

Synthesis and crystal structures of some cobalt halide derivatives containing alkyl or silanolato groups

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Abstract

The alkylcobalt halide $[(2-C_5H_4N)Me_2Si](Me_3Si)_2CCoCl)_2$ (**2**) and the lithium silanolatocobaltates $Li(THF)_2(\mu-Br)_2Co(\mu-OSiMe_3)_2Co(\mu-Br)_2Li(THF)_2$ (**4**) and $[LiBr\{Li(THF)\}_2\{CoBr(OSiMe_3)_3\}]_2$ (**5**) form centrosymmetrical halogen-bridged dimers in the crystalline state. Compound **4** shows bromide bridges between lithium and cobalt, and silanolato bridges between the cobalt atoms. Below 200 K there are significant antiferromagnetic interactions between the cobalt centres. Compound **5** crystallises in a novel structure in which two cubane-like fragments containing silanolato bridges are linked together through a Li_2Br_2 ring.

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1. Introduction

Organometallic compounds of the general type RMX , where M is a metal other than magnesium and X is halogen, are described as ‘Grignard analogues’. Some have been prepared from halides MX_2 and organolithium or -magnesium compounds, and used in situ as carbanion sources that are more selective than are Grignard reagents themselves. Although extensive structural data on Grignard reagents have been published [1], little information is available about structures of Grignard analogues. During our work on organometallic compounds containing the ligand $C(Si-$

$Me_3)_2(SiMe_2C_5H_4N-2)$, we have shown that compounds of the type RMX are formed by a range of elements. Those that have been isolated include the Grignard reagent $RMgX \cdot THF$ [2], the monomeric compounds $RMCl$ (where $M = Hg$ [3], Ge , Sn or Pb [4]), the dimeric halogen-bridged derivatives $(RZnBr)_2$ and $(RCdCl)_2$ [3] containing tetrahedrally coordinated metal centres, and $(RMCl)_2$, (where $M = Cr$ [2] or Pd [5]) with square planar coordination at the metal. Some dimeric compounds containing the related ligand $R' = C(SiMe_3)_2(SiMe_2NMe_2)$ viz $R'MBr$ ($M = Co$ [6] or Zn [7]) and $R'MnCl$ [6] have also been reported.

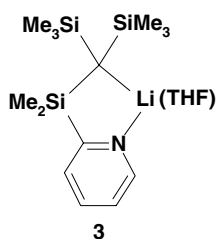
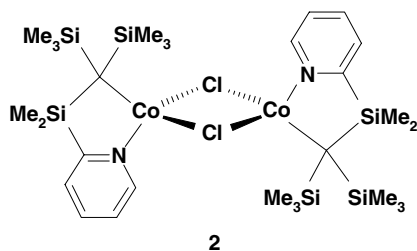
Despite the importance of organocobalt compounds as carbanion sources in nature few cobalt analogues of alkylmagnesium halides have been reported. Reactions of the dimeric compounds $(C_5Me_5CoX)_2$ ($X = Cl, Br$ or I) have been studied [8] but only the monomeric pyridine complex $C_5Me_5CoClPy$ [9] and a dimeric arylcobalt(II) bromide $[\{C_6H_3(C_6H_2Me_3-2,4,6)_2-$

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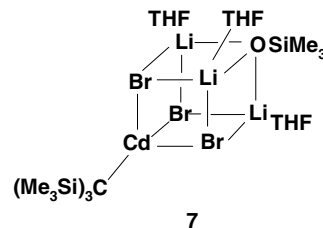
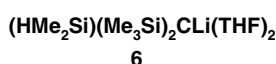
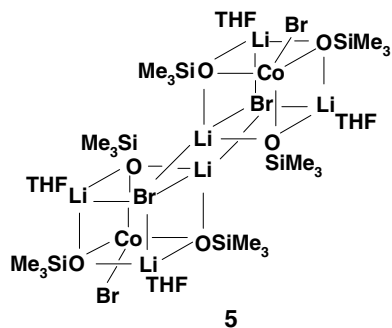
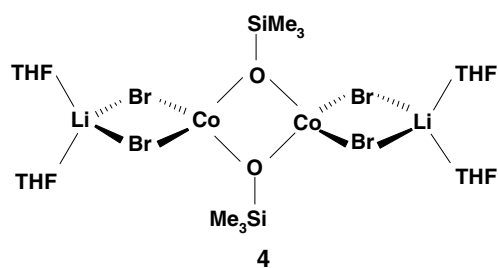
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¹ Died 22.02.04.

