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Synthesis and Molecular Structure of a Hydrogen-Bonded Dinuclear Species, $[\{Fe(C_5H_5)(CO)_2PPh\text{-}t\text{-}BuO\}_2H]BPh_4$, and Some Acid–Base Chemistry of This Complex and Related Complexes

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The compounds $[Fe(C_5H_5)(CO)_2PPhRCl]X$ (R = Ph, *t*-Bu, X = several anions) were prepared. Hydrolysis (using Et_3N and H_2O in acetone) gave the dinuclear hydrogen-bridged species $[\{Fe(C_5H_5)(CO)_2(PPhRO)\}_2H]X$. The protonation of these species with HBr(g) gave $[Fe(C_5H_5)(CO)_2PPhROH]Br$ while deprotonation with additional Et_3N gave $Fe(C_5H_5)(CO)_2(PPhRO)$ or, for R = *tert*-butyl only, $[Fe(C_5H_5)(CO)_2PPh\text{-}t\text{-}BuOHNEt_3]^+$. Titration data for aqueous acetone solutions of $[Fe(C_5H_5)(CO)_2(PPhROH)]Br$ and for the dinuclear species suggest that these complexes are acids of moderate strength. The data further suggest that the dinuclear species is substantially dissociated to $[Fe(C_5H_5)(CO)_2(PPhROH)]^+$ and $Fe(C_5H_5)(CO)_2(PPhRO)$ in aqueous acetone. The formation and isolation of the dinuclear complexes are presumably a consequence of the solvent choice in synthesis. A crystal structure study on the complex $[\{Fe(C_5H_5)(CO)_2(PPh\text{-}t\text{-}BuO)\}_2H]BPh_4$ was carried out. Crystal data: monoclinic space group $C2/c$, $Z = 8$, with unit cell parameters $a = 36.71$ (2) Å, $b = 12.991$ (3) Å, $c = 22.67$ (2) Å, $\beta = 102.80$ (4)°. Diffraction data (4992 independent data with $I \geq 2\sigma(I)$) were collected on a Syntex P$\bar{1}$ four-circle automated diffractometer, with use of graphite-monochromated Mo Kα radiation. The structure was solved by direct methods and refined by isotropic and anisotropic least-squares programs to $R_1 = 0.045$. The structure of the cation consists of two $Fe(C_5H_5)(CO)_2(PPh\text{-}t\text{-}BuO)$ groups linked via a hydrogen bond. The O–H–O distance is 2.403 (4) Å, in the range formally designated as "very short", implying that the bond is somewhat stronger than average and likely to be symmetric.

Introduction

Previous workers in our research group have prepared complexes of the general formula $[Fe(C_5H_5)(CO)_2(Phos)]X$ (Phos = primary, secondary, and tertiary phosphines).[1,2] One goal of these syntheses was to provide compounds for further study of reactions that occur at coordinated phosphorus ligands. Earlier studies were directed to the acid–base chemistry of compounds having P–H groups.

This paper describes the synthesis of two further complexes of this general type, having formulas $[Fe(C_5H_5)(CO)_2(PPhRCl)]^+$ (R = Ph, *t*-Bu), isolated as salts of several anions. Our interest in these complexes is again directed toward their reaction chemistry at the ligand site. This paper focuses on hydrolysis of the P–Cl bond of these complexes. These reactions produce compounds with P–OH groups which shown unexpected acid–base behavior, giving isolable dinuclear hydrogen-bridged complexes $[\{Fe(C_5H_5)(CO)_2(PPhRO)\}_2H]X$. A crystal structure study on one of these complexes is detailed in this paper.

Kraihanzel and several coworkers have also been interested in reactions occurring at phosphorus in metal complexes having halophosphine ligands. There are two papers which relate specifically to our work, on solvolyses of $Mo(CO)_5PR_2Cl$[3] and $Mo(CO)_4(PR_2Cl)_2$[4] by several protonic reagents including H_2O. There is a review on reactions at coordinate phosphorus ligands which covers general work in this area up to 1974[5] and a more recent review on metal complexes of phosphinous acids[6] which is related to this work.

Experimental Section

Syntheses of $Fe(C_5H_5)(CO)_2X$ (X = Cl,[7] I[8]), $[Fe(C_5H_5)(CO)_2(THF)]BF_4$,[9] $P(C_6H_5)(t\text{-}C_4H_9)Cl$,[10] and PPh_2OMe[11] were carried out by using methods described in cited references. Other reagents were obtained commercially. Dry solvents were deaerated with a stream of N_2, and general precautions were used to exclude air in reactions and subsequent manipulations.

Melting points were determined with a Thomas-Hoover melting point apparatus in sealed capillaries. Infrared spectra were obtained with a Beckman Acculab-7 spectrometer and NMR spectra were run on a JEOL MH-100 spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Synthesis of $[Fe(C_5H_5)(CO)_2(PPh\text{-}t\text{-}BuCl)]PF_6$. The preparation of this compound was carried out by the method used to prepare many other similar complexes.[1,2] A mixture of $Fe(C_5H_5)(CO)_2Cl$ (10.0 g, 47.2 mmol) and $PPh\text{-}t\text{-}BuCl$ (9.4 g, 47.0 mmol) in 125 mL of benzene was stirred for 3 days at room temperature. The brown solid that formed was filtered out, washed with benzene, and dissolved in water. Addition of excess NH_4PF_6 in water caused immediate precipitation of the PF_6^- salt. This material was purified by crystallization from acetone/H_2O, as yellow crystals: yield 10.1 g (41%); mp 192 °C dec.

Anal. Calcd for $C_{17}H_{19}FeO_2P_2F_6Cl$: C, 39.06; H, 3.64; Fe, 10.68. Found: C, 38.96; H, 3.71; Fe, 10.49. IR (CH_3CN): ν(CO) 2050 s, 2010 s cm^{-1}. ^{1}H NMR (acetone-d_6): δ 7.84 m, C_6H_5; δ 5.72 d (J = 3 Hz), C_5H_5; δ 1.33 d (J = 18 Hz), $t\text{-}C_4H_9$.

The BF_4^- and BPh_4^- salts were prepared in a similar manner substituting 50% aqueous HBF_4 or $NaBPh_4$ for NH_4PF_6 at the metathesis step. Isolated yields were 28% and 45%, respectively. Identity and purity of these products were confirmed by ν(CO) and proton NMR data.

Synthesis of $[\{Fe(C_5H_5)(CO)_2(PPh\text{-}t\text{-}BuO)\}_2H]PF_6$. A 5.0 g (9.6 mmol) sample of $[Fe(C_5H_5)(CO)_2(PPh\text{-}t\text{-}BuCl)]PF_6$ was dissolved in 50 mL of acetone, and 1.5 mL of H_2O and 1.5 g (14.9 mmol) of $(C_2H_5)_3N$ were added. This solution was refluxed for 5 h. The volume of solution was reduced to 5 mL; filtration removed a white solid, presumed to be a $[(C_2H_5)_3NH]^+$ salt. Water (25 mL) was added to the filtrate, precipitating a yellow solid. This material was filtered and dried under vacuum: yield 2.8 g (68%); mp 211–212 °C.

Anal. Calcd for $C_{34}H_{41}P_3O_6Fe_2F_6$: C, 47.35; H, 4.57; Fe, 12.95; P, 10.77. Found: C, 47.34; H, 4.50; Fe, 11.55; P, 11.83. IR (CH_2Cl_2): ν(CO) 2030 vs, 1990 vs cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.59 m, C_6H_5; δ 5.5–7.5 br s, concentration dependent, P–OH; δ 5.46 s, C_5H_5; δ 1.21 d (J = 16 Hz), $t\text{-}C_4H_9$.

The BF_4^- (mp 148–154 °C) and BPh_4^- (mp 145–149 °C) salts of this cation were also prepared in similar reactions of precursors

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containing these anions. In the preparation of the BPh_4^- salt it is desirable to use Bu_3N rather than Et_3N; otherwise difficulties are encountered in purification owing to similar solubilities of the product and $[NEt_3H]BPh_4$.

