New Nitrosylrhenium Hydrides as Precursors of “Diazo” Complexes: Preparation of Hydrazine and Diazene Derivatives

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The reaction of $[ReCl_2(OCH_3)(NO)(PPh_3)_2]$ with phosphane in the presence of $NaBH_4$ gives different dihydride $[ReH_2(NO)\{PPh_2(OEt)\}_3]$ (**1**) and alkoxy-hydride $[ReH(OR^1)(NO)P_3]$ (**2**, **3**) [$R^1 = CH_3, C_2H_5$; $P = PPh(OEt)_2, P(OEt)_3$] derivatives depending on the nature of the phosphane and the solvent used. The protonation reactions of the new hydrides with Brønsted acid were performed and led to thermally unstable $[Re(OR^1)(\eta^2\text{-}H_2)(NO)P_3]^+$ (**2***, **3***) dihydrogen cations. Hydrazine complexes $[ReH(RNHNH_2)(NO)\{PPh_2(OEt)\}_3]BPh_4$ (**4**) (R = H, CH_3,C_6H_5) and $[Re(OR^1)(RNHNH_2)(NO)P_3]BPh_4$ (**5**, **6**) [$R^1 = CH_3, C_2H_5$; R = H, CH_3,C_6H_5; $P = PPh(OEt)_2$] were prepared by allowing the hydrides $[ReH_2(NO)P_3]$ and $[ReH(OR^1)(NO)P_3]$ to react first with triflic acid and then with hydrazine. The complexes were characterized spectroscopically and by the X-ray crystal structure determination of $[Re(OC_2H_5)(NH_2NH_2)(NO)\{PPh(OEt)_2\}_3]BPh_4$ (**5a**). Oxidation of the hydrazine complexes **4**–**6** was studied with $Pb(OAc)_4$ at –30 °C and, depending on the nature of the hydrazine and the stoichiometry of the complexes, led to aryldiazene $[ReH(C_6H_5N{=}NH)(NO)\{PPh_2(OEt)\}_3]BPh_4$ (**7c**), $[Re(OC_2H_5)(C_6H_5N{=}NH)(NO)\{PPh(OEt)_2\}_3]BPh_4$ (**8c**), methyldiazene $[ReH(CH_3N{=}NH)(NO)\{PPh_2(OEt)\}_3]BPh_4$ (**7b**) and a mixture of methyldiazene $[Re(OCH_3)(CH_3N{=}NH)(NO)\{PPh_2(OEt)\}_3]BPh_4$ (**9b**) and methyleneimine $[Re(OCH_3)(\eta^1\text{-}NH{=}CH_2)(NO)\{PPh_2(OEt)\}_3]BPh_4$ (**9*b**) derivatives. Mono- and binuclear aryldiazene complexes $[ReH(ArN{=}NH)(NO)\{PPh_2(OEt)\}_3]BPh_4$ (**10**), $[\{ReH(NO)[PPh_2(OEt)]_3\}_2(\mu\text{-}HN{=}NAr\text{–}ArN{=}NH)](BPh_4)_2$ (**11**), $[Re(OR^1)(ArN{=}NH)(NO)P_3]BPh_4$ (**12**, **14**, **16**) and $[\{Re(OR^1)(NO)P_3\}_2(\mu\text{-}HN{=}NAr\text{–}ArN{=}NH)](BPh_4)_2$ (**13**, **15**) [$R^1 = CH_3, C_2H_5$; $P = PPh(OEt)_2, P(OEt)_3$; Ar = C_6H_5, 4-$CH_3C_6H_4$; Ar-Ar = 4,4′-C_6H_4-C_6H_4] were also prepared by allowing hydrides $[ReH_2(NO)[PPh_2(OEt)]_3]$ and $[ReH(OR^1)(NO)P_3]$ to react with mono- and bis-aryldiazonium cations.

Introduction

The chemistry of transition metal complexes containing partially reduced dinitrogen ligands such as aryldiazenido, ArN_2, diazene, RN=NH, or hydrazine, $RNHNH_2$, has developed considerably in the past 25 years,[1−3] not only because of the similarity of these derivatives with the intermediates in nitrogen fixation, but also for the interesting reactivity modes and structural properties that this class of compounds may exhibit.[1−4]

Among the metal centers used to bind diazo molecules, rhenium plays a prominent role and a number of studies on aryldiazenido $[Re]{-}N_2Ar$ complexes have been reported.[5] Less attention, however, has been devoted to hydrazine and diazene chemistry. A glance through the literature shows, in fact, that hydrazine or substituted hydrazine complexes are rather rare and include, apart from the pioneering work on $[Re(NCO)(CO)_2(NH_2NH_2)P_2]$ (P = tertiary phosphane) complexes,[6] only two papers[7] on $[ReCp^*Me_3(NH_2NH_2)]CF_3SO_3$ (Cp* = pentamethylcyclopentadienyl) and $[Re(NH_2NH_2)(CO)_3(PPh_3)_2]CF_3SO_3$ hydrazine derivatives, and another on the substituted hydrazine complex $[ReCl_2(PPh_3)_2\{NNC(O)Ph\}\{H_2NNHC(S)Ph\}]$.[8]

Only a few studies on aryldiazene complexes have been reported and include, apart from chelate organodiazene complexes[9] such as $[ReCl(HN{=}Npy)(NNpy)(PPhMe_2)_2]^+$, $[ReCl_2(NNC_4H_2N_2CF_3)(HN{=}NC_4H_2N_2CF_3)(PPh_3)]$, and $[ReCl_3(NNC_5H_4NH)(HN{=}NC_5H_4N)]$, only two types[10] of stable aryldiazene complexes — $[Re(\eta^5\text{-}C_5H_5)(CO)_2(HN{=}NR)]$ (R = 4-$CH_3C_6H_4$, 4-$CH_3OC_6H_4$) and $[Re(NH{=}NPh)(CO)_3(PPh_3)]BF_4$.

We are active in this field[3] and have recently reported[11,12] on the synthesis and reactivity of aryldiazene and hydrazine complexes of rhenium stabilized by mixed phosphane-carbonyl ligands of the type $[Re(ArN{=}NH)(CO)_nP_{5-n}]BPh_4$ and $[Re(RNHNH_2)(CO)_nP_{5-n}]BPh_4$ [$P = P(OEt)_3$, $PPh(OEt)_2$ and PPh_2OEt; $n = 1{-}4$] obtained from the hydride $[ReH(CO)_nP_{5-n}]$[13] as precursor. We now extend these studies to include nitrosyl and phosphane as supporting ligands with the aim both to increase the knowledge of the “diazo” chemistry of rhenium and to determine

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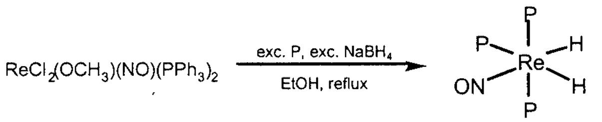
the influence of these ligands on the stability and on the properties of both diazene and hydrazine derivatives. The precursors for these syntheses needed to be mixed-ligand hydride complexes with the phosphanes $P(OEt)_3$, $PPh(OEt)_2$, PPh_2OEt and nitrosyl, whose synthesis has not previously been reported.[14,15] We therefore began to study how to prepare rhenium hydrides containing both phosphane and nitrosyl ligands to use as precursors in diazo chemistry. The results of these studies, which include the preparation of new rhenium hydrides and their use as precursor for the synthesis of new diazene and hydrazine complexes, are reported here.

Results and Discussion

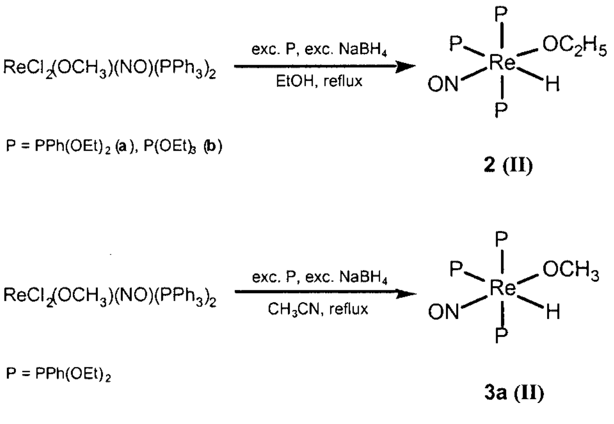
Preparation of Hydride Complexes

The outcome of the reaction of the dichloro complex $[ReCl_2(OCH_3)(NO)(PPh_3)_2]$ with phosphanes and $NaBH_4$ depends on the nature of the phosphorus ligands and the solvent used, as shown in Schemes 1 and 2.



1 (I)

Scheme 1. P = PPh_2OEt



Scheme 2

In the presence of ethoxydiphenylphosphane PPh_2OEt, the reaction of $[ReCl_2(OCH_3)(NO)(PPh_3)_2]$ with $NaBH_4$ in ethanol proceeds to give the dihydride $[ReH_2(NO)P_3]$ (**1**; P = PPh_2OEt) which was isolated as white microcrystals in about 83% yield (Scheme 1). In the presence of $PPh(OEt)_2$ and $P(OEt)_3$ the reaction proceeds to give exclusively the monohydride $[ReH(OC_2H_5)(NO)P_3]$ (**2**) [P = $PPh(OEt)_2$ (**a**), $P(OEt)_3$ (**b**)] containing the ethoxide group OC_2H_5 as a supporting ligand (Scheme 2). The presence of this OC_2H_5 ligand in the final complex **2** as well as the absence of traces of the dihydride $[ReH_2(NO)P_3]$ in the raw reaction product prompted us to use a different solvent for the reaction. The reaction of $[ReCl_2(OCH_3)(NO)(PPh_3)_2]$ with $NaBH_4$ in acetonitrile, in the presence of $PPh(OEt)_2$ and $P(OEt)_3$, however, also only gives the monohydride $[ReH(OCH_3)(NO)P_3]$ (**3**) [P = $PPh(OEt)_2$ (**a**)] which, in this case, contains the OCH_3 group as a ligand. The hydride was isolated as a stable solid with $PPh(OEt)_2$ (**3a**), while with $P(OEt)_3$ only an oily product was obtained (Scheme 2). The reaction of $[ReCl_2(OCH_3)(NO)(PPh_3)_2]$ with $NaBH_4$, in the presence of ethoxydiphenylphosphane PPh_2OEt, in acetonitrile solvent was also performed and gave the dihydride $[ReH_2(NO)P_3]$ (**1**), as in the reaction in ethanol but with a lower yield.

These results seem to indicate that the nature of the phosphane ligand determines the stoichiometry of the hydride obtained from the reaction of $[ReCl_2(OCH_3)(NO)(PPh_3)_2]$ with $NaBH_4$. The dihydride **1** can be obtained under all conditions with PPh_2OEt, which is a bulkier ligand[16] than $PPh(OEt)_2$ and $P(OEt)_3$, but less π-acid, while only the alkoxy-monohydrides $[ReH(OR^1)(NO)P_3]$ (**2**, **3**) were obtained with the ligands $PPh(OEt)_2$ and $P(OEt)_3$. The good π-acceptor ability[16] of these latter phosphanes probably requires the presence of an alkoxy ligand bonded to an $\{ReNO\}^6$-metal fragment[17] for the stabilization of the complexes. The nature of the solvent is important in determining the type of OR^1 group in the monohydride species.

Although a number of mono- and polyhydride complexes of rhenium have been reported,[14,15] few of them contain phosphanes as an ancillary ligand and none, to the best of our knowledge, an alkoxy group. The use of $[ReCl_2(OCH_3)(NO)(PPh_3)_2]$ as a precursor in the reaction with phosphanes and $NaBH_4$ allows the synthesis of new types of nitrosyl-hydride complexes to be achieved.

The hydride complexes **1**−**3** are white diamagnetic solids that are stable in air and in solution in the more common organic solvents, where they behave as non-electrolytes. Analytical and spectroscopic data (Table 1) support the proposed formulation and a geometry in solution was also established. The IR spectrum of $[ReH_2(NO)(PPh_2OEt)_3]$ (**1**) show two ν_{ReH} bands at 1914 and 1841 cm^{-1} suggesting a mutually *cis* position of the two hydride ligands. A strong band at 1637 cm^{-1} attributed to the ν_{NO} of the nitrosyl ligand is also present. In the temperature range between +20 and −80 °C the $^{31}P\{^1H\}$ NMR spectra of the complex appear as an AB_2 multiplet, in agreement with the presence of two magnetically equivalent phosphanes that are different to the third. The ^1H NMR spectrum confirms the presence of the hydride ligand showing, besides the signals of the PPh_2OEt groups, a multiplet between $\delta = -2$ and -4 ppm. Taking into account the AB_2 pattern of the ^{31}P NMR spectra, the hydride multiplet can be simulated using an AB_2XY model (X, Y = H) with the parameters reported in Table 1. This model involves two inequivalent hydride ligands, one hydride with two very similar $J_{P,H}$ values, while the other has different $J_{P,H}$ values (29.5 and 39.8 Hz). On the basis of these data a geometry of type **I** (Scheme 1) can reasonably be proposed for the dihydride complex.

