Diazo Complexes of Rhenium with Phosphite Ligands: Facile Synthesis of Bis(dinitrogen) [Re(N₂)₂P₄]BPh₄ Derivatives

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Introduction

Previous reports¹ from our laboratory dealt with studies of the reaction of rhenium trichloro complexes, ReCl₃[PPh(OEt)₂]₃, with hydrazines, which gives new "diazo" derivatives, including the first bis(dinitrogen) complex for this metal, [Re(N₂)₂P₄]BPh₄. 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 ReCl₃P₃ 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 ReCl₃P₃ 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 CH₃NHNH₂, BuNHNH₂•HCl, PhNHNH₂, and NH₂•H₂O 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, ³¹P) were obtained on a Bruker AC200 spectrometer at temperatures between +30 and -90 °C, unless otherwise noted. ¹H spectra are referred to internal tetramethylsilane; ³¹P{¹H} chemical shifts are reported with respect to 85% H₃PO₄, with downfield shifts considered positive. The SwaN-MR software package⁵ was used to treat NMR data. The conductivity of 10^{-3} M solutions of the complexes in CH₃NO₂ at 25 °C were measured with a CDM 83 Radiometer.

Synthesis of Complexes. Compound ReOCl₃(AsPh₃)₂ was prepared as previously reported.⁶

 $[\text{Re}(N_2)_2P_4]$ BPh₄ (1) $[P = P(OEt)_3$ (a), $P(OMe)_3$ (b)]. An excess of the appropriate phosphite (6 mmol) was added to a solution of ReOCl₃(AsPh₃)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 NEt₃ (20 mmol, 2.8 mL), and then an excess of solid 'BuNHNH2+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 NaBPh4 (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 CH₂Cl₂ (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, ν(N₂)] cm⁻¹. ¹H NMR [(CD₃)₂CO, 25 °C; δ]: 7.35-6.70 (m, 20 H, Ph), 4.21 (m, 24 H, CH₂), 1.41 (t, 36 H, CH₃). $^{31}P\{^{1}H\}$ NMR [(CD₃)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. $\Lambda_{\rm M} = 56.3$ $\Omega^{-1}\ mol^{-1}\ cm^2.$ 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, CH₃). ³¹P{¹H} NMR [CD₂Cl₂, 25 °C; δ]: 113.8 s.

[ReCl(PhN₂){P(OEt)₃}₄]BPh₄ (2). An excess of triethyl phosphite (6 mmol, 1 mL) was added to a solution of ReOCl₃(AsPh₃)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 NEt₃ (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 NaBPh₄ (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 CH2Cl2 (5 mL) and, after filtration and concentration, adding enough ethanol (5 mL) to give separation of the solid; yield $\geq 40\%$. 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. $\Lambda_{\rm M} = 55.5 \ \Omega^{-1} \ {\rm mol}^{-1} \ {\rm cm}^2$. IR (KBr): 1603 [m, $\nu(N_2)$] cm⁻¹. ¹H NMR [(CD₃)₂CO, 25 °C; δ]: 7.60–6.80 (m, 25 H, Ph), 4.06 (m, 24 H, CH₂), 1.23 (t, 36 H, CH₃). ³¹P{¹H} NMR [(CD₃)₂-CO, 25 °C; δ]: 95.9 s.

[{Re[P(OEt)₃]₄}₂(μ -NH₂NH₂)₂](BPh₄)₂ (3). An excess of P(OEt)₃ (6 mmol, 1 mL) was added to a solution of ReOCl₃(AsPh₃)₂ (1 mmol, 0.92 g) in 10 mL of thf, and the reaction mixture was stirred for 1 h. An excess of NH₂NH₂·H₂O (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 NaBPh₄ (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 CH₂Cl₂ (2 mL) and ethanol (4 mL);

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^{*a*} P = P(OEt)₃ (**a**), P(OMe)₃ (**b**); (*i*) = in thf/ROH (R = Et, Me) (1:2) solution containing an excess of NEt₃ (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. $\Lambda_M = 124.9 \ \Omega^{-1} \ mol^{-1} \ cm^2$. IR (KBr): 3367, 3346 [m, ν (NH)], 1616 [δ (NH₂)] cm⁻¹. ¹H NMR [CD₂Cl₂, 25 °C; δ]: 7.40–6.84 (m, 40 H, Ph), 4.02, 3.87 (m, 48 H, CH₂), 2.30 (br, 8 H, NH₂), 1.26, 1.19 (t, 72 H, CH₃). ³¹P{¹H} NMR [CD₂Cl₂, -55 °C; δ]: spin system A₂B₂, δ_A 120.3, δ_B 115.7, $J_{AB} = 36.5 \ Hz$.

[Re(PhN₂)(PhNHNH₂){P(OMe)₃}₄](BPh₄)₂ (4). To a solution of ReOCl₃(AsPh₃)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 NEt₃ (10 mmol, 1.4 mL), an excess of PhNHNH₂ (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 NaBPh4 (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 CH₂Cl₂. The extracts were evaporated to dryness, giving a pink solid which was crystallized from ethanol; yield \geq 35%. Anal. Calcd: C, 56.37; H, 5.85; N, 3.65. Found: C, 56.24; H, 5.93; N, 3.55. $\Lambda_{\rm M} = 128.7 \ \Omega^{-1} \ {\rm mol}^{-1} \ {\rm cm}^2$. IR (KBr): 3356 w, 3325 m, 3263 m [ν(NH)], 1755 [s, ν(N₂)] cm⁻¹. ¹H NMR [CD₂Cl₂, 25 °C; δ]: 7.50-6.80 (m, 50 H, Ph), 4.65 (br, 2 H, NH₂), 3.61 (m, 36 H, CH₃). ³¹P{¹H} NMR [CD₂Cl₂, 25 °C; δ]: spin system ABC₂, 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.

