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Stereochemical Lability of (CO)$_3$Fe(μ-ER$_2$)$_2$Fe(CO)$_2$PR$_3$. Evidence for Two Distinct CO Averaging Processes without Bridge Opening

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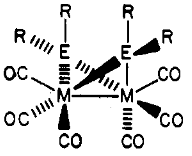
Photochemical incorporation of the phosphines PPhMe$_2$ or PPhBzMe into (CO)$_3$Fe(μ-AsMe$_2$)$_2$Fe(CO)$_3$ forms the title compounds which are shown by ^{1}H and ^{13}C NMR spectra to have stereochemical nonrigidity very similar to that of the parent hexacarbonyl. The arsenide methyl groups average with $\Delta G^{\ddagger}_{298} \approx$ 15–16 kcal/mol. The ^{13}C NMR spectrum of (CO)$_3$Fe(μ-AsMe$_2$)$_2$Fe(CO)$_2$(PPhBzMe) exhibits diastereotopic CO groups on the Fe(CO)$_2$L terminus which average with $\Delta G^{\ddagger}_{298}$ = 15.6 kcal/mol. The ^{13}C NMR spectrum of (CO)$_3$Fe(μ-PPh(CH$_2$)$_3$-μ-PPh)Fe(CO)$_2$(PPhBzMe), in which the μ-phosphide ligands are constrained by a –(CH$_2$)$_3$– bridge, shows no indication of averaging of the diastereotopic CO ligands. These data lead to the conclusions that (1) there is no intramolecular metal–metal CO ligand interchange, (2) there are two processes which average the CO ligands on a given metal terminus, (3) neither of these CO averaging processes is a formal Berry pseudorotation, at least for the Fe(CO)$_2$L terminus, and (4) averaging of the bridge ligand alkyl groups is more likely to arise via a nondissociative molecular deformation than by a bridge-opening process.

Introduction

Grobe[2] first observed that the ^{19}F NMR spectrum of (CO)$_3$Fe[μ-P(CF$_3$)$_2$]$_2$Fe(CO)$_3$ contained two doublets at 40 °C, while at 120 °C only a single doublet was present. Subsequently[3,4] it was found that molecules of general formula **1**, which are well-known to have the bent structure shown,[2-4]



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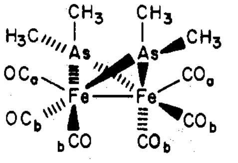

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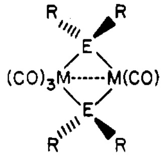
M = Fe; E = P, As
M = Co; E = Ge, Sn

and some triply bridged species (CO)$_3$Fe(μ-ER$_2$)$_2$(μ-CO)-Fe(CO)$_3$ (E = Si, Ge, Sn)[5,6] all exhibit the same kind of stereochemically nonrigid behavior, with $\Delta G^{\ddagger}_{298}$ varying from 11–19 kcal/mol. Adams and Cotton[3] showed that there are two types of magnetically nonequivalent CO ligands in molecules of type **1** and calculated a $\Delta G^{\ddagger}_{298}$ of 9.7 ± 0.7 kcal/mol for their site exchange in **2**.

There are, however, several questions which remain regarding the nonrigidity of these molecules: (1) by what path are the alkyl groups of the bridging ligand exchanging sites, (2) by what path are the CO ligands exchanging sites, and (3) are the CO ligands exchanged between the two metals?

The most contested of these questions is the first. Cotton and co-workers, for reasons which they discuss,[3] favor what has been called a "butterfly" mechanism[4] wherein the four heavy atoms simply flatten with a transition state resembling **3**. Muetterties[7] has proposed a bridge-opening mechanism which presumably would proceed via an intermediate of structure **4**.



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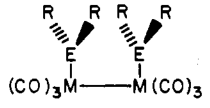

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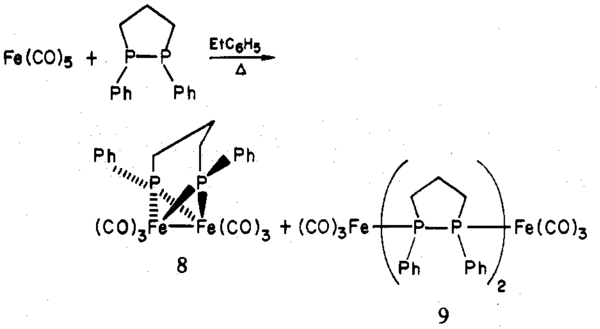
As part of our program to examine uses of chirality in the investigation of organometallic mechanisms, we have employed chiral phosphines as ligands to reduce the symmetry of metal complexes, thereby increasing the information available concerning configurational dynamics.[8] It seemed to us that studies of systems of type **1** would profit from such a technique and would thereby provide another example of the general utility of this approach.

