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Article

Tautomerization of Methyldiazene to Formaldehyde-Hydrazone in Ruthenium and Osmium Complexes

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Mixed-ligand hydrazine complexes $[M(CO)(RNHNH_2)P_4](BPh_4)_2$ (**1**, **2**) [M = Ru, Os; R = H, CH_3, C_6H_5; P = $P(OEt)_3$] with carbonyl and triethyl phosphite were prepared by allowing hydride $[MH(CO)P_4]BPh_4$ species to react first with $HBF_4{\cdot}Et_2O$ and then with hydrazines. Depending on the nature of the hydrazine ligand, the oxidation of $[M(CO)(RNHNH_2)P_4](BPh_4)_2$ derivatives with $Pb(OAc)_4$ at –30 °C gives acetate $[M(\kappa^1\text{-}OCOCH_3)(CO)P_4]BPh_4$ (**3a**), phenyldiazene $[M(CO)(C_6H_5N{=}NH)P_4](BPh_4)_2$ (**3c**, **4c**), and methyldiazene $[M(CO)(CH_3N{=}NH)P_4](BPh_4)_2$ (**3b**, **4b**) derivatives. Methyldiazene complexes **3b** and **4b** undergo base-catalyzed tautomerization of the $CH_3N{=}NH$ ligand to formaldehyde-hydrazone $NH_2N{=}CH_2$, giving the $[M(CO)(NH_2N{=}CH_2)P_4](BPh_4)_2$ (**5**, **6**) derivatives. Complexes **5** and **6** were characterized spectroscopically and by the X-ray crystal structure determination of the $[Ru(CO)(NH_2N{=}CH_2)\{P(OEt)_3\}_4](BPh_4)_2$ (**5**) derivative. Acetone-hydrazone $[M(CO)\{NH_2N{=}C(CH_3)_2\}P_4](BPh_4)_2$ (**7**, **8**) complexes were also prepared by allowing hydrazine $[M(CO)(NH_2NH_2)P_4](BPh_4)_2$ derivatives to react with acetone.

Introduction

The chemistry of coordinate diazene (NH=NH or RN=NH) has been extensively developed in the past 20 years, and a number of related transition metal complexes have been reported.[1,2] Interest in these studies stems not only from the different coordination modes and chemical reactivities that this class of compounds may exhibit[1,2] but also from the possible relevance of coordinate diazenes in inorganic and bioinorganic N_2-reducing systems.[3]

In the free state, diazenes are reactive and thermally unstable molecules which decompose with the evolution of nitrogen at room temperature.[4] Coordination on a metal fragment strongly enhances their stability and often leads to new properties.[1,2] Among these, we can highlight the easy deprotonation of the diazene hydrogen atom to give a diazenido $[M]{\cdots}N{\equiv}N{-}R$ derivative[1a,2b,2j,5] and the reduction to hydrazine or NH_3 under mild conditions.[1a,6] Tautomerization of a coordinate methyldiazene to give the hydrazone $[W(NH_2N{=}CH_2)(CO)_2(NO)(PPh_3)_2]^+$ complex has also been described,[7] but no experimental data for this reaction and

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(1) (a) Sutton, D. *Chem. Rev.* **1993**, *93*, 995–1022. (b) Kisch, H.; Holzmeier, P. *Adv. Organomet. Chem.* **1992**, *34*, 67–109. (c) Zollinger, H., Ed. *Diazo Chemistry II*; VCH: Weinheim, Germany, 1995.

(2) For some papers on coordinate diazene, see: (a) Sellmann, D.; Brandl, A.; Endell, R. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 1019. (b) Albertin, G.; Antoniutti, S.; Pelizzi, G.; Vitali, F.; Bordignon, E. *J. Am. Chem. Soc.* **1986**, *108*, 6627–6634. (c) Smith, M. R., III; Hillhouse, G. L. *J. Am. Chem. Soc.* **1988**, *110*, 4066–4068. (d) Sellmann, D.; Soglowek, W.; Knoch, F.; Moll, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1271–1272. (e) Collmann, J. P.; Hutchinson, J. E.; Lopez, M. A.; Guilard, R.; Reed, R. A. *J. Am. Chem. Soc.* **1991**, *113*, 2794–2796. (f) Sellmann, D.; Käppler, J.; Moll, M.; Knoch, F. *Inorg. Chem.* **1993**, *32*, 960–964. (g) Smith, M. R., III; Cheng, T.-Y.; Hillhouse, G. L. *J. Am. Chem. Soc.* **1993**, *115*, 8638–8642. (h) Cheng, T.-Y.; Ponce, A.; Rheingold, A. L.; Hillhouse, G. L. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 657–659. (i) Cheng, T.-Y.; Peters, J. C.; Hillhouse, G. L. *J. Am. Chem. Soc.* **1994**, *116*, 204–207. (j) Albertin, G.; Antoniutti, S.; Bacchi, A.; Bordignon, E.; Busatto, F.; Pelizzi, G. *Inorg. Chem.* **1997**, *36*, 1296–1305. (k) Sellmann, D.; Engl, K.; Heinemann, F. W.; Sieler, J. *Eur. J. Inorg. Chem.* **2000**, 1079–1089.

(3) (a) MacKay, B. A.; Fryzuk, M. D. *Chem. Rev.* **2004**, *104*, 385–401. (b) Fryzuk, M. D.; Johnson, S. A. *Coord. Chem. Rev.* **2000**, *200–202*, 379–409. (c) Hidai, M.; Mizobe, Y. *Chem. Rev.* **1995**, *95*, 1115–1133. (d) Sellmann, D.; Sutter, J. *Acc. Chem. Res.* **1997**, *30*, 460–469. (e) Malinak, S. M.; Coucouvanis, D. *Prog. Inorg. Chem.* **2001**, *49*, 599–662.

(4) (a) Wiberg, N.; Bachhuber, H.; Fischer, G. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 829. (b) Patai, S., Ed. *The Chemistry of Hydrazo, Azo, and Azoxy Groups*; Wiley: New York, 1975.

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for the resulting hydrazone complex were provided. We now report the first documented example of base-catalyzed tautomerization of a coordinate methyldiazene to formaldehyde-hydrazone, giving the corresponding $[M]{-}NH_2N{=}CH_2$ derivative.

Our interest in the chemistry of "diazo" complexes has been extensively devoted to the synthesis and the reactivity of hydrazine and diazene complexes of the iron triad[2b,8] stabilized by $P(OEt)_3$ and $PPh(OEt)_2$ phosphite ligands of the $[M(RNHNH_2)_2P_4]^{2+}$, $[M(RNHNH_2)P_5]^{2+}$, $[M(RN{=}NH)_2P_4]^{2+}$, and $[M(RN{=}NH)P_5]^{2+}$ ($M = Ru, Os$; $R = H, CH_3, C_6H_5$) types. Recently,[2j,6c,9] we have shown that Mn(I) and Re(I) also form stable hydrazine and diazene complexes of the $[M(RNHNH_2)(CO)_nP_{5-n}]^+$ and $[M(RN{=}NH)(CO)_nP_{5-n}]^+$ (P = phosphite; $n = 1-4$) types which, in part, parallel the chemistry of the isoelectronic d^6 ruthenium and osmium diazo species, while also exhibiting new properties, unknown for the related Ru(II) and Os(II) derivatives. This unusual reactivity of Mn(I) and Re(I) diazo complexes may be attributed to the presence of the strong π-acceptor carbonyl ligands, which modify the properties of the mixed-ligand $M(CO)_nP_{5-n}$ fragment bonded to the diazo molecule. We, therefore, decided to extend our studies on diazo complexes by introducing a carbonyl ligand into the chemistry of Ru(II) and Os(II) derivatives with the aim of testing how this ligand may change the properties of coordinate diazo molecules.

The results of these studies, which involve the synthesis of new hydrazine and diazene complexes and the first well-characterized example of tautomerization of methyldiazene to formaldehyde-hydrazone in a metal complex, are reported here.

Experimental Section

General Comments. All synthetic work was carried out in an appropriate atmosphere (Ar, 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 stored in 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. $RuCl_3 \cdot 3H_2O$ and $(NH_4)_2OsCl_6$ salts were Pressure (USA) products, used as received. Phosphine $PPh(OEt)_2$ was prepared by the method of Rabinowitz and Pellon,[10] while $P(OEt)_3$ was an Aldrich product purified by distillation under nitrogen. Diazonium salts were prepared in the usual way.[11] Hydrazine NH_2NH_2 was prepared by the decomposition of hydrazine cyanurate (Fluka), following the reported method.[12] High-grade (99.99%) lead(IV) acetate was purchased from Aldrich. The other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on Nicolet Magna 750 FT-IR or Perkin-Elmer Spectrum One spectrophotometers. NMR spectra (^1H, ^{31}P, and ^{13}C) were obtained on AC200 or AVANCE 300 Bruker spectrometers at temperatures between −90 and +30 °C, unless otherwise noted. The COSY, NOESY, HMQC, and HMBC NMR experiments were performed using their standard programs. ^1H and ^{13}C spectra are referred to internal tetramethylsilane; $^{31}P\{^1H\}$ chemical shifts are reported with respect to 85% H_3PO_4 with downfield shifts considered positive. The SwaN-MR software package[13] was used to treat NMR data. The conductivities of 10^{-3} mol dm^{-3} solutions of the complexes in CH_3NO_2 at 25 °C were measured with a Radiometer CDM 83.

