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Synthesis and crystal structures of novel lithium- and palladium-1-azaallyls

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Abstract

Treatment of $(RH_2C)_2C_5H_3N$-2,6 (R = $SiMe_3$) with Bu^nLi followed by addition of Me_3SiCl gave the tetrasilyl pyridine derivative $(R_2HC)_2C_5H_3N$-2,6 **1** in high yield. Further lithiation of **1** with Bu^nLi and reaction of the intermediate with PhCN led to the new lithium-1-azaallyl $[Li\{N(R)C(Ph)C(R)(C_5H_3N\text{-}2,6)(CHR_2)\}]_2$ **2**, while metallation of the previously described di-lithium compounds $[Li\{N(R)C(R')CH\}_2(C_5H_3\text{-}2,6)]Li(tmen)_n$ (R = $SiMe_3$, R′ = Bu^t, $n = 1$ or R = $SiMe_3$, R′ = Ph, $n = 2$) with $PdCl_2(PhCN)_2$ yielded the novel metallacycles $[Pd\{\{N(H)(R)C(R')CH\}\{N(SiMe_2CH_2)C(R')CH\}C_5H_3N\text{-}2,6\}]$ **3** (R′ = Bu^t) and $[Pd\{\{N(R)C(R')CH\}\{N(R)(H)C(R')CH\}C_5H_3N\text{-}2,6\}_2]$ (R′ = Ph) **4** in moderate to low yield. Compound **3** is unusual in being the first example of a crystallographically characterised PdNSiC heterocycle which is believed to be formed via an intramolecular CH-activation of a trimethylsilyl group by Pd(II). All four compounds were fully characterised by NMR-spectroscopy, microanalysis (not **4**) and X-ray diffraction.
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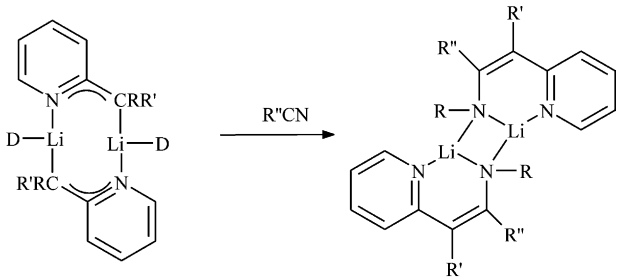
Keywords: Lithium; Palladium; 1-azaallyl; X-ray; Metallacycle

1. Introduction

The organometallic chemistry of the bulky bis-silylated alkyl ligand, $(2\text{-pyr})(R)_2C^-$ (R = $SiMe_3$), has been extensively investigated [1]. As noted previously, this is in part due to the ligand having several attractive features: (i) it is devoid of a β-H, thereby negating the possibility of β-H elimination and, (ii) it has the available stabilising of a nearby pyridyl N, and there is kinetic protection offered by two R groups [2]. In contrast, the mono-silylated ligand, $(2\text{-pyr})(R)CH^-$, is less bulky and only retains the possible stabilising effect of the pyridyl N, which is possibly the reason for the structural chemistry of this ligand being less developed [2,3]. Insertion of a nitrile into the Li–C bond of these ligands has demonstrated the synthetic utility of these ligands in preparing pyridyl substituted azaallyls. The 1-azaallyls $[Li\{N(R)C(R')C(H)(2\text{-pyr})\}]_2$ [R′ = Ph (**A**) or Bu^t (**B**)] were prepared from $[Li\{C(R)(H)(2\text{-pyr})(Et_2O)\}]_2$ and PhCN or Bu^tCN, respectively, while $[Li\{N(R)C(Ph)C(R)(2\text{-pyr})\}]_2$ (**C**) was derived from $[Li\{C(R)_2(2\text{-pyr})\}]_2$ and PhCN (Eq. (1)) [4]. Such reactions involve a 1, 2-insertion of the nitrile into the Li–C bond followed by a 1, 3-trimethylsilyl shift. Not only did the preparation of zirconium(IV) and hafnium(IV) complexes $[M\{N(R)C(R')C(R'')(2\text{-pyr}$ or $C_9H_6N\text{-}2)\}_{4-m}Cl_m]$ were effective catalysts when treated with methylaluminoxane for the polymerisation of ethylene [R′ = Bu^t or Ph, R″ = H or R and $m = 1$ or 2] [5].



R = $SiMe_3$, R' = H, D = Et_2O
R = R' = $SiMe_3$, no donor

A, R = $SiMe_3$, R' = H, R" = Ph
B, R = $SiMe_3$, R' = H, R" = Bu^t
C, R = R' = $SiMe_3$, R" = Ph

(1)

