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Synthesis and Multinuclear Magnetic Resonance Study of Stereochemically Nonrigid Derivatives of Iron Pentacarbonyl Containing Bidentate Ligands

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Received June 19, 1975 AIC50436H

In order to examine the stereochemical behavior of iron tricarbonyl derivatives of several bidentate ligands a multinuclear NMR investigation was carried out on the following ligands and corresponding iron tricarbonyl derivatives: $(CH_3)_2PCF_2CH_2P(CH_3)_2$, $Fe[(CH_3)_2PCF_2CH_2P(CH_3)_2](CO)_3$, $(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2$, $Fe[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2](CO)_3$, *o*-$C_6H_4(As(CH_3)_2)_2$ (diars), and Fe(diars)$(CO)_3$. Nuclei studied include ^1H, ^{19}F, ^{31}P, and ^{13}C. Results indicate stereochemical nonrigidity on the NMR time scale down to −70°C for all the complexes studied. Because of evidence showing the structure of Fe(diars)$(CO)_3$ to be close to idealized trigonal bipyramidal, this complex was further investigated and found to be stereochemically nonrigid on the NMR time scale down to −140°C.

Introduction

Iron pentacarbonyl and its *mono*dentate phosphine derivatives, $Fe(R_3P)_2(CO)_3$, appear to be stereochemically nonrigid molecules at ambient temperature and below.[3-5] Although it seems reasonable to expect that the barrier to intramolecular isomerization might be increased if a *bi*dentate ligand rather than two *mono*dentate ligands is employed, we have recently shown[6] that, at least in the compound $Fe[(CH_3)_2PCH_2CH_2P(CH_3)_2](CO)_3$ over the limited temperature range investigated, this is not the case. On the NMR time scale this species behaves as a nonrigid molecule down to −80°.[6]

In a recent study of bidentate derivatives of iron pentacarbonyl Fe(L-L)$(CO)_3$, variable-temperature ^1H NMR data of Fe(diars)$(CO)_3$ [diars = *o*-phenylenebis(dimethylarsine), *o*-$C_6H_4(As(CH_3)_2)_2$] was interpreted as suggesting that these compounds are stereochemically rigid,[7] since the spectrum of Fe(diars)$(CO)_3$ was invariant between +20 and −80°. This observation is, of course, equally consistent with a system which is stereochemically nonrigid in this temperature range.

Discussions of mechanisms of stereochemical nonrigidity have assumed an idealized polytopal form rearranging through one or more intermediates to the original form with concurrent permutation of sites. The idealized forms discussed with regard to five-coordination have been the trigonal bipyramid and the square pyramid although a recent X-ray crystallographic structural determination of tricarbonyl[bis(diphenylphosphino)methane]iron(0), $Fe[(C_6H_5)_2PCH_2P(C_6H_5)_2](CO)_3$, by Cotton and coworkers[8] casts doubt upon this approach in describing the stereochemical nonrigidity of these Fe(L-L)$(CO)_3$ species. They reported that the coordination geometry about the iron atom was intermediate between trigonal bipyramidal and square pyramidal. On the basis of this structure, these authors concluded that consideration of the Berry pseudorotation mechanism[9] or some other permutationally equivalent mechanism[10] to explain rapid site interconversion was possible but not necessary. Only relatively slight bends or twists would be needed to average the sites and it was indicated that the carbonyl groups were equivalent on the NMR time scale down to −70°.[8]

In contrast to this indication of an intermediate structure in derivatives of $Fe(CO)_5$ with bidentate ligands, a single-crystal X-ray study[11] indicated that the geometry of Fe(diars)$(CO)_3$ is only slightly distorted from trigonal bipyramidal, the distortion from the ideal arrangement being only a few degrees. This observation, together with the fact that a slight bending of the diars ligand would probably have to occur in a facile Berry-type intramolecular isomerization step, suggested that Fe(diars)$(CO)_3$ might become stereochemically rigid at temperatures higher than those for other iron tricarbonyl derivatives with bidentate ligands.

The present study was undertaken in order to ascertain whether stereochemical nonrigidity on the NMR time scale is a general property of $Fe(CO)_5$ derivatives with bidentate ligands at least down to moderately low temperatures. Due to the possibility that Fe(diars)$(CO)_3$ might be stereochemically rigid at low temperature, vide supra, this compound was of prime concern. In order to determine whether or not nonrigidity of $Fe[(CH_3)_2PCH_2CH_2P(CH_3)_2](CO)_3$ was unique to this compound, the related new compound $Fe[(CH_3)_2PCF_2CH_2P(CH_3)_2](CO)_3$ was synthesized and studied. Both of these compounds have phosphine ligands in which $(CH_3)_2P$ groups are separated by two carbons. To explore the effect of further structural changes in the phosphine ligand and hence the extent to which the complex might approach that of an undistorted trigonal bipyramid in its ground state, the new complex $Fe[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2](CO)_3$ in which the phosphorus atoms are separated by three carbon atoms was also synthesized and investigated by NMR techniques.

