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Preparation, X-ray Structure, and Reactivity of an Osmium-Hydroxo Complex Stabilized by an N-Heterocyclic Carbene Ligand: A Base-Free Catalytic Precursor for Hydrogen Transfer from 2-Propanol to Aldehydes

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Complex [(η^6-*p*-cymene)OsCl(IPr)]OTf (**1**; IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolylidene; OTf = CF_3SO_3) reacts with NaOH to give [(η^6-*p*-cymene)Os(OH)(IPr)]OTf (**2**), which under hydrogen atmosphere affords [(η^6-*p*-cymene)OsH_3(IPr)]OTf (**3**). The hydride ligands of **3** undergo exchange coupling, decreasing the H−H coupling constant from 206 to 74 Hz in the temperature range 213−178 K. Complex **3** is also obtained in a two-step procedure involving the reaction of **2** with $NaBH_4$ to give (η^6-*p*-cymene)OsH_2(IPr) (**4**) and the protonation of the latter with HOTf. Attempts to obtain **4** directly from **1** or (η^6-*p*-cymene)$OsCl_2$(IPr) (**5**) are unsuccessful. In both reactions (η^6-*p*-cymene)OsHCl(IPr) (**6**) is formed. Complex **2** also reacts with methanol and 2-propanol. At −30 °C, the reaction with the first of them leads to [(η^6-*p*-cymene)Os(OMe)(IPr)]OTf (**7**), while with the second one, [(η^6-*p*-cymene)OsH{κ^1-$OC(CH_3)_2$}(IPr)]OTf (**8**) is obtained. Complex **2** is a catalyst precursor for the hydrogen transfer from 2-propanol to aldehydes, which does not need a base. The obtained TOF values are between 950 and 3500 h^{-1}. The X-ray structures of **2** and **6** are also reported.

Introduction

N-Heterocyclic carbenes (NHC) are an emergent class of versatile ancillary ligands, which are receiving increased attention due to their ability to stabilize a variety of transition-metal complexes, some of which are very active in catalytic reactions.[1] As regards the iron triad, most of the known NHC catalysts are ruthenium-based derivatives, which have been applied to C−C coupling and hydrogenation reactions including hydrogen transfer from alcohols to carbonyl compounds.[2]

Aldehydes, in contrast to ketones, are hard to reduce successfully by transfer hydrogenation from a solvent such as refluxing 2-propanol.[3] The difficulty resides in the side reactions that may occur during the process, usually performed in basic media. In addition to metal-promoted C−H bond activation, the α-CH group is susceptible to deprotonation, which may degenerate into aldol condensation products.[4] Furthermore, the substrates may also undergo decarbonylation reactions, which cause catalyst deactivation by coordination of carbon monoxide to the metal center.[5]

The NHC-osmium complexes are very scarce, and most of them have been reported during the last two years.[6] Thus, the NHC-osmium catalysts were unknown until 2005. That year, as a part of our work on half-sandwich transition-metal compounds,[7] we reported that the dimer [(η^6-*p*-cymene)$OsCl_2$]$_2$

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reacts with 1,3-bis(2,6-diisopropylphenyl)imidazolylidene (IPr) and 1,3-bis(2,4,6-trimethylphenyl)imidazolylidene (IMes) to give the mononuclear derivatives (η^6-*p*-cymene)$OsCl_2$(NHC), which afford the alkylidene compounds [(η^6-*p*-cymene)-OsCl(=CHPh)(NHC)]OTf (OTf = CF_3SO_3) by treatment with AgOTf and subsequent addition of phenyldiazomethane to the corresponding 16-electron intermediate [(η^6-*p*-cymene)OsCl(NHC)]OTf.[8] These alkylidene species are a rare case of efficient third-row initiators for olefin metathesis reactions.

A few osmium catalyst precursors for transfer hydrogenation from alcohols to carbonyl compounds have been reported,[9] including the synthesis of chiral benzyl-α-*d* alcohols by reduction of benzaldehyde-α-*d* substrates.[10] In general, it has been proposed that the catalysis proceeds via a metal-alkoxide intermediate, which generates a hydride species by β-elimination.[11] A base is required when the precursor does not contain a hydride ligand. Its function is to generate the alkoxide group from the solvent, affording the active species by coordination to the metal center.[12] Undoubtedly, the cleanest method to obtain it is the direct protonation of a coordinated Brønsted base stronger than the alkoxide ligand.[13] In this context, the transition-metal hydroxide complexes should play an important role as transfer hydrogenation precursors.

The osmium-hydroxo compounds are extremely rare in comparison with other metals. Those known include high-oxidation-state derivatives independently reported by Shapley[14] and Meyer,[15] the osmium(II) species OsH(OH)(CO)$(PR_3)_2$ (PR_3 = P^iPr_3,[16] P^tBu_2Me[17]), and few dimers.[18] Now, we report a novel unsaturated osmium-hydroxo compound, stabilized by a NHC ligand, which is the entry point to new hydride derivatives and an efficient catalyst precursor for the hydrogen transfer from 2-propanol to aldehydes.

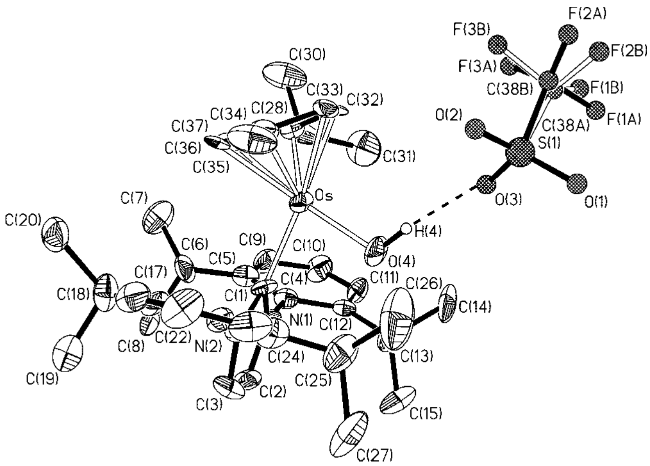
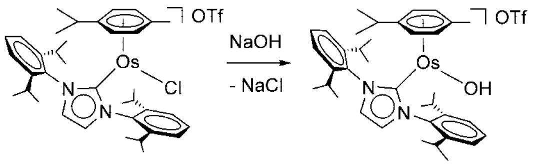


Figure 1. Molecular diagram of **2**. Selected bond lengths (Å) and angles (deg): Os−C(1) 2.034(13), Os−O(4) 1.925(12), H(4)−O(3) 1.97; C(1)−Os−O(4) 80.9(5).

