Formation of N–C Bonds *via* Alkylation of Transition Metal Nitrosyls. Reaction of Ruthenium and Other Transition Metal Nitrosyls with Benzyl Bromide

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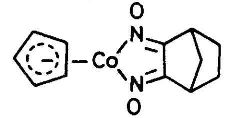
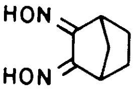
$[Ru(NO)_2(PPh_3)_2]$ reacts with benzyl bromide in refluxing toluene under CO to give $[RuBr(CO)(NO)(PPh_3)_2]$, $[RuBr_2(CO)_2(PPh_3)_2]$, PhCH=NOH, PhCN, $PhCONH_2$, PhCHO, and $PhCH_2OH$. In the absence of CO, $[Ru(NO)_2(PPh_3)_2]$ reacts with benzyl bromide to give $[RuBr_2(NCPh)_2(PPh_3)_2]$, $[RuBr_3(NO)(PPh_3)_2]$, PhCN, $PhCONH_2$, $(PhCH_2)_2$, and PhCHO, but in amounts smaller than those obtained under CO. In the absence of a metal, NO gas reacts with benzyl bromide in refluxing toluene to give $PhCH_2NO_2$ (major product, 45%) and small amounts of PhCN, PhCHO, and $PhCH_2OH$. Reaction of $[Ru(NO)_2(PPh_3)_2]$ with $PhCH_2Cl$ and other alkyl bromides, and of $[Ru(NO)_2(Ph_2PCH_2CH_2PPh_2)]$, $[Ru(NO)_2\{P(OPh)_3\}_2]$, $[Co(NO)\{P(OEt)_3\}_3]$, $[Rh(NO)(PPh_3)_3]$, and $[RhCl_2(NO)(PPh_3)_2]$ with $PhCH_2Br$ are briefly discussed.

The reactivity of metal-co-ordinated NO has been reviewed,[1] and it is apparent that there are relatively few homogeneous reactions which lead to the formation of N–C bonds. A selective list of these, indicating general reaction types, is given in Table 1. Related to these reactions is the heterogeneously catalysed formation of acrolein oxime (CH_2=CHCH=NOH) and acrylonitrile (CH_2=CHCN) from propene and NO over nickel oxide.[2] Most of the processes indicated in Table 1 involve ionic nitrosyl complexes which function in strongly polar reaction media. Only the reactions of $[CoBr(CO)_2(NO)]^-$ with benzyl bromide[3] and of $[Co(\eta\text{-}C_5H_5)(NO)]^-$ with RI[4] involve the direct alkylation, *via* an alkyl halide, of co-ordinated NO. However, NO undergoes 'insertion' reactions with d^0, d^1, and d^{10} transition metal alkyls affording species containing RNO or $[ON(R)NO]^-$ (R = *e.g.* Me or Pr^n), and some of these reactions occur in non-polar solvents.[4,5] It has also been observed recently that thermolysis of $[Ru(\eta\text{-}C_5Me_5)(NO)(CH_2R')_2]$ (R′ = H or Me) in benzene at 150 °C in the presence of PMe_3 gave $[Ru(\eta\text{-}C_5Me_5)(CN)(PMe_3)_2]$ (where R′ = H) and $[Ru(\eta\text{-}C_5Me_5)(PMe_3)_2(ON{=}CHMe)]$.[6]

While looking for potential routes to the formation of organonitrogen compounds by the direct alkylation of readily prepared transition metal nitrosyl complexes in non-polar solvents we were intrigued by the simplicity of the reaction between $[CoBr(CO)_2(NO)]^-$ and $PhCH_2Br$[3] in dimethylformamide. The organic reaction products were mainly PhCH=NOH and $PhCH_2CO_2H$, and the mechanism of formation of the oxime was thought to involve addition of $PhCH_2Br$ to NO, perhaps *via* oxidative addition of benzyl bromide to the Co species followed by group migration, giving $PhCH_2NO$ which then tautomerised to PhCH=NOH. A disadvantage of this reaction was the parallel, but not unexpected, formation of the carbonylation product $PhCH_2CO_2H$ produced, presumably, *via* CO 'insertion' into a $CoCH_2Ph$ bond. It occurred to us that such an undesirable side-reaction could be eliminated by using non-carbonyl-containing metal complexes, *e.g.* the readily available nitrosyl triphenylphosphine complexes of ruthenium or rhodium, $[Ru(NO)_2(PPh_3)_2]$ or $[Rh(NO)(PPh_3)_3]$. These nitrosyls are particularly easy to prepare and are soluble in hydrocarbon solvents.[7]

We reasoned that benzylation of co-ordinated NO should occur readily to form the easily identified benzyl oxime and, indeed, preliminary experiments indicated that addition of $PhCH_2Br$ to $[Ru(NO)_2(PPh_3)_2]$ did cause loss of the NO groups. However, isolation and characterisation of the products proved initially difficult, but introduction of CO into