Syntheses of the Complexes. Hydrides RuH_2P_4 and OsH_2P_4 [$P = P(OEt)_3$, $PPh(OEt)_2$] were prepared following previously reported methods.[14,15] The hydride-carbonyl $[MH(CO)P_4]BPh_4$ complexes [$M = Ru, Os$; $P = P(OEt)_3$] were prepared by a modification of the method reported for the related $[RuH(CO)\{PPh(OEt)_2\}_4]BPh_4$ derivative,[16] as follows:

(A) $[RuH(CO)\{P(OEt)_3\}_4]BPh_4$. An equimolar amount of triflic acid (0.26 mmol, 23 μL) was added to a solution of $RuH_2[P(OEt)_3]_4$ (0.26 mmol, 0.200 g) in 10 mL of ethanol cooled to −196 °C and placed under a CO atmosphere (1 atm). The reaction mixture was brought to room temperature and stirred for about 2 h, and then, the solvent was removed under reduced pressure. The oil obtained was triturated with ethanol (2 mL) containing an excess of $NaBPh_4$ (0.52 mmol, 0.18 g). A white solid slowly separated out and was filtered and crystallized from CH_2Cl_2 and ethanol. Yield ≥ 90%. Anal. Calcd for $C_{49}H_{81}BO_{13}P_4Ru$: C, 52.83; H, 7.33. Found: C, 53.05; H, 7.49. $\Lambda_M = 50.4\ \Omega^{-1}\ mol^{-1}\ cm^2$. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.40−6.85 (m, 20 H, Ph), 4.10−3.90 (m, 24 H, CH_2), 1.33, 1.31 (t, 36 H, CH_3), −8.52 to −8.95 (m, 1 H, RuH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: A_2BC spin syst, δ_A 137.2, δ_B 136.3, δ_C 136.0, $J_{AB} = 43.7$, $J_{AC} = 65.5$, $J_{BC} = 50.5$. IR (KBr) cm^{-1}: 2032 s (νCO), 1890 s (νRuH).

(B) $[OsH(CO)\{P(OEt)_3\}_4]BPh_4$. An equimolar amount of methyltriflate, $CF_3SO_3CH_3$ (0.26 mmol, 29 μL), was added to a solution of $OsH_2[P(OEt)_3]_4$ (0.26 mmol, 0.22 g) in 10 mL of toluene cooled to −196 °C and placed under a CO atmosphere (1 atm). The reaction mixture was brought to room temperature and stirred for about 2 h, and then, the solvent was removed under reduced pressure. The oil obtained was triturated with ethanol (2 mL) containing an excess of $NaBPh_4$ (0.52 mmol, 0.18 g). A white solid slowly separated out and was filtered and crystallized from CH_2Cl_2 and ethanol. Yield ≥ 90%. Anal. Calcd for

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(5) (a) Haymore, B. L.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 2784−2795. (b) Laing, K. R.; Robinson, S. D.; Uttley, M. F. *J. Chem. Soc., Chem. Commun.* **1973**, 176−177.

(6) (a) Parshall, G. W. *J. Am. Chem. Soc.* **1967**, *89*, 1822−1826. (b) Schrock, R. R.; Glassman, T. E.; Vale, M. G. *J. Am. Chem. Soc.* **1991**, *113*, 725−726. (c) Albertin, G.; Antoniutti, S.; Giorgi, M. T. *Eur. J. Inorg. Chem.* **2003**, 2855−2866.

(7) Smith, M. R., III; Keys, R. L.; Hillhouse, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 8312−8314.

(8) (a) Albertin, G.; Antoniutti, S.; Pelizzi, G.; Vitali, F.; Bordignon, E. *Inorg. Chem.* **1988**, *27*, 829−835. (b) Albertin, G.; Antoniutti, S.; Bacchi, A.; Bordignon, E.; Pelizzi, G.; Ugo, P. *Inorg. Chem.* **1996**, *35*, 6245−6253. (c) Albertin, G.; Antoniutti, S.; Bacchi, A.; Bordignon, E.; Dolcetti, P. M.; Pelizzi, G. *J. Chem. Soc., Dalton Trans.* **1997**, 4435−4444. (d) Albertin, G.; Antoniutti, S.; Bacchi, A.; Bergamo, M.; Bordignon, E.; Pelizzi, G. *Inorg. Chem.* **1998**, *37*, 479−489. (e) Albertin, G.; Antoniutti, S.; Bacchi, A.; Boato, M.; Pelizzi, G. *J. Chem. Soc., Dalton Trans.* **2002**, 3313−3320.

(9) (a) Albertin, G.; Antoniutti, S.; Bacchi, A.; Ballico, G. B.; Bordignon, E.; Pelizzi, G.; Ranieri, M.; Ugo, P. *Inorg. Chem.* **2000**, *39*, 3265−3279. (b) Albertin, G.; Antoniutti, S.; Bordignon, E.; Perinello, G. *J. Organomet. Chem.* **2001**, *625*, 217−230. (c) Albertin, G.; Antoniutti, S.; Bacchi, A.; Bordignon, E.; Giorgi, M. T.; Pelizzi, G. *Angew. Chem., Int. Ed.* **2002**, *41*, 2192−2194.

(10) Rabinowitz, R.; Pellon, J. *J. Org. Chem.* **1961**, *26*, 4623−4626.

(11) Vogel, A. I. *Practical Organic Chemistry*, 3rd ed.; Longmans, Green and Co.: New York, 1956.

(12) Nachbaur, E.; Leiseder, G. *Monatsh. Chem.* **1971**, *102*, 1718−1723.

(13) Balacco, G. *J. Chem. Inf. Comput. Sci.* **1994**, *34*, 1235−1241.

(14) Peet, W. G.; Gerlach, D. H. *Inorg. Synth.* **1974**, *15*, 38−42. Gerlach, D. H.; Peet, W. G.; Muetterties, E. L. *J. Am. Chem. Soc.* **1972**, *94*, 4545−4549.

(15) Albertin, G.; Antoniutti, S.; Bordignon, E. *J. Chem. Soc., Dalton Trans.* **1989**, 2353−2358.

(16) Amendola, P.; Antoniutti, S.; Albertin, G.; Bordignon, E. *Inorg. Chem.* **1990**, *29*, 318−324.

$C_{49}H_{81}BO_{13}OsP_4$: C, 48.92; H, 6.79. Found: C, 48.74; H, 6.80. $\Lambda_M = 49.5\ \Omega^{-1}\ mol^{-1}\ cm^2$. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.31−6.87 (m, 20 H, Ph), 4.01 (m, 24 H, CH_2), 1.31 (t, 36 H, CH_3), −10.61 (m, 1 H, OsH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −70 °C) δ: ABC_2 spin syst, δ_A 99.0, δ_B 98.0, δ_C 96.6, $J_{AB} = 47.7$, $J_{AC} = 32.0$, $J_{BC} = 33.5$. IR (KBr) cm^{-1}: 2012 s (νCO).