Table 1. IR and NMR spectroscopic data of the rhenium complexes

Compound	IR[a] (cm^{-1})	Assignment	^1H NMR[b] δ (*J*/Hz)	Assignment	Spin system	$^{31}P\{^1H\}$ NMR[b] [c] δ (*J*/Hz)
$[ReH_2(NO)\{PPh_2(OEt)\}_3]$ (**1**)	1914 m	ν(ReH)	3.59 m	CH_2	AB_2	$\delta_A = 118.3$
	1841 m		3.06 qnt			$\delta_B = 117.5$
	1637 s	ν(NO)	1.17 t	CH_3		$J_{A,B} = 14.5$
			1.00 t			
			AB_2XY spin system	ReH		
			$\delta_X = -2.08$			
			$\delta_Y = -3.95$			
			$J_{A,X} = 29.5$			
			$J_{A,Y} = 39.8$			
			$J_{B,X} = 28.6$			
			$J_{B,Y} = 28.7$			
			$J_{X,Y} = 6.20$			
$[ReH(OC_2H_5)(NO)\{PPh(OEt)_2\}_3]$ (**2a**)	1832 m	ν(ReH)	4.21−3.70 m	CH_2 phos	A_2B	$\delta_A = 142.3$
	1635 s	ν(NO)	2.82 q	CH_2		$\delta_B = 135.0$
			1.34 t	CH_3 phos		$J_{A,B} = 19.6$
			1.27 t			
			1.25 t			
			0.018 t	CH_3		
			A_2BX spin system	ReH		
			$\delta_X = 0.26$			
			$J_{A,X} = 26.0$			
			$J_{B,X} = 92.5$			
$[Re(\eta^2\text{-}H_2)(OC_2H_5)(NO)\{PPh(OEt)_2\}_3]BF_4$ (**2*a**)			4.19−3.88 m[d]	CH_2 phos	A_2B[d]	$\delta_A = 147.4$
			2.92 q	CH_2		$\delta_B = 144.9$
			1.38 t	CH_3 phos		$J_{A,B} = 16.6$
			1.34 t			
			0.31 t	CH_3		
$[ReH(OC_2H_5)(NO)\{P(OEt)_3\}_3]$ (**2b**)	1864 m	ν(ReH)	4.03 m[e]	CH_2 phos		126.5 s, br
	1657 s	ν(NO)	3.27 q	CH_2		
			1.23 t	CH_3 phos	A_2B[e]	$\delta_A = 127.8$
			1.20 t			$\delta_B = 126.4$
			0.55 t	CH_3		$J_{A,B} = 27.1$
			A_2BX spin system	ReH		
			$\delta_X = 0.86$			
			$J_{A,X} = 8.0$			
			$J_{B,X} = 36.1$			
$[ReH(OCH_3)(NO)\{PPh(OEt)_2\}_3]$ (**3**)	1848 s	ν(ReH)	3.90 m	CH_2	A_2B	$\delta_A = 141.6$
	1650 s	ν(NO)	2.81 s	CH_3O		$\delta_B = 135.3$
			1.30 t	CH_3		$J_{A,B} = 19.2$
			1.27 t			
			A_2BX spin system	ReH		
			$\delta_X = 0.51$			
			$J_{A,X} = 26$			
			$J_{B,X} = 92$			
$[Re(\eta^2\text{-}H_2)(OCH_3)(NO)\{PPh(OEt)_2\}_3]BF_4$ (**3***)			4.05 m	CH_2	A_2B[d]	$\delta_A = 148.0$
			3.84 m			$\delta_B = 144.7$
			2.56 s	CH_3O		$J_{A,B} = 17.0$
			1.37 t	CH_3		
			1.33 t			
			1.28 t			
$[ReH(NH_2NH_2)(NO)\{PPh_2(OEt)\}_3]BPh_4$ (**4a**)	3341 w	ν(NH)	5.75 br	NH_2	AB_2	$\delta_A = 110.0$
	3304 w		3.74 br	NH_2		$\delta_B = 101.1$
	3215 m		3.45 br	CH_2		$J_{A,B} = 13.0$
	1683 s	ν(NO)	3.10 qnt			
			1.06 t	CH_3		
			0.58 t			
			AB_2X spin system	ReH		
			$\delta_X = -3.48$			
			$J_{A,X} = 30$			
			$J_{B,X} = 20$			
$[ReH(CH_3NHNH_2)(NO)\{PPh_2(OEt)\}_3]BPh_4$ (**4b**)	3609 w	ν(NH)	5.60 br	NH_2	AB_2	$\delta_A = 110.8$
	3289 w		4.13 br	NH		$\delta_B = 100.6$
	1683 s	ν(NO)	3.51 m	CH_2		$J_{A,B} = 15.5$
			3.16 qnt			
			2.47 d	CH_3 hydraz		
			$J_{H,H} = 6$			
			1.12 t	CH_3		
			0.63 t			
			AB_2X spin system	ReH		
			$\delta_X = -3.40$			
			$J_{A,X} = 20$			
			$J_{B,X} = 32$			

Table 1. *(continued)*

Compound	IR[a] (cm^{-1})	Assignment	^1H NMR[b] δ (*J*/Hz)	Assignment	Spin system	$^{31}P\{^1H\}$ NMR[b] [c] δ (*J*/Hz)
$[ReH(C_6H_5NHNH_2)(NO)\{PPh_2(OEt)\}_3]BPh_4$ (**4c**)	3601 m	ν(NH)	6.71 br, m	NH_2	AB_2	$\delta_A = 109.8$
	3289 m		6.53 br, m	NH		$\delta_B = 101.6$
	3217 w		3.41 m	CH_2		$J_{A,B} = 14.5$
	1690 s	ν(NO)	3.14 qnt			
			0.97 t	CH_3		
			0.66 t			
$[Re(OC_2H_5)(NH_2NH_2)(NO)\{PPh(OEt)_2\}_3]BPh_4$ (**5a**)	3356 m	ν(NH)	5.61 br	NH_2	AB_2	$\delta_A = 128.3$
	3329 m		4.00 m	CH_2 phos		$\delta_B = 122.6$
	3270 m		3.58 m			$J_{A,B} = 22.8$
	1690 s	ν(NO)	3.21 q	CH_2		
			1.26 t	CH_3 phos		
			1.22 t			
			1.01 t			
			0.81 t	CH_3		
$[Re(OC_2H_5)(CH_3NHNH_2)(NO)\{PPh(OEt)_2\}_3]CF_3SO_3$ (**5b$_2$**)	3335 m	ν(NH)	5.84 br	NH_2	AB_2	$\delta_A = 128.1$
	3302 m		4.00 m	CH_2 phos		$\delta_B = 122.9$
	3217 w		3.56 m			$J_{A,B} = 24.0$
	1690 s	ν(NO)	3.32 q	CH_2		
			2.81 d	CH_3 hydraz		
			$J_{H,H} = 6$			
			1.34 t	CH_3 phos		
			1.30 t			
			1.12 t			
			0.88 t	CH_3		
$[Re(OC_2H_5)(C_6H_5NHNH_2)(NO)\{PPh(OEt)_2\}_3]BPh_4$ (**5c**)	3375 m	ν(NH)	6.34 m	NH_2	AB_2	$\delta_A = 131.5$
	3302 m		3.86 m	CH_2 phos		$\delta_B = 123.1$
	3237 w		3.69 m			$J_{A,B} = 23.6$
	1696 s	ν(NO)	3.41 q	CH_2		
	1618 m	δ(NH_2)	1.27 t	CH_3 phos		
			1.25 t			
			1.22 t			
			0.88 t	CH_3		
$[Re(OCH_3)(NH_2NH_2)(NO)\{PPh(OEt)_2\}_3]BPh_4$ (**6a**)	3368 w	ν(NH)	5.73 br	NH_2	AB_2	$\delta_A = 127.8$
	3322 m		3.97 m	CH_2		$\delta_B = 122.2$
	3270 m		3.44 m			$J_{A,B} = 23.1$
	1683 s	ν(NO)	3.23 s	CH_3O		
			1.35 t	CH_3		
			1.31 t			
			1.10 t			
$[Re(OCH_3)(CH_3NHNH_2)(NO)\{PPh(OEt)_2\}_3]BPh_4$ (**6b**)	3323 m	ν(NH)	5.75 s br	NH_2	AB_2	$\delta_A = 127.6$
	3296 m		3.96 m	CH_2		$\delta_B = 122.6$
	1670 s	ν(NO)	3.65 m			$J_{A,B} = 23.4$
			3.45 s	CH_3O		
			3.30 m, br	NH		
			2.78 d	CH_3 hydraz		
			$J_{H,H} = 6$			
			1.36 t	CH_3		
			1.33 t			
			1.11 t			
$[Re(OCH_3)(C_6H_5NHNH_2)(NO)\{PPh(OEt)_2\}_3]BPh_4$ (**6c**)	3302 m	ν(NH)	6.31 s, br	NH_2	AB_2	$\delta_A = 131.0$
	3243 w		3.86 m	CH_2		$\delta_B = 122.5$
	1697 s	ν(NO)	3.50 m			$J_{A,B} = 23.9$
	1604 m	δ(NH_2)	3.28 s	CH_3O		
			1.24 t	CH_3		
			1.20 t			
$[ReH(CH_3N{=}NH)(NO)\{PPh_2(OEt)\}_3]BPh_4$ (**7b**)	1696 s	ν(NO)	15.74 d, br	NH	AB_2	$\delta_A = 109.9$
			4.17 s	$CH_3N{=}$		$\delta_B = 101.7$
			3.67 q	H hydride		$J_{A,B} = 16.0$
			$J_{P,H\mathit{cis}} = 6$			
			$J_{P,H\mathit{trans}} = 6$			
			3.29 m	CH_2		
			3.14 m			
			1.02 t	CH_3		
			0.92 t			
$[ReH(C_6H_5N{=}NH)(NO)\{PPh_2(OEt)\}_3]BPh_4$ (**7c**)	1736 s	ν(NO)	17.32 d, br	NH	AB_2	$\delta_A = 117.0$
			3.66 q	H hydride		$\delta_B = 105.7$
			$J_{P,H\mathit{cis}} = 6$			$J_{A,B} = 16.0$
			0.90 t			
$[Re(OC_2H_5)(C_6H_5N{=}NH)(NO)\{PPh(OEt)_2\}_3]BPh_4$ (**8c**)	1729 s	ν(NO)	17.26 d, br	NH	A_2B	$\delta_A = 133.2$
			3.90 m	CH_2		$\delta_B = 132.6$
			1.34 t	CH_3		$J_{A,B} = 18.9$

Table 1. *(continued)*

Compound	IR[a] (cm^{-1})	Assignment	^{1}H NMR[b] δ (*J*/Hz)	Assignment	Spin system	^{31}P{^{1}H} NMR[b] [c] δ (*J*/Hz)
			1.27 t			
			1.23 t			
			1.17 t			
$[Re(OCH_3)(CH_3N{=}NH)(NO)\{PPh(OEt)_2\}_3]BPh_4$ (**9b**)[f]	1723 s	ν(NO)	18.73 d	HN=N	AB$_2$	$\delta_A = 133.1$
+	1690 s		15.68 d	HN=C		$\delta_B = 127.6$
$[Re(OCH_3)(\eta^1\text{-}NH{=}CH_2)(NO)\{PPh(OEt)_2\}_3]BPh_4$ (**9*b**) [f]			4.06 s, br	$CH_2{=}N$		$J_{A,B} = 26.0$
			3.85 m	CH_2		
			3.73 s	$CH_3N{=}$	AB$_2$	$\delta_A = 132.6$
			3.30 s	CH_3O		$\delta_B = 126.7$
			1.31 m	CH_3		$J_{A,B} = 28.0$
$[ReH(C_6H_5N{=}NH)(NO)\{PPh_2(OEt)\}_3]BPh_4$ (**10c**)	1729 s	ν(NO)	13.83 d	NH	AB$_2$	$\delta_A = 112.1$
			13.61 d			$\delta_B = 111.1$
			3.55−3.25 m	CH_2		$J_{A,B} = 24.0$
			AB$_2$X spin system	H hydride		
			$\delta_X = 2.83$		AB$_2$	$\delta_A = 108.5$
			$J_{A,X} = 29.5$			$\delta_B = 93.2$
			$J_{B,X} = 20.0$			$J_{A,B} = 19.5$
			1.03 t	CH_3		
			0.83 t			
			0.78 t			
			0.66 t			
$[ReH(C_6H_5N{=}^{15}NH)(NO)\{PPh_2(OEt)\}_3]BPh_4$ ($\mathbf{10c_1}$)	1723 s	ν(NO)	13.84 dd	NH	AB$_2$Y	$\delta_A = 112.1$
			$J^{15}{}_{NH} = 65$			$\delta_B = 111.1$
			13.62 dd			$J_{A,B} = 24.1$
			$J^{15}{}_{NH} = 64.0$			$J_{A,Y} = 28.8$
			3.55−3.25 m	CH_2		$J_{B,Y} = 2.2$
			AB$_2$X spin system	H hydride		
			$\delta_X = 2.82$		AB$_2$Y	$\delta_A = 108.9$
			$J_{A,X} = 29.0$			$\delta_B = 93.5$
			$J_{B,X} = 19.7$			$J_{A,B} = 19.5$
			1.01 t	CH_3		$J_{A,Y} = 39.3$
			0.85 t			$J_{B,Y} = 1.8$
			0.79 t			
			0.68 t			
$[ReH(4\text{-}CH_3C_6H_5N{=}NH)(NO)\{PPh_2(OEt)\}_3]BPh_4$ (**10d**)	1729 s, br	ν(NO)	13.62 d, br	NH	AB$_2$	$\delta_A = 112.2$
	1705 sh		13.45 d, br			$\delta_B = 111.3$
			3.62−3.20 m	CH_2		$J_{A,B} = 23.0$
			2.40 s	CH_3 *p*-tolyl		
			2.38 s		AB$_2$	$\delta_A = 108.7$
			1.18−0.65 m	CH_3		$\delta_B = 92.1$
						$J_{A,B} = 18.1$
$[\{ReH(NO)[PPh_2(OEt)]_3\}_2(\mu\text{-}4,4'\text{-}HN{=}NHC_6H_4\text{-}C_6H_4N{=}NH)](BPh_4)_2$ (**11a**)	1696 s	ν(NO)	13.45 d, br	NH	AB$_2$	$\delta_A = 112.1$
			3.45 m	CH_2		$\delta_B = 110.6$
			AB$_2$X spin system	H hydride		$J_{A,B} = 24.3$
			$\delta_X = 2.93$			
			$J_{A,X} = 20.4$			
			$J_{B,X} = 29.4$			
			0.84 t	CH_3		
			0.81 t			
$[\{ReH(NO)[PPh_2(OEt)]_3\}_2\text{- }(\mu\text{-}4,4'\text{-}H^{15}N{=}NC_6H_4\text{-}C_6H_4N{=}^{15}NH)](BPh_4)_2$ ($\mathbf{11a_1}$)	1696 s	ν(NO)	13.44 dd	NH	AB$_2$Y	$\delta_A = 112.6$
			$J^{15}{}_{NH} = 64.0$			$\delta_B = 111.3$
			3.45 m	CH_2		$J_{AB} = 24.3$
			AB$_2$X spin system	H hydride		$J_{AY} = 29.1$
			$\delta_X = 2.95$			$J_{BY} = 1.0$
			$J_{A,X} = 20.0$			
			$J_{B,X} = 29.5$			
			0.85 m	CH_3		
$[Re(OC_2H_5)(C_6H_5N{=}NH)(NO)\{PPh(OEt)_2\}_3]BF_4$ (**12c**)	1736 s	ν(NO)	13.67 d, br	NH	AB$_2$	$\delta_A = 127.1$
			3.96 m	CH_2		$\delta_B = 116.7$
			3.78 m			$J_{A,B} = 26.0$
			1.24 t	CH_3		
			1.20 t			
			1.15 t			
$[Re(OC_2H_5)(NO)(C_6H_5N{=}^{15}NH)\{PPh(OEt)_2\}_3]BF_4$ ($\mathbf{12c_1}$)	1734 s	ν(NO)	13.68 dd	NH	AB$_2$Y	$\delta_A = 127.1$
			$J^{15}{}_{NH} = 64.5$			$\delta_B = 116.8$
			3.96 m	CH_2		$J_{A,B} = 26.0$
			3.78 m			$J_{A,Y} = 43.5$
			1.25 t	CH_3		$J_{B,Y} = 4.0$
			1.13 t			
$[Re(OC_2H_5)(4\text{-}CH_3C_6H_4N{=}NH)(NO)\{PPh(OEt)_2\}_3]BF_4$ (**12d**)	1722 s	ν(NO)	13.47 d, br	NH	AB$_2$	$\delta_A = 127.3$
			3.93 m	CH_2		$\delta_B = 116.9$
			3.60 m			$J_{A,B} = 26.0$
			2.43 s	CH_3 *p*-tolyl		

