Isocyanide Complexes of Zerovalent Ruthenium. Proton Addition to a Transition-metal Base offering Alternative Base Sites

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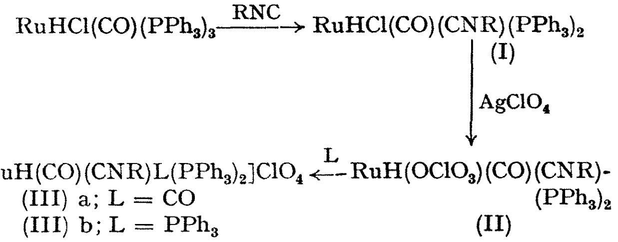
Summary $Ru(CO)_2(CNR)(PPh_3)_2$, $Ru(CO)(CNR)(PPh_3)_3$, and the dioxygen complex $Ru(O_2)(CO)(CNR)(PPh_3)_2$, ($R = p$-tolyl) have been prepared by the action of bases on $[RuH(CO)_2(CNR)(PPh_3)_2]^+$ and $[RuH(CO)(CNR)(PPh_3)_3]^+$; protonation of $Ru(CO)_2(CNR)(PPh_3)_2$ occurs specifically *trans* to isocyanide.

WE have examined isocyanide complexes of zerovalent ruthenium in order to compare their chemistry with that of the related carbonyl compounds. Since $Ru(CO)_3(PPh_3)_2$[1] is very inert to further substitution, direct replacement of a carbonyl group by an isocyanide is a poor route to the required compounds and attempted reductions of $RuCl_2(CNR)_2(PPh_3)_2$[2] have also failed. We have now found a successful approach involving formal deprotonation of ruthenium(II) hydrido-cations which already incorporate the isocyanide ligand. This has a marked experimental advantage in that the very reactive products are obtained in a final step which can be carried out in ethanol, a solvent from which the products crystallise immediately upon formation. The scheme we have utilised for the preparation of the hydrido-cations is as follows:



$$\begin{tikzcd}
RuHCl(CO)(PPh_3)_3 \arrow[r, "RNC"] & RuHCl(CO)(CNR)(PPh_3)_2 \text{ (I)} \arrow[d, "AgClO_4"] \\
{[RuH(CO)(CNR)L(PPh_3)_2]ClO_4} & RuH(OClO_3)(CO)(CNR)(PPh_3)_2 \text{ (II)} \arrow[l, "L"']
\end{tikzcd}$$

(III) a; L = CO
(III) b; L = PPh_3

Compound (II) is unusual in having co-ordinated perchlorate as a ligand, but this is readily displaced by carbon monoxide and triphenylphosphine producing (IIIa) and (IIIb), respectively. That compounds (I), (II), and (III) all have a *trans*-arrangement of phosphines is shown by their ^1H n.m.r. spectra, which have a high-field triplet due to the single hydrogen on the ruthenium coupling with two equivalent phosphorus atoms (see Table). The i.r. spectrum of (IIIa) indicates a *cis*-arrangement of carbonyl groups (see Table) and the ^1H n.m.r. spectrum of (IIIb) shows a doublet of triplets due to a third phosphine *trans* to hydrogen. Thus the stereochemistries of (IIIa) and (IIIb) are completely determined.

The action of sodium hydroxide upon an ethanol solution of (IIIa) produces bright yellow crystals of $Ru(CO)_2(CNR)(PPh_3)_2$ (IV).

Since this reaction is not fast, it seems that the mechanism must be more complicated than proton transfer, and hydroxy- or alkoxy-intermediates of the type $RuH(OH)(CO)(CNR)(PPh_3)_2$ or $RuH(OEt)(CO)(CNR)(PPh_3)_2$ are likely. The zerovalent complex would result from elimination of water or ethanol, followed by co-ordination of carbon monoxide. There is support for an alkoxy-intermediate in that dihydrides, *e.g.* $RuH_2(CO)(PPh_3)_3$, are occasionally produced under these same experimental conditions and among the related osmium compounds it has been possible to isolate $OsH(OEt)(CO)(CNR)(PPh_3)_2$.[3] The yellow compound, $Ru(CO)_2(CNR)(PPh_3)_2$ is presumably of the same geometry as $Ru(CO)_3(PPh_3)_2$ and $Os(CO)_3(PPh_3)_2$[4] with an isocyanide replacing one equatorial carbonyl group. The observed i.r. spectrum, showing two carbonyl bands of equal intensity (see Table) is compatible with this structure. Reaction of $Ru(CO)_2(CNR)(PPh_3)_2$ with dioxygen results in the oxidation of one carbonyl group and the formation of $Ru(CO_3)(CO)(CNR)(PPh_3)_2$, (VII).