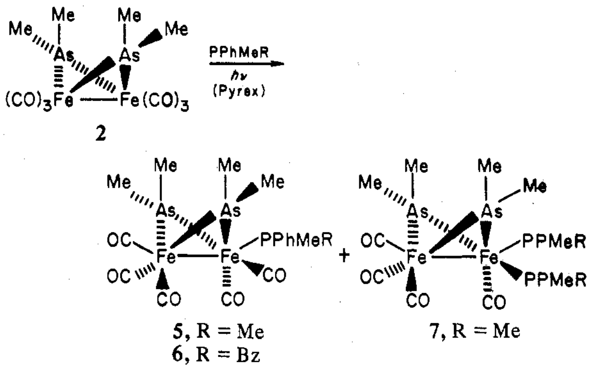
Results and Discussion

Preparations. The method of Hayter[9] was used to prepare **2**. Similarly, reaction of iron pentacarbonyl with 1,2-diphenyl-1,2-diphosphacyclopentane formed **8**, along with some of the bis-bridged species **9** (eq 1).[10] Both **2** and **8** were



(1)

isotopically enriched by photolysis in a ^{13}CO atmosphere. Incorporation of dimethyl(phenyl)phosphine (PPhMe$_2$) and benzyl(phenyl)(methyl)phosphine (PBzPhMe) was accomplished by irradiation of **2** or **8** in the presence of a substantial deficiency of phosphine to minimize disubstitution (eq 2 and 3). For example, using a **2**:PPhMe$_2$ ratio of 2.7, the products were (based on starting **2**) recovered **2** (66%), **5** (15%), and **7** (4% yield).



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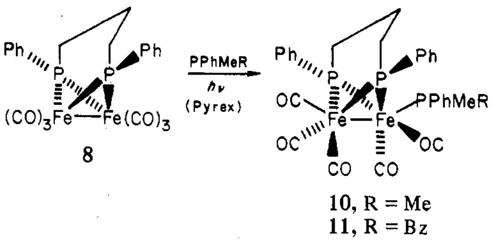

(3)

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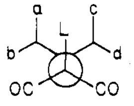
NMR Spectra. At −20 °C the proton spectrum of **5** contains two distinct arsine methyl resonances. Coalescence of these resonances occurs at ca. 34 °C, and at 80 °C, there is one sharp As–Me resonance. Line-shape analysis yields $\Delta G^{\ddagger}_{298} = 15.0 \pm 0.4$. Substitution of the phosphine for the carbonyl thus lowers the $\Delta G^{\ddagger}_{298}$ for methyl exchange by ca. 2 kcal/mol compared to the reported value for **2**.[3]

The CO region of the ^{13}C NMR spectrum of **5** from ambient temperature to −80 °C consists of a singlet and a doublet (3:2 ratio). Below −80 °C, the singlet broadens and by −127 °C has sharpened to two singlets in a 2:1 ratio, but the doublet does not change. Clearly axial–basal exchange of CO ligands on the $Fe(CO)_3$ terminus occurs in **5** as it does in **2**. However, on the $Fe(CO)_2(PPhMe_2)$ terminus either only one rotamer is visibly populated (with the phosphine axial as shown in eq 2) or the barrier to axial–basal exchange is lowered by phosphine substitution to the point that no broadening is evident even at −127 °C. Also, up to 123 °C the singlet and doublet remain distinct, so that well beyond the temperature of As–Me averaging there is no CO interchange between the two iron atoms.

