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Preliminary communication

CYCLIC TRANSITION-METAL CARBENE COMPLEXES FROM RING-CLOSING REACTIONS ON THE π-BOUND SUBSTRATES CS_2 AND CSe_2. 1,3-DITHIOLAN-2-YLIDENE AND 1,3-DISELENOLAN-2-YLIDENE COMPLEXES OF RUTHENIUM(II) AND OSMIUM(II)

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Summary

$Os(CS_2)(CO)_2(PPh_3)_2$, $Os(CS_2)(CO)(CNR)(PPh_3)_2$, $Ru(CS_2)(CO)(CNR)(PPh_3)_2$ and $Ru(CSe_2)(CO)_2(PPh_3)_2$ react with 1,2-dibromoethane to give cationic and neutral 1,3-dithiolan-2-ylidene and 1,3 diselenolan-2-ylidene complexes.

Complexes involving the 1,3-dioxolan-2-ylidene ligand result from intramolecualr cyclisation of the product from $Mn(CO)_5^-$ and 2-chloroethyl chloroformate [1]. We describe here the synthesis of compounds containing sulphur and selenium analogues of the 1,3-dioxolan-2-ylidene ligand. The formation of $[OsI(C[SMe]_2)(CO)_2(PPh_3)_2]^+$ from $Os(CS_2)(CO)_2(PPh_3)_2$ and methyl iodide [2] suggested the possibility that with suitable difunctional alkyl halides, $X(CH_2)_nX$, heterocyclic carbene complexes might result. Accordingly, the reaction of $Ru(CS_2)(CO)(CNR)(PPh_3)_2$ [3], $Ru(CSe_2)(CO)_2(PPh_3)_2$ [4], $Os(CS_2)(CO)_2(PPh_3)_2$ [2], and $Os(CS_2)(CO)(CNR)(PPh_3)_2$ [5] with such reagents was investigated.

$Os(CS_2)(CO)_2(PPh_3)_2$ dissolves on warming in 1,2-dibromoethane to give a pale straw-coloured solution from which can be isolated, after the addition of $NaClO_4$, $[OsBr(\overline{CSCH_2CH_2S})(CO)_2(PPh_3)_2]ClO_4$. The IR spectrum (see Table 1) of this compound exhibits strong ν(CO) bands at 2060 and 1985 cm^{-1} and bands attributable to the cyclic carbene ligand at 955 m and 860 cm^{-1}. Conclusive evidence for ring closure having occurred is derived from the ^1H NMR spectrum (see Table 1) which exhibits a singlet at τ 6.77 ppm for the 4 ring protons. This can be compared with the value of τ 6.00 ppm obtained for the carbene ligand in $[OsCl(\overline{COCH_2CH_2O})(CO)(CNR)(PPh_3)_2]ClO_4$ [5].

