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Preliminary communication

NEUTRAL, CATIONIC, AND DICATIONIC RUTHENIUM(II) COMPLEXES OF THE SECONDARY CARBENES $CHNH(p\text{-}C_6H_4CH_3)$ AND $CHN(CH_3)(p\text{-}C_6H_4CH_3)$

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Summary

The formimidoyl complex, $Ru(CH{=}NR)(O_2CCH_3)(CO)(PPh_3)_2$ (R = *p*-tolyl) is converted to neutral, cationic, and dicationic compounds containing the coordinated secondary carbenes CHNHR and $CHN(CH_3)R$ by protonation and methylation respectively.

Carbene complexes with a hydrogen atom bound to the carbene carbon have been named secondary carbene complexes [1]. Well characterised examples of this type of complex are few in number but are represented by the chelate complexes of Mo^{II}, Mn^{I}, and Fe^{II} containing the system $MCHN(CH_3)BH_2N(CH_3)CH$ [2], and various complexes of chromium, iron, rhodium and platinum derived from oxidative addition of chloroform-iminium chlorides [1]. The ruthenium(II) formimidoyl complex $Ru(CH{=}NR)(O_2CCH_3)(CO)(PPh_3)_2$ (I), (R = *p*-tolyl) which we have described from the reaction of $Ru(O_2)(CO)(CNR)(PPh_3)_2$ with ethanol [3] is a suitable precursor for the synthesis of a variety of secondary carbene complexes.

A high-yield preparation of the formimidoyl compound I which avoids isolation of the dioxygen complex was devised as follows:

$$\begin{tikzcd}
RuH_2(PPh_3)_4 \arrow[r, "CNR"] & RuH_2(CNR)(PPh_3)_3 \arrow[d, "CH_3CO_2H"] \\
Ru(CH{=}NR)(O_2CCH_3)(CO)(PPh_3)_2 & RuH(O_2CCH_3)(CNR)(PPh_3)_2 \arrow[l, "CO"']
\end{tikzcd}$$

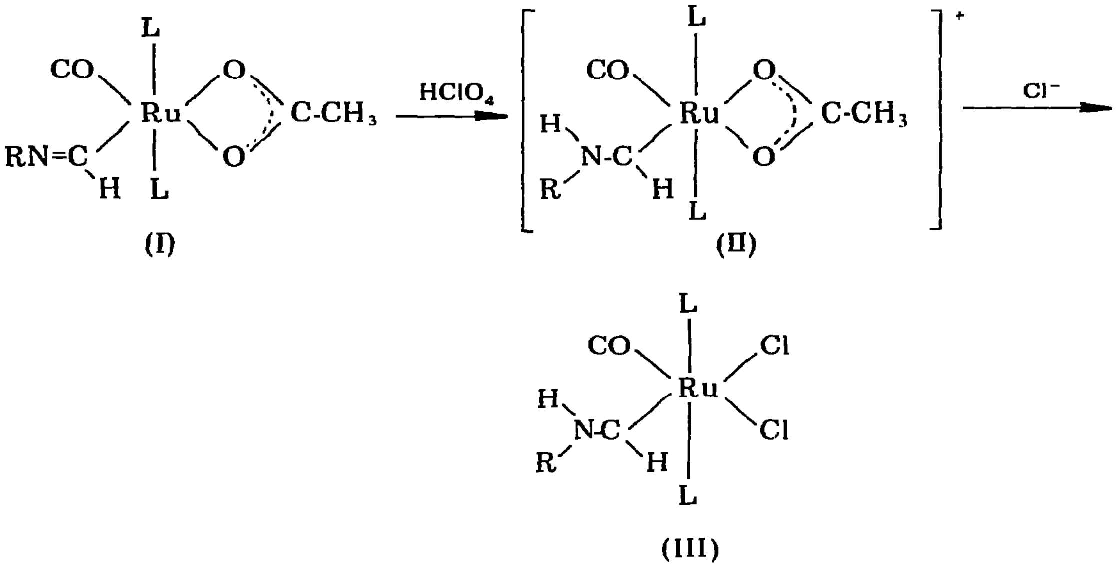
Protonation of I with acids which have non-coordinating anions e.g. $HClO_4$ produces cation II containing CHNHR and retaining the chelate acetate group according to Scheme 1. Reaction of I directly with HCl or of II with LiCl yields a neutral species III.

TABLE 1

INFRARED DATA FOR RUTHENIUM(II) SECONDARY CARBENE COMPLEXES

	Compounds [a,b]	ν(CN) [c] (cm^{-1})	ν(CN) [d] (cm^{-1})	ν(CO)(cm^{-1})	ν(NH)(cm^{-1})
II	$[Ru(CHNHR)(O_2CCH_3)(CO)(PPh_3)_2]^+$	—	1550s	1970vs	3200m
IV	$[Ru(CHN(CH_3)R)(O_2CR)(CO)(PPh_3)_2]^+$	—	1542m	1960vs	—
III	$RuCl_2(CHNHR)(CO)(PPh_3)_2$	—	1540m	1980s, 1960vs [e]	—
V	$RuCl_2(CHN(CH_3)R)(CO)(PPh_3)_2$	—	1505m	1968vs, 1950vs [f]	—
VI	$[Ru(O_2CCH_3)(CO)(CNR)(CHNHR)(PPh_3)_2]^+$	2165vs	1545s	1985vs	—
VII	$[Ru(OClO_3)(CO)(CNR)(CHNHR)(PPh_3)_2]^+$	2180vs	1550m	2030vs	3200m
VIII	$[Ru(CO)_2(CNR)(CHNHR)(PPh_3)_2]^{2+}$	2200s	1560m	2100vs, 2070vs	—
IX	$[Ru(CO)(CNR)_2(CHNHR)(PPh_3)_2]^{2+}$	2205s, 2175vs	1552m	2050vs	—

