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Synthesis and structural characterisation of nickel(II) alkyl complexes NiR_2, $[Ni(Cp)R]_2$ and a 'head-to-tail' coupled alkyl intermediate compound $[NiR(Cl)(R{-}R)]$ [$R = C(SiMe_3)_2C_5H_4N$-2, $CPh(SiMe_3)C_5H_4N$-2 or $CH(SiMe_3)C_5H_4N$-2; $Cp = \eta^5$-C_5H_5]

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Abstract

Thermally stable nickel(II) alkyls NiR_2 [$R = R^1 = C(SiMe_3)_2C_5H_4N$-2 (**1**); $R = R^2 = CPh(SiMe_3)C_5H_4N$-2 (**2**),] and $[CpNiR]_2$ [$Cp = \eta^5$-C_5H_5; $R = R^3 = CH(SiMe_3)C_5H_4N$-2 (**4**)] containing pyridine-functionalised α-substituted alkyl ligands have been prepared by the alkylation of nickel(II) dihalide complexes $[NiX_2L_2]$ ($X = Cl$, Br; $L_2 = 2\ PPh_3$, *N,N,N′,N′*-tetramethylethylenediamine) or nickelocene with appropriate lithium alkyls. However, similar alkylation reaction of $[LiR^1]_2$ with $[NiCl_2(diphos)]$ ($diphos = Ph_2PCH_2CH_2PPh_2$) afforded a novel nickel(II)alkylchloride complex $[NiR^1(Cl)(R^1{-}R^1)]$ (**3**), in which a 'head-to-tail' coupled organic compound 2-$CH(SiMe_3)_2C_5H_4N$-5-$C(SiMe_3)_2C_5H_4N$ ($R^1{-}R^1$) remained coordinated to the nickel centre via one of the pyridyl nitrogens. Compounds **1–4** have been confirmed by X-ray structure analysis. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Nickel(II); Alkyls; Pyridine substituted alkyls; Cyclopentadienyl

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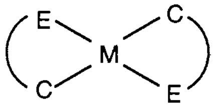
1. Introduction

Organonickel species are known to be the intermediate compounds in nickel catalyzed coupling reaction of organic halides [1]. Thermally stable nickel(II) complexes of the types $[NiR(X)L_2]$, $[NiR_2L_2]$, and $[(\eta^5$-$C_5H_5)NiR(L)]$ (R = alkyl or aryl; X = halides; L = nitrogen- or phosphorus-containing ligands) have been known [1,2]. In contrast, nickel dialkyls of the type $[NiR_2]$ which contain Ni–C σ-bonds being isolated and fully characterised are scarcely reported. Using sterically demanding alkyl or aryl ligands, thermally stable nickel dialkyl and diaryl complexes such as bis(trityl)nickel(II) $[Ni(CPh_3)_2]$ and bis(mesityl)nickel(II) $[Ni(Mes)_2]$ [1–4] have been synthesised. The stability of these complexes is attributed to the use of bulky and β-elimination stabilized ligands which shield the central metal and block the decomposition pathway.

In addition to the use of bulky ligands, it has been known that chelating ligands also impose a stabilizing effect on the corresponding nickel(II) complexes. For example, a large number of metallacycle compounds of composition $[Ni(C{-}E)_2]$ (**I**) and $[\{Ni(C{-}E)Cl\}_2]$ (**II**) (E = N, P, O, S) with anionic *C,N*- or *C,P*-chelates are known [5–7]. Complexes **I** are prepared by direct reaction of metal halides with the appropriate organolithium or Grignard reagents, whilst complexes **II** are usually obtained by direct metallation of C–H bonds. Organo-nickel compounds of type **II** are scarcely found, although their palladium(II) and platinum(II) analogues have been extensively studied [8–10].



I

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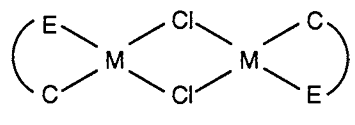
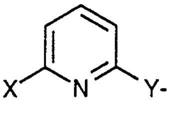


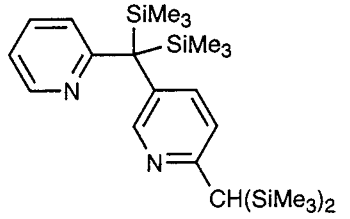
II

Pyridine-functionalised bulky alkyl ligands of type **III** were of particular interest over the past few years as they have been used in the synthesis of some novel main-group metal alkyl complexes [11–20]. They usually form *Y*,*N*-chelates with the metals resulting in the formation of four-membered metallacycle rings.

