Steric Effects in Enantioselective Allylic Alkylation Catalysed by Cationic (η^3-Allyl)palladium Complexes Bearing Chiral Pyridine-Aziridine Ligands

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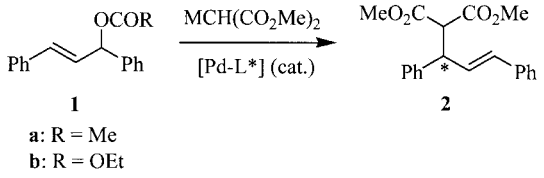
Enantiopure *N*,*N*′-bidentate ligands (*N*,*N*′)*, containing substituted aziridine and aza-aromatic rings, were prepared from imines derived from (*S*)-valinol or (*R*)-phenylglycinol and heteroaromatic aldehydes (2-pyridine-, 6-benzyl-2-pyridine-, 2- and 8-quinolinecarbaldehyde) by the addition of *i*PrMgCl and subsequent cyclisation of the 1,2-amino alcohol moiety to aziridine. Crystalline [(*N*,*N*′)*(η^3-allyl)Pd][SbF_6] complexes were prepared from these ligands and used as catalysts in the alkylation of sodium dimethyl malonate with 1,3-diphenyl-2-propenyl acetate and carbonate. By comparing the performances of two complexes bearing similar pyridine-aziridine ligands but with a different C2-aziridine substituent (Ph vs. *i*Pr), a better enantioselectivity was provided by the Ph-substituted ligand (90% vs. 41% *ee*), whereas the presence of a C6-pyridine benzyl substituent caused inversion of the enantioselectivity.

Introduction

C_2-Symmetric enantiopure *N*,*N*-bidentate ligands have been used in Pd-catalysed allylic substitution reactions, typically the reaction of 1,3-diphenylpropenyl acetate (**1a**) with the dimethyl malonate anion, in the presence of allylpalladium chloride dimer to give the substitution product **2** (Scheme 1). Selected examples of ligands containing either an aziridine or a pyridine ring are shown below as they will be compared with the ligands prepared in this paper. Notably, the C_2-symmetric bis(aziridine) **3**[1] affords complete enantioselectivity. Substituted pyridines, for example the ligand **4**, where the pyridine substituent bears the *trans*-2,5-disubstituted pyrrolidine ring,[2] provide greater enantioselectivity (64% *ee*) than C_2-symmetric 6,6′-disubstituted-2,2′-bipyridines.[3] With C_1-symmetric 2-(2′-pyridyl)oxazolines **5a**,**b**[4] and **6**[4c,5] a remarkable effect of the substituent in both rings was observed. In fact, substitution of Ph for the *i*Pr group in the oxazoline was beneficial for enantioselectivity as, with the same pyridine substituent (R = H), a better *ee* was provided by **6**. Most importantly, the presence of a (chiral) bulky substituent at the pyridine-C6 of both ligands, or the presence of a benzo[*b*]-fused ring as in **7**, caused an increase in the enantioselectivity.[4,5] It should be noted that the ligands **5**–**7** form a rigid, five-membered chelate ring in the cationic (η^3-allyl)palladium complexes, whereas six-membered chelate rings are formed with the ligands **8**–**10**. In the case of 8-quinolineoxazolines **8**, an unexpected effect of the substitution was observed, as when R = Me[6] and with the benzo[*b*]-derivative (acridininyloxazoline)[4] the opposite enantiomer of **2** was produced. Similarly, the 2-(quinolylmethyl)oxazoline **10** displayed the opposite enantioselectivity with respect to **9**.[6]



1
a: R = Me
b: R = OEt

2

Scheme 1.

We observed that (*N*,*N*′)* ligands containing both pyridine and aziridine rings had not been described in the literature and envisioned a simple two-step route to (*S*)-1-[(*S*)-(2-pyridyl)alkyl]isopropylaziridines, such as **11**, from *N*-(2-pyridylmethylidene)-(*S*)-valinol.[7] In a preliminary report we have described the preparation of **11** and its cationic (η^3-allyl)palladium complex **12**, which is more effective than the free base in the above mentioned Pd-catalysed allylic substitution reaction, and provides (*R*)-**2** with moderate yield and 41% *ee* (Table 1, entry 1).[8] The ligand **11** differs from **3**–**10** in the presence of a stereocentre in the carbon chain linking the two nitrogen atoms, besides the one present on the aziridine carbon. The two stereocentres in **11** have a combined role and compel the aziridine nitrogen to

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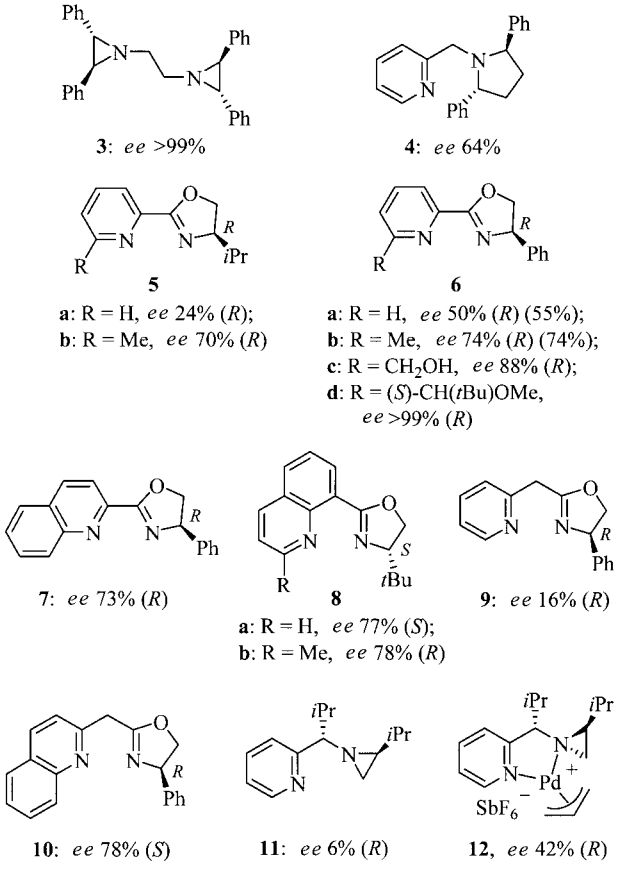
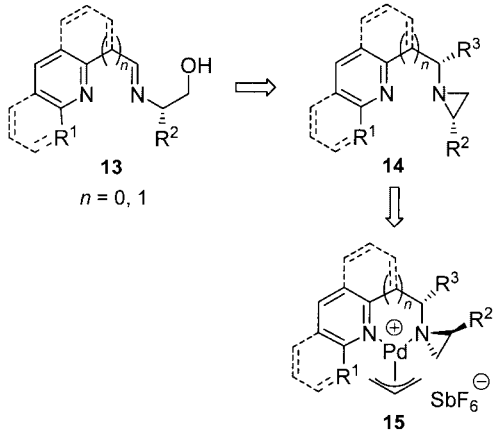


assume the N_R configuration when forming the Pd complex, as shown by the X-ray structural analysis of **12**. This happens to avoid the severe interaction of the two *i*Pr substituents that would occur in the alternative complex with the N_S configuration.

Since then, we have directed our efforts to the preparation of other C_1-symmetrical (*N*,*N*′)* ligands and their palladium complexes (general structures **14** and **15**, respectively) by the same route. This is described in Scheme 2 and involves the preliminary organometallic addition step to the imine **13** to give the 1,2-amino alcohol **14**, from which the aziridine ring is constructed. This route is flexible, as it allows variation of the ligand skeleton, the size of the Pd chelate ring (starting from the appropriate aldehyde) and all the substituents, especially those in the heterocyclic rings (ring-substituted aza-heteroaromatic aldehyde and chiral 1,2-amino alcohol) and in the tether connecting them (organometallic reagent). Similarly, the influence of a new substituent R^1 or a benzo[*b*]-fused pyridine ring can be studied by preparing the ligand from a suitable aldehyde. As a corollary of this study, owing to the low reactivity of the acetate **1** in the reaction catalysed by **12**, we have checked the more reactive 1,3-diphenyl-2-propenyl ethyl carbonate **1b** as the substrate in the same substitution reaction.



Scheme 2.

