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Chiral platinum and palladium complexes containing functionalized C_2-symmetric bisaminoaryl 'Pincer' ligands

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Dedicated to Professor Jean Normant on the occasion of his 65th anniversary in admiration of his great contribution to the application of organocopper chemistry.

Abstract

The synthesis of enantiopure (oxo-functionalized) C_2-symmetric NCN pincer ligands is described. A key step is the symmetric functionalization of the benzylic positions, which was achieved by enantioselective ketone reduction and subsequent stereoselective substitution protocols. The introduction of α-alkyl substituents has a pronounced effect on the cavity for metal binding. For example, lithiation of the α-ethyl-functionalized pincer ligand afforded mixed (alkyl)(aryl)lithium aggregates rather than dinuclear bis(aryl) lithium $[Li(NCN)]_2$ species as usually observed for NCN–lithium complexes. Similar effects were established for the (*trans*)-metalation reaction, which proceeded significantly slower when the steric demand of the α-substituent is increased. The potential of the corresponding enantiopure palladium and ruthenium complexes as enantioselective catalyst has been probed in the asymmetric aldol condensation and hydrogen transfer reactions. The low enantiomeric excess of the products of both reactions indicated that face-discrimination of substrates is not induced by these catalysts and that the chiral information must be located in closer proximity to the metal center. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Asymmetric synthesis; Homogeneous catalysis; Pincer N ligand; Ligand tuning; Platinum

1. Introduction

Chiral transition metal complexes containing C_2-symmetric ligands have found widespread application in asymmetric catalysis [1]. Frequently, the catalyst precursor consists of a late transition metal bound to a (set of) bidentate coordinating ligand(s), of which derivatives of chiral bis-oxazolines, salen-, and binap-type ligands are prominent examples [2]. Terdentate bonding, C_2-symmetric ligands having a neutral donor array (e.g. η^3-*N*,*N*,*N*-coordinating pybox ligands) are less frequently used, although good to excellent (asymmetric) catalyst performance (stereo-, regio-, chemoselectivity) was established for some inorganic complexes [3]. Recently, various research groups started to explore catalysts derived from related organometallic analogs with monoanionic 'pincer' ligands ECE (C = aromatic carbanion; E = heteroatom, e.g. P, N, S) [4]. This class of complexes offers interesting opportunities for the design of chiral catalysts: (i) the metal is bonded to the ligand via a direct metal-to-carbon σ-bond, thus preventing leaching of the metal from the complex; (ii) both the benzylic carbon and the two N or P donor sites are potentially stereogenic centers; and (iii) the active metal center in such complexes has a distinct steric surrounding as a result of bis(*ortho*)-chelation of the ligand (Fig. 1).

Dependent on the choice of the metal M and the donor E, various reactions were catalyzed, such as hydrogenation [5], alkane dehydrogenation [6], C–C bond formation [7–13], C–C bond cleavage [14], and polymerization [15]. Early approaches towards asymmetric catalysis involved the replacement of the NMe_2

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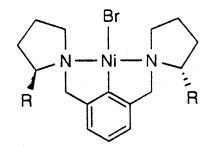
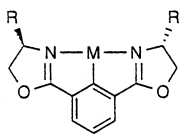
groups in the NCN pincer ligand by asymmetrically substituted pyrrolidines (**A** in Chart 1) [16]. A nickel catalyst with this chiral ligand was used in atom transfer radical (Kharasch) addition reaction, which provided, however, 1:1 addition products with low enantiomeric excess. Detailed studies have shown that this ATRA catalysis involves inner sphere radical formation and quenching at the nickel-stabilized halide atom. According to a crystal structure determination on the catalyst precursor, this atom is localized remote from the stereogenic centers of the chiral ligand [16]. In a similar approach, C_2-symmetric Phebox ligands (**B** in Chart 1) were prepared and used in asymmetric catalysis, however, with only limited success (ee typically below 35%) [9–11]. A markedly improved asymmetric induction was observed by the enantioselective functionalization of the benzylic positions of PCP pincer ligands (ee up to 80%; **C** in Chart 1) [12,13,17].



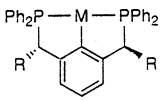
A

R = Me, *i*Pr, OCOMe [16]



B

M = PdBr, R = Me, *i*Pr, ... [9]
M = PdBr, R = *i*Pr [10]
M = Rh(cod), R = *i*Pr [11]



C

M = PdBr, R = acetale [12a]
M = PdCl, PtCl, R = Me [12b]
M = RuCl(PPh3), R = Me, Et [17]

Chart 1.

Recently, we set out to explore the synthesis of a series of enantiopure α-alkylated NCN pincer ligands (E = NMe_2) containing chiral information on the benzylic carbons, and their platinum(II) and palladium(II) complexes [18], since the NCN and PCP metal complexes often have different and sometimes complementary activity [5]. Moreover, the high kinetic stability generally observed for NCN–platinum species, makes them ideal candidates for detailed structural analyses, while the corresponding palladium(II) complexes are kinetically active and catalyze a wide range of synthetically important C–C coupling reactions. Furthermore, the functionalization of the aryl moiety of these chiral NCN pincer ligands is reported, which offers attractive opportunities for the anchoring of such (catalytically active) chiral complexes to soluble (e.g. dendritic) [19] or insoluble heterogeneous (e.g. activated oxide surface) [20] supports as well as for the synthesis of molecular networks for crystal engineering.

2. Results and discussion

2.1. Enantioselective pincer ligand synthesis

Alkylated benzylic alcohols such as **1** (Scheme 1) were selected as key intermediates for the synthesis of different types of chiral NCN pincer ligands [21]. The various elegant methods [22] for the enantioselective preparation of such benzylic alcohols include the asymmetric reductive alkylation of aldehydes with dialkyl zinc reagents catalyzed by enantiopure *ortho*-arenethiolate zinc catalysts, e.g. [Zn(*S*-SC_6H_4{CH_2NMe_2}-2)]$_2$ [23]. Hence, the diol **1b** was prepared from isophthaldehyde and $ZnEt_2$ (Scheme 1). Chiral HPLC analysis of the products obtained after work-up revealed a mixture of *S*,*S*-**1b** (74%), *R*,*R*-**1b** (2%) and *meso*-**1b** (24%). Substitution of the NMe_2 groups in the catalyst by *N*-pyrrolidinyl or *N*-piperidinyl moieties increased the stereoselectivity, because these changes enhanced the rate of the catalyzed reaction and resulted in a more pronounced chiral pocket [23b]. Using these catalysts, the stereoisomeric compounds were obtained in 90:2:8 molar ratio (*S*,*S*:*R*,*R*:*meso*).

However, when $ZnMe_2$ was used as the alkylating agent in order to prepare diol **1a**, the reaction was

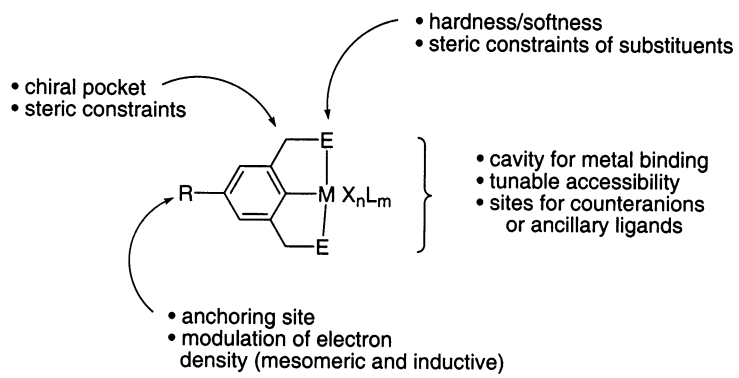
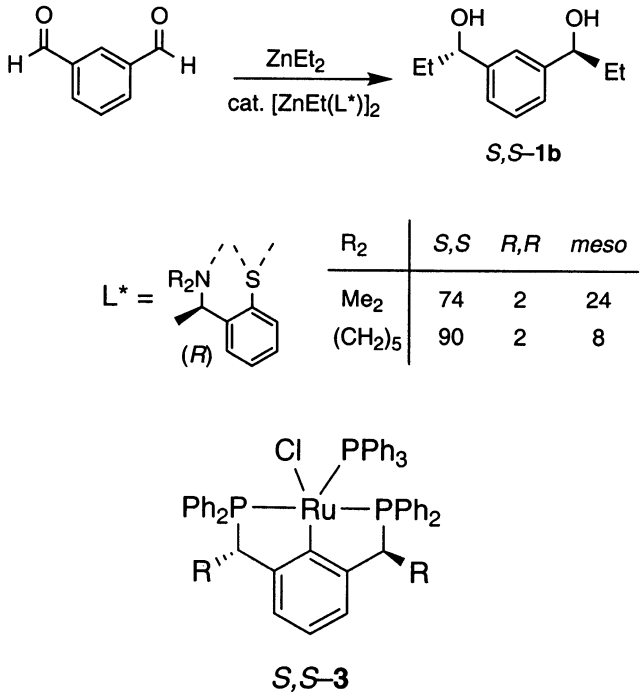


Fig. 1. Basic concepts for steric and electronic tuning of metal properties in complexes containing a pincer-type ligand (E = NR_2, PR_2, SR).



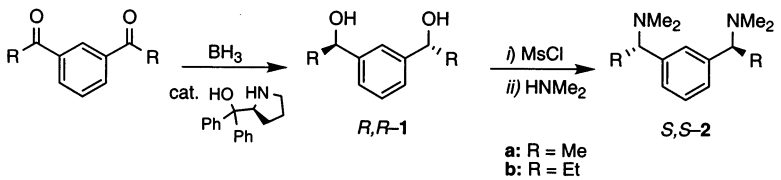
Scheme 1.

much slower (90% consumption of aldehyde after 7 days); moreover, the optical purity of the formed product mixture was considerably lower than in the corresponding ethyl case. This is a result of achiral product formation via the uncatalyzed (non-stereoselective) reaction, which also promoted the formation of difficult to separate byproducts, e.g. monoalkylated diols.

