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CYCLOPENTADIENYL-RUTHENIUM AND -OSMIUM COMPLEXES

VI *. FORMATION AND PROPERTIES OF DIHYDRIDO-(η-CYCLOPENTADIENYL)BIS(TRIPHENYLPHOSPHINE)OSMIUM(IV) CATION. REACTION OF HYDRIDO(η-CYCLOPENTADIENYL)-BIS(TRIPHENYLPHOSPHINE)OSMIUM(II) AND DIHYDRIDO-(η-CYCLOPENTADIENYL)BIS(TRIPHENYLPHOSPHINE)OSMIUM(IV) HALOGENATES WITH HX ACIDS, X_2 DIHALOGENO AND HALOGENATED HYDROCARBONS

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Summary

Several new compounds of the type $[CpOsH_2(PPh_3)_2]^+ X^-$, where X = Cl, Br, I, I_3, BPh_4, *p*-toluenesulphonate, *d*(+)-campho-10-sulphonate, have been obtained in the form of ion pairs or salts. The above compounds form during oxidative addition by HX acids to $CpOsH(PPh_3)_2$. The reactions are complete after several seconds, with a quantitative yield. This is in contrast to the behaviour of $CpRuH(PPh_3)_2$, where covalent $CpRuX(PPh_3)_2$ forms. Reaction of $CpOsH(PPh_3)_2$ with DCl acid (excess) gives $[CpOsD_2(PPh_3)_2]Cl$, but no $[CpOsHD(PPh_3)_2]Cl$ is formed.

Refluxing $CpOsBr(PPh_3)_2$, in ethylene glycol for instance, gives a $[CpOsH_2(PPh_3)_2]^+$ cation as a result of the dehydrogenation of the glycol. Compounds of the type, $[CpOsH_2(PPh_3)_2]X$, in solutions of polar solvents (MeOH) or halogenated hydrocarbons (e.g. CH_2X_2) undergo transformation to $CpOsX(PPh_3)_2$ during the reductive elimination process. In this way novel $CpOsI(PPh_3)_2$ has been obtained. In the case of the reaction of a mixture of HX + X_2 with $CpOsH(PPh_3)_2$, $[CpOsHBr(PPh_3)_2]Br_3$ (for Br_2) and $[CpOsH_2(PPh_3)_2]I_3$ (for I_2) have been obtained in the form of sparingly soluble ion pairs with yields of about 90%.

Introduction

The compound $CpRuH(PPh_3)_2$ which was discovered in 1971 by Blackmore, Bruce and Stone [1], undergoes a reaction in polar media with halogenohydro acids

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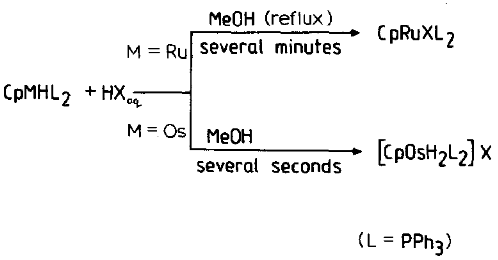
* For part V see ref. 18.



SCHEME 1

HX (or pseudohalogenohydro acids) giving halogeno(η-cyclopentadienyl)bis(triphenylphosphine)ruthenium(II) in a high yield [2,3], Scheme 1.

Quite a different way in which CpOsH(PPh$_3$)$_2$ reacts was discovered in 1982 [4], where reaction with HX acids resulted in the dihydrido(η-cyclopentadienyl)bis(triphenylphosphine)osmium(IV) cation. The reaction is very fast in polar media (MeOH) lasting only several seconds, and gives a practically quantitative yield. In aqueous media, however, the process is significantly slower, because the [CpOsH$_2$(PPh$_3$)$_2$]X formed is sparingly soluble in water and hinders contact by the CpOsH(PPh$_3$)$_2$ substrate with HX$_{aq}$. In a previous preliminary communication [4], the reactions and schemes were erroneously presented and the formula CpOsCl(PPh$_3$)$_2$ should read [CpOsH$_2$(PPh$_3$)$_2$]Cl.

During the oxidative addition reaction of HBF$_4$ with a solution of CpOsBr(PPh$_3$)$_2$ Bruce obtained dark red-brown crystals of [CpOsHBr(PPh$_3$)$_2$]BF$_4$ [5,6].

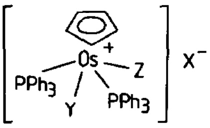
In the case of the ruthenium series however, the use of a strong organic acid, pentakis(methoxycarbonylcyclopentadiene), HC$_5$(CO$_2$Me)$_5$ [7], in a reaction with CpRuH(PPh$_3$)$_2$ causes the formation of the [CpRuH$_2$(PPh$_3$)$_2$]$^+$ cation which was isolated as its colourless salt [CpRuH$_2$(PPh$_3$)$_2$][C$_5$(CO$_2$Me)$_5$] [8].

Results and discussion

CpOsH(PPh$_3$)$_2$ reacts in polar solvents with HX acids (where X = Cl, Br, I, *p*-toluenesulphonate, campho-10-sulphonate) giving compounds of the type [CpOsH$_2$(PPh$_3$)$_2$]$^+$ X$^-$ with an ion pair or salt-like character. At high reagent concentrations the reactions are exothermic. In the above oxidative-addition reaction a change in the oxidation state of osmium to Os^{IV} is observed. The same [CpOsH$_2$(PPh$_3$)$_2$]$^+$ cation is formed when glycols are dehydrogenated during the reflux of CpOsBr(PPh$_3$)$_2$ in these high boiling-point solvents.

As can be seen from the proton decoupled ^{31}P NMR spectra, the location of the singlet at about δ 9 ppm of two equivalent phosphorus atoms is almost independent of the kind of X$^-$ anion and the type of solvent present (Table 2).

Regarding the probable *trans*-configuration of the hydrogen atoms in the [CpOsH$_2$(PPh$_3$)$_2$]$^+$ cation a diagonal configuration in accordance with Bruce [6] is proposed. In the up-field regions of the ^{1}H NMR spectra of compounds I–V, VII, and X (Table 2) a triplet is observed, the position of which (δ −11.3 ppm) and the coupling constants (J(PH) 29 Hz) are also almost independent of the kind of the X$^-$ anion present. The triplet nature of these signals arises from coupling to the ^{31}P nuclei and indicates the equivalency of both phosphorus atoms, which is as expected for the diagonal structure of the complex cation.



	Y	Z	X
I	H	H	Cl
II	H	H	Br
III	H	H	I
IV	H	H	I_3
V	H	H	BPh_4
VI	D	D	BPh_4
VII	H	H	*p*-toluenesulphonate
VIII	D	D	p-toluenesulphonate
IX	H	Br	Br_3
X	H	H	*d*(+)-campho-10-sulphonate

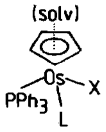
The properties of the novel osmium compounds are summarized in Tables 1 and 2.

The $[CpOsH_2(PPh_3)_2]^+$ cation can be easily isolated as sparingly soluble ion pairs with an excess of BPh_4^- or I_3^- anions, (compounds IV, V, see Experimental, iv–viii) from solutions in polar solvents (methanol, ethanol or glycols) in a yield of over 90%. Compounds of the dihydride type (I–III) are very stable in the solid state. For instance, compound I, despite storage for over 4 years, showed virtually no changes in its ^1H NMR and ^{31}P NMR spectra.

