

Preparations, Structures, and Electrochemical Studies of Aryldiazene Complexes of Rhenium: Syntheses of the First Heterobinuclear and Heterotrinnuclear Derivatives with Bis(diazene) or Bis(diazenido) Bridging Ligands

Gabriele Albertin,^{*,†} Stefano Antoniutti,[†] Alessia Bacchi,[‡] Giovanni B. Ballico,[†] Emilio Bordignon,[†] Giancarlo Pelizzi,[‡] Maria Ranieri,[†] and Paolo Ugo[§]

Dipartimento di Chimica, Università Ca'Foscari di Venezia, Dorsoduro 2137, 30123 Venezia, Italy, Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Centro CNR di Strutturistica Diffattometrica, Università di Parma, Viale delle Scienze, 43100 Parma, Italy, and Dipartimento di Chimica Fisica, Università Ca'Foscari di Venezia, Dorsoduro 2137, 30123 Venezia, Italy

Received December 3, 1999

The mono- and binuclear aryldiazene complexes $[\text{Re}(\text{C}_6\text{H}_5\text{N}=\text{NH})(\text{CO})_{5-n}\text{P}_n]\text{BY}_4$ (**1–5**) and $[\{\text{Re}(\text{CO})_{5-n}\text{P}_n\}_2(\mu\text{-HN}=\text{NAr}-\text{ArN}=\text{NH})](\text{BY}_4)_2$ (**6–12**) [$\text{P} = \text{P}(\text{OEt})_3$, $\text{PPh}(\text{OEt})_2$, PPh_2OEt ; $n = 1-4$; $\text{Ar}-\text{Ar} = 4,4'\text{-C}_6\text{H}_4\text{-C}_6\text{H}_4$, $4,4'\text{-(2-CH}_3\text{)C}_6\text{H}_3\text{-C}_6\text{H}_3(2\text{-CH}_3)$, $4,4'\text{-C}_6\text{H}_4\text{-CH}_2\text{-C}_6\text{H}_4$; $\text{Y} = \text{F, Ph}$] were prepared by reacting the hydride species $\text{ReH}(\text{CO})_{5-n}\text{P}_n$ with the appropriate mono- and bis(aryldiazonium) cations. These compounds, as well as other prepared compounds, were characterized spectroscopically (IR; ^1H , ^{31}P , ^{13}C , and ^{15}N NMR data), and **1a** was also characterized by an X-ray crystal structure determination. $[\text{Re}(\text{C}_6\text{H}_5\text{N}=\text{NH})(\text{CO})\{\text{P}(\text{OEt})_3\}_4]\text{BPh}_4$ (**1a**) crystallizes in space group $P\bar{1}$ with $a = 15.380(5)$ Å, $b = 13.037(5)$ Å, $c = 16.649(5)$ Å, $\alpha = 90.33(5)^\circ$, $\beta = 91.2(1)^\circ$, $\gamma = 89.71(9)^\circ$, and $Z = 2$. The “diazene–diazonium” complexes $[\text{M}(\text{CO})_3\text{P}_2(\text{HN}=\text{NAr}-\text{ArN}=\text{N})](\text{BF}_4)_2$ (**13–15**, **17**) [$\text{M} = \text{Re, Mn}$; $\text{P} = \text{PPh}_2\text{OEt}$, PPh_2OMe , PPh_3 ; $\text{Ar}-\text{Ar} = 4,4'\text{-C}_6\text{H}_4\text{-C}_6\text{H}_4$, $4,4'\text{-C}_6\text{H}_4\text{-CH}_2\text{-C}_6\text{H}_4$] and $[\text{Re}(\text{CO})_4(\text{PPh}_2\text{OEt})(4,4'\text{-HN}=\text{NC}_6\text{H}_4\text{-C}_6\text{H}_4\text{N}=\text{N})](\text{BF}_4)_2$ (**16b**) were synthesized by allowing the hydrides $\text{MH}(\text{CO})_3\text{P}_2$ or $\text{ReH}(\text{CO})_4\text{P}$ to react with equimolar amounts of bis(aryldiazonium) cations under appropriate conditions. Reactions of diazene–diazonium complexes **13–17** with the metal hydrides $\text{M}_2\text{H}_2\text{P}'_4$ and $\text{M}_2'\text{H}(\text{CO})_{5-n}\text{P}''_n$ afforded the heterobinuclear bis(aryldiazene) derivatives $[\text{M}_1(\text{CO})_3\text{P}_2(\mu\text{-HN}=\text{NAr}-\text{ArN}=\text{NH})\text{M}_2\text{HP}'_4](\text{BPh}_4)_2$ (**ReFe**, **ReRu**, **ReOs**, **MnRu**, **MnOs**) and $[\text{M}_1(\text{CO})_3\text{P}_2(\mu\text{-HN}=\text{NAr}-\text{ArN}=\text{NH})\text{M}_2'(\text{CO})_{5-n}\text{P}''_n](\text{BPh}_4)_2$ (**ReMn**, **MnRe**) [$\text{M}_1 = \text{Re, Mn}$; $\text{M}_2 = \text{Fe, Ru, Os}$; $\text{M}_2' = \text{Mn, Re}$; $\text{P} = \text{PPh}_2\text{OEt}$, PPh_2OMe ; $\text{P}', \text{P}'' = \text{P}(\text{OEt})_3$, $\text{PPh}(\text{OEt})_2$; $\text{Ar}-\text{Ar} = 4,4'\text{-C}_6\text{H}_4\text{-C}_6\text{H}_4$, $4,4'\text{-C}_6\text{H}_4\text{-CH}_2\text{-C}_6\text{H}_4$; $n = 1, 2$]. The heterotrinnuclear complexes $[\text{Re}(\text{CO})_3(\text{PPh}_2\text{OEt})_2(\mu\text{-4,4}'\text{-HN}=\text{NC}_6\text{H}_4\text{-C}_6\text{H}_4\text{N}=\text{NH})\text{M}\{\text{P}(\text{OEt})_3\}_4(\mu\text{-4,4}'\text{-HN}=\text{NC}_6\text{H}_4\text{-C}_6\text{H}_4\text{N}=\text{NH})\text{Mn}(\text{CO})_3(\text{PPh}_2\text{OEt})_2](\text{BPh}_4)_4$ ($\text{M} = \text{Ru, Os}$) (**ReRuMn**, **ReOsMn**) were obtained by reacting the heterobinuclear complexes **ReRu** and **ReOs** with the appropriate diazene–diazonium cations. The heterobinuclear complex with a bis(aryldiazenido) bridging ligand $[\text{Mn}(\text{CO})_2(\text{PPh}_2\text{OEt})_2(\mu\text{-4,4}'\text{-N}_2\text{C}_6\text{H}_4\text{-C}_6\text{H}_4\text{N}_2)\text{Fe}\{\text{P}(\text{OEt})_3\}_4]\text{BPh}_4$ (**MnFe**) was prepared by deprotonating the bis(aryldiazene) compound $[\text{Mn}(\text{CO})_3(\text{PPh}_2\text{OEt})_2(\mu\text{-4,4}'\text{-HN}=\text{NC}_6\text{H}_4\text{-C}_6\text{H}_4\text{N}=\text{NH})\text{Fe}(4\text{-CH}_3\text{C}_6\text{H}_4\text{CN})\{\text{P}(\text{OEt})_3\}_4](\text{BPh}_4)_3$. Finally, the binuclear compound $[\text{Re}(\text{CO})_3(\text{PPh}_2\text{OEt})_2(\mu\text{-4,4}'\text{-HN}=\text{NC}_6\text{H}_4\text{-C}_6\text{H}_4\text{N}_2)\text{Fe}(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2](\text{BPh}_4)_2$ (**ReFe**) containing a diazene–diazenido bridging ligand was prepared by reacting $[\text{Re}(\text{CO})_3(\text{PPh}_2\text{OEt})_2(4,4'\text{-HN}=\text{NC}_6\text{H}_4\text{-C}_6\text{H}_4\text{N}=\text{N})]^+$ with the $\text{FeH}_2(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2$ hydride derivative. The electrochemical reduction of mono- and binuclear aryldiazene complexes of both rhenium (**1–12**) and the manganese, as well as heterobinuclear **ReRu** and **MnRu** complexes, was studied by means of cyclic voltammetry and digital simulation techniques. The electrochemical oxidation of the mono- and binuclear aryldiazenido compounds $\text{Mn}(\text{C}_6\text{H}_5\text{N}_2)(\text{CO})_2\text{P}_2$ and $\{\text{Mn}(\text{CO})_2\text{P}_2\}_2(\mu\text{-4,4}'\text{-N}_2\text{C}_6\text{H}_4\text{-C}_6\text{H}_4\text{N}_2)$ ($\text{P} = \text{PPh}_2\text{OEt}$) was also examined. Electrochemical data show that, for binuclear compounds, the diazene bridging unit allows delocalization of electrons between the two different redox centers of the same molecule, whereas the two metal centers behave independently in the presence of the diazenido bridging unit.

Introduction

Although a large number of studies on the syntheses, structures, and reactivity of aryldiazene and aryldiazenido complexes of transition metals have been reported,^{1,2} very few of them involve binuclear species with bis(diazene) or bis(diazenido)

bridging ligands,³ and none containing two different metals have ever been reported. In the course of our studies on the reactivity of rhenium hydride complexes with mono- and bis(aryldiazonium) cations, we prepared the mononuclear aryldiazene

[†] Dipartimento di Chimica, Università Ca'Foscari di Venezia.

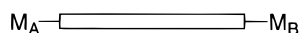
[‡] Università di Parma.

[§] Dipartimento di Chimica Fisica, Università Ca'Foscari di Venezia.

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Chart 1



complexes $[\{\text{Re}\}-\text{HN}=\text{NAr}-\text{ArN}=\text{N}\}^{2+}$, still containing a diazonium $-\text{N}=\text{N}$ group potentially able to react with another metal hydride, affording heterobinuclear bis(aryldiazene) derivatives (Chart 1).

The syntheses, characterizations, and electrochemical studies of this new class of binuclear complexes, also including bis(aryldiazenido) and diazene-diazenido bridging ligands, are the subject of this report.

Furthermore, in view of current interest^{1,2,4} in the chemistry of "diazo" complexes, due not only to their importance in nitrogen fixation processes but also to their diverse reactivity modes and structural properties, in this paper we report an extensive study on the reactivity of the hydride species $\text{ReH}(\text{CO})_5-n\text{P}_n$ (P = phosphite) toward aryldiazonium cations, which allows mono- and homobinuclear bis(aryldiazene) complexes to be prepared.

Diazo complexes of rhenium have been widely studied^{1,2} and include mainly aryldiazenido⁵ $[\text{Re}]-\text{N}_2\text{Ar}$, arylhydrazido,^{5i,k,6-8} and hydrazine⁹ derivatives, whereas there have been fewer investigations on the aryldiazene complexes. In fact, apart from chelate organodiazene complexes¹⁰ of the type $[\text{ReCl}(\text{HN}=\text{Npy})(\text{NNpy})(\text{PPhMe}_2)_2]^+$, $[\text{ReCl}_2(\text{NNC}_4\text{H}_2\text{N}_2\text{CF}_3)(\text{HN}=\text{NC}_4\text{H}_2\text{N}_2\text{CF}_3)(\text{PPh}_3)]$, and $[\text{ReCl}_3(\text{NNC}_5\text{H}_4\text{NH})(\text{HN}=\text{NC}_5\text{H}_4\text{N})]$, obtained from the reaction of NaReO_4 or ReOCl_3P_2 (P = tertiary phosphine) with hydrazinopyridine or hydrazinopyrimidine, only

one type of stable aryldiazene complex, $[\text{Re}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{HN}=\text{NR})]$ (R = 4- $\text{CH}_3\text{C}_6\text{H}_4$, 4- $\text{CH}_3\text{OC}_6\text{H}_4$), has been described,^{6,7b} prepared by reacting an aryldiazenido $[\text{Re}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{N}_2\text{R})]\text{BF}_4$ complex with NaBH_4 .

It therefore seemed of interest to report some new results on the aryldiazene chemistry of rhenium, including an X-ray crystal structure determination and an electrochemical study aimed at comparing the obtained results with those for related manganese complexes^{3b} and shedding light on the different electrochemical behaviors shown by bis(aryldiazene) and bis(aryldiazenido) binuclear derivatives.^{3a,c}

Experimental Section

General Materials and Methods. All synthetic work was carried out under an appropriate atmosphere (Ar or N_2) using standard Schlenk techniques or a vacuum atmosphere drybox. Once isolated, the complexes were found to be relatively stable in air but were nevertheless stored under an inert atmosphere at -25°C . All solvents were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. Triethyl phosphite was an Aldrich product, purified by distillation under nitrogen. The phosphines $\text{PPh}(\text{OEt})_2$, PPh_2OEt , and PPh_2OMe were prepared by the method of Rabinowitz and Pellon.¹¹ The complex $\text{Re}_2(\text{CO})_{10}$ was purchased from Pressure Chemical Co. (Pittsburgh, PA) and used as received. Diazonium salts were obtained in the usual way.¹² The related bis(diazonium) salts $[\text{N}_2\text{Ar}-\text{ArN}_2](\text{BF}_4)_2$ [$\text{Ar}-\text{Ar}$ = 4,4'- $\text{C}_6\text{H}_4-\text{C}_6\text{H}_4$, 4,4'-(2- CH_3)- C_6H_3 -(2- CH_3) C_6H_3 , 4,4'- $\text{C}_6\text{H}_4-\text{CH}_2-\text{C}_6\text{H}_4$] were prepared by treating the amine precursors $\text{H}_2\text{NAr}-\text{ArNH}_2$ with NaNO_2 , as described in the literature for common mono(diazonium) salts.¹² The labeled diazonium tetrafluoroborates $[\text{C}_6\text{H}_5\text{N}=\text{N}^{15}\text{N}]\text{BF}_4$ and $[\text{4,4}'\text{-}^{15}\text{N}=\text{NC}_6\text{H}_4-\text{C}_6\text{H}_4\text{N}=\text{N}^{15}\text{N}](\text{BF}_4)_2$ were prepared from $\text{Na}^{15}\text{NO}_2$ (99% enriched, CIL) and the appropriate amine. Alternatively, the $[\text{C}_6\text{H}_5\text{N}=\text{N}^{15}\text{N}]\text{BF}_4$ salt was prepared from NaNO_2 and $\text{C}_6\text{H}_5^{15}\text{NH}_2$. Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on a Nicolet Magna 750 FT-IR spectrophotometer. NMR spectra (^1H , ^{31}P , ^{13}C , ^{15}N) were obtained on a Bruker AC200 spectrometer at temperatures between -90 and $+30^\circ\text{C}$, unless otherwise noted. ^1H and ^{13}C NMR spectra refer to internal tetramethylsilane; $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shifts are reported with respect to 85% H_3PO_4 , with downfield shifts considered positive; ^{15}N NMR spectra refer to external $\text{CH}_3^{15}\text{NO}_2$, with downfield shifts considered positive. The SwaN-MR software package¹³ was used to treat NMR data. The conductivities of 10^{-3} M solutions of the complexes in CH_3NO_2 at 25°C were measured with a Radiometer CDM 83.

Syntheses of the Complexes. The hydride species $\text{ReH}(\text{CO})_4$, $\text{ReH}(\text{CO})_2\text{P}_3$, $\text{ReH}(\text{CO})_3\text{P}_2$, $\text{ReH}(\text{CO})_4\text{P}$, and $\text{MnH}(\text{CO})_3\text{P}_2$ [P = $\text{P}(\text{OEt})_3$, $\text{PPh}(\text{OEt})_2$, PPh_2OEt , PPh_2OMe] were prepared according to literature procedures.^{14,15} The dihydride compounds $\text{FeH}_2[\text{P}(\text{OEt})_3]_4$,¹⁶ $[\text{FeH}(\text{4-CH}_3\text{C}_6\text{H}_4\text{CN})\{\text{P}(\text{OEt})_3\}_4]\text{BPh}_4$,^{17c} $\text{RuH}_2[\text{P}(\text{OEt})_3]_4$,¹⁸ OsH_2P_4 ¹⁹ [P = $\text{P}(\text{OEt})_3$, $\text{PPh}(\text{OEt})_2$], and $\text{FeH}_2(\text{CO})_2[\text{P}(\text{OPh})_3]_2$ ²⁰ were also prepared by following reported methods.

