Preparation and Reactivity of Hydrazine Complexes of Rhenium: Synthesis of 1,2-Diazene (NH=NH) and Methyleneimine (CH_2=NH) Derivatives

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The hydrazine complexes $[Re(RNHNH_2)(CO)_nP_{5-n}]BPh_4$ [R = H, CH_3, Ar; n = 1–4; P = $P(OEt)_3$, $PPh(OEt)_2$, PPh_2OEt] 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 $[Re(NH_2NH_2)(CO)_nP_{5-n}]BPh_4$ or $[Re(ArNHNH_2)(CO)_nP_{5-n}]BPh_4$ with $Pb(OAc)_4$ at –40 °C proceeds with the selective oxidation of the hydrazine ligand to yield either $[Re(NH=NH)(CO)_nP_{5-n}]BPh_4$ or $[Re(ArN=NH)(CO)_nP_{5-n}]BPh_4$. 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 $[Re(\eta^1\text{-}NH=CH_2)(CO)_nP_{5-n}]BPh_4$. Reduction reactions of both hydrazine and diazene complexes with Zn amalgam were also studied and yielded ammonia in moderate yield (20–25%).

Introduction

Complexes containing partially reduced dinitrogen molecules such as hydrazine ($RNHNH_2$), hydrazido (RNHNH), diazene (RN=NH), and diazenido (RN_2) 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 NH_2NH_2 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 NH_2NH_2 or substituted hydrazine $RNHNH_2$ 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] one on $[ReCp^*Me_3(NH_2NH_2)]CF_3SO_3$ (Cp^* = pentamethylcyclopentadienyl) and $[Re(NH_2NH_2)(CO)_3(PPh_3)_2]CF_3SO_3$, and another on the substituted-hydrazine complex $[ReCl_2(PPh_3)_2\{NNC(O)Ph\}\{H_2NNHC(S)Ph\}]$.[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 (CH_2=NH) derivatives, are reported here. A preliminary paper on part of this work has previously been published.[12]

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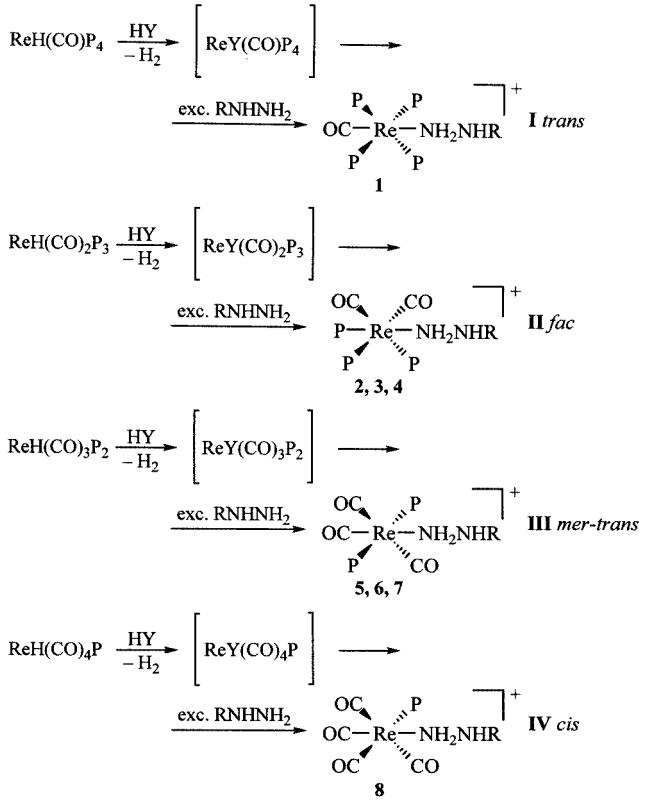
Results and Discussion

Preparation of Hydrazine Complexes

The hydrazine complexes $[Re(RNHNH_2)(CO)_nP_{5-n}]BPh_4$ (**1**–**8**) were prepared by reacting the hydride species $[ReH(CO)_nP_{5-n}]$ first with an equimolar amount of a Brønsted acid (CF_3SO_3H or HBF_4) and then with an excess of hydrazine, as shown in Scheme 1.

Treatment of the hydrides $[ReH(CO)_nP_{5-n}]$ with the Brønsted acid CF_3SO_3H or HBF_4 (HY) gives the dihydrogen-containing cationic complexes $[Re(\eta^2\text{-}H_2)(CO)_nP_{5-n}]^+$,[13] which are thermally unstable and easily lose H_2 yielding either the neutral $ReY(CO)_nP_{5-n}$ species, containing the labile Y^- ligand, or the coordinatively unsaturated $[Re(CO)_nP_{5-n}]^+$ cations. Reaction of these intermediates with an excess of hydrazine gives the final derivatives $[Re(RNHNH_2)(CO)_nP_{5-n}]^+$ (**1**–**8**), which were isolated as their BPh_4^- 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,



Scheme 1. P = $P(OEt)_3$ (**1**, **2**, **5**), $PPh(OEt)_2$ (**3**, **6**), PPh_2OEt (**4**, **7**, **8**); Y = $CF_3SO_3^-$, BF_4^-; R = H (**a**), CH_3 (**b**), C_6H_5 (**c**), 4-$NO_2C_6H_4$ (**d**); $(CH_3)_2NNH_2$ (**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 ν(NH) bands between 3366 and 3202 cm^{-1}. In some complexes the δ(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 NH_2 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 NH_2NH_2 complexes, two NH_2 proton signals are present, thus excluding the formation of a dimeric complex with an NH_2NH_2 bridging ligand.

In the temperature range between +30 and −80 °C the ^{31}P 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 ν(CO) band at 1887−1888 cm^{-1}.

