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Iron(II) Aryldiazene Complexes: Preparation, Characterization, and Ligand-Substitution Reactions with Ketones, Nitriles, and Isocyanides. Crystal Structure of the Diazene Precursor, the New Hydride *trans*-[FeH(CO){P(OEt)₃]₄]BPh₄^{1,2}

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Iron hydride complexes, *trans*-[FeH(CO)L₄]BPh₄ (L = P(OMe)₃, P(OEt)₃, PhP(OEt)₂), were prepared by allowing [FeX(CO)L₄]⁺ (X = Cl, Br) derivatives to react with zinc in acetonitrile solution; the crystal structure of *trans*-[FeH(CO){P(OEt)₃]₄]BPh₄ was determined. The compound crystallized in the orthorhombic space group *P*2₁2₁2₁ with four molecules per unit cell and lattice parameters *a* = 23.658 (14) Å, *b* = 23.671 (13) Å, and *c* = 10.507 (6) Å. The structure was solved by the heavy-atom technique and refined to *R* = 0.0756 for 2813 independent reflections having *I* > 2σ(*I*). The environment of the iron atom is that of a distorted octahedron, the ligands being one hydride ion, one carbonyl group, and four phosphite groups. The complex [FeH(CO){P(OEt)₃]₄⁺ undergoes insertion reactions with aryldiazonium cations to afford the first iron(II) diazene derivatives, *trans*-[Fe(ArNNH)(CO)L₄](BPh₄)₂ (Ar = 4-CH₃C₆H₄, 4-ClC₆H₄). The ¹H NMR spectrum of the ¹⁵N-labeled complex (*J*_{15NH} = 67 Hz) excludes the existence of an arylhydrazido(2-) derivative. The reaction of these diazene compounds with ketones was examined and led to the synthesis of new O-bonded *trans*-[Fe(CO)(RR'CO)L₄](BPh₄)₂ (R = R' = CH₃; R = CH₃, R' = C₂H₅; R = CH₃, R' = C₆H₅; R, R' = (CH₂)₅ (cyclohexanone)) ketone complexes. Furthermore, carbonyl, isocyanide, and nitrile derivatives of the type *cis*-[Fe(CO)₂L₄](BPh₄)₂, *cis*-[Fe(CO)(RNC)L₄](BPh₄)₂ (R = C₆H₅, 4-CH₃C₆H₄, 4-CH₂OC₆H₄, 2,6-(CH₃)₂C₆H₃, 4-NO₂C₆H₄), and *trans*-[Fe(CO)(RCN)L₄](BPh₄)₂ (R = C₆H₅, 4-CH₃C₆H₄, 2-CH₃C₆H₄, CH₃, NC(CH₂)₄) were obtained; their characterization by infrared and ¹H and ³¹P NMR data is also reported. The nitrile complexes show ν(CN) increased in comparison to the free-ligand value.

Introduction

There has recently been considerable interest in the chemistry of aryldiazene and aryldiazene complexes,³⁻⁶ in part due to the close relationship of the aryldiazene group with nitrosyl and dinitrogen ligand. Furthermore, since several studies⁷ have confirmed the role of transition-metal ions in biological nitrogen fixation, the diazene-metal system could be considered as an intermediate of such N₂ reduction. A large number of studies on the synthesis, structure, and reactivity of aryldiazene (Ar-N=NH) derivatives has been reported, including platinum,^{5,6} ruthenium, rhodium, iridium, rhenium, etc. as the central metal.^{5,6} However, no data are available on iron diazene complexes, although iron is a molybdenum cometal in the nitrogenase enzyme. In this paper we report the reactivity of the new hydride [FeH(CO)L₄]⁺ toward diazonium cations, which allowed the synthesis of the first aryldiazene complexes of iron(II). Moreover, study of their properties shows that a new route to the preparation of ketone as well as carbonyl, isocyanide, and nitrile complexes has been achieved, and the results are also reported here.

Experimental Section

Solvents and Reagents. Solvents were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuumtight storage flasks. Ethanol and methanol were dried over calcium hydride, diethyl ether was dried over sodium/benzophenone, and dichloromethane and 1,2-dichloroethane were dried by reflux over phosphorus pentoxide. Acetonitrile was distilled over activated molecular sieves. Trimethyl and triethyl phosphites (Ega Chemie) were purified by distillation under nitrogen while diethyl phenyl phosphite was prepared by the reported method.⁸ Diazonium salts were prepared in the usual way as described in the literature.⁹ All ketones and nitriles used were purified by distillation over activated molecular sieves. Substituted phenyl isocyanides were obtained by the phosgene method¹⁰ of Ugi et al. Other reagents were purchased from commercial sources in the highest available purity and used as received.

Physical Measurements. Solution ¹H NMR spectra were obtained with Varian EM-390 or Varian FT-80 A spectrometers. Spectra were recorded at ambient temperature unless otherwise noted and are referred to internal tetramethylsilane. Fourier-mode, proton-noise-decoupled ³¹P NMR spectra were collected on a Varian FT-80 A spectrometer operating at 32.203 MHz. All chemical shifts are reported with respect to 85% H₃PO₄, with downfield shifts considered positive.

Infrared spectra were recorded on a Perkin-Elmer Model 683 instrument. Solid-state spectra were obtained with use of potassium bromide pellets.

Conductivities of 10⁻³ M solutions of the complexes in nitromethane at 25 °C were measured with a "Halosis" bridge.

- (1) This paper is dedicated to Ugo Croatto on the occasion of his 70th birthday.
- (2) A preliminary communication on part of this work has appeared: Albertin, G.; Antoniutti, S.; Bordignon, E. *J. Chem. Soc., Chem. Commun.* **1984**, 1688.
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Synthesis of the Complexes. All the preparative work was performed under an inert atmosphere with use of standard Schlenk techniques. Once isolated, the compounds were shown to be stable in air for 2–3 days.

trans-[FeH(CO)₄]BPh₄ (L = P(OMe)₃, P(OEt)₃, PhP(OEt)₂). Zinc dust in excess (0.5 g) was added to a yellow solution of [FeCl(CO)₄]-BPh₄ (2 mmol) in acetonitrile (200 mL), and the reaction mixture was stirred until the solution turned colorless. After filtration, the solvent was removed by evaporation to yield a brown oil, which was stirred with methanol or ethanol for 1 h to produce a light brown product, which was crystallized from alcohol; yield ≥60%. The physical constants and the elemental analyses for the hydride complexes follow. Anal. Calcd for L = P(OMe)₃: C, 49.35; H, 6.38. Found: C, 49.41; H, 6.28; mp 198 °C. $\Delta_M = 54.1 \text{ cm}^2 \text{ M}^{-1} \Omega^{-1}$. ¹H NMR (acetone-*d*₆): δ 7.33 (m), 6.90 (m), 3.76 (m), -8.97 (quintet). Anal. Calcd for L = P(OEt)₃: C, 55.07; H, 7.64. Found: C, 54.90; H, 7.78; mp, 194 °C. $\Delta_M = 49.9 \text{ cm}^2 \text{ M}^{-1} \Omega^{-1}$. ¹H NMR (acetone-*d*₆): δ 6.91 (m), 6.85 (m), 4.11 (m), 1.32 (t), -8.89 (quintet). Anal. Calcd for L = PhP(OEt)₂: C, 65.23; H, 6.82. Found: C, 65.31; H, 6.70; mp 165 °C. $\Delta_M = 47.5 \text{ cm}^2 \text{ M}^{-1} \Omega^{-1}$. ¹H NMR (acetone-*d*₆): δ 7.39 (m), 3.69 (m), 1.14 (t), -7.92 (quintet).

trans-[FeH(CO)]P(OEt)₃]Br. This complex has been prepared by following the method reported above, starting from the *cis*-[FeBr(CO)]P(OEt)₃]Br derivative; yield ≥20%. Anal. Calcd: C, 36.20; H, 7.41. Found: C, 36.02; H, 7.52; mp, 87 °C. $\Delta_M = 52.4 \text{ cm}^2 \text{ M}^{-1} \Omega^{-1}$. ¹H NMR (acetone-*d*₆): δ 4.13 (m), 1.33 (t), -8.89 (quintet).

[Fe(ArN=NH)(CO)]P(OEt)₃]4(BPh₄)₂ (Ar = 4-CH₃C₆H₄, 4-ClC₆H₄). The appropriate diazonium salt (ArN₂⁺BF₄⁻) (6 mmol) was added to a solution of [FeH(CO)]P(OEt)₃]4BPh₄ (2 mmol, 2.14 g) in dichloromethane (30 mL). The reaction mixture was stirred for 24 h and then filtered through a Schlenk filter funnel to separate the unreacted diazonium salt. The solvent was removed under reduced pressure, leaving an oil, which was then treated with ethanol (20 mL) containing NaBPh₄ (2 mmol, 0.69 g). A yellow product separated out, which was filtered, washed with ethanol, and dried under vacuum. Recrystallization was carried out by dissolving the product in dichloromethane (5 mL) and, after filtration, adding ethanol drop by drop until a white solid separated out; yield ≥10%. Anal. Calcd for Ar = 4-CH₃C₆H₄: C, 63.75; H, 7.22; N, 1.86. Found: C, 63.28; H, 7.14; N, 2.00; mp, 157 °C. $\Delta_M = 131.6 \text{ cm}^2 \text{ M}^{-1} \Omega^{-1}$. ¹H NMR (Me₂SO-*d*₆): δ 13.3 (br), 6.93 (m), 6.84 (m), 4.43 (m), 2.26 (s), 1.43 (t). Anal. Calcd for Ar = 4-ClC₆H₄: C, 62.11; H, 6.93; N, 1.83. Found: C, 62.41; H, 7.00; N, 1.79; mp, 176 °C. $\Delta_M = 128.2 \text{ cm}^2 \text{ M}^{-1} \Omega^{-1}$. ¹H NMR (Me₂SO-*d*₆): δ 13.4 (br), 7.17 (m), 6.83 (m), 4.28 (m), 1.39 (t).