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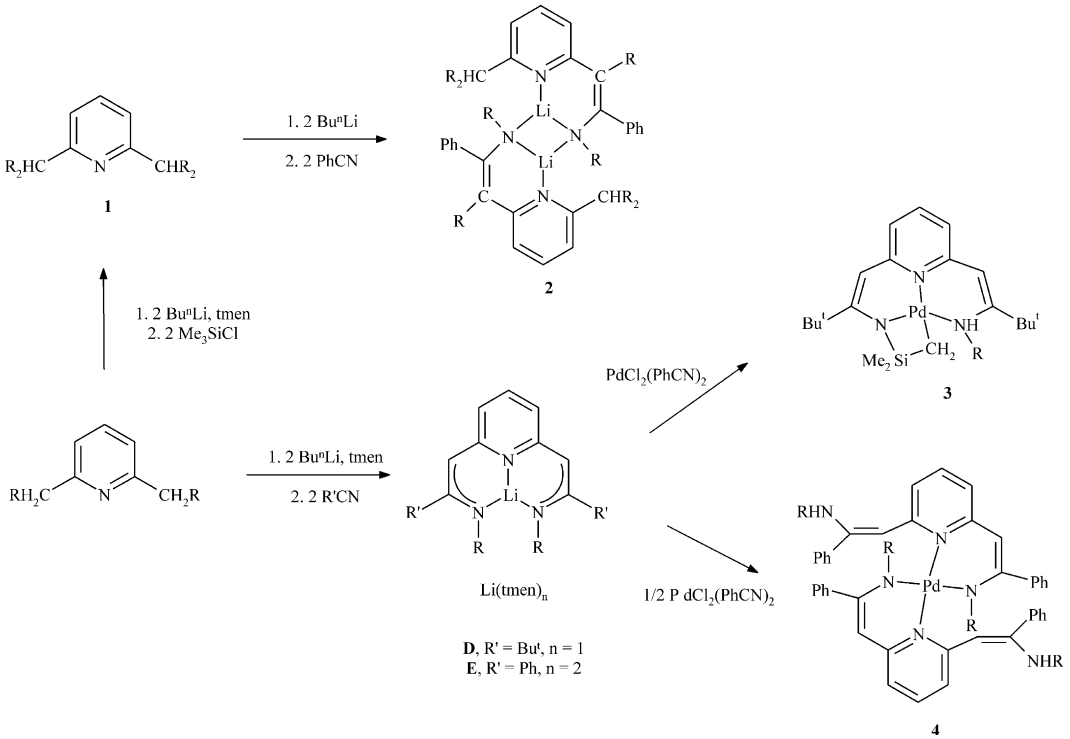
Recently, as an extension to the work on (2-pyr)(R)-CH^-, reactions of the dilithium dialkyl [{$(RHC)_2$-C_5H_3N-2,6}{$Li(tmen)\}_2$] [6] derived from the dilithiation of 2,6-bis(trimethylsilyl)lutidine, with organic nitriles R′CN (R′ = Bu^t or Ph) were reported [7]. The reactions afforded the 2,6-pyridyl-bridged bis-azaallyl complexes, [{$\{N(R)C(Bu^t)CH\}_2C_5H_3N$-2,6}{$Li_2(tmen)\}$] **D** and [Li-{$\{N(R)C(Ph)CH\}_2C_5H_3N$-2,6}][$Li(tmen)_2$] **E**, respectively (Scheme 1), with the latter being a solvent separated ion complex. Transmetallation of the tmen (*N*,*N*′-tetramethylethylendiamine) analogue of the former with $KOBu^t$ generated a dimeric dipotassium compound [{$\{N(R)C(Bu^t)CH\}_2C_5H_3N$-2,6}{$K_2(Bu^t$-CN)(tmen)}]$_2$, while transmetallation of the dilithium dialkyl [{$(RHC)_2C_5H_3N$-2,6}{$Li(tmen)\}_2$] with $KOBu^t$, followed by PhCN insertion, afforded a mixture, with **E**, a mixed lithium-potassium complex [{$\{N(R)$-$C(Ph)CH\}_2C_5H_3N$-2,6}{$Li(Et_2O)$}{$K(tmen)\}$] and a dipotassium complex [{$\{N(R)C(Ph)CH\}_2C_5H_3N$-2,6}-{$K(tmen)\}_2$] being isolated upon fractional crystallisation.

The present study complements the previous (2-pyr)$(R)_2C^-$/nitrile insertion investigations by extending the system to include reactions of the anion prepared by the in situ lithiation of the hitherto unknown dialkyl ligand, $(R_2HC)_2(C_5H_3N$-2,6), with PhCN. Full details on the synthesis and characterisation (including X-ray crystallography) of $(R_2HC)_2(C_5H_3N$-2,6) and the insertion complex containing a new unsolvated *N*,*N*′-chelating, monoanionic ligand are provided. Unsolvated lithium-1-azaallyls are rare and since these ligands have been utilised as precursors for the preparation of cyclic phosphonium salts [8,9] it was envisaged that the new monoionic ligand could yield similar lipophilic cations. Lipophilic cations (for examples see [10]), including phophonium salts [11] are a promising class of antitumor agents and the evaluation of the above mentioned phosphonium salts as antitumour agents will be discussed elsewhere. Owing to the scarcity of structurally authenticated Pd complexes containing the 1-azaallyl ligand, the versatility of [{$\{N(R)C(Bu^t)CH\}_2C_5H_3N$-2,6}{$Li_2(tmen)\}$] **D** and [{$\{N(R)C(Ph)CH\}_2C_5H_3N$-2,6}{$Li(tmen)_2\}$] **E** as ligand transfer agents was confirmed by generating the Pd^{II} derivatives. The preparation and characterisation (including X-ray crystallography) of these novel palladacycles is included. Characterisation data of previously reported palladium 1-azaallyls are restricted to NMR and occasionally elemental analysis and mass spectrometry. These complexes include [Pd{$N(R)C(Ph)C(H)R\}_2$] [12], [Pd{$N(R)C(Bu^t)C(H)R$}I] [13] and [Pd{$N(R)C(Bu^t)$-$C(H)R$}I(PPh_3)] [13], while for the β-diketiminates, [Pd{$N(R)C(Ph)_2CH\}_2$] [14], [Pd{$(N(R)C(Ph))_2CH$}(η^3-CH_2CHCH_2)] [14] and [Pd{$(N(C_6H_3{}^iPr_2$-2,6)$C(Me))_2$-$C(H)Pd(NCMe)_3$}$(NCMe)_2$][BF_4]$_3$ [15], X-ray data have been reported.



Scheme 1. Synthesis of compounds **1**–**4** (R = $SiMe_3$).

