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Ionic Liquids as a Convenient New Medium for the Catalytic Asymmetric Dihydroxylation of Olefins Using a Recoverable and Reusable Osmium/Ligand

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The use of room-temperature ionic liquids (RTILs) in the Sharpless catalytic asymmetric dihydroxylation (AD) as a cosolvent or replacement of the *tert*-butanol was studied in detail by screening 11 different RTILs. The AD reaction is faster in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate [C_4mim][PF_6] as a cosolvent than in the conventional system of *tert*-butanol/H_2O. For the range of six substrates tested, comparable or even higher yields and enantiomeric excess (ee) were found using [C_4mim][PF_6] or 1-*n*-octyl-3-methylimidazolium hexafluorophosphate [C_8mim][PF_6] compared to the conventional solvent system. Due to high affinity of the catalytic osmium/quiral ligand system to the ionic liquid, the use of ionic liquid/water (biphasic) or ionic liquid/water/*tert*-butanol (monophasic) solvent systems provides a recoverable, reusable, robust, efficient, and simple system for the AD reaction. Using 1-hexene and [C_4mim][PF_6] as RTIL it was possible to reuse the catalytic system for 9 cycles with only a 5% of yield reduction from the first cycle, allowing an overall yield of 87%, TON = 1566, and with similar ee. Additionally, for each cycle, after extraction of the reaction mixture with diethyl ether, the osmium content in the organic phase (containing the AD product) and in the aqueous phase was in the range of the detection limit (≤3%, ≤7 ppb) and 3−6% of initial amount, respectively. In contrast, the ionic liquid phase retained more than 90% of the osmium content of the previous cycle.

Introduction

The Sharpless catalytic asymmetric dihydroxylation (AD) of olefins is a well-established and robust methodology for the synthesis of a wide range of enantiomerically pure vicinal diols.[1] However, the high cost of osmium and chiral ligands, as well as the high toxicity of osmium, which can contaminate the desired product, has made difficult the application of the AD reaction to large-scale processes.[2] To explore the possibility of the recycle and reuse of the osmium/ligand catalytic system, several approaches have been studied.[3] The early remarkable success with the immobilization of the chiral ligand onto soluble and insoluble polymers has also shown the need of long synthesis of each chiral ligand, reduction of the enantioselectivity, and uncompleted recovery and reuse of the osmium−ligand catalytic system due to the occurrence of osmium leaching.[4] On the other hand, more recently it has been demonstrated that the immobilization of the osmium catalyst by microencapsulation of OsO_4 in polystyrene,[5] polyurea,[6] and poly(ethylene glycol)[7] matrixes, on silica-anchored tetrasubstituted olefins (limited to achiral version),[8] by ion exchangers[9] or by anchoring in Amberlite[10] have allowed a recoverable and reusable system for the osmium-catalyzed AD reaction. Although recycling experiments have been successfully performed for three,[5] five,[7] and six[6] cycles, the catalyst amount used of 5 mol %[5,6] and 1 mol %[10] is higher than the amount needed for homogeneous AD reaction (0.2−

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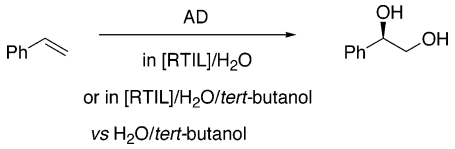
0.5 mol %),[1,11] or the addition of chiral ligand after each cycle is necessary.[7]

Room-temperature ionic liquids (RTILs),[12] especially those based on the 1,3-dialkylimidazolium cation[12,13] have been adopted as a new approach for catalyst recycling, in a broad range of catalytic reactions[14] including biocatalysis,[15] which is based on catalyst immobilization in the ionic liquid due to their higher partition into the ionic liquid phase. Additionally, the reaction product can be selectively removed from the ionic liquid phase by water or organic solvent,[16] supercritical CO_2[17] extraction, pervaporation,[18] and potentially using supported liquid membranes.[19] Very recently, has been described in two

SCHEME 1



communications the recyclable and reusable OsO_4-catalyzed olefin dihydroxylation using the cooxidant *N*-methylmorpholine oxide (NMO) in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate [C_4mim][PF_6]/water/*tert*-butanol[20] solvent system and in 1-ethyl-3-methylimidazolium tetrafluoroborate [emim][BF_4].[21] Later we[22] and Song et al.[23] reported a simple and practical approach to reuse and recycle the catalytic system of the AD reaction using the ionic liquid [C_4mim][PF_6] as a cosolvent and the cooxidants $K_3Fe(CN)_6$ and NMO, respectively. For the reuse and recycle experiments using *trans*-stilbene in a solvent system of [C_4mim][PF_6]/acetone/water (1.1:10:1 v/v/v) Song et al.[23] reported a total turnover number of 391 and 2370, respectively, using 1 mol % of OsO_4 for five cycles and 0.1 mol % of OsO_4 for three cycles. Additionally, using 1-hexene as substrate model and the solvent system of [C_4mim][PF_6]/water (1:1 v/v) and [C_4mim][PF_6]/water/*tert*-butanol (1:1:1 v/v) using 0.5 mol % of $K_2OsO_4(OH)_4$, we observed a total turnover number respectively of 1500 for 11 cycles and 1910 for 12 cycles.[22] In both solvent systems, we observed that more than 90% of the osmium of the previous cycle was retained in the ionic liquid phase, while in the organic phase containing the chiral diol product the osmium content was found in the range of detection limit ($\leq$3% or $\leq$7 ppb) for all cycles tested. Encouraged by these preliminary observations, we then performed a systematic and detailed study of the AD reaction by comparing the effect of several experimental parameters such as temperature, concentration, solvent system (ionic liquid structure), catalyst, quiral ligand, cooxidant, and substrate scope using the new RTIL/H_2O and RTIL/H_2O/*tert*-butanol with the reported optimized H_2O/*tert*-butanol solvent system.[1]

Results and Discussion

All studies performed to disclose the effect of several reaction parameters in the AD reaction were done using styrene as substrate model as presented in Scheme 1.

1. Reaction Conditions: Temperature, Catalyst, and Substrate Concentration Effect in the AD Reaction using [C_4mim][PF_6]/H_2O. In Table 1 is presented the AD reaction conditions effect on styrene in biphasic solvent system ([C_4mim][PF_6]/H_2O) using the ligand $(DHQD)_2PHAL$ and the cooxidant $K_3Fe(CN)_6$, by changing the temperature (5 °C, rt, 45, and 75 °C), catalyst type (OsO_4 or $K_2OsO_2(OH)_4$), catalytic amount

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TABLE 1. Effect of AD Reaction Conditions on Styrene in [C_4mim][PF_6]/H_2O Using $(DHQD)_2PHAL$[a]

entry	[styrene] (M)	catalyst[b] (mol %)	RTIL/H_2O	temp	yield[c] (%)	ee (%)
1	0.33	0.5	1:2	5 °C	67	63
2	0.33	0.5	1:2	rt	87	62
3	0.33	0.5	1:2	45 °C	80	68
4	0.33	0.5	1:2	75 °C	48	64
5	0.33	2.0	1:2	rt	91	67
6	0.33	5.0	1:2	rt	94	70
7	0.33	0.5	1:1	rt	84	71
8	0.67	0.5	1:1	rt	82	68
9	0.33	0.5 OsO_4	1:1	rt	84	76

[a] All reactions were carried out using styrene (0.5 or 1.0 mmol), catalyst $K_2OsO_2(OH)_4$ (0.5, 2.0 or 5.0 mol %) or OsO_4, and ligand $(DHQD)_2PHAL$ (1.0 mol %), $K_3Fe(CN)_6$ (3.0 molar equiv), K_2CO_3 (3.0 molar equiv), [C_4mim][PF_6]/H_2O (1:2, 1.5 mL or 1:1, 1.0 mL), 24 h. [b] $K_2OsO_2(OH)_4$ or OsO_4 (entry 9). [c] Isolated yields after purification by flash chromatography.

(0.5, 2.0, and 5.0 mol %), and substrate concentration (0.33 and 0.67 M).

