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Asymmetric Transfer Hydrogenation of Ketones Catalyzed by Enantiopure Osmium(II) Pybox Complexes

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Supporting Information

ABSTRACT: The complexes *trans*-[$OsCl_2$(L){(*S*,*S*)-^{i}Pr-pybox}] ((*S*,*S*)-^{i}Pr-pybox = 2,6-bis[4′-(*S*)-isopropyloxazolin-2′-yl]pyridine, L = $P(OMe)_3$ (**1a**), $P(OEt)_3$ (**2a**), $P(O^iPr)_3$ (**3a**), $P(OPh)_3$ (**4a**), and *cis*-[$OsCl_2$(L){(*S*,*S*)-^{i}Pr-pybox}] (L = PPh_3 (**5a**), P^iPr_3 (**6a**), and PCy_3 (**7a**)) have been synthesized from the complex *trans*-[$OsCl_2(\eta^2$-C_2H_4){(*S*,*S*)-^{i}Pr-pybox}] via substitution of ethylene by phosphites and phosphines, respectively, under toluene reflux conditions. On the other hand, the synthesis of the complexes *trans*-[$OsCl_2$(L){(*R*,*R*)-Ph-pybox}] (L = $P(OMe)_3$ (**1b**) and *cis*-[$OsCl_2$(L){(*R*,*R*)-Ph-pybox}] (L = PPh_3 (**5b**), P^iPr_3 (**6b**), and PCy_3 (**7b**)) has been achieved from the complex *trans*-[$OsCl_2(\eta^2$-C_2H_4){(*R*,*R*)-Ph-pybox}] ((*R*,*R*)-Ph-pybox = 2,6-bis[4′-(*R*)-phenyloxazolin-2′-yl]pyridine under microwave irradiation. Complexes **1a**–**6a**, **1b**, **5b**, and **6b** have been assayed as catalysts for the asymmetric transfer hydrogenation (ATH) of ketones. Among the catalysts tested, the ^{i}Pr-pybox complexes *trans*-[$OsCl_2$(L){(*S*,*S*)-^{i}Pr-pybox}] (L = $P(OMe)_3$ (**1a**), $P(OEt)_3$ (**2a**), $P(O^iPr)_3$ (**3a**), $P(OPh)_3$ (**4a**)) have proven to be the most active catalysts for the reduction of a variety of aromatic ketones as nearly complete conversion and high enantioselectivity (up to 94%) are reached.

INTRODUCTION

Asymmetric transfer hydrogenation (ATH) of carbonyl compounds with chiral molecular catalysts is currently recognized as one of the most powerful and versatile tools to access enantiopure alcohols. While homogeneous ruthenium, rhodium, and iridium complexes are usually employed as catalysts,[1] much less attention has been devoted to other transition-metal-based systems. In particular, osmium catalysts are usually considered less active than ruthenium analogues and, thus, have been employed only occasionally.[2] An interesting example has recently been reported by Baratta and co-workers, who found that osmium complexes, generated in situ from [$OsCl_2(PPh_3)_3$], 1-(pyridin-2-yl)methanamine (Pyme), or the racemic (±)-RPyme (R = Me, ^{t}Bu) and diphosphine (*S*,*R*)-Josiphos or (*S*,*R*)-Josiphos* (see Figure 1), efficiently catalyze the ATH of methyl, aryl ketones (high TOF values and up to 96% ee).[3] These values are close to those obtained using analogous ruthenium complexes (95%–99% ee).[4]

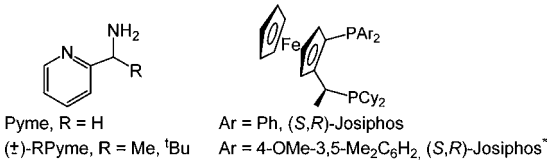

Figure 1. Pyme, (±)-RPyme, (*S*,*R*)-Josiphos, and (*S*,*R*)-Josiphos*.

On the other hand, the same authors reported that the CN′N pincer complexes [OsCl(CN′N)(P_2)] (P_2 = (*S*,*R*)-Josiphos or (*S*,*R*)-Josiphos*), obtained from either 2-aminomethylbenzo[*h*]quinoline[5] or 1-(6-arylpyridin-2-yl)methanamines[6] (HCN′N), also behave very efficiently for transfer hydrogenation of acetophenone (80–90% ee) and aryl ketones (74%–97% ee), respectively, with very low catalyst loading. Particularly, the complexes [MCl(CN′N){(*R*,*S*)-Josiphos*}] (M = Ru, Os; HCN′N = (*S*)-2-(1-aminoethyl)-6-(2-naphtyl)-pyridine) provide the best results, in terms of rate and enantioselectivity (up to 99% ee), for the conversion of different alkyl, aryl ketones into the corresponding alcohols.[7] All of these results seem to indicate that certain osmium complexes would be able to catalyze the ATH of ketones with comparable efficiency to that reported for analogous ruthenium systems. According to the authors the catalytic activity of these pincer complexes is ascribed to the Os-NH_2 linkage. The presence of the Os-NH_2 linkage favors a hydrogen-bonding network involving the alkoxyde and the alcohol.[5]

Interestingly, we have recently found that enantiopure pybox-derived ligands show great efficiency in the case of ruthenium complexes.[8] Thus, the ruthenium complexes *trans*- and *cis*-[$RuCl_2$(L){(*R*,*R*)-Ph-pybox}] ((*R*,*R*)-Ph-pybox = 2,6-bis(4′-(*R*)-phenyloxazolin-2′-yl)pyridine, L = phosphine) catalyze the ATH of aromatic ketones with up to 94% ee and very high TOF. It should be noted that only a few osmium/pybox

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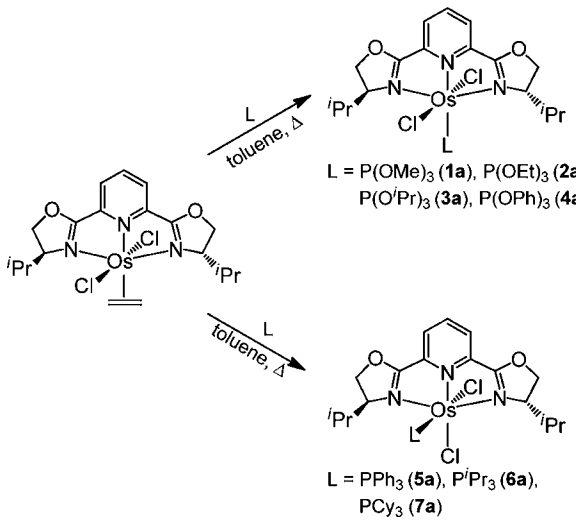
complexes have been synthesized as yet[9] and no essays have been reported dealing with their catalytic activity in asymmetric synthesis.[10] Herein, we report the synthesis and catalytic application of the osmium(II)-pybox complexes bearing phosphine and phosphite ligands as well as a comparative study of their catalytic activity in the ATH of ketones. In particular, the activity of ligands lacking the N−H function (pybox ligands in this work), relative to that of ligands containing the N−H function (ancillary ligands in refs 3, 5, 6, and 7; see above) is studied.

