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Organopalladium complex promoted asymmetric synthesis of a P-chiral phosphanorbornene in ionic liquids and in organic solvents

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Abstract

The organopalladium(II) complex containing the (*S*)-form of *ortho*-palladated (1-(dimethylamino)ethyl)naphthylalene has been successfully utilised as a chiral template to promote the asymmetric *endo*-cycloaddition reaction between coordinated 3,4-dimethyl-1-phenylphosphole and acrolein. The rate of this chiral template promoted reaction is dramatically affected by the solvent and temperature. In dichloromethane, the intermolecular cycloaddition reaction at room temperature gave a 2:1 mixture of the diastereomeric *endo*-substituted formyl-phosphanorbornene template complexes in 35 days. The major diastereomer could be isolated by fractional crystallization. The absolute configurations and the coordination properties of the *endo*-formylphosphines in the isolated template complex have been established by X-ray crystallography. The enantiomerically pure *endo*-cycloadduct (−)-5-(formyl)-2,3-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-2-ene was obtained by the treatment of the major product with dppe. When the *endo*-cycloaddition reaction was conducted in the ionic liquid 1-hexyl-3-methylimidazolium tetrafluoroborate ([hmim][BF_4]), the same 2:1 diastereomeric mixture was obtained in two days. When the reaction temperature was raised to 85 °C, the reaction generated the two diastereomeric *endo*-cycloadducts as a 1:1 mixture in 2 h. Similarly, a 1:1 mixture was obtained when the reaction was heated at 85 °C in 1,2-dichloroethane for 2 days.

Keywords: Asymmetric synthesis; P-Chiral phosphanorbornene; Ionic liquids; Organopalladium complex; *endo*-Cycloaddition; Acrolein

1. Introduction

We are interested in developing novel functionalized phosphine–gold(I) complexes that exhibit anti-cancer activities [1]. We believe that the biological properties of these gold complexes can be controlled by selected functionalities and designed chirality of the phosphine ligands. In order to establish the structure–activity relationship systematically, we have recently synthesized a range of enantiomerically pure functionalized P-chiral phosphanorbornenes which can be used as gold-drug supporters [2]. The phosphanorbornenes were prepared via the palladium complex promoted asymmetric Diels–Alder reaction between 3,4-dimethyl-1-phenylphosphole (DMPP) and selected dienophiles in the presence of the enantiomerically pure forms of dimethyl[1-(2-naphthyl)ethyl]amine as the chiral auxiliaries [2–4]. In this series of phosphines synthesis, the *exo* or *endo* cycloaddition pathways can be selected just by controlling the number of coordination sites on the chiral palladium template. For example, in the designed *exo*-cycloaddition reactions, both the reacting dienophile and DMPP are allowed to coordinate simultaneously onto the palladium template during the course of the reaction. The common inactive dienophiles are thus activated via the dienophile–metal interaction and the intra-molecular *exo*-cycloaddition reactions usually proceed smoothly at room temperature in organic solvents. Such dienophile–metal interactions, however, would not be permitted in the

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analogous inter-molecular *endo*-cycloaddition reactions. As such, the reaction usually proceeds rather slowly with the less reactive dienophiles [3]. In several cases, it took 1–2 months to form the desired *endo*-substituted cycloadducts [4]. Acceleration of these asymmetric syntheses using higher temperatures usually resulted in poor stereoselectivity. In an effort to improve the synthesis of these phosphines, we decided to explore the possibility of using ionic liquids for the slow *endo*-cycloaddition reactions. It is well known that the utilization of ionic liquids in organic synthesis is beneficial with regards to environmental and economical considerations [5]. These green solvents have been used successfully in many transition metal complex catalyzed synthetic processes [5,6]. It has been reported that an ionic liquid may activate a metal ion promoted reaction by forming hydrogen bonds with the substrates or function as a co-catalyst by interacting with the metal ion to form a more reactive and stable species in the reaction transition state [7]. We herein report the asymmetric *endo*-cycloaddition reaction between acrolein and the coordinated DMPP on the chiral template (S_c)-**1**, in both ionic liquids and in organic solvents.

