

Preparation of Hydroxylamine and *O*-Methylhydroxylamine Complexes of Manganese and Rhenium

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Hydroxylamine and *O*-methylhydroxylamine complexes $[M(NH_2OH)(CO)_n P_{5-n}]BPh_4$ and $[M(NH_2OCH_3)(CO)_n P_{5-n}]BPh_4$ [$M = Mn, Re$; $n = 1, 2, 3$; $P = P(OEt)_3, PPh(OEt)_2, PPh_2OEt$] were prepared by allowing hydrides $MH(CO)_n P_{5-n}$ to react first with triflic acid and then with an excess of hydroxylamine. Bidentate phosphane and phosphite can also be used to prepare both NH_2OH and NH_2OCH_3 complexes of manganese and rhenium of the $[M(NH_2OR)(CO)_2(P-P)-P(OEt)_3]BPh_4$ and $[M(NH_2OR)(CO)_3(P-P)]BPh_4$ [$R = H, CH_3$; $P-P = Ph_2POCH_2CH_2OPPh_2, Ph_2PO(CH_2)_3OPPh_2, Ph_2PN(CH_3)CH_2CH_2N(CH_3)PPh_2$] types with the use of $MH(CO)_2-$

$(P-P)\{P(OEt)_3\}$ and $MH(CO)_3(P-P)$ as precursors. The complexes were characterized spectroscopically and by the X-ray crystal-structure determination of $[Re(NH_2OCH_3)(CO)_2\{PPh(OEt)_2\}_3]BPh_4$ and $[Re(NH_2OCH_3)(CO)_3(Ph_2PO(CH_2)_3OPPh_2)]BPh_4$. Oxidation of the hydroxylamine complexes with $Pb(OAc)_4$ was studied at $-40^\circ C$ and led to an unstable compound tentatively characterized as a nitroxyl $[M]-N(H)=O$ derivative.

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Introduction

Despite the very large number of transition-metal complexes that contain monodentate nitrogenous ligands^[1] such as ammonia, amines, imine, nitrile, nitrogen monoxide, hydrazine, etc., the coordination chemistry of hydroxylamine, NH_2OH , may be considered somewhat unexplored. A glance through the literature, in fact, shows that hydroxylamine complexes are very scarce,^[2] and only recently have some examples of complexes of the $[MX(NH_2OH)(CO)_2(PPh_3)_2]CF_3SO_3$ ($M = Ru, Os$; $X = Cl, Br$) and $[Re(NH_2OH)(CO)_3(PPh_3)_2]CF_3SO_3$ types been reported.^[3]

This feature is rather surprising in view of the fact that the hydrazine molecule, NH_2NH_2 , which is isoelectronic to and somewhat similar to NH_2OH forms a number of stable and isolable transition-metal complexes.^[4,5] A reason for the scarce number of hydroxylamine derivatives may be a result of the presence of the OH group that is bonded to NH_2 , which makes the NH_2OH a poor ligand either as an *N*-bonded, or as an *O*-bonded group. However, the instability of the NH_2OH molecule in the free state may also contribute to the fact that the synthesis of hydroxylamine derivatives is somewhat difficult.

We have interest in the chemistry of transition metal complexes with nitrogen-containing ligands and have reported the synthesis and the reactivity of hydrazine com-

plexes of Mn, Re, Fe, Ru, and Os stabilized by phosphite ligands.^[6] Recently, we have focused our attention on the NH_2OH molecule and reported the preparation of both mono- and bis(hydroxylamine) complexes of ruthenium and osmium of the $[MH(NH_2OH)P_4]^+$ and $[M(NH_2OH)_2-P_4]^{2+}$ types ($M = Ru, Os$; $P = phosphites$).^[7]

These studies have now been extended to manganese and rhenium as a central metal to determine whether the synthesis of hydroxylamine complexes can be achieved for these metals and, if possible, to compare these complexes with related hydrazine derivatives.^[6a,6g] The results of these studies, which allow the synthesis of the first hydroxylamine and methylhydroxylamine complexes of manganese and of new examples for rhenium, are reported here.

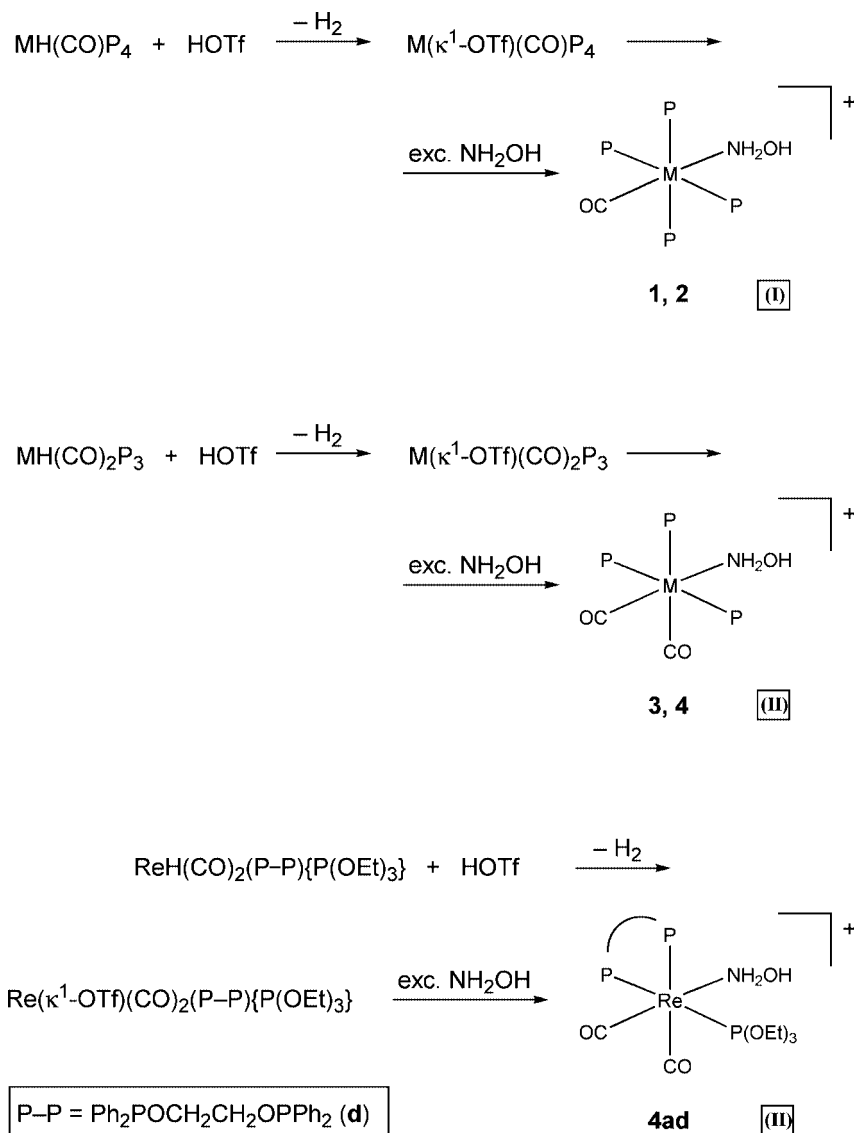
Results and Discussion

The synthesis of hydroxylamine complexes of manganese(I) and rhenium(I) was achieved by the reaction of the $MH(CO)_n P_{5-n}$ hydride^[6a,8] first with an equimolar amount of triflic acid (HOTf) and then with an excess of hydroxylamine, as shown in Scheme 1 and Scheme 2.

Protonation of the $MH(CO)_n P_{5-n}$ hydride with HOTf leads to the evolution of H_2 and the formation of the triflate complexes $M(\kappa^1-OTf)(CO)_n P_{5-n}$.^[6a,8] Substitution of the labile κ^1-OTf ligand with NH_2OH afforded the final hydroxylamine complexes, which were isolated in good yields and characterized. Crucial for the success of the synthesis is to carry out the reaction at $0^\circ C$ for 5–8 hours and to use a large excess of free NH_2OH . Otherwise, either intractable

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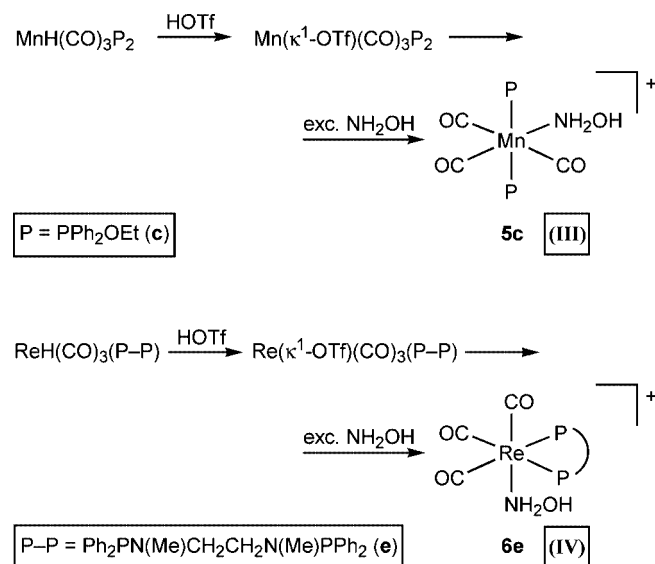
Scheme 1. M = Mn (1, 3), Re (2, 4); P = P(OEt)₃ (a), PPh(OEt)₂ (b); OTf = CF₃SO₃.

mixtures of products, or very low yields in the complexes are obtained. It should also be noted that only the mono-[M(CO)P₄] and the dicarbonyl [M(CO)₂P₃] fragments with P(OEt)₃ and PPh(OEt)₂ ligands allow the synthesis of hydroxylamine complexes. With tricarbonyl complexes [M(CO)₃P₂], a different phosphane such as PPh₂OEt or Ph₂PN(Me)CH₂CH₂N(Me)PPh₂ (P–P) must be used to yield hydroxylamine complexes [Mn(NH₂OH)(CO)₃-(PPh₂OEt)₂]BPh₄ (**5c**) and [Re(NH₂OH)(CO)₃(P–P)]BPh₄ (**6e**) [Scheme 2].