Results and Discussion

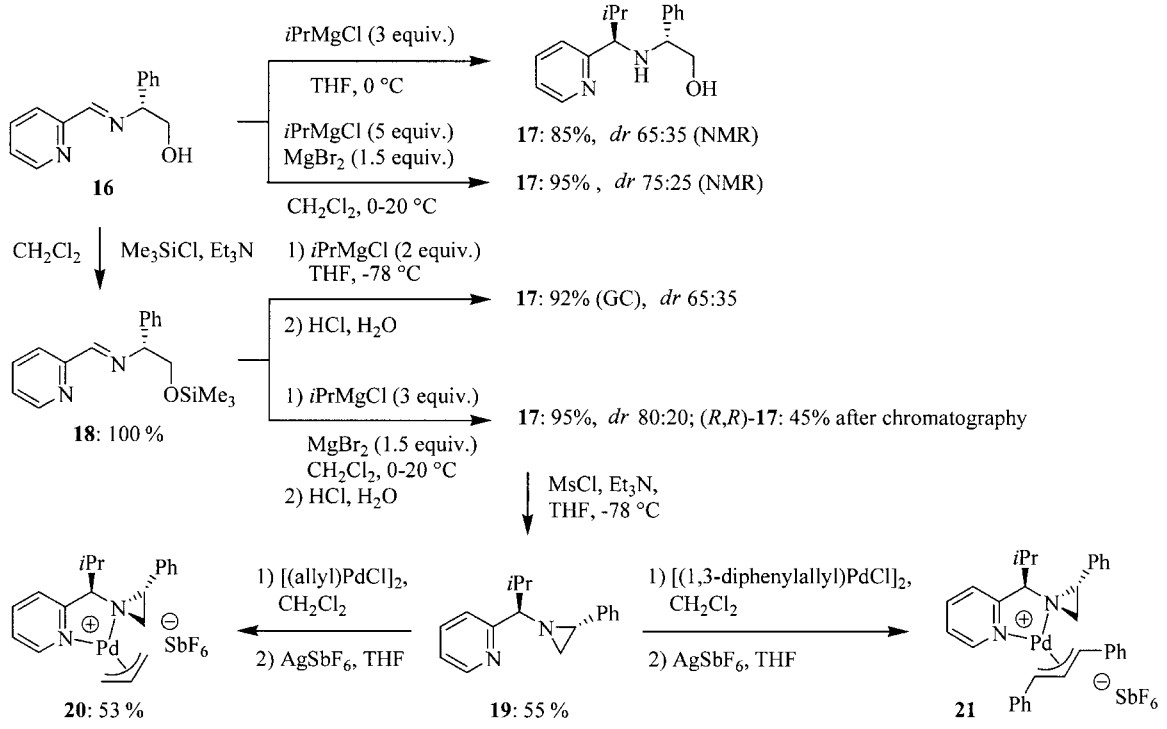
Influence of the Aziridine Ring Substituent

In order to determine the effect of the aziridine C2-substituent on the enantioselectivity we chose to replace the *i*Pr group, present in the prototypical ligand **2**, with a phenyl group. This was accomplished by preparing the free imine **16** and the *O*-protected one (**18**), from 2-pyridinylaldehyde and (*R*)-phenylglycinol, and optimising the preparation of the amino alcohol **17** from them (Scheme 3). Although phenylglycinol has been widely exploited for the diastereoselective addition of organometallic reagents to imines,[9] in our hands the addition of *i*PrMgCl to **16** in THF at 0 °C gave the secondary amines **17** with moderate stereocontrol.

Table 1. Pd-catalysed enantioselective allylic substitution reactions of 1,3-diphenyl-2-propenyl acetate and carbonate **1a**,**b** with sodium dimethyl malonate (1.5 equiv., THF, 25 °C).

Entry	Substrate	Catalyst [equiv.]	Time [h]	Product	Yield [%]	*ee* [%]
1	**1a**	**12** (0.1)	36	(*R*)-**2**	50	42
2	**1b**	**12** (0.05)	3	(*R*)-**2**	85	19
3	**1b**	**20** (0.1)	12	(*S*)-**2**	70[a]	90
4	**1b**	[(allyl)PdCl]$_2$ (0.05), **19** (0.1)	12	(*S*)-**2**	74	86
5	**1a**	**25a** (0.1)	36	(*R*)-**2**	22	<5
6	**1a**	**25b** (0.1)	24	(*S*)-**2**	35	23
7	**1b**	**25c** (0.1)	18	(*S*)-**2**	43	42
8	**1b**	**25c** (0.1)	6[b]	(*S*)-**2**	75	35

[a] Almost no reaction occurred at 0 °C or when using 10 mol-% of sodium hydride. [b] The reaction was performed at 50 °C.



Scheme 3.

No attempt was made to separate the main (*S*,*S*)-diastereomer. The experimental conditions used by Spero[10] for similar Grignard reactions with 2-pyridylketimines were then applied to **16**, with the use of CH_2Cl_2 as the solvent and the presence of $MgBr_2$.[10] In this manner a 95% yield and a 75:25 *dr* (^{1}H NMR spectroscopy) were obtained for **17**. Also, the addition of *i*PrMgCl to the *O*-protected imine **18** in THF at –78 °C gave **17** with a moderate diastereoselectivity (65:35), although a better *dr* (80:20) was finally obtained by applying the Spero protocol to the protected imine **18**, and the main diastereomer of **17** was isolated pure in 45% yield by column chromatography of the reaction mixture.

The conversion of the amino alcohol **17** to the aziridine **19** by treatment with carbonyl diimidazole (CDI)[8,11] was not satisfactory. In this case, a better result was achieved from the reaction with mesyl chloride and triethylamine at –78 °C, which gave **19** in 55% yield. The cationic (η^3-allyl) palladium complex **20** was then prepared by the routine procedure. The complex **20** (10 mol-%) was used for the catalytic allylation of sodium dimethyl malonate with the acetate **1a**, but almost no reaction was observed after one day at 25 °C. However, using the carbonate **1b**, almost complete conversion (TLC) after 12 h at 25 °C in THF was observed and the product (*S*)-**2** was isolated by column chromatography with 70% yield and 90% *ee* (Table 1, entry 3). It is noteworthy that with **12** as the catalyst (5 mol-%) the malonate **2** was obtained with 85% yield from the carbonate **1b** after only 3 h at 25 °C, but with lower *ee* (19%, entry 2) with respect to the reaction with the acetate **1a** (entry 1); unfortunately, almost no reaction took place with **1b** at 0 °C. The reaction of carbonate **1b** with dimethyl malonate in the presence of 10 mol-% each of sodium hydride[12] and complex **20** at 25 °C stopped after a few hours when a black Pd precipitate had formed; only small amounts of **2** were detected by TLC analysis. The reaction of **1b** with sodium dimethyl malonate (1.5 equiv.) in the presence of allylpalladium chloride dimer (5 mol-%) and ligand **19** (10 mol-%), i.e. forming the reactive complex **21** in situ, gave (*S*)-**2** with 74% yield and 86% *ee* (entry 4). On the other hand, the reaction of **1b** with dimethyl malonate salt (2.5 equiv.), bis(trimethylsilyl)acetamide (BSA, 3 equiv.), potassium acetate (1 mol-%) and the palladium complex **20** (10 mol-%) gave a largely incomplete conversion to (*S*)-**2**, which was isolated after 12 h with only 33% yield although with high *ee* (90%). It should be underlined that the two complexes **12** and **20** have opposite chirality. Consequently, they induce the same sense of asymmetric induction in the formation of (*R*)-**2** and (*S*)-**2**, respectively.

Influence of the Ligand Skeleton and C6-Pyridine Substituent

We aimed to assess the effect of the modified *N*,*N*-ligand skeleton or pyridine-substitution pattern on the enantioselectivity of the substitution reaction, hence we prepared the imines **22a**–**c** from commercially available 2- and 8-quinolinaldehydes and ad hoc prepared 6-benzyl-2-pyridinal-

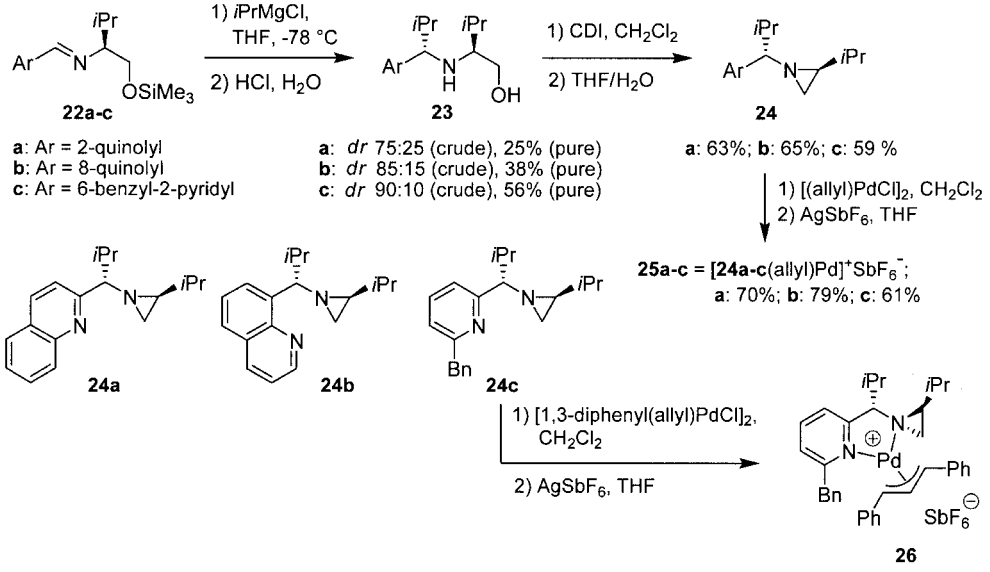
dehyde, respectively. In the case of **22a** and **22c** we envisioned a steric interaction of the pyridine-fused benzene ring or the C6-benzyl substituent with the phenyl group of the η^3-allyl ligand in the reactive allylic complex. A six-membered Pd-chelation complex should be formed with the ligand **24b** derived from **22b**, which might result in a modified structure of the allylic complex.

