Inorg. Chem. **2001,** *40,* 5465−5467 **5465**

Diazo Complexes of Rhenium with Phosphite Ligands: Facile Synthesis of Bis(dinitrogen) $[Re(N_2)_2P_4]BPh_4$ Derivatives

Gabriele Albertin,* Stefano Antoniutti,
Emilio Bordignon, and Eros Visentin

Dipartimento di Chimica, Università Ca' Foscari di Venezia,
Dorsoduro 2137, 30123 Venezia, Italy

Received April 27, 2001

Introduction

Previous reports[1] from our laboratory dealt with studies of the reaction of rhenium trichloro complexes, $ReCl_3[PPh(OEt)_2]_3$, with hydrazines, which gives new “diazo” derivatives, including the first bis(dinitrogen) complex for this metal, $[Re(N_2)_2P_4]BPh_4$. However, the compound was obtained as a byproduct in low yield. We have now extended these studies to include the reaction of phosphite $P(OR)_3$ (R = Me, Et) containing $ReCl_3P_3$ derivatives, and we have found a rapid and easy method for the preparation, in high yield, of bis(dinitrogen) complexes.

In view of current interest[2,3] in the chemistry of N_2 derivatives, which may be considered the first stage of the N_2 fixation processes,[3,4] this paper reports the synthesis and characterization of new bis(dinitrogen) complexes of rhenium. A study on the influence of phosphite ligands in the reaction of $ReCl_3P_3$ species with hydrazines, which allows new aryldiazenido and hydrazine complexes to be prepared, is also reported.

Experimental Section

All synthetic work was carried out in an inert atmosphere (Ar or N_2) using standard Schlenk techniques or a vacuum atmosphere drybox. Once isolated, the complexes were found to be relatively stable in air, but were nevertheless stored 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. Metallic rhenium was a Chempur (Germany) product and used as received. Phosphites $P(OMe)_3$ and $P(OEt)_3$ were Aldrich products, which were purified by distillation under nitrogen. Hydrazines CH_3NHNH_2, $^tBuNHNH_2{\cdot}HCl$, $PhNHNH_2$, and $NH_2NH_2{\cdot}H_2O$ were also Aldrich products and used as received. 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 +30 and −90 °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[5] was used to treat NMR data. The conductivity of 10^{-3} M solutions of the complexes in CH_3NO_2 at 25 °C were measured with a CDM 83 Radiometer.

Synthesis of Complexes. Compound $ReOCl_3(AsPh_3)_2$ was prepared as previously reported.[6]

$[Re(N_2)_2P_4]BPh_4$ (1) [P = $P(OEt)_3$ (a), $P(OMe)_3$ (b)]. An excess of the appropriate phosphite (6 mmol) was added to a solution of $ReOCl_3(AsPh_3)_2$ (1 mmol, 0.92 g) in 8 mL of tetrahydrofuran (thf), and the reaction mixture stirred for 1 h. Ethanol or methanol (16 mL), an excess of NEt_3 (20 mmol, 2.8 mL), and then an excess of solid $^tBuNHNH_2{\cdot}HCl$ (10 mmol, 1.25 g) were sequentially added to the solution, which was stirred for about 4 h. After filtration, the solvent was removed under reduced pressure, giving an oil which was treated with ethanol (10 mL) containing an excess of $NaBPh_4$ (6.5 mmol, 2.2 g). The white solid that separated out from the resulting solution was filtered off and discarded. A yellow solid appeared after the remaining solution had been concentrated to 3−4 mL and cooled to −25 °C, which was filtered and crystallized from CH_2Cl_2 (2 mL) and ethanol (5 mL); yield 40−60%. Anal. Calcd for **1a**: C, 47.02; H, 6.58; N, 4.57. Found: C, 47.16; H, 6.44; N, 4.70. $\Lambda_M = 52.9\ \Omega^{-1}\ mol^{-1}\ cm^2$. IR (KBr): 2108 [s, $\nu(N_2)$] cm^{-1}. ^1H NMR [$(CD_3)_2CO$, 25 °C; δ]: 7.35−6.70 (m, 20 H, Ph), 4.21 (m, 24 H, CH_2), 1.41 (t, 36 H, CH_3). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$, 25 °C; δ]: 110.3 s. Anal. Calcd for **1b**: C, 40.88; H, 5.34; N, 5.30. Found: C, 41.05; H, 5.49; N, 5.24. $\Lambda_M = 56.3\ \Omega^{-1}\ mol^{-1}\ cm^2$. IR (KBr): 2109 [s, $\nu(N_2)$] cm^{-1}. ^1H NMR [CD_2Cl_2, 25 °C; δ]: 7.40−6.84 (m, 20 H, Ph), 3.72 (t, 36 H, CH_3). $^{31}P\{^1H\}$ NMR [CD_2Cl_2, 25 °C; δ]: 113.8 s.

