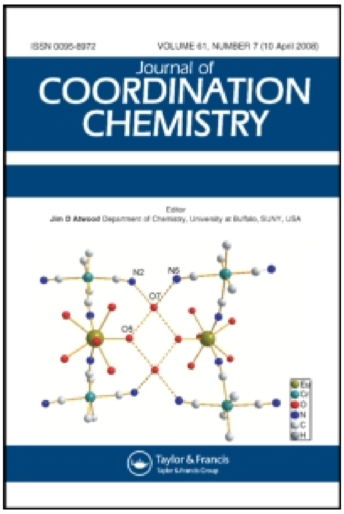

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HOMOGENOUS HYDROGENATION USING OSMIUM COMPLEXES

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$Os(II)ClH(PPh_3)_3$ (I) was generated and its catalytic properties were investigated. Solutions of 1 catalysed the hydrogenation of 1-alkenes, and of some internal alkenes with activated double bonds. Stereoselective *cis* addition of hydrogen was demonstrated with suitable model compounds. In some cases the hydrogenation reaction was accompanied by *cis-trans* or positional isomerization.

Some reactions of 1 are reported and the nmr data of 1 and related complexes are presented.

INTRODUCTION

Relatively few osmium complexes are known as homogeneous hydrogenation catalysts.[1] Attention has largely focussed on $Os(II)(CO)ClH(PPh_3)_3$;[2b,3] other catalytically active systems include $Os(III)Cl_2H(PPh_3)_3$ and $Os(III)H_3(PPh_3)_3$.[4]

We have investigated the catalytic properties of $Os(II)ClH(PPh_3)_3$ (**1**), since we expected this complex to be active under milder conditions than are required for $Os(II)(CO)ClH(PPh_3)_3$.[5] Moreover it should be noted that **1** constitutes the osmium analogue of the known hydrogenation catalyst $Ru(II)ClH(PPh_3)_3$.[6]

In the present paper we report several methods to prepare compound **1**, together with its properties as a catalyst for homogeneous hydrogenation. The mechanism of hydrogenation catalyzed by **1** will be discussed on the basis of deuteration experiments. We also report the spectroscopic properties of compound **1** as well as those of some related complexes.

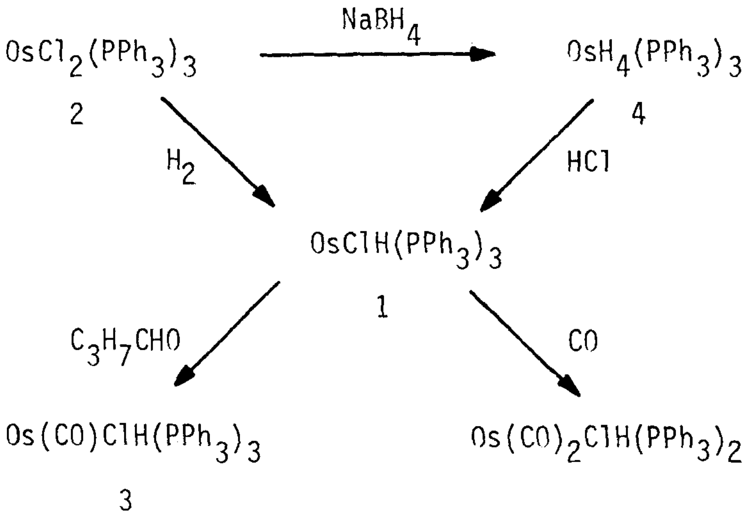
PREPARATION AND STRUCTURAL ANALYSIS

Preparation of $Os(III)Cl_2H(PPh_3)_3$ from Na_2OsCl_6 and PPh_3 in boiling ethanol has been claimed.[4] In our hands, the reaction of Na_2OsCl_6 and PPh_3 under the above conditions yielded a complex which was identified by elemental analysis and nmr spectroscopy as $Os(II)Cl_2(PPh_3)_3$ (**2**). Treatment of **2** with hydrogen afforded **1**, as shown amongst others by the appearance of a hydride signal at $\delta = -9.34$ ppm in the ^1H nmr spectrum. Aldehydes, *e.g.* butanal, reacted with **1** to give $Os(II)(CO)ClH(PPh_3)_3$ (**3**) (cf. Scheme 1), which complex was also obtained by reacting Na_2OsCl_6 and alcoholic PPh_3 at elevated temperatures.[2a]

