Synthesis and crystal structures of the first C_2-symmetric bis-aldimine NCN–pincer complexes of platinum and palladium

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Abstract

(S,S)-2,6-bis[(N-α-methylbenzyl)imino]phenylpalladium bromide was synthesised by oxidative addition of palladium(0) to (S,S)-1-bromo-2,6-bis[(N-α-methylbenzyl)imino]benzene. In contrast, (S,S)-2,6-bis[(N-α-methylbenzyl)imino]phenylplatinum chloride was synthesised by direct C–H activation from the reaction of potassium tetrachloroplatinate with (S,S)-1,3-bis[(N-α-methylbenzyl)imino]benzene. The X-ray crystal structures of both pincer complexes were obtained. Treatment of both complexes with silver hexafluoroanimonate gave effective but not stereoselective catalysts for a Michael reaction between methyl vinyl ketone and methyl 2-cyanopropanoate.
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Keywords: Pincer complex; NCN; Platinum; Palladium; Catalysis; Aldimine

1. Introduction

Nitrogen donor pincer complexes are of increasing interest in materials and chemical science. Complexes of general formulas **1**–**3** have been used in applications ranging from gas sensing to asymmetric catalysis [1–16]. The most promising NCN–pincer chiral catalysts consist of an sp^2 central carbon ligand flanked by heterocyclic ligands (oxazolines [11] and bis-pyrroloimidazolone [7]), where nitrogen may be either sp^2 or sp^3 hybridised. To the best of our knowledge, chiral non-heterocyclic, all sp^2 donor NCN–pincer complexes are unreported. In this note we report the first chiral bis-aldimine NCN–pincer complexes (see Fig. 1).

2. Results and discussion

Iso-structural palladium and platinum halide complexes of α-methylbenzylamine derived imines were prepared by different procedures. Demonstrating the utility of Echaverran's direct platination protocol [17] that we adopted for the synthesis of non-chiral NCN bis-iminyl [18] and bis-oxazolinyl platinum complexes [19,20], the platinum complex **3b** is available in only two steps from commercially available starting materials. In contrast, the palladium complex **3a** required the synthesis of a more synthetically demanding 1,2,3-trisubstituted benzene **4a**.

2-Bromoisophthalaldehyde **4a** or commercially available isophthalaldehyde **4b** were converted to the corresponding aldimines **6a/b** by reaction with (S)-α-methylbenzylamine **5** in ethanol heated at reflux (Scheme 1). Addition of Pd$_2$(dba)$_3$ to bis-aldimine **6a** resulted in oxidative addition of palladium(0) to give the palladium(II) pincer complex **3a**. In contrast, heating at reflux a mixture of **6b** and potassium tetrachloroplatinate in dry acetic acid afforded the corresponding platinum(II) pincer complex **3b**.

Slow diffusion of hexane into ethyl acetate solutions of **3a** and **3b**, with no particular precautions regarding air or moisture exclusion, readily provided X-ray crystallographic quality crystal of palladium and platinum complexes **3a** and **3b**, Figs. 2 and 3.

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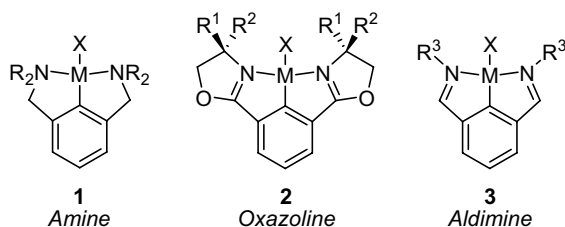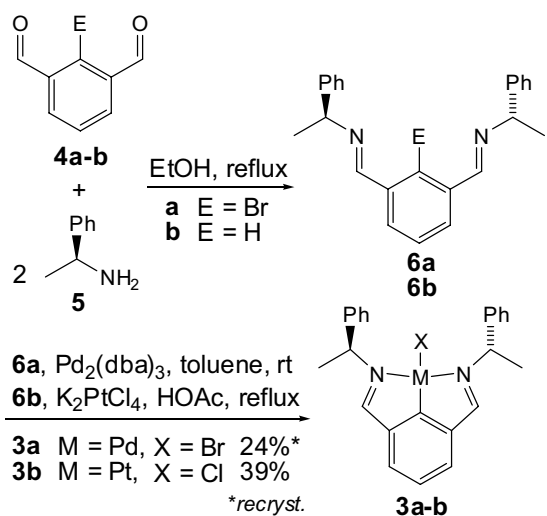 *E-mail address:* j.fossey@bath.ac.uk (J.S. Fossey).