$[ReCl(PhN_2)\{P(OEt)_3\}_4]BPh_4$ (2). An excess of triethyl phosphite (6 mmol, 1 mL) was added to a solution of $ReOCl_3(AsPh_3)_2$ (1 mmol, 0.92 g) in 10 mL of thf, and the reaction mixture was stirred for 1 h. Ethanol (10 mL), an excess of NEt_3 (10 mmol, 1.4 mL), and then an excess of phenylhydrazine (10 mmol, 1.1 mL) were sequentially added to the solution, which was refluxed for 30 min. The solvent was removed under reduced pressure, giving an oil which was treated with ethanol (10 mL) containing an excess of $NaBPh_4$ (6 mmol, 2.05 g). A reddish−brown solid slowly separated out after vigorous stirring of the resulting solution, which was filtered and crystallized by dissolving in CH_2Cl_2 (5 mL) and, after filtration and concentration, adding enough ethanol (5 mL) to give separation of the solid; yield ≥40%. Anal. Calcd: C, 49.49; H, 6.54; N, 2.14; Cl, 2.71. Found: C, 49.38; H, 6.48; N, 2.20; Cl, 2.88. $\Lambda_M = 55.5\ \Omega^{-1}\ mol^{-1}\ cm^2$. IR (KBr): 1603 [m, $\nu(N_2)$] cm^{-1}. ^1H NMR [$(CD_3)_2CO$, 25 °C; δ]: 7.60−6.80 (m, 25 H, Ph), 4.06 (m, 24 H, CH_2), 1.23 (t, 36 H, CH_3). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$, 25 °C; δ]: 95.9 s.

$[\{Re[P(OEt)_3]_4\}_2(\mu\text{-}NH_2NH_2)_2](BPh_4)_2$ (3). An excess of $P(OEt)_3$ (6 mmol, 1 mL) was added to a solution of $ReOCl_3(AsPh_3)_2$ (1 mmol, 0.92 g) in 10 mL of thf, and the reaction mixture was stirred for 1 h. An excess of $NH_2NH_2{\cdot}H_2O$ (6 mmol, 0.29 mL) and 10 mL of ethanol were then added to the solution, which was stirred at room temperature for 3 h. The solvent was removed under reduced pressure, giving an oil which was treated with ethanol (10 mL) containing an excess of $NaBPh_4$ (6 mmol, 2.05 g). The white solid (probably the hydrazinium salt) that separated out from the resulting solution was filtered off and discarded. A reddish−brown solid slowly appeared after the remaining solution had been concentrated to 5 mL and cooled to −25 °C. This was filtered and crystallized from CH_2Cl_2 (2 mL) and ethanol (4 mL);

---

* To whom correspondence should be addressed.

(1) Albertin, G.; Antoniutti, S.; Bacchi, A.; Bordignon, E.; Miani, F.; Pelizzi, G. *Inorg. Chem.* **2000**, *39*, 3283.

