$[H(EtOH)_2][\{OsCl(\eta^4\text{-COD})\}_2(\mu\text{-H})(\mu\text{-Cl})_2]$ as an Intermediate for the Preparation of $[OsCl_2(COD)]_x$ and Its Activity as an Ionic Hydrogenation and Etherification Catalyst

Miguel A. Esteruelas,* Cristina García-Yebra,* and Enrique Oñate

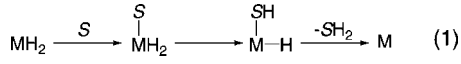
Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain

Received February 19, 2008

Complex $[H(EtOH)_2][\{OsCl(\eta^4\text{-COD})\}_2(\mu\text{-H})(\mu\text{-Cl})_2]$ (**1**) reacts with 1-hexene, acetone, and acetophenone to give the corresponding reduced organic substrates and the osmium polymer $[OsCl_2(COD)]_x$ (**2**, COD = 1,5-cyclooctadiene), which regenerates **1** in ethanol. The reaction of **2** with acetonitrile leads to the mononuclear derivative $OsCl_2(\eta^4\text{-COD})(CH_3CN)_2$ (**3**). On the other hand, treatment of **1** with acetonitrile affords the neutral dimer $\{Os(CH_3CN)(\eta^4\text{-COD})\}(\mu\text{-H})(\mu\text{-Cl})_2\{OsCl(\eta^4\text{-COD})\}$ (**4**), which has been characterized by X-ray diffraction analysis. The reaction of **4** with triisopropylphosphine gives $\{Os(P\textit{i}\text{-}Pr_3)(\eta^4\text{-COD})\}(\mu\text{-H})(\mu\text{-Cl})_2\{OsCl(\eta^4\text{-COD})\}$ (**5**). Complex **1** is an active catalyst for the ionic hydrogenation of aldehydes and ketones, using 2-propanol as hydrogen source. The reductions of aromatic compounds are easier than those of aliphatic ones, and the hydrogenations of aldehydes are also easier than those of ketones. Complex **1** also promotes the alcohol etherification and one-pot synthesis of isopropyl ethers starting from 2-propanol and the corresponding aldehyde or ketone through catalytic hydrogenation−etherification tandem processes.

Introduction

The traditional homogeneous catalytic hydrogenation of unsaturated organic substrates (*S*) by hydride transition metal complexes takes place on the coordination sphere of the metal center via insertion and subsequent reductive elimination (eq 1).[1]



(1)

However, there have been reports where a transition metal can add a hydrogen molecule to unsaturated organic substrates by a different mechanism involving proton and hydride transfer steps (eq 2).[2] Such an ionic hydrogenation mimics biological reductions, which heterolytically cleaves the hydrogen molecule, and H^- and H^+ are separately added to the substrates.[3] Hydrogenation by an ionic mechanism potentially offers the advantage of the compatibility with ionizing solvents such as water and alcohols.[4]

Aldehydes and ketones are organic compounds that incorporate a carbonyl functional group susceptible to hydrogenation

(2)

by an ionic mechanism.[5] The hydrogenation of the C═O double bond has found widespread application in organic chemistry, and it is particularly relevant in the preparation of compounds of interest to the pharmaceutical and agricultural industries.[6]

Reductive etherification is another interesting transformation of this type of compound, which is known as an elegant alternative method to the Williamson ether synthesis. The reductive etherification of ketones and aldehydes with alcohols to afford unsymmetrical ethers is promoted by Lewis acids. Molecular hydrogen, trialkylsilanes, and decaborane have been used as reducing agents.[7]

Osmium is less often used in catalysis compared with the platinum metals,[8] and its organometallic chemistry[9] is also lesser known. This is in part a consequence of the little effort done to find starting materials from commercially available inorganic salts and to optimize the synthetic procedures leading to them. The osmium-1,5-cyclooctadiene polymer $[OsCl_2(COD)]_x$ is an example of a precursor that should be useful to develop a wide series of derivatives in both stoichiometric and catalytic transformations. However, the procedure for its preparation does not appear to be clear. In 1966, Winkhaus et al.[10] reported that the treatment of H_2OsCl_6 with 1,5-cyclooctadiene in boiling

* Corresponding authors. E-mail: maester@unizar.es (M.A.E.); cgaryeb@unizar.es (C.G.-Y.).

(1) (a) Chaloner P. A.; Esteruelas, M. A.; Joó, F.; Oro, L. A. *Homogenous Hydrogenation*; Kluwer Academic Publ.: Dordrecht, The Netherlands, 1994. (b) de Vries, J. G., Elsevier, C. J., Eds. *Handbook of Homogeneous Hydrogenation*; Wiley-VCH: Weinheim, Germany, 2006.

(2) See for example: (a) Papish E. T.; Magoo, M. P.; Norton, J. R. In *Recent Advances in Hydride Chemistry*; Peruzzini, M., Poli, R., Eds.; Elsevier: Amsterdam, The Netherlands, 2001; Chapter 2, Section 2.5. (b) Chapham, S. E.; Hadzovic, A.; Morris, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2201. (c) Bullock, R. M. *Chem.−Eur. J.* **2004**, *10*, 2366. (d) Samec, J. S. M.; Bäckvall, J.-E.; Andersson, P. G.; Brandt, P. *Chem. Soc. Rev.* **2006**, *35*, 237. (e) Kubas, G. J. *Chem. Rev.* **2007**, *107*, 4152.

(3) (a) Vignais, P. M.; Billoud, B. *Chem. Rev.* **2007**, *107*, 4206. (b) Fontecilla-Camps, J.-C.; Volbeda, A.; Cavazza, C.; Nicolet, Y. *Chem. Rev.* **2007**, *107*, 4273.

(4) See for example: (a) Akbayeva, D. N.; Gonsalvi, L.; Oberhauser, W.; Peruzzini, M.; Vizza, F.; Brüggeller, P.; Romerosa, A.; Sava, G.; Bergamo, A. *Chem. Commun.* **2003**, 264. (b) Frost, B. J.; Mebi, C. A. *Organometallics* **2004**, *23*, 5317. (c) Guan, H.; Limura, M.; Magee, M. P.; Norton, J. R.; Zhu, G. *J. Am. Chem. Soc.* **2005**, *127*, 7805.

(5) See for example: (a) Bullock, R. M.; Voges, M. H. *J. Am. Chem. Soc.* **2000**, *122*, 12594. (b) Yamakawa, M.; Ito, H.; Noyori, R. *J. Am. Chem. Soc.* **2000**, *122*, 1466. (c) Magee, M. P.; Norton, J. R. *J. Am. Chem. Soc.* **2001**, *123*, 1778. (d) Casey, C. P.; Singer, S. W.; Powell, D. R.; Hayashi, R. K.; Kavana, M. *J. Am. Chem. Soc.* **2001**, *123*, 1090.

(6) Noels, A. F.; Hubert, A. J. *In Industrial Applications of Homogeneous Catalysis*; Mortreux, A.; Petit, F., Eds.; D. Reidel Publishing Company: Dordrecht, The Netherlands, 1988.

10.1021/om800150z CCC: $40.75
Publication on Web 06/05/2008

isoamyl alcohol afforded the compound in 35% yield. In 1974, Schrock and co-workers[11] described a high-yield procedure (90%) that involved heating OsO_4 in a mixture of concentrated HCl and isoamyl alcohol, adding 1,5-cyclooctadiene, and distilling off the solvent to afford the yellow-brown product. On the other hand, by this procedure, Girolami's group[12] has obtained yields of only 15−20%.