RESULTS AND DISCUSSION

Synthesis of Complexes *trans*-[$OsCl_2$(L){(*S*,*S*)-^{i}Pr-pybox}] (L = $P(OMe)_3$ (1a), $P(OEt)_3$ (2a), $P(O^iPr)_3$ (3a), $P(OPh)_3$ (4a)) and *cis*-[$OsCl_2$(L){(*S*,*S*)-^{i}Pr-pybox}] (L = PPh_3 (5a), P^iPr_3 (6a), PCy_3 (7a)). The reaction of the complex *trans*-[$OsCl_2(\eta^2$-$C_2H_4)$}{(*S*,*S*)-^{i}Pr-pybox}] and phosphites $P(OR)_3$ (R = Me, Et, ^{i}Pr, Ph) in refluxing toluene resulted in the stereoselective formation of the *trans* complexes **1a**−**4a**, which were isolated as solids in good yields (80%−88%). On the other hand, the *cis* complexes **5a**−**7a** were formed when phosphines PR_3 (R = Ph, ^{i}Pr, Cy), instead of phosphites, were reacted under similar reaction conditions (84%−92% yield) (see Scheme 1).

Scheme 1

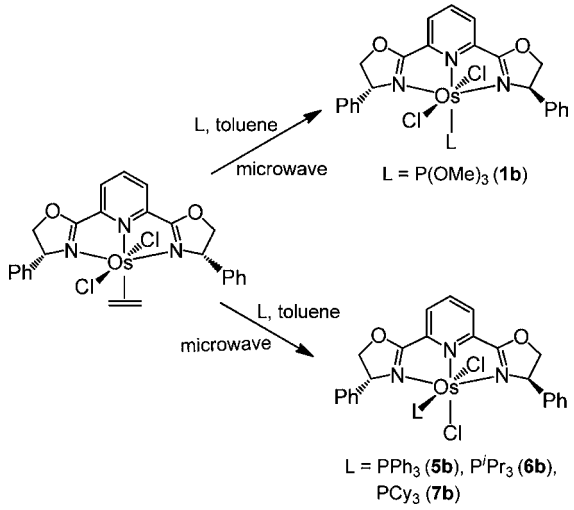


The complexes thus synthesized were characterized by infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy and elemental analysis (see Experimental Section for details).

The stereochemistry of complexes **1a**−**7a** was readily determined based on the ^{1}H and ^{13}C{^{1}H} NMR spectra. In accordance with the presence of a C_2 symmetry axis for complexes **1a**−**4a**, single resonance signals were observed for the C-5 (CH_2) and C-4 (CH^{i}Pr) carbon atoms of both oxazoline rings. On the other hand, the ^{1}H and ^{13}C{^{1}H} NMR spectra of **5a**−**7a** reveal the loss of the C_2 symmetry axis. Thus, their ^{13}C{^{1}H} NMR spectra show double resonance signals for the nonequivalent carbon nuclei of the oxazoline rings (C-5/C-5′ and C-4/C-4′) and for the nonequivalent carbon nuclei of the pyridine ring (C-2/C-6 and C-3/C-5). Moreover, these data are in accordance with those reported for the complex *cis*-[$RuCl_2(PPh_3)$}{(*S*,*S*)-^{i}Pr-pybox}], whose structure was confirmed by a single-crystal X-ray diffraction (XRD) study.[11]

Synthesis of Complexes *trans*-[$OsCl_2${$P(OMe)_3$}{(*R*,*R*)-Ph-pybox}] (1b) and *cis*-[$OsCl_2$(L){(*R*,*R*)-Ph-pybox}] (L = PPh_3 (5b), P^iPr_3 (6b), and PCy_3 (7b)). The substitution of ethylene by phosphines and phosphites in the complex *trans*-[$OsCl_2(\eta^2$-$C_2H_4)$}{(*R*,*R*)-Ph-pybox}] was accomplished in toluene under microwave irradiation affording *trans*- (**1b**, 84% yield) and *cis*-complexes (**5b**−**7b**, 81%−88% yield), respectively. The process is depcited in Scheme 2 (see the Experimental Section for further details).

Scheme 2



Catalytic Asymmetric Transfer Hydrogenation of Ketones. On the basis of comparative purposes, we first explored the catalytic activity of both (*R*,*R*)-Ph-pybox and (*S*,*S*)-^{i}Pr-pybox complexes. Regarding the enantioselectivity, the C-4 substituents (Ph and ^{i}Pr) of the oxazoline rings have been shown to be crucial.[8,12] In a representative run, the osmium catalyst precursor (0.2 mol %) was added to a solution containing 5 mmol of acetophenone and 2-propanol (75 mL), and the mixture was stirred for 15 min at 82 °C. NaOH then was added (ketone/catalyst/NaOH ratio = 500:1:24), and the resulting mixture was monitored by gas chromatography. Table 1 summarizes the conversion of acetophenone into 1-phenylethanol using the catalysts (*S*,*S*)-^{i}Pr-pybox) (**1a**, **5a**, **6a**) and (*R*,*R*)-Ph-pybox (**1b**, **6b**). Interestingly, selective access to both *R*- and *S*-configured secondary alcohols was achieved by using (*S*,*S*)- and (*R*,*R*)-pybox ligands, respectively. We also found that the ^{i}Pr-pybox osmium derivatives display higher efficiency than the corresponding Ph-pybox catalysts (Table 1; see entries: 1 vs 4, 3 vs 5). This result is in sharp contrast with those reached with analogous ruthenium-pybox complexes for which the Ph-pybox complexes are the most active catalysts.[8] Importantly, the efficiency of the catalyst depends not only on the chiral ligand but also on the auxiliary nonchiral ligand (phosphine or phosphite) coordinated to metal. Thus, the osmium complex containing the phosphite ligand ($P(OMe)_3$) led to the best results, in terms of reaction rate and enantiomeric excess (Table 1; see entries 1 vs 2, 3; 4 vs 5). Unfortunately, the influence of the stereoisomeric arrangement of the complex (*cis*-catalysts vs *trans*-catalysts) could not be ascertained, because only phosphine-containing *cis*-isomers and phosphite-containing *trans*-isomers are available.