Results and Discussion

1. Preparation and Characterization of [(η^6-*p*-cymene)-Os(OH)(IPr)]OTf. Although complex [(η^6-*p*-cymene)OsCl(IPr)]OTf (**1**) is a cationic 16-electron species, the treatment at room temperature of its tetrahydrofuran solutions with 14.0 equiv of NaOH produces the replacement of the chloride ligand by a hydroxo group, instead of the coordination of the latter to the unsaturated metal center. As a result, the cationic 16-electron hydroxo derivative [(η^6-*p*-cymene)Os(OH)(IPr)]OTf (**2**) is formed according to eq 1.



1 **2** (1)

Complex **2**, which is isolated as a brown solid in 73% yield, was characterized by elemental analysis, IR, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, and an X-ray crystallographic study. A view of the structure is shown in Figure 1. The geometry around the osmium atom is the typical two-legged piano stool for 16-electron half-sandwich complexes of this type,[8,19] with an O(4)−Os−C(1) angle of 80.9(5)°.

The Os−O(4) distance of 1.925(12) Å is about 0.2 Å shorter than that in the saturated bis-phosphine compound OsH(OH)(η^2-CH_2=$CHCO_2CH_3$)(CO)$(P^iPr_3)_2$ (2.111(3) Å),[16] indicating that the ground state of the complex involves O → Os π-donation and is thus going toward a formal 18-valence-electron ground state. The H(4) atom points toward the O(3) atom of the trifluoromethanesulfonate anion. The separation between them

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of 1.97 Å is shorter than the sum of the van der Waals radii of hydrogen and oxygen (r_{vdw}(H) = 1.20 Å; r_{vdw}(O) = 1.40 Å).[20] This suggests that there is an O(4)−H(4)···O(3) hydrogen bond.

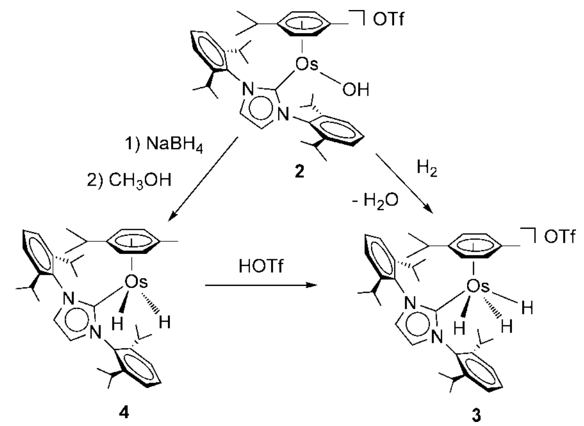
The Os−C(1) bond length of 2.034(13) Å compares well with the reported distances for the few NHC-osmium compounds characterized by X-ray diffraction analysis,[6,8,21] those found in the tautomerized-quinoline derivatives $OsCl_2(\eta^2\text{-}H_2)\{\kappa\text{-}C\text{-}[HNC_{10}H_8]\}(P^iPr_3)_2$ (2.005(6) Å)[22] and $OsCl_2(\eta^2\text{-}H_2)\{\kappa\text{-}C\text{-}[HNbq]\}(P^iPr_3)_2$ (bq = benzo[*h*]quinoline; 2.0055(11) and 2.030(10) Å)[23] and in the tautomerized-pyridine complexes $[\overline{OsH_2\{C_6H_4C(O})Ph\}\{\kappa\text{-}C\text{-}[HNC_5H_3Et]\}(P^iPr_3)_2]BF_4$ (2.110(5) Å) and $[OsH\{\kappa\text{-}C\text{-}[HNC_5H_3Et]\}(CH_3CN)_2(P^iPr_3)_2]BF_4$ (1.993(6) Å).[24]

In agreement with the presence of a hydroxo ligand in **2**, the IR of this compound shows a ν(O−H) band at 3366 cm^{-1}. In the ^1H NMR spectrum in dichloromethane-d_2 at room temperature, the resonance corresponding to the OH-proton appears at 13.97 ppm as a broad signal, which is converted into a singlet at −40 °C. This resonance is shifted 9.5 ppm toward lower field with regard to that of the unsaturated bis-phosphine complex $OsH(OH)(CO)(P^iPr_3)_2$ (δ, 4.5),[16] but only 3.2 ppm with regard to that of $[Cp^*W(OH)(\mu\text{-}S)_2RuH(PPh_3)_2]OTf$, where the OH-hydrogen atom is also involved in a O−H···O hydrogen bond with the trifluoromethanesulfonate anion.[25] The $^{13}C\{^1H\}$ NMR spectrum shows the C(1) resonance at 175.9 ppm.

2. Hydride Compounds. In dichloromethane complex **2** reacts with molecular hydrogen to give the trihydride derivative $[(\eta^6\text{-}p\text{-cymene})OsH_3(IPr)]OTf$ (**3**), which is isolated as a white solid in 89% yield. We assume a piano-stool geometry for this compound (Scheme 1), since previous studies on phosphine complexes of the form $[(\eta^6\text{-}C_6H_6)OsH_3(PR_3)]^+$ have established this ligand disposition, with H−H separations of about 1.7 Å.[26]

The ^1H NMR spectrum in the hydride region anticipated for this structure would consist of two resonances in the intensity ratio 2:1. However, the room-temperature ^1H NMR spectrum of **3** in dichloromethane-d_2 exhibits a singlet at −11.8 ppm. This observation is consistent with the operation of a thermally activated site exchange process, which proceeds at rates sufficient to lead to a single hydride resonance. In accordance with this, lowering the sample temperature leads to broadening of the resonance. At low temperature (213 K), decoalescence occurs and a pattern corresponding to the expected A_2B spin system is observed, which becomes well resolved at 203 K and below (Figure 2). The values of the chemical shifts of the A (δ, −11.7) and B (δ, −11.1) sites show no significant temperature dependence. However, the magnitudes of the observed H−H coupling constants are very sensitive to temperature, decreasing from 206 to 74 Hz as temperature decreases from 213 to 178 K. The trihydride character of the complex is supported by the T_1(min) value of 127 ms, which is observed at 228 K, at higher temperature than the decoalescence.

