New Mononitrosyl Derivatives of Iron, Ruthenium and Osmium†

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Hydride nitrosyl complexes $[MH(NO)L_4][PF_6]_2$ **1** [M = Ru or Os; L = $P(OEt)_2Ph$] were prepared by allowing $[MH(\eta^2-H_2)L_4]BF_4$ to react with $NO^+PF_6^-$ at −80 °C in CH_2Cl_2. Five-co-ordinate $[Fe(NO)L_4]PF_6$ **2** was obtained from the same reaction in the case of iron. Deprotonation of cations $[MH(NO)L_4]^{2+}$ **1** with NEt_3 or OH^- led to the formation of new mononitrosyl cations $[M(NO)L_4]^+$ **2** (M = Ru or Os). All **2** react with $HBF_4 \cdot Et_2O$ to give $[MH(NO)L_4]^{2+}$ derivatives, according to the equilibrium $[MH(NO)L_4]^{2+} \rightleftharpoons [M(NO)L_4]^+$. Characterization of nitrosyls **1** and **2** by infrared, ^1H and ^{31}P NMR spectra is reported. The reaction of $[M(NO)L_4]^+$ **2** (M = Fe, Ru or Os) with isocyanides and CO was examined and led to the synthesis of $[M(NO)(CNR)_2L_2]^+$ (M = Fe), $[M(CNR)_4L_2]^{2+}$ (M = Ru or Os), and $[M(NO)(CO)_2L_2]^+$ (M = Fe or Ru) derivatives (R = $4-MeC_6H_4$ or $4-MeOC_6H_4$). The $[M(NO)L_4]PF_6$ complexes are also oxidized by bromine to produce $[RuBr_2(NO)L_3]^+$ and $[OsBr(NO)L_4]^{2+}$.

A number of ruthenium and osmium nitrosyl phosphine complexes[1] have been reported in recent years, and the study of their properties has been stimulated by the knowledge that NO can co-ordinate to transition-metal ions in either a linear or a bent manner,[1d,2] that certain nitrosyl derivatives have been found to be catalytically active,[3] and that co-ordinated nitric oxide can undergo both nucleophilic and electrophilic attack.[4] For octahedral d^6 complexes the known types are $[MX_3(NO)L_2]$,[5] $[MX_2(NO)L_3]^+$,[5d,6] and $[MX(NO)L_4]^{2+}$ (ref. 7) (X = halide, L = phosphine and/or CO), but no hydridenitrosyl derivative of ruthenium and osmium, except $[OsH_2(NO)(PPh_3)_3]BPh_4$,[8] has been reported. Conversely, several five-co-ordinate mononitrosyl d^8 complexes[9] have been described, mainly with carbonyl and phosphine ligands, such as $[M(NO)(CO)_2L_2]^+$, $[MCl(NO)L_3]$, $[M(NO)(CO)L_3]^+$, *etc.*, while $[M(NO)(dppe)_2]^+$ (dppe = $Ph_2PCH_2CH_2PPh_2$) is the only known example of a complex[10] containing the $(NO)P_4$ donor set.

We are interested in the chemistry of nitrosyl and aryldiazo complexes containing phosphite ligands[11] and, as part of our studies, we now report on the reactivity of molecular hydrogen derivatives $[MH(\eta^2-H_2)L_4]^+$ (L = phosphite) with nitrosonium hexafluorophosphate which allow the synthesis of the first $[MH(NO)L_4]^{2+}$ derivatives. Studies on the chemistry of these derivatives were also undertaken and the synthesis and properties of new five-co-ordinate mononitrosyl $[M(NO)L_4]^+$ complexes containing phosphite ligands are also described.

Experimental

General Comments.—Unless otherwise noted, all manipulations were carried out in a nitrogen and/or argon atmosphere by using standard Schlenk and syringe techniques or a Vacuum Atmosphere dry-box. All solvents used were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. Diethoxyphenylphosphine was prepared by the method of Rabinowitz and Pellon;[12] triethyl and trimethyl phosphite were Ega Chemie products purified by distillation under nitrogen. Nitrosonium hexafluorophosphate was an Alfa Inorganic product used as received. Substituted phenyl isocyanides were obtained by the phosgene method of Ugi *et al.*[13] Other reagents were purchased from commercial sources in the highest available purity and used as received.

Infrared spectra were recorded on a Perkin-Elmer model 683 spectrophotometer, solution ^1H NMR spectra on Varian EM-390 and FT-80A spectrometers at temperatures varying between −85 and +34 °C unless otherwise noted and referred to internal tetramethylsilane. Fourier-mode, proton-noise-decoupled ^{31}P NMR spectra were collected on a Varian FT-80A spectrometer operating at 32.203 MHz. All chemical shifts are reported with respect to 85% H_3PO_4, with downfield shifts considered positive. Conductivities of 10^{-3} mol dm^{-3} solutions of the complexes in nitromethane at 25 °C were measured on a Radiometer CDM 83 instrument. Solution susceptibilities were determined by the Evans method.[14]

Synthesis of Complexes.—Molecular hydrogen complexes $[MH(\eta^2-H_2)L_4]^+$ (M = Fe, Ru or Os) were prepared according to the procedures previously reported.[11f,g,15]