Table 1. Formation of N–C bonds *via* transition metal nitrosyls

Reactants[a]	Intermediate or stable product	Organic product
$[Fe(CN)_5(NO)]^{2-}$, acetone, OH^-	$[Fe(CN)_5\{N(=O)CH_2COMe\}]^{2-}$	MeCOCH=NOH
$[RuCl(bipy)_2(NO)]^{2+}$, $PhNMe_2$	$[RuCl(bipy)_2\{N(=O)C_6H_4NMe_2\text{-}p\}]^{2+}$	—
$[Ru(NO)(NH_3)_5]^{3+}$, $^{\bullet}CH_2CMe_2(OH)$	$[Ru(NH_3)_5\{N(=O)CH_2CMe_2(OH)\}]^{2+}$	—
$[CoBr(CO)_2(NO)]^-$, $PhCH_2Br$	—	PhCH=NOH, $PhCH_2CO_2H$
$[\{M(\eta\text{-}C_5H_5)(NO)\}_n]$, $LiBu^t$	$\{M\text{–}NHBu^t\text{–}M\}$, *etc.*[b]	—
$[WMe_6]$, NO	$[WMe_4\{ON(Me)N{=}O\}_2]$	—
$[\{Co(\eta\text{-}C_5H_5)(NO)\}_2]$, 2-norbornene		
$[\{Ni(\eta\text{-}C_3H_5)Br\}_2]$, NO	$[\{Ni(CH_2{=}CHCH{=}NOH)Br\}_n]$	—
$[Ru(\eta\text{-}C_3H_5)(NO)(PPh_3)_2]$, CO	$[Ru(C_3H_5)(CO)(NO)(PPh_3)_2]$	CH_2=CHCH=NOH
$[Co(\eta\text{-}C_5H_5)(NO)]^-$, RI, PPh_3	$[Co(\eta\text{-}C_5H_5)\{N(=O)R\}(PPh_3)]$	—
$[Ru(\eta\text{-}C_5Me_5)(NO)Et_2]$, PMe_3 (150 °C)	$[Ru(\eta\text{-}C_5Me_5)(PMe_3)_2(ON{=}CHMe)]$ $[Ru(\eta\text{-}C_5Me_5)(PMe_3)_2(NHCOMe)]$	

[a] 2-Norbornene = bicyclo[2.2.1]hept-2-ene, bipy = 2,2′-bipyridyl. [b] Cluster species of Co and Ni containing μ-$NHBu^t$ and μ_3-NBu^t.

the reaction system permitted us not only to identify the metal-containing species formed at various stages of the reaction, but also to recover smoothly the organic products. A preliminary account of this work has been given,[1,8] and in this paper we describe in full our studies of reactions between benzyl bromide and various nitrosyl ruthenium complexes.

Results

1. *Reactions under* CO *Gas.*—The complex $[Ru(NO)_2(PPh_3)_2]$ reacted smoothly with $PhCH_2Br$ under CO in toluene at various temperatures, giving $[RuBr(CO)(NO)(PPh_3)_2]$ and $[RuBr_2(CO)_2(PPh_3)_2]$, the former appearing in the early stages of the reaction and being converted into the latter as the reaction proceeded (Table 2). These complexes were readily identified by their i.r. spectra, and by isolation followed by elemental analyses of the solids obtained.

The organic products of the reaction were identified, by a combination of gas–liquid chromatography and mass spectrometric techniques, as mainly PhCH=NOH, PhCN, and $PhCONH_2$ together with small amounts of PhCHO and $PhCH_2OH$ as well as, depending on conditions, unreacted $PhCH_2Br$.

From a study of the relative concentrations of the organic compounds formed in the reaction at 90 °C over 30 h (Table 2), we observed that the concentration of $PhCH_2Br$ decreased and PhCH=NOH, PhCN, PhCHO, and $PhCH_2OH$ quickly appeared. The concentrations of these new products gradually increased at the expense of the benzyl bromide, and it was only after 30 h at 90 °C that significant quantities of the $PhCONH_2$ appeared. These results indicated that $PhCONH_2$ is *not* a primary product of the reaction, and must be produced from either PhCH=NOH or PhCN, probably the latter. We also noted that the amount of $PhCH_2OH$ steadily increased during the reaction, and since great care was taken to exclude moisture, both from the solvent and the CO gas, we conclude that the production of the alcohol occurs *via* hydrolysis of $PhCH_2Br$. The water could originate from the dehydration of PhCH=NOH to PhCN, perhaps in a metal-assisted process. At 90 °C this dehydration must be a relatively slow and inefficient process, since the concentration of PhCH=NOH is significantly greater than PhCN. Clearly, after some considerable time and a significant decrease in the amount of $PhCH_2Br$, rehydrolysis of PhCN to $PhCONH_2$ must become competitive with alcohol formation.

Table 2. Reaction of $[Ru(NO)_2(PPh_3)_2]$ with $PhCH_2Br$ (1:2) at 90 °C in toluene: inorganic and organic products as a variable with time

	Time (h)					
Compound	1	2	4	6	23	30
$[Ru(NO)_2(PPh_3)_2]$[a]	4	4	1	1	0	0
$[RuBr(CO)(NO)(PPh_3)_2]$[a]	1	2	2	1.5	0	0
$[RuBr_2(CO)_2(PPh_3)_2]$[a]	0	1	1	4	1	1
$PhCH_2Br$[b]	94.8	79.7	64.5	53.8	39.4	39.4
PhCH=NOH[b]	1.4	14.5	28.4	36.2	37.0	35.9
PhCN[b]	2.8	4.2	3.9	6.3	10.0	9.5
$PhCONH_2$[b]	0	0	0	0	0	1.7
PhCHO[b]	0.7	1.1	1.4	1.5	5.8	5.7
$PhCH_2OH$[b]	0.3	0.5	1.6	2.1	7.8	8.3

[a] Relative ratios, established by i.r. spectral methods. [b] Relative percentages, established by v.p.c. methods.