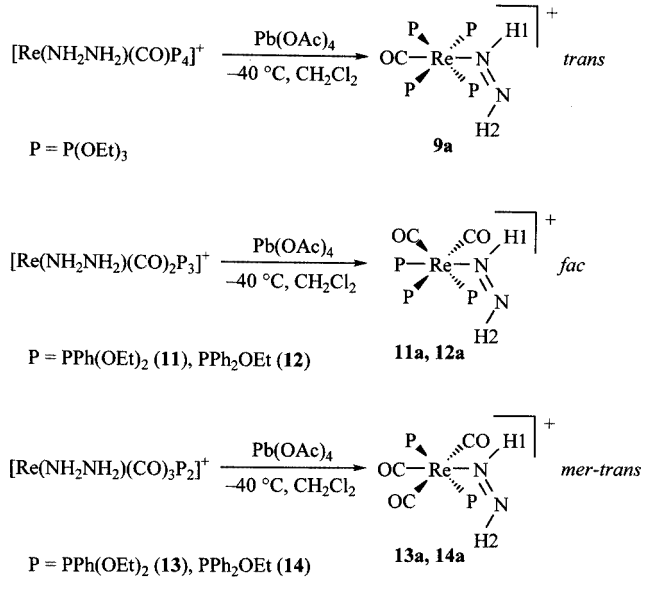
The IR spectra of the dicarbonyl complexes **2**−**4** show two strong bands in the ν(CO) region indicating the mutual *cis* position of the two carbonyl ligands. The ^{13}C NMR spectra also indicate that the two CO groups are magnetically equivalent, showing only one multiplet for **2b** in the carbonyl carbon region at δ = 194.2 ppm. Furthermore, the $^{31}P\{^1H\}$ NMR spectra display either an A_2B- or an AB_2-type 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 ^{31}P 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 ν(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 ν(CO) bands in the carbonyl region of its IR spectrum strongly suggests a *cis* geometry (**IV**) for the tetracarbonyl derivative $[Re(NH_2NH_2)(CO)_4(PPh_2OEt)]^+$ (**8**).

Oxidation Reactions

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).



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 $[Re(CO)_nP_{5-n}]$ (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-

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

Compound	IR[a] $\tilde{\nu}$, cm^{-1}	Assgnt	^1H NMR[b][c] δ (*J*/Hz)	Assgnt	Spin system	$^{31}P\{^1H\}$ NMR[b] [d] δ (*J*/Hz)
$[Re(NH_2NH_2)(CO)\{P(OEt)_3\}_4]BPh_4$ (**1a**)	3366m	ν(NH)	4.45 (br. m)	$ReNH_2$	A_4	118.1 (s)
	3313m		4.07 (m)	CH_2		
	3283w		1.30 (t)	CH_3		
	3218m					
	1887s	ν(CO)				
$[Re(C_6H_5NHNH_2)(CO)\{P(OEt)_3\}_4]BPh_4$ (**1c**)	3341m	ν(NH)	6.22 (br. t)	NH	A_4	117.8 (s)
	3285m		5.16 (br. m)	$ReNH_2$		
	1888s	ν(CO)	4.08 (m)	CH_2		
	1611m	δ(NH_2)	1.31 (t)	CH_3		
$[Re\{(CH_3)_2NNH_2\}(CO)\{P(OEt)_3\}_4]BPh_4$ (**1e**)	3327w	ν(NH)	4.24 (br)	$ReNH_2$	A_4	116.7 (s)
	3283m		4.06 (m)	CH_2		
	1887s	ν(CO)	2.39 (s)	$(CH_3)_2N$		
			1.29 (t)	CH_3		
$[Re(CH_3NHNH_2)(CO)_2\{P(OEt)_3\}_3]BPh_4$ (**2b**)[e]	3325m	ν(NH)	4.44 (br)	$ReNH_2$	A_2B	δ_A = 114.7
	3285m		3.36 (br)	NH		δ_B = 113.3
	3213w		4.13 (m)	CH_2		J_{AB} = 49
	1982s	ν(CO)	2.59 (d, $J_{H,H}$ = 6)	CH_3N		
	1902s		1.38 (t)	CH_3		
			1.34 (t)			
$[Re(NH_2NH_2)(CO)_2\{PPh(OEt)_2\}_3]BPh_4$ (**3a**)	3357w	ν(NH)	3.55 (br. m)	$ReNH_2$	AB_2	δ_A = 139.3
	3298m		3.90 (m)	CH_2		δ_B = 136.4
	3262w		2.71 (br)	NH_2		J_{AB} = 35
	3219w		1.35 (t)	CH_3		
	1999s	ν(CO)	1.33 (t)			
	1905s		1.31 (t)			
$[Re(CH_3NHNH_2)(CO)_2\{PPh(OEt)_2\}_3]BPh_4$ (**3b**)	3335w	ν(NH)	3.27 (br. m)	$ReNH_2$	AB_2	δ_A = 139.4
	3289w		3.93 (m)	CH_2		δ_B = 137.1
	3276m		2.27 (m)	NH		J_{AB} = 35
	1989s	ν(CO)	1.79 (d, $J_{H,H}$ = 6)	CH_3N		
	1905s		1.38 (t)	CH_3		
			1.32 (t)			
$[Re(C_6H_5NHNH_2)(CO)_2\{PPh(OEt)_2\}_3]BPh_4$ (**3c**)	3354w	ν(NH)	4.87 (br. t)	NH	AB_2	δ_A = 139.9
	3268m		4.04 (br. m)	$ReNH_2$		δ_B = 136.6
	1982s	ν(CO)	3.88 (m)	CH_2		J_{AB} = 35
	1905s		1.31 (t)	CH_3		
	1617m	δ(NH_2)	1.30 (t)			
			1.27 (t)			
$[Re(4\text{-}NO_2C_6H_4NHNH_2)(CO)_2\{PPh(OEt)_2\}_3]BPh_4$ (**3d**)	3295m	ν(NH)	6.13 (m)	$ReNH_2$	AB_2	δ_A = 144.4
	3276w		6.10 (m)	NH		δ_B = 144.1
	1986s	ν(CO)	4.10−3.80 (m)	CH_2		J_{AB} = 40
	1894s		1.39 (t)	CH_3		
			1.32 (t)			
			1.25 (t)			
$[Re\{(CH_3)_2NNH_2\}(CO)_2\{PPh(OEt)_2\}_3]BPh_4$ (**3e**)	3299w	ν(NH)	4.05−3.80 (m)	CH_2	AB_2	δ_A = 138.7
	3262w		3.74 (m)	$ReNH_2$		δ_B = 135.1
	1980s	ν(CO)	2.05 (s)	$(CH_3)_2N$		J_{AB} = 38
	1868s		1.37 (t)	CH_3		
			1.35 (t)			
			1.28 (t)			
$[Re(NH_2NH_2)(CO)_2(PPh_2OEt)_3]BPh_4$ (**4a**)	3358m	ν(NH)	3.69 (br. m)	$ReNH_2$	AB_2	δ_A = 113.4
	3290m		3.60−3.30 (m)	CH_2		δ_B = 109.1
	3271w		2.60 (br. t)	NH_2		J_{AB} = 30
	3224w		0.99 (t)	CH_3		
	1970s	ν(CO)	0.63 (t)			
	1872s					
$[Re(CH_3NHNH_2)(CO)_2(PPh_2OEt)_3]BPh_4$ (**4b**)	3332m	ν(NH)	3.80−3.15 (m)	CH_2	AB_2	δ_A = 113.7
	3262m		2.97 (m)	$ReNH_2$		δ_B = 109.4
	1970s	ν(CO)	2.04 (m)	NH		J_{AB} = 30
	1881s		1.61 (d, $J_{H,H}$ = 6)	CH_3N		
			0.97 (t)	CH_3		
			0.62 (t)			

