Preparation of Hydroxylamine Complexes of Ruthenium(II), Osmium(II) and Iridium(III)

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The hydroxylamine complexes $[MH(NH_2OH)P_4]BPh_4$ (M = Ru, Os) and $[Ru(NH_2OH)_2P_4](BPh_4)_2$ [P = $P(OEt)_3$, $PPh(OEt)_2$] were prepared by allowing the triflate species $MH(\kappa^1\text{-}OSO_2CF_3)P_4$ and $[Ru(\kappa^2\text{-}O_2SOCF_3)P_4]^+$ to react with an excess of hydroxylamine. The iridium complexes $[IrCl_2(NH_2OH)PL_2]BPh_4$ [P = $P(OEt)_3$, $PPh(OEt)_2$; L = PPh_3, $AsPh_3$] and $[IrH_2(NH_2OH)(PPh_3)_3]BPh_4$ were also prepared by reacting the hydride species $[IrHCl_2PL_3]$ and $[IrH_3(PPh_3)_3]$ first with triflic acid and then with an excess of NH_2OH. The *O*-iminoacylated hydroxylamine complexes $[M\{\eta^2\text{-}NH{=}C(R)ONH_2\}P_4](BPh_4)_2$ and $[M\{\eta^2\text{-}NH{=}C(R)ONH(CH_3)\}P_4](BPh_4)_2$ (M = Ru, Os; R = CH_3, 4-$CH_3C_6H_4$) were prepared by allowing the nitrile complexes $[M(RCN)_2P_4](BPh_4)_2$ to react with hydroxylamine (NH_2OH) or *N*-methylhydroxylamine [$NH(CH_3)OH$]. The compounds were characterised spectroscopically (IR, ^1H, ^{13}C and ^{31}P NMR) and a geometry in solution was also established.

Introduction

Hydroxylamine is a bifunctional molecule of simple constitution and structure, which has a somewhat unexplored coordination chemistry. Apart from the proposed $[IrCl_3(NH_2OH)(PPh_3)_2]$ compound,[1] obtained by protonation of $[Ir(NO)(PPh_3)_3]$ with HCl, and the $[Fe(TPP)(NH_2OH)_2]$ derivative (TPP = tetraphenylporphyrinate),[2] prepared by reacting Fe(TPP) with NH_2OH at low temperature, only recently[3] have some examples of hydroxylamine complexes of the type $[MX(NH_2OH)(CO)_2(PPh_3)_2]CF_3SO_3$ (M = Ru, Os; X = Cl, Br) and $[Re(NH_2OH)(CO)_3(PPh_3)_2]CF_3SO_3$ been reported. In contrast with numerous studies on hydrazine derivatives,[4,5] no further studies have been reported on the chemistry of hydroxylamine complexes, although NH_2OH is isoelectronic and somewhat similar to NH_2NH_2.

We have previously reported[6] the synthesis and the reactivity of mono- and bis(hydrazine) complexes of transition metals such as Mn, Fe, Ru, Os and Ir and have now extended these studies to hydroxylamine and methylhydroxylamine with the aim of testing the behaviour of these molecules as a ligand on appropriate metal fragments and, if possible, of carrying out a comparison with related hydrazine complexes. The results of these studies, which also include hydroxylamine reactions with coordinated nitriles,[7] are reported here.

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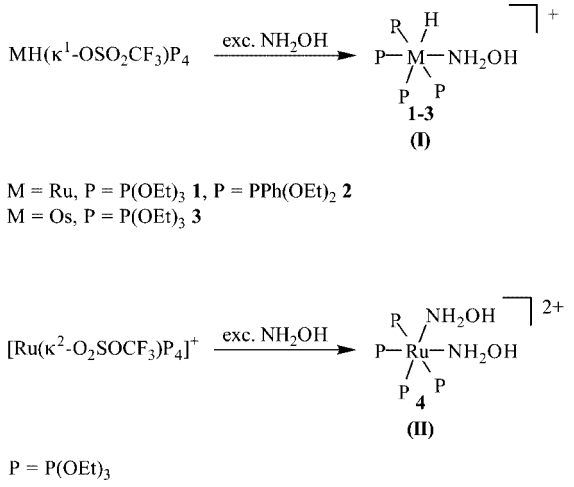
Results and Discussion

Preparation of Hydroxylamine Complexes

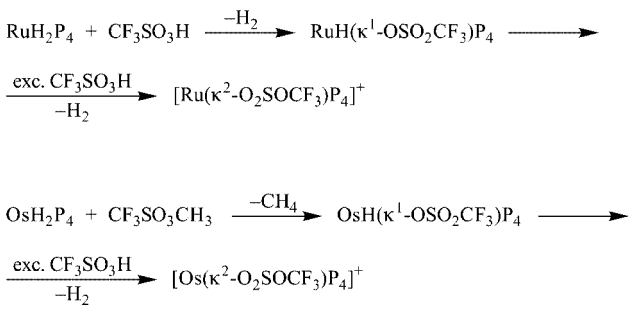
Mono- and bis(hydroxylamine) complexes of ruthenium and osmium $[MH(NH_2OH)P_4]BPh_4$ (**1**−**3**) and $[M(NH_2OH)_2P_4](BPh_4)_2$ (**4**) [P = $P(OEt)_3$, $PPh(OEt)_2$], were prepared by substituting the triflato ligand in the corresponding precursors, as shown in Scheme 1.



Scheme 1

The triflate precursors $[MH(\kappa^1\text{-}OSO_2CF_3)P_4]$ and $[M(\kappa^2\text{-}O_2SOCF_3)P_4]^+$ were generated in situ, in the case of ruthenium,[6a] by reacting the hydride complexes $[MH_2P_4]$ with an equimolar or an excess amount of triflic acid, while

with osmium[6c] the reaction first with methyl triflate and then with CF_3SO_3H was used (Scheme 2).



Scheme 2. P = $P(OEt)_3$, $PPh(OEt)_2$

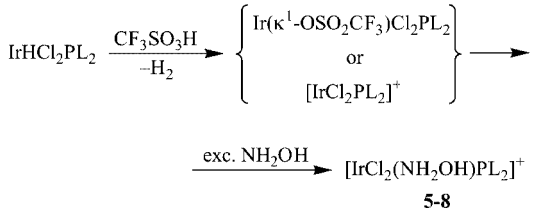
Substitution of the triflato ligand was easy for ruthenium, allowing the preparation of both mono- (**1, 2**) and bis(hydroxylamine) (**4**) complexes. In the case of osmium, however, only the mono-substituted derivative **3** was obtained in pure form. Attempts to prepare the bis-species, in fact, gave white solids, which probably contain (by NMR) a mixture of $[Os(NH_2OH)_2P_4]^{2+}$, $[Os(\kappa^1\text{-}OSO_2CF_3)(NH_2OH)P_4]^+$ and decomposition products whose separation was unsuccessful.

The hydroxylamine complexes **1**−**4** are white or pale-yellow solids that are stable in air and in solution in polar organic solvents, where they behave as 1:1 (**1**−**3**) or as 1:2 (**4**) electrolytes.[8] Analytical and spectroscopic data (Table 1) support the proposed formulations. Both the IR and ^1H NMR spectroscopic data are diagnostic for the presence of the NH_2OH ligand. The IR spectra, in fact, show a slightly broad medium-intensity band at 3487−3318 cm^{-1}, attributed to ν(OH), and two ν(NH) absorptions at 3326−3223 cm^{-1} of the hydroxylamine ligand. In the spectra of the mono-substituted derivatives **1**−**3** one weak band is also present at 1955−1820 cm^{-1}, due to the ν(MH) absorption of the hydride ligand. Its presence is confirmed by the ^1H NMR spectra, which show the characteristic high-field multiplet due to the coupling with the phosphorus nuclei, simulated using an AB_2CX model (X = H) with the parameters reported in Table 1.

