Preparation and Reactivity of Hydrazine Complexes of Rhenium: Synthesis of 1,2-Diazene (NH=NH) and Methyleneimine (CH₂=NH) Derivatives

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The hydrazine complexes [Re(RNHNH₂)(CO)_nP_{5-n}]BPh₄ [R = H, CH₃, Ar; n = 1-4; P = P(OEt)₃, PPh(OEt)₂, PPh₂OEt] were prepared by allowing the hydride species [ReH(CO)_nP_{5-n}] to react first with a Brønsted acid and then with hydrazine. The reaction of either [Re(NH₂NH₂)(CO)_nP_{5-n}]BPh₄ or [Re(ArNHNH₂)(CO)_nP_{5-n}]BPh₄ with Pb(OAc)₄ at -40 °C proceeds with the selective oxidation of the hydrazine ligand to yield either [Re(NH=NH)(CO)_nP_{5-n}]BPh₄ or [Re(ArN=NH)(CO)_nP_{5-n}]BPh₄. The oxidation of [Re-

 $(CH_3NHNH_2)(CO)_nP_{5-n}]BPh_4$ (n = 1, 2) with $Pb(OAc)_4$ at -40 °C gives both $[Re(CH_3N=NH)(CO)_nP_{5-n}]BPh_4$ and $[Re(\eta^1-NH=CH_2)(CO)_nP_{5-n}]BPh_4$. Reduction reactions of both hydrazine and diazene complexes with Zn amalgam were also studied and yielded ammonia in moderate yield (20–25%).

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Introduction

Complexes containing partially reduced dinitrogen molecules such as hydrazine (RNHNH₂), hydrazido (RNHNH), diazene (RN=NH), and diazenido (RN₂) as ligands continue to be studied not only for their relationship with the nitrogen-fixation process intermediates, but also because their properties lead us to consider this class of compounds as having an identity and chemistry of their own,^[1-3] with potentially interesting developments.

The hydrazine complexes are the least studied^[1,2] among these diazo species even though NH₂NH₂ has been shown to be a substrate^[4] as well as a product of functioning nitrogenase and has been isolated by quenching the enzyme.^[5] Furthermore, rhenium complexes containing NH₂NH₂ or substituted hydrazine RNHNH₂ are very rare and include, apart from the pioneering work on [Re(NCO)- $(CO)_2(NH_2NH_2)P_2$] (P = tertiary phosphane),^[6] only two papers,^[7,8] on [ReCp*Me₃(NH₂NH₂)]CF₃SO₃ one $(Cp^* = pentamethylcyclopentadienyl)$ and $[Re(NH_2NH_2)-$ (CO)₃(PPh₃)₂]CF₃SO₃, and another on the substitutedhydrazine complex [ReCl₂(PPh₃)₂{NNC(O)Ph}{H₂NNHC-(S)Ph}].^[9]

We have previously reported the synthesis and reactivity of mono- and bis(hydrazine) complexes of the iron triad^[10] and manganese^[11] of the type $[MH(RNHNH_2)P_4]BPh_4$, $[M(RNHNH_2)_2P_4](BPh_4)_2$ (M = Fe, Ru, Os) and $[Mn(RNHNH_2)(CO)_nP_{5-n}]BPh_4$ (P = phosphites). We have now extended these studies to rhenium with the aim of preparing hydrazine complexes and studying their reactivity toward oxidizing and reducing reagents in an attempt to test whether the rhenium fragments are able to stabilize diazene species. The results of these studies, which include the synthesis of stable 1,2-diazene complexes and the unprecedented methyleneimine (CH₂=NH) derivatives, are reported here. A preliminary paper on part of this work has previously been published.^[12]

Results and Discussion

Preparation of Hydrazine Complexes

The hydrazine complexes $[\text{Re}(\text{RNHNH}_2)(\text{CO})_n P_{5-n}]$ -BPh₄ (1-8) were prepared by reacting the hydride species $[\text{ReH}(\text{CO})_n P_{5-n}]$ first with an equimolar amount of a Brønsted acid (CF₃SO₃H or HBF₄) and then with an excess of hydrazine, as shown in Scheme 1.

Treatment of the hydrides $[ReH(CO)_n P_{5-n}]$ with the Brønsted acid CF₃SO₃H or HBF₄ (HY) gives the dihydrogen-containing cationic complexes $[\text{Re}(\eta^2 H_2(CO)_n P_{5-n}^{+,[13]}$ which are thermally unstable and easily lose H₂ yielding either the neutral $\text{ReY}(\text{CO})_n P_{5-n}$ species, containing the labile Y⁻ ligand, or the coordinatively unsaturated $[\text{Re}(\text{CO})_n P_{5-n}]^+$ cations. Reaction of these intermediates with an excess of hydrazine gives the final derivatives $[\text{Re}(\text{RNHNH}_2)(\text{CO})_n P_{5-n}]^+$ (1-8), which were isolated as their BPh₄⁻ salts and characterised. 1,1-Dimethylhydrazine reacts with these rhenium intermediates giving the final derivatives $[Re{(CH_3)_2NNH_2}(CO)_nP_{5-n}]BPh_4$ (1e and 3e).

Good analytical data were obtained for all the hydrazine complexes 1-8, which are white or pale-yellow solids,

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Scheme 1. P = P(OEt)₃ (1, 2, 5), PPh(OEt)₂ (3, 6), PPh₂OEt (4, 7, 8); Y = CF₃SO₃⁻, BF₄⁻⁻; R = H (a), CH₃ (b), C₆H₅ (c), 4-NO₂C₆H₄ (d); (CH₃)₂NNH₂ (e)

stable in air and in solution in polar organic solvents, where they behave as 1:1 electrolytes.^[14] The IR and NMR spectroscopic data (Table 1) support the proposed formulation and allow a geometry in solution to be established.

The presence of a hydrazine ligand in the complexes is confirmed by the IR spectra, which show the characteristic v(NH) bands between 3366 and 3202 cm⁻¹. In some complexes the $\delta(NH_2)$ absorption at 1624–1611 cm⁻¹ is also observed. Furthermore, the ¹H NMR spectra confirm the presence of the hydrazine ligand, showing the characteristic NH and NH₂ signals, which were clearly assigned by accurate integration and homodecoupling experiments, and are reported in Table 1. The spectra also show that, in the case of the NH₂NH₂ complexes, two NH₂ proton signals are present, thus excluding the formation of a dimeric complex with an NH₂NH₂ bridging ligand.

In the temperature range between +30 and -80 °C the ³¹P NMR spectra of the monocarbonyl complexes 1 show a sharp singlet suggesting a mutual *trans* position (geometry I) of the carbonyl and hydrazine ligands. This is confirmed by the IR spectra, which show the v(CO) band at 1887 - 1888 cm⁻¹.

The IR spectra of the dicarbonyl complexes 2-4 show two strong bands in the v(CO) region indicating the mutual cis position of the two carbonyl ligands. The ¹³C NMR spectra also indicate that the two CO groups are magnetically equivalent, showing only one multiplet for 2b in the carbonyl carbon region at $\delta = 194.2$ ppm. Furthermore, the ${}^{31}P{}^{1}H$ NMR spectra display either an A₂B- or an AB₂type coupling pattern, suggesting the magnetic equivalence of two P atoms, different from the third. On this basis a fac geometry (II) may be proposed for the dicarbonyl derivatives.

In the temperature range between +30 and -80 °C, the ³¹P NMR spectra of the tricarbonyl compounds 5-7 show a sharp singlet, in agreement with two magnetically equivalent phosphane ligands. The IR spectra show three v(CO)bands, two strong and one of medium intensity, suggesting a mer arrangement of the carbonyl ligands. On this basis, a *mer-trans* geometry (III) in solution may be reasonably proposed for the tricarbonyl derivatives.

Finally, the presence of four v(CO) bands in the carbonyl region of its IR spectrum strongly suggests a cis geometry (IV) for the tetracarbonyl derivative [Re(NH₂NH₂)- $(CO)_4(PPh_2OEt)]^+$ (8).