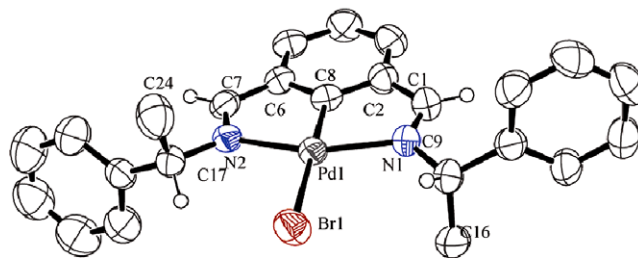Fig. 1. General formula for three classes of Group 10 NCN–pincer complexes.

Fig. 2. Representation of the crystal structure of **3a** (hydrogens adjacent to nitrogen included for clarity). See Table 1 for representative bond lengths, angles and torsions.

The X-ray diffraction data for **3a** and **3b** show the solid state structures to be essentially identical. In both cases the chiral *arms* of the ligand are rotated in such a manner to present the proton towards the halide (see Table 1).

A small but distinct difference between the two iso-structural complexes is observed on comparison of their NMR spectra. The aldimine ^{1}H and ^{13}C NMR signals for **3a** are 7.65 and 172.2 ppm, respectively, for **3b** these signals are at 7.79 and 182.2 ppm. In this case, the aldimine serves as a useful NMR handle allowing direct comparison between the two complexes, and suggests the platinum complex as being more Lewis acidic than its palladium congener.

Clearly the expeditious direct platination of 1,3-substituted bis-imines with K_2PtCl_4 provides access to the pincer architecture with considerably more ease than the oxidative addition route required for the synthesis of the palladium derivative. We have previously discussed the merits and contradictory evidence surrounding palladation *versus* platination in a number of systems [20]. In our hands direct palladation *via* C–H activation failed to give bis-iminyl pincer complexes, consistent with the findings of Echavarren for bis-pyridyl systems [17].

Taking the crystallographic structures as starting coordinates for compounds **3a** and **3b**. These structures were examined using DFT to investigate the energy required to rotate the pendant arms of the compounds. GAUSSIAN03 [21] was employed for the study using the DFT functional B3LYP [22–25] with the LANL2DZ basis set [26–29]. The structures were initially minimised without constraint and verified through vibrational frequency analysis, after which the relevant orbitals were examined. As can be seen within Fig. 4, the HOMO is sited principally upon the halide ion, whilst the LUMO is centred more on the metal–ligand complex.

3. Catalysis

Michael reactions employing α-cyanocarboxylates as nucleophiles have been shown to proceed in high yields with modest asymmetric induction catalysed by a number of chiral cationic NCN–pincer complexes [16]. Notably recent reports of Takenaka et al. have pushed the bench mark up to 83% ee when these reactions are catalysed by their bis-pyrroloimidazolone NCN palladium pincer complexes [7,30].

We were interested to see how our chiral imine pincers fair in asymmetric catalysis particularly in the reaction of most interest to us, the Michael reaction given in Scheme 2. Whilst halide abstraction gave active catalysts for the model asymmetric Michael reaction we have studied previously, racemic products were obtained (quantitative conversion), Scheme 2 [11,12].

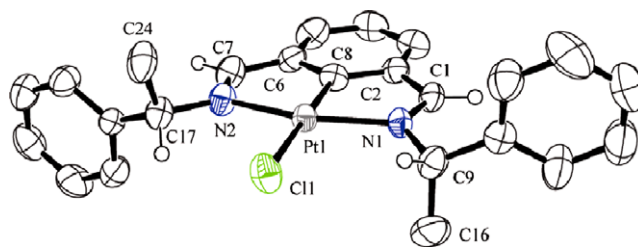Scheme 1. Synthesis of palladium and platinum bis(aldimine) NCN–pincer complexes.

Fig. 3. Representation of the crystal structure of **3b** (hydrogens adjacent to nitrogen included for clarity). See Table 1 for representative bond lengths, angles and torsions.