The PBh_4^- salt, used in the crystal structure study, was also analyzed. Anal. Calcd for $C_{58}H_{59}O_6P_2Fe_2B$: C, 67.20; H, 5.75; Fe, 10.78; P, 5.98. Found: C, 67.39; H, 5.95; Fe, 10.73; P, 5.84. Infrared (ν(CO)) and proton NMR data for the BF_4^- and BPh_4^- salts were the same as for the PF_6^- salt except that the NMR spectrum showed additional intensity in the phenyl proton region associated with the protons of the BPh_4^- anion.

Synthesis of [Fe(C_5H_5)(CO)$_2$(PPh-*t*-BuOH)]Br. A sample of [{Fe(C_5H_5)(CO)$_2$(PPh-*t*-BuO)}$_2$H]PF_6 (0.5 g, 0.58 mmol) was dissolved in 25 mL of CH_2Cl_2; HBr(g) was slowly bubbled through the solution for 15 min. Ether (40 mL) was added, and the solution was filtered. Cooling the filtrate caused precipitation of the yellow solid product: 0.33 g (65%); mp 169–171 °C.

Anal. Calcd for $C_{17}H_{20}FeO_3PBr$: C, 46.50; H, 4.60; Fe, 12.72. Found: C, 45.50; H, 4.84; Fe, 11.93. IR (CH_2Cl_2): ν(OH) 2643 m, br; ν(CO) 2050 vs, 2003 vs cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.1 br s, OH; δ 7.50 m, C_6H_5; δ 5.36 d (J = 4 Hz), C_5H_5; δ 1.17 d (J = 17 Hz), *t*-C_4H_9.

Synthesis of [Fe(C_5H_5)(CO)$_2$(PPh-*t*-BuOHNEt$_3$)]PF_6 and Fe(C_5H_5)(CO)$_2$(PPh-*t*-BuO). A 2.0-g (2.3-mmol) sample of [{Fe(C_5H_5)(CO)$_2$(PPh-*t*-BuO)}$_2$H]PF_6 was dissolved in 50 mL of $CHCl_3$, and 0.24 g (2.4 mmol) of N(C_2H_5)$_3$ was added. Diethyl ether (25 mL) was added immediately and the solution cooled, to give yellow crystals of [Fe(C_5H_5)(CO)$_2$(PPh-*t*-BuOHNEt$_3$)]PF_6: 1.25 g (89%); mp 113–123 °C (evacuated capillary, some decomposition apparent; this result appears reproducible).

Anal. Calcd for $C_{23}H_{35}F_6FeNO_3P_2$: C, 45.63; H, 5.84; N, 2.31. Found: C, 45.56; H, 5.92; N, 2.23. IR (CH_2Cl_2): ν(CO) 2020 s, 1990 s; ν(NH···O) 2400 m, vbr cm^{-1}. ^1H NMR (acetone-d_6): δ 7.52 m, C_6H_5; δ 5.19 s, C_5H_5; δ 3.9–4.6 br s, concentration dependent, OH; δ 3.39 q (J = 7 Hz), NCH_2; δ 1.43 t (J = 7 Hz), NCH_2CH_3; δ 1.11 d (J = 15 Hz), *t*-C_4H_9.

The filtrate from the above procedure was treated with more ether and cooled, giving a second crop of crystals. Visual inspection indicated crystals of two compounds, one which appeared to be the product identified above. Crystals of the second substance were separated mechanically, and IR and NMR data were obtained. These data supported the formulation of this compound as Fe(C_5H_5)(CO)$_2$(PPh-*t*-BuO). Good analytical data could not be obtained.

IR (CH_2Cl_2): ν(CO) 2010, 1975 vs cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.17 m, C_6H_5; δ 4.88 s, C_5H_5; δ 1.10 d (J = 15 Hz), *t*-C_4H_9.

Synthesis of [Fe(C_5H_5)(CO)$_2$(PPh$_2$Cl)]X. These complexes could not be obtained by the direct reaction of PPh_2Cl and Fe(C_5H_5)(CO)$_2$Cl. We were first successful in making this compound in a two-step process, initially forming [Fe(C_5H_5)(CO)$_2$(PPh$_2$OMe)]PF_6 and then treating this complex with HCl. Later we found that the complex could be prepared more easily from [Fe(C_5H_5)(CO)$_2$(THF)]BF_4. Both syntheses are described below.

Method 1, via [Fe(C_5H_5)(CO)$_2$(PPh$_2$OMe)]PF_6. Samples of Fe(C_5H_5)(CO)$_2$I (1.44 g, 6.8 mmol) and PPh_2OMe (1.47 g, 6.8 mmol) were stirred in 30 mL of benzene for 7.5 h in the dark. A yellow precipitate, [Fe(C_5H_5)(CO)$_2$(PPh$_2$OMe)]Cl, formed. This was separated by filtration and dried. For the purpose of analysis this compound was converted to a PF_6^- salt. It was dissolved in warm water, and an excess of NH_4PF_6 (saturated aqueous solution) was added to precipitate the PF_6^- salt. This material was separated by filtration. It was recrystallized from acetone/H_2O: 2.03 g (55%); mp 174–176 °C.

Anal. Calcd for $C_{20}H_{18}F_6FeP_2O_3$: C, 44.64; H, 3.37; Fe, 10.38. Found: C, 44.78; H, 3.09; Fe, 10.25. IR (CH_3CN): ν(CO) 2050, 2010 cm^{-1}. ^1H NMR (acetone-d_6): δ 7.71 m, C_6H_5; δ 5.56 d (J = 2 Hz), C_5H_5; δ 3.67 d (J = 14 Hz), OCH_3.

A sample of [Fe(C_5H_5)(CO)$_2$(PPh$_2$OMe)]Cl (1.50 g, 3.07 mmol) was dissolved in 60 mL of $CHCl_3$, and HCl(g), was bubbled through the solution for 1.5 h. The solution was then refluxed for 4 h. Evaporation in vacuo gave an oil. This was dissolved in ethanol, and 0.5 g of NH_4PF_6 was added. The solution was again evaporated and the residue extracted with $CHCl_3$, separating the product from insoluble NH_4Cl and NH_4PF_6. The $CHCl_3$ was removed in vacuo. Addition of acetone dissolved part of the product. The insoluble part was separated and characterized as [Fe(C_5H_5)(CO)$_2$(PPh$_2$Cl)]Cl: 0.33 g (27%); mp 204–207 °C.

Anal. Calcd for $C_{19}H_{15}FeO_2PCl_2$: C, 52.69; H, 3.50; Fe, 12.90. Found: C, 53.00; H, 3.81; Fe, 13.05. IR (CH_3CN): ν(CO) 2040, 1995 cm^{-1}. NMR ($CDCl_3$): δ 7.52 m, C_6H_5; δ 5.48 d (J = 5 Hz), C_5H_5.

Partial evaporation of the acetone extract from above and addition of ether gave 0.35 g (22%) of yellow plates, identified as [Fe(C_5H_5)(CO)$_2$PPh$_2$Cl]PF_6. Identification was based on infrared (ν(CO) and ν(P–F)) evidence.

Method 2, from [Fe(C_5H_5)(CO)$_2$(THF)]BF_4. The compounds [Fe(C_5H_5)(CO)$_2$(THF)]BF_4 (5.0 g, 15 mmol) and PPh_2Cl (3.30 g, 15 mmol) were dissolved in 100 mL of CH_2Cl_2, and the solution was stirred for 4 h. After the solution was filtered, its volume was reduced to 50 mL by evaporation in vacuo and 10 mL of ether was added. Cooling this mixture produced large yellow crystals mixed with a small amount of unidentified product. Recrystallization of the product was carried out with use of CH_2Cl_2/ether, giving 4.13 g (57%) of the product [Fe(C_5H_5)(CO)$_2$(PPh$_2$Cl)]BF_4, mp 154–158 °C. IR (CH_2Cl_2): ν(CO) 2068, 2028 cm^{-1}. ^1H NMR (acetone-d_6): δ 7.62 m, C_6H_5; δ 5.71 d (J = 2 Hz), C_5H_5.