Oxidation Reactions

 $P = PPh(OEt)_2$ (11), PPh_2OEt (12)

The hydrazine complexes $[Re(NH_2NH_2)(CO)_nP_{5-n}]BPh_4$ react with Pb(OAc)₄ at -40 °C to give the 1,2-diazene derivatives $[Re(NH=NH)(CO)_nP_{5-n}]BPh_4$, which were isolated in the solid state and characterised (Scheme 2).



$$[\text{Re}(\text{NH}_{2}\text{NH}_{2})(\text{CO})_{3}\text{P}_{2}]^{+} \xrightarrow{\text{Pb}(\text{OAc})_{4}}_{-40 \text{ °C}, \text{ CH}_{2}\text{Cl}_{2}} \xrightarrow{\text{P}}_{OC} \xrightarrow{\text{N}}_{N} \xrightarrow{\text{CO}}_{H1} \xrightarrow{\text{H1}}_{+} mer-trans$$

$$P = \text{PPh}(\text{OEt})_{2} (13), \text{PPh}_{2}\text{OEt} (14)$$

$$13a, 14a$$

Scheme 2

The reaction proceeds with the selective oxidation of the hydrazine ligand to 1,2-diazene, which is stabilized by coordination to all the $[\operatorname{Re}(\operatorname{CO})_n \operatorname{P}_{5-n}]$ (n = 1, 2, 3) fragments, thus allowing the complexes to be isolated. The use of a temperature below -30 °C during the reaction course is crucial for a successful synthesis, as is crystallisation of the products at 0 °C. If these temperatures are not maintained, large amounts of decomposition products are obtained that contain only traces of the diazene complexes. In pure form, however, the NH=NH compounds 9-14 are stable at room temperature both as a solid and in solution in polar organic solvents, where they behave as 1:1 electrolytes.^[14] Analytical and spectroscopic data (Table 1) support the proposed for-

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Table 1. Selected IR and NMR spectroscopic data for rhenium complexes

Compound	$IR^{[a]}$ \tilde{v} , cm ⁻¹	Assgnt	1 H NMR ^{[b][c]} δ (<i>J</i> /Hz)	Assgnt	Spin system	${}^{31}P{^{1}H} NMR^{[b] [d]} \delta (J/Hz)$
$[Re(NH_2NH_2)(CO){P(OEt)_3}_4]BPh_4 (1a)$	3366m 3313m 3283w 3218m	v(NH)	4.45 (br. m) 4.07 (m) 1.30 (t)	ReNH ₂ CH ₂ CH ₃	A_4	118.1 (s)
$[Re(C_6H_5NHNH_2)(CO){P(OEt)_3}_4]BPh_4 (1c)$	1887s 3341m 3285m 1888s	v(CO) v(NH) v(CO)	6.22 (br. t) 5.16 (br. m) 4.08 (m)	NH ReNH ₂ CH ₂	A_4	117.8 (s)
$[Re\{(CH_{3})_{2}NNH_{2}\}(CO)\{P(OEt)_{3}\}_{4}]BPh_{4} (1e)$	1611m 3327w 3283m 1887s	$\delta(NH_2)$ v(NH) v(CO)	1.31 (t) 4.24 (br) 4.06 (m) 2.39 (s)	CH ₃ ReNH ₂ CH ₂ (CH ₃) ₂ N	A ₄	116.7 (s)
[Re(CH ₃ NHNH ₂)(CO) ₂ {P(OEt) ₃ } ₃]BPh ₄ (2b) ^[e]	3325m 3285m 3213w 1982s 1902s	ν(NH) ν(CO)	1.29 (t) 4.44 (br) 3.36 (br) 4.13 (m) 2.59 (d, $J_{H,H} = 6$) 1.38 (t)	CH ₃ ReNH ₂ NH CH ₂ CH ₃ N CH ₃	A ₂ B	$\delta_{A} = 114.7$ $\delta_{B} = 113.3$ $J_{AB} = 49$
[Re(NH ₂ NH ₂)(CO) ₂ {PPh(OEt) ₂ } ₃]BPh ₄ (3a)	3357w 3298m 3262w 3219w 1999s	ν(NH) ν(CO)	1.34 (t) 3.55 (br. m) 3.90 (m) 2.71 (br) 1.35 (t) 1.33 (t)	ReNH ₂ CH ₂ NH ₂ CH ₃	AB ₂	$\delta_{A} = 139.3$ $\delta_{B} = 136.4$ $J_{AB} = 35$
[Re(CH ₃ NHNH ₂)(CO) ₂ {PPh(OEt) ₂ } ₃]BPh ₄ (3b)	1905s 3335w 3289w 3276m 1989s 1905s	ν(NH) ν(CO)	1.31 (t) 3.27 (br. m) 3.93 (m) 2.27 (m) 1.79 (d, $J_{H,H} = 6$) 1.38 (t) 1.32 (t)	ReNH ₂ CH ₂ NH CH ₃ N CH ₃	AB ₂	$\delta_{A} = 139.4$ $\delta_{B} = 137.1$ $J_{AB} = 35$
$[Re(C_6H_5NHNH_2)(CO)_2\{PPh(OEt)_2\}_3]BPh_4 (3c)$	3354w 3268m 1982s 1905s 1617m	ν(NH) ν(CO) δ(NH ₂)	4.87 (br. t) 4.04 (br. m) 3.88 (m) 1.31 (t) 1.30 (t)	NH ReNH ₂ CH ₂ CH ₃	AB ₂	$\delta_{A} = 139.9$ $\delta_{B} = 136.6$ $J_{AB} = 35$
$[Re(4-NO_2C_6H_4NHNH_2)(CO)_2\{PPh(OEt)_2\}_3]BPh_4 (3d)$	3295m 3276w 1986s 1894s	v(NH) v(CO)	1.27 (t) 6.13 (m) 6.10 (m) 4.10-3.80 (m) 1.39 (t) 1.32 (t) 1.25 (t)	ReNH ₂ NH CH ₂ CH ₃	AB ₂	$\delta_{A} = 144.4$ $\delta_{B} = 144.1$ $J_{AB} = 40$
$[Re{(CH_3)_2NNH_2}(CO)_2{PPh(OEt)_2}_3]BPh_4 (3e)$	3299w 3262w 1980s 1868s	v(NH) v(CO)	4.05-3.80 (m) 3.74 (m) 2.05 (s) 1.37 (t) 1.35 (t) 1.28 (t)	CH ₂ ReNH ₂ (CH ₃) ₂ N CH ₃	AB ₂	$\delta_{A} = 138.7$ $\delta_{B} = 135.1$ $J_{AB} = 38$
[Re(NH ₂ NH ₂)(CO) ₂ (PPh ₂ OEt) ₃]BPh ₄ (4a)	3358m 3290m 3271w 3224w 1970s	ν(NH) ν(CO)	3.69 (br. m) 3.60-3.30 (m) 2.60 (br. t) 0.99 (t) 0.63 (t)	ReNH ₂ CH ₂ NH ₂ CH ₃	AB ₂	$\delta_{A} = 113.4$ $\delta_{B} = 109.1$ $J_{AB} = 30$
[Re(CH ₃ NHNH ₂)(CO) ₂ (PPh ₂ OEt) ₃]BPh ₄ (4b)	3332m 3262m 1970s 1881s	v(NH) v(CO)	3.80-3.15 (m) 2.97 (m) 2.04 (m) 1.61 (d, $J_{\text{H,H}} = 6$) 0.97 (t) 0.62 (t)	CH ₂ ReNH ₂ NH CH ₃ N CH ₃	AB ₂	$\delta_{A} = 113.7$ $\delta_{B} = 109.4$ $J_{AB} = 30$

Table 1 (Continued)