Table 1
X-ray crystallographic data summary for compounds **3a** and **3b**

	3a (M = Pd, X = Br)	**3b** (M = Pt, X = Cl)
Molecular formula	$C_{24}H_{23}BrN_2Pd$	$C_{24}H_{23}ClN_2Pt$
Formula weight	525.78	569.98
Crystal system	Orthorhombic	Orthorhombic
Space Group	$P2_12_12_1$	$P2_12_12_1$
Cell lengths		
a	11.157(3)	10.966(2)
b	13.7956(15)	13.945(2)
c	14.313(2)	13.963(3)
Z	4	4
C(8)–M(1) (Å)	1.910(4)	1.901(7)
M(1)–X(1) (Å)	2.5278(6)	2.397(2)
N(1)–M(1) (Å)	2.071(3)	2.027(5)
N(2)–M(1) (Å)	2.054(3)	2.049(6)
N(1)–C(1) (Å)	1.275(5)	1.287(9)
N(2)–C(7) (Å)	1.286(5)	1.282(10)
M(1)–N(1)–C(9) (°)	123.5(2)	121.4(6)
M(1)–N(2)–C(17) (°)	123.2(2)	123.6(5)
C(2)–C(1)–N(1)–C(9) (°)	+175.08	+172.14
C(6)–C(7)–(N2)–C(17) (°)	+172.12	+175.67
C(1)–N(1)–C(9)–C(16) (°)	−101.60	−93.24
C(7)–(N2)–C(17)–C(24) (°)	−93.79	−100.09

An explanation for the lack of stereocontrol is provided by Graph 1 which shows the calculated relative energies between the structures' dihedral angles M(1)–N(1)–C(9)–H(9) for **3a** and **3b** (M = Pd and Pt, respectively *cf* Figs. 2 and 3) when rotated through fixed degrees, with the rest of the structure freely optimised. Both **3a** and **3b** display essentially identical profiles. It can be seen that the two minima place both of the 'smaller' functional groups (methyl and proton) gauche to the halide. The energy difference between the two minima in both **3a** and **3b** is small (*circa* 6.0 and 9.5 kJ mol^{-1}, respectively) and that the barrier to inter-conversion between these two minima is 24.0 and 26.0 kJ mol^{-1}, respectively, thus these two rotomers are able to inter-convert with relative ease. Conversely to rotate the ancillary phenyl rings past the halide a barrier of over 55 kJ mol^{-1} would need to be overcome, which is thermally inaccessible. It is also noteworthy that variation of this torsion angle results in little change of the minimised structure of the other half of the molecule.

The LUMO of the cationic aquo-platinum complex (the *in situ* catalyst) has a high coefficient on the metal (Fig. 5) consistent with enhanced ligand exchange rate (H_2O *versus* chloride **3b**) whilst the pincer ligand architecture is unaffected.

Computational data in conjunction with the crystallographic observations suggests conformational flexibility (when extrapolated to solution phase) lies at the root of the poor selectivity displayed in the catalytic Michael reaction. Although disappointed that no asymmetric induction was observed in these trial reactions, we provided a rationale for this and are pleased to note that the reaction proceed with only 2 mol% catalyst. Our future efforts will focus on generating more suitable chiral pockets about

the site of interest for catalysis. Cyclic ketimines, ancillary donors and hydrogen bonding domains are reasoned to aid asymmetric induction [7,30], owing to the versatility of the catalyst synthesis they will receive attention in due course.

4. Experimental

General: Cyclometallation reactions were performed under an atmosphere of dry nitrogen employing standard Schlenk techniques. Disopropylethylamine was distilled form KOH, glacial acetic acid of 99.8% purity was distilled from Ac_2O/P_2O_5 under nitrogen [31], dichloromethane was distilled from calcium hydride under nitrogen and toluene was distilled from molten sodium under nitrogen and was freeze-thaw-degassed. Other solvents employed were not specifically dried. Column chromatography was performed on (silica) SiO_2 (40–63 μm). Coupling to ^{195}Pt ($^xJ_{Pt}$) in NMR spectrums is reported as the 34% component of the peak. Compounds **4a** and **7** were prepared by the literature procedures [32–34]. NMR data for **9** matched previously reported data [32].

4.1. (S,S)-1,3-Bis[(N-α-methylbenzyl)imino]-2-bromobenzene (**6a**)

