

Methyleneimine $\text{CH}_2=\text{NH}$ as a Unidentate Ligand in Rhenium Complexes**

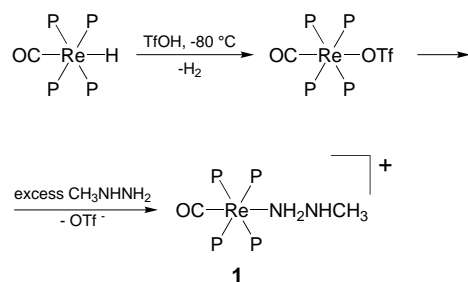
Gabriele Albertin,* Stefano Antoniutti, Alessia Bacchi, Emilio Bordignon, Maria Teresa Giorgi, and Giancarlo Pelizzi

Coordinated hydrazines RNHNH_2 are reported to react with oxidizing agents, such as $[\text{Pb}(\text{OAc})_4]$ and H_2O_2 , to give the corresponding diazenes $\text{RN}=\text{NH}$, 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 $[\text{Pb}(\text{OAc})_4]$ to give a $\eta^1\text{-NH}=\text{CH}_2$ methyleneimine derivative.

The $\text{CH}_2=\text{NH}$ 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] $[\text{ReH}(\text{CO})\{\text{P}(\text{OEt})_3\}_4]$ with triflic acid (TfOH) gives the thermally unstable $[\text{Re}(\eta^2\text{-H}_2)(\text{CO})\{\text{P}(\text{OEt})_3\}_4]^+(\text{CF}_3\text{SO}_3)^-$ species, which loses H_2 , affording the compound $[\text{Re}(\kappa^1\text{-OTf})(\text{CO})\{\text{P}(\text{OEt})_3\}_4]$. Substitution of the weakly bound triflate ligand with methylhydrazine gives *trans*- $[\text{Re}(\text{CH}_3\text{NHNH}_2)(\text{CO})\{\text{P}(\text{OEt})_3\}_4]^+$ (**1**), which was isolated as a BPh_4 salt (**1-BPh₄**) in about 70% yield (Scheme 1).

Complex **1-BPh₄** was characterized by standard methods (IR, NMR, Λ_M , elemental analysis). The IR spectra show the ν_{NH} bands at 3343 and 3291 cm^{-1} of the methylhydrazine



Scheme 1. $\text{P} = \text{P}(\text{OEt})_3$.

[*] Prof. G. Albertin, S. Antoniutti, E. Bordignon, Dr. M. T. Giorgi
Dipartimento di Chimica
Università Ca' Foscari di Venezia
Dorsoduro 2137, 30123 Venezia (Italy)
Fax: (+39)041-234-8917
E-mail: albertin@unive.it

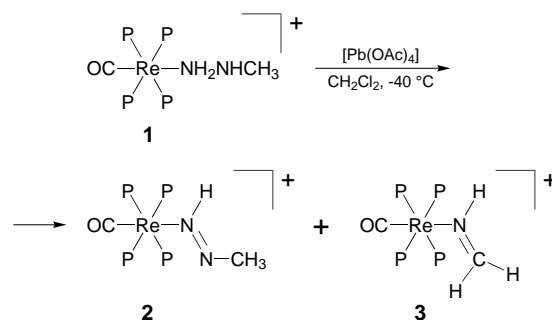
Prof. A. Bacchi, G. Pelizzi
Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica
Chimica Fisica, Università di Parma
Parco Area delle Scienze 17/a, 43100 Parma (Italy)

[**] This work was supported by MIUR (Rome)—Programmi di Ricerca Scientifica di Rilevante Interesse Nazionale, Cofinanziamento 2000–2001. We thank Daniela Baldan for technical assistance.

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ligand, whereas the ^1H NMR spectrum exhibits resonance signals at $\delta = 4.35$ (s, br; $\text{ReNH}_2\text{NHCH}_3$), 3.93 (m, br; $\text{ReNH}_2\text{NHCH}_3$), and 2.49 ppm (d; $\text{ReNH}_2\text{NHCH}_3$) of the CH_3NHNH_2 group.

Treatment of methylhydrazine complex **1-BPh₄** with an equimolar amount of $[\text{Pb}(\text{OAc})_4]$ at low temperature (-40°C) in CH_2Cl_2 gives a mixture of methyl diazene $[\text{Re}(\text{CH}_3\text{N}=\text{NH})(\text{CO})\{\text{P}(\text{OEt})_3\}_4]\text{BPh}_4$ (**2-BPh₄**) and methyleneimine $[\text{Re}(\eta^1\text{-NH}=\text{CH}_2)(\text{CO})\{\text{P}(\text{OEt})_3\}_4]\text{BPh}_4$ (**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.