(C) [M(CO)(RNHNH$_2$){P(OEt)$_3$}$_4$](BPh$_4$)$_2$ (1, 2) [M = Ru (1), Os (2); R = H (a), CH$_3$ (b), C$_6$H$_5$ (c)]. An excess of $HBF_4 \cdot Et_2O$ (0.72 mmol, 104 μL of a 54% solution in diethyl ether) was added to a solution of the appropriate $[MH(CO)\{P(OEt)_3\}_4]BPh_4$ hydride (0.18 mmol) in 10 mL of CH_2Cl_2 cooled to −196 °C. A large excess of the appropriate hydrazine $RNHNH_2$ (1.8 mmol) was added, and the solution was brought to room temperature and stirred for 24 h. The solvent was removed under reduced pressure to give an oil which was triturated with ethanol (2 mL) containing an excess of $NaBPh_4$ (0.54 mmol, 0.185 g). A white solid slowly separated out and was filtered and crystallized from CH_2Cl_2 and ethanol. Yield from 55 to 68%. (**1a**) Anal. Calcd for $C_{73}H_{104}B_2N_2O_{13}P_4Ru$: C, 59.88; H, 7.16; N, 1.91. Found: C, 59.79; H, 7.20; N, 1.95. $\Lambda_M = 114.5\ \Omega^{-1}\ mol^{-1}\ cm^2$. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.40−6.88 (m, 40 H, Ph), 4.10 (m, 24 H, CH_2), 3.92 (m, br, 2 H, $RuNH_2$), 2.45 (m, br, 2 H, NH_2), 1.39, 1.37, 1.33 (t, 36 H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB_2C spin syst, δ_A 124.1, δ_B 114.5, δ_C 111.6, $J_{AB} = 51.6$, $J_{AC} = 58.3$, $J_{BC} = 65.4$. IR (KBr) cm^{-1}: 3342 m, 3322 m, 3260 sh, 3256 m (νNH), 2065 s (νCO). (**1b**) Calcd for $C_{74}H_{106}B_2N_2O_{13}P_4Ru$: C, 60.13; H, 7.23; N, 1.90. Found: C, 59.98; H, 7.26; N, 1.87. $\Lambda_M = 120.2\ \Omega^{-1}\ mol^{-1}\ cm^2$. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.33−6.85 (m, 40 H, Ph), 4.37 (br, 2 H, NH_2), 4.17, 4.05 (m, 24 H, CH_2), 3.27 (q, br, 1 H, NH), 2.58 (d, 3 H, CH_3N, $J_{HH} = 6$ Hz), 1.38, 1.36, 1.34 (t, 36 H, CH_3 phos). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB_2C spin syst, δ_A 123.5, δ_B 114.1, δ_C 110.9, $J_{AB} = 53.6$, $J_{AC} = 55.4$, $J_{BC} = 66.2$. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 191.8 (m, CO), 165−122 (m, Ph), 65.5 (m, CH_2), 44.7 (s, CH_3N), 16.3 (m, CH_3 phos). IR (KBr) cm^{-1}: 3316 m, 3296 m, 3263 m (νNH), 2060 s (νCO). (**1c**) Calcd for $C_{79}H_{108}B_2N_2O_{13}P_4Ru$: C, 61.60; H, 7.07; N, 1.82. Found: C, 61.79; H, 7.15; N, 1.75. $\Lambda_M = 119.8\ \Omega^{-1}\ mol^{-1}\ cm^2$. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.44−6.72 (m, 45 H, Ph), 5.16 (m, br, 1 H, NH), 5.12 (m, br, 2 H, NH_2), 4.10 (m, 24 H, CH_2), 1.34, 1.32 (t, 36 H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB_2C spin syst, δ_A 122.4, δ_B 113.8, δ_C 110.2, $J_{AB} = 53.9$, $J_{AC} = 56.6$, $J_{BC} = 65.3$. IR (KBr) cm^{-1}: 3337 m, 3304 w, 3275 m (νNH), 2063 s (νCO). (**2a**) Calcd for $C_{73}H_{104}B_2N_2O_{13}OsP_4$: C, 56.45; H, 6.75; N, 1.80. Found: C, 56.55; H, 6.81; N, 1.85. $\Lambda_M = 117.2\ \Omega^{-1}\ mol^{-1}\ cm^2$. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.36−6.87 (m, 40 H, Ph), 4.38 (m, br, 2 H, $OsNH_2$), 4.21−4.00 (m, 24 H, CH_2), 2.64 (m, br, 2 H, NH_2), 1.38, 1.36 (t, 36 H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB_2C spin syst, δ_A 80.5, δ_B 77.9, δ_C 77.1, $J_{AB} = 54.9$, $J_{AC} = 43.8$, $J_{BC} = 36.9$. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 176.1 (m, CO), 163−122 (m, Ph), 65.3, 64.5 (m, CH_2), 16.2 (m, CH_3). IR (KBr) cm^{-1}: 3340 m, 3312 m, 3262 m (νNH), 2037 s (νCO). (**2b**) Calcd for $C_{74}H_{106}B_2N_2O_{13}OsP_4$: C, 56.71; H, 6.82; N, 1.79. Found: C, 56.58; H, 7.00; N, 1.75. $\Lambda_M = 123.5\ \Omega^{-1}\ mol^{-1}\ cm^2$. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.37−6.87 (m, 40 H, Ph), 4.84 (m, br, 2 H, NH_2), 4.18 (m), 4.05 (qnt, 24 H, CH_2), 3.35 (m, 1 H, NH), 2.56 (d, 3 H, CH_3N, $J_{HH} = 6$ Hz), 1.38, 1.35, 1.33 (t, 36 H, CH_3 phos). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB_2C spin syst, δ_A 79.5, δ_B 77.4, δ_C 76.3, $J_{AB} = 54.7$, $J_{AC} = 43.7$, $J_{BC} = 37.3$. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 176.4 (m, CO), 163−122 (m, Ph), 65.7, 64.9 (m, CH_2), 44.9 (m, CH_3N), 16.3 (m, CH_3 phos). IR (KBr) cm^{-1}: 3308 m, 3298 w, 3261 m (νNH), 2045 s (νCO). (**2c**) Calcd for $C_{79}H_{108}B_2N_2O_{13}OsP_4$: C, 58.23; H, 6.68; N, 1.72. Found: C, 57.99; H, 6.84; N, 1.70. $\Lambda_M = 115.6\ \Omega^{-1}\ mol^{-1}\ cm^2$. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.40−6.81 (m, 45 H, Ph), 5.60 (m, br, 1 H, NH), 5.19 (m, br, 2 H, NH_2), 4.08 (m, 24 H, CH_2), 1.36, 1.33 (t, 36 H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB_2C spin syst, δ_A 78.5, δ_B 76.6, δ_C 73.9, $J_{AB} = 56.4$, $J_{AC} = 42.0$, $J_{BC} = 37.5$. IR (KBr) cm^{-1}: 3318 w, 3298 m (νNH), 2040 s (νCO).

(D) [M(CO)(C$_6$H$_5$N=NH){P(OEt)$_3$}$_4$](BPh$_4$)$_2$ (3c, 4c) [M = Ru (3), Os (4)]. A solid sample of the phenylhydrazine $[M(CO)(C_6H_5NHNH_2)\{P(OEt)_3\}_4](BPh_4)_2$ complex (0.135 mmol) was placed in a three-necked 25-mL flask fitted with a solid-addition sidearm containing $Pb(OAc)_4$ (0.135 mmol, 60 mg). The apparatus was evacuated, CH_2Cl_2 (10 mL) was added, the solution was cooled to −30 °C, and $Pb(OAc)_4$ was added portionwise over 10−20 min to the cold stirring solution. The reaction mixture was then allowed to warm to 0 °C and was stirred for 20 min, and then, the solvent was removed under reduced pressure. The oil obtained was treated at 0 °C with ethanol (2 mL) containing $NaBPh_4$ (0.27 mmol, 92 mg). A white solid slowly separated out and was filtered and twice crystallized from CH_2Cl_2 and ethanol. Yield ≥ 65%. (**3c**) Anal. Calcd for $C_{79}H_{106}B_2N_2O_{13}P_4Ru$: C, 61.68; H, 6.95; N, 1.82. Found: C, 61.55; H, 7.03; N, 1.75. $\Lambda_M = 116.4\ \Omega^{-1}\ mol^{-1}\ cm^2$. ^1H NMR (CD_2Cl_2, 25 °C) δ: 13.19 (m, 1 H, NH), 7.80−6.88 (m, 45 H, Ph), 4.21−4.00 (m, 24 H, CH_2), 1.38, 1.26 (t, 36 H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB_2C spin syst, δ_A 123.3, δ_B 112.3, δ_C 110.1, $J_{AB} = 52.7$, $J_{AC} = 60.0$, $J_{BC} = 65.1$. IR (KBr) cm^{-1}: 2065 s (νCO). (**4c**) Calcd for $C_{79}H_{106}B_2N_2O_{13}OsP_4$: C, 58.30; H, 6.56; N, 1.72. Found: C, 58.15; H, 6.69; N, 1.75. $\Lambda_M = 120.8\ \Omega^{-1}\ mol^{-1}\ cm^2$. ^1H NMR (CD_2Cl_2, 25 °C) δ: 13.56 (m, br, 1 H, NH), 7.40−6.86 (m, 45 H, Ph), 4.10 (m, 24 H, CH_2), 1.37, 1.35 (t, 36 H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB_2C spin syst, δ_A 79.6, δ_B 77.1, δ_C 75.4, $J_{AB} = 55.8$, $J_{AC} = 43.6$, $J_{BC} = 38.6$. IR (KBr) cm^{-1}: 2042 s (νCO).

