Reaction of 1,2,3-Triphenyl-1,2,3-triphosphaindan with Nonacarbonyldiiron and Dodecacarbonyltriiron Revisited. Structures of Three P_3Fe_3 Clusters[1]

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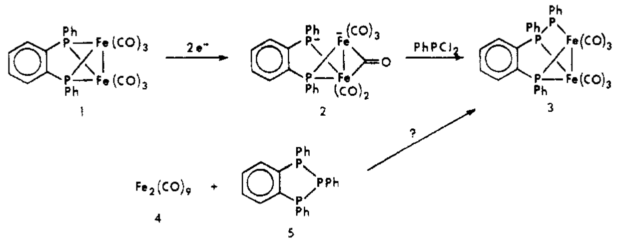
The reaction of 1,2,3-triphenyltriphosphaindan (1) with nonacarbonyldiiron or dodecacarbonyltriiron occurs rapidly in benzene at reflux to give a mixture of at least five components, as monitored by HPLC. In addition to [μ-1,2-phenylenebis(phosphido)]hexacarbonyldiiron and octacarbonyl[1,2,3-triphenyl-1,2,3-triphosphaindan-κP^1,κP^3]diiron(0), three Fe_3 species were isolated and their structures determined by X-ray crystallography, two of which were P_3Fe_3 clusters and the other, a P_3Fe_3 cluster precursor. The two clusters 3,3,3,4,4,4,6,6,6-nonacarbonyl-2,5,7-triphenyl-2,5,7-triphospha-3,4,6-triferrapentacyclo[6.4.0.0.^{2,5}0.^{3,7}0.^{4,6}]dodeca-8(1),9,11-triene (8) and 3,3,3,4,4,4,6,6,6-nonacarbonyl-2,5,7-triphenyl-2,5,7-triphospha-3,4,6-triferrapentacyclo[6.4.0.0.^{2,6}0.^{3,5}0.^{4,7}]dodeca-8(1),9,11-triene (11) are trigonal-prismatic structures with an edge of a three-membered ring expanded by the benzo moiety. The third complex whose structure was determined was [4,4,4,5,5,5-hexacarbonyl-2,3,6-triphenyl-2,3,6-triphospha-4,5-diferratetracyclo[5.4.0.0.^{3,5}0.^{4,6}]undeca7(1),8,10-triene]tetracarbonyliron (9) which contains a disymmetric bis(μ-phosphido)hexacarbonyldiiron moiety and a proximal, pendant (phosphido)tetracarbonyliron moiety. Species 9 decomposes thermally in benzene with first-order kinetics [$\tau_{1/2}$(80.5 °C) = 79.4 min^{-1}] to give 8 in quantitative yield during the early stages of the reaction. Complex 8 rearranges in benzene into the isomeric 11 also in a first-order process with $\tau_{1/2}$ (80.5 °C) = 75.4 min^{-1}. Crystal structures at −110 °C have been determined for 8, 9, and 11. X-ray data were collected on a Syntex $P2_1$ autodiffractometer and refined by full-matrix least-squares methods. For 8: $a = 15.635$ (3) Å, $b = 11.856$ (2) Å, $c = 18.982$ (4) Å, $\beta = 112.85$ (2)°, monoclinic, $P2_1/c$, $Z = 4$, $R = 0.0450$, $R_w = 0.0382$ for 5251 reflections with $I \geq 2\sigma_I$. An unusually long Fe–Fe bond, 2.862 Å, is observed at the fusion of two four-membered rings. For 9, $a = 10.499$ (1) Å, $b = 10.371$ (2) Å, $c = 34.046$ (7) Å, $\alpha = 104.55$ (1)°, $\beta = 89.43$ (1)°, $\gamma = 106.20$ (1)°, triclinic, $P\bar{1}$, $Z = 4$, $R = 0.0516$, $R_w = 0.0431$ for 6893 reflections with $I \geq 2.5\sigma_I$. The two crystallographically independent molecules differ in that the coordination geometry about the $Fe(CO)_4P$ moiety is trigonal bipyramidal with P equatorial in one molecule and square pyramidal with P basal in the other. For 11, $a = 9.885$ (2) Å, $b = 17.412$ (4) Å, $c = 9.799$ (7) Å, $a = 96.78$ (2)°, $\beta = 95.46$ (2)°, $\gamma = 89.97$ (2)°, triclinic, $P\bar{1}$, $Z = 2$, $R = 0.0391$, $R_w = 0.0369$ for 4126 reflections with $I \geq 2.5\sigma_I$. The structure contains a highly symmetrical P_3Fe_3 core with a long Fe–Fe bond, 2.830 Å, between two metal atoms bearing eclipsed carbonyl groups.

Introduction

Recently we have been developing transition-metal coordination chemistry of linked, bis(μ-phosphido) and related ligands. We have described the dianion 2 derived from 1 and its reaction with the electrophiles MeI and trifluoroacetic or acetic acid.[2] We also noted that the reaction of 2 with phenylphosphonous dichloride gave 3, albeit in low yields (ca. 10%, eq 1).[3] This species was of interest to us because of the potential for the synthesis of higher nuclearity complexes, via the free lone pair and/or metal insertion into the phosphinidene–iron bond. Since we had prepared 1 from the reaction of nonacarbonyldiiron (4) and 1,2-bis(phenylphosphino)benzene, we wondered whether or not we might be able to synthesize 3 in better yield by the reaction of 4 and 1,2,3-triphenyltriphosphaindan (5).[4]



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Results

Addition of 3 equiv of nonacarbonyldiiron to a hot (70 °C) benzene solution of the benzotriphosphole 5, followed by heating the reaction mixture at reflux for 10–30 min gave rise to a complex mixture as monitored by HPLC (UV detector at 280 nm, silica). Figure 1 illustrates a typical HPLC chromatogram, which did not appear to change drastically after the first 10 min of reaction, although some significant changes did occur on heating for several hours (vide infra). The major components were separated by preparative HPLC utilizing hexane–ethyl acetate (49:1, v/v) as eluent. Table I presents yields and ^{31}P NMR and IR data for some of the components (W–Z) labeled in Figure 1.

Peak V is at the solvent front, which contains benzene as well as unidentified material. The other peaks (W–Z) identified in Figure 1 were found to correspond to materials isolated by one of us earlier from the reaction of dodecacarbonyltriiron and 5.[5] Peak W corresponded to 1, first prepared in 3% yield[5] and later in about 60%.[2]

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[1] (a) Linked Bis(μ-phosphido) and Related Ligands for Metallic Clusters. 4. For the preceding paper in this series, see: Kyba, E. P.; Mather, J. D.; Hassett, K. L.; McKennis, J. S.; Davis, R. E. *J. Am. Chem. Soc.* **1984**, *106*, 5371. (b) A preliminary account of this work has appeared. Kyba, E. P.; Davis, R. E.; Hassett, K. L.; McKennis, J. S.; Sheikh, B. *Phosphorus Sulfur* **1983**, *18*, 275.

