Table II. Electronic Spectral Data for **1** and **2** as a Function of Solvent

complex	solvent	electronic spectral data[a]
1 (M = Mo)	MeOH	467, 613
	EtOH	467, 595
	MeCN	460, 565
	DMF	450, 555
	CH_2Cl_2	465, 555
1 (M = W)	MeOH	418, 490
	MeCN	405, 460
	CH_2Cl_2	412, 470
2 (M = Mo)	MeOH	457, 687
	MeCN	455, 675
	CH_2Cl_2	457, 669
2 (M = W)	MeOH	426, 549
	MeCN	426, 545
	CH_2Cl_2	424, 535

[a] Values in nanometers.

$V^{-1/2}$ mol^{-1} for the known one-electron transfer in $[Mo(S_2C_4N_2)_4]^{3-}$[23] at the same temperature. Assignment of the reduction waves to relatively localized electron transfer to the coordinated M(VI) MS_4 moiety is consistent with previous electrochemical data on Fe–Mo–S species. Thus, $[(o\text{-xyl-}S_2)FeS_2MS_2]^{2-}$ complexes (*o*-xyl-S_2 = $C_6H_4(CH_2S)_2$; M = Mo, W), which contain formally M(VI) tetrathiometalates bound to an Fe(II)–thiolate moiety, undergo reversible reduction at −1.6 V (M = Mo) and −1.8 V (M = W), events postulated[24] on the basis of EPR spectroscopic evidence to involve formation of M(V). The similarity of the potentials for the reductions in this system and those in **1** and **2** indicate that assignment of the reversible reductions to M(VI)/M(V) couples is reasonable. It is also worthwhile to note (a) that the shift to more negative reduction potentials on substitution of tungsten for molybdenum is consistent with the electrochemistry of both the above (*o*-xyl-S_2)Fe system[24] and the $[Fe(MS_4)_2]^{3-}$ ions[25] and (b) that the addition of a second $Mo(CO)_4$ unit to **1** results in a shift of the reduction wave to more positive potential, an effect presumably due to a lowering of the electron density at the MS_4 center via donation to the extra Mo(0) moiety. The irreversible wave at ca. +0.2 V for these complexes is likely to be due to a $Mo(CO)_4$-centered oxidation of Mo(0) to Mo(I) and is about 0.4 V more positive than the net two-electron Mo(0)/Mo(I) couple in $[M_2(CO)_8(SR)_2]^{2-}$ (M = Mo, W)[13-15] and the one-electron oxidation of $[Mo(CO)_4(SR)_2]^{2-}$.[16] It is interesting that the oxidation wave of trinuclear **2** is a *one-electron* Mo(0)/Mo(I) redox event, while the similar couple in the trinuclear, thiolate-bridged complex $[(CO)_4Mo(SR)_2M'(SR)_2Mo(CO)_4]^{2-}$ accounted for the simultaneous transfer of *two electrons*,[17] this latter phenomenon postulated[17] to be due to the formation of two M′–Mo bonds. The lack of ability of the central Mo(VI) in **2** to participate in metal–metal bonding is consistent with the observed one-electron behavior. Thus, as noted above, the electrochemical data are consistent with the presence of both high-valent Mo or W and low-valent Mo in the same polynuclear complex.

Complexes that contain metals in such widely differing oxidation states should be candidates for internal charge-transfer (CT) behavior. Indeed, the visible spectra of both dinuclear and trinuclear species are characterized by several intense bands (Table I), with the low-energy transitions particularly good candidates for charge transfer since they are characterized by solvatochromic behavior (Table II). Solvent-dependent CT bands are well-documented for a number of structurally related, but neutral, M(0) complexes of the forms $Mo(CO)_4$(N--N) (N--N = 2,2′-bipyridyl, 1,10-phenanthroline, 1,4-diazabutadiene, 2,3-bis(2-pyridyl)pyrazine, etc.),[26-29] $W(CO)_5L$, and $W(CO)_4L_2$ (L = substituted pyridine).[30] However, for these neutral compounds, the CT bands shift to ***higher energy*** with ***increasing solvent polarity***, "negative" solvatochromism as described by tom Dieck and Renk,[28] while compounds **1** and **2** in general show the opposite shift on solvent variation (Table II). The "positive" solvatochromic effect[28] in **1** and **2** could indicate that the CT transitions for these species are $MS_4 \rightarrow$ Mo(0) in character (rather than Mo(0) → L in the $Mo(CO)_4L_2$ systems[28]), but this hypothesis is seemingly inconsistent with the above electrochemical data, which would predict that Mo(0) → MS_4 charge-transfer behavior is more likely for **1** and **2**. In addition, it is possible that specific hydrogen-bonding interactions between the alcohols (where the largest solvatochromic effects are observed) and the MS_4 sulfurs could be at least partially responsible for this different trend.

