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Note

Synthesis and catalytic properties of the complex $[OsH(CO)(NCMe)_2(PPh_3)_2]BF_4$

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Abstract

The cationic complex $[OsH(CO)(NCMe)_2(PPh_3)_2]^+$ (4), isolated as its BF_4^- salt, was synthesized in high yields by reaction of $OsHCl(CO)(PPh_3)_3$ (3) with acetonitrile in the presence of $NaBF_4$. The spectroscopic data are consistent with an octahedral geometry around the osmium atom, with two phosphines mutually *trans* and the acetonitriles mutually *cis*. Complex 4 is shown to be an efficient precatalyst for the hydrogenation of benzaldehyde, cyclohexanone, cyclohexene and quinoline. For the hydrogenation of carbonyl compounds to their corresponding alcohols in 2-methoxyethanol, complex 4 showed a catalytic activity somewhat lower than 3 and than their analogous complexes of ruthenium. However, for the hydrogenation of cyclohexene to cyclohexane and for the quinoline reduction to 1,2,3,4-tetrahydroquinoline, in xylene solvent, the activities were higher for the osmium complexes. The results show that the cationic osmium complex is a more efficient precatalyst for the hydrogenation of C=C and C=N bonds than for C=O bonds in selected substrates.

Keywords: Homogeneous hydrogenation; Osmium complexes; Hydrido complexes; Acetonitrile complexes; Carbonyl complexes

1. Introduction

The chemistry of triphenylphosphine complexes of ruthenium(II) has attracted much attention in view of their catalytic activity in a variety of reactions [1]. Thus, for example, $RuHCl(CO)(PPh_3)_3$ (1) [2,3] and $[RuH(CO)(NCMe)_2(PPh_3)_2]BF_4$ (2) [2–7] are efficient precatalysts for a variety of organic reactions. On the other hand, the use of osmium complexes as precatalysts has been limited, perhaps because the third row transition metals usually form more stable species than their second row congeners, which has led to the general assumption that reactions typically forming catalytic cycles are too slow for 5d metal complexes to be of any practical use in catalysis. However, some organic reactions (isomerization, hydrogenation, hydrosilylation, dimerization, hydroformylation and asymmetric dihydroxylation reactions) catalyzed by osmium complexes have emerged in the literature in the past few years. Examples of osmium complexes used as precatalysts in organic transformations have been recently reviewed; the complex $OsHCl(CO)(PPh_3)_3$ (3) and other $OsHX(CO)(PR_3)_n$ compounds have been used by the groups of Sanchez-Delgado and Oro mostly in hydrogenation reactions [8].

In this paper we present the synthesis and spectroscopic characterization of a cationic osmium complex, namely $[OsH(CO)(NCMe)_2(PPh_3)_2]BF_4$ (4). The catalytic activity of this complex is explored in the hydrogenation of cyclohexene, benzaldehyde, cyclohexanone and quinoline. A comparison of its catalytic activities with those of the corresponding neutral complex 3 and their ruthenium analogues 1 and 2 was also carried out. To the best of our knowledge, 4 is one of very few cationic phosphine–osmium complexes used in a catalytic process; there is one report of Bianchini et al. [9] on the use of complexes of the type $[OsHL(P(CH_2CH_2PPh_2)_3)]^+$ ($L=H_2$, N_2) for the reduction of α,β-unsaturated ketones and for the stereoselective dimerization of acetylenes.

2. Experimental

2.1. Instruments and materials

All manipulations were carried out with rigorous exclusion of air. This condition is required for successful hydrogenation. Cyclohexene, benzaldehyde, cyclohexanone and quinoline were purified by distillation at reduced pressure. Solvents of analytical grade were dried by known procedures and distilled under inert atmosphere prior to use; other com-

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mercially available reagents were used without further purification. Complexes **1** [10] and **2** [2] were prepared by published procedures. NMR (in $CDCl_3$) and IR (in KBr discs) spectra were recorded on a Bruker AM-300 spectrometer and Nicolet FT-IR 5DXC instrument, respectively. Conductivity data were measured with a 122 model Orion apparatus using nitromethane as the solvent. Elemental analysis were carried out by means of an EA 1108 model Fisons Instrument apparatus.

2.2. $OsHCl(CO)(PPh_3)_3$ (3)

Complex **3** was obtained by the method previously reported in the literature [10], using $OsCl_3 \cdot 3H_2O$ (410 mg, 1.38 mmol) in the place of $K_2[OsCl_6]$ (yield 90%).