(2) (a) Caselli, A.; Solari, E.; Scopelliti, R.; Floriani, C.; Re, N.; Rizzoli, C.; Chiesi-Villa, A. *J. Am. Chem. Soc.* **2000**, *122*, 3652. (b) Clentsmith, G. K. B.; Bates, V. M. E.; Hitchcock, P. B.; Cloke, F. G. N. *J. Am. Chem. Soc.* **1999**, *121*, 10444. (c) Peters, J. C.; Cherry, J.-P. F.; Thomas, J. C.; Baraldo, L.; Mindiola, D. J.; Davis, W. M.; Cummins, C. C. *J. Am. Chem. Soc.* **1999**, *121*, 10053. (d) Fryzuk, M. D.; Johnson, S. A.; Rettig, S. J. *J. Am. Chem. Soc.* **1998**, *120*, 11024. (e) Nishibayashi, Y.; Iwai, S.; Hidai, M. *J. Am. Chem. Soc.* **1998**, *120*, 10559. (f) Roussel, P.; Scott, P. *J. Am. Chem. Soc.* **1998**, *120*, 1070. (g) O’Donoghue, M. B.; Zanetti, N. C.; Davis, W. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 2753. (h) Hahn, J.; Landis, C. R.; Nasluzov, V. A.; Neyman, K. M.; Rösch, N. *Inorg. Chem.* **1997**, *36*, 3947.

(3) (a) Hidai, M.; Mizobe, Y. *Chem. Rev.* **1995**, *95*, 1115. (b) Leigh, G. J. *New J. Chem.* **1994**, *18*, 157. (c) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589.

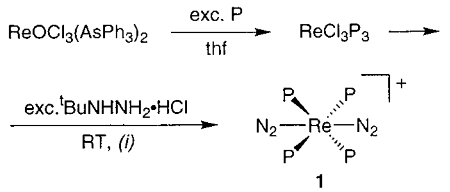
(4) (a) Shilov, A. E. *Metal Complexes in Biomimetic Chemical Reactions*; C.R.C.: Boca Raton, FL, 1997. (b) Sellmann, D.; Sutter, J. *Acc. Chem. Res.* **1997**, *30*, 460. (c) Richards, R. L. *Coord. Chem. Rev.* **1996**, *154*, 83. (d) Leigh, G. J. *Science* **1995**, *268*, 827.

(5) Balacco, G. *J. Chem. Inf. Comput. Sci.* **1994**, *34*, 1235. Upgrades via the Internet at: http://qobrue.usc.es/jsgroup/swan/index.html.

(6) Garcia-Fontán, S.; Marchi, A.; Marvelli, L.; Rossi, R.; Antoniutti, S.; Albertin, G. *J. Chem. Soc., Dalton Trans.* **1996**, 2779.

10.1021/ic0104508 CCC: \$20.00

Scheme 1[a]



[a] P = P(OEt)$_3$ (**a**), P(OMe)$_3$ (**b**); *(i)* = in thf/ROH (R = Et, Me) (1:2) solution containing an excess of NEt$_3$ (20:1 ratio).

yield ≥20%. Anal. Calcd: C, 47.96; H, 7.04; N, 2.33. Found: C, 48.14; H, 6.95; N, 2.27. $\Lambda_M = 124.9\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. IR (KBr): 3367, 3346 [m, ν(NH)], 1616 [δ(NH$_2$)] cm^{-1}. ^{1}H NMR [CD$_2$Cl$_2$, 25 °C; δ]: 7.40−6.84 (m, 40 H, Ph), 4.02, 3.87 (m, 48 H, CH$_2$), 2.30 (br, 8 H, NH$_2$), 1.26, 1.19 (t, 72 H, CH$_3$). ^{31}P{^{1}H} NMR [CD$_2$Cl$_2$, −55 °C; δ]: spin system A$_2$B$_2$, δ_A 120.3, δ_B 115.7, J_{AB} = 36.5 Hz.

