

Synthesis of an Organolanthanoid Complex with a Novel High-strain Anionic Cyclohexen-4-yne Ligand and Crystal Structure of $[(\eta^5\text{-Cp})_2\text{Sm}(\eta^5\text{-C}_6\text{H}_5)(\text{thf})]$

Shaowu Wang,^a Yongfei Yu,^a Zhongwen Ye,^{a*} Changtao Qian^b and Xianglin Jin^c

^a Institute of Organic Chemistry, Anhui Normal University, Wuhu, Anhui 241000, China

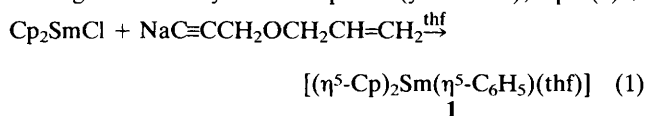
^b Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fengling Lu, Shanghai 200032, China

^c Chemistry Department, Peking University, Beijing 100871, China

An organosamarium complex, $[(\eta^5\text{-Cp})_2\text{Sm}(\eta^5\text{-C}_6\text{H}_5)(\text{thf})]$, with a novel high-strain anionic cyclohexen-4-yne ligand, a new benzene isomer, has been synthesised.

The exploration of the structure limitations in cyclic organic compounds has attracted considerable interest.¹⁻⁴ With regard to the unstrained cycloalkenyne, Meier *et al.*⁵ pointed out that the lowest ring size n is 13 for multiple bonds situated in positions 1 and 3; while n is 12 for those multiple bonds in the 1 and 4 positions. This implies that a cycloalkenyne with multiple bonds in positions 1 and 4 is more stable than one with multiple bonds in positions 1 and 3. In 1990, Shakespeare and Johnson⁶ described evidence for the existence of cyclohexen-3-yne by trapping, but it is very unstable and reactive.

We now report that reaction of dicyclopentadienylsamarium chloride with sodium allyloxypropynylide ($\text{NaC}\equiv\text{CCH}_2\text{OCH}_2\text{CH}=\text{CH}_2$) in thf at -78°C under pure argon for 8 h, followed by removal of solvent and crystallisation by cooling affords the yellow complex **1** (yield 12%, eqn. (1)).[†]



$[(\eta^5\text{-Cp})_2\text{Sm}(\eta^5\text{-C}_6\text{H}_5)(\text{thf})]$ **1** consists of discrete monomer units. A perspective drawing of the complex molecule is shown in Fig. 1.[‡] The tetrahedron around the samarium ion is formed by the two centroids of the cyclopentadienyl rings, the centroid of the plane formed by C(16), C(17), C(18), C(19), C(20) and one oxygen atom of thf.

The ligand $\eta^5\text{-C}_6\text{H}_5$ is the anionic form of cyclohexen-4-yne;

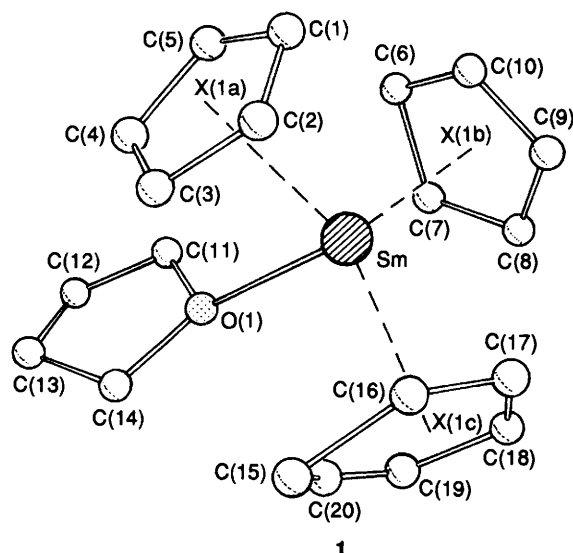


Fig. 1 Molecular structure and atom numbering scheme for **1**. Bond distances (\AA) and angles ($^\circ$); Sm–O(1) 2.536(8), Sm–X(1a)(Cp) 2.492, Sm–X(1b)(Cp) (2.509), Sm–X(1c) 2.500, C(15)–C(20) 1.483(26), C(19)–C(20) 1.183(26), C(15)–C(16) 1.495(27), C(16)–C(17) 1.273(26), C(17)–C(18) 1.382(30), C(18)–C(19) 1.379(28), C(15)–C(20)–C(19) 142.2(21), C(20)–C(19)–C(18) 116.7(20), C(19)–C(18)–C(17) 114.8(17), C(18)–C(17)–C(16) 114.1(19), C(17)–C(16)–C(15) 139.7(20), C(16)–C(15)–C(20) 85.9(15). [X(1a), X(1b) represent the centroids of cyclopentadienyl rings, X(1c) of the plane formed by C(16), C(17), C(18), C(19) and C(20)].