Previous studies by Coucouvanis and co-workers[31] have shown the utility of a substitution-labile Mo(0) starting material as a source of reactive $Mo(CO)_3$ fragments. Their reaction of $Mo(CO)_3(MeCN)_3$ with the hexairon prismane species $[Fe_6S_6X_6]^{3-}$ (X = Cl, OR) yielded novel complexes with a $[Fe_6Mo_2S_6]^{3+/2+}$ core, which are exciting in that they may be susceptible to oxidative decarbonylation[32] to produce species that mimic certain aspects of the iron molybdenum cofactor of nitrogenase.[4,33] Our results on the utilization of $Mo(CO)_4$(norbornadiene), as described both herein and elsewhere,[15,16] complement this synthetic concept and suggest that the reactivity of Mo(0) species with Fe–S complexes (or vice versa) may result in the synthesis of a variety of new heterometallic clusters.

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Registry No. **1** (M = Mo), 110015-34-4; **1** (M = W), 110015-36-6; **2** (M = Mo), 110026-45-4; **2** (M = W), 110015-38-8; $Mo(CO)_4(C_4H_8)$, 12146-37-1; $[Et_4N]_2[MoS_4]$, 14348-09-5; $[Et_4N]_2[WS_4]$, 14348-05-1.

Supplementary Material Available: Figures showing cyclic voltammograms of **1** (M = Mo) and **2** (M = Mo) and the electronic spectra of **1** (M = Mo) in MeOH and CH_2Cl_2 (2 pages). Ordering information is given on any current masthead page.

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Preparation and Characterization of Bis(aryldiazenido) Complexes of Iron

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In a previous paper[1] we described the reaction of the dihydride $FeH_2[P(OEt)_3]_4$ toward aryldiazonium cations, which gave the first bis(aryldiazene) complexes $[Fe(ArN{=}NH)_2\{P(OEt)_3\}_4]^{2+}$. In order to clarify the influence of the phosphite ligands in this reaction, we extended our studies to other FeH_2L_4 dihydrides and, in the case of the $PhP(OEt)_2$ ligand, found the bis(aryldiazenido) complexes $[Fe(ArN_2)_2\{PhP(OEt)_2\}_3]^{2+}$ as final products. Such a class of derivative is very rare, and to date only Mo, Ru, and Mn complexes[2-4] have been described. In view of current interest in the chemistry of aryldiazenido complexes,[5] in this paper we report the synthesis and characterization of the first example of an iron compound containing two aryldiazenido groups bound to the same central metal. The reaction between $FeH_2[PhP(OEt)_2]_4$ and ArN_2^+ with regard to the nature of the aryldiazene and aryldiazenido intermediates is also described.

Experimental Section

General Considerations. All the solvents used were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuumtight storage flasks. Ethanol was dried over calcium hydride, dichloromethane by reflux over phosphorus pentoxide, and diethyl ether over sodium/benzophenone. Diethoxyphenylphosphine and ethoxydiphenylphosphine were prepared by following the method of Rabinowitz and Pellon.[6] Diazonium salts were obtained in the usual way, as described in the literature.[7] The labeled diazonium salt $[4\text{-}CH_3C_6H_4N{\equiv}{}^{15}N]BF_4$ was prepared from $Na^{15}NO_2$ (99% enriched, Stohler Isotope Chemicals) and arylamine. Triethylamine was dried with CaH_2. Other reagents were purchased from commercial sources in the highest available purity and used as received.

