Synthesis of Ammonium Ions and Nitrosylation Reactions using Nitrosyl Chloride and Alkyl Nitrites

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Nitrosyl chloride (NOCl) reacts with $RuCl_3{\cdot}xH_2O$ in the presence of PPh_3 in different alcohols leading to the formation of ammonium ions and $[Ru(NO)Cl_3(PPh_3)_2]$ under mild experimental conditions, through reductive deoxygenation. Some parameters affecting the reactivity of the redox system have been qualitatively defined. Similar reactions in tetrahydrofuran do not yield $[NH_4]^+$ ions. Alkyl nitrites (RONO, R = Me or Et) have also been successfully employed as nitrosylating agents for the syntheses of nitrosyl complexes of Ru^{II}, Ru^{III}, Rh^I, and Ir^I.

Ammonium ion synthesis[1] by the reduction of nitric oxide, NO with $RuCl_3{\cdot}xH_2O$ in the presence of PPh_3 has led us to enquire into the various factors affecting the reaction dynamics. It is envisaged that the reaction should be affected, mainly, by four factors: (*i*) concentrations of the metal ions and/or triphenylphosphine (PPh_3); (*ii*) nature of the reaction medium; (*iii*) nature of the nitrogen source; and (*iv*) reaction temperature. The present work describes the results of experiments carried out to investigate these effects. Furthermore, a literature survey indicated the use of pentyl and isopentyl nitrites, as nitrosylating agents, in only a few reactions.[2-7] A comprehensive study of how alkyl nitrites in general can be used for nitrosylating metal ions is lacking. Such a study may be useful in its application to a general method for the synthesis of metal nitrosyls. The results of the reactions of alkyl nitrites in alcohols and tetrahydrofuran (thf) with $RuCl_3{\cdot}xH_2O$, $RhCl_3{\cdot}xH_2O$, and $IrCl_3{\cdot}xH_2O$ in the presence of PPh_3 or $AsPh_3$, and with a number of their complexes, are also presented herein. The results, indirectly, provide some evidence for the various factors affecting ammonium ion formation.

Experimental

The reagents used were of Analar or chemically pure grade. Solvents were freshly distilled and degassed according to the standards methods. All the reactions were carried out under dry nitrogen or argon atmospheres unless otherwise described. Nitrosyl chloride, methyl nitrite (MeONO), ethyl nitrite (EtONO), n-butyl nitrite (Bu^nONO), dinitrogen trioxide (N_2O_3), Zn–Cu couple, nitric oxide, *N*-methyl-*N*-nitroso-toluene-*p*-sulphonamide (mnts), $[RuCl_2(PPh_3)_3]$, $[RuCl_2(PPh_3)_4]$, $[RuCl_3(PPh_3)_2]{\cdot}MeOH$, $[RuCl_3(AsPh_3)_2(MeOH)]$, $[RhCl(PPh_3)_3]$, $[RhH(CO)(PPh_3)_3]$, $[RhH(PPh_3)_4]$, $[IrH(CO)(PPh_3)_3]$, and $[Ir(CO)Cl(PPh_3)_2]$ were prepared by the literature methods.[8-18]

Carbon, hydrogen, and nitrogen analyses were performed by the Microanalytical Laboratory of the Indian Institute of Technology, Kanpur, India. Chloride, bromide, phosphorus, arsenic, and caesium analyses of the complexes were performed by the methods described elsewhere.[19,20] A Schimadzu 420 i.r. spectrophotometer, Fisher John's melting point apparatus, Gouy balance, and Elico conductivity bridge were used to record i.r. spectra, melting points, and measuring magnetic behaviour and conductivity of the complexes, respectively.

Reactions involving Ammonium Ion Formation (Route I).—Reactions of NOCl *with* $RuCl_3{\cdot}xH_2O$ *and* PPh_3 *in alcohols.* A typical method of carrying out these reactions is described by Khan *et al.*[1] The reactions were performed under different conditions which are given in the Table.

Nitrosylation Reactions of Alkyl Nitrites (Route II).—These reactions were carried out by a method similar to that given by Johnson and Segal,[6] except that RONO (R = Me or Et) gas was allowed to pass simultaneously into boiling solutions of the metal ions and of their complexes. In the case of Ru^{II} and Ru^{III} the addition of methanol was found to be necessary in order to obtain the nitrosyl complex. In the absence of MeOH, the reaction mixture did not give the desired complex. Apparently it is post-treatment with an alcohol that leads to the nitrosyl product.