Scheme 2. $\text{P} = \text{P}(\text{OEt})_3$.

The complexes were characterized by spectroscopy and in two X-ray diffraction studies.^[9–12] Figure 1 shows the crystal structure of the cation $[\text{Re}(\eta^1\text{-NH}=\text{CH}_2)(\text{CO})\{\text{P}(\text{OEt})_3\}_4]^+$ (**3**). The most relevant feature of the complex is the presence

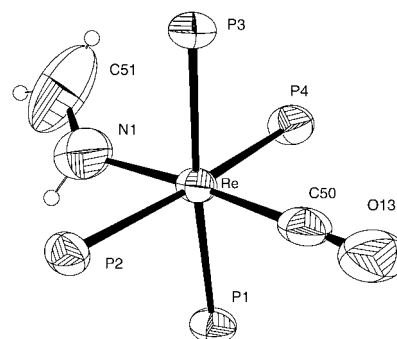


Figure 1. Structure of the core of the cation **3** (thermal ellipsoids drawn at the 30% level; ethoxy groups are omitted for clarity). Selected bond lengths [\AA] and angles [$^\circ$]: $\text{Re}-\text{C}51$ 1.956(8), $\text{Re}-\text{N}1$ 2.32(1), $\text{Re}-\text{P}3$ 2.362(2), $\text{Re}-\text{P}1$ 2.362(2), $\text{Re}-\text{P}4$ 2.374(2), $\text{Re}-\text{P}2$ 2.378(2), $\text{O}13-\text{C}51$ 1.108(8), $\text{N}1-\text{C}51$ 1.26(1); $\text{C}50-\text{Re}-\text{N}1$ 175.9(3), $\text{C}50-\text{Re}-\text{P}3$ 87.7(2), $\text{N}1-\text{Re}-\text{P}3$ 95.9(2), $\text{C}50-\text{Re}-\text{P}1$ 86.9(2), $\text{N}1-\text{Re}-\text{P}1$ 89.5(2), $\text{P}3-\text{Re}-\text{P}1$ 174.44(6), $\text{C}50-\text{Re}-\text{P}4$ 94.4(2), $\text{N}1-\text{Re}-\text{P}4$ 87.6(2), $\text{P}3-\text{Re}-\text{P}4$ 90.00(7), $\text{P}1-\text{Re}-\text{P}4$ 89.25(7), $\text{C}50-\text{Re}-\text{P}2$ 92.9(2), $\text{N}1-\text{Re}-\text{P}2$ 85.0(2), $\text{P}3-\text{Re}-\text{P}2$ 91.44(6), $\text{P}1-\text{Re}-\text{P}2$ 90.01(6), $\text{P}4-\text{Re}-\text{P}2$ 172.56(6), $\text{O}13-\text{C}50-\text{Re}$ 177.2(6), $\text{C}51-\text{N}1-\text{Re}$ 134(1).

of the methyleneimine ligand, *trans* to the carbonyl group, and coordinated with the metal in a bent mode, as required by the sp^2 character of the N atom ($\text{Re}-\text{N}-\text{C}$ 139(1) $^\circ$), with $\text{Re}-\text{N}$ 2.32(1) and $\text{N}-\text{C}$ 1.26(1) \AA . This is, in fact, the first example of η^1 coordination of a $\text{CH}_2=\text{NH}$ molecule to a transition metal, the only other similar case being the deprotonated $\text{CH}_2=\text{N}=\text{M}$ fragment found in (μ^2 -methyleneamido)tricarbonylbis-

(η^5 -pentamethylcyclopentadienyl)methyleneamidodimolybdenum,^[13] in which the system is practically linear (M-N-C 163°). The bent geometry found for our terminal methyleneimine group fits the common structural features of alkylic and arylc $R_2C=NH$ 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 catenabis(isopropylideneamine)gold trifluoromethanesulfonate complex at 173 K^[14]). 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 $\delta = 13.98$ ppm, which is attributed to the =NH imine proton. Substituted imine $R_2C=NH$, 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 $\delta = 3.66$ ppm, which is coupled with the imine proton and was assigned to one of the two protons of the methylene =CH₂ group. The other is probably masked by the methylene signals of the P(OCH₂CH₃)₃ 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 methyldiazene 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 $\delta = 15.99$ ppm and one doublet at $\delta = 4.37$ ppm, attributed to the methyl group. A mutual *trans* position of carbonyl and methyldiazene ligands is also suggested in solution by the presence of only one singlet at $\delta = 116.7$ ppm in the ³¹P{¹H} NMR spectrum.