[Fe(CO)(RR'CO)]P(OEt)₃]4(BPh₄)₂ (R = R' = CH₃; R = CH₃, R' = C₆H₅; R = CH₃, R' = C₆H₅; R, R' = (CH₂)₅ (Cyclohexanone)). A solution of [FeH(CO)₄]BPh₄ (1 mmol, 1.07 g) in dichloromethane (20 mL) was added to a suspension of [4-CH₃C₆H₄N₂]BF₄ (3 mmol, 0.62 g) in CH₂Cl₂ (10 mL). The reaction mixture was stirred for 24 h and filtered, and then an excess of the appropriate ketone (10 mmol) was added. After 20 h the red-brown solution was evaporated to dryness and the oil obtained was stirred with ethanol (20 mL). The addition of NaBPh₄ (2 mmol, 0.69 g) caused the separation of a yellow product, which was crystallized from CH₂Cl₂/ethanol (1:10); yield ≥40%. In the case of the acetone complex the reaction can be carried out with acetone as solvent instead of CH₂Cl₂, giving a better yield of the [Fe(CO)]OC(CH₃)₂]4(BPh₄)₂ derivative. The physical constants and the elemental analyses for the ketone complexes follow. Anal. Calcd for the (CH₃)₂CO derivative: C, 63.17; H, 7.39. Found: C, 62.92; H, 7.43; mp, 162 °C. $\Delta_M = 126.1 \text{ cm}^2 \text{ M}^{-1} \Omega^{-1}$. ¹H NMR (Me₂SO-*d*₆): δ 7.19 (m), 6.89 (m), 4.18 (m), 2.31 (s), 1.29 (t). Anal. Calcd for the CH₃(C₂H₅)CO derivative: C, 63.38; H, 7.46. Found: C, 63.32; H, 7.49; mp, 160 °C. $\Delta_M = 125.9 \text{ cm}^2 \text{ M}^{-1} \Omega^{-1}$. ¹H NMR (Me₂SO-*d*₆): δ 7.18 (m), 6.88 (m), 4.19 (m), 2.45 (quartet), 2.34 (s), 1.30 (t), 1.07 (t). Anal. Calcd for the CH₃(C₆H₅)CO derivative: C, 64.55; H, 7.22. Found: C, 64.64; H, 7.07; mp, 137 °C. $\Delta_M = 122.5 \text{ cm}^2 \text{ M}^{-1} \Omega^{-1}$. ¹H NMR (Me₂SO-*d*₆): δ 7.8 (m), 7.18 (m), 6.89 (m), 4.20 (m), 2.90 (s), 1.28 (t). Anal. Calcd for the C₆H₁₀CO derivative: C, 63.89; H, 7.47. Found: C, 64.28; H, 7.67; mp, 163 °C. $\Delta_M = 127.4 \text{ cm}^2 \text{ M}^{-1} \Omega^{-1}$. ¹H NMR (Me₂SO-*d*₆): δ 7.17 (m), 6.90 (m), 4.20 (m), 2.49 (m), 1.70 (m), 1.31 (t).

[Fe(CO)]{(CH₃)₂CO}P(OMe)₃]4(BPh₄)₂. The complex has been prepared by following the method reported above starting from the *trans*-[FeH(CO)]P(OMe)₃]4BPh₄ hydride; yield ≥40%. Anal. Calcd: C, 60.21; H, 6.47. Found: C, 60.11; H, 6.42; mp, 215 °C. $\Delta_M = 136.2 \text{ cm}^2$

$\text{M}^{-1} \Omega^{-1}$. ¹H NMR (Me₂SO-*d*₆): δ 7.20 (m), 6.88 (m), 3.85 (m), 2.30 (s).

[Fe(CO)]{(CD₃)₂CO}P(OEt)₃]4(BPh₄)₂. This compound was prepared by ligand exchange, with dissolution of a sample of [Fe(CO)]{(CH₃)₂CO}P(OEt)₃]4(BPh₄)₂ in hexadeuterioacetone: after 10 h the solution was cooled to -30 °C, giving yellow crystals of the product.

[Fe(OH₂)(CO)]P(OEt)₃]4(BPh₄)₂. To a solution of [Fe(CO)]{(CH₃)₂CO}P(OEt)₃]4(BPh₄)₂ (0.35 mmol, 0.5 g) in dichloromethane/ethanol (1:1, 10 mL) was added 0.70 mmol (12.6 μ L) of distilled water, and the mixture was stirred for 1 day. Addition of diethyl ether caused the precipitation of a yellow compound, which was washed with ethanol and dried under vacuum; yield ≥70%. This compound was also obtained in the synthesis of diazene and ketone complexes and separated from the main products by fractional crystallization. Anal. Calcd: C, 62.40; H, 7.32. Found: C, 62.45; H, 7.32. $\Delta_M = 130.1 \text{ cm}^2 \text{ M}^{-1} \Omega^{-1}$. ¹H NMR (acetone-*d*₆): δ 7.32 (m), 6.89 (m), 4.37 (m), 3.76 (br), 1.44 (t), 1.39 (t), 1.35 (t).

[Fe(CO)₂]P(OEt)₃]4(BPh₄)₂. A solution of [Fe(CO)]{(CH₃)₂CO}P(OEt)₃]4(BPh₄)₂ (0.7 mmol, 1 g) in dichloromethane (30 mL) was allowed to stand under CO for 24 h. Removal of the solvent under vacuum by rotary evaporation gave a residual oil, which was stirred with ethanol (20 mL) to give a white solid. The product was crystallized from dichloromethane/ethanol (1:15); yield ≥75%. Anal. Calcd: C, 62.81; H, 7.12. Found: C, 62.71; H, 7.19; mp, 172 °C. $\Delta_M = 128 \text{ cm}^2 \text{ M}^{-1} \Omega^{-1}$. ¹H NMR (acetone-*d*₆): δ 7.35 (m), 6.90 (m), 4.52 (m), 1.44 (t), 1.40 (t).

[Fe(CO)(RNC)]P(OEt)₃]4(BPh₄)₂ (R = C₆H₅, 4-CH₃C₆H₄, 4-CH₃OC₆H₄, 4-NO₂C₆H₄, 2,6-(CH₃)₂C₆H₃). The appropriate isocyanide (1 mmol) was added to a solution of [Fe(CO)]{(CH₃)₂CO}P(OEt)₃]4(BPh₄)₂ (0.35 mmol, 0.5 g) in dichloromethane (25 mL), and the mixture was stirred for 36 h. The solvent was removed, and the resulting oil was triturated with ethanol (10 mL) to give white crystals of the product, which was further purified by crystallization from dichloromethane/ethanol (1:10); yield ≥80%. The physical constants and the elemental analyses for the isocyanide complexes follow. Anal. Calcd for R = C₆H₅: C, 64.48; H, 7.10; N, 0.94. Found: C, 64.13; H, 7.18; N, 1.09; mp 179 °C. $\Delta_M = 119.7 \text{ cm}^2 \text{ M}^{-1} \Omega^{-1}$. ¹H NMR (acetone-*d*₆): δ 7.62 (s), 7.32 (m), 6.88 (m), 4.44 (m), 1.45 (t), 1.41 (t), 1.39 (t). Anal. Calcd for R = 4-CH₃C₆H₄: C, 64.68; H, 7.17; N, 0.93. Found: C, 64.26; H, 7.11; N, 1.06; mp, 178 °C. $\Delta_M = 123.7 \text{ cm}^2 \text{ M}^{-1} \Omega^{-1}$. ¹H NMR (acetone-*d*₆): δ 7.33 (m), 6.89 (m), 4.37 (m), 2.37 (s), 1.43 (t), 1.40 (t), 1.37 (t). Anal. Calcd for R = 4-CH₃OC₆H₄: C, 64.00; H, 7.10; N, 0.92. Found: C, 64.03; H, 7.18; N, 1.05; mp, 180 °C. $\Delta_M = 125.1 \text{ cm}^2 \text{ M}^{-1} \Omega^{-1}$. ¹H NMR (acetone-*d*₆): δ 7.32 (m), 6.88 (m), 4.44 (m), 3.82 (s), 1.45 (t), 1.42 (t), 1.40 (t). Anal. Calcd for R = 4-NO₂C₆H₄: C, 62.59; H, 6.83; N, 1.83. Found: C, 62.03; H, 6.64; N, 2.01; mp, 171 °C. $\Delta_M = 121.5 \text{ cm}^2 \text{ M}^{-1} \Omega^{-1}$. ¹H NMR (acetone-*d*₆): δ 8.17 (AA'BB'), 7.32 (m), 6.89 (m), 4.45 (m), 1.46 (t), 1.42 (t), 1.40 (t). Anal. Calcd for R = 2,6-(CH₃)₂C₆H₃: C, 64.87; H, 7.24; N, 0.92. Found: C, 65.16; H, 7.02; N, 1.06; mp, 185 °C. $\Delta_M = 133.5 \text{ cm}^2 \text{ M}^{-1} \Omega^{-1}$. ¹H NMR (acetone-*d*₆): δ 7.31 (m), 6.89 (m), 4.40 (m), 2.58 (s), 1.45 (t), 1.32 (t).

[Fe(CO)(4-CH₃C₆H₄NC)]P(OEt)₃]4(BPh₄)₂. This compound was prepared by following the method reported above; yield ≥70%. Anal. Calcd: C, 62.04; H, 6.26; N, 1.05. Found: C, 62.12; H, 6.17; N, 1.01; mp, 196 °C. $\Delta_M = 128.6 \text{ cm}^2 \text{ M}^{-1} \Omega^{-1}$. ¹H NMR (acetone-*d*₆): δ 7.34 (m), 6.89 (m), 4.04 (m), 2.41 (s).