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[Re(C₆H₅N=NH)(CO){P(OEt)₃}₄]BPh₄ (**1a**), [Re(C₆H₅N=NH)(CO)₂(PPh₂OEt)₃]BF₄ (**2a**), and [Re(C₆H₅N=NH)(CO)₃P₂](BF₄)₂ (**3**, **4**, **5**) [P = P(OEt)₃ (**3a**), PPh(OEt)₂ (**4a**), PPh₂OEt (**5a**)]. The appropriate hydride ReH(CO)_{5-n}P_n (*n* = 2, 3, 4) (0.15 mmol) and the phenyldiazonium salt [C₆H₅N₂](BF₄)₂ (0.15 mmol, 29 mg) were placed in a 25-mL three-necked flask, and after the mixture was cooled to -196 °C, 10 mL of (CH₃)₂CO was added. The reaction mixture was brought to room temperature and stirred for 4 h, and the solvent was then removed under reduced pressure. The resulting oil was treated with ethanol (2 mL), affording a yellow solution that slowly deposited a crystalline solid, which was filtered off and crystallized by cooling to -25 °C a saturated solution in ethanol prepared at 30 °C; yield ≥ 65%. The yield could be increased (to about 90%) by adding to the yellow solution in ethanol an excess of NaBF₄ (0.30 mmol, 33 mg) in 2 mL of ethanol. In the case of **1**, the complex was precipitated as its BPh₄ salt by adding an excess of NaBPh₄ (0.3 mmol, 103 mg) in 2 mL of ethanol. After filtration and crystallization from a mixture of CH₂-Cl₂ (2 mL) and ethanol (3 mL), the yield was ≥ 75%. Anal. Calcd for C₅₅H₈₆N₂BO₁₃P₄Re (**1a**): C, 50.65; H, 6.65; N, 2.15. Found: C, 50.47; H, 6.54; N, 2.10. $\Lambda_M = 51.2 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. Anal. Calcd for C₅₀H₅₁N₂BF₄O₅P₃Re (**2a**): C, 53.34; H, 4.57; N, 2.49. Found: C, 53.45; H, 4.46; N, 2.43. $\Lambda_M = 89.7 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. Anal. Calcd for C₂₁H₃₆N₂BF₄O₉P₂Re (**3a**): C, 31.71; H, 4.56; N, 3.52. Found: C, 31.54; H, 4.64; N, 3.45. $\Lambda_M = 92.2 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. Anal. Calcd for C₂₉H₃₆N₂BF₄O₇P₂Re (**4a**): C, 40.52; H, 4.22; N, 3.26. Found: C, 40.44; H, 4.15; N, 3.25. $\Lambda_M = 86.7 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. Anal. Calcd for C₃₇H₃₆N₂BF₄O₅P₂Re (**5a**): C, 48.11; H, 3.93; N, 3.03. Found: C, 47.98; H, 3.97; N, 3.13. $\Lambda_M = 85.9 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$.

[Re(C₆H₅N=¹⁵NH)(CO)₃][PPh(OEt)₂]₂]BF₄ (**4a***) and [Re(C₆H₅¹⁵N=NH)(CO)₃][PPh(OEt)₂]₂]BF₄ (**4a****). These complexes were prepared exactly like the related compound **4a** using labeled [C₆H₅N=¹⁵N]BF₄ and [C₆H₅¹⁵N=NH]BF₄ diazonium salts, respectively; yield ≥ 65%.

[[Re(CO)[P(OEt)₃]₄]₂(μ -HN=NAr-ArN=NH)](BPh₄)₂ (**6b**, **6d**), [[Re(CO)₂P₃]₂(μ -HN=NAr-ArN=NH)](BPh₄)₂ (**7b**, **7d**, **8b**) [P = PPh(OEt)₂ (**7**), PPh₂OEt (**8**)], [[Re(CO)₃P₂]₂(μ -HN=NAr-ArN=NH)](BPh₄)₂ (**10c**, **11d**) [P = PPh(OEt)₂ (**10**), PPh₂OEt (**11**)], and [[Re(CO)₄(PPh₂OEt)₂]₂(μ -HN=NAr-ArN=NH)](BPh₄)₂ [Ar-Ar = 4,4'-C₆H₄-C₆H₄ (**b**), 4,4'-(2-CH₃)C₆H₃-C₆H₃(2-CH₃) (**c**), 4,4'-C₆H₄-CH₂-C₆H₄ (**d**)]. The appropriate hydride ReH(CO)_{5-n}P_n (*n* = 4, 3, 2, 1) (0.3 mmol) and bis(aryldiazonium) salt [N₂Ar-ArN₂](BF₄)₂ (0.15 mmol) were placed in a 25-mL three-necked flask, and the mixture was cooled to -196 °C, after which 10 mL of acetone was added. The reaction mixture was brought to room temperature and stirred for 4 h, and the solvent was then removed under reduced pressure. The resulting oil was triturated with 2 mL of ethanol, giving a yellow solution, from which the complex was precipitated by adding a slight excess of NaBPh₄ (0.4 mmol, 137 mg) in 1 mL of ethanol. After crystallization from CH₂Cl₂/ethanol/diethyl ether (1/3/5 mL), the complex was filtered off and dried under vacuum; the yields were between 60 and 80%. Anal. Calcd for C₁₁₀H₁₇₀N₄B₂O₂₆P₈Re₂ (**6b**): C, 50.69; H, 6.57; N, 2.15. Found: C, 50.56; H, 6.65; N, 2.20. $\Lambda_M = 114.5 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. Anal. Calcd for C₁₁₁H₁₇₂N₄B₂O₂₆P₈Re₂ (**6d**): C, 50.88; H, 6.62; N, 2.14. Found: C, 51.03; H, 6.74; N, 2.07. $\Lambda_M = 107.0 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. Anal. Calcd for C₁₂₄H₁₄₀N₄B₂O₁₆P₆Re₂ (**7b**): C, 59.05; H, 5.59; N, 2.22. Found: C, 59.22; H, 5.55; N, 2.16. $\Lambda_M = 105.6 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. Anal. Calcd for C₁₂₅H₁₄₂N₄B₂O₁₆P₆Re₂ (**7d**): C, 59.19; H, 5.64; N, 2.21. Found: C, 59.25; H, 5.71; N, 2.09. $\Lambda_M = 109.1 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. Anal. Calcd for C₁₄₈H₁₄₀N₄B₂O₁₀P₆Re₂ (**8b**): C, 65.48; H, 5.20; N, 2.06. Found: C, 65.60; H, 5.12; N, 1.96. $\Lambda_M = 104.8 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. Anal. Calcd for C₁₀₈H₁₁₄N₄B₂O₁₄P₄Re₂ (**10c**): C, 58.70; H, 5.20; N, 2.54. Found: C, 58.81; H, 5.23; N, 2.41. $\Lambda_M = 113.3 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. Anal. Calcd for C₁₂₃H₁₁₂N₄B₂O₁₀P₄Re₂ (**11d**): C, 63.56; H, 4.86; N, 2.41. Found: C, 63.41; H, 4.99; N, 2.40. $\Lambda_M = 103.6 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. Anal. Calcd for C₉₆H₈₀N₄B₂O₁₀P₂Re₂ (**12b**): C, 60.51; H, 4.23; N, 2.94. Found: C, 61.88; H, 4.11; N, 2.49. $\Lambda_M = 106.4 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$.

[[Re(CO)₃P₂]₂(μ -HN=NAr-ArN=NH)](BF₄)₂ (**9b**, **10b**, **10d**, **11b**, **11c**) [P = P(OEt)₃ (**9**), PPh(OEt)₂ (**10**), PPh₂OEt (**11**); Ar-Ar =

4,4'-C₆H₄-C₆H₄ (**b**), 4,4'-(2-CH₃)C₆H₃-C₆H₃(2-CH₃) (**c**), 4,4'-C₆H₄-CH₂-C₆H₄ (**d**)]. These complexes were prepared like the related BPh₄ derivatives **10** and **11** by reacting the appropriate hydride ReH(CO)₃P₂ (0.3 mmol) and [N₂Ar-ArN₂](BF₄)₂ salt at low temperature (-196 °C) in acetone solution (10 mL). The reaction mixture, evaporated to dryness under reduced pressure, gave an oil, which was triturated with ethanol (2 mL). In this case, a yellow solid slowly appeared in the resulting solution. This was filtered off and crystallized by cooling to -25 °C a saturated solution in ethanol prepared at 30 °C; yield ≥ 70%. Anal. Calcd for C₄₂H₇₀N₄B₂F₈O₁₈P₄Re₂ (**9b**): C, 31.75; H, 4.44; N, 3.53. Found: C, 31.98; H, 4.51; N, 3.48. $\Lambda_M = 186.2 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. Anal. Calcd for C₅₈H₇₀N₄B₂F₈O₁₄P₄Re₂ (**10b**): C, 40.57; H, 4.11; N, 3.26. Found: C, 40.72; H, 4.19; N, 3.25. $\Lambda_M = 177.1 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. Anal. Calcd for C₅₉H₇₂N₄B₂F₈O₁₄P₄Re₂ (**10d**): C, 40.94; H, 4.19; N, 3.24. Found: C, 40.82; H, 4.28; N, 3.18. $\Lambda_M = 160.7 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. Anal. Calcd for C₇₄H₇₀N₄B₂F₈O₁₀P₄Re₂ (**11b**): C, 48.17; H, 3.82; N, 3.04. Found: C, 48.09; H, 3.90; N, 3.11. $\Lambda_M = 186.4 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. Anal. Calcd for C₇₆H₇₄N₄B₂F₈O₁₀P₄Re₂ (**11c**): C, 48.73; H, 3.98; N, 2.99. Found: C, 48.61; H, 4.05; N, 3.04. $\Lambda_M = 180.7 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$.

[[Re(CO)₂(PPh₂OEt)₃]₂(μ -4,4'-H¹⁵N=NC₆H₄-C₆H₄N=¹⁵NH)](BPh₄)₂ (**8b***) and [[Re(CO)₃(PPh(OEt)₂)₂]₂(μ -4,4'-H¹⁵N=NC₆H₄-C₆H₄N=¹⁵NH)](BF₄)₂ (**11b***). These complexes were prepared by following the method described for the related compounds **8b** and **11b** using the labeled [4,4'-¹⁵N=NC₆H₄-C₆H₄N=¹⁵N]BF₄ bis(diazonium) salt; yield ≥ 75%.

ReH(CO)₃(PPh₃)₂. In a 25-mL three-necked Pyrex Schlenk flask were placed 0.3 mL (2.1 mmol) of ReH(CO)₅, an excess of PPh₃ (5.9 mmol, 1.6 g), and 25 mL of toluene, and the resulting solution was irradiated at room temperature for 6 h using a standard 400 W medium-pressure mercury arc lamp. A white solid began to precipitate during irradiation, and after concentration of the reaction mixture to 10 mL, this solid was filtered off, washed with toluene, and dried under vacuum; yield ≥ 30%. Anal. Calcd for C₃₉H₃₁O₃P₂Re: C, 58.86; H, 3.93. Found: C, 58.67; H, 4.12. IR (KBr): 2080 m, 1914 br [$\nu(\text{CO})$] cm⁻¹. ¹H NMR (C₆D₆, 25 °C): δ 7.90-6.90 (m, 30 H, Ph), -4.45 (t, 1 H, hydride, $J_{\text{PH}} = 18$ Hz). ³¹P{¹H} NMR (C₆D₆, 25 °C): δ 22.54 (s).

[Re(CO)₃P₂(HN=NAr-ArN=N)](BF₄)₂ (**13b**, **13d**, **14b**, **15b**) [P = PPh₂OEt (**13**), PPh₂OMe (**14**), PPh₃ (**15**); Ar-Ar = 4,4'-C₆H₄-C₆H₄ (**b**), 4,4'-C₆H₄-CH₂-C₆H₄ (**d**)] and [Re(CO)₄(PPh₂OEt)(4,4'-HN=NC₆H₄-C₆H₄N=N)](BF₄)₂ (**16b**). A solution of the appropriate hydride ReH(CO)₃P₂ or ReH(CO)₄P (0.3 mmol) in 40 mL of acetone was cooled to -80 °C and quickly transferred by needle into a solution of an [N₂Ar-ArN₂](BF₄)₂ bis(aryldiazonium) salt (0.3 mmol) in 30 mL of acetone cooled to -196 °C. The reaction mixture was brought to 0 °C and stirred for 5 h. The solvent was removed under reduced pressure, giving an oil which was rather difficult to transform into a solid. However, after crystallization of the oil from CH₂Cl₂/ethanol (2/5 mL), solid products were obtained in the case of compounds **13** and **15**. These were filtered off and dried under vacuum. Gummy orange products were obtained for compounds **14** and **16**, which were also characterized and used for further reactions. The yields were between 60 and 80%. Anal. Calcd for C₄₃H₃₉N₄B₂F₈O₅P₂Re (**13b**): C, 46.38; H, 3.53; N, 5.03. Found: C, 46.46; H, 3.60; N, 5.12. $\Lambda_M = 184.7 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. Anal. Calcd for C₄₄H₄₁N₄B₂F₈O₅P₂Re (**13d**): C, 46.87; H, 3.66; N, 4.97. Found: C, 46.71; H, 3.68; N, 5.11. $\Lambda_M = 191.4 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. Anal. Calcd for C₄₁H₃₅N₄B₂F₈O₅P₂Re (**14b**): C, 45.37; H, 3.25; N, 5.16. Found: C, 45.59; H, 3.34; N, 5.25. $\Lambda_M = 185.6 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. Anal. Calcd for C₅₁H₃₉N₄B₂F₈O₅P₂Re (**15b**): C, 52.02; H, 3.34; N, 4.76. Found: C, 52.16; H, 3.46; N, 4.88. $\Lambda_M = 182.9 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. Anal. Calcd for C₃₀H₂₄N₄B₂F₈O₃PRe (**16b**): C, 39.54; H, 2.65; N, 6.15. Found: C, 39.35; H, 2.69; N, 6.30. $\Lambda_M = 188.4 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$.

[Re(CO)₃(PPh₂OEt)₂(4,4'-H¹⁵N=NC₆H₄-C₆H₄N=¹⁵N)](BF₄)₂ (**13b***) and [Re(CO)₃(PPh₃)₂(4,4'-H¹⁵N=NC₆H₄-C₆H₄N=¹⁵N)](BF₄)₂ (**15b***). These complexes were prepared exactly like the related compounds **13b** and **15b** using the labeled [4,4'-¹⁵N=NC₆H₄-C₆H₄N=¹⁵N]BF₄ bis(diazonium) salt; yield ≥ 70%.

[Mn(CO)₃(PPh₂OEt)₂(4,4'-HN=NC₆H₄-C₆H₄N=N)](BF₄)₂ (**17b**). This compound was prepared by following the method used for the related rhenium complex **13b** by reacting MnH(CO)₅(PPh₂OEt)₂ (0.34 mmol, 200 mg) with [4,4'-N₂C₆H₄-C₆H₄N₂](BF₄)₂ (0.34 mmol, 127

mg) in acetone at $-196\text{ }^{\circ}\text{C}$. After crystallization from CH_2Cl_2 /ethanol (2/6 mL), the yield of the gummy orange product was about 75%. Anal. Calcd for $\text{C}_{43}\text{H}_{39}\text{N}_4\text{B}_2\text{F}_8\text{MnO}_5\text{P}_2$: C, 52.58; H, 4.00; N, 5.70. Found: C, 52.75; H, 3.88; N, 5.86. $\Lambda_M = 179.5\ \Omega^{-1}\ \text{mol}^{-1}\ \text{cm}^2$.

[Mn(CO)₃(PPh₂OEt)₂(μ -4,4'-H¹⁵N=NC₆H₄-C₆H₄N¹⁵N)](BF₄)₂ (17b*). This compound was prepared exactly like **17b** using the labeled [$4,4'$ -¹⁵N=NC₆H₄-C₆H₄N¹⁵N](BF₄)₂ salt; yield $\geq 75\%$.

[Re(CO)₃P₂(μ -HN=NAr-ArN=NH)RuHP'₄](BPh₄)₂ (Re₁₃Ru-b, Re₁₃Ru-d, Re₁₄Ru-b) [P = PPh₂OEt (Re₁₃), PPh₂OMe (Re₁₄); P' = P(OEt)₃; Ar-Ar = 4,4'-C₆H₄-C₆H₄ (b), 4,4'-C₆H₄-CH₂-C₆H₄ (d)] and [Re(CO)₄(PPh₂OEt)(μ -4,4'-HN=NC₆H₄-C₆H₄N=NH)RuH-{P(OEt)₃]₄(BPh₄)₂ (Re₁₆Ru-b). The hydride $\text{RuH}_2[\text{P}(\text{OEt})_3]_4$ (0.13 mmol, 0.10 g) and the appropriate diazene-diazonium complex $[\text{Re}(\text{CO})_{5-n}\text{P}_n(\text{HN}=\text{NAr}-\text{ArN}=\text{N})](\text{BF}_4)_2$ (**13**, **14**, **16**) (0.13 mmol) were placed in a 25-mL three-necked flask and cooled to $-196\text{ }^{\circ}\text{C}$, after which 10 mL of acetone was added. The reaction mixture was brought to room temperature and stirred for about 2 h, and the solvent was then removed under reduced pressure. The resulting oil was treated with ethanol (5 mL) containing an excess of NaBPh₄ (0.52 mmol, 178 mg), giving a red solid, which was filtered off and crystallized from a mixture of CH_2Cl_2 (2 mL) and ethanol (7 mL); yield $\geq 70\%$. Anal. Calcd for $\text{C}_{115}\text{H}_{141}\text{N}_4\text{B}_2\text{O}_{17}\text{P}_6\text{ReRu}$ (**Re₁₃Ru-b**): C, 58.87; H, 6.06; N, 2.39. Found: C, 58.99; H, 6.12; N, 2.50. $\Lambda_M = 100.6\ \Omega^{-1}\ \text{mol}^{-1}\ \text{cm}^2$. Anal. Calcd for $\text{C}_{116}\text{H}_{143}\text{N}_4\text{B}_2\text{O}_{17}\text{P}_6\text{ReRu}$ (**Re₁₃Ru-d**): C, 59.03; H, 6.11; N, 2.37. Found: C, 58.88; H, 6.20; N, 2.37. $\Lambda_M = 97.8\ \Omega^{-1}\ \text{mol}^{-1}\ \text{cm}^2$. Anal. Calcd for $\text{C}_{113}\text{H}_{137}\text{N}_4\text{B}_2\text{O}_{17}\text{P}_6\text{ReRu}$ (**Re₁₄Ru-b**): C, 58.55; H, 5.96; N, 2.42. Found: C, 58.76; H, 6.04; N, 2.34. $\Lambda_M = 103.1\ \Omega^{-1}\ \text{mol}^{-1}\ \text{cm}^2$. Anal. Calcd for $\text{C}_{102}\text{H}_{126}\text{N}_4\text{B}_2\text{O}_{17}\text{P}_5\text{ReRu}$ (**Re₁₆Ru-b**): C, 57.14; H, 5.92; N, 2.61. Found: C, 57.29; H, 5.98; N, 2.70. $\Lambda_M = 100.1\ \Omega^{-1}\ \text{mol}^{-1}\ \text{cm}^2$.