When $Ru(CO)_2(CNR)(PPh_3)_2$ is reprotonated *e.g.* with

Physical properties of ruthenium isocyanide complexes[a]

		$\nu(CO)(cm^{-1})$[b]	$\nu(CN)(cm^{-1})$[b]	^1H n.m.r.[c] τ	^1H n.m.r.[c] J(P–H)(Hz)
(I)	$RuHCl(CO)(CNR)(PPh_3)_2$	1935(s) 1922(s)	2140(s)	15·5	19[e]
(II)	$RuH(OClO_3)(CO)(CNR)(PPh_3)_2$[d]	1947(s)	2184(s)	15·4	18[e]
(IIIa)	*cis*-$[RuH(CO)_2(CNR)(PPh_3)_2]^+$	2085(s), 2045(s)	2205(m)	16·0	17[e]
(IIIc)	*trans*-$[RuH(CO)_2(CNR)(PPh_3)_2]^+$	2122(w), 2045(s)	2213(m)	17·3	14[e]
(IIIb)	$[RuH(CO)(CNR)(PPh_3)_3]^+$	1990(s)	2170(s)	18·3	23[e], 72[f]
(IV)	$Ru(CO)_2(CNR)(PPh_3)_2$	1899(s) 1865(s)	2062(m) 2042(m)		
(V)	$Ru(CO)(CNR)(PPh_3)_3$	1901(s)	2090(s)		
(VI)	$Ru(O_2)(CO)(CNR)(PPh_3)_2$[g]	1920(s)	2115(s)		
(VII)	$Ru(CO_3)(CO)(CNR)(PPh_3)_2$	1950(s)	2130(s)		

[a] Satisfactory elemental analyses have been obtained for all compounds reported. They are colourless, except for (IV) (yellow), (V) (orange), and (VI) (pale yellow).
[b] Recorded as Nujol mulls.
[c] In $CDCl_3$ relative to Me_4Si.
[d] I.r. bands for co-ordinated perchlorate at 1115(s), 1050(s) cm^{-1}.
[e] *cis* P-coupling.
[f] *trans* P-coupling.
[g] $\nu Ru{-}O_2$ at 838 cm^{-1}.

perchloric acid, the hydrido-cation produced is of different geometry from that used in its preparation. The i.r. and n.m.r. data (see Table) suggest that the new hydrido-cation has *trans*-carbonyl groups, and upon heating in ethanol solution it isomerizes to the original cation with *cis*-carbonyl groups. Protonation occurs specifically at a site *trans* to the isocyanide ligand and not *trans* to a carbonyl. This appears to be the first instance of proton addition to a transition-metal base[5] where more than one base site presents itself and where it is possible to isolate more than one geometrical isomer of the resulting hydride species. The fact that protonation occurs *trans* to isocyanide may be a consequence of the bonding demands of this ligand since it is known to be a better σ-donor and weaker π-acceptor than carbon monoxide.[6]

The action of sodium hydroxide upon (IIIb) produces orange crystals of $Ru(CO)(CNR)(PPh_3)_3$, (V). Again the reaction is slow and is likely to involve the co-ordinatively unsaturated intermediate, $Ru(CO)(CNR)(PPh_3)_2$ resulting from elimination of ethanol from $RuH(OEt)(CO)(CNR)(PPh_3)_2$. If the reaction is carried out in the presence of dioxygen, the complex, $Ru(O_2)(CO)(CNR)(PPh_3)_2$, (VI) results. Complex (VI) also results from reaction of $Ru(CO)(CNR)(PPh_3)_3$ with dioxygen in benzene, but in chloroform $RuCl_2(CO)(CNR)(PPh_3)_2$ is formed. Both ν(CO) and ν(CN) for $Ru(CO)(CNR)(PPh_3)_3$ are higher than the corresponding absorptions for $Ru(CO)_2(CNR)(PPh_3)_2$ and we take this to indicate a *trans*-arrangement of carbonyl and isocyanides leaving the three phosphines at equatorial sites in a trigonal bipyramid. Crystal structure determinations of other related tris-phosphine complexes, *e.g.* $RhH(CO)(PPh_3)_3$,[7] $[IrH(NO)(PPh_3)_3]^+$,[8] and $RuH(NO)(PPh_3)_3$[9] all reveal equatorial phosphine arrangements, perhaps for steric reasons.

The compound (VI), when heated with triphenylphosphine, produces triphenylphosphine oxide and $Ru(CO)(CNR)(PPh_3)_3$, and like $Ru(O_2)(NCS)(NO)(PPh_3)_2$,[10] it functions as a catalyst for this oxidation.

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