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Reactions of pyridine-functionalized lithium alkyls with nickelocenes and nickel(II) chloride: respective formation of cyclopentadienyl-nickelalkyls and coupled organic products. X-Ray crystal structures of [(η^5-C$_5$H$_5$)Ni{C(SiMe$_3$)$_2$C$_5$H$_5$N-2}] and {CH(SiMe$_3$)C$_5$H$_4$N-2}$_2$*

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Abstract

Reactions of the pyridine-functionalized lithium alkyls LiR^n [R^1 = CH(SiMe$_3$)C$_5$H$_4$N-2, R^2 = C(SiMe$_3$)$_2$C$_5$H$_4$N-2] with nickelocenes Ni(Cp^R)$_2$[Cp^R = η^5-C$_5$H$_5$ or η^5-C$_5$H$_3$(SiMe$_3$)$_2$] gave thermally stable cyclopentadienylnickel alkyl complexes [Cp^{R}NiR^n]. The reaction of LiR^1 with NiCl$_2$ afforded the coupled organic product (R^1)$_2$. The crystal structures of [(η^5-C$_5$H$_5$)Ni{C(SiMe$_3$)$_2$-C$_5$H$_4$N-2}][Ni–C$_\alpha$ = 2.018(2), Ni–N = 1.856(2) Å] and the coupled organic product {CH(SiMe$_3$)C$_5$H$_4$N-2}$_2$ have been determined.

1. Introduction

Nickel dialkyls are thermally unstable but can be stabilized by π-bonding ligands such as pyridine, phosphines and π-cyclopentadienyl [1]; for example, mixed-ligand nickel compounds of the type [NiR(X)L$_2$] and [NiR$_2$L$_2$] [R = alkyl, X = halide, L = nitrogen- or phosphorus-containing ligand] are known [2]. We previously described the preparation of the cobalt(II) dialkyl compound CoR$_2^2$ [R^2 = C(SiMe$_3$)$_2$C$_5$H$_4$N-2] and an X-ray crystal structure determination showed that the pair of sterically-hindered, pyridine-functionalized ligands R^2 is *trans*-chelated to the central planar four-co-ordinate cobalt(II) atom [3]. In the light of this chelating nature of the ligand R^2 and by analogy with the preparation of the known nickel(II) dialkyl complex [Ni(CH$_2$SiMe$_3$)$_2$(py)$_2$], we attempted to prepare NiR$_2^n$ by the reaction of LiR^n [R^1 = CH(SiMe$_3$)C$_5$H$_4$N-2, R^2 = C(SiMe$_3$)$_2$C$_5$H$_4$N-2, R^3 = CH$_2$C$_5$H$_4$N-2] with NiCl$_2$. The desired nickel dialkyl compounds were not, however, isolated but instead the coupled alkyl derivatives (R^n)$_2$. Subsequently, we investigated the reaction

of LiR^n with nickelocenes Ni(Cp^R)$_2$, which yielded the corresponding cyclopentadienylnickelalkyl compounds. In this paper, we report (i) the reactions of LiR^n with NiCl$_2$, (ii) the synthesis of cyclopentadienylnickelalkyl compounds of the type [Cp^{R}NiR^n], (iii) the synthesis of nickelocene Ni{η^5-C$_5$H$_3$(SiMe$_3$)$_2$}$_2$, and (iv) the crystal structures of [(η^5-C$_5$H$_5$)Ni{C(SiMe$_3$)$_2$C$_5$H$_4$N-2}] and {CH(SiMe$_3$)C$_5$H$_4$N-2}$_2$.

2. Results and discussion

The reaction of LiR^n [R^1 = CH(SiMe$_3$)C$_5$H$_4$N-2, R^3 = CH$_2$C$_5$H$_4$N-2] with NiCl$_2$ in THF gave the coupling products (R^1)$_2$ (1) and (R^3)$_2$ (2) (eqn. (1)).