In the search for a new method to prepare $[OsCl_2(COD)]_x$, which avoids the toxic and dangerous compound OsO_4, we have recently carried out the reaction of $OsCl_3 \cdot 3H_2O$ with 1,5-cyclooctadiene in refluxing ethanol.[13] Instead of the desired product, the Brønsted acid $[H(EtOH)_2][\{OsCl(\eta^4\text{-COD})\}_2(\mu\text{-H})(\mu\text{-Cl})_2]$ was obtained. Now we have observed that this compound is a safe hydrogen storage, which transfers a hydrogen molecule to some unsaturated organic substrates to give, via ionic hydrogenation, the reduced organic compounds and the osmium polymer. This paper reports an efficient procedure to obtain the osmium polymer $[OsCl_2(COD)]_x$, in good yield, a catalytic system for the ionic hydrogenation of aldehydes and ketones, and the catalytic formation of unsymmetrical ethers from 2-propanol and alcohols, aldehydes, and ketones.

Results and Discusion

1. Stoichiometric Reductions: Formation of $[OsCl_2(COD)]_x$. Several coordinatively saturated hydride transition metal complexes have shown to be efficient hydride donors to unsaturated organic molecules. Thus, stoichiometric ionic hydrogenations of aldehydes, ketones, olefins, and imines have been observed with mixtures formed by these hydride compounds and Brønsted acids, such as CF_3CO_2H, $CH_3C_6H_4SO_3H$, $C_6F_5CO_2H$, and CF_3SO_3H, of considerably different strengths.[14]

Complex $[H(EtOH)_2][\{OsCl(\eta^4\text{-COD})\}_2(\mu\text{-H})(\mu\text{-Cl})_2$ (**1**) mimics these systems due to its ambivalent nature: the cation gives a proton, whereas the anion transfers the hydride ligand. This property converts **1** into an intermediate species on the way from $OsCl_3 \cdot 3H_2O$ to the osmium polymer $[OsCl_2(COD)]_x$ (**2**). Treatment of toluene solutions of **1** with 1-hexene, acetone, or acetophenone produces the reduction of the corresponding organic substrate and the precipitation of the osmium polymer. The yield of the reaction depends on the time and the organic substrate. Thus, after 60 h an 86% of polymer is obtained with 1-hexene, while with acetone and acetophenone 72 h are necessary to form about 50% of the solid. Since the reaction of formation of the precursor **1** from $OsCl_3 \cdot 3H_2O$ takes place with a 76% yield, complex **2** can be prepared by a two-step method from the commercially available $OsCl_3 \cdot 3H_2O$ in 65% yield, via the reaction shown in eq 3 using 1-hexene as hydrogen acceptor.

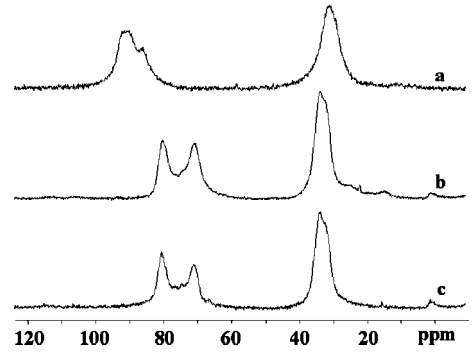


Figure 1. Solid-state $^{13}C\{^1H\}$ NMR spectra for $[RuCl_2(COD)]_x$ (a) and $[OsCl_2(COD)]_x$ obtained by reaction of **1** with 1-hexene (b) and acetone (c).

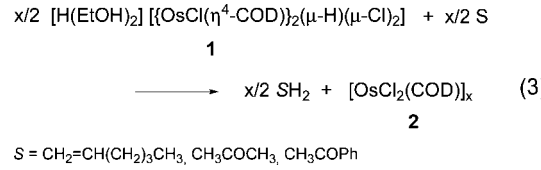
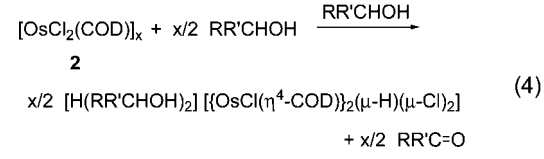


Figure 1 shows the solid-state $^{13}C\{^1H\}$ NMR spectra of the ruthenium polymer $[RuCl_2(COD)]_x$ (a) and those of the solids obtained from the reactions with 1-hexene (b) and acetone (c). In agreement with the spectrum of the ruthenium compound, which shows olefinic resonances between 100 and 80 ppm and a broad aliphatic signal at about 30 ppm, the $^{13}C\{^1H\}$ NMR spectra of the osmium solids contain olefinic resonances between 85 and 65 ppm and an aliphatic signal at about 30 ppm. The displacement observed for the osmium-olefinic resonances toward higher field with regard to ruthenium is consistent with the stronger π-back-donor character of osmium compared to ruthenium, due to the better overlap established between the osmium valence orbitals and the ligand orbitals.

In the presence of **2** primary and secondary alcohols undergo dehydrogenation, according to eq 4. The treatment of **2** in refluxing ethanol regenerates **1**, whereas in 2-propanol the hydride anion and the cation $[H\{(CH_3)_2CHOH\}_2]^+$ are formed. However in *tert*-butanol the polymer is inert. In agreement with this, complex **2** can be obtained from $OsCl_3 \cdot 3H_2O$ in a one-pot synthesis using 1,5-cyclooctadiene itself as hydrogen acceptor and *tert*-butanol as solvent. Unfortunately, by this procedure, the osmium polymer is obtained in only 56% yield. Furthermore, it is contaminated with traces of an insoluble material, most probably poly cyclooctene. In this context, it should be noted that several organometallic osmium compounds have shown to be active catalysts for cyclodiolefins ROMP reactions.[15]



(7) (a) Doyle, M. P.; DeBruyn, D. J.; Kooistra, D. A. *J. Am. Chem. Soc.* **1972**, *94*, 3659. (b) Lee, S. H.; Park, Y. J.; Yoon, C. M. *Tetrahedron Lett.* **1999**, *40*, 6049. (c) Wada, M.; Nagayama, S.; Mizutani, K.; Hiroi, R.; Miyoshi, N. *Chem. Lett.* **2002**, *248*, 7. (d) Bajwa, J. S.; Jiang, X.; Slade, J.; Prasad, K.; Repiè, O.; Blacklock, T. J. *Tetrahedron Lett.* **2002**, 6709. (e) Evans, P. A.; Cui, J.; Gharpure, S. J. *Org. Lett.* **2003**, *5*, 3883. (f) Evans, P. A.; Cui, J.; Gharpure, S.; Hinkle, R. J. *J. Am. Chem. Soc.* **2003**, *125*, 11456. (g) Jia, H.-M.; Fang, D.-C.; Scheunemann, M. *J. Org. Chem.* **2005**, *70*, 4478. (h) Iwanami, K.; Yano, K.; Oriyama, T. *Synthesis* **2005**, 2669. (i) Iwanami, K.; Seo, H.; Tobita, Y.; Oriyama, T. *Synthesis* **2005**, 183. (j) Goobe, L. J.; Linder, C. *Synlett* **2006**, 3489. (k) Iwanami, K.; Yano, K.; Oriyama, T. *Chem. Lett.* **2007**, *36*, 38.

(8) (a) Sánchez-Delgado, R. A.; Rosales, M.; Esteruelas, M. A.; Oro, L. A. *J. Mol. Catal. A: Chem.* **1995**, *96*, 231. (b) Esteruelas, M. A.; Oro, L. A. *Chem. Rev.* **1998**, *98*, 577.

(9) (a) Esteruelas, M. A.; Oro, L. A. *Adv. Organomet. Chem.* **2001**, *47*, 1. (b) Esteruelas, M. A.; López, A. M. *Organometallics* **2005**, *24*, 3584. (c) Esteruelas, M. A.; López, A. M.; Oliván, M. *Coord. Chem. Rev.* **2007**, *251*, 795. (d) Jia, G. *Coord. Chem. Rev.* **2007**, *251*, 2167.