It seems, therefore, that the electronic properties of the [M(CO)_nP_{5–n}] (M = Mn, Re) fragment are important in determining the synthesis and the stabilization of the NH₂OH complexes. In particular, it seems that an electron-poor metal center is not able to stabilize the coordination of NH₂OH. With good π-acceptor^[9] phosphanes such as P(OEt)₃ and PPh(OEt)₂ only mono- and dicarbonyl compounds [M(NH₂OH)(CO)P₄]⁺ and [M(NH₂OH)(CO)₂P₃]⁺ were obtained, while stable tricarbonyl cations

[M(NH₂OH)(CO)₃P₂]⁺ could only be prepared through the use of phosphanes that are less π-acidic than PPh(OEt)₂, such as PPh₂OEt and P–P, which were used in complexes **5c** and **6e**. The presence of four strong π-acceptor carbonyl ligands in the [M(CO)₄P] fragment makes the metal center so electron-poor that it does not allow for the preparation of hydroxylamine complexes with any phosphane used.

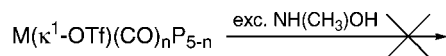
A comparison between the behavior of NH₂OH and the somewhat related NH₂NH₂ ligands toward the [M(CO)_nP_{5–n}] fragment reveals that when hydrazine was used the synthesis of mixed-ligand complexes of manganese and rhenium with carbonyl and phosphite compounds was easily achieved with every [M(CO)_nP_{5–n}] fragment,^[6a,6g] and stable complexes were even obtained with the tetracarbonyl [M(NH₂NH₂)(CO)₄P]⁺ cation, but hydroxylamine was found to be a more problematic ligand. Only appropriate fragments, in fact, allow for the synthesis of the corresponding hydroxylamine derivatives, which highlights the fact that NH₂OH is a molecule that is hard to coordinate.



Scheme 2.

However, the use of the triflate complex $\text{M}(\kappa^1\text{-OTf})(\text{CO})_n\text{P}_{5-n}$ ($n = 1, 2, 3$) as a precursor allows for the synthesis of the first hydroxylamine complexes of manganese, in addition to new examples of rhenium derivatives. Only one example, in fact, of NH_2OH complexes of rhenium^[3b] is reported in the literature, while only quantum chemical calculations^[10] are reported for hydroxylamine complexes of manganese.

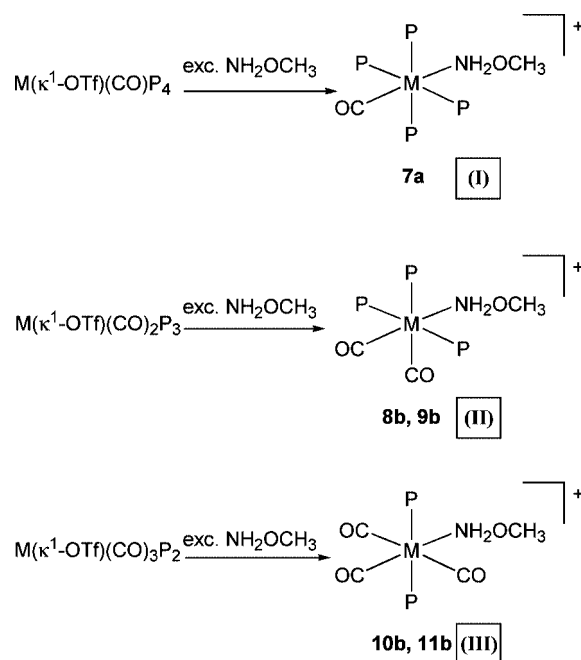
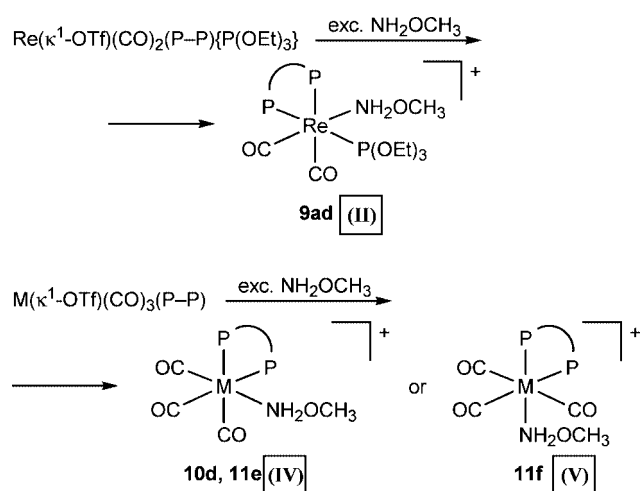
The results obtained with hydroxylamine prompted us to extend our study to the use of both *N*- and *O*-substituted NH_2OH as a ligand. We began to investigate the behavior of the *N*-methyl, $\text{NH}(\text{CH}_3)\text{OH}$, and hydroxylamine towards the triflate complex $\text{M}(\kappa^1\text{-OTf})(\text{CO})_n\text{P}_{5-n}$, but in no case was an *N*-methylhydroxylamine complex obtained. The steric hindrance of the methyl group probably prevents the *N*-coordination of the $\text{NH}(\text{CH}_3)\text{OH}$ molecule.



The *O*-methylhydroxylamine, on the other hand, quickly reacts with the triflate complexes $\text{M}(\kappa^1\text{-OTf})(\text{CO})_n\text{P}_{5-n}$ containing monodentate phosphite ligands (P) to give the NH_2OCH_3 derivatives **7–11** which were isolated in good yield and characterized (Scheme 3).

The reaction also proceeds with triflate precursors $\text{Re}(\kappa^1\text{-OTf})(\text{CO})_2(\text{P-P})\{\text{P}(\text{OEt})_3\}$ and $\text{Re}(\kappa^1\text{-OTf})(\text{CO})_3(\text{P-P})$, containing bidentate phosphane ligands, to yield the related NH_2OCH_3 complexes **9–11**, as shown in Scheme 4.

The syntheses of the NH_2OCH_3 complexes **7–11** can be carried out at room temperature and do not need particular attention to give the final complexes in good yields. Furthermore, in contrast to NH_2OH , the tricarbonyl fragment $\text{M}(\text{CO})_3\text{P}_2$ afforded stable *O*-methylhydroxylamine complexes with all the phosphites used. These results may be attributed to the presence of the methoxy group in NH_2OCH_3 , which makes *O*-methylhydroxylamine a better σ -donor than NH_2OH . As a result, more thermally stable

Scheme 3. M = Re (**7**, **9**, **11**), Mn (**8**, **10**); P = $\text{P}(\text{OEt})_3$ (**a**), $\text{PPh}(\text{OEt})_2$ (**b**).Scheme 4. M = Mn (**10**), Re (**11**); P–P = $\text{Ph}_2\text{POCH}_2\text{CH}_2\text{OPPh}_2$ (**d**), $\text{Ph}_2\text{PN}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{PPh}_2$ (**e**), $\text{Ph}_2\text{PO}(\text{CH}_2)_3\text{OPPh}_2$ (**f**).

complexes were obtained with the NH_2OCH_3 ligand, and suitable crystals for X-ray crystal-structure determination were also obtained with the *O*-methylhydroxylamine complexes **9b** and **11f**.

Once crystallized, both the hydroxylamine complexes **1–6** and the *O*-methylhydroxylamine complexes **7–11** are stable as solids and in a solution of polar organic solvents, in which they behave like 1:1 electrolytes.^[11] The complexes were characterized spectroscopically (Table 1 and Table 2) and by the X-ray crystal-structure determination of $[\text{Re}(\text{NH}_2\text{OCH}_3)(\text{CO})_2\{\text{PPh}(\text{OEt})_2\}_3]\text{BPh}_4$ (**9b**) and $[\text{Re}(\text{NH}_2\text{OCH}_3)(\text{CO})_3\{\text{Ph}_2\text{PO}(\text{CH}_2)_3\text{OPPh}_2\}]\text{BPh}_4$ (**11f**), whose ORTEP drawings are shown in Figure 1 and Figure 2.