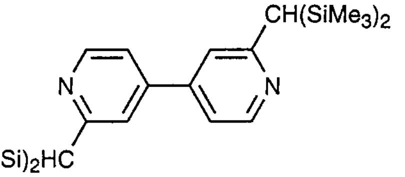


X = H, aryls, alkyls or halogens;
Y = aryls, alkyls, O, S, NR or PR (R = alkyls)

III



"Head-to-tail" coupled alkyl



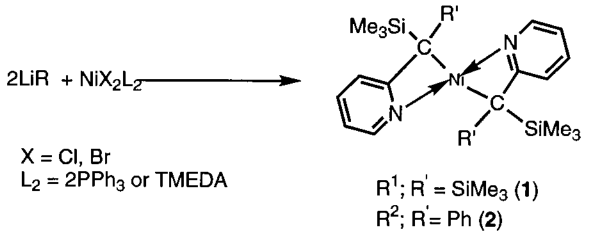
"Tail-to-tail" coupled alkyl

We have recently reported the synthesis and structures of the thermally stable iron(II) and cobalt(II) dialkyls $[\mathrm{MR}^1_2]$ [M = Fe and Co] and η^5-cyclopentadienylnickel alkyl complexes $[\eta^5\text{-Cp}''\mathrm{NiR}]$ [$\mathrm{Cp}'' = \mathrm{C_5H_5}$ or $\mathrm{C_5H_3(SiMe_3)_2}$; $\mathrm{R = R^3 = CH(SiMe_3)C_5H_4N}$ or $\mathrm{R^1}$] [21–24]. It is noteworthy that the attempted synthesis of $\mathrm{NiR^3_2}$ by the reaction of $[\{\mathrm{LiR^3(Et_2O)}\}_2]$ with $\mathrm{NiCl_2}$, gave the 'head-to-head' coupled organic product $[\{\mathrm{CH(SiMe_3)C_5H_4N\text{-}2}\}_2]$ and nickel metal as the by-product. In this paper, we report the synthesis and structures of nickel(II) alkyl complexes based on the pyridine-functionalised alkyl ligands $\mathrm{R^1}$, $\mathrm{R^2}$ and $\mathrm{R^3}$.

2. Results and discussion

2.1. Synthesis of nickel(II) alkyls $\mathrm{NiR_2}$

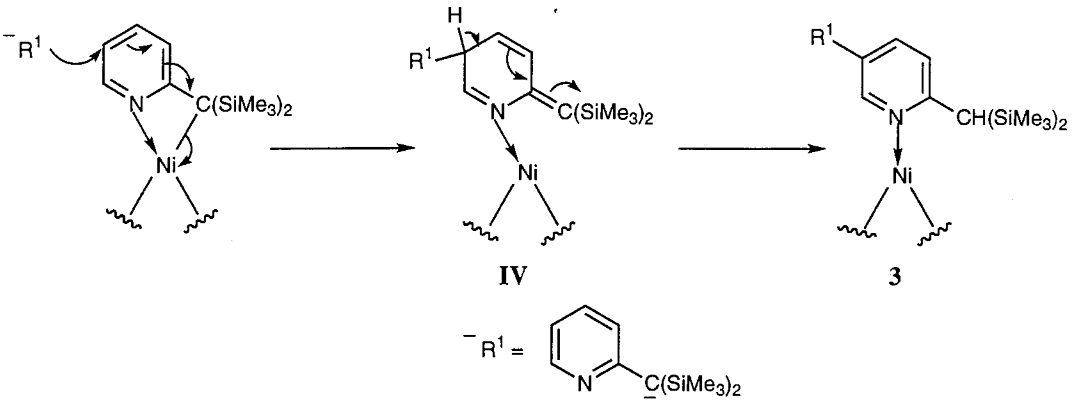
The reaction of $[\{\mathrm{LiR^1}\}_2]$ with $\mathrm{NiCl_2}$ in THF at ambient temperature afforded a reddish-brown solution with a black precipitate, apparently metallic nickel. The solution was filtered, chromatographed and cooled to give a red crystalline compound, $[\mathrm{NiR^1_2}]$ (**1**) in 6% yield. This result is similar to the 5% yield of the same compound reported by Thornton and co-workers by treating $[\mathrm{NiCl_2(PEt_3)_2}]$ with $[\{\mathrm{LiR^1}\}_2]$, but the structure of **1** has not been given [25]. In this work, we have found that the yield of **1** can be improved significantly to 50% by the reaction of $[\{\mathrm{LiR^1}\}_2]$ with $[\mathrm{NiCl_2(TMEDA)}]$ or $[\mathrm{NiCl_2(PPh_3)_2}]$ (Eq. 1).



Similarly, compound **2**, $[\mathrm{NiR^2_2}]$, was obtained in 40% yield by treating $[\mathrm{NiCl_2(TMEDA)}]$ with $[\mathrm{LiR^2(TMEDA)}]$. Compound **1** is more soluble in hydrocarbon solvents and stable in air than compound **2**. Using $[\mathrm{NiCl_2L_2}]$ as the starting materials, no metallic nickel, an obvious sign of reduction was observed during the course of the reactions. Organolithium compounds are well-known reducing reagents in alkylation reactions. The use of $[\mathrm{NiCl_2(TMEDA)}]$ in the preparation of nickel diaryl complexes has previously been reported in the literature. Longoni and co-workers have studied the reaction of $[\mathrm{NiCl_2(TMEDA)}]$ with *o*-lithio-*N*,*N*-dimethylbenzylamine and isolated the corresponding diaryl compound $[\mathrm{Ni}(o\text{-}\mathrm{C_6H_4CH_2NMe_2})_2]$ which probably has a trans square-planar geometry [5]. However, thermal stability of the compound was very low and was not fully characterised. Moreover, Issleib and co-workers have synthesized the nickel diaryl $[\mathrm{Ni}(o\text{-}\mathrm{CH_2C_6H_4PPh_2})_2]$ in satisfactory yield by treating $[\mathrm{NiCl_2(TMEDA)}]$ with the appropriate lithium aryl [6]. Both compounds were believed to have a five-membered metallacycle ring from *C*,*N*- or *C*,*P*-chelation.