By varying the temperature and time of the reaction (Table 3), we established that the most efficient conversion of the NO in the dinitrosyl complexes into organonitrogen derivatives occurred at 110 °C (refluxing toluene) over 48 h. Indeed, under these conditions, the major organonitrogen product was $PhCONH_2$, and production of $PhCH_2OH$ was totally suppressed.

For comparison purposes, we investigated the reaction of $PhCH_2Br$ with NO gas in toluene (Table 4). At 80 °C, conversion to other organic products was very inefficient, but we identified PhCN, PhCHO, $PhCH_2OH$, and two species not found in the reaction mediated by $[Ru(NO)_2(PPh_3)_2]$, namely $(PhCH_2)_2$ and $PhCH_2NO_2$. At 110 °C over 48 h, however, reaction with NO led to conversion of more than half of the benzyl bromide into a significant amount of $PhCH_2NO_2$ as well as to $PhCH_2OH$, PhCHO, and PhCN. The absence of nitrobenzyl would seem to suggest that in reactions involving $[Ru(NO)_2(PPh_3)_2]$, dissociation of NO from the complex prior to reaction with $PhCH_2Br$ does not occur or, in other words, that alkylation of NO occurs while the nitrosyl group is co-ordinated to the metal. This is consistent with the observation that $[Ru(NO)_2(PPh_3)_2]$ does not react with CO in refluxing toluene, the complex being recovered unchanged after 25 h. We also observed that there was no significant reaction between NO and toluene at 110 °C.

Because mononitrosyl species are formed during the reaction between $[Ru(NO)_2(PPh_3)_2]$ and $PhCH_2Br$, we investigated the reactions of several known mononitrosyl halide complexes of ruthenium with $PhCH_2Br$ (Table 5). $[RuBr(CO)(NO)(PPh_3)_2]$ was identified as the mononitrosyl complex formed in reactions under CO, but treatment of the readily prepared $[RuCl(CO)(NO)(PPh_3)_2]$ with $PhCH_2Br$ in refluxing benzene under nitrogen gave only a very small conversion to organic products, possibly reflecting the relatively unreactive nature of this species. However, reaction of the co-ordinatively unsaturated $[RuCl(NO)(PPh_3)_2]$ with benzyl bromide in benzene under nitrogen at room temperature, when oxidative addition, presumably to give $[RuBrCl(CH_2Ph)(NO)(PPh_3)_2]$, is known to occur,[9] followed by treatment of the mixture with CO under refluxing conditions did afford PhCHNOH, PhCN, PhCHO, and traces of $PhCONH_2$, $PhCH_2OH$, and $(PhCH_2)_2$. These observations imply that oxidative addition of $PhCH_2Br$ to the ruthenium may occur at an early stage of these overall reactions,

Table 3. Reaction of $[Ru(NO)_2(PPh_3)_2]$ with $PhCH_2Br$ (1:2) in toluene: variation of organic products (relative percentages) with time and temperature

Temp. (°C)	50	65	80	110	65	80	110[a]	90[b]	90
Time (h)	90	20	20	20	48	48	48	20	23
$PhCH_2Br$	63.0	96.0	70.9	19.1	59.6	23.9	0	39.1	39.4
PhCH=NOH	0	0	22.4	4.1	4.1	42.3	9.0	50.2	37.0
PhCN	1.5	0.4	4.4	54.0	12.8	10.8	17.2	5.0	10.0
$PhCONH_2$	0	trace	trace	9.2	6.2	19.4	77.0	trace	0
PhCHO	11.2	0.8	1.7	7.2	7.3	2.2	5.4	4.0	5.8
$PhCH_2OH$	11.3	0.9	1.0	5.2	9.4	0.6	0	1.0	7.8

[a] 1:1 Molar ratio. [b] In the presence of $MgSO_4$.

and is followed by a migration of the benzyl group to the coordinated NO. Such an oxidative addition process is unlikely to occur with $PhCH_2Br$ and $[RuCl_3(NO)(PPh_3)_2]$ and, indeed, under CO in refluxing toluene, only very small amounts of organic products are formed from these reactants.

As both PhCN and PhCH=NOH are produced rapidly in the treatment of $[Ru(NO)_2(PPh_3)_2]$ with $PhCH_2Br$ under CO, we investigated their reactions with nitrosyl complexes which may be formed as intermediates during the overall reaction. Benzonitrile does not react with $[RuCl(CO)(NO)(PPh_3)_2]$ even in refluxing toluene, but may, judging by colour changes, form a weak adduct with $[RuCl(NO)(PPh_3)_2]$, *viz.* $[RuCl(NO)(NCPh)(PPh_3)_2]$. However, when treated with CO this adduct is rapidly converted to $[RuCl(CO)(NO)(PPh_3)_2]$. There was similarly no significant reaction between $[RuCl(CO)(NO)(PPh_3)_2]$ and PhCH=NOH, but the results obtained using $[RuCl(NO)(PPh_3)_2]$ are summarised in Table 6. When PhCH=NOH is allowed to react with the chloro-nitrosyl it is presumed that an adduct is formed but on passage of CO some of this is removed before dehydration can occur. This could explain the recovery of nearly 27% of the unreacted oxime when the reaction mixture is refluxed under CO. However, it is clear that dehydration of the oxime to the nitrile is significantly assisted by $[RuCl(NO)(PPh_3)_2]$, as judged from the results obtained in the absence of CO. It may also be noted that benzaldehyde can be formed from either the oxime or the nitrile under these conditions.