2.3. $[OsH(CO)(NCMe)_2(PPh_3)_2][BF_4]$ (4)

Complex **3** (250 mg, 0.24 mmol), $NaBF_4$ (40 mg, 0.24 mmol) and MeCN (15 ml) were placed in a 100 ml two-necked round-bottom flask equipped with a magnetic stirring bar. The suspension was initially heated to mild reflux for 2 h. The solution was filtered under nitrogen and evaporated to dryness in vacuo. The crude solid was washed with diethyl ether (3×5 ml) in order to remove free PPh_3, and then dissolved in the minimum amount of dichloromethane and finally precipitated by slow addition of n-pentane, to obtain white microcrystals of **4**, which were washed with diethyl ether and pentane and dried in vacuo (70% yield). IR, ν(Os–H) 2125 (m), ν(CO) 1935 (s) and ν(BF) 1080 (vs) cm^{-1}; m.p. 180–182°C (dec.). *Anal.* Calc. for $OsC_{41}H_{37}N_2BF_4OP_2$: C, 54.0; H, 4.1; N, 3.1. Found: C, 54.4; H, 4.1; N, 2.8%.

2.4. Procedure for hydrogenation experiments

In a typical experiment the catalyst and the substrate, dissolved in the appropiate solvent (50 ml total volume), and a stirring bar were introduced into a glass-lined stainless steel autoclave (125 ml) fitted with a high precision manometer. Air was removed by flushing three times with argon, then the vessel was equilibrated for ~30 min in a silicone-oil bath which was thermostatted at the reaction temperature, and subsequently charged to the desired pressure. During the catalytic run, the consumption of hydrogen was periodically measured and the total pressure of the system was continuously adjusted to a constant value by admitting hydrogen from a high pressure reservoir. The catalytic mixtures at the end of the reaction were cooled in ice and were immediately analyzed by means of a 610 Series UNICAM gas chromatograph fitted with a thermal conductivity detector and a 3 m 10% SE-30 glass column using helium as the carrier gas. The results were quantified with a UNICAM 4815 computing integrator using the internal standard method.

The consumption of hydrogen was converted to molar concentration of the corresponding product taking into account the stoichiometry of the reaction, and then plotted versus time to yield straight lines which were fitted by conventional linear regression programs. Initial rates of the reaction were obtained from the corresponding slopes. The percentage of hydrogenation in the catalytic reactions was restricted to 5–10% in order to employ the initial rate method [11].

Each reaction was repeated at least twice in order to ensure reproducibility of the results. Statistical analyses were carried out using analysis of variance (ANOVA) to test the difference between means. Significant difference was considered when $P < 0.05$.

3. Results and discussion

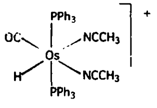
3.1. The complex $[OsH(CO)(NCMe)_2(PPh_3)_2][BF_4]$ (4)

As $OsHX(CO)(PPh_3)_3$ have been shown to be efficient precatalysts in a number of important catalytic reactions [8], we have turned our attention toward the synthesis of more soluble cationic derivatives containing acetonitrile ligands, which are often more labile than phosphines and may result in an enhanced activity. Surprisingly, the chemistry of cationic osmium complexes has been little developed; Roper and co-workers briefly mentioned the formation of the cationic complex $[OsH(CO)(NCMe)_2(PPh_3)_2]ClO_4$ by reaction of $OsHCl(CO)(PPh_3)_3$ with $AgClO_4$ in acetonitrile, without synthetic and spectroscopic details [12]. However, we found that this compound is more conveniently obtained in high yields by using $NaBF_4$ instead of the potentially explosive perchlorate salts.

Complex **4** may be isolated in high yields from the reaction of **3** with $NaBF_4$ in acetonitrile. This compound is an air stable, white crystalline material which melts with decomposition at 180–182°C. It is very soluble in acetonitrile, acetone, chloroform and dichloromethane, and moderately soluble in toluene, tetrahydrofuran and alcohols. The conductivity of a 10^{-3} M solution of the osmium complex **4** in nitromethane was 68 $cm^2\ ohm^{-1}\ mol^{-1}$ (or 85 $cm^2\ ohm^{-1}\ mol^{-1}$ at infinite dilution), which corresponds well to that of a 1:1 electrolyte [13]. The IR spectrum of **4** (KBr disc) shows a medium intensity band at 2125 cm^{-1} due to the Os–H stretch, a strong ν(CO) band at 1935 cm^{-1}, and a very strong band at 1080 cm^{-1} characteristic of the BF_4^- anion.

The ^1H NMR spectrum shows, besides the coordinated PPh_3 signals, two singlets at 1.8 and 1.5 ppm corresponding to two inequivalent bound acetonitriles, plus a triplet at -13.8 ppm (^2J(H–P) = 16 Hz), consistent with a metal hydride in a *cis* disposition with respect to two equivalent phosphine ligands. These signals are in the corresponding relative integrals 30:3:3:1. Correspondingly, the $^{31}P\{^1H\}$ NMR spectrum consists of a singlet at 16.6 ppm which confirms the equivalence of the triphenylphosphine ligands.