The proton spectrum of **6** exhibits the same temperature dependence as that of **5**, with essentially the same coalescence temperature (ca. 40 °C). However, the presence of the chiral phosphine renders all four As–Me groups inequivalent so that at −20 °C there are four resonances which have averaged to two at 100 °C. This is explicable in terms of the interchange of **12** and **13** which will average site a with d and site b with c. This averaging pattern is consistent either with the butterfly mechanism (**3**) or with bridge opening (**4** in which arsine inversion is slow). Line-shape analysis of this process yields $\Delta G^{\ddagger}_{298} = 15.7 \pm 0.5$ kcal/mol; within experimental error the same value is obtained for **5**.



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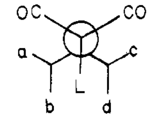

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The variable-temperature ^{13}C spectrum of the CO region of **6** is shown in Figure 1, along with calculated spectra. The observation of two doublets at lower field at 3 °C again is consistent with the presence of only one rotamer, or, if rotamer interconversion is rapid, it must be occurring in a propeller-like fashion since the two diastereotropic CO ligands remain distinct. At 70 °C these two doublets have averaged to one sharp doublet. This is a nondissociative process since the P–C coupling remains at the high-temperature limit. Line-shape analysis yields $\Delta G^{\ddagger}_{298} = 15.6 \pm 0.4$ kcal/mol. This high-temperature coalescence either is the same process that occurs at ca. −100 °C on the $Fe(CO)_3$ terminus (except that the phosphine substituent raises the energy barrier) or is a second and separate averaging process. Since the activation barriers for methyl averaging in **5** ($\Delta G^{\ddagger}_{298} = 15.0 \pm 0.4$ kcal/mol) and **6** ($\Delta G^{\ddagger}_{298} = 15.7 \pm 0.5$ kcal/mol) and CO averaging in **6** ($\Delta G^{\ddagger}_{298} = 15.6 \pm 0.4$ kcal/mol) are the same, the implication is that these two processes are linked and that there are, therefore, two distinct CO averaging processes operating.

In order to test this last idea, the molecules **8**, **10**, and **11** were prepared in which the two bridging ligands are themselves connected by a trimethylene bridge. In this case, the butterfly mechanism (via **3**) could not operate, but there is little reason to believe that the bridge-opening mechanism (via an intermediate like **4**, in this case **14**) could not.[11]

Figure 1. Temperature-dependent 100-MHz ^{13}C NMR spectra and calculated spectra of the CO ligands of $(CO)_3Fe(\mu\text{-}AsMe_2)_2Fe(CO)_2(PPhBzMe)$ (**6**).

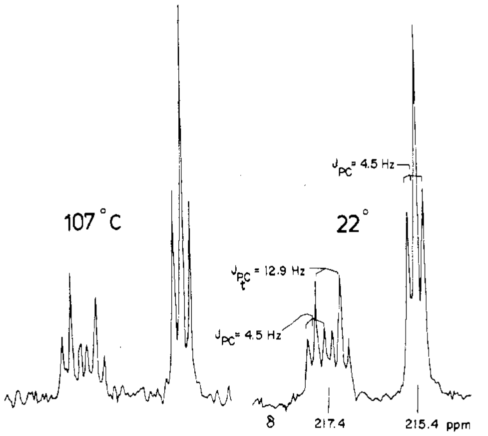

Figure 2. ^{13}C NMR spectra of the CO ligands of $(CO)_3Fe(\mu\text{-}PPh(CH_2)_3\text{-}\mu\text{-}PPh)Fe(CO)_2(PPhMe_2)$ (**10**) at 22 and 107 °C.

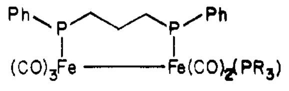

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Figure 2 shows that the CO ligands of **10** are fully averaged on the $Fe(CO)_3$ terminus so that the $-(CH_2)_3-$ bridge has no effect on this process. The CO ligands on the $Fe(CO)_2(PMe_2Ph)$ end either are averaged or are staticly equivalent and appear as a virtually coupled triplet. Incorporation of the chiral phosphine in compound **11** removes the molecular symmetry, resulting in the ^{13}C NMR spectrum of the CO ligands shown in Figure 3. As anticipated, the $Fe(CO)_3$ CO ligands appear as a triplet. At 67 °C the two CO resonances on the $Fe(CO)_2(PPhBzMe)$ terminus show independent cis and trans coupling with the bridging phosphides and a diastereotopic chemical shift difference. The spectrum can be