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Table 1. Transfer Hydrogenation of Acetophenone Catalyzed by (*S*,*S*)-^{i}Pr-pybox)- and (*R*,*R*)-Ph-pybox)-Containing Osmium Complexes[a]

	catalyst	time, *t* (min)	conv (%)[b]	ee (%)[b]
1	$[OsCl_2\{P(OMe)_3\}(^{i}Pr\text{-pybox})]$ (**1a**)	90	96	75 (*R*)
2	$[OsCl_2(PPh_3)(^{i}Pr\text{-pybox})]$ (**5a**)	360	26	45 (*R*)
3	$[OsCl_2(P^{i}Pr_3)(^{i}Pr\text{-pybox})]$ (**6a**)	360	96	62 (*R*)
4	$[OsCl_2\{P(OMe)_3\}(Ph\text{-pybox})]$ (**1b**)	90 (120)	73 (91)	64 (62) (*S*)
5	$[OsCl_2(P^{i}Pr_3)(Ph\text{-pybox})]$ (**6b**)	360	92	26 (*S*)

[a]Reactions were carried out at 82 °C using 5 mmol of acetophenone and 2-propanol (75 mL), 0.2 mol % catalyst, and NaOH (ketone/catalyst/NaOH = 500:1:24). [b]As determined by gas chromatography (GC), using a Supelco *β*-DEX 120 chiral capillary column.

We then focused on the optimization of the reaction conditions for the reduction of acetophenone catalyzed by ^{i}Pr-pybox complexes **1a**, **5a**, **6a** (Table 2). The following parameters were explored:

(i) *Concentration of the solution*: The best results were obtained using 5 mmol of acetophenone and 2-propanol (75 mL). Higher concentration of the substrate led to either similar (compare entries 1 vs 2, 8 vs 9) or poorer (compare entries 10 vs 11) results, in terms of conversion and asymmetric induction.

(ii) *Acetophenone/catalyst/base ratio*: Increasing the ratio of catalyst and base, with respect to the ketone, from 500:1:24 to 500:2:48 (ketone:catalyst:base) results in slightly higher ee values (compare entries 1 vs 3).

(iii) *Base of choice*: KO^{t}Bu was found to be superior to NaOH (entries: 1 vs 4; 3 vs 5) and Cs_2CO_3 (entries: 5 vs 7).

Finally, the optimized acetophenone/catalyst/KO^{t}Bu ratio was found to be 500:3:60 (0.6 mol % of catalyst) (compare entries 6 vs 4, 6 vs 5).

We next assessed the influence of the nature of the phosphite on the process in the case of (*S*,*S*)-^{i}Pr-pybox complexes under optimized reaction conditions (5 mmol of acetophenone and 75 mL of 2-propanol; temp = 82 °C; 0.6 mol % of catalyst; ketone/catalyst/KO^{t}Bu molar ratio = 500:3:60). Table 3 summarizes the conversion of acetophenone into 1-phenylethanol using catalysts **1a**−**4a**. The reactions were almost complete in 60 min providing very high enantiomeric excess (entries 1−4, 90%−94%). It then becomes apparent that the electronic nature and the bulkiness of the phosphite do not exert much influence in the process in terms of conversion and enantiomeric excess. For comparative purposes, the results obtained using a lower catalyst loading (0.4 mol %; ketone/catalyst/KO^{t}Bu molar ratio = 500:2:48) are also collected in Table 3 (see entries 5−8).

Table 3. Transfer Hydrogenation of Acetophenone Catalyzed by (*S*,*S*)-^{i}Pr-pybox) Phosphite Osmium Complexes under Optimized Conditions[a]

	catalyst	time, *t* (min)	conv (%)	ee (%) (*R*)[b]
1	$[OsCl_2\{P(OMe)_3\}(^{i}Pr\text{-pybox})]$ (**1a**)	60	98	94
2	$[OsCl_2\{P(OEt)_3\}(^{i}Pr\text{-pybox})]$ (**2a**)	60	99	90
3	$[OsCl_2\{P(O^{i}Pr)_3\}(^{i}Pr\text{-pybox})]$ (**3a**)	60	99	91
4	$[OsCl_2\{P(OPh)_3\}(^{i}Pr\text{-pybox})]$ (**4a**)	60	98	92
5	$[OsCl_2\{P(OMe)_3\}(^{i}Pr\text{-pybox})]$ (**1a**)[c]	75	98	89
6	$[OsCl_2\{P(OEt)_3\}(^{i}Pr\text{-pybox})]$ (**2a**)[c]	75	97	86
7	$[OsCl_2\{P(O^{i}Pr)_3\}(^{i}Pr\text{-pybox})]$ (**3a**)[c]	75	96	89
8	$[OsCl_2\{P(OPh)_3\}(^{i}Pr\text{-pybox})]$ (**4a**)[c]	75	98	89

[a]Reactions were carried out at 82 °C using 5 mmol of acetophenone and 2-propanol (75 mL), 0.6 mol % catalyst, and KO^{t}Bu (acetophenone/catalyst/KO^{t}Bu = 500:3:60). [b]Determined by GC with a Supelco *β*-DEX 120 chiral capillary column. [c]Reactions were carried using 0.4 mol % catalyst and KO^{t}Bu (acetophenone/catalyst/KO^{t}Bu = 500:2:48).

