Metallocene-Appended Imidazoles Displaying Virtual Planar Chirality

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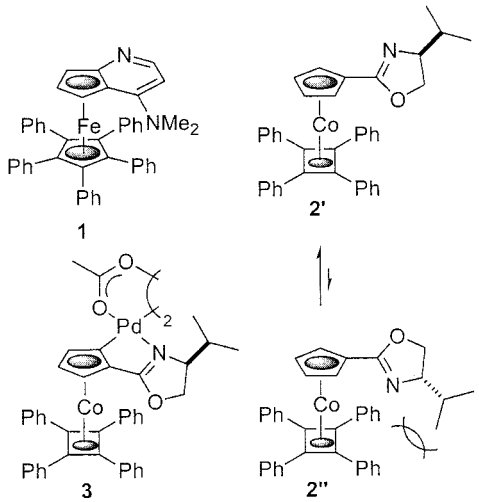
Summary: (S)-1-(1-Alkylethyl)imidazoles ***6a/b*** *(alkyl = cyclohexyl, tert-butyl) containing a 2-(η⁵-cyclopentadienyl)(η⁴-tetraphenylcyclobutadiene)cobalt substituent are readily synthesized. The effect of the bulky metallocene is to place the imidazoles in an environment of virtual planar chirality as revealed by X-ray crystallography (of* ***6a****), NOE difference NMR spectroscopy, and also their highly diastereoselective reactions with Pd(OAc)₂ resulting in new palladacycles* ***7a/b*** *with (S)-(ₚR) configurations. The ability of the imidazole complexes to act as nucleophilic catalysts was investigated, weak activity being found for the promotion of the reaction between ethanol and dimethylchlorophosphate.*

The development of nonenzymatic methods for enantioselective acyl transfer reactions has involved the use of both stoichiometric chiral acylating agents[1] and nucleophilic catalysts employed for acyl transfer.[2] In both of these categories significant attention has focused on the use of chiral DMAP derivatives and related structures. These are typically generated by attaching a stereogenic center to the 2-position of a pyridine nucleus[1d,e] or by incorporation of this heterocycle into structures displaying either axial[2a,e,i] or planar chiality.[1b,2c,f−h,k] Illustrative of the latter category is the pentaphenyl ferrocene derived structure **1**, which has proved especially effective for the kinetic resolution by acylation of a range of secondary alcohols and represents the best nonenzymatic method for carrying out this transformation. In contrast imidazole, which has also been extensively used as a nucleophilic catalyst for acyl transfer,[3] has been little studied with respect to its potential applications in asymmetric catalysis. The only notable exception is the incorporation of histidine into minimal acylase-like peptides that have been successfully applied to the kinetic resolution of *trans*-2-acetamidocyclohexanol.[4]

We recently reported the synthesis of the metallocene-appended oxazoline **2**, which on reaction with $Pd(OAc)_2$ led exclusively to the ortho-palladated product **3** of (*S*)-($_pR$) configuration.[5a] This outcome was rationalized by palladation occurring on rotamer **2′** rather than the alternative **2″** due to the unfavorable interaction in the latter of the isopropyl substituent with the tetraphenylcyclobutadiene floor. We have utilized this rotamer imbalance in related 4-(hydroxymethyl)oxazoline ligands for use in asymmetric catalysis.[5b] A further consequence of this effect is that the oxazoline nitrogen is in an environment similar to that of the pyridine nitrogen in the DMAP derivative **1**. Although the oxazoline is clearly unsuitable for use as a nucleophilic catalyst, we were intrigued by the possibility of instead attaching a 2-imidazoyl group to the metallocene and examining the ability of a stereogenic center attached to position 1 to control the stereochemical outcome of reactions occurring at the nucleophilic and basic nitrogen of this heterocycle. Our initial results are reported in this note.[6]



Results and Discussion

Carboxylic acid **4**, readily prepared from the reaction of diphenylacetylene and sodium carbomethoxycyclopentadienylide with $CoCl(PPh_3)_3$ followed by ester hy-