Infrared spectra were recorded on a Perkin-Elmer Model 683 spectrometer. ^1H NMR spectra were obtained on a Varian EM 390 instrument with $(CH_3)_4Si$ as an internal standard. Fourier-mode, proton-noise-decoupled ^{31}P NMR spectra were collected on a Varian FT 80A spectrometer operating at 32.203 MHz. All chemical shifts are reported with respect to 85% H_3PO_4, downfield shifts being considered positive. Conductivities of 10^{-3} M solutions of the complexes in CH_3NO_2 at 25 °C were measured with a "Halosis" bridge. Solution susceptibilities were determined by the Evans method.[8]

Synthesis of the Complexes. All synthetic procedures were carried out under an inert N_2 atmosphere unless otherwise noted. Dihydride species $FeH_2[PhP(OEt)_2]_4$ and $FeH_2(dppe)_2$ (dppe = 1,2-bis(diphenylphosphino)ethane) were prepared according to the procedure previously reported.[9] The compound $FeH_2[Ph_2P(OEt)]_4$ was synthesized by following the method described for the related $PhP(OEt)_2$ derivative. Anal. Calcd: C, 73.52; H, 6.83. Found: C, 73.40; H, 6.89. ^1H NMR (CD_2Cl_2, 34 °C): δ 7.24 m (40 H, C_6H_5); 3.1 br (8 H, CH_2); 1.08 br (12 H, CH_3); −13.5 qi br (2 H, FeH_2).

$[Fe(ArN_2)_2\{PhP(OEt)_2\}_3](BPh_4)_2$ (Ar = $4\text{-}CH_3C_6H_4$ (4a), $4\text{-}CH_3OC_6H_4$ (4b), $4\text{-}FC_6H_4$ (4c)). A solution of $FeH_2\{PhP(OEt)_2\}_4$ (2 g, 2.35 mmol) in dichloromethane (20 mL) at −80 °C was quickly transferred into a reaction flask containing an excess of the appropriate diazonium salt (8 mmol) previously cooled to ca. −90 °C. The reaction mixture was brought to 0 °C (in 10–15 min) and stirred for 30 min. After filtration to remove the unreacted diazonium salt, the solution was evaporated under reduced pressure, giving a brown oil, which was treated with ethanol (20 mL). The addition of $NaBPh_4$ (1.7 g, 5 mmol) to the resulting solution caused the separation of a red solid containing $[Fe(ArN_2)_2L_3]^{2+}$ (**4**) and $[Fe(ArN{=}NH)_2L_4]^{2+}$ (**2**) compounds (ratio ca. 2:1 by ^1H NMR), from which the bis(aryldiazenido) complex **4** can be separated in pure form by extraction with ethanol/diethyl ether. In a typical separation the more soluble complex **4** was extracted from the crude product with five 10-mL portions of ethanol/diethyl ether (6:4). The solvent was removed under reduced pressure, giving a red oil, which was triturated with ethanol (10 mL). After 2 h of stirring at 0 °C, microcrystals of the bis(aryldiazenido) complex separated out, which were filtered and dried under vacuum; yield ≥ 30%. However, this separation does not allow pure samples of the bis(aryldiazene) complex **2** to be obtained from the solid remaining after extraction.

An alternative procedure involves the reaction of the dihydride $FeH_2[PhP(OEt)_2]_4$ (2 g, 2.35 mmol) with an excess of the appropriate diazonium salt (8 mmol) in 20 mL of CH_2Cl_2 at −80 °C, but the reaction mixture, once brought to 0 °C (in 10–15 min), was exposed to air and stirred for 1 h. The unreacted diazonium salt was removed by filtration and the solution evaporated to dryness. The red-brown oil obtained was vigorously stirred with ethanol (20 mL) containing $NaBPh_4$ (1.7 g, 5 mmol), affording a red product that was repeatedly crystallized from ethanol (between +25 and −30 °C); yield ≥60%.

The physical constants and elemental analyses for the bis(aryldiazenido) complexes are as follows. **4a**: mp 102 °C dec; Λ_M = 112.1 $cm^2\ \Omega^{-1}\ M^{-1}$. Anal. Calcd: C, 72.35; H, 6.53; N, 3.67. Found: C, 72.07; H, 6.64; N, 3.52. **4b**: mp 61 °C dec; Λ_M = 114.3 $cm^2\ \Omega^{-1}\ M^{-1}$. Anal. Calcd: C, 70.87; H, 6.40; N, 3.59. Found: C, 70.72; H, 6.41; N, 3.35. **4c**: mp 94 °C dec; Λ_M = 108.6 $cm^2\ \Omega^{-1}\ M^{-1}$. Anal. Calcd: C, 70.41; H, 6.11; N, 3.65. Found: C, 70.17; H, 6.21; N, 3.58.