(E) [Ru(κ^1-OCOCH$_3$)(CO){P(OEt)$_3$}$_4$]BPh$_4$ (3a). This complex was obtained from the oxidation of the $[Ru(CO)(NH_2NH_2)\{P(OEt)_3\}_4](BPh_4)_2$ (**1a**) hydrazine complex with $Pb(OAc)_4$ following the method reported above for the related $C_6H_5NHNH_2$ derivatives. Yield ≥ 70%. Anal. Calcd for $C_{51}H_{83}BO_{15}P_4Ru$: C, 52.27; H, 7.14. Found: C, 52.39; H, 7.22. $\Lambda_M = 51.8\ \Omega^{-1}\ mol^{-1}\ cm^2$. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.35−6.94 (m, 20 H, Ph), 4.22−3.98 (m, 24 H, CH_2), 1.92 (s, 3 H, CH_3COO), 1.34, 1.31, 1.29 (t, 36 H, CH_3 phos). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: ABC_2 spin syst, δ_A 129.5, δ_B 120.8, δ_C 120.7, $J_{AB} = 62.7$, $J_{AC} = 54.2$, $J_{BC} = 53.2$. IR (KBr) cm^{-1}: 2058 s (νCO), 1615 m (νCOO).

(F) [M(CO)(CH$_3$N=NH){P(OEt)$_3$}$_4$](BPh$_4$)$_2$ (3b, 4b) [M = Ru (3), Os (4)]. A solid sample of the methylhydrazine $[M(CO)(CH_3NHNH_2)\{P(OEt)_3\}_4](BPh_4)_2$ complex (0.2 mmol) was placed in a three-necked 25-mL flask fitted with a solid-addition sidearm containing $Pb(OAc)_4$ (0.2 mmol, 89 mg). The apparatus was evacuated, CH_2Cl_2 (10 mL) was added, the solution was cooled to −30 °C, and $Pb(OAc)_4$ was added portionwise over 10−20 min to the cold stirring solution. The reaction mixture was then allowed to warm to 0 °C and was stirred for 20 min, and then, the solvent was removed under reduced pressure at 0 °C. The oil obtained was treated at the same temperature with ethanol (2 mL) containing $NaBPh_4$ (0.4 mmol, 137 mg). A pale-yellow solid slowly separated out and was filtered and dried under vacuum. Crystallization by cooling to −25 °C of a saturated solution of the solid in CH_2Cl_2 and ethanol prepared at 0 °C gave white microcrystals of pure methyldiazene derivative. Yield ≥ 60%. (**3b**) Anal. Calcd for $C_{74}H_{104}B_2N_2O_{13}P_4Ru$: C, 60.21; H, 7.10; N, 1.90. Found: C, 60.18; H, 7.22; N, 1.85. $\Lambda_M = 118.6\ \Omega^{-1}\ mol^{-1}\ cm^2$. ^1H NMR (CD_2Cl_2, 25 °C) δ: 13.04 (d, br, 1 H, NH), 7.40−6.89 (m, 40 H, Ph), 4.20−4.00 (m, 24 H, CH_2), 3.75 (s, 3 H, CH_3N), 1.35, 1.32 (t, 36 H, CH_3 phos). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB_2C spin syst, δ_A 123.5,

δ_B 112.3, δ_C 109.7, J_{AB} = 52.8, J_{AC} = 58.3, J_{BC} = 65.6. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 191.3 (m, CO), 164−135 (m, Ph), 68.6 (s, $CH_3N{=}$), 65.5 (m, CH_2), 16.4 (m, CH_3 phos). IR (KBr) cm^{-1}: 2050 s (νCO). (**4b**) Calcd for $C_{74}H_{104}B_2N_2O_{13}OsP_4$: C, 56.78; H, 6.70; N, 1.79. Found: C, 56.91; H, 6.88; N, 1.75. Λ_M = 115.9 Ω^{-1} mol^{-1} cm^2. ^1H NMR (CD_2Cl_2, 25 °C) δ: 13.45 (s, br, 1 H, NH), 7.32−6.86 (m, 40 H, Ph), 4.10 (m, 24 H, CH_2), 3.72 (s, 3 H, CH_3N), 1.38, 1.36, 1.34 (t, 36 H, CH_3 phos). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB_2C spin syst, δ_A 82.9, δ_B 78.7, δ_C 74.2, J_{AB} = 51.1, J_{AC} = 40.5, J_{BC} = 39.0. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 171.2 (m, CO), 165−122 (m, Ph), 68.4 (s, $CH_3N{=}$), 65.8 (m), 63.8 (d, CH_2), 16.3 (m, CH_3 phos). IR (KBr) cm^{-1}: 2037 s (νCO).

(G) [M(CO)($NH_2N{=}CH_2$){$P(OEt)_3$}$_4$](BPh_4)$_2$ (5, 6) [M = Ru (5), Os (6)]. Triethylamine (0.03 mmol, 4 μL) was added to a solution of [M(CO)($CH_3N{=}NH$){$P(OEt)_3$}$_4$](BPh_4)$_2$ (**3b**, **4b**) methyldiazene complex (0.135 mmol) in 10 mL of CH_2Cl_2 cooled to −196 °C. The reaction mixture was then brought to 0 °C and stirred for 30 min. The solvent was removed under reduced pressure, giving an oil which was triturated with ethanol (2 mL) at 0 °C. A pale-pink solid slowly separated out and was filtered and crystallized from CH_2Cl_2 and ethanol. Yield ≥ 92%. (**5**) Anal. Calcd for $C_{74}H_{104}B_2N_2O_{13}P_4Ru$: C, 60.21; H, 7.10; N, 1.90. Found: C, 60.08; H, 7.23; N, 1.95. Λ_M = 124.4 Ω^{-1} mol^{-1} cm^2. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.34−6.86 (m, 40 H, Ph), AB spin syst δ_A 6.74, δ_B 6.60, J_{AB} = 9.3 Hz (2 H, $={CH_2}$), 5.86 (s, br, 2 H, NH_2), 4.12 (m, 24 H, CH_2 phos), 1.38, 1.35 (t, 36 H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB_2C spin syst, δ_A 124.0, δ_B 114.6, δ_C 111.4, J_{AB} = 52.5, J_{AC} = 56.5, J_{BC} = 66.1. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 193.5 (m, CO), 149.2 (s, $={CH_2}$), 165−122 (m, Ph), 65.0 (m, CH_2 phos), 16.3 (m, CH_3). IR (KBr) cm^{-1}: 3310 m (νNH), 2064 s (νCO). (**6**) Calcd for $C_{74}H_{104}B_2N_2O_{13}OsP_4$: C, 56.78; H, 6.70; N, 1.79. Found: C, 56.59; H, 6.81; N, 1.78. Λ_M = 119.6 Ω^{-1} mol^{-1} cm^2. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.33−6.85 (m, 40 H, Ph), AB spin syst δ_A 6.60, δ_B 6.49, J_{AB} = 9.1 Hz (2 H, $={CH_2}$), 6.26 (s, br, 2 H, NH_2), 4.00 (m, 24 H, CH_2 phos), 1.37, 1.35, 1.32 (t, 36 H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB_2C spin syst, δ_A 79.7, δ_B 77.7, δ_C 74.8, J_{AB} = 55.3, J_{AC} = 42.6, J_{BC} = 37.5. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 177.2 (m, CO), 150.6 (s, $={CH_2}$), 165−122 (m, Ph), 65.7 (m), 64.9 (d, CH_2 phos), 16.2 (m, CH_3). IR (KBr) cm^{-1}: 3298 m, 3261 w (νNH), 2050 s (νCO).

Suitable crystals for X-ray analysis were obtained by slow cooling from 20 to −25 °C of a solution of complex **5** (100 mg) prepared by adding 10 mL of ethanol and enough CH_2Cl_2 to obtain a saturated solution at room temperature.

