Inorg. Chem. **1996,** *35,* 6245−6253 **6245**

Binuclear Iron and Ruthenium Complexes with Bis(diazene) or Bis(diazenido) Bridging Ligands: Synthesis, Characterization, X-ray Crystal Structure, and Electrochemical Studies

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Received February 8, 1996[⊗]

Binuclear complexes $[(MHP_4)_2(\mu\text{-HN=NAr−ArN=NH})](BPh_4)_2$ [M = Fe, Ru; P = $P(OMe)_3$, $P(OEt)_3$, $PPh(OEt)_2$; Ar−Ar = 4,4′-C_6H_4−C_6H_4, 4,4′-(2-CH_3)C_6H_3−C_6H_3(2-CH_3), 4,4′-C_6H_4−CH_2−C_6H_4] were prepared by allowing hydride species MH_2P_4 to react with bis(diazonium) salts $(N_2Ar−ArN_2)(BF_4)_2$ in a 2:1 ratio at low temperature. The compounds were characterized by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy (including ^{15}N isotopic substitution) and an X-ray crystal structure determination. The complex $[\{FeH(P(OEt)_3)_4\}_2\{\mu\text{-4,4′-HN=N(2-CH}_3)C_6H_3−C_6H_3(2\text{-CH}_3)N=NH\}](BPh_4)_2$ crystallizes in the space group $P\bar{1}$ with $a = 16.105(5)$, $b = 17.551(6)$, $c = 11.539(3)$ Å; $\alpha = 96.41(2)$, $\beta = 84.49(2)$, $\gamma = 97.97(2)$°; and $Z = 2$. The structure is centrosymmetric and consists of binuclear cations with the two iron atoms in an octahedral environment having the hydride and the diazene ligands in mutually *cis* positions. The $[(MHP_4)_2(\mu\text{-HN=NAr−ArN=NH})]^{2+}$ cations reacted with mono(diazonium) $(RN_2)BF_4$ salts to give the binuclear bis(diazene) derivatives $[\{M(RN=NH)P_4\}_2(\mu\text{-HN=NAr−ArN=NH})](BPh_4)_4$ (R = C_6H_5, 4-$CH_3C_6H_4$, 4-$CH_3OC_6H_4$). Binuclear bis(diazenido) complexes $[(MP_4)_2(\mu\text{-}N_2Ar−ArN_2)](BPh_4)_2$ [M = Fe, Ru; P = $P(OEt)_3$; Ar−Ar = 4,4′-C_6H_4−C_6H_4, 4,4′-C_6H_4−CH_2−C_6H_4] were also prepared by deprotonation with triethylamine of the diazene−nitrile $[M\{4\text{-}CH_3C_6H_4CN\}P_4\}_2(\mu\text{-HN=NAr−ArN=NH})](BPh_4)_4$ derivatives. Characterization of all the complexes by infrared and ^1H and ^{31}P NMR spectroscopy is discussed. Cyclic voltammetry of the binuclear $[(MHP_4)_2(\mu\text{-HN=NAr−ArN=NH})]^{2+}$ and of the related mononuclear $[MH(RN=NH)P_4]^+$ derivatives was also investigated. Electrochemical reduction of binuclear compounds, where conjugation between the metal centers is possible, proceeds *via* two well-separated one-electron reduction steps whereas, when conjugation is hindered, the two consecutive reductions tend to merge into a one-step reduction process.

Introduction

The interest in the chemistry of transition metal complexes containing diazene RN=NH, diazenido RN_2, or other partially reduced dinitrogen ligands stems from their relationship with the intermediates of the dinitrogen fixation process. These "diazo" complexes, in fact, may be potential models to study the numerous steps of inorganic and biological N_2 reduction or to design nitrogen fixation catalysts.[1,2]

A number of aryldiazene and aryldiazenido complexes have been reported in recent years,[1a,b,3] and their synthesis often involves the use of the mono(aryldiazonium) salts RN_2^+ which, through insertion into a metal−hydride bond or substitution reactions, can give the "diazo" derivatives. However, despite the numerous studies, only one report[4] is known on the reactivity toward transition metal complexes of bis(diazonium) cations, while no studies include salts of types **A**−**C** (Chart 1) and the possible complexes containing the related bis(diazenido) and bis(diazene) ligands. These ligands may behave potentially as though they are bidentate, affording bi- or polynuclear complexes in which the bridging unit may induce new properties on the same NN groups or on the corresponding complexes. It has in fact been reported that organometallic compounds containing a π-conjugated unsaturated chain may show unusual properties such as those of electronic conductors or those of nonlinear optical materials.[5−7]

We previously reported[8] on the reactivity of several metal hydrides with mono(aryldiazonium) cations RN_2^+ which allowed

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[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1996.

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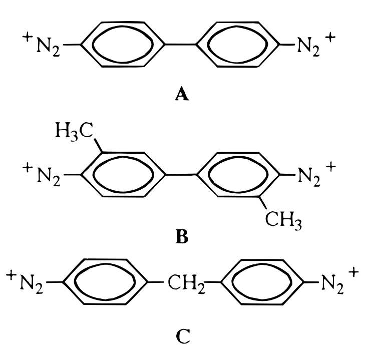
S0020-1669(96)00138-3 CCC: $12.00

Chart 1



A

B

C

the synthesis of new aryldiazene and aryldiazenido complexes, and now, as an extension of these studies, we have begun an investigation on the reactivity of bis(diazonium) cations of types **A**−**C** toward several metal hydrides. In the present paper, we report the syntheses of the first binuclear iron and ruthenium complexes containing a bis(diazene) or bis(diazenido) bridging ligand, together with some electrochemical studies and an X-ray crystal structure determination.

Experimental Section

All synthetic work was carried out under an inert atmosphere using standard Schlenk techniques or a Vacuum Atmospheres drybox. Once isolated, the complexes were found to be sufficiently air-stable and were stored under an inert atmosphere at −25 °C. All solvents used were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. The phosphite PPh(OEt)$_2$ was prepared by the method of Rabinowitz and Pellon,[9] while P(OMe)$_3$ and P(OEt)$_3$ (Aldrich) were purified by distillation under nitrogen. The bis(diazonium) salts $(N_2Ar{-}ArN_2)(BF_4)_2$ [Ar−Ar = 4,4′-$C_6H_4{-}C_6H_4$ (**A**); 4,4′-(2-CH$_3$)C$_6$H$_3$−C$_6$H$_3$(2-CH$_3$) (**B**); 4,4′-$C_6H_4{-}CH_2{-}C_6H_4$ (**C**)] were obtained in the usual way by treating the amine $H_2NAr{-}ArNH_2$ with $NaNO_2$ as described in the literature for the common mono(diazonium) salts.[10] The labeled diazonium salt (4,4′-$^{15}N{\equiv}NC_6H_4{-}C_6H_4N{\equiv}^{15}N)(BF_4)_2$ was prepared from $Na^{15}NO_2$ (99% enriched, CIL) and the diamine. Triethylamine was dried with CaH$_2$ and distilled before use. Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on a Digilab Bio-Rad FTS-40 spectrophotometer. NMR spectra (^{1}H, ^{31}P) were obtained on a Bruker AC200 spectrometer at temperatures varying between −90 and +30 °C, unless otherwise noted. ^{1}H spectra are referred to internal tetramethylsilane, while $^{31}P\{^1H\}$ chemical shifts are reported with respect to 85% H_3PO_4, with downfield shifts considered positive. The conductivities of 10^{-3} M solutions of the complexes in CH_3NO_2 at 25 °C were measured with a Radiometer CDM 83 instrument.

Synthesis of Complexes. The hydride species FeH_2P_4 [P = P(OEt)$_3$, PPh(OEt)$_2$] and RuH_2P_4 [P = P(OMe)$_3$, P(OEt)$_3$, PPh(OEt)$_2$] were prepared by following the methods previously reported.[11,12] The nitrile complexes [FeH(4-CH$_3$C$_6$H$_4$CN){P(OEt)$_3$}$_4$]BPh$_4$ and [RuH(4-CH$_3$C$_6$H$_4$CN){P(OEt)$_3$}$_4$]BPh$_4$ were obtained from the dihydrogen species [MH(η^2-H$_2$){P(OEt)$_3$}$_4$]BPh$_4$ (M = Fe, Ru) as previously described.[8e,f]

[{FeH(P(OEt)$_3$)$_4$}$_2$(μ-HN=NAr−ArN=NH)](BPh$_4$)$_2$ (1) [Ar−Ar = 4,4′-C$_6$H$_4$−C$_6$H$_4$ (a), 4,4′-(2-CH$_3$)C$_6$H$_3$−C$_6$H$_3$(2-CH$_3$) (b), 4,4′-C$_6$H$_4$−CH$_2$−C$_6$H$_4$ (c)]. A solution of FeH$_2$[P(OEt)$_3$]$_4$ (2.8 mmol, 2 g) in 10 mL of CH$_2$Cl$_2$ was cooled to −80 °C and quickly transferred by needle into a suspension of the appropriate bis(diazonium) salt (N$_2$Ar−ArN$_2$)(BF$_4$)$_2$ (1.4 mmol) in 10 mL of CH$_2$Cl$_2$ cooled to −80 °C. The reaction mixture was brought to room temperature and stirred for 2 h, and then the solvent was removed under reduced pressure. The oil obtained was treated with 10 mL of ethanol, giving a red solution from which the complex was precipitated as a red solid by adding a slight excess of NaBPh$_4$ (3 mmol, 1.03 g) in 5 mL of EtOH. After crystallization from CH$_2$Cl$_2$/EtOH (4/15 mL), the complexes were filtered off and dried under vacuum; yield ≥80%. Anal. Calcd for **1a**: C, 56.60; H, 7.57; N, 2.44. Found: C, 56.32; H, 7.42; N, 2.47. Mp: 125 °C. $\Lambda_M = 106.3\ \Omega^{-1}\ mol^{-1}\ cm^2$. Anal. Calcd for **1b**: C, 56.95; H, 7.65; N, 2.42. Found: C, 56.27; H, 7.67; N, 2.31. Mp: 131 °C. $\Lambda_M = 106.6\ \Omega^{-1}\ mol^{-1}\ cm^2$. Anal. Calcd for **1c**: C, 56.78; H, 7.61; N, 2.43. Found: C, 56.35; H, 7.53; N, 2.39. Mp: 129 °C. $\Lambda_M = 107.4\ \Omega^{-1}\ mol^{-1}\ cm^2$.