The following facts support the postulated formulation of the cation $[CpOsH_2(PPh_3)_2]^+$ with two hydride atoms:

(i) In the IR (KBr) spectra of the compound, $[CpOsH_2(PPh_3)_2]BPh_4$ (V), there are two very weak bands (2163 and 2130 cm^{-1}) showing antisymmetric and symmetric ν(Os–H) vibration, as is also the case in chloroform solutions (2185vw,

(Continued on p. 312)



	X	L	(solv)
XI	H	PPh_3	-
XII	D	PPh_3	-
XIII	Br	CO	-
XIV	Cl	PPh_3	CH_2Cl_2
XV	Br	PPh_3	CH_2Br_2
XVI	Cl	PPh_3	CS_2
XVII	Br	PPh_3	CS_2
XVIII	Cl	PPh_3	-
XIX	Br	PPh_3	-
XX	I	PPh_3	-

TABLE 1

YIELDS, MELTING POINTS AND MASS SPECTRAL DATA FOR THE COMPOUNDS OBTAINED

Compound	Mol. wt. (calc.)	MS(FD) Parent ion m/e [a]	Colour	Yield (%)	M.p. [c] (°C)	Substrate used for synthesis
$[CpOsH_2(PPh_3)_2]Cl$ (I)	817.3	783, 816 [b]	white-yellow	100	207–210 d	$CpOsH(PPh_3)_2$
$[CpOsH_2(PPh_3)_2]Br$ (II)	861.8	783, 860 [b]	white-grey	100	182–187 d	$CpOsH(PPh_3)_2$
$[CpOsH_2(PPh_3)_2]I$ (III)	908.8	783, 908 [b]	yellow-grey	100	256–264 d	$CpOsH(PPh_3)_2$
$[CpOsH_2(PPh_3)_2]I_3$ (IV)	1162.6	783, 908 [b]	yellow-brown	82	182–186 d	$CpOsBr(PPh_3)_2$
		783, 908 [b]	yellow-brown	74	172–178 d	$CpOsH(PPh_3)_2$
$[CpOsH_2(PPh_3)_2]BPh_4$ (V)	1101.1	783, 782 [b]	white	91	226–232 d	$CpOsBr(PPh_3)_2$
			white	84	222–224 d	$[CpOsH_2(PPh_3)_2]Cl$
$[CpOsD_2(PPh_3)_2]BPh_4$ (VI)	1103.1	785, 783 [b]	white	69	216–228 d	$CpOsH(PPh_3)_2$
$[CpOsH_2(PPh_3)_2]SO_3C_6H_4Me$ (VII)	953.1	783, 952 [b]	white	100	165–178 d	$CpOsH(PPh_3)_2$
$[CpOsHBr(PPh_3)_2]Br_3$ (IX)	1100.5	861	yellow-brown	95	113–115 d	$CpOsH(PPh_3)_2$
		861	lemon-yellow	88	113–115 d	$CpOsBr(PPh_3)_2$
$[CpOsH_2(PPh_3)_2]SO_3C_{10}H_{15}O$ (X)	1013.2	783, 1012 [b]	white	100	214–221 d	$CpOsH(PPh_3)_2$
$CpOsH(PPh_3)_2$ (XI)	780.9	782	lemon-yellow	89	204–206	$CpOsBr(PPh_3)_2$
$CpOsBr(CO)PPh_3$ (XIII)	625.5	626	yellow	10	not measured	$CpOsBr(PPh_3)_2$
$CpOsCl(PPh_3)_2 \cdot CH_2Cl_2$ (XIV)	900.3	816	yellow	42	197–212 d	$[CpOsH_2(PPh_3)_2]Cl$
$CpOsBr(PPh_3)_2 \cdot CH_2Br_2$ (XV)	1033.6	860	yellow-brown	42	230–240 d	$[CpOsH_2(PPh_3)_2]BPh_4$
$CpOsI(PPh_3)_2$ (XX)	906.8	908	yellow-orange	29	188–192	$CpOsBr(PPh_3)_2$
			yellow-brown	68	184–192	$CpOsH(PPh_3)_2$

[a] Data for ^{192}Os, ^{35}Cl, ^{79}Br, ^{32}S isotopes. [b] As a result of rearrangement of compound $[CpOsH_2(PPh_3)_2]X$ to $CpOsX(PPh_3)_2$. [c] d = decomposition.

TABLE 2

NMR DATA OF THE NEW CYCLOPENTADIENYLOSMIUM COMPLEXES (chemical shifts δ in ppm)

Compound	^{1}H NMR (TMS)						^{31}P NMR (H_3PO_4)	
	Solvent	Cp	PPh_3	Os–H,	J(PH) Hz	Others	Solvent	PPh_3
$[CpOsH_2(PPh_3)_2]Cl$ (I)	$CDCl_3$	5.06s	7.29m	−11.3t	29		CH_2Cl_2	8.9s
	$(CD_3)_2SO$	5.23s	7.36m	−11.6t	29			
$[CpOsH_2(PPh_3)_2]Br$ (II)	$CDCl_3$	5.08s	7.30m	−11.3t	29		CH_2Cl_2	9.1s
							MeOH [a]	9.0s
$[CpOsH_2(PPh_3)_2]I$ (III)	$CDCl_3$	5.10s	7.30m	−11.3t	29		$CHCl_3$	9.0s
							CH_2Cl_2	9.0s
$[CpOsH_2(PPh_3)_2]I_3$ (IV)	$CDCl_3$	5.10s	7.36m	−11.3t	29		$CHCl_3$	8.9s
							C_5H_5N	8.6s
$[CpOsH_2(PPh_3)_2]BPh_4$ (V)	$CDCl_3$	4.50s	7.24m	−11.6t	29	BPh_4: 7.00m, 6.90m	CH_2Cl_2	8.9s
	$(CD_3)_2CO$	5.29s	7.46m	not measured [b]		BPh_4: 7.00m, 6.90m		
	$(CD_3)_2SO$	5.19s	7.32m	−11.6t	29	BPh_4: 7.00m, 6.85m		
	C_5D_5N	5.00s	7.23m	−11.4t	29	BPh_4: 7.95m, 6.97m		
$[CpOsH_2(PPh_3)_2]SO_3C_6H_4Me$ (VII)	$CDCl_3$	5.02s	7.26m	−11.4t	29	C_6H_4: 7.88d, 7.03d	MeOH	8.9s
						J(HH) 8 Hz, Me: 2.30s	CH_2Cl_2	9.0s
$[CpOsHBr(PPh_3)_2]Br_3$ (IX)	$CDCl_3$	5.52s	7.35m	−12.3t	33		$CHCl_3$	−12.2s
$[CpOsH_2(PPh_3)_2]SO_3C_{10}H_{15}O$ (X)	$CDCl_3$	5.11s	7.30m	−11.5t	29	$C_{10}H_{15}O$: 3.5–0.8m	$CHCl_3$	8.9s
$CpOsH(PPh_3)_2$ (XI)	$CDCl_3$	4.26s	7.12m	−14.4t	28		CH_2Cl_2	20.6s
	CS_2	4.07s	6.97m	not measured				
	CH_2Cl_2	not measured		−14.4t	27 [c]			
$CpOsBr(PPh_3)_2 \cdot CH_2Br_2$ (XV)	$CDCl_3$	4.36s	7.26m			CH_2: 5.00s	C_5H_5N	−5.7s
	CS_2	4.16s	7.19m			CH_2: 4.96s	$CHCl_3$	−4.9s
							CH_2Br_2	−4.4s
$CpOsI(PPh_3)_2$ (XX)	$CDCl_3$	4.38s	7.23m				C_5H_5N	−8.9s
	CS_2	4.13s	7.21m				$CHCl_3$	−8.2s
							CH_2I_2	−6.7bs

[a] Mixture with ethylene glycol. [b] Owing to the poor solubility of V in acetone-d_6. [c] Measured on a Perkin–Elmer R12B spectrophotometer.

2125sh cm^{-1}), and in Nujol. Likewise this occurs for compounds I–III; 2110, 2076; 2114, 2079; 2120, 2080 cm^{-1}; respectively.

(ii) Integration of the δ(Os–H) triplet intensity in the ^{1}H NMR spectra of compounds I–V, VII and X, compared with the intensity of the Cp singlet, gives values of about 2 H.

(iii) The off-resonance ^{1}H-decoupled ^{31}P NMR spectra of compounds I–III, V and VII showed broad massive bands, and were unchanged from −90 to 30 °C. In these spectra the triplet contours could scarcely be seen, but the estimated coupling constants from that band were generally consistent with the J(PH) values obtained from the ^{1}H NMR spectra.