$2,6\text{-Co}(\text{THF})\text{Br}_2$ (**1**) [10] have been structurally characterised.



In this paper we describe the structure of the Grignard analogue $[\{(2\text{-C}_5\text{H}_4\text{N})\text{Me}_2\text{Si}\}(\text{Me}_3\text{Si})_2\text{CCoCl}]_2$, **2**, made from the reaction between CoCl_2 and the lithium derivative **3**. We also describe the structures of two silanolato derivatives, **4** and **5**, obtained from the reaction between CoBr_2 and the organolithium precursor **6** [11]. Compound **4** was subsequently made more simply from CoBr_2 , methyl lithium and hexamethyldisiloxane.

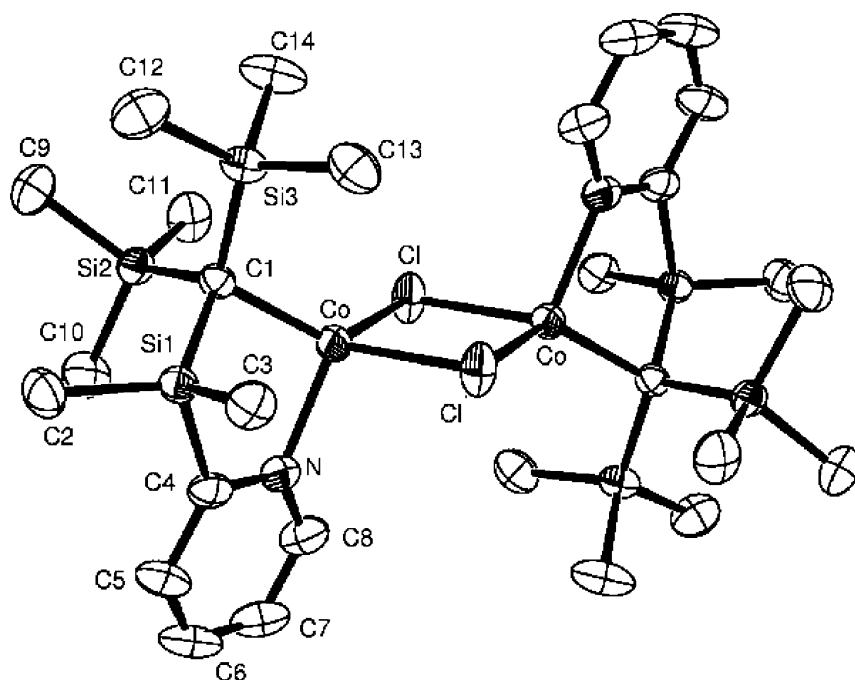


2. Results and discussion

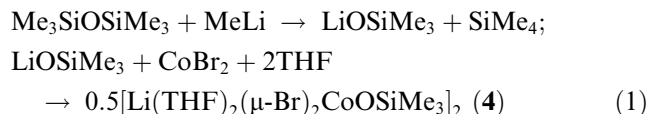
2.1. Syntheses

The reaction between the lithium derivative **3** and cobalt (II) chloride gave blue crystals of the alkylcobalt halide **2**. The sample isolated was not analytically pure (C, H and N values were about 3% low), but there is no doubt that compound **2** was formed since good quality X-ray data were obtained from a single crystal and peaks that could be assigned to dimeric molecules were observed in the mass spectrum. The molecular structure is shown in Fig. 1 and selected bond lengths and angles are given in Table 1. This work led us to consider whether analogous compounds $(\text{HMe}_2\text{Si})(\text{Me}_3\text{Si})_2\text{CCoX}$ could be obtained from cobalt halides and the lithium derivative **6**. We surmised that such compounds might be stabilised by $\text{Co}\cdots\text{H}\cdots\text{Si}$ interactions in the same way as compound **2** is stabilised by formation of the CoCSiCN metallacycle. The reaction between cobalt(II) bromide and **6** gave dark green crystals that proved to be difficult to purify. A solution in toluene became blue at 50°C and the crystals obtained when the blue solution was allowed to cool were shown by an X-ray structure determination to be the silanolato derivative **4**. The molecular structure is shown in Fig. 2 and selected bond lengths and angles are given in Table 2. In an attempt to suppress the conversion of the green into the blue product, the reaction was repeated with very careful exclusion of moisture and without heating the green crystals above room temperature. These were still unsuitable for an X-ray structure determination but a crystal from a minor product was identified as a second silanolato derivative **5**, in which Me_3SiO groups are incorporated into cubane cages that are linked by lithium halide bridges (Fig. 3). A trimethylsilylanolato derivative **7** was obtained about 20 years ago from CdBr_2 and $(\text{Me}_3\text{Si})_3\text{CLi}$ [12].

