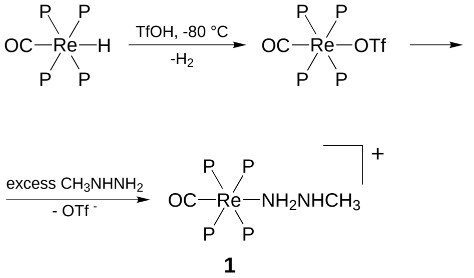
Methyleneimine CH_2=NH as a Unidentate Ligand in Rhenium Complexes[**]

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 $[Pb(OAc)_4]$ and H_2O_2, 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 η^1-NH=CH_2 methyleneimine derivative.

The CH_2=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.

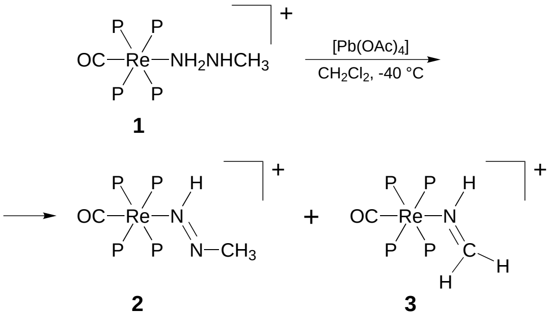
The reaction of the hydride[8] $[ReH(CO)\{P(OEt)_3\}_4]$ with triflic acid (TfOH) gives the thermally unstable $[Re(\eta^2\text{-}H_2)(CO)\{P(OEt)_3\}_4]^+(CF_3SO_3)^-$ species, which loses H_2, affording the compound $[Re(\kappa^1\text{-}OTf)(CO)\{P(OEt)_3\}_4]$. Substitution of the weakly bound triflato ligand with methylhydrazine gives *trans*-$[Re(CH_3NHNH_2)(CO)\{P(OEt)_3\}_4]^+$ (**1**), which was isolated as a BPh_4 salt (**1**-BPh_4) in about 70% yield (Scheme 1).



Scheme 1. $P = P(OEt)_3$.

Complex **1**-BPh_4 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 ligand, whereas the ^1H NMR spectrum exhibits resonance signals at $\delta = 4.35$ (s, br; $ReNH_2NHCH_3$), 3.93 (m, br; $ReNH_2NHCH_3$), and 2.49 ppm (d; $ReNH_2NHCH_3$) of the CH_3NHNH_2 group.

Treatment of methylhydrazine complex **1**-BPh_4 with an equimolar amount of $[Pb(OAc)_4]$ at low temperature (−40 °C) in CH_2Cl_2 gives a mixture of methyldiazene $[Re(CH_3N{=}NH)(CO)\{P(OEt)_3\}_4]BPh_4$ (**2**-BPh_4) and methyleneimine $[Re(\eta^1\text{-}NH{=}CH_2)(CO)\{P(OEt)_3\}_4]BPh_4$ (**3**-BPh_4) derivatives (Scheme 2). These were separated by fractional crystallization in moderate yields (42% for **2**-BPh_4, 24% for **3**-BPh_4) as analytically pure white crystalline solids.



Scheme 2. $P = P(OEt)_3$.

The complexes were characterized by spectroscopy and in two X-ray diffraction studies.[9–12] Figure 1 shows the crystal structure of the cation $[Re(\eta^1\text{-}NH{=}CH_2)(CO)\{P(OEt)_3\}_4]^+$ (**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 sp^2 character of the N atom (Re-N-C 139(1)°), with Re–N 2.32(1) and N–C 1.26(1) Å. This is, in fact, the first example of η^1 coordination of a CH_2=NH molecule to a transition metal, the only other similar case being the deprotonated CH_2=N=M fragment found in (μ^2-methyleneamido)tricarbonylbis-