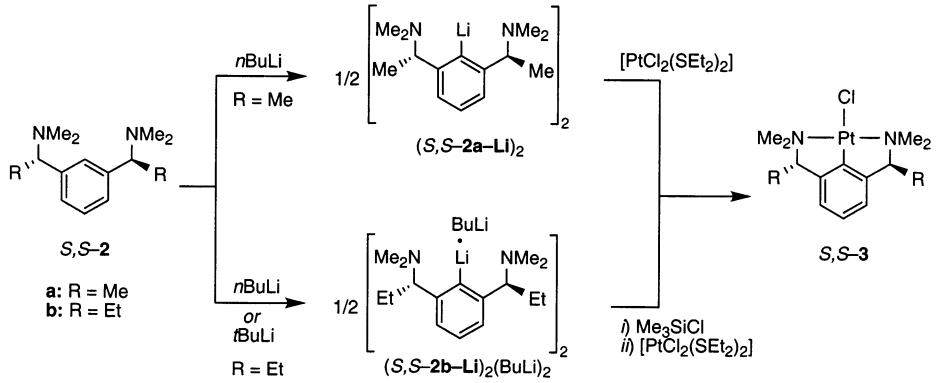
A method, which circumvents these limitations, is the borane-mediated reduction of ketones using an optically active β-amino alcohol as chiral auxiliary (CBS reduction) [24]. Incubation of BH_3 with *S*-diphenyl prolinol afforded a chiral oxazoborolidine which was used for the asymmetric reduction of 1,3-diacetyl benzene, giving the diol *R*,*R*-**1a** in high chemical yield (92%) and optical purity (>90% of the enantiopure diasteroisomer) [25]. Application of the same procedure starting from 1,3-dipropionyl benzene afforded the desired ethyl-substituted diol *R*,*R*-**1b** in slightly lower optical purity in a typical 85% yield (Scheme 2). The absolute configuration of the diols was determined by chiral HPLC and also by comparison of the specific rotation of the product mixtures with reported data [2a,26]. The *R*,*R*-configuration is in full accordance with the mechanism of the CBS reduction as proposed by Corey and Helal [24]. Stereoselective transformation [12b] of the diol **1** involved dropwise addition of $MeSO_2Cl$ (MsCl) to a cold (−80°C) solution of **1** in the presence of NEt_3, affording the corresponding bis(-mesylate) compound (Scheme 2). Subsequent nucleophilic substitution with $HNMe_2$ was performed in situ and proceeded with inversion at the stereogenic carbon centers affording the target bisaminoarene *S*,*S*-**2** [27].

2.2. C_2-Symmetric lithium and platinum NCN complexes

Generally, heteroatom-directed lithiation of the bisaminoarene pincer ligand precursors and subsequent transmetalation allows for the preparation of a large variety of transition metal pincer complexes [4b]. Hence, reaction of *S*,*S*-**2a** with *n*-BuLi in alkane solvents followed by transmetalation with $[PtCl_2(SEt_2)_2]$ afforded the chiral arylplatinum(II) complex *S*,*S*-**3a** in 78% yield. While lithiation of *S*,*S*-**2a** was straightforward, different product formation was observed when the α-ethyl substituted bisaminoarene **2b** was used. Lithiation of **2b** under similar conditions did not exceed 50% even after prolonged reaction times (Scheme 3) [18a]. It appeared that addition of a second equivalent of *n*-BuLi was necessary to obtain complete *ortho*-lithiation. Quenching experiments with aliquots of the reaction mixture confirmed that quantitative formation of either **2b-D** (D_2O added) or **2b-SMe** (MeS–SMe added) had occurred. Also changing the lithiating agent to *t*-BuLi, which is much more reactive and sterically significantly more demanding than the *n*-Bu group in *n*-BuLi [28], did not drive the reaction beyond 50% conversion, i.e. again two mole equivalents of *t*-BuLi were necessary to achieve complete litihiation. This pointed to the formation of similar mixed aryl–alkyl lithium aggregates, i.e. [(*S*,*S*-**2b-Li**)(*t*-BuLi)]. Recent studies of these reactions showed that the reaction of **2b** with one mole equivalent of *n*-BuLi stops at the stage of a stable mixed aryl–alkyl lithium dimer [(**2b-Li**)$_2$(BuLi)$_2$] (see Fig. 2 for the molecular structures in the solid state). The two NCN ligands are each bridging between two Li-atoms via 3c–2e bonds, thus resulting in two $[NCN{\cdot}Li_2]^+$ motifs which are bridged by two butyl anions in an electron-deficient CLi_2 bonding [18a]. These structural features are remarkable, since



Scheme 2.



Scheme 3.

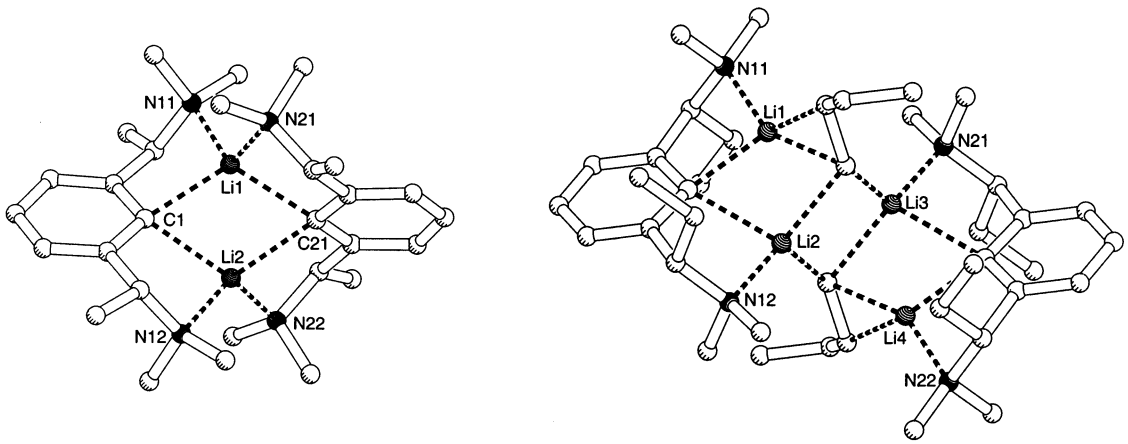


Fig. 2. Lithium adduct formation of NCN pincer ligands in dependence of the α-alkyl substituents: (a) crystal structure of (**2a-Li**)$_2$, an aryllithium dimer containing α-methyl substituents; and (b) crystal structure of the lithiated, α-ethyl functionalized ligand **2b** showing the formation of a mixed aryl–alkyl lithium aggregate [(**2b-Li**)$_2$(*n*-BuLi)$_2$]. Note that the crystal, obtained from racemic solutions, comprises one pincer ligand in the *S,S*- and the other in the *R,R*-configuration.

the Li(NCN) compounds form typically dinuclear [Li(NCN)]$_2$ lithium aggregates, both in solution and in the solid state [29]. Similar aggregation of **2b-Li** was anticipated but appeared to give tetranuclear lithium aggregates even when *t*-BuLi was used. Apparently, the steric demand of the α-alkyl substituents dictates the aggregation process, since dimer formation as observed for the α-methyl ligand is obviously prevented by the larger α-ethyl substituents, which is elevated in the [(NCN–Li)$_2$(RLi)$_2$] structure by the incorporation of bridging alkyl groups.

For obvious reasons, it was essential to remove the *t*-BuLi species in [(**2b-Li**)$_2$(*t*-BuLi)$_2$] prior to attempting any transmetalation. Interestingly, Me_3SiCl was found to react selectively with the *t*-BuLi groups of the tetranuclear aggregates, thus leaving the [Li(NCN)] moieties unaffected [30]. Apparently, the two bulky *ortho*-aminomethyl substituents in [Li(NCN)] shield the C–Li bond efficiently (cf. the quantitative reaction of Me_3SiCl with LiPh). Moreover, separate experiments have shown that the silicon center in Me_3SiCl has too low a electrophilicity to react with [Li(NCN)]$_2$. [31] It is important to note that the resulting NCN–Li reagent has the composition [(**2b-Li**)$_2$(LiCl)$_2$] and has structural features that are most probably similar to those observed in [(**2b-Li**)$_2$(BuLi)$_2$] (Fig. 2) but with bridging chloride ligands instead of butyl groups.

Following this BuLi–Me_3SiCl protocol, alkyl lithium-free *S,S*-**2b-Li**·LiCl was successfully transmetalated with [$PtCl_2(SEt_2)_2$] to give the chiral platinum(II) complex *S,S*-**3b** in good yield (Scheme 3). Notably, the reaction time for complete platination was much longer (4 days) than is required for the formation of the corresponding methyl analog *S,S*-**3a** (1 day) [18b]. This is another indication for the way metal binding and reactivity of a metal center in the cavity of these pincer ligands can be engineered by small steric modifications in the ligand array.

Both the ^{1}H and ^{13}C{^{1}H}-NMR spectra of enantiopure *S,S*-**3a** show the NMe_2 groups as two well-resolved signals ($\delta_H = 3.14$, $^3J_{HPt} = 36.6$ Hz, $\delta_H = 2.81$, $^3J_{HPt} = 42.4$ Hz; $\delta_C = 51.9$ and 47.0). Diastereotopicity of these groups points to a rigid conformation of the metallacycles, where Pt–N bond dissociation is negligible and

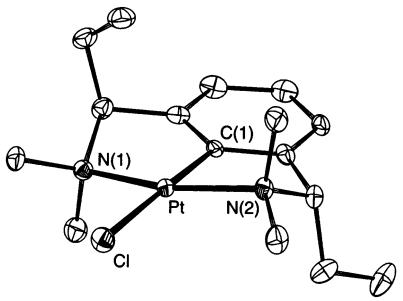


Fig. 3. Perspective view (ORTEP, 50% probability) of the C_2-symmetric arylplatinum complex *S,S*-**3b**. Pertinent bond lengths (Å) and angles (°) are: Pt–Cl 2.4165(16), Pt–C(1) 1.927(5), Pt–N(1) 2.099(5), Pt–N(2) 2.088(5); Cl–Pt–C(1) 178.57(18), N(1)–Pt–N(2) 162.1(2), C(1)–Pt–N(1) 80.8(2), C(1)–Pt–N(2) 81.4(2), Cl–Pt–N(1) 99.74(14), Cl–Pt–N(2) 98.06(15).

puckering processes are slow on the NMR time scale, cf. the different chemical shifts and H–Pt coupling constants of the axially and equatorially positioned methyl groups and benzylic protons.

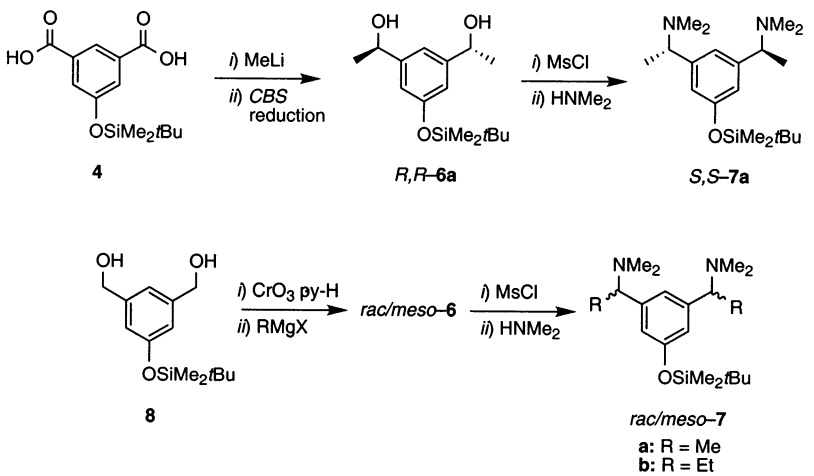
The NMR spectra of the diastereoisomeric mixture of **3a** showed two qualitatively similar, well-resolved signal patterns, one for each enantiopair [32]. The spectroscopic characteristics of *R,S*:*SR*-**3a** were conveniently extracted by subtracting the set of signals identified as *S,S*-**3a**. Only small shift differences were observed (i.e. $|\delta_{RR:SS} - \delta_{RS:SR}| < 0.1$ ppm), which were most pronounced for the two singlets assigned to the diastereotopic NMe_2 groups: in *R,S*:*SR*-**3a** they are located at $\delta_H = 3.07$ and 2.85, and are separated by only 0.22 ppm (cf. 0.33 ppm in *S,S*-**3a**). Moreover, the coupling constants of these two resonances to platinum are equal ($^3J_{HPt} = 39.6$ Hz for both signals), which points to a less pronounced axial–equatorial orientation of the nitrogen-bound methyl groups than in the C_2-symmetric complex, thus approaching a conformation with mirror-plane symmetry.