(iv) The MS(FD) spectra of compound V contain only one group of signals centered at $m/e = 783$, and this fits the $[CpOsH_2(PPh_3)_2]^+$ cation, as follows from the above spectra with an internal standard included. The maximum intensity of the signals may also occur at lower values of m/e (782), but this depends on the procedure (temperature and time of heating by the emitter device of the MS apparatus). This indicates the possibility of an internal rearrangement of the cation in compound V to $CpOsH(PPh_3)_2$ (compound XI) $m/e = 782$. Similar results were obtained for the dideuteride $[CpOsD_2(PPh_3)_2]BPh_4$ (compound VI, Table 1).

The FD mass spectra of compounds I–IV, VII and X also confirm the possibility of rearrangement on the MS emitter device to corresponding covalent compounds of the type $CpOsX(PPh_3)_2$ (eq. 1) where the X group in $CpOsX(PPh_3)_2$ originates from the X$^-$ anion, connected with the $[CpOsH_2(PPh_3)_2]^+$ cation. In the MS(FD) spectra of these compounds the $[CpOsH_2(PPh_3)_2]^+$ cation signal ($m/e = 783$) is also present, less intense, or equivalent to the signal of the compound formed as the result of the rearrangement (Table 1).

$$[CpOsH_2(PPh_3)_2]X \rightarrow CpOsX(PPh_3)_2 + H_2 \tag{1}$$

The following processes may occur simultaneously on the MS emitter device:

(i) dissociation of the ion-pair and acceleration of the $[CpOsH_2(PPh_3)_2]^+$ cation, $m/e = 783$, as is expected for typical onium compounds [9],

(ii) rearrangement of the ion pair, leading to the formation of a covalent compound of the type $CpOsX(PPh_3)_2$, and then its acceleration (after field ionisation).

The rearrangement phenomenon of the ion pair which occurs at the MS emitter device is probably a rule for compounds of the ion pair type given in Table 1. For $[CpOsYZ(PPh_3)_2]X$ rearrangement, the following stages of the process are likely:

(i) Release of the covalent molecule YZ from the coordination sphere of osmium(IV) in the reductive-elimination process, this is connected with a formal transference of 2 electrons to the osmium atom,

$$[CpOsYZ(PPh_3)_2]X \rightarrow CpOsX(PPh_3)_2 + YZ \tag{2}$$

(ii) Stabilization of the unstable $[CpOs^+(PPh_3)_2]$ cation by formation of a covalent bond with the X$^-$ anion. For instance, only the signal at $m/e = 861$ has been observed for the compound $[CpOsHBr(PPh_3)_2]Br_3$ (compound IX), this corresponds to that of the $[CpOsHBr(PPh_3)_2]^+$ cation. But there are no signals at $m/e = 781$–783 and this precludes the possibility of fragmentation of the $[CpOsHBr(PPh_3)_2]^+$ cation under these conditions.

The expected rearrangement of compound IX may lead to the formation of: (i)

$CpOsBr(PPh_3)_2$ $m/e = 860$, or (ii) $CpOsH(PPh_3)_2$ $m/e = 782$. Experimental data however exclude the second possibility. The covalent compound $CpOsBr(PPh_3)_2$ (XIX) formed due to the rearrangement of compound IX would have signals centered at $m/e = 860$, which would superpose on the signals group with a maximum m/e at 861, corresponding to the $[CpOsHBr(PPh_3)_2]^+$ cation, which originated due to the dissociation of compound IX. Thus, in practice it is impossible to state for certain whether rearrangement of compound IX follows equation 3,

$$[CpOsHBr'(PPh_3)_2]Br_3 \rightarrow CpOsBr(PPh_3)_2 + HBr' + Br_2 \qquad (3)$$

however, as the behaviour of the remaining compounds is analogous, this is very likely. In the above case the source of the bromine atom in $CpOsBr(PPh_3)_2$, is postulated as the Br_3^- anion, which is similar to that observed in the case of the rearrangement of $[CpOsH_2(PPh_3)_2]I_3$ (compound IV), leading to the $CpOsI(PPh_3)_2$ signal at $m/e = 908$, Table 1.

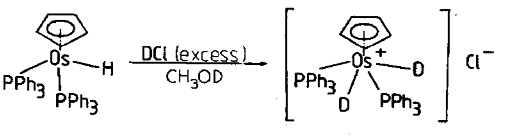
When the X anions in the ion pair are the derivatives of sulphonic acids, e.g. *p*-toluenesulphonic acid (VII) and *d*(+)-campho-10-sulphonic acid (X), in the MS(FD) spectra, signals at $m/e = 952$ and 1012 (Table 1) are observed. They were ascribed to the covalent compounds $CpOsOSO_2C_6H_4Me(PPh_3)_2$ and $CpOsOSO_2C_{10}H_{15}O(PPh_3)_2$, formed on the MS emitter device as the result of reductive elimination, according to equations 1 or 2.

Covalent halogenides of the type $CpOsX(PPh_3)_2$ (compounds XVIII–XX) only give the parent ion signal, while fragmentation to $[CpOs^+(PPh_3)_2]$ $m/e = 781$, is not observed.

It seems that both hydrogen ions, H^- are very labile, because for instance, in the reaction of $CpOsH(PPh_3)_2$ with chlorodeuterium acid (excess) one does not obtain a mixed compound, containing hydrogen and deuterium, but a fully deuterated cation (Scheme 2).

Using partially deuterated ethylene glycol (from an exchange reaction with D_2O) and carrying out a reflux of $CpOsBr(PPh_3)_2$ (see Experimental, viii) only a symmetrical cation was obtained, that was isolated as the tetraphenyl borate $[CpOsD_2(PPh_3)_2]BPh_4$ in a mixture with $[CpOsH_2(PPh_3)_2]BPh_4$. The isolated compounds V and VI were found to have characteristic IR (KBr) spectra in the range of 600–400 cm^{-1}, thus allowing the evaluation of the ratio of compound V to VI (Fig. 1). Several bands in the IR spectrum disappear when the content of $[CpOsD_2(PPh_3)_2]BPh_4$ in the mixture is increased. A similar phenomenon also occurs in the IR spectra of the solutions of the mixture V and VI in chloroform (Fig. 2). How the exchange of H^- with D^- in the compounds affects the shape of the vibration bands of triphenylphosphine is not clear.

The heterogenic reaction of $CpOsH(PPh_3)_2$ with HX_{aq} acids in methanol proceeds rapidly (several seconds). It was observed that after evaporation of the



SCHEME 2

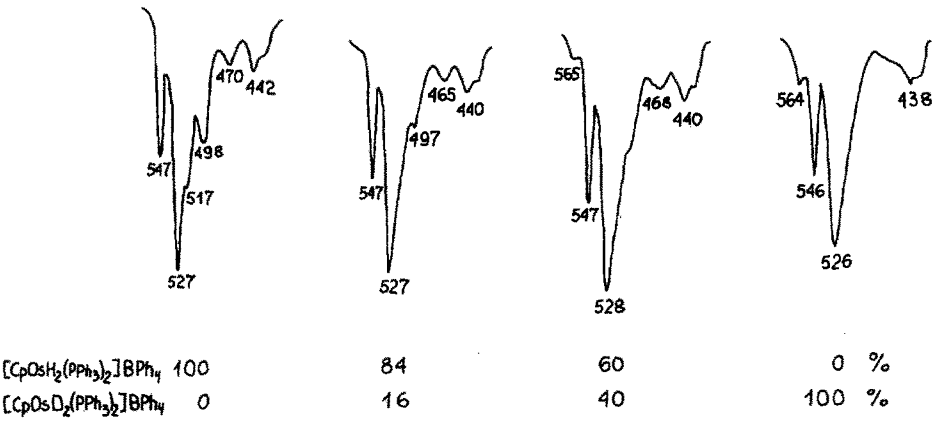


Fig. 1. The IR(KBr) spectra in the region of 600–400 cm^{-1} for the mixture $[CpOsH_2(PPh_3)_2]BPh_4$ and $[CpOsD_2(PPh_3)_2]BPh_4$.

obtained solution, containing $[CpOsH_2(PPh_3)_2]X$ and HX (excess), where X = Cl, Br, a colourless, vitreous substance, is obtained, to which the formulae I · HCl and II · HBr can be ascribed. The HX bound cannot be removed even when dried over KOH in a vacuum. Action by water decomposes the adducts and after removal of the acidic aqueous filtrate, pure I and II remain (see Experimental, i, ii). This phenomenon however has not been observed for X = I, probably owing to the lack of stability of the hypothetical III · HI compound.