[Re(PhN$_2$)(PhNHNH$_2$){P(OMe)$_3$}$_4$](BPh$_4$)$_2$ (4). To a solution of ReOCl$_3$(AsPh$_3$)$_2$ (1 mmol, 0.92 g) in 10 mL of thf were added first an excess of P(OMe)$_3$ (6 mmol, 0.74 mL) and, after 1 h of stirring, then an excess of NEt$_3$ (10 mmol, 1.4 mL), an excess of PhNHNH$_2$ (10 mmol, 1.1 mL), and 10 mL of methanol. The reaction mixture was stirred for 3 h, and then the solvent was removed under reduced pressure, giving an oil which was treated with 7 mL of methanol containing an excess of NaBPh$_4$ (6 mmol, 2.05 g). An orange solid separated out from the resulting solution, which was cooled to −25 °C. This was filtered, and the complex extracted with three 5 mL portions of CH$_2$Cl$_2$. The extracts were evaporated to dryness, giving a pink solid which was crystallized from ethanol; yield ≥35%. Anal. Calcd: C, 56.37; H, 5.85; N, 3.65. Found: C, 56.24; H, 5.93; N, 3.55. $\Lambda_M = 128.7\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. IR (KBr): 3356 w, 3325 m, 3263 m [ν(NH)], 1755 [s, ν(N$_2$)] cm^{-1}. ^{1}H NMR [CD$_2$Cl$_2$, 25 °C; δ]: 7.50−6.80 (m, 50 H, Ph), 4.65 (br, 2 H, NH$_2$), 3.61 (m, 36 H, CH$_3$). ^{31}P{^{1}H} NMR [CD$_2$Cl$_2$, 25 °C; δ]: spin system ABC$_2$, δ_A 108.8, δ_B 100.3, δ_C 96.6, J_{AB} = 59.7, J_{AC} = 34.9, J_{BC} = 52.4 Hz.

[ReCl(CH$_3$N$_2$)(CH$_3$NHNH$_2$){P(OMe)$_3$}$_3$]BPh$_4$ (5). To a solution of ReOCl$_3$(AsPh$_3$)$_2$ (1 mmol, 0.92 g) in 10 mL of thf were added, first an excess of P(OMe)$_3$ (6 mmol, 0.74 mL) and, after 1 h of stirring, an excess of NEt$_3$ (10 mmol, 1.4 mL), an excess of methylhydrazine (10 mmol, 0.53 mL), and 10 mL of methanol. The reaction mixture was stirred at room temperature for 3 h, and then the solvent was removed under reduced pressure. The oil obtained was treated with methanol (7 mL) containing an excess of NaBPh$_4$ (6 mmol, 2.05 g). A dark green solid slowly separated out from the resulting solution, which was filtered and crystallized from CH$_2$Cl$_2$ (2 mL) and ethanol (4 mL); yield ≥20%. Anal. Calcd: C, 41.94; H, 5.63; N, 5.59; Cl, 3.54. Found: C, 41.78; H, 5.76; N, 5.45; Cl, 3.72. $\Lambda_M = 54.9\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. IR (KBr): 3331 w, 3230 sh, 3217 m [ν(NH)], 1734 [m, ν(N$_2$)] cm^{-1}. ^{1}H NMR [CD$_2$Cl$_2$, 25 °C; δ]: 7.40−6.87 (m, 20 H, Ph), 5.20 (br, 2 H, NH$_2$), 3.70 t, 3.62 d (27 H, CH$_3$ phos), 3.21 (s, 3 H, CH$_3$N$_2$), 3.15 (br, 1 H, NH), 2.43 (d, 3 H, CH$_3$NH). ^{31}P{^{1}H} NMR [CD$_2$Cl$_2$, 25 °C; δ]: spin system AB$_2$, δ_A 112.3, δ_B 99.8, J_{AB} = 35.0 Hz.

