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Article

Redox Isomerization of Allylic Alcohols Catalyzed by Osmium and Ruthenium Complexes Containing a Cyclopentadienyl Ligand with a Pendant Amine or Phosphoramidite Group: X-ray Structure of an η^3-1-Hydroxyallyl-Metal-Hydride Intermediate

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Complexes $[MCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (M = Os (**1a**), Ru (**1b**)) react with $Li(C_5H_4CH_2CH_2NHMe)$ ($LiCp^N$) and KPF_6 to give the sandwich derivatives $[M(\eta^5\text{-}Cp^N)(\eta^6\text{-}p\text{-cymene})]PF_6$ (M = Os (**2a**), Ru (**2b**)). Treatment of **2a** and **2b** with (2,2′-biphenol)PCl leads to $[M(\eta^5\text{-}Cp^P)(\eta^6\text{-}p\text{-cymene})]PF_6$ (M = Os (**3a**), Ru (**3b**); $Cp^P = C_5H_4CH_2CH_2N(Me)P(2,2'\text{-biphenol})$). The photolysis of **2a**, **2b**, **3a**, and **3b** in acetonitrile produces the release of the *p*-cymene group and the coordination of the cyclopentadienyl pendant substituent to the metal center to afford $[M(\eta^5\text{-}C_5,\kappa\text{-}N\text{-}Cp^N)(CH_3CN)_2]PF_6$ (M = Os (**4a**), Ru (**4b**)) and $[M(\eta^5\text{-}C_5,\kappa\text{-}P\text{-}Cp^P)(CH_3CN)_2]PF_6$ (M = Os (**5a**), Ru (**5b**)). Complex **4a**, which has been characterized by X-ray diffraction analysis, is a more efficient catalyst precursor than **4b** for the redox isomerization of primary allylic alcohols, while the latter is more efficient than the former for the redox isomerization of secondary allylic alcohols. From the catalytic solutions containing **4a** and 2-methyl-2-propen-1-ol, the η^3-1-hydroxyallyl complex $[OsH(\eta^5\text{-}C_5,\kappa\text{-N-}Cp^N)\{\eta^3\text{-}CH_2C(CH_3)CH\text{-}OH\}]PF_6$ (**6**) has been crystallized and characterized by spectroscopic methods and X-ray diffraction analysis. The structure shows a N−H···O hydrogen bond (2.22 Å) between the NH-hydrogen atom of the coordinated pendant amine group and the oxygen atom of the hydroxy substituent of the allyl ligand.

Introduction

The one-pot internal redox isomerization of allylic alcohols mediated by transition metal complexes represents a useful and elegant shortcut to carbonyl compounds (eq 1), which otherwise would require a two-step sequence of oxidation and reduction reactions.[1]

(1)

Primary allylic alcohols[2] are harder to isomerize successfully than secondary allylic alcohols,[3] due to the side reactions that may occur during the process, in particular when a basic medium is used. In addition to metal-promoted C−H bond activation,[4] the α-CH group of the resulting aldehyde is susceptible to deprotonation, which may degenerate into aldol condensation products.[5] Furthermore, the products may also undergo decarbonylation reactions, which cause catalyst deactivation by coordination of carbon monoxide to

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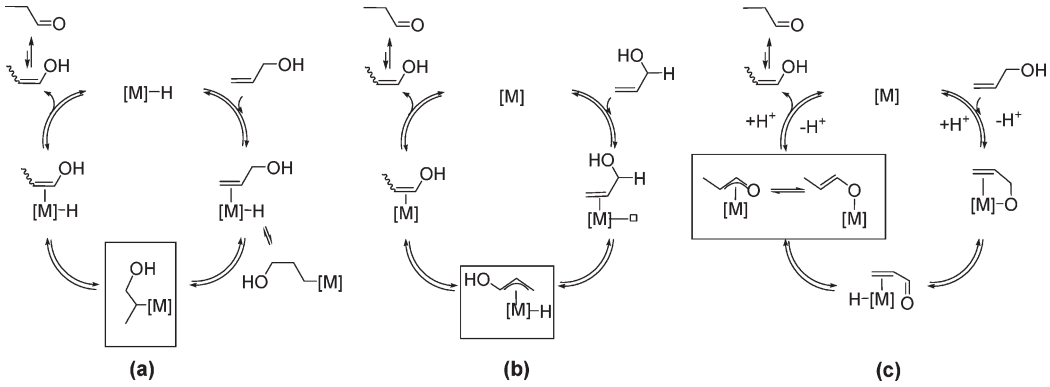

Figure 1

the metal center.[6] The development of efficient catalysts for the isomerization of primary allylic alcohols to aldehydes is of great interest.

Three types of mechanisms have been proposed for these reactions[1,3c,l] (Figure 1). A metal hydride addition−elimination mechanism is usually invoked for metal-hydride catalysts (a), while a π-allyl-metal-hydride mechanism has been proposed for low-valent metal complexes that can accommodate a π-allyl ligand (b). The third type of mechanism involves alcoholate species, which are generated in a basic reaction medium (c). These mechanisms have, however, been proposed with scarce experimental evidence, and all previous attempts to isolate and characterize catalytic intermediates unambiguously have been unsuccessful.

The overwhelming majority of catalysts belong to either group 8 or 9.[1,3g] From the iron triad, ruthenium dominates these reactions.[3b−f,h−j,l−t] Osmium has received little attention.[7] It is more reducing than ruthenium and prefers coordination saturation and redox isomers with more metal−carbon bonds.[8] This appears to be a handicap from a catalytic point of view. Thus, the catalytic osmium chemistry is poor. In addition to the Sharpless osmium-catalyzed asymmetric olefin dihydroxylation,[9] only a few homogeneous processes have been reported.[5,7,10,11]

Ruthenium-cyclopentadienyl complexes have been found to be very efficient catalysts for the redox isomerization of allylic alcohols, in particular for secondary alcohols.[3c,e,f,l−n,t] A modification of the cyclopentadienyl system is the use of a pendant donor substituent. The complexes containing this type of ligands are expected to perform chemistry different from that of usual cyclopentadienyl complexes. Indeed, the reversible coordination of the pendant donor group increases the stability of highly reactive centers.[12] This has a strong influence on the catalytic properties of the active systems and facilitates the study of the catalytic mechanisms.[13] As a consequence of this, complexes containing

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cyclopentadienyl ligands with a pendant donor substituent are attracting increased interest from those who study the chemistry of metals.[14]

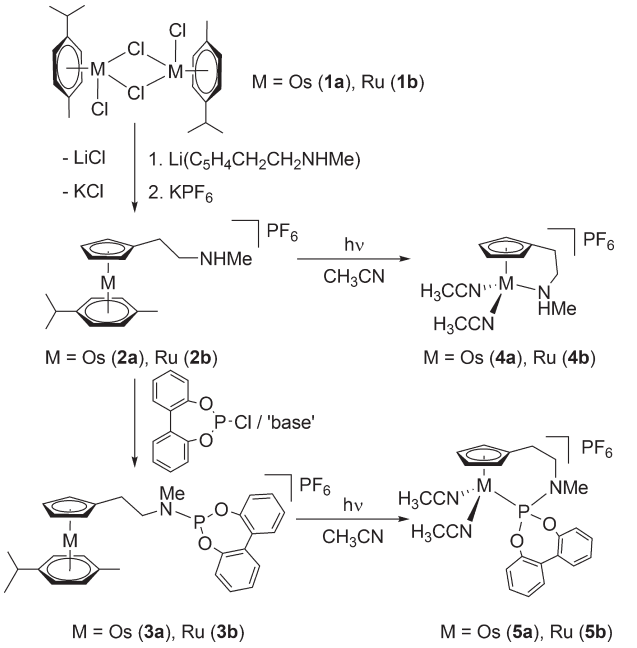
Our group is actively interested in this type of compounds.[15] As a part of our work in this field, we now report the preparation and characterization of new osmium and ruthenium complexes containing cyclopentadienyl ligands with pendant amine and phosphoramidite groups and their catalytic behavior in the isomerization of primary and secondary allylic alcohols. Furthermore, we propose a catalytic cycle on the basis of the isolation and full characterization of a hydroxyallyl intermediate.

Results and Discussion

1. Osmium and Ruthenium Complexes Containing Cyclopentadienyl Ligands with Pendant Amine and Phosphoramidite Groups. Osmium-cyclopentadienyl compounds[15d] are harder to prepare than the ruthenium counterparts. This is due to the greater inertness of the octahedral osmium(II) complexes, which is a consequence of the dependence of the crystal field activation energy on Δ_o. Two successful methods have been used to obtain this type of derivative: (i) the treatment of phosphine-metal-halide complexes with cyclopentadiene or a cyclopentadienyl derivative of an s- or p-block element[15b,c,16] and (ii) the photolysis of sandwich cyclopentadienyl-metal-arene derivatives in acetonitrile.[17] The former method has a major disadvantage in that displacement of the phosphine ligands is often difficult. Therefore, we have used the latter as it also allows the ruthenium counterparts to be obtained (Scheme 1).

Treatment at room temperature of the dimer $[OsCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (**1a**) with 2.5 equiv of $Li(C_5H_4CH_2CH_2NHCH_3)$ ($LiCp^N$) in tetrahydrofuran for 4 h and the subsequent addition of 2.0 equiv of KPF_6 to the dichloromethane/acetone (1:1) solution of the resulting residue affords the sandwich derivative $[Os(\eta^5\text{-}Cp^N)(\eta^6\text{-}p\text{-cymene})]PF_6$ (**2a**). Under the same conditions, the reaction of the ruthenium dimer $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (**1b**) with $LiCp^N$ and KPF_6 yields $[Ru(\eta^5\text{-}Cp^N)(\eta^6\text{-}p\text{-cymene})]PF_6$ (**2b**). Both compounds were isolated as brown oils in 80% yield.