[Re(CO)₃(PPh₂OEt)₂(μ -4,4'-H¹⁵N=NC₆H₄-C₆H₄N¹⁵NH)-RuH{P(OEt)₃]₄(BPh₄)₂ (Re₁₃Ru-b*). This compound was prepared like the related compound **Re₁₃Ru-b** using the labeled $[\text{Re}(\text{CO})_3(\text{PPh}_2\text{OEt})_2(\text{H}^{15}\text{N}=\text{NC}_6\text{H}_4-\text{C}_6\text{H}_4\text{N}^{15}\text{N})](\text{BF}_4)_2$ derivative; yield $\geq 70\%$.

[Mn(CO)₃(PPh₂OEt)₂(μ -4,4'-HN=NC₆H₄-C₆H₄N=NH)RuH-{P(OEt)₃]₄(BPh₄)₂ (Mn₁₇Ru-b). The complex was prepared like the related complex **Re₁₃Ru-b** by reacting RuH_2P_4 with $[\text{Mn}(\text{CO})_3(\text{PPh}_2\text{OEt})_2(\mu-4,4'\text{-HN}=\text{NC}_6\text{H}_4-\text{C}_6\text{H}_4\text{N}=\text{N})](\text{BF}_4)_2$ (**17b**) in acetone at $-196\text{ }^{\circ}\text{C}$; yield $\geq 65\%$. Anal. Calcd for $\text{C}_{115}\text{H}_{141}\text{N}_4\text{B}_2\text{MnO}_{17}\text{P}_6\text{Ru}$: C, 62.36; H, 6.42; N, 2.53. Found: C, 62.55; H, 6.55; N, 2.41. $\Lambda_M = 107.5\ \Omega^{-1}\ \text{mol}^{-1}\ \text{cm}^2$.

[Re(CO)₃(PPh₂OEt)₂(μ -4,4'-HN=NC₆H₄-C₆H₄N=NH)OsHP'₄]- (BPh₄)₂ (Re₁₃Os-b, Re₁₃Os-b) [P' = P(OEt)₃ (Os), PPh(OEt)₂ (Os₁)] and **[Mn(CO)₃(PPh₂OEt)₂(μ -4,4'-HN=NC₆H₄-C₆H₄N=NH)OsH-{P(OEt)₃]₄(BPh₄)₂ (Mn₁₇Os-b). These heterobinuclear complexes were prepared like the related complex **Re₁₃Ru** by reacting the hydride OsH_2P_4 with the appropriate diazene-diazonium $[\text{M}(\text{CO})_3\text{P}_2(\mu-4,4'\text{-HN}=\text{NC}_6\text{H}_4-\text{C}_6\text{H}_4\text{N}=\text{N})](\text{BF}_4)_2$ (M = Re, Mn) derivatives; yield $\geq 65\%$. Anal. Calcd for $\text{C}_{115}\text{H}_{141}\text{N}_4\text{B}_2\text{O}_{17}\text{OsP}_6\text{Re}$ (**Re₁₃Os-b**): C, 56.72; H, 5.84; N, 2.30. Found: C, 56.65; H, 5.95; N, 2.24. $\Lambda_M = 104.3\ \Omega^{-1}\ \text{mol}^{-1}\ \text{cm}^2$. Anal. Calcd for $\text{C}_{131}\text{H}_{141}\text{N}_4\text{B}_2\text{O}_{15}\text{OsP}_6\text{Re}$ (**Re₁₃Os₁-b**): C, 61.38; H, 5.54; N, 2.19. Found: C, 61.57; H, 5.68; N, 2.27. $\Lambda_M = 102.8\ \Omega^{-1}\ \text{mol}^{-1}\ \text{cm}^2$. Anal. Calcd for $\text{C}_{115}\text{H}_{141}\text{N}_4\text{B}_2\text{MnO}_{17}\text{OsP}_6$ (**Mn₁₇Os-b**): C, 59.95; H, 6.17; N, 2.43. Found: C, 60.12; H, 6.28; N, 2.35. $\Lambda_M = 99.6\ \Omega^{-1}\ \text{mol}^{-1}\ \text{cm}^2$.**

[Re(CO)₃P₂(μ -4,4'-HN=NC₆H₄-C₆H₄N=NH)Mn(CO)₃P'₂]- (BPh₄)₂ (Re₁₃Mn-b, Re₁₅Mn-b) [P = PPh₂OEt (Re₁₃), PPh₃ (Re₁₅); P' = PPh(OEt)₂]. These complexes were prepared according to the general method, by reacting the hydride $\text{MnH}(\text{CO})_3\text{P}'_2$ with the appropriate $[\text{Re}(\text{CO})_3\text{P}_2(\mu-4,4'\text{-HN}=\text{NC}_6\text{H}_4-\text{C}_6\text{H}_4\text{N}=\text{N})](\text{BF}_4)_2$ complexes in acetone; yield $\geq 70\%$. Anal. Calcd for $\text{C}_{114}\text{H}_{110}\text{N}_4\text{B}_2\text{MnO}_{12}\text{P}_4\text{Re}$ (Re₁₃Mn-b**): C, 64.75; H, 5.24; N, 2.65. Found: C, 64.93; H, 5.38; N, 2.57. $\Lambda_M = 112.5\ \Omega^{-1}\ \text{mol}^{-1}\ \text{cm}^2$. Anal. Calcd for $\text{C}_{122}\text{H}_{110}\text{N}_4\text{B}_2\text{MnO}_{10}\text{P}_4\text{Re}$ (**Re₁₅Mn-b**): C, 67.25; H, 5.09; N, 2.57. Found: C, 67.33; H, 5.12; N, 2.67. $\Lambda_M = 108.7\ \Omega^{-1}\ \text{mol}^{-1}\ \text{cm}^2$.**

[Mn(CO)₃(PPh₂OEt)₂(μ -4,4'-HN=NC₆H₄-C₆H₄N=NH)Re(CO)-{P(OEt)₃]₄(BPh₄)₂ (Mn₁₇Re-b) and [Mn(CO)₃(PPh₂OEt)₂(μ -4,4'-H¹⁵N=NC₆H₄-C₆H₄N¹⁵NH)Re(CO){P(OEt)₃]₄(BPh₄)₂ (Mn₁₇Re-b*). These complexes were also prepared according to the general method, by reacting $\text{ReH}(\text{CO})[\text{P}(\text{OEt})_3]_4$ with the unlabeled and labeled diazene-diazonium $[\text{Mn}(\text{CO})_3(\text{PPh}_2\text{OEt})_2(\mu-4,4'\text{-HN}=\text{NC}_6\text{H}_4-\text{C}_6\text{H}_4\text{N}=\text{N})]$

$[\text{N}]^{2+}$ cations; yield $\geq 80\%$. Anal. Calcd for $\text{C}_{116}\text{H}_{140}\text{N}_4\text{B}_2\text{MnO}_{18}\text{P}_5\text{Re}$ (**Mn₁₇Re-b**): C, 59.87; H, 6.06; N, 2.41. Found: C, 59.77; H, 6.15; N, 2.48. $\Lambda_M = 103.2\ \Omega^{-1}\ \text{mol}^{-1}\ \text{cm}^2$.

[Re(CO)₃(PPh₂OEt)₂(μ -4,4'-HN=NC₆H₄-C₆H₄N=NH)FeH-{P(OEt)₃]₄(BPh₄)₂ (Re₁₃Fe-b). A solution of $[\text{Re}(\text{CO})_3(\text{PPh}_2\text{OEt})_2(\mu-4,4'\text{-HN}=\text{NC}_6\text{H}_4-\text{C}_6\text{H}_4\text{N}=\text{N})](\text{BF}_4)_2$ (0.277 mmol, 308 mg) in 10 mL of CH_2Cl_2 was cooled to $-80\text{ }^{\circ}\text{C}$ and quickly transferred by needle into a 25-mL three-necked flask containing 200 mg (0.277 mmol) of $\text{FeH}_2[\text{P}(\text{OEt})_3]_4$ cooled to $-196\text{ }^{\circ}\text{C}$. The reaction mixture was brought to room temperature and stirred for 4 h, and the solvent was then removed under reduced pressure. The resulting oil was triturated with 3 mL of ethanol, giving a red-brown solution, from which the complex was precipitated by adding an excess of NaBPh₄ (1 mmol, 342 mg) in 2 mL of ethanol. After crystallization from a mixture of CH_2Cl_2 (2 mL) and ethanol (5 mL), the complex was filtered off and dried under vacuum; yield $\geq 60\%$. Anal. Calcd for $\text{C}_{115}\text{H}_{141}\text{N}_4\text{B}_2\text{FeO}_{17}\text{P}_6\text{Re}$: C, 60.03; H, 6.18; N, 2.43. Found: C, 60.20; H, 6.24; N, 2.35. $\Lambda_M = 104.1\ \Omega^{-1}\ \text{mol}^{-1}\ \text{cm}^2$.

[Re(CO)₃(PPh₂OEt)₂(μ -4,4'-HN=NC₆H₄-C₆H₄N=NH)Ru-{P(OEt)₃]₄(μ -4,4'-HN=NC₆H₄-C₆H₄N=NH)Mn(CO)₃(PPh₂OEt)₂]- (BPh₄)₄ (Re₁₃RuMn₁₇). A solution of the diazene-diazonium complex $[\text{Mn}(\text{CO})_3(\text{PPh}_2\text{OEt})_2(\mu-4,4'\text{-HN}=\text{NC}_6\text{H}_4-\text{C}_6\text{H}_4\text{N}=\text{N})](\text{BF}_4)_2$ (**17b**) (0.25 mmol, 254 mg) in 10 mL of acetone was cooled to $-80\text{ }^{\circ}\text{C}$ and quickly transferred into a 25-mL three-necked flask containing $[\text{Re}(\text{CO})_3(\text{PPh}_2\text{OEt})_2(\mu-4,4'\text{-HN}=\text{NC}_6\text{H}_4-\text{C}_6\text{H}_4\text{N}=\text{NH})\text{RuH}\{[\text{P}(\text{OEt})_3]_4\}(\text{BPh}_4)_2$ (**Re₁₃Ru-b**) (0.25 mmol, 586 mg) in 10 mL of acetone cooled to $-80\text{ }^{\circ}\text{C}$. The reaction mixture was brought to room temperature and stirred for 8 h, and the solvent was then removed under reduced pressure. The resulting oil was triturated with ethanol (5 mL) containing an excess of NaBPh₄ (0.50 mmol, 170 mg), affording a red-brown solid, which was filtered off and crystallized from a mixture of CH_2Cl_2 (2 mL) and ethanol (7 mL); yield $\geq 60\%$. Anal. Calcd for $\text{C}_{206}\text{H}_{220}\text{N}_8\text{B}_4\text{MnO}_{22}\text{P}_8\text{ReRu}$: C, 65.23; H, 5.85; N, 2.95. Found: C, 65.39; H, 5.96; N, 2.87. $\Lambda_M = 244\ \Omega^{-1}\ \text{mol}^{-1}\ \text{cm}^2$.

[Re(CO)₃(PPh₂OEt)₂(μ -4,4'-HN=NC₆H₄-C₆H₄N=NH)Os-{P(OEt)₃]₄(μ -4,4'-HN=NC₆H₄-C₆H₄N=NH)Mn(CO)₃(PPh₂OEt)₂]- (BPh₄)₄ (Re₁₃OsMn₁₇). This compound was prepared like the related trinuclear **Re₁₃RuMn₁₇** complex; yield $\geq 45\%$. Anal. Calcd for $\text{C}_{206}\text{H}_{220}\text{N}_8\text{B}_4\text{MnO}_{22}\text{OsP}_8\text{Re}$: C, 63.73; H, 5.71; N, 2.89. Found: C, 63.89; H, 5.83; N, 2.84. $\Lambda_M = 235\ \Omega^{-1}\ \text{mol}^{-1}\ \text{cm}^2$.

[Mn(CO)₃(PPh₂OEt)₂(μ -4,4'-HN=NC₆H₄-C₆H₄N=NH)Fe(4-CH₃C₆H₄CN){P(OEt)₃]₄(BPh₄)₃ (Mn₁₇Fe₁-b). In a 25-mL three-necked flask were placed the hydride $[\text{FeH}(4\text{-CH}_3\text{C}_6\text{H}_4\text{CN})\{[\text{P}(\text{OEt})_3]_4\}]\text{-BPh}_4$ (0.2 mmol, 230 mg) and the diazene-diazonium complex $[\text{Mn}(\text{CO})_3(\text{PPh}_2\text{OEt})_2(\mu-4,4'\text{-HN}=\text{NC}_6\text{H}_4-\text{C}_6\text{H}_4\text{N}=\text{N})](\text{BF}_4)_2$ (**17b**) (0.2 mmol, 196 mg), and the mixture was cooled to $-196\text{ }^{\circ}\text{C}$, after which 10 mL of acetone was added. The reaction mixture was brought to room temperature and stirred for about 5 h, and the solvent was then removed under reduced pressure. The resulting oil was triturated with ethanol (5 mL) containing an excess of NaBPh₄ (0.4 mmol, 137 mg). A yellow solid slowly precipitated. This was filtered off and crystallized from a mixture of CH_2Cl_2 (2 mL) and ethanol (5 mL); yield $\geq 60\%$. Anal. Calcd for $\text{C}_{147}\text{H}_{167}\text{N}_3\text{B}_3\text{FeMnO}_{17}\text{P}_6$: C, 67.78; H, 6.46; N, 2.69. Found: C, 67.63; H, 6.55; N, 2.60. $\Lambda_M = 181.8\ \Omega^{-1}\ \text{mol}^{-1}\ \text{cm}^2$.

[Mn(CO)₃(PPh₂OEt)₂(μ -4,4'-H¹⁵N=NC₆H₄-C₆H₄N¹⁵NH)Fe(4-CH₃C₆H₄CN){P(OEt)₃]₄(BPh₄)₃ (Mn₁₇Fe₁-b*). This compound was prepared exactly like the related unlabeled complex **Mn₁₇Fe₁-b** starting from the labeled $[\text{Mn}(\text{CO})_3(\text{PPh}_2\text{OEt})_2(\mu-4,4'\text{-H}^{15}\text{N}=\text{NC}_6\text{H}_4-\text{C}_6\text{H}_4\text{N}=\text{N})](\text{BF}_4)_2$ (**17b***) complex; yield $\geq 60\%$.

[Mn(CO)₂(PPh₂OEt)₂(μ -4,4'-N₂C₆H₄-C₆H₄N₂)Fe{P(OEt)₃]₄-BPh₄ (MnFe-b). An excess of NEt_3 (0.5 mmol, 69 μL) was added to a solution of $[\text{Mn}(\text{CO})_3(\text{PPh}_2\text{OEt})_2(\mu-4,4'\text{-HN}=\text{NC}_6\text{H}_4-\text{C}_6\text{H}_4\text{N}=\text{NH})\text{-Fe}(4\text{-CH}_3\text{C}_6\text{H}_4\text{CN})\{[\text{P}(\text{OEt})_3]_4\}(\text{BPh}_4)_3$ (**Mn₁₇Fe₁-b**) (0.1 mmol, 260 mg) in 5 mL of CH_2Cl_2 , and the reaction mixture was stirred for about 50 min. After filtration to remove the $[\text{NHEt}_3]\text{BPh}_4$ salt, the solution was evaporated to dryness and the resulting oil triturated with 2 mL of ethanol. The red-brown solid that slowly formed was filtered off and crystallized from a mixture of CH_2Cl_2 (2 mL) and ethanol (5 mL); yield $\geq 60\%$. Anal. Calcd for $\text{C}_{90}\text{H}_{118}\text{N}_4\text{BFeMnO}_{16}\text{P}_6$: C, 59.42; H, 6.54; N, 3.08. Found: C, 59.56; H, 6.64; N, 3.00. $\Lambda_M = 52.6\ \Omega^{-1}\ \text{mol}^{-1}\ \text{cm}^2$.