Table 1. Selected IR and 300 MHz NMR spectroscopic data for manganese and rhenium complexes.

	Compound	IR ^[a] $\tilde{\nu}$ [cm ⁻¹]	Assign- ment	¹ H NMR ^[b,c]		Spin system	³¹ P{ ¹ H}NMR ^[b,d] δ [ppm] J [Hz]
				δ [ppm] J [Hz]	Assign- ment		
1b	[Mn(NH ₂ OH)(CO){PPh(OEt) ₂ } ₄]BPh ₄	3415 m, br	ν_{OH}	6.11 br ^[e]	OH	A ₄ ^[e]	196.4 s
		3303 m	ν_{NH}	5.30 br	NH ₂		
		3222 m		3.48 m, br	CH ₂		
		1884 s	ν_{CO}	3.19 m, br			
2a	[Re(NH ₂ OH)(CO){P(OEt) ₃ } ₄]BPh ₄	3434 m, br	ν_{OH}	1.11 t	CH ₃	A ₄ ^[e]	118.0 s
		3316 w	ν_{NH}	6.39 t ^[e]	OH		
		3230 m		$J_{\text{H,H}} = 2.3$ 6.17 m, br	NH ₂		
		1888 s	ν_{CO}	$J_{\text{P,H}} = 3.0$ 4.01 q	CH ₂		
3b	[Mn(NH ₂ OH)(CO) ₂ {PPh(OEt) ₂ } ₃]BPh ₄	3414 m	ν_{OH}	1.27 t	CH ₃	A ₂ B ^[f]	P _A : 189.6 P _B : 182.0 $J_{\text{A,B}} = 84.0$
		3289 m	ν_{NH}	6.16 br ^[f]	OH		
		3217 m		5.68 t, br	NH ₂		
		2000 s	ν_{CO}	3.78 m	CH ₂		
4a	[Re(NH ₂ OH)(CO) ₂ {P(OEt) ₃ } ₃]BPh ₄	1909 s		1.25 m	CH ₃	AB ₂ ^[e]	P _A : 142.0 P _B : 135.1 $J_{\text{A,B}} = 36.7$
		3390 m	ν_{OH}	5.50 t, br ^[e]	OH		
		3277 m	ν_{NH}	5.05 m, br	NH ₂		
		3221 m		4.10–3.30 m	CH ₂		
4b	[Re(NH ₂ OH)(CO) ₂ {PPh(OEt) ₂ } ₃]BPh ₄	1986 s	ν_{CO}	1.31 m	CH ₃	AB ₂	P _A : 139.3 P _B : 137.4 $J_{\text{A,B}} = 36.1$
		1902 s		1.14 t			
		3417 m	ν_{OH}	5.79 t, br	OH		
		3287 m	ν_{NH}	5.60 m, br	NH ₂		
4ad	[Re(NH ₂ OH)(CO) ₂ (Ph ₂ POCH ₂ CH ₂ OPPh ₂){P(OEt) ₃ }]BPh ₄	3218 m		3.94 m	CH ₂	ABC	P _A : 124.0 P _B : 121.3 P _C : 112.6 $J_{\text{A,B}} = 34.0$ $J_{\text{A,C}} = 248.1$ $J_{\text{B,C}} = 27.2$
		1998 s	ν_{CO}	3.84 m			
		1915 s		1.37 m	CH ₃		
				1.35 t			
5c	[Mn(NH ₂ OH)(CO) ₃ (PPh ₂ OEt) ₂]BPh ₄	3383 m, br	ν_{OH}	4.95 m, br	NH ₂	A ₂ B ^[f]	158.1
		3348 m	ν_{NH}	4.59 m, br	OH		
		3215 m		4.50–3.88 m	CH ₂		
		1988 s	ν_{CO}	4.10 m			
6e	[Re(NH ₂ OH)(CO) ₃ {Ph ₂ PN(CH ₃)CH ₂ CH ₂ N(CH ₃)PPh ₂ }]BPh ₄	1889 s		1.16 t	CH ₃	A ₂	66.1 s
7a	[Re(NH ₂ OCH ₃)(CO){P(OEt) ₃ } ₄]BPh ₄	3381 m, br	ν_{OH}	4.87 t, br	OH	A ₂	
		3243 m	ν_{NH}	3.54 m, br	NH ₂		
		3212 m		3.80 m	CH ₂		
		2047 s	ν_{CO}	3.28 m			
7b	[Mn(NH ₂ OCH ₃)(CO) ₂ {PPh(OEt) ₂ } ₃]BPh ₄	1979 s		2.50 s	NCH ₃	A ₂ B ^[f]	P _A : 194.1 P _B : 187.9 $J_{\text{A,B}} = 93.0$
		1913 s					
		3269 m	ν_{NH}	4.88 t ^[g]	NH ₂		
		3223 m		$J_{\text{P,H}} = 6$			
8b	[Mn(NH ₂ OCH ₃)(CO) ₂ {PPh(OEt) ₂ } ₃]BPh ₄	1993 s	ν_{CO}	3.95 m	CH ₂	A ₂ B ^[f]	P _A : 194.1 P _B : 187.9 $J_{\text{A,B}} = 93.0$
		1907 s		2.88 s	OCH ₃		
				1.36 m	CH ₃ phos		
				1.34 t			
9b	[Re(NH ₂ OCH ₃)(CO) ₂ {PPh(OEt) ₂ } ₃]BPh ₄			1.30 t		AB ₂ ^[g]	P _A : 139.1 P _B : 138.4 $J_{\text{A,B}} = 34.9$
		3238 m	ν_{NH}	4.75 t ^[g]	NH ₂		
		2025 s	ν_{CO}	$J_{\text{P,H}} = 6$			
		1909 s		4.09–3.80 m	CH ₂		
9c	[Mn(NH ₂ OCH ₃)(CO) ₂ {PPh(OEt) ₂ } ₃]BPh ₄			2.70 s	OCH ₃	AB ₂ ^[g]	P _A : 139.1 P _B : 138.4 $J_{\text{A,B}} = 34.9$
				1.37 m	CH ₃ phos		
				1.32 t			

Table 1. Continued

Compound		IR ^[a] $\tilde{\nu}$ [cm ⁻¹]	Assign- ment	¹ H NMR ^[b,c] δ [ppm] J [Hz]	Assign- ment	Spin system	³¹ P{ ¹ H} NMR ^[b,d] δ [ppm] J [Hz]	
9ad	[Re(NH ₂ OCH ₃)(CO) ₂ (Ph ₂ POCH ₂ CH ₂ OPPh ₂){P(OEt) ₃ }]BPh ₄	3245 m	ν_{NH}	4.32 m, br	NH ₂	ABC	P _A : 131.0	
		3215 m		4.08 m	CH ₂		P _B : 113.1	
		1995 s	ν_{CO}	4.55–4.27 m			P _C : 109.4	
		1891 s		2.64 s 1.14 t	OCH ₃ CH ₃ phos		$J_{\text{A,B}}$ = 33.2 $J_{\text{A,C}}$ = 245.2 $J_{\text{B,C}}$ = 30.2	
10b	[Mn(NH ₂ OCH ₃)(CO) ₃ {PPh(OEt) ₂ } ₂]BPh ₄	3261 m		4.83 t ^[e]	NH ₂	A ₂ ^[e]	188.7 s, br	
		3228 m		$J_{\text{P,H}}$ = 6				
		2056 m		4.05 m	CH ₂			
		1975 s		2.90 s	OCH ₃			
10d	[Mn(NH ₂ OCH ₃)(CO) ₃ (Ph ₂ POCH ₂ CH ₂ OPPh ₂)]BPh ₄	1943 s		1.38 t	CH ₃ phos	A ₂	165.8 s	
		3257 m	ν_{NH}	4.58 m, br	NH ₂			
		3225 m		4.35–4.00 m	CH ₂			
		2042 s	ν_{CO}	3.23 s	OCH ₃			
11b	[Re(NH ₂ OCH ₃)(CO) ₃ {PPh(OEt) ₂ } ₂]BPh ₄	1977 s				A ₂	135.2 s	
		1945 s						
		3259 m	ν_{NH}	5.48 t	NH ₂			
		3215 m		$J_{\text{P,H}}$ = 4.5				
11e	[Re(NH ₂ OCH ₃)(CO) ₃ {Ph ₂ PN(CH ₃)CH ₂ CH ₂ N(CH ₃)PPh ₂ }]BPh ₄	2072 w	ν_{CO}	4.08 m	CH ₂	A ₂	66.1 s	
		1981 s		2.99 s	OCH ₃			
		1949 s		1.44 s	CH ₃ phos			
		3271 w	ν_{NH}	4.32 m	NH ₂			
11f	[Re(NH ₂ OCH ₃)(CO) ₃ (Ph ₂ POCH ₂ CH ₂ CH ₂ OPPh ₂)]BPh ₄	3235 w		3.81 m	CH ₂	AB	P _A : 110.0 P _B : 115.0 $J_{\text{A,B}}$ = 32.5	
		2044 s	ν_{CO}	3.26 m				
		1971 s		2.54 s, br	OCH ₃ + NCH ₃			
		1925 s						
		3246 m	ν_{NH}	4.76 s, br	NH ₂			
		3217 m		3.72 m	OCH ₂			
		2066 m	ν_{CO}	3.50 m				
		1971 s		2.39 s	OCH ₃			
		1950 s		1.95 m	CH ₂			

[a] In KBr pellets. [b] In CD₂Cl₂ at 20 °C, unless otherwise noted. [c] Phenyl proton resonances omitted. [d] Positive shift downfield from 85% H₃PO₄. [e] At –30 °C. [f] At –70 °C. [g] At 0 °C.

