*Inorg. Chem.* **1987**, *26*, 1357-1361

**X-ray Structural Determination.** Intensity data were collected at room temperature on a Nonius CAD-4 automated diffractometer with Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å), and corrected for absorption by the empirical method described in ref 22.

Crystal data for compounds **8A** and **12c** (**12**$\cdot 2CH_3C_6H_5$) are summarized in Table IV, together with some experimental details. The unit cell parameters for both crystals were determined by least-squares refinement of the setting angles of 25 reflections. Both structures were solved by conventional Patterson and Fourier methods and refined by full-matrix least squares as described in Table IV.

Anisotropic thermal factors were refined for all the atoms with the exception of the phenyl carbon atoms and the solvent molecules. Scattering factors and anomalous dispersion corrections were taken from ref 23. The hydrogen atoms of the phenyl rings and of the pyrazolato ligand (wherever their positioning was not ambiguous) were placed in calculated positions (C–H distance 0.95 Å), and their contribution to the structure factors were computed. A set of three difference Fourier syntheses was finally computed at increasing values of limiting $(\sin\theta)/\lambda$, to test whether residual peaks attributable to the hydridic hydrogen atoms were present close to the metal atom.[24] For compound **8A** only peaks due to a residual contribution of the metal atom were detected, so that the hydrides were introduced in approximate calculated positions in the plane N(1), Ir, C, trans to N(1) and C only for sake of clarity in the drawing. For **12c** the test reveals two peaks approximately close to the expected positions for the two hydrides at 1.66 and 1.65 Å from the iridium atom. All computations were carried out on a PDP11/34 computer using the SDP-Plus structure determination package and the physical constants listed therein.[25]

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**Supplementary Material Available:** Tables of general temperature factors, calculated positions for hydrogen atoms in **8A** and **12c**, and atomic positions for solvent molecules in **12c** (5 pages); listings of structure factors for **8A** and **12c** (55 pages). Ordering information is given on any current masthead page.

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# Properties and X-ray Structure of $PPN^+[cis\text{-}HFe(CO)_3P(OPh)_3]^-$: An Unexpected Structural Isomer

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The preparation of $[PPN][HFe(CO)_3P(OPh)_3]$ (**1**) has been carried out by using an alcoholic hydroxide reaction with $Fe(CO)_4P(OPh)_3$; the same synthesis was reported earlier for *trans*-$HFe(CO)_3PR_3^-$ salts. After spectral and chemical differences were observed between the anion of **1** and all other $HFe(CO)_3PR_3^-$ anions, which have been shown to exist in a trans configuration of H and $PR_3$ (TBP geometry), an X-ray structural determination was performed. **1** crystallizes in the triclinic system, space group $P\bar{1}$, with cell parameters $a$ = 10.491 (3) Å, $b$ = 13.963 (4) Å, $c$ = 18.687 (6) Å, $\alpha$ = 108.19 (2)°, $\beta$ = 105.47 (2)°, $\gamma$ = 93.16 (2)°, $V$ = 2478 (1) Å$^3$, and $Z$ = 2. The hydride ligand was located in the axial position of a distorted trigonal bypyramid, but curiously the $P(OPh)_3$ ligand is in the equatorial plane, cis to the hydride. Unique properties of **1** include its air stability and its rigidity as the cis isomer. The spectral properties of **1** including ion pairing and isotopic H/D exchange effects were examined. In contrast to other anion trigonal-bipyramidal complexes that show equatorial $CO\cdots Na^+$ interaction, an axial $CO\cdots Na^+$ site interaction was observed for **1**. Hydrogen/deuterium substitution in this anion revealed a large $\nu$(MH) to $\nu$(CO) coupling to the trans carbonyl group.

## Introduction

Recently we synthesized a series of phosphine and phosphite derivatives of the well-known $HFe(CO)_4^-$ anion.[1] An X-ray crystal structure determination carried out on the $Et_4N^+HFe(CO)_3PPh_3^-$ salt found the anion to be of distorted trigonal-bipyramidal geometry, with the $PPh_3$ ligand in an axial position and trans to the likely position for the unlocated hydride ligand. The distortion results from a bending of the CO groups away from the $PPh_3$ ligand, $\angle$(P–Fe–CO) = 99.5°, and into the void where the hydride ligand presumably lies. Since this angle is identical with the $\angle(CO)_{ax}\text{–}Fe\text{–}(CO)_{eq}$ of $HFe(CO)_4^-$,[2] the distortion is not a result of the large steric bulk of the $PPh_3$ substituent.

An alternate view of the structure of $HFe(CO)_3PPh_3^-$ is that of a tetrahedral $Fe(CO)_3PPh_3^{2-}$ anion that has been distorted by protonation in the all-carbonyl face. As a distorted TBP the relative positioning of the ligands is as expected according to the thesis of Rossi and Hoffmann[3] that the equatorial plane is the site of preference of weaker $\sigma$-donating and better $\pi$-accepting ligands in d$^8$, TBP complexes.

