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Organometallic complexes with chiral cyclometallated ligands. The synthesis of cycloplatinated complexes containing the (*S*)- or (*R*)-2-$NMe_2C_6H_4CH(SiR_3)$ (R = Me, Ph) monoanion. X-Ray crystal and molecular structure of $[PtCl[CH(SiMe_3)C_6H_4\text{-}2\text{-}NMe_2](Et_2S)]$

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Abstract. Cyclometallated platinum complexes of the monoanionic ligand 2-$NMe_2C_6H_4CH(SiR_3)^-$ (R = Me, Ph; dmat-SiR_3^-) have been synthesized via the reaction of the organolithium reagent with both $[PtCl_2(Et_2S)_2]$ and $[PtCl_2COD]$ (COD = 1,5-cyclooctadiene). The 1:1 reaction of Li(dmat-SiR_3) with $[PtCl_2(Et_2S)_2]$ affords the mono-alkylated platinum complexes [PtCl(dmat-SiR_3)Et_2S]. The X-ray crystal structure of one of these (R = Me) was determined. The platinum centre has a square-planar geometry with a *trans*-C–Pt–Cl arrangement and the chelate dmat-$SiMe_3$ ring has a conformation that places the bulky $SiMe_3$ substituent out of the aryl ring plane. From the 2:1 reaction of Li(dmat-SiR_3) with $[PtCl_2(Et_2S)_2]$ no stable organoplatinum compound could be isolated. However with $[PtCl_2COD]$ this 2:1 reaction affords complexes of $[Pt(dmat\text{-}SiR_3)_2COD]$ stoichiometry. These latter monomeric complexes contain one cyclometallated dmat-SiR_3 ligand and a COD ligand that, after having undergone an addition of the second dmat-SiR_3 ligand to one of its double bonds, is η^2,η^1-bound to the metal.

Introduction

Cyclometallated compounds of the nickel triad, in particular of nickel and palladium, have received much interest in studies of their organic synthetic utility[1]. Reaction of nucleophiles[2] or electrophiles[3] with the cyclometallated palladium or nickel compounds often leads directly to organic heterocyclic products, whereas with organoplatinum analogues stable organometallic compounds usually result. In some cases these latter compounds can be used as models for the intermediates (transient species) in corresponding reactions of the cyclometallated palladium and nickel species.

We recently found that α-silylated 2-(dimethylamino)-toluene, 2-$NMe_2C_6H_4CH_2SiR_3$, (R = Me, Ph; dmat-SiR_3; dmat = 2-(dimethylamino)toluene) could be lithiated at the α-benzylic carbon atom, without displacement of the triorganosilyl group[4]. Using this new monomeric species Li(dmat-SiR_3) we have synthesised cyclometallated compounds of the nickel triad and embarked on a study of the reactivity of the chiral α-carbon centre with electrophiles. The synthesis and reactivity of the cyclonickelated compounds containing the dmat-$SiMe_3$ group has already been described[6] and preliminary results regarding a series of organopalladium have been published[5]. One of the palladium complexes was found to give an unexpected C–C coupling reaction with hexafluorobutyne[5a] and to afford a new type of μ-benzylidenepalladium complex with $[PdCl_2(Et_2S)_2]$[5b].

Herein we describe the synthesis of some new organoplatinum compounds containing dmat-SiR_3 ligands. The structure of $[PtCl[CH(SiMe_3)C_6H_4\text{-}2\text{-}NMe_2](Et_2S)]$ (**1c**) in the solid state has been determined to help us rationalize the high reactivity of the cyclopalladated compound $[Pd(dmat\text{-}SiMe_3)(\mu\text{-}Cl)]_2$ towards alkynes[5a,7].

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Experimental

Syntheses were carried out using standard Schlenk techniques in an atmosphere of purified nitrogen. The solvents were dried prior to use. The following compounds were prepared by literature methods: $[PtCl_2(Et_2S)_2]$[19], $(PtCl_2COD)$[20], Li(dmat-SiR_3)[4].
^1H NMR spectra were obtained on Bruker AC 100 and WM 250 spectrometers. Elemental analyses were carried out by the section Elemental Analyses of the Institute for Applied Chemistry, Zeist, The Netherlands. Field Desorption (FD) mass spectra were obtained with a Varian MAT 711 double focussing mass spectrometer equipped with a combined EI/FI/FD source. 10-µm tungsten wire emitters containing carbon micro-needles with an average length of 30 µm were used. The samples were dissolved in chloroform and then loaded onto the emitter with the dipping technique. The emitter currents used to desorb the samples are given in the experimental section in the part FD-MS in parenthesis. The ion-source temperature was generally 80°C.

Crystal structure determination of [PtCl(dmat-$SiMe_3$)(Et_2S)] (**1c**)

Crystals of [[2-(dimethylamino)phenyl)](trimethylsilyl)methyl]platinum chloride (diethyl sulphide) (**1c**) $PtC_{16}H_{30}NClSSi$, obtained from a saturated hexane solution at −20°C, were monoclinic, space group $P2_1/c$, $Z = 4$, $a = 15.844(4)$, $b = 10.859(4)$, $c = 21.711(3)$ Å, $\beta = 110.03(2)°$, $V = 2055(2)$ Å^3, $\mu(MoK_\alpha) = 71.8$ cm^{-1}, $d_{calc} = 1.70$ g·cm^{-3}.
The intensities (6236) were measured on a NONIUS CAD4 diffractometer using graphite monochromated Mo-Kα radiation ($1.1 < \theta < 30°$; h −22 to 22, k 0 to 15, l 0 to 17; crystal dimensions 0.2 × 0.3 × 0.3 mm) of which 2780 were below the 2.5 $\sigma(I)$ level and were treated as unobserved. The structure was solved by means of the heavy-atom method. After isotropic block-diagonal least-squares refinement an empirical absorption correction was applied (DIFABS[21]). Continued anisotropic refinement converged to $R = 0.046$ ($R_w = 0.051$). Unit weights were used and the anomalous dispersion of Pt, S, Cl and Si was taken into account.
The calculations were carried out with XRAY76[22]. The scattering factors were taken from *Cromer* and *Mann*[23], the dispersion corrections from International Tables for X-ray Crystallography[24].

Synthesis of [PtCl(dmat-SiR_3)(Et_2S)] (**1c**, **2c**)

A solution of 0.50 g of $[PtCl_2(Et_2S)_2]$ (1.1 mmole) in toluene (20 ml) was added dropwise to a solution of an equimolar amount of the organolithium compound Li(dmat-SiR_3) dissolved in toluene (20 ml) at −60°C. The temperature of the reaction mixture was slowly raised to room temperature, followed by stirring of the brown reaction mixture for another 3 h. The solvent was removed *in vacuo* and the residue extracted with hexane (100 ml) which was filtered through Celite. Evaporation of the hexane yielded a brownish powder. Yield **1c**, R = Me, 50%; **2c**, R = Ph, 33%.
Elemental analyses: **1c** $C_{16}H_{30}NClSSiPt$ ($M = 527.16$) calcd.: 36.46, H 5.74, Cl 6.72, N 2.66, S 6.08; found: C 36.39, H 5.61, Cl 6.71, N 2.53, S 6.03%. FD-MS (0 mA): 526 (M^+).
2c $C_{31}H_{36}NClSSiPt$ ($M = 713.37$) calcd.: C 52.19, H 5.09, Cl 4.97, N 1.96, S 4.49; found: C 52.39, H 5.06, Cl 5.35, N 1.95, S 4.49%. FD-MS (20 mA): 712 (M^+).