Table 1 *(Continued)*

Compound	IR[a] $\tilde{\nu}$, cm^{-1}	Assgnt	^1H NMR[b][c] δ (*J*/Hz)	Assgnt	Spin system	$^{31}P\{^1H\}$ NMR[b] [d] δ (*J*/Hz)
$[Re(NH_2NH_2)(CO)_3\{P(OEt)_3\}_2]BPh_4$ (**5a**)	3347w	ν(NH)	4.11 (m)	CH_2	A_2	110.9 (s)
	3261m		3.47 (br. m)	$ReNH_2$		111.3 (s)[f]
	3223w		2.83 (br. m)	NH_2		
	2076m	ν(CO)	1.38 (t)	CH_3		
	1971s					
	1947s					
	1612m	$\delta(NH_2)$				
$[Re(NH_2NH_2)(CO)_3\{PPh(OEt)_2\}_2]BPh_4$ (**6a**)	3348m	ν(NH)	3.97 (m)	CH_2	A_2	132.3 (s)
	3287m		3.22 (br. m)	$ReNH_2$		
	3268w		2.57 (br. t)	NH_2		
	3219m		1.38 (t)	CH_3		
	2072w	ν(CO)				
	1968s					
	1944s					
	1624m	$\delta(NH_2)$				
$[Re(4\text{-}NO_2C_6H_4NHNH_2)(CO)_3\{PPh(OEt)_2\}_2]BPh_4$ (**6d**)	3285m	ν(NH)	6.30 (m)	NH	A_2	133.0 (s)
	3270sh		6.24 (m)	$ReNH_2$		
	3230w		4.10 (m)	CH_2		
	2084w	ν(CO)	1.42 (t)	CH_3		
	1984s					
	1938s					
$[Re(NH_2NH_2)(CO)_3(PPh_2OEt)_2]BPh_4$ (**7a**)	3354m	ν(NH)	3.61 (m)	CH_2	A_2	107.1 (s)
	3281w		3.43 (br. m)	$ReNH_2$		
	3267m		2.67 (br. t)	NH_2		
	3217w		1.16 (t)	CH_3		
	2075w	ν(CO)				
	1970s					
	1933s					
$[Re(CH_3NHNH_2)(CO)_3(PPh_2OEt)_2]BPh_4$ (**7b**)	3322w	ν(NH)	3.76 (br. m)	$ReNH_2$	A_2	109.0 (s)
	3263m		3.68 (m)	CH_2		
	2076m	ν(CO)	2.77 (m)	NH		
	1969s		1.97 (d, $J_{H,H}$ = 6)	CH_3N		
	1926s		1.21 (t)	CH_3		
$[Re(NH_2NH_2)(CO)_4(PPh_2OEt)]BPh_4$ (**8a**)	3328w	ν(NH)	3.58 (qnt)	CH_2	A	102.9 (s)
	3282w		2.31 (m)	$ReNH_2$		
	3267w		1.94 (br. t)	NH_2		
	3202m		1.18 (t)	CH_3		
	2113m	ν(CO)				
	2024sh					
	2009s					
	1975s					
	1614m	$\delta(NH_2)$				
$[Re(NH{=}NH)(CO)\{P(OEt)_3\}_4]BPh_4$ (**9a**)	1887s	ν(CO)	A_4XY spin syst.	NH=NH	A_4	123.6 (s)
			δ_X = 16.70	ReNH		123.4 (s)[f]
			δ_Y = 15.84	N=NH		
			J_{XY} = 33.0	CH_2		
			J_{AX} = 1.26	CH_3		
			J_{AY} = 2.86			
			4.06 (m)			
			1.32 (t)			
$[Re(C_6H_5N{=}NH)(CO)\{P(OEt)_3\}_4]BPh_4$ (**9c**)	1899s	ν(CO)	14.39 (qnt, J_{PH} = 4)	NH	A_4	116.8 (s)
			4.08 (m)	CH_2		
			1.27 (t)	CH_3		
$[Re(CH_3N{=}NH)(CO)_2\{P(OEt)_3\}_3]BPh_4$ (**10b**)[g]	1992s	ν(CO)	15.86 (br. s)	ReNH	A_2B[f]	δ_A = 114.1
	1911s		4.10 (m)	CH_2		δ_B = 111.3
			4.44 (d)	$=NCH_3$		J_{AB} = 48.3
			1.36 (t)	CH_3		
$[Re(\eta^1\text{-}NH{=}CH_2)(CO)_2\{P(OEt)_3\}_3]BPh_4$ (**10*b**)[h]	2002s	ν(CO)	13.82 (br. s)	ReNH	A_2B[f]	δ_A = 120.9
	1915s		4.05 (m)	CH_2		δ_B = 118.7
			3.75 (q)	$N=CH_2$		J_{AB} = 47.8
			1.31 (t)	CH_3		

