Nitrosoarene Complexes of Ruthenium and Platinum and their Reactions with NO and NO^+

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Addition of RNO (R = Ph or *o*-MeC_6H_4) to [RuCl(NO)$(PPh_3)_2$] afforded the complex [RuCl(NO)(RNO)$(PPh_3)_2$] which reacted with I_2 to give [RuClI$_2$(NO)$(PPh_3)_2$]. The RNO ligand was readily displaced by O_2, and treatment with PPh_3 or CO caused extensive decomposition without formation of a Ru{ON(R)NO} chelate ring. Treatment of [Pt(PhNO)$(PPh_3)_2$] with NO^+ afforded [Pt{ON(Ph)NO}$(PPh_3)_2$]$^+$ isolated as the PF_6^- salt. The complexes [M{ON(R)NO}-$(PPh_3)_2$] (M = Pt or Pd; R = Ph or *p*-MeC_6H_4) were prepared by reaction of [$MCl_2(PPh_3)_2$] with Ag[ON(R)NO].

It has been suggested[1–4] that the formation of *N*-alkyl-*N*-nitrosohydroxylaminato-species, [ON(R)NO]$^-$, by 'double insertion' of NO into d^0, d^8, or d^{10} transition metal–alkyl bonds may proceed in two stages: (*i*) addition of NO to the metal–alkyl and migration of the alkyl group to NO giving a paramagnetic nitrosoalkane intermediate, M(RNO), and (*ii*) second addition of NO to M(RNO) affording the diamagnetic chelated species M{ON(R)NO}.

That nitrosoalkane complexes can be formed by migration of an alkyl group to metal-co-ordinated NO has been elegantly demonstrated by Weiner and Bergman,[5] using [Co(η-C_5H_5)-R(NO)] (R = Me or Et) which can be readily converted into [Co(η-C_5H_5)(RNO)(PPh_3)] by addition to the former of PPh_3.

The requirement that a second NO 'insertion' requires a *paramagnetic* nitrosoalkane intermediate is implied by the reactions of d^1 transition metal–alkyls, where it seems that only one NO 'insertion' takes place, leading presumably to a *diamagnetic* nitrosoalkane intermediate. Thus treatment of $ReOMe_4$[6] and [Nb(η-C_5H_5)$_2$Me$_2$][7] with NO probably led to the diamagnetic intermediates [ReOMe$_3$(MeNO)] and [Nb(η-C_5H_5)$_2$Me(MeNO)] respectively. These intermediates were unstable, breaking down to ReO_2Me_3 and [Nb(η-C_5H_5)$_2$Me-(=O)] with loss of MeN. The nitrene, MeN, was trapped as 1-methyl-2-phenylaziridine using styrene. In the reaction involving niobium the diamagnetic metal-containing residue, [Nb(η-C_5H_5)$_2$Me(=O)], underwent further NO insertion to give [Nb(η-C_5H_5)$_2$(=O){ON(Me)NO}].[7]

In further exploring the nature of these NO 'insertion' and coupling reactions, we wondered whether, in diamagnetic species containing co-ordinated NO and RNO, coupling could be induced to give the ON(R)NO ligand. We also considered the possibility that treatment of diamagnetic metal-co-ordinated RNO species with NO^+ could lead to [M{ON(R)NO}]$^+$ chelate rings.

Experimental

The compounds Ag[ON(R)NO] (R = Ph or *p*-MeC_6H_4),[8] [RuCl(NO)$(PPh_3)_2$],[9] PhNO,[10] and [Pt(PhNO)$(PPh_3)_2$][11] were prepared as described in the literature. *o*-MeC_6H_4NO was supplied by the Aldrich Chemical Co. Ltd., and was used without further purification. NO gas was generated as described elsewhere[12] and was purified by passage through 10 mol dm^{-3} KOH, KOH pellets, and through a trap containing molecular sieves cooled at −117 °C (ethanol–liquid N_2 slush-bath). CO gas was supplied by B.O.C. Ltd., and purified by passage through KOH pellets. All solvents were degassed prior to use and all reactions were carried out under nitrogen.

I.r. spectra were recorded using a PE 297 spectrophotometer and ^1H n.m.r. spectra were obtained with Varian XL100 or JEOL JMN-PMX 60 instruments. Elemental analyses were carried out by the Microanalytical Laboratory of this Department. All yields are quoted relative to the metal-containing starting material.