2-Bromoisophthaldehyde (0.69 g, 2.64 mmol) and (S)-α-methylbenzylamine (0.4 mL, 3.09 mmol) were heated at reflux in absolute ethanol (50 mL) for 30 min. The volume of solvent was reduced *in vacuo* to approximately 10 mL and cooled, a colourless solid allowed to crystallise and this was collected by filtration to give **6a** (0.42 g, 38% recrystallised yield). Mp 95 °C; IR (v_{max}; thin film) 1631 (C=N) cm^{-1}; ^1H NMR (δ; 400 MHz, CDCl$_3$) 1.53 (6H, d, *J* 6.6, C*H*$_3$), 4.58 (2H, q, *J* 6.6, C*H*CH$_3$), 7.19 (1H, t, *J* 6.6, Ar
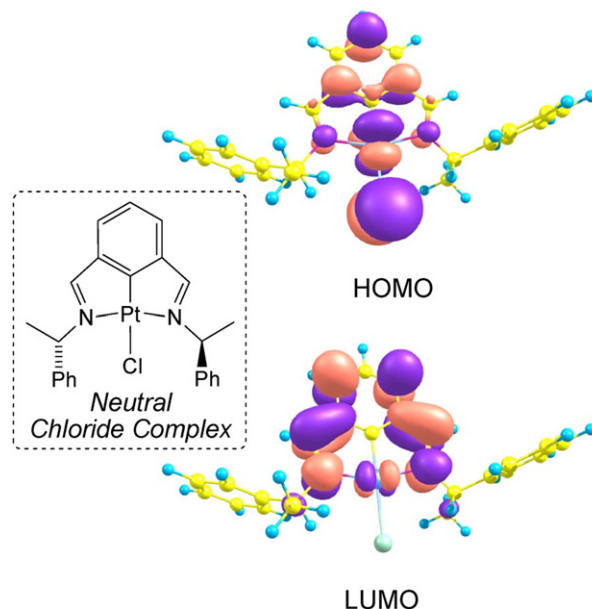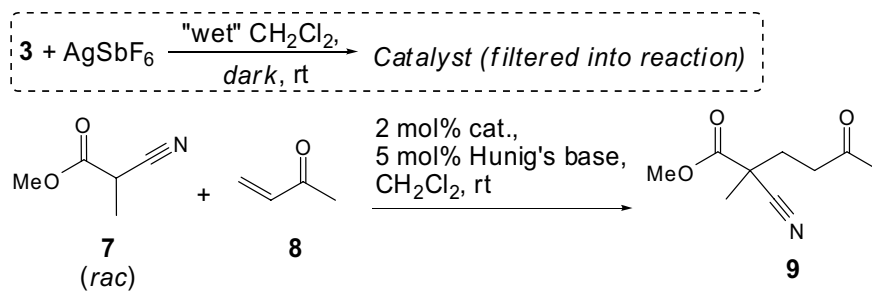

HOMO

LUMO

Fig. 4. Representation of the HOMO and LUMO for **3a**.

Scheme 2. Activation by halide abstraction and asymmetric catalysis trial.

5-H), 7.30 (6H, m, Ar, Ph), 7.38 (4H, d, J 7.6, Ar CH), 8.01 (2H, d, J 7.6, Ar, CH), 8.76 (2H, s, C=N); ^{13}C{^{1}H} NMR (δ; 100 MHz, CDCl$_3$) 27.4 (CH_3), 72.4 (CH$_3$CH), 128.4 (Ar C), 129.1 (Ar C), 129.5 (Ar C), 130.0 (Ar C), 131.0 (Ar C), 133.7 (Ar C), 137.8 (Ar C), 147.3 (Ar C), 160.9 (N=C); MS (m/z; FAB) 419 (M + H, 74%). High-resolution MS (m/z, FAB): Found for M + H 419.1110. C$_{24}$H$_{24}$BrN$_2$ requires 419.1123. $[\alpha]_D^{20}$ − 52 (c 0.001, CHCl$_3$).

4.2. (S,S)-1,3-Bis[(N-α-methylbenzyl)imino]benzene (6b)

Isophthalaldehyde (13.4 g, 0.1 mol) and (S)-α-methyl-benzylamine (26.25 g, 0.22 mol) were heated at reflux in absolute ethanol (400 mL) for 45 min. The solvent was removed *in vacuo* and the residue rapidly filtered through a short plug of silica eluting with ethyl acetate, followed by solvent removal *in vacuo* to give **6b** as a colourless solid (33.88 g, >99% yield). Mp 81 °C; IR (ν_{max}; thin film) 1643 (N=C) cm^{-1}; ^{1}H NMR (δ; 400 MHz, CDCl$_3$) 1.50 (6H, d, J 6.7, CH_3), 4.46 (2H, q, J 6.6, CH$_3$CH), 7.16 (2H, t, J 6.5, Ar, Ph), 7.26 (4H, t, J 7.5, Ar, Ph), 7.32–7.35 (5H, m, Ar), 7.77 (2H, dd, J 7.5 and 1.0, Ar, 3- and 5-H), 8.15 (1H, s, Ar, 1-H), 8.32 (2H, s, C=N); ^{13}C{^{1}H} NMR (δ; 100 MHz, CDCl$_3$) 25.2 (CH_3), 70.2 (CH$_3$CH), 127.1 (Ar C), 127.3 (Ar C), 128.8 (Ar C), 128.9 (Ar, C), 129.2 (Ar C), 130.5 (Ar C), 137.2 (Ar, 3- and 5-C), 145.4 (Ar, 1-C), 159.5 (N=C); MS (m/z; FAB) 341 (M + H, 76%). High-