Initially we observed that the AD reaction depends strongly on temperature used, with 20% and 39% in yield reduction relative to that at room temperature (entry 2), respectively, at lower (5 °C, entry 1) and higher (75 °C, entry 4) temperatures. The range of temperature between room temperature (25 °C) and 45 °C seems to be the best for this type of reaction (entries 2 and 3). In contrast to the considerable effect of the reaction temperature used on the yield, the observed enantiomeric excess (ee) was almost constant (65 ± 3%) for different temperatures tested (5−75 °C).

Despite the fact that the catalyst OsO_4 allows ee's better than the catalyst $K_2OsO_2(OH)_4$ (entry 9 vs entry 7) we decided to use only the catalyst $K_2OsO_2(OH)_4$ because this is a potentially less toxic catalyst as a result of being nonvolatile. The increase of the catalyst amount between 0.5 and 5 mol % provoked some increase in yield (7%) and ee (8%) performance (Table 1, entries 2, 5, and 6). However, this increase does not justify the use of a catalyst amount over 0.5 mol %.

On the other hand, the reaction concentrations tested do not have any major influence in observed yield and ee (0.33 M, 84%, ee 71% for entry 7 vs 0.67 M, 82%, ee 68% for entry 8). On the basis of the preliminary study above presented for the substrate-model styrene, we used in the following studies 0.5 mol % of $K_2OsO_2(OH)_4$ as catalyst and 0.33 M as reaction concentration, at room temperature.

2. Reaction Conditions: Solvent, Cooxidant, and Ligand Effect. In Table 2 is presented the effect of reaction conditions of AD reaction on styrene using the catalyst $K_2OsO_2(OH)_4$ and the cooxidant $K_3Fe(CN)_6$, by changing two different parameters: (1) solvent system - biphasic system RTIL/H_2O (1:1; 1:2, and 1:5 ratios) and monophasic system RTIL/H_2O/*t*-BuOH (1:1:2 and 1:2:4 ratios) in opposition to conventional system *t*-BuOH/H_2O (1:1, 1:2 and 1:5 ratios) and (2) ligand effect - $(DHQD)_2$-PHAL or $(DHQD)_2$PYR. In Chart 1 is presented the range of ionic liquids tested in the AD reaction.

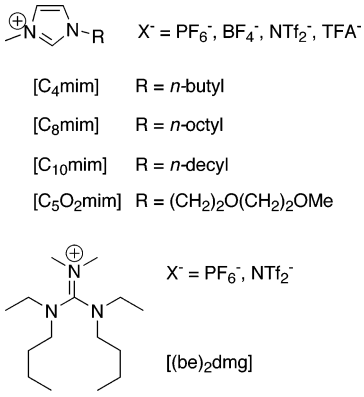
Analyzing the solvent type effect, we compared two kinds of solvent system with the conventional system *t*-BuOH/H_2O. A biphasic system RTIL/H_2O was used with 1:1 (1 mL), 1:2 (1.5 mL), and 1:5 (3 mL) solvent ratios,

TABLE 2. Effect of Solvent and Ligand Type in the AD of Styrene Using $K_2OsO_2(OH)_4/K_3Fe(CN)_6$[a]

entry	solvent system[b]	solvent ratio	ligand[c]	yield[d] (%)	ee (%)
1	[C_4mim][PF_6]/H_2O	1:1	PHAL	84	71
2	[C_4mim][PF_6]/H_2O	1:2	PHAL	86	62
3	[C_4mim][PF_6]/H_2O	1:2	PYR	86	75
4	[C_4mim][PF_6]/H_2O	1:5	PHAL	85	67
5	[C_4mim][BF_4]/H_2O	1:2	PHAL	45	71
6	[C_4mim][NTf_2]/H_2O	1:2	PHAL	67	77
7	[C_8mim][PF_6]/H_2O	1:2	PHAL	81	78
8	[C_8mim][PF_6]/H_2O	1:2	PYR	83	87
9	[C_8mim][BF_4]/H_2O	1:2	PHAL	64	79
10	[C_8mim][BF_4]/H_2O	1:2	PYR	82	88
11	[C_{10}mim][PF_6]/H_2O	1:2	PHAL	72	82
12	[C_5O_2mim][PF_6]/H_2O	1:2	PHAL	70	74
13	[C_5O_2mim][BF_4]/H_2O	1:2	PHAL	61	74
14	$[(be)_2dmg][PF_6]/H_2O$	1:2	PHAL	35	84
15	[C_4mim][PF_6]/H_2O/*t*-BuOH	1:1:2	PHAL	86	94
16	[C_4mim][PF_6]/H_2O/*t*-BuOH	1:2:4	PHAL	88	92
17	[C_4mim][PF_6]/H_2O/*t*-BuOH	1:1:2	PYR	90	90
18	[C_4mim][PF_6]/H_2O/*t*-BuOH	1:2:4	PYR	92	93
19	[C_4mim][PF_6]/H_2O/EtOH	1:1:3	PHAL	68	82
20	[C_4mim][NTf_2]/H_2O/*t*-BuOH	1:1:2	PHAL	69	99
21	[C_4mim][TFA]/H_2O/*t*-BuOH	1:2:4	PHAL	68	82
22	[C_8mim][PF_6]/H_2O/*t*-BuOH	1:1:2	PHAL	85	92
23	[C_8mim][PF_6]/H_2O/*t*-BuOH	1:1:2	PYR	87	96
24	[C_8mim][BF_4]/H_2O/*t*-BuOH	1:1:2	PHAL	71	94
25	[C_8mim][BF_4]/H_2O/*t*-BuOH	1:1:2	PYR	83	88
26	[C_{10}mim][BF_4]/H_2O/*t*-BuOH	1:1:2	PHAL	71	96
27	[C_{10}mim][BF_4]/H_2O/*t*-BuOH	1:2:4	PHAL	66	93
28	[C_{10}mim][BF_4]/H_2O/*t*-BuOH	1:1:2	PYR	79	96
29	[C_5O_2mim][PF_6]/H_2O/*t*-BuOH	1:2:4	PHAL	73	76
30	[C_5O_2mim][BF_4]/H_2O/*t*-BuOH	1:2:4	PHAL	67	77
31	$[(be)_2dmg]$ [PF_6]/H_2O/*t*-BuOH	1:2:4	PHAL	53	86
32	$[(be)_2dmg][NTf_2]/H_2O$/*t*-BuOH	1:2:4	PHAL	23	89
33	*t*-BuOH/H_2O	1:1	PHAL	90	97
34	*t*-BuOH/H_2O	1:2	PHAL	88	97
35	*t*-BuOH/H_2O	1:5	PHAL	85	91
36	*t*-BuOH/H_2O	1:1	PYR	93	95
37	*t*-BuOH/H_2O	1:2	PYR	91	93

[a] All reactions were carried out using styrene (0.5 or 1.0 mmol), catalyst $K_2OsO_2(OH)_4$ (0.5 mol %), ligand $(DHQD)_2PHAL$ or $(DHQD)_2PYR$ (1.0 mol %), $K_3Fe(CN)_6$ (3.0 molar equiv), K_2CO_3 (3.0 molar equiv), solvent, rt, 24 h. [b] RTIL/H_2O (1:1, 1 mL; 1:2, 1.5 mL, and 1:5, 3 mL); RTIL/H_2O/*t*-BuOH (1:1:2, 2 mL; 1:2:4, 3.5 mL), and *t*-BuOH/H_2O (1:1, 1 mL; 1:2, 1.5 mL, and 1:5, 3 mL). [c] PHAL or PYR refers, respectively, to $(DHQD)_2PHAL$ and $(DHQD)_2PYR$. [d] Isolated yields after purification by flash chromatography.