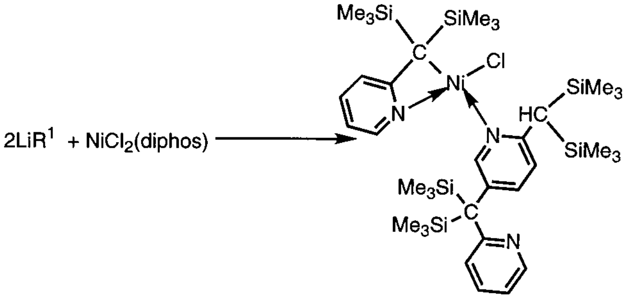
2.2. Synthesis of $[\mathrm{NiR^1(Cl)(R^1\text{–}R^1)}]$ (3)

When $[\mathrm{NiCl_2(diphos)}]$ was used as the starting material in the alkylation reaction with $[\{\mathrm{LiR^1}\}_2]$, the



Scheme 1.

chloroalkylnickel(II) compound, $[\mathrm{NiR^1(Cl)(R^1{-}R^1)}]$ (**3**) $[\mathrm{R^1{-}R^1} = 2\text{-}\mathrm{CH(SiMe_3)_2C_5H_4N}\text{-}5\text{-}\mathrm{C(SiMe_3)_2C_5H_4N}]$ was isolated in 35% yield (Eq. 2).



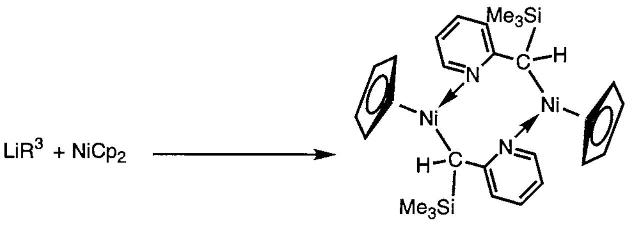
3

X-ray structure analysis has revealed that compound **3** contains a 'head-to-tail' coupled product $\mathrm{R^1{-}R^1}$ (**3b**) coordinated to the nickel centre via one of the pyridine-nitrogen atoms. Unlike **1**, the monoalkyl complex **3** is only sparingly soluble in hydrocarbon solvents. It is also unstable towards oxygen in solution, although the solid-form of **3** can be handled in air for a short period of time. We have reported earlier that the reaction of $\mathrm{LiR^3}$ with $\mathrm{NiCl_2}$ afforded a 'head-to-head' coupled product $2\text{-}\mathrm{C_5H_4NCH(SiMe_3)CH(SiMe_3)C_5H_4N(R^3{-}R^3)}$ [23]. The more sterically demanding nature of $\mathrm{R^1}$ renders 'head-to-head' coupling of this ligand unfavourable. The 'head-to-tail' coupling of $\mathrm{R^1}$, on the other hand, has been reported by Raston and co-workers in their attempted alkylation reaction of $\mathrm{BiCl_3}$ ([11]k). Furthermore, a 'tail-to-tail' coupled product (**3c**) was isolated at their studies of the monomeric dialkyl-aluminum and -gallium radical species $[\mathrm{MR^2_2}]^{\cdot}$ (M = Al, Ga) ([11]j). Compound **3** is one of the rare examples of an intermediate compound being isolated in a nickel catalysed reaction. The formation of different coupled products is apparently dependent on steric factors of the alkyl ligands at the α-carbon.

A mechanism for the formation of the 'head-to-tail' coupling product was proposed in which a C-centred carbanionic alkyl ligand $\mathrm{R^1}$ attacked position 5 of the pyridyl ring of a nickelocycle to give the intermediate compound **IV** which then re-aromatizes to give the species containing the 'head-to-tail' coupled product **3** (Scheme 1). Nevertheless, the mechanism for the formation of compound **IV** as well as the reason why the formation of the coupled alkyl ligand $[\mathrm{R^1{-}R^1}]$ was not observed in the reactions of $[\{\mathrm{R^1Li}\}_2]$ with $[\mathrm{NiCl_2(TMEDA)}]$ and $[\mathrm{NiCl_2(PPh_3)_2}]$ still remained unknown. However, $[\mathrm{NiCl_2(diphos)}]$ is known to be a good catalyst for coupling reactions in organic synthesis.

