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Preliminary communication

ALKOXIDE ATTACK AT CARBONYL AND HYDROSULPHIDE ATTACK AT ISOCYANIDE IN THE MIXED CARBONYL-ISOCYANIDE CATION $[OsCl(CO)_2(CNR)(PPh_3)_2]^+$. A NEW SYNTHESIS OF π-BOUND ISOTHIOCYANATE (RNCS) COMPLEXES

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Summary

$[OsCl(CO)_2(CNR)(PPh_3)_2]^+$ (R = *p*-tolyl) reacts with OMe^- to give $OsCl(CO_2Me)(CO)(CNR)(PPh_3)_2$ but reaction with SH^- produces the π-bound *p*-tolylisothiocyanate complex, $Os(\eta^2\text{-}SCNR)(CO)_2(PPh_3)_2$, which can be protonated or methylated at N to yield complexes containing bidentate thiocarboxamido-ligands.

Carbonyl and isocyanide ligands both show increased susceptibility to nucleophilic attack when they are coordinated in cationic complexes. However, few studies have been directed towards determining the relative reactivities of these two ligands when in comparable environments, and in a mixed carbonyl-isocyanide complex it is not always possible to predict which ligand will be attacked by a given nucleophile [1].

$OsHCl(CO)(CNR)(PPh_3)_2$ (R = *p*-tolyl) results from reaction of $OsHCl(CO)(PPh_3)_3$ with CNR and further reaction with perchloric acid gives $OsCl(OClO_3)(CO)(CNR)(PPh_3)_2$ which in turn yields the compound $[OsCl(CO)_2(CNR)(PPh_3)_2]ClO_4$ (I) upon carbonylation. I exhibits high values for ν(CO) and ν(CN) (see Table 1) suggesting that this compound may be susceptible to nucleophilic attack at one of the ligands and we report here reactions with alkoxide and hydrosulphide.

I reacts reversibly with basic methanol to form a methoxycarbonyl compound.

$$[OsCl(CO)_2(CNR)(PPh_3)_2]^+ + MeOH \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} OsCl(CO_2Me)(CO)(CNR)(PPh_3)_2$$

$[OsCl(CO)_3(PPh_3)_2]^+$ behaves in a similar fashion [2]. When 2-chloroethanol is employed as the alcohol with triethylamine as the base, the cyclic carbene

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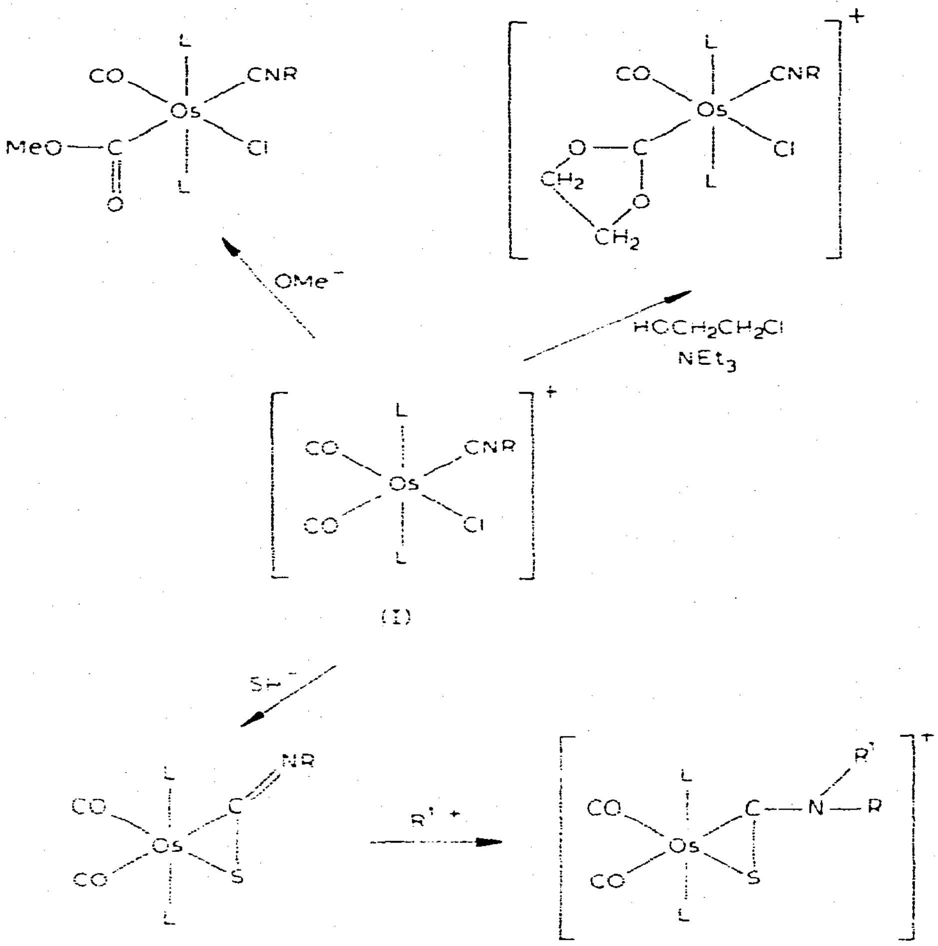
TABLE 1