[{FeH(P(OEt)$_3$)$_4$}$_2$(μ-4,4′-H^{15}N=NC$_6$H$_4$−C$_6$H$_4$N=^{15}NH)](BPh$_4$)$_2$ (1*a). This complex was prepared analogously to the related unlabeled **1a** using the (4,4′-$^{15}N{\equiv}NC_6H_4{-}C_6H_4N{\equiv}^{15}N)(BF_4)_2$ bis(diazonium) salt; yield ≥70%. Anal. Calcd: C, 56.55; H, 7.56; N, 2.53. Found: C, 56.42; H, 7.45; N, 2.48. Mp: 120 °C. $\Lambda_M = 106.1\ \Omega^{-1}\ mol^{-1}\ cm^2$.

[(RuHP$_4$)$_2$(μ-HN=NAr−ArN=NH)](BPh$_4$)$_2$ (2−4) [P = P(OMe)$_3$ (2), P(OEt)$_3$ (3), PPh(OEt)$_2$ (4); Ar−Ar = 4,4′-C$_6$H$_4$−C$_6$H$_4$ (a), 4,4′-(2-CH$_3$)C$_6$H$_3$−C$_6$H$_3$(2-CH$_3$) (b), 4,4′-C$_6$H$_4$−CH$_2$−C$_6$H$_4$ (c)]. A dichloromethane solution (10 mL) of the appropriate hydride RuH$_2$P$_4$ (0.7 mmol) cooled to −80 °C was transferred by needle into a suspension of the appropriate bis(diazonium) salt (N$_2$Ar−ArN$_2$)(BF$_4$)$_2$ (0.35 mmol) in 10 mL of CH$_2$Cl$_2$ cooled to −80 °C. The reaction mixture was brought to room temperature and stirred for 3 h, and then the solvent was removed under reduced pressure. The oil obtained was triturated with 5 mL of ethanol, giving a yellow solution from which the complex was precipitated as a yellow solid by adding a slight excess of NaBPh$_4$ (0.8 mmol, 0.27 g) in 5 mL of ethanol. After crystallization from CH$_2$Cl$_2$/EtOH (3/10 mL), the complexes were filtered off and dried under vacuum; yield ≥80%. Anal. Calcd for **2a**: C, 49.32; H, 6.11; N, 2.74. Found: C, 49.20; H, 6.07; N, 2.70. Mp: 128 °C. $\Lambda_M = 107.5\ \Omega^{-1}\ mol^{-1}\ cm^2$. Anal. Calcd for **2b**: C, 49.81; H, 6.22; N, 2.70. Found: C, 49.63; H, 6.00; N, 2.62. Mp: 132 °C. $\Lambda_M = 108.2\ \Omega^{-1}\ mol^{-1}\ cm^2$. Anal. Calcd for **3a**: C, 54.45; H, 7.28; N, 2.35. Found: C, 54.29; H, 7.21; N, 2.21. Mp: 132 °C. $\Lambda_M = 101.3\ \Omega^{-1}\ mol^{-1}\ cm^2$. Anal. Calcd for **3b**: C, 54.82; H, 7.36; N, 2.32. Found: C, 54.44; H, 7.29; N, 2.34. Mp: 130 °C. $\Lambda_M = 102.2\ \Omega^{-1}\ mol^{-1}\ cm^2$. Anal. Calcd for **3c**: C, 54.64; H, 7.32; N, 2.34. Found: C, 54.46; H, 7.35; N, 2.40. $\Lambda_M = 96.9\ \Omega^{-1}\ mol^{-1}\ cm^2$. Anal. Calcd for **4a**: C, 63.73; H, 6.57; N, 2.12. Found: C, 63.53; H, 6.54; N, 2.17. Mp: 115 °C. $\Lambda_M = 100.3\ \Omega^{-1}\ mol^{-1}\ cm^2$. Anal. Calcd for **4b**: C, 63.96; H, 6.65; N, 2.10. Found: C, 64.09; H, 6.67; N, 2.12. Mp: 110 °C. $\Lambda_M = 121.5\ \Omega^{-1}\ mol^{-1}\ cm^2$. Anal. Calcd for **4c**: C, 63.85; H, 6.61; N, 2.11. Found: C, 63.70; H, 6.68; N, 2.02. Mp: 55 °C. $\Lambda_M = 102.4\ \Omega^{-1}\ mol^{-1}\ cm^2$.

[{RuH(P(OEt)$_3$)$_4$}$_2$(μ-4,4′-H^{15}N=NC$_6$H$_4$−C$_6$H$_4$N=^{15}NH)](BPh$_4$)$_2$ (3*a). This compound was prepared by the method described for the related **3a** using the labeled (4,4′-$^{15}N{\equiv}NC_6H_4{-}C_6H_4N{\equiv}^{15}N)(BF_4)_2$ bis(diazonium) salt; yield ≥80%. Anal. Calcd: C, 54.41; H, 7.27; N, 2.43. Found: C, 53.71; H, 7.25; N, 2.31. Mp: 127 °C. $\Lambda_M = 99.2\ \Omega^{-1}\ mol^{-1}\ cm^2$.

[{Fe(4-CH$_3$C$_6$H$_4$N=NH)(P(OEt)$_3$)$_4$}$_2$(μ-HN=NAr−ArN=NH)](BPh$_4$)$_4$ (5) [Ar−Ar = 4,4′-C$_6$H$_4$−C$_6$H$_4$ (a), 4,4′-(2-CH$_3$)C$_6$H$_3$−C$_6$H$_3$(2-CH$_3$) (b), 4,4′-C$_6$H$_4$−CH$_2$−C$_6$H$_4$ (c)]. An excess of the *p*-tolyldiazonium salt (4-CH$_3$C$_6$H$_4$N$_2$)BF$_4$ (3 mmol, 0.62 g) and the appropriate bis(diazene) complex [{FeH(P(OEt)$_3$)$_4$}$_2$(μ-HN=NAr−ArN=NH)](BPh$_4$)$_2$ (**1**) (0.5 mmol) were placed in a three-necked flask (50 mL) cooled to 0 °C, and 20 mL of acetone was slowly added. The suspension obtained was stirred for 3 h at 0 °C, and then the solvent removed under reduced pressure. The oil obtained was treated with 15 mL of ethanol containing an excess of NaBPh$_4$ (2 mmol, 0.68 g), giving a red-brown solid which was filtered off and crystallized by

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dissolving in 5 mL of CH$_2$Cl$_2$. After filtration, the complex was precipitated with 10 mL of ethanol; yield ≥60%. Anal. Calcd for **5a**: C, 64.44; H, 7.19; N, 3.54. Found: C, 64.20; H, 7.08; N, 3.50. Mp: 110 °C. $\Lambda_\mathrm{M} = 198.0\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. Anal. Calcd for **5b**: C, 64.63; H, 7.25; N, 3.51. Found: C, 64.49; H, 7.12; N, 3.43. Mp: 112 °C. $\Lambda_\mathrm{M} = 205.3\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. Anal. Calcd for **5c**: C, 64.54; H, 7.22; N, 3.52. Found: C, 64.37; H, 7.32; N, 3.46. Mp: 105 °C. $\Lambda_\mathrm{M} = 206.3\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$.

[{Ru(RN=NH)P$_4$}$_2$(*μ*-HN=NAr−ArN=NH)](BPh$_4$)$_4$ (6−8) [P = P(OMe)$_3$ (6), P(OEt)$_3$ (7), PPh(OEt)$_2$ (8); Ar−Ar = 4,4′-C$_6$H$_4$−C$_6$H$_4$ (a), 4,4′-(2-CH$_3$)C$_6$H$_3$−C$_6$H$_3$(2-CH$_3$) (b), 4,4′-C$_6$H$_4$−CH$_2$−C$_6$H$_4$ (c); R = C$_6$H$_5$ (a), 4-CH$_3$C$_6$H$_4$ (b), 4-CH$_3$OC$_6$H$_4$ (c)]. An excess of the appropriate aryldiazonium salt RN$_2^+$BF$_4^-$ (1.2 mmol) and the bis(diazene) complex [(RuHP$_4$)$_2$(*μ*-HN=NAr−ArN=NH)](BPh$_4$)$_2$ (**2**−**4**) (0.2 mmol) were placed in a 50-mL three-necked flask, and 15 mL of CH$_2$Cl$_2$ was added. The reaction mixture was stirred at room temperature for 4 h and filtered to remove the unreacted diazonium salt. The filtrate was then evaporated to dryness under reduced pressure. The oil obtained was treated with ethanol (10 mL), and the addition of NaBPh$_4$ (0.8 mmol, 0.27 g) in 5 mL of ethanol caused the precipitation of an orange solid, which was filtered off and crystallized from CH$_2$Cl$_2$/EtOH (3/8 mL); yield ≥80%. Anal. Calcd for **6ac**: C, 59.36; H, 6.07; N, 3.79. Found: C, 59.50; H, 6.02; N, 3.54. Mp: 133 °C. $\Lambda_\mathrm{M} = 209.8\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. Anal. Calcd for **7ab**: C, 62.65; H, 6.99; N, 3.44. Found: C, 60.83; H, 7.00; N, 3.26. Mp: 135 °C. $\Lambda_\mathrm{M} = 204.4\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. Anal. Calcd for **7ac**: C, 62.05; H, 6.92; N, 3.40. Found: C, 61.75; H, 6.88; N, 3.33. Mp: 135 °C. $\Lambda_\mathrm{M} = 210.3\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. Anal. Calcd for **7bb**: C, 62.85; H, 7.05; N, 3.41. Found: C, 63.01; H, 7.00; N, 3.29. Mp: 126 °C. $\Lambda_\mathrm{M} = 212.0\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. Anal. Calcd for **7cb**: C, 62.75; H, 7.02; N, 3.42. Found: C, 62.59; H, 7.15; N, 3.49. Mp: 130 °C. $\Lambda_\mathrm{M} = 206.5\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. Anal. Calcd for **8aa**: C, 68.89; H, 6.42; N, 3.21. Found: C, 68.57; H, 6.35; N, 3.25. Mp: 127 °C. $\Lambda_\mathrm{M} = 199.9\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. Anal. Calcd for **8ab**: C, 69.02; H, 6.48; N, 3.19. Found: C, 68.76; H, 6.51; N, 3.36. Mp: 140 °C. $\Lambda_\mathrm{M} = 208.6\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. Anal. Calcd for **8ac**: C, 68.40; H, 6.42; N, 3.16. Found: C, 68.09; H, 6.44; N, 3.00. Mp: 135 °C. $\Lambda_\mathrm{M} = 201.7\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. Anal. Calcd for **8cb**: C, 69.09; H, 6.51; N, 3.17. Found: C, 68.88; H, 6.45; N, 3.25. Mp: 133 °C. $\Lambda_\mathrm{M} = 188.9\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$.

