Journal of Organometallic Chemistry, 142 (1977) C1—C6

Preliminary Communication

FIVE AND SIX CO-ORDINATE σ-ARYL DERIVATIVES OF Ru(II) AND Os(II) AND THE EQUILIBRIUM $RuRX(CO)_2(PPh_3)_2 \rightleftharpoons Ru[C(O)R]X(CO)(PPh_3)_2$

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(Received September 27th, 1977)

Summary

Reaction of $MHCl(CO)(PPh_3)_3$ (M = Ru or Os) with HgR_2 (R = *p*-tolyl) yields red, five co-ordinate, $MRCl(CO)(PPh_3)_2$, (square pyramidal, R apical) and Hg; uptake of CO gives colourless $MRCl(CO)_2(PPh_3)_2$ and in CH_2Cl_2 the ruthenium dicarbonyl complex is in equilibrium with the acyl derivative, $Ru[C(O)R]Cl(CO)(PPh_3)_2$, for which evidence suggests a possible *dihapto*-acyl ligand.

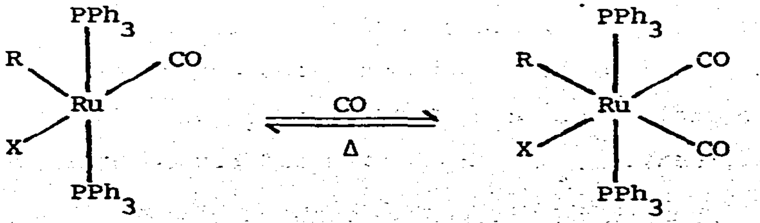
The preparation and structure of a five co-ordinate Ru(II) σ-aryl derivative from orthometallation of a N,N^1-di-arylimidazolidin-2-ylidene ligand has recently been reported[1] but no simple co-ordinatively unsaturated aryls of Ru(II) or Os(II) are known although related hydrido-compounds exist, e.g. $RuHCl(PPh_3)_3$ [2] and $OsHCl(CO)[P(c\text{-hexyl})_3]_2$. [3] Both five and six co-ordinate alkyl and acyl compounds of rhodium(III) and iridium(III) are well-known.[4,5] We report here a high yield route to five co-ordinate σ-aryl compounds through reaction of $MHCl(CO)(PPh_3)_3$ (M = Ru, Os) with HgR_2 (R = *p*-tolyl).

Reaction between $MHCl(CO)(PPh_3)_3$ and HgR_2 proceeds smoothly in toluene under reflux, depositing Hg and forming a deep red solution from which can be isolated red crystals of $MRCl(CO)(PPh_3)_2$ in approximately 95% yield.

$$MHCl(CO)(PPh_3)_3 + HgR_2 \longrightarrow MRCl(CO)(PPh_3)_2 + PPh_3 + Hg + RH$$

HgRCl is also an effective reagent for the preparation of $RuRCl(CO)(PPh_3)_2$ but not for $OsRCl(CO)(PPh_3)_2$. Other derivatives with X = Br or I are formed by reaction with $AgClO_4$ followed by NaX. Like other five co-ordinate compounds of Ru(II) and Os(II),[6] square pyramidal geometry is expected and this has been confirmed for $RuRCl(CO)(PPh_3)_2$ by x-ray crystal structure determination.[7] The R group is apical and the phosphine ligands mutually *trans*.

Red solutions of $MRX(CO)(PPh_3)_2$ (X = Cl, Br, I) are immediately decolourised by CO forming octahedral $MRX(CO)_2(PPh_3)_2$ with *cis* carbonyl ligands, (see Table for I.R. data). For the ruthenium compounds this CO uptake is reversible and heating in benzene under reflux returns $RuRX(CO)(PPh_3)_2$.



$OsRCl(CO)_2(PPh_3)_2$ does not readily undergo a migratory-insertion reaction and may be recovered unchanged after 24 hours heating under reflux in toluene. Also the solution I.R. spectrum in CH_2Cl_2 does not change after three days heating under reflux. In marked contrast, solution spectra of $RuRX(CO)_2(PPh_3)_2$ in CH_2Cl_2 indicate that the dicarbonyl is in equilibrium with the monocarbonyl-acyl, $Ru[C(O)R]X(CO)(PPh_3)_2$ in almost equal amounts. The acyl form is favoured for $X = I > Br > Cl$. Solubility differences and a rapid rate of interconversion make it possible to isolate crystalline samples of almost pure aryl-dicarbonyl for X = Cl and almost pure acyl-monocarbonyl for X = I. When either pure solid $RuRCl(CO)_2(PPh_3)_2$ or pure solid $Ru[C(O)R]I(CO)(PPh_3)_2$ is redissolved in CH_2Cl_2, the solution I.R. spectra reveal that equilibrium between aryl and acyl is immediately established. I.R. data (see Table) show that the acyl ν_{CO} occurs at 1550 cm^{-1} which is much lower than typical *monohapto*-acyl ligands but is exactly where ν_{CO} occurs for a structurally verified *dihapto*-acyl in $Zr(\eta^5-C_5H_5)[\eta^2-C(O)Me]Me$.[8] The approximately octahedral co-ordination which would result from a *dihapto*-acyl ligand is also in keeping with the very pale colour of the acyl compound compared with the dark red of the five co-ordinate aryl, $RuRCl(CO)(PPh_3)_2$.

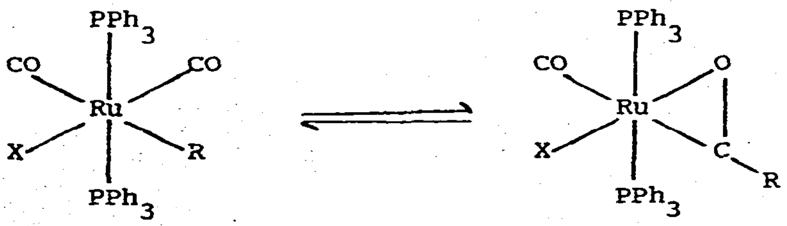


TABLE PHYSICAL PROPERTIES OF Ru(II) AND Os(II) σ-ARYL DERIVATIVES

Compound [a]	Colour	ν_{CO} [b] (cm^{-1})	Other I.R. bands
$RuRCl(CO)(PPh_3)_2$	Red	1923	
$RuRCl(CO)_2(PPh_3)_2$	Colourless	2055, 1952	
$Ru[C(O)R]I(CO)(PPh_3)_2$	Pale yellow	1905	ν_{CO}(Acyl), 1550
$OsRCl(CO)(PPh_3)_2$	Red	1906	
$OsRCl(CO)_2(PPh_3)_2$	Colourless	2025, 1935	

[a] All compounds have satisfactory elemental analyses.

[b] Nujol mulls.

Other *dihapto*-acyl derivatives of Ru(II) have been claimed previously [9] but the physical properties reported for these compounds are identical with those of the corresponding *dihapto*-carboxylates [10] and in the absence of confirming structural information, the existence of these acyl compounds must be regarded as doubtful.

Methyl derivatives of Ru(II) also undergo conversion to acetyl compounds although no *dihapto*-acetyl has been suggested for this system [11] or for the related Rh(III) system.[12]

We thank the New Zealand Universities Grants Committee for grants towards instrumental facilities and the award of a Postgraduate Scholarship to L.J.W.

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