The adducts obtained (I · HCl and II · HBr), are more soluble in polar solvents than their analogues (I and II). The IR (KBr) spectra of I · HCl and II · HBr are

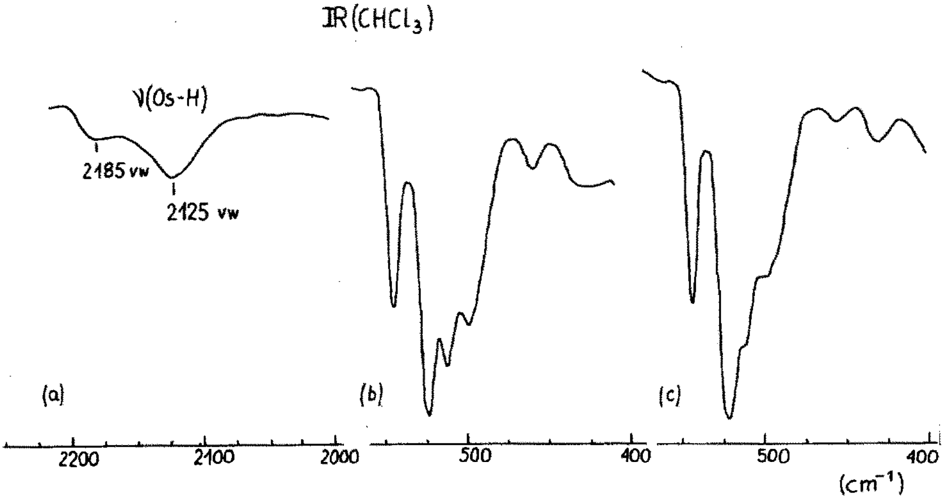
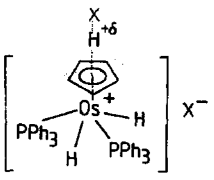


Fig. 2. The IR(CHCl$_3$) spectra of compounds V and VI. (a) The IR spectrum of $[CpOsH_2(PPh_3)_2]BPh_4$ (V), in the region 2200–2000 cm^{-1}. (b) The same as above but in region 600–400 cm^{-1}. (c) The IR spectrum in the region 600–400 cm^{-1} of the mixture containing 60% of $[CpOsH_2(PPh_3)_2]BPh_4$ (V) and 40% of $[CpOsD_2(PPh_3)_2]BPh_4$ (VI).

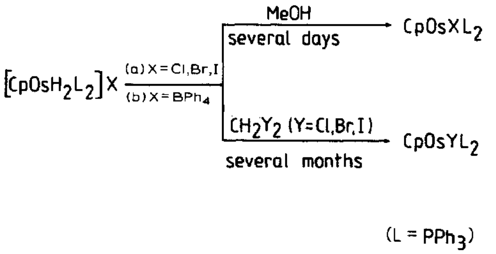


SCHEME 3

virtually the same as the spectra of I and II, except for a 900–800 cm^{-1} difference in the signal. The signal in that part of the spectrum (between 840–850 cm^{-1}) is taken to be the Cp signal [1]. In ruthenocene the CH band occurs at 806 cm^{-1} [10]. The distinguishing property of the adducts obtained (I · HCl and II · HBr) is the occurrence of an intense band at 852–850 cm^{-1} and a markedly weak band at 880 cm^{-1}. For compounds I–III the picture in the spectrum range is opposite, and the band at 880 cm^{-1} predominates. The same associate (or solvate) attribute in the IR spectra occurs for compounds XIV–XVII (solvates with CH_2Cl_2, CH_2Br_2 and CS_2).

Because the formation of the adduct causes disturbances in the cyclopentadienyl ring part of the spectrum, it is probable that the HX (or H_3O^+ X^-) bonding occurs from the other free side of the Cp ring (Scheme 3) with participation of the π Cp-ring electrons. It is known that hydrogen bonding involves the Cp ring in ruthenocene as a π-electron donor in a $CHCl_3$ solution [11,12]. Assuming that an important requirement for the formation of the Cp → H–X bonds is the posession a hydrogen atom with a partial positive charge (δ^+) (Scheme 3) facilitating the withdrawal of the electron cloud from the Cp ring, the charge decreases in large steps in the order Cl > Br > I ($\delta^+ = 0.80$, 0.55 and 0.23, respectively). Bonding in the HI molecule has an insignificant ionic character (5%) and this may explain the fact of not obtaining the III · HI adduct.

The above-mentioned tendency of $[CpOsH_2(PPh_3)_2]X$ to rearrange into $CpOsX(PPh_3)_2$ (eq. 1) observed while obtaining the MS(FD) spectra, also occurs in non-chlorinated solutions of polar solvents. Solutions of $[CpOsH_2(PPh_3)_2]X \cdot HX$ adducts as well as $[CpOsH_2(PPh)_3)_2]X$ compounds are not stable in methanol. After several days of storage, crystals of $CpOsX(PPh_3)_2$ compounds were obtained in accordance with equation 1. When another anion, Y^-, was introduced into the $[CpOsH_2(PPh_3)_2]^+$ (X^-) polar solvent system at a concentration many times higher than that of the X^- anion, mainly $CpOsY(PPh_3)_2$ was obtained along with a small amount of $CpOsX(PPh_3)_2$ (see Experimental, xvii). A process of rearrangement was



SCHEME 4

$$[CpOsH_2L_2]X + CH_2Y_2 \xrightarrow{\text{2 months}} CpOsXL_2 + CpOsYL_2$$

X	Y	%	%
Cl	Cl	42	
Cl	Br	0	63
Cl	I	0	70
Br	Cl	24	17
Br	Br	57	
Br	I	0	80
I	Cl	68	25
I	Br	36	28
I	I	87	

SCHEME 5

also observed in halogenated hydrocarbons, e.g. CH_2Y_2, where covalent $CpOsY(PPh_3)_2$ halogenides formed (Scheme 4). In the case of pathway "a" the atom of the halogen in $CpOsX(PPh_3)_2$ originates from the anion, X^-, in the case of path "b" it originates from halogenated hydrocarbons used as solvents (CHY_3, CH_2Y_2).

By allowing the rearrangement of the dihydrides into covalent halogenides where X does not equal Y, to occur (Scheme 5) both possible halogen atom sources reveal themselves, although with different yields. The tendency to form $CpOsI(PPh_3)_2$ is especially high.

The easiest way to the identification of the compound, $CpOsX(PPh_3)_2$, is by means of TLC or ^{31}P NMR spectral data (Scheme 6). Also a distinct increase in the R_F value for the sequence; Cl, Br, I ($R_F = 0.09$, 0.30 and 0.55, respectively) is a reflection of the increasing covalent nature of the Os–X bonding in $CpOsX(PPh_3)_2$ compounds. In accordance with Pearson's theory the osmium atom can be considered a soft acid. Thus, the softer the base (in this case, I^-), the more covalent is the bond that is formed.

The compound $[CpOsH_2(PPh_3)_2]SO_3C_{10}H_{15}O$ (X) contains as the anion, the rest of the optically active, *d*(+)-campho-10-sulphonic acid. In accord with expectations in the circular dichroism (CD) spectrum, a band at λ_{max} 294 nm thus occurs in the positive part of the spectrum. This indicates the existence of one anion of the *d*(+)-campho-10-sulphonic acid with an unchanged configuration in compound X.