Presented herein are the results of a multinuclear NMR investigation of the following ligands and their corresponding iron tricarbonyl complexes: 1,2-bis(dimethylphosphino)-1,1-difluoroethane, $(CH_3)_2PCF_2CH_2P(CH_3)_2$; tricarbonyl-1,2-bis(dimethylphosphino)-1,1-difluoroethaneiron(0), $Fe[(CH_3)_2PCF_2CH_2P(CH_3)_2](CO)_3$; 1,3-bis(diphenylphosphino)propane, $(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2$; tricarbonyl-1,3-bis(diphenylphosphino)propaneiron(0), $Fe[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2](CO)_3$; *o*-phenylenebis(dimethylarsine), "diars"; tricarbonyl-*o*-phenylenebis(dimethylarsino)iron(0), Fe(diars)$(CO)_3$.

Experimental Section

All operations were carried out under a dry nitrogen atmosphere or by using standard high-vacuum techniques. The solvents were dried over lithium aluminum hydride and were distilled under nitrogen immediately before use.

Fluorine-19 NMR spectra were recorded at 94.1 MHz with Varian HA 100D and XL-100-15 NMR spectrometers. Proton NMR spectra were obtained at 100 MHz with the Varian XL-100-15 spectrometer operating in both continuous-wave (CW) and Fourier-transform (FT) modes. Carbon-13 and phosphorus-31 NMR spectra were measured with the XL-100-15 NMR spectrometer operating at 25.2 MHz in the FT mode and at 40.5 MHz in the CW mode, respectively. The lower temperature (−140°C) ^{13}C spectra were measured with a Varian CFT-20 spectrometer operating at 20.0 MHz in the FT mode. Further experimental details concerning the operating conditions of the Fourier transform mode have been described previously.[6]

Approximately 10–20% by weight solutions were employed for all NMR spectral studies. Ambient probe temperature (31°) NMR spectra were recorded in benzene-d_6 or in methylene-d_2 chloride, while low-temperature spectra were recorded in toluene-d_8 or in a dichlorofluoromethane–methylene-d_2 chloride mixture. The phosphorus-decoupled ^{13}C spectrum of $(CH_3)_2PCF_2CH_2P(CH_3)_2$ was determined on an 85% sample in C_6D_6. All ^{13}C resonances are reported relative to the ^{13}C resonance of TMS. Phosphorus-31 chemical shifts are reported relative to triphenylphosphine oxide. Fluorine-19 chemical shifts are reported relative to 1,2-dibromotetrafluoroethane. For the sake of consistency the authors have chosen to use the chemical shift sign convention employed in ^1H and ^{13}C NMR spectroscopy for the ^{19}F and ^{31}P chemical shifts. The authors respectfully apologize to the users of the more rational sign convention. *A positive sign in chemical shift denotes resonances to lower shielding.*

Iron pentacarbonyl, tetramethyldiphosphine, 1,3-bis(diphenylphosphino)propane, and "diars" were obtained from Strem Chemicals, Inc., and 1,1-difluoroethylene was from the Matheson Co., Inc. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. 11377. The mass spectrum was obtained by the Analytical and Physical Measurements Service, E. I. du Pont de Nemours and Co., Inc., Wilmington, Del. 19898, using a Du Pont 21-110 high-resolution mass spectrometer with a direct-introduction system. A sample inlet temperature of approximately 225° was employed.

1,2-Bis(dimethylphosphino)-1,1-difluoroethane, $(CH_3)_2PCF_2CH_2P(CH_3)_2$. This compound was synthesized according to the method of Cooper, Fields, and Haszeldine[12] with some changes in the reaction conditions. Tetramethyldiphosphine (3.02 g, 24.8 mmol) and 1,1-difluoroethylene (2.00 g, 21.2 mmol) were exposed to ultraviolet radiation (Hanovia 100-W lamp, No. 608A-36) in a 25-ml quartz tube for 10 hr at room temperature. The reaction products were separated by trap-to-trap distillation with continuous pumping; pure $(CH_3)_2PCF_2CH_2P(CH_3)_2$ (4.34 g, 23.3 mmol, 94.0%) was collected at −23°. Anal. Calcd for $C_6H_{14}P_2F$: C, 38.72; H, 7.58; P, 33.28; F, 20.41. Found: C, 38.74; H, 7.59; P, 33.00; F, 20.07. Excess $CF_2{=}CH_2$ was collected at −196°.

Tricarbonyl-1,2-bis(dimethylphosphino)-1,1-difluoroethaneiron(0), $Fe[(CH_3)_2PCF_2CH_2P(CH_3)_2](CO)_3$. A solution of $(CH_3)_2PCF_2CH_2P(CH_3)_2$ (0.51 g, 2.7 mmol) in toluene (10 ml) was added, with stirring, to a solution of $Fe(C_8H_8)(CO)_3$[13] (0.67 g, 2.8 mmol) in toluene (20 ml). After the mixture had refluxed under nitrogen for 1 hr, the dark red color of $Fe(C_8H_8)(CO)_3$ in the reaction mixture had changed to pale yellow. After 6 hr of refluxing, the solvent was removed under vacuum and the gummy residue was placed on the top of an alumina chromatographic column (pentane liquid phase) under nitrogen and was eluted with a 4:1 pentane–dichloromehane mixture. From the resulting pale yellow solution light yellow crystalline material (0.75 g, 2.3 mmol, 85%) was obtained on removal of solvent in vacuo; mp 75–76°. Anal. Calcd for $FeC_9H_{14}P_2F_2O_3$: Fe, 17.11; C, 33.16; H, 4.34; P, 19.02; F, 11.66. Found: Fe, 17.77; C, 33.62; H, 4.41; P, 18.57; F, 11.36.