Scheme 1



The $^{13}C\{^1H\}$ and ^1H NMR spectra of **2a** and **2b** are consistent with the presence of a free pendant substituent in the complexes. This allows, in solution, the five-membered ring to rotate around the M−Cp axis. Thus, the $^{13}C\{^1H\}$ NMR spectra in dichloromethane-d_2 shows three Cp singlets for each complex, at 75.8, 76.5, and 98.1 (**2a**) and 66.2, 80.4, and 81.5 (**2b**) ppm, whereas in the ^1H NMR spectra two Cp signals, at 5.48 and 5.60 (**2a**) and 5.08 and 5.17 (**2b**) ppm, are observed. The free character of the pendant substituent is also revealed by the CH_2 resonances of the CH_2-CH_2 chain in the ^1H NMR spectra, which appear as triplets, at 2.50 and 2.71 (**2a**) and 2.34 and 2.64 (**2b**) ppm, with H−H coupling constants of 6.6 (**2a**) and 7.1 (**2b**) Hz.

An effective method to prepare phosphoramidite ligands involves the reaction of $(RO)_2PCl$ compounds with primary or secondary amines in the presence of a base.[18] In agreement with this, the treatment at 0 °C of dichloromethane solutions of **2a** and **2b** with 1.3 equiv of (2,2′-biphenol)PCl in the presence of 2.4 equiv of piperidinomethyl polystyrene for 12 h leads to $[M(\eta^5\text{-}Cp^P)(\eta^6\text{-}p\text{-cymene})]PF_6$ (M = Os (**3a**), Ru (**3b**); $Cp^P = C_5H_4CH_2CH_2N(Me)P(2,2'\text{-biphenol})$) containing a phosphoramidite pendant substituent at the cyclopentadienyl group. Complexes **3a** and **3b** were isolated as pale brown solids in 75% and 68% yield, respectively. The formation of the phosphoramidite group is strongly supported by the $^{31}P\{^1H\}$ NMR spectra of these compounds, in acetonitrile-d_3 at room temperature, which show singlets at 150 (**3a**) and 148 (**3b**) ppm.

The photolysis at −5 °C of acetonitrile solutions of **2a**, **2b**, **3a**, and **3b** for 6 h, with a 400 W medium-pressure mercury lamp, produces the release of the *p*-cymene group and the coordination to the metal center of the pendant substituent of the cyclopentadienyl groups. The resulting unsaturated metal fragments are stabilized by coordination of two solvent molecules. The formed half-sandwich derivatives $[M(\eta^5\text{-}C_5,\kappa\text{-}N\text{-}Cp^N)(CH_3CN)_2]PF_6$ (M = Os (**4a**), Ru (**4b**)) and $[M(\eta^5\text{-}C_5,\kappa\text{-}P\text{-}Cp^P)(CH_3CN)_2]PF_6$ (M = Os (**5a**),

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(18) See for example: Bartels, B.; García-Yebra, C.; Helmchen, G. *Eur. J. Org. Chem.* **2003**, 1097, and references therein.

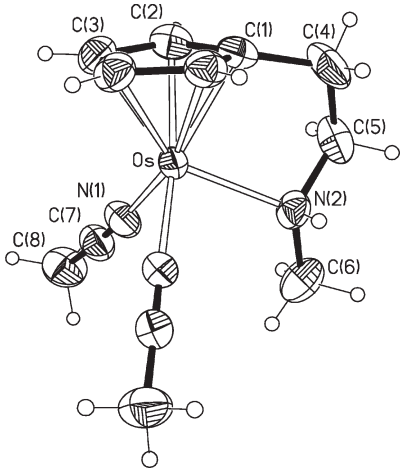


Figure 2. Molecular diagram of complex **4a**. Selected bond lengths (Å) and angles (deg): Os−C(1) 2.095(8); Os−C(2) 2.144(6); Os−C(3) 2.161(6); Os−N(1) 2.049(5); Os−N(2) 2.176(8); C(1)−Os−N(2) 82.3(3); N(1)−Os−N(2) 83.3(3).

Ru (**5b**)) were obtained as yellow (**4a**, **4b**, and **5a**) or white (**5b**) solids in 40−44% yield.

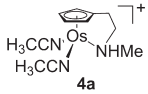
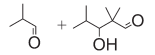
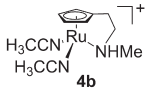
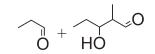
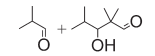
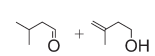
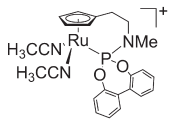
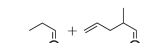
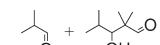
The coordination of the pendant group to the metal center of these compounds was confirmed by an X-ray diffraction study of **4a** (Figure 2). The geometry around the osmium center can be described as a distorted octahedron, with the cyclopentadienyl ring occupying the three sites of a face. The N−Os−N angles are close to 90°, whereas the separation between the pendant amine group and the metal center (Os−N(2)) is 2.176(8) Å.

The $^{13}C\{^1H\}$ and ^1H NMR spectra in acetonitrile-d_3 of **4a** and **4b** are temperature invariant between 25 and 80 °C. They are consistent with the structure shown in Figure 2 and reveal that the bond between the metal center and the amine nitrogen atom is strong; therefore the metal−pendant interaction remains in acetonitrile solution. In agreement with this the $^{13}C\{^1H\}$ NMR spectra contain five cyclopentadienyl resonances at 52.1, 58.7, 60.0, 68.3, and 96.6 (**4a**) and 57.4, 62.9, 67.0, 74.6, and 102.5 (**4b**) ppm, whereas the ^1H NMR spectra show ABCD spin systems between 4.10 and 4.78 (**4a**) and between 3.85 and 4.30 (**4b**) ppm for the cyclopentadienyl ring protons. The ^1H NMR spectra also reflect the rigidity of the CH_2-CH_2 chain, which is a consequence of the coordination of the amine pendant group. Thus, they show four resonances at 2.03, 2.21, 3.24, and 3.87 (**4a**) and 2.10−2.27, 3.27, and 3.62 (**4b**) for the diastereotopic ethylene protons.

The coordination of the phosphoramidite pendant substituent to the metal center of **5a** and **5b** is mainly supported by the $^{31}P\{^1H\}$ NMR spectra, which show singlets at 114 (**5a**) and 169 (**5b**) ppm. The first of them is displaced by 36 ppm toward higher field with regard to **3a**, while the second one appears displaced by 19 ppm toward lower field with regard to **3b**. These chemical shifts agree well with those previously reported for osmium-[11d] and ruthenium-phosphoramidite[19] derivatives. The ^1H NMR spectra also reflect the rigidity of the CH_2-CH_2 chain. Thus, similarly to the ^1H NMR spectra of **4a** and **4b**, they contain four complex resonances at 2.23−2.30 and 3.05−3.19 (**5a**) and 2.15−2.22 and 3.09−3.23 (**5b**) ppm, for the ethylene protons.

(19) Huber, D.; Mezzetti, A. *Tetrahedron: Asymmetry* **2004**, *15*, 2193.

Table 1. [a]

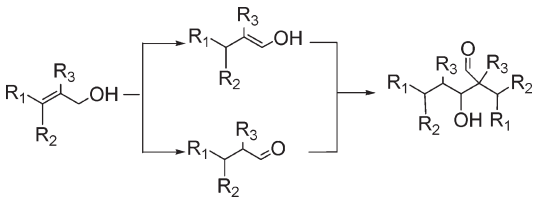
Entry	Catalyst	Substrate	(C/S) x100	t (min)	Products[b]	TOF_{50}[c] (h^{-1})
1	 **4a**		4	6	 (98 %)	232
2			4	180 (3 h)	 (69 %) (31 %)	-
3			4	80 (1.3 h)	 (93 %)	21
4			4	780 (13 h)	 (98 %)	1.8
5	 **4b**		2	20	 (27 %) (68 %)	-
6			2	40	 (68 %) (32 %)	-
7			4	320 (3.5 h)	 (16 %) (31 %)	-
8			4	84 (1.4 h)	 (36 %)	-
9	 **5b**		5	65	 (41 %) (59 %)	-
10			2	91 (1.5 h)	 (38 %) (62 %)	-

[a] All reactions were performed in THF-d_8 (0.08 M in substrate) at 60 °C in an NMR tube. [b] Yields referred to starting alcohol. [c] Turnover frequencies calculated at 50% of conversion.

2. Isomerization of Primary Allylic Alcohols. The osmium complex **4a** is an efficient catalyst precursor for the redox isomerization of 2-propen-1-ol, 2-methyl-2-propen-1-ol, 3-methyl-2-buten-1-ol, and 2-methyl-3-phenyl-2-propen-1-ol into the corresponding aldehydes. The reactions were performed under argon atmosphere in tetrahydrofuran at 60 °C.