$[Fe(4\text{-}CH_3C_6H_4N{\equiv}{}^{15}N)_2\{PhP(OEt)_2\}_3](BPh_4)_2$ ($4a_1$). This compound was prepared exactly as for 4, by using the $[4\text{-}CH_3C_6H_4N{\equiv}{}^{15}N]BF_4$ salt: yield ≥ 55%; mp 102 °C dec; Λ_M = 111.4 $cm^2\ \Omega^{-1}\ M^{-1}$. Anal. Calcd: C, 72.26; H, 6.53; N, 3.79. Found: C, 72.04; H, 6.61; N, 3.65.

$[FeH(4\text{-}CH_3C_6H_4N{=}NH)\{PhP(OEt)_2\}_4]BPh_4$ (1). The hydride $FeH_2\{PhP(OEt)_2\}_4$ (1.70 g, 2 mmol) and the diazonium salt $[4\text{-}CH_3C_6H_4N_2]BF_4$ (0.41 g, 2 mmol) were placed in a reaction flask and cooled to −90 °C. Dichloromethane (20 mL) was slowly added and the reaction mixture stirred until its temperature reached 0 °C. The solvent was removed by evaporation, leaving an oily product, which was dissolved in ethanol (20 mL). The addition of $NaBPh_4$ (0.68 g, 2 mmol) caused the separation of a red solid, which was crystallized from ethanol; yield ≥85%.

Spectroscopic studies (^1H and ^{31}P NMR) on this crystalline product showed that both the cis and trans isomers of $[FeH(4\text{-}CH_3C_6H_4N{=}NH)\{PhP(OEt)_2\}_4]BPh_4$ are present in the ratio ca. 1:10. Chromatographic separation through a silica gel column (height 50 cm, diameter 2 cm) with ether/dichloromethane/ethanol (50:45:5) as eluent gave the trans complex in pure form. In fact, by concentration of the first red-orange eluate fraction to a small volume (10 mL), the *trans*-$[FeH(4\text{-}CH_3C_6H_4N{=}NH)L_4]^+$ compound was recovered. The cis derivative, in contrast, decomposed during separation. Physical data for **1**: mp 115 °C dec; Λ_M = 59.3 $cm^2\ \Omega^{-1}\ M^{-1}$. Anal. Calcd: C, 66.15; H, 6.96; N, 2.17. Found: C, 65.94; H, 7.05; N, 2.02.

$[Fe(4\text{-}CH_3C_6H_4N{=}NH)_2\{PhP(OEt)_2\}_4](BPh_4)_2$ (2). To a solution of the $[FeH(4\text{-}CH_3C_6H_4N{=}NH)\{PhP(OEt)_2\}_4]^+$ cation (1.29 g, 1 mmol) in 20 mL of CH_2Cl_2 was added the diazonium salt $[4\text{-}CH_3C_6H_4N_2]BF_4$ (0.21 g, 1 mmol) in the ratio 1:1. The reaction mixture was stirred for 2 h and the solvent removed under reduced pressure to give a brown oil. The addition of ethanol (20 mL) containing $NaBPh_4$ (0.34 g, 1 mmol) afforded a red product, which was filtered, washed with four 5-mL portions of ethanol to remove the small amount of the bis(aryldiazenido) complex present in the crude product, and dried under vacuum. Crystallization was carried out by dissolving the product in dichloromethane (5 mL) and adding ethanol drop by drop until a red-orange solid separated out: yield ≥65%; mp 117 °C dec; Λ_M = 114.8 $cm^2\ \Omega^{-1}\ M^{-1}$. Anal. Calcd: C, 70.92; H, 6.77; N, 3.44. Found: C, 70.71; H, 6.81; N, 3.29.