CHART 1. Structure of Ionic Liquids Tested in the AD Reaction



concluding that for the [C_4mim][PF_6]/H_2O system the increase in water volume (1:1 to 1:2) corresponded to a decrease in enantiomeric excess (ee) of the reaction without variation in yield observed (Table 2, entry 1 vs

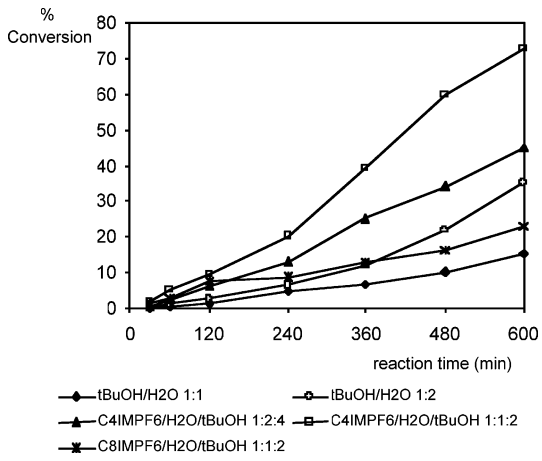


FIGURE 1. Kinetic studies of AD reaction on styrene for monophasic solvent system RTIL/H_2O/*t*-BuOH (1:1:2 and 1:2:4) and conventional solvent system *t*-BuOH/H_2O (1:1 and 1:2).

entry 2). In following studies, we choose for the biphasic system RTIL/H_2O (1:2, 1.5 mL) because this ratio better solubilizes overall reaction components. When we modified the RTIL used [C_4mim][PF_6] for [C_8mim][PF_6] this provoked an increase of 16% in ee value (62% in entry 2 vs 78% in entry 7) but with small reduction in yield value (86% entry 2 vs 81% entry 7, see also Figure 1). Of a general approach, the increase in cation chain of RTIL of *n*-butyl (C_4), *n*-octyl (C_8), and *n*-decyl (C_{10}) influenced strongly the ee value by an increase of 20% and decreased the yield by 14%. In relation to the anion effect, as can be seen in Table 2 for biphasic conditions, by changing PF_6 for BF_4 or NTf_2 resulted in higher ee values (62% for [C_4mim][PF_6], entry 2, vs 71% for [C_4mim][BF_4], entry 5, and 77% for [C_4mim][NTf_2], entry 6) but with an abrupt reduction in the yield obtained (86% for [C_4mim][PF_6], entry 2, vs 45% for [C_4mim][BF_4], entry 5, and 67% [C_4mim][NTf_2], entry 6). In the case of the monophasic system RTIL/H_2O/*t*-BuOH, by using two different solvent ratios 1:1:2 (entry 15) and 1:2:4 (entry 16), it was observed that by comparison with the conventional system *t*-BuOH/H_2O (entry 34) the introduction of *t*-BuOH in the system improved significantly the ee values (94% and 92% vs 97%) and without observed considerable variation in the yield value (86% and 88% vs 88%). This monophasic RTIL/H_2O/*t*-BuOH solvent system can be seen as an alternative to the conventional system *t*-BuOH/H_2O (1:2, entry 34) mainly for the ionic liquids [C_4mim][PF_6] (entry 15) and [C_8mim][PF_6] (entry 22).

When we studied the ligand effect using $(DHQD)_2$PHAL or $(DHQD)_2$PYR (1.0 mol %), we concluded that for the three solvent systems tested the ligand $(DHQD)_2$PYR (1.0 mol %) presented the best results of yield and with ee values considerably higher (except in the case of conventional system), with more relevance for the biphasic system RTIL/H_2O ([C_4mim][PF_6] with 62% for PHAL, entry 2 and 75% for PYR, entry 3; [C_8mim][PF_6] with 78% for PHAL, entry 7 and 87% for PYR, entry 8). In contrast, for the conventional *tert*-butanol/H_2O solvent system the PYR ligand gave slightly lower ee (2−4%) than for the PHAL ligand.

In Table 3 is presented the effect of reaction conditions of AD reaction on styrene using the catalyst $K_2OsO_2(OH)_4$ and the cooxidant NMO, by changing the two different parameters discussed above: (1) solvent system - biphasic system RTIL/H_2O (1:1 and 1:2 ratios) and monophasic system RTIL/H_2O/*t*-BuOH (1:1:2 ratio) in opposition to conventional system *t*-BuOH/H_2O (1:1 and 1:2 ratios) and (2) ligand effect - $(DHQD)_2$PHAL or $(DHQD)_2$PYR.

TABLE 3. Effect of Solvent and Ligand Type in the AD of Styrene Using $K_2OsO_2(OH)_4$/NMO[a]

entry	solvent system[b]	solvent ratio	ligand[c]	yield (%)	ee (%)
1	[C_4mim][PF_6]/H_2O	1:1	PHAL	84	75
2	[C_4mim][PF_6]/H_2O	1:2	PHAL	56 (60[d])	88 (62[e])
3	[C_4mim][PF_6]/H_2O	1:1	PYR	52	85
4	[C_4mim][PF_6]/H_2O	1:2	PYR	85	89
5	[C_8mim][PF_6]/H_2O	1:2	PHAL	86 (39[d])	94 (75[e])
6	[C_8mim][PF_6]/H_2O	1:2	PYR	39	76
7	[C_4mim][PF_6]/H_2O/*t*-BuOH	1:1:2	PHAL	89 (71[d])	85 (65[e])
8	[C_4mim][PF_6]/H_2O/*t*-BuOH	1:1:2	PYR	85	94
9	[C_8mim][PF_6]/H_2O/*t*-BuOH	1:1:2	PHAL	64 (65[d])	67 (66[e])
10	[C_8mim][PF_6]/H_2O/*t*-BuOH	1:1:2	PYR	61	74
11	*t*-BuOH/H_2O	1:1	PHAL	96 (80[d])	98 (73[e])
12	*t*-BuOH/H_2O	1:2	PHAL	88 (70[d])	91 (84[e])
13	*t*-BuOH/H_2O	1:2	PYR	87	64

[a] All reactions were carried out using a slow addition of styrene (0.5 mmol), catalyst $K_2OsO_2(OH)_4$ (0.5 mol %), ligand $(DHQD)_2$-PHAL or $(DHQD)_2$PYR (1.0 mol %), NMO (1.0 molar equiv), solvent, rt, 24 h. [b] RTIL/H_2O (1:1, 1 mL; 1:2, 1.5 mL); RTIL/H_2O/*t*-BuOH (1:1:2, 2 mL), and *t*-BuOH/H_2O (1:1, 1 mL; 1:2, 1.5 mL). [c] PHAL or PYR refers respectively to $(DHQD)_2$PHAL and $(DHQD)_2$-PYR. [d] Yields of the reactions that were carried out using styrene (0.5 mmol) without slow addition. [e] Enantiomeric excess (ee) of the reactions that were carried out using styrene (0.5 mmol) without slow addition.

The results presented in Table 3 show that the replacement of the cooxidant $K_3Fe(CN)_6$ by *N*-methylmorpholine oxide (NMO) is also feasible in the presence of ionic liquids. In general, using NMO instead of $K_3Fe(CN)_6$, higher ee values were obtained for both solvent system (monophasic and biphasic). However, the use of NMO presents the additional disadvantage of requiring a slow addition of substrate. In fact, as it was reported for conventional *tert*-butanol/H_2O solvent system, the ee is drastically lower (ca. 20%) without slow addition of the olefin (results in brackets). In the biphasic system the best results have been obtained for [C_8mim][PF_6]/H_2O 1:2 (entry 5) when compared with the conventional system *t*-BuOH/H_2O 1:2 (entry 12). In contrast, in the monophasic system the best results have corresponded to [C_4mim][PF_6]/H_2O/*t*-BuOH 1:1:2 (entry 7). The replacement of $(DHQD)_2$PHAL by $(DHQD)_2$PYR under the conventional *tert*-butanol/H_2O solvent system resulted in a considerable reduction in the ee (91% for PHAL, entry 12 vs 64% for PYR, entry 13). However, in the case of the biphasic and monophasic RTILs systems studied here, the ee value was higher for ligand $(DHQD)_2$PYR (with exception for the system [C_8mim][PF_6]/H_2O 1:2).