$$NiCl_2 + LiR^n \xrightarrow{-LiCl} R^n - R^n + Ni^0 \qquad (1)$$

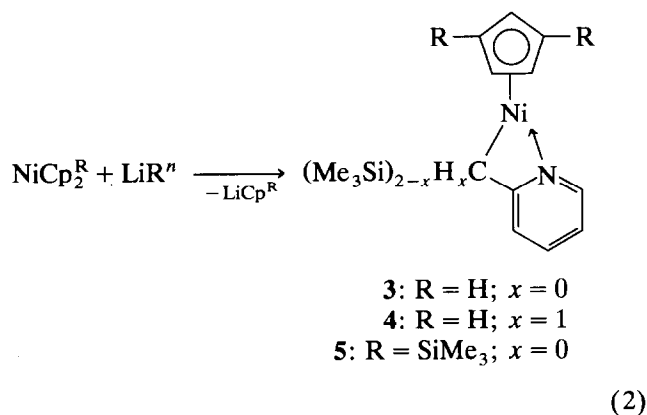$$1: R^1 = CH(SiMe_3)C_5H_4N-2$$
$$2: R^3 = CH_2C_5H_4N-2$$
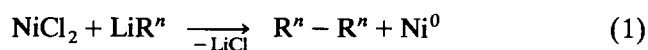
These organic products were separated from the reaction mixture by filtration followed by chromatographic separation on silica gel. They were characterized by their NMR spectra and elemental analysis. For compound **1**, a single crystal X-ray structural study was carried out. The formation of (R^n)$_2$ is due to in-

tramolecular reductive coupling of the alkyl groups within the thermally unstable nickel alkyl compounds formed initially. The thermal decomposition of the benzylnickel(II) compound, $PhCH_2Ni(Br)(PPh_3)$ is known to give the coupled product $PhCH_2CH_2Ph$ in quantitative yield [4]. Furthermore, coupled products of butane and biaryls are the major products from the reductive coupling reactions of thermally stable organonickel(II) complexes cis-diethyl(bipyridine)-nickel(II) and trans-$Ar_2Ni(PEt_3)_2$ [1]. In the case of the reaction of LiR^2 with $NiCl_2$ in THF, direct coupling between the bulky alkyl ligands R^2 is difficult to envisage. The organic product present in the reaction mixture was not identified.

Subsequently, the reaction of LiR^n [$R^1 = CH(SiMe_3)C_5H_4N-2$, $R^2 = C(SiMe_3)_2C_5H_4N-2$,] with nickelocenes $Ni(Cp^R)_2$ in THF afforded the thermally stable compound [Cp^RNiR^n] (eqn. (2)).

$$R\text{—}\underset{\displaystyle \overset{\displaystyle Ni}{\diagup \ \nwarrow}}{\bigcirc}\text{—}R$$

$$NiCp_2^R + LiR^n \xrightarrow[-LiCp^R]{} (Me_3Si)_{2-x}H_xC\underset{\diagdown N}{\diagup}$$

3: R = H; x = 0
4: R = H; x = 1
5: R = SiMe₃; x = 0

(2)

In the case of the reaction of LiR^2 with the nickelocene bearing the more bulky cyclopentadienyl ligand $[C_5H_3(SiMe_3)_2]^-$, the rate was found to be relatively low, possibly owing to steric hindrance around the metal centre. Lack of reactivity for steric reasons has been observed in the reaction of $CpNi(PPh_3)I$ with alkyl lithium compounds other than MeLi [5]. Compounds 3–5 are diamagnetic and achieve the eighteen-electron configuration required by the EAN rule. The compounds were characterized by microanalysis, mass spectroscopy, and ¹H and ¹³C NMR spectroscopy. In the case of 3 the X-ray crystal structure was determined.

The intermediate compound, cyclopentadienylnick-elmethyl {CpNiCH₃}, formed in the reaction of NiCp₂ with MeLi at −78°C, has been reported to be unstable and to react further with MeC≡CMe to give the thermolabile complex CpNiCH₃(MeC≡CMe) [6]. Nevertheless, compounds of the type CpNiR′(R″) [R′ = Me, Et, cyclopropyl, iso- and n-butyl, isopropyl, Ph; R″ = ethylene, propene, butadiene, 2,3-dimethylbutadiene] have been prepared by treatment of NiCp₂ with appro-

priate alkyllithium in the presence of alkenes or butadienes at low temperature [7–9]. It was also found that cyclopentadienylnickelalkyl can be stabilized by tertiary phosphine, and the nickel compounds $Cp^*Ni(PPh_3)$ (R)(Cp* = η⁵-C_5Me_5, R = Me, PhC≡C [10] or Cp* = η⁵-C_5H_5, R = CH_2SPh, SPh [11]) have been prepared by the reaction of $Cp^*Ni(PPh_3)X$ (X = Cl or I) with LiR or by treatment of a mixture of $NiCp_2$ and PPh_3 with LiR.