Further support for the presence of the NH_2OH ligand comes from the ^1H NMR spectra, which show, for compounds **1** and **2**, a slightly broad multiplet at δ = 6.13−6.02 ppm, attributed to the NH_2 protons, and a broad signal at δ = 4.98−4.44 ppm, attributed to the OH hydrogen atom of the hydroxylamine ligand. These assignments are confirmed by integration and ^1H COSY experiments. In the spectra of compounds **3** and **4**, on the other hand, only the NH_2 proton signal at δ = 6.61−5.80 ppm is unambiguously attributable, while the OH signal is masked by the signals of the CH_2 protons. The low-frequency values observed for our proton OH signals as compared with those (δ = 8−9 ppm) of known hydroxylamine derivatives[1,3] may suggest an O-coordination of the NH_2OH ligand. However, the ^1H NMR spectra show a small coupling ($^3J_{P,H} \approx 1$ Hz) of the NH_2 protons with the phosphorus nuclei which seems to support, like the known hydroxylamine complexes,[3] an N-bonded NH_2OH ligand. Therefore, in the absence of an X-ray structure determination, the N-coordination (Scheme 1) should be considered more likely in this case.

In the temperature range between +30 and −80 °C the $^{31}P\{^1H\}$ NMR spectra of mono-hydroxylamine complexes **1**−**3** appear as AB_2C multiplets, which can be simulated using the parameters reported in Table 1, suggesting a mutual *cis* arrangement (**I**) of the hydride and NH_2OH ligands (Scheme 1). An A_2B_2 multiplet, instead, is present in the spectra of the bis(hydroxylamine) complex **4**, in agreement with a mutually *cis* position (**II**) of the two NH_2OH ligands.

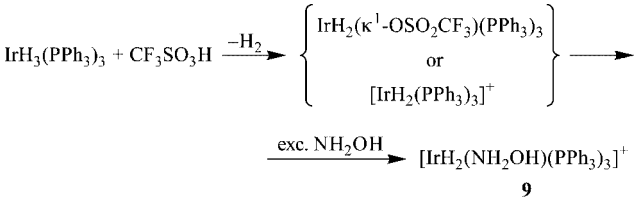
These studies on the synthesis of NH_2OH complexes have been extended to other metals with a d^6 configuration. We found that, in the case of iridium, the use of appropriate precursors containing mixed phosphite-phosphane (or arsane) ligands allows the synthesis of stable hydroxylamine derivatives. Treatment of $[IrHCl_2PL_2]$, first with triflic acid and then with an excess of NH_2OH, gives the hydroxylamine complexes $[IrCl_2(NH_2OH)PL_2]^+$ (**5**−**8**) [P = $P(OEt)_3$, $PPh(PEt)_2$; L = PPh_3, A_5Ph_3], which were isolated as their BPh_4 salts and characterised (Scheme 3).



Scheme 3. L = PPh_3, P = $P(OEt)_3$ **5**, P = $PPh(OEt)_2$ **6**; L = $AsPh_3$, P = $P(OEt)_3$ **7**, P = $PPh(OEt)_2$ **8**

Protonation of $[IrHCl_2PL_2]$ with CF_3SO_3H leads[6d] to the evolution of H_2 and probable formation of either the triflate $[Ir(\kappa^1\text{-}OSO_2CF_3)Cl_2PL_2]$ or the pentacoordinate cations $[IrCl_2PL_2]^+$, which, when treated with an excess of hydroxylamine, give the final complexes **5**−**8**.

The $IrCl_2PL_2$ fragment seems to be peculiar to the formation of stable hydroxylamine complexes, since the use of other precursors such as $[IrHCl_2(PPh_3)_3]$, $[IrHCl_2(AsPh_3)_3]$ or $[IrH_2Cl(PPh_3)_3]$ does not allow the preparation of NH_2OH derivatives. The only other fragment we found to be able to bind NH_2OH is $[IrH_2(PPh_3)_3]$, which gives the stable and isolable complex $[IrH_2(NH_2OH)(PPh_3)_2]BPh_4$ (**9**). In fact, treatment of the trihydride $[IrH_3(PPh_3)_3]$, first with an equimolar amount of triflic acid and then with an excess of NH_2OH, produces the hydroxylamine complex **9**, which was isolated and characterised (Scheme 4).



Scheme 4

Table 1. IR and NMR spectroscopic data for hydroxylamine complexes

Complex	IR cm^{-1}	Assignment	^1H NMR[b][c] δ (*J*/Hz)	Assignment	Spin system	$^{31}P\{^1H\}$NMR[b][d] δ (*J*/Hz)
$[RuH(NH_2OH)\{P(OEt)_3\}_4]BPh_4$ (**1**)	3487 m	ν(OH)	6.13 m, br	NH_2	AB_2C	δ_A = 147.5
	3326 m	ν(NH)	4.44 br	OH		δ_B = 141.1
	3259 m		4.24−3.88 m	CH_2		δ_C = 136.7
	1820 m	ν(RuH)	1.36 t	CH_3		J_{AB} = 63.0
			1.32 t			J_{AC} = 42.2
			1.27 t			J_{BC} = 45.0
			−7.71 to −8.68 m	RuH		
			6.27 m, br [e]	NH_2		
			5.26 m	OH		
			4.19 m	CH_2		
			3.95 qnt			
			1.33 t	CH_3		
			1.30 t			
			1.26 t			
			AB_2CX	RuH		
			δ_X −8.19			
			J_{AX} = 24.2			
			J_{BX} = 24.5			
			J_{CX} = 122.1			
$[RuH(NH_2OH)\{PPh(OEt)_2\}_4]BPh_4$ (**2**)	3407 m	ν(OH)	6.02 m, br	NH_2	AB_2C	δ_A = 169.7
	3299 m	ν(NH)	4.98 br	OH		δ_B = 164.1
	3223 w		4.00−3.15 m	CH_2		δ_C = 159.4
	1946 m	ν(RuH)	1.28 t	CH_3		J_{AB} = 46.9
			1.23 t			J_{AC} = 29.7
			1.19 t			J_{BC} = 31.4
			0.92 t			
			AB_2CX	RuH		
			δ_X −8.02			
			J_{AX} = 24.5			
			J_{BX} = 24.0			
			J_{CX} = 105.2			
$[OsH(NH_2OH)\{P(OEt)_3\}_4]BPh_4$ (**3**)	3481 m, br	ν(OH)	6.61 br	NH_2	AB_2C	δ_A = 102.4
	3321 m	ν(NH)	4.22−3.84 m	CH_2		δ_B = 102.0
	3265 w		1.36 t	CH_3		δ_C = 96.3
	1955 w	ν(OsH)	1.31 t			J_{AB} = 34.3
			1.28 t			J_{AC} = 26.9
			AB_2CX	OsH		J_{BC} = 43.7
			δ_X −9.14			
			J_{AX} = 45.8			
			J_{BX} = 21.6			
			J_{CX} = −107.9			
$[Ru(NH_2OH)_2\{P(OEt)_3\}_4](BPh_4)_2$ (**4**)	3318 m	ν(OH)	5.80 m, br	NH_2	A_2B_2	δ_A = 129.6
	3290 m, br	ν(NH)	4.05 m	CH_2		δ_B = 119.8
			1.35 t	CH_3		J_{AB} = 60.3
			1.29 t			
$[IrCl_2(NH_2OH)\{P(OEt)_3\}(PPh_3)_2]BPh_4$ (**5**)	3258 m	ν(NH)	5.45 m, br	NH_2	AB_2	δ_A = 32.1
	3215 m		3.42 qnt	CH_2		δ_B = −19.2
	1601 m	δNH_2	1.00 t	CH_3		J_{AB} = 27.5
	393 m [f]	νIrCl				
$[IrCl_2(NH_2OH)\{PPh(OEt)_2\}(PPh_3)_2]BPh_4$ (**6**)	3490 m	ν(OH)	5.62 m	NH_2	AB_2	δ_A = 64.3
	3258 m	ν(NH)	3.50 m	CH_2		δ_B = −22.5
	3215 m		1.08 t	CH_3		J_{AB} = 21.0
	1616 m	$\delta(NH_2)$				
$[IrCl_2(NH_2OH)\{P(OEt)_3\}(AsPh_3)_2]BPh_4$ (**7**)	3254 m	ν(NH)	5.73 br	NH_2	A	32.84 s
	3213 m		3.55 qnt	CH_2		
	1624 m	$\delta(NH_2)$	1.00 t	CH_3		
$[IrCl_2(NH_2OH)\{PPh(OEt)_2\}(AsPh_3)_2]BPh_4$ (**8**)	3256 m	ν(NH)	5.83 m	NH_2	A	64.3 s
	3213 m		3.52 qnt	CH_2		
	1616 m	$\delta(NH_2)$	1.05 t	CH_3		
	386 m [f]	ν(IrCl)				
$[IrH_2(NH_2OH)(PPh_3)_3]BPh_4$ (**9**)	3275 m	ν(NH)	5.26 br	NH_2	A_2B	δ_A = 9.81
	3219 m		3.39 br	OH		δ_B = 5.46
	2179 w	νIrH)	A_2BXY	IrH		J_{AB} = 12.8
	2130 w		δ_X −12.19			
	1614 m	$\delta(NH_2)$	δ_Y −20.68			
			J_{AX} = 21.3			
			J_{AY} = 16.8			
			J_{BX} = 120			
			J_{BY} = 12.5			
			J_{XY} = 46.3			