To disclose the effect of the replacement of the conventional *t*-BuOH/H_2O (1:1 or 1:2) solvent system by monophasic RTIL/H_2O/*t*-BuOH (1:1:2 or 1:2:4) solvent system on the rate of AD reaction, we carried out a kinetic study of AD on styrene using the catalyst $K_2OsO_2(OH)_4$, the ligand $(DHQD)_2$PHAL, and the cooxidant $K_3Fe(CN)_6$, at room temperature during the first 600 min

TABLE 4. AD of Olefins Using Ionic Liquids as Cosolvent[a]

			yield (ee)[g]					
solvent[b]	cooxidant	ligand[c]	styrene[d]	α-methyl styrene[d]	1-hexene[d]	1-methylcyclohexene[e]	*trans*-stilbene[f]	*trans*-5-decene[f]
$[C_4mim][PF_6]/H_2O$ (1:2)	$K_3Fe(CN)_6$	PHAL	87(62)	80(66)	71(90)	47**(92)**	87(98)	69(87)
		PYR	86(75)	77(71)	**96**(90)	66(86)	81(96)	52(63)
	NMO	PHAL	84(75)	53(81)	92(82)	**92**(68)	56(91)	73(60)
		PYR	85(89)					
$[C_8mim][PF_6]/H_2O$ (1:2)	$K_3Fe(CN)_6$	PHAL	78(81)	77(67)	77(80)	56**(92)**	**97**(96)	66(66)
		PYR	83(87)	76(76)	94(89)	67(86)	73(84)	65(60)
	NMO	PHAL	64(94)					
		PYR	39(76)					
$[C_4mim][PF_6]/H_2O$/*t*-BuOH (1:1:2)	$K_3Fe(CN)_6$	PHAL	86(94)	85(84)	88(89)	53(87)	92**(99)**	**96**(92)
		PYR	90(89)	**97**(80)	**96**(91)	57(83)	79(77)	92**(96)**
	NMO	PHAL	89(85)	63**(90)**	85(94)	95(88)	65**(99)**	81(78)
		PYR	85(94)					
$[C_8mim][PF_6]/H_2O$/*t*-BuOH (1:1:2)	$K_3Fe(CN)_6$	PHAL	85(92)	65(86)	89**(97)**	87(86)	81(97)	81(79)
		PYR	87**(96)**	84(80)	95(91)	89(69)	89**(96)**	74(74)
	NMO	PHAL	56(67)					
		PYR	61(74)					
t-BuOH/H_2O (1:2)	$K_3Fe(CN)_6$	PHAL	88**(97)**	83**(92)**	92(90)	**91**(87)	89(96)	94**(94)**
		PYR	**91**(93)	**95**(77)	93(94)	63(90)	**94**(87)	79(75)
	NMO	PHAL	88(91)	83(88)	81(93)	87**(99)**	75(86)	**98**(80)
		PYR	87(95)					

[a] All reactions were carried out using olefin (0.5 or 1.0 mmol), catalyst $K_2OsO_2(OH)_4$ (0.5 mol %), ligand $(DHQD)_2PHAL$ or $(DHQD)_2PYR$ (1.0 mol %), cooxidant $K_3Fe(CN)_6$ (3.0 molar equiv), K_2CO_3 (3.0 molar equiv) or NMO (1 molar equiv), solvent, rt, 24 h. [b] RTIL/H_2O (1:2 1.5 mL); RTIL/H_2O/*t*-BuOH (1:1:2, 2 mL), and *t*-BuOH/H_2O (1:2, 1.5 mL). [c] PHAL or PYR refers respectively to $(DHQD)_2PHAL$ and $(DHQD)_2PYR$. [d] Absolute configuration of the diol is (*R*). [e] Absolute configuration of the diol is (1*S*,2*R*). [f] Absolute configuration of the diol is (*R*,*R*). [g] Yield and enantiomeric excess (in brackets) of the diol) (%); in **bold** are presented the best results using RTIL and in conventional solvent systems.

(10 h) of reaction, as indicated in Figure 1. The figure clearly shows that the reaction is faster for the AD performed in the presence of the RTIL $[C_4mim][PF_6]$. In contrast, the more hydrophobic $[C_8mim][PF_6]$ gave a rate similar to that of the *t*-BuOH/H_2O conventional solvent.

3. Substrate Scope of the AD Reaction in the Presence of RTIL. For the best conditions observed for the AD reaction on styrene was carried out a study of the asymmetric dihydroxylation of different olefins. In these experiments were used the biphasic systems $[C_4mim][PF_6]/H_2O$ and $[C_8mim][PF_6]/H_2O$ (1:2) and the monophasic systems $[C_4mim][PF_6]/H_2O$/*t*-BuOH and $[C_8mim][PF_6]/H_2O$/*t*-BuOH (1:1:2) using two different cooxidants, $K_3Fe(CN)_6$ and NMO, and two ligands, $(DHQD)_2PHAL$ and $(DHQD)_2PYR$. In Table 4 are presented the results obtained for several olefins.

The experiments done using $K_3Fe(CN)_6$ and for the biphasic system RTIL/H_2O (1:2) gave yield and ee values similar to the conventional system *t*-BuOH/H_2O (1:2), in the case of 1-hexene and 1-methylcyclohexene (using ligand $(DHQD)_2PHAL$) and *trans*-stilbene (using ligand $(DHQD)_2PYR$). In case of the monophasic system RTIL/H_2O/*t*-BuOH (1:1:2) were observed higher yield and ee values for the substrates styrene, 1-hexene, *trans*-stilbene, and *trans*-5-decene (using both ligands) and α-methylstyrene (using ligand $(DHQD)_2PYR$). In the experiments with NMO as cooxidant we observed for biphasic system $[C_4mim][PF_6]/H_2O$ (1:2) yield and ee values similar to those for the conventional system *t*-BuOH/H_2O (1:2), for 1-hexene (using ligand $(DHQD)_2PHAL$). While for the monophasic system $[C_4mim][PF_6]/H_2O$/*t*-BuOH (1:1:2) we observed similar yield and ee values, in the case of styrene (using ligand $(DHQD)_2PYR$) and methylcyclohexene (using ligand $(DHQD)_2PHAL$), yield and ee values were higher in the case of substrates 1-hexene and *trans*-stilbene (using ligand $(DHQD)_2PHAL$). In Table 4 is presented in bold the best results obtained for each substrate using RTIL and conventional *t*-BuOH/H_2O solvent systems. The comparison has clearly shown that for the substrates tested was obtained a similar, or even better, yield and ee than in case of conventional *t*-BuOH/H_2O (1:2) solvent system.

4. Recycling and Reuse of the Catalyst. The results presented above demonstrate that the AD reaction works well in the presence of ionic liquids, namely, $[C_4mim][PF_6]$ and $[C_8mim][PF_6]$, using monophasic or biphasic solvent systems. The observation that the Os/ligand catalytic system is soluble in the ionic liquid allowed us to explore the possibility to reuse the catalytic system and to reduce the osmium contamination in the reaction products by careful extraction of the reaction media using an appropriate solvent. In extension of our preliminary results,[22] we performed a detailed study of catalyst reuse by using $[C_4mim][PF_6]$ and $[C_8mim][PF_6]$ as ionic liquids (3 mL) in two solvent systems: biphasic RTIL/H_2O and monophasic RTIL/H_2O/*tert*-butanol. In all reuse experiments 1-hexene was used as a substrate model and $(DHQD)_2PHAL$ as chiral ligand. After each reaction cycle of 24 h, organic solvent was added, and the aqueous and the organic layers were removed, followed by the addition to the remaining RTIL phase of additional 1-hexene and aqueous solution containing $K_3Fe(CN)_6$ and K_2CO_3 or NMO as cooxidants. For each solvent system presented in Tables 5−7, two parallel experiments were necessary. One experiment was used to determine the isolated yield and the ee. The other parallel experiment was used for osmium content determination (relative to initial amount) in the aqueous, organic, and ionic liquid phases. In the case of osmium determination in the RTIL phase, 50 μL of ionic liquid, for each cycle, was taken before the addition of reagents to next cycle. As a result of this, the ionic liquid phase became smaller than in the case of the

TABLE 5. Effect of Organic Extraction Solvent (Diethyl Ether, *tert*-Butyl Methyl Ether (TBME) and Hexane) on Reuse of Catalyst for the AD of 1-Hexene in [C_4mim][PF_6]/H_2O (1:1) Solvent System Using $K_2OsO_2(OH)_4$/$(DHQD)_2PHAL$ as Catalyst and $K_3Fe(CN)_6$ as Cooxidant[a]

run	yield (%) Et_2O/TBME/hexane[c]	ee (%) Et_2O/TBME/hexane[c]	Os in H_2O (%)[b] Et_2O/TBME/hexane[c]	Os in RTIL (%)[b] Et_2O/TBME/hexane[c]
1	78/80/79	88/84/82	14/21/18	91/98/92
2	74/78/77	85/81/81	4/5/11	88/90/82
3	76/81/61	81/80/75	3/3/4	88/88/64
4	72/74/56	84/81/69	3/2/3	93/90/54
5	71/77/43	87/82/64	3/2/2	90/84/35
6	74/72/20[d]	83/76/37	4/2/2	69/74/32