The hitherto unknown nickelocene $Ni(Cp^R)_2$ [Cp^R = η⁵-$C_5H_3(SiMe_3)_2$] was prepared by the reaction of $LiCp^R$ with 'activated' $NiBr_2$ [12]. The same compound can be prepared by the reaction of $LiCp^R$ and $NiCl_2$ in THF, but the reaction was relatively slow and gave only a low yield of $Ni\{η^5-C_5H_3(SiMe_3)_2\}_2$. The preparation of crowded nickelocenes by using the more reactive $NiCl_2(THF)_{1.65}$ has been reported [13].

The ¹H NMR spectra of 3 and 4 displayed singlets due to SiMe₃ groups from the alkyl ligands R^1 or R^2 and the Cp protons. For compound 5 signals from the various SiMe₃ groups in the Cp^R ligand and R^2 were observed. The ¹H NMR spectrum of 5 at low temperature (−80°C) was not significantly changed, indicating that the bulky ligand R^2 does not detectably interfere with the free rotation of the Cp^R ring at the temperature studied. Interestingly, the chemical shift of δ 4.39 for the methine proton of 4 is significantly different from that of δ 2.31 for the free ligand $CH_2(SiMe_3)$-C_5H_4N-2. This down-field shift suggests that 'η³-aza-allyl' type bonding, similar to that in the zirconium compound [$Zr(R^1)Cl(η^5-C_5H_5)_2$] [$R^1 = CH(SiMe_3)$-C_5H_4N-2], is present [14].

The molecular structures of 1 and 3 with numbering schemes are shown in Figs. 1 and 2, respectively; atomic coordinates, selected bond distances and bond angles are given in Tables 1–4. Compound 3 is a
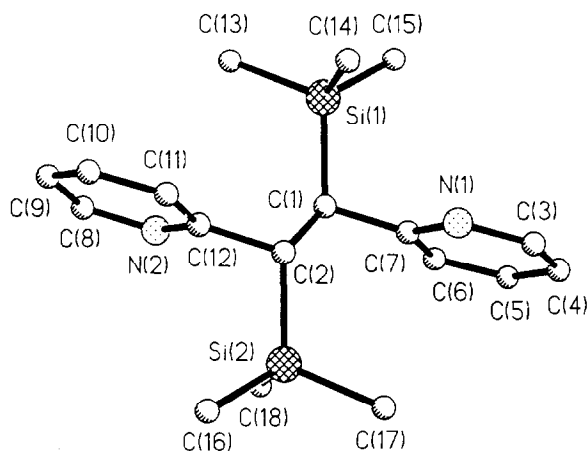

Fig. 1. Molecular structure of {CH(SiMe₃)C₅H₄N-2}₂ (1)
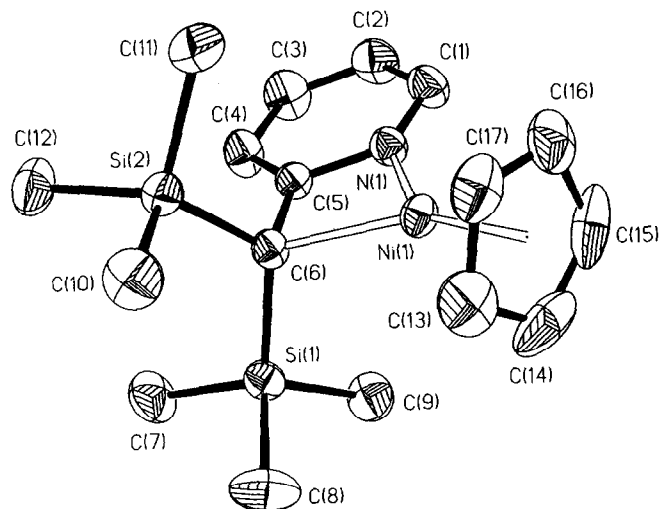
Fig. 2. Molecular structure of $[(\eta^5\text{-}C_5H_5)\overline{Ni\{C(SiMe_3)_2C_5H_4N\text{-}2\}}]$ (3)

