DALTON

Synthesis and structural characterisation of mono- and bi-nuclear cobalt(II) alkyls†

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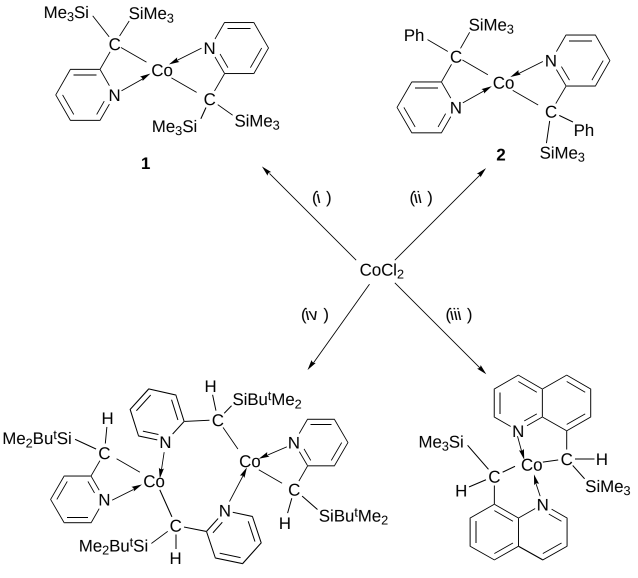
Treatment of $CoCl_2$ with the organolithium compounds $[(LiR^1)_2]$, $[\{LiR^2(tmen)\}_2]$, $[\{LiR^3(tmen)\}_2]$ and $[LiR^4(tmen)]$ $[R^1 = C(SiMe_3)_2(C_5H_4N\text{-}2)$, $R^2 = CPh(SiMe_3)(C_5H_4N\text{-}2)$, $R^3 = CH(SiMe_3)(C_9H_6N\text{-}8)$, $R^4 = CH(SiBu^tMe_2)(C_5H_4N\text{-}2)$; tmen = $Me_2NCH_2CH_2NMe_2]$ afforded the corresponding cobalt(II) dialkyls $[Co\{C(SiMe_3)_2(C_5H_4N\text{-}2)\}_2]$ **1**, $[Co\{CPh(SiMe_3)(C_5H_4N\text{-}2)\}_2]$ **2**, $[Co\{CH(SiMe_3)(C_9H_6N\text{-}8)\}_2]$ **3** and $[\{Co[CH(SiBu^tMe_2)(C_5H_4N)]_2\}_2]$ **4**. X-Ray diffraction analyses revealed that **1**–**3** are four-co-ordinated mononuclear compounds, each cobalt(II) centre adopting a square-planar environment with a pair of alkyl ligands bound in a *trans* chelating fashion. In contrast **4** is a four-co-ordinated binuclear compound, with one pair of alkyl ligands forming two interligand bridges between the tetrahedral cobalt centres to give an eight-membered 'chair' conformation. The cobalt to α-carbon and cobalt to nitrogen distances are in the ranges 2.01–2.13 and 1.90–2.10 Å, respectively. Magnetic moment measurements of **1**–**3** are consistent with a low-spin d^7 electronic configuration having one unpaired electron, whilst **4** showed antiferromagnetic coupling between two cobalt(II) centres. The electrochemical behaviour of these cobalt(II) compounds was studied by cyclic voltammetry.

