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Preliminary communication

REACTIONS OF OSMIUM COORDINATED FORMALDEHYDE. SYNTHESIS OF COMPLEXES OF SELENOFORMALDEHYDE AND TELLUROFORMALDEHYDE

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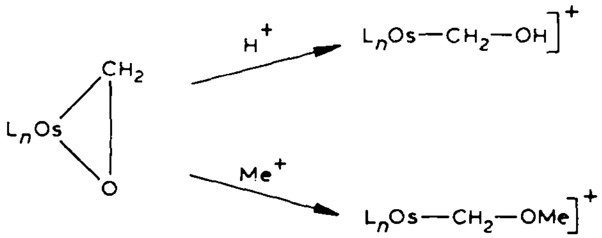
Summary

$Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$ reacts with CSe_2 to form a metallacycle $\overline{Os(CH_2OC[Se}]Se)(CO)_2(PPh_3)_2$. This compound breaks down to $Os(\eta^2\text{-}CH_2Se)(CO)_2(PPh_3)_2$ with probable loss of COSe. An alternative route to $Os(\eta^2\text{-}CH_2Se)(CO)_2(PPh_3)_2$ and also $Os(\eta^2\text{-}CH_2Te)(CO)_2(PPh_3)_2$ is through reaction of $Os(CH_2I)I(CO)_2(PPh_3)_2$ with SeH^- and TeH^-, respectively. HCl with $Os(\eta^2\text{-}CH_2E)(CO)_2(PPh_3)_2$ (E = Se or Te) gives $OsCl(EMe)(CO)_2(PPh_3)_2$ while methyl iodide gives $[Os(\eta^2\text{-}CH_2EMe)(CO)_2\text{-}(PPh_3)_2]I$. BH_4^- reacts with these cations to cleave the C—E bond and form $Os(CH_3)(EMe)(CO)_2(PPh_3)_2$.

The simple transformations undergone by a metal-bound formaldehyde molecule are of interest because coordinated formaldehyde may play a significant role in CO reduction [1]. We have shown that for the well-characterised formaldehyde complex $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$ [2,3] reaction with the electrophiles H^+ and Me^+ results in ring opening and the formation of oxymethylene derivatives [2,3,4].



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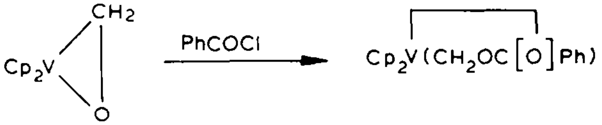
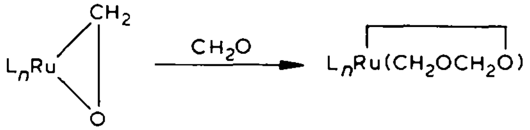
Similarly, for a vanadium-formaldehyde complex conversion to acyloxymethylene derivatives has been demonstrated [5]:



In addition, while attempting to produce a formaldehyde complex of $\mathrm{Ru(CO)(PPh_3)_3}$ we observed formation of $\mathrm{Ru(CH_3)(\eta^2\text{-}O_2CH)(CO)(PPh_3)_2}$ [6] and suggested that this product might possibly have arisen from the intermediate formation of a metallacycle from addition of two molecules of formaldehyde, viz.



To demonstrate the formation of stable examples of such five-membered rings we have examined reaction between $\mathrm{Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2}$ and the powerful electrophile, $\mathrm{CSe_2}$. This reaction is described here together with the characterisation of stable complexes of monomeric selenoformaldehyde and telluroformaldehyde thus completing the series $\mathrm{Os(\eta^2\text{-}CH_2X)(CO)_2(PPh_3)_2}$ for X = O [2,3], S [7], Se, and Te.