$CpMX(PPh_3)_2$		NMR δ (ppm)	
M	X	^1H (CS_2)	^{31}P (CH_2Cl_2)
Ru	H	4.06 s	67.1 s
Ru	Cl	3.89	38.6
Ru	Br	3.92	37.2
Ru	I	3.99	36.2
Os	H	4.07	20.6
Os	Cl	4.12	-2.8
Os	Br	4.16	-5.1
Os	I	4.13	-8.2

SCHEME 6

TABLE 3

THE KNOWN COMPOUNDS OF THE TYPE $CpMX(PPh_3)_2$

M	X	Colour	Discovered in
Ru	H	yellow	1971
Ru	Cl	orange-yellow	1969
Ru	Br	orange	1969
Ru	I	deep-red	1971
Os	H	pale-yellow	1982
Os	Cl	yellow	1983
Os	Br	yellow-orange	1971
Os	I	yellow-brown	1985

The comparison of the reactivity of $CpMX(PPh_3)_2$ type complexes

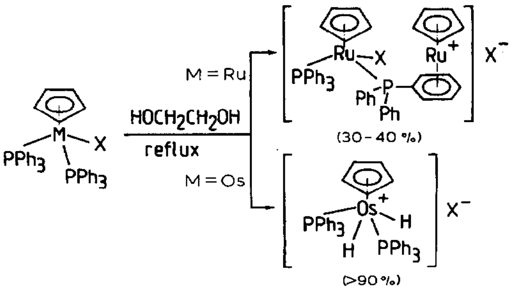
Recently, the following compounds of ruthenium and osmium halogeno(η-cyclopentadienyl)bis(triphenylphosphine)-ruthenium and -osmium were obtained, Table 3). The compounds shown in this Table are stable. Their representatives, i.e. chloro(η-cyclopentadienyl)bis(triphenylphosphine)ruthenium and the bromo-osmium analogue were obtained by Bruce in 1977 in high yield (over 90%) in one-pot syntheses from ruthenium and osmium halides, the tertiary phosphine and cyclopentadiene [13]. The full X-ray structures were obtained for $CpRuCl(PPh_3)_2$ and $CpOsCl(PPh_3)_2 \cdot CH_2Cl_2$ [14,15]. The differences between them are slight. The coordination about the metal may be described as a distorted octahedron or distorted tetrahedron, if the cyclopentadienyl ligand is considered to occupy one coordination position.

There are no significant differences between ruthenium and osmium compound series, when the infrared spectra, R_F values (TLC), colours or melting points are taken into account. This is due to the structural similarities of the representatives of both series. A more significant differentiation occurs in the proton and phosphorus NMR spectra with respect to the location of the cyclopentadienyl groups and triphenylphosphine signals, Scheme 6.

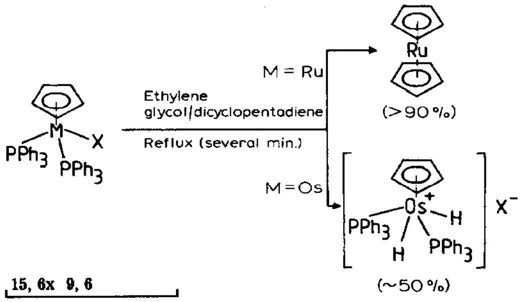
The $CpMX(PPh_3)_2$ compounds can be easily converted into their hydrides. In the reaction with the alkoxy anion in an alcoholic medium an intermediate alkoxy complex is formed, and an intramolecular hydride shift occurs, and the expected hydrides are formed with yields of over 90%. In this manner both ruthenium and osmium hydrides have been obtained [2–4]. But the reactions of the hydrides with HX acids in polar media follow quite different routes, Scheme 1.

The most significant difference occurs in the behaviour of the $CpMX(PPh_3)_2$ in boiling ethylene glycol. In the case of osmium the dihydride cation is obtained as the result of the dehydrogenation of ethylene glycol, Scheme 7, [9]. Also a significant difference occurs when in the presence of dicyclopentadiene the method of refluxing mentioned previously, is used. In the case of osmium, even traces of osmocene were not found, while for ruthenium the yield of ruthenocene exceeded 90%, Scheme 8.

It is clear that the cause of these differences in behaviour of the ruthenium and osmium series of compounds is due to greater dimensions of the osmium atom. One may thus take osmium to be:



SCHEME 7



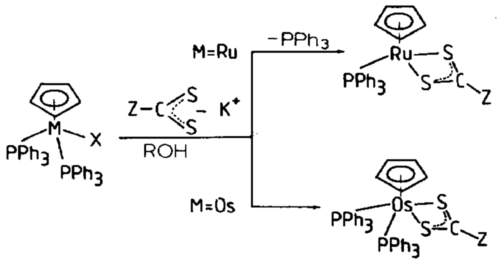
15, 6x 9, 6

SCHEME 8

(i) A poorer transmitter of nuclear spin–spin coupling effects compared to ruthenium. E.g., in proton NMR spectra of hydrides, the triplet in the up-field part of the spectrum has coupling constants equal to 27 Hz for osmium, and 34 Hz for ruthenium [4].

(ii) The easier polarizability of the osmium atom. According, to Pearson's theory it is a softer acid than the ruthenium atom.

(iii) When the group X is an extended substituent, e.g. xanthogenates or dithiocarbamates, in the osmium series, complexes with two PPh_3 are favoured, whereas for ruthenium, one PPh_3 is favoured, Scheme 9. However, under exceptional conditions it is possible to obtain an osmium derivative with one PPh_3, and two PPh_3 for ruthenium, in certain cases [2,4,16].



(Z = OR, NR_2)

SCHEME 9

Conclusions

Only a few cases of obtaining dihydride derivatives of ruthenium(IV) are known. Beside the case of the cation $[CpRuH_2(PPh_3)_2]^+$ as the salt of a strong organic acid [8], mentioned above, Blackmore, Bruce and Stone obtained $CpRuBH_4(PPh_3)_2$ by treating $CpRuCl(PPh_3)_2$ with $NaBH_4$ [1]. Spectral data indicate, that two hydrogen atoms are attached to ruthenium. Davies, Moon and Simpson obtained a stable ruthenium(IV) trihydride, which was formulated as $CpRuH_3PPh_3$ [17].

It is possible, to obtain the ruthenium(IV) dihydride directly by reaction of HX with $CpRuH(PPh_3)_2$. The final result is the compound $CpRuX(PPh_3)_2$, owing to a fast intramolecular reductive elimination process. Because PPh_3 is a σ-donor ligand of medium strength, the substitution of PPh_3 by the more nucleophilic PMe_3 ligand, should facilitate the production of Ru^{IV} derivatives. In this way it is possible to obtain $[CpRuCl_2(PMe_3)_2]^+$, for instance [6].

The few known Ru^{IV} derivatives containing a PPh_3 ligand (along with the H^- ligand) are, however, not stable in solution. The compound $[CpRuH_2(PPh_3)_2]$-$[C_5(CO_2Me)_5]$ is insoluble in most common solvents, but rapidly decomposes when an attempt is made to dissolve it in chlorinated solvents, giving $CpRuCl(PPh_3)_2$ [8]. In the case of the osmium analogue, the same reaction is considerably slower.

When a suspension of $CpOsH(PPh_3)_2$ in MeOH, is treated with an $HX + X_2$ mixture also in MeOH; in the case of $HI + I_2$ it is possible to isolate the $[CpOsH_2(PPh_3)_2]^+$ cation in the form of a sparingly soluble ion pair with the I_3^- anion (see Experimental, iv). However when an $HBr + Br_2$ mixture is used, a sparingly soluble ion pair with the Br_3^- anion was obtained, but the presence of Br_2 is marked by the introduction of Br^- into the coordination sphere of osmium(IV). The ^{31}P NMR spectrum of the $[CpOsHBr(PPh_3)_2]^+$ cation obtained showed a significant shift for the PPh_3, group of δ -12.2 ppm (see Experimental, x). Under more rigorous reaction conditions another substitution product $[CpOsBr_2(PPh_3)_2]^+$ is probably also formed. Its signal found in the ^{31}P NMR spectrum was shifted even more to the right, δ -39.5 ppm, but this compound is not yet well documented.