[Fe(CO)(RCN)]P(OEt)₃]4(BPh₄)₂ (R = CH₃, C₆H₅, 4-CH₃C₆H₄, 2-CH₃C₆H₄, NC(CH₂)₄). To a solution of [Fe(CO)]{(CH₃)₂CO}P(OEt)₃]4(BPh₄)₂ (0.35 mmol, 0.5 g) in dichloromethane (30 mL) was added the appropriate nitrile (3.5 mmol), and the solution was stirred for 3 days. The mixture was concentrated to 5 mL, and then ethanol was added drop by drop until a yellow-white precipitate separated out. The solid was filtered, washed with ethanol, and crystallized from dichloromethane/ethanol (1:10); yield ≥80%. The physical constants and the elemental analyses for the nitrile complexes follow. Anal. Calcd for R = CH₃: C, 63.08; H, 7.27; N, 0.98. Found: C, 62.90; H, 7.30; N, 1.14; mp, 178 °C. $\Delta_M = 126.9 \text{ cm}^2 \text{ M}^{-1} \Omega^{-1}$. ¹H NMR (CD₂Cl₂): δ 7.32 (m), 6.97 (m), 4.04 (m), 2.20 (br), 1.30 (t). Anal. Calcd for R = C₆H₅: C, 64.48; H, 7.10; N, 0.94. Found: C, 63.82; H, 6.80; N, 0.90; mp, 202 °C. $\Delta_M = 133.6 \text{ cm}^2 \text{ M}^{-1} \Omega^{-1}$. ¹H NMR (CD₂Cl₂): δ 7.30 (m), 6.96 (m), 4.14 (m), 1.33 (t). Anal. Calcd for R = 4-CH₃C₆H₄: C, 64.68; H, 7.17; N, 0.93. Found: C, 64.00; H, 6.93; N, 1.10; mp, 173 °C. $\Delta_M = 125.5 \text{ cm}^2 \text{ M}^{-1} \Omega^{-1}$. ¹H NMR (CD₂Cl₂): δ 7.29 (m), 6.96 (m), 4.18 (m), 2.43 (s), 1.32 (t). Anal. Calcd for R = 2-CH₃C₆H₄: C, 64.68; H, 7.17; N, 0.93. Found: C, 65.03; H, 7.12; N, 0.96; mp, 182 °C. $\Delta_M = 135.9 \text{ cm}^2 \text{ M}^{-1} \Omega^{-1}$. ¹H NMR (CD₂Cl₂): δ 7.29 (m), 6.96 (m), 4.16 (m), 2.49 (s), 1.33 (t). Anal. Calcd for R = NC(CH₂)₄: C, 63.46; H, 7.28; N, 1.87. Found: C, 64.00; H, 7.17; N, 2.00; mp, 147 °C. $\Delta_M = 130.3 \text{ cm}^2 \text{ M}^{-1} \Omega^{-1}$. ¹H NMR (acetone-*d*₆): δ 7.35 (m), 6.89 (m), 4.30 (m), 2.90 (br), 2.33 (m), 1.72 (m), 1.40 (t).

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Table I. Selected Infrared and NMR Data for Iron(II) Complexes

comps	$\nu(\text{CO}),^a \text{ cm}^{-1}$	$\nu(\text{OC}),^a \text{ cm}^{-1}$	$^1\text{H NMR}$		$^{31}\text{P}\{^1\text{H}\}$ NMR chem shifts, ^{b,d} δ
			assign	chem shifts, ^b δ	
<i>trans</i> -[FeH(CO){P(OMe) ₃] ₄]BPh ₄	1990 s (1988 s)		FeH	-8.97 qi (51.5) ^c	+164.6 s ^c
<i>trans</i> -[FeH(CO){P(OEt) ₃] ₄]BPh ₄	1985 s (1980 s)		FeH	-8.89 qi (53.3) ^c	+159.2 s ^c
<i>trans</i> -[FeH(CO){PhP(OEt) ₂] ₄]BPh ₄	1966 s (1960 s)		FeH	-7.92 qi (49.0) ^c	+180.4 s ^c
<i>trans</i> -[FeH(CO){P(OEt) ₃] ₄]Br	1980 s (1977 s)		FeH	-8.89 qi (53.3) ^c	+159.1 s ^c
[Fe(4-CH ₃ C ₆ H ₄ N=NH)(CO){P(OEt) ₃] ₄ (BPh ₄) ₂	2002 s (2000 s)		NH CH ₃ C ₆ H ₄ N=NH	13.3 br 2.26 s	+135.17 s
[Fe(4-ClC ₆ H ₄ N=NH)(CO){P(OEt) ₃] ₄ (BPh ₄) ₂	2002 s (2001 s)		NH	13.4 br	+135.6 s
[Fe(CO){(CH ₃) ₂ CO}{P(OMe) ₃] ₄ (BPh ₄) ₂	2009 s (2003 s)	1680 s (1678 s)	(CH ₃) ₂ CO	2.30 s	+136.27 s
[Fe(CO){(CH ₃) ₂ CO}{P(OEt) ₃] ₄ (BPh ₄) ₂	2000 s (1997 s)	1685 s (1682 s)	(CH ₃) ₂ CO	2.31 s	+130.84 s
[Fe(CO){(CH ₃)(C ₆ H ₅)CO}{P(OEt) ₃] ₄ (BPh ₄) ₂	2004 s (1998 s)	1632 s (1633 s)	CH ₃ (C ₆ H ₅)CO	2.90 s	+130.53 s
[Fe(CO){(CD ₃) ₂ CO}{P(OEt) ₃] ₄ (BPh ₄) ₂	2003 s (1998 s)	1672 s (1675 s)			+130.36 s
[Fe(CO){(CH ₃)(C ₂ H ₅)CO}{P(OEt) ₃] ₄ (BPh ₄) ₂	2001 s (1998 s)	1675 s (1674 s)	CH ₃ (C ₂ H ₅)CO C ₂ H ₅ (CH ₃)CO	2.34 s 2.45 q, 1.07 t	+130.7 s
[Fe(CO){(C ₅ H ₁₀)CO}{P(OEt) ₃] ₄ (BPh ₄) ₂	2003 s (1995 s)	1675 s (1680 s)	C ₅ H ₁₀ CO	2.49 m 1.70 m	+130.67 s
[Fe(H ₂ O)(CO){P(OEt) ₃] ₄ (BPh ₄) ₂	2035 s (2034 s)		H ₂ O	3.76 br	+134 m

^aFrequencies in parentheses are from spectra of KBr pellets of complexes in the solid state; all other values are from spectra of CH₂Cl₂ solutions.

^bAt room temperature in (CD₃)₂SO. ^cSpectra in (CD₃)₂CO; the J_{PH} value in hertz is given in parentheses. ^dPositive shift downfield from 85% H₃PO₄.

Table II. Selected Infrared and ^{31}P NMR Data for Carbonyl, Isocyanide, and Nitrile Complexes

comps ^a	$\nu(\text{CO}),^b \text{ cm}^{-1}$	$\nu(\text{CN}),^b \text{ cm}^{-1}$	$\nu(\text{CN}),^c \text{ cm}^{-1}$ (free ligand)	spin syst	$^{31}\text{P}\{^1\text{H}\}$ NMR chem. shifts, ^{d,e} δ (coupling const, Hz)		
					δ_{A}	δ_{B}	δ_{C}
[Fe(CO) ₂ {P(OEt) ₃] ₄] ²⁺	2053 s (2045 s) 2090 s (2080 s)			A ₂ B ₂	$\delta_{\text{A}} = 130.1$ ($J_{\text{AB}} = 121.3$)	$\delta_{\text{B}} = 127.8$	
[Fe(CO)(4-CH ₃ C ₆ H ₄ NC){P(OMe) ₃] ₄] ²⁺	2057 s (2052 s)	2180 s (2180 s)	2128 s	AB ₂ C	$\delta_{\text{A}} = 142.0$ ($J_{\text{AB}} = 123$)	$\delta_{\text{B}} = 141.5$ ($J_{\text{AC}} = 128$)	$\delta_{\text{C}} = 139.5$ ($J_{\text{BC}} = 130$)
[Fe(CO)(4-CH ₃ C ₆ H ₄ NC){P(OEt) ₃] ₄] ²⁺	2048 s (2040 s)	2175 s (2170 s)	2128 s	AB ₂ C	$\delta_{\text{A}} = 135.6$ ($J_{\text{AB}} = 115$)	$\delta_{\text{B}} = 134.1$ ($J_{\text{AC}} = 130$)	$\delta_{\text{C}} = 133.0$ ($J_{\text{BC}} = 126$)
[Fe(CO)(C ₆ H ₅ NC){P(OEt) ₃] ₄] ²⁺	2052 s (2047 s)	2175 s (2175 s)	2128 s	AB ₂ C	$\delta_{\text{A}} = 136.5$ ($J_{\text{AB}} = 109$)	$\delta_{\text{B}} = 136.3$ ($J_{\text{AC}} = 121$)	$\delta_{\text{C}} = 132.2$ ($J_{\text{BC}} = 116$)
[Fe(CO)(4-CH ₃ OC ₆ H ₄ NC){P(OEt) ₃] ₄] ²⁺	2049 s (2042 s)	2176 s (2177 s)	2126 s	AB ₂ C	$\delta_{\text{A}} = 135.8$ ($J_{\text{AB}} = 115$)	$\delta_{\text{B}} = 134.3$ ($J_{\text{AC}} = 130$)	$\delta_{\text{C}} = 133.2$ ($J_{\text{BC}} = 125$)
[Fe(CO)(4-NO ₂ C ₆ H ₄ NC){P(OEt) ₃] ₄] ²⁺	2052 s (2045 s)	2162 s (2160 s)	2125 s	AB ₂ C	$\delta_{\text{A}} = 134.3$ ($J_{\text{AB}} = 118$)	$\delta_{\text{B}} = 133.1$ ($J_{\text{AC}} = 128$)	$\delta_{\text{C}} = 131.9$ ($J_{\text{BC}} = 127$)
[Fe(CO)[2,6-(CH ₃) ₂ C ₆ H ₃ NC]{P(OEt) ₃] ₄] ²⁺	2048 s (2041 s)	2168 s (2168 s)	2121 s	AB ₂ C	$\delta_{\text{A}} = 135.9$ ($J_{\text{AB}} = 122$)	$\delta_{\text{B}} = 134.0$ ($J_{\text{AC}} = 116$)	$\delta_{\text{C}} = 132.3$ ($J_{\text{BC}} = 138$)
[Fe(CO)(4-CH ₃ C ₆ H ₄ CN){P(OMe) ₃] ₄] ²⁺	2022 s (2020 s)	2268 m (2265 m)	2230 m			+138.81 s ^f	
[Fe(CO)(4-CH ₃ C ₆ H ₄ CN){P(OEt) ₃] ₄] ²⁺	2023 s (2020 s)	2268 m (2270 m)	2230 m			+134.03 s ^f	
[Fe(CO)(C ₆ H ₅ CN){P(OEt) ₃] ₄] ²⁺	2023 s (2018 s)	2272 m (2275 m)	2231 m			+129.63 s ^f	
[Fe(CO)(2-CH ₃ C ₆ H ₄ CN){P(OEt) ₃] ₄] ²⁺	2021 s (2018 s)	2261 m (2260 m)	2227 m			+130.06 s ^f	
[Fe(CO)(CH ₃ CN){P(OEt) ₃] ₄] ²⁺	2020 s (2023 s)		2291 m 2252 m			+134.26 s ^f	
[Fe(CO){NC(CH ₂) ₄ CN}{P(OEt) ₃] ₄] ²⁺	2025 s (2022 s)	2296 w (2297 w) 2248 w (2246 w)	2248 w			+133.51 s	