Preparation of [RuCl(NO)(PhNO)$(PPh_3)_2$].—To an emerald green solution of [RuCl(NO)$(PPh_3)_2$] {obtained by Zn/Cu reduction of [RuCl$_3$(NO)$(PPh_3)_2$] (0.50 g) in benzene (30 cm^3)} was added PhNO (0.07 g) in a mixture of benzene and light petroleum (b.p. 80—100 °C) (1:1 v/v, 50 cm^3). The colour of the solution immediately became deep orange-red. After stirring for 2 h, the volume of the solution was reduced *in vacuo* and an orange-red solid began to precipitate. Addition of light petroleum (b.p. 80—100 °C) afforded more solid which was then filtered off, washed with n-hexane (2 × 2.5 cm^3), and dried overnight *in vacuo* giving the complex as an orange-red powder (yield 0.43 g, 83%).

[RuCl(NO)(*o*-MeC_6H_4NO)$(PPh_3)_2$] was prepared similarly using *o*-nitrosotoluene (0.79 g) (yield 0.38 g, 72%). Both complexes were stored under N_2.

Reaction of [RuCl(NO)(PhNO)$(PPh_3)_2$] *with* I_2:[RuClI$_2$-(NO)$(PPh_3)_2$].—A suspension of [RuCl(NO)(PhNO)$(PPh_3)_2$] (0.5 g) in light petroleum (b.p. 60—80 °C; 20 cm^3) was stirred with iodine (0.16 g) for 24 h. A brown solid formed which was filtered off, washed with light petroleum (b.p. 60—80 °C), and dried *in vacuo* (yield 0.48 g, 81%).

Reaction of [RuCl(NO)(RNO)$(PPh_3)_2$] (R = Ph *or o*-MeC_6H_4) *with* NO *Gas*.—A solution of the complex in benzene was treated with pure dry NO for 30 min. The resulting solution was flushed with N_2 and then evaporated *in vacuo*. The solid residue which formed was washed with n-hexane, and dried *in vacuo*, but could not be further purified.

Preparation of [Pt(*o*-MeC_6H_4NO)$(PPh_3)_2$].—A suspension of [Pt(C_2H_4)$(PPh_3)_2$] (1.0 g) and *o*-nitrosotoluene (0.15 g) in n-hexane was stirred for 2—3 h and the resulting yellow solid filtered off. The *complex* was washed with n-hexane and dried *in vacuo* (yield 0.88 g, 79%).

Reaction of [Pt(PhNO)$(PPh_3)_2$] *with* $NOPF_6$: [Pt{ON(Ph)-NO}$(PPh_3)_2$][PF_6].—The initially orange-yellow solution obtained by reacting $NOPF_6$ (0.14 g) and [Pt(PhNO)$(PPh_3)_2$] (0.50 g) in benzene–methanol mixtures (3:1 v/v; 60 cm^3) became cloudy within a few minutes, and was stirred at room temperature for 3 h. The mixture was evaporated to dryness *in vacuo* and the residue extracted with dichloromethane. The solution was filtered and the filtrate stirred with decolourising charcoal for 30 min, and then re-filtered. The colourless filtrate was treated with methanol and n-hexane and partially evaporated *in vacuo*. A white solid precipitated which was recrystallised from dichloromethane–methanol–n-hexane (*ca.* 1 : 1 : 1) affording $[Pt\{ON(Ph)NO\}(PPh_3)_2][PF_6]$ as white microcrystals which were dried *in vacuo* (yield 0.25 g, 42%).

Alternative Method for $[Pt\{ON(Ph)NO\}(PPh_3)_2][PF_6]$.—Ag[ON(Ph)NO] (0.16 g) and $AgPF_6$ (0.16 g) were added in rapid succession to a suspension of $[PtCl_2(PPh_3)_2]$ (0.50 g) in benzene and methanol (3:1 v/v; 60 cm^3). The mixture was stirred vigorously for 3 h and then evaporated to dryness *in vacuo*. The residue was treated with dichloromethane and after filtration, methanol and n-hexane were added to the filtrate, the volume of solvent then being reduced partially *in vacuo*. The white solid which formed was filtered off, recrystallised from dichloromethane–methanol–n-hexane (1 : 1 : 1) giving the *complex* as white microcrystals which were dried *in vacuo* at 50 °C (yield 0.48 g, 76%).

Preparation of $[Pt\{ON(C_6H_4Me\text{-}p)NO\}(PPh_3)_2][PF_6]$.—This complex was obtained similarly to the R = Ph analogue, using $Ag[ON(C_6H_4Me\text{-}p)NO]$ (0.18 g), to give a white solid (yield 0.45 g, 70%).

