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Enantiomerically enriched ‘carbanions’: Studies on the stereochemical course of selective transformations of metal alkyls

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Dedicated to Professor Helmut Werner in recognition of his lifetime achievements in the field of organometallic chemistry

Abstract

Two (aminomethyl)(lithiomethyl)silanes $Ph_2Si(CH_2Li)(CH_2NC_5H_{10})$ (NC_5H_{10} = 1-piperidinyl) (**2**) and $Me_2Si\{[R]\text{-}[CHLiPh]\}(CH_2SMP)$ {SMP = 1-[(*S*)-2-(methoxymethyl)pyrrolidinyl]} [(*R*,*S*)-**17**] are presented including their solid state structures, the first one non-chiral, the latter highly diastereomerically enriched. By metathesis reactions with metal(II) halides (metal = Mg, Ga, Pd, Cd and Hg), the corresponding bis{[(aminomethyl)silyl]methyl}metal(II) compounds or the [(aminomethyl)silyl]methylmetal(II) halides were obtained. In the case of highly diastereomerically enriched (aminomethyl)(lithiomethyl)silane (*R*,*S*)-**17**, the ‘carbanionic’ fragment could be transferred with high stereoselectivities on the metals Hg and Pd. For all of the compounds, the solid state molecular structures were determined.

Keywords: Organolithium; Organometallic chemistry; Solid state structures; Carbanion; Diastereomerically enriched

1. Introduction

The synthesis of enantiomerically[1] enriched metal alkyls with a stereogenic metalated carbon center has been intensively studied for the last 20 years [1]. In selective transformations, these types of compounds can act as chiral alkyl transfer reagents, the stereogenic metalated carbon center has been transferred to organic molecules and hetero element centers. But furthermore, compounds of this type are valuable ‘tools’ for studies on the stereochemical course of transmetallations and metathesis reactions. Our recent results on this will be summarized in the following.

Stereogenic metalated carbon centers are usually generated starting from the corresponding lithium alkyls. These are mostly synthesized by deprotonation using alkyllithium bases, e.g. butyllithium [1]. The stereochemical information is either introduced *inter*molecularly by chiral auxiliaries, like (−)-sparteine [2,3], or *intra*molecularly by side-arm donation [4] of chiral substituents [5], like the [(*S*)-2-(methoxymethyl)pyrrolidinomethyl] substituent (CH_2SMP). Moreover, the stereochemical information can also be introduced prior to the deprotonation reaction by using enantiomerically enriched C–H acidic precursors bearing only one proton at the stereogenic carbon center [1b,2a].

The latter chiral (aminomethyl) substituent is an important part of our concept for the synthesis of enantiomerically enriched metal alkyls: (amino-

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[1] *Remark:* In general, we speak of *enantiomerically enriched* metal alkyls, when we focus our interest on the stereogenic metalated carbon center. In the real case, these molecules are almost always *diastereomerically enriched* metal alkyls, due to the presence of more stereogenic centers than only the metalated one.

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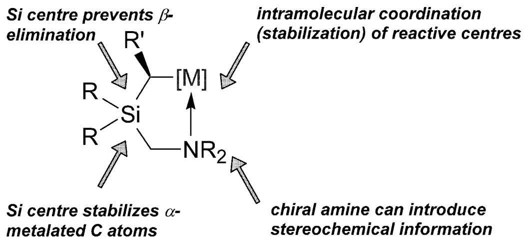


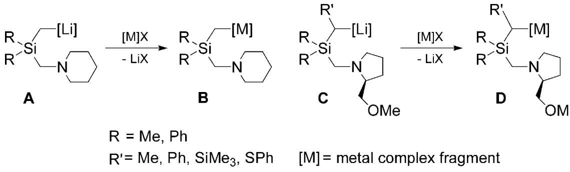
Fig. 1. Stabilization effects in (aminomethyl)(metallomethyl)silanes on their metalated centers.

methyl)(metallomethyl)silanes (Fig. 1). The side-arm donor SMP fulfills two important tasks. First of all, it introduces the stereochemical information into the coordination sphere of the metal fragment by coordination to the metal. Secondly, also by coordination, it stabilizes the absolute configuration of the stereogenic carbon center by fixing the metal fragment to the metalated carbon center. Without this ‘trick’, unstabilized stereogenic metal centers would lose their stereochemical information even at low temperatures due to the small barrier of inversion of metalated carbon centers (‘carbanions’ are isoelectronic to amines, which are known to have an unstable absolute configuration).

The silicon center of the (aminomethyl)(metallomethyl)silane also has two important functions. It stabilizes α-metalated carbon centers by polarization effects [6]. Moreover, it prevents the β-elimination, which is often observed for polar organo metal compounds.

In the field of enantiomerically enriched metal alkyls, the determination of the absolute configuration at the metalated stereogenic center and the clarification of the stereochemical course of further transformations are most important. However, this is often difficult to realize without speculation. In many cases, stereochemical assumptions have been made that are not always generally applicable. Furthermore, many aspects of the reaction mechanisms have not been understood yet.

In order to optimize the synthetic methods and to understand the structure/reactivity patterns, the aggregation behavior and the involved reaction mechanisms, it is important to start with lithium alkyls which have a defined structure in solution and the solid state. This is why we studied the influence of different metals and substituents or ligands with non-chiral (aminomethyl)(metallomethyl)silanes of type **B** first (Scheme 1).



Scheme 1.

2. Non-chiral metal alkyls

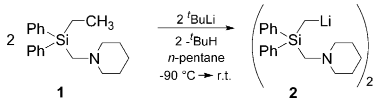
The starting lithium alkyl for the synthesis of the non-chiral metal alkyls, (aminomethyl)(lithiomethyl)silane (**2**), is generated in *n*-pentane at low temperatures, using *tert*-butyllithium (Scheme 2). After warming up to room temperature, single crystals of **2** were obtained, suitable for X-ray diffraction studies on the solid state structure of the lithium compound [7].

