the lines is also illustrated in Figure 2. The two components of ν_{10} are separated by 10 ± 1 cm^{-1}, in agreement with the low-temperature data.

An interpretation based on a core-size difference rather than a difference in planarity of the macrocycle is unlikely because the shifts in ν_3, ν_2, and ν_{10} (−5, −7, −11 cm^{-1}) of the ruffled form relative to the planar form in solution are proportional to the shifts of the tetragonal crystalline form relative to either the triclinic A form (−7, −11, −18 cm^{-1}) or the B form (−11, −13, −21 cm^{-1}). Also, the shift in ν_2 is larger than the shift in ν_3. In contrast, the shifts predicted from an increase in core size are smaller for ν_2 than for ν_3;[17] thus, the observed pattern of shifts in the core-size markers favors the ruffling interpretation. The differences in core-size marker line frequencies for the two solution forms comprise 50–70% of the differences observed for the two crystalline forms. The smaller frequency differences observed in solution suggest that the degree of ruffling is less in solution.

The enhanced contribution from the ruffled form at 406.7 nm indicates a red shift in the Soret absorption maximum for the ruffled form of NiOEP, relative to the absorption maximum of the planar solution form at 393 nm. Although we have not detected a shoulder in the absorption spectrum at 295 K or at 77 K, iterative extended Hückel calculations for the planar and the ruffled structures predict a red shift for the Soret and α bands of 410 and 360 cm^{-1}, respectively. IEH MO calculations were carried out with a program provided by M. Gouterman and E. R. Davidson. The molecular geometries used were those of the triclinic A and tetragonal crystal structures. The shift in the positions of the observed Q (α) and B (Soret) transitions was determined by using the predicted energies of the four frontier orbitals (a_{1u}, a_{2u}, and e_g*). The shifts were calculated by the method of Gouterman[18] and Shelnutt.[19] The primary effect of ruffling is destabilization of all of the frontier orbitals. In detail, both the a_{1u} and a_{2u} orbitals are destabilized more than the e_g*, so that the separation between the HOMOs and LUMOs is smaller for the ruffled structure. This accounts for the red shift in the spectrum.

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The full implication of ruffled conformations on nickel–tetrapyrrole chemistry is unclear at present. Multiple forms have recently been detected in nickel tetrapyrroles related to cofactor F_{430}.[22,23] Native F_{430} is expected to be more planar than its heat-extracted form, the 12,13-diepimer.[11,24] It is thought that the degree of planarity in these two F_{430} forms determines their relative axial ligand affinities[11] and may affect other properties including catalytic activity. An increased degree of ruffling can also explain the observed differences in the dynamics of axial ligand photodissociation for the reduced nickel tetrapyrroles (such as the F_{430} model compound)[23,25] compared with the more planar nickel porphyrins.[26]

In particular, for NiOEP the presence of multiple forms at room temperature strongly suggests that a reinterpretation of previous work on the vibrational analysis of porphyrins may be necessary, especially since NiOEP has been used as a reference structure. Because of the existence of multiple forms in solution and because of the large differences between the low-frequency vibrations of the tetragonal and triclinic forms,[7] some vibrations may have been identified incorrectly in the past. Also, the existence of a ruffled equilibrium conformation suggests that a normal coordinate analysis based on the nonplanar structure might aid in assignment of the out-of-plane vibrational modes.[3] The existence of both planar and ruffled species in solution also explains some of the anomalous spectroscopic behavior of nickel porphyrins that occurs upon aggregation[27] and upon π–π complex formation.[28]

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New Molecular Hydrogen Iron(II) Complexes: Synthesis, Characterization, and Reactivity with Aryldiazonium Cations

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Abstract: Dihydrogen complexes of the type $[FeH(\eta^2\text{-}H_2)P_4]BPh_4$ [P = $PhP(OEt)_2$ and $P(OEt)_3$] were prepared by allowing the dihydride FeH_2P_4 to react at −80 °C with $HBF_4{\cdot}Et_2O$ in ethanol. Variable-temperature ^{1}H and $^{31}P\{^1H\}$ NMR spectra and T_1 measurements of the complexes are reported. Ligand-substitution reactions with CO, isocyanide, nitrile, and phosphite afforded the new monohydrides $[FeHLP_4]BPh_4$ [L = CO, 4-$CH_3C_6H_4NC$, 4-$CH_3OC_6H_4NC$, 4-ClC_6H_4NC, 2,6-$(CH_3)_2C_6H_3NC$, 4-$CH_3C_6H_4CN$, $CH_3(CH_2)_2CN$, $P(OEt)_3$, and $PhP(OEt)_2$]. Furthermore, the reactivity with aryldiazonium cations of both molecular hydrogen $[FeH(\eta^2\text{-}H_2)P_4]^+$ and hydride $[FeHLP_4]^+$ derivatives was examined and led to the synthesis of bis(aryldiazenido) $[Fe(ArN_2)_2P_3]^{2+}$ (Ar = 4-$CH_3C_6H_4$ and 4-$CH_3OC_6H_4$) and monodiazene $[Fe(ArN{=}NH)LP_4]^{2+}$ (L = nitrile) complexes, respectively. Their characterization by infrared, ^{1}H, and $^{31}P\{^1H\}$ NMR data is also reported.

There has recently been considerable interest in the chemistry of dihydrogen complexes of the transition metals, not only because they may serve as models for the important process of oxidative addition of the dihydrogen, but also because of their relevance

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to homogeneous catalysis.[1-10] In this context, a number of molecular hydrogen complexes of several metals have been reported, mainly with tertiary phosphine ligands.[1-5] However, no example of such a complex containing phosphite $P(OR)_3$ ligands is known, although their different electronic and steric properties may give further information on the properties of this new class of compounds, as well as on the factors governing the dihydrogen vs dihydride equilibrium. In this paper we report the synthesis and characterization of new iron(II) molecular hydrogen complexes with phosphite ligands. We are also interested in the chemistry of aryldiazo and aryldiazene complexes and have previously reported[11] the reactivity of mono- and dihydride iron(II) complexes with aryldiazonium cations, which allowed the synthesis of the first bis(diazene) complexes. However, no data are available on the reaction of dihydrogen derivatives toward ArN_2^+, and an investigation on the reactivity of our hydride–dihydrogen iron(II) complexes with aryldiazonium cations was therefore undertaken, with the aim of comparing the results with those obtained with "classical" dihydride FeH_2P_4 derivatives. Furthermore, the presence of both H_2 and H^- bonded to an iron atom may give information on the possibilities of the reduction, in this system, of an ArN=N group to an arylhydrazine molecule. The results of these studies are also presented here.