Other methylhydrazine complexes, such as dicarbonyls [Re(CH₃NHNH₂)(CO)₂P₃]BPh₄ (P = P(OEt)₃ or PPh(OEt)₂), were prepared, and their reaction with [Pb(OAc)₄] led, at -40 °C, to a mixture of methyldiazene [Re(CH₃N=NH)(CO)₂P₃]⁺ and methyleneimine [Re(η^1 -NH=CH₂)(CO)₂P₃]⁺ derivatives which, in the case of P(OEt)₃, were separated in pure form or, for PPh(OEt)₂, were detected by spectroscopy. The reaction affording the coordinated η^1 -NH=CH₂ molecule seems to be general for the [Re(CO)_nP_{5-n}] (*n* = 1, 2) fragment containing a methylhydrazine ligand, but appears to be specific for [Pb(OAc)₄], as attempts to carry out the reaction with other oxidants such as MnO₂ or H₂O₂ were unsuccessful.

The formation of species **2**-BPh₄ and **3**-BPh₄ from the reaction of methylhydrazine complexes **1**-BPh₄ (Scheme 2) suggests that [Pb(OAc)₄] gives rise to two parallel reactions involving selective oxidation of CH₃NHNH₂ to methyldiazene CH₃N=NH, giving **2**-BPh₄, in one case, whereas a completely new reaction involving cleavage of the N=N bond and formation of the CH₂=NH moiety takes place in the other. Although coordinated hydrazine is known to undergo oxidation by [Pb(OAc)₄] or other reagents to the corresponding diazene,^[1-3] the reaction affording coordinated η^1 -NH=CH₂ 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^[18] 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-NH=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: CF₃SO₃H (TfOH) (0.23 mmol, 20 μ L) was added to a solution of [ReH(CO){P(OEt)₃]₄]^[8] (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. CH₃NHNH₂ (0.6 mmol, 32 μ L) was added and stirring was continued for 24 h. The solvent was removed under reduced pressure to give an oil which was triturated with ethanol (3 mL) containing NaBPh₄ (0.6 mmol, 205 mg). A white solid slowly separated out, which was crystallized from CH₂Cl₂ and ethanol to give **1**-BPh₄ (210 mg; yield 73%). IR (KBr): $\bar{\nu} = 3343$ (m), 3291 (m) (ν_{NH}), 1880 cm⁻¹ (s) (ν_{CO}); ¹H NMR (200 MHz, CD₂Cl₂, 293 K, TMS): $\delta = 7.40$ –6.86 (m, 20H; Ph), 4.35 (s, br, 2H; NH₂), 4.05 (m, 24H; CH₂); 3.93 (m, br, 1H; NH), 2.49 (d, ³J_{H,H} = 6 Hz, 3H; CH₃N), 1.29 ppm (t, 36H; CH₃); ³¹P{¹H} (200 MHz, CD₂Cl₂, 293 K, H₃PO₄ 85% ext.): $\delta = 117.9$ ppm (s); elemental analysis (%) calcd for C₅₀H₈₆BN₂O₁₃P₄Re (1244.14): C 48.27, H 6.97, N 2.25; found: C 48.15, H 7.01, N 2.13.

2-BPh₄, **3**-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 evacuated, 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 NaBPh₄ (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.

2-BPh₄: IR (KBr): $\bar{\nu} = 1890$ cm⁻¹ (s) (ν_{CO}); ¹H NMR (200 MHz, CD₂Cl₂, 293 K, TMS): $\delta = 15.99$ (s, br, 1H; NH), 7.40–6.70 (m, 20H; Ph), 4.37 (d, 3H; =NCH₃), 4.06 (m, 24H; CH₂), 1.33 ppm (t, 36H; CH₃); ³¹P{¹H} (200 MHz, CD₂Cl₂, 293 K, H₃PO₄ ext.): $\delta = 116.7$ ppm (s); elemental analysis (%) calcd for C₅₀H₈₄BN₂O₁₃P₄Re (1242.12): C 48.35, H 6.82, N 2.26; found: C 48.19, H 6.95, N 2.30;

3-BPh₄: IR (KBr): $\bar{\nu} = 1894$ cm⁻¹ (s) (ν_{CO}); ¹H NMR (200 MHz, CD₂Cl₂, 293 K, TMS): $\delta = 13.98$ (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.): $\delta = 123.6$ ppm (s); elemental analysis (%) calcd for C₅₀H₈₃BN₂O₁₃P₄Re (1227.11): C 48.94, H 6.82, N 1.14; found: C 49.08, H 6.96, N 1.10.