Tricarbonyl-1,3-bis(diphenylphosphino)propaneiron(0), $Fe[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2](CO)_3$. The ligand, $(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2$ (1.65 g, 4.00 mmol), and $Fe(C_8H_8)(CO)_3$[13] (0.75 g, 3.1 mmol) were refluxed in toluene (50 ml) for 14 hr under nitrogen. After this time the reaction mixture was reddish yellow. The solvent was removed under vacuum and the residue chromatographed on an alumina column under nitrogen using a 4:1 pentane–dichloromethane mixture. A yellow crystalline material (1.10 g, 1.99 mmol, 64.2%) was obtained when the solvent was removed in vacuo. It was characterized by means of its mass spectrum which showed a strong parent ion peak at *m/e* 552.07040 (calcd 552.07065) in addition to the expected (P − CO), [P − 2(CO)] and [P − 3(CO)] peaks. Additional high-resolution measurements were made on the [P − $Fe(CO)_3$] peak at *m/e* 412.15790 (calcd 412.15098) and on the [P − $Fe(CO)_3C_6H_5$] peak at *m/e* 335.11120 (calcd 335.11185). Only two very weak peaks of a mass number higher than that of the parent ion were observed. The infrared and ^{13}C NMR spectra of the compound were consistent with the proposed structure.

Tricarbonyl-*o*-phenylenebis(dimethylarsino)iron(0), Fe(diars)(CO)$_3$. This compound was synthesized according to the method of Nigam et al.;[14] mp 131°, lit.[14] mp 131°. Anal. Calcd for $FeC_{13}H_{16}As_2O_3$: Fe, 13.11; C, 36.65; H, 3.79. Found: Fe, 13.22; C, 36.87; H, 3.79.

Results

1,2-Bis(dimethylphosphine)-1,1-difluoroethane. Tetramethyldiphosphine reacts with 1,1-difluoroethylene to give $(CH_3')_2P'CF_2CH_2P(CH_3)_2$ as indicated previously,[12] though the yield can be improved significantly by using excess $CF_2{=}CH_2$ and irradiating for a shorter period of time (10 hr vs. 120 hr). The infrared spectrum (liquid film using KBr windows and a Perkin-Elmer 137B Infracord spectrophotometer) showed major absorption bands at 3020 (s), 2950 (s), 2850 (w), 1430 (s), 1400 (w), 1298 (m), 1282 (m), 1245 (m), 1216 (m), 1138 (vs), 1025 (sh), 1018 (vs), 988 (vs), 945 (s), 908 (sh), 896 (s), 868 (m), 825 (m), 796 (w), 784 (vs), 738 (m), 712 (s), and 700 (sh) cm^{-1}.

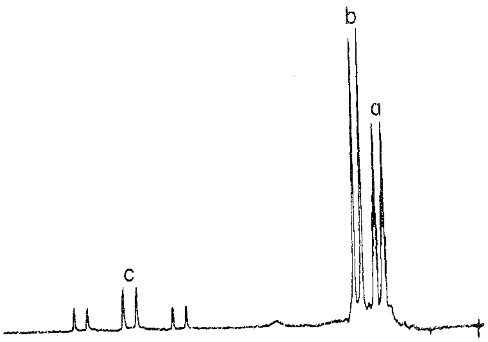

Figure 1. ^1H NMR spectrum of $(CH_3')_2P'CF_2CH_2P(CH_3)_2$: (a) CH_3 resonance; (b) CH_3' resonance; (c) CH_2 resonance

The ^1H NMR spectrum of $(CH_3')_2P'CF_2CH_2P(CH_3)_2$ is shown in Figure 1. At 31°, an expanded spectrum of the most shielded multiplet (τ 9.07), a doublet of triplets of doublets, is assigned to the CH_3 group ($^2J_{HP} = 3.3$ Hz, $^5J_{HF} = 0.7$ Hz, $^5J_{HP} = 0.3$ Hz). The adjacent doublet (τ 8.94) is assigned to the CH_3' group ($^2J_{HP} = 3.1$ Hz). The methylene signal (τ 8.08) is a triplet of doublets of doublets ($^3J_{HF} = 2.01$ Hz, $^2J_{HP} = 5.3$ Hz, $^3J_{HP'} = 0.4$ Hz). The overall appearance of the spectrum remained unchanged between +90° and −70°, although small changes in chemical shifts and coupling constants were noted: at 90°, $\delta_{CH_3} = 8.97\ \tau$ ($^2J_{H'P'} = 3.5$ Hz), $\delta_{CH_3'} = 8.88\ \tau$ ($^2J_{HP} = 3.8$ Hz), $\delta_{CH_2} = 7.96\ \tau$ ($^2J_{HP} = 5.6$ Hz, $^3J_{HF} = 20.1$ Hz); at −70°, $\delta_{CH_3} = 9.09\ \tau$ ($^2J_{H'P'} = 3.0$ Hz), $\delta_{CH_3'} = 8.96\ \tau$ ($^2J_{HP} = 3.0$ Hz), $\delta_{CH_2} = 8.15\ \tau$ ($^2J_{HP} = 5.2$ Hz, $^3J_{HF} = 20.1$ Hz).