Table 1. *(Continued)*

Complex	IR[a] cm^{-1}	Assignment	^{1}H NMR[b][c] δ (*J*/Hz)	Assignment	Spin system	^{31}P{^{1}H}NMR[b][d] δ (*J*/Hz)
[Ru(η^2-NH=C(CH$_3$)ONH$_2$){P(OEt)$_3$}$_4$](BPh$_4$)$_2$ (**10a**)	3375 m 3290 m 3227 m 1668 m	ν(NH) δ(NH$_2$)	8.02 m 4.02 m 1.88 s 1.33 t 1.30 t	NH + NH$_2$ CH$_2$ CH$_3$ CH$_3$ phos	ABC$_2$	δ$_A$ = 131.9 δ$_B$ = 129.3 δ$_C$ = 116.8 *J*$_{AB}$ = 76.1 *J*$_{AC}$ = 61.4 *J*$_{BC}$ = 57.3
			9.06 br [e] 8.97 m, br 4.26 m 2.91 s 1.38 t 1.37 t	NH NH$_2$ CH$_2$ CH$_3$ CH$_3$ phos	ABC$_2$ [e]	δ$_A$ = 134.5 δ$_B$ = 131.2 δ$_C$ = 119.3 *J*$_{AB}$ = 76.8 *J*$_{AC}$ = 62.0 *J*$_{BC}$ = 57.3
{Ru(η^2-NH=C(4-CH$_3$C$_6$H$_4$)ONH$_2$)[P(OEt)$_3$]$_4$}(BPh$_4$)$_2$ (**10b**)	3381 m 3290 m 3217 m 1653 m	ν(NH) δ(NH$_2$)	8.32 m 4.17−3.94 m 2.46 s 1.36 t 1.32 t 1.24 t	NH + NH$_2$ CH$_2$ CH$_3$ CH$_3$ phos	ABC$_2$ [e]	δ$_A$ = 133.7 δ$_B$ = 131.1 δ$_C$ = 118.9 *J*$_{AB}$ = 75.9 *J*$_{AC}$ = 61.4 *J*$_{BC}$ = 57.2
			9.28 m, br [e] 8.79 br 4.28 m 2.42 s 1.42 t 1.40 t 1.29 t	NH NH$_2$ CH$_2$ CH$_3$ CH$_3$ phos		
[Ru{η^2-NH=C(CH$_3$)ONH(CH$_3$)}{P(OEt)$_3$}$_4$](BPh$_4$)$_2$ (**11**)	3408 m 3302 w 1608 m	ν(NH) δ(NH$_2$)	7.0 br 4.75 s, br 4.07 m 3.27 s 2.08 s 1.34 t 1.30 t 1.28 t	=NH NH CH$_2$ CH$_3$ CH$_3$ CH$_3$ phos	ABC$_2$	δ$_A$ = 132.4 δ$_B$ = 129.7 δ$_C$ = 120.6 *J*$_{AB}$ = 6.9 *J*$_{AC}$ = 58.8 *J*$_{BC}$ = 60.8
[Os{η^2-NH=C(CH$_3$)ONH$_2$}{P(OEt)$_3$}$_4$](BPh$_4$)$_2$ (**12a**)	3330 m 3217 w 1668 m	ν(NH) δ(NH$_2$)	7.48 s, br 4.08−6.84 m 2.07 s 1.29 t 1.25 t	NH + NH$_2$ CH$_2$ CH$_3$ CH$_3$ phos	A$_2$B$_2$	δ$_A$ = 82.7 δ$_B$ = 81.0 *J*$_{AB}$ = 41.5
			12.36 br [e,g] 8.56 s 4.04 m 2.44 s 1.21 t 1.16 t	NH NH$_2$ CH$_2$ CH$_3$ CH$_3$ phos	A$_2$BC [e,g]	δ$_A$ = 86.8 δ$_B$ = 84.7 δ$_C$ = 83.8 *J*$_{AB}$ = 41.5 *J*$_{AC}$ = 41.0 *J*$_{BC}$ = 54.2
[Os{η^2-NH=C(4-CH$_3$C$_6$H$_4$)ONH$_2$}{P(OEt)$_3$}$_4$](BPh$_4$)$_2$ (**12b**)	3481 m, br 3310 m 1636 m	ν(NH) δ(NH$_2$)	8.38 s, br 4.10−3.90 m 2.46 s 1.29 t 1.20 t	NH + NH$_2$ CH$_2$ CH$_3$ CH$_3$ phos	A$_2$BC	δ$_A$ = 81.9 δ$_B$ = 80.6 δ$_C$ = 80.4 *J*$_{AB}$ = 41.5 *J*$_{AC}$ = 41.6 *J*$_{BC}$ = 53.8
			10.12 br [g] 8.28 s 4.03−3.88 m 2.44 s 1.23 t 1.15 t	NH NH$_2$ CH$_2$ CH$_3$ CH$_3$ phos	A$_2$BC [g]	δ$_A$ = 82.9 δ$_B$ = 81.7 δ$_C$ = 81.6 *J*$_{AB}$ = 42.3 *J*$_{AC}$ = 41.5 *J*$_{BC}$ = 54.3
			11.79 s, br [e] [g] 8.71 s, br 4.17 m 2.38 s 1.29 t 1.22 t	NH NH$_2$ CH$_2$ CH$_3$ CH$_3$ phos	A$_2$BC [e,g]	δ$_A$ = 83.4 δ$_B$ = 82.9 δ$_C$ = 82.1 *J*$_{AB}$ = 41.5 *J*$_{AC}$ = 41.9 *J*$_{BC}$ = 54.5
[Os{η^2-NH=C(CH$_3$)ONH(CH$_3$)}{P(OEt)$_3$}$_4$](BPh$_4$)$_2$ (**13**)	3408 m 3294 m 1610 m	ν(NH) δ(NH$_2$)	7.4 br 5.24 s, br 4.00 m 3.29 s 2.08 s 1.28 t 1.26 t 1.24 t	=NH NH CH$_2$ CH$_3$ CH$_3$ phos	ABC$_2$	δ$_A$ = 93.8 δ$_B$ = 89.3 δ$_C$ = 82.2 *J*$_{AB}$ = 4.3 *J*$_{AC}$ = 45.4 *J*$_{BC}$ = 46.3

[a] In KBr pellets. [b] In CD_2Cl_2 at 25 °C, unless otherwise noted. [c] Phenyl proton resonances are omitted. [d] Positive shift downfield from 85% H_3PO_4. [e] In $(CD_3)_2CO$. [f] In polyethylene (far-IR). [g] At −70 °C.

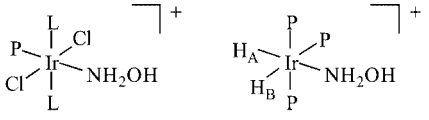
The reaction of $[IrH_3(PPh_3)_3]$ with CF_3SO_3H proceeds also in this case with the evolution of H_2 and probable formation of either κ^1-OSO_2CF_3 or pentacoordinate intermediates which, on treatment with NH_2OH, afford the final hydroxylamine derivative **9**. We also attempted to prepare bis(hydroxylamine) derivatives by reacting $[IrH_3(PPh_3)_3]$ sequentially, first with two equivalents of CF_3SO_3H and then with NH_2OH, but only a mixture of products not containing the NH_2OH ligand was isolated.