2. *Reactions in the Absence of* CO.—Our early studies of the reaction between $[Ru(NO)_2(PPh_3)_2]$ and $PhCH_2Br$ were frustrated by difficulties in product purification and characterisation, although we did establish that $PhCONH_2$ could be formed when the reagents were refluxed in toluene under nitrogen. Once we understood the nature of the products formed under CO however, it was relatively easy to reinvestigate those reactions involving less reactive gases, *e.g.* C_2H_4 and N_2. We chose to use ethylene partly because of the possibility of alkene insertion into M–C bonds which might be concomitant with 'NO insertion' but in the event, this did not happen. The results of our study are summarised in Table 7.

Table 4. Percentage yields for the products of the reaction of $PhCH_2Br$ with NO in toluene

Compound	80 °C/19 h	110 °C/48 h
$PhCH_2Br$	91.5	40.0
PhCH=NOH	—	—
PhCN	0.4	0.4
$PhCONH_2$	—	—
PhCHO	1.8	3.5
$PhCH_2OH$	2.4	9.2
$(PhCH_2)_2$	0.1	—
$PhCH_2NO_2$	1.8	45.1

In these reactions, which give results broadly similar to each other, it was clear that there was only a *ca.* 30% yield of 'free' organic product, taking into account that in the reaction under N_2, an excess of $PhCH_2Br$ was used. However, the inorganic products were shown to be $[RuBr_2(NCPh)_2(PPh_3)_2]$ and $[RuBr_3(NO)(PPh_3)_2]$, which accounted for the overall consumption of benzyl bromide. We also noted that dibenzyl was formed in these three reactions, a species conspicuously absent in those processes carried out under CO. Also PhCH=NOH and $PhCH_2OH$ were absent, and the relative yields of PhCHO were low. It is clear, however, that when CO is present, the organic products of the reaction are readily released from their Ru complexes.

3. *Reactions with Other Organic Halides.*—Benzyl chloride reacted with $[Ru(NO)_2(PPh_3)_2]$ under CO in refluxing toluene but much less efficiently than its bromo analogue, the organic products being PhCN (3.0%), PhCH=NOH (7.0%), and unreacted $PhCH_2Cl$ (9.0%). The inorganic products, identified spectroscopically, were unreacted starting material, $[RuCl(CO)(NO)(PPh_3)_2]$, and $[RuCl_2(CO)_2(PPh_3)_2]$. $PhCH_2CH_2Br$, o-$C_6H_4(CH_2Br)_2$, and $(CH_3)_2CHBr$ also reacted with $[Ru(NO)_2(PPh_3)_2]$, as evidenced by denitrosylation, but only extremely low yields of new organic products were formed, which were not identified. When $[Ru(NO)_2(PPh_3)_2]$ was refluxed for 17 and 26 h in toluene under CO with PhMeCHBr, which cannot form an oxime or a nitrile, the organohalide was recovered virtually qualitatively, although traces of PhMeCHOH were detected.

4. *Reactions with Other Ruthenium Phosphine and Phosphite Complexes.*—$[Ru(NO)_2(dppe)]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) and $[Ru(NO)_2\{P(OPh)_3\}_2]$ both reacted with benzyl bromide in refluxing toluene under CO, but not as effectively as $[Ru(NO)_2(PPh_3)_2]$ (Table 8). In general, the same organic products were identified, although with the triphenyl phosphite complex, $PhCH_2NO_2$ was also observed.

Reaction of the hydrido-acetate $[RuH(O_2CMe)(PPh_3)_3]$ with benzyl bromide in refluxing toluene under NO (Table 8) also afforded organic products whose nature and distribution were strongly reminiscent of the reaction between free NO and benzyl bromide in refluxing toluene alone (Table 4).

Table 5. Reactions of ruthenium nitrosyl halides with benzyl bromide

Organic products	$[RuCl(CO)(NO)(PPh_3)_2]$, N_2, benzene[a] 80 °C/1 h	80 °C/17 h	$[RuCl(NO)(PPh_3)_2]$, N_2, benzene[b] (10 min; then reflux + CO, 17 h)	$[RuCl_3(NO)(PPh_3)_2]$, CO, toluene[c] (110 °C/17 h)
$PhCH_2Br$	85.0	75.0	64.1	96.4
PhCH=NOH	—	—	10.3	—
PhCN	1.0	0.5	8.0	1.0
$PhCONH_2$	—	—	trace	—
PhCHO	7.0	10.0	14.2	1.4
$PhCH_2OH$	0.5	0.5	trace	—
$(PhCH_2)_2$	—	—	trace	—
$PhCH_2NO_2$	—	—	—	—
Inorganic products	unreacted s.m.c.[d] + trace $[RuX_2(CO)_2(PPh_3)_2]$[e]		$[RuX_2(CO)_2(PPh_3)_2]$[e]	unreacted s.m.c.[d] + trace $[RuX_2(CO)_2(PPh_3)_2]$[e]

[a] Metal complex: $PhCH_2Br$ ratio 1:2. [b] Metal complex: $PhCH_2Br$ ratio 1:1.5. [c] Metal complex: $PhCH_2Br$ ratio 1:1. [d] s.m.c. = Starting metal complex. [e] X = Cl and/or Br.