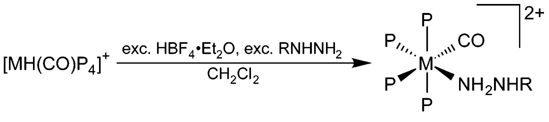
(H) [M(CO){$NH_2N{=}C(CH_3)_2$}{$P(OEt)_3$}$_4$](BPh_4)$_2$ (7, 8) [M = Ru (7), Os (8)]. A solution of the appropriate [M(CO)(NH_2NH_2){$P(OEt)_3$}$_4$](BPh_4)$_2$ (**1a**, **2a**) hydrazine complex (0.14 mmol) in 10 mL of acetone was refluxed for about 12 h. The solvent was removed under reduced pressure, giving an oil which was triturated with ethanol (3 mL) containing an excess of $NaBPh_4$ (0.28 mmol, 96 mg). A white solid slowly separated out and was filtered and crystallized from CH_2Cl_2 and ethanol. Yield ≥ 65%. (**7**) Anal. Calcd for $C_{76}H_{108}B_2N_2O_{13}P_4Ru$: C, 60.68; H, 7.24; N, 1.86. Found: C, 60.55; H, 7.30; N, 1.91. Λ_M = 120.2 Ω^{-1} mol^{-1} cm^2. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.35−6.85 (m, 40 H, Ph), 5.56 (s, br, 2 H, NH_2), 4.10 (m, 24 H, CH_2), 2.00, 1.85 (s, 6 H, $(CH_3)_2C{=}$), 1.36, 1.35, 1.34 (t, 36 H, CH_3 phos). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB_2C spin syst, δ_A 125.1, δ_B 115.4, δ_C 111.6, J_{AB} = 53.4, J_{AC} = 54.9, J_{BC} = 67.3. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 182.5 (m, CO), 166.3 (s, $N{=}C$), 165−122 (m, Ph), 65.5 (m), 65.0 (d, CH_2), 25.2, 16.2 (s, $(CH_3)_2C{=}$), 16.3 (m, CH_3 phos). IR (KBr) cm^{-1}: 3314 m (νNH), 2056 s (νCO). (**8**) Anal. Calcd for $C_{76}H_{108}B_2N_2O_{13}OsP_4$: C, 57.29; H, 6.83; N, 1.76. Found: C, 57.24; H, 6.91; N, 1.79. Λ_M = 118.0 Ω^{-1} mol^{-1} cm^2. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.40−6.85 (m, 40 H, Ph), 5.97 (s, br, 2 H, NH_2), 4.12 (m, 24 H, CH_2), 2.05, 1.86 (s, 6 H, $(CH_3)_2C{=}$), 1.39, 1.37, 1.35 (t, 36 H, CH_3 phos). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AB_2C spin syst, δ_A 79.5, δ_B 77.0, δ_C 75.8, J_{AB} = 55.6, J_{AC} = 41.7, J_{BC} = 38.5. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 178.2 (m, CO), 168.4 (s, $N{=}C$), 165−122 (m, Ph), 65.5 (m, CH_2), 24.9, 16.1 (s, $(CH_3)_2C{=}$), 16.2 (m, CH_3 phos). IR (KBr) cm^{-1}: 3314 m, 3240 w (νNH), 2039 s (νCO).

X-ray Crystal Structure Determination of [Ru(CO)($NH_2N{=}CH_2$){$P(OEt)_3$}$_4$](BPh_4)$_2$ (5). Single crystals of **5** were obtained by recrystallization from CH_2Cl_2 and ethanol. X-ray diffraction data were collected with a SMART AXS 1000 CCD diffractometer (Mo Kα radiation, λ = 0.71073 Å, T = 293 K). Lorentz, polarization, and absorption corrections were applied.[17] The structure was solved by direct methods using SIR97[18] and refined by full-matrix least-squares analysis on all F^2 using SHELXL97[19] as implemented in the WingX package.[20] Hydrogen atoms belonging to the formaldehyde-hydrazone ligand were located on Fourier difference maps and refined isotropically, and all the others were introduced in calculated positions. Anisotropic displacement parameters were refined for all non-hydrogen atoms. The Cambridge Crystallographic Data Centre packages[21] were used for the analysis of crystal geometry. *Crystal data*: **5**·0.5CH_2Cl_2, $C_{74.50}H_{105}B_2ClN_2O_{13}P_4Ru$, FW = 1518.62, 0.3 × 0.1 × 0.1 mm^3, orthorhombic, space group $Pca2_1$, a = 22.239(1), b = 19.041(1), c = 19.538(1) Å, V = 8273.4(7) Å^3, ρ = 1.219 Mg m^{-3}, 9553 unique reflections [R(int) = 0.0687], 6881 observed ($I > 2\sigma(I)$), 824 parameters, R1 = 0.0465, wR2 = 0.1137 ($I > 2\sigma(I)$).

Results and Discussion

Preparation of the Hydrazine Complexes. The synthesis of the hydrazine complexes of ruthenium(II) and osmium(II) of the [M(CO)($RNHNH_2$){$P(OEt)_3$}$_4$](BPh_4)$_2$ (**1**, **2**) type was achieved by reacting the [MH(CO){$P(OEt)_3$}$_4$]BPh_4 hydride first with an excess of HBF_4·Et_2O and then with the appropriate hydrazine, as shown in Scheme 1. Treatment of the hydride [MH(CO)P_4]$^+$ with an excess of HBF_4·Et_2O probably leads to the evolution[22] of H_2 and the formation of

Scheme 1 [a]



1, 2 (I)

[a] M = Ru (**1**), Os (**2**); P = $P(OEt)_3$; R = H (**a**), CH_3 (**b**), C_6H_5 (**c**).

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(17) (a) *SAINT: SAX, Area Detector Integration;* Siemens Analytical Instruments INC.: Madison, WI, Bruker AXS Copyright 1997−1999. (b) Sheldrick, G. *SADABS: Siemens Area Detector Absorption Correction Software;* University of Göttingen: Göttingen, Germany, 1996.

(18) Altomare, A.; Burla, M. C.; Cavalli, M.; Cascarano, G.; Giacovazzo, C.; Gagliardi, A.; Moliterni, A. G.; Polidori, G.; Spagna, R. *Sir97: A New Program for Solving and Refining Crystal Structures;* Istituto di Ricerca per lo Sviluppo di Metodologie Cristallografiche CNR: Bari, Italy, 1997.

(19) Sheldrick, G. *Shelxl97. Program for structure refinement;* University of Göttingen: Göttingen, Germany, 1997.

(20) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837−838.

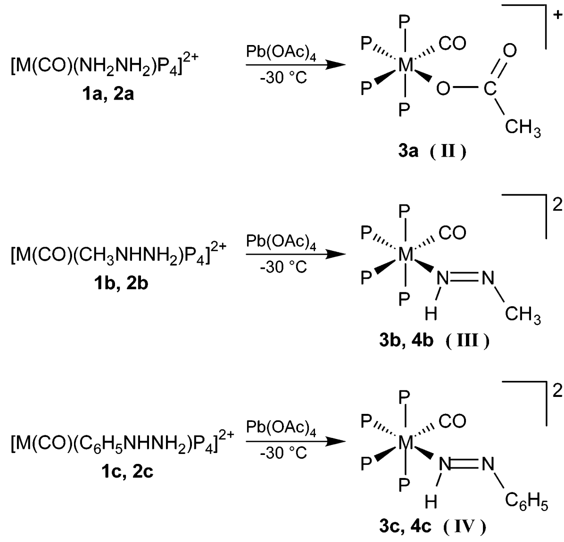
(21) (a) Allen, F. H.; Kennard, O.; Taylor, R. *Acc. Chem. Res.* **1983**, *16*, 146−153. (b) Bruno, I. J.; Cole, J. C.; Edgington, P. R.; Kessler, M.; Macrae, C. F.; McCabe, P.; Pearson, J.; Taylor, R. *Acta Crystallogr.* **2002**, *B58*, 389−397.

a coordinatively unsaturated[23] $[M(CO)P_4]^{2+}$ intermediate which, by reaction with $RNHNH_2$, gives the final hydrazine complexes **1** and **2**. It is worth noting that only with $P(OEt)_3$ as a supporting ligand can the carbonyl-hydrazine complexes **1** and **2** be prepared. With the $PPh(OEt)_2$ and PPh_2OEt phosphines, which are bulkier than $P(OEt)_3$, instead, the reaction of the hydride $[MH(CO)P_4]^+$ cation first with $HBF_4{\cdot}Et_2O$ and then with hydrazine always gives decomposition products.

Good analytical data were obtained for all the compounds **1**−**2**, which are white solids that are stable in air and in solutions of polar organic solvents where they behave like 1:2 electrolytes.[24] The infrared and NMR data support the proposed formulation. The IR spectra show one strong band at 2065−2037 cm^{-1} attributed to the ν_{CO} of the carbonyl ligand, while three or four medium-intensity bands, attributable to the ν_{NH} of the hydrazine ligand, were observed in the 3342−3256 cm^{-1} region. The presence of the $RNHNH_2$ ligand, however, is confirmed by the ^1H NMR spectra, which show the characteristic NH and NH_2, slightly broad signals between 5.60 and 2.45 ppm. The decoupling experiments and COSY spectra confirm the proposed attribution and also indicate that the doublet at 2.58 ppm for **1b** and at 2.56 ppm for **2b** is due to the methyl group of the CH_3NHNH_2 ligand. The proton spectra also show that, in the case of NH_2NH_2 complexes **1a** and **2a**, two NH_2 signals are present, suggesting η^1-coordination for the hydrazine ligand. Furthermore, in the ^{13}C NMR spectra, the carbonyl carbon signal appears as a multiplet at 192−176 ppm, while a singlet at 44.9−44.7 ppm of the methyl substituent of the CH_3NHNH_2 group is also observed for methylhydrazine complexes **1b** and **2b**. Finally, in the temperature range between +20 and −80 °C, the $^{31}P\{^1H\}$ NMR spectra of the hydrazine complex appear as an AB_2C multiplet, suggesting that a geometry (I, Scheme 1) with the carbonyl and the hydrazine ligands in a mutually cis position can reasonably be proposed for our derivatives **1** and **2**.