^aAll the compounds are BPh₄⁻ salts. ^bFrequencies in parentheses are from spectra of KBr pellets of complexes in the solid state; all other values are from spectra of CH₂Cl₂ solutions (dicarbonyl and isocyanide complexes) or ClCH₂CH₂Cl solutions (nitrile derivatives). ^cIn CH₂Cl₂ solutions (isocyanides) and in ClCH₂CH₂Cl solutions (nitriles). ^dPositive shift downfield from 85% H₃PO₄. ^eAt room temperature in (CD₃)₂CO. ^fIn CD₂Cl₂.

[Fe(CO)(4-CH₃C₆H₄CN){P(OMe)₃]₄(BPh₄)₂. This complex was prepared by following the method reported above; yield $\geq 55\%$. Anal. Calcd: C, 62.04; H, 6.26; N, 1.05. Found: C, 61.90; H, 6.30; N, 0.96; mp 205 °C. $\Delta_{\text{M}} = 127.2 \text{ cm}^2 \text{ M}^{-1} \Omega^{-1}$. $^1\text{H NMR}$ (CD₂Cl₂): δ 7.32 (m), 6.96 (m), 3.68 (m), 2.43 (s).

Crystallography of *trans*-[FeH(CO){P(OEt)₃]₄]BPh₄. Collection and Reduction of X-ray Diffraction Data. All measurements were performed on a Siemens AED three-circle diffractometer in conjunction with a Jumbo 220 computer, by using niobium-filtered molybdenum radiation. The cell dimensions and crystal lattice were obtained from automatic

Table III. Data for Crystal Structure Analysis of *trans*-[FeH(CO)[P(OEt)₃]₄]BPh₄

formula	C ₄₉ H ₈₁ BF ₆ O ₁₃ P ₄
fw	1068.72
space group ^a	P2 ₁ 2 ₁ 2 ₁
a, Å	23.658 (14)
b, Å	23.671 (13)
c, Å	10.507 (6)
V, Å ³	5884 (6)
Z	4
radiation (λ, Å)	Mo Kα (λ = 0.710 69)
d _{calcd.} g cm ⁻³	1.206
μ(Mo Kα), cm ⁻¹	4.14
cryst color and habit	colorless rectangular parallelepipeds
cryst size, mm	0.36 × 0.36 × 1.10
scan method	θ-2θ
takeoff angle, deg	4
abs cor (min-max)	0.802-1.292
extinction cor (min-max)	0.936-1.217
θ range, deg	3.0-23.0
std reflection	971
freq	every 75 measmts
variation	negligible
no. of data collected ^c	4933
no. of indep data	4831
internal consistency index ^d	0.0201
no. of unique obsd reflcns	2813
σ criterion	I > 2σ(I)
max shift/esd (last cycle)	0.20
no. of params refined	449
ratio of observns to params	6.3/1
R ^e	0.0756
R _w ^f	0.0818
R _g ^g	0.1021
GOF	0.8227

^a Based upon systematic absences: $h00, h = 2n + 1; 0k0, k = 2n + 1; 00l, l = 2n + 1$. In view of the nearly identical observed *a* and *b* dimensions and the pseudosymmetry of the molecule, a tetragonal space group was also considered, but it was rejected on the basis of a careful inspection of the intensities of the reflections. ^b Final lattice parameters were determined by least-squares analysis of the θ values for 17 strong reflections. ^c Including 29 systematically absent reflections and 73 duplicate hkl reflections. ^d $R_{av} = \sum(I - \langle I \rangle) / \sum I$. ^e $R = \sum |\Delta F| / \sum |F_o|$. ^f $R_w = \sum (\Delta F)^2 w^{1/2} / \sum w^{1/2} F_o$. ^g $R_g = [\sum w (\Delta F)^2 / \sum w F_o^2]^{1/2}$.

peak-search and indexing procedures. Pertinent crystal data and basic information about data collection and structure refinement are summarized in Table III. The intensities were measured with the profile technique and corrected for Lorentz and polarization factors. Corrections for absorption and extinction were also made, with use of the Walker and Stuart method.¹¹

Structure Analysis and Refinement. The iron atom position was revealed by the inspection of a Patterson map. Subsequent least-squares difference Fourier cycles allowed the location of all other non-hydrogen atoms. The structure was refined by full-matrix least-squares methods, minimizing the function $\sum w(\Delta F)^2$, where w was taken as $[\sigma^2(F_o) + 0.005F_o^2]^{-1}$. Attempts to refine the ethyl C atoms anisotropically resulted in non-positive-definite conditions for most of them. Accordingly, these atoms were refined in the isotropic form, while all the other non-hydrogen atoms were assigned anisotropic thermal parameters. The phenyl rings were treated as rigid groups (with attached H) of D_{6h} symmetry. The hydrogen atoms from the cation were ignored, except the hydride, which was directly located in a difference map based mainly on low-angle ($\sin \theta / \lambda = 0.3$) reflections. Even if the isotropic thermal parameter is rather high, the position of the hydride has been refined in the last cycle and, in our opinion, the structural parameters obtained may be considered chemically reasonable. The final residuals were $R = 0.0784$, $R_w = 0.0846$, and $R_g = 0.1057$ defined as in Table III. At this point, the absolute configuration of the complex was tested by inverting the signs of all the coordinates and by performing another refinement. The resulting residuals given in Table III provide evidence that the correct crystal chirality is defined by the "inverted" coordinates, which are listed in Table IV. The large thermal parameters of some ethyl carbon atoms could be suggestive of positional disorder, but attempts to locate alter-

native positions with fractional occupancies for these atoms led to no satisfactory results. We attribute the not so satisfactory *R* indices to the intense thermal motion of most atoms as well as to the weakly diffracting nature of the crystal. In the final ΔF map, the largest peaks had electron densities of $0.5 \text{ e } \text{Å}^{-3}$ and were located near the ethyl groups. Atomic scattering factors for the non-hydrogen atoms were corrected for real and imaginary contributions from anomalous scattering.¹² For major computations the SHELX-76 package of crystallographic programs¹³ was used, as well as PARST,¹⁴ ASSORB,¹⁵ and ORTEP¹⁶ programs. The more important bond distances and angles are summarized in Table V.

The calculations were carried out on the Cyber 76 computer of CIN-ECA (Casalecchio, Bologna, Italy) and the Gould-SEL 32/77 computer of the Centro di Studio per la Strutturistica Diffraattometrica del CNR (Parma, Italy).

Results and Discussion

Preparation and Characterization of [FeH(CO)L₄]⁺ Cations. Zinc dust reduction of both *cis*- and *trans*-[FeX(CO)L₄]BPh₄ (X = Cl, Br; L = P(OMe)₃, P(OEt)₃, PhP(OEt)₂) complexes¹⁷ in acetonitrile solution gives the [FeH(CO)L₄]⁺ derivatives. Attempts to prepare the hydrides by reaction with NaBH₄ in ethanol failed because the starting carbonyls are unreactive under these conditions and only with zinc dust can the [FeH(CO)L₄]⁺ be prepared.¹⁸ These monohydrides are white, diamagnetic, soluble in all polar solvents, and very air-stable, both as solids or in solution. Some spectroscopic properties are reported in Table I. The infrared spectra show a strong band at 1966-1990 cm⁻¹ due to $\nu(\text{CO})$, and no absorption attributable to $\nu(\text{Fe-H})$ is observed in the 1700-2300-cm⁻¹ region. In the hydride region the ¹H NMR spectra show a well-resolved quintet at $\delta -7.92$ to -8.97 ($J_{\text{PH}} = 53.3-49.0 \text{ Hz}$) due to the coupling of the hydride with four equivalent phosphorus nuclei. The ³¹P{¹H} NMR spectra are singlets at 30 °C and remain unchanged when the temperature is lowered to -80 °C. On this basis a *trans* geometry in solution can be proposed for the complexes, as observed in the solid state.