The $\nu$(CO) infrared spectra observed for *trans*-$HFe(CO)_3PPh_3^-$ was consistent with $C_{3v}$ symmetry of the CO groups (i.e., one weak and one very strong band). Six other derivatives ($PEt_3$, $PMe_3$, $PPh_2Me$, $PPhMe_2$, $P(OMe)_3$, $P(OEt)_3$) had analogous $\nu$(CO) band patterns.[1] The proton NMR spectra of the series showed an interesting and dramatic dependence of $J_{PH}$ on solvent polarity and temperature, varying from a maximum of $|J_{PH}|$ = 15 Hz to a minimum of 0.0 Hz. Surprisingly, the eighth member of this series, $HFe(CO)_3P(OPh)_3^-$, showed anomalous spectral and chemical behavior. Whereas the other hydrides were air-sensitive as expected for anionic hydrides, the $P(OPh)_3$ derivative was stable to air, even in solution for extended periods of time. The $\nu$(CO) IR spectrum was comprised of three bands, of a medium, strong, and medium (sh) pattern. Furthermore, the Fe–H stretch at 1895 cm$^{-1}$ was surprisingly intense. The $^1$H NMR hydride resonance was a doublet of $J_{PH}$ = 55 Hz, which was invariant with temperature. This derivative has also been subjected to a molecular

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structure determination, the results of which are given in this report.

## Experimental Section

**A. Methods and Materials.** An argon atmosphere glovebox and standard Schlenk techniques were used in all reactions and sample preparations. All solvents were distilled under nitrogen from an appropriate drying agent (THF and hexane from $Na^0$/benzophenone, diethyl ether from $LiAlH_4$, and methanol from $Mg/I_2$) and then stored over activated 3A molecular sieves. Deuteriated solvents were obtained from Aldrich Chemical Co. and degassed prior to use.

**B. Instrumentation.** Infrared spectra were recorded on an IBM FTIR Model 32 or 85 instrument using 0.1-mm $CaF_2$ sealed cells. Nuclear magnetic resonance spectra were performed on either a Varian XL-200 or XL-200E spectrometer. Temperatures reported are ±1 °C.

**C. Preparations.** The preparation of $Fe(CO)_4P(OPh)_3$ was carried out according to that described by Albers and Coville by using $CoI_2\cdot 2H_2O$ as the substitution catalyst.[4] The preparation of $PPN^+HFe(CO)_3P(OPh)_3^-$ was carried out in a manner identical with that of all other $HFe(CO)_3PR_3^-$ complexes.[1] A typical preparation involved mixing 1 g of $Fe(CO)_4P(OPh)_3$ with a 1:1 molar ratio of (PPN)Cl and 8 equiv of KOH in a 50-mL Schenk flask. Approximately 12 mL of methanol was then added, and a bright yellow solid appeared in only a few minutes. The reaction was left stirring for 1.5 h to ensure reaction completion. The yellow solid was collected on a fritted glass filter and washed with 100 mL of methanol. The yellow product was dried in vacuo for 3 h. The hydride was then recrystallized from THF/diethyl ether. The percentage yields were typically 70–80%. Single crystals for X-ray analysis were grown by layering diethyl ether onto a saturated THF solution of $PPN^+HFe(CO)_3P(OPh)_3^-$ in a 5-mm NMR tube. The corresponding deuteride was prepared in a similar manner to the hydride except that $CH_3OD$ (99.5% isotopically labeled) and NaOD (40 wt % solution in $D_2O$, 99+ atom % D) were replaced for MeOH and KOH, respectively. All glassware was prewashed with $D_2O$ and dried prior to use.

**D. Force Constant Calculations.** Trial force constants for the CO stretching vibrations of *cis*-$HFe(CO)_3P(OPh)_3^-$ were calculated by using a modified Cotton-Kraihanzel approach[5] employing three observed frequencies ($A'_1$, $A'_2$, and $A''$) in THF. The $A'_2$ band was found to couple into the $\nu$(MH) band; therefore, its position was taken from the corresponding deuterio analogue where $\nu$(MD) to $\nu$(CO) coupling should be greatly reduced. The $A'_2$ band is actually a shoulder on the $A''$ band; therefore, its position is only an estimate (±5 $cm^{-1}$). The trial force constants ($k_{1(eq)}$, $k_{2(ax)}$, $k_{c(eq-eq)}$, $k_{c'(ax-eq)}$) were calculated by assuming a $k_c/k_{c'}$ ratio of unity. To release this assumption an interactive computer program based on the work of Schachtschneider and Snyder[6] was employed that allowed for the input of more observations, namely $\nu(^{13}CO)$ bands. On $^{13}CO$ labeling of **1** (vide infra), a well-defined mono-$^{13}CO$-substitution $A'_1$ band was apparent at 1948 $cm^{-1}$. The program took the four observed frequencies and adjusted the force constants to fit the observed data. The final $k_c/k_{c'}$, ratio obtained was 1.26 with $k_c$ and $k_{c'}$ being 0.53 and 0.42 mdyn/Å, respectively.

The force constants for *trans*-$HFe(CO)_3PR_3^-$ complexes were also obtained by using a Cotton–Kraihanzel approach.[5] The $A_1$ and E $\nu$(CO) band positions for $C_{3v}$ symmetry were taken from THF solutions in which the cation was either $PPN^+$ or Na(18-Cr-6)$^+$. The value of $k_c$ was on average 0.51 (1) mdyn/Å.

**E. $^{13}$CO Enrichment of *cis*-$HFe(CO)_3P(OPh)_3^-$.** $Fe(CO)_4P(OPh)_3$ was enriched with $^{13}CO$ by using the procedure described by Darensbourg et al.[7] Enrichment was monitored by $\nu$(CO) IR spectroscopy and stopped when the enrichment level of the sample reached ca. 25%. This $^{13}CO$-enriched $Fe(CO)_4P(OPh)_3$ compound was then converted to the hydride by using the same procedure described above.