Organocobalt(II) compounds which contain cobalt–carbon σ bonds have received little attention due to the hitherto low thermal stability which renders their isolation and characterisation difficult. A few homoleptic neutral and functionalised aryls of cobalt have been reviewed by Koschmieder and Wilkinson.[1] In general, alkyl or aryl derivatives of cobalt(II) can be obtained by the reaction of a cobalt(II) halide with the appropriate organolithium or Grignard reagents.[1] Stable diaryl complexes of cobalt(II) of the type *trans*-$[CoR_2(PEt_2Ph)_2]$ (R = *ortho*-substituted phenyl group) have been prepared by Chatt and Shaw[2] using this method. It was believed that *ortho* substituents on the aryl ligands hindered nucleophilic attacks on the metal centres. Based on dipole-moment and magnetic moment measurements, a *trans* square-planar geometry was assigned to the cobalt(II) compounds. In the case of cobalt(II) dialkyl compounds, only the five-co-ordinate $[CoMe_2(PMe_3)_3]$ has been reported.[3] Homoleptic cobalt(II) diaryls or dialkyls are scarcely found. The ionic complex $Li[Co(mes)_3]\cdot 4thf$ prepared by the reaction of $CoCl_2$ with an excess of mesityllithium in tetrahydrofuran (thf) was used to prepare the dinuclear homoleptic cobalt(II) diaryl $[\{Co(mes)_2\}_2]$ *via* protonation.[4,5] The cobalt(II) diaryl complex of the more bulky $2,4,6\text{-}Bu^t{}_3C_6H_2{}^-$ has been reported to be unstable and to decompose readily under ambient conditions.[6] Although the complex $[Co\{C(CN)(CF_3)_2\}_2]$ has been formulated with cobalt–carbon σ bonds and may be considered as a homoleptic dialkyl of cobalt(II), concrete evidence of its existence is still equivocal.[7]

Stabilisation of transition-metal alkyls using *N*-functionalised alkyl ligands has been reported by Manzer and Guggenberger.[8] Main Group and Groups 11 and 12 metal alkyls containing pyridine-functionalised alkyl ligands have been reviewed.[9] Recently, we have reported the synthesis and structures of a cobalt alkyl and some iron(II) alkyl complexes, *viz*. $[FeR^1{}_2]$, $[FeR^2{}_2]$, $[FeR^3{}_3]$, $[(FeR^4{}_2)_2]$ and $[Fe(R^2)Cl(tmen)]$ $[R^1 = C(SiMe_3)_2(C_5H_4N\text{-}2)$, $R^2 = CPh(SiMe_3)(C_5H_4N\text{-}2)$, $R^3 = CH(SiMe_3)(C_9H_6N\text{-}8)$, $R^4 = CH(SiBu^tMe_2)(C_5H_4N\text{-}2)$; tmen = $Me_2NCH_2CH_2NMe_2]$.[10–12] Our interest has extended to cobalt(II) compounds of R^1–R^4. We describe herein the synthesis, structural characterisation, magnetic susceptibilities and electrochemical behaviours of a series of thermally stable cobalt(II) dialkyl compounds.



Scheme 1 (*i*) $[(LiR^1)_2]$; (*ii*) $[LiR^2(tmen)]$; (*iii*) $2[LiR^3(tmen)]$; (*iv*) $[\{LiR^4(tmen)\}_2]$

Results and Discussion

The reaction of 2 equivalents of the organolithium reagents with anhydrous $CoCl_2$ in diethyl ether afforded the corresponding mononuclear cobalt(II) dialkyls $[CoR^i{}_2]$ $[R^1 = C(SiMe_3)_2\text{-}(C_5H_4N\text{-}2)$ **1**, $R^2 = CPh(SiMe_3)(C_5H_4N\text{-}2)$ **2**, $R^3 = CH(SiMe_3)\text{-}(C_9H_6N\text{-}8)$ **3**] or the binuclear dialkyl compound $[(CoR^4{}_2)_2]$ **4** $[R^4 = CH(SiBu^tMe_2)(C_5H_4N\text{-}2)]$ (Scheme 1). These compounds have been characterised by their elemental analyses, mass

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† *Non-SI unit employed:* $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