$[Fe(4\text{-}CH_3C_6H_4N_2)\{PhP(OEt)_2\}_4]BPh_4$ (3). Triethylamine (0.21 mL, 1.5 mmol) was added to a solution of the bis(aryldiazene) complex $[Fe(4\text{-}CH_3C_6H_4N{=}NH)_2L_4](BPh_4)_2$ (0.86 g, 0.5 mmol) in 10 mL of CH_2Cl_2 and the reaction mixture stirred for 1 h and then filtered. The solvent was removed by evaporation, giving a brown oil, which was treated with ethanol (10 mL). The resulting white solid, $(Et_3NH)BPh_4$, was filtered off and the red solution cooled to −30 °C to obtain red

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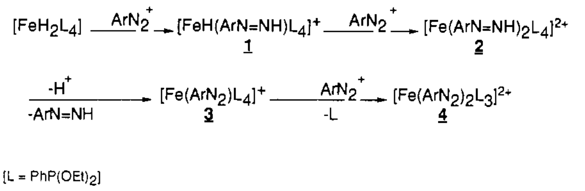
Scheme I



[L = PhP(OEt)$_2$]

crystals of the complex: yield ≥70%; mp 125 °C dec; Λ_M = 60.0 cm^2 Ω^{-1} M^{-1}. Anal. Calcd: C, 66.26; H, 6.81; N, 2.18. Found: C, 66.02; H, 6.84; N, 2.09.

Results and Discussion

The hydride $FeH_2[PhP(OEt)_2]_4$ reacts in CH_2Cl_2 with an excess of aryldiazonium cations to yield a mixture of $[Fe(ArN_2)_2L_3]^{2+}$ (cation of **4**) and $[Fe(ArN{=}NH)_2L_4]^{2+}$ (cation of **2**) complexes, from which the bis(aryldiazenido) compounds **4** (Ar = 4-$CH_3C_6H_4$ (**4a**), 4-$CH_3OC_6H_4$ (**4b**), 4-FC_6H_4 (**4c**)) can be isolated and characterized. Studies carried out on the progress of the reaction allow us to hypothesize the reaction path shown in Scheme I. The mono(diazene) complex $[FeH(ArN{=}NH)L_4]^+$ (cation of **1**) is formed as the first product of the reaction between the hydride FeH_2L_4 and the $ArN_2^+BF_4^-$ salt and may be obtained in almost quantitative yields (≥90%) by operating with stoichiometric amounts of reagents. The subsequent reaction of the mono(diazene) complex **1** with the aryldiazonium cation was studied by IR and NMR spectroscopy, with the $[FeH(ArN{=}NH)L_4]^+{:}ArN_2^+$ molar ratio being changed in the range 1:0.2 to 1:4. In every case the bis(diazene) compound **2** was observed to be the initial reaction product, though after 5–10 min a small amount of the bis(aryldiazenido) complex **4** also appeared at low $[FeH(ArN{=}NH)L_4]^+{:}ArN_2^+$ ratios. However, no other intermediates except **2** and **4** were detected in the course of the reaction. On samples independently prepared (see below), we have demonstrated that the bis(diazene) **2** can easily be deprotonated with base to give only the mono(diazenido) derivative $[Fe(ArN_2)L_4]^+$ (cation of **3**) and that this compound quickly reacts with aryldiazonium cation to produce the bis(diazenido) complex **4** and free $PhP(OEt)_2$ ligand. On this basis the proposed mechanism (**2** → **3** → **4**) seems to be plausible.[10]

A question arises, however, about the nature of the deprotonating agent on the intermediate **2** in the absence of added base. Traces of water present in the solvent and free $PhP(OEt)_2$ released in the reaction course may reasonably be invoked. Deprotonation of aryldiazene complexes in solutions of common organic solvents, without addition of base, to give the corresponding aryldiazenido derivatives, is a feature previously observed for Ru and Rh compounds.[11] Moreover, in the case of molybdenum[2a] it was observed that exposure to air converted solutions of $[Mo(ArN_2)(ArNHNH)(dtc)_2]$ into $[Mo(ArN_2)_2(dtc)_2]$ derivatives. It may be noted that, in our case too, exposure to air of the reaction mixture favors the formation of **4** from the bis(diazene) complex **2**.