Results and Discussion

Bis(dinitrogen) complexes [Re(N$_2$)$_2$P$_4$]BPh$_4$ (**1**) may be prepared in 40−60% yield by treating ReOCl$_3$(AsPh$_3$)$_2$ first with phosphites P(OR)$_3$ and then with an excess of *t*-butylhydrazine, as shown in Scheme 1.

The reaction of ReOCl$_3$(AsPh$_3$)$_2$ with phosphites probably proceeds to give the ReCl$_3$P$_3$ complexes, which cannot be isolated as solids but only as oily products. The NMR data, however, show the proton resonances at unusual chemical shifts (between +20 and +6 ppm), as observed in the related ReCl$_3$[PPh(OEt)$_2$]$_3$ compound[6] and due to second-order paramagnetism of an octahedral Re(III) ReCl$_3$P$_3$ complex.[7] Treatment of these ReCl$_3$P$_3$ complexes with *t*-butylhydrazine gave exclusively bis(dinitrogen) derivatives **1**, which were isolated as yellow solids and characterized. This result contrasts with those obtained[1] for the reaction of the related ReCl$_3$P$_3$ complex containing PPh(OEt)$_2$ ligand, which afforded the neutral monodiazoto ReCl(N$_2$)P$_4$ compound in the reaction with *t*-butylhydrazine; but the bis(dinitrogen) complex with PPh(OEt)$_2$ ligand was obtained as a byproduct in low yield (15%) from the reaction of ReCl$_3$P$_3$ with methylhydrazine. Instead, with phosphites P(OEt)$_3$ and P(OMe)$_3$, bis(dinitrogen) complexes **1** may easily be prepared in pure form and in good yield.

Dinitrogen complexes **1** were also obtained by operating in both argon and dinitrogen atmospheres, and therefore, the N$_2$ ligand must come from the *t*-butylhydrazine, which can liberate N$_2$ in the reduction reaction of the central metal from Re(III) to Re(I).

Bis(dinitrogen) complexes **1** are yellow solids that are stable in air and in solutions of polar organic solvents, in which they behave as 1:1 electrolytes.[8] The analytical and spectroscopic data support the proposed formulation and suggest a mutually trans position for the two dinitrogen ligands.

The IR spectra show only one strong νN$_2$ band at 2108 for **1a** and 2109 cm^{-1} for **1b**, whereas the ^{31}P{^{1}H} NMR spectra appear as sharp singlets, in the temperature range +30 to −90 °C, fitting the proposed geometry.

Reactivity studies indicate that **1** are very robust complexes, in which the N$_2$ ligand cannot be substituted by CO, phosphites, halogenide, or other donor molecules, and starting complexes were found unchanged after 48 h of reaction at room temperature. The N$_2$ groups are also unreactive toward both electrophilic and nucleophilic reagents. Treatment with an excess of Brønsted acid (CF$_3$SO$_3$H, HBF$_4$•Et$_2$O, CF$_3$COOH) as well as with CF$_3$SO$_3$CH$_3$ always gives unreacted dinitrogen compound **1**, even after 48 h of reaction. Treatment with an excess of methyl- or buthyllithium at room temperature or in refluxing thf also gives unreacted complex **1**, and only after long reaction times was some decomposition observed, thus confirming the noteworthy stability of bis(dinitrogen) derivatives.

Results obtained with *t*-buthylhydrazine prompted us to extend the study of the reactivity of phosphite-containing ReCl$_3$P$_3$ complexes to other hydrazines to determine the influence of the phosphite ligands on these reactions. The results are reported in Scheme 2.