Reaction of [$PtCl_2COD$] with Li(dmat-$SiMe_3$) affording **1d**

[$PtCl_2COD$] (1.32 g, 3.5 mmol) was added to a solution of 1.72 g of Li(dmat-$SiMe_3$) (8.1 mmol) in diethyl ether (50 ml). The mixture was refluxed for 2 h and subsequently filtered through Celite. The resulting solution was evaporated to dryness and the residue recrystallized from hexane affording brown crystals. Yield 0.28 g (11%).
Elemental analysis $C_{32}H_{52}N_2Si_2Pt$ ($M = 716.13$) calcd.: C 53.66, H 7.33, N 3.91; found: C 53.61, H 7.29, N 4.05%. FD-MS (0 mA): 716 (M^+).

Reaction of [$PtCl_2COD$] with Li(dmat-$SiPh_3$) affording **2d**

$PtCl_2$(COD) (0.8 g, 2.1 mmol) was added to a solution of 1.6 g of Li(dmat-$SiPh_3$) in diethyl ether (25 ml). The mixture was stirred for 4 h, filtered through Celite and the yellow solution was evaporated to dryness. The residue was dissolved in diethyl ether and to this solution hexane was added affording a light yellow precipitate. Yield 0.46 g (20%).
Elemental analyses $C_{58}H_{64}N_2Si_2Pt$ ($M = 1088.55$) calcd.: C 68.40, H 5.94, N 2.57; found: C 68.88, H 5.98, N 2.27%.

Synthesis of 2-$NMe_2C_6H_4CH(OH)$(t-Bu)

A solution of 6.30 g of Li(dmat) (50 mmol) in diethyl ether (50 ml) was added dropwise to trimethylacetaldehyde (4.74 g, 55 mmol) in diethyl ether (50 ml) at −60°C. The temperature was allowed to raise slowly to room temperature and stirred for another 3 h. Water (50 ml) was added to the solution and after 5 min of stirring the two layers were separated. The water layer was washed with two portions of diethyl ether (25 ml each). The combined organic fractions were dried over $MgSO_4$ and the diethyl ether was removed *in vacuo* affording a light yellow liquid which was distilled *in vacuo* (b.p. 95–110°C, 3 mm Hg). Yield 8.33 g of a pale yellow oil (72%).

Synthesis of 2-$NMe_2C_6H_4CH_2$(t-Bu) (**3a**)

To a mixture obtained after dissolution of 2.5 g of Li, cut in small pieces, in THF (100 ml) and liquid ammonia (100 ml) was slowly added a solution of 5.9 g of dmatOH-*t*-Bu (28 mmol) in THF (30 ml). After stirring for 30 min, NH_4Cl was added until the deep blue colour had disappeared. The temperature was raised to room temperature, after which the white precipitate was filtered and thoroughly washed with several portions of diethyl ether. The combined diethyl ether fractions were dried on $MgSO_4$ and the solvent was removed *in vacuo* affording a colourless oil which was used for reactions without further purification. Yield 4.39 g of **3a** (82%).

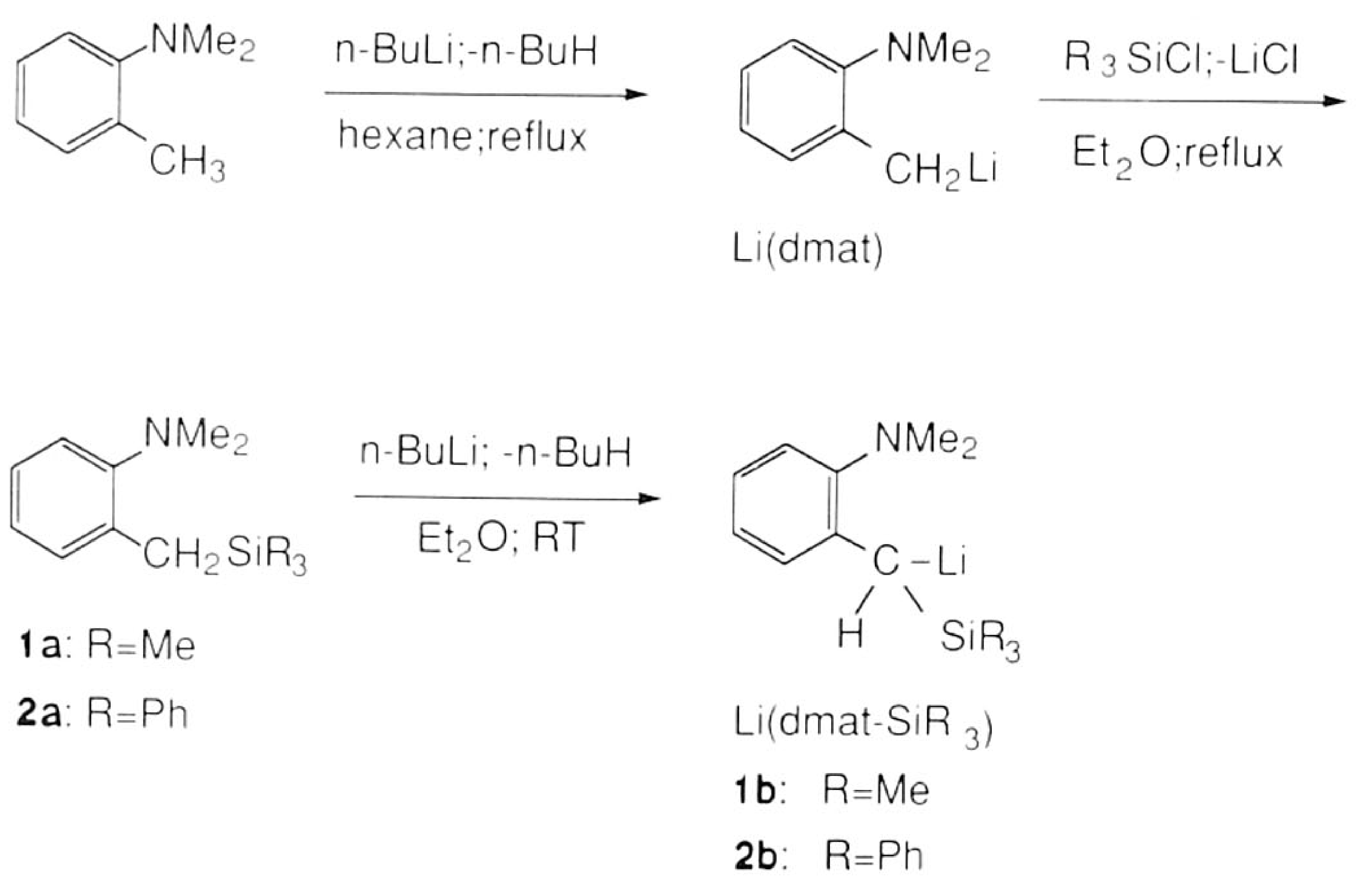
Table I Fractional coordinates of the atoms with standard deviations in parentheses of **1c**.