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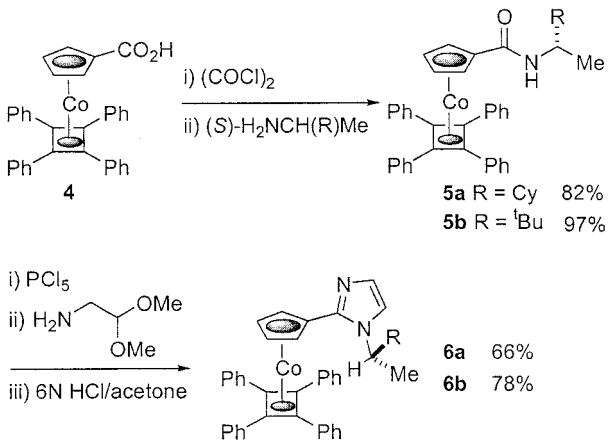
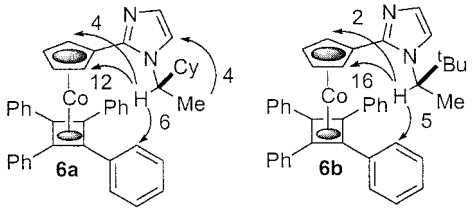
Scheme 1



drolysis,[5] was readily transformed into the amides **5a**/**b**. Subsequent reaction of these yellow complexes with PCl_5 in CH_2Cl_2 resulted in their conversion into intermediate red imidyl chlorides. These were immediately reacted with 2,2-dimethoxyethylamine to give, in both cases, amidines isolated by chromatography as a mixture of isomers. These were not separated but were instead converted with 6 N HCl into metallocene-appended imidazoles **6a**/**b** in good overall yield (Scheme 1). This methodology was found to be inapplicable to the corresponding amide derived from α-methylbenzylamine due to the quantitative formation of (η^5-cyclopentadienylnitrile)(η^4-tetraphenylcyclobutadiene)cobalt[7] on reaction with PCl_5, as a result of a retro-Ritter reaction.



The structure of **6a** was confirmed by an X-ray crystal structure analysis (Figure 1).[8]As anticipated, the smallest substituent attached to the stereogenic center, hydrogen, is pointing toward the bulky metallocene, with the smaller of the two remaining substituents oriented toward the tetraphenylcyclobutadiene floor. To aid accommodation of this methyl substituent, one of the phenyls lies essentially perpendicular to the cyclobutadiene group, to which it is attached at C(9). A consequence of this arrangement is the proximity of the active nitrogen N(2) to C(2), one of the two diastereotopic α-positions of the cyclopentadienyl ring, and the

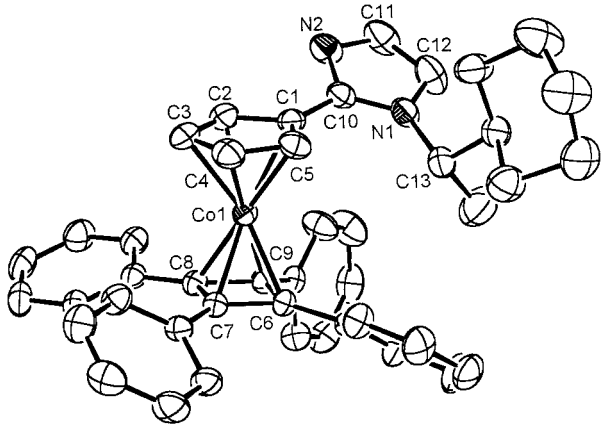
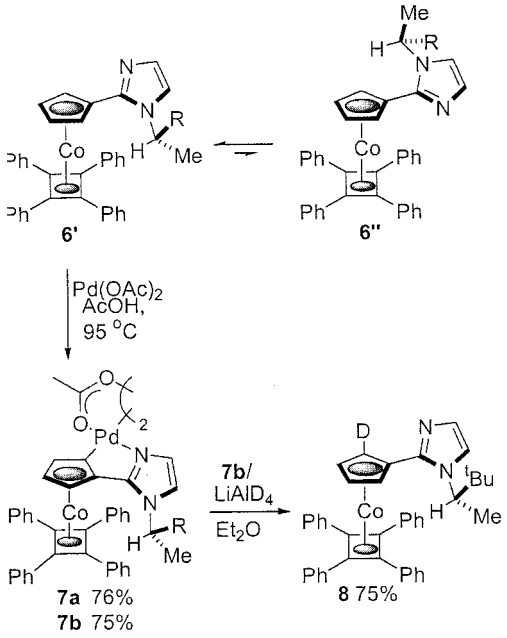


Figure 1. Molecular structure of **6a**.