Oxidation Reactions. The reactivity of hydrazine complexes **1** and **2** with $Pb(OAc)_4$ at low temperatures was studied, and the results are summarized in Scheme 2. The reaction of the hydrazine $[M(CO)(NH_2NH_2)P_4]^{2+}$ (**1a**, **2a**) cations with $Pb(OAc)_4$ at −30 °C in CH_2Cl_2 proceeds to give a pale-yellow solution from which the κ^1-acetate $[Ru(\kappa^1\text{-}OCOCH_3)(CO)P_4]BPh_4$ (**3a**) complex was, in the case of ruthenium, isolated in pure form and characterized. With osmium, an intractable oily mixture was obtained. The formation of the acetate complex may suggest that the reaction with $Pb(OAc)_4$ proceeds through the selective oxidation of NH_2NH_2 to give the unstable 1,2-diazene $[M(CO)(NH{=}NH)P_4]^{2+}$ derivative, which undergoes substitution of the labile NH═NH ligand with the CH_3COO^- to give the final species **3a**. The reaction was also carried out, either at a low temperature (−50 °C) or using less than the stoichiometric amount of $Pb(OAc)_4$, but only traces of the diazene complex were detected in the reaction product. However, since the starting hydrazine **1a** and **2a** compounds do not react with the acetate ion, the formation of an unstable 1,2-diazene intermediate is plausible and is supported both by several of the precedents[1,2,6c,8e] reported in the literature and by the results obtained with substituted hydrazines (see Scheme 2).

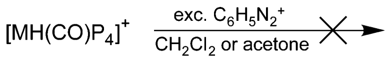
Scheme 2 [a]



[a] M = Ru (**3**), Os (**4**); P = $P(OEt)_3$.

Phenylhydrazine $[M(CO)(C_6H_5NHNH_2)P_4]^{2+}$ (**1c**, **2c**) complexes react with $Pb(OAc)_4$ to give, in contrast with the case of hydrazine, the related phenyldiazene $[M(CO)(C_6H_5N{=}NH)P_4](BPh_4)_2$ (**3c**, **4c**) derivatives, which are stable and were isolated in good yield and characterized. The stability of **3c** and **4c** toward decomposition of the diazene ligand prompted us to attempt the synthesis of the same aryldiazene **3c** and **4c** complexes following a different route involving the insertion of aryldiazonium cations into the M−H bond of the $[MH(CO)P_4]^+$ hydride precursor (Scheme 3). The reaction was studied extensively but, at room temperature, did not proceed, and the starting hydride was quantitatively recovered. This unreactivity toward the insertion of ArN_2^+ into the M−H bond may be attributed to the positive charge of the complexes, although the influence of the ancillary ligands must not be underestimated.

Scheme 3 [a]



[a] M = Ru, Os; P = $P(OEt)_3$.

The insertion of ArN_2^+ does take place, as previously reported by us, in cationic complexes such as the pentakis(phosphite) $[MHP_5]^+$ or the mixed-ligand $[MH(N{-}N)P_3]^+$ [M = Fe, Ru, Os; N−N = 1,2-bipyridine, 1,10-phenanthroline; P = $P(OEt)_3$] derivatives,[8e,25] giving stable and isolable phenyldiazene complexes. The unreactivity of our $[MH(CO)P_4]^+$ derivatives is somewhat unexpected and may be

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(22) For reactions of hydride complexes with Brønsted acids, see: Kubas, G. J. *Metal Dihydrogen and σ-Bond Complexes*; Kluwer Academic: New York, 2001, and references therein.

(23) The intermediate formed by reacting $[MH(CO)P_4]^+$ with $HBF_4{\cdot}Et_2O$ may also contain a labile BF_4^- ligand of the $[M(BF_4)(CO)P_4]^+$ type. However, an agostic interaction between the metal center and the C−H bond of the ethyl group of one $P(OEt)_3$ ligand to stabilize the $[M(CO)P_4]^{2+}$ intermediate is also plausible.

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

attributed to the presence of stronger π-acceptor ligands such as CO, which probably decreases the hydridic character of the M$-$H group, preventing the insertion of the ArN_2^+ cation to give the ArN=NH aryldiazene group. It seems, therefore, that only the oxidation of arylhydrazine allows the synthesis of aryldiazene ligands bonded to the $M(CO)P_4$ fragment in complexes of the type **3c** and **4c**.

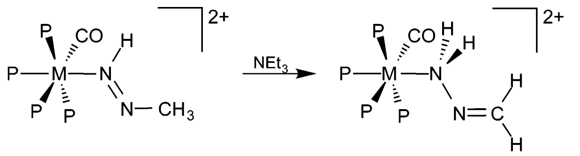
Methylhydrazine $[M(CO)(CH_3NHNH_2)P_4](BPh_4)_2$ (**1b**, **2b**) complexes react with $Pb(OAc)_4$ at -30 °C to give, after workup, a pale-yellow solid. Crystallization from CH_2Cl_2 and ethanol yielded white microcrystals of pure methyldiazene $[M(CO)(CH_3N{=}NH)P_4](BPh_4)_2$ (**3b, 4b**) derivatives in about 60% yield.

Both the phenyldiazene (**3b**, **4b**) and the methyldiazene (**3c**, **4c**) complexes were isolated as white or pale-yellow solids that are stable in air and in solutions of polar organic solvents, where they behave like 2:1 electrolytes.[24] The acetate complex **3a** is also stable both in the solid state and in solution, where it behaves like a 1:1 electrolyte. Analytical and spectroscopic data support the proposed formulation for the compounds.

The IR spectra of the acetate $[Ru(\kappa^1\text{-}OCOCH_3)(CO)P_4]BPh_4$ (**3a**) complex show a strong band at 2058 cm^{-1} due to the CO ligand and a medium-intensity absorption at 1615 cm^{-1} attributed to ν_{CO} of the coordinate acetate ion. The presence of the CH_3COO^- ligand is confirmed by the ^1H NMR spectrum, which shows, besides the signals of the phosphite and the BPh_4 anion, a singlet at 1.92 ppm attributable to the methyl group of the acetate ligand. In the temperature range between $+20$ and -80 °C, the $^{31}P\{^1H\}$ specta appear as a ABC_2 multiplet, suggesting the mutually cis position of the carbonyl and the acetate ligands. On the basis of these data, a geometry of type II (Scheme 2) can reasonably be proposed.

The ^1H NMR spectra of both the methyldiazene (**3b**, **4b**) and the phenyldiazene (**3c**, **4c**) complexes show, in the high-frequency region, a slightly broad signal at 13.56$-$13.04 ppm attributed to the NH proton of the substituted diazene ligand. In the spectra of the methyldiazene complexes **3b** and **4b**, a singlet at 3.75$-$3.72 ppm of the methyl substituent is also present, which correlates (^1H COSY) to the broad NH signal near 13 ppm, which in turn is in agreement with the presence of the diazene ligand. A NOESY experiment was also carried out and indicated a cis arrangement of the $CH_3N{=}NH$ group. In the ^{13}C NMR spectra, one singlet at 68.6$-$68.4 ppm appears and was attributed to the CH_3 group of the methyldiazene, while the multiplet between 191.3 and 171.2 ppm was attributed to the carbonyl carbon resonance. The infrared spectra of all the diazene complexes show a strong absorption at 2065$-$2037 cm^{-1} attributed to ν_{CO} of the carbonyl ligand. In the temperature range between $+20$ and -80 °C, the $^{31}P\{^1H\}$ NMR spectra appear as AB_2C multiplets which can be simulated with the reported parameters. On the basis of these data, a mutually cis position of the carbonyl and the diazene ligands in a type III or IV geometry can reasonably be proposed for the diazene derivatives **3b**, **3c**, **4b**, and **4c**.

Scheme 4 [a]



3b, 4b **5, 6 (V)**

[a] M = Ru (**3b**, **5**), Os (**4b**, **6**); P = $P(OEt)_3$.

Tautomerization of Methyldiazene to Formaldehyde-Hydrazone. The addition of traces of base (NEt_3) to a dichloromethane solution of the methyldiazene $[M(CO)(CH_3N{=}NH)P_4](BPh_4)_2$ (**3b**, **4b**) complexes leads to the tautomerization of the coordinate methyldiazene to formaldehyde-hydrazone, yielding the $[M(CO)(NH_2N{=}CH_2)P_4](BPh_4)_2$ (**5**, **6**) derivatives, which were isolated with an excellent yield ($\geq$92%) and characterized (Scheme 4). The complexes are stable pale-pink solids which were characterized by standard spectroscopic methods (IR and NMR) and by a single-crystal X-ray diffraction study of the $[Ru(CO)(NH_2N{=}CH_2)\{P(OEt)_3\}_4](BPh_4)_2$ (**5**) derivative.