2. Experimental

Reactions involving air-sensitive compounds were performed under a positive pressure of purified nitrogen. Routine ^{1}H and ^{31}P NMR spectra were recorded at 500 and 202 MHz, respectively, on the Bruker AMX 500 spectrometer. Optical rotations were measured in the specified solution in a 1-cm cell at 25 °C with a Perkin–Elmer Model 341 polarimeter. Melting points were determined using an Electrothermal IA 9200 apparatus. All FT-IR spectra were obtained from a FTs-165 meter. Elemental analyses were performed by the Elemental Analysis Laboratory of the Department of Chemistry at the National University of Singapore. Both enantiomeric forms of the chiral complexes **1** [4,8] and **4** [9] were prepared as previously described. The ionic solvent [hmim][BF_4] was purchased from commercial sources and was used directly without further purification.

*2.1. Endo-cycloaddition reaction in dichloromethane: isolation of chloro {(S)-1-[1-(dimethylamino)ethyl]-2-naphthyl-C^2,N}{(1α, 4α, 5β, 7S)-5-(formyl)-2,3-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-2-ene-P^7}-palladium(II) ((S_c, S_p)-**2**)*

A solution of the neutral chloro complex (S_c)-**1**(1.00 g, 1.89 mmol) in dichloromethane (50 mL) was treated with excess acrolein (0.76 mL, 11.34 mmol). The reaction mixture was then stirred at room temperature for 35 days. The ^{31}P NMR spectrum of the crude product in $CDCl_3$ indicated the presence of two singlets at δ 124.5 and 125.8 with an intensity ratio of 2:1, respectively. The solvent was removed under reduced pressure and the residue was crystallized from dichloromethane–acetone to yield the less soluble major diastereomer (S_c, S_p)-**2** as pale yellow prisms: yield 0.58 g (52%); m.p. 213–214 °C; $[\alpha]_D$ + 33.2° (*c* 1.0, CH_2Cl_2); Anal. Calc. for $C_{29}H_{33}ClNOPPd$: C, 59.6; H, 5.7; N, 2.4. Found: C, 59.5; H, 5.6; N, 2.3%. ^{1}H NMR ($CDCl_3$) δ 1.40 (s, 3H, C=C*Me*), 1.75 (s, 3H, C=C*Me*), 1.90 (d, 3H, $^3J_{HH}$ = 6.4 Hz, CH*Me*), 1.97 (dddd, 1H, $^3J_{PH}$ = 33.8, $^2J_{HH}$ = 12.6, $^3J_{HH}$ = 4.6, $^3J_{HH}$ = 1.6 Hz, *H6*(*endo*)), 2.26–2.30 (m, 1H, *H6*(*exo*)), 2.55 (d, 3H, $^4J_{PH}$ = 1.1 Hz, N*Me*), 2.87 (d, 3H, $^4J_{PH}$ = 3.2 Hz, N*Me*), 3.07 (s, 1H, *H4*), 3.99 (m, 1H, *H1*), 4.27 (dq, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.4 Hz, C*H*Me), 4.42–4.46 (m, 1H, *H5*), 7.09–7.93 (m, 11H, *aromatics*), 9.72 (s, 3H, C*H*O); ^{31}P NMR ($CDCl_3$) δ 124.5 (s, 1P); IR (KBr) υ 1716 cm^{-1} (uncoordinated C=O).

The minor diastereomer (S_c, R_p)-**2** could not be induced to crystallize in all solvent systems attempted.

2.2. Endo-cycloaddition reaction in 1-hexyl-3-methylimidazolium tetrafluoroborate

The chloro complex (S_c)-**1** (0.50 g, 0.95 mmol) in [hmim][BF_4] (2 mL) was treated with excess acrolein (0.35 mL, 5.68 mmol). The reaction mixture was then stirred at room temperature for 2 days. The ^{31}P NMR spectrum of the crude product in $CDCl_3$ indicated the presence of two cycloadducts (S_c, R_p)-**2** and (S_c, S_p)-**2** in ratio of 1:2, respectively. Addition of methanol precipitated the product, which was then isolated by filtration and recrystallized from dichloromethane–acetone to yield the less soluble di astereomer (S_c, S_p)-**2** in 45 % yield.

*2.3. Liberation of (1α, 4α, 5β, 7R)-5-(formyl)-2,3-dimethyl-7-phenyl-7-phosphabicyclo [2.2.1]hept-2-ene ((R_p)-**3**)*

A solution of (S_c, S_p)-**2** (0.4 g, 0.68 mmol) in dichloromethane (20 mL) was treated with a solution of 1,2-bis(diphenylphophino)ethane (0.27 g, 0.68 mmol) in the same solvent (20 mL) for 1 h. The resulting yellowish mixture was passed through a column which was packed successively with silica gel (2 g) and florisil (20 g), with dichloromethane as the eluent to yield a colorless solution. Removal of solvent under reduced pressure gave (R_p)-**3** as a highly air-sensitive pale yellow solid,: Yield 0.16 g (97%); $[\alpha]_{365}$−22.9° (*c* 0.4, $CHCl_3$); $[\alpha]_D$ −2.9° (*c* 0.4, $CHCl_3$). ^{31}P NMR ($CDCl_3$) δ 109.0 (s, 1P).

