Inorg. Chem. **2000,** *39,* 3283−3293

Diazo Complexes of Rhenium: Preparations and Crystal Structures of the Bis(dinitrogen), $[Re(N_2)_2\{PPh(OEt)_2\}_4][BPh_4]$ and Methyldiazenido $[ReCl(CH_3N_2)(CH_3NHNH_2)\{PPh(OEt)_2\}_3][BPh_4]$ Derivatives

Gabriele Albertin,*,† Stefano Antoniutti,† Alessia Bacchi,‡ Emilio Bordignon,† Francesca Miani,† and Giancarlo Pelizzi‡

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

Received August 11, 1999

Depending on experimental conditions and the nature of the hydrazine, the reactions of $ReCl_3P_3$ [P = $PPh(OEt)_2$] with $RNHNH_2$ (R = H, CH_3, ^tBu) afford the bis(dinitrogen) $[Re(N_2)_2P_4]^+$ ($\mathbf{2}^+$), dinitrogen $ReClN_2P_4$ (**3**), and methyldiazenido $[ReCl(CH_3N_2)(CH_3NHNH_2)P_3]^+$ ($\mathbf{1}^+$) derivatives. In contrast, reactions of $ReCl_3P_3$ [P = $PPh(OEt)_2$, PPh_2OEt] with arylhydrazines $ArNHNH_2$ (Ar = Ph, *p*-tolyl) give the aryldiazenido cations $[ReCl(ArN_2)(ArNHNH_2)P_3]^+$ ($\mathbf{4}^+$) and $[ReCl(ArN_2)P_4]^+$ ($\mathbf{7}^+$) and the bis(aryldiazenido) cations $[Re(ArN_2)_2P_3]^+$ ($\mathbf{5}^+$, $\mathbf{6}^+$). These complexes were characterized spectroscopically (IR; ^1H and ^{31}P NMR), and the BPh_4 complexes **1**, **2**, and **7** were characterized crystallographically. The methyldiazenido derivative $[ReCl(CH_3N_2)(CH_3NHNH_2)\{PPh(OEt)_2\}_3][BPh_4]$ (**1**) crystallizes in space group $P\bar{1}$ with $a = 15.396(5)$ Å, $b = 16.986(5)$ Å, $c = 11.560(5)$ Å, $\alpha = 93.96(5)°$, $\beta = 93.99(5)°$, $\gamma = 93.09(5)°$, and $Z = 2$ and contains a singly bent CH_3N_2, group bonded to an octahedral central metal. One methylhydrazine ligand, one Cl^- trans to the CH_3N_2, and three $PPh(OEt)_2$ ligands complete the coordination. The complex $[Re(N_2)_2\{PPh(OEt)_2\}_4][BPh_4]$ (**2**) crystallizes in space group *Pbaa* with $a = 23.008(5)$ Å, $b = 23.367(5)$ Å, $c = 12.863(3)$ Å, and $Z = 4$. The structure displays octahedral coordination with two end-on N_2 ligands in mutually trans positions. $[ReCl(PhN_2)\{PPh(OEt)_2\}_4][BPh_4]$ (**7**) crystallizes in space group $P2_1/n$ with $a = 19.613(5)$ Å, $b = 20.101(5)$ Å, $c = 19.918(5)$ Å, $\beta = 115.12(2)°$, and $Z = 4$. The structure shows a singly bent phenyldiazenido group trans to the Cl^- ligand in an octahedral environment. The dinitrogen complex $ReClN_2P_4$ (**3**) reacts with $CF_3SO_3CH_3$ to give the unstable methyldiazenido derivative $[ReCl(CH_3N_2)P_4][BPh_4]$. Reaction of the methylhydrazine complex $[ReCl(CH_3N_2)(CH_3NHNH_2)P_3][BPh_4]$ (**1**) with $Pb(OAc)_4$ at −30 °C results in selective oxidation of the hydrazine, affording the corresponding methyldiazene derivative $[ReCl(CH_3N{=}NH)(CH_3N_2)P_3][BPh_4]$ (**8**). In contrast, treatment with $Pb(OAc)_4$ of the related arylhydrazines $[ReCl(ArN_2)(ArNHNH_2)P_3][BPh_4]$ (**4**) [P = $PPh(OEt)_2$] gives the bis(aryldiazenido) complexes $[Re(ArN_2)_2P_3][BPh_4]$ (**5**). Possible protonation reactions of Brønsted acids HX with all diazenides, **1**, **4**, **5**, **6,** and **8**, were investigated and found to proceed only in the cases of the bis(aryldiazenido) complexes **5** and **6**, affording, with HCl, the octahedral $[ReCl(ArN{=}NH)(ArN_2)P_3][BPh_4]$ or $[ReCl\{Ar(H)NN\}(ArN_2)P_3][BPh_4]$ (**10**) (Ar = Ph; P = PPh_2OEt) derivative.

Introduction

Dinitrogen complexes[1−3] are an important class of compounds which continue to attract interest because of their relevance to nitrogen fixation processes.[4−11] A number of N_2 complexes have been synthesized,[1−3,12−20] and several studies on their chemical, electronic, and structural properties have been carried out, with the aim of obtaining insight into N_2 binding and activation through metal complexation.

Complexes containing partially reduced dinitrogen ligands such as diazene, NH═NH, diazenides, $RN{\equiv}N^+$, or hydrazide, $NHNH_2^-$, were also prepared and studied as models for the intermediates of N_2 reduction.[21−24] The goal of these studies

---

† Università Ca'Foscari di Venezia.

‡ Università di Parma.

(1) Hidai, M.; Mizobe, Y. *Chem. Rev.* **1995**, *95*, 1115.

(2) Leigh, G. J. *New J. Chem.* **1994**, *18*, 157.

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

(4) Shilov, A. E. *Metal Complexes in Biomimetic Chemical Reactions*; CRC: Boca Raton, FL, 1997.

(5) Sellmann, D.; Sutter, J. *Acc. Chem. Res.* **1997**, *30*, 460.

(6) Richards, R. L. *Coord. Chem. Rev.* **1996**, *154*, 83.

(7) Leigh, G. J. *Science* **1995**, *268*, 827.

(8) Eady, R. R. *Chem. Rev.* **1996**, *96*, 3013.

(9) Howard, J. B.; Rees, D. C. *Chem. Rev.* **1996**, *96*, 2965.

(10) Burgess, B. K.; Lowe, D. J. *Chem. Rev.* **1996**, *96*, 2983.

(11) Dilworth, M. J., Glenn, A. R., Eds. *Biology and Biochemistry of Nitrogen Fixation*; Elsevier: New York, 1991.

(12) Fryzuk, M. D.; Johnson, S. A.; Rettig, S. J. *J. Am. Chem. Soc.* **1998**, *120*, 11024.

(13) Nishibayashi, Y.; Iwai, S.; Hidai, M. *J. Am. Chem. Soc.* **1998**, *120*, 10559.

(14) Odom, A. L.; Arnold, P. L.; Cummins, C. C. *J. Am. Chem. Soc.* **1998**, *120*, 5836.

(15) Zanotti-Gerosa, A.; Solari, E.; Giannini, L.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1998**, *120*, 437.

(16) Roussel, P.; Scott, P. *J. Am. Chem. Soc.* **1998**, *120*, 1070.

(17) O'Donoghue, M. B.; Zanetti, N. C.; Davis, W. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 2753.

(18) Hahn, J.; Landis, C. R.; Nasluzov, V. A.; Neyman, K. M.; Rösch, N. *Inorg. Chem.* **1997**, *36*, 3947.

(19) Hirano, M.; Akita, M.; Morikita, T.; Kubo, H.; Fukuoka, A.; Komiya, S. *J. Chem. Soc., Dalton Trans.* **1997**, 3453.

(20) Laplaza, C. E.; Johnson, M. J. A.; Peters, J. C.; Odom, A. L.; Kim, E.; Cummins, C. C.; George, G. N.; Pickering, I. J. *J. Am. Chem. Soc.* **1996**, *118*, 8623 and references therein.

(21) Zollinger, H. *Diazo Chemistry II*; VCH: Weinheim, Germany, 1995.

10.1021/ic990970r CCC: $19.00

on diazo complexes was not only to provide insight into the N$_2$ fixation mechanism and the nature of the intermediate but also to design a dinitrogen reduction process operating under mild conditions. Development of synthetic methods for obtaining organonitrogen compounds directly from N$_2$ as the nitrogen source under mild conditions was a further target of these studies. Despite the number of research studies, none of these goals have yet been achieved, but it is generally believed that systematic in-depth studies on dinitrogen and diazo transition metal complexes will soon lead to the activation of N$_2$ and its exploitation to produce NH$_3$ under milder conditions than those of the Haber−Bosch process.

As part of our contribution[25−33] to this field, we report here the syntheses, crystal structures and reactivity studies both of the first bis(dinitrogen) complexes of rhenium and of other diazo derivatives, including a rare example of a methyldiazenido complex.

(Dinitrogen)rhenium complexes with tertiary phosphine and carbonyl groups as ancillary ligands, of the types ReX(N$_2$)P$_4$,[34,35] ReX(CO)$_2$(N$_2$)P$_2$,[35,36] ReX(N$_2$)(P-P)$_2$,[34,35,37] [ReCl(N$_2$)(P-P)$_2$][FeCl$_4$],[38] and Re(S$_2$CNR$_2$)(N$_2$)(PPhMe$_2$)$_3$[39] ($X = Cl^-, Br^-, H^-$; P = monodentate phosphine; P-P = bidentate phosphine),[40−44] and with cyclopentadienyl groups as ligands, of the types CpRe(CO)$_2$(N$_2$),[45,46] Cp*Re(CO)$_2$(N$_2$),[47,48] and Cp*Re(CO)(N$_2$)(PR$_3$)[49] (Cp = η^5-C$_5$H$_5$, Cp* = η^5-C$_5$Me$_5$), have been reported. Except for ReCl(PPhMe$_2$)$_4$(μ-N$_2$)MoCl$_4$(OMe)[50] and Tp(CO)$_2$Re(μ-N$_2$)Re(CO)$_2$Tp (Tp = hydridotris(pyrazolyl)borate),[51] the reported compounds are all mononuclear and are often obtained by reactions of aryldiazenido [Re]−N$_2$COPh and [Re]−N$_2$Ar species. They contain only one molecule of N$_2$; bis(dinitrogen)rhenium derivatives are still without precedent.

Diazo complexes of rhenium are also known[21−24] and mainly include aryldiazenide species,[52−62] as hydrazine[63−65] and diazene[66−70] complexes are rather rare. No example of a methyldiazenido complex has ever been reported.

New studies on diazo complexes of rhenium are therefore of interest not only for their importance in nitrogen fixation processes, but also because of their diverse reactivity modes and structural properties.[21−24,52−70] This paper reports a systematic investigation of reactions of ReCl$_3$P$_3$ complexes with hydrazines that afford a series of new diazo derivatives.

Experimental Section

General Materials and Procedures. All synthetic work was carried out under 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 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. Metallic rhenium was a Chempur (Heraeus) product, used as received. Phosphines PPh(OEt)$_2$ and the PPh$_2$OEt were prepared by the method of Rabinowitz and Pellon.[71] Hydrazines CH$_3$NHNH$_2$, ^{t}BuNHNH$_2$·HCl, PhNHNH$_2$, and NH$_2$NH$_2$·H$_2$O were Aldrich products, used as received. The compound *p*-tolNHNH$_2$ (*p*-tol = *p*-tolyl) was prepared by treating under nitrogen the corresponding RNHNH$_2$·HCl salt with a slight excess of NaOH in aqueous solution. A solid separated out which, after 15 min of stirring, was filtered off, washed with water, and dried over P$_2$O$_5$ under vacuum

---

(22) Sutton, D. *Chem. Rev.* **1993**, *93*, 995.

(23) Kisch, H.; Holzmeier, P. *Adv. Organomet. Chem.* **1992**, *34*, 67.