The results collected in Table 1 clearly show that this osmium catalyst is very sensitive to the number of substituents at the carbon−carbon double bond of the alcohol, their positions, and their aliphatic or aromatic nature. Using 4 mol % of catalyst precursor, the almost quantitative formation of propanal occurs after 6 min (entry 1), while the isomerization of the trisubstituted substrates requires hours. 3-Methylbutanal, resulting from a double C^3-alkyl-substituted alcohol, is formed in 93% yield after 1.3 h (entry 3), whereas 2-methyl-3-phenylpropanal, resulting from a C^2-alkyl,C^3-aryl-substituted alcohol, is obtained in 98% after 13 h (entry 4). The isomerization of the disubstituted 2-methyl-2-propen-1-ol into 2-methylpropanal is not a clean process. In this case, the metal center catalyzes not only the redox isomerization but also the aldol-type reaction. Thus, after 3 h, 2-methylpropanal is obtained in only 69% yield; the rest of the substrate (31%) is transformed into 3-hydroxy-2,2,4-trimethylpentanal (entry 2). The formation of the latter, which can be rationalized according to Scheme 2, involves the initial isomerization of the starting alcohol to both the aldehyde and the enol, followed by the formal

Scheme 2



insertion of the carbon−carbon double bond of the enol into the C^2−H bond of the aldehyde. In agreement with a direct participation of the enol in the aldol reaction, its transitory formation in amounts lower than 10% is observed during the process.

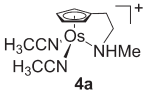
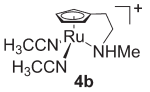
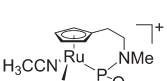
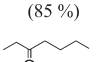
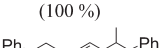
The osmium complex **4a** is surprisingly more efficient than the ruthenium counterpart **4b**. In the presence of the latter, the yields of the redox isomerizations of the primary alcohols of this study are in all cases lower than 69%. Several ruthenium complexes have shown to be active catalysts for the aldol reaction between aldehydes and allylic alcohols.[20] Complex **4b** is a new member of this family. In addition to the redox isomerization of the corresponding primary alcohols, it effects the aldol-type reactions. After 20 min in the presence of 2 mol % of **4b**, 68% of 2-propen-1-ol is transformed into 3-hydroxy-2-methylpentanal, while only 27% of the starting alcohol is isomerized (entry 5). Under the same conditions, 32% of 2-methyl-2-propen-1-ol is converted into 3-hydroxy-2,2,4-trimethylpentanal and 68% of the substrate isomerizes to 2-methylpropanal (entry 6). In both cases, the transitory formation of the corresponding enols was also observed. In the presence of 3-methyl-2-buten-1-ol and 2-methyl-3-phenyl-2-propen-1-ol, complex **4b** undergoes deactivation. 3-Methylbutanal and 2-methyl-3-phenylpropanal can be obtained in only very low yields of 16% and 36%, respectively (entries 7, 8). 3-Methyl-2-buten-1-ol also undergoes a position isomerization process of the C−C double bond to afford 3-methyl-3-buten-1-ol in 31% yield (entry 7). This is a reaction typically catalyzed by a metal-hydride intermediate.[21]

The phosphoramidite complex **5b** also leads to mixture of products. After 65 min, in the presence of 5 mol % of **5b**, 41% of 2-propen-1-ol is isomerized to propanal. However, the 59% of alcohol is transformed into 2-methyl-4-pentenal according to eq 2 (R = H) (entry 9). A similar reaction has been observed during the redox isomerization of several allylic alcohols catalyzed by $[Ru(\eta^5\text{-Cp})(PR_3)(CH_3CN)_2]PF_6$. It has been proposed that these products are a consequence of the oxidative addition of the C−O bond of the alcohol to the metal center. Thus, the resulting allyl-M-hydroxy intermediate can generate an allyl-M-enolate species, which affords the product by C−C coupling of the allyl and enolate ligands.[3e] 2-Methyl-2-propen-1-ol undergoes redox isomerization (38%) and aldol reaction (68%). The osmium counterpart **5a** does not catalyze any of these reactions, and the substrates

(20) See for example: (a) Uma, R.; Davies, M.; Crésivy, C.; Grée, R. *Tetrahedron Lett*. **2001**, *42*, 3069. (b) Wang, M.; Li, C.-J. *Tetrahedron Lett*. **2002**, *43*, 3589. (c) Yang, X.-F.; Wang, M.; Varma, R. S.; Li, C.-J. *Org. Lett*. **2003**, *5*, 657. (d) Wang, M.; Yang, X.-F.; Li, C.-J. *Eur. J. Org. Chem*. **2003**, 998. (e) Yang, X.-F.; Wang, M.; Varma, R. S.; Li, C.-J. *J. Mol. Catal. A: Chem*. **2004**, *214*, 147. (f) Bartoszewick, A.; Livendahl, M.; Martín-Matute, B. *Chem.—Eur. J*. **2008**, *14*, 10547.

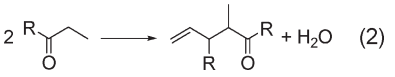
(21) Chaloner, P. A.; Esteruelas, M. A.; Joó, F.; Oro, L. A. *Homogeneous Hydrogenation*; Kluwer: Dordrecht, The Netherlands, 1994.

Table 2. [a]

Entry	Catalyst	Substrate	(C/S) x100	t (min)	Products[b]	TOF_{50}[c] (h^{-1})
1	 **4a**		4	91 (1.5 h)	 (87 %)	33
2			4	105 (1.7 h)	 (92 %)	38
3			4	92 (1.5 h)	 (100 %)	35
4			4	92 (1.5 h)	 (87 %)	39
5	 **4b**		0.5	9	 (100 %)	1200
6			0.5	13	 (98 %)	960
7			0.5	7	 (97 %)	1470
8			0.5	48	 (91 %)	1038
9			0.5	10	 (85 %)	1205
10	 **5b**		10	37	 (100 %)	20
11			4	115 (1.9 h)	 (64 %) (36 %)	-
12			4	300 (5 h)	 (97 %)	28

[a] All reactions were performed in THF-d_8 (0.08 M in substrate) at 60 °C in an NMR tube. [b] Yields referred to starting alcohol. [c] Turnover frequencies calculated at 50% of conversion.

are recovered unchanged from their tetrahydrofuran-d_8 solutions.



3. Isomerization of Secondary Allylic Alcohols. The osmium complex **4a** is certainly more efficient for the redox isomerization of primary allylic alcohols than for the redox isomerization of secondary allylic alcohols. While the turnover frequency calculated at 50% of conversion (TOF_{50}) for the transformation of 2-propen-1-ol into propanal is 232 h^{-1} (Table 1, entry 1), the TOF_{50} for the redox isomerization of secondary allylic alcohols monosubstituted at the olefin, such as 1-hepten-3-ol, 1-hexen-3-ol, 1-penten-3-ol, and α-vinylbenzyl alcohol, into the corresponding ketones ranges from 33 to 39 h^{-1} (Table 2, entries 1−4).

The ruthenium counterpart **4b** is more efficient than **4a** for the redox isomerization of secondary allylic alcohols, in contrast to that observed for the primary alcohols. Thus, the TOF_{50} values obtained with **4b** are in the range 960−1470 h^{-1}. The isomerization of 2-cyclohexen-1-ol to cyclohexanone with a TOF_{50} of 1205 h^{-1} is noteworthy. This substrate is particularly difficult to isomerize into the ketone. We note that bis(allyl)-ruthenium(IV) catalyst precursors,

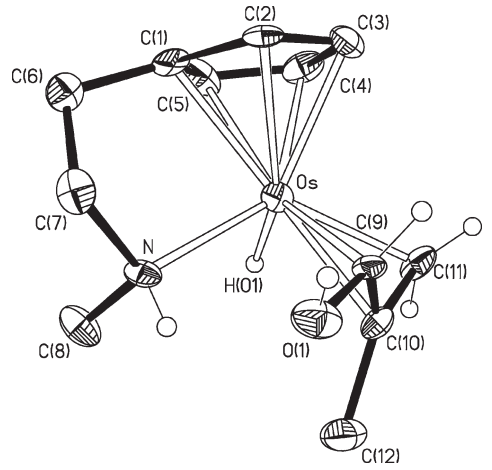
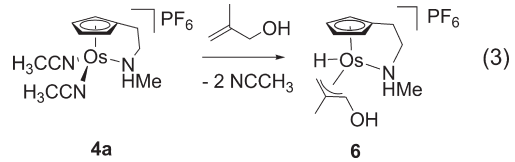


Figure 3. Molecular diagram of complex **6**. Selected bond lengths (Å) and angles (deg): Os−C(1) 2.241(7); Os−C(2) 2.261(7); Os−C(3) 2.216(8); Os−C(4) 2.180(9); Os−C(5) 2.220(8); Os−C(11) 2.157(7); Os−C(10) 2.138(8); Os−C(9) 2.215(9); Os−N 2.159(6); C(9)−C(10) 1.385(12); C(10)−C(11) 1.425(10); O(1)−H 2.22; N−Os−C(1) 78.5(3); C(9)−Os−C(11) 64.8(3); C(9)−C(10)−C(11) 113.0(8).

which reach turnover frequencies of 3000 h^{-1} for the isomerization of secondary alcohols monosubstituted at the olefin, isomerize 2-cyclohexen-1-ol with turnover frequencies lower than 1 h^{-1}.[3r]

The phosphoramidite complex **5b** is also an efficient precursor for the redox isomerization of secondary allylic alcohols. However, the obtained TOF_{50} values, between 20 and 30 h^{-1}, are significantly lower than those for **4b**. In the presence of this precursor, the isomerization of α-vinylbenzyl alcohol is not clean. After 115 min in the presence of 4 mol % of **5b**, 64% of the alcohol is isomerized, while the rest of substrate (36%) is transformed into 2-methyl-1,3-diphenyl-4-penten-1-one according to eq 2 (R = Ph) (Table 2, entry 11).