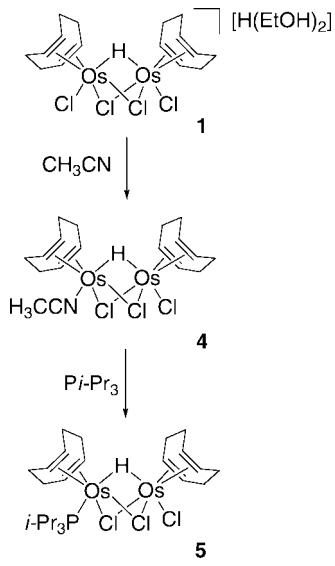
(10) Winkhaus, G.; Sanger, H.; Kricke, M. *Z. Naturforsch., B: Chem. Sci.* **1966**, *21*, 1109.

(11) Schrock, R. R.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1974**, 951.

(12) Dickinson, P. W.; Girolami, G. S. *Inorg. Chem.* **2006**, *45*, 5215.

(13) Esteruelas, M. A.; García-Yebra, C.; Oliván, M.; Oñate, E. *Inorg. Chem.* **2006**, *45*, 10162.

Scheme 1



2. Reactions with Acetonitrile. The formation of the osmium polymer according to eq 3 was confirmed by reaction of the solids obtained with acetonitrile. Like the bromine counterpart $[OsBr_2(COD)]_x$,[12] they are dissolved in refluxing acetonitrile, in this case, to afford the adduct $OsCl_2(\eta^4\text{-COD})(CH_3CN)_2$ (**3**), which is isolated as a yellow solid in 70% yield, according to eq 5. The NMR spectroscopic data of this compound are consistent with those of $OsBr_2(\eta^4\text{-COD})(CH_3CN)_2$. The ^1H NMR spectrum shows a multiplet at 4.04 ppm and two complex signals at 2.33 and 1.94 ppm corresponding to the olefinic and aliphatic protons, respectively, of the diene. The acetonitrile resonance appears at 2.69 ppm. In the $^{13}C\{^1H\}$ NMR spectrum the olefinic carbon atoms give rise to a singlet at 76.3 ppm.

$$\underset{\mathbf{2}}{[OsCl_2(COD)]_x} \xrightarrow{CH_3CN} x\ \underset{\mathbf{3}}{OsCl_2(\eta^4\text{-COD})(CH_3CN)_2} \quad (5)$$

In contrast to **2**, in acetonitrile, complex **1** reacts with the solvent to give the neutral dinuclear derivative $\{Os(CH_3CN)(\eta^4\text{-COD})\}(\mu\text{-H})(\mu\text{-Cl})_2\{OsCl(\eta^4\text{-COD})\}$ (**4**) as a result of the displacement of one of the terminal chloride ligands by an acetonitrile molecule (Scheme 1). In this case the reduction of the unsaturated organic substrate is not observed. The difference in behavior between 1-hexene or acetone and acetonitrile can be related to the higher coordinating power of the latter substrate with regard to the first ones. In fact, the coordination of the nitrogen atom of the nitrile produces its deactivation for the protonation, and at the same time, the neutral nature of the resulting species reduces the ability of the metal fragment to transfer the hydride ligand.

Complex **4** was isolated as a brown solid in 70% yield and characterized by X-ray diffraction analysis. Figure 2 shows a view of its structure. The molecule can be described as an asymmetrical dimer formed by the conical $Os(CH_3CN)(\eta^4\text{-COD})$ and $OsCl(\eta^4\text{-COD})$ moieties, which are joined by two bridging chlorine atoms and a bridging hydride ligand. The separation between the metal centers, 2.8084(4) Å, agrees well with that of **1** (2.8065(6) Å) and related $Os(\eta^4\text{-COD})$ dimers.[13] Although both separations are consistent with the osmium−osmium single bond distance found in the triosmium cluster $Os_3(\mu\text{-H})(\mu\text{-}\eta^2\text{-HapyPh-N,N})(CO)_9$ (H_2apyPh = 2-amino-6-phenylpyridine; 2.8141(6), 2.7765(6), and 2.7873(6) Å),[16] analysis of the Laplacian of the electron density and calculations of critical

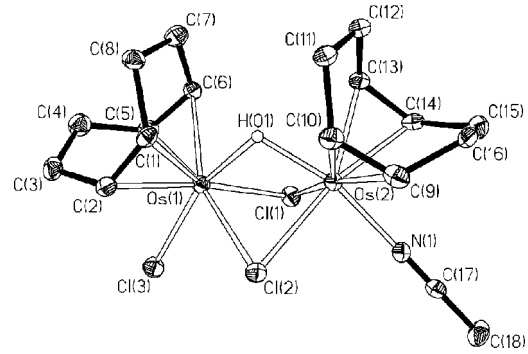


Figure 2. Molecular diagram of complex **4**. Selected bond lengths (Å) and angles (deg): Os(1)···Os(2) 2.8084(4), Os(1)−Cl(3) 2.3978(15), Os(1)−Cl(1) 2.4673(15), Os(1)−Cl(2) 2.4819(16), Os(2)−Cl(1) 2.4402(16), Os(2)−Cl(2) 2.4447(15), C(1)−C(2) 1.417(9), C(5)−C(6) 1.407(9), C(9)−C(10) 1.409(10), C(13)−C(14) 1.427(9), Os(1)−C(5) 2.138(7), Os(1)−C(2) 2.138(6), Os(1)−C(1) 2.156(6), Os(1)−C(6) 2.157(6), Os(2)−C(10) 2.156(7), Os(2)−C(9) 2.164(8), Os(2)−C(13) 2.170(6), Os(2)−C(14) 2.177(7), H(01)−Os(1)−Cl(3) 164(3), H(01)−Os(2)−N(1) 165(3).

points in the region between the osmium atoms of **1** indicate the absence of any direct metal−metal interaction.[13]

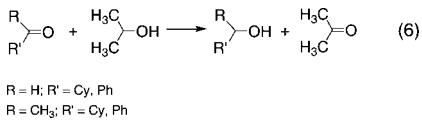
The hydride ligand is pseudo-*trans*-disposed to both the acetonitrile molecule and the terminal chlorine atom, with H(01)−Os(2)−N(1) and H(01)−Os(1)−Cl(3) angles of 165(3)° and 164(3)°, respectively. The terminal Os(1)−Cl(3) distance of 2.3978(15) Å is about 0.07 Å shorter than the bridging Os(1)−Cl distances (2.4673(15) and 2.4819(16) Å) and about 0.04 Å shorter than the bridging Os(2)−Cl bond lengths (2.4402(16) and 2.4447(15) Å). The 1,5-cyclooctadiene ligands take their customary "tub" conformation. The olefinic bond lengths, between 1.407(9) and 1.427(9) Å, lie within the range reported for transition metal olefin complexes (1.340−1.455 Å).[17] They are statistically identical and longer than those found in the free 1,5-cyclooctadiene molecule (1.34 Å),[18] in agreement with the usual Chatt, Dewar, and Duncanson metal-bonding scheme. The osmium−diene coordination exhibits Os−C distances between 2.138(7) and 2.177(7) Å, which agree well with those found in other osmium−olefin complexes (2.13−2.28 Å).[13,19]

The NMR spectroscopic data of **4** are consistent with the structure shown in Figure 2. In agreement with the presence of a hydride ligand in the complex, the ^1H NMR spectrum in dichloromethane-d_2 shows a singlet at −19.18 ppm. In the $^{13}C\{^1H\}$ NMR spectrum, the $C(sp^2)$ resonances of the diene appear at 67.1, 66.7, 66.2, and 61.9 ppm.

The acetonitrile ligand of **4** is easily displaced by triisopropylphosphine to afford the phosphine derivative $\{Os(Pi\text{-}Pr_3)(\eta^4\text{-COD})\}(\mu\text{-H})(\mu\text{-Cl})_2\{OsCl(\eta^4\text{-COD})\}$ (**5**), which is isolated as a brown solid in 81% yield (Scheme 1). The substitution process is strongly supported by the ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of **5**. In the ^1H NMR spectrum, the hydride resonance appears at −17.45 ppm as a doublet with a H−P coupling constant of 24.3 Hz. In the $^{13}C\{^1H\}$ NMR spectrum the (Csp^2) resonances of the coordinated olefin are observed at 66.6, 63.7, and 59.9 ppm as singlets and at 56.1 ppm as a doublet with a C−P coupling constant of 5.4 Hz. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at −27.8 ppm.