Table 2. Optimization of Reaction Conditions for Transfer Hydrogenation of Acetophenone Catalyzed by ^{i}Pr-pybox Osmium Complexes[a]

	catalyst	catalyst amount (mol %)	time, *t* (min)	conv (%)	ee (%) (*R*)[h]
1	$[OsCl_2\{P(OMe)_3\}(^{i}Pr\text{-pybox})]$ (**1a**)	0.2	90	96	75
2	**1a**[b]	0.2	120	96	73
3	**1a**[c]	0.4	75	97	81
4	**1a**[d]	0.2	75	95	86
5	**1a**[e]	0.4	75	98	89
6	**1a**[f]	0.6	60	98	94
7	**1a**[g]	0.4	240	90	71
8	$[OsCl_2(PPh_3)(^{i}Pr\text{-pybox})]$ (**5a**)	0.2	360 (600)	26 (36)	45 (38)
9	**5a**[b]	0.2	360 (600)	23 (32)	41 (36)
10	$[OsCl_2(P^{i}Pr_3)(^{i}Pr\text{-pybox})]$ (**6a**)	0.2	360	96	62
11	**6a**[b]	0.2	480	79	52
12	**6a**[d]	0.2	360 (480)	81 (94)	58 (56)

[a]Reactions were carried out at 82 °C using 0.2 mol % catalyst, 5 mmol of acetophenone, 2-propanol (75 mL) and NaOH (ketone/catalyst/NaOH = 500:1:24). [b]5 mmol of acetophenone, 2-propanol (50 mL). [c]Reactions carried out using 0.4 mol % catalyst (ketone/catalyst/NaOH 500:2:48). [d]Reactions carried out using 0.2 mol % catalyst (ketone/catalyst/KO^{t}Bu = 500:1:24) [e]Reactions carried out using 0.4 mol % catalyst (ketone/catalyst/KO^{t}Bu = 500:2:48). [f]Reactions carried out using 0.6 mol % catalyst (ketone/catalyst/KO^{t}Bu = 500:3:60. [g]Reactions carried out using 0.4 mol % catalyst (ketone/catalyst/Cs_2CO_3 = 500:2:48). [h]Determined by GC with a Supelco *β*-DEX 120 chiral capillary column.

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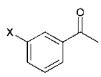
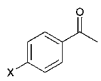
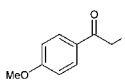
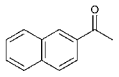
Furthermore, the selected catalysts **1a**−**4a** were screened in the catalytic reduction of various aryl ketones to the corresponding secondary alcohols under optimized conditions. Representative examples are given in Table 4 (additional results using catalysts **1a**−**4a** are provided in the Supporting Information). All the reactions went to completion in 60 min (96%−99% conversion). Most secondary alcohols have the *R* configuration, except those derived from *o*-substituted aryl ketones and 2′-acetonaphtone, wherein the *S* enantiomer was formed as the major isomer. Although the ee values are influenced by the nature and the position of substituents of the aryl group of the ketone, a general trend in terms of steric and/or electronic effects cannot be advanced at this stage. Whereas *o*-bromoacetophenone and 2′-acetonaphtone were reduced with moderate ee values (55%−57% ee, entries 8−9 and 22−23), excellent enantioselectivity was reached for acetophenone (92%−94% ee, see entries 1−2), propiophenone (92%−94% ee, entries 3−5), 3-bromoacetophenone (91%−92% ee, entries 13−14), 4-methoxyacetophenone (93% ee, entries 15−16), and 4-methoxypropiophenone (93.5%−94% ee, entries 19−21). The ee values for the remaining ketones ranged from 74% to 80% (entries 6−7, 10−12, 17−18). On the other hand, no appreciable variation in ee was observed when different phosphite auxiliary ligands were used. This is in contrast to the trend found in the series of ruthenium pybox complexes, wherein the complexes containing $P(OPh)_3$ are much less active than those containing $P(OMe)_3$ ($[RuCl_2\{P(OMe)_3\}\{(R,R)\text{-Ph-pybox}\}]$, 5 min, 97% conversion, 63% ee; $[RuCl_2\{P(OPh)_3\}\{(R,R)\text{-Ph-pybox}\}]$, 60 min, 25% conversion, 5% ee).[8]

Table 4. Selected Examples of Transfer Hydrogenation of Ketones Catalyzed by (*S*,*S*)-^{i}Pr-pybox Complexes under Optimized Conditions[a]

	Ketone		Catalyst	Conv. (%)	*e.e.* (%)[b]
1		R = Me	**1a**	98	94 (*R*)
2			**4a**	98	92 (*R*)
3		R = Et	**2a**	98	92(*R*)
4			**3a**	99	92(*R*)
5			**4a**	98	94(*R*)
6		X = OMe	**1a**	99	74 (*S*)
7			**2a**	99	74 (*S*)
8		X = Br	**1a**	98	57 (*S*)
9			**2a**	99	55 (*S*)
10		X = OMe	**1a**	97	79 (*R*)
11			**3a**	97	79 (*R*)
12			**4a**	97	80 (*R*)
13		X = Br	**1a**	99	92 (*R*)
14			**2a**	99	91 (*R*)
15		X = OMe	**1a**	98	93 (*R*)
16			**3a**	98	93 (*R*)
17		X = Br	**1a**	97	72 (*R*)
18			**2a**	97	73 (*R*)
19			**1a**	97	94 (*R*)
20			**2a**	96	93.5 (*R*)
21			**3a**	96	94 (*R*)
22			**1a**	99	54 (*S*)
23			**3a**	99	55 (*S*)

[a]Reactions were carried out at 82 °C during 60 min, using 5 mmol of ketone and 75 mL of 2-propanol, 0.6 mol % catalyst, and KO^{t}Bu (ketone/catalyst/KO^{t}Bu = 500:3:60). [b]Determined by GC with a Supelco *β*-DEX 120 chiral capillary column. The absolute configuration of the major enantiomer is given in parentheses.

SUMMARY

We have synthesized the osmium complexes *trans*-$[OsCl_2(L)\text{-(R-pybox)}]$ (L = phosphite) and *cis*-$[OsCl_2(L)\text{(R-pybox)}]$ (L = phosphine) and their catalytic activity toward the asymmetric transfer hydrogenation (ATH) of aryl ketones has been compared with that of analogous ruthenium complexes already reported from our group.[8] In particular, the complexes *trans*-$[OsCl_2(L)\{(S,S)\text{-}^i\text{Pr-pybox}\}]$ (L = $P(OMe)_3$ (**1a**), $P(OEt)_3$ (**2a**), $P(O^iPr)_3$ (**3a**), $P(OPh)_3$ (**4a**)) are highly efficient in the reduction of aryl ketones (nearly quantitative conversion and 90%−94% ee have been reached in the reduction of acetophenone, propiophenone, 3-bromoacetophenone, 4-methoxyacetophenone, and 4-methoxypropiophenone). Interestingly, the efficiency of these catalysts, as well as that of the ruthenium analogues, depends not only on the chiral ligand but also on the nonchiral auxiliary ligand. In the case of osmium complexes, the best results were reached using the ligand combination (*S*,*S*)-^{i}Pr-pybox)/ $P(OR)_3$, whereas the complexes *cis*-$[RuCl_2(L)\{(R,R)\text{-Ph-pybox}\}]$ (L = PPh_3, P^iPr_3) were the best catalysts for ruthenium catalysts (ee values of up 95%).[8] Herein, new examples based on osmium catalysts are presented that catalyze the ATH of ketones with comparable efficiency as similar ruthenium systems. On the other hand, it should be emphasized that osmium complexes based on aprotic nitrogen ligands are shown for the first time to efficiently catalyze the ATH of ketones (>90% ee).