A number of iron(II) hydrides have been prepared in recent years, with either mono- or polydentate tertiary phosphine ligands.¹⁹ With phosphites (P(OR)₃, PhP(OR)₂), however, except for the [FeH{P(OMe)₃}]⁺ complex,²⁰ only dihydrides of the type [FeH₂L₄] are obtained, and their properties have been studied extensively.²¹ In our case, the use of zinc dust as reducing agent in acetonitrile allowed us to synthesize a new series of cationic monohydrides containing monodentate phosphites and carbonyl ligands. Study of the chemical properties of the monohydrides indicated relatively robust complexes. No evidence for phosphite dissociation was detected by NMR data over a 2-week period at 25 °C. Moreover, neither isomerization to give the *cis* derivative nor a substitution reaction with isocyanides and phosphites in boiling 1,2-dichloroethane takes place. Treatment with nitric oxide or CO does not modify the starting hydrides after a 2-week period of reaction. With an equimolecular amount of Br₂ in CH₂Cl₂,

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Table IV. Fractional Atomic Coordinates ($\times 10^4$)

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Fe	-2177 (1)	-2978 (1)	-3976 (2)	C(41)	-3346 (5)	1672 (4)	-2252 (10)
P(1)	-2868 (2)	-2374 (1)	-4211 (4)	C(42)	-3863 (5)	1827 (4)	-2788 (10)
P(2)	-2618 (2)	-3564 (2)	-5244 (4)	C(43)	-4203 (5)	1420 (4)	-3366 (10)
P(3)	-1751 (2)	-2415 (1)	-2612 (4)	C(44)	-5050 (5)	609 (5)	-4585 (13)
P(4)	-1378 (2)	-3377 (2)	-4435 (4)	C(45)	-5065 (5)	925 (5)	-5706 (13)
O(1)	-2512 (5)	-3681 (5)	-1830 (11)	C(46)	-5572 (5)	1166 (5)	-6113 (13)
C(1)	-2390 (6)	-3388 (7)	-2678 (15)	C(47)	-6063 (5)	1092 (5)	-5399 (13)
O(2)	-2665 (4)	-1741 (4)	-4024 (11)	C(48)	-6048 (5)	777 (5)	-4277 (13)
O(3)	-3121 (4)	-2376 (4)	-5620 (10)	C(49)	-5541 (5)	535 (5)	-3870 (13)
O(4)	-3427 (4)	-2396 (5)	-3384 (12)	H	-1926 (64)	-2522 (65)	-5009 (168)
O(5)	-3274 (4)	-3599 (5)	-4883 (12)	C(2)	-3037 (9)	-1283 (9)	-3922 (24)
O(6)	-2622 (5)	-3500 (4)	-6739 (9)	C(3)	-2661 (10)	-726 (10)	-3825 (26)
O(7)	-2402 (5)	-4192 (4)	-5052 (14)	C(4)	-3634 (12)	-2206 (11)	-5947 (30)
O(8)	-1376 (4)	-1897 (5)	-2979 (9)	C(5)	-3728 (9)	-2223 (8)	-7446 (22)
O(9)	-1333 (4)	-2762 (4)	-1751 (10)	C(6)	-3527 (12)	-2724 (11)	-2269 (27)
O(10)	-2187 (4)	-2165 (4)	-1617 (9)	C(7)	-4064 (10)	-2667 (10)	-1732 (24)
O(11)	-854 (4)	-2950 (6)	-4443 (15)	C(8)	-3694 (11)	-3867 (11)	-5687 (27)
O(12)	-1370 (4)	-3621 (4)	-5830 (10)	C(9)	-4179 (10)	-3957 (11)	-4744 (27)
O(13)	-1115 (7)	-3887 (6)	-3681 (15)	C(10)	-2317 (7)	-3101 (7)	-7469 (17)
B	-4419 (7)	364 (7)	-4108 (18)	C(11)	-2435 (7)	-3229 (7)	-8841 (19)
C(26)	-4522 (4)	-113 (4)	-2881 (9)	C(12)	-2536 (10)	-4664 (13)	-5725 (27)
C(27)	-4644 (4)	101 (4)	-1675 (9)	C(13)	-2562 (11)	-5161 (11)	-4626 (26)
C(28)	-4685 (4)	-264 (4)	-636 (9)	C(14)	-1354 (8)	-1603 (8)	-4119 (22)
C(29)	-4604 (4)	-843 (4)	-803 (9)	C(15)	-909 (9)	-1132 (10)	-3986 (25)
C(30)	-4482 (4)	-1057 (4)	-2010 (9)	C(16)	-901 (10)	-2499 (10)	-1018 (25)
C(31)	-4441 (4)	-692 (4)	-3048 (9)	C(17)	-490 (12)	-2895 (12)	-464 (29)
C(32)	-4129 (6)	59 (4)	-5327 (9)	C(18)	-2064 (7)	-1689 (7)	-785 (18)
C(33)	-3576 (6)	176 (4)	-5703 (9)	C(19)	-2622 (10)	-1513 (9)	-203 (23)
C(34)	-3344 (6)	-99 (4)	-6756 (9)	C(20)	-279 (16)	-3019 (16)	-4633 (37)
C(35)	-3666 (6)	-491 (4)	-7432 (9)	C(21)	-35 (14)	-2580 (15)	-5294 (38)
C(36)	-4219 (6)	-608 (4)	-7056 (9)	C(22)	-1009 (8)	-4094 (8)	-6255 (20)
C(37)	-4451 (6)	-333 (4)	-6003 (9)	C(23)	-1113 (10)	-4212 (11)	-7674 (24)
C(38)	-4027 (5)	857 (4)	-3408 (10)	C(24)	-1197 (20)	-4088 (26)	-2657 (50)
C(39)	-3510 (5)	702 (4)	-2872 (10)	C(25)	-918 (12)	-4633 (13)	-2212 (29)
C(40)	-3170 (5)	1110 (4)	-2294 (10)				

Table V. Selected Bond Distances (Å) and Angles (deg)

Fe-P(1)	2.185 (4)	P(1)-O(2)	1.584 (9)	P(3)-O(8)	1.562 (12)
Fe-P(2)	2.187 (4)	P(1)-O(3)	1.597 (11)	P(3)-O(9)	1.573 (11)
Fe-P(3)	2.202 (4)	P(1)-O(4)	1.583 (11)	P(3)-O(10)	1.583 (10)
Fe-P(4)	2.169 (4)	P(2)-O(5)	1.599 (11)	P(4)-O(11)	1.599 (12)
Fe-C(1)	1.75 (1)	P(2)-O(6)	1.578 (10)	P(4)-O(12)	1.576 (11)
Fe-H	1.64 (16)	P(2)-O(7)	1.586 (11)	P(4)-O(13)	1.572 (15)
C(1)-O(1)	1.16 (2)				
P(1)-Fe-P(2)	89.4 (2)	O(2)-P(1)-O(3)	103.4 (6)	O(11)-P(4)-O(12)	102.6 (7)
P(1)-Fe-P(3)	91.1 (2)	O(2)-P(1)-O(4)	102.5 (6)	O(11)-P(4)-O(13)	100.5 (8)
P(1)-Fe-P(4)	155.8 (2)	O(3)-P(1)-O(4)	101.2 (6)	O(12)-P(4)-O(13)	100.5 (7)
P(1)-Fe-C(1)	103.7 (5)	Fe-P(2)-O(5)	110.5 (5)	P(1)-O(2)-C(2)	123 (1)
P(1)-Fe-H	76 (5)	Fe-P(2)-O(6)	123.2 (5)	P(1)-O(3)-C(4)	126 (1)
P(2)-Fe-P(3)	176.9 (2)	Fe-P(2)-O(7)	111.3 (5)	P(1)-O(4)-C(6)	127 (1)
P(2)-Fe-P(4)	90.2 (2)	O(5)-P(2)-O(6)	103.6 (6)	P(2)-O(5)-C(8)	123 (1)
P(2)-Fe-C(1)	89.2 (5)	O(5)-P(2)-O(7)	103.5 (6)	P(2)-O(6)-C(10)	127 (1)
P(2)-Fe-H	101 (6)	O(6)-P(2)-O(7)	102.6 (6)	P(2)-O(7)-C(12)	129 (1)
P(3)-Fe-P(4)	90.5 (2)	Fe-P(3)-O(8)	125.1 (4)	P(3)-O(8)-C(14)	129 (1)
P(3)-Fe-C(1)	87.7 (5)	Fe-P(3)-O(9)	110.3 (4)	P(3)-O(9)-C(16)	122 (1)
P(3)-Fe-H	82 (5)	Fe-P(3)-O(10)	110.9 (4)	P(3)-O(10)-C(18)	124 (1)
P(4)-Fe-C(1)	100.5 (5)	O(8)-P(3)-O(9)	101.2 (6)	P(4)-O(11)-C(20)	133 (2)
P(4)-Fe-H	80 (5)	O(8)-P(3)-O(10)	103.9 (5)	P(4)-O(12)-C(22)	124 (1)
C(1)-Fe-H	170 (6)	O(9)-P(3)-O(10)	103.0 (6)	P(4)-O(13)-C(24)	134 (3)
Fe-P(1)-O(2)	112.3 (4)	Fe-P(4)-O(11)	113.7 (5)	Fe-C(1)-O(1)	177 (1)
Fe-P(1)-O(3)	112.5 (4)	Fe-P(4)-O(12)	112.1 (4)		
Fe-P(1)-O(4)	122.7 (5)	Fe-P(4)-O(13)	124.6 (6)		

however, the reaction $[\text{FeH}(\text{CO})\text{L}_4]^+ + \text{Br}_2 \rightarrow [\text{FeBr}(\text{CO})\text{L}_4]^+ + \text{HBr}$ was observed and the *trans*- $[\text{FeBr}(\text{CO})\text{L}_4]^+$ complex was isolated.

Figure 1 shows the molecular structure of the cation of one of the new Fe(II) hydrides, *trans*- $[\text{FeH}(\text{CO})\{\text{P}(\text{OEt})_3\}_4]\text{BPh}_4$. The iron atom is surrounded by four triethyl phosphite molecules, one carbonyl group, and one hydride ion in an approximately octahedral configuration. The distortion of the coordination sphere from the ideal octahedral geometry is a steric effect undoubtedly associated with the small size of the hydride ligand and is mainly evidenced by the remarkable deviation from 180° of the P(1)-

Fe-P(4) angle, which is $155.8 (2)^\circ$, and by the C-Fe-P and H-Fe-P angles all falling in the range 76 - 104° . The four Fe-P bond distances are nearly equal and agree closely with those found in six-coordinate phosphite iron(II) complexes.²²⁻²⁵ Longer Fe-P

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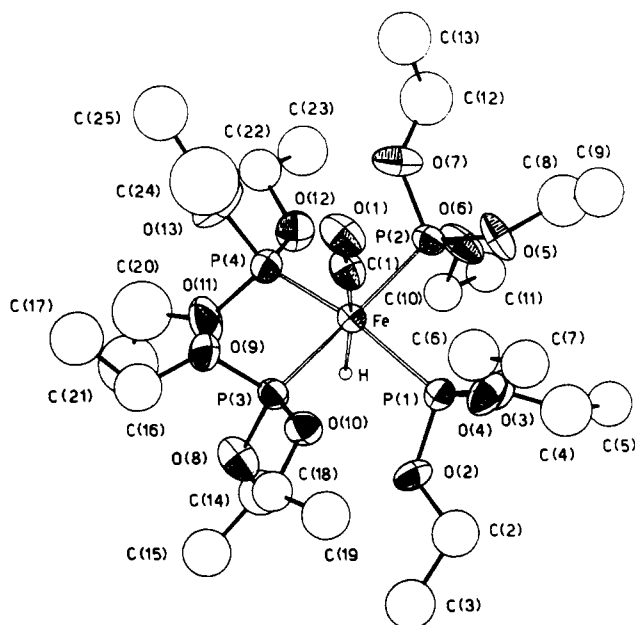