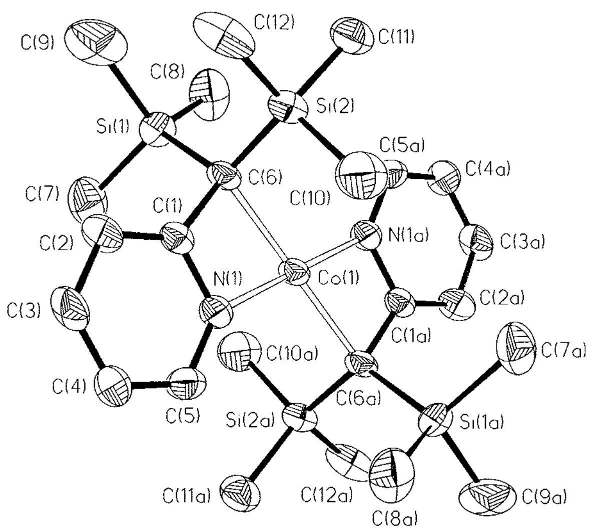

Fig. 1 Molecular structure of $[Co\{C(SiMe_3)_2(C_5H_4N-2)\}_2]$ **1** with the atom numbering scheme for each of the two nearly identical molecules in the asymmetric unit. Thermal ellipsoids are shown as the 35% probability level. Selected bond distances (Å) and angles (°): Co(1)–C(6) 2.092(6), Co(1)–N(1) 1.923(4), C(1)–C(2) 1.386(8), N(1)–C(1), 1.345(8), C(2)–C(3) 1.371(9), C(3)–C(4) 1.36(1), C(4)–C(5) 1.361(8), C(1)–C(6) 1.482(7), N(1)–C(5) 1.339(7), Si(1)–C(6) 1.878(6) and Si(2)–C(6) 1.858(5); N(1)–Co(1)–C(1) 32.7(2), N(1)–Co(1)–C(6) 69.3(2), C(1)–Co(1)–C(6) 36.7(2), Co(1)–N(1)–C(1) 96.8(3), Co(1)–N(1)–C(5) 143.3(4) and Co(1)–C(6)–C(1) 85.8(3)

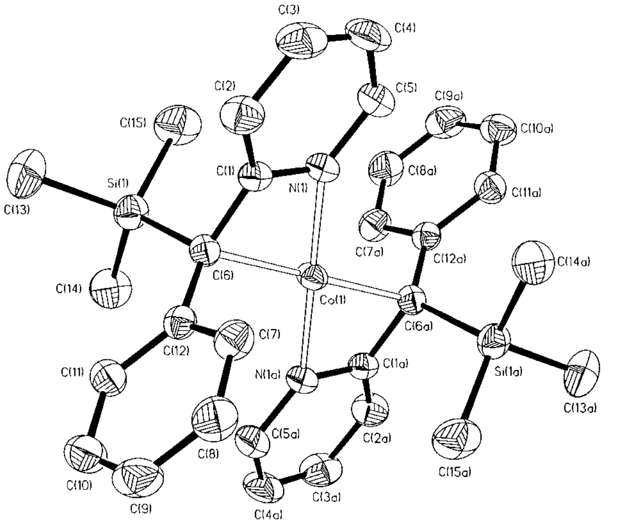

Fig. 2 Molecular structure of $[Co\{CPh(SiMe_3)(C_5H_4N-2)\}_2]$ **2** with the atom numbering scheme. Thermal ellipsoids are shown at the 35% probability level. Selected bond distances (Å) and angles (°): Co(1)–C(6) 2.071(3), Co(1)–N(1) 1.897(3), C(1)–C(6), 1.484(5), C(6)–C(12) 1.502(4), C(1)–C(2) 1.395(5), C(2)–C(3) 1.392(6), C(3)–C(4) 1.370(7), C(4)–C(5) 1.369(6), N(1)–C(1) 1.358(5) and N(1)–C(5) 1.347(5); N(1)–Co(1)–C(6) 70.5(1), N(1)–Co(1)–N(1a) 180.0(1), C(1)–Co(1)–N(1a) 145.9(1), C(6)–Co(1)–N(1a) 109.5(1), N(1)–Co(1)–C(1a) 145.9(1), C(6)–Co(1)–C(1a) 142.4(1), Co(1)–N(1)–C(1) 94.4(2), Co(1)–C(6)–C(1) 83.9(2), Co(1)–C(6)–C(12) 112.8(2) and Co(1)–C(6)–Si(1) 104.9(2)

spectra and single-crystal structure analyses. They are notably stable, in particular **1** can be sublimed at *ca.* 160 °C under vacuum (10^{-2} mmHg, *ca.* 1.33 Pa). In contrast, most of the cobalt(II) dialkyl compounds reported hitherto readily decompose at ambient temperature.[1] The stability of these compounds is attributed to the bulkiness of the *N*-functionalised alkyl ligands R^i which protects the central metal from attacks by other reagents or solvents. It also hinders decomposition *via* reductive coupling of two alkyl ligands. In addition, the intramolecular electron donation from the pyridyl nitrogens of the ligand also contributes to the thermal stability of these compounds.