EXPERIMENTAL SECTION

General Comments. The reactions were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques or microwave reaction conditions. The reagents were obtained from commercial suppliers and used without further purification. Solvents were dried by standard methods and distilled under nitrogen before use. The complexes *trans*-$[OsCl_2(\eta^2\text{-}C_2H_4)\{(S,S)\text{-}^i\text{Pr-pybox}\}]$ and *trans*-$[OsCl_2(\eta^2\text{-}C_2H_4)\{(R,R)\text{-Ph-pybox}\}]$ were prepared by reported methods.[9] IR spectra were recorded on a Perkin−Elmer Model 1720-XFT spectrometer. The C, H, N analyses were carried out with a LECO Model CHNS-TruSpec microanalyzer and a Perkin−Elmer Model 240-B microanalyzer (inconsistent analyses were found for complexes **7a** and **7b**, because of incomplete combustion). A CEM Discover S-Class microwave synthesizer was used. NMR spectra were recorded on Bruker spectrometers (Model AV400 operating at 400.13 MHz (^{1}H), 100.61 MHz (^{13}C), and 161.95

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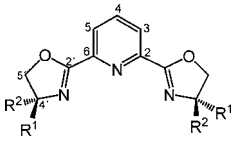
(^{31}P) MHz or Model DPX300 operating at 300.13 MHz (^{1}H) and 75.45 MHz (^{13}C)). DEPT experiments were carried out for all of the compounds. Chemical shifts are reported in parts per million and referenced to TMS or 85% H_3PO_4 as standards. Coupling constants (J) are given in hertz (Hz). The following atom labels have been used for the ^{1}H and ^{13}C{^{1}H} spectroscopic data of the pybox ligands.



*Synthesis of Complexes trans-[OsCl$_2$(L){(S,S)-^{i}Pr-pybox}] (L = P(OMe)$_3$ (**1a**), P(OEt)$_3$ (**2a**), P(O^{i}Pr)$_3$ (**3a**), P(OPh)$_3$ (**4a**).* To a solution of complex *trans*-[OsCl$_2$(η^2-C$_2$H$_4$){(*S*,*S*)-^{i}Pr-pybox}] (100 mg, 0.173 mmol) in toluene (25 mL), the corresponding phosphite (0.259 mmol) was added and the mixture heated under reflux during 5 h. The solvent was then evaporated under reduced pressure and the solid residue was purified by chromatography over silica gel, using dichloromethane/methanol (50:2) as the eluent.

Complex 1a. Yield: 95 mg, 80%. Purple solid. Anal. Calcd. for $C_{20}H_{32}Cl_2N_3O_5OsP$ (686.59 g/mol): C, 34.99; H, 4.70; N, 6.12. Found: C, 34.97; H, 4.91; N, 6.15. ^{31}P{^{1}H} NMR (161.95 MHz, CD_2Cl_2, 298 K): δ 89.4. ^{1}H NMR (400.13 MHz, CD_2Cl_2, 298 K): δ 6.91 (br s, 3H, H^{3,4,5} C_5H_3N), 4.95 (m, 4H, OCH_2), 4.21 (m, 2H, C*H*^{i}Pr), 3.85 (br s, 9H, P(OMe)$_3$), 2.74 (br s, 2H, C*H*Me$_2$), 1.02 (d, J_{HH} = 8.7 Hz, 6H, CH*Me*$_2$), 0.82 (d, J_{HH} = 8.7 Hz, 6H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (100.61 MHz, CD_2Cl_2, 298 K): δ 171.4 (br s, OCN), 147.3 (s, C^{2,6} C_5H_3N), 137.3 (s, C^{4} C_5H_3N), 118.7 (s, C^{3,5} C_5H_3N), 73.4 (s, C*H*^{i}Pr), 71.6 (s, OCH_2), 52.1 (s, P(OMe)$_3$), 28.6 (s, C*H*Me$_2$), 19.5, 14.9 (2*s*, CH*Me*$_2$).

Complex 2a. Yield: 103 mg, 82%. Purple solid. Anal. Calcd. for $C_{23}H_{38}Cl_2N_3O_5OsP$ (728.67 g/mol): C, 37.91; H, 5.26; N, 5.77. Found: C, 37.67; H, 5.50; N, 5.80. ^{31}P{^{1}H} NMR (161.95 MHz, CD_2Cl_2, 298 K): δ 76.3. ^{1}H NMR (400.13 MHz, CD_2Cl_2, 298 K): δ 7.02 (d, J_{HH} = 7.8 Hz, 2H, H^{3,5} C_5H_3N), 6.82 (t, J_{HH} = 7.8 Hz, 1H, H^{4} C_5H_3N), 4.42 (m, 2H, OCH_2), 4.07 (m, 4H, OCH_2 and C*H*^{i}Pr), 3.83 (m, 6H, CH_2 P(OEt)$_3$), 2.86 (m, 2H, C*H*Me$_2$), 1.26 (m, 9H, CH_3 P(OEt)$_3$), 1.03 (d, J_{HH} = 6.7 Hz, 6H, CH*Me*$_2$), 0.93 (d, J_{HH} = 6.7 Hz, 6H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (75.46 MHz, CD_2Cl_2, 298 K): δ 172.1 (br s, OCN), 146.7 (s, C^{2,6} C_5H_3N), 136.3 (s, C^{4} C_5H_3N), 119.2 (s, C^{3,5} C_5H_3N), 73.4 (s, C*H*^{i}Pr), 71.0 (s, OCH_2), 60.5 (s, CH_2 P(OEt)$_3$), 28.0 (s, C*H*Me$_2$), 19.0 (s, CH*Me*$_2$), 16.4 (s, CH_3 P(OEt)$_3$), 14.7 (s, CH*Me*$_2$).

