Preparation, Characterization and Crystal Structure of the Dinuclear Chromium Complex $\{(C_5H_5)Cr[\mu\text{-}CH_2SiMe_2{-}N(SiMe_3)]\}_2$

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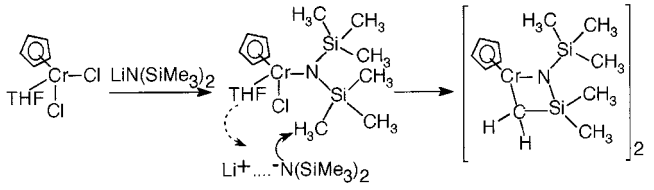
The complex $\{(C_5H_5)Cr[\mu\text{-}CH_2SiMe_2{-}N(SiMe_3)]\}_2$ (**1**) was obtained by reacting lithium bis(trimethylsilyl)amide (**2**) with $CpCrCl_2{\cdot}THF$. A single crystal X-ray diffraction study revealed that the complex is dimeric with two [μ-CH_2SiMe_2–$N(SiMe_3)$] bridging units and a *cis* configuration of the two cyclopentadienyl ligands. Bond distances and angles are compared with those observed in $[(C_5Me_5)Cr^{I\text{-}I}Me]_2$ and $[(C_5H_5)Cr^{III}Me_2]_2$.

Introduction

Chromium-based heterogeneous catalysts have a long-standing use in the commercial polymerization of small olefins. The search for soluble analogues has led Theopold et al. to synthesize a variety of low valent chromium complexes.[1] In this context, different permethylated cyclopentadienyl complexes of Cr^{II} and Cr^{III} have been fully identified as monomeric and/or dimeric species,[2] revealing new structures and reactivities towards olefins.[3]

We now report the first example of a cyclopentadienyl complex of chromium(III) containing a bidentate alkyl-amido ligand. Although amido derivatives of Si, Ti, V, Fe and Cr have been reported,[4] amide complexes of chromium are rare and, to date, never simultaneously ligated to a Cp ligand.

The new complex was readily obtained from $CpCrCl_2{\cdot}THF$ (or $[CpCrCl_2]_n$) and $LiN(SiMe_3)_2$, (**2**). Reaction of $CpCrCl_2{\cdot}THF$ with three equivalents of $LiN(SiMe_3)_2$ in THF produced a dark violet solution from which, instead of the expected complex $[(C_5H_5)Cr(NSiMe_3)_2]$, an unprecedented dimeric complex $\{(C_5H_5)Cr[\mu\text{-}CH_2SiMe_2{-}N(SiMe_3)]\}_2$ **(1)** (Scheme 1) was isolated as a crystalline material in 55% yield after purification.



Scheme 1. Synthesis of di-Cr^{III} complex **1**

At this preliminary stage, complex **1** appears to result from a C–H σ bond metathesis similar to that described by Berno et al. for a similar vanadium complex,[5] the deprotonation being performed by $LiN(SiMe_3)_2$ which acts as a base rather than as a nucleophile.

The ^1H NMR spectrum of paramagnetic **1** displays broadened, intense absorptions which are characteristic of the CH_3 groups [δ = 0.62 (*C20, C21* and *C22*, 9 H); δ = 2.28 (s, 3 H), −1.79 (s, 3 H), *C 19, C 18*; δ = 27.2 (μ-CH_2)]. The ^{13}C NMR spectrum displays three broad absorptions at 46.3, 35.1 and 2.7 ppm and a doublet at 89 ppm. The FTIR spectrum shows the characteristic absorptions of the Si–N and Si–CH_3 stretching at 850 and 1250 cm^{-1}.

The molecular structure of **1** has been unambiguously established by an X-ray structure analysis.

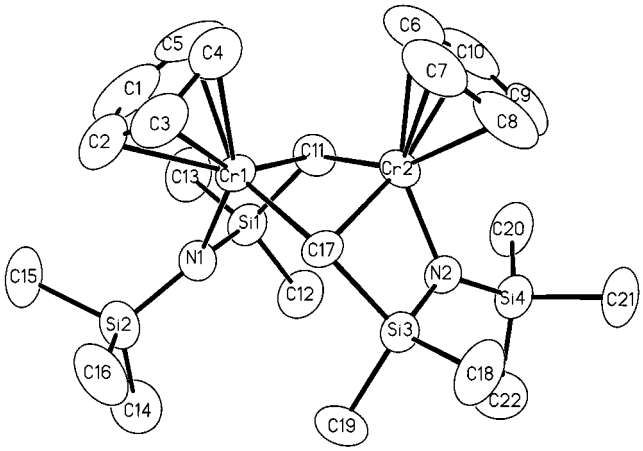


Figure 1. X-ray structure of **1** with atom labelling scheme

Figure 1 shows the geometry and the atom labelling scheme for the molecule. It appears indeed that **1** is a dimer consisting of two $[(C_5H_5)Cr]$ moieties bridged by two [μ-$CH_2SiMe_2{-}N(SiMe_3)$] units. The two Cp ligands are unexpectedly in a *cis* arrangement. Selected bond lengths and