The corresponding α-ethyl analog, *S,S*-**3b** displayed similar spectroscopic properties. Rigid conformation of the benzylic groups, i.e. a frozen wagging of the metallacycles, was clearly indicated by ^{1}H-NMR spectroscopy, since the benzylic protons appeared as doublet of doublets, owing to different and well-defined vicinal coupling constants with the two CH_2 protons of the ethyl substituent ($^3J_{HH} = 8.7$ and 3.9 Hz). This unambiguously implies a fixed conformation of the metallacycles. In addition, the absolute stereochemistry of *S,S*-**3b** was assessed by single crystal X-ray analysis (Fig. 3) and by determining the specific optical rotation. These results underline the stereoselectivity of the synthetic protocol, i.e. the *R,R*-enantiomer of the benzylic alcohol as the product of the CBS reduction and inversion of the stereocenters upon nucleophilic substitution of the mesylate by $HNMe_2$. Comparison of the molecular structure of *S,S*-**3b** (Fig. 2) and the earlier reported structure of *R,R*-**3b** [18b] does not show significant differences, and bond lengths and angles as well as the unit cell parameters of the two enantiopairs are identical within standard deviations.

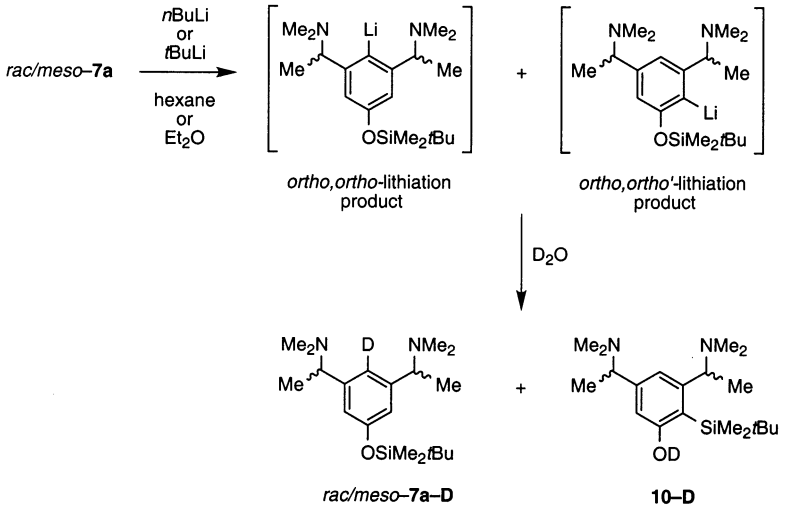
2.3. Functionalized C_2-symmetric pincer ligands

Recent work in connection with our interest in nanosize (multisite) immobilized (grafted) homogeneous catalysts [19a,33] has shown that a hydroxy group on the pincer arene moiety in *para* position with respect to the M–C_{aryl} bond is a suitable anchoring point to tether NCN–metal catalysts to dendritic peripheries and focal points of dendritic wedges [33e,34]. In addition, such hydroxy groups in combination with metal-bound chloride ions have been shown to provide a particularly attractive synthon for hydrogen bonding and crystal engineering [35].

The synthesis of the oxo-functionalized precursor **7** is shown in Scheme 4 and starts from 5-siloxyisophthalic



Scheme 4.

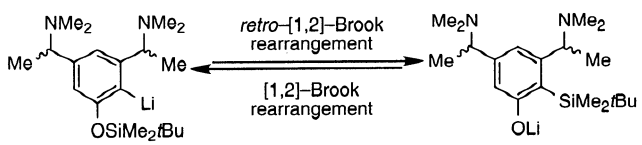


Scheme 5.

acid **4** containing a silyl-protected phenol functional group as a potential linker unit to a tether (Scheme 4). The acid functionalities in **4** were selectively converted into methyl ketones by treatment with an excess of MeLi without affecting the silyl-protecting group [36]. Subsequent CBS-type oxazoborolidine-mediated reduction of the diketone **5** using identical conditions as for the preparation of **1** afforded the C_2-symmetric diol *R,R*-**6a** in high optical purity (typically 90% of the desired stereoisomer). Residual undesired products from partial reduction as well as minor quantities of *meso*-**6a** (significantly less than 10%) were at this stage conveniently separated by column chromatography. Diastereoisomeric mixtures of *rac*/*meso*-**6** were prepared from the readily accessible primary diol **8** by oxidation with pyridinium chlorochromate [37] and subsequent reductive alkylation using EtMgBr or MeMgI, with retention of the silyl-protecting group on the phenol. Stereoselective amination, performed following the MsCl–$HNMe_2$ protocol, finally gave *S,S*-**7a** and *rac*/*meso*-**7**, respectively.

2.4. Lithiation of oxo-functionalized chiral pincer ligands

Surprisingly, following the usually successful reaction protocol (viz. *n*-BuLi in hexane), lithiation of the oxo-functionalized bisaminoarene *rac*/*meso*-**7a** did not occur regioselectively. According to ^{1}H-NMR spectroscopy on a sample obtained from D_2O quenching experiments of the reaction mixture, which showed two sets of clearly resolved resonance patterns in a 1:1 molar ratio, two different products were formed during lithiation. One of these resonance patterns was assigned to **7a-D**, as all signals were identical to those of *rac*/*meso*-**7a** except for the absence of the resonance at 6.78 ppm due to the proton in mutual *ortho,ortho* position in **7a** (Scheme 5) [38]. The second signal pattern is characterized by two singlets in the aromatic region. Moreover, the proton resonances due to the $SiMe_2$ group are located at $\delta_H = 0.40$, and are shifted considerably downfield (cf. $\delta_H = 0.18$ in **7a**), pointing to a rearrangement of the silyl-protecting group. Lower symmetry than the parent species **7a** was also indicated, e.g. by two inequivalent benzylic protons and nitrogen-bound methyl groups. All these data are in good agreement with the formation of phenol **10-D**, which results from oxygen-to-arene migration of the silyl group (Scheme 5). This migration can be explained by lithiation in *ortho,ortho'* position [38], because of competitive directing properties of the O- and N-heteroatom-containing aryl substituents. This lithiation is followed by a fast retro-[1,2]-Brook rearrangement, involving sequential Si–O bond cleavage and Si–C_{aryl} bond formation (Eq. (1)) [39]. The product **10-D** showed a diagnostic downfield shift of the singlet of the silicon-bound methyl protons. This resonance provided a sensitive probe for the products formed by a retro-Brook rearrangement.



(1)

The choice of solvent and lithiating agent had a pronounced influence on the regioselectivity of the lithiation of **7a**. The use of more reactive *t*-BuLi instead of *n*-BuLi promoted the formation of **10-D** rather than that of **7a-D** (after D_2O quench, molar ratio 6:1). Similar effects were observed when the solvent was changed from hexane to coordinating solvents such as Et_2O, which enhanced the selectivity for **10-D** (molar ratio 11:2). These results point to a kinetically con-

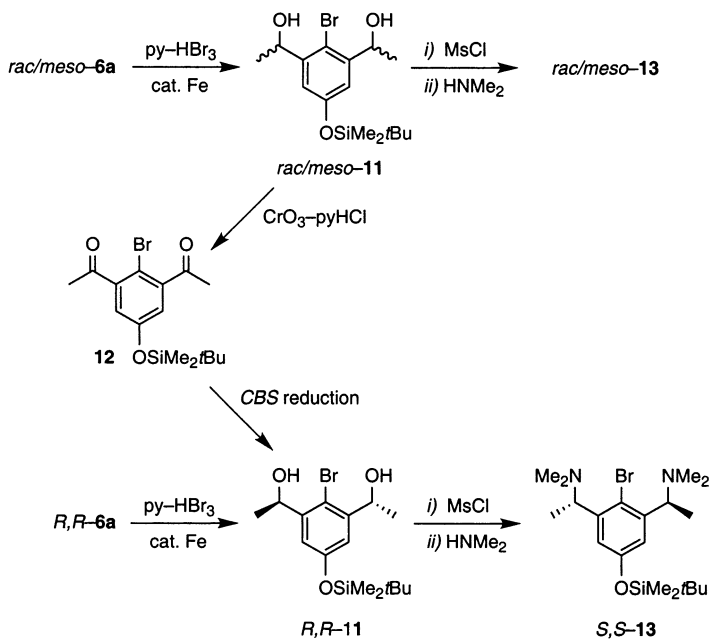
trolled product distribution and clearly reveal that lithiation of **7** is predominantly directed by oxygen lone pairs — either intramolecularly present or originating from the solvent — rather than by tertiary amines [40], in spite of the steric shielding of the silyl substituent in, e.g. Ar-O-$SiMe_2$tBu. This is corroborated by earlier results from studies of the selective lithiation of NC(H)N (i.e. the achiral version of **2**; see Scheme 2, R=H) [41]. Significant lithiation of the thermodynamically less stabilized *ortho*,*ortho′* position was noted in Et_2O, whereas in hexane intramolecular nitrogen-assistance by both CH_2NMe_2 groups directed the regioselectivity, hence giving *ortho*,*ortho*-lithiation exclusively. Obviously, the two lithiated species (Scheme 5) do not equilibrate and an (in)direct interconversion of the lithiated precursors of **7a-D** and **10-D** does apparently not occur [42].

These results prompted us to also reinvestigate the lithiation of NC(H)N-$OSiMe_2$tBu, i.e. the achiral analog of **7** (Scheme 4, R=H) in hexane [27b]. The NMR spectrum of samples after quenching of the reaction mixture with D_2O pointed to the presence of ca. 10% of products originating from a retro-[1,2]-Brook rearrangement [43]. This is significantly lesser than that observed during lithiation of **7a** under similar conditions. Obviously, the introduction of substituents at the benzylic carbon restricts the population of the C_{aryl}–C_{benzyl} rotamers and consequently decreases the required conformational flexibility of the nitrogen lone pairs to become involved in the regioselective lithiation process.

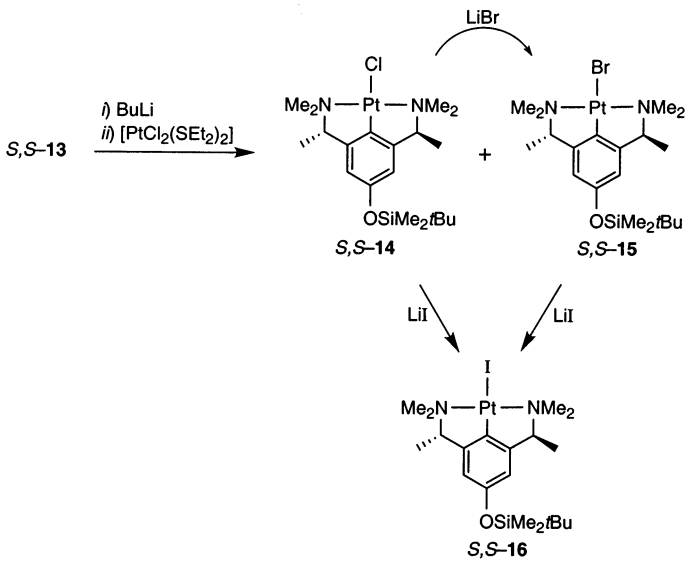
2.5. Brominated ligand precursors

Since the selective lithiation of the desired *ortho*,*ortho* position in **7a** via H/Li exchange failed, the Br/Li exchange route was attempted [44]. To this end, a bromide substituent had to be introduced first in the designated *ipso* position. This was achieved by regioselective bromination of diol *R*,*R*-**6a** with pyrH-Br_3 and catalytic amounts of iron (Scheme 6) [45]. The corresponding diol *R*,*R*-**11** was obtained in moderate yields (54%), since slow Si–O bond cleavage was observed during the bromination, presumably due to dissolved HBr. Purification of *R*,*R*-**11** from undesired side products by column chromatography was necessary prior to nucleophilic amination (vide supra) [46].