(24) Johnson, B. F. G.; Haymore, B. L.; Dilworth, J. R. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, U.K., 1987; Vol. 2, p 130.

(25) Albertin, G.; Antoniutti, S.; Bacchi, A.; Barbera, D.; Bordignon, E.; Pelizzi, G.; Ugo, P. *Inorg. Chem.* **1998**, *37*, 5602.

(26) Albertin, G.; Antoniutti, S.; Bacchi, A.; Bergamo, M.; Bordignon, E.; Pelizzi, G. *Inorg. Chem.* **1998**, *37*, 479.

(27) Albertin, G.; Antoniutti, S.; Bordignon, E.; Pattaro, S. *J. Chem. Soc., Dalton Trans.* **1997**, 4445.

(28) Albertin, G.; Antoniutti, S.; Bacchi, A.; Bordignon, E.; Busatto, F.; Pelizzi, G. *Inorg. Chem.* **1997**, *36*, 1296.

(29) Albertin, G.; Antoniutti, S.; Bacchi, A.; Bordignon, E.; Pelizzi, G.; Ugo, P. *Inorg. Chem.* **1996**, *35*, 6245.

(30) Albertin, G.; Antoniutti, S.; Baldan, D.; Bordignon, E. *Inorg. Chem.* **1995**, *34*, 6205.

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

(32) Albertin, G.; Antoniutti, S.; Bordignon, E. *J. Am. Chem. Soc.* **1989**, *111*, 2072.

(33) Albertin, G.; Antoniutti, S.; Pelizzi, G.; Vitali, F.; Bordignon, E. *Inorg. Chem.* **1988**, *27*, 829.

(34) Chatt, J.; Dilworth, J. R.; Leigh, G. J. *J. Chem. Soc., Chem. Commun.* **1969**, 687.

(35) Chatt, J.; Dilworth, J. R.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1973**, 612.

(36) Chatt, J.; Dilworth, J. R.; Leigh, G. J. *J. Organomet. Chem.* **1970**, *21*, P49.

(37) Tully, M. E.; Ginsberg, A. P. *J. Am. Chem. Soc.* **1973**, *95*, 2042.

(38) Chatt, J.; Dilworth, J. R.; Gunz, H. P.; Leigh, G. J.; Sanders, J. R. *J. Chem. Soc., Chem. Commun.* **1970**, 90.

(39) Chatt, J.; Crabtree, R. H.; Dilworth, J. R.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1974**, 2358.

(40) Chin, R. M.; Barrera, J.; Dubois, R. H.; Helberg, L. E.; Sabat, M.; Bartucz, T. Y.; Lough, A. J.; Morris, R. H.; Harman, W. D. *Inorg. Chem.* **1997**, *36*, 3553.

(41) Dilworth, J. R.; Hu, J.; Miller, J. R.; Hughes, D. L.; Zubieta, J. A.; Chen, Q. *J. Chem. Soc., Dalton Trans.* **1995**, 3153.

(42) Orth, S. D.; Barrera, J.; Sabat, M.; Harman, W. D. *Inorg. Chem.* **1994**, *33*, 3026.

(43) Chatt, J.; Hussain, W.; Leigh, G. J.; Ali, H. M.; Pickett, C. J.; Rankin, D. A. *J. Chem. Soc., Dalton Trans.* **1985**, 1131.

(44) Leigh, G. J.; Morris, R. H.; Pickett, C. J.; Stanley, D. R.; Chatt, J. *J. Chem. Soc., Dalton Trans.* **1981**, 800.

(45) Sellmann, D. *J. Organomet. Chem.* **1972**, *36*, C27.

(46) Barrientos-Penna, C. F.; Einstein, F. W. B.; Sutton, D.; Willis, A. C. *Inorg. Chem.* **1980**, *19*, 2740.

(47) Einstein, F. W. B.; Klahn-Oliva A. H.; Sutton, D.; Tyers, K. G. *Organometallics* **1986**, *5*, 53.

(48) Cusanelli, A.; Sutton, D. *Organometallics* **1995**, *14*, 4651.

(49) Klahn, A. H.; Sutton, D. *Organometallics* **1989**, *8*, 198.

(50) Mercer, M.; Crabtree, R. H.; Richards, R. L. *J. Chem. Soc., Chem. Commun.* **1973**, 808.

(51) Gunnoe, T. B.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 8747.

(52) da Costa, M. T. A. R. S.; Dilworth, J. R.; Duarte, M. T.; da Silva, J. J. R. F.; Galvão, A. M.; Pombeiro, A. J. L. *J. Chem. Soc., Dalton Trans.* **1998**, 2405.

(53) Garcia-Minsal, A.; Sutton, D. *Organometallics* **1996**, *15*, 332.

(54) Nicholson, T.; Cook, J.; Davison, A.; Rose, D. J.; Maresca, K. P.; Zubieta, J. A.; Jones, A. G. *Inorg. Chim. Acta* **1996**, *252*, 421.

(55) Coutinho, B.; Dilworth, J. R.; Jobanputra, P.; Thompson, R. M.; Schmid, S.; Strähle, J.; Archer, C. M. *J. Chem. Soc., Dalton Trans.* **1995**, 1663.

(56) Richards, T. C.; Bard, A. J.; Cusanelli, A.; Sutton, D. *Organometallics* **1994**, *13*, 757.

(57) Cusanelli, A.; Batchelor, R. J.; Einstein, F. W. B.; Sutton, D. *Organometallics* **1994**, *13*, 5096.

(58) Kettler, P. B.; Chang, Y.-D.; Zubieta, J. *Inorg. Chem.* **1994**, *33*, 5864.

(59) Hitchcock, P. B.; Meidine, M. F.; Nixon, J. F.; Pombeiro, A. J. L. *J. Chem. Soc., Chem. Commun.* **1991**, 1031.

(60) Carr, S. W.; Fontaine, X. L. R.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1988**, 769.

(61) Hsieh, T.-C.; Nicholson, T.; Zubieta, J. *Inorg. Chem.* **1988**, *27*, 241.

(62) Nicholson, T.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1985**, 367.

(63) Moelwyn-Hughes, J. T.; Garner, A. W. B.; Howard, A. S. *J. Chem. Soc. A* **1971**, 2361.

(64) Vale, M. G.; Schrock, R. R. *Organometallics* **1991**, *10*, 1661.

(65) Moehlenkamp, A.; Mattes, R. *Z. Naturforsch., B* **1992**, *47*, 969.

(66) Moehlenkamp, A.; Mattes, R. *Z. Naturforsch., B* **1990**, *45*, 1167.

(67) Cheng, T.-Y.; Peters, J. C.; Hillhouse, G. L. *J. Am. Chem. Soc.* **1994**, *116*, 204.

(68) Kettler, P. B.; Chang, Y.-D.; Chen, Q.; Zubieta, J.; Abrams, M. J.; Larsen, S. K. *Inorg. Chim. Acta* **1995**, *231*, 13.

(69) Hirsch-Kuchma, M.; Nicholson, T.; Davison, A.; Davis, W. M.; Jones, A. G. *Inorg. Chem.* **1997**, *36*, 3237.

(70) Hirsch-Kuchma, M.; Nicholson, T.; Davison, A.; Davis, W. M.; Jones, A. G. *J. Chem. Soc., Dalton Trans.* **1997**, 3185.

(71) Rabinowitz, R.; Pellon, J. *J. Org. Chem.* **1961**, *26*, 4623.

for 24 h. The product was stored under nitrogen at −25 °C. Hydrazine, NH_2NH_2, was prepared by decomposition of hydrazine cyanurate (Fluka) following the reported method.[72] A solution of HCl (0.1 M) in Et_2O was prepared by treating Me_3SiCl with CH_3OH. 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) were obtained on a Bruker AC200 spectrometer at temperatures between −90 and +30 °C, unless otherwise noted. ^1H 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[73] 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 instrument.

Syntheses of the Complexes. The compounds $ReCl_3P_3$ [P = PPh(OEt)$_2$, PPh$_2$OEt] were prepared as previously reported.[74]

[ReCl(CH_3N_2)(CH_3NHNH_2){PPh(OEt)$_2$}$_3$][BPh$_4$] (1). To a suspension of ReCl$_3$[PPh(OEt)$_2$]$_3$ (1 g, 1.13 mmol) in 15 mL of ethanol *under an argon atmosphere* were added first an excess of methylhydrazine (0.6 mL, 11.3 mmol) and then an excess of NEt$_3$ (1.57 mL, 11.3 mmol), and the reaction mixture was stirred for about 2 h. The solvent was removed under reduced pressure, giving a brown oil, which was treated with 5 mL of ethanol. The addition of an excess of NaBPh$_4$ (2.33 g, 6.8 mmol) in 3 mL of ethanol to the resulting solution caused the separation of a yellow solid, from which compound **1** was extracted with three 4-mL portions of CH_2Cl_2. The extracts were evaporated to dryness, giving an oil, which was crystallized from ethanol; yield ≥40%. Anal. Calcd for $C_{56}H_{74}BClN_4O_6P_3Re$: C, 54.92; H, 6.09; N, 4.57; Cl, 2.89. Found: C, 54.84; H, 5.89; N, 4.49; Cl, 2.89. $\Lambda_M = 60.8\ \Omega^{-1}\ mol^{-1}\ cm^2$.

[Re(N$_2$)$_2${PPh(OEt)$_2$}$_4$][BPh$_4$] (2). A 25-mL three-necked round-bottomed flask was charged with 1 g (1.13 mmol) of ReCl$_3$[PPh(OEt)$_2$]$_3$ and 15 mL of ethanol *under a dinitrogen atmosphere*. First an excess of methylhydrazine (0.6 mL, 11.3 mmol), then an excess of NEt$_3$ (1.57 mL, 11.3 mmol), and last a slight excess of free PPh(OEt)$_2$ (0.44 mL, 2.26 mmol) were added, and the reaction mixture, was stirred for about 90 min. The solvent was removed under reduced pressure, giving an oil, which was treated with ethanol (7 mL) containing an excess of NaBPh$_4$ (2.33 g, 6.8 mmol). A yellow solid slowly separated out from the resulting solution, which was treated with four 3-mL portions of CH_2Cl_2 to extract the rhenium complexes that were formed. The extracts were evaporated to dryness, giving an oil, which was triturated with ethanol until a solid separated out. This solid was a mixture of methyldiazenido **1**, bis(dinitrogen) **2**, and traces of ReCl(N$_2$)P$_4$ (**3**), from which **2** was separated by repeated fractional crystallization from ethanol; yield ≥15%. Anal. Calcd for $C_{64}H_{80}BN_4O_8P_4Re$: C, 56.76; H, 5.95; N, 4.14. Found: C, 56.69; H, 5.95; N, 4.02. $\Lambda_M = 58.2\ \Omega^{1-}\ mol^{-1}\ cm^2$.

ReCl(N$_2$)[PPh(OEt)$_2$]$_4$ (3). To a suspension of ReCl$_3$[PPh(OEt)$_2$]$_3$ (1 g, 1.13 mmol) in 15 mL of ethanol under a dinitrogen atmosphere were added first an excess of ^{t}BuNHNH$_2$·HCl (1.4 g, 11.3 mmol), then an excess of NEt$_3$ (3.14 mL, 22.6 mmol), and last a slight excess of PPh(OEt)$_2$ (0.4 mL, 2 mmol). The reaction mixture was refluxed for 30 min, and the solvent was then removed under reduced pressure, giving an oil, which was treated with ethanol (5 mL). A pale-yellow solid slowly separated out after vigorous stirring of the resulting solution and was collected and crystallized from ethanol; yield ≥40%. Anal. Calcd for $C_{40}H_{60}ClN_2O_8P_4Re$: C, 46.09; H, 5.80; N, 2.69; Cl, 3.40. Found: C, 45.90; H, 5.83; N, 2.60; Cl, 3.21.