**F. X-ray Structure Determination.** Crystallographic data are summarized in Table I. The sample was mounted on a glass fiber with epoxy cement. Preliminary photographic characterization revealed no symmetry higher than triclinic. The centrosymmetric alternative $P\bar{1}$ was initially assumed and later proved correct by the computationally stable and chemically sensible results obtained. No correction for absorption was needed (small $\mu$ and $T$(max)/$T$(min) = 1.13).

**Table I.** Summary of Crystallographic Data for $PPN^+[$*cis*-$HFe(CO)_3P(OPh)_3]^-$

| | | | |
|---|---|---|---|
| | (a) Crystal Parameters | | |
| empirical formula | $FeP_3NC_{57}H_{46}O_6$ | $\gamma$, deg | 93.16 (2) |
| $M_r$ | 989.77 | $V$, Å$^3$ | 2478 (1) |
| cryst syst | triclinic | $Z$ | 2 |
| space group | $P\bar{1}$ | $D$(calcd), g cm$^{-3}$ | 1.326 |
| $a$, Å | 10.491 (3)[a] | color | yellow |
| $b$, Å | 13.963 (4) | size, mm | 0.25 × 0.35 × 0.41 |
| $c$, Å | 18.687 (6) | | |
| $a$, deg | 108.19 (2) | $\mu$(Mo K$\alpha$), cm$^{-1}$ | 4.48 |
| $\beta$, deg | 105.47 (2) | temp, K | 296 |
| | (b) Data Collection | | |
| diffractometer | Nicolet R3M/$\mu$ | no. of reflcns collcd | 7193 |
| radiation | Mo K$\alpha$ | no. of indep reflcns | 6942 |
| wavelength, Å | 0.71073 | $R$(int), % | 2.2 |
| monochromator | graphite | no. of indep reflcns with $4\sigma(F_0)$ | 3729 |
| scan method | Wyckoff | | |
| scan limits, deg | $4 \le 2\theta \le 45$ | std reflcns | 3 std/97 reflcns |
| scan speed, deg/min | 5–20 variable | decay, % | ≤1.5 |
| | (c) Refinement | | |
| $R(F)$, % | 5.20 | $\Delta/\sigma$ (final) | 0.07 |
| $R(wF)$, % | 5.31 | $\Delta(\rho)$, e Å$^{-3}$ | 0.31 |
| GOF | 1.203 | $N_v/N_o$ | 6.3 |

[a] Unit cell parameters were obtained from the best fit of the angular settings of 25 reflections, 20° ≤ $2\theta$ ≤ 28°.

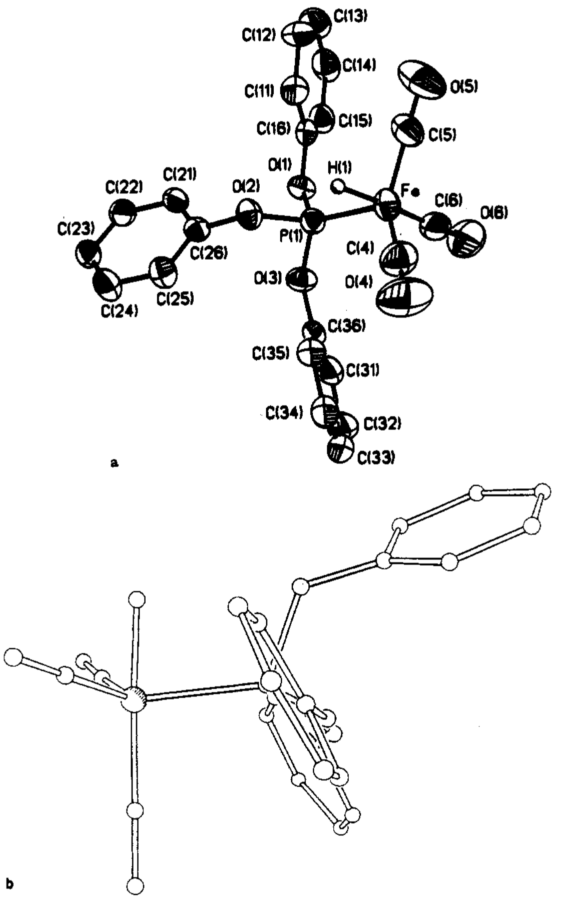

**Figure 1.** (a) ORTEP drawing of the anion of $PPN^+[$*cis*-$HFe(CO)_3P(OPh)_3]^-$ (**1**) showing atom-numbering scheme. (b) Alternate view of the anion of **1**.

The structure was solved by a Patterson synthesis and subsequent difference Fourier synthesis. All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were treated as idealized isotropic contributions except for H(1), which was found and isotropically refined. The phenyl rings of both the cation and anion were constrained to rigid, planar hexagons.