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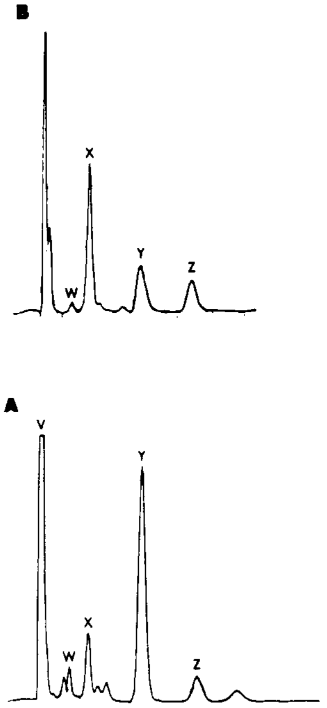


Figure 1. HPL chromatograms of A, the reaction of **5** + $Fe_2(CO)_9$, and B, the reaction of **5** + $Fe_3(CO)_{12}$. Conditions, retention volumes, and yields are given in the Experimental Section.

Table I. ^{31}P NMR and IR Spectra of Benzotriphosphole 5 and Carbonyliron Complexes Derived from It

	^{31}P NMR, ppm	IR ν_{CO}, cm^{-1}
5	32.0 (2 P), −38.9 (1 P) (J_{AB} = 262 Hz)[b]	
6	90.0 (2 P), −29.0 (1 P) (J_{AB} = 262 Hz)	2055 (m), 1984 (m), 1956, 1952 (s, overlapping)
8 (≡ Z)	133.8 (dd, J = 264, 23 Hz, 1 P), 72.3 (d, J = 23 Hz, 1 P), 53.2 (d, J = 264, 1 P)	2056 (m), 2025 (s), 1997 (s)
9 (≡ X1)	129.7 (dd, J = 235, 185 Hz, 1 P), 113.1 (dd, J = 185, 15 Hz, 1 P), 30.7 (dd, J = 236, 15 Hz, 1 P)[c]	2067 (m), 2055 (ms), 2028 (s), 2003 (m), 1992 (m), 1973 (m), 1956 (m)
11 (≡ X2)	55.6 (1 P), −16.8 (2 P) (J = 185 Hz)[d]	2046 (s), 2015 (s), 1998 (m), 1966 (m), 1955 (m)

[a] NMR spectra were determined on 0.05 M $CDCl_3$ solutions at an operating frequency of 32.2 MHz. See Experimental Section for further details. IR spectra were taken on 1% (w/v) CH_2Cl_2 solutions, using an abscissa expansion mode. [b] Second-order A_2B spectrum, matched exactly by calculation using the chemical shifts and coupling constant given. [c] The spectrum determined at 36.4 MHz was essentially identical with that reported above, and the coupling constants at the two operating frequencies agreed within 1 Hz. [d] Second-order AB_2 spectrum, matched exactly by calculation using the chemical shifts and coupling constants given.

Peak X caused some difficulties for us until we determined that two products of the reaction (X1 and X2) had exactly the same retention volumes. This problem was solved by carrying out the analyses on an alumina HPLC column, utilizing dichloromethane–hexane (3:97, v/v) as the eluent, which gave base-line separation of components V–Z. When the reaction was run only for a short period (0.5 h), only XI was produced, whereas long reaction times (10 h) gave both X1 and X2. Both materials were crystallized and recrystallized from 2% ethyl acetate in hexane (XI was more soluble than X2) to give crystals of X-ray quality. Care had to be taken in the recrystallization of X1 to minimize the heating time (ca. 10 min) as well as the temperature of the solvent during dissolution of the solid (ca. 55 °C), because X1 was transformed into Z if these conditions were exceeded significantly (see below). Manipulation of X1 was further complicated by the fact that in solvents which were not largely hexane (e.g., pure benzene, dichloromethane, ethyl acetate), it was transformed quite cleanly at room temperature in the dark into **1** (peak W) and Z (mol ratio ca. 1:10), with a half-life on the order of 1 day.

In a control experiment, pure X1 was heated in benzene at reflux and the course of the reaction was followed by HPLC. At reasonably high dilution (8.92×10^{-5} M), it exhibited clean first-order decomposition kinetics, with $k_1 = 9.15 \times 10^{-3}$ min^{-1} ($\tau_{1/2}$ = 75.4 min). The transformation of X1 to Z is essentially quantitative in the early stages of the reaction ($<0.3\tau_{1/2}$), but the yield of Z falls off as a function of time since it decomposes at about the same rate as X1 (see below). In a similar experiment, it was found that no X2 was lost during a 24-h period in benzene at reflux.

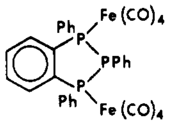
Complex Y was obtained as a yellow powder which appeared to be somewhat unstable, particularly in solution. This material was heated in boiling benzene in the presence and absence of $Fe_2(CO)_9$. During a period of 1 h, in neither case was there appreciable loss of Y, nor the appearance of any of the other components shown in Figure 1A.

Finally, complex Z was crystallized and recrystallized from toluene to give reddish purple hexagonal X-ray quality crystals. When Z was heated in benzene at reflux, it gave clean first-order kinetics of disappearance, with $k_1 = 8.73 \times 10^{-3}$ min^{-1} ($\tau_{1/2}$ = 79.0 min). The yield of X2, based on the amount of Z lost, was about 50%, and no other components were detected with the HPLC solvent system utilized.

The reaction of **5** with dodecacarbonyltriiron gave the same products but a significantly different distribution than the reaction of **5** with **4**, as shown in Figure 1b. That the X peak was indeed X1 was established unambiguously with the alumina HPLC column (see above).

Discussion

The products W–Z described in Table I are those isolated and described earlier by one of us,[5] but obtained from the reaction of **5** and dodecacarbonyltriiron. The structures of W and of Y originally assigned as **1** and **6** are



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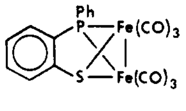

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entirely reasonable. Although we do not have an X-ray structure on **1**, we have determined the structure of **7**, whose spectral properties are very similar to **1**.[2,6] The structural assignment of Y as **6** rests on combustion analytical, as well as IR (no bridging CO) and ^{31}P NMR data. The ^{31}P NMR spectrum of **5** exhibits a second-order A_2B pattern (Table I) which can be matched exactly by calculation.[7] It has been established that **5** exists as a single, meso isomer.[8] Coordination of the benzo phosphorus atoms by the $Fe(CO)_4$ moieties gives rise to expected changes in the ^{31}P NMR spectrum. The A_2 portion of the

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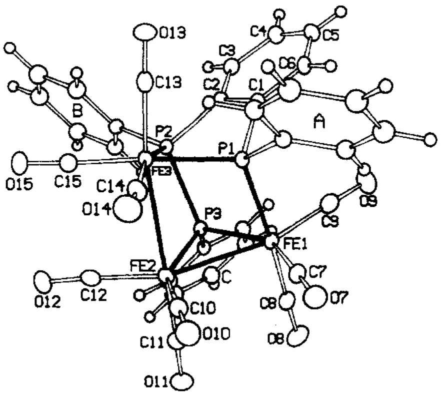
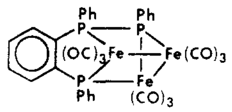