$[RuH(NO)\{P(OEt)_2Ph\}_4][PF_6]_2$ **1b**. A solution of $[RuH(\eta^2-H_2)\{P(OEt)_2Ph\}_4]BF_4$ (1.02 mmol, 1 g) in CH_2Cl_2 (10 cm^3) was cooled to −80 °C and quickly transferred, at the same temperature, to a reaction flask containing $NO^+PF_6^-$ (1.02 mmol, 0.18 g) in CH_2Cl_2 (5 cm^3). The reaction mixture was brought to room temperature and stirred for about 90 min. The solvent was removed under reduced pressure to give a yellow oil, which was treated with ethanol. Addition of an excess of $NaPF_6$ (3 mmol, 0.5 g) to the resulting solution caused the precipitation of a yellow solid, which was crystallized from CH_2Cl_2 (5 cm^3)–ethanol (15 cm^3); yield ⩾80%. $\delta_H(CD_2Cl_2)$ 7.52 (20 H, m, Ph), 3.84 (16 H, m, CH_2) and 1.29 (24 H, t, CH_3).

$[OsH(NO)\{P(OEt)_2Ph\}_4][PF_6]_2$ **1c**. A solution of $[OsH(\eta^2-H_2)\{P(OEt)_2Ph\}_4]BF_4$ (0.28 mmol, 0.30 g) in CH_2Cl_2 (10 cm^3) was cooled to −80 °C and transferred to a reaction flask at −80 °C containing $NO^+PF_6^-$ (0.28 mmol, 0.05 g) in CH_2Cl_2 (5 cm^3). The reaction mixture was brought to room temperature and stirred for 3 h. The solvent was removed at reduced pressure, giving an oil which was treated with ethanol (10 cm^3). Addition of $NaPF_6$ (0.84 mmol, 0.14 g) to the resulting solution caused the precipitation of a yellow solid, which was filtered off and crystallized from CH_2Cl_2 (2 cm^3)–ethanol (8 cm^3); yield ⩾75%. $\delta_H(CD_2Cl_2)$ 7.50 (20 H, m, Ph), 3.80 (16 H, m, CH_2), 1.30 (24 H, t, CH_3).

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† *Non-SI unit employed:* atm = 101 325 Pa.

$[OsH(NO)\{P(OEt)_2Ph\}_4][BPh_4]_2$ **1c′**. This compound was prepared exactly as for **1c**, using $NaBPh_4$ as precipitating agent. $\delta_H(CD_2Cl_2)$ 7.47, 7.28, 6.94 (60 H, m, Ph), 3.66 (16 H, m, CH_2) and 1.21 (24 H, t, CH_3).

$[Fe(NO)\{P(OEt)_2Ph\}_4]PF_6$ **2a**. A solution of $[FeH(\eta^2\text{-}H_2)\{P(OEt)_2Ph\}_4]BF_4$ (1.07 mmol, 1 g) in CH_2Cl_2 (10 cm^3) was cooled to −80 °C and quickly transferred, at the same temperature, to a reaction flask containing an excess of $NO^+PF_6^-$ (3.2 mmol, 0.56 g) in CH_2Cl_2 (5 cm^3). The reaction mixture was brought to room temperature, stirred for 2 h and then filtered. The solvent was removed under reduced pressure, leaving an oil which was triturated with ethanol. A green-brown solid separated after 30 min and was filtered off and crystallized from CH_2Cl_2 (5 cm^3)–ethanol (15 cm^3); yield $\geqslant$40%. $\delta_H(CD_2Cl_2)$ 7.39 (20 H, m, Ph), 3.64 (16 H, m, CH_2) and 1.09 (24 H, t, CH_3).

$[Ru(NO)\{P(OEt)_2Ph\}_4]PF_6$ **2b**. An excess of $LiOH{\cdot}H_2O$ (1.5 mmol, 0.06 g) in ethanol (5 cm^3) was added to a suspension of $[RuH(NO)\{P(OEt)_2Ph\}_4][PF_6]_2$ (0.5 mmol, 0.61 g) in ethanol (10 cm^3) and the reaction mixture was stirred for 4 h at room temperature. As the reaction proceeded, a red-brown solid separated which was finally filtered off and crystallized from CH_2Cl_2 (3 cm^3)–ethanol (10 cm^3); yield $\geqslant$80%. $\delta_H(CD_2Cl_2)$ 7.36 (20 H, m, Ph), 3.60 (16 H, m, CH_2) and 1.14 (24 H, t, CH_3).

$[Ru(NO)\{P(OEt)_2Ph\}_4]BPh_4$ **2b′**. This compound can be prepared by metathetic exchange, by adding a solution of $NaBPh_4$ in ethanol to a saturated solution of $[Ru(NO)\{P(OEt)_2Ph\}_4]PF_6$ in EtOH and enough CH_2Cl_2. The pale red solid obtained was filtered off and crystallized from CH_2Cl_2 (3 cm^3)–ethanol (100 cm^3); yield $\geqslant$90%. $\delta_H(CD_2Cl_2)$ 7.35, 6.96 (40 H, m, Ph), 3.60 (16 H, m, CH_2) and 1.12 (24 H, t, CH_3).