Table 1. Crystal Data and Structure Refinement Details for [Re(C₆H₅N=NH)(CO){P(OEt)₃}₄]BPh₄ (**1a**)

empirical formula	C ₅₅ H ₈₆ BN ₂ O ₁₃ P ₄ Re
fw	1304.15
temp (°C)	20(2)
wavelength (Å)	0.710 69
crystal system, space group	triclinic, <i>P</i> $\bar{1}$
unit cell dimensions (Å; deg)	<i>a</i> = 15.380(5), <i>b</i> = 13.037(5), <i>c</i> = 16.649(5), α = 90.33(5), β = 91.2(1), γ = 89.71(9)
volume (Å ³)	3337(2)
Z, calcd density (g/cm ³)	2, 1.298
abs coeff (cm ⁻¹)	19.71
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] ^a	<i>R</i> 1 = 0.0384, <i>wR</i> 2 = 0.0811
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0970, <i>wR</i> 2 = 0.0970

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}; w = 1 / \{ \sigma^2(F_o^2) + [0.17(2F_c^2 + F_o^2)/3] \}.$$

[Mn(CO)₂(PPh₂OEt)₂(μ -4,4'-¹⁵N≡NC₆H₄-C₆H₄N≡¹⁵N)Fe-**P(OEt)₃}_4]BPh₄ (MnFe-b^{*}). This compound was prepared exactly like the related unlabeled complex MnFe-b by deprotonation with NEt₃ of the labeled [Mn(CO)₂(PPh₂OEt)₂(μ -4,4'-H¹⁵N≡NC₆H₄-C₆H₄N≡¹⁵N)Fe(4-CH₃C₆H₄CN){P(OEt)₃}_4](BPh₄)₃ (Mn₁₇Fe₁-b^{*}) derivative; yield \geq 60%.**

[Re(CO)₃(PPh₂OEt)₂(μ -4,4'-HN=NC₆H₄-C₆H₄N=N)Fe(CO)₂-**P(OEt)₃}_2](BPh₄)₂ (Re₁₃Fe₂). A solution of [Re(CO)₃(PPh₂OEt)₂(4,4'-HN=NC₆H₄-C₆H₄N=N)](BF₄)₂ (0.277 mmol, 308 mg) in 10 mL of acetone was cooled to -80 °C and quickly transferred by a cannula into a 25-mL three-necked flask containing 203 mg (0.277 mmol) of FeH₂(CO)₂[P(OEt)₃]₂ cooled to -196 °C. The reaction mixture was brought to room temperature and stirred for about 20 h, and the solvent was then removed under reduced pressure. The resulting oil was triturated with 3 mL of ethanol, giving a red-brown solution, from which the complex was precipitated by adding an excess of NaBPh₄ (0.8 mmol, 274 mg) in 2 mL of ethanol. After crystallization from a mixture of CH₂Cl₂ (2 mL) and ethanol (5 mL), the gummy solid obtained was filtered off and dried under vacuum; yield \geq 55%. Anal. Calcd for C₁₂₉H₁₀₉N₄B₂FeO₁₃P₄Re: C, 67.05; H, 4.75; N, 2.42. Found: C, 67.31; H, 4.73; N, 2.34. $\Lambda_M = 105.1 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$.**

X-ray Structure Determination of [Re(C₆H₅N=NH)(CO){P(OEt)₃}_4]BPh₄ (1a**).** Suitable crystals for X-ray analysis were obtained by recrystallization from ethanol. The data were collected at room temperature on a Philips PW 1100 diffractometer using graphite-monochromatized Mo K α radiation. Despite the values of the angles, all near 90°, a cell reduction program failed to show the presence of a higher symmetry, and the choice of the triclinic centric space group *P* $\bar{1}$ was justified by the intensity distribution statistics and the satisfactory refinement of the structure. No crystal decay was observed. Pertinent crystallographic parameters are summarized in Table 1. The data were processed with a peak-profile procedure and corrected for Lorentz and polarization as well as for absorption effects, using the ψ -scan method. A total of 19 477 reflections ($\pm h, \pm k, \pm l$) were measured by using the θ - 2θ scan technique to a maximum 2θ value of 60°.

The structure was solved by direct methods²¹ and refined by a full-matrix least-squares procedure on *F*² with SHELXL97.²² All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were inserted at calculated positions using a riding model, with the exception of the hydrogen belonging to the nitrogen in the phenyldiazene group, which was detected in a ΔF map and refined freely. Phenyl groups of the anion were refined as rigid bodies.

Neutral-atomic scattering factors were employed, and anomalous dispersion terms were included for non-hydrogen atoms. The refinement for 653 parameters converged with *R*1 = 0.0384 (for 10 297 observed data), *wR*2 = 0.0970, and GOF = 0.829. The final difference map

showed no significant features. All calculations were performed on a Digital Alpha 255 workstation at the Centro di Studio per la Strutturistica Diffraattometrica del CNR in Parma. The final geometry was analyzed with the program PARST97,²³ and the drawing of the structure was made with ZORTEP.²⁴

Electrochemical Apparatus and Procedures. Voltammetric experiments were carried out in a three-electrode cell. The working electrode was a glassy-carbon (area 0.2 cm²) or platinum disk (area 0.07 cm²), mirror-polished with graded alumina powder. The voltammetric patterns of the tested compounds showed similar characteristics on both Pt and glassy-carbon electrodes (apart from large peak current values, which are on scale with respect to electrode area). All data presented here were obtained using a glassy-carbon disk as the working electrode. The working electrode was surrounded by a platinum spiral counter electrode. The reference electrode (aqueous KCl-saturated Ag/AgCl) was placed in a Luggin capillary reference electrode compartment. All potentials are referred to this Ag/AgCl reference electrode. The *E*_{1/2} value for the ferrocene/ferrocenium (Fc/Fc⁺) couple, measured in the supporting electrolyte used in this work, (0.1 M tetrabutylammonium hexafluorophosphate, TBAH, in dichloroethane, DCE) was +0.520 V vs Ag/AgCl. The specific resistance of the electrolyte solution, measured with a Crison CM 2202 conductometer, was 1250 Ω cm. All measurements were carried out at room temperature under a nitrogen atmosphere. The voltammetric equipment used was an EG&G PAR Model 273 potentiostat controlled by a personal computer via M 270 software, using a positive feedback correction of uncompensated *IR* drops.

Digital simulations of experimental voltammograms were performed with Digisim 2.1 (Bas Inc.), a cyclic voltammetric simulation program, running on an HP 735/90 CPU Pentium computer. The voltammograms of the binuclear compounds were simulated by the following reaction sequence, where A is the starting binuclear compound:



The voltammograms of the relevant mononuclear compounds were simulated by a similar mechanism from which, however, reactions 3 and 4 were excluded. For all the compounds studied in this work, the fits between simulated and experimental data were optimized using the simulation parameters listed in Table 2. For digital simulation of the oxidation of mono- and binuclear Mn aryldiazene compounds, the following mechanism was adopted:



where A was always the starting complex; reaction 6 was excluded in the case of the mononuclear compound. The fits between simulated and experimental data were optimized by the simulation parameters listed in Table 3.

Although a positive feedback correction of the ohmic drop of the solution was used to obtain the experimental data, slightly better fits between experimental and simulated voltammograms were achieved by introducing a residual uncompensated resistance of 200 Ω in the simulations. A double-layer capacitance of 5×10^{-6} farad was employed.

Results and Discussion

Aryldiazene Complexes. The rhenium hydride complexes ReH(CO)_{5-n}P_n quickly react with both mono- and bis(aryldiazonium) cations to give the aryldiazene derivatives [Re-

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Table 2. Fitting Parameters Used in the Digital Simulations of the Reductions of Selected Aryldiazene Complexes^a

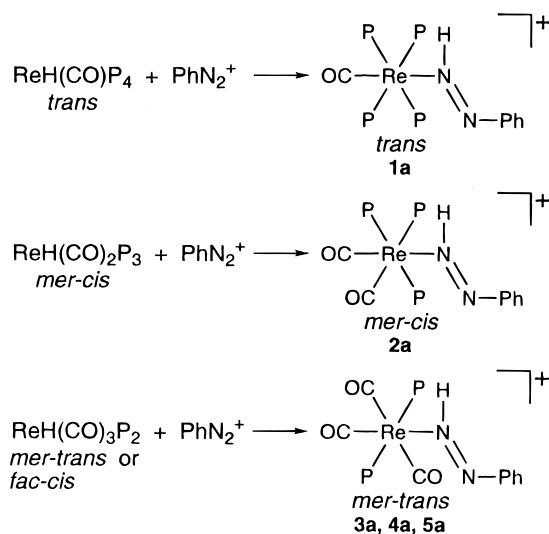
cmpd	$E^{\circ}(1)$ (V)	$\alpha(1)$	$k_s(1)$ (cm s^{-1})	$K_{\text{eq}}(2)$	$k_f(2)$ (s^{-1})	$E^{\circ}(3)$ (V)	$\alpha(3)$	$10^3 k_s(3)$ (cm s^{-1})	$K_{\text{eq}}(4)$	$k_f(4)$ (s^{-1})	$10^6 D(A)$ ($\text{cm}^2 \text{s}^{-1}$)	$10^6 D(B)$ ($\text{cm}^2 \text{s}^{-1}$)	$10^6 D(C)$ ($\text{cm}^2 \text{s}^{-1}$)	$10^6 D(D)$ ($\text{cm}^2 \text{s}^{-1}$)	$10^6 D(E)$ ($\text{cm}^2 \text{s}^{-1}$)
5a	-0.79	0.2	0.005	300	100						2.0	2.0	2.0		
11b	-0.70	0.37	0.017	30	400	-0.83	0.22	9	3×10^5	100	2.4	2.4	2.4	2.0	2.0
Re₁₃Ru-b	-0.66	0.2	0.002	500	100	-1.24	0.3	5	3×10^4	500	2.0	1.8	2.0	2.0	2.0
Mn₁	-0.89	0.2	0.0015	300	100						1.5	1.0	1.0		
Mn₂	-0.73	0.2	0.001	300	1	-0.95	0.2	1	3×10^4	150	1.0	1.0	1.0	1.0	1.0
Mn₁₇Ru-b	-0.85	0.2	0.0012	3×10^5	100	-1.24	0.3	3	3×10^4	500	1.2	1.8	8.0	8.0	8.0

^a α = transfer coefficient, k_s = standard heterogeneous rate constant, D = diffusion coefficient, and the other symbols have their usual meanings. **Mn₁** = $[\text{Mn}(\text{C}_6\text{H}_5\text{N}=\text{NH})(\text{CO})_3(\text{PPh}_2\text{OEt})_2]\text{BF}_4$; **Mn₂** = $\{[\text{Mn}(\text{CO})_3(\text{PPh}_2\text{OEt})_2]_2(\mu\text{-}4,4'\text{-HN}=\text{NC}_6\text{H}_4\text{-C}_6\text{H}_4\text{N}=\text{NH})\}(\text{BPh}_4)_2$.^{3b}

Table 3. Fitting Parameters Used in the Digital Simulations of the Oxidations of Aryldiazenido Compounds of Manganese

cmpd	$E^{\circ}(5)$ (V)	$\alpha(5)$	$10^4 k_s(5)$ (cm s^{-1})	$E^{\circ}(6)$ (V)	$\alpha(6)$	$10^4 k_s(6)$ (cm s^{-1})	$10^6 D(A)$ ($\text{cm}^2 \text{s}^{-1}$)	$10^6 D(B)$ ($\text{cm}^2 \text{s}^{-1}$)	$10^6 D(C)$ ($\text{cm}^2 \text{s}^{-1}$)
Mn₃	0.425	0.4	1.5				6.5	6.5	
Mn₄	0.44	0.35	1.5	0.48	0.35	2.0	5	5	5

^a **Mn₃** = $\text{Mn}(\text{C}_6\text{H}_5\text{N}_2)(\text{CO})_2(\text{PPh}_2\text{OEt})_2$; **Mn₄** = $\{\text{Mn}(\text{CO})_2(\text{PPh}_2\text{OEt})_2\}_2(\mu\text{-}4,4'\text{-N}_2\text{C}_6\text{H}_4\text{-C}_6\text{H}_4\text{N}_2)$.^{3b}

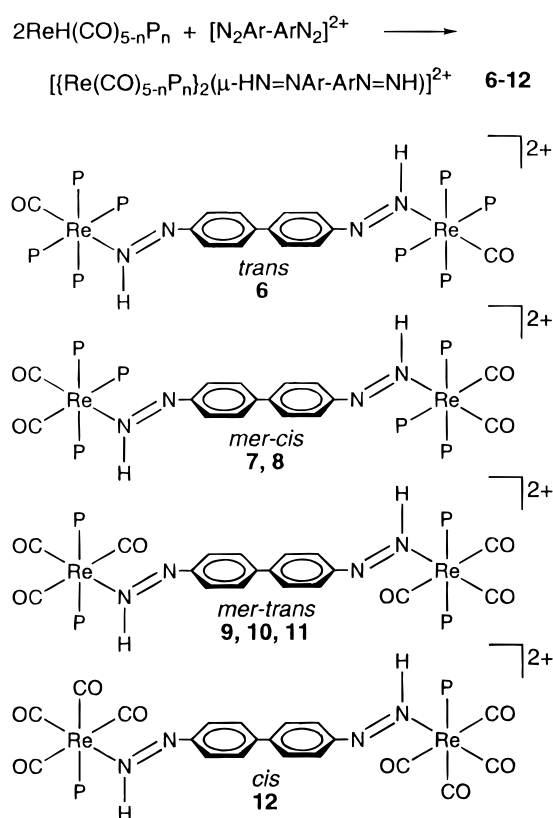
Scheme 1^a

^a P = P(OEt)₃ (**1**, **3**), PPh(OEt)₂ (**4**), PPh₂OEt (**2**, **5**).

$(\text{PhN}=\text{NH})(\text{CO})_{5-n}\text{P}_n$ (**1–5**) and $\{[\text{Re}(\text{CO})_{5-n}\text{P}_n]_2(\mu\text{-HN}=\text{NAr}-\text{ArN}=\text{NH})\}^{2+}$ (**6–12**), which were isolated as BF_4^- or BPh_4^- salts and characterized (Schemes 1 and 2).

An exact stoichiometric ratio between the reagents and the start of the reaction at low temperature seems to be crucial for successful synthesis of the aryldiazene derivatives. Otherwise, some decomposition products or oily substances were found in the final reaction products.

Good analytical data were obtained for all the aryldiazene complexes, which are yellow or orange solids and are stable in air and in solutions of polar organic solvents, where they behave as 1:1 or 2:1 electrolytes.²⁵ The IR and NMR data (Table 4) support the proposed formulations and allow geometries in solution to be established for all the complexes (Schemes 1 and 2). In particular, the presence of the diazene ligand was confirmed by the ¹H NMR spectra, which showed the characteristic NH proton signal as a broad resonance at 14.51–12.21 ppm. For the related labeled compounds **4a***, **4a****, **8b***, and **11b***, this signal was split into a sharp doublet with $^1J_{\text{NH}} = 62\text{--}66$ Hz and $^2J_{\text{NH}} = 3.5$ Hz, in agreement with the proposed formulations.^{1,2,26} The ¹⁵N NMR spectra of labeled compounds **8b*** and **11b*** further support the assignments, showing a doublet of triplets for the ¹⁵NH resonance (Table 5) due to coupling with the proton and phosphorus nuclei.

Scheme 2^a

P = P(OEt)₃ (**6**, **9**), PPh(OEt)₂ (**7**, **10**), PPh₂OEt (**8**, **11**, **12**); Ar–Ar = 4,4'-C₆H₄–C₆H₄ (**b**), 4,4'-(2-CH₃)C₆H₃–C₆H₃(2-CH₃) (**c**), 4,4'-C₆H₄–CH₂–C₆H₄ (**d**).

In the temperature range between +30 and –80 °C, the ³¹P NMR spectra of the monocarbonyl complexes **1** and **6** appeared as sharp singlets, indicating the magnetic equivalence of the four phosphite ligands, whereas the IR spectra showed only one $\nu(\text{CO})$ band. On this basis, the mutual trans positions of the diazene and carbonyl ligands may be proposed.

For both the mononuclear dicarbonyl complexes **2** and the binuclear dicarbonyl complexes **7** and **8**, the IR spectra showed two strong $\nu(\text{CO})$ bands, suggesting a cis arrangement of the

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Table 4. IR and NMR Data for Selected Mono-, Bi-, and Trinuclear Complexes^a