Compound	$IR^{[a]}$ $\tilde{\nu}, cm^{-1}$	Assgnt	¹ H NMR ^{[b][c]} δ (J/Hz)	Assgnt	Spin system	$^{31}P{^{1}H} NMR^{[b] [d]} \delta (J/Hz)$
$[Re(NH_2NH_2)(CO)_3 \{P(OEt)_3\}_2]BPh_4 (5a)$	3347w 3261m 3223w 2076m 1971s	ν(NH) ν(CO)	4.11 (m) 3.47 (br. m) 2.83 (br. m) 1.38 (t)	CH ₂ ReNH ₂ NH ₂ CH ₃	A ₂	110.9 (s) 111.3 (s) ^[f]
[Re(NH ₂ NH ₂)(CO) ₃ {PPh(OEt) ₂ } ₂]BPh ₄ (6a)	1612m 3348m 3287m 3268w 3219m 2072w 1968s	$ \begin{aligned} &\delta(NH_2)\\ &\nu(NH) \end{aligned} \\ &\nu(CO) \end{aligned}$	3.97 (m) 3.22 (br. m) 2.57 (br. t) 1.38 (t)	CH ₂ ReNH ₂ NH ₂ CH ₃	A ₂	132.3 (s)
$[Re(4-NO_2C_6H_4NHNH_2)(CO)_3\{PPh(OEt)_2\}_2]BPh_4$ (6d)	1944s 1624m 3285m 3270sh 3230w 2084w	$ \begin{aligned} &\delta(\mathrm{NH}_2) \\ &\nu(\mathrm{NH}) \end{aligned} \\ &\nu(\mathrm{CO}) \end{aligned} $	6.30 (m) 6.24 (m) 4.10 (m) 1.42 (t)	NH ReNH ₂ CH ₂ CH ₃	A ₂	133.0 (s)
[Re(NH ₂ NH ₂)(CO) ₃ (PPh ₂ OEt) ₂]BPh ₄ (7a)	1984s 1938s 3354m 3281w 3267m 3217w 2075w 1970s	ν(NH) ν(CO)	3.61 (m) 3.43 (br. m) 2.67 (br. t) 1.16 (t)	CH ₂ ReNH ₂ NH ₂ CH ₃	A ₂	107.1 (s)
[Re(CH ₃ NHNH ₂)(CO) ₃ (PPh ₂ OEt) ₂]BPh ₄ (7b)	1933s 3322w 3263m 2076m 1969s	v(NH) v(CO)	3.76 (br. m) 3.68 (m) 2.77 (m) 1.97 (d. $J_{H,H} = 6$)	ReNH ₂ CH ₂ NH CH ₂ N	A ₂	109.0 (s)
$[Re(NH_2NH_2)(CO)_4(PPh_2OEt)]BPh_4 (8a)$	1926s 3328w 3282w 3267w 3202m	v(NH)	1.21 (t) 3.58 (qnt) 2.31 (m) 1.94 (br. t) 1.18 (t)	$CH_3 \\ CH_2 \\ ReNH_2 \\ NH_2 \\ CH_3$	А	102.9 (s)
[Re(NH=NH)(CO){P(OEt) ₃ } ₄]BPh ₄ (9a)	2113m 2024sh 2009s 1975s 1614m 1887s	ν(CO) δ(NH ₂) ν(CO)	A ₄ XY spin syst. $\delta_X = 16.70$ $\delta_Y = 15.84$ $J_{XY} = 33.0$ $J_{AX} = 1.26$ $J_{AY} = 2.86$ 4.06 (m) 1.22 (i)	NH=NH ReNH N=NH CH ₂ CH ₃	A ₄	123.6 (s) 123.4 (s) ^[f]
$[Re(C_6H_5N=NH)(CO){P(OEt)_3}_4]BPh_4 (9c)$	1899s	v(CO)	1.32 (t) 14.39 (qnt, $J_{\rm PH} = 4$) 4.08 (m)	NH CH ₂	A_4	116.8 (s)
$[Re(CH_3N=NH)(CO)_2\{P(OEt)_3\}_3]BPh_4 \ (10b)^{[g]}$	1992s 1911s	v(CO)	1.27 (t) 15.86 (br. s) 4.10 (m) 4.44 (d)	CH_3 $ReNH$ CH_2 $=NCH_3$	$A_2B^{[f]}$	$\delta_{A} = 114.1$ $\delta_{B} = 111.3$ $J_{AB} = 48.3$
$[Re(\eta^{1}-NH=CH_{2})(CO)_{2}\{P(OEt)_{3}\}_{3}]BPh_{4} (10*b)^{[h]}$	2002s 1915s	v(CO)	1.36 (t) 13.82 (br. s) 4.05 (m) 3.75 (q) 1.31 (t)	CH_3 ReNH CH_2 N=CH_2 CH_3	A ₂ B ^[f]	$\delta_A = 120.9$ $\delta_B = 118.7$ $J_{AB} = 47.8$

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Table 1 (Continued)

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Compound	$IR^{[a]}$ $\tilde{\nu}, cm^{-1}$	Assgnt	¹ H NMR ^{[b][c]} δ (<i>J</i> /Hz)	Assgnt	Spin system	$^{31}P{^{1}H} NMR^{[b] [d]} \delta (J/Hz)$
$[Re(NH=NH)(CO)_{2}{PPh(OEt)_{2}}_{3}]BPh_{4} (11a)$	1998s 1906s	v(CO)	$\begin{array}{l} A_2B_2XY \text{ spin syst.} \\ \delta_X = 16.07 \\ \delta_Y = 15.28 \\ J_{XY} = 33.3 \\ J_{AX} = 2.15 \\ J_{AY} = 3.15 \\ J_{BX} = 1.15 \\ J_{BY} = 1.45 \end{array}$	NH=NH ReNH N=NH	A ₂ B	$\delta_{A} = 142.8$ $\delta_{B} = 140.0$ $J_{AB} = 35$
			3.92 (m) 1.38 (t) 1.35 (t) 1.33 (t)	CH ₂ CH ₃		
$[\text{Re}(\text{CH}_3\text{N}=\text{NH})(\text{CO})_2\{\text{PPh}(\text{OEt})_2\}_3]\text{BPh}_4$ (11b) and	1992s 1911s	v(CO)	15.94 (br. s) 12.08 (br. s)	N=NH C=NH	AB_2 AB_2	142 - 140 (m) 135 - 132 (m)
$[Re(\eta^{1}-NH=CH_{2})(CO)_{2}{PPh(OEt)_{2}_{3}}BPh_{4}$ (11*b)	19110		4.29 (d) 3.90 (m) 3.70 (m) 1.35 (m)	$= NCH_3$ CH_2 $N=CH_2$ CH_3	1102	100 102 (III)
$[Re(C_6H_5N=NH)(CO)_2\{PPh(OEt)_2\}_3]BPh_4 (11c)$	1970s 1887s	v(CO)	12.22 (d) 3.35 (m) 0.84 (t) 0.67 (t)	NH CH ₂ CH ₃	AB ₂	$\delta_{A} = 113.2$ $\delta_{B} = 108.6$ $J_{AB} = 28$
[Re(NH=NH)(CO) ₂ (PPh ₂ OEt) ₃]BPh ₄ (12a)	1972s 1887s	v(CO)	$\begin{array}{l} AB_2XY \ \text{spin syst.} \\ \delta_X = 15.31 \\ \delta_Y = 14.42 \\ J_{XY} = 33.5 \\ J_{AX} = 2.38 \\ J_{AY} = 3.74 \\ J_{BX} = 1.16 \\ J_{BY} = 1.88 \end{array}$	NH=NH ReNH N=NH	AB ₂	$\delta_{A} = 113.5$ $\delta_{B} = 109.1$ $J_{AB} = 30$
			3.45 (m) 0.99 (t) 0.64 (t)	CH ₂ CH ₃		
$[Re(NH=NH)(CO)_{3}\{PPh(OEt)_{2}\}_{2}]BPh_{4} (13a)$	2071w 1969s 1944s	v(CO)	$\begin{array}{l} A_2XY \text{ spin syst.} \\ \delta_X = 13.03 \\ \delta_Y = 11.89 \\ J_{XY} = 26.5 \\ J_{AX} = 2.4 \\ J_{AY} = 1.3 \end{array}$	NH=NH ReNH N=NH	A ₂	131.0 (s) 131.6 (s) ^[f]
			3.88 (m) 1.30 (t)	CH ₂ CH ₂		
$[Re(4-NO_2C_6H_4N=NH)(CO)_3\{PPh\{OEt)_2\}_2]BPh_4 (13d)$	2076m 1982s 1951s	v(CO)	13.14 (br) 4.10 (m) 1.43 (t)	NH CH ₂ CH ₃	A ₂	133.5 (s)
[Re(NH=NH)(CO) ₃ (PPh ₂ OEt) ₂]BPh ₄ (14a)	2069w 1967s 1940s	v(CO)	$\begin{array}{l} A_2 XY \text{ spin syst.} \\ \delta_X = 13.16 \\ \delta_Y = 12.40 \\ J_{XY} = 26.6 \\ J_{AX} = 2.20 \\ J_{AY} = 1.04 \end{array}$	NH=NH ReNH N=NH	A ₂	110.8 (s)
$[Re(CH_3NH_2)(CO)_2 \{P(OEt)_3\}_3]BPh_4 (15)^{[i]}$	3329m 3283m 2005s 1894s	v(NH) v(CO)	3.48 (m) 1.14 (t) 4.04 (m) 2.73 (t) 2.65 (br) 1.37 (t) 1.32 (t)	$\begin{array}{c} \mathrm{CH}_2\\ \mathrm{CH}_3\\ \mathrm{CH}_2\\ \mathrm{CH}_3\mathrm{N}\\ \mathrm{NH}_2\\ \mathrm{CH}_3\end{array}$	A ₂ B	$\delta_{A} = 172.1$ $\delta_{B} = 171.3$ $J_{AB} = 49$

