus atoms and many $J(PF)$ and $J(PP)$ coupling constants that the signal-to-noise ratio was marginal to observe the fine structure. Therefore even tentative assignments could not be made.

The mass spectrum of I was extremely complex in view of the complicated structure of this molecule and the asymmetry of the system leading to many possible fragmentation processes. For this reason a detailed analysis was not attempted. However, the expected molecular ion at *m/e* 576 could be identified. The most intense fragment ions appear at *m/e* 548, 381, and 296, corresponding to the successive losses of CO, $CH_3N(PF_2)_2$, and $POF_2$ in that order. A relatively intense ion also appears at *m/e* 287 corresponding to $C_{12}H_{13}NP_2F_2O^+$ formed by elimination of a neutral $FeF_2$ fragment from $C_{12}H_{13}NP_2F_4OFe^+$ (*m/e* 381). Similar eliminations of neutral $FeF_2$ and other metal fluoride fragments have been reported in the mass spectra of other fluorinated metal complexes.[13]

## Discussion

The formation of $[C_6H_5CH{=}CHC(CH_3){=}C[P(O)F_2]N(CH_3)PF_2]Fe(CO)(PF_2)_2NCH_3$ (I) from the reaction of benzalacetonetricarbonyliron with $CH_3N(PF_2)_2$ can be rationalized by the scheme outlined in Figure 3. In the first proposed step one of the phosphorus atoms in a $CH_3N(PF_2)_2$ ligand displaces the $\pi$-bonded ketone carbonyl group in benzalacetonetricarbonyliron (A) to form complex B containing *C,C*-dihapto benzalacetone and monoligate monometallic $CH_3N(PF_2)_2$ ligands. Related reactions of benzalacetonetricarbonyliron (A) with simple trivalent phosphorus ligands such as phosphines and phosphites have been reported to proceed in such a manner.[14] In the second proposed step the uncomplexed $PF_2$ group in B attacks the carbon of an adjacent carbonyl group to form a five-membered chelate ring leading to C. The oxygen atom of the carbonyl group incorporated into the chelate ring in C is bent in the direction of one of the remaining adjacent carbonyl groups, thereby facilitating loss of $CO_2$ to form D. Since such $CO_2$ loss vacates one of the iron coordination positions, the benzalacetone carbonyl group recoordinates to the iron atom in D to regenerate a *C,C,C,O*-tetrahapto benzalacetone ligand. The coordinated ketonic carbonyl in this tetrahapto benzalacetone ligand in D can be displaced by a new $CH_3N(PF_2)_2$ ligand to form E completely analogous to the conversion of A to B. The phosphorus-carbon bond in the chelate ring of D which is retained in E is analogous to a phosphorus-carbon bond in a phosphonium ylide (Wittig reagent) except for the nature of the substituents. This phosphorus-carbon bond can therefore react with the uncomplexed ketone in E in an intramolecular Wittig-type reaction with the formation of a new carbon-carbon double bond and a new phosphorus-oxygen bond to give the observed product F (=I). Formation of the former bond leads to the 1,3-diene whereas formation of the latter bond leads to the $POF_2$ substituent. Thus all of the five steps necessary to form the observed product I from benzalacetonetricarbonyliron and $CH_3N(PF_2)_2$ as outlined in Figure 3 are fully consistent with known chemistry: two steps involve simple displacement of a $\pi$-bonded ketone carbonyl with a trivalent phosphorus ligand (A → B and D → E), one step involves a decarboxylation (C → D), one step involves attack of a metal carbonyl carbon by a conveniently situated nucleophile (B → C), and one step involves an intramolecular version of the Wittig reaction (E → F). The following two features of the reaction sequence in Figure 3 are particularly novel: (1) an intramolecular Wittig reaction where both the phosphonium ylide and the ketone reactants are attached to the same transition metal through appropriate linkages; (2) the flexibility of the benzalacetone ligand to act as either a two- or a four-electron donor depending on the available number of metal coordination sites (i.e., the ketone