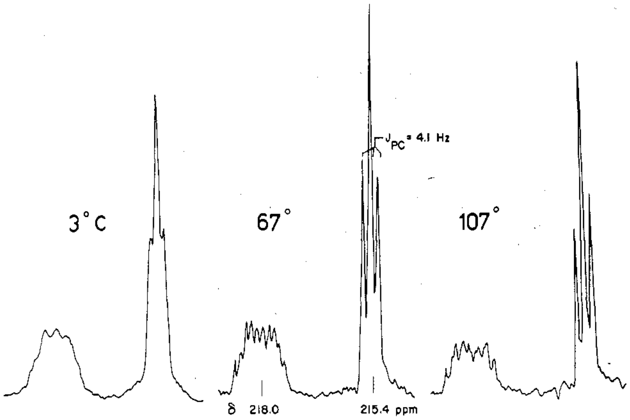


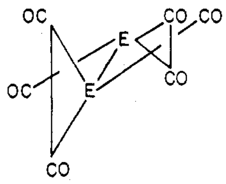
Figure 3. ^{13}C NMR spectra of the CO ligands of (CO)$_3$Fe(μ-PPh(CH$_2$)$_3$-μ-PPh)Fe(CO)$_2$(PPhBzMe) (**11**) at 3, 67, and 107 °C.

accounted for by the apparent constants: $J_{CP_{bridge}}$(cis) = 6, $J_{CP_{bridge}}$(trans) = 3, $J_{CP_{terminal}}$ = 12, and $\Delta\delta_{diastereotopic}$ = 6, all to the nearest Hz.[12] Clearly, the two CO ligands are not exchanging sites, and they do not do so even at 107 °C.

Connection of the two bridging phosphorus atoms in **11** thus prevents mutual exchange of the two diastereotopic CO ligands, confirming that methyl averaging and diastereotopic CO averaging in **6** are coupled processes. There are, therefore, two distinct paths for stereochemical lability of CO ligands in these molecules. The lower energy process is probably a propeller-like or pseudo-C_3 rotation, although this is still not certain since it cannot be determined whether any of the rotamers wherein the phosphine ligand is basal are populated, and therefore it cannot be said whether stereochemical lability is prevented on the Fe(CO)$_2$PR$_3$ terminus by the presence of the phosphine.[15]

The second CO averaging process is of interest with regard to distinguishing between mechanisms involving **3** or **4**. It is clear that if the butterfly mechanism obtains, then both alkyl averaging and diastereotopic CO averaging while present in **6** above 50 °C will be prohibited in **11**. If bridge opening operates in **6** (intermediate **4**), it should also operate in **11** (intermediate **14**) and both **4** and **14** would contain coordinatively unsaturated (16-valence-electron) pentacoordinate iron centers.[11] It must be argued that the iron centers of **4** would be stereochemically nonrigid, since simple rotation around the Fe–Fe bond in **4** would not account for the averaging processes observed in **6**. Evidence is accumulating that such fluxional behavior of unsaturated pentacoordinate intermediates in many cases is fast with respect to S$_N$1 ligand substitution reactions.[16] Inasmuch as **4** could undergo pseudorotation of some type, there is no reason to believe that **14** could not as well. Since the diastereotopic CO ligands of **11** do not undergo mutual site exchange even above 100 °C, this is significant (albeit circumstantial) additional evidence that the butterfly mechanism is operating and not the bridge-opening path.

A few observations can be made about the mode of rearrangement involving **3**. Adams and Cotton[3] have proposed a process which is the inverse of the Berry pseudorotation[17] (BPR) as one possible route for inversion of molecules of type **1**. If the geometry around each iron is viewed as a square pyramid (ignoring the Fe–Fe bond), then transition state **3** would appear to be approximated by **15**, where the bridge R groups have been omitted for clarity. Accepting the strict definition of the BPR formalism that the three equatorial ligands of a trigonal bipyramid transform to the axial and two trans-basal ligands of a square pyamid, **15** can be strictly ruled out as an intermediate, at least for the Fe(CO)$_2$(PR$_3$) terminus, because the BPR transformation would result only in a pseudo-C_3 type of motion of the three terminal ligands. That is, a synchronous motion would result which could *not* cause mutual site exchange of the diastereotopic CO ligands in **6**, contrary to our observation. Whether the motion of the three ligands will be the same for Fe(CO)$_2$(PR$_3$) as for Fe(CO)$_3$ cannot be determined from our data. However, if the BPR occurs at the Fe(CO)$_3$ terminus, while a different ligand permutation occurs at the Fe(CO)$_2$(PR$_3$) terminus, then clearly there is a set of permutational paths available which are close to one another in energy, and delineation of these paths will not be a simple matter.