4. Mechanism of the Redox Isomerizations. The ^{1}H NMR spectra of the catalytic solutions of **4a** show a weak singlet between −10 and −13 ppm, revealing the presence of a hydride intermediate during the course of the isomerizations. At −20 °C, from the solutions containing 2-methyl-2-propen-1-ol a few yellow crystals suitable for an X-ray diffraction study were formed. The structure (Figure 3) proves the formation of the hydroxyallyl complex $[OsH(\eta^5\text{-}C_5,\kappa\text{-N-}Cp^N)\{\eta^3\text{-}CH_2C(CH_3)CHOH\}]PF_6$ (**6**) according to eq 3. 2-Methylpropanal formation was observed when solutions of pure **6** in THF-d_8 were allowed to stand at room temperature.



(3)

4a **6**

The distribution of ligands around the osmium atom of **6** is consistent with that found in $[OsH(\eta^5\text{-Cp})(\eta^3\text{-allyl})(P^iPr_3)]^+$ compounds[22] and can be described as a four-legged piano-stool geometry, where the allyl ligand occupies two *cisoid* positions with a C(9)−Os−C(11) angle of 64.8(3)°.

The allyl group coordinates to the metal center in the *endo* form, which is preferred for d^4 $M(\eta^5\text{-}C_5R_5)L_2(\eta^3\text{-allyl})$ complexes[23] (L ≠ CO), with the C(9) atom *cisoid* disposed to the coordinated pendant amine group and its hydroxy substituent in *syn* position with regard to the *meso* carbon atom C(10). The C_3 skeleton is bonded in an asymmetric fashion. The separation between the central carbon atom, C(10), and the metal (2.138(8) Å) is shorter than the separation between the metal and the terminal carbon atoms C(9) (2.215(9) Å) and C(11) (2.157(7) Å). The carbon−carbon distances within the allylic skeleton are 1.385(12) Å for C(9)−C(10) and 1.425(10) Å for C(10)−C(11). The angle C(9)−C(10)−C(11) is 113.0(8)°.

The coordination of the pendant amine atom is strong, as in **4a**. The separation between the nitrogen atom and the metal, 2.159(6) Å, is statistically identical with the Os−N distance in the latter. The NH hydrogen atom points toward the oxygen of the hydroxy substituent of the allyl group. The separation between these atoms, 2.22 Å, is about 0.5 Å 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), indicating the presence of an intramolecular N−H···O hydrogen bond.[24]

The interaction appears to stabilize the structure. Although for this ligand disposition two orientations of the amine are possible, hydrogen toward oxygen or methyl toward oxygen, the stereoisomer shown in Figure 3 is also the obtained one when, at Schlenk tube scale, strongly concentrated tetrahydrofuran solutions of **4a** are treated with 5 equiv of 2-methyl-2-propen-1-ol at 60 °C for 10 min. By this procedure, complex **6** is isolated as a yellow solid in 60% yield.

The ^{1}H NMR spectra in dichloromethane-d_2 at 253 K of the crystals and the solid, as well as the $^{13}C\{^1H\}$ NMR spectra, are identical and consistent with Figure 3. In agreement with the catalytic solutions, the hydride resonance appears at −12.20 ppm, whereas the OH signal is observed at 4.69 ppm. The allyl skeleton displays three resonances at 2.74 and 3.22 (CH_2) and 6.91 (CH) ppm. As expected for the coordination of the nitrogen atom of the amine to the metal center, the cyclopentadienyl protons give rise to an ABCD spin system between 4.21 and 6.51 ppm, whereas the CH_2CH_2 chain displays four resonances at 2.37, 2.47, 3.58, and 3.76 ppm. In the $^{13}C\{^1H\}$ NMR spectrum, the resonances corresponding to the allyl carbon atoms are observed at 17.4 (C(11)), 78.4 (C(9)), and 93.0 (C(10)) ppm. In accordance with **4a**, the spectrum contains five cyclopentadienyl signals at 68.0, 81.6, 81.7, 92.5, and 122.2 ppm.

A limited number of η^3-hydroxyallyl complexes have been isolated.[25] The regioisomer η^3-1-hydroxyallyl is particularly

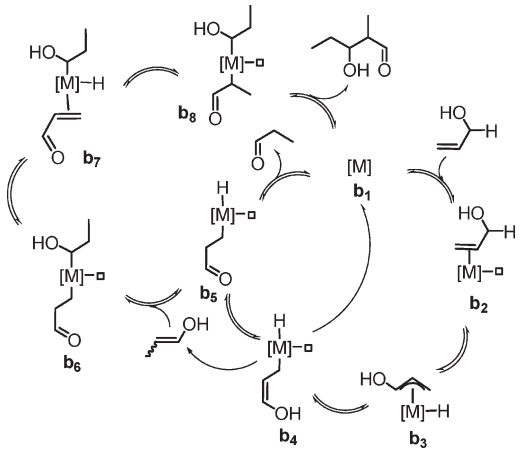
(22) (a) Esteruelas, M. A.; González, A. I.; López, A. M.; Oliván, M.; Oñate, E. *Organometallics* **2006**, *25*, 693. (b) Esteruelas, M. A.; Hernández, Y. A.; López, A. M.; Oliván, M.; Oñate, E. *Organometallics* **2007**, *26*, 2193.

(23) (a) Albers, M. O.; Liles, D. C.; Robinson, D. J.; Shaver, A.; Singleton, E. *Organometallics* **1987**, *6*, 2347. (b) Itoh, K.; Fukahori, T. *J. Organomet. Chem.* **1988**, *349*, 227. (c) Nagashima, H.; Mukai, K.; Shiota, Y.; Yamaguchi, K.; Ara, K.-I.; Fukahori, T.; Suzuki, H.; Akita, M.; Moro-oka, Y.; Itoh, K. *Organometallics* **1990**, *9*, 799. (d) Hubbard, J. L.; Zoch, C. R. *J. Organomet. Chem.* **1995**, *487*, 65. (e) Mui, H. D.; Brumaghim, J. L.; Gross, C. L.; Girolami, G. S. *Organometallics* **1999**, *18*, 3264. (f) Kondo, H.; Yamaguchi, Y. *Chem. Commun.* **2000**, 1075. (g) Bi, S.; Ariafard, A.; Jia, G.; Lin, Z. *Organometallics* **2005**, *24*, 680.

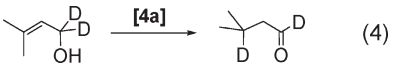
(24) (a) Esteruelas, M. A.; Lledós, A.; Oliván, M.; Oñate, E.; Tajada, M. A.; Ujaque, G. *Organometallics* **2003**, *22*, 3753. (b) Barrio, P.; Esteruelas, M. A.; Lledós, A.; Oñate, E.; Tomàs, J. *Organometallics* **2004**, *23*, 3008.

(25) (a) Huang, T.-M.; Hsu, R.-H.; Yang, C.-S.; Chen, J.-T.; Lee, G.-H.; Wang, Y. *Organometallics* **1994**, *13*, 3657. (b) Hui, J. W.-S.; Wong, W.-T. *Polyhedron* **1996**, *15*, 541. (c) Pasch, R.; Koelle, U.; Ganter, B.; Englert, U. *Organometallics* **1997**, *16*, 3950. (d) Hsu, R.-H.; Chen, J.-T.; Lee, G.-H.; Wang, Y. *Organometallics* **1997**, *16*, 1159. (e) Casey, C. P.; Nash, J. R.; Yi, C. S.; Selmeczy, A. D.; Chung, S.; Powell, D. R.; Hayashi, R. K. *J. Am. Chem. Soc.* **1998**, *120*, 722.

Scheme 3



rare. Only two palladium complexes containing this group have been characterized.[26] Complex **6** is the first species of this type isolated from a catalytic solution and is overwhelming evidence for mechanism b shown in Figure 1, which is also consistent with eq 4. In agreement with the relatively high stability of the hydride-η^3-hydroxyallyl intermediates, the reaction shown in eq 4 has an inverse kinetic isotope effect of 0.36 at 333 K. This is strong evidence supporting that the migration of the hydride ligand from the osmium atom to the hydroxyallyl group is the rate-determining step of the isomerization.



(4)

The pendant amine group appears to favor the formation of the π-allyl-metal-hydride intermediate, probably as a consequence of the increase of stability resulting from the N−H···O hydrogen bond. In this context, it should be mentioned that the Cp counterpart [Os(η^5-Cp)($CH_3CN)_3$]PF_6 is a much less efficient catalyst precursor than **4a**. For instance, in the presence of 4 mol % of Cp complex, 2-propen-1-ol gives mixtures of propanal and 3-hydroxy-2-methylpentanal, whereas, after 12 h, the isomerization of 1-hepten-3-ol to 3-heptanone occurs only in 58% yield.