**Table IV.** Bond Angles (deg) for $[C_6H_5CH{=}CHC(CH_3){=}C(POF_2)N(CH_3)PF_2]Fe(CO)[(PF_2)_2NCH_3]$

| | | | |
|---|---|---|---|
| $P_1$-Fe-$P_3$ | 98.43 (5) | Fe-$P_1$-$F_1$ | 115.1 (1) |
| $P_1$-Fe-$C_1$ | 104.3 (2) | Fe-$P_2$-$F_2$ | 116.7 (1) |
| $P_1$-Fe-$C_2$ | 148.5 (1) | Fe-$P_1$-$N_1$ | 126.2 (2) |
| $P_1$-Fe-$C_3$ | 113.5 (1) | $F_1$-$P_1$-$F_2$ | 95.5 (2) |
| $P_1$-Fe-$C_4$ | 96.4 (1) | $F_1$-$P_1$-$N_1$ | 98.7 (2) |
| $P_1$-Fe-$C_5$ | 104.1 (1) | $F_2$-$P_1$-$N_1$ | 99.1 (2) |
| $P_3$-Fe-$C_1$ | 97.3 (1) | $F_3$-$P_2$-$F_4$ | 93.9 (2) |
| $P_3$-Fe-$C_2$ | 67.4 (1) | $F_3$-$P_2$-$N_1$ | 98.7 (3) |
| $P_3$-Fe-$C_3$ | 87.7 (1) | $F_4$-$P_2$-$N_1$ | 99.3 (2) |
| $P_3$-Fe-$C_4$ | 126.7 (1) | Fe-$P_3$-$F_5$ | 123.0 (2) |
| $P_3$-Fe-$C_5$ | 154.4 (1) | Fe-$P_3$-$F_6$ | 129.6 (2) |
| $C_1$-Fe-$C_2$ | 105.2 (2) | Fe-$P_3$-$N_2$ | 94.8 (1) |
| $C_1$-Fe-$C_3$ | 140.6 (2) | $F_5$-$P_3$-$F_6$ | 94.6 (2) |
| $C_1$-Fe-$C_4$ | 127.6 (2) | $F_5$-$P_3$-$N_2$ | 106.7 (2) |
| $C_5$-Fe-$C_1$ | 88.8 (2) | $F_6$-$P_3$-$N_2$ | 105.9 (2) |
| $C_2$-Fe-$C_3$ | 41.5 (1) | $F_7$-$P_4$-$F_8$ | 97.4 (1) |
| $C_4$-Fe-$C_2$ | 73.6 (1) | $F_7$-$P_4$-$O_1$ | 112.3 (2) |
| $C_2$-Fe-$C_5$ | 87.0 (2) | $F_7$-$P_4$-$C_2$ | 106.3 (2) |
| $C_3$-Fe-$C_4$ | 39.8 (1) | $F_8$-$P_4$-$O_1$ | 113.6 (2) |
| $C_3$-Fe-$C_5$ | 72.3 (2) | $F_8$-$P_4$-$C_2$ | 104.9 (2) |
| $C_4$-Fe-$C_5$ | 39.2 (2) | $O_1$-$P_4$-$C_2$ | 119.8 (2) |
| $P_1$-$N_1$-$P_2$ | 119.4 (3) | Fe-$C_4$-$C_5$ | 73.5 (2) |
| $P_1$-$N_1$-$C_{13}$ | 120.2 (4) | Fe-$C_4$-$C_3$ | 68.5 (2) |
| $P_2$-$N_1$-$C_{13}$ | 120.3 (4) | $C_5$-$C_4$-$C_3$ | 122.5 (3) |
| $P_3$-$N_2$-$C_2$ | 96.7 (3) | Fe-$C_1$-$O_2$ | 175.8 (4) |
| $P_3$-$N_2$-$C_{14}$ | 133.6 (3) | Fe-$C_5$-$C_4$ | 67.3 (2) |
| $C_2$-$N_2$-$C_{14}$ | 126.5 (3) | Fe-$C_5$-$C_6$ | 124.4 (3) |
| Fe-$C_2$-$P_4$ | 120.9 (2) | $C_4$-$C_5$-$C_6$ | 120.6 (3) |
| Fe-$C_2$-$N_2$ | 101.1 (3) | $C_5$-$C_6$-$C_7$ | 124.3 (5) |
| Fe-$C_2$-$C_3$ | 68.7 (2) | $C_5$-$C_6$-$C_{11}$ | 117.6 (4) |
| $P_4$-$C_2$-$N_2$ | 112.5 (3) | $C_7$-$C_6$-$C_{11}$ | 118.1 (4) |
| $P_4$-$C_2$-$C_3$ | 127.3 (3) | $C_6$-$C_7$-$C_8$ | 120.0 (6) |
| $N_2$-$C_2$-$C_3$ | 115.7 (4) | $C_7$-$C_8$-$C_9$ | 121.3 (5) |
| Fe-$C_3$-$C_{12}$ | 129.6 (3) | $C_8$-$C_9$-$C_{10}$ | 118.3 (5) |
| Fe-$C_3$-$C_4$ | 71.7 (2) | $C_9$-$C_{11}$-$C_{10}$ | 120.5 (6) |
| Fe-$C_3$-$C_2$ | 69.8 (2) | $C_6$-$C_{11}$-$C_{10}$ | 121.8 (4) |
| $C_2$-$C_3$-$C_4$ | 120.4 (4) | | |
| $C_2$-$C_3$-$C_{12}$ | 120.7 (3) | | |
| $C_4$-$C_3$-$C_{12}$ | 118.9 (3) | | |