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Experimental Section

General Methods and Materials. All reactions were carried out under an atmosphere of prepurified nitrogen. THF was distilled from a purple solution of benzophenone dianion just before use. Benzene was distilled under N$_2$ atmosphere. All other solvents were degassed by vigorously bubbling N$_2$ gas through them. As$_2$Me$_4$,[18] Fe$_2$(CO)$_6$(μ-AsMe$_2$)$_2$,[9] PPhCH$_2$CH$_2$CH$_2$PPh,[19] and PPhBzMe[20] were all prepared by described procedures. Melting points are uncorrected. Infrared spectra were taken on a Perkin-Elmer 337 spectrophotometer. Preparative photolyses were performed using a Hanovia 450-W medium-pressure mercury arc lamp in a quartz immersion apparatus using a Pyrex filter sleeve. Microanalyses were performed by Elek Microanalytical Laboratories, Torrance, Calif.

(CO)$_3$Fe(μ-AsMe$_2$)$_2$Fe(CO)$_2$(PPhMe$_2$) (5). A solution of **2** (3.76 g), dimethyl(phenyl)phosphine (0.4 g), 120 mL of THF, and 120 mL of ether was irradiated in the immersion apparatus for 1 h. The solvent was evaporated, and the residue was taken up in benzene and run on an alumina column (6.5 × 25 cm). Starting material (yellow band) was eluted with 10% benzene/hexane (2.5 g, 66%). The product (orange band) was eluted with 30% benzene/hexane (0.67 g, 44% based on unrecovered starting material). A sample was crystallized from hexane for analysis: mp 118.5–119 °C; ^{1}H NMR (benzene-d_6) δ 0.6–1.8 (m, 12), 1.35 (d, J = 8 Hz, 6), 9.6–7.5 (m, 5) ppm; IR (benzene) 2007 (s), 1941 (m), 1924 (sh), 1910 (sh) (CO) cm^{-1}; ^{13}C NMR (carbonyl region, CDCl$_3$) δ 212.7 (s, 3), 215.1 (d, J_{PC} = 9 Hz, 2) ppm. Anal. Calcd for C$_{17}$H$_{23}$As$_2$Fe$_2$PO$_5$: C, 34.04; H, 3.86. Found: C, 34.10; H, 3.83. A third red-orange band, **7**, was eluted with benzene (13% based on unrecovered **2**) and was purified by chromatography on a second alumina column (substantial loss of material) and recrystallized from ether/hexane to yield deep orange crystals: mp 127–129 °C; ^{1}H NMR (toluene-d_8) δ 1.03 (s, 3), 1.31 (d, J_{PC} = 8 Hz, 3), 1.36 (d, J_{PC} = 8 Hz, 3), 1.38 (s, 3), 7.4 (m, 10) ppm; IR (CHCl$_3$) 1998 (s), 1927 (s, br), 1882 (sh) cm^{-1}; ^{13}C NMR (carbonyl region, CDCl$_3$) δ 217.0 (s, 3), 219.9 (t, J_{PC} = 19 Hz) ppm. Anal. Calcd for C$_{24}$H$_{34}$As$_2$Fe$_2$P$_2$O$_4$: C, 40.59; H, 4.83. Found: C, 41.04; H, 4.75.

(CO)$_3$Fe(μ-AsMe$_2$)$_2$Fe(CO)$_2$(PPhBzMe) (6). This was prepared in the same manner as **5** (see above) using 2.5 g of **2**, 0.3 g of P(CH$_3$)(CH$_2$Ph)Ph,[20] 120 mL of THF, and 120 mL of ether and irradiating for 40 min. The product, eluted with 50% benzene/hexane, amounted to 370 mg (46% based on unrecovered starting material). A sample was crystallized from hexane for analysis: mp 134–135.5 °C; ^{1}H NMR (toluene-d_8) δ 0.4–2.4 (m, 12), 1.25 (d, J = 8 Hz, 3), 3.27 (ABX pattern, J_{AP} = 8 Hz, J_{BP} = 6 Hz, $J_{AB} \approx$ 15 Hz, Δδ(apparent) = 18 Hz, 2), 6.4–7.4 (m, 10) ppm; IR (benzene) 2005 (s), 1937 (m), 1926 (sh) cm^{-1} (CO); ^{13}C NMR (carbonyl region, CDCl$_3$) δ 214.0 (s, 3), 214.9 (m, 2) ppm. Anal. Calcd for C$_{23}$H$_{27}$As$_2$Fe$_2$PO$_5$: C, 40.87; H, 4.03. Found: C, 41.02; H, 4.01. A red-orange band, presumably the bis-substituted material analogous to **7**, did not survive the column.