The origin of the oxygen in these silanolato products is not clear. It is possible that the CoBr_2 contained traces of $\text{CoBr}(\text{OH})$. Compound **4** could then be obtained by migration of the SiMe_3 group from carbon to oxygen (a process that is well known [13]) and rupture of the $\text{Co}\text{-C}$ bond. Alternatively the source of the oxygen could be the THF solvent. It has been shown that metal halides may catalyse the reaction between $(\text{Me}_3\text{Si})_3\text{CLi}$ and THF

Fig. 1. Molecular structure of **2**.

[14]. In the presence of traces of moisture the 5,5,5-tris(trimethylsilyl)pentoxymetal product may give $(\text{Me}_3\text{Si})_3\text{C}(\text{CH}_2)_4\text{OH}$, which rearranges with migration of SiMe_3 from carbon to oxygen [15] to give $(\text{Me}_3\text{Si})_2\text{CH}(\text{CH}_2)_4\text{OSiMe}_3$. This may then react with LiOH to give LiOSiMe_3 [12]. If LiOSiMe_3 is formed similarly from THF and **6**, it is possible to explain the formation of **4** and **5**. Compound **4** was obtained in good yield from cobalt bromide and hexamethyldisiloxane by the reaction sequence shown in Eq. (1). It is possible that compound **5** is formed similarly from different proportions of CoBr_2 and LiOSiMe_3 , but we have not yet examined whether this reaction can be used in a high-yield synthesis.



Compounds **2**, **4** and **5** form centrosymmetrical halide-bridged dimers in the crystalline state. Even though only compound **4** has been obtained as an analytically pure bulk sample, we report the structures of all three compounds now since the X-ray data are of good quality and there are few previous examples of derivatives containing the CoX_2Co ($\text{X} = \text{halogen}$) core.

Table 1
Selected bond lengths [Å] and angles [°] for $[\{(2\text{-C}_3\text{H}_4\text{N})\text{Me}_2\text{Si}\}(\text{Me}_3\text{Si})_2\text{CCoCl}]_2$ (**2**)

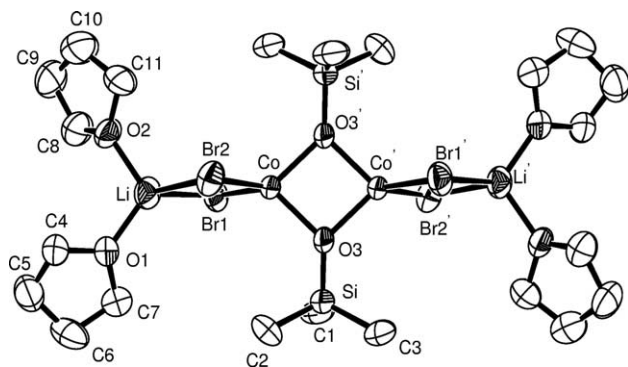
Co–N	2.043(4)	Si–Cl	1.870(4) ^a
Co–C	2.048(4)	Si–Me	1.877(5) ^a
Co–Cl	2.323(1)	Si–C4	1.911(5)
Co–Cl'	2.368(1)	C4–N	1.348(6)
Cl–Co–Cl'	91.20(4)	C–Co–Cl	126.82(12)
Co–Cl–Co'	88.80(4)	C–Co–Cl'	124.32(13)
Co–N–C4	111.5(3)	Si2–C–Co	107.2(2)
C4–Si–C1	103.55(19)	Si3–C–Co	112.6(2)
Si1–C–Co	96.20(19)	Cl–Si–Me	110.8(2)–117.9(2)
C–Co–N	96.43(16)	Me–Si–Me	103.2(3)–108.3(3)
N–Co–Cl	114.39(12)	Me–Si–C4	104.8(2), 108.8(2)
N–Co–Cl'	102.57(12)	Si–C–Si	110.4(2)–116.3(2)

