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A new paradigm in *N*-heterocyclic carbenoid ligands

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Abstract

We report a new class of very readily prepared chiral *N*-heterocyclic carbenoid ligand that also contains two different types of chirality: an asymmetric centre and an atropoisomeric unit, but contained in two separate N-substituents, such that both can easily be varied. In addition to its simplicity and flexibility, this approach has potential advantages over systems containing only atropoisomeric units, because the inclusion of an additional fixed asymmetric centre means that the atropoisomers are diastereoisomers and therefore chemically distinct entities. Complexation to a metal centre increases the barrier to rotation in the atropoisomeric unit so that the two diastereoisomers may be separable by simple methods such as standard chromatography. In addition, a novel *cis*-substituted palladium complex has been characterised by X-ray crystallography.

Keywords: Carbene; Benzimidazolylidene; Imidazolylidene; Atropoisomerism; Chirality; Asymmetry

1. Introduction

The use of *N*-heterocyclic carbenoid (NHC) ligands in organic and inorganic chemistry has grown exponentially over the last 10 years [1]. The majority of reactions have, however, been concerned with relatively simple achiral carbenes containing aniline-derived amine units. Several approaches to chiral carbene ligands have appeared over this time: for example Hermann [2] and Grubbs [3] have both employed chiral N-substituted imidazolium salts as a means of accessing enantiomerically enriched ligands and complexes. More recently, interest in the area of chiral *N*-heterocyclic carbene ligands has increased [4], but the preparation and use of chiral benzimidazolylidene examples remain rare (vide infra). Of particular relevance to this paper is Hoveyda's use of axial chirality in an *N*-heterocyclic carbene metal complex [5]; planar chiral elements have also been used [6]. We report here our initial findings regarding a new class of very readily prepared chiral *N*-heterocyclic carbenoid ligand that also contains two different types of chirality: an asymmetric centre and an atropoisomeric unit, but contained in two separate N-substituents, such that both can easily be varied. In addition to its simplicity and flexibility, this approach has potential advantages over systems containing only atropoisomeric units, because the inclusion of an additional fixed asymmetric centre means that the atropoisomers are diastereoisomers and therefore chemically distinct entities. We further conjectured that complexation to a metal centre might increase the barrier to rotation in the atropoisomeric unit so that the two diastereoisomers would in principle be separable by simple methods such as standard chromatography.

Diver has recently reported the use of C_2 symmetric carbenes based on a benzimidazole structure [7], and this prompts us to describe our own results in this area. Such a design of ligand is attractive because both of the enantiomers are in principle available, and because the ligands can be readily accessed through a short synthetic sequence; for example, the bis-α-methylbenzylamine-derived benzimidazolium salt **1** was easily prepared as shown in Schemes 1

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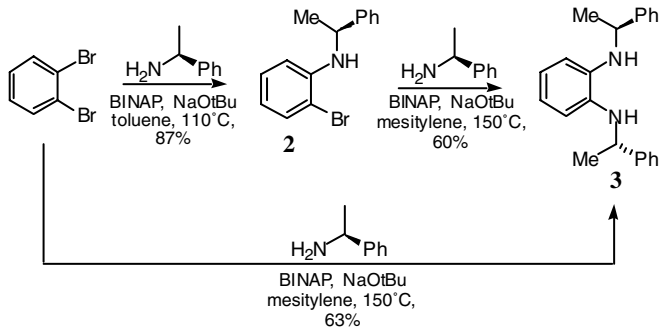


Scheme 1.

and 2. Nevertheless, an in situ double Buchwald–Hartwig coupling provided the diamine product in only 63% yield, and the use of two sequential Buchwald–Hartwig couplings proved frustrating as the second reaction consistently gave a lower yield than expected; reaction of (*S*)-α-methylbenzylamine with 1,2-dibromobenzene gave the monosubstituted product **2** in an excellent 87% yield, but attempts to introduce the second amine gave the desired product **3** in no more than a respectable 60% yield in our hands.

Generation of a palladium–carbene complex **4** was achieved by heating the imidazolium salt in the presence of $Pd_2(dba)_3$ under the conditions described by Faller and Crabtree (Scheme 2) [8]. Single crystal X-ray analysis (Fig. 1) showed that in this *trans* complex the two imidazolylidene rings are almost orthogonal to the central plane containing the Pd atom, and are close to coplanarity, in each case with the two benzyl substituents oriented so that their two phenyl groups project over opposite faces of the imidazolylidene ring. The phenyl groups of adjacent benzyl substituents in different imidazolylidene rings are also oriented to project towards different faces of the ring system.