2.3. Synthesis of $[(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{NiR^3}]_2$ (4)

In our previous study, the reaction of $\mathrm{Ni}(\eta^5\text{-}\mathrm{C_5H_5})_2$ with $[\{\mathrm{LiR^1}\}_2]$ gave the η^5-cyclopentadienylnickel alkyl complex $[(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{NiR^1}]$ [23]. However, attempts to prepare dialkyl **1** by treatment of $[(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{NiR^1}]$ with one equivalent of $[\{\mathrm{LiR^1}\}_2]$ were unsuccessful. The starting compounds were recovered quantitatively. Similarly, the reaction of $\mathrm{LiR^3}$ $[\mathrm{R^3} = \mathrm{CH(SiMe_3)C_5H_4N}]$ with $\mathrm{Ni}(\eta^5\text{-}\mathrm{C_5H_5})_2$ afforded a less soluble compound and was suggested to be $[(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{NiR^3}]$ (**4**). Based on the down-field shift of the methine proton signal in the ^{1}H-NMR spectrum, it was believed that $\mathrm{R^3}$ in **4** behaved as an aza-ally type ligand. We have recently obtained the X-ray structure and confirmed that compound to be $[(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{NiR^3}]_2$ (**4**), a dimeric compound with the alkyl ligand forming a bridge between the two nickel centres (Eq. 3).



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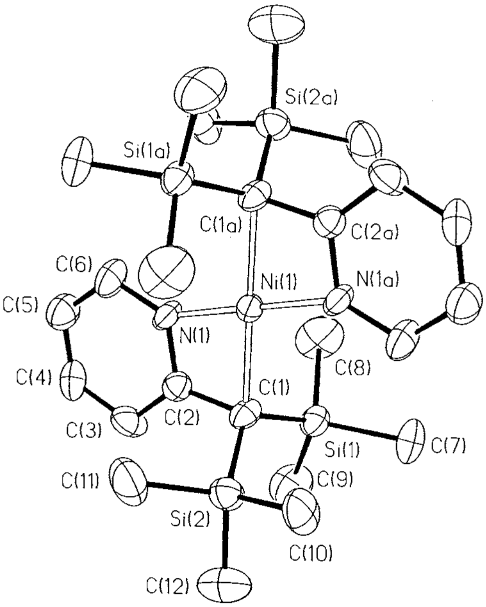


Fig. 1. Crystal structure of **1**, non-hydrogen atoms are shown with 35% thermal ellipsoids. Selected bond distances (Å) and angles are shown in Table 1.

2.4. X-ray structures

The molecular structures of **1**–**4** with the atom numbering schemes and selected bond distances and angles are shown in Figs. 1–4 and Tables 1–4.

Compound **1** crystallizes in a triclinic system with space group $P\bar{1}$. It contains two independent molecules of identical structure with each being located in a crystallographic inversion centre. Compound **2** crystallizes in a monoclinic system in the space group $P2/_1$. Both compounds exhibit a square-planar coordination geometry around each nickel(II) centre, with each pair of alkyl ligands bonded in trans chelate fashion. The structures are similar to their cobalt(II) analogues CoR$^1_2$ and CoR$^2_2$ [22–24]. The Ni–C$_\alpha$ and Ni–N distances of 2.075(8) and 1.889(2) Å in **1**, 2.065(7) and 1.871(5) Å in **2** are shorter than the corresponding distances in [CoR$^1_2$] [2.092(6) and 1.923(4) Å] and [CoR$^2_2$] [2.071(3) and 1.897(3) Å]. Furthermore, the Ni–C$_\alpha$ distances in **1** and **2** are slightly longer than the corresponding Ni–C$_\alpha$ distance of 2.018(2) Å in [η^5-CpNiR^1] (**5**) [23], but is much longer than that of 1.89(1) Å in *cis*-[Ni(CH$_2$SiMe$_3$)$_2$Py$_2$] (**6**) [26] although the coordination environments provided by the ligands in **6** are close to those in **1** and **2**. The mean Ni–N distances in **1** (1.889(2)) and **2** (1.871(5) Å) are comparable to that of

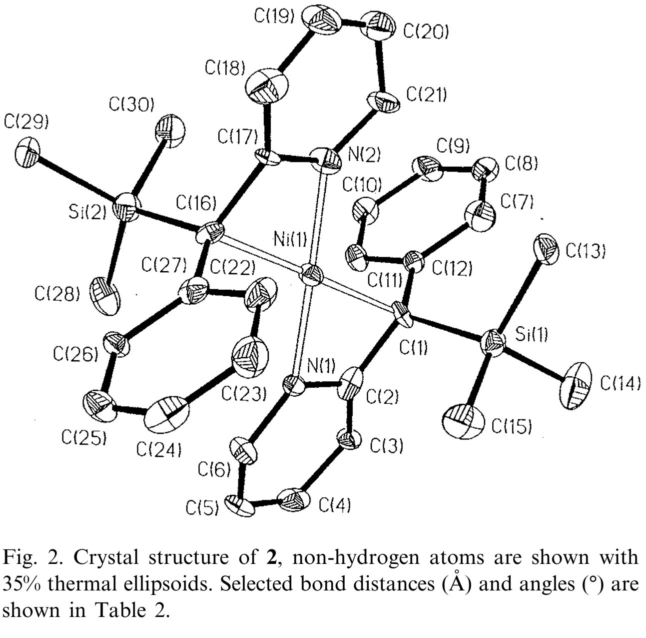


Fig. 2. Crystal structure of **2**, non-hydrogen atoms are shown with 35% thermal ellipsoids. Selected bond distances (Å) and angles (°) are shown in Table 2.