The infrared spectra show the ν_{CO} band at 2064 (**5**) and at 2050 cm^{-1} (**6**), while the ν_{NH} of the hydrazone appears at 3310$-$3261 cm^{-1}. The ^1H NMR spectra show a slightly broad signal at 5.86 (**5**) and 6.26 ppm (**6**) attributed to the NH_2 group of the $NH_2N{=}CH_2$ ligand, while the methylene protons, which are not magnetically equivalent, appear as an AB quartet ($J_{AB} = 9.3$ Hz) at 6.67 (**5**) and at 6.54 ppm (**6**). The ^{13}C NMR spectra show, besides the signals of the $P(OEt)_3$ ligands and the BPh_4^- anion, a multiplet at 177$-$193 ppm attributed to the carbonyl carbon resonance and a singlet at 149.2 (**5**) and at 150.6 ppm (**6**), which splits into a doublet of doublets in the proton-coupled ^{13}C spectra ($^1J_{^{13}CH} = 163$ Hz). This signal at 149$-$150 ppm is correlated, in the HMQC experiments, to the proton signal at 5.86$-$6.26 ppm and was attributed to the methylene carbon resonance of the $NH_2N{=}CH_2$ ligand. In the temperature range between $+20$ and -80 °C, the $^{31}P\{^1H\}$ NMR spectra of the formaldehyde-hydrazone complexes **5** and **6** appear as AB_2C multiplets, suggesting a cis arrangement of the CO and the hydrazone ligand, in agreement with a geometry (V) similar to that of the solid state.

Compound **5** crystallizes as a $[Ru(CO)(NH_2N{=}CH_2)(P(OEt)_3)_4](BPh_4)_2\cdot{}^1/_2CH_2Cl_2$ solvate. The molecular structure and labeling scheme are reported in Figure 1. The relevant geometrical data of the octahedral cation are in Table 1. The $NH_2N{=}CH_2$ and the CO ligands are in a cis position, and the N$-$N bond is perfectly eclipsed with respect to the C$-$O bond (C25$-$Ru$-$N1$-$N2 = 10.3(5)°), while the $N{=}CH_2$ bond is practically perpendicular to the plane containing the equatorial ligands P3, P4, C25, O13, N1, and N2 (Ru$-$N1$-$N2$-$C26 = $-$113.1(8)°). In the cation, the Ru$-$P bond distances are in accord with the trans influence of the ligands, where the one trans to the hydrazone moiety is the shortest (Ru$-$P4 = 2.270(2) Å). This is the first structural example of a coordinated formaldehyde-hydrazone.

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(25) (a) Albertin, G.; Antoniutti, S.; Bortoluzzi, M. *Inorg. Chem.* **2004**, *43*, 1328$-$1335. (b) Albertin, G.; Antoniutti, S.; Pizzol, S. *J. Organomet. Chem.* **2004**, *689*, 1639$-$1647.

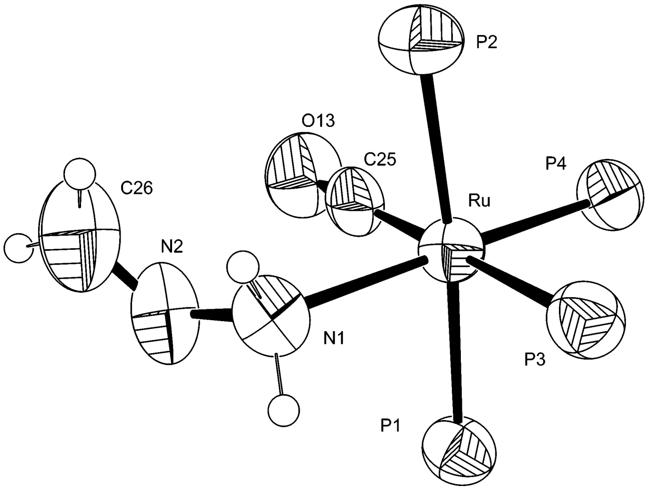
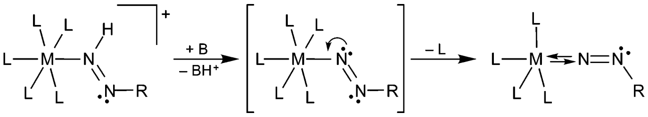


Figure 1. Molecular structure of *cis*-[Ru(CO)($NH_2N{=}CH_2$){$P(OEt)_3$}$_4$]$^{2+}$ (**5**). The ethoxy groups are omitted for clarity.

Table 1. Relevant Bond Lengths (Å) and Angles (deg) for Compound **5**·$^1/_2CH_2Cl_2$

Ru−C(25)	1.90(1)	P(4)−Ru−P(1)	91.16(8)
Ru−N(1)	2.226(7)	C(25)−Ru−P(2)	89.9(2)
Ru−P(4)	2.270(2)	N(1)−Ru−P(2)	86.6(2)
Ru−P(1)	2.343(2)	P(4)−Ru−P(2)	96.01(8)
Ru−P(2)	2.347(2)	P(1)−Ru−P(2)	172.83(8)
Ru−P(3)	2.369(2)	C(25)−Ru−P(3)	177.4(2)
N(1)−N(2)	1.454(9)	N(1)−Ru−P(3)	87.9(2)
N(2)−C(26)	1.22(1)	P(4)−Ru−P(3)	95.44(7)
C(25)−Ru−N(1)	89.7(3)	P(1)−Ru−P(3)	90.31(8)
C(25)−Ru−P(4)	87.0(2)	P(2)−Ru−P(3)	88.76(8)
N(1)−Ru−P(4)	175.8(2)	N(2)−N(1)−Ru	112.5(4)
C(25)−Ru−P(1)	90.7(2)	C(26)−N(2)−N(1)	115.8(9)
N(1)−Ru−P(1)	86.3(2)		

Scheme 5

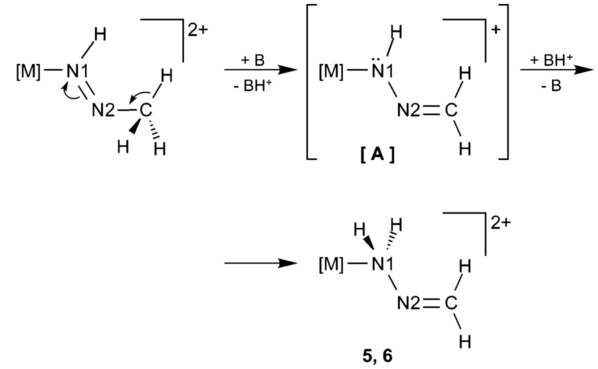


A comparison with the Ru complexes of the related acetone-hydrazone ligand[26] shows that the N═CH$_2$ bond (1.22(1) Å) is remarkably shorter than the one observed for the Ru−NH$_2$−N═C(CH$_3$)$_2$ system (1.27−1.28 Å), while the N−N bond is not significantly different.

Coordinate diazene [{M}−NH═NR]$^+$ is known to undergo a deprotonation reaction in the presence of a base to give a diazenido derivative,[1a,2b,2j,5] as shown in Scheme 5. The reaction is reported[2b,2j] to involve the rearrangement of the RN$_2^-$ ligand to RN$_2^+$ with concurrent 2 e$^-$ reduction of the metal center and consequent dissociation of one ligand.

A different behavior is shown by the metal-bonded methyldiazene[27] group in our complexes **3b** and **4b**, which undergoes base-catalyzed tautomerization to hydrazone. The reaction also allows one to prepare and stabilize by coordination a simple but elusive molecule[28] such as CH$_2$N═NH$_2$ formaldehyde-hydrazone. This species, in fact, has been prepared in solution from the reaction of CH$_3$OCH$_2$OH with hydrazine[28] and is stable in the free state only below −30 °C. The tautomerization of methyldiazene establishes a further method for the preparation of this molecule, which, in this case, is stabilized by coordination, can be isolated as a coordination compound, and is the first well-characterized example of a formaldehyde-hydrazone complex. It may also be noted that substituted hydrazone derivatives of ruthenium and osmium are rare[1a] and were obtained from the reaction of hydrazine [M]−NH$_2$NH$_2$ complexes[29] with acetone, yielding the [M]−NH$_2$N═C(CH$_3$)$_2$ final species.