The hydride $FeH_2[P(OEt)_3]_4$, which contains the $P(OEt)_3$ ligand instead of $PhP(OEt)_2$, was previously shown to react with aryldiazonium cations to give mono- and bis(aryldiazene) derivatives,[1] but no evidence of the formation of a bis(aryldiazenido) complex has ever been detected even by exposing the reaction mixture to the air. Since deprotonation of the bis(diazene) to give the $[Fe(ArN_2)\{P(OEt)_3\}_4]^+$ complex is also easy in this case, the different behavior observed as the phosphite ligand is changed may be attributed (on the basis of the proposed mechanism) to unreactivity of the $[Fe(ArN_2)\{P(OEt)_3\}_4]^+$ complex toward substitution by ArN_2^+ to give the bis(aryldiazenido) derivative. To

Table I. Selected Infrared and NMR Data for Iron Complexes

compds[a]	$\nu(N{\equiv}N)$,[b] cm^{-1}	^{1}H NMR,[c,d] δ NH	CH$_2$ (phos)	CH$_3$	CH$_3$ (phos)	spin syst	$^{31}P\{^1H\}$ NMR,[c,e] δ (coupling const, Hz)
$[Fe(4\text{-}CH_3C_6H_4N_2)_2L_3]^{2+}$ (**4a**)	1798 sh, 1774 s (1795 sh, 1770 s)		3.96 m [12]	2.46 s [6]	1.19 t [18]	AB$_2$[f]	δ_A = 159.5, δ_B = 150.0 (J_{AB} = 77.6)
$[Fe(4\text{-}CH_3C_6H_4N{\equiv}^{15}N)_2L_3]^{2+}$ (**4a$_1$**)	1741 s (1738 s)		4.06 m [12]	2.52 s [6]	1.24 t [18]	AB$_2$X$_2$[g]	δ_A = 159.6, δ_B = 150.2 (J_{AB} = 77.1, J_{AX} = 2.0, J_{BX} = 13.9)
$[Fe(4\text{-}CH_3OC_6H_4N_2)_2L_3]^{2+}$ (**4b**)	1770 s (1766 s)		4.06 m [12]	3.93 s [6]	1.25 t [18]	AB$_2$[f]	δ_A = 160.7, δ_B = 150.5 (J_{AB} = 76.3)
$[Fe(4\text{-}FC_6H_4N_2)_2L_3]^{2+}$ (**4c**)	1766 s (1762 s)		3.98 m [12]		1.26 t [18]	AB$_2$[f]	δ_A = 158.2, δ_B = 148.6 (J_{AB} = 79.6)
$[Fe(4\text{-}CH_3C_6H_4N_2)L_4]^+$ (**3**)	1660 s (1658 s)		3.8 br [16]	2.38 s [3]	1.17 br [24]	ABC$_2$[f]	δ_A = 191.9, δ_B = 187.2, δ_C = 172.5 (J_{AB} = −12.4, J_{BC} = 99.5, J_{AC} = 85.0)
cis-$[Fe(4\text{-}CH_3C_6H_4N{=}NH)_2L_4]^{2+}$ (**2**)		13.6 br [2]	4.00 m [16]	2.40 s [6]	1.55 t [12] 1.12 t [12]	A$_2$B$_2$	δ_A = 179.5, δ_B = 168.5 (J_{AB} = 94.1)
trans-$[FeH(4\text{-}CH_3C_6H_4N{=}NH)L_4]^+$ (**1**)		14.3 br [1]	3.80 m [16]	2.38 s [3]	1.17 t[h] [24]		182.9

[a] All compounds are BPh_4^- salts; L = $PhP(OEt)_2$. [b] In CH_2Cl_2 and KBr (in parentheses). [c] At room temperature in $(CD_3)_2CO$. [d] Relative integration in brackets. [e] Positive shift downfield from 85% H_3PO_4. [f] At −60 °C in $(CD_3)_2CO$. [g] At −60 °C in CD_2Cl_2; X = ^{15}N. [h] FeH resonance at δ −14.50 qi [1] (J_{PH} = 50.5 Hz).

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(10) It may be noted that the presence of the hydrocarbon ArH in the reaction mixture, which was demonstrated to be the decomposition product of the free diazene (see ref 1), further supports the deprotonation of **2** to give **3** in the course of the reaction.