Scheme 1



Line-shape analysis of the spectra of Figure 2 allows the calculation of the rate constants for the thermal exchange process at different temperatures. The activation parameters obtained from the Eyring analysis are $\Delta H^\ddagger = 9.7 \pm 1$ kcal·mol^{-1} and $\Delta S^\ddagger = 1.7 \pm 1.5$ cal·K^{-1}·mol^{-1}. The value for the entropy of activation close to zero is in agreement with an intramolecular process, while the value for the enthalpy of activation lies in

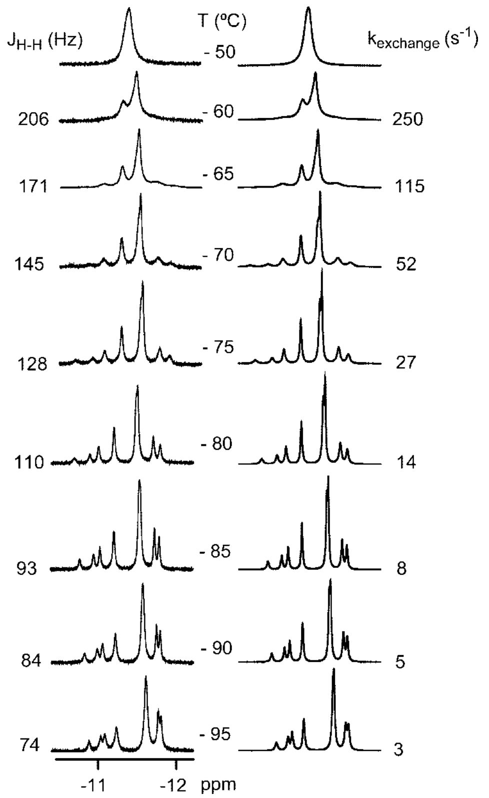


Figure 2. Variable-temperature ^1H NMR spectra in the hydride region of **3**: experimental (left) and calculated (right).

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the range reported for similar thermal exchange processes in other trihydride- and hydride-dihydrogen-osmium derivatives.[27]

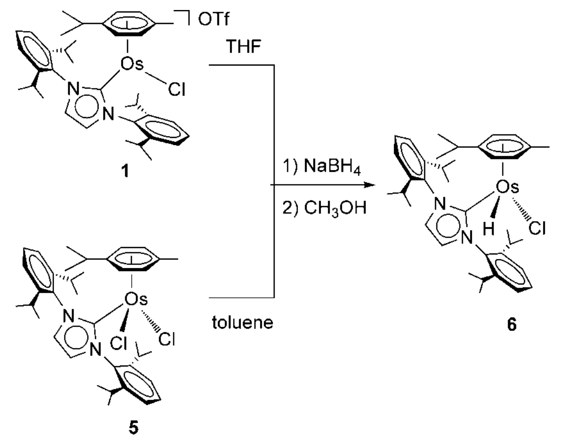
The large temperature-dependent coupling constant is similar to that reported for the related phosphine complexes $[(\eta^6\text{-}C_6H_6)OsH_3(PR_3)]^+$,[26] which is explained in terms of exchange coupling between the hydride ligands. Although the phenomenon has been observed in numerous phosphine complexes,[28] only two NHC examples are known: the ruthenium derivatives $RuH_3(\eta^5\text{-}C_5Me_5)$(IMes) and $RuH_3(\eta^5\text{-}C_5Me_4Et)$(IMes).[29]

The values of the exchange coupling are critically dependent on the nature of the ligands. In general, they decrease as the ligand basicity defined by Tolman increases.[30] There is no apparent contribution to the phenomenon from steric factors. The H−H coupling constant in **3** at 178 K (74 Hz) is similar to that observed in the tricyclohexylphosphine derivative $[(\eta^6\text{-}C_6H_6)OsH_3(PCy_3)]^+$ (98 Hz) and significantly smaller than that found in the triphenylphosphine counterpart $[(\eta^6\text{-}C_6H_6)OsH_3(PPh_3)]^+$ (374 Hz at 173 K). This suggests that the IPr ligand has a Tolman basicity similar to PCy_3.

A ν(Os−H) band at 2130 cm^{-1} in the IR and a singlet at 153 ppm in the $^{13}C\{^1H\}$ NMR spectrum, due to the metalated carbon atom of the NHC ligand, are also characteristic of **3**. In this context, it should be mentioned that this resonance appears shifted about 20 ppm toward higher field with regard to those of the osmium(II) derivatives reported here, indicating that the chemical shift of the resonance corresponding to the metalated carbon atom in this type of compounds is very sensitive to the formal oxidation state of the metal center.

Complex **3** can also be prepared by a two-step procedure, which involves the treatment at room temperature of tetrahydrofuran solutions of **2** with 10 equiv of sodium tetrahydroborate, and some drops of methanol, and the subsequent protonation of the resulting dihydride (η^6-p-cymene)OsH_2(IPr) (**4**) with the stoichiometric amount of triflouromethanesulfonic acid (Scheme 1). The intermediate complex **4** is isolated as a yellow solid in 62% yield. In agreement with the presence of the hydride ligands, its IR shows two ν(Os−H) bands at 2078 and 2021 cm^{-1}, whereas the ^1H NMR spectrum in dichloromethane-d_2 contains a singlet at −10.93 ppm. A T_1(min) value of 404 ms was found for this resonance at 223 K, which supports the dihydride character of the complex. The $^{13}C\{^1H\}$ NMR spectrum shows the OsC resonance of the NHC ligand at 173.5 ppm.

Scheme 2



Attempts to obtain **4** directly from **1** or its dichloro precursor (η^6-*p*-cymene)$OsCl_2$(IPr) (**5**) and sodium tetrahydroborate were unsuccessful (Scheme 2). In both cases the reactions lead to the hydride-chloro species (η^6-*p*-cymene)OsHCl(IPr) (**6**).

Complex **6**, which is isolated as a yellow solid in 66% yield, was characterized by elemental analysis, IR, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, and an X-ray crystallographic study. Figure 3 shows a view of the structure. The geometry around the osmium center is close to octahedral, with the arene ligand occupying three sites of a face. The angles C(1)−Os−Cl(1), C(1)−Os−H(01), and Cl(1)−Os−H(01) are 85.5(2)°, 71(3)°, and 79(3)°, respectively. The Os−C(1) bond length of 2.047(9) Å agrees well with that found in **2**.

The IR and ^1H and $^{13}C\{^1H\}$ NMR spectra of **6** are consistent with the structure shown in Figure 3. In the IR the most noticeable feature is the presence of the ν(Os−H) band, which is observed at 2125 cm^{-1}. The ^1H NMR spectrum shows the hydride resonance at −6.25 ppm, as a singlet. In the $^{13}C\{^1H\}$ NMR spectrum, the OsC resonance of the NHC ligand appears at 171.6 ppm.