Synthesis of [{Fe(C_5H_2)(CO)$_2$(PPh$_2$O)}$_2$H]BF_4. A sample of [Fe(C_5H_5)(CO)$_2$(PPh$_2$Cl)]BF_4 (10.0 g, 20.6 mmol) was dissolved in 100 mL of acetone; then 3.1 g (31 mmol) of N(C_2H_5)$_3$ and 6 mL of H_2O were added. The mixture was stirred at room temperature for 4.5 h. Additional water (100 mL) was added, and the solution was filtered. Cooling the filtrate precipitated the yellow product: 5.5 g (63%); mp 158–161 °C.

Anal. Calcd for $C_{38}H_{31}BF_4FeP_2O_6$: C, 54.00; H, 3.70; Fe, 13.22. Found: C, 54.22; H, 3.79; Fe, 13.01. IR (CH_2Cl_2): ν(CO) 2040, 1996 cm^{-1}. ^1H NMR (acetone-d_6): δ 7.59 m, C_6H_5; δ 5.46 s, C_5H_5; δ 4.5–5.5 broad, concentration dependent, OH.

Synthesis of Fe(C_5H_5)(CO)$_2$(PPh$_2$O). Solid [{Fe(C_5H_5)(CO)$_2$PPh$_2$O}$_2$H]BF_4 (1.96 g, 2.3 mmol) was dissolved in 25 mL of nitromethane, and 0.42 g (4.2 mmol) of N(C_2H_5)$_3$ was added. After several minutes of stirring, 10 mL of ether was added to the solution. Cooling led to precipitation of the yellow crystalline product: 0.66 g (38%); mp 208–210 °C.

Anal. Calcd for $C_{19}h_{15}FeO_3P$: C, 60.26; H, 4.00; Fe, 14.75 (mol wt 378). Found: C, 60.44; H, 4.07; Fe, 15.05 (mol wt (osmometric in $CHCl_3$) 356). IR (CH_2Cl_2): ν(CO) 2009, 1974 vs; ν(PO) 12.27 m cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.24, 7.53 m, C_6H_5; δ 4.93 d (J = 4 Hz), C_5H_5.

Synthesis of [Fe(C_5H_5)(CO)$_2$(PPh$_2$OH)]Br. Gaseous HBr was slowly bubbled into a solution of Fe(C_5H_5)(CO)$_2$(PPh$_2$O) (1.77 g, 4.03 mmol) in 40 mL of CH_2Cl_2. The reaction could be followed by monitoring the infrared spectrum (ν(CO)). After ~20 min, addition of HBr was stopped. Ether (25 mL) was added, and upon cooling yellow crystals precipitated from solution. This compound was separated by filtration; 1.8 g (84%). The compound is air stable and not particularly hygroscopic, but it is light sensitive. It is soluble in alcohols but noticeably less soluble in solvents other than other ionic compounds encountered in this work.

Anal. Calcd for $C_{14}H_{16}BrFeO_3P$: C, 49.71; H, 3.52; Fe, 12.17. Found: C, 49.71; H, 3.57; Fe, 12.03. IR (CH_2Cl_2): ν(CO) 2053, 2003 vs; ν(OH) 2520 m, br cm^{-1}. ^1H NMR (Me_2SO-d_6): δ 7.52 m, C_6H_5; δ 6.3 br s, OH; δ 5.50 s, C_5H_5.

Acid–Base Titrations

Titrations of [{Fe(C_5H_5)(CO)$_2$(PPh-*t*-BuO)}$_2$H]PF_6, [{Fe(C_5H_5)(CO)$_2$(PPh$_2$O)}$_2$H]BF_4, and [Fe(C_5H_5)(CO)$_2$(PPh$_2$OH)]Br vs. standard base were carried out. The complexes were dissolved in 60–80% aqueous acetone and titrated with ~0.10 M aqueous NaOH. A Corning Model 7 pH meter with a glass electrode, calibrated at pH 4.0 and 9.93 with standard buffer solutions, was used to follow the reaction and detect the end point.

Titration of the dinuclear complexes was undertaken initially to ascertain the stoichiometry of these complexes, before the identity of these substances had been fully established. The dimeric formulas of the complexes were verified by the determination that 1 equiv of base was required to deprotonate each complex as formulated. Representative data are listed below (Table I).

There are several qualitative features of the titration data which stand out. First, pH values for solutions of the three complexes at various stages of the titration (initial pH, pH at half-neutralization point, pH at end point) indicate that all these species are moderately strong acids. Calculations from these data suggest K_a values in the 10^{-2}–10^{-3} range with the values for [{Fe(C_5H_5)(CO)$_2$(PPh-*t*-

Table I. Data on Stoichiometry of Acid-Base Titration[a]

compd	mmol of compd	mL of 0.1007 M NaOH	mmol of NaOH	mmol of compd/ mmol of NaOH
$[Fe(C_5H_5)(CO)_2\text{-}(PPh_2OH)]Br$	0.984	9.68	0.965	1.02
$[Fe(C_5H_5)(CO)_2\text{-}(PPh_2O)_2H]BF_4$	0.399	3.85	0.391	1.03
$[Fe(C_5H_5)(CO)_2\text{-}(PPh\text{-}t\text{-}BuO)_2H]PF_6$	0.452	4.40	0.443	1.02

[a] See text for details. A ratio of 1.0 for mmol of compound/mmol of NaOH establishes the defined stoichiometry.

Table II. Crystal Data for X-ray Diffraction Study

chem formula	$C_{58}H_{59}O_6P_2Fe_2B$
crystallizn method	precipitation at 0 °C with H_2O in acetone
cryst color and shape	irregular yellow plate cut from larger crystal
cryst face indices (dist from centroid, mm)	100 (0.015), 012 (0.025), 423 (0.225), $23\bar{4}$ (0.275), 0.052 (0.30)
linear abs coeff, μ, cm^{-1}	6.080
estd variation of intens	5%
cell parameters (error)	
a, Å	36.71 (2)
b, Å	12.991 (3)
c, Å	22.67 (2)
β, deg	102.80 (4)
cell vol (error), $Å^3$	10545 (9)
no. of reflctns used in cell parameter determination	15
Laue symmetry	monoclinic
space group	$C2/c$
d_{calcd}, g/cm^3	1.306
d_{obsd}, g/cm^3	1.309 ± 0.003 (flotation in C_6H_5Cl/C_6H_5Br)
no. of molecules/unit cell, Z	8

$BuO)\}_2H]BF_4$ being smaller than the values for the diphenylphosphinato complexes. It is noted that phosphinic acids R_2POOH have K_a values in the range 10^{-2}–10^{-4} and that alkylphosphinic acids are less acidic than arylphosphinic acids.[12] A second observation is that in the titration of $[Fe(C_5H_5)(CO)_2PPh_2OH]Br$ there is no indication of an equivalence point after 0.5 equiv of base has been added. Moreover the titration curves for this compound and for the dimeric species $[\{Fe(C_5H_5)(CO)_2(PPh_2O)\}_2H]BF_4$ are qualitatively and quantitatively very similar. It may be that this dimeric species is substantially dissociated in solution; i.e., the equilibrium

$$[\{Fe(C_5H_5)(CO)_2(PPh_2O)\}_2H]^+ \rightleftharpoons [Fe(C_5H_5)(CO)_2(PPh_2OH)]^+ + Fe(C_5H_5)(CO)_2(PPh_2O)$$

favors the products on the right, in this solvent system and under the defined conditions.