Atom	X	Y
Pt	0.20118(3)	0.39245(4)
Si	0.3724(2)	0.2007(3)
Cl	0.1262(2)	0.5683(3)
S	0.2908(2)	0.5134(3)
N	0.1106(6)	0.2668(8)
C1	0.2598(7)	0.2381(10)
C2	0.1951(7)	0.1322(9)
C3	0.1271(7)	0.1427(10)
C4	0.0715(8)	0.0447(11)
C5	0.0830(9)	−0.0701(13)
C6	0.1463(9)	−0.0790(11)
C7	0.2033(8)	0.0191(12)
C8	0.1175(9)	0.2705(13)
C9	0.0162(7)	0.3069(13)
C10	0.3663(10)	0.2123(19)
C11	0.4646(8)	0.3048(17)
C12	0.4129(11)	0.0392(15)
C13	0.2109(10)	0.5795(13)
C14	0.2569(12)	0.6643(17)
C15	0.3823(12)	0.6213(21)
C16	0.3220(10)	0.6535(13)

Results and discussion

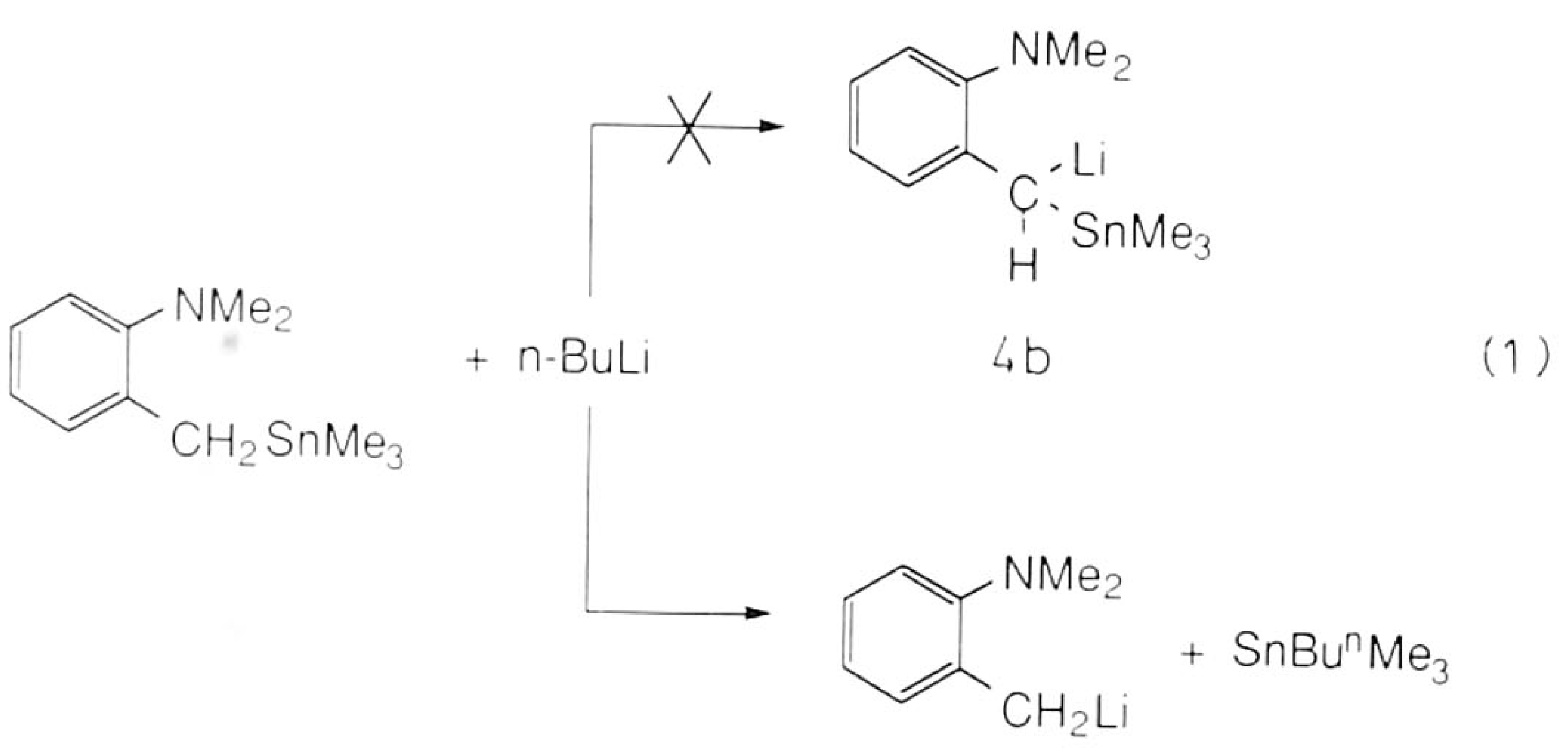
Preparation of 2-$NMe_2C_6H_4CH_2SiR_3$ and their lithiation

The silylated starting materials 2-$NMe_2C_6H_4CH_2SiR_3$ (R = Me **1a**, Ph **1b**) used in this study were easily accessible from the reaction of the appropriate triorganosilyl chloride and [[2-(dimethylamino)phenyl]methyl]lithium, Li(dmat).
Both **1a** and **2a** could be easily lithiated with *n*-butyllithium in diethyl ether at room temperature. The resulting organolithium compounds, (2-$NMe_2C_6H_4CHSiR_3$)Li [R = Me; **1b** Li(dmat-$SiMe_3$); R = Ph; **2b** Li(dmat-$SiPh_3$)] were isolated as air-sensitive solids that could be stored for some days at low temperature (−20°C). These reactions are summarized in Scheme 1[8].
Various attempts to prepare **3b**, the analogous lithiated species of the tertiary butyl compound 2-$NMe_2C_6H_4CH_2$-



