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Preparation and Reactivity of Mixed-Ligand Iron(II) Hydride Complexes with Phosphites and Polypyridyls

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Hydride complexes $[FeH(N\text{-}N)P_3]BPh_4$ (**1**, **2**) [N-N = 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen); P = $P(OEt)_3$, $PPh(OEt)_2$, and PPh_2OEt] were prepared by allowing $FeCl_2(N\text{-}N)$ to react with phosphite in the presence of $NaBH_4$. The hydrides $[FeH(bpy)_2P]BPh_4$ (**3**) [P = $P(OEt)_3$ and $PPh(OEt)_2$] were prepared by reacting the tris-(2,2′-bipyridine) $[Fe(bpy)_3]Cl_2{\cdot}5H_2O$ complex with the appropriate phosphite in the presence of $NaBH_4$. The protonation reaction of **1** and **2** with acid was studied and led to thermally unstable (above –20 °C) dihydrogen $[Fe(\eta^2\text{-}H_2)(N\text{-}N)P_3]^{2+}$ (**4**, **5**) derivatives. The presence of the H_2 ligand is indicated by short T_{1min} values (3.1–3.6 ms) and by J_{HD} measurements (31.2–32.5 Hz) of the partially deuterated derivatives. Carbonyl $[Fe(CO)(bpy)\{P(OEt)_3\}_3](BPh_4)_2$ (**6**) and nitrile $[Fe(CH_3CN)(N\text{-}N)P_3](BPh_4)_2$ (**7**, **8**) [N-N = bpy, phen; P = $P(OEt)_3$ and $PPh(OEt)_2$] complexes were prepared by substituting the H_2 ligand in the η^2-H_2 **4**, **5** derivatives. Aryldiazene complexes $[Fe(ArN{=}NH)(N\text{-}N)P_3](BPh_4)_2$ (**9**, **10**, **11**) (Ar = C_6H_5, 4-$CH_3C_6H_4$) were also obtained by allowing hydride $[FeH(N\text{-}N)P_3]BPh_4$ derivatives to react with aryldiazonium cations in CH_2Cl_2 at low temperature.

Introduction

The chemistry of iron(II) classical and nonclassical hydride complexes has developed considerably in the last 30 years, highlighting the syntheses of a number of complexes with interesting properties.[1,2] The ancillary ligands used in this chemistry involve mainly π-acceptors such as tertiary phosphine, carbon monoxide, and cyclopentadienyl ligands, which are associated with classical neutral FeH_2P_4, $FeH_2(CO)_2P_2$, $FeHXP_4$ (X = Cl, CN), $FeH(CO)_2(\eta^5\text{-}C_5H_5)$, and $FeHP_2(\eta^5\text{-}C_5H_5)$ [P = mono- to tetradentate phosphorus ligands] as well as classical or nonclassical cationic $[FeH_3P_4]^+$, $[FeH(\eta^2\text{-}H_2)P_4]^+$, $[FeH(CO)P_4]^+$, $[FeHP_5]^+$, $[Fe(\eta^2\text{-}H_2)(CO)P_4]^{2+}$, or neutral FeH_4P_3 hydride derivatives.[1−5]

Less attention, however, has been devoted to the use of nitrogen-donor ancillary ligands, and, to the best of our knowledge, no iron(II) hydride complexes containing polypyridyl or mixed-ligand polypyridyl-phosphine as supporting ligands have ever been reported.

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Changes in the nature of the ancillary ligands may greatly change both the reactivity of the M−H bond and the properties of the M−(η^2-H_2) group. In dihydrogen complexes, for example, the following are important: stability regarding the loss of H_2, the bonding mode which may make η^2-H_2 stretched or unstretched, and the acidity of the η^2-H_2 ligand. These properties have been raised in recently reported[6] dicationic dihydrogen such as $[Fe(\eta^2\text{-}H_2)(CO)(dppe)_2]^{2+}$, $[Os(\eta^2\text{-}H_2)(dppe)_2(NCCH_3)]^{2+}$ (dppe = 1,2-bis(diphenylphosphino)ethane), $[Os(\eta^2\text{-}H_2)(P^iPr_3)_2(NCCH_3)_3]^{2+}$, $[M(\eta^2\text{-}H_2)(dppp)(CO)]^{2+}$ [M = Ru, Os; dppp = 1,3-bis(diphenylphosphino)propane], and $[Os(\eta^2\text{-}H_2)(PR_3)_2(CO)(bpy)]^{2+}$ (R = Ph, ^{i}Pr).

For several years we have developed the chemistry of classical and nonclassical metal hydride complexes of the iron[7] and manganese[8] triads of the $[MH(\eta^2\text{-}H_2)P_4]^+$, $[MX(\eta^2\text{-}H_2)P_4]^+$ (M = Fe, Ru, Os; X^- = Cl^-, Br^-, I^-), $MH(CO)_nP_{5-n}$, and $[M(\eta^2\text{-}H_2)(CO)_nP_{5-n}]^+$ (M = Mn, Re; n = 1−4) types using phosphites as ancillary ligands. We have now extended these studies with the aim of introducing nitrogen-donor ligands such as 2,2′-bipyridine and 1,10-phenanthroline in the iron hydride chemistry. The results of these studies, which allow the synthesis and reactivity of the unprecedented mixed-ligand iron(II) hydrides and dicationic η^2-H_2 derivatives with phosphites and polypyridyls, are reported here.

Experimental Section

All synthetic work was carried out under an appropriate atmosphere (Ar, H_2) using standard Schlenk techniques or a Vacuum Atmospheres drybox. Once isolated, the complexes were found to be relatively stable in air, but were stored under an inert atmosphere at −25 °C. All solvents were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. Triethyl phosphite was an Aldrich product, purified by distillation under nitrogen, while the phosphines $PPh(OEt)_2$ and PPh_2OEt were prepared by the method of Rabinowitz and Pellon.[9] Diazonium salts were obtained in the usual way.[10] Labeled diazonium tetrafluoroborates $(C_6H_5N{\equiv}^{15}N)BF_4$ were prepared from $Na^{15}NO_2$ (99% enriched, CIL) and aniline. 2,2′-Bipyridine (bpy) and 1,10-phenanthroline (phen), $HBF_4{\cdot}Et_2O$ (54% solution in Et_2O), CF_3SO_3H, and CF_3SO_3D were Aldrich products, used without any further purification. Infrared spectra were recorded on a Nicolet Magna 750 FT-IR spectrophotometer. NMR spectra (^1H, ^{13}C, ^{31}P, ^{15}N) were obtained on a Bruker AC200 or an AVANCE 300 spectrometer at temperatures varying between +30 and −90 °C, unless otherwise noted. ^1H and ^{13}C spectra are referred to internal tetramethylsilane. $^{31}P\{^1H\}$ chemical shifts are reported with respect to 85% H_3PO_4, while ^{15}N shifts are referred to external $CH_3{}^{15}NO_2$, in both cases with downfield shifts considered positive. The COSY, HMQC, and HMBC NMR experiments were performed using their standard programs. The SwaN-MR software package[11] was used in treating the NMR data. Proton T_1 values were measured in CD_2Cl_2 at 200 MHz by the inversion−recovery method between +30 and −90 °C with a standard 180°−τ−90° pulse sequence. The conductivity of 10^{-3} mol dm^{-3} solutions of the complexes in CH_3NO_2 at 25 °C was measured with a Radiometer CDM 83 instrument. Elemental analyses were determined in the Microanalytical Laboratory of the Dipartimento di Scienze Farmaceutiche of the University of Padova (Italy).

Synthesis of Complexes. Both the red[12,13a] and the orange[13b] isomers of $FeCl_2(bpy)$ were prepared following the method previously reported. Also the $FeCl_2(phen)$ was obtained using the same method.[12,13] The tris(2,2′-bipyridine) $[Fe(bpy)_3]Cl_2{\cdot}5H_2O$ complex was prepared by a procedure previously described.[14] The spectroscopic data (IR and NMR) of the new complexes are reported in Tables 1 and 2.