The cycle b of Figure 1 does not rationalize any of the results of this study. Thus, it should be modified. The clean isomerization processes do not show the enol as an intermediate species. However significant concentrations of the enol form are present in a transitory manner when the isomerization competes with the aldol reaction. This suggests that the enol tautomerization occurs on the coordination sphere of the metal. Scheme 3 summarizes a proposal that allows the rationalization of this fact and the aldol reactions. Once the η^3-hydroxyallyl-metal-hydride key intermediate (**b$_3$**) is formed, it could evolve into a σ-3-hydroxyallyl-metal-hydride species (**b$_4$**), which could undergo reductive elimination to give the enol form, regenerating the catalyst (**b$_1$**), or alternatively the enol part of the σ-3-hydroxyallyl group could tautomerize. In the latter case, a reductive elimination in the resulting intermediate **b$_5$** should directly lead to the carbonyl compounds. The reductive elimination reactions in **b$_4$** and **b$_5$** are favored by the unsaturated character of these intermediates.[27]

The reaction of the enol form present in the catalytic solution with **b$_5$** could be responsible for the formation of the aldol products. The unsaturated character of this intermediate should favor the Markovnikov insertion of the C−C double bond of the enol into the metal−hydride bond. Subsequently, the M-CH_2CH_2CHO unit of the resulting intermediate **b$_6$** could undergo a position isomerization, via **b$_7$**, to afford **b$_8$**. The latter should give the aldol product by reductive elimination.

Why is the osmium complex **4a**, a catalyst precursor, more efficient than its ruthenium counterpart, **4b**, for the isomerization of primary alcohols, while the latter is more efficient than the former for the isomerization of secondary alcohols? This is because osmium is more reducing than ruthenium and prefers coordination saturation and redox isomers with more metal−carbon bonds; that is, ruthenium favors intermediates **b$_4$** and **b$_5$** and the steps involving reductive elimination reactions.

Concluding Remarks

This study shows the preparation and characterization of new half-sandwich osmium and ruthenium derivatives containing cyclopentadienyl ligands with coordinated amine and phosphoramidite pendant substituents. Furthermore, it reveals that the osmium complex [Os(η^5-C_5,κ-N-Cp^N)-($CH_3CN)_2$]PF_6 is a more efficient catalyst precursor than its ruthenium counterpart for the redox isomerization of primary alcohols to aldehydes, while the latter is more efficient than the former for the redox isomerization of secondary allylic alcohols to ketones. Complex [Os(η^5-C_5,κ-N-Cp^N)($CH_3CN)_2$]PF_6 is more efficient than its Cp counterpart [Os(η^5-Cp)($CH_3CN)_3$]PF_6 for the redox isomerization of both primary and secondary allylic alcohols.

From the catalytic solutions containing [Os(η^5-C_5,κ-N-Cp^N)($CH_3CN)_2$]PF_6 and 2-methyl-2-propen-1-ol, the η^3-hydroxyallyl complex [OsH(η^5-C_5,κ-N-Cp^N){η^3-$CH_2C(CH_3)$-CHOH}]PF_6 has been isolated and characterized by X-ray diffraction analysis. This supports a π-allyl-metal-hydride mechanism. However, some modifications should be made to the classical proposal since the enol form, the released product from the metal according to this proposal, is not detected during clean isomerization processes. The enol is formed in a transitory manner only when the redox isomerization vies with an aldol reaction. The pendant amine group appears to increase the stability of the η^3-hydroxyallyl intermediate by means of a N−H···O hydrogen bond.

Experimental Section

Materials and General Methods. The preparation of the metal complexes was carried out using Schlenk tube techniques under argon with rigorous exclusion of air. Solvents were dried by the usual procedures and distilled under argon prior to use or obtained oxygen- and water-free from an MBraun solvent purification apparatus. The photochemical reactions were performed in a 200 mL quartz immersion well reactor (RQ 400) with a 400 W medium-pressure mercury lamp. ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra were recorded on either a Varian Gemini 2000, a Bruker ARX 300, a Bruker Avance 300 MHz, a Bruker

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Avance 400 MHz, or a Bruker Avance 500 MHz instrument. ^{1}H chemical shifts are referenced to residual solvent peaks CD_2Cl_2 (δ = 5.32 ppm) and CD_3CN (δ = 1.94 ppm). $^{13}C\{^1H\}$ chemical shifts are referenced to residual solvent peaks CD_2Cl_2 (δ = 53.8 ppm), CD_3CN (δ = 1.39, 118.7 ppm), and $CDCl_3$ (δ = 7.25, 77.0 ppm). An external H_3PO_4 reference was used for $^{31}P\{^1H\}$ NMR spectra. Coupling constants, *J*, are given in hertz. Spectral assignments were achieved by $^1H-^1H$ COSY, $^1H\{^{31}P\}$, ^{13}C APT, $^1H-^{13}C$ HSQC, and $^1H-^{13}C$ HMBC experiments. Infrared spectra were recorded on a Spectrum One spectrometer as neat solids or KBr pellets. High-resolution electrospray mass spectra were acquired using a MicroTOF-Q hybrid quadrupole time-of-flight spectrometer (Bruker Daltonics, Bremen, Germany). MALDI-MS measurements were performed on a reflex time-of-flying instrument (Bruker Daltonics Microflex analyzer) equipped with a target micro-SCOUT ion source. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O and a Fisons EA-1108 analyzer. Allyl alcohols were obtained from commercial suppliers. Alcohol 3-methyl-2-buten-1-ol-1,1-d_2 was prepared by following a previously reported method.[28] Complexes $[OsCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (**1a**)[10w] and $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (**1b**)[29] were prepared according to published methods. (2,2′-Biphenol)PCl was prepared from PCl_3 and 2,2′-biphenol by following a previously reported procedure.[30]

Preparation of $[Os(\eta^5\text{-}Cp^N)(\eta^6\text{-}p\text{-cymene})]PF_6$ (2a). THF (30 mL) was added to a mixture of $[OsCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (1.00 g, 1.26 mmol) and $Li(C_5H_4CH_2CH_2NHCH_3)$ (0.409 g, 3.162 mmol) and the mixture stirred for 4 h at rt. The solvent was then removed under vacuum and the residue extracted with dichloromethane (15 mL). A solution of KPF_6 (466 mg, 2.53 mmol) in acetone (15 mL) was then added to the filtrate and the mixture stirred for 12 h. The solvent was evaporated to dryness, the residue extracted with dichloromethane (15 mL), and the filtrate evaporated to dryness to give a brown oil, which was washed with diethyl ether (3 × 10 mL) and dried *in vacuo* (1.19 g, 2.02 mmol, 80% yield). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 1.29 [d, $^3J_{H,H}$ = 6.9 Hz, 6 H, $CH(CH_3)_2$], 2.20 (s, 3 H, CH_3, *p*-cymene), 2.45 (s, 3 H, $NHCH_3$), 2.50 [t, $^3J_{H,H}$ = 6.6 Hz, 2 H, $CH_2(C_5H_4)$], 2.50 (br s, 1 H, $NHCH_3$), 2.61 [sept, $^3J_{H,H}$ = 6.9 Hz, 1 H, $CH(CH_3)_2$], 2.71 (t, $^3J_{H,H}$ = 6.6 Hz, 2 H, CH_2N), 5.48, 5.60 (both br s, 2 H, C_5H_4), 6.06 (4 H, *CH*-arom, *p*-cymene). $^{13}C\{^1H\}$ NMR (75.45 MHz, CD_2Cl_2, 298 K): δ 20.0 (s, CH_3, *p*-cymene), 23.5 [s, $CH(CH_3)_2$], 28.6 (s, $C_5H_4CH_2$), 32.5 [s, *C*H-$(CH_3)_2$], 36.3 (s, $NHCH_3$), 53.0 (s, CH_2N), 75.8, 76.5 (both s, *C*H, C_5H_4), 78.0, 78.2 (both s, *C*H-arom, *p*-cymene), 93.2 (s, $-CH_3C_{ipso}$, *p*-cymene), 98.1 (s, C_{ipso}-C_5H_4), 104.1 [s, $(CH_3)_2CHC_{ipso}$, *p*-cymene]. HRMS (electrospray, *m*/*z*): calcd for $C_{18}H_{26}NOs$ $[M]^+$ 448.1675; found 448.1684. IR (ATR, cm^{-1}): ν(NH) 3119 (w), $\nu(PF_6)$ 819 (s). Anal. Calcd for $C_{18}H_{26}F_6NOsP\cdot CH_2Cl_2$: C 33.73, H 4.17, N 2.07. Found: C 34.01, H 4.06, N 2.13.

Preparation of $[Ru(\eta^5\text{-}Cp^N)(\eta^6\text{-}p\text{-cymene})]PF_6$ (2b). Complex **2b** was synthesized from $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (1.00 g, 1.63 mmol) and $Li(C_5H_4CH_2CH_2NHCH_3)$ (0.528 g, 4.075 mmol) following an identical procedure to that described for the synthesis of $[Os(\eta^5\text{-}Cp^N)(\eta^6\text{-}p\text{-cymene})]PF_6$ (**2a**). Yield: 81% (1.33 g, 2.65 mmol). ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 1.18 [d, $^3J_{H,H}$ = 7.0 Hz, 6 H, $CH(CH_3)_2$], 2.21 (s, 3 H, CH_3, *p*-cymene), 2.33 (s, 3 H, $NHCH_3$), 2.34 (t, $^3J_{H,H}$ = 7.1 Hz, 2 H, $CH_2C_5H_4$), 2.62 [sept, $^3J_{H,H}$ = 7.0 Hz, 1 H, $CH(CH_3)_2$], 2.64 (t, $^3J_{H,H}$ = 7.1 Hz, 2 H, CH_2N), 4.5 (s, 1 H, $NHCH_3$), 5.08, 5.17 (both br s, 2 H, C_5H_4), 5.92 (AB spin system, $\Delta\nu$ = 8.70, J_{AB} = 6.34, 4 H, *CH*-arom, *p*-cymene). $^{13}C\{^1H\}$ NMR (75.45 MHz, CD_2Cl_2, 298 K): δ 19.9 (s, CH_3, *p*-cymene), 23.6 [s, $CH(CH_3)_2$], 28.0 (s, $C_5H_4CH_2$), 32.4 (s, $NHCH_3$), 36.1 [s, $CH(CH_3)_2$], 52.3 (s, CH_2N), 66.2 (s, C_{ipso}-C_5H_4), 80.4, 81.5 (both s, *C*H, C_5H_4), 84.9, 87.3 (both s, *C*H-arom, *p*-cymene), 102.1 (s, CH_3C_{ipso}, *p*-cymene), 113.0 [s, $(CH_3)_2CHC_{ipso}$, *p*-cymene]. HRMS (electrospray, *m*/*z*): calcd for $C_{18}H_{26}NRu$ $[M]^+$ 358.1108; found 358.1091. IR (ATR, cm^{-1}): ν(NH) 3120 (w), $\nu(PF_6)$ 822 (s). Anal. Calcd for $C_{18}H_{26}F_6NRuP\cdot CH_2Cl_2$: C 38.85, H 4.80, N 2.38. Found: C 38.96, H 4.46, N 2.44.