Compound **9b** does not show any interaction between the complex cation and the BPh₄[–] anion, but in the case of **11f** an interionic interaction, with parameters: distance H $\cdots$ Ct1 = 2.66(3) Å, distance N $\cdots$ Ct1 = 3.530(3) Å and angle NH $\cdots$ Ct1 = 167(3)° (where Ct1 is the centroid of one of the phenyl rings of the anion) indicates an NH– π hydrogen bond between the nitrogen of the *O*-methylhydroxylamine and a phenyl ring of the BPh₄[–] anion. Compound **11f** crystallized with a molecule of CH₂Cl₂ solvent to give a supramolecular arrangement of the crystal through a hydrogen-bonded network involving the cation [parameters, H $\cdots$ Ct2 = 2.98 Å, C $\cdots$ Ct2 = 3.805(4) Å, angle CH $\cdots$ Ct2 = 141.2°; H $\cdots$ O4' = 2.74 Å, C $\cdots$ O4' = 3.649(5) Å, angle CHO4' = 152.4°. Symmetry operation 2–*x*, 2–*y*, 2–*z*; Ct2 stands for the centroid of the phenyl ring labeled as C31 to C36.]

In both cationic complexes the rhenium atom is coordinated in a slightly distorted octahedral fashion. In **9b** there are three meridional phosphonite ligands PPh(OEt)₂, two *cis* carbonyl ligands and an *N*-coordinated *O*-methylhydroxylamine. In **11f** there are three *mer* carbonyl ligands, two phosphorus atoms of the bidentated phosphinite ligand PPh₂{O(CH₂)₃O}PPh₂, and an *N*-coordinated *O*-methylhydroxylamine. The coordination polyhedra in **11f** is more irregular; the *cis* angles range from 86.26(9) to 95.47(3)°, and

95.47(3) is the largest value that corresponds to the chelate angle of the bidentate ligand. This fact was already observed in other compounds that bear this ligand^[8d] and it is probably due to the steric requirement of the ligand.

For **11f**, the eight-membered ring adopts the disposition of a chair, in such a way that the phosphorus and the oxygen atoms are in a planar situation (rms deviation of 0.0229) with the rhenium atom slightly below the plane [0.463(2) Å], and the three carbon atoms form another almost parallel plane, [dihedral angle of 4.5(4)°] at 1.21(1) Å (average for the two nearest carbon atoms). This conformation was previously found for complexes with this ligand.^[8d]

The Re–P bond lengths are in the range observed for complexes with phosphonite or phosphinite ligands.^[8d,12] For **9b**, the Re–P distances for the mutually *trans* phosphonite ligands [2.381(3) Å (average)] are shorter than that of the phosphonite *trans* to a carbonyl ligand [2.413(3) Å] because of the stronger π -acceptor character of the CO group. The same behavior is observed in compound **11f** in which the Re–P1 distance is shorter [2.3647(8) Å] than Re–P2 [2.4608(8) Å].

The Re–C bond lengths in **9b** also show the different *trans* influence of the ligand: Re–C2 (*trans* to a P atom) is 0.063 Å longer than Re–C3 (*trans* to an N atom) because

Table 2. 300 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopic data for selected manganese and rhenium complexes.

	Compound	$^{13}\text{C}\{^1\text{H}\}$ NMR ^[a] δ [ppm], J [Hz]	Assignment
3b	$[\text{Mn}(\text{NH}_2\text{OH})(\text{CO})_2\{\text{PPh}(\text{OEt})_2\}_3]\text{BPh}_4^{[\text{b}]}$	221.1 m	CO
		216.5 m	
		65.7 d	CH ₂
		64.8 d	
		16.3 s	CH ₃
4b	$[\text{Re}(\text{NH}_2\text{OH})(\text{CO})_2\{\text{PPh}(\text{OEt})_2\}_3]\text{BPh}_4^{[\text{b}]}$	16.1 s	
		198.3 m	CO
		195.5 m	
		63.5 m	CH ₂
		16.3 m	CH ₃
4ad	$[\text{Re}(\text{NH}_2\text{OH})(\text{CO})_2(\text{Ph}_2\text{POCH}_2\text{CH}_2\text{OPPh}_2)\{\text{P}(\text{OEt})_3\}]\text{BPh}_4^{[\text{c}]}$	196.9 m	CO
		193.2 m	
		65.2 s, br	CH ₂ bident.
		64.8 s, br	
		63.0 d, $J_{\text{C,P}} = 8$	CH ₂
7a	$[\text{Re}(\text{NH}_2\text{OCH}_3)(\text{CO})\{\text{P}(\text{OEt})_3\}_4]\text{BPh}_4^{[\text{b}]}$	15.7 d, $J_{\text{C,P}} = 6$	CH ₃
		196.3 qnt	CO
		66.8 s	OCH ₃
		61.7 t	CH ₂
		16.3 s	CH ₃
8b	$[\text{Mn}(\text{NH}_2\text{OCH}_3)(\text{CO})_2\{\text{PPh}(\text{OEt})_2\}_3]\text{BPh}_4^{[\text{b}]}$	221.8 m	CO
		217.9 m	
		67.1 s	OCH ₃
		65.2 d	CH ₂
		64.1 d	
9ad	$[\text{Re}(\text{NH}_2\text{OCH}_3)(\text{CO})_2(\text{Ph}_2\text{POCH}_2\text{CH}_2\text{OPPh}_2)\{\text{P}(\text{OEt})_3\}]\text{BPh}_4^{[\text{c}]}$	16.5 s	CH ₃
		16.2 s	
		197.3 m	CO
		193.4 m	
		66.7 s	OCH ₃
11b	$[\text{Re}(\text{NH}_2\text{OCH}_3)(\text{CO})_3\{\text{PPh}(\text{OEt})_2\}_2]\text{BPh}_4^{[\text{b}]}$	65.3 s, br	CH ₂ bident.
		64.1 s, br	
		62.9 d, $J_{\text{C,P}} = 8$	CH ₂
		15.8 d, $J_{\text{C,P}} = 7$	CH ₃
		190.1 t, $J_{\text{C,P}} = 8$	CO
11e	$[\text{Re}(\text{NH}_2\text{OCH}_3)(\text{CO})_3\{\text{Ph}_2\text{PN}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{PPh}_2\}]\text{BPh}_4^{[\text{c}]}$	189.8 t, $J_{\text{C,P}} = 10$	
		67.9 s	OCH ₃
		64.7 m	CH ₂
		16.3 m	CH ₃
		194.2 m	CO
11f	$[\text{Re}(\text{NH}_2\text{OCH}_3)(\text{CO})_3(\text{Ph}_2\text{POCH}_2\text{CH}_2\text{CH}_2\text{OPPh}_2)]\text{BPh}_4^{[\text{c}]}$	188.3 m	
		66.2 s	OCH ₃
		52.1 t, $J_{\text{C,P}} = 7$	CH ₂
		39.5 t, $J_{\text{C,P}} = 3$	NCH ₃
		191.0 m	CO
		189.1 m	
		65.4 s	OCH ₃
		64.7 s, br	OCH ₂
		63.4 s, br	
		29.6 s, br	–CH ₂ –

[a] Phenyl resonances omitted. [b] In CD_2Cl_2 at 20 °C. [c] In CDCl_3 at 20 °C.

of the stronger π -acceptor character of the phosphonite ligand.

In both cases, the geometrical parameters of the *O*-methylhydroxylamine ligand are in accordance with an sp^3 character for both the oxygen and the nitrogen atom,^[13] and the conformation of the ligand is such that all the atoms belong to the same plane (Re–N1–O1–C1) (rms deviation of 0.0173 and 0.0405, respectively). The Re–N bonds are similar to those found in previously reported^[3b] hydroxylaminerhenium(I) complexes.