 $[ReCl(CH_3N_2)(CH_3NHNH_2)\{P(OMe)_3\}_3]BPh_4$ (5). To a solution of ReOCl₃(AsPh₃)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 NEt₃ (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 NaBPh4 (6 mmol, 2.05 g). A dark green solid slowly separated out from the resulting solution, which was filtered and crystallized from CH2Cl2 (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. $\Lambda_M = 54.9 \ \Omega^{-1} \ mol^{-1} \ cm^2$. IR (KBr): 3331 w, 3230 sh, 3217 m [ν (NH)], 1734 [m, ν (N₂)] cm⁻¹. ¹H NMR [CD₂Cl₂, 25 °C; δ]: 7.40–6.87 (m, 20 H, Ph), 5.20 (br, 2 H, NH₂), 3.70 t, 3.62 d (27 H, CH₃ phos), 3.21 (s, 3 H, CH₃N₂), 3.15 (br, 1 H, NH), 2.43 (d, 3 H, CH₃NH). ${}^{31}P{}^{1}H}$ NMR [CD₂Cl₂, 25 °C; δ]: spin system AB₂, δ_A 112.3, δ_B 99.8, $J_{AB} = 35.0$ Hz.

Results and Discussion

Bis(dinitrogen) complexes $[Re(N_2)_2P_4]BPh_4$ (1) may be prepared in 40–60% yield by treating ReOCl₃(AsPh₃)₂ first with phosphites P(OR)₃ and then with an excess of *t*-butylhydrazine, as shown in Scheme 1.

The reaction of ReOCl₃(AsPh₃)₂ with phosphites probably proceeds to give the ReCl₃P₃ 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 ReCl₃-[PPh(OEt)₂]₃ compound⁶ and due to second-order paramagnetism of an octahedral Re(III) ReCl₃P₃ complex.⁷ Treatment of these ReCl₃P₃ complexes with *t*-butylhydrazine gave exclusively bis(dinitrogen) derivatives **1**, which were isolated as yellow solids and characterized. This result contrasts with those obtained¹ for the reaction of the related ReCl₃P₃ complex containing PPh(OEt)₂ ligand, which afforded the neutral monodiazoto ReCl(N₂)P₄ 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 ReCl₃P₃ 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 ³¹P{¹H} 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 N₂ 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 N₂ groups are also unreactive toward both electrophilic and nucleophilic reagents. Treatment with an excess of Brønsted acid (CF₃SO₃H, HBF₄·Et₂O, CF₃COOH) as well as with CF₃SO₃CH₃ 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 ReCl₃P₃ 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 ReCl₃P₃ with phenylhydrazine afforded the [ReCl(PhN₂)P₄]BPh₄ (**2**) compound in the case of P(OEt)₃; the hydrazine–phenyl-diazenido [Re(PhN₂)(PhNHNH₂)P₄](BPh₄)₂ (**4**) derivative was separated by operating at room temperature with P(OMe)₃. Various experimental conditions in the reaction between ReCl₃P₃ and phenylhydrazine, i.e. 25 °C with P(OEt)₃ and under reflux with P(OMe)₃, afforded only intractable oils.

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

Finally, the reaction of ReCl₃P₃ with the hydrazine NH₂NH₂· H₂O afforded binuclear [{ReP₄}₂(μ -NH₂NH₂)₂](BPh₄)₂ (**3**) species in the case of P(OEt)₃, and an intractable mixture of products with P(OMe)₃.

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Scheme 2^a



^{*a*} Prepared in situ by reacting ReOCl₃(AsPh₃)₂ with an excess (6:1 ratio) of the appropriate phosphite; (*i*) in thf/EtOH (1:1) solution containing an excess of NEt₃ (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 NEt₃ (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 different⁹ 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 ones1 on the reactivity of ReCl₃P₃ 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 airstable 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(ArN₂)P₄]BPh₄ (2) showed only one ν N₂ band at 1603 cm⁻¹. By comparison with the ν N₂ values of other diazenido complexes,^{1,10,11} this value suggests the presence of a singly bent ArN₂ ligand. In the temperature range +30 to -80 °C, the ³¹P{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 $[\text{Re}(\text{PhN}_2)(\text{PhNHNH}_2)\text{P}_4]^{2+}$ (4) cation according to the ABC₂ multiplet observed in the ³¹P{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 ν NN of ArN₂ ligand and three medium-weak absorptions between 3356 and 3263 cm⁻¹ due to the ν NH of the PhNHNH₂ 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 NH₂ group. The NH signal is probably masked by the signals of the phenyl protons.

The IR spectra of methylhydrazine complex **5** show the ν N₂ band at 1734 cm⁻¹ and ν NH absorptions of the hydrazine ligand at 3331–3217 cm⁻¹. The ¹H NMR data confirm the presence of the CH₃NHNH₂ group, showing the characteristic NH₂ 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 ³¹P{¹H} NMR spectra appear as an AB₂ 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(CH₃N₂)(CH₃NHNH₂){PPh(OEt₂)₃]BPh₄ 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(μ -NH_2NH_2)_2](BPh_4)_2 (**3**) shows only two ν NH 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)_2-CO, or CDCl_3]. Finally, an A_2B_2 multiplet was observed in the ³¹P{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**.

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