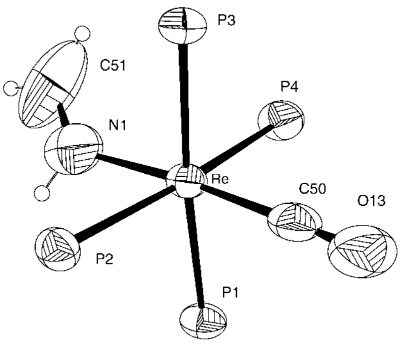


Figure 1. Structure of the core of the cation **3** (thermal ellipsoids drawn at the 30% level; ethoxy groups are omitted for clarity). Selected bond lengths [Å] and angles [°]: Re-C50 1.956(8), Re-N1 2.32(1), Re-P3 2.362(2), Re-P1 2.362(2), Re-P4 2.374(2), Re-P2 2.378(2), O13-C50 1.108(8), N1-C51 1.26(1); C50-Re-N1 175.9(3), C50-Re-P3 87.7(2), N1-Re-P3 95.9(2), C50-Re-P1 86.9(2), N1-Re-P1 89.5(2), P3-Re-P1 174.44(6), C50-Re-P4 94.4(2), N1-Re-P4 87.6(2), P3-Re-P4 90.00(7), P1-Re-P4 89.25(7), C50-Re-P2 92.9(2), N1-Re-P2 85.0(2), P3-Re-P2 91.44(6), P1-Re-P2 90.01(6), P4-Re-P2 172.56(6), O13-C50-Re 177.2(6), C51-N1-Re 134(1).

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[*] 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)

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(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 arylic $R_2C{=}NH$ 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 ^{1}H NMR spectra of **3**-BPh_4 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 $=CH_2$ group. The other is probably masked by the methylene signals of the $P(OCH_2CH_3)_3$ ligands. In the temperature range between +30 and −80 °C the $^{31}P\{^1H\}$ 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**-BPh_4, 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 ^{1}H NMR spectra of **2**-BPh_4 further support the presence of the $CH_3N{=}NH$ 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 $^{31}P\{^1H\}$ NMR spectrum.

Other methylhydrazine complexes, such as dicarbonyls $[Re(CH_3NHNH_2)(CO)_2P_3]BPh_4$ ($P = P(OEt)_3$ or $PPh(OEt)_2$), were prepared, and their reaction with $[Pb(OAc)_4]$ led, at −40 °C, to a mixture of methyldiazene $[Re(CH_3N{=}NH)(CO)_2P_3]^+$ and methyleneimine $[Re(\eta^1\text{-}NH{=}CH_2)(CO)_2P_3]^+$ 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-$NH{=}CH_2$ 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 MnO_2 or H_2O_2 were unsuccessful.

The formation of species **2**-BPh_4 and **3**-BPh_4 from the reaction of methylhydrazine complexes **1**-BPh_4 (Scheme 2) suggests that $[Pb(OAc)_4]$ gives rise to two parallel reactions involving selective oxidation of CH_3NHNH_2 to methyldiazene $CH_3N{=}NH$, giving **2**-BPh_4, in one case, whereas a completely new reaction involving cleavage of the N=N bond and formation of the $CH_2{=}NH$ 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-$NH{=}CH_2$ 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 $M{-}NH{=}CH_2$ 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-BPh_4: CF_3SO_3H (TfOH) (0.23 mmol, 20 µL) was added to a solution of $[ReH(CO)\{P(OEt)_3\}_4]$[8] (200 mg, 0.23 mmol) in CH_2Cl_2 (5 mL) cooled to −196 °C, and the reaction mixture was allowed to warm to room temperature, and stirred for 1 h. CH_3NHNH_2 (0.6 mmol, 32 µL) 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 $NaBPh_4$ (0.6 mmol, 205 mg). A white solid slowly separated out, which was crystallized from CH_2Cl_2 and ethanol to give **1**-BPh_4 (210 mg; yield 73%). IR (KBr): $\tilde{\nu} = 3343$ (m), 3291 (m) (ν_{NH}), 1880 cm^{-1} (s) (ν_{CO}); ^{1}H NMR (200 MHz, CD_2Cl_2, 293 K, TMS): $\delta = 7.40–6.86$ (m, 20H; Ph), 4.35 (s, br, 2H; NH_2), 4.05 (m, 24H; CH_2); 3.93 (m, br, 1H; NH), 2.49 (d, $^3J_{H,H} = 6$ Hz, 3H; CH_3N), 1.29 ppm (t, 36H; CH_3); $^{31}P\{^1H\}$(200 MHz, CD_2Cl_2, 293 K, H_3PO_4 85% ext.): $\delta = 117.9$ ppm (s); elemental analysis (%) calcd for $C_{50}H_{86}BN_2O_{13}P_4Re$ (1244.14): C 48.27, H 6.97, N 2.25; found: C 48.15, H 7.01, N 2.13.