[ReCl(ArN$_2$)(ArNHNH$_2$){PPh(OEt)$_2$}$_3$][BPh$_4$] (4) [Ar = Ph (4a), *p*-tolyl (4b)]. An excess of the appropriate hydrazine ArNHNH$_2$ (11.3 mmol) was added to a suspension of ReCl$_3$[PPh(OEt)$_2$]$_3$ (1 g, 1.13 mmol) in 20 mL of ethanol, and the reaction mixture was stirred at room temperature for 2 h. The solvent was removed under reduced pressure, giving an oil, which was treated with ethanol (5 mL) containing an excess of NaBPh$_4$ (1.54 g, 4.5 mmol). The white solid (probably the hydrazinium salt) that separated out from the resulting solution was filtered off and discarded. The solution was cooled to −25 °C. After 24 h, an orange solid appeared. This was filtered off and crystallized from a mixture of CH_2Cl_2 (3 mL) and ethanol (5 mL); yield ≥60%. Anal. Calcd for $C_{66}H_{78}BClN_4O_6P_3Re$, **4a**: C, 58.77; H, 5.83; N, 4.15; Cl, 2.63. Found: C, 58.61; H, 5.70; N, 4.29; Cl, 2.70. $\Lambda_M = 56.2\ \Omega^{1-}\ mol^{-1}\ cm^2$. Anal. Calcd for $C_{68}H_{82}BClN_4O_6P_3Re$, **4b**: C, 59.32; H, 6.00; N, 4.07; Cl, 2.57. Found: C, 59.41; H, 5.92; N, 4.14; Cl, 2.68. $\Lambda_M = 54.9\ \Omega^{1-}\ mol^{-1}\ cm^2$.

[Re(ArN$_2$)$_2$P$_3$][BPh$_4$] (5, 6) [P = PPh(OEt)$_2$, Ar = Ph (5a); P = PPh(OEt)$_2$, Ar = *p*-tol (5b); PPh$_2$OEt, Ar = Ph (6)]. An excess of the appropriate arylhydrazine ArNHNH$_2$ (11.3 mmol) was added to a suspension of ReCl$_3$P$_3$ (1.13 mmol) in 20 mL of ethanol, and the reaction mixture was refluxed for about 1 h. The solvent was removed under reduced pressure, giving an oil, which was treated with ethanol (5 mL) containing an excess of NaBPh$_4$ (1.5 g, 4.5 mmol). The white solid (probably the hydrazinium salt) that separated out from the resulting solution was filtered off and discarded. An orange solid appeared after the remaining solution was cooled to −25 °C. This was filtered off and crystallized from a mixture of CH_2Cl_2 (3 mL) and ethanol (5 mL); yield ≥45%. Anal. Calcd for $C_{66}H_{75}BN_4O_6P_3Re$, **5a**: C, 60.50; H, 5.77; N, 4.28. Found: C, 60.51; H, 5.74; N, 4.29. $\Lambda_M = 57.9\ \Omega^{1-}\ mol^{-1}\ cm^2$. Anal. Calcd for $C_{68}H_{79}BN_4O_6P_3Re$, **5b**: C, 61.03; H, 5.95; N, 4.19. Found: C, 61.16; H, 5.94; N, 4.21. $\Lambda_M = 56.0\ \Omega^{1-}\ mol^{-1}\ cm^2$. Anal. Calcd for $C_{78}H_{75}BN_4O_3P_3Re$, **6**: C, 66.61; H, 5.38; N, 3.98. Found: C, 66.51; H, 5.54; N, 4.19. $\Lambda_M = 58.5\ \Omega^{1-}\ mol^{-1}\ cm^2$.

[ReCl(PhN$_2$){PPh(OEt)$_2$}$_4$][BPh$_4$] (7). To a suspension of ReCl$_3$[PPh(OEt)$_2$]$_3$ (1 g, 1.13 mmol) in 20 mL of ethanol were added first an excess of PPh(OEt)$_2$ (0.79 mL, 4 mmol) and then an excess of phenylhydrazine (1.15 mL, 11.3 mmol), and the reaction mixture was refluxed for 1 h. The solvent was removed under reduced pressure, giving an oil, which was treated with ethanol (5 mL) containing an excess of NaBPh$_4$ (1.54 g, 4.5 mmol). The white solid (probably the hydrazinium salt) that slowly separated out from the resulting solution was filtered off and discarded. An orange solid appeared after the remaining solution was cooled to −25 °C. This was filtered off and crystallized from ethanol; yield ≥60%. Anal. Calcd for $C_{70}H_{85}BClN_2O_8P_4Re$: C, 58.43; H, 5.95; N, 1.95; Cl, 2.46. Found: C, 58.64; H, 6.09; N, 2.07; Cl, 2.68. $\Lambda_M = 60.7\ \Omega^{1-}\ mol^{-1}\ cm^2$.

[ReCl(CH$_3$N═NH)(CH$_3$N$_2$){PPh(OEt)$_2$}$_3$][BPh$_4$] (8). A sample of [ReCl(CH$_3$N$_2$)(CH$_3$NHNH$_2$){PPh(OEt)$_2$}$_3$][BPh$_4$] (**1**) (0.10 g, 0.082 mmol) was placed in a 25-mL three-necked round-bottomed flask fitted with a solids-addition sidearm containing an equimolar amount of Pb(OAc)$_4$ (36 mg, 0.082 mmol). Dichloromethane (10 mL) was added, the resulting solution was cooled to −30 °C, and Pb(OAc)$_4$ was added portionwise over 30−40 min to the cold stirred solution. The reaction mixture was brought to 0 °C, and the solvent was removed under reduced pressure to give an oil. The addition at 0 °C of cold ethanol (2 mL) containing an excess of NaBPh$_4$ (55 mg, 0.16 mmol) caused the precipitation of a yellow-orange solid, which was filtered off and crystallized at 0 °C from a mixture of CH_2Cl_2 (1 mL) and ethanol (3 mL); yield ≥65%. Anal. Calcd for $C_{56}H_{72}BClN_4O_6P_3Re$: C, 55.02; H, 5.94; N, 4.58; Cl, 2.90. Found: C, 55.17; H, 5.86; N, 4.44; Cl, 3.01. $\Lambda_M = 53.6\ \Omega^{1-}\ mol^{-1}\ cm^2$.

[ReCl(PhN═NH)(PhN$_2$)(PPh$_2$OEt)$_3$][BPh$_4$] (10). To a solution of [Re(PhN$_2$)$_2$(PPh$_2$OEt)$_3$][BPh$_4$] (**6**) (0.10 g, 0.071 mmol) in 10 mL of CH_2Cl_2, cooled to −196 °C, was added a slight excess of HCl (0.078 mmol, 0.78 mL of a 0.1 M solution in diethyl ether), and the reaction mixture, brought to room temperature, was stirred for about 2 h. The solvent was removed under reduced pressure, giving an oil, which was triturated with 3 mL of ethanol containing an excess of NaBPh$_4$ (68 mg, 0.20 mmol). The red-brown solid that slowly precipitated out from the resulting solution was filtered off and crystallized from ethanol; yield ≥70%. Anal. Calcd for $C_{78}H_{76}BClN_4O_3P_3Re$: C, 64.93; H, 5.31; N, 3.88; Cl, 2.46. Found: C, 64.81; H, 5.42; N, 3.76; Cl, 2.59. $\Lambda_M = 49.7\ \Omega^{1-}\ mol^{-1}\ cm^2$.

X-ray Crystal Structure Determinations. Crystals suitable for X-ray diffraction analysis were obtained for compounds **1**, **2**, and **7** by slow cooling of saturated solutions of the complexes in ethanol. Diffraction data for all compounds were acquired at room temperature

---

(72) Nachbaur, E.; Leiseder, G. *Monatsh. Chem.* **1971**, *102*, 1718.
(73) Balacco, G. *J. Chem. Inf. Comput. Sci.* **1994**, *34*, 1235.
(74) Garcia-Fontán, S.; Marchi, A.; Marvelli, L.; Rossi, R.; Antoniutti, S.; Albertin, G. *J. Chem. Soc., Dalton Trans.* **1996**, 2779.

Table 1. Crystal Data and Structure Refinement Details for $[ReCl(CH_3N_2)(CH_3NHNH_2)\{PPh(OEt)_2\}_3][BPh_4]$ (**1**), $[Re(N_2)_2\{PPh(OEt)_2\}_4][BPh_4]$ (**2**), and $[ReCl(PhN_2)\{PPh(OEt)_2\}_4][BPh_4]$ (**7**)

	1	**2**	**7**
formula	$C_{56}H_{74}BClN_4O_6P_3Re$	$C_{64}H_{80}BN_4O_8P_4Re$	$C_{70}H_{85}BClN_2O_8P_4Re$
fw	1224.61	1354.26	1254.64
crystal dimensions (mm)	0.9 × 0.8 × 0.2	1 × 0.3 × 0.3	0.9 × 0.3 × 0.2
temp (k)	293(2)	293(2)	293(2)
wavelength (Å)	0.710 69	0.710 69	0.710 69
crystal system, space group	triclinic, $P\bar{1}$	orthorhombic, *Pbaa*	monoclinic, $P2_1/n$
color	orange	yellow	red
unit cell dimensions (Å; deg)	$a = 15.396(5)$, $b = 16.986(5)$, $c = 11.560(5)$ $\alpha = 93.96(5)$, $\beta = 93.99(5)$, $\gamma = 93.09(5)$	$a = 23.008(5)$, $b = 23.367(5)$, $c = 12.863(3)$	$a = 19.613(5)$, $b = 20.101(5)$, $c = 19.918(5)$; $\beta = 115.12(2)$
volume (Å^3)	3003(2)	6916(3)	7110(3)
Z, calcd density (Mg/m^3)	2, 1.354	4, 1.301	4, 1.344
abs coeff (mm^{-1})	2.196	1.901	1.889
max/min transmission factors	1.000/0.861	1.000/0.442	1.000/0.796
θ range for data collection (deg)	3−30	3−30	3−28
no. of collected/unique reflns	17 456/17 456	19 904/10 103 [R(int) = 0.0826]	16 450/16 450
no. od unique obsd reflns [$I > 2\sigma(I)$]	12 407	3846	7496
no. of data/restraints/parameters	17 456/2/679	10 103/22/406	16 450/0/800
goodness-of-fit on F^2	0.889	0.920	1.030
final R1, wR2 indices^a [$I > 2\sigma(I)$]	0.0340, 0.0661	0.0463, 0.1047	0.0414, 0.0768

^{a} $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$, $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

on a Philips PW100 diffractometer using Mo Kα ($\lambda = 0.710\,73$ Å) radiation, a graphite monochromator, and $\theta/2\theta$ scans. In each case, the intensity of one standard reflection was monitored every 100 measurements, and intensity decay corrections were found to be necessary for **1** and **2**. Empirical ψ-scan corrections for absorption effects were applied in all cases. The intensity data were processed with peak-profile procedures and corrected for Lorentz and polarization effects. Table 1 lists the most important details of the data collections and structure refinements for the compounds. In all cases, phase problems were solved by direct methods, using SIR97,[75] which allowed all non-hydrogen atoms to be retrieved. For **1**, it was necessary to consider the $P1$ space group to solve the phase problem, although intensity statistics indicated centrosymmetric structure. The structure showed the presence of the center of symmetry, and refinement was carried out in the $P\bar{1}$ space group. Neutral-atomic scattering factors were employed, those for non-hydrogen atoms being corrected for anomalous dispersion. Structures were successively refined on F^2 by a full-matrix least-squares program using SHELXL97.[76] In the last stages of refinement, anisotropic displacement parameters were used for all non-hydrogen atoms. In general, the substituents on the phosphites showed considerable anisotropic motion, and in one case, **1**, one atom appeared in two positions. Hydrogen atoms were introduced into calculated positions, riding on their carrier atoms, with the exception of hydrazine hydrogens in **1**, which were located on a difference Fourier map and refined isotropically, with restraints on bonding geometry. For **2** and **7**, isolated systems of residual peaks with significant electronic density were found and were introduced into the final refinements as disordered solvent molecules. Nevertheless, the final maps still revealed spurious features. In **2**, one of the two coordination sites for N_2 ligands (N1−N2) had a sausage-like electronic density and the N1−N2 distance refined to the extremely short value of 0.7 Å. This indicated substitutional disorder between N_2 and Cl^- due to contamination[77] of **2** with the mono(dinitrogen) complex $ReCl(N_2)[PPh(OEt)_2]_4$ (**3**), obtained together with **2** from the reaction of $ReCl_3[PPh(OEt)_2]_3$ with hydrazine (see below). The complementary site occupancies of N_2 and Cl^- were consequently refined (for stoichiometric consistence, the same occupancies were assigned to N_2 and BPh_4^-), and convergence was achieved by restraining the N1−N2 distance to 1.03 Å and that of Re−Cl to 2.52 Å, in agreement with average literature values, and by applying rigid-bond and similar thermal motion restraints for N_2 and Cl^-. The final amount of chloride was 9%. The second dinitrogen site (N3−N4) was not involved in disorder and was refined independently, with rigid-bond restraints on the thermal anisotropic parameters.