TABLE 2. Atomic coordinates ($\times 10^5$ for Ni and Si; $\times 10^4$ for others) for $[(\eta^5\text{-}C_5H_5)Ni\{C(SiMe_3)_2C_5H_4N\text{-}2\}]$ (3)

Atom	x	y	z	U_{eq}
Ni(1)	33922(3)	48542(3)	18788(2)	400(1)
Si(1)	24418(7)	69176(7)	34596(4)	432(2)
Si(2)	63818(7)	83496(6)	28674(4)	444(2)
N(1)	2870(2)	6048(2)	959(1)	41(1)
C(1)	2225(3)	5940(3)	12(2)	54(1)
C(2)	2057(3)	7242(3)	-354(2)	62(1)
C(3)	2537(3)	8640(3)	257(2)	68(1)
C(4)	3203(3)	8762(3)	1232(2)	57(1)
C(5)	3359(2)	7422(2)	1572(1)	38(1)
C(6)	3977(2)	7091(2)	2548(1)	37(1)
C(7)	2583(4)	8964(3)	3868(2)	72(1)
C(8)	2827(4)	6015(4)	4597(2)	81(2)
C(9)	145(3)	5615(3)	2864(2)	65(1)
C(10)	7257(3)	7733(3)	3986(2)	66(1)
C(11)	7510(3)	8164(3)	1805(2)	66(1)
C(12)	7013(3)	10595(3)	3109(2)	72(1)
C(13)	3880(5)	3408(3)	2846(2)	81(2)
C(14)	2133(4)	2507(3)	2429(3)	91(2)
C(15)	2137(4)	2280(3)	1429(3)	87(1)
C(16)	3891(3)	2944(3)	1236(2)	71(1)
C(17)	4930(3)	3578(3)	2110(2)	68(1)

TABLE 1. Atomic coordinates ($\times 10^4$) for $[\{CH(SiMe_3)C_5H_4N\text{-}2\}_2]$ (1)

Atom	x	y	z	U_{eq}
Si(1)	3432(3)	7145(2)	681(2)	49(1)
Si(2)	6958(3)	6180(2)	2632(2)	51(1)
Si(3)	2365(3)	561(2)	4017(2)	49(1)
N(1)	6174(9)	8443(6)	918(5)	63(4)
N(2)	4105(8)	4919(6)	2402(5)	61(3)
N(3)	-1391(10)	464(8)	3251(5)	100(5)
C(1)	5340(9)	6686(6)	1079(5)	43(4)
C(2)	5057(8)	6657(6)	2227(5)	41(4)
C(3)	7217(14)	9104(8)	488(8)	76(6)
C(4)	8596(13)	8778(9)	-254(8)	83(6)
C(5)	8977(11)	7731(9)	-577(7)	73(5)
C(6)	7952(10)	7043(7)	-141(6)	55(4)
C(7)	6566(10)	7402(7)	600(6)	46(4)
C(8)	3015(12)	4277(7)	2832(7)	66(5)
C(9)	1620(11)	4649(8)	3528(7)	73(5)
C(10)	1348(11)	5679(9)	3863(6)	70(5)
C(11)	2402(10)	6354(7)	3447(6)	57(4)
C(12)	3803(10)	5950(7)	2708(5)	47(4)
C(13)	2269(9)	6017(6)	774(6)	72(4)
C(14)	2154(9)	8333(6)	1416(6)	66(4)
C(15)	4045(10)	7494(7)	-654(5)	79(5)
C(16)	6324(9)	5830(7)	3963(5)	76(5)
C(17)	8173(9)	7297(6)	2493(5)	63(4)
C(18)	8188(9)	4967(6)	1913(5)	68(4)
C(19)	-2437(12)	1258(10)	2885(7)	83(6)
C(20)	-2892(12)	2269(9)	3282(7)	80(6)
C(21)	-2306(12)	2508(8)	4045(7)	76(5)
C(22)	-1316(9)	1815(6)	4394(5)	31(3)
C(23)	-880(9)	842(7)	4040(5)	46(4)
C(24)	353(9)	61(7)	4393(4)	50(4)
C(25)	4073(9)	-540(6)	4016(5)	72(3)
C(26)	2364(9)	1701(6)	4833(5)	64(4)
C(27)	2664(10)	1076(7)	2743(5)	82(5)