Reactions of NOCl *with* $RuCl_3{\cdot}xH_2O$ *and* PPh_3 *in the Presence of the* Zn–Cu *Couple in Ethanol (Route III).*—A solution of $RuCl_3{\cdot}xH_2O$ (0.5 mmol) in ethanol (10 cm^3) was mixed with a hot ethanolic solutions (15 cm^3) of PPh_3 (2.5 mmol), followed by addition of the freshly prepared Zn–Cu couple (0.6 g) and a saturated CH_2Cl_2 solution of NOCl (15 cm^3). The resulting solution was gently heated on a water-bath for about 2 h. The solution was filtered to remove unreacted Zn–Cu couple and any other insoluble material. To the filtrate NOCl (10 cm^3) was added. The solution was concentrated, nearly to dryness, and the resulting mass was washed thoroughly with ethanol to yield wine-red washings. A pink water-soluble compound remained which was identified as $[NH_4][Ru(NO)Cl_5]$. Ethanolic washings, on evaporation, gave an oily mass which on treatment with an excess of PPh_3 in CH_2Cl_2, followed by addition of methanol, yielded shiny crystals of $[Ru(NO)Cl_3(PPh_3)_2]$.

Results and Discussion

All the complexes known from the literature described herein have been confirmed by their microanalyses and by comparing their m.p., mixed-m.p., and spectral (i.r., u.v., and visible) data with those of authentic samples.

The experimental results given in the Table can be discussed in terms of the following parameters.

(*i*) *Role of* PPh_3.—The results suggest that PPh_3 has two roles in these reactions: (*a*) as a base during the formation of $[Ru(NO)Cl_3(PPh_3)_2]$ and (*b*) generating a nitrene intermediate by deoxygenating either free or bonded NO (*cf.* alkyl nitrite). The latter is subsequently hydrolysed by the solvent, or HCl, to yield $[NH_4]^+$ ions. Role (*b*) is also consistent with the formation of $Ph_3P{=}O$ in experiments where the ammonium ion is one of the reaction products.

It is interesting that a molar ratio of PPh_3 to metal of less than 5:1 results in preferential formation of $[Ru(NO)Cl_3(PPh_3)_2]$, with a practically negligible yield of ammonium ions. Increase in the PPh_3:metal ratio with simultaneous increase in the NOCl concentration increases the yields of both $[Ru(NO)Cl_3(PPh_3)_2]$ and ammonium ions. Thus it can be postulated that at least two competitive, parallel reactions, *viz.* deoxygenation and nitrosylation of metal ions, occur simultaneously, and are PPh_3-concentration dependent. The deoxygenation reaction predominates over that of $[Ru(NO)Cl_3(PPh_3)_2]$ formation at a metal: PPh_3 ratio greater than 1:16, yielding the nitrosyl complex in negligible amounts, while the converse is true at a molar ratio $\leqslant$1:5 {the ideal ratio for obtaining the maximum yield of $[Ru(NO)Cl_3(PPh_3)_2]$ has been found to be 1:5}. Additionally, ruthenium has a tendency to form $[Ru(NO)Cl_4L]^{n-}$ ($L = Cl^-$, H_2O, or NH_3, n = 1 or 2). Further confirmation of the deoxygenation reaction by PPh_3 comes from the formation of $[H_3O]_2[Ru(NO)Cl_5]$ or $Cs_2[Ru(NO)Cl_5]$ in large quantities, instead of ammonium ions, when $M:PPh_3 = 1:0$.

(*ii*) *Role of the Reaction Medium.*—Results for the reaction in different solvents suggest that ammonium ion formation, as opposed to formation of $[Ru(NO)Cl_3(PPh_3)_2]$ or $[Ru(NO)Cl_4L]^{n-}$, depends upon the nature of the alcohols used. Higher alcohols like n-butyl, isobutyl, t-butyl, amyl, and octyl alcohols give rather poor yields of $[Ru(NO)Cl_3(PPh_3)_2]$ (2—5%). It is well established that the rate of nitrite ester formation is slower in higher alcohols compared to that in lower ones. This will result in a lower concentration of an alkyl nitrite in higher alcohols, in a particular reaction time, compared to that in lower alcohols. Consequently the higher PPh_3 concentration in the presence of relatively low alkyl nitrite concentration leads to a higher rate of deoxygenation, with relatively higher yields of $[NH_4]^+$ ions. The results of nitrosylation reactions using n-butyl nitrite or amyl nitrites as nitrosylating agents support this.