3. Catalytic Transfer Hydrogenation of Aldehydes and Ketones. The reactions shown in eqs 3 and 4 form cycles for the ionic hydrogenation of unsaturated organic molecules, using alcohols as a hydrogen source. In accordance with this, complex **1** catalyzes the hydrogen transfer from 2-propanol to aldehydes

(cyclohexanecarbaldehyde and benzaldehyde) and ketones (cyclohexyl methyl ketone and acetophenone) according to eq 6.



(6)

The reactions were performed under reflux in the hydrogen donor as solvent using 1 mol % of dimer. Under those conditions, at later stages of the reductions, some amount of alcohols is converted to the ethers $RR'CHOCH(CH_3)_2$, in all cases less than 20%. The alcohol etherification is generally seen as a side process, which sometimes goes with the ionic hydrogenation of aldehydes and ketones. It has been also observed at later stages of the reduction of 3-pentanone with $[Cp(CO)_2(PPh_3)M(\kappa^1\text{-}OCEt_2)]^+$ (M = Mo, W) under hydrogen atmosphere[5a] and in the reductions of cholestan-3-one and 4-*tert*-butylcyclohexanone by 2-propanol in the presence of iridium sulfoxide catalysts.[20]

Aromatic compounds are more easily reduced than aliphatic ones (Table 1). After 1 h, 78% of benzaldehyde is reduced while only 32% of cyclohexylmethanol is formed. After 4 h, 66% of acetophenone is converted into 1-phenylethanol, while only 32% of cyclohexyl methyl ketone is reduced to 1-cyclohexylethanol. This preference is consistent with the ionic nature of the process.

Table 1. Ionic Hydrogenation of Aldehydes and Ketones According to Eq 6[a]

Entry	Substrate	*t* (h)	Yield[b] (%)
1		1	32
2		1	78
3		4	32
4		4	66

[a] Reactions were performed at 90 °C, by using a 1 mol% of the catalyst (**1**) and 2-propanol as solvent (for further details, see experimental section). [b] Yields are given on the basis of ^{1}H NMR experiments.

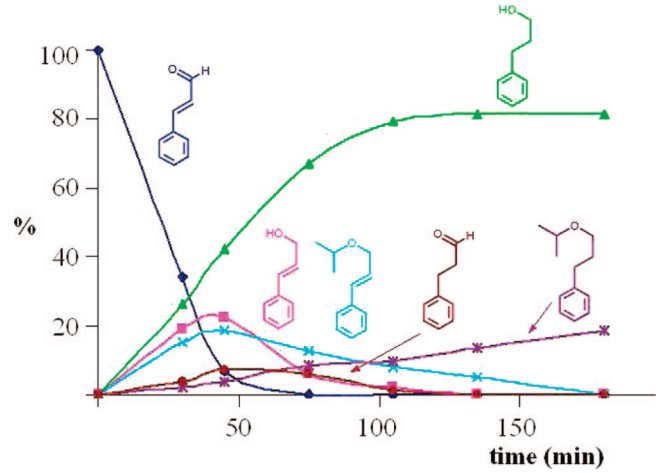


Figure 3. Course of the catalytic hydrogenation of cinnamaldehyde.

In this context, it should be noted that a phenyl group delocalizes the positive charge of the cation resulting from protonation of the carbonyl group of the substrates better than an aliphatic substituent. The hydrogenation of aldehydes is also, in general, easier than that of ketones, in agreement with the lower steric demand of aldehydes than the corresponding ketone (cyclohexanecarbaldehyde versus cyclohexyl methyl ketone and benzaldehyde versus acetophenone). Once the cation is formed, the approach of the aldehydes to the hydride-metal fragment is easier than the approach of the ketones, due to the smaller size of a hydrogen atom with regard to a methyl group. As a result, the necessary hydride transfer step to the hydrogenation is more favored for the aldehyde than for the ketone.

Figure 3 shows the composition of products as a function of the time for the reduction of cinnamaldehyde. As expected for an ionic hydrogenation and for the small size of the hydrogen atom bonded to the carbonyl group, the direct addition of H^+ and H^- to the CO double bond is favored with regard to the reduction of the C−C double bond. Thus, cinnamyl alcohol is the main intermediate compound. It should be also mentioned that the etherification of this alcohol appears to be very easy, and therefore, amounts of about 18% of (3-isopropoxyprop-1-enyl)benzene are formed after 45 min, which are transformed into (3-isopropoxypropyl)benzene by reduction of the C−C double bond.

(14) (a) Gibson, D. H.; El-Omrani, Y. S. *Organometallics* **1985**, *4*, 1473. (b) Gaus, P. L.; Kao, S. C.; Youngdahl, K.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1985**, *107*, 2428. (c) Geraty, S. M.; Harkin, P.; Vos, J. G. *Inorg. Chim. Acta* **1987**, *131*, 217. (d) Bullock, R. M.; Rappoli, B. J. *J. Chem Soc., Chem. Commun.* **1989**, 1447. (e) Song, J.-S.; Szalda, D. J.; Bullock, R. M.; Lawrie, C. J. C.; Rodkin, M. A.; Norton, J. R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1233. (f) Bullock, R. M.; Song, J.-S. *J. Am. Chem. Soc.* **1994**, *116*, 8602. (g) Smith, K. T.; Norton, J. R.; Tilset, M. *Organometallics* **1996**, *15*, 4515. (h) Bakhmutov, V. I.; Vorontsov, E. V.; Antonov, D. Y. *Inorg. Chim. Act* **1998**, *278*, 122. (i) Minato, M.; Fujiwara, Y.; Koga, M.; Matsumoto, N.; Kurishima, S.; Natori, M.; Sekizuka, N.; Yoshioka, K.-i.; Ito, T. *J. Organomet. Chem.* **1998**, *569*, 139.

(15) See for example: (a) Brumahim, J. L.; Girolami, G. S. *Organometallics* **1999**, *18*, 1929. (b) Cobo, N.; Esteruelas, M. A.; González, F.; Herrero, J.; López, A. M.; Lucio, P.; Oliván, M. *J. Catal.* **2004**, *223*, 319. (c) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2005**, *24*, 4343. (d) Esteruelas, M. A.; González, F.; Herrero, J.; Lucio, P.; Oliván, M.; Ruiz Labrador, B. *Polym. Bull.* **2007**, *58*, 923.

(16) Cabeza, J. A.; del Río, I.; Riera, V.; Suárez, M.; García-Granda, S. *Organometallics* **2004**, *23*, 1107.

(17) Allen, F. H.; Davies, J. E.; Galloy, J. J.; Johnson, O.; Kennard, O.; Macrae, C. F.; Mitchell, E. M.; Mitchell, G. F.; Smith, J. M.; Watson, D. G. *J. Chem. Inf. Comput. Sci.* **1991**, *31*, 187.

(18) Churchill, M. R.; Bezman, S. A. *Inorg. Chem.* **1973**, *12*, 531.