TABLE 3. Selected bond distances (Å) and angles (°) for 1

Si(1)-C(1)	1.905(8)	Si(1)-C(13)	1.866(9)
Si(1)-C(14)	1.857(7)	Si(1)-C(15)	1.882(7)
Si(2)-C(2)	1.907(8)	N(1)-C(3)	1.345(13)
N(1)-C(7)	1.355(12)	C(1)-C(2)	1.585(11)
C(1)-C(7)	1.517(11)	C(3)-C(4)	1.371(13)
C(4)-C(5)	1.363(16)	C(5)-C(6)	1.360(14)
C(6)-C(7)	1.382(10)		
C(1)-Si(1)-C(13)	110.9(4)	C(2)-Si(2)-C(16)	108.2(3)
C(3)-N(1)-C(7)	116.7(7)	C(3)-C(4)-C(5)	119.8(9)
N(1)-C(7)-C(1)	115.3(6)	N(2)-C(12)-C(2)	117.3(6)
C(2)-C(12)-C(11)	121.5(8)		

TABLE 4. Selected bond distances (Å) and angles (°) for 3

Ni(1)-N(1)	1.856(2)	Ni(1)-C(5)	2.416(2)
Ni(1)-C(6)	2.018(2)	Ni(1)-C(13)	2.060(3)
Ni(1)-C(14)	2.137(13)	Ni(1)-C(15)	2.128(2)
Ni(1)-C(16)	2.149(3)	Ni(1)-C(17)	2.147(2)
Si(1)-C(6)	1.872(2)	Si(1)-C(7)	1.872(3)
Si(1)-C(8)	1.866(3)	Si(1)-C(9)	1.878(2)
N(1)-C(1)	1.343(3)	N(1)-C(5)	1.346(2)
C(1)-C(2)	1.374(4)	C(2)-C(3)	1.363(4)
C(3)-C(4)	1.380(3)	C(4)-C(5)	1.389(3)
C(5)-C(6)	1.487(3)	C(13)-C(14)	1.406(4)
C(13)-C(17)	1.391(5)	C(14)-C(15)	1.374(6)
C(15)-C(16)	1.423(4)	C(16)-C(17)	1.356(4)
Cp-Ni(1)	1.765		
N(1)-Ni(1)-C(6)	71.5(1)	Ni(1)-N(1)-C(1)	142.2(2)
Ni(1)-N(1)-C(5)	96.6(1)	Ni(1)-C(6)-C(5)	85.7(1)
Ni(1)-C(6)-Si(1)	110.8(1)	Ni(1)-C(6)-Si(2)	110.7(1)
N(1)-C(5)-C(6)	106.2(2)	N(1)-Ni(1)-Cp	142.4
C(6)-Ni(1)-Cp	146.1		

'half-sandwich', with the pyridine-functionalized alkyl ligand R^2-bonded in a chelate fashion. The five Ni–C(Cp) distances are not identical, ranging from 2.060 to 2.149 Å, revealing that the η^5 coordination is not symmetrical. The Ni–Cp(centroid) distance is 1.765(2) Å, and the average Ni–C(Cp) distance is 2.124(2) Å, significantly shorter than the corresponding distance in NiCp₂ [15]. The Ni–C$_\alpha$ distance of 2.018(2) Å in **3** is longer than the corresponding distance of 1.89(1) Å in cis-[Ni(CH₂SiMe₃)₂(py)₂] [2], which contains a pair of the less bulky alkyl ligands CH₂SiMe₃. However, the Ni–N(py) distance of 1.856(2) Å in **3** is significantly shorter than that of 1.957(8) Å in cis-[Ni(CH₂SiMe₃)₂-(py)₂]. The crystal of **1** comprises two nearly identical molecules, one of which is located at a centre of symmetry; the bond distances and angles in both molecules are normal.

