

Preliminary communication

CYCLOPENTADIENYL RUTHENIUM AND OSMIUM COMPLEXES

II*. THE REACTIVITY OF π -CYCLOPENTADIENYL(TRIPHENYL-PHOSPHINE)-RUTHENIUM(II) AND -OSMIUM(II) COMPLEXES

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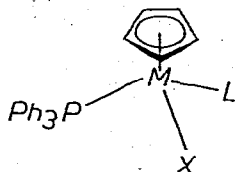
Summary

Ruthenium and osmium complexes of the type $\text{CpMX}(\text{PPh}_3)_2\text{L}$ ($\text{M} = \text{Ru}$; $\text{X} = \text{Cl}, \text{H}, \text{S}_2\text{COC}_{10}\text{H}_{19}, \text{S}_2\text{COMe}$; $\text{L} = \text{PPh}_3$ and PPh_2 ; $\text{M} = \text{Os}$, $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{H}, \text{D}$, xanthogenate, dithiocarbamate, BPh_4 , $\text{L} = \text{PPh}_3$) are obtained. The compound $\text{CpOsCl}(\text{PPh}_3)_2$ is readily soluble in MeOH and in the solution the cation $[\text{CpOs}(\text{PPh}_3)_2]^+$ is present. Upon addition of NaBPh_4 a white compound $\text{CpOs}(\text{PPh}_3)_2\text{BPh}_4$ immediately precipitates, which can not be solved in MeOH, contrary to the behaviour of the corresponding ruthenium compound.

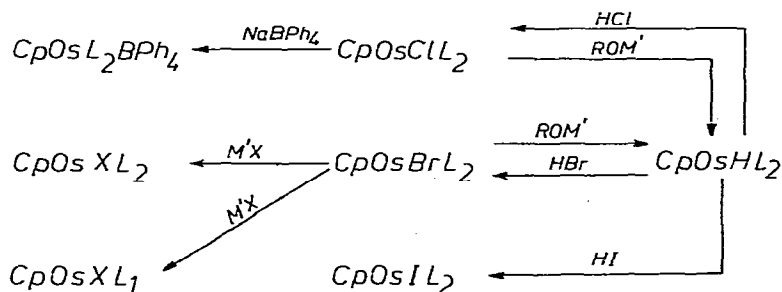
- Blackmore, Bruce and Stone [1] had obtained in 1971 pale yellow-orange $\text{CpOsBr}(\text{PPh}_3)_2$ in the reaction of $\text{OsBr}_2(\text{PPh}_3)_3$ with cyclopentadiene (m.p. 182–185°C, yield 77%). In 1977 Bruce and Windsor [2] presented a rapid method of synthesis for this compound (m.p. 180–185°C, yield 74%). Attempts were made to repeat Bruce's synthesis [2] which were unsuccessful. Instead in a sealed capillary a yellow-orange compound (II, m.p. 248–254°C, yield 91%) was obtained. The compound was formed independently of the solvent (MeOH or 95% EtOH) and of the type of osmium(IV) bromide used in the synthesis. Also in the reaction of $\text{CpOsH}(\text{PPh}_3)_2$ with HBr compound II was formed (m.p. 232–238°C, yield 8%, see Scheme 1).

A similar phenomenon was observed earlier for $\text{CpRuCl}(\text{PPh}_3)_2$ [3]. Since then the complete structure of $\text{CpRuCl}(\text{PPh}_3)_2$ (m.p. 244–248°C) was determined [4] (Fig. 1), an earlier assumption [3] about the similarity of the structure of $\text{CpRuCl}(\text{PPh}_3)_2$ and the structure of the rhodium cation $[(\pi\text{-C}_5\text{Me}_5)\text{RhH}$

*For part I see ref. 3.



	M	X	L
I	Os	Cl	PPh_3
II	Os	Br	PPh_3
III	Os	I	PPh_3
IV	Os	H	PPh_3
V	Os	D	PPh_3
VI	Os	S_2C-OMe	PPh_3
VII	Os	S_2C-OEt	PPh_3
VIII	Os	$S_2C-O-nPr$	PPh_3
IX	Os	$S_2C-N(CH_2)_4$	PPh_3
X	Os	$S_2C-N(CH_2)_4(MeOH)$	PPh_3
XI	Os	$S_2C-N(CH_2)_4$	—
XII	Ru	Cl	PPh_2
XIII	Ru	H	PPh_2
XIV	Ru	$S_2C-OC_{10}H_{19}$	PPh_3
XV	Os	$S_2C-OC_{10}H_{19}$	PPh_3
XVI	Os	BPh_4	PPh_3
XVII	Ru	S_2C-OMe	—



SCHEME 1. R = Me, Et, $CH_2=CH$, L = PPh_3 , M' = alkali metal, X = xanthogenate, dithiocarbamate.

$(PPh_3)_2]^+$ [5] was confirmed. Analogously, if the structure of compound II is similar to that of $CpRuCl(PPh_3)_2$ then the possibility of compound II and of that described in refs. 1 and 2 to be isomers should be excluded.

Recently Bruce, Wong and co-workers [8] reported that they also determined the structure of $CpRuCl(PPh_3)_2$.