[a] All reactions were carried out using 1-hexene (0.5 mmol), $K_2OsO_2(OH)_4$ (0.5 mol %), $(DHQD)_2PHAL$, 1.0 mol %), $K_3Fe(CN)_6$ (3.0 molar equiv), K_2CO_3 (3.0 molar equiv), [C_4mim][PF_6]/H_2O (1:1, 6 mL), rt, 24 h followed by extraction with the appropriate organic solvent, removal of both phases, and reload with 1-hexene, water (3 mL), cooxidant, and K_2CO_3. [b] Percentage of osmium relative to initial amount detected by ICP in the aqueous and in the RTIL phases; for the organic phases no osmium was detected for all cycles, error of the ICP method was ±3%. [c] Results obtained by extraction of each separate reaction with diethyl ether (see also Table 6 for complete set of experiments), *tert*-butyl methyl ether (TBME), and hexane. [d] After extraction with hexane, the remaining ionic liquid phase was extracted with TBME to give more diol (0.42 mmol, 83%).

TABLE 6. Reuse of Catalyst for the AD of 1-Hexene in RTIL/H_2O (1:1) Solvent System Using $K_2OsO_2(OH)_4$/$(DHQD)_2PHAL$ as Catalyst and $K_3Fe(CN)_6$ or NMO (in Brackets) as Cooxidants[a]

	[C_4mim][PF_6]/H_2O				[C_8mim][PF_6]/H_2O			
run	yield (%)	ee (%)	Os in H_2O (%)[b]	Os in RTIL (%)[b]	yield (%)	ee (%)	Os in H_2O (%)[b]	Os in RTIL (%)[b]
1	78 (86)	88 (93)	14 (4)	91 (99)	74	82	23	84
2	74 (82)	85 (96)	4 (2)	88 (96)	70	74	5	86
3	76 (81)	81 (92)	3 (2)	88 (96)	72	78	2	78
4	72 (83	84 (95)	3 (2)	93 (93)	68	75	3	83
5	71 (74)	87 (90)	3 (2)	90 (87)	59	73	3	85
6	74 (72)	83 (88)	4 (1)	69 (85)	52	70	4	63
7	75 (65)	86 (86)	3 (1)	57 (73)	48	68	2	45
8	77 (58)	85 (76)	3 (2)	51 (63)	45	60	2	41
9	70 (50)	83 (70)	3 (1)	46 (57)	39	41	3	16
10	59 (87[c])	71 (91)	3 (4)	44 (99)	16	27	3	19
11	24 (84)	61 (95)	4 (2)	44 (98)	3	15	3	11
12	73[c] (80)	87 (92)	19 (2)	87 (94)	81[c]	79	19	89
13	75[d] (81)	84[d] (93)	5 (1)	83 (90)	72	77	7	80

[a] All reactions were carried out using 1-hexene (0.5 mmol), $K_2OsO_2(OH)_4$ (0.5 mol %), $(DHQD)_2PHAL$, 1.0 mol %), $K_3Fe(CN)_6$ (3.0 molar equiv), K_2CO_3 (3.0 molar equiv) or NMO (1.0 molar equiv, in brackets), RTIL/H_2O (1:1, 6 mL), rt, 24 h followed by extraction with diethyl ether, removal of both phases, and reload with 1-hexene, water (3 mL), cooxidant, and K_2CO_3. [b] Percentage of osmium relative to initial amount detected by ICP in the aqueous and in the RTIL phases; for the ethereal phases no osmium was detected for all cycles, error of the ICP method was ±3%. [c] New addition of $K_2OsO_2(OH)_4$ (0.5 mol %) and $(DHQD)_2PHAL$ (1.0 mol %). [d] More cycles were performed (ee in brackets): run 14, 74% (84%); run 15, 71% (85%); run 16, 72% (82%).

other parallel experiment. The reuse experiments were repeated until lower diol yield was observed. Then more $K_2OsO_2(OH)_4$ and $(DHQD)_2PHAL$ were added to the next cycle and high yield and enantioselectivity were again restored. In Table 5 is presented a comparison of reuse of the catalytic system for six cycles using three different organic solvents for the extraction procedures, namely, diethyl ether (see also Table 6 for the remaining cycles), *tert*-butyl-methyl ether (TBME), and hexane. The results presented show that the reuse of the catalytic system is possible using diethyl ether or TBME, both giving similar yields and ee. In contrast, hexane is not appropriate because of lower overall yield (total of six cycles, 74% for Et_2O and 77% for TBME vs 70% for hexane), higher erosion of ee (6 run, 83% for Et_2O and 76% for TBME vs 37% for hexane), and less efficient extraction of the product from the ionic liquid (83% more diol was obtained by further extraction of the [C_4mim][PF_6] phase with TBME after the last run). Additionally, less osmium was retained in the ionic liquid phase (6 run, 69% for Et_2O and 74% for TBME vs 32% for hexane). The reduction of the RTIL phase as a result of some solubility of the ionic liquid in the aqueous and organic phases is also an important issue. After six cycles was observed a volume reduction of the [C_4mim][PF_6] phase of 16%, 48%, and 13%, respectively, for diethyl ether, TBME, and hexane. From these comparisons it was concluded that diethyl ether was the more appropriate solvent for the next reuse experiments.

In Tables 6 and 7 are presented the maximum cycles performed for each solvent system. For the last cycle tested of each reuse experiment, the recovered ionic liquid had spectroscopic data (^1H, and ^{13}C) identical to that of the initial RTIL stock sample (see Supporting Information). These results demonstrate that the ionic liquid is an efficient and stable reaction cosolvent for the AD reaction. The results presented in Table 6 (biphasic) and in Table 7 (monophasic) clearly show that the reuse of catalytic system is more advantageous for the ionic liquid [C_4mim][PF_6] than for [C_8mim][PF_6]. In fact, for [C_4mim]-[PF_6] using biphasic and monophasic systems, the yield and ee were permanently high until 9 and 10 cycles, respectively (biphasic, run 1, 78%, ee 88%; run 9, 70%, ee 83%; monophasic, run 1, 88%, ee 90%; run 10, 77%, ee 82%). In clear contrast, for the ionic liquid [C_8mim]-[PF_6] a considerable drop in the yield and ee was observed after the 7th and 5th cycles, respectively, for biphasic and monophasic systems (biphasic, run 1, 74%, ee 82%; run 7, 48%, ee 68%; monophasic, run 1, 88%, ee 93%; run 5, 766%, ee 85%). These considerable differences between

TABLE 7. Reuse of Catalyst for the AD of 1-Hexene in RTIL/H_2O/*t*-BuOH (1:1:2) Solvent System Using $K_2OsO_2(OH)_4$/$(DHQD)_2PHAL$ as Catalyst and $K_3Fe(CN)_6$ or NMO (in Brackets) as Cooxidants[a]

	[C_4mim][PF_6]/H_2O/*t*-BuOH				[C_8mim][PF_6]/H_2O/*t*-BuOH			
run	yield (%)	ee (%)	Os in H_2O (%)[b]	Os in RTIL (%)[b]	yield (%)	ee (%)	Os in H_2O (%)[b]	Os in RTIL (%)[b]
1	88 (95)	90 (85)	6 (5)	98 (99)	88	93	5	98
2	90 (90)	85 (87)	6 (3)	97 (95)	82	91	4	97
3	91 (85)	87 (83)	4 (2)	93 (96)	80	96	4	84
4	85 (82)	83 (84)	4 (2)	93 (95)	79	90	3	53
5	84 (79)	88 (78)	3 (2)	90 (93)	66	85	3	41
6	87 (74)	84 (75)	3 (1)	84 (90)	55	83	4	38
7	89 (68)	91 (76)	3 (1)	82 (88)	38	59	3	24
8	86 (63)	92 (72)	3 (1)	71 (83)	12	33	2	15
9	83 (60)	89 (71)	4 (1)	61 (72)	86[c]	96	8	91
10	77 (94[c])	82 (86)	4 (5)	55 (99)	85	95	4	92
11	63 (92)	75 (83)	4 (4)	56 (95)	79	91	2	76
12	32 (89)	64 (81)	4 (2)	47 (96)	74	87	1	69
13	85[c,d] (85)	86[d] (81)	8 (2)	96 (91)	62	78	1	64

