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Bis(aryldiazene) Derivatives of Iron(II): Preparation, Characterization, and Properties of the First Complexes Containing Two Diazene Ligands Bonded to the Same Central Metal. The X-ray Crystal Structures of Hexacoordinate $[FeH(4\text{-}CH_3C_6H_4NNH)\{P(OEt)_3\}_4]^+$ and Pentacoordinate $[Fe(4\text{-}CH_3C_6H_4N_2)\{P(OEt)_3\}_4]^+$ Cations

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Abstract: The complexes $[FeH(ArN{=}NH)L_4]BPh_4$ (**1**) and $[Fe(ArN{=}NH)_2L_4](BPh_4)_2$ (**2**) [$L = P(OEt)_3$; Ar = $4\text{-}CH_3C_6H_4$ (**a**), $4\text{-}CH_3OC_6H_4$ (**b**), $4\text{-}FC_6H_4$ (**c**)] were prepared by reacting hydride FeH_2L_4 with aryldiazonium cations in CH_2Cl_2 at −80 °C. Their characterization by ^1H and $^{31}P\{^1H\}$ NMR (with ^{15}N isotopic substitution) is reported. The reaction of bis(diazene) **2** with triethylamine was investigated and led to the synthesis of new pentacoordinate $[Fe(ArN_2)L_4]^+$ (**3**) [Ar = $4\text{-}CH_3C_6H_4$ (**a**), $4\text{-}CH_3OC_6H_4$ (**b**), $4\text{-}FC_6H_4$ (**c**)] aryldiazenido complexes, which were isolated and characterized by infrared and $^{31}P\{^1H\}$ NMR spectroscopy. The structures of compounds **1a** and **3a** were determined crystallographically. The compounds crystallize in the space group $P2_1/n$ ($a = 21.271$ (8) Å, $b = 15.727$ (4) Å, $c = 20.580$ (7) Å, $\beta = 112.77$ (3)°, and $Z = 4$) and $P\bar{1}$ ($a = 14.834$ (8) Å, $b = 18.942$ (10) Å, $c = 11.738$ (6) Å, $\alpha = 100.59$ (4)°, $\beta = 90.36$ (5)°, $\gamma = 95.52$ (4)°, and $Z = 2$), respectively. Both structures were solved by heavy-atom techniques and were refined by least-squares calculations to $R = 0.0839$ and 0.0779, respectively. In **1a** the iron cation is six-coordinate with the diazene and the hydride ligand in mutually cis position. The structure of **3a** consists of discrete cations and anions. The cation is five-coordinate with coordination geometry close to trigonal bipyramidal with an equatorial single-bent aryldiazenido group. Significant angles and distances are the following: Fe–N(1) = 1.672 (9) Å, N(1)–N(2) = 1.224 (13) Å; Fe–N(1)–N(2) = 166.6 (9)°, N(1)–N(2)–C(*p*-tolyl) = 120.3 (10)°.

A number of studies on the synthesis, structure, and reactivity of aryldiazene complexes have been reported in recent years.[2] However, no data are yet available on metal derivatives containing two ArN=NH groups bonded to the same central metal.

We recently described the synthesis of the first aryldiazene derivatives of iron(II) obtained by "apparent" insertion of an aryldiazonium cation into the Fe–H bond of a new monohydride.[3] The peculiarity of these results has now led us to extend our studies to include the dihydride $FeH_2[P(OEt)_3]_4$ compound with the aim of testing the possiblity that the "insertion" of two ArN_2^+ groups into the FeH_2 moiety could take place.

The reaction of hydrides such as $MH_2(CO)(PPh_3)_3$ (M = Ru, Os),[4] $IrH_3(PPh_3)_3$,[5] $RhH_2Cl(PPh_3)_2S$ (S = solvent),[5] Cp_2WH_2,[2f,6] and $CpRe(CO)_2H_2$[6] with aryldiazonium cations has previously been studied, but the insertion of only one ArN_2^+ group was always observed, giving monodiazene, monoarylhydrazido, and monodiazenido complexes, respectively. In this paper we describe the results of our investigations, which gave the first examples of bis(aryldiazene) complexes. Furthermore, relatively few crystal structures of 3d transition-metal aryldiazene and aryldiazenido complexes have been reported, as compared with the corresponding 4d and 5d metals. Only three aryldiazenido X-ray studies of $[Fe(CO)_2(N_2C_6H_5)(PPh_3)_2]BF_4$, $[PhNNMn(CO)_4]_2$, and $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(o\text{-}N_2C_6H_4CF_3)]BF_4$ have been made,[7-9] whereas no data on 3d aryldiazene derivatives are known. The structural characterization of the new iron aryldiazene $[FeH(ArNNH)L_4]BPh_4$ and aryldiazenido $[Fe(ArN_2)L_4]BPh_4$ complexes was therefore undertaken and the results are also reported.

Experimental Section

Solvents and Reagents. All the solvents used were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. Ethanol was dried over calcium hydride, diethyl ether over sodium/benzophenone, and dichloromethane by reflux over phosphorus pentoxide. Acetone and nitromethane were distilled over activated molecular sieves. Triethyl phosphite (Ega Chemie) was purified by distillation under nitrogen. Diazonium salts were obtained in the usual way, as described in the literature.[10] The labeled diazonium salt $[4\text{-}CH_3C_6H_4N^{15}N]BF_4$ was prepared from $Na^{15}NO_2$ (99% enriched, Stohler Isotope Chemicals) and the arylamine. Triethylamine was dried with, and distilled from, CaH_2 and BaO before use. Other reagents were purchased from commercial sources in the highest available purity and used as received.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer Model 683. Solid-state spectra were obtained with potassium bromide pellets, while solution spectra were obtained from KBr solution cells (path length 0.5 mm). Proton magnetic resonance spectra were recorded on a Varian EM390 or a Varian FT-80A instrument with tetramethylsilane as an internal standard. Fourier-mode, proton-noise-decoupled ^{31}P NMR spectra were collected on a Varian FT-80A spec-

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trometer 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 nitromethane at 25 °C were measured with a "Halosis" bridge. Solution susceptibilities were determined by the Evans method.[11]

Synthesis of the Complexes. All synthetic work was performed under an inert atmosphere with standard Schlenk techniques. The dihydride species $[FeH_2L_4]$ [L = $P(OEt)_3$] was prepared according to the procedure previously reported.[12]

$[FeH(ArN{=}NH)\{P(OEt)_3\}_4]BPh_4$ (1) and $[Fe(ArN{=}NH)_2\{P(OEt)_3\}_4](BPh_4)_2$ (2) [Ar = 4-$CH_3C_6H_4$ (a), 4-$CH_3OC_6H_4$ (b), 4-FC_6H_4 (c)]. A solution of $FeH_2\{P(OEt)_3\}_4$ (2.0 g, 2.77 mmol) in 20 mL of CH_2Cl_2 was cooled to −80 °C and quickly transferred, at the same temperature, into a reaction flask containing an excess of the appropriate diazonium salt (10 mmol). The reaction mixture was stirred for 10 min, brought to 0 °C in 10–15 min, 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 treated with ethanol (20 mL) to give a red-brown solution. The addition of $NaBPh_4$ (2.0 g, 6 mmol) caused the separation of a red solid containing $[FeH(ArN{=}NH)L_4]BPh_4$ and $[Fe(ArN{=}NH)_2L_4](BPh_4)_2$ compounds, which were separated by fractional crystallization. In a typical separation, the more soluble monodiazene complex **1** was extracted from the crude product with three 20-mL portions of diethyl ether. The solvent was removed under reduced pressure, giving a red oil which, by crystallization with ethanol, afforded red crystals of the compound. Microcrystals of $[Fe(ArN{=}NH)_2L_4](BPh_4)_2$ were obtained by dissolving the yellow-orange residue in dichloromethane (5 mL) and, after filtration, adding ethanol in excess (50–70 mL). The ratio between the two complexes depends on the reaction time; the total yield is, however, about 80%.

Bis(diazene) $[Fe(ArN{=}NH)_2L_4]^{2+}$ derivatives can also be prepared by reacting monodiazenes $[FeH(ArN{=}NH)L_4]^+$ with $[ArN_2]BF_4$. A typical preparation involved the addition of an excess of the appropriate diazonium salt (3 mmol) to a solution of $[FeH(ArN{=}NH)L_4]BPh_4$ (1 mmol) in 20 mL of CH_2Cl_2. The reaction mixture was stirred for 1 h at 0 °C and then filtered, and the solvent was removed by evaporation. The oil obtained was treated with ethanol containing $NaBPh_4$ (0.34 g, 1 mmol), affording an orange product, which was crystallized from CH_2Cl_2 (5 mL)/ethanol (50 mL); yield ≥70%.