resolution MS (m/z, FAB): Found for M + H 341.2010. C$_{24}$H$_{25}$N$_2$ requires 341.2018. $[\alpha]_D^{20}$ − 38 (c 0.02, CHCl$_3$).

4.3. (S,S)-2,6-Bis[(N-α-methylbenzyl)imino]phenyl-palladium bromide (3a)

Pd$_2$(dba)$_3$ (0.26 g, 0.28 mmol) was dissolved in freshly distilled toluene (65 mL), with **6a** (0.196 g, 0.47 mmol). The reaction mixture was freeze-thaw-degassed and stirred at room temperature under nitrogen for 60 h. After removal of the solvent *in vacuo*, the black/yellow residue was taken up in dichloromethane and filtered through silica eluting with more dichloromethane. The solvent was removed *in vacuo* and the yellow residue triturated with hexane to remove dba (which was confirmed by ^{1}H and ^{13}C NMR spectroscopy). The yellow residue was recrystallised (slow diffusion of hexane into an ethyl acetate solution) to give **3a** as a crystalline yellow solid suitable for X-ray diffraction analysis (0.059 g, 24% recrystallised yield). Mp 195 °C; IR (ν_{max}; CH$_2$Cl$_2$) 1650 (C=N) cm^{-1}; ^{1}H NMR (δ; 400 MHz, CDCl$_3$) 1.77 (6H, d, J 6.9, CH_3), 5.73 (2H, q, J 6.7, CH$_3$CH), 6.93 (1H, dd, J 7.02 and 7.98, Ar, 4-H), 7.03 (2H, d, J 7.8, Ar, 3- and 5-H), 7.28–7.50 (10H, m, Ar, Ph), 7.65 (2H, s, N=CH); ^{13}C{^{1}H} NMR (δ; 100 MHz, CDCl$_3$) 21.3 (CH_3), 66.3 (CH$_3$CH), 124.4 (Ar C), 127.3 (Ar C), 128.7 (Ar C), 129.0 (Ar C), 129.3 (Ar C), 139.8 (Ar, 2- and 6-C), 144.1 (Ar, 1-C),
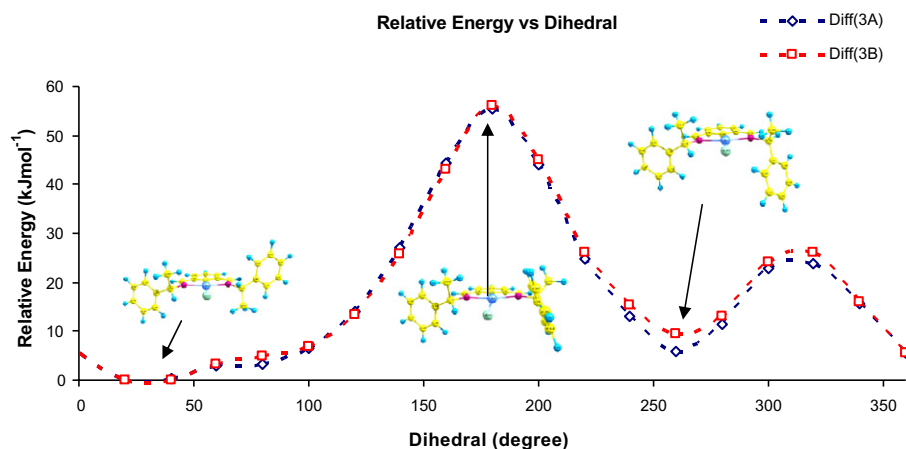
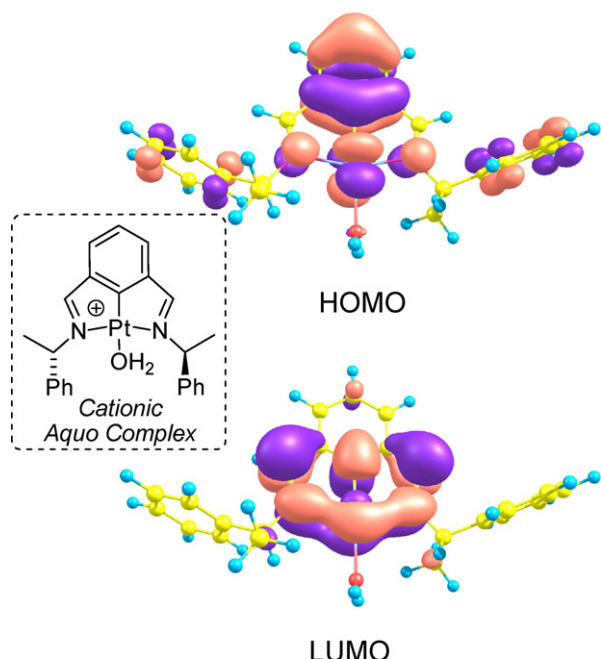Graph 1. Relative energy *vs.* dihedral angle M(1)–N(1)–C(9)–H(9) for **3a** and **3b** (M = Pd and Pt, respectively).