The ^{19}F and ^1H-noise-decoupled ^{31}P spectra of $(CH_3')_2P'CF_2CH_2P(CH_3)_2$ are both first order. The ^{19}F spectrum is a doublet of triplets of doublets (δ −32.86 ppm, $^2J_{FP'} = 62.8$ Hz, $^3J_{HF} = 20.0$, $^3J_{FP} = 16.5$ Hz), retaining this multiplet structure from +80 to −70°. However, a slight increase in shielding (~1.1 ppm) was noted as the temperature was lowered. The ^{31}P resonance (^1H decoupled) displays a triplet of doublets for the P' resonance (δ −58.8 ppm, $^2J_{P'F} = 63.0$ Hz, $^3J_{P'P} = 39.3$ Hz) and a doublet of triplets for the P resonance (δ −91.9 ppm, $^3J_{PP'} = 39.3$ Hz, $^3J_{PF} = 16.7$ Hz). The ^{31}P spectrum showed no changes between +25 and −70°. The ^1H-noise-decoupled ^{13}C spectrum (Figure 2) is first order. The more shielded methyl resonance (Figure 2a), a doublet of triplets of doublets, is assigned to the CH_3' group (δ 8.4 ppm, $J_{C'P'} = 15$ Hz, $^3J_{C'F} = 6$ Hz, $^4J_{C'P} = 3$ Hz). The adjacent doublet is assigned to the CH_3 group (δ 15.2 ppm, $J_{CP} = 14$ Hz). The methylene resonance (Figure 2b) is a quartet of doublets, the quartet arising from an overlapping doublet of triplets (δ 41.3 ppm, $J_{CP} = 22.4$ Hz, $^2J_{CF} = 22.4$ Hz, $^2J_{CP'} = 19.9$ Hz). The least shielded ^{13}C resonance, a triplet of doublets assigned to the CF_2 group, is not shown (δ 130.8 ppm, $J_{CF} = 269$ Hz, $J_{CP'} = 29$ Hz, $^2J_{CP} = 10$ Hz).

Tricarbonyl-1,2-bis(dimethylphosphino)-1,1-difluoroethaneiron(0). The new compound $Fe[(CH_3)_2PCF_2CH_2P(CH_3)_2](CO)_3$ was obtained in good yields, by the reaction of $Fe(C_8H_8)(CO)_3$ with $(CH_3)_2PCF_2CH_2P(CH_3)_2$. The infrared spectrum in the carbonyl region is given in Table I. Other major absorption bands appeared at (Nujol mull using KBr windows and a Perkin-Elmer 137B Infracord spectrophotometer): 1309 (w), 1296 (w), 1244 (m), 1144 (m), 1058 (s), 988 (s), 946 (s), 920 (s), 894 (w), 844 (w), 763 (s), 724 (s), and 698 (m) cm^{-1}.

The ^1H NMR spectra (at 31°) of $Fe[(CH_3')_2P'$-

Table I. CO Stretching Frequencies[a]

Compd	Phase	Freq, cm^{-1}
$Fe[(CH_3')_2P'CF_2CH_2P(CH_3)_2](CO)_3$	Nujol	1998 s, 1928 ms, 1910 vs
	CH_2Cl_2 soln	1994 s, 1925 ms, 1910 vs
$Fe[(CH_3)_2PCH_2CH_2P(CH_3)_2](CO)_3$	Nujol	1982 s, 1911 ms, 1895 vs
	CH_2Cl_2 soln	1970 s, 1896 ms, 1877 vs
$Fe[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2](CO)_3$	Nujol	1980 s, 1908 s, 1885 vs
	CH_2Cl_2 soln	1986 s, 1914 ms, 1884 vs
Fe(diars)$(CO)_3$[b]	Nujol	1982 vs, 1908 sh, s, 1885 vs
	C_6H_{12} soln	1985 s, 1915 ms, 1905 vs
	CH_2Cl_2 soln	1982 vs, 1908 ms, 1885 s

[a] Recorded with a Perkin-Elmer 521 double-beam grating spectrophotometer using cells fitted with KBr windows. [b] $\nu_{^{13}CO}$ 1840 (m) cm^{-1}.