Compound **2** crystallized from *n*-pentane in the monoclinic crystal system, space group $P2_1/n$. It forms a dimer in the solid state with a central four-membered C–Li–C–Li ring (Fig. 2).

Compared to non-metalated silanes, the bond Si–C(1) = 1.806(2) Å is shortened, indicating the stabilizing effect of the silicon center on the α-metalated carbon center [6]. Thus, this bonding situation is an indicator on the polarity of the C(1)–Li contact, which is underlined by an N–Li contact of 2.049(4) Å.

Starting from lithium alkyl **2**, the bis{[diphenyl(piperidinomethyl)silyl]methyl}metal compounds **3**–**5** [metal = magnesium (**3**) [9], cadmium (**4**) [9] and mercury (**5**)] where synthesized in different solvents (toluene, THF) by metathesis reactions, using the corresponding metal(II) halides (Scheme 3) [10].

At a temperature of −90 °C, a cooled solution of two equivalents of the lithium alkyl **2** was added to the cooled solution (suspension) of the metal(II) halide and the reaction mixture was warmed to room temperature. After separation of the lithium halide and removing the solvent, single crystals of compounds **3**, **4** and **5** were



Scheme 2.

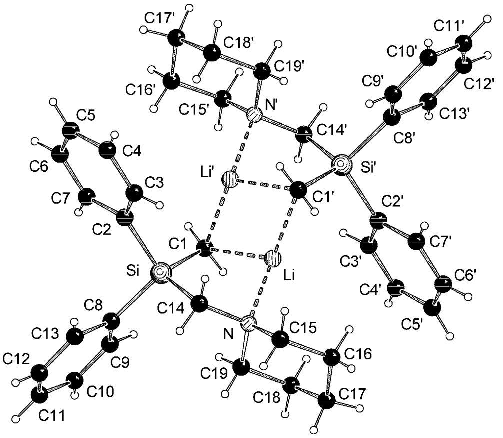
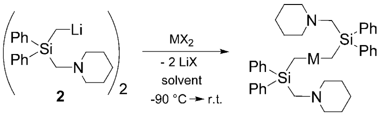


Fig. 2. Molecular structure and numbering scheme of compound **2** in the crystal (*Schakal plot*) [8]. Selected bond distances (Å) and angles (°): Si–C(1) 1.806(2), Li–C(1) 2.207(4), Li–C(1)′ 2.178(4), N–Li 2.049(4), C(1)–Si–C(14) 108.36(10), C(1)′–Li–C(1) 113.76(15).



MX_2	solvent	compound
$[Mg(thf)_4]Br_2$	toluene,THF	**3**
$CdCl_2$	THF	**4**
$HgCl_2$	toluene	**5**

Scheme 3.

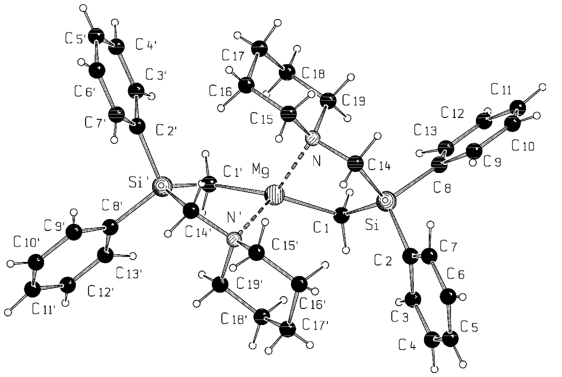


Fig. 3. Molecular structure and numbering scheme of compound **3** in the crystal (*Schakal plot*) [8]. Selected bond distances (Å) and angles (°): Si–C(1) 1.820(2), Mg–C(1) 2.181(2), Mg–N 2.254(2), C(1)–Si–C(14) 106.78(8), C(1)′–Mg–C(1) 123.29(11).

obtained, suitable for single crystal X-ray diffraction analyses.

Monomeric magnesium compound **3** crystallized from toluene in the monoclinic crystal system, space group *C*2/*c* [9]. The coordination situation at the magnesium center of a distorted tetrahedron, resulting in a C_2 symmetry of the molecule, is formed by two magnesium carbon contacts and two magnesium nitrogen contacts (Fig. 3). The Si–C(1) = 1.820(2) Å bond length is again shortened in this molecule, the Mg–N distance is of 2.254(2) Å. The C(1)′–Mg–C(1) angle of 123.3(1)° lies within the normal range for compounds of this type [10].

Monomeric cadmium compound **4** crystallized from toluene–*n*-pentane in the monoclinic crystal system, space group *C*2/*c* [9]. Like in magnesium compound **3**, the coordination situation is described by a distorted tetrahedron and the molecule is of C_2 symmetry (Fig. 4). The decreased polarity of the cadmium carbon bond is represented by an Si–C(1) distance of 1.831(3) Å and a Cd–N distance of 2.537(2) Å. To the best of our knowledge, the C(1)–Cd–C(1)′ angle of 140.6(2)° is unusually small and the shortest angle, that has been observed by X-ray diffraction methods for this type of compounds [10].

Monomeric mercury compound **5** crystallized from toluene–*n*-pentane in the monoclinic crystal system, space group $P2_1/c$. Compared to compounds **3** and **4**, the situation in compound **5** with mercury(II) as the metal center is different (Fig. 5). The two coordinating nitrogen atoms are no longer equivalent, the Hg–N(1) distance is 3.026(6) Å, the Hg–N(2) distance is 3.643(7) Å. Thus, no symmetry elements can be found for the molecular structure of compound **5** in the solid state. Moreover, the structure is mainly determined by the T-shape coordination geometry formed by two mercury carbon bonds and one stronger mercury nitrogen contact, typical for mercury compounds of this type. The weak Hg–N(2) interaction seems to merely complete the coordination sphere of the central metal. With the angle C(20)–Hg–C(1) = 177.1(3)°, the mercury center is almost linearly coordinated by the two carbon centers.