Experimental Section

General Comments. Unless otherwise noted, all manipulations were carried out in air-free atmosphere (e.g. H_2 and/or argon) by using standard Schlenk and syringe techniques or in a Vacuum Atmosphere drybox. All solvents used were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. Diethoxyphenylphosphine was prepared by the method of Rabinowitz and Pellon;[12] triethyl phosphite was an Ega Chemie product and purified by distillation under nitrogen. Deuterium was obtained[13] from D_2O and Na; high-purity HD was prepared from $LiAlH_4$ and D_2O (99.8%) following the reported method.[14] Diazonium salts were obtained in the usual way described in the literature.[15] The labeled diazonium salt $[4\text{-}CH_3C_6H_4N{\equiv}^{15}N]BF_4$ was prepared from $Na^{15}NO_2$ (99% enriched, Stohler Isotope Chemicals) and the arylamine. Substituted phenyl isocyanides were obtained by the phosgene method of Ugi et al.[16] Other reagents were purchased from commercial sources in the highest available purity and used as received.

Infrared spectra were recorded on a Perkin-Elmer Model 683. Solution ^1H NMR spectra were obtained with Varian EM-390 and Varian FT-80A spectrometers. Spectra were recorded at temperature varying between −85 and +34 °C unless otherwise noted, and are referred to internal tetramethylsilane. Fourier-mode, proton-noise-decoupled ^{31}P NMR spectra were collected on a Varian FT-80A spectrometer operating at 32.203 MHz. All chemical shifts are reported with respect to 85% H_3PO_4, with downfield shifts considered positive. Conductivities of 10^{-3} M solutions of the complexes in acetone at 25 °C were measured with a Radiometer CDM 83 instrument. Solution susceptibilities were determined by the Evans method.[17]

Synthesis of the Complexes. Dihydride species FeH_2P_4 [P = $PhP(OEt)_2$ and $P(OEt)_3$] were prepared according to the procedure previously reported.[18] Deuterides FeD_2P_4 were obtained in the same way by using $NaBD_4$ as reagent.

$[FeH(\eta^2\text{-}H_2)P_4]BPh_4$ [P = $PhP(OEt)_2$ (1), $P(OEt)_3$ (1*)]. A slight excess of $HBF_4\cdot Et_2O$ (54% solution) (ca. 1.2 mmol, 0.17 mL) was slowly added to a suspension of FeH_2P_4 (1 mmol) in 20 mL of ethanol cooled to −80 °C. The reaction mixture was brought to 0 °C in 10–15 min and stirred until a pale-yellow solution was obtained (5–10 min). The addition of $NaBPh_4$ (1.2 mmol, 0.41 g) afforded a pale-yellow precipitate, which was filtered and crystallized by dissolving in CH_2Cl_2 (4–5 mL) and, after filtration, adding ethanol in excess (20–40 mL); yield ≥75%.

Anal. Calcd for **1**: C, 65.65; H, 7.15. Found: C, 65.41; H, 7.06. Λ_M = 93.5 Ω^{-1} M^{-1} cm^2. ^1H NMR (CD_2Cl_2) δ 7.41, 6.95 (m, 40 H, Ph), 3.36 (m, 16 H, CH_2), 1.00 (t, 24 H, CH_3).

Calcd for **1***: C, 55.29; H, 8.02. Found: C, 55.10; H, 7.90. Λ_M = 95.3 Ω^{-1} M^{-1} cm^2. ^1H NMR (CD_2Cl_2) δ 7.29, 6.95 (m, 20 H, Ph), 3.95 (m, 24 H, CH_2), 1.24 (t, 36 H, CH_3).

$[FeH(\eta^2\text{-}H_2)\{PhP(OEt)_2\}_4]BF_4$ (1a). To a solution of $FeH_2[PhP(OEt)_2]_4$ (1 mmol, 0.85 g) in 20 mL of diethyl ether a slight excess of $HBF_4\cdot Et_2O$ (ca. 1.2 mmol, 0.17 mL) was added at −80 °C and the reaction mixture was brought to 0 °C. After about 10 min of stirring a white solid separated out, which was filtered and crystallized from CH_2Cl_2 (5 mL) and diethyl ether (30–40 mL); yield ≥60%.

Anal. Calcd: C, 51.19; H, 6.77. Found: C, 51.08; H, 6.83. Λ_M = 141 Ω^{-1} M^{-1} cm^2. ^1H NMR (CD_2Cl_2) δ 7.39 (m, 20 H, Ph), 3.34 (m, 16 H, CH_2), 0.99 (t, 24 H, CH_3), −8.02 (qi, J_{PH}(app) = 22 Hz, H hydride).

$[FeH(RNC)\{PhP(OEt)_2\}_4]BPh_4$ (2: R = 4-$CH_3C_6H_4$ (a), 4-$CH_3OC_6H_4$ (b), 2,6-$(CH_3)_2C_6H_3$ (c), 4-ClC_6H_4 (d), 4-$NO_2C_6H_4$ (e)). The appropriate isocyanide (0.5 mmol) was added to a solution of $[FeH(\eta^2\text{-}H_2)\{PhP(OEt)_2\}_4]BPh_4$ (0.43 mmol, 0.5 g) in 10 mL of dichloromethane and the reaction mixture was stirred for 1 h. The solvent was removed under reduced pressure and the resulting oil was triturated with ethanol (5 mL) to give a white solid that was crystallized from CH_2Cl_2 (5 mL) and ethanol (20 mL); yield ≥90%. The physical constants and elemental analyses follow.

Anal. Calcd for **2a**: C, 67.24; H, 6.90; N, 1.09. Found: C, 66.92; H, 6.92; N, 1.02. mp 175 °C. Λ_M = 83.2 Ω^{-1} M^{-1} cm^2. ^1H NMR (CD_2Cl_2) δ 7.24, 7.00 (m, 44 H, Ph), 3.64 (m, 16 H, CH_2), 2.41 (s, 3 H, CH_3), 1.11 (t, 24 H, CH_3 phos).

Calcd for **2b**: C, 66.42; H, 6.81; N, 1.08. Found: C, 66.34; H, 6.85; N, 1.01. mp 78 °C. Λ_M = 90.2 Ω^{-1} M^{-1} cm^2. ^1H NMR [$(CD_3)_2CO$] δ 7.56, 7.33, 6.88 (m, 44 H, Ph), 3.75 (m, 16 H, CH_2), 3.89 (s, 3 H, CH_3), 1.16 (t, 24 H, CH_3 phos).

Calcd for **2c**: C, 67.44; H, 6.98; N, 1.08. Found: C, 67.50; H, 6.84; N, 0.95. mp 152 °C. Λ_M = 84.3 Ω^{-1} M^{-1} cm^2. ^1H NMR (CD_2Cl_2) δ 7.17, 6.87 (m, 43 H, Ph), 3.51 (m, 16 H, CH_2), 2.34 (s, 6 H, CH_3), 0.99 (t, 24 H, CH_3 phos).