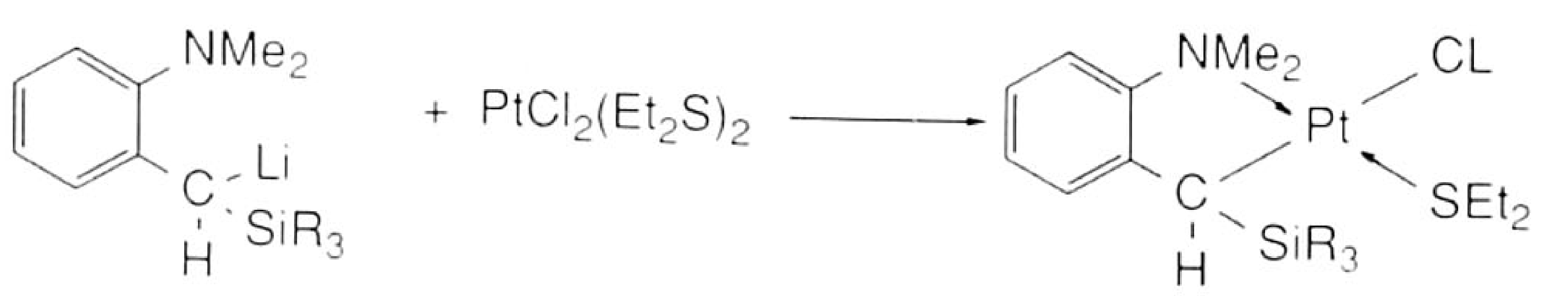
Scheme 1. Synthesis of the lithium starting compounds.

t-Bu **3a**, were unsuccessful (see Scheme 2). Lithiation of 2-$NMe_2C_6H_4CH_2SnMe_3$ (**4a**) with *n*-butyllithium (Eqn. 1), did not afford Li(dmat-$SnMe_3$) (**4b**), but instead resulted in transmetallation of the 2-$NMe_2C_6H_4CH_2$ unit from tin to lithium, affording Li(dmat) and Me_3BuSn. It is unfortunate that neither **3b** nor **4b** could be prepared since comparison of the influence of the substituent at the α-carbon atom upon their reactivity towards alkynes would have been interesting.



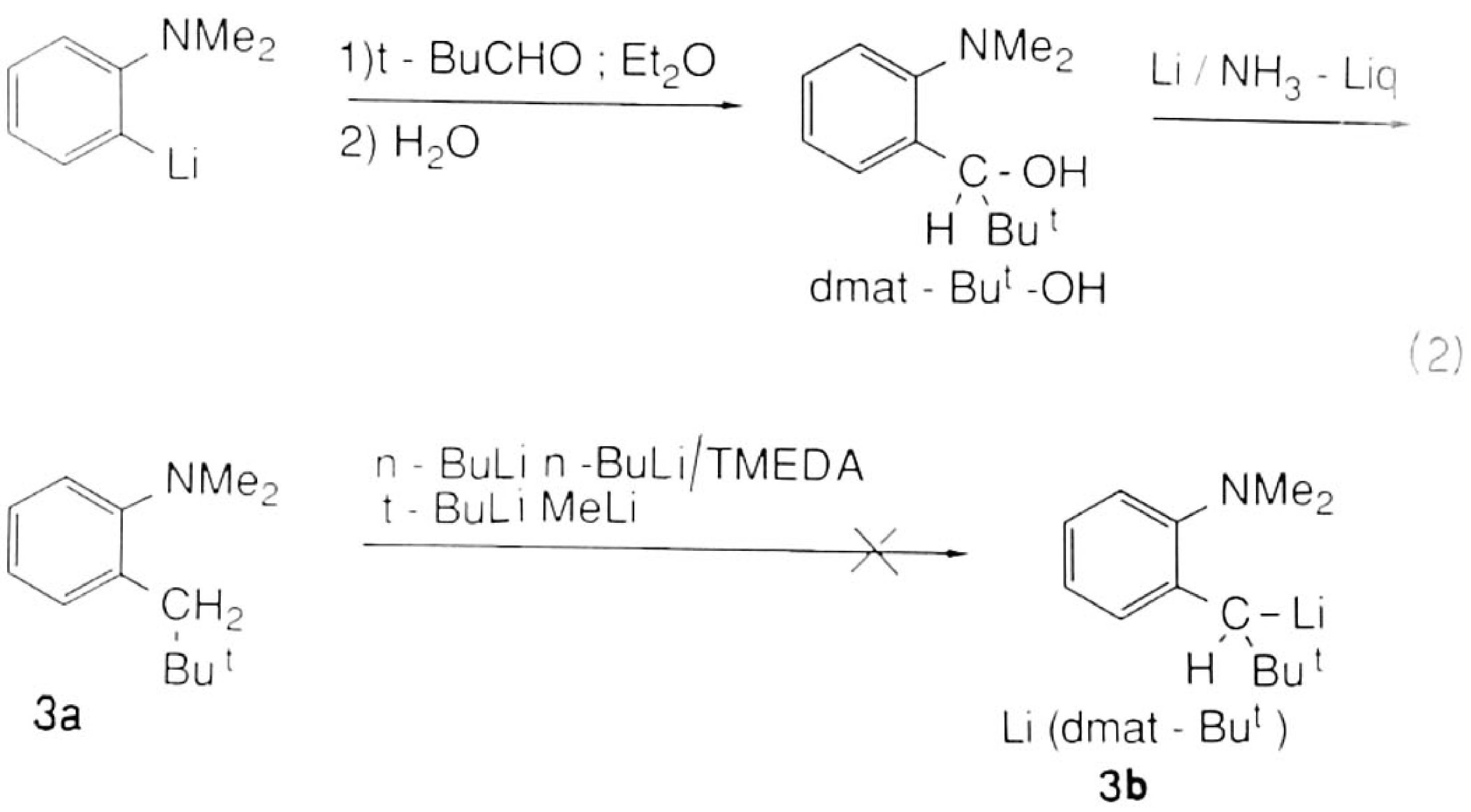
Synthesis of the platinum compounds [PtCl(dmat-SiR$_3$)(Et$_2$S)] (**1c**, **2c**)

The 1:1 reaction of the organolithium compounds **1b** and **2b** with $[PtCl_2(Et_2S)]_2$ at −60°C in toluene afforded the extremely soluble monochloro-substituted organoplatinum compounds [PtCl(dmat-SiR_3)(Et_2S)] (R = Me, **1c**; R = Ph, **2c**), which could be isolated as off-white, air-stable solids. Their stoichiometry was derived from elemental analysis and mass spectral data and the presence of coordinated diethyl sulphide was confirmed by 100-MHz ^1H NMR spectroscopy. Although in general reaction of $[PtCl_2L_2]$ (L = Et_2S, PR_3) with organolithium compounds leads directly to disubstituted organoplatinum compounds[9b], monosubstitution has also been found before with some heteroatom-containing aryllithium compounds related to Li(dmat)[9,10].



PtCl(dmat)-SiR$_3$)SEt$_2$
1c: R=Me
2c: R=Ph

The ^1H NMR spectrum of the dmat-SiR_3 platinum complexes **1c** and **2c** showed anisochronous signals for the dimethylamino group. This anisochronicity indicates the presence of rigid Pt−N coordination which thus renders the N centre a stable prochiral assembly that can reflect the chirality of the silyl-substituted α-carbon atom of the toluidine group[11]. The NMe_2 signals of **1c** and **2c** also show $^3J(^{195}Pt-{}^1H)$ of 33 Hz, which is comparable to the value of 32 Hz found for an analogous monocycloplatinated compound with the 8-(dimethylamino)naphthyl group[10]. The presence of ^{195}Pt satellites is an independent proof of the rigidity of the N−Pt coordination on the ^1H NMR time scale. Whereas in **1c** there is a chemical shift difference of only 0.1 ppm between the diastereotopic methyl groups, in **2c** it is 0.8 ppm. This large difference in **2c** most probably arises from a specific shielding of one of the amino-methyl groups by the phenyl groups of the triphenylsilyl substituent.