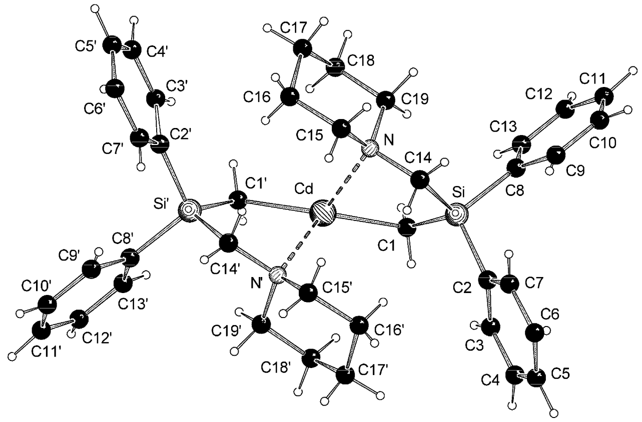


Fig. 4. Molecular structure and numbering scheme of compound **4** in the crystal (*Schakal plot*) [8]. Selected bond distances (Å) and angles (°): Si–C(1) 1.831(3), Cd–C(1) 2.202(3), Cd–N 2.537(2), C(1)–Si–C(14) 108.63(13), C(1)–Cd–C(1)′ 140.58(15).

When one equivalent of the lithium compound **2** is reacted with mercury(II) chloride in toluene at low temperatures, formally only one chloride is substituted to give {[diphenyl(piperidinomethyl)silyl]methyl}mer-

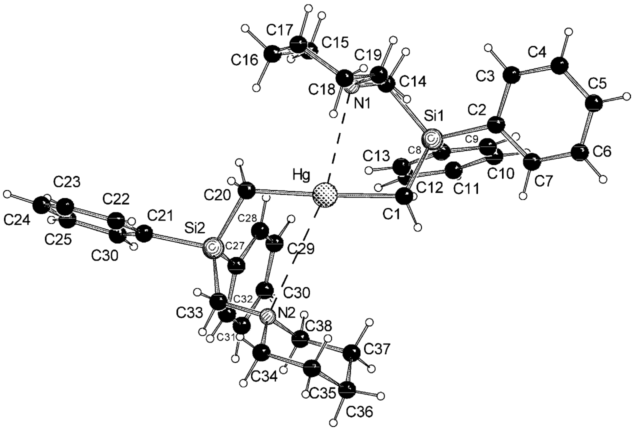
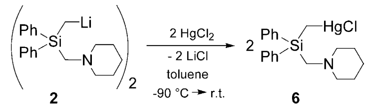


Fig. 5. Molecular structure and numbering scheme of compound **5** in the crystal (*Schakal plot*) [8]. Selected bond distances (Å) and angles (°): Si(1)–C(1) 1.858(8), Si(2)–C(20) 1.852(8), Hg–C(1) 2.095(7), Hg–C(20) 2.087(9), Hg–N(1) 3.026(6), Hg–N(2) 3.643(7), C(1)–Si(1)–C(14) 109.6(4), C(20)–Si(2)–C(33) 111.1(4), C(20)–Hg–C(1) 177.1(3).



Scheme 4.

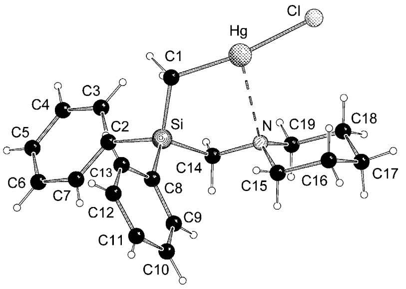


Fig. 6. Molecular structure and numbering scheme of compound **6** in the crystal (*Schakal plot*) [8]. Selected bond distances (Å) and angles (°): Si–C(1) 1.859(8), Hg–C(1) 2.066(7), Hg–N 2.778(6), C(1)–Si–C(14) 109.1(3), C(1)–Hg–Cl 170.5(2).

cury(II) chloride (**6**) (Scheme 4). After separation of lithium chloride and removing the solvent, single crystals of compound **6** were obtained, suitable for single crystal X-ray diffraction analysis.

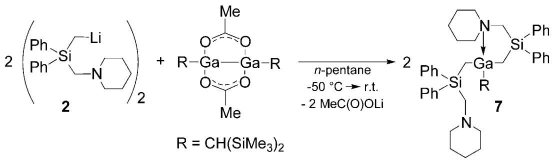
Monomeric compound **6** crystallized from acetone in the monoclinic crystal system, space group $P2_1/n$. Like in compound **5**, the mercury center is almost linearly coordinated by C(1) and Cl with an angle C(1)–Hg–Cl of 170.5(2)°. By the Hg–N contact of 2.778(6) Å, the T-shape coordination geometry, typical for mercury compounds, is obtained (Fig. 6). The more covalent character of the metal carbon bond in both mercury alkyls is underlined by the length of the bond Si–C(1) of both compounds [1.858(8) Å for **5** and 1.859(8) Å for **6**]. Compared to lithium compound **2** or magnesium compound **3**, these distances are of almost the same value than in non-metalated (aminomethyl)silanes due to minimal stabilizing effects by the vicinal silicon center.

The carbanionic {[(aminomethyl)diphenylsilyl]-methyl} fragment of lithium alkyl **2** can also be transferred to Group 13 main group elements (e.g. gallium), shown in Scheme 5 [11].