The hydroxylamine complexes of iridium (**5**−**8**) are yellow solids, while **9** is white, and all are stable in air and in solution in polar organic solvents, where they behave as 1:1 electrolytes.[8] Good analytical data were obtained for all compounds, and their IR and NMR spectroscopic data (Table 1) confirm the proposed formulations.

The IR spectra show the characteristic ν(NH) bands at 3275−3213 cm^{-1} and one of medium intensity at 1624−1607 cm^{-1}, attributed to δ(NH_2) of the NH_2OH ligands. The ν(OH) absorption in these complexes is weak and rather broad, and was unambiguously assigned only for **6** at 3490 cm^{-1}. In the spectrum of hydride complex **9** two weak bands at 2179 and 2130 cm^{-1} are also present. These were assigned to the ν(IrH) absorption of the two H^- ligands in a mutually *cis* position.

The presence of the hydroxylamine ligand in complexes **5**−**9** was further confirmed by the ^1H NMR spectra, which show the characteristic signal at δ = 5.83−5.25 ppm of the NH_2 protons of the hydroxylamine ligand. The OH proton is clearly observed at δ = 3.39 ppm only in the case of **9**; in the other complexes it is probably masked by the methylene protons of the phosphite ligands.

In the temperature range between +30 and −80 °C the $^{31}P\{^1H\}$ NMR spectra of the phosphane-phosphite complexes $[IrCl_2(NH_2OH)PL_2]BPh_4$ (**5** and **6**) [P = $P(OEt_3$, $PPh(OEt)_2$; L = PPh_3] appear as AB_2 multiplets in agreement with the magnetic equivalence of the two PPh_3 ligands. Taking into account that the far-IR spectrum of **5** shows only one ν(IrCl) band at 393 cm^{-1}, indicating that the two Cl^- ligands are in a mutually *trans* position, we may propose a *mer-trans* geometry (**III**) for our hydroxylamine derivatives **5** and **6** (Chart 1).



III **IV**

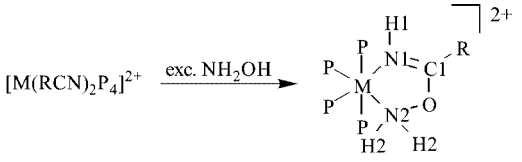
The $^{31}P\{^1H\}$ NMR spectra of the related arsane complexes $[IrCl_2(NH_2OH)PL_2]BPh_4$ (**7** and **8**) [P = $P(OEt)_3$, $PPh(OEt)_2$; L = $AsPh_3$] show only one singlet at δ = 32.8 and 64.3 ppm, respectively, for the phosphite ligand, and therefore no plausible hypothesis for the geometry of complexes can be made. However, taking into account that the far-IR spectra show only one ν(IrCl) band, we propose, by analogy with the related complexes **5** and **6**, a *mer-trans* geometry (**III**) for compounds **7** and **8** as well.

In the temperature range between +30 and −80 °C the $^{31}P\{^1H\}$ NMR spectra of $[IrH_2(NH_2OH)(PPh_3)_3]BPh_4$ (**9**) show an A_2B multiplet indicating the presence of two magnetically equivalent phosphanes, different from the third. In the hydride region, the ^1H NMR spectra also appear as a complicated multiplet, which can be simulated as the XY part (X, Y = H) of an A_2BXY spin system, with the parameters reported in Table 1. On this basis, we can reasonably propose a *mer-cis* geometry of type **IV** for our hydride-hydroxylamine complex **9**.

A comparison between the results for the NH_2OH complexes and those for related hydrazine NH_2NH_2 complexes shows that these two ligands are very similar in their behaviour toward metal fragments containing phosphite as supporting ligand. Similar complexes of Ru[6a] and Ir,[6d] containing either NH_2NH_2 or NH_2OH as monodentate ligand, can be isolated in the solid state. Furthermore, in the case of iridium only the mixed phosphane-phosphite fragment $IrCl_2PL_2$ can give stable hydrazine complexes, so the hydroxylamine derivative can be prepared exclusively with the same mixed-ligand fragment. Some differences, however, can be observed with osmium, which allows the synthesis of only mono-hydroxylamine complexes (**3**) with $P(OEt)_3$ phosphite ligand, whereas both mono- and bis(hydrazine) derivatives[6c] $[OsH(NH_2NH_2)P_4]^+$ and $[Os(NH_2NH_2)_2P_4]^{2+}$ can easily be prepared. In every case, although the comparison is still restricted to a few complexes, it seems that when a metal fragment is able to bind hydrazine, it can also coordinate hydroxylamine, affording the corresponding stable derivatives. Support for this hypothesis comes from the results on other complexes[3] suggesting a synthetic pathway for NH_2OH derivatives.

O-Iminoacylated Hydroxylamine Complexes

The synthesis of hydroxylamine complexes by substituting a labile ligand has prompted us to extend these studies to other precursors, such as the nitrile complexes $[M(RCN)_2P_4]^{2+}$ with the aim of testing whether new hydroxylamine derivatives may be prepared. Surprisingly, the reaction of bis(nitrile) complexes of ruthenium and osmium with hydroxylamine does not produce NH_2OH complexes, but affords a yellow solid which was characterised as containing an *O*-iminoacylated ligand of the type shown in Scheme 5.



10, 12
(V)

Scheme 5. P = $P(OEt)_3$, M = Ru **10**, Os **12**, R = CH_3 **a**, 4-$CH_3C_6H_4$ **b**

The reaction proceeds easily at room temperature, affording complexes **10** and **12** in good yields. However, only the $P(OEt)_3$-containing *O*-iminoacylated complexes were pre-

Table 2. $^{13}C\{^1H\}$ NMR spectroscopic data for selected complexes[a]

Compd.	δ	Assignment
$[Ru(\eta^2\text{-}NH{=}C(CH_3)ONH_2)\{P(OEt)_3\}_4](BPh_4)_2$ (**10a**)	172.8 s	C=N
	163−122 m	Ph
	63.4 m	CH_2
	15.9 s	CH_3C=
	16.1 m	CH_3 phos
$[Ru\{\eta^2\text{-}NH{=}C(CH_3)ONH(CH_3)\}\{P(OEt)_3\}_4](BPh_4)_2$ (**11**)	154.7 s	C=N
	164−121 m	Ph
	61.9 m	CH_2
	39.2 s	CH_3N
	19.3 s	CH_3C=
	15.9 m	CH_3 phos
$[Os\{\eta^2\text{-}NH{=}C(4\text{-}CH_3C_6H_4)ONH_2\}\{P(OEt)_3\}_4](BPh_4)_2$ (**12b**)	156.3 s	C=N
	165−122 m	Ph
	62.6 m	CH_2
	21.3 s	CH_3 *p*-tolyl
	15.8 m	CH_3 phos

[a] In $(CD_3)_2CO$ at 203 K.

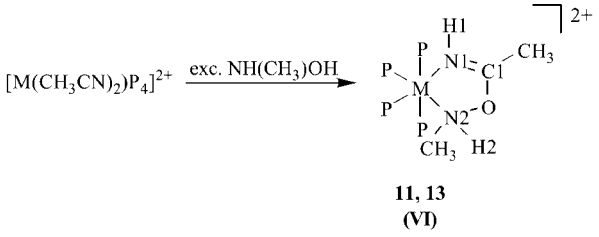
pared in pure form, while with the related $PPh(OEt)_2$ compounds only intractable mixtures of product were obtained. Compounds **10** and **12** are pale-yellow solids stable in air and in solution in polar organic solvents, diamagnetic and 1:1 electrolytes.[8] The analytical and spectroscopic data (IR and NMR, Table 1 and 2) support the proposed formulation. The infrared spectra show, in the 3481−3217 cm^{-1} region, two or three medium-intensity bands, attributed to ν(NH) of the η^2-HN=C(R)ONH_2 ligand. The $\delta(NH_2)$ absorptions at 1668−1636 cm^{-1} also appear in the spectra. At room temperature, in CD_2Cl_2 as solvent, the ^1H NMR spectra of complexes **10** and **12** show, in the high-frequency region, a broad resonance at δ = 8.32−7.84 ppm. In $(CD_3)_2CO$, however, this resonance splits into two slightly broadened signals at δ = 12.36−9.06 and at 8.97−8.28 ppm, respectively, of intensity ratio 1:2. This split is observed at room temperature, except for compound **12a**, for which a lowering of the temperature to −20 °C is required. The highest frequency signal is assigned to the iminic =NH proton (H1), while the lowest is assigned to the ONH_2 (H2) group of the *O*-iminoacylated ligand. In the ^1H NMR spectra one sharp singlet between δ = 1 and 3 ppm due to the methyl group of the substituent R (CH_3 or 4-$CH_3C_6H_4$) of the η^2-ligand is also present.