Complex 3a. Yield: 118 mg, 81%. Purple solid. Anal. Calcd. for $C_{26}H_{44}Cl_2N_3O_5OsP$ (770.75 g/mol): C, 40.52; H, 5.75; N, 5.45. Found: C, 40.53; H, 5.45; N, 5.20. ^{31}P{^{1}H} NMR (161.95 MHz, CD_2Cl_2, 298 K): δ 84.2. ^{1}H NMR (400.13 MHz, CD_2Cl_2, 298 K): δ 7.00 (d, J_{HH} = 7.8 Hz, 2H, H^{3,5} C_5H_3N), 6.34 (t, J_{HH} = 7.2 Hz, 1H, H^{4} C_5H_3N), 4.43 (m, 2H, OCH_2), 4.33 (m, 3H, CH P(O^{i}Pr)$_3$), 3.83 (m, 4H, OCH_2 and C*H*^{i}Pr), 1.86 (m, 2H, C*H*Me$_2$), 1.06 (m, 18H, CH_3 P(O^{i}Pr)$_3$), 0.83 (d, J_{HH} = 7.7 Hz, 6H, CH*Me*$_2$), 0.42 (d, J_{HH} = 8.4 Hz, 6H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (75.45 MHz, CD_2Cl_2, 298 K): δ 171.0 (br s, OCN), 147.3 (s, C^{2,6} C_5H_3N), 136.9 (s, C^{4} C_5H_3N), 118.3 (s, C^{3,5} C_5H_3N), 73.5 (s, C*H*^{i}Pr), 71.0 (s, OCH_2), 61.2 (s, CH P(O^{i}Pr)$_3$), 28.1 (s, C*H*Me$_2$), 19.7 (s, CH*Me*$_2$), 16.7 (s, CH_3 P(O^{i}Pr)$_3$), 15.0 (s, CH*Me*$_2$).

Complex 4a. Yield: 131 mg, 88%. Purple solid. Anal. Calcd. for $C_{35}H_{38}Cl_2N_3O_5OsP$ (872.80 g/mol): C, 48.16; H, 4.39; N, 4.81. Found: C, 48.31; H, 4.41; N, 4.85. ^{31}P{^{1}H} NMR (161.95 MHz, CD_2Cl_2, 298 K): δ 84.0. ^{1}H NMR (300.13 MHz, CD_2Cl_2, 298 K): δ 7.40 (m, 6H, P(OPh)$_3$), 7.24 (m, 9H, P(OPh)$_3$), 7.02 (d, J_{HH} = 7.8 Hz, 2H, H^{3,5} C_5H_3N), 6.82 (t, J_{HH} = 7.8 Hz, 1H, H^{4} C_5H_3N), 4.92 (m, 4H, OCH_2), 3.82 (m, 2H, C*H*^{i}Pr), 2.73 (m, 2H, C*H*Me$_2$), 0.83 (d, J_{HH} = 6.6 Hz, 6H, CH*Me*$_2$), 0.64 (d, J_{HH} = 5.7 Hz, 6H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (100.61 MHz, CD_2Cl_2, 298 K): δ 172.0 (s, OCN), 156.5, 152.7 (2*s*, C^{2,6} C_5H_3N), 130.0−121.7 (5*s*, C^{4} C_5H_3N, P(OPh)$_3$), 120.9 (s, C^{3,5} C_5H_3N), 73.2 (s, OCH_2), 71.3 (s, C*H*^{i}Pr), 32.8 (s, C*H*Me$_2$), 19.3, 14.4 (2*s*, CH*Me*$_2$).

*Synthesis of Complexes cis-[OsCl$_2$(L){(S,S)-^{i}Pr-pybox}] (L = PPh$_3$ (**5a**), PiPr$_3$ (**6a**), and PCy$_3$ (**7a**)).* A solution of complex *trans*-[OsCl$_2$(η^2-C$_2$H$_4$){(*S*,*S*)-^{i}Pr-pybox}] (100 mg, 0.169 mmol) and the corresponding phosphine (0.259 mmol) in toluene (25 mL) was heated under reflux during 5 h. The solvent was then evaporated under reduced pressure and the solid residue was purified by chromatography over silica gel using dichloromethane/methanol (50:2) as the eluent.

Complex 5a. Yield: 128 mg, 92%. Garnet solid. Anal. Calcd. for $C_{35}H_{38}Cl_2N_3O_2OsP$ (824.80 g/mol): C, 50.97; H, 4.64; N, 5.09. Found: C, 50.88; H, 4.89; N, 5.00. ^{31}P{^{1}H} NMR (161.95 MHz, CD_2Cl_2, 298 K): δ −29.4 (s). ^{1}H NMR (300.13 MHz, CD_2Cl_2, 298 K): δ 7.68 (m, 3H, PPh_3), 7.27−7.23 (m, 12H, PPh_3), 6.89 (m, 1H, H^{4} C_5H_3N), 6.63 (m, 2H, H^{3,5} C_5H_3N), 4.78 (m, 2H, OCH_2), 4.70 (m, 1H, OCH_2), 4.41 (m, 1H, OCH_2), 4.18 (m, 1H, C*H*^{i}Pr), 3.95 (m, 1H, C*H*^{i}Pr), 2.94 (m, 1H, C*H*Me$_2$), 2.49 (m, 1H, C*H*Me$_2$), 1.01 (d, $^{2}J_{HH}$ = 7.2 Hz, 3H, CH*Me*$_2$), 0.90 (d, $^{2}J_{HH}$ = 8.4 Hz, 6H, CH*Me*$_2$), 0.01 (d, J_{HH} = 8.2 Hz, 3H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (100.61 MHz, CD_2Cl_2, 298 K): δ = 176.6, 175.7 (2*s*, OCN), 154.2, 153.8 (2*s*, C^{2,6} C_5H_3N), 133.8−132.3 (6*s*, PPh_3), 128.1−127.9 (6*s*, PPh_3), 125.4, 124.7, 124.1 (3*s*, C^{3,4,5} C_5H_3N), 72.4, 72.0 (2*s*, OCH_2), 71.3, 70.6 (2*s*, C*H*^{i}Pr), 28.7, 27.9 (2*s*, C*H*Me$_2$), 19.9, 19.5, 13.9, 13.3 (4*s*, CH*Me*$_2$).