Two equivalents of **2** react with di{[bis(trimethylsilyl)methyl](μ-acetato)}digallan in *n*-pentane at low temperatures, yielding the unsymmetrically substituted triorgano gallium compound **7** (Scheme 5). In this compound with a coordination number of four at the gallium center, one of the {[bis(trimethylsilyl)methyl] groups of the starting material is left. Moreover, two {[(aminomethyl)diphenylsilyl]methyl} substituents are found at the gallium center, only one coordinating it in a chelating manner by an additional Ga–N contact, as the crystal structure of **7** reveals (Fig. 7).

Monomeric compound **7** crystallized from *n*-pentane in the triclinic crystal system, space group $P\bar{1}$. The coordination geometry at the gallium center is of a distorted tetrahedron. As only one of the {[(aminomethyl)diphenylsilyl]methyl} substituents acts as a chelating ligand, only one Ga–N contact Ga–N(1) = 2.198(6) Å is of interest, comparable to that of magnesium alkyl **3**. Nevertheless, two contacts between silicon and a metalated carbon center can be found: Si(1)–C(1) = 1.840(8) and Si(2)–C(20) = 1.853(8). Both distances are in the range of cadmium compound **4** and mercury compounds **5** and **6**, indicators for a more covalent C–Ga bond in this molecule.

As a conclusion, the {[diphenyl(piperidinomethyl)silyl]methyl} fragment was successfully transferred to the metals magnesium, gallium, cadmium and mercury. Since the nitrogen center of the (aminomethyl) substituent is intramolecularly coordinating the metal center, it is strongly determining the molecular structures. Thus, no additional solvent molecules are found intermolecularly coordinating to the central metal. As a regularity, the Si–C bond length is in accordance with the polarity of the C–M bond: the more polar the C–M bond is, the shorter is the Si–C bond between the silicon and the metalated carbon center. Finally, some exciting structural features could be observed [e.g. the small C(1)–Cd–C(1)′ angle in cadmium compound **4**].



Scheme 5.

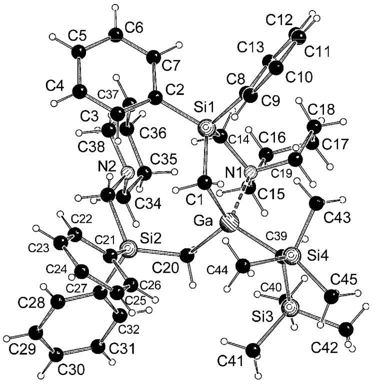
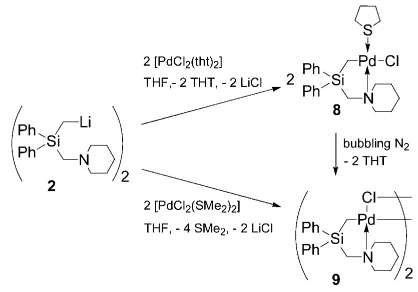


Fig. 7. Molecular structure and numbering scheme of compound **7** in the crystal (*Schakal plot*) [8]. Selected bond distances (Å) and angles (°): Si(1)–C(1) 1.840(8), Si(2)–C(20) 1.853(8), Ga–C(1) 2.018(7), Ga–C(20) 2.015(9), Ga–N(1) 2.198(6), Ga–C(39) 2.041(6), C(1)–Si(1)–C(14) 104.1(4), C(20)–Si(2)–C(33) 114.7(4), C(20)–Ga–C(1) 115.9(3), Si(1)–C(33)–N(2) 119.4(3).

3. Synthesis and reactivity of non-chiral palladium alkyls

Since palladium was the first metal that we used for enantiomerically enriched metal alkyls, reactions of lithium alkyl **2** with palladium(II) compounds were intensively studied [12]. The following questions had to be answered: (1) Can the {[diphenyl(piperidinomethyl)-silyl]methyl} fragment be transferred to palladium? (2) Is the Pd–C bond stable towards ligand exchange reactions? (3) Is the coordination of the (aminomethyl) substituent a structure-determining factor?

The reaction of lithium alkyl **2** with *trans*-[$PdCl_2(SMe_2)_2$] directly leads to dimeric {Pd[CH_2SiPh_2-($CH_2NC_5H_{10}$)](μ-Cl)}$_2$ (**9**), where the [$CH_2SiPh_2(CH_2$-$NC_5H_{10})$] ligand forms a palladacycle (Scheme 6). When *trans*-[$PdCl_2(tht)_2$] is used, the corresponding monomeric (aminomethyl)(palladiomethyl)silane **8** with one tht ligand coordinated to the palladium center can be isolated. The chloro bridged dimer **9** crystallizes as the *trans* isomer from CH_2Cl_2–*n*-hexane (monoclinic crystal system, space group $P2_1/n$), as both carbon donor atoms or both nitrogen donor atoms are at opposite sides of the molecule (Fig. 8). However, the compound exists as a mixture of the *cis* isomer and the *trans* isomer in solution.



Scheme 6.

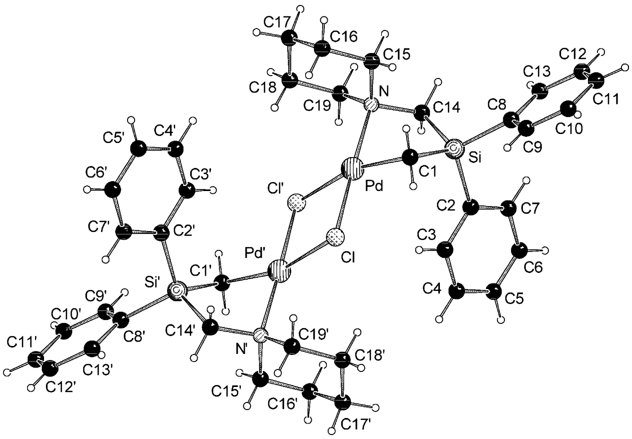


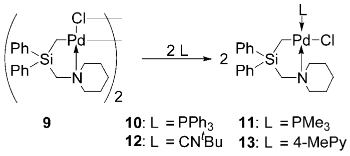
Fig. 8. Molecular structure and numbering scheme of compound **9** in the crystal (*Schakal plot*) [8]. Selected bond distances (Å) and angles (°): Si–C(1) 1.855(3), Pd–C(1) 2.034(2), Pd–N 2.126(2), C(1)–Si–C(14) 104.40(11).