A larger concentration of NO or alkyl nitrite increases the yield of $[Ru(NO)Cl_3(PPh_3)_2]$. However, this observation is contradicted when the reaction medium is changed to methanol, in which the yield of $[Ru(NO)Cl_3(PPh_3)_2]$ is reduced compared to that in higher alcohols. An explanation of this contradiction may be the precipitation of $[RuCl_2(PPh_3)_3]$ in methanol, in addition to the formation of $[Ru(NO)Cl_3(PPh_3)_2]$. {A slight delay in the addition of NOCl results largely in precipitation of $[RuCl_2(PPh_3)_3]$, thereby decreasing the yield of $[Ru(NO)Cl_3(PPh_3)_2]$.} The presence of a large excess of PPh_3 in the reaction medium, however, yielded some $[NH_4]^+$ ions. Similar behaviour was observed when alkyl nitrite was used as nitrosylating agent.

Reaction in thf. Reactions carried out in thf did not yield $[Ru(NO)Cl_3(PPh_3)_2]$, $[Ru(NO)Cl_4L]^{n-}$, or $[NH_4]^+$ ions. On the contrary, the yellowish reactant solution turned black on exposure to the atmosphere for 1 h or more. All attempts to precipitate a pure solid material from the black solution were unsuccessful.

This suggested a special efficacy of alcohols as a reaction medium for formation of $[NH_4]^+$ ions and $[Ru(NO)Cl_3(PPh_3)_2]$. One of the possible rationales for this behaviour is that formation of alkyl nitrite is essential for the generation of both $[NH_4]^+$ ions and the nitrosyl complexes. Thus, it is not NOCl but, possibly, alkyl nitrites which are responsible for nitrosylation reactions, and the role of NOCl is to esterify alcohols. The latter presumption is supported by the successful

Table. Reaction conditions of nitrosylation reactions and their reaction product(s)

Reaction number	Metal chloride or complex	Reaction medium	Nitrosylating agent	Co-ligand (L)	M:L ratio	Reflux/ stirring time (min)	Reaction products (yields)[a]		Synthetic route[b]	Comments
							X	Y		
(1)	$RuCl_3{\cdot}xH_2O$[c]	EtOH[d]	NOCl	PPh_3[e]	1:5	2—5	(**A**) (l)	(**B**) (m)	I	—
(2)					1:8	2—5	(**A**) (s)	[(**B**) + (**C**)] (l)	I	—
(3)					1:12	2—5	(**A**) (n)	[(**B**) + (**C**)] (l)	I	—
(4)					1:16	2—5	(**A**) (no)	(**C**) (l)	I	—
(5)					1:20	2—5	(**A**) (no)	(**C**) (l)	I	—
(6)		Pr^nOH[d]			1:5	2—5	(**A**) (m)	(**C**)	I	—
(7)					1:8	2—5	(**A**) (s)	(**C**)	I	—
(8)					1:20	2—5	(**A**) (no)	(**C**)	I	—
(9)		Bu^nOH[d]			1:5	2—5	(**A**) (s)	(**B**) (m)	I	—
(10)					1:8	2—5	(**A**) (s)	(**D**) (m)	I	—
(11)					1:16	2—5	(**A**) (s)	(**D**) (m)	I	—
(12)		Bu^iOH			1:5	2—5	(**A**) (s)	(**C**) (l)	I	—
(13)		Bu^tOH			1:5	2—5	(**A**) (n)	(**C**) (l)	I	—
(14)		$C_5H_{11}OH$			1:5	2—5	(**A**) (n)	(**D**) (l)	I	—
(15)		$C_8H_{17}OH$			1:5	2—5	(**A**) (n)	(**D**) (l)	I	—
(16)		thf			1:5	2—5	(**A**) (no)	—	I	—
(17)		MeOH[f]			1:5	2—5	(**A**) (n)	—	I	—
(18)		Bu^nOH	n-BuONO		1:5	5—7	(**A**) (m)	—	I	*g*
(19)		thf			1:5	5—7	(**A**) (n)	(**B**) (s)	I	—
(20)					1:5	5—7	(**A**) (m)	(**B**) (m)	I	*h*
(21)		EtOH	EtONO		1:5	5	(**A**) (l)	—	I	*i*
(22)					1:5	5	(**A**) (l)	(**B**) (s)	I	*h*
(23)				—	1:0	10	(**A**) (no)	(**E**) (m)	*j*	*h*
(24)					0:1	10	(**A**) (no)	(**F**) (m)	*k*	*h*
(25)		thf			1:5	5	(**A**) (l)	(**B**) (m)	I	*h*
(26)				—	1:0	5	(**A**) (no)	(**G**) (m)	I	*h*
(27)					0:1	10	(**A**) (no)	(**F**) (s)	*l*	*h*
(28)		EtOH	NOCl		1:5	120	(**A**) (no)	(**B**) (l)	III	*m*
(29)			NO		1:5	5	(**A**) (l)	—	I	—
(30)					1:5	5	(**A**) (l)	(**B**) (m)	I	*h*