carbonyl group can "reserve" an iron coordination site needed for a later step of the reaction).

In summary this work indicates that benzalacetonetricarbonyliron, although it can serve as a convenient source of $Fe(CO)_3$ groups under mild conditions for reactions with dienes[6] and acetylenes,[15] can undergo more complicated reactions involving the benzalacetone unit in the cases of other ligands as exemplified by $CH_3N(PF_2)_2$ in this work. There are thus some clear limitations in the use of benzalacetonetricarbonyliron as a source of $Fe(CO)_3$ groups in synthetic transition metal organometallic chemistry.

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## References and Notes

(1) For part 8 of this series see R. B. King and S. Goel, *Synth. React. Inorg. Met-Org. Chem.*, in press.
(2) Portions of this work were presented at the 9th Central Regional Meeting of the American Chemical Society, Charleston, W.Va., Oct 1977, Abstracts, No. INOR 60.
(3) M. G. Newton, R. B. King, M. Chang, and J. Gimeno, *J. Am. Chem. Soc.*, **99**, 2802 (1977).
(4) R. B. King and J. Gimeno, *Inorg. Chem.*, **17**, 2390 (1978).
(5) M. G. Newton, R. B. King, M. Chang, and J. Gimeno, *J. Am. Chem. Soc.*, **100**, 326 (1978).
(6) J. A. S. Howell, B. F. G. Johnson, P. L. Josty, and J. Lewis, *J. Organomet. Chem.*, **39**, 329 (1972).
(7) C. R. Graham, G. Scholes, and M. Brookhart, *J. Am. Chem. Soc.*, **99**, 1180 (1977).
(8) J. F. Nixon, *J. Chem. Soc. A*, 2689 (1968).
(9) The computer program MULTAN was written by P. Main and M. M. Woolfson, University of York, York, England, and G. Germain, Université de Louvain, Louvain, Belgium.
(10) F. A. Cotton, V. W. Day, B. A. Frenz, K. I. Hardcastle, and J. M. Troup, *J. Am. Chem. Soc.*, **95**, 4522 (1973).
(11) M. G. Newton, N. S. Pantaleo, R. B. King, and C. K. Chu, *J. Chem. Soc., Chem. Commun.*, 10 (1979).
(12) R. B. King and J. Gimeno, *Inorg. Chem.*, **17**, 2396 (1978).
(13) R. B. King, *J. Am. Chem. Soc.*, **89**, 6368 (1967).
(14) G. Cardaci and G. Concetti, *J. Organomet. Chem.*, **90**, 49 (1974); A. Vessieres and A. Dixneuf, *Tetrahedron Lett.*, 1499 (1974).
(15) R. B. King and M. N. Ackermann, *J. Organomet. Chem.*, **60**, C57 (1973).