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verify this hypothesis, we reacted the known $[Fe(ArN_2)\{P(OEt_3)\}_4]^+$ with excess ArN_2^+ in CH_2Cl_2 and did observe the absence of phosphite substitution to give the bis(aryldiazenido) derivative.

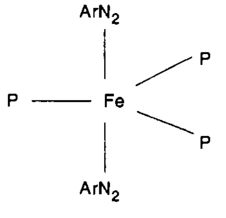
We may therefore conclude that, although the difference in π-acceptor properties and/or steric hindrance between the two $P(OEt)_3$ and $PhP(OEt)_2$ phosphite ligands is small,[12] different products are finally obtained in the reaction of FeH_2L_4 with aryldiazonium cations.

Selected properties of the bis(aryldiazenido) complexes, which are diamagnetic red-orange solids, relatively stable in the solid state and in solution, are reported in Table I. In the NN stretching region the infrared spectra show only one band at 1762–1774 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, **4a**, this band at 1774 cm^{-1} (CH_2Cl_2) is shifted to 1741 cm^{-1} on labeling with ^{15}N (using the $4\text{-}CH_3C_6H_4{}^{14}N{\equiv}{}^{15}N^+BF_4^-$ ligand). These $\nu(NN)$ values seem to indicate that the ArN_2 ligands are singly bent, in agreement with the empirical rules proposed by Haymore and Ibers.[13] Support for this assertion comes from a comparison of our infrared data with those of the previously reported aryldiazenido complexes $[Fe(C_6H_5N_2)(CO)_2(PPh_3)_2]BF_4$,[14] $[RuCl_3(4\text{-}CH_3C_6H_4N_2)(PPh_3)_2]$,[13,15] $[Mn(CO)_2(\eta^5\text{-}C_5H_4CH_3)(2\text{-}CF_3C_6H_4N_2)]BF_4$,[16] and $[Fe(4\text{-}CH_3C_6H_4N_2)\{P(OEt)_3\}_4]BPh_4$,[1] whose X-ray structure is known.

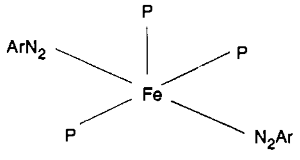
The two aryldiazenido ligands in **4** should be bonded to the central metal as separated groups and do not couple to give a metal/tetrazene system.[17] In fact, compound **4** reacts with free $PhP(OEt)_2$ to give $[Fe(ArN_2)L_4]^+$ and ArN_2^+ (eq 1), as expected

$$[Fe(ArN_2)_2L_3]^{2+} + L \rightarrow [Fe(ArN_2)L_4]^+ + ArN_2^+ \quad (1)$$

for a bis(diazenido) rather than a tetrazene complex. At room temperature the $^{31}P\{^1H\}$ NMR spectra of **4** consist of broad signals, which, by lowering the sample temperature to −60 °C, appear as AB_2 multiplets (parameters in Table I). Furthermore, the labeled $[Fe(4\text{-}CH_3C_6H_4N{\equiv}{}^{15}N)_2L_3]^{2+}$ complex, at −60 °C as well, shows an AB_2X_2 multiplet in the ^{31}P spectra, which may be simulated with the values reported in Table I. When we take into account that the presence of only one band in the $\nu(NN)$ region for **4** seems to indicate two mutually trans aryldiazenido ligands, trigonal-bipyramidal (TBP) geometry (I) in solution seems to be improbable, because in this case a singlet (triplet for the labeled compound) should be expected in the ^{31}P NMR spectra. On the other hand, the IR and ^{31}P NMR data could be interpreted on the basis of type II square-pyramidal (SP) geometry. The X-ray crystal structures of the complexes were not determined, owing to the poor quality of the crystals obtained, and therefore any proposed geometry can only be tentative. We believe, however, that a distortion of TBP (I) toward SP geometry would make the three equatorial phosphorus atoms inequivalent (i.e., for example, one different from the other two), resulting in AB_2 spectra. Distorted TBP geometry for pentacoordinate aryldiazenido complexes has previously been reported for the $[Fe(ArN_2)\{P(OEt)_3\}_4]BPh_4$[1] and $[IrCl(C_6H_5N_2)\{P(CH_3)(C_6H_5)_2\}_3]PF_6$[18] derivatives.