3. Reactions with Methanol and 2-Propanol. The hydroxo ligand of **2** is easily replaced by an alkoxide group. In methanol at −30 °C, complex **2** evolves into the methoxy derivative $[(\eta^6$-

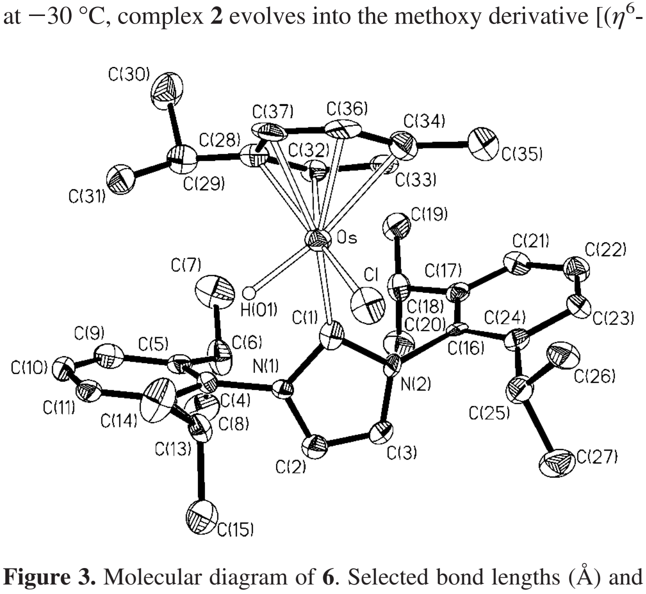


Figure 3. Molecular diagram of **6**. Selected bond lengths (Å) and angles (deg): Os−C(1) 2.047(9), Os−H(01) 1.62(9); Cl−Os−C(1) 85.5(2), Cl−Os−H(01) 79(3), C(1)−Os−H(01) 71(3).

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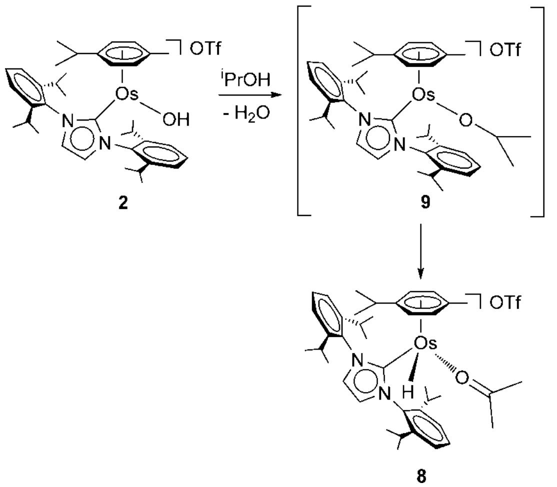
(27) See for example: (a) Esteruelas, M. A.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A.; Ruiz, N.; Sola, E.; Tolosa, J. I. *Inorg. Chem.* **1996**, *35*, 7811. (b) Castillo, A.; Esteruelas, M. A.; Oñate, E.; Ruiz, N. *J. Am. Chem. Soc.* **1997**, *119*, 9691. (c) Barea, G.; Esteruelas, M. A.; Lledós, A.; López, A. M.; Oñate, E.; Tolosa, J. I. *Organometallics* **1998**, *17*, 4065. (d) Castillo, A.; Barea, G.; Esteruelas, M. A.; Lahoz, F. J.; Lledós, A.; Maseras, F.; Modrego, J.; Oñate, E.; Oro, L. A.; Ruiz, N.; Sola, E. *Inorg. Chem.* **199938**, 1814. (e) Baya, M.; Crochet, P.; Esteruelas, M. A.; Gutiérrez-Puebla, E.; Ruiz, N. *Organometallics* **1999**, *18*, 5034. (f) Barrio, P.; Castarlenas, R.; Esteruelas, M. A.; Lledós, A.; Maseras, F.; Oñate, E.; Tomàs, J. *Organometallics* **2001**, *20*, 442. (g) Barrio, P.; Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 2635. (h) Barrio, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2004**, *23*, 3627. (i) Baya, M.; Eguillor, B.; Esteruelas, M. A.; Lledós, A.; Oliván, M.; Oñate, E. *Organometallics* **2007**, *26*, 5140.

(28) Sabo-Etienne, S.; Chaudret, B. *Chem. Rev* **1998**, *98*, 2077.

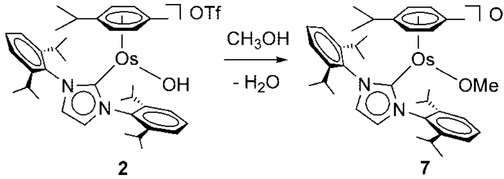
(29) Jones, A. L.; McGrady, G. S.; Sirsch, P.; Steed, J. W. *Chem. Commun.* **2005**, 5994.

(30) See for example: (a) Heinekey, D. M.; Millar, J. M.; Koetzle, T. F.; Payne, N. G.; Zilm, K. W. *J. Am. Chem. Soc.* **1990**, *112*, 909. (b) Heinekey, D. M.; Payne, N. G.; Sofield, C. D. *Organometallics* **1990**, *9*, 2643. (c) Gusev, D. G.; Kuhlman, R.; Sini, G.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1994**, *116*, 2685. (d) Sabo-Etienne, S.; Chaudret, B.; el Makarim, H. A.; Barthelat, J.-C.; Daudey, J.-P.; Ulrich, S.; Limbach, H.-H.; Moïse, C. *J. Am. Chem. Soc.* **1995**, *117*, 11602. (e) Heinekey, D. M.; Hinkle, A. S.; Close, J. D. *J. Am. Chem. Soc.* **1996**, *118*, 5353. (f) Kuhlman, R.; Clot, E.; Leforestier, C.; Streib, W. E.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1997**, *119*, 10153. (g) Yandulov, D. V.; Huang, D.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **2000**, *39*, 1919.

Scheme 3



p-cymene)Os(OCH_3)(IPr)]OTf (**7**), which is isolated at −30 °C as a brown solid in 84% yield according to eq 2.



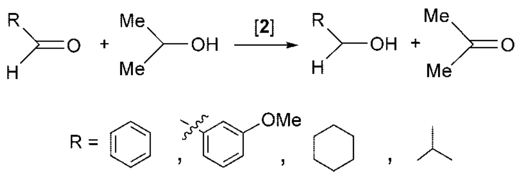
(2)

The presence of a methoxy ligand in this compound is supported by singlets at 4.56 and 82.2 ppm in the ^1H and $^{13}C\{^1H\}$ NMR spectra, respectively. In agreement with **2**, **4**, and **6**, the OsC resonance of the NHC ligand in the $^{13}C\{^1H\}$ NMR spectrum appears at 173.5 ppm.

The isopropoxy counterpart is much less stable than **7**, as expected. Thus, at −30 °C in dichloromethane-d_2, the addition of 6 equiv of 2-propanol to **2** gives the hydride-acetone species [(η^6-*p*-cymene)OsH{κ^1-OC(CH_3)$_2$}(IPr)]OTf (**8**) via the isopropoxy intermediate [(η^6-*p*-cymene)Os{OCH(CH_3)$_2$}(IPr)]OTf (**9**), which rapidly evolves by hydrogen β-elimination and it is not detected (Scheme 3).