Scheme 2



orientation of this nitrogen away from the bulk of the metallocene (C(2)−C(1)−C(10)−N(2) = 23.9°).

To examine if this conformation is maintained in solution, ^{1}H NMR NOE difference spectra of **6a**/**b** were recorded in $CDCl_3$ at room temperature, revealing, in both cases, the proximity of the stereogenic center methines to predominantly one of the two diastereotopic α-positions of the cyclopentadienyl rings. The disparity in the population of rotamers is greater for the *tert*-butyl-containing derivative **6b**. Support for there being two, essentially conjugated, rotameric minima is provided by the proximity of the stereogenic center methines to the ortho-hydrogens of the tetraphenycyclobutadiene moieties. To test the relative accessibility of the active nitrogen N(2) in these rotamers, **6a**/**b** were heated separately with $Pd(OAc)_2$ for 30 min under the same conditions previously employed for the palladation of oxazoline **2**. After cooling of the reaction mixtures to room temperature, both led to isolation by filtration of new palladated complexes **7a**/**b** formed as single diastereoisomers, as revealed by the single sets of peaks observed in their ^{1}H/^{13}C NMR spectra (Scheme 2). Examination of the mother liquors revealed, in both cases, the presence of only the same diastereoisomer as isolated by filtration. The assumption that these reac-

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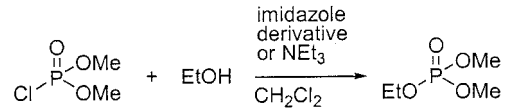
(8) For the structural details of **6a** and **7b** and a representation of the latter complex, see Supporting Information.

Scheme 3



tions are under kinetic control was tested by heating **6a** with $Pd(OAc)_2$ for only 2 min prior to examination of the reaction mixture by NMR spectroscopy. Peaks corresponding to palladacycle **7a** could clearly be identified, and there was no evidence to suggest the presence of the alternative diastereoisomer.

The configuration of the new element of planar chirality in these complexes was established as $_pR$ by an X-ray crystal structure analysis of **7b**.[8] Treatment of **7b** with $LiAlD_4$ in Et_2O gave clean conversion to **8** with ~56% deuterium incorporation, as determined by the reduction in the signal intensity for the peak at 5.45 ppm in the ^1H NMR spectum. This confirms the NOE assignments made for **6a**/**b** and the identity of **6′** as the major rotamer present in solution. Although the torsion angle C(2)−C(1)−C(10)−N(2) cannot be specified exactly, there is a clear preference for the active nitrogen N(2) to be in proximity to C(2) rather than the alternative C(5). That palladation occurred exclusively via this rotamer enables the imidazole to be regarded as being in an environment of virtual planar chirality,[5b] with one face of the heterocycle blocked by the tetraphenylcyclobutadiene moiety of the adjoined complex. The alternative minor rotamer **6″** likely features nitrogen N(2) being tipped toward the tetraphenyl floor to minimize interaction of either the cyclohexyl or *tert*-butyl substituents with this bulky moiety, with the inaccessibility of the N(2) lone pair accounting for the inactivity of this rotamer.