$[Os(NO)\{P(OEt)_2Ph\}_4]BPh_4$ **2c′**. An excess of $LiOH{\cdot}H_2O$ (1.2 mmol, 0.05 g) in ethanol (5 cm^3) was added to a suspension of $[OsH(NO)\{P(OEt)_2Ph\}_4][BPh_4]_2$ (0.12 mmol, 0.20 g) in ethanol (10 cm^3) and CH_2Cl_2 (3 cm^3). The reaction mixture was stirred for 1 d at room temperature, concentrated to 5 cm^3 and cooled to −30 °C. The red solid obtained was filtered off and crystallized from CH_2Cl_2 (2 cm^3)–ethanol (10 cm^3); yield $\geqslant$80%. $\delta_H(CD_2Cl_2)$ 7.34, 6.96 (40 H, m, Ph), 3.59 (16 H, m, CH_2) and 1.14 (24 H, t, CH_3).

$[Os(NO)\{P(OEt)_2Ph\}_4]PF_6$ **2c**. This compound was prepared exactly as the related BPh_4^- derivative **2c′**, starting from $[OsH(NO)\{P(OEt)_2Ph\}_4][PF_6]_2$ in ethanol; yield $\geqslant$80%. $\delta_H(CD_2Cl_2)$ 7.37 (20 H, m, Ph), 3.60 (16 H, m, CH_2) and 1.15 (24 H, t, CH_3).

$[Fe(NO)(CNR)_2\{P(OEt)_2Ph\}_2]PF_6$ **3a** (R = 4-MeC_6H_4 **3a$_1$** *or* 4-$MeOC_6H_4$ **3a$_2$**). An excess of the appropriate isocyanide (1.2 mmol) was added to a suspension of $[Fe(NO)\{P(OEt)_2Ph\}_4]PF_6$ (0.39 mmol, 0.40 g) in ethanol (15 cm^3), and the reaction mixture was refluxed for about 3 h. The resulting red solution was concentrated to $\approx$5 cm^3 and cooled to 0 °C. Red microcrystals separated after 20 min of stirring; they were filtered off and crystallized from ethanol; yield $\geqslant$80%. For **3a$_1$**: $\delta_H[(CD_3)_2CO]$ 7.85, 7.63, 7.31 (18 H, m, Ph), 4.34 (8 H, m, CH_2), 2.39 (6 H, s, CH_3 of isocyanide) and 1.42 (12 H, t, CH_3). For **3a$_2$**: $\delta_H(CD_2Cl_2)$ 7.64, 7.54, 6.98 (18 H, m, Ph), 4.14 (8 H, m, CH_2), 3.84 (6 H, s, CH_3 of isocyanide) and 1.39 (12 H, t, CH_3).

$[Ru(4\text{-}MeC_6H_4NC)_4\{P(OEt)_2Ph\}_2][PF_6]_2$ **4b**. An excess of 4-tolyl isocyanide (1.65 mmol, 0.2 cm^3) was added to a solution of $[Ru(NO)\{P(OEt)_2Ph\}_4]PF_6$ (0.37 mmol, 0.40 g) in CH_2Cl_2 (10 cm^3) and the reaction mixture was stirred for 2 h. The solvent was removed under reduced pressure, giving an oil which was treated with ethanol (5 cm^3). By slow cooling of the resulting solution to −30 °C, white microcrystals of the complex were obtained; yield $\geqslant$45%. Derivative **4b** can also be prepared by adding an excess of 4-tolyl isocyanide (1.65 mmol, 0.2 cm^3) to a solution of $[RuH(NO)\{P(OEt)_2Ph\}_4][PF_6]_2$ (0.33 mmol, 0.40 g) in ethanol (10 cm^3) and refluxing the reaction mixture for 1 h. The solution was then concentrated to about 5 cm^3 and cooled to −30 °C to give white microcrystals of the complex; yield $\geqslant$80%. $\delta_H(CD_2Cl_2)$ 7.56, 7.23 (26 H, m, Ph), 4.14 (8 H, m, CH_2), 2.42 (12 H, s, CH_3 of isocyanide) and 1.38 (12 H, t, CH_3).

$[Os(4\text{-}MeC_6H_4NC)_4\{P(OEt)_2Ph\}_2][BPh_4]_2$ **4c′**. To a suspension of $[Os(NO)\{P(OEt)_2Ph\}_4]BPh_4$ (0.2 mmol, 0.27 g) in ethanol (10 cm^3) was added an excess of 4-tolyl isocyanide (0.85 mmol, 0.1 cm^3) and the reaction mixture refluxed for 20 min. The solution was then concentrated to about 5 cm^3 and cooled to −30 °C to give white microcrystals of the complex; yield $\geqslant$45%. Complex **4c′** can also be prepared by refluxing for 1 h a suspension of $[OsH(NO)\{P(OEt)_2Ph\}_4][BPh_4]_2$ (0.2 mmol, 0.33 g) in ethanol (10 cm^3) containing an excess (0.85 mmol, 0.1 cm^3) of 4-MeC_6H_4NC. By slow cooling to −30 °C of the resulting concentrated (5 cm^3) solution, crystals of the compound were obtained; yield $\geqslant$80%. $\delta_H(CD_2Cl_2)$ 7.30, 6.94 (66 H, m, Ph), 4.02 (8 H, m, CH_2), 2.40 (12 H, s, CH_3 of isocyanide) and 1.35 (12 H, t, CH_3).