The presence of the hydride and acetone ligands in **8** is evident in the ^1H and $^{13}C\{^1H\}$ NMR spectra. In the ^1H NMR spectrum the hydride resonance appears at −6.49 ppm as a singlet. The coordination of acetone by the oxygen atom[31] is supported by the $^{13}C\{^1H\}$ NMR spectrum, where the carbonyl resonance is observed at 226.3 ppm, shifted 19.8 ppm to lower field with regard to the resonance of the free acetone. In accordance with an osmium(II) metal center, the OsC resonance of the NHC ligand appears at 168.5 ppm.

4. Hydrogen Transfer from 2-Propanol to Aldehydes. It has been proposed that the inner-sphere transfer hydrogenation mechanism for the reduction of carbonyl compounds with 2-propanol involves four steps:[11] (i) coordination of the substrate to a coordinatively unsaturated metal-hydride species, (ii) formation of an alkoxy-metal intermediate by hydrogen migration from the metal to the carbonyl carbon atom, (iii) exchange of the alkoxy group by reaction with the alcohol, which acts as solvent, and (iv) a β-elimination process. The formation of **8** according to Scheme 3 represents stoichiometric evidence for the steps iii and iv. The substitution of the acetone ligand of **8** by an aldehyde molecule and the subsequent insertion of the latter into the osmium−hydride bond close this cycle. Thus, one should expect that the hydroxo derivative **2** was a useful catalytic precursor for the reaction in absence of base. In fact, in the presence of **2**, the 2-propanol solutions of aldehydes afford primary alcohols and acetone (eq 3).



(3)

The reactions were carried out at 80 °C using 1:1000 and 1:3000 catalyst:substrate molar ratios. Under these conditions almost quantitative yields of alcohols are obtained after 1−6 h. At 50% conversion the TOF values are between 950 and 3500 h^{-1} (Table 1). They are similar to those obtained by Crabtree with some neopentyl-substituted NHC-iridium complexes and a carbonate base[3k] and lower than those reported by Baratta using 0.01−0.05 mol % of the ruthenium complex RuCl(CNN)(dppb) (HCNN = 6-(4′-methylphenyl)-2-pyridylmethylamine, dppb = $Ph_2P(CH_2)_4PPh_2$) in the presence of 1−10 mol% of potassium carbonate.[3n]

The substituent of the aldehyde has a marked influence on the TOF values. Aliphatic aldehydes are more easily reduced than benzaldehydes. The presence of a methoxy substituent in *meta* position with regard to the carbonyl group of the benzaldehyde increases the reduction rate of the substrate. Cyclohexanecarbaldehyde is more easily reduced than isovaleraldehyde.

The addition of 100 equiv of *p*-cymene to the catalytic solution does not modify significantly the activity of the system for the reduction of 3-methoxybenzaldehyde (entry 5), suggesting that during the catalysis the decoordination of the arene does not takes place. This is in contrast with that observed in the olefin metathesis reactions initiated by the related alkylidene precursor [(η^6-*p*-cymene)OsCl(=CHPh)(IPr)]OTf, which is activated by means of the arene decoordination.[8]

Under the catalytic conditions acetophenone is also reduced. However the activity of the system is very poor. At 50% conversion the obtained TOF value is only 12 h^{-1}.

Concluding Remarks

This study has revealed that the reaction of [(η^6-*p*-cymene)OsCl(IPr)]OTf with NaOH affords [(η^6-*p*-cymene)Os(OH)(IPr)]OTf. Under hydrogen atmosphere, this compound gives rise to the trihydride [(η^6-*p*-cymene)OsH_3(IPr)]OTf, where the hydride ligands undergo exchange coupling with a similar intensity to that of the hydride ligands of the tricyclohexylphosphine complex [(η^6-C_6H_6)OsH_3(PCy_3)]$^+$. In 2-propanol, the hydroxo compound affords the monohydride [(η^6-*p*-cymene)OsH{κ^1-OC(CH_3)$_2$}(IPr)]OTf, which is an active catalyst for the reduction of aldehydes by transfer hydrogenation.

In conclusion, we report the preparation and the X-ray structure of a novel half-sandwich osmium-hydroxo complex stabilized with a NHC ligand, which is the entry to a trihydride-NHC species with exchange coupling between the hydride

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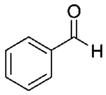
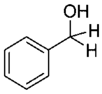
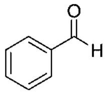
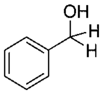
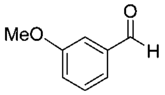
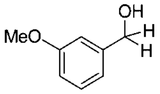
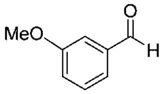
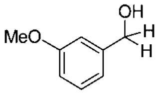
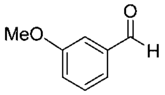
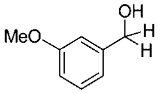
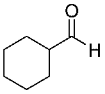
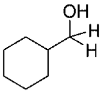
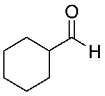
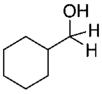
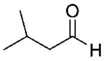
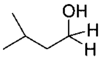
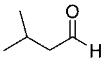
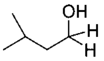
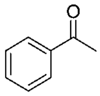
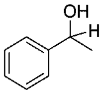
[31] (a) Esteruelas, M. A.; Gómez, A. V.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A. *Organometallics* **1996**, *15*, 3423. (b) Bohanna, C.; Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Martinez, M.-P. *Organometallics* **1997**, *16*, 4464. (c) Esteruelas, M. A.; Hernández, Y. A.; López, A. M.; Oliván, M.; Oñate, E. *Organometallics* **2005**, *24*, 5989. (d) Esteruelas, M. A.; Hernández, Y. A.; López, A. M.; Oliván, M.; Oñate, E. *Organometallics* **2007**, *26*, 2193. (e) Castro-Rodrigo, R.; Esteruelas, M. A.; López, A. M.; Oliván, M.; Oñate, E. *Organometallics* **2007**, *26*, 4498.

Table 1. Transfer Hydrogenation Catalyzed by 2[a]

Entry	Substrate	Product	Ratio[b]	Time (h)	Yield(%)[c]	TOF (h^{-1})[d]
1			1000	2	98	1360
2			3000	6	88	950
3			1000	3	98	1670
4			3000	6	95	1640
5			1000+cy[e]	3	97	1720
6			1000	1	98	3530
7			3000	2	98	2730
8			1000	1	98	2300
9			3000	4	96	1550
10			100	22	72	12

[a] Performed under argon atmosphere in 10 mL of 2-propanol at 80 °C. [Substrate] = 0.34 M. [b] [Substrate]/[Catalyst]. [c] Determined by GC-MS. [d] Determined at 50% conversion. [e] 100 equiv of *p*-cymene related to catalyst was added.

ligands and a useful catalytic precursor for the hydrogen transfer from 2-propanol to aldehydes that does not need the help of a base.