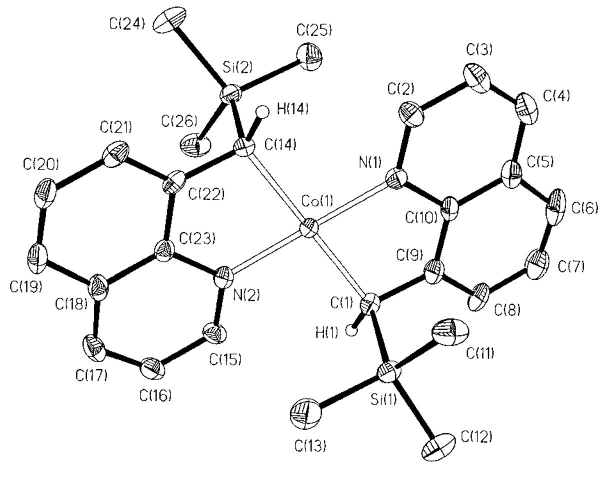

Fig. 3 Molecular structure of $[Co\{CH(SiMe_3)(C_9H_6N-8)\}_2]$ **3** with the atom numbering scheme. Thermal ellipsoids are shown at the 35% probability level. Selected bond distances (Å) and angles (°): Co(1)–C(1) 2.009(4), Co(1)–N(1) 1.930(2), Co(1)–C(14), 2.041(4), Co(1)–N(2) 1.940(2), C(1)–C(9) 1.476(4), C(14)–C(22) 1.485(4), N(1)–C(2) 1.344(3), N(1)–C(10) 1.390(5), C(2)–C(3) 1.393(4), C(3)–C(4) 1.360(6), C(4)–C(5) 1.404(4), C(5)–C(6) 1.443(6), C(6)–C(7) 1.352(3), C(7)–C(8) 1.403(4), C(8)–C(9) 1.392(5) and C(9)–C(10) 1.395(3); N(1)–Co(1)–N(2) 179.5(1), N(1)–Co(1)–C(1) 83.4(1), N(2)–Co(1)–C(1) 96.1(1), N(1)–Co(1)–C(14) 96.7(1), N(2)–Co(1)–C(14) 83.8(1), C(1)–Co(1)–C(14) 179.6(1), Co(1)–C(1)–C(9) 106.7(2) and Co(1)–N(1)–C(10) 113.9(1)