5. Reactions of Benzyl Bromide with Other Transition Metal Nitrosyls.—On the basis of the successful denitrosylation of $[Ru(NO)_2(PPh_3)_2]$ by benzyl bromide under CO, we thought that the reaction could be made more general providing that a reaction pathway leading to a stable metal carbonyl bromide could be envisaged, equations (1)—(3).

$$[M(NO)L_m] + RX + CO \longrightarrow [M(CO)L_mX] + \text{‘RNO’} \tag{1}$$

$$[M(NO)L_mX_n] + RX + CO \longrightarrow [M(CO)L_mX_{n+1}] + \text{‘RNO’} \tag{2}$$

$$[M(NO)_2L_mX] + 2RX + 2CO \longrightarrow [M(CO)_2L_mX_3] + 2\text{‘RNO’} \tag{3}$$

Accordingly, we studied the behaviour of $[Co(NO)\{P(OEt)_3\}_3]$, $[Rh(NO)(PPh_3)_3]$, and $[RhCl_2(NO)(PPh_3)_2]$ with $PhCH_2Br$ under CO in refluxing toluene (Table 9).

The reactions with $[Co(NO)\{P(OEt)_3\}_3]$ and $[RhCl_2(NO)(PPh_3)_2]$ gave only low conversion to organic products, but indicated a product distribution essentially similar to those reactions involving $[Ru(NO)_2(PPh_3)_2]$. With [Rh(NO)-

Table 6. Reaction of $[RuCl(NO)(PPh_3)_2]$ with PhCH=NOH (1:1) in toluene*

Organic products	Reaction conditions	
	At r.t. under N_2, 10 min; reflux under CO, 20 h	Reflux under N_2, 20 h
PhCH=NOH	26.5	—
PhCN	51.0	95.0
PhCHO	5.1	5.0
$PhCONH_2$	9.8	—

* Relative percentages of products as determined by v.p.c.; r.t. = room temperature.

Table 7. Reactions of $[Ru(NO)_2(PPh_3)_2]$ with $PhCH_2Br$ under C_2H_4 and under N_2 in toluene*

Organic products	Reaction conditions		
	Under C_2H_4 mole ratio 1:2		Under N_2, mole ratio 1:3, 65 °C/20 h
	65 °C/20 h	110 °C/20 h	
$PhCH_2Br$	7.6	—	30.1
PhCN	3.2	14.2	5.1
$PhCONH_2$	19.2	4.9	9.6
$(PhCH_2)_2$	0.7	8.2	6.0
$PhCH_2OH$	—	—	—
PhCHO	0.3	2.0	4.3
Total	31.3	30.0	55.1
Inorganic products	$[RuBr_2(NCPh)_2(PPh_3)_2]$ $[RuBr_3(NO)(PPh_3)_2]$		$[RuBr_2(NCPh)_2(PPh_3)_2]$ $[RuBr_3(NO)(PPh_3)_2]$

* Relative percentages of products as determined by v.p.c.

Table 8. Reactions of various ruthenium complexes with benzyl bromide and NO in toluene*

Organic products	$[Ru(NO)_2(dppe)]$, mole ratio 1:2, under CO, 90 °C/18 h	$[Ru(NO)_2\{P(OPh)_3\}_2]$, mole ratio 1:2, under CO, 110 °C/18 h	$[RuH(O_2CMe)(PPh_3)_3]$, mole ratio 1:2, under NO, 110 °C/18 h
$PhCH_2Br$	42.5	61.0	42.6
PhCH=NOH	27.7	trace	—
PhCN	5.3	13.0	0.5
$PhCONH_2$	1.1	—	—
$PhCH_2NO_2$	—	23.0	26.6
PhCHO	8.4	1.0	1.6
$PhCH_2OH$	5.0	trace	18.1
$(PhCH_2)_2$	—	—	0.1

* Relative percentages of products as determined by v.p.c.

Table 9. Reactions of cobalt and rhodium nitrosyls with benzyl bromide (1:1) under CO in refluxing toluene (110 °C)[a]

Organic products	$[Co(NO)\{P(OEt)_3\}_3]$, 17 h	$[Rh(NO)(PPh_3)_3]$, 20 h	$[RhCl_2(NO)(PPh_3)_2]$, 48 h
$PhCH_2Br$	80.0	19.5	71.1
PhCH=NOH	—	—	—
PhCN	—	18.4	6.0
$PhCONH_2$	3.3	—	4.0
PhCHO	3.3	11.2	18.0
$PhCH_2OH$	5.9	9.4	2.0
$PhCH_2NO_2$	—	—	—
$(PhCH_2)_2$	5.6	—	—
Others	—	[b]	—

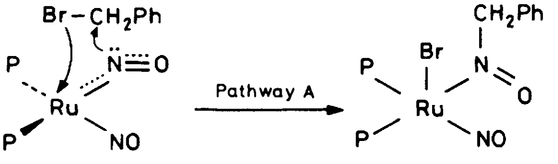
[a] Relative percentages of products as determined by v.p.c. [b] Two unidentified products with column retention times of 42 and 45 min.

$(PPh_3)_3]$, significant conversion of benzyl bromide occurred, although two unidentified organic species were detected. In this reaction, however, the inorganic products were $[RhBr(CO)(PPh_3)_2]$ and $[PPh_3(CH_2Ph)]Br$ (identified spectroscopically).