Experimental Section

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Organic solvents were dried by standard procedures and distilled under argon prior to use. The starting material **1** was prepared as previously described in the literature.[8] ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on either a Varian Gemini 2000, a Bruker ARX 300, or a Bruker Avance 400 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^1H, $^{13}C\{^1H\}$) or external H_3PO_4 ($^{31}P\{^1H\}$). Coupling constants, *J*, are given in hertz. Infrared spectra were run on a Perkin-Elmer 1730 spectrometer (Nujol mulls on polyethylene sheets). C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. GC experiments were run on an Agilent 6890 series gas chromatograph system, using a HP-5MS 5% phenyl methyl siloxane column (30 m × 250 μm with a 0.25 μm film thickness).

Preparation of [(η^6-*p*-Cymene)Os(OH)(IPr)]OTf (2). A green solution of **1** (400 mg, 0.447 mmol) in 10 mL of tetrahydrofuran was treated with NaOH (250 mg, 6.25 mmol) and was kept stirring for 1 h at room temperature. The resulting brown suspension was filtered through Celite and evaporated to dryness. Then 10 mL of CH_2Cl_2 was added, and it was filtered through Celite. The solvent was removed under vacuum, and addition of diethyl ether caused the precipitation of a reddish-brown solid, which was washed with diethyl ether (3 × 3 mL) and dried in vacuo. Yield: 285 mg (73%). Anal. Calcd for $C_{38}H_{51}N_2SF_3O_4Os$: C, 51.92; H, 5.85; N, 3.19; S, 3.65. Found: C, 51.53; H, 5.53; N, 3.44; S, 3.80. IR (cm^{-1}): ν(Os−OH) 3366; $\nu_a(SO_3)$ 1285 (s); $\nu_s(CF_3)$ 1224 (m); $\nu_a(CF_3)$ 1153 (s); $\nu_s(SO_3)$ 1031 (s); $\delta_a(SO_3)$ 637 (s). ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 13.97 (br, 1H, OH), 7.55 (m, 2H, H_{ph}), 7.40 (m, 4H, H_{ph}), 7.12 (s, 2H, =CHN), 6.37 and 6.31 (both d, J_{H-H} = 6.4, 4H, H_{cym}), 2.83 (sept, J_{H-H} = 6.4, 4H, $C\underline{H}Me_{IPr}$), 1.40 and 1.15 (both d, J_{H-H} = 6.4, 24H, $CH\underline{Me}_{IPr}$), 1.14 (m, 1H, $C\underline{H}Me_{cym}$), 0.89 (s, 3H, Me_{cym}), 0.86 (d, J_{H-H} = 6.3, 6H, $CH\underline{Me}_{cym}$). $^{13}C\{^1H\}$-APT NMR plus HSQC and HMBC (75.4 MHz, CD_2Cl_2, 293 K): δ 175.9 (s, OsC), 146.8 (s, C_q), 135.2 (s, C_qN), 131.5 and 124.9 (s, CH_{ph}), 125.2 (s, =CHN), 121.3 (q, J_{C-F} = 320.4, CF_3), 87.6 and 77.2 (both s, $C_{q\text{-}cym}$), 79.6 and 76.0 (both s, CH_{cym}), 32.6 (s, $\underline{C}HMe_{cym}$), 29.2 (s, $\underline{C}HMe_{IPr}$), 26.5 and 22.7 (both s, $CH\underline{Me}_{IPr}$), 22.6 (s, $CH\underline{Me}_{cym}$), 19.1 (s, Me_{cym}).

Preparation of [(η^6-*p*-Cymene)OsH_3(IPr)]OTf (3). A brown solution of **2** (200 mg, 0.227 mmol) in 10 mL of methylene chloride was stirred for 3 h under hydrogen atmosphere. The resulting colorless solution was evaporated to dryness, and then addition of diethyl ether caused the precipitation of a white solid, which was washed with diethyl ether (3 × 3 mL) and dried in vacuo. Yield: 175 mg (89%). Anal. Calcd for $C_{38}H_{53}N_2SF_3O_3Os$: C, 52.76; H, 6.17; N, 3.24; S, 3.71. Found: C, 52.63; H, 6.36; N, 3.25; S, 3.80.

IR (cm^{-1}): ν(Os−H) 2130 (m); $\nu_a(SO_3)$ 1274 (s); $\nu_s(CF_3)$ 1221 (m); $\nu_a(CF_3)$ 1145 (s); $\nu_s(SO_3)$ 1031 (s); $\delta_a(SO_3)$ 636 (s). ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.59 (m, 2H, H_{ph}), 7.41 (m, 4H, H_{ph}), 7.14 (s, 2H, =CHN), 5.53 (s, 4H, H_{cym}), 2.38 (sept, J_{H-H} = 6.9, 4H, $C\underline{H}Me_{IPr}$), 2.08 (sept, J_{H-H} = 6.9, 1H, $C\underline{H}Me_{cym}$), 1.90 (s, 3H, Me) 1.40 and 1.12 (both d, J_{H-H} = 6.9, 24H, $CH\underline{Me}_{IPr}$), 0.94 (d, J_{H-H} = 6.9, 6H, $CH\underline{Me}_{cym}$), −11.18 (s, 1H, OsH). $^{13}C\{^1H\}$-APT NMR plus HSQC and HMBC (75.4 MHz, CD_2Cl_2, 293 K): δ 153.9 (s, OsC), 146.2 (s, C_q), 137.3 (s, C_qN), 131.3, 125.1, and 124.8 (s, CH_{Ph}), 130.0 and 119.6 (both s, $C_{q\text{-}cym}$), 120.8 (q, J_{C-F} = 320.2, CF_3), 88.6 and 85.0 (both s, CH_{cym}), 32.8 (s, $\underline{C}HMe_{cym}$), 29.5 (s, $\underline{C}HMe_{IPr}$), 25.8 and 22.5 (both s, $CH\underline{Me}_{IPr}$), 23.7 (s, $CH\underline{Me}_{cym}$), 19.1 (s, Me_{cym}).