[{Fe(4-CH$_3$C$_6$H$_4$CN)(P(OEt)$_3$)$_4$}$_2$(*μ*-HN=NAr−ArN=NH)](BPh$_4$)$_4$ (9) [Ar−Ar = 4,4′-C$_6$H$_4$−C$_6$H$_4$ (a), 4,4′-C$_6$H$_4$−CH$_2$−C$_6$H$_4$ (c)]. The appropriate bis(diazonium) salt (N$_2$Ar−ArN$_2$)(BF$_4$)$_2$ (0.43 mmol) and the nitrile complex [FeH(4-CH$_3$C$_6$H$_4$CN){P(OEt)$_3$}$_4$]BPh$_4$ (0.86 mmol, 1.0 g) were placed in a 50-mL three-necked flask, and 20 mL of acetone was added. The reaction mixture was stirred at room temperature for 8 h, and then the solvent was removed under reduced pressure. The oil obtained was treated with 10 mL of ethanol containing an excess of NaBPh$_4$ (2 mmol, 0.68 g). A red solid slowly precipitated from the resulting solution, which was filtered off and crystallized from CH$_2$Cl$_2$/EtOH (4/12 mL); yield ≥75%. Anal. Calcd for **9a**: C, 65.33; H, 7.14; N, 2.66. Found: C, 65.05; H, 7.03; N, 2.55. Mp: 126 °C. $\Lambda_\mathrm{M} = 210.7\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. Anal. Calcd for **9c**: C, 65.42; H, 7.17; N, 2.65. Found: C, 65.26; H, 7.10; N, 2.53. Mp: 115 °C. $\Lambda_\mathrm{M} = 208.4\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$.

[{Ru(4-CH$_3$C$_6$H$_4$CN)(P(OEt)$_3$)$_4$}$_2$(*μ*-HN=NAr−ArN=NH)](BPh$_4$)$_4$ (10) [Ar−Ar = 4,4′-C$_6$H$_4$−C$_6$H$_4$ (a), 4,4′-C$_6$H$_4$−CH$_2$−C$_6$H$_4$ (c)]. These compounds were prepared analogously to the related iron complexes **9** by reacting [RuH(4-CH$_3$C$_6$H$_4$CN){P(OEt)$_3$}$_4$]BPh$_4$ (0.42 mmol, 0.5 g) with the appropriate bis(diazonium) salt (N$_2$Ar−ArN$_2$)(BF$_4$)$_2$ (0.21 mmol) in acetone for 8 h; yield ≥80%. Anal. Calcd for **10a**: C, 63.51; H, 6.94; N, 2.58. Found: C, 63.35; H, 6.88; N, 2.50. Mp: 126 °C. $\Lambda_\mathrm{M} = 209.2\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. Anal. Calcd for **10c**: C, 63.60; H, 6.97; N, 2.57. Found: C, 63.49; H, 6.92; N, 2.53. Mp: 120 °C. $\Lambda_\mathrm{M} = 206.8\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$.

[{Ru(4-CH$_3$C$_6$H$_4$CN)(P(OEt)$_3$)$_4$}$_2$(*μ*-4,4′-H^{15}N=NC$_6$H$_4$−C$_6$H$_4$N=^{15}NH)](BPh$_4$)$_4$ (10*a). This complex was prepared analogously to the related **10a** using the labeled (4,4′-^{15}N≡NC$_6$H$_4$−C$_6$H$_4$N≡^{15}N)(BF$_4$)$_2$ bis(diazonium) salt as a reagent; yield ≥80%. Anal. Calcd: C, 63.47; H, 6.94; N, 2.64. Found: C, 63.44; H, 6.85; N, 2.57. Mp: 123 °C. $\Lambda_\mathrm{M} = 207.5\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$.

[{Fe(P(OEt)$_3$)$_4$}$_2$(*μ*-N$_2$Ar−ArN$_2$)](BPh$_4$)$_2$ (11) [Ar−Ar = 4,4′-C$_6$H$_4$−C$_6$H$_4$ (a), 4,4′-C$_6$H$_4$−CH$_2$−C$_6$H$_4$ (c)]. An excess of triethylamine (1.9 mmol, 0.25 mL) was added to a solution of the appropriate bis(diazene) complex [{Fe(4-CH$_3$C$_6$H$_4$CN)(P(OEt)$_3$)$_4$}$_2$(*μ*-HN=NAr−ArN=NH)](BPh$_4$)$_4$ (**9**) (0.2 mmol) in 10 mL of dichloromethane. The ammonium salt [NHEt$_3$]BPh$_4$ began to precipitate as a white solid, which was removed by filtration after 2 h of stirring. The resulting solution was evaporated to dryness, giving an oil which was treated with 10 mL of ethanol. The red solution obtained was vigorously stirred until a solid appeared which was removed by filtration. The filtrate was then cooled to −25 °C. Red microcrystals of the complex slowly formed which were collected and dried under vacuum; yield ≥40%. Anal. Calcd for **11a**: C, 58.35; H, 4.72; N, 2.52. Found: C, 58.09; H, 4.70; N, 2.47. Mp: 145 °C. $\Lambda_\mathrm{M} = 129.5\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. Anal. Calcd for **11c**: C, 56.88; H, 7.44; N, 2.43. Found: C, 56.55; H, 7.38; N, 2.34. Mp: 125 °C. $\Lambda_\mathrm{M} = 120.9\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$.

Table 1. Crystallographic Data for Compound **1b**

empirical formula: C$_{55}$H$_{88}$BFeN$_2$O$_{12}$P$_4$	$\alpha = 96.41(2)°$
fw: 1159.9	$\beta = 84.49(2)°$
crystal system: triclinic	$\gamma = 97.97(2)°$
space group: $P\bar{1}$	$V = 3199$ Å^3
$T = 20$ °C	$Z = 2$
$\lambda = 0.710\,78$ Å	$\rho_\mathrm{calcd} = 1.204$ g cm^{-3}
$a = 16.105(5)$ Å	$\mu = 3.78$ cm^{-1}
$b = 17.551(6)$ Å	$F(000) = 1238$
$c = 11.539(3)$ Å	$R(F_\mathrm{o})^a = 0.0809$
	$R_\mathrm{w}(F_\mathrm{o}^2)^b = 0.2938$

[a] $R(F_\mathrm{o}) = \Sigma|F_\mathrm{o} - F_\mathrm{c}|/\Sigma|F_\mathrm{o}|$, calculated on reflections with $F_\mathrm{o} > 4\sigma(F_\mathrm{o})$. [b] $R_\mathrm{w}(F_\mathrm{o}^2) = \{\Sigma[w(F_\mathrm{o}^2 - F_\mathrm{c}^2)^2]/\Sigma w(F_\mathrm{o}^2)\}^{1/2}$. $w = 1/[\Sigma\sigma^2(F_\mathrm{o}^2) + 0.01P]$; $P = [\mathrm{Max}(F_\mathrm{o}^2,0) + 2F\mathrm{c}^2]/3$.

[{Ru(P(OEt)$_3$)$_4$}$_2$(*μ*-N$_2$Ar−ArN$_2$)](BPh$_4$)$_2$ (12) [Ar−Ar = 4,4′-C$_6$H$_4$−C$_6$H$_4$ (a), 4,4′-C$_6$H$_4$−CH$_2$−C$_6$H$_4$ (c)]. These complexes were prepared analogously to the related iron derivatives **11** by reacting [{Ru(4-CH$_3$C$_6$H$_4$CN)(P(OEt)$_3$)$_4$}$_2$(*μ*-HN=NAr−ArN=NH)](BPh$_4$)$_4$ (**10**) (0.2 mmol) with an excess of NEt$_3$ in CH$_2$Cl$_2$; yield ≥60%. Anal. Calcd for **12a**: C, 54.55; H, 7.12; N, 2.36. Found: C, 55.00; H, 7.15; N, 2.33. $\Lambda_\mathrm{M} = 119.6\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. Anal. Calcd for **12c**: C, 54.73; H, 7.16; N, 2.34. Found: C, 54.55; H, 7.01; N, 2.20. $\Lambda_\mathrm{M} = 123.3\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$.

[{Ru(P(OEt)$_3$)$_4$}$_2$(*μ*-4,4′-^{15}N≡NC$_6$H$_4$−C$_6$H$_4$N≡^{15}N)](BPh$_4$)$_2$ (12*a). This complex was prepared analogously to the related **12a** by starting from the labeled [{Ru(4-CH$_3$C$_6$H$_4$CN)(P(OEt)$_3$)$_4$}$_2$(*μ*-4,4′-H^{15}N=NC$_6$H$_4$−C$_6$H$_4$N=^{15}NH)](BPh$_4$)$_4$ (**10*a**) complex; yield ≥60%. Anal. Calcd: C, 54.50; H, 7.12; N, 2.44. Found: C, 54.45; H, 7.12; N, 2.39. $\Lambda_\mathrm{M} = 118.7\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$.