Preparation of $[Pd\{ON(R)NO\}(PPh_3)_2][PF_6]$ (R = Ph *or* p-MeC_6H_4).—These complexes were prepared in the same way as their Pt analogues above, using $[PdCl_2(PPh_3)_2]$ (0.50 g), Ag[ON(R)NO] (0.18 g), and $AgPF_6$ (0.18 g), and were obtained as yellow-orange microcrystals (yield 0.42 g, 65% and 0.40 g, 61% respectively).

Reaction of $[Pt(RNO)(PPh_3)_2]$ (R = Ph *or* o-MeC_6H_4) *with* NO *Gas*.—$[Pt(RNO)(PPh_3)_2]$ (0.5 g) in benzene (30 cm^3) was treated with NO gas for 30 min. The resulting solution was flushed with N_2 affording a pale yellow solid and an orange-red solution. The solid was filtered off and the orange-red filtrate evaporated to dryness *in vacuo*. Attempts to recrystallise the residue so formed using various solvent pairs were unsuccessful, but both it and the yellow solid had very similar i.r. spectra.

Results and Discussion

Ruthenium Complexes.—Reaction of the co-ordinatively unsaturated emerald green $[RuCl(NO)(PPh_3)_2]$ with RNO (R = Ph or o-MeC_6H_4) afforded the unstable orange-red complexes $[RuCl(NO)(RNO)(PPh_3)_2]$ (elemental analytical data in the Table). These complexes exhibited ν(NO) at 1 740 cm^{-1}, which may be compared with 1 670 cm^{-1} in the precursor, $[RuCl(NO)(PPh_3)_2]$, 1 765 cm^{-1} in $[RuCl(NO)(O_2)(PPh_3)_2]$, 1 778 cm^{-1} in $[Ru(CF_3C_2CF_3)Cl(NO)(PPh_3)_2]$, and 1 730 cm^{-1} in $[Ru(C_2F_4)Cl(NO)(PPh_3)_2]$.[13] A series of ruthenium nitrosoarene complexes, of the type $[RuCl(RNO)(bipy)_2]^+$ (bipy = 2,2′-bipyridine; R = Ph, p-MeC_6H_4, or p-$O_2NC_6H_4$) are known to contain a Ru←N(=O)R group, and exhibit ν(N=O) in the range 1 330—1 383 cm^{-1}.[14] No such bands were observed for $[RuCl(NO)(RNO)(PPh_3)_2]$, nor could we detect absorptions in the region of 1 000 cm^{-1} which would be consistent with an η^2-ONR group. The compounds were generally too unstable and air-sensitive to permit molecular-weight measurements, and/or informative n.m.r. spectral measurements. Notwithstanding these comments, we think it reasonable to assume that the complexes contain η^2-ONR groups.

Reaction of $[RuCl(NO)(RNO)(PPh_3)_2]$ with I_2 afforded the orange-brown $[RuClI_2(NO)(PPh_3)_2]$ with loss of the RNO ligand. This species exhibited ν(NO) at 1 872 cm^{-1}, in a region typical of $[RuX_3(NO)(PPh_3)_2]$ type complexes.[15]

In an attempt to induce coupling of the NO and RNO groups by reaction with neutral two-electron donor ligands, L, *e.g.* $[RuCl(NO)(RNO)(PPh_3)_2] + L \rightarrow [RuCl\{ON(R)NO\}(PPh_3)_2L]$, we investigated reactions of the new nitrosoarene complexes with PPh_3 and CO. Treatment of both complexes with PPh_3 in benzene afforded brown solutions which gave, after work-up, $PPh_3(O)$ (identified by i.r. spectroscopy and mixed m.p.), but we were quite unable to characterise other products. From an i.r. spectral examination of the residue, it was apparent that species containing the ligand ON(R)NO were not present. Treatment of an orange-red

Table. Analytical and i.r. spectroscopic data obtained from Ru, Pt, and Pd complexes