(19) (a) Johnson, T. J.; Albinati, A.; Koetzle, T. F.; Ricci, J.; Eisenstein, O.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1994**, *33*, 4966. (b) Edwards, A. J.; Esteruelas, M. A.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A.; Tolosa, J. I. *Organometallics* **1997**, *16*, 1316. (c) Edwards, A. J.; Elipe, S.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Valero, C. *Organometallics* **1997**, *16*, 3828. (d) Crochet, P.; Esteruelas, M. A.; Gutiérrez-Puebla, E. *Organometallics* **1998**, *17*, 3141. (e) Buil, M. L.; Esteruelas, M. A.; García-Yebra, C.; Gutiérrez-Puebla, E.; Oliván, M. *Organometallics* **2000**, *19*, 2184. (f) Esteruelas, M. A.; García-Yebra, C.; Oliván, M.; Õate, E. *Organometallics* **2000**, *19*, 3260. (g) Baya, M.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2002**, *21*, 5681. (h) Esteruelas, M. A.; González, A. I.; López, A. M.; Oñate, E. *Organometallics* **2003**, *22*, 414. (i) Esteruelas, M. A.; Lledós, A.; Maseras, F.; Oliván, M.; Oñate, E.; Tajada, M. A.; Tomàs, J. *Organometallics* **2003**, *22*, 2087. (j) Barrio, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2003**, *22*, 2472. (k) Baya, M.; Buil, M. L.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2004**, *23*, 1416. (l) Barrio, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2004**, *23*, 3267. (m) Baya, M.; Buil, M. L.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2005**, *24*, 2030. (n) Baya, M.; Buil, M. L.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2005**, *24*, 5180. (o) Esteruelas, M. A.; Fernández-Álvarez, F. J.; Oliván, M.; Oñate, E. *J. Am. Chem. Soc.* **2006**, *128*, 4596.

(20) Haddad, Y. M. Y.; Henbest, H. B.; Husbands, J.; Mitchell, T. R. B.; Trocha-Grimshaw, J. *J. Chem. Soc., Perkin Trans. 1* **1974**, *5*, 596.

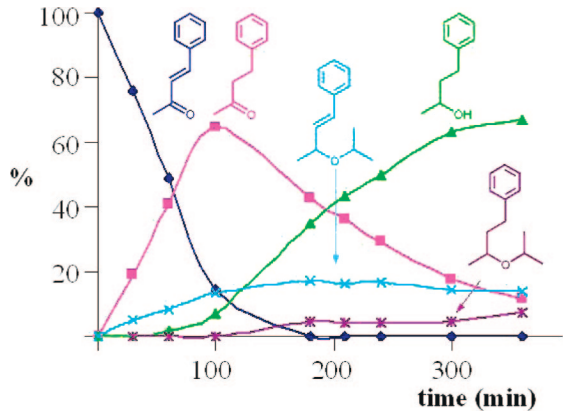
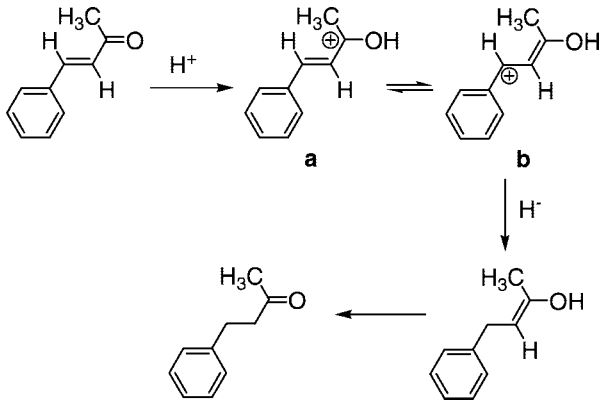


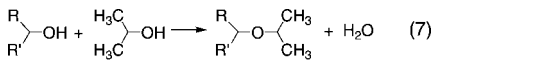
Figure 4. Course of the catalytic hydrogenation of 4-phenyl-3-buten-2-one.

Scheme 2



The hydrogenation of 4-phenyl-3-buten-2-one is sequential with an intermediate selectivity toward the saturated ketone of about 60% (Figure 4). Like it has been shown in a recent work,[21] the formation of the saturated ketone involves a 1,4-hydrogen addition to the oxygen and C_β atoms of the α,β-unsaturated ketone. This fact can be rationalized according to Scheme 2. The initial protonation of the oxygen atom of the α,β-unsaturated substrate affords the carbocation **a**, which has the resonance form **b**. The hydride transfer to **b** is certainly easier than to **a**, since in **b** the positive charge is on a less protected carbon atom than in **a**. In this case the allylic alcohol is not detected. However, the product of its etherification, (3-isopropoxybut-1-enyl)benzene, is formed in about 18% yield after 100 min. This suggest that the etherification of 4-phenyl-3-buten-2-ol is even faster than that of cinnamyl alcohol.

4. Formation of Isopropyl Ethers. The transition metal catalysis is a nice method for the selective etherification of alcohols. However few transition metal catalysts have been reported for this reaction.[22] The formation of isopropyl ethers at the later stages of the hydrogenation reactions of aldehydes and ketones prompted us to investigate the capacity of **1** to promote the etherification of benzyl alcohol, 3-phenylpropanol, and 1-phenylethanol with 2-propanol, according to eq 7.



R = H; R' = Ph, $PhCH_2CH_2$
R = CH_3; R' = Ph

The reactions were carried out in a 5:3 toluene/2-propanol mixture as solvent, under reflux, using 5 mol % of **1** and a Dean−Stark apparatus to remove the water formed. Under these conditions high yields of products are obtained (Table 2), at lower rates than those observed for reduction reactions. Partial decomposition of the organometallic complex to a black solid occurs at times longer than 12 h.

Table 2. Etherification of Alcohols, Aldehydes, and Ketones[a]

Entry	Substrate	Product	*t* (h)	Yield[b](%)
1			5.5	85
2			12	80
3			7	82[c]
4			6.5	95
5			7	70
6			7	95

[a] Reactions were performed at 130 °C, by using 5 mol % of the catalyst (**1**) and a 5:3 toluene/2-propanol mixture as solvent (for further details, see Experimental Section). [b]Yields are given on the basis of ^1H NMR measurements. [c]Yield of isolated product (flash column chromatography).

Figure 5 describes the course of the etherification reaction of benzaldehyde. The graphic clearly shows that the hydrogenation rate of the carbonyl group is significantly faster than the etherification rate of the resulting alcohol. The course of the etherification reaction of acetophenone is similar. On the other hand, the intermediate stages of the cinnamaldehyde etherification are more complex (Figure 6). In agreement with Figure 3, the main intermediate compound is 3-phenylpropan-1-ol, which leads to (3-isopropoxypropyl)benzene by etherification. Cinnamyl alcohol is formed even faster than 3-phenylpropan-1-ol. Subsequently, it undergoes a rapid etherification to give (3-isopropoxyprop-1-enyl)benzene. The reduction of the C−C double bond of the latter ether also leads to (3-isopropoxypropyl)benzene.

Concluding Remarks

This study has revealed that complex $[H(EtOH)_2][\{OsCl(\eta^4\text{-}COD)\}_2(\mu\text{-}H)(\mu\text{-}Cl)_2]$ is an intermediate in the two-step synthesis of $[OsCl_2(COD)]_x$ (65% yield) from $OsCl_3 \cdot 3H_2O$ and 1,5-cyclooctadiene. The osmium polymer is formed as a result of

(21) Esteruelas, M. A.; Hernández, Y. A.; López, A. M.; Oliván, M.; Oñate, E. *Organometallics* **2005**, *24*, 5989.

(22) (a) Zhu, Z.; Espenson, J. H. *J. Org. Chem.* **1996**, *61*, 324. (b) Salehi, P.; Iranpoor, N.; Bahbahani, F. K. *Tetrahedron* **1998**, *54*, 943. (c) Sharma, G. V. M.; Mahalingam, A. K. *J. Org. Chem.* **1999**, *64*, 8943. (d) Bouquillon, S.; Hénin, F.; Muzart, J. *Organometallics* **2000**, *19*, 1434. (e) Sharma, G. V. M.; Prasad, T. R.; Mahalingam, A. K. *Tetrahedron Lett.* **2001**, *42*, 759. (f) Miller, K. J.; Abu-Omar, M. M. *Eur. J. Org. Chem.* **2003**, 1294. (g) Cuenca, A. B.; Mancha, G.; Asensio, G.; Medio-Simón, M. *Chem.−Eur. J.* **2008**, *14*, 1518.