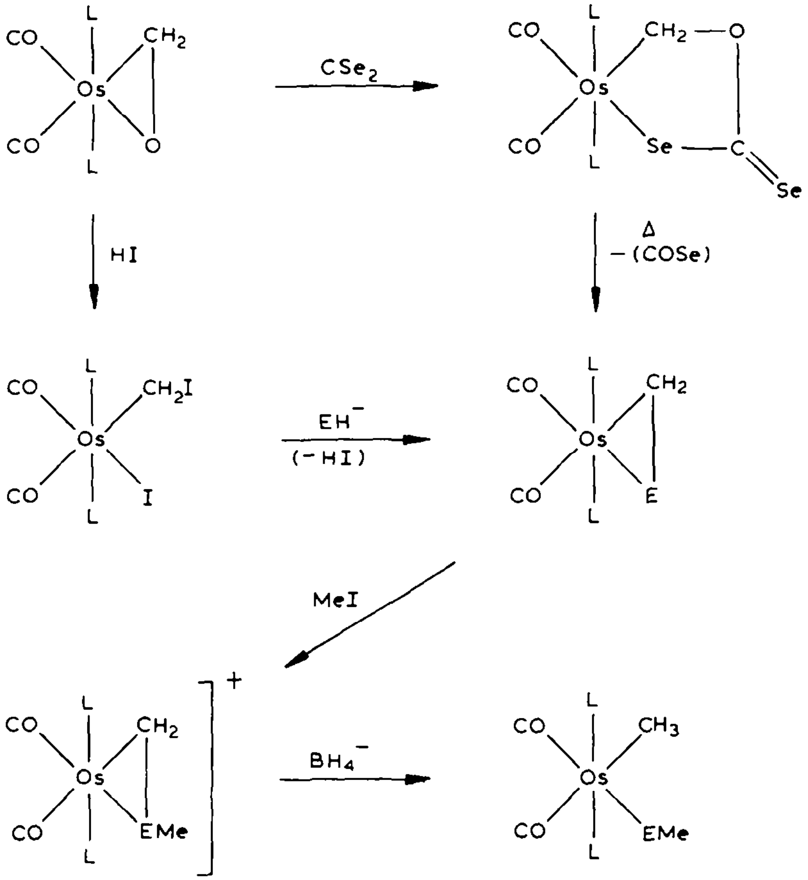
Reaction between $\mathrm{CSe_2}$ and $\mathrm{Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2}$ affords, after chromatography on florisil, a yellow-crystalline product having the composition of a 1/1 adduct and with an IR spectrum (see Table 1) compatible with the metallacycle, $\mathrm{\overline{Os(CH_2OC[Se]Se})(CO)_2(PPh_3)_2}$. Heating a $\mathrm{CH_2Cl_2}$ solution of this compound under reflux for several hours resulted in the formation of $\mathrm{Os(\eta^2\text{-}CH_2Se)(CO)_2(PPh_3)_2}$, isolated as pale yellow crystals, presumably with simultaneous elimination of COSe (see Scheme 1). A superior preparative

TABLE 1

IR [a] AND ^{1}H NMR [b] DATA FOR CHALCOFORMALDEHYDE COMPLEXES OF OSMIUM AND DERIVATIVES

Compound [c]	ν(CO) (cm^{-1})	Chemical shift (τ) and coupling constant (Hz)
$\mathrm{Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2}$	1977, 1902	7.44(t), ^3J(H—P) 4.0
$\mathrm{Os(\eta^2\text{-}CH_2S)(CO)_2(PPh_3)_2}$	1985, 1915	9.10(t), ^3J(H—P) 4.6
$\mathrm{Os(\eta^2\text{-}CH_2Se)(CO)_2(PPh_3)_2}$	1986, 1919	8.22(t), ^3J(H—P) 4.8
$\mathrm{Os(\eta^2\text{-}CH_2Te)(CO)_2(PPh_3)_2}$	1991, 1922	7.92(t), ^3J(H—P) 6.0
$\mathrm{\overline{Os(CH_2OC[Se]Se})(CO)_2(PPh_3)_2}$ [d]	2015, 1953	
$\mathrm{[Os(\eta^2\text{-}CH_2SeMe)(CO)_2(PPh_3)_2]I}$	2020, 1953	7.58(t), ^3J(H—P) 10.5; 8.57(s) (SeMe)
$\mathrm{[Os(\eta^2\text{-}CH_2TeMe)(CO)_2(PPh_3)_2]I}$	2024, 1947	7.41(t), ^3J(H—P) 10.0; 8.98(s) (TeMe)
$\mathrm{Os(CH_3)(SeMe)(CO)_2(PPh_3)_2}$	1981, 1912	10.16(t) ^3J(H—P) 7.8; 9.23(s) (SeMe)
$\mathrm{Os(CH_3)(TeMe)(CO)_2(PPh_3)_2}$	2000, 1936	10.27(t) ^3J(H—P) 7.4; 9.43(s) (TeMe)