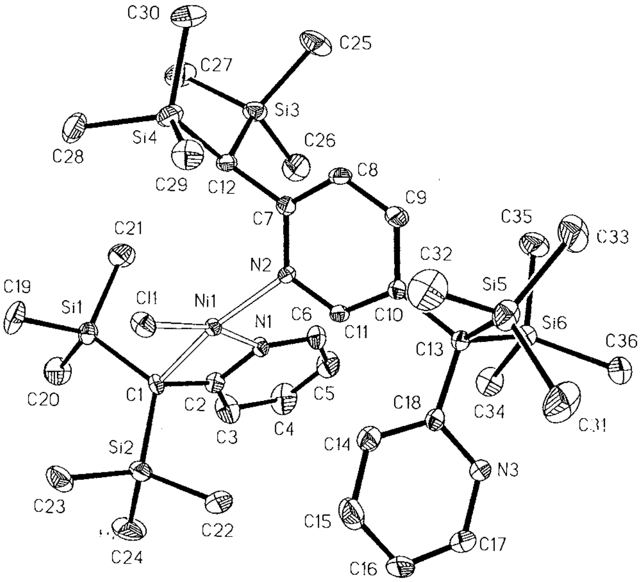


Fig. 3. Crystal structure of **3**, non-hydrogen atoms are shown with 35% thermal ellipsoids. Selected bond distances (Å) and angles (°) are shown in Table 3.

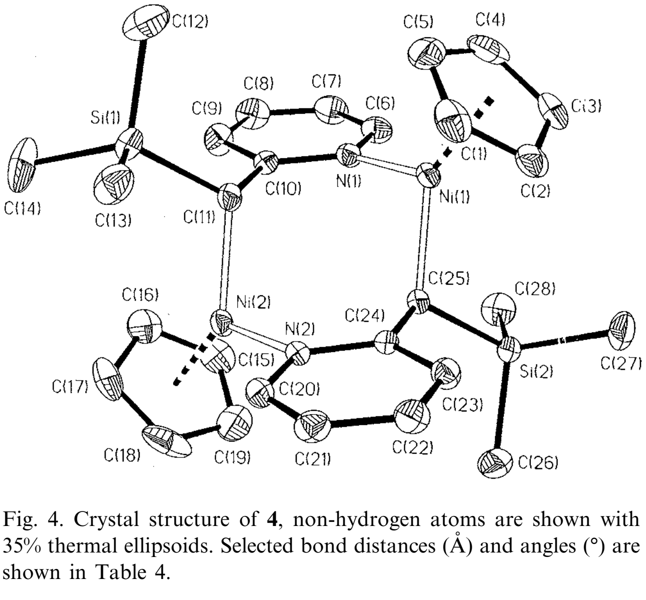


Fig. 4. Crystal structure of **4**, non-hydrogen atoms are shown with 35% thermal ellipsoids. Selected bond distances (Å) and angles (°) are shown in Table 4.

Table 1
Selected bond distances (Å) and angles (°) for structure **1**

Bond lengths (Å)			
Ni(1)–N(1)	1.887(2)	Ni(1)–C(1)	2.078(3)
C(1)–C(2)	1.486(3)	N(1)–C(2)	1.350(4)
N(1)–C(6)	1.344(3)	C(2)–C(3)	1.392(3)
C(3)–C(4)	1.385(3)	C(4)–C(5)	1.368(5)
C(5)–C(6)	1.379(4)	Si(1)–C(1)	1.867(2)
Si(2)–C(1)	1.872(3)		
Bond angles (°)			
N(1)–Ni(1)–C(1)	70.6(1)	N(1)–Ni(1)–N(1A)	180.0(1)
C(1)–Ni(1)–N(1A)	109.4(1)	N(1)–Ni(1)–C(1A)	109.4(1)
C(1)–Ni(1)–C(1A)	180.0(1)	N(1A)–Ni(1)–C(1A)	70.6(1)°

1.856(2) Å in **5** but are much shorter than the Ni–N distance of 1.957(8) Å in **6** [23,26].

Crystals of **3** are monoclinic with space group *C*2/*c*. The alkyl ligand R^1 bonds to the nickel centre in a *C*,*N*-chelating manner with Ni–C(1) and Ni–N(1) distance being 2.024(6) and 1.871(4) Å, respetively, with a bite angle of 70.7(2)°. The coupled product R^1–R^1 is bound to the nickel centre via the pyridyl nitrogen N(2) and is trans to C(1) of ligand R^1. The observed Ni–N(2) distance is 2.000(5) and the Ni–Cl(1) distance is 2.166(2) Å. The bidentate ligand R^1, N(2) and Cl(1) constitute a distorted square planar coordination geometry around the nickel centre with the metal atom located slightly above the plane formed by the four groups. The maximum overlap between the pyridyl nitrogen and the metal would involve the metal and the heterocyclic ring atoms lying coplanar with each other as in the case of **1**, **2**, and the cobalt dialkyls [CoR$^1_2$] and [CoR$^2_2$] [22,24]. This slight deformation in **3** is believed to take place in order to relieve steric strain at the metal centre without necessarily decreasing the pyridine-metal bonding.