Table 1 *(Continued)*

Compound	IR[a] ν̃, cm^{-1}	Assgnt	^1H NMR[b][c] δ (*J*/Hz)	Assgnt	Spin system	$^{31}P\{^1H\}$ NMR[b] [d] δ (*J*/Hz)
$[Re(NH{=}NH)(CO)_2\{PPh(OEt)_2\}_3]BPh_4$ (**11a**)	1998s 1906s	ν(CO)	A_2B_2XY spin syst. δ_X = 16.07 δ_Y = 15.28 J_{XY} = 33.3 J_{AX} = 2.15 J_{AY} = 3.15 J_{BX} = 1.15 J_{BY} = 1.45 3.92 (m) 1.38 (t) 1.35 (t) 1.33 (t)	NH=NH ReNH N=NH CH_2 CH_3	A_2B	δ_A = 142.8 δ_B = 140.0 J_{AB} = 35
$[Re(CH_3N{=}NH)(CO)_2\{PPh(OEt)_2\}_3]BPh_4$ (**11b**) and $[Re(\eta^1\text{-}NH{=}CH_2)(CO)_2\{PPh(OEt)_2\}_3]BPh_4$ (**11*b**)	1992s 1911s	ν(CO)	15.94 (br. s) 12.08 (br. s) 4.29 (d) 3.90 (m) 3.70 (m) 1.35 (m)	N=NH C=NH $=NCH_3$ CH_2 $N{=}CH_2$ CH_3	AB_2 AB_2	142−140 (m) 135−132 (m)
$[Re(C_6H_5N{=}NH)(CO)_2\{PPh(OEt)_2\}_3]BPh_4$ (**11c**)	1970s 1887s	ν(CO)	12.22 (d) 3.35 (m) 0.84 (t) 0.67 (t)	NH CH_2 CH_3	AB_2	δ_A = 113.2 δ_B = 108.6 J_{AB} = 28
$[Re(NH{=}NH)(CO)_2(PPh_2OEt)_3]BPh_4$ (**12a**)	1972s 1887s	ν(CO)	AB_2XY spin syst. δ_X = 15.31 δ_Y = 14.42 J_{XY} = 33.5 J_{AX} = 2.38 J_{AY} = 3.74 J_{BX} = 1.16 J_{BY} = 1.88 3.45 (m) 0.99 (t) 0.64 (t)	NH=NH ReNH N=NH CH_2 CH_3	AB_2	δ_A = 113.5 δ_B = 109.1 J_{AB} = 30
$[Re(NH{=}NH)(CO)_3\{PPh(OEt)_2\}_2]BPh_4$ (**13a**)	2071w 1969s 1944s	ν(CO)	A_2XY spin syst. δ_X = 13.03 δ_Y = 11.89 J_{XY} = 26.5 J_{AX} = 2.4 J_{AY} = 1.3 3.88 (m) 1.30 (t)	NH=NH ReNH N=NH CH_2 CH_3	A_2	131.0 (s) 131.6 (s)[f]
$[Re(4\text{-}NO_2C_6H_4N{=}NH)(CO)_3\{PPh\{OEt)_2\}_2]BPh_4$ (**13d**)	2076m 1982s 1951s	ν(CO)	13.14 (br) 4.10 (m) 1.43 (t)	NH CH_2 CH_3	A_2	133.5 (s)
$[Re(NH{=}NH)(CO)_3(PPh_2OEt)_2]BPh_4$ (**14a**)	2069w 1967s 1940s	ν(CO)	A_2XY spin syst. δ_X = 13.16 δ_Y = 12.40 J_{XY} = 26.6 J_{AX} = 2.20 J_{AY} = 1.04 3.48 (m) 1.14 (t)	NH=NH ReNH N=NH CH_2 CH_3	A_2	110.8 (s)
$[Re(CH_3NH_2)(CO)_2\{P(OEt)_3\}_3]BPh_4$ (**15**)[i]	3329m 3283m 2005s 1894s	ν(NH) ν(CO)	4.04 (m) 2.73 (t) 2.65 (br) 1.37 (t) 1.32 (t)	CH_2 CH_3N NH_2 CH_3	A_2B	δ_A = 172.1 δ_B = 171.3 J_{AB} = 49

[a] In KBr. [b] In CD_2Cl_2 at 25 °C, unless otherwise noted. [c] Phenyl proton resonances are omitted. [d] Positive shift downfield from 85% H_3PO_4. [e] $^{13}C\{^1H\}$ NMR (**2b**): δ = 194.2 (m) CO, 165−122 (m) Ph, 62.9 (m) CH_2, 44.6 (s) CH_3N, 16.3 (m) CH_3 ppm. [f] At −80 °C. [g] $^{13}C\{^1H\}$ NMR (**10b**): δ = 196.2 (m) CO, 165−120 (m) Ph, 71.7 (s) $CH_3N{=}$, 62.7 (m) CH_2, 16.3 (m) CH_3 ppm. [h] $^{13}C\{^1H\}$ NMR (**10* b**): δ = 194.7 (m) CO, 165−122 (m) Ph, 67.8 (s) $N{=}CH_2$, 62.4 (m) CH_2, 16.1 (m) CH_3 ppm. [i] $^{13}C\{^1H\}$ NMR (**15**): δ = 194.2 (m) CO, 165−122 (m) Ph, 62.8 (m) CH_2, 38.5 (br. s) CH_3N, 16.3 (s) CH_3 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 ^{1}H 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 A_2XY, AB_2XY or A_4XY 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]

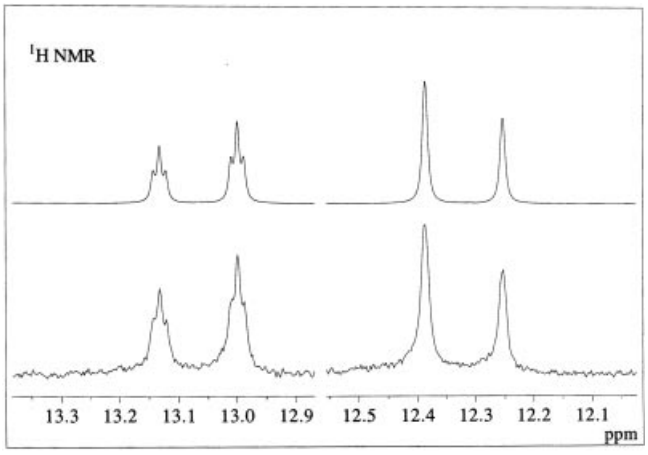
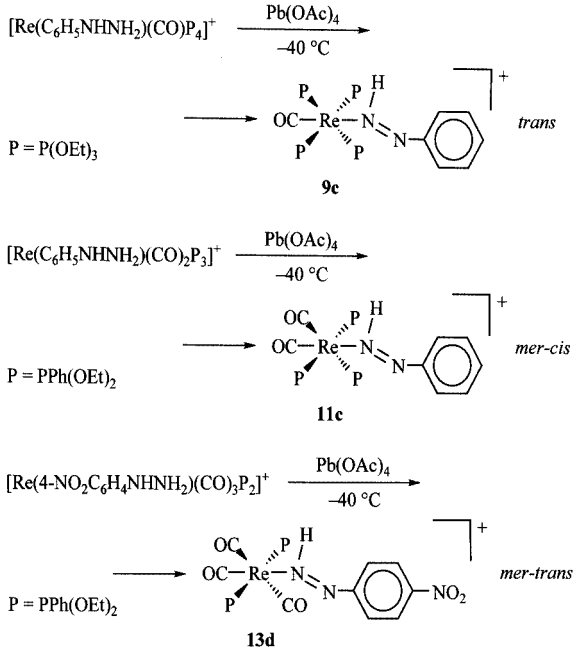