Table (*continued*)

Reaction number	Metal chloride or complex	Reaction medium	Nitrosylating agent	Co-ligand (L)	M:L ratio	Reflux/ stirring time (min)	Reaction products (yields)[a] X	Y	Synthetic route[b]	Comments
(31)			mnts		1:5	20	(**A**) (l)	—	I	*n*
(32)			N_2O_3		1:5	20	(**A**) (m)	(**B**) (s)	I	*o*
(33)		EtOH	MeONO		1:5	10	(**A**) (l)	—	II	—
(34)			EtONO–MeONO		1:6	25	(**H**) (l)	—	II	*p*
(35)			EtONO		1:4	10	(**I**) (l)	—	II	—
(36)		$MeOCH_2CH_2OH$	EtONO–MeONO	$AsPh_3$	1:4	45	(**J**) (l)	—	II	—
(37)	$RhBr_3\cdot xH_2O$		EtONO–MeONO	$AsPh_3$	1:4	45	(**K**) (l)	—	II	—
(38)	$IrCl_3\cdot xH_2O$		EtONO–MeONO		1:4	45	(**O**) (m)	—	II	—
(39)	$RhCl_3\cdot xH_2O$		MeONO		1:4	10	(**I**)[q] (l)	—	II	—
(40)	$[RuCl_2(PPh_3)_3]$	CH_2Cl_2	MeONO–EtONO	—	—	10	(**A**) (s)	—	II	—
(41)	$[RuCl_2(PPh_3)_3]$			—	—	10	(**A**) (l)	—	II	*h*
(42)	$[RuCl_2(PPh_3)_4]$			—	—	180	(**A**) (s)	—	II	—
(43)	$[RuCl_2(PPh_3)_4]$			—	—	180	(**A**) (l)	—	II	*h*
(44)	$[RuCl_3(PPh_3)_2]\cdot MeOH$			—	—	30	(**A**) (m)	—	II	—
(45)	$[RuCl_3(AsPh_3)_2]\cdot MeOH$			—	—	120	(**P**) (m)	—	II	*r*
(46)	$[RhCl(PPh_3)_3]$	CH_2Cl_2–MeOH (2:1 v/v)	EtONO	—	—	30	(**I**) (m)	—	II	*h*
(47)	$[RhH(CO)(PPh_3)_3]$	EtOH		—	—	30	(**Q**) (m)	—	II[s]	*h*
(48)	$[RhH(PPh_3)_4]$			—	—	15	(**R**) (l)	—	II[t]	*h*
(49)	$[IrH(CO)(PPh_3)_3]$	C_6H_6		—	—	30	(**T**) (m)	—	II[u]	—
(50)	$[Ir(CO)Cl(PPh_3)_2]$	EtOH		—	—	120	(**O**) (m)	—	II[s]	*h*