(CO)$_3$Fe(μ-PPh(CH$_2$)$_3$-μ-PPh)Fe(CO)$_3$ (8). A solution of 2.5 g (10 mmol) of PPhCH$_2$CH$_2$CH$_2$PPh,[19] 3.79 g (20 mmol) of iron pentacarbonyl, and 125 mL of ethylbenzene was heated at reflux with stirring for 60 h. Solvent was distilled at atmospheric pressure until ca. 30 mL remained. This was diluted with hexane and submitted to column chromatography (alumina, hexane). A large yellow band (**8**) was eluted with 40% benzene/hexane, and a small green band was eluted with benzene. From evaporation of the eluate containing the yellow band was obtained 4.4 g (82%) of yellow solid: mp 182–184 °C (lit.[10] mp 184–187 °C); ^{13}C NMR (carbonyl region, CDCl$_3$) δ 212.0 (t, J_{PC} = 4.7 Hz) ppm. The green material which amounted to 0.5 g was not characterized. In another experiment, 2.7 g (10.5 mmol) of $\overline{\text{PPhCH}_2\text{CH}_2\text{CH}_2\text{PPh}}$ and 2.8 mL (10.5 mmol) of iron pentacarbonyl in 100 mL of ethylbenzene were heated at reflux for 47 h. About 30 mL of ethylbenzene was distilled at atmospheric pressure and another 20 mL under aspirator vacuum. The remainder of the solution was diluted with hexane and this was submitted to column chromatography (alumina, hexane). Product **8** was eluted with 50% benzene/hexane (3.4 g, 60%). The orange band was eluted with 80% benzene/hexane. (There was a very small green band present.) Evaporation of solvent left 0.25 g of an orange oil which was crystallized from hexane: mp 178–180 °C; ^{1}H NMR (CDCl$_3$) δ 0.6–3.30 (m, 12), 7.2–8.05 (m, 20) ppm; IR (benzene) 2025 (s), 1962 (m), 1930 (s), 1879 (m) cm^{-1} (CO). Anal. Calcd for C$_{36}$H$_{32}$Fe$_2$P$_4$O$_6$: C, 54.31; H, 4.05. Found: C, 54.75; H, 4.27. These data are consistent with structure **9** (see text).

(CO)$_3$Fe(μ-PPh(CH$_2$)$_3$-μ-PPh)Fe(CO)$_2$(PPhMe$_2$) (10). A solution of 4.3 g of **8**, 0.4 g of P(CH$_3$)$_2$Ph, 120 mL of THF, and 120 mL of ether was irradiated in the immersion apparatus for 1 h. Solvent was evaporated and the residue was submitted to column chromatography (alumina, hexane). Starting material (yellow band) was eluted with 50% benzene/hexane. Product (orange band) was eluted with benzene (1.47 g, 78% based on unrecovered starting material), and a sample was purified for analysis by boiling in toluene for 6 h, chromatographing on alumina, and crystallizing from hexane: mp 164–165 °C; ^{1}H NMR (CDCl$_3$) δ 1.0–2.5 (m, 6), 1.77 (d, J_{PH} = 8 Hz, 6), 7.11–8.0 (m, 15) ppm; IR (CHCl$_3$) 2016 (s), 1970 (s), 1940 (sh), 1917 (sh) cm^{-1} (CO); ^{13}C NMR (carbonyl region, toluene-d_8) δ 215.4 (t, J_{PC} = 4.5 Hz, 3), 217.4 (doublet of triplets, J_{P_1C} = 12.9 Hz, J_{P_2C} = 4.5 Hz, 2) ppm. Anal. Calcd for C$_{28}$H$_{27}$Fe$_2$P$_3$O$_5$: C, 51.89; H, 4.20. Found: C, 52.13; H, 4.40.