All computer software and sources of scattering factors are from the SHELXTL (5.1) library of programs (Nicolet Corp., Madison, WI). Table II contains atomic coordinates and Table III selected bond distances and angles. Additional crystallographic data including complete tables of

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**Table II.** Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for PPN$^+$[*cis*-HFe(CO)$_3$P(OPh)$_3$]$^-$

| | *x* | *y* | *z* | $U^a$ | | *x* | *y* | *z* | $U^a$ |
|---|---|---|---|---|---|---|---|---|---|
| Fe | 4671 (1) | 2865 (1) | 2272 (1) | 62 (1) | C(43) | −1575 | 6409 | 3878 | 70 (4) |
| P(1) | 5478 (2) | 1555 (1) | 2341 (1) | 50 (1) | C(44) | −2317 | 6390 | 3132 | 70 (3) |
| P(2) | 328 (1) | 8073 (1) | 2576 (1) | 39 (1) | C(45) | −1774 | 6925 | 2738 | 56 (3) |
| P(3) | 2083 (1) | 6497 (1) | 2290 (1) | 40 (1) | C(46) | −488 | 7480 | 3091 | 43 (2) |
| N | 1515 (4) | 7537 (3) | 2342 (3) | 46 (2) | C(51) | −1638 (4) | 8932 (3) | 1772 (2) | 58 (3) |
| O(1) | 5065 (4) | 472 (3) | 1602 (2) | 53 (2) | C(52) | −2531 | 8993 | 1090 | 75 (4) |
| O(2) | 5298 (4) | 1192 (3) | 3062 (2) | 56 (2) | C(53) | −2676 | 8253 | 360 | 72 (3) |
| O(3) | 7041 (4) | 1423 (3) | 2427 (2) | 61 (2) | C(54) | −1928 | 7451 | 311 | 82 (4) |
| O(4) | 6037 (6) | 4661 (4) | 3635 (4) | 136 (3) | C(55) | −1036 | 7390 | 992 | 65 (3) |
| O(5) | 1827 (5) | 2648 (5) | 1529 (3) | 135 (4) | C(56) | −891 | 8131 | 1723 | 42 (2) |
| O(6) | 5700 (6) | 3049 (5) | 1015 (4) | 121 (4) | C(61) | 193 (3) | 9894 (3) | 3675 (2) | 53 (3) |
| C(4) | 5496 (7) | 3944 (5) | 3071 (5) | 92 (4) | C(62) | 624 | 10921 | 4129 | 64 (3) |
| C(5) | 2971 (7) | 2724 (6) | 1824 (4) | 80 (4) | C(63) | 1817 | 11414 | 4129 | 63 (3) |
| C(6) | 5302 (7) | 2980 (5) | 1534 (5) | 79 (4) | C(64) | 2580 | 10879 | 3676 | 64 (3) |
| C(11) | 2671 (5) | 147 (3) | 1419 (2) | 71 (3) | C(65) | 2149 | 9852 | 3223 | 51 (3) |
| C(12) | 1411 | −347 | 912 | 98 (5) | C(66) | 955 | 9359 | 3223 | 40 (2) |
| C(13) | 1267 | −937 | 132 | 109 (5) | C(71) | 569 (4) | 4859 (3) | 1011 (2) | 59 (3) |
| C(14) | 2384 | −1032 | −142 | 90 (4) | C(72) | −514 | 4075 | 614 | 70 (3) |
| C(15) | 3645 | −538 | 365 | 68 (3) | C(73) | −1330 | 3810 | 1023 | 72 (3) |
| C(16) | 3789 | 52 | 1146 | 56 (3) | C(74) | −1063 | 4328 | 1830 | 65 (3) |
| C(21) | 5526 (4) | −590 (3) | 2842 (2) | 56 (3) | C(75) | 21 | 5112 | 2227 | 54 (3) |
| C(22) | 6035 | −1330 | 3147 | 64 (3) | C(76) | 837 | 5377 | 1818 | 46 (3) |
| C(23) | 6894 | −1041 | 3916 | 63 (3) | C(81) | 4008 (4) | 5626 (3) | 1655 (2) | 57 (3) |
| C(24) | 7244 | −12 | 4379 | 73 (3) | C(82) | 4903 | 5552 | 1213 | 70 (3) |
| C(25) | 6735 | 729 | 4074 | 62 (3) | C(83) | 5017 | 6261 | 839 | 69 (3) |
| C(26) | 5876 | 440 | 3305 | 48 (3) | C(84) | 4237 | 7043 | 907 | 63 (3) |
| C(31) | 9222 (5) | 2157 (4) | 2594 (3) | 83 (4) | C(85) | 3343 | 7117 | 1349 | 48 (3) |
| C(32) | 10348 | 2897 | 3021 | 114 (6) | C(86) | 3228 | 6408 | 1723 | 40 (2) |
| C(33) | 10354 | 3653 | 3718 | 116 (6) | C(91) | 3717 (4) | 7420 (3) | 3794 (3) | 63 (3) |
| C(34) | 9235 | 3669 | 3988 | 96 (4) | C(92) | 4431 | 7480 | 4556 | 92 (4) |
| C(35) | 8109 | 2929 | 3562 | 71 (3) | C(93) | 4441 | 6608 | 4771 | 101 (5) |
| C(36) | 8103 | 2173 | 2865 | 54 (3) | C(94) | 3736 | 5677 | 4223 | 95 (5) |
| C(41) | 255 (3) | 7499 (3) | 3837 (2) | 53 (3) | C(95) | 3022 | 5616 | 3461 | 69 (3) |
| C(42) | −289 | 6963 | 4230 | 67 (3) | C(96) | 3013 | 6488 | 3246 | 47 (3) |

$^a$ Equivalent isotropic *U* is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