(23) Wasilke, J.-C.; Obrey, S. J.; Baker, R. T.; Bazan, G. C. *Chem. Rev.* **2005**, *105*, 1001.

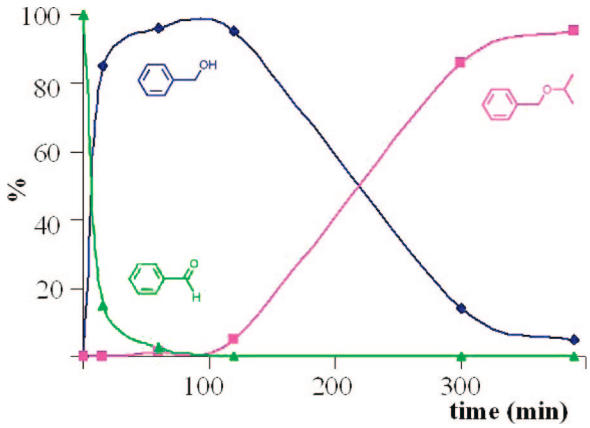


Figure 5. Course of the catalytic etherification of benzaldehyde.

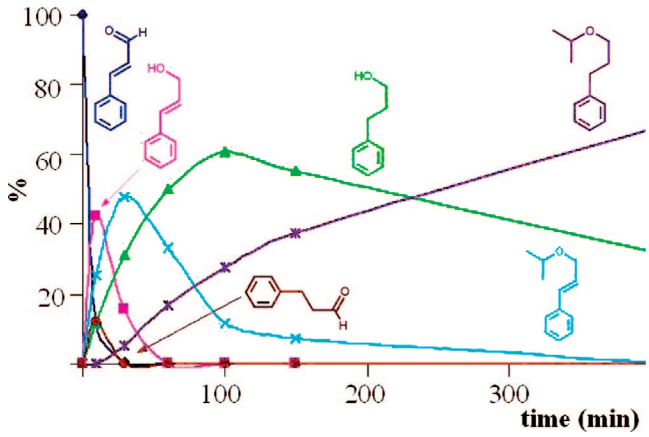


Figure 6. Course of the catalytic etherification of cinnamaldehyde.

Table 3. Crystal Data and Data Collection and Refinement for 4

formula	$C_{18}H_{28}Cl_3NOS_2$
molecular wt	745.16
color and habit	irregular block, black
size, mm	0.12,0.10,0.10
symmetry, space group	monoclinic, *P*2(1)/*c*
a, Å	15.4555(11)
b, Å	9.2944(7)
c, Å	13.9390(10)
β, deg	100.5180(10)
V, Å^3	1968.7(2)
Z	4
D_{calc}, g cm^{-3}	2.514
Data Collection and Refinement	
diffractometer	Bruker Smart APEX
λ(Mo Kα), Å	0.71073
monochromator	graphite oriented
scan type	*ω* scans
μ, mm^{-1}	13.304
2*θ*, range deg	4, 58
temp, K	105.0(1)
no. of data collect	23 817
no. of unique data	4810 (R_{int} = 0.0564)
no. of params/restraints	246/0
R_1[a] [$F^2 > 2\sigma(F^2)$]	0.0352
wR_2[b] [all data]	0.0796
S[c] [all data]	1.077

[a] $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] Goof = $S = \{\sum[F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

the H$^-$ transfer from the dimer anion to a protonated organic species, resulting from the interaction of weakly coordinating unsaturated organic molecules such as olefins, aldehydes, and ketones with the cation. In contrast to these substrates, a stronger coordinating molecule such as acetonitrile displaces the terminal chloride ligand of one of the osmium atoms of the dimer, to give the neutral species {Os(CH$_3$CN)(η^4-COD)}(μ-H)(μ-Cl)$_2${OsCl(η^4-COD)}. The osmium polymer regenerates the cation−anion species in primary and secondary alcohols. These reactions and the combined H$^+$ and H$^-$ transfer from the cation and anion to olefins, aldehydes, and ketones form cycles for the transfer hydrogenation of weakly coordinating unsaturated organic molecules, using alcohols as hydrogen source. In agreement with this, complex [H{(CH$_3$)$_2$CHOH}$_2$][{OsCl(η^4-COD)}$_2$(μ-H)(μ-Cl)$_2$] catalyzes the hydrogen transfer from 2-propanol to aldehydes and ketones. Using a Dean−Stark apparatus, alcohols can be transformed into isopropyl ethers in high yields, at rates lower than those of the hydrogenation reactions. In accordance with this, isopropyl ethers are prepared by a one-pot synthesis starting from the corresponding carbonyl compounds and 2-propanol. The reactions are described as hydrogenation−etherification tandem processes.

In conclusion, we report an efficient method to prepare the starting complex [OsCl$_2$(COD)]$_x$ from the commercially available OsCl$_3$·3H$_2$O and the discovery of an osmium catalytic system for the ionic hydrogenation of aldehydes and ketones, using 2-propanol as hydrogen source, which is also able to catalyze the etherification of alcohols and the one-pot synthesis of isopropyl ethers from 2-propanol and aldehydes or ketones.

Experimental Section

All reactions were carried out under an argon atmosphere using Schlenk tube techniques. THF, dichloromethane, pentane, and toluene were obtained oxygen- and water-free from an MBraun solvent purification apparatus. Other solvents were dried and purified by known procedures and distilled under argon prior to use. Infrared spectra were recorded on a Spectrum One spectrometer as neat solids or KBr pellets. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on a Varian Gemini 2000−300 MHz, a Bruker Avance 300, or a Bruker ARX Avance 400 spectrometer. Chemical shifts are referenced to residual solvent peaks (^{1}H, ^{13}C{^{1}H}) or external H$_3$PO$_4$ (85%) (^{31}P{^{1}H}). Coupling constants, *J*, are given in hertz. The solid-state CP MAS experiments were performed on a Bruker ARX Avance 400 spectrometer at 100.62 MHz frequency for ^{13}C, equipped with a MAS probe head using 4 mm ZrO$_2$ rotors. The samples were spun at 8000 Hz, and the conventional spectra were recorded with a proton 90° pulse length of 5.10 μs and a contact time of 1.5 ms. The repetition delay was 5 s. MALDI-MS measurements were performed on a reflex time-of-flight instrument (Bruker Daltonics Microflex analyzer) equipped with a target micro-SCOUT ion source, operating in the negative reflection mode with pulsed extraction. Ions were formed by a pulsed UV laser beam (nitrogen laser, λ = 337 nm) and using dithranol (DIT) or 2-[3-(4-*tert*-butylphenyl)-2-methylallylidene]malononitrile (DCTB) as a matrix. High-resolution electrospray mass spectra were acquired using a MicroTOF-Q hybrid quadrupole time-of-flight spectrometer (Bruker Daltonics, Bremen, Germany). Samples were introduced as methanol (or acetonitrile) solutions using an Agilent 1100 HPLC operated at a flow rate of 0.2 mL/min. A 10 mM solution of sodium formate in 1:1 2-propanol/water was used as external standard for accurate mass measurements. C, H, and, N analyses were measured on a Perkin-Elmer 2400 CHNS/O analyzer. Catalysis experiments were followed in an Agilent 4890D series gas chromatograph with a flame ionization detector, using a cross-linked polyethylene glycol column HP INNOWAX (25 m × 0.2 mm, with 0.4 μm film thickness). The reaction products were identified by comparison of their retention

times with those observed for pure samples and by NMR and GC-MS experiments run on an Agilent 5973 mass selective detector interfaced to an Agilent 6890 series gas chromatograph system. Samples were injected into a 30 m × 250 mm HP-5MS 5% phenyl methyl siloxane column with a film thickness of 0.25 mm (Agilent). Complex $[H(EtOH)_2][\{OsCl(\eta^4\text{-COD})\}_2(\mu\text{-H})(\mu\text{-Cl})_2]$ (**1**) was prepared according to the published method.[13] All ketones, aldehydes, and alcohols either are commercially available or have been previously described in the literature.[24] Ethers reported in this paper are known in the literature.[22b,f,25] Spectroscopic data for some ethers are given below. The GC oven temperature was programmed depending on the ketone or aldehyde as follows: cinnamaldehyde, 1 min 140 °C,12 °C/min, 10 min 200 °C; benzaldehyde, 1 min 120 °C, 15 °C/min, 18 min 180 °C; cyclohexanecarbaldehyde, 3 min 120 °C, 15 °C/min, 1 min 180 °C; acetophenone, 3 min 120 °C, 15 °C/min, 5 min 200 °C; 4-phenyl-3-buten-2-one, 1 min 120 °C, 15 °C/min, 15 min 200 °C; cyclohexylmethylketone, 3 min 120 °C, 15 °C/min, 3 min 180 °C.