	compd	IR(KBr) ν (cm ⁻¹)	assgnt	¹ H NMR ^{b,c} δ (ppm; <i>J</i> , Hz)	assgnt	spin system	³¹ P{ ¹ H} NMR ^{b,d} δ (ppm; <i>J</i> , Hz)
1a	[Re(C ₆ H ₅ N=NH)(CO){P(OEt) ₃ } ₄]BPh ₄	1903 (s)	ν (CO)	14.37 (qi) <i>J</i> _{PH} = 4	NH CH ₂ 4.04 (m) 1.26 (t) CH ₃	A ₄	116.4 (br) [117.6 (s)] ^e
2a	[Re(C ₆ H ₅ N=NH)(CO) ₂ (PPh ₂ OEt) ₃]BF ₄ ^f	1968 (s) 1889 (s)	ν (CO)	12.21 (d) 3.34 (m) 0.84 (t) 0.65 (t)	NH CH ₂ CH ₃	AB ₂	δ _A = 115.5 δ _B = 108.8 <i>J</i> _{AB} = 28
4a	[Re(C ₆ H ₅ N=NH)(CO) ₃ {PPh(OEt) ₂ } ₂]BF ₄	2072 (m) 1979 (s) 1960 (s)	ν (CO)	14.30 (s, br) ^g 3.97 (m) 1.24 (t)	NH CH ₂ CH ₃	A ₂ ^g	136.0 (s) [137.9 (s)] ^e
4a*	[Re(C ₆ H ₅ N= ¹⁵ NH)(CO) ₃ {PPh(OEt) ₂ } ₂]BF ₄	2078 (m) 1979 (s) 1960 (s)	ν (CO)	14.31 (d) ^g <i>J</i> ¹⁵ NH = 63 3.98 (m) 1.24 (t)	NH CH ₂ CH ₃	A ₂ X ^{e,g}	137.8 (d) ² <i>J</i> ³¹ P ¹⁵ N = 2.5
5a	[Re(C ₆ H ₅ N=NH)(CO) ₃ (PPh ₂ OEt) ₂]BF ₄	2071 (m) 1979 (s) 1948 (s)	ν (CO)	12.55 (s) 3.65 (m) 1.18 (t)	NH CH ₂ CH ₃	A ₂	110.9 (s)
11b	[{Re(CO) ₃ (PPh ₂ OEt) ₂] ₂ (μ -4,4'-HN=NC ₆ H ₄ -C ₆ H ₄ N=NH)(BF ₄) ₂	2075 (m) 1981 (s) 1925 (s)	ν (CO)	13.46 (s) 3.67 (m) 1.22 (t)	NH CH ₂ CH ₃	A ₂	110.5 (s)
12b	[{Re(CO) ₄ (PPh ₂ OEt) ₂] ₂ (μ -4,4'-HN=NC ₆ H ₄ -C ₆ H ₄ N=NH)(BPh ₄) ₂	2115 (m) 2033 (s) 2017 (s) 1980 (s)	ν (CO)	12.78 (s) 3.70 (qi) 1.21 (t)	NH CH ₂ CH ₃	A	106.3 (s)
13b	[Re(CO) ₃ (PPh ₂ OEt) ₂ (4,4'-HN=NC ₆ H ₄ -C ₆ H ₄ N=N)](BF ₄) ₂	2266 (m) 2071 (m) 1979 (s) 1942 (s)	ν (N=N) ν (CO)	13.70 (s) 13.55 (s) 3.64 (qi) 1.22 (t)	NH CH ₂ CH ₃	A ₂	110.4 (s)
13b*	[Re(CO) ₃ (PPh ₂ OEt) ₂ (4,4'-H ¹⁵ N=NC ₆ H ₄ -C ₆ H ₄ N= ¹⁵ N)](BF ₄) ₂	2232 (m) 2072 (m) 1979 (s) 1942 (s)	ν (N=N) ν (CO)	13.71 (d) 13.54 (d) <i>J</i> ¹⁵ NH = 66 3.64 (br) 1.21 (br)	NH CH ₂ CH ₃	A ₂ X	110.6 (s, br)
17b	[Mn(CO) ₃ (PPh ₂ OEt) ₂ (4,4'-HN=NC ₆ H ₄ -C ₆ H ₄ N=N)](BF ₄) ₂	2265 (m) 2061 (m) 1984 (s) 1952 (s)	ν (N=N) ν (CO)	13.11 (s) 12.95 (s) 3.58 (br) 1.20 (br)	NH CH ₂ CH ₃	A ₂ + A ₂ ^h	161.9 (s, br)
Re₁₃Ru-b	[Re(CO) ₃ (PPh ₂ OEt) ₂ (μ -4,4'-HN=NC ₆ H ₄ -C ₆ H ₄ N=NH)RuH{P(OEt) ₃ } ₄](BPh ₄) ₂	2072 (m) 1978 (s) 1943 (s)	ν (CO)	13.98 (s, br) 12.72 (s) 12.68 (s) 4.05 (m) 3.62 (q) 1.30 (t) 1.26 (t) 1.24 (t) 1.19 (t) -6.89 to -7.90 (m)	NH, Ru NH, Re CH ₂ CH ₃ H, hydride	A ₂ + A ₂ AB ₂ C	109.8 (s), Re 109.6 (s) δ _A = 149.5, Ru δ _B = 141.7 δ _C = 136.7 <i>J</i> _{AB} = 62.0 <i>J</i> _{AC} = 41.5 <i>J</i> _{BC} = 43.0
Re₁₃Ru-b*	[Re(CO) ₃ (PPh ₂ OEt) ₂ (μ -4,4'-H ¹⁵ N=NC ₆ H ₄ -C ₆ H ₄ N= ¹⁵ NH)RuH{P(OEt) ₃ } ₄](BPh ₄) ₂	2071 (m) 1978 (s) 1941 (s)	ν (CO)	13.99 (d) 12.71 (d) 12.66 (d) 4.05 (m) 3.62 (qi) 1.30 (t) 1.26 (t) 1.23 (t) 1.19 (t) -6.88 to -7.89 (m)	NH, Ru NH, Re CH ₂ CH ₃ H, hydride	A ₂ X + A ₂ X AB ₂ CX	109.8 (s, br) Re δ _A = 149.5, Ru δ _B = 141.6 δ _C = 136.7 <i>J</i> _{AB} = 62.6 <i>J</i> _{AC} = 41.7 <i>J</i> _{AX} = 52.4 <i>J</i> _{BC} = 43.0 <i>J</i> _{BX} = 4.6 <i>J</i> _{CX} = 3.8
Mn₁₇Ru-b	[Mn(CO) ₃ (PPh ₂ OEt) ₂ (μ -4,4'-HN=NC ₆ H ₄ -C ₆ H ₄ N=NH)RuH{P(OEt) ₃ } ₄](BPh ₄) ₂	2060 (m) 1981 (s) 1954 (s)	ν (CO)	14.14 (s, br) ^g 14.06 (s) 13.98 (s) 4.27 (br) 4.08 (br) 3.70 (qi) 1.34 (t) 1.30 (t) 1.26 (t) 1.22 (t) -6.76 to -7.70 (m)	NH, Ru NH, Mn CH ₂ CH ₃ H, hydride	A ₂ + A ₂ AB ₂ C ^g	162.6 (s, br), Mn δ _A = 151.6, Ru δ _B = 145.0 δ _C = 137.4 <i>J</i> _{AB} = 61.3 <i>J</i> _{AC} = 41.5 <i>J</i> _{BC} = 41.0

Table 4 (Continued)

compd	IR(KBr) ν (cm ⁻¹)	assgnt	¹ H NMR ^{b,c}		spin system	³¹ P{ ¹ H} NMR ^{b,d} δ (ppm; <i>J</i> , Hz)
			δ (ppm; <i>J</i> , Hz)	assgnt		
Re₁₃Os-b [Re(CO) ₃ (PPh ₂ OEt) ₂ (μ -4,4'-HN=NC ₆ H ₄ -C ₆ H ₄ N=NH)OsH{P(OEt) ₃ } ₄](BPh ₄) ₂	2071 (m) 1978 (s) 1947 (s)	ν (CO)	14.61 (s, br)	NH, Os	A ₂ + A ₂ A ₂ BC	109.7 (s), Re
			12.59 (s)	NH, Re		109.5 (s)
			12.54 (s)			[110.7 (s)] ⁱ
			[12.60 (s)]			110.5 (s)] ⁱ
			12.53 (s)] ⁱ			$\delta_A = 103.9$, Os
			4.17–3.94 (m)	CH ₂		$\delta_B = 101.2$
			3.64 (m)			$\delta_C = 100.4$
			1.30 (t)	CH ₃		$J_{AB} = 47.3$
			1.23 (t)			$J_{AC} = 29.6$
			1.20 (t)			$J_{BC} = -32.7$
	-8.32 to -8.82 (m)	H, hydride				
Re₁₃Mn-b [Re(CO) ₃ (PPh ₂ OEt) ₂ (μ -4,4'-HN=NC ₆ H ₄ -C ₆ H ₄ N=NH)Mn(CO) ₃ {PPh(OEt) ₂] ₂](BPh ₄) ₂	2064 (w) 1978 (s, br) 1950 (s, br)	ν (CO)	12.75 (s)	NH, Re	A ₂ A ₂ + A ₂	186.6 (s), Mn
			12.73 (s)			[187.6 (s)] ⁱ
			12.55 (s)	NH, Mn		109.7 (s, br), Re
			4.09 (br)	CH ₂		[110.8 (s, br)] ⁱ
			3.65 (m)			
			1.37 (t)	CH ₃		
Mn₁₇Re-b [Mn(CO) ₃ (PPh ₂ OEt) ₂ (μ -4,4'-HN=NC ₆ H ₄ -C ₆ H ₄ N=NH)Re(CO){P(OEt) ₃ } ₄](BPh ₄) ₂	2060 (m) 1981 (s) 1954 (s) 1865 (s)	ν (CO), Mn	14.47 (br)	NH, Re	A ₂ + A ₂ A ₄	161.4 (s, br), Mn ^e
			12.47 (br)	NH, Mn		123.6 (s), Re
			4.06 (m)	CH ₂		
			3.60 (m)			
			1.30 (m br)	CH ₃		
			1.18 (t br)			
Re₁₃RuMn₁₇ [Re(CO) ₃ (PPh ₂ OEt) ₂ (μ -4,4'-HN=NC ₆ H ₄ -C ₆ H ₄ N=NH)Ru{P(OEt) ₃ } ₄ (μ -4,4'-HN=NC ₆ H ₄ -C ₆ H ₄ N=NH)Mn(CO) ₃ (PPh ₂ OEt) ₂](BPh ₄) ₄	2060 (m, br) 1980 (s, br) 1947 (s, br)	ν (CO)	14.12 (br)	NH, Ru	A ₂ + A ₂ A ₂ + A ₂ A ₂ B ₂	160.7 (br), Mn
			12.85 (s)	NH, Mn		110.0 (s), Re
			12.73 (s)			109.9 (s)
			12.51 (s)	NH, Re		$\delta_A = 126.5$, Ru
			12.39 (s)			$\delta_B = 116.7$
			4.05 (m)	CH ₂		$J_{AB} = 61.5$
			3.62 (m)			
			1.30 (m)	CH ₃		
			1.18 (m)			
			14.62 (br)	NH, Os		A ₂ + A ₂
12.92 (s)	NH, Mn	A ₂ + A ₂	109.9 (s, br), Re			
12.91 (s)		A ₂ BC	$\delta_A = 102.8$, Os			
12.56 (s)	NH, Re		$\delta_B = 101.0$			
12.42 (s)			$\delta_C = 100.5$			
4.10 (m)	CH ₂		$J_{AB} = 31.0$			
3.62 (m)			$J_{AC} = 45.5$			
1.37–1.15 (m)	CH ₃		$J_{BC} = 29.8$			
MnFe-b [Mn(CO) ₂ (PPh ₂ OEt) ₂ (μ -4,4'-N ₂ C ₆ H ₄ -C ₆ H ₄ N ₂)Fe{P(OEt) ₃ } ₄](BPh ₄)	1931 (s) 1853 (s) 1653 (m) 1617 (m) 1560 (m) 1585 (m)	ν (CO)	4.05 (br)	CH ₂	A ₂ + ABC ₂ ^b	174.1 (s), Mn
			3.69 (br)			$\delta_A = 169.2$, Fe
			1.30 (br)	CH ₃		$\delta_B = 166.8$
						$\delta_C = 152.6$
						$J_{AB} = -3.75$
				ν' (N≡N), Mn		$J_{AC} = 122.5$
MnFe-b* [Mn(CO) ₂ (PPh ₂ OEt) ₂ (μ -4,4'- ¹⁵ N≡NC ₆ H ₄ -C ₆ H ₄ N≡ ¹⁵ N)Fe{P(OEt) ₃ } ₄](BPh ₄)	1931 (s) 1854 (s) 1604 (m) 1580 (m) 1541 (m) 1558 (m)	ν (CO)	4.05 (br)	CH ₂	A ₂ X + ABC ₂ X	174.7 (s, br), Mn
			3.70 (br)			170–150 (m), Fe
			1.31 (br)	CH ₃		
				ν' (N≡N), Mn		
				ν' (N≡N), Mn		
Re₁₃Fe₂ [Re(CO) ₃ (PPh ₂ OEt) ₂ (μ -4,4'-HN=NC ₆ H ₄ -C ₆ H ₄ N ₂)Fe(CO) ₂ {P(OPh) ₃] ₂](BPh ₄) ₂	2073 (m) 1978 (s) 1944 (s) 2054 (m) 2000 (sh) 1752 (m)	ν (CO), Re	14.37 (br) ^g	NH	A ₂ + A ₂ A ₂ ^g	145.9 (s), Re
			3.78 (m)	CH ₂		111.0 (s, br), Fe
			1.21 (t)	CH ₃		
				ν (CO), Fe		
				ν (N≡N)		

^a IR and NMR data for all the prepared complexes are reported in Table S1 (Supporting Information). ^b In CD₂Cl₂ at 25 °C unless otherwise noted. ^c Phenyl proton resonances are omitted. ^d Positive shift downfield from 85% H₃PO₄. ^e At -90 °C. ^f ¹³C{¹H} NMR, δ : 202.2 (dt, $J_{\text{CP, cis}} = J_{\text{CP, cis}} = 8.5$ Hz, CO), 193.7 (dt, $J_{\text{CP, cis}} = 8.2$, $J_{\text{CP, trans}} = 67$ Hz, CO), 135–120 (m, Ph), 65.35 (d), 64.95 (t), (CH₂), 15.8 (t), 15.5 (d) (CH₃). ^g In (CD₃)₂CO. ^h At -30 °C. ⁱ At -70 °C.

two carbonyl ligands. However, these two ligands are not magnetically equivalent, as shown by the two well-separated multiplets due to the carbonyl carbon atom that appear at 202.2 (dt) and 193.7 (dt) ppm in the ¹³C NMR spectrum of [Re(C₆H₅N=NH)(CO)₂(PPh₂OEt)₃](BF₄) (2a). Furthermore, the ³¹P{¹H} NMR spectra appear as an AB₂ multiplet, suggesting a mer-cis geometry for the dicarbonyl derivatives.

The IR spectra of complexes **3**, **4**, **5**, **9**, **10**, and **11**, containing the tricarbonyl fragment Re(CO)₃P₂, showed three bands (one medium and two of strong intensity) in the ν (CO) region, indicating a mer rearrangement of the three carbonyl ligands. In the temperature range between +30 and -80 °C, the ³¹P{¹H} NMR spectra consisted of sharp singlets, indicating the magnetic equivalence of the two phosphite ligands. On this basis,

Table 5. ^{15}N NMR Data for Selected Labeled Complexes^a

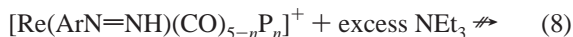
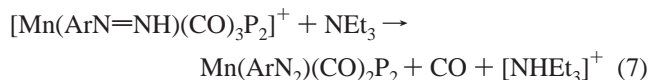
	compd	δ^b (ppm; <i>J</i> , Hz)	assgnt
8b*	$[\{\text{Re}(\text{CO})_2(\text{PPh}_2\text{OEt})_3\}_2(\mu\text{-}4,4'\text{-H}^{15}\text{N}=\text{N}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{N}^{15}\text{NH})](\text{BPh}_4)_2$	-11.5 (dt) $^2J^{15}_{\text{NP}} = 4$ $^1J^{15}_{\text{NH}} = 62$	^{15}NH
11b*	$[\{\text{Re}(\text{CO})_3(\text{PPh}_2\text{OEt})_2\}_2(\mu\text{-}4,4'\text{-H}^{15}\text{N}=\text{N}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{N}^{15}\text{NH})](\text{BF}_4)_2$	-17.6 (dt) $^2J^{15}_{\text{NP}} = 4$ $^1J^{15}_{\text{NH}} = 66$	^{15}NH
13b*	$[\text{Re}(\text{CO})_3(\text{PPh}_2\text{OEt})_2(4,4'\text{-H}^{15}\text{N}=\text{N}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{N}^{15}\text{N})](\text{BF}_4)_2$	-8.3 (d, br) -16.6 (d, br) $J^{15}_{\text{NH}} = 66$	^{15}NH
15b*	$[\text{Re}(\text{CO})_3(\text{PPh}_3)_2(4,4'\text{-H}^{15}\text{N}=\text{N}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{N}^{15}\text{N})](\text{BF}_4)_2$	-70.0 (s) -15.0 (d) -20.0 (d) $J^{15}_{\text{NH}} = 66$	N^{15}N ^{15}NH
17b*	$[\text{Mn}(\text{CO})_3(\text{PPh}_2\text{OEt})_2(4,4'\text{-H}^{15}\text{N}=\text{N}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{N}^{15}\text{N})](\text{BF}_4)_2$	16.8 (d, br) 11.6 (d, br) $J^{15}_{\text{NH}} = 65$	N^{15}N ^{15}NH
MnFe-b*	$[\text{Mn}(\text{CO})_2(\text{PPh}_2\text{OEt})_2(\mu\text{-}4,4'\text{-H}^{15}\text{N}=\text{N}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{N}^{15}\text{N})\text{Fe}\{\text{P}(\text{OEt})_3\}_4\text{BPh}_4$	-70.0 (s) 58.0 (t) $J^{15}_{\text{NP}} = 13$ 27.0 (m, br)	N^{15}N $\text{Mn}^{15}\text{N}=\text{N}$ $\text{Fe}^{15}\text{N}=\text{N}$

^a In CD_2Cl_2 at 25 °C. ^b Positive shift downfield from $\text{CH}_3^{15}\text{NO}_2$.

a mer-trans geometry of the type in Schemes 1 and 2 may be proposed for the tricarbonyl compounds. It may also be noted that exclusively mer-trans complexes were obtained by reacting both mer-trans and fac-cis isomers of the $\text{ReH}(\text{CO})_3\text{P}_2$ hydride precursors prepared in the case of the PPh_2OEt ligand.

Finally, mutual cis positions for the phosphite and diazene ligands of the tetracarbonyl $[\{\text{Re}(\text{CO})_4(\text{PPh}_2\text{OEt})_2\}_2(\mu\text{-}4,4'\text{-HN}=\text{NC}_6\text{H}_4-\text{C}_6\text{H}_4-\text{N}=\text{NH})](\text{BPh}_4)_2$ (**12b**) complex may be proposed on the basis of the presence of four $\nu(\text{CO})$ bands in the infrared spectra.