Treatment of **2** with $NaBH_4$ afforded $Os(IV)H_4(PPh_3)_3$ (**4**), which compound was identified by ^1H and ^{31}P nmr.[7][§] Reaction of complex **4** with hydrochloric acid gave **1**; similarly, treatment of **4** with hydrobromic or hydroiodic acid yielded $Os(II)BrH(PPh_3)_3$ (**5**) and $Os(II)HI(PPh_3)_3$ (**6**), respectively. Upon treatment with butanal, **5** and **6** yielded the corresponding carbonyl complexes.

Upon treatment of **1** with pyridine a signal belonging to free PPh_3 appeared; apparently one PPh_3 ligand is substituted by pyridine. We suggest that $Os(II)ClH(PPh_3)_2(py)_2$ is formed, which assignment is in agreement with the observed ^1H nmr spectrum. Reaction of **2** and **5** with pyridine gave similar results. Carbon monoxide reacted with **1** to yield $Os(II)(CO)_2ClH(PPh_3)_2$. The nmr data of the complexes **1-6** and the reaction products are compiled in Table I; the ^{31}P nmr data of the known complex $Os(II)(CO)H_2(PPh_3)_3$ (**7**)[8] have been included.

The pentaco-ordinate complexes **1**,**2**,**5**, and **6**, and the heptaco-ordinate complex **4** show equivalence of the phosphine and – in the case of **4** – hydride ligands. This is accounted for by intramolecular exchange due to polytopal rearrangements[9-11] of these complexes. The observed mean coupling constant $^2J\,|POsH| = (3.{}^2J\,|POsH|_{cis} + {}^2J\,|POsH|_{trans})/4$ is apt to



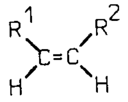
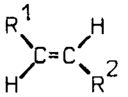
SCHEME 1

TABLE I
Nmr data of osmium complexes[a]

Compound	Os-H	Os-P
1^{b}	-9.34 {q(3Hz)}	+8.0 (br.s)
$OsClH(PPh_3)_2(py)_2^{b}$	-10.34 {t(13Hz)}	
$Os(CO)_2ClH(PPh_3)_2^{c}$	-3.46 {t(20Hz)}	
$Os(CO)ClH(PPh_3)_3^{d}$	-6.90 {d(88Hz){t(25Hz)}}	
2^{b}		+3.3 (s)
$OsCl_2(PPh_3)_2(py)_2^{b}$		-13.2 (s)
3	-7.01 {d(86Hz){t(25Hz)}}[d]	+11.3 {d(25Hz){d(11Hz)}}[c] -4.3 {d(86Hz){t(11Hz)}}
4^{c}	-8.33 {q(8Hz)}	+27.0 {quint(8Hz)}
5^{b}	-9.58 {q(6Hz)}	
$OsBrH(PPh_3)_2(py)_2^{b}$	-10.67 {t(13Hz)}	
$OsBr(CO)H(PPh_3)_3^{c}$	-7.34 {d(87Hz){t(26Hz)}}	
6^{b}	-10.10 {q(2Hz)}	
$Os(CO)HI(PPh_3)_3^{b}$	-8.07 {d(80Hz){t(25Hz)}}	
7^{c}		+23.7 {t(28Hz){d(12Hz)}} +19.4 {d(60Hz){d(16Hz){t(12Hz)}}}

[a] Varian XL-100; δ values in ppm downfield from TMS (^{1}H) or from PPh_3 (^{31}P), in parenthesis the multiplicity (d = doublet, t = triplet, q = quartet, quint = quintuplet) and the coupling constants are given.
[b] C_6H_6 solution. [c] $ChCl_3$ solution. [d] CH_2Cl_2 solution.