We were interested to assess whether this unsatisfactory yield in the second coupling reaction was a function of steric interactions between the monosubstituted amine substrate and the nucleophile, or due to electronic factors. We therefore used a structurally very different amine, 2-isopropyl aniline, as the coupling partner. A fascinating additional possibility was the enhanced potential in this system for atropoisomerism in the imidazolium carbenoid as a result of hindered rotation around the new carbon–nitrogen

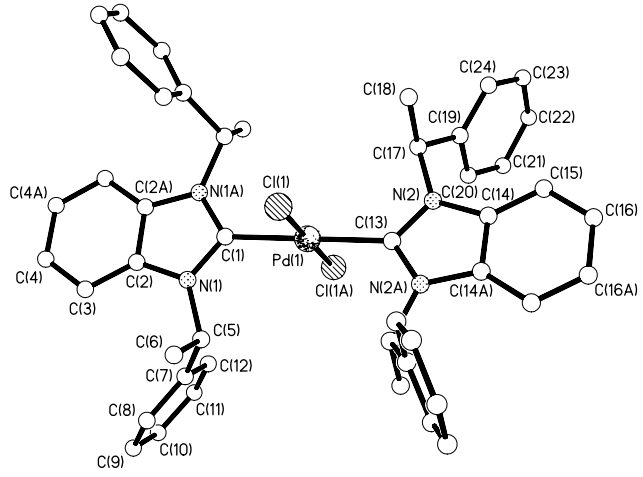
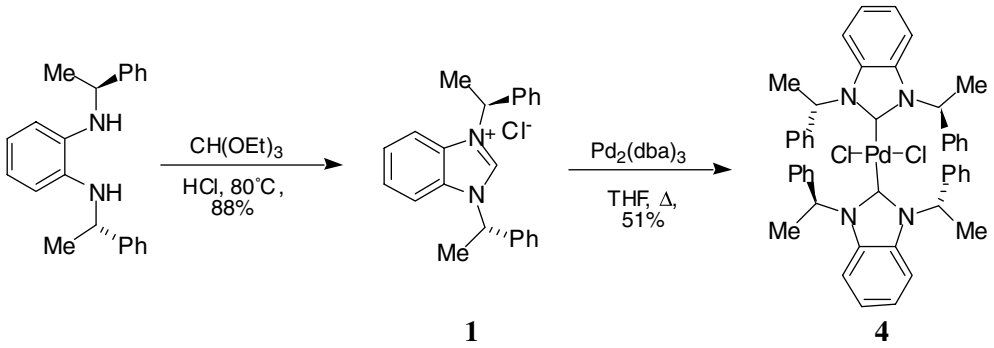


Fig. 1. Pd–carbene complex of the bis-α-methylbenzylamine-derived benzimidazolylidene **4** [9].

bond. We were intrigued to find that the second Buchwald–Hartwig coupling proceeded well with this substituted aniline, producing the differentially substituted bis-amine **5** in an excellent 95% yield. Insertion of the final carbon atom was achieved by reaction with triethyl orthoformate under acidic conditions, producing the benzimidazolium salt **6** in 84% yield (Scheme 3).