X-ray Crystallography. Suitable crystals for X-ray analysis were obtained by slow cooling between +30 and +5 °C of a saturated solution of [{FeH(P(OEt)$_3$)$_4$}$_2${*μ*-4,4′-HN=N(2-CH$_3$)C$_6$H$_3$−C$_6$H$_3$(2-CH$_3$)N=NH}](BPh$_4$)$_2$ (**1b**) in ethanol/CH$_2$Cl$_2$ (20/5 mL). An orange crystal of approximate dimensions 0.42 × 0.37 × 0.21 mm was mounted on an Enraf-Nonius CAD4 diffractometer, which was used to measure cell dimensions and diffraction intensities by means of graphite-monochromatized Mo Kα radiation. Automatic peak search and indexing procedures yielded a triclinic reduced primitive cell. Inspection of Niggli values revealed no conventional cells of higher symmetry. The intensity statistics suggested that the crystal was centric, and a successful model was found with the space group $P\bar{1}$. Table 1 summarizes the principal experimental data regarding X-ray crystallographic analysis.

The unit-cell dimensions and their standard deviations were determined and refined from the angular positions of 25 carefully measured reflections. A total of 11 257 data were collected by the $\theta-2\theta$ scan technique for one hemisphere ($\pm h,\pm k,+l$) of reciprocal space over the range 6−50° in 2θ.

The number of observed reflections is quite small due to a rapid falloff of high-angle data intensities and to the thinness of the sample. No correction for crystal decay or loss of alignment was required. The reflections were processed with the peak profile analysis procedure and corrected for Lorentz, polarization, and absorption effects.

The structure was solved by direct methods (SIR92)[13] and refined

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(13) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

Table 2. Selected Bond Distances (Å) and Angles (deg) with Esd's in Parentheses

	Distances		
Fe−P1	2.150(5)	C1−C2	1.341(23)
Fe−P2	2.159(5)	C1−C6	1.388(25)
Fe−P3	2.196(5)	C2−C3	1.407(21)
Fe−P4	2.201(5)	C3−C4	1.375(22)
Fe−N1	1.918(10)	C4−C5	1.348(21)
Fe−H1	1.669(77)	C5−C6	1.452(21)
N1−N2	1.273(16)	C6−C7	1.507(21)
N2−C1	1.415(19)		
	Angles		
N1−Fe−H1	79.3(28)	P1−Fe−P3	100.8(2)
P4−Fe−H1	90.4(28)	P1−Fe−P2	89.2(2)
P4−Fe−N1	88.0(3)	N2−C1−C6	112.0(14)
P3−Fe−H1	169.9(28)	N2−C1−C2	126.1(15)
P3−Fe−N1	93.0(4)	C2−C1−C6	120.9(16)
P3−Fe−P4	95.8(2)	C1−C2−C3	123.8(15)
P2−Fe−H1	80.8(27)	C2−C3−C4	117.5(13)
P2−Fe−N1	86.2(3)	C3−C4−C5	118.9(14)
P2−Fe−P4	170.2(2)	C4−C5−C6	124.6(14)
P2−Fe−P3	92.4(2)	C1−C6−C5	114.1(14)
P1−Fe−H1	86.5(28)	C5−C6−C7	121.1(13)
P1−Fe−N1	165.6(3)	C1−C6−C7	124.8(14)
P1−Fe−P4	94.6(2)		

by full-matrix least squares based on F^2 (SHELXL93).[14] In view of the large fraction of unobserved reflections, only the iron, the phosphorus atoms, and the non-hydrogen atoms of the [μ-4,4′-HN=N-(2-CH_3)C_6H_3−C_6H_3(2-CH_3)N=NH] ligand were refined anisotropically. Rigid-group refinement was used for the phenyl rings of the anion. H atom positions were calculated except for that of the hydride ligand, which was located in the difference map. The final residual indices for 340 variables are R1 = 0.0809 on 1538 observed reflections ($F_o > 4\sigma(F_o)$) and wR2 = 0.2938 for all data. The final difference map was essentially featureless. Neutral-atom scattering factors were employed, and anomalous dispersion terms were included for all non-hydrogen atoms. Calculations were performed on Gould Powernode 6040 and Encore 91 computers; programs PARST[15] and ZORTEP[16] were used for molecular geometry calculations and drawings. Extensive use was made of the program packages of the Cambridge Structural Database at the Centro di Studio per la Strutturistica Diffrattometrica del CNR in Parma. Selected bond distances and angles are listed in Table 2.

Electrochemical Apparatus and Procedures. Voltammetric and chronoamperometric experiments were carried out in a three-electrode cell. The working electrode was a glassy-carbon disk (diameter 0.5 cm) mirror-polished with graded alumina powder. It was surrounded by a platinum spiral counter electrode. The potential of the working electrode was probed by a Luggin capillary reference electrode compartment. All potentials were measured and are referred to an aqueous-KCl-saturated Ag/AgCl reference electrode.

All measurements were carried out at room temperature under a nitrogen atmosphere on 1,2-dichloroethane (DCE) solutions that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte.

The voltammetric equipment used was an Amel Model 552 potentiostat, with positive feedback correction of the uncompensated resistance, in conjunction with an Amel Model 568 digital logic function generator and with a Yokogawa 3023 X-Y recorder. Chronoamperometric measurements were carried out with the same apparatus, but using a Nicolet 3091 oscilloscope with analogue output for X-Y recorders as the recording device.

Results and Discussion

Preparation of the Complexes. Binuclear complexes [$(MHP_4)_2$(μ-HN=NAr−ArN=NH)]$(BPh_4)_2$ (**1**−**4**) with a bis(diazene) bridging unit can be easily prepared by reacting the hydride species MH_2P_4 with bis(diazonium) salts (N_2Ar−ArN_2)-$(BF_4)_2$ in a 2:1 ratio, as shown in eq 1. Good yields of

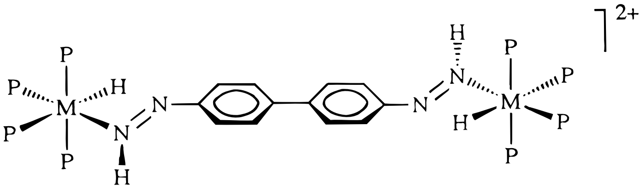
$$2MH_2P_4 + [N_2Ar{-}ArN_2]^{2+} \xrightarrow[-80\ ^\circ C]{CH_2Cl_2} [(MHP_4)_2(\mu\text{-}HN{=}NAr{-}ArN{=}NH)]^{2+} \quad (1)$$

1−**4**

M = Fe (**1**), Ru (**2**−**4**); P = $P(OMe)_3$ (**2**), $P(OEt)_3$ (**1**, **3**), $PPh(OEt)_2$ (**4**); Ar−Ar = 4,4′-C_6H_4−C_6H_4 (**a**), 4,4′-(2-CH_3)C_6H_3−C_6H_3(2-CH_3) (**b**), 4,4′-C_6H_4−CH_2−C_6H_4 (**c**)

analytically pure solid compounds were obtained with all the MH_2P_4 species, except $FeH_2[PPh(OEt)_2]_4$. In this case, oils were always obtained whose ^1H NMR spectra seem to suggest the presence of a mixture of products. The formation of an oily product containing more than one compound may be explained by taking into account that the reaction of the hydride $FeH_2[PPh(OEt)_2]_4$ with the mono(diazonium) salts gives as the first insertion product the *trans* derivatives [FeH(RN=NH){$PPh(OEt)_2$}$_4$]$^+$ instead of the *cis*.[8c] If the bis(diazonium) salts give the same reaction, the *trans*-[$(FeHP_4)_2$(μ-HN=NAr−ArN=NH)]$^{2+}$ cations can further easily react with other bis(diazonium) salts present in the reaction mixture giving polynuclear complexes.

Chart 2



The complexes are diamagnetic, air stable 2:1 electrolytes,[17] and their formulation is confirmed by NMR data, reported in the Supporting Information. In the ^1H NMR spectra, the diazene resonance appears as only one, slightly broad signal at high frequency (15−12 ppm) which is replaced by a sharp doublet ($^1J_{^{15}NH}$ = 65 Hz) in the spectra of the labeled [$(MHP_4)_2$(μ-$H^{15}N$=NAr−ArN=$N^{15}H$)]$^{2+}$ (**1*a**) and (**3*a**) derivatives, thus confirming the presence of the diazene ligand.[1a,8] Furthermore, in the low-frequency region (−6 to −10 ppm), the hydride ligand exhibits a complicated multiplet due to the coupling with the four phosphorus *nuclei* of the phosphite ligands. Finally, in the temperature range between +30 and −80 °C, the $^{31}P\{^1H\}$ NMR spectra appear as AB_2C multiplets, suggesting a *cis* geometry for the complexes of the type schematized in Chart 2.

Support for the existence of such types of binuclear bis(diazene) complexes comes from an X-ray study of one of them, the [{$FeH(P(OEt)_3)_4$}$_2${μ-4,4′-HN=N(2-CH_3)C_6H_3−C_6H_3(2-CH_3)N=NH}]$(BPh_4)_2$ (**1b**) derivative, whose crystal structure is shown in Figure 1 and will be discussed below.