When $HCl + Cl_2$ are used, serious difficulties are encountered with the isolation of compounds of the above type.

Attempts to isolate the sparingly soluble ion pair by the use of $NaBPh_4$ were not successful. The decomposition of the osmium(IV) complexes to osmium(II) complexes is observed.

Experimental

The procedure and apparatus were applied as in ref. 9. The SPECORD M80 IR spectrometer and VARIAN EM-360A ^1H NMR apparatus were also used. TLC (Silufol) plates of dimensions 25 × 75 mm covered with a 0.1 mm layer of silicagel bound with starch, which were developed with iodine vapour were applied.

i. Preparation of $[CpOsH_2(PPh_3)_2]Cl$ (I)

0.9721 g of $CpOsH(PPh_3)_2$ (1.24 mmol) and 0.5 cm^3 of 12 *M* HCl_{aq} (6 mmol) were added to 20 cm^3 of MeOH. The volume of the warm solution obtained (due to exothermic reaction) was reduced. The viscous, colourless compound $[CpOsH_2$-$(PPh_3)_2]Cl \cdot HCl$ obtained was washed with water (3×50 cm^3) until the aqueous decanted solutions were neutral. The compound was dissolved once more in 20 cm^3 of MeOH, and after filtration, the volume of solution obtained was evaporated to dryness. After drying over solid KOH, 1.0925 g of I was obtained. IR (KBr) ν(Os–H) 2110vw, 2076vw cm^{-1}, the remaining part of the spectrum is identical with that of compound III.

ii. Preparation of [CpOsH$_2$(PPh$_3$)$_2$]Br (II)

0.2310 g of CpOsH(PPh$_3$)$_2$ (0.29 mmol), 10 cm^3 of MeOH and 0.1 cm^3 of 6.8M HBr$_{aq}$ (0.68 mmol) were heated at 40 °C for 40 minutes and stirred once in a while. Next the solution was evaporated at 40 °C and dried. 0.3054 g of [CpOsH$_2$(PPh$_3$)$_2$]Br · HBr was obtained as a vitreous yellow-brown substance. This substance was washed with 10 cm^3 of water and pulverized, next the acidic aqueous layer was decanted (it contained 0.25 mmol of HBr). To the solid substance obtained was added 10 cm^3 of MeOH and the suspension was repeatedly evaporated at 40 °C. After drying under vacuum, 0.2626 g of II were obtained. Methanol is not essential for the [CpOsH$_2$(PPh$_3$)$_2$]Br synthesis. So, proceeding as above, but using n-hexane instead of MeOH and heating the suspension at 55 °C for 20 minutes (with stirring) compound II was obtained in a quantitative yield. In the ^{31}P NMR spectrum of the above compound no signals were found, which could indicate the presence of CpOsBr(PPh$_3$)$_2$. IR (KBr) ν(Os–H) 2114vw, 2079vw cm^{-1}, the remaining part of the spectrum is identical with that of compound III.

iii. Preparation of [CpOsH$_2$(PPh$_3$)$_2$)]I (III)

0.1686 g of CpOsH(PPh$_3$)$_2$ (0.21 mmol), 10 cm^3 of MeOH and 0.1 cm^3 of 4.37M HI$_{aq}$ (0.44 mmol) were heated at 40 °C for 20 minutes. After evaporation at 40 °C and drying, 0.2284 g of III was obtained. Next 10 cm^3 of water was added and III was pulverized, the remaining procedure was as for ii, but the aqueous decanted solution was neutral. After drying 0.1982 g of III was obtained. IR (KBr) 2120vw, 2080vw ν(Os–H), 1592vw, 1580vw, 1487s, 1440s, 1422w, 1317m, 1190m, 1165m, 1126w, 1097s, 1080w, 1033w, 1006m, 880m, 852w, 803m, 768s, 752s, 704vs, 622w, 548s, 527s, 517s, 506m, 464m, 447w, 428w cm^{-1}.

iv. Preparation of [CpOsH$_2$(PPh$_3$)$_2$]I$_3$ (IV)

0.1101 g of CpOsBr(PPh$_3$)$_2$ (0.13 mmol) was refluxed in 10 cm^3 of ethylene glycol for 5 min. After cooling 20 cm^3 of MeOH was added to the white suspension obtained. Next, a mixture containing 0.2339 g of iodine I$_2$, 0.2337 g of potassium iodide KI, 1 cm^3 of water and 10 cm^3 of MeOH, was added to this colourless solution. After 20–30 s, yellow-brown needle-shaped crystals began to form and after 20 min these were filtered, washed with MeOH (10 cm^3), n-hexane and dried, giving 0.1221 g of compound IV.

It is also possible to obtain compound IV by treating CpOsH(PPh$_3$)$_2$ with an HI/I$_2$ mixture. Thus, to a solution of 0.0357 g of I$_2$ and 0.5 cm^3 of 4.37M HI$_{aq}$ (2.2 mmol) in 10 cm^3 of MeOH, 0.1083 g of CpOsH(PPh$_3$)$_2$ (0.14 mmol) was added. The suspension was heated at 40 °C with stirring, for 15 min. After filtration, washing and drying, 0.1197 g of IV was obtained.

v. Preparation of [CpOsH$_2$(PPh$_3$)$_2$]BPh$_4$ (V), method A

0.5274 g of CpOsBr(PPh$_3$)$_2$ (0.61 mmol) and 25 cm^3 of ethylene glycol were refluxed for 5 min then 50 cm^3 of MeOH was added and filtered, and 0.4 g of

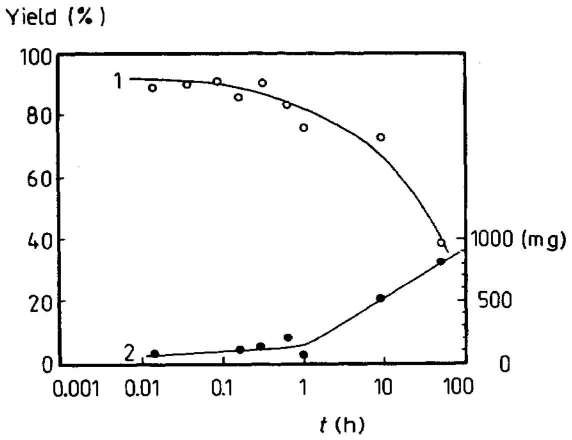


Fig. 3. The dependence of $[CpOsH_2(PPh_3)_2]BPh_4$ yield on the time for which $CpOsBr(PPh_3)_2$ is refluxed in ethylene glycol; curve 1. Weight of the evaporated benzene extracts (mg); curve 2.

$NaBPh_4$ in 5 cm^3 of MeOH was added to the filtrate. After 10 min a white precipitate was filtered off, washed and dried, giving 0.6120 g of compound V. IR (Nujol) 2142vw, 2108vw ν(Os–H), 1574m, 1476s, 1430s, 1305w, 1258w, 1179w, 1150vw, 1128w, 1086s, 1060w, 1028m, 997m, 964w, 910w, 838s, 758w, 740s, 725s, 695vs cm^{-1}.

The yield of compound V is only slightly dependent on the reflux time when it lies in the range of 0.01–1 h. The measurement of the reflux time was started when ethylene glycol began to boil. For longer reflux times the post-reaction mixture must be extracted with benzene (2 × 25 cm^3), discarding the benzene extracts. Residual benzene must be evaporated from the remaining glycol phase, and the procedure further followed as above. The dependence of the $[CpOsH_2(PPh_3)_2]BPh_4$ yield on the time of reflux is shown in Fig. 3.

Compound V can be obtained in the form of well-developed crystals in two ways.

(a) 0.1980 g of compound V (obtained according to version A) was dissolved in 5 cm^3 of chloroform. To the clear yellow solution 10 cm^3 of MeOH were added. A white, microcrystalline compound slowly began to separate out. After 5 min it was filtered, washed with 15 cm^3 of MeOH and dried. 0.1654 g of V, was obtained in the form of white, small crystals (m.p. 228–233°C dec, 83% yield of the crystallization process).