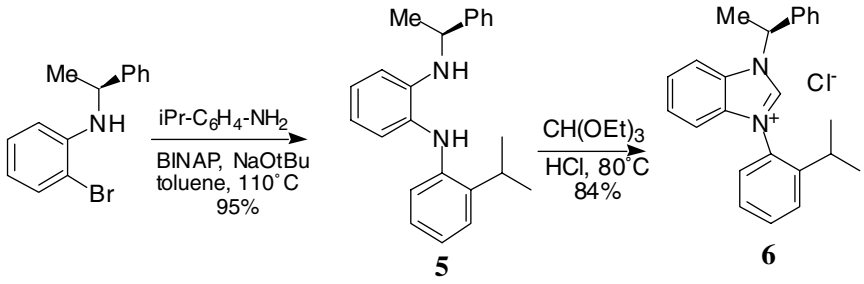
Examination of the benzimidazolium salt **6** by ^{1}H NMR spectroscopy at room temperature did indeed show two sets of signals corresponding to the presence of two isomers in an approximately 1:1 ratio. The distinct central benzimidazole proton signals at 10.892 and 10.833 ppm ($\delta\upsilon = 23.6$ Hz at 400 MHz) coalesce at 55 °C, which corresponds to an experimentally derived conformational barrier of $\Delta G^{\ddagger} = 68.8$ kJ mol^{-1} [10]. The two diastereotopic methyl signals of the isopropyl unit remained distinct at lower temperatures, only reaching near-coalescence at 115 °C, which corresponds to $\Delta G^{\ddagger} = 80$ kJ mol^{-1}. The relative energy difference between the two isomers was obtained using the classic Boltzman equation and the ratio of the two benzimidazole protons, giving $\Delta G = 0.5$ kJ mol^{-1}.

Nuclear Overhauser effect (nOe) experiments provided further evidence of this hindered rotation. Irradiation of the benzimidazole proton shows an enhancement in the



1 **4**

Scheme 2.



Scheme 3.

proton, methyl and phenyl group of the α-methyl benzylamine substituents, suggesting that this side chain is freely rotating at room temperature. The enhancement in the *o*-isopropylaryl group is, however, much more specific: the isopropyl methine proton is enhanced, but the methyl groups are very little affected, again suggesting that rotation around the aryl-isopropyl C–C bond is severely restricted (Fig. 2).

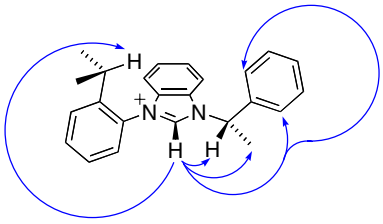


Fig. 2. The nOe enhancement in the differentially substituted benzimidazolium salt.

We thus attribute the lower conformational barrier to atropoisomerism by rotation about the C–N bond between the 2-isopropylphenyl group and the central heterocyclic ring (Fig. 1), and the higher rotational barrier to rotation about the isopropyl group C2–arene bond. This conclusion is supported by molecular modelling, which suggests a very high barrier (>49 kJ mol^{-1}, semi-empirical, AM1 level) in both cases [11]. Ab initio calculations at the UHF/6-31G* level for a fully optimized structure suggest that the 2-isopropylaniline group lies nearly orthogonal to the benzimidazole ring, with $\Delta G = 0.5$ kJ mol^{-1} between the two atropoisomeric structures (Fig. 3) [12].

With the carbene precursor **6** in hand, we next investigated the formation of metal complexes of the carbenoid ligand. Reaction with Pd(0) as before did indeed provide a palladium–carbene complex in 44% yield, and ^{1}H NMR spectroscopy at room temperature indicated the presence of a mixture of three conformational isomers in a 1:1:1 ratio (Scheme 4). The signals in the proton NMR

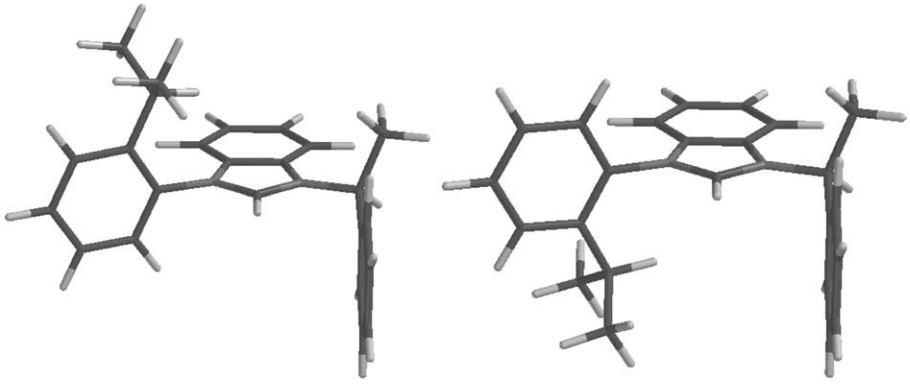
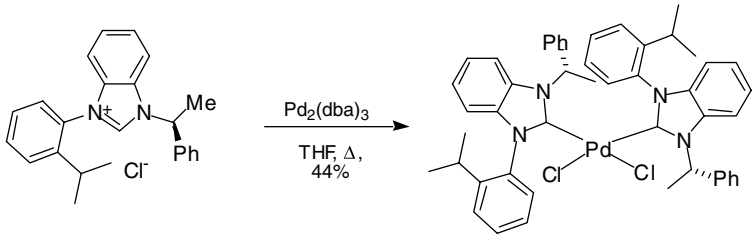


Fig. 3. Two conformations of the *o*-isopropropyl aryl group with respect to the benzimidazolium unit.