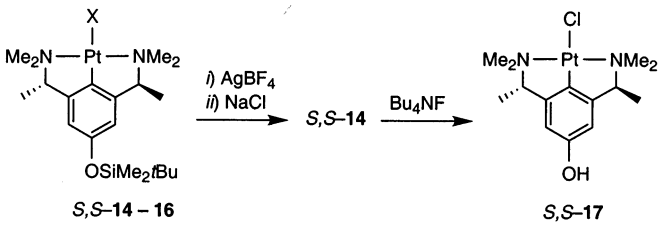
The bis-aminoarene *S*,*S*-**13** was lithiated at low temperature (-80°C) using two equivalents of *t*-BuLi in hexane. According to ^{1}H-NMR spectroscopy of an aliquot of the reaction mixture that was quenched with D_2O, the Li/Br exchange was complete after 30 min reaction time. No traces of products raising from lithiation at other positions could be detected. When the reaction mixture was kept at RT for 2 days, a new product was formed in minor quantities (less than 10%), which was characterized (after D_2O quench) by a set of proton resonances that was qualitatively related to that of **7a-D**. However, the diagnostic signal for the $SiMe_2$ group at 0.40 ppm and the conservation of the overall molecular symmetry (no additional resonances or couplings were observed) strongly point to partial formation of a product originating from a retro-[1,4]-



Scheme 6.



Scheme 7.



Scheme 8.

Table 1
Selected NMR spectroscopic data for the chiral complexes **14–16**

Complex	X	^{1}H-NMR		^{13}C-NMR	
		ArCHN	NMe_2	ArCHN	NMe_2
S,S-**14**	Cl	4.11	3.07, 2.75	78.8	52.0, 47.2
S,S-**15**	Br	4.14	3.18, 2.84	78.5	53.1, 47.7
S,S-**16**	I	4.10	3.26, 2.91	78.1	55.1, 49.0

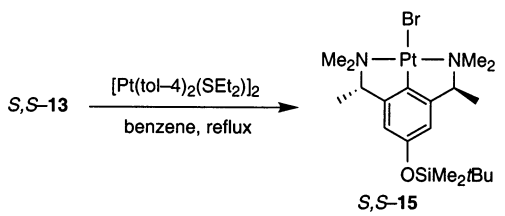
Brook rearrangement [39,47]. These results emphasize that the Li–C_{aryl} bond in complexes such as **13-Li** is inert to migratory processes, since no residues due to, e.g. *ortho*,*ortho*′-lithiation [38] and subsequent retro-[1,2]-Brook rearrangement were observed even after prolonged reaction times.

2.6. Tethered chiral organoplatinum complexes

Transmetalation of the lithium complex *S,S*-**13-Li**, obtained from selective Br/Li exchange, with $[PtCl_2(SEt_2)_2]$ gave a mixture of two related platinum complexes (NMR). The observed chemical shift differences for the NMe_2 resonances of these compounds were typical for platinum complexes containing different metal-bound halides [34] and suggested the formation of the chloride complex *S,S*-**14**, and the corresponding bromide complex *S,S*-**15** (Scheme 7). Indeed, addition of excess NaBr to an acetone solution of the crude product mixture gave *S,S*-**15** as the single platinum complex. The same result was obtained when LiBr was added during the transmetalation reaction. The driving force for this conversion was attributed to the better solubility properties of LiBr in Et_2O compared to that of the formed LiCl. Accordingly, the presence of LiI, which is even better soluble in Et_2O, quantitatively generated the iodide complex *S,S*-**16** (Scheme 7). Obviously, the reverse process, i.e. the exchange of a platinum-bound iodide by chloride (or bromide) required a different procedure. Halide abstraction by addition of stoichiometric amounts of $AgBF_4$ in wet acetone resulted in instantaneous precipitation of the silver salt AgX and formation of a cationic platinum aqua complex, which was converted into the desired neutral species **14**, **15** or **16** by treatment with the corresponding halide anion X^-, e.g. as aqueous NaX solution (Scheme 8).

The two NMe_2 resonances (vide supra) in the ^{1}H-NMR spectra are diagnostic for the determination of the type of halide present [34], since a systematic downfield shift was observed for these signals in the series Cl to Br to I (Table 1). A similar trend was established for the ^{13}C chemical shift values of these groups. Remarkably, the benzylic carbons showed an opposite behavior and the resonances shifted systematically to higher field.

The presence of a reactive C–Br bond in *S,S*-**13** also provides access to the alternative preparation of *S,S*-**15** via oxidative addition with an equimolar amount of $[Pt(tol\text{-}4)_2(SEt_2)]_2$ in benzene at reflux temperature (Eq. (2)) [48]. Residual bitolyl was removed either by repeated recrystallization from CH_2Cl_2–pentane mixtures or by gradient column chromatography on silica. Obviously, this oxidative addition route does not suffer from the halide scrambling as observed during the transmetalation reaction. The fact that no lithium intermediates are required might become particularly relevant for the construction of multifunctional species, for example nanosize metallodendrimers, containing labile groups that are sensitive towards strong nucleophiles such as carbanions.



(2)

Deprotection of the phenol by fluoride-mediated selective Si–O bond cleavage was accomplished in high yields with Bu_4NF followed by a few drops of water

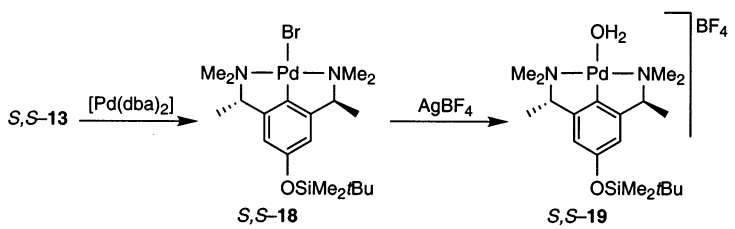
(Scheme 8) [49]. The pertinent ^{1}H-NMR data of *S,S*-**17** ($\delta_H = 4.17$ for the benzylic ArCHN protons; $\delta_H = 3.12$ and 2.81 with $^3J_{HPt} = 34.9$ and 41.6 Hz, respectively, for the diastereotopic NMe_2 groups; absence of any resonance upfield from 2 ppm) confirmed clean removal of the $SiMe_2$-*t*-Bu group without affecting the organoplatinum site. Interestingly, complex **17** is soluble in aromatic solvents (benzene, toluene; solubility $> 10\ g\ l^{-1}$), which is in marked contrast to the solubility properties of the parent achiral complex [PtCl(NCN–OH)] without α-methyl substituents [34]. The latter self-assembles in the solid state and in solution via intermolecular $Pt-Cl\cdots H-O$ hydrogen bonding to α-type networks [35]. In contrast, IR spectroscopy ($CHCl_3$ or KBr) on *S,S*-**17** only showed vibrations for the O–H bond that are in the range for free phenolic groups. No signals were observed, however, in the characteristic region that would indicate hydrogen-bond association. Obviously, the α-methyl substituents not only enhance the solubility but also restrict the hydrogen-bond-mediated self-assembly. The excellent solubility of *S,S*-**17** is an unexpected advantage when using the phenolic functionality for the attachment to soluble supports via a tether. In the case of the achiral analog [PtCl(NCN–OH)], its low solubility slows down most coupling reactions and therefore enhances the probability of formation of undesired byproducts.

2.7. Chiral ruthenium(II) and palladium(II) catalysts

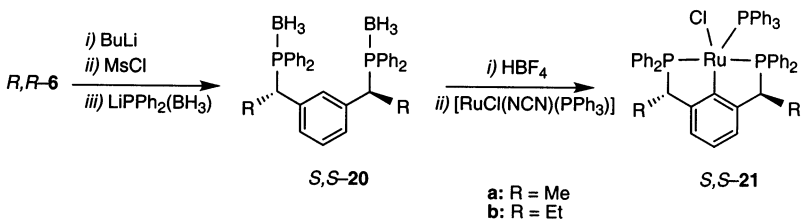
An analogous C_2-symmetric arylpalladium(II) complex *S,S*-**18** was prepared by oxidative addition of the aryl bromide *S,S*-**13** to [Pd(dba)$_2$] (Scheme 9). Due to the stability of NCN–palladium complexes towards silica, residual dba could be removed from *S,S*-**18** by gradient column chromatography. The pure aqua complex *S,S*-**19** was prepared in situ by $AgBF_4$-mediated halide abstraction and then used as a catalyst in the palladium-catalyzed aldol condensation reaction of benzaldehyde with methyl isocyanoacetate [50]. Monitoring of the reaction progress by GC indicated that the catalytic performance (turnover number and frequency) compares well with those of related achiral catalysts and is not significantly influenced by the α-methyl substituents in the organopalladium complex [50]. Analysis of the product solution by NMR [12] however revealed only 12% ee (*trans* isomer).

The synthesis of the enantiopure α-ethyl substituted PCHP pincer ligand *S,S*-**20b** followed a modified procedure which was developed by Zhang et al. [12b] for the corresponding α-methyl ligand precursor *S,S*-**20a** (Scheme 10). The detailed preparation and characterization have been reported elsewhere [17]. Acidic removal (HBF_4) of the borane-protecting groups afforded the enantiopure PCHP ligands, which were converted in situ to the corresponding ruthenium complexes *S,S*-**21** by using a transcyclometalation protocol as established recently [17,51]. Notably, the formation of *S,S*-**21b** was considerably slower than the transcycloruthenation of the corresponding methylated analog. This is another indication for the high sensitivity of the metal binding pocket (Fig. 1) towards small ligand modifications.

Application of the chiral ruthenium complex as catalyst in the hydrogen transfer reaction of acetophenone and *i*-PrOH revealed a very high catalytic activity similar to that observed for the achiral analog [5]. However, analysis of the product solution by chiral HPLC showed that the asymmetric induction of the catalyst is very poor (14% ee).



Scheme 9.



Scheme 10.

3. Conclusions

The cavity for metal binding of NCN pincer ligands was tuned by (enantioselective) ligand functionalization of the benzylic positions. For example, lithiation of α-methyl substituted pincer ligands results in dimer formation, similar to non-functionalized pincer ligands, while α-ethyl groups prevent direct dimerization and promoted the formation of mixed alkyl–aryl lithium aggregates. The pronounced effect of α-alkyl substitution on the accessibility of the *ipso* carbon is also reflected by the reaction rates observed for direct cyclometalation of PCP pincer ligands or transmetalation of the NCN–lithium complexes by platinum which are considerably lower for ethyl- than for methyl-functionalized pincer ligands.