^a Average value, with e.s.d.'s of individual measurements in parentheses. None differs significantly from the mean.

Table 2

Selected bond lengths [Å] and angles [°] for [Li(THF)₂(μ-Br)₂Co(OSiMe₃)₂]₂ (**4**) and [LiBr{Li(THF)₂{CoBr(OSiMe₃)₃}]₂ (**5**)

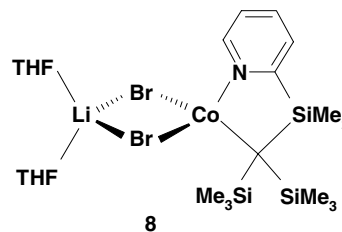
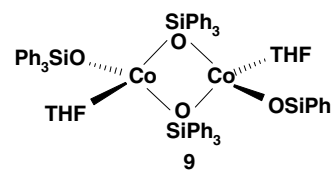
	4	5		5
Co–O	1.972(6) ^a	1.987(5) ^{a,b}	Li–O	1.984(15) ^{c,a,b}
Co–Br	2.4146(18) ^a	2.3539(14)	Li–Br	2.634(15) ^{a,b}
Li–Br	2.56(2) ^a	2.476(12) ^c		
Li–THF	1.87(2) ^a	1.869(15) ^a	Li1–Br2–Li1'	79.2(5) ^c
Si–O	1.615(7)	1.628(5)	Li–Br–Li	66.7(4) ^{a,b}
Si–Me ^a	1.854(13)	1.856(12)	Li2,3–Br–Li'	127.8(4), 130.8(5)
Co–O–Co	93.8(3)		Co–O–Li	87.0(4) ^{a,b}
O–Co–O	86.2(3)	92.9(2) ^{a,b}	Si–O–Li	121.8(5)–130.2(5)
O–Co–Br	115.0(2)–120.5(2)	123.21(16) ^a	Li–O–Li	93.7(6) ^{a,b}
Li–Br–Co	81.7(4), 83.1(5)		O–Li–THF	121.3(7)–129.5(8)
Br–Co–Br	101.55(6)		Br–Li–THF	106.5(7), 112.3(6)
Br–Li–Br'	93.5(6)	100.8(5) ^c	Br–Li–O	96.3(6)–100.8(6)
Br–Li–O	108.1(9)–118.4(10)	129.2(7)	O–Li–O	93.0(6) ^{a,b}
Si–O–Co	133.0(4), 131.2(4)	122.8(3)–127.8(3)	Br2–Li–O	98.6(6) ^{a,b}
THF–Li–THF	109.3(10)		Br2'–Li–O	128.2(7) ^a

^a Average value, with e.s.d.'s of individual measurements in parentheses.^b In cubane cage.^c In central Li₂Br₂ ring.Fig. 2. Molecular structure of **4**.

2.2. The alkylcobalt chloride **2**

Compound **2** is the first alkylcobalt(II) halide to be structurally characterised. The dimeric molecules are similar to those of the cadmium analogue described earlier [3], with the chelate ring bent at the Co...Si axis and the carbon atom C1 standing out of the CoNCSi plane. Cobalt(II) is a stronger Lewis acid than cadmium(II), so that, whereas the Cd–C is shorter than the Cd–N bond, the Co–N and Co–C distances are almost the same. The C–Co–N angle is wider and the C1–Si–C4 angle narrower than corresponding angles in the cadmium analogue. There is a significant difference between the Co–Cl [2.323(1) Å] and Co–Cl' [2.368(1) Å] bond lengths, as expected since the ligand is not symmetrically disposed about the CoNCSi plane. Both these distances are greater than those in the monomeric organocobalt halide C₅Me₅CoClPy [2.223(1) Å] [9]. The weak transfer of charge from cobalt to the CSi₃ core of the organic group [16] is shown