The physical constants and elemental analyses for the monodiazene $[FeH(ArN{=}NH)\{P(OEt)_3\}_4]BPh_4$ complexes follow.

Anal. Calcd for Ar = 4-$CH_3C_6H_4$: C, 56.90; H, 7.73; N, 2.41. Found: C, 56.42; H, 7.75; N, 2.38. 106 °C dec. Λ_M 57.55 cm^2 Ω^{-1} M^{-1}.

Anal. Calcd for Ar = 4-$CH_3OC_6H_4$: C, 56.13; H, 7.62; N, 2.38. Found: C, 55.75; H, 7.83; N, 2.12. 128 °C dec. Λ_M 52.80 cm^2 Ω^{-1} M^{-1}.

Anal. Calcd for Ar = 4-FC_6H_4: C, 55.68; H, 7.44; N, 2.41. Found: C, 54.86; H, 7.74; N, 2.11. 132 °C dec. Λ_M 66.62 cm^2 Ω^{-1} M^{-1}.

The physical constants and elemental analyses for the $[Fe(ArN{=}NH)_2\{P(OEt)_3\}_4](BPh_4)_2$ derivatives follow.

Anal. Calcd for Ar = 4-$CH_3C_6H_4$: C, 64.58; H, 7.31; N, 3.50. Found: C, 64.90; H, 7.39; N, 3.50. 117 °C dec. Λ_M 121.9 cm^2 Ω^{-1} M^{-1}.

Anal. Calcd for Ar = 4-$CH_3OC_6H_4$: C, 63.32; H, 7.17; N, 3.44. Found: C, 62.98; H, 7.16; N, 3.24. 120 °C dec. Λ_M 124.0 cm^2 Ω^{-1} M^{-1}.

Anal. Calcd for Ar = 4-FC_6H_4: C, 62.77; H, 6.90; N, 3.49. Found: C, 62.62; H, 6.96; N, 3.40. 108 °C dec. Λ_M 121.9 cm^2 Ω^{-1} M^{-1}.

$[Fe(4\text{-}FC_6H_4N{=}NH)(4\text{-}CH_3OC_6H_4N{=}NH)\{P(OEt)_3\}_4](BPh_4)_2$. This complex was prepared following the procedure above reported for bis(diazene) complexes, by reacting the $[FeH(4\text{-}FC_6H_4N{=}NH)\{P(OEt)_3\}_4]BPh_4$ compound in CH_2Cl_2 at 0 °C with an excess of $[4\text{-}CH_3OC_6H_4N_2]BF_4$ salt.

Anal. Calcd: C, 63.05; H, 7.03; N, 3.46. Found: C, 62.77; H, 7.07; N, 3.38. 112 °C dec. Λ_M 117.1 cm^2 Ω^{-1} M^{-1}.

$[Fe(ArN_2)\{P(OEt)_3\}_4]BPh_4$ [Ar = 4-$CH_3C_6H_4$ (a), 4-$CH_3OC_6H_4$ (b), 4-FC_6H_4 (c)]. Triethylamine (0.18 mL, 1.2 mmol) was added to a solution of the appropriate bis(diazene) complex $[Fe(ArN{=}NH)_2L_4]^{2+}$ (0.7 mmol) in dichloromethane (15 mL). A color change of the solution from orange to dark-red was observed, and after 30 min, the reaction mixture was filtered. The solvent was removed by evaporation, and the brown oil remaining was treated with ethanol (15 mL) to give a white solid ($[Et_3NH]BPh_4$) and a red solution. The solid was removed by filtration, and after slow cooling of the red solution to −30 °C, crystals of $[Fe(ArN_2)\{P(OEt)_3\}_4]BPh_4$ were obtained; yield ≥80%.

The physical constants and elemental analyses for aryldiazenido complexes follow.

Table I. Summary of Crystal Data, Intensity Collection, and Refinement for $[FeH(4\text{-}CH_3C_6H_4N{=}NH)\{P(OEt)_3\}_4]BPh_4$ (**1a**) and $[Fe(4\text{-}CH_3C_6H_4N_2)\{P(OEt)_3\}_4]BPh_4$ (**3a**)

	1a	**3a**
formula	$C_{55}H_{89}BFeN_2O_{12}P_4$	$C_{55}H_{87}BFeN_2O_{12}P_4$
formula wt	1160.87	1158.85
cryst color and habit	yellow-orange prisms	red-brown parallelepipeds
cryst dimensions, mm	0.23 × 0.49 × 0.58	0.36 × 0.46 × 0.59
space group	$P2_1/n^a$	$P\bar{1}$
cell constants^b		
a, Å	21.271 (8)	14.834 (8)
b, Å	15.727 (4)	18.942 (10)
c, Å	20.580 (7)	11.738 (6)
α, deg	90	100.59 (4)
β, deg	112.77 (3)	90.36 (5)
γ, deg	90	95.52 (4)
V, Å^3	6348 (4)	3226 (3)
Z	4	2
d_{calcd}, g cm^{-3}	1.215	1.193
μ (Mo Kα), cm^{-1}	3.89	3.82
scan method	θ–2θ	ω–2θ
scan speed	3–12 deg/min	0.075 deg/s
2θ limits, deg	5.0–48.0	6.0–47.0
quadrants collected	$+h+k\pm l$	$\pm h\pm k+l$
standard reflcn	3, 2, 6	4, $\bar{2}$, 2
freq	every 50 measurements	every 120 min
variatn	negligible	negligible
no. of data collected	9568	9393
No. of unique obsd data	4365	3431
σ criterion	$I > 2\sigma(I)$	$I > 3\sigma(I)$
no. of unique data used (last cycle)	4329	3367
no. of variables	494	544
ratio of observations to variables	8.8/1	6.2/1
R^c	0.0839	0.0779
$R_w{}^d$	0.0914	0.0828
$R_g{}^e$	0.1143	0.1003
GOF	1.240	1.777

[a] A nonstandard setting of $^5C_{2h}$, no. 14; coordinates of equivalent positions: $\pm(x, y, z; {}^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z)$. [b] Based on least-squares fit to θ values for 19 reflections with $11 < \theta < 15°$ for **1a** and 25 reflections with $7 < \theta < 19°$ for **3a**. [c] $R = \sum|\Delta F|/\sum|F_o|$. [d] $R_w = \sum(\Delta F)w^{1/2}/\sum w^{1/2}F_o$. [e] $R_g = [\sum w(\Delta F)^2/\sum wF_o{}^2]^{1/2}$.

Anal. Calcd for Ar = 4-$CH_3C_6H_4$: C, 57.00; H, 7.57; N, 2.42. Found: C, 57.64; H, 7.72; N, 2.46. 153 °C dec. Λ_M 60.60 cm^2 Ω^{-1} M^{-1}.

Anal. Calcd for Ar = 4-$CH_3OC_6H_4$: C, 56.23; H, 7.47; N, 2.39. Found: C, 56.83; H, 7.55; N, 2.33. 114 °C dec. Λ_M 65.90 cm^2 Ω^{-1} M^{-1}.

Anal. Calcd for Ar = 4-FC_6H_4: C, 55.78; H, 7.28; N, 2.41. Found: C, 56.04; H, 7.43; N, 2.42. 133 °C dec. Λ_M 67.40 cm^2 Ω^{-1} M^{-1}.

Crystallography of $[FeH(4\text{-}CH_3C_6H_4N{=}NH)\{P(OEt)_3\}_4]BPh_4$ (1a) and $[Fe(4\text{-}CH_3C_6H_4N_2)\{P(OEt)_3\}_4]BPh_4$ (3a). Data Collection and Processing. X-ray measurements of compound **1a** were carried out on a Siemens AED computer-controlled diffractometer by using Nb-filtered Mo Kα radiation; those of compound **3a** were performed on a Philips PW 1100 diffractometer equipped with graphite monochromator and Mo Kα radiation. The results from automatic peak search, centering, and indexing procedures were consistent with a monoclinic cell in the case of **1a** and a triclinic cell in the case of **3a**. For **1a** the space group $P2_1/n$ was unquestionably defined by systematic absences $h0l, h + l = 2n + 1$ and $0k0, k = 2n + 1$. For **3a** the ambiguity in the space group, $P1$ or $P\bar{1}$, was resolved by means of statistics on normalized structure factors E, which showed the crystal to be centrosymmetric, so $P\bar{1}$ was chosen and later confirmed by the satisfactory refinement of the structure. Lattice parameters are listed in Table I, together with summaries of crystal data and details concerning data collection and structure refinement. Standard reflections measured during the course of the experiment showed no variation with time for either compound. For **1a** the intensities of the reflections were obtained from the diffraction profile by a modification of the Lehmann and Larsen procedure,[13] while for **3a** the three-point technique was used. The data were corrected for Lorentz and

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polarization factors, and an empirical correction for absorption effects was applied.