Preliminary solid state studies on the enantiopure platinum complex *S*,*S*-**17** revealed no indication for a hydrogen-bond-mediated self-assembly of these complexes and no NLO activity was detected with the material investigated thus far. Moreover, catalytic application of the enantiopure complexes *S*,*S*-**19** and *S*,*S*-**21** in the palladium-catalyzed aldol condensation and the ruthenium-catalyzed hydrogen transfer reaction, respectively, did not show significant asymmetric induction on product formation (ee < 15% in either reaction). Apparently, benzylic substitution of the pincer ligand affects the metal binding cavity and hence the accessibility of the *ipso* carbon, but not the metal environment, since the chiral pocket is too large for efficient asymmetric catalysis. Transfer of the chiral information into closer proximity of the metal center, i.e. on the nitrogen or phosphorus donor atoms, is expected to improve the asymmetric induction for catalysis.

4. Experimental

4.1. General

All reactions involving organolithium reagents were performed using standard Schlenk techniques unless stated otherwise. Benzene, pentane, THF, and Et_2O were distilled from Na-benzophenone, CH_2Cl_2 and NEt_3 from CaH_2. $HNMe_2$ was freshly distilled and condensed directly into the reaction vessel. The syntheses of the diols *R*,*R*-C_6H_4[CHR(OH)]$_2$-1,3 (**1** and **8**) [22a,25–27], the acid *t*-$BuMe_2SiO$-$C_6H_3(COOH)_2$-3,5 (**4**) [52], the metal precursors [$PtCl_2(SEt_2)_2$] [34], [Pt(tol-4)$_2$(SEt_2)]$_2$ [48], and [Pd(dba)$_2$] [53] are described elsewhere. All other reagents were obtained commercially and were used without further purification. Elemental analyses were performed by Kolbe, Mikroanalytisches Laboratorium (Mülheim, Germany). ^{1}H and ^{13}C{^{1}H}-NMR spectra were recorded on a Varian Inova 300 spectrometer operating at 300 and 75 MHz, respectively. Spectra were obtained in $CDCl_3$ solution at room temperature, unless specified otherwise, and were referenced to external $SiMe_4$ ($\delta = 0.00$ ppm, *J* in Hz). Melting points are uncorrected. Optical rotations (α_D) were measured at 22°C on a Perkin–Elmer 241 polarimeter. The optical purity of new organic compounds was determined by chiral HPLC (chiracel OD column, hexane–*i*-PrOH (2%) as eluent, UV–vis detection), those of known compounds were determined by comparison of the observed values with those of authentic samples. Standard procedures have been used for the catalytic reductive alkylation [23], the palladium-catalyzed aldol condensation [50] and the ruthenium-catalyzed hydrogen transfer reaction [5]. Most of the non-stereoselective syntheses were carried out as described in detail for the corresponding enantiopure compounds and are therefore not mentioned separately.

4.2. Syntheses

4.2.1. *S*,*S*-C_6H_4[CH(Me)NMe_2]$_2$-1,3 (*S*,*S*-**2a**)

A solution of *R*,*R*-**1a** (2.56 g, 15 mmol) and NEt_3 (5.4 ml, 38 mol) were dissolved in CH_2Cl_2 (30 ml) and cooled to −80°C. MsCl (3.0 ml, 38 mmol) was added dropwise within 20 min and the mixture was stirred at low temperature for 20 min. Subsequently, $HNMe_2$ (10 ml, large excess) was added and then left overnight to warm up to room temperature. The formed suspension was poured onto an aqueous HCl solution (2 M, 50 ml) and extracted. The aqueous layer was washed with EtO_2 (2 × 30 ml) and made basic (solid KOH, pH > 12). The product was extracted with pentane (3 × 40 ml) and the combined organic layers were washed with brine and dried over Na_2SO_4. Removal of the solvent in vacuo yielded crude **2a**, which was further purified by bulb-to-bulb destillation. This afforded 2.88 g (85%) of *S*,*S*-**2a** as a colorless oil.

^{1}H-NMR: $\delta = 7.27$–7.14 (m, 4H, Ar*H*), 3.24 (q, $^3J_{HH} = 7.4$ Hz, 2H, ArCHN), 2.09 (s, 12H, NMe_2), 1.36 (d, $^3J_{HH} = 7.4$ Hz, 6H, ArCHC*H*$_3$); ^{13}C{^{1}H}-NMR: $\delta = 143.7$ (C_{aryl}–C), 127.8 (C_{aryl}–H), 126.5 (C_{aryl}–H), 125.8 (C_{aryl}–H), 65.8 (ArCHN), 43.0 (NMe_2), 20.2 (ArCH*C*H$_3$); $[\alpha]_D = -95.0°$ ($c = 0.39$, pentane); Anal. Found: C, 76.22; H, 11.09; N, 12.79. Calc. for $C_{14}H_{24}N_2$: C, 76.31; H, 10.98; N, 12.71%.

4.2.2. *S*,*S*-C_6H_4[CH(Et)NMe_2]$_2$-1,3 (*S*,*S*-**2b**)

The procedure was analogous to the preparation of **2a**, starting from *R*,*R*-**1b** (5.16 g, 26 mmol), NEt_3 (9.0 ml, 65 mmol), MsCl (5.0 ml, 65 mmol) and $HNMe_2$ (30 ml, large excess). After bulb-to-bulb distillation, 4.46 g (68%) of *S*,*S*-**2b** were isolated as colorless, air-sensitive oil.

^{1}H-NMR: $\delta = 7.23$ (t, $^3J_{HH} = 7$ Hz, 1H, Ar*H*), 7.09–7.05 (m, 3H, Ar*H*), 3.03–2.98 (m, 2H, ArCHN), 2.15

(s, 12H, NMe_2), 1.96–1.64 (m, 4H, CH_2CH_3), 0.68 (t, $^3J_{HH} = 7.4$ Hz, 6H, CH_2CH_3); $^{13}C\{^1H\}$-NMR: $\delta =$ 140.3 (C_{aryl}–C), 128.8 (C_{aryl}–H), 127.6 (C_{aryl}–H), 127.2 (C_{aryl}–H), 72.7 (ArCHN), 43.1 (NMe_2), 26.3 (CH_2CH_3), 10.8 (CH_2CH_3); $[\alpha]_D = -40.4°$ ($c = 3.0$, pentane); Anal. Found: C, 77.22; H, 11.26; N, 11.15. Calc. for $C_{16}H_{28}N_2$: C, 77.36; H, 11.36; N, 11.28%.

4.2.3. S,S-[PtCl{C$_6$H$_3${CH(Me)NMe$_2$}-2,6)] (S,S-**3a**)

At −80°C, *n*-BuLi (3.0 ml, 1.5 M in pentane, 4.5 mmol) was added to a solution of *S*,*S*-**2a** (1.00 g, 4.5 mmol) in pentane (30 ml). The solution was stirred for 12 h, while the temperature was allowed to increase to ambient temperature. All volatiles were removed in vacuo and the residue was redissolved in Et_2O (40 ml). To this solution was added $[PtCl_2(SEt_2)_2]$ (2.01 g, 4.5 mmol) and the mixture was stirred at room temperature over 4 days, during which a precipitate had formed. The volatiles were removed in vacuo and the residue was washed with hexane (3 × 40 ml) and extracted with CH_2Cl_2 (3 × 20 ml). The product was filtered through a short pad of SiO_2 (CH_2Cl_2–acetone, 3:1), and recrystallized from toluene–pentane to give *S*,*S*-**3a** as a colorless crystalline solid. Yield: 1.58 g, 78%.

^{1}H-NMR: $\delta = 7.02$ (t, $^3J_{HH} = 7.5$ Hz, 1H, Ar*H*), 6.68 (d, $^3J_{HH} = 7.5$ Hz, 2H, Ar*H*), 4.21 (q, $^3J_{HH} = 6.9$ Hz, 2H, ArCHN), 3.14 (s, $^3J_{HPt} = 36.0$ Hz, 6H, $NMeCH_3$), 2.81 (s, $^3J_{HPt} = 42.4$ Hz, 6H, NCH_3Me), 1.39 (d, $^3J_{HH} = 6.9$ Hz, 6H, ArCHC*H*$_3$); $^{13}C\{^1H\}$-NMR: $\delta =$ 146.9 (C_{aryl}–C), 145.5 (C_{aryl}–Pt), 122.9 (C_{aryl}–H), 120.6 ($^3J_{CPt} = 40.8$ Hz, C_{aryl}–H), 78.8 ($^2J_{CPt} = 63.3$ Hz, ArCHN), 51.9 ($^2J_{CPt} = 18.9$ Hz, $NMeCH_3$), 47.0 ($^2J_{CPt} = 19.9$ Hz, NCH_3Me), 12.9 ($^3J_{CPt} = 31.7$ Hz, ArCH*C*H$_3$); $[\alpha]_D = -57.1°$ ($c = 1.3$, CH_2Cl_2); Anal. Found: C, 37.29; H, 5.22; N, 6.18. Calc. for $C_{14}H_{23}ClN_2Pt$: C, 37.38; H, 5.15; N, 6.23%.

Spectroscopic data of *R*,*S*:*SR*-**3a**: ^{1}H-NMR: $\delta = 6.98$ (t, $^3J_{HH} = 7.5$ Hz, 1H, Ar*H*), 6.69 (d, $^3J_{HH} = 7.5$ Hz, 2H, Ar*H*), 4.03 (q, $^3J_{HH} = 6.6$ Hz, $^3J_{HPt} = 35.7$ Hz, 2H, ArCHN), 3.07 (s, $^3J_{HPt} = 39.3$ Hz, 6H, $NMeCH_3$), 2.85 (s, $^3J_{HPt} = 39.6$ Hz, 6H, NCH_3Me), 1.40 (d, $^3J_{HH} = 6.9$ Hz, 6H, ArCHC*H*$_3$); $^{13}C\{^1H\}$-NMR: $\delta = 147.8$ (C_{aryl}–C), 144.5 (C_{aryl}–Pt), 122.8 (C_{aryl}–H), 120.2 ($^3J_{CPt} = 38.6$ Hz, C_{aryl}–H), 79.4 ($^2J_{CPt} = 61.9$ Hz, ArCHN), 53.1 ($^2J_{CPt} = 17.7$ Hz, $NMeCH_3$), 47.6 ($^2J_{CPt} = 17.7$ Hz, NCH_3Me), 16.1 ($^3J_{CPt} = 24.3$ Hz, ArCH*C*H$_3$).