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angles are reported hereafter. The two bridging units form two almost p1anar (within 0.10 Å) four-membered metallaazasilacyclobutane rings (an example where a cyclobutane ring is made up of four different elements!), and form the dimeric unit by sharing the CH_2 groups with the two Cr atoms. The two bridging carbon atoms are almost symmetrically placed between the two Cr atoms [Cr1−C11 = 2.163(5), Cr1−C17 = 2.221(5), Cr2−C11 = 2.217(5), Cr2−C17 = 2.172(5) Å] but are significantly longer than typical Cr^{III}−C alkyl σ-bonds (2.09 Å).[6] The coordination about each chromium has approximate C_{3v} symmetry with the center of the Cp ring at the apex and the bridging methyl carbons and the nitrogen at the base of a distorted tetrahedron. The two tetrahedrons are joined by sharing a C−C edge. The Cr−C bond lengths of C_5H_5Cr are in the range expected for η^5-coordinated cyclopentadienyl rings. The distortion of the coordination polyhedrons is reflected by the angles subtended at the chromium atoms. While the C−Cr−C and N−Cr−C angles are less than 109°, the Cp−Cr−C and Cp−Cr−N angles are nearly identical but greater than 109°. The Cr−C (bridging) mean distance of 2.193(5) Å is in agreement with the mean value of 2.186 Å observed in $[(C_5Me_5)Cr^{II}Me]]_2$ [1b] and 2.188 Å observed in $[(C_5H_5)(CH_3)Cr^{III}Me]_2$.[2b] The chromium−chromium distance of 2.662(2) Å is fairly short and close to the value (2.606 Å) reported for the dimeric complex $\{(C_5H_5)(CH_3)Cr^{III}Me\}_2$.[2b] In light of the theoretical MO-analysis of metal−metal bonding in related paramagnetic chromium(III) complexes by Janiak et al.,[6] such short distances are consistent with metal−metal interactions, although we do not care to speculate about the exact bond order or bond strength of this interaction. This Cr−Cr bond remains, however, considerably longer than that of a Cr^{III} bis(μ-alkylidene) complex (2.262 Å) recently described by Theopold et al., the shortest metal−metal distance found so far in Cr^{III} alkyls.[7]

Complex **1** alone is inactive in the polymerization of ethylene and addition of an alkylaluminium is required to initiate ethylene polymerization. Polymerization results will be reported in due course.

Experimental Section

All reactions were carried out under an atmosphere of purified nitrogen. Solvents were distilled, dried and kept under nitrogen before use.

$(C_5H_5)CrCl_2\cdot THF$: Finely divided $CrCl_3\cdot THF_3$ (10 g) was poured into 200 mL of dry deoxygenated THF. A solution of CpNa in THF (1 M, 20 mL) at 0° C was added to this suspension and the resulting green solution stirred for 1 hour at 0 °C. The solution was then warmed to 20 °C and kept for one hour at that temperature. The green solution turned blue. The solution was then taken to dryness under low pressure to yield a blue product. This dark solid was washed with pentane (100 mL) at 20 °C to yield a blue, hygroscopic powder after drying under vacuum at 30 °C. Yield 95%.

$\{(C_5H_5)Cr[\mu\text{-}CH_2SiMe_2\text{−}N(SiMe_3)]\}_2$ (1): $(C_5H_5)CrCl_2\cdot THF$ (0.1 g) was dissolved in 50 mL of purified THF under an inert atmosphere. To this solution was added a solution of $LiN(SiMe_3)_2$ (1 M, 2.7 mL) in THF at 10 °C. The reaction mixture was then stirred at 20° C for 4 hours after which the solution was taken to dryness under low pressure, yielding a black solid. This dark product was extracted with pentane (20 mL) and then with toluene (2 × 30 mL). The combined toluene filtrate was kept at −20 °C for 2 days to yield a dark-violet solid. Yield 55%.

X-ray Crystallographic Study:[8] Crystal data for $C_{22}Cr_2N_2Si_4$ (M_r = 508.6): monoclinic system with cell dimensions at 20 °C of a = 14.847(3)Å, b = 11.172(2) Å, c = 17.889(3) Å, β = 93.43(3)°; V = 2962(1) Å^3; μ(Mo-K_α) = 0.904 mm^{-1}; F(000) = 1000; space group $P2_1/c$ with Z = 4 and $D_{calcd.}$ = 1.141 g/cm^3. A selected specimen (0.45 × 0.35 × 0.35 mm.) was sealed in a thin-walled glass capillary under argon. The X-ray diffraction data were obtained with a Siemens R3m/V four-circle computer-controlled X-ray diffractometer (graphite-monochromated Mo-K_α radiation: λ = 0.71073 Å) at 293 K. The unit cell parameters and standard deviations were calculated for the setting angles of 25 reflections with 10° < 2θ < 35°. The space group $P2_1/c$ was unequivocally established from systematic absences. The intensities of 7519 reflections corresponding to 3823 independent reflections ($R_{int.}$ = 0.038) were measured by the ω scan technique in the range 3.5° < 2θ < 45.0° (h: −15 → 15, k: −12 → 12, l: −19 → 19). Three standard reflections were monitored every 97 reflections to check crystal stability. No decrease of intensity during data collection was observed. Data were corrected for Lorentz polarization and absorption effects, the latter with a semi-empirical method. The transmission factors range from 0.765 to 0.967. The structure was solved by direct methods and Fourier techniques. Full-matrix least-squares refinement was carried out against F^2. The thermal behavior of the nonhydrogen atoms was treated anisotropically. Riding H atoms, with C−H bond lengths of 0.95 Å and a fixed isotropic U of 0.08 Å were included in the refinement. The final agreement factors were 0.056 for 2914 reflections with $F_o^2 > 2\sigma(F_o^2)$ and 271 parameters. The maximum shift/e.s.d. in the final cycle was less than 0.001. The highest peak in the final difference Fourier map was 0.703 eÅ^{-3}. Calculations were performed with Siemens SHELXTL PLUS package programs.[9]

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[8] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC-117153. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].
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