Table 1. *(continued)*

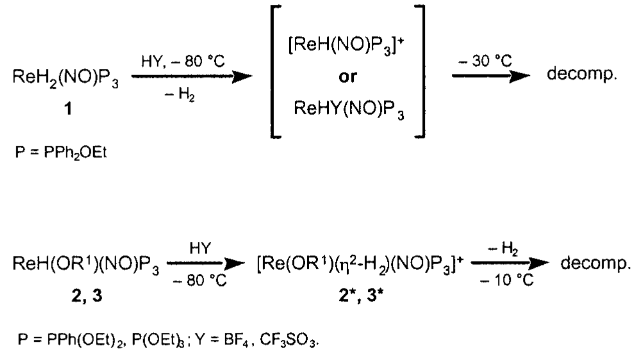
Compound	IR[a] (cm^{-1})	Assignment	^{1}H NMR[b] δ (*J*/Hz)	Assignment	Spin system	^{31}P{^{1}H} NMR[b] [c] δ (*J*/Hz)
			1.25 t	CH_3		
			1.22 t			
			1.13 t			
$[\{Re(OC_2H_5)(NO)[PPh(OEt)_2]_3\}_2(\mu\text{-}4,4'\text{-}HN{=}NC_6H_4{-}C_6H_4N{=}NH)](BF_4)_2$ (**13a**)	1728 s	ν(NO)	13.77 d, br	NH	AB_2	$\delta_A = 127.5$
			13.66 d, br			$\delta_B = 117.3$
			4.00 m	CH_2		$J_{A,B} = 26.1$
			3.68 m			
			1.31 t	CH_3	AB_2	$\delta_A = 127.3$
			1.28 t			$\delta_B = 117.0$
			1.24 t			$J_{A,B} = 26.2$
			1.21 t			
$[\{Re(OC_2H_5)(NO)[PPh(OEt)_2]_3\}_2(\mu\text{-}4,4'\text{-}H^{15}N{=}NC_6H_4{-}C_6H_4N{=}^{15}NH)](BF_4)_2$ (**13a$_1$**)	1729 s	ν(NO)	13.79 dd	NH	AB_2Y	$\delta_A = 127.6$
			$J^{15}{}_{NH} = 64.5$			$\delta_B = 117.3$
			13.65 dd			$J_{A,B} = 26.2$
			$J^{15}{}_{NH} = 64.5$			$J_{A,Y} = 45.0$
			4.00 m	CH_2		$J_{B,Y} = 4.0$
			3.66 m			
			1.30 t	CH_3	AB_2Y	$\delta_A = 127.4$
			1.25 t			$\delta_B = 117.1$
			1.24 t			$J_{A,B} = 26.1$
			1.21 t			$J_{A,Y} = 45.2$
						$J_{B,Y} = 4.0$
$[Re(OCH_3)(4\text{-}CH_3C_6H_4N{=}NH)(NO)\{PPh(OEt)_2\}_3]BPh_4$ (**14d**)	1736 s	ν(NO)	13.67 d, br	NH	AB_2	$\delta_A = 127.3$
			13.52 d, br			$\delta_B = 116.9$
			3.98 m	CH_2		$J_{AB} = 25.6$
			3.70 m			
			2.51 s	CH_3	AB_2	$\delta_A = 126.9$
			2.46 s			$\delta_B = 117.2$
			1.32 t	CH_3 phos		$J_{A,B} = 26.0$
			1.29 t			
			1.27 t			
			1.24 t			
			1.17 t			
$[\{Re(OCH_3)(NO)[PPh(OEt)_2]_3\}_2(\mu\text{-}4,4'\text{-}HN{=}NC_6H_4{-}C_6H_4N{=}NH)](BPh_4)_2$ (**15a**)	1742 s	ν(NO)	13.76 d, br	NH	AB_2	$\delta_A = 126.9$
			13.63 d, br			$\delta_B = 116.7$
			4.00 m	CH_2		$J_{A,B} = 26.3$
			3.72 m			
			1.32 t	CH_3	AB_2	$\delta_A = 127.1$
			1.26 t			$\delta_B = 116.8$
			1.20 t			$J_{AB} = 24.5$
$[\{Re(OCH_3)(NO)[PPh(OEt)_2]_3\}_2(\mu\text{-}4,4'\text{-}H^{15}N{=}NC_6H_4{-}C_6H_4N{=}^{15}NH)](BPh_4)_2$ (**15a$_1$**)	1736 s	ν(NO)	13.76 dd	NH	AB_2Y	$\delta_A = 127.4$
			$J^{15}{}_{NH} = 64.0$			$\delta_B = 117.1$
			13.63 dd			$J_{A,B} = 26.4$
			$J^{15}{}_{NH} = 64.0$			$J_{A,Y} = 45.1$
			4.00 m	CH_2		$J_{B,Y} = 2.9$
			3.75 m			
			1.31 t	CH_3	AB_2Y	$\delta_A = 127.0$
			1.25 t			$\delta_B = 116.7$
			1.20 t			$J_{A,B} = 26.0$
						$J_{A,Y} = 45.0$
						$J_{B,Y} = 3.0$
$[Re(OC_2H_5)(4\text{-}CH_3C_6H_4N{=}NH)(NO)\{P(OEt)_3\}_3]BF_4$ (**16d**)	1722 s	ν(NO)	14.03 d, br	NH	AB_2	$\delta_A = 108.3$
			4.10 m	CH_2		$\delta_B = 96.3$
			2.49 s	CH_3 *p*-tolyl		$J_{A,B} = 36.5$
			1.32 t	CH_3		
			1.25 t			

[a] In KBr pellets. [b] In CD_2Cl_2 at 25 °C unless otherwise noted. [c] Positive shift downfield from 85% H_3PO_4. [d] At −30 °C. [e] At −70 °C. [f] $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 165-121$ (m, Ph), 64.0 (br, s, $CH_2{=}NH$), 63.0 (m, CH_2), 62.5 (s, $CH_3N{=}NH$), 16.6 (m, CH_3) ppm.

The infrared spectra of the alkoxide complexes $[ReH(OR^1)(NO)P_3]$ (**2**, **3**) show only one medium-intensity band at 1864−1832 cm^{-1} attributed to ν_{ReH} of the hydride ligand and one strong absorption at 1657−1635 cm^{-1} due to the ν_{NO} of the nitrosyl group. In the temperature range between +20 and −80 °C the $^{31}P\{^1H\}$ NMR spectra appear, for each of the hydrides, as an A_2B multiplet in agreement with the presence of two magnetically equivalent phosphanes that are different from the third. The ^{1}H NMR spectra confirm the presence of both the hydride and the alkoxide ligand showing, besides the signals of the phosphane protons, a multiplet at $\delta = 0.86-0.26$ ppm attributed to the hydride ligand and the characteristic signals of either an OC_2H_5 or an OCH_3 group. The multiplet of the hydride can be easily simulated using an A_2BX model (X = H) with the parameters reported in Table 1. The values of the two $J_{P,H}$ coupling constants deduced from this simulation are rather different between each other and suggest that the hydride occupies a *trans* position with respect to one phosphane and a *cis* position with respect to the other two. On this basis a geometry of type **II** (Scheme 2) can be reasonably proposed in solution for all the monohydride [ReH(OR^1)(NO)P$_3$] (**2**, **3**) derivatives.

Protonation Reactions

The protonation reaction of the new hydrides **1−3** with Brønsted acids was studied in an NMR tube at temperatures between +20 and −80 °C. The results are summarized in Scheme 3.



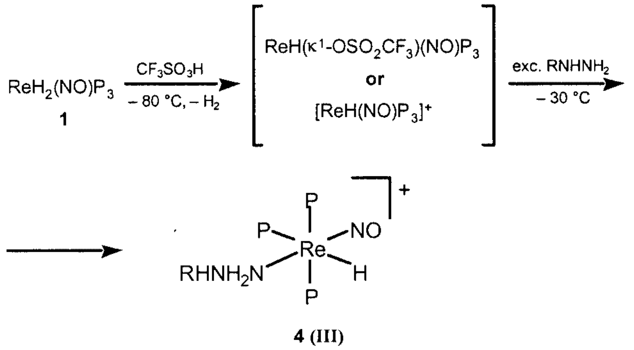
Scheme 3

Addition of an equimolar amount of CF_3SO_3H or $HBF_4{\cdot}Et_2O$ to a solution of the dihydride [ReH$_2$(NO)P$_3$] (**1**) in CD_2Cl_2 at −80 °C causes a change in the ^{1}H and ^{31}P NMR spectra of the solution with evolution of H_2 at this temperature. The formation of H_2 suggests that the protonation forms a dihydrogen [ReH(η^2-H$_2$)(NO)P$_3$]$^+$ intermediate[18] which is unstable to the loss of H_2 even at −80 °C, yielding either a coordinatively unsaturated [ReH(NO)P$_3$]$^+$ cation or a neutral [ReHY(NO)P$_3$] species (Y = BF$_4$ or CF$_3$SO$_3$). The formation of a dichloromethane complex[19] of the type [ReH(CH$_2$Cl$_2$)(NO)P$_3$]$^+$, however, cannot be excluded. These complexes are thermally unstable and decompose above −30 °C, preventing their isolation in the solid state. The loss of H_2 at low temperatures (−70 °C) was also observed in the protonation with CF_3COOH of similar[15c] [ReH$_2$(CO)(NO)L$_2$] [L = P(*i*Pr)$_3$, P(O*i*Pr)$_3$] hydride complexes which yield, in this case, the trifluoroacetate [ReH(OOCCF$_3$)(CO)(NO)L$_2$] derivatives.

The protonation of the alkoxy-hydride [ReH(OR^1)(NO)P$_3$] (**2**, **3**) with CF_3SO_3H or $HBF_4{\cdot}Et_2O$ at −80 °C proceeds with the disappearance of the hydride multiplet in the ^{1}H NMR spectra at δ = 0.86−0.26 ppm and a simultaneous change in chemical shift of all the other signals of both the phosphanes and the alkoxide groups. The ^{31}P{^{1}H} NMR spectra also show the disappearance of the A$_2$B multiplet of the hydride precursor and the appearance of a new A$_2$B pattern (Table 1). These data may be interpreted on the basis of the formation of a dihydrogen[18] complex of the type [Re(OR^1)(η^2-H$_2$)(NO)P$_3$]$^+$ obtained by the attack of the acid on the hydride ligand. In the ^{1}H NMR spectra, however, no signal attributable to the η^2-H$_2$ resonance was clearly observed, and this may make the presence of the dihydrogen complex uncertain. In order to obtain further information, we increased the temperature of the sample and observed no change in the profile of the spectra until −10 °C. At this temperature a signal at δ = 4.58 ppm due[20] to free H_2 appears in the ^{1}H NMR spectra, which increases in intensity with time with the simultaneous lowering of all the other signals. The ^{31}P NMR spectra also show a decrease in the intensity of the A$_2$B multiplet and the formation of decomposition products near −10 °C. The appearance of free H_2 as the temperature is increased seems to confirm the formation of the [Re(OR^1)(η^2-H$_2$)(NO)P$_3$]$^+$ (**2***, **3***) dihydrogen cation whose η^2-H$_2$ signal is probably masked by the intense methyl multiplet of the phosphane ligands. The chemical shift of the η^2-H$_2$ ligand,[18] in fact, generally falls at lower values than those of the related hydride precursor, making the signal, in our case, probably superimposed by the methyl multiplet of the phosphane. The formation of the dihydrogen complexes **2*** and **3*** also indicates that among the three potential sites for protonation in [ReH(OR^1)(NO)P$_3$] complexes — the alkoxy, the hydride or the NO — the hydride is probably the most accessible and affords the corresponding η^2-H$_2$ complex. Unfortunately, this species is thermally unstable and the loss of H_2 already at −10 °C prevents its isolation in the solid state.

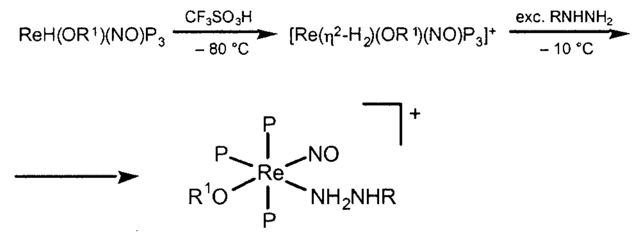
Preparation of Hydrazine Complexes

The unstable complexes formed by the protonation of the hydrides **1−3** are either coordinatively unsaturated or contain one labile ligand (Y or η^2-H$_2$) and should therefore react easily with the appropriate ligands, allowing the synthesis of new complexes. This reaction does occur with hydrazine and a series of new complexes was prepared and characterized (Schemes 4 and 5).



Scheme 4. P = PPh$_2$OEt; R = H (**a**), CH$_3$ (**b**), C$_6$H$_5$ (**c**)

The new hydrazine complexes **4a−c**, **5a−c**, **6a−c** were isolated in good yields as BPh$_4^-$ salts and are white or pale-yellow solids that are stable in air and in solution in polar organic solvents, where they behave as 1:1 electrolytes.[21] Their characterization is supported by analytical and spectroscopic data (IR, NMR, Table 1) and by the X-ray crystal structure determination (Table 2) of the derivative [Re(OC$_2$H$_5$)(NH$_2$NH$_2$)(NO){PPh(OEt)$_2$}$_3$]BPh$_4$ (**5a**).