Figure 2. the ORTEP plot of 8 (≡ Z), showing the non-hydrogen atoms as 35% equiprobability ellipsoids. Selected bond lengths (Å): Fe1–Fe2, 2.7136 (10); Fe1–P1, 2.2939 (11); Fe1–P3, 2.2159 (11); Fe2–Fe3, 2.8616 (9); Fe2–P3, 2.1787 (14); Fe3–P2, 2.2362 (13); Fe3–P1, 2.2735 (13); P2–P3, 2.1755 (14); P1···P2, 2.834 (2). Selected bond angles (deg): Fe1–P3–Fe2, 76.26 (4); Fe1–Fe2–P3, 52.49 (3); P1–Fe3–P2, 77.86 (4); Fe3–P2–P3, 93.89 (5); P2–P3–Fe2, 101.43 (6); P3–Fe2–Fe3, 78.23 (3); Fe2–Fe3–P2, 81.77 (3); Fe3–P1–Fe1, 109.54 (5); P1–Fe1–Fe2, 83.41 (4); Fe1–Fe2–Fe3, 83.96 (3); Fe2–Fe3–P1, 80.44 (3); C13–Fe3–Fe2, 170.7 (2); C11–Fe2–Fe3, 169.98 (14); P1–Fe1–C8, 174.00 (13). Selected angles between planes: (P1–Fe3–Fe1)–(Fe3–Fe1–Fe2), 161.1°; (P2–Fe3–P3)–(Fe3–P3–Fe2), 157.4°.

spectrum now appears at δ 88 (Δ_A = 56 ppm) and the B portion at δ 31 (Δ_B = 8 ppm), but the coupling constant remains at 262 Hz, and the NMR pattern is essentially identical with that of **5**. The coordination chemical shifts Δ_A and Δ_B are somewhat less than observed for $Fe(CO)_4(Ph_2PPPh_2)$,[9] but nonetheless within the expected range.[10]

The ^{31}P NMR spectrum of product Z (Table I) was consistent only with a species in which one of the original P–P bonds had been broken (only one large coupling constant, 266 Hz). The analytical data were in accord with the formulation $5{\cdot}Fe_3(CO)_9$, and a priori, there were several possible structures of this species consistent with the data, one of which has been described.[5] In order to ascertain the nature of Z, we determined the X-ray crystal structure of this species. Figure 2 presents an ORTEP drawing of Z, and structure **8** presents a conventional drawing of it. The



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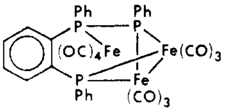
P_3Fe_3 core is a distorted trigonal prism with one edge expanded by the two carbon atoms of the benzo link. The five P–Fe bond lengths (Figure 2) are in the range observed for chelated phosphines[11] and bridging phosphides[12] bound to a carbonyliron moiety. The Fe1–Fe3 bond length (2.714 Å) is typical of phosphido-bridged species, especially where the nuclearity of the complex is higher than two.[12c–e] In contrast, the Fe2–Fe3 bond length (2.862 Å) is among the longest observed[11c] in such complexes. Presumably, an important factor in this long bond is that it is not bridged by a single atom; i.e., it is the edge of a pair of four-membered rings and is not the edge of a three-membered ring, as is the shorter Fe1–Fe3 bond (see also further discussion below).

Component X1 (Figure 1) required care in its manipulation due to its propensity to be transformed thermally into Z (see below). As suggested previously, the ^{31}P NMR spectrum conceivably could have been consistent with a mixture of two isomers: isomer 1, δ 135 (d, J = 236 Hz), 112 (d, J = 15 Hz), and 33 (dd, J = 236, 15 Hz); isomer 2, δ 129 (d, J = 236 Hz), 11, (d, J = 15 Hz), and 33 (dd, J = 236, 15 Hz). For this to be true, both isomers must have one identical phosphorus chemical shift (δ 33) as well as identical coupling constants (J = 236, 15 Hz). The alternative would be that the material is homogeneous in solution with the resonances and coupling constants reported in Table I. This latter case was found to obtain by determining the spectrum at two different operating frequencies (32.2 and 36.4 MHz), wherein the same three coupling constants (236, 185, and 15 Hz) were observed in both spectra. The coupling constant of 185 Hz was particularly intriguing, since it seemed to indicate directly bound phosphorus atoms, but apeared to be too low by perhaps 15–75 Hz for such a bonding arrangement.

Structural questions were resolved by a single-crystal X-ray study. The results for the two crystallographically independent molecules are shown in the ORTEP plots in Figure 3 as well as structure **9**. The molecules contain a



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di-μ-phosphido diiron, as well as a proximal (phosphine)tetracarbonyliron moiety. The bond lengths and angles in the P_2Fe_2 core (Figure 3) are quite comparable to those in the unlinked analogue of **1**.[12a] The only significant difference between the two crystallographically independent molecules involves the coordination geometry about Fe_3. In one molecule (Figure 3a), the iron displays a trigonal-bipyramidal coordination. It is one of a rather small group in which the phosphorus ligand is in an equatorial[13] rather than the expected axial[14,15] position in the trigonal bipyramid. All of the *neutral*[16] phosphine-type ligands which are equatorially located in a $Fe(CO)_4PR_3$ complex are extremely bulky. It is difficult to use Tolman's technique[17] to determine the cone angle of the P3 ligand in **9**, but it appears to be substantially in excess of

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[10] In general, coordination chemical shifts of tertiary phosphines with the $Fe(CO)_4$ moiety are in the 75–90 range. See ref 9 and (a) Keiter, R. L.; Rheingold, A. L.; Hamerski, J. J.; Castle, C. K. *Organometallics* **1983**, *2*, 1635. (b) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

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[12] (a) Ginsburg, R. E.; Rothrock, R. K.; Finke, R. G.; Collman, J. P.; Dahl, L. F. *J. Am. Chem. Soc.* **1979**, *101*, 6550. (b) Mathey, F.; Comarmond, M.-B.; Moras, D. *J. Chem. Soc., Chem. Commun.* **1979**, 417. (c) Cook, S. L.; Evans, J.; Gray, L. R.; Webster, M. *J. Organomet. Chem.* **1982**, *236*, 367. (d) Vahrenkamp, H.; Wucherer, E. J.; Wolters, D. *Chem. Ber.* **1983**, *116*, 1219. (e) Kouba, J. K.; Muetterties, E. L.; Thompson, M. R.; Day, V. W. *Organometallics* **1983**, *2*, 1065.

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[14] (a) For a recent summary of structures of axial-phosphine $(CO)_4Fe$ species see: Keiter, R. L.; Rheingold, A. L.; Hamerski, J. J.; Castle, C. K. *Organometallics* **1983**, *2*, 1635. (b) Stalick, J. K.; Corfield, P. W. R.; Meek, D. W. *Inorg. Chem.* **1973**, *12*, 1668.

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[16] The structure of a cationic phosphenium tetracarbonyliron species has been determined recently, in which the dicoordinate ligand is in the equatorial plane for electronic[15] reasons: Cowley, A. H.; Kemp, R. A.; Ebsworth, E. A. V.; Rankin, D. W. H.; Walkinshaw, M. D. *J. Organomet. Chem.* **1984**, *265*, C19.

