

Journal of Organometallic Chemistry, 141 (1977) C5-C9
 © Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary Communication

A FOUR-MEMBERED OSMIUM METALLOCYCLE FROM INTER-LIGAND REACTION BETWEEN THIOCARBOXAMIDO- AND THIOCARBONYL LIGANDS. STRUCTURE OF $\text{Os}(\text{CS}_2\text{CNMeptolyl})\text{H}(\text{CO})(\text{PPh}_3)_2$.

G.R. Clark, T.J. Collins, D. Hall, S.M. James and W.R. Roper*

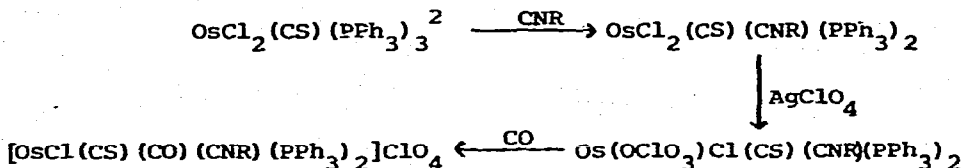
Department of Chemistry, University of Auckland, Auckland (New Zealand)

(Received August 23rd, 1977)

Summary

The thiocarboxamido-thiocarbonyl cation, $[\text{Os}(\eta^2\text{-SCNMeptolyl})(\text{CS})(\text{CO})(\text{PPh}_3)_2]^+$, upon reaction with NaBH_4 , forms $\text{Os}(\text{CS}_2\text{CNMeptolyl})\text{H}(\text{CO})(\text{PPh}_3)_2$ through an inter-ligand reaction; x-ray crystal structure analysis of $\text{Os}(\text{CS}_2\text{CNMeptolyl})\text{H}(\text{CO})(\text{PPh}_3)_2$ confirms the presence of a four-membered metallocycle and further reaction with MeI produces what is formally a chelate di-carbene ligand in $[\text{Os}(\text{C}(\text{SMe})\text{SCNMeptolyl})\text{H}(\text{CO})(\text{PPh}_3)_2]^+$.

We have previously reported that reaction of the mixed carbonyl-isocyanide cation, $[\text{OsCl}(\text{CO})_2(\text{CNR})(\text{PPh}_3)_2]^+$, ($\text{R} = p\text{-tolyl}$), with SH^- produces $\text{Os}(\eta^2\text{-SCNR})(\text{CO})_2(\text{PPh}_3)_2$.¹ Recent developments in the synthesis of thiocarbonyl complexes of osmium² have made it possible to produce a mixed thiocarbonyl-carbonyl-isocyanide cation and it was of interest to determine which ligand is attacked by SH^- in such a cation. $[\text{OsCl}(\text{CS})(\text{CO})(\text{CNR})(\text{PPh}_3)_2]\text{ClO}_4$ was prepared as follows:



I.R. data for these compounds are shown in the Table.