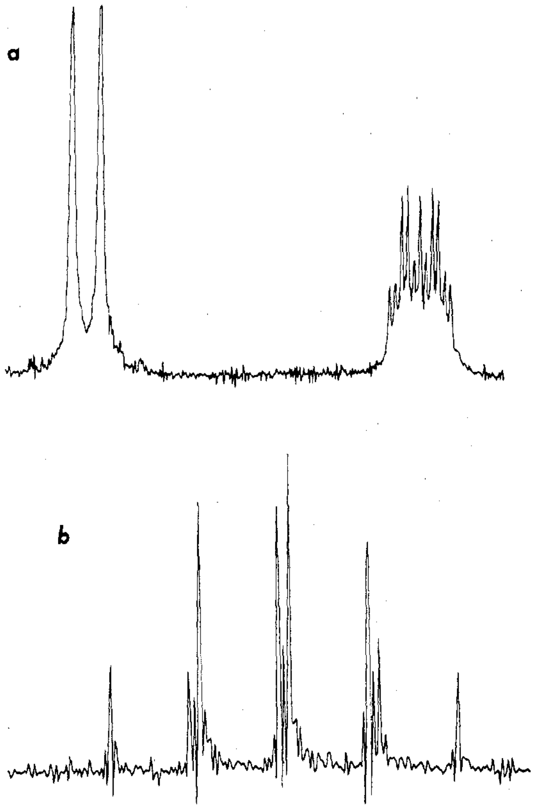

Figure 2. The alkyl region of the ^{13}C FT NMR spectrum of $(CH_3')_2P'CF_2CH_2P(CH_3)_2$ under conditions of resolution enhancement: (a) methyl region with the most shielded multiplet being the CH_3' resonance; (b) methylene carbon resonance [the wiggle beats at the base of the major peaks are artifacts of the resolution enhancement technique].

$CF_2CH_2P(CH_3)_2](CO)_3$ is shown in Figure 3. The resonances for both the CH_3 and CH_3' groups are resolved, each consisting of a doublet of quartets. The more shielded multiplet is assigned to the CH_3 group (δ_{CH_3} = 8.91 τ, $^2J_{HP}$ = 9.4 Hz, $^5J_{HP'}$ = 0.7 Hz, $^5J_{HF}$ = 0.5 Hz; $\delta_{CH_3'}$ = 8.79 τ, $^2J_{H'P'}$ = 9.0 Hz, $^5J_{H'P}$ = 0.8 Hz, $^4J_{H'J}$ = 0.7 Hz). The ^1H resonance of the CH_2 group (Figure 3b) is an overlapping triplet of doublets of doublets (δ_{CH_2} = 8.42 τ, $^3J_{HF}$ = 15.2 Hz, $^2J_{HP}$ = 14.8 Hz, $^3J_{HP'}$ = 9.0 Hz). The multiplet structure of the ^1H spectrum did not change in the temperature range of +90 to −50°. Significant changes in chemical shifts, however, were noted: at 90°, $\delta_{CH_3'}$ = 8.59 τ, δ_{CH_3} = 8.71 τ, δ_{CH_2} = 8.18 τ; at −50°, $\delta_{CH_3'}$ = 8.79 τ, δ_{CH_3} = 8.95 τ, δ_{CH_2} = 8.64 τ.

The ^{19}F spectrum of $Fe[(CH_3')_2P'CF_2CH_2P(CH_3)_2](CO)_3$ is a doublet of quartets (δ −44.68 ppm, $^2J_{FP'}$ = 47.4 Hz, $^3J_{FP}$ = 15.8 Hz, $^3J_{HF}$ = 15.8 Hz). The ^{31}P spectrum (^1H noise decoupled) is first order, the signal of each phosphorus being a doublet of triplets. The less shielded resonance is assigned to P' ($\delta_{P'}$ 51.1 ppm, $^2J_{PP}$ = 77.7 Hz, $^2J_{P'F}$ = 46.7 Hz); the more shielded multiplet is assigned to P (δ_P 2.5 ppm, $^2J_{PP'}$ = 77.3 Hz, $^3J_{PF}$ = 16.3 Hz). The overall appearance of the ^{19}F and ^{31}P spectra did not change in the temperature range +31 to −70°.

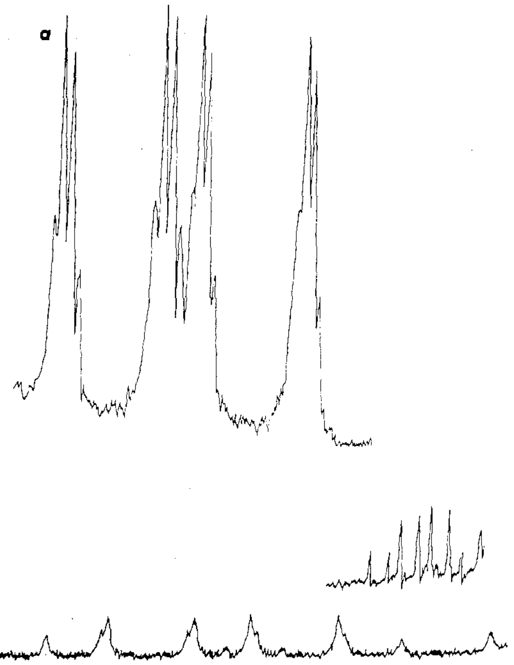

Figure 3. ^1H NMR spectrum of $Fe[(CH_3')_2P'CF_2CH_2P(CH_3)_2](CO)_3$: (a) methyl region; (b) methylene region, sweep width 100 Hz (inset, methylene region, sweep width 250 Hz).