4.2.4. S,S-[PtCl(C$_6$H$_3${CH(Et)NMe$_2$}$_2$-2,6)] (S,S-**3b**) [18b]

To a solution of *S*,*S*-**2b** (1.00 g, 4.0 mmol) in pentane (30 ml) was added *t*-BuLi (2.75 ml, 1.5 M in pentane, 4.0 mmol) at −80°C. The solution was stirred for 16 h, while the temperature was allowed to raise to room temperature. At this stage, ^{1}H-NMR indicated only 45% lithiation and therefore, the mixture was treated with a second amount of *t*-BuLi (2.75 ml, 4.0 mmol). After stirring for 24 h, Me_3SiCl (1.5 ml, 12 mmol) was added within 5 min and stirring continued for 6 h, during which a white precipitate formed. All volatiles were then removed in vacuo, and the residue was redissolved in EtO_2 (30 ml) and $[PtCl_2(SEt_2)_2]$ (2.01 g, 4.5 mmol) was added. This mixture was stirred at room temperature for 4 days. The volatiles were removed in vacuo and the residue was washed with pentane (3 × 40 ml) and extracted with CH_2Cl_2 (3 × 20 ml). The combined extracts were evaporated to dryness at the brown residue was purified by column chromatography (SiO_2; acetone–$CHCl_3$ 1:2) and recrystallized from CH_2Cl_2–pentane to give *S*,*S*-**3b** as a colorless solid. Yield: 1.15 g, 60%.

^{1}H-NMR: $\delta = 6.94$ (t, $^3J_{HH} = 7.2$ Hz, 1H, ArH), 6.78 (d, $^3J_{HH} = 7.2$ Hz, 2H, ArH), 3.58 (dd, $^3J_{HH} = 3.9$ Hz, $^3J_{HH} = 8.7$ Hz, $^3J_{HPt} = 73.5$ Hz, 2H, ArCHN), 3.00 (s, $^3J_{HPt} = 44.5$ Hz, 6H, $NMeCH_3$), 2.92 (s, $^3J_{HPt} = 32.8$ Hz, 6H, NCH_3Me), 2.05–1.80 (m, 4H, CH_2CH_3), 0.97 (t, $^3J_{HH} = 7.2$ Hz, 6H, CH_2CH_3); $^{13}C\{^1H\}$-NMR: $\delta =$ 146.1 (C_{aryl}–C), 145.7 (C_{aryl}–Pt), 121.7 (C_{aryl}–H), 121.0 ($^3J_{CPt} = 35.1$ Hz, C_{aryl}–H), 85.5 ($^2J_{CPt} = 52.2$ Hz, ArCHN), 55.4 ($^2J_{CPt} = 18$, $NMeCH_3$), 48.6 ($^2J_{CPt} = 16$, NCH_3Me), 26.1 (CH_2CH_3), 10.4 (CH_2CH_3); $[\alpha]_D = +106.4°$, ($c = 2.0$, CH_2Cl_2); Anal. Found: C, 40.11; H, 5.63; N, 5.81. Calc. for $C_{16}H_{27}ClN_2Pt$: C, 40.21; H, 5.69; N, 5.81%.

4.2.5. t-BuMe$_2$SiO-C$_6$H$_3$(CHO)$_2$-3,5 (**9**)

The diol **8** (4.0 g, 14.9 mmol) was dissolved in CH_2Cl_2 (80 ml) and added to a suspension of pyridinium chlorochromate (9.64 g, 44.0 mmol) in CH_2Cl_2 (20 ml). The mixture was stirred at RT for 2 h. The solution was removed from the solids by decantation and the solvent removed in vacuo. All the solids were washed with Et_2O (5 × 80 ml). The washings were passed through a short column of Fluorosil. The solvents were removed in vacuo to give the product as a colorless oil (3.86 g, 98%), which solidified at −20°C.

^{1}H-NMR: $\delta = 10.04$ (s, 2H, CHO), 7.97 (t, 1H, $^4J_{HH} = 1.4$ Hz, Ar*H*), 7.58 (d, $^4J_{HH} = 1.4$ Hz, 2H, Ar*H*), 1.00 (s, 9H, SiC*Me*$_3$), 0.25 (s, 6H, $SiCH_3$); $^{13}C\{^1H\}$-NMR: $\delta = 190.9$ (CHO), 157.3 (C_{aryl}–O), 138.5 (C_{aryl}–C), 125.4 (C_{aryl}–H), 124.7 (C_{aryl}–H), 25.5 (SiC*Me*$_3$), 18.2 (Si*C*Me$_3$), −4.4 ($SiCH_3$); Anal. Found: C, 63.46; H, 7.73. Calc. for $C_{14}H_{20}O_3Si$: C, 63.60; H, 7.62%.

4.2.6. t-BuMe$_2$SiO-C$_6$H$_3$[C(=O)Me]$_2$-3,5 (**5**)

MeLi (60 ml, 96 mmol) was added within 1 h to the diacid **4** (5.95 g, 20 mmol) dissolved in THF (200 ml). The suspension was stirred for 4 h at reflux temperature and then poured onto a cold solution of NH_4Cl (1 M, 300 ml) under vigorous stirring. EtO_2 (50 ml) was added and the phases were separated. The inorganic

phase was extracted with EtO_2 (2 × 100 ml) and the combined organic layers were washed with brine, dried (Na_2SO_4) and evaporated to dryness. The residue was purified by column chromatography (SiO_2, hexane–Et_2O 3:1), thus affording analytically pure **5** as a white solid (3.40 g, 58%).

^{1}H-NMR: $\delta = 8.10$ (t, 1H, $^4J_{HH} = 1.5$ Hz, Ar*H*), 7.59 (d, $^4J_{HH} = 1.5$ Hz, 2H, Ar*H*), 2.62 (s, 6H, C(O)CH_3), 1.00 (s, 9H, SiCMe_3), 0.24 (s, 6H, $SiCH_3$); $^{13}C\{^1H\}$-NMR: $\delta = 197.0$ (C=O), 156.4 (C_{aryl}–O), 138.8 (C_{aryl}–C), 123.8 (C_{aryl}–H), 121.2 (C_{aryl}–H), 26.8 (C(O)*C*H_3), 25.6 (SiC*Me*$_3$), 18.2 (Si*C*Me_3), −4.4 ($SiCH_3$); m.p. = 55–58°C; Anal. Found: C, 65.65; H, 8.20. Calc. for $C_{16}H_{24}O_3Si$: C, 65.71; H, 8.27%.

4.2.7. *R,R-t-BuMe$_2$SiO-C$_6$H$_3$[CH(Me)OH]$_2$-3,5 (R,R-**6a**)*

To a solution of $BH_3{\cdot}SMe_2$ (3.5 ml, 2 M in toluene, 7 mmol) was added *S*-diphenyl prolinol (0.13 g, 0.5 mmol) in THF (3.5 ml). The solution was stirred for 16 h at 45°C in a closed system. After 16 h, a solution of **5** (1.36 g, 4.7 mmol) in THF (9 ml) was added dropwise over 1 h. The reaction mixture was subsequently stirred 1 h at 45°C and 2 h at RT, then quenched with MeOH (2 ml, dropwise addition). Stirring was continued for 2 h before all volatiles were evaporated under reduced pressure. Column chromatography (SiO_2; hexane–Et_2O 4:1) gave pure *R,R*-**6a** as a white solid (0.92 g, 66%).

^{1}H-NMR: $\delta = 6.96$ (s, 1H, Ar*H*), 6.75 (s, 2H, Ar*H*), 4.82 (q, $^3J_{HH} = 6.4$ Hz, 2H, ArCH-O), 2.07 (br s, 2H, OH), 1.46 (d, $^3J_{HH} = 6.4$ Hz, 6H, ArCHC*H*$_3$), 0.99 (s, 9H, SiC*Me*$_3$), 0.20 (s, 6H, $SiCH_3$); $^{13}C\{^1H\}$-NMR: $\delta =$ 156.0 (C_{aryl}–O), 147.7 (C_{aryl}–H), 116.0 (C_{aryl}–H), 115.3 (C_{aryl}–C), 70.2 (ArCH-O), 31.7 (ArCH*C*H_3), 25.7 (SiC*Me*$_3$), 18.2 (Si*C*Me_3), −4.4 ($SiCH_3$); m.p. = 92–94°C; $[\alpha]_D = +21.1°$ ($c = 1.3$, THF); Anal. Found: C, 64.76; H, 9.44. Calc. for $C_{16}H_{28}O_3Si$: C, 64.82; H, 9.52%.

4.2.8. *rac/meso-t-BuMe$_2$SiO-C$_6$H$_3$[CH(Et)OH]$_2$-3,5 (rac/meso-**6b**)*

To a solution of EtMgBr (60 ml, 1 M in Et_2O, 60 mmol) was added dropwise a solution of **3** (5.58 g, 21 mmol) in Et_2O (50 ml). The reaction mixture was stirred 2 h at reflux temperature and then poured onto aqueous NH_4Cl (1 M, 100 ml). After phase separation, the aqueous layer was extracted with EtO (2 × 60 ml) and the combined organic phases were washed with brine, $NaHSO_3$, H_2O, and brine, dried over $MgSO_4$ and evaporated under reduced pressure to leave *rac/meso*-**6b** as a waxy solid (5.91 g, 86%).

^{1}H-NMR: $\delta = 6.88$ (s, 1H, Ar*H*), 6.72 (s, 2H, Ar*H*), 4.52 (t, $^3J_{HH} = 6.4$ Hz, 2H, ArCH-O), 2.01 (br s, 2H, OH), 1.82–1.62 (m, 4H, C*H*$_2$CH$_3$), 0.98 (s, 9H, SiC*Me*$_3$), 0.89 (t, $^3J_{HH} = 7.2$ Hz, 6H, CH$_2$C*H*$_3$), 0.19 (s, 6H, $SiCH_3$); $^{13}C\{^1H\}$-NMR: $\delta = 155.8$ (C_{aryl}–O), 146.3 (C_{aryl}–C), 116.7 (C_{aryl}–H), 116.6 (C_{aryl}–H), 75.8 (ArCH-O), 31.8 (*C*H$_2$CH$_3$), 25.7 (SiC*Me*$_3$), 18.2 (Si*C*Me_3),10.1 (CH$_2$*C*H$_3$), −4.4 ($SiCH_3$); Anal. Found: C, 66.47; H, 10.08. Calc. for $C_{18}H_{32}O_3Si$: C, 66.62; H, 9.94%.

4.2.9. *rac/meso-t-BuMe$_2$SiO-C$_6$H$_3$[CH(Me)NMe$_2$]$_2$-3,5 (rac/meso-**7a**)*

The procedure was analogous to the preparation of **2a**, starting from *rac/meso*-**6a** (0.76 g, 2.6 mmol) in CH_2Cl_2 (15 ml), NEt_3 (0.84 ml, 6.0 mmol), MeCl (0.46 ml, 6.0 mmol) and $HNMe_2$ (10 ml, large excess). The resulting suspension was poured onto NaOH (1 N, 50 ml) and extracted with pentane (3 × 40 ml). After drying the combined organic layers over Na_2SO_4 and evaporation of all volatiles resulted 0.83 g (91%) of *rac/meso*-**7a** as a yellowish oil.

^{1}H-NMR: $\delta = 6.78$ (s, 1H, Ar*H*), 6.66 (s, 2H, Ar*H*), 3.16 (q, $^3J_{HH} = 6.6$ Hz, 2H, ArCHN), 2.17 (s, 12 H, NMe_2), 1.34 (d, $^3J_{HH} = 6.6$ Hz, 6H, ArCHC*H*$_3$), 0.98 (s, 9H, *t*-SiCMe_3), 0.18 (s, 6H, $SiCH_3$); $^{13}C\{^1H\}$-NMR: $\delta = 155.3$ (C_{aryl}–O), 145.1 (C_{aryl}–C), 120.2 (C_{aryl}–H), 117.8 (C_{aryl}–H), 65.9 (ArCHN), 43.3 (NMe_2), 25.7 (SiC*Me*$_3$), 20.5 (ArC*C*H$_3$), 18.2 (Si*C*Me_3), −4.4 ($SiCH_3$); Anal. Found: C, 68.36; H, 11.06; N, 8.03. Calc. for $C_{20}H_{38}N_2OSi$: C, 68.51; H, 10.92; N 7.99%.