Fig. 5. Representation of the HOMO and LUMO for a cationic platinum aquo complex.

172.2 (N=C*H*); MS (*m/z*; APCI) 444.0 (M$^+$, 100%). $[\alpha]_D^{20}$ + 87 (*c* 0.001, CHCl$_3$).

4.4. *(S,S)-2,6-Bis[(N-α-methylbenzyl)imino]-phenylplatinum chloride (3b)*

K$_2$PtCl$_4$ (0.26 g, 0.63 mmol) was suspended in freshly distilled acetic acid (30 mL) to which **6b** (0.29 g, 0.85 mmol) was added. The reaction mixture was stirred at reflux under nitrogen for 24 hours. The solvent was removed *in vacuo* and the residue passed through silica eluting with ethyl acetate. The orange band was collected, the solvent removed and the product dried *in vacuo* to give **3b** as an orange solid (0.14 g, 39% yield): Mp 204 °C. Anal. Calc. for C$_{24}$H$_{23}$ClN$_2$Pt: C, 50.57; H, 4.07; N, 4.91. Found: C, 50.80; H, 4.12; N, 4.76%. IR (ν_{max}; thin film) 1589.2 (C=N) cm^{-1}; ^{1}H NMR (δ; 400 MHz, CDCl$_3$) 1.82 (6H, d, *J* 6.9, C*H*$_3$), 5.81 (2H, q, *J* 6.7, CH$_3$C*H*), 7.20 (3H, overlapping d and t, Ar), 7.29 (2H, t, *J* 7.1, Ar), 7.35 (4H, t, *J* 7.5, Ar), 7.41 (2H, d, *J* 7.4, Ar), 7.97 (2H, (66%) s, (34%) d, $^3J_{PtH}$ 148.1, N=C*H*); ^{13}C{^{1}H} NMR (δ; 100 MHz, CDCl$_3$) 28.6 (*C*H$_3$), 73.3 (CH$_3$*C*H), 130.0 (Ar *C*), 134.4 (Ar *C*), 136.0 (Ar *C*), 136.2 (Ar *C*), 136.6 (Ar *C*), 147.2 (Ar *C*), 149.3 (Ar, 2- and 6-H), 182.2 (N=C*H*) (Pt coupling not observed in dilute sample); MS (*m/z*; APCI) 533.3 (M$^+$, 100%). $[\alpha]_D^{20}$ + 65 (*c* 0.003, CHCl$_3$).

*Procedure for catalysed reactions of methyl 2-cyanopropanoate **7** with methyl vinyl ketone **8*** – Equimolar amounts of AgSbF$_6$ and pincer complexes **3a** or **3b** were stirred protected from light for 24 h in non-anhydrous CH$_2$Cl$_2$, then the solution was filtered through celite, to remove precipitated silver halides, into the reaction flask which already contained methyl 2-cyanopropanoate (corresponding to

2 mol% catalyst loading). The volume was adjusted to 0.15 M with respect to methyl 2-cyanopropanoate, then methyl vinyl ketone and a catalytic amount of Hünig's base (5 mol%) were added in rapid succession. The reaction mixtures were stirred at room temperature. Aliquots were filtered through silica (to remove catalyst) and analysed by ^{1}H NMR spectroscopy, both reactions had essentially reached completion (>95% conversion by NMR) at 34 h. Filtration through silica and analysis by chiral GC revealed racemic product in both cases.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem. 2007.06.066.

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