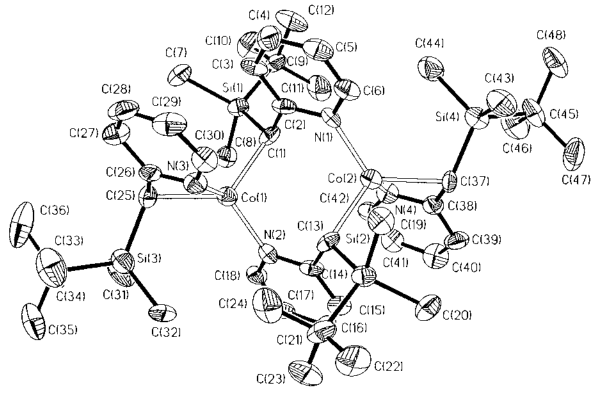

Fig. 4 Molecular structure of $[\{Co[CH(SiBu^tMe_2)(C_5H_4N-2)]_2\}_2]$ **4** with the atom numbering scheme. Thermal ellipsoids are shown at the 35% probability level. Selected bond distances (Å) and angles (°): Co(1)–C(1) 2.10(1), Co(1)–N(2) 2.02(1), Co(1)–N(3) 2.10(1), Co(1)–C(25) 2.11(1), Co(2)–N(1) 2.04(1), Co(2)–C(13) 2.10(1), Co(2)–N(4) 2.10(1), Co(2)–C(37) 2.13(1), N(1)–C(6) 1.36(2), C(1)–C(2) 1.49(2), C(2)–C(3) 1.39(2), C(3)–C(4) 1.36(2), C(4)–C(5) 1.38(2), C(5)–C(6) 1.35(2), N(1)–C(2) 1.38(2) and C(25)–C(26) 1.42(2); C(1)–Co(1)–N(2) 102.1(5), C(1)–Co(1)–N(3) 109.4(5), C(1)–Co(1)–C(25) 123.9(5), N(2)–Co(1)–N(3) 128.4(4), N(3)–Co(1)–C(25) 68.2(5), N(2)–Co(1)–C(25) 123.3(5), N(1)–Co(2)–C(13) 102.2(4), N(1)–Co(2)–N(4) 127.3(4), C(13)–Co(2)–N(4) 107.5(4), N(1)–Co(2)–C(37) 125.9(5), C(13)–Co(2)–C(37) 123.7(5), N(4)–Co(2)–C(37) 67.6(4), Co(1)–C(25)–C(26) 83.9(8), Co(1)–N(3)–C(26) 85.6(8) and Co(1)–C(1)–C(2) 107.5(8)

The molecular structures of compounds **1**–**4** with atom numbering schemes and selected bond distances and angles are shown in Figs. 1–4. For **1** the asymmetric unit consists of two independent half-molecules. Compounds **1**–**3** are mononuclear and exhibit a square-planar co-ordination geometry around each cobalt(II) centre, with each pair of alkyl ligands bonded in *trans* chelate fashion. Each of the molecules contains a crystallographically imposed C_2 axis making each pair of alkyl ligands equivalent. The cobalt to α-carbon distances for **1**–**3** are in the

Table 1 Electrochemical data[a] for cobalt(II) dialkyls **1**–**3**

Compound	$E_p{}^a$/V	$E_p{}^c$/V	$E_{\frac{1}{2}}$/V	$\Delta E_p{}^b$/mV
1 [CoR$^1_2$]	−3.04	−2.14	−2.59	90
	0.86	—	—	—
2 [CoR$^2_2$]	—	−1.66	—	—
	−0.04	−0.15	−0.10	0.11
3 [CoR$^3_2$]	−2.13	−2.30	−2.22	170

[a] Solvent: thf. Supporting electrolyte: 0.4 mol dm^{-3} NBu$_4$BF$_4$ solution at room temperature. Scan rate: 100 mV s^{-1}. [b] $\Delta E_p = E_p{}^a - E_p{}^c$.

sequence of **1** > **2** > **3** and parallel the steric crowding at the α-carbon due to the size of the substituents and extent of substitution. These distances are in the range 2.01–2.09 Å slightly longer than the similar distances of 1.931(5) Å in [Co(C$_6$F$_5$)$_2$-(η^6-C$_6$H$_5$Me)] and 1.994(2) Å in *trans*-[Co(mes)$_2$(PPhEt$_2$)$_2$].[13,14] The longer Co–C distance in **1**–**3** is a consequence of the steric demand of the bulky ligands R^1–R^3. The cobalt–nitrogen distances are in the range of 1.90–1.94 Å. That in **1** is longer than that in **2** due to the more bulky R^1 which prevents closer approach to the metal centre.

The molecular structure of compound **1** has shown that the fifth and sixth pseudo-octahedral sites are blocked by two SiMe$_3$ groups, one from each of the ligands R^1. This effectively protects the cobalt(II) from attacks by potential reactants and thus accounts for the remarkable stability of the compound. This also accounts for the stability of the cobalt(II) diaryls *trans*-[CoR$_2$(PEt$_2$Ph)$_2$], in which the bulky *ortho* substituents on ligand R hinder attacks on the metal.[2] The inertness towards a few bulky alcohols and benzenethiols is unusual, as [FeR$^1_2$] reacts readily with alcohols such as 2,6-Bu$^t_2$-4-Me-C$_6$H$_2$OH and the benzenethiol 2,4,6-Bu$^t_3$C$_6$H$_2$SH to form [Fe(OC$_6$H$_2$Bu$^t_2$-2,6-Me-4)$_2$(R^{1}H)] and [Fe(SC$_6$H$_2$Bu$^t_3$-2,4,6)$_2$(R^{1}H)].[11] Its stability, both thermal and chemical, is presumably due to the effective shielding by the sterically encumbered alkyl ligand R^1.