5, 6 (IV)

Scheme 5. P = $PPh(OEt)_2$; R = C_2H_5 (**5**), CH_3 (**6**); R^1 = H (**a**), CH_3 (**b**), C_6H_5 (**c**)

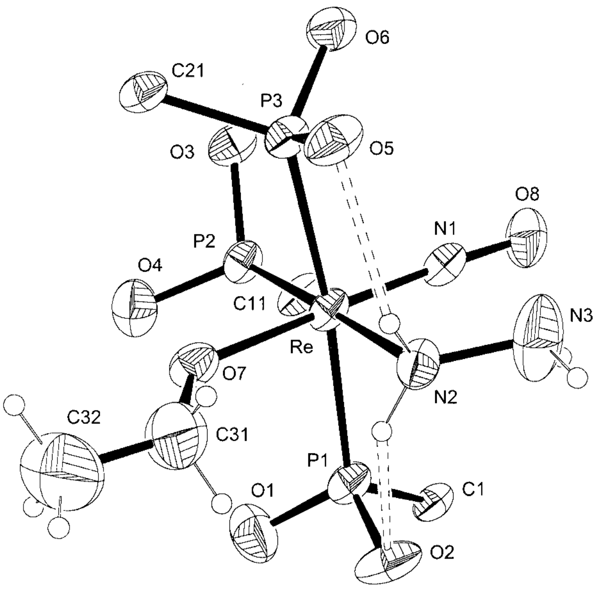


Figure 1. Perspective view and labelling scheme of the cation $[Re(OC_2H_5)(NH_2NH_2)(NO)\{PPh(OEt)_2\}_3]^+$ in the crystal structure of **5a**; thermal ellipsoids at the 30% level; phenyl and ethyl groups of phosphane ligands are omitted for clarity; intramolecular hydrogen bonds are dashed

Table 2. Crystal data and structure refinement for $[Re(OCH_2CH_3)(NH_2NH_2)(NO)\{PPh(OEt)_2\}_3]^+$ (**5a**)

Empirical formula	$C_{56}H_{74}BN_3O_8P_3Re$
Molecular mass	1207.10
Temperature	293(2) K
Wavelength	0.71069 Å
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 9.6930(10) Å b = 18.093(3) Å β = 84.276(3)° c = 33.710(5) Å
Volume	5882.4(14) Å³
Z	4
Density (calculated)	1.363 Mg/m³
Absorption coefficient	2.199 mm⁻¹
F(000)	2480
θ range for data collection	1−26°
Index ranges	$-11 \leq h \leq 11$, $-22 \leq k \leq 22$, $-41 \leq l \leq 39$
Reflections collected	50057
Independent reflections	11598 [R(int) = 0.0969]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	11598/1/576
Goodness-of-fit on F^2	1.182
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0722, $wR2$ = 0.1125
R indices (all data)	$R1$ = 0.1319, $wR2$ = 0.1309

Table 3. Selected bond lengths (Å) and angles (°) for compound **5a**

Re−N(1)	1.763(7)	Re−P(1)	2.418(2)
Re−O(7)	2.016(5)	Re−P(3)	2.443(2)
Re−N(2)	2.256(6)	N(1)−O(8)	1.215(8)
Re−P(2)	2.352(2)	N(2)−N(3)	1.44(1)
N(1)−Re−O(7)	176.2(3)	P(2)−Re−P(1)	91.35(8)
N(1)−Re−N(2)	92.0(3)	N(1)−Re−P(3)	95.0(2)
O(7)−Re−N(2)	84.3(2)	O(7)−Re−P(3)	84.1(2)
N(1)−Re−P(2)	89.7(2)	N(2)−Re−P(3)	86.9(2)
O(7)−Re−P(2)	94.0(2)	P(2)−Re−P(3)	92.96(8)
N(2)−Re−P(2)	178.3(2)	P(1)−Re−P(3)	169.87(8)
N(1)−Re−P(1)	94.2(2)	O(8)−N(1)−Re	174.2(6)
O(7)−Re−P(1)	86.4(2)	N(3)−N(2)−Re	114.1(5)
N(2)−Re−P(1)	88.5(2)		

The molecular structure adopted by the cation in the solid state is shown in Figure 1, along with the labelling scheme. The metal coordination is octahedral, with the nitrosyl ligand placed *trans* to the ethoxy group, while the hydrazine molecule is coordinated *trans* to a phosphane. The ligands NO^+, NH_2NH_2 and $CH_3CH_2O^-$ are in a *mer* arrangement, and two more phosphanes complete the coordination. The relevant bond lengths and angles for the cationic complex are in Table 3.

The hydrazine ligand is in a *Z* configuration relative to the nitrosyl molecule and is almost perfectly coplanar with it [N1−Re−N2−N3 = 2.5(6)°]. The Re−N2 and N2−N3 bonds (Table 3) are typical of coordination by a single σ-bond via the terminal -NH_2 group, with a bonding geometry similar to that observed previously for the coordination of methylhydrazine to rhenium [Re−N = 2.235(3), N−N = 1.445(4) Å].[3d] The nitrosyl bonding mode [Re−N1 = 1.763(7), N1−O8 = 1.215(9) Å] agrees with the average geometry found in the literature {e.g. Re−N = 1.765, N−O = 1.200 Å in $[ReCl_3(NO)(PPh_3)_2]$}.[22] The ethoxy group is also roughly coplanar with the hydrazine, and the α-carbon is oriented towards N2 [C31−O7−Re−N2 = −12.8(8)°].

The Re−P bond *trans* to the hydrazine ligand is significantly shorter [Re−P2 = 2.352(2) Å] than the Re−P bond of the phosphanes *trans* to each other [Re−P3 = 2.443(2) and Re−P1 = 2.418(2) Å, respectively], which are similar to those observed for *trans* $PPh(OEt)_2$ groups bonded to rhenium, ranging between 2.41 and 2.46 Å.[3d] This trend has already been observed in $[ReCl(CH_3N_2)(CH_3NHNH_2)\{PPh(OEt)_2\}_3]BPh_4$,[3d] where the Re−P distance *trans* to the methylhydrazine [2.362(1) Å] is remarkably shorter than those observed for the phosphanes situated *trans* to each other [2.406(1) and 2.412(1) Å]. As also pointed out in the above paper, the Re−P elongation is supported by a system of intramolecular hydrogen bonds between the hydrazine NH groups and the ethoxy substituents carried by the adjacent phosphanes [N2···O5 = 2.871(9) Å, N2−H···O5 = 131.6(4)°, N2···O2 = 2.941(9) Å, N2−H···O2 = 139.2(4)°], and is accompanied by a bending of the phosphanes P1 and P3 towards the hydrazine [P3−Re−N2 = 86.9(2)° and P1−Re−N2 = 88.5(2)°].

The IR spectra of all the hydrazine complexes **4**−**6** show, besides the bands of the phosphane and the BPh_4 anion, a strong absorption at 1697−1670 cm^{-1} due to the ν_{NO} of the nitrosyl ligand and three or four medium-intensity bands between 3609 and 3215 cm^{-1} attributed to the ν_{NH} of the hydrazine ligand. In some compounds the δ_{NH_2} band is also observed at 1630−1620 cm^{-1}.

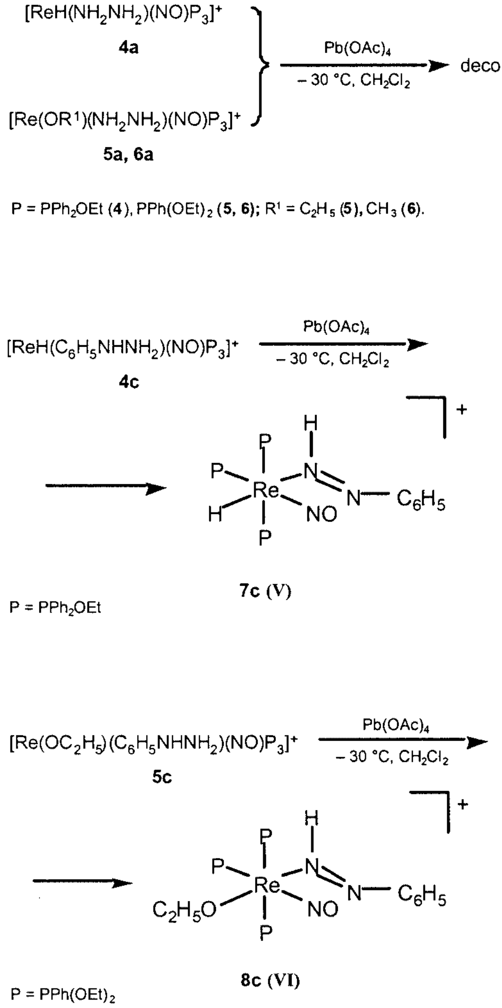
The presence of the hydrazine ligand is confirmed by the ^1H NMR spectrum, which show the characteristic broad multiplets between δ = 6 and 3 ppm (Table 1) of the NH_2 and NH protons of the $RNHNH_2$ ligand. Integration measurements and ^1H COSY experiments confirm the proposed attributions.

In the ^1H NMR spectra of complexes $[ReH(RNHNH_2)(NO)P_3]BPh_4$ (**4**) one multiplet at δ = −3.40 and at −3.48 ppm is also present, attributed to the hydride ligand, and can be simulated by using an AB_2X (X = H) model with the parameters reported in Table 1. The two $J_{P,H}$ coupling constants have different values (20 and 30 Hz) which suggests that the hydride should be *trans* to one phosphane and *cis* to the other two. In the temperature range between +20 and −80 °C the $^{31}P\{^1H\}$ NMR spectra appear as an AB_2 multiplet, in agreement with the presence of two magnetically equivalent phosphanes that are different from the third. On this basis a geometry of type **III** can be reasonably proposed for the hydride-hydrazine complexes **4**.

The ^1H NMR spectra of the alkoxy derivative **5** and **6** show, besides the signals of the phosphanes and of the hydrazine, the resonance of the OR^1 ligands, which appear as a triplet and a quadruplet for OC_2H_5 and as a singlet for OCH_3. The $^{31}P\{^1H\}$ NMR spectra also indicate that for these complexes an AB_2 multiplet is present. These data, however, do not allow us to unambiguously assign a geometry for the alkoxy complexes although, by analogy with the solid state, a complex of type **IV** can reasonably be proposed. The preparation of complexes **4**−**6** highlights the fact that both hydride $[ReH(NO)P_3]$ and alkoxy $[Re(OR^1)(NO)P_3]$ nitrosyl fragments can bind the hydrazine molecule to give stable derivatives that can be isolated.

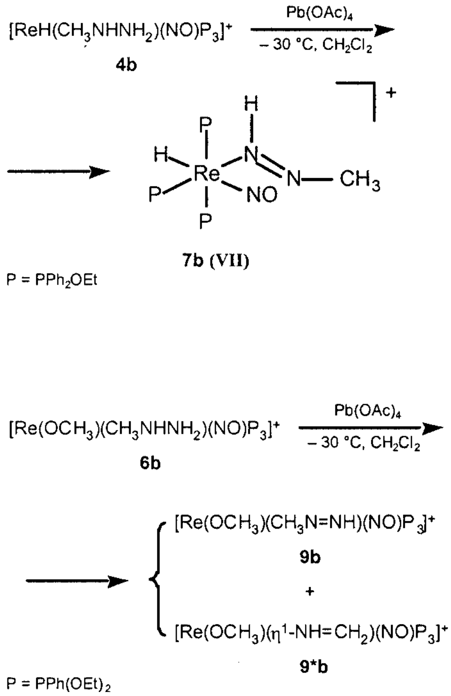
Oxidation of Hydrazine Complexes

The oxidation reaction of the hydrazine complexes **4**−**6** with $Pb(OAc)_4$ was studied extensively and the results are summarized in Schemes 6 and 7.



Scheme 6

The outcome of the oxidation reactions depends on the nature of both the metal fragment and the hydrazine used. The NH_2NH_2 complexes **4a**, **5a** and **6a** do not give any diazene complexes in the reaction with $Pb(OAc)_4$ and only decomposition products were obtained. The reaction proceeds with a color change of the reaction mixture but probably leads to unstable species. Instead, the phenylhydrazine is selectively oxidized in both the hydride (**4c**) and the ethoxy (**5c**) derivatives to the corresponding phenyldiazene compounds (**7c** and **8c**, respectively), which were isolated in the solid state and characterized. Surprisingly, the reaction of methylhydrazine gives the methyldiazene complex **7b** in the oxidation of the hydride $[ReH(CH_3NHNH_2)(NO)P_3]^+$ (**4b**), while a mixture of the methyldiazene complex $[Re(OCH_3)(CH_3N{=}NH)(NO)P_3]^+$ (**9b**) and the methyleneimine[11] complex $[Re(OCH_3)(\eta^1\text{-}NH{=}CH_2)(NO)P_3]^+$ (**9*b**) was obtained in the reaction with the methoxy-methylhydrazine derivative $[Re(OCH_3)(CH_3NHNH_2)(NO)P_3]^+$ (**6b**). The hydride-methyldiazene complex **7b** was isolated in the solid state and in a pure form, whereas the two compounds **9b** and **9*b** were obtained as a mixture and were not sepa-



Scheme 7

rated. The spectroscopic data, however, strongly support their formulation (see below).

The different behavior of the hydrazine complexes towards oxidation may be explained by taking into account that, whereas coordinated aryldiazenes[1–3] are generally stable and can be easily isolated, 1,2-diazene complexes [M]−NH=NH are rare and few metal fragments are able to stabilize the unstable NH=NH species.[23] Our [ReH(NO)P$_3$] and [Re(OR^1)(NO)P$_3$] fragments are not among these, although they are able to stabilize the methyldiazene CH$_3$N=NH giving **7b** and **9b**. Furthermore, the oxidation of methylhydrazine bonded to the [Re(OCH$_3$)(NO)P$_3$] fragment with Pb(OAc)$_4$ shows a second example of a new reaction[11] of coordinated methylhydrazine, which can give both methyldiazene and methyleneimine η^1-NH=CH$_2$ species. This reaction depends on the nature of the metal fragment, and only in the case of the alkoxy precursor [Re(OCH$_3$)(CH$_3$N=NH)(NO)P$_3$]$^+$ were both **9b** and **9*b** obtained; with the hydride derivative [ReH(CH$_3$N=NH)(NO)P$_3$]$^+$ only the formation of methyldiazene **7b** was observed. These results show that the substitution of only one ligand — H$^-$ with OCH$_3$$^-$ — in the rhenium nitrosyls changes the nature of the reaction course in the oxidation of the methylhydrazine ligand with Pb(OAc)$_4$. Furthermore, a comparison with related carbonyl complexes[11] highlights the fact that both the nitrosyl [Re(OCH$_3$)(CH$_3$NHNH$_2$)(NO)P$_3$]$^+$ and the carbonyl [Re(CH$_3$NHNH$_2$)(CO)$_2$P$_3$]$^+$ methylhydrazine derivatives react with Pb(OAc)$_4$ to give a mixture of η^1-NH=CH$_2$ and CH$_3$N=NH complexes. A different behavior is shown by the hydride-nitrosyl [ReH(CH$_3$NHNH$_2$)(NO)P$_3$]$^+$ cation, which only gives the methyldiazene **7b**. Studies were also carried out to identify the product of the reaction with Pb(OAc)$_4$ in order to obtain information on a possible reaction path giving **9*b**. Unfortunately, apart from acetic acid and traces of NH$_3$, no other nitrogen-containing products were unambiguously identified in the reaction mixture and therefore no proposal can be made about the mechanism of the reaction, which involves the cleavage of the N−N bond of methylhydrazine to give an η^1-NH=CH$_2$ species.

Good analytical data were obtained for all the diazene complexes **7−9** which are pale-yellow solids stable in air and in solutions of polar organic solvents, where they behave as 1:1 electrolytes.[21] The IR and NMR spectra (Table 1) support the proposed formulation and a geometry in solution was also established. The presence of the diazene ligand is confirmed by the ^{1}H NMR spectra, which show the characteristic, slightly broad NH signal at δ = 16−18 ppm.