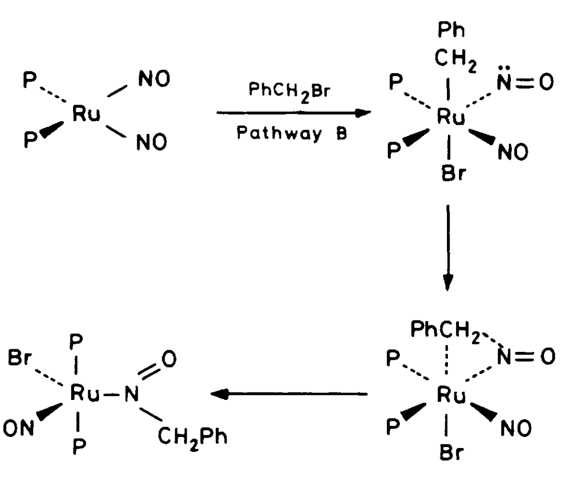
Discussion

Irrespective of whether the attack of benzyl bromide on $[Ru(NO)_2(PPh_3)_2]$ occurs under CO, N_2, or C_2H_4, we consider that ruthenium-co-ordinated $PhCH_2NO$ must be formed very rapidly. This may occur either by nucleophilic attack on benzyl bromide by a co-ordinated NO group, Scheme 1, with concomitant attachment of Br to the metal, or by oxidative addition of the benzyl bromide, giving a transient intermediate, containing a bent RuNO group which then undergoes a NO 'insertion' reaction (Scheme 2).

The known distortion of the Ru–N–O bonds detected in the structure of $[Ru(NO)_2(PPh_3)_2]$[10] would be consistent with pathway A. However, coupling of the allyl group and NO by treatment of $[Ru(\eta^3\text{-}C_3H_5)(NO)(PPh_3)_2]$ with CO,[11] which may involve the intermediate $[Ru(\sigma\text{-}C_3H_5)(CO)(NO)(PPh_3)_2]$ would seem to be consistent with pathway B. We cannot differentiate between the two pathways. Alternative routes involving either oxidative addition to give $[RuBr_2(CH_2Ph)(NO)(PPh_3)_2]$ with release of $PhCH_2NO$, or a reaction that results in loss of NO which subsequently combines with $PhCH_2Br$, can be dismissed since these could not account for the early observation of $[RuBr(CO)(NO)(PPh_3)_2]$, the failure to observe ν(NO) values being commensurate with the presence of $[Ru(NO)]^{3+}$ species (> 1 800 cm^{-1}), the fairly rapid appearance of PhCN, the absence of acyl products derived from CO insertion into Ru–C bonds, and the fact that $PhCH_2NO_2$ (expected and usually found in reactions of 'free' NO and $PhCH_2Br$) was not detected in the products of the denitrosylation reactions carried out under CO. Another possible intermediate, $[Ru(CH_2Ph)(NO)_2(PPh_3)_2]Br$, also seems unlikely since it proved impossible to isolate or obtain any evidence for the existence of $[Ru(NO)_2(PPh_3)_2R][BF_4]$ (R = Me or Et), analogous to $[Ru(NO)_2(PPh_3)_2X]^+$ (X = Cl or OH),[12] in the reaction between $[Ru(NO)_2(PPh_3)_2]$ and $[R_3O][BF_4]$ and because, in toluene, $PhCH_2Br$ bond cleavage to give such ionic species would seem to be disfavoured.



Scheme 1.



Scheme 2.

It seems highly probable that the nitrosobenzyl in the intermediate $[RuBr(NO)\{N(=O)CH_2Ph\}(PPh_3)_2]$ undergoes rapid tautomerisation, giving the oxime species $[RuBr(NO)\{N(OH)=CHPh\}(PPh_3)_2]$, which is then quickly dehydrated to the nitrile complex $[RuBr(NO)(NCPh)(PPh_3)_2]$. That PhCH=NOH can be rapidly dehydrated in the presence of ruthenium nitrosyl complexes was demonstrated by reaction of $[RuCl(NO)(PPh_3)_2]$ with the oxime in refluxing toluene. Under N_2, the yield of PhCN was almost quantitative, while under CO it was the major species formed, some hydrolysis products and unreacted oxime also being present. The lower yield of benzonitrile in the reaction under CO might be expected because of competition of oxime and CO for the site at the metal in the co-ordinatively unsaturated $[RuX(NO)(PPh_3)_2]$ (X = Cl or Br). These processes are related to those reported for the thermolysis of $[Ru(\eta\text{-}C_5Me_5)(NO)Et_2]$ in the presence of PMe_3, where both the oximato species $[Ru(\eta\text{-}C_5Me_5)(PMe_3)_2(ON{=}CHMe)]$ and the acetamidato compound $[Ru(\eta\text{-}C_5Me_5)(PMe_3)_2(NHCOMe)]$ could be formed.[6] Thus, we propose that the initial steps in the reaction of $[Ru(NO)_2(PPh_3)_2]$ with $PhCH_2Br$, irrespective of the gaseous atmosphere, are as in equations (4)—(6). Under CO, two reactions can cause relatively slow release of PhCH=NOH and PhCN, respectively (7) and (8). Subsequent denitrosylation under CO will presumably follow according to reactions (9)—(12). Reaction between $[RuCl(CO)(NO)(PPh_3)_2]$ and $PhCH_2Br$ under N_2 in refluxing toluene was very slow, yielding some PhCHO, traces of PhCN, and $[RuX_2(CO)_2(PPh_3)_2]$. These data are consistent with the observation that $[Ru(NO)_2(PPh_3)_2]$ is rapidly converted into $[RuBr(CO)(NO)(PPh_3)_2]$ but that the latter only slowly forms $[RuBr_2(CO)_2(PPh_3)_2]$.