A comparison of these results for rhenium aryldiazene complexes with those previously reported by us for related manganese derivatives^{3b} showed that, in both cases, aryldiazene complexes can be obtained by “apparent” insertions of aryldiazonium cations into the $\text{M}-\text{H}$ bonds of the monohydride species $\text{MH}(\text{CO})_{5-n}\text{P}_n$ ($\text{M} = \text{Mn}, \text{Re}$) containing phosphites as ancillary ligands. However, whereas stable diazene complexes of rhenium can be obtained for all $\text{CO}:\text{P}$ ratios in the $[\text{Re}(\text{ArN}=\text{NH})(\text{CO})_{5-n}\text{P}_n]^+$ ($n = 1-4$) complexes, only the tricarbonyl fragment $\text{Mn}(\text{CO})_3\text{P}_2$ allowed stable aryldiazene derivatives to be prepared. Furthermore, the $[\text{Mn}(\text{ArN}=\text{NH})(\text{CO})_3\text{P}_2]^+$ cations can easily be deprotonated with NEt_3 , affording aryldiazenido $\text{Mn}(\text{ArN}_2)(\text{CO})_2\text{P}_2$ derivatives, in agreement with eq 7. Surprisingly, no reaction [as in (8)] was



observed when the related rhenium aryldiazene complexes **1-12** were treated with base. The starting $[\text{Re}]-\text{NH}=\text{NAr}$ compound, in fact, could be recovered unchanged even after 10–12 h of reaction with an excess of NEt_3 at room temperature, whereas longer reaction times or reflux conditions only caused decomposition of the aryldiazene derivative. This unreactivity was rather unexpected in view of the known properties of aryldiazene complexes^{3,17} and may be explained by taking into account eq 7, which involves deprotonation of $\text{ArN}=\text{NH}$ and concurrent dissociation of one ligand, affording a pentacoordinate $\text{Mn}(-\text{I})$ aryldiazenido derivative. In agreement with this path, the probable reluctance of the rhenium complexes to dissociate one

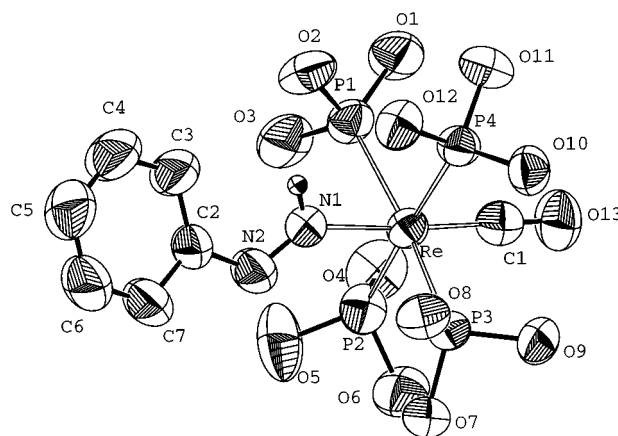


Figure 1. ORTEP view of the cation $[\text{Re}(\text{C}_6\text{H}_5\text{N}=\text{NH})(\text{CO})\{\text{P}(\text{OEt})_3\}_4]^+$ (**1a**⁺) with thermal ellipsoids drawn at the 50% probability level. Ethyl groups of phosphite ligands are omitted for clarity.

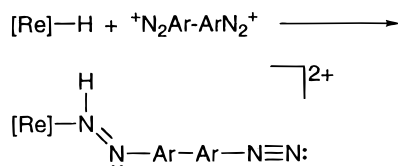
CO or one phosphite ligand may explain the different behaviors of the aryldiazene complexes of the two metals.

X-ray Crystal Structure of 1a. The crystal structure of **1a** consists of discrete $[\text{Re}(\text{C}_6\text{H}_5\text{N}=\text{NH})(\text{CO})\{\text{P}(\text{OEt})_3\}_4]^+$ cations and BPh_4^- anions, which interact only by means of electrostatic and dispersive forces. The complex cation showing the atom-labeling scheme used is depicted in Figure 1. Selected bond distances and angles are given in Table 6. The coordination polyhedron is a distorted octahedron in which the rhenium atom is coordinated by four phosphite groups, one phenyldiazene molecule, and one carbonyl group, the two last ligands being mutually trans. The angles in the coordination sphere range from 169.91(3) to 176.24(4)° (trans) and from 82.7(1) to 97.6(1)° (cis). The orientation of the phosphite groups containing P1 and P4 is determined by an intramolecular bifurcated hydrogen bond involving two ethoxy oxygens and the hydrazidic $-\text{NH}$: $\text{N1}-\text{H}\cdots\text{O2}$ (2.924(5) Å, 108(3)°) and $\text{N1}-\text{H}\cdots\text{O12}$ (2.902(4) Å, 120(3)°). This compound is the first case in which the structure of the $\text{Re}-\text{NH}=\text{N}-\text{Ph}$ system has been determined.

Like that of the phenyldiazene ligand, this structure may be compared with the structure of the similar complex^{3b} $[\text{Mn}(\text{CO})_3(4\text{-CH}_3\text{C}_6\text{H}_4\text{N}=\text{NH})\{\text{PPh}(\text{OEt})_2\}_2]^+$, in which the metal envi-

Table 6. Selected Bond Distances (Å) and Angles (deg) for $[\text{Re}(\text{C}_6\text{H}_5\text{N}=\text{NH})(\text{CO})\{\text{P}(\text{OEt})_3\}_4]^+$ (**1a**⁺)

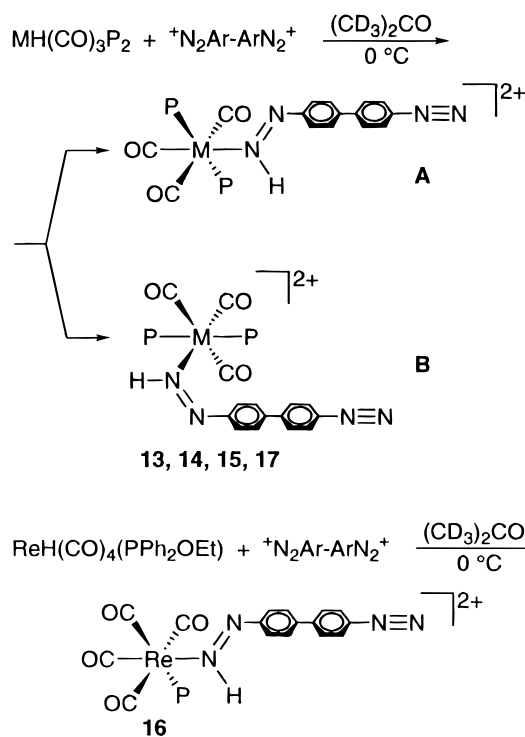
Distances			
Re–C1	1.887(5)	Re–P4	2.366(2)
Re–N1	2.136(4)	O13–C1	1.180(4)
Re–P1	2.370(1)	N1–N2	1.229(4)
Re–P2	2.372(2)	N2–C2	1.424(5)
Re–P3	2.368(1)		
Angles			
C1–Re–N1	175.6(1)	P3–Re–P1	169.91(3)
C1–Re–P4	89.6(1)	C1–Re–P2	86.7(1)
N1–Re–P4	86.1(1)	N1–Re–P2	97.6(1)
C1–Re–P3	93.2(1)	P4–Re–P2	176.24(4)
N1–Re–P3	87.8(1)	P3–Re–P2	92.86(9)
P4–Re–P3	87.82(9)	P1–Re–P2	91.61(9)
C1–Re–P1	96.1(1)	N2–N1–Re	135.4(3)
N1–Re–P1	82.7(1)	N1–N2–C2	118.6(3)
P4–Re–P1	88.30(9)	O13–C1–Re	178.6(3)

Scheme 3

ronment consists of two phosphite ligands trans to each other, three carbonyl groups, and one *p*-tolylidiazene moiety, and with the structure of chlorodicarbonyl(*cis*-phenyldiazene)bis(triphenylphosphine)ruthenium(1+).^{5k} The structural parameters of the Re–NH=N–C system (Re–N = 2.136(4), N–N = 1.229(4), N–C = 1.424(5) Å; Re–N–N = 135.4(3), N–N–C = 118.6(3)°) agree with sp² hybridization for both N atoms. In the aryldiazene ligand of the above-mentioned Mn derivative, the distances are slightly longer (N–N = 1.263(10), N–C = 1.438(11) Å) and the bond angles more regular (Mn–N–N = 125.1(5), N–N–C = 119.8(7)°). The geometry of the Ru complex (N–N = 1.218, N–C = 1.409 Å; Ru–N–N = 129, N–N–C = 118°), is not significantly different from that of the Re compound, apart from the M–N–N angle. It is interesting to compare the geometry of Re–NH=N–Ph with that of the Re–N=N–Ph system found in dibromo(phenyldiazene)(phenylhydrazido)bis(triphenylphosphine)rhenium,²⁷ where the shift of the proton from N1 to N2 produces shortening of the Re–N bond (1.922 Å) and lengthening of the N–N bond (1.276 Å).

“Diazene–Diazonium” Derivatives. In the course of synthesizing the binuclear $[\{\text{Re}(\text{CO})_{5-n}\text{P}_n\}_2(\mu\text{-HN}=\text{NAr}-\text{ArN}=\text{NH})]^{2+}$ cations, we observed that, in some cases, the ¹H NMR spectra of the raw products showed a new NH signal of low intensity besides that of the binuclear species. This observation led us to hypothesize that the reactions between the hydrides $\text{ReH}(\text{CO})_{5-n}\text{P}_n$ and bis(aryldiazonium) cations may also afford mononuclear species of the type $[\text{Re}(\text{CO})_{5-n}\text{P}_n(\text{HN}=\text{NAr}-\text{ArN}\equiv\text{N})]^{2+}$ as marginal products, obtained by reactions of only one end of the ${}^+\text{N}_2\text{Ar}-\text{Ar}-\text{N}_2^+$ ligands with the hydrides (Scheme 3).

To test this hypothesis and to attempt to isolate these mononuclear compounds containing a diazene–diazonium ligand in pure form, we studied the reactions between $\text{ReH}(\text{CO})_{5-n}\text{P}_n$ and ${}^+\text{N}_2\text{Ar}-\text{Ar}-\text{N}_2^+$ species extensively and found that hydrides containing PPh_2OEt , PPh_2OMe , and PPh_3 , under appropriate conditions, reacted with equimolar amounts of bis(aryldiazonium) cations to give the mononuclear diazene–diazonium

Scheme 4^a

^a Top: M = Re (**13**, **14**, **15**), Mn (**17**); P = PPh_2OEt (**13**, **17**), PPh_2OMe (**14**), PPh_3 (**15**). Bottom: Ar–Ar = 4,4'-C₆H₄–C₆H₄ (**b**), 4,4'-C₆H₄–CH₂–C₆H₄ (**d**).

complexes $[\text{Re}(\text{CO})_{5-n}\text{P}_n(\text{HN}=\text{NAr}-\text{ArN}\equiv\text{N})]^{2+}$ ($n = 2, 1$) (**13–16**), which were isolated in pure form and characterized (Scheme 4). The ¹H, ³¹P, and ¹⁵N NMR data of complexes **13–15** indicate the presence of two stereoisomers of types **A** and **B** (Scheme 4), which will be discussed below.

Investigations of the reactions between $\text{ReH}(\text{CO})_{5-n}\text{P}_n$ species containing phosphines with *ethoxy groups* and bis(diazonium) salts showed that the mononuclear diazene–diazonium complexes were obtained exclusively with hydrides containing the PPh_2OEt ligand, whereas all other hydrides containing $\text{P}(\text{OEt})_3$ or $\text{PPh}(\text{OEt})_2$ always afforded the binuclear derivatives under any conditions. These results may be related to the electronic and steric properties²⁸ of PPh_2OEt as compared to other phosphites, which induce a unique reactivity in $\text{ReH}(\text{CO})_3\text{-}(\text{PPh}_2\text{OEt})_2$ toward the bis(diazonium) cations. Furthermore, the formation of the diazene–diazonium complexes $[\text{Re}(\text{CO})_3\text{P}_2\text{-}(4,4'\text{-HN}=\text{NC}_6\text{H}_4\text{-C}_6\text{H}_4\text{N}\equiv\text{N})](\text{BF}_4)_2$ with P = PPh_2OMe (**14**) and P = PPh_3 (**15**) confirmed that phosphine ligands with large steric hindrance and rather weak π -acceptor properties²⁸ allow the mononuclear derivatives **13–16** to be prepared.

The properties shown by the rhenium hydrides $\text{ReH}(\text{CO})_{5-n}\text{P}_n$ containing bulky PPh_2OR or PPh_3 ligands prompted us to investigate the reactivity of the related manganese complexes $\text{MnH}(\text{CO})_3\text{P}_2$ toward bis(aryldiazonium) cations under appropriate experimental conditions, in an attempt to prepare similar diazene–diazonium derivatives. Binuclear $[\{\text{Mn}(\text{CO})_3\text{P}_2\}_2(\mu\text{-HN}=\text{NAr}-\text{ArN}=\text{NH})]^{2+}$ species have recently been synthesized.^{3b} Results showed that also the manganese diazene–diazonium complex $[\text{Mn}(\text{CO})_3(\text{PPh}_2\text{OEt})_2(4,4'\text{-HN}=\text{NC}_6\text{H}_4\text{-C}_6\text{H}_4\text{N}\equiv\text{N})](\text{BF}_4)_2$ (**17b**) can be prepared as a mixture of the two isomers **A** and **B** (Scheme 4) and characterized.

(28) (a) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313. (b) Rahman, M. M.; Liu, H.-Y.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1989**, *8*, 1.

(27) Haymore, B. L.; Ibers, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 5369.

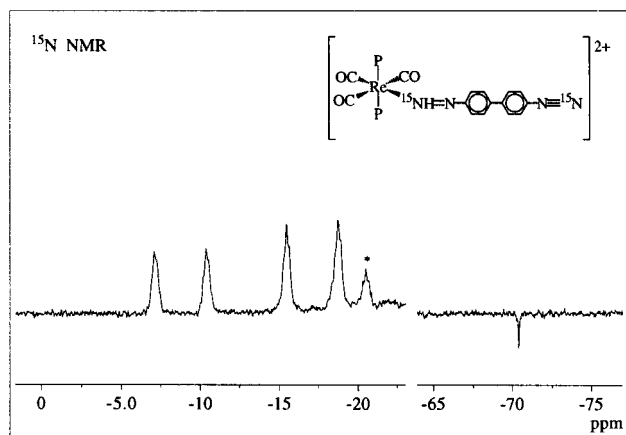


Figure 2. ^{15}N NMR spectrum of $[\text{Re}(\text{CO})_3(\text{PPh}_2\text{OEt})_2(4,4'\text{-H}^{15}\text{N}=\text{NC}_6\text{H}_4\text{-C}_6\text{H}_4\text{N}\equiv^{15}\text{N})](\text{BF}_4)_2$ (**13b***) derivative, in CD_2Cl_2 at 25°C . The peak marked with the asterisk is due to an impurity.

The reactions of both the rhenium and manganese hydrides $\text{MH}(\text{CO})_{5-n}\text{P}_n$ with bis(aryldiazonium) cations can therefore proceed (with special phosphite ligands and under appropriate conditions) through the insertion of only one $\text{N}\equiv\text{N}$ group, affording the mononuclear diazene–diazonium complexes **13–17**. However, also in the case of PPh_2OR or PPh_3 complexes, the reactions give the mononuclear complexes **13–17** as the main products, since the binuclear $[\{\text{M}(\text{CO})_{5-n}\text{P}_n\}_2(\mu\text{-HN}=\text{NAr}-\text{ArN}\equiv\text{N})]^{2+}$ cations are always present in the reaction products as secondary species (10–25%). In contrast, with hydrides containing $\text{P}(\text{OEt})_3$ and $\text{PPh}(\text{OEt})_2$ ligands, the binuclear derivatives **6–11** were obtained exclusively.

These results may tentatively be explained on the basis of rather low rates of $^+\text{N}_2\text{Ar}-\text{ArN}_2^+$ insertion into the $\text{M}-\text{H}$ bonds in the cases of $\text{MH}(\text{CO})_{5-n}\text{P}_n$ hydrides containing PPh_2OR or PPh_3 ligands. As the second insertion involving a $[\text{M}(\text{CO})_{5-n}\text{P}_n(\text{HN}=\text{NAr}-\text{ArN}\equiv\text{N})]^{2+}$ cation is probably slower than the first, the use of diluted reaction mixtures at low temperatures with hydrides that react slowly with $^+\text{N}_2\text{Ar}-\text{ArN}_2^+$ allows diazene–diazonium complexes to be prepared.

The mononuclear $[\text{M}(\text{CO})_{5-n}\text{P}_n(\text{HN}=\text{NAr}-\text{ArN}\equiv\text{N})](\text{BF}_4)_2$ derivatives (**13–17**) are obtained as orange solid or gummy products, stable both in air and in solutions of polar organic solvents, where they behave as 1:2 electrolytes.²⁵ Elemental analyses and IR and NMR data (Tables 4 and 5) support the proposed formulation. The spectroscopic data also indicate the existence of stereoisomers **A** and **B** for each mononuclear complex, with the geometries shown in Scheme 4.

Besides the $\nu(\text{CO})$ bands, the IR spectra of the mononuclear compounds **13–17** show one medium-intensity absorption band between 2281 and 2265 cm^{-1} , attributed to $\nu(\text{N}\equiv\text{N})$ of the $\text{HN}=\text{NAr}-\text{ArN}\equiv\text{N}$ group. This band falls at a lower frequency than that of the free species $[\text{N}_2\text{Ar}-\text{ArN}_2](\text{BF}_4)_2$ [$\nu(\text{N}_2)$ at 2315 cm^{-1}] and is shifted to a lower frequency (about 35 cm^{-1}) for the labeled $[\text{M}(\text{CO})_3(\text{PPh}_2\text{OEt})_2(4,4'\text{-H}^{15}\text{N}=\text{NC}_6\text{H}_4\text{-C}_6\text{H}_4\text{N}\equiv^{15}\text{N})](\text{BF}_4)_2$ [$\text{M} = \text{Re}$ (**13b***), Mn (**17b***)] complexes, in agreement with the proposed formulation.