4.2.10. *rac/meso-t-BuMe$_2$SiO-C$_6$H$_3$[CH(Et)NMe$_2$]$_2$-3,5 (rac/meso-**7b**)*

The procedure was analogous to the preparation of **2a**, starting from *rac/meso*-**6b** (3.13 g, 9.6 mmol) in CH_2Cl_2 (30 ml), NEt_3 (3.1 ml, 22 mmol), MeCl (1.7 ml, 22 mmol) and $HNMe_2$ (15 ml, large excess). The resulting suspension was poured onto NaOH (1 N, 40 ml) and extracted with pentane (3 × 40 ml). The combined organic layers were dried (Na_2SO_4) and evaporated, resulting in 3.20 g (88%) of *rac/meso*-**7b** as a yellowish oil.

^{1}H-NMR: $\delta = 6.68$ (s, 1H, Ar*H*), 6.62 (s, 2H, Ar*H*), 2.98–2.93 (m, 2H, ArCHN), 2.16 (s, 12 H, NMe_2), 2.0–1.6 (m, 4H, C*H*$_2$CH$_3$), 0.97 (s, 9H, *t*-SiCMe_3), 0.69 (t, $^3J_{HH} = 7.2$ Hz, 6H, CH$_2$C*H*$_3$), 0.18 (s, 6H, $SiCH_3$); $^{13}C\{^1H\}$-NMR: $\delta = 155.1$ (C_{aryl}–O), 141.6 (C_{aryl}–C), 122.4 (C_{aryl}–H), 119.1 (C_{aryl}–H), 72.7 (ArCHN), 43.2 (NMe_2), 26.6 (*C*H$_2$CH$_3$), 25.7 (SiC*Me*$_3$), 18.2 (Si*C*Me_3), 10.9 (CH$_2$*C*H$_3$), −4.4 ($SiCH_3$); Anal. Found: C, 69.65; H, 11.12; N, 7.31. Calc. for $C_{22}H_{42}N_2OSi$: C, 69.78; H, 11.18; N 7.40%.

4.2.11. *rac/meso-C$_6$H$_3$OD-[CH(Me)NMe$_2$]$_2$-3,5-SiMe$_2$t-Bu-2 (rac/meso-**10-D**)*

A solution of *rac/meso*-**7a** (0.35 g, 1.0 mmol) in pentane (8 ml) was cooled to −80°C and treated with *n*-BuLi (0.63 ml, 1.6 M in hexane, 1.0 mmol) and allowed to warm to RT during 4 h. The solution was

stirred additional 12 h and then quenched with D_2O (0.5 ml, large excess). The suspension was dried over $MgSO_4$, filtered through Celite and evaporated to dryness to afford a mixture of deuterated *rac*/*meso*-**7a-D** (vide supra) and *rac*/*meso*-**10-D**.

^{1}H-NMR: $\delta = 7.06$ (d, $^4J_{HH} = 1.4$ Hz, 1H, Ar*H*), 6.59 (d, $^4J_{HH} = 1.5$ Hz, 1H, Ar*H rac* and *meso*), 3.46 (q, $^3J_{HH} = 6.2$ Hz, 1H, ArCHN), 3.18 (q, $^3J_{HH} = 6.6$ Hz, 1H, ArCHN), 2.21 (s, 6 H, NMe_2), 2.18 (s, 6 H, NMe_2), 1.35 (d, $^3J_{HH} = 6.6$ Hz, 3H, ArCHCH_3), 1.29 (d, $^3J_{HH} = 6.3$ Hz, 3H, ArCHCH_3), 0.97 (s, 9H, *t*-SiCMe$_3$), 0.40 (s, 6H, $SiCH_3$).

4.2.12. *R,R*-C_6H_2Br-[CH(Me)OH]$_2$-2,6-$OSiMe_2t$-Bu-4 (*R,R*-**11**)

A mixture of *R,R*-**6a** (2.50 g, 8.5 mmol) in CH_2Cl_2 (40 ml) and pyridinium-Br_3 (2.90 g, 9.0 mmol) in MeOH (10 ml) was stirred in the presence of a catalytic amount of Fe (0.18 g, 3 mmol) until TLC indicated complete consumption of the starting material. All volatiles were removed and the residue was purified by column chromatography (SiO_2; hexane–Et_2O 2:1) to give 1.72 g (54%) *R,R*-**11** as a white solid.

^{1}H-NMR: $\delta = 7.03$ (s, 2H, Ar*H*), 5.26 (d of q, $^3J_{HH} = 6.3$ Hz, $^3J_{HH} = 2.7$ Hz, 2H, ArCH-O), 1.89 (d, $^3J_{HH} = 2.7$ Hz, 2H, OH), 1.45 (d, $^3J_{HH} = 6.3$ Hz, 6H, ArCHCH_3), 0.99 (s, 9H, SiCMe_3), 0.22 (s, 6H, $SiCH_3$); ^{13}C{^{1}H}-NMR: $\delta = 155.9$ (C_{aryl}–O), 146.3 (C_{aryl}–C), 117.3 (C_{aryl}–H), 112.0 (C_{aryl}–Br), 69.2 (ArCH-O), 25.7 (SiCMe_3), 23.6 (ArCHCH_3), 18.2 (SiCMe$_3$), −4.4 ($SiCH_3$); m.p. = 137–140°C; $[\alpha]_D = 37.7°$ ($c = 1.3$, $CHCl_3$); Anal. Found: C, 51.11; H, 7.20. Calc. for $C_{16}H_{27}BrO_3Si$: C, 51.19; H, 7.25%.

4.2.13. C_6H_2Br-[C(=O)Me]$_2$-2,6-$OSiMe_2t$-Bu-4 (**12**)

A solution of *rac*/*meso*-**11** (1.88 g, 5.0 mmol) was dissolved in CH_2Cl_2 (40 ml) and added to a suspension of pyridinium chlorochromate (2.68 g, 12 mmol) in CH_2Cl_2 (20 ml). The mixture was stirred at RT for 4 h, and then, all volatiles were removed under reduced pressure. The residue was extracted with Et_2O (8 × 30 ml). The ethereal extracts were passed through a short column of Fluorosil and evaporated to dryness to give **12** as a colorless solid (1.82 g, 98%).

^{1}H-NMR: $\delta = 6.84$ (s, 2H, Ar*H*), 2.58 (s, 6H, C(O)CH_3), 0.97 (s, 9H, SiCMe_3), 0.21 (s, 6H, $SiCH_3$); ^{13}C{^{1}H}-NMR: $\delta = 201.4$ (ArCO), 155.4 (C_{aryl}–O), 144.8 (C_{aryl}–C), 120.8 (C_{aryl}–H), 104.5 (C_{aryl}–Br), 30.6 (C(O)CH_3), 25.5 (SiCMe_3), 18.1 (SiCMe$_3$), −4.5 ($SiCH_3$); m.p. = 36–37°C; Anal. Found: C, 51.86; H, 6.26. Calc. for $C_{16}H_{23}BrO_3Si$: C, 51.75; H, 6.24%.

4.2.14. *S,S*-C_6H_2Br-[CH(Me)NMe_2]$_2$-2,6-$OSiMe_2t$-Bu-4 (*S,S*-**13**)

The procedure was analogous to the preparation of **2a**, starting from *R,R*-**11** (0.70 g, 1.9 mmol) in CH_2Cl_2 (15 ml), NEt_3 (0.64 ml, 4.6 mmol), MeCl (0.36 ml, 4.6 mmol) and $HNMe_2$ (10 ml, large excess). The resulting suspension was poured onto NaOH (1 N, 20 ml) and extracted with pentane (3 × 20 ml). Drying of the combined organic layers over Na_2SO_4 and evaporation of all volatiles resulted in 0.64 g (80%) of *S,S*-**13** as a colorless waxy solid.

^{1}H-NMR: $\delta = 6.93$ (s, 2H, Ar*H*), 3.77 (q, $^3J_{HH} = 6.5$ Hz, 2H, ArCHN), 2.20 (s, 12H, NMe_2), 1.22 (d, $^3J_{HH} = 6.5$ Hz, 6H, ArCHCH_3), 0.95 (s, 9H, SiCMe_3), 0.16 (s, 6H, $SiCH_3$); ^{13}C{^{1}H}-NMR: $\delta = 155.1$ (C_{aryl}–O), 145.5 (C_{aryl}–C), 118.9 (C_{aryl}–H), 117.0 (C_{aryl}–Br), 64.4 (ArCHN), 43.5 (NMe_2), 25.7 (SiCMe_3), 20.1 (ArCHCH_3), 18.2 (SiCMe$_3$), −4.5 ($SiCH_3$); $[\alpha]_D = -83.4°$ ($c = 1.5$, acetone); Anal. Found: C, 56.08; H, 8.55; N, 6.46. Calc. for $C_{20}H_{37}BrN_2OSi$: C, 55.93; H, 8.68; N, 6.52%.

4.2.15. [PtCl(*S,S*-C_6H_2-{CH(Me)NMe_2}$_2$-2,6-$OSiMe_2t$-Bu-4)] (*S,S*-**14**)

To a solution of *S,S*-**15** (88.5 mg, 0.14 mmol) in acetone (5 ml) was added $AgBF_4$ (35.0 mg, 0.18 mmol) and the mixture was stirred for 30 min under exclusion of light. The formed precipitate was filtered off (Celite) and all volatiles removed under reduced pressure. The residue was suspended in CH_2Cl_2 (15 ml) and brine (3 ml) and rigorously stirred for 30 min and then treated with $MgSO_4$. After filtration and evaporation of the volatiles, *S,S*-**14** was obtained as a colorless solid (66.3 mg, 81%).

^{1}H-NMR: $\delta = 6.18$ (s, 2H, Ar*H*), 4.11 (q, $^3J_{HH} = 7.0$ Hz, 2H, ArCHN), 3.07 (s, $^3J_{HPt} = 35.8$ Hz, 6H, NMeCH_3), 2.75 (s, $^3J_{HPt} = 42.8$ Hz, 6H, NCH_3Me), 1.30 (d, $^3J_{HH} = 6.6$ Hz, 6H, ArCHCH_3), 0.93 (s, 9H, SiCMe_3), 0.12 (s, 6H, $SiCH_3$); ^{13}C{^{1}H}-NMR: $\delta = 152.2$ (C_{aryl}–O), 147.3 (C_{aryl}–C), 136.2 (C_{aryl}–Pt), 112.8 (C_{aryl}–H), 78.8 ($^2J_{CPt} = 59.7$ Hz, ArCHN), 52.0 (NMeCH_3), 47.2 (NCH_3Me), 25.6 (SiCMe_3), 18.0 (SiCMe$_3$), 13.0 ($^3J_{CPt} = 31.5$ Hz, ArCHCH_3), −4.5 ($SiCH_3$); $[\alpha]_D = -66.3°$ ($c = 1.0$, CH_2Cl_2); Anal. Found: C, 41.28; H, 6.36; N, 4.82. Calc. for $C_{20}H_{37}ClN_2OSiPt$: C, 41.41; H, 6.43; N, 4.83%.