2. Experimental

All manipulations were carried out under argon, using standard Schlenk techniques. Solvents were distilled from drying agents and degassed. The NMR spectra were recorded in C_6D_6 or $CDCl_3$ at ambient probe temperature using the following Bruker instruments: DRX 400 (^{1}H, 400.32 MHz), DXP 300 (^{1}H, 300.1; ^{13}C 75.5 MHz) or AC200 (^{1}H, 200.13 MHz) and referenced internally to residual solvent resonances (chemical shift data in δ). ^{13}C-NMR spectra were all proton-decoupled. Melting points were taken in sealed capillaries (an unsealed capillary was used for **1**) and are uncorrected. Elemental analyses were determined by the Institute for Soil, Climate and Water, Pretoria, South Africa. The following abbreviations are used throughout Section 2: vd = virtual doublet, vt = virtual triplet, bs = broad singlet, m = multiplet, Ar = C_5H_3N. Coupling constants (J) are given in Hz.

2.1. Preparations

2.1.1. $(R_2HC)_2(C_5H_3N\text{-}2,6)$ **1**

tmen (2.2 g, 19.08 mmol) was added over 1 min to a solution of Bu^{n}Li (1.505 M, 12.68 cm^3) in hexane (20 cm^3). The reaction mixture was cooled to −50 °C, followed by the rapid addition of a hexane (15 cm^3) solution of $(RH_2C)_2(C_5H_3N\text{-}2,6)$ (2.0 g, 7.96 mmol). Concomitant precipitation occurred as the reaction warmed to room temperature over ca. 1 h. Dissolution of the precipitate was achieved by the addition of thf (15 cm^3). The resulting orange coloured solution was then cooled to −70 °C, Me_3SiCl (2.07 g, 19.08 mmol) added rapidly via syringe, followed by gradual warming of the reaction to room temperature over ca. 16 h. The mixture was concentrated in vacuo, Et_2O (20 cm^3) and ice cold water (20 cm^3) added, followed by separation of the organic phase and repeated extraction of the aqueous phase with Et_2O. The combined ethereal fractions were dried (over $MgSO_4$), filtered, giving a yellow viscous liquid upon removal of volatiles in vacuo. Crystallisation was accomplished by sequential freezing and warming of the sample to room temperature under prolonged evacuation. Recrystallisation of the light yellow solid from hexane at −60 °C over ca. 6 weeks gave colourless crystals of the title compound (2.8 g, 89%) (Found: C, 56.9; H, 10.52; N, 3.62. $C_{19}H_{41}NSi_4$ requires C, 57.6; H, 10.44; N, 3.54%), m.p.: 39–40 °C; ^{1}H-NMR ($CDCl_3$): δ 0.018 (s, 36 H, $SiMe_3$), 1.85 (s, 2 H, C HR_2), 6.54 (d, 2 H, $J = 7.5$, m-Ar), 7.25 (t, 1 H, $J = 6.0$, p-Ar); ^{13}C-NMR ($CDCl_3$): δ 0.30 (s, $SiMe_3$), 33.5 (s, CHR), 117.2 (s, m-C), 135.3 (s) (s, p-C), 162.9 (s, *ipso*-C).

2.1.2. $[Li\{(N(R)C(Ph)C(R)(C_5H_3N\text{-}2,6)(CHR_2)\}]_2$ **2**

Bu^{n}Li in hexane was added dropwise to a cooled (−70 °C) solution of **1** (0.5 g, 1.26 mmol) in Et_2O (35 cm^3). The reaction was allowed to warm to room temperature over 1 h and stirring was continued for a further hour. The orange solution was then cooled to −30 °C and PhCN in Et_2O was added dropwise with the reaction being allowed to warm to room temperature over night. Removal of volatiles in vacuo and extraction of the residue with hexane (35 cm^3), filtration of the extract and concentration of the filtrate gave, upon cooling at −60 °C for ca. 6 weeks, pale yellow crystals of **2**. The liquor was decanted, concentrated and cooled (at −60 °C), thereby affording another crop of **2** (overall yield: 0.9 g, 60%). (Found: C, 60.6; H, 9.16; N, 5.34. $C_{52}H_{90}Li_2N_4Si_8[O(C_2H_5)_2]$ requires C, 62.1; H, 9.29; N, 5.19%), m.p.: 99–105 °C (dec.). ^{1}H-NMR (C_6D_6): δ 0.04 (bs, 9 H, $CSiMe_3$), 0.15 (s, 9 H, CH R), 0.17 (s, 9 H, CHR), 0.3 (bs, 9 H, NR), 2.11 (s, 1 H, C H), 6.8 (vd, 1 H, 5-Ar H), 7.19 (m, 1 H, m-Ph), 7.37 (vt, 2H, p-Ph), 7.43 (vt, 1H, 3-ArH), 7.58 (m, 1 H, 4-ArH), 7.87 (m, 2 H, o-Ph); ^{13}C-NMR (C_6D_6): δ 0.3 (s), 0.7 (s), 0.8 (s), 1.2 (CHR), 1.6 (s), 1.8 (s) (CR), 2.5 (s), 4.8 (s) (NR), 33.6 (s), 33.8 (s) (CHR), 118.9 (s), 119.0 (s) (C, Ar/Ph), 119.8 (s) (CR), 121.8 (s), 127.1 (s), 131.3 (s), 136.1 (s), 151.2 (s), 161.9 (s), 165.9 (s), (C, Ar/Ph), 173.0 (s) (NCPh).