Scheme 4.

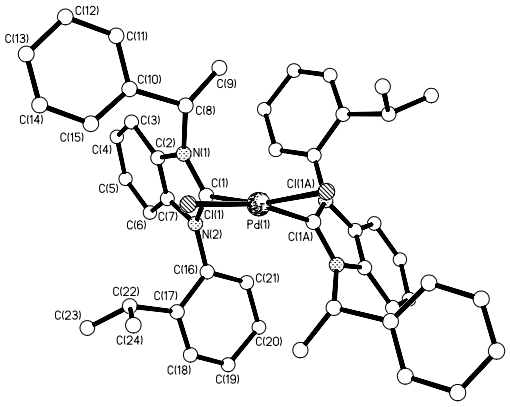


Fig. 4. Pd–carbene complex of the differentially substituted benzimidazolylidene **7** [14].

spectrum were unaffected by heating the sample, suggesting that the rotational barrier about the C–N bond is significantly greater than for the uncomplexed adduct, as a result of the large steric effect of the metal. However, selective recrystallization did provide a single complex **7** by ^{1}H NMR spectroscopy, and this was suitable for X-ray crystallographic analysis.

Single crystal X-ray analysis (Fig. 4) showed that this is, unexpectedly, a *cis* complex, most *cis* Pd complexes of *N*-heterocyclic carbenes having chelated structures [13]. The solid-state structure is C_2 symmetric, with the phenyl groups of the benzylamine units orientated away from the metal centre, and the methine protons of the isopropyl groups orientated towards the imidazolylidene moiety, as expected. The two imidazolylidene rings are not in this case orthogonal to the central plane containing the Pd atom.

We have in the past successfully prepared complexes of NHC ligands with cobalt alkyne complexes [15]. Application of this procedure using our new chiral ligand, by generation of the free carbene followed by reaction with the cobalt complex of diphenylacetylene, gave *two* new isomeric complexes in a 1:1 ratio, Scheme 5. Separation of these complexes by silica gel chromatography now proved possible, and ^{1}H NMR spectroscopy of the separated complexes indicates that the two complexes are indeed diastereoisomeric; we again attribute this to the presence of atropoisomers differentiated by rotation about the C–N bond.

In conclusion, we have prepared a new type of *N*-heterocyclic carbene ligand that contains two different types of chirality, an asymmetric centre and an atropoisomeric axis, contained in separate N-substituents that are readily varied. We believe this is the first time this has been achieved with a benzimidazole skeleton. A significant barrier to rotation results in two atropoisomeric diastereoisomers being produced, and this is carried forward into the resulting metal complexes. In addition, a novel *cis*-substituted palladium complex has been characterized by X-ray crystallography.

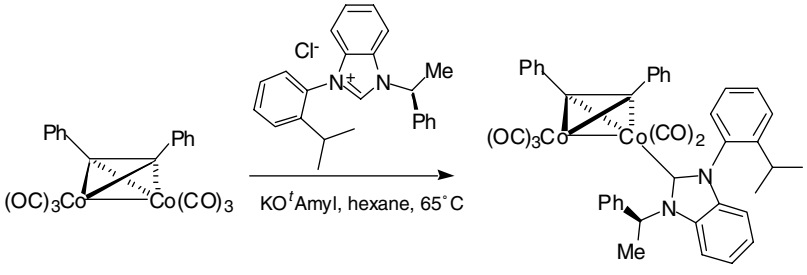
2. Experimental

2.1. (2-Bromophenyl)-(*S*)-α-methylbenzylamine (*2*)