Structure Solution and Refinement. Both structures were solved with use of the heavy-atom method. In each case the iron atom position was deduced from a three-dimensional Patterson map, while the remaining non-hydrogen atoms were located in successive difference Fourier syntheses. Refinement was by full-matrix least-squares calculations based on *F*, minimizing the function $\sum w|\Delta F^2|$ and treating all non-hydrogen atoms anisotropically, except three O atoms in **1a** [those bonded to P(2)], which had high thermal motion, and all the ethyl C atoms in both **1a** and **3a**. A regular hexagon with C–C fixed at 1.395 Å was fitted to all the phenyl rings of the anion, which were then refined as rigid bodies with attached H. Toward the end of refinement, a ΔF map showed the hydride ligand at a distance of 1.58 Å from Fe. Since this structure was of relatively poor quality, we chose not to refine the hydride position but to introduce this atom as a fixed contribution with positional parameters from the ΔF map. The hydrogen atoms from the cation were not included. In both structures, but especially in **3a**, some degree of disorder was observed for the ethyl groups. While no satisfactory model was found for this disorder in **1a**, it was possible to locate two alternative positions and to refine their occupancies for seven C atoms in **3a**. The somewhat high values of the final residues, defined as in Table I, may be a result of both disorder and weak diffracting power of the crystals. It should be noted that two independent data sets were collected for **1a** with use of two different crystals, which led to the same results. After refinement had been completed, a careful check of the data revealed that in both structures some reflections at the limit of observation (36 for **1a** and 64 for **3a**) had large values of $F_o - F_c$; accordingly, it seemed reasonable to remove them from the final refinement cycle. The final ΔF map in both structures contained some ripples (0.3–0.4 e Å^{-3}), mainly in regions close to the ethyl groups, suggesting that the models for these moieties are not fully adequate. Weighting schemes applied were of the form $w = k/[\sigma^2(F_o) + g|F_o|^2]$. Scattering factors with corrections for the effects of anomalous dispersion were taken from ref[14].

The final fractional atomic coordinates are given in Tables III and IV, and relevant interatomic distances and angles are listed in Tables V and VI. The remaining structural information, including thermal parameters, observed and calculated structure factors, and all bond distances and angles, is reported as supplementary material.

Calculations were carried out with the SHELX-76 system of programs[15] partly on the Cyber 76 computer of CINECA (Casalecchio, Bologna) and partly on the Gould-SEL 32/77 computer of the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R. (Parma).

Results and Discussion

Preparation and Characterization of Monodiazene and Bis(diazene) Complexes. The reaction of hydride $FeH_2\{P(OEt)_3\}_4$ with an excess of aryldiazonium cations $ArN_2^+BF_4^-$ in dichloromethane at −80 °C proceeds to give first monodiazene $[FeH(ArN{=}NH)\{P(OEt)_3\}_4]^+$ complexes **1**, which further react with $ArN_2^+BF_4^-$ to yield bis(diazene) derivatives **2**, as reported in Scheme I. Both complexes **1** and **2** were isolated from the reaction mixture as BPh_4^- salts and separated by fractional crystallization.[16] Some spectroscopic properties of these compounds, which are diamagnetic red or orange solids, relatively stable in the solid state and in solution of polar organic solvents, are given in Table II. Furthermore, the presence of the diazene ligand[17] in both **1** and **2** was confirmed by ^1H NMR studies, using ^{15}N labeled ($ArN{=}^{15}NH$) and unlabeled complexes. Thus, the broad signal at δ 13.8 appearing in the ^1H NMR spectra of **1a**, attributable to the diazene[18] hydrogen atom, is replaced by a sharp doublet ($J_{^{15}NH}$ = 65 Hz) in the labeled $[FeH(ArN{=}^{15}NH)L_4]^+$ complex, thus confirming the existence of the diazene ligand. In the case of unlabeled bis(diazene) complex **2a**, only one broad signal at δ 14.6 is present, due to NH resonance, which is still replaced by a

Table II. Selected Infrared and NMR Data for Iron Complexes

compd no.	compounds[a]	$\nu(N{=}N)$,[b] cm^{-1}	^1H NMR,[c] δ: NH	CH$_2$ phosph	CH$_3$	CH$_3$ phosph	FeH	spin syst	$^{31}P\{^1H\}$ NMR chem shifts,[c,d] δ (coupling const, Hz)		
1a	$[FeH(4\text{-}CH_3C_6H_4N{=}NH)\{P(OEt)_3\}_4]^+$		13.8 br	4.07 m	2.35 s	1.27 m	−9.30 m	AB$_2$C	δA = 170.3 (J_{AB} = 124.0)	δB = 162.7 (J_{AC} = 76.7)	δC = 158.1 (J_{BC} = 71.0)
1b	$[FeH(4\text{-}CH_3OC_6H_4N{=}NH)\{P(OEt)_3\}_4]^+$		13.6 br	4.09 m	3.77 s	1.26 m	−9.22 m	AB$_2$C	δA = 167.6 (J_{AB} = 123.0)	δB = 159.6 (J_{AC} = 75.2)	δC = 155.3 (J_{BC} = 71.0)
1c	$[FeH(4\text{-}FC_6H_4N{=}NH)\{P(OEt)_3\}_4]^+$		13.9 br	4.13 m		1.28 m	−9.35 m	AB$_2$C	δA = 169.9 (J_{AB} = 123.0)	δB = 162.2 (J_{AC} = 76.9)	δC = 157.7 (J_{BC} = 69.5)
2a	$[Fe(4\text{-}CH_3C_6H_4N{=}NH)_2\{P(OEt)_3\}_4]^{2+}$		14.6 br	4.44 m 4.16 m	2.45 s	1.45 t 1.13 t		A$_2$B$_2$	δA = 148.1 (J_{AB} = 129.9)	δB = 137.6	
2b	$[Fe(4\text{-}CH_3OC_6H_4N{=}NH)_2\{P(OEt)_3\}_4]^{2+}$		14.2 br	4.40 m 4.11 m	3.87 s	1.43 t 1.11 t		A$_2$B$_2$	δA = 150.1 (J_{AB} = 128.9)	δB = 138.8	
2c	$[Fe(4\text{-}FC_6H_4N{=}NH)_2\{P(OEt)_3\}_4]^{2+}$		14.6 br	4.42 m 4.15 m		1.43 t 1.12 t		A$_2$B$_2$	δA = 147.3 (J_{AB} = 130.4)	δB = 136.9	
2d	$[Fe(4\text{-}CH_3OC_6H_4N{=}NH)(4\text{-}FC_6H_4N{=}NH)\text{-}\{P(OEt)_3\}_4]^{2+}$		14.7 br 14.2 br	4.25 m	3.83 s	1.26 m		ABC$_2$	δA = 148.7 (J_{AB} = 56.0)	δB = 147.9 (J_{AB} = 124.9)	δC = 137.6 (J_{BC} = 135.1)
3a	$[Fe(4\text{-}CH_3C_6H_4N_2)\{P(OEt)_3\}_4]^+$	1668 s 1654 sh (1670 s 1660 sh)		4.13 m	2.34 s	1.25 t		ABC$_2$[e]	δA = 167.4 (J_{AB} = −4.8)	δB = 165.5 (J_{AC} = 126.0)	δC = 152.5 (J_{BC} = 125.0)
3b	$[Fe(4\text{-}CH_3OC_6H_4N_2)\{P(OEt)_3\}_4]^+$	1664 s (1667 s)		4.11 m	3.81 s	1.27 t		ABC$_2$[e]	δA = 167.2 (J_{AB} = −5.5)	δB = 166.1 (J_{AC} = 128.0)	δC = 153.4 (J_{BC} = 123.5)
3c	$[Fe(4\text{-}FC_6H_4N_2)\{P(OEt)_3\}_4]^+$	1660 s (1662 s)		4.12 m		1.29 t		ABC$_2$[e]	δA = 166.2 (J_{AB} = −4.0)	δB = 165.6 (J_{AC} = 124.1)	δC = 152.3 (J_{BC} = 127.0)

[a] All the compounds are BPh_4^- salts. [b] In CH_2Cl_2 and (KBr). [c] At room temperature in $(CD_3)_2CO$. [d] Positive shift downfield from 85% H_3PO_4. [e] At −50 °C in $(CD_3)_2CO$.