2.1.3. $[Pd\{\{N(H)(R)C(Bu^t)CH\}\{N(SiMe_2CH_2)\text{-}C(Bu^t)CH\}C_5H_3N\text{-}2,6\}]$ **3**

$PdCl_2(PhCN)_2$ (0.36 g, 0.936 mmol) was added to a cooled (−80 °C) hexane suspension of **D** (0.62 g, 0.936 mmol), and the reaction was allowed to warm to room temperature over 16 h, resulting in a red coloured reaction mixture. Removal of volatiles in vacuo and extraction of the residue with hexane (35 cm^3), filtration of the extract and concentration of the filtrate gave, upon cooling to −20 °C for ca. 24 h, red crystalline material (**13**, 0.28 g, 57%). (Found: C, 53.0; H, 7.99; N, 8.57. $C_{23}H_{41}N_3PdSi_2$ requires C, 52.9; H, 7.91; N, 8.05%), m.p.: 137–144 °C (dec.). ^{1}H-NMR (C_6D_6): δ −0.93 [d, $^2J(^1H\text{–}^1H) = 9.9$, 1 H, $SiCH_2$], −0.83 [d, $2J(^1H\text{–}^1H) = 9.9$, 1 H, $SiCH_2$], 0.06 (s, 9 H, R), 0.72 (s, 3 H, $SiMe_2$), 0.76 (s, 3 H, $SiMe_2$), 0.95 (s, 9 H, CMe_3), 1.4 (s, 9 H, CMe_3), 3.68 (bs, 1 H, N H), 5.62 (s, 1 H, C H), 5.67 (s, 1 H, C H), 6.13 (d, $J = 6.3$, 1 H, 3 or 5-Ar H), 6.78 (d, $J = 7.3$, 1 H, 3 or 5-Ar H), 6.87 (t, $J = 7$, 1 H, 4-Ar H). ^{13}C-NMR (C_6D_6): δ, 1.84 (s, $NSiMe_3$), 6.8 (s, $SiMe_2$), 12.1 (s, Si CH_2), 31.8, 29.0 (s, CMe_3), 36.5, 39.4 (s, CMe_3), 94.7 (s) (CH), 112.2, 114.3 (s, m-C), 123.6, 132.8 (s, p-C), 149.8, 151.7 (s, *ipso*-C), 155.3, 165.2 (s, N CBu^t).

2.1.4. $[Pd\{\{N(R)C(Ph)CH\}\{N(R)(H)C(Ph)CH\}\text{-}C_5H_3N\text{-}2,6\}_2]$ **4**

$PdCl_2(PhCN)_2$ (0.27 g, 0.712 mmol) was added to a cooled (−80 °C) hexane suspension of **E** (0.5 g, 0.712 mmol), and the reaction was allowed to warm to room temperature over 16 h, resulting in a red coloured reaction mixture. Removal of volatiles in vacuo and extraction of the residue with hexane (70 cm^3), filtration of

the extract and concentration of the filtrate gave, upon cooling to 0 °C for ca. 48 h, a fine, red crystalline material (**4**, 0.13 g, 17%). m.p.: 161–166 °C (dec.). ^{1}H-NMR (C_6D_6): δ 0.23 (s, 18 H, $NSiMe_3$), 0.39 (s, 18 H, PdN*R*), 5.34 (s, 2 H, C *H*), 5.72 (s, 2 H, C *H*), 6.70–8.84 (m, Ar *H*/Ph *H*). ^{13}C-NMR (C_6D_6): δ 1.4, 1.7 (s, $NSiMe_3$), 65.9, 102.5 (s, *C*H), 116.0, 118.4, 128.5, 128.7, 129.0, 137.0, 150.3, 157.0, 158.5, 159.5, 160.1, 161.0 (s,*C*, Ar/Ph), not observed *C*Ph.

2.2. Crystallography

Data sets for compounds **1**–**4** were collected on a Bruker SMART 1K CCD area detector, using monochromatic Mo-Kα radiation. Single crystals were enclosed in mineral oil and cooled in a stream of nitrogen gas to 173(2) K. Data reduction was carried out using the program SAINT [16a] and absorption corrections (not **1**) were made using the program SADABS [16b]. The structures were solved by direct methods using SHELXTL [17]. Refinement was based on F^2 with hydrogen atoms in riding mode, using SHELXTL [17]. The solid state structure of **4** had two highly disordered hexane molecule in the asymmetric unit which were incorporated in the refinement using SQUEEZE [18]. Correction of the X-ray data for **4** by SQUEEZE (189 electron/cell) was close to the required value (200 electron/cell) for the two hexane molecules. Diagrams (all drawn at 50% probability level) and publication materials were generated using SHELXTL [18], PLATON [19] and ORTEP3 [20]. Further details are found in Table 1.

Crystallographic data has been deposited at the Cambridge Crystallographic Data Centre (CCDC reference numbers: 204926 (**1**), 204928 (**2**), 204927 (**3**) and 204925 (**4**)). Copies of this information may 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 http://www.ccd.cam.ac.uk).

3. Results and discussion

3.1. Synthesis of 1-azaallyls

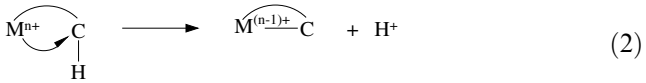
The reaction of the dilithium dialkyl [{(RHC)$_2$C$_5$H$_3$N-2,6}{Li(tmen)}$_2$] with an excess of Me_3SiCl at low temperature gave the hydrocarbon soluble precursor (R_2HC)$_2$(C_5H_3N-2,6) (**1**) in high yield (Scheme 1). Metallation of **1** with $Bu^nLi \cdot tmen$ or Bu^nLi in hexane followed by attempted nitrile insertion failed. An evaluation of the reactivity of the more extensively