Figure 1. Observed (bottom) and calculated (top) ^{1}H NMR spectrum in the diazene region of $[Re(NH=NH)(CO)_3(PPh_2OEt)_2]BPh_4$ (**14a**), in CD_2Cl_2 at 25 °C; the simulated spectrum was obtained using the parameters reported in Table 1

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 NH_2NH_2 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 ^{31}P NMR spectrum. A *fac* structure is proposed for the dicarbonyl complexes **11a** and **12a**, as their IR spectra show two ν(CO) bands, while an AB_2 multiplet appears in the ^{31}P NMR spectra. Finally, the presence of three ν(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 ^{31}P 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 $[Re(ArNHNH_2)(CO)_nP_{5-n}]BPh_4$ also react with $Pb(OAc)_4$ to give the corresponding aryldiazene complexes $[Re(ArN=NH)(CO)_nP_{5-n}]BPh_4$, which were isolated and characterised (Scheme 3).



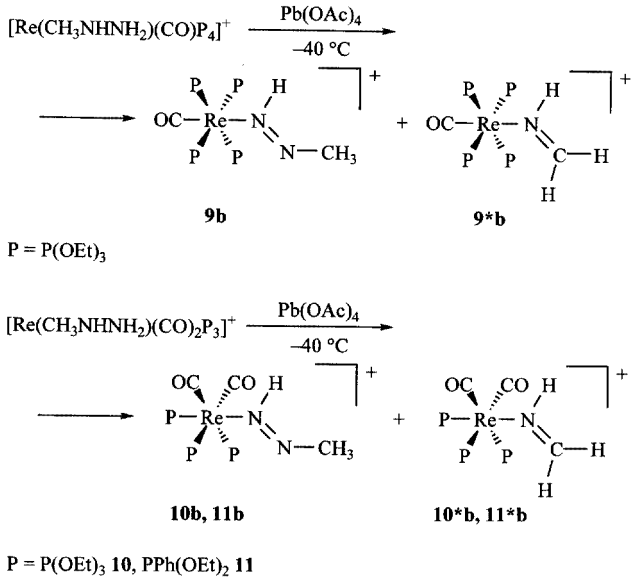
Scheme 3

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 $ReH(CO)P_4$ 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 ^{1}H 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 $[Re(C_6H_5N=NH)(CO)_2(PPh_2OEt)_3]BPh_4$,[18] can be proposed for the carbonyl complex **11c**. The IR spectra, in fact, show two ν(CO) bands, while an AB_2 multiplet is observed in the ^{31}P NMR spectrum.

In the temperature range between +20 and −80 °C the ^{31}P 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 ν(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 $[Re(CH_3N{=}NH)(CO)_nP_{5-n}]^+$ and methyleneimine $[Re(\eta^1\text{-}NH{=}CH_2)(CO)_nP_{5-n}]^+$ derivatives, which were separated and characterised (Scheme 4).



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 δ = 13.82 ppm and the two inequivalent CH_2 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 ^{13}C NMR spectrum shows only one multiplet at δ = 194.7 ppm for the carbonyl carbon atoms. A singlet at δ = 67.8 ppm is also present in the ^{13}C NMR spectrum and is attributed to the methylene carbon atom of the $CH_2{=}NH$ ligand. A ^1H, ^{13}C HMQC experiment correlates this signal with that at δ = 3.75 ppm for the $=CH_2$ protons, in agreement with the proposed assignment. In the temperature range between +20 and −80 °C the ^{31}P NMR spectrum appears as an A_2B 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.

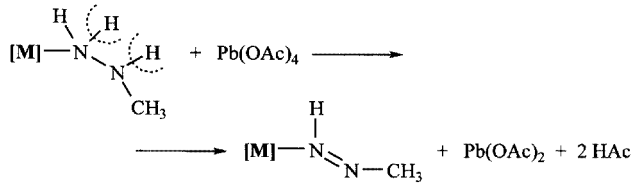
A similar *fac* geometry can also be proposed for the methyldiazene derivative **10b** on the basis of the presence of two ν(CO) bands in the IR spectrum and only one multiplet for the carbonyl carbon atoms at δ = 196.2 ppm in the ^{13}C NMR spectrum, indicating the magnetic equivalence of the two *cis* carbonyl ligands. A singlet at δ = 71.7 ppm is also present in the ^{13}C NMR spectrum; it was attributed, with the help of an HMQC experiment, to the methyl carbon atom of the $CH_3N{=}NH$ ligand. The presence of this ligand is confirmed by the ^1H NMR spectrum, which shows the characteristic diazene signal at δ = 15.86 ppm and the methyl protons as a doublet at δ = 4.44 ppm. The ^{31}P NMR spectrum appears as an A_2B 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 = $P(OEt)_3$, $PPh(OEt)_2$] fragments containing the CH_3NHNH_2 ligand, but appears to be specific for $Pb(OAc)_4$, as attempts to carry out the reaction with other oxidants like MnO_2 or H_2O_2 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.