$[FeH(bpy)P_3]BPh_4$ (1) [P = $P(OEt)_3$ (1a), $PPh(OEt)_2$ (1b), PPh_2OEt (1c)]. In a 50-mL three-necked round-bottomed flask were placed 0.500 g (1.8 mmol) of $FeCl_2(bpy)$ (orange isomer), 15 mL of ethanol, and an excess of the appropriate phosphite (8 mmol). An excess of $NaBH_4$ (10 mmol, 0.38 g) in 20 mL of ethanol was slowly added, and the reaction mixture was stirred at room temperature for 150 min. The resulting red-brown solution was filtered through silica gel (TLC standard grade) and the solvent removed under reduced pressure to give a brown oil. The addition of an excess of $NaBPh_4$ (0.68 g, 2 mmol) in 5 mL of ethanol caused the separation of a red-brown solid, which was filtered and crystallized from CH_2Cl_2 and ethanol; ≥55%. Anal. Calcd for $C_{52}H_{74}BFeN_2O_9P_3$ (**1a**): C, 60.59; H, 7.24; N, 2.72. Found: C, 60.40; H, 7.35; N, 2.79. Λ_M = 53.6 Ω^{-1} mol^{-1} cm^2. Calcd for $C_{64}H_{74}BFeN_2O_6P_3$ (**1b**): C, 68.22; H, 6.62; N, 2.49. Found: C, 68.01; H, 6.57; N, 2.43. Λ_M = 55.8 Ω^{-1} mol^{-1} cm^2. Calcd for $C_{76}H_{74}BFeN_2O_3P_3$ (**1c**): C, 74.64; H, 6.10; N, 2.29. Found: C, 74.86; H, 6.19; N, 2.25. Λ_M = 49.8 Ω^{-1} mol^{-1} cm^2.

$[FeH(bpy)P_3]CF_3SO_3$ (1-CF_3SO_3) [P = $P(OEt)_3$ (1a-CF_3SO_3), $PPh(OEt)_2$ (1b-CF_3SO_3), PPh_2OEt (1c-CF_3SO_3)]. In a 50-mL three-necked round-bottomed flask were placed 0.500 g (1.8 mmol) of $FeCl_2(bpy)$ (orange isomer), 15 mL of ethanol, and an excess of the appropriate phosphite (8 mmol). An excess of $NaBH_4$ (10 mmol, 0.38 g) in 20 mL of ethanol was slowly added, and the reaction mixture was stirred at room temperature for 150 min. The solvent was removed under reduced pressure to give an oil, from which the hydride $[FeH(bpy)P_3]Cl$ was extracted with three 10-mL portions of CH_2Cl_2. The extracts were evaporated to dryness to give an oil, which was treated with an excess of $LiCF_3SO_3$ (7 mmol, 1.1 g) in 4 mL of ethanol. The resulting solution was stirred for 1 h and then the solvent removed under reduced pressure to give a red-brown oil, from which the complex was extracted with three 5-mL portions of diethyl ether. By cooling to −25 °C of the

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Table 1. Selected IR and NMR Data for Iron Complexes