*2.4. Crystal structure determination of (S_c, S_p)-**2***

Crystal data for complex (S_c, S_p)-**2** and a summary of the crystallographic analysis are given in Table 1. Diffraction data were collected on a Siemen SMART CCD diffractometer using graphite monochromated Mo Kα radiation. The structure was solved by direct methods, and all non-hydrogen atoms refined anisotropically. Hydrogen atoms were introduced at fixed distances from carbon atoms and assigned on a Silicon Graphics workstation using programs by Siemens [10].

Table 1
Crystallographic data for the complex (S_c, S_p)-**2**

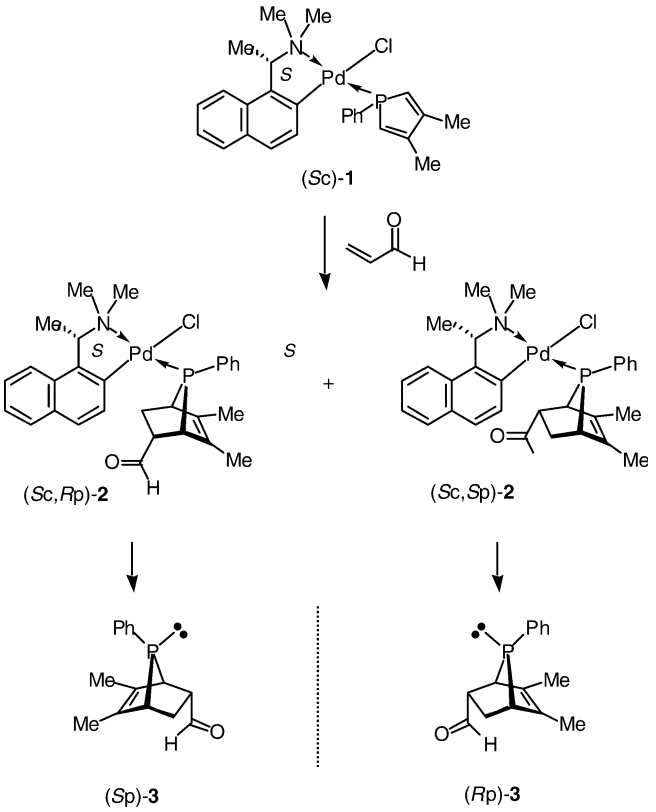
Formula	$C_{29}H_{33}ClNOPPd$
Molecular weight	584.38
Space group	$P2_12_12_1$
Crystal system	Orthorhombic
a (Å)	11.583(1)
b (Å)	15.186(1)
c (Å)	15.319(1)
Z	4
T (K)	223
D_c (g cm^{-3})	1.421
λ (Å)	0.71073
μ (mm^{-1})	0.869
F(000)	1200
R_1 (obsd. data)[a]	0.0254
WR_2 (obsd. data)[b]	0.0606

[a] $R_1 = \sum \| F_o \| - \| F_c \| / \sum \| F_o \|$.
[b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}1/2;\ w^{-1} = \sigma^2(F_o)^2 + (aP)^2 + bP$.