Electronic density maps were examined with the XtalView program,[78] running on a Silicon Graphics workstation. The final geometries were analyzed with the PARST97 program,[79] and the drawings of the structures were made with ZORTEP.[80] All calculations were performed on a Digital Alpha 255 computer at the Centro di Studio per la Strutturistica Diffrattometrica del CNR in Parma. Besides those of the original literature, data for comparison with other compounds were retrieved and analyzed by the software packages of the Cambridge Structural Database.[81] Complete lists of final atomic fractional coordinates, atomic displacement parameters, and bond distances and angles are deposited in CIF format as Supporting Information.

Results and Discussion

The outcomes of the reactions of the trichlororhenium complexes $ReCl_3P_3$ with hydrazines depend on the experimental conditions and the natures of the reagents, as shown in Schemes 1 and 2.

Under an argon atmosphere, the $ReCl_3P_3$ complex reacted with methylhydrazine to give the methyldiazenido $[ReCl(CH_3N_2)(CH_3NHNH_2)P_3]^+$ derivative $\mathbf{1}^+$, which was isolated as its BPh_4 salt and characterized (eq 1). In contrast, under a dinitrogen atmosphere, the reaction proceeded to give both methyldiazenido **1** and bis(dinitrogen) $[Re(N_2)_2P_4][BPh_4]$ (**2**) complexes, which were separated by fractional crystallization and characterized (eq 2). These results indicate that the N_2 ligand comes from the atmosphere of the reaction and is not due to

---

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

(76) Sheldrick G. M. *SHELXL97: Program for Structure Refinement*; University of Goettingen: Goettingen, Germany, 1997.

(77) Davis, B. R.; Ibers, J. A. *Inorg. Chem.* **1971**, *10*, 578.

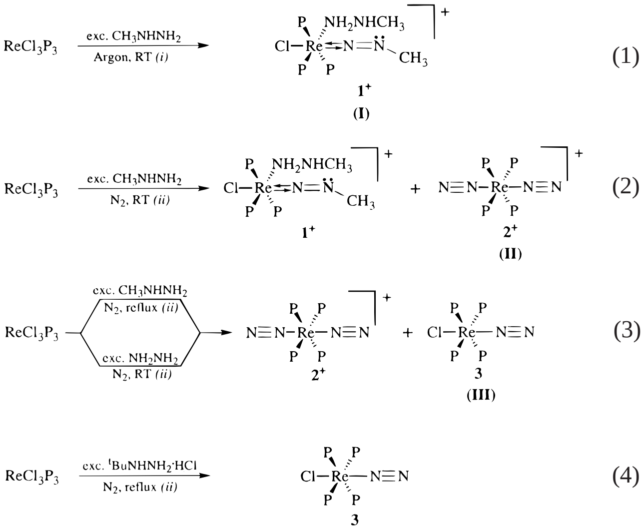
(78) McRee, D. E. *XtalView*, Release 3.2; The Scripps Research Institute, La Jolla, CA, 1997.

(79) Nardelli, M. PARST97, updated version of PARST95. *J. Appl. Crystallogr.* **1995**, *28*, 659.

(80) Zsolnai, L.; Pritzkow, H. *ZORTEP: ORTEP Original Program Modified for PC*; University of Heidelberg: Heidelberg, Germany, 1994.

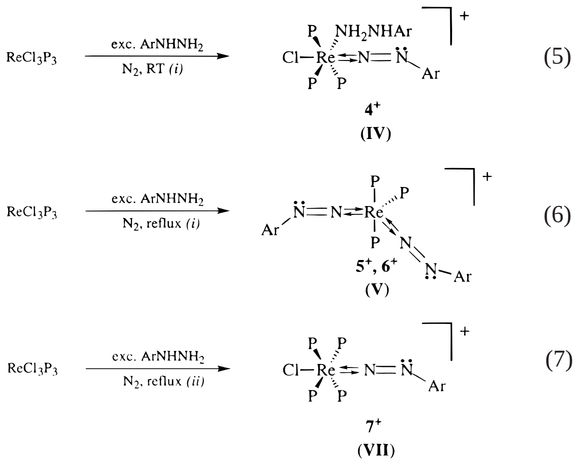
(81) Allen, F. H.; Kennard, O. Cambridge Structural Database. *Chem. Des. Autom. News* **1993**, *8*, 1, 31−37.

Scheme 1



P = PPh(OEt)$_2$; *(i)* = in C_2H_5OH solution containing an excess of NEt_3 (10:1 ratio); *(ii)* = in C_2H_5OH solution containing an excess of NEt_3 (10:1 ratio) and a slight excess of PPh(OEt)$_2$ (2:1 ratio)

Scheme 2



P = PPh(OEt)$_2$ **4**, **5**, **7**; PPh$_2$OEt **6**; Ar = Ph **a**; *p*-tolyl **b**; *(i)* = in C_2H_5OH solution; *(ii)* = in C_2H_5OH solution containing an excess of PPh(OEt)$_2$ (3:1 ratio)

degradation of methyldiazenido complex **1** or the dinitrogen formed by decomposition of the oxidation product of CH_3NHNH_2. The reduction of the central metal from Re(III) to Re(I) probably involves the methylhydrazine, whose oxidation product can liberate N_2, affording the dinitrogen complex. In the raw product of the reaction carried out under argon, traces of dinitrogen complex **2** were observed, but it was only when the reaction was conducted under N_2 that a reasonable amount of **2** was obtained.

Addition of free phosphite ligand PPh(OEt)$_2$ and varying amounts of NEt_3 to the reaction mixture only resulted in a slight variation of the ratio between **1** and **2** (eq 2), with an increase in bis(dinitrogen) complex **2** in the presence of PPh(OEt)$_2$ and an excess of NEt_3. We also attempted to isolate some intermediates, to collect information on the reaction path and the nature of the intermediate rhenium fragment which binds N_2, but the solids isolated at the initial stage of the reaction or with the use of a low CH_3NHNH_2:Re ratio contained a mixture of paramagnetic species, preventing any clear identification. However, in the final reaction product, we always observed a white solid identified as the ammonium salt [NHEt$_3$][BPh$_4$], which indicated that protons are liberated in the reaction course, as expected for the formation of the methyldiazenido ligand, $CH_3N{\equiv}N$, in **1** from the reaction of $ReCl_3P_3$ with CH_3NHNH_2.

Rhenium(V) complexes of the type $ReOCl_3P_2$ (P = tertiary phosphine) are reported to react with arylhydrazines,[52,54,82−84] affording mono- or bis(aryldiazenido) ($ReCl_2(N_2COPh)P_2$ or $ReCl(ArN_2)_2P_2$) derivatives. The use of methylhydrazine with Re(III) $ReCl_3P_3$ starting materials allows both the first bis(dinitrogen) and the first methyldiazenido−methylhydrazine complexes, **1** and **2**, to be prepared. However, to test the influence of the ancillary ligands on these reactions, other studies are in progress on $ReCl_3P_3$ complexes containing both tertiary phosphine, PR_3, and phosphite, $P(OR)_3$, which will be the subject of a forthcoming paper.

Bis(dinitrogen) complex **2** was also obtained by treating $ReCl_3P_3$ complexes either with hydrazine at 25 °C or with methylhydrazine at reflux, but in these cases, the mono(dinitrogen) complex $ReCl(N_2)P_4$ (**3**) (eq 3) was also formed and had to be separated from **2** by fractional crystallization. In contrast, only the mono(dinitrogen) compound $ReCl(N_2)P_4$ (**3**) was produced upon reacting $ReCl_3P_3$ complexes with *tert*-butylhydrazine (eq 4), and it was isolated in good yield and characterized.

No dinitrogen complex was obtained after treating $ReCl_3P_3$ complexes with arylhydrazines (Scheme 2), aryldiazenido derivatives **4**−**6** being the only products. . At room temperature, in fact, the $ReCl_3P_3$ complexes reacted with arylhydrazines to give aryldiazenido $[ReCl(ArN_2)(ArNHNH_2)P_3]^+$ (**4**$^+$) cations (eq 5), while under reflux, the reactions proceeded to give bis(aryldiazenido) $[Re(ArN_2)_2P_3]^+$ (**5**$^+$, **6**$^+$) derivatives (eq 6). Last, treatment of an $ReCl_3P_3$ complex with an excess of an arylhydrazine at reflux in the presence of free phosphite PPh(OEt)$_2$ afforded the $[ReCl(ArN_2)P_4]^+$ (**7**$^+$) cation (eq 7), which was isolated as its BPh_4^- salt and characterized.

Good analytical data were obtained for all rhenium complexes **1**−**7**. They are air-stable diamagnetic solids and are soluble in organic polar solvents in which they (except **3**) behave as 1:1 electrolytes.[85] The IR and NMR data (Table 2) support the proposed formulations.

At 3325−3205 cm^{-1}, the IR spectrum of methyldiazenido complex **1** shows three bands of weak intensity due to the ν(NH$_2$) and ν(NH) of the methylhydrazine ligand and a medium-intensity absorption at 1714 cm^{-1} attributed to ν(NN) of the methyldiazenido ligand. This value, falling above 1600 cm^{-1}, also indicates a singly bent diazenido ligand,[86] formally present as $CH_3N_2^+$, with the central metal in an oxidation state of I. The X-ray structure confirms this assignment (Figure 1). In the NMR proton spectra, the methylhydrazine shows the NH$_2$ and NH groups as broad multiplets at 5.74 and 3.28 ppm, respectively, and the methyl substituent as a doublet at 2.61 ppm. These assignments were confirmed by integration data and homodecoupling experiments. In the temperature range between +30 and −80 °C, the $^{31}P\{^1H\}$ NMR spectrum of **1** appears as an AB$_2$ multiplet, indicating that two phosphines are magnetically equivalent and different from the third. The spectroscopic data, however, do not allow a geometry in solution for **1** to be unambiguously assigned, since **I**, **Ia**, and **Ib** (Chart 1) equally fit both IR and NMR data.

---

(82) Dilworth, J. R.; Harrison, S. A.; Walton, D. R. M.; Schweda, E. *Inorg. Chem.* **1985**, *24*, 2594.
(83) Nicholson, T.; Lombardi, P.; Zubieta, J. *Polyhedron* **1987**, *6*, 1577.
(84) Chatt, J.; Dilworth, J. R.; Leigh, G. J.; Gupta, V. D. *J. Chem. Soc. A* **1971**, 2631.
(85) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.
(86) Haymore, B. L.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 3060.