Compound **4** displays a binuclear structure. A pair of alkyl ligands R^4 are co-ordinated to each of the metals in a C,N chelate fashion and the other pair are bonded in interligand bridging fashion between the two cobalt centres. This leads to the formation of an eight-membered Co$_2$R$^4_2$ ring which adopts a 'chair' conformation. The geometry at the cobalt centre is tetrahedral with Co–C distances of 2.11 Å (average) comparatively longer than in the mononuclear compounds. This structure is isostructural to its iron(II) analogue reported recently.[11] In addition to [(FeR$^4_2$)$_2$], such eight-membered 'chair' conformations have been reported for a few dimeric organolithium compounds containing C,N-bridging pyridylmethyl ligands.[11,15] The formation of a binuclear structure in **4** is probably due to the less bulky nature of R^4. It is also noteworthy that the structural data had shown that the geometry at the cobalt centre for compounds **1**–**3** is square planar, while in **4** the cobalt is in a tetrahedral geometry. Chatt and Shaw[2] suggested that the adoption of a square-planar geometry for d^7 organocobalt(II) complexes is due to the large gains in ligand-field stabilisation energy over other molecular geometries.

Magnetic properties and electrochemical studies

The magnetic moments of compounds **1**–**3** in benzene, as measured by the NMR method of Evans,[16] are 3.11, 2.31 and 2.40 μ_B, respectively. In general, magnetic moments of square-planar cobalt(II) compounds usually fall in the range 2.1–2.9 μ_B owing to a large orbital contribution to the magnetic moment for such complexes which contain one unpaired electron.[2,17] The values for **2** and **3** fall well within this range, albeit that of **1** is marginally higher. It is believed that each of these d^7 planar dialkylcobalt(II) complexes has one unpaired electron. The magnetic moment of 1.63 μ_B per cobalt atom for **4**, much lower than the expected value for tetrahedral cobalt(II), is most likely a result of antiferromagnetic coupling between each pair of cobalt(II) centres.

Cyclic voltammetry (CV) of compounds **1**–**3** has been studied. All potentials were measured using thf as solvent, tetrabutylammonium tetrafluoroborate as the supporting electolyte, and were internally referenced to the ferrocemium–ferrocene couple. The electrochemical data for **1**–**3** are shown in Table 1. The cyclic voltammogram of **1**, sweeping initially in the anodic direction, shows a reversible one-electron reduction at $E_{\frac{1}{2}} = -2.59$ V (scan rate 100 mV s^{-1}, $\Delta E_p = 90$ mV). The sweep-rate dependence shows that the cobalt(I) species is stable on the CV time-scale. An irreversible oxidation peak with $E_p = 0.86$ V (at 100 mV s^{-1}) was also recorded. The cyclic voltammogram of **2** is complex. It shows a quasi-reversible anodic wave at $E_{\frac{1}{2}} = -0.10$ V which is probable due to oxidation to the cobalt(III) species. The irreversible cathodic peak at −1.66 V was presumably due to reduction of **2** to the corresponding electrochemically unstable cobalt(I) species. The CV of **3** displays a quasi-reversible one-electron cathodic wave at $E_{\frac{1}{2}} = -2.22$ V. No evidence of oxidation or reduction was observed for the binuclear compound **4** down to the limits of background decomposition.

Experimental

General procedures

All manipulations were carried out under an argon or dinitrogen atmosphere using standard Schlenk techniques or in a dry-box. Solvents were dried over and distilled from sodium–benzophenone (thf, diethyl ether, toluene), calcium hydride (hexane), or lithium aluminium hydride (pentane) under nitrogen and degassed twice before use. Anhydrous cobalt(II) chloride was prepared by a standard procedure.[18] The organolithium reagents [(LiR^1)$_2$] [R^1 = C(SiMe$_3$)$_2$(C$_5$H$_4$N-2)],[8] [LiR^i(tmen)] [R^2 = CPh(SiMe$_3$)(C$_5$H$_4$N-2), R^3 = CH(SiMe$_3$)(C$_9$H$_6$N-8), R^4 = CH(SiBu^{t}Me$_2$)(C$_5$H$_4$N-2)] were described previously.[19,20]