[a] (**A**), $[Ru(NO)Cl_3(PPh_3)_2]$; (**B**), $[NH_4]_2[Ru(NO)Cl_5]$; (**C**), $[NH_4][Ru(NO)Cl_4(H_2O)]$; (**D**), $[NH_4][Ru(NO)Cl_4(NH_3)]$; (**E**), $Cs_2[Ru(NO)Cl_5]$; (**F**), NH_4Cl; (**G**), $[H_3O]_2[Ru(NO)Cl_5]$; (**H**), $[Ru(NO)_2(PPh_3)_2]$; (**I**), $[Rh(NO)Cl_2(PPh_3)_2]$; (**J**), $[Rh(NO)Cl_2(AsPh_3)_2]$; (**K**), $[Rh(NO)Br_2(AsPh_3)_2]$; (**O**), $[Ir(NO)Cl_2(PPh_3)_2]$; (**P**), $[Ru(NO)Cl_3(AsPh_3)L]$ (L = PPh_3 or $AsPh_3$); (**Q**), $[Rh(CO)(NO)Cl_2(PPh_3)_2]$; (**R**), $[RhCl(PPh_3)_3]$; (**T**), $[Ir(CO)(NO)(PPh_3)_2]$; l, m, s, n, no mean large, modest, small, negligible, and not observed for the yield, respectively. [b] For routes I—III see Experimental section. [c] The same amount (0.13 g, 0.5 mmol) of $RuCl_3\cdot xH_2O$ was used in all its reactions, unless indicated otherwise. [d] At a molar ratio of PPh_3 to $RuCl_3\cdot xH_2O$ lower than 5 there is a drastic reduction in the yield of product Y compared to that of X.[e] L = PPh_3 unless otherwise stated. [f] Change of medium from ethanol to methanol reduced the yield of (**A**) with simultaneous precipitation of $[RuCl_2(PPh_3)_3]$. [g] Initial treatment with 10 cm^3 of Bu^nONO, followed by heating, yielded (**A**). The filtrate after being further treated with Bu^nONO, followed by slow heating, resulted in an oily mass which contained $[NH_4]^+$ and O=PPh_3. No other ionic compound could be isolated from this mass. [h] Reaction was carried out in the presence of a slow stream of dry HCl gas through the reaction mixture. [i] As *g* above, except that a slow stream of EtONO was used in place of Bu^nONO. [j] Passing HCl and EtONO gases simultaneously for 10 min through the reaction mixture and concentrating it to half its volume, followed by the addition of an aqueous solution of CsCl, precipitated the Cs salt. [k] Evaporation of the reaction mixture, followed by washing the residue with CH_2Cl_2, yielded NH_4Cl. O=PPh_3 was isolated from CH_2Cl_2 washings. [l] As in *k*, except that O=PPh_3 was not found. [m] Initial reaction mixture was refluxed for 2 h with the Zn–Cu couple (0.6 g) and filtered. The filtrate, after treating further with NOCl, was concentrated to near dryness. The resulting mass, on extraction with ethanol, yielded (**B**) and ethanol washings precipitated (**A**) after its treatment with CH_2Cl_2, PPh_3 (2 mmol), and methanol. [n] Reaction mixture was refluxed for 20 min with mnts (1 mmol). [o] After separating (**A**), the filtrate was further treated with N_2O_3 followed by its evaporation to an oily mass from which (**B**) was isolated by washing with CH_2Cl_2. [p] Triethylamine (8 cm^3) was added dropwise to the reaction mixture (containing 1 mmol of $RuCl_3\cdot xH_2O$ and 6 mmol of PPh_3), before passing alkyl nitrite, until its colour changed to deep purple. [q] Blood red filtrate upon treatment with PPh_3 (2 mmol) yielded a brick-red crystalline compound which was analyzed for $[\{RhCl(PPh_3)_2\}_2]$ after filtration, washing, and drying *in vacuo*. The latter compound (0.1 mmol), upon refluxing with PPh_3 (0.26 g, 1 mmol) in ethanol (15 cm^3) for 90 min, yielded $[RhCl(PPh_3)_3]$. [r] Bright yellow reaction mixture, after being treated with alkyl nitrite, was stirred for 2 h and methanol (40 cm^3) added. Treatment of half of the solution with $AsPh_3$ (2 mmol), followed by slow heating, precipitated $[Ru(NO)Cl_3(AsPh_3)_2]$ while addition of PPh_3 to the remaining solution yielded $[Ru(NO)Cl_3(AsPh_3)(PPh_3)]$. Product crystallized after concentrating the reaction mixture on a steam-bath. [s] Product separated on cooling the reaction mixture. [t] To the reaction mixture, after concentrating it to one quarter of its volume, MeOH, CH_2Cl_2, and PPh_3 (3.0 mmol) (5 cm^3 of each) were added in succession to obtain the product. [u] Product obtained on concentrating the reaction mixture to one-fifth its original volume, followed by addition of dry ethanol.