The Pd–C distance of 2.034(2) Å is in the typical range found for Pd–C(sp^3) single bonds (from 2.0 to 2.1 Å) [13]. The difference in the Pd–Cl distances of 2.491(1) and 2.329(1) Å reflects the strong electron donating properties of the (silylmethyl) ligand, being an indicator for a high *trans* influence.

The reactivity of complex **9** was studied in order to determine the behavior of the [(aminomethyl)(silylmethyl)] ligand coordinated to palladium. A wide variety of mono- and bidentate ligands of different geometric and electronic characteristics, neutral or anionic, were used.

Monodentate ligands cleave the chloro bridges to give compounds of type Pd[$CH_2SiPh_2(CH_2NC_5H_{10})$]ClL [L = PPh_3 (**10**), PMe_3 (**11**), CN^{t}Bu (**12**), 4-methylpyridine (4-MePy) (**13**)], where the incoming ligand and the carbon center of the cyclometalated ligand are coordinated *cis* (Scheme 7). One of these compounds (**10**) was crystallographically examined by X-ray diffraction studies.

As an example, the molecular structure of PPh_3 complex **10** is shown in Fig. 9. The compound crystallized from CH_2Cl_2–*n*-hexane in the orthorhombic crystal system, space group $P2_12_12_1$. The coordination geometry at the palladium center is square planar with the PPh_3 ligand in *cis* position to the metalated carbon center. As can be seen, the five-membered palladacycle remains intact during the reaction with the phosphine.



Scheme 7.

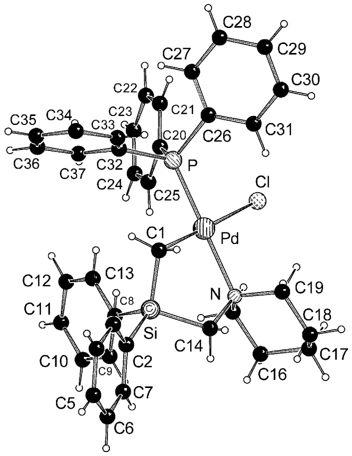


Fig. 9. Molecular structure and numbering scheme of compound **10** in the crystal (*Schakal plot*) [8]. Selected bond distances (Å) and angles (°): Pd–C(1) 2.067(5), Si–C(1) 1.824(4), Pd–N 2.212(4), C(1)–Si–C(14) 100.4(2).

The cationic complex {Pd[$CH_2SiPh_2(CH_2NC_5H_{10})$]-(4-MePy)$_2$}$BF_4$ (**14**) with two 4-MePy ligands at the palladium center is obtained by treating the starting dimer **9** with $TlBF_4$ and 4-MePy in a redox reaction (Scheme 8). The solid state structure of **14** was determined.

The molecular structure of the 4-MePy complex **14** is shown in Fig. 10. The compound crystallized from CH_2Cl_2–Et_2O in the monoclinic crystal system, space group $P2_1/n$. Two different Pd–N(sp^2) distances are found in the crystal [Pd–N(2) = 2.180(4), Pd–N(3) = 2.046(3)], indicating a 4-MePy ligand more covalently bound and one with a more dative bond to the palladium center.

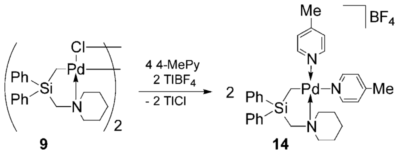
A chelate complex Pd[$CH_2SiPh_2(CH_2NC_5H_{10})$]($S_2C$-$NEt_2$) (**15**) is obtained when reacting the starting chloro bridged dimer **9** with NaS_2CNEt_2 (Scheme 9). The solid state structure of compound **15** could be determined.

Compound **15** crystallized from CH_2Cl_2–*n*-hexane in the monoclinic crystal system space group $P2_1/c$. The coordination geometry at the palladium center is again square planar, but with some greater distortion than in the monodentate complexes **10**–**14**. A value of 75.12(3)° is found for S(1)–Pd–S(2), 104.35(6)° for N(1)–Pd–S(2) (Fig. 11).

The reactions of lithium alkyl **2** with *trans*-[$PdCl_2(SMe_2)_2$] show that the {[diphenyl(piperidinomethyl)silyl]methyl} fragment can also be transferred to palladium and that in all of the reactions a five-membered palladacycle is formed. This palladacycle remains intact during all of the reactions, where bridging chloro ligands are cleaved by neutral ligands or substituted by anionic bidentate ligands. However, Si–C and Pd–N cleavages are detected during the attempts to synthesize cationic complexes, the complexes with 4-methylpyridine being the only ones to be cleanly obtained. X-ray structural analyses of each type of compound show the strong *trans* influence of the [(piperidinomethyl)silylmethyl] fragment, regardless of neutral or cationic complexes. Again, the nitrogen centers of the (aminomethyl) substituent can be regarded as strongly structure determining.

4. Enantiomerically enriched metal alkyls

Summarizing the results on the transformations with non-chiral (aminomethyl)(lithiomethyl)silane **2**, the requirements on structure and reactivity have been met. All the synthesized non-chiral metal alkyls are well-defined compounds in the solid state. By reaction of a metal halide with a highly diastereomerically enriched alkyl lithium compound, diastereomerically enriched metal alkyls should be accessible. The high diastereoselectivities of lithiated (aminomethyl)benzylsilane (*R*,*S*)-**17** in trapping reactions with organic electrophiles [14] (e.g. alkyl halides) and organotinhalides made us choose this molecule for alkyl transfer reactions on other metals. This alkyl lithium compound is again obtained by deprotonation of the corresponding (aminomethyl)benzylsilane **16** with *tert*-butyllithium in non-polar solvents at low temperatures (Scheme 10).