The usual route was followed to prepare the new (*N*,*N*′)* ligands (Scheme 4). However, the addition of *i*PrMgCl to **24a** was plagued by poor chemoselectivity, affording the β-amino alcohol **23a** with 25% yield after chromatographic separation from several unidentified by-products and its diastereomer (75:25 *dr*, as determined by GC-MS analysis of the crude product). A more selective addition of the same Grignard reagent was observed to the 8-quinolineimine **22b** (85:15 *dr*) and the pure diastereomer **23b** was isolated with 38% yield. Finally, the imine **22c** was prepared from 6-benzyl-2-bromopyridine[13] by bromine–lithium exchange at low temperature, followed by reaction with DMF. The reaction of **22c** with *i*PrMgCl gave the amino alcohol **23c** with good yield and diastereoselectivity (90:10 *dr*), and the pure diastereomer was isolated with 56% yield by column chromatography. The aziridines **24a**–**c** and their cationic (η^3-allyl)palladium complexes **25a**–**c** were readily prepared by the routine sequence in good yields (Scheme 4). X-ray analyses of the recrystallised salts **25a**,**b** (see Supporting Information) showed structures similar to that of **12**.[8] However, two independent cations are present in the crystals of the 2-quinoline derivative **25a**, and in both of them the *endo*-allyl rotamer predominates. In the crystal of the 8-quinoline derivative **25b**, which features a six-membered Pd chelate ring, a 56:44 *exo*/*endo* ratio of the allyl rotamers was observed. It is noteworthy that the ligands in the salts **12**[8] and **25a**,**b** present similar envelope or puckered conformations.

The reactions carried out with the acetate **1a** catalysed by complexes **25a**–**c** gave unexpected results. A low enantioselectivity for (*R*)-**2** was obtained using **25a** (4% *ee*, Table 1, entry 5), and an inversion of the enantioselectivity was observed in the reaction catalysed by **25b**: in fact, (*S*)-**2** was prevalently formed, although with low *ee* (23%, entry 6). In both cases, the pyridine substituent caused an increase of the reaction time needed to achieve a satisfactory conversion. An even more sluggish reaction was observed with the 6-benzylpyridine derivative **25c**, so in this case we worked with the more-reactive carbonate **1b** and obtained (*S*)-**2** with reasonable yield and moderate enantioselectivity (47% *ee*, entry 7). When the same reaction was performed at higher temperature (50 °C) the reaction rate increased considerably and (*S*)-**2** was isolated with 75% yield, but slightly lower *ee* (37%, entry 8).

X-ray Studies of (η^3-1,3-Diphenylallyl)palladium Complexes: A Tentative Explanation of the Divergent Enantioselectivity

The stereochemical outcomes of the reactions catalysed by the (*N*,*N*′)*(η^3-allyl)palladium salts **12** and **25a**,**b** are not correlated to their crystallographic parameters (bond lengths and angles).[14] Therefore, with the aim of finding clues to explain the remarkable inverted enantioselectivity obtained with catalyst **25c** with respect to **20**, we prepared the corresponding cationic (η^3-1,3-diphenylallyl)palladium complexes, which are the possible intermediates in the enantio-discriminating steps, as their hexafluoroantimonate salts **26** (Scheme 4) and **21** (Scheme 3), respectively. X-ray diffraction analysis (Figure 1 for **21** and Figure 2 for **26**) showed that the structures of these complexes are similar to



Scheme 4.

each other as well as to those of **12**[8] and **25a**,**b**.[14] However, only the *endo* rotamers of the 1,3-diphenylallyl ligand are present in **21** and **26**. For clarity, throughout the paper the aziridine and pyridine nitrogen atoms are indicated as N_A and N_P, respectively, and the allylic carbons C_A (*trans* to aziridine) and C_P (*trans* to pyridine).

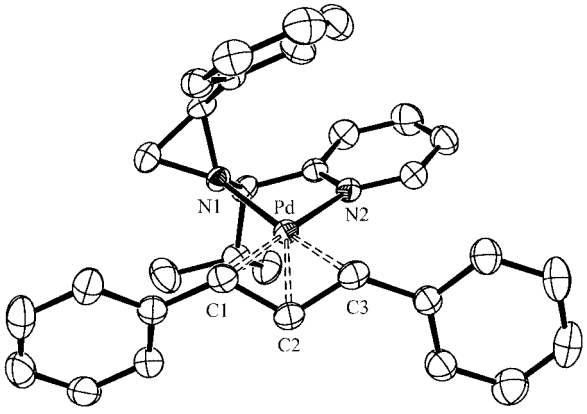


Figure 1. ORTEP drawing of one of the cations of **21**. Thermal ellipsoids at 30% probability level. The following conventions have been adopted: N1 = N_A, N2 = N_P, C2 = C_{endo}, C1 = C_P, C3 = C_A.

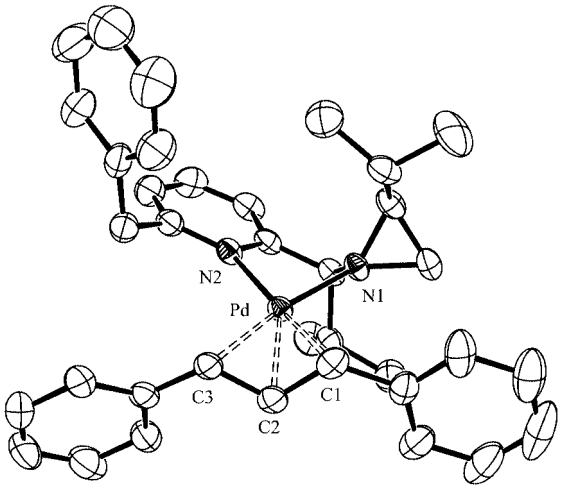
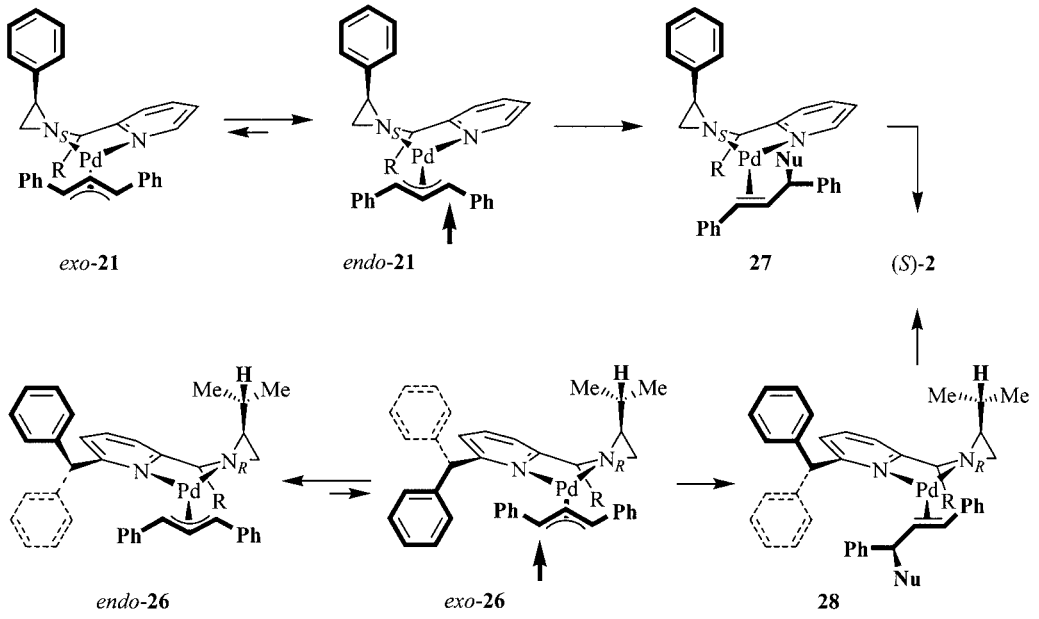


Figure 2. ORTEP drawing of one of the independent cations of **26**. Thermal ellipsoids at 30% probability level. The following conventions have been adopted: N1 = N_A, N2 = N_P, C2 = C_{endo}, C1 = C_P, C3 = C_A.