Calcd for **2d**: C, 65.27; H, 6.56; N, 1.07. Found: C, 65.13; H, 6.48; N, 0.95. mp 174 °C. Λ_M = 83.3 Ω^{-1} M^{-1} cm^2. ^1H NMR (CD_2Cl_2) δ 7.33, 7.16, 6.87 (m, 44 H, Ph), 3.56 (m, 16 H, CH_2), 1.03 (t, 24 H, CH_3).

Calcd for **2e**: C, 64.75; H, 6.51; N, 2.13. Found: C, 64.49; H, 6.50; N, 2.04. mp 175 °C. Λ_M = 86.3 Ω^{-1} M^{-1} cm^2. ^1H NMR (CD_2Cl_2) δ 8.26, 7.18, 6.87 (m, 44 H, Ph), 3.59 (m, 16 H, CH_2), 1.05 (t, 24 H, CH_3).

$[FeH(4\text{-}CH_3C_6H_4NC)\{P(OEt)_3\}_4]BPh_4$ (2a*). This compound was

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prepared following the method reported above, starting from $[FeH(\eta^2\text{-}H_2)\{P(OEt)_3\}_4]BPh_4$; yield ≥85%.

Anal. Calcd: C, 58.09; H, 7.66; N, 1.21. Found: C, 58.12; H, 7.60; N, 1.28. mp 126 °C dec. Λ_M = 92.0 Ω^{-1} M^{-1} cm^2. ^1H NMR [$(CD_3)_2CO$] δ 7.26, 6.87 (m, 24 H, Ph), 4.13 (m, 24 H, CH_2), 2.32 (s, 3H, CH_3), 1.28 (t, 36 H, CH_3 phos).

$[FeH(RCN)\{PhP(OEt)_2\}_4]BPh_4$ (3: R = 4-$CH_3C_6H_4$ (a), $CH_3CH_2CH_2$ (b)). To a solution of $[FeH(\eta^2\text{-}H_2)\{PhP(OEt)_2\}_4]BPh_4$ (0.43 mmol, 0.5 g) in dichloromethane (15 mL) a slight excess of the appropriate nitrile (0.6 mmol) was added and the solution stirred for 2 h. Removal of the solvent under reduced pressure gave an oily product that was treated with ethanol (8 mL). The pale-yellow solid obtained was filtered and crystallized from CH_2Cl_2 (5 mL)/ethanol (20 mL); yield ≥80%.

Anal. Calcd for **3a**: C, 67.24; H, 6.90; N, 1.09. Found: C, 67.09; H, 6.92; N, 1.02. mp 141 °C. Λ_M = 84.4 Ω^{-1} M^{-1} cm^2. ^1H NMR [$(CD_3)_2CO$] δ 7.47, 7.31, 6.87 (m, 44 H, Ph), 3.74 (m, 16 H, CH_2), 2.46 (s, 3 H, CH_3), 1.16 (t, 24 H, CH_3 phos).

Calcd for **3b**: C, 66.02; H, 7.09; N, 1.13. Found: C, 65.81; H, 7.21; N, 1.08. mp 126 °C. Λ_M = 83.6 Ω^{-1} M^{-1} cm^2. ^1H NMR [$(CD_3)_2CO$] δ 7.34, 6.87 (m, 40 H, Ph), 3.69 (m, 16 H, CH_2 phos), 3.33 m, 2.81 t (4 H, CH_2 nitrile), 1.75 (q, 3 H, CH_3 nitrile), 1.14 (t, 24 H, CH_3 phos).

$[FeH(4\text{-}CH_3C_6H_4CN)\{P(OEt)_3\}_4]BPh_4$ (3a*). This compound was prepared exactly as for **3** starting from $[FeH(\eta^2\text{-}H_2)\{P(OEt)_3\}_4]BPh_4$; yield ≥75%.

Anal. Calcd: C, 58.09; H, 7.66; N, 1.21. Found: C, 58.07; H, 7.81; N, 1.09. mp 85 °C dec. Λ_M = 98.1 Ω^{-1} M^{-1} cm^2. ^1H NMR [$(CD_3)_2CO$] δ 7.31, 6.88 (m, 24 H, Ph), 4.17 (m, 24 H, CH_2), 2.38 (s, 3 H, CH_3), 1.28, 1.24 (t, 36 H, CH_3 phos).

$[FeHP_5]BPh_4$ (4: P = $PhP(OEt)_2$ (a), $P(OEt)_3$ (a*)). The appropriate phosphite (0.5 mmol) was added to a solution of $[FeH(\eta^2\text{-}H_2)P_4]BPh_4$ (0.43 mmol) in dichloromethane (20 mL) and the mixture was stirred for 1 h. The solvent was removed and the resulting oil was triturated with ethanol (8 mL) to give a white solid that was crystallized from ethanol; yield ≥80%.

Anal. Calcd for **4a**: C, 65.01; H, 7.08. Found: C, 64.89; H, 7.01. mp 91 °C dec. Λ_M = 83.2 Ω^{-1} M^{-1} cm^2. ^1H NMR [$(CD_3)_2CO$] δ 7.35, 6.86 (m, 45 H, Ph), 3.53 (m, 20 H, CH_2), 1.16 (t, 30 H, CH_3).

Calcd for **4a***: C, 53.74; H, 8.02. Found: C, 53.74; H, 8.02. mp 125 °C. Λ_M = 92.1 Ω^{-1} M^{-1} cm^2. ^1H NMR [$(CD_3)_2CO$] δ 7.33, 6.88 (m, 20 H, Ph), 4.10 (m, 30 H, CH_2), 1.29 (t, 45 H, CH_3).

$[FeH\{P(OEt)_3\}\{PhP(OEt)_2\}_4]BPh_4$ (4b) and $[FeH\{PhP(OEt)_2\}\{P(OEt)_3\}_4]BPh_4$ (4b*). These compounds were prepared following the method reported above for **4a**.

Anal. Calcd for **4b**: C, 62.97; H, 7.25. Found: C, 63.09; H, 7.14. mp 110 °C dec. Λ_M = 84.0 Ω^{-1} M^{-1} cm^2. ^1H NMR [$(CD_3)_2CO$] δ 7.77, 7.37, 6.88 (m, 40 H, Ph), 3.75 (m, 22 H, CH_2), 1.22, 1.18, 1.16, 1.09 (t, 33 H, CH_3).

Calcd for **4b***: C, 56.23; H, 7.81. Found: C, 55.97; H, 7.75. mp 105 °C. Λ_M = 89.0 Ω^{-1} M^{-1} cm^2. ^1H NMR [$(CD_3)_2CO$], δ: 8.04, 7.38, 6.88 (m, 25 H, Ph), 4.08 (m, 28 H, CH_2), 1.33, 1.25, 1.19 (t, 42 H, CH_3).