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(14) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99 and 149.

(15) Sheldrick, G. M. *SHELX-76: a program for crystal structure determination*; University of Cambridge: England, 1976.

(16) The same compounds **1** and **2** were also obtained with acetone instead of CH_2Cl_2 as solvent, but in this case yields were lower.

(17) In the infrared spectra of both complexes **1** and **2** the ν(NN) band cannot be unambiguously assigned.

(18) It may be noted that this value, as well as the $^1J_{^{15}NH}$ value, falls in the range of that of the previously reported aryldiazene derivatives (δ 11.60–15.1 and 65–92 Hz, respectively). See ref 2a and: Carrol, J. A.; Sutton, D.; Xiaoheng, Z. *J. Organomet. Chem.* **1982**, *244*, 73.

Table III. Fractional Atomic Coordinates ($\times 10^4$) for Compound **1a**

atom	x/A	y/B	z/C	atom	x/A	y/B	z/C
Fe	452 (1)	2326 (1)	2522 (1)	C47	7092 (4)	6130 (5)	202 (4)
P1	−389 (1)	2269 (2)	2856 (1)	C48	7652 (4)	6422 (5)	71 (4)
P2	−169 (1)	2875 (2)	1492 (1)	C49	8150 (4)	6915 (5)	573 (4)
P3	1124 (1)	1642 (2)	3446 (1)	C50	9085 (4)	7108 (5)	2543 (4)
P4	952 (1)	3539 (2)	2937 (1)	C51	8899 (4)	6272 (5)	2610 (4)
O1	−431 (4)	1485 (4)	3330 (4)	C52	9245 (4)	5822 (5)	3231 (4)
O2	−1093 (3)	2214 (5)	2191 (4)	C53	9777 (4)	6207 (5)	3783 (4)
O3	−475 (4)	3010 (4)	3334 (4)	C54	9964 (4)	7043 (5)	3716 (4)
O7	1074 (3)	629 (4)	3502 (3)	C55	9618 (4)	7493 (5)	3095 (4)
O8	1100 (4)	1898 (4)	4175 (3)	B	8660 (6)	7696 (8)	1836 (6)
O9	1896 (3)	1790 (5)	3525 (3)	O4	328 (4)	3282 (5)	1181 (4)
O10	1598 (4)	3652 (5)	2733 (4)	O5	−613 (5)	2290 (7)	865 (6)
O11	1321 (4)	3735 (5)	3756 (3)	O6	−704 (7)	3570 (10)	1336 (7)
O12	494 (4)	4345 (4)	2629 (4)	C1	−591 (6)	621 (8)	3051 (6)
N1	1095 (4)	2079 (6)	2111 (4)	C2	−407 (7)	50 (9)	3681 (7)
N2	1095 (5)	1492 (6)	1702 (5)	C3	−1769 (7)	2224 (8)	2241 (7)
C25	1635 (6)	1497 (7)	1452 (6)	C4	−2263 (8)	1973 (10)	1534 (8)
C26	1477 (6)	1161 (8)	774 (6)	C5	−920 (9)	2997 (11)	3730 (9)
C27	1986 (7)	1184 (8)	501 (7)	C6	−729 (8)	3614 (10)	4272 (8)
C28	2620 (6)	1518 (8)	881 (7)	C7	128 (9)	3550 (11)	448 (9)
C29	2775 (6)	1837 (8)	1553 (7)	C8	744 (10)	3909 (12)	386 (10)
C30	2279 (6)	1831 (8)	1837 (7)	C9	−762 (9)	1494 (12)	823 (9)
C31	3160 (7)	1545 (11)	565 (7)	C10	−1268 (10)	1170 (12)	177 (10)
C32	8223 (4)	8453 (5)	2042 (3)	C11	−1048 (12)	4043 (16)	1564 (12)
C33	7830 (4)	9010 (5)	1514 (3)	C12	−1586 (11)	4560 (14)	1062 (11)
C34	7458 (4)	9654 (5)	1667 (3)	C13	1113 (6)	96 (8)	2935 (6)
C35	7478 (4)	9740 (5)	2350 (3)	C14	1099 (7)	−838 (9)	3159 (7)
C36	7870 (4)	9183 (5)	2879 (3)	C15	1263 (7)	1389 (9)	4816 (7)
C37	8243 (4)	8540 (5)	2725 (3)	C16	905 (8)	1721 (10)	5228 (8)
C38	9250 (4)	8107 (4)	1579 (5)	C17	2452 (8)	1455 (10)	4121 (8)
C39	9684 (4)	7526 (4)	1449 (5)	C18	3064 (10)	1422 (13)	3919 (10)
C40	10187 (4)	7814 (4)	1224 (5)	C19	2237 (8)	4075 (10)	3171 (8)
C41	10256 (4)	8682 (4)	1129 (5)	C20	2679 (9)	4135 (12)	2776 (9)
C42	9822 (4)	9263 (4)	1259 (5)	C21	932 (6)	3936 (8)	4176 (7)
C43	9320 (4)	8975 (4)	1484 (5)	C22	1463 (8)	4106 (10)	4927 (8)
C44	8090 (4)	7115 (5)	1207 (4)	C23	736 (7)	5220 (9)	2730 (7)
C45	7531 (4)	6823 (5)	1338 (4)	C24	752 (9)	5522 (11)	2041 (9)
C46	7032 (4)	6331 (5)	835 (4)	H1	107	1483	2125

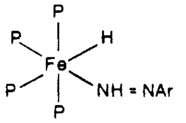
doublet ($J_{^{15}NH}$ = 65 Hz) in the case of the labeled $[Fe(ArN{=}^{15}NH)_2L_4]^{2+}$ complex.

Scheme I

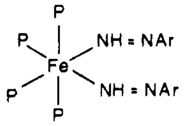
$$FeH_2L_4 \xrightarrow{ArN_2^+} \underset{\mathbf{1}}{[FeH(ArN{=}NH)L_4]^+} \xrightarrow{ArN_2^+} \underset{\mathbf{2}}{[Fe(ArN{=}NH)_2L_4]^{2+}}$$

$L = P(OEt)_3$; $Ar = 4\text{-}CH_3C_6H_4$ (**a**), $4\text{-}CH_3OC_6H_4$ (**b**), $4\text{-}FC_6H_4$ (**c**)

The $^{31}P\{^1H\}$ NMR spectra of monodiazene complexes **1**, in the temperature range +30 to −80 °C, are AB_2C multiplets, which can be simulated with the values reported in Table II. Cis geometry (I) can therefore be proposed in solution for these complexes, as observed in the solid state. On the other hand, the $^{31}P\{^1H\}$ NMR spectra of bis(diazene) derivatives **2** at +30 °C consist of A_2B_2 patterns (Table II), which remain unchanged when the temperature is lowered to −80 °C. These data confirm the presence of two diazene moieties bonded to the same central metal in a mutual cis position, as indicated in type II geometry. To further confirm the presence of two ArN=NH groups in our compounds, we prepared the mixed $[Fe(4\text{-}CH_3OC_6H_4N{=}NH)(4\text{-}FC_6H_4N{=}NH)\{P(OEt)_3\}_4](BPh_4)_2$ complex, **2d**, which contains two different diazene ligands. In this case, the ^1H NMR spectrum shows two NH resonances at δ 14.7 and 14.2, while the ^{31}P spectrum is an ABC_2 multiplet, in agreement with the proposed stoichiometry for the complex.