Support for these assignments comes from a ^1H COSY spectrum of compound **10a**, which shows that the iminic HN= proton (H1) correlates with the methyl substituent of the iminic carbon atom HN=$C(CH_3)$ of the ligand. No correlation was observed between the iminic H1 and the aminic H2 proton resonances, in agreement with an *O*-iminoacylated molecule.

The ^{13}C NMR spectra confirm the formulation of the complexes showing, apart from the signals of the $P(OEt)_3$ and the BPh_4 anion, the imine carbon (C1) resonance of the η^2-ligand as a singlet at δ = 172.8 ppm for **10a** and at δ = 156.3 ppm for **12b**. An HMBC experiment for compound **10a** correlates the imine carbon signal at δ = 172.8 ppm with the methyl proton resonances at δ = 2.91 ppm of the methyl group bonded to the iminic C1 carbon atom, in agreement with the proposed assignment.

In the osmium complex **12b** the HMBC experiment shows a correlation between the iminic C1 carbon resonance and the signals of the phenyl protons of the *p*-tolyl substituent. On the basis of these data, and taking into account that in any solvent and in the temperature range between +20 and −80 °C the $^{31}P\{^1H\}$ NMR spectra of the *O*-iminoacylated derivatives **10**, **12** appear as an ABC_2 or A_2BC multiplet, a type-**V** geometry can reasonably be proposed.

We then thought to extend the studies to other hydroxylamines and treated the bis(nitrile) complexes $[M(CH_3CN)_2P_4]^{2+}$ with *N*-methylhydroxylamine $NH(CH_3)OH$. We observed that the reaction proceeds as with NH_2OH to give the chelated $[M(\eta^2\text{-}HN{=}C(CH_3)ONH(CH_3)\}P_4]^{2+}$ cations **11** and **13**, which were isolated as their BPh_4^- salts and characterised (Scheme 6).



11, 13
(VI)

Scheme 6. P = $P(OEt)_3$, M = Ru **11**, Os **13**

The IR spectra of complexes **11** and **13** show the characteristic ν(NH) absorption at 3408−3294 cm^{-1} and

$\delta[NH(CH_3)]$ at 1610−1608 cm^{-1} for the HN=$C(CH_3)ONH(CH_3)$ ligand.

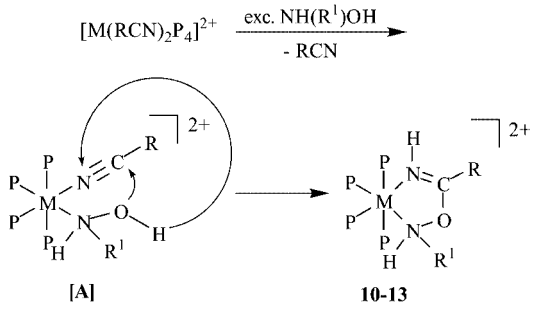
In the ^1H NMR spectra (Table 1) of both compounds **11** and **13** two singlets between δ = 3.29 and 2.08 ppm appear, due to the two methyl groups of the η^2-ligand. One broad signal at δ = 4.75 ppm (**11**) and at δ = 5.24 ppm (**13**) is also present in the spectra, which was attributed to the aminic $ONHCH_3$ (H2) proton. A ^1H COSY spectrum of **11** confirms this assignment, showing a strong correlation between the signal at δ = 4.75 ppm and the methyl singlet at δ = 2.08 ppm of CH_3N2. A weak correlation was also observed between the other methyl singlet at δ = 3.27 ppm (CH_3C1) and a signal near δ = 7.0 ppm, which appears to be masked by the phenyl protons of the BPh_4 anion and can be attributed to the iminic proton (H1) of the ligand.

The $^{13}C\{^1H\}$ NMR spectrum of **11** (Table 2) shows, besides the signals of the phosphites and the BPh_4 anion, two singlets at δ = 39.2 and 19.3 ppm attributed to the two methyl carbons of the $N2CH_3$ and $C1CH_3$ groups, respectively, and one singlet at δ = 154.7 ppm due to the iminic C=N carbon atom (C1). An HMBC experiment confirms this attribution showing a strong correlation between the imino carbon signal at δ = 154.7 ppm and the proton signal at δ = 2.08 ppm of the methyl $N2CH_3$ substituent and also a weak correlation with the ^1H signal at δ = 3.27 ppm of the $C1CH_3$ methyl group. Furthermore, the methyl carbon resonance of the HN=CCH_3 group at δ = 19.3 ppm correlates with the aminic H2 proton signal at δ = 4.75 ppm, in agreement with the presence of the *O*-iminoacylated ligand.

In the temperature range between +30 and −80 °C, the $^{31}P\{^1H\}$ NMR spectra of both the ruthenium and osmium complexes **11** and **13** appear as ABC_2 multiplets; these spectra can be simulated with the parameters reported in Table 1. On the basis of these data, we can reasonably propose a geometry of type **VI** for our *O*-iminoacylated methylhydroxylamine derivatives.

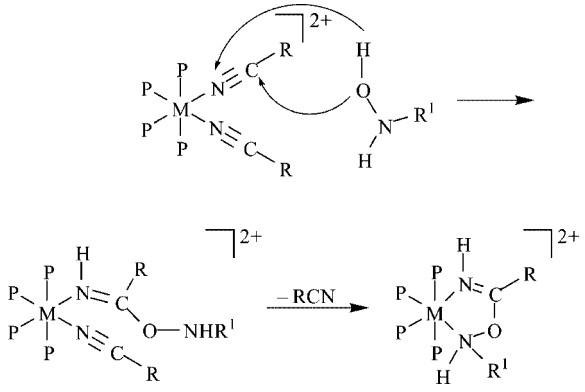
Formation of *O*-iminoacylated hydroxylamine complexes from the reaction of a coordinated nitrile with NH_2OH or $NH(CH_3)OH$ is not surprising, taking into account that a metal-bonded RCN molecule can undergo nucleophilic attack by alcohols, amines and carbanions to give iminoether-, amidine- and imine derivatives.[7,9−12] Furthermore, nitrile precursors $[Ru(RCN)_2P_4]^{2+}$ are reported[6a−6c] to react with hydrazine or methylhydrazine to give amidrazone complexes $[M\{\eta^2\text{-}NH{=}C(R)N(R^1)NH_2\}P_4]^{2+}$ (R^1 = H, CH_3), probably through the nucleophilic attack of the hydrazine on the cyanide carbon atom of the coordinated nitriles, followed by an H-shift, giving a five-membered metallacycle. Finally, it is well documented[13−15] that NH_2OH can react with free nitriles through the more usual N-addition, giving amide oximes $RC(NH_2)$=NOH, or through O-addition, affording carboxamides $RC(=O)NH_2$ as the final products.

A nucleophilic attack of the hydroxylamine by the oxygen atom on the coordinated nitrile can therefore also be proposed in our case for the formation of *O*-iminoacylated hydroxylamine complexes **10**−**13**, which represents the first example[7] of the addition of hydroxylamine NH_2OH to a coordinated nitrile. Doubts remain, however, regarding the reaction path. Treatment of bis(nitrile) complexes $[M(RCN)_2P_4]^{2+}$ with $NH(R^1)OH$ (R^1 = H, CH_3) could result in the substitution of only one nitrile ligand to afford the $[M(RCN)(NH_2OH)P_4]^{2+}$ intermediate **A**. The *O*-iminoacylated hydroxylamine complex can be obtained (Scheme 7) by a nucleophilic attack of the coordinated hydroxylamine's oxygen atom on the coordinated RCN's nitrile carbon atom, followed by an H-shift.