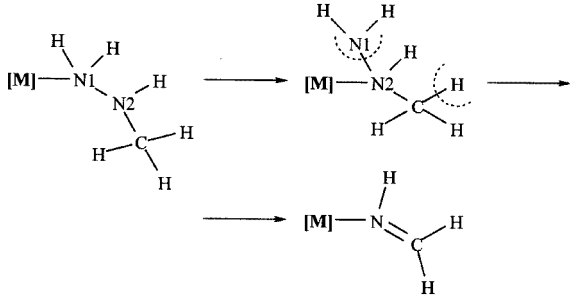
We have also investigated the products of the oxidation of methylhydrazine complexes in order to establish a stoichiometry and/or a possible reaction path. In the reaction mixture we have unambiguously identified, beside the methyldiazene complexes **9b** and **10b** and the methyleneimine complexes **9*b** and **10b***, only acetic acid, dinitrogen and traces of NH_3. 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

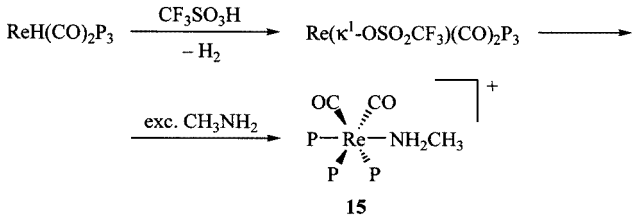


Scheme 6

In light of the reagent and the η^1-NH=CH_2 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 NH_3 and formation of the methyleneimine ligand may be hypothesized. The presence of only traces of NH_3 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.

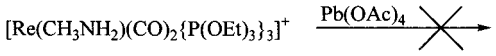
The stabilization of the methyleneimine molecule by coordination to appropriate metal fragments prompted us to attempt to prepare similar η^1-NH=CH_2 complexes following a different method involving, for example, the reaction of a methylamine (CH_3NH_2) derivative with $Pb(OAc)_4$. The synthesis of the precursor complex $[Re(CH_3NH_2)(CO)_2\{P(OEt)_3\}_3]BPh_4$ (**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 CH_3NH_2, as shown in Scheme 7.



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

The complex was isolated as its BPh_4 salt and characterised in the usual way (Table 1). The IR spectrum shows two strong ν(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 ν(NH) of the methylamine ligand. The presence of this ligand is confirmed by the ^1H NMR spectrum, which shows a triplet at δ = 2.73 ppm for the CH_3 group and a broad signal at δ = 2.65 ppm for the NH_2 group of the CH_3NH_2 ligand. The ^{13}C 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 δ = 194.2 ppm for the carbonyl carbon atom. In the temperature range between +20 and −80 °C, the ^{31}P NMR spectrum appears as an A_2B 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 CH_3NH_2 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.



Scheme 8

Reduction Reactions

The hydrazine complexes $[Re(NH_2NH_2)(CO)_2P_3]BPh_4$ [P = $PPh(OEt)_2$ and PPh_2OEt] are reduced by zinc amalgam in tetrahydrofuran (THF) in the presence of 2,6-lutidine hydrochloride (Lu·HCl) to give NH_3 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 NH_2NH_2 does not increase the conversion into NH_3, 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 NH_3 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 $[Re(CH_3NHNH_2)(CO)_2\{PPh(OEt)_2\}_3]BPh_4$ and this result may be connected with the

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

Compd	Mol	NH_3[a][b] (mol)[a]	Time (h)	Conv. (%)
$[Re(NH_2NH_2)(CO)_2\{PPh(OEt)_2\}_3]BPh_4$ (**3a**)	$1.82\cdot10^{-4}$	$1.81\cdot10^{-5}$	23	5
$[Re(NH_2NH_2)(CO)_2\{PPh(OEt)_2\}_3]BPh_4$ (**3a**)	$9.25\cdot10^{-5}$	$3.71\cdot10^{-5}$	48	20
$[Re(NH_2NH_2)(CO)_2\{PPh_2OEt\}_3]BPh_4$ (**4a**)	$8.87\cdot10^{-5}$	$4.41\cdot10^{-5}$	72	25
$[Re(CH_3NHNH_2)(CO)_2\{PPh(OEt)_2\}_3]BPh_4$ (**3b**)	$1.20\cdot10^{-4}$	$3.18\cdot10^{-5}$	26	27
$[Re(NH{=}NH)(CO)_2\{PPh(OEt)_2\}_3]BPh_4$ (**11a**)	$7.17\cdot10^{-5}$	$0.97\cdot10^{-5}$	48	7
$[Re(NH_2NH_2)(CO)_2\{PPh(OEt)_2\}_3]BPh_4$ (**3a**)[c]	$9.33\cdot10^{-5}$	$2.26\cdot10^{-4}$	96	12
Zn(Hg)/Lut·HCl		$2.6\cdot10^{-6}$	24	
NH_2NH_2/Zn(Hg)/Lut·HCl	$1.02\cdot10^{-4}$ [d]	$3.1\cdot10^{-6}$	24	1.5

[a] At 25 °C. [b] Mean value from two or three experiments. [c] Containing added NH_2NH_2 ($9.4\cdot10^{-4}$ mol, ratio 10:1). [d] Mol of NH_2NH_2.

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=CH_2 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 $ReH(CO)_nP_{5-n}$ 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 $[Re(\eta^1\text{-}NH{=}CH_2)(CO)_nP_{5-n}]BPh_4$ as well as the methyldiazene derivative $[Re(CH_3N{=}NH)(CO)_nP_{5-n}]BPh_4$. Also, 1,2-diazene can be stabilized by the $Re(CO)_nP_{5-n}$ 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 NH_3 in low yield.

Experimental Section

General: All synthetic work was carried out under an inert atmosphere (Ar, N_2) 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. $Re_2(CO)_8$ 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 PPh_2OEt were prepared by the method of Rabinowitz and Pellon.[24] The hydrazines CH_3NHNH_2, $C_6H_5NHNH_2$, 4-$NO_2C_6H_4NHNH_2$, and $(CH_3)_2NNH_2$ are Aldrich products and were used as received. High purity (99.99%) $Pb(OAc)_4$ is an Aldrich product was used as received. Hydrazine (NH_2NH_2) 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, ^{31}P, ^{13}C) 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 $^{31}P\{^1H\}$ chemical shifts are reported with respect to 85% H_3PO_4, with downfield shifts considered positive. The SwaN-MR software package[26] was used in treating the NMR spectroscopic data. The conductivities of 10^{-3} M solutions of the complexes in CH_3NO_2 at 25 °C were measured with a Radiometer CDM 83 instrument.