In the ^{1}H NMR spectra of the complexes [ReH(RN=NH)(NO)P$_3$]BPh$_4$ (**7b**, **7c**) a quadruplet at δ = 3.68−3.67 ppm also appears, which can be attributed to the hydride ligand coupled to the phosphorus nuclei of the phosphanes. This attribution was confirmed by ^{1}H, ^{31}P NMR spectra and HMQC experiments. The two $J_{P,H}$ coupling constants have the same value of 6 Hz, suggesting that the hydride should be in the same position relative to all the phosphane ligands. It should also be noted that the chemical shifts of the hydride fall at very high frequencies as compared to known rhenium hydrides,[14,15] and this feature may be due to the combined influences of both the diazene and the NO ligands. In the temperature range between +20 and −80 °C the ^{31}P{^{1}H} NMR spectra of **7b** and **7c** appear as AB$_2$ multiplets, in agreement with the presence of two magnetically equivalent phosphanes that are different from the third. These data do not allow us to unambiguously assign a geometry to the complexes. However, further information comes from a comparison of the IR spectra of the diazene compounds **7b** and **7c** with those of the precursors **4b** and **4c**, which shows that the ν_{NO} values are similar for **4b** and **7b** (1683 and 1696 cm^{-1}, respectively) whereas a higher value is found in the phenyldiazene complex [ReH(C$_6$H$_5$N=NH)(NO)P$_3$]BPh$_4$ (**7c**) (ν_{NO} = 1736 cm^{-1}) than in the precursor **4c** (1690 cm^{-1}). This high ν_{NO} value for **7c** seems to indicate that the NO ligand is *trans* to a good π-acceptor ligand such as the phosphane and therefore, taking into account the ^{1}H and the ^{31}P NMR spectra, a geometry such as **V** can be proposed. In the methyldiazene complex **7b** the NO group should be *trans* to a σ-donor ligand as in a type-**VII** geometry.

The IR spectrum of the alkoxy complex [Re(OC$_2$H$_5$)(C$_6$H$_5$N=NH)(NO)P$_3$]BPh$_4$ (**8c**) shows the ν_{NO} at higher value (1729 cm^{-1}) than its hydrazine precursor **5c** (1685 cm^{-1}) suggesting, also in this case, the mutually *trans* position of NO and one phosphane ligand. Taking into account that the ^{31}P NMR spectra is an A$_2$B multiplet, a type-**VI** geometry may be proposed.

The IR spectrum of the oxidation product of [Re(OCH$_3$)(CH$_3$NHNH$_2$)(NO)P$_3$]BPh$_4$ (**6b**) shows two ν_{NO} bands at 1723 and 1650 cm^{-1} and two AB$_2$ multiplets in the ^{31}P{^{1}H} NMR spectra, suggesting the presence of two compounds formulated as a mixture of $[\mathrm{Re(OCH_3)(CH_3N{=}NH)(NO)P_3}]^+$ (**9b**) and $[\mathrm{Re(OCH_3)(\eta^1\text{-}NH{=}CH_2)(NO)P_3}]^+$ (**9*b**). The ^{1}H NMR spectra show, besides the phosphane and $\mathrm{BPh_4}$ signals, two slightly broad signals at $\delta = 18.69$ and 15.73 ppm attributed to two NH groups. A singlet at $\delta = 3.73$ ppm and a slightly broad signal at $\delta = 4.05$ ppm are also present. The singlet at $\delta = 3.73$ ppm is correlated to the broad signal at $\delta = 18.69$ ppm (^{1}H COSY experiment) and can be attributed to the $\mathrm{CH_3N{=}NH}$ group. An APT experiment confirmed this attribution. The slightly broad signal at $\delta = 4.05$ ppm is correlated to the proton resonance at $\delta = 15.73$ ppm (^{1}H COSY) and an APT experiment indicated a $\mathrm{CH_2}$ group attributable to the $\mathrm{CH_2{=}NH}$ ligand. The $^{13}\mathrm{C}\{^1\mathrm{H}\}$ spectra show, besides the signals of the phosphane and $\mathrm{BPh_4}$ anion, two singlets at $\delta = 62.5$ and 64.0 ppm, and HMBC and HMQC experiments allow the attribution of these carbon resonances to the $\mathrm{CH_3N{=}NH}$ and $\mathrm{CH_2{=}NH}$ groups, respectively, and are thus in agreement with the proposed formulation for the mixture of the two compounds **9b** and **9*b**. These attributions, indeed, are strongly supported by a comparison with the data we previously reported on methyleneimine $[\mathrm{Re(\eta^1\text{-}NH{=}CH_2)(CO)P_4}]\mathrm{BPh_4}$ and methyldiazene $[\mathrm{Re(CH_3N{=}NH)(CO)P_4}]\mathrm{BPh_4}$ complexes.[11] In conclusion, although the two compounds **9b** and **9*b** cannot be separated, the strong similarity of their spectroscopic data with those of known complexes[11] supports their proposed formulation.

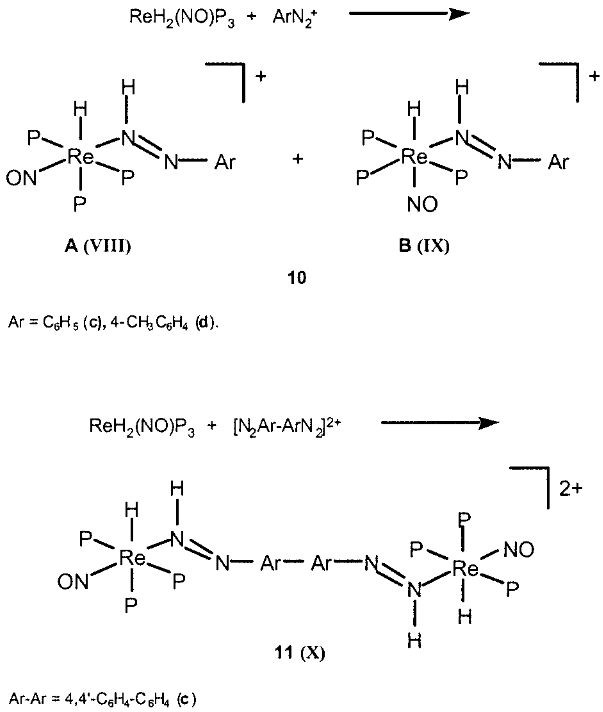
Reactions with Aryldiazonium Cations

The synthesis of the aryldiazene complexes **7c** and **8c** prompted us to test whether analogous compounds can be prepared by the insertion reaction of aryldiazonium cations into the Re−H bond of our hydrides **1−3**. The reaction was studied extensively and the results can be summarized in Schemes 8 and 9.

Aryldiazonium cations react quickly with an equimolar amount of dihydride $[\mathrm{ReH_2(NO)P_3}]$ to give the aryldiazene complexes **10**, which were isolated and characterized as $\mathrm{BPh_4}$ salts. The reaction was also studied in the presence of an excess of $\mathrm{ArN_2}^+$ to test whether the insertion of two diazonium salts can take place giving bis(aryldiazene) complexes. Although the reaction proceeds, the solid obtained contains several products which decomposed during crystallization and were not separated. The NMR spectra reveal the presence of new diazene complexes besides **10**, but also of large amounts of decomposition products which prevent any further investigation.

Bis(aryldiazonium) cations $[\mathrm{N_2Ar{-}ArN_2}]^{2+}$ also react with the hydride $[\mathrm{ReH_2(NO)P_3}]$ yielding the binuclear complexes **11** containing the bis(diazene) $\mathrm{NH{=}NAr{-}ArN{=}NH}$ as a bridging unit (Scheme 8).

Parallel to the behavior of the dihydride, the hydride-alkoxy complexes $[\mathrm{ReH(OR^1)(NO)P_3}]$ also react with both mono- $[\mathrm{ArN_2}]^+$ and bis(aryldiazonium) $[\mathrm{N_2Ar{-}ArN_2}]^{2+}$ cations to give the corresponding aryldiazene derivatives **12−16**, which were isolated and characterized (Scheme 9).



Scheme 8. P = $\mathrm{PPh_2OEt}$

$$\mathrm{ReH(OR^1)(NO)P_3 + ArN_2^+ \longrightarrow [Re(OR^1)(ArN{=}NH)(NO)P_3]^+}$$

12, 14, 16

P = $\mathrm{PPh(OEt)_2}$, $\mathrm{R^1 = C_2H_5}$ (**12**), $\mathrm{CH_3}$ (**14**)
P = $\mathrm{P(OEt)_3}$, $\mathrm{R^1 = C_2H_5}$ (**16**), Ar = $\mathrm{C_6H_5}$ (**c**), 4-$\mathrm{CH_3C_6H_4}$ (**d**)

$$\mathrm{2ReH(OR^1)(NO)P_3 + [N_2Ar\text{-}ArN_2]^{2+} \longrightarrow [\{Re(OR^1)(NO)P_3\}_2(\mu\text{-}NH{=}NAr\text{-}ArN{=}NH)]^{2+}}$$

13, 15

P = $\mathrm{PPh(OEt)_2}$, Ar-Ar = 4,4'-$\mathrm{C_6H_4}$-$\mathrm{C_6H_4}$,
$\mathrm{R^1 = C_2H_5}$ (**13**), $\mathrm{CH_3}$ (**15**)

Scheme 9

These results highlight that the same aryldiazene complexes of rhenium (**7c** and **10c**) and (**8c** and **12c**) can be prepared both by the oxidation of the arylhydrazine derivative with $\mathrm{Pb(OAc)_4}$ and by the insertion of an aryldiazonium cation into the Re−H bond of the appropriate hydride. The two methods, however, give isomers with a different geometry, as will be discussed below. Furthermore, a comparison of the results obtained in the reaction of our nitrosyl hydrides **1−3** with $\mathrm{ArN_2}^+$ with those we[12] previously reported on the carbonyls $[\mathrm{ReH(CO)}_n\mathrm{P}_{5-n}]$ shows that, in both cases, aryldiazene rhenium complexes can be obtained by "apparent" insertion of aryldiazonium cations into the

Re−H bond of all the hydride species. The reaction seems to be general for both the carbonyl and nitrosyl hydrides yielding stable aryldiazene complexes. Some differences, however, were observed in the reaction with bis(aryldiazonium) salts, which allow, in the case of carbonyls $[ReH(CO)_nP_{5-n}]$ containing the bulky PPh_2OEt ligand, the preparation of "diazo-diazene" $[Re(CO)_nP_{5-n}(HN{=}NAr{-}ArN{\equiv}N)]^{2+}$ (n = 1, 2) derivatives[12] through the insertion of only one end of the $^{+}N_2Ar{-}ArN_2{}^{+}$ ligand with the hydride. The same mononuclear compounds were not obtained with the nitrosyl-hydride $[ReH_2(NO)(PPh_2OEt)_3]$ which gives exclusively binuclear bis(aryldiazene) derivatives, under all conditions.

The aryldiazene complexes **10**, **11**, **14** and **15** were isolated with the BPh_4 anion whereas the ethoxy derivatives **12**, **13** and **16** were obtained as BF_4 salts. All are yellow or pale-yellow solids, stable in air and in solution in polar organic solvents where they behave as 1:1 or 2:1 electrolytes, respectively. Some decomposition was observed for the alkoxy derivatives **12**, **13** and **16** in solutions of ethanol. Analytical and spectroscopic data (Table 1) support the proposed formulation for the complexes and for the hydride-diazene derivatives **10** and **12** a geometry in solution can also be established.

The ^1H NMR spectra of the cations $[ReH(ArN{=}NH)(NO)P_3]^+$ (**10**) show two slightly broad signals in the high-frequency region (δ = 13.84−13.45 ppm) attributed to two diazene protons. This attribution is confirmed by the spectra of the labeled complex **10c$_1$** which show two high-frequency doublets centered at the same chemical shift of the two slightly broad signals of unlabeled **10c** and with a $^1J^{15}{}_{N,H}$ coupling constant of 65 Hz, in agreement with the presence of two diazene ligands. This is also confirmed by the $^{15}N\{^1H\}$ NMR spectrum of **10c$_1$** which shows two AB_2Y (Y = ^{15}N) multiplets at δ = −2.57 and at δ = −8.70 ppm (Table 4) due to the coupling with the phosphorus nuclei. Because the compounds contain only one aryldiazene ligand, the presence of two NH signal may suggest the existence of two isomers. This was confirmed by the ^{31}P NMR spectra, which show two AB_2 multiplets which can be simulated using the parameters reported in Table 1. The formation of two isomers for **10** is not unexpected due to the chemical non-equivalence of the two hydrides in the $[ReH_2(NO)P_3]$ precursors which give two isomers through the insertion of only one $ArN_2{}^+$ into each of the two Re−H bonds. Whether or not an isomerization may be excluded, the insertion should only give the two isomers **A** and **B** (Scheme 8) which were isolated in a 30:70 ratio. This ratio is probably related to the different insertion rate of $ArN_2{}^+$ into the two different hydrides.

In the ^1H NMR spectra of **10c** one AB_2X (X = H) multiplet at δ = 2.83 ppm is also present which can be attributed to one of the hydride ligands. The H^- signal of the other isomer probably overlaps the multiplet of the methylene protons, as well as those of **10d**. Furthermore, the ν_{NO} band observed in the IR spectrum appears slightly broad in **10c** and also contains a shoulder in **10d** in agreement with the presence of more nitrosyl compounds. These data confirm the formulation proposed for the hydride-aryldiazene complexes, but do not allow us to unambiguously propose a geometry in solution. However, a comparison of the spectroscopic data of **10c** with those of the related complex **7c** obtained by the oxidation of phenylhydrazine shows different chemical shift values for both the NH proton signals and the ^{31}P nucleus suggesting that the complex **7c** has a geometry that is different from those of the two isomers. Since a geometry of type **V** (Scheme 6) for **7c** had been proposed and the structure of the $[ReH(ArN{=}NH)(NO)P_3]^+$ complex can be discussed in terms of only three geometries, it follows that **VIII** and **XI** should be proposed for the two isomers **A** and **B** of complexes **10**.

Table 4. $^{15}N\{^1H\}$ NMR spectroscopic data for selected rhenium compounds

Compound	$^{15}N\{^1H\}$ NMR[a] δ (J/Hz)
$[ReH(C_6H_5N{=}^{15}NH)(NO)\{PPh_2(OEt)\}_3]BPh_4$ (**10c$_1$**)	AB_2Y spin system $\delta_Y = -2.57$ $J_{A,Y} = 28.8$ $J_{B,Y} = 2.0$ AB_2Y spin system $\delta_Y = -8.70$ $J_{A,Y} = 39.3$ $J_{B,Y} = 2.0$
$[\{ReH(NO)[PPh_2(OEt)]_3\}_2(\mu\text{-}4,4'\text{-}H^{15}N{=}NC_6H_4{-}C_6H_4N{=}^{15}NH)](BPh_4)_2$ (**11a$_1$**)	AB_2Y spin system $\delta_Y = -3.0$ $J_{A,Y} = 29.1$ $J_{B,Y} = 1.0$
$[Re(OC_2H_5)(NO)\{PPh(OEt)_2\}_3(C_6H_5N{=}^{15}NH)]BF_4$ (**12c$_1$**)	AB_2Y spin system $\delta_Y = -7.9$ $J_{A,Y} = 44.0$ $J_{B,Y} = 4.0$
$[\{Re(OC_2H_5)(NO)[PPh(OEt)_2]_3\}_2(\mu\text{-}4,4'\text{-}H^{15}N{=}NC_6H_4{-}C_6H_4N{=}^{15}NH)](BF_4)_2$ (**13a$_1$**)	AB_2Y spin system $\delta_Y = -8.20$ $J_{A,Y} = 45.0$ $J_{B,Y} = 4.0$ AB_2Y spin system $\delta_Y = -12.2$ $J_{A,Y} = 45.0$ $J_{B,Y} = 4.0$
$[\{Re(OCH_3)(NO)[PPh(OEt)_2]_3\}_2(\mu\text{-}4,4'\text{-}H^{15}N{=}NC_6H_4{-}C_6H_4N{=}^{15}NH)](BPh_4)_2$ (**15a$_1$**)	AB_2Y spin system $\delta_Y = -8.05$ $J_{A,Y} = 45.0$ $J_{B,Y} = 3.0$ AB_2Y spin system $\delta_Y = -12.4$ $J_{A,Y} = 45.0$ $J_{B,Y} = 2.9$

[a] In CD_2Cl_2 at 25 °C. Positive shifts downfield from $CH_3{}^{15}NO_2$.