A common feature of all the ionic Pd complexes is the unique configuration of N_A, which is (*R*) for the complexes **12**, **25a**,**b** and **26** derived from (*S*)-valinol, and (*S*) for the complex **21** derived from (*R*)-phenylglycinol.[15] This avoids the steric interaction between the *i*Pr group present in the tether linking the nitrogen atoms and the aziridine substituent (*i*Pr or Ph). It should also be noted that in all our cationic allylic Pd complexes, apart from **21**, the Pd–N_P bonds are longer than the corresponding Pd–N_A bonds. For example, in the (η^3-1,3-diphenylallyl)palladium complex **26**, where two independent cations are present, the Pd–N_P bonds are in the range 2.180–2.200(5) Å and are considerably longer than the Pd–N_A bonds [2.133–2.152(6) Å]. This is noteworthy because N_P and N_A use sp^2- and sp^3-type orbitals, respectively. The lengths of the two Pd–N_A bonds in the calculated structure of the complex [(η^3-1,3-diphenylallyl)Pd(**3**)][SbF_6] are 2.131 and 2.134 Å,[1b,1f] which are similar to the values observed in **21** and **26**. On the contrary, in the reported X-ray structure of an [(*N*,*N*′)(η^3-1,3-diphenylallyl)Pd]$^+$ cation, the metal forms a longer



Scheme 5.

bond with pyrrolidine (2.15 Å) than with pyridine (2.08 Å).[2a] Moreover, the two Pd–N bonds in the [(sparteine)(η^3-1,3-diphenylallyl)Pd]$^+$ cation are 2.19 and 2.24 Å.[16] Hence, it appears that the aziridine nitrogen generally forms a shorter bond a with palladium cation than other sp^3-hybridised nitrogen atoms.

In order to understand the enantioselectivity of the alkylation reaction, several points should be considered. In all the *endo* and *exo* rotamers of the unsubstituted allyl complexes **12** and **25a**,**b**, and particularly in *endo*-**21** and *endo*-**26**, the C_A–Pd bond is longer than the C_P–Pd bond, thus indicating an apparently greater *trans* influence of aziridine with respect to pyridine and a more electrophilic character of C_A.[17–19] It should also be considered that complexes **21** and **26** in $CDCl_3$ solution are present as *syn*,*syn*-*endo*/*syn*,*syn*-*exo* mixtures (72:28 and 85:15, respectively), and that in no case were *anti*,*syn*-allyl species detected. The *endo*/*exo* ratios and the Pd–C bond lengths are determined by steric effects, i.e. the non-bonding interactions of the (*N*,*N*′)* and allyl ligands, whereas electronic effects are not relevant.

In the hypothesis that the *endo* and *exo* rotamers have the same reactivity and undergo a completely regioselective attack, the *ee*'s of the product should be correlated to the *endo*/*exo* ratio. This is true, for example, in reactions catalysed by 8-(2-oxazoline)quinoline ligands.[20] In the case of our ligands, the preferred formation of (*R*)-**2** with **12** and (*S*)-**2** with **20** can be rationalised by assuming a highly regioselective attack at the more electrophilic allylic termini C_A of the most abundant rotamers, e.g. *endo*-**21**, as shown in Scheme 5. Conversely, the opposite enantioselectivity obtained in the case of **26**, which has the same chirality as **12** but mainly affords (*S*)-**2**, requires a different interpretation. In this case, the relative ratio and reactivity of *endo* and *exo* rotamers of **26** must be considered.[21] This different reactivity is probably associated to the relative stability of the late transition states leading to the alternative η^2-complexes, which are precursors of the product **2** (Scheme 5). It should be noted that the formation of the η^2-complex **28** by attack on the less-abundant rotamer *exo*-**26** occurs by "preferential rotation"[22] and does not suffer from severe steric interactions, contrary to the alternative η^2-complex derived from *endo*-**26**. In our opinion, the high enantioselectivity observed for (*S*)-**2** in the reaction catalysed by complex **20** is the result of two convergent factors: the prevalence of the rotamer *endo*-**21** in solution, and the relatively low activation energy of the transition state derived from the nucleophilic attack at the more electrophilic C_A allylic terminus leading to the η^2-complex **27**.

Conclusions

We have investigated a synthetic route to enantiopure C_1-symmetric *N*,*N*′-bidentate ligands carrying either a 1,2-disubstituted aziridine or an aza-aromatic ring. The ligands were prepared from imines derived from pyridine- and quinolinecarbaldehydes and optically pure β-amino alcohols. The ligands were then converted into the [(*N*,*N*′)*(η^3-allyl)Pd][SbF_6] complexes, which were used as catalysts in the allylic substitution reaction of 1,3-diphenyl-2-propenyl esters with sodium dimethyl malonate in THF.[16,23] Although the synthetic route to the ligand proved to be more efficient and stereoselective when starting from (*S*)-valinol as the chiral precursor, it was observed that the analogous ligand prepared from (*R*)-phenylglycinol was considerably more enantioselective in the catalytic application (90% *ee*), as a consequence of the more-demanding steric effects of the phenyl substituent in the aziridine ring, which is oriented towards the allyl ligand. On the other hand, structural variations in the starting heterocyclic aldehyde, the capability of the ligand to form either a five- or six-membered ring with palladium and the substitution pattern in the aza-heteroaromatic ring affect either the reactivity and/or stereocontrol. In particular, inversion of enantioselectivity was observed using the ligand bearing a 6-benzyl-substituted pyridine. The X-ray diffraction studies of the two [(*N*,*N*′)*(η^3-1,3-diphenylallyl)Pd][SbF_6] complexes that afforded the most marked difference in enantioselectivity showed the similarity of their structures and the presence of only the *endo*-allylic rotamers, contrary to the unsubstituted allylpalladium complexes. Hence, the solid-state structure does not always correspond to the more reactive conformer in solution, and the steric effects of the different skeleton or substituents on the regio- and stereoselectivity are not easily evaluated.[24] Interestingly, the Pd–N(aziridine) bonds in most allylic complexes studied are shorter than the Pd–N(pyridine) bonds.

A lack of reactivity was observed with cyclohexenyl acetate, as previously reported for the reaction catalysed by the bis(aziridine) **3**.[1] The moderate efficiency of the alkylation reactions catalysed by our ligands/complexes can be attributed to the weakness of the Pd–N(pyridine) bond(s), which affects the stability of the chelated [(*N*,*N*′)*(η^3-allyl)Pd]$^+$ cations. Similarly, the absence of a π-acceptor N ligand in (*N*,*N*′)* probably does not allow the effective stabilization/dissolution of the Pd^0 species that are formed by nucleophilic attack on the intermediate cationic complex. With regard to this, it would be worthwhile to study the effect of electron-withdrawing substituents on the pyridine ring of the ligand, particularly at C4, where steric effects are absent.

Experimental Section

General Remarks: Melting points are uncorrected. Solvents were distilled from the appropriate drying agent under N_2 before use: THF (sodium benzophenone ketyl, then $LiAlH_4$), CH_2Cl_2 (P_2O_5). Optical rotations were measured on a digital polarimeter in a 1-dm cell and $[\alpha]_D$ values are given in 10^{-1} deg cm^3 g^{-1}. ^{1}H NMR spectra were recorded on a Varian Gemini instrument at 300 or 200 MHz for samples in $CDCl_3$ which was stored over Mg. ^{1}H chemical shifts are reported in ppm relative to $CHCl_3$ (δ_H = 7.27 ppm) and coupling constants are given in hertz. Mass spectra were measured at an ionising voltage of 70 eV on a Hewlett–Packard 5970 or 5890

spectrometer with GLC injection. Chromatographic separations were performed on columns of SiO_2 (Merck, 230–400 mesh) at medium pressure. The following materials were purchased from Aldrich: *n*BuLi (1.6 M in hexanes), *i*PrMgCl (2 M in THF), $[(allyl)PdCl]_2$, $AgSbF_6$, 3-methyl-2-butenyl bromide, 2-pyridinaldehyde, 2-quinolinaldehyde, (*S*)-valinol, (*S*)-phenylglycinol, 1,1′-carbonyldiimidazole, thionyl chloride. 8-Quinolinecarbaldehyde was prepared from 8-methylquinoline by oxidation with SeO_2.[25] η^3-(1,3-Diphenylallyl)palladium chloride dimer was prepared from the allyl chloride by reaction with $PdCl_2/SnCl_2/NaCl$ in DMF following a procedure described for the preparation of different η^3-allylpalladium(II) complexes.[26] All the organometallic reactions were performed in a flame-dried apparatus under a static atmosphere of dry N_2.

Preparation of the Imines: The imines were prepared on a 5 mmol scale by a previously described procedure[27] and used without further purification.

(*S*)-*N*-[(2-Pyridyl)methylidenephenylglycinol (16):[28] Yellow oil: 100%. $[\alpha]_D^{20}$ = +19.6 (*c* = 0.83, $CHCl_3$). We observed a 55:45 mixture of imine and 1,3-oxazolidine by ^1H NMR in $CDCl_3$ (200 MHz): δ = 8.49 (s, 1 H, CH=N), 5.65 (s, 1 H, NCHO) ppm. The ^1H NMR spectra in $CDCl_3$ and [D$_8$]THF have been partially described previously.[28]

(*S*)-*N*-[(2-Pyridyl)methylidene]-*O*-trimethylsilylphenylglycinol (18): Yellow oil: 84%. $[\alpha]_D^{20}$ = –15.5 (*c* = 0.62, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.63 (d, *J* = 4 Hz, 1 H, Py), 8.43 (s, 1 H, CH=N), 8.15 (d, *J* = 8 Hz, 1 H, Py), 7.73 (t, *J* = 8 Hz, Py), 7.55–7.20 (m, 6 H, Py and Ph), 4.50 (m, 1 H, C*H*Ph), 3.84 (m, 2 H, CH_2O), 0.0 (s, 9 H, $SiMe_3$) ppm. GC-MS: *m*/*z* (%) = 195 (100) [M^+ – CH_2OSiMe_3], 92 (30), 73 (18), 66 (12), 163 (10), 298 (4) [M^+ – 1].