The presence of the NH_2OH or NH_2OCH_3 ligand in the complexes can be determined by IR and NMR spectroscopy (Table 1). The IR spectra of the hydroxylamine derivatives show one medium-intensity band at $\tilde{\nu} = 3381\text{--}3434\text{ cm}^{-1}$ for the νOH stretch, and two bands at $\tilde{\nu} = 3212\text{--}3348\text{ cm}^{-1}$ attributed to the νNH stretch of the NH_2OH ligand. In the spectra of the related NH_2OCH_3 complexes only two medium-intensity bands at $\tilde{\nu} = 3215\text{--}3271\text{ cm}^{-1}$ for the νNH stretch were observed.

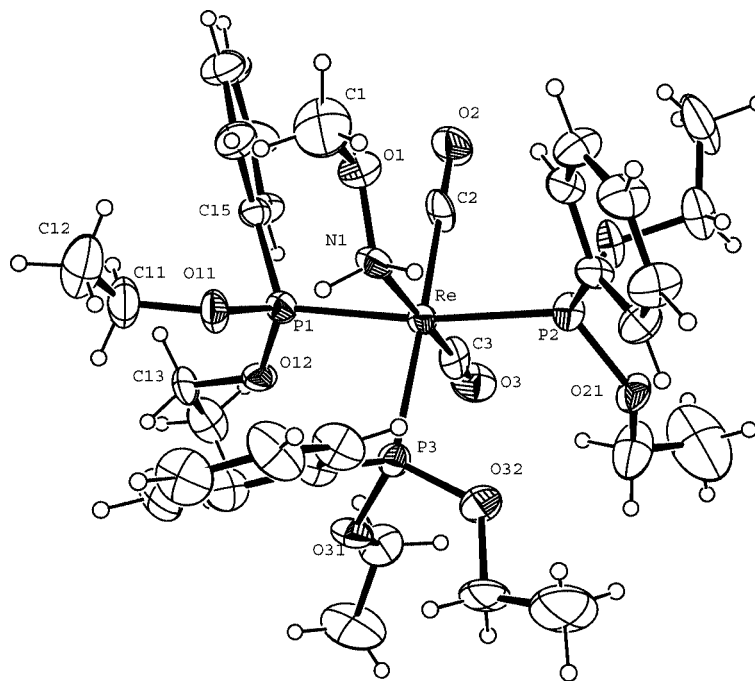


Figure 1. The cation of $[\text{Re}(\text{NH}_2\text{OCH}_3)(\text{CO})_2\{\text{PPh}(\text{OEt})_2\}_3]\text{BPh}_4$ (**9b**) drawn at 30% probability level.

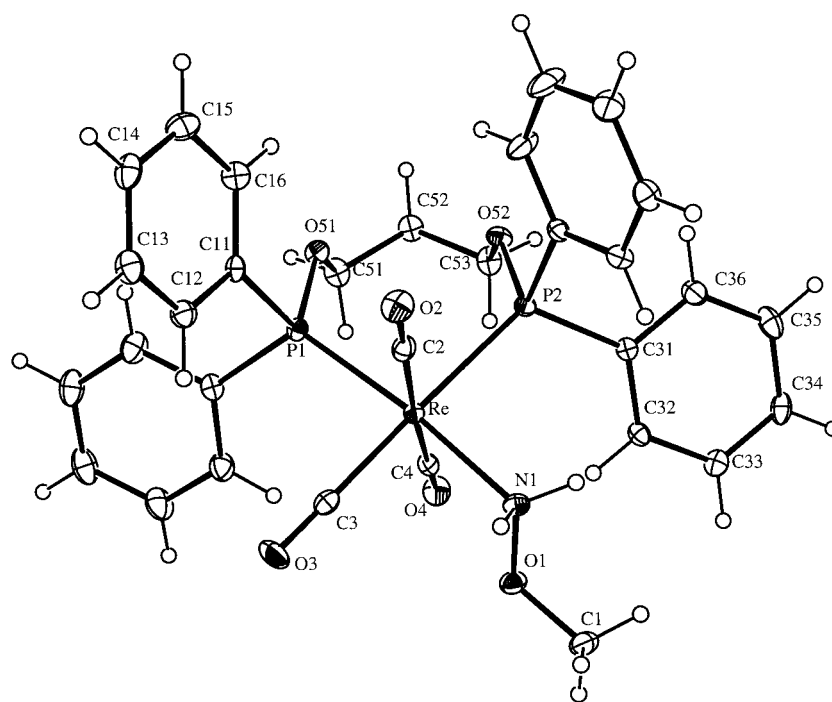


Figure 2. The cation of $[\text{Re}(\text{NH}_2\text{OCH}_3)(\text{CO})_3\{\text{Ph}_2\text{PO}(\text{CH}_2)_3\text{OPPh}_2\}]\text{BPh}_4$ (**11f**) drawn at 30% probability level.

The NMR spectra of the NH_2OH complexes **1–5**, which contain monodentate phosphite ligands, indicate that they are fluxional. The slightly broad signal that appears at room temperature in the proton spectra, in fact, resolves into two signals for the ligands at 243 K. At this temperature the spectra show, besides the signals for the phosphite and the BPh_4 anion, a triplet at $\delta = 4.41\text{--}6.39$ ppm ($J_{\text{H-H}} = 2.3$ Hz) attributed to the OH protons of

the NH_2OH ligand and one slightly broad multiplet at $\delta = 3.54\text{--}6.17$ ppm for the NH_2 protons of NH_2OH group. Decoupling experiments and COSY spectra were used to confirm these assignments and to determine the value of $J_{\text{H,P}}$ for the NH_2 protons. Values between $J_{\text{H,P}} = 2$ and 3 Hz were determined for the NH_2OH complexes **1–5**, which strongly supports the presence of an *N*-bonded NH_2OH ligand.

The proton spectra of complexes **4ad** and **6c**, which contain the bidentate phosphane ligand show, apart from no fluxionality, the characteristic signals for the NH_2 and the OH protons, in agreement, also in this case, with the presence of the hydroxylamine ligand.

The ^1H NMR spectra of the NH_2OCH_3 derivatives show a singlet at $\delta = 2.39\text{--}3.49$ ppm attributed to the methoxy group, OCH_3 , and a multiplet at $\delta = 4.32\text{--}6.19$ ppm for the NH_2 protons of the *O*-methylhydroxylamine ligand. Decoupling experiments indicate that the multiplet for the NH_2 protons is a result of the coupling of the phosphorus nuclei of the phosphane to the NH_2OCH_3 ligand with $J_{\text{H,P}} = 4\text{--}6$ Hz, which is in agreement with the *N*-bonded coordination of the NH_2OCH_3 ligand.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the monocarbonyl complexes $[\text{M}(\text{NH}_2\text{OH})(\text{CO})\text{P}_4]^+$ and $[\text{M}(\text{NH}_2\text{OCH}_3)(\text{CO})\text{P}_4]^+$ (**1**, **2**, **7**) appear as a slightly broad signal at room temperature, which resolves into a sharp singlet at 243 K, in agreement with the magnetic equivalence of the four phosphite ligands. On the basis of these data, a geometry of type **I** (Scheme 1 and Scheme 3), with the carbonyl and the hydroxylamine ligands in a mutually *trans* position, can reasonably be proposed.

The IR spectra of the dicarbonyl complexes $[\text{M}(\text{NH}_2\text{OR})(\text{CO})_2\text{P}_3]^+$ (**3**, **4**, **8**, **9**) ($\text{R} = \text{H}$, CH_3) show two strong νCO bands which indicate a mutually *cis* position of the two carbonyl ligands. These two CO groups, however, are not magnetically equivalent, because they show two well-separated multiplets at 221.8 and 193.2 ppm in the ^{13}C NMR spectra (Table 2). At room temperature, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the dicarbonyl complexes that contain the monodentate phosphite ligands (**3b**, **4a**, **4b**, **8b**, **9b**) show a rather broad multiplet which resolves into an AB_2 pattern at temperatures between 0 and -70°C . This indicates that there are two phosphites that are magnetically equivalent but different from the third phosphite. On the basis of these data, a *mer-cis* geometry of type **II** (Scheme 1 and Scheme 3) similar to that observed in the solid state for **9b** can reasonably be proposed for these dicarbonyl-hydroxylamine derivatives.

In the temperature range between $+20$ and -80°C , the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the dicarbonyl complexes **4ad** and **9ad** appear as an ABC multiplet, which can be easily simulated with the parameters reported in Table 1. These parameters indicate that, while two of the $J_{\text{P,P}}$ values are comparable ($J_{\text{P,P}} = 27\text{--}34$ Hz) the third is considerably higher than the others ($J_{\text{P,P}} = 245\text{--}248$ Hz), which suggests that two of the three phosphanes are in a mutually *trans* position. Taking into account that the IR spectra suggest the presence of two CO groups in a mutually *cis* position, we can then reasonably propose a *mer-cis* geometry of type **II** (Scheme 1 and Scheme 4) for the complexes containing a bidentate phosphane ligand.