$[Fe(ArN_2)_2\{P(OEt)_3\}_3](BPh_4)_2$ (5*: Ar = 4-$CH_3C_6H_4$ (a), 4-$CH_3OC_6H_4$ (b)). A solution of $[FeH(\eta^2\text{-}H_2)\{P(OEt)_3\}_4]BPh_4$ (0.7 mmol, 0.73 g) in dichloromethane (20 mL) was cooled to −80 °C and quickly transferred into a reaction flask containing an excess of the appropriate diazonium salt (2.2 mmol). The reaction mixture was brought to room temperature in 10–15 min and stirred for 1 h. The unreacted diazonium salt was removed by filtration and the resulting solution evaporated to dryness. The brown oil obtained was treated with ethanol (10 mL) containing $NaBPh_4$ (1 mmol, 0.34 g) to give a red solid that was filtered and crystallized by dissolving the product in CH_2Cl_2 (5 mL) and, after filtration, adding ethanol drop by drop until a solid separated out; yield ≥65%.

Anal. Calcd for **5a***: C, 67.14; H, 6.97; N, 3.92. Found: C, 66.95; H, 6.89; N, 3.74. mp 100 °C dec. Λ_M = 160.6 Ω^{-1} M^{-1} cm^2. ^1H NMR [$(CD_3)_2CO$] δ 7.59, 7.33, 6.88 (m, 48 H, Ph), 4.34 (m, 18 H, CH_2), 2.46 (s, 6 H, CH_3), 1.29 (t, 27 H, CH_3 phos).

Calcd for **5b***: C, 65.67; H, 6.82; N, 3.83. Found: C, 65.40; H, 6.79; N, 3.71. mp 73 °C dec. Λ_M = 164.0 Ω^{-1} M^{-1} cm^2. ^1H NMR [$(CD_3)_2CO$] δ 7.33, 6.88 (m, 48 H, Ph), 4.22 (m, 18 H, CH_2), 3.84 (s, 6 H, CH_3), 1.41, 1.28 (t, 27 H, CH_3 phos).

$[Fe(4\text{-}CH_3C_6H_4N{\equiv}^{15}N)_2\{P(OEt)_3\}_3](BPh_4)_2$ (5a$_1$*). This compound was prepared following the method reported above, using the $[4\text{-}CH_3C_6H_4N{\equiv}^{15}N]BF_4$ diazonium salt; yield ≥65%.

Anal. Calcd: C, 67.05; H, 6.96; N, 4.05. Found: C, 66.89; H, 7.00; N, 3.92. mp 97 °C dec. Λ_M = 178.0 Ω^{-1} M^{-1} cm^2. ^1H NMR [$(CD_3)_2CO$] δ 7.52, 7.33, 6.88 (m, 48 H, Ph), 4.27 (m, 18 H, CH_2), 2.41 (s, 6 H, CH_3), 1.25 (t, 27 H, CH_3 phos).

$[Fe(4\text{-}CH_3C_6H_4N_2)_2\{PhP(OEt)_2\}_3](BPh_4)_2$ (5a). This compound was prepared exactly as for **5a*** starting from $[FeH(\eta^2\text{-}H_2)\{PhP(OEt)_2\}_4]BPh_4$; yield ≥70%.

Anal. Calcd: C, 72.35; H, 6.53; N, 3.67. Found: C, 72.20; H, 6.60; N, 3.58. mp 102 °C dec. Λ_M = 172 Ω^{-1} M^{-1} cm^2. ν(NN) (CH_2Cl_2), 1798 sh, 1774 s cm^{-1}. It should be noted that the same compound had previously been prepared by us from reaction of the hydride $FeH_2[PhP(OEt)_2]_4$ with aryldiazonium cations.[11b]

$[Fe(4\text{-}CH_3C_6H_4N{=}NH)(4\text{-}CH_3C_6H_4CN)P_4](BPh_4)_2$ [P = $PhP(OEt)_2$ (6), $P(OEt)_3$ (6*)]. An excess of the aryldiazonium salt $[4\text{-}CH_3C_6H_4N_2]BF_4$ (1.2 mmol, 0.25 g) was added to a solution of $[FeH(4\text{-}CH_3C_6H_4CN)P_4]BPh_4$ (0.4 mmol) in 20 mL of dichloromethane. The reaction mixture was stirred for 3 h and then filtered to remove the unreacted diazonium salt. The resulting solution was evaporated to dryness and the oil obtained was stirred with ethanol (10 mL) containing $NaBPh_4$ (0.8 mmol, 0.27 g). A yellow solid separated out, which was filtered and crystallized by dissolving the product in CH_2Cl_2 (5 mL) and, after filtration, adding ethanol drop by drop until a solid separated out; yield ≥65%. Anal. Calcd for **6**: C, 71.74; H, 6.72; N, 2.44. Found: C, 71.27; H, 6.80; N, 2.32. mp 121 °C. Λ_M = 176.0 Ω^{-1} M^{-1} cm^2. ^1H NMR [$(CD_3)_2CO$] δ 13.63 (m, 1 H, NH), 7.76, 7.25, 6.85 (m, 68 H, Ph), 4.05 (m, 16 H, CH_2), 2.42, 2.36 (s, 6 H, CH_3 diazene and CH_3 nitrile), 1.39, 0.96 (t, 24 H, CH_3 phos).

Calcd for **6***: C, 65.46; H, 7.26; N, 2.63. Found: C, 65.25; H, 7.08; N, 2.47. mp 124 °C. Λ_M = 181.0 Ω^{-1} M^{-1} cm^2. ^1H NMR [$(CD_3)_2CO$] δ 14.18 (m, 1 H, NH), 7.55, 7.33, 6.87 (m, 48 H, Ph), 4.33 (m, 24 H, CH_2), 2.44, 2.42 (s, 6 H, CH_3 diazene and CH_3 nitrile), 1.43, 1.22 (t, 36 H, CH_3 phos).

Results and Discussion

Synthesis and Properties of Dihydrogen Complexes. Hydrides FeH_2P_4 [P = $PhP(OEt)_2$ and $P(OEt)_3$] react at low temperature (−80 °C) in ethanol, in both stoichiometric and excess amounts of $HBF_4{\cdot}Et_2O$, to give dihydrogen complexes $[FeH(\eta^2\text{-}H_2)P_4]^+$ (**1**, **1***), which were isolated as BPh_4^- salts and characterized. The protonation reaction may also be carried out with a different acid such as CF_3COOH, or in diethyl ether or THF as solvent, affording in all cases $[FeH(\eta^2\text{-}H_2)P_4]^+$ compounds but in lower yields.