3. Experimental section

All manipulations were carried out under dinitrogen or *in vacuo* by standard Schlenk techniques. Solvents were dried over and distilled from CaH₂ (hexane), and Na (THF, OEt₂). Elemental (C, H, N) analyses of the compounds were performed by MEDAC Ltd., Brunel University, or at the Shanghai Institute of Organic Chemistry, People's Republic of China. The ¹H and ¹³C NMR spectra were recorded at 250 and 62.90 MHz, respectively, using a Brüker WM-250 spectrometer. The chemical shifts, δ were recorded relative to SiMe₄. The organolithium reagents LiR'' [R¹ = CH(SiMe₃)C₅H₄N-2] [16], R² = C(SiMe₃)₂C₅H₄N-2, R³ = CH₂C₅H₄N-2] [17] and NiCp₂ [12] were prepared by published methods.

3.1. Synthesis of Ni{η⁵-C₅H₃(SiMe₃)₂}₂

Method A—by reaction of nickel(II) chloride with Li{C₅H₃(SiMe₃)₂}. A solution of Li{C₅H₃(SiMe₃)₂} (1.84 g, 8.5 mmol) in 25 ml of THF was added to a slurry of nickel(II) chloride (0.55 g, 4.24 mmol) in 10 ml THF. The mixture was heated under reflux for 2.5 h, during which the colour changed to dark green. The volatiles were then removed *in vacuo* and the residue was extracted with hexane. Filtration of the extract followed by concentration and cooling to −30°C yielded dark green crystals of Ni{η⁵-C₅H₃(SiMe₃)₂}₂(0.84 g, 42% yield).

Method B—by the reaction of 'activated' nickel(II) bromide with Li{C₅H₃(SiMe₃)₂}. Bromine (0.53 ml, 10.3 mmol) was added to a stirred suspension of nickel powder (0.57 g, 9.65 mmol) in 30 ml of dimethoxyethane, and the resulting mixture was stirred until colourless. (During this period, a yellow precipitate was observed.) The solvent was then removed *in vacuo*, 20

ml of THF was added, and a solution of Li{C₅H₃-(SiMe₃)₂} (4.15 g, 19.2 mmol) in 70 ml THF was added with stirring, the reaction mixture immediately turning green. After 6 h stirring at room temperature, the solvent was removed *in vacuo* and the residue was Soxhlet-extracted with pentane. The extract was concentrated and dark green crystals were obtained (3.7 g, 81%), m.p. 112–114°C. Mass spectrum: m/e, 477 [M]⁺, 404 [M − SiMe₃]⁺; Anal. Found: C, 55.42; H, 8.57. Calc. for C₂₂H₄₂Si₄Ni: C, 55.33; H, 8.86%.

3.2. Synthesis of [(η⁵-C₅H₅)Ni{C(SiMe₃)₂C₅H₄N-2}] (3)

A solution of NiCp₂ (0.75 g, 4 mmol) in 15 ml of THF was added to one of {LiR²}₂ (0.97 g, 4 mmol) in 20 ml of THF at 0°C. After 30 min stirring at 0°C the solution had turned from dark green to brown. It was stirred for a further 6 h at room temperature and the solvent was then removed *in vacuo*. The residue was extracted with hexane and the insoluble LiCp, as a white precipitate, was filtered off. The filtrate was concentrated at room temperature, then set aside to give brownish-green crystals (1.1 g, 77%), m.p. 186–188°C (dec.). Mass spectrum: m/e, 359 [M]⁺, 344 [M − CH₃]⁺, 294 [M − Cp]⁺; Anal. Found: C, 56.73; H, 7.53, N, 3.97. Calc. for C₁₇H₂₇Si₂NNi: C, 56.67; H, 7.55, N, 3.89%. ¹H NMR (250 MHz, C₆D₆): δ 0.30 (s, Me₃Si, 18H); 5.25 (s, C₅H₅, 5H); 5.90–5.96 (m, pyridyl, 1H); 6.05–6.09 (m, pyridyl, 1H); 6.80–6.87 (m, pyridyl, 1H); 7.11–7.15 (m, pyridyl, 1H). ¹³C NMR (¹H-decoupled, C₆D₆); δ 2.20 (Me₃Si), 89.06 (C₅H₅), 117.74, 121.96, 134.77, 152.63, 176.96 (C₅H₄N).