TABLE II
Hydrogenation of alkenes catalyzed by 1[a]

Compound	R^1	R^2	Initial[b] rate	Initial[c] concentration
$R^1\text{-}C_H\text{=}CH_2$	$n\text{-}C_4H_9$	-	72	0.5
	$t\text{-}C_4H_9$	-	74	0.5
	C_6H_5	-	64	0.8
	$CH_2C_6H_5$	-	64	0.8
	$COOCH_3$	-	22	0.8
	$COOCH_3$	$COOCH_3$	6.0	0.8
	C_6H_5	$COOCH_3$	8.3	0.1
	C_6H_5	CH_3	<0.1	0.8
	$(CH_2)_6$		13.6	0.8
	$COOCH_3$	$COOCH_3$	4.2	0.1
	C_6H_5	$COOCH_3$	1.1[d]	0.1
	CH_3	$COOCH_3$	1.9	0.1
	C_6H_5	CH_3	<0.1	0.8
$R^1\text{-}(C_H\text{=}C_H)_2\text{-}R^2$	CH_3	$COOH$	1.1[e]	0.1

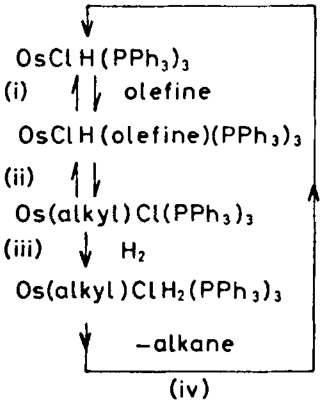
[a] 1, 0.04 mmole; benzene, 10 ml; 50°, 1 atm. [b] M min^{-1} x 10^3. [c] M. [d] Promoted with 0.4 ml of 0.1 N KOH in MeOH. [e] 2 equivalents of hydrogen consumed.

become very small since $^2J\,|\,\mathrm{POsH}\,|_{trans} \simeq -3.{}^2J\,|\,\mathrm{POsH}\,|_{cis}$.

HYDROGENATION

Complex 1, as prepared from 2 by reaction with hydrogen, catalyzed the homogeneous hydrogenation of 1-alkenes at 40-50° and 1 atm in benzene solution. Some internal alkenes were hydrogenated at a lower rate. Kinetic data are given in Table II.

As a catalyst for terminal double bond hydrogenation, 1 is about 20 times less active than its ruthenium counterpart Ru(II)ClH(PPh$_3$)$_3$. This latter catalyst exhibited a high degree of selectivity for the hydrogenation of terminal alkenes, which was attributed to steric effects.[6] A similar preference is apparent in the case of **1**, but the effect is less pronounced.† As a basis for discussion, we suggest the reaction mechanism depicted in Scheme 2, which is similar to the mechanism of hydrogenation proposed for the ruthenium complex. It cannot be excluded that the bis(triphenylphosphine) complex plays a role.[6]



SCHEME 2

The order of the reaction varied, *e.g.* ethyl acrylate and dimethly maleate showed zero order kinetics in alkene, whereas styrene (Fig. 1) followed a first order reation. The latter observation, as well as the absence of a kinetic isotope effect in the deuteration of styrene, indicates that co-ordination of alkene is the rate-determining step. On the other hand, the zero order kinetics of ethyl acrylate and dimethyl maleate suggest that in these cases one of the steps (ii)-(iv) is rate-determining.

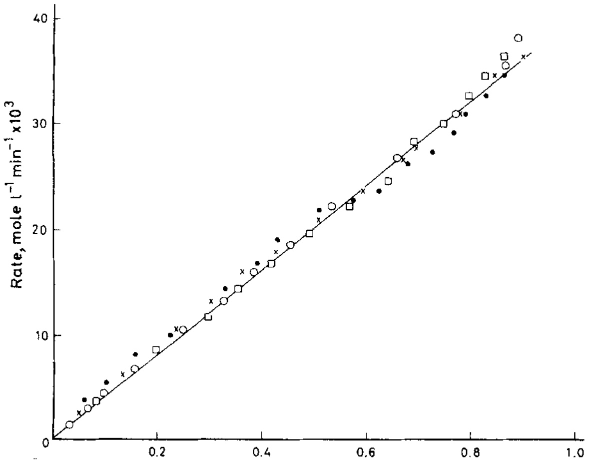


FIGURE 1 Hydrogenation of styrene (10 mmoles) with **1** (0.04 mmole) in toluene (10 ml) at 40° and 1 atm. Run 1 (○), run 2 (□), run 3 (X), run 4 (●).