$[Ru(NO)(CO)_2\{P(OEt)_2Ph\}_2]PF_6$ **5b**. A solution of $[Ru(NO)\{P(OEt)_2Ph\}_4]PF_6$ (0.2 mmol, 0.21 g) in CH_2Cl_2 (5 cm^3) was stirred under CO (1 atm) for 30 min, and then, maintaining the CO atmosphere, diethyl ether was slowly added until a white solid separated. The solid was filtered off, washed with diethyl ether, and dried under vacuum; yield $\geqslant$80%. $\delta_H(CD_2Cl_2)$ 7.60 (10 H, m, Ph), 3.88 (8 H, m, CH_2) and 1.27 (12 H, t, CH_3).

$[RuBr_2(NO)\{P(OEt)_2Ph\}_3]PF_6$ **6b**. Bromine (0.29 mmol, 15 µl) was added to a solution of $[Ru(NO)\{P(OEt)_2Ph\}_4]PF_6$ (0.29 mmol, 0.31 g) in CH_2Cl_2 (10 cm^3) cooled to −80 °C, and the reaction mixture was slowly brought to 0 °C (10 min). The solvent was evaporated under reduced pressure to give a yellow oil, which was treated with ethanol containing $LiPF_6$ (0.29 mmol, 44 mg). The solid obtained was filtered off and its spectral data (IR and NMR) showed that, besides **6b**, it also contained other species which, being neutral, could be separated by extraction with benzene. The solid was therefore washed with three 5 cm^3 portions of benzene and crystallized by slow cooling to −30 °C of a saturated solution of the complex in ethanol–dichloromethane (15 cm^3, 3 cm^3); yield $\geqslant$55%. $\delta_H[(CD_3)_2CO]$ 7.76, 7.60 (15 H, m, Ph), 4.34 (12 H, m, CH_2), 1.54 and 1.46 (18 H, t, CH_3).

$[OsBr(NO)\{P(OEt)_2Ph\}_4][PF_6]_2$ **7c**. A solution of bromine (0.1 mmol, 5.1 µl) in CH_2Cl_2 (5 cm^3) was added to a solution of $[Os(NO)\{P(OEt)_2Ph\}_4]PF_6$ (0.1 mmol, 116 mg) in CH_2Cl_2 (5 cm^3) cooled to −80 °C, and the reaction mixture was slowly brought to 0 °C (10 min). The solvent was evaporated under reduced pressure to give a yellow oil which was triturated with ethanol (5 cm^3) containing $LiPF_6$ (0.10 mmol, 15 mg). The solid obtained was filtered off and crystallized from CH_2Cl_2 (2 cm^3)–ethanol (5 cm^3); yield $\geqslant$80%. $\delta_H(CD_2Cl_2)$ 7.72 (20 H, m, Ph), 4.13 (16 H, m, CH_2), 1.54, 1.45 and 1.36 (24 H, t, CH_3).

Results and Discussion

Molecular hydrogen complexes $[MH(\eta^2\text{-}H_2)L_4]BF_4$ [M = Ru or Os; L = $P(OEt)_2Ph$] react at −80 °C in CH_2Cl_2 with both stoichiometric or excess amounts of nitrosonium cation to give mononitrosyl derivatives $[MH(NO)L_4]^{2+}$ **1**, as shown in equation (1). Instead, from the reaction of the related iron complex $[FeH(\eta^2\text{-}H_2)L_4]BF_4$ with excess of $NO^+PF_6^-$, only five-co-ordinate $[Fe(NO)L_4]^+$ **2a** can be isolated. The reaction between NO^+ and other η^2-H_2 complexes, containing different phosphites such as $P(OEt)_3$ and $P(OMe)_3$, were also studied, but no stable nitrosyl complex was isolated. We also attempted to prepare nitrosyls $[MH(NO)L_4]^{2+}$ by treating molecular hydrogen complexes $[MH(\eta^2\text{-}H_2)L_4]^+$ with other nitrosylating agents such as $NBu^n{}_4NO_2$ and *N*-methyl-*N*-nitrosotoluene-*p*-sulfonamide (mnts). While with an excess of nitrite in ethanol

$$[MH(\eta^2\text{-}H_2)L_4]^+ + NO^+ \longrightarrow [MH(NO)L_4]^{2+} + H_2 \quad (1)$$
$$M = Ru\ \mathbf{1b}\ \text{or}\ Os\ \mathbf{1c}$$

