Solid-State Structural Investigation of an Organolithium (−)-Sparteine Complex: η^3-*N*-Boc-*N*-(*p*-methoxyphenyl)-3-phenylallyllithium · (−)-Sparteine[**]

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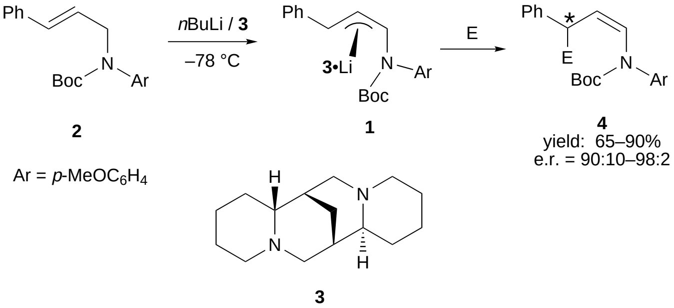
A number of organolithium compounds have been found to be of remarkable value for the enantioselective formation of carbon–carbon bonds under the influence of (−)-sparteine.[1] Definitive information about the structure of the lithiated species that are involved in these reactions is needed to understand and improve the methodology. Herein we report the isolation and X-ray crystallographic analysis of η^3-*N*-Boc-*N*-(*p*-methoxyphenyl)-3-phenylallyllithium · (−)-sparteine (**1**). This configurationally stable complex, which results from the asymmetric deprotonation of *N*-Boc-*N*-(*p*-methoxyphenyl)-cinnamylamine (**2**) by *n*BuLi in the presence of (−)-sparteine (**3**), undergoes reactions with alkylating and acylating reagents and 1,4-additions to afford products **4** with high enantioenrichments.[2] The determination of the structure of this key intermediate allows definative conclusions about the stereochemical course of the conversions of **1** into **4**.



The organolithium species **1** crystallizes in the triclinic space group *P*1.[3] The unit cell contains two nearly identical complexes along with four molecules of uncoordinated diethyl ether.[6] The crystal structure for one of the complexes of **1** is shown in Figure 1. It is interesting that Li1 in **1** is associated in a η^3 fashion to the allyl unit (Li1 – C7 258.2(1.3), Li1 – C8 244.2(1.3), Li1 – C9 274.0(1.4) pm). This is in contrast to an analogous carbamoyloxy-3-trimethylsilylallyllithium (−)-sparteine complex in which the Li cation is coordinated in an η^1 manner.[7a] Dimeric, 3-metalated (3*S*)-3-lithio-1-[(*S*)-2-(methoxymethyl)pyrrolidino]-1,3-diphenylpropene has also been characterized as an unbridged structure in the solid state.[7b] The 1-butylindenidelithium · (−)-sparteine complex characterized by Boche and Hoppe is similar to **1** but with a closer association between the lithium cation and the η^3-allyl carbon atoms.[7c]

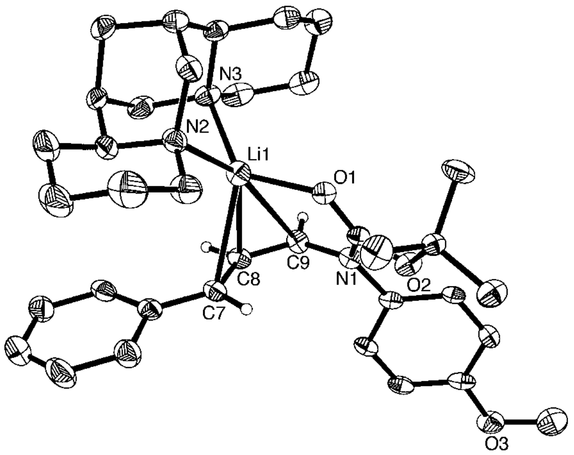


Figure 1. Molecular structure of **1** in the crystal.[3, 6] Important distances [pm] as well as bond and torsional angles [°]: C7 – C8 141.0(0.9), C8 – C9 137.5(0.9), Li1 – C7 258.2(1.3), Li1 – C8 244.2(1.3), Li1 – C9 274.0(1.4), Li1 – N2 212.3(1.3), Li1 – N3 212.3(1.2), Li1 – O1 191.7(1.2), C9 – N1 142.6(0.8), N1 – C17 137.4(0.8), O1 – C17 123.4(0.7), C17 – O2 134.2(0.7); C7-C8-C9 129.3(0.6), Li1-C7-C8-C9 77.1(0.7).