$Pd_2(dba)_3$ (0.081 g, 0.088 mmol) and (±)-BINAP (0.11 g, 0.18 mmol) were dissolved in toluene (6 ml) and the solution degassed for 15 min before being heated at 110 °C for 10 min (solution turns from deep purple to dark orange). Upon cooling sodium *tert*-butoxide (0.43 g, 4.51 mmol), (*S*)-α-methylbenzylamine (0.67 g, 5.5 mmol) and 1,2-dibromobenzene (0.52 g, 2.2 mmol) were added and the reaction mixture heated under reflux for 1.5 h. The solution was allowed to cool and filtered through a pad of celite. Solvents were removed under reduced pressure and the crude material purified by column chromatography eluting with light petroleum/ethyl acetate (99:1). Colourless oil (0.53 g, 87%). ν_{max} (film)/cm^{-1} 3050, 2964, 1734, 1596, 1507, 1449, 1320, 1282, 1203, 1016, 741, 699, 665; δ_H (400 MHz; $CDCl_3$) 1.57 (3H, d *J* 6.8 Hz), 4.51 (1H, q, *J* 6.8 Hz), 6.29 (1H, dd, *J* 1.5 and 8.2 Hz), 6.42 (1H, dt, *J* 1.5 and 7.4 Hz), 6.89 (1H, dt, *J* 1.5 and 7.4 Hz), 7.12–7.16 (1H, m), 7.21–7.26 (4H, m), 7.32 (1H, dd, *J* 1.5 and 7.8 Hz); δ_C (100 MHz; $CDCl_3$) 25.2, 53.6, 109. 7, 112.7, 117.8, 125.8, 127.1, 128.4, 128.8, 132.3, 144.0, 144.6.

2.2. (+)-*N*- (2-Isopropylphenyl)-*N*′-(*S*)-α-methylbenzyl-1,2-diaminobenzene (*5*)

$Pd_2(dba)_3$ (0.081 g, 0.088 mmol) and (±)-BINAP (0.11 g, 0.18 mmol) were dissolved in mesitylene (6 ml) and the solution degassed for 15 min before being heated at 150 °C for 10 min (solution turns from deep purple to



Scheme 5.

dark orange). Upon cooling sodium *tert*-butoxide (0.43 g, 4.51 mmol), 2-isopropyl-phenylamine (0.74 g, 5.5 mmol) and (2-Bromo-phenyl)-(*S*)-α-methylbenzylamine (0.50 g, 2.2 mmol) were added and the reaction mixture heated at 150 °C for 12 h. The solution was allowed to cool and filtered through a pad of celite. Solvents were removed under reduced pressure and the crude material purified by column chromatography eluting with light petroleum/ethyl acetate (99:1). Yellow oil (0.69 g, 95%). $[\alpha]_D + 93.2$ (*c* 1.49, $CHCl_3$); ν_{max} (film)/cm^{-1} 3060, 2960, 1598, 1511, 1450, 1322, 1277, 1307, 745, 700; δ_H (400 MHz; $CDCl_3$) 1.33 (3H, d, *J* 6.8 Hz), 1.35 (3H, d, *J* 6.8 Hz), 1.43 (3H, d, *J* 6.4 Hz), 3.12 (1H, sep, *J* 6.8 Hz), 4.30–4.70 (1H, m), 6.61–6.70 (1H, m), 6.46–6.56 (1H, m), 6.60–6.68 (2H, m), 6.87–6.93 (2H, m), 6.96 (1H, dd, *J* 1.2 and 7.6 Hz), 7.07 (1H, dt, *J* 1.6 and 8.0 Hz), 7.16–7.40 (6H, m); δ_C (100 MHz; $CDCl_3$) 22.7, 23.0, 27.6, 31.6, 53.5, 112.6, 116.2, 117.5, 120.3, 124.6, 125.5, 125.9, 126.6, 127.2, 128.6, 128.7, 129.2, 134.9, 135.0, 142.5, 142.7; *m*/*z* (ES^+) 330 (M^+ 100%), 225 (24%) 208 (71%), 105 (100%); 330.2091; $C_{23}H_{26}N_2$ requires 330.2096.