Single-Crystal X-ray Diffraction Study on $[\{Fe(C_5H_5)(CO)_2(PPh\text{-}t\text{-}BuO)\}_2H]BPh_4$

Crystals of this compound were grown by slow addition of water to an acetone solution of the compound at 0 °C. The sample used, cut from a platelet of irregular shape, was mounted on a glass fiber. The crystal was accurately centered on a Syntex P$\bar{1}$ four-circle automated diffractometer. With use of Mo Kα radiation, preliminary data were collected on 15 well-defined diffraction maxima. Preliminary Syntex routines indicated a monoclinic lattice (space group $C2/c$ or Cc; $C2/c$ was eventually chosen and led to a satisfactory solution). This choice was verified by partial rotation photographic projections along the reciprocal axes.[13] Lattice dimensions were a = 36.71 (2) Å, b = 12.991 (3) Å, c = 22.67 (2) Å, $\alpha = \gamma = 90°$, β = 102.80 (4)°, and V = 10545 (9) $Å^3$. For Z = 8 this gives a calculated density of 1.306 g cm^{-3}; density determined by flotation in C_6H_5Cl/C_6H_5Br mixtures is 1.309 (3) g cm^{-3}, in good agreement with the calculated value. Crystal data are presented in Table II.

Table III. Data Collection and Reduction of the X-ray Diffraction Data and Solution and Refinement of Structure

temp, °C	20 ± 2
radiation (graphite monochromated)	Mo Kα
width of ω scan at half-height	0.18
takeoff angle, deg	4
scan speed (T_r), deg/min	2–24
scan range, deg	1.0
bkgd/scan time ratio (B_r)	0.67
scan method	ω
no./freq of std reflctns	2/50
intens variations of std reflctns	2% decrease
2θ limits, deg	3–45
cutoff of obsd data	$2\sigma(I)$
no. of total data	7437
no. of unique data	7197
no. of nonzero data	4992
technique of soln	direct method[15]
Wilson-Debye statistics	centric
method of refinement	block-diagonal least-squares matrix[17,18]
anisotropic convergence	$R_1 = 0.045$; $R_2 = 0.052$
error of fit	1.22
data/parameters	4992/622
anomalous dispersion cor[17]	
$\Delta f'$ (real)	0.301 (Fe); 0.090 (P)
$\Delta f''$ (imaginary)	0.845 (Fe); 0.095 (P)

Table IV. Selected Bond Lengths and Angles

A. Bond Lengths, Å			
Fe(1)–P(1)	2.264 (1)	Fe(2)–P(2)	2.241 (1)
Fe(1)–C(1)	1.764 (5)	Fe(2)–C(3)	1.752 (5)
Fe(1)–C(2)	1.772 (5)	Fe(2)–C(4)	1.756 (6)
P(1)–O(1)	1.546 (3)	P(2)–O(2)	1.565 (3)
P(1)–C(5)	1.873 (5)	P(2)–C(9)	1.876 (4)
P(1)–C(1A)	1.823 (4)	P(2)–C(1B)	1.820 (4)
C(1)–O(3)	1.144 (5)	C(3)–O(5)	1.139 (6)
C(2)–O(4)	1.136 (5)	C(4)–O(6)	1.136 (6)
B. Bond Angles, Deg			
P(1)–Fe(1)–C(1)	95.7 (2)	P(2)–Fe(2)–C(3)	96.4 (2)
P(1)–Fe(1)–C(2)	91.1 (2)	P(2)–Fe(2)–C(4)	91.1 (2)
C(1)–Fe(1)–C(2)	96.5 (2)	C(3)–Fe(2)–C(4)	97.7 (3)
Fe(1)–P(1)–O(1)	111.0 (1)	Fe(2)–P(2)–O(2)	111.1 (1)
Fe(1)–P(1)–C(5)	118.7 (1)	Fe(2)–P(2)–C(9)	120.3 (1)
Fe(1)–P(1)–C(1A)	113.0 (1)	Fe(2)–P(2)–C(1B)	111.5 (1)
O(1)–P(1)–C(5)	105.0 (2)	O(2)–P(2)–C(9)	102.4 (2)
O(1)–P(1)–C(1A)	105.2 (2)	O(2)–P(2)–C(1B)	106.0 (2)
C(5)–P(1)–C(1A)	102.6 (2)	C(9)–P(2)–C(1B)	104.2 (2)
Fe(1)–C(1)–O(3)	177.0 (4)	Fe(2)–C(3)–O(5)	174.4 (5)
Fe(1)–C(2)–O(4)	175.0 (4)	Fe(2)–C(4)–O(6)	175.5 (5)

Diffraction data were collected with use of the ω-scan method. Absorption corrections were deemed unnecessary since two standard peaks, monitored after every 50 reflections, showed no significant deviation in intensity (±2%). A total of 7437 reflections were collected for which $I \geq 2\sigma(I)$, data reduction yielding 4992 independent reflections which were used in the eventual solution of the structure.[14]

The structure was solved by direct methods[15] which first yielded

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(12) Crofts, P. C.; Kosolapoff, G. M. *J. Am. Chem. Soc.* **1953**, *75*, 3379–3383.

(13) Sparks, R. A.;, et al. "P$\bar{1}$ Autodiffractometer Operations Manual"; Syntex Analytical Instruments Division: Cuperatino, CA, 1970.

(14) The crystallographic programs used were written by J. C. Calabrese of this department. Plots were made with use of the ORTEP program (C. K. Johnson).

(15) MULTAN: Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368–376.

(16) The integrated intensity (I) was calculated according to the expression $I = [S - (B_1 + B_2)/B_r]T_r$ where S is the scan count and B_1 and B_2 are the background counts. B_r is the ratio of the background time to scan time, and T_r is the ω-scan rate in deg/min. The standard deviation of I was calculated as $\sigma(I) = T_r[S + (B_1 + B_2)/B_r^2 + (pI)^2]^{1/2}$.

(17) All least-squares refinements were based on the minimization of $\sum w_i||F_o| - |F_c||^2$ with the individual weights $w_i = 1/(\sigma(F_o))^2$ Atomic scattering factors used for all nonhydrogen atoms are from: Hanson, H. P.; Herman, F.; Lea, J. D.; Skillman, S. *Acta Crystallogr.* **1964**, *17*, 1040–1044. Those for the hydrogen atoms are from: Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–3187.