Another significant feature of the structure is the 68° angle between the planes formed by the allyl unit (C7-C8-C9) and the amide functionality (O1-C17-N1). This twist allows bonding of the carbonyl group to the bridging lithium atom and relieves the repulsive pair – pair interactions between the electrons in the HOMOs of the amide π bond and the sp^2 carbanion.[8]

To verify that the isolated intermediate is the same as the major species present in solution during the standard reaction sequence, isolated crystalline **1** was dissolved in diethyl ether at −78 °C, and benzyl bromide was added. The reaction yielded (*S*)-**4a** with an enantiomeric ratio (e.r.) of 99:1. The absolute configuration of the major enantiomer was identical to that observed from the normal lithiation/substitution sequence as determined by the elution order from HPLC on a chiral stationary phase. Thus, the crystallization also provides an opportunity for increased enantioenrichment.[9]

From the configuration of **1**, which has the lithium · (−)-sparteine complex on the *re* face of the allyl unit, the stereochemical course of substitution with different types of electrophiles is evident. Reaction with the alkyl halide benzyl bromide proceeds with inversion of configuration to give product (*S*)-**4a.** In contrast, reactions with the Michael acceptor 5,6-dihydro-2*H*-pyran-2-one and the carbonyl electrophile cyclohexanone proceed with retention of configuration to give (*R*,*R*)-**4b** and (*R*)-**4c**. The latter cases are considered to involve precomplexation between the carbonyl group and lithium cation; this type of interaction is not favorable in the trigonal-bipyramidal transition structure for the reaction of **1** with an alkyl halide electrophile.[10]

We have reported a transmetalation sequence with trimethyltin chloride which provides access to the enantiomers with the opposite configuration to the reaction products **4**.[2]

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Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.

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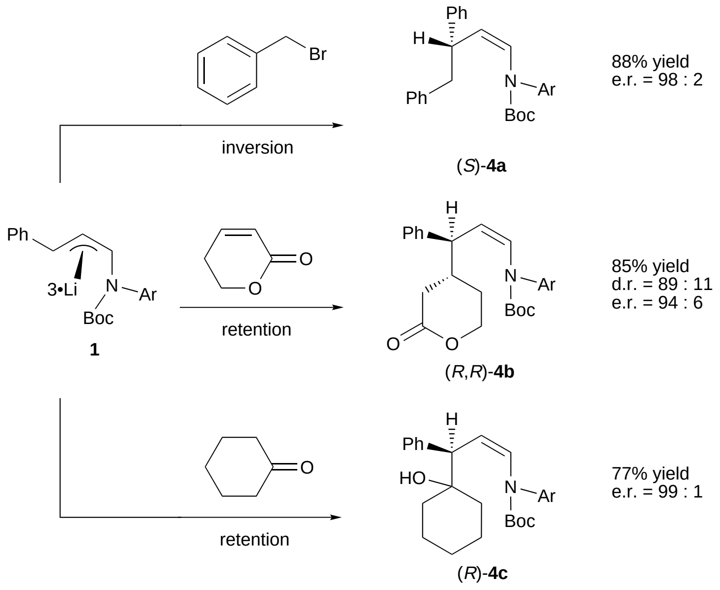
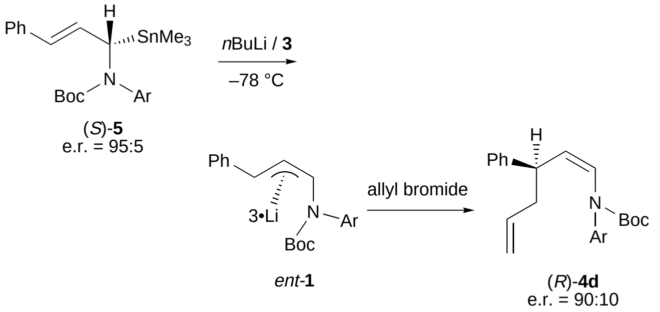