(*S*)-*N*-[(2-Quinolyl)methylidene]-*O*-trimethylsilylvalinol (22a): Yellow oil; 94%. $[\alpha]_D^{20}$ = –23.2 (*c* = 1.1, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ = 8.48 (s, 1 H, CH=N), 8.15 (m, 3 H, quinoline), 7.90–7.50 (m, 3 H, quinoline), 3.92 (dd, *J* = 4.2 and 10.5 Hz, 1 H, CH_2O), 3.75 (dd, *J* = 8.1 and 10.5 Hz, 1 H, CH_2O), 3.18 (m, 1 H, CHN), 2.0 (m, 1 H, C*H*Me$_2$), 0.95 (2 d, *J* = 6.7 Hz, 6 H, CH*Me*$_2$), 0.05 (s, 9 H, $SiMe_3$) ppm. GC-MS: *m*/*z* (%) = 211 (100) [M^+ – CH_2OSiMe_3], 169 (42), 142 (34), 73 (31), 181 (25), 271 (10), 115 (5), 299 (5) [M^+ – Me]

(*S*)-*N*-[(8-Quinolyl)methylidene]-*O*-trimethylsilylvalinol (22b): Yellow oil: 98%. $[\alpha]_D^{20}$ = –32 (*c* = 1.80, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ = 9.58 (s, 1 H, CH=N), 8.98 (dd, *J* = 2.0 and 4.2 Hz, 1 H, quinoline), 8.46 (dd, *J* = 1.6 and 7.4 Hz, 1 H, quinoline), 8.19 (dd, *J* = 4.8 and 8.0 Hz, 1 H, quinoline), 7.90 (dd, *J* = 1.4 Hz0 and 8.0 Hz, 1 H, quinoline), 7.60 (t, *J* = 7.4 Hz, 1 H, quinoline), 7.44 (dd, *J* = 4.4 and 8.4 Hz, 1 H, quinoline), 3.95 (dd, *J* = 6.6 and 10.6 Hz, 1 H, CH_2O), 3.75 (dd, *J* = 7.8 and 10.2 Hz, 1 H, CH_2O), 3.25 (m, 1 H, N–CH), 2.05 (m, 1 H, C*H*Me$_2$), 1.00 (d. *J* = 7.0 Hz, 6 H, CH*Me*$_2$), 0.07 (s, 9 H, $SiMe_3$) ppm. GC-MS: *m*/*z* (%) = 155 (100), 211 (38) [M^+ – CH_2OSiMe_3], 142 (36), 156 (18), 73 (17), 299 (4) [M^+ – Me].

(*S*)-*N*-[(6-Benzyl-2-pyridyl)methylidene]-*O*-trimethylsilylvalinol (22c): 6-Benzyl-2-bromopyridine was prepared from 2,6-dibromopyridine according to the reported procedure:[13] yellowish oil (61%). ^1H NMR (200 MHz, $CDCl_3$): δ = 7.48–7.18 (m, 7 H, Ar), 7.00 (d, *J* = 7.0 Hz, 1 H, Py), 4.15 (s, 2 H, CH_2) ppm. MS: *m*/*z* (%) = 248 (100), 246 (95), 247 (44), 167 (43), 249 (41), 166 (27), 168 (24), 65 (11), 83 (10), 139 (9). *n*BuLi (1.6 M *in* hexanes, 3.44 mL, 5.5 mmol) was slowly added to the solution of this compound (1.36 g, 5.5 mmol) in THF (8 mL) cooled to –78 °C while magnetically stirring. The mixture was stirred for 1 h at –78 °C, then dry DMF (0.66 mL) was directly added to the solution. After stirring for 1 h, H_2O (10 mL) was added and the organic phase was extracted with Et_2O (3 × 10 mL). The collected organic layers were dried (Na_2SO_4) and concentrated to leave an oily residue. Chromatography on a silica gel column, eluting with cyclohexane/ethyl acetate (10:1), gave 6-benzyl-2-pyridinecarbaldehyde as an oil (0.65 g, 60%). ^1H NMR (200 MHz, $CDCl_3$): δ = 10.10 (s, 1 H, CHO), 7.80 (m, 2 H, Py), 7.48–7.10 (m, 6 H, Ar), 4.27 (s, 2 H, CH_2). MS: *m*/*z* (%) 196 (100), 197 (28), 167 (21), 168 (15), 166 (14), 91 (9), 65 (7), 115 (5). The imine **22c** was then obtained from the aldehyde by the previously described procedure as a yellowish oil (1.08 g, 90%). $[\alpha]_D^{20}$ = –9.4 (*c* = 0. 38, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ = 8.32 (s, 1 H, CH=N), 7.89 (d, *J* = 7.6 Hz, 1 H, Py),7.60 (t, *J* = 7.6 Hz, 1 H, Py), 7.40–7.17 (m, 5 H, Ph), 7.08 (d, *J* = 7.8 Hz, 1 H, Py), 4.20 (s, 2 H, CH_2), 3.87 (dd, *J* = 4.4 and 10.2 Hz, 1 H, CH_2O), 3.67 (t, *J* = 10.2 Hz, 1 H, CH_2O), 3.09 (m, 1 H, NC*H*CH_2O), 1.97 (m, 1 H, C*H*Me$_2$), 0.94 and 0.93 (2 d, *J* = 6.6 Hz, 6 H, CH*Me*$_2$), 0.06 (s, 9 H, $SiMe_3$) ppm. GC-MS: *m*/*z* (%) = 251 (100), 73 (26), 209 (18), 183 (11), 221 (10), 354 (9) [M^+], 339 (7), 311 (5).

Preparation of Secondary Amines by Addition of *i*PrMgCl to Imines. Synthesis of (*R*)-*N*-[(*R*)-2-methyl-1-(2-pyridyl)propyl]phenylglycinol (17): Anhydrous $MgBr_2$ (1.656 g, 9 mmol) was added to the solution of the imine **18** (1.782 g, 6 mmol) in CH_2Cl_2 (60 mL), cooled to 0 °C, and the mixture was stirred for 1 h while the temperature rose to 20 °C. Then, *i*PrMgCl (2 M in Et_2O, 9.0 mL, 18 mmol) was added over 10 min, the mixture was stirred for a further 3 h, and then quenched with sat. $NaHCO_3$ (20 mL). The organic layer was separated and the organic material was extracted from the aqueous phase with CH_2Cl_2 (3 × 20 mL). The collected organic layers were concentrated and the residue was treated with NH_4F (2.0 g) in MeOH/H_2O (1:1, 20 mL) for 6 h, then solid NaOH was added to reach pH 11 and the organic material was extracted with Et_2O (3 × 20 mL). The collected ethereal layers were dried (Na_2SO_4) and concentrated to leave an oily residue. The diastereomeric ratio (80:20) was determined by GC-MS and ^1H NMR spectroscopy. Chromatography on a SiO_2 column eluting with cyclohexane/ethyl acetate (85:15) gave compound **17** as a pure diastereomer. Yellowish oil: 0.736 g, (45%);. $[\alpha]_D^{20}$ = –23.3 (*c* = 1.0, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.46 (d, *J* = 4.8 Hz, 1 H, Py), 7.46 (t, *J* = 7.6 Hz, 1 H, Py), 7.2–7.0 (m, 6 H, Ar), 7.95 (d, *J* = 7.6 Hz, Py), 3.8–3.5 (m, 3 H, $CHCH_2$), 3.41 (d, *J* = 7.2 Hz, 1 H, C*Hi*Pr), 2.01 (m, 1 H, C*H*Me$_2$), 1.25 (broad, 2 H, OH and NH), 1.05 and 0.79 (2 d, *J* = 6.9 Hz, CH*Me*$_2$). $C_{17}H_{22}N_2O$: calcd. C 75.52; H 8.20, N 10.36; found C 75.30, H 8.10, N 10.31. The product decomposed during GC-MS analysis. The minor diastereomer could not be isolated in a pure state by column chromatography.

Preparation of the Amines 23a–c: *i*PrMgCl (6 mmol) was added to a solution of the imine (3 mmol) in THF (10 mL) and magnetically stirred and cooled to –78 °C. After 1.5 h, the reaction mixture was quenched by adding saturated aq. $NaHCO_3$ (10 mL) and the organic phase was extracted with diethyl ether (3 × 10 mL). The collected ethereal phases were dried with Na_2SO_4 and concentrated to leave a yellowish oil. Treatment with 1 N HCl (6 mL) at 25 °C for 2 h, addition of NaOH until pH 11, extraction with Et_2O (3 × 5 mL), drying (Na_2SO_4) and evaporation of the solvent gave a thick, yellow oil. The diastereomeric ratios were determined byGC-MS and ^1H NMR analysis: **23a** 75:25, **23b** 85:15, **23c** 90:10. The major diastereomers of **23a**–**c** were separated by column

chromatography (SiO_2; hexane/ethyl acetate with increasing polarity) with *dr* > 95:5 and were used as such in the subsequent step. For analytical purposes, the pure diastereomers were obtained by repeated chromatography with slightly decreased yield. No attempt was made to isolate the minor diastereomers as they could not be isolated in a pure state by column chromatography.