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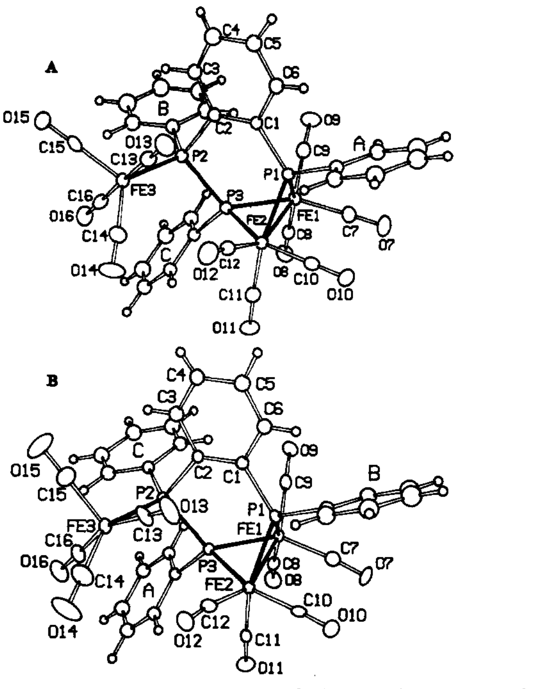
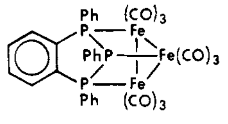


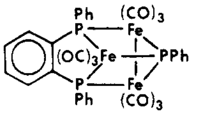
Figure 3. A. The ORTEP plot of **9** (tbp) (≡ X1), showing the non-hydrogen atoms as 29% equiprobability ellipsoids. Selected bond lengths (Å): Fe1–Fe2, 2.613 (2); Fe1–P1, 2.235 (2); Fe1–P3, 2.232 (3); Fe2–P1, 2.229 (2); Fe2–P3, 2.214 (2); P2–P3, 2.217 (3); Fe3–P2, 2.242 (2). Selected bond angles (deg): Fe1–P1–Fe2, 71.64 (6); Fe1–P3–Fe2, 71.98 (7); Fe1–Fe2–P1, 54.29 (5); Fe1–Fe2–P3, 54.33 (6); Fe2–P3–P2, 116.65 (9); Fe1–P3–P2, 124.39 (11); P3–P2–Fe3, 112.73 (10); P2–Fe3–C13, 87.2 (3); P2–Fe3–C16, 92.4 (3); P2–Fe3–C14, 125.6 (3); P2–Fe3–C15, 118.4 (3); C14–Fe3–C15, 115.9 (4); C13–Fe3–C16, 177.8 (4). Angle between planes: (P3–Fe2–Fe1)–(Fe2–Fe1–P1), 101.5°. B. The ORTEP plot of **9** (sp) (≡ X1), showing the non-hydrogen atoms as 29% equiprobability ellipsoids. Selected bond lengths (Å): Fe1–Fe2, 2.6032 (13); Fe1–P1, 2.232 (2); Fe1–P3, 2.222 (2); Fe2–P1, 2.236 (2); Fe2–P3, 2.211 (2); P2–P3, 2.217 (2); Fe3–P2, 2.255 (2). Selected bond angles (deg): Fe1–P1–Fe2, 71.28 (6); Fe1–P3–Fe2, 71.92 (7); Fe1–Fe2–P1, 54.29 (5); Fe1–Fe2–P3, 54.23 (5); Fe2–P3–P2, 115.54 (9); Fe1–P3–P2, 124.21 (10); P3–P2–Fe3, 115.53 (9); P2–Fe3–C13, 85.5 (2); P2–Fe3–C16, 93.5 (2); P2–Fe3–C14, 146.1 (3); P2–Fe3–C15, 104.5 (3); C14–Fe3–C15, 109.2 (4); C13–Fe3–C16, 159.9 (4); Fe3–C15, 98.0 (4); C16–Fe3–C15, 101.7 (4). Angle between planes: (P3–Fe2–Fe1)–(Fe2–Fe1–P1), 101.7°.

180° and thus the equatorial position is occupied because it is sterically more forgiving than is the axial one. In the other independent molecule, the tetracarbonyliron moiety is in a square-pyramidal configuration with the phosphine ligand in a basal position (Figure 3b). A case has been reported in which $(DPPE)_2CoCl^+$ exists as either a trigonal bipyramid or a square pyramid as determined by X-ray crystallography.[14b] With the structure of **9** in hand it is now unambiguous that the multi-two-bond coupling constant in this dissymmetric bis(phosphido)diiron system is 185 Hz. We show below another instance of a two-bond P–P coupling constant in the same range.

The final complex isolated in this study X2 (Figure 1) had exactly the same HPLC retention volume as X1 on silica using 2% EtOAc in hexane as eluent. Base-line separation of X1 and X2 could easily be achieved, however, on alumina with 3% CH_2Cl_2 in hexane as eluent. Component X2 was not produced in the early stages of the reaction, as monitored by this chromatographic system. The FAB mass spectrum and combustion analysis of X2 were consistent with the formulation **5**·$Fe_3(CO)_9$; i.e., it was isomeric with **8**. The ^{31}P NMR spectrum was an AB_2 (J_{AB} = 185 Hz) type, very similar in appearance to those of **6** and **5** except that the unique phosphorus atom was quite deshielded (Δ = 95 ppm), and the two identical ones (benzo) were highly shielded (Δ = −49 ppm), relative to the uncomplexed **5**. One of us[5] had suggested previously that X2 might be **10**, which would be consistent with the



10



11

observed AB_2 ^{31}P NMR spectrum. Since we knew from **9** that two-bond P–P coupling constants could be in the 185-Hz range, we felt that **11** was also a viable alternative for X2 and in fact might be more reasonable, given the J_{P-P} in **5** and **6** (ca. 262 Hz).

An X-ray crystal structure of X2 resolved the connectivity question in favor of **11**, as illustrated in the ORTEP plot shown in Figure 4. The structure has a highly symmetrical P_3Fe_3 core with bond lengths that are not unusual except, perhaps, for Fe1–Fe2, 2.830 Å; an analogous bond length in **8** (Fe1–Fe2) is 2.714 Å. A possible explanation for this long bond stems from the observation that the distance between the nonbonded P1 and P2 atoms is 2.899 Å. If the Fe1–Fe2 bond length were in the 2.7 Å range and P2–Fe1–C8 and P1–Fe2–C11 were linear, then the C8–O8 and C11–O11 bonds, which are eclipsed, would suffer significant repulsion. The nonbonded distance, C8···C11, is 2.79 Å and O8···O11 is 2.97 Å, indicating a significant repulsion between the electron-rich oxygen atoms. The system has responded to this nonbonded repulsive interaction by lengthening the Fe1–Fe2 bond, as well as moving the O8 and O11 atoms away from each other. By contrast, the nonbonded distancd C7···C10 is a comfortable 3.20 Å.