At room temperature, the ^{31}P NMR spectra of the tricarbonyl cations $[\text{M}(\text{NH}_2\text{OH})(\text{CO})_3\text{P}_2]^+$ (**5c**) and $[\text{M}(\text{NH}_2\text{OCH}_3)(\text{CO})_3\text{P}_2]^+$ (**10b**, **11b**) appear as a rather broad signal which resolves into a sharp singlet as the temperature is lowered, which indicates the magnetic equivalence

of the two phosphane ligands. The IR spectra show, in the νCO region, three bands; one band of medium intensity and two strong bands, which suggests a *mer* arrangement of the three carbonyl ligands. On the basis of these data, a *mer-trans* geometry **III** may be proposed for the tricarbonyl complexes **5c**, **10b**, **11b**.

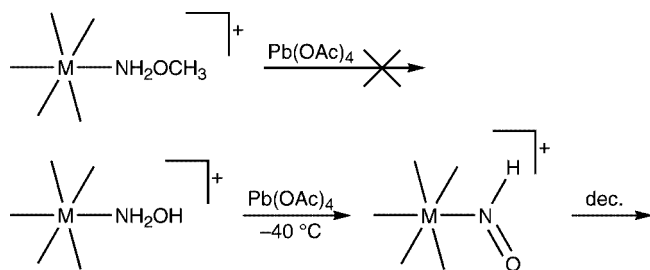
The IR spectra of the tricarbonyl complexes **6e**, **10d** and **11e**, containing bidentate phosphane ligands, show three strong absorptions in the νCO region, which indicates a *fac* arrangement of the three carbonyl ligands. In the temperature range between $+20$ and -80°C the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra appear as a sharp singlet, in agreement with the magnetic equivalence of the two phosphite ligands. On the basis of these data, a *fac* geometry (**IV**) can reasonably be proposed for these hydroxylamine complexes. Finally, a *mer-cis* geometry of type **V** (Scheme 4), like that found in the solid state, can be proposed for the tricarbonyl complex $[\text{Re}(\text{NH}_2\text{OCH}_3)(\text{CO})_3\{\text{Ph}_2\text{PO}(\text{CH}_2)_3\text{OPPh}_2\}]\text{BPh}_4$ (**11f**), whose IR spectrum shows one medium-intensity band and two strong bands in the νCO region. The ^{31}P NMR spectrum has an AB multiplet.

The *mer-cis* geometry observed for compound **11f** is unusual as compared with those of related complexes **10d**, **11e** that contain bidentate phosphane ligands and may be attributed to the steric requirement of the $\text{Ph}_2\text{PO}(\text{CH}_2)_3\text{OPPh}_2$ ligand, because the π -acceptor properties of the P–P phosphites are very similar in complexes **10d** and **11f**.

The fluxional behavior observed in some of our hydroxylamine complexes may be due to an intermolecular process that involves dissociation of NH_2OR or phosphite ligands. NMR experiments in the presence of free phosphite or hydroxylamine, however, seem to exclude such a process. Therefore, it is plausible to assume that the fluxional process simply results in the inter-exchange of the position of both the P- and the NH_2OR ligands at room temperature, and the progressive decrease of this change as the temperature is lowered leads to a static A_2B or ABC system at -70°C .

Reactivity studies of the hydroxylamine complexes were undertaken, and the preliminary results indicate that they are relatively robust complexes. Substitution of the NH_2OH or NH_2OCH_3 ligand by carbonyl or phosphane is very slow at room temperature, while reflux conditions cause the decomposition of the complexes.

Oxidation reactions with $\text{Pb}(\text{OAc})_4$ were also tested, and the results show (Scheme 5) that, while the *O*-methylhydroxylamine complexes **7–11** do not react with $\text{Pb}(\text{OAc})_4$ under any conditions, hydroxylamines **1–6** quickly react with $\text{Pb}(\text{OAc})_4$ at -40°C to give a pale-yellow solution. Unfortunately, the solid separated from this solution is not a pure species, but its ^1H NMR spectrum shows, in the case of the oxidation of complex $[\text{Re}(\text{NH}_2\text{OH})(\text{CO})_2\{\text{PPh}(\text{OEt})_2\}_3]\text{BPh}_4$ (**4b**), a slightly broad signal at $\delta = 19.7$ ppm. This resonance may be attributed^[2b,3b] to the NH proton of the $\text{N}(\text{H})=\text{O}$ group of the $[\text{Re}\{\text{N}(\text{H})=\text{O}\}(\text{CO})_2\{\text{PPh}(\text{OEt})_2\}_3]^+$ cation, formed by selective oxidation of the NH_2OH ligand, as shown in Scheme 5.



Scheme 5. M = Mn, Re.

Unfortunately, the nitroxyl $[\text{Re}\{\text{N}(\text{H})=\text{O}\}(\text{CO})_2\text{P}_3]^+$ derivatives are unstable even at -40°C and were separated only as traces. The IR spectrum of the separated solid did not show a signal for the nitrosyl $[\text{Re}]\text{--NO}$ complex, which would result from the deprotonation of $[\text{Re}]\text{--N}(\text{H})=\text{O}$. This observation suggests that the deprotonation does not take place. Our results, therefore, prove that the $\text{M}(\text{CO})_n\text{P}_{5-n}$ fragment is able to stabilize the coordination of the hydroxylamine group, but not that of the nitroxyl ligand.

Conclusions

In this report we have highlighted that the synthesis of the unprecedented hydroxylamine and the *O*-methylhydroxylamine complexes of manganese can be achieved through the use of mixed-ligand $\text{Mn}(\text{OTf})(\text{CO})_n\text{P}_{5-n}$ complexes with mono- or bidentate phosphites and carbonyls as precursors. New NH_2OH and NH_2OCH_3 derivatives of rhenium were also prepared which allowed for the first structural parameters of an *O*-methylhydroxylamine complex to be obtained. Oxidation of the hydroxylamine complexes with $\text{Pb}(\text{OAc})_4$ at -40°C was also studied and led to the unstable $[\text{M}]\text{--N}(\text{H})\text{O}$ nitroxyl derivative.

Experimental Section

General: All synthetic work was carried out under an inert atmosphere by using standard Schlenk techniques or a flaccuum 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 with appropriate drying agents, degassed on a vacuum line and distilled into vacuum-tight storage flasks. The phosphite $\text{P}(\text{OEt})_3$ (Aldrich) was purified by distillation under nitrogen, while $\text{PPh}(\text{OEt})_2$ and PPh_2OEt were prepared by the method of Rabinowitz and Pellon.^[14] The bidentate phosphanes $\text{Ph}_2\text{PO}(\text{CH}_2)_n\text{OPPh}_2$ ($n = 2, 3$) and $\text{Ph}_2\text{PN}(\text{CH}_3)\text{--CH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{PPh}_2$ were prepared by the reported methods.^[8c,8d,15] $\text{Re}_2(\text{CO})_{10}$ was purchased from Pressure Chemical Co. (U.S.A.) while $\text{Mn}_2(\text{CO})_{10}$ was purchased from Aldrich, and both compounds were used as received. Hydroxylamine (NH_2OH), *N*-methylhydroxylamine [$\text{NH}(\text{CH}_3)\text{OH}$], and *O*-methylhydroxylamine (NH_2OCH_3) were prepared by a slight modification of a reported method,^[16] which involved the treatment of hydroxylamine hydrochloride with sodium ethylate in ethanol. The free NH_2OH was isolated as a white solid, while $\text{NH}(\text{CH}_3)\text{OH}$ and NH_2OCH_3 were prepared in solution just prior to use. Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded with a Nicolet

Magna 750 FT-IR or Perkin–Elmer Spectrum One spectrophotometer. NMR spectra (^1H , ^{13}C , ^{31}P) were obtained with Bruker AC200, AVANCE 300, and ARX 400 spectrometers at temperatures varying between -90 and $+30^\circ\text{C}$, unless otherwise noted. ^1H - and ^{13}C spectra are referred to internal tetramethylsilane, while $^{31}\text{P}\{^1\text{H}\}$ chemical shifts are reported with respect to 85% H_3PO_4 , with downfield shifts considered positive. The COSY, HMQC, and HMBC NMR experiments were performed with their standard programs. The SwaN-MR and g-NMR software packages^[17] were used to treat the NMR spectroscopic data and for the simulation. The conductivity of $10^{-3}\text{ mol}\cdot\text{dm}^{-3}$ solutions of the complexes in CH_3NO_2 at 25°C was measured with a Radiometer CDM 83 instrument.