2.3. (+)-N,N′-bis-(S)-α-Methylbenzyl-1,2-diaminobenzene (3)

$Pd_2(dba)_3$ (0.036 g, 0.04 mmol) and (±)-BINAP (0.05 g, 0.08 mmol) were dissolved in mesitylene (6 ml) and the solution degassed for 15 min before being heated at 150 °C for 10 min (solution turns from deep purple to dark orange). Upon cooling sodium *tert*-butoxide (0.39 g, 4.0 mmol), (*S*)-α-methyl benzylamine (0.61 g, 5.0 mmol) and 1,2-dibromobenzene (0.26 g, 1.0 mmol) were added and the reaction mixture heated under reflux for 16 h. The solution was allowed to cool and filtered through a pad of celite. Solvents were removed under reduced pressure and the crude material purified by column chromatography eluting with light petroleum/ethyl acetate (99:1). Yellow oil (0.20 g, 63%). $[\alpha]_D + 177.6$ (*c* 0.94 $CHCl_3$), (lit.[7] $[\alpha]_D + 182$ (*c* 0.76 $CHCl_3$); ν_{max} (film)/cm^{-1} 3054, 2962, 2865, 1597, 1508, 1490, 1443, 1432, 738, 699; δ_H (250 MHz; $CDCl_3$) 1.59 (6H, d *J* 6.7 Hz), 4.49 (2H, q, *J* 6.5 Hz), 6.42–6.46 (2H, m), 6.55–6.59 (2H, m), 7.22–7.42 (10H, m); δ_C (100 MHz; $CDCl_3$) 25.4, 53.5, 113.7, 118.8, 125.8, 126.6, 128.7, 136.3, 145.4.

2.4. (+)-N,N′-bis-(S)-α-Methylbenzyl benzimidazolium chloride (1)

(+)-*N*,*N*′-Bis-(*S*)-α-methylbenzyl-1,2-diaminobenzene (0.30 g, 0.95 mmol) was dissolved in $CH(OEt)_3$ (10 ml), and 12.1 N HCl (0.08 ml, 0.95 mmol) added dropwise over 5 min. The resulting solution was stirred at room temperature for 30 min under nitrogen and then heated to 80 °C until condensation was observed on the neck of the flask. At this point the rubber septum was removed and the solution was allowed to stir open to the air for 2 h. After cooling to room temperature, the suspension obtained was diluted with diethyl ether (30 ml) and filtered. The off white solid obtained was washed with diethyl ether and the residual solvents removed under high reduced pressure. Colourless powder (0.30 g, 88%). M.p. 241.4–243.7 °C, (lit.[7] 242–243 °C); $[\alpha]_D + 22.9$ (*c* 1.07, MeOH), (lit.[7] $[\alpha]_D + 24.0$ (*c* 1.0 MeOH); ν_{max} (film)/cm^{-1} 3026, 2988, 2945, 2904, 1546, 1442, 1385, 1242, 750, 703; δ_H (250 MHz; $CHCl_3$) 2.45 (6H, d, *J* 7.2 Hz), 6.30 (2H, q, *J* 7.0 Hz), 7.30–7.45 (10H, m) 7.50–7.57 (4H, m), 12.46 (1H, s); δ_C (100 MHz; $CHCl_3$) 20.9, 59.5, 114.5, 126.7, 126.8, 128.2, 129.7, 133.1, 135.0, 142.7; *m*/*z* (FAB^+) 327 (M^+ 100%), 223 (14%), 119 (59%), 105 (85%); 327.1861; $C_{24}H_{25}N_2$ (cation) requires 327.1861.

2.5. (−)-(S)-3-(2-Isopropylphenyl)-1-(S)-α-methylbenzylbenzimidazolium chloride (6)