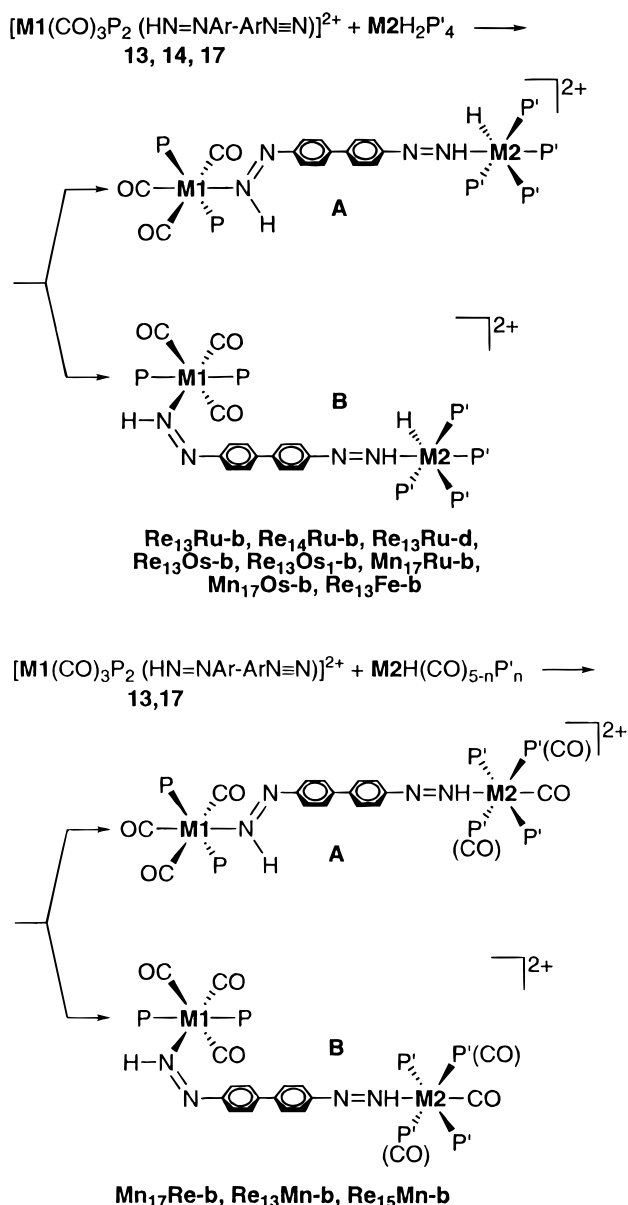
The ^1H NMR spectra of diazene–diazonium derivatives show the NH diazene signal in the high-frequency region, appearing as two slightly broad resonances at $14.44\text{--}12.95\text{ ppm}$, both split into doublets for the labeled $[\text{M}(\text{CO})_3(\text{PPh}_2\text{OEt})_2(4,4'\text{-H}^{15}\text{N}=\text{NC}_6\text{H}_4\text{-C}_6\text{H}_4\text{N}\equiv^{15}\text{N})]^{2+}$ [$\text{M} = \text{Re}$ (**13b***), Mn (**17b***)] cations with $J_{\text{NH}} = 66\text{ Hz}$. The proton-coupled (Figure 2) and decoupled ^{15}N NMR spectra of **13b*** parallel the proton spectrum, showing two ^{15}NH resonances in the coupling spectra,

appearing as slightly broad doublets due to slight coupling with the two magnetically equivalent phosphite ligands. The spectra also show a singlet at -70 ppm (Table 5), attributed to the diazonium ^{15}N resonance of the $4,4'\text{-}^{15}\text{N}\equiv\text{NC}_6\text{H}_4\text{-C}_6\text{H}_4\text{N}\equiv^{15}\text{N}$ group. The presence of two NH resonances is probably due to two isomers of the types shown in Scheme 4, with H and aryl substituents mutually in trans and cis positions with respect to the $\text{N}=\text{N}$ moiety. For these two isomers, two proton NH and two ^{15}N NMR resonances are expected; the difference in chemical shifts of the farther $^{15}\text{N}\equiv\text{N}$ group in the two isomers is probably smaller than the line width, giving only one ^{15}N signal. Furthermore, the two NH resonances do not coalesce into only one signal as temperature increases, indicating that the two stereoisomers do not interconvert between $+50$ and -60°C . Support for this hypothesis is given by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra which, in the temperature range between $+30$ and -80°C , show two singlets for each diazene–diazonium compound with close chemical shift values (Table 4), as expected for the two isomers.

In contrast with the results obtained for the diazene–diazonium derivatives **13–17**, all of the mono- and binuclear aryldiazene cations $[\text{Re}(\text{ArN}=\text{NH})(\text{CO})_{5-n}\text{P}_n]^+$ (**1–5**) and $[\{\text{Re}(\text{CO})_{5-n}\text{P}_n\}_2(\mu\text{-HN}=\text{NAr}-\text{ArN}=\text{NH})]^{2+}$ (**6–12**), including those containing the PPh_2OEt ligand, show only one ^1H and ^{15}N NH resonance, in agreement with the presence of only one stereoisomer involving the $\text{N}=\text{N}$ group. The solid-state structure of $[\text{Re}(\text{C}_6\text{H}_5\text{N}=\text{NH})(\text{CO})\{\text{P}(\text{OEt})_3\}_4]\text{BPh}_4$ (**1a**) confirms the existence of only one isomer of type **A**. The formation of two stereoisomers in the case of the $[\text{Re}(\text{CO})_3\text{P}_2(\text{HN}=\text{NAr}-\text{ArN}\equiv\text{N})]^{2+}$ complexes (**13–17**) and only one for the other aryldiazene derivatives (**1–12**) is rather surprising and may be explained on the basis of the different reaction conditions (reagent ratios, temperature, concentration) used in the two syntheses, which may also cause two different mechanisms to operate in the reactions. Preparing the binuclear $[\{\text{Re}(\text{CO})_3(\text{PPh}_2\text{OEt})_2\}_2(\mu\text{-}4,4'\text{-HN}=\text{NC}_6\text{H}_4\text{-C}_6\text{H}_4\text{N}=\text{NH})]^{2+}$ complex (**11b**) under dilute conditions at 0°C afforded a mixture of $[\text{Re}(\text{CO})_3(\text{PPh}_2\text{OEt})_2(4,4'\text{-HN}=\text{NC}_6\text{H}_4\text{-C}_6\text{H}_4\text{N}\equiv\text{N})]^{2+}$ (**13b**) and the binuclear complex **11b**, both showing two proton NH resonances probably due to two stereoisomers for each compound. This fact partly supports the hypothesis of the influence of experimental conditions on reaction mechanism.

Heterobinuclear and Heterotrinnuclear Aryldiazene Complexes. The diazene–diazonium $[\text{M}(\text{CO})_{5-n}\text{P}_n(\text{HN}=\text{NAr}-\text{ArN}\equiv\text{N})]^{2+}$ cations (**13–17**) contain an $-\text{N}\equiv\text{N}$ group which may potentially react with a new metal hydride to afford binuclear bis(aryldiazene) complexes. We therefore treated these complexes with several metal hydrides whose reactivity with aryldiazonium cations is well-known,^{3,17} obtaining the first heterobinuclear complexes with bis(aryldiazene) bridging ligands, as shown in Scheme 5.

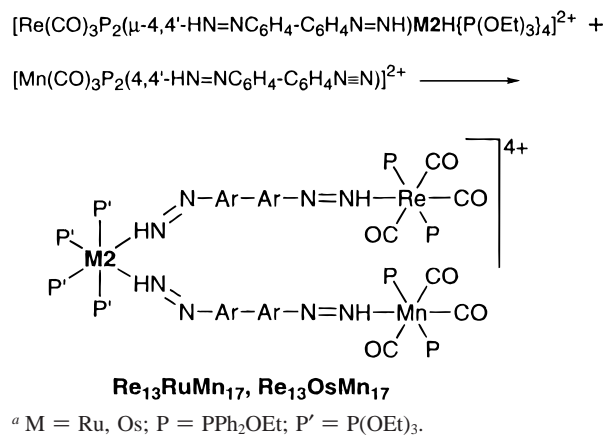
The complexes were obtained as orange or reddish-brown solids, stable in air and in solution of polar organic solvents, where they behave as 1:2 electrolytes.²⁵ Analytical and spectroscopic data (Table 4) confirm the proposed formulation and also indicate the geometries shown in Scheme 5. The binuclear complexes were in fact obtained as mixtures of the two stereoisomers **A** and **B**, like those observed for the diazene–diazonium precursors with the H and aryl substituents mutually trans or cis to the $\text{N}=\text{N}$ moiety. However, this isomerism only involves the metal-bonded diazene of the $[\text{M}(\text{CO})_3\text{P}_2(\text{HN}=\text{NAr}-\text{ArN}\equiv\text{N})]^{2+}$ precursors, since the other diazene is present in only one isomer. The ^1H NMR spectra of the heterobinuclear complexes show two sets of NH proton resonances in the high-

Scheme 5^a

^a Top: **M1** = Mn, Re; **M2** = Fe, Ru, Os; P = PPh₂OEt, PPh₂OMe; P' = P(OEt)₃, PPh(OEt)₂ (**Os₁**). Bottom: **M1** = Mn, Re; **M2** = Re, Mn; P = PPh₂OEt, PPh₃; P' = P(OEt)₃, PPh(OEt)₂.

frequency region, one appearing as a broad signal and the other as two slightly broad singlets. The latter are very similar to those of the $[\text{M1}(\text{CO})_3\text{P}_2(\text{HN}=\text{NAr}-\text{ArN}=\text{N})]^{2+}$ precursors (**13–17**) and fall at similar chemical shift values, indicating the presence of two isomers with H and aryl substituents mutually in *cis* and *trans* positions with respect to the $-\text{NH}=\text{N}(\text{R})$ moiety. The heterobinuclear nature of our complexes is also confirmed by the ³¹P spectra, which show two groups of signals of phosphites bonded to two different metals. In particular, the spectra of **ReRu**, **MnRu**, **ReOs**, **ReFe**, and **MnOs** show complicated AB₂C multiplets due to the *cis*-**M2HP**₄ (**M2** = Ru, Os) fragment and a doublet due to stereoisomers **A** and **B** of the **M1**(CO)₃P₂ (**M1** = Re, Mn) center of the binuclear complexes. The proton spectra of these complexes also have multiplets, at low frequency, attributed to the hydride resonance of the **M2HP**₄ fragment, in agreement with the proposed formulation.

Complexes $[\text{M1}(\text{CO})_3\text{P}_2(\mu\text{-HN}=\text{NAr}-\text{ArN}=\text{NH})\text{M2HP}'_4]^{2+}$ still contain a metal–hydride group accessible for further

Scheme 6^a

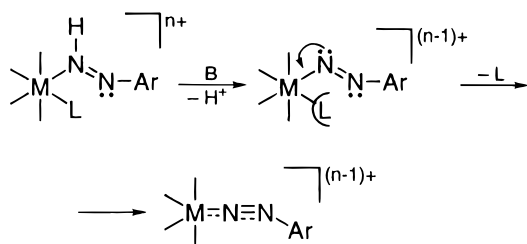
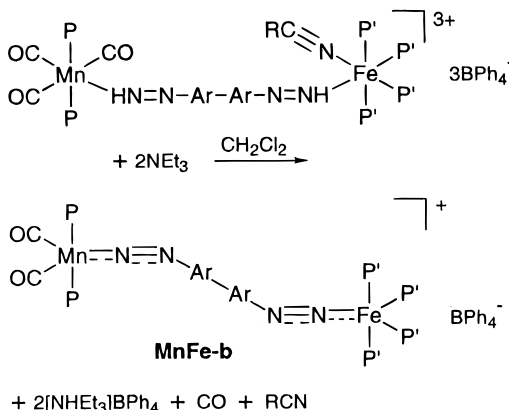
reaction with a diazenido group, and we therefore reacted these complexes with diazene–diazonium $[\text{M}(\text{CO})_3\text{P}_2(\text{HN}=\text{NAr}-\text{ArN}=\text{N})]^{2+}$ derivatives in an attempt to obtain heterotrimeric complexes. Although the reactions were rather slow, they did yield, after workup, $[\text{Re}(\text{CO})_3(\text{PPh}_2\text{OEt})_2(\mu\text{-}4,4'\text{-HN}=\text{NC}_6\text{H}_4\text{-C}_6\text{H}_4\text{N}=\text{NH})\text{M2}\{\text{P}(\text{OEt})_3\}_4(\mu\text{-}4,4'\text{-HN}=\text{NC}_6\text{H}_4\text{-C}_6\text{H}_4\text{N}=\text{NH})\text{-Mn}(\text{CO})_3(\text{PPh}_2\text{OEt})_2](\text{BPh}_4)_4$ (**M2** = Ru, Os) (**Re₁₃RuMn₁₇**, **Re₁₃OsMn₁₇**) derivatives, which were isolated as solids and characterized (Scheme 6).

The IR spectra show three $\nu(\text{CO})$ bands (two strong and one weak) which are quite broad due to the overlap of $\text{Re}(\text{CO})_3$ and $\text{Mn}(\text{CO})_3$ fragments. In the proton NMR spectra, apart from the signals of the phosphites and BPh_4 , three groups of NH resonances appear, attributed to the diazene bonded to the three metals. Two of these groups of resonances, attributed to $\text{ReN}=\text{NH}$ and $\text{MnN}=\text{NH}$ proton signals, appear as a set of two signals, again indicating the presence of several isomers. The ³¹P{¹H} NMR data support the formulation of the complexes as trinuclear species, showing three groups of signals at chemical shift values near those expected for the $\text{Re}(\text{CO})_3\text{P}_2$, RuP_4 (or OsP_4), and $\text{Mn}(\text{CO})_3\text{P}_2$ fragments, in agreement with the proposed formulation.

Heterobinuclear Bis(aryldiazenido) Complexes. The known properties of some aryldiazene complexes^{3,17} of transition metals, which may be deprotonated with base to give aryldiazenido compounds, prompted us to attempt to synthesize a heterobinuclear complex with a bis(aryldiazenido) bridging ligand. The strategy used for this synthesis should therefore have involved the initial preparation of a binuclear bis(aryldiazene) species containing two metal fragments, each able to convert the diazene ligand into the related diazenido ligand. However, the properties shown by the rhenium aryldiazene complexes **1–12**, which are unreactive toward base and do not give aryldiazenido complexes, exclude the use of an Re aryldiazene as one end of the binuclear complexes. Instead, only aryldiazene species containing a rather labile ligand are reported^{3a,b,17b,d,e} to afford, by deprotonation, aryldiazenido complexes, according to Scheme 7, which involves rearrangement of the ArN_2 group and dissociation of one ligand to give a singly bent ArN_2^+ species with a 2 e reduction of the central metal.

We therefore prepared the new heterobinuclear complex $[\text{Mn}(\text{CO})_3(\text{PPh}_2\text{OEt})_2(\mu\text{-}4,4'\text{-HN}=\text{NC}_6\text{H}_4\text{-C}_6\text{H}_4\text{N}=\text{NH})\text{Fe}(4\text{-CH}_3\text{C}_6\text{H}_4\text{CN})\{\text{P}(\text{OEt})_3\}_4](\text{BPh}_4)_3$ (**Mn₁₇Fe-b**) by reacting $[\text{Mn}(\text{CO})_3(\text{PPh}_2\text{OEt})_2(4,4'\text{-HN}=\text{NC}_6\text{H}_4\text{-C}_6\text{H}_4\text{N}=\text{N})](\text{BF}_4)_2$ with the hydride^{17e} $[\text{FeH}(4\text{-CH}_3\text{C}_6\text{H}_4\text{CN})\{\text{P}(\text{OEt})_3\}_4]\text{BPh}_4$ and studied the deprotonation reaction with an excess of NEt_3 . The reaction proceeds at room temperature in CH_2Cl_2 with a rapid color

Scheme 7

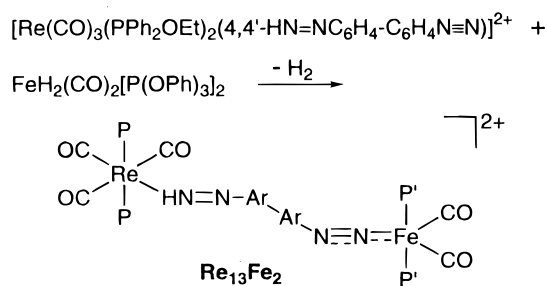
Scheme 8^a

^a P = PPh₂OEt; P' = P(OEt)₃; R = 4-CH₃C₆H₄.

change of the solution and the separation of (NH₄)₃BPPh₄ as a white solid, according to Scheme 8.

After workup, the heterobinuclear **MnFe-b** complex with a bis(aryldiazene) bridging ligand was isolated as a stable reddish-orange solid and characterized in the usual way. The compound is a diamagnetic solid and behaves as a 1:1 electrolyte in solution.²⁵ IR spectrum shows two strong bands in the ν -(CO) region due to the two carbonyl ligands cis to the M(CO)₂P₂ end of the complex. The spectrum also shows one medium-intensity band at 1653 cm⁻¹ and two others at 1617 and 1560 cm⁻¹. These bands shift to lower frequencies (1604 and 1580, 1541 cm⁻¹, respectively) in the spectrum of the labeled [Mn(CO)₂P₂(μ -4,4'-¹⁵N≡NAr-ArN≡¹⁵N)FeP'₄]BPPh₄ (**MnFe-b***) derivative and are attributed to ν (N₂) of the FeN₂Ar- (1654 cm⁻¹) and MnN₂Ar- (1617, 1560 cm⁻¹) groups, respectively. Attributions are based on comparison with the IR spectra of the mononuclear Mn(CO)₂P₂(ArN₂) and [FeP'₄(ArN₂)]⁺ derivatives, previously reported by us,^{3b,17b} which contain a singly bent aryldiazene ArN₂⁺ ligand bonded to the formal Mn(-I) or Fe(0) central metal. This probably also applies to the binuclear **MnFe-b** derivative and is confirmed^{29,30} by the ¹⁵N NMR data (Table 5).