^[a] In KBr. ^[b] In CD₂Cl₂ at 25 °C, unless otherwise noted. ^[c] Phenyl proton resonances are omitted. ^[d] Positive shift downfield from 85% H₃PO₄. ^[e] ¹³C{¹H} NMR (**2b**): δ = 194.2 (m) CO, 165–122 (m) Ph, 62.9 (m) CH₂, 44.6 (s) CH₃N, 16.3 (m) CH₃ ppm. ^[f] At -80 °C. ^[g] ¹³C{¹H} NMR (**10b**): δ = 196.2 (m) CO, 165–120 (m) Ph, 71.7 (s) CH₃N=, 62.7 (m) CH₂, 16.3 (m) CH₃ ppm. ^[h] ¹³C{¹H} NMR (**10*** b): δ = 194.7 (m) CO, 165–122 (m) Ph, 67.8 (s) N=CH₂, 62.4 (m) CH₂, 16.1 (m) CH₃ ppm. ^[i] ¹³C{¹H} NMR (**15**): δ = 194.2 (m) CO, 165–122 (m) Ph, 62.8 (m) CH₂, 38.5 (br. s) CH₃N, 16.3 (s) CH₃ ppm.

mulation and a geometry in solution can also be established from the IR and NMR spectroscopic data.

Diagnostic evidence for the presence of the NH=NH ligand are the ¹H NMR spectra, which show a multiplet of the type shown in Figure 1 in the high-frequency region, which can reasonably be attributed to the H1 and H2 protons of the diazene ligand coupled to the phosphorus nucleus of the phosphane. This multiplet, in fact, can easily be simulated by using A₂XY, AB₂XY or A₄XY models (X, Y = H), with the parameters reported in Table 1. The value of ³J_{H,H} was found to fall in the range 35–27 Hz, suggesting a probable *trans*-NH=NH geometry of the ligand.^[16a]



Figure 1. Observed (bottom) and calculated (top) ¹H NMR spectrum in the diazene region of $[Re(NH=NH)(CO)_3(PPh_2O-Et)_2]BPh_4$ (14a), in CD₂Cl₂ at 25 °C; the simulated spectrum was obtained using the parameters reported in Table 1

IR and NMR spectroscopic data support the geometry shown in Scheme 2 for the diazene complexes 9-14, which proves to be the same as that of the related hydrazine precursors. The oxidation of the NH₂NH₂ ligand does not change the geometry of the complexes, and a *trans* geometry is proposed for the monocarbonyl complex 9a on the basis of the sharp singlet present in the ³¹P NMR spectrum. A *fac* structure is proposed for the dicarbonyl complexes 11a and 12a, as their IR spectra show two v(CO) bands, while an AB₂ multiplet appears in the ³¹P NMR spectra. Finally, the presence of three v(CO) bands, one medium and two strong, in the IR spectra of the tricarbonyl complexes 13a and 14a, and only one sharp singlet in the ³¹P NMR spectra, suggest a *mer-trans* geometry for the complexes.

The stabilization of the very reactive molecule NH=NH by coordination to a transition metal has been achieved in a few cases, mainly in bimetallic complexes containing a μ -NH=NH ligand.^[15] Stable derivatives containing a monodentate diazene have been reported,^[16] but they are rather rare and include only one example for rhenium.^[17] The use of a mixed-ligand phosphite-carbonyl Re(CO)_nP_{5-n} fragment allows new examples of the stabilization of monodentate diazene to be achieved. It should be noted that the related manganese complexes $[Mn(NH_2NH_2)(CO)_nP_{5-n}]BPh_4$ also react with $Pb(OAc)_4$,^[11] but give only thermally unstable diazene complexes, which cannot be isolated.

The arylhydrazine complexes $[\text{Re}(\text{ArNHNH}_2)(\text{CO})_n$ - $P_{5-n}]\text{BPh}_4$ also react with Pb(OAc)_4 to give the corresponding aryldiazene complexes $[\text{Re}(\text{ArN}=\text{NH})(\text{CO})_n P_{5-n}]\text{BPh}_4$, which were isolated and characterised (Scheme 3).



Scheme 3

These complexes are yellow or orange solids that are stable in air and in solution in polar organic solvents, where they behave as 1:1 electrolytes.^[14] Analytical and spectroscopic data (Table 1) confirm the proposed formulation. Furthermore, the spectroscopic data of complex **9c** are identical to those of samples we have previously prepared by reacting the ReH(CO)P₄ hydride with a phenyldiazonium cation;^[18] this feature strongly supports the proposed formulation. Moreover, this result highlights that stable aryldiazene complexes of rhenium can be prepared following two different methods, which involve the oxidation of a coordinated arylhydrazine, in one case, and the insertion of an aryldiazonium cation into the Re–H bond of the appropriate hydride complex, in the other.

The presence of the aryldiazene ligand in complexes 9c, 11c and 13d is confirmed by the ¹H NMR spectra, which show the characteristic high-frequency signal of the ArN= NH ligand. The IR and NMR spectra also allow a geometry in solution to be established (Scheme 3). Apart from the *trans* geometry of the monocarbonyl complex 9c,^[18] a *mer-cis* arrangement of the ligands, like that of the related compound [Re(C₆H₅N=NH)(CO)₂(PPh₂OEt)₃]BPh₄,^[18] can be proposed for the carbonyl complex 11c. The IR spectra, in fact, show two v(CO) bands, while an AB₂ multiplet is observed in the ³¹P NMR spectrum. In the temperature range between +20 and -80 °C the ³¹P NMR spectrum of the tricarbonyl compound **13d** appears as a sharp singlet, while the IR spectrum shows one medium-intensity and two strong bands in the v(CO) region. On this basis, a *mer-trans* geometry for the complex can be proposed.

Surprisingly, the reaction of methylhydrazine complexes with an equimolar amount of Pb(OAc)₄ gives a mixture of methyldiazene [Re(CH₃N=NH)(CO)_nP_{5-n}]⁺ and methyleneimine [Re(η^1 -NH=CH₂)(CO)_nP_{5-n}]⁺ derivatives, which were separated and characterised (Scheme 4).





 $P = P(OEt)_3 10, PPh(OEt)_2 11$

Scheme 4

The two monocarbonyl complexes **9b** and **9*b** were characterised not only spectroscopically (IR and NMR spectroscopic data) but also by two X-ray crystal structure determinations. These structures were reported in a preliminary communication^[12] and will not be discussed further.

The dicarbonyl complexes 10b and 10*b, containing the P(OEt)₃ ligand, can be separated by fractional crystallisation or by the Pasteur method, obtaining the methyldiazene (10b) and the methyleneimine (10*b) species as white microcrystalline solids, while the related PPh(OEt)₂ derivatives 11b and 11*b were characterised spectroscopically as a mixture of the two species. The presence of the $CH_2 = NH$ ligand in 10*b is confirmed by the ¹H NMR spectrum, which shows the NH signal at $\delta = 13.82$ ppm and the two inequivalent CH₂ protons as an AB quadruplet at δ = 3.75 ppm. The IR spectra show two strong bands at 2002 and 1915 cm⁻¹ attributed to two CO ligands in a mutually cis position. These two carbonyls are also magnetically equivalent, since the ¹³C NMR spectrum shows only one multiplet at $\delta = 194.7$ ppm for the carbonyl carbon atoms. A singlet at $\delta = 67.8$ ppm is also present in the ¹³C NMR spectrum and is attributed to the methylene carbon atom of the CH₂=NH ligand. A ¹H, ¹³C HMQC experiment correlates this signal with that at $\delta = 3.75$ ppm for the =CH₂ protons, in agreement with the proposed assignment. In the temperature range between +20 and -80 °C the ³¹P NMR spectrum appears as an A₂B multiplet indicating that two of the phosphites are magnetically equivalent and different from the third. On the basis of these data a *fac* geometry (Scheme 4) can reasonably be proposed.