IR[a] ($\mathrm{cm^{-1}}$)	assgnt	^{1}H NMR[b,c] (ppm; J, Hz)	assgnt	spin syst	^{31}P{^{1}H} NMR[b,d] (ppm; J, Hz)
		$\mathrm{[FeH(bpy)\{P(OEt)_3\}_3]BPh_4}$ (**1a**)			
1857 w	ν_{FeH}	4.04 m[e]	$\mathrm{CH_2}$	$\mathrm{AB_2}$[f]	δ_A 179.4
		3.67 m			δ_B 161.3
		3.46 m			$J_{AB} = 129.7$
		1.28 t	$\mathrm{CH_3}$		
		0.94 t			
		$\mathrm{AB_2X}$	H hydride		
		δ_X −18.34			
		$J_{AX} = 70$			
		$J_{BX} = 56$			
		$\mathrm{[FeH(bpy)\{PPh(OEt)_2\}_3]BPh_4}$ (**1b**)			
1886 w	ν_{FeH}	3.87 m	$\mathrm{CH_2}$	$\mathrm{AB_2}$	δ_A 204.1
		3.64 m			δ_B 187.2
		3.44 m			$J_{AB} = 94.0$
		1.32 t	$\mathrm{CH_3}$		
		1.05 t			
		$\mathrm{AB_2X}$	H hydride		
		δ_X −18.01			
		$J_{AX} = J_{BX} = 62$			
		$\mathrm{[FeH(bpy)\{PPh_2OEt\}_3]BPh_4}$ (**1c**)			
1863 w	ν_{FeH}	3.29 m	$\mathrm{CH_2}$	$\mathrm{AB_2}$	δ_A 177.0
		3.02 m			δ_B 167.0
		0.70 t	$\mathrm{CH_3}$		$J_{AB} = 74.0$
		0.47 t			
		$\mathrm{AB_2X}$	H hydride		
		δ_X −16.87			
		$J_{AX} = J_{BX} = 56$			
		$\mathrm{[FeH(phen)\{P(OEt)_3\}_3]BPh_4}$ (**2a**)			
1890 w	ν_{FeH}	4.21 qnt	$\mathrm{CH_2}$	$\mathrm{AB_2}$	δ_A 180.3
		3.69 m			δ_B 160.0
		3.45 m			$J_{AB} = 130.0$
		1.42 t	$\mathrm{CH_3}$		
		0.90 t			
		$\mathrm{AB_2X}$	H hydride		
		δ_X −17.95			
		$J_{AX} = 70$			
		$J_{BX} = 56$			
		$\mathrm{[FeH(phen)\{PPh(OEt)_2\}_3]BPh_4}$ (**2b**)			
1887 w	ν_{FeH}	3.98 m	$\mathrm{CH_2}$	$\mathrm{AB_2}$	δ_A 205.9
		3.50 m			δ_B 187.9
		1.38 t	$\mathrm{CH_3}$		$J_{AB} = 95.0$
		0.97 t			
		$\mathrm{AB_2X}$	H hydride		
		δ_X −17.74			
		$J_{AX} = J_{BX} = 62$			
		$\mathrm{[FeH(bpy)_2\{P(OEt)_3\}]BPh_4}$ (**3a**)			
1782 w	ν_{FeH}	3.65 qnt	$\mathrm{CH_2}$		168.6 s
		1.00 t	$\mathrm{CH_3}$		
		−13.13 d	H hydride		
		$J_{PH} = 116$			
		$\mathrm{[FeH(bpy)_2\{PPh(OEt)_2\}]BPh_4}$ (**3b**)			
1798 w	ν_{FeH}	3.85 m	$\mathrm{CH_2}$		193.8 s
		1.18 t	$\mathrm{CH_3}$		
		1.04 t			
		−12.86 d	H hydride		
		$J_{PH} = 102$			
		$\mathrm{[Fe(\eta^2\text{-}H_2)(bpy)\{P(OEt)_3\}_3]^{2+}}$ (**4a**)			
		3.96 m[e]	$\mathrm{CH_2}$	$\mathrm{AB_2}$[f]	δ_A 151.8
		3.44 m			δ_B 140.4
		1.33 br	$\mathrm{CH_3}$		$J_{AB} = 127.5$
		1.00 br			
		−15.7 br	η^2-$\mathrm{H_2}$		
		$\mathrm{[Fe(\eta^2\text{-}H_2)(bpy)\{PPh(OEt)_2\}_3]^{2+}}$ (**4b**)			
		3.88 m[e]	$\mathrm{CH_2}$	$\mathrm{AB_2}$[f]	δ_A 179.8
		3.66 m			δ_B 172.3
		3.41 m			$J_{AB} = 99.7$
		1.29 t	$\mathrm{CH_3}$		
		1.17 t			
		1.14 t			
		−16.3 br	η^2-$\mathrm{H_2}$		
		$\mathrm{[Fe(\eta^2\text{-}H_2)(bpy)\{PPh_2OEt\}_3]^{2+}}$ (**4c**)			
		3.5 br[e]	$\mathrm{CH_2}$	$\mathrm{AB_2}$[e]	δ_A 156.8
		0.80 br	$\mathrm{CH_3}$		δ_B 154.1
		0.50 br			$J_{AB} = 57.1$
		−13.3 br	η^2-$\mathrm{H_2}$		
		$\mathrm{[Fe(\eta^2\text{-}H_2)(phen)\{P(OEt)_3\}_3]^{2+}}$ (**5a**)			
		4.15 qnt[e]	$\mathrm{CH_2}$	$\mathrm{AB_2}$[e]	δ_A 152.9
		3.82 m			δ_B 140.5
		1.30 t	$\mathrm{CH_3}$		$J_{AB} = 128.0$
		0.84 t			
		−15.7 br	η^2-$\mathrm{H_2}$		
		$\mathrm{[Fe(\eta^2\text{-}H_2)(phen)\{PPh(OEt)_2\}_3]^{2+}}$ (**5b**)			
		3.73 m[e]	$\mathrm{CH_2}$	$\mathrm{AB_2}$[e]	δ_A 181.3
		1.35 t	$\mathrm{CH_3}$		δ_B 172.8
		1.24 t			$J_{AB} = 99.0$
		0.75 t			
		−16.2 br	η^2-$\mathrm{H_2}$		
		$\mathrm{[Fe(CO)(bpy)\{P(OEt)_3\}_3](BPh_4)_2}$[g] (**6a**)			
2033 s	ν_{CO}	4.20 m	$\mathrm{CH_2}$	$\mathrm{A_2B}$	δ_A 147.0
		3.59 m			δ_B 129.2
		1.41 t	$\mathrm{CH_3}$		$J_{AB} = 148.0$
		1.02 t			
		$\mathrm{[Fe(CH_3CN)(bpy)\{P(OEt)_3\}_3](BPh_4)_2}$ (**7a**)			
		4.25 qnt	$\mathrm{CH_2}$	$\mathrm{AB_2}$	δ_A 153.4
		3.72 m			δ_B 137.0
		2.07 s	$\mathrm{CH_3CN}$		$J_{AB} = 133.6$
		1.42 t	$\mathrm{CH_3}$ phos		
		1.01 t			
		$\mathrm{[Fe(CH_3CN)(bpy)\{PPh(OEt)_2\}_3](BPh_4)_2}$ (**7b**)			
		4.30 m	$\mathrm{CH_2}$	$\mathrm{AB_2}$	δ_A 191.5
		3.84 m			δ_B 170.1
		1.34 s	$\mathrm{CH_3CN}$		$J_{AB} = 100.0$
		1.49 t	$\mathrm{CH_3}$ phos		
		1.23 t			
		0.98 t			
		$\mathrm{[Fe(CH_3CN)(phen)\{PPh(OEt)_2\}_3](BPh_4)_2}$[h] (**8b**)			
		4.30 m	$\mathrm{CH_2}$	$\mathrm{AB_2}$	δ_A 190.8
		3.70 m			δ_B 170.2
		1.42 s	$\mathrm{CH_3CN}$		$J_{AB} = 97.2$
		1.56 t	$\mathrm{CH_3}$phos		
		1.17 t			
		0.89 t			
		$\mathrm{[Fe(C_6H_5N{=}NH)(bpy)\{P(OEt)_3\}_3](BPh_4)_2}$ (**9a**)			
		13.88 s, br	NH	$\mathrm{AB_2}$	δ_A 148.1
		4.19 m	$\mathrm{CH_2}$		δ_B 134.2
		3.69 m			$J_{AB} = 136.9$
		1.35 t	$\mathrm{CH_3}$		
		1.01 t			
		$\mathrm{[Fe(C_6H_5N{=}^{15}NH)(bpy)\{P(OEt)_3\}_3](BPh_4)_2}$[i] (**9a-^{15}N**)			
		13.87 d	NH	$\mathrm{AB_2Y}$	δ_A 147.9
		$^1J_{^{15}NH} = 68$		($Y = {}^{15}$N)	δ_B 134.2
		4.18 m	$\mathrm{CH_2}$		$J_{AB} = 136.8$
		3.69 m			$J_{AY} = 8.6$
		1.32 t	$\mathrm{CH_3}$		$J_{BY} = 8.4$
		0.99 t			
		$\mathrm{[Fe(4\text{-}CH_3C_6H_4N{=}NH)(bpy)\{P(OEt)_3\}_3](BPh_4)_2}$ (**10a**)			
		13.68 s, br	NH	$\mathrm{AB_2}$	δ_A 148.6
		4.20 m	$\mathrm{CH_2}$		δ_B 134.6
		3.70 m			$J_{AB} = 136.6$
		2.49 s	$\mathrm{CH_3}$ *p*-tolyl		
		1.35 t	$\mathrm{CH_3}$ phos		
		1.01 t			
		$\mathrm{[Fe(4\text{-}CH_3C_6H_4N{=}NH)(bpy)\{PPh(OEt)_2\}_3](BPh_4)_2}$ (**10b**)			
		13.37 s, br	NH	$\mathrm{AB_2}$	δ_A 181.6
		4.20 m	$\mathrm{CH_2}$		δ_B 168.7
		3.78 m			$J_{AB} = 104.6$
		2.50 s	$\mathrm{CH_3}$ *p*-tolyl		
		1.51 t	$\mathrm{CH_3}$ phos		
		1.14 t			

Table 1. Continued

IR[a] (cm^{-1})	assgnt	^1H NMR[b,c] (ppm; J, Hz)	assgnt	spin syst	$^{31}P\{^1H\}$ NMR[b,d] (ppm; J, Hz)	IR[a] (cm^{-1})	assgnt	^1H NMR[b,c] (ppm; J, Hz)	assgnt	spin syst	$^{31}P\{^1H\}$ NMR[b,d] (ppm; J, Hz)
	$[Fe(4\text{-}CH_3C_6H_4N{=}NH)(phen)\{P(OEt)_3\}_3](BPh_4)_2$ (**11a**)						$[Fe(4\text{-}CH_3C_6H_4N{=}NH)(phen)\{PPh(OEt)_2\}_3](BPh_4)_2$ (**11b**)				
		13.85 s, br	NH	AB_2	δ_A 130.2			13.77 s, br	NH	AB_2	δ_A 181.3
		4.26 m	CH_2		δ_B 115.3			4.32 m	CH_2		δ_B 168.9
		3.53 m			$J_{AB} = 136.5$			3.58 m			$J_{AB} = 105.0$
		2.51 s	CH_3 *p*-tolyl					2.55 s	CH_3 *p*-tolyl		
		1.41 t	CH_3 phos					1.61 t	CH_3 phos		
		0.82 t						1.19 t			

[a] In KBr pellets. [b] In CD_2Cl_2 at 25 °C unless otherwise noted. [c] Phenyl proton resonances omitted; for the OC_2H_5 group of the phosphine $J_{HH} = 7$ Hz. [d] Positive shifts downfield from 85% H_3PO_4. [e] At −70 °C. [f] At −30 °C. [g] ^{13}C NMR (CD_2Cl_2, 25 °C): 207.8 (dt, CO, $J_{CP_{cis}} = J_{CP_{trans}} = 55$ Hz), 165−122 (m, Ph + bpy), 65.9 (m, CH_2), 16.2 (m, CH_3). [h] ^{13}C NMR (CD_2Cl_2, 25 °C): 165−122 (m, Ph + phen), 137.8 (s, CH_3CN), 67.2 (m, CH_2), 17.1 (m, CH_3 phos), 3.65 (s, CH_3CN). [i] ^{15}N NMR (CD_2Cl_2, 25 °C; δ from $CH_3{}^{15}NO_2$): AB_2Y spin system. δ_Y 17.6, $J_{AY} = 8.6$, $J_{BY} = 8.4$ Hz.