Physical measurements

Mass spectra were obtained on a Bruker APEX 47e FTMS mass spectrometer. Melting points were recorded in sealed glass capillaries under argon and are uncorrected. Elemental (C, H, N) analyses were performed by MEDAC Ltd., Brunel University, UK. The UV/VIS spectra were recorded on a Hitachi U-2000 spectrometer with quartz cells of 1 cm path length. Magnetic moments were determined using Evan's NMR method in C$_6$D$_6$ solution and a JEOL PMX 60si NMR spectrometer. Cyclic voltammetric measurements were performed by using a BAS CV-50W Voltammetric Analyzer. The electrochemical cell comprised a platinum-wire working electrode, a silver-wire reference electrode, and a tungsten-wire counter electrode. All measurements were made in an argon atmosphere. All sample solutions (thf) contained 0.4 mol dm^{-3} NBu$^n_4$BF$_4$ (supporting electrolyte) and *ca.* 4 × 10^{-3} mol dm^{-3} complex. Chemical potentials were internally referenced to the ferrocenium–ferrocene redox system.

Syntheses

[Co{C(SiMe$_3$)$_2$(C$_5$H$_4$N-2)}$_2$] 1. To a stirred suspension of CoCl$_2$ (0.32 g, 2.5 mmol) in diethyl ether (20 cm^3) was added a solution of [(LiR^1)$_2$] (1.21 g, 2.5 mmol) in ether (30 cm^3) at 0 °C. After stirring at room temperature for 8 h a deep red solution with a grey precipitate was obtained. This mixture was filtered and the filtrate concentrated *in vacuo* and placed at −30 °C to afford dark red *crystals* (1.13 g, 85%), m.p. 116–118 °C. Mass spectrum: *m/z* 531 (M^+, 36), 296 ([M − R^1]$^+$, 52), 236 (31) and 222 (100%). UV/VIS (thf): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 231 (4600), 265 (4400), 368 (2800) and 532 (1500) (Found: C, 54.15;

Table 2 Selected crystallographic and data-collection parameters for compounds **1**–**4**

	1	**2**	**3**	**4**
Molecular formula	$C_{24}H_{44}CoN_2Si_4$	$C_{30}H_{36}CoN_2Si_2$	$C_{26}H_{32}CoN_2Si_2$	$C_{48}H_{80}Co_2N_4Si_4$
M	531.99	539.7	487.6	943.34
Colour and habit	Dark red plate	Red prism	Dark green prism	Dark green plate
Crystal size/mm	0.26 × 0.24 × 0.34	0.18 × 0.24 × 0.42	0.18 × 0.26 × 0.44	0.05 × 0.30 × 0.40
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	*Pn* (no. 7)	$P2_1/n$ (no. 14)
a/Å	8.519(2)	9.777(2)	6.586(1)	13.358(3)
b/Å	11.906(6)	10.762(2)	8.608(1)	24.990(5)
c/Å	16.212(6)	14.065(3)	22.196(2)	16.458(3)
α/°	70.12(3)			
β/°	80.74(3)	91.40(3)	94.18(1)	93.92
γ/°	82.96(3)			
U/Å^3	1522(1)	1479.6(4)	1254.9(6)	5481(3)
Z	2	2	2	4
D_c/g cm^{-3}	1.161	1.211	1.290	1.143
μ/mm^{-1}	0.730	0.681	0.791	0.730
Scan type	ω	ω	ω	ω
Scan rate/° min^{-1}	3.005–15.625	7.00–60.00	4.0–26.0	2–16
$2\theta_{max}$/°	50	52	50	50
Unique data measured	4850	2663	3945	5838
No. observed reflections [$\|F_o\| \geqslant n\sigma(\|F_o\|)$], *n*	3356, 6	1839, 3	2559, 6	2809, 4
No. variables	283	160	279	524
R	0.061	0.047	0.036	0.078
R′	0.063	0.055	0.051	0.074
g in weighting scheme*	0.0003	0.0006	0.0012	0

* $w^{-1} = \sigma^2|F_o| + g|F_o|^2$.