The rate of styrene hydrogenation was considerably enhanced by the addition of trace amounts of water, tertiary amine, or potassium hydroxide. We ascribe this effect to the scavenging of hydrogen chloride from the reaction of **2** with hydrogen.[6] Whereas first order kinetics are maintained with amine, the hydroxylic activators show a different picture (Fig. 2).

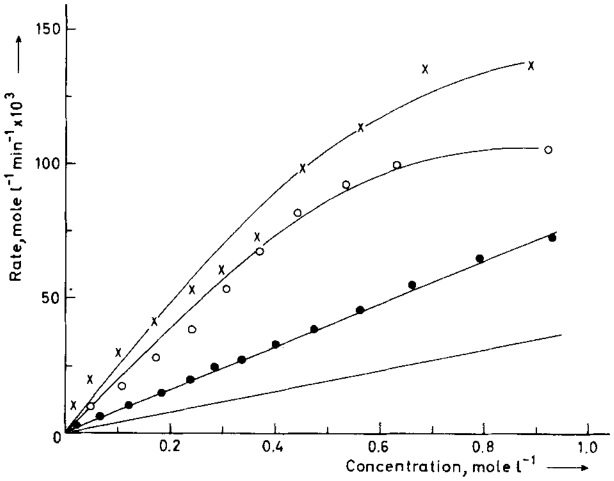


FIGURE 2 Base-promoted hydrogenation of styrene (10 mmoles) with **1** (0.04 mmole) in toluene (10 ml) at 40° and 1 atm. 0.2 ml of 0.1 N KOH in methanol (X); 0.2 ml of 1.2% H_2O in methanol (○); 0.05 ml of ethyl-diisopropylamine (●); unlabeled line, no activation.

Hydrogenation of methyl (*E*)-2-phenylethenecarboxylate (methyl *trans*-cinnamate) – which reaction required promotion of the catalyst – gave methyl 2-phenylethanecarboxylate. Deuteration afforded methyl *threo*-1,2-dideutero-2-phenylethanecarboxylate (as determined by ms and nmr) showing *cis* addition of deuterium. This would be expected, since the metal atom is involved in the transfer of both hydrogen atoms (steps (ii) and (iv)). Hydrogenation of methyl (*Z*)-2-phenylethenecarboxylate (methyl *cis*-cinnamate) was accompanied by approximately 15% isomerization to the *E*-isomer. Deuteration afforded methyl *erythro*-1,2-dideutero-2-phenylethanecarboxylate. The stereospecificity, as well as the isotopic analyses of the deuterated products by ms and nmr (see experimental part), indicate that the hydrogenation is a rather straightforward process. Isotopic exchange does not occur to an important degree, unless in combination with isomerization; from the stereospecificity as well as from the small amounts of trideuterated products it appears that isomerized product does not participate in further reaction. Isomerization can be effected by reversal of steps (ii) and (i) (Scheme 2) and should be accompanied by incorporation of one deuterium atom. Accordingly, the isotopic contents of the *E*-isomer formed in the deuteration experiment was as follows d$_0$ 10%,1-d$_1$ 45%,2-d$_1$ 45%,d$_2$ 0% (obtained by ^{1}H nmr). The results seem to indicate that transfer of the first hydrogen atom (step ii) occurs equally on C$_1$ and C$_2$[5].

Migration of the double bond can be visualized by reversal of steps (ii) and (i) if in the reversed *cis* ligand migration (step (ii)) a hydrogen atom is abstracted from an adjacent position. This is observed with 3-phenylpropene: hydrogenation afforded 1-phenylpropane (73%), (*E*)-1-phenylpropene (24%), and (*Z*)-1-phenylpropene (3%).