[a] All reactions were carried out using 1-hexene (0.5 mmol), $K_2OsO_2(OH)_4$ (0.5 mol %), $(DHQD)_2PHAL$, (1.0 mol %), $K_3Fe(CN)_6$ (3.0 molar equiv), K_2CO_3 (3.0 molar equiv) or NMO (1 molar equiv in brackets), RTIL/H_2O/*t*-BuOH (1:1:2, 7.5 mL), rt, 24 h followed by extraction with diethyl ether, removal of both phases, and reload with 1-hexene, water (3 mL), cooxidant, and K_2CO_3. [b] Percentage of osmium relative to initial amount detected by ICP in the aqueous and in the RTIL phases; for the ethereal phases no osmium was detected for all cycles, error of the ICP method was ±3%. [c] New addition of $K_2OsO_2(OH)_4$ (0.5 mol %) and $(DHQD)_2PHAL$, (1.0 mol %). [d] More cycles were performed (ee in brackets): run 14, 88% (89%); run 15, 89% (85%); run 16, 87% (90%).

both ionic liquids are due to the occurrence of higher solubility for the ethereal phase of [C_8mim][PF_6] compared to that of [C_4mim][PF_6], implying more leaching of the catalytic system. This justification is also based on two additional observations. The first one is due to the occurrence of a volume reduction in the ionic liquid [C_4mim][PF_6] phase after the overall 13 cycles, which were 35% and 28%, respectively, for biphasic and monophasic and for [C_8mim][PF_6] were 51% and 43%, respectively, for biphasic and monophasic. The second observation is related to the Os measured in the RTIL phase, which has been seen from Tables 6 and 7 as decreasing faster for [C_8mim][PF_6] than for [C_4mim][PF_6] (biphasic, run 11, 44% for [C_4mim][PF_6] vs 11% for [C_8mim][PF_6]; monophasic run 8, 71% for [C_4mim][PF_6] vs 15% for [C_8mim][PF_6]). The product reaction contamination by osmium is an important issue in the AD reaction. In this context, for all of the cycles performed by us, the osmium content in the crude ethereal phase has been found to be in the detection limit range of the method used (≤3% or ≤7 ppb by ICP). It is also noteworthy that for the RTIL [C_4mim][PF_6], the ionic liquid phase retains more than 90 % of the osmium of the previous cycle. Additionally, the osmium content in the aqueous phase is lower than 6 %. The only exception was in each first run after osmium/chiral ligand addition, with higher leaching (≤19%) observed, which is probably due to preferential partition into the aqueous phase of the free osmium. To check this possibility we measured the osmium content for AD reaction on 1-hexene in the case of [C_4mim][PF_6]/H_2O (1:2) biphasic system using 0.5 mol % of $K_2OsO_2(OH)_4$ and changing the equivalents of the ligand $(DHQD)_2PHAL$ to 0.5, 1.0, and 1.5 under the previous standard conditions. Under these conditions were obtained the following osmium contents according to the amount of chiral ligand present: 0.5 equiv, Os in water 20%, osmium in the RTIL 79%; 1.0 equiv, Os in water 14%, osmium in the RTIL 92%; 1.5 equiv, Os in water 9%, osmium in the RTIL 97%. The observed leaching of osmium is clearly dependent on chiral ligand amount, which is consistent with the presence in the reaction of some noncomplexed osmium/ligand, which is expected to be less hydrophobic and in consequence more soluble in the aqueous phase. In clear contrast to the observed osmium content in the aqueous and organic phases using the RTIL [C_4mim][PF_6] as a cosolvent, by performing the AD reaction on 1-hexene using the conventional solvent system of H_2O/*tert*-butanol, followed by partion between the aqueous and the ethereal phase, the osmium content in each phase was 96% and 6%, respectively. Because of the peculiar property of higher affinity of the catalytic osmium/chiral ligand system to the ionic liquid, it was possible to perform the AD reaction in high yield and ee and for a remarkable number of runs as well with a high overall TON number (biphasic, run 1, 78%, ee 88%; run 9, 70%, ee 83%, TON (runs 1−9) = 1334; monophasic, run 1, 88%, ee 90%; run 10, 77%, ee 82%, TON (runs 1−10) = 1720). The reuse of the catalytic system immobilized in the RTIL is also feasible using the cooxidant NMO (Tables 6 and 7, results in brackets) instead of $K_3Fe(CN)_6$. However, for both solvent system used, less efficient cycles were achieved for the same catalyst.

Conclusions

The systematic study presented here on the use of ionic liquids as a cosolvent in the AD reaction clearly demonstrates that among the range of ionic liquids tested, [C_4mim][PF_6] and [C_8mim][PF_6] allow yields and enantioselectivities comparable or higher than those of the conventional H_2O/*tert*-butanol solvent system for a representative range of substrates tested. More important is that as a result of high affinity of the catalytic system for the ionic liquid phase, the presence of ionic liquid in the reaction mixture allows a simple, robust, efficient, and unique system for the reuse of the catalyst where remarkably low contamination of the product by osmium occurred.

Experimental Section

General Procedure for the Asymmetric Dihydroxylation (AD) in Biphasic System (RTIL/H_2O), using $K_3Fe(CN)_6$ as Cooxidant. A 10 mL flask was charged with

$K_3[Fe(CN)_6]$ (495 mg; 1.5 mmol); K_2CO_3 (210 mg; 1.5 mmol); water (1, 2, or 5 mL) ,and ionic liquid (1 mL), and under stirring were added the ligand [$(DHQD)_2PHAL$ or $(DHQD)_2PYR$ (1 mol %)] and the catalyst $K_2OsO_2(OH)_4$ (0.5 mol %), resulting in the formation of two phases. Then, different olefins (0.5 mmol) were added to the two-phase system and the reaction mixture stirred at room temperature for 24 h (for other conditions see Tables 1 and 2). The reaction mixture was extracted with dichloromethane (3 × 25 mL), and the resulting solution was dried ($MgSO_4$), evaporated in vacuo, and purified by TLC or flash chromatography.

General procedure for the AD in Monophasic System (RTIL/H_2O/*t*-BuOH), using $K_3Fe(CN)_6$ as Cooxidant. A 10 mL flask was charged with $K_3[Fe(CN)_6]$ (495 mg; 1.5 mmol), K_2CO_3 (210 mg; 1.5 mmol), water (1 or 2 mL), ionic liquid (1 mL), and *tert*-butyl alcohol (2 or 4 mL), and under stirring were added the ligand [(1 mol %) $(DHQD)_2PHAL$ or $(DHQD)_2PYR$] and the catalyst $K_2OsO_2(OH)_4$ (0.5 mol %). Different olefins (0.5 mmol) were then added to the homogeneous mixture, and the reaction mixture was stirred at room temperature for 24 h. (For other conditions see Table 2). The reaction mixture was extracted with dichloromethane (3 × 25 mL), and the resulting solution was dried ($MgSO_4$), evaporated in vacuo, and purified by TLC or flash chromatography as described before.

General Procedure for the Asymmetric Dihydroxylation (AD) in Ionic Liquids [C_4mim][PF_6]/H_2O and [C_8mim][PF_6]/H_2O systems, using NMO as Cooxidant. A 10 mL flask was charged with NMO (100 mg; 0.5 mmol), water (2 mL), and 1-*n*-butyl-3-methylimidazolium hexafluorophosphate [C_4mim][PF_6] or 1-*n*-octyl-3-methylimidazolium hexafluorophosphate [C_8mim][PF_6] (1 mL), and under stirring were added the ligand [$(DHQD)_2PHAL$ or $(DHQD)_2PYR$ (1 mol %)] and the catalyst $K_2OsO_2(OH)_4$ (0.5 mol %), resulting in the formation of two phases. Then, different olefins (0.5 mmol) were added slowly to the two-phase system, and the reaction mixture was stirred at room temperature for 24 h (for other conditions see Table 3). The reaction mixture was extracted with dichloromethane (3 × 25 mL), and the resulting solution was dried ($MgSO_4$), evaporated in vacuo, and purified by TLC or flash chromatography.