Table V. Atomic Coordinates for $[\{Fe(C_5H_5)(CO)_2PPh\text{-}t\text{-}BuO\}_2H]BPh_4$[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Fe(1)	3253.8 (2)	1691.0 (5)	4391.2 (3)	C(1H)	4295 (1)	−3395 (4)	5560 (2)
Fe(2)	4229.3 (2)	−1871.0 (5)	5839.1 (3)	C(2H)	4262 (1)	−2723 (4)	5067 (2)
P(1)	2986.3 (3)	116.8 (8)	4364.4 (5)	C(3H)	3913 (1)	−2231 (4)	4980 (2)
P(2)	3885.9 (3)	−757.6 (8)	6241.4 (5)	C(4H)	3728 (1)	−2600 (4)	5418 (2)
O(1)	3199 (1)	−571 (2)	4884 (1)	C(5H)	3962 (2)	−3307 (4)	5781 (2)
O(2)	3662 (1)	−15 (2)	5748 (1)	H(6)	1965	277	3872
O(3)	2598 (1)	2775 (3)	3726 (2)	H(6)	2263	1026	3725
O(4)	3149 (1)	2110 (3)	5601 (2)	H(6)	2256	−88	3502
O(5)	4785 (1)	−2346 (5)	6920 (2)	H(7)	2151	−1146	4591
O(6)	4615 (1)	−229 (4)	5369 (2)	H(7)	2573	−1278	4932
C(1)	2850 (1)	2326 (4)	3988 (2)	H(7)	2446	−1529	4254
C(2)	3176 (1)	1924 (3)	5123 (2)	H(8)	2160	673	4947
C(3)	4560 (2)	−2121 (5)	6509 (2)	H(8)	2462	1417	4840
C(4)	4466 (1)	−855 (4)	5576 (2)	H(8)	2582	532	5293
C(5)	2484 (1)	28 (3)	4410 (2)	H(10)	4512	1251	6950
C(6)	2215 (1)	335 (4)	3823 (2)	H(10)	4588	359	6551
C(7)	2405 (2)	−1083 (4)	4566 (3)	H(10)	4282	1140	6276
C(8)	2414 (1)	719 (4)	4925 (2)	H(11)	3920	1324	7296
C(9)	4117 (1)	159 (3)	6849 (2)	H(11)	3694	1207	6633
C(10)	4398 (2)	793 (5)	6636 (3)	H(11)	3633	437	7124
C(11)	3812 (2)	847 (4)	6988 (2)	H(12)	4415	78	7729
C(12)	4301 (2)	−409 (5)	7435 (2)	H(12)	4119	−813	7565
C(1A)	2994 (1)	−592 (3)	3673 (2)	H(12)	4493	−845	7357
C(2A)	2912 (1)	−136 (4)	3099 (2)	H(2A)	2853	578	3061
C(3A)	2919 (1)	−714 (4)	2592 (2)	H(3A)	2866	−396	2205
C(4A)	3002 (1)	−1746 (4)	2639 (2)	H(4A)	3006	−2139	2286
C(5A)	3079 (1)	−2214 (4)	3198 (2)	H(5A)	3135	−2931	3234
C(6A)	3076 (1)	−1633 (3)	3714 (2)	H(6A)	3132	−1959	4100
C(1B)	3539 (1)	−1418 (3)	6565 (2)	H(2B)	3087	−622	6107
C(2B)	3154 (1)	−1158 (3)	6394 (2)	H(3B)	2644	−1479	6519
C(3B)	2900 (1)	−1674 (4)	6636 (2)	H(4B)	2825	−2809	7206
C(4B)	3006 (2)	−2453 (4)	7041 (3)	H(5B)	3453	−3262	7504
C(5B)	3379 (2)	−2727 (4)	7215 (2)	H(6B)	3894	−2442	7077
C(6B)	3639 (1)	−2232 (4)	6970 (2)	H(2C)	3706	−6447	7256
B	4146 (1)	−5520 (4)	8285 (2)	H(3C)	3772	−6648	6267
C(1C)	4161 (1)	−5548 (3)	7561 (2)	H(4C)	4274	−5910	5957
C(2C)	3912 (1)	−6126 (4)	7136 (2)	H(5C)	4701	−4943	6636
C(3C)	3952 (2)	−6253 (4)	6542 (2)	H(6C)	4630	−4692	7617
C(4C)	4245 (2)	−5815 (4)	6361 (2)	H(2D)	3425	−5027	7564
C(5C)	4494 (1)	−5250 (4)	6758 (2)	H(3D)	2855	−4718	7805
C(6C)	4453 (1)	−5105 (4)	7351 (2)	H(4D)	2778	−4955	8791
C(1D)	3720 (1)	−5412 (3)	8402 (2)	H(5D)	3290	−5488	9530
C(2D)	3404 (1)	−5114 (3)	7971 (2)	H(6D)	3864	−5760	9300
C(3D)	3060 (1)	−4935 (4)	8114 (2)	H(2E)	4873	−6216	8729
C(4D)	3013 (1)	−5073 (4)	8695 (2)	H(3E)	5128	−7807	9036
C(5D)	3316 (1)	−5382 (4)	9127 (2)	H(4E)	4750	−9247	9004
C(6D)	3660 (1)	−5546 (3)	8987 (2)	H(5E)	4107	−9069	8674
C(1E)	4327 (1)	−6633 (3)	8537 (2)	H(6E)	3846	−7470	8396
C(2E)	4711 (1)	−6788 (4)	8724 (2)	H(2F)	4226	−3457	7991
C(3E)	4864 (1)	−7747 (5)	8901 (2)	H(3F)	4463	−2026	8544
C(4E)	4643 (2)	−8594 (4)	8884 (2)	H(4F)	4762	−2178	9560
C(5E)	4267 (2)	−8486 (4)	8693 (2)	H(5F)	4801	−3796	10012
C(6E)	4111 (1)	−7526 (3)	8525 (2)	H(6F)	4567	−5229	9459
C(1F)	4363 (1)	−4533 (3)	8651 (2)	H(1G)	3509	3215	3725
C(2F)	4344 (1)	−3542 (3)	8406 (2)	H(2G)	3478	1395	3330
C(3F)	4486 (1)	−2681 (4)	8734 (3)	H(3G)	3759	237	4214
C(4F)	4660 (1)	−2766 (4)	9331 (3)	H(4G)	3934	1349	5142
C(5F)	4684 (1)	−3723 (4)	9596 (2)	H(5G)	3790	3179	4831
C(6F)	4542 (1)	−4577 (4)	9265 (2)	H(1H)	4502	−3829	5722
C(1G)	3592 (1)	2620 (4)	3961 (3)	H(2H)	4444	−2619	4832
C(2G)	3575 (1)	1603 (5)	3737 (3)	H(3H)	3818	−1733	4676
C(3G)	3728 (2)	961 (4)	4228 (3)	H(4H)	3486	−2399	5458
C(4G)	3828 (1)	1579 (5)	4742 (3)	H(5H)	3909	−3670	6116
C(5G)	3746 (1)	2600 (4)	4569 (3)				

[a] $B_{iso} = 6.0$ Å^2 for all hydrogens.

the positions of the two iron and two phosphorus atoms. Application of Fourier techniques then yielded the positions of all nonhydrogen atoms. Idealized hydrogen atoms (with the exception of the single bridging hydrogen) were included as fixed atom contributions at this point with d(C–H) = 0.95 Å and bond angles of 120 or 109.5°, the hydrogen atoms being placed in a staggered configuration. After several cycles of isotropic refinement, the final refinement was carried out anisotropically, for all nonhydrogen atoms, with use of the block-diagonalized-matrix least-squares program,[14] to values of R_1 = 0.045 and R_2 = 0.052.

Further details specific to the collection and reduction of data and to the solution and final refinement of the structure are provided in Table III. Selected bond distances and angles are given in Table

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(18) (a) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. (b) $R_2 = [\sum w_i||F_o| - |F_c||^2/\sum w_i|F_o|^2]^{1/2}$. (c) The standard deviation of an observation of unit weight is defined as $[\sum w_i||F_o| - |F_c||^2/(m - n)]^{1/2}$, where m is the number of observations and n is the number of parameters fitted to the data set.

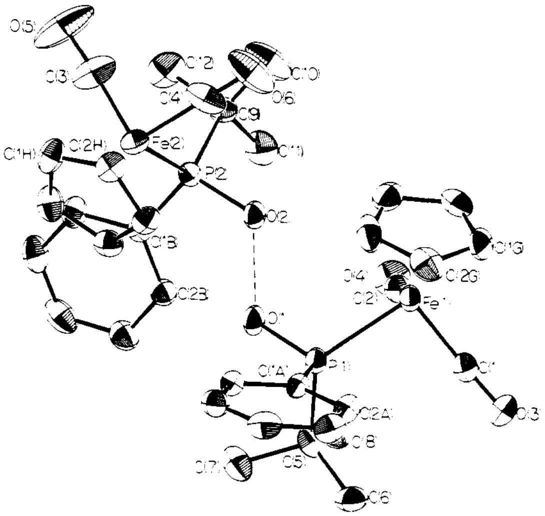

Figure 1. Molecular structure of the cation of [{Fe(C_5H_5)(CO)$_2$PPh-*t*-BuO}$_2$H]BPh$_4$. Atoms are shown with 30% probability ellipsoids; hydrogens have been omitted.

IV, and final positional and thermal parameters are given in Tables V and VI. Observed and calculated structure factors are available in the supplementary material for this paper.

Figure 1 presents one perspective of the molecular cation, emphasizing the hydrogen-bond linkage between halves of this species.

Discussion

The complex [Fe(C_5H_5)(CO)$_2$(PPh-*t*-BuCl)]$^+$ was prepared by displacement of chloride ion in Fe(C_5H_5)(CO)$_2$Cl by the designated phosphorus ligand. Metathesis of the chloride salt provided salts of this cation with several anions. It was not possible to prepare the analogous complex of PPh$_2$Cl by this route, but this complex was obtained by two reactions: (1) the reaction of [Fe(C_5H_5)(CO)$_2$(PPh$_2$OMe)]$^+$ with HCl and (2) the displacement of THF from [Fe(C_5H_5)(CO)$_2$(THF)]BF$_4$ using PPh$_2$Cl. The latter route is the easier of the two.