Figure 1. ORTEP diagram and atom-labeling scheme for the $[\text{FeH}(\text{CO})\text{P}(\text{OEt})_3]_4^+$ cation. Thermal ellipsoids are drawn at the 30% probability level. Anisotropic parameters were used only for shaded atoms. H is represented by an arbitrarily small sphere.

bonds had been found previously in $[\text{FeCl}(\text{4-CH}_3\text{C}_6\text{H}_4\text{NC})_2\{\text{PhP}(\text{OEt})_2\}_3]\text{ClO}_4$,²⁶ where the strong π -acceptor effects of the isocyanide group weaken the π -acceptor ability of the phosphite. Most closely relevant to the structure of the present compound are those of $[\text{FeH}_2\{\text{PhP}(\text{OEt})_2\}_4]$ ²⁴ and $[\text{FeH}(\text{N}_2)(\text{P}_4)]\text{Br}\cdot\text{C}_2\text{H}_5\text{OH}$,²⁷ which are both hydrido complexes containing a six-coordinate iron(II) bonded to four P atoms. The former compound differs from ours in having two hydrogen atoms in a cis disposition and consequently the two axial ligands farther away from the iron atom. In the latter compound, in which one of the axial positions is occupied by one atom of the dinitrogen molecule, the marked lengthening of the Fe–P bond distances (~ 0.04 Å) with respect to the present ones is fully consistent with the weaker π -acceptor ability of the phosphines (P_4 = hexaphenyl-1,4,7,10-tetraphosphadecane) when compared with phosphites.

The carbonyl group is trans to the hydride ion and coordinates in the linear mode (Fe–C(1)–O(1) = $177(1)^\circ$). The Fe–C bond distance is 1.75 (1) Å and is within the normal limits found for terminally bonded CO groups.^{25,28} The Fe–H bond distance of 1.64 (16) Å compares favorably with those reported for terminal Fe–H bonds.^{28,29}

Although no symmetry is imposed upon the cation, it has a pseudo- C_{2v} symmetry. In fact, there is a pseudotwofold axis passing through the O(1), C(1), Fe, and H atoms and two approximate mirror planes, each containing two oppositely placed P atoms and two OEt groups, one for each P. In particular, the P(1)O(4)C(6)C(7) and P(4)O(13)C(24)C(25) groupings lie approximately in one of the two mirrors and eclipse the Fe–C bond, while the P(2)O(6)C(10)C(11) and P(3)O(8)C(14)C(15) systems are contained in the other mirror, thus eclipsing the Fe–H bond. Moreover, within each phosphite, two OEt chains adopt an anti-periplanar conformation (Fe–P–O–C torsion angles range from $-174(2)$ to $177(2)^\circ$); the third is syn-periplanar (Fe–P–O–C torsion angles range from $-17(4)$ to $19(2)^\circ$).

The anion is not unusual in any respect, the B–C distances averaging 1.67 (2) Å.

The molecular packing produces no exceptionally short interionic contacts. The two shortest distances are O(1)⋯C(11) ($x, y, z + 1$), 3.32 (2) Å, and C(14)⋯C(41) ($\bar{x} - 1/2, \bar{y}, z - 1/2$), 3.37 (3) Å.

Reactivity with Diazonium Salts. The hydride $[\text{FeH}(\text{CO})\text{P}(\text{OEt})_3]_4^+$ slowly reacts with diazonium salts $\text{ArN}_2^+\text{BF}_4^-$ ($\text{Ar} = 4\text{-CH}_3\text{C}_6\text{H}_4, 4\text{-ClC}_6\text{H}_4$) in dichloromethane to give the diazene complexes $[\text{Fe}(\text{ArNNH})(\text{CO})\text{P}(\text{OEt})_3]_4^{2+}$, which can be isolated as white solids. Monitoring the progress of the reaction by infrared spectra reveals replacement of the $\nu(\text{CO})$ band at 1985 cm^{-1} of the hydride with a new absorption at 2002 cm^{-1} due to the $\nu(\text{CO})$ of the diazene complex. Furthermore, after 8–10 h a new weak band, near 2035 cm^{-1} , appears, attributable to the aqua complex $[\text{Fe}(\text{OH}_2)(\text{CO})\text{L}_4]^{2+}$ formed by substitution of the ArNNH ligand with the small fraction of water present in the solvent used. The $\text{P}(\text{OMe})_3$ and $\text{PhP}(\text{OEt})_2$ hydride derivatives also react with diazonium cations, but the slowness of the reactions prevents separation of pure samples of aryl diazenes.

The new $[\text{Fe}(\text{ArNNH})(\text{CO})\text{P}(\text{OEt})_3]_4^{2+}$ complexes are diamagnetic and 2:1 electrolytes,³⁰ moderately stable as solids, while their solutions decompose in all polar solvents. In addition, elemental analyses and IR and NMR spectra (Table I) are consistent with the proposed formulation. Infrared spectra show $\nu(\text{CO})$ at 2002 cm^{-1} in dichloromethane solution and at $2002\text{--}2001\text{ cm}^{-1}$ in the solid state. A band of medium intensity at 3330 cm^{-1} is also present and may be attributed³¹ to $\nu(\text{NH})$. Furthermore, the presence of the diazene ligand was confirmed by ^1H NMR studies using ^{15}N -labeled ($\text{ArN}=\text{NH}$) and unlabeled complexes. Measurement of the ^{15}N coupling constant for the diazene complexes gives a reliable means of detecting and locating the protonated nitrogen site. The $[\text{Fe}(\text{ArNNH})(\text{CO})\text{L}_4]^{2+}$ complex ($\text{Ar} = 4\text{-CH}_3\text{C}_6\text{H}_4$) shows a broad resonance near δ 13.3 (at δ 13.4 for $\text{Ar} = 4\text{-ClC}_6\text{H}_4$) attributable to the nitrogen-bound proton of the $\text{ArN}=\text{NH}$ moiety. In the ^{15}N -labeled $[\text{Fe}(4\text{-CH}_3\text{C}_6\text{H}_4\text{N}=\text{NH})(\text{CO})\text{L}_4]^{2+}$ derivative³² this broad signal is replaced by a sharp doublet centered at δ 13.26 with $J_{^{15}\text{N}} = 67$ Hz, which is consistent with the presence of the diazene ligand. Finally, a trans geometry can be proposed in solution for these complexes on the basis of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, which, in the temperature range $+30$ to -80 °C, appear as sharp singlets.

Although analogous aryl diazene complexes of Ru,^{5g} Os,^{6b} Pt,^{5a,c} and Rh^{5d,g} are reported to undergo deprotonation to give aryl diazenido derivatives, no evidence of such a type of reaction was obtained in our case. In fact, the reaction of the $[\text{Fe}(\text{ArNNH})(\text{CO})\text{L}_4]^{2+}$ derivatives with triethylamine in CH_2Cl_2 does not occur and the starting material can be recovered unchanged.

The diazene ligand in the $[\text{Fe}(\text{ArNNH})(\text{CO})\text{L}_4]^{2+}$ complexes is a good leaving group and can easily be substituted by several ligands such as CO, isocyanides, and nitriles (see below). In these substitution reactions the $\text{ArN}=\text{NH}$ moiety decomposes to give N_2 and toluene or chlorobenzene, as detected by gas chromatography. The presence of hydrocarbon may also be observed when the diazene complexes spontaneously decompose in solution. Unfortunately, the instability of these diazene derivatives prevents study on the reactivity of the coordinated $\text{ArN}=\text{NH}$ group toward reduction or hydrogenation reactions.

Surprisingly, when the reaction between the $[\text{FeH}(\text{CO})\text{L}_4]^+$ ($\text{L} = \text{P}(\text{OEt})_3$) hydride and the diazonium cations $\text{ArN}_2^+\text{BF}_4^-$ was carried out with acetone as solvent instead of CH_2Cl_2 , the yellow complex $[\text{Fe}\{(\text{CH}_3)_2\text{CO}\}(\text{CO})\text{L}_4](\text{BPh}_4)_2$ was isolated, containing acetone as ligand. The same complex can also be obtained from the diazene derivatives by adding acetone to their dichloromethane solution. Because the hydride does not react with acetone, it is reasonable to presume that, in acetone too, the reaction first gives the diazene complex, which by substitution

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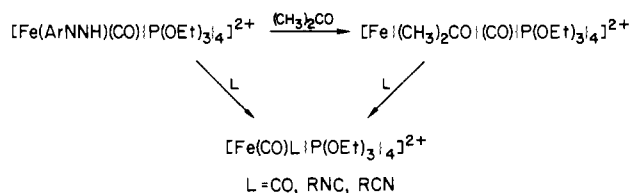
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(31) The $[\text{Ir}(\text{FC}_6\text{H}_3\text{NNH})\text{Cl}(\text{CO})(\text{PPh}_3)_2]^+$ complex exhibited $\nu(\text{NH})$ at 3150 cm^{-1} .^{5e}

(32) The ^{15}N isotope was introduced with use of the labeled diazonium salt $[4\text{-CH}_3\text{C}_6\text{H}_4\text{N}^{15}\text{N}]\text{BF}_4$ prepared from $\text{Na}^{15}\text{NO}_2$ (99% enriched, Stohler Isotope Chemicals) and the arylamine.

Scheme I



reaction with $(\text{CH}_3)_2\text{CO}$ then gives the acetone complex. The $\text{P}(\text{OMe})_3$ and $\text{PhP}(\text{OEt})_2$ hydride derivatives also react in acetone with ArN_2^+ to give the ketone complexes, but the reaction rate is slow and only the $[\text{Fe}\{(\text{CH}_3)_2\text{CO}\}(\text{CO})\{\text{P}(\text{OMe})_3\}_4]^{2+}$ cation can be separated in pure form.