We have established now by X-ray crystallographic analysis of (*S*)-**5** that trimethyltin chloride reacts with inversion of configuration.[3, 11] Transmetalation of (*S*)-**5** with *n*BuLi and subsequent reaction with allyl bromide gives (*R*)-**4d**, with the configuration of the major enantiomer opposite to that observed in the normal lithiation/substitution protocol. This result establishes that the tin–lithium transmetalation proceeds with retention of configuration.[12]



In summary, we have isolated and crystallographically characterized the important η^3-allyllithium · (–)-sparteine complex **1**. This structural determination allows assignment of the stereochemical course for carbon–carbon bond forming reactions which proceed with high enantioselectivity. We believe these definitive structural assignments will aid in further developing the synthetic potential of these species.

Experimental Section

1: Single crystals of **1** were prepared in an oven-dried Schlenk flask under dry argon. *N*-Boc-*N*-(*p*-methoxyphenyl)cinnamylamine (**2**) (187 mg, 0.551 mmol) was dissolved in diethyl ether (13 mL, freshly distilled from sodium/benzophenone). (–)-Sparteine (**3**, 0.127 mL, 0.551 mmol) was added to the clear solution at room temperature. The reaction mixture was then cooled to –78 °C, and *n*BuLi (0.404 mL, 1.5 M, 0.606 mmol) was added. After 1 h under argon, the yellow homogenous solution was placed under vacuum (0.04 torr) with continued stirring at –78 °C for 1.5 h. The flask was then back-filled with argon, and the homogenous yellow solution was allowed to sit undisturbed at –78 °C for 36 h. During this period, brilliant yellow crystals of **1** formed. In a test reaction, the crystals were separated by filtration and redissolved in pre-cooled diethyl ether (10 mL). Treatment of the solution with benzyl bromide (4 equiv) for 1.5 h at –78 °C gave (*S*)-**4a** (33 % yield based on **2**, e.r. = 99:1). The supernatant was also allowed to react with benzyl bromide (1.8 equiv) for 1.5 h at –78 °C, to give (*S*)-**4a** (35 % yield based on **2**, e.r. = 89:11).

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[3] X-ray data were collected with 0.3° steps in the ω scan mode on a Siemens SMART system equipped with a CCD detector (Mo$_{K\alpha}$ radiation, $\lambda = 71.073$ pm). The structures were solved by direct methods and refined with full-matrix least squares on all reflections, based on F_o^2, with SHELXTL.[4] Crystallographic data for **1** · 2 Et$_2$O ($C_{36}H_{50}LiN_3O_3 \cdot 2\,C_4H_{10}O$, $M_r = 727.97$): A yellow crystal with the dimensions 0.30 × 0.44 × 1.10 mm was mounted on a 0.7-mm cryoloop at 163(2) K. Triclinic space group $P1$, $a = 946.57(7)$, $b = 1395.39(10)$, $c = 1796.55(12)$ pm, $\alpha = 111.6920(10)$, $\beta = 96.5740(10)$, $\gamma = 92.4160(10)$°, $V = 2181.2(3) \times 10^6$ pm^3; $Z = 2$, $\rho_{calcd} = 1.108$ g cm^{-3}; $\mu = 0.071$ mm^{-1} (no absorption correction was applied); 10258 data, 8549 unique ($R_{int} = 0.0361$), $2\theta < 50.8°$, 973 free parameters; $R_1 = 0.075$, $wR_2 = 0.178$ for 7309 data observed ($I > 2\sigma(I)$); max./min. residual electron density +0.357/–0.349 eÅ^{-3}. Allylic H atoms were independently refined; the remaining H atoms were included as fixed idealized contributors. Crystallographic data for **5** ($C_{24}H_{33}N_1O_3Sn$, $M_r = 502.21$): A colorless crystal with the dimensions 0.10 × 0.20 × 0.30 mm was mounted in paratone oil at 198(2) K. Monoclinic space group $P2_1$, $a = 1040.63(6)$, $b = 682.02(4)$, $c = 1748.85(11)$ pm, $\beta = 101.690(2)$, $V = 1215.47(13) \times 10^6$ pm^3; $Z = 2$, $\rho_{calcd} = 1.372$ g cm^{-3}; $\mu = 1.073$ mm^{-1} (an empirical absorption correction was applied, transmission 0.4830–0.9369); 7723 data, 5242 unique ($R_{int} = 0.0840$), $2\theta < 56.8°$, 269 free parameters; $R_1 = 0.083$, $wR_2 = 0.192$ for 4314 data observed ($I > 2\sigma(I)$), Flack parameter –0.08(7); min./max. residual electron density +1.592/–1.699 e Å^{-3}. All H atoms were included as fixed idealized contributors.[5]