Preparation of (η^6-*p*-Cymene)OsH$_2$(IPr) (4). A brown solution of **2** (200 mg, 0.227 mmol) in 10 mL of tetrahydrofuran was treated with sodium borohydride (100 mg, 2.7 mmol) and two drops of MeOH. The color changed immediately to yellow, and after the evolution of gas had ceased, the solvent was removed in vacuo. Then, 10 mL of toluene was added and the suspension was filtered through Celite. The solution was evaporated to dryness, and addition of pentane at −78 °C caused the precipitation of a yellow solid, which was washed with cold pentane (2 × 2 mL) and dried in vacuo. Yield: 100 mg (62%). Anal. Calcd for $C_{37}H_{52}N_2Os$: C, 62.15; H, 7.33; N, 3.92. Found: C, 61.79; H, 6.92; N, 3.76. IR (cm^{-1}): ν(Os−H) 2078, 2021 (m). ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.42 (m, 2H, H_{Ph}), 7.27 (m, 4H, H_{Ph}), 6.78 (s, 2H, =CHN), 4.41 and 4.19 (both d, J_{H-H} = 5.4, 4H, H_{cym}), 2.86 (sept, J_{H-H} = 6.4, 4H, $C\underline{H}Me_{IPr}$), 2.06 (sept, J_{H-H} = 6.9, 1H, $C\underline{H}Me_{cym}$), 2.02 (s, 3H, Me_{cym}), 1.34 and 1.07 (both d, J_{H-H} = 6.4, 24H, $CH\underline{Me}_{IPr}$), 1.00 (d, J_{H-H} = 6.9, 6H, $CH\underline{Me}_{cym}$), −10.93 (s, 2H, OsH). $^{13}C\{^1H\}$-APT NMR plus HSQC and HMBC (75.4 MHz, CD_2Cl_2, 293 K): δ 173.5 (s, OsC), 147.0 (s, C_q), 140.5 (s, C_qN), 129.1 and 124.0 (both, CH_{ph}), 122.2 (s, =CHN), 102.2 and 87.7 (both s, $C_{q\text{-}cym}$), 76.6 and 69.2 (both s, CH_{cym}), 32.6 (s, $\underline{C}HMe_{cym}$), 29.0 (s, $\underline{C}HMe_{IPr}$), 25.4 and 22.8 (both s, $CH\underline{Me}_{IPr}$), 25.1 (s, $CH\underline{Me}_{cym}$), 21.0 (s, Me_{cym}).

Preparation of (η^6-*p*-Cymene)OsHCl(IPr) (6). A green solution of **1** (400 mg, 0.447 mmol) in 10 mL of tetrahydrofuran was treated with sodium borohydride (100 mg, 2.7 mmol) and two drops of MeOH. The color changed immediately to yellow, and after the evolution of gas had ceased, the solvent was removed in vacuo. Then, 10 mL of toluene was added, and the suspension was filtered through Celite. The solution was evaporated to dryness, and the addition of pentane caused the precipitation of a yellow solid, which was washed with cold pentane (2 × 2 mL) and dried in vacuo. Yield: 220 mg (66%). Anal. Calcd for $C_{37}H_{51}N_2ClOs$: C, 59.29; H, 6.86; N, 3.74. Found: C, 59.29; H, 6.42; N, 3.91. IR (cm^{-1}): ν(Os−H) 2125 (m). ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 7.3 (m, 6H, H_{ph}), 6.62 (s, 2H, =CHN), 5.21 and 4.33 (both d, J_{H-H} = 6.0, 2H, H_{cym}), 4.86 and 4.01 (both d, J_{H-H} = 4.8, 2H, H_{cym}), 3.35 and 3.17 (both m, 4H, $C\underline{H}Me_{IPr}$), 1.73 (sept, J_{H-H} = 6.9, 1H, $C\underline{H}Me_{cym}$), 1.63 (s, 3H, Me_{cym}), 1.49, 1.38, 1.05 and 1.01 (all d, J_{H-H} = 6.6, 24H, $CH\underline{Me}_{IPr}$), 1.06 and 0.88 (both d, J_{H-H} = 6.9, 6H, $CH\underline{Me}_{cym}$), −6.52 (s, 1H, OsH). $^{13}C\{^1H\}$-APT NMR plus HSQC and HMBC (75.4 MHz, C_6D_6, 293 K): δ 171.6 (s, OsC), 148.0 and 147.1 (both s, C_q), 139.5 (s, C_qN), 129.6 and 124.1 (both s, CH_{ph}), 123.5 (s, =CHN), 95.7 and 88.1 (both s, $C_{q\text{-}cym}$), 85.5, 84.0, 72.6 and 60.8 (all s, CH_{cym}), 32.5 (s, $\underline{C}HMe_{cym}$), 28.6 and 28.5 (both s, $\underline{C}HMe_{IPr}$), 26.4, 26.2, 23.1, 22.4 (all s, $CH\underline{Me}_{IPr}$), 25.8 and 22.5 (both s, $CH\underline{Me}_{cym}$), 17.9 (s, Me_{cym}).

Preparation of [(η^6-*p*-Cymene)Os(OMe)(IPr)]OTf (7). Complex **3** (200 mg, 0.227 mmol) was dissolved in 5 mL of MeOH at −30 °C with activated molecular sieves (4 Å) and was kept stirring for 30 min at low temperature. Then, it was filtered through Celite, and the resulting brown solution was evaporated to dryness under −30 °C. Addition of cold diethyl ether caused the precipitation of a brown solid, which was washed at −30 °C with diethyl ether (3 × 3 mL) and dried in vacuo. Yield: 170 mg (84%). Anal. Calcd for $C_{39}H_{53}N_2SF_3O_4Os$: C, 52.45; H, 5.98; N, 3.14; S, 3.52. Found: C, 52.21; H, 5.88; N, 2.99; S, 3.46. IR (cm^{-1}): $\nu_a(SO_3)$ 1272 (s); $\nu_s(CF_3)$ 1223 (m); $\nu_a(CF_3)$ 1154 (s); $\nu_s(SO_3)$ 1029 (s); $\delta_a(SO_3)$ 637 (s). ^{1}H NMR (300 MHz, CD_2Cl_2, 243 K): δ 7.53 (m, 2H, H_{ph}), 7.36 (m, 4H, H_{ph}), 7.12 (s, 2H, =CHN), 6.22 and 6.14 (both d, J_{H-H} = 6.4, 4H, H_{cym}), 4.56 (s, 3H, OMe), 2.64 (sept, J_{H-H} = 6.6, 4H, $C\underline{H}Me_{IPr}$), 1.35 and 1.09 (both d, J_{H-H} = 6.6, 24H, $CH\underline{Me}_{IPr}$), 1.14 (m, 1H, $C\underline{H}Me_{cym}$), 0.89 (s, 3H, Me_{cym}), 0.87 (d, J_{H-H} = 6.6, 6H, $CH\underline{Me}_{cym}$). $^{13}C\{^1H\}$-APT NMR plus HSQC and HMBC (75.4 MHz, CD_2Cl_2, 243 K): δ 173.5 (s, Os−C), 145.8 (s, C_q), 134.3 (s, C_qN), 131.3 and 124.5 (s, CH_{ph}), 125.3 (s, =CHN), 120.6 (q, J_{C-F} = 319.3, CF_3), 83.9 and 74.5 (both s, $C_{q\text{-}cym}$), 82.2 (s, OMe), 78.7 and 75.4 (both s, CH_{cym}), 32.4 (s, $\underline{C}HMe_{cym}$), 28.8 (s, $\underline{C}HMe_{IPr}$), 26.2 and 22.4 (both s, $CH\underline{Me}_{IPr}$), 22.2 (s, $CH\underline{Me}_{cym}$), 18.6 (s, Me_{cym}).