Table 2. Selected IR and NMR Data for the Rhenium Complexes

compound				^{1}H NMR^{b,c}		spin	^{31}P{^{1}H} NMR^{b,d}
no.	formula	IR^a (cm^{-1})	assgnt	(ppm; J, Hz)	assgnt	syst	(ppm; J, Hz)
1	$[ReCl(CH_3N_2)(CH_3NHNH_2)\{PPh(OEt)_2\}_3][BPh_4]$	3325 w	ν(NH)	5.74 m, br	NH_2	AB_2	$\delta_A = 130.5$
		3287 m		3.28 m	NH		$\delta_B = 121.0$
		3205 w		4.15−3.50 m	CH_2		$J_{AB} = 22$
		1714 s	$\nu(N_2)$	3.16 s	CH_3N_2		
				2.61 d	CH_3NH		
				$J_{HH} = 6.2$			
				1.33, 1.29, 1.21 t	CH_3		
2	$[Re(N_2)_2\{PPh(OEt)_2\}_4][BPh_4]$	2094 s	$\nu(N_2)$	3.69 m	CH_2	A_4	130.3 s
				1.26 t	CH_3		
3	$[ReCl(N_2)\{PPh(OEt)_2\}_4]$	2027 s	$\nu(N_2)$	3.96, 3.64 m	CH_2	A_4	129.0 s
				1.19 t	CH_3		
4a	$[ReCl(C_6H_5N_2)(C_6H_5NHNH_2)\{PPh(OEt)_2\}_3][BPh_4]$	3354 w	ν(NH)	6.57 br	NH_2	AB_2	$\delta_A = 131.2$
		3287 m		5.89 t, br	NH		$\delta_B = 118.7$
		3214 w		4.00, 3.65 m	CH_2		$J_{AB} = 22$
		1653 s	$\nu(N_2)$	1.22, 1.19, 1.12 t	CH_3		
4b	$[ReCl(4\text{-}CH_3C_6H_4N_2)(4\text{-}CH_3C_6H_4NHNH_2)\{PPh(OEt)_2\}_3][BPh_4]$	3353 w	ν(NH)	6.53 br	NH_2	AB_2	$\delta_A = 133.5$
		3288 m		5.78 t, br	NH		$\delta_B = 123.2$
		3219 w		4.10−3.60 m	CH_2		$J_{AB} = 22$
		1653 s	$\nu(N_2)$	2.44, 2.33 s	$CH_3C_6H_4$		
				1.23, 1.19, 1.13 t	CH_3		
5a	$\{Re(C_6H_5N_2)_2\{PPh(OEt)_2\}_3][BPh_4]$	1642 m	$\nu(N_2)$	3.58 m	CH_2	$AB_2{}^g$	$\delta_A = 143.5$
		1616 s		1.26, 1.23, 1.06 t	CH_3		$\delta_B = 123.5$
							$J_{AB} = 15$
5b	$[Re(4\text{-}CH_3C_6H_4N_2)_2\{PPh(OEt)_2\}_3][BPh_4]^f$	1635 m	$\nu(N_2)$	3.70 m	CH_2	AB_2	$\delta_A = 144.3$
		1617 s		2.52 s	$CH_3C_6H_4$		$\delta_B = 125.2$
				1.27, 1.22, 1.06 t	CH_3		$J_{AB} = 15$
6	$[Re(C_6H_5N_2)_2(PPh_2OEt)_3][BPh_4]^f$	1653 sh	$\nu(N_2)$	3.37 m	CH_2	AB_2	$\delta_A = 125.3$
		1620 s		0.72 t	CH_3		$\delta_B = 104.0$
							$J_{AB} = 12$
7	$[ReCl(C_6H_5N_2)\{PPh(OEt)_2\}_4][BPh_4]^f$	1662 s	$\nu(N_2)$	3.69 m	CH_2	A_4	118.6 s
				1.22 t	CH_3		134−105 m^e
8	$[ReCl(CH_3N{=}NH)(CH_3N_2)\{PPh(OEt)_2\}_3][BPh_4]$	1695 s	$\nu(N_2)$	15.89 d, br	NH	AB_2	$\delta_A = 129.0$
				3.90 m	CH_2		$\delta_B = 119.6$
				3.34 s	CH_3N_2		$J_{AB} = 26$
				4.05 s	$CH_3N{=}NH$		
				1.31, 1.30, 1.28 t	CH_3		
10	$[ReCl(C_6H_5N{=}NH)(C_6H_5N_2)(PPh_2OEt)_3][BPh_4]$	1670 s	$\nu(N_2)$	14.20 d, br	NH	AB_2	$\delta_A = 105.6$
				3.50−3.30 m	CH_2		$\delta_B = 93.0$
				1.03, 0.99, 0.85 t	CH_3		$J_{AB} = 20$

[a] In KBr. [b] In CD_2Cl_2 at 25 °C. [c] Phenyl proton resonances are omitted. [d] Positive shift downfield from 85% H_3PO_4. [e] At −90 °C. [f] In $(CD_3)_2CO$. [g] At −30 °C.

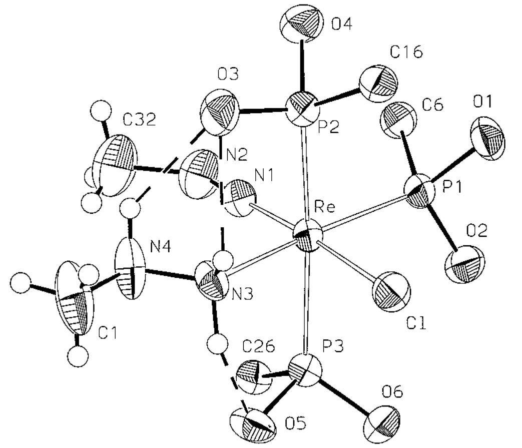
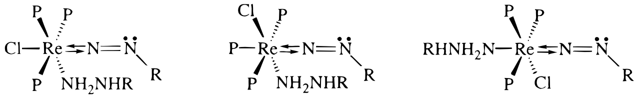


Figure 1. Perspective view of the crystal structure of the cation $[ReCl(CH_3N_2)(CH_3NHNH_2)\{PPh(OEt)_2\}_3]^+$ (**1**$^+$), with thermal ellipsoids drawn at the 50% probability level. The ethyl and phenyl groups of the phosphites are omitted for clarity. The network of intramolecular hydrogen bonds between methylhydrazine and ethoxy groups is represented as dashed bonds.

The solid-state structure (Figure 1) shows that the halide Cl^- is in a trans position with respect to the good π-acceptor $CH_3N_2{}^+$ group, and it is therefore probable that such geometry (type **I**) is also preserved in solution.

Chart 1



I **Ia** **Ib**

R = CH_3, Ph, *p*-tolyl

Methyldiazenido complexes are rather rare[87−92] and have often been obtained by reactions of diazomethane with transition metal hydrides. The use of methylhydrazine with $ReCl_3[PPh(OEt)_2]_3$ allowed us to synthesize the first complex containing both a methyldiazenido and a methylhydrazine ligand bonded to the same central metal.

Closely related to the methyldiazenido complex **1** are the aryldiazenido−arylhydrazine complexes $[ReCl(ArN_2)(ArNHNH_2)P_3][BPh_4]$ (**4**), which were obtained with the phenyl (**4a**) and *p*-tolyl (**4b**) substituents at the diazo groups (Scheme 2).

---

(87) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 355.
(88) Herrmann, W. A.; Ziegler, M. L.; Weidenhammer, K. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 368.
(89) Hillhouse, G. L.; Haymore, B. L.; Herrmann, W. A. *Inorg. Chem.* **1979**, *18*, 2423.
(90) Turney, T. W. *Inorg. Chim. Acta* **1982**, *64*, L141.
(91) Day, V. W.; George, T. A.; Iske, S. D. A. *J. Am. Chem. Soc.* **1975**, *97*, 4127.
(92) Tatsumi, T.; Hidai, M.; Uchida, Y. *Inorg. Chem.* **1975**, *14*, 2530.

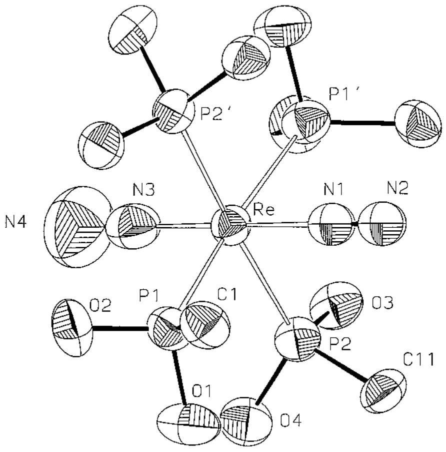


Figure 2. Perspective view of the crystal structure of the cation $[Re(N_2)_2\{PPh(OEt)_2\}_4]^+$ ($\mathbf{2}^+$), with thermal ellipsoids drawn at the 50% probability level. The ethyl and phenyl groups of the phosphites are omitted for clarity. Substitutional disorder between N1−N2 (91%) and Cl (9%) is not shown. The cation has 2-fold crystallographic symmetry.

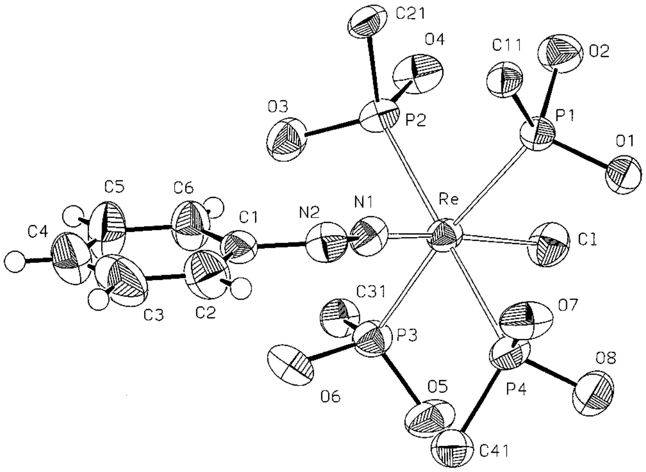


Figure 3. Perspective view of the crystal structure of the cation $[ReCl(PhN_2)\{PPh(OEt)_2\}_4]^+$ ($\mathbf{7}^+$), with thermal ellipsoids drawn at the 50% probability level. The ethyl and phenyl groups of the phosphites are omitted for clarity.

The spectroscopic data (Table 2) support the proposed formulation for **4** and suggest the presence of a singly bent aryldiazenido ligand ($\nu(N_2)$ at 1653 cm^{-1}) formally present as ArN_2^+ bonded to a Re(I) central metal.[86] However, the IR and NMR data (AB_2 multiplet in the $^{31}P\{^1H\}$ NMR spectra) do not allow us to assign a geometry among the three shown in Chart 1, although, by analogy with the related methyldiazenido compound **1**, we tentatively propose structure **I** for our aryldiazenido derivatives **4**, with the Cl^- and ArN_2^+ ligands in mutually trans positions.

The IR spectrum of the bis(dinitrogen) complex $[Re(N_2)_2\{PPh(OEt)_2\}_4][BPh_4]$ (**2**) shows only one strong $\nu(N_2)$ band[93] at 2094 cm^{-1}, suggesting mutually trans positions for the two dinitrogen ligands (geometry **II**, Scheme 1). This is confirmed by the $^{31}P\{^1H\}$ NMR spectra which, between +30 and −80 °C, display only one sharp singlet near 130 ppm. A similar trans geometry was observed in the solid state (Figure 2).

The mono(dinitrogen) complex $ReClN_2[PPh(OEt)_2]_4$ (**3**) also shows $\nu(N_2)$ as a sharp strong band at 2027 cm^{-1} whereas, between +30 and −90 °C, the $^{31}P\{^1H\}$ NMR spectra show a sharp singlet, suggesting mutually trans positions for the Cl^- ligand and the dinitrogen ligand (geometry **III**, Scheme 1).