(+)-*N*-(2-Isopropyl-phenyl)-*N*′-(*S*)-α-methylbenzyl-1,2-diaminobenzene (0.50 g, 1.5 mmol) was dissolved in $CH(OEt)_3$ (10 ml), and 12.1 N HCl (0.12 ml, 1.5 mmol) added dropwise over 5 min. The resulting solution was stirred at room temperature for 30 min under nitrogen and then heated to 80 °C until condensation was observed on the neck of the flask. At this point the rubber septum was removed and the solution was allowed to stir open to the air for 2 h. After cooling to room temperature, the suspension obtained was diluted with diethyl ether (30 ml) and filtered. The off white solid obtained was washed with diethyl ether and the residual solvents removed under high reduced pressure. Colourless powder (0.475 g, 84%). M.p. 178.3–180.1 °C; $[\alpha]_D$ −30.6 (*c* 1.15, $CHCl_3$); ν_{max} (film)/cm^{-1} 3050, 2964, 1614, 1547, 1493, 1421, 1327, 1276, 1203, 1079, 1030, 753, 729, 703; δ_H (400 MHz; DMSO 100 °C, mixture of isomers) 1.05 (6H, d, *J* 6.8 Hz), 2.10 (3 H, d, *J* 7.2 Hz), 2.40–2.60 (1H, m), 6.31 (1H, q, *J* 6.4 Hz), 7.32–7.41 (4H, m), 7.45–7.56 (3 H, m), 7.58–7.74 (5 H m), 7.84–8.20 (1H, m), 10.46 (1H, s); δ_C (100 MHz; $CDCl_3$, mixture of isomers) 19.8, 20.4, 23.3, 24.5, 24.6, 28.4, 28.5, 58.3, 113.4, 113.5, 114.8, 115.0, 127.05, 127.09, 127.11, 127.15, 127.47, 127.50, 127.55, 127.66, 127.84, 127.90, 128.04, 128.24, 129.00, 129.10, 129.34, 129.38, 129.78, 129.89, 129.92, 129.98, 132.04, 132.06, 137.3, 137.4, 145.51, 145.57. ; *m*/*z* (ES^+) 341 (M^+ 45%), 238 (60%), 237 (100%), 105 (75%); 341.2009; $C_{24}H_{25}N_2$ (cation) requires 341.2012.

2.6. (−)-bis-[N,N′-bis-(S)-α-Methylbenzyl-benzimidazolylidene] palladium dichloride (4)

$Pd_2(dba)_3$ (0.136 g, 0.15 mmol) was dissolved in THF (10 ml) under a nitrogen atmosphere, and (+)-*N*,*N*′-Bis-(*S*)-α-methylbenzylbenzimidazolium chloride (0.095 g, 0.26 mmol) added. The reaction mixture was heated under reflux for 3 h, allowed to cool to room temperature, and a scoop of silica added. The solvent was removed under reduced pressure to give the reaction mixture adsorbed onto silica. Column chromatography eluting with

dichloromethane/light petroleum (5:1) gave the product as a colourless solid. Recrystallized from dichloromethane/light petroleum, colourless crystals (0.053 g, 51%). M.p. 273.1 °C (dec.); $[\alpha]_D$ –344.6 (*c* 0.91, $CHCl_3$); ν_{max} (film)/cm^{-1} 3057, 3030, 2975, 1605, 1495, 1448, 1396, 1379, 1282, 1079, 1056, 741, 700; δ_H (250 MHz; $CHCl_3$) 2.07 (12H, d, *J* 7.2 Hz), 6.75–6.85 (8H, m), 7.20–7.40 (12H, m), 7.45 (4H, q, 7.0 Hz), 7.65–7.69 (8H, m); δ_C (100 MHz; $CHCl_3$) 17.8, 59.1, 112.7, 122.11, 127.6, 127.8, 128.7, 133.2, 139.1, 182.0.

2.7. (−)-bis-N-(2-Isopropyl-phenyl)-N′-(S)-α-methylbenzyl-1,2-diamino-benzimidazolylidene palladium dichloride (7)

$Pd_2(dba)_3$ (0.07 g, 0.08 mmol) was dissolved in THF (10 ml) under a nitrogen atmosphere, and (+)-*N*,*N*′-Bis-(*S*)-α-methylbenzylbenzimidazolium chloride (0.05 g, 0.14 mmol) added. The reaction mixture was heated under reflux for 3 h, allowed to cool to room temperature, and a scoop of silica added. The solvent was removed under reduced pressure to give the reaction mixture adsorbed onto silica. Column chromatography eluting with dichloromethane/light petroleum (5:1) gave the product as a colourless solid. Recrystallized from dichloromethane/light petroleum, colourless crystals (0.05 g, 44%). M.p. 284.3 °C (dec.); $[\alpha]_D$ –139.7 (*c* 0.73, $CHCl_3$); ν_{max} (film)/cm^{-1} 3060, 2960, 1603, 1490, 1448, 1380, 1284, 1067, 1031, 745, 665; δ_H (400 MHz; $CHCl_3$) 0.75 (6H, d, *J* 6.9 Hz), 1.06 (6H, d, 7.2 Hz), 1.59 (6H, d, 6.7 Hz), 3.11 (2H, quin, 6.5 Hz), 6.02 (2H, dd, *J* 0.8 and 7.6 Hz), 6.46 (2H, dt, 1.2 and 7.6 Hz), 6.52 (2H, d, 8.0 Hz), 6.65 (2H, d, *J* 8.0 Hz), 6.75 (2H, d, *J* 8.8 Hz), 7.14–7.28 (8H, m), 7.34–7.37 (4H, m), 7.44 (2H, t, *J* 7.6 Hz), 7.67 (2H, dd, *J* 1.2 and 7.6 Hz), 7.72 (2H, q, *J* 7.2 Hz); δ_C (100 MHz; $CHCl_3$) 23.9, 24.3, 27.9, 53.4, 59.0, 111.1, 113.6, 123.3, 123.4, 126.1, 126.4, 127.4, 128.1, 128.9, 130.9, 131.9, 134.6, 137.6, 137.5, 139.3, 149.3, 172.4; *m*/*z* (FAB^+) 820 (5%), 784 (6%), 445 (6%), 339 (100%), 235 (75%), 105 (93%); 820.2629; $C_{48}H_{48}N_4PdCl$ ($M^+ - Cl$) requires 820.2618.

