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Preliminary communication

Cyclic cobaltadisiloxane compounds. Crystal structures of a pyridinolithium [bis(cyclosiloxy)cobalt] cobalt chloride and a bis(tetramethylethylenediaminolithium)-bis(cyclosiloxy)cobaltate

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Abstract

Reaction of $CoCl_2$ and dilithio tetraphenyldisiloxanediolate $Ph_4Si_2O(OLi)_2$ in tetrahydrofuran (THF) followed by removal of the THF, extraction of the residue with toluene, and treatment of the toluene solution with tetramethylethylenediamine (TMEDA) or pyridine (Py) has given the compounds bis [tetramethylethylenediaminolithium]-μ-[octaphenyltetrasiloxyspiro[5.5]cobalt], $[TMEDALi]_2$-μ-$[\overline{Co(OSiPh_2OSiPh_2O)}_2]$ and bispyridinolithium-μ-[octaphenyltetrasiloxyspiro[5.5]pyridinocobalt]-μ-pyridinocobalt chloride, $[Py_2Li]$-μ-$[\overline{Co(OSiPh_2OSiPh_2O)}_2]$-μ-CoPyCl. Both compounds have been characterized by X-ray crystallography.

We recently reported [1] the formation of the compound *cis*-$Py_2[\overline{Ti(OSiPh_2(OSiPh_2)_2O)}_2]$ from $TiCl_4$ and $Ph_4Si_2O(OLi)_2$ (**1**) in a reaction involving chain expansion of the siloxane. A similar chain expansion was not observed in the case of zirconium [2]. We have now extended our studies to other transition metals and report here on the products obtained from reactions between **1** and $CoCl_2$ in 1/1 molar ratio, in the presence of (a) tetramethylethylenediamine (TMEDA), and (b) pyridine (Py). These reactions led to the isolation of products that differed in an unexpected manner in their composition.

Results and discussion

A solution of $Ph_4Si_2O(OLi)_2$ and $CoCl_2$ (1/1) in tetrahydrofuran (THF) was stirred at 0 °C for 12 h, and after removal of THF the residue was extracted into toluene. On addition of TMEDA to the toluene extracts the olive-green compound $[TMEDALi]_2$-μ-$[\overline{Co(OSiPh_2OSiPh_2O)}_2]$ (**2**), m.p. 266–269 °C, was immediatelty

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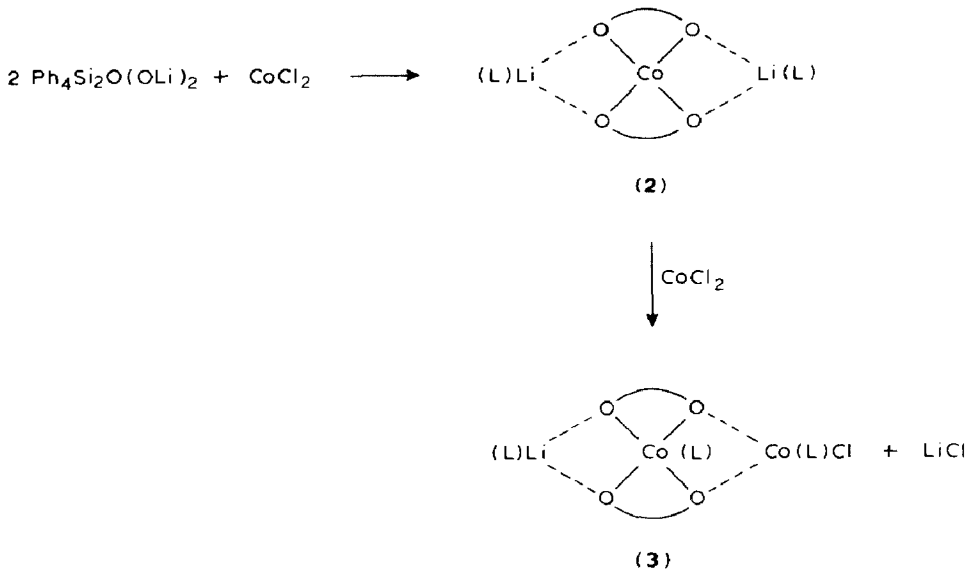

Scheme 1. $\widehat{\mathrm{O\quad O}}$ = OSiPh$_2$OSiPh$_2$O; L = THF (complex not isolated), TMEDA, or Py.

deposited (and isolated in yields of ca. 36–45%). Some of the complex CoCl$_2$ · TMEDA remained in solution and was subsequently identified. In contrast addition of pyridine to the toluene extract initially gave deposit of some pyridinated cobalt