Complexes **1**−**4** still contain one hydride ligand for each metal center which can undergo a further insertion reaction, thus potentially allowing the build-up of a complex molecular structure using the [N_2Ar−ArN_2]$^{2+}$ unit. We have therefore studied the reaction of the binuclear complexes [$(MHP_4)_2$(μ-HN=NAr−ArN=NH)]$^{2+}$ (**1**−**4**) with both mono- and bis(diazonium) salts and observed first of all that this second insertion reaction is very slow, as compared to the first, mainly in the case of iron. Furthermore, only with mono(diazonium) salts RN_2^+ can the reaction of binuclear derivatives **1**−**4** give, after workup, pure samples of bis(diazene), while the bis-

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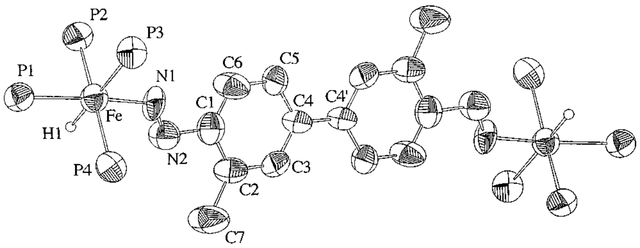
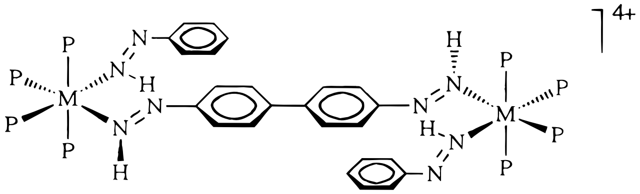


Figure 1. ORTEP diagram for $[\{FeH(P(OEt)_3)_4\}_2\{\mu\text{-}4,4'\text{-}HN{=}N(2\text{-}CH_3)C_6H_3{-}C_6H_3(2\text{-}CH_3)N{=}NH\}]^{2+}$ (cation of **1b**) with thermal ellipsoids drawn at the 50% probability level. Ethoxy groups have been omitted for clarity.

Chart 3



(diazonium) $[N_2Ar{-}ArN_2]^{2+}$ reactions gave oily products or intractable mixtures. Finally, the resulting bis(diazene) complexes are rather unstable and decompose during the course of the reaction, giving often impure products in low yields. Nevertheless, bis(diazene) derivatives $[\{M(RN{=}NH)P_4\}_2(\mu\text{-}HN{=}NAr{-}ArN{=}NH)](BPh_4)_4$ (**5**−**8**) were prepared by reacting bis(diazene) complexes **1**−**4** with an excess of mono(diazonium) RN_2^+ salts in $(CH_3)_2CO$ at 0 °C as shown in the following:

$$[(MHP_4)_2(\mu\text{-}HN{=}NAr{-}ArN{=}NH)]^{2+} \xrightarrow[(CH_3)_2CO,\ 0\ °C]{\text{excess } RN_2^+} [\{M(RN{=}NH)P_4\}_2(\mu\text{-}HN{=}NAr{-}ArN{=}NH)]^{4+}$$

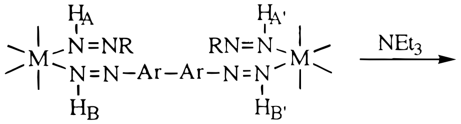
5−**8**

$$M = Fe\ (\mathbf{5}),\ Ru\ (\mathbf{6}{-}\mathbf{8});$$
$$R = C_6H_5,\ 4\text{-}CH_3C_6H_4,\ 4\text{-}CH_3OC_6H_4$$

It can be noted that while, in the case of ruthenium, the binuclear bis(diazene) complexes can be easily prepared with several mono(diazonium) salts, in the case of iron, only with the $4\text{-}CH_3C_6H_4N_2^+$ salt can the bis(diazene) **5** be obtained in pure form and as a solid sample. Furthermore, the binuclear bis(diazene) complexes **5**−**8** may also be obtained by reacting the mono(diazene) $[MH(RN{=}NH)P_4]^+$ cations with the appropriate bis(diazonium) salt $(N_2Ar{-}ArN_2)(BF_4)_2$ in a 2:1 ratio using $(CH_3)_2CO$ as solvent.

The compounds are orange or yellow solids, moderately stable, both as solids and in solution of polar organic solvents, where they behave as 4:1 electrolytes. The NMR spectra confirm their formulation. In the high-frequency region the ^1H NMR spectra show two diazene signals while the resonances of the methyl or methoxy substituents of the N=NH moiety are present as singlets between 4 and 2 ppm. The $^{31}P\{^1H\}$ NMR spectra appear as ABC_2 multiplets, suggesting that the two diazenes are in mutually *cis* positions, as schematized in Chart 3. A comparison of the results obtained on the reactivity of the dihydride species MH_2P_4 toward mono-[8a,d] and bis(diazonium) salts, shows that the first insertion into the M−H bond is easy, giving mononuclear mono(diazene) cations[8a,d] $[MH(RN{=}NH)P_4]^+$ with RN_2^+ and binuclear derivatives **1**−**4** with the bis(diazonium) salts. Differences were observed in the reactivities of these hydride−diazene complexes toward diazonium cations, probably owing to steric factors which make the second insertion into the M−H bond more difficult with the binuclear complexes **1**−**4** than with the related $[MH(RN{=}NH)P_4]^+$ mononuclear ones. Only a little difference, however, was observed in the ^1H and ^{31}P NMR spectra of the mono- and binuclear diazene derivatives.

Chart 4



$$\longrightarrow [(MP_4)_2(\mu\text{-}N_2Ar\text{-}ArN_2)]^{2+} + [M(RN_2)P_4]^+ + [M(HAr\text{-}ArN_2)P_4]^+ + [NHEt_3]^+ + N_2 + RH + HAr\text{-}ArH$$

The hydrogen atom in the diazene ligands is generally acidic,[1a,b,3,8] and treatment with base of the mononuclear bis(diazene) $[M(RN{=}NH)_2P_4]^{2+}$ derivatives[8a,d] gave the pentacoordinate aryldiazenido $[M(RN_2)P_4]^+$ cations according to a pathway that involves the deprotonation of one diazene group and the concurrent dissociation of the other (which decomposes to N_2 and the hydrocarbon RH) to give aryldiazenido final products. Accordingly, we tried to prepare the binuclear bis(diazenido) $[(MP_4)_2(\mu\text{-}N_2Ar{-}ArN_2)]^{2+}$ derivatives by treatment of the bis(diazenes) **5**−**8** with an excess of triethylamine and observed that the reactions did proceed but gave solids whose IR and NMR spectra indicated the presence of a mixture of products. Among them, we have clearly identified the mononuclear $[M(RN_2)P_4]^+$ and the binuclear $[(MP_4)_2(\mu\text{-}N_2Ar{-}ArN_2)]^{2+}$ diazenido complexes, together with other unidentified products. This result suggests that also in these binuclear complexes the deprotonation proceeds to give the diazenido derivatives, but the difference in acidity between the two diazenes bonded to the same central metal is not sufficient (even in **7ac** or **8ac**) to allow the deprotonation exclusively of the same diazene in the molecule giving only one compound. In other words, the deprotonation involving H_B and $H_{B'}$ (Chart 4) should give $[(MP_4)_2(\mu\text{-}N_2Ar{-}ArN_2)]^{2+}$ and the deprotonation involving H_A and $H_{A'}$ should give $[M(RN_2)P_4]^+$, while $[M(HAr{-}ArN_2)P_4]^+$ and $[M(RN_2)P_4]^+$ should be formed by removing H_B and $H_{A'}$ or $H_{B'}$ and H_A.

The formation of a mixture of products by deprotonation of bis(diazenes) **5**−**8** is therefore plausible but does not allow us to prepare pure samples of the bis(diazenido) complexes.

A different strategy was therefore employed in order to prepare binuclear complexes containing bis(diazenido) $^+N_2Ar{-}ArN_2^+$ bridging ligands, involving the synthesis of binuclear bis(diazene) compounds containing a labile ligand such as a nitrile bonded to each central metal. This ligand can dissociate as a result of the deprotonation reaction of the diazene group giving the expected complexes. Such derivatives are the nitrile−diazene compounds $[\{M(4\text{-}CH_3C_6H_4CN)P_4\}_2(\mu\text{-}HN{=}NAr{-}ArN{=}NH)](BPh_4)_4$ (**9**, **10**) which were prepared as orange microcrystalline solids by reacting the $[MH(4\text{-}CH_3C_6H_4CN)P_4]BPh_4$ compounds with the bis(diazonium) salts $(N_2Ar{-}ArN_2)(BF_4)_2$, as shown in eq 2.

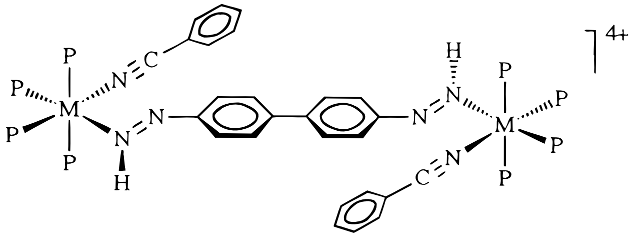
$$2[MH(4\text{-}CH_3C_6H_4CN)P_4]^+ + [N_2Ar{-}ArN_2]^{2+} \rightarrow [\{M(4\text{-}CH_3C_6H_4CN)P_4\}_2(\mu\text{-}HN{=}NAr{-}ArN{=}NH)]^{4+} \quad (2)$$

9, **10**

$$M = Fe\ (\mathbf{9}),\ Ru\ (\mathbf{10});\ P = P(OEt)_3;$$
$$Ar{-}Ar = 4,4'\text{-}C_6H_4{-}C_6H_4\ (\mathbf{a}),$$
$$4,4'\text{-}C_6H_4{-}CH_2{-}C_6H_4\ (\mathbf{c})$$

The reaction giving the related compounds **9b** and **10b** with the $4,4'\text{-}HN{=}N(2\text{-}CH_3)C_6H_3{-}C_6H_3(2\text{-}CH_3)N{=}NH$ bridging

Chart 5



ligand is very slow, probably owing to the insolubility of the bis(diazonium) salt **B** and does not allow the preparation of pure compounds.

The formulation of the new complexes is confirmed by IR and NMR spectra, which also suggest mutually *cis* positions for the nitrile and the diazene ligands as in Chart 5. In particular the IR spectra exhibit the ν(CN) band at 2265−2258 cm^{-1} while the ^1H NMR shows the diazene proton resonance as only one broad signal between 14.41 and 13.97 ppm [substituted by a doublet in the ^{15}N-labeled $[\{Ru(4\text{-}CH_3C_6H_4CN)P_4\}_2(\mu\text{-}4,4'\text{-}H^{15}N{=}NC_6H_4{-}C_6H_4N{=}^{15}NH)]^{4+}$ (**10*a**) compound with $^1J_{NH}$ of 61 Hz]. Furthermore, the $^{31}P\{^1H\}$ NMR spectra are ABC_2 multiplets in agreement with the *cis* geometry of Chart 5.