Table 2. T_{1min} (200 MHz) and J_{HD} NMR Data for Some Dihydrogen and Hydride Complexes and Calculated H−H Distances

	compound	T (K)	δ	T_{1min} (ms)	J_{HD} (Hz)	r_{H-H} (Å)		
4a	$[Fe(\eta^2\text{-}H_2)(bpy)\{P(OEt)_3\}_3]^{2+}$	210	−15.7 br	3.1	31.5	0.92[a]	0.73[b]	0.91[c]
4b	$[Fe(\eta^2\text{-}H_2)(bpy)\{PPh(OEt)_2\}_3]^{2+}$	218	−16.3 br	3.6	32.5	0.94	0.75	0.89
5a	$[Fe(\eta^2\text{-}H_2)(phen)\{P(OEt)_3\}_3]^{2+}$	213	−15.7 br	3.3	31.2	0.93	0.74	0.92
5b	$[Fe(\eta^2\text{-}H_2)(phen)\{PPh(OEt)_2\}_3]^{2+}$	225	−16.2 br	3.1	32.0	0.92	0.73	0.90
1a	$FeH(bpy)\{P(OEt)_3\}_3]^+$	193	−18.34 dt	196				

[a,b] The H−H distances were calculated[18,20] from the T_{1min} values for fast rotation[b] or static regimes[a] of the H_2 ligand. [c] H−H distances calculated from the J_{HD} values for HD complexes using the equation[6c,8] $r_{H-H} = 1.44 - 0.0168\ (J_{HD})$.

exctracts, red-brown microcrystals of the product separated out, which were filtered and dried under vacuum; yield ≥15%. Anal. Calcd for $C_{29}H_{54}F_3FeN_2O_{12}P_3S$ (**1a-CF$_3$SO$_3$**): C, 40.48; H, 6.32; N, 3.26. Found: C, 40.63; H, 6.25; N, 3.20. $\Lambda_M = 76.8\ \Omega^{-1}\ mol^{-1}\ cm^2$. IR (KBr): 1890 w [$\nu$(FeH)] cm^{-1}. ^1H NMR [CD_2Cl_2, 25 °C; δ]: 9.58−7.28 (m, 8 H, bpy), 4.00 qnt, 3.65 m, 3.47 m (18 H, CH_2), 1.23, 0.90 (t, 27 H, CH_3), spin system AB_2X (X = H), δ_X −18.41 (1 H, Fe−H, $J_{AX} = 70$, $J_{BX} = 58$ Hz). $^{31}P\{^1H\}$ NMR [CD_2Cl_2, 25 °C; δ]: spin system AB_2, δ_A 178.9, δ_B 160.1, $J_{AB} = 127.9$ Hz. $^{13}C\{^1H\}$ NMR [CD_2Cl_2, 25 °C; δ]: 159−117 (m, bpy), 120.5 (q, CF_3, $^1J_{CF} = 319$ Hz), 61.9 d, 60.7 t (CH_2), 16.2 d, 16.0 t (CH_3). Calcd for $C_{41}H_{54}F_3FeN_2O_9P_3S$ (**1b-CF$_3$SO$_3$**): C, 51.47; H, 5.69; N, 2.93. Found: C, 51.28; H, 5.55; N, 3.02. $\Lambda_M = 80.4\ \Omega^{-1}\ mol^{-1}\ cm^2$. IR (KBr): 1886 w [$\nu$(FeH)] cm^{-1}. ^1H NMR [CD_2Cl_2, 25 °C; δ]: 9.21−7.12 (m, 15 H, Ph and 8 H, bpy), 3.86, 3.61, 3.38 (m, 12 H, CH_2), 1.30, 1.05, 1.03 (t, 18 H, CH_3), spin system AB_2X (X = H), δ_X −18.04 (1 H, Fe−H, $J_{AX} = J_{BX} = 62$ Hz). $^{31}P\{^1H\}$ NMR [CD_2Cl_2, 25 °C; δ]: spin system AB_2, δ_A 204.0, δ_B 187.2, $J_{AB} = 93.5$ Hz. Calcd for $C_{53}H_{54}F_3FeN_2O_6P_3S$ (**1c-CF$_3$SO$_3$**): C, 60.46; H, 5.17; N, 2.66. Found: C, 60.28; H, 5.29; N, 2.55. $\Lambda_M = 78.8\ \Omega^{-1}\ mol^{-1}\ cm^2$. IR (KBr): 1865 w [$\nu$(FeH)] cm^{-1}. ^1H NMR [CD_2Cl_2, 25 °C; δ]: 9.32−7.05 (m, 30 H, Ph and 8 H, bpy), 3.32 m, 2.99 qnt (6 H, CH_2), 0.72, 0.47 (t, 9 H, CH_3), spin system AB_2X (X = H), δ_X −16.86 (1 H, Fe−H, $J_{AX} = J_{BX} = 56.2$ Hz). $^{31}P\{^1H\}$ NMR [CD_2Cl_2, 25 °C; δ]: spin system AB_2, δ_A 177.5, δ_B 167.0, $J_{AB} = 74.0$ Hz.

[FeH(phen)P$_3$]BPh$_4$ (2) [P = P(OEt)$_3$ (2a), PPh(OEt)$_2$ (2b)]. These red-brown complexes were prepared exactly like the related bipyridine complexes **1** starting from the $FeCl_2$(phen) precursor; yield ≥45%. Anal. Calcd for $C_{54}H_{74}BFeN_2O_9P_3$ (**2a**): C, 61.49; H, 7.07; N, 2.66. Found: C, 61.35; H, 6.95; N, 2.54. $\Lambda_M = 56.0\ \Omega^{-1}\ mol^{-1}\ cm^2$. Calcd for $C_{66}H_{74}BFeN_2O_6P_3$ (**2b**): C, 68.88; H, 6.48; N, 2.43. Found: C, 68.97; H, 6.56; N, 2.49. $\Lambda_M = 51.8\ \Omega^{-1}\ mol^{-1}\ cm^2$.

[FeH(phen){P(OEt)$_3$}$_3$]CF$_3$SO$_3$ (2a-CF$_3$SO$_3$). This complex was prepared like the related triflate complex **1a-CF$_3$SO$_3$** using $LiCF_3SO_3$ as precipitating agent; yield ≥15%. Anal. Calcd for $C_{31}H_{54}F_3FeN_2O_{12}P_3S$: C, 42.09; H, 6.15; N, 3.17. Found: C, 42.27; H, 6.25; N, 3.10. $\Lambda_M = 82.5\ \Omega^{-1}\ mol^{-1}\ cm^2$. IR (KBr): 1890 w [$\nu$(FeH)] cm^{-1}. ^1H NMR [CD_2Cl_2, 25 °C; δ]: 9.11−7.05 (m, 8 H, phen), 4.25 qnt, 3.55 m (18 H, CH_2), 1.47, 0.90 (t, 27 H, CH_3), spin system AB_2X (X = H), δ_X −17.91 (1 H, Fe−H, $J_{AX} = 70$, $J_{BX} = 56$ Hz). $^{31}P\{^1H\}$ NMR [CD_2Cl_2, 25 °C; δ]: spin system AB_2, δ_A 180.5, δ_B 159.8, $J_{AB} = 130.5$ Hz.