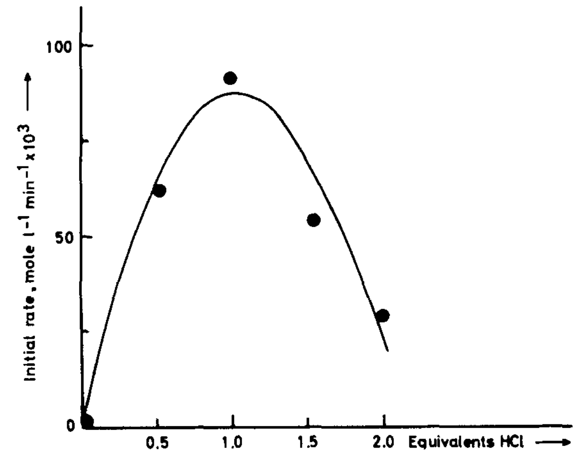


FIGURE 3 Hydrogenation of styrene (10 mmoles) with 4 (0.02 mmole) in benzene (10 ml) promoted with HCl in methanol (0.2 ml) containing 1% H$_2$O at 40° and 1 atm.

The tetrahydrido complex 4 showed no catalytic activity, but hydrogenations proceeded upon treatment of benzene solutions of 4 with hydrogen halide HX(X = Cl,Br,I). In the case of HCl optimum activity was attained when 1 equivalent was used (see Fig. 3). We suggest that oxidative protonation occurs, yielding Os(VI)H$_5$(PPh$_3$)$_3$$^+$. Cl$^-$, followed by reductive elimination of 2 moles of hydrogen[12] leading to 1. This is supported by the comparable activities of 1 and HCl-treated solutions of 4. Treatment of 4 with 0.5 equivalent of iodine gave the same results as activation with 1 equivalent of HI. *Inter alia* we would like to note that Os(IV)Cl$_4$(PPh$_3$)$_2$ showed catalytic activity upon treatment with 2 equivalents of potassium hydroxide. In this case we also believe the active species to be an osmium hydrido complex formed by reaction of Os(IV)Cl$_4$(PPh$_3$)$_2$ with hydrogen, followed by elimination of hydrochloric acid.

EXPERIMENTAL

Materials

Disodium hexachloroosmate(IV) was supplied by Drijfhout, Amsterdam; triphenylphosphine was purchased from Fluka. All solvents were reagent grade *ex* UCB and Merck. Nitrogen was purified over BTS catalyst, hydrogen was passed through a Deoxo unit.

Preparation of Complexes

All reactions were carried out in a closed apparatus under nitrogen. Compounds 3 and 7 were prepared according to the literature[2,8].

Dichlorotris(triphenylphosphine)osmium(II) (2): A solution of disodium hexachloroosmate(IV) (0.50 g, 1 mmole) in 95% ethanol (15 ml) was added dropwise to a boiling, stirred solution of triphenylphosphine (1.53 g, 6 mmoles) in 95% ethanol (40 ml). The solution was stirred and heated under reflux for 6 hr and filtered; the solid was washed successively with ethanol, water, and ethanol and dried *in vacuo* (0.84 g, 80%).

Anal. Calcd. for C$_{54}$Cl$_2$H$_{45}$OsP$_3$:C, 61.89; Cl, 6.77; H, 4.33. Found: C, 61.43; Cl, 7.11; H, 4.34.

Tetrahydridotris(triphenylphosphine)osmium(IV) (4): To a stirred, boiling suspension of 2 (0.5 g, 0.5 mmole) in ethanol (40 ml) was added dropwise a solution of sodium borohydride (0.5 g, 13.5 mmoles) in ethanol (20 ml). The colour of the suspension changed from green to white immediately. The suspension was stirred and heated under reflux for 5 hr; the solid was filtered, washed with ethanol, water, and ethanol and dried *in vacuo* (0.45 g, 95%).

Anal. Calcd. for C$_{54}$H$_{49}$OsP$_3$: C, 66.11; H, 5.03.Found: C, 66.39; H, 5.04.

Tetrachlorobis(triphenylphosphine)osmium(IV): A solution of triphenylphosphine (0.79 g, 3 mmoles) in ethyl methyl ketone (10 ml) was added dropwise to a stirred solution of disodium hexachloroosmate(IV) (0.25 g, 0.5 mmole) in ethyl methyl ketone (15 ml). The resulting mixture was heated under reflux for

4 hr. After 0.5 hr a light-brown product precipitated which was eventually filtered, washed with ethanol, water, and ethanol and dried *in vacuo* (0.24 g, 55%).