Our observations and interpretations of the chemical transformations in this system can be summarized as follows. The reaction between **5** and $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ is rapid in benzene at 80 °C; it is essentially complete in 15 min, and the products observed by HPLC account for ca. 80% of the starting **5** (Table I). In the former reaction, the yields are a function of the starting concentration of reactants: at 3.3×10^{-3} M, **1**, **8**, and **9** account for only a 3.2% cumulative yield, whereas at 33×10^{-3} M, they rep-

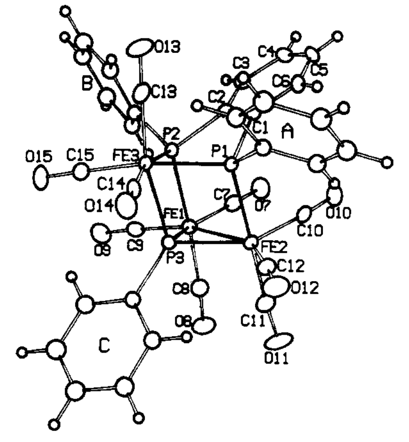


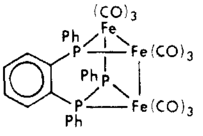
Figure 4. The ORTEP plot of **11** (≡ X2), showing the non-hydrogen atoms as 25% equiprobability ellipsoids. Selected bond lengths in Å: Fe1–Fe2, 2.8285 (11); Fe1–P3, 2.2083 (14); Fe1–P2, 2.2920 (13); Fe2–P1, 2.3023 (13); Fe2–P3, 2.2110 (14); Fe3–P1, 2.2867 (13); Fe3–P2, 2.3110 (13); Fe3–P3, 2.3196 (13); P1···P2, 2.899 (2). Selected bond angles (deg): Fe1–P3–Fe2, 79.59 (5); Fe1–Fe2–P3, 50.16 (4); P1–Fe3–P2, 78.14 (5); Fe1–P2–Fe3, 102.26 (5); P2–Fe3–P3, 75.21 (5); Fe1–P3–Fe3, 104.62 (5); P2–Fe1–P3, 77.76 (5); Fe2–P1–Fe3, 102.52 (5); P1–Fe3–P3, 75.63 (5); Fe3–P3–Fe2, 104.36 (5); P3–Fe2–P1, 77.45 (5); C13–Fe3–P3, 165.7 (2); C8–Fe1–P2, 173.5 (2); C11–Fe2–P1, 176.0 (2). Selected angles between planes: (P1–Fe3–Fe2)–(Fe3–Fe2–P3), 177.5°; (P2–Fe3–Fe1)–(Fe3–Fe1–P3), 175.2°.

resent a 13.5% combined yield. The $Fe_3(CO)_{12}$ reaction was not so affected. It is possible that products **1**, **8**, and **9** arise from $Fe_3(CO)_{12}$ even in the $Fe_2(CO)_9$ reaction by the transformation of the diiron into the triiron species under the reaction conditions. We have not addressed this question experimentally except to note that in the $Fe_2(CO)_9$ reaction, at no time was there any green coloration [$Fe_3(CO)_{12}$] of the reaction solution.

It seems reasonable that $Fe_2(CO)_9$ is acting primarily as a source of $Fe(CO)_4$,[18] two of which react with **5** to give **6**. Complex **6** represents a "dead end" in that it does not give any of the other observed products, even when treated with 1 equiv of $Fe_2(CO)_9$ in benzene under reflux. In fact, the addition of nonacarbonyldiiron does not affect the stability of **6** in benzene at 80 °C. Presumably the products other than **6** arise from di- or triironcarbonyl species. Although mechanisms can be advanced which would, for example, transform a single $Fe_3(CO)_{12}$ into **9**, i.e., all three iron atoms derived from the same starting cluster, such detailed speculation is unwarranted on the basis of the experimental evidence at hand.

The chemistry of this system was particularly difficult to sort out because two of the primary products **8** and **9** decompose under the reaction conditions, both with half-lives slightly over 1 h. In addition, **9** generates **8** essentially quantitatively. It is possible that **8** is a secondary product, derived only from **9**, but if this were so, one should be able to predict with reasonable accuracy the ratio of **8**/**9** at an early stage (e.g., 15 min) in the reaction of **5** and either $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$. Given the rate constants for the decomposition of **8** and **9** (see Results), the maximum expected ratio of **8**/**9** at a reaction time of 15 min is 0.15, assuming **8** does not decompose. The actual expected ratio would be somewhat less, since **8** does indeed decompose. The ratios **8**/**9** determined at 15 min are 0.50 for the $Fe_2(CO)_9$ reaction and 0.26 for the $Fe_3(CO)_{12}$ reaction. Thus it seems clear that **8** is both a primary and a secondary product.

Structure **9** is also of interest because it allows us to speculate about at least one pathway to the P_3Fe_3 cluster **8**. The distance from Fe3 to the midpoint of the Fe1–P2 bond is 4.72 Å. If the $(CO)_4Fe$ moiety were to lose a carbonyl group thermally, a reactive iron intermediate (L_4Fe) isolobal with carbene[19] would be generated in a good position to insert into the Fe1–P2 bond, to give **8** directly. Alternatively, the reactive iron center could insert into the Fe1–P1 bond to give **12**, a complex that was not isolated,

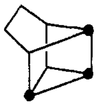


12

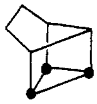
but which could have been one of the unidentified minor components shown in Figure 1. Examination and comparison of molecular models of **12**, **8**, and **9** indicate that there would be considerable angle strain in having the 1,2-bis(phosphino)benzene moiety span a four-membered ring of the trigonal prism. Elimination of [$PhP{=}Fe(CO)_3$] from **12** would then generate **1**.

In order to probe the mechanism of transformation of **8** into **11**, the decomposition of **8** was studied at 80 °C in benzene at two concentrations which differed by a factor of 21; the rates were cleanly first order in both cases and agreed within 10%. The yields of **11** in this reaction are a function of starting concentration of **8**, however, being ca. 50% at an initial [**8**] = 1.29×10^{-3} M and ca. 30% at an initial [**8**] = 6.02×10^{-5} M. Presumably, in the rate-determining step an intermediate is formed, which in fast subsequent concentration-dependent reactions, can partition either to **11** or to undetermined decomposition products. It is certain that **11** is the thermodynamic isomer, since it gave no evidence of **8** upon heating at 80 °C for 21 h.

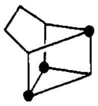
From a topological viewpoint, there are four isomeric $C_2P_3Fe_3$ cores, illustrated by **8C**, **10C**, **11C**, and **12C**, where



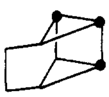
8C



10C



11C



12C

the filled circles represent Fe atoms, and we have characterized fully two of these (**8** and **11**). A search of the Cambridge Crystallographic Data Centre Structural Database[20] revealed no examples of these types of core structures. Examination of models of **10** and **12** indicates that in the latter case, repulsive interactions between eclipsed carbonyl groups could lead to considerable instability. In the former case (**10**), there appears to be considerable distortion from "normal" bond angles for the 1,2-phenylenebis(phosphide) group to span the four-membered ring edge of the trigonal prism.