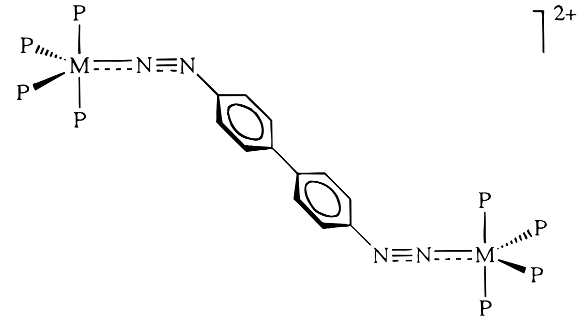
Treatment of $[\{M(4\text{-}CH_3C_6H_4CN)P_4\}_2(\mu\text{-}HN{=}NAr{-}ArN{=}NH)]^{4+}$ (**9**, **10**) derivatives with an excess of triethylamine gave, after workup, the binuclear bis(diazenido) complexes $[(MP_4)_2(\mu\text{-}N_2Ar{-}ArN_2)](BPh_4)_2$ (**11**, **12**) (eq 3) as red or orange solids in about 40−60% yields. Studies on this reaction support the stoichiometry reported in eq 3. The ammonium salt $[NHEt_3]BPh_4$ is in fact formed as a white solid and can be recovered in quantitative yield, while the IR spectra of the reaction mixture show the appearance of the band of the free nitrile at 2230 cm^{-1} besides the absorptions of the bis(diazenido) complexes **11** and **12** at 1663−1646 cm^{-1}. Furthermore, the IR spectrum of the final reaction mixture in the 2300−1600 cm^{-1} region is identical with that of a 1:1 solution of **11a** and $4\text{-}CH_3C_6H_4CN$. On this basis, it seems to be confirmed that the deprotonation of the two diazene moieties in the binuclear complexes giving the diazenido $N_2Ar{-}ArN_2$ group is followed by the dissociation of the nitrile ligand, affording **11** and **12** as final products.

$$[\{M(4\text{-}CH_3C_6H_4CN)P_4\}_2(\mu\text{-}HN{=}NAr{-}ArN{=}NH)]^{4+} + 2NEt_3 \rightarrow \underset{\mathbf{11},\ \mathbf{12}}{[(MP_4)_2(\mu\text{-}N_2Ar{-}ArN_2)]^{2+}} + 2NHEt_3^{+} + 2(4\text{-}CH_3C_6H_4CN) \quad (3)$$

$$M = Fe\ (\mathbf{11}),\ Ru\ (\mathbf{12});\quad Ar{-}Ar = 4,4'\text{-}C_6H_4{-}C_6H_4\ (\mathbf{a}),\ 4,4'\text{-}C_6H_4{-}CH_2{-}C_6H_4\ (\mathbf{c})$$

The new bis(diazenido) $[(MP_4)_2(\mu\text{-}N_2Ar{-}ArN_2)](BPh_4)_2$ derivatives are red or orange solid, diamagnetic 2:1 electrolytes. The IR spectra exhibit only one medium-intensity band at 1663−1653 cm^{-1} (KBr) for **11** and at 1646 cm^{-1} (CH_2Cl_2) for **12** attributed to $\nu(N_2)$ of the diazenido $N_2Ar{-}ArN_2$ ligand as confirmed by the lowering of 21 cm^{-1} observed for the labeled $[\{Ru(P(OEt)_3)_4\}_2(\mu\text{-}4,4'\text{-}^{15}N{\equiv}NC_6H_4{-}C_6H_4N{\equiv}^{15}N)](BPh_4)_2$ (**12*a**) complex, which shows $\nu(^{15}N_2)$ at 1625 cm^{-1}. For the related mononuclear complex[8d] $[Ru(C_6H_5N_2)\{P(OEt)_3\}_4]BPh_4$, this $\nu(N_2)$ band falls at 1646 cm^{-1} (CH_2Cl_2) with a shift at 1626 cm^{-1} for the labeled compound. These values for the N≡N stretching frequency suggest a singly bent aryldiazenido ligand[1,3,8,18] in agreement with a formal oxidation number of “zero” for the central metal.

Chart 6



The $^{31}P\{^1H\}$ spectra of **11** and **12** change with temperature, and the rather broad signal that appears for all the complexes at room temperature resolves into an ABC_2 multiplet at −40 °C which can be simulated with the parameters reported in the Supporting Information. Such a spectrum seems to exclude a regular TBP geometry, for example of the type of Chart 6, for which an A_2B_2 spectrum should be expected. Also a regular TBP geometry with the diazenido ligand in the apical position can be excluded on the basis of the expected AB_3- or A_3B-type ^{31}P spectra. Instead, a distorted TBP toward SP geometry could result in an ABC_2-type spectrum, as previously proposed for the related mononuclear[8b] iron $[Fe(RN_2)P_4]BPh_4$ derivatives. However, a restricted rotation at low temperature of the ArNN group placed in the equatorial plane of a regular TBP (Chart 6) may cause either the two apical or the two equatorial phosphorus *nuclei* to be mutually magnetically inequivalent, resulting in an ABC_2-type ^{31}P spectrum.

X-ray Crystal Structure of 1b. The structure is constituted by binuclear cations $[\{FeH(P(OEt)_3)_4\}_2\{\mu\text{-}4,4'\text{-}HN{=}N(2\text{-}CH_3)\text{-}C_6H_3{-}C_6H_3(2\text{-}CH_3)N{=}NH\}]^{2+}$ and BPh_4^- anions. The binuclear moieties are discrete, displaying no significant interactions with neighboring units. The halves of the binuclear cation are related by the crystallographically imposed center of symmetry situated in the middle of the C4−C4′ bond. A perspective drawing of the cation is shown in Figure 1. The iron atom is six-coordinated in a distorted octahedral geometry which involves four phosphite groups, two of which are *trans* to one another, one diazene molecule, and one hydride ion. The variations observed in the angular geometry are mainly due to the small steric bulk of the hydride ligand. *Cis* bond angles range from 79(3)° for N1−Fe−H1 to 100.8(2)° for P1−Fe−P3, and the range of *trans* bond angles extends from 165.6(3)° for P1−Fe−N1 to 170.2(2)° for P2−Fe−P4. In this respect, the geometry around Fe is very similar to that observed in the mononuclear structure.[8b] The mono- and binuclear cations differ essentially in the reciprocal orientation of the octahedral coordination and the ligand: the N−N bond is practically eclipsed with respect to the Fe−H bond in the mononuclear cation, whereas it is tilted in the binuclear (torsion angles H−Fe−N−N = 3.0 and −26.4°, respectively). The structural parameters in the Fe−N−N system agree with sp^2 hybridization for both N atoms.

In the octahedral coordination, the two Fe−P bonds *trans* to each other are significantly different [Fe−P2 = 2.159(5) Å and Fe−P4 = 2.201(5) Å]; and this effect is present also in the mononuclear structure, but to a lesser extent. Since the most evident structural difference between the mono- and the binuclear compound is the torsion angle between the octahedral

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(18) (a) Haymore, B. L.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 3060. (b) Haymore, B. L.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 1369. (c) McArdle, J. V.; Schultz, A. J.; Corden, B. J.; Eisenberg, R. *Inorg. Chem.* **1973**, *12*, 1676.

Table 3. Comparison of Bond Lengths and Angles for Selected Diazene Compounds[a]

compound	d_1(M−P) (Å)	d_2(M−P) (Å)	P−M−N1−N2 (deg)	relative stretching (%)	ref
$[IrCl\{HNNC_6H_3(4\text{-}F)\}(CO)(PPh_3)_2]BF_4\cdot(CH_3)_2CO$	2.399	2.374	88.36	1.018	19a
$[MoCl(HNNCOPh)(N_2COPh)(PMe_2Ph)_2]$	2.542	2.524	84.98	0.683	19b
$[MoCl(HNNCOPh)(N_2COPh)(PMe_2Ph)_2]$	2.544	2.522	88.84	0.875	19b
$[Ir\{NHNHC_6H_3(2\text{-}NO_2)\}(CO)(PPh_3)_2]BF_4$	2.376	2.376	93.29	0.000	19c
$[RuCl(CO)_2(HNNC_6H_5)(PPh_3)_2]ClO_4\cdot CH_2Cl_2$	2.439	2.415	80.83	0.979	19d
$[IrCl_2(HNNC\{C(O)Ph\}_2)(PPh_3)_2]$	2.394	2.388	89.23	0.274	19e
$[FeH\{HNNC_6H_4(4\text{-}CH_3)\}\{P(OEt)_3\}_4]BPh_4$	2.195	2.171	78.65	1.089	7b
$[RuBr\{3\text{-}CH_3(2\text{-}O)C_6H_3NNC_6H_4\}(PPh_3)_2]$	2.408	2.395	92.50	0.511	19f
$[IrHCl(C_6H_4NNC_6H_5)(PPh_3)_2]$	2.348	2.333	91.23	0.679	19g
$[IrHI\{HNNC_6H_4(4\text{-}CH_3O)\}(PPh_3)_2]\cdot CDCl_3$	2.326	2.315	89.96	0.475	19h
$[W(HNNMe)(CO)_2(NO)(PPh_3)_2]PF_6\cdot (CH_3)_2CO\cdot Et_2O$	2.546	2.539	90.67	0.296	19i
$[OsBr(NHNH)(CO)_2(PPh_3)_2]CF_3SO_3$	2.431	2.422	93.53	0.379	19j
$[IrCl_2\{HNNC_6H_3(4\text{-}CH_3O)\}(PPh_3)_2]\cdot CHCl_3$	2.375	2.362	88.89	0.565	19k
$[\{FeH(P(OEt)_3)_4\}_2\{\mu\text{-}4,4'\text{-}HN{=}N(2\text{-}CH_3)C_6H_3{-}C_6H_3(2\text{-}CH_3)N{=}NH\}](BPh_4)_2$	2.201	2.159	64.34	1.927	this work