Table 1
Crystal data and refinement for compounds **1**–**4**

Compound	**1**	**2**	**3**	**4**
Formula	$C_{19}H_{41}NSi_4$	$C_{52}H_{90}Li_2N_4Si_8$ (Et_2O)	$C_{23}H_{41}N_3PdSi_2$	$C_{54}H_{68}N_6PdSi_4$ (C_6H_{14})$_2$
Formula weight	395.89	1084.00	522.17	1192.25
Temperature (K)	173(2)	173(2)	173(2)	173(2)
Crystal system	Tricilinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$C2/C$ (No. 15)	$P2_1/n$ (No. 14)
a (Å)	8.959(1)	14.010(2)	32.268(3)	13.766(7)
b (Å)	9.637(1)	15.328(2)	9.1579(9)	9.176(5)
c (Å)	16.867(2)	17.693(3)	22.623(2)	24.549(12)
α	75.783(3)	71.300(3)	90	90
β	80.281(3)	80.742(3)	128.736(2)	96.195(8)
γ	67.989(3)	81.013(3)	90	90
U (Å^3)	1303.9(3)	3529.7(9)	5214.6(9)	3083(3)
Z	2	2	8	2
D (Mg/m^3)	1.008	1.020	1.330	1.284
μ (mm^{-1})	0.231	0.187	0.818	0.424
F(0 0 0)	436	1180	2192	1272
Theta range (°)	1.25 to 28.38	1.22 to 26.00	1.62 to 28.30	1.49 to 25.00
Index ranges	$-10 \leqslant h \leqslant 11$, $-12 \leqslant k \leqslant 12$, $-22 \leqslant l \leqslant 17$	$-15 \leqslant h \leqslant 17$, $-18 \leqslant k \leqslant 17$, $-21 \leqslant l \leqslant 21$	$-42 \leqslant h \leqslant 43$, $-9 \leqslant k \leqslant 12$, $-28 \leqslant l \leqslant 30$	$-16 \leqslant h \leqslant 16$, $-8 \leqslant k \leqslant 10$, $-29 \leqslant l \leqslant 25$
Reflections collected	9118	21045	17716	13720
Unique refl., R_{int}	6267, 0.0263	13736, 0.0307	6467, 0.0233	5364, 0.1122
Refl. with $I > 2\sigma(I)$	3627	8824	5460	3187
Data/restraints/parameter	6267/0/229	13736/0/626	6467/0/293	5364/0/303
Final R indices (for $I > 2\sigma(I)$)	$R_1 = 0.048$ $wR_2 = 0.115$	$R_1 = 0.058$ $wR_2 = 0.147$	$R_1 = 0.028$ $wR_2 = 0.061$	$R_1 = 0.088$ $wR_2 = 0.218$
R indices (all data)	$R_1 = 0.099$ $wR_2 = 0.134$	$R_1 = 0.104$ $wR_2 = 0.172$	$R_1 = 0.037$ $wR_2 = 0.063$	$R_1 = 0.146$ $wR_2 = 0.244$
Largest diff peak/hole (e Å^{-3})	0.322, −0.308	0.864, −0.331	0.696, −0.458	0.126, −0.193

studied monoalkyl precursor (2-pyr)$(R)_2$CH revealed that even though the pyridine ring should provide sufficient intramolecular activation, the metallation of (2-pyr)$(R)_2$CH with Bu^{n}Li in hexane yielded a 1:1 adduct of (2-pyr)$(R)_2$CH and lithium alkyl, whereas (2-pyr)$(R)_2$CH with BuLi$^n \cdot$ tmen in hexane afforded (2-pyr)$(R)_2$CLi(tmen) [21,22]. (Ph)$(R)_2$CH which is isoelectronic to (2-pyr)$(R)_2$CH was found to be unreactive towards Bu^{n}Li in hexane and was not metallated at the tertiary carbon atom with BuLi$^n \cdot$ tmen, even though this is the expected site of lithiation on the basis of relative thermodynamic acidities. In the presence of a catalytic amount of Et_2O, however, the 1:1 adduct of (2-pyr)$(R)_2$CH and lithium alkyl reacted with further Bu^{n}Li to form (2-pyr)$(R)_2$CLi [21]. Since complex (2-pyr)$(R)_2$CLi is free of a coordinating solvent [giving rise to the carbanion form of the ligand, rather than the η^3-azaallyl or the unknown enamide form of (2-pyr)$(R)_2C^-$; cf. [2,23], nitrile insertion is believed to be facilitated owing to the enhancement of C-centred nucleophilicity. Consequently, using Et_2O as solvent, the solvent free azaallyl **2**, was prepared in good yield (60%) from **1** and two equivalents of Bu^{n}Li and PhCN. Since 2,6-pyridyl-bridged dilithium bis-azaallyl complexes have previously been generated from the precursor $(RH_2C)_2(C_5H_3N$-2,6) [7], while we have demonstrated that the incorporation of additional R groups led to the mono-azaallyllithium compound **2** [from a precursor $(R_2HC)_2(C_5H_3N$-2,6) (**1**)], it seems likely that the observed difference in reactivity may be attributed to steric reasons.

The reactions of **D** and **E** with $PdCl_2(PhCN)_2$ at low temperature in hexane gave the crystalline materials **3** in a 1:1 ligand to metal (L:M) stoichiometry or **4** in a 2:1 L:M stiochiometry in moderate (57%) and low (17%) yields, respectively (Scheme 1). The repeated reaction of two equivalents of **E** with $PdCl_2(PhCN)_2$ gave no improvement in the yield of **4**. It is believed that **3** and **4** are initially formed by transmetallation, which is followed in the case of **3** by cyclometallation involving intramolecular C–H bond activation to form a four-membered palladacycle and in the case of **4** by hydrogenation of the terminal nitrogen involving the possibility of intermolecular C–H bond activation or hydrolysis. In this respect, it may be possible to view a PdN_4 complex, such as **4,** as a precursor to the cyclometallated product. Previously, it had been noted that for P,P containing pincer ligands, some metal complexes failed to induce C–H bond activation even after prolonged heating, and coordination complexes containing a $\eta^2 - P,P$ bidentate coordinating pincer ligand were formed. Such species were suggested to be intermediates preceding cyclometallation [24,25]. While cyclopalladation is generally considered an electrophilic process (Eq. (2)), the absence of a hydrogen coordinated to the Pd (II) centre in **3**, is not necessarily diagnostic of this mechanism, since oxidative-addition followed by rapid reductive-elimination (Eq. (3)) [26] could also yield **3**.