I



II

Studies on the chemical properties of both complexes **1** and **2** show that the aryldiazene ligand is rather inert to substitution by several ligands such as CO, isonitrile, nitrile, and phosphite. For example, after 3–4 days of reaction with CO (1 atm) or excess isocyanide at room temperature, starting bis(diazene) compounds **2** can be recovered with a yield ≥90%. The use of longer reaction time as well as reflux conditions is limited, however, by decomposition of starting derivatives **2**. In this case, the reaction gave a mixture of products, the aryldiazenido complexes $[Fe(ArN_2)L_4]^+$ being the main one. The monodiazene complex **1** is also unreactive toward substitution of the ArN=NH group; these results contrast with those obtained by the closely related *trans*-$[Fe(ArN{=}NH)(CO)\{P(OEt)_3\}_4]^{2+}$ compound,[3] whose diazene ligand is a very good leaving group. The different behaviors of the two monodiazene complexes may be explained on the basis of the strong trans influence of the CO group in one case as compared to the phosphite group in **1**. However, also the presence of the hydride ligand in determining the stability of ArN=NH in **1** cannot be underestimated. It can be observed in addition that the stable dinitrogen iron(II) complexes often contain the hydride ligand.[19]

Several attempts were made to prepare crystals of **1** and **2** for X-ray analysis, but only in the case of monodiazene **1a** were suitable crystals obtained. An ORTEP drawing of the iron environment of the $[FeH(4\text{-}CH_3C_6H_4N{=}NH)\{P(OEt)_3\}_4]BPh_4$ (**1a**) complex[20] is shown in Figure 1. The iron atom is hexacoordinated to four phosphite groups, one diazene molecule, and one hydride

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(19) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589.

(20) In both compounds **1a** and **3a** the BPh_4 anion is ordered and well-behaved. It is not involved in significant interactions with the cation atoms. The closest of these contacts occurs between C atoms and is in the range 3.5–3.6 Å.

Table IV. Fractional Atomic Coordinates (×10^4) for Compound **3a**

atom	*x*/*A*	*y*/*B*	*z*/*C*	atom	*x*/*A*	*y*/*B*	*z*/*C*
Fe	2477 (1)	2580 (1)	1418 (1)	C46	1391 (6)	6176 (6)	347 (9)
P1	1175 (2)	2246 (2)	2132 (3)	C47	1835 (6)	6348 (6)	−626 (9)
P2	3810 (2)	2848 (2)	689 (3)	C48	2445 (6)	6966 (6)	−518 (9)
P3	2054 (2)	3645 (2)	1423 (3)	C49	2612 (6)	7412 (6)	563 (9)
P4	3123 (2)	2574 (2)	3115 (3)	C50	2553 (8)	7225 (7)	3771 (9)
O1	239 (5)	2428 (4)	1621 (7)	C51	3179 (8)	6722 (7)	3474 (9)
O2	1085 (5)	1387 (4)	1979 (6)	C52	3351 (8)	6253 (7)	4220 (9)
O3	1050 (5)	2542 (4)	3455 (7)	C53	2897 (8)	6288 (7)	5263 (9)
O4	3664 (6)	3028 (5)	−557 (7)	C54	2271 (8)	6792 (7)	5561 (9)
O5	4436 (6)	3512 (5)	1368 (9)	C55	2099 (8)	7260 (7)	4815 (9)
O6	4518 (6)	2273 (5)	496 (8)	C1	13 (9)	2283 (7)	333 (11)
O7	2855 (6)	4259 (4)	1414 (8)	C2^{a}	−408 (27)	1498 (17)	−47 (28)
O8	1415 (6)	3962 (4)	2432 (7)	C2′^{b}	−791 (59)	1650 (39)	226 (63)
O9	1407 (5)	3702 (4)	344 (7)	C3	348 (9)	996 (7)	2511 (11)
O10	2778 (6)	1940 (7)	3788 (11)	C4	384 (10)	189 (8)	1981 (13)
O11	4170 (6)	2506 (5)	2986 (7)	C5	192 (11)	2706 (9)	4044 (15)
O12	3047 (8)	3177 (7)	4250 (9)	C6	468 (12)	3190 (9)	5179 (15)
N1	2238 (6)	1964 (5)	213 (8)	C7	4367 (14)	3055 (11)	−1377 (19)
N2	2034 (6)	1637 (5)	−768 (9)	C8^{c}	3904 (20)	2784 (26)	−2592 (27)
C25	2184 (8)	876 (7)	−1105 (11)	C8′^{d}	4093 (37)	3271 (42)	−2361 (48)
C26	2261 (8)	443 (7)	−277 (12)	C9^{a}	5343 (22)	3702 (21)	1158 (53)
C27	2393 (9)	−300 (7)	−671 (14)	C9′^{b}	5484 (45)	3572 (42)	1594 (102)
C28	2429 (9)	−531 (8)	−1919 (15)	C10	5724 (11)	4326 (9)	2111 (15)
C29	2370 (11)	−72 (10)	−2686 (15)	C11	4329 (13)	1527 (11)	135 (17)
C30	2208 (10)	644 (8)	−2292 (12)	C12	5091 (14)	1108 (11)	350 (18)
C31	2544 (12)	−1373 (8)	−2325 (16)	C13	2710 (11)	4999 (9)	1358 (14)
B	2367 (10)	7757 (8)	2831 (14)	C14	3609 (12)	5309 (9)	937 (14)
C32	1427 (7)	8179 (4)	3272 (7)	C15	672 (14)	4407 (11)	2303 (17)
C33	578 (7)	7969 (4)	2734 (7)	C16^{e}	290 (48)	4719 (29)	3462 (35)
C34	−166 (7)	8332 (4)	3137 (7)	C16′^{e}	769 (48)	4982 (30)	3334 (36)
C35	−60 (7)	8905 (4)	4077 (7)	C17	1711 (11)	3509 (8)	−833 (14)
C36	789 (7)	9115 (4)	4615 (7)	C18^{c}	1082 (28)	3908 (12)	−1514 (20)
C37	1533 (7)	8752 (4)	4212 (7)	C18′^{d}	1565 (92)	3971 (42)	−1593 (69)
C38	3182 (7)	8399 (7)	2839 (9)	C19^{c}	2945 (15)	1250 (14)	3397 (20)
C39	3027 (7)	8971 (7)	2289 (9)	C19′^{d}	2596 (38)	1681 (31)	4674 (56)
C40	3706 (7)	9533 (7)	2289 (9)	C20	2658 (12)	836 (10)	4474 (17)
C41	4541 (7)	9524 (7)	2838 (9)	C21	4765 (12)	2560 (9)	4033 (15)
C42	4696 (7)	8952 (7)	3388 (9)	C22	5490 (14)	2096 (11)	3648 (18)
C43	4016 (7)	8390 (7)	3389 (9)	C23	3228 (15)	3887 (14)	4229 (20)
C44	2169 (6)	7240 (6)	1535 (9)	C24^{a}	3649 (27)	4324 (15)	5386 (26)
C45	1558 (6)	6622 (6)	1427 (9)	C24′^{b}	2904 (46)	4283 (27)	5460 (45)

[a] Occupancy 0.65. [b] Occupancy 0.35. [c] Occupancy 0.70. [d] Occupancy 0.30. [e] Occupancy 0.50.

Table V. Selected Bond Distances (Å) and Angles (deg) for Compound **1a**

Fe–P(1)	2.153 (4)	N(1)–N(2)	1.250 (14)	N(2)–C(25)	1.427 (19)
Fe–P(2)	2.194 (3)	P(1)–O(1)	1.596 (8)	P(3)–O(7)	1.604 (7)
Fe–P(3)	2.171 (3)	P(1)–O(2)	1.593 (6)	P(3)–O(8)	1.572 (8)
Fe–P(4)	2.190 (3)	P(1)–O(3)	1.581 (8)	P(3)–O(9)	1.604 (8)
Fe–N(1)	1.907 (11)	P(2)–O(4)	1.569 (10)	P(4)–O(10)	1.594 (9)
Fe–H(1)	1.58	P(2)–O(5)	1.570 (10)	P(4)–O(11)	1.591 (7)
		P(2)–O(6)	1.520 (16)	P(4)–O(12)	1.575 (7)
P(1)–Fe–P(2)	93.5 (2)	Fe–N(1)–N(2)	129.6 (8)	N(1)–N(2)–C(25)	116.6 (10)
P(1)–Fe–P(3)	92.6 (2)	Fe–P(1)–O(1)	118.5 (4)	Fe–P(3)–O(7)	121.1 (3)
P(1)–Fe–P(4)	104.5 (2)	Fe–P(1)–O(2)	110.4 (3)	Fe–P(3)–O(8)	117.1 (3)
P(1)–Fe–N(1)	163.9 (3)	Fe–P(1)–O(3)	118.6 (3)	Fe–P(3)–O(9)	108.5 (3)
P(2)–Fe–P(3)	170.8 (2)	O(1)–P(1)–O(2)	103.1 (4)	O(7)–P(3)–O(8)	99.1 (4)
P(2)–Fe–P(4)	93.1 (1)	O(1)–P(1)–O(3)	98.2 (4)	O(7)–P(3)–O(9)	103.3 (4)
P(2)–Fe–N(1)	85.3 (3)	O(2)–P(1)–O(3)	106.2 (4)	O(8)–P(3)–O(9)	106.0 (4)
P(3)–Fe–P(4)	92.0 (1)	Fe–P(2)–O(4)	107.8 (4)	Fe–P(4)–O(10)	109.4 (3)
P(3)–Fe–N(1)	86.9 (3)	Fe–P(2)–O(5)	120.6 (4)	Fe–P(4)–O(11)	123.2 (3)
P(4)–Fe–N(1)	91.5 (3)	Fe–P(2)–O(6)	127.5 (6)	Fe–P(4)–O(12)	114.4 (3)
		O(4)–P(2)–O(5)	100.9 (5)	O(10)–P(4)–O(11)	97.8 (4)
		O(4)–P(2)–O(6)	100.8 (7)	O(10)–P(4)–O(12)	105.4 (4)
		O(5)–P(2)–O(6)	94.8 (7)	O(11)–P(4)–O(12)	104.2 (4)