[a] The relative bond stretching is defined as $200(d_1 - d_2)/(d_1 + d_2)$.

coordination and the N−N bond, a survey on related systems was carried out on the Cambridge Structural Database (version March 1995) in order to investigate possible correlations between differences in the lengths of *trans* metal−phosphorus bonds and orientation of the diazo group. All the structures containing a chemical fragment consisting of a six-coordinated transition metal bound to a N=N moiety and two chemically equivalent *trans* P atoms were retrieved.[19] The compounds containing, besides the fragment under examination, other analogous groups which could bias the analysis and an evident outlier[20] were discarded. For each of the 13 remaining fragments, the difference between the two metal−phosphorus bonds, divided by the bond average, was plotted versus the torsion angle P−M−N−N involving the longer bond. The results are listed in Table 3. A significant correlation results, suggesting that as the torsion angle decreases, the corresponding metal−phosphorus bond stretches (Figure 2). The point representing the title compound, even if located far outside the range comprising the points corresponding to the compounds retrieved in the Database, is surprisingly well predicted by the least-squares line fitting the distribution of the remaining points. Care must be taken in trying to correlate the linear fit of the data to some specific physical effect, since the results are more likely an expression of the synergic contribution of more than one factor; it is possible anyway to point out that there is a general trend for these systems to weaken one of the two chemically equivalent *trans* M−P bonds in response to a torsion of the azo group.

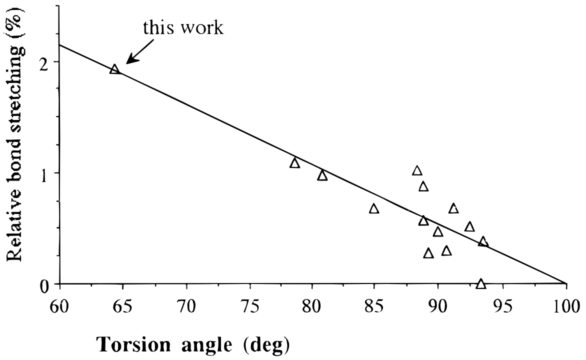

Figure 2. Scatterplot of relative bond stretching *versus* the P−Fe−N−N torsion angle for the *trans* P−Fe−P systems of selected diazene compounds. The regression line (intercept = 5.8, slope = −5.9, correlation coefficient = −0.762) was calculated for the compounds in the Database; the point for the title compound **1b** is identified.

Electrochemical Studies. Figure 3a shows the cyclic voltammetric behavior of $[\{RuH(PPh(OEt)_2)_4\}_2(\mu\text{-}4,4'\text{-}HN{=}NC_6H_4{-}C_6H_4N{=}NH)](BPh_4)_2$ (**4a**) recorded immediately after the dissolution of this compound in 0.1 M TBAH/DCE solution. It is characterized by two reduction peaks, A at −1090 and B at −1340 mV, with which the reoxidation peaks A′ and B′ are associated, respectively. Oxidation scans toward positive potential values do not show any peculiar feature apart from the irreversible oxidation of the BPh_4^- anion (E_p about +970 mV), this last process narrowing the accessible positive potential limit to +700 mV. Reduction scans which extend toward potential values more negative than −1600 mV, show the appearance of a small and broad irreversible peak at about −1750 mV which appears as a shoulder over the reduction process involving the reduction of the electrolyte (the accessible negative limit is about −1800 mV). The value of the $I_p(v^{-1/2})$ product is independent of the scan rate for both reduction peaks A and B as well as the $I_p(A')/I_p(A)$ ratio, this last quantity being equal to 0.94 ± 5 in the range 20−500 mV s^{-1}.

The half-wave potentials $E_{1/2} = (E_p^f + E_p^b)/2$ (where E_p^f and E_p^b are the peak potentials for associated peaks in the forward and backward scans, respectively) are −1040 and −1260 mV at any scan rate explored, while the separation between the associated reduction and oxidation peaks is slightly dependent on the scan rate for both peak systems, being for instance 70 mV at 50 mV s^{-1} and 100 mV at 500 mV s^{-1} for the A−A′ peaks. These findings indicate that both reduction processes are not perfectly reversible,[21] however they involve transfer coefficient values α within the range 0.3−0.7, which allows one to evaluate the half-wave potentials by the above reported simple relationship.

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(19) (a) Einstein, F. W. B.; Sutton, D. *J. Chem. Soc., Dalton Trans.* **1973**, 434. (b) Butcher, A. V.; Chatt, J.; Dilworth, J. R.; Leigh, G. J.; Hursthouse, M. B.; Jayaweera, S. A. A.; Quik, A. *J. Chem. Soc., Dalton Trans.* **1979**, 921. (c) Carroll, J. A.; Cobbledick, R. E.; Einstein, F. W. B.; Farrell, N.; Sutton, D.; Vogel, P. L. *Inorg. Chem.* **1977**, *16*, 2462. (d) Haymore, B. L.; Ibers, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 5369. (e) Cowie, M.; Loeb, S. J.; McKeer, I. R. *Organometallics* **1986**, *5*, 854. (f) Lahiri, G. K.; Bhattacharya, S.; Mukherjee, M.; Mukherjee, A. K.; Chakravorty A. *Inorg. Chem.* **1987**, *26*, 3359. (g) van Baar, J. F.; Meij, R.; Olie, K. *Cryst. Struct. Commun.* **1974**, *3*, 587. (h) Bellon, P. L.; Demartin, F.; Manassero, M.; Sansoni, M.; Caglio, G. *J. Organomet. Chem.* **1978**, *157*, 209. (i) Smith, M. R., III; Keys, R. L.; Hillhouse, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 8312. (j) Cheng, T.-Y.; Ponce, A.; Rheingold, A. L.; Hillhouse, G. L. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 657. (k) Bellon, P. L.; Caglio, G.; Manassero, M.; Sansoni, M. *J. Chem. Soc., Dalton Trans.* **1974**, 897.

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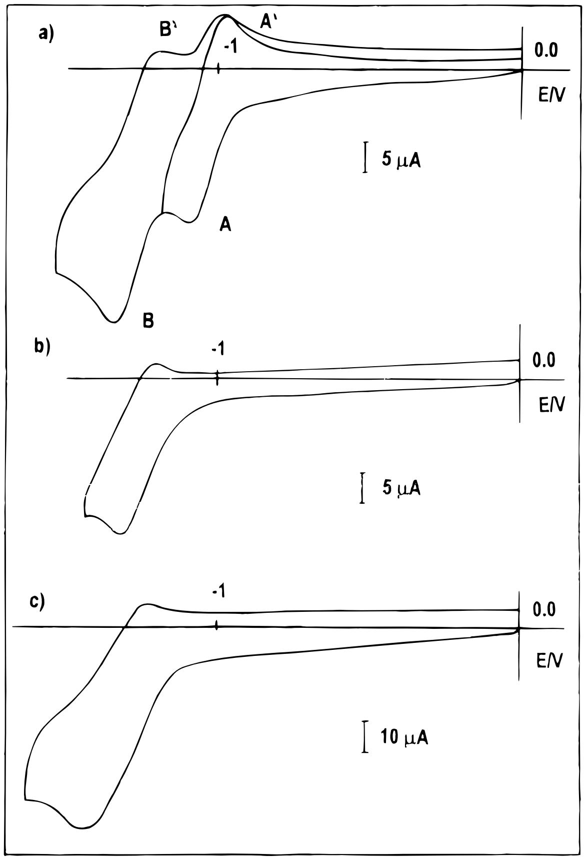

Figure 3. Cyclic voltammograms recorded at a glassy-carbon electrode at 200 mV s^{-1} in dichloroethane (DCE)/0.1 M tetrabutylammonium hexafluorophosphate (TBAH): (a) 0.6 mM $[\{RuH(PPh(OEt)_2)_4\}_2(\mu\text{-}4,4'\text{-}HN{=}NC_6H_4{-}C_6H_4N{=}NH)](BPh_4)_2$ **4a**; (b) 0.6 mM $[RuH(C_6H_5N{=}NH)\{PPh(OEt)_2\}_4]BPh_4$; (c) 1.0 mM $[\{RuH(PPh(OEt)_2)_4\}_2(\mu\text{-}4,4'\text{-}HN{=}NC_6H_4{-}CH_2{-}C_6H_4N{=}NH)](BPh_4)_2$, **4c**.

The cyclic voltammetric pattern described above changes slowly with time, showing the progressive appearance of a new reduction peak at about −750 mV. After a longer time, other peaks emerge and the formation of insoluble products is evident. Such an instability of the solutions has been observed also for the other compounds studied here, and therefore all the data discussed below will concern only freshly prepared solutions.

Attempts to carry out controlled-potential electrolyses were unsuccessful because the time scales of these experiments were comparable to the lifetimes of the starting electroactive substances in the electrolytic solutions.

In order to determine the number of electrons (n) involved, an alternative to coulometry was used,[22,23] which gives n from the combination of voltammetric and chronoamperometric responses according to eq 4, where K is the Randles−Sevcik

$$n = \{I_p(v^{-1/2})F/I_c(t^{1/2})K\}^2(1/\pi) \qquad (4)$$

constant, I_c is the chronoamperometric current at time t, and all the other symbols have their usual meaning. Concerning the first reduction process, by substituting in eq 4 the slope of the I_p *vs* $v^{1/2}$ plot for cyclic voltammetric experiments and the slope of the I_c *vs* $t^{-1/2}$ linear plot obtained from chronoamperometric data, one calculates an n value of about 1. Comparison of currents of peaks A and B shows that the process taking place at peak B is a one-electron reduction.