A similar *fac* geometry can also be proposed for the methyldiazene derivative **10b** on the basis of the presence of two v(CO) bands in the IR spectrum and only one multiplet for the carbonyl carbon atoms at $\delta = 196.2$ ppm in the ¹³C NMR spectrum, indicating the magnetic equivalence of the two *cis* carbonyl ligands. A singlet at $\delta = 71.7$ ppm is also present in the ¹³C NMR spectrum; it was attributed, with the help of an HMQC experiment, to the methyl carbon atom of the CH₃N=NH ligand. The presence of this ligand is confirmed by the ¹H NMR spectrum, which shows the characteristic diazene signal at $\delta = 15.86$ ppm and the methyl protons as a doublet at $\delta = 4.44$ ppm. The ³¹P NMR spectrum appears as an A₂B multiplet, in agreement with the proposed geometry.

The results on the oxidation of methylhydrazine complexes seem to indicate that the formation of an η^1 -NH= CH_2 ligand is general for the $[Re(CO)_nP_{5-n}]$ [n = 1, 2; P =fragments containing $P(OEt)_3$, $PPh(OEt)_2$] the CH₃NHNH₂ ligand, but appears to be specific for $Pb(OAc)_4$, as attempts to carry out the reaction with other oxidants like MnO₂ or H₂O₂ were unsuccessful. Furthermore, while oxidation of a coordinated hydrazine to the related diazene is a known reaction, the formation of the methyleneimine molecule in the reaction of methylhydrazine with Pb(OAc)₄ is completely new and involves the cleavage of the N-N bond.^[19] Finally, it is worth noting that methyleneimine is a very reactive molecule which has never been isolated since it is unstable above -80 °C in the free state.^[20] It has been detected in outer space.^[21] and has been proposed as a possible precursor^[22] of the simplest α amino acid glycine. As a ligand, it has been found in only one case, through π -coordination to an osmium centre,^[23] and no other report has been found on this molecule, which displays a simple constitution and structure and whose chemical properties are still unknown.

We have also investigated the products of the oxidation of methylhydrazine complexes in order to establish a stoichiometry and/or a possible reaction path. In the reaction mixture we have unambiguously identified, beside the methyldiazene complexes **9b** and **10b** and the methyleneimine complexes **9*b** and **10b***, only acetic acid, dinitrogen and traces of NH₃. Both the NMR spectra and GC analysis of the reaction mixture also revealed the presence of other species, but all were present in very small amounts and were not identified.

The oxidation of methylhydrazine to methyldiazene by $Pb(OAc)_4$ probably proceeds to give acetic acid and lead(II) acetate (Scheme 5) and should involve the loss of two hydrogen atoms and two electrons with cleavage of two N-H bonds to give the final methyldiazene species. The formation of the coordinated methyleneimine, however, seems to be much more complicated and should involve the cleavage

of one N-N and one C-H bond (Scheme 6), with the loss of fragments such as H or NH_2 to give the final species. However, the lack of identified reaction products, as well as of any intermediates, does not allow us to determinate either the stoichiometry or to propose a path for the reaction.



Scheme 5



Scheme 6

In light of the reagent and the η^1 -NH=CH₂ species formed, an N1 to N2 shift in the coordination of the methylhydrazine followed by N–N and C–H bond cleavage with loss of NH₃ and formation of the methyleneimine ligand may be hypothesized. The presence of only traces of NH₃ in the reaction mixture, however, seems to exclude such a mechanism in which the Pb(OAc)₄ does not behave as an oxidant, but only as a catalyst.

Further studies on other metal complexes will, therefore, be required to shed light on the mechanism of this new reaction.

The stabilization of the methyleneimine molecule by coordination to appropriate metal fragments prompted us to attempt to prepare similar η^1 -NH=CH₂ complexes following a different method involving, for example, the reaction of a methylamine (CH₃NH₂) derivative with Pb(OAc)₄. The synthesis of the precursor complex [Re(CH₃NH₂)(CO)₂{P(OEt)₃}₃]BPh₄ (**15**) was achieved by reacting the hydride complex [ReH(CO)₂{P(OEt)₃}₃] first with triflic acid and then with an excess of CH₃NH₂, as shown in Scheme 7.



Scheme 7. $P = P(OEt)_3$

The complex was isolated as its BPh₄ salt and characterised in the usual way (Table 1). The IR spectrum shows two strong v(CO) bands at 2005 and 1894 cm^{-1} due to two carbonyls in a mutually cis position. Two absorptions of medium intensity are also present at 3329 and 3283 cm⁻¹, attributed to v(NH) of the methylamine ligand. The presence of this ligand is confirmed by the ¹H NMR spectrum, which shows a triplet at $\delta = 2.73$ ppm for the CH₃ group and a broad signal at $\delta = 2.65$ ppm for the NH₂ group of the CH₃NH₂ ligand. The ¹³C NMR spectrum further supports the proposed formulation for the complex and indicates that the two CO ligands are magnetically equivalent, showing only one multiplet at $\delta = 194.2$ ppm for the carbonyl carbon atom. In the temperature range between +20 and -80 °C, the ³¹P NMR spectrum appears as an A₂B multiplet indicating that two of the phosphanes are magnetically equivalent and different from the third. On the basis of these data, a *fac* geometry can be proposed for our methylamine complex 15.

The reaction of this complex with Pb(OAc)₄ was studied extensively in an attempt to prepare a methyleneimine complex by selective oxidation of the CH₃NH₂ ligand. Unfortunately, the reaction does not proceed under any conditions [at -40 or at +20 °C, with an equimolar or an excess amount of Pb(OAc)₄; Scheme 8], and the starting amine complex was recovered almost quantitatively. The coordinated methylamine does not react with Pb(OAc)₄ and this reaction, therefore, cannot be used to prepare methyleneimine complexes. Until a new method can be found, only the reaction of coordinated methylhydrazine can give a stable complex containing methyleneimine as a unidentate ligand, even though it is formed as a mixture.

$$[\text{Re}(\text{CH}_3\text{NH}_2)(\text{CO})_2\{\text{P}(\text{OEt})_3\}_3]^+ \xrightarrow{\text{Pb}(\text{OAc})_4}$$

Scheme 8

Reduction Reactions

The hydrazine complexes [Re(NH₂NH₂)(CO)₂P₃]BPh₄ $[P = PPh(OEt)_2 \text{ and } PPh_2OEt]$ are reduced by zinc amalgam in tetrahydrofuran (THF) in the presence of 2,6-lutidine hydrochloride (Lu·HCl) to give NH₃ in about a 20-25% yield (Table 2). The reaction was carried out at room temperature under argon and found to be relatively slow, with the formation of NH_3 in appreciable amounts after 24 h. The conversion is, however, rather low and the addition of free NH₂NH₂ does not increase the conversion into NH₃, thus excluding any catalytic involvement of the rhenium complexes. Also, the related 1,2-diazene complex $[Re(NH=NH)(CO)_{2}{PPh(OEt)_{2}_{3}}BPh_{4}$ is reduced by zinc amalgam to give NH₃ but, as expected, with a lower yield (about 7%) than the hydrazine precursors. Instead, a relatively high conversion (about 27%) was observed with the methylhydrazine complex [Re(CH₃NHNH₂)(CO)₂{PPh- $(OEt)_{2}_{3}$ BPh₄ and this result may be connected with the

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Table 2. Reduction reactions of hydrazine, methylhydrazine and diazene complexes to give ammonia