The ^1H and ^{31}P NMR spectra of the dinuclear complexes **11** indicate the presence of only one isomer. In fact, only one diazene signal at δ = 13.45 ppm is present in the ^1H NMR spectrum of **11a**, which is split into a doublet with a $^1J^{15}{}_{N,H}$ coupling constant of 64 Hz in the labeled compound **11a$_1$**. In the ^1H NMR spectrum one AB_2X (X = H) multiplet, simulated with the parameters reported in

Table 1, is also present which was attributed to the hydride ligand. The two $J_{P,H}$ coupling constants deduced from the spectra have different values of 20.4, 29.4 Hz, respectively, suggesting that the hydride should be in *trans* to one phosphane and *cis* to the other two. In the temperature range between +20 and −80 °C the ^{31}P NMR spectra show only one AB_2 multiplet in agreement with the presence of only one isomer with two magnetically equivalent phosphanes that are different from the third. On the basis of these data a geometry of type **IX** can reasonably be proposed for the binuclear complex **11a**.

The formation of only one isomer with the bis(aryldiazonium) cation may be explained on the basis of the faster insertion rate of the aryldiazonium cation into one of the two Re−H bonds which affords, in the case of the dinuclear complexes, only traces of the other isomers that were discarded by crystallization.

The ^1H NMR spectra of the alkoxy complexes **12−16** confirm the presence of the diazene ligand showing the characteristic high-frequency NH signal which splits into a doublet in the ^{15}N-labeled complexes (Table 1). In the spectra the characteristic resonance of the alkoxy OR^1 ligand is also present, along with the signals of the phosphane and BPh_4 anion. The $^{31}P\{^1H\}$ NMR spectra show, for some complexes, the presence of only one AB_2 multiplet, while two AB_2 multiplets are present in the spectra of **13**, **14** and **15**, suggesting the probable presence of two isomers. These data support the proposed formulation for the complexes but, in the absence of an X-ray determination, do not allow us to unambiguously propose a geometry in solution for these aryldiazene derivatives.

Conclusion

In this contribution we have reported the synthesis of new rhenium nitrosyl hydrides of the $[ReH_2(NO)P_3]$ and $[ReH(OR^1)(NO)P_3]$ type containing both phosphane and alkoxy groups as supporting ligands. Their protonation with Brønsted acids allows thermally unstable η^2-H_2 complexes to be obtained. Both classical and non-classical rhenium hydrides behave with an easy entry into "diazo" chemistry and allow the synthesis of the first hydrazine and diazene complexes stabilized by nitrosyl ligands. The structural parameters for one hydrazine complex, $[Re(OC_2H_5)(NH_2NH_2)(NO)\{PPh(OEt)_2\}_3]BPh_4$, are also reported. Reactivity studies also show that aryldiazene $[ReH(ArN{=}NH)(NO)P_3]BPh_4$ and $[Re(OR^1)(ArN{=}NH)(NO)P_3]BPh_4$ complexes can be prepared both by insertion of an aryldiazonium cation into the Re−H bond of an appropriate hydride and by the oxidation of the related arylhydrazine derivatives with $Pb(OAc)_4$. Furthermore, the oxidation of the methylhydrazine complex $[Re(OCH_3)(CH_3NHNH_2)(NO)\{PPh(OEt)_2\}_3]BPh_4$ with $Pb(OAc)_4$ shows a new example of formation of a methyleneimine $[Re(OCH_3)(\eta^1\text{-}NH{=}CH_2)(NO)\{PPh(OEt)_2\}_3]BPh_4$ derivative.

Experimental Section

General: All synthetic work was carried out under an inert atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres 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. The phosphanes $PPh(OEt)_2$ and PPh_2OEt were prepared by the method of Rabinowitz and Pellon,[24] whereas $P(OEt)_3$ was an Aldrich product, purified by distillation under nitrogen. Diazonium salts were obtained in the usual way.[25] The related di-diazonium salts $[N_2Ar{-}ArN_2](BF_4)_2$ (Ar−Ar = 4,4′-C_6H_4-C_6H_4) were prepared by treating the amine precursors H_2NAr-$ArNH_2$ with $NaNO_2$ as described in the literature for the common monodiazonium salts.[25] The labeled diazonium tetrafluoroborate $[C_6H_5N{\equiv}^{15}N]BF_4$ and $[4,4'\text{-}^{15}N{\equiv}NC_6H_4{-}C_6H_4N{\equiv}^{15}N](BF_4)_2$ were prepared from $Na^{15}NO_2$ (99% enriched, CIL) and the appropriate amine. The hydrazines $C_6H_5NHNH_2$, $C_6H_5CONHNH_2$ and CH_3NHNH_2 were Aldrich products and used as received. Hydrazine (NH_2NH_2) was prepared by decomposition of hydrazine cyanurate (Fluka) following the reported method.[26] High-grade (99.99%) lead(IV) acetate was purchased from Aldrich. 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, ^{13}C, ^{31}P, ^{15}N) were obtained on Bruker AC200 or Avance 300 spectrometers at temperatures varying between −90 and +30 °C, unless otherwise noted. ^1H and ^{13}C chemical shifts 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. ^{15}N NMR spectra are referenced to external $CH_3{}^{15}NO_2$, with downfield shifts considered positive. The SwaN-MR software package[27] was used to treat 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: $[ReCl_2(OCH_3)(NO)(PPh_3)_2]$ was prepared following a reported method.[15a]

$[ReH_2(NO)(PPh_2OEt)_3]$ (1): An excess of PPh_2OEt (2.05 mL, 8.9 mmol) and then an excess of $NaBH_4$ (0.404 g, 10.68 mmol) in 15 mL of ethanol were added to a suspension of $[ReCl_2(OCH_3)(NO)(PPh_3)_2]$ (1.5 g, 1.78 mmol) in 30 mL of ethanol. Upon refluxing the reaction mixture both a color change of the solution from red-brown to yellow and the separation of a yellow solid were observed. After about 90 min of reflux the mixture was cooled and the solid obtained was filtered and crystallized from CH_2Cl_2 and ethanol; yield 1.34 g (83%). $C_{42}H_{47}NO_4P_3Re$ (908.96): calcd. C 55.5, H 5.2, N 1.5; found C 55.7, H, 5.3, N 1.4.

$[ReH(OC_2H_5)(NO)P_3]$ (2) [P = $PPh(OEt)_2$ (a), $P(OEt)_3$ (b)]: An excess of the appropriate phosphane (12 mmol) and then an excess of $NaBH_4$ (0.45 g, 12 mmol) in 15 mL of ethanol were added to a suspension of $[ReCl_2(OCH_3)(NO)(PPh_3)_2]$ (2 g, 2.37 mmol) in 45 mL of ethanol. The reaction mixture was refluxed for 1 h, cooled to room temperature, filtered and concentrated to about 20 mL by evaporation of the solvent under reduced pressure. At this point, the method to obtain solid samples of the complexes depends on the nature of the phosphane ligand. In the case of $PPh(OEt)_2$ yellow crystals of **2a** were obtained by cooling the resulting solution to −25 °C. These were filtered and dried under vacuum. In the case of $P(OEt)_3$, the solid obtained by cooling the solution to −25 °C gave PPh_3. Finally, by further concentrating

and cooling of the solution, yellow crystals of **2b** separated out, which were filtered and dried under vacuum; yield 1.58 g for **2a** (78%); 0.36 g for **2b** (20%).
2a: $C_{32}H_{51}NO_8P_3Re$ (856.88): calcd. C 44.9, H 6.0, N 1.6; found C 44.7, H 6.0, N 1.5.
2b: $C_{20}H_{51}NO_{11}P_3Re$ (760.74): calcd. C 31.6, H 6.8, N 1.8; found C 31.4, H 6.9, N 1.8.

[ReH(OCH$_3$)(NO){PPh(OEt)$_2$}$_3$] (3): An excess of $PPh(OEt)_2$ (2.76 g, 12 mmol) and then an excess of $NaBH_4$ (0.45 g, 12 mmol) in 20 mL of CH_3CN were added to a solution of $[ReCl_2(OCH_3)(NO)(PPh_3)_2]$ (2 g, 2.37 mmol) in 30 mL of CH_3CN. The reaction mixture was refluxed for about 2 h and then the solvent was removed by evaporation under reduced pressure. The oil obtained was treated with 8 mL of ethanol and the resulting solution, after filtration, was allowed to stand at −25 °C. A yellow-green solid slowly separated out which was filtered and crystallized from CH_2Cl_2 and ethanol; yield 1.04 g (52%). $C_{31}H_{49}NO_8P_3Re$ (842.85): calcd. C 44.2, H 5.9, N 1.7; found C 44.3, H 5.7, N 1.6.

[ReH(RNHNH$_2$)(NO)(PPh$_2$OEt)$_3$]BPh$_4$ (4) [R = H (a), CH$_3$ (b), C$_6$H$_5$ (c)]: An equimolar amount of CF_3SO_3H (9.7 µL, 0.11 mmol) was added to a solution of $[ReH_2(NO)(PPh_2OEt)_3]$ (100 mg, 0.11 mmol) in 8 mL of CH_2Cl_2 cooled to −196 °C. The reaction mixture was warmed to about −10 °C, stirred for 1 h and then an excess of the appropriate hydrazine (0.22 mmol) was added. After two hours of stirring at −10 °C, the solvent was removed under reduced pressure to give an oil which was treated with ethanol (2 mL) containing an excess of $NaBPh_4$ (75 mg, 0.22 mmol). A yellow solid slowly separated out from the resulting solution which was filtered and crystallized from CH_2Cl_2 and ethanol; yield 93 mg for **4a** (67%), 91 mg for **4b** (65%), 100 mg for **4c** (98%).
4a: $C_{66}H_{70}BN_3O_4P_3Re$ (1259.2): calcd. C 63.0, H 5.6, N 3.3; found C 63.2, H 5.7, N 3.2. $\Lambda_M = 48.7\ \Omega^{-1}\ mol^{-1}\ cm^2$.
4b: $C_{67}H_{72}BN_3O_4P_3Re$ (1273.3): calcd. C 63.2, H 5.7, N 3.3; found C 63.0, H 5.6, N 3.2. $\Lambda_M = 51.8\ \Omega^{-1}\ mol^{-1}\ cm^2$.
4c: $C_{72}H_{74}BN_3O_4P_3Re$ (1335.3): calcd. C 64.8, H 5.6, N 3.2; found C 64.6, H 5.7, N 3.1. $\Lambda_M = 50.3\ \Omega^{-1}\ mol^{-1}\ cm^2$.

[Re(OC$_2$H$_5$)(RNHNH$_2$)(NO){PPh(OEt)$_2$}$_3$]BPh$_4$ (5) [R = H (a), C$_6$H$_5$ (c)]: An equimolar amount of CF_3SO_3H (10.3 µL, 0.117 mmol) was added to a solution of $[ReH(OC_2H_5)(NO)\{PPh(OEt)_2\}_3]$ (100 mg, 0.117 mmol) in 8 mL of CH_2Cl_2 cooled to −196 °C and the reaction mixture brought to 0 °C and stirred for 1 h. The solution was cooled to −196 °C again and an excess of the appropriate hydrazine (0.24 mmol) added. The reaction mixture was brought to 0 °C, stirred for about 2 h and then the solvent removed under reduced pressure. The solid obtained was treated with ethanol (3 mL) containing an excess of $NaBPh_4$ (85 mg, 0.25 mmol). A pale-yellow solid slowly separated out from the resulting solution, which was filtered and crystallized from CH_2Cl_2 and ethanol; yield 80 mg for **5a** (55%), 86 mg for **5c** (58%).
5a: $C_{56}H_{74}BN_3O_8P_3Re$ (1207.2): calcd. C 55.7, H 6.2, N 3.5; found C 55.5, H 6.3, N 3.5. $\Lambda_M = 49.5\ \Omega^{-1}\ mol^{-1}\ cm^2$.
5c: $C_{62}H_{78}BN_3O_8P_3Re$ (1283.2): calcd. C 58.0, H 6.1, N 3.3; found C 57.8, H 6.0, N 3.3. $\Lambda_M = 51.4\ \Omega^{-1}\ mol^{-1}\ cm^2$.

[Re(OC$_2$H$_5$)(CH$_3$NHNH$_2$)(NO){PPh(OEt)$_2$}$_3$]CF$_3$SO$_3$ (5b$_2$): This complex was prepared following the method used for the related BPh_4 complex **5a** by reacting $[ReH(OC_2H_5)(NO)\{PPh(OEt)_2\}_3]$ first with CF_3SO_3H and then with an excess of CH_3NHNH_2 in CH_2Cl_2 as a solvent. After the reaction was finished, the solvent was removed under reduced pressure to give a pale-yellow solid which was triturated with ethanol (1.5 mL). A yellow solid slowly separated out from the resulting solution, which was cooled to −25 °C to complete the precipitation. The solid was filtered, washed with cold ethanol and dried under vacuum; yield 52 mg (42%). $C_{34}H_{56}F_3N_3O_{11}P_3ReS$ (1051.01): calcd. C 38.9, H 5.4, N 4.0; found C 39.0, H 5.5, N 3.9. $\Lambda_M = 78.5\ \Omega^{-1}\ mol^{-1}\ cm^2$.

[Re(OCH$_3$)(RNHNH$_2$)(NO){PPh(OEt)$_2$}$_3$]BPh$_4$ (6) [R = H (a), CH$_3$ (b), C$_6$H$_5$ (c)]: These complexes were prepared exactly like the related ethoxy complexes **5a** and **5c** by reacting $[ReH(OCH_3)(NO)\{PPh(OEt)_2\}_3]$ first with CF_3SO_3H and then with an excess of the appropriate hydrazine. After precipitation with $NaBPh_4$ in ethanol, the yields were 95 mg for **6a** (65%), 89 mg for **6b** (63%) and 101 mg for **6c** (68%).
6a: $C_{55}H_{72}BN_3O_8P_3Re$ (1193.1): calcd. C 55.4, H 6.1, N 3.5; found C 55.2, H 6.0, N 3.5. $\Lambda_M = 54.8\ \Omega^{-1}\ mol^{-1}\ cm^2$.
6b: $C_{56}H_{74}BN_3O_8P_3Re$ (1207.2): calcd. C 55.7, H 6.2, N 3.5; found C 55.6, H 6.3, N 3.4. $\Lambda_M = 53.3\ \Omega^{-1}\ mol^{-1}\ cm^2$.
6c: $C_{61}H_{76}BN_3O_8P_3Re$ (1269.2): calcd. C 57.7, H 6.0, N 3.3; found C 57.9, H 6.2, N 3.3. $\Lambda_M = 49.6\ \Omega^{-1}\ mol^{-1}\ cm^2$.