Complex 6a. Yield: 111 mg, 91%. Garnet solid. Anal. Calcd. for $C_{26}H_{44}Cl_2N_3O_2OsP$ (722.76 g/mol): C, 43.21; H, 6.14; N, 5.81. Found: C, 43.19; H, 6.10; N, 5.80. ^{31}P{^{1}H} NMR (161.95 MHz, CD_2Cl_2, 298 K): δ 57.4. ^{1}H NMR (400.13 MHz, CD_2Cl_2, 298 K): δ 7.11 (m, 2H, H^{3,5} C_5H_3N), 6.48 (m, 1H, H^{4} C_5H_3N), 4.92 (m, 4H, OCH_2), 4.20 (m, 2H, C*H*^{i}Pr), 2.95 (m, 1H, C*H*Me$_2$), 2.80 (m, 1H, C*H*Me$_2$), 2.12 (m, 3H, P(C*H*Me$_2$)$_3$), 1.24 (m, 6H, P(C*H*Me$_2$)$_3$), 1.10 (m, 12H, P(CH*Me*$_2$)$_3$), 0.99 (d, $^{2}J_{HH}$ = 7.6 Hz, 6H, CH*Me*$_2$), 0.89 (d, $^{2}J_{HH}$ = 6.4 Hz, 6H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (100.61 MHz, CD_2Cl_2, 298 K): δ 179.0, 176.9 (2*s*, OCN), 157.3, 156.9 (2*s*, C^{2,6} C_5H_3N), 124.7, 124.4, 124.1 (3*s*, C^{3,4,5} C_5H_3N), 74.9, 72.8 (2*s*, C*H*^{i}Pr), 71.4, 71.0 (2*s*, OCH_2), 29.9, 29.0 (2*s*, C*H*Me$_2$), 27.5 (br s, P(C*H*Me$_2$)$_3$), 21.0, 20.3, 19.8, 19.1 (4*s* CH*Me*$_2$, P(CH*Me*$_2$)$_3$), 16.1, 15.5 (2*s*, CH*Me*$_2$).

Complex 7a. Yield: 124 mg, 84%. Garnet solid. ^{31}P{^{1}H} NMR (161.95 MHz, CD_2Cl_2, 298 K): δ 57.3. ^{1}H NMR (300.13 MHz, CD_2Cl_2, 298 K): δ 7.88 (br s, 1H, H^{3,5} of C_5H_3N), 7.64 (br s, 1H, H^{3,5} of C_5H_3N), 7.54 (br s, 1H, H^{4} C_5H_3N), 6.07 (br s, 1H, OCH_2), 5.88 (br s, 1H, OCH_2), 5.78 (br s, 1H, OCH_2), 5.45 (br s, 1H, OCH_2), 4.78 (br s, 1H, C*H*^{i}Pr), 4.51 (br s, 1H, C*H*^{i}Pr), 3.78 (br s, 1H, C*H*Me$_2$), 3.08 (br s, 1H, C*H*Me$_2$), 1.81−1.31 (m, 33H, PCy$_3$), 0.99 (br s, 6H, CH*Me*$_2$), 0.89 (br s, 6H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (100.61 MHz, CD_2Cl_2, 298 K): δ 175.6 (br s, OCN), 158.8, 156.6 (2*s*, C^{2,6} C_5H_3N), 126.6 (s, C^{4} C_5H_3N), 124.1, 123.9 (2*s*, C^{3,5} of C_5H_3N), 72.1, 71.4 (2*s*, OCH_2), 68.4, 68.0 (2*s*, C*H*^{i}Pr), 37.9 (d, $^{2}J_{CP}$ = 25 Hz, PCH), 35.1 (d, $^{2}J_{CP}$ = 50 Hz, PCH), 31.3 (d, $^{2}J_{CP}$ = 45 Hz, PCH), 29.4, 29.2 (2*s*, C*H*Me$_2$), 26.8−23.3 (4*s*, CH_2 PCy$_3$), 22.3, 21.2, 17.4, 16.7 (4*s*, CH*Me*$_2$).

*Synthesis of Complex trans-[OsCl$_2${P(OMe)$_3$}{(R,R)-Ph-pybox}] (**1b**).* Under a nitrogen atmosphere, a pressure-resistant septum-sealed glass vial was charged with the complex *trans*-[OsCl$_2$(η^2-C$_2$H$_4$){(*R*,*R*)-Ph-pybox}] (100 mg, 0.161 mmol), P(OMe)$_3$ (30 mg, 0.241 mmol), a magnetic stirring bar, and toluene (2 mL). The vial was then placed inside the cavity of the microwave synthesizer, and the power was held at 300 W until the desired temperature (107 °C) was reached. Microwave power was automatically regulated for the remainder of the experiment to maintain the temperature (monitored by a built-in infrared (IR) sensor). After completion of the reaction (3 h), the vial was cooled, the solvent was evaporated under reduced pressure, and the solid residue was purified by chromatography over silica gel using dichloromethane/methanol (50:2) as the eluent. Yield: 84% (0.101 g). Purple solid. Anal. Calcd. for $C_{26}H_{28}Cl_2N_3O_5OsP$ (754.63 g/mol): C, 41.38; H, 3.74; N, 5.57. Found: C, 41.28; H, 3.61; N, 5.23. ^{31}P{^{1}H} NMR (161.95 MHz, $CDCl_3$, 298 K): δ 88.9. ^{1}H NMR (400.13 MHz, CD_2Cl_2, 298 K): δ 7.46 (m, 4H, Ph), 7.25 (m, 6H, Ph), 6.91 (br s, 3H, H^{3,4,5} C_5H_3N), 5.05 (m, 4H, OCH_2), 4.71 (m, 2H, C*H*Ph), 3.74 (br s, 9H, P(OMe)$_3$). ^{13}C{^{1}H} NMR (100.61 MHz, CD_2Cl_2, 298 K): δ 172.8 (br s, OCN), 147.8 (s, C^{2,6} C_5H_3N), 139.6 (s, C^{ipso} Ph), 137.0

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(s, C^4 C_5H_3N), 128.3−127.7 (6*s*, Ph), 118.5 (s, $C^{3,5}$ C_5H_3N), 79.6 (s, OCH_2), 72.7 (*s*, *C*HPh), 51.2 (s, $P(OMe)_3$).