Scheme 8.

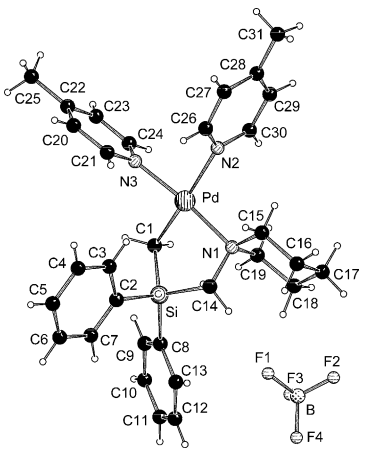
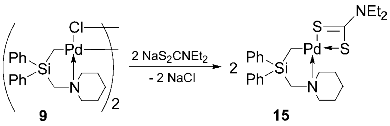


Fig. 10. Molecular structure and numbering scheme of compound **14** in the crystal (*Schakal plot*) [8]. Selected bond distances (Å) and angles (°): Si–C(1) 1.846(5), Pd–C(1) 2.050(5), Pd–N(1) 2.124(3), Pd–N(2) 2.180(4), Pd–N(3) 2.046(3),C(1)–Si–C(14) 102.8(2).



Scheme 9.

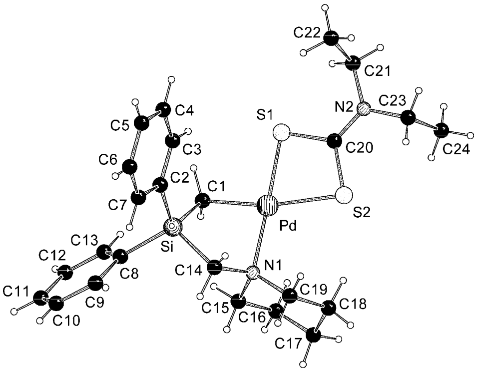
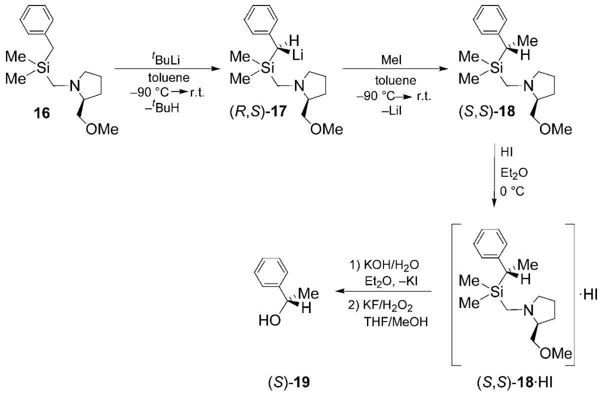


Fig. 11. Molecular structure and numbering scheme of compound **15** in the crystal (*Schakal plot*) [8]. Selected bond distances (Å) and angles (°): Si–C(1) 1.843(2), Pd–C(1) 2.074(2), Pd–N(1) 2.155(2), C(1)–Si–C(14) 105.19(10).



Scheme 10.

The amazingly high selectivity of reactions of lithium alkyl (*R*,*S*)-**17**, which was first investigated by Chan et al. [14a], and the apparent stability of configuration make a closer look at the stereochemical course of its transformations necessary. Thus, it was of great interest to determine the molecular structure and the absolute configuration of lithium alkyl (*R*,*S*)-**17** in the crystal, since both had not been known yet [15].

Compound (*R*,*S*)-**17** crystallized from toluene in the hexagonal crystal system, space group $P3_2$. Three crystallographically independent molecules are found in the asymmetric unit, each building up infinite chain structures of (*R*,*S*)-**17** in the solid state. These chains are formed by π-interactions between a lithium center and the phenyl group of an adjoining silane molecule (Fig. 12). The metalated stereogenic carbon center C(3) is planar but is nevertheless—due to the metal–carbon contact Li(1)–C(3)—a stereogenic center. The sum of the angles around C(3) is 360(3)°, regarding only the 'carbanionic' moiety [15].

The reaction sequence of the metalation, followed by methylation and direct Si–C cleavage reaction to the correspending benzyl alcohol (*S*)-**19** was already studied by Chan et al. [14a]. The stereochemical pathway of this reaction remained unclear and was based on stereochemical speculations due to the absence of knowledge of the solid state structure for (*R*,*S*)-**17**.

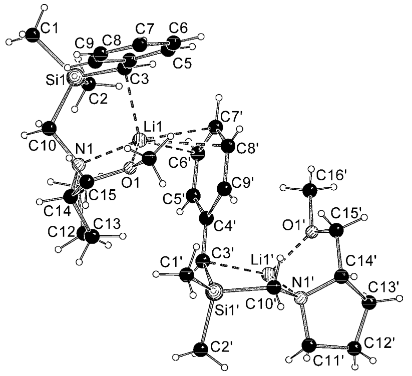


Fig. 12. Molecular structure and numbering scheme of compound (*R*,*S*)-**17** (molecule A) in the crystal (*Schakal plot*) [8]. Selected bond distances (Å) and angles (°): Si(1)–C(3) 1.797(7), Li(1)–C(3) 2.269(14), C(3)–C(4) 1.419(9), N(1)–Li(1) 2.183(12), C(3)–Si(1)–C(10) 107.9(3).