The ³¹P{¹H} NMR spectrum of the complex agrees with the proposed formulation, showing two groups of signals attributed to the phosphorus nuclei of the MnP₂ and FeP'₄ fragments. The spectrum is also temperature dependent, and whereas the singlet due to MnP₂ at 174 ppm remains unchanged between +30 and -90 °C, the rather broad resonance observed at room temperature for the FeP'₄ phosphorus nuclei resolves into an ABC₂ multiplet at -30 °C. This type of spectrum seems to exclude a regular TBP geometry of the type shown in Scheme 8, for which an A₂B₂ spectrum would be expected. However, a TBP distorted

Scheme 9^a

^a P = PPh₂OEt; P' = P(OPh)₃.

toward SP geometry may result in an ABC₂-type spectrum, as previously proposed for the related mononuclear^{17b} [Fe(ArN₂-P₄)]⁺ and binuclear^{3a} [(FeP₄)₂(μ -N₂Ar-ArN₂)]²⁺ cations. This distortion may have occurred in our case too, although restricted rotation at low temperature of the Ar-ArNN group placed in the equatorial plane of a regular TBP (Scheme 8) may also result in an ABC₂-type ³¹P spectrum.

The easy deprotonation of the aryldiazene complexes of manganese [Mn(CO)₃P₂(HN=NAr)]⁺, on one hand, and the unreactivity of the rhenium complexes [Re(CO)₃P₂(HN=NAr)]⁺, on the other, suggested treating a binuclear [Re(CO)₃P₂(μ -HN=NAr-ArN≡N)Mn(CO)₂P₂](BPPh₄)₂ complex with base to prepare a binuclear complex with a diazene-diazenido bridging ligand of the type in [Re(CO)₃P₂(μ -HN=NAr-ArN≡N)Mn(CO)₂P₂](BPPh₄). However, although the reaction with NEt₃ proceeded easily at room temperature, no stable complex could be obtained.

A different strategy was therefore employed in order to prepare heterobinuclear complexes with an aryldiazene-aryldiazene bridging ligand, involving the reaction of the diazene-diazenido [Re(CO)₃(PPh₂OEt)₂(4,4'-HN=NC₆H₄-C₆H₄N≡N)]²⁺ cation with the dihydride FeH₂(CO)₂[P(OPh)₃]₂ (Scheme 9), whose reactions with aryldiazene cations are reported^{3c} to give aryldiazene [Fe(ArN₂)(CO)₂{P(OPh)₃]₂]⁺ derivatives. The reaction proceeded slowly, affording the [Re(CO)₃(PPh₂OEt)₂(μ -4,4'-HN=NC₆H₄-C₆H₄N≡N)Fe(CO)₂[P(OPh)₃]₂-(BPPh₄)₂ (**Re₁₃Fe₂**) complex (Scheme 9), which was isolated in moderate yield and characterized.

Diagnostic for the presence of the diazene-diazenido bridging ligand μ -HN=NAr-ArN≡N are both IR and ¹H NMR spectra which show, respectively, a medium-intensity ν (N₂) band at 1752 cm⁻¹ and a slightly broad NH signal at 14.37 ppm. Furthermore, the ν (CO) region of the IR spectrum contains five bands which may be attributed, by spectral comparison with the related mononuclear complexes, to the CO ligands of the two ends of the complex. In particular, the two bands at 2054 and 2000 cm⁻¹ are assigned to the two carbonyl ligands cis to the Fe(CO)₂ moiety, whereas the three at 2073(w), 1978(s), and 1944(s) cm⁻¹ are attributed to the Re(CO)₃ fragment with the carbonyls in a mer arrangement. In the temperature range between +30 and -80 °C, the ³¹P{¹H} NMR spectra show the signals of the phosphorus nuclei of the two end groups as singlets, in agreement with the presence of two magnetically equivalent phosphite ligands for both metals. On these bases, a geometry of the type reported in Scheme 9 can be proposed for this binuclear **Re₁₃Fe₂** complex with a diazene-diazenido bridging ligand.

Electrochemical Reductions of Aryldiazene Complexes. Voltammograms for the electrochemical reductions of the mononuclear compounds **5a** and [Mn(C₆H₅N=NH)(CO)₃(PPh₂OEt)₂]BF₄ (**Mn₁**) in 0.1 M TBAH/DCE, recorded at 0.05 V

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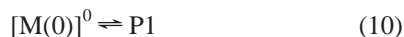
(30) Dilworth, J. R.; Kan, C. T.; Richards, R. L.; Mason, J.; Stenhouse, I. *J. Organomet. Chem.* **1980**, 201, C24.

s^{-1} , are characterized by one irreversible reduction peak located at -0.81 V for **5a** and -0.92 V for **Mn₁**. Increasing the scan rate (ν) to >1 V s^{-1} causes the progressive appearance of a return peak with a concomitant increase in the I_{pb}/I_{pf} ratio (where I_{pb} and I_{pf} are the currents of the peaks recorded in the backward and forward scans, respectively), which approaches unity at a scan rate of 30 V s^{-1} .

$I_{pf} \nu^{-1/2}$ values decrease slightly (by about 15%) when the scan rate is increased from 1 to 30 V s^{-1} . The peak potential recorded in the forward scan (E_{pf}) shifts negatively with scan rate, with a shift of about 80 mV when the scan rate is increased from 0.1 to 1 V s^{-1} .

These findings indicate that the reduction follows an EC mechanism, which involves a quasi-reversible electron-transfer step followed by a chemical reaction. The quasi-reversibility of the charge transfer is supported by the evidence that, when $\nu \leq 1$ V s^{-1} , the shift in peak potentials with scan rate is higher than the 30 mV/decade value expected for an EC process with reversible electron transfer. The value of almost unity for the I_{pb}/I_{pf} ratio at 30 V s^{-1} indicates that, at this scan rate, almost pure diffusion-controlled conditions hold. Comparison of peak currents recorded at this scan rate with reduction peak currents of mononuclear ruthenium complexes with one aryldiazene ligand, which have been shown to undergo one-electron reduction,^{3a} indicates that the process is a one-electron reduction. Half-wave potentials ($E_{1/2}$), calculated as $(E_{pf} + E_{pb})/2$ (where E_{pb} is the potential of the peak recorded in the backward scan) from the voltammograms at 30 V s^{-1} , are -0.80 V for **5a** and -0.88 V for **Mn₁**. Satisfactory agreement between experimental and simulated data is achieved using the (1)–(2) mechanism and the fitting parameters listed in Table 2.

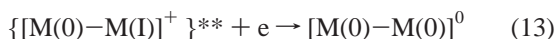
These findings indicate that, for mononuclear compounds, the reduction mechanism is the following:



where $M = \text{Re}$ or Mn and $P1$ is an unknown product.

Voltammetric patterns for the reduction of the binuclear compounds **11b** and $[\{\text{Mn}(\text{CO})_3(\text{PPh}_2\text{OEt})_2\}_2(\mu\text{-}4,4'\text{-HN}=\text{NC}_6\text{H}_4\text{-C}_6\text{H}_4\text{N}=\text{NH})](\text{BPh}_4)_2$ (**Mn₂**), recorded at $0.05 \leq \nu \leq 10$ V s^{-1} , are characterized by two irreversible reduction peaks; associated return peaks can only be detected at 30 V s^{-1} . At 0.05 V s^{-1} , E_{pf} values for the two peaks are -0.70 and -0.77 V for **11b** and -0.84 and -1.00 V for **Mn₂**. The change in voltammetric parameters with scan rate (E_{pf} values, appearance of return peaks, etc.) follows the same trend as that observed for the mononuclear compounds; a satisfactory fit between experimental and simulated data is achieved via mechanism (1)–(4), using the fitting parameters of Table 2.

These findings indicate that the following reduction mechanism is operative for the binuclear compounds:



where $M = \text{Re}$ or Mn , $\{[M(0)\text{-}M(I)]^+\}^*$ and $\{[M(0)\text{-}M(I)]^+\}^{**}$ are two forms of the mixed-valence complex in equilibrium with each other, and $P10$ is an unknown product.

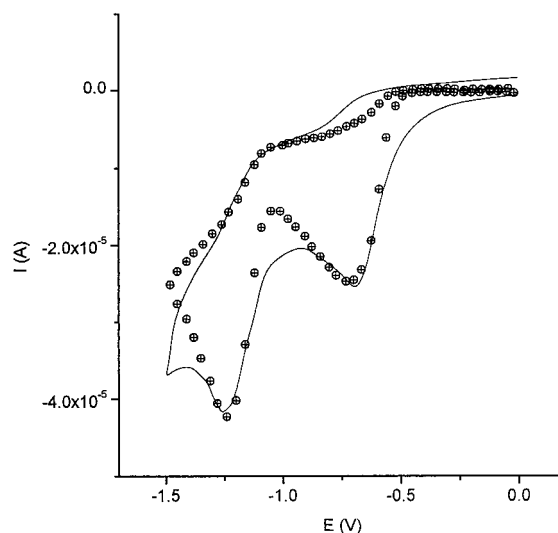


Figure 3. Experimental (full line) and simulated (dotted line) cyclic voltammograms obtained for 2×10^{-3} M $[\text{Re}(\text{CO})_3(\text{PPh}_2\text{OEt})_2(\mu\text{-}4,4'\text{-HN}=\text{NC}_6\text{H}_4\text{-C}_6\text{H}_4\text{N}=\text{NH})\text{RuH}\{\text{P}(\text{OEt})_3\}_4](\text{BPh}_4)_2$ (**Re₁₃Ru-b**) at 0.05 V s^{-1} . Supporting electrolyte: 0.1 M tetrabutylammonium hexafluorophosphate/dichloroethane. Working electrode: glassy carbon (area 0.2 cm^2). Potentials are referred to an aqueous Ag/AgCl reference electrode.

The chemical reactions coupled with the electron transfer could be proton-transfer reactions, isomeric equilibria, or (for reactions 10 and 14) simple decomposition reactions. In any case, they are well fitted in the simulations as simple first-order processes.

The main point is that, for both the Re and Mn binuclear compounds, the two electron-transfer processes take place at different potential values: delocalization of the electron between the two metal centers makes the first reduction process easier than in the case of the mononuclear compounds. Moreover, in the homobinuclear complex, the addition of the first electron makes the second reduction process more energy demanding. This situation is comparable to that observed previously for ruthenium–diazene binuclear complexes,^{3a} confirming that the ability to provide electronic communication between the two metal centers in the binuclear compounds is a property typical of the diazene ligand.

The importance of delocalization of the electron between the two redox centers via the diazene bridging ligand is also confirmed by the electrochemical behavior of heterobinuclear compounds containing rhenium–ruthenium or manganese–ruthenium redox centers. The full-line voltammogram of Figure 3 shows the pattern for the **Re₁₃Ru-b** heterobinuclear complex. The dotted-line voltammogram refers to data obtained by digital simulation (see Table 2 for fitting parameters). A similar pattern is observed for the **Mn₁₇Ru-b** binuclear complex (at 0.05 V s^{-1} the potentials of the two peaks are -0.81 and -1.29 V).

The first reduction process clearly involves the reduction of either rhenium or manganese, while the second reduction peak involves the ruthenium center.^{3a} At variance with results relevant to previously studied homobinuclear ruthenium complexes,^{3a} at all the scan rates employed in this work, the Ru reduction peak is irreversible (a broad reoxidation peak starts to appear at 30 V s^{-1}). This indicates that, in the heterobinuclear compounds, electron transfer to the Ru center is followed by a chemical reaction. At variance with Ru homobinuclear compounds,^{3a} the presence of a different metal center (Re or Mn) makes the reduction products more unstable, thus decreasing their lifetimes and hindering the possibility of observing their reoxidations on a voltammetric time scale.

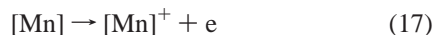
Electrochemical Oxidations of Aryldiazenido Complexes.

Results obtained from voltammetric studies of mono- and binuclear complexes with bis(aryldiazene) bridging ligands prompted us to extend investigations also to binuclear aryldiazenido complexes of manganese, with the aim of clarifying the different electrochemical behaviors observed between bis(aryldiazene) and bis(aryldiazenido) complexes of iron^{3c} and whether this behavior is typical of iron complexes or if it also involves other central metals.

Voltammetric patterns for electrochemical oxidations of the mononuclear Mn(C₆H₅N₂)(CO)₂(PPh₂OEt)₂ (**Mn**₃) and binuclear {Mn(CO)₂(PPh₂OEt)₂}₂(μ-4,4'-N₂C₆H₄-C₆H₄N₂) (**Mn**₄) compounds are characterized by an oxidation peak with which a small reduction peak (shifted toward much less positive potential values) is associated in the return scan. Values of the oxidation peak potentials at 0.05 V s⁻¹ are 0.680 and 0.570 V for the mononuclear and binuclear compounds, respectively. Both of these peak values shift toward more positive potential values with increasing scan rate; for instance, at 0.500 V s⁻¹ they are 0.940 V for **Mn**₃ and 0.670 V for **Mn**₄. Peak currents increase linearly with the square root of the scan rate; *I*_{pb}/*I*_{pr} values remain almost constant at 0.64–0.67, i.e. always much lower than unity, independent of the scan rate. All these findings, together with the satisfactory fitting with simulated voltammograms [see Table 3 and mechanisms (5)–(6) for simulation parameters], indicate that the charge-transfer process is irreversible. Comparison of the **Mn**₃ and **Mn**₄ oxidation peak currents indicates that the process for Mn(C₆H₅N₂)(CO)₂(PPh₂OEt)₂ is a one-electron oxidation, whereas that for the binuclear compound {Mn(CO)₂(PPh₂OEt)₂}₂(μ-4,4'-N₂C₆H₄-C₆H₄N₂) is a two-electron oxidation. The shape of the voltammogram (*E*_{pr} - *E*_{pr}/2 values, where *E*_{pr}/2 is the half-peak potential) and the fitting with mechanism (5)–(6) indicate that, as already observed for similar aryldiazenido compounds of iron,^{3c} oxidation of the binuclear complex of manganese is composed of two separate one-electron processes, in which the two Mn centers behave as localized redox centers not interacting with each other. Under these conditions, the peak parameters are the same as those for a one-electron-transfer process, the only difference being an increase in peak current.^{31,32} The scheme for oxidation of the binuclear compound that matches experimental and simulated voltammograms is



In the case of the mononuclear compound Mn(C₆H₅N₂)(CO)₂(PPh₂OEt)₂, oxidation is limited to the one-electron irreversible process



Comparison of aryldiazenido-Mn(-I) compound data with those for the Fe(0) complexes studied previously^{3c} reveals that oxidations of Mn complexes occur at less positive potential values. This may be explained by the fact that the starting Mn

complexes were neutral species, whereas the Fe complexes studied in ref 3c were cationic. Moreover, electrochemical oxidations of Mn compounds are less irreversible than those of Fe compounds, as evidenced by both the presence of small return peaks and the *k*_s values used in the simulations which, for Mn complexes, are roughly 1 order of magnitude higher than those obtained previously for the Fe case.^{3c}

It must be emphasized that oxidation of diazenido binuclear complexes with both Fe(0) and Mn(-I) metal centers proceeds in such a way that each metal center does not show any interaction with the other metal center of the same molecule, since both centers are oxidized at potential values which may be compared with each other as well as with that of the mononuclear compound. These results contrast with those observed for binuclear bis(aryldiazene) complexes of Fe(II),^{3a} Ru(II),^{3a} Mn(I),^{3b} and Re(I) and may be attributed to the different electronic properties of the aryldiazenido N≡NAr-ArN≡N (singly bent coordination)^{3b,c} as compared to the aryldiazene HN=NAr-ArN=NH bridging ligand, which prevent electronic communication between the two metal centers in bis(aryldiazenido) derivatives.

Conclusions

The present studies show that aryldiazene complex cations of rhenium of the types [Re(ArN=NH)(CO)_{5-n}P_n]⁺ and [{Re(CO)_{5-n}P_n}₂(μ-HN=NAr-ArN=NH)]²⁺ may easily be prepared by insertions of mono- and bis(aryldiazonium) cations into the Re-H bonds of the hydride species ReH(CO)_{5-n}P_n. The first "diazene-diazonium" derivatives [M(CO)_{5-n}P_n(HN=NAr-ArN≡N)]²⁺ (M = Re, Mn) were prepared through the insertions of only one -N≡N group of the bis(aryldiazonium) cations [N≡NAr-ArN≡N]²⁺ into the MH(CO)_{5-n}P_n hydrides containing bulky phosphite ligands. These diazene-diazonium derivatives are building blocks for heterobinuclear **M1**-**M2** and heterotrimeric **M1**-M-**M2** complexes with bis(aryldiazene) bridging ligands. In fact, the reactions of [**M1**(CO)_{5-n}P_n(HN=NAr-ArN≡N)]²⁺ with **M2**H₂P'₄ or **M2**'H(CO)₃P''₂ metal hydrides allow several examples of this new class of bi- and trinuclear complexes, of the type Re-Ru, Re-Os, Mn-Ru, Ru-Mn, Re-Ru-Mn, etc., to be prepared. Furthermore, syntheses of the heterobinuclear complexes incorporating a bis(aryldiazenido) bridging ligand [Mn(CO)₂P₂(μ-N₂Ar-ArN₂)-FeP'₄]BPh₄ were also achieved, together with syntheses of the "diazene-diazenido" [Re(CO)₃P₂(μ-HN=NAr-ArN≡N)Fe(CO)₂P'₂]²⁺ cationic species. Finally, the structural parameters of an aryldiazene complex of rhenium were determined and electrochemical studies were conducted for both mono- and binuclear derivatives prepared in this work.

Acknowledgment. The financial support of MURST, Rome (Programmi di Ricerca Scientifica di Rilevante Interesse Nazionale, Cofinanziamento 1998/99), is gratefully acknowledged. We thank Daniela Baldan and Danilo Rudello for technical assistance.

Supporting Information Available: An X-ray crystallographic file, in CIF format for **1a**, complete lists of IR and NMR data for all complexes (Table S1), infrared spectra of **13b** and **13b*** (Figure S1), and cyclic voltammograms of **5a** and **11b** (Figure S2) and **Mn**₃ and **Mn**₄ (Figure S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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