$$[Ru(NO)_2(PPh_3)_2] + PhCH_2Br \longrightarrow [RuBr(NO)\{N(=O)CH_2Ph\}(PPh_3)_2] \text{ (fast)} \quad (4)$$

$$[RuBr(NO)\{N(=O)CH_2Ph\}(PPh_3)_2] \longrightarrow [RuBr(NO)\{N(OH)=CHPh\}(PPh_3)_2] \quad (5)$$

$$[RuBr(NO)\{N(OH)=CHPh\}(PPh_3)_2] \longrightarrow [RuBr(NO)(NCPh)(PPh_3)_2] + H_2O \text{ (fast)} \quad (6)$$

$$[RuBr(NO)\{N(OH)=CHPh\}(PPh_3)_2] + CO \longrightarrow [RuBr(CO)(NO)(PPh_3)_2] + PhCH{=}NOH \quad (7)$$

$$[RuBr(NO)(NCPh)(PPh_3)_2] + CO \longrightarrow [RuBr(CO)(NO)(PPh_3)_2] + PhCN \quad (8)$$

$$[RuBr(CO)(NO)(PPh_3)_2] + PhCH_2Br \longrightarrow [RuBr_2(CO)\{N(OH)=CHPh\}(PPh_3)_2] \text{ (slow)} \quad (9)$$

$$[RuBr_2(CO)\{N(OH)=CHPh\}(PPh_3)_2] + CO \longrightarrow [RuBr_2(CO)_2(PPh_3)_2] + PhCH{=}NOH \quad (10)$$

$$[RuBr_2(CO)\{N(OH)=CHPh\}(PPh_3)_2] \longrightarrow [RuBr_2(CO)(NCPh)(PPh_3)_2] + H_2O \text{ (slow)} \quad (11)$$

$$[RuBr_2(CO)(NCPh)(PPh_3)_2] + CO \longrightarrow [RuBr_2(CO)_2(PPh_3)_2] + PhCN \quad (12)$$

The occurrence of $PhCONH_2$, PhCHO, and $PhCH_2OH$ in the organic reaction products can be rationalised as arising from (metal-assisted) hydrolysis of PhCN, PhCH=NOH, and $PhCH_2Br$. All of the reactions described were carried out under strictly anhydrous conditions, but the metal-assisted dehydration of PhCH=NOH [reactions (6) and (11)] will provide sufficient water to accomplish these hydrolyses. There is ample evidence of the metal-catalysed hydration of nitriles to amides.[13]

When the benzylation reaction is carried out in the absence of CO, that is under N_2 or ethylene, we believe that the reaction sequence (4)—(6) is repeated. However, after that point we propose that reactions (13)—(17) can occur. It may be noted that $[RuCl(NO)(PPh_3)_2]$ is known to undergo oxidative addition reactions with alkyl halides,[9] and that a mixture of benzyl bromide and $[RuBrCl(CH_2Ph)(NO)(PPh_3)_2]$ in refluxing toluene afforded small amounts of $(PhCH_2)_2$, which is consistent with the proposed reactions (13) and (14). The slow benzylation of NO would lead, by analogy with reactions (9)—(12), to formation of benzonitrile, which remains co-ordinated to the metal. Thus reactions (13)—(17) may account for the relatively low yields of 'free' organic products and for the appearance of $[RuBr_2(NCPh)_2(PPh_3)_2]$ and $[RuBr_3(NO)(PPh_3)_2]$.

$$[\mathrm{RuBr(NO)(NCPh)(PPh_3)_2}] + \mathrm{PhCH_2Br} \longrightarrow [\mathrm{RuBr_2(CH_2Ph)(NO)(PPh_3)_2}] + \mathrm{PhCN} \quad (13)$$

$$[\mathrm{RuBr_2(CH_2Ph)(NO)(PPh_3)_2}] + \mathrm{PhCH_2Br} \longrightarrow [\mathrm{RuBr_3(NO)(PPh_3)_2}] + (\mathrm{PhCH_2})_2 \quad (14)$$

$$[\mathrm{RuBr(NO)(NCPh)(PPh_3)_2}] + \mathrm{PhCH_2Br} \longrightarrow [\mathrm{RuBr_2\{N({=}O)CH_2Ph\}(NCPh)(PPh_3)_2}] \quad (15)$$

$$[\mathrm{RuBr_2\{N({=}O)CH_2Ph\}(NCPh)(PPh_3)_2}] \longrightarrow [\mathrm{RuBr_2\{N(OH){=}CHPh\}(NCPh)(PPh_3)_2}] \quad (16)$$

$$[\mathrm{RuBr_2\{N(OH){=}CHPh\}(NCPh)(PPh_3)_2}] \longrightarrow [\mathrm{RuBr_2(NCPh)_2(PPh_3)_2}] + \mathrm{H_2O}\ (\text{slow}) \quad (17)$$

From a comparison of the apparent speed with which organic products are formed in the reactions under CO with those under N_2 or ethylene, it seems that the role of CO is to facilitate the liberation of the nitrosobenzyl derivatives without generating compounds which are themselves significantly reactive. Indeed, the original intention of using CO was to deactivate $[RuBr(NO)(PPh_3)_2]$ which, we thought, might be formed in the reaction after elimination of $PhCH_2NO$. Indeed, it has been suggested that in related reactions between $[Ru(NO)_2(PPh_3)_2]$ and halogens, in which $[Ru(NO)(PPh_3)_2X_3]$ is the final product, a likely intermediate is $[Ru(NO)(PPh_3)_2X]$.[14] We reasoned that the ability of such a species to undergo oxidative addition with $PhCH_2Br$ would complicate the intended nitrosylation processes. Another significant point is that, under CO, no dibenzyl is formed, suggesting that, unlike the reactions in the absence of CO, radical processes are unimportant in the overall mechanism.