ion in a slightly distorted octahedral array. The major source of distortion to regular octahedral geometry arises from the small steric bulk of the hydride ligand. Such distortion is mainly reflected in the P(1)–Fe–N(1) and P(1)–Fe–P(4) angles, which are 163.9 (3) and 104.5 (2)° rather than the expected 180 and 90°. The other angles at Fe are all within 10° of the expected idealized values.

Least-squares calculations through the three coordination planes show that the set of P(1)N(1)P(4)H(1) atoms, as well as that of P(2)P(3)P(4)H(1) atoms, forms an almost perfect plane, while P(1)N(1)P(2)P(3) has a slight tetrahedral distortion.

The two P atoms trans to each other are bonded at 2.171 (3) and 2.194 (3) Å, with a mean value of 2.183 Å, practically identical with that observed for the P atom opposite the hydride ligand, 2.190 (3) Å, while the P atom trans to the diazene moiety is slightly closer to the metal at a distance of 2.153 (4) Å. These bonds are similar and slightly but not significantly shorter than those observed in the analogous complex [FeH(CO){P-

Table VI. Selected Bond Distances (Å) and Angles (deg) for Compound **3a**

Fe-P(1)	2.194 (4)	P(1)-O(1)	1.601 (9)	P(3)-O(7)	1.582 (9)
Fe-P(2)	2.211 (4)	P(1)-O(2)	1.596 (8)	P(3)-O(8)	1.588 (9)
Fe-P(3)	2.169 (4)	P(1)-O(3)	1.570 (8)	P(3)-O(9)	1.610 (9)
Fe-P(4)	2.207 (4)	P(2)-O(4)	1.580 (10)	P(4)-O(10)	1.601 (13)
Fe-N(1)	1.672 (9)	P(2)-O(5)	1.574 (9)	P(4)-O(11)	1.577 (10)
N(1)-N(2)	1.224 (13)	P(2)-O(6)	1.572 (11)	P(4)-O(12)	1.600 (11)
N(2)-C(25)	1.461 (16)				
P(1)-Fe-P(2)	176.5 (2)	Fe-P(1)-O(1)	121.2 (4)	Fe-P(3)-O(7)	114.8 (4)
P(1)-Fe-P(3)	90.4 (2)	Fe-P(1)-O(2)	107.5 (4)	Fe-P(3)-O(8)	117.6 (4)
P(1)-Fe-P(4)	88.4 (2)	Fe-P(1)-O(3)	116.0 (4)	Fe-P(3)-O(9)	114.9 (4)
P(1)-Fe-N(1)	90.0 (4)	O(1)-P(1)-O(2)	104.8 (5)	O(7)-P(3)-O(8)	105.4 (5)
P(2)-Fe-P(3)	93.1 (2)	O(1)-P(1)-O(3)	99.7 (5)	O(7)-P(3)-O(9)	104.3 (5)
P(2)-Fe-P(4)	90.8 (2)	O(2)-P(1)-O(3)	106.3 (5)	O(8)-P(3)-O(9)	97.8 (5)
P(2)-Fe-N(1)	88.1 (4)	Fe-P(2)-O(4)	109.2 (4)	Fe-P(4)-O(10)	117.8 (5)
P(3)-Fe-P(4)	108.6 (2)	Fe-P(2)-O(5)	117.9 (4)	Fe-P(4)-O(11)	110.7 (4)
P(3)-Fe-N(1)	116.6 (4)	Fe-P(2)-O(6)	119.9 (4)	Fe-P(4)-O(12)	124.7 (5)
P(4)-Fe-N(1)	134.8 (4)	O(4)-P(2)-O(5)	105.1 (5)	O(10)-P(4)-O(11)	103.9 (6)
Fe-N(1)-N(2)	166.6 (9)	O(4)-P(2)-O(6)	103.8 (5)	O(10)-P(4)-O(12)	91.8 (6)
N(1)-N(2)-C(25)	120.3 (10)	O(5)-P(2)-O(6)	99.2 (6)	O(11)-P(4)-O(12)	104.8 (6)

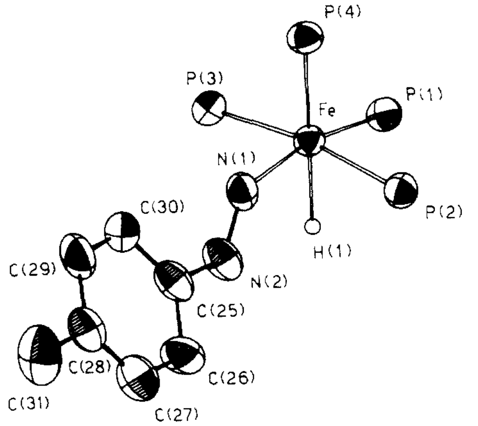

Figure 1. Perspective view of the $[FeH(4-CH_3C_6H_4N=NH)\{P(OEt)_3\}_4]^+$ cation (**1a**) with the numbering scheme used. Thermal ellipsoids are drawn at 40% probability level except for that of the hydride ion which is drawn artificially small. OEt groups have been omitted for clarity.

$(OEt)_3\}_4]BPh_4$, whose structure, which we have earlier reported,[3b] has strong similarities to the present one. Perhaps the only significant difference between the two structures involves the hydride ligand which in the title compound is trans to a phosphite group, while in the CO derivative it is trans to the carbonyl group which has replaced the diazene molecule. The structural parameters in the Fe-N-N system [Fe-N(1) = 1.907 (11) Å, N(1)-N(2) = 1.250 (14) Å, Fe-N(1)-N(2) = 129.6 (8)°, N(1)-N(2)-C(25) = 116.6 (10)°] strongly suggest sp^2 hybridization for both nitrogen atoms. The dimensions in the diazene moiety are in good agreement with the corresponding values found in two other hexacoordinated metal complexes containing an aryldiazene ligand, namely $[RuCl(CO)_2(PhNNH)(PPh_3)_2][ClO_4]\cdot CH_2Cl_2$[2b] and $[IrCl(CO)(FC_6H_3NNH)(PPh_3)_2][BF_4]$.[21]

Preparation and Characterization of Monoaryldiazenido Complexes. Bis(diazene) complexes **2** react in dichloromethane solution with 1 equiv of triethylamine to give pentacoordinate aryldiazenido $[Fe(ArN_2)\{P(OEt)_3\}_4]^+$ complexes **3**, as shown in eq 1. Compounds **3** can also be obtained by operating with an excess of triethylamine.

$$[Fe(ArN=NH)_2L_4]^{2+} + NEt_3 \rightarrow \underset{\mathbf{3}}{[Fe(ArN_2)L_4]^+} + Et_3NH^+ + N_2 + ArH \quad (1)$$

$$Ar = 4\text{-}CH_3C_6H_4\ (\mathbf{a}),\ 4\text{-}CH_3OC_6H_4\ (\mathbf{b}),\ 4\text{-}FC_6H_4\ (\mathbf{c})$$

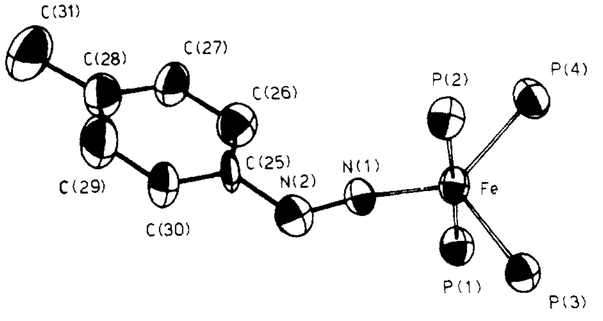

Figure 2. Perspective view of the $[Fe(4-CH_3C_6H_4N_2)\{P(OEt)_3\}_4]^+$ cation (**3a**) with the numbering scheme used. Thermal ellipsoids are drawn at 40% probability level. OEt groups have been omitted for clarity.