Figure 3b shows the voltammogram recorded in a 0.6 mM solution of $[RuH(C_6H_5N{=}NH)\{PPh(OEt)_2\}_4]BPh_4$ in 0.1 M TBAH/DCE. It is characterized by a reduction peak at −1310 mV with which a reoxidation peak at −1230 mV is associated. It is worth noting that the ratio $I_p{}^f/I_p{}^b$ is constantly equal to 1 only for scan rates higher than 100 mV s^{-1} and it decreases to 0.7 at 50 mV s^{-1}. For this reason, the calculation of n by eq 4 was carried out in this case by using both voltammetric and chronoamperometric data gained in a time window not longer than 0.25 s.

The analysis of voltammetric data indicates the operativity of a one-electron quasi-reversible reduction process whose characteristic features are listed in Table 4, together with those of compound **4a** and all the other products studied.

In Figure 3c, the voltammetric pattern recorded in a 1.0 mM $[\{RuH(PPh(OEt)_2)_4\}_2(\mu\text{-}4,4'\text{-}HN{=}NC_6H_4{-}CH_2{-}C_6H_4N{=}NH)](BPh_4)_2$ (**4c**) solution is reported. The reduction peak appears broader than in previous cases, and larger ($E_p{}^b - E_p{}^f$) values are observed. The $I_p(v^{-1/2})$ product is again independent of the scan rate, while the $I_p(A')/I_p(A)$ ratio becomes smaller than unity, being almost constantly equal to 0.7 in the range 0.020−0.500 V s^{-1}. Comparison of the peak currents of Figure 3c and Figure 3a indicates that the peak current relevant to **4c** is roughly double that of the current of peak A relevant to compound **4a**. Assuming that the diffusion coefficients of the two compounds do not differ significantly, such evidence indicates that the process involving compound **4c** is a two-electron reduction reaction.

As shown by the data reported in Table 4, the reduction of all the binuclear compounds examined, apart from **4c**, is characterized by two one-electron steps which, according to eqs 5 and 6, are characterized by different standard potential values.

$$[(MHP_4)_2(\mu\text{-}HN{=}NAr{-}ArN{=}NH)]^{2+} + e \rightleftarrows [(MHP_4)_2(\mu\text{-}HN{=}NAr{-}ArN{=}NH)]^{+} \qquad E^\circ{}_A \quad (5)$$

$$[(MHP_4)_2(\mu\text{-}HN{=}NAr{-}ArN{=}NH)]^{+} + e \rightleftarrows [(MHP_4)_2(\mu\text{-}HN{=}NAr{-}ArN{=}NH)] \qquad E^\circ{}_B \quad (6)$$

$$E^\circ{}_A > E^\circ{}_B$$

In the case of the mononuclear complexes only a one reduction process is operative (eq 7). The reduction product

$$[MH(RN{=}NH)P_4]^+ + e \rightleftarrows [MH(RN{=}NH)P_4] \qquad (7)$$

in this case is less stable, since its reoxidation peak tends to lower during voltammetric experiments carried out at scan rates lower than 100 mV s^{-1}.

In the case of **4c**, the analysis of voltammetric data indicates that the two-electron reduction observed (eq 8) is really an EE

$$[(RuHP_4)_2(\mu\text{-}4,4'\text{-}HN{=}NC_6H_4{-}CH_2{-}C_6H_4N{=}NH)]^{2+} + 2e \rightleftarrows [(RuHP_4)_2(\mu\text{-}4,4'\text{-}HN{=}NC_6H_4{-}CH_2{-}C_6H_4N{=}NH)] \qquad (8)$$

process,[24] involving at least one quasi-reversible step[25] with $E^\circ{}_A$ only some tens of a millivolt more positive than $E^\circ{}_B$.

The evidence indicates that, for all the examined compounds, in the negative potential window studied, any Ru(II)-centered

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Table 4. Selected Electrochemical Data

complex	cation	$E_{1/2}{}^{A\,a}$ (mV)	n^b	$E_{1/2}{}^{B}$ (mV)	n	$\Delta E_{1/2}{}^{c}$ (mV)
4a	$[RuH\{PPh(OEt)_2\}_4]_2(\mu\text{-}4,4'\text{-}HN{=}NC_6H_4{-}C_6H_4N{=}NH)]^{2+}$	−1040	1	−1260	1	220
	$[RuH(HN{=}NC_6H_5)\{PPh(OEt)_2\}_4]^{+}$	−1270	1			
4b	$[RuH\{PPh(OEt)_2\}_4]_2\{\mu\text{-}4,4'\text{-}HN{=}N(2\text{-}CH_3)C_6H_3{-}C_6H_3(2\text{-}CH_3)N{=}NH\}]^{2+}$	−1050	1	−1240	1	190
4c	$[RuH\{PPh(OEt)_2\}_4]_2(\mu\text{-}4,4'\text{-}HN{=}NC_6H_4{-}CH_2{-}C_6H_4N{=}NH)]^{2+}$	−1330	1.8			*d*
3a	$[RuH\{P(OEt)_3\}_4]_2(\mu\text{-}4,4'\text{-}HN{=}NC_6H_4{-}C_6H_4N{=}NH)]^{2+}$	−1094	1	−1280	1	186
	$[RuH(HN{=}NC_6H_5)\{P(OEt)_3\}_4]^{+}$	−1250	1			
3b	$[RuH\{P(OEt)_3\}_4]_2\{\mu\text{-}4,4'\text{-}HN{=}N(2\text{-}CH_3)C_6H_3{-}C_6H_3(2\text{-}CH_3)N{=}NH\}]^{2+}$	−1130	1	−1350	1	220
	$[RuH\{HN{=}NC_6H_4(4\text{-}CH_3)\}\{P(OEt)_3\}_4]^{+}$	−1430	1			
1b	$[FeH\{P(OEt)_3\}_4]_2\{\mu\text{-}4,4'\text{-}HN{=}N(2\text{-}CH_3)C_6H_3{-}C_6H_3(2\text{-}CH_3)N{=}NH\}]^{2+}$	−1240	1	−1420	1	180

[a] Obtained by use of $^1/_2(E_p{}^f + E_p{}^b)$ recorded at 200 mV s^{-1}. [b] Calculated from voltammetric and chronoamperometric data by the relationship $n = \{I_p(v^{-1/2})F/I_c(t^{1/2})K\}^2\,(1/\pi)$. [c] Calculated as $E_{1/2}{}^A - E_{1/2}{}^B$ (see eqs 5 and 6). [d] See text.

moiety can accept one electron. For binuclear compounds, where electron delocalization between the two ruthenium moieties is possible, the first reduction process is easier than the one electron reduction of the mononuclear parent compound; moreover, for the binuclear conjugated compounds, addition of the first electron makes the second reduction process more energy demanding since the perturbation caused by the first reduction process propagates over both reduced ruthenium centers. This is not the case when conjugation between the two ruthenium centers is not possible, as for the **4c** compound. Also in this case each ruthenium-centered moiety can accept one electron, but with a very small difference in reduction potentials of the two ruthenium centers.

Concerning the influence of the nature of the metal center, it can be noted that the reduction of the iron compound **1b** takes place at a slightly more negative potential than the reduction of the related ruthenium compound **3b**. A change in the phosphine ligand from $PPh(OEt)_2$ to $P(OEt)_3$ has a similar effect as well as a change in the aryl group from benzyl to tolyl in the bis(diazene) ligand.

Conclusions. The present studies have shown that bis(diazonium) cations of the type $(N_2Ar{-}ArN_2)^{2+}$ can give, with appropriate hydrides, the insertion of both the NN groups into the MH bond to give the unprecedented binuclear complexes with bis(diazene) bridging units of the types $[(MHP_4)_2(\mu\text{-}HN{=}NAr{-}ArN{=}NH)](BPh_4)_2$ (**1**−**4**) and $[\{M(4\text{-}CH_3C_6H_4CN)P_4\}_2(\mu\text{-}HN{=}NAr{-}ArN{=}NH)](BPh_4)_4$ (**11**, **12**). The formulation as binuclear complexes is also confirmed by an X-ray structure determination of the $[\{FeH(P(OEt)_3)_4\}_2\{\mu\text{-}4,4'\text{-}HN{=}N(2\text{-}CH_3)C_6H_3{-}C_6H_3(2\text{-}CH_3)N{=}NH\}](BPh_4)_2$ (**1b**) derivative.

Among the properties of these bis(diazene) complexes, we should emphasize the electrochemical behavior, which showed that the reduction of **1**−**4** to $[(MHP_4)_2(\mu\text{-}HN{=}NAr{-}ArN{=}NH)]$ involves two one-electron quasi-reversible processes with $\Delta E_{1/2}$ of about 200 mV in the case of $4,4'\text{-}HN{=}NC_6H_4{-}C_6H_4N{=}NH$ and $4,4'\text{-}HN{=}N(2\text{-}CH_3)C_6H_3{-}C_6H_3(2\text{-}CH_3)N{=}NH$ bridging ligands, while only one reduction process is observed voltammetrically for the two-electron reduction of the compound **4c** with the $4,4'\text{-}HN{=}NC_6H_4{-}CH_2{-}C_6H_4N{=}NH$ bridging unit.

Furthermore, the diazene derivatives **1**−**4** allowed us to prepare bis(diazene) binuclear cations of the type $[\{M(RN{=}NH)P_4\}_2(\mu\text{-}HN{=}NAr{-}ArN{=}NH)]^{4+}$ whereas, from the nitrile−diazene $[\{M(4\text{-}CH_3C_6H_4CN)P_4\}_2(\mu\text{-}HN{=}NAr{-}ArN{=}NH)]^{4+}$ derivatives, the synthesis of new binuclear compounds incorporating a bis(diazenido) bridging ligand $[(MP_4)_2(\mu\text{-}N_2Ar{-}ArN_2)](BPh_4)_2$ was also achieved.

Acknowledgment. The financial support of the MURST and CNR, Rome, is gratefully acknowledged. We thank Danilo Rudello and Daniela Baldan for technical assistance.

Supporting Information Available: Tables S1−S5, listing ^1H and ^{31}P NMR data, anisotropic displacement parameters, atomic coordinates for hydrogen and non-hydrogen atoms, and complete bond lengths and angles (13 pages). Ordering information is given on any current masthead page.

IC960138B