Preparation of $[Os(\eta^5\text{-}Cp^P)(\eta^6\text{-}p\text{-cymene})]PF_6$ (3a). A cold solution (0 °C) of $[Os(\eta^5\text{-}Cp^N)(\eta^6\text{-}p\text{-cymene})]PF_6$ (0.5 g, 1.0 mmol) in dichloromethane (8 mL) was added to a stirred suspension of (2,2′-biphenol)PCl (254 mg, 1.01 mmol) and piperidinomethyl polystyrene (579 mg, 2.02 mmol) in dichloromethane (8 mL) at 0 °C. The reaction mixture was stirred for 12 h at room temperature and then filtered through a glass frit. The filtrate was evaporated to dryness and the residue extracted with CH_3CN. After removal of the solvent, the residue was washed with diethyl ether (3 × 10 mL) and dried *in vacuo* to yield a pale brown solid (0.511 g, 0.63 mmol, 75% yield). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 1.16 [d, $^3J_{H,H}$ = 6.7 Hz, 6 H, $CH(CH_3)_2$], 2.29 (s, 3 H, CH_3, *p*-cymene), 2.39 (t, $^3J_{H,H}$ = 6.6 Hz, 2 H, $CH_2C_5H_4$), 2.50 (d, $^3J_{P,H}$ = 8.1 Hz, 3 H, NCH_3), 2.59 [sept, $^3J_{H,H}$ = 6.6 Hz, 1 H, $CH(CH_3)_2$], 3.11 (dt, $^3J_{H,P}$ = 11.0, $^3J_{H,H}$ = 6.6 Hz, 2 H, CH_2N), 5.40−5.60 (4 H, C_5H_4), 5.90−6.20 (4 H, *CH*-arom, *p*-cymene), 7.18 (ddd, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 1.3 Hz, $J_{H,P}$ = 1.0 Hz, 2 H, *CH*-arom), 7.31 (dddd, $^3J_{H,H}$ = $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 1.3 Hz, $J_{H,P}$ = 0.7 Hz, 2 H, *p*-*CH*-arom), 7.40 (ddd, $^3J_{H,H}$ = $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 1.8 Hz, 2 H, *CH*-arom), 7.50 (dd, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 1.8 Hz, 2 H, *CH*-arom). $^{13}C\{^1H\}$ NMR (75.45 MHz, CD_2Cl_2, 298 K): δ 20.1 (s, CH_3, *p*-cymene), 23.6 [s, $CH(CH_3)_2$], 27.4 (d, $^3J_{C,P}$ = 2.6 Hz, $CH_2C_5H_4$), 32.5 [s, $CH(CH_3)_2$], 33.0 (d, $^2J_{C,P}$ = 16.8 Hz, NCH_3), 50.0 (d, $^2J_{C,P}$ = 24.0 Hz, CH_2N), 75.8, 78.2 (both s, *C*H-arom, *p*-cymene), 76.6, 77.9 (both s, *C*H, C_5H_4), 93.2 (s, CH_3C_{ipso}, *p*-cymene), 96.7 (s, C_{ipso}-C_5H_4), 104.2 [s, $(CH_3)_2CHC_{ipso}$, *p*-cymene], 122.5, 125.3, 130.0, 130.2 (all s, *C*H-arom), 131.3 (d, $^3J_{C,P}$ = 3.0 Hz, C_{ipso}-arom), 151.8 (d, $^2J_{C,P}$ = 5.0 Hz, *C*OP-arom). $^{31}P\{^1H\}$ NMR (121.479 MHz, CD_3CN, 298 K): δ 149.8 (s). HRMS (electrospray, *m*/*z*): calcd for $C_{30}H_{33}NO_2OsP$ $[M]^+$ 662.1860; found 662.1906. Anal. Calcd for $C_{30}H_{33}F_6NO_2OsP_2\cdot 0.5C_4H_{10}O$: C 45.60, H 4.54, N 1.66. Found: C 45.69, H 4.12, N 1.71.

Preparation of $[Ru(\eta^5\text{-}Cp^P)(\eta^6\text{-}p\text{-cymene})]PF_6$ (3b). Complex **3b** was prepared from $[Ru(\eta^5\text{-}Cp^N)(\eta^6\text{-}p\text{-cymene})]PF_6$ (0.5 g, 1.0 mmol), (2,2′-biphenol)PCl (299 mg, 1.2 mmol), and piperidinomethyl polystyrene (686 mg, 2.4 mmol) in dichloromethane at 0 °C following an identical procedure to that described for the synthesis of $[Os(\eta^5\text{-}Cp^P)(\eta^6\text{-}p\text{-cymene})]PF_6$ (**3a**). A pale brown solid was obtained (0.487 g, 0.68 mmol, 68% yield). ^{1}H NMR (300 MHz, CD_3CN, 298 K): δ 1.19 [d, $^3J_{H,H}$ = 6.9 Hz, 6 H, $CH(CH_3)_2$], 2.22 (s, 3 H, CH_3, *p*-cymene), 2.42 (t, $^3J_{H,H}$ = 7.0 Hz, 2 H, $CH_2C_5H_4$), 2.55 (d, $^3J_{P,H}$ = 7.3 Hz, 3 H, NCH_3), 2.64 [sept, $^3J_{H,H}$ = 6.9 Hz, 1 H, $CH(CH_3)_2$], 3.16 (dt, $^3J_{P,H}$ = 11.2, $^3J_{H,H}$ = 7.0 Hz, 2 H, CH_2N), 5.13−5.23 (4 H, C_5H_4), 5.90−5.97 (4 H, *CH*-arom, *p*-cymene), 7.18 (ddd, $^3J_{H,H}$ = 7.6, $^4J_{H,H}$ = 1.3, $J_{H,P}$ = 1.0 Hz, 2 H, *CH*-arom), 7.30 (dddd, $^3J_{H,H}$ = $^3J_{H,H}$ = 7.6, $^4J_{H,H}$ = 1.3, $J_{H,P}$ = 0.7 Hz, 2 H, *p*-*CH*-arom), 7.41 (ddd, $^3J_{H,H}$ = $^3J_{H,H}$ = 7.6, $^4J_{H,H}$ = 1.8 Hz, 2 H, *CH*-arom), 7.52 (dd, $^3J_{H,H}$ = 7.6, $^4J_{H,H}$ = 1.8 Hz, 2 H, *CH*-arom). $^{13}C\{^1H\}$ NMR (75.45 MHz, CD_3CN, 298 K): δ 19.7 (s, CH_3, *p*-cymene), 23.5 [s, $(CH_3)_2CH$], 27.2 (d, $^3J_{C,P}$ = 3.0 Hz, $CH_2C_5H_4$), 32.5 (s, NCH_3), 32.6 [s, $CH(CH_3)_2$], 50.1 (d, $^2J_{C,P}$ = 28.6 Hz, CH_2N), 80.9, 82.0 (both s, *C*H, C_5H_4), 85.2, 87.6 (both s, *C*H-arom, *p*-cymene), 101.2 (s, C_{ipso}-C_5H_4), 102.1 (s, CH_3C_{ipso}, *p*-cymene), 113.0 [s, $(CH_3)_2CHC_{ipso}$, *p*-cymene], 122.8, 125.8, 130.5, 130.7 (all s, *CH*-arom), 131.6 (s, C_{ipso}-arom), 152.1 (d, $^2J_{C,P}$ = 4.8 Hz, *C*OP-arom). $^{31}P\{^1H\}$ NMR (121.479 MHz, CD_3CN, 298 K): δ 148.2 (s). HRMS (electrospray, *m*/*z*): calcd for $C_{30}H_{33}NO_2PRu$ $[M]^+$ 572.1295; found 572.1327. Anal. Calcd for $C_{30}H_{33}F_6NO_2P_2Ru$: C 50.28, H 4.64, N 1.95. Found: C 49.94, H 4.99, N 2.03.