[a] Measured as Nujol mulls. [b] In $\mathrm{CDCl_3}$. [c] All compounds have satisfactory elemental analyses.
[d] Bands at 1148, 935 associated with metallacycle.

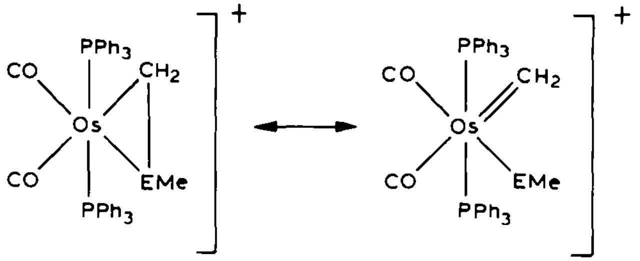


SCHEME 1. Synthesis and reactions of selenoformaldehyde and telluroformaldehyde complexes of osmium (L = PPh_3, E = Se or Te).

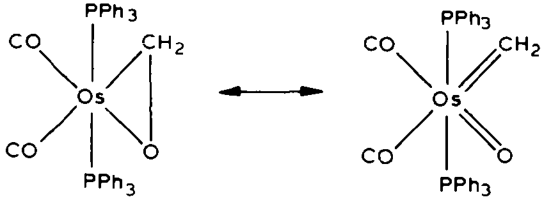
route to the selenoformaldehyde complex is through reaction of the iodomethyl complex, $Os(CH_2I)I(CO)_2(PPh_3)_2$ [3] with SeH^-. The immediate product of this reaction is $Os(CH_2SeH)I(CO)_2(PPh_3)_2$ but attempted recrystallisation of this leads to rapid loss of HI and formation of $Os(\eta^2\text{-}CH_2Se)(CO)_2(PPh_3)_2$. The same approach using TeH^- leads to $Os(\eta^2\text{-}CH_2Te)(CO)_2(PPh_3)_2$ as bright yellow air-stable crystals. Various polymeric forms of selenoformaldehyde have been prepared and characterised, e.g. the cyclic trimer 1,3,5-triselenane [8] but monomeric selenoformaldehyde is unknown. A trimer of telluroformaldehyde has also been reported but was not characterised [9]. Spectral data for the complete series of chalcoformaldehyde complexes are collected in Table 1.

Treatment of $Os(\eta^2\text{-}CH_2E)(CO)_2(PPh_3)_2$ (E = Se or Te) with HCl yields $OsCl(EMe)(CO)_2(PPh_3)_2$ probably via initial protonation at the metal. This behaviour is exactly that observed for $Os(\eta^2\text{-}CH_2S)(CO)_2(PPh_3)_2$ [7].

In contrast to the acid reaction, alkylation with methyl iodide occurred at the selenium or tellurium atom to yield $[Os(\eta^2\text{-}CH_2EMe)(CO)_2(PPh_3)_2]I$. The reaction of these cations with $NaBH_4$ did not yield the expected ringopened hydride-containing derivative $Os(\eta^1\text{-}CH_2EMe)H(CO)_2(PPh_3)_2$ but instead gave methylosmium complexes $OsCH_3(EMe)(CO)_2(PPh_3)_2$ (see Scheme 1). This surprising reaction perhaps suggests that the following resonance forms both contribute to the bonding in $[Os(\eta^2\text{-}CH_2EMe)(CO)_2(PPh_3)_2]^+$



In this connection, it can also be noted that the very long C—O bond distance of 1.584(11) Å found in $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$ [3] likewise implies a contribution to the bonding in this molecule from a "methylidene-oxide" resonance form



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