Mononuclear complexes containing two dinitrogen ligands are scarce[1−7] and include the well-known Mo and W complexes $M(N_2)_2(P\text{-}P)_2$ and $M(N_2)_2P_4$ (P, P-P = mono-, bidentate phosphine)[94−99] and the $Na[V(N_2)_2(Me_2PCH_2CH_2PMe_2)]$ compound,[100] the related rhenium bis(dinitrogen) derivatives being unknown. The use of methylhydrazine as a reducing agent for the Re(III) complex $ReCl_3[PPh(OEt)_2]_3$ allows both bis(dinitrogen) **2** and the new mono(dinitrogen) **3** rhenium derivatives to be prepared.

The NMR data for the aryldiazenido $[ReCl(PhN_2)P_4]^+$ cation $\mathbf{7}^+$ indicate temperature-dependent behavior in solution. The broad singlet appearing at 118 ppm in the ^{31}P NMR spectrum at 25 °C does change as temperature falls and resolves into a complicated multiplet at −90 °C. This result implies the presence of inequivalent phosphorus nuclei and, in contrast with the trans structure observed in the solid state, suggests a cis arrangement for the Cl^- and ArN_2^+ ligands. However, the ^{31}P spectra may also be interpreted on the basis of a trans geometry, in which the four $PPh(OEt)_2$ ligands are made inequivalent by the different arrangement of the phenyl and ethoxy groups of one phosphite with respect to the other. Examples of inequivalent phosphorus nuclei in octahedral complexes containing four $PPhMe_2$ or $PPh(OEt)_2$ ligands in a plane were recently reported for $[IrCl_2(PPhMe_2)_4]ClO_4$,[101] $FeHCl[PPh(OEt)_2]_4$,[102] and $MnH(CO)[PPh(OEt)_2]_4$[103] derivatives. Taking into account these precedents and the crystal structure shown in Figure 3, discussed below, we find that the trans octahedral geometry **VII** (Scheme 2) may also be proposed in solution for the $[ReCl(PhN_2)\{PPh(OEt)_2\}_4][BPh_4]$ compound (**7**). A singly bent aryldiazenido PhN_2^+ ligand is also present in the complex, fitting the $\nu(N_2)$ value of 1662 cm^{-1} observed in the IR spectra.

The bis(aryldiazenido) $[Re(ArN_2)_2P_3][BPh_4]$ derivatives (**5**, **6**) show two medium-intensity $\nu(N_2)$ bands at 1653−1616 cm^{-1}, indicating the mutually cis positions of the two ArN_2 ligands. The absorption values also indicate a singly bent coordination for both aryldiazenido ligands, which are therefore formally bonded as ArN_2^+ to a metal center, resulting in the formal oxidation state of −I [Re(−I)]. Between +30 and −80 °C, the $^{31}P\{^1H\}$ NMR spectra of complexes **5** and **6** appear as AB_2 multiplets, indicating that two phosphites are magnetically equivalent and different from the third. However, the IR and NMR data do not allow us unambiguously to assign a geometry in solution to the compounds, since both geometries **V** and **VI** (Chart 2) fit the spectroscopic data.

---

(93) Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1970.

(94) Hidai, M.; Tominari, K.; Uchida, Y. *J. Am. Chem. Soc.* **1972**, *94*, 110.

(95) Chatt, J.; Pearman, A. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1977**, 2139.

(96) Carmona, E.; Marin, J. M.; Poveda, M. L.; Atwood, J. L.; Rogers, R. D. *J. Am. Chem. Soc.* **1983**, *105*, 3014.

(97) Dadkhah, H.; Dilworth, J. R.; Faiman, K.; Kan, C. T.; Richards, R. L.; Hughes, D. L. *J. Chem. Soc., Dalton Trans.* **1985**, 1523.

(98) Anderson, S. N.; Richards, R. L.; Hughes, D. L. *J. Chem. Soc., Dalton Trans.* **1986**, 245.

(99) George, T. A.; De Bord, J. R. D.; Kaul, B. B.; Pickett, C. J.; Rose, D. J. *Inorg. Chem.* **1992**, *31*, 1295.

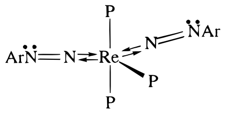
(100) Rehder, D.; Woitha, C.; Priebsch, W.; Gailus, H. *J. Chem. Soc., Dalton Trans.* **1992**, 364.

(101) Deeming, A. J.; Doherty, S.; Marshall, J. E.; Powell, N. I. *J. Chem. Soc., Chem. Commun.* **1989**, 1351.

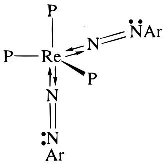
(102) Albertin, G.; Antoniutti, S.; Bordignon, E. *J. Organomet. Chem.* **1996**, *513*, 147.

(103) Albertin, G.; Antoniutti, S.; Bettiol, M.; Bordignon, E.; Busatto, F. *Organometallics* **1997**, *16*, 4959.

Chart 2



V



VI

As comparisons with the data reported for other pentacoordinate aryldiazenido complexes whose X-ray structures are known[21−25,104] indicate that singly bent aryldiazenido ligands generally occupy equatorial positions in bipyramidal geometries, we tentatively propose cis geometry **V** for our bis(aryldiazenido) complexes **5** and **6**.

X-ray Crystal Structures. In the cationic complex $[ReCl(CH_3N_2)(CH_3NHNH_2)\{PPh(OEt)_2\}_3]^+$ ($\mathbf{1}^+$), the metal coordinates one methyldiazenido, N1−N2−C32, and one methylhydrazine, N3−N4−C1, molecule; octahedral coordination is completed by a chloride, trans to the methyldiazenido ligand, and three phosphites (Figure 1). Table 3 lists relevant geometric features of $\mathbf{1}^+$. The structure is completed by a BPh_4^- counteranion. This is the first known crystal structure of a rhenium complex containing either an $NNCH_3$ or an NH_2NHCH_3 ligand. The diazenido fragment shows a linear arrangement around N1 (Re−N1−N2 = 173.3(3)°) and an sp^2 geometry around N2 (N1−N2−C32 = 125.0(3)°). This suggests a marked double-bond character for the Re−N and N−N bonds, as indicated by the very short bond distances Re−N1 = 1.817(3) and N1−N2 = 1.199(4) Å, explained by π back-donation from the metal to the ligand, fitting the geometry found for dicarbonyl(η^5-cyclopentadienyl)(methyldiazenido)tungsten[89] (W−N = 1.850, N−N = 1.281 Å; W−N−N = 173, N−N−C = 116°). The situation is different when the diazenido group is protonated, as in *trans,trans*-dicarbonyl(methylhydrazine)nitrosylbis(triphenylphosphine)tungsten hexafluorophosphate,[105] where the bond geometry is bent around the metal−nitrogen bond and the increase in bond strength is shifted toward the terminal methyl (W−N = 2.215, N−N = 1.330, N−C = 1.336 Å; W−N−N = 117, N−N−C = 119°). These two complexes[89,105] are the only other structurally known compounds containing the $NNCH_3$ ligand. The mode of coordination of the diazenido ligand influences the Re−Cl bond, situated trans to N1, which is longer (2.438(1) Å) than the mean distance found for terminal chlorides in octahedral Re complexes (2.391 Å). The methylhydrazine molecule, N3−N4−C1, is coordinated to rhenium by a typical σ single bond via the terminal $-NH_2$ group, with a bonding geometry similar to that observed for *trans*-carbonyl(methylhydrazine)bis(triphenylphosphine)rhodium perchlorate[106] (N−N = 1.454, N−C = 1.459 Å; Rh−N−N = 110, N−N−C = 113°), the only other structurally known metal complex containing this ligand. The Re−N3 and N−N bond lengths agree with those found for similar systems. The coordination of phosphites in **1** is an interesting example of the influence that nonbonding interactions may have on the bonding of metal complexes. It has been shown that these effects can induce distortions of up to 0.02 Å and 1−2° in coordination geometry; among others, "second-order effects" have been described, which affect bond lengths by deforming bond angles.[107] In compound **1**, the distance Re−P1 = 2.362(1) Å, trans to N3, is comparable to those observed for **2** and **7** (see below). The distances Re−P2 = 2.406(1) Å and Re−P3 = 2.412(1) Å are significantly longer, due to a system of strong intramolecular hydrogen bonds between the hydrazine NH groups and the ethoxy substituents carried by P2 and P3: N3−H1···O3 (N3···O3 = 2.855(4) Å, N3−H1···O3 = 102(2)°), N3−H2···O5 (N3···O5 = 2.807(4) Å, N3−H···O5 = 130(3)°), N4−H···O3 (N3···O3 = 3.165(4)

Table 3. Selected Bond Distances (Å) and Angles (deg), with Esd's in Parentheses

$[ReCl(CH_3N_2)(CH_3NHNH_2)\{PPh(OEt)_2\}_3][BPh_4]$ (**1**)			
Distances			
Re−Cl	2.438(1)	P2−O3	1.610(2)
Re−P1	2.362(1)	P2−O4	1.593(3)
Re−P2	2.406(1)	P3−O5	1.610(2)
Re−P3	2.412(1)	P3−O6	1.602(2)
Re−N1	1.817(3)	N1−N2	1.199(4)
Re−N3	2.235(3)	N2−C32	1.431(6)
P1−O1	1.601(2)	N3−N4	1.445(4)
P1−O2	1.601(2)	N4−C1	1.480(6)
Angles			
Cl−Re−P1	92.86(3)	P3−Re−N3	85.43(8)
Cl−Re−P2	89.38(3)	N1−Re−N3	95.4(1)
Cl−Re−P3	86.66(3)	Re−P1−O1	119.37(9)
Cl−Re−N1	175.66(9)	Re−P1−O2	112.38(9)
Cl−Re−N3	80.65(7)	Re−P2−O3	105.10(9)
P1−Re−P2	91.78(4)	Re−P2−O4	121.19(9)
P1−Re−P3	94.97(3)	Re−P3−O5	106.67(9)
P1−Re−N1	91.14(9)	Re−P3−O6	126.00(9)
P1−Re−N3	173.47(8)	Re−N1−N2	173.3(3)
P2−Re−P3	172.33(4)	N1−N2−C32	125.0(3)
P2−Re−N1	92.17(8)	Re−N3−N4	115.6(2)
P2−Re−N3	87.45(7)	N3−N4−C1	108.8(3)
P3−Re−N1	91.34(8)		
$[Re(N_2)_2\{PPh(OEt)_2\}_4][BPh_4]$ (**2**)			
Distances			
Re−N3	1.970(9)	Re−P1	2.445(2)
Re−N1	2.025(7)	N1−N2	1.022(2)
Re−P2	2.434(1)	N3−N4	1.09(1)
Re−Cl	2.44(2)		
Angles			
N3−Re−N1	180	P2′−Re−P1′	90.02(5)
N3−Re−P2	92.22(4)	N3−Re−P1	93.25(4)
N1−Re−P2	87.78(4)	N1−Re−P1	86.75(4)
N3−Re−P2′	92.22(4)	P2−Re−P1	90.03(5)
N1−Re−P2′	87.78(4)	P2′−Re−P1	89.72(5)
P2−Re−P2′	175.56(8)	P1′−Re−P1	173.50(9)
N3−Re−P1′	93.25(4)	Re−N1−N2	180
N1−Re−P1′	86.75(4)	Re−N3−N4	180
P2−Re−P1′	89.72(5)		
$[ReCl(PhN_2)]\{PPh(OEt)_2\}_4][BPh_4]$ (**7**)			
Distances			
Re−P1	2.441(2)	Re−Cl	2.437(2)
Re−P2	2.448(2)	Re−N1	1.799(6)
Re−P3	2.440(2)	N1−N2	1.220(7)
Re−P4	2.462(2)	N2−C1	1.44(1)
Angles			
P1−Re−P2	85.73(7)	P3−Re−P4	86.94(7)
P1−Re−P3	168.76(7)	P3−Re−Cl	84.05(7)
P1−Re−P4	92.78(7)	P3−Re−N1	93.9(2)
P1−Re−Cl	84.72(7)	P4−Re−Cl	89.32(7)
P1−Re−N1	97.2(2)	P4−Re−N1	86.6(2)
P2−Re−P3	94.90(7)	Cl−Re−N1	175.5(2)
P2−Re−P4	177.55(7)	Re−N1−N2	170.9(6)
P2−Re−Cl	92.48(7)	N1−N2−C1	125.8(7)
P2−Re−N1	91.7(2)		

---

[104] Albertin, G.; Antoniutti, S.; Pelizzi, G.; Vitali, F.; Bordignon, E. *J. Am. Chem. Soc.* **1986**, *108*, 6627.