Hydrolyses of [Fe(C_5H_5)(CO)$_2$(PPh-*t*-BuCl)]X (X = PF$_6$, BF$_4$, BPh$_4$) and [Fe(C_5H_5)(CO)$_2$(PPh$_2$Cl)]PF$_6$ were carried out in acetone in the presence of triethylamine. The conditions chosen are similar to those used in previously studied hydrolyses of Mo(CO)$_5$PR$_2$Cl (R = Ph, Me)[3] and Mo(CO)$_4$(PPh$_2$Cl)$_2$.[4] However acetone had to be used as a solvent instead of THF because of the insolubility of the reactants in THF, and with the complexes of PPh-*t*-BuCl the reaction was slow at room temperature so the solution had to be heated. The products isolated are the hydrogen-bridged dinuclear species [{Fe(C_5H_5)(CO)$_2$(PPhRO)}$_2$H]X (eq 1). These results

$$2[\mathrm{Fe(C_5H_5)(CO)_2(PPhRCl)}]^+ + 2\mathrm{H_2O} + 3\mathrm{NEt_3} \rightarrow [\{\mathrm{Fe(C_5H_5)(CO)_2(PPhRO)}\}_2\mathrm{H}]^+ + 3\mathrm{NEt_3H}^+ + 2\mathrm{Cl}^- \quad (1)$$

contrast with the results from hydrolyses of the Mo(CO)$_5$(PR$_2$Cl) compounds (R = Ph, Me), from which the compounds [Mo(CO)$_5$PPh$_2$O]NEt$_3$H and Mo(CO)$_5$(PMe$_2$OH) were isolated. It bears a closer resemblance to the formation of [Mo(CO)$_4${(PPh$_2$O)$_2$}H]NEt$_3$H from the hydrolysis of Mo(CO)$_4$(PPh$_2$Cl)$_2$. That compound was characterized as having an intramolecular hydrogen bond, the hydrogen linking the oxygens of cis PPh$_2$O groups. Many complexes having similar structural units are also known.[6]

Table VI. Thermal Parameters of [{Fe(C_5H_5)(CO)$_2$PPh-*t*-BuO}$_2$H]BPh$_4$

atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe(1)	7.0 (1)	41.7 (4)	22.7 (1)	0.8 (1)	3.2 (1)	5.9 (2)
Fe(2)	6.8 (1)	67.5 (5)	12.8 (1)	1.3 (1)	1.5 (1)	−3.3 (2)
P(1)	7.7 (1)	40.4 (7)	15.8 (2)	0.7 (2)	1.8 (1)	3.1 (4)
P(2)	6.6 (1)	46.9 (7)	12.6 (2)	−1.1 (2)	2.0 (1)	−0.3 (3)
O(1)	12 (1)	46 (2)	16 (1)	0 (1)	0 (1)	6 (1)
O(2)	9 (1)	48 (2)	17 (1)	0 (1)	2 (1)	7 (1)
O(3)	10 (1)	82 (3)	41 (1)	6 (1)	−1 (1)	19 (1)
O(4)	14 (1)	105 (3)	26 (1)	3 (1)	4 (1)	−15 (1)
O(5)	19 (1)	304 (6)	25 (1)	44 (1)	−9 (1)	−23 (2)
O(6)	21 (1)	149 (4)	43 (1)	−31 (1)	19 (1)	−27 (2)
C(1)	9 (1)	58 (3)	26 (1)	−1 (1)	4 (1)	6 (2)
C(2)	8 (1)	58 (3)	24 (1)	1 (1)	3 (1)	−3 (2)
C(3)	11 (1)	152 (5)	22 (1)	16 (1)	1 (1)	−18 (2)
C(4)	10 (1)	107 (4)	28 (1)	−13 (1)	8 (1)	−23 (2)
C(5)	9 (1)	52 (3)	20 (1)	−4 (1)	5 (1)	−4 (2)
C(6)	6 (1)	101 (4)	33 (1)	−1 (1)	2 (1)	9 (2)
C(7)	13 (1)	71 (4)	38 (1)	−6 (1)	9 (1)	−2 (2)
C(8)	11 (1)	78 (4)	32 (1)	−4 (1)	9 (1)	−7 (2)
C(9)	8 (1)	66 (3)	17 (1)	−2 (1)	1 (1)	−8 (2)
C(10)	18 (1)	138 (5)	33 (1)	−27 (1)	10 (1)	−36 (2)
C(11)	14 (1)	78 (4)	24 (1)	−2 (1)	4 (1)	−15 (2)
C(12)	15 (1)	109 (5)	22 (1)	5 (1)	−1 (1)	−18 (2)
C(1A)	6 (1)	48 (3)	16 (1)	3 (1)	2 (1)	4 (1)
C(2A)	8 (1)	68 (3)	18 (1)	5 (1)	4 (1)	5 (2)
C(3A)	8 (1)	94 (4)	18 (1)	2 (1)	4 (1)	4 (2)
C(4A)	8 (1)	91 (4)	25 (1)	1 (1)	3 (1)	−14 (2)
C(5A)	8 (1)	51 (3)	30 (1)	1 (1)	3 (1)	−8 (2)
C(6A)	7 (1)	48 (3)	21 (1)	1 (1)	1 (1)	2 (2)
C(1B)	7 (1)	45 (3)	13 (1)	−1 (1)	2 (1)	−4 (1)
C(2B)	7 (1)	57 (3)	21 (1)	0 (1)	3 (1)	0 (2)
C(3B)	8 (1)	68 (3)	34 (1)	0 (1)	7 (1)	−3 (2)
C(4B)	12 (1)	79 (4)	34 (1)	−10 (1)	11 (1)	−8 (2)
C(5B)	16 (1)	68 (3)	22 (1)	−3 (1)	8 (1)	13 (2)
C(6B)	10 (1)	65 (3)	18 (1)	2 (1)	5 (1)	11 (2)
B	6 (1)	65 (4)	15 (1)	1 (1)	2 (1)	4 (2)
C(1C)	7 (1)	58 (3)	17 (1)	3 (1)	2 (1)	8 (1)
C(2C)	11 (1)	70 (4)	21 (1)	0 (1)	4 (1)	1 (2)
C(3C)	16 (1)	77 (4)	20 (1)	−1 (1)	2 (1)	−8 (2)
C(4C)	17 (1)	86 (4)	18 (1)	7 (1)	7 (1)	2 (2)
C(5C)	11 (1)	120 (5)	23 (1)	4 (1)	8 (1)	13 (2)
C(6C)	8 (1)	91 (4)	17 (1)	3 (1)	3 (1)	8 (2)
C(1D)	7 (1)	35 (3)	18 (1)	0 (1)	1 (1)	3 (1)
C(2D)	7 (1)	45 (3)	23 (1)	0 (1)	2 (1)	4 (2)
C(3D)	7 (1)	57 (3)	32 (1)	2 (1)	1 (1)	1 (2)
C(4D)	8 (1)	54 (3)	37 (1)	1 (1)	7 (1)	−6 (2)
C(5D)	10 (1)	69 (4)	24 (1)	1 (1)	7 (1)	−1 (2)
C(6D)	8 (1)	62 (3)	18 (1)	3 (1)	3 (1)	4 (2)
C(1E)	8 (1)	64 (3)	12 (1)	3 (1)	4 (1)	5 (1)
C(2E)	8 (1)	73 (3)	24 (1)	3 (1)	4 (1)	2 (2)
C(3E)	10 (1)	109 (4)	26 (1)	15 (1)	3 (1)	0 (2)
C(4E)	15 (1)	67 (3)	25 (1)	16 (1)	6 (1)	5 (2)
C(5E)	14 (1)	55 (3)	20 (1)	2 (1)	7 (1)	1 (2)
C(6E)	9 (1)	58 (3)	15 (1)	4 (1)	4 (1)	3 (1)
C(1F)	5 (1)	60 (3)	17 (1)	2 (1)	2 (1)	5 (1)
C(2F)	7 (1)	61 (3)	24 (1)	0 (1)	3 (1)	9 (2)
C(3F)	9 (1)	57 (3)	37 (1)	−2 (1)	5 (1)	10 (2)
C(4F)	9 (1)	73 (4)	38 (1)	−8 (1)	3 (1)	−12 (2)
C(5F)	8 (1)	95 (4)	24 (1)	−4 (1)	0 (1)	−7 (2)
C(6F)	8 (1)	66 (3)	22 (1)	−3 (1)	2 (1)	1 (2)
C(1G)	10 (1)	72 (4)	35 (1)	−1 (1)	7 (1)	21 (2)
C(2G)	11 (1)	101 (4)	34 (1)	−4 (1)	11 (1)	−1 (2)
C(3G)	10 (1)	60 (4)	69 (2)	7 (1)	17 (1)	21 (2)
C(4G)	7 (1)	117 (5)	42 (1)	0 (1)	4 (1)	34 (2)
C(5G)	9 (1)	91 (4)	40 (2)	−11	3 (1)	8 (2)
C(1H)	12 (1)	61 (3)	21 (1)	11 (1)	4 (1)	−1 (2)
C(2H)	10 (1)	76 (3)	16 (1)	3 (1)	4 (1)	−8 (2)
C(3H)	9 (1)	64 (3)	14 (1)	3 (1)	0 (1)	−6 (2)
C(4H)	8 (1)	64 (3)	22 (1)	−1 (1)	3 (1)	−10 (2)
C(5H)	13 (1)	60 (3)	24 (1)	0 (1)	8 (1)	2 (2)