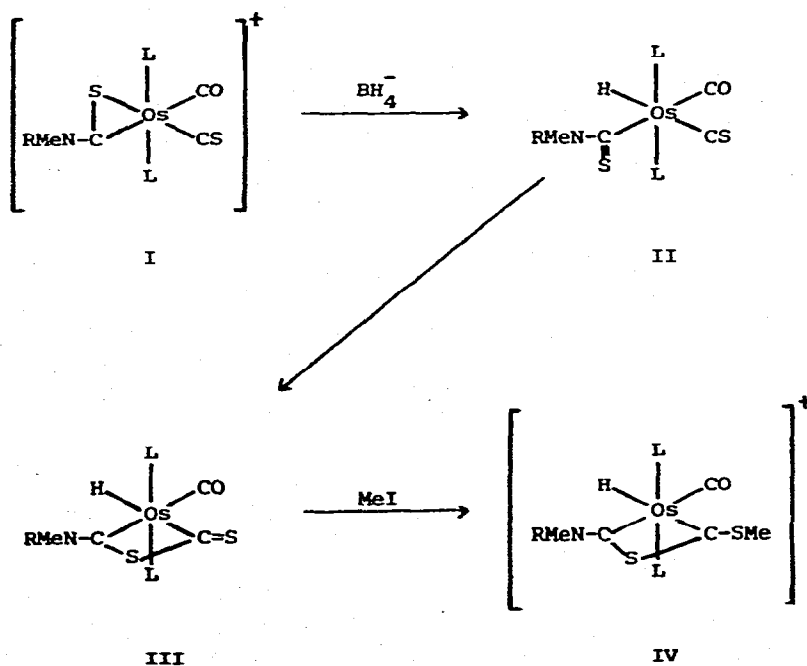
In fact, the reaction of $[\text{OsCl}(\text{CS})(\text{CO})(\text{CNR})(\text{PPh}_3)_2]^+$ with SH^- was complicated and the products showed a solvent dependence. In acetone the product was exclusively $\text{Os}(\eta^2\text{-SCNR})(\text{CS})(\text{CO})(\text{PPh}_3)_2$ but in dichloromethane-ethanol (1:1) the products were $\text{Os}(\eta^2\text{-SCNR})(\text{CS})(\text{CO})(\text{PPh}_3)_2$ (approximately 85%) and $\text{Os}(\eta^2\text{-CS}_2)(\text{CO})(\text{CNR})(\text{PPh}_3)_2$ (approximately 15%) indicating attack by SH^- at both CNR and CS ligands.

The η^2 -*p*-tolylisothiocyanate complex is readily methylated by MeI to form a dihapto-thiocarboxamido-cation, $[\text{Os}(\eta^2\text{-SCNMe})(\text{CS})(\text{CO})(\text{PPh}_3)_2]^+$, (I). The related cations with dihapto-dithioester ligands react with NaBH_4 to form neutral metal hydride complexes with monhapto-dithioester-ligands.³ In expectation of a similar dihapto to monhapto rearrangement, I was reacted with NaBH_4 . The neutral, red, crystalline product was identified as an osmium(II) hydride from ^1H N.M.R. (CDCl_3 , τ , 19.51, triplet, $^2\text{J}(\text{H-P}) = 23.5\text{Hz.}$), but no ν_{CS} band appeared in the I.R. spectrum. Accordingly the anticipated product II (see Scheme) was formulated instead as III with the monhapto-thiocarboxamido- and the thiocarbonyl ligands having combined to form a four-membered metallocycle. Confirmation was sought through x-ray crystal structure determination.

The red crystals of III are orthorhombic, $a = 18.298(1)$, $b = 18.474(7)$, $c = 24.583(2)$ Å, $Z = 8$, space group Pnma . Intensity data were collected on a Hilger-Watts 4-circle diffractometer using Ni-filtered Cu-K_α radiation. A total of 1544 unique reflections with $I > 3\sigma(I)$ were recorded, and

absorption corrections have been applied. The structure was solved by Patterson and Fourier syntheses and has been partially refined by least squares techniques to $R = 0.096$. All atoms heavier than oxygen have been assigned anisotropic thermal parameters. The hydrogen atom bonded to Os has not yet been located. The Figure illustrates the molecular geometry of III as determined, and includes the important bond lengths and angles.

It is interesting that the dithioester analogue of compound II, *viz.* $\text{Os}(\eta^1\text{-CS}_2\text{Me})\text{H}(\text{CS})(\text{CO})(\text{PPh}_3)_2$ does not show this same rearrangement. The increased nucleophilicity of the sulphur atom of a monohapto-thiocarboxamido- compared with a monohapto-dithioester ligand has been noted previously.^{4,5}