3.3. Synthesis of {η⁵-C₅H₅}Ni[CH(SiMe₃)C₅H₄N-2] (4)

A solution of [R¹Li(Et₂O)]₂ (0.72 g, 2.94 mmol) in THF (20 ml) was added with stirring to a solution of NiCp₂ (0.55 g, 2.94 mmol) in THF (20 ml) at 0°C. The solution turned from blue-green to dark brown. After 6 h stirring, the solvent was removed *in vacuo* and the residue extracted with hexane. The white precipitate of LiCp was filtered off and the extract concentrated, to give dark red crystals which were recrystallized from benzene (yield 0.61 g, 72%), m.p. 170–172°C (dec). Mass spectrum: m/e, 287 [M]⁺, 272 [M − CH₃]⁺, 214 [M − SiMe₃]⁺; Anal. Found: C, 58.61; H, 6.62 N, 4.85%. Calc for C₁₄H₁₉SiNNi: C, 58.37; H, 6.65; N, 4.86%. ¹H NMR (250 MHz, C₆D₆): δ 0.43 (s, Me₃Si, 9H), 4.39 (s, CHSi, 1H); 4.76 (s, C₅H₅, 5H); 6.02–6.05 (m, pyridyl, 1H); 6.27–6.30 (m, pyridyl, 1H); 6.48–6.55 (m, pyridyl, 1H); 8.45–8.46 (m, pyridyl, 1H). ¹³C NMR (¹H-decoupled, C₆D₆), δ 1.94 (Me₃Si); (CH)obscured; 92.03 (C₅H₅); 113.60, 120.80, 134.95, 139.40, 156.17 (C₅H₄N).

3.4. Synthesis of {η⁵-C₅H₃(SiMe₃)₂}Ni[C(SiMe₃)₂-C₅H₄N-2] (5)

[LiR²]₂ (0.51 g, 2.12 mmol) in 20 ml THF was added to a stirred solution of Ni{η⁵-C₅H₃(SiMe₃)₂}₂ in 20 ml of THF at 0°C. The colour changed slowly from yellowish-green to brownish-green. It was stirred for a further 10 h and solvent was then removed and the brown residue extracted with hexane. The white precipitate was filtered off and the extract concentrated and cooled to −30°C to give dark brown crystals (0.9 g, 84%), m.p. 99–101°C. Mass spectrum: m/e, 503 [M]⁺, 488 [M − CH₃]⁺, 430 [M − SiMe₃]⁺, 294 [M − C₅H₃(SiMe₃)₂]⁺; Anal. Found: C, 54.67; H, 8.48, N, 2.64%. Calc. for C₂₃H₄₃Si₄NNi: C, 54.72; H, 8.59, N, 2.78%. ¹H NMR (250 MHz, C₇D₈): δ 0.49 (s, Me₃Si, 18H); 0.55 (s, Me₃Si, 18H); 5.15–5.16 (m, C₅H₃, 1H); 5.20–5.21 (m, C₅H₃, 2H); 6.17–6.28 (m, pyridyl, 2H); 7.03–7.10 (m, pyridyl, 1H); 7.42–7.44 (m, pyridyl, 1H). ¹³C NMR (¹H-decoupled, C₇D₈); δ 1.80 (Me₃Si); 3.23 (Me₃Si); 90.67 (C₅H₃); 96.78 (C₅H₃); 111.29 (C₅H₃); 118.51, 122.70, 135.96, 153.27, 178.29 (C₅H₄N).

3.5. Reaction of R¹Li(Et₂O) with nickel(II) chloride

To a slurry of NiCl₂ (0.26 g, 4 mmol) in 20 ml THF at 0°C was added [R¹Li(Et₂O)]₂ (0.98 g, 4 mmol) in THF (25 ml). The colour turned from light brown to dark brown. After two days' stirring, a pale green solution and black precipitate had been formed. The solvent was then removed and the residue extracted

with hexane. After filtration of the extract and evaporation of the solvent the residue was chromatographed (silica gel) with 3/1 hexane/ethyl acetate mixture as eluent to give {CH(SiMe₃)C₅H₄N-2}₂ as white crystals (0.51 g, 39%), m.p. 130–132°C. Mass spectrum: m/e, 328 [M]⁺, 313 [M − CH₃]⁺, 254 [M − SiMe₃]⁺; Anal. Found: C, 65.63; N, 8.34; H, 8.49. Calc. for C₁₈H₂₈N₂Si₂: C, 65.79; N, 8.52; H, 8.59%. ¹H NMR (250 MHz, CDCl₃): δ −0.43 (s, Me₃Si, 18H), 3.25 (s, CHSi, 2H), 6.96–7.01 (m, pyridyl, 2H), 7.11–7.14 (m, pyridyl, 2H), 7.49–7.50(5) (m, pyridyl, 2H), 8.48–8.50 (m, pyridyl, 2H). ¹³C NMR (¹H-decoupled, CDCl₃): δ −1.55 (Me₃Si), 40.22(CHSi), 119.87, 123.98, 135.57, 149.11, 164.71(C₅H₄N).