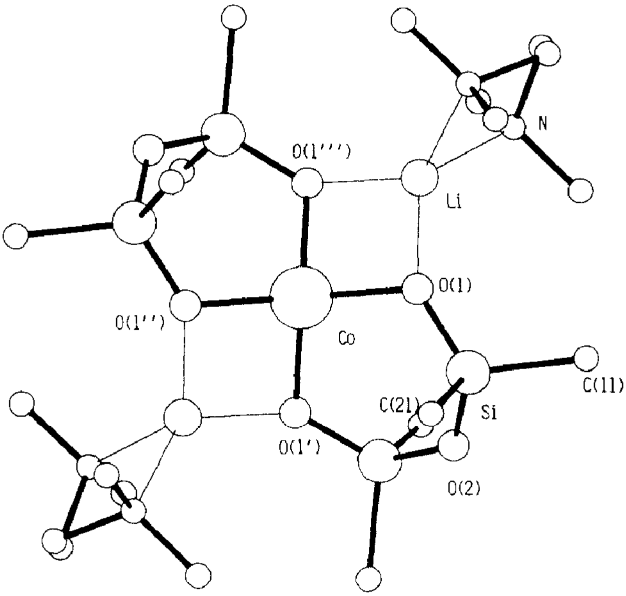

Fig. 1. Structure of [TMEDALi]$_2$-μ-[$\overline{\mathrm{Co(OSiPh_2OSiPh_2O)}}_2$] (**2**), (phenyl carbon atoms omitted for clarity); selected bond lengths (Å) and angles (°) Co(1)–O(1) 1.974(4), O(1)–Si(1) 1.600(5), O(2)–Si(1), 1.641(4), Li–N 2.150(5), Li–O(1) 1.940(9), C(11)–Si(1) 1.886(5), C(21)–Si(1) 1.895(5), O(1)–Co(1)–O(1′) 104.1(2), O(1)–Co(1)–O(1″) 137.2(1) O(1)–Co(1)–O(1‴) 91.3(2), O(2)–Si(1)–O(1) 110.5(2), Si(1)–O(2)–Si(1) 132.7(2), Si(1)–O(1)–Co(1) 120.2(2), O(1)–Li(1)–O(1) 93.3(5), C(11)–Si(1)–O(1) 114.6(2), C(11)–Si(1)–O(2) 104.8(2), C(21)–Si(1)–O(1) 110.5(2), C(21)–Si(1)–O(2) 108.4(2).