The nature of the phosphite ligand seems to be crucial in determining the reaction course and stoichiometry of the resulting diazo complexes. Thus, under reflux, the reaction of ReCl$_3$P$_3$ with phenylhydrazine afforded the [ReCl(PhN$_2$)P$_4$]BPh$_4$ (**2**) compound in the case of P(OEt)$_3$; the hydrazine−phenyldiazenido [Re(PhN$_2$)(PhNHNH$_2$)P$_4$](BPh$_4$)$_2$ (**4**) derivative was separated by operating at room temperature with P(OMe)$_3$. Various experimental conditions in the reaction between ReCl$_3$P$_3$ and phenylhydrazine, i.e. 25 °C with P(OEt)$_3$ and under reflux with P(OMe)$_3$, afforded only intractable oils.

Treatment of ReCl$_3$[P(OMe)$_3$]$_3$ with methylhydrazine gave a mixture of bis(dinitrogen) complex **1b** and methyldiazenido [ReCl(CH$_3$N$_2$)(CH$_3$NHNH$_2$)P$_3$]BPh$_4$ (**5**) derivative, which were separated by fractional crystallization. In the case of P(OEt)$_3$, the reaction gave only decomposition products.

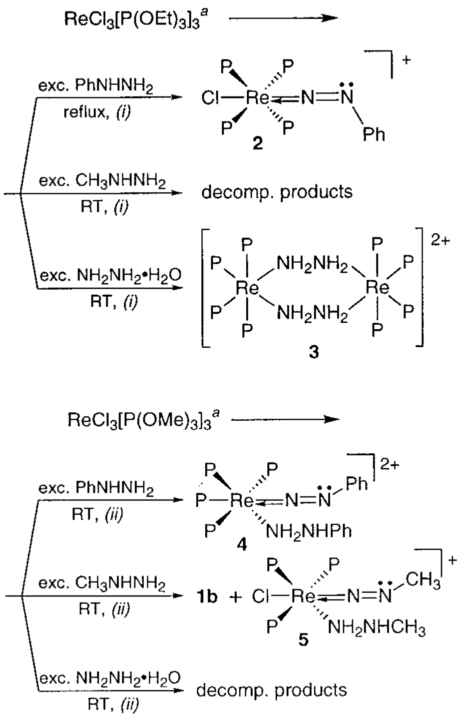
Finally, the reaction of ReCl$_3$P$_3$ with the hydrazine NH$_2$NH$_2$•H$_2$O afforded binuclear [{ReP$_4$}$_2$(μ-NH$_2$NH$_2$)$_2$](BPh$_4$)$_2$ (**3**) species in the case of P(OEt)$_3$, and an intractable mixture of products with P(OMe)$_3$.

---

(7) (a) Chatt, J.; Leigh, G. J.; Mingos, D. M. P.; Randall, E. W.; Shaw, D. *J. Chem. Soc., Chem. Commun.* **1968**, 419. (b) Chatt, J.; Leigh, G. J.; Mingos, D. M. P. *J. Chem. Soc. A* **1969**, 1674. (c) Randall, E. W.; Shaw, D. *J. Chem. Soc. A* **1969**, 2867.

(8) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

Scheme 2[a]



[a] Prepared in situ by reacting $ReOCl_3(AsPh_3)_2$ with an excess (6:1 ratio) of the appropriate phosphite; *(i)* in thf/EtOH (1:1) solution containing an excess of NEt_3 (10:1 ratio) and a slight excess of $P(OEt)_3$ (2:1); *(ii)* in thf/MeOH (1:1) solution containing an excess of both NEt_3 (10:1 ratio) and $P(OMe)_3$ (3:1).

The formation of various diazo species upon changing the ancillary phosphite ligand is not surprising but difficult to rationalize in our case, because the electronic and steric properties of $P(OMe)_3$ and $P(OEt)_3$ are not sufficiently different[9] as to explain the results shown in Scheme 2. However, the yields of the isolated diazo complexes are quite low, and the final product often contains only decomposition products, thus hindering clear-cut comparisons among reactions involving the two phosphites. Also, comparisons among these results and previous ones[1] on the reactivity of $ReCl_3P_3$ containing PPh(OEt)$_2$ with hydrazines confirm the important role of the ancillary ligand in determining the nature of the resulting diazo species, although no reasonable trend can be deduced. It seems that every phosphite leads to its own stable complex, according to a reaction course, and depending on the peculiar properties of all the ligands.