	Elemental analyses (%) Found (Calc.)			
	C	H	N	I.r.[a] (cm^{-1})
$[RuCl(NO)(PhNO)(PPh_3)_2]$	63.5 (63.2)	4.6 (4.4)	3.7 (3.5)	1 740 [ν(NO)]
$[RuCl(NO)(o\text{-}MeC_6H_4NO)(PPh_3)_2]$	63.9 (63.6)	4.6 (4.9)	3.3 (3.5)	1 740 [ν(NO)]
$[RuClI_2(NO)(PPh_3)_2]$	44.4 (45.8)	3.6 (3.2)	1.5 (1.5)	1 872 [ν(NO)]
$[Pt(o\text{-}MeC_6H_4NO)(PPh_3)_2]$	61.4 (61.4)	4.7 (4.4)	1.7 (1.7)	975 [ν(NO)]
$[Pt\{ON(Ph)NO\}(PPh_3)_2][PF_6]$[b]	50.2 (50.4)	3.8 (3.5)	2.6 (2.8)	1 375s, 1 315m, 1 275s, 910s {ON(Ph)NO}; 840vs [ν(P–F)]
$[Pt\{ON(Ph)NO\}(PPh_3)_2][PF_6]$[c]	50.3 (50.4)	3.8 (3.5)	2.7 (2.8)	
$[Pt\{ON(C_6H_4Me\text{-}p)NO\}(PPh_3)_2][PF_6]$	50.7 (50.8)	4.0 (3.7)	2.6 (2.8)	1 380s, 1 315m, 1 275s, 915s {ON(R)NO}; 840vs [ν(P–F)]
$[Pd\{ON(Ph)NO\}(PPh_3)_2][PF_6]$	55.1 (55.3)	4.0 (3.9)	3.3 (3.1)	1 372s, 1 280s, 1 165m, 905s {ON(Ph)NO}; 840vs [ν(P–F)]
$[Pd\{ON(C_6H_4Me\text{-}p)NO\}(PPh_3)_2][PF_6]$	55.7 (55.7)	4.0 (4.0)	2.9 (3.0)	1 360m, 1 280s, 1 160m, 902s {ON(R)NO}; 840vs [ν(P–F)]
$[Pt(NO_2)_2(PPh_3)_2]\cdot C_6H_6$	57.1 (56.7)	4.1 (4.1)	3.0 (3.2)	1 420 [$\nu_{asym}(NO_2)$]; 1 340 [$\nu_{sym}(NO_2)$]; 825 [δ(ONO)]

[a] In KBr discs. [b] From $[Pt(PhNO)(PPh_3)_2] + NOPF_6$. [c] From $[PtCl_2(PPh_3)_2] + Ag[ON(Ph)NO]$.

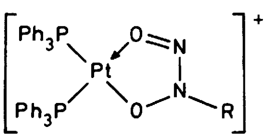
solution of $[\mathrm{RuCl(NO)}(o\text{-}\mathrm{MeC_6H_4NO})(\mathrm{PPh_3})_2]$ in benzene with CO caused the colour to change to golden yellow, and a green-yellow compound could be isolated. The i.r. spectrum of this material exhibited a strong band at 1 965 $\mathrm{cm^{-1}}$, which is presumably ν(CO) but there was no evidence for ν(NO); the known $[\mathrm{RuCl(CO)(NO)(PPh_3)_2}]$ exhibits ν(NO) at 1 595 and ν(CO) at 1 925 $\mathrm{cm^{-1}}$. Chromatography on silica gel using dichloromethane–n-hexane mixtures afforded a yellow fraction from which a yellow solid was isolated. ^{1}H N.m.r. and i.r. examination showed that $o\text{-}\mathrm{MeC_6H_4NO}$ was absent in this species, and since elemental analyses were irreproducible, we are unable to formulate this product. It appears, however, that coupling between NO and RNO at the metal is not induced by CO.

Reaction of $[\mathrm{RuCl(NO)(RNO)(PPh_3)_2}]$ with NO gas afforded an orange-yellow solid exhibiting ν(NO) at 1 880 $\mathrm{cm^{-1}}$. This suggested that a species of the type $\mathrm{Ru(NO)(PPh_3)_2XYZ}$ had been formed, and bands at 1 330 m, 1 265s, and 820w $\mathrm{cm^{-1}}$ could be assigned to $\nu_{\mathrm{asym}}(\mathrm{NO_2})$, $\nu_{\mathrm{sym}}(\mathrm{NO_2}$ of $\mathrm{NO_3})$, and $\delta(\mathrm{ONO}$ for $\mathrm{NO_2})$, indicating that the complex might be $[\mathrm{RuCl(NO)(NO_2)(NO_3)(PPh_3)_2}]$. However, elemental analyses failed to provide consistent data for this or any other formulation, although ^{1}H n.m.r. spectra of the product obtained from $[\mathrm{RuCl(NO)}(o\text{-}\mathrm{MeC_6H_4NO})(\mathrm{PPh_3})_2]$ indicated that the nitrosoarene had been lost.