Scheme L = PPh_3 , R = *p*-tolyl

Compound ^a	$\nu_{\text{CO}}(\text{cm}^{-1})$ ^b	$\nu_{\text{CS}}(\text{cm}^{-1})$	$\nu_{\text{CN}}(\text{cm}^{-1})$
$\text{OsCl}_2(\text{CS})(\text{CNR})(\text{PPh}_3)_2$	-	1305	2150
$\text{OsCl}(\text{OCIO}_3)(\text{CS})(\text{CNR})(\text{PPh}_3)_2$	-	1310	2160
$[\text{OsCl}(\text{CS})(\text{CO})(\text{CNR})(\text{PPh}_3)_2]^+$	2060	1323	2205
$\text{Os}(\eta^2\text{-SCNR})(\text{CS})(\text{CO})(\text{PPh}_3)_2$	1980	1285	1620, 1570
$\text{Os}(\eta^2\text{-CS}_2)(\text{CO})(\text{CNR})(\text{PPh}_3)_2$	1905	1095, 1070	2120
$[\text{Os}(\eta^2\text{-SCN RMe})(\text{CS})(\text{CO})(\text{PPh}_3)_2]^+$	2040	1308	1540
$\text{Os}(\text{CS}_2\text{CNRMe})\text{H}(\text{CO})(\text{PPh}_3)_2$	1930	1110	1500
$[\text{Os}(\text{CS}_2\text{MeCNRMe})\text{H}(\text{CO})(\text{PPh}_3)_2]^+$	1945	-	1530

^a All compounds have satisfactory elemental analyses and ¹H N.M.R. data consistent with the formulations given. Cations characterised as ClO_4^- or CF_3SO_3^- salts.

^b Nujol mulls, all absorptions quoted are strong.

The *exo*-sulphur atom in III is rapidly methylated by reaction with methyl iodide forming IV in which the ligand is formally a bidentate dicarbene.

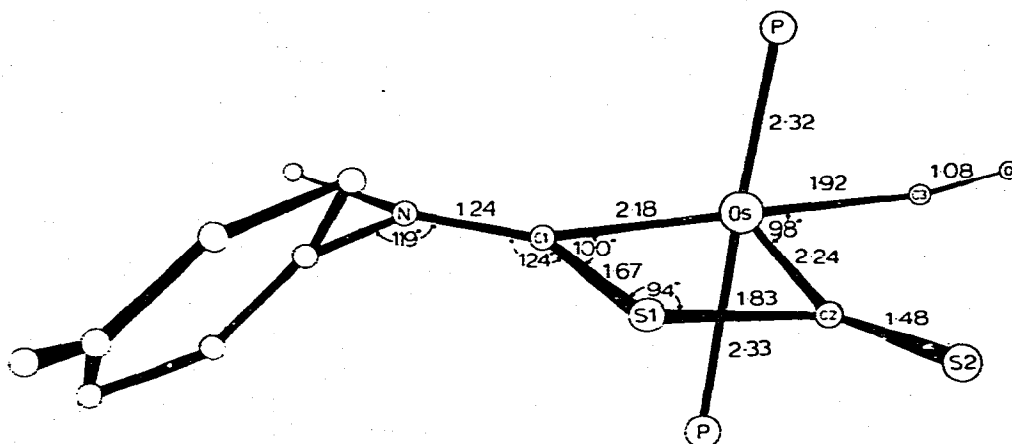


Figure. Structure of $\text{Os}(\text{CS}_2\text{CNMeptolyl})\text{H}(\text{CO})(\text{PPh}_3)_2$

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

References

1. K.R. Grundy and W.R. Roper, J. Organometal. Chem., **113**, (1976), C45.
2. T.J. Collins and W.R. Roper, J. Organometal. Chem., submitted for publication.
3. T.J. Collins, W.R. Roper and K.G. Town, J. Organometal. Chem., **121**, (1976), C41.
4. W.K. Dean, J.B. Wetherington and J.W. Moncrief, Inorg. Chem., **15**, (1976), 1566.
5. G.R. Clark, T.J. Collins, S.M. James and W.R. Roper, J. Organometal. Chem., **125**, (1977), C23.