Preparation of $[Os(\eta^4\text{-COD})Cl_2]_x$ (2). Method A. To a solution of $[H(EtOH)_2][\{OsCl(\eta^4\text{-COD})\}_2(\mu\text{-H})(\mu\text{-Cl})_2]$ (**1**) (444 mg, 0.53 mmol) in toluene (10 mL) was added 1-hexene (2 mL, 15.9 mmol), and the mixture was refluxed for 60 h. The brown-yellow precipitate thus formed was isolated by filtration, washed once with ethanol and three times with diethyl ether, and dried *in vacuo* (337 mg, 0.45 mmol, 86% yield, 66% overall yield starting from $OsCl_3 \cdot 3H_2O$). **Method B**. To a solution of $[H(EtOH)_2][\{OsCl(\eta^4\text{-COD})\}_2(\mu\text{-H})(\mu\text{-Cl})_2]$ (**1**) (311 mg, 0.37 mmol) in toluene (5 mL) was added acetone (0.8 mL, 11 mmol), and the mixture was refluxed for 72 h. The brown-yellow precipitate thus formed was isolated by filtration, washed once with ethanol and three times with diethyl ether, and dried *in vacuo* (142 mg, 0.14 mmol, 51% yield). **Method C.** To a solution of $[H(EtOH)_2][\{OsCl(\eta^4\text{-COD})\}_2(\mu\text{-H})(\mu\text{-Cl})_2]$ (**1**) (150 mg, 0.18 mmol) in toluene (3 mL) was added acetophenone (0.63 mL, 5.4 mmol), and the mixture was refluxed for 72 h. The reddish-brown precipitate thus formed was isolated by filtration, washed once with ethanol and three times with diethyl ether, and dried *in vacuo* (70 mg, 0.09 mmol, 53% yield). **Method D.** A solution of $OsCl_3 \cdot 3H_2O$ (500 mg, 1.42 mmol) and 1,5-cyclooctadiene (1.4 mL, 11.4 mmol) in oxygen-free *t*-BuOH (10 mL) was refluxed for three days. After that, the reaction mixture was cooled and left to stand, and the brown-green precipitate was isolated by filtration, washed with ethanol and finally with diethyl ether, and dried under vacuum (300 mg, 0.40 mmol, 56% yield). Anal. Calcd for $C_{16}H_{24}Cl_4Os_2$: C, 26.02; H, 3.28. Found: C, 25.99; H, 3.21. IR (neat compound, cm^{-1}): 2944 (m), 2906 (m), 2886 (m), 2860 (m), 2841 (m), 1630 (w), 1470 (m), 1435 (m), 1366 (w), 1328 (s), 1298 (m), 1163 (m), 1070 (w), 1009 (s), 922 (w), 873 (m), 842 (m), 789 (m), 728 (m), 694 (m), 602 (vw), 531 (m), 491 (s), 464 (w), 375 (s), 305 (s). MS (MALDITOF): *m*/*z* 775 (33), [M] + [Cl]; 741 (100), [M] + [H]; 405 (13), [M/2] + [Cl]; 370 (51) [M/2]. $^{13}C\{^1H\}$ NMR (100.62 MHz, solid state, 293 K): δ 80.0, 70.6 (both br s, *C*H-COD), 33.5 (br s, CH_2-COD).

Reaction of $[Os(\eta^4\text{-COD})Cl_2]_x$ (2) with Ethanol. An emulsion of $[Os(\eta^4\text{-COD})Cl_2]_x$ (50 mg, 0.07 mmol) in ethanol (5 mL) was heated at 90 °C for 18 h. The clear dark green solution thus obtained was evaporated to dryness and the crude washed with pentane to precipitate a green solid, which was identified as complex **1**. Yield: 80% (47 mg, 0.06 mmol).

Preparation of $Os(\eta^4\text{-COD})(CH_3CN)_2Cl_2$ (3). A suspension of $[Os(\eta^4\text{-COD})Cl_2]_x$ (**2**) (369 mg, 0.34 mmol) in acetonitrile (10 mL) was refluxed for 3 days. After this time, the initial mixture turned into a clear bright yellow solution that was filtered hot. The solvent of the liquids was evaporated, giving rise to a yellow solid that was washed with pentane and dried *in vacuo* (109 mg, 0.24 mmol, 70% yield). Anal. Calcd for $C_{12}H_{18}Cl_2N_2Os$: C, 31.93; H, 4.02; N, 6.21. Found: C, 32.05; H, 3.95; N, 6.15. IR (neat, cm^{-1}): 2330, 2305 [ν_{CN}]. MS (HR-electrospray): $[M - Cl - (CH_3CN)]^+ = C_{10}H_{15}ClNOs$ calcd 376.0502; found 376.0501. ^1H NMR (300 MHz, CD_3CN, 293 K): δ 4.04 (m, 4 H, CH-COD), 2.69 (s, 6 H, CH_3CN), 2.33 (m, 4 H, CH_2−COD), 1.94 (m, 4 H, CH_2-COD). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_3CN, 293 K): δ 123.9 (s, CH_3CN), 76.3 (s, CH-COD), 32.3 (s, CH_2-COD), 4.8 (s, CH_3CN).

Preparation of $\{Os(CH_3CN)(\eta^4\text{-COD})\}(\mu\text{-H})(\mu\text{-Cl})_2\{OsCl(\eta^4\text{-COD})\}$ (4). A solution of $[H(EtOH)_2][\{OsCl(\eta^4\text{-COD})\}_2(\mu\text{-H})(\mu\text{-Cl})_2]$ (**1**) (274 mg, 0.33 mmol) in acetonitrile (5 mL) was refluxed for 3 h, the color changing from dark green to orange-brown. The brown precipitate thus formed was isolated by filtration from the cold mixture, washed with pentane, and dried *in vacuo* (177 mg, 0.23 mmol, 70% yield). Anal. Calcd for $C_{18}H_{28}Cl_3NOs_2$: C, 29.01; H, 3.79; N, 1.88. Found: C, 29.11; H, 3.73; N, 1.90. IR (KBr, cm^{-1}): 2311, 2290 [ν_{CN}]. MS (MALDITOF): *m*/*z* 706 (22), [M] − [CH_3CN]; 671 (100), [M] − [CH_3CN] − [Cl]. ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 4.21 (m, 2 H, C*H*-*C*OD), 4.08 (m, 4 H, C*H*-*C*OD), 3.99 (m, 2 H, C*H*-*C*OD), 2.83 (s, 3 H, CH_3CN), 2.60−2.00 (16 H, CH_2-COD), −19.18 (s, 1 H, Os-H). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 293 K): δ 128.0 (s, CH_3CN), 67.1, 66.7, 66.2, 61.9 (all s, *C*H-COD), 36.1, 35.2, 31.5, 31.1 (all s, *C*H_2-COD), 5.6 (s, *C*H_3CN).