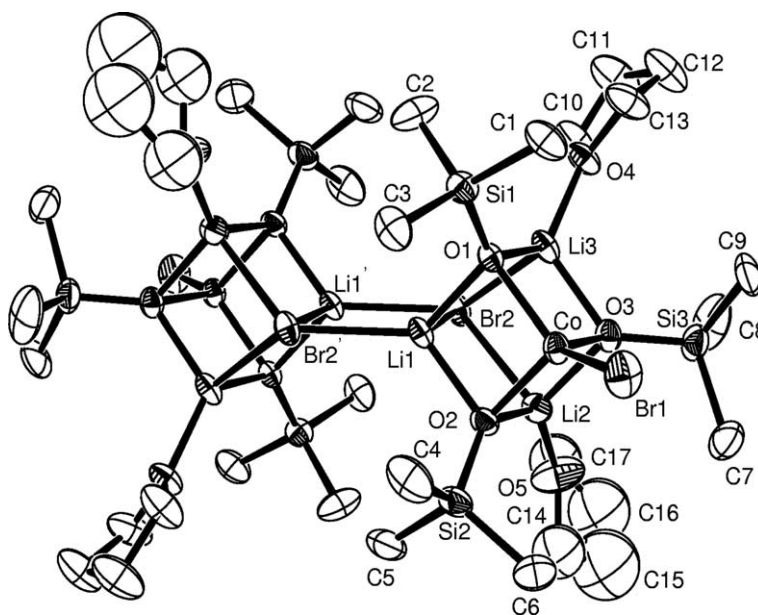
by the similarity between the average Si–C1 [1.870(4) Å] and Si–Me [1.877(5) Å] distances; the distances in the organolithium reagent **3** are Si–C1 1.819(4) Å and Si–Me 1.888(4) Å [2].

**8****9**

2.3. The silanolato derivatives **4** and **5**

The blue colour of the silanolato compounds **4** and **5** suggests that they contain tetrahedral Co^{II} and thus may be viewed as lithium cobaltates Li(THF)₂[CoBr₂(O–SiMe₃)] and Li₃(THF)₂[CoBr(OSiMe₃)₃]Br, respectively. This conclusion is confirmed by crystal structure determinations. Selected bond lengths and angles are given in Table 2.

The structure of the silanolato compound **4** (Fig. 2) shows bromide bridges between lithium and cobalt

Fig. 3. Molecular structure of **5**.

and oxygen bridges between cobalt atoms. The LiBr_2Co rings [mean Li–Br 2.56(2), Co–Br 2.4146(18) and Li–O 1.87(2) Å] are similar to those in the previously described cobaltate **8** [mean Li–Br 2.528(13), Co–Br 2.4532(11) and Li–O 1.903(13) Å] [2]. They are almost planar and the angles at bromine [81.7(4)° and 83.1(5)°] are narrower than 90°, as the transannular repulsions between Br are larger than those between Co atoms. Similarly in the planar CoO_2Co ring the angles at cobalt [86.2(3)°] are narrower than those at oxygen [93.8(3)°]. The CoBr_2Li rings are almost perpendicular to the CoO_2Co ring so that the $\text{O}_2\text{LiBr}_2\text{CoO}_2\text{CoBr}_2\text{LiO}_2$ framework has close to D_{2h} symmetry. The three-coordinate oxygen is almost planar (sum of angles 358°).