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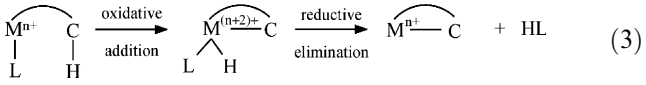

(3)

Compounds **1**–**4** are soluble in hydrocarbons. Crystals of these compounds suitable for X-ray analysis were obtained from concentrated hexane solutions, with the solutions of **1** and **2** requiring prolonged cooling (ca. 6 weeks) at −60 °C. Compounds **1** and **2** are colourless, air stable and yellow, air sensitive solids, respectively. The deep red solids **3** and **4** were air stable for the period of observation (ca. 1 h).

3.2. Structural studies

The molecular structures of **1**–**4** with the atom numbering Scheme are shown in Figs. 1–4, while selected bond distances and angles (not compound **1**) are listed in Tables 2–4.

Compound **2** crystallises as a dimer (Fig. 2) with approximate twofold rotational symmetry. The molecule has a central Li_2N_2 rhombus and bridging $NSiMe_3$ groups, the Li atoms being three coordinate. These features are similar to those of the molecular structures of $[Li\{N(R)C(Ph)C(H)C(Ph)N(R)\}]_2$ [27] and $[Li\{(N-(R)C(Ph)C(R)(C_5H_4N$-2)$\}]_2$ (**C**) [4]. A comparison to the crystal structure of the ligand precursor **1** (Fig. 1) reveals that the aromaticity of the pyridyl ring is unchanged and that the bonding within the NCCCN backbone, as for **C**, is localised with discrete PhC=C double bonds. Furthermore, the C1–C6 [C31–C36] bond distance of 1.494(4) [1.499(4)] Å is comparable to the corresponding single bonds substituted at C5 [1.515(4) Å] in **2** and C5–C13 [1.505(3) Å], C1–C6 [1.521(3) Å] in

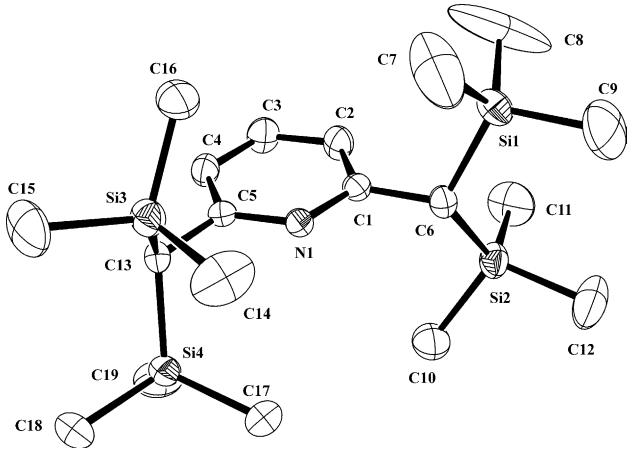

Fig. 1. Molecular structure of compound **1**.

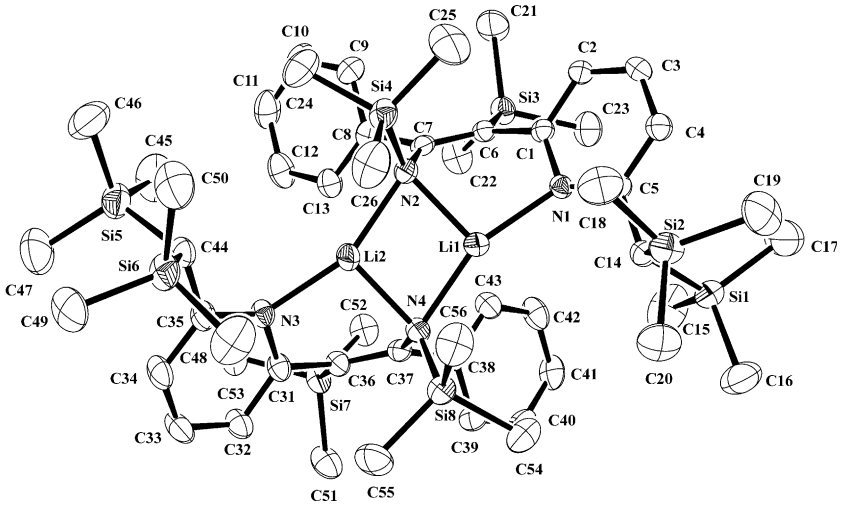

Fig. 2. Molecular structure of compound **2**.

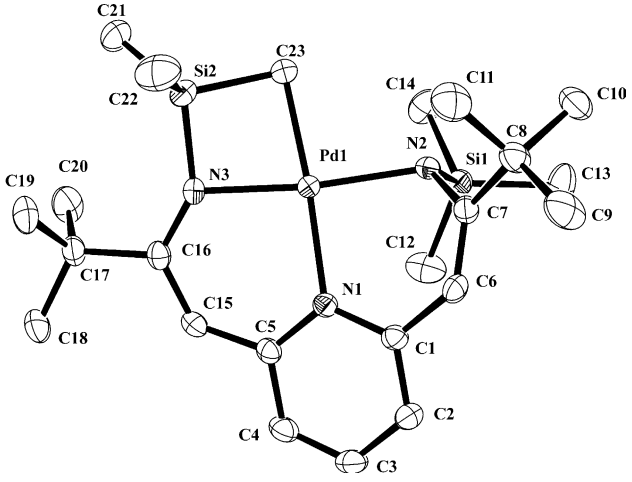

Fig. 3. Molecular structure of compound **3**.