Experimental Section

General Information. Proton magnetic resonance spectra were obtained on a Varian EM-390 or a Varian FT-80 spectrometer. Carbon-13 NMR spectra were determined on a Varian FT-80 spectrometer at 20.1 MHz. Proton-decoupled ^{31}P NMR spectra were determined on a Varian PT-80 or Bruker WH90 spectrometer at 32.2 and 36.4 MHz, respectively. Chemical shifts are given in parts per million relative to Me_4Si for ^{13}C and relative to 85% H_3PO_4 for ^{31}P NMR spectra. Chemical shifts upfield of the standard are defined as negative. Analytical HPLC determinations were carried out on a Waters ALC 204 instrument, equipped with a UV detector (280 nm). Quantitative analyses of components W–Z were performed by using a digital integrator (Hewlett-Packard 3390A reporting integrator). Response factors were determined for these components at 280 nm utilizing pure samples of W–Z and are as follows (mmol/area unit × 10^{-3}): W (2.60), X1 (3.22) X2 (1.85), Y (4.0), Z (1.94). The columns and solvent systems used and retention volumes of W–Z are as follows: Waters μ-Porasil 10 μM, 3.9 mm i.d. × 30 cm column; hexane–ethyl acetate (49:1, v/v), flow rate 2.0 mL/min, retention volumes W, 6.4, X1 = X2, 8.2, Y, 14.0, Z, 20.0 mL; and Alltech Associates Spherisorb A5Y (Alumina) 5 μM, 4.6 mm i.d. × 25 cm column; hexane–dichloromethane (97:3, v/v), flow rate 2.0 mL/min; retention volumes W, 5.9, X1, 8.1, X2, 9.0, Y, 10.5, Z, 12.7 mL. Preparative HPLC was carried out on a Waters Prep 500 instrument.

All of the reactions were performed under dry nitrogen or argon atmosphere. All concentrations of solutions were carried out on a rotary evaporator under water aspirator pressures unless otherwise noted. Solutions were dried with anhydrous magnesium sulfate.

Reaction of 1,2,3-Triphenyl-1,2,3-triphosphaindan (5) with Nonacarbonyldiiron (4). A. Preparative Run: Isolation of Components W, X1, Y, Z. Nonacarbonyldiiron (13.7 g, 37.7 mmol) was added in one portion to a solution of **5** (5.00 g, 12.5 mmol) in benzene (50 mL) at 70 °C, and the resulting mixture was heated to reflux with an oil bath held at 100 °C. After 0.5

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[18] Braterman, P. S.; Wallace, W. J. *J. Organomet. Chem.* **1971**, *30*, C17.

[19] Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.

[20] The Structural Database is maintained by the Cambridge Crystallographic Data Centre, Department of Chemistry, Cambridge CB2 1EW, England. Our searches were carried out on a local copy of the April 1983 issue of the database, using programs originating at the Data Centre.

Table II. Crystallographic Summary for **8**, **9**, and **11**

	8	**9**	**11**
	A. Crystal Data (−110 °C)[a]		
crystallizatn solv	toluene	hexane–ethyl acetate (49:1)	hexane–ethyl acetate (49:1)
a, Å	15.635 (3)	10.499 (1)	9.885 (2)
b, Å	11.856 (2)	10.371 (2)	17.412 (4)
c, Å	18.982 (4)	34.046 (7)	9.799 (2)
α, deg	90.	104.55 (1)	96.78 (2)
β, deg	112.85 (2)	89.43 (1)	95.46 (2)
γ, deg	90.	106.20 (1)	89.97 (2)
V, $Å^3$	3242.5	3438.8	1667.0
d_{calcd}, g cm^{-1} (−110 °C)	1.679	1.638	1.633
empirical formula	$Fe_3P_3C_{33}O_9H_{19}$	$Fe_3P_3C_{34}O_{10}H_{19}$	$Fe_3P_3C_{33}O_9H_{19}$
fw	819.94	847.95	819.94
cryst system	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
Z	4	4	2
F(000), electrons	1648	1704	824
	B. Data Collection (−110 °C)[b]		
radiatn, λ (Å)	Mo Kα, 0.710 69		
mode	ω scan		
scan range	symmetrically over 1.0° about $Kα_{1,2}$ maximum		
background	offset 1.0 and −1.0° in ω from $Kα_{1,2}$ maximum		
scan rate, deg min^{-1}	3.0–6.0	3.0–6.0	3.0–6.0
exposure time, h	104.3	143.5	145.15
stability analysis computed *s*, *t*	0.001 13 (15), −0.000 012 (1)	−0.001 12 (20), 0.000 014 (3)[c]	0.000 04 (13), 0.000 001 (1)
correctn range (on *I*)	0.974–1.000	1.000–1.023[c]	not applied
2θ range, deg	4.0–55.0	4.0–50.0	4.0–50.0
total reflectns measd	7466	12 120	5869
data cryst vol, mm^3	0.013 06	0.005 45	0.005 96
data cryst faces	8	10	7
abs coeff μ(Mo Kα), cm^{-1}	15.6	14.8	15.2
transmissn factor factor range	0.659–0.798	0.739–0.809	0.675–0.945
	C. Structure Refinement[d]		
ignorance factor *p*	0.02	0.02	0.02
reflctns used, $I > n(\sigma_I)$	5251, 2.0	6893, 2.5	4126, 2.5
no. of variables	326	622	323
R_1, R_2	0.0450, 0.0382	0.0516, 0.0431	0.0391, 0.0369
R_1 for all data	0.0761	0.114	0.0645
max shift/esd (non-H)	0.036	0.550	0.006
max shift/esd (H)	0.109	0.317	0.012
max peak in diff map, e $Å^3$	0.73	0.99	0.64
goodness of fit	1.36	1.30	1.55

[a] Unit-cell parameters were obtained by least-squares refinement of the setting angle of 45 reflections with $22.0 < 2\theta < 24.8°$ for **8**, 60 reflections with $16.1 < 2\theta < 19.9°$ for **9**, and 61 reflections with $20.0 < 2\theta < 29.9°$ for **11**. [b] Syntex $P2_1$ autodiffractometer with a graphite monochromator and a Syntex LT-1 inert-gas (N_2) low-temperature delivery system. Data reduction was carried out as described in: Riley, P. E.; Davis, R. E. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Commun.* **1976**, *B32*, 381. Crystal and instrument stability were monitored by remeasurement of four check reflections after every 96 reflections. These data were analyzed as detailed in: Henslee, W. H.; Davis, R. E. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Commun.* **1975**, *B31*, 1511. [c] Tabulated values were applied to the first 5449 reflections; corresponding values of *s*, *t*, and correction range for the remainder of the data set are −0.000 21 (10), 0.000 002 (1), and 1.000–1.005. [d] Relevant expressions are as follows, where in this footnote F_o and F_c represent, respectively, the observed and calculated structure factor amplitudes. Function minimized was $\Sigma w(F_o - F_c)^2$, where $w = (\sigma_F)^{-2}$, $R_1 = \Sigma \text{abs}(F_o - F_c)/\Sigma F_o$, and $R_2 = [\Sigma w(F_o - F_c)^2/\Sigma w F_o^2]^{1/2}$.

h, the mixture was cooled and passed through a short column (75 g) of silica gel using hexane–ethyl acetate (49:1, v/v) and the eluent was concentrated to 40 mL. A small sample was diluted with benzene by a factor of 10^2 and analyzed on the silica gel HPLC system described above. The chromatogram was similar to that shown in Figure 1A. The mixture was separated on a Waters Prep 500 instrument (silica gel, hexane–ethyl acetate (49:1, v/v)) to give, after concentration of each fraction, the following amounts: W, 215 mg (3%); X1, 530 mg (5%); Y, 4.13 g (45%); and Z, 820 mg (8%). It was necessary to rechromatograph X1 to minimize impurities. Table I summarizes pertinent spectroscopic and other data concerning these complexes, and comparison of these data with those of complexes described previously[5] revealed the following correspondence: isomer A$^5 \equiv$ X1; isomer B$^5 \equiv$ Z; isomer C$^5 \equiv$ X2. The following solvents were used to recrystallize the isolated products: W, X1, X2 (vide infra), and Y, hexane–ethyl acetate (49:1, v/v); Z, toluene.