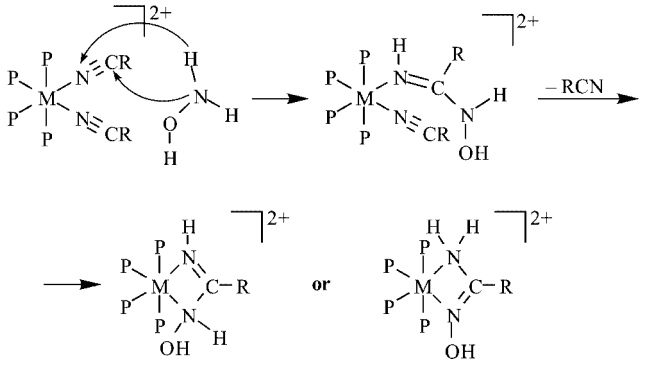
Scheme 7. P = $P(OEt)_3$, R = CH_3, 4-$CH_3C_6H_4$, R^1 = H, CH_3

The hydroxylamine, however, could react with one of the coordinated nitriles through the oxygen atom without being bonded to the central metal, resulting in the *O*-iminoacylated ligand, which, by substitution of the second RCN ligand, yields the final chelate complexes (Scheme 8).



Scheme 8

The formation of complexes **10**−**13**, in fact, means that hydroxylamine, which possesses two sites of attack, reacts with the coordinated nitrile through the oxygen atom. The N-addition of hydroxylamine should give different products, such as complexes containing either the imine NH=C(R)NHOH or the tautomer amide oxime $RC(NH_2)$=NOH as a ligand (Scheme 9).



Scheme 9

We have studied the reactions between $[M(RCN)_2P_4]^{2+}$ cations and hydroxylamine by NMR spectroscopy and observed that no signals attributable to a nitrile-hydroxylamine intermediate of the type $[M(RCN)(NH_2OH)P_4]^{2+}$ were detected, with the resonances of the initial and the final products and of free nitrile being the only signals observed in the spectra. However, since the reaction of this intermediate would be intramolecular, one could expect it to be much faster than substitution of one RCN to give $[M(RCN)(NH_2OH)P_4]^{2+}$, making this intermediate undetectable. On this basis, although our data do not give conclusive information, a mechanism involving the initial substitution of one RCN with NH_2OH (Scheme 7) may be reasonably proposed.

Apart from the mechanism, the behaviour of both the hydroxylamine and the hydrazine toward a coordinated nitrile of the $[M(RCN)_2P_4]^{2+}$ cations containing $P(OEt)_3$ as ancillary ligand is very similar. In both cases they result in a nucleophilic attack on the nitrile carbon atom followed by an H-shift, yielding a new chelate ligand. A different atom, however, is used by the two nucleophiles, i.e. N-addition with hydrazine and O-addition with hydroxylamine, affording different molecules which behave, in every case, as bidentate ligands. The attack of the oxygen atom of the hydroxylamine in these reactions is rather surprising, since the reaction with free nitriles involves, in the majority of cases, N-addition.[13–15] An O-addition has been reported[16] in the reaction of the platinum complex $[PtCl_4(CH_3CN)_2]$ with *N*-substituted hydroxylamine R_2NOH, but the steric hindrance at the N-atom makes the O-attack plausible in this case. This is the only known example[16] of the reaction of a substituted hydroxylamine with coordinated RCN. In our $[M(RCN)_2P_4]^{2+}$ complexes the coordination of the nitrile to the MP_4 fragment probably makes the nitrile carbon increasingly susceptible to nucleophilic attack by the more electronegative oxygen, yielding the *O*-iminoacylated derivatives.

Conclusions

In this contribution we have reported the synthesis of several new hydroxylamine complexes of Ru, Os and Ir, including the first bis(hydroxylamine) $[Ru(NH_2OH)_2P_4](BPh_4)_2$ derivatives. The preparation of *O*-iminoacylated complexes $[M\{\eta^1\text{-}HN{=}C(R)ONHR^1\}P_4](BPh_4)_2$ (M = Ru, Os) was also achieved by O-addition of hydroxylamine to an organonitrile in a metal-assisted reaction.

Experimental Section

General: All synthetic work was carried out under an inert atmosphere using standard Schlenk techniques or a Vacuum Atmosphere dry-box. Once isolated, the complexes were found to be relatively stable in air, but were stored under an inert atmosphere at −25 °C. All solvents were dried over appropriate drying agents, degassed on a vacuum line and distilled into vacuum-tight storage flasks. The phosphite $P(OEt)_3$ (Aldrich) was purified by distillation under nitrogen, while $PPh(OEt)_2$ was prepared by the method of Rabinowitz and Pellon.[17] $RuCl_3{\cdot}3H_2O$ was obtained from Chempur, while $[(NH_4)_2(OsCl_6)]$ was purchased from Johnson Matthey and $IrCl_3{\cdot}3H_2O$ from Pressure Chemical Co.; all salts were used as received. Hydroxylamine (NH_2OH) and *N*-methylhydroxylamine [$NH(CH_3)OH$] were prepared by slight modification of a reported method,[18] involving treatment of hydroxylamine hydrochloride with sodium ethoxide in ethanol. The free NH_2OH was isolated as a white solid, while $NH(CH_3)OH$ was 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 on a Nicolet Magna 750 FT-IR spectrophotometer. NMR spectra (^1H, ^{13}C, ^{31}P) were obtained on Bruker AC200 and AVANCE 300 spectrometers at temperatures varying between −90 °C and +30 °C, unless otherwise noted. ^1H and ^{13}C spectra are referred to internal tetramethylsilane, while $^{31}P\{^1H\}$ chemical shifts are reported with respect to 85% H_3PO_4, with downfield shifts considered positive. The SWAN-MR software package[19] was used to treat NMR spectroscopic data and for the simulation. The conductivity of 10^{-3} M 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 RuH_2P_4 and OsH_2P_4 and the nitrile complexes $[Ru(RCN)_2P_4](BPh_4)_2$ and $[Os(RCN)_2P_4](BPh_4)_2$ [R = CH_3, 4-$CH_3C_6H_4$; P = $P(OEt)_3$, $PPh(OEt)_2$] were prepared following the reported methods.[6,20] The iridium complexes $[IrHCl_2P(PPh_3)_2]$, $[IrHCl_2P(AsPh_3)_2]$ [P = $P(OEt)_3$, $PPh(OEt)_2$] and $[IrH_3(PPh_3)_3]$ were synthesised by published methods.[6d,21]

$[RuH(NH_2OH)P_4]BPh_4$ [P = $P(OEt)_3$ 1, $PPh(OEt)_2$ 2]: An equimolar amount of CF_3SO_3H (0.40 mmol, 35 μL) was added to a solution of the appropriate hydride RuH_2P_4 (0.40 mmol) in 10 mL of ethanol cooled to −196 °C and the reaction mixture, after warming to 0 °C, was stirred for 1 h. An excess of hydroxylamine (0.60 mmol, 0.43 mL of a 1.4 M solution in ethanol) was then added and the resulting solution stirred for about 2 h. The solvent was removed under reduced pressure to give an oil, which was treated with ethanol (2 mL) containing an excess of $NaBPh_4$ (0.8 mmol, 0.27 g). A white solid slowly separated out upon stirring the resulting solution. This solid was filtered off and recrystallised from CH_2Cl_2 and ethanol; yield 336 mg for **1** (75%); 384 mg for **2** (77%).
1: $C_{48}H_{84}BNO_{13}P_4Ru$ (1118.97): calcd. C 51.52, H 7.57, N 1.25; found C 51.41, H 7.60, N 1.18. Λ_M = 57.4 S cm^2 mol^{-1}.
2: $C_{64}H_{84}BNO_9P_4Ru$ (1247.14): calcd. C 61.64, H 6.79, N 1.12; found C 61.48, H 6.82, N 1.17. Λ_M = 58.6 S cm^2 mol^{-1}.

