Methyleneimine CH₂=NH as a Unidentate Ligand in Rhenium Complexes**

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Coordinated hydrazines RNHN₂ are reported to react with oxidizing agents, such as [Pb(OAc)₄] and H₂O₂, to give the corresponding diazenes RN=NH, the stabilization of which on an appropriate metal fragment allows their separation as coordinated species.[1–3] We now report a new reaction of coordinated methylhydrazine, which reacts with [Pb(OAc)₄] to give a η¹-NH=CH₂ methyleneimine derivative.

The CH₂=NH molecule is a reactive species which was first obtained in 1933 from the low-temperature reaction of HCN with hydrogen.[4] It has been detected in several galactic objects[5] and proposed as a possible precursor[6] of the simplest α-amino acid, glycine. As a ligand, it is present in only one case, through π coordination[7] to an osmium center; no other report has been found on this molecule, which displays a simple constitution and structure, and has still unknown properties.

The reaction of the hydride[8] [ReH(CO){P(OEt)₃}₄] with triflic acid (TfOH) gives the thermally unstable [Re[η²-H₂]CO(P(OEt)₃)₄]⁺(CF₃SO₃)⁻ species, which loses H₂, affording the compound [Re(κ¹-OTf)(CO)(P(OEt)₃)₄]. Substitution of the weakly bound triflato ligand with methylhydrazine gives trans-[Re(CH₂(NH)NH₂)(CO)(P(OEt)₃)₄]⁺ (I), which was isolated as a BPh₄ salt (1-BPh₄) in about 70% yield (Scheme 1).

Complex 1-BPh₄ was characterized by standard methods (IR, NMR, Aₑ₅₀, elemental analysis). The IR spectra show the νₐ₅ bands at 3343 and 3291 cm⁻¹ of the methylhydrazine ligand, whereas the ³H NMR spectrum exhibits resonance signals at δ = 4.35 (s, br; ReNH₂-NHCH₃), 3.93 (m, br; ReNH₂-NHCH₃), and 2.49 ppm (d; ReNH₂-NHCH₃) of the CH₂NHNH₂ group.

Treatment of methylhydrazine complex 1-BPh₄ with an equimolar amount of [Pb(OAc)₄] at low temperature (−40 °C) in CH₂Cl₂ gives a mixture of methyldiazenes [Re(CH₃N=NH)(CO)(P(OEt)₃)₄]BPh₄ (2-BPh₄) and methyleneimine [Re(η¹-NH=CH₂)(CO)(P(OEt)₃)₄]BPh₄ (3-BPh₄) derivatives (Scheme 2). These were separated by fractional crystallization in moderate yields (42% for 2-BPh₄, 24% for 3-BPh₄) as analytically pure white crystalline solids.

The complexes were characterized by spectroscopy and in two X-ray diffraction studies.[9–12] Figure 1 shows the crystal structure of the cation [Re(η¹-NH=CH₂)(CO)(P(OEt)₃)₄]⁺ (3). The most relevant feature of the complex is the presence of the methyleneimine ligand, trans to the carbonyl group, and coordinated with the metal in a bent mode, as required by the sp² character of the N atom (Re-N-C 139(1)°), with Re=N 2.32(1) Å and N=C 1.26(1) Å. This is, in fact, the first example of η¹ coordination of a CH₂=NH molecule to a transition metal, the only other similar case being the deprotonated CH₂=N=M fragment found in (η²-methyleneamido)tricarbonylbris-

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Scheme 1. P = P(OEt)₃.

Scheme 2. P = Pb(OAc)₄.

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(η²-pentamethylcyclopentadienyl)methyleneamidodimolybdenum,[19] in which the system is practically linear (M-N=C 163°). The bent geometry found for our terminal methylene-imine group fits the common structural features of alkyl and aryl R₅C=NH ligands, which show similar M-N-C angles and generally larger N-C distances (ranging from 1.25 to 1.30 Å; the shortest ones are found in the catenabisisopropylidenediamine|gold trilfluoromethanesulfonate complex at 173 K[16]). The plane of the methyleneimine ligand (Re-N1-C51) forms a dihedral angle of 38(1)° with the equatorial coordination plane containing the N donor (Re-C50-P1-P3-N1).