The extension of the concept [3] for the synthesis of hydrido complexes of ruthenium and osmium in reactions of the respective halides I, II and XII with the alkoxide anion led to compounds IV and XIII. It is of interest

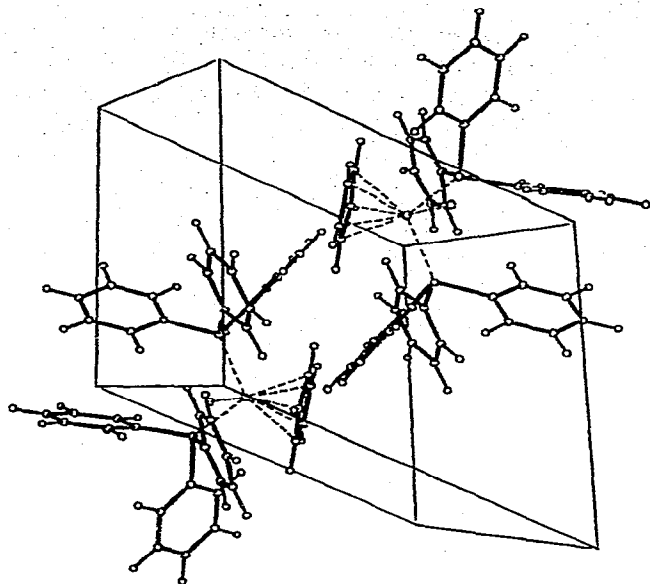


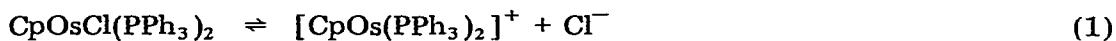
Fig. 1. Structure of $\text{CpRuCl}(\text{PPh}_3)_2$ (m.p. $244\text{--}248^\circ\text{C}$).
Angles: $\text{P}(1)\text{RuP}(2)$ 103.88° , $\text{ClRuP}(1)$ 90.52° , $\text{ClRuP}(2)$ 88.90° .

that the hydride IV is stable in the solid state. As in the case of the ruthenium analogue compound IV has the expected higher melting point ($204\text{--}206^\circ\text{C}$) which is higher than that of $\text{CpRuH}(\text{PPh}_3)_2$ (m.p. $181\text{--}184^\circ\text{C}$). The ^1H NMR spectrum of compound IV showed the presence of a triplet of Os—H (δ -14.4 ppm, $J(\text{PH})$ 27 Hz (for $\text{CpRuH}(\text{PPh}_3)_2$ $J(\text{PH})$ 34 Hz). The data indicated that the osmium in compound IV was a poorer transmitter of nuclear spin—spin coupling effects compared to ruthenium. A similar effect for ruthenium and iron was observed by Blackmore, Bruce and Stone [1, cf. 6].

The performance of the reaction of compound II with sodium deuteromethoxide in CD_3OD afforded the deuteride V. The IR band $\nu(\text{Os—D})$ was obscured in the region $1470\text{--}1425\text{ cm}^{-1}$ by other intensive bands.

In the reaction of the hydride IV with acids in polar solvents (e.g. MeOH) complexes were obtained in high yield, in which the hydride ligand was replaced by an anion from the respective acids [cf. 3]. In this way also $\text{CpOsCl}(\text{PPh}_3)_2$ which is readily soluble in MeOH, was obtained. Probably this explains the fact, that until now compound I in the reaction of H_2OsCl_6 with cyclopentadiene and PPh_3 in accordance with the method given by Bruce [2] was not obtained.

Compound I, now obtained, is an analogue of $\text{CpRuCl}(\text{PPh}_3)_2$ and shows practically ionic behaviour in MeOH, indicating that the equilibrium 1 is



shifted almost completely to the right.

For example: upon addition of a solution of NaBPh_4 in MeOH a white, microcrystalline compound $\text{CpOs}(\text{PPh}_3)_2\text{BPh}_4$ (XVI) immediately precipitated. Also the results of conductometric titration on solution of NaBPh_4 in MeOH con-

firmed the formula of compound XVI. In contrast, the analogous ruthenium compound obtained in 20% yield is $\text{CpRu}(\text{MeOH})(\text{PPh}_3)_2\text{BPh}_4$ [7].

By replacing the bromo group for a bromide ion in compound II in a polar medium (MeOH, EtOH) with salts of $\text{M}'\text{X}$ type (where M' = alkali metal) a series of new compounds was obtained, i.e. compounds VI—XI and XIV—XVII.

Performing the exchange process in the two phase system (solid state $\text{CpOsBr}(\text{PPh}_3)_2$ —solution of $\text{M}'\text{X}$ in MeOH) and isolating the solid reaction product obtained by filtration, pure compounds would not be obtained. The kind of alkali metal cation affected the yield and by-products. For example: if using for the synthesis of compound VII lithium, sodium or potassium ethyl-xanthogenate, compound VII was obtained in 13, 58 and 67% yields, respectively.

In exchange reactions of compound II with sodium *l*-menthylxanthogenate the optically active compounds XIV and XV, ($[\alpha]_D^{20}$ +89° and +38° (benzene)) were obtained. The ^{31}P NMR spectrum showed non-equivalency of the phosphorus atoms in compound XV, δ -2.62 ppm, $d(\text{P}(1))$ and -3.31 ppm, $d(\text{P}(2))$, $J(\text{P}(1)\text{P}(2))$ 36 Hz. In the case of the ruthenium analogue XIV δ +40.28 s ppm.

Previously compound $\text{CpRuS}_2\text{COMe}(\text{PPh}_3)_2$ was obtained [3], while the further derived compounds (ethyl-, *n*-propyl-, *n*-butyl-xanthogenate) contained only one PPh_3 per molecule [3]. Now the expected compound containing one PPh_3 per molecule (XVII, m.p. 141–142°C) was obtained.

References

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