Complexes **1**, **1*** are pale-yellow solids and relatively stable under nitrogen or argon, both as solids and in solution of polar organic solvents. Evolution of H_2 does not take place at room temperature, and only by heating of their acetone or 1,2-dichloroethane solution over 70 °C was a slow loss of H_2 detected. Exchange of H_2 ligand with D_2 gas in solution at 20 °C occurs[19] with a half-life ($t_{1/2}$) of about 3.5 h. At the end of the reaction, however, only the $[FeD(\eta^2\text{-}D_2)P_4]^+$ complex was isolated.

Selected spectroscopic properties of the hydride–dihydrogen derivatives, which are diamagnetic and 1:1 electrolytes, are reported in Table I. The infrared spectra of complexes **1**, **1*** reveal only weak modes at 1715–1720 cm^{-1}, which may be attributed to the terminal Fe–H stretches, whereas the modes of most interest, ν(HH) and ν(MH_2), were not observed, probably due to overlap in the IR by ν(CH) and ν(CC), respectively.[1d]

In the high-field region of the ^1H NMR spectra the $[FeH(\eta^2\text{-}H_2)\{PhP(OEt)_2\}_4]^+$ complex at −85 °C in CD_2Cl_2 shows a multiplet at δ −10.34 with a T_1 value[20] of 54 ms attributed to hydride resonance[21,22] and a broad singlet at δ −7.2 with a very

(19) The replacement of the metal-bonded hydrogen in the complex by D_2 gas at room temperature (20 °C) was achieved by dissolving the $[FeH(\eta^2\text{-}H_2)P_4]BPh_4$ complex in $(CD_3)_2CO$ (20 mg/mL), degassing the solution, and then adding D_2 (1 atm). The progress of the exchange was followed by ^1H NMR on samples of the solution removed by a syringe at different times.

(20) Determined by the inversion–recovery method at 79.542 MHz. Errors are ±20% in T_1 values.

(21) Because at this temperature (−85 °C) the ^{31}P NMR spectrum of the compound suggests the existence of both cis and trans isomers, the presence of only one multiplet for the hydride resonance is probably due to the quintet of the trans isomer superimposed on the AB_2CX (or ABC_2X) pattern of the cis isomer. Several T_1 measurements on the multiplet gave a mean value of 54 ms for the apparent relaxation time. In order to confirm the existence of the two isomers, we attempted to analyze the ^1H resonance by observing the spectra during the T_1 determinations. We hoped that the differences in T_1 between the hydride resonance of the cis and trans isomers would annul the ^1H signal for only one isomer, allowing clear observation of the signal of the other. Unfortunately, in repeated T_1 determinations using an inversion–recovery pulse sequence, we observed no variation of the profile of the spectra; furthermore when the resonance was nulled out, it involved the whole pattern, perhaps because the relaxation times of the two isomers are similar. In the absence of further data, the existence of the two isomers must therefore be considered as probable.

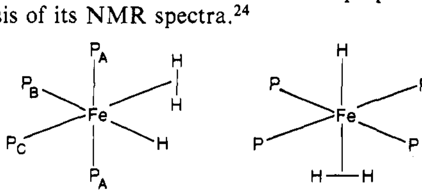
Table I. Selected Infrared and NMR Data for Iron Complexes

no.	cation[a]	IR[b] ν, cm^{-1}	IR[b] assign	^{1}H NMR,[d,e] δ H hydride	spin syst	^{31}P{^{1}H} NMR[d,g] δ (coupling const, Hz)
1	$[FeH(\eta^2\text{-}H_2)\{PhP(OEt)_2\}_4]^+$	1715 w[c]	ν(MH)	+34 °C; −8.00 qi J_{PH}(app) = 22 −85 °C; −7.2 br (η^2-H_2) −10.34 m (H hydr)		187.0 s 187.8 s, 186.4 m
1*	$[FeH(\eta^2\text{-}H_2)\{P(OEt)_3\}_4]^+$	1720 w[c]	ν(MH)	+34 °C; −10.40 qi J_{PH}(app) = 17 −85 °C; −9.6 br	 A_2B_2	164.7 s δ_A = 172.2, δ_B = 168.5 (J_{AB} = 115.0)
2a	*trans*-$[FeH(4\text{-}CH_3C_6H_4NC)\{PhP(OEt)_2\}_4]^+$	2075 s (2075 s)	ν(NC)	−9.88 qi J_{PH} = 48.3		185.8 s
2b	*trans*-$[FeH(4\text{-}CH_3OC_6H_4NC)\{PhP(OEt)_2\}_4]^+$	2079 s, 2045 sh (2072 s, 2042 sh)	ν(NC)	−9.87 qi[f] J_{PH} = 49.5		185.1 s[f]
2c	*trans*-$[FeH\{2,6\text{-}(CH_3)_2C_6H_3NC\}\{PhP(OEt)_2\}_4]^+$	2056 s (2052 s)	ν(NC)	−10.45 qi J_{PH} = 50.5		185.5 s
2d	*trans*-$[FeH(4\text{-}ClC_6H_4NC)\{PhP(OEt)_2\}_4]^+$	2062 s, 2023 sh (2060 s, 2020 sh)	ν(NC)	−9.65 qi J_{PH} = 48.0		185.1 s
2e	*trans*-$[FeH(4\text{-}NO_2C_6H_4NC)\{PhP(OEt)_2\}_4]^+$	2048 s, 2013 sh (2042 s, 2010 sh)	ν(NC)	−9.01 qi J_{PH} = 47.8		184.0 s
2a*	*trans*-$[FeH(4\text{-}CH_3C_6H_4NC)\{P(OEt)_3\}_4]^+$	2096 s, 2047 sh (2085 s, 2040 sh)	ν(NC)	−10.49 qi[f] J_{PH} = 53.1		164.2 s[f]
3a	*trans*-$[FeH(4\text{-}CH_3C_6H_4CN)\{PhP(OEt)_2\}_4]^+$	2208 m (2206 m) 1920 w	ν(CN) ν(MH)	−18.24 qi[f] J_{PH} = 50.7		185.6 s[f]
3b	*trans*-$[FeH(n\text{-}PrCN)\{PhP(OEt)_2\}_4]^+$	2232 m (2225 m) 1930 w	ν(CN) ν(MH)	−19.54 qi[f] J_{PH} = 51.4		186.4 s[f]
3a*	*cis*-$[FeH(4\text{-}CH_3C_6H_4CN)\{P(OEt)_3\}_4]^+$	2245 m (2248 m) 1880 w	ν(CN) ν(MH)	−9.6 m	ABC_2	δ_A = 171.3, δ_B = 166.2, δ_C = 162.1 (J_{AB} = 128.0) (J_{AC} = 95.3) (J_{BC} = 63.0)
4a	$[FeH\{PhP(OEt)_2\}_5]^+$	(1940 w)	ν(MH)	−12.2 m[f]	A_4B[f]	δ_A = 186.1, δ_B = 183.4 (J_{AB} = 58.8)
4b	*cis*-$[FeH\{P(OEt)_3\}\{PhP(OEt)_2\}_4]^+$	(1910 w)	ν(MH)	−11.9 m[f]		185 m[f], 160 m[f]
4a*	$[FeH\{P(OEt)_3\}_5]^+$	(1902 w)	ν(MH)	−12.8 m[f]	A_4B[f]	δ_A = 163.6, δ_B = 160.7 (J_{AB} = 84.0)
4b*	*cis*-$[FeH\{PhP(OEt)_2\}\{P(OEt)_3\}_4]^+$	(1910 w)	ν(MH)	−12.5 m[f]		186 m[f], 162 m[f]
5a*	$[Fe(4\text{-}CH_3C_6H_4N_2)_2\{P(OEt)_3\}_3]^{2+}$	1780 s (1773 s)	ν(NN)		AB_2[h]	δ_A = 131.0, δ_B = 122.5 (J_{AB} = 114.4)
5a$_1$*	$[Fe(4\text{-}CH_3C_6H_4N{\equiv}^{15}N)_2\{P(OEt)_3\}_3]^{2+}$	1753 s (1740 s)	ν(NN)		AB_2X_2[h]	δ_A = 130.9, δ_B = 122.4 (J_{AB} = 114.7) (J_{AX} = 7.3) (J_{BX} = 16.8)
5b*	$[Fe(4\text{-}CH_3OC_6H_4N_2)_2\{P(OEt)_3\}_3]^{2+}$	1779 s (1775 s)	ν(NN)		AB_2[h]	δ_A = 132.4, δ_B = 123.0 (J_{AB} = 115.9)
6	*cis*-$[Fe(4\text{-}CH_3C_6H_4N{=}NH)(4\text{-}CH_3C_6H_4CN)\{PhP(OEt)_2\}_4]^{2+}$	2263 w (2258 w)	ν(CN)		ABC_2[f]	δ_A = 182.1, δ_B = 180.1, δ_C = 171.5 (J_{AB} = 90.0) (J_{BC} = 99.0) (J_{AC} = 95.0)
6*	*cis*-$[Fe(4\text{-}CH_3C_6H_4N{=}NH)(4\text{-}CH_3C_6H_4CN)\{P(OEt)_3\}_4]^{2+}$	2261 w (2250 w)	ν(CN)		ABC_2[f]	δ_A = 151.8, δ_B = 146.9, δ_C = 138.2 (J_{AB} = 134.7) (J_{BC} = 145.0) (J_{AC} = 121.0)