Anal. Calcd. for $C_{36}Cl_4\ H_{30}OsP_2$: C, 50.48; Cl, 16.55; H, 3.53. Found: C, 51.78; Cl, 15.55; H, 3.58.

Carbonylation Reactions

Carbonylation reactions were performed with active catalyst solutions, obtained by dissolving **2** under hydrogen or deuterium in benzene.

With carbon monoxide: Carbon monoxide (20 ml, ambient conditions) was injected into a solution of $Os(II)ClD(PPh_3)_3$ (0.1 mmole) in benzene (10 ml) under deuterium. The solution was stirred during 1 hr at 50°. Upon addition of ethanol, dicarbonylchlorodeuteridobis(triphenylphosphine)osmium(II) was precipitated as a white product, filtered, washed with ethanol, water, and ethanol and dried *in vacuo* (0.66 g, 76%). IR(KBr)ν_{CO}: 1955, 2040 cm^{-1}.

Anal. Calcd. for $C_{38}ClDH_{30}O_2OsP_2$: C, 56.47; Cl, 4.39; H, 3.99. Found: C, 55.00; Cl, 6.59; H, 3.78.

With butanal: Butanal (3 ml) was injected into a solution containing **1** (0.43 mmole) in benzene (10 ml). The resulting solution was stirred for 3 hr at 50°. The product **3** was precipitated by addition of ethanol, filtered, washed with ethanol, water, and ethanol and dried *in vacuo* (0.28 g, 62%), IR (KBr) ν_{CO}: 1910, ν_H: 2100 cm^{-1}.

Anal. Calcd. for $C_{55}ClH_{46}OOsP_3$: C, 63.42; Cl, 3.40; H, 4.45. Found: C, 63.45; Cl, 3.55; H, 4.78.

Hydrogenation Experiments

Hydrogenation experiments were conducted in a double-walled, thermostatted vessel, equipped with a magnetic stirrer, a revolver for the addition of solids, and a serum cap. **2** was dissolved under hydrogen in benzene or toluene and substrate (purified over alumina) was injected.

When using **4** as a precursor of **1**, 1 equivalent of acid (1 N in methanol containing 1% water) was injected, the solution stirred for 1 hr and the substrate injected.

Deuteration of Methyl 2-phenylethenecarboxylate

Methyl (*E*)-2- and (*Z*)-2-phenylethenecarboxylate were deuterated according to the procedure described above. The saturated products were analyzed by ^1H nmr and ms (apparatus Varian-Mat SM1); the data are compiled in Table III.

The diastereomers of the product methyl 1,2-dideutero-2-phenylethanecarboxylate were assigned on the basis of ^1H nmr. The products were compared with *bona fide* methyl *erythro*- and *threo*-1,2-dideutero-2-phenylethanecarboxylate prepared from the methyl 2-phenylethenecarboxylates by reaction with dideuterodi-imide[13]. The ^1H nmr spectra of these products showed unresolved multiplets of the methylene moities; upon decoupling of deuterium these signals collapsed into AB systems with J_{AB} = 8.8 Hz (*erythro*) and 6.5 Hz (*threo*), respectively. These data are in agreement with the values which were calculated from the spectrum of methyl 2-phenylethanecarboxylate.[14]

TABLE III
Deuteration of methyl 2-phenylethenecarboxylates[a]

Substrate	nmr position (at D)			ms isotopic contents (%)				
	1	2	$\bar{D}$	d_0	d_1	d_2	d_3	$\bar{D}$
(E)	0.85	1.1	1.95	0.9	16.6	75.6	6.8	1.88
(Z)	1.0	0.8	1.8	3.0	20.4	71.0	5.2	1.78

[a] $Os(II)\ Cl_2\ (PPh_3)_3$ 0.04 mmole; substrate 2 mmoles; benzene 10 ml; 50°, 1 atm.

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[§] Presumably, the complex reported as $Os(III)H_3(PPh_3)_3$, and prepared from the alleged product $Os(III)Cl_2H(PPh_3)_3$, has to be revised into $Os(IV)H_4(PPh_3)_3$.

[†] Cf. the ratio of reaction rates found for $Ru(II)ClH(PPh_3)_3$[6]: 1-hexene/cyclohexene = 1.4×10^3; whereas for **1** 1-hexene/cyclooctene = 5.3.