N-Methyl imidazole (NMI) has been reported to be 130 times more effective than pyridine as a catalyst for the acylation of secondary alcohols with acetyl chloride, but displays less than 1% of the activity of DMAP in the same reaction.[9] A further feature of imidazole and its derivatives is the switch between general base catalysis and nucleophilic catalysis for acyl transfer, depending on the nature of the acylating agent and the solvent(s) employed.[3] Using both acetic anhydride and *p*-nitrophenyl acetate as acyl sources, we were unable to observe any accelerated reactivity when they were combined with 1-phenylethanol in the presence of **6a** dissolved in a variety of different solvent combinations. Instead our attention focused on the alcoholysis of chlorophosphates, for which an accelaration in half-life time of 7×10^4 was reported for the ethanolysis of diethylchlorophosphate in the presence of 1 equiv of NMI.[10] This is reported to act as a nucleophilic catalyst in this reaction and is a true catalyst as substoichiometric quantities may be employed with NEt_3 acting as a base. When dimethylchlorophosphate was combined with ethanol (1 equiv) in dry CH_2Cl_2 containing **6a** (1 equiv) at room temperature (20 °C), a half-life for the formation of dimethylethyl phosphate was determined as 100 h (Scheme 3/Table 1). Complex **6b** gave an identical result, but when these imidazoles were replaced by NEt_3, no reaction product was observed. The half-life time could be cut by carrying out the reaction at 40 °C, and under these conditions no reaction was observed when **6b** was again replaced by NEt_3. However attempts to use 10 mol % of either **6a**/**b** as a true catalyst in the presence of NEt_3 failed to give a measurable conversion to product within a meaningful timespan. In comparison, use of 1 equiv of 2-(9-anthryl)-1-(1-(*tert*-butyl)ethyl)imidazole, **9**, as promotor resulted in a half-life of 65 min, a time that further reduced to 27 min with the use of 1 equiv of *N*-methylimidazole.

Table 1. Reaction of Ethanol with Dimethylchlorophosphate

conditions	half-life
1 equiv **6a** (20 °C)	100 h
1 equiv **6b** (20 °C)	100 h
1 equiv NEt_3 (20 °C)	no reaction (after 120 h)
1 equiv **6b** (40 °C)	50 h
1 equiv NEt_3 (40 °C)	no reaction (after 65 h)
1 equiv **9** (20 °C)	65 min
1 equiv NMI (20 °C)	27 min

In conclusion, we have demonstrated that bulky metallocene-appended imidazoles are readily synthesized and that the heterocycle may be regarded as being in an environment of virtual planar chirality. Although the size of the metallocene has a signifiant effect on attenuating the activity of the complexes as nucleophilic catalysts, it is anticipated that the chiral relay principle demonstrated here will be readily extended to related complexes displaying significantly higher activity.

Experimental Section

Dichloromethane was distilled from calcium hydride. Petroleum ether refers to that fraction boiling in the range 40−60 °C. Column chromatography was performed on Matrix silica 60 (35−70 μm). All reactions, with the exception of the imidazole cyclizations, were performed under a nitrogen atmosphere. Assignment of ^{13}C resonances was made with the aid of DEPT.

(η^5-(*S*)-*N*-1-Cyclohexylethylcarboxamidecyclopentadienyl)(η^4-tetraphenylcyclobutadiene)cobalt, 5a. To a solution of **4** (0.805 g, 1.54 mmol) in CH_2Cl_2 (10 mL) was added oxalyl chloride (0.27 mL, 3.1 mmol), and the resulting red solution was stirred at room temperature for 20 min. The solvent and excess oxalyl chloride were removed in vacuo, and the crude acid chloride was dissolved in CH_2Cl_2 (10 mL) and added to a solution of (*S*)-1-cyclohexylethylamine (0.195 g, 1.54 mmol) in triethylamine (0.21 mL) and CH_2Cl_2 (5 mL). The resulting orange reaction mixture was stirred at room temperature for 3 h, the solvent removed in vacuo, and the residue column chromatographed (CH_2Cl_2) to give **5a** as an orange solid (0.797 g, 82%): mp 127−129 °C; $[\alpha]^{20}_D$ −9 (*c* 0.72, $CHCl_3$); ν_{max}/cm^{-1} (Nujol) 1620 (C═O); δ_H (400 MHz, $CDCl_3$) 0.68 (d, *J* 6.8, 3H, C*H*$_3$), 0.70−1.69 (m, 11H, Cy), 3.57 (sextet, *J* 7, 1H, C*H*CH$_3$), 4.56 (br s, 1H, Cp), 4.61 (br s, 1H, Cp), 4.81 (br s, 1H, Cp), 5.00 (d, *J* 8.67, 1H, N*H*), 5.05 (br s, 1H, Cp), 7.13−7.21 (m, 12H, Ph), 7.37−7.39 (m, 8H, Ph); δ_C {^1H} (100 MHz, $CDCl_3$) 17.5 (*C*H$_3$), 26.6 (*C*H$_2$ × 2), 26.8 (*C*H$_2$), 29.1 (*C*H$_2$), 29.8 (*C*H$_2$), 43.1 (*C*HCH$_2$), 49.7 (NH*C*H), 76.4 (*C*$_4$Ph$_4$), 81.9 (Cp), 82.7 (Cp), 86.7 (Cp × 2), 91.7 (Cp − ipso), 127.1 (Ph − para), 128.6 (Ph), 129.2 (Ph), 135.8 (Ph − ipso), 165.6 (*C*═O); *m*/*z* (APCI) 634 (MH^+, 100%), 415 (30); HRMS (ES) *m*/*z* found for MH^+, 634.2525; calcd for $C_{42}H_{41}CoNO$, 634.2520.