[a] All compounds are BPh_4^- salts. [b] In CH_2Cl_2 and (KBr). [c] In Nujol mull. [d] At room temperature in CD_2Cl_2, unless otherwise noted. [e] Coupling constant (J_{PH}) in Hz. [f] In $(CD_3)_2CO$ at +34 °C. [g] Positive shift downfield from 85% H_3PO_4. [h] In $(CD_3)_2CO$ at −60 °C.

short T_1 value (3 ms), which is characteristic of a η^2-H_2 ligand.[2] However, no resolvable coupling to phosphorus atoms was shown by this resonance associated with η^2-H_2 in the complex. Increasing the sample temperature caused a variation of the spectra until coalescence of the resonances to a broad singlet at δ −8.2 occurred[23] at −30 °C. An intramolecular exchange process of the unique hydride with the two hydrogens may reasonably explain this fluxional process, as previously observed in the $[MH(\eta^2\text{-}H_2)(depe)_2]BPh_4$ (M = Fe, Os) derivatives.[3]

The ^{31}P{^{1}H} NMR spectra of **1** change with temperature and, while at +34 °C only one signal at δ 187.0 is present, at −85 °C a sharp singlet at δ 187.8 and a multiplet at δ 186.4 appear. These data may be interpreted on the basis of the existence in solution of two isomers with geometry of the cis (I) and trans (II) types, respectively, because the multiplet may be attributed to the cis isomer, while the singlet is expected for the trans. It may also be noted that, for the dihydride precursor $FeH_2[PhP(OEt)_2]_4$, the presence of both cis and trans isomers has been proposed in solution on the basis of its NMR spectra.[24]



I II

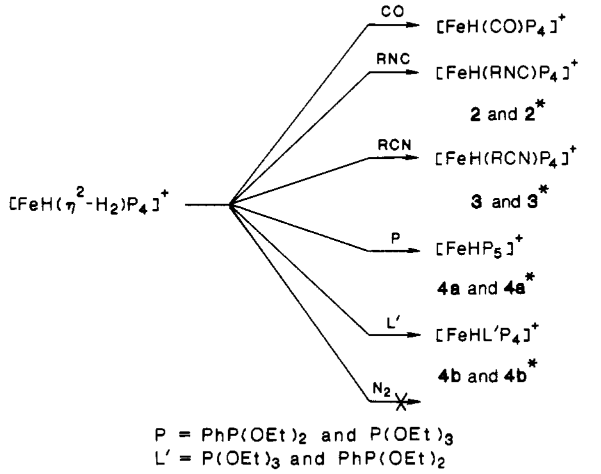
In the high-field region of the ^{1}H NMR spectra, the $[FeH(\eta^2\text{-}H_2)\{P(OEt)_3\}_4]BPh_4$ (**1***) derivative shows a quintet at room temperature that collapses at −10 °C to a broad signal. However, further lowering of the temperature does not change the profile of the spectra and even at −85 °C in CD_2Cl_2 only one broad resonance is present. Measurements of T_1 at this temperature give a mean value of 4 ms, in agreement in this case too with a molecular hydrogen rather than a trihydride complex. Probably further reduction of the temperature below −85 °C should show both the hydride and η^2-H_2 resonances, in the ^{1}H NMR spectra,

(22) It must be noted that the T_1 values for both hydride and hydrogen resonances in **1** are lower than those generally found in previously reported hydrides[22a] and η^2-H_2 complexes;[1-6] however, these figures seem to be characteristic of complexes containing $PhP(OEt)_2$ or $P(OEt)_3$ as coligands.[22b] (a) Crabtree, R. H.; Segmuller, B. E.; Uriarte, R. J. *Inorg. Chem.* **1985**, *24*, 1949. (b) Antoniutti, S.; Albertin, G.; Amendola, P.; Bordignon, E. *J. Chem. Soc., Chem. Commun.*, in press.

(23) A sharp quintet results on increasing the sample temperature further.

(24) Meakin, P.; Guggenberg, L. J.; Jesson, J. P.; Gerlach, D. H.; Tebbe, F. N.; Peet, W. G.; Muetterties, E. L. *J. Am. Chem. Soc.* **1970**, *92*, 3482.