[4] The Siemens X-ray structure refinement package consists of SAINT Version 4, SHELXTL Version 5, and SMART Version 4 and is marketed by Siemens Industrial Automation, Inc., Madison, WI.

[5] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101316. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk)..

[6] The greatest difference in bond lengths between **1** and **2** is 3.5 pm for an aromatic C–C bond on the *p*-OMeC_6H_4 ring. Bond lengths and angles reported here are for complex **1**.

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[11] The absolute configurations of **4b** and **5** are opposite to our earlier provisional assignments.[2a] The determination of the absolute configuration for **4b** is detailed in the supporting information.
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Generation of a Silylene Complex by the 1,2-Migration of Hydrogen from Silicon to Platinum**

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Intramolecular migrations in transition metal silicon compounds have attracted considerable attention in recent years.[1] Many of the catalytic cycles and the most interesting transformations for metal–silicon systems appear to feature such migrations,[1, 2] but discrete examples of these steps have proven difficult to observe and characterize. Silylene complexes of the type [$L_nM{=}SiR_2$] are commonly featured as key intermediates in mechanistic speculations on 1,2- and 1,3-migrations.[1–3] Silylene complexes have only recently been isolated,[4] but despite great effort the formation of a silylene ligand through an intramolecular migration has not yet been observed. We recently described a reversible 1,2-hydrogen migration which interconverts *cis*-[$(PEt_3)_2Pt(H)Si(S\mathit{t}Bu)_2$][OTf] and *cis*-[$(PEt_3)_2Pt(NCMe)SiH(S\mathit{t}Bu)_2$][OTf] (Tf = SO_2CF_3), probably via an intermediate silylene complex.[5] Here we report the first observation of a facile 1,2-hydride migration which generates an observable platinum silylene complex.

In the search for a 1,2-migration that might produce a silylene ligand, we targeted the synthesis of an alkylsilyl complex of the type [$L_2PtR(SiHR'_2)$]. It was thought that migration of a hydrogen atom to a platinum center to produce the alkyl hydride [$L_2Pt(R)(H)({=}SiR'_2)$] might result in elimination of alkane[6] to produce a silylene complex of the type [$L_2Pt{=}SiR_2$]. Thus, the reaction of [(dippe)PtMeCl] (dippe = $\mathit{i}Pr_2PCH_2CH_2P\mathit{i}Pr_2$) with [$(thf)_2LiSiHMes_2$][7] (Mes = 2,4,6-$Me_3C_6H_2$) in diethyl ether yielded a light brown solution, from which the platinum silyl complex [(dippe)Pt(Me)-$SiHMes_2$] (**1**) was isolated in a 79% yield as colorless crystals that were suitable for an X-ray diffraction study (Figure 1).[8] The Pt–Si distance of 2.388(3) Å is similar to that observed for *cis*-[$(MePh_2P)_2PtMe(SiPh_3)$] (2.381(2) Å),[9] and the silicon-bound hydrogen atom was located and refined at a distance of 1.36(3) Å from the silicon atom.