(CO)$_3$Fe(μ-PPh(CH$_2$)$_3$-μ-PPh)Fe(CO)(PPhBzMe) (11). This was prepared in the same manner as **10** (see above) using 3.0 g of **8**, 0.4 g of P(CH$_3$)(CH$_2$Ph)Ph,[20] 120 mL of THF, and 120 mL of ether. Product (eluted with 75% benzene/hexane) amounted to 0.89 g (66% based on unrecovered starting material). A small sample was purified for analysis by boiling in toluene for 2 h, chromatographing on alumina, and crystallizing from hexane: mp 137–138 °C; ^{1}H NMR (toluene-d_8) δ 1.17 (d, J_{PH} = 8 Hz, 3), 1.65 (m, 6), 3.40 (ABX pattern, J_{AP} = 7 Hz, J_{BP} = 4 Hz, J_{AB} = 15 Hz, $\Delta\delta$(apparent) = 22 Hz, 2), 6.30–7.87 (m, 20) ppm; IR (CHCl$_3$) 2117 (s), 1976 (s), 1958 (sh), 1919 (sh) cm^{-1} (CO); ^{13}C NMR (carbonyl region, toluene-d_8) δ 215.4 (t, J_{PC}(av) = 4.1 Hz, 3), 218.0 (m, 2) ppm. Anal. Calcd for C$_{34}$H$_{31}$Fe$_2$P$_3$O$_5$: C, 56.39; H, 4.31. Found: C, 56.09; H, 4.40.

Carbon-13 Enrichment of 2 and 8. Enrichment was achieved by dissolving ca. 4 g of either **2** or **8** in 200 mL of benzene in a 500-mL Pyrex flask. After the solvent was frozen at −78 °C and the flask was evacuated, ^{13}CO (Merk Sharp and Dohme; 90% ^{13}C) was admitted. The solution was stirred and externally irradiated by the Hanovia 450-W medium-pressure mercury arc lamp for 6 h. The solution was filtered through a short alumina column, and solvent removal afforded pure enriched material. Mass spectral analysis revealed enrichment to be ca. 4% for **2** and ca. 15% for **8**.

NMR Spectra. ^{1}H NMR and ^{13}C NMR spectra were measured on a Varian XL-100 NMR spectrometer. The temperature of the probe was monitored with a Varian control unit which was calibrated with a standard thermocouple. Errors in reported temperatures are ±2 °C at a maximum. Values of δ for ^{1}H and ^{13}C spectra are reported positive downfield with respect to internal Me$_4$Si. Coupling constants in ^{13}C spectra are reported to ±2 Hz and to ±1 Hz for ^{1}H NMR spectra. All samples were prepared under an N$_2$ atmosphere using degassed CD$_2$Cl$_2$, CDCl$_3$, or CD$_3$C$_6$D$_5$.

Computer simulations of ^{1}H NMR spectra were performed using DNMR4 and INMR.[21] The rate constants obtained from the line-shape analysis were used in a weighted least-squares program to calculate $\Delta G^{\ddagger}$.

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Registry No. **2**, 15525-09-4; **5**, 66161-31-7; **6**, 66161-30-6; **7**, 66161-29-3; **8**, 37451-26-6; **9**, 66161-28-2; **10**, 66161-27-1; **11**, 66161-36-2; Fe(CO)$_5$, 13463-40-6; ^{13}C, 14762-74-4.

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(12) Assignment of the larger $J_{\mathrm{CP}_{\mathrm{terminal}}}$ to the cis pair is arbitrary and is based on the observation that J_{CP}(cis) > J_{CP}(trans) for basal ligands of square-pyramidal molecules.[8,13] Generally, the opposite holds for octahedral molecules.[14]

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(21) DNMR4 was prepared by J. Brunelle and L. J. Letendre and is a modification of a program originally written by G. Binsch and D. A. Kleier. We thank C. H. Bushweller for providing us with a copy of this program. INMR is an iterative line-shape program written by W. B. Jennings.[22] We thank Dr. Jennings for suggesting the use of INMR, and we thank Drs. Jennings and H. Hargis for providing us with a program deck.

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