The Ni–C$_\alpha$ distance in the monoalkyl species **3** (2.024(6) Å) is only 0.054 Å shorter than that of the dialkyl **1** but is comparable to that of **5** [23]. However, it is significantly longer than that of **6** [26]. The Ni–N(1) distance of 1.871(4) Å in **3** is shorter than the Ni–N(2) distance of 2.000(5) Å for the coupled dialkyl ligand. The former is comparable to the corresponding distance in **5** but is significantly shorter than the Ni–N distance in **6** [23,26].

Table 2
Selected bond distances (Å) and bond angles (°) for structure **2**

Bond distances			
Ni(1)–C(1)	2.065(7)	Ni(1)–N(1)	1.871(5)
Ni(1)–C(16)	2.044(6)	Ni(1)–N(2)	1.862(6)
Si(1)–C(1)	1.899(7)	C(1)–C(2)	1.442(11)
C(1)–C(12)	1.496(7)	N(1)–C(2)	1.369(10)
N(1)–C(6)	1.360(9)	C(2)–C(3)	1.394(10)
C(3)–C(4)	1.432(10)	C(4)–C(5)	1.392(12)
C(5)–C(6)	1.313(10)		
Bond angles			
C(1)–Ni(1)–N(1)	70.9(3)	C(1)–Ni(1)–C(16)	178.5(2)
N(1)–Ni(1)–C(16)	107.9(2)	C(1)–Ni(1)–N(2)	109.5(3)
N(1)–Ni(1)–N(2)	178.8(2)	C(16)–Ni(1)–N(2)	71.7(2)

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

Bond distances (Å)			
Ni(1)–Cl(1)	2.166(2)	Ni(1)–C(1)	2.024(6)
Ni(1)–N(1)	1.871(4)	Ni(1)–N(2)	2.000(5)
Si(1)–C(1)	1.874(5)	C(1)–C(2)	1.486(7)
N(1)–C(2)	1.334(8)	N(1)–C(6)	1.334(8)
C(2)–C(3)	1.382(9)	C(3)–C(4)	1.375(10)
C(4)–C(5)	1.360(13)	C(5)–C(6)	1.369(9)
Bond angles (°)			
Cl(1)–Ni(1)–C(1)	99.3(2)	Cl(1)–Ni(1)–N(1)	167.8(2)
C(1)–Ni(1)–N(1)	70.7(2)	Cl(1)–Ni(1)–C(2)	136.5(2)
Cl(1)–Ni(1)–N(2)	91.6(1)	C(1)–Ni(1)–N(2)	168.3(2)
N(1)–Ni(1)–N(2)	97.9(2)	C(2)–Ni(1)–N(2)	130.9(2)

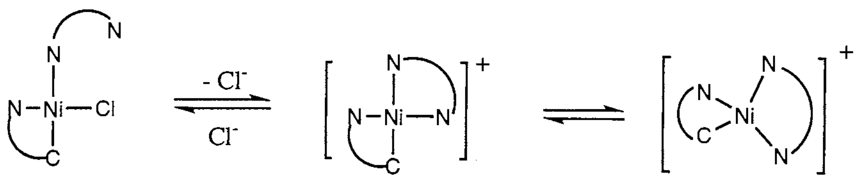
X-ray structure analysis of cyclopentadienylnickel(II) alkyl complex **4** had shown that it is a dimer. The asymmetric unit consists of one and a half molecules. The pyridine-functionalised alkyl ligand R^3 acts as an inter-bridging ligand between two nickel centres and forms a ‘chair-like’ eight-membered ring. Such bonding mode had been found in the dimeric structures of [FeR$^4_2$]$_2$ and [CoR$^4_2$]$_2$ [R^4 = CH(SiBu^{t}Me$_2$)C$_5$H$_4$N-2]. The cyclopentadienyl ligand in **4** is bonded to the nickel metal in a usual pentahapto mode of the metallocene ‘half-sandwich’ ([21]b[24]). The analogous compound **5** bearing the bis(trimethylsily)-substituted ligand R^1 is a monomer. The average Ni–C$_\alpha$ and Ni–N distances in **4** are 2.002 and 1.923 Å, respectively. The corresponding distances in **5** are 2.018(2) and 1.856(2) Å.

2.5. NMR spectroscopy

The ^{1}H-NMR spectrum of compound **1** displayed only one set of SiMe$_3$ peaks, this is consistent with the

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

Bond distances (Å)			
Ni(1)–C(1)	2.159(4)	Ni(1)–C(2)	2.071(4)
Ni(1)–C(3)	2.164(5)	Ni(1)–C(4)	2.158(5)
Ni(1)–C(5)	2.172(5)	Ni(1)–N(1)	1.920(3)
Ni(1)–C(25)	2.000(3)	Ni(2)–C(11)	2.004(4)
C(10)–C(11)	1.473(4)	C(1)–C(2)	1.419(6)
C(2)–C(3)	1.391(6)	C(3)–C(4)	1.385(7)
C(4)–C(5)	1.414(6)	N(1)–C(6)	1.343(4)
N(1)–C(10)	1.365(5)	C(6)–C(7)	1.374(6)
C(7)–C(8)	1.381(7)	C(8)–C(9)	1.383(5)
C(9)–C(10)	1.390(5)		



Scheme 2.