Scheme I

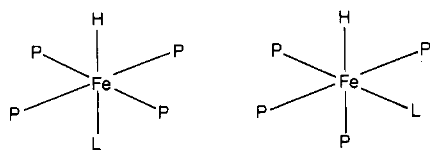


as shown by the related $PhP(OEt)_2$ derivative. At −85 °C the $^{31}P\{^1H\}$ NMR spectra show an A_2B_2 multiplet that may be simulated with the values reported in Table I. This result is unexpected, because an A_2BC (or AB_2C) multiplet is predicted for a cis structure (I). However, the presence of an A_2B_2 spectrum may be tentatively explained by taking into account the fact that the hydride–hydrogen exchange, being still rapid on the NMR time scale at −85 °C, may make the two P_B and P_C nuclei magnetically equivalent at this temperature.

We attempted to detect the resonances for η^2-HD in a mixture of $[FeH(\eta^2\text{-}HD)P_4]^+$ and $[FeD(\eta^2\text{-}HD)P_4]^+$ formed together with other isotopomers from the reaction of D_2 or HD with **1** or by protonation with HBF_4 of FeD_2P_4 species. In every case, a broad resonance[2b,3a] beside the hydride pattern was always observed in the high-field region of the ^1H NMR spectra between −85 and +34 °C.

Studies on the chemical properties of both dihydrogen complexes **1** and **1*** showed that the deprotonation reaction takes place with triethylamine at room temperature to give the FeH_2P_4 dihydride precursor. Furthermore, the H_2 group in **1** and **1*** may easily be substituted by several ligands, affording a new series of monohydride complexes, as reported in Scheme I. Exchange of H_2 ligand with N_2 to give $[FeH(N_2)P_4]^+$ was not detected.

All complexes were isolated as stable white or pale-yellow solids, diamagnetic, and 1:1 electrolytes. A trans geometry of type III may be proposed in solution for carbonyl[11c] $[FeH(CO)P_4]^+$ and isocyanide complexes **2** and **2*** on the basis of the sharp singlet that appears in their $^{31}P\{^1H\}$ NMR spectra (between −80 and +34 °C). On the other hand, a geometry depending on the nature of the phosphite ligand was observed in the nitrile $[FeH(RCN)P_4]^+$ complexes. While a trans geometry (III) is proposed in solution

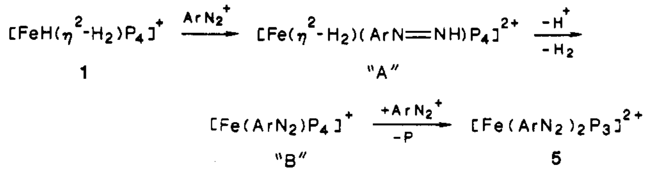


III IV

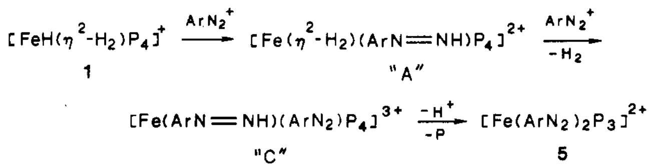
for $PhP(OEt)_2$ derivatives **3** (singlet in the ^{31}P spectra), the presence of an AB_2C multiplet in the ^{31}P NMR spectra of $P(OEt)_3$ compound **3*** suggests a cis geometry (IV) for this complex. Lastly, compound $[FeHL'P_4]^+$ (**4b** and **4b***), containing two different phosphite ligands, shows a complicated pattern in the ^{31}P NMR spectra, i.e. two multiplets at δ 185–186 and 160–162, which may be interpreted on the basis of the existence in solution of a cis geometry (IV) for the compound. A trans structure, in fact, should give a doublet and a quintet in the ^{31}P spectra.

The ^1H NMR spectra of all these complexes show the hydride resonance as a quintet or multiplet between δ −12.8 and −9.01, except for trans nitrile derivatives **3a** and **3b**, whose resonances occur at δ −18.24 and −19.54. These different chemical shifts may be explained on the basis of the different trans influence of the nitrile ligand which, being a better σ-donor but a poorer π-acceptor than both isocyanide and phosphite, probably caused the shift of the hydride resonance.

Scheme II



Scheme III



The isocyanide complexes show the ν(CN) band in the infrared spectra at 2048–2096 cm^{-1} (CH_2Cl_2 solution), while the ν(CN) peak appears at 2208–2245 cm^{-1} in the nitrile derivative. This frequency is lowered by about 20 cm^{-1} as compared to the free ligand value and suggests some back-donation of electrons from iron into the nitrile ligands. Monohydrides of iron(II) with phosphite are rare[11c] and no such compounds containing nitrile or isocyanide ligands have been described. The use of dihydrogen complexes as precursors represents a convenient method of synthesis of a new series of RCN and RNC monohydride Fe(II) phosphite derivatives.

Reactivity with Aryldiazonium Cation. The $[FeH(\eta^2\text{-}H_2)P_4]^+$ complexes react with an excess of aryldiazonium cations to yield the bis(aryldiazenido) $[Fe(ArN_2)_2P_3]^{2+}$ (**5** and **5***) derivatives, which were isolated and characterized. Studies on the progress of the reaction by infrared and ^1H NMR spectra, changing the $[FeH(\eta^2\text{-}H_2)P_4]^+{:}ArN_2^+$ ratio in the range 1:0.5 to 1:4, did not allow a reaction path to be defined unambiguously. In every case the IR spectra showed two ν(NN) bands at 1780–1774 and 1668–1660 cm^{-1}, attributed to the $[Fe(ArN_2)_2P_3]^{2+}$ and $[Fe(ArN_2)P_4]^+$ (Ar = 4-$CH_3C_6H_4$) derivatives, respectively. As the reaction proceeded, the 1780–1774-cm^{-1} band increased, and the 1668–1660-cm^{-1} absorption remained almost unchanged in the case of the $P(OEt)_3$ derivatives, while it decreased in the $PhP(OEt)_2$ compound and disappeared after 1 h. At the end of the reaction, therefore, compound **5** was observed in the case of P = $PhP(OEt)_2$, while both complexes **5*** and $[Fe(ArN_2)P_4]^+$ were present with $P(OEt)_3$ as ligand and both were contained in the raw final product. However, no other aryldiazenido compounds were detected.