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Preparation of [Os(η^5-*C*$_5$,κ-*N*-Cp^N)(CH$_3$CN)$_2$]PF$_6$ (4a). An acetonitrile (200 mL) solution of [Os(η^5-Cp^N)(η^6-*p*-cymene)]PF$_6$ (1.0 g, 1.69 mmol) and biphenyl (2.42 g, 15.73 mmol) was placed in a photochemical reactor and irradiated with a 400 W medium-pressure mercury lamp for 6 h at −5 °C. After removal of the solvent, the residue was chromatographed on neutral aluminum oxide (activity V) with a mixture of CH_3CN/Et_2O (85:15) as eluent. The resulting yellow solution was then evaporated to dryness and the residue washed with diethyl ether (3 × 10 mL) and dried *in vacuo* to yield a yellow microcrystalline solid (401 mg, 0.74 mmol, 44% yield). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 2.03 (m, 1 H, −CH_2−), 2.21 (m, 1 H, −CH_2−), 2.56, 2.58 (both s, 3 H, NCCH_3), 2.72 (d, $^3J_{H,H}$ = 6.1 Hz, 3 H, NHCH_3), 3.24 (m, 1 H, −CH_2−), 3.87 (m, 1 H, −CH_2−), 4.10, 4.22, 4.74, 4.78 (ABCD system, all br s, 1 H, C$_5H_4$), 5.34 (br s, 1 H, N*H*CH$_3$). ^{13}C{^{1}H} NMR (75.45 MHz, CD_2Cl_2, 298 K): δ 4.02, 4.18 (both s, NC*C*H$_3$), 27.1 (s, *C*H$_2$C$_5$H$_4$), 41.5 (s, NH*C*H$_3$), 52.1, 58.7, 60.0, 68.3 (all s, *C*H, C$_5$H$_4$), 72.1 (s, −*C*H$_2$N), 96.6 (s, C_{ipso}-C$_5$H$_4$), 121.6, 122.8 (both s, N*C*CH$_3$). HRMS (electrospray, *m*/*z*): calcd for $C_{10}H_{15}N_2Os$ [M − CH_3CN]$^+$ 355.0845; found 355.0871; calcd for $C_8H_{12}NOs$ [M − 2CH_3CN]$^+$ 314.0579; found 314.0586. IR (ATR, cm^{-1}): ν(NH) 3293 (w), ν(NC) 2273 (w), ν(PF$_6$) 825 (s). Anal. Calcd for $C_{12}H_{18}F_6N_3OsP$: C 26.72, H 3.36, N 7.79. Found: C 26.63, H 3.55, N 7.80.

Preparation of [Ru(η^5-*C*$_5$,κ-*N*-Cp^N)(CH$_3$CN)$_2$]PF$_6$ (4b). An acetonitrile (200 mL) solution of [Ru(η^5-Cp^N)(η^6-*p*-cymene)]PF$_6$ (665 mg, 1.32 mmol) was placed in a photochemical reactor and irradiated with a 400 W medium-pressure mercury lamp for 6 h at −5 °C. Complex **4b** was isolated and purified following an identical procedure to that described for [Os(η^5-*C*$_5$,κ-*N*-Cp^N)(CH$_3$CN)$_2$]PF$_6$ (**4a**) and obtained as a yellow solid (594 mg, 0.55 mmol, 42% yield). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 2.10−2.27 (2 H, CH_2), 2.39 (s, 6 H, NCCH_3), 2.46 (d, $^3J_{H,H}$ = 6.5 Hz, 3 H, NHCH_3), 3.27 (m, 1 H, CH_2), 3.62 (m, 1 H, CH_2), 3.75 (br s, 1 H, N*H*CH$_3$), 3.85, 3.96, 4.15, 4.30 (ABCD system, all br s, 1 H, C$_5H_4$). ^{13}C{^{1}H} NMR (75.45 MHz, CD_2Cl_2, 298 K): δ 4.20, 4.25 (both s, NC*C*H$_3$), 27.7 (s, *C*H$_2$C$_5$H$_4$), 41.1 (s, NH*C*H$_3$), 67.7 (s, *C*H$_2$N), 57.4, 62.9, 67.0, 74.6 (all s, *C*H, C$_5$H$_4$), 102.5 (s, C_{ipso}-C$_5$H$_4$), 125.9, 126.6 (both s, N*C*CH$_3$). HRMS (electrospray, *m*/*z*): calcd for $C_{10}H_{15}N_2Ru$ [M − CH_3CN]$^+$ 265.0276; found 265.0252; calcd for $C_8H_{12}NRu$ [M − 2CH_3CN]$^+$ 224.0010; found 223.9977. IR (ATR, cm^{-1}): ν(NH) 3299 (w), ν(NC) 2276 (w), ν(PF$_6$) 831 (s). Anal. Calcd for $C_{12}H_{18}F_6N_3PRu$: C 32.01, H 4.03, N 9.33. Found: C 32.57, H 3.95, N 9.09.

Preparation of [Os(η^5-*C*$_5$,κ-*P*-Cp^P)(CH$_3$CN)$_2$]PF$_6$ (5a). An acetonitrile (200 mL) solution of [Os(η^5-Cp^P)(η^6-*p*-cymene)]PF$_6$ (300 mg, 0.372 mmol) and biphenyl (533 mg, 3.46 mmol) was placed in a photochemical reactor and irradiated with a 400 W medium-pressure mercury lamp for 6 h at −5 °C. After removal of the solvent, the residue was chromatographed on neutral aluminum oxide (activity V) with a mixture of CH_3CN/Et_2O (85:15) as eluent. The resulting yellow solution was then evaporated to dryness and the residue washed with diethyl ether (3 × 10 mL) and dried under vacuum to yield a white solid (112 mg, 0.149 mmol, 40% yield). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 2.23−2.30 (2 H, CH_2C$_5$H$_4$), 2.36 (d, $J_{H,P}$ = 1.6 Hz, 6 H, NCCH_3), 2.56 (d, $^3J_{P,H}$ = 6.4 Hz, 3 H, NCH_3), 3.05−3.19 (2 H, CH_2N), 4.68−4.70 (2 H, C$_5H_4$), 5.33−5.36 (2 H, C$_5H_4$), 7.26 (ddd, $^3J_{H,H}$ = 7.8, $^4J_{H,H}$ = 1.3, $J_{H,P}$ = 1.3 Hz, 2 H, C*H*-arom), 7.37 (dddd, $^3J_{H,H}$ = 7.8, $^3J_{H,H}$ = 7.8, $^4J_{H,H}$ = 1.3, $J_{H,P}$ = 1.3 Hz, 2 H, C*H*-arom), 7.48 (ddd, $^3J_{H,H}$ = $^3J_{H,H}$ = 7.6, $^4J_{H,H}$ = 1.7 Hz, 2 H, C*H*-arom), 7.60 (dd, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 1.7 Hz, 2 H, C*H*-arom). ^{13}C{^{1}H} NMR (75.45 MHz, CD_2Cl_2, 298 K): δ 4.6 (s, NC*C*H$_3$), 24.9 (d, $^2J_{C,P}$ = 1.8 Hz, *C*H$_2$C$_5$H$_4$), 36.7 (d, $^2J_{C,P}$ = 4.3 Hz, NCH$_3$), 55.8 (d, $^2J_{C,P}$ = 23.6 Hz, *C*H$_2$N), 66.1 (s, *C*H, C$_5$H$_4$), 83.7 (d, $J_{C,P}$ = 9.7 Hz, *C*H, C$_5$H$_4$), 92.3 (s, C_{ipso}-C$_5$H$_4$), 122.8 (d, $^4J_{C,P}$ = 3.0 Hz, *C*H-arom), 122.9 (s, N*C*CH$_3$), 125.9 (s, *C*H-arom), 130.0 (s, *C*H-arom), 130.5 (s, *C*H-arom), 130.6 (s, C$_{ipso}$-arom), 151.5 (d, $^2J_{C,P}$ = 10.7 Hz, *C*OP-arom). ^{31}P{^{1}H} NMR (121.479 MHz, CD_2Cl_2, 298 K): δ 114.4 (s). HRMS (electrospray, *m*/*z*): calcd for $C_{22}H_{22}N_2O_2OsP$ [M − CH_3CN]$^+$ 569.1029; found 569.1046; calcd for $C_{20}H_{19}NO_2OsP$ [M − 2(CH_3CN)]$^+$ 528.0763; found 528.0780. IR (ATR, cm^{-1}): ν(NC) 2280 (w), ν(PF$_6$) 834 (s). Anal. Calcd for $C_{24}H_{25}F_6N_3O_2OsP_2$: C 38.25, H 3.34, N 5.58. Found: C 38.73, H 3.20, N 5.75.