The ¹H NMR spectra of 3-BPh₄ are diagnostic for the presence of the methyleneimine ligand, showing a broad high-frequency signal at δ = 13.98 ppm, which is attributed to the =NH imine proton. Substituted imine R₅C=NH, and RHC=NH bonded to a metal center[14, 15] are also reported to give rise to a high-frequency NH proton resonance signal. A slightly broad multiplet is also present at δ = 3.66 ppm, which is coupled with the imine proton and was assigned to one of the two protons of the methylene =CH₃ group. The other is probably masked by the methylene signals of the P(OCH₂CH₂)₂ ligands. In the temperature range between +30 and –80 °C the ³¹P{¹H} NMR spectrum displays a sharp singlet, which is assigned to a trans geometry like that found in the solid state.

In the crystal structure of 2-BPh₄, the methyldiazeno and carbonyl ligands in the cation are exchanged between two trans coordination positions, with 50% substitutional disorder, and their refinement was possible only by restraining them to conform to a plausible geometry.[16]

The ¹H NMR spectra of 2-BPh₄ further support the presence of the CH₃N=NH ligand, showing the NH resonance signal at δ = 15.99 ppm and one doublet at δ = 4.37 ppm, attributed to the methyl group. A mutual trans position of carbonyl and methyleneimine ligands is also suggested in solution by the presence of only one singlet at δ = 116.7 ppm in the ³¹P{¹H} NMR spectrum.

Other methyldiazenyl complexes, such as dicarbonyls [Re(CH₃NHNH₂)(CO)₂P(OEt)₃]BPh₄ (P = PO(OEt)₃ or PPh(OEt)₂), were prepared, and their reaction with [Pb(OAc)₄] led, at 25°C, to give rise to a high-frequency NH proton resonance signal. The mechanism[17] may be, cleavage of the N bond[18] of a diazene,[1±3] the reaction affording coordinated NH₂CH₂ is new, unexpected, and interesting—not only because it allows us to prepare, and stabilize by coordination, an elusive molecule such as methyleneimine, but also because, whatever the mechanism[17] may be, cleavage of the N=N bond[19] of a coordinated hydrazine[19] takes place in the presence of an oxidizing species.

Studies are currently in progress to explore the reaction chemistry of the M=N=CH₂ systems, mainly in terms of deprotonation and substitution reactions.

Experimental Section

All reactions were carried out under an inert atmosphere using dry, air-free solvents.

1-BPh₄: CF₃SO₂H (TIOH) (0.23 mmol, 20 μL) was added to a solution of [ReH(CO){P(OEt)₃}₄]L (200 mg, 0.23 mmol) in CH₂Cl₂ (5 mL) cooled to –196 °C, and the reaction mixture was allowed to warm to room temperature, and stirred for 1 h. CH₂NHNH₂ (0.66 mmol, 32 μL) was added and stirring continued for 24 h. The solvent was removed under reduced pressure to give an oil which was triturated with ethanol (3 mL) containing Na₂B₄O₇ (0.6 mmol, 205 mg). A white solid slowly separated out, which was crystallized from CH₂Cl₂ and ethanol to give 1-BPh₄ (210 mg, 75% yield). IR (KBr): ν = 3343 (m), 3291 (m) (νOH), 1894 cm⁻¹ (νCO); ¹H NMR (200 MHz, CD₂Cl₂, 293 K, TMS): δ = 7.54–6.86 (m, 20H; Ph), 4.35 (s, br, 2H; NH), 4.05 (m, 24H; CH₂); 3.93 (m, br, 1H; NH), 2.49 (d, J̇ = 11 Hz, 3H; CH₃); ³¹P{¹H}(200 MHz, CD₂Cl₂, 293 K, H₃PO₄ ext.): δ = 117.9 ppm (s); elemental analysis (%) calcd for C₅₀H₈₄BN₂O₁₃P₄Re (1242.12): C 48.35, H 6.82, N 2.30; found: C 48.19, H 6.95, N 2.30;