Preparation of $\{Os(P\textit{i}\text{-}Pr_3)(\eta^4\text{-COD})\}(\mu\text{-H})(\mu\text{-Cl})_2\{OsCl(\eta^4\text{-COD})\}$ (5). To a solution of $\{Os(CH_3CN)(\eta^4\text{-COD})\}(\mu\text{-H})(\mu\text{-Cl})_2\{OsCl(\eta^4\text{-COD})\}$ (**4**) (75 mg, 0.1 mmol) in THF (4 mL) was added P*i*-Pr_3 (118 μL, 96.5 mg, 0.6 mmol), and the mixture was refluxed overnight. The solvent was removed to give a brown oil, which was precipitated with diethyl ether, isolated by filtration, and dried *in vacuo* (70 mg, 0.08 mmol, 81% yield). Anal. Calcd for $C_{25}H_{46}Cl_3Os_2P$: C, 34.74; H, 5.36. Found: C, 34.85; H, 5.41. MS (HR-electrospray): $[M + Na]^+ = C_{25}H_{46}Cl_3NaOs_2P$ calcd. 889.1451; found 889.1525. ^1H NMR (400 MHz, CD_2Cl_2, 293 K): δ 4.21 (m, 2 H, C*H*-*C*OD), 4.05 (m, 4 H, C*H*-*C*OD), 3.73 (m, 2 H, C*H*-*C*OD), 3.01 {m, 3 H, P[C*H*$(CH_3)_2]_3$}, 2.47 (m, 8 H, CH_2-COD), 2.28 (m, 2 H, CH_2-COD), 2.16 (m, 6 H, CH_2-COD),1.43 {dd, $^3J_{HP} = 12.9$, $^3J_{HH} = 7.2$ Hz, 18 H, P[CH(C$H_3)_2]_3$}, −17.45 (d, $^2J_{HP} = 24.3$ Hz, 1 H, Os-H). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 293 K): δ −27.8 (s). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 293 K): δ 66.6, 63.7, 59.9 (all s, *C*H-COD), 56.1 (d, $^3J_{CP} = 5.4$ Hz, *C*H-COD), 35.6, 34.3, 33.5, 30.7 (all s, *C*H_2−COD), 27.9 {d, $^1J_{CP} = 21.7$ Hz, P[*C*H$(CH_3)_2]_3$}, 21.0 {d, $^2J_{CP} = 2.9$ Hz, P[CH(*C*$H_3)_2]_3$}.

General Procedure for the Transfer Hydrogenation of Aldehydes and Ketones. The hydrogen transfer reactions were carried out in a 50 mL two-necked flask fitted with a condenser and containing a magnetic stirring bar. The second neck was capped with a Suba-seal to allow samples to be removed by syringe without opening the system. Within the described system, a mixture of the catalysts **1** (0.02 mmol, 16.7 mg), the substrate (2 mmol), and 2-propanol (8 mL) was stirred under reflux. Time of reaction and yields are given in Table 1.

General Procedure for the Etherification of Alcohols, Aldehydes, and Ketones. Reactions were carried out in a 50 mL two-necked flask fitted with a condenser and containing a magnetic stirring bar as described above. The reaction system was then modified by introducing a Dean-Stark between the flask and the condenser that is filled with toluene and allows the removal of water formed in the condensation reaction. A mixture of the catalysts **1** (0.1 mmol, 83 mg), the substrate (2 mmol), 2-propanol (3 mL), and toluene (5 mL) was stirred under reflux. Time of reaction and yields are given in table 2.

(24) 4-Phenyl-3-buten-1-ol: Onaran, M. B.; Seto, C. T. *J. Org. Chem.* **2003**, *68*, 8136. 3-Phenylpropanal: Caló, V.; Nacci, A.; Monopoli, A.; Ferola, V. *J. Org. Chem.* **2007**, *72*, 2596.

(25) (Isopropoxymethyl) benzene: Barluenga, J.; Alonso-Cires, L.; Campos, P. J.; Asensio, G. *Synthesis* **1983**, 53. (3-Isopropoxyprop-1-enyl)benzene: Kim, H.; Lee, C. *Org. Lett.* **2002**, *4*, 4369. (3-Isopropoxypropyl)benzene: Lashdaf, M.; Nieminen, V.-V.; Tiitta, M.; Venäläinen, T.; Österholm, H.; Krause, O. *Microporous Mesoporous Mater.* **2004**, *75*, 149.

Spectroscopic Data for (3-Isopropoxybut-1-enyl)benzene. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ 1.19 [d, $^3J_{HH}$ = 4.8 Hz, 6 H, $(CH_3)_2$CHO-], 1.33 [d, $^3J_{HH}$ = 6.0 Hz, 3 H, CH_3CH(O*i*-Pr)], 3.73 [m, 1 H, $(CH_3)_2$CHO-], 4.15 (m, 1 H, CH_3CH(O*i*-Pr)], 6.15 (dd, $^3J_{HH}$ = 7.2, 16.0 Hz, 1 H, =CHCHO), 6.53 (d, $^3J_{HH}$ = 16.0 Hz, 1 H, PhCH=), 7.20−7.45 (5 H, C_6H_5). ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$, 293 K): δ 21.8 [s, CH_3CH(O*i*-Pr)], 22.2, 23.3 [both s, $(CH_3)_2$CHO], 68.4 [s, $(CH_3)_2$CHO], 73.4 [s, CH(O*i*-Pr)] 126.4, 127.4, 128.3 [all s, arom-CH] 130.1 (s, PhCH=), 132.9 (s, =CHCHO), 139.1 (arom. ipso-*C*).

Spectroscopic Data for (3-Isopropoxypropyl)benzene. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ 1.18 [d, $^3J_{HH}$ = 6.4 Hz, 6 H, $(CH_3)_2$CHO−], 1.91 (m, 2 H, CH_2CH_2O), 2.72 (m, 2 H, PhCH_2), 3.44 (t, $^3J_{HH}$ = 6.8 Hz, 2 H, CH_2O-), 3.57 [sept, 1 H, *J* = 6.4 Hz, $(CH_3)_2$CHO], 7.23 (m, 2 H, C_6H_5), 7.31 (m, 3 H, C_6H_5). ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$, 293 K): δ 22.1 [s, $(CH_3)_2$CHO], 31.5 (s, CH_2CH_2O), 32.7 (s, CH_2Ph), 67.2 [s, CH_2(O*i*-Pr)], 71.5 [s, CH(O*i*-Pr)] 125.7, 128.3, 128.5 [all s, arom-CH], 129.4 (arom. ipso-*C*).

Structural Analysis of Complex 4. X-ray data were collected on a Bruker Smart APEX CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube source (Mo radiation, λ = 0.71073 Å) operating at 50 kV and 30 mA. Data were collected over the complete sphere. Each frame exposure time was 10 s covering 0.3° in ω. Data were corrected for absorption by using a multiscan method applied with the SADABS program.[26] The structure was solved by the Patterson method and refined by full-matrix least-squares on F^2 with SHELXL97,[27] including isotropic and subsequently anisotropic displacement parameters for non-hydrogen atoms. Hydrogen atoms were observed in the difference Fourier maps and refined as free isotropic atoms or included in calculated positions and refined riding on their respective carbon atoms with the thermal parameter related to the bonded atoms. The hydride ligand of **4** was observed and refined as a free isotropic atom with a fixed thermal parameter. Crystal data and details of the data collection and refinement are given in Table 3.

Acknowledgment. Financial support from the MEC of Spain (Proyect CTQ2005-00656) and Consolider Ingenio 2010 (CDS2007-00006) is acknowledged. C.G.-Y. thanks the Spanish MEC and the University of Zaragoza for funding through the "Ramón y Cajal" program.

Supporting Information Available: Table of crystallographic data and bond lengths and angles of complex **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800150Z

(26) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33. *SADABS*: Area-detector absorption correction; Bruker-AXS: Madison, WI, 1996.

(27) *SHELXTL* Package v. 6.10; Bruker-AXS: Madison, WI, 2000. Sheldrick, G. M. SHELXS-86 and SHELXL-97; University of Göttingen: Göttingen, Germany, 1997.