(b) 0.4890 g of $CpOsBr(PPh_3)_2$ and 25 cm^3 of diethylene glycol $(HOCH_2CH_2)_2O$ were refluxed during 2.4 min. In the interim about 0.5 cm^3 of a colourless liquid was distilled off. After cooling, the glycol phase was extracted with benzene (3 × 25 cm^3). After the rest of the benzene was removed from the glycol phase, 50 cm^3 of MeOH was added, the residue filtered and 0.3 g of $NaBPh_4$ in 5 cm^3 of MeOH was added. After several minutes long needle-shaped crystals began to form. After 40 minutes the compound was filtered, washed with MeOH, n-hexane and dried. 0.3132 g of a whitish-yellow crystalline compound of V (50% yield, m.p. 229–232°C, d) was obtained. IR ($CHCl_3$) ν(Os–H) 2185vw, 2125vw. IR (KBr) 3058m, 2995w, 2930w, 2860w, 2163vw, 2130vw ν(Os–H), 1582m, 1486s, 1440s, 1317w, 1272w, 1193w, 1140w, 1098s, 1085w, 1039m, 1010m, 850s, 756s, 742s, 710vs, 615s, 547m, 527vs, 517w, 498m, 470m, 442m cm^{-1}.

The remaining benzene extracts were combined, filtered and evaporated at 40 °C, giving a yellow-brown liquid (3.57 g). Chromatographic separation was carried out in a column (silicagel, benzene) rejecting the first colourless fraction (30 cm^3 of benzene). The lemon-yellow second fraction (100 cm^3 of benzene) was evaporated giving a lemon-yellow, vitreous substance (0.0566 g). 10 cm^3 of n-hexane was added and after pulverization of the n-hexane layer was decanted and discarded. The washed yellow residue contained $CpOsBr(CO)PPh_3$ (compound XIII; 10% yield) and $CpOsBr(PPh_3)_2$ (with 4% recovery of the substrate). Identification of $CpOsBr(CO)PPh_3$, obtained previously by Blackmore, Bruce and Stone in 1971 [1] was carried out on the basis of ^1H NMR, IR (KBr) and MS(FD) spectra. IR (KBr) ν(CO) 1930vs cm^{-1}.

vi. Preparation of $[CpOsH_2(PPh_3)_2]BPh_4$ *(V), method B*

0.1502 g of $[CpOsH_2(PPh_3)_2]Cl$ (0.18 mmol) was dissolved in 25 cm^3 of MeOH and after filtration, a solution of 0.16 g of $NaBPh_4$ (0.47 mmol) in 10 cm^3 of MeOH was added. The white precipitate was immediately filtered, giving 0.1663 g of V.

vii. Preparation of $[CpOsD_2(PPh_3)_2]BPh_4$ *(VI)*

1 cm^3 of D_2O was saturated with gaseous HCl at room temperature for 15 min. Then 0.0428 g of $CpOsH(PPh_3)_2$ (0.055 mmol) was added and the suspension stirred at room temperature for 30 min, afterwards D_2O and DCl were evaporated at 30 °C. The yellow slurry was dried under vacuum over solid KOH overnight. 1 cm^3 of CH_3OD was then added and the solution heated for 15 min at 40 °C, and CH_3OD as well as the residual D_2O were evaporated. To the colourless, sticky crystals obtained 5 cm^3 of MeOH was added and then filtered. The white precipitate obtained, when 0.08 g of $NaBPh_4$ in 2 cm^3 of MeOH was added, was filtered after 10 min, giving 0.0415 g of VI. The IR (KBr) spectrum bands at 2163 and 2130 cm^{-1} were however not observed, and in the ^1H NMR spectrum only a residual signal at δ −11.7 ppm (traces of $[CpOsH_2(PPh_3)_2]BPh_4$) was seen. The amount of non-deuterated compound V was estimated to be far below 10%. No differences in the signal locations of Cp, PPh_3 and BPh_4 in the low-field part of the ^1H NMR spectrum of the above compound, were found this compares well with the spectrum of $[CpOsH_2(PPh_3)_2]BPh_4$.

viii. Preparation of partially deuterated $[CpOsH_2(PPh_3)_2]BPh_4$ *(mixture of V + VI)*

25 cm^3 of ethylene glycol and 10 cm^3 of D_2O were refluxed for 8 h. On the next day, D_2O, H_2O were distilled off, and ca. 9.7 cm^3 of distillate was collected. To the partially deuterated ethylene glycol that remained in the distillation vessel, 0.5090 g of $CpOsBr(PPh_3)_2$ (0.59 mmol) was added, and refluxed for 18 min. The glycol phase was then extracted with benzene (2 × 25 cm^3), discarding the extracts. The residual benzene was removed from the glycol phase and 50 cm^3 of MeOH and 0.3 g of $NaBPh_4$ in 5 cm^3 of MeOH, were added. The white precipitate was filtered after 20 min, 0.5918 of the mixture containing 65% of V and 35% of VI were obtained (with a total yield of 91%, m.p. 225–235 °C dec).

In the ^1H-decoupled ^{31}P NMR spectrum of this mixture, there was a sharp singlet at δ 8.812 ppm. In the off-resonance ^1H-decoupled ^{31}P NMR spectrum of the same sample gave a broad band in the range 9.7 to 7.8 ppm.

ix. Preparation of [CpOsH$_2$(PPh$_3$)$_2$]SO$_3$C$_6$H$_4$Me (VII)

To 0.1598 g of *p*-toluenesulphonic acid $C_7H_6O_3S \cdot H_2O$ (0.84 mmol) in 10 cm^3 MeOH, 0.1576 g of CpOsH(PPh$_3$)$_2$ (0.20 mmol) was added. The mixture was heated for 2 min at 40 °C and then evaporated. The vitreous, white residue obtained was washed with water (2 × 20 cm^3). The decanted aqueous solutions together contained 0.57 mmol of acid. After drying, 0.1933 g of VII were obtained. IR (KBr) 3060m, 2122vw, 2085vw ν(Os–H), 1489m, 1442s, 1420vw, 1320vw, 1278vw, 1230m, 1208vs ν(S=O), 1191m, 1125m, 1099s, 1040m, 1018m, 852m, 821w, 753s, 704vs, 680w, 565m, 550m, 529s, 515m, 504w, 465w, 435w cm^{-1}.

x. Preparation of [CpOsHBr(PPh$_3$)$_2$]Br$_3$ (IX)

To a suspension of 0.2226 g of CpOsH(PPh$_3$)$_2$ (0.28 mmol) in 10 cm^3 of MeOH, a solution containing 0.5 cm^3 of 6.8 *M* HBr$_{aq}$ (3.4 mmol), 0.7315 g of dibromine Br$_2$ in 5 cm^3 of MeOH, was added. The suspension obtained was stirred at room temperature for 1 h. The yellow-brown precipitate was filtered, washed with 5 cm^3 of MeOH and dried and 0.2969 g of IX was obtained. Found C, 44.2; H, 2.9; Br, 28.5. $C_{41}H_{36}P_2Br_4Os$ calc. C, 44.7; H, 3.3; Br, 29.0%.