2-BPh₄: A sample of 1 (124 mg, 0.1 mmol) was placed in a three-necked 25-mL flask fitted with a solid-addition sidearm containing Pb(OAc)₄ (0.1 mmol, 44 mg). The system was evaporated. CH₂Cl₂ (8 mL) was added, the solution cooled to –40 °C, and [Pb(OAc)₄] was added portionwise over 10–20 min to the cold stirring solution. The reaction mixture was then allowed to warm to 0 °C, stirred for 10 min, and the solvent removed under reduced pressure. The oil obtained was treated at 0 °C with ethanol (2 mL) containing Na₂B₄O₇ (0.2 mmol, 68 mg). A white solid slowly separated out which was filtered and crystallized fractionally. A typical separation involved slow cooling from +20 to +25 °C of a saturated solution of the complexes prepared by adding ethanol (8 mL) to the white solid and enough CH₂Cl₂ to obtain a saturated solution at room temperature. The first crystals are of 2-BPh₄, the second a mixture of 2-BPh₄ and 3-BPh₄, which was recrystallized. A total of 52 mg of 2-BPh₄ (yield 42%) was separated. By further cooling of the solution, 29 mg of white crystals of 3-BPh₄ (yield 24%) were obtained. Pure samples of 2-BPh₄ and 3-BPh₄ can also be obtained by Pasteur separation of crystals obtained by cooling a saturated solution of the reaction product in ethanol to –25 °C.

1-BPh₄: IR (KBr): ν = 1890 cm⁻¹ (s) (νCO); ¹H NMR (200 MHz, CD₂Cl₂, 293 K, TMS): δ = 15.99 (s, br, 1H; NH), 7.40–6.70 (m, 20H; Ph), 4.37 (d, 3H; =NCH₂), 4.06 (m, 24H; CH₂); ³¹P{¹H}(200 MHz, CD₂Cl₂, 293 K, H₃PO₄ ext.): δ = 116.7 ppm (s); elemental analysis (%) calcd for C₅₀H₈₄BN₂O₁₃P₄Re (1242.12): C 48.35, H 6.82; found: C 48.19, H 6.95, N 2.30;

3-BPh₄: IR (KBr): ν = 1894 cm⁻¹ (s) (νCO); ¹H NMR (200 MHz, CD₂Cl₂, 293 K, TMS): δ = 13.98 (s, br, 1H; NH), 7.60–6.80 (m, 20H; Ph), 4.06 (m, 24H; CH₂); 3.66 (m, br, 1H; N=CH₂), 1.34 ppm (t, 36H; CH₃); ³¹P{¹H}(200 MHz, CD₂Cl₂, 293 K, H₃PO₄ ext.): δ = 112.6 ppm (s); elemental analysis (%) calcd for C₅₀H₈₄BN₂O₁₃P₄Re (12271.11): C 48.94, H 6.82, N 1.14; found: C 49.08, H 6.96, N 1.10.

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Preliminary investigations show the presence of traces of ammonia in the final reaction mixture, but no other nitrogen-containing compound was unambiguously identified, and therefore no reaction path may be reasonably proposed.


Total Synthesis of the Amaryllidaceae Alkaloid (+)-Plicamine and Its Unnatural Enantiomer by Using Solid-Supported Reagents and Scavengers in a Multistep Sequence of Reactions**

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Amaryllidaceae alkaloids are an important class of natural products especially as many members of the series display a wide range of potent biological activity. These properties include anticholinergic, antitumor, immunosuppressive, and analgesic activity, and they have also been shown to inhibit various cell cycle mechanisms (including HIV-1 activity), and have found recent application in the therapeutic treatment of Alzheimer’s disease.11,12 Thus extensive synthetic studies of this family have been carried over a number of years.12,13 Furthermore, the search for new members of the series has proved to be extremely profitable.1,4 The recently isolated compound (+)-plicamine (1) is especially attractive as it exemplifies many of the structural features of these natural components.