The stoichiometry of reaction **1** is substantiated by the following results: (a) aryldiazenido derivatives **3** and ammonium salt $Et_3NH^+BPh_4^-$ are formed in equivalent amounts and can be recovered in quantitative yield; (b) gas chromatographic analysis of the reaction mixture shows the presence of N_2 and the aromatic hydrocarbon ArH. Taking into account that the N_2 and ArH are the decomposition products of the free diazene ligand,[3] we can hypothesize that the reaction with NEt_3 involves the deprotonation of only one aryldiazene ligand in **2** with concurrent dissociation of the other ArN=NH group to give pentacoordinate **3** as the final product. Deprotonation of both the diazene ligands to give a bis(aryldiazenido) complex has never been observed, **3** being the only observed product also operating in excess of base (NEt_3 or KOH). The reaction of the mixed complex $[Fe(4-CH_3OC_6H_4N=NH)(4-FC_6H_4N=NH)\{P(OEt)_3\}_4]^{2+}$ with NEt_3 afforded only the $[Fe(4-FC_6H_4N_2)L_4]^+$ compound and showed, as expected, that deprotonation takes place on the more acidic diazene ligand.

On the contrary, monodiazene complexes **1** are unreactive toward bases, and the starting compounds can be recovered unchanged even after long reaction times with an excess of base. Analogous behavior had also been shown by the previously reported monodiazene $[Fe(ArN=NH)(CO)\{P(OEt)_3\}_4]^+$ derivatives.[3] These different behaviors shown by monodiazene and bis(diazene) may tentatively be explained on the basis of the nature of the coligands around the central metal, rather than in a great difference of acidity between monodiazene and bis(diazene) complexes. The deprotonation giving pentacoordinate complex **3** must involve the dissociation of one ligand, the second ArNNH group, to reach pentacoordination. In the case of monodiazenes **1** and $[Fe(ArNNH)(CO)L_4]^{2+}$, the presence of CO, $P(OEt)_3$, or hydride coligand in the complexes, whose dissociation is probably more difficult than the second ArNNH group in **2**, prevents the formation of aryldiazenido derivatives.

We studied the reaction of the new $[Fe(ArN_2)L_4]^+$ complexes toward hydrogen chloride or HBF_4 in order to test whether

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(21) Einstein, F. W. B.; Gilchrist, A. B.; Rayner-Canham, G. W.; Sutton, D. *J. Am. Chem. Soc.* **1972**, *94*, 645.

protonation of the ArN_2 group can take place to give an aryldiazene derivative. Although color change was observed when a dichloromethane solution of **3** was treated with dry gaseous HCl or HBF_4, no stable products could be isolated. Furthermore, also studying the in situ reaction by ^1H NMR spectroscopy in the temperature range −80 to +34 °C, no evidence of the formation of a diazene species was detected.

Figure 2 shows the molecular structure of the cation of one of the new aryldiazenido complexes,[20] $[Fe(4\text{-}CH_3C_6H_4N_2)\{P(OEt)_3\}_4]BPh_4$ (**3a**). The iron stereochemistry is close to trigonal bipyramidal with two phosphite groups taking two of the equatorial sites, while the third is occupied by the diazenido ligand. The other two phosphite groups span the axial position. The Fe atom lies out of the trigonal plane by only 0.015 Å. The principal angular distortions that occur in the trigonal bipyramidal description are localized in the trigonal plane; the most significant distortions are found in the P(4)–Fe–N(1) and P(3)–Fe–P(4) angles with the former opened to 134.8 (4)° and the latter closed to 108.6 (2)°. These values suggest slight distortion in the coordination polyhedron toward a square-pyramidal configuration. The axial unit, on the other hand, is essentially linear, with the P(1)–Fe–P(2) angle bent 3.5° from the idealized linear arrangement, and the angles between the axial and equatorial ligands show only slight distortions from the expected 90°, ranging from 88.1 (4) to 93.1 (2)°. No significant difference occurs between the axial and equatorial Fe–P bond distances, which average 2.202 and 2.188 Å, respectively. Longer distances, 2.261 (2) and 2.266 (2) Å, have been found by Haymore and Ibers[7] in the closely related complex $[Fe(CO)_2(N_2C_6H_5)(PPh_3)_2][BF_4]$, in which distorted trigonal-bipyramidal coordination geometry is also observed for the iron cation and the two P ligands are axial. As regards the Fe–N–N system, the Fe–N(1) and N(1)–N(2) bond distances, 1.672 (9) and 1.224 (13) Å, respectively, are consistent with significant double bonding and suggest electron delocalization slightly more marked than that found in the above-mentioned iron complex where the Fe–N and N–N distances are 1.702 (6) and 1.201 (7) Å, respectively. The Fe–N(1)–N(2) and N(1)–N(2)–C(25) bond angles found here are 166.6 (9) and 120.3 (10)°, respectively [the respective values in Haymore and Ibers' compound are 179.2 (5) and 124.2 (6)°]. The structural parameters in the Fe–N–N skeleton indicate approximate sp hybridization about the coordinated nitrogen and sp^2 hybridization about the uncoordinated nitrogen. The diazenido ligand essentially displays the singly bent geometry and may therefore be considered to coordinate to the iron atom formally as ArN_2^+, the oxidation state of the metal being 0. The structural parameters in the diazenido moiety are in the range of values previously reported[8] for singly bent aryldiazenido complexes, with the only exception of the Fe–N–N angle which is slightly smaller than those usually observed for M–N–N angles (range 170.6–179.2°).

As in general for metal phosphite complexes, the coordination around the P atoms is distorted tetrahedral. The Fe–P–O and O–P–O angles on average show significant expansion and contraction, respectively, relative to the idealized tetrahedral value.

Selected infrared and NMR data for the new diamagnetic aryldiazenido complexes are reported in Table II. The IR spectra show, in the ν(NN) region, only one band at 1660–1670 cm^{-1}, both in the solid state and in CH_2Cl_2 solution. In the case of the $4\text{-}CH_3C_6H_4N_2$ derivative, **3a**, this band at 1668 cm^{-1} (CH_2Cl_2) shifts to 1637 cm^{-1} on labeling with ^{15}N [using the $Ar^{14}N{\equiv}^{15}N^+$ ligand]. These values for the (NN) stretching frequency are indicative of a singly bent aryldiazenido ligand, whether or not adjusted according to the empirical rules suggested by Haymore and Ibers.[22] This assertion has been shown to be correct by an X-ray structure determination of **3a**, as discussed above. A higher ν(NN) value (1724 cm^{-1}) was observed in the previously reported $[Fe(CO)_2(C_6H_5N_2)(PPh_3)_2]BF_4$ complex,[7,23] in agreement with the slightly higher π-bonding of the ArN_2 ligand in our derivatives.

At room temperature the $^{31}P\{^1H\}$ NMR spectra of **3** consist of broad signals which, by lowering the sample temperature to −50 °C, appear as multiplets of the type shown in Figure 3A. The experimental spectra can be simulated (Figure 3B) with an ABC_2 model using the values listed in Table II. These spectra are rather unexpected because a trigonal-bipyramidal geometry, like that observed in the solid state (Figure 2), should give an A_2B_2 pattern, whereas the ABC_2 spectra could be interpreted on the basis of a square-pyramidal geometry. However, slight distortion of TBP toward SP geometry, already observed in the solid state, would make the two equatorial (or the two apical) P nuclei magnetically not equivalent, with a resulting ABC_2 ^{31}P spectra. Further support for the existence of a distorted TBP structure for **3** in solution can be obtained from a comparison of the ^{31}P values (δ and J_{PP}) of our compounds (Table II), also taking into account the studies of Meek and Du Bois[24] on the relationship existing between the structures and the J_{PP} values for phosphorus ligands at different sites of TBP and SP. The chemical shifts of the two nuclei A and B in these ABC_2 systems show very close values ($\Delta\delta$ about 2 ppm), different from the third (*C*), whereas the J_{AB} (ca. −5 Hz) appear very small as compared to J_{AC} and J_{BC} (124–128 Hz), in agreement with a distorted TBP structure rather that a SP one, in which a higher J_{AB} and $\Delta\delta$ (from *A* and *B*) values would be expected. Lastly, on the basis of these data,[25] interaction with the solvent to give octahedral geometry can reasonably be excluded.