General Procedure for the AD in Ionic Liquids [C_4mim][PF_6]/H_2O/*t*-BuOH and [C_8mim][PF_6]/H_2O/*t*-BuOH systems, using NMO as Cooxidant. A 10 mL flask was charged with NMO (100 mg; 0.5 mmol), water (1 mL), 1-*n*-butyl-3-methylimidazolium hexafluorophosphate [C_4mim][PF_6] or 1-*n*-octyl-3- methylimidazolium hexafluorophosphate [C_8mim][PF_6] (1 mL), and *tert*-butyl alcohol (2 mL), and under stirring were added the ligand [(1 mol %) $(DHQD)_2PHAL$ or $(DHQD)_2PYR$] and the catalyst $K_2OsO_2(OH)_4$ (0.5 mol %). Different olefins (0.5 mmol) were then added slowly to the homogeneous mixture, and the reaction mixture was stirred at room temperature for 24 h (for other conditions see Table 3). The reaction mixture was extracted with dichloromethane (3 × 25 mL), and the resulting solution was dried ($MgSO_4$), evaporated in vacuo, and purified by TLC or flash chromatography as described before.

General Procedure for the Reaction Rate Profile of the AD Reaction during the First 10 h. The conversions for the solvent systems RTIL/H_2O/*t*-BuOH (1:1:2 and 1:2:4) and *t*-BuOH/H_2O (1:1 and 1:2) were obtained by performing the AD reaction on styrene (57 μL) following each general procedure described above. The course of the reaction was followed by GLC by taking 50 μL samples of the reaction media at determined time intervals (30, 60, 120, 240, 360, 480, and 600 min) and extraction of the product with diethyl ether (2 × 1 mL), followed by injection into a gas chromatograph [carrier gas flow 0.9 mL/min, *T*(oven) = 140 °C; *T*(injector) = 270 °C; *T*(detector) = 270 °C]: t_R = 25.2 min (minor); t_R = 26.3 min (major)]. The conversion of the reaction for each sample was determined by comparing the peak areas of the diol (*(R)*-1-phenyl-1,2-ethanediol) with dodecane as external standard.

Description of Procedure for Several Olefins using the Best Ionic Liquids Conditions of the AD Reaction. (Best results of yield and ee presented in bold; see Table 4). *(R)*-1-Phenyl-1,2-ethanediol. $K_3[Fe(CN)_6]$ (495 mg), K_2CO_3 (210 mg), $(DHQD)_2PYR$ (4.5 mg), $K_2OsO_2(OH)_4$ (1 mg), and styrene (57 μL) in ionic liquid [C_4mim][PF_6]/water/*t*-BuOH 1:1:2 (4 mL) were stirred for 24 h. Purification by flash chromatography using diethyl ether gave *(R)*-1-phenyl-1,2-ethanediol as a white solid (62.2 mg, 90%; 60.1 mg, 87% in the case of [C_8mim][PF_6]/water/*t*-BuOH system).The enantiomeric excess (ee) was determined by GC analysis [carrier gas flow 0.9 mL/min, *T*(oven) = 140 °C; *T*(injector) = 270 °C; *T*(detector) = 270 °C]: t_R = 25.2 min (minor); t_R = 26.3 min (major); spectral data are identical to those of an authentic sample and to those previously reported.[5b]

***(R)*-2-Phenyl-1,2-propanediol.** $K_3[Fe(CN)_6]$ (495 mg), K_2CO_3 (210 mg), $(DHQD)_2PYR$ (4.5 mg), $K_2OsO_2(OH)_4$ (1 mg), and α-methylstyrene (65 μL) in ionic liquid [C4mim][PF_6]/water/*t*-BuOH 1:1:2 (4 mL) were stirred for 24 h. Purification by flash chromatography using diethyl ether gave *(R)*-2-phenyl-1,2-propanediol as a white solid (73.8 mg, 97%). The enantiomeric excess (ee) was determined by HPLC analysis [eluent hexane/*i*-PrOH 99.5:0.5; flow rate 1.2 mL/min]: t_R = 7.0 min (minor); t_R = 7.8 min (major); spectral data are identical to those of an authentic sample and to those previously reported.[5b]

***(R)*-1,2-Hexanediol.** $K_3[Fe(CN)_6]$ (495 mg), K_2CO_3 (210 mg), $(DHQD)_2PYR$ (4.5 mg), $K_2OsO_2(OH)_4$ (1 mg), and 1-hexene (63 μL) in ionic liquid [C_4mim][PF_6]/water/*tert*-butyl alcohol 1:1:2 (4 mL) were stirred for 24 h. Purification by flash chromatography using diethyl ether gave *(R)*-1,2-hexanediol as a colorless oil (56.7 mg, 96%). The enantiomeric excess (ee) was determined by GC analysis [carrier gas flow 0.9 mL/min, *T*(oven) = 102 °C; *T*(injector) = 270 °C; *T*(detector) = 270 °C]: t_R = 25.4 min (minor); t_R = 27.1 min (major); spectral data are identical to those of an authentic sample and to those previously reported.[5b]

(1*S*,2*R*)-1-Methyl-1,2-cyclohexanediol. NMO (100 mg), $(DHQD)_2PHAL$ (4 mg), $K_2OsO_2(OH)_4$ (1 mg), and 1-methylcyclohexene (60 μL) in ionic liquid [C_4mim][PF_6]/water/*tert*-butyl alcohol 1:1:2 (4 mL) were stirred for 24 h. Purification by flash chromatography using diethyl ether gave (1*S*,2R)-1-methyl-1,2-cyclohexanediol as a white solid (61.9 mg, 95%). The enantiomeric excess (ee) was determined by GC analysis [carrier gas flow 0.9 mL/min, *T*(oven) = 115 °C; *T*(injector) = 270 °C; *T*(detector) = 270 °C]: t_R = 16.0 min (minor); t_R = 16.8 min (major); spectral data are identical to those of an authentic sample.

(*R*,*R*)-1,2-Diphenyl-1,2-ethanediol. $K_3[Fe(CN)_6]$ (495 mg), K_2CO_3 (210 mg), $(DHQD)_2PHAL$ (4 mg), $K_2OsO_2(OH)_4$ (1 mg) and *trans*-stilbene (90.2 mg) in ionic liquid [C_8mim][PF_6]/water 1:2 (3 mL) were stirred for 24 h. Purification by flash chromatography using diethyl ether gave (*R*,*R*)-1,2-diphenyl-1,2-ethanediol as a colorless oil (104 mg, 97%). The enantiomeric excess (ee) was determined by HPLC analysis [eluent hexane/*i*-PrOH 95:5; flow rate 1.0 mL/min]: t_R = 29.6 min (minor); t_R = 31.1 min (major); spectral data are identical to those of an authentic sample and to those previously reported.[20]

(*R*,*R*)-5,6-Decanediol. $K_3[Fe(CN)_6]$ (495 mg), K_2CO_3 (210 mg), $(DHQD)_2PHAL$ (4 mg), $K_2OsO_2(OH)_4$ (1 mg), and *trans*-5-decene (95 μL) in ionic liquid [C_4mim][PF_6]/water/*tert*-butyl alcohol 1:1:2 (4 mL) were stirred for 24 h. Purification by flash chromatography using diethyl ether gave (*R*,*R*)-5,6-decanediol as a white solid (80.3 mg, 92%; 83.8 mg, 96% in the case of $(DHQD)_2PYR$)). The enantiomeric excess (ee) was determined by GC analysis [carrier gas flow 0.9 mL/min, *T*(oven) = 105 °C; *T*(injector) = 270 °C; *T*(detector) = 270 °C]: t_R = 8.1 min (minor); t_R = 9.8 min (major); spectral data are identical to those of an authentic sample and to those previously reported.[5b]

General Procedure for the Recycling and Reuse of Os−Ionic Liquids in [C_4mim][PF_6]/H_2O and [C_8mim]-