Initial characterization of these dinuclear products was accomplished via elemental analyses. The stoichiometry was further defined by titration of the single acid proton with base, 1 equiv of base being required/1 equiv of compound. The yellow crystalline products are stable to air and moisture and soluble in polar solvents. They show two strong ν(CO) absorptions in their infrared spectra at 2030 and 1990 cm^{-1} for the phenyl-*tert*-butylphosphinato complex and at 2040 and 1996 cm^{-1} for the diphenylphosphinato species. NMR spectra were recorded, and they show the expected pattern of resonances for phenyl, *tert*-butyl, and cyclopentadienyl protons.

Ultimate characterization was accomplished by an X-ray crystallographic study; vide infra.

It was possible to convert both dinuclear complexes to the mononuclear complexes $[Fe(C_5H_5)(CO)_2(PPhROH)]Br$ (R = Ph, *t*-Bu) by reaction with HBr(g) in CH_2Cl_2. These yellow solid compounds have ν(CO) values at 2050 and 2003 cm^{-1} (for the PPh-*t*-BuOH compound) and at 2053 and 2003 cm^{-1} (for the PPh_2OH compound); in addition they possess a broad ν(OH) absorption around 2520 cm^{-1}. They are moderately strong acids. Titration data in aqueous acetone suggest that pK_a values for these compounds are in the range of 2–3. Generally the pK_a values for phosphinic acids, R_2POOH, fall in the range of 2–4.[12]

In the titrations of $[Fe(C_5H_5)(CO)_2(PPhROH)]Br$ there was no evidence for the intermediacy of the dinuclear species $[\{Fe(C_5H_5)(CO)_2(PPhRO)\}_2H]^+$ after addition of 0.5 equiv of base. Also, there was a substantial similarity between these titration data and titration data for the dinuclear species. We believe that this means that the dinuclear species have low stability in this solvent system and that they probably dissociate readily according to eq 2.

$$[\{Fe(C_5H_5)(CO)_2(PPhRO)\}_2H]^+ \rightleftharpoons [Fe(C_5H_5)(CO)_2(PPhROH)]^+ + Fe(C_5H_5)(CO)_2(PPhRO) \quad (2)$$

Deprotonation of $[\{Fe(C_5H_5)(CO)_2(PPh_2O)\}_2H]BF_4$ could be effected in nitromethane upon triethylamine addition, the neutral species $Fe(C_5H_5)(CO)_2(PPh_2O)$ being isolated and fully characterized. Another compound having a diphenylphosphinito ligand, $NEt_3H[Mo(CO)_5(PPh_2O)]$, had been made in the same fashion.[3] The reaction of Et_3N with $[\{Fe(C_5H_5)(CO)_2(PPh\text{-}t\text{-}BuO)\}_2H]PF_6$ in $CHCl_3$ gave a mixture of two products, $[Fe(C_5H_5)(CO)_2(PPh\text{-}t\text{-}BuOHNEt_3]PF_6$ and $Fe(C_5H_5)(CO)_2(PPh\text{-}t\text{-}BuO)$. Characterization of the former species was made from analytical and spectroscopic data; the latter compound was not obtained pure enough to get a good analysis, and its identification rests primarily on its NMR spectrum. The former species is presumed to have a hydrogen bond linking the hydrogen of NEt_3H to the oxygen on phosphorus; this result implies substantial basicity at the oxygen site. A higher basicity for this compound than what is implied in $Fe(C_5H_5)(CO)_2(PPh_2O)$ is expected on the basis of the relative donor abilities of alkyl (*tert*-butyl) and aryl (phenyl) groups. This result accords well with the earlier observations that hydrolyses of two $Mo(CO)_5(PR_2Cl)$ compounds (R = Ph, Me) give, respectively, $Mo(CO)_5(PPh_2O)$ and $Mo(CO)_5PMe_2OH$ under similar conditions.[3]

We return to the existence of the dinuclear species $[\{Fe(C_5H_5)(CO)_2(PPhRO)\}_2H]^+$ and to its possible intermediacy in the protonation–deprotonation processes relating $[Fe(C_5H_5)(CO)_2(PPhROH)]^+$ and $Fe(C_5H_5)(CO)_2(PPhRO)$. The fact that these species were isolated in hydrolysis reactions is probably a consequence of the reaction conditions and specifically of solvent choice. Many examples of the association of an acid (HA) and its anion [A$^-$] in certain systems to give [AHA]$^-$ species can be found.[19] This type of behavior is ordinarily encountered with use of aprotic basic solvents such as acetonitrile and acetone, the solvent used in this work. Association usually occurs when solvation of the conjugate base of the acid via a hydrogen bond is not possible; in such a situation the conjugate base can choose to hydrogen bond to the acid from which it is derived.

In the acid–base titrations a different solvent system, aqueous acetone, was used. In this solvent mixture the solvation of $Fe(C_5H_5)(CO)_2PPhRO$ by water is likely to be favored. If so, it is reasonable that the dimer dissociates substantially, so that titration is effectively carried out on $[Fe(C_5H_5)(CO)_2(PPhROH)]^+$ rather than on the dimeric species.

As mentioned earlier a crystal structure study was carried out on one of the dinuclear complexes $[\{Fe(C_5H_5)(CO)_2(PPh\text{-}t\text{-}BuO)\}_2H]BPh_4$. This work verified the stoichiometry for this compound and further established the structural features relating to the association of the halves of this molecule. The structure of the cation is shown in Figure 1. Significant bond lengths and angles are given in Table IV.

The cation in this compound consists of two $Fe(C_5H_5)(CO)_2(PPh\text{-}t\text{-}BuO)$ groups with the oxygens of the phosphinato ligands being the only atoms at a distance appropriate for linking the halves of the molecule. The highest peak in the final difference Fourier map was located between these oxygens and was presumed to be the hydrogen. No attempt was made to further define the position of this atom, and it was doubtful that this could be done to a useful degree of precision. The O···O distance is 2.403 (4) Å, an appropriate length to designate this as a "very short" hydrogen bond (vide infra). The four atoms P(1), O(1), P(2), and O(3) are very nearly coplanar as is common for this type of system.