Preparation of the Complexes: The hydride complexes $\text{MH}(\text{CO})_n\text{P}_{5-n}$ [M = Mn, Re; P = $\text{P}(\text{OEt})_3$, $\text{PPh}(\text{OEt})_2$, PPh_2OEt ; $n = 1, 2, 3, 4$] were prepared by following the previously reported method.^[6c,8a,8b] The related complexes $\text{MH}(\text{CO})_2(\text{P}(\text{P}))\{\text{P}(\text{OEt})_3\}$ and $\text{MH}(\text{CO})_3(\text{P}(\text{P}))$ [P–P = $\text{Ph}_2\text{POCH}_2\text{CH}_2\text{OPPh}_2$, $\text{Ph}_2\text{PO}(\text{CH}_2)_3\text{OPPh}_2$, $\text{Ph}_2\text{PN}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{PPh}_2$] were also obtained by a known method.^[8c,8d]

$[\text{Mn}(\text{NH}_2\text{OH})(\text{CO})_n\text{P}_{5-n}]\text{BPh}_4$ (1b, 3b, 5c) [P = $\text{PPh}(\text{OEt})_2$ (b), PPh_2OEt (c); $n = 1$ (1); $n = 2$ (3); $n = 3$ (5)]: An equimolar amount of $\text{CF}_3\text{SO}_3\text{H}$ (0.2 mmol, 18 μL) was added to a solution of the appropriate hydride $\text{MnH}(\text{CO})_n\text{P}_{5-n}$ (0.2 mmol) in CH_2Cl_2 (10 mL) cooled to -196°C . The reaction mixture was brought to room temperature, stirred for 1 h, and then cooled again to -196°C . An excess of hydroxylamine (1 mmol, 0.91 mL of a 1.1 M solution in ethanol) was added, and the resulting solution was brought to 0°C and stirred for 8 h. The solvent was removed under reduced pressure. The oil that was obtained was treated with ethanol (1.5 mL) containing an excess amount of NaBPh_4 (0.4 mmol, 137 mg). A yellow solid slowly separated out from the resulting solution, which was allowed to stand at -25°C overnight to complete the precipitation. The solid was filtered and crystallized at 0°C from CH_2Cl_2 and ethanol. Yield: 115 mg for 1b (47%), 131 mg for 3b (62%), and 103 mg for 5c (54%).

1b: $\text{C}_{65}\text{H}_{83}\text{BMnNO}_{10}\text{P}_4$ (1228.01): calcd. C 63.58, H 6.81, N 1.14; found C 63.82, H 6.95, N 1.10. $A_M = 55.5\ \Omega^{-1}\text{ mol}^{-1}\text{ cm}^2$.

3b: $\text{C}_{56}\text{H}_{68}\text{BMnNO}_9\text{P}_3$ (1057.82): calcd. C 63.58, H 6.48, N 1.32; found C 63.45, H 6.57, N 1.27. $A_M = 56.0\ \Omega^{-1}\text{ mol}^{-1}\text{ cm}^2$.

5c: $\text{C}_{55}\text{H}_{53}\text{BMnNO}_6\text{P}_2$ (951.72): calcd. C 69.41, H 5.61, N 1.47; found C 69.35, H 5.75, N 1.44. $A_M = 51.9\ \Omega^{-1}\text{ mol}^{-1}\text{ cm}^2$.

$[\text{Re}(\text{NH}_2\text{OH})(\text{CO})_n\text{P}_{5-n}]\text{BPh}_4$ (2a, 4a, 4b) [P = $\text{P}(\text{OEt})_3$ (a), $\text{PPh}(\text{OEt})_2$ (b); $n = 1$ (2); $n = 2$ (4)]: These complexes were prepared as per the related manganese complexes 1, 3, 5 with the use of hydride $\text{ReH}(\text{CO})_n\text{P}_{5-n}$ as a precursor. The reaction mixture was stirred for 4 h at room temperature. Yield: 175 mg for 2a (71%), 142 mg for 4a (65%), and 147 mg for 4b (62%).

2a: $\text{C}_{49}\text{H}_{83}\text{BNO}_{14}\text{P}_4\text{Re}$ (1231.10): calcd. C 47.81, H 6.80, N 1.14; found C 48.02, H 6.90, N 1.06. $A_M = 53.8\ \Omega^{-1}\text{ mol}^{-1}\text{ cm}^2$.

4a: $\text{C}_{44}\text{H}_{68}\text{BNO}_{12}\text{P}_3\text{Re}$ (1092.95): calcd. C 48.35, H 6.27, N 1.28; found C 48.44, H 6.25, N 1.19. $A_M = 54.3\ \Omega^{-1}\text{ mol}^{-1}\text{ cm}^2$.

4b: $\text{C}_{56}\text{H}_{68}\text{BNO}_9\text{P}_3\text{Re}$ (1189.09): calcd. C 56.57, H 5.76, N 1.18; found C 56.66, H 5.90, N 1.12. $A_M = 54.7\ \Omega^{-1}\text{ mol}^{-1}\text{ cm}^2$.

$[\text{Re}(\text{NH}_2\text{OH})(\text{CO})_2(\text{Ph}_2\text{POCH}_2\text{CH}_2\text{OPPh}_2)\{\text{P}(\text{OEt})_3\}]\text{BPh}_4$ (4ad): This complex was prepared as per the related rhenium complexes 2 and 4 with the use of $\text{ReH}(\text{CO})_2(\text{Ph}_2\text{POCH}_2\text{CH}_2\text{OPPh}_2)\{\text{P}(\text{OEt})_3\}$ as a precursor. The reaction mixture was stirred at room temperature for 6 h. Yield: 131 mg (55%). $\text{C}_{58}\text{H}_{62}\text{BNO}_8\text{P}_3\text{Re}$

(1191.06): calcd. C 58.49, H 5.25, N 1.18; found C 58.62, H 5.29, N 1.15. $A_M = 50.0 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$.

[Re(NH₂OH)(CO)₃(Ph₂PN(Me)CH₂CH₂N(Me)PPh₂)]BPh₄ (6e): This complex was prepared as per the related rhenium complexes with the use of hydride ReH(CO)₃(Ph₂PN(CH₃)CH₂CH₂N(CH₃)PPh₂). The reaction was stirred for 7 h at 0 °C; yield 175 mg (81%). C₅₅H₅₃BN₃O₄P₂Re (1079.00): calcd. C 61.22, H 4.95, N 3.89; found C 61.05, H 4.88, N 3.68. $A_M = 52.6 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$.

[Re(NH₂OMe)(CO)_nP_{5-n}]BPh₄ (7a, 9b, 11b) and [Mn(NH₂OMe)(CO)_nP_{5-n}]BPh₄ (8b, 10b) [P = P(OEt)₃ (a), PPh(OEt)₂ (b); n = 1 (7); n = 2 (8, 9); n = 3 (10, 11)]: An equimolar amount of CF₃SO₃H (0.2 mmol, 18 µL) was added to a solution of the appropriate hydride MH(CO)_nP_{5-n} (0.2 mmol) in CH₂Cl₂ (5 mL) cooled to –196 °C. The reaction mixture was brought to room temperature, stirred for 1 h, and then cooled again to –196 °C. An excess of NH₂OCH₃ (2 mmol, 1.54 mL of a 1.3 M solution in ethanol) was added, and the resulting solution was brought to room temperature and stirred for about 5 h. The solvent was removed under reduced pressure. The oil that was obtained was treated with ethanol (1.5 mL) containing an excess of NaBPh₄ (0.4 mmol, 137 mg). A white or pale-yellow solid slowly separated out from the resulting solution, which was allowed to stand at –25 °C overnight to complete the precipitation. The solid was filtered and crystallized from CH₂Cl₂ and ethanol. Yield: 167 mg for **7a** (67%), 133 mg for **8b** (62%), 176 mg for **9b** (73%), 123 mg for **10b** (68%), and 155 mg for **11b** (75%).

7a: C₅₀H₈₅BN₄O₁₄P₄Re (1245.12): calcd. C 48.23, H 6.88, N 1.12; found C 48.45, H 6.94, N 1.08. $A_M = 56.9 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$.

8b: C₅₇H₇₀BMnNO₉P₃ (1071.85): calcd. C 63.87, H 6.58, N 1.31; found C 63.80, H 6.67, N 1.27. $A_M = 55.9 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$.

9b: C₅₇H₇₀BNO₉P₃Re (1203.11): calcd. C 56.90, H 5.86, N 1.16; found C 57.04, H 5.95, N 1.11. $A_M = 53.5 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$.

10b: C₄₈H₅₅BMnNO₈P₂ (901.66): calcd. C 63.94, H 6.15, N 1.55; found C 64.10, H 6.41, N 1.49. $A_M = 52.1 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$.

11b: C₄₈H₅₅BNO₈P₂Re (1032.92): calcd. C 55.82, H 5.37, N 1.36; found C 55.60, H 5.35, N 1.25. $A_M = 55.0 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$.

[Re(NH₂OMe)(CO)₂(Ph₂POCH₂CH₂OPPh₂){P(OEt)₃}]BPh₄ (9ad): This compound was prepared as per the related rhenium complexes **7**, **9**, **11** with the use of hydride ReH(CO)₂(Ph₂POCH₂CH₂OPPh₂){P(OEt)₃}. Yield: 137 mg (57%). C₅₉H₆₄BNO₈P₃Re (1205.09): calcd. C 58.80, H 5.35, N 1.16; found C 59.04, H 5.49, N 1.18. $A_M = 49.6 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$.