Scheme 2. Attempts to prepare Li(dmat-tBu).

Geometry of [PtCl[CH(SiMe$_3$)C$_6$H$_4$-2-NMe$_2$](Et$_2$S)], **1c**

The molecular structure of **1c** is shown in Fig. 1 together with the adopted numbering scheme. The molecule has a regular square-planar coordination geometry about the platinum atom, with a *cis*-chelated *C,N*-2-$NMe_2C_6H_4CHSiMe_3$ ligand forming a five-membered $PtC^1C^2C^3N$ ring. The chloride atom is *trans* to the platinum–carbon and the diethyl sulphide ligand *trans* to the $-NMe_2$ group (see Fig. 1). The positioning of this set of ligands has also been found in other related monosubstituted platinum compounds and has been proposed as the most common geometry for compounds of the type

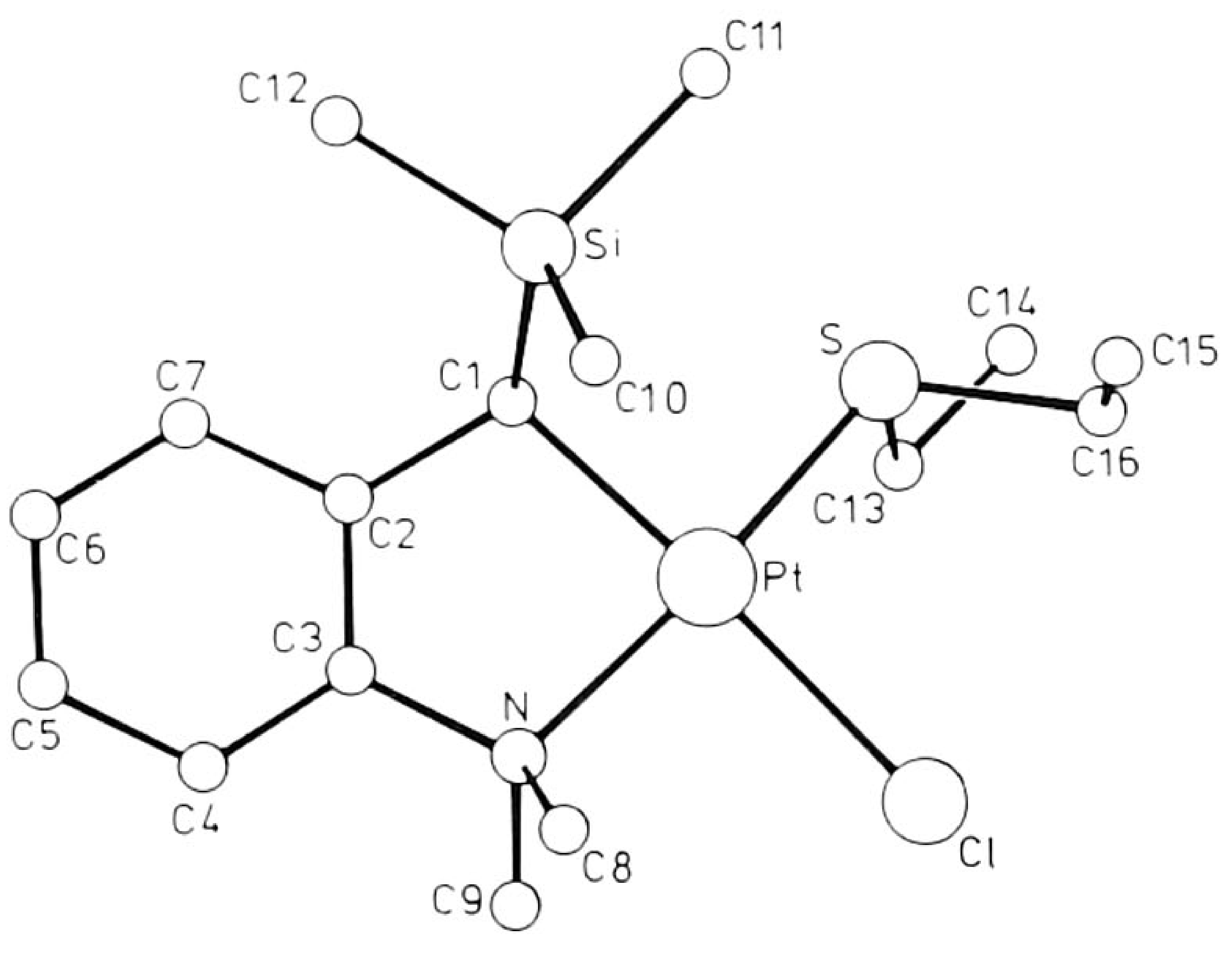
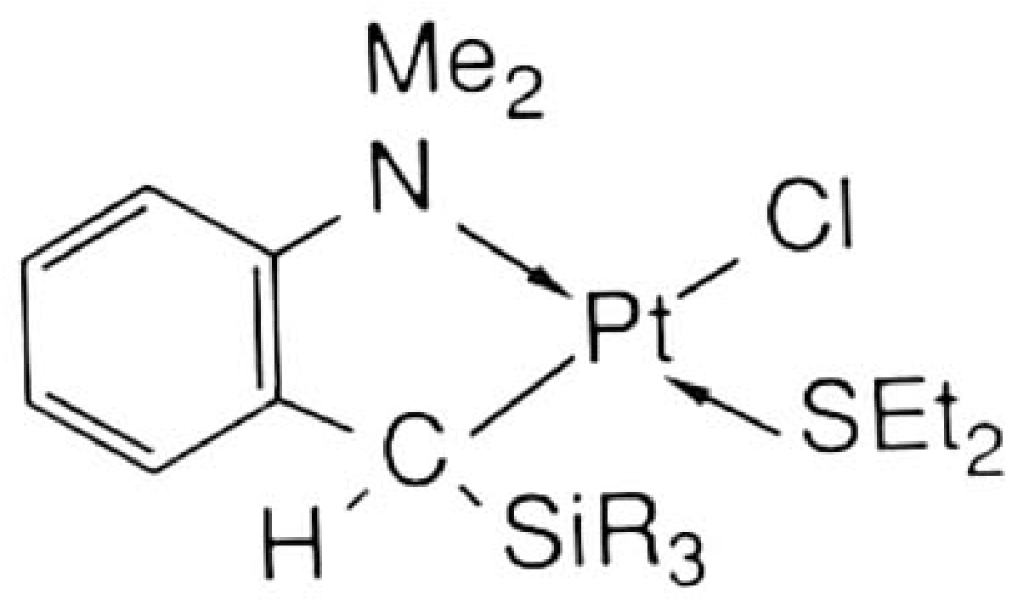
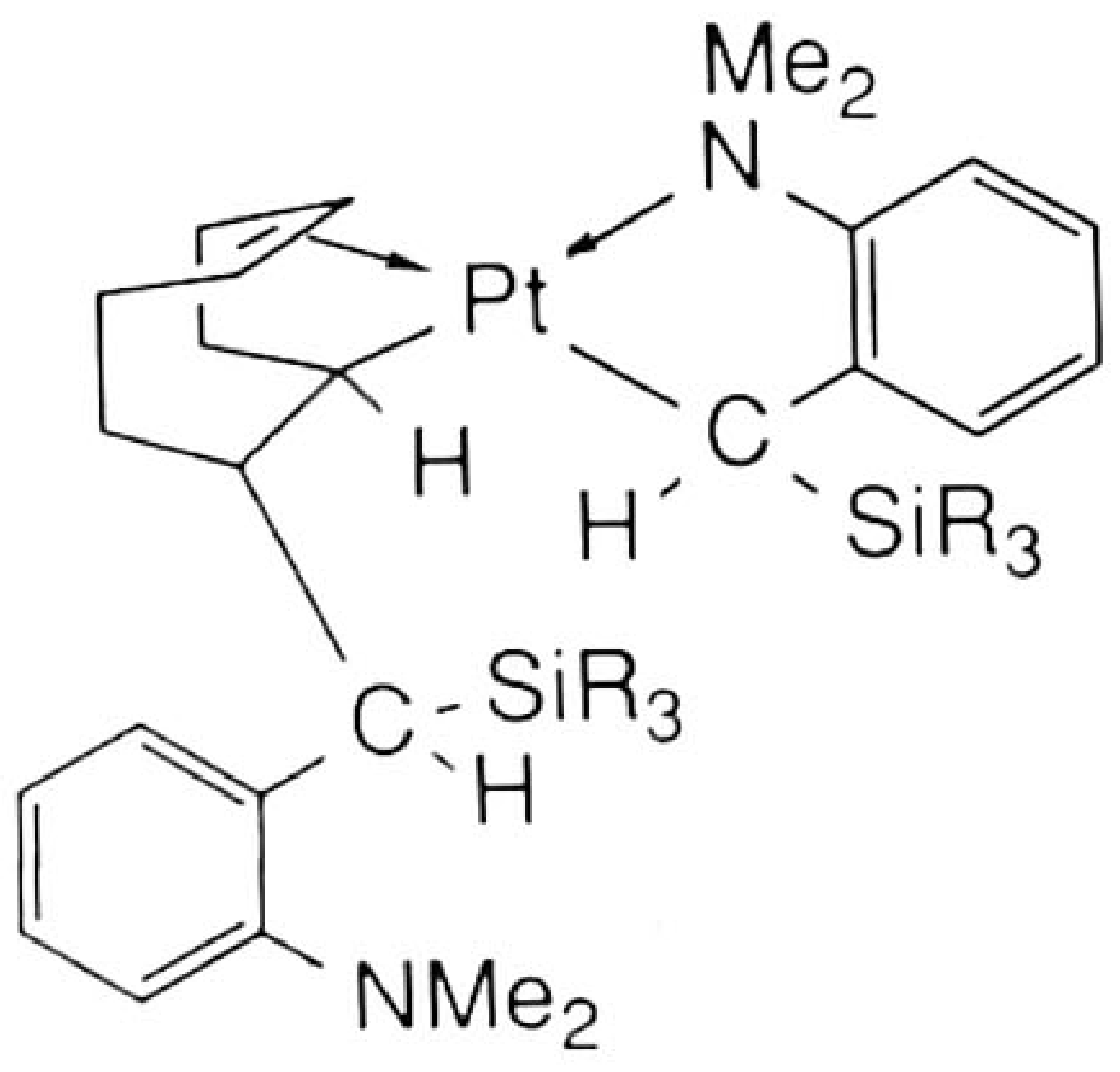
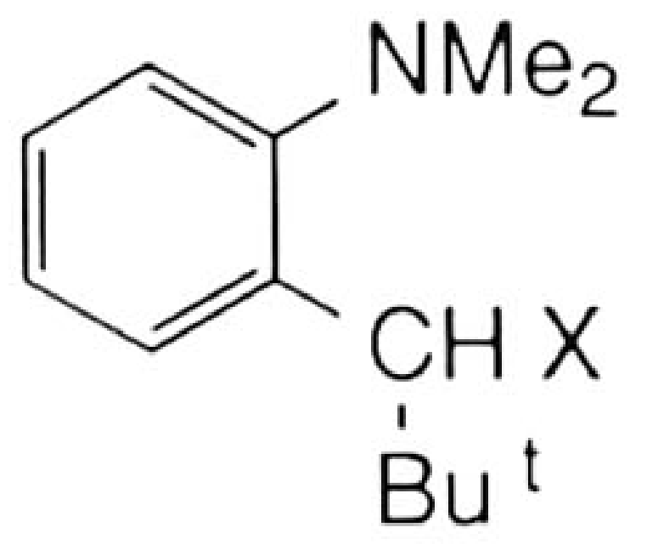