**Table III.** Interatomic Distances and Angles for the *cis*-HFe(CO)$_3$P(OPh)$_3$$^-$ Anion

| | | | |
|---|---|---|---|
| | (a) Bond Lengths (Å) | | |
| Fe–P(1) | 2.083 (2) | Fe–H(1) | 1.560 (70) |
| Fe–C(4) | 1.736 (6) | Fe–C(5) | 1.727 (6) |
| Fe–C(6) | 1.728 (10) | O(4)–C(4) | 1.181 (8) |
| O(5)–C(5) | 1.163 (8) | O(6)–C(6) | 1.180 (13) |
| P(1)–O(1) | 1.639 (3) | P(1)–O(2) | 1.630 (5) |
| P(1)–O(3) | 1.631 (4) | O(1)–C(16) | 1.362 (5) |
| O(2)–C(26) | 1.378 (6) | O(3)–C(36) | 1.363 (6) |
| | (b) Bond Angles (deg) | | |
| P(1)–Fe–H(1) | 82.0 (22) | P(1)–Fe–C(4) | 112.6 (3) |
| H(1)–Fe–C(4) | 76.8 (17) | P(1)–Fe–C(5) | 117.3 (3) |
| H(1)–Fe–C(5) | 80.9 (19) | C(4)–Fe–C(5) | 121.0 (4) |
| P(1)–Fe–C(6) | 95.7 (3) | H(1)–Fe–C(6) | 177.4 (22) |
| C(4)–Fe–C(6) | 103.0 (4) | C(5)–Fe–C(6) | 101.3 (4) |
| Fe–C(4)–O(4) | 177.1 (8) | Fe–C(5)–O(5) | 178.8 (7) |
| Fe–C(6)–O(6) | 178.2 (6) | Fe–P(1)–O(1) | 122.7 (2) |
| Fe–P(1)–O(2) | 115.0 (2) | Fe–P(1)–O(3) | 124.6 (2) |
| O(1)–P(1)–O(2) | 101.6 (2) | O(1)–P(1)–O(3) | 87.9 (2) |
| O(2)–P(1)–O(3) | 99.4 (2) | P(1)–O(1)–C(16) | 124.8 (3) |

bond distances and angles are available.[20]

## Results and Discussion

**X-ray Diffraction Study of PPN$^+$HFe(CO)$_3$P(OPh)$_3$$^-$.** An ORTEP drawing and an alternate perspective view of the anion HFe(CO)$_3$P(OPh)$_3$$^-$ are shown in Figure 1. The molecular structure of **1** is that of a distorted trigonal bipyramid with the located hydride in an axial position and the P(OPh)$_3$ ligand equatorial. The cation shows an interesting interleafing of the phenyl groups of PPN$^+$ with the phenyl groups of the P(OPh)$_3$ ligand (Figure 1S[20]); nevertheless, there were no close interionic contacts that might suggest that the cation stabilized the anion in this particular form. The structure of the anion of **1** is amazingly similar to that of the previously determined *trans*-HFe(CO)$_3$PPh$_3$$^-$ (**2**), except for the exchange of P ligand and CO positions. The L$_{ax}$–Fe–(CO)$_{eq}$ angles in both **1** and **2** are 100 ± 3°; i.e., the CO groups bend toward the hydride as is generally observed for metal carbonyl hydrides. The P(OPh)$_3$ ligand in **1** also bends toward the hydride with ∠P–Fe–H = 82.0 (22)°. The fact that the coordination sphere interligand angles of both **1** and **2** are hardly different from those of HFe(CO)$_4$$^-$ (**3**, ∠(CO)$_{ax}$–Fe–(CO)$_{eq}$ = 99.5°),[2] suggests a remarkably small steric influence of the bulky P-donor ligands. The structure of **1** showed no significant difference in Fe–C or C–O distances for the CO ligands trans to hydride and those cis.

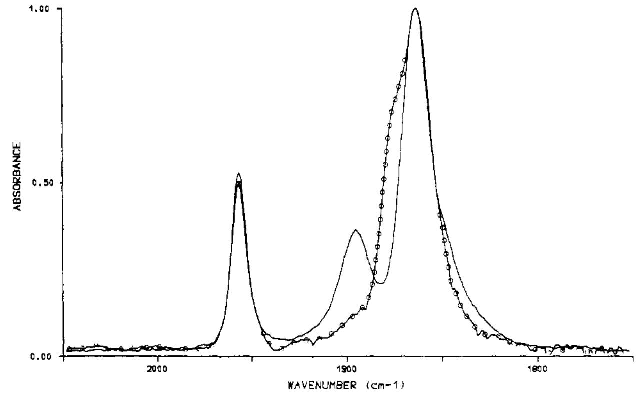

**Figure 2.** $\nu$(CO) infrared spectrum of PPN$^+$[*cis*-HFe(CO)$_3$P(OPh)$_3$]$^-$ (—) and of PPN$^+$[*cis*-DFe(CO)$_3$P(OPh)$_3$]$^-$ (-o-o-) in THF.

**Spectroscopy.** Figure 2 shows the infrared spectrum of PPN$^+$[*cis*-HFe(CO)$_3$P(OPh)$_3$]$^-$ in THF solution. An identical pattern and similar band positions were observed when the spectrum was taken as a KBr pellet. The band of medium intensity at 1895 cm$^{-1}$ was determined to be the Fe–H stretch on the basis of H/D isotopic exchange. The remaining $\nu$(CO) bands were assigned to the ($C_s$ symmetry) vibrational modes A$'_1$ (1958 (m) cm$^{-1}$), A$''$ (1864 (s) cm$^{-1}$), and A$'_2$ (1851 (sh) cm$^{-1}$) (Figure 3) according to the arguments of Cotton and Kraihanzel.[5] The DFe(CO)$_3$P(OPh)$_3$$^-$ analogue was prepared as described in the