(*S*)-*N*-[(*S*)-2-Methyl-1-(2-quinolyl)propyl]valinol (23a): Yellowish oil; 0.215 g (25%). $[\alpha]_D^{20}$ = –70.7 (*c* = 1.05, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ = 8.08 (dd, *J* = 5.4 and 8.0 Hz, Ar), 7.80 (dd, *J* = 1.2 and 8.0 Hz, 1 H, Ar), 7.70 (m, 1 H, Ar), 7.51 (m, 1 H, Ar), 7.31 (d, *J* = 8.4 Hz, 1 H, Ar), 3.70 (dd, *J* = 3.6 and 10.6 Hz, 1 H, CH_2O), 3.61 (d, *J* = 6.6 Hz, 1 H, ArC*H*N), 3.45 (dd, *J* = 3.8 and 10.8 Hz, 1 H, CH_2OH), 2.5 (broad, 2 H, OH and NH), 2.13 (m, 1 H, CHN), 2.06 (m, 1 H, C*H*Me_2), 1.32 (s, 1 H, NH), 1.65 (m, 1 H, C*H*Me_2), 1.04 (d, *J* = 6.6 Hz, 3 H, CH*Me*$_2$), 0.86, 0.84 and 0.77 (3 d, *J* = 7.0 Hz, 9 H, CH*Me*$_2$) ppm. GC-MS: *m*/*z* (%) = 243 (100) [M^+ – *i*Pr], 184 (98), 142 (51), 199 (50), 154 (30), 158 (28), 157 (20), 169 (19), 170 (18), 255 (10) [M^+ – CH_2OH]. $C_{18}H_{26}N_2O$: calcd. C 75.48; H 9.15, N 9.78; found C 75.55, H 9.18, N 9.70.

(*S*)-*N*-[(*S*)-2-methyl-1-(8-quinolyl)propyl]valinol (23b): Yellowish oil; 0.325 g (1.14 mmol, 38%). $[\alpha]_D^{20}$ = –49.1 (*c* = 1.05, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ = 8.87 (dd, *J* = 1.8 and 4.4 Hz, Ar), 8.16 (dd, *J* = 1.8 and 8.4 Hz, 1 H, Ar), 7.72 (m, 1 H, Ar), 7.47 (d, *J* = 5.2 Hz, 2 H, Ar), 7.39 (dd, *J* = 4.4 and 8.0 Hz, 1 H, Ar), 3.95 (broad, 1 H, OH), 3.71 (dd, *J* = 4.0 and 10.6 Hz, 1 H, CH_2O), 3.43 (dd, *J* = 1.8 and 10.6 Hz, 1 H, CH_2O), 2.55 (m, 2 H, ArC*H*N and NH), 1.99 (m, 1 H, C*H*Me_2), 1.55 (m, 1 H, C*H*Me_2), 1.24 (d, *J* = 6.6 Hz, 3 H, CH*Me*), 0.64, 0.59 and 0.56 (3 d, *J* = 6.6 Hz, 9 H, CH*Me*$_2$) ppm. GC-MS: *m*/*z* (%) = 243 (100) [M^+ – *i*Pr], 184 (98), 142 (51), 199 (51), 158 (28), 154 (26), 157 (20), 167 (19), 168 (18). $C_{18}H_{26}N_2O$: calcd. C 75.48; H 9.15, N 9.78; found C 75.34, H 9.17, N 9.72.

(*S*)-*N*-[(*S*)-1-(6-Benzyl-2-pyridyl)-2-methylpropyl]valinol (23c): Yellowish oil; 0.546 g (56%). $[\alpha]_D^{20}$ = –64.4 (*c* = 0.68, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ = 7.49 (t, *J* = 7.6 Hz, 1 H, Py), 7.36–7.14 (m, 5 H, Ph), 6.94 (t, *J* = 7.6 Hz, 2 H, Py), 4.14 (s, 2 H, CH_2Ph), 3.60 and 3.41 (2 dd, *J* = 3.8 and 10.8 Hz, 2 H, CH_2O), 3.30 (d, *J* = 7.4 Hz, 1 H, ArC*H*N), 2.15 (m, 1 H, NC*H*CH_2), 1.96 and 1.56 (2 m, 2 H, C*H*Me_2), 1.42 (broad, 2 H, NH and OH), 1.04, 0.77, 0.75 and 0.74 (4 d, *J* = 7.0 Hz, 12 H, CH*Me*$_2$) ppm. $C_{21}H_{30}N_2O$: calcd. C 77.25; H 9.26, N 8.58; found C 77.33, H 9.32, N 8.52. The product decomposed during the GC-MS analysis.

(*R*)-1-[(*R*)-2-methyl-1-(2-pyridyl)propyl]phenylaziridine (19): Triethylamine (0.755 g, 7.4 mmol) and methanesulfonyl chloride (0.493 g, 4,44 mmol) were added to a solution of the diastereomerically pure amino alcohol **17** (0.400 g, 1.48 mmol) in CH_2Cl_2 (12 mL) cooled to –78 °C and the mixture was stirred for 3 h. After quenching with sat. $NaHCO_3$ (5 mL), the organic layer was separated and the organic bases were extracted from the aqueous layer with CH_2Cl_2 (3 × 5 mL). The collected organic layers were dried ($CaCl_2$) and concentrated to leave an oil, which was chromatographed on a SiO_2 column eluting with cyclohexane/ethyl acetate (85:15) to obtain compound **19** as a yellowish oil. Yield: 0.202 g, (55%). $[\alpha]_D^{20}$ = –129.6 (*c* = 0.44, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.51 (d, *J* = 4.5 Hz, 1 H, Py), 7.56 (dt, *J* = 1.5 and 7.5 Hz, 1 H, Py), 7.42 (d, *J* = 7.5 Hz, 1 H, Py), 7.35–7.0 (m, 6 H, Ar), 2.71 (d, *J* = 6.0 Hz, 1 H, NC*H*Py), 2.35 (dd, *J* = 3.3 and 6.5 Hz, PhC*H*CH_2), 2.28 (m, 1 H, C*H*Me_2), 2.16 (d, *J* = 3.3 Hz, 1.H, CHCH_2), 2.02 (d, *J* = 6.5 Hz, 1 H, CHCH_2), 1.10 and 0.97 (2 d, *J* = 6.6 Hz, 6 H, CH*Me*$_2$) ppm. GC-MS: *m*/*z* (%) = 118 (100) [PhCHCH_2N], 91 (86), 136 (21), 119 (8), 78 (6), 182 (5), 104 (5), 209 (4) [M^+ – *i*Pr]. $C_{17}H_{20}N_2$: calcd. C 80.91, H 7.99, N 11.10; found C 80.97, H 8.04, N 11.05.

Preparation of the Aziridines 24a–c: A solution of 1,2-amino alcohol (3 mmol) and 1,1′-carbonyldiimidazole (0.540 g, 3.3 mmol) in dry CH_2Cl_2 (10 mL) was stirred at room temperature for 1.5 h, then the solvent was evaporated and the yellow-brown residue was dissolved in a 1:3 THF/H_2O mixture (80 mL). The mixture was vigorously stirred overnight, then THF was evaporated under reduced pressure and the organic phase was extracted with Et_2O (3 × 30 mL). The collected organic phases were dried (Na_2SO_4), then evaporated to leave an oily residue, which was chromatographed on a SiO_2 column, eluting with cyclohexane/ethyl acetate mixtures.

(*S*)-1-[(*S*)-2-Methyl-1-(2-quinolyl)propyl]isopropylaziridine (24a): Yellowish oil; 0.507 g (63%), *dr* = 95:5 (GC/MS). $[\alpha]_D^{20}$ = –32.6 (*c* = 1.05, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ = 8.12 (dd, *J* = 8.8 Hz and 15.8 Hz, 1 H, Ar), 7.82 (d, *J* = 8.0 Hz, 1 H, Ar), 7.71 (d, *J* = 8.4 Hz, 2 H, Ar), 7.53 (t, *J* = 7.6 Hz, 1 H, Ar), 2.41 (m, 1 H, NC*H*CH_2), 2.20 (d, *J* = 8.5 Hz, 1 H, PyC*H*), 1.85 (d, *J* = 3.6 Hz, 1 H, NCH_2), 1.64 (d, *J* = 6.2 Hz, 1 H, NCH_2), 1.22 (d, *J* = 5.6 Hz, 3 H, CH*Me*$_2$), 1.22 (m, 1 H, C*H*Me_2), 1.15 (m, 1 H, C*H*Me_2), 0.74 (t, *J* = Hz, 6 H, CH*Me*$_2$), 0.35 (d, *J* = 6.4 Hz, 3 H, ArCHCH*Me*$_2$) ppm. GC-MS: *m*/*z* (%) = 155 (100), 197 (60), 142 (50), 168 (22), 225 (18) [M^+ – *i*Pr]. $C_{18}H_{24}N_2$: calcd. C 80.55; H 9.01, N 10.40; found C 80.59, H 9.06, N 10.42.