Compd	Mol	NH3 ^{[a][b]} (mol) ^[a]	Time (h)	Conv. (%)
$[Re(NH_2NH_2)(CO)_2\{PPh(OEt)_2\}_2]BPh_4 (3a)$	$1.82 \cdot 10^{-4}$	$1.81 \cdot 10^{-5}$	23	5
$[Re(NH_2NH_2)(CO)_2\{PPh(OEt)_2\}_3]BPh_4$ (3a)	$9.25 \cdot 10^{-5}$	$3.71 \cdot 10^{-5}$	48	20
$[Re(NH_2NH_2)(CO)_2\{PPh_2OEt\}_3]BPh_4$ (4a)	$8.87 \cdot 10^{-5}$	$4.41 \cdot 10^{-5}$	72	25
$[\text{Re}(\text{CH}_3\text{NHNH}_2)(\text{CO})_2\{\text{PPh}(\text{OEt})_2\}_3]\text{BPh}_4$ (3b)	$1.20 \cdot 10^{-4}$	$3.18 \cdot 10^{-5}$	26	27
$[Re(NH=NH)(CO)_{2}{PPh(OEt)_{2}_{3}}BPh_{4} (11a)$	$7.17 \cdot 10^{-5}$	$0.97 \cdot 10^{-5}$	48	7
$[\text{Re}(\text{NH}_2\text{NH}_2)(\text{CO})_2\{\text{PPh}(\text{OEt})_2\}_3]\text{BPh}_4 (3a)^{[c]}$	$9.33 \cdot 10^{-5}$	$2.26 \cdot 10^{-4}$	96	12
Zn(Hg)/Lut·HCl		$2.6 \cdot 10^{-6}$	24	
NH ₂ NH ₂ /Zn(Hg)/Lut·HCl	$1.02 \cdot 10^{-4}$ [d]	$3.1 \cdot 10^{-6}$	24	1.5

^[a] At 25 °C. ^[b] Mean value from two or three experiments. ^[c] Containing added NH₂NH₂ (9.4·10⁻⁴ mol, ratio 10:1). ^[d] Mol of NH₂NH₂.

observed easy cleavage of the N–N bond of methylhydrazine bonded to $[Re(CO)_2P_3]$ or $[Re(CO)P_4]$ fragments. In the presence of Pb(OAc)₄, in fact, the methyleneimine species $[Re]\eta^1$ -NH=CH₂ is formed, whereas ammonia is obtained with Zn amalgam and Lut·HCl; in both cases cleavage of the N–N bond of the coordinated methylhydrazine takes place.

Although these data must be considered as preliminary results, they indicate that both hydrazine and diazene molecules bonded to the $[Re(CO)_2P_3]$ fragment can be reduced to ammonia by zinc amalgam, and this seems to be an interesting observation in organometallic diazo chemistry.

Conclusions

In this contribution we have shown that a series of hydrazine complexes of rhenium of the type $[Re(RNHNH_2)(CO)_nP_{5-n}]BPh_4$ can easily be prepared from precursor $\text{ReH}(\text{CO})_n P_{5-n}$ hydrides. Among the properties shown by these complexes we can highlight the reaction of the methylhydrazine species with $Pb(OAc)_4$, which gives the unprecedented methyleneimine derivative $[\text{Re}(\eta^1-\text{NH}=\text{CH}_2)(\text{CO})_n\text{P}_{5-n}]\text{BPh}_4$ as well as the methyldiazene derivative [Re(CH₃N=NH)(CO)_nP_{5-n}]BPh₄. Also, 1,2-diazene can be stabilized by the $\text{Re}(\text{CO})_n P_{5-n}$ fragment, allowing stable $[Re(NH=NH)(CO)_nP_{5-n}]BPh_4$ complexes to be obtained through the selective oxidation of the hydrazine precursors with Pb(OAc)₄. Finally, reduction of hydrazine and diazene complexes with zinc amalgam in the presence of Lu·HCl was also tested and found to give NH₃ in low yield.

Experimental Section

General: All synthetic work was carried out under an inert atmosphere (Ar, N₂) using standard Schlenk techniques or a Vacuum Atmosphere dry-box. Once isolated, the complexes were found to be relatively stable in air, but were stored under 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. Re₂(CO)₈ was a Pressure Chem. (USA) product, and used as received. Triethylphosphite P(OEt)₃ (Aldrich) was purified by distillation under nitrogen, while PPh(OEt)₂ and PPh₂OEt were prepared by the method of Rabinowitz and Pellon.^[24] The hydra-

zines CH3NHNH2, C6H5NHNH2, 4-NO2C6H4NHNH2, and (CH₃)₂NNH₂ are Aldrich products and were used as received. High purity (99.99%) Pb(OAc)₄ is an Aldrich product was used as received. Hydrazine (NH₂NH₂) was prepared by decomposition of hydrazine cyanurate (Fluka) following the reported method.^[25] 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, ¹³C) were obtained on Bruker AC200 or Bruker AVANCE 300 spectrometers at temperatures varying between -90 and +30 °C, unless otherwise noted. ¹H spectra are referenced to internal tetramethylsilane, while ³¹P{¹H} chemical shifts are reported with respect to 85% H₃PO₄, with downfield shifts considered positive. The SwaN-MR software package^[26] was used in treating the NMR spectroscopic data. The conductivities of 10^{-3} м solutions of the complexes in CH₃NO₂ at 25 °C were measured with a Radiometer CDM 83 instrument.

Synthesis of Complexes: The hydrides $[ReH(CO)_n P_{5-n}]$ $[n = 1-4; P = P(OEt)_3, PPh(OEt)_2, PPh_2OEt]$ were prepared following the method reported previously.^[13]

[Re(NH₂NH₂)(CO){P(OEt)₃}₄]BPh₄ (1a) and [Re{(CH₃)₂NNH₂} (CO){P(OEt)₃}₄]BPh₄ (1e): An equimolar amount of CF₃SO₃H (0.2 mmol, 18 μ L) was added to a solution of the hydride [ReH(CO){P(OEt)₃}₄] (0.2 mmol, 196 mg) in 8 mL of CH₂Cl₂ cooled to -196 °C, and the reaction mixture warmed to room temperature and stirred for about 1 h. An excess of the appropriate hydrazine (0.6 mmol) was added to the resulting solution which was stirred for a time varying between 3 (1a) and 24 (1e) h and then the solvent was removed under reduced pressure. The oil obtained was triturated with 3 mL of ethanol containing an excess of NaBPh₄ (0.4 mmol, 137 mg). Upon cooling of the resulting solution to -25 °C, a white solid separated out which was filtered off and recrystallised from CH₂Cl₂ (3 mL) and ethanol (3 mL); yield between 80% (1a) and 15% (1e).

1a: $C_{49}H_{84}BN_2O_{13}P_4Re$ (1230.11): calcd. C 47.84, H 6.88, N 2.28; found C 47.58, H 6.94, N 2.20. $\Lambda_M = 55.4 \ \Omega^{-1} \ mol^{-1} \ cm^2$ **1e:** $C_{51}H_{88}BN_2O_{13}P_4Re$ (1258.17): calcd. C 48.69, H 7.05, N 2.23; found C 48.92, H 7.24, N 2.08. $\Lambda_M = 58.6 \ \Omega^{-1} \ mol^{-1} \ cm^2$.

[Re(C₆H₅NHNH₂)(CO){P(OEt)₃}₄]BPh₄ (1c): An equimolar amount of HBF₄·Et₂O (0.2 mmol, 28 μ L) was added to a solution of the hydride [ReH(CO){P(OEt)₃}₄] (0.2 mmol, 176 mg) in 5 mL of CH₂Cl₂ cooled to -196 °C, and the reaction mixture warmed to room temperature and stirred for 1 h. An excess of C₆H₅NHNH₂ (0.6 mmol, 60 μ L) was added to the resulting solution, which was stirred for about 150 min, and then the solvent was removed under reduced pressure. The oil obtained was treated with ethanol (3 mL), and then an excess of NaBPh₄ (0.4 mmol, 137 mg) in 3 mL of ethanol was added. A white solid slowly separated out which was filtered off and recrystallised from CH₂Cl₂ (2 mL) and ethanol (2 mL); yield \geq 40%. C₅₅H₈₈BN₂O₁₃P₄Re (1306.21): calcd. C 50.57, H 6.79, N 2.14; found C 50.49, H 6.87, N 2.10. $\Lambda_{\rm M} = 55.8 \ \Omega^{-1} \ {\rm mol}^{-1} \ {\rm cm}^2$.