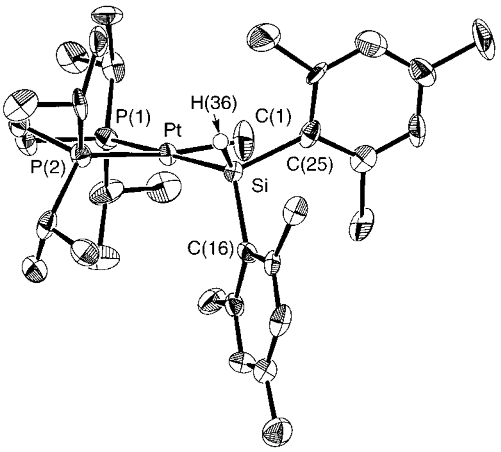
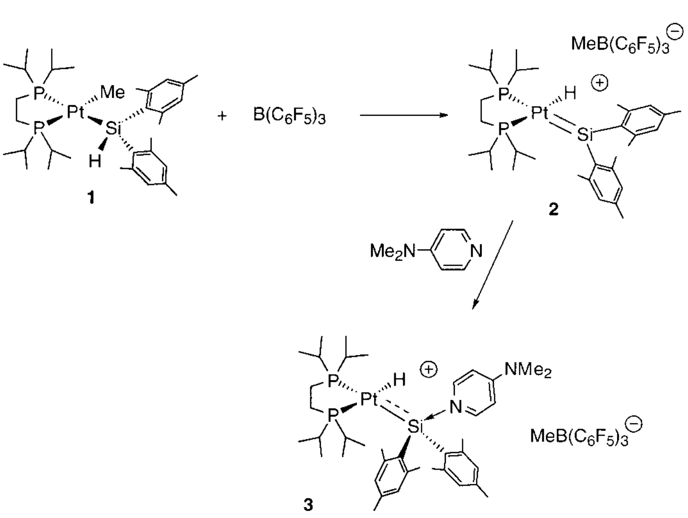


Figure 1. Molecular structure of **2**. Selected interatomic distances [Å] and angles [°]: Pt–Si 2.388 (3), Pt–P(1) 2.329 (3), Pt–P(2) 2.285 (3), Pt–C(1) 2.09 (1), Si–H(36) 1.46 (3), Si–C(16) 1.93 (1), Si–C(25) 1.91 (1); P(1)-Pt-P(2) 86.1 (1), P(1)-Pt-Si 177.7 (1), P(1)-Pt-C(1) 91.0 (4), P(2)-Pt-Si 96.1 (1), P(2)-Pt-C(1) 172.0 (4), Si-Pt-C(1) 86.8 (4), Pt-Si-C(16) 119.3 (4), Pt-Si-C(25) 117.7(4).

Compound **1** is remarkably stable. Heating a solution of **1** in [D_8]toluene at 110 °C for two weeks resulted in no detectable decomposition (^1H and ^{31}P NMR spectroscopy). Also, no reaction was observed between **1** and diphenylacetylene or 2-butyne after heating at 100 °C in [D_8]toluene for three days. However, **1** does react with H_2 at 110 °C over a period of one month to give $MeSi(H)Mes_2$[7] (GC/MS and ^1H NMR spectroscopy), presumably by reductive elimination and formation of a Si–C bond. These results suggest that a 1,2-hydrogen migration from the silicon atom to produce a five-coordinate platinum silylene species might be disfavored.

The reaction of **1** with $B(C_6F_5)_3$ in [D_2]dichloromethane resulted in the rapid generation of a clear yellow solution and formation of primarily (>95%) one new compound (^1H and ^{31}P NMR spectroscopy). The Si–H resonance of **1** ($\delta = 6.21$) was replaced by a Pt–H signal at $\delta = -1.50$ ($^1J(H,Pt) = 743$ Hz), suggesting that a 1,2-hydride shift had taken place to generate the silylene complex [$(dippe)(H)Pt{=}SiMes_2$]-[$MeB(C_6F_5)_3$] (**2**, Scheme 1). This was confirmed by observa-



Scheme 1. Generation of the platinum silylene complex **2** and its conversion into **3**.

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