(*S*)-1-[(*S*)-2-Methyl-1-(8-quinolyl)propyl]isopropylaziridine (24b): Yellowish oil; 0.523 g (65%), *dr* = 96:4 (GC/MS). $[\alpha]_D^{20}$ = +15.7 (*c* = 0.53, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ = 8.89 (m, 1 H, Ar), 8.15 (d, *J* = 8.1 Hz, 1 H, Ar), 8.05 (d, *J* = 6.4 Hz, 1 H, Ar), 7.70 (d, *J* = 8.1 Hz, 1 H, Ar), 7.60 (m, 1 H, Ar), 7.38 (m, 1 H, Ar), 3.86 (d, *J* = 8.7 Hz, 1 H, ArCHN), 2.38 (m, 1 H, NC*H*CH_2), 1.80 (m, 2 H, NCHCH_2), 1.22 (d, *J* = 6.6 Hz, 3 H, CH*Me*$_2$), 1.03 (m, 2 H, C*H*Me_2), 0.67 and 0.66 (2 d, *J* = 6.6 Hz, 6 H, CH*Me*$_2$), 0.26 (d, *J* = 6.6 Hz, 3 H, CH*Me*$_2$) ppm. GC-MS: *m*/*z* (%) = 155 (100), 197 (60), 142 (50), 225 (18), 168 (15), 184 (13), 268 (10) [M^+], 253 (5). $C_{18}H_{24}N_2$: calcd. C 80.55; H 9.01, N 10.44; found C 80.61, H 9.03, N 10.42.

(*S*)-1-[(*S*)-1-(6-Benzyl-2-pyridyl)-2-methylpropyl]isopropylaziridine (24c): Yellowish oil; 0.545 g (59%), *dr* 98:2 (GC/MS). $[\alpha]_D^{20}$ = –44.5 (*c* = 0.63, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ = 7.53 (t, *J* = 7.8 Hz, 1 H, 7.35–7–13 (m, 6 H, Ar), 6.93 (d, *J* = 7.8 Hz, 1 H, Py), 4.14 (s, 2 H, CH_2Ph), 2.28 (m, 1 H, C*H*CH_2), 2.18 (d, *J* = 8.8 Hz, 1 H, NC*H*Ar), 1.77 (d, *J* = 3.6 Hz, 1 H, CHCH_2), 1.54 (d, *J* = 6.2 Hz, 1 H, CHCH_2), 1.20 and 1.05 (2 m, 2 H, C*H*Me_2), 1.14, 0.74, 0.69 and 0.34 (4 d, *J* = 6.6 Hz, 12 H, CH*Me*$_2$) ppm. GC-MS: *m*/*z* (%) = 225 (100), 265 (88), 210 (58), 84 (47), 236 (35), 197 (33), 91 (20), 55 (17), 182 (16), 167 (13). $C_{21}H_{28}N_2$: calcd. C 81.77; H 9.15, N 9.08; found C 81.83, H 9.18, N 9.04.

Preparation of [(*N*,*N*′)*(η³-allyl)Pd][SbF_6] Complexes: Allylpalladium chloride dimer (0.157 g, 0.43 mmol) was added to a solution of the aziridine (0.86 mmol) in CH_2Cl_2 (15 mL). After stirring for 1 h the solution became green, then a solution of silver hexafluoroantimonate (0.300 g, 0.86 mmol) in THF (6 mL) was added and the mixture was stirred for 30 min, during which time a white precipitate formed. The solid was filtered off through a small pad of celite. The organic phase was washed with brine, dried (Na_2SO_4) and evaporated to leave a solid residue, which was then crystallised. Complex **12** has been described previously.[8]

Complex 20: Colourless crystals (CH_2Cl_2/Et_2O), 57% yield; m.p. 213–214 °C (dec.). $[\alpha]_D^{20}$ = –31.6 (*c* = 0.4, $CHCl_3$). The ^1H NMR spectrum (300 MHz, $CDCl_3$) shows the presence of two rotamers in a 60:40 ratio (the absorptions of the prevalent rotamer are reported in bold): δ = **8.58** and 8.46 (2 d, *J* = 5.6 Hz, 1 H, Ar), 8.08 (m, 1 H, Ar), 7.77 (m, 1 H, Ar), **7.52** (m, 1 H, Ar), 7.47 (m, 1 H,

Ar), 7.30 (m, 4 H, Ar), **7.10** (m, 1 H, Ar), 6.96 (m, 1 H, Ar), **5.53** and 4.55 (m, 1 H, CH_2CHCH_2), **3.93** and 3.73 (2 d, J = 6.6 Hz, 1 H, CH_2CHCH_2), 3.68 and **3.59** (2 d, J = 6.6 Hz, 1 H, PyC*H*), **3.58** and 3.26 (2 d, J = 6.6 Hx, 1 H, CH_2CHCH_2), **3.50** and 3.38 (2 dd, J = 7.3 and 5.0 Hz, 1 H, NC*H*CH_2), 3.11 and **3.0** (2 m, 2 H, NCHCH_2), 2.85 and **2.56** (2 d, J = 12.6 Hz, 1 H, CH_2CHCH_2), 2.55 and **2.27** (2 m, 1 H, C*H*Me_2), 1.44 (d, J = 12.6 Hz, 1 H, CH_2CHCH_2), 1.23, **1.16**, 1.09 and **0.87** (4 d, J = 6.8 Hz, CHMe_2) ppm.

Complex 21: Orange crystals (MeOH), 72% yield; m.p. 225–227 °C (dec.). $[\alpha]_D^{20}$ = +26.5 (c = 0.58, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 2980, 1607, 1533, 1490, 1474, 1446, 1388, 1159, 1015, 758, 698 cm^{-1}. The ^1H NMR spectrum (200 MHz, $CDCl_3$) shows the presence of two rotamers in a 70:30 ratio (the absorptions of the prevalent rotamer are reported in bold): δ = 7.95 (t, J = 6.6 Hz, 1 H, Ar), 7.80–6.95 (m, 17 H, Ar), 6.50 and **6.31** (2 d, J = 5.2 and 7.4 Hz, 1 H, Ar), **6.25** and 5.67 (2 dd, J = **11.0** and **11.4** Hz, 12.4 and 10.6 Hz, 1 H, CHC*H*CH), 5.03 and **3.82** (2 d, J = 12.4 and **11.4** Hz, 1 H, C*H*CHCH), 4.47 and **2.82** (2 d, J = 10.6 and **11.0** Hz, 1 H, C*H*CHCH), 3.73 and **3.37** (d, J = 6.8 and **7.2** Hz,1 H, C*H*Py), 3.33 and 2.90 (2 m, 2 H, NCHCH_2), 2.83 and **2.11** (m, 1 H, C*H*Me_2), 2.43 and **2.27** (2 dd, J = 2.2, 8.0 Hz, **2.2** and **7.4** Hz, 1 H, NC*H*CH_2), 1.34, 1.0, **0.96** and **0.86** (4 d, J = 6.6 and **7.0** Hz, 6 H, CHMe_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ (major diastereomer) = 159.7, 149.0, 139.2, 136.2, 136.1, 132–126 (m), 125.0, 124.7, 106.0, 81.4, 75.8, 45.2, 34.85, 20.1, 18.8 ppm. $C_{32}H_{33}F_6N_2PdSb$: calcd. C 48.79; H 4.22, N 3.56; found C 48.68, H 4.40, N 3.48.

Complex 25a: Colourless crystals (CH_2Cl_2/Et_2O), 70% yield; m.p. 182–185 °C (dec.). $[\alpha]_D^{20}$ = +101.1 (c = 1.06, $CHCl_3$). The ^1H NMR spectrum (300 MHz, $CDCl_3$) shows the presence of two rotamers in a 65:35 ratio (the absorptions of the prevalent rotamer are reported in bold): δ = 8.50 (2 d, J = 8 Hz, 1 H, Ar), 8.18–7.88 (m, 3 H, Ar), 7.70 (m, 2 H, Ar), 5.88 and **5.75** (2 m, 1 H, CH_2CHCH_2), 4.79 and **4.50** (2 d, J = 7.2 and 7.2 Hz, 1 H, CH_2CHCH_2), **4.13** and 3.95 (2 d, J = **6.6** and 7.2 Hz, 1 H, CH_2CHCH_2), 3.53 and **3.43** (2 d, J = 7.8 Hz, 1 H, ArC*H*), **3.45**, 3.38, 3.32 and **3.16** (4 d, J = 12.6 Hz, 2 H, CH_2CHCH_2), 2.82 and **2.49** (2 m, 1 H, NC*H*CH_2), 2.75 and 2.40 (2 m, 2 H, NCHCH_2), **1.92** and 1.86 (2 m, 1 H, C*H*Me_2), 1.41, **1.28**, 1.10, **1.00**, **0.93**, 0.91, **0.74** and 0.51 (8 d, J = 6.6 Hz, 12 H, CHMe_2) ppm.

