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Preliminary Communication

A *dihapto*-IMINOACYL DERIVATIVE OF RUTHENIUM(II). SYNTHESIS AND STRUCTURE OF $Ru[\eta^2\text{-}C(NR)R]Cl(CO)(PPh_3)_2$

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SUMMARY

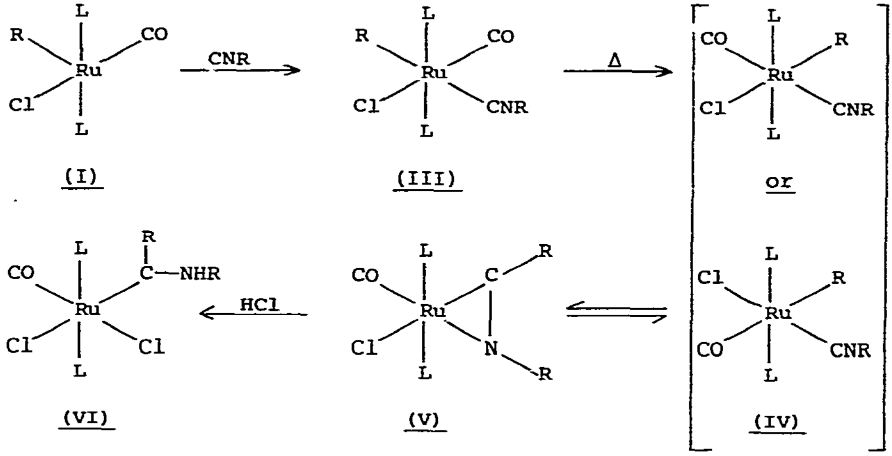
The ruthenium iminoacyl complex, $Ru[C(NR)R]Cl(CO(PPh_3)_2$, (R = *p*-tolyl), which results from a migratory-insertion rearrangement of $RuRCl(CO)(CNR)(PPh_3)_2$ is shown by X-ray crystal structure analysis to contain the iminoacyl ligand attached to ruthenium through C and N in an almost symmetrical manner.

We recently reported the five co-ordinate ruthenium(II) aryl, $RuRX(CO)(PPh_3)_2$, I, and the further reaction with CO to form $RuRX(CO)_2(PPh_3)_2$, II, (ref. 1). A solution of II was shown to be in equilibrium with the acyl-derivative $Ru[C(O)R]X(CO)(PPh_3)_2$ for which a *dihapto*-arrangement of the acyl group was suggested. In an extension of this work we describe here reaction of I with CNR and the ensuing migratory-insertion reaction to yield $Ru[C(NR)R]X(CO)(PPh_3)_2$.

I, (X = Cl), reacts rapidly with CNR to form the colourless octahedral complex $RuRCl(CO)(CNR)(PPh_3)_2$ for which the most likely geometry, based on the known geometry of I, is III (see Scheme). When a solution of III in dichloromethane is heated under reflux the solution becomes orange and the orange crystalline product, V, has no isocyanide ν_{CN} band in the I.R. spectrum but instead has a band at 1654 cm^{-1} appropriate for an iminoacyl ligand (see Table for other I.R. data).

A dichloromethane solution of V is in equilibrium with a very small amount of a compound having ν_{CO} and ν_{CN} close to but not identical with those of compound III. This must be one of the two possible isomers of III with *cis* R and CNR ligands, IV.

Compound V does not have the intense colour of other five co-ordinate Ru(II) complexes nor does it readily react with further CO or CNR. It therefore seemed likely that the iminoacyl ligand was occupying two co-ordination sites as has been demonstrated for the iminoacyl ligand in the molybdenum complex, $Mo[\eta^2\text{-}C(NC_6H_5)CH_3](\eta^5\text{-}C_5H_5)(CO)_2$ (ref. 2). Confirmation was sought through an X-ray structure determination.



SCHEME: (L = PPh_3; R = *p*-tolyl)

TABLE: I.R. data for ruthenium(II) complexes

Compound[a]	ν_{CO}[b] (cm^{-1})	ν_{CN}[b] (cm^{-1})
$RuRCl(CO)(CNR)(PPh_3)_2$ III	1948	2125
$RuRCl(CO)(CNR)(PPh_3)_2$ IV	1970	2145
$Ru[\eta^2\text{-}C(NR)R]Cl(CO)(PPh_3)_2$ V	1902	1654
$RuCl_2[C(NHR)R](CO)(PPh_3)_2$ VI	1975	1510

[a] All compounds have satisfactory elemental analyses and ^1H N.M.R. data consistent with formulations given.

[b] Nujol mulls

$Ru[\eta^2\text{-}C(NR)R]Cl(CO)(PPh_3)_2$ crystallizes in the monoclinic system with a = 12.769(8), b = 23.938(2), c = 14.825(2) Å, β = 104.182(6)°, Z = 4, space group $P2_1/c$. Intensity data were collected on a Hilger-Watts four-circle diffractometer using Cu-K_α radiation and a total of 3688 unique reflections with $I > 3\sigma(I)$ were recorded. The structure was solved by Patterson and Fourier methods and has been refined to R = 0.052 based on a disordered model. Full details will be published separately.

The figure shows the co-ordination geometry with the iminoacyl-group bound as a *dihapto*-ligand. The Ru-C(2) and Ru-N distances are 2.031(8) and 2.123(7) Å respectively; the C(2)-N bond length of 1.30(1) Å is indistinguishable from an unco-ordinated CN double bond. The angles C(2)-N-C(4) and N-C(2)-C(3) have been

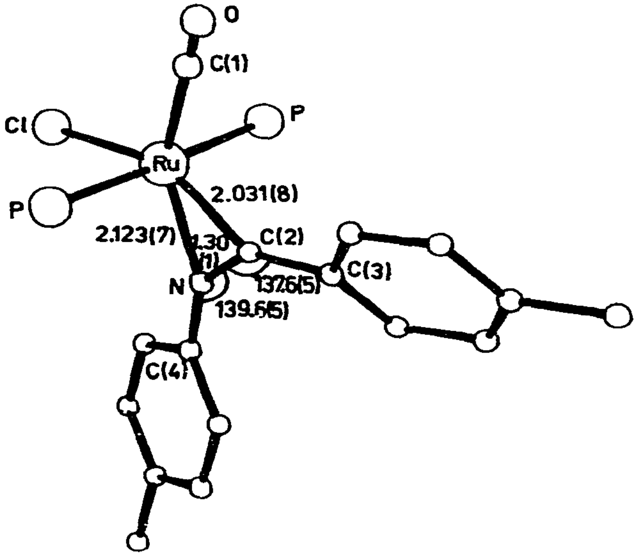


FIGURE: Co-ordination geometry of Ru[η^2-C(NR)R]Cl(CO)(PPh_3)$_2$

increased from those expected for a *monohapto*-iminoacyl ligand to 139.6(5) and 137.6(5) respectively as was also found in the similar complex Mo[η^2-C(NC_6H_5)CH_3](η^5-C_5H_5)$(CO)_2$ (ref. 2).

The nitrogen atom of the *dihapto*-iminoacyl ligand is not readily alkylated, even with methyl triflate, but is rapidly protonated and reaction with HCl gives the amino-carbene complex, $RuCl_2$[C(NHR)R](CO)(PPh_3)$_2$,VI.

REFERENCES

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