existence of one geometrical form, the trans-geometry of the square-planar complex in solution. For compound **2**, due to the substitution at the α-carbon, there are four possible diastereomers, viz. (*R*,*R*), (*S*,*S*), (*R*,*S*), and (*S*,*R*). The ^{1}H-NMR spectrum of **2** displayed two sets of $SiMe_3$ signals, which is consistent with the existence of two sets of diastereoisomers in the ratio of 1:1. They are assignable to the (*R*,*R*)/(*S*,*S*) and (*R*,*S*)/(*S*,*R*) diastereoisomers. Broad signals were observed in the ^{1}H-NMR spectrum of compound **3**. This may suggest the presence of dynamic behaviour in solution by which a tetrahedral species could be formed as shown in Scheme 2. Magnetic moment measurement by Evan's NMR method carried out for compound **3** had shown no significant paramagnetic property.

3. Experimental

3.1. General procedures

All manipulations were carried out under an argon or dinitrogen atmosphere. Solvents were dried over and distilled from CaH_2 (hexane), and sodium benzophenone (THF, ether, toluene) and degassed twice prior to use. Anhydrous $NiCl_2$ was prepared by standard procedure [27]. Samples of $[NiCl_2(PPh_3)_2]$ (Fluka), $[NiCl_2(diphos)]$ (Aldrich), were used as purchased. The organolithium reagents $[\{LiR^1\}_2]$ $[R^1 = C(SiMe_3)_2C_5H_4N\text{-}2]$, $[LiR^2(TMEDA)]$ $[R^2 = CPh(SiMe_3)C_5H_4N\text{-}2]$ were prepared by published methods [11,20].

3.2. Physical measurements

All NMR spectra were recorded with a Brüker WM-250 spectrometer. Chemical shifts are referenced to residual solvent protons of 7.15 ppm for C_6D_6 and 7.24 ppm for $CDCl_3$. Mass spectra (EI 70 eV) were obtained on a VG7070F mass spectrometer. Melting points were recorded on an Electrothermal Melting Point Apparatus and were uncorrected. Elemental (C, H, N) analyses were performed by MEDAC, Brunel University, UK.

*3.3. X-ray crystallography for compounds **1–4***

The crystals selected for study were mounted in glass capillaries and sealed under purified nitrogen. Data were collected on a Siemens P4/PC diffractometer at 294 K using graphite-monochromatized Mo–K_α radiation ($\lambda = 0.71073$ Å) with a $\omega/2\theta$ scan model (for compounds **1**, **3**, **4**,) or taking oscillation IP photos (for compounds **2**). *N* unique reflections were measured, and N_0 observed reflections with $|F_0| = n\sigma(|F_0|)$ where $n = 3$ for **1**, 10 for **2**, 4 for **3** and **4** were used in the structure solution refinement. The weighing scheme $w = [\sigma^2|F_0| + x|F_0|^2]^{-1}$ was used with $x = 0.002$ for **1**, 0.001 for **2** and **4**, and 0.0003 for **3**. Computations were performed using the SHELXTL PC program package on a PC 486 computer. The structures were solved by direct phase determination 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 assigned isotropic temperature factors. Tables of atomic coordinates, thermal parameters and complete lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Center.

*3.4. Synthesis of $[Ni\{C(SiMe_3)_2C_5H_4N\text{-}2\}_2]$ (**1**)*

3.4.1. Method A

A sample of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (0.23 g, 2.0 mmol) was stirred with a suspension of $NiCl_2$ (0.26 g, 2.0 mmol) in THF (20 ml) at 25°C for 8 h. A solution of $[\{LiR^1\}_2]$ (0.97 g, 2.0 mmol) in THF (20 ml) was then added slowly to the above suspension at −40°C. After the addition was completed, the mixture was stirred at ambient temperature for a further 8 h to give a reddish brown solution. The solvent was removed in vacuo and the residue was extracted with hexane followed by filtration and concentration. The concentrate was chromatographed on silica gel using pentane as eluent. All the red fraction was collected. The solvent was removed under reduced pressure to give **1** as red crystals (yield 0.53 g, 50%). M.p.: 158–160°C. EI-MS m/z (%) = 531 (9.3) $[M]^+$, 295 (54) $[M\text{–}R^1]^+$. Anal. Found: C, 54.22; H, 8.37; N, 5.18%. Calc. for $C_{24}H_{44}Si_4N_2Ni$: C, 54.22; H, 8.34; N, 5.27%. ^{1}H-NMR (250 MHz, C_6D_6): δ 0.47 (s, 18H), 6.01–6.06 (m, 1H), 3.32 (m, 1H), 6.73–6.79 (dt,$J = 1.7$ and 7.9 Hz, 1H), 7.56–7.58 (m, 1H). $^{13}C\{^1H\}$-NMR (62.89 MHz, C_6D_6): δ 4.10 ($SiMe_3$), 117.64, 125.58, 136.43, 149.15, 179.68 (C_5H_4N).

3.4.2. Method B

A solution of [{LiR^1}$_2$] (0.97 g, 2.0 mmol) in THF (20 ml) was added slowly to a suspension of [NiCl$_2$(PPh$_3$)$_2$] (1.31 g, 2.0 mmol) in THF (30 ml) at −40°C. The mixture was stirred at room temperature (r.t.) for 8 h. The resulting reddish brown solution was worked up by a similar procedure as described in Method A to give 0.51 g (48%) of the title compound.