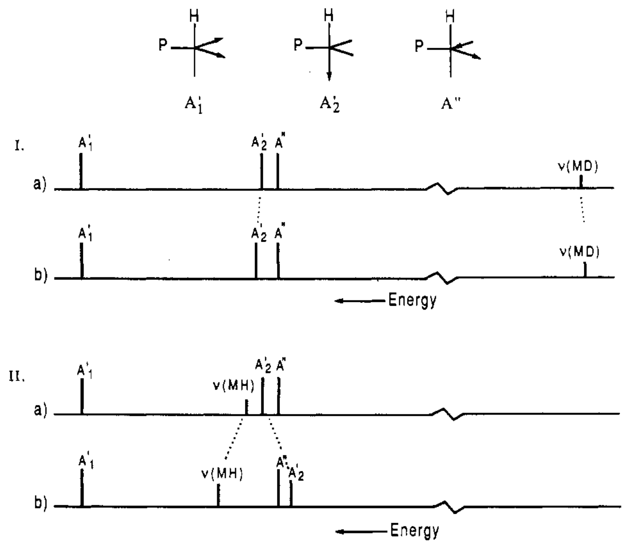

**Figure 3.** Infrared vibrational analysis for $PPN^+[cis\text{-}DFe(CO)_3P(OPh)_3]^-$ (I) and $PPN^+[cis\text{-}HFe(CO)_3P(OPh)_3]^-$ (II). The uncoupled and coupled $\nu(CO)$ to $\nu(MH(D))$ spectral representations are designated as a and b, respectively.

Experimental Section. Its infrared spectrum in this region (Figure 2) showed loss of the 1895-cm$^{-1}$ band and a concurrent shift of the shoulder at 1851 cm$^{-1}$ to the high-energy side of the most intense band at 1864 cm$^{-1}$. That is, the $A'_2$ $\nu(CO)$ position in **1**-*d* is positioned at 1874 cm$^{-1}$.

In fact, the shift in the $A'_2$ position upon H/D isotopic exchange provides further evidence for the cis geometry of **1** in solution. As shown in Figure 3, the $A'_2$ mode corresponds to the motion of the CO group trans to the hydride ligand. Kaesz and co-workers have shown that metal–hydrogen vibrations can couple to symmetrical CO stretches by a factor of up to 400 times greater when the CO group is trans to the hydride than when it is cis.[8] Such coupling is apparent in $HM(CO)_4^-$ (M = Fe, Ru, Os) where the greatest $\nu(CO)$ position change on isotopic exchange of hydrogen for deuterium was in the position of the $A_1{}^2$ band, due primarily to the stretch of the axial or trans CO group.[9] Consistent with this, the $A'_2$ band in **1** is the only band that was seen to shift on deuteriation. The shift is large (23 cm$^{-1}$) and qualitatively explains the large intensity of the $\nu$(Fe–H) band. (The intensity of the Fe–H stretch of **1** is quite exceptional in hydridometal carbonylates.[10]) In the process of deuteriation the $\nu(CO)$ $A'_2$ band appears to have gained some intensity, although severe overlap does not permit quantification. The $\nu$(Fe–D) to $\nu(CO)$ coupling is expected to be smaller due to the greater energy difference in the two vibrations. The $\nu$(Fe–D) band is therefore expected to be of lower intensity than the $\nu$(Fe–H) band, and indeed, when the KBr solid spectra of **1** is subtracted from that of PPN (**1**-*d*), a very weak and broad absorption centered at 1320 cm$^{-1}$ was observed and assigned to $\nu$(Fe–D).

We note that in the *trans*-$HFe(CO)_3PR_3^-$ complexes, the $\nu$(Fe–H) band is of low intensity.[1] This would indicate little coupling with the symmetrical stretch of the three equatorial CO groups. On the deuteriation of the trans derivatives there is hardly any shift in the $\nu(CO)$ bands, confirming little coupling. Due to absorbances of solvent and counteranion in the region where the $\nu$(Fe–D) band was expected, we were unable to verify its position.

**Ion Pairing and Force Constant Calculations.** The interaction of a $Na^+$ ion with the title anion was probed by using $\nu(CO)$ IR spectroscopy. Tetrahydrofuran solution spectra of $PPN^+$ (a large cation known not to interact with organometallic anions in a specific, perturbing manner) and $Na^+$ salts of $HFe(CO)_3P(OPh)_3^-$ are shown in Figure 4. We note that only one band shifts in the presence of $Na^+$ ions, and it is the one assigned to the $A'_2$ $\nu(CO)$ vibration. Since this vibrational mode is due primarily to the trans CO stretch, the contact ion pair is indicated to be of the form axial-CO···$Na^+$. This contact ion pairing can be removed upon addition of 18-crown-6. The resulting spectrum is identical with that of **1** and indicates there is no change in anion configuration with change in counterion.

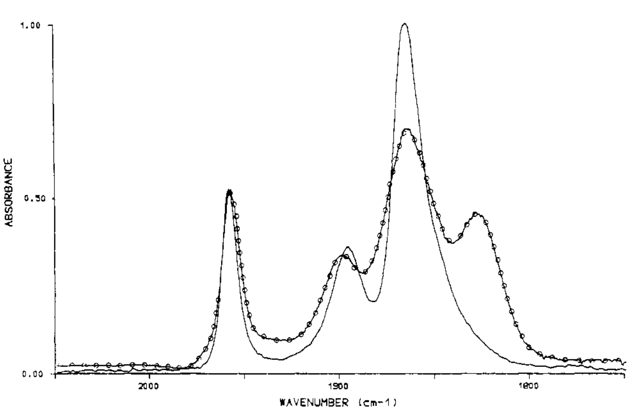

**Figure 4.** Overlay of the infrared spectrum of $PPN^+[cis\text{-}HFe(CO)_3P(OPh)_3]^-$ (—) and $Na^+[cis\text{-}HFe(CO)_3P(OPh)_3]^-$ (-o-o-) in THF.