[FeH(bpy)$_2$P]BPh$_4$ (3) [P = P(OEt)$_3$ (3a), PPh(OEt)$_2$ (3b)]. To a solution of $[Fe(bpy)_3]Cl_2\cdot5H_2O$ (1 g, 1.46 mmol) in 15 mL of ethanol were added first an excess of the appropriate phosphite (2 mmol) and then an excess of $NaBH_4$ (10 mmol, 0.38 g) in 10 mL of ethanol. The reaction mixture was stirred at room temperature for 2 h, and then the resulting red-brown solution was filtered through silica gel (TLC standard grade). The solvent was removed under reduced pressure to give an oil, which was triturated at 0 °C with ethanol (5 mL) containing an excess of $NaBPh_4$ (2.5 mmol, 0.86 g). A red-brown solid slowly separated out, which was filtered and crystallized from CH_2Cl_2 and ethanol; yield ≥50%. Anal. Calcd for $C_{50}H_{52}BFeN_4O_3P$ (**3a**): C, 70.27; H, 6.13; N, 6.56. Found: C, 70.02; H, 6.10; N, 6.49. $\Lambda_M = 54.3\ \Omega^{-1}\ mol^{-1}\ cm^2$. Calcd for $C_{54}H_{52}BFeN_4O_2P$ (**3b**): C, 73.15; H, 5.91; N, 6.32. Found: C, 72.96; H, 6.00; N, 6.25. $\Lambda_M = 48.6\ \Omega^{-1}\ mol^{-1}\ cm^2$.

[Fe(η^2-H$_2$)(bpy)P$_3$]$^{2+}$Y^{2-} (4), [Fe(η^2-H$_2$)(phen)P$_3$]$^{2+}$Y^{2-} (5) [P = P(OEt)$_3$ (4a, 5a), PPh(OEt)$_2$ (4b), PPh$_2$OEt (4c); Y = 2CF$_3$SO$_3$$^-$] and [Fe($\eta^2$-H$_2$){PPh(OEt)$_2$}$_3$(phen)]$^{2+}$Y^{2-} (5b) (Y^{2-} = BPh$_4$$^-$ and CF$_3$SO$_3$$^-$). These complexes were prepared in solution in an NMR tube at a temperature below −20 °C. A typical experiment involves the preparation of a solution of the appropriate hydride (0.04 mmol) in CD_2Cl_2 (0.5 mL) in an NMR tube which was cooled to −80 °C. An excess (0.08 mmol, 7.1 μL) of triflic acid was added and the tube transferred into the probe of the NMR instrument, precooled to −80 °C. The progress of the reaction was monitored by ^1H and $^{31}P\{^1H\}$ spectra recorded from −80 to 20 °C.

[Fe(CO)(bpy){P(OEt)$_3$}$_3$](BPh$_4$)$_2$ (6a). An excess of $HBF_4\cdot Et_2O$ (0.6 mmol, 86 μL of a 54% solution in Et_2O) was added to a solution of $[FeH(bpy)\{P(OEt)_3\}_3]BPh_4$ (0.200 g, 0.19 mmol) in 10 mL of CH_2Cl_2 cooled to −80 °C and placed under a CO atmosphere (1 atm). The reaction mixture was allowed to reach room temperature overnight with stirring. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (3 mL) containing an excess of $NaBPh_4$ (0.4 mmol, 0.137 g). An orange solid slowly separated out from the resulting solution, which was filtered and crystallized from CH_2Cl_2 and ethanol; yield ≥60%. Anal. Calcd for $C_{77}H_{93}B_2FeN_2O_{10}P_3$: C, 67.17; H, 6.81; N, 2.03. Found: C, 67.32; H, 6.88; N, 1.95. $\Lambda_M = 119.5\ \Omega^{-1}\ mol^{-1}\ cm^2$.

$[Fe(CH_3CN)(bpy)P_3](BPh_4)_2$ (7) [P = $P(OEt)_3$ (7a), $PPh(OEt)_2$ (7b)]. To a solution of the appropriate hydride (0.19 mmol) in 10 mL of CH_3CN cooled to −80 °C was added an excess of $HBF_4\cdot Et_2O$ (0.6 mmol, 86 μL of a 54% solution in Et_2O), and the reaction mixture was allowed to reach room temperature and stirred for 2 h. The solvent was removed under reduced pressure to give an oil, which was treated with ethanol (3 mL) containing an excess of $NaBPh_4$ (0.4 mmol, 0.137 g). An orange solid slowly separated out, which was filtered and crystallized from CH_2Cl_2 and ethanol; yield ≥65%. Anal. Calcd for $C_{78}H_{96}B_2FeN_3O_9P_3$ (**7a**): C, 67.40; H, 6.96; N, 3.02. Found: C, 67.21; H, 7.04; N, 2.93. $\Lambda_M = 124.0\ \Omega^{-1}\ mol^{-1}\ cm^2$. Calcd for $C_{90}H_{96}B_2FeN_3O_6P_3$ (**7b**): C, 72.74; H, 6.51; N, 2.83. Found: C, 72.93; H, 6.60; N, 2.87. $\Lambda_M = 119.7\ \Omega^{-1}\ mol^{-1}\ cm^2$.

$[Fe(CH_3CN)(phen)\{PPh(OEt)_2\}_3](BPh_4)_2$ (8b). This orange complex was prepared exactly like the related bipyridine complexes **7**; yield ≥60%. Anal. Calcd for $C_{92}H_{96}B_2FeN_3O_6P_3$: C, 73.17; H, 6.41; N, 2.78. Found: C, 73.04; H, 6.50; N, 2.69. $\Lambda_M = 112.6\ \Omega^{-1}\ mol^{-1}\ cm^2$.

$[Fe(ArN{=}NH)(bpy)P_3](BPh_4)_2$ (9, 10) [Ar = C_6H_5 (9), 4-$CH_3C_6H_4$ (10); P = $P(OEt)_3$ (a), $PPh(OEt)_2$ (b)]. In a 25-mL three-necked round-bottomed flask were placed solid samples of the appropriate hydride (0.34 mmol) and an excess of the appropriate aryldiazonium salt (1 mmol), and the flask was cooled to −196 °C. Dichloromethane (10 mL) was slowly added, and the reaction mixture was allowed to reach room temperature and stirred for 2 h. The solvent was removed under reduced pressure to give an oil, which was treated with ethanol (3 mL) containing an excess of $NaBPh_4$ (0.88 mmol, 0.30 g). A yellow-orange solid slowly separated out from the resulting solution, which was filtered and crystallized from CH_2Cl_2 and ethanol; yield ≥70%. Anal. Calcd for $C_{82}H_{99}B_2FeN_4O_9P_3$ (**9a**): C, 67.69; H, 6.86; N, 3.85. Found: C, 67.89; H, 6.95; N, 4.02. $\Lambda_M = 118.7\ \Omega^{-1}\ mol^{-1}\ cm^2$. Calcd for $C_{83}H_{101}B_2FeN_4O_9P_3$ (**10a**): C, 67.86; H, 6.93; N, 3.81. Found: C, 67.80; H, 7.02; N, 3.74. $\Lambda_M = 126.6\ \Omega^{-1}\ mol^{-1}\ cm^2$. Calcd for $C_{95}H_{101}B_2FeN_4O_6P_3$ (**10b**): C, 72.90; H, 6.50; N, 3.58. Found: C, 72.68; H, 6.55; N, 3.51. $\Lambda_M = 119.9\ \Omega^{-1}\ mol^{-1}\ cm^2$.

$[Fe(C_6H_5N{=}^{15}NH)(bpy)\{P(OEt)_3\}_3](BPh_4)_2$ (9a-^{15}N). This compound was prepared exactly like the related unlabeled complex **9a** using the $[C_6H_5N{\equiv}^{15}N]BF_4$ as a reagent; yield ≥65%.