[105] Smith, M. R., III; Keys, R. L.; Hillhouse, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 8312.

[106] Davies, C. J.; Dodd, I. M.; Harding, M. M.; Heaton, B. T.; Jacob, C.; Ratnam, J. *J. Chem. Soc., Dalton Trans.* **1994**, 787.

[107] Martìn, A. M.; Orpen, A. G. *J. Am. Chem. Soc.* **1996**, *118*, 1464.

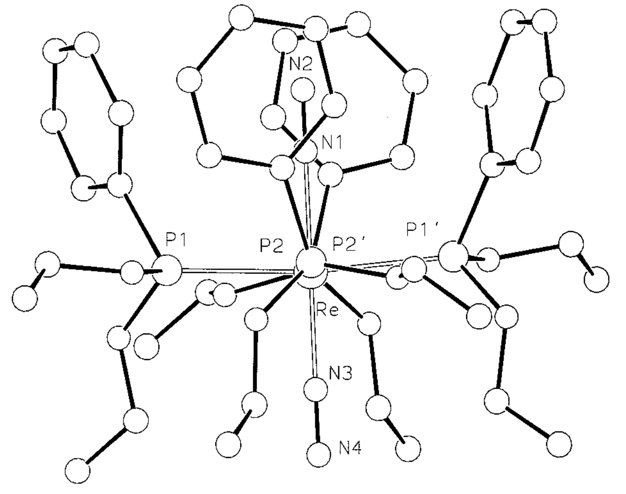


Figure 4. Complete sketch of the cation $[Re(N_2)_2\{PPh(OEt)_2\}_4]^+$ (**2**$^+$), showing the arrangement of phenyl groups around coordination site N1−N2.

Å, N4−H···O3 = 135(5)°). The same effect was observed in the complex bis(hydrazine)tetrakis(triethoxyphosphine)osmium bis(tetraphenylborate),[26] where a network of intramolecular hydrogen bonds induced a lengthening of about 0.06 Å in the Os−P distances. These interactions cause the bending of the phosphite toward N3 (P2−Re−N3 = 87.45(7), P3−Re−N3 = 85.43(8), Re−P2−O3 = 105.10(9), Re−P3−O5 = 106.67(9)°), slightly hindering the overlap of bonding orbitals between Re and P and producing the elongation of the Re−P bonds.

The complex cation $[Re(N_2)_2\{PPh(OEt)_2\}_4]^+$ (**2**$^+$) shows C_2 point group symmetry, the metal and the two dinitrogen molecules being collinear on a crystallographic 2-fold axis along *z* (Figure 2). The geometry around the metal is completed by four phosphite groups, symmetrically related in pairs, giving octahedral coordination. Table 3 lists principal bond distances and angles for the complex. The overall geometry of the cation is close to C_4 symmetry, the two independent phosphites being related by a pseudo-4-fold axis coinciding with the crystallographic 2-fold axis along *z*, and the cell constants simulate a tetragonal setting. The octahedral geometry is highly regular in the equatorial plane containing the P atoms, and it is slightly distorted along the *z* axis, as the angles P−Re−N3 are 93.25(4) and 92.22(4)° for P1 and P2, respectively. The bending of the phosphites toward N1−N2 is related to the peculiar arrangement of the ethoxy and phenyl groups, shown in Figure 4. The aromatic moieties define a 4-fold corolla around N1−N2, with the torsion angles N1−Re−P−C = 26.3(3) and 15.3(3)° for P1 and P2, respectively, and with a dihedral angle of 85° between the two independent rings C1−C6 and C11−C16. The ethoxy groups surround the N3−N4 molecule on the other side of the complex. A cavity with a volume of about 134 Å^3 is located on the molecular 2-fold axis, centered about 3.1 Å from N4, and contains approximately 5 electrons. This blurry electronic density has been explained in terms of a disordered solvent, whose loss might be the cause of the crystal decay observed during X-ray exposure. As mentioned in the Experimental Section, the coordination site of the molecule N1−N2 is partially occupied by a chloride anion and this prevents satisfactory definition of local bonding geometry. The distances Re−N3 = 1.970(9) Å and N3−N4 = 1.09(1) Å agree with other values observed for dinitrogen complexes of rhenium.

A search of the Cambridge Crystallographic Database[81] (October 1998 release) revealed that 13 other molecules containing the Re−N═N system are structurally known. However, ours is the first case in which the metal is coordinated to two N_2 molecules. The Re−N and N−N distances tend to be anticorrelated, according to a possible π back-donation from Re d occupied orbitals to the π^* LUMO of N_2. The extreme cases are *mer*-tris(dimethylphenylphosphine)(dinitrogen-*N*)(diphenyldithiophosphinato-*S*)(methyl isocyanide)rhenium[108] (Re−N = 1.828, N−N = 1.128 Å; Re−N−N = 174°), in which back-donation is significant, and tetrakis(diethylphenylphosphine)(dinitrogen-*N*)hydridorhenium[109] (Re−N = 2.055, N−N = 1.018 Å; Re−N−N = 180°), in which the N−N distance, trans to H$^-$, is apparently shorter than the N_2 internuclear distance in the gas phase (1.0976 Å). Compound **2** falls in the intermediate range, typical of complexes in which the dinitrogen is bonded trans to a chloride or a PMe_3 ligand.

The asymmetric unit also contains half of a BPh_4^- counteranion, with the B atom lying on a crystallographic 2-fold axis; crystal packing does not show any other important features except for van der Waals interactions.

In the cation $[ReCl(PhN_2)\{PPh(OEt)_2\}_4]^+$ (**7**$^+$), rhenium is bonded to a phenyldiazenido group, trans to a chloride ligand, and four phosphites complete the octahedral coordination (Figure 3). The crystal structure is completed by a BPh_4^- anion. Table 3 lists the most important bonding parameters for the cation. Comparison between the bonding situations of the diazenido ligands in **1** and **7** shows that replacement of the methyl substituent in the former with a phenyl group in the latter slightly shortens the Re−N bond (1.817(3) and 1.799(5) Å, respectively) and lengthens the N−N bond (1.199(4) and 1.220(7) Å, respectively), according to the greater π-acceptor capability of the phenyldiazenido with respect to the methyldiazenido ligand.[89] As already observed for **1**, the geometry of the diazenido group is essentially linear on N1 (Re−N1−N2 = 170.9(6)°) and bent on N2 (N1−N2−C1 = 125.8(7)°). The Re−Cl distance (2.437(2) Å) is the same as that in **1**, indicating similar trans effects of the two diazenido ligands, and the Re−P bonds clearly resemble those observed in **2**, where bonding is not perturbed by intramolecular hydrogen bonds. The phenyl group is slightly rotated around the N2−C1 bond (N1−N2−C1−C6 = −17(1)°), allowing optimization of the intramolecular interaction C6−H···O3 (C6···O3 = 3.440(8) Å, C6−H···O3 = 170.0(5)°). Other nonnegligible intramolecular interactions involving different phosphites may partially account for the temperature-dependent behavior observed in the solution ^{31}P NMR spectrum, which indicates that the four phosphites are not magnetically equivalent; i.e., their free rotation around the Re−P bonds is somewhat hindered. In the solid state, the substituents on the P atoms are differently oriented and the shortest contacts observed are C12−H···N2 (C···N = 3.22(1) Å, C−H···N = 118.4(5)°), C19−H···Cl (C···Cl = 3.39(1) Å, C−H···Cl = 122.4(5)°), and C39−H···O1 (C···O = 3.10(1) Å, C−H···O = 135.6(6)°), where C12 belongs to the phenyl at P1, C19 is bonded to O4, and C39 is bonded to O8.

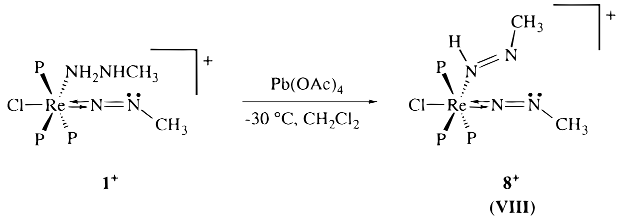
In the crystallographic literature, 15 cases of rhenium complexes with phenyldiazenido ligands are known, containing different substituents on the aromatic ring. In only one case (bis(1,2-bis(dimethylphosphino)ethane)bis((4-chlorophenyl)diazenido)rhenium(III) hexafluorophosphate)[55] is the coordination bent (Re−N−N = 147 and 149° for two independent ligands, acting as 1-electron donors); the geometry is generally linear

---

(108) Pombeiro, A. J. L.; Hitchcock, P. B.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1987**, 319.

(109) Chiu, K. W.; Howard, C. G.; Rzepa, H. S.; Sheppard, R. N.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *Polyhedron* **1982**, *1*, 441.

Scheme 3



P = PPh(OEt)2

in the remaining molecules, with Re−N−N angles ranging from 159 to 178°. In all cases, the N−N−C angles range from 116 to 126°.

Reactivity. The new dinitrogen complexes $[Re(N_2)_2P_4][BPh_4]$ (**2**) and $ReCl(N_2)P_4$ (**3**) are very stable, both as solids and in solution, and the N_2 group cannot easily be substituted by ligands such as CO or phosphite even after long reaction times. For example, bis(dinitrogen) complex **2** showed no substitution of N_2 after 24 h of reaction with CO (1 atm) at room temperature. Protonation with HBF_4 or CF_3SO_3H and methylation with $CF_3SO_3CH_3$ were also investigated and found to cause decomposition of compound **2**, with loss of N_2. However, in the case of $ReCl(N_2)P_4$ (**3**), while protonation resulted in decomposition, methylation with $CF_3SO_3CH_3$ proceeded slowly to give a rather unstable compound, which was isolated as a BPh_4^- salt and whose IR and NMR data support its formulation as the methyldiazenido derivative $[ReCl(CH_3N_2)P_4][BPh_4]$ (eq 8). The IR spectrum shows a medium-intensity band at 1739

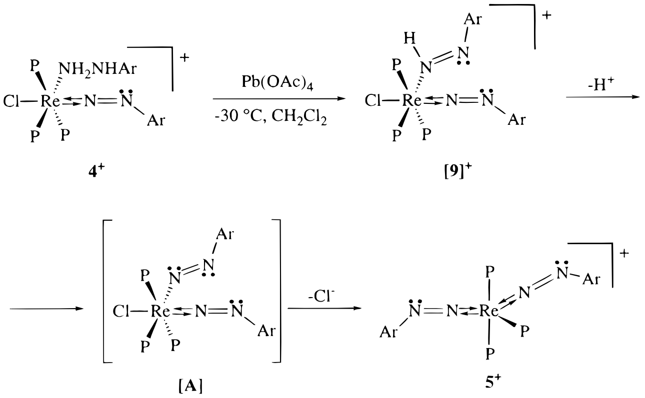
$$ReClN_2P_4 \xrightarrow{CF_3SO_3CH_3} [ReCl(CH_3N_2)P_4]^+ \qquad (8)$$

cm^{-1}, attributed to νN_2 of the CH_3N_2 group formed by methylation of the N_2 ligand. In the ^1H NMR spectrum, the singlet of the methyl substituent appears at 3.12 ppm, but in the $^{31}P\{^1H\}$ NMR spectrum, a multiplet appears, indicating a cis arrangement for the Cl^- and CH_3N_2 ligands. In contrast to the related $[ReCl(CH_3N_2)(CH_3NHNH_2)P_3][BPh_4]$ (**1**) complex, the new methyldiazenido $[ReCl(CH_3N_2)P_4]^+$ cation is unstable, both as a solid and in solution, and this prevents its complete characterization. However, the spectroscopic data and the precedent of compound **1** strongly support the formation of a methyldiazenido species by electrophilic attack[110] of CH_3^+ on the coordinate N_2 molecule in **3**.