Fig. 1. Molecular structure of [PtCl(dmat-SiMe$_3$)Et$_2$S] (**1c**) *along with the adopted numbering scheme.*

Table II ^1H *NMR data*[a] *of the complexes.*

		NMe_2[b]	CH[b]	$SiMe_3$	Aromatic	Other groups
	**1c**: R = Me	3.31 (s, 33) and 3.25 (s, 33)	2.60 (s, 48)	− 0.06	7.15–6.92 (m, 4)	1.37 (t, SCH_2CH_3)[e]
	2c: R = Ph	3.27 (s, 33) and 2.46 (s, 33)	3.47 (s, 52)		7.52–6.75 (m, 19)	1.36 (b) and 0.75 (b, SCH_2CH_3)[e]
	**1d**: R = Me	2.89 (s, 3)[c] and 2.85 (s, 3)[c]; 2.61 (s, 6)[d]	3.25 (s, 55) and 3.12 (s)	0.02 and 0.00	7.05–6.75 (m, 8)	4.32 (COD-olef); 3.16 (s, 56) and 2.50–1.50 (COD-aliphatic)
	2d: R = Ph	2.39 (s, 3)[c] and 2.24 (s, 3)[c]; 2.01 (s, 6)[d]	3.20 (s) and 3.05 (s)		7.64–6.81 (m, 38)	4.50–4.00 (COD-olef); 2.98 and 1.80–1.20 (COD-aliphatic)
	X = OH **3a**: X = H	2.63 (s) 2.63 (s)	4.60 (s) 2.67 (s)		7.33–6.93 (m, 4) 7.33–7.00 (m, 4)	6.60 (s, OH); 0.97 (s, t-Bu) 0.97 (s, t-Bu)

[a] Recorded in $CDCl_3$; shifts relative to Me_4Si internal; s = singlet, m = multiplet, b = broad. [b] $^3J(^{195}Pt-^1H)$ in parentheses. [c] Diastereotopic groups. [d] Enantiotopic groups. [e] Signal of CH_2 was not observed. The strongly broadened signal due to the inequivalence of the groups and ^{195}Pt coupling coincides with NMe_2 signals.