The ^{13}C spectrum (^1H noise decoupled) of $Fe[(CH_3')_2P'CF_2CH_2P(CH_3)_2](CO)_3$ is complex. The CH_3' and CH_3 groups each show a broad doublet, the CH_3' resonance being the more shielded ($\delta_{CH_3'}$ 16.2 ppm, $J_{CP'}$ = 24 Hz; δ_{CH_3} 20.3 ppm, J_{CP} = 29 Hz). The CH_2 resonance is a doublet of quintets, the quintets arising from two overlapping triplets (δ_{CH_2} 37.6 ppm, J_{CP} = 42 Hz, $^2J_{CP'}$ = 28 Hz, $^2J_{CF}$ = 21 Hz). The ^{13}C spectrum of the CF_2 carbon is the X portion of an ABX spectrum each line of which is split into a triplet by the two magnetically equivalent fluorines. Because of the reduced intensity and longer relaxation time, only the central portion of this triplet was observed (δ_{CF_2} 133.5 ppm, $J_{CP'}$ = 33 Hz, $^2J_{CP}$ = 26 Hz). The proton-coupled and -decoupled spectra of the carbonyl carbons are identical, showing a partially resolved doublet of doublets. The resonance is unchanged down to the lowest temperature at which studies were performed, −70° (δ_{CO} 220.0 ppm, $^2J_{CP}$ = 10.1 Hz, $^2J_{C'P}$ = 5.7 Hz).

***o*-Phenylenebis(dimethylarsine).** The ^1H spectrum of diars gave a methyl singlet at τ 8.84 at 31°; at −90° it had broadened somewhat (δ = 8.83 τ). The ^{13}C spectrum of the ligand in toluene-d_8 exhibited a singlet in the methyl region (δ 10.99 ppm). The ^1H and ^{13}C resonances in the aromatic region were not assigned.

Tricarbonyl-*o*-bis(dimethylarsino)iron(0). The methyl protons of Fe(diars)$(CO)_3$ gave a single, sharp resonance at τ 8.37 at 31° in toluene-d_8. The signal was relatively sharp at +90° but started broadening at temperatures below −30°. The chemical shift was somewhat temperature dependent (τ 8.60 at +90° and τ 8.77 at −50°); however, it was much less temperature dependent in methylene-d_2 chloride (τ 8.37 at +31° and τ 8.34 at −50°). The resonance also started broadening below −30° in this solvent.

The ^{13}C spectrum of the carbonyl carbons of Fe(diars)$(CO)_3$ in toluene-d_8 was a single, sharp line down to −70° (δ 221.4 ppm), the ^1H-coupled and -decoupled spectrum being unchanged. At −84° the line had broadened somewhat but was still a single resonance. The spectrum of the carbonyl carbons was also investigated in a low-temperature solvent system, $CHCl_2F$–CD_2Cl_2 (90:10) and found to remain a single line down to −140°. The ^{13}C spectrum of the methyl carbons was also observed to be a single line down to −140° (δ 16.7 ppm).

1,3-Bis(diphenylphosphino)propane. The ^1H spectrum of the methylene protons of $(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2$ was second order and was not analyzed. The ^1H-decoupled ^{31}P spectrum consisted of a single line (δ −19.0 ppm). The ^1H-decoupled ^{13}C spectrum in the methylene region consisted of two triplets. The more shielded triplet is assigned to C-2 (δ 22.8 ppm, J_{CP} = 7.5 Hz); the less shielded triplet (X portion of an AA'X spectrum) is assigned to C-1 and C-3 (δ 30.0 ppm, $^1/_2(J_{CP} + {}^3J_{CP})$ = 13.4 Hz).

Tricarbonyl-1,3-bis(diphenylphosphino)propaneiron(0). The ^1H spectrum of the methylene region of $Fe[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2](CO)_3$ is second order and was not analyzed. The ^1H-decoupled ^{31}P spectrum consisted of a single line (δ 44.3 ppm). The ^1H-decoupled ^{13}C spectrum of the methylene region consisted of a singlet (δ 19.8 ppm) assigned to C-2 and a triplet (δ 29.9 ppm, $^1/_2(J_{CP} + {}^3J_{CP})$ = 15.6 Hz) assigned to C-1 and C-3. The ^{13}C spectrum of the carbonyl region consists of a triplet (δ 219.9 ppm, $^2J_{CP}$ = 8.9 Hz) down to −80°, with some broadening of the lines at the low temperature.

Discussion

As seen in Table I, all complexes studied have three carbonyl stretching vibrations in their infrared spectrum both as solid mulls and in solution. This is consistent with trigonal-bipyramidal structures with one ligand being axial and one equatorial. As pointed out previously[6] this appears to be the most favored structure for molecules of this type and, indeed, is the observed structure[11] of Fe(diars)$(CO)_3$.