$[OsH(NH_2OH)\{P(OEt)_3\}_4]BPh_4$ (3): An equimolar amount of $CF_3SO_3CH_3$ (0.12 mmol, 11 μL) was added to a solution of $[OsH_2\{P(OEt)_3\}_4]$ (0.12 mmol, 0.100 g) in 5 mL of toluene cooled to −196 °C and the reaction mixture, after warming to room temperature, was stirred for 1 h. An excess of NH_2OH (0.3 mmol, 0.48 mL of a 0.63 M solution in ethanol) was added and the solution stirred for about 4 h. The solvent was then removed under reduced pressure to give an oil which was treated with ethanol (2 mL) containing an excess of $NaBPh_4$ (0.24 mmol, 0.082 g). Upon stirring the resulting solution, a white solid separated out which was filtered off and recrystallised from CH_2Cl_2 and ethanol; yield 104 mg (72%). $C_{48}H_{84}BNO_{13}OsP_4$ (1208.10): calcd. C 47.72, H 7.01, N 1.16; found C 47.89, H 7.08, N 1.09. Λ_M = 55.0 S cm^2 mol^{-1}.

$[Ru(NH_2OH)_2\{P(OEt)_3\}_4](BPh_4)_2$ (4): An equimolar amount of CF_3SO_3H (0.40 mmol, 35 μL) was added to a solution of $[RuH_2\{P(OEt)_3\}_4]$ (0.40 mmol, 0.307 g) in 10 mL of toluene cooled to −196 °C. The reaction mixture was warmed to 0 °C, stirred for 1 h, and then cooled to −196 °C again. Triflic acid (0.40 mmol, 35 μL) was added and the solution, after warming to 0 °C, was stirred for 90 min. An excess of hydroxylamine (1.60 mmol, 1.14 mL of a 1.4 M solution in ethanol) was then added and the solution stirred for about 20 min. The solvent was removed under reduced pressure to give an oil which was treated with ethanol (2 mL). Addition of an excess of $NaBPh_4$ (1.60 mmol, 0.55 g) in ethanol (2 mL) to the resulting solution caused the separation of a white solid, which was filtered off and recrystallised from CH_2Cl_2 and ethanol; yield 476 mg (81%). $C_{72}H_{106}B_2N_2O_{14}P_4Ru$ (1470.22): calcd. C 58.82, H 7.27, N 1.47; found C 58.65, H 7.38, N 1.58. Λ_M = 119.6 S cm^2 mol^{-1}).

$[IrCl_2(NH_2OH)P(PPh_3)_2]BPh_4$ [P = $P(OEt)_3$ 5, $PPh(OEt)_2$ 6]: An equimolar amount of CF_3SO_3H (0.12 mmol, 11 μL) was added to a solution of the appropriate hydride $[IrHCl_2P(PPh_3)_2]$ (0.12 mmol) in 8 mL of CH_2Cl_2 cooled to −196 °C, and the reaction mixture was warmed to room temperature and stirred for 90 min. An excess of hydroxylamine (1.20 mmol, 1.46 mL of 0.82 M solution in ethanol) was added and the resulting mixture stirred for about 4 h. The solvent was removed under reduced pressure giving an oil, which was triturated with ethanol (2 mL) containing an excess of $NaBPh_4$ (0.24 mmol, 0.082 g). A yellow solid slowly separated out from the resulting solution, which was filtered off and recrystallised from CH_2Cl_2 in ethanol; yield 98 mg (63%) for **5**; 109 mg (68%) for **6**.
5: $C_{66}H_{68}BCl_2IrNO_4P_3$ (1306.12): calcd. C 60.69, H 5.25, N 1.07, Cl 5.43; found C 60.55, H 5.32, N 1.06, Cl 5.37. Λ_M = 58.2 S cm^2 mol^{-1}.
6: $C_{70}H_{68}BCl_2IrNO_3P_3$ (1338.17): calcd. C 62.83, H 5.12, N 1.05, Cl 5.30; found C 63.01, H 5.24, N 1.10, Cl 5.08. Λ_M = 61.6 S cm^2 mol^{-1}.

$[IrCl_2(NH_2OH)P(AsPh_3)_2]BPh_4$ [P = $P(OEt)_3$ 7, $PPh(OEt)_2$ 8]: These complexes were prepared exactly as for compounds **5** and **6**; yield 113 mg (68%) for **7**; 125 mg (73%) for **8**.
7: $C_{66}H_{68}As_2BCl_2IrNO_4P$ (1394.02): calcd. C 56.87, H 4.92, N 1.00, Cl 5.09; found C 56.64, H 5.01, N 0.92, Cl 5.27. Λ_M = 55.7 S cm^2 mol^{-1}.
8: $C_{70}H_{68}As_2BCl_2IrNO_3P$ (1426.07): calcd. C 58.96, H 4.81, N 0.98, Cl 4.97; found C 59.13, H 4.70, N 1.06, Cl 4.79. Λ_M = 59.0 S cm^2 mol^{-1}.

$[IrH_2(NH_2OH)(PPh_3)_3]BPh_4$ (9): An equimolar amount of CF_3SO_3H (0.12 mmol, 11 μL) was added to a solution of $[IrH_3(PPh_3)_3]$ (0.12 mmol, 0.118 g) in 5 mL of toluene cooled to −196 °C, and the reaction mixture warmed to room temperature and stirred for 10 min. An excess of hydroxylamine (1.20 mmol, 1.46 mL of 0.82 M solution in ethanol) was added and the solution stirred for 4 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (3 mL) containing an excess of $NaBPh_4$ (0.24 mmol, 0.082 g). A white solid separated out from the resulting solution, which was filtered off and recrystallised from CH_2Cl_2 and ethanol; yield 128 mg (80%). $C_{78}H_{70}BIrNOP_3$ (1333.37): calcd. C 70.26, H 5.29, N 1.05; found C 70.35, H 5.37, N 1.11. Λ_M = 54.8 S cm^2 mol^{-1}.

$[Ru\{\eta^2\text{-}NH{=}C(R)ONH_2\}\{P(OEt)_3\}_4](BPh_4)_2$ (R = CH_3 10a, 4-$CH_3C_6H_4$ 10b): An excess of NH_2OH (0.52 mmol, 0.62 mL of a 0.84 M solution in ethanol) was added to a solution of the appropriate nitrile complex $[Ru(RCN)_2\{P(OEt)_3\}_4](BPh_4)_2$ (0.13 mmol) in 10 mL of CH_2Cl_2 and the reaction mixture was stirred for 24 h. The solvent was removed under reduced pressure to give an oil which was treated with ethanol (2 mL). The addition of an excess of $NaBPh_4$ (0.26 mmol, 0.089 g) in 2 mL of ethanol to the resulting solution caused the separation of a white solid, which was filtered off and recrystallised from CH_2Cl_2 and ethanol; yield 123 mg (64%) for **10a**; 135 mg (67%) for **10b**.
10a: $C_{74}H_{106}B_2N_2O_{13}P_4Ru$ (1478.24): calcd. C 60.13, H 7.23, N 1.90; found C 59.97, H 7.17, N 1.86. Λ_M = 117.4 S cm^2 mol^{-1}.
10b: $C_{80}H_{110}B_2N_2O_{13}P_4Ru$ (1554.34): calcd. C 61.82, H 7.13, N 1.80; found C 61.98, H 7.20, N 1.75. Λ_M = 120.7 S cm^2 mol^{-1}.

$[Ru\{\eta^2\text{-}NH{=}C(CH_3)ONH(CH_3)\}\{P(OEt)_3\}_4](BPh_4)_2$ (11): This complex was prepared similarly to **10** by reacting $[Ru(CH_3CN)_2\{P(OEt)_3\}_4](BPh_4)_2$ (0.17 mmol, 0.250 g in 10 mL of CH_2Cl_2) with an excess of $NH(CH_3)OH$ (1.7 mmol, 2.9 mL of 0.58 M solution in ethanol) for 24 h; yield 140 mg (55%). $C_{75}H_{108}B_2N_2O_{13}P_4Ru$ (1492.27): calcd. C 60.37, H 7.29, N 1.88; found C 60.49, H 7.35, N 1.80. Λ_M = 119.1 S cm^2 mol^{-1}.