B. Preparative Run: Isolation of X2. A reaction which employed exactly the same reagents in the same amounts as described above was carried out except that the reaction was heated for 15 h. Workup and separation of the mixture on the preparative HPLC instrument gave X2, 308 mg (3%). Spectroscopic data concerning X2 are presented in Table I.

C. HPLC Quantitative Analysis: Low Concentration. A solution of 5 (4.00 mg, 10.0 μmol) and 4 (11.0 mg, 30 μmol) in benzene (3.0 mL) was heated at reflux for 0.75 h. HPLC analyses of the reaction mixture were carried out at 0.25, 0.50, and 0.75 h, utilizing the alumina system (see General Information, above). There was a trace of a peak at a retention volume of 9.0 mL (X2) at 0.25 h. The following analyses were determined at 0.25 (0.5) h: W, 0.3% (0.4%); X1, 1.5% (2.0%); X2, 0.1% (0.1%); Y, 66% (73%); Z, 0.7% (0.8%). The analysis at 0.75 h was essentially the same as at 0.5 h.

D. HPLC Quantitative Analysis: High Concentration. A solution of 5 (26.3 mg, 65.8 μmol) and 4 (70 mg, 193 μmol) in benzene (2.0 mL) was heated at reflux for 0.75 h. HPLC analyses of the reaction mixture after being diluted by a factor of 10 were carried out at 0.28 and 0.60 h as described immediately above. The following analyses were determined at 0.28 (0.60) h: W, 1.3%; (1.4%); X1, 7.4% (8.7%); Y, 68%; (68%); Z, 2.0% (2.4%).

Thermolysis of 8 in Benzene at Reflux. A. Low Concentration. Isomer 8 (2.47 mg, 3.01 × 10^{-3} mmol) was dissolved in dry, degassed benzene (50.0 mL) to give a 6.02 × 10^{-5} M solution, and four 8.0-μL aliquots were analyzed on the alumina HPLC system described in the General Information. The average variation from injection to injection was 1.1% of the area determined. The above solution, in a 100 mL round-bottomed flask equipped with a magnetic stirring bar and condenser, was immersed in an oil bath held at 100 °C. The temperature of the benzene solution was 80.5 ± 0.2 °C and was reached in 2.5 min. Seven aliquots were removed and analyzed by HPLC over a 136-min period to give the following data [time in min (area units X 10^{-3} per 8.0-μL injection—average of three injections)]: 0 (2181), 10.0 (2038), 20.0 (1865), 31.1 (1721), 48.0 (1410), 70.1 (1214), 102 (914), 136 (679). These data were found to fit the standard first-order kinetic equation $\ln (a/(a - n)) = k_1t$ where a = the area determined at t = 0 (i.e., 2181) and $a - n$ = the areas determined at each time listed above. A least-squares analysis of a plot of t vs. $\ln (a/(a - n))$ gave the following: intercept, –0.02; slope, 8.73 × 10^{-3} min^{-1}; correlation coefficient, 0.999. Analysis for 11 during the course of the reaction indicated that the yield of 11 (based on amount of 8 reacted) increased during the course of the reaction. At 20 min the yield was 16%, whereas from 70 to 136 min the yield was in the 30–32% range.

B. High Concentration. Isomer 8 (5.30 mg, 6.46 × 10^{-3} mmol) was dissolved in dry, degassed benzene 5.0 mL) to give a 1.29 × 10^{-3} M solution. This solution was treated as in part A, except that each aliquot was diluted by a factor of 21.0 prior to HPLC analysis, to give the following data [time in min (area units × 10^{-3} per 8.0-μL injection—average of three injections)]: 0 (1503), 10.0 (1425), 23.0 (1302), 45.0 (1090), 76.0 (850), 100.0 (704). Treatment of the data as described above gave the following: intercept, –0.03; slope, 7.89 × 10^{-3} min^{-1}, correlation coefficient, 0.999. Analysis for 11 during the course of the reaction indicated that its yield based on amount of 8 consumed increased as the reaction proceeded. At 23 min the yield of 11 was 40%, and increased to 56% at 76 and 100 min.

Thermolysis of 9 in Benzene at Reflux. Complex 9 (3.78 mg, 4.46 × 10^{-3} mmol) was dissolved in dry, degassed benzene (50.0 mL) and treated as described for 8 above. HPLC analyses as a function of time gave the following data [time in min (area units × 10^{-3} per 8.0-μL injection—average of three injections)]: 0 (2819), 11.5 (2324), 25.5 (2022), 45.0 (1728), 73.0 (1451), 253.0 (256). Treatment of the data as described above for 8 gave the following: intercept, 0.07; slope, 9.15 × 10^{-3} min^{-1}; correlation coefficient, 0.999. Quantitative analysis for the percentage of 8 produced based on the amount of 9 consumed gave the following [time in min (% 8)]: 11.5 (100), 25.5 (83), 45.0 (67), 73.0 (56), 253 (28).

Attempted Thermolysis of 11 in Benzene at Reflux. Complex 11 (3.25 mg, 3.96 × 10^{-3} mmol) in benzene (5.0 mL) was heated under reflux for 16 h. Analysis by HPLC as described for the thermolysis of 8 (part B) showed no loss of the complex in this period.

Attempted Thermolysis of 6 in Benzene at Reflux. A. In the Absence of $Fe_2(CO)_9$. A solution of 6 (10.1 mg, 13.7 × 10^{-3} mmol) in benzene (3.0 mL) was heated under reflux for 1 h. Analysis by HPLC revealed no decrease in the concentration of 6 during this time.

B. In the Presence of $Fe_2(CO)_9$. Nonacarbonyldiiron (5.0 mg, 13.7 × 10^{-3} mmol) was added to the solution described in part A, and the resulting mixture was heated under reflux for an additional hour. HPLC analysis showed no decrease in the concentration of 6 during this time.

Crystallogrpahic Analysis. Crystals were grown by cooling or evaporation from the solvents indicated in Table II. For each compound, a single crystal was affixed to a glass fiber attached to a goniometer head and then transferred to a Syntex P2_1 autodiffractometer, where it was maintained in a cold (–110 °C) stream of dry nitrogen for the duration of the diffraction experiments.[21] Preliminary diffraction studies allowed determination of crystal symmetry and verification of the suitable quality of the crystals for intensity data collection. A summary of the pertinent crystal data and details of the X-ray diffraction data collection and processing is presented in Table II. The measured intensities were reduced and assigned standard deviations as described elsewhere,[22] including corrections for absorption based on measured crystal shape.