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TABLE 1

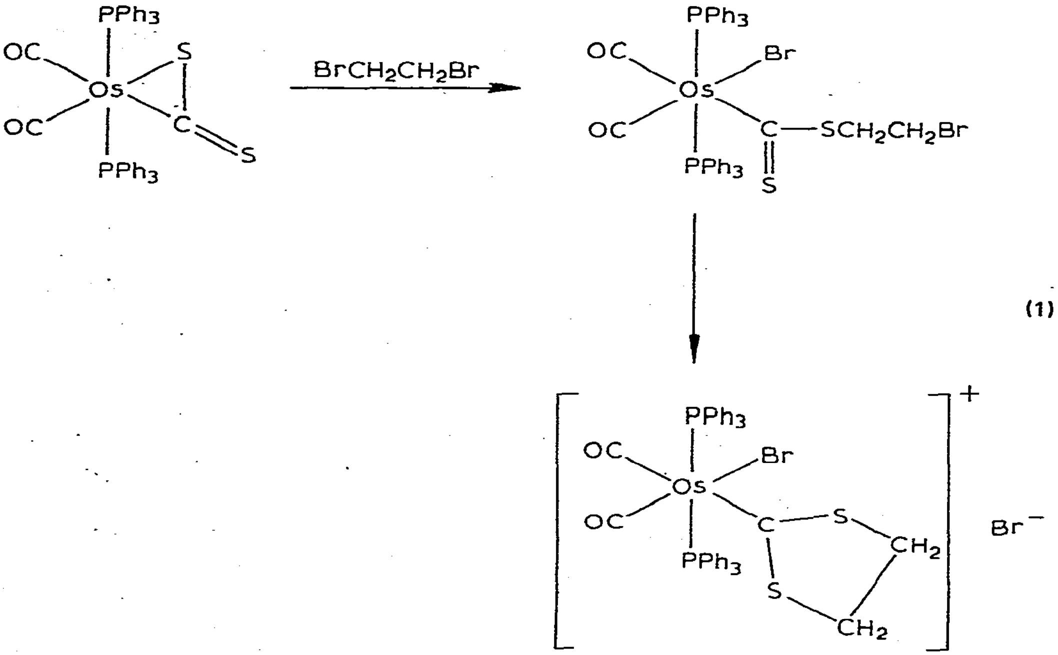
IR[a] (cm^{-1}) AND ^1H NMR[b] (τ, ppm) DATA FOR CYCLIC CARBENE COMPLEXES

Complex[c]	ν (CO)	ν (CN)	Chemical shifts
$[OsBr(\overline{CSCH_2CH_2S})(CO)_2(PPh_3)_2]^+$	2060, 1985		6.77
$[OsBr(\overline{CSCH_2CH_2S})(CO)(CNR)(PPh_3)_2]^{+d}$	1975	2150	6.87
$OsBr_2(\overline{CSCH_2CH_2S})(CO)(PPh_3)_2$	1940		
$[RuBr(\overline{CSCH_2CH_2S})(CO)(CNR)(PPh_3)_2]^{+d}$	1990	2150	6.85
$[RuBr(\overline{CSeCH_2CH_2Se})(CO)_2(PPh_3)_2]^+$	2060, 1997		6.40
$RuBr_2(\overline{CSeCH_2CH_2Se})(CO)(PPh_3)_2$	1968		

[a] Nujol mulls. [b] $CDCl_3$ solution. [c] All compounds reported have satisfactory elemental analyses. Cations characterised as perchlorate salts. [d] R = p-tolyl.

The other CS_2 adducts and also $Ru(CSe_2)(CO)_2(PPh_3)_2$ react similarly with 1,2-dibromoethane producing the compounds described in Table 1. The two dicarbonyl cations are labile with respect to replacement of carbonyl with bromide and the neutral compounds $RuBr_2(\overline{CSeCH_2CH_2Se})(CO)(PPh_3)_2$ and $OsBr_2(\overline{CSCH_2CH_2S})(CO)(PPh_3)_2$ have also been characterised.

The mechanism of this reaction probably proceeds as shown in eq. 1.



(1)

The CS_2 adducts undergo similar reactions with 1,3-dibromopropane yielding 1,3-dithian-2-ylidene complexes. We have tried unsuccessfully to extend this reaction to the synthesis of thiazolidin-2-ylidene complexes through ring-closing reactions on π-bound isothiocyanate (RNCS) complexes.

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References

1 D.H. Bowen, M. Green, D.M. Grove, J.R. Moss and F.G.A. Stone, J. Chem. Soc., (1974) 1189.
2 K.R. Grundy, R.O. Harris and W.R. Roper, J. Organometal. Chem., 90 (1975) C34.
3 D.F. Christian, Thesis, University of Auckland, 1973.
4 G.R. Clark, K.R. Grundy, R.O. Harris, S.M. James and W.R. Roper, J. Organometal. Chem., 90 (1975) C37.
5 K.R. Grundy, Thesis, University of Auckland, 1975.