$[Fe(4\text{-}CH_3C_6H_4N{=}NH)(phen)P_3](BPh_4)_2$ (11) [P = $P(OEt)_3$ (11a), $PPh(OEt)_2$ (11b)]. These orange complexes were prepared following the method used for the related bipyridine derivatives **10**; yield ≥65%. Anal. Calcd for $C_{85}H_{101}B_2FeN_4O_9P_3$ (**11a**): C, 68.37; H, 6.82; N, 3.75. Found: C, 68.44; H, 6.91; N, 3.88. $\Lambda_M = 121.0\ \Omega^{-1}\ mol^{-1}\ cm^2$. Calcd for $C_{97}H_{101}B_2FeN_4O_6P_3$ (**11b**): C, 73.31; H, 6.41; N, 3.53. Found: C, 73.08; H, 6.54; N, 3.49. $\Lambda_M = 115.8\ \Omega^{-1}\ mol^{-1}\ cm^2$.

Acidity Measurements. The protonation of $[FeH(N\text{-}N)P_3]CF_3SO_3$ complexes **1-CF_3SO_3** and **2-CF_3SO_3** was studied in an NMR tube by ^{31}P and ^{1}H NMR mesurements in CD_2Cl_2 at low temperature. The concentrations of $[FeH(N\text{-}N)P_3]^+$ and $[Fe(\eta^2\text{-}H_2)(N\text{-}N)P_3]^{2+}$ were determined by integration of the inverse-gated decoupled ^{31}P spectra using a delay time of 10 s between pulses. A typical experiment involved the addition of 30−40 mg (0.03−0.04 mmol) of the appropriate hydride $[FeH(N\text{-}N)P_3]CF_3SO_3$ in a screw-cap NMR tube placed in a Vacuum Atmospheres drybox. CD_2Cl_2 (0.5 mL) was added, the solid was dissolved and the tube was sealed by the screw-cap. After standard NMR measurements, incremental amounts of CF_3SO_3H were added (from 0.5 to 4 equiv) by a microsyringe to the NMR tube cooled to −80 °C and then transferred into the probe precooled to −80 °C. Approximately 1.5 equiv of CF_3SO_3H is required to completely generate the $[Fe(\eta^2\text{-}H_2)(N\text{-}N)P_3]^{2+}$ dicationic species for all the hydrides **1** and **2**.

Results and Discussion

Preparation of Hydride Complexes. Dichloro complexes $FeCl_2(bpy)$ and $FeCl_2(phen)$ react with phosphites in the presence of $NaBH_4$ to give the mixed-ligand hydride cations $[FeH(bpy)P_3]^+$ (**1**) and $[FeH(phen)P_3]^+$ (**2**), which were isolated as BPh_4 or CF_3SO_3 salts and characterized (eq 1).

$$FeCl_2(N\text{-}N) \xrightarrow[\text{EtOH}]{\text{excess P, excess NaBH}_4} \underset{\mathbf{1,\,2}}{[FeH(N\text{-}N)P_3]^+} \qquad (1)$$

N-N = bpy (**1**), phen (**2**); P = $P(OEt)_3$ (**a**),
$PPh(OEt)_2$ (**b**), PPh_2OEt (**c**)

Studies on the reaction course showed that both the isomers of $FeCl_2(N\text{-}N)$ compounds, which were reported to be a chain polymer containing either a six-coordinated (red isomer) or a five-coordinated (orange isomer) iron(II) unit,[13] did not react with phosphites in ethanol, and only the addition of $NaBH_4$ led the reaction to proceed yielding the final species **1** or **2**. These compounds, however, were the only hydrides we isolated from the reaction, and changes in the experimental conditions, i.e. change of the ratio among the reagents, addition of free bpy or phen, or the lowering of the reaction temperature, resulted only in a lowering of the yield of the final complexes **1** and **2**.

The tris(bipyridine) complex $[Fe(bpy)_3]Cl_2\cdot 5H_2O$ also reacted with $NaBH_4$ in the presence of phosphites and gave the bis(bipyridine) $[FeH(bpy)_2P]^+$ (**3**) hydride cations, which were isolated as BPh_4 salts and characterized (eq 2). The reaction of the related phenanthroline $[Fe(phen)_3]^{2+}$ cation, instead, gave under all conditions the tris(phosphite) complexes $[FeH(phen)P_3]^+$ (**2**), isolable either in pure form or as a mixture containing the starting $[Fe(phen)_3]^{2+}$ derivative.

$$[Fe(bpy)_3]^{2+} \xrightarrow[\text{EtOH}]{\text{excess P, excess NaBH}_4} \underset{\mathbf{3}}{[FeH(bpy)_2P]^+} \qquad (2)$$

P = $P(OEt)_3$ (**a**), $PPh(OEt)_2$ (**b**)

The new hydrides **1**−**3** are red-brown solids moderately stable in air and in a solution of polar organic solvents, where they behave as 1:1 electrolytes.[15] The analytical and spectroscopic data (Table 1) support the proposed formulation, and a geometry in solution was also established. The IR spectra show a weak band at 1890−1782 cm^{-1} attributed to the ν(FeH) of the hydride ligand. Its presence is confirmed

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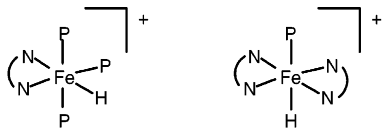
(15) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81−122.

Chart 1



I *mer* **II** *trans*

by the ^{1}H NMR spectra which show the characteristic low-frequency multiplet between −12 and −19 ppm. This pattern appears as an AB_2X (X = H) multiplet for the $[FeH(N\text{-}N)P_3]^+$ (**1**, **2**) cations, due to the coupling with the phosphorus nuclei. A simulation of the spectra can be obtained with the parameters reported in Table 1, which show that the values of the two J_{PH} are equal in some cases or comparable in magnitude (i.e. 70 and 56 Hz) in the others, suggesting that the hydride should occupy the same mutual position with all the phosphite ligands. Taking into account that in the temperature range between +20 and −80 °C the $^{31}P\{^1H\}$ NMR spectra appear as an AB_2 multiplet, a *mer* geometry of type **I** (Chart 1) can reasonably be proposed for the tris(phosphite) **1**, **2** derivatives.

Support for this proposal comes from the X-ray crystal structure determination[16] of the related ruthenium complex $[RuH(bpy)\{P(OEt)_3\}_3]BPh_4$, whose spectroscopic data are very similar, and a *mer* geometry was established.

The hydride signals for the bis(bipyridine) $[FeH(bpy)_2P]^+$ complexes **3a** and **3b** each appear as a doublet (at −13.13 and at −12.86 ppm) with J_{PH} values of 116 and 102 Hz. These values are somewhat higher than those observed in the related $[FeH(N\text{-}N)P_3]^+$ complexes (**1**, **2**) and may suggest a mutually trans position of the hydride and phosphite ligands as in a type **II** geometry (Chart 1).

Protonation Reactions. Hydride $[FeH(N\text{-}N)P_3]^+$ (**1**, **2**) complexes react with the Brønsted acid CF_3SO_3H (or HBF_4) at low temperature to give the dihydrogen $[Fe(\eta^2\text{-}H_2)(N\text{-}N)P_3]^{2+}$ (**4**, **5**) derivatives, as shown in eq 3. The protonation

$$\underset{\mathbf{1,\,2}}{[FeH(N\text{-}N)P_3]^+} \xrightarrow{CF_3SO_3H} \underset{\mathbf{4,\,5}}{[Fe(\eta^2\text{-}H_2)(N\text{-}N)P_3]^{2+}} \tag{3}$$