[Mn(NH₂OMe)(CO)₃(Ph₂POCH₂CH₂OPPh₂)]BPh₄ (10d) and [Re(NH₂OMe)(CO)₃(P–P)]BPh₄ (11e, 11f) [P–P = Ph₂PN(Me)CH₂CH₂N(Me)PPh₂ (e), Ph₂PO(CH₂)₃OPPh₂ (f)]: These complexes were prepared as per the related complexes **7–11** with the use of hydride MH(CO)₃(P–P). The reaction was stirred for 5 h. Yield: 108 mg for **10d** (58%), 168 mg for **11e** (77%), and 162 mg for **11f** (75%).

10d: C₅₄H₄₉BMnNO₆P₂ (935.25): calcd. C 69.32, H 5.28, N 1.50; found C 69.25, H 5.43, N 1.47. $A_M = 55.6 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$.

11e: C₅₆H₅₅BN₃O₄P₂Re (1093.03): calcd. C 61.54, H 5.07, N 3.84; found C 61.49, H 5.13, N 3.80. $A_M = 52.3 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$.

11f: C₅₅H₅₁BNO₆P₂Re (1080.97): calcd. C 61.11, H 4.76, N 1.30; found C 61.25, H 4.87, N 1.24. $A_M = 50.7 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$.

Oxidation Reaction: The oxidation of the hydroxylamine and *O*-methylhydroxylamine complexes was carried out at low temperature (–40 °C) by using Pb(OAc)₄ as a reagent. In a typical experi-

Table 3. Crystal data and structure refinement for [Re(NH₂OCH₃)(CO)₂{PPh(OEt)₂}]₃BPh₄ (**9b**) and [Re(NH₂OCH₃)(CO)₃{Ph₂PO(CH₂)₃OPPh₂}]BPh₄ (**11f**).

Identification code	9b	11f
Empirical formula	C ₅₇ H ₇₀ BNO ₉ P ₃ Re	C ₅₆ H ₅₃ BCl ₂ NO ₆ P ₂ Re
Formula weight	1203.06	1165.84
Temperature	293(2) K	173(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	monoclinic	triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
Unit cell dimensions	<i>a</i> = 12.707(2) Å <i>b</i> = 27.279(5) Å <i>c</i> = 17.486(3) Å <i>α</i> = 90° <i>β</i> = 106.130(5)° <i>γ</i> = 90°	<i>a</i> = 10.0187(7) Å <i>b</i> = 15.7038(11) Å <i>c</i> = 17.9835(13) Å <i>α</i> = 94.267(1)° <i>β</i> = 104.823(1)° <i>γ</i> = 105.249(1)°
Volume	5822.9(18) Å ³	2608.3(3) Å ³
<i>Z</i>	4	2
Density (calculated)	1.372 Mg/m ³	1.484 Mg/m ³
Absorption coefficient	2.222 mm ^{–1}	2.544 mm ^{–1}
<i>F</i> (000)	2464	1176
Crystal size	0.14 × 0.11 × 0.07 mm	0.36 × 0.23 × 0.22 mm
Theta range for data collection	1.42 to 28.08°	1.36 to 28.01°
Index ranges	–15 ≤ <i>h</i> ≤ 16; –35 ≤ <i>k</i> ≤ 27; –20 ≤ <i>l</i> ≤ 22	–12 ≤ <i>h</i> ≤ 13; –20 ≤ <i>k</i> ≤ 18; –23 ≤ <i>l</i> ≤ 18
Reflections collected	30713	17230
Independent reflections	12872 [<i>R</i> (int) = 0.1441]	11960 [<i>R</i> (int) = 0.0424]
Reflections observed (>2σ)	3713	10213
Data completeness	0.908	0.949
Max. and min. transmission	1.000 and 0.753	1.000 and 0.739
Data/restraints/parameters	12872/0/656	11960/0/632
Goodness-of-fit on <i>F</i> ²	0.637	0.953
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0555 <i>wR</i> ₂ = 0.0631	<i>R</i> ₁ = 0.0301 <i>wR</i> ₂ = 0.0608
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.2593 <i>wR</i> ₂ = 0.1031	<i>R</i> ₁ = 0.0400 <i>wR</i> ₂ = 0.0629
Largest diff. peak and hole	0.837 and –0.600 e·Å ^{–3}	0.989 and –0.890 e·Å ^{–3}

ment, a sample of the appropriate complex, $[\text{M}(\text{NH}_2\text{OH})(\text{CO})_n\text{P}_{5-n}\text{BPh}_4]$ or $[\text{M}(\text{NH}_2\text{OCH}_3)(\text{CO})_n\text{P}_{5-n}\text{BPh}_4]$ (0.10 mmol), was placed in a three-necked, 25-mL, round-bottomed flask fitted with a solid-addition sidearm containing an equimolar amount of $\text{Pb}(\text{OAc})_4$ (44 mg, 0.10 mmol). The system was evacuated, CH_2Cl_2 (10 mL) was added, the solution cooled to -40°C , and the $\text{Pb}(\text{OAc})_4$ was added portionwise over 10–20 min to the cold solution with stirring. The reaction mixture was then warmed to 0°C , stirred for 10 min, and the solvent was removed under reduced pressure. The oil obtained was treated at 0°C with ethanol (2 mL) containing NaBPh_4 (42 mg, 0.12 mmol), but no solid compound was separated from the resulting solution.

X-ray Crystal-Structure Determination of $[\text{Re}(\text{NH}_2\text{OCH}_3)(\text{CO})_2\{\text{PPh}(\text{OEt})_2\}_3\text{BPh}_4$ (9b) and $[\text{Re}(\text{NH}_2\text{OCH}_3)(\text{CO})_3\{\text{Ph}_2\text{PO}(\text{CH}_2)_3\text{OPPh}_2\}_3\text{BPh}_4$ (11f): Suitable crystals for X-ray analysis were obtained by slow cooling of a saturated solution of the complexes in ethanol and CH_2Cl_2 . The data was collected with a SIEMENS Smart CCD area-detector diffractometer with graphite-monochromated $\text{Mo-K}\alpha$ radiation, at room temperature in the case of **9b** and at -100°C in the case of **11f**. Absorption corrections were carried out with SADABS with the use of semi-empirical methods from equivalents.^[18] The structures were solved by direct methods in the case of **9b** and by Patterson methods in the case of **11f**. Both were refined by a full-matrix least-squares analysis based on F^2 .^[19] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions and refined with isotropic displacement parameters, except those bonded to the nitrogen atom in **11f**, which were located on the density map and refined isotropically. Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from the International Tables for X-ray Crystallography (Tables 3, 4 and 5).^[20]

Table 4. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$] for $[\text{Re}(\text{NH}_2\text{OCH}_3)(\text{CO})_2\{\text{PPh}(\text{OEt})_2\}_3\text{BPh}_4$ (**9b**).

Re–C3	1.838(12)	Re–C2	1.901(10)
Re–N1	2.223(8)	Re–P1	2.378(3)
Re–P2	2.385(3)	Re–P(3)	2.413(3)
O1–C1	1.426(11)	O1–N1	1.432(8)
C3–Re–C2	86.1(5)	C3–Re–N1	176.3(4)
C2–Re–N1	91.3(4)	C3–Re–P1	91.5(3)
C2–Re–P1	87.6(3)	N1–Re–P1	85.6(2)
C3–Re–P2	91.0(3)	C2–Re–P2	85.4(3)
N1–Re–P2	91.5(2)	P1–Re–P2	172.41(10)
C3–Re–P3	96.2(3)	C2–Re–P3	177.6(3)
N1–Re–P3	86.33(19)	P1–Re–P3	91.53(9)
P2–Re–P3	95.31(9)	C1–O1–N1	111.2(8)
O1–N1–Re	110.5(5)		

Table 5. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$] for $[\text{Re}(\text{NH}_2\text{OCH}_3)(\text{CO})_3\{\text{Ph}_2\text{PO}(\text{CH}_2)_3\text{OPPh}_2\}_3\text{BPh}_4$ (**11f**).

Re–C3	1.962(4)	Re–C4	1.977(3)
Re–C2	1.998(3)	Re–N1	2.232(3)
Re–P1	2.3647(8)	Re–P2	2.4608(8)
N1–O1	1.440(3)	O1–C1	1.436(3)
C3–Re–C4	92.80(13)	C3–Re–C2	91.70(13)
C4–Re–C2	175.41(13)	C3–Re–N1	86.45(12)
C4–Re–N1	90.57(11)	C2–Re–N1	90.62(11)
C3–Re–P1	86.98(9)	C4–Re–P1	91.47(9)
C2–Re–P1	87.85(9)	N1–Re–P1	173.21(9)
C3–Re–P2	176.74(9)	C4–Re–P2	89.29(9)
C2–Re–P2	86.26(9)	N1–Re–P2	91.03(8)
P1–Re–P2	95.47(3)	O1–N1–Re	107.26(16)
C1–O1–N1	111.3(2)		

Details of crystal data and structural refinement are given in Table 3; selected bond lengths and angles are listed in Table 4 and Table 5. CCDC-297494 and -297495 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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