2.8. Dicobaltpentacarbonyl-3-(2-isopropylphenyl)-1-(S)-α-methylbenzyl-benzimidazolium–diphenylacetylene

(+)-*N*,*N*′-Bis-(*S*)-α-methylbenzylbenzimidazolium chloride (0.074 g, 0.19 mmol) was dissolved in hexane (10 ml) under a nitrogen atmosphere, and potassium-*tert*-pentoxide (0.22 ml, 0.38 mmol) (25% solution in toluene) added dropwise. The resulting solution was stirred for 30 min at room temperature. Dicobalt hexacarbonyl-diphenylacetylene (0.176 g, 0.38 mmol) was then added as a solid. The solution was then heated to 65 °C for 40 min. The solution was then filtered through a pad of celite and silica, and then solvent was removed under reduced pressure. Column chromatography eluting with diethyl ether/light petroleum (5:95) gave the product as a dark purple liquid. Two separate diastereoisomers (1:1) (0.103 g, 68% combined yield); ν_{max} (film)/cm^{-1} 3089, 2963, 2925, 2869, 2052, 2003, 1990, 1955, 1712, 1600, 1494, 1261, 1025, 691;

2.9. First eluting diastereoisomer

δ_H (400 MHz; $CDCl_3$) 1.07 (3H, d, *J* 6.8 Hz), 1.31 (3H, d, *J* 6.8 Hz), 1.74 (3H, d, *J* 6.8 Hz), 2.26 (1H, sept, *J* 6.8 Hz), 6.29 1H, (q, *J* 6.8 Hz), 6.4–6.48 (1H, m), 6.50–6.76 (4H, m), 6.95–7.04 (3H, m), 7.09–7.16 (4H, m), 7.20–7.28 (3H, m), 7.30–7.39 (2H, m), 7.52–7.57 (4H, m); δ_C (100 MHz; $CDCl_3$); 18.8, 23.4, 23.9, 29.0, 58.4, 86.4, 89.5, 111.3, 112.6, 122.1, 122.4, 125.8, 125.9, 126.2, 126.7, 127.3, 127.4, 128.0, 128.1, 128.2, 128.9, 129.7, 129.8, 130.5.

2.10. Second eluting diastereoisomer

δ_H (400 MHz; $CDCl_3$; 1.05 (3H, d, *J* 6.8 Hz), 1.23 (3H, d, *J* 6.8 Hz), 1.24 (3H, d, *J* 6.8 Hz), 2.20 (1H, sept, *J* 6.8 Hz), 6.02 (1H, m), 6.44 (1H, q, *J* 6.8 Hz), 6.51–6.63 (1H, m), 6.71–6.99 (5H, m), 7.01–7.12 (2H, m), 7.13–7.34 (8H, m), 7.37–7.63 (5H, m); δ_C (100 MHz; $CDCl_3$); 18.0, 32.1, 23.5, 27.9, 58.5, 85.1, 87.9, 112.0, 112.2, 122.2, 122.4, 125.2, 125.6, 126.0, 126.9, 127.0, 127.1, 127.8, 128.0, 128.3, 129.0, 129.4, 129.5, 130.2.

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