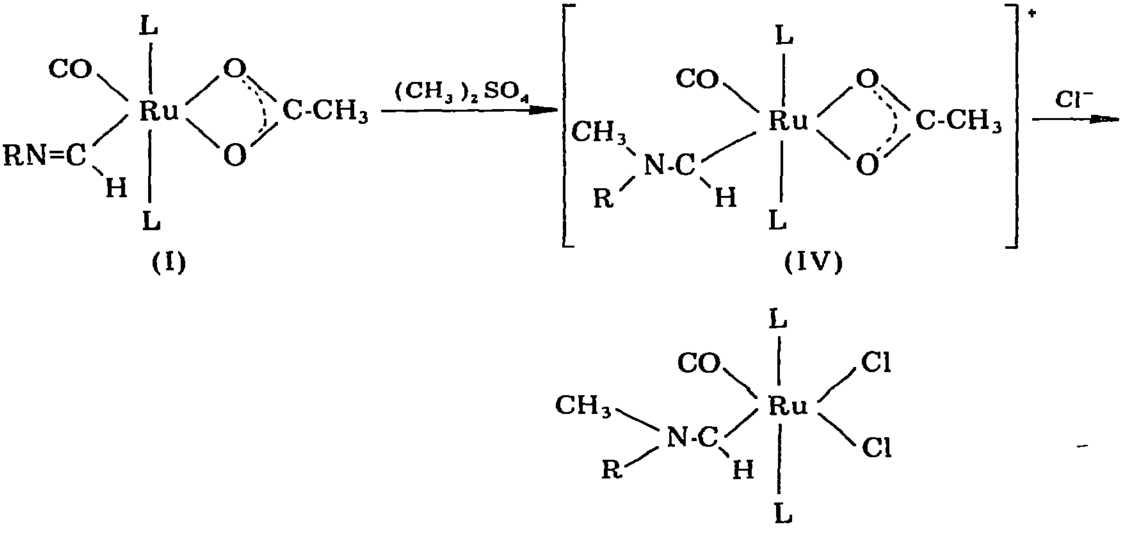
[a] All compounds are colourless. Cations were isolated as perchlorate salts and all compounds characterised by IR and NMR spectroscopy, and by elemental analyses. [b] Measured as nujol mulls. [c] CNR. [d] Carbene ligand. [e] Singlet in CH_2Cl_2, 1970vs. [f] Singlet in CH_2Cl_2, 1060vs.



Scheme 1 (L = PPh_3)

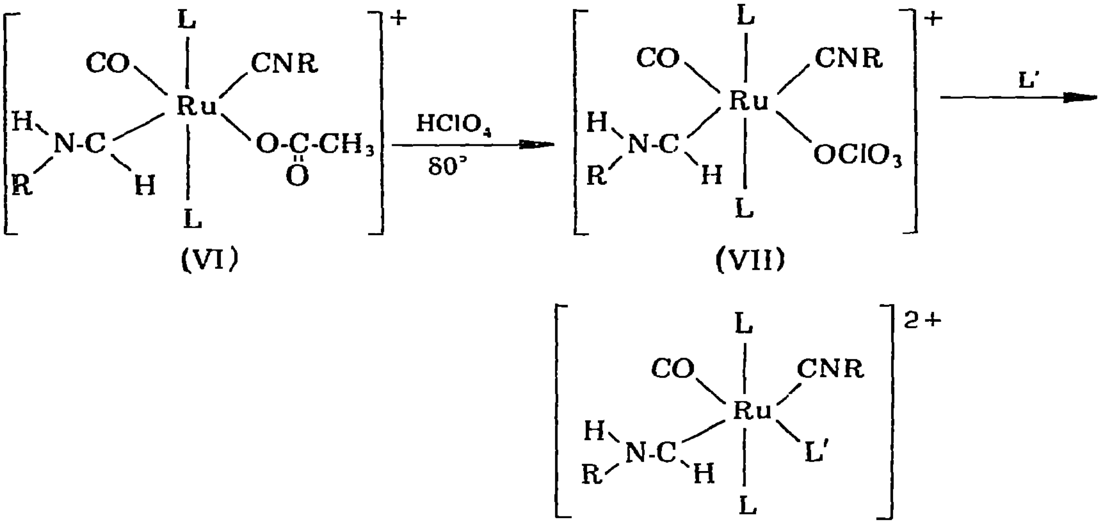
The ^{1}H NMR spectra of these derivatives all show the C_{carb}—H at low-field (τ, 0.15 to −1.2) coupling with N—H (τ, −1.1 to −6.4) J(H—H) (17—21 Hz).

The formimidoyl group is also readily methylated by dimethyl sulphate to form the corresponding complexes containing $CHN(CH_3)R$ (Scheme 2); see Table 1 for IR data.



Scheme 2 (L = PPh_3)

The chelating acetate ligand in the cation II (or IV) is opened by reaction with further CNR producing VI and the monodentate acetate in this cation is resistant to further direct substitution by CO or CNR but is cleaved by $HClO_4$ to an unusual perchlorato-cation VII. This perchlorato-cation reacts readily with CO or CNR producing the dicationic species VIII and IX (Scheme 3).



(VIII)(L' = CO)
(IX) (L' = CNR)

Scheme 3 (L = PPh$_3$)

All of the secondary carbene complexes reported here have ν(CN) (carbene ligand) at approx. 1550 cm^{-1} (see Table 1). This high value, together with the C_{carb}—H ^{1}H NMR signal at very low-field suggests a particularly high bond order for the C—N bond within the secondary carbene ligand.

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