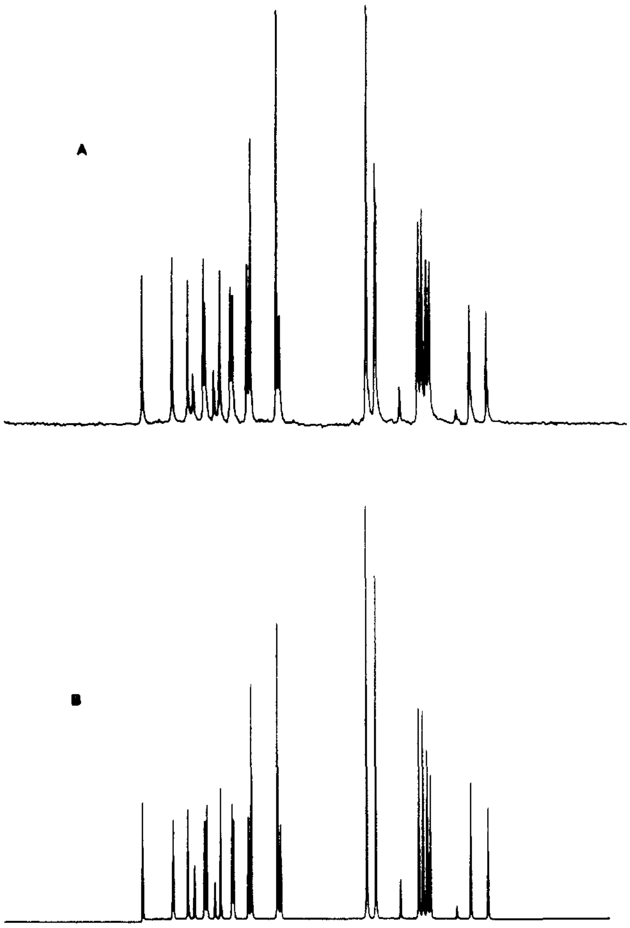

Figure 3. Observed (A) and calculated (B) $^{31}P\{^1H\}$ NMR spectra at −50 °C for a $(CD_3)_2CO$ solution of $[Fe(4\text{-}CH_3C_6H_4N_2)\{P(OEt)_3\}_4]BPh_4$. The simulated spectrum was obtained with an ABC_2 model, and the NMR parameters are given in Table II.

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[24] DuBois, D. L.; Meek, D. W. *Inorg. Chem.* **1976**, *15*, 3076.

[25] An ABC_2 pattern with analogous parameters (δ_A = 168.9 ppm, δ_B = 166.2 ppm, δ_C = 153.2 ppm; J_{AB} = −5.7 Hz, J_{AC} = 125.0 Hz, J_{BC} = 126.1 Hz) is also observed at −50 °C in CD_2Cl_2 for **3a**. The subsequent addition of acetone does not change the profile of the spectrum.

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Registry No. **1a**, 103835-81-0; **1b**, 103835-83-2; **1c**, 103835-85-4; **2a**, 103835-87-6; **2b**, 103835-89-8; **2c**, 103835-91-2; **2d**, 103835-93-4; **3a**, 103835-95-6; **3b**, 103835-97-8; **3c**, 103835-99-0; $FeH_2\{P(OEt)_3\}_4$, 34503-40-7.

Supplementary Material Available: Tables of thermal parameters and a full list of bond lengths, bond angles, and torsion angles for **1a** and **3a** (18 pages); tables of structure factors (32 pages). Ordering information is given on any current masthead page.

Fluorides and Fluoro Acids. 12.[1] Complex-Anion Homology and Isomerism in the Crystal Structures of Two Potassium Poly(hydrogen fluorides), KF·2.5HF and KF·3HF[2]

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Contribution from the Institut für Anorganische Chemie und Strukturchemie, Universität Düsseldorf, D-4000 Düsseldorf, Federal Republic of Germany. *Received May 21, 1986*

Abstract: The compounds KF·2.5HF and KF·3HF were prepared as single crystals and characterized by structure analysis from Mo Kα diffractometer data measured at −100 °C. The structures found are those of poly(hdyrogen fluorides) with anions $H_nF_{n+1}^-$ of three types, formed by strong F–H···F hydrogen bonds. The structural formula of KF·2.5HF (monoclinic, space group $P2_1/a$, $Z = 8$ formula units per unit cell) is $K_2[H_2F_3][H_3F_4]$ with two different, homologous anions. An isomeric $H_3F_4^-$ anion is present in the structure of KF·3HF or KH_3F_4 (rhombohedral, $R\bar{3}c$, $Z = 6$ with hexagonal axes). Evidence for the subsolidus existence below −100 °C of a new, dimorphic compound of the system KF–HF with a very high HF content (KF·7HF?) was obtained by difference thermal analysis.

The system potassium fluoride–hydrogen fluoride is of practical importance for the electrolytic production of elemental fluorine. Its melting diagram[3] shows the existence of five intermediary compounds KF·*x*HF with *x* = 1, 2, 2.5, 3, and 4. Those with *x* = 1, 2, and 4 have been subjected to crystal structure analysis and characterized as complex acid fluorides KHF_2: α[4] and β[5], KH_2F_3[2,6] and KH_4F_5,[7] respectively. The present paper deals with the crystal and in particular the anionic structures of the remaining compounds, KF·2.5HF and KF·3HF.

Experimental and Calculations

The solid phases in the system potassium fluoride–hydrogen fluoride in the region 60–100 mol % HF and their melting behavior were checked by difference thermal analysis with apparatus and techniques as described and referred to elsewhere.[8] The samples were prepared by combining in PTFE vessels and ampules weighed amounts of potassium hydrogen difluoride of controlled purity and hydrogen fluoride distilled from 70–75% technical grade hdyrofluoric acid.

For crystal growth of KF·2.5HF and KF·3HF, molten samples of 72 and 78 mol % HF, respectively, were introduced into polyethylene tubings (ca. 10 mm long, 0.3 mm diameter), which then were sealed at both ends by melting the polymer and fixed in thin-walled glass capillaries. In a temperature-controlled gas stream, single crystals were obtained by simple cooling or miniature zone melting using focused heat radition from a halogen lamp.[9] The crystal symmetry, unit cell dimensions, and reflection intensities were determined on a Syntex P2₁ diffractometer (Mo Kα radiation, graphite monochromator, ω scan). The instrument was equipped with a modified LT-1 low-temperature attachment, and all measurements were carried out at −100 °C.

Table I. Crystallographic Data and Some Numbers Related to the Crystal Structure Determinations

	KF·2.5HF	KF·3HF
mp,[a] °C	64.3	65.8
measuring temp, °C	−100	−100
crystal system	monoclinic	trigonal
space group; *Z*	$P2_1/a$; 8	$R\bar{3}c$; 6
lattice const		
a, pm	831.5 (6)	745.8 (4)
b, pm	838.4 (5)	
c, pm	1003.1 (7)	1181.8 (6)
β, deg	101.63 (5)	
calcd density, g/cm³	2.10	2.07
θ scan range, deg	1.5–30	1.5–30
unique data: obsd;[b] all	1850; 1998	188; 189
parameters refined[c]	102	12
c in weighting scheme[d]	0.0004	0.0
R: obsd; all	0.035; 0.041	0.011; 0.011
R_w: obsd; all	0.065; 0.067	0.015; 0.015

[a] See ref 3. [b] $|F_o| \geq 3.92\sigma_F$. [c] Minimizing $\sum w(|F_o| - |F_c|)^2$. [d] $w = 1/(\sigma_F^2 + c|F_o|^2)$.

Crystals of KF·2.5HF were invariably twinned as indicatd by pseudoorthorhombic symmetry with nonconventional space group extinctions. The twin law (twin plane (001), $a \simeq -4c \cos \beta$) and true symmetry (monoclinic) could be recognized and were used to collect an appropriate data set of a twin specimen (twin ratio 6.8:1 as determined from noncoinciding reflections) and to reduce it to that of a single crystal for the subsequent structure analysis.

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(1) Number 11 of this series: ref 8.

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