Whether the unique hydrogen is symmetrically disposed between O(1) and O(2) cannot be determined unequivocally. The location of this atom was not precisely determined, and the crystal system places no symmetry constraints on the molecule. The differences in P–O and Fe–P distances within a molecule are small and cannot be judged to be significant to establish an unsymmetric structure; approximately equal distances are expected for either a symmetric structure or a disordered asymmetric structure.

The compound has two chiral phosphorus atoms, and it can be seen from Figure 2 that the isomer studied is the *meso* form. It has not been established whether a *dl* form is also present in the sample. Infrared data (two ν(CO) peaks) favor one diastereomer. All crystals measured had the same density which, while not conclusive, suggests only one diastereomer. However, the isolation of the meso isomer could be a consequence of its lower solubility. Titration data suggested a facile dissociation of the dinuclear species; such a process could readily interconvert *meso* and *dl* forms.

There are several reviews on compounds that contain a single intramolecular hydrogen bond that acts exclusively to hold the molecule together.[20-23] Speakman[20] has divided these compounds into two general classes, a type B class in which the two parts of the molecule are crystallographically distinguishable and are best represented as A:HA and a type A class in which the oxygen–oxygen distance is "short" (2.38–2.51 Å, with the majority of examples between 2.44 and 2.48 Å). The distance for our compound, 2.403 (4) Å, is clearly among the shorter bond lengths encountered. Compounds with shorter oxygen–oxygen distances (type A) appear more likely to have symmetric O–H–O units.

Two recent papers describe structures of related compounds $Pd(PPh_2S_2)[(PPh_2O)_2H]$[24] and $Pd_2(SCN)_2[(PPh_2O)_2H]_2$.[25] Both species have cis phosphinato groups bridged by a hydrogen, and both also have short oxygen–oxygen distances, 2.42 Å.

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determination of the title compound.

Registry No. $[Fe(C_5H_5)(CO)_2(PPh\text{-}t\text{-}BuCl)]PF_6$, 76498-86-7; $[Fe(C_5H_5)(CO)_2(PPh\text{-}t\text{-}BuCl)]BF_4$, 76498-87-8; $[Fe(C_5H_5)(CO)_2(PPh\text{-}t\text{-}BuCl)]BPh_4$, 76498-88-9; $[\{Fe(C_5H_5)(CO)_2(PPh\text{-}t\text{-}BuO)\}_2H]PF_6$, 76498-90-3; $[\{Fe(C_5H_5)(CO)_2(PPh\text{-}t\text{-}BuO)\}_2H]BF_4$, 76498-91-4; $[\{Fe(C_5H_5)(CO)_2(PPh\text{-}t\text{-}BuO)\}_2H]BPh_4$, 76498-92-5; $[Fe(C_5H_5)(CO)_2(PPh\text{-}t\text{-}BuOH)]Br$, 76498-93-6; $[Fe(C_5H_5)(CO)_2(PPh\text{-}t\text{-}BuOHNEt_3)]PF_6$, 76498-94-7; $Fe(C_5H_5)(CO)_2(PPh\text{-}t\text{-}BuO)$, 76498-89-0; $[Fe(C_5H_5)(CO)_2(PPh_2OMe)]I$, 76498-95-8; $[Fe(C_5H_5)(CO)_2(PPh_2OMe)]PF_6$, 76498-97-0; $[Fe(C_5H_5)(CO)_2(PPh_2Cl)]Cl$, 76498-98-1; $[Fe(C_5H_5)(CO)_2(PPh_2Cl)]PF_6$, 76499-00-8; $[Fe(C_5H_5)(CO)_2(PPh_2Cl)]BF_4$, 76499-01-9; $[\{Fe(C_5H_5)(CO)_2(PPh_2O)\}_2H]BF_4$, 76499-03-1; $Fe(C_5H_5)(CO)_2(PPh_2O)$, 76499-02-0; $[Fe(C_5H_5)(CO)_2(PPh_2OH)]Br$, 76499-04-2; $Fe(C_5H_5)(CO)_2Cl$, 12107-04-9; $[Fe(C_5H_5)(CO)_2(THF)]BF_4$, 63313-71-3; $Fe(C_5H_5)(CO)_2I$, 12078-28-3.

Supplementary Material Available: Listing of structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

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Cationic Pyrazole Complexes of Palladium and Platinum. Characterization of Dynamic Stereochemistry by ^1H and ^{31}P NMR and the Crystal and Molecular Structure of *cis*-Chlorobis(triethylphosphine)(3,5-dimethylpyrazole)palladium(II) Tetrafluoroborate

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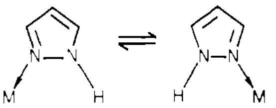
Synthesis of the complex cations *cis*-$[MCl(PEt_3)_2L]^+$, M = Pd or Pt, L = pyrazole (pzH), 3,5-dimethylpyrazole (3,5-DMP), 3,4,5-trimethylpyrazole (3,4,5-TMP), or 4-bromo-3,5-dimethylpyrazole (Br-3,5-DMP), is reported. In solution at ambient temperatures, the platinum complexes are static on the NMR time scale but the palladium compounds exhibit rapid averaging of the two nonequivalent phosphorus nuclei and of the 3,5 proton or methyl positions on the pyrazole ligands. Detailed study of the M = Pd, L = Br-3,5-DMP derivative suggests pyrazole dissociation as the rate-determining step in the phosphorus averaging. The mechanism of 3,5-methyl averaging is less clearly established but may involve deprotonation followed by an intramolecular, metallotropic, 1,2 (equivalent to 1,5) shift. X-ray diffraction study of the M = Pd, L = 3,5-DMP cation as its BF_4^- salt shows approximately square-planar coordination with a monodentate 3,5-DMP ligand. Both nitrogen atoms are displaced to the same side of the basic coordination plane by an important hydrogen bond from N(2), which bears the proton, to F(2) in the anion. The Pd atom is significantly displaced (0.348 Å) from the plane of the 3,5-DMP ligand, an effect probably caused by steric interaction of the pyrazole with a PEt_3 ligand.

Introduction

Fluxional processes involving metal transfer between two nitrogen donor sites on an organic ring have been of recent interest to coordination chemists from two points of view. First, the observation of such processes in imidazole complexes of metalloporphyrins has been considered important for its potential biochemical significance.[1] Second, a relationship has been suggested[2] between a 1,2 metal-transfer process between adjacent nitrogen sites in 1-metallopyrazolyls and the well-established fluxional character of (η^1-cyclopentadienyl)metal complexes. That the latter are fluxional by virtue of a 1,5 (equivalent to 1,2) shift, with 1,3 shifts being forbidden, has been substantiated by recent work in these laboratories.[3]

We became interested in these processes through our previous demonstration that phenanthroline in the complex cation *cis*-$[PtCl(PEt_3)_2(phen)]^+$ is essentially monodentate and fluxional by virtue of a metal transfer between the nitrogen donor sites[4] and our extension of these studies to naphthyridine[5] and phthalazine[6] complexes and to palladium.[7] Pyrazole complexes, however, present a different situation in that a proton transfer is necessary in addition to the metal exchange between nitrogen sites, and if the ring exhibits any significant double-bond localization, then electron reorganization will also be necessary during the transfer (see eq 1).



(1)

Several studies of pyrazole complexes of platinum and palladium have been published recently, especially $[M(pz)_2(L\text{-}L)]$ and $[M(pzH)_2(L\text{-}L)]^{2+}$, where M = Pt or Pd, pzH = pyrazole or substituted pyrazole, and L-L = 1,2-bis(diphenylphosphino)ethane, 2,2′-bipyridine, or cycloocta-1,5-diene.[8-10] However, no fluxional behavior has been reported in any of these studies. Fluxional behavior in the rhodium complex $[RhCl(pzH)CO)_2]$ has been noted in a preliminary communication, but no details have been published.[11] In the present paper we describe the synthesis of a series of cationic pyrazole and substituted-pyrazole complexes of platinum and palladium. The monodentate nature of the pyrazole ligands is demonstrated by an X-ray structure determination for the

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