IR[a] (cm^{-1}) AND ^1H NMR[b] (τ, ppm) DATA FOR OSMIUM ALKOXYCARBONYL, ISOTHIOCYANATE AND THIOCARBOXAMIDO COMPLEXES

Compound[c]	ν(CO) (cm^{-1})	ν(CN) (cm^{-1})	Chemical shifts
$OsHCl(CO)(CNR)(PPh_3)_2$	1920, 1910	2125	14.76 t, J(H—P) 20Hz (Os—H)
$OsCl(OClO_3)(CO)(CNR)(PPh_3)_2$	1955	2160	
$[OsCl(CO)_2(CNR)(PPh_3)_2]^+$	2050, 2000	2225	
$OsCl(CO_2Me)(CO)(CNR)(PPh_3)_2$	1950, 1630	2150	
$[OsCl(\overline{COCH_2CH_2O})(CO)(CNR)(PPh_3)_2]^+$	1995, 1980	2175	6.0s (—OC_2H_4O—)
$Os(\eta^2\text{-}SCNPh)(CO)_2(PPh_3)_2$	2000, 1935	1620, 1600, 1580	
$Os(\eta^2\text{-}SCNR)(CO)_2(PPh_3)_2$	2000, 1935	1625, 1600, 1580	
$[Os(\eta^2\text{-}SCNHR)(CO)_2(PPh_3)_2]^+$	2050, 1975	1550	−2.43s (br) (NH)
$[Os(\eta^2\text{-}SCNMeR)(CO)_2(PPh_3)_2]^+$	2040, 1975	1555	6.6 s (NCH_3)

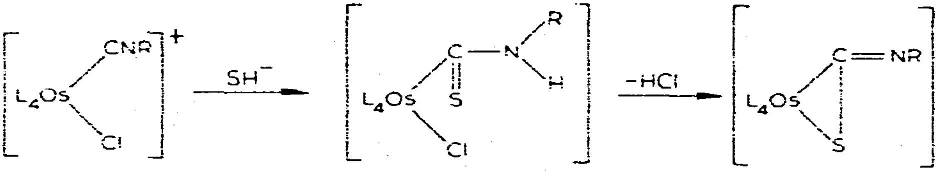
[a] Nujol mulls. [b] $CDCl_3$ solution. [c] All compounds reported have satisfactory elemental analyses. Cations characterised as perchloric salts.



SCHEME 1. Reactions of $[\mathrm{OsCl(CO)_2(CNR)(PPh_3)_2}]^+$ ($L = \mathrm{PPh_3}$, R = *p*-tolyl, R^1 = H or Me; yields in all reactions are high).

complex $[\mathrm{OsCl}(\overline{\mathrm{COCH_2CH_2O}})(\mathrm{CO})(\mathrm{CNR})(\mathrm{PPh_3})_2]\mathrm{ClO_4}$ can be isolated (see Scheme 1). In the ^{1}H NMR spectrum the 1,3-dioxolan-2-ylidene ligand exhibits a singlet at τ 6.0 ppm integrating for four protons. Manganese complexes of this same ligand are known [3] and have been characterised by crystal structure determination of $\mathrm{MnCl}(\overline{\mathrm{COCH_2CH_2O}})(\mathrm{CO})_4$ [3].

In contrast to the above results, reaction of I with hydrosulphide ion results in attack at the isocyanide ligand and formation of $\mathrm{Os}(\eta^2\text{-SCNR})(\mathrm{CO})_2(\mathrm{PPh_3})_2$. This formulation is confirmed by elemental analysis, further reactions, and the IR spectrum (see Table 1) which bears a striking resemblance to that of $\mathrm{Os}(\eta^2\text{-SCNPh})(\mathrm{CO})_2(\mathrm{PPh_3})_2$ prepared directly from $\mathrm{Os(C_2H_4)(CO)_2(PPh_3)_2}$ [4] and phenylisothiocyanate. A possible reaction path involves initial formation of a thiocarboxamido-complex followed by elimination of HCl:



$L_4 = (CO)_2(PPh_3)_2$

In a closely related reaction, SH^- adds to $[Pt(CNMe)_2(PPh_3)_2]^{2+}$ to give a thiocarboxamido-complex [5]. $Os(\eta^2\text{-}SCNR)(CO)_2(PPh_3)_2$ is protonated by perchloric acid forming a bidentate thiocarboxamido complex $[Os(\eta^2\text{-}SCNHR)(CO)_2(PPh_3)_2]ClO_4$. This is readily deprotonated by base. $Os(\eta^2\text{-}SCNR)(CO)(PPh_3)_2$ also reacts with MeI to form $[Os(\eta^2\text{-}SCNMeR)(CO)_2\text{-}(PPh_3)_2]^+$ (see Scheme 1). Other bidentate thiocarboxamido complexes have been characterised by structure determination, e.g. $RhCl(S_2CNMe_2)(SCNMe_2)\text{-}PPh_3$ [6].

Since osmium dithioester complexes have been shown to yield thiocarbonyls on acid hydrolysis [7] we are investigating these thiocarboxamido derivatives as possible thiocarbonyl precursors.

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