Besides the ArN_2 compounds, the ^1H NMR spectra of the reaction mixture showed a diazene intermediate on the basis of the appearance of a broad singlet near δ 14.2. Since such a diazene does not seem to be either the $[FeH(ArN{=}NH)P_4]^+$ or the $[Fe(ArN{=}NH)_2P_4]^{2+}$ derivatives, which are known to be formed by reaction of the hydride FeH_2P_4 with aryldiazonium cations,[11a,b] the existence in solution of the equilibrium

$$[FeH(\eta^2\text{-}H_2)P_4]^+ \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} FeH_2P_4$$

may reasonably be excluded. Taking into account the lability of the H_2 ligand in **1** and **1*** and the presence of a diazene as intermediate, a reaction path of the type reported in Scheme II may be proposed.

However, in the case of the $P(OEt)_3$ derivative at least, our previous results[11b] seem to exclude the possibility of such a mechanism giving the bis(aryldiazenido) derivative, because the substitution of a $P(OEt)_3$ ligand by ArN_2^+ in the $[Fe(ArN_2)P_4]^+$ ("B" compound) does not take place. The presence of a small amount of monoaryldiazenido "B" in the reaction mixture and in the final product may, however, indicate that the reaction path **1** → "A" → "B" is also partly operating. An alternative mechanism of the type shown in Scheme III, involving an intermediate diazene–diazenido iron(II) complex, would be stimulating, but the absence of further data makes any discussion purely speculative.

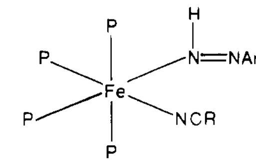
We hoped that the presence of a H_2 molecule bonded to the iron atom would allow reduction of the N=N function, i.e. formation of arylhydrazine or arylhydrazido(−1) complexes. We therefore studied the reaction of **1** with aryldiazonium cation under H_2 too, but in no case was evidence of the formation of such a derivative observed, nor did we find free arylhydrazine in the reaction mixture.

Table I reports selected properties of the bis(aryldiazenido) complexes. It may be noted that only the $PhP(OEt)_2$ derivatives had been previously prepared,[11b] whereas now, using **1*** as precursor, the $P(OEt)_3$ compounds can also be prepared with ease. The chemical and spectroscopic properties of these new $[Fe(ArN_2)_2\{P(OEt)_3\}_3]^{2+}$ derivatives are very similar to those of the related $PhP(OEt)_2$ complexes. The IR spectra show only one ν(NN) band at 1779–1780 cm^{-1} (CH_2Cl_2), which is shifted by 27 cm^{-1} at lower frequencies on labeling with ^{15}N. The $^{31}P\{^1H\}$ NMR spectra show a broad signal at room temperature, but an AB_2 multiplet appears at −60 °C, and this was simulated with the parameters reported in Table I. As for the related $PhP(OEt)_2$ derivatives,[11b] these data still seem to suggest a slightly distorted TBP geometry, with singly bent aryldiazenido ligands in the mutually trans position for $[Fe(ArN_2)_2\{P(OEt)_3\}_3]^{2+}$ too.

We also studied the reactivity of the new monohydrides $[FeHLP_4]^+$ with aryldiazonium cations. The results obtained show that, apart from the monocarbonyl[11c] $[FeH(CO)P_4]^+$, only the nitrile $[FeH(RCN)P_4]^+$ complexes quickly react with ArN_2^+ in CH_2Cl_2 to give the new diazene $[Fe(ArN{=}NH)(RCN)P_4]^{2+}$ (**6** and **6***) derivatives, which can be isolated and characterized. Instead, both isocyanide **2, 2*** and pentakis phosphite **4, 4*** are unreactive toward ArN_2^+ cation and can be recovered unaltered after a 24 h period of reaction.

The new diazene compounds **6, 6*** are orange-yellow solids, diamagnetic, and 2:1 electrolytes. Their ^1H NMR spectra confirm the presence of the ArN=NH ligand, showing a broad singlet at δ 14.18–13.63 attributed to diazene hydrogen atoms split into a sharp doublet ($J_{^{15}NH}$ = 65 Hz) in the labeled $[Fe(ArN{=}^{15}NH)(RCN)P_4]^{2+}$ compound. On the basis of the ABC_2 multiplets which appear in the $^{31}P\{^1H\}$ NMR spectra, a geometry of type V with the nitrile and diazene ligands in a mutually cis position may be proposed for these derivatives in solution.

Mono diazene complexes **6, 6*** react in dichloromethane solution with triethylamine (ratio 1:1) to give the monoaryldiazenido



V

$[Fe(ArN_2)P_4]^+$ complexes, as shown in eq 1. Studies on the

$$[Fe(ArN{=}NH)(RCN)P_4]^{2+} + NEt_3 \rightarrow [Fe(ArN_2)P_4]^+ + RCN + Et_3NH^+ \quad (1)$$

progress of the reaction by infrared spectra showed the appearance of a band at 1668–1660 cm^{-1}, due to the $[Fe(ArN_2)P_4]^+$ complexes and the band of the free nitrile at 2230 cm^{-1}. Furthermore, the IR spectrum of the final reaction mixture in the 2300–1600-cm^{-1} region is identical with that of a 1:1 solution of $[Fe(ArN_2)P_4]^+$ and $4\text{-}CH_3C_6H_4CN$. Lastly, the ammonium salt $Et_3NH^+BPh_4^-$ can be recovered in quantitative yield and the stoichiometry of reaction 1 therefore seems to be confirmed.

The deprotonation of a monodiazene complex is somewhat surprising, because such complexes of Fe(II)[11] or of Ru(II)[25] do not react with base to give aryldiazenido derivatives. This unreactivity has been explained on the basis of the nature of the coligands in the complexes, whose probably difficult dissociation prevents the formation of the pentacoordinate aryldiazenido derivatives. The reactivity of our new monodiazene complexes may therefore be attributed to the presence of the nitrile ligand, whose facile dissociation allows reaction 1 to proceed. This confirms the hypothesis[11a] that, in octahedral diazene complexes, deprotonation is related to the possible dissociation of one of the ligands in the starting complexes.

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Registry No. 1, 118460-63-2; **1***, 118460-65-4; **1a**, 118460-66-5; **2a**, 118460-68-7; **2a***, 118460-78-9; **2b**, 118460-70-1; **2c**, 118460-72-3; **2d**, 118460-74-5; **2e**, 118460-76-7; **3a**, 118460-80-3; **3a***, 118460-84-7; **3b**, 118460-82-5; **4a**, 118460-86-9; **4a***, 118474-30-9; **4b**, 118460-88-1; **4b***, 118460-90-5; **5a**, 109365-33-5; **5a***, 118474-32-1; **5a$_1$***, 118460-94-9; **5b***, 118460-92-7; **6**, 118474-34-3; **6***, 118474-36-5; $FeH_2(PhP(OEt)_2)_4$, 28755-83-1; $FeH_2(P(OEt)_3)_4$, 34503-40-7; $[4\text{-}CH_3C_6H_4N{\equiv}^{15}N]BF_4$, 118460-61-0.

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