Platinum Complexes.—The *o*-nitrosotoluene complex $[\mathrm{Pt}(o\text{-}\mathrm{MeC_6H_4NO})(\mathrm{PPh_3})_2]$ was prepared in the same way as the known nitrosobenzene complex,[11] by treating $[\mathrm{Pt(C_2H_4)(PPh_3)_2}]$ with $o\text{-}\mathrm{MeC_6H_4NO}$ in n-hexane. The i.r. spectra of $[\mathrm{Pt(RNO)(PPh_3)_2}]$ showed absorptions at 973 (R = Ph) and 975 $\mathrm{cm^{-1}}$ (R = $o\text{-}\mathrm{MeC_6H_4}$), respectively, which are assigned to ν(NO) of an η^2-RNO group.[11,16] The ^{1}H n.m.r. spectrum of $[\mathrm{Pt}(o\text{-}\mathrm{MeC_6H_4NO})(\mathrm{PPh_3})_2]$ exhibited a broad group of signals at δ 6.2—7.8 (relative intensity 11.4) due to the $\mathrm{C_6}\mathit{H}_4\mathrm{Me}$ and $\mathrm{P(C_6}\mathit{H}_5)_3$ protons, and a sharp singlet at δ 1.56 (relative intensity 1) due to the methyl protons.

Treatment of $[\mathrm{Pt(PhNO)(PPh_3)_2}]$ with $\mathrm{NOPF_6}$ in benzene–methanol mixtures afforded $[\mathrm{Pt\{ON(Ph)NO\}(PPh_3)_2}][\mathrm{PF_6}]$. This complex, and its Pd analogue, and the related *p*-tolyl species, could be alternatively synthesised by reacting $[\mathrm{MCl_2(PPh_3)_2}]$ (M = Pd or Pt) with $\mathrm{Ag[ON(R)NO]}$ (R = Ph or $p\text{-}\mathrm{MeC_6H_4}$). The i.r. spectra of $[\mathrm{Pt\{ON(Ph)NO\}(PPh_3)_2}][\mathrm{PF_6}]$ prepared by the two methods were identical, exhibiting bands at 1 375s, 1 315m, 1 275s and 910s $\mathrm{cm^{-1}}$, typical of the co-ordinated ON(Ph)NO ligand.[17] The ^{1}H n.m.r. spectrum of $[\mathrm{Pt\{ON(C_6H_4Me}\text{-}p\mathrm{)NO\}(PPh_3)_2}]^+$ consisted of a broad set of aryl proton resonances in the range δ 6.8—7.5 (relative intensity 34) and a sharp singlet due to the methyl group at δ 2.33 (relative intensity 3), consistent with our formulation of the complex.

From these data it is clear that $\mathrm{NO^+}$ addition to $[\mathrm{Pt(RNO)(PPh_3)_2}]$ resulted in the formation of the chelate ring system $\overline{\mathrm{PtON(R)NO}}$, as shown below. It may be noted that



Cenini[18] has observed other additions to the nitrosoarene ligand in $[\mathrm{Pt(PhNO)(PEt_3)_2}]$, *e.g.* with $\mathrm{CS_2}$ and $\mathrm{CO_2}$ to give $[\mathrm{Pt\{ON(Ph)C({=}E)E\}(PEt_3)_2}]$ (E = O or S).

Treatment of $[\mathrm{Pt(RNO)(PPh_3)_2}]$ with NO in benzene afforded a pale yellow precipitate and a red-brown solution. The i.r. spectrum of the yellow solid exhibited bands at 1 420, 1 340, and 825 $\mathrm{cm^{-1}}$, in addition to those associated with $\mathrm{PPh_3}$. These absorptions may be due to $\nu_{\mathrm{asym}}(\mathrm{NO_2})$, $\nu_{\mathrm{sym}}(\mathrm{NO_2})$, and δ(ONO) in a *N*-bonded nitro-complex, $[\mathrm{Pt(NO_2)_2(PPh_3)_2}]$. ^{1}H N.m.r. examination of the product derived from the nitrosotoluene complex showed that the $o\text{-}\mathrm{MeC_6H_4}$ group was absent. Microanalytical data, i.r., and m.p. comparison with authentic $[\mathrm{Pt(NO_2)_2(PPh_3)_2}]$, prepared by treatment of $[\mathrm{PtCl_2(PPh_3)_2}]$ with $\mathrm{AgNO_2}$ in chloroform,[19] indicate that the species formed is indeed a bis-nitro-complex, as a benzene solvate (see Table). Precisely how the nitro-species is formed is not known, but it may be noted that $[\mathrm{PtMe_2(L)_2}]$ (L = $\mathrm{PMe_2Ph}$ or $\mathrm{PEt_3}$) reacted with NO giving $[\mathrm{PtMe_2(NO_2)_2(L)_2}]$.[20] However, the generation of nitro- and nitrato-species by reaction of NO with Pt and Pd tertiary phosphine complexes will be discussed in a later paper.[19]

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