4.2.16. [PtBr(*S,S*-C_6H_2-{CH(Me)NMe_2}$_2$-2,6-$OSiMe_2t$-Bu-4)] (*S,S*-**15**)

A mixture of *S,S*-**13** (0.45 g, 1.05 mmol) and [Pt(tol-4)$_2$(SEt_2)]$_2$ (0.51 g, 1.05 mmol) in C_6H_6 (8 ml) was stirred at reflux temperature for 4 h. All volatiles were removed in vacuo and the residue was purified by gradient column chromatography (SiO_2; CH_2Cl_2, then CH_2Cl_2–acetone 19:1) to yield *S,S*-**15** as a colorless solid (0.28 g, 43%).

^{1}H-NMR: $\delta = 6.23$ (s, 2H, Ar*H*), 4.14 (q, $^3J_{HH} = 6.6$ Hz, 2H, ArCHN), 3.18 (s, $^3J_{HPt} = 36.9$ Hz, 6H, NMeCH_3), 2.84 (s, $^3J_{HPt} = 41.8$ Hz, 6H, NCH_3Me), 1.36 (d, $^3J_{HH} = 6.9$ Hz, 6H, ArCHCH_3), 0.98 (s, 9H,

SiCMe_3), 0.18 (s, 6H, $SiCH_3$); $^{13}C\{^1H\}$-NMR: $\delta =$ 152.4 (C_{aryl}–O), 147.4 (C_{aryl}–C), 137.0 (C_{aryl}–Pt), 113.0 (C_{aryl}–H), 78.5 ($^2J_{CPt} = 60.5$ Hz, ArCHN), 53.1 ($NMeCH_3$), 47.7 (NCH_3Me), 25.7 (SiCMe_3), 18.1 (SiCMe$_3$), 13.4 ($^3J_{CPt} = 26$, ArCHCH_3), -4.4 ($SiCH_3$); $[\alpha]_D = -60.7°$ ($c = 1.15$, CH_2Cl_2); Anal. Found: C, 38.52; H, 6.05; N, 4.41. Calc. for $C_{20}H_{37}BrN_2OSiPt$: C, 38.46; H, 5.97; N, 4.49%.

4.2.17. [PtI(S,S-C_6H_2-{CH(Me)NMe_2}$_2$-2,6-OSiMe_2t-Bu-4)] (S,S-16)

A mixture of *S,S*-**14** (125 mg, 0.20 mmol) and NaI (0.3 g, 2 mmol) in acetone (10 ml) was stirred for 12 h and subsequently evaporated to dryness. The residue was extracted with CHCl (3×20 ml) and the organic fractions concentrated to 5 ml. Addition of pentane afforded microcrystalline *S,S*-**16** (126 mg, 94%).

^{1}H-NMR: $\delta = 6.22$ (s, 2H, ArH), 4.10 (q, $^3J_{HH} = 6.2$ Hz, $^3J_{HPt} = 23.0$ Hz, 2H, ArCHN), 3.26 (s, $^3J_{HPt} = 38.0$ Hz, 6H, $NMeCH_3$), 2.91 (s, $^3J_{HPt} = 40.9$ Hz, 6H, NCH_3Me), 1.38 (d, $^3J_{HH} = 6.7$ Hz, 6H, ArCHCH_3), 0.97 (s, 9H, SiCMe_3), 0.17 (s, 6H, $SiCH_3$); $^{13}C\{^1H\}$-NMR: $\delta = 152.4$ (C_{aryl}–O), 147.8 (C_{aryl}–C), 139.7 (C_{aryl}–Pt), 113.0 (C_{aryl}–H), 78.1 ($^2J_{CPt} = 60.5$ Hz, ArCHN), 55.1 ($NMeCH_3$), 49.0 (NCH_3Me), 25.7 (SiCMe_3), 18.1 (SiCMe$_3$), 14.6 ($^3J_{CPt} = 30.6$ Hz, ArCHCH_3), -4.3 ($SiCH_3$); $[\alpha]_D = -33.4°$ ($c = 0.1$, CH_2Cl_2); Anal. Found: C, 35.49; H, 5.48; N, 4.17. Calc. for $C_{20}H_{37}IN_2OSiPt$: C, 35.77; H, 5.55; N, 4.17%.

4.2.18. [PtCl(S,S-C_6H_2-{CH(Me)NMe_2}$_2$-2,6-OH-4)] (S,S-17)

A solution of Bu_4NF (0.11 ml, 1.0 M in THF, 0.11 mmol) was added to a solution of *S,S*-**14** (66.2 mg, 0.11 mmol) in THF (4 ml). After stirring for 10 min, H_2O (60 μl) was added and the mixture stirred for 40 h at RT. The product was extracted from H_2O (20 ml) and CH_2Cl_2 (3×15 ml). The combined organic layers were washed with brine, dried ($MgSO_4$) and evaporated to dryness. The residue was precipitated twice from CH_2Cl_2 (2 ml) and hexane (70 ml) to afford *S,S*-**17** as an analytically pure, colorless solid (43.7 mg, 82%).

^{1}H-NMR: $\delta = 6.30$ (s, 2H, ArH), 4.16 (q, $^3J_{HH} = 6.8$ Hz, 2H, ArCHN), 3.12 (s, $^3J_{HPt} = 35.0$ Hz, 6H, $NMeCH_3$), 2.81 (s, $^3J_{HPt} = 41.5$ Hz, 6H, NCH_3Me), 1.36 (d, $^3J_{HH} = 6.9$ Hz, 6H, ArCHCH_3); $^{13}C\{^1H\}$-NMR: $\delta = 152.8$ (C_{aryl}–O), 147.6 (C_{aryl}–C), 135.5 (C_{aryl}–Pt), 108.6 (C_{aryl}–H), 78.8 ($^2J_{CPt} = 63.2$ Hz, ArCHN), 52.0 ($NMeCH_3$), 47.2 (NCH_3Me), 12.9 ($^3J_{CPt} = 31.7$ Hz, ArCHCH_3); $[\alpha]_D = -67.8°$ ($c = 0.73$, CH_2Cl_2); Anal. Found: C, 35.88; H, 5.09; N, 7.46. Calc. for $C_{14}H_{23}ClN_2OPt$: C, 36.09; H, 4.98; N, 7.61%.

4.2.19. [PdBr(S,S-C_6H_2-{CH(Me)NMe_2}$_2$-2,6-OSiMe_2t-Bu-4)] (S,S-18)

A mixture of ***S,S*-13** (150 mg, 0.35 mmol) and [Pd(dba)$_2$] (200 mg, 0.35 mmol) in C_6H_6 (3 ml) was stirred at reflux temperature for 4 h. The resulting suspension was filtered through Celite and evaporated to dryness. The residue was purified by gradient column chromatography (SiO_2; CH_2Cl_2, then CH_2Cl_2–acetone 4:1) to yield ***S,S*-17** as a yellowish solid (98 mg, 52%). Analytically pure product was obtained by recrystallization from benzene–pentane.

^{1}H-NMR: $\delta = 6.21$ (s, 2H, ArH), 4.11 (br q, $^3J_{HH}$ not resolved, 2H, ArCHN), 3.00 (s, 6H, $NMeCH_3$), 2.75 (s, 6H, NCH_3Me), 1.38 (d, $^3J_{HH} = 6.6$ Hz, 6H, ArCHCH_3), 0.97 (s, 9H, SiCMe_3), 0.17 (s, 6H, $SiCH_3$); $^{13}C\{^1H\}$-NMR: $\delta = 153.2$ (C_{aryl}–O), 149.8 (C_{aryl}–C), 113.0 (C_{aryl}–H), 75.8 (ArCHN), 52.1 ($NMeCH_3$), 46.4 (NCH_3Me), 25.7 (SiCMe_3), 18.1 (SiCMe$_3$), 15.0 (ArCHCH_3), -4.4 ($SiCH_3$), C_{aryl}–Pd not resolved; $[\alpha]_D = -29.0°$ ($c = 0.32$, CH_2Cl_2); Anal. Found: C, 48.78; H, 7.18; N, 4.75. Calc. for $C_{20}H_{37}BrN_2OSiPd \cdot 2/3\ C_6H_6$: C, 49.02; H, 7.03; N, 4.76%.

Prior to the catalytic runs, the neutral organopalladium complex *S,S*-**18** (8.7 mg, 16 μmol) was dissolved in acetone (5 ml) and water (0.2 ml) and treated with an equimolar amount of $AgBF_4$ (3.2 mg, 16 μmol, dissolved in 1 ml acetone). The suspension was stirred for 30 min in the absence of light and subsequently filtered through Celite. The filtrate was evaporated to dryness to give the cationic catalyst precursor *S,S*-**19** in quantitative yield as an off-white solid. This solid was used in situ for the catalytic experiments [50].

4.3. X-ray structure determination of S,S-3b

Intensities were measured on an Enraf–Nonius CAD4-T diffractometer with rotating anode (Mo–K_α, $\lambda = 0.71073$ Å) at a temperature of 150 K. The structure was solved with Patterson methods (DIRDIF-97 [54]) and refined with the program SHELXL-97 [55] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters, hydrogen atoms were refined as rigid groups. All calculations, graphical illustrations and checking for higher symmetry were performed with the PLATON [56] package.

Crystal data for *S,S*-**3b**: $[C_{16}H_{27}ClN_2Pt]$, $M_r = 477.93$, colorless cubes, monoclinic $P2_1$ (no. 4), $a = 6.6377(11)$, $b = 10.2267(17)$, $c = 12.4420(16)$, $\beta = 99.635(11)$, $V = 832.7(2)$ Å^3, $Z = 2$, $D_{calcd} = 1.906$ g cm^{-3}, $T = 150$ K, $\mu = 8.579$ mm^{-1} (Mo–K_α radiation, $\lambda = 0.71073$ Å), empirical absorption correction (PLATON/DELABS, transmission range 0.225–0.689), 4364 reflections measured of which 2017 unique, $R_{int} = 0.035$, final $R_1 = 0.0208$ (for data $I > 2\sigma(I)$, 0.0214 for all data). wR_2 0.0649, $S = 1.052$, Flack parameter 0.017(11), residual density $-1.43 < 1.74$ e Å^{-3}.

5. Supplementary material

Crystallographic data for the structural analysis of *S*,*S*-**3b** (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 151430. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www/ccdc/cam/ac/uk).

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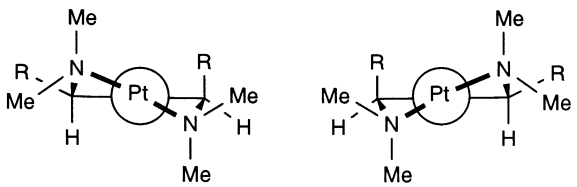
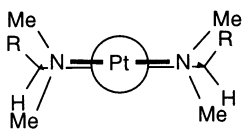


S,R–**3**

R,S–**3**



meso–**3**

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