These spectroscopic data are consistent with the stereochemistry shown as **4**, containing one hydride ligand *cis* to two equivalent triphenylphosphines, and the two acetonitrile mutually *cis*.



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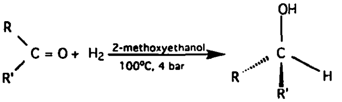
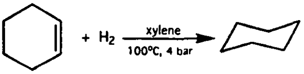
3.2. Catalytic properties of complex 4

The complex $[OsH(CO)(NCMe)_2(PPh_3)_2]BF_4$ (**4**) was chosen as the precatalyst on the basis of the known catalytic activity of its ruthenium analogue **2** for some hydrogenation reactions and of the versatility found for some osmium complexes.

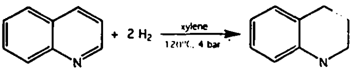
This complex proved to be an efficient catalyst precursor for the homogeneous hydrogenation of unsaturated organic substrates such as carbonyl compounds (Eq. (1)), cyclohexene (Eq. (2)) and N-aromatic compounds such as quinoline (Eq. (3)), under mild conditions of temperature and pressure.



(1)



(2)



(3)

The hydrogenation of carbonyl compounds (benzaldehyde and cyclohexanone) to their corresponding alcohols in 2-methoxyethanol solvent, was efficiently carried out using complexes **1**–**4** (Table 1). Although the values for initial rates are all rather similar, some significant differences are observed. For the hydrogenation of benzaldehyde, no significant differences ($P = 0.01$) were observed for complexes **1**–**3**, while the cationic Os complex **4** showed a catalytic activity two times lower ($P = 0.05$) than that of the corresponding neutral osmium complex **3** and those of the analogous ruthenium complexes (**1** and **2**). For the cyclohexanone substrate, identical trends have been obtained for complexes **1**–**4**. Similar differences between neutral complexes of ruthenium and osmium have been obtained by Sánchez-Delgado et al. for the hydrogenation of propionaldehyde and acetone [14].

For the hydrogenation of cyclohexene to cyclohexane at 100°C and 4 bar of H_2 in xylene solution (Eq. (2)), the osmium complexes showed significantly higher activities ($P = 0.01$). Representative examples of the catalytic runs for this reaction are shown in Fig. 1, and the values of initial rates are collected in Table 2. Analysis of these results reveals that both the ruthenium and osmium complexes tested are very efficient precatalysts for the hydrogenation of cyclohexene. The cationic osmium complex **4** showed a catalytic activity statistically lower ($P = 0.01$) than that of its neutral precursor **3**. and five times more active than that of the corresponding cationic ruthenium complex **2**.

Table 1
Hydrogenation of carbonyl compounds catalyzed by ruthenium and osmium complexes

Catalyst	Benzaldehyde		Cyclohexanone	
	$10^5\ r_i\ (M\ s^{-1})$ [a,b]	TN [b,c]	$10^5\ r_i\ (M\ s^{-1})$ [b,d]	TN [b,c]
1	(2.24 ± 0.18)	84 ± 7	(2.00 ± 0.10)	77 ± 4
2	(1.99 ± 0.08)	75 ± 3	(1.54 ± 0.09)	59 ± 3
3	(1.98 ± 0.06)	74 ± 2	(1.98 ± 0.06)	76 ± 2
4	(1.12 ± 0.21)	42 ± 8	(0.74 ± 0.12)	28 ± 5

[a] 100°C, bar, [benzaldehyde] = 0.96 M, [catalyst] = 9.6×10^{-4} M, 2-methoxyethanol.

[b] (mean ± s.e.m.).

[c] Turnover number in 1 h.

[d] 100°C, 4 bar, [cyclohexanone] = 0.94 M, [catalyst] = 9.4×10^{-4} M, 2-methoxyethanol.

The reduction of C=N bonds requires somewhat more drastic reaction conditions than that of the C=O and C=C bonds. Thus, the regioselective reduction of quinoline to give exclusively 1,2,3,4-tetrahydroquinoline (THQ) under mild conditions (120°C and 4 bar H_2) in xylene solvent (Eq. (3)) was efficiently carried out by using **4** as the precatalyst. Representative examples of quinoline hydrogenation are shown in Fig. 2, and the values of initial rates are collected in Table 3. The cationic osmium complex showed significantly higher catalytic activity for this reaction. Thus, **4** presented an activity statistically higher ($P = 0.01$) than that of its ruthenium analogue and showed to be twenty times more active than the neutral osmium complex **3**. Hydrogenation of the benzene ring of quinoline does not take place to any detectable extent during the hydrogenation runs. Sánchez-Delgado and González found that the ruthenium complex **1** was somewhat more active than its analogous osmium complex **3**, under more drastic conditions [15].