Having determined the molecular structure in the solid state and the absolute configuration at the metalated α-carbon center, we experimentally examined and explained the stereochemical course of an integral sequence of transformations, starting from the unmetalated silane **16** (Scheme 10). The absolute configuration at the α-carbon center of compound (*S*,*S*)-**18** was determined by conversion into the ammonium iodide (*S*,*S*)-**18**·HI and subsequent determination of the crystal structure. The selectivity of the Si–C cleavage reaction and the absolute configuration of benzyl alcohol (*S*)-**19** could be determined by NMR methods with the help of chiral lanthanide shift reagents $[Er(tfc)_3]$ [15].

In the literature, both the (*R*,*S*) and the (*S*,*S*) diastereomer of lithium alkyl **17** have been proposed as the major diastereomer [5,14]. Based on these predictions, both retention and inversion of the configuration at C(3) have been postulated for the reactions of (*R*,*S*)-**17** with alkyl halides [14]. Our X-ray structural analysis of (*R*,*S*)-**17** shows that (*R*) configuration at the metalated carbon center and inversion of configuration [for the reaction of (*R*,*S*)-**17** with methyl iodide in toluene] are in fact the case.

A look in the literature reveals that both retention and inversion of the configuration have been observed for the reactions of lithiated benzylic and related systems with various electrophiles [16]. In most cases no solid state structure of the corresponding lithium alkyl could be determined to confirm the absolute configuration of the stereogenic metalated carbon center. The stereochemical course of the reaction of our lithium alkyl with the electrophile MeI in toluene can be understood on the basis of the solid state structure of compound (*R*,*S*)-**17**, which was crystallized from the same solvent used in the substitution reaction with the alkyl iodide, in the combination with computational studies.

The modelling of monomeric (*R*,*S*)-**17** [B3LYP/6-31+G(d)] indicates that the highest occupied molecular orbital (HOMO) is chiefly located at the metalated carbon center and the aromatic ring system (Fig. 13). It can be deduced from the calculated orbital coefficients that both inversion and retention of configuration are almost equally likely to result from electrophilic attack. Only the fact that the site opposite to the lithium center is sterically accessible to attack by electrophiles (the coordination polymer of the solid state structure should be broken up in solution) makes it possible for (*R*,*S*)-**17** to react selectively with inversion of configuration at C(3) under kinetic control in non-polar solvents.

When lithiated benzyl silane (*R*,*S*)-**17** is reacted with one equivalent of $HgCl_2$ in the solvent diethyl ether, mercury compound (*S*,*S*)-**20** is obtained mainly with

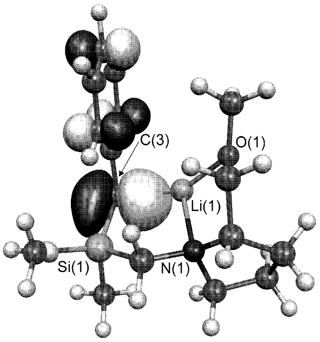
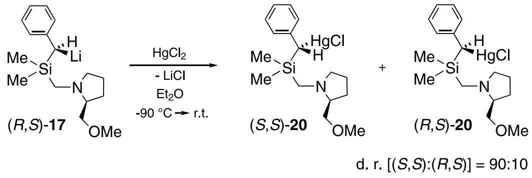


Fig. 13. B3LYP/6-31+G(d)-optimized structure of monomeric (*R*,*S*)-**17** and visualization of the highest occupied molecular orbital (HOMO) (*Molekel plot* [17]; numbering scheme adopted from Fig. 12).

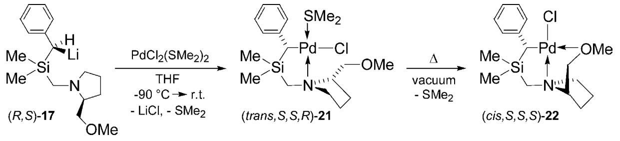
inversion of configuration at the metalated carbon center in a diastereomeric ratio of d.r.[(*S*,*S*):(*R*,*S*)] = 90:10 (Scheme 11).

The molecular structure of (*S*,*S*)-**20** in the solid state could be determined and associated with the corresponding NMR data (Fig. 14). The compound crystallized from toluene–*n*-pentane in the orthorhombic crystal system, space group $P2_12_12_1$. The molecular structure of (*S*,*S*)-**20** is similar to that of non-chiral mercury compound **6**. Only the nitrogen donor center of the SMP ligand is coordinating to the Group 12 metal center, the oxygen center does not act as a ligand.

By the reaction of lithium alkyl (*R*,*S*)-**17** with one equivalent of *trans*-$[PdCl_2(SMe_2)_2]$, two interesting compounds were isolated in high d.r. values from the reaction mixture (Scheme 12). In the first step at low temperatures, palladium compound (*trans*,*S*,*S*,*R*)-**21** was isolated in a diastereomeric ratio of d.r. ≥ 98:2. In this compound, one labile SMe_2 ligand of the starting material is left *cis* to the metalated carbon center, as well as the intramolecularly coordinating nitrogen center of the SMP substituent. In *trans* position to the metalated carbon center is the substitutable chloro ligand. Upon warming (*trans*,*S*,*S*,*R*)-**21** in vacuo, *cis*–*trans* isomerization and inversion at the nitrogen center takes place, the chloro substituent now in *cis* position to the metalated carbon center and both donor centers of the amine substituent intramolecularly coordinating to the metal center of palladium compound (*cis*,*S*,*S*,*S*)-**22**. Also this compound can be isolated in a diastereomeric ratio of d.r. ≥ 98:2.



Scheme 11.



Scheme 12.