[$PtXRL_2$] (X = halogen, R = organo group, L = neutral ligand)[9,10,12]. However, **16** is the first example of a cyclometallated organoplatinum compound for which *trans*-Cl–Pt–C positioning has been firmly established. The bonding distances around platinum, which are shown in Table III, are normal for square-planar Pt^{II} species[12]. The five-membered cyclometallated $PtC^1C^2C^3N$ ring is puckered (a feature which is commonly observed in cyclometallated compounds[13,14]) and the Me_3Si group is placed in the more sterically favoured axial position that also places it out of the phenyl ring plane (see Fig. 2). So positioned, almost perpendicular to this plane, it lies above the coordination plane of this otherwise approximately flat molecule and protects one side of the metal centre from attack in possible further reactions.

Table III Bond distances of the atoms (Å) with standard deviations in parentheses of **1c**.

Pt–Cl	2.431(3)	N–C8	1.524(10)
Pt–S	2.255(3)	N–C9	1.521(11)
Pt–N	2.118(6)	C1–C2	1.513(11)
Pt–C1	2.048(8)	C2–C3	1.390(11)
Si–C1	1.911(9)	C2–C7	1.421(12)
Si–C10	1.898(11)	C3–C4	1.396(12)
Si–C11	1.894(12)	C4–C5	1.414(13)
Si–C12	1.897(13)	C5–C6	1.420(15)
S–C13	1.848(12)	C6–C7	1.396(13)
S–C16	1.834(11)	C13–C14	1.514(16)
N–C3	1.471(10)	C15–C16	1.519(19)

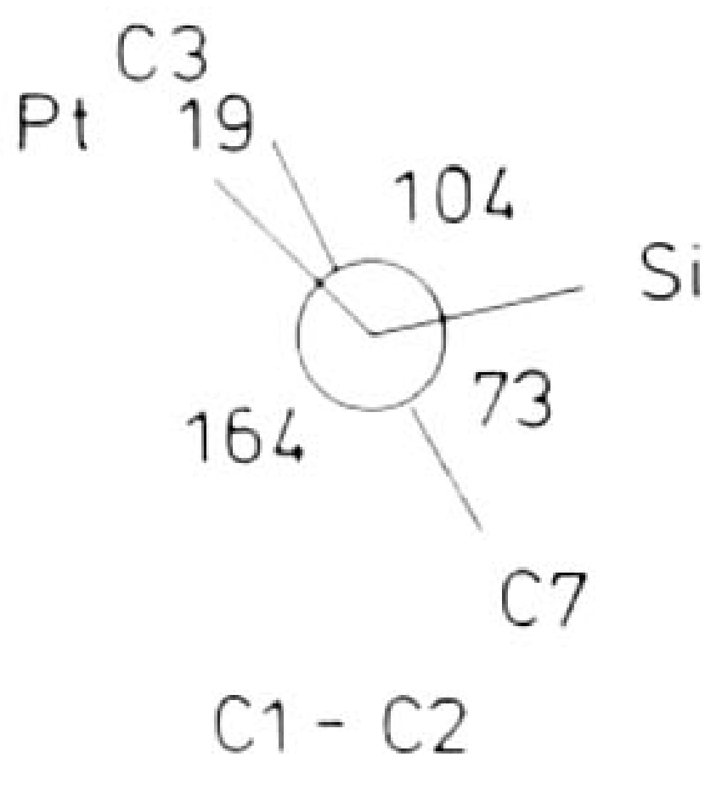


Fig. 2. Newman projection of **1c** *along the* C^1-C^2 *axis showing the positioning of the* $SiMe_3$ *group.*

This structural feature has also been observed in the tin complex [(dmat-$SiMe_3$)SnMePhBr][4] and the diastereochemically pure diorganopalladium compounds [Pd(S)-[C_6H_4-2-CH(Me)NMe_2](dmat-$SiMe_3$)][15].

Reactions of the lithiated species with [$PtCl_2COD$]

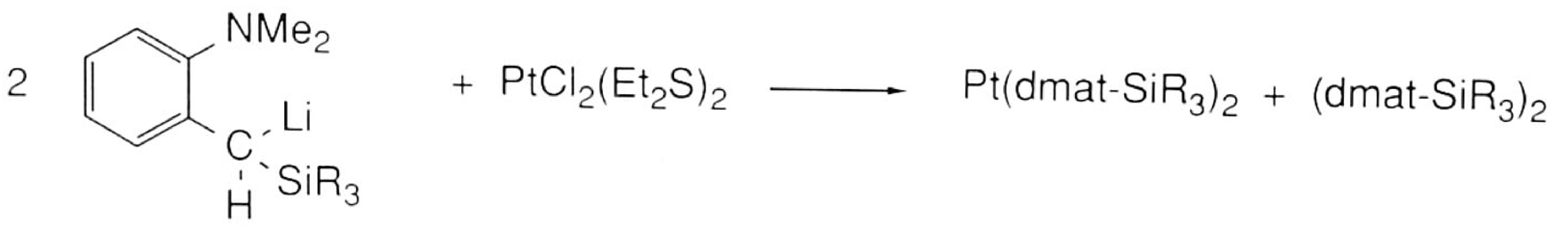
Reaction of [$PtCl_2(Et_2S)_2$] with two equivalents of Li(dmat-$SiMe_3$) (**1b**), afforded crude reaction mixtures whose ^1H NMR spectrum was complicated and contained several inequivalent dimethylamino signals with ^{195}Pt satellites. We were unable to isolate any pure organoplatinum species from this mixture which we believe on the basis of earlier results with [$PdCl_2(Et_2S)_2$] to contain both mono- and diorgano platinum species as well as the C–C-coupled dimer (dmat-SiR_3)$_2$.[16]

Table IV Bond angles of the atoms (°) with standard deviations in parentheses of **1c**.