3. Results and discussion

3.1. Metal template promoted endo-cycloaddition reaction between acrolein and DMPP

The cycloadduct product was not formed when acrolein and DMPP were stirred together in the absence of a transition metal ion in both CH_2Cl_2 and ionic liquid. However, the cycloaddition reaction proceeded smoothly at room temperature when the coordinated DMPP in (S_c)-**1** was treated with excess acrolein (Scheme 1). As the Pd–Cl bond in (S_c)-**1** is thermodynamically stable and kinetically inert, displacement of the chloro ligand by acrolein to form a palladium–acrolein interaction is not possible [11]. Thus acrolein could only react with the coordinated cyclic diene via the intermolecular cycloaddition pathway. In general, acrolein is considered to be a reactive dienophile. We were therefore surprised to observe that the *endo*-cycloaddition reaction proceeded rather slowly when the reaction was conducted at room temperature in dichloromethane. The reaction was monitored by ^{31}P NMR spectroscopy and was found to take as long as 35 days to complete. Presumably, the steric hindrances originating from the P–Ph and P → Pd moieties of the coordinated DMPP impeded the interaction between acrolein and the cyclic diene to form the necessary transitional structure for the [4 + 2] cycloaddition reaction. Under similar conditions, however, the *endo*-cycloaddition was found to proceed significantly faster when ionic liquid, 1-hexyl-3-methylimidazolium tetrafluoroborate ([hmim][BF_4], Fig. 1), was used as the solvent. Formation of the *endo*-cycloadduct in [hmim][BF_4] was found to be complete within 2 days. Interestingly, although ionic liquid indeed accelerated the rate of the cycloaddition reaction, the ^{31}P NMR studies showed that the two different solvent systems employed in these syntheses did not affect the reaction stereoselectivity noticeably as very similar spectra were recorded from the two reaction mixtures. Prior to purification, the ^{31}P NMR ($CDCl_3$) spectra of both reaction mixtures exhibited two sharp singlets at δ 124.5 and 125.8 in the ratio of 2:1. No other ^{31}P NMR signals were detected in these 202 MHz spectra, thus confirming that only two diastereomeric complexes were formed in the cycloaddition reaction. The diastereomers could be isolated efficiently from the reaction mixtures. For the synthesis in which [hmim][BF_4] was used as the solvent, the crude product was isolated by precipitation with methanol followed by filtration. Fractional recrystallization of the crude product from dichloromethane–acetone afforded the pure major isomer in 45% isolated yield, $[\alpha]_D + 33.2$ (CH_2Cl_2). It is noteworthy that [hmim][BF_4] could be recycled into its pure form by evaporation of methanol followed by the removal of the excess acrolein with diethyl-ether. For the reaction in dichloromethane, evaporation of the solvent followed by recrystallization of the crude product from dichloromethane–acetone gave the major isomer in 52% yield. In $CDCl_3$, the ^{31}P NMR spectrum of this isolated major product exhibited a sharp



Scheme 1.

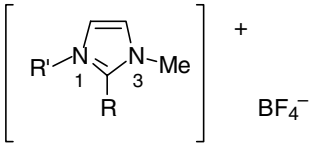


Fig. 1. Ionic liquid used in this work. [hmim]$^+$: R = H, R′ = *n*-hexyl; [bdimim]$^+$: R = methyl, R′ = *n*-butyl.

singlet at δ 124.5. The more soluble minor product, which exhibited the ^{31}P NMR resonance signal at δ 125.8, could not be isolated from a wide range of solvent systems.

The molecular structure and the absolute stereochemistry of the major isomer isolated from the above asymmetric cycloaddition reaction were determined by X-ray crystallography (Fig. 2). The structural analysis confirmed that the compound was indeed (S_c, S_p)-**2** as depicted in Scheme 1. Selected bond distances and angles of (S_c, S_p)-**2** are given in Table 2. The absolute configurations of the four new stereogenic centers at P(3), C(22), C(25) and C(27) are *S*, *R*, *S* and *R*, respectively. The chiral phosphanorbornene cycloadduct coordinates as a monodentate ligand via its phosphorus donor atom. The formyl group is attached to the *endo* position at C(27) of the rigid bicyclic ring with the P–Ph group orientated in the *syn* orientation. The formyl-oxygen is not involved in any metal interactions. The geometry of the phosphanorbornene skeleton is typical, with the angel at phosphorus being acute [81.2(1)°]. The geometry at the palladium center is slightly distorted square planar.

3.2. Liberation and enantiomerical purity of the formyl-substituted phosphanorbornene

As illustrated in Scheme 1, the formyl-substituted phosphanorbornene could be liberated efficiently from the palladium template (S_c, S_p)-**2** by treating the enantiomerically pure complex with 1,2-bis(diphenylphosphino)ethane. The liberated ligand (R_p)-**3** was obtained as a highly air-sensitive pale yellow solid in 97% yield, $[\alpha]_D$ −22.1 (CH_2Cl_2). The apparent inversion of configuration that takes place at the phosphorus center when the functionalised phosphine is liberated from the reaction promoter is merely a consequence of the Cahn–Ingold–Prelog (CIP) sequence rules [12]. The ^{31}P NMR spectrum of the free phosphine in $CDCl_3$ exhibited a sharp singlet at δ 109.0. The low field ^{31}P NMR signal confirms that the *endo–syn* stereochemistry of the phosphanorbornene skeleton is retained [4,8].