H, 8.3; N, 5.3. $C_{24}H_{44}CoN_2Si_4$ requires C, 54.25; H, 8.3; N, 5.25%).

[Co{CPh(SiMe$_3$)(C$_5$H$_4$N-2)}$_2$] 2. To a suspension of anhydrous $CoCl_2$ (1.22 g, 0.9 mmol) in ether (10 cm^3) was added dropwise a solution of [LiR^2(tmen)] (0.67 g, 1.9 mmol) in ether (20 cm^3) at room temperature. The reaction mixture was stirred for 6 h at room temperature and gave a dark red mixture. The red supernatant solution was filtered, concentrated *in vacuo*, followed by cooling at −30 °C to give complex **2** as red crystals (0.31 g, 63%), m.p. >180 °C (decomp.). Mass spectrum: *m/z* 539 (M^+, 23) and 300 (100%) (Found: C, 66.2; H, 6.7; N, 5.05. $C_{30}H_{36}CoN_2Si_2$ requires C, 66.75; H, 6.7; N, 5.2%).

[Co{CH(SiMe$_3$)(C$_9$H$_6$N-8)}$_2$] 3. To a slurry of $CoCl_2$ (0.26 g, 2.0 mmol) in ether (10 cm^3) at 0 °C was added dropwise a solution of [LiR^3(tmen)] (1.35 g, 4.0 mmol) in ether (40 cm^3). Stirring was continued for 20 h at ambient temperature. The dark green reaction mixture was filtered and the filtrate concentrated under reduced pressure. Upon cooling to −30 °C for 18 h, 0.68 g (70% yield) of dark green crystals of complex **3** was obtained by filtration, m.p. 183–185 °C (decomp.). Mass spectrum: *m/z* 487 (M^+, 9.7), 413 (37), 341 (100) and 199 (90%) (Found: C, 63.95; H, 6.6; N, 5.3. $C_{26}H_{32}CoN_2Si_2$ requires C, 64.05; H, 6.6; N, 5.75%). UV/VIS (thf): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 227 (5600), 273 (5400), 283 (5400), 440 (4100) and 665 (2800).

[{Co[CH(SiBu^{t}Me$_2$)(C$_5$H$_4$N-2)]$_2$}$_2$] 4. To a suspension of $CoCl_2$ (0.20 g, 1.5 mmol) in ether (20 cm^3) was added a solution of [{LiR^4(tmen)}$_2$] (0.97 g, 1.5 mmol) in ether (45 cm^3) at room temperature. After stirring for 10 min the dark green mixture was filtered and the filtrate allowed to stand at ambient temperature for 2 d. Dark green crystals of complex **4** were obtained (0.28 g, 40%), m.p. 169–170 °C (decomp.). Mass spectrum: *m/z* 471 ($\frac{1}{2}M^+$, 23), 357 (40) and 150 (100%) (Found: C, 60.7; H, 8.5; N, 5.85. $C_{48}H_{80}Co_2N_4Si_4$ requires C, 61.1; H, 8.55; N, 5.95%).

X-Ray crystallography

The crystals selected for study were mounted in glass capillaries and sealed under argon. Details of crystal parameters, data collection and structure refinement are summarised in Table 2. For complex **1** the structure was solved by the Patterson method at room temperature (294 K) using the computer program SHELXTL PLUS[21] on a DEC Mivro VAX II computer and refined by full-matrix least squares with anisotropic thermal parameters for the non-hydrogen atoms. The asymmetric unit comprises two independent half-molecules with the cobalt atoms on centres of symmetry. For **2**–**4** raw intensities were collected on a Rigaku AFC7R four-circle diffractometer at room temperature (294 K) and corrected for absorption using ψ-scan data. Patterson superposition yielded the positions of all non-hydrogen atoms, which were subjected to anisotropic refinement. All hydrogens were generated geometrically (C−H bonds fixed at 0.96 Å) and allowed to ride on their respective parent C atoms; they were assigned appropriate isotropic thermal parameters and included in the structure-factor calculations. Computations with refinement on *F* were performed using the SHELTXL PC program[22] on a PC 486 computer. Analytical expressions were incorporated.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/353.

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