For the rest of the heteroaromatic nitrogen compounds under the same conditions of quinoline reduction, complex **4** is also an efficient catalyst precursor for the hydrogenation of isoquinoline (9.33×10^{-6} M s^{-1}) and acridine (1.72×10^{-5} M s^{-1}).

4. Conclusions

The catalysis results show that the cationic osmium complex, $[OsH(CO)(NCCH_3)_2(PPh_3)_2]BF_4$, is a more efficient catalyst precursor for the hydrogenation of C=C and C=N bonds than for C=O bonds. This enhanced selectivity can be

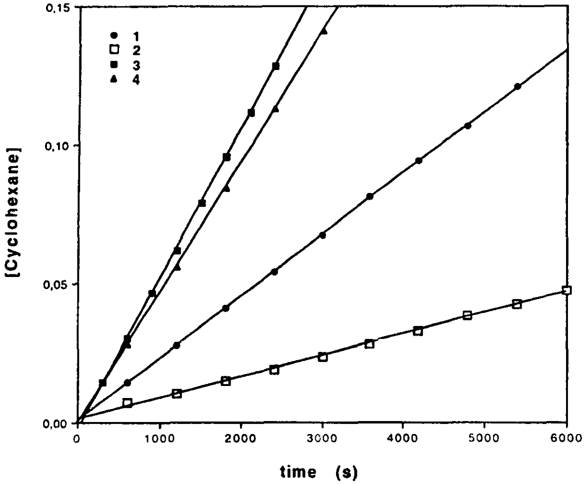


Fig. 1. Representative examples of the cyclohexene hydrogenation catalyzed by ruthenium and osmium complexes. Conditions as in Table 2.

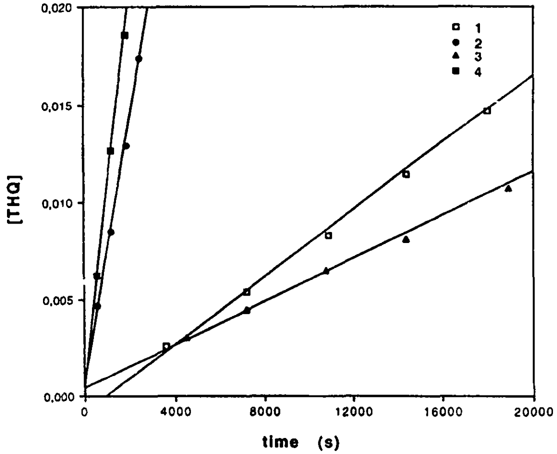


Fig. 2. Representative examples of the quinoline reduction catalyzed by ruthenium and osmium complexes. Conditions as in Table 3.

rationalized in terms of a greater ability of this charged osmium complex to coordinate the C=C and C=N functional groups of the substrates to the appropiate extent to promote subsequent hydrogen transfer. These features ratify the possibility of using osmium complexes for the catalytic treatme of more sophisticated unsaturated molecules, as propose elsewhere [8]. In this sense, kinetic, coordination chemist and theoretical investigations are in progress in our laborato

Table 2
Hydrogenation of cyclohexene catalyzed by ruthenium and osmium complexes

Catalyst	$10^5 r_i$ (M s^{-1}) [a,b]	TN [b,c]
1	(2.16 ± 0.05)	79 ± 2
2	(0.82 ± 0.06)	30 ± 2
3	(5.21 ± 0.23)	191 ± 8
4	(4.55 ± 0.03)	167 ± 6

[a] 100°C, 4 bar, [cyclohexene] = 0.98 M, [catalyst] = 9.8×10^{-4} M, xylene.
[b] (mean ± s.e.m.).
[c] Turnover number in 1 h.

Table 3
Hydrogenation of quinoline catalyzed by ruthenium and osmium complexes

Catalyst	$10^6 r_i$ (M s^{-1}) [a]	TN [b]
1	(0.84 ± 0.08)	4 ± 1
2	(7.73 ± 0.23)	33 ± 1
3	(0.53 ± 0.03)	2 ± 1
4	(9.77 ± 0.01)	42 ± 2

[a] 120°C, 4 bar, [quinoline] = 0.17 M, [catalyst] = 8.4×10^{-4} M, xylene.
[b] (mean ± s.e.m.).
[c] Turnover number in 1 h.

in order to gain deeper insight into the catalytic behavior of these osmium complexes.

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