[ReH(CH$_3$N=NH)(NO)(PPh$_2$OEt)$_3$]BPh$_4$ (7b) and [ReH(C$_6$H$_5$N=NH)(NO)(PPh$_2$OEt)$_3$]BPh$_4$ (7c): A sample of the appropriate hydrazine complex $[ReH(RNHNH_2)(NO)(PPh_2OEt)_3]BPh_4$ (**4**) (R = CH_3 or C_6H_5; 0.07 mmol) was placed in a three-necked 25-mL round-bottomed flask fitted with a solid-addition sidearm containing an equimolar amount of $Pb(OAc)_4$ (31 mg, 0.07 mmol). The system was evacuated, CH_2Cl_2 (10 mL) was added, the solution cooled to −30 °C and the $Pb(OAc)_4$ was added portionwise over 10−20 min. The reaction mixture was then allowed to warm to 0 °C, stirred for 10 min and the solvent removed under reduced pressure. The oil obtained was treated at 0 °C with ethanol (2 mL) containing $NaBPh_4$ (34 mg, 0.10 mmol). A white solid slowly separated out upon stirring the resulting solution at 0 °C, which was filtered and crystallized at 0 °C from CH_2Cl_2 and ethanol; yield 64 mg for **7b** (72%) and 65 mg for **7c** (70%).
7b: $C_{67}H_{70}BN_3O_4P_3Re$ (1271.2): calcd. C 63.3, H 5.6, N 3.3; found C 63.1, H 5.4, N 3.2. $\Lambda_M = 49.9\ \Omega^{-1}\ mol^{-1}\ cm^2$.
7c: $C_{72}H_{72}BN_3O_4P_3Re$ (1333.3): calcd. C 64.9, H 5.4, N 3.2; found C 64.6, H 5.3, N 3.0. $\Lambda_M = 52.1\ \Omega^{-1}\ mol^{-1}\ cm^2$.

[Re(OC$_2$H$_5$)(C$_6$H$_5$N=NH)(NO){PPh(OEt)$_2$}$_3$]BPh$_4$ (8c): This complex was prepared exactly like the related complexes **7** by oxidation of the phenylhydrazine derivative $[Re(OC_2H_5)(C_6H_5NHNH_2)(NO)\{PPh(OEt)_2\}_3]BPh_4$ (**5c**) with $Pb(OAc)_4$ at −30 °C; yield 56 mg (62%). $C_{62}H_{76}BN_3O_8P_3Re$ (1281.2): calcd. C 58.1, H 6.0, N 3.3; found C 57.9, H 6.1, N 3.2. $\Lambda_M = 52.0\ \Omega^{-1}\ mol^{-1}\ cm^2$.

[Re(OCH$_3$)(CH$_3$N=NH)(NO){PPh(OEt)$_2$}$_3$]BPh$_4$ (9b) and [Re(OCH$_3$)(η^1-NH=CH$_2$)(NO){PPh(OEt)$_2$}$_3$]BPh$_4$ (9*b): These complexes were obtained as a mixture by oxidation of the methylhydrazine compound $[Re(OCH_3)(CH_3NHNH_2)(NO)\{PPh(OEt)_2\}_3]BPh_4$ (**6b**) with $Pb(OAc)_4$ at −30 °C following the method used for the related **7** and **8** complexes.

[ReH(ArN=NH)(NO)(PPh$_2$OEt)$_3$]BPh$_4$ (10) [Ar = C$_6$H$_5$ (c), 4-CH$_3$C$_6$H$_4$ (d)]: Solid samples of $[ReH_2(NO)(PPh_2OEt)_3]$ (0.1 g, 0.11 mmol) and the appropriate aryldiazonium salt $[ArN_2]BF_4$ (0.11 mmol) were placed into a 25-mL three-necked round-bottomed flask. The mixture was cooled to −196 °C and CH_2Cl_2 (8 mL) slowly added. The reaction mixture was allowed to warm to room temperature, stirred for about 8 h and then the solvent removed under reduced pressure. The oil obtained was treated with ethanol (2 mL) containing an excess of $NaBPh_4$ (75 mg, 0.22 mmol). A yellow solid slowly separated out from the resulting solution which was filtered and crystallized from CH_2Cl_2 and ethanol; yield 107 mg for **10c** (73%) and 105 mg for **10d** (71%).

10c: $C_{72}H_{72}BN_3O_4P_3Re$ (1333.3): calcd. C 64.9, H 5.4, N 3.2; found C 64.8, H 5.5, N 3.0. $\Lambda_M = 49.4\ \Omega^{-1}\ mol^{-1}\ cm^2$.
10d: $C_{73}H_{74}BN_3O_4P_3Re$ (1347.3): calcd. C 65.1, H 5.5, N 3.1; found C 65.3, H 5.6, N 3.0. $\Lambda_M = 53.8\ \Omega^{-1}\ mol^{-1}\ cm^2$.

$[ReH(C_6H_5N{=}^{15}NH)(NO)(PPh_2OEt)_3]BPh_4$ (10c$_1$): This complex was prepared exactly like the related compound **10** using the labeled diazonium salt $[C_6H_5N{\equiv}^{15}N]BF_4$; yield 95 mg (65%).

$[\{ReH(NO)(PPh_2OEt)_3\}_2(\mu\text{-}4,4'\text{-}HN{=}NC_6H_4\text{-}C_6H_4N{=}NH)](BPh_4)_2$ (11a): Solid samples of $[ReH_2(NO)(PPh_2OEt)_3]$ (0.1 g, 0.11 mmol) and the bis(aryldiazonium) salt $[4,4'\text{-}N_2C_6H_4\text{-}C_6H_4N_2](BF_4)_2$ (21 mg, 0.055 mmol) were placed into a 25-mL three-necked flask. The mixture was cooled to −196 °C and CH_2Cl_2 (12 mL) added. The reaction mixture was brought to room temperature, stirred for about 12 h and then the solvent removed by evaporation under reduced pressure. The oil obtained was triturated with ethanol (3 mL) containing an excess of $NaBPh_4$ (75 mg, 0.22 mmol). A red solid separated out from the resulting solution which was filtered and crystallized from CH_2Cl_2 and ethanol; yield 217 mg (74%). $C_{144}H_{142}B_2N_6O_8P_6Re_2$ (2664.6): calcd. C 64.9, H 5.4, N 3.2; found C 64.7, H 5.5, N 3.2. $\Lambda_M = 115\ \Omega^{-1}\ mol^{-1}\ cm^2$.

$[\{ReH(NO)(PPh_2OEt)_3\}_2(\mu\text{-}4,4'\text{-}H^{15}N{=}NC_6H_4{-}C_6H_4\text{-}N{=}^{15}NH)](BPh_4)_2$ (11a$_1$): This complex was prepared exactly like the related compound **11a** using the labeled bis(aryldiazonium) salt $[4,4'\text{-}^{15}N{\equiv}NC_6H_4{-}C_6H_4N{\equiv}^{15}N](BF_4)_2$; yield 194 mg (66%).

$[Re(OC_2H_5)(ArN{=}NH)(NO)\{PPh(OEt)_2\}_3]BF_4$ (12) [Ar = C_6H_5 (c), 4-$CH_3C_6H_4$ (d)]: Equimolar amounts of $[ReH(OC_2H_5)(NO)\{PPh(OEt)_2\}_3]$ (100 mg, 0.117 mmol) and the appropriate aryldiazonium salt $[ArN_2]BF_4$ (0.117 mmol) were placed into a 25-mL three-necked flask. The mixture was cooled to −196 °C and CH_2Cl_2 (8 mL) added. The reaction mixture was brought to room temperature, stirred for 8 h and then the solvent was removed under reduced pressure. The oil obtained was triturated with diethyl ether (10 mL) until a pale-yellow solid separated out, which was filtered and dried under vacuum; yield 112 mg for **12c** (91%) and 109 mg for **12d** (88%).
12c: $C_{38}H_{56}BF_4N_3O_8P_3Re$ (1048.8): calcd. C 43.5, H 5.4, N 4.0; found C 43.4, H 5.5, N 3.9. $\Lambda_M = 88.7\ \Omega^{-1}\ mol^{-1}\ cm^2$.
12d: $C_{39}H_{58}BF_4N_3O_8P_3Re$ (1062.8): calcd. C 44.1, H 5.5, N 4.0; found C 44.23, H 5.37, N 4.02. $\Lambda_M = 93.1\ \Omega^{-1}\ mol^{-1}\ cm^2$.

$[Re(OC_2H_5)(NO)(C_6H_5N{=}^{15}NH)\{PPh(OEt)_2\}_3]BF_4$ (12c$_1$): This complex was prepared exactly like the related compound **12c** using the labeled aryldiazonium salt $[C_6H_5N{\equiv}^{15}N]BF_4$; yield 104 mg (85%).

$[\{Re(OC_2H_5)(NO)[PPh(OEt)_2]_3\}_2(\mu\text{-}4,4'\text{-}HN{=}NC_6H_4{-}C_6H_4N{=}NH)](BF_4)_2$ (13a): This complex was prepared following the method used for the related mononuclear compound **12** by reacting $[ReH(OC_2H_5)(NO)\{PPh(OEt)_2\}_3]$ with $[4,4'\text{-}N_2C_6H_4\text{-}C_6H_4N_2](BF_4)_2$ in CH_2Cl_2 with a reaction time of 12 h; yield 218 mg (89%). $C_{76}H_{110}B_2F_8N_6O_{16}P_6Re_2$ (2095.6): calcd. C 43.6, H 5.3, N 4.0; found C 43.7, H 5.2, N 3.9. $\Lambda_M = 188\ \Omega^{-1}\ mol^{-1}\ cm^2$.

$[\{Re(OC_2H_5)(NO)[PPh(OEt)_2]_3\}_2(\mu\text{-}4,4'\text{-}H^{15}N{=}NC_6H_4{-}C_6H_4N{=}^{15}NH)](BF_4)_2$ (13a$_1$): This complex was prepared exactly like the related compound **13a** using the labeled bis(aryldiazonium) salt $[4,4'\text{-}^{15}N{\equiv}NC_6H_4\text{-}C_6H_4N{\equiv}^{15}N](BF_4)_2$; yield 206 mg (84%).

$[Re(OCH_3)(4\text{-}CH_3C_6H_4N{=}NH)(NO)\{PPh(OEt)_2\}_3]BPh_4$ (14d): Solid samples of $[ReH(OCH_3)(NO)\{PPh(OEt)_2\}_3]$ (100 mg, 0.119 mmol) and the diazonium salt $[4\text{-}CH_3C_6H_4N_2]BF_4$ (23 mg, 0.119 mmol) were placed into a 25-mL three-necked round-bottomed flask and the mixture cooled to −196 °C. Dichloromethane (8 mL) was added and the reaction mixture brought to room temperature and stirred for 9 h. The solvent was removed under reduced pressure to give an oil which was treated with ethanol (2 mL) containing an excess of $NaBPh_4$ (82 mg, 0.24 mmol). A yellow solid slowly separated out from the resulting solution which was filtered and crystallized from CH_2Cl_2 and ethanol; yield 126 mg (83%). $C_{62}H_{76}BN_3O_8P_3Re$ (1281.2): calcd. C 58.1, H 6.0, N 3.3; found C 58.2, H 5.9, N 3.2. $\Lambda_M = 52.7\ \Omega^{-1}\ mol^{-1}\ cm^2$.

$[\{Re(OCH_3)(NO)[PPh(OEt)_2]_3\}_2(\mu\text{-}4,4'\text{-}HN{=}NC_6H_4{-}C_6H_4\text{-}N{=}NH)](BPh_4)_2$ (15a): This complex was prepared following the method used for the related mononuclear compound **14d** by reacting $[ReH(OCH_3)(NO)\{PPh(OEt)_2\}_3]$ with the bis(aryldiazonium) salt $[4,4'\text{-}N_2C_6H_4\text{-}C_6H_4N_2](BF_4)_2$ in CH_2Cl_2 for about 13 h; yield 205 mg (68%). $C_{122}H_{146}B_2N_6O_{16}P_6Re_2$ (2532.4): calcd. C 57.9, H 5.8, N 3.3; found C 57.7, H 5.7, N 3.4. $\Lambda_M = 113\ \Omega^{-1}\ mol^{-1}\ cm^2$.

$[\{Re(OCH_3)(NO)[PPh(OEt)_2]_3\}_2(\mu\text{-}4,4'\text{-}H^{15}N{=}NC_6H_4{-}C_6H_4N{=}^{15}NH)](BPh_4)_2$ (15a$_1$): This complex was prepared exactly like the related compound **15a** using the labeled bis(aryldiazonium) salt $[4,4'\text{-}^{15}N{\equiv}NC_6H_4\text{-}C_6H_4N{\equiv}^{15}N](BF_4)_2$; yield 196 mg (65%).

$[Re(OC_2H_5)(4\text{-}CH_3C_6H_4N{=}NH)(NO)\{P(OEt)_3\}_3]BF_4$ (16d): Equimolar amounts of solid samples of $[ReH(OC_2H_5)(NO)\{P(OEt)_3\}_3]$ (100 mg, 0.13 mmol) and $[4\text{-}CH_3C_6H_4N_2]BF_4$ (27 mg, 0.13 mmol) were placed in a 25-mL three-necked round-bottomed flask and the mixture cooled to −196 °C. Dichloromethane (8 mL) was added and the reaction mixture brought to 0 °C and stirred for 9 h. The solvent was removed under reduced pressure to give an oil which was triturated with diethyl ether (7 mL). A pale-yellow solid slowly separated out which was filtered and dried under vacuum; yield 103 mg (82%). $C_{27}H_{58}BF_4N_3O_{11}P_3Re$ (966.69): calcd. C 33.6, H 6.1, N 4.4; found C 33.7, H 6.2, N 4.3. $\Lambda_M = 89.4\ \Omega^{-1}\ mol^{-1}\ cm^2$.

Protonation Reactions: The protonation of the hydrides $[ReH_2(NO)(PPh_2OEt)_3]$ (**1**) and $[ReH(OR^1)(NO)P_3]$ (**2**, **3**) was carried out in a 5-mm NMR tube at temperatures of between −80 and +20 °C. A typical experiment involved the preparation, in an argon-filled dry-box, of a solution of the appropriate hydride (0.04 mmol) in CD_2Cl_2 (0.5 mL). The solution was placed in a screw-cap NMR tube, cooled to −80 °C, and then an equivalent amount (0.04 mmol, 3.5 µL) of CF_3SO_3H was added. The tube was transferred into the NMR probe (pre-cooled to −80 °C) and the ^1H and ^{31}P NMR spectra of the solution were recorded.

