Synthesis and Crystal Structure of Triscyclopentadienyl(triphenyltin)uranium. The First Example of a Uranium–Tin Bond

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The uranium–tin complex $(cp)_3U{-}SnPh_3$ ($cp = \eta^5{-}C_5H_5$) has been prepared from $(cp)_3UNEt_2$ and $HSnPh_3$, and its crystal structure determined; it provides the first example of a compound with a uranium–tin bond.

The organometallic chemistry of actinoid elements has developed widely during last decade, but no compounds unequivocally containing uranium–metal bonds have been described until now.[1] Structurally characterized complexes containing both direct[2] and bridged[3] Th–(d metal) bonds have recently been reported, and this prompted us to publish our preliminary data concerning the synthesis and structural characterization of $(cp)_3USnPh_3$ ($cp = \eta^5{-}C_5H_5$).

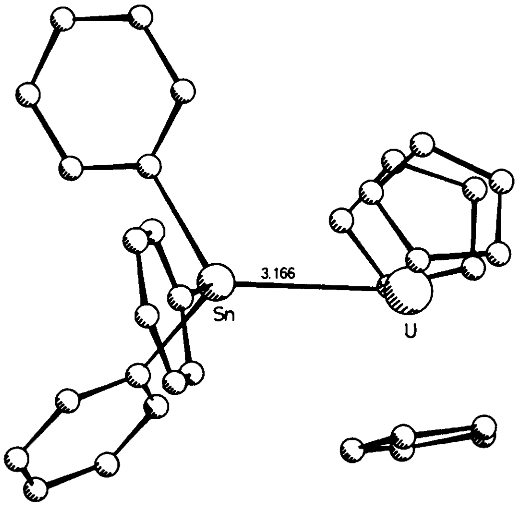

Figure 1. Crystal structure of $(cp)_3USnPh_3$, composed of monomeric dinuclear molecules with a direct U–Sn bond of 3.166(1) Å. Both metal ions are four-co-ordinate (considering the cp centroids) in a distorted tetrahedral arrangement. The U–C bond lengths are in the range 2.68—2.79 Å; mean Sn–C distance 2.21 Å.

Reaction of $(cp)_3UNEt_2$[4] with a small excess of $HSnPh_3$ in toluene solution at room temperature gave a brown powder almost quantitatively after removal of solvent. After washing with n-hexane it gave satisfactory elemental analyses.† The reaction (1) proved to be a more suitable preparative method than others attempted, *i.e.* reaction of $(cp)_3UMe$ or $(cp)_3UBH_4$ with $HSnPh_3$ and of $(cp)_3UCl$ with $LiSnPh_3$, which appeared to be too slow or complicated by formation of other inseparable products. Similar experiments carried out with $HSnBu_3$ were unsuccessful.

$$(cp)_3UNEt_2 + HSnPh_3 \rightarrow (cp)_3USnPh_3 + HNEt_2 \quad (1)$$

The brown $(cp)_3USnPh_3$ dissolves in benzene or toluene giving a reasonably stable bright green solution, while in diethyl ether or tetrahydrofuran fast reaction with solvent occurs. The complex is stable at room temperature but decomposes at 60—70 °C. Crystals suitable for an *X*-ray

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† ^{1}H N.m.r. (C_6D_6, 27 °C, C_6D_5H internal standard 7.2 p.p.m. from $SiMe_4$): δ 10.8 (15H, s, cp), 13.5 (6H, br. d), and 2.9 (9H, m). ^{119}Sn–H coupling was not observed. I.r. (Nujol, in KBr discs) $\nu_{max.}$ 1010, 790 (cp), 1570, 1060, 700, and 730 cm^{-1} (Ph). Under our conditions, the i.r. spectrum did not give any information about U–Sn stretching frequencies. The mass spectrum did not show M^+ ions; the most intense peak was at *m/z* 350 ($SnPh_3^+$); other intense peaks: *m/z* 700 ($Sn_2Ph_6^+$), 623 ($Sn_2Ph_5^+$), 546 ($Sn_2Ph_4^+$), 433 (cp_3U^+), and 368 (cp_2U^+).

structure determination‡ were obtained by addition of cooled n-hexane to a saturated solution in toluene. The structure (Figure 1) consists of two pseudo-tetrahedral groups [$(cp)_3U$–Sn and Ph_3Sn–U]. Angles and Sn–C_{Ph} and U–C_{cp} bond lengths are typical of Ph_3Sn [5] and $(cp)_3U$ [6] moieties. The main feature is the U–Sn bond length of 3.166 Å, comparable with those in other Ph_3Sn–(d metal) compounds[7] if the larger size of the uranium atom is taken into account.

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References

1 T. J. Marks and R. D. Ernst, in 'Comprehensive Organometallic Chemistry,' eds G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, Oxford, 1982. The shortest U–U non-interactive distance is 3.576 Å (F. A. Cotton, D. O. Marler, and W. Schwotzer, *Inorg. Chim. Acta*, 1984, **85**, L31) while a U–U bond has been suggested for the complex $U_6O_4(OH)_4(SO_4)_6$, U–U distance 3.85 Å (G. Lundgren, *Ark. Kemi*, 1953, **5**, 247, quoted by V. Gutmarnn, 'Halogen Chemistry,' Academic Press, New York, 1967, vol. 3, p. 49).

2 R. S. Sternal, C. P. Brock, and T. J. Marks, *J. Am. Chem. Soc.*, 