A purer sample of IX was obtained by refluxing 0.2645 g of CpOsBr(PPh$_3$)$_2$ (0.31 mmol) in 10 cm^3 of ethylene glycol for 5 min. Next, 10 cm^3 of MeOH were added followed by the addition of 0.8754 g of dibromine Br$_2$ in 5 cm^3 of MeOH. After 1 d of storage, the yellow precipitate was filtered, giving 0.2960 g of IX.

xi. Preparation of [CpOsH$_2$(PPh$_3$)$_2$]OSO$_2$C$_{10}$H$_{15}$O (X)

To a solution of 0.1077 g of *d*(+)-campho-10-sulphonic acid $C_{10}H_{16}O_4S \cdot H_2O$ (0.43 mmol) in 5 cm^3 of MeOH, 0.1561 g of CpOsH(PPh$_3$)$_2$ (0.20 mmol) was added and the mixture heated for 1 min at 40 °C, then evaporated to dryness. To the colourless, solid residue was added 10 cm^3 of water and the substance pulverized. After 3 h the acidic solution was decanted and the residue was dried. To this solid was added 5 cm^3 of MeOH, and the solution obtained filtered and evaporated to dryness, giving 0.2049 g of X. IR (KBr) 3070bm, 2960bm, 2180vw, 2100vw ν(Os–H), 1745vs ν(C=O), 1490s, 1441s, 1422w, 1398w, 1380w, 1320w, 1270w, 1237m, 1201vs ν(S=O), 1188w, 1130w, 1100s, 1042s, 1008m, 852s, 791w, 758s, 708vs, 618m, 586w, 550s, 530vs, 517m, 504w, 468m, 445w, 430w cm^{-1}.

xii. Preparation of CpOsH(PPh$_3$)$_2$ (XI)

To 120 cm^3 of MeOH, 0.55 g of metallic sodium (23.9 mmol) were added and after formation of MeONa, 1.2779 g of CpOsBr(PPh$_3$)$_2$ (1.48 mmol) were added. The suspension was heated at 55 °C for 10 h, with occasional shaking. The white-yellow, microcrystalline preparate was then filtered, washed with MeOH and n-hexane, and dried, giving 1.0331 g of XI. IR (Nujol) 2060w cm^{-1} ν(Os–H); IR (KBr) 2085w ν(Os–H) cm^{-1}.

The use of CD$_3$OD instead of CH$_3$OH causes the formation of CpOsD(PPh$_3$)$_2$ (XII) [4].

xiii. Preparation of CpOsCl(PPh$_3$)$_2$ · CH$_2$Cl$_2$ (XIV)

0.3492 g of CpOsH(PPh$_3$)$_2$ (0.45 mmol), 10 cm^3 of MeOH and 1 cm^3 of 1 *M* HCl$_{aq}$ (1 mmol) were heated at 40 °C for 15 min. MeOH, H$_2$O and HCl were then evaporated and dried. The [CpOsH$_2$(PPh$_3$)$_2$]Cl · HCl obtained, was dissolved in 2 cm^3 of CH_2Cl_2 and the yellow solution was left to stand for 2 weeks at room temperature, then, during 6 hours, CH_2Cl_2 was slowly evaporated from the solution thus obtained. The yellow, platelike crystals formed, were collected and washed with 5 drops of CH_2Cl_2, and finally dried, giving 0.1695 g of XIV. IR (KBr) 3080vw, 3055m, 1590w, 1576vw, 1485s, 1439s, 1408w, 1317w, 1274m (CH_2Cl_2), 1190m, 1160w, 1095s, 1074w, 1034w, 1005m, 922w, 848s, 809w, 748s, 738m; ν(C–Cl), 705vs, 621w, 590w, 542s, 527vs, 515s, 500m, 465m, 425m cm^{-1}. ^1H NMR (CS_2) 7.02m, PPh_3; 5.17s, CH_2; 4.05s, Cp. The X-ray structure of $CpOsCl(PPh_3)_2 \cdot CH_2Cl_2$ was determined by Bruce [15].

The reaction of $[CpOsH_2(PPh_3)_2]BPh_4$ with CH_2Cl_2, after storage of the solution for 1 month, gave $CpOsCl(PPh_3)_2$ which was isolated by extraction, and subjected to chromatographic separation (yield 22%). The substrate $[CpOsH_2(PPh_3)_2]BPh_4$ was also regenerated (36% recovery).

xiv. Preparation of $CpOsBr(PPh_3)_2 \cdot CH_2Br_2$ *(XV)*

0.5823 g of $[CpOsH_2(PPh_3)_2]BPh_4$ (0.53 mmol) were dissolved in 4 cm^3 of dibromomethane and the colourless solution was left to stand at room temperature for 25 days. The large crystals were filtered, giving 0.2310 g of XV. IR (Nujol) 1580w, 1560w, 1470s, 1428s, 1302w, 1260vw, 1194m (CH_2Br_2), 1175w, 1150m, 1083s, 1060w, 1020m, 990m, 968w, 912m, 850vw, 838s, 814w (CH_2Br_2), 798m, 737s, 690vs, 632m ν(C–Br), 586w, 576w (CH_2Br_2), 535m, 525m, 509s, 494m, 461m, 439m, 419m cm^{-1}.

xv. Preparation of $CpOsCl(PPh_3)_2 \cdot CS_2$ *(XVI) and* $CpOsBr(PPh_3)_2 \cdot CS_2$ *(XVII)*

About 0.1 g of $CpOsCl(PPh_3)_2 \cdot CH_2Cl_2$ or $CpOsBr(PPh_3)_2 \cdot CH_2Br_2$ was dissolved in 1 cm^3 of CS_2 and these solutions were left to slowly evaporate at room temperature. Compounds XVI and XVII were obtained in form of golden-yellow crystals. In the IR (Nujol) spectra a band originating from CS_2 (1510s cm^{-1} in both cases), a slight shift was found when compared with the free CS_2 band (1516s cm^{-1}). Bands indicating the presence of CH_2Cl_2 or CH_2Br_2 in the IR spectra of compounds XVI and XVII were not found. The bands in the range 900–800 cm^{-1} are typical for solvates of the type $CpOsX(PPh_3)_2 \cdot$(solv), where X = Cl, Br; (solv) = CH_2X_2, CS_2, benzene.

xvi. Preparation of $CpOsI(PPh_3)_2$ *(XX)*

0.1612 g of $CpOsBr(PPh_3)_2$ (0.19 mmol) and 10 cm^3 of ethylene glycol were refluxed for 5 minutes. After cooling, 20 cm^3 of MeOH was added, then, into the colourless solution obtained a mixture containing 0.4787 g of potassium iodide KI and 10 cm^3 of MeOH was introduced. The clear colourless solution was left to stand for 7 d. Afterwards the yellow-brown crystals were filtered, giving 0.0492 g of XX. R_F(benzene) 0.55. IR (KBr) 3060bm, 1590w, 1580vw, 1488m, 1441s, 1410w, 1320w, 1195w, 1168w, 1130vw, 1095s, 1078vw, 1038w, 1010w, 940w, 850m, 804m, 750s, 706vs, 624w, 592m, 544s, 526vs, 518s, 505m, 474m, 428m cm^{-1}.

It is also possible to obtain the compound $CpOsI(PPh_3)_2$, using $CpOsH(PPh_3)_2$ as the starting compound to rearrange $[CpOsH_2(PPh_3)_2]$ I. Thus, 0.2143 g of $CpOsH(PPh_3)_2$, 10 cm^3 of MeOH and 0.2 cm^3 of 4.37 *M* HI_{aq} were mixed, and after storage at 40°C for 20 min, evaporated to dryness. Then 10 cm^3 of MeOH were added and the solution left to stand for 5 d. Afterwards 0.0805 g of $CpOsI(PPh_3)_2$

(32% yield) was filtered off. The filtrate, after a further 50 days of storage was filtered once more, giving 0.0890 g of XX (36% yield).

xvii. The $[CpOsH_2(PPh_3)_2]^+ Br^-$ *(ethylene glycol) MeOH system*

0.3679 g of $CpOsBr(PPh_3)_2$ (0.43 mmol) and 15 cm^3 of ethylene glycol were refluxed for 5 minutes. After cooling, 5 cm^3 of MeOH were added. From the clear, colourless standard solution obtained, 5 cm^3 was taken and left to stand for 1 month, after which, 0.0107 g of crystals of $CpOsBr(PPh_3)_2$ were filtered off (12% yield).

When a further 5 cm^3 of the standard solution was added to a 5 cm^3 solution containing 0.67 g of NaBr in MeOH and left to stand, after one month, 0.0080 g of $CpOsBr(PPh_3)_2$ (9% yield) were obtained.

Using the method given above, and adding a 5 cm^3 of MeOH solution containing 0.94 g of $LiCl \cdot H_2O$ instead, when left to stand for one month, mainly $CpOsCl(PPh_3)_2$ (9% yield) and traces of $CpOsBr(PPh_3)_2$ (1.5% yield) were obtained.

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