cyclohexen-4-yne is probably more stable than cyclohexen-3-yne.⁶ In the present structure, C(16), C(17), C(18), C(19) and C(20) are coplanar with a least squares deviation of 0.0233 \AA , whereas C(15) is 0.3655 \AA away from the plane. The dihedral angle between the planes formed by C(16), C(15), C(20) and C(16), C(17), C(18), C(19) and C(20) is 19° , which is smaller than the corresponding angles in η^5 -cyclohexadienyl transition metal complexes.⁷⁻¹⁰ This is presumably because of the existence of high strain in the six-membered ring in **1**. The difference in bond lengths between C(15)–C(20) (1.483 \AA) and C(15)–C(16) (1.495 \AA) results from the different hybridisation ($\text{sp}^3\text{-sp}$ and $\text{sp}^3\text{-sp}^2$ respectively).

We are studying the mechanism of the formation of the complex. Cleavage of C–O bonds must be involved, in accordance with the reported C–O cleavage catalysed by a samarium complex.¹¹⁻¹⁴

This work was supported by the Foundation of Laboratory of Organometallic Chemistry in Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. Thanks are also due to Professor Yao-zeng Huang, a member of the Chinese Academy of Sciences, for helpful discussions and encouragement.

Received, 2nd December 1993; Com. 3/07140E

Footnotes

[†] Spectroscopic data: **1**, IR(KBr) ν/cm^{-1} = $\eta^5\text{-Cp}$, 3087, 1440, 1015, 788, 240, C=C, 1675, C \equiv C, 2100.

[‡] Crystal data for $\text{C}_{20}\text{H}_{23}\text{OSm}$ **1**, M_r = 429.7, yellow monoclinic crystal, space group $C2/c$, a = 12.866(5), b = 10.468(5), c = 24.945(16) \AA , β = 97.95(6) $^\circ$, V = 3327(3) \AA^3 , Z = 8, D_c = 1.716 g cm^{-3} , $F(000)$ = 1704. Data were collected on a Siemens R3m/v diffractometer at 0°C using a graphite monochromator and corrected for Lorentz-polarisation effects and empirical absorption. 4681 reflections were collected within the range $3.0^\circ \leq 2\theta \leq 45.0^\circ$. 2172 independent reflections were measured and 1972 unique reflections with $F > 4\sigma(F)$ were used in the refinement. Mo-K α radiation (λ = 0.71073 \AA), scan speed varied in the range 5.45–29.30 $^\circ\text{min}^{-1}$. The structure was solved by direct methods, and full-matrix least-squares refinement led to R = 0.0522, R_w = 0.0569. The nonhydrogen atoms were treated anisotropically. Hydrogen atom positions were calculated from a riding model (fixed isotropic U) and isotropic thermal parameters were refined. All calculations were made on Micro-VAX-II computer using the Siemens SHELTXL-PLUS program package. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

- 1 K. Wilberg, *Chem. Rev.*, 1989, **89**, 975.
- 2 P. M. Warner, *Chem. Rev.*, 1989, **89**, 1067.
- 3 W. T. Borden, *Chem. Rev.*, 1989, **89**, 1095.
- 4 W. E. Billups, M. M. Haley and G. A. Lee, *Chem. Rev.*, 1989, **89**, 1147.
- 5 H. Meier, N. Harold, T. Molz, H. J. Bissinger, H. Koshorn and J. Hounstas, *Tetrahedron*, 1986, **42**, 1711.
- 6 W. C. Shakespeare and R. P. Johnson, *J. Am. Chem. Soc.*, 1990, **112**, 8578.
- 7 P. H. Bird and M. R. Churchill, *Chem. Commun.*, 1967, 777.

- 8 A. Mawby, P. J. C. Walker and R. J. Mawby, *J. Organomet. Chem.*, 1973, **55**, C39.
- 9 M. F. Semmelhack, H. T. Hall, Jr. R. Farina, M. Yoshifuji, G. Clark, T. Bargar, K. Hirotsu and J. Clardy, *J. Am. Chem. Soc.*, 1979, **101**, 3535.
- 10 P. J. Van Vuuren, R. J. Fletterick, J. Meinwald and R. E. Hughes, *J. Am. Chem. Soc.*, 1971, **93**, 4394.
- 11 J. Prandi, J. L. Namy, G. Meroret and H. B. Kagan, *J. Organomet. Chem.*, 1985, **285**, 449.
- 12 G. A. Molander and G. Hahn, *J. Org. Chem.*, 1986, **51**, 1135.
- 13 P. Girard, T. L. Namy and H. B. Kagan, *J. Am. Chem. Soc.*, 1980, **102**, 2693.
- 14 T. Tabuchi, J. Inanaga and M. Yamaguchi, *Chem. Lett.*, 1987, 2275.