

Synthesis, Crystal Structure and Homogeneous Catalytic Activity towards Ethylene Polymerisation of the Spirocyclic Chromium(II) Siloxane

$[\text{Cr}\{\overline{(\text{OSiPh}_2\text{OSiPh}_2\text{O})-\mu\text{-Na}(\text{thf})_2\}_2] (\text{thf} = \text{tetrahydrofuran})$

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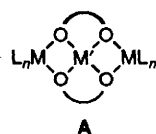
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The chromium(II) compound $[\text{Cr}\{\overline{(\text{OSiPh}_2\text{OSiPh}_2\text{O})-\mu\text{-Na}(\text{thf})_2\}_2] \mathbf{1}$ has been isolated and structurally characterised; in combination with trimethylaluminium, it is a precatalyst for the polymerisation of ethene to linear polyethylene.

In a programme aimed at establishing a range of structural types for compounds with metallasiloxane rings based on linked R_2SiO_2 groups we discovered that the structural type **A** is kinetically stable towards rearrangement to cyclic siloxanes and have already reported on examples having Co^{II} **2** and Cu^{II} **3** at the spiro sites.¹ We now report on the orange crystalline sodium ion-bridged compound **1** with Cr^{II} at the spiro site obtained as indicated Scheme 1 using standard Schlenk techniques.

Crystals suitable for X-ray crystallography were obtained from concentrated toluene solutions of **1** at room temperature. The structure of **1** is shown in Fig. 1† along with selected bond lengths and angles. The siloxane rings are coplanar and the geometry at the chromium site is consequently square planar. This contrasts with the related lithium ion-bridged compounds **2** and **3** where the ring twists are 75 and 50° respectively and the geometries at the spiro sites distorted tetrahedral and flattened tetrahedral. The siloxane framework is thus flexible enough to accommodate a range of metal stereochemistries at the spiro atom sites. The Si–O–Si angles are relatively small and this probably indicates some degree of ring strain. The angles at the silicon atoms are close to regular tetrahedral values. To our knowledge no other Cr^{II} compounds with siloxy ligands have been structurally characterised although related alkoxide chemistry is well established.²



- 1** $L_nM = (\text{thf})_2\text{Na}$, $M = \text{Cr}$
2 $L_nM = (\text{tmeda})\text{Li}$, $M = \text{Co}$
3 $L_nM = (\text{py})_2\text{Li}$, $M = \text{Cu}$



Scheme 1 tmeda = tetramethylethylenediamine; py = pyridine. Conditions: toluene, thf (–NaCl).

Data for **1**: m.p. 249–256 °C; $\lambda_{\text{max}}/\text{nm}$ 660 (ϵ 60) and 460 (ϵ 50); $\mu_{\text{eff}} = 3.97 \mu_B$

† Crystal Data for compound **1**: $\text{C}_{64}\text{H}_{60}\text{O}_{10}\text{Si}_4\text{Na}_2\text{Cr}$, $M = 1199.492$, triclinic, $a = 13.008(3)$, $b = 13.289(5)$, $c = 22.106(3) \text{ \AA}$, $\alpha = 83.70(2)$, $\beta = 81.70(1)$, $\gamma = 60.94(2)^\circ$, $U = 3301.80(1.65) \text{ \AA}^3$, $Z = 2$, space group $P1$, $D_c = 1.206 \text{ g cm}^{-3}$; λ (Mo-K α) = 0.71069 \AA , $\mu = 3.025 \text{ cm}^{-1}$, $F(000) = 1252$. Measurements were made on a crystal sealed in a glass capillary under nitrogen using a CAD4 diffractometer operating in the ω – 2θ scan mode. The structure was solved by standard heavy atom techniques and refined by least squares. A total of 9502 reflections were measured of which 9179 were unique and 5263 ‘observed’ ($F_o > 3\sigma F_o$). The phenyl rings were treated as rigid regular hexagons (C–C 1.395 \AA), with hydrogen atoms included at fixed distance (C–H 0.96 \AA). $R = 0.068$, $R_w = 0.066$ for 656 refined parameters.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Heterogeneous silica-supported chromium catalysts for the polymerisation of olefins have long been known but are still poorly defined. The most notable of these are the Phillips chromium catalyst, derived essentially from CrO_3 on $\text{SiO}_2/\text{Al}_2\text{O}_3$ and the Union Carbide chromium catalyst from $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}^{\text{II}}$ on SiO_2 .³ There is some evidence to suggest that the active site in the latter case is a Cr^{II} species. In addition to these heterogeneous systems a chromium(VI)-containing polyhedral oligometallasilsesquioxane in combination with AlMe_3 was also found to be an active precatalyst for the polymerisation of ethylene.⁴