I



II

As previously observed for other aryldiazenido complexes of iron,[1,19] no evidence for the formation of diazene derivatives was detected by reacting **4** with gaseous HCl or HBF_4 solutions.

The reaction of the hydride $FeH_2[PhP(OEt)_2]_4$ with aryldiazonium cations also allowed synthesis of the mono(aryldiazene) $[FeH(4\text{-}CH_3C_6H_4N{=}NH)L_4]^+$ (cation of **1**) and bis(aryldiazene) $[Fe(4\text{-}CH_3C_6H_4N{=}NH)_2L_4]^{2+}$ (cation of **2**) complexes, which were isolated and characterized (Table I). Both the cis and trans isomers (ratio ca. 1:10) were shown by NMR spectroscopy to be present in the case of the mono(diazene) **1**. Chromatographic separation on silica gel, however, allowed us to separate only one compound in pure form, whose $^{31}P\{^1H\}$ NMR data (sharp singlet at δ 182.9) suggest a trans arrangement of the hydride and $ArN{=}NH$ ligands. In contrast, a mutually cis position of the two diazene groups seems to be present in compound **2**, because an A_2B_2 multiplet (between −70 and +34 °C) is shown by its $^{31}P\{^1H\}$ NMR spectra. Lastly, the presence of the diazene ligand in both **1** and **2** is deduced from ^1H NMR spectra of labeled and unlabeled complexes. In the nonaromatic diazene proton region (δ 15.1–11.6) a broad signal is present at δ 14.3 for **1** and at δ 13.6 for **2**, which is replaced by a sharp doublet ($J_{^{15}NH}$ = 65 Hz) in the labeled $ArN{=}{}^{15}NH$ complexes, thus confirming the presence of the diazene ligand.

The reactivity of both diazene complexes with base was studied: while the mono(diazene) **1** is unreactive toward NEt_3, the $[Fe(ArN{=}NH)_2L_4]^{2+}$ complex reacts with triethylamine to give the mono(diazenido) complex $[Fe(4\text{-}CH_3C_6H_4N_2)\{PhP(OEt)_2\}_4]^+$ (cation of **3**). This reaction parallels those previously observed in the closely related $[Fe(ArN{=}NH)_2\{P(OEt)_3\}_4]^{2+}$ derivatives.[1] In the same way, the spectroscopic properties of **3** ($\nu(NN)$ 1660 cm^{-1} (CH_2Cl_2) and ABC_2 $^{31}P\{^1H\}$ NMR spectra; see Table I) agree with those of the related $[Fe(ArN_2)\{P(OEt)_3\}_4]^+$ derivatives,[1] previously described by us, and suggest slightly distorted TBP geometry with a singly bent aryldiazenido ligand in the equatorial position for **3** as well.

We also studied the reaction of other dihydrides such as $FeH_2[Ph_2P(OEt)]_4$ and $FeH_2(dppe)_2$ (dppe = $Ph_2PC_2H_4PPh_2$) with aryldiazonium cations. The results show that both hydrides react with ArN_2^+ in stoichiometric or excess amounts, but only intractable products were obtained, whose IR and NMR spectra show neither diazene nor diazenido complexes. In only one case, however, by reaction of $FeH_2(dppe)_2$ with the salt $ArN_2^+BF_4^-$ at −80 °C in a 1:1 ratio, was an impure green product isolated, whose IR spectrum (band at 1630 cm^{-1}) seems to indicate the presence of an aryldiazenido complex. Unfortunately, the instability of the product, which decomposed on attempted crystallization, prevented any formulation.

On the basis of the results obtained in this and previous[1] studies, we may conclude that, though the number of hydrides is limited, only with good π-acceptor phosphite ligands such as $P(OEt)_3$ and $PhP(OEt)_2$ can diazene complexes be prepared by reacting the dihydride FeH_2L_4 with aryldiazonium cations.

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Registry No. **1**, 109390-33-2; **2**, 109365-35-7; **3**, 109365-31-3; **4a**, 109365-33-5; **4b**, 109390-29-6; **4c**, 109390-31-0; ^{15}N, 14390-96-6; $FeH_2\{PhP(OEt)_2\}_4$, 28755-83-1.

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