Synthesis and X-Ray Crystal Structure of $Sm(C_8H_8)(2,4\text{-}C_7H_{11})\cdot thf$

Jizhu Jin, Songchun Jin, Zhongsheng Jin and Wenqi Chen*

Changchun Institute of Applied Chemistry, Academia Sinica, Changchun 130022, Jilin, PR China

$SmCl_3$ reacts with $K_2C_8H_8$ to yield the complex $Sm(C_8H_8)Cl\cdot 2thf$, which reacts with $K(2,4\text{-}C_7H_{11})$ ($2,4\text{-}C_7H_{11}$ = 2,4-dimethylcyclopentadienyl) to form $Sm(C_8H_8)(2,4\text{-}C_7H_{11})\cdot thf$; the X-ray crystal structure of $Sm(C_8H_8)(2,4\text{-}C_7H_{11})\cdot thf$ shows that the 2,4-dimethylcyclopentadienyl has a 'U' conformation.

Hodgson *et al.* reported the synthesis of $[Sm(C_8H_8)Cl\cdot 2thf]_2$[1] in 1973. In 1974 Jamerson *et al.* reported the synthesis of $Sm(C_8H_8)C_5H_5\cdot thf$ (thf = tetrahydrofuran).[2] Recently, Schumann *et al.* reported the syntheses and crystal structures of $Lu(C_8H_8)(C_5Me_5)$[3] and $Lu(C_8H_8)[C_5(CH_2Ph)_5]$.[4] $Pr(C_8H_8)(C_5H_5)\cdot 2thf$ and $Pr(C_8H_8)(C_9H_7)\cdot 2thf$ were also prepared and their crystal structures were determined by Chen *et al.*[5] In this communication, we report the first synthesis and crystal structure of $Sm(C_8H_8)(2,4\text{-}C_7H_{11})\cdot thf$.

The complex $Sm(C_8H_8)(2,4\text{-}C_7H_{11})\cdot thf$ was synthesized as follows: 0.8 g (3.11 mmol) solid $SmCl_3$ and 20 ml thf were mixed, and the solution was stood overnight. Then $K_2C_8H_8$ (3.07 mmol) in thf was added at −78 °C. After stirring for 10 h, $K(2,4\text{-}C_7H_{11})$[6] (3.07 mmol) was added at room temperature and the reaction continued for 10 h. The solution was centrifuged to remove solids, and hexane was added to the clear solution. Deep-brown crystals (38%) formed once the solution was cooled. The reaction is represented by eqn.(1)

$$SmCl_3 + K_2C_8H_8 \xrightarrow{thf} Sm(C_8H_8)Cl\cdot 2thf \xrightarrow{K(2,4\text{-}C_7H_{11})} Sm(C_8H_8)(2,4\text{-}C_7H_{11})\cdot thf + 3KCl \quad (1)$$

The crystal was characterized by complexometric metal analysis (Sm, found: 35.6%; calcd.: 35.69%), IR spectroscopy [(KBr): 3080w, 3000s, 2970m, 2870m, 1635w, 1580w, 1555w, 1445m, 1375m, 1225w, 1070s, 1045s, 890s, 800s, 670s and 625s cm^{-1}] and X-ray crystallography.†

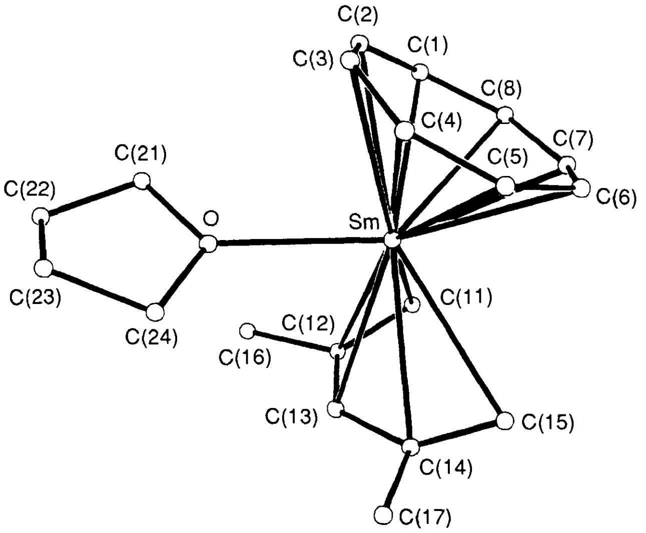

Fig. 1 Structure of $Sm(C_8H_8)(2,4\text{-}C_7H_{11})\cdot(thf)$. Important bond distances (Å) and angles (°): Sm–O 2.50(1), Sm–C(η^8-C_8H_8) average 2.66, Sm–(centroid C_8H_8) 1.92, Sm–C(13) 2.71(1), Sm–C(11,15) average 2.88, Sm–C(12,14) average 2.84, Sm–[centroid C(11) to C(17)] 2.43; (centroid C_8H_8)–Sm–[centroid C(11) to C(17)] 131.1, (centroid C_8H_8)–Sm–O 125.4, [centroid C(11) to C(17)]–Sm–O 85.7.