Complex 25b: Colourless crystals ($CHCl_3$), 79% yield; m.p. 215–218 °C (dec.). $[\alpha]_D^{20}$ = +54.5 (c = 0.58, $CHCl_3$). The ^1H NMR spectrum (200 MHz, CD_2Cl_2) shows the presence of two rotamers in a 55:45 ratio (the absorptions of the prevalent rotamer are reported in bold): δ = **9.29** and 9.21 (2 d, J = 5.0 Hz, 1 H, Ar), 8.51 (t, J = 8.7 Hz, 1 H, Ar), 7.99 (d, J = 5.7 Hz, 1 H, Ar), 7.63 (m, 3 H, Ar), 6.12 (m, 1 H, CH_2CHCH_2), **4.12** and 4.01 (2 d, J = **7.4** and 5.8 Hz, 1 H, CH_2CHCH_2), 3.76 (m, 1 H, CH_2CHCH_2), 3.53 (d, J = 7.0 Hz, 1 H, ArC*H*), **3.43** and 3.31 (2 d, J = **12.2** and 12.4 Hz, 1 H, CH_2CHCH_2), 3.10 (m, 1 H, NC*H*CH_2), **3.09** and 3.67 (2 d, J = **11.8** and 10.4 Hz, 1 H, CH_2CHCH_2), 2.55 and 2.42 (2 m, 2 H, NCHCH_2), 1.61 and 1.25 (2 m, 2 H, C*H*Me_2), 1.50, **1.33**, **0.91**, 0.84, 0.61, **0.57**, **0.20**, 0.07 (8 d, J = 6.6 Hz, 12 H, CHMe_2) ppm.

Complex 25c: Colourless crystals (MeOH), 61% yield; m.p. 223–224 °C (dec.). $[\alpha]_D^{20}$ = +4.2 (c = 1.0, $CHCl_3$). The ^1H NMR spectrum (300 MHz, $CDCl_3$) shows the presence of two rotamers in 55:45 ratio (the absorptions of the prevalent rotamer are reported in bold): δ = 7.85 (2 t, J = 7.8 Hz, 1 H, Py), 7.53–7.28 (m, 4 H, Ar), 7.15 (m (3 H, Ar), 5.72 (m, 1 H, CH_2CHCH_2), **4.36** and 4.27 (2 s, 2 H, CH_2Ph), 4.35 and 4.28 (2 d, J = 6.6 Hz, 1 H, CH_2CHCH_2), **4.06** and 3.89 (2 d, J = 6.6 Hz, 1 H, CH_2CHCH_2), 3.34, 3.22, 3.14 and 3.10 (4 d, J = 12.4 Hz, 2 H, 2 CH_2CHCH_2), 3.24 and 3.13 (2 d, J = 8.2 Hz, 1 H, NC*H*Ar), 2.84 and **2.50** (2 m, 1 H, NC*H*CH_2), 2.68 and **2.38** (2 m, 2 H, CHCH_2), 1.88, 1.81, 1.45 and 1.18 (4 m, 2 H, C*H*Me_2), 1.37, **1.25**, 1.05, 1.03, 0.94, **0.90**, **0.89** and 0.65 (8 d, J = 6.7 Hz, 12 H, CHMe_2) ppm.

Complex 26: Orange crystals (MeOH), 77% yield; m.p. 218–219 °C (dec.). $[\alpha]_D^{20}$ = +84.9 (c = 0.68, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 2950, 1607, 1570, 1540, 1491, 1464, 1023, 889, 756, 697 cm^{-1}. The ^1H NMR spectrum (300 MHz, $CDCl_3$) shows the presence of two rotamers in an 85:15 ratio (the absorptions of the prevalent rotamer are reported in bold): δ = 7.80–7.10 (m, 16 H, Ar), 6.90–6.60 (m, 2 H, Ar), 6.55 and **6.44** (2 dd, J = 11.2 and **11.4** Hz, 1 H, CHC*H*CH), 5.33 and **4.86** (2 d, J = 10.8 Hz, 1 H, C*H*CHCH), 4.78 and **4.72** (d, J = 12.0 Hz, 1 H, C*H*CHCH), **4.29**, **3.75**, 3.21 and 3.01 (4 d, J = **17.0** and 14.0 Hz, 2 H, CH_2Ph), **2.91** (d, J = 8.7 Hz, 1 H, NC*H*Py), 2.72 (m, 1 H, NC*H*CH_2), 1.60–1.40 (m, 4 H, 2 C*H*Me_2 and NCHCH_2), **1.14**, 1.02, **0.91**, **0.89**, **0.87**, 0.55. 0.50 and 0.40 (8 d, J = 6.6 Hz, CHMe_2) ppm. ^{13}C NMR (75 MHz, [D_6]DMSO): δ (major diastereomer) = 162.1, 160.5, 139.8, 137.2, 136.1, 132–128, 123.8, 122.6, 107.9, 81.8, 80.0, 76.9, 45.9, 35.9, 33.1, 21.1, 21.0, 20.0, 19.6 ppm. $C_{36}H_{41}F_6N_2PdSb$: calcd. C 51.24, H 4.90, N 3.32; found C 51.35, H 5.02, N 3.42.

X-ray Crystallography: The diffraction experiments for **21** were carried out at room temperature on a Bruker AXS SMART 2000 CCD diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Intensity data were measured over full diffraction spheres using 0.3°-wide ω scans at a crystal-to-detector distance of 5.0 cm. The SMART[29] software package was used for collecting frames of data, indexing reflections and determination of lattice parameters. The collected frames were then processed for integration with SAINT[29] and an empirical absorption correction was applied with SADABS.[30] The diffraction experiments for **26** were carried out on an Enraf–Nonius CAD4 diffractometer at room temperature, using graphite-monochromatized Mo-K_α radiation (λ = 0.71069 Å). The unit cell was determined by a least-squares fitting procedure using 25 randomly selected strong reflections. The diffracted intensities were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using the azimuthal scan method. The structures were solved by direct methods (SIR 97)[31] and subsequent Fourier syntheses, and refined by full-matrix least-squares calculations on F^2 (SHELXTL)[32] with anisotropic thermal parameters for the non-hydrogen atoms. One of the two SbF_6^- anions present in the asymmetric unit of **26** was found to be disordered over two orientations yielding two distinct F_6 octahedra around the Sb centre (0.59 and 0.41 occupation factors, respectively). The methyl, methylene and aromatic hydrogen atoms were placed in calculated positions and refined with idealized geometry, whereas the other H-atoms were located in the Fourier map and refined isotropically. Crystal data and details of the data collection for both structures are reported in Table S2 (see Supporting Information). CCDC-244030 ... -244033 (for **21**, **26** and **25a**,**b** respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Further data are available as Supporting Information[14].

Ethyl (*E*)-1,3-Diphenyl-2-propen-1-yl Carbonate: Ethyl chloroformate (1.84 g, 17 mmol) was slowly added to a stirred solution of 1,3-diphenyl-2-propen-1-ol (1.05 g, 5 mmol), pyridine (1.5 g, 19 mmol), and 4-(dimethylamino)pyridine (10 mg) in THF (10 mL) at 0 °C. The mixture was stirred at 20 °C for 48 h, after which time

H_2O was added and the organic phase extracted with Et_2O (3 × 10 mL). The collected organic layers were washed with 1 N HCl (10 mL), with sat. $NaHCO_3$ and brine, then dried (Na_2SO_4) and concentrated to leave **1b** in almost quantitative yield. The compound decomposed during GC analysis, but a purity of >95% was determined by ^1H NMR analysis and therefore the product was used without further purification. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.60–7.20 (m, 10 H, Ph), 6.82 (d, J = 15.4 Hz, 1 H, PhCH=CH), 6.42 (d, J = 8.4 Hz, 1 H, CHO), 6.27 (dd, J = 15.4 and 8.4 Hz, 1 H, PhCH=CHCHPh), 4.21 (dq, J = 1.0 and 6.2 Hz, CH_2O), 1.31 (t, J = 6.2 Hz, 3 H, CH_3) ppm.

Palladium-Catalysed Allylic Substitution Reactions. Preparation of (*S*)-2: The palladium salt **20** (0.061 g, 0.1 mmol) was added to a stirred solution of **1b** (0.28 g, 1 mmol) in THF (5 mL) under Ar at room temperature. Then, a solution of sodium dimethyl malonate, generated from dimethyl malonate (0.198 g, 1.5 mmol) and NaH (0.036 g, 1.5 mmol) in THF 6 mL), was added dropwise and the mixture was magnetically stirred overnight. 1 N HCl (5 mL) was added and the mixture was extracted with Et_2O (3 × 10 mL), the organic phase was dried (Na_2SO_4) and the solvents evaporated. Chromatography of the residue on a SiO_2 column eluting with cyclohexane/ethyl acetate (15:1) gave the product (*S*)-**2**: 0.227 g (70%). $[\alpha]_D^{25}$ = –15.4 (c = 0.42, EtOH); the *ee* (90%) was determined by HPLC analysis (Daicel Chiralcel™ OD column, *n*-hexane/*i*PrOH, 99:1, flow rate 0.5 mL min^{-1}; the product eluted at 21.15 [(*R*)-enantiomer] and 22.22 min [(*S*)-enantiomer].

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