Table 1 Selected infrared and NMR data for iron, ruthenium and osmium complexes

	IR[a]		^1H NMR[b]		$^{31}P\text{-}\{^1H\}$ NMR[c]	
Compound	ν/cm^{-1}	Assignment	δ (hydride)	$J(PH)_{app}$/Hz	Spin system	δ (*J*)
1b $[RuH(NO)\{P(OEt)_2Ph\}_4][PF_6]_2$	1972w (1965w) 1826s 1698m (1830s) (1685m)	ν(MH) ν(NO)	−4.69 (qnt)	17.4	ABC_2	δ_A 140.9, δ_B 140.3, δ_C 130.4 (J_{AB} = 4.0, J_{AC} = 33.0, J_{BC} = 37.0)
1c $[OsH(NO)\{P(OEt)_2Ph\}_4][PF_6]_2$	2041w (2035w) 1814s (1823s)	ν(MH) ν(NO)	−3.33 (qnt)	21.6		96 (d of m)
1c′ $[OsH(NO)\{P(OEt)_2Ph\}_4][BPh_4]_2$	2040w (2035w) 1812s (1808s)	ν(MH) ν(NO)	−3.66 (qnt)	21.6		96 (d of m)
2a $[Fe(NO)\{P(OEt)_2Ph\}_4]PF_6$	1723s (1710s)	ν(NO)			A_2B_2	δ_A 183.3, δ_B 169.7 (J_{AB} = 104.1)
2b $[Ru(NO)\{P(OEt)_2Ph\}_4]PF_6$	1698s (1685s)	ν(NO)			A_2B_2	δ_A 162.9, δ_B 151.0 (J_{AB} = 46.3)
2b′ $[Ru(NO)\{P(OEt)_2Ph\}_4]BPh_4$	1699s (1690s)	ν(NO)			A_2B_2	δ_A 163.1, δ_B 151.1 (J_{AB} = 46.3)
2c $[Os(NO)\{P(OEt)_2Ph\}_4]PF_6$	1690s (1684s)	ν(NO)			A_2B_2	δ_A 121.9, δ_B 105.8 (J_{AB} = 37.2)
2c′ $[Os(NO)\{P(OEt)_2Ph\}_4]BPh_4$	1690s (1680s)	ν(NO)			A_2B_2	δ_A 121.8, δ_B 105.6 (J_{AB} = 37.2)
3a$_1$ $[Fe(NO)(4\text{-}MeC_6H_4NC)_2\{P(OEt)_2Ph\}_2]PF_6$	2131m 2089s (2137s) (2088s) 1750s (1753s)	ν(CN) ν(NO)				177.3 (s)[d]
3a$_2$ $[Fe(NO)(4\text{-}MeOC_6H_4NC)_2\{P(OEt)_2Ph\}_2]PF_6$	2132m 2092s (2135s) (2095s) 1748s (1740s)	ν(CN) ν(NO)				179.7 (s)
4b $[Ru(4\text{-}MeC_6H_4NC)_4\{P(OEt)_2Ph\}_2][PF_6]_2$	2172s (2170s)	ν(CN)				143.7 (s)
4c′ $[Os(4\text{-}MeC_6H_4NC)_4\{P(OEt)_2Ph\}_2][BPh_4]_2$	2168s (2163s)	ν(CN)				102.1 (s)
5b $[Ru(NO)(CO)_2\{P(OEt)_2Ph\}_2]PF_6$	2055m 1989s (2045m) (1985s) 1728s (1722s)	ν(CO) ν(NO)				139.2 (s)[d]
6b $[RuBr_2(NO)\{P(OEt)_2Ph\}_3]PF_6$	1876s (1870s)	ν(NO)			AB_2[b]	δ_A 119.8, δ_B 113.1 (J_{AB} = 30.0)
7c $[OsBr(NO)\{P(OEt)_2Ph\}_4][PF_6]_2$	1885s (1884s)	ν(NO)			AB_2C[b]	δ_A 95.1, δ_B 80.6, δ_C 80.3 (J_{AB} = 46.9,J_{AC} = 49.4, J_{BC} = 31.6)

[a] In CH_2Cl_2 and (KBr). [b] At room temperature in CD_2Cl_2. [c] Positive shift downfield from 85% H_3PO_4, at −80 °C in CD_2Cl_2; *J* in Hz. [d] At −80 °C in $(CD_3)_2CO$.

Table 2 Physical and analytical data for the iron, ruthenium and osmium complexes

			Analysis[b] (%)		
Compound	M.p./°C	Λ_M[a]/S cm^2 mol^{-1}	C	H	N
1b	131	184.1	39.65 (39.55)	5.00 (5.05)	1.20 (1.15)
1c	160	169.2	37.05 (36.85)	4.75 (4.70)	1.05 (1.05)
1c′	141	122.5	63.65 (63.95)	6.05 (6.15)	0.80 (0.85)
2a	96	83.7	46.75 (46.95)	6.00 (5.90)	1.50 (1.35)
2b	108	81.3	44.80 (44.95)	5.65 (5.65)	1.25 (1.30)
2b′	105	50.5	61.65 (61.85)	6.45 (6.50)	1.25 (1.15)
2c		82.3	41.35 (41.50)	5.30 (5.20)	1.30 (1.20)
2c′	151	55.6	57.65 (57.70)	6.05 (6.05)	1.00 (1.05)
3a$_1$	139	87.4	49.95 (50.20)	5.20 (5.15)	4.95 (4.90)
3a$_2$	130	89.5	48.55 (48.40)	4.95 (4.95)	4.75 (4.70)
4b	122	166.5	49.35 (49.70)	4.65 (4.65)	4.30 (4.45)
4c′	159	116.2	70.70 (70.90)	5.80 (5.85)	3.10 (3.30)
5b		85.8	36.45 (36.25)	4.10 (4.15)	1.80 (1.90)
6b	155	86.0	34.70 (34.95)	4.30 (4.40)	1.20 (1.35)
7c	154	185.2	34.60 (34.75)	4.30 (4.35)	1.10 (1.00)

[a] In nitromethane solution (10^{-3} mol dm^{-3}) at 25 °C. [b] Calculated values in parentheses.

the reaction proceeds to give **1** in good yield, with mnts only a mixture of $[MH(NO)L_4]^{2+}$ and $[M(NO)L_4]^+$ derivatives is obtained.