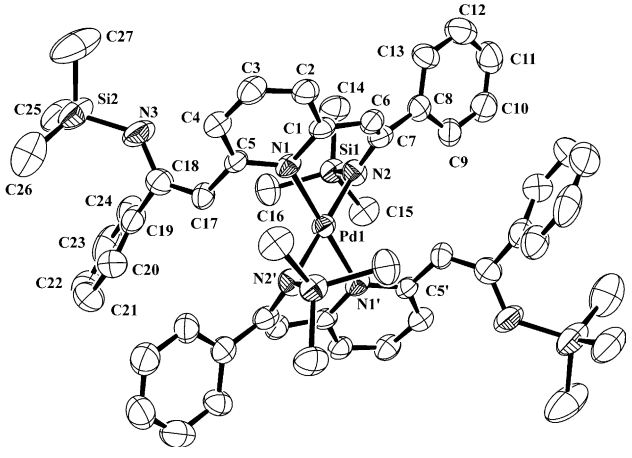

Fig. 4. Molecular structure of compound **4**.

Table 2
Selected bond distances (Å) for compound **2**

Li1–N1	2.040(6)	Li2–N2	2.055(6)
Li1–N2	2.017(6)	Li2–N3	2.038(6)
Li1–N4	2.060(6)	Li2–N4	2.008(6)
N2–C7	1.399(4)	N4–C37	1.399(4)
C1–C6	1.494(4)	C31–C36	1.499(4)
C6–C7	1.371(4)	C36–C37	1.371(4)
C7–C8	1.509(4)	C37–C38	1.509(4)
C5–C15	1.515(4)	C35–C44	1.518(4)

Table 3
Selected bond distances (Å) and angles (°) for compound **3**

Pd1–N1	2.086(2)	Pd1–N3	2.015(2)
Pd1–N2	2.105(2)	Pd1–C23	2.065(2)
Si1–N2	1.816(2)	Si2–N3	1.746(2)
Si2–C21	1.877(2)	Si2–C22	1.874(3)
Si2–C23	1.835(2)		
N2–C7	1.450(3)	N3–C16	1.343(3)
C1–C6	1.477(3)	C5–C15	1.436(3)
C6–C7	1.343(3)	C15–C16	1.386(3)
N1–Pd1–N2	90.90(6)	N2–Pd1–C23	93.26(8)
N1–Pd1–N3	95.93(7)	N3–Pd1–C23	79.94(8)

Table 4
Selected bond distances (Å) and angles (°) for compound **4**

Pd1–N1	2.016(5)	Pd1–N2	2.021(6)
N2–C7	1.344(9)	N3–C18	1.37(1)
C1–C6	1.44(1)	C5–C17	1.45(1)
C6–C7	1.37(1)	C17–C18	1.35(1)
N1–Pd1–N1′	180.0(3)	N1–Pd1–N2	85.4(2)
N1–Pd1–N2′	94.6(2)		

the neutral ligand **1**. This contrasts the apparent delocalisation in the ligand backbone for $[Li\{N(R)C(Ph)C(H)C(Ph)N(R)\}]_2$ [27]. The bulky R

groups in **2** are directed away from the centre of the complex as expected for the minimisation of non-bonding interactions, while for the neutral ligand **1** the trimethylsilyl groups are above and below the plane of the pyridyl ring. Viewing **1** perpendicular to the plane of the aromatic ring reveals that an approximately eclipsed conformation is adopted by the $SiMe_3$ groups above and below the pyridyl ring [torsion angles for MeSiSiMe range from 7.2° to 37.1°] with the C–H bonds of the bistrimethylsilylmethyl substituents being in the plane of the ring and pointing in the same direction.

The Li–N distances within the Li_2N_2 rhombus are similar [N2–Li1 2.017(6), N4–Li2 2.008(6) versus N2–Li2 2.055(6), N4–Li1 2.060(6) Å] and are in the same region as those involving the N atoms of the pyridine rings [2.040(6), 2.038(6) Å]. These bond distances are unexceptional but slightly longer (possibly a consequence of the additional $SiMe_3$ group in **2**) than in the related three-coordinate lithium compounds [Li{2-$C(R)_2C_5H_4N$}{$CH(R)_2C_5H_4N$-2}] [3a] [2.01(1) Å] and **C** [1.981(7) Å] [4]. The LiNCCCN metallacycles are puckered and the attached phenyl groups are rotated out of the plane described by the atoms C6, C7, C8 [66.7(2)°] or C36, C37, C38 [69.3(2)°] thereby preventing effective conjugation with the C=C double bonds [cf. C7–C8 and C37–C38 1.509(4) Å] [4,28]. Similar geometrical features have been described for [Li{2-$C(R)_2C_5H_4N$}{$CH(R)_2C_5H_4N$-2}] [3a] and **C** [4].

While the integrity of the neutral ligand is retained in solution, ^{13}C-NMR data revealed that some dissociation of **2** occurs in solution as evident by minor additional unassigned peaks in the alkyl region of the spectrum (see Section 2). This behaviour is consistent with the relief of steric congestion in the absence of packing forces.