Since the nitrogen center has a coordination number of four in both palladium compounds (Scheme 12, Figs. 15 and 16), it is a stereogenic center with inverted absolute configuration for compound (*trans*,*S*,*S*,*R*)-**21** and (*cis*,*S*,*S*,*S*)-**22**. By analysis of the NMR spectra of the crude product, it is assumed that the molecule is formed as mixture of epimers with different absolute configurations at the nitrogen centers. In one of these epimers, intramolecular OMe coordination is possible, followed by conversion into palladium compound (*cis*,*S*,*S*,*S*)-**22**. In the other epimer, an intramolecular OMe coordination is not possible, what probably makes the compound crystallize as this stereoisomer (Fig. 15).

Compound (*trans*,*S*,*S*,*R*)-**21** crystallized from CH_2Cl_2–*n*-pentane in the orthorhombic crystal system, space group $P2_12_12_1$. The absolute configuration at the metalated carbon center C(3) is (*S*). Thus, the stereochemical course of the metathesis reaction with the palladium(II) halide is *inversion of configuration*.

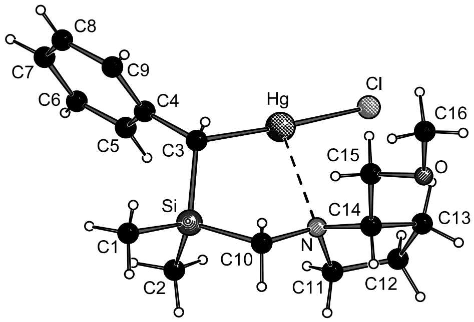


Fig. 14. Molecular structure and numbering scheme of compound (*S*,*S*)-**20** in the crystal (*Schakal plot*) [8]. Selected bond distances (Å) and angles (°): Si–C(3) 1.875(8), Hg–C(3) 2.105(6), Hg–N 2.905(6), C(3)–Si–C(10) 109.8(4), C(3)–Hg–Cl 173.8(2).

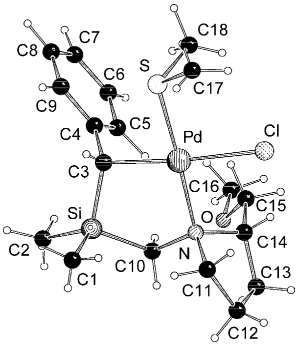


Fig. 15. Molecular structure and numbering scheme of compound (*trans*,*S*,*S*,*R*)-**21** in the crystal (*Schakal plot*) [8]. Selected bond distances (Å) and angles (°): Si–C(3) 1.872(5), Pd–C(3) 2.117(4), Pd–N 2.183(3), C(3)–C(4) 1.501(6), C(3)–Si–C(10) 103.7(2).

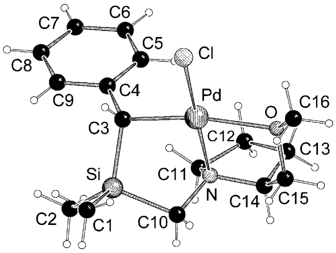


Fig. 16. Molecular structure and numbering scheme of compound (*cis*,*S*,*S*,*S*)-**22** in the crystal (*Schakal plot*) [8]. Selected bond distances (Å) and angles (°): Si–C(3) 1.907(8), Pd–C(3) 2.071(7), Pd–N 2.112(6), C(3)–C(4) 1.521(9), C(3)–Si–C(10) 104.5(3).

Compound (*cis*,*S*,*S*,*S*)-**22** crystallized from CH_2Cl_2–*n*-pentane in the orthorhombic crystal system, space group $P2_12_12_1$ (Fig. 16). When compound (*trans*,*S*,*S*,*R*)-**21** is transformed into compound (*cis*,*S*,*S*,*S*)-**22**, the absolute configuration at C(3) does not change, as can be seen from Fig. 16. Thus, the isomerization at the palladium center does not influence the stereochemistry at the metalated carbon center.

Both palladium compounds (*trans*,*S*,*S*,*R*)-**21** and (*cis*,*S*,*S*,*S*)-**22** are reactive molecules (labile ligands in either *cis* or *trans* position) that bear a stereogenic carbon center in α-position to the active metal fragment. Very selective reactions at either the metal center or the Pd–C bond should be the consequence.

5. Conclusions

Our studies on [(aminomethyl)silylmethyl]metal compounds have shown that it is possible to transfer the ‘carbanionic’ fragment of non-chiral (aminomethyl)(lithiomethyl)silane **2** to other metals, like magnesium, gallium, palladium, cadmium or mercury. The corresponding bis{[diphenyl(piperidinomethyl)silyl]methyl}metal(II) compounds have been obtained for Mg, Ga, Cd and Hg, and the molecular structures have been determined. In case of Hg and Pd, the [diphenyl(piperidinomethyl)silyl]methylmetal(II) chlorides were synthesized and the molecular structures were determined. All of the compounds are well-defined in solution and the solid state.

For highly diastereomerically enriched (aminomethyl)(lithiomethyl)silane (*R*,*S*)-**17**, high diastereoselectivities could be observed for the metathesis reactions with mercury and palladium compounds. Furthermore, the stereochemical course for the reaction sequence of deprotonation, nucleophilic substitution (alkylation of the lithium alkyl) and oxidative Si–C cleavage, starting from unmetalated (aminomethyl)benzylsilane **16**, was solved.

In the special case of (aminomethyl)(palladiomethyl)silanes, it could be shown that the five-membered palladacycle remains intact during ligand exchange reactions and neutral or cationic palladium complexes can be obtained. When the ‘carbanionic’ fragment of lithium alkyl (*R*,*S*)-**17** is transferred to palladium, two reactive diastereomerically enriched palladium alkyls were isolated that bear a stereogenic carbon center directly bound to an active metal (labile ligands at the palladium center). We are hopeful to observe stereoselective reactions at the active metal site or at the Pd–C bond of palladium compounds (*trans*,*S*,*S*,*R*)-**21** and (*cis*,*S*,*S*,*S*)-**22**.

Acknowledgements

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