The methylhydrazine ligand in the $[ReCl(CH_3N_2)(CH_3NHNH_2)P_3][BPh_4]$ (**1**) complex was selectively oxidized by $Pb(OAc)_4$ at low temperature to give the corresponding methyldiazene derivative $[ReCl(CH_3N{=}NH)(CH_3N_2)P_3][BPh_4]$ (**8**), which was isolated in good yield and characterized (Scheme 3).

Complex **8** is an orange-yellow stable solid, which is also stable in solutions of polar organic solvents, where it behaves as a 1:1 electrolyte.[85] Analytical and spectroscopic data (Table 2) support the proposed formulation. In particular, the presence of the diazene ligand is confirmed by the ^1H NMR spectrum, which shows the characteristic NH signal as a broad doublet at 15.89 ppm. The spectrum also contains two singlets at 4.05 and at 3.34 ppm, attributed to the methyl substituents of the $CH_3N{=}NH$ and CH_3N_2 ligands, respectively. The sharp singlet at 4.05 ppm and the rather high frequency of the NH proton signal (15.89 ppm) also seem to exclude the presence of a methylhydrazido(2−), $NN(H)CH_3$, ligand[26,82,111] formed by oxidation of the methylhydrazine molecule. A doublet due to the coupling with the NH proton should in fact be present for the CH_3 signal of a $NN(H)CH_3$ ligand, with the NH signal at a lower frequency than 15 ppm (11−12 ppm), as observed for other methylhydrazido(2-) complexes.[82,111,112]

Scheme 4



P = PPh(OEt)2; Ar = Ph, *p*-tolyl

The infrared spectrum of **8** shows the νN_2 band of the methyldiazenido ligand at 1695 cm^{-1} whereas, between −80 and +30 °C, the $^{31}P\{^1H\}$ NMR spectra display an AB_2 multiplet. These spectroscopic data (IR and NMR) fit the proposed structure (**VIII**), which is based on the hypothesis that oxidation of CH_3NHNH_2 does not change the geometry from that of precursor **1** to that of the final diazene derivative **8**.

Methyldiazene complexes are rare,[26,105,113] and no examples are reported for rhenium. The easy oxidation of **1** with $Pb(OAc)_4$ allows the synthesis of the first complex containing both one methyldiazene and one methyldiazenido ligand bonded to the same central metal.

Arylhydrazine−aryldiazenido complexes **4** also react with $Pb(OAc)_4$ at −30 °C to give, after workup, red-orange solids, which turn out to be the bis(aryldiazenido) $[Re(ArN_2)_2P_3][BPh_4]$ derivatives (**5**) and not the expected $[ReCl(ArN{=}NH)(ArN_2)P_3][BPh_4]$ complexes. However, this result is not completely surprising, taking into account the known properties of aryldiazene complexes,[21−25,28,29,32,33,104] which can easily be deprotonated to give the corresponding aryldiazenido derivatives. On this basis, it is plausible to hypothesize the path shown in Scheme 4 for the formation of the bis(aryldiazenido) complexes **5** from the oxidation of complexes **4**.

In fact, in this case too, reactions of complexes **4** with $Pb(OAc)_4$ probably give the aryldiazene−aryldiazenido cations **[9]**$^+$, which can lose the diazene proton to give intermediates **[A]**, each containing two aryldiazenido ligands, one singly bent (ArN_2^+) and one doubly bent (ArN_2^-). The deprotonating agent may be the acetate ion present in the reaction mixtures. Upon rearrangement of ArN_2^- to ArN_2^+ and concurrent formal reduction of the central metal to Re(−I), the bis(aryldiazenido) complexes are formed and probably lose one ligand to reach the more stable 18-electron configuration, as in **5**. Although the intermediates **[9]**$^+$ were not detected in these reactions, the closely related complex $[ReCl(PhN{=}NH)(PhN_2)(PPh_2OEt)_3][BPh_4]$ (**10**) can be obtained by protonation of $[Re(PhN_2)_2(PPh_2$-

---

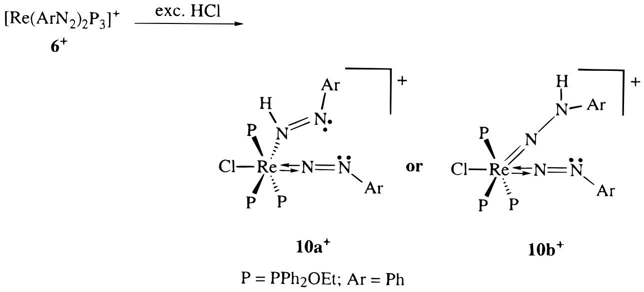
[110] Diamantis, A. A.; Chatt, J.; Heath, G. A.; Hooper, N. E.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1977**, 688.

[111] Barrientos-Penna, C. F.; Campana, C. F.; Einstein, F. W. B.; Jones, T.; Sutton, D.; Tracey, A. S. *Inorg. Chem.* **1984**, *23*, 363.

[112] Albertin, G.; Antoniutti, S.; Bacchi, A.; Bordignon, E.; Giorgi, M. T.; Pelizzi, G. Manuscript in preparation.

[113] Ackerman, M. N. *Inorg. Chem.* **1971**, *10*, 272.

Scheme 5



OEt)$_3$][BPh$_4$] (**6**) with HCl (see below). The subsequent treatment of **10** with NEt$_3$ gives back the bis(aryldiazenido) complex **6**, thus strongly supporting the path shown in Scheme 4.

These results prompted us to treat the methyldiazene complex [ReCl(CH$_3$N═NH)(CH$_3$N$_2$){PPh(OEt)$_2$}$_3$][BPh$_4$] (**8**) with an excess of NEt$_3$ in an attempt to prepare a bis(methyldiazenido) [Re(CH$_3$N$_2$)$_2$P$_3$][BPh$_4$] complex related to **5** (eq 9). However,

$$[\mathrm{ReCl(CH_3N{=}NH)(CH_3N_2)P_3}]^+ + \mathrm{NEt_3} \not\longrightarrow [\mathrm{Re(CH_3N_2)_2P_3}]^+ + \mathrm{NHEt_3}^+\mathrm{Cl}^- \qquad (9)$$

in this case, no reaction occurred and starting complex **8** was recovered unchanged after 24 h at 25 °C. This result was rather unexpected but may be explained as being due to the absence of acidity in methyldiazene in contrast to the properties of the related aryldiazene. However, as previously reported results[21−25,28,29,31−33,104] indicate that deprotonation of a diazene is often closely linked to one rearrangement, one reduction and the dissociation of one ligand (see Scheme 4), the lack of reactivity of **8** toward a base may be related to the whole sequence of reactions and not only to the low acidity of the diazene. Furthermore, the properties of the final aryldiazenido compounds can also influence the deprotonation reactions, and the nonreactivity of **8** may also be due to a reluctance to form a bis(methyldiazenido) Re(−I) derivative. In any case, the natures of the substituents on the NN groups in these diazene and diazenido rhenium complexes seem to be significant in determining their chemical properties.

Aryldiazenido complexes are reported to react with Brønsted acids to give the corresponding aryldiazene derivatives,[21−33] and we therefore tested this type of reaction using HCl, CF$_3$SO$_3$H, and CF$_3$COOH, for both the methyldiazenido complexes **1** and **8** and the aryldiazenido complexes **4**−**7** derivatives. Results show that only bis(aryldiazenido) complexes **5** and **6** react with strong acids to give new derivatives of the type **10**, which, in the case of the reaction with HCl, was isolated in the solid state and characterized (Scheme 5).

The other mono(diazenido) complexes **1**, **8**, **4** and **7** do not react toward protonation (as ascertained by NMR) and may be isolated unchanged even after treatment with excess acid.

The new compound **10** is an air-stable orange solid that is diamagnetic and behaves as a 1:1 electrolyte. Its spectroscopic data indicate that only one aryldiazenido ligand in **6** is protonated, affording an aryldiazene, ArN═NH, or an arylhydrazido(2−), Ar(H)NN, derivative of type **10a** or **10b**, respectively. However, the observed spectroscopic properties are not sufficient to distinguish between the two possible protonation sites on the aryldiazenide ligand, and the absence of any X-ray structure prevents conclusive assignment of the geometry. The IR spectrum shows a νN$_2$ absorption of the aryldiazenido ligand at 1670 cm^{-1}, whereas the ^{1}H NMR spectrum shows an NH signal due to the ArN═NH or Ar(H)NN ligand present as a broad doublet at 14.20 ppm. Two phosphines, magnetically equivalent and different from the third, are also present in the complex, as indicated by the AB$_2$ multiplet observed in the ^{31}P-{^{1}H} NMR spectrum. The ν(N$_2$) adsorption at 1670 cm^{-1} also indicates a singly bent ArN$_2^+$ ligand. On this basis, the aryldiazene [ReCl(ArN═NH)(ArN$_2$)P$_3$]$^+$ (**10a**$^+$) should contain a formal Re(I) central metal and the arylhydrazide(2−) [ReCl{Ar(H)NN}(ArN$_2$)P$_3$]$^+$ (**10b**$^+$) a formal Re(III), indicating that the protonation reaction of a singly bent aryldiazenido ligand in [Re(ArN$_2$)$_2$P$_3$]$^+$ (**6**$^+$) results in 2 e$^-$ or 4 e$^-$ oxidation of the central metal.

This feature may also explain the lack of reactivity toward acid of all the mono(aryldiazenido) Re(I) complexes **1**, **4**, **7**, and **8**, whose probable reluctance to give rhenium complexes in a high oxidation state (III or V) prevents protonation from taking place.

Conclusions

This paper reports some new aspects of the diazo chemistry of rhenium. In particular, the syntheses of both the unprecedented bis(dinitrogen) [Re(N$_2$)$_2$P$_4$][BPh$_4$] (**2**) and methyldiazenido [ReCl(CH$_3$N$_2$)(CH$_3$NHNH$_2$)P$_3$][BPh$_4$] (**1**) derivatives were easily achieved using methylhydrazine as the reducing agent for the trichloro Re(III) complex ReCl$_3$P$_3$. Diazo complexes such as the mono(dinitrogen) ReCl(N$_2$)P$_4$ (**3**), the bis(aryldiazenido) [Re(ArN$_2$)$_2$P$_3$][BPh$_4$], and the mono(aryldiazenido) [ReCl(ArN$_2$)(ArNHNH$_2$)P$_3$][BPh$_4$] and [ReCl(ArN$_2$)P$_4$][BPh$_4$] derivatives were prepared. The first structural parameters for both bis(dinitrogen) **2** and methyldiazenido−methylhydrazine **1** complexes of rhenium were also obtained. Reactivity studies carried out on these new complexes highlighted their interesting properties, including selective oxidation of the methylhydrazine ligand in **1** by lead tetraacetate to give the corresponding methyldiazene derivative [ReCl(CH$_3$N═NH)(CH$_3$N$_2$){PPh(OEt)$_2$}$_3$][BPh$_4$] (**8**). The methylation reaction of the dinitrogen ligand in **3**, affording an unstable species characterized as methyldiazenido [ReCl(CH$_3$N$_2$)P$_4$]$^+$, was also detected.

Acknowledgment. The financial support of MURST (Rome) is gratefully acknowledged. We thank Dr. G. Balacco (Menarini Ricerche S.p.A.) for the use of his NMR software SwaN-MR and D. Baldan for technical assistance.

Supporting Information Available: X-ray crystallographic files, in CIF format, for the structure determinations of complexes **1**, **2**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC990970R