[Pd{{N(H)(R)C(Bu^t)CH}{$N(SiMe_2CH_2)$C(Bu^t)CH}-C_5H_3N-2,6}] **3** crystallises as a monomer with one molecule in the asymmetric unit (Fig. 3). The Pd(II) atom is coordinated in an approximately square planar fashion by the three nitrogen atoms and the carbon atom [largest deviation from plane N_3PdC for N3 2.62(1) pm]. The ligand therefore behaves as a tetradentate chelate with N3 and C23 each been formally carrying a negative charge while N1 and N2 act as neutral donor atoms. Compound **3** is to the best of our knowledge the first structurally characterised compound that features a PdCSiN heterocycle. The related PdCCN systems have, however, been described previously [29]. For the known PdCCN systems, unlike in **3**, N typically functions as a neutral donor, while examples of N functioning as an anionic donor include [Pd{PhNC(O)CHC(O)Ph}(bipy)] [29a] and rac-[(*N*,*N*′-bis(3, 5-dinitrophenylo)-3, 6, 9-trithiaundecane-diamide-C, N, S, S′)-palladium] [29e]. In both these cases, the approximately square planar PdN_3C and $PdNCS_2$ coordination spheres are stabilised by the amide form of the ligand. The three metallacycles in **3** are all puckered with a maximum deviation from the corresponding planes of more than 10 pm. The angles subtended at Pd are close to 90°/180° with the exemption of the angle N3–Pd–C23 which is with 79.94(8)° much more acute. The latter angle is largely imposed by the geometry of the four membered ring and is within the range of other four membered alkylpalladacycles [29b,30]. The PdCCN derivatives display comparatively smaller angles (smaller atomic radius of C) as for example in [Pd{PhNC(O)CHC(O)Ph}(bipy)] [67.1(2)°] [29a], *rac*-[(*N*,*N*′-bis(3, 5-Dinitrophenylo)-3, 6, 9-trithiaundecane-diamide-C, N, S, S′)-palladium] [66.4(2)°] [29e], and 70.9° and 64.3(3)° for the neutral N-donor containing palladacycles, chloro[2-(dimethylamino)-1-methylpropyl-C,N](dimethylamine)palladium [29b] and *cis*-[$Pd(C_6F_5)_2(C_6H_5CH_2NMe_2)$] [29f], respectively. The acute angle of the latter was attributed to the C,N-chelating nature of the benzyldimethylamine ligand. The coordination sphere around the exocyclic N atom in **3** deviates significantly from a trigonal planar arrangement (Σ° 338.15 for N2) and is consistent with a protonated pyramidal nitrogen resulting from the abstraction of an activated H (see above) hereby confirming the notion of Pd–N2 being a dative bond. This proton at N2 was observed in the ^{1}H-NMR spectrum at δ 3.68.

The Pd1–N3 bond distance of 2.015(2) Å compares well with the corresponding bond in [Pd{PhNC(O)-CHC(O)Ph}(bipy)] [2.021(5) Å] [29a], but is significantly shorter than Pd1–N2 [2.105(2) Å] and other derivatives containing neutral N-alkyl donors (cf. chloro[2-(dimethylamino)-1-methylpropyl-C,N](dimethylamine)palladium [2.060(5) Å] [29b] and *cis*-[$Pd(C_6F_5)_2(C_6H_5$-$CH_2NMe_2)$] [2.314(6) Å] [29f,29g]). The Pd1–C23 bond distance [2.065(2) Å] in **3** is comparable to Pd–C bond distances reported for [Pd{PhNC(O)CHC(O)Ph}(bipy)] [2.054(6) Å] [29a], *rac*-[(*N*,*N*′-bis(3, 5-Dinitrophenylo)-3, 6, 9-trithiaundecane-diamide-C, N, S, S′)-palladium] [2.033(7) Å] [29e] and chloro[2-(dimethylamino)-1-methylpropyl-C,N](dimethylamine)palladium [2.023(6) Å] [29b] and corresponds to a typical Pd–C σ-bond (1.9–2.1 Å) [29f]. The bond between Si2 and the anionic carbon atom C23 [1.835(2) Å] is shorter than those between Si2 and the methyl groups C21 [1.877(2) Å] and C22 [1.874(2) Å]. The exocyclic double bond C15–C16 in the anionic part of the ligand shows a considerable degree of delocalisation as is evident by the bond distances C15–C16 [1.386(3) Å] and N3–C16 [1.343(3) Å] which may be compared to the bond distances in the neutral part of the ligand [C6–C7 1.343(3), N2–C7 1.450(3) Å] that are indicative of C=C double and N–C single bonds, respectively.

Compound **4** crystallises as a monomer (Fig. 4) in which the Pd atom is bound in a bidentate fashion (N, N) to two monoionic ligands [31]. The Pd atom occupies a crystallographic centre of inversion and the metal is coordinated in a square planar fashion by four nitrogen atoms. The six-membered PdNCCCN-metallacycle

adopts a boat conformation with Pd1 and C6 being located 1.137 and 0.230 Å above the plane defined by N1, C1, C7 and N2 [largest deviation from least square plane 0.2 pm for C7]. As in the case of compound **3** there is a considerable amount of delocalisation found between the C=C double and N–C single bond of the anionic part of the ligand [C6–C7 1.37(1), N2–C7 1.344(9) Å] which is less pronounced for the non-chelating part of the ligand [C17–C18 1.35(1), N3–C18 1.37(1) Å].

In both **3** and **4**, all C atoms attached to the aromatic rings are single bonds, and the aromaticity of the aryl rings is unchanged. The N(aryl)-Pd bond length for **3** [2.086 (2) Å] is comparable with those given for some other square planar Pd(II) pyridyl coordinated complexes [32], while in **4** [2.016(5) Å] some shortening is observed, presumably facilitated by the *trans* orientation of the ligands coordinated around the metal.

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