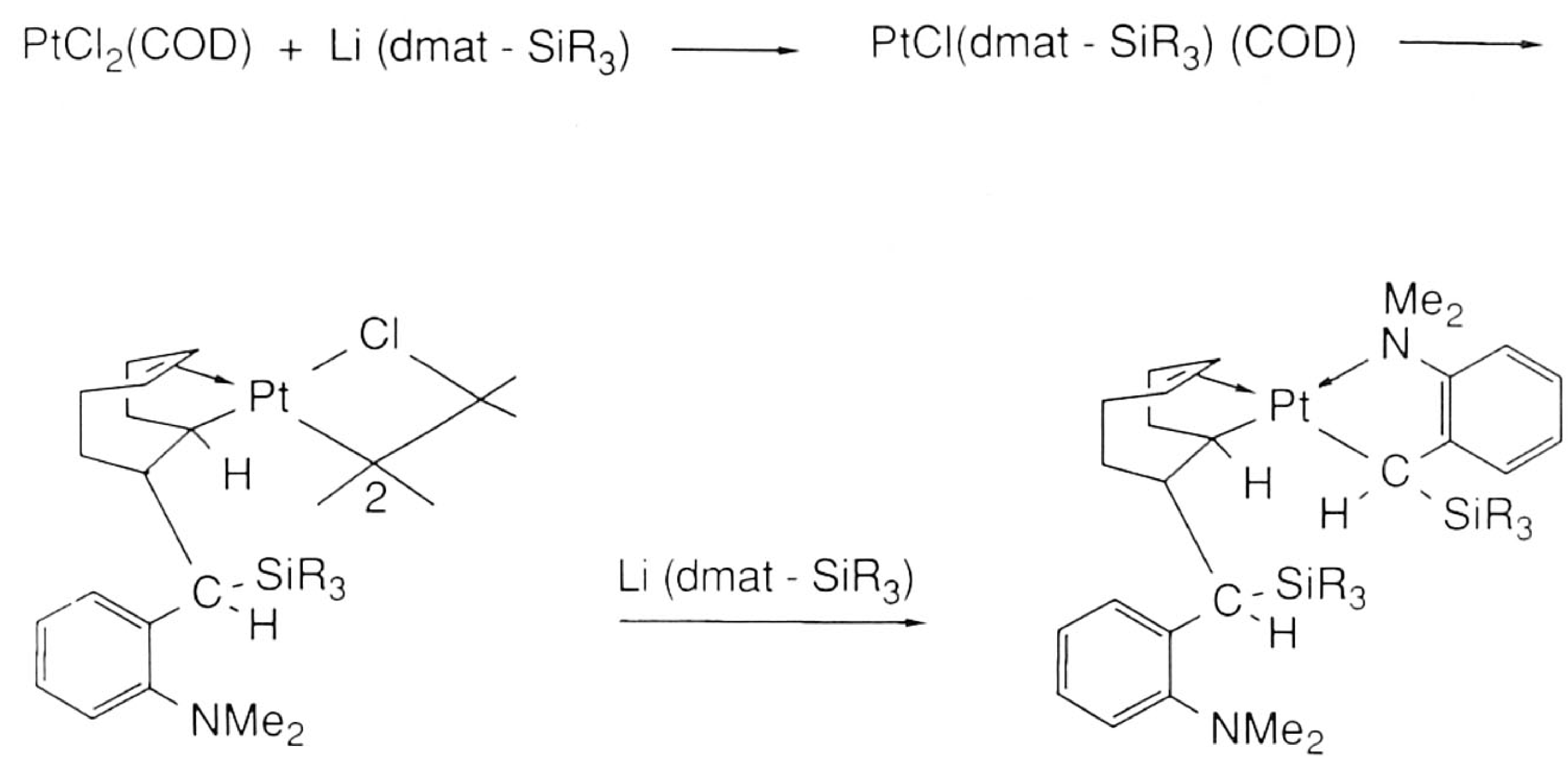
Cl–Pt–S	92.6(2)
Cl–Pt–N	92.2(3)
Cl–Pt–C1	176.8(2)
S–Pt–N	171.2(2)
S–Pt–C1	90.6(3)
N–Pt–C1	84.7(4)
C1–Si–C10	111.9(6)
C1–Si–C11	111.2(6)
C1–Si–C12	112.6(7)
C10–Si–C11	109.7(7)
C10–Si–C12	106.6(9)
C11–Si–C12	104.4(8)
Pt–S–C13	102.3(5)
Pt–S–C16	110.8(5)
C13–S–C16	99.7(7)
Pt–N–C3	109.2(6)
Pt–N–C8	111.2(6)
Pt–N–C9	107.3(7)
C3–N–C8	112.2(8)
C3–N–C9	109.0(8)
C8–N–C9	107.8(9)
Pt–C1–Si	112.4(5)
Pt–C1–C2	107.4(7)
Si–C1–C2	109.8(7)
C1–C2–C3	119.5(8)
C1–C2–C7	122.4(9)
C3–C2–C7	118.1(9)
N–C3–C2	116.5(8)
N–C3–C4	120.3(8)
C2–C3–C4	123.1(8)
C3–C4–C5	118.8(10)
C4–C5–C6	118.7(10)
C5–C6–C7	121.1(11)
C2–C7–C6	119.9(10)
S–C13–C14	112.0(10)
S–C16–C15	110.1(11)

The reaction of **1b** and **2b** with [$PtCl_2COD$] affords compounds which have, based on elemental analyses and FD mass spectroscopical results, a [Pt(dmat-SiR_3)$_2$COD] stoichiometry. Owing to their high solubility, isolation and purification of these complexes were difficult and resulted in rather low yields of isolated product.

The ^1H NMR spectra of these [Pt(dmat-SiR_3)$_2$COD] products show some interesting features. For the two dimethylamino groups two sets of signals in a 1:1 ratio were observed. One set consisted of two anisochronous, equal-intensity singlets having poorly resolved ^{195}Pt satellites indicative of a diastereotopic NMe_2 group of a cyclometallated ligand. The other set was an isochronous signal without satellites attributed to a non-coordinated dimethylamino group. The presence of different dmat-SiR_3 groupings is confirmed by the observation of two signals for the $SiMe_3$ groups. The integral of the resonances in the olefinic COD part of the spectrum is consistent with only two olefinic protons, thus indicating the removal of one olefinic COD bond. This data can be interpreted in terms of a structure which contains one cyclometallated ligand system, whereas the second dmat-SiR_3 group is bonded to the COD molecule that is believed, as a result of addition of this second dmat-SiR_3 molecule to one double bond, now to be η^1,η^2-bonded via a new Pt–C bond and a Pt–C=C π bond



(3)



1d: R=Me
2d: R=Ph

Scheme 3. Proposed reaction path for formation of [Pt(dmat-SiR$_3$)$_2$COD].

(see Scheme 3). This product can originate from nucleophilic addition of a dmat-SiMe$_3$ anion to a double bond of the coordinated COD ligand. The activation of such coordinated olefins towards nucleophilic attack has been attributed to electron withdrawal by the metal[17] and it is generally believed that these nucleophilic additions proceed via an intramolecular rather than an intermolecular pathway[18]. Scheme 3 shows a possible reaction sequence. Unfortunately attempted crystallization of **1d** and **2d**, however has not yielded crystals suitable for X-ray diffraction measurements.

Further investigations will be directed to the study of the reactivity of the platinum– and palladium–carbon bond of the cyclometallated system in complexes containing the 2-NMe$_2$C$_6$H$_4$CH(SiMe$_3$) ligand towards electrophiles and alkynes. Preliminary experiments have shown that the Pd compounds show unusual behaviour patterns, caused by the presence of the R$_3$Si group[7].

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