Solution and Refinement of the Structures.[23] The structures were solved by the heavy-atom method, using heavy-atom positions determined from a sharpened Patterson map. All structures were refined by full-matrix least-squares methods, using the program SHELX. Neutral atom scattering factors[24] for H, C, O, P, and Fe were used, including real and imaginary corrections for anomalous dispersion. In each structure, phenyl rings were treated as rigid groups, constrained with C–C = 1.395 Å, C–H = 1.00 Å, and C–C–C = C–C–H = 120°. Other non-hydrogen atoms were refined anisotropically and H atoms isotropically, except as noted. For each structure, refinement was continued until shifts in all parameters were less than one estimated standard deviation in the respective parameter.[25] Further details of the refinements appear in Table II. Observed and calculated structure amplitudes, final crystallographic coordinates and thermal parameters, and

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[21] Because of the extreme difficulty in obtaining the weakly scattering data crystal of 11, a room-temperature data set was collected first as a precaution. This data set was used to solve the structure while the low-temperature data set was being collected.

[22] Riley, P. E.; Davis, R. E. *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Commun.* 1976, *B32*, 381.

[23] Principal computer programs: least-squares lattice parameters, LSLAT by K. N. Trueblood; absorption correction, SYABS, a local version of ORABS by W. R. Busing and H. A. Levy as modified by J. M. Williams; full-matrix least squares and Fourier calculations, SHELX-76 by G. M. Sheldrick; least-squares planes, LSMP by M. E. Pippy; thermal ellipsoid plots, ORTEP-II by C. K. Johnson. Various data processing programs of local origin, including the following: statistical analysis of check reflections, SYSTD by T.-H. Hseu; data reduction, INCON by R. E. Davis; preparation of computer-typed tables of atomic parameters, bond lengths, bond angles, and torsion angles for publicaiton, FUER by S. B. Larson; listing of structure factor amplitudes, FTABLE by R. E. Davis.

[24] Scattering factors for H, C, O, and P were used as programmed in SHELX-76. Values for Fe were obtained from: "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

[25] Because of the large number of parameters in structure 9 due to the presence of two molecules/asu, this structure refinement was carried out as follows. In the final stages of refinement, the parameters were divided into blocks: block 1 (369 parameters) included all Fe (anisotropic), all P (anisotropic), five C═O from each molecule (anisotropic), benzo bridges from both molecules (all C and H isotropic), and scale factor; block 2 (361 parameters) included all Fe (anisotropic), all P (anisotropic), five C═O from each molecule (anisotropic), and three rigid phenyl rings from each molecule (C isotropic, H *U*'s set equal to those of C in the penultimate refinement). Parameters in these two blocks were varied on alternate cycles.

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full tables of bond lengths, bond angles, and selected torsion angles are available.[26]

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Registry No. 1, 57139-08-9; 4, 15321-51-4; 5, 89104-79-0; 6, 57139-05-6; 8, 89087-33-2; 9, 89210-02-6; 11, 95891-62-6; $Fe_3(CO)_{12}$, 17685-52-8.

Supplementary Material Available: Tables of observed and calculated structure factor amplitudes, fractional crystallographic coordinates, thermal parameters, and full listings of bond lengths and angles (137 pages). Ordering information is given on any current masthead page.

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[26] See note at the end of the paper regarding availability of supplementary material.

Proton-Initiated Opening of the Heterocyclic Ring in η^5-$C_5H_5(CO)_2Fe\overline{CHCH_2N(SO_2CH_3)SN(SO_2CH_3)CH}_2$ and η^5-$C_5H_5(CO)_2Fe\overline{CHCH_2N(SO_2CH_3)S(O)CH}_2$ and Deprotonation of Resultant Cationic Iron–η^2-Alkene Complexes†

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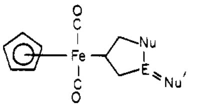
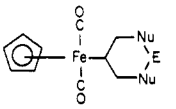
Reaction of η^5-$C_5H_5(CO)_2Fe\overline{CHCH_2N(SO_2CH_3)SN(SO_2CH_3)CH}_2$ (3) with $HPF_6\cdot(C_2H_5)_2O$ in CH_2Cl_2 results in the cleavage of the six-membered heterocyclic ring to afford the cationic complex $[\eta^5$-$C_5H_5(CO)_2Fe(\eta^2$-$CH_2{=}CHCH_2N(SO_2CH_3)SNH(SO_2CH_3))]^+PF_6^-$ (4) essentially quantitatively. Complex 4 was characterized by elemental analysis, ^1H and ^{13}C NMR and IR spectroscopy, and single-crystal X-ray diffraction techniques. Crystals of 4 are monoclinic of space group $P2_1/c$ with $a = 8.753$ (6) Å, $b = 23.74$ (1) Å, $c = 10.45$ (1) Å, $\beta = 98.56$ (5)°, and $Z = 4$. The structure was solved and refined to $R = 0.038$ and $R_w = 0.040$ by using 2317 independent reflections. The crystal structure of 4 consists of discrete iron–η^2-alkene complex cations and PF_6^- anions. Complex 4 reacts with 1,8-bis(dimethylamino)naphthalene (Proton Sponge) to regenerate 3 in 86% yield. There are no reactions between the oxonium salts $(CH_3)_3OBF_4$ and $(C_2H_5)_3OPF_6$ and 3 in CH_2Cl_2 solution at room temperature. The five-membered heterocyclic ring of η^5-$C_5H_5(CO)_2Fe\overline{CHCH_2N(SO_2CH_3)S(O)CH}_2$ (5) undergoes a similar protonation reaction with $HPF_6\cdot(C_2H_5)_2O$ to afford $[\eta^5$-$C_5H_5(CO)_2Fe(\eta^2$-$CH_2{=}CHCH_2S(O)NH(SO_2CH_3))]^+PF_6^-$ (6), which reacts with Proton Sponge to give back 5.

Introduction

Complexes of the type 1 and 2 (E = electrophilic part; Nu and Nu′ = nucleophilic parts), obtained by cycloaddition reaction of η^5-$C_5H_5(CO)_2Fe(\eta^1$-$CH_2CH{=}CH_2)$ with the heterocumulenes Nu=E=Nu′ (i.e., RN=C=O[1,2] and RN=S=O[3]) and Nu=E=Nu (i.e., RN=S=NR[3]), respectively, present themselves as potential precursors of heterocyclic organic compounds.[4,5] In an attempt to ascertain possible applications of these cycloadducts to organic synthesis, we examined their reactions with protic acids. Cleavage of the Fe–C σ bond in η^5-$C_5H_5(CO)_2FeR$ on protonation generally is a facile process when R = alkyl, aryl, and cycloalkyl.[6-9]



1



2

Our previous, cursory, studies on reactions of 1 and related cycloadducts with acids led to the observation[1,10] that cleavage of the Fe–C σ bond therein occurs less readily than in the corresponding iron alkyls and cycloalkyls.

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† Inquiries concerning the X-ray crystallographic work should be directed to the Trieste address.

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