We have not found structural data for any other trimethylsilanolato-bridged cobalt(II) derivatives. The mean Co–O bond length [1.972(6) Å] is longer than those in the monomeric tris(3,5-diisopropylpyrazolyl)boratocobalt(II) derivatives $\text{Tp}^i\text{Pr}_2\text{CoOSiR}_3$ ($\text{Tp}^i\text{Pr}_2 = \text{HB}(\mu\text{-N}_2\text{C}_3\text{HPr}^i_2)_3$, R = Me or Ph) [1.834(3) and 1.846(7) Å, respectively] [17] and the Co^{I} derivative $\text{Co}(\text{PPh}_3)_3\text{OSiMe}_3$ [Co–O 1.862(4) Å] [18]. It is similar to the distance [mean 1.988(3) Å] between cobalt and bridging oxygen in the compound $[\text{Co}(\text{OSiPh}_3)_2(\text{THF})_2]$ (**9**) [19] or that in the tris(trimethylsilyl)silanolato derivative $[\text{Co}\{\text{OSi}(\text{SiMe}_3)_3\}_2]_2$ [mean 1.953(7) Å] [20], and falls between the longest bond to 4-coordinate cobalt [1.964(7) Å] and the shortest bond to 5-coordinate cobalt [1.982(7) Å] in the cobaltate $[\text{LiPy}_2\text{CoPy}(\text{OSiPh}_2\text{OSiPh}_2\text{O})_2\text{CoPyCl}]$ [1.917(8) to 2.067(7) Å] [21]. The Si–O and Si–Me bonds in **4** are normal.

The molar magnetic susceptibility χ_M of **4** was measured over the range 5–300 K. A plot of χ_M^{-1} against

T showed normal Curie–Weiss behaviour ($\theta = 12$ K) and a value of $\mu_{\text{eff}} = 4.31 \mu_B$ was calculated from the slope. A plot of $\chi_M T$ against T indicated antiferromagnetic interactions at low temperatures ($\mu_{\text{eff}} = 2.83 \mu_B$ at 5 K). As with other tetrahedral Co^{II} complexes, the contribution from temperature-dependent paramagnetism is small, but the value of the moment is significantly raised above the spin-only value by spin–orbit coupling. As the magnetic properties of only a few binuclear cobalt(II) complexes have been studied over a wide range of temperature, there are few data in the literature for comparison with those obtained for **4**. Compounds, e.g., **1** [10] and $[\text{C}_{10}\text{H}_6(\text{NMe}_2)_2\text{H}][\text{Co}_2\{\text{OOC}(\text{CO})_9\}_5]$ (**10**) [22], in which the $\text{Co}\cdots\text{Co}$ distance is ca. 3.5 Å, have moments of ca. $4.5 \mu_B$, in the range quoted for tetrahedral Co^{II} compounds generally (4.4–4.8 μ_B) [23]. [Compound **10** shows ferromagnetic interactions at low temperature.] The value of the moment in **4** ($\text{Co}\cdots\text{Co}$ 2.880 Å) is slightly greater than that in $[\text{Co}(\text{C}_9\text{H}_7\text{N})(\text{OOCPh})_2]_2$ ($\text{C}_9\text{H}_7\text{N} = \text{quinoline}$) [$\text{Co}\cdots\text{Co}$ 2.83 Å; $\mu_{\text{eff}} = 4.11 \mu_B$ at 293 K, $1.71 \mu_B$ at 98 K] [24]. In $[\text{Co}(\text{mes})_2]_2$ the mean $\text{Co}\cdots\text{Co}$ distance is 2.515(2) Å and the moment $3.80 \mu_B$ at 300 K [25]. Still lower moments (1.19–2.60 μ_B) are observed in the complexes $[\text{C}_5\text{Me}_5\text{CoX}]_2$, [8], and $[\text{Co}\{\text{CH}(\text{SiBu}^i\text{Me}_2)\text{C}_3\text{H}_4\text{N-2}\}_2]_2$, [26]. The compound $\text{Co}_2[(p\text{-MeC}_6\text{H}_4)\text{NNN}(\text{C}_6\text{H}_4\text{Me-p})_4]$ ($\text{Co}\cdots\text{Co}$ 2.265(2) Å) is diamagnetic with a Co–Co bond [27].

The centrosymmetrical structure of **5** (Fig. 3) contains two $\text{CoO}_3\text{Li}_3\text{Br}$ cubane cages, linked by Li–Br interactions. The Co–O3 bonds lie close to the plane defined by the Li_2Br_2 ring. This is rectangular with the intercage bonds [Li–Br 2.476(12) Å] slightly stronger than the intracage bonds [mean Li–Br 2.634(15) Å].