Received: March 13, 2002 [Z18883]

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[9] X-ray structural analysis: Philips PW1100 diffractometer equipped with a scintillation counter, graphite-monochromated MoK_{α} radiation ($\lambda = 0.71069 \text{ \AA}$). Data correction for absorption effects by the ψ scan method^[10] for both compounds, and intensity decay correction (40%) for **2-BPh₄**. Structural determination: direct methods^[11] and full-matrix least-squares refinement on all F^2 .^[12] Anisotropic displacement parameters refined in both cases for all non-hydrogen atoms; hydrogen atoms were introduced in idealized positions. Phosphite and phenyl groups were restrained to agree with typical bonding geometry from the literature. Crystal data for **2-BPh₄**: $\text{C}_{50}\text{H}_{84}\text{BN}_2\text{O}_{13}\text{P}_4\text{Re}$, $M_w = 1242.12$, crystal dimensions $0.3 \times 0.2 \times 0.2 \text{ mm}^3$, space group $P2_1/c$, monoclinic, $a = 13.002(2)$, $b = 24.570(5)$, $c = 20.054(4) \text{ \AA}$, $\beta = 95.49(2)^\circ$, $V = 6377(2) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.308 \text{ g cm}^{-3}$, $\theta_{\text{max}} = 30^\circ$, 18990 measured reflections (18537 unique), 4388 unique observed ($I > 2\sigma(I)$), $R_1 = 0.095$, $wR_2 = 0.26$ (on observed data), 176 restraints, 601 parameters, $GOF = 0.845$. Crystal data for **3-BPh₄**: $\text{C}_{50}\text{H}_{83}\text{BNO}_{13}\text{P}_4\text{Re}$, $M_w = 1227.11$, crystal dimensions $0.4 \times 0.3 \times 0.2 \text{ mm}^3$, space group $P\bar{1}$, triclinic, $a = 15.393(5)$, $b = 16.977(5)$, $c = 12.916(5) \text{ \AA}$, $\alpha = 100.02(5)$, $\beta = 91.63(5)$, $\gamma = 71.08(5)^\circ$, $V = 3143(2) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calcd}} = 1.290 \text{ g cm}^{-3}$, $\theta_{\text{max}} = 28^\circ$, 15138 measured unique reflections, 8634 unique observed ($I > 2\sigma(I)$), $R_1 = 0.048$, $wR_2 = 0.115$ (on observed data), 611 parameters, 79 restraints, $GOF = 0.912$. CCDC-181120 (**2-BPh₄**) and CCDC-181121 (**3-BPh₄**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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[16] Coordination geometry for **2**: Re–N 2.12(1), Re–CO 2.14(1), Re–P 2.354(4), NH–N 1.251(4), N–C 1.36(2), C–O 1.12(1) Å; Re–N–N 145(2), N–N–C 123(2)°.

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

Ian R. Baxendale, Steven V. Ley,* and Claudia Piutti

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.^[1] Thus extensive synthetic studies of this family have been carried out over a number of years.^[2, 3] Furthermore, the search for new members of the series has proved to be extremely profitable.^[3, 4] The recently isolated compound (+)-plicamine (**1**) is especially attractive as it exemplifies many of the structural features of these natural

[*] Prof. S. V. Ley, I. R. Baxendale
Department of Chemistry
University of Cambridge
Lensfield Road, Cambridge CB2 1EW (UK)
Fax: (+44)1223-336-442
E-mail: svl1000@cam.ac.uk
C. Piutti
Department of Chemistry
Pharmacia S.p.A
Discovery Research Oncology
Viale Pasteur, 10, 20014 Nerviano (MI) (Italy)

** We gratefully acknowledge financial support from Pfizer Central Research for a Postdoctoral Fellowship (to I.R.B.), the BP endowment and the Novartis Research Fellowship (to S.V.L.), and Pharmacia & Upjohn (to C.P.).