*Synthesis of Complexes cis-[OsCl$_2$(L){(R,R)-Ph-pybox}] (L = PPh$_3$ (**5b**), P^{i}Pr$_3$ (**6b**), and PCy$_3$ (**7b**).* Under nitrogen atmosphere, a pressure-resistant septum-sealed glass vial was charged with the complex *trans*-[$OsCl_2(\eta^2$-$C_2H_4)$\{(*R*,*R*)-Ph-pybox\}] (100 mg, 0.161 mmol), the phosphine (0.241 mmol), a magnetic stirring bar, and toluene (2 mL). The vial was then placed inside the cavity of the microwave synthesizer, and the power was held at 300 W until the desired temperature (107−112 °C) was reached. Microwave power was automatically regulated for the remainder of the experiment to maintain the temperature (monitored by a built-in IR sensor). After completion of the reaction (2 h), the vial was cooled, the solvent was evaporated under reduced pressure, and the solid residue was purified by chromatography over silica gel, using dichloromethane/methanol (50:2) as the eluent.

Complex 5b. Yield: 126 mg, 88%. Garnet solid. Anal. Calcd. for $C_{41}H_{34}Cl_2N_3O_2OsP$ (892.84 g/mol): C, 55.15; H, 3.84; N, 4.71. Found: C, 55.18; H, 3.88; N, 4.78. $^{31}P\{^1H\}$ NMR (161.95 MHz, CD_2Cl_2, 298 K): δ −26.3. ^1H NMR (400.13 MHz, CD_2Cl_2, 298 K): δ 7.55 (m, 2H), 7.34 (m, 8H), 7.27−7.14 (m, 12H), 7.02 (m, 3H, Ph and PPh_3), 6.96 (m, 2H, $H^{3,5}$ C_5H_3N), 6.70 (m, 1H, H^4 C_5H_3N), 5.32 (m, 1H, OCH_2), 5.14 (m, 1H, OCH_2), 4.74 (m, 1H, OCH_2), 4.61−4.57 (m, 3H, *CH*Ph, OCH_2). $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, 298 K): δ 179.2, 177.7 (2*s*, OCN), 154.8, 154.7 (2*s*, $C^{2,6}$ C_5H_3N), 138.9, 137.6 (2*s*, C^{ipso} Ph), 133.7−127.6 (10*s*, Ph, PPh_3), 125.5, 125.4, 125.2 (3*s*, $C^{3,4,5}$ C_5H_3N), 81.2, 78.3 (2*s*, OCH_2), 70.8, 70.7 (2*s*, *C*HPh).

Complex 6b. Yield: 106 mg, 84%. Garnet solid. Anal. Calcd. for $C_{32}H_{40}Cl_2N_3O_2OsP$ (790.79 g/mol): C, 48.60; H, 5.10; N, 5.31. Found: C, 48.68; H, 4.53; N, 5.32. $^{31}P\{^1H\}$ NMR (161.95 MHz, CD_2Cl_2, 298 K): δ 59.9. ^1H NMR (300.13 MHz, CD_2Cl_2, 298 K): δ 7.69 (m, 2H, Ph), 7.60 (m, 2H, Ph), 7.35−7.15 (m, 8H, $H^{3,5}$ C_5H_3N, Ph), 6.47 (m, 1H, H^4 C_5H_3N), 5.37 (m, 2H, OCH_2), 5.23 (m, 2H, OCH_2), 4.73 (m, 2H, *CH*Ph), 2.15 (m, 3H, $P(CHMe_2)_3$), 1.32−1.12 (m, 18H, $P(CHMe_2)_3$). $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, 298 K): δ 170.4 (br s, OCN), 159.9, 158.7 (2*s*, $C^{2,6}$ C_5H_3N), 147.3 (s, C^{ipso} Ph), 135.4 (s, C^4 C_5H_3N), 132.1 (s, C^{ipso} Ph), 128.4−127.5 (6*s*, Ph), 118.8, 117.9 (2*s*, $C^{3,5}$ C_5H_3N), 79.7, 78.5 (2*s*, CHPh), 72.4, 72.0 (2*s*, OCH_2), 28.1 (s, $P(CHMe_2)_3$), 21.7, 20.1 (2*s*, $P(CHMe_2)_3$).

Complex 7b. Yield: 128 mg, 81%. Garnet solid. $^{31}P\{^1H\}$ NMR (161.95 MHz, CD_2Cl_2, 298 K): δ 59.1. ^1H NMR (400.13 MHz, CD_2Cl_2, 298 K): δ 7.57 (m, 2H, Ph), 7.46 (m, 2H, Ph), 7.37−7.20 (m, 8H, $H^{3,5}$ C_5H_3N, Ph), 6.73 (m, 1H, H^4 C_5H_3N), 5.09 (m, 4H, OCH_2), 4.67−4.39 (m, 2H, *CH*Ph), 1.80−1.62 (2m, 33H, PCy_3). $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, 298 K): δ 170.4 (br s, OCN), 159.2, 158.7 (2*s*, $C^{2,6}$ C_5H_3N), 135.8 (s, C^{ipso} Ph), 134.3 (s, C^4 C_5H_3N), 132.0 (s, C^{ipso} Ph), 128.7−127.3 (4*s*, Ph), 122.9 (s, $C^{3,5}$ C_5H_3N), 79.8 (s, OCH_2), 70.9 (s, CHPh), 36.3 (d, $^2J_{CP}$ = 48 Hz, PCH), 35.3 (d, $^2J_{CP}$ = 54 Hz, PCH), 32.8 (d, $^2J_{CP}$ = 43 Hz, PCH), 27.9−26.2 (5*s*, CH_2 PCy_3).

General Procedure for Hydrogen Transfer Reactions. The ketone (5 mmol) and the catalyst (0.01−0.03 mmol) were placed in a three-bottomed Schlenk flask under a dry nitrogen atmosphere and 2-propanol (75 mL) was added. The solution was heated at 82 °C, and the corresponding amount of base (0.08 M solution in 2-propanol) was added after 15 min. The reaction was monitored by gas chromatography using Agilent Model HP-6890 equipment. The corresponding alcohol and acetone were the only products detected in all cases. The conversions and ee values were determined by gas chromatography (GC) with a Supelco β-DEX 120 chiral capillary column.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional catalytic results using catalysts **1a**−**4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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