The contact ion pair formed in $Na^+HFe(CO)_4^-$ exhibited equatorial CO site selectivity,[11] as expected on basis of the predicted electron distribution in d$^8$, TBP structures.[3] That is, better electron-withdrawing ligands are in theory positioned in the equatorial plane of TBP structures, and the CO···$Na^+$ ligand is clearly a better $\pi$-acceptor than CO itself. All other previously studied TBP metal carbonyl anions (e.g., $Mn(CO)_5^-$ and $Mn(CO)_4PR_3^-$)[12] have also shown equatorial carbonyl site selectivity for interactions with alkali-metal cations.

We conclude then that the exchange of an equatorial CO group by $P(OPh)_3$ does not drastically increase the electron density in the remaining equatorial carbonyls. In fact, carbonyl force constant calculations showed a greater similarity in so-called "equatorial" and "axial" carbonyl groups for *cis*-$HFe(CO)_3P(OPh)_3^-$, $k_{1(eq)} = 14.56$ and $k_{2(ax)} = 14.57$ mdyn/Å, than for $HFe(CO)_4^-$, $k_{1(eq)} = 14.72$ and $k_{2(ax)} = 15.02$ mdyn/Å.

The difference in the calculated $k_1$ and $k_2$ values for **1** is insignificant given the inaccuracy of the $A_2'$ $\nu(CO)$ band position used in the force constant calculation. Nevertheless, the largest lowering of force constant on substituting the $P(OPh)_3$ ligand for an equatorial CO is for the CO group trans to the hydride. That is, as compared to the $HFe(CO)_4^-$, a greater portion of electron density donated by the $P(OPh)_3$ ligand is distributed to the axial CO group.

An interesting observation was made upon calculating a value for $k_{1(eq)}$ for the *hypothetical* trans isomer of **1**. This was carried out by first determining $k_{1(eq)}$ values for all other known *trans*-$HFe(CO)_3PR_3^-$ complexes ($PR_3$, $k_1$ (mdyn/Å): $P(OMe)_3$, 14.20; $P(OEt)_3$, 14.13; $PPh_3$, 14.00; $PPh_2Me$, 13.94; $PPhMe_2$, 13.89; $PMe_3$, 13.82; $PEt_3$, 13.79). These values were compared with those for the corresponding parent compounds, $Fe(CO)_4PR_3$.[7] A plot of $k_{1(eq)}$ for $Fe(CO)_4PR_3$ vs. $k_{1(eq)}$ for the respective *trans*-$HFe(CO)_3PR_3^-$ was linear with $r = 0.994$. From $k_{1(eq)}$ for $Fe(CO)_4P(OPh)_3$, a value of 14.39 mdyn/Å was extrapolated for *trans*-$HFe(CO)_3P(OPh)_3^-$. This is a significantly smaller value than that obtained for $k_1$ or $k_2$ in *cis*-$HFe(CO)_3P(OPh)_3^-$, leading to the conclusion that the $P(OPh)_3$ ligand is *accepting* a substantial amount of electron density when in the cis position. We expect the stability of the cis isomer is associated with the ability of the $P(OPh)_3$ ligand to accept electron density.

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**Nuclear Magnetic Resonance.** The hydride ligand of **1** has the largest $^1$H upfield shift of all HFe(CO)$_3$PR$_3^-$ derivatives thus prepared, at $\delta = -9.89$ in THF-$d_8$. As previously mentioned, the $J_{PH}$ value (d) 54.8 Hz, is about five times that of the average $J_{PH}$ of *trans*-HFe(CO)$_3$PR$_3^-$ derivatives, and is invariant with temperature and solvent. The $^2$H resonance for PPN$^+$[*cis*-DFe(CO)$_3$P(OPh)$_3$]$^-$ is also at -9.9 ppm in THF, and the $J_{PH}$ is precisely 1/6.5 that of $J_{PH}$, i.e., 8.4 Hz, as expected.

Both at room temperature and at -110 °C only one $^{13}$C resonance is observed for the carbonyl carbons: $\delta$ +223 in THF (d of d, $J_{HC} = 10.7$ Hz, $J_{PC} = 5.3$ Hz). There are two possible explanations of the single resonance. A magnetic and electronic degeneracy of the carbonyl carbons could be argued on the basis of the structural data (equal Fe–CO bond lengths) as well as the infrared results (equal force constants). Alternatively, a rapid low-barrier intramolecular site exchange may be operative. Mechanisms for the latter could include the well-known Berry pseudorotation, a trigonal twist of the CO groups relative to the P and H sites, or a movement of the hydride ligand among the three faces of the distorted PFe(CO)$_3$ tetrahedron.