Preparation of [(η^6-*p*-Cymene)OsH{O=C(CH$_3$)$_2$}(IPr)]OTf (8). An NMR tube in CD_2Cl_2 at −30 °C was charged with complex **3** (60 mg, 0.068 mmol) and 30 μL (0.392 mmol) of ^{i}PrOH and was sealed under argon atmosphere. NMR data were colleted immediately at −30 °C. ^{1}H NMR (300 MHz, CD_2Cl_2, 243 K): δ 7.52 (m, 2H, H_{ph}), 7.36 (m, 4H, H_{ph}), 7.17 (s, 2H, =CHN), 5.50 and 3.95 (both d, J_{H-H} = 6.4, 2H, H_{cym}), 4.88 and 4.81 (both d, J_{H-H} = 4.8, 2H, H_{cym}), 2.70 and 2.59 (both sept, J_{H-H} = 6.6, 4H, $C\underline{H}Me_{IPr}$), 2.27 (s, 6H, $OC(CH_3)_2$), 1.62 (s, 3H, Me_{cym}), 1.50 (sept, J_{H-H} = 6.6, 1H, $C\underline{H}Me_{cym}$), 1.44, 1.28, 1.14, and 1.08 (all d, J_{H-H} = 6.6, 24H, $CH\underline{Me}_{IPr}$), 0.92 and 0.78 (both d, J_{H-H} = 6.6, 6H, $CH\underline{Me}_{cym}$), −6.49 (s, 1H, OsH). $^{13}C\{^1H\}$-APT NMR plus HSQC and HMBC (75.4 MHz, CD_2Cl_2, 243 K): δ 226.3 (s, Os−O=C), 168.5 (s, OsC), 146.2 and 146.1 (both s, C_q), 137.4 (s, C_qN), 130.0 and 123.8 (both s, CH_{ph}), 124.2 (s, =CHN), 120.3 (q, J_{C-F} = 318.9, CF_3), 98.6 and 88.7 (both s, $C_{q\text{-}cym}$), 84.7, 80.6, 74.3, and 57.1 (all s, CH_{cym}), 32.9 {s, Os−O=C($\underline{C}H_3$)$_2$}, 32.1 (s, $\underline{C}HMe_{cym}$), 29.0 and 28.7 (both s, $\underline{C}HMe_{IPr}$), 26.4, 26.2, 22.1, 21.8 (all s, $CH\underline{Me}_{IPr}$), 24.2 and 22.3 (both s, $CH\underline{Me}_{cym}$), 17.9 (s, Me_{cym}).

Determination of the Exchange Coupling Constants and Rate Constants for the Thermal Exchange Process of Hydrides in 3. Complete line-shape analysis of the hydride region of ^{1}H NMR spectra of **3** was achieved using the program gNMR (Cherwell Scientific Publishing Limited). The rate constants for various temperatures were obtained by fitting calculated to experimental spectra by full line-shape iterations. The transverse relaxation time, T_2, was estimated at the lowest temperature. Activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were obtained by least-squares fit of the Eyring plot. Errors were computed by published methods.[34]

Typical Transfer Hydrogenation Catalytic Reactions. An adequate amount of catalyst (0.033−0.1% mol) was added to a 0.34 M solution of substrate in 10 mL of 2-propanol under argon atmosphere. The Schlenk were placed under a thermostatic bath at 80 °C and was kept stirring for the determined time. The crude product was filtrated through neutral alumina and analyzed by GC-MS and NMR.

Structural Analysis of Complexes 2 and 6. 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 40 mA. Each frame exposure time was 60 s (**2**) or 30 s (**6**) covering 0.3° in ω. Data were corrected for absorption by using a multiscan method applied with the SADABS program.[32] The structures were solved by the Patterson method and refined by full-matrix least-squares on F^2 with SHELXL97,[33] including isotropic and subsequently anisotropic displacement parameters for non-hydrogen atoms and nondisordered

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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. In both molecules the observed displacement parameters of some carbon atoms have refined to unreasonable values. In both the rigid-bond restraint DELU was used to make the ADP values more reasonable.

Crystal data for **2**: $C_{38}H_{51}F_3N_2O_4OsS$, M_w 879.07, needle, light orange (0.20 × 0.04 × 0.01 mm), monoclinic, space group *Cc*, $a = 10.7729(15)$ Å, $b = 22.084(3)$ Å, $c = 16.445(2)$ Å, $\beta = 93.904(3)°$, $V = 3903.4(9)$ Å^3, $Z = 4$, $D_{calc} = 1.496$ g cm^{-3}, $F(000) = 1776$, $T = 100.0(2)$ K; $\mu = 3.374$ mm^{-1}; 12 492 measured reflections ($2\theta = 3-50°$), 6641 unique ($R_{int} = 0.0703$); min./max. transm factors = 0.819/0.967. Final agreement factors were R1 = 0.0638 (5661 observed reflections, $I > 2\sigma(I)$) and $wR^2 = 0.1448$; Flack parameter 0.043(18); data/restraints/parameters 6641/50/433; GoF = 1.009. Largest peak and hole = 1.768 and −2.767 e/Å^3. In the last cycles of refinement, the $CF_3SO_3^-$ anion was observed disordered and was refined with two moieties for the CF_3 unit (angle C−O−C of about 10°) with restraints in geometry and thermal ellipsoids. The OH hydrogen was refined with fixed geometry but free to rotate about the O−H axes.

Crystal data for **6**: $C_{37}H_{51}ClN_2Os$, M_w 749.45, needle, yellow (0.20 × 0.04 × 0.03 mm), monoclinic, space group $P2_1/n$, $a = 16.127(3)$ Å, $b = 12.312(3)$ Å, $c = 18.753(4)$ Å, $\beta = 114.684(5)°$, $V = 3383.3(12)$ Å^3, $Z = 4$, $D_{calc} = 1.471$ g cm^{-3}, $F(000) = 1520$, $T = 100.0(2)$ K; $\mu = 3.875$ mm^{-1}; 21 929 measured reflections ($2\theta = 3-50°$), 5956 unique ($R_{int} = 0.0968$); min./max. transm factors = 0.499/0.892. Final agreement factors were R1 = 0.0630 (4377 observed reflections, $I > 2\sigma(I)$) and $wR^2 = 0.1157$; data/restraints/parameters 5956/12/384; GoF = 1.110. Largest peak and hole = 2.026 and −2.438 e/Å^3. The hydride ligand was observed and refined as a free isotropic atom with a fixed thermal parameter.

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Supporting Information Available: The crystal structure determinations and a CIF file giving crystal data for compounds **2** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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