(η^5-(*S*)-2-(1-{1-Cyclohexylethyl})imidazoyllcyclopentadienyl)(η^4-tetraphenylcyclobutadiene)cobalt, 6a. To a solution of **5a** (2.853 g, 4.50 mmol) in CH_2Cl_2 (65 mL) was added PCl_5 (0.94 g, 4.5 mmol), and the resulting red solution

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was heated at reflux for 1 h. The solvent was removed in vacuo, the crude imidyl chloride was dissolved in CH_2Cl_2 (60 mL), and amino acetaldehyde dimethyl acetal (0.48 g, 4.57 mmol) was added. The resulting orange reaction mixture was stirred at room temperature for 2 h, the solvent was then removed in vacuo, and the residue was column chromatographed (10% MeOH/EtOAc) to give the intermediate amidines as a dark orange solid (2.53 g). This in turn was dissolved in THF (65 mL), to which was added 5 M HCl (0.94 mL, 4.7 mmol), and the orange reaction mixture was then heated at reflux for 12 h. After cooling to room temperature, 6 M NaOH was added until a pH of 10 was reached, followed by extraction with CH_2Cl_2 (100 mL). The organic phase was dried (Na_2SO_4), filtered, and evaporated in vacuo, and the residue was column chromatographed (30% EtOAc/petroleum ether) to give **6a** as an orange solid (1.940 g, 66%): mp 193−195 °C; $[\alpha]^{20}_D$ −183 (*c* 0.2, $CHCl_3$); ν_{max}/cm^{-1} (Nujol) 1594; δ_H (400 MHz, $CDCl_3$) 0.74 (d, *J* 6.8, 3H, C*H*$_3$), 0.67−1.59 (m, 11H, Cy), 3.90 (pent, *J* 6.7, 1H, C*H*CH$_3$), 4.69 (br s, 2H, Cp), 4.71 (br s, 1H, Cp), 5.40 (br s, 1H, Cp), 6.69 (d, *J* 1.1, 1H, imidazole 5-H), 6.84 (d, *J* 1.1, 1H, imidazole 4-H), 7.04−7.15 (m, 12H, Ph), 7.25−7.27 (m, 8H, Ph); δ_C {^{1}H} (100 MHz, $CDCl_3$) 15.3 (*C*H$_3$), 24.9 (*C*H$_2$), 25.1 (*C*H$_2$ × 2), 26.3 (*C*H$_2$), 28.7 (*C*H$_2$), 43.2 (*C*HCH$_2$), 54.9 (NH*C*H), 74.7 (*C*$_4$Ph$_4$), 79.6 (Cp), 81.7 (Cp), 82.0 (Cp), 83.8 (Cp), 89.3 (Cp − ipso), 116.0 (imidazole 5 − C), 125.2 (Ph − para), 126.9 (Ph), 126.9 (imidazole C − 4), 127.7 (Ph), 134.6 (Ph − ipso), 148.8 (*C*═N); *m*/*z* (EI) 657 (M^+, 100%), 181 (44), 163 (31). Anal. Found: C, 80.23; H, 6.28; N, 4.14. Calcd for $C_{44}H_{41}CoN_2$: C, 80.47; H, 6.29; N, 4.27.