Some spectroscopic properties of hydridenitrosyl compounds **1**, which are air-stable as solids but rather unstable in solution, diamagnetic and 2:1 electrolytes, are reported in Table 1. Physical and analytical data for all complexes are given in Table 2. At room temperature the ^1H NMR spectra of both the ruthenium **1b** and osmium **1c** complexes show a quintet hydride resonance, whereas the $^{31}P\text{-}\{^1H\}$ NMR spectra display only one singlet. Lowering of the sample temperature resulted in a variation in the spectra showing, at −80 °C, a multiplet for the hydride resonance in the proton spectra, and a multiplet in the ^{31}P spectra for both complexes which, in the case of Ru, can also be simulated using an ABC_2 model. The presence of non-equivalent phosphite ligands is proposed on the basis of the mutually *cis* positions of the hydride and the nitrosyl. However, a *trans* geometry in which rotation of the four phosphites is restricted by steric interaction may also show inequivalent phosphorus ligands as the temperature is lowered, resulting in a multiplet in the ^{31}P NMR spectrum. One such example, *trans*-$[IrCl_2(PMe_2Ph)_4]ClO_4$, has recently been reported.[16] The X-ray crystal structures of our complexes were not determined and therefore, in the absence of other data, no conclusive assignment of the geometry of **1b** and **1c** can be proposed. Furthermore, Table 1 shows that the two osmium complexes **1c** and **1c′**, which differ only in the anion, *i.e.* PF_6^- and BPh_4^-, reveal a change in the chemical shift of the hydride resonance of about 25 Hz. This variation is rather unusual, because the known phosphitehydride complexes[11,15] generally show little variation (2–3 Hz) of chemical shift with change of anion.

The infrared spectra show a weak band at 1972 cm^{-1} for complex **1b** and at 2041 cm^{-1} for **1c** (CH_2Cl_2), attributable to ν(MH). Furthermore, in the ν(NO) stretching region, where the osmium complex in both the solid state and in CH_2Cl_2 solution shows only one strong band at 1814 cm^{-1} (CH_2Cl_2), the related $[RuH(NO)L_4]^{2+}$ exhibits two bands, a strong one at 1826 cm^{-1} and a medium-intensity one at 1698 cm^{-1} (CH_2Cl_2). However, the latter band falls at exactly the same frequency as that of the mononitrosyl $[Ru(NO)L_4]^+$ complex, which may therefore be present in the sample of $[RuH(NO)L_4]^{2+}$. In fact, synthesis of the five-co-ordinate complex is easy (see below) and the band at 1698 cm^{-1} may simply represent a protonation–deprotonation equilibrium involving some impurity acting as a base. Therefore, the existence of a rapid linear $\rightleftharpoons$ bent equilibrium [1a,2a,b] of the metal nitrosyl invoked to explain the presence of two ν(NO) bands for mononitrosyl complexes may reasonably be excluded for our compounds.

Cations $[MH(NO)L_4]^{2+}$ react with bases such as LiOH or NEt_3 to give five-co-ordinate mononitrosyls $[M(NO)L_4]^+$ **2**, which can be isolated and characterized. Protonation of complexes **2** with $HBF_4{\cdot}Et_2O$ gives the starting $[MH(NO)L_4]^{2+}$ cations [equation (2)]. The complex $[Fe(NO)L_4]^+$ **2a** also reacts with $HBF_4{\cdot}Et_2O$ in CH_2Cl_2 to give a yellow solution, the IR spectrum of which shows ν(NO) at 1833 cm^{-1} and ν(MH) at 1930 cm^{-1}, reasonably attributable to the $[FeH(NO)L_4]^{2+}$ derivative. However, the instability of this complex prevents its isolation and may also explain why, in contrast to Ru and Os, the reaction of $[FeH(\eta^2\text{-}H_2)L_4]^+$ with NO^+ only gives the $[Fe(NO)L_4]^+$ derivative.

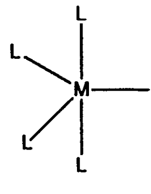
$$\underset{\mathbf{1}}{[MH(NO)L_4]^{2+}} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} \underset{\mathbf{2}}{[M(NO)L_4]^{+}} \qquad (2)$$

The equilibrium (2) shown by our complexes allows easy transformation between a six-co-ordinate d^6 complex and a five-co-ordinate d^8 derivative and *vice versa* by simple reaction with base or strong acid respectively. It should also be noted that this reaction is new for the iron-triad nitrosyl complexes and its extension may give new synthetic methods for this class of compounds.