[PF_6]/H_2O Systems, using $K_3Fe(CN)_6$ as Cooxidant. A 10 mL flask was charged with $K_3[Fe(CN)_6]$ (495 mg; 1.5 mmol), K_2CO_3 (210 mg; 1.5 mmol), water (3 mL), 1-*n*-butyl-3-methylimidazolium hexafluorophosphate [C_4mim][PF_6], or 1-*n*-octyl-3- methylimidazolium hexafluorophosphate [C_8mim][PF_6] (3 mL), and under stirring were added the ligand [$(DHQD)_2PHAL$] (4 mg; 1 mol %) and the catalyst $K_2OsO_2(OH)_4$ (1.0 ± 0.1 mg; 0.5 mol %). 1-Hexene (63 μL) was then added, and the resulting mixture stirred for 24 h at room temperature. The aqueous phase was then removed, and the osmium content was determined by ICP analysis. The ionic liquid phase was extracted with diethyl ether (1 × 7 mL), and the ethereal layer was dried ($MgSO_4$), evaporated in vacuo, and purified by flash chromatography using diethyl ether. Then, more 1-hexene (63 μL), $K_3[Fe(CN)_6]$ (495 mg; 1.5 mmol); K_2CO_3 (210 mg; 1.5 mmol), and water (3 mL) were added to the recycled [C_4mim][PF_6] and the cycle was repeated. The obtained yield and ee are presented in Table 2. In case of entry 12 a new portion of catalyst (0.5 mol %) and ligand (1.0 mol %) was added into the ionic reaction mixture. The other parallel experiment was performed as described before and used for the determination of the osmium content (in relation to initial amount) in the aqueous, ethereal, and ionic liquid phases. In the case of the ionic liquid phase, 50 μL of the [C_4mim][PF_6] or [C_8mim][PF_6] was taken before the addition of the reagents to the next cycle.

General Procedure For the recycling and Reuse of Os−Ionic Liquid in [C_4mim][PF_6]/H_2O using NMO as Cooxidant. A 10 mL flask was charged with NMO (100 mg; 0.5 mmol), water (3 mL), and 1-*n*-butyl-3-methylimidazolium hexafluorophosphate [C_4mim][PF_6] (3 mL), and under stirring were added the ligand [$(DHQD)_2PHAL$] (4 mg; 1 mol %) and the catalyst $K_2OsO_2(OH)_4$ (1.0 ± 0.1 mg; 0.5 mol %). 1-Hexene (63 μL) was then added slowly to the resulting mixture, which was stirred for 24 h at room temperature. The aqueous phase was then removed, and the osmium content was determined by ICP analysis. The ionic liquid phase was extracted with diethyl ether (1 × 7 mL), and the ethereal layer was dried ($MgSO_4$), evaporated in vacuo, and purified by flash chromatography using diethyl ether. Then, more 1-hexene (63 μL), NMO (100 mg; 0.5 mmol), and water (3 mL) were added to the recycled [C_4mim][PF6] and the cycle was repeated. The obtained yield and ee are presented in Table 6. In case of entry 10 a new portion of catalyst (0.5 mol %) and ligand (1.0 mol %) was added into the ionic reaction mixture. The other parallel experiment was performed as described before and used for the determination of the osmium content (in relation to initial amount) in the aqueous, ethereal, and ionic liquid phases. In the case of the ionic liquid phase, 50 μL of the [C_4mim][PF_6] was taken before the addition of the reagents to the next cycle.

General Procedure for the Recycling and Reuse of Os−Ionic Liquids in [C_4mim][PF_6]/H_2O/*t*-BuOH and [C_8mim][PF_6]/H_2O/*t*-BuOH Systems, using $K_3Fe(CN)_6$ as Cooxidant. A 10 mL flask was charged with $K_3[Fe(CN)_6]$ (495 mg; 1.5 mmol), K_2CO_3 (210 mg; 1.5 mmol), water (2.5 mL), *tert*-butanol (2.5 mL), and 1-*n*-butyl-3-methylimidazolium hexafluorophosphate [C_4mim][PF_6] (2.5 mL) or 1-*n*-octyl-3-methylimidazolium hexafluorophosphate [C_8mim][PF_6], and under stirring were added the ligand [$(DHQD)_2PHAL$] (4 mg; 1 mol %) and the catalyst $K_2OsO_2(OH)_4$ (1.0 ± 0.1 mg; 0.5 mol %). 1-Hexene (63 μL) was then added, and the resulting mixture was stirred for 24 h at room temperature. Water (2 mL) was added, and the aqueous phase was removed and the osmium content was determined by ICP analysis. The remaining phase was extracted with diethyl ether (1 × 7 mL), and the ethereal layer was dried ($MgSO_4$), evaporated in vacuo, and purified by flash chromatography using diethyl ether. Then, more 1-hexene (63 μL), $K_3[Fe(CN)_6]$ (495 mg; 1.5 mmol), K_2CO_3 (210 mg; 1.5 mmol), water (2.5 mL), and *tert*-butyl alcohol (5 mL) were added to the recycled [C_4mim][PF_6], and the cycle was repeated. The obtained yields and ee are presented in Table 6. In case of entries 13 ([C_4mim][PF_6]) and 9 ([C_8mim][PF_6]) a new portion of catalyst (0.5 mol %) and ligand (1.0 mol %) was added into the ionic reaction mixture. The other parallel experiment was performed as described before and used for the determination of the osmium content (in relation to initial amount) in the aqueous, ethereal, and ionic liquid phases. In the case of the ionic liquid phase 50 μL of the [C_4mim][PF_6] or [C_8mim][PF_6] was taken before the addition of the reagents to the next cycle.

General Procedure for the Recycling and Reuse of Os−Ionic Liquid in [C_4mim][PF_6]/H_2O/*t*-BuOH System, using NMO as Cooxidant. A 10 mL flask was charged with NMO (100 mg; 0.5 mmol), water (2.5 mL), *tert*-butanol (2.5 mL), and 1-*n*-butyl-3-methylimidazolium hexafluorophosphate [C_4mim][PF_6] (2.5 mL), and under stirring were added the ligand [$(DHQD)_2PHAL$] (4 mg; 1 mol %) and the catalyst $K_2OsO_2(OH)_4$ (1.0 ± 0.1 mg; 0.5 mol %). 1-Hexene (63 μL) was then added, and the resulting mixture was stirred for 24 h at room temperature. Water (2 mL) was added, the aqueous phase was removed, and the osmium content was determined by ICP analysis. The remaining phase was extracted with diethyl ether (1 × 7 mL,) and the ethereal layer was dried ($MgSO_4$), evaporated in vacuo, and purified by flash chromatography using diethyl ether. Then, more 1-hexene (63 μL), NMO(100 mg; 0.5 mmol), water (2.5 mL), and *tert*-butyl alcohol (5 mL) were added to the recycled [C_4mim][PF_6], and the cycle was repeated. The obtained yields and ee are presented in Table 6. In the case of entry 10 a new portion of catalyst (0.5 mol %) and ligand (1.0 mol %) was added into the ionic reaction mixture. The other parallel experiment was performed as described before and used for the determination of the osmium content (in relation to initial amount) in the aqueous, ethereal, and ionic liquid phases. In the case of the ionic liquid phase 50 μL of the [C_4mim][PF_6] was taken before the addition of the reagents to the next cycle.

General Procedure for the Determination of Os in Each Phase of the Recycling and Reuse Experiments. For the determination of the osmium content, an initial aqueous solution of osmium (100 ppm) was prepared, using $K_2OsO_2(OH)_4$ as the Os source. Then, different solutions were prepared: 40, 20, 10, 5, 2, 1, and 0.4 ppm, which were used to obtain a calibration curve. The observed detection limit was 1 ppb, which corresponds to 7 ppb for each original phase. After each recycling experiment, the aqueous phase (3 or 2.5 mL) was removed and diluted in 100 mL of distilled water. Each ethereal layer was evaporated in vacuo, and the residue was diluted in 50 mL of distilled water (containing 2% of methanol). For each recycling experiment 50 μL of the ionic liquid was taken and diluted in 50 or 25 mL of distilled water (containing 2% methanol). The aqueous, organic, and ionic liquid phases prepared were analyzed by inductively coupled plasma spectroscopy (ICP) for osmium content (λ = 228.226 nm), using the calibration curve described above.

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Supporting Information Available: General experimental information and spectral data of initial and reused room temperature ionic liquids. This material is available free of charge via the Internet at http://pubs.acs.org.

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