X-ray Crystal Structure Determination of $[Re(OC_2H_5)(NH_2NH_2)(NO)\{PPh(OEt)_2\}_3]BPh_4$ (5a): A pale-yellow single crystal was mounted on a glass fiber and X-ray diffraction data were collected on a Bruker-Siemens SMART AXS 1000 equipped with CCD detector, using graphite monochromated Mo-K_α radiation (λ = 0.71069 Å). Data collection details are: crystal to detector distance = 5.0 cm, 2424 frames collected (complete sphere mode), time per frame = 30 s, oscillation $\Delta\omega$ = 0.300°. Crystal decay resulted negligible. Data reduction was performed up to d = 0.90 Å with the SAINT package[28] and data were corrected for absorption effects by the SADABS[29] procedure (T_{max} = 1.000, T_{min} = 0.746). The phase problem was solved by direct methods[30] and refined by full-matrix least-squares on all F^2,[31] implemented in the WinGX package.[32] Anisotropic displacement parameters were refined for all non hydrogen atoms, while hydrogen atoms were introduced in calculated positions, except for hydrazine hydrogens, which were located from Fourier maps and refined isotropically. Use of the Cambridge Crystallographic Database[33] facilities was made for structure discussion. The final map was featureless. Data collection and refinement results are summarized in Table 2.

CCDC-220153 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] [1a] D. Sutton, *Chem. Rev.* **1993**, *93*, 995−1022. [1b] H. Zollinger, *Diazo Chemistry II*, VCH, Weinheim, Germany, **1995**. [1c]H. Kisch, P. Holzmeier, *Adv. Organomet. Chem.* **1992**, *34*, 67−109.

[2] [2a] B. F. G. Johnson, B. L. Haymore, J. R. Dilworth, in *Comprehensive Coordination Chemistry* (Eds.: G. Wilkinson, R. D. Gillard, J. A. McCleverty), Pergamon Press, Oxford, UK, **1987**, vol. 2, pp. 130−141. [2b]R. A. Henderson, G. J. Leigh, C. Pickett, *Adv. Inorg. Chem. Radiochem.* **1983**, *27*, 197−292. [2c] W. A. Nugent, B. L. Haymore, *Coord. Chem. Rev.* **1980**, *31*, 123−175.

[3] [3a] G. Albertin, S. Antoniutti, A. Bacchi, M. Boato, G. Pelizzi, *J. Chem. Soc., Dalton Trans.* **2002**, 3313−3320. [3b] G. Albertin, S. Antoniutti, E. Bordignon, E. Visentin, *Inorg. Chem.* **2001**, *40*, 4565−4567. [3c] G. Albertin, S. Antoniutti, E. Bordignon, G. Perinello, *J. Organomet. Chem.* **2001**, *625*, 217−230. [3d] G. Albertin, S. Antoniutti, A. Bacchi, E. Bordignon, F. Miani, G. Pelizzi, *Inorg. Chem.* **2000**, *39*, 3283−3293. [3e] G. Albertin, S. Antoniutti, A. Bacchi, D. Barbera, E. Bordignon, G. Pelizzi, P. Ugo, *Inorg. Chem.* **1998**, *37*, 5602−5610, and references cited therein. [3f] G. Albertin, S. Antoniutti, A. Bacchi, E. Bordignon, F. Busatto, G. Pelizzi, *Inorg. Chem.* **1997**, *36*, 1296−1305.

[4] [4a] X. Yan, R. J. Batchelor, F. W. B. Einstein, X. Zhang, R. Nagelkerke, D. Sutton, *Inorg. Chem.* **1997**, *36*, 1237−1246. [4b] D. Sellmann, K. Engl, F. W. Heinemann, J. Sieler, *Eur. J. Inorg. Chem.* **2000**, 1079−1089.

[5] [5a] A. R. Cowley, J. R. Dilworth, P. S. Donnelly, *Inorg. Chem.* **2003**, *42*, 929−931. [5b] M. T. A. R. S. da Costa, J. R. Dilworth, M. T. Duarte, J. J. R. F. da Silva, A. M. Galvão, A. J. L. Pombeiro, *J. Chem. Soc., Dalton Trans.* **1998**, 2405−2410. [5c] A. Garcia-Minsal, D. Sutton, *Organometallics* **1996**, *15*, 332−336. [5d] D. J. Rose, K. P. Maresca, P. B. Kettler, Y.-D. Chang, V. Soghomomian, Q. Chen, M. J. Abrams, S. K. Larsen, J. Zubieta, *Inorg. Chem.* **1996**, *35*, 3548−3558. [5e] B. Coutinho, J. R. Dilworth, P. Jobanputra, R. M. Thompson, S. Schmid, J. Strähle, C. M. Archer, *J. Chem. Soc., Dalton Trans.* **1995**, 1663−1669. [5f] A. Cusanelli, D. Sutton, *Organometallics* **1995**, *14*, 4651−4660. [5g] A. Cusanelli, R. J. Batchelor, F. W. B. Einstein, D. Sutton, *Organometallics* **1994**, *13*, 5096−5112. [5h] P. B. Kettler, Y.-D. Chang, J. Zubieta, *Inorg. Chem.* **1994**, *33*, 5864−5871. [5i] S. W. Carr, X. L. R. Fontaine, B. L. Shaw, *J. Chem. Soc., Dalton Trans.* **1987**, 3067−3071. [5j] H. M. Ali, G. J. Leigh, *J. Chem. Soc., Dalton Trans.* **1986**, 213−215. [5k] C. F. Barrientos-Penna, A. B. Gilchrist, A. H. Klahn-Oliva, A. J. L. Hanlan, D. Sutton, *Organometallics* **1985**, *4*, 478−485. [5l] J. R. Dilworth, S. A. Harrison, D. R. M. Walton, E. Schweda, *Inorg. Chem.* **1985**, *24*, 2594−2595.

[6] J. T. Moelwyn-Hughes, A. W. B. Garner, A. S. Howard, *J. Chem. Soc. (A)* **1971**, 2361−2370.

[7] [7a] M. G. Vale, R. R. Schrock, *Organometallics* **1991**, *10*, 1661−1662. [7b] T.-Y. Cheng, J. C. Peters, G. L. Hillhouse, *J. Am. Chem. Soc.* **1994**, *116*, 204−207.

[8] A. Moehlenkamp, R. Mattes, *Z. Naturforsch., Teil B* **1992**, *47*, 969.

[9] [9a] P. Perez-Lourido, J. Romero, J. A. Garcia-Vasquez, A. Souza, K. P. Maresca, J. Zubieta, *Inorg. Chem.* **1999**, *38*, 1511−1519. [9b] M. Hirsch-Kuchma, T. Nicholson, A. Davison, W. M. Davis, A. G. Jones, *Inorg. Chem.* **1997**, *36*, 3237−3241. [9c] M. Hirsch-Kuchma, T. Nicholson, A. Davison, W. M. Davis, A. G. Jones, *J. Chem. Soc., Dalton Trans.* **1997**, 3185−3188. [9d] T. Nicholson, J. Cook, A. Davison, D. J. Rose, K. P. Maresca, J. A. Zubieta, A. G. Jones, *Inorg. Chim. Acta* **1996**, *252*, 421−426. [9e] P. B. Kettler, Y.-D. Chang, Q. Chen, J. A. Zubieta, M. J. Abrams, S. K. Larsen, *Inorg. Chim. Acta* **1996**, *252*, 427−430. [9f] P. B. Kettler, Y.-D. Chang, Q. Chen, J. A. Zubieta, M. J. Abrams, S. K. Larsen, *Inorg. Chim. Acta* **1995**, *231*, 13.

[10] [10a] C. F. Barrientos-Penna, F. W. B. Einstein, T. Jones, D. Sutton, *Inorg. Chem.* **1982**, *21*, 2578−2585. [10b] C. F. Barrientos-Penna, C. F. Campana, F. W. B. Einstein, T. Jones, D. Sutton, A. S. Tracey, *Inorg. Chem.* **1984**, *23*, 363−368. [10c] R. Melenkivitz, J. S. Southern, G. L. Hillhouse, T. E. Concolino, L. M. Liable-Sands, A. L. Rheingold, *J. Am. Chem. Soc.* **2002**, *124*, 12068−12069.

[11] [11a] G. Albertin, S. Antoniutti, M. T. Giorgi, *Eur. J. Inorg. Chem.* **2003**, 2855−2866. [11b] G. Albertin, S. Antoniutti, A. Bacchi, E. Bordignon, M. T. Giorgi, G. Pelizzi, *Angew. Chem.* **2002**, *114*, 2296; *Angew. Chem. Int. Ed.* **2002**, *41*, 2192−2194.

[12] G. Albertin, S. Antoniutti, A. Bacchi, G. B. Ballico, E. Bordignon, G. Pelizzi, M. Ranieri, P. Ugo, *Inorg. Chem.* **2000**, *39*, 3265−3279.

[13] G. Albertin, S. Antoniutti, S. Garcia-Fontán, R. Carballo, F. Padoan, *J. Chem. Soc., Dalton Trans.* **1998**, 2071−2081.

[14] For rhenium polyhydrides see: [14a] D. Gusev, A. Llamazares, G. Artus, H. Jacobsen, H. Berke, *Organometallics* **1999**, *18*, 75−89. [14b] D. M. Heynekey, C. E. Radzewich, M. H. Voges, B. M. Schomber, *J. Am. Chem. Soc.* **1997**, *119*, 4172−4181. [14c] Y. Kim, H. Deng, J. C. Gallucci, A. Wojcicki, *Inorg. Chem.* **1996**, *35*, 7166−7173. [14d] A. L. Ondracek, W. Wu, P. E. Fanwick, R. A. Walton, *Inorg. Chem.* **1996**, *35*, 5249−5253. [14e] X. L. R. Fontaine, T. P. Layzell, B. L. Shaw, *J. Chem. Soc., Dalton Trans.* **1994**, 917−924. [14f] M. Kohli, D. J. Lewis, R. L. Luck, J. V. Silverton, K. Sylla, *Inorg. Chem.* **1994**, *33*, 883. [14g] M. Leeaphon, K. Rohl, R. J. Thomas, P. E. Fanwick, R. A. Walton, *Inorg. Chem.* **1993**, *32*, 5562−5568. [14h] D. Michos, X.-L. Luo, J. A. K. Howard, R. H. Crabtree, *Inorg. Chem.* **1992**, *31*, 3914−3916. [14i] Y. Kim, H. Deng, D. W. Meek, A. Wojcicki, *J. Am. Chem. Soc.* **1990**, *112*, 2798−2800. [14j] F. A. Cotton, R. L. Luck, *J. Am. Chem. Soc.* **1989**, *111*, 5757−5761. [14k] K. A. Earl, G. Jia, P. A. Maltby, R. H. Morris, *J. Am. Chem. Soc.* **1991**, *113*, 3027−3039. [14l] D. M. Heynekey, B. M. Schomber, C. E. Radzewich, *J. Am. Chem. Soc.* **1994**, *116*, 4515−4516.

[15] The known nitrosyl rhenium hydrides are of the types $[ReH_2(NO)(PPh_3)_3]$, $[ReH_2(NO)(CO)P_2]$ and $[ReH(NO)_2P_2]$ [$P = PMe_3, P\mathit{i}Pr_3, P(O\mathit{i}Pr)_3$]: [15a] T. S. Cameron, K. R. Grundy, K. N. Robertson, *Inorg. Chem.* **1982**, *21*, 4149−4155. [15b] N. V. Belkova, E. S. Shubina, A. V. Ionidis, L. M. Epstein, H. Jacobsen, A. Messmer, H. Berke, *Inorg. Chem.* **1997**, *26*, 1522−1525. [15c] S. Feracin, T. Bürgi, V. I. Bakhmutov, I. Eremenko, E. V. Vorontsov, A. B. Vimenits, H. Berke, *Organometallics* **1994**, *13*, 4194−4202. [15d] D. G. Gusev, D. Nietlispach, I. L. Eremenko, H. Berke, *Inorg. Chem.* **1993**, *32*, 3628−3636.

[16] [16a] C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313−348. [16b] M. M. Rahman, H.-Y. Lin, K. Eriks, A. Prock, W. P. Giering, *Organometallics* **1989**, *8*, 1−7.

[17] J. H. Enemark, R. D. Feltham, *Coord. Chem. Rev.* **1974**, *13*, 339−406.

[18] [18a] G. J. Kubas, *Acc. Chem. Res.* **1988**, *21*, 120−128. [18b] P. G. Jessop, R. H. Morris, *Coord. Chem. Rev.* **1992**, *121*, 155−284. [18c] R. H. Crabtree, *Angew. Chem. Int. Ed. Engl.* **1993**, *92*, 789−805. [18d] D. M. Heynekey, W. J. Oldham Jr., *Chem. Rev.* **1993**, *93*, 913−926.

[19] J. Huhmann-Vincent, B. L. Scott, G. J. Kubas, *Inorg. Chem.* **1999**, *38*, 115−124, and references cited therein.

[20] R. H. Crabtree, M. Lavin, L. Bonneviot, *J. Am. Chem. Soc.* **1986**, *108*, 4032−4037.
[21] W. G. Geary, *Coord. Chem. Rev.* **1971**, *7*, 81−122.
[22] T. J. Bartczak, W. Czurak, J. O. Dziemagegielewski, B. Machura, A. Jankowska, J. Kusz, J. Warczewski, *Polyhedron* **1999**, *18*, 2313−2320.
[23] [23a] M. R. Smith III, T.-Y. Cheng, G. L. Hillhouse, *J. Am. Chem. Soc.* **1993**, *115*, 8638−8642. [23b] T.-Y. Cheng, A. L. Ponce, A. L. Rheingold, G. L. Hillhouse, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 657−659. [23c] T.-Y. Cheng, J. C. Peters, G. L. Hillhouse, *J. Am. Chem. Soc.* **1994**, *116*, 204−207.
[24] R. Rabinowitz, J. Pellon, *J. Org. Chem.* **1961**, *26*, 4623−4626.
[25] A. I. Vogel, *Practical Organic Chemistry*, 3rd ed., Longmans, Green and Co., New York, **1956**.
[26] E. Nachbaur, G. Leiseder, *Monatsh. Chem.* **1971**, *102*, 1718−1723.
[27] G. Balacco, *J. Chem. Inf. Comput. Sci.* **1994**, *34*, 1235−1241.
[28] SAINT: SAX, *Area Detector Integration*, Siemens Analytical instruments INC., Madison, Wisconsin, USA.
[29] G. Sheldrick *SADABS: Siemens Area Detector Absorption Correction Software*, University of Göttingen, Germany, **1996**.
[30] A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. Moliterni, G Polidori, R. Spagna, *Sir97: A New Program For Solving And Refining Crystal Structures*, Istituto di Ricerca per lo Sviluppo di Metodologie Cristallografiche C N R, Bari, Italy, 1997.
[31] G. Sheldrick, *Shelxl97. Program for structure refinement*, University of Göttingen, Germany, **1997**.
[32] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837−838.
[33] F. H. Allen, O. Kennard, R. Taylor, *Acc. Chem. Res.* **1983**, *16*, 146−153.

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