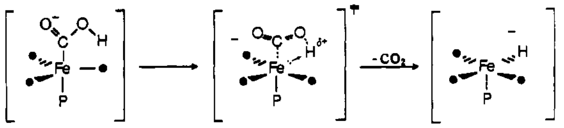
**Attempts To Prepare *trans*-HFe(CO)$_3$P(OPh)$_3^-$ (*trans*-1$^-$).** The above results suggested that we might be able to detect the *trans*-**1** isomeric form by $\nu$(CO) and IR $\nu$(Fe-H) IR values and J$_{PH}$ values in the $^1$H NMR spectra. In fact we have been unable to isomerize *cis*-**1** to *trans*-**1**. No isomerization or decomposition of **1** was observed over a 24-h period in refluxing THF. When **1** was heated to 160 °C in diglyme, substantial decomposition of **1**, yielding HFe(CO)$_4^-$ as the major product, occurred within 1 h. Remaining **1** was of the cis isomeric form. Attempts to exchange P(OPh)$_3$ for poorer acceptor PR$_3$ ligands in *trans*-HFe(CO)$_3$PR$_3^-$ yielded, according to the PR$_3$ ligand, various organometallic products (Fe(CO)$_4$PR$_3$, HFe(CO)$_4^-$, etc.) but little to no HFe(CO)$_3$P(OPh)$_3^-$. When **1** was formed by this method it was of the cis isomeric form. The test of the supposition that deprotonation to the dianion and reprotonation might lead to the trans isomer was also thwarted by hydrolysis of P(OPh)$_3$.

The preparation of the Et$_4$N$^+$ salt of **1** was attempted according to eq 1. The resulting hydride product, however, contained a P(OMe)$_3$ ligand rather than the original P(OPh)$_3$ ligand. Further

$$(PhO)_3PFe(CO)_4 + KOH \xrightarrow{MeOH/Et_4N^+Br^-} Et_4N^+HFe(CO)_3P(OMe)_3^- + CO_2 \quad (1)$$

studies by $\nu$(CO)IR showed Et$_4$N(*cis*-**1**) to be the first-formed product in this synthesis. It subsequently underwent ligand hydrolysis in basic MeOH solution. Phenoxide anion was identified as a product in this reaction. The isolation of pure **1** as its PPN$^+$ salt is attributed to its insolubility in alcoholic KOH solutions, while the Et$_4$N$^+$ salt of **1** is soluble in these solutions and underwent further reaction.

**Comments and Conclusions.** The preparation of these anionic hydrides[13,14] undoubtedly proceeds by nucleophilic attack of hydroxide on the axial CO carbon of the starting materials, Fe(CO)$_4$PR$_3$ (eq 2). Isolated products of nucleophilic addition of



(2)

carbanions (RMgX or RLi as R$^-$ source)[15] or hydride (HBEt$_3^-$ as H$^-$ source)[16] yields trans addition products. For example, Casey et al. have reported the X-ray structures of Et$_4$N$^+$ salts of *trans*-(PhO)$_3$PFe(CO)$_3$CHO$^-$ (**4**) and *trans*-(PhO)$_3$PFe(CO)$_3$C(O)Me$^-$ (**5**).[16] We have prepared **4** as its PPN$^+$ salt and observed its thermal decomposition to a hydride that is identical with **1**, i.e., the cis isomer. We conclude that the stereochemical course involves OH$^-$ attack on the trans CO carbon, generating a metallo carboxylic acid intermediate[17] that follows a decarboxylation path as shown in eq 2. Simple motions of the ligands in the square-pyramid intermediate generate either of the isomeric forms observed.

The failure to permute the cis isomer of **1** into the trans isomer, the fact that **1** might be fluxional as suggested by $^{13}$C NMR and comparison to all other known TBP carbonyl compounds, and the fact that solution structural probes are consistent with the same isomeric form in solution as in the solid state, leads to the fated conclusion that *cis*-**1** is not the kinetic isomer but is rather the choice of thermodynamics. The fact that no other Fe(CO)$_4$PR$_3$ derivative yields *cis*-HFe(CO)$_3$PR$_3^-$ as the thermodynamically stable form suggests a unique electronic character for the P(OPh)$_3$ ligand. Certainly of all the HFe(CO)$_3$PR$_3^-$ derivatives prepared, the P(OPh)$_3$ ligand is electronically the best suited for the equatorial position. Nevertheless, the P(OPh)$_3$ ligand is not anticipated to rival a CO group in $\pi$-accepting ability. Furthermore, we would expect a gradation in electronic/structural effects. That is, the P(OMe)$_3$ derivative might be expected to exist as a mixture of cis/trans isomeric forms. It does not, however. Recently we attempted to reduce the $\pi$-accepting character of P(OPh)$_3$ by preparing the P(O-*o*-tolyl)$_3$ derivative. The spectroscopic data again best fit the cis arrangement for hydride and P donor ligand.[18]

We close with a comment about the formal use of the trigonal-bipyramidal (TBP) geometry and the use of theory[3] derived for orbital overlap appropriate to this geometry. Much of the overlap that *favors* the positioning of $\pi$-acceptors in the equatorial plane is expected to be lost as the coordination sphere moves toward a face-capped tetrahedron. In fact the distortion of the "equatorial" ligands positions them favorably for direct interaction with the hydride ligand. A "direct donation"[19] of hydride electron density to the empty $\pi^*$ orbitals of "equatorial" CO or acceptor orbitals of P(OPh)$_3$ could very well account for the observed favored geometry as well as the very large phosphorus–hydrogen coupling constant.

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**Supplementary Material Available:** Listings of bond distances (Table 1S), bond angles (Table 2S), anisotropic temperature factors (Table 3S), and hydrogen atom coordinates (Table 4S) and a unit cell packing diagram (Figure 1S) (6 pages); a listing of observed and calculated structure factors (Table 5S) (22 pages). Ordering information is given on any current masthead page.

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