3.4.3. [Ni{CPh(SiMe$_3$)C$_5$H$_4$N-2}$_2$], (**2**)

N,*N*,*N*′,*N*′-tetramethylethylenediamine (0.16 g, 1.4 mmol) was stirred with a suspension of NiCl$_2$ (0.18 g, 1.4 mmol) in 20 ml THF at 25°C for 8 h. A solution of [LiR^2(TMEDA)] (1.02 g, 2.8 mmol) in THF (30 ml) was added to the above mixture at −30°C. The solution was allowed to warm to r.t. and stirring was continued for 20 h. All volatiles were then removed in vacuo and the residue was extracted with toluene. The combined extract was reduced in volume to ca. 10 ml under reduced pressure. Upon cooling to −30°C, deep red crystals of **2** were obtained, yielded 0.34 g, 45%. M.p.: 232–233°C (dec.); EI-MS m/z (%) = 539 (23) [M]$^+$, 299 (64) [M−R^2]$^+$, 240 (16) [R^2]$^+$, 225 (100) [R^2−CH$_3$]$^+$. ^{1}H-NMR (250 MHz, C$_6$D$_6$): δ 0.38 (s, 9H), 5.87–5.93 (dd, $J = 1.1$, 5.4, and 7.4 Hz, 1H), 6.33–6.37 (dt, $J = 1.1$ and 8.0 Hz, 1H), 6.64–6.71 (dt, $J = 1.7$ and 7.7 Hz, 1H), 7.01–7.08 (dt, $J = 1.1$ and 7.3 Hz, 1H), 7.20–7.26 (dt, $J = 1.7$ and 7.9 Hz, 2H), 7.27–7.31 (dd, $J = 1.1$, and 1.7, and 5.4 Hz, 2H), 7.76–7.81 (dd, $J = 1.4$ and 8.3 Hz, 1H). ^{13}C{^{1}H}-NMR (62.89 MHz, C$_6$D$_6$): δ 1.78 (Si*Me*$_3$), 116.81, 118.01 (*C*$_5$H$_4$N), 121.86 (*C*$_6$H$_5$), 122.05, (*C*$_5$H$_4$N) 123.75 (*C*$_6$H$_5$), 136.53, 137.24 (*C*$_6$H$_5$), 144.76, 145.94 (*C*$_5$H$_4$N).

3.4.4. Synthesis of [Ni{C(SiMe$_3$)$_2$C$_5$H$_4$N-2}(Cl){5-(2′-C$_5$H$_4$NC(SiMe$_3$)$_2$)C$_5$H$_4$N-2-CH(SiMe$_3$)$_2$}] (**3**)

A solution of [{LiR^1}$_2$] (0.73 g, 1.5 mmol) in ether (30 ml) was added dropwise to a slurry of [NiCl$_2$(diphos)] (0.79 g, 1.5 mmol) in ether (20 ml) at 0°C. Stirring was continued at 0°C for an additional 15 min and then at 25°C for 8 h. The reddish brown supernatant solution was filtered through Celite. The filtrate was concentrated in vacuo followed by cooling to −30°C for 18 h to give dark reddish brown microcrystalline substance which was recrystallised from toluene to give **3** as dark red crystals (yield 0.42g, 35%). M.p.: 220–222°C (dec.). EI-MS m/z (%) = 472 (49) [R^1−R^1]$^+$, 457 (16) [R^1−R^1−CH$_3$]$^+$, 399 (10) [R^1−R^1−SiMe$_3$]$^+$, 236 (20) [R^1]$^+$, 222 (100) [R^1−CH$_3$]$^+$.

3.4.5. Synthesis of [{(η^5-C$_5$H$_5$)Ni{CH(SiMe$_3$)C$_5$H$_4$N-2}}$_2$] (**4**)

A solution of [{R^{3}Li(Et$_2$O)}$_2$] (0.72 g, 2.94 mmol) in THF (20 ml) was added with stirring to a solution of [Ni(η^5-C$_5$H$_5$)$_2$] (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 recrystallised from benzene (yield 0.61 g, 72%). M.p.: 170–172°C (dec.). EI-MS: m/z (%) = 287 (35) [M]$^+$, 272 (9) [M−CH$_3$]$^+$, 214 (23) [M−SiMe$_3$]$^+$. Anal. Found: C, 58.61; H, 6.62; N, 4.85%. Calc. for C$_{14}$H$_{19}$NSiNi: C, 58.37; H, 6.65; N, 4.86%. ^{1}H-NMR (250 MHz, C$_6$D$_6$): δ 0.43 (s, SiMe$_3$, 9H), 4.39 (s, CHSi, 1H), 4.76 (s, C$_5$H$_5$, 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). ^{13}C{^{1}H}-NMR (62.89 MHz, C$_6$D$_6$): δ 1.94 (SiMe$_3$), (CH) obscured, 92.03 (*C*$_5$H$_5$), 113.60, 120.80, 134.95, 139.40, 156.17 (*C*$_5$H$_4$N).

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