---

† *Crystal data*: $Sm(C_8H_8)(2,4\text{-}C_7H_{11})\cdot thf$, M = 421.8, monoclinic, space group $P2_1$, a = 8.632(3), b = 10.968(3), c = 9.744(3) Å, β = 104.24(2)°, V = 899.3(4) $Å^3$, Z = 2, $F(000)$ = 422, μ = 33.2 cm^{-1}, D_c = 1.56 g cm^{-3}. Data were collected on a Nicolet R3m/E four circle X-ray diffractometer at room temperature, using graphite monochromated Mo-$K\alpha$ radiation (λ = 0.71069 Å). Scan type ω–2θ, $2\theta_{max}$ = 56°. 2438 independent reflections were measured and 2021 reflections with $I > 2\sigma(I)$ were used in the refinement, R = 0.041. The intensities were corrected for Lorentz-polarization effects and empirical absorption. The structure was solved by Patterson and Fourier methods. Residues in the final difference Fourier ranged from 0.91 to −1.35 $eÅ^{-3}$. All non-hydrogen atoms except C(1), C(2) and C(22) were refined anisotropically by block-diagnonal matrix least-squares. Non-positive parameters for C(1), C(2) and C(22) appeared during refinement, so isotropic thermal refinement was used for them. All hydrogen atoms were placed in calculated positions 0.96 Å from carbon atoms to which they are bonded except for C(11) and C(15). All calculations were performed on an Eclipse S/140 computer using SHELXTL programs. 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.

The reaction of $SmCl_3$ with $K(2,4\text{-}C_7H_{11})$ at a molar ratio of 1:1 in thf gives $Sm(2,4\text{-}C_7H_{11})_3$ instead of $Sm(2,4\text{-}C_7H_{11}Cl_2 \cdot 3thf$. Using the method shown in eqn. (1) $Sm(C_8H_8)(2,4\text{-}C_7H_{11}) \cdot thf$ can easily be prepared.

The molecular structure is shown in Fig. 1. The X-ray structure shows the compound is a mononuclear samarium complex with the central metal atom coordinated by the cyclooctatetraenyl and by the 2,4-dimethylcyclopentadienyl in η-8 and η-5 bonded fashion, respectively. Both the cyclooctatetraenyl ring and 2,4-dimethylpentadienyl 'open ring' are planar. The two planes form a dihedral angle of 114.6°.

The $Sm\text{-}C(2,4\text{-}C_7H_{11})$ distances range from 2.71(1) to 2.89(1) Å. The Sm–C(13) distance is the shortest [2.71(1) Å], the average Sm–C(12,14) distance is intermediary (2.84 Å) and the average Sm–C(11,15) distance is the longest (2.88 Å). This order is different from those in $Ln(2,4\text{-}C_7H_{11})_3$ (Ln = Nd[7], Gd[8]).

The carbon–carbon bond distances within the pentadienyl ligand fall essentially in two sets.[7,8] The external C–C bond [C(11)–C(12) and C(14)–C(15)] distances average 1.37 Å, and the internal C–C bond [C(12)–C(13) and C(13)–C(14)] distances average 1.50 Å.

The angle of centroid (C_8H_8)–Sm–centroid$(2,4\text{-}C_7H_{11})$ is 131.1°, which is smaller than those of $Lu(C_8H_8)(C_5Me_5)$ (173.0°)[3] and $Lu(C_8H_8)[C_5(CH_2Ph)_5]$ (167.7°).[4] This is due to the presence of thf in $Sm(C_8H_8)(2,4\text{-}C_7H_{11}) \cdot thf$ and absence of thf in $Lu(C_8H_8)(C_5Me_5)$[3] and $Lu(C_8H_8)[C_5(CH_2Ph)_5]$.[4]

Received, 21st February 1991; Com. 1/00836F

References

1 K. O. Hodgson, F. Mares, D. F. Starks and A. Streitwieser, *J. Am. Chem. Soc.*, 1973, **95**, 8650.
2 J. D. Jamerson, A. P. Masion and J. Takats, *J. Organomet. Chem.*, 1974, **65**, C33.
3 H. Schumann, R. D. Kohn, F. W. Reier, A. Dietrich and J. Pickardt, *Organometallics*, 1989, **8**, 1388.
4 H. Schumann, C. Janiak, R. D. Kohn, J. Loebel and A. Dietrich, *J. Organomet. Chem.*, 1989, **365**, 137.
5 K. Wen, Z. Jin and W. Chen, *J. Chem. Soc., Chem. Commun.*, 1991, 680.
6 H. Yasuda, Y. Ohnuma, M. Tamauchi, H. Tani and A. Nakamura, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 2036.
7 R. D. Ernst and T. H. Cymbaluk, *Organometallics*, 1982, **1**, 708.
8 N. Hu, L. Gong, Z. Jin and W. Chen, *J. Inorg. Chem. (China)*, 1989, **5**(**3**), 107.