N-N = bpy (**1**, **4**), phen (**2**, **5**); P = $P(OEt)_3$ (**a**), $PPh(OEt)_2$ (**b**), PPh_2OEt (**c**)

reaction was carried out at variable temperatures and was monitored by ^{1}H and ^{31}P NMR spectra. The addition of the Brønsted acid to **1** or **2** caused the disappearance of the hydride multiplet and the appearance of a broad signal (half-height width of about 200 Hz) between −13 and −17 ppm attributed to the η^2-H_2 ligand. Measurements of T_1 on these signals gave a T_{1min} value of about 3 ms (Table 2) in agreement[17] with the presence of a dihydrogen derivative. Further support for the presence of the η^2-H_2 ligand came from the measurement of the J_{HD} values of the isotopomer $[Fe(\eta^2\text{-}HD)(N\text{-}N)P_3]^{2+}$ derivatives. These HD complexes were prepared by the addition of deuterated triflic acid CF_3SO_3D to the hydrides **1**, **2** in CD_2Cl_2. Their ^{1}H NMR spectra exhibit, in the hydride region, a relatively sharp triplet of doublets of intensity ratio 1:1.3:1. The increased intensity of the center peak of the triplet of the HD resonances is due to the presence of a small amount of H_2 species, resulting from the incomplete deuteration of the triflic acid, while the doubling of each signal of the triplet is attributable to the coupling with the phosphorus nuclei of the phosphites with $^2J_{PH_{HD}}$ of 12 Hz for **4a**, **4b** and 14 Hz for **5a**. From this triplet a value between 31.5 and 32.5 Hz for J_{HD} was measured, which confirms the formation of the dihydrogen derivatives. From the J_{HD} values the H−H distances[18] were calculated, and they are reported in Table 2. Values between 0.89 and 0.92 Å were observed for our η^2-H_2 complexes **4**, **5**, which fall in the range found in the previously reported dicationic dihydrogen derivatives[6] of iron and ruthenium. The presence of the poor π-acceptor bpy or phen ligands does not seem to have a strong influence on the H−H distances of dicationic η^2-H_2 complexes. The H−H bond length in the H_2 ligand can also be calculated[19] from the T_{1min} values. The results for our complexes (Table 2) show that there is a general agreement between the distance calculated from the J_{HD} values and those determined by the T_1 method using a static rotation model. For a fast rotation of H_2, instead, the observed T_{1min} values give rather short H−H lengths, which are also not comparable with the known dihydrogen derivatives. An analysis of J_{HD} and T_{1min} data of known dihydrogen complexes that have J_{HD} values ≥25 Hz has been recently reported[20] and shows as in only a few cases, namely those with general formula *trans*-$[MH(\eta^2\text{-}H_2)(P\text{-}P)_2]^+$ (M = Fe, Ru; P-P = chelating phosphine) it is necessary to invoke the fast-rotation model to produce a reasonable H−H distance in the H_2 ligand. In general, the H−H distances should be calculated from T_{1min} data using a static rotation model, as observed in our case. However, the dicationic dihydrogen complex $[Fe(\eta^2\text{-}H_2)(CO)(dppe)_2]^{2+}$ [dppe = 1,2-bis(diphenylphosphinoethane)] recently reported by Morris and coworkers[6d] shows that the H−H distances obtained from the J_{HD} are consistent with those calculated from T_{1min} data using a fast-spinning model. Our mixed-ligand dicationic dihydrogen complexes **4** and **5** differ from that of Morris in this aspect.

In the temperature range between −80 and −20 °C the $^{31}P\{^1H\}$ NMR spectra of η^2-H_2 complexes **4** and **5** appear as an AB_2 multiplet. Taking into account that the ^{1}H NMR spectra of the isotopomers $[Fe(\eta^2\text{-}HD)(N\text{-}N)P_3]^{2+}$ recorded

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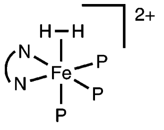
Chart 2



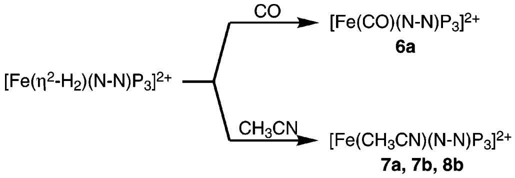
III

at −40 °C show a strong coupling ($^{2}J_{HP}$ of 12 and 14 Hz) between HD and one phosphorus nucleus suggesting a mutually trans position between the hydrogen and one phosphite ligand, a *fac* geometry **III** (Chart 2) can reasonably be proposed for our derivatives **4** and **5**. The protonation of the hydrides **1** and **2**, therefore, involves an isomerization as well, giving a final complex containing the H_2 trans to the π-acceptor phosphite ligand.

The variable-temperature ^{1}H NMR spectra of **4** and **5** also show that the complexes are thermally unstable and, already at −20 °C, the signal of free H_2 at 4.6 ppm appears in the proton spectra. Unfortunately, this thermal instability prevents the isolation of the complexes **4** and **5** in the solid state. This instability, however, is somewhat unexpected in light of the relatively long H−H distances and of the behavior of the comparable $[Fe(\eta^2\text{-}H_2)(CO)(P\text{-}P)_2]^{2+}$ dicationic complex,[6d] which does not lose H_2 in solution at room temperature. Probably, either the trans influence of the phosphite ligand in our compounds **4** and **5** as compared to CO in $[Fe(\eta^2\text{-}H_2)(CO)(P\text{-}P)_2]^{2+}$ derivative, or the nature of the $Fe(N\text{-}N)P_3$ fragment makes the $[Fe(\eta^2\text{-}H_2)(N\text{-}N)P_3]^{2+}$ derivative unstable toward the loss of H_2.

Studies on the protonation of the $[FeH(N\text{-}N)P_3]^+$ complexes indicated that less than 1.5 equiv of CF_3SO_3H is required to completely generate the $[Fe(\eta^2\text{-}H_2)(N\text{-}N)P_3]^{2+}$ (**4**, **5**) species. This result indicates that our dicationic dihydrogen complexes **4** and **5** are less acidic than the related dicationic η^2-H_2 derivatives[6b,d] such as $[Os(\eta^2\text{-}H_2)(CO)(dppe)_2]^{2+}$ and $[Fe(\eta^2\text{-}H_2)(CO)(dppe)_2]^{2+}$, which require at least 10 equiv of CF_3SO_3H for their preparation. The relatively low acidity observed in our complexes **4**, **5** is probably due to the presence of the bpy or phen ligands, which can delocalize the total charge of the complexes making the η^2-H_2 ligand less acidic. However, all the compared complexes contain CO as a ligand, whose π-acceptor properties in those M(CO)(dppe)$_2$ fragments should lead to a strong acidity of the η^2-H_2 ligand. A qualitative comparison can also be made with $[Os(\eta^2\text{-}H_2)(CH_3CN)(dppe)_2](BF_4)_2$ [6a] and $[M(\eta^2\text{-}H_2)(PR_3)_2(bpy)(CO)]^{2+}$ (M = Ru, Os),[6c] whose formation from the monohydride required a large excess of $HBF_4{\cdot}Et_2O$ for the former and 4 equiv of CF_3SO_3H for the latter, suggesting that the mixed-ligand iron(II) dihydrogen complexes $[Fe(\eta^2\text{-}H_2)(N\text{-}N)P_3]^{2+}$ (**4**, **5**) can be estimated as the least acidic among the above-reported[6] dicationic dihydrogen derivatives. Only the dicationic[21] $[Os(\eta^2\text{-}H_2)(NH_3)_5]^{2+}$ is less acidic than our **4** and **5** derivatives, probably owing to the presence of the σ-donor NH_3 ligands, which make the amino complex stable toward base.

Scheme 1[a]



[a] P = P(OEt)$_3$, N-N = bpy (**6a**, **7a**); P = PPh(OEt)$_2$, N-N = phen (**7b**, **8b**).

We have also studied the protonation of the monophosphite $[FeH(bpy)_2P]^+$ (**3**) at low temperatures with both CF_3SO_3H and $HBF_4{\cdot}Et_2O$, but in this case no formation of η^2-H_2 species was detected by ^{1}H NMR spectra. The addition of the Brønsted acid at low temperature causes a color change of the solution followed by the separation of solid products indicating that decomposition takes place. It seems therefore that only complexes containing three phosphites and one bipyridine or phenanthroline like **1**, **2** can stabilize the η^2-H_2 derivatives, at least at low temperature.