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

$[Re(NH_2NH_2)(CO)\{P(OEt)_3\}_4]BPh_4$ (1a) and $[Re\{(CH_3)_2NNH_2\}(CO)\{P(OEt)_3\}_4]BPh_4$ (1e): An equimolar amount of CF_3SO_3H (0.2 mmol, 18 μL) was added to a solution of the hydride $[ReH(CO)\{P(OEt)_3\}_4]$ (0.2 mmol, 196 mg) in 8 mL of CH_2Cl_2 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 $NaBPh_4$ (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 CH_2Cl_2 (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. Λ_M = 55.4 Ω^{-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. Λ_M = 58.6 Ω^{-1} mol^{-1} cm^2.

$[Re(C_6H_5NHNH_2)(CO)\{P(OEt)_3\}_4]BPh_4$ (1c): An equimolar amount of $HBF_4\cdot Et_2O$ (0.2 mmol, 28 μL) was added to a solution of the hydride $[ReH(CO)\{P(OEt)_3\}_4]$ (0.2 mmol, 176 mg) in 5 mL of CH_2Cl_2 cooled to −196 °C, and the reaction mixture warmed to room temperature and stirred for 1 h. An excess of $C_6H_5NHNH_2$ (0.6 mmol, 60 μL) 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 $NaBPh_4$ (0.4 mmol, 137 mg) in 3 mL of etha-

nol was added. A white solid slowly separated out which was filtered off and recrystallised from CH_2Cl_2 (2 mL) and ethanol (2 mL); yield ≥40%. $C_{55}H_{88}BN_2O_{13}P_4Re$ (1306.21): calcd. C 50.57, H 6.79, N 2.14; found C 50.49, H 6.87, N 2.10. Λ_M = 55.8 Ω^{-1} mol^{-1} cm^2.

[Re(CH$_3$NHNH$_2$)(CO)$_2${P(OEt)$_3$}$_3$]BPh$_4$ (2b): An equimolar amount of $HBF_4{\cdot}Et_2O$ (0.2 mmol, 28 μL) was added to a solution of [ReH(CO)$_2${P(OEt)$_3$}$_3$] (0.2 mmol, 143 mg) in 5 mL of CH_2Cl_2 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 $NaBPh_4$ (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 CH_2Cl_2 (2 mL) and ethanol (2 mL); yield ≥65%. $C_{45}H_{71}BN_2O_{11}P_3Re$ (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} cm^2.

[Re(RNHNH$_2$)(CO)$_2$P$_3$]BPh$_4$ 3, 4 [R = H a, CH$_3$ b, 4-NO$_2$C$_6$H$_4$ d; P = PPh(OEt)$_2$ 3, PPh$_2$OEt 4]: These complexes were prepared similarly to **1** by reacting the appropriate hydride $ReH(CO)_2P_3$ (0.2 mmol) first with an equimolar amount of CF_3SO_3H 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 ≥ 60% $C_{56}H_{69}BN_2O_8P_3Re$ (1188.10): calcd. C 56.61, H 5.85, N 2.36; found C 56.43, H 5.89, N 2.28. Λ_M = 58.9 Ω^{-1} mol^{-1} cm^2.

3b: Yield ≥ 70% $C_{57}H_{71}BN_2O_8P_3Re$ (1202.13): calcd. C 56.95, H 5.95, N 2.33; found C 57.11, H 6.03, N 2.20. Λ_M = 58.1 Ω^{-1} mol^{-1} cm^2.

3d: Yield ≥ 80% $C_{62}H_{72}BN_3O_{10}P_3Re$ (1309.20): calcd. C 56.88, H 5.54, N 3.21; found C 56.95, H 5.62, N 3.17.. Λ_M = 49.3 Ω^{-1} mol^{-1} cm^2.

4a: Yield ≥ 75% $C_{68}H_{69}BN_2O_5P_3Re$ (1284.23): calcd. C 63.60, H 5.42, N 2.18; found C 63.46, H 5.51, N 2.15. Λ_M = 49.4 Ω^{-1} mol^{-1} cm^2.

4b: Yield ≥ 65% $C_{69}H_{71}BN_2O_5P_3Re$ (1298.26): calcd. C 63.84, H 5.51, N 2.16; found C 63.66, H 5.59, N 2.20. Λ_M = 60.0 Ω^{-1} mol^{-1} cm^2.

[Re(C$_6$H$_5$NHNH$_2$)(CO)$_2${PPh(OEt)$_2$}$_3$]BPh$_4$ (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 $HBF_4{\cdot}Et_2O$ and then with an excess of $C_6H_5NHNH_2$. The reaction time was 150 min; yield approx. 40%. $C_{62}H_{73}BN_2O_8P_3Re$ (1264.20): calcd. C 58.91, H 5.82, N 2.22; found C 59.05, H 5.90, N 2.27. Λ_M = 51.3 Ω^{-1} mol^{-1} cm^2.

[Re{(CH$_3$)$_2$NNH$_2$)(CO)$_2${PPh(OEt)$_2$}$_3$]BPh$_4$ (3e): This compound was also prepared similarly to complexes **3** and **4** using CF_3SO_3H as the protonating agent, but in this case a large excess of $(CH_3)_2NNH_2$ was used; yield approx. 75%. $C_{58}H_{73}BN_2O_8P_3Re$ (1216.15): calcd. C 57.28, H 6.05, N 2.30; found C 57.37, H 6.12, N 2.28. Λ_M = 49.5 Ω^{-1} mol^{-1} cm^2.

[Re(RNHNH$_2$)(CO)$_3$P$_2$]BPh$_4$ 5−7 [R = H a, CH$_3$ b, 4-NO$_2$C$_6$H$_4$ d; P = P(OEt)$_3$ 5, PPh(OEt)$_2$ 6, PPh$_2$OEt 7]: An equimolar mount of CF_3SO_3H (0.2 mmol, 18 μL) was added to a solution of the appropriate hydride $ReH(CO)_3P_2$ (0.2 mmol) in 7 mL of CH_2Cl_2 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 $NaBPh_4$ (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 CH_2Cl_2 and ethanol; yield between 55 and 80%.

5a: Yield ≥ 55% $C_{39}H_{54}BN_2O_9P_2Re$ (953.82): calcd. C 49.11, H 5.71, N 2.94; found C 48.94, H 5.80, N 3.02. Λ_M = 56.6 Ω^{-1} mol^{-1} cm^2.

6a: Yield ≥ 65% $C_{48}H_{56}BN_2O_7P_2Re$ (1031.94): calcd. C 55.87, H 5.47, N 2.71; found C 55.74, H 5.55, N 2.79. Λ_M = 54.8 Ω^{-1} mol^{-1} cm^2.