Many structures containing Li_4O_4 [28] and Li_4X_4 (X = halogen) [29,30] cages have been reported and Li–O bond lengths in the data base at the Cambridge Crystallographic Data Centre (CCDC) range from 1.847(11) to 2.11 Å (e.s.d. not given). Structures containing Co_4O_4 cages are less well known but a few examples of Co^{II} compounds, in which the metal is six-coordinate, have been reported [31], as well as some containing Co^{III} [32] and mixed valence systems [33]. As far as we are aware, **5** is the first compound containing a mixed Li–Co cubane cage to be structurally characterised.

The cubane cage has close to threefold symmetry about the Br1CoBr2 axis with no significant difference within the three Co–O, the six Li–O, or the three Li–Br bonds. The similarity between the Li–O [mean 1.984(15) Å] and Co–O [mean 1.987(5) Å] bond lengths in **5** appears to facilitate the formation of a mixed Li–Co cage. In the Co^{II} –O cages reported hitherto the Co–O bonds are somewhat longer [1.99–2.27 Å, e.s.d.'s not given] [31]. The Li–Br bonds [mean 2.634 Å] are similar to those in $[\text{LiBrOEt}_2]_4$ [2.54(2)–2.62(2) Å] [30], so the cage in **5** is elongated along the quasi-threefold axis, with Li–Br2–Li angles [mean 66.7(4)°] considerably narrower than the O–Co–O angles [92.9(2)°].

2.4. Conclusions

We have shown that the Grignard analogue **1** has a structure like those of the previously isolated chromium, palladium and zinc derivatives. We have isolated two compounds with empirical formulae $\text{LiOSiMe}_3 \cdot \text{CoBr}_2 \cdot 2\text{THF}$ (**4**) and $(\text{LiOSiMe}_3)_3 \cdot \text{CoBr}_2 \cdot 2\text{THF}$ (**5**). Compound **4** has been isolated in good yield but conditions for the formation of **5** have not yet been optimised. X-ray structural determinations indicate that **4** and **5** are lithium silanolatocobaltates, $\text{Li}(\text{THF})_2[\text{CoBr}_2(\text{OSiMe}_3)]$ and $\text{Li}_3(\text{THF})_2[\text{CoBr}(\text{OSiMe}_3)_3]\text{Br}$, respectively, the first examples of this class of compounds to be reported. It is likely that more derivatives of this type will be accessible from syntheses in which the $\text{CoBr}_2/\text{LiOSiMe}_3$ mole ratio is varied.

3. Experimental

Air and moisture were excluded as far as possible by use of Schlenk techniques with flame dried glassware and argon as blanket gas. Commercially available anhydrous cobalt(II) chloride and bromide were dried in vacuum (10^{-3} mmHg) at 70 °C and used without further treatment. The lithium compounds **3** and **6** were made as described previously [2,11]. The magnetic data on **2** were obtained by use of a Quantum Design SQUID MPMS5 magnetometer at 0.5 T with field cooling. A correction was made for diamagnetism [34].

3.1. $[\{(\text{2-C}_3\text{H}_4\text{N})\text{Me}_2\text{Si}\}(\text{Me}_3\text{Si})_2\text{CCoCl}\}_2$ (**2**)

A solution of **3** (2.41 mmol) in THF (20 mL) was added at –78 °C to a slurry of CoCl_2 (0.31 g, 2.41 mmol) in THF (20 mL). The mixture was stirred for 1 h and the deep blue solution was then allowed to warm to room temperature. Solvent was removed under vacuum and the residue was extracted with a mixture of hexane (50 mL) and toluene (50 mL). The green solution was filtered and the volume of the filtrate reduced to 20 mL to give blue crystals of **2** (0.80 g, 51%). MS: $m/z = 776$ (20) [M_2], 761 (35) [$\text{M}_2 - \text{Me}$], 703 (20, $\text{M}_2 - \text{SiMe}_3$), 668 (15, $\text{M}_2 - \text{SiMe}_3\text{Cl}$), 376 (50), 353 (95, $\text{M} - \text{Cl}$), 316 (85), 294 (100) [R], 266 (50), 248 (50), 221 (95) [R – SiMe_3] 164 (35), 136 (65), 73 (90).