$[Os\{\eta^2\text{-}NH{=}C(R)ONH_2\}\{P(OEt)_3\}_4](BPh_4)_2$ (R = CH_3 12a, 4-$CH_3C_6H_4$ 12b): An excess of hydroxylamine (1.3 mmol, 1.8 mL of a 0.72 M solution in ethanol) was added to a solution of the appropriate nitrile complex $[Os(RCN)_2\{P(OEt)_3\}_4](BPh_4)_2$ (0.13 mmol) in 8 mL of CH_2Cl_2 and the reaction mixture stirred for 20 h. The solvent was removed under reduced pressure to give an oil, which was treated with ethanol (2 mL) containing an excess of $NaBPh_4$ (0.26 mmol, 0.089 g). Upon stirring the resulting solution a white solid slowly separated out, which was filtered off and recrystallised from CH_2Cl_2 and ethanol; yield 124 mg (62%) for **12a**; 126 mg (59%) for **12b**.
12a: $C_{74}H_{106}B_2N_2O_{13}OsP_4$ (1567.37): calcd. C 56.71, H 6.82, N 1.79; found C 56.59, H 6.98, N 1.68. Λ_M = 123.4 S cm^2 mol^{-1}.
12b: $C_{80}H_{110}B_2N_2O_{13}OsP_4$ (1643.47): calcd. C 58.47, H 6.75, N 1.70; found C 58.30, H 6.81, N 1.62. Λ_M = 121.6 S cm^2 mol^{-1}.

$[Os\{\eta^2\text{-}NH{=}C(CH_3)ONH(CH_3)\}\{P(OEt)_3\}_4](BPh_4)_2$ (13): This complex was prepared similarly to **12** by reacting $[Os(CH_3CN)_2\{P(OEt)_3\}_4](BPh_4)_2$ with a 10-fold excess of *N*-methylhydroxylamine; yield 93 mg (45%). $C_{75}H_{108}B_2N_2O_{13}OsP_4$ (1581.40): calcd. C 56.96, H 6.88, N 1.77; found C 57.13, H 6.96, N 1.69. Λ_M = 115.9 S cm^2 mol^{-1}.

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[1] [1a] K. R. Grundy, C. A. Reed, W. R. Roper, *J. Chem. Soc., Chem. Commun.* **1970**, 1501. [1b] R. Melenkivitz, G. Hillhouse, *Chem. Commun.* **2002**, 660.
[2] D.-W. Feng, M. D. Ryan, *Inorg. Chem.* **1987**, *26*, 2480.
[3] [3a] T.-Y. Cheng, A. Ponce, A. L. Rheingold, G. L. Hillhouse, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 657. [3b] J. S. Southern, G. L. Hillhouse, A. L. Rheingold, *J. Am. Chem. Soc.* **1997**, *119*, 12406.
[4] [4a] D. Sutton, *Chem. Rev.* **1993**, *93*, 995. [4b] B. F. G. Johnson, B. L. Haymore, J. R. Dilworth, in *Comprehensive Coordination Chemistry*, (Eds.: G. Wilkinson, R. D. Gillard and J. A. McCleverty), Pergamon Press, Oxford, 1987, Vol. 2. [4c] R. A. Henderson, G. J. Leigh, C. J. Pickett, *Adv. Inorg. Chem. Radiochem.* **1983**, *27*, 197. [4d] F. Bottomley, *Q. Rev. Chem. Soc.* **1970**, *24*, 617.
[5] [5a] K. D. Demadis, S. M. Malinak, D. Coucouvanis, *Inorg. Chem.* **1996**, *35*, 4038. [5b] C. J. Davies, I. M. Dodd, M. M. Harding, B. T. Heaton, C. Jacob, J. Ratnam, *J. Chem. Soc., Dalton Trans.* **1994**, 787. [5c] D. Sellmann, K. Engl, F. W. Heinemann, *Eur. J. Inorg. Chem.* **2000**, 423. [5d] T. E. Glassman, M. G. Vale, R. R. Schrock, *J. Am. Chem. Soc.* **1992**, *114*, 8098. [5e] M. Kawano, C. Hoshino, K. Matsumoto, *Inorg. Chem.* **1992**, *31*, 5158.
[6] [6a] G. Albertin, S. Antoniutti, A. Bacchi, E. Bordignon, P. M. Dolcetti, G. Pelizzi, *J. Chem. Soc., Dalton Trans.* **1997**, 4435. [6b] G. Albertin, S. Antoniutti, E. Bordignon, S. Pattaro, *J. Chem. Soc., Dalton Trans.* **1997**, 4445. [6c] G. Albertin, S. Antoniutti, A. Bacchi, M. Bergamo, E. Bordignon, G. Pelizzi, *Inorg. Chem.* **1998**, *37*, 479. [6d] G. Albertin, S. Antoniutti, E. Bordignon, F. Menegazzo, *J. Chem. Soc., Dalton Trans.* **2000**, 1181. [6e] G. Albertin, S. Antoniutti, E. Bordignon, G. Perinello, *J. Organomet. Chem.* **2001**, *625*, 217.
[7] V. Yu. Kukushkin, A. J. L. Pombeiro, *Chem. Rev.* **2002**, *102*, 1771.
[8] W. J. Geary, *Coord. Chem. Rev.* **1971**, *7*, 81.
[9] R. A. Michelin, M. Mozzon, R. Bertani, *Coord. Chem. Rev.* **1996**, *147*, 299.
[10] R. Cini, F. P. Fanizzi, F. P. Intini, L. Maresca, G. Natile, *J. Am. Chem. Soc.* **1993**, *115*, 5123; P. Paul, K. Nag, *Inorg. Chem.* **1987**, *26*, 1586; D. L. Thorn, J. C. Calabrese, *J. Organomet. Chem.* **1994**, *272*, 283.
[11] A. Syamale, A. R. Chakravarty, *Inorg. Chem.* **1991**, *30*, 4699; S. G. Feng, P. S. White, J. L. Templeton, *Organometallics* **1993**, *12*, 1765; D. P. Fairlie, W. G. Jackson, *Inorg. Chem.* **1990**, *29*, 140.
[12] Z. Kanda, Y. Nakamura, S. Kawaguchi, *Inorg. Chem.* **1978**, *17*, 910; P. Braunstein, D. Matt, Y. Dusausoy, J. Fischer, *Organometallics* **1983**, *2*, 1410; J. Vicente, M.-T. Chicote, J. Fernandez-Baeza, F. J. Lahoz, J. A. Lopez, *Inorg. Chem.* **1991**, *30*, 3617; R. A. Michelin, M. Mozzon, P. Berin, R. Bertani, F. Benetollo, G. Bombieri, R. J. Angelici, *Organometallics* **1994**, *13*, 1341.
[13] S. Dayagi, Y. Degani, in *The Chemistry of the Carbon-Nitrogen Double Bond* (Ed.: S. Patai), Interscience, London, 1970, p. 111.
[14] B. P. Iudkins, D. G. Allen, T. A. Cook, B. Evans, T. E. Sardharwala, *Synth. Commun.* **1996**, *26*, 4351.
[15] L. Stephenson, W. K. Warburton, M. J. Wilson, *J. Chem. Soc., C* **1969**, 861.
[16] G. Wagner, A. J. L. Pombeiro, Y. N. Kukushkin, T. B. Pakhomova, A. D. Ryabov, V. Yu. Kukushkin, *Inorg. Chim. Acta* **1999**, *292*, 272.
[17] R. Rabinowitz, J. Pellon, *J. Org. Chem.* **1961**, *26*, 4623.
[18] C. Hurd, *Inorg. Synth.* **1939**, *1*, 87.
[19] G. Balacco, *J. Chem. Inf. Comput. Sci.* **1994**, *34*, 1235.
[20] [20a] W. G. Peet, D. H. Gerlach, *Inorg. Synth.* **1974**, *15*, 38. [20b] D. H. Gerlach, W. G. Peet, E. L. Muetterties, *J. Am. Chem. Soc.* **1972**, *94*, 4545. [20c] G. Albertin, S. Antoniutti, E. Bordignon, *J. Chem. Soc., Dalton Trans.* **1989**, 2353.
[21] S. Park, A. J. Lough, R. H. Morris, *Inorg. Chem.* **1996**, *35*, 3001 and references therein.

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