Reactivity. The lability of the η^2-H_2 ligand in complexes **4**, **5** prompted us to test the substitution reaction with several ligands, and the results are summarized in Scheme 1. Although the reaction proceeds easily with CO, phosphite, isocyanide, H_2O, CH_3CN, etc., only the carbonyl **6a** and the nitrile **7**, **8** complexes were obtained in pure form. In the other cases, mixtures of products were obtained from which the detected complexes were not separated.

The new iron(II) complexes **6**−**8** were isolated as BPh_4 salts and are orange solids stable in the air and in a solution of polar organic solvents in which they behave as 2:1 electrolytes.[15] Analytical and spectroscopic data (Table 1) support their formulation. The IR spectrum of the carbonyl complex **6a** shows, besides the absorptions of the BPh_4^- anion and of the bpy and P(OEt)$_3$ ligands, one strong band at 2033 cm^{-1} attributed to the ν(CO) of the carbonyl group. The $^{13}C\{^{1}H\}$ NMR spectrum confirms the presence of the CO ligand showing one doublet of triplets at 207.8 ppm due to the carbonyl carbon atom coupled with the phosphorus nuclei of the phosphites. The two $^{2}J_{CP}$ have the same value of 55 Hz, suggesting that the carbonyl ligand should occupy the same mutual position with all the phosphite ligands. In the temperature range between +20 and −80 °C the $^{31}P\{^{1}H\}$ NMR spectrum appears as an A_2B multiplet. On this basis a *mer* geometry **IV** can be reasonably proposed for the carbonyl complex **6a**.

The IR spectra of the nitrile complexes **7**, **8** do not show any band attributable to ν(CN) probably owing to their very low intensity.[22] However, the presence of this ligand is confirmed by the ^{1}H NMR spectra which show a singlet at 1.34−2.07 ppm of the methyl group of the CH_3CN. The $^{13}C\{^{1}H\}$ NMR spectra of **8b** further support the presence of the nitrile showing a singlet at 3.65 ppm due to the methyl carbon resonance and a singlet at 137.8 ppm of the C≡N carbon atom. The HMQC and HMBC experiments confirm this attribution showing the correlation between the methyl proton signal at 1.42 ppm of CH_3CN with the ^{13}C signal at 3.65

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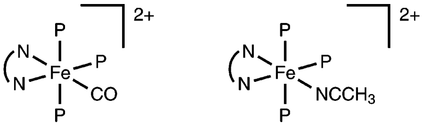
Chart 3



IV **V**

ppm in HMQC and with those at 137.8 ppm in HMBC, in agreement with the proposed formulation.

In the temperature range between +30 and −80 °C the $^{31}P\{^1H\}$ NMR spectra of the nitrile complexes **7**, **8** appear as AB_2 multiplets which were simulated with the parameters reported in Table 1. These data, however, do not allow us to unambiguously assign a geometry in solution to these complexes, although by analogy with the carbonyl **6a**, a *mer* type **V** (Chart 3) may be tentatively proposed.

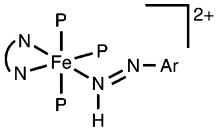
Reactivity studies on the new hydrides $[FeH(N\text{-}N)P_3]BPh_4$ (**1**, **2**) and $[FeH(N\text{-}N)_2P]BPh_4$ (**3**) were devoted also to an insertion reaction into the Fe−H bond. Several unsaturated molecules were tested such as terminal alkynes, heteroallenes (CO_2, CS_2, ArNCS) and aryldiazonium cations. The results showed that only aryldiazonium cations ArN_2^+ react with $[FeH(N\text{-}N)P_3]BPh_4$ to give isolable aryldiazene[23] $[Fe(ArN{=}NH)(N\text{-}N)P_3](BPh_4)_2$ (**9**, **10**, **11**) derivatives (eq 4). Decomposition products were obtained with the other reagents in the reaction with the mixed-ligand hydrides **1**−**3**, except with carbon dioxide, which does not react with either tris(phosphite) $[FeH(N\text{-}N)P_3]^+$ or the mono(phosphite) $[FeH(bpy)_2P]^+$ hydride derivative.

$$[FeH(N\text{-}N)P_3]^+ \xrightarrow{ArN_2^+} \underset{\mathbf{9},\ \mathbf{10},\ \mathbf{11}}{[Fe(ArN{=}NH)(N\text{-}N)P_3]^{2+}} \qquad (4)$$

N-N = bpy (**9**, **10**), phen (**11**); P = $P(OEt)_3$ (**a**),
$PPh(OEt)_2$ (**b**); Ar = C_6H_5 (**9**), 4-$CH_3C_6H_4$ (**10**, **11**)

Good analytical data were obtained for aryldiazene complexes **9**, **10**, **11**, which are orange solids stable in air and in a solution of polar organic solvents where they behave as 2:1 electrolytes.[15] The spectroscopic data (Table 1) support the proposed formulation, and a geometry in solution was also established. Diagnostic for the presence of the diazene ligand are the ^1H NMR spectra which show the characteristic slightly broad NH signal between 13 and 14 ppm. Support for this attribution comes from the ^1H spectra of the labeled **9a-^{15}N** complex which shows the ^{15}NH resonance as a high frequency doublet at 13.87 ppm with $^1J_{NH}$ of 68 Hz in agreement[23,24] with the presence of the diazene ligand. In the proton spectra the signals of the phosphite, the polypyridyl ligand, and the BPh_4 anion are also present, while the ^{31}P spectra appear as an AB_2 multiplet suggesting that two phosphites are magnetically equivalent and different from the third. Furthermore, we also recorded the $^{15}N\{^1H\}$ NMR spectra of the labeled $[Fe(C_6H_5N{=}^{15}NH)(bpy)\{P(OEt)_3\}_3](BPh_4)_2$ (**9a-^{15}N**) complex, which appear as an AB_2Y multiplet (Y = ^{15}N) due to the coupling with the phosphorus nuclei. The two coupling constants $^2J_{NP}$ show very similar values (8.4 and 8.6 Hz) as expected for a diazene ligand which is in the same mutual position with all the phosphite ligands. On this basis a geometry of type **VI** (Chart 4) can be reasonably proposed for the aryldiazene derivatives **9**−**11**.

Chart 4



VI

Aryldiazene complexes of iron(II) are known,[23,25] but contain exclusively phosphites as supporting ligands. The synthesis of complexes **9**−**11** shows that also polypyridyls such as phen and bpy are able to stabilize aryldiazene iron(II) derivatives.

Conclusions

An easy route for the synthesis of the first iron(II) hydride complexes containing both polypyridyl and phosphite as supporting ligands of the $[FeH(N\text{-}N)P_3]BPh_4$ and $[FeH(bpy)_2P]BPh_4$ type is described. Mixed-ligand dihydrogen complexes $[Fe(\eta^2\text{-}H_2)(N\text{-}N)P_3]^{2+}$ were obtained by protonation of the $[FeH(N\text{-}N)P_3]BPh_4$ hydride precursors with Brønsted acid. Measurements of T_{1min} and J_{HD} values give information on the H−H distances of the η^2-H_2 ligand, while protonation studies suggests a strong acidic character of the dihydrogen ligand. However, the presence of the polypyridyl ligand makes the $[Fe(\eta^2{-}H_2)(N\text{-}N)P_3]^{2+}$ complexes among the least acidic of the known dicationic dihydrogen derivatives. New polypyridyl iron(II) complexes can also be prepared using both classical and nonclassical hydride complexes as precursors. Thus, carbonyl $[Fe(CO)(bpy)\{P(OEt)_3\}_3](BPh_4)_2$, nitrile $[Fe(CH_3CN)(N\text{-}N)P_3](BPh_4)_2$, and aryldiazene $[Fe(ArN{=}NH)(N\text{-}N)P_3](BPh_4)_2$ complexes were obtained.

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Supporting Information Available: Observed and calculated $^{31}P\{^1H\}$ NMR spectra of compound **5b** (Figure S1). The hydride part of the proton spectrum of compound **1a** (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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