2-BPh_4, **3**-BPh_4: 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, CH_2Cl_2 (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 $NaBPh_4$ (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 CH_2Cl_2 to obtain a saturated solution at room temperature. The first crystals are of **2**-BPh_4, the second a mixture of **2**-BPh_4 and **3**-BPh_4 which was recrystallized. A total of 52 mg of **2**-BPh_4 (yield 42%) was separated. By further cooling of the solution, 29 mg of white crystals of **3**-BPh_4 (yield 24%) were obtained. Pure samples of **2**-BPh_4 and **3**-BPh_4 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-BPh_4: IR (KBr):$\tilde{\nu} = 1890$ cm^{-1} (s) (ν_{CO}); ^{1}H NMR (200 MHz, CD_2Cl_2, 293 K, TMS): $\delta = 15.99$ (s, br, 1H; NH), 7.40–6.70 (m, 20H; Ph), 4.37 (d, 3H; $=NCH_3$), 4.06 (m, 24H; CH_2), 1.33 ppm (t, 36H; CH_3); $^{31}P\{^1H\}$ (200 MHz, CD_2Cl_2, 293 K, H_3PO_4 ext.): $\delta = 116.7$ ppm (s); elemental analysis (%) calcd for $C_{50}H_{84}BN_2O_{13}P_4Re$ (1242.12): C 48.35, H 6.82, N 2.26; found: C 48.19, H 6.95, N 2.30;

3-BPh_4: IR (KBr): $\tilde{\nu} = 1894$ cm^{-1} (s) (ν_{CO}); ^{1}H NMR (200 MHz, CD_2Cl_2, 293 K, TMS): $\delta = 13.98$ (s, br, 1H; NH), 7.60–6.80 (m, 20H; Ph), 4.06 (m, 24H; CH_2), 3.66 (m, br, 1H; $N{=}CH_2$), 1.34 ppm (t, 36H; CH_3); $^{31}P\{^1H\}$ (200 MHz, CD_2Cl_2, 293 K, H_3PO_4 ext.): $\delta = 123.6$ ppm (s); elemental analysis (%) calcd for $C_{50}H_{83}BNO_{13}P_4Re$ (1227.11): C 48.94, H 6.82, N 1.14; found: C 49.08, H 6.96, N 1.10.

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[9] X-ray structural analysis: Philips PW1100 diffractometer equipped with a scintillation counter, graphite-monochromated $\mathrm{Mo}_{K\alpha}$ radiation ($\lambda = 0.71069$ Å). Data correction for absorption effects by the ψ scan method[10] for both compounds, and intensity decay correction (40%) for **2**-BPh$_4$. 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**-BPh$_4$: $C_{50}H_{84}BN_2O_{13}P_4Re$, $M_W = 1242.12$, crystal dimensions $0.3 \times 0.2 \times 0.2$ mm^3, space group $P2_1/c$, monoclinic, $a = 13.002(2)$, $b = 24.570(5)$, $c = 20.054(4)$ Å, $\beta = 95.49(2)^\circ$, $V = 6377(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.308$ g cm^{-3}, $\theta_{max} = 30^\circ$, 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**-BPh$_4$: $C_{50}H_{83}BNO_{13}P_4Re$, $M_W = 1227.11$, crystal dimensions $0.4 \times 0.3 \times 0.2$ mm^3, space group $P\bar{1}$, triclinic, $a = 15.393(5)$, $b = 16.977(5)$, $c = 12.916(5)$ Å, $\alpha = 100.02(5)$, $\beta = 91.63(5)$, $\gamma = 71.08(5)^\circ$, $V = 3143(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.290$ g cm^{-3}, $\theta_{max} = 28^\circ$, 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**-BPh$_4$) and CCDC-181121 (**3**-BPh$_4$) 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)°.

[17] 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.

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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, immunosuppresive, 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

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[*] 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)

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