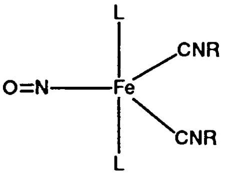
Mononitrosyl complexes of the type $[RuX(NO)L_2]^+$ [X = Cl or Br, L = 2,2′-bipyridine (bipy) or a diarsine] are reported to undergo to a variety of nucleophilic reactions at the co-ordinated NO,[4b,17] and the corresponding nitrito complexes $[RuX(NO_2)L_2]$ were obtained with OH^-. These nitrosyl complexes, which behave as electrophiles, have high ν(NO) frequencies, generally in the range 1945–1886 cm^{-1}. Our $[MH(NO)L_4]^{2+}$ derivatives also show electrophilic behaviour, but nucleophilic attack by OH^- does not take place at the NO ligand, in view of the low ν(NO) frequencies (1826–1812 cm^{-1}), giving rather a simple deprotonation reaction.

The five-co-ordinate $[M(NO)L_4]^+$ (M = Fe, Ru or Os) complexes are stable solids, diamagnetic and soluble in polar organic solvents, in which they behave as 1 : 1 electrolytes (Table 2). The IR spectra display only one ν(NO) band at 1723–1680 cm^{-1} (Table 1), both in the solid state and in CH_2Cl_2 solution. These values, compared with those previously reported for related d^8 complexes,[5g] seem to suggest a linear M–N=O group. The $^{31}P\text{-}\{^1H\}$ NMR spectra show a singlet at room temperature but an A_2B_2 multiplet at −80 °C, in agreement with the existence in solution of a trigonal-bipyramidal geometry with NO in the equatorial position (**I**).

A comparison of nitrosyl $[M(NO)L_4]^+$ cations with related aryldiazenido $[M(RN_2)L_4]^+$ derivatives, previously reported by us,[11b,d,e] shows that, whereas the nitrosyls have trigonal-bipyramidal geometry in solution, such a geometry distorted toward square planar seems to be present for the aryldiazenides. The ν(NO) values for the nitrosyls (range 1723–1690 cm^{-1}) are about 50 cm^{-1} higher than for ν(NN) (range 1668–1640 cm^{-1}), as is generally observed for related nitrosyl and arenediazonium complexes. Both react with strong acid (HBF_4), but while protonation seems to take place at the central metal in all the nitrosyls to give the hydride complexes $[MH(NO)L_4]^{2+}$, with the aryldiazenido $[M(RN_2)L_4]^+$ (M = Ru or Os) derivatives protonation takes place at the N^1 atom of the RN_2 ligand to afford the aryldiazene $[M(RN{=}NH)L_4]^{2+}$ compounds.



I



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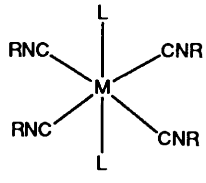
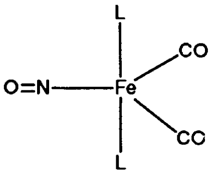
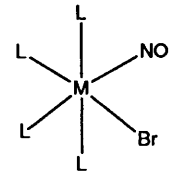


III



IV



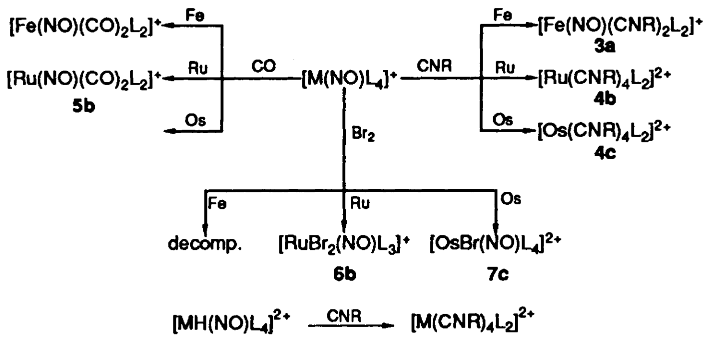
V

Some reactions of $[M(NO)L_4]^+$ and $[MH(NO)L_4]^{2+}$ complexes with various reagents were investigated and the results are summarized in Scheme 1. While the five-co-ordinate $[M(NO)L_4]^+$ derivatives show a rich and varied chemistry, the six-co-ordinate $[MH(NO)L_4]^{2+}$ are rather robust complexes and substitution reactions with CO, halogenide, and phosphine are very slow. The reaction proceeds only with isocyanides, giving $[M(CNR)_4L_2]^{2+}$ complexes.

The iron nitrosyl $[Fe(NO)L_4]^+$ slowly reacts with isocyanides at room temperature, but under reflux conditions the derivatives $[Fe(NO)(CNR)_2L_2]^+$ **3a** can easily be obtained. Their IR spectra exhibit a ν(NO) band at 1750–1748 cm^{-1} and two absorptions at 2131–2132 and 2089–2092 cm^{-1}, attributed to the two isocyanides in mutually *cis* positions. In the temperature range +30 to −80 °C the $^{31}P\text{-}\{^1H\}$ NMR spectra show only one sharp singlet, whereas in the ^1H NMR spectra a complicated multiplet appears in the CH_2 region, suggesting that the two phosphite ligands are *trans*. A trigonal-bipyramidal geometry in solution of the type **II** can therefore reasonably be proposed for this mixed-ligand derivative, as we had previously proposed for the related complexes [18] containing $P(OMe)_3$ and $P(OEt)_3$ as coligands.