Consideration of assignment of the NMR parameters of $(CH_3')_2P'CF_2CH_2P(CH_3)_2$ and $Fe[(CH_3')_2P'CF_2CH_2P(CH_3)_2](CO)_3$ deserves comment. Assignment requires correlation of a resonance with a specific magnetically active nucleus in the molecule by comparison with previously determined NMR parameters and then associating other resonances with the determined one to extend the assignment to the entire spectrum of the molecule. As an example, in $(CH_3')_2P'CF_2CH_2P(CH_3)_2$ the ^{13}C resonances due to the CF_2 and CH_2 groups are readily assigned due to chemical shifts and J_{CF}. However, it is unclear how to associate the above-mentioned assignments to an unequivocal assignment of the two methyl resonances. Hence, use of ^{13}C experiments alone appears to be an impractical way to distinguish the CH_3' resonance from the CH_3 resonance.

Table II. ^1H, ^{19}F, and ^{31}P NMR Parameters for $(CH_3')_2P'CF_2CH_2P(CH_3)_2$ and $Fe[(CH_3')_2P'CF_2CH_2P(CH_3)_2](CO)_3$[a,b]

	$(CH_3')_2P'CF_2CH_2P(CH_3)_2$			$Fe[(CH_3')_2P'CF_2CH_2\text{-}P(CH_3)_2](CO)_3$		
	^1H	^{19}F	^{31}P	^1H	^{19}F	^{31}P
$\tau_{CH_3'}$	8.94			8.79		
τ_{CH_3}	9.07			8.91		
τ_{CH_2}	8.08			8.42		
δ_{CF_2}		−32.86			−44.68	
$\delta_{P'}$			−58.8			51.1
δ_P			−91.9			2.5
$^2J_{H'P'}$	3.1			9.0		
$^5J_{H'P}$	*c*			0.8		
$^4J_{H'F}$	*c*			0.7		
$^2J_{HP}$	3.3			9.4		
$^5J_{HP'}$	0.3			0.7		
$^5J_{HF}$	0.7			0.5		
$^3J_{HF}$	20.1	20.0		15.2	15.8	
$^2J_{HP}$	5.3			14.8		
$^3J_{HP'}$	0.4			9.0		
$^2J_{FP'}$		62.8	63.0		47.4	46.7
$^3J_{FP}$		16.5	16.7		15.8	16.3
$^2J_{PP'}$						77.5
$^3J_{PP'}$			39.3			

[a] ^{19}F chemical shifts are in ppm with 1,2-dibromotetrafluoroethane as an external standard. Proton chemical shifts are given in τ units with TMS as an internal standard. Triphenylphosphine oxide was used as the external standard for ^{31}P chemical shifts in ppm. Coupling constants are in Hz. [b] Coupling constant values derived from ^1H spectra have maximum error limits of ±0.2 Hz. Coupling constants determined by either ^{19}F or ^{31}P spectra have a maximum uncertainty of ±0.5 Hz. [c] Not observed.

Table III. ^{13}C NMR Parameters[a,b]

	$(CH_3')_2P'CF_2CH_2P(CH_3)_2$				$Fe[(CH_3')_2P'CF_2CH_2\text{-}P(CH_3)_2](CO)_3$			
	δ_C	J_{CP}	$J_{CP'}$	J_{CF}	δ_C	J_{CP}	$J_{CP'}$	J_{CF}
CH_3'	8.4	3	15	6	16.2	*c*	24	*c*
CH_3	15.2	14	*c*	*c*	20.3	29	*c*	*c*
CH_2	41.3	22.4	19.9	22.4	37.6	42	28	21
CF_2	130.8	10	29	269	133.5	26	33	*c*
CO					220.0	10.1	5.7	

[a] Chemical shifts are in ppm with respect to TMS. Coupling constants are in Hz. Fe(diars)$(CO)_3$: δ_{CO} 221.4, δ_{CH_3} 16.7. $Fe[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2](CO)_3$: δ_{CO} 219.9, $^2J_{P-(CO)}$ = 8.9. [b] Primes denote the dimethylphosphino group on C-1 in $(CH_3')_2P'CF_2CH_2P(CH_3)_2$. [c] Not observed.

The nucleus chosen as the basis of assignment for $(CH_3')_2P'CF_2CH_2P(CH_3)_2$ was ^{31}P. The two ^{31}P resonances can be assigned from the known information that generally $|^2J_{PF}| > |^3J_{PF}|$.[15] Thus the less shielded ^{31}P resonance is assigned to P'. The assignment was extended to the methyl proton resonances by observing ^1H while selectively decoupling ^{31}P and viewing the results with the assumption that $|^2J_{PH}| > |^5J_{PH}|$. This experiment indicates the less shielded methyl ^1H resonance to be due to CH_3'. In addition it was possible to assign the methyl ^{13}C resonances while decoupling phosphorus with the assumption that $|J_{PC}| > |^4J_{PC}|$. This established assignment of the more shielded methyl ^{13}C resonance to CH_3'. The observed pattern of chemical shifts underscores the notion that the factors which determine the chemical shift of one nucleus (e.g., ^1H) do not necessarily control the chemical shift of another nucleus (e.g., ^{13}C).

To determine the origin of the triplet structure in the more shielded methyl ^1H resonance, this resonance was observed while decoupling ^{19}F. These experiments indicated the triplet structure was due to the fluorines rather than the methylene protons, hence $|^5J_{HF}| > |^4J_{HH}|$. The ^1H, ^{19}F, and ^{31}P NMR parameters of this ligand are given in Table II; the ^{13}C NMR parameters are given in Table III.