In a synthetic procedure similar to that reported for the $(\text{C}_6\text{H}_5)_2\text{CO}$ complex, a series of stable ketone complexes, *trans*- $[\text{Fe}(\text{CO})\text{L}\{\text{P}(\text{OEt})_3\}_4]^{2+}$ ($\text{L} = (\text{CH}_3)(\text{C}_2\text{H}_5)\text{CO}$, $(\text{CH}_3)(\text{C}_6\text{H}_5)\text{CO}$, $\text{C}_6\text{H}_5\text{CO}$), was prepared. It can be noted that only with methyl alkyl or methyl aryl ketones can the complexes be prepared, whereas with diethyl or ethyl phenyl ketones the synthesis failed, probably owing to the major steric hindrance of these ketones. The properties of the new complexes are shown in Table I. They are all yellow solids, air-stable in both the solid and solution, in which they are diamagnetic and 2:1 electrolytes ($\Lambda_M = 136.1\text{--}126.2 \text{ M}^{-1} \Omega^{-1} \text{ cm}^2$). The infrared spectra show $\nu(\text{CO})$ at $2000\text{--}2009 \text{ cm}^{-1}$ in CH_2Cl_2 solution, while that of the coordinated ketone was observed at $1632\text{--}1685 \text{ cm}^{-1}$. These stretching frequencies are reduced by about 30 cm^{-1} as compared to that of the free ligand.

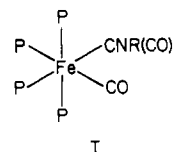
The ^1H NMR spectra of $[\text{Fe}(\text{CO})(\text{RR}'\text{CO})\text{L}_4]^{2+}$ cations in $(\text{CD}_3)_2\text{SO}$ show not only the resonances of four equivalent $\text{P}(\text{OEt})_3$ ligands but also the signals of the ketone protons, generally shifted to low field. Furthermore, in the case of the acetone complexes $[\text{Fe}\{(\text{CH}_3)_2\text{CO}\}(\text{CO})\text{L}_4]^{2+}$, the ligand exchange in hexa-deuterioacetone is observed with the disappearance of the δ 2.31 singlet of the coordinated $(\text{CH}_3)_2\text{CO}$ ligand and the appearance of the signal of the free acetone at δ 2.05. The deuterated $[\text{Fe}\{(\text{CD}_3)_2\text{CO}\}(\text{CO})\text{L}_4]^{2+}$ complex was also prepared, and while the IR spectrum shows $\nu(\text{OC})$ at 1672 cm^{-1} (CH_2Cl_2) for the coordinated $(\text{CD}_3)_2\text{CO}$ ligand, the singlet at δ 2.31 is absent in the NMR spectra. Finally, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra in the temperature range -70 to $+35 \text{ }^\circ\text{C}$ show only one singlet, indicating a *trans* geometry for these ketone complexes too.

Two different bond modes of the carbonyl group to the metal can be considered for these complexes, i.e., a σ -bonded oxygen atom or a π -bonded carbonyl group. The last mode is less common but was proposed for Pd and Pt complexes³³ with dibenzylideneacetone on the basis of the unaltered ^1H NMR spectra of the ligand on complex formation and the disappearance of $\nu(\text{OC})$. In our case, the shift at low field (about 0.2 ppm) shown by the CH_3 group of the ketones together with the presence of $\nu(\text{OC})$ at $1632\text{--}1685 \text{ cm}^{-1}$ suggests a σ -bonded oxygen for the complexes.³⁴ Further support for this coordination mode is given by a comparison of our spectroscopic data with those reported for the $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{L}]^+$ complex³⁵ ($\text{L} = \text{ketones}$), whose crystal structure³⁶ indicates a σ -bonded carbonyl ligand.

Substitution Reactions. The diazene ligand was shown to be a good leaving group in the $[\text{Fe}(\text{ArNNH})(\text{CO})\text{L}_4]^{2+}$ complexes, and reactivity with carbon monoxide, isocyanides, and nitriles allowed us to prepare a new series of cationic iron(II) complexes, as shown in Scheme I. The ketone ligand can also be substituted

by CO, RNC, and RCN in $[\text{Fe}(\text{CO})(\text{RR}'\text{CO})\text{L}_4]^{2+}$ to give the same compounds obtained from the diazene derivatives. Thus, in preparative work, the acetone complex, which is more stable than the diazene complex, was used instead of the ArNNH derivative.

Carbon monoxide reacts with the $[\text{Fe}(\text{ArNNH})(\text{CO})\{\text{P}(\text{OEt})_3\}_4]^{2+}$ cation to give the $[\text{Fe}(\text{CO})_2\text{L}_4]^{2+}$ species, whose infrared spectrum in the CO stretching region shows two strong bands at 2053 and 2090 cm^{-1} in CH_2Cl_2 solution, indicating a *cis* arrangement of the two carbonyl ligands. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum in $(\text{CD}_3)_2\text{CO}$ is an A_2B_2 pattern with $\delta_A = 130.1$, $\delta_B = 127.8$, and $J_{AB} = 121.3 \text{ Hz}$, confirming *cis* geometry I for this compound.



The reaction between aryl isocyanides and both $[\text{Fe}(\text{ArNNH})(\text{CO})\text{L}_4]^{2+}$ and $[\text{Fe}\{(\text{CH}_3)_2\text{CO}\}(\text{CO})\text{L}_4]^{2+}$ in the molar ratio 1:1 proceeds slowly to give the $[\text{Fe}(\text{CO})(\text{RNC})\text{L}_4]^{2+}$ complexes ($\text{L} = \text{P}(\text{OEt})_3$, $\text{P}(\text{OMe})_3$; $\text{R} = \text{C}_6\text{H}_5$, $4\text{-CH}_3\text{C}_6\text{H}_4$, $4\text{-CH}_3\text{OC}_6\text{H}_4$, $4\text{-NO}_2\text{C}_6\text{H}_4$, $2,6\text{-(CH}_3)_2\text{C}_6\text{H}_3$). By increasing the amount of the isocyanide (ratio 1:10), a faster reaction rate results, but no further substitution takes place, $[\text{Fe}(\text{CO})(\text{RNC})\text{L}_4]^{2+}$ being the only product formed. The complexes are diamagnetic, 2:1 electrolytes, and the infrared spectra of dichloromethane solutions (Table II) show $\nu(\text{CO})$ at $2048\text{--}2057 \text{ cm}^{-1}$ and $\nu(\text{CN})$ at $2175\text{--}2162 \text{ cm}^{-1}$, the highest observed for isocyanide complexes³⁷ of iron(II). Their structure in solution can be discussed in terms of *cis* geometry I, as shown by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. An AB_2C multiplet appears for all the isocyanide complexes, which can be simulated with the values listed in Table II.

Aryl cyanides of the type $\text{C}_6\text{H}_5\text{CN}$, $4\text{-CH}_3\text{C}_6\text{H}_4\text{CN}$, and $2\text{-CH}_3\text{C}_6\text{H}_4\text{CN}$ react with both diazene or acetone complexes to give the dicationic $[\text{Fe}(\text{CO})(\text{RCN})\text{L}_4]^{2+}$ derivatives, whose BPh_4^- salts were separated and characterized. The infrared spectra show the $\nu(\text{CN})$ peak at $2261\text{--}2272 \text{ cm}^{-1}$, increased by $34\text{--}41 \text{ cm}^{-1}$ as compared with those of the free nitriles (Table II). This is generally observed for the RCN coordination to a transition metal via σ donation of the lone pair of electrons of the nitrile nitrogen atom.³⁸ In some cases, however, the π -back-bonding ability of the metal gives rise to complexes in which $\nu(\text{CN})$ is generally lowered in coordination.³⁹ Compounds of this type are the iron nitrile $[\text{FeCl}(\text{RCN})(\text{depe})_2]^+$ ($\text{R} = \text{Ph}$; $\text{depe} = 1,2\text{-bis}(\text{diethylphosphino})\text{ethane}$) complexes,⁴⁰ with a reduction of 12 cm^{-1} from the free ligand value.

The different behavior in $\nu(\text{CN})$ shown by our complexes compared to that of the previously reported one, $[\text{FeCl}(\text{RCN})(\text{depe})_2]^+$, can be partly attributed to the great formal charge on the metal ion. Moreover, the presence of good π -acceptor ligands such as the CO and phosphite $\text{P}(\text{OR})_3$ in our complexes should decrease the back-donation of electrons from iron into the nitrile ligands. The increase of $\nu(\text{CN})$ observed in the $[\text{Fe}(\text{CO})(\text{RCN})\text{L}_4]^{2+}$ complexes can also explain why dinitrogen complexes cannot be obtained from the diazene derivatives. In fact, dinitrogen analogues of organonitrile complexes can generally be prepared when $\nu(\text{CN})$ is lowered in coordination.³⁹

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The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the nitrile complexes appear as sharp singlets at 129.6–138.8 ppm, indicating the presence of four equivalent phosphorus nuclei, as expected for the trans arrangement of the carbonyl and nitrile ligands in the complexes.

Acetonitrile reacts with the diazene complexes to give yellow-white products whose elemental analyses and conductivity data agree with those of the $[\text{Fe}(\text{CO})(\text{CH}_3\text{CN})\text{L}_4]^{2+}$ derivative. Although the infrared spectra of both solid and solution samples do not show any absorption in the CN stretching region,⁴¹ the ^1H NMR spectra in hexadeuterioacetone or CD_2Cl_2 , besides the phosphite and BPh_4 signals, show a broad resonance near δ 2.20 attributable to the methyl protons of the acetonitrile ligand. Furthermore, in CD_3CN solvent ligand exchange is observed with the appearance, after 10–20 min, of the singlet at δ 1.96 of the free acetonitrile ligand, thus confirming the proposed formulation for the compound.