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# Structural and Chemical Characterization of a Phosphine Bound M–H–M Bridged Carbonylate: $Et_4N^+(\mu\text{-}H)[Mo_2(CO)_9PPh_3]^-$

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**Abstract:** An X-ray crystal structure determination of $Et_4N^+(\mu\text{-}H)[Mo_2(CO)_9PPh_3]^-$ (**1**) has affirmed the positioning of $PPh_3$ to be cis to the hydride bridge in a (bent, staggered) molecular anion framework. The compound crystallizes in the monoclinic space group $P2_1/n$ with unit cell parameters of $a$ = 16.386 (6) Å, $b$ = 13.470 (5) Å, $c$ = 17.085 (8) Å, and $\beta$ = 92.10 (7)°; $\rho_{\text{calcd}} = 1.48$ g cm$^{-3}$ for $Z$ = 4. The refinement led to a final $R$ value of 0.034 based on 3518 observed reflections. The Mo–Mo separation is 3.4736 (7) Å, the bend of the molecular anion framework is 162.7°, the Mo–H–Mo angle is 127 (3)°, and the hydride is located asymmetrically between the Mo atoms, the shorter Mo–H distance (by 0.5 Å) being to the $Mo(CO)_5$ moiety. The quite long Mo–P bond (2.565 (1) Å) corroborated the solution chemistry of **1**, which was kinetically dominated by a labile Mo–$PPh_3$ bond. The kinetically determined Mo–P bond enthalpy in **1** is 23 ± 2.4 kcal/mol. The title compound may be used as precursor to more highly substituted dimer anions and/or neutral complexes, $L_2Mo(CO)_4$.

## Introduction

Previous investigations of $(\mu\text{-}H)[M(CO)_5]_2^-$ (M = group 6B) and related compounds have placed particular emphasis on the structural chemistry of such M–H–M bridged systems, while investigations of the dynamic chemistry of these carbonylates have remained limited. We have recently reported ligand lability studies of $Et_4N^+(\mu\text{-}H)[M(CO)_5]_2^-$ and have suggested that simple CO dissociation from an equatorial position is rate determining in ligand substitution reactions.[2,3] Group 5A donor ligands react with $(\mu\text{-}H)[M(CO)_5]_2^-$ in refluxing THF or EtOH to form $L_2M(CO)_4$ products. A kinetic investigation of this process implicated coordinatively unsaturated intermediates of the type $(OC)_5M\text{-}H\text{-}M(CO)_4^-$, with dimer disruption occurring only after substitution onto the available coordination site. For the reaction of $Et_4N^+(\mu\text{-}H)[Mo(CO)_5]_2^-$ with $PPh_3$ in THF, an intermediate, $Et_4N^+(\mu\text{-}H)[Mo_2(CO)_9PPh_3]^-$ (**1**), was isolated prior to dimer disruption and was tentatively identified as an equatorially substituted Mo dimer.[3]

Subsequent work has intimated that the effects of M–M interaction in these bridged hydride–dinuclear carbonylates make tenuous the local symmetry approximation used in the $\nu$(CO) infrared-based structure assignment.[4] An X-ray crystal structure determination was initiated to ascertain the geometry of the substituted anion as well as the details of structural modification on substitution of CO by the relatively enormous $PPh_3$ ligand. The refined structure of **1** (including the hydride position), the kinetic determination of the Mo–P bond strength in **1**, and the use of **1** as a precursor to other substituted dinuclear hydrides are reported here.

A recent review of structural transition metal hydride chemistry included an excellent and clarifying section on the six or so structures of 6B M–H–M carbonylates and derivatives.[5] A brief synopsis of the current status of these structural

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