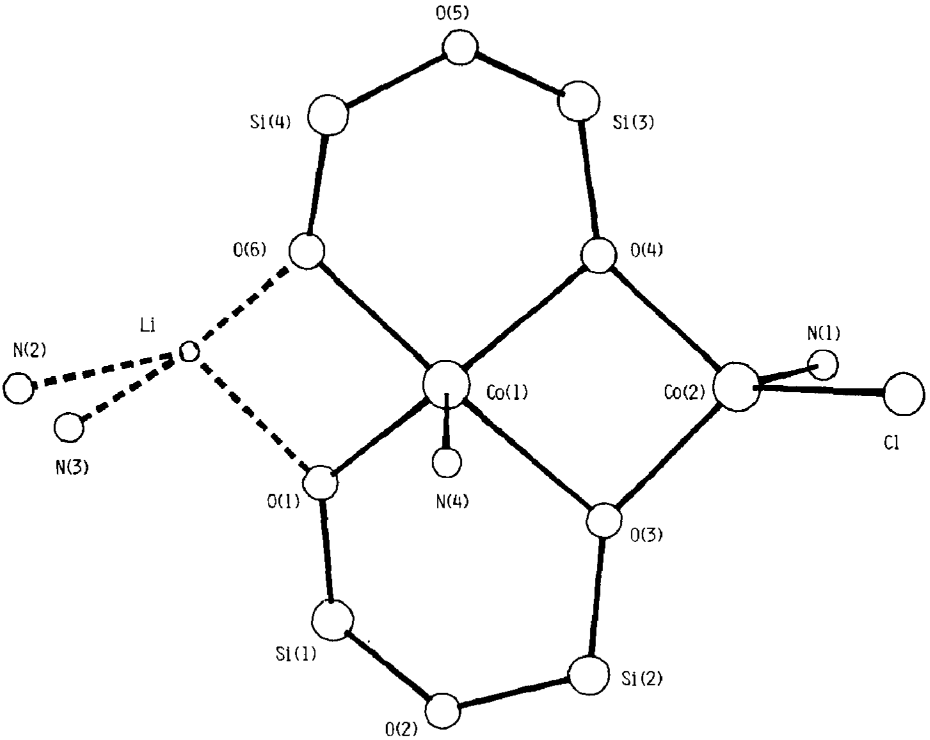

Fig. 2. Structure of (μ-LiPy2)-Py$\overline{\mathrm{Co(OSiPh_2OSiPh_2O})_2}$-$\mu$-CoClPy·0.5 toluene·0.5 pyridine (**2**) (toluene, phenyl and pyridine carbon atoms omitted for clarity) selected bond lengths (Å) and angles (°): Co(1)–O(1) 1.982(7), Co(1)–O(3) 2.198(7), Co(1)–O(4) 2.067(7), Co(1)–O(6) 2.014(7), Co(1)–N(4) 2.098(12), Co(2)–O(3) 1.917(8), Co(2)–O(4) 1.964(7), Co(2)–Cl 2.249 (5), Co(2)–N(1) 2.051(10), Li–O(6) 1.863(19), Si(1)–O(1) 1.592(8), Si(1)–O(2) 1.642(8), Si(2)–O(2) 1.649(8), Si(2)–O(3) 1.597(8), Si(3)–O(4) 1.620(8), Si(3)–O(5) 1.612(8), Si(4)–O(5) 1.648(8), Si(4)–O(6) 1.589(8); Co(1)–O(1)–Li 90.53(3), Co(1)–O(6)–Li 91.4(6), Co(1)–O(3)–Co(2) 94.3(3), Co(1)–O(4)–Co(2) 97.1(3), O(1)–Co(1)–O(6) 86.1(3), O(3)–Co(1)–O(4) 137.8(2), N(4)–Co(1)–O(1) 110.0(4), N(4)–Co(1)–O(6) 98.6(4), N(4)–Co(1)–O(3) 87.8(4), N(4)–Co(1)–O(4) 111.0(4), O(3)–Co(2)–O(4) 88.9(3), O(3)–Co(2)–Cl 119.8(3), O(3)–Co(2)–N(1) 113.4 (4), O(4)–Co(2)–Cl 119.3(3), O(4)–Co(2)–N(1) 110.4(4), Cl–Co(2)–N(1) 104.8(3).

dichloride and after filtration and concentration of the solutions the navy blue compound [$\mathrm{Py_2Li}$]-μ-[$\overline{\mathrm{Co(OSiPh_2OSiPh_2O})_2}$]-$\mu$-CoPyCl (**3**), m.p. 144–145 °C separated (37% based on cobalt). The products obtained were probably formed in the manner indicated in Scheme 1.

It is likely that species **2** and **3** with L = THF, though not isolated, are present (probably in equilibrium) in the toluene solutions of the reaction mixture, but only species **2** was isolated on subsequent addition of TMEDA and only **3** when Py was used. The structures determined for compounds **2** and **3** are shown in Fig. 1 and 2.

Crystallography. Data were recorded with a CAD4 diffractometer operating in the $\omega/2\theta$ scan mode. The structures were solved by standard heavy atom techniques and refined by least squares (with phenyl groups treated as rigid hexagons (C–C 1.395 Å) and with inclusion of hydrogen atoms at fixed positions (C–H 0.96 Å)).

Crystal data for 2. $\mathrm{C_{60}H_{72}CoLi_2N_4O_6Si_4}$, $M = 1130.388$, Tetragonal, a, b 18.575(2), c 34.468(3) Å, $\alpha = \beta = \gamma = 90°$, U 11892.52 Å^3, space group $I4_1/acd$, $Z = 8$, $D_c = 1.26$ g cm^{-3}, λ(Mo-K_α) 0.71069 Å, μ 4.155 cm^{-1}, 2623 unique reflections measured giving 1745 with ($F > 3\sigma F_0$). $R = 0.0581$, $R_w = 0.0480$ for 181 parameters.

Crystal data for 3. $C_{68}H_{60}Si_4O_6N_4Co_2Cl \cdot 0.5C_5H_5N \cdot 0.5C_7H_8$, $M = 1386.94$, Monoclinic, a 25.185(7), b 13.156(9), c 21.947(4) Å, β 95.66(2)°, U 7236.37 Å^3, space group $P2_1/a$, $Z = 4$, $D_c = 1.27$ g cm^{-3}, λ(Mo-K_α) 0.71069 Å, μ 5.64 cm^{-1}, Data recorded as for **1** above; 7759 unique reflections measured 3935 with ($F > 4\sigma F_0$). $R = 0.06231$, $R_w = 0.0574$ for 384 parameters.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Data Centre. The cobalt atom in compound **2** lies on a site of 222 (D_2) symmetry. The two cobaltadisiloxane rings of the central spiro section are twisted by 55.14(3)° with respect to each other. The distorted (i.e. flattened) tetrahedron around the Co atom is bridged by lithium along the shorter pair of open edges. In compound **3** the central chelated cobalt atom has distorted square pyramidal geometry in which the apical site is occupied by a pyridine group. The basal chelating oxygen atoms are also bridged on one side by lithium and on the other by the second cobalt atom with both bridging metal atoms in distorted tetrahedral environments.

These are the first examples of simple cyclic cobaltadiloxane systems (the polymeric ionic compound $Na_6[(PhSiO_{1.5})_{22}Co_3O_6] \cdot 7H_2O$ was recently reported) [3]. The Co–O(Si) bond lengths in compound **2** are similar to the bridging Co–O distances reported for the compound $[Co(OSiPh_3)_2THF]_2$ [4] but the bonds in compound **3** are slightly longer. The Si–O(Co) and Si–O(Si) bond lengths are similar in compounds **2** and **3**. The bond angles within the central ring systems are also similar, except that one of the sets of *trans*-O–Co–O angles in **3** is widened to 173°, probably to accomodate the pyridine group. Studies of the spectroscopic and chemical properties of these compounds are in progress.

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