Stereospecific displacement of the formyl-substituted phosphanorbornene was confirmed by the quantitative repreparation of (S_c, S_p)-**2** from the liberated (R_p)-**3** and the dimeric complex (S_c)-**4** (Scheme 2). Prior to purification, the 202 MHz ^{31}P NMR spectrum of the crude product exhibited the expected singlet at δ 124.5 arising from the regenerated diastereomer (S_c, S_p)-**2**. The enantiomerical purity of (R_p)-**3** was further tested by the preparation of the non-equivalent diastereomer (R_c, S_p)-**2** from the liberated ligand and the equally accessible (R_c)-**4**. The ^{31}P NMR spectrum of the crude product exhibited only one singlet at δ 125.8. More importantly, no resonance signal was observed at δ 124.5 in this NMR spectrum. The above NMR studies confirmed that the two diastereomeric complexes indeed show distinct ^{31}P NMR signals and (R_p)-**3** is enantiomerically pure. In the second NMR experiment, a singlet would have been observed at δ 124.5 if the liberated phosphanorbornene contained the enantiomer (S_p)-**3** as impurity. It is noteworthy that the new diastereomer (R_c, S_p)-**2** is enantiomeric to (S_c, R_p)-**2** as depicted in Scheme 1. In achiral solvents, these two enantiomeric complexes should exhibit identical NMR signals. The minor product in the original asymmetric synthesis indeed exhibited a singlet at δ 125.8. These NMR experiments thus confirm that the more soluble minor isomer that was generated from the asymmetric cycloaddition reaction is (S_c, R_p)-**2**. However, attempts to crystallize this minor isomer from a wide range of solvent systems were not successful.

3.3. Mechanism, stereoselectivity, solvent and temperature effects

The stereoselectivity of the current asymmetric synthesis was found to be the same in both dichloromethane and in [hmim][BF_4]. It would appear that reaction proceeded via the same intermolecular *endo*-cycloaddition reaction mech-

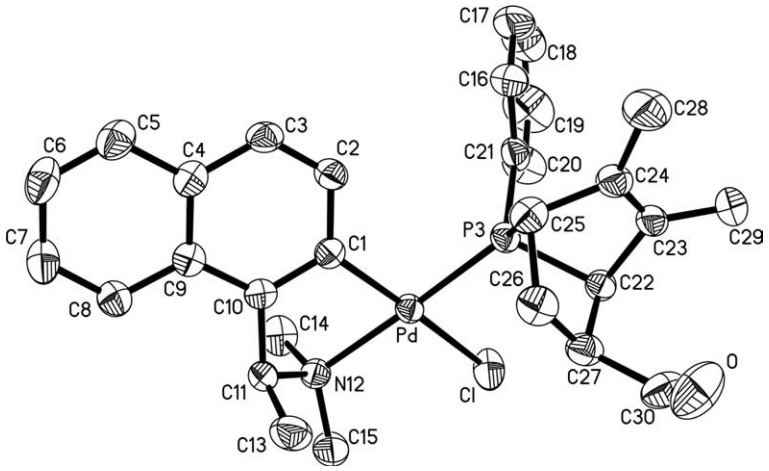
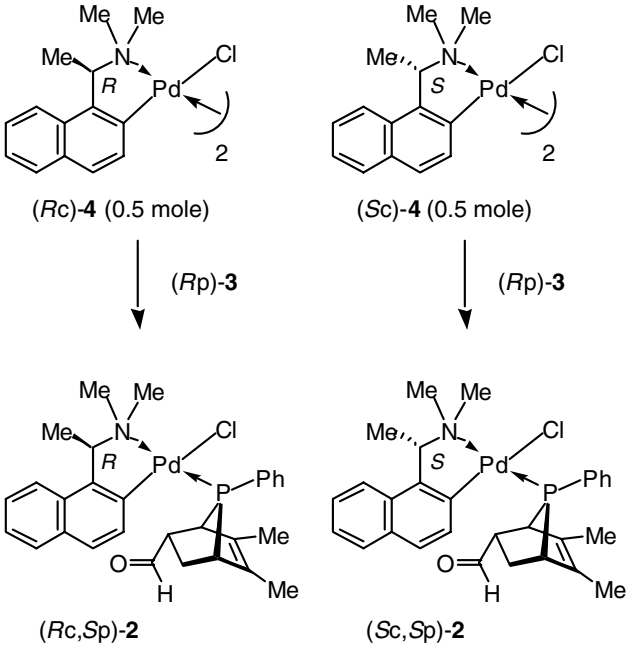


Fig. 2. Molecular structure and absolute stereochemistry of (S_c, S_p)-**2**.

Table 2
Selected bond distances (Å) and bond angles (°) for (S_c, S_p)-**2**

Pd–C(1)	2.005(2)	C(22)–C(23)	1.520(3)
Pd–P(3)	2.214(1)	C(23)–C(24)	1.331(3)
Pd–N(12)	2.144(2)	C(24)–C(25)	1.522(3)
Pd–Cl	2.392(1)	C(25)–C(26)	1.557(3)
C(1)–C(10)	1.385(3)	C(26)–C(27)	1.547(3)
P(3)–C(21)	1.806(2)	C(27)–C(22)	1.566(3)
P(3)–C(22)	1.855(2)	C(27)–C(30)	1.501(3)
P(3)–C(25)	1.848(2)	C(30)–O	1.194(3)
C(1)–Pd–N(12)	81.3(1)	C(22)–C(23)–C(24)	110.4(2)
C(1)–Pd–P(3)	94.2(1)	C(22)–C(23)–C(29)	120.4(2)
C(1)–Pd–Cl	174.1(2)	C(23)–C(24)–C(25)	111.1(2)
N(12)–Pd–P(3)	174.6(1)	C(22)–C(27)–C(30)	110.0(2)
P(3)–Pd–Cl	90.1(1)	C(22)–C(27)–C(26)	106.1(2)
C(22)–P(3)–C(25)	81.2(1)	C(25)–C(26)–C(27)	106.0(2)
C(25)–C(24)–C(28)	120.6(2)	C(27)–C(30)–O	125.7(3)



Scheme 2.

anism in both solvents. The stereoselectivity was controlled only by the *ortho*-palladated naphthylamine auxiliary. It has been reported that this organometallic C–N chelate is kinetically and thermodynamically stable and the unique absolute stereochemistry of the five-membered ring is not dissipated in solution [13]. Similarly, due to the strong electronic influence originating from the coordinated naphthylene-carbon, the *trans* Pd–Cl ligands in this class of organopalladium complexes are also stable and inert. The fourth coordination site of the chiral palladium template should be occupied by DMPP throughout the cycloaddition reaction as uncoordinated DMPP itself is not a reactive cyclic diene for the Diels–Alder reaction. Since there were no empty coordination sites available in this chiral template promoted synthesis, acrolein could not have been activated by metal complexation. Acrolein could only react with the coordinated DMPP in (S_c)-**1** via a simple intermolecular mechanism. With similar stability and coordination chemistry considerations, we believe that the ionic liquid [hmim][BF_4] was not involved in any carbene-type metal complexation with the palladium template during the course of the cycloaddition reaction. We envisage that, however, the ionic liquid activated the acrolein by forming a hydrogen bond between the carbonyl oxygen of the dienophile and the [hmim] cation. Apparently the proton attached to C(2) of the [hmim] cation is responsible for this important hydrogen bonding. Indeed, no noticable acceleration was observed for the Diels–Alder reaction conducted in the analogous ionic liquid butyldimethylimidazolium tetrafluoroborate [bdimim][BF_4] in which the H–C(2) proton was replaced by a methyl group.

In a typical intermolecular process, the *endo*-cycloaddition reaction between (S_c)-**1** and acrolein could be accelerated by conducting the reaction at higher temperatures. Indeed, the reaction was found to be complete within 2 days when it was conducted at 85 °C in 1,2-dichloroethane. Under similar heating conditions in [hmim][BF_4], the *endo*-cycloadducts were generated quantitatively within 2 h. It should be noted that, however, poor setereoselectivity resulted in these stronger reaction conditions. In both solvent systems, the two diastereomeric cycloadducts (S_c, R_p)- and (S_c, S_p)-**2** were generated in ca. equal quantities. We are currently investigating the application of a range of ionic liquids in other prolonged asymmetric syntheses.

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Appendix A. Supplementary data

For (S_c, S_p)-**2**, tables of crystal data and data collection and solution and refinement details, final positional parameters, bond distances and angles, thermal parameters of non-hydrogen atoms, and calculated hydrogen parameters. This material is available free of charge via the Internet at http://www.rsc.org. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.08.009.

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