Preparation of [Ru(η^5-*C*$_5$,κ-*P*-Cp^P)(CH$_3$CN)$_2$]PF$_6$ (5b). An acetonitrile (200 mL) solution of [Ru(η^5-Cp^P)(η^6-*p*-cymene)]PF$_6$ (300 mg, 0.419 mmol) was placed in a photochemical reactor and irradiated with a 400 W medium-pressure mercury lamp for 6 h at −5 °C. Complex **5b** was isolated and purified following an identical procedure to that described for [Os(η^5-*C*$_5$,κ-*P*-Cp^P)(CH$_3$CN)$_2$]PF$_6$ (**5a**) and obtained as a white solid (111 mg, 0.167 mmol, 40% yield). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 2.08 (s, 6 H, NCCH_3), 2.15−2.22 (2 H, CH_2C$_5$H$_4$), 2.58 (d, $^3J_{P,H}$ = 6.0 Hz, 3 H, NCH_3), 3.09−3.23 (2 H, CH_2N), 4.31−4.37 (2 H, C$_5H_4$), 5.18−5.24 (2 H, C$_5H_4$), 7.22 (ddd, $^3J_{H,H}$ = 7.6, $^4J_{H,H}$ = 1.0, $J_{H,P}$ = 1.1 Hz, 2 H, C*H*-arom), 7.37 (dddd, $^3J_{H,H}$ = $^3J_{H,H}$ = 7.6, $^4J_{H,H}$ = 1.0, $J_{P,H}$ = 1.0 Hz, 2 H, C*H*-arom), 7.48 (ddd, $^3J_{H,H}$ = $^3J_{H,H}$ = 7.6, $^4J_{H,H}$ = 1.7 Hz, 2 H, C*H*-arom), 7.60 (dd, $^3J_{H,H}$ = 7.6, $^4J_{H,H}$ = 1.7 Hz, 2 H, C*H*-arom). ^{13}C{^{1}H} NMR (75.45 MHz, CD_2Cl_2, 298 K): δ 4.3 (s, NC*C*H$_3$), 25.1 (s, *C*H$_2$C$_5$H$_4$), 36.7 (d, $^2J_{C,P}$ = 5.6 Hz, NCH$_3$), 55.1 (d, $^2J_{C,P}$ = 27.8 Hz, *C*H$_2$N), 71.5 (s, *C*H, C$_5$H$_4$), 85.6 (d, $J_{C,P}$ = 9.1 Hz, *C*H, C$_5$H$_4$), 94.5 (s, C_{ipso}-C$_5$H$_4$), 122.8 (d, $^4J_{C,P}$ = 3.0 Hz, *C*H-arom), 126.0 (s, *C*H-arom), 127.7 (s, N*C*CH$_3$), 130.1 (s, *C*H-arom), 130.5 (s, *C*H-arom), 130.6 (s, C_{ipso}-arom), 151,4 (d, $^2J_{C,P}$ = 10.6 Hz, *C*OP-*arom*). ^{31}P{^{1}H} NMR (121.479 MHz, CD_2Cl_2, 298 K): δ 168.9 (s). HRMS (electrospray, *m*/*z*): calcd for $C_{22}H_{22}N_2O_2$-PRu [M − CH_3CN]$^+$ 479.0463; found 479.0497; calcd for $C_{20}H_{19}NO_2PRu$ [M − 2(CH_3CN)]$^+$ 438.0197; found 438.0232. IR (ATR, cm^{-1}): ν(NC) 2284 (w), ν(PF$_6$) 832 (s). Anal. Calcd for $C_{24}H_{25}F_6N_3O_2P_2Ru$: C 43.38, H 3.79, N 6.32. Found: C 43.60, H 3.66, N 6.30.

Preparation of [OsH(η^5-*C*$_5$,κ-*N*-Cp^N){η^3-CH$_2$C(CH$_3$)CH(OH)}]PF$_6$ (6). A solution of [Os(η^5-*C*$_5$,κ-*N*-Cp^N)(CH$_3$CN)$_2$]PF$_6$ (100 mg, 0.185 mmol) and 2-methyl-2-propen-1-ol (78 μL, 0.926 mmol) in THF (3 mL) was stirred for 10 min at 60 °C. The solvent was then removed al 0 °C and the residue obtained washed with diethyl ether (3 × 3 mL) and dried under vacuum to give a light brown solid (61 mg, 0.115 mmol, 62% yield). ^{1}H NMR (400 MHz, CD_2Cl_2, 253 K): δ −12.20 (s, 1 H, Os-*H*), 2.37, 2.47 (both m, 1 H, CH_2C$_5$H$_4$), 2.61 [s, 3 H, CH$_2$C(CH_3)CH(OH)], 2.74 [s, 1 H, CH_2C(CH$_3$)CH(OH)], 2.86 (d, $J_{H,H}$ = 5.0 Hz, 3 H, NHCH_3), 3.22 [s, 1 H, CH_2C(CH$_3$)CH(OH)], 3.58, 3.76 (both m, 1 H, −CH_2N), 4.19 (br s, 1 H, N*H*CH$_3$), 4.21, 5.20, 6.27, 6.51 (ABCD system, all br s, 1 H, C$_5H_4$), 4.69 [s, 1 H, CH$_2$C(CH$_3$)CH-(O*H*)], 6.91 [s, 1 H, CH$_2$C(CH$_3$)C*H*(OH)]. ^{13}C{^{1}H} NMR (125.75 MHz, CD_2Cl_2, 253 K): δ 16.3 [s, CH$_2$C(*C*H$_3$)CH(OH)], 17.4 [s, *C*H$_2$C(CH$_3$)CH(OH)], 24.6 (s, *C*H$_2$C$_5$H$_4$), 52.7 (s, NH*C*H$_3$), 68.0 (s, *C*H, C$_5$H$_4$), 74.3 (s, −*C*H$_2$N), 78.4 [s, CH$_2$C(CH$_3$)*C*H(OH)], 81.6, 81.7 (both s, *C*H, C$_5$H$_4$), 92.5 (s, *C*H, C$_5$H$_4$), 93.0 [s, CH$_2$*C*-(CH$_3$)CH(OH)], 122.2 (s, C_{ipso}-C$_5$H$_4$). MS (MALDI-TOF): *m*/*z* 386 (100), [M + H]$^+$. IR (KBr, cm^{-1}): ν(OsH) 2079 (w), ν(PF$_6$) 842 (s). Anal. Calcd for $C_{12}H_{19}F_6NOOsP$: C 27.27, H 3.62, N 2.65. Found: C 27.79, H 3.44, N 2.77.

Typical Procedure for Catalytic Isomerization of Allylic Alcohols. The required amount of catalyst and THF-d_8 (0.5 mL) as solvent were placed in an NMR tube. Then, the corresponding allylic alcohol (0.4 mmol) was added to the solution, and the course of the reactions was monitored by ^{1}H NMR at 60 °C.

Determination of the Kinetic Isotope Effect (KIE). The isomerizations of 3-methyl-2-buten-1-ol and 3-methyl-2-buten-1-ol-1,1-d_2 were performed by following the typical procedure described above and followed by ^{1}H NMR spectroscopy in THF-d_8 at 333 K and constant concentrations of the osmium catalyst **4a** (0.032 M). The decrease of the intensity (*I*) of a chosen signal corresponding to the substrate, related to an internal patron, vs the time (min) fits an exponential decay

function. $Ln(I_o/I)$ (where I_o represents the first measured intensity value) vs time fits a linear function from which k_{obs}^{H} for 3-methyl-2-buten-1-ol and k_{obs}^{D} for 3-methyl-2-buten-1-ol-1,1-d_2 can be obtained. The k_{obs}^{H}/k_{obs}^{D} gives a KIE value of 0.36.

Structural Analysis of Complexes 4a 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, $\lambda = 0.71073$ Å) operating at 50 kV and 30 (**4a**)/40 (**6**) mA. Data were collected over the complete sphere by a combination of four sets. Each frame exposure time was 10 s (**4a**)/20 s (**6**), covering 0.3° in ω. Data were corrected for absorption by using a multiscan method applied with the SADABS program.[31] The structures were solved by the Patterson method. Refinement of both complexes was performed by full-matrix least-squares on F^2 with SHELXL97,[32] including isotropic and subsequently anisotropic displacement parameters. For **4a**, the pendant amine group of the Cp ligand and the PF_6 anion were observed disordered about a plane of symmetry. All the highest electronic residuals were observed in close proximity to the metal centers and make no chemical sense.

Crystal data for **4a**: $C_{12}H_{18}N_3Os\cdot PF_6$, M_w 539.46, irregular block, yellow (0.12 × 0.08 × 0.08), orthorhombic, space group *Pbcm*, $a = 7.2245(19)$ Å, $b = 13.747(4)$ Å, $c = 16.602(4)$ Å, $V = 1648.8(8)$ Å^3, $Z = 4$, $D_{calc} = 2.173$ g cm^{-3}, $F(000) = 1024$, $T = 150(2)$ K, $\mu = 7.891$ mm^{-1}; 17 316 measured reflections (2θ: 3−58°, ω scans 0.3°), 2163 unique ($R_{int} = 0.0317$); min./max. transmn factors 0.451/0.570. Final agreement factors were $R_1 = 0.0361$ (2013 observed reflections, $I > 2\sigma(I)$) and $wR_2 = 0.0938$; data/restraints/parameters 2163/18/135; GoF = 1.086. Largest peak and hole: 1.617 and −1.420 e/Å^3.

Crystal data for **6**: $C_{12}H_{20}NO_2Os\cdot PF_6\cdot OC_4H_8$, M_w 601.56, irregular block, yellow (0.08 × 0.06 × 0.02), orthorhombic, space group *Pna*2$_1$, $a = 12.497(2)$ Å, $b = 19.794(4)$ Å, $c = 8.1791(15)$ Å, $V = 2023.2(7)$ Å^3, $Z = 4$, $D_{calc} = 1.975$ g cm^{-3}, $F(000) = 1168$, $T = 100(2)$ K, $\mu = 6.446$ mm^{-1}; 18 640 measured reflections (2θ: 3−58°, ω scans 0.3°), 4917 unique ($R_{int} = 0.0668$); min./max. transmn factors 0.583/0.882. Final agreement factors were $R_1 = 0.0433$ (4055 observed reflections, $I > 2\sigma(I)$) and $wR_2 = 0.0781$; data/restraints/parameters 4917/2/257; GoF = 1.041. Largest peak and hole: 1.086 and −2.281 e/Å^3. Absolute structure parameter was 0.000(11).

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Supporting Information Available: CIF files giving crystal data for compounds **4a** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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