Scheme 6



A possible mechanism, which requires the 1−3 shift of one hydrogen atom, may be considered to explain the tautomerization reaction (Scheme 6). This involves the direct deprotonation of the methyl group of CH$_3$N═NH to give a coordinate methylenehydrazido(1−) [M]−NH−N═CH$_2$ [**A**] intermediate, which can undergo protonation to the basic N1 nitrogen atom with BH$^+$ to yield the final **5** and **6** species (Scheme 6). To obtain information on the reaction path, we monitored the reaction at −80 °C by NMR techniques, but the reaction was very fast even at this temperature, preventing the observation of any intermediate species. The formation of an intermediate of type **A**, however, is plausible and is supported by numerous precedents[30,31] reported in the literature on coordinate hydrazido(1−) complexes. The protonation of this intermediate to the N1 nitrogen atom should easily afford the final formaldehyde-hydrazone molecule.

The path of Scheme 6 entails the coordination of the methyldiazene to the M(CO)P$_4$ fragment to activate the

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(26) (a) Nolte, M. J.; Singleton, E. *J. Chem. Soc., Dalton Trans.* **1974,** 2406−2410. (b) Day, V. W.; Everspacher, T. A.; Klemperer, W. G.; Planalp, R. P.; Schiller, P. W.; Yagasaki, A.; Zhong, B. *Inorg. Chem.* **1993**, *32*, 1629−1637.

(27) Free methyldiazene, CH$_3$N═NH, is reported to decompose upon warming to give N$_2$ and CH$_4$. Decomposition via a CH$_2$═NNH$_2$ intermediate was also proposed, but only methane was detected: Ackermann, M. N.; Ellenson, J. L.; Robison, D. H. *J. Am. Chem. Soc.* **1968**, *90*, 7173−7174.

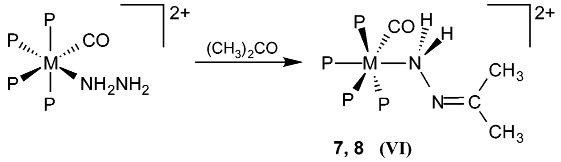
(28) Heaton, B. T.; Jacob, C.; Monks, G. L.; Hursthouse, M. B.; Ghatak, I.; Somerville, R. G.; Heggie, W.; Page, P. R.; Villax, I. *J. Chem. Soc., Dalton Trans.* **1996**, 61−67.

(29) (a) Ashworth, T. V.; Singleton, E.; Hough, J. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1809−1815. (b) Oosthuizen, H. E.; Singleton, T.; Fields, J. S.; Van Niekerk, G. G. *J. Organomet. Chem.* **1985**, *279*, 433−446.

(30) (a) McCleverty, J. A.; Rae, A. E.; Wolochowicz, I.; Bailey, N. A.; Smith, J. M. A. *J. Chem. Soc., Dalton Trans.* **1983**, 71−80. (b) Sellmann, D.; Kern, W.; Pohlmann, G.; Knoch, F.; Moll, M. *Inorg. Chim. Acta* **1991**, *185*, 155−162. (c) Chatt, J.; Dilworth, J. R.; Dahlstrom, P. L.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1980**, 786−787. (d) Glassman, T. E.; Vale, M. G.; Schrock, R. R. *J. Am. Chem. Soc.* **1992**, *114*, 8098−8109.

(31) (a) Nicholson, T.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1985**, 367−368. (b) Barrientos-Penna, C. F.; Gilchrist, A. B.; Klahn-Oliva, A. H.; Hanlan, A. J. L.; Sutton, D. *Organometallics* **1985**, *4*, 478−485.

Scheme 7 [a]



[a] M = Ru (**7**), Os (**8**); P = P(OEt)$_3$.

methyl CH bond to give the final $NH_2N{=}CH_2$ molecule, and this activation is probably attributable to the introduction of a carbonyl ligand into the coordination sphere of the methyldiazene derivatives. Comparable methyldiazene complexes[8c−e] of Ru and Os of the $[M(CH_3N{=}NH)_2P_4](BPh_4)_2$ and $[M(CH_3N{=}NH)(CH_3NHNH_2)P_4](BPh_4)_2$ [P = P(OEt)$_3$] types, in fact, are very stable in the presence of a base, and the methyldiazene does not show any trend of tautomerization to formaldehyde-hydrazone. Introducing a strong π-acceptor ligand (CO) beside the P(OEt)$_3$ decreases the electronic density on the metal center and probably makes the $M(CO)P_4$ fragment able to activate the $CH_3N{=}NH$ group toward the tautomerization.

It can be noted that the presence of the CO ligand, however, activates neither the methyldiazene nor the phenyldiazene toward the deprotonation of the NH group to give a diazenido derivative (see Scheme 5). Treatment of the phenyldiazene complexes **3c** and **4c** with an excess of NEt_3, in fact, did not give any reactions, and the starting complexes were recovered unchanged. The excess of base, instead, caused exclusive tautomerization in the methyldiazene **3b** and **4b** derivatives. Therefore, the properties of our $M(CO)P_4$ fragment seem to involve the activation of the methyl substituent instead of the NH group of the methyldiazene to give the final formaldehyde-hydrazone complex.

Acetone-Hydrazone Complexes. The stability of formaldehyde-hydrazone complexes **5** and **6** prompted us to test whether other hydrazone complexes containing the $M(CO)P_4$ fragment can be prepared. We, therefore, reacted hydrazine $[M(CO)(NH_2NH_2)P_4](BPh_4)_2$ (**1a**, **2a**) derivatives with acetone and observed that the reaction proceeded to give the corresponding hydrazone $[M(CO)\{NH_2N{=}C(CH_3)_2\}P_4](BPh_4)_2$ (**7**, **8**) complexes, which were isolated as white solids and characterized (Scheme 7). Hydrazone complexes of ruthenium and osmium stabilized by the $M(CO)P_4$ fragment can therefore be prepared not only by the tautomerization of methyldiazene but also by the reaction of coordinate hydrazine with a ketone.

The complexes are stable in the solid state and in solutions of polar organic solvents, where they behave like 2:1 electrolytes.[24] The analytical and spectroscopic data support the proposed formulation.

The IR spectra of the hydrazone complexes **7** and **8** show a strong absorption at 2056−2039 cm^{-1} due to the ν_{CO} of the carbonyl ligand, while the bands of medium intensity at 3314−3240 cm^{-1} are attributed to ν_{NH} of the $NH_2N{=}C(CH_3)_2$ group. The presence of the hydrazone ligand, however, is confirmed by the proton NMR spectra, which show a slightly broad signal at 5.56 (**7**) and at 5.97 ppm (**8**) attributed to the NH_2 of the $NH_2N{=}C(CH_3)_2$ moiety. Two singlets at 2.00 and 1.85 ppm for **7** and at 2.05 and 1.86 ppm for **8** are also present in the spectra; these are due to the methyl substituents of the hydrazone. Curiously, only one of these singlets correlates in the COSY experiment with the broad signal between 6 and 5 ppm of the NH_2 moiety. The ^{13}C NMR spectra further support the formulation of the complexes showing a multiplet at 182.5 (**7**) and 178.2 ppm (**8**) of the carbonyl carbon atom, one singlet at 166.3 (**7**) and at 168.4 ppm (**8**) of the hydrazone carbon atoms, and two singlets between 25 and 16 ppm of the methyl substituents of the $NH_2N{=}C(CH_3)_2$ ligand. The HMQC and HMBC experiments confirm the attribution of these signals. In the temperature range between +20 and −80 °C, the $^{31}P\{^1H\}$ NMR spectra appear as AB_2C multiplets, suggesting the mutually cis position of the carbonyl and the hydrazone ligands. A type VI geometry (Scheme 7) can therefore be proposed for the acetone-hydrazone derivatives.

Conclusions

In this paper, we have reported the synthesis of a series of hydrazine complexes of ruthenium and osmium stabilized by the mixed-ligand $M(CO)P_4$ fragment with phosphites and carbonyls. The introduction of the CO group in the diazo chemistry of ruthenium and osmium induces new properties on the diazo molecule. Among these, we can highlight the first documented example of base-catalyzed tautomerization of coordinate methyldiazene, $CH_3N{=}NH$, to formaldehyde-hydrazone, giving the $[M(CO)(NH_2N{=}CH_2)P_4](BPh_4)_2$ derivatives. Furthermore, acetone-hydrazone $[M(CO)\{NH_2N{=}C(CH_3)_2\}P_4](BPh_4)_2$ derivatives can also be prepared from the reaction of hydrazine complexes with acetone.

Acknowledgment. The financial support of MIUR (Rome)—PRIN 2004—is gratefully acknowledged. We thank Daniela Baldan for technical assistance.

Supporting Information Available: Crystallographic data: CIF and PDF files of Tables S1−S5 and Figures S1 and S2 for complex **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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