Formation of Organonitrogen Compounds *via* Neutral Ruthenium Nitrosyl Complexes

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Summary $[Ru(NO)_2(PPh_3)_2]$ reacts with $PhCH_2Br$ in hot toluene under CO to give $[RuBr(CO)(NO)(PPh_3)_2]$, $[RuBr_2(CO)_2(PPh_3)_2]$, PhCH=NOH, PhCN, and $PhCONH_2$, together with small amounts of PhCHO and $PhCH_2OH$; in the absence of CO, under N_2 or C_2H_4, the yields of organonitrogen products are reduced, and $[RuBr_2(NCPh)_2(PPh_3)_2]$ and $[RuBr_3(NO)(PPh_3)_2]$ are formed.

THE formation of N–C bonds *via* the intermediacy of ruthenium nitrosyl complexes has been described in two instances: (i) the reaction of $[Ru(bipyridyl)_2(NO)X]^{2+}$ (X = Cl or NO_2) with 'activated' arylamines,[1] *e.g.* $PhNMe_2$, when Ru-co-ordinated p-$Me_2NC_6H_4NO$ is formed, and (ii) the radiolysis of $[Ru(NH_3)_5(NO)]^{3+}$ in solutions containing Bu^tOH,[2] when metal-bound $Me_2C(CH_2NO)(OH)$ is produced. However, by virtue of the use of charged ruthenium nitrosyl precursors, these interesting reactions must, of necessity, take place in polar solvents. In attempting to find routes for the alkylation of nitric oxide *via* metal complex intermediates in hydrocarbon solvents, we have investigated the reaction of $[Ru(NO)_2(PPh_3)_2]$ with benzyl bromide† in toluene.

Under an atmosphere of CO in hot toluene, $[Ru(NO)_2(PPh_3)_2]$ was converted into $[RuBr(CO)(NO)(PPh_3)_2]$ 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). The organic products were identified‡ as mainly PhCH:NOH, PhCN, and $PhCONH_2$., with smaller amounts of PhCHO and $PhCH_2OH$. From the data in the Table, it is clear that efficient conversion of co-ordinated NO into organonitrogen compounds is temperature dependent, being optimal at 110 °C after 48 h.

TABLE. Nitrosylation of $PhCH_2Br$ in toluene

$$\underset{(A)}{[Ru(NO)_2(PPh_3)_2]} + 2\ PhCH_2Br \xrightarrow{CO} \underset{(B)}{[RuBr(CO)(NO)(PPh_3)_2]} + \underset{(C)}{[RuBr_2(CO)_2(PPh_3)_2]} + \text{organic products}$$

	(A) under CO								(A) under C_2H_4	$PhCH_2Br+NO$[a]	
	65 °C	90 °C					110 °C		110 °C	80 °C	110 °C
Organic products (%)	20 h	1 h	2 h	6 h	23 h	30 h	20 h	48 h	20 h	19 h	48 h
$PhCH_2Br$	96·0	94·8	79·7	53·8	39·4	39·7	19·1	—	—	91·5	40·0
PhCH=NOH	—	1·4	14·5	36·2	37·0	35·9	4·1	9·0	—	—	—
PhCN	0·4	2·8	4·2	6·3	10·0	9·5	54·0	17·2	14·2	0·4	0·4
$PhCONH_2$	—	—	—	—	—	1·7	9·2	77·0	4·9	—	—
PhCHO	0·8	0·7	1·1	1·5	5·8	5·7	7·2	5·4	2·0	1·8	3·5
$PhCH_2OH$	0·9	0·3	0·5	2·1	7·8	8·3	5·2	—	—	2·4	9·2
$(PhCH_2)_2$	—	—	—	—	—	—	—	—	8·2	0·1	—
$PhCH_2NO_2$	—	—	—	—	—	—	—	—	—	1·8	45·1
(A) : (B) : (C)[c]	—	4:1:0	4:2:1	1:1·5:4	0:0:1	0:0:1	—	0:0:1	d	—	—

[a] In the absence of (A). [b] Ratio of (A) to $PhCH_2Br$ 1:1. [c] Ratio of organometallic products. [d] Products are $[RuBr_2(NCPh)_2(PPh_3)_2]$ and $[RuBr_3(NO)(PPh_3)_2]$.

If the reaction is carried out under N_2 or C_2H_4 instead of CO, the yield of free organonitrogen compounds is greatly reduced and some bibenzyl is also formed, but the total nitrogen content of the system can be accounted for by the isolation of $[RuBr_2(NCPh)_2(PPh_3)_2]$ and $[RuBr_3(NO)(PPh_3)_2]$. In the absence of ruthenium compounds, $PhCH_2Br$ reacts less efficiently with NO in toluene (Table) to give $PhCH_2NO_2$ as the main organonitrogen compound, a species not detected in the other reactions reported herein. We have also established that $[Ru(NO)_2(PPh_3)_2]$ does not react with CO in hot toluene and that, in the absence of ruthenium compounds, NO does not react with toluene.

A plausible overall explanation for this reaction may involve the formation of ruthenium-co-ordinated PhCH:NOH [derived presumably by tautomerisation of a species containing $[Ru{-}N(:O)CH_2Ph]$. This oxime could either be displaced by CO {leading to $[RuBr(CO)(NO)(PPh_3)_2]$ and/or $[RuBr_2(CO)_2(PPh_3)_2]$} or undergo dehydration to give compounds containing the group Ru–NCPh.[3] The isolation of $[RuBr_2(NCPh)_2(PPh_3)_2]$ is consistent with this view, and nitrile may be displaced from this complex by CO, giving $[RuBr_2(CO)_2(PPh_3)_2]$. Hydration of nitrile could occur,[4] the water originating from dehydration of the oxime, perhaps with participation of ruthenium complexes, to give $PhCONH_2$; in view of the relative rates of appearance of the various organonitrogen products, it seems unlikely that $PhCONH_2$ arises from a metal-catalysed Beckmann rearrangement of PhCH:NOH.[3] Benzaldehyde and benzyl alcohol probably are formed by hydrolysis of PhCH:NOH and $PhCH_2Br$ respectively.

It was observed that the distribution of products, and the rate of their formation, was not changed by addition of dibenzoyl peroxide. Furthermore, organonitrogen compounds were not produced when $[Ru(NO)_2(PPh_3)_2]$ was photolysed in the presence of $(PhCO)_2$. These results suggest that a radical pathway is not a major route to the benzylation of NO in this system.

It may be noted that other ruthenium dinitrosyls, *e.g.* $[Ru(NO)_2\{P(OPh)_3\}_2]$ and $[Ru(NO)_2(Ph_2PCH_2CH_2PPh_2)]$, and $[Co(NO)(PR_3)_3]$ (R = Ph or OEt), $[Rh(NO)(PPh_3)_3]$, and $[RhCl_2(NO)(PPh_3)_2]$ also may be denitrosylated by benzyl bromide but the yields of organonitrogen products are significantly lower than in the reaction with $[Ru(NO)_2(PPh_3)_2]$. Finally, denitrosylation of $[Ru(NO)_2(PPh_3)_2]$ was observed also with $PhCH_2Cl$, $PhCH_2CH_2Br$, and EtBr, but not with PhMeCHBr.

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† $PhCH_2Br$ was chosen as a model substrate since it can presumably form $PhCH_2NO$ which, in turn, may tautomerise to the readily characterised oxime, PhCH:NOH.

‡ Procedures involved a combination of g.l.c., i.r. and ^1H n.m.r. spectroscopy, and mass spectrometry.

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