use of alkyl nitrites as nitrosylating reagents. Furthermore, it also suggests that the deoxygenation reaction proceeds *via* the alkyl nitrite rather than NOCl. Further support derives from the fact that direct reaction of NOCl with PPh_3 yields O=PPh_3, and organic nitro and nitroso derivatives are, in general, deoxygenated by PPh_3 with the formation of nitrene and $\geqslant$P=O groups.[21–23]

The role of thf in the formation of complexes and ammonium ions has further been examined by using alkyl nitrites, in place of NOCl, as nitrosylating agents, both in the presence and in the absence of PPh_3. In the absence of HCl, the reactions of ethyl or butyl nitrite with $RuCl_3\cdot xH_2O$ in the presence of PPh_3 afforded $[Ru(NO)Cl_2(PPh_3)_2]$ in relatively large yield and $[NH_4]^+$ ions in low or negligible yield, whereas the presence of HCl gas substantially enhanced the yields of both species. This observation suggests the need for a hydrogen source in the formation of these products. The involvement of quadrivalent phosphorus in the reductive deoxygenation process is also indicated by the formation of NH_4Cl in the reaction of alkyl nitrite with PPh_3 in thf, even in the absence of $RuCl_3\cdot xH_2O$. Ammonium chloride is not formed in the absence of PPh_3. Furthermore, the ratio of the products (complex:$[NH_4]^+$) is a function of PPh_3 concentration.

A ratio of $RuCl_3\cdot xH_2O$ to PPh_3 of less than 1:5 yields largely ammonium ions and a negligible amount of $[Ru(NO)Cl_3(PPh_3)_2]$, while a ratio greater than 1:5 shifted the yields in the opposite direction. A large excess of Cl^- ions is also essential for a better yield of $[Ru(NO)Cl_5]^{2-}$ and/or $[Ru(NO)Cl_4L]^-$ ($L = H_2O$ or NH_3).

Previous studies[13] have reported the reduction of $[Ru(NO)Cl_3(PPh_3)_2]$ by the Zn–Cu couple, affording a soluble species, $[Ru(NO)Cl(PPh_3)_2]$. Accordingly, the likelihood of increasing the yields of $[NH_4]_2[Ru(NO)Cl_5]$ or $[NH_4][Ru(NO)Cl_4L]$ if the reaction is carried out in the presence of the Zn–Cu couple can be assumed. Besides the reductive deoxygenation process, the Zn–Cu couple may assist in the reduction of NO also. Experimental results in the presence of the Zn–Cu couple (Table) suggests a definite trend in the positive direction.

(*iii*) *Role of the* NO *Source*.—The generalized behaviour described in the foregoing paragraphs was examined by performing the reactions in the presence of other nitrosylating agents (NO or N_2O_3). They all afforded the complex $[Ru(NO)Cl_3(PPh_3)_2]$ and, in the presence of a large excess of chloride ions, the complex $[Ru(NO)Cl_5]^{2-}$ also. Although NO and N_2O_3 were reductively deoxygenated with the formation of $[NH_4]^+$ ions, mnts behaved differently.

It is suggested that the formation of ammonium ions and metal nitrosyls using NOCl is based on formation of alkyl nitrite as a reaction intermediate, the concentration of which determines the extent of the nitrosylation reaction. Support for this comes from the results of nitrosylation reactions using various alkyl nitrites, which provide a new and milder method for the synthesis of metal nitrosyls.

The reactions of methyl or ethyl nitrite with $RhCl_3{\cdot}xH_2O$ in the presence of PPh_3 or $AsPh_3$ in ethanol or 2-methoxyethanol gave a brown complex $[Rh(NO)X_2(APh_3)_2]$ [X = Cl or Br, A = As or P]. On further reaction with PPh_3 the filtrate obtained from the reaction with methyl nitrite yielded a brick red complex $[\{RhCl(PPh_3)_2\}_2]$ (m.p. 120 °C) and, in refluxing conditions, the complex $[RhCl(PPh_3)_3]$.