3.2. The reaction between

$(\text{HMe}_2\text{Si})(\text{Me}_3\text{Si})_2\text{CLi}(\text{THF})_2$ and CoBr_2

A solution of **6** (1.69 g, 4.59 mmol) in THF (20 mL) at –78 °C was added to a suspension of CoBr_2 (1.006 g, 4.59 mmol) in THF (20 mL) also at –78 °C. The mixture was left to warm up slowly overnight and the solvents were removed. The dark green residue was extracted with toluene, but when the extract was heated to 50 °C the colour became blue. The toluene was removed and the residue extracted with hexane (50 mL). This solution was kept at –30 °C to give blue crystals, shown to be $[\text{Li}(\text{THF})_2(\mu\text{-Br})_2\text{Co}(\text{OSiMe}_3)]_2$ (**4**), m.p. 145 °C. Anal. Calc. for $\text{C}_{22}\text{H}_{50}\text{Br}_4\text{Co}_2\text{Li}_2\text{O}_6$: C, 30.65; H, 5.85. Found: C, 30.02; H, 6.00%. This experiment was repeated with the same quantities of starting materials as before but after removal of solvent the residue was extracted with hexane, without heating above room temperature. The volume of the extract was reduced to 10 mL and kept at –30 °C to give two kinds of crystals. Those of the green major product were unsuitable for an X-ray structure determination, but the minor product, which gave blue crystals, was identified as the trimethylsilanolato compound $[\text{CoLi}_3(\text{THF})_2\text{Br}_2(\text{OSiMe}_3)_3]$.

3.3. Independent synthesis of $[\text{Li}(\text{THF})_2(\mu\text{-Br})_2\text{Co}(\text{OSiMe}_3)]_2$ (**4**)

A solution of LiMe (4.8 mmol) in Et_2O (3 mL) was added dropwise to a solution of $(\text{Me}_3\text{Si})_2\text{O}$ (1.0 mL 4.72 mmol) in THF (20 mL) and the mixture was heated under reflux overnight. This solution was then added to a mixture of CoBr_2 (1.0 g, 4.59 mmol) in THF (20 mL) at room temperature to give a deep blue solution, which was stirred for 3 h, then filtered. The solvents were removed from the filtrate under vacuum and the residue was recrystallized from hexane to give blue crystals of **4** (Yield 2.55 g, 60%).

Table 3
Crystal data for compounds **2**, **4** and **5**

	2	4	5
Chemical formula	C ₂₆ H ₅₆ Cl ₂ Co ₂ NSi ₃	C ₂₂ H ₅₀ Br ₄ Co ₂ Li ₂ O ₆ Si ₂	C ₃₄ H ₈₆ Br ₄ Co ₂ Li ₆ O ₁₀ Si ₆
Formula weight	655.7	918.2	1302.7
<i>T</i> (K)	173(2)	173(2)	223(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i> No. 14	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	9.5484(3)	10.8412(8)	10.1872(4)
<i>b</i> (Å)	9.1992(3)	13.4162(11)	21.6882(9)
<i>c</i> (Å)	23.0809(8)	13.2827(11)	14.9880(6)
β (°)	96.488(2)	93.025(4)	91.645(3)
<i>U</i> (Å ³)	2014.4(1)	1929.2(3)	3310.1(2)
<i>Z</i>	2	2	2
μ (mm ⁻¹)	1.06	5.09	3.06
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.058, 0.143	0.063, 0.145	0.065, 0.135
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.063, 0.146	0.095, 0.161	0.115, 0.155
Measured/independent reflections/ <i>R</i> _{int}	14255/3479/0.057	6225/2338/0.101	16020/4535/0.094
Reflections with <i>I</i> > 2 σ (<i>I</i>)	3143	1685	2927

3.4. Crystallography

Crystal data for **2**, **4** and **5** were collected on a Kappa CCD diffractometer and absorption corrections were made by MULTISCAN. Full-matrix least-squares refinement was by the SHELXL-97 programs. Non-hydrogen atoms were isotropic and hydrogen atoms were refined in riding mode. Further details are given in Table 3.

4. Supplementary material

Crystallographic data are available in files CCDC Nos. 250007–250009. These can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK: fax +441223 336033; e-mail deposit@ccdc.cam.ac.uk.

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