[Re(CH₃NHNH₂)(CO)₂{P(OEt)₃}]BPh₄ (2b): An equimolar amount of HBF₄·Et₂O (0.2 mmol, 28 μL) was added to a solution of [ReH(CO)₂{P(OEt)₃}] (0.2 mmol, 143 mg) in 5 mL of CH₂Cl₂ cooled to −196 °C, and the reaction mixture warmed to room temperature and stirred for 1 h. An excess of methylhydrazine (0.3 mmol, 16 μL) was added to the resulting solution which was stirred for 3 h and then the solvents evaporated to dryness. The oil obtained was treated with ethanol (2 mL) containing an excess of NaBPh₄ (0.4 mmol, 137 mg). Upon cooling the resulting solution to −25 °C a white solid slowly separated out which was filtered off and recrystallised from CH₂Cl₂ (2 mL) and ethanol (2 mL); yield ≥65%. C₄₅H₇₁BN₂O₁₁P₃Re (1105.99): calcd. C 48.87, H 6.47, N 2.53; found C 48.80, H 6.55, N 2.48. Λ_M = 50.8 Ω⁻¹ mol⁻¹ cm².

[Re(RNHNH₂)(CO)₂P₃]BPh₄ 3, 4 [R = H a, CH₃ b, 4-NO₂C₆H₄ d; P = PPh(OEt)₂ 3, PPh₂OEt 4]: These complexes were prepared similarly to 1 by reacting the appropriate hydride ReH(CO)₂P₃ (0.2 mmol) first with an equimolar amount of CF₃SO₃H and then with an excess (0.6 mmol) of the appropriate hydrazine. The reaction time was 20 h for 3a, 3b, 4a and 24 h for 3d and 4b; yields between 60 and 80%.

3a: Yield $\geq 60\%$ C₅₆H₆₉BN₂O₈P₃Re (1188.10): calcd. C 56.61, H 5.85, N 2.36; found C 56.43, H 5.89, N 2.28. $\Lambda_M = 58.9 \ \Omega^{-1} \ mol^{-1} \ cm^2$.

3b: Yield \geq 70% C₅₇H₇₁BN₂O₈P₃Re (1202.13): calcd. C 56.95, H 5.95, N 2.33; found C 57.11, H 6.03, N 2.20. $\Lambda_M =$ 58.1 Ω^{-1} mol⁻¹ cm².

3d: Yield $\geq 80\%$ C₆₂H₇₂BN₃O₁₀P₃Re (1309.20): calcd. C 56.88, H 5.54, N 3.21; found C 56.95, H 5.62, N 3.17.. $\Lambda_{\rm M} = 49.3 \ \Omega^{-1} \ {\rm mol}^{-1} \ {\rm cm}^2$.

4a: Yield $\geq 75\%$ C₆₈H₆₉BN₂O₅P₃Re (1284.23): calcd. C 63.60, H 5.42, N 2.18; found C 63.46, H 5.51, N 2.15. $\Lambda_{\rm M} = 49.4 \ \Omega^{-1} \ {\rm mol}^{-1} \ {\rm cm}^2$.

4b: Yield $\geq 65\%$ C₆₉H₇₁BN₂O₅P₃Re (1298.26): calcd. C 63.84, H 5.51, N 2.16; found C 63.66, H 5.59, N 2.20. $\Lambda_{\rm M} = 60.0 \ \Omega^{-1} \ {\rm mol}^{-1} \ {\rm cm}^2$.

[Re(C₆H₅NHNH₂)(CO)₂{PPh(OEt)₂}₃]BPh₄ (3c): This complex was prepared similarly to 2b by treating [ReH(CO)₂{PPh(OEt)₂}₃] (0.2 mmol) first with an equimolar mount of HBF₄·Et₂O and then with an excess of C₆H₅NHNH₂. The reaction time was 150 min; yield approx. 40%. C₆₂H₇₃BN₂O₈P₃Re (1264.20): calcd. C 58.91, H 5.82, N 2.22; found C 59.05, H 5.90, N 2.27. $\Lambda_{\rm M} = 51.3 \ \Omega^{-1} \ {\rm mol}^{-1} \ {\rm cm}^2$.

[Re{(CH₃)₂NNH₂)(CO)₂{PPh(OEt)₂}]BPh₄ (3e): This compound was also prepared similarly to complexes 3 and 4 using CF₃SO₃H as the protonating agent, but in this case a large excess of (CH₃)₂NNH₂ was used; yield approx. 75%. C₅₈H₇₃BN₂O₈P₃Re (1216.15): calcd. C 57.28, H 6.05, N 2.30; found C 57.37, H 6.12, N 2.28. $\Lambda_{\rm M} = 49.5 \ \Omega^{-1} \ {\rm mol}^{-1} \ {\rm cm}^2$.

[Re(RNHNH₂)(CO)₃P₂]BPh₄ 5–7 [R = H a, CH₃ b, 4-NO₂C₆H₄ d; P = P(OEt)₃ 5, PPh(OEt)₂ 6, PPh₂OEt 7]: An equimolar mount of CF₃SO₃H (0.2 mmol, 18 μ L) was added to a solution of the appropriate hydride ReH(CO)₃P₂ (0.2 mmol) in 7 mL of CH₂Cl₂ cooled to –196 °C, and the reaction mixture warmed to room temperature and stirred for 1 h. An excess of the appropriate hydrazine (0.6 mmol) was added and the resulting solution was stirred for 3 h for 5a, 6a, 7a; 8 h for 6d and 15 h for 7b. The solvent was removed under reduced pressure to give a yellow oil, which was triturated with ethanol containing an excess of NaBPh₄ (0.4 mmol, 137 mg). Upon cooling of the resulting solution to -25 °C a white solid separated out, which was filtered off and recrystallised from CH₂Cl₂ and ethanol; yield between 55 and 80%.

5a: Yield \geq 55% C₃₉H₅₄BN₂O₉P₂Re (953.82): calcd. C 49.11, H 5.71, N 2.94; found C 48.94, H 5.80, N 3.02. $\Lambda_{\rm M} =$ 56.6 Ω^{-1} mol⁻¹ cm².

6a: Yield $\geq 65\%$ C₄₈H₅₆BN₂O₇P₂Re (1031.94): calcd. C 55.87, H 5.47, N 2.71; found C 55.74, H 5.55, N 2.79. $\Lambda_M = 54.8 \ \Omega^{-1} \ mol^{-1} \ cm^2$.

6d: Yield $\geq 80\%$ C₅₃H₅₇BN₃O₉P₂Re (1139.01): calcd. C 55.89, H 5.04, N 3.69; found C 55.71, H 5.18, N 3.59. $\Lambda_M = 51.6 \ \Omega^{-1} \ mol^{-1} \ cm^2$.

7a: Yield $\geq 60\%$ C₅₅H₅₄BN₂O₅P₂Re (1082.00): calcd. C 61.05, H 5.03, N 2.59; found C 61.23, H 5.15, N 2.68. $\Lambda_M = 60.2 \ \Omega^{-1} \ mol^{-1} \ cm^2$.

7b: Yield \geq 70% C₅₆H₅₆BN₂O₅P₂Re (1096.03): calcd. C 61.37, H 5.15, N 2.56; found C 61.19, H 5.25, N 2.62. $\Lambda_M =$ 57.4 Ω^{-1} mol⁻¹ cm².

[Re(NH₂NH₂)(CO)₄(PPh₂OEt)]BPh₄ (8a): This complex was prepared similarly to complexes **5a**, **6a** and **7a**; yield approx. 65%. C₄₂H₃₉BN₂O₅PRe (879.76): calcd. C 57.34, H 4.47, N 3.18; found C 57.13, H 4.50, N 3.10. $\Lambda_{\rm M} = 57.0 \ \Omega^{-1} \ {\rm mol}^{-1} \ {\rm cm}^2$.

[Re(NH=NH)(CO){P(OEt)_3}_4]BPh_4 (9a): A solid sample of the hydrazine complex [Re(NH₂NH₂)(CO){P(OEt)_3}_4]BPh_4 (1a; 0.1 mmol, 123 mg) was placed in a three-necked 25-mL round-bot-tomed flask fitted with a solid-addition sidearm containing a slight excess of Pb(OAc)_4 (0.12 mmol, 53 mg). Dichloromethane (10 mL) was added, the solution cooled to -40 °C and the Pb(OAc)_4 added portionwise over 20-30 min to the cold stirring solution. The solution was then warmed to 0 °C, stirred for 15 min and the solvent removed under reduced pressure. The oil obtained was treated at 0 °C with ethanol (2 mL) containing an excess of NaBPh_4 (0.2 mmol, 68 mg) and the white solid separated was filtered off and recrystallised at 0 °C from CH₂Cl₂ (2 mL) and ethanol (2 mL); yield approx. 45%. C₄₉H₈₂BN₂O₁₃P₄Re (1228.10): calcd. C 47.92, H 6.73, N 2.28; found C 48.01, H 6.77, N 2.19. $\Lambda_{\rm M} = 54.8 \ \Omega^{-1} \, {\rm mol}^{-1} \, {\rm cm}^2$.