All diazo complexes **2**−**5** were isolated as diamagnetic air-stable solids, soluble in polar organic solvents, in which they behave as 1:1 (**2**, **5**) or 2:1 (**3**, **4**) electrolytes.[8] Analytical and spectroscopic data support the proposed formulation, and a geometry in solution of the type shown in Scheme 2 may also be assigned for the diazo derivatives.

The IR spectrum of the compound $[ReCl(ArN_2)P_4]BPh_4$ (**2**) showed only one νN_2 band at 1603 cm^{-1}. By comparison with the νN_2 values of other diazenido complexes,[1,10,11] this value suggests the presence of a singly bent ArN_2 ligand. In the temperature range +30 to −80 °C, the $^{31}P\{^1H\}$ NMR spectra showed a sharp singlet, which was compatible with the presence of four equivalent phosphite ligands. On this basis, a trans geometry was proposed for the aryldiazenido species **2**.

The mutually cis position of the aryldiazenido and hydrazine ligands occurs in the $[Re(PhN_2)(PhNHNH_2)P_4]^{2+}$ (**4**) cation according to the ABC_2 multiplet observed in the $^{31}P\{^1H\}$ NMR spectra. The IR spectra support the presence of diazenido and hydrazine ligands, showing a medium-intensity band at 1755 cm^{-1} attributed to the νNN of ArN_2 ligand and three medium-weak absorptions between 3356 and 3263 cm^{-1} due to the νNH of the $PhNHNH_2$ group. The presence of the hydrazine ligand is also confirmed by the ^1H NMR spectrum, which shows a broad signal at 4.65 ppm due to the NH_2 group. The NH signal is probably masked by the signals of the phenyl protons.

The IR spectra of methylhydrazine complex **5** show the νN_2 band at 1734 cm^{-1} and νNH absorptions of the hydrazine ligand at 3331−3217 cm^{-1}. The ^1H NMR data confirm the presence of the CH_3NHNH_2 group, showing the characteristic NH_2 and NH signals at 5.20 and 3.15 ppm and the methyl substituent as a doublet at 2.43 ppm. These assignments were confirmed by integration data and homodecoupling experiments. In the temperature range +30 to −80 °C, the $^{31}P\{^1H\}$ NMR spectra appear as an AB_2 multiplet, indicating two magnetically equivalent phosphite ligands which are different from the third. The spectroscopic data do not allow an unambiguous assignment of geometry in solution for this compound, but comparison with the related $[ReCl(CH_3N_2)(CH_3NHNH_2)\{PPh(OEt)_2\}_3]BPh_4$ compound,[1] whose structure is known, suggests a cis geometry for complex **5** (Scheme 2).

The IR spectrum of hydrazine complex $[\{Re[P(OEt)_3]_4\}_2(\mu\text{-}NH_2NH_2)_2](BPh_4)_2$ (**3**) shows only two νNH bands at 3367 and 3346 cm^{-1} of the NH_2NH_2 ligand. In addition, in the temperature range +30 to −80 °C, the ^1H NMR spectra shows only one signal for the NH_2 protons in any solvent used [CD_2Cl_2, $(CD_3)_2CO$, or $CDCl_3$]. Finally, an A_2B_2 multiplet was observed in the $^{31}P\{^1H\}$ NMR spectra of **3**, which can be simulated with the parameters reported in Experimental Section. On these bases, a symmetric geometry of type of Scheme 2, with two bridging NH_2NH_2 ligands, is proposed for hydrazine complex **3**.

Acknowledgment. The financial support of MURST, Rome (Programmi di Ricerca Scientifica di Rilevante Interesse Nazionale, Cofinanziamento 2000/2001) is gratefully acknowledged.

IC0104508

---

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

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

(11) Haymore, B. L.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 3060.