In contrast, the $[Ru(NO)L_4]^+$ complex quickly reacts at room temperature with an excess of 4-tolyl isocyanide to give a pale yellow solution, the IR spectrum of which does not show the presence of ν(NO) bands, but only those due to the isocyanide groups. From this solution we isolated a white solid, characterized as $[Ru(4\text{-}MeC_6H_4NC)_4L_2][PF_6]_2$ **4b**.

The reaction of the complex $[Os(NO)L_4]^+$ with isocyanides is slower than that of the ruthenium complex, but it always produces the tetrakis(isocyanide) compound $[Os(CNR)_4L_2]^{2+}$. These isocyanide complexes, which can also be prepared by treating the $[MH(NO)L_4]^{2+}$ compounds with isocyanides, are 1 : 2 electrolytes and their IR spectra in CH_2Cl_2 solution show only one ν(CN) absorption at 2172 (Ru) and 2168 cm^{-1} (Os), suggesting the existence of a *trans* structure **III**. The formation of complexes of Ru^{II} and Os^{II} is rather unexpected, because it must imply two-electron oxidation of the central metal. Taking



Scheme 1 L = Ph(OEt)$_2$Ph, R = 4-MeC$_6$H$_4$ or 4-MeOC$_6$H$_4$

into account the nature of the ligands present [CNR, P(OEt)$_2$Ph and NO], the nitrosyl ligand probably operates as the oxidizing agent.

Carbon monoxide (1 atm) quickly reacts at room temperature with [Ru(NO)L$_4$]$^+$ in CH$_2$Cl$_2$ to give the [Ru(NO)(CO)$_2$L$_2$]$^+$ cation, which can be isolated and characterized. Its infrared spectrum shows two ν(CO) bands at 2055 and 1989 cm^{-1}, whereas NO stretching appears at 1728 cm^{-1}. In the temperature range -80 to $+20$ °C the ^{31}P-{^{1}H} NMR spectra exhibit only one singlet at δ 139.2, in agreement with two magnetically equivalent phosphorus nuclei. Moreover, the ^{1}H NMR spectra show a complicated multiplet for the methylene protons of the phosphine ligand, suggesting that these ligands are *trans*. On this basis, a type **IV** geometry can reasonably be proposed for the [Ru(NO)(CO)$_2$L$_2$]$^+$ derivative.

The complex [Fe(NO)L$_4$]PF$_6$ also reacts with CO (1 atm) at room temperature to afford a yellow solution from which only an oily product was isolated. However, its IR spectrum shows the presence of one ν(NO) band at 1760 cm^{-1} and two ν(CO) absorptions at 2060 and 1973 cm^{-1}, which seem to indicate, by comparison with the related ruthenium complex, the formation in this case too of the dicarbonyl derivative [Fe(NO)(CO)$_2$L$_2$]$^+$.

In contrast, the osmium compound [Os(NO)L$_4$]$^+$ reacts very slowly with CO (1 atm) at room temperature, while under reflux conditions the reaction proceeds with the formation of a carbonyl species not containing a nitrosyl ligand, as may be deduced by the disappearance of the ν(NO) band in the IR spectra.

The reaction of the mononitrosyls [M(NO)L$_4$]$^+$ with bromine at -80 °C in CH$_2$Cl$_2$ depends on the nature of the central metal, as reported in Scheme 1. While the [OsBr(NO)L$_4$]$^{2+}$ derivative was isolated in high yield, in the case of ruthenium we obtained the [RuBr$_2$(NO)L$_3$]$^+$ cation, together with a small amount of a yellow compound not containing nitrosyl ligand, of probable formulation RuBr$_2$L$_4$. With the iron complex, although the oxidation reaction proceeded to give a yellow solution whose IR spectrum showed the presence of nitrosyl species [ν(NO) at 1850 cm^{-1}], no stable compound was isolated, probably owing to the instability of these nitrosyl derivatives.

The [OsBr(NO)L$_4$][PF$_6$]$_2$ complex is a stable orange solid, soluble in polar organic solvents, in which it behaves as a 2:1 electrolyte. Its IR spectrum shows a ν(NO) band at 1885 cm^{-1}, whereas the ^{31}P-{^{1}H} NMR spectrum is an AB$_2$C multiplet which can be simulated with the parameters reported in Table 1. On this basis, a type **V** geometry, with NO and Br ligands mutually *cis*, can reasonably be proposed. The related ruthenium compound [RuBr$_2$(NO)L$_3$]PF$_6$ is a 1:1 electrolyte and a ν(NO) band appears at 1876 cm^{-1} in its IR spectrum. However, no ν(MBr) absorption could be unambiguously assigned and therefore, although the ^{31}P NMR spectrum displays an AB$_2$ multiplet, we could not distinguish between a *fac* or *mer* geometry in solution for this complex.

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