Assignments of NMR spectral parameters for $Fe[(CH_3')_2P'CF_2CH_2P(CH_3)_2](CO)_3$ are also based on coupling involving ^{31}P. Again the ^{31}P resonances were assigned on the basis that $|^2J_{PF}| > |^3J_{PF}|$.[15] Also, the assignment that the more shielded phosphorus in the ligand is also the more shielded in the complex is consistent with work showing a linear relationship between the ^{31}P chemical shift of free phosphine ligands and the change in chemical shift upon complexation.[16] The methyl ^{1}H resonances were assigned by observing them while decoupling ^{31}P. This established the assignment of the less shielded methyl ^{1}H resonance to CH_3'. Due to the limited solubility of the iron complex, it was impractical to observe ^{13}C while decoupling ^{31}P.

The ^{31}P and ^{1}H assignments for both the free and complexed ligand were analogous. In both cases P' was less shielded than P and the protons of CH_3' were less shielded than those of CH_3. To assign the methyl ^{13}C resonances the analogy was extended to the ^{13}C spectrum. Thus, since $^{13}C\{^{31}P\}$ decoupling experiments resulted in assignment of the more shielded ^{13}C methyl resonance to CH_3' for the ligand, the more shielded ^{13}C methyl resonance of the complex is also assigned to CH_3'. The ^{1}H, ^{19}F, and ^{31}P NMR data for the complex are listed in Table II and the ^{13}C NMR data are listed in Table III.

The spectral assignments of the methyl and carbonyl resonances for diars and $Fe(diars)(CO)_3$ follow from chemical shift arguments.

The methylene ^{13}C resonances in the ^{13}C spectrum of $(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2$ are assigned on the basis of relative intensities as are the methylene ^{13}C resonances for the complex $Fe[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2](CO)_3$. In addition the C-1 and C-3 carbons of this ligand and complex are expected to be less shielded than the C-2 carbons because of the greater number of carbons β to the C-1 and C-3 carbons.[17]

In the metal complexes studied, there are no indications of the attainment of stereochemical rigidity on the NMR time scale. The carbonyl region in the ^{13}C spectrum of each compound displays one resonance down to the lowest temperatures at which studies were performed: −70° for $Fe[(CH_3')_2P'CF_2CH_2P(CH_3)_2](CO)_3$, −80° for $Fe[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2](CO)_3$, and −140° for $Fe[o\text{-}C_6H_4\{As(CH_3)_2\}_2](CO)_3$. No static structure of any of these molecules can be constructed which has all three carbonyl groups equivalent.

Although the crystal structure of $Fe(diars)(CO)_3$ indicates[11] the methyl groups on the ligand are nonequivalent in the solid sample their ^{13}C NMR spectrum consisted of a single resonance down to −140°, thus indicating site averaging as for the carbonyl resonance.

The lack of differentiation between the carbonyl groups in these compounds on the basis of their ^{13}C NMR spectra indicates either that site equivalence is being accomplished by fluxional behavior or that the different carbonyl groups of a static structure are accidentally chemical shift equivalent. The latter possibility is considered highly unlikely due to the sensitivity of the ^{13}C chemical shift of carbonyl carbons in other transition metal complexes studied.[18] Thus the carbonyl ^{13}C NMR data are considered indicative of fluxional behavior as we have observed previously for $Fe[(CH_3)_2PCH_2CH_2P(CH_3)_2](CO)_3$.[6] The temperature dependence of the ^{1}H chemical shifts can be rationalized in terms of medium effects as also previously discussed.[6]

We believe that arguments similar to those stated previously[6,19,20] may be applied to explain the fluxionality of the compounds studied in this investigation. Furthermore we believe that, in general, $(L\text{-}L)Fe(CO)_3$ derivatives containing a bidentate ligand will exhibit fluxional behavior similar to $L_2Fe(CO)_3$ complexes containing two monodentate ligands.

Acknowledgment. The University of South Carolina group and the University of Pennsylvania group gratefully acknowledge Grants GP42454X and GP9562, respectively, from the National Science Foundation for financial support of this study.

Registry No. $(CH_3)_2PCF_2CH_2P(CH_3)_2$, 34250-95-8; $Fe[(CH_3)_2PCF_2CH_2P(CH_3)_2](CO)_3$, 56700-28-8; $(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2$, 6737-42-4; $Fe[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2](CO)_3$, 56700-29-9; diars, 13246-32-7; $Fe(diars)(CO)_3$, 56760-75-9; $Fe[(CH_3)_2PCH_2CH_2P(CH_3)_2](CO)_3$, 38504-43-7; $Fe(C_8H_8)(CO)_3$, 12093-05-9; ^{31}P, 7723-14-0; ^{13}C, 14762-74-4; $(CH_3)_2PP(CH_3)_2$, 3676-91-3; $CF_2{=}CH_2$, 75-38-7.

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(1) (a) University of South Carolina. (b) University of Pennsylvania.

(2) Taken in part from the thesis of G. R. Langford submitted to the Graduate School of the University of South Carolina in partial fulfillment of the requirements for the M.S. degree.

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