3.6. Reaction of LiR³ with nickel(II) chloride

A solution of LiR³, freshly prepared by treating 1.6 ml (16.2 mmol) of α-picoline with 10.6 ml (17.0 mmol) of ⁿBuLi in a 1:1 mixture of THF and hexane, was added dropwise to a stirred suspension 1.1 g of NiCl₂ (8.1 mmol) in 20 ml of THF at 0°C. The reaction mixture was stirred at room temperature for two days and the solvent then removed under reduced pressure and the residue extracted with hexane. The black precipitate was filtered off and the filtrate concentrated then chromotographed (silica gel) with 3/1 hexane/ethyl acetate mixture as eluent to remove impurities. Finally elution with pure ethyl acetate gave (CH₂C₅H₄N-2)₂ as white crystals (0.15 g, 10.1%), m.p. 39–40°C.

TABLE 5. Summary of crystal data

	1	3
Complex	[(CH(SiMe₃)C₅H₄N-2)₂]	[(η⁵-C₅H₅)Ni{C(SiMe₃)₂C₅H₄N-2}]
Formula	C₁₈H₃₀N₂Si₂	C₁₇H₂₇NSi₂Ni
M	330.62	360.3
Crystal system	triclinic	triclinic
Space group	P1̄ (No. 2)	P1̄ (No. 2)
$a/\text{Å}$	8.764(4)	8.695(1)
$b/\text{Å}$	12.565(5)	9.140(1)
$c/\text{Å}$	4.270(7)	13.679(1)
$\alpha/°$	87.63(4)	92.73(1)
$\beta/°$	73.36(4)	95.45(1)
$\gamma/°$	79.81(4)	116.74(1)
$V/\text{Å}^3$	1482.0(1)	961(1)
Z	3	2
$D_c/\text{g cm}^{-3}$	1.11	1.245
Crystal size/mm	0.18 × 0.24 × 0.3	0.24 × 0.36 × 0.45
$\mu(\text{Mo K}\alpha)/\text{mm}^{-1}$	1.80	1.13
$2\theta_{max}$	45	60
N	3649	5579
N_o	1876	4130
R	0.063	0.031
wR	0.055	0.040

Mass spectrum: m/e 184 $[M]^+$, 169 $[M - CH_3]^+$, 154 $[M - 2CH_3]^+$, 106 $[M - C_5H_4N]^+$. ^{1}H NMR (250 MHz, CDCl$_3$): δ 3.21 (s, CH$_2$, 2H), 7.05–7.11 (m, pyridyl, 2H), 7.49–7.56 (m, pyridyl, 1H), 8.51–8.53 (m, pyridyl, 1H).

3.7. Crystallography

Crystal data are given in Table 5. Crystals of **1** and **3** were grown from hexane. X-ray data were collected from single crystals sealed in capillaries under dinitrogen on a Nicolet R3m/V diffractometer using graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) in the conventional $\omega/2\theta$ scan mode. N unique reflections were measured, and N_o observed reflections with $|F_o| \geq 3\sigma$ ($|F_o|$) were used in the structure solution and refinement. The weighting scheme $w = [\sigma^2 |F_o| + 0.0012 |F_o|^2]^{-1}$ was used for **3** and $w = [\sigma^2 |F_o| + 0.0015 |F_o|^2]^{-1}$ was used for **1**. The structures were solved by the Patterson method using the computer program SHELXTL-PLUS [18] on a DEC MicroVax II computer and refined by full matrix least-squares with anisotropic thermal parameters for the non-hydrogen atoms. Hydrogen atoms were introduced in their idealized positions and included in structure factor calculations with isotropic temperature factors. Complete lists of bond lengths and angles, and tables of the thermal parameters and H-atom coordinates have been deposited with the Cambridge Crystallographic Data Centre.

Acknowledgements

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