6d: Yield ≥ 80% $C_{53}H_{57}BN_3O_9P_2Re$ (1139.01): calcd. C 55.89, H 5.04, N 3.69; found C 55.71, H 5.18, N 3.59. Λ_M = 51.6 Ω^{-1} mol^{-1} cm^2.

7a: Yield ≥ 60% $C_{55}H_{54}BN_2O_5P_2Re$ (1082.00): calcd. C 61.05, H 5.03, N 2.59; found C 61.23, H 5.15, N 2.68. Λ_M = 60.2 Ω^{-1} mol^{-1} cm^2.

7b: Yield ≥ 70% $C_{56}H_{56}BN_2O_5P_2Re$ (1096.03): calcd. C 61.37, H 5.15, N 2.56; found C 61.19, H 5.25, N 2.62. Λ_M = 57.4 Ω^{-1} mol^{-1} cm^2.

[Re(NH$_2$NH$_2$)(CO)$_4$(PPh$_2$OEt)]BPh$_4$ (8a): This complex was prepared similarly to complexes **5a**, **6a** and **7a**; yield approx. 65%. $C_{42}H_{39}BN_2O_5PRe$ (879.76): calcd. C 57.34, H 4.47, N 3.18; found C 57.13, H 4.50, N 3.10. Λ_M = 57.0 Ω^{-1} mol^{-1} cm^2.

[Re(NH=NH)(CO){P(OEt)$_3$}$_4$]BPh$_4$ (9a): A solid sample of the hydrazine complex [Re(NH$_2$NH$_2$)(CO){P(OEt)$_3$}$_4$]BPh$_4$ (**1a**; 0.1 mmol, 123 mg) was placed in a three-necked 25-mL round-bottomed 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 CH_2Cl_2 (2 mL) and ethanol (2 mL); yield approx. 45%. $C_{49}H_{82}BN_2O_{13}P_4Re$ (1228.10): calcd. C 47.92, H 6.73, N 2.28; found C 48.01, H 6.77, N 2.19. Λ_M = 54.8 Ω^{-1} mol^{-1} cm^2.

[Re(C$_6$H$_5$N=NH)(CO){P(OEt)$_3$}$_4$]BPh$_4$ (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%. $C_{55}H_{86}BN_2O_{13}P_4Re$ (1304.20): calcd. C 50.65, H 6.65, N 2.15; found C 50.43, H 6.70, N 2.09. Λ_M = 52.8 Ω^{-1} mol^{-1} cm^2.

[Re(CH$_3$N=NH)(CO)$_2${P(OEt)$_3$}$_3$]BPh$_4$ (10b) and [Re(η^1-NH=CH$_2$)(CO)$_2${P(OEt)$_3$}$_3$]BPh$_4$ (10*b): A sample of [Re(CH$_3$NHNH$_2$)(CO)$_2${P(OEt)$_3$}$_3$]BPh$_4$ (**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 $NaBPh_4$ (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 CH_2Cl_2 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/CH_2Cl_2; 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. Λ_M = 51.1 Ω^{-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. Λ_M = 58.9 Ω^{-1} mol^{-1} cm^2.

[Re(CH$_3$N=NH)(CO)$_2${PPh(OEt)$_2$}$_3$]BPh$_4$ (11b) and [Re(η^1-NH=CH$_2$)(CO)$_2${PPh(OEt)$_2$}$_3$]BPh$_4$ (11*b): These complexes were also prepared by oxidation of the methylhydrazine complex [Re(CH$_3$NHNH$_2$)(CO)$_2${PPh(OEt)$_2$}$_3$]BPh$_4$ (**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)$_2$P$_3$]BPh$_4$ [P = PPh(OEt)$_2$ 11a, PPh$_2$OEt 12a]: These complexes were prepared by oxidation of the hydrazine precursors [Re(NH$_2$NH$_2$)(CO)$_2$P$_3$]BPh$_4$ (**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. Λ_M = 59.2 Ω^{-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. Λ_M = 57.7 Ω^{-1} mol^{-1} cm^2.

[Re(NH=NH)(CO)$_3$P$_2$]BPh$_4$ [P = PPh(OEt)$_2$ 13a, PPh$_2$OEt 14a]: These complexes were obtained similarly to the related complexes **9a**, **11a** and **12a** by oxidation of the related hydrazine derivatives [Re(NH$_2$NH$_2$)(CO)$_3$P$_2$]BPh$_4$ (**6a**, **7a**) with Pb(OAc)$_4$ at −40 °C; yield approx. 65%.
13a: $C_{47}H_{52}BN_2O_7P_2Re$ (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} cm^2
14a: $C_{55}H_{52}BN_2O_5P_2Re$ (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} cm^2.

[Re(4-NO$_2$C$_6$H$_4$N=NH)(CO)$_3${PPh(OEt)$_2$}$_2$]BPh$_4$ (13d): This compound was prepared exactly like the related phenyldiazene compound **9c** by oxidation of the related *p*-nitrophenylhydrazine derivative; yield approx. 55%. $C_{53}H_{55}BN_3O_9P_2Re$ (1136.99): calcd. C 55.99, H 4.88, N 3.70; found C 56.17, H 5.00, N 3.79. Λ_M = 56.0 Ω^{-1} mol^{-1} cm^2.

[Re(CH$_3$NH$_2$)(CO)$_2${P(OEt)$_3$}$_3$]BPh$_4$ (15): An equimolar amount of HBF$_4$·Et$_2$O (0.27 mmol, 39 μL of a 54% solution in Et$_2$O) was added to a solution of [ReH(CO)$_2${P(OEt)$_3$}$_3$] (200 mg, 0.27 mmol) in 10 mL of CH_2Cl_2 cooled to −196 °C, and the reaction mixture warmed to room temperature and stirred for 1 h. An excess of CH_3NH_2 (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 NaBPh$_4$ (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 CH_2Cl_2 and ethanol; yield approx. 70%. $C_{45}H_{70}BNO_{11}P_3Re$ (1090.98): calcd. C 49.54, H 6.47, N 1.28; found C 49.35, H 6.55, N 1.29. Λ_M = 58.5 Ω^{-1} mol^{-1} 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 Et$_2$O) 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 H_2O and, after filtration, ammonia from the solution was quantified by the indophenol method.[27]

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