Adiponitrile also reacts with the starting Fe(II) complexes but only gives the monosubstituted dication $[\text{Fe}(\text{CO})\{\text{NC}(\text{CH}_2)_4\text{CN}\}\text{L}_4]^{2+}$ at all ligand:complex ratios. The infrared spectrum shows two $\nu(\text{CN})$ bands at 2296 and 2248 cm^{-1} , attributable to the coordinated and free CN group, respectively. An increase of 48 cm^{-1} as compared to the free ligand value is observed, like that found for the aryl cyanide complexes, and suggests similar bonding properties. Finally, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra also show that the alkyl cyanide derivatives have the carbonyl and RCN ligands in the trans position.

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Registry No. *trans*- $[\text{FeH}(\text{CO})\{\text{P}(\text{OMe})_3\}_4]\text{BPh}_4$, 100112-66-1; *trans*- $[\text{FeH}(\text{CO})\{\text{P}(\text{OEt})_3\}_4]\text{BPh}_4$, 95738-79-7; *trans*- $[\text{FeH}(\text{CO})\{\text{PhP}(\text{OEt})_2\}_4]\text{BPh}_4$, 100112-68-3; *trans*- $[\text{FeH}(\text{CO})\{\text{P}(\text{OEt})_3\}_4]\text{Br}$, 100112-69-4; $[\text{Fe}(4\text{-CH}_3\text{C}_6\text{H}_4\text{N}=\text{NH})(\text{CO})\{\text{P}(\text{OEt})_3\}_4](\text{BPh}_4)_2$, 95738-81-1; $[\text{Fe}(4\text{-ClC}_6\text{H}_4\text{N}=\text{NH})(\text{CO})\{\text{P}(\text{OEt})_3\}_4](\text{BPh}_4)_2$, 100112-71-8; $[\text{Fe}(\text{CO})\{(\text{CH}_3)_2\text{CO}\}\{\text{P}(\text{OMe})_3\}_4](\text{BPh}_4)_2$, 100112-73-0; $[\text{Fe}(\text{CO})\{(\text{CH}_3)_2\text{CO}\}\{\text{P}(\text{OEt})_3\}_4](\text{BPh}_4)_2$, 95738-89-9; $[\text{Fe}(\text{CO})\{(\text{CH}_3)(\text{C}_6\text{H}_5)\text{CO}\}\{\text{P}(\text{OEt})_3\}_4](\text{BPh}_4)_2$, 100112-75-2; $[\text{Fe}(\text{CO})\{(\text{CD}_3)_2\text{CO}\}\{\text{P}(\text{OEt})_3\}_4](\text{BPh}_4)_2$, 100112-77-4; $[\text{Fe}(\text{CO})\{(\text{CH}_3)(\text{C}_2\text{H}_5)\text{CO}\}\{\text{P}(\text{OEt})_3\}_4](\text{BPh}_4)_2$, 100112-79-6; $[\text{Fe}(\text{CO})\{(\text{C}_5\text{H}_{10})\text{CO}\}\{\text{P}(\text{OEt})_3\}_4](\text{BPh}_4)_2$, 100112-81-0; $[\text{Fe}(\text{H}_2\text{O})(\text{CO})\{\text{P}(\text{OEt})_3\}_4](\text{BPh}_4)_2$, 100112-83-2; $[\text{FeCl}(\text{CO})\{\text{P}(\text{OMe})_3\}_4]\text{BPh}_4$, 100112-85-4; $[\text{FeCl}(\text{CO})\{\text{P}(\text{OEt})_3\}_4]\text{BPh}_4$, 100112-87-6; $[\text{FeCl}(\text{CO})\{\text{PhP}(\text{OEt})_2\}_4]\text{BPh}_4$, 100112-89-8; *cis*- $[\text{FeBr}(\text{CO})\{\text{P}(\text{OEt})_3\}_4]\text{Br}$, 100112-90-1; $[\text{Fe}(\text{CO})(4\text{-CH}_3\text{C}_6\text{H}_4\text{NC})\{\text{P}(\text{OEt})_3\}_4]^{2+}$, 100227-13-2; $[\text{Fe}(\text{CO})(\text{C}_6\text{H}_5\text{NC})\{\text{P}(\text{OEt})_3\}_4]^{2+}$, 100112-91-2; $[\text{Fe}(\text{CO})(4\text{-CH}_3\text{OC}_6\text{H}_4\text{NC})\{\text{P}(\text{OEt})_3\}_4]^{2+}$, 100112-92-3; $[\text{Fe}(\text{CO})(4\text{-NO}_2\text{C}_6\text{H}_4\text{NC})\{\text{P}(\text{OEt})_3\}_4]^{2+}$, 100112-93-4; $[\text{Fe}(\text{CO})\{2,6\text{-}(\text{CH}_3)_2\text{C}_6\text{H}_3\text{NC}\}\{\text{P}(\text{OEt})_3\}_4]^{2+}$, 100112-94-5; $[\text{Fe}(\text{CO})(4\text{-CH}_3\text{C}_6\text{H}_4\text{CN})\{\text{P}(\text{OMe})_3\}_4]^{2+}$, 100112-95-6; $[\text{Fe}(\text{CO})(4\text{-CH}_3\text{C}_6\text{H}_4\text{CN})\{\text{P}(\text{OEt})_3\}_4]^{2+}$, 100227-14-3; $[\text{Fe}(\text{CO})(\text{C}_6\text{H}_5\text{CN})\{\text{P}(\text{OEt})_3\}_4]^{2+}$, 100112-96-7; $[\text{Fe}(\text{CO})(2\text{-CH}_3\text{C}_6\text{H}_4\text{CN})\{\text{P}(\text{OEt})_3\}_4]^{2+}$, 100112-97-8; $[\text{Fe}(\text{CO})(\text{CH}_3\text{CN})\{\text{P}(\text{OEt})_3\}_4]^{2+}$, 100112-98-9; $[\text{Fe}(\text{CO})\{\text{NC}(\text{CH}_2)_4\text{CN}\}\{\text{P}(\text{OEt})_3\}_4]^{2+}$, 100112-99-0; $[\text{Fe}(\text{CO})_2\{\text{P}(\text{OEt})_3\}_4]^{2+}$, 100227-15-4; $[\text{Fe}(\text{CO})(4\text{-CH}_3\text{C}_6\text{H}_4\text{NC})\{\text{P}(\text{OMe})_3\}_4]^{2+}$, 100113-00-6; $4\text{-CH}_3\text{C}_6\text{H}_4\text{N}_2^+\text{BF}_4^-$, 459-44-9; $4\text{-ClC}_6\text{H}_4\text{N}_2^+\text{BF}_4^-$, 673-41-6; Zn, 7440-66-6.

Supplementary Material Available: Tables of structure factors and thermal parameters and a full list of bond lengths, bond angles, and torsion angles (20 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, and ^{195}Pt NMR Solution Studies of a Reactive Binuclear Platinum(III) Complex: $[\text{Pt}_2(\text{en})_2(\text{C}_5\text{H}_4\text{NO})_2(\text{NO}_2)(\text{NO}_3)](\text{NO}_3)_2 \cdot 0.5\text{H}_2\text{O}$

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Oxidation of the α -pyridonate- ($\text{C}_5\text{H}_4\text{NO}^-$) bridged diplatinum(II) complex $[\text{Pt}_2(\text{en})_2(\text{C}_5\text{H}_4\text{NO})_2]^{2+}$ (2), where en = ethylenediamine, in nitric acid leads to the formation of a metal-metal-bonded diplatinum(III) complex, $[\text{Pt}_2(\text{en})_2(\text{C}_5\text{H}_4\text{NO})_2(\text{NO}_2)(\text{NO}_3)]^{2+}$ (1). In the structure of 1, two (ethylenediamine)diplatinum(III) units are linked by a metal-metal single bond and two α -pyridonate ligands bridging in a head-to-head fashion. The 2.6382 (6) Å Pt-Pt bond axis is capped by nitrite, Pt-N = 2.109 (1) Å, and nitrate, Pt-O = 2.307 (9) Å, ligands. These Pt-axial ligand distances nicely illustrate a structural trans influence mediated by the metal-metal bond. The coordinated nitrite group is disordered over two positions about the Pt-N axis and is bonded to the platinum atom having two N- and two O-donor ligands. As shown by ^{195}Pt NMR spectroscopy, 1 has a binuclear, metal-metal-bonded structure in freshly prepared aqueous or dimethylformamide (DMF) solutions. In DMF the platinum resonances occur at +541 (PtN_3O_2) and -1141 (PtN_4O) ppm from $[\text{PtCl}_6]^{2-}$, with $J(^{195}\text{Pt}-^{195}\text{Pt}) = 6850$ Hz. Decomposition of 1 to form 2 occurs slowly in solution, as revealed by ^{195}Pt NMR spectroscopy. Reductive elimination of nitrite (NO_2^-) to form the nitronium (NO_2^+) ion is postulated to explain this decomposition, since nitrobenzene or *p*-nitrophenol is generated in aqueous solutions of 1 containing tetraphenylborate or phenol, respectively. The nitrate salt of compound 1, $[\text{Pt}(\text{en})_2(\text{C}_5\text{H}_4\text{NO})_2(\text{NO}_2)(\text{NO}_3)](\text{NO}_3)_2 \cdot 0.5\text{H}_2\text{O}$, crystallizes in the monoclinic space group $P2_1/c$ with $a = 17.934$ (1) Å, $b = 11.491$ (1) Å, $c = 13.507$ (1) Å, $\beta = 108.84$ (1)°, $V = 2634$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 2.369$ g cm⁻³, and $\rho_{\text{obsd}} = 2.379$ (5) g cm⁻³. The structure was refined to $R = 0.035$ using 2686 diffractometer data with $F_o > 4\sigma(F_o)$.

Introduction

Until recently, there were few examples of complexes containing platinum in the +3 oxidation state. Binuclear species comprise the vast majority of structurally characterized platinum(III) complexes and therefore provide the best opportunity to probe the structural properties and chemical reactivity of this oxidation state.¹ Platinum-platinum single-bond formation is a natural consequence of the d^7-d^7 electronic configuration in these binuclear complexes, all of which contain two or more bridging ligands.

Binuclear *cis*-diammineplatinum(III) complexes, bridged by two 1-methyluracilate² or two α -pyridonate³ ligands in either a head-to-head or head-to-tail manner, have been previously described. They can be prepared by chemical or electrochemical oxidation of the corresponding platinum(II) dimers³ or tetranuclear

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