The preferential formation of $[RhCl(PPh_3)_3]$ on reaction of ethyl nitrite with an ethanolic suspension of $[RhH(PPh_3)_4]$ in the presence of HCl was surprising, when, under similar conditions, an ethanolic suspension of $[RhH(CO)(PPh_3)_3]$ yielded the well characterized complex $[Rh(CO)(NO)Cl_2(PPh_3)_2]$. Presumably the reaction paths in the two cases are different. Iridium could also be nitrosylated by RONO (R = Me or Et) to yield a well known yellow-orange complex $[Ir(NO)Cl_2(PPh_3)_2]$.[17] Under similar conditions $[IrH(CO)(PPh_3)_2]$, in boiling benzene, afforded $[Ir(CO)(NO)(PPh_3)_2]$.[17]

In ethanol the nitrosylation of Vaska's complex by ethyl nitrite gave $[Ir(NO)Cl_2(PPh_3)_2]$. The metal ions are oxidized in a few of the nitrosylation reactions in the presence of HCl. It appears that under the reaction conditions, NOCl is formed because of the thermal breaking of the O–N bond of alkyl nitrite which will oxidize metal ions to their higher oxidation states. Although in the absence of HCl both $[RuCl_2(PPh_3)_3]$ and $[RuCl_2(PPh_3)_4]$ gave $[Ru(NO)Cl_3(PPh_3)_2]$, the yield was very poor. Perhaps under these conditions the Cl^- ion concentration was insufficient for nitrosyl complex formation which could occur only at the expense of the reactants (ruthenium complex). In the presence of HCl, sufficient Cl^- ions were present to form the nitrosyl complex and thereby enhance the yield. Hydrogen chloride is apparently an important constituent in all the nitrosylation reactions.

It is assumed that a mechanism[6,7] similar to that proposed by Johnson and Segal, Robinson and Uttley for the nitrosylation of $[Fe(CO)_3(PPh_3)_2]$ by R–O–NO is also operative in the systems discussed here.

References

1 M. I. Khan, R. Saheb, and U. C. Agarwala, *Ind. J. Chem., Sect. A*, 1983, **22**, 417.
2 W. Heiber, W. Beck, and H. Tengler, *Z. Naturforsch., Teil B*, 1960, **15**, 411.
3 W. Heiber and H. Tengler, *Z. Anorg. Allg. Chem.*, 1962, **318**, 136.
4 S. Trofimenco, *Inorg. Chem.*, 1971, **10**, 504.
5 S. Trofimenco, *Inorg. Chem.*, 1969, **8**, 2675.
6 B. F. G. Johnson and J. A. Segal, *J. Chem. Soc., Dalton Trans.*, 1972, 1268.
7 S. D. Robinson and M. F. Uttley, *J. Chem. Soc., Dalton Trans.*, 1972, 1; *J. Chem. Soc. A*, 1971, 1254.
8 Shell Internat. Research Maats Chappij, N.U., Neth. Appl. 61512661 (CI CO15), 1967, **31**, 3.
9 W. H. Hartung and F. Crossley, *Org. Synth.*, 1943, Coll. vol. 2, 363.
10 W. L. Semon and V. R. Damerell, *Org. Synth.*, 1943, Coll. vol. 2, 204.
11 W. A. Noyes, *Org. Synth.*, 1943, Coll. vol. 2, 108.
12 G. Brauer, 'Handbook of Preparative Inorganic Chemistry,' vol. 1, Academic Press, New York, 1963, p. 406.
13 J. Reed, C. G. Pierpont, and R. Isenberg, *Inorg. Synth.*, 1976, **16**, 21.
14 T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1966, **28**, 945.
15 J. A. Osborn and G. Wilkinson, *Inorg. Synth.*, 1967, **10**, 67.
16 N. Ahmad, J. J. Levison, S. D. Robinson, and M. F. Uttley, *Inorg. Synth.*, 1974, **15**, 45.
17 C. A. Reed and W. R. Roper, *J. Chem. Soc. A*, 1970, 3054.
18 D. Evans, J. A. Osborn, and G. Wilkinson, *Inorg. Synth.*, 1968, **11**, 99.
19 J. Basset, R. C. Denny, G. H. Geffry, and J. Mendham, 'Vogel's Textbook of Quantitative Inorganic Analysis,' 4th edn., Longman, London, 1978.
20 R. M. Engelbrecht and F. A. McCoy, *Anal. Chem.*, 1956, **28**, 1772.
21 R. S. Edmundson, in, 'Comprehensive Organic Chemistry,' vol. 2, eds. D. Barton and W. D. Ollis, Pergamon, Oxford, 1979, pp. 1205—1206.
22 J. H. Boyer, in 'Nitrene,' ed. W. Lwowski, Interscience, New York, 1970, p. 163.
23 R. G. Coombers, in ref. 21, p. 163.

Received 21*st September* 1987; *Paper* 7/1688