Finally, we may conclude that the reaction between gaseous NO and $PhCH_2Br$ in solution is inefficient in comparison to that when the NO is co-ordinated by ruthenium, and that the nature of the products is significantly modified by that co-ordination.

Experimental

The complexes $[RuCl(NO)(PPh_3)_2]$, $[RuX(CO)(NO)(PPh_3)_2]$ (X = Cl or Br), $[RuX_3(NO)(PPh_3)_2]$ (X = Cl or Br), $[Ru(NO)_2(dppe)]$, $[Ru(NO)_2\{P(OPh)_3\}_2]$, $[Rh(NO)(PPh_3)_3]$, $[RhCl_2(NO)(PPh_3)_2]$ and $[Co(NO)\{P(OEt)_3\}_3]$ were prepared by methods readily available in the literature. CO and NO gas were supplied by Air Products Ltd., and passed through H_2SO_4, KOH pellets, and molecular sieves. The allyl and aryl halides were distilled over $CaBr_2$ and stored under argon over anhydrous $MgSO_4$. Infrared spectra were obtained using PE-257, -457, and -180 spectrophotometers. ^1H N.m.r. spectra were obtained using a Varian HA100 spectrometer. Analytical vapour pressure chromatographic (v.p.c.) separations were performed by a PEF11 gas chromatograph fitted with a flame ionization detector. Glass columns (183 cm × 3 mm internal diameter) were packed with free fatty acid phase with 5% w/w loading on Chromasorb G (80—100 mesh) acid-washed $SiHClMe_2$. The carrier gas (N_2) flow rate was 30 cm^3 min^{-1} and column temperature varied from 60—230 °C with a programmed rise of 6 °C min^{-1}. Quantitative measurements were made by comparison with standard v.p.c. runs using predetermined concentrations of known compounds. Mass spectra (m.s.) and gas chromatographic (g.c.) m.s. measurements were made using an AEMS12 instrument fitted with a Biemann Separator. For g.c.m.s., the carrier gas was helium, and column conditions were as for conventional v.p.c. For conventional mass spectrometry the ionising voltage was 70 eV ($eV \approx 1.60 \times 10^{-19}$ J) but for g.c.m.s, 30 eV.

Reaction conditions are as described in Tables 1—9. The metal compounds formed were separated, and characterised by microanalysis (C, H, N, halogen) and i.r. spectral studies. The organic compounds were determined by v.p.c. (comparison with authentic compounds) and g.c.m.s.

Typical Reactions: Treatment of $[Ru(NO)_2(PPh_3)_2]$ *with Benzyl Bromide in Toluene under* CO.—$[Ru(NO)_2(PPh_3)_2]$ (0.7 g) and $PhCH_2Br$ (0.25 cm^3) (1:2 mole ratio) were heated at 90 °C in CO-saturated dry toluene (50 cm^3) for 48 h. The mixture was stirred and CO passed continuously through the toluene to maintain saturation. The pale yellow solution which formed was evaporated *in vacuo* to *ca.* 5 cm^3, cooled to 0 °C and treated with cold EtOH. The $[RuBr_2(CO)_2(PPh_3)_2]$ which precipitated was filtered off and the filtrate evaporated *in vacuo* to leave an organic residue analysed by v.p.c. and g.c.m.s. (Found: C, 54.4; H, 3.3; Br, 19.6. $C_{38}H_{30}Br_2O_2P_2Ru$ requires C, 54.2; H, 3.6; Br, 19.0%). I.r. (KBr disc): 2 070, 1 990 cm^{-1}.

When the reaction was stopped after 12 h, the solid filtered off contained $[RuBr(CO)(NO)(PPh_3)_2]$ and $[RuBr_2(CO)_2(PPh_3)_2]$, identified by i.r. spectroscopy. The former was separated from the latter by recrystallisation from CH_2Cl_2–MeOH mixtures: $[RuBr(CO)(NO)(PPh_3)_2]$ (Found: C, 48.6; H, 3.4; Br, 10.3; N, 1.8. $C_{37}H_{30}BrNO_2P_2Ru$ requires C, 48.5; H, 3.9; Br, 10.5; N, 1.8%). I.r. (KBr disc): 1 925 (ν_{CO}), 1 595 cm^{-1} (ν_{NO}).

Treatment of $[Ru(NO)_2(PPh_3)_2]$ *with* $PhCH_2Br$ *in Toluene under Nitrogen.*—$[Ru(NO)_2(PPh_3)_2]$ (0.5 g) and $PhCH_2Br$ (0.25 g) (1:2 mole ratio) were refluxed in toluene (80 cm^3) under N_2 for 5 h. A yellow powder was precipitated and was collected and recrystallised from toluene–n-hexane to give $[RuBr_2(NCPh)_2(PPh_3)_2]$ (Found: C, 61.9; H, 4.2; Br, 16.7; N, 2.8. $C_{50}H_{40}Br_2N_2P_2Ru$ requires C, 62.3; H, 4.2; Br, 16.6; N, 2.9%). I.r. (KBr disc): 2 223 cm^{-1} (ν_{CN}).

Concentration of the filtrate and addition of n-hexane afforded a brown solid, identified as $[RuBr_3(NO)(PPh_3)_2]$ (Found: C, 48.9; H, 3.7; Br, 26.9; N, 1.9. $C_{36}H_{30}Br_3NOP_2Ru$ requires C, 48.2; H, 3.3; Br, 26.8; N, 1.6%). I.r. (KBr disc): 1 870 cm^{-1} (ν_{NO}).

After removal of all solvents, the organic residue was subjected to v.p.c. and g.c.m.s analysis.

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