[Re(C₆H₅N=NH)(CO){P(OEt)₃}₄]BPh₄ (9c): This complex was prepared by oxidation of the corresponding hydrazine derivatives with Pb(OAc)₄ at low temperature (-40 °C) following the method used for the related 1,2-diazene derivative **9a**; yield approx. 55%. C₅₅H₈₆BN₂O₁₃P₄Re (1304.20): calcd. C 50.65, H 6.65, N 2.15; found C 50.43, H 6.70, N 2.09. $\Lambda_{\rm M} = 52.8 \ \Omega^{-1} \ {\rm mol}^{-1} \ {\rm cm}^2$.

 $[Re(CH_3N=NH)(CO)_2{P(OEt)_3}]BPh_4$ (10b) and $[Re(\eta^1-NH=$ (10*b): CH₂)(CO)₂{P(OEt)₃}₃]BPh₄ Α sample of [Re(CH₃NHNH₂)(CO)₂{P(OEt)₃}₃]BPh₄ (**2b**; 200 mg, 0.18 mmol) was placed in a three-necked 25-mL round-bottomed flask fitted with a solid-addition sidearm containing Pb(OAc)₄ (0.18 mmol, 80 mg). Dichloromethane (8 mL) was added, the solution cooled to -40 °C and the Pb(OAc)₄ added portionwise over 10-20 min to the cold stirring solution. The solution was then warmed 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 an excess of NaBPh₄ (0.2 mmol, 68 mg). A white solid slowly separated out, which was filtered and crystallised fractionally to separate the two complexes. A typical separation involved the slow cooling from +25 to -25 °C of a saturated solution of the complexes prepared by adding 10 mL of ethanol to the white solid and enough CH₂Cl₂ to obtain a saturated solution at room temperature. The first crystals obtained were 10b, and the second

a mixture, which was further recrystallised. Upon further cooling, white microcrystals of 10*b were obtained. Pure samples of 10b and 10*b were also obtained by Pasteur separation of the crystals obtained by cooling a saturated solution of the reaction product in ethanol/CH₂Cl₂; yield: 38% for 10b and 25% for 10*b

10b: $C_{45}H_{69}BN_2O_{11}P_3Re$ (1103.98): calcd. C 48.96, H 6.30, N 2.54; found C 49.11, H 6.23, N 2.43. $\Lambda_M = 51.1 \ \Omega^{-1} \ mol^{-1} \ cm^2$.

10*b: $C_{45}H_{68}BNO_{11}P_3Re$ (1088.96): calcd. C 49.63, H 6.29, N 1.29; found C 49.45, H 6.37, N 1.35. $\Lambda_M = 58.9 \ \Omega^{-1} \ mol^{-1} \ cm^2$.

[Re(CH₃N=NH)(CO)₂{PPh(OEt)₂}₃]BPh₄ (11b) and [Re(η^1 -NH= CH₂)(CO)₂{PPh(OEt)₂}₃]BPh₄ (11*b): These complexes were also prepared by oxidation of the methylhydrazine complex [Re(CH₃NHNH₂)(CO)₂{PPh(OEt)₂}₃]BPh₄ (3b) with Pb(OAc)₄ at -40 °C following exactly the same method as used for the synthesis of 10b and 10*b. The reaction afforded a mixture of the two species which, in this case, could not be separated. The IR and NMR spectroscopic data, however, confirm the formation of both the methyldiazene (11b) and methyleneimine (11*b) derivatives.

[Re(NH=NH)(CO)₂P₃]BPh₄ [P = PPh(OEt)₂ 11a, PPh₂OEt 12a]: These complexes were prepared by oxidation of the hydrazine precursors [Re(NH₂NH₂)(CO)₂P₃]BPh₄ (**3a**, **4a**) with Pb(OAc)₄ at -40 °C following the method used for the related compound **9a**; yield between 40 and 55%.

11a: $C_{56}H_{67}BN_2O_8P_3Re$ (1186.09): calcd. C 56.71, H 5.69, N 2.36; found C 56.58, H 5.73, N 2.29. $\Lambda_M = 59.2 \ \Omega^{-1} \ mol^{-1} \ cm^2$.

12a: $C_{68}H_{67}BN_2O_5P_3Re$ (1282.22): calcd. C 63.70, H 5.27, N 2.18; found C 63.56, H 5.33, N 2.08. $\Lambda_M = 57.7 \ \Omega^{-1} \ mol^{-1} \ cm^2$.

[Re(NH=NH)(CO)₃P₂]BPh₄ [P = PPh(OEt)₂ 13a, PPh₂OEt 14a]: These complexes were obtained similarly to the related complexes 9a, 11a and 12a by oxidation of the related hydrazine derivatives [Re(NH₂NH₂)(CO)₃P₂]BPh₄ (6a, 7a) with Pb(OAc)₄ at -40 °C; yield approx. 65%.

13a: C₄₇H₅₂BN₂O₇P₂Re (1015.89): calcd. C 55.57, H 5.16, N 2.76; found C 55.38, H 5.05, N 2.64. Λ_M = 58.1 Ω⁻¹ mol⁻¹ cm² **14a:** C₅₅H₅₂BN₂O₅P₂Re (1079.98): calcd. C 61.17, H 4.85, N 2.59; found C 61.06, H 4.97, N 2.50. Λ_M = 56.5 Ω⁻¹ mol⁻¹ cm².

[Re(4-NO₂C₆H₄N=NH)(CO)₃{PPh(OEt)₂}]BPh₄ (13d): This compound was prepared exactly like the related phenyldiazene compound **9c** by oxidation of the related *p*-nitrophenylhydrazine derivative; yield approx. 55%. C₅₃H₅₅BN₃O₉P₂Re (1136.99): calcd. C 55.99, H 4.88, N 3.70; found C 56.17, H 5.00, N 3.79. $\Lambda_{\rm M}$ = 56.0 Ω^{-1} mol⁻¹ cm².

[Re(CH₃NH₂)(CO)₂{P(OEt)₃}₃]BPh₄ (15): An equimolar amount of HBF₄·Et₂O (0.27 mmol, 39 μL of a 54% solution in Et₂O) was added to a solution of [ReH(CO)₂{P(OEt)₃}₃] (200 mg, 0.27 mmol) in 10 mL of CH₂Cl₂ cooled to -196 °C, and the reaction mixture warmed to room temperature and stirred for 1 h. An excess of CH₃NH₂ (0.88 mmol, 0.44 mL of a 2 M solution in THF) was added and, after 3 h of stirring, the solvent was removed under reduced pressure to give an oil which was treated with ethanol (1 mL). The addition of an excess of NaBPh₄ (0.54 mmol, 0.185 g) in 2 mL of ethanol to the resulting solution caused the separation of a white solid, which was filtered off and recrystallised from CH₂Cl₂ and ethanol; yield approx. 70%. C₄₅H₇₀BNO₁₁P₃Re (1090.98): calcd. C 49.54, H 6.47, N 1.28; found C 49.35, H 6.55, N 1.29. \Lambda_{\rm M} = 58.5 \ \Omega^{-1} \ {\rm mol}^{-1} \ {\rm cm}^2.

Reduction Reactions: The reduction of hydrazine and diazene complexes was carried out in THF at room temperature under argon using an excess of Zn/Hg as reducing agent in the presence of lutidine hydrochloride. A typical experiment involved the addition of a 10-fold excess of Zn (20 mmol), as 2% zinc amalgam, to a solution of the appropriate diazo complex (about 0.1 mmol) in 10 mL of THF. A 16-fold excess of lutidine hydrochloride in 10 mL of THF was then added to the reaction mixture, which was stirred at room temperature under an argon atmosphere for a reaction time varying from 23 to 96 h. An excess of hydrochloric acid (1 mL of 1 M solution in Et₂O) was added to the reaction mixture, which was stirred for 1 h. The solvent was then removed under reduced pressure. The solid obtained was treated with five 5-mL portions of H₂O and, after filtration, ammonia from the solution was quantified by the indophenol method.^[27]

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