In view of the activity of the above-mentioned chromium-containing systems we investigated olefin polymerisation in the presence of compound **1**. Orange toluene solutions of compound **1** (10^{-4} mol in 20 cm^3) failed to give any polymer in the presence of ethylene (3 bar) (1 bar = 10^5 Pa). On addition of trimethylaluminium (12 equiv.) the solutions of **1** turned green and when charged with ethylene (used as purchased) to 3 bar, the solution gelled after 2 h. The differential scanning calorimetry melting curve of the polymer formed showed the onset of melting occurred at 129 °C. The polymer was too insoluble in 1,2-dichlorobenzene for reliable average

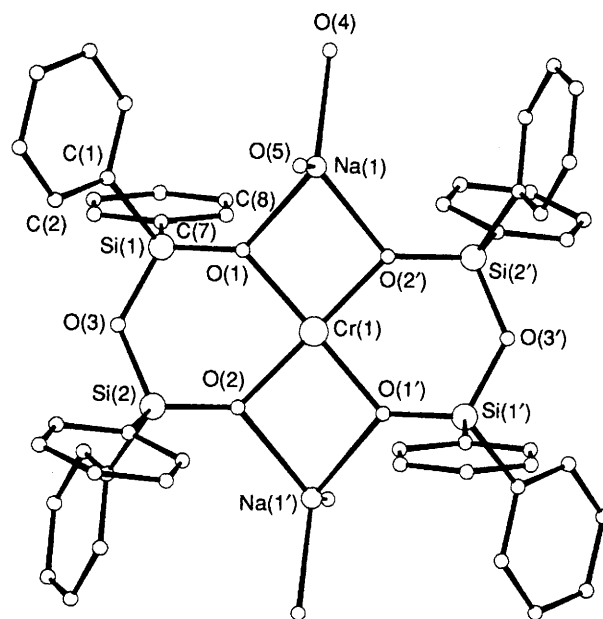


Fig. 1 Molecular structure of one of the molecules **1** in the asymmetric unit (thf groups omitted for clarity). Selected bond lengths (\AA) and angles ($^\circ$) are: Cr(1)–O(1) 1.987(7), Cr(1)–O(2) 1.985(6), Si–O(1) 1.589(6), Si–O(Si) av. 1.637(7), Na–O(Si) av. 2.226(7), Na–O(thf) av. 2.271(8); O(1)–Cr(1)–O(1') 180.0(3), O(2)–Cr(1)–O(2') 180.0(3), O(1)–Cr(1)–O(2) 93.2(3), O(1)–Cr(1)–O(2') 86.8(3), Cr(1)–O(1)–Na(1) 96.5(4), Cr(1)–O(2)–Na(1) 96.9(4), O(1)–Na(1)–O(2') 75.7(3), O(4)–Na(1)–O(5), 110.9(5), O(4)–Na(1)–O(1) 123.9(4), Si–O–Cr(1) av. 131.3(3), Si(1)–O(3)–Si(2) 128.0(4), O(1)–Si(1)–O(3) 112.8(4), O(2)–Si(2)–O(3) 111.9(3), C(1)–Si(1)–O(3) 106.6(3), C(1)–Si(1)–O(1) 110.5(4), C(1)–Si(1)–C(7) 109.4(3).

molecular mass determination. Catalytic activity was rather low [10^2 g polyethylene (g Cr) $^{-1}$ h $^{-1}$] and this may in part be due to the extreme air- and moisture-sensitivity of the Cr^{II} solutions.

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