Di-*μ*-acetatobis[(*η*^{5}-(*S*)-(*$_p$R*)-2-(2′-(1′-{1-cyclohexylethyl}-imidazoyl)cyclopentadienyl,1-*C*,3′-*N*)(*η*^{4}-tetraphenylcyclobutadiene)cobalt]dipalladium, 7a. A solution of **6a** (0.241 g, 0.37 mmol) and $Pd(OAc)_2$ (0.082 g, 0.37 mmol) in glacial acetic acid (1 mL) was heated for 30 min at a temperature of 95 °C. After the resultant orange mixture had cooled to room temperature, it was diluted with cold glacial acetic acid (1 mL), and the product was isolated by filtration and washed with further glacial acetic acid (1 mL). After drying in vacuo, complex **7a** was obtained as an orange crystalline solid (0.229 g, 76%): mp 254−255 °C (decomp); $[\alpha]^{20}_D$ +133 (*c* 0.215, $CHCl_3$); ν_{max}/cm^{-1} (Nujol) 1577; δ_H (400 MHz, $CDCl_3$) 0.52 (d, *J* 6.7, 3H, C*H*$_3$), 0.45−1.62 (m, 11H, Cy), 2.06 (s, 3H, O$_2$CC*H*$_3$), 3.17 (pent, 1H, *J* 6.6, C*H*CH$_3$), 3.77 (t, *J* 2.4, 1H, Cp), 4.06 (d, *J* 2.0, 1H, Cp), 4.09 (d, *J* 2.0, 1H, Cp), 6.25 (d, *J* 1.5, 1H, imidazole), 6.28 (d, *J* 1.4, 1H, imidazole), 7.02−7.11 (m, 12H, Ph), 7.26−7.29 (m, 8H, Ph); δ_C {^{1}H} (100 MHz, $CDCl_3$) 15.7 (*C*H$_3$), 21.8 (O$_2$C*C*H$_3$), 23.1 (*C*H$_2$), 25.0 (*C*H$_2$), 25.3 (*C*H$_2$), 27.3 (*C*H$_2$), 28.2 (*C*H$_2$), 42.8 (*C*HCH$_2$), 56.9 (NH*C*H), 74.0 (*C*$_4$Ph$_4$), 81.4 (Cp), 83.7 (Cp), 88.9 (Cp), 97.1 (Cp), 111.8 (imidazole), 124.6 (Ph − para), 124.9 (imidazole), 126.8 (Ph), 127.7 (Ph), 135.5 (Ph − ipso), 148.5 (*C*═N), 179.7 (O$_2$*C*CH$_3$); *m*/*z* (APCI) 1643 (MH^+, 3%), 657 (18), 75 (100). Anal. Found: C, 66.90; H, 5.04; N, 3.08. Calcd for $C_{92}H_{86}Co_2N_4O_4Pd_2$: C, 67.28; H, 5.28; N, 3.41.

Catalysis Experiments. To a solution of the imidazole (0.61 mmol) in dry CH_2Cl_2 (8 mL) was added dimethylchlorophosphate (0.074 g, 0.066 mmol) followed by ethanol (0.028 g, 0.61 mmol). The resulting solution was stirred under nitrogen, and the progress of the reaction was monitored by removal of aliquots for examination by ^{1}H NMR (δ_H (400 MHz, $CDCl_3$) EtOH, 1.14 (t, *J* 7.0, 3H), 3.46 (q, *J* 7.0, 3H); EtOP(O)(OMe)$_2$, 1.27 (td, *J* 7.0, 0.8, 3H, −CH$_2$C*H*$_3$), 4.05 (pent, *J* 7.4, 2H, −C*H*$_2$-CH$_3$).

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Supporting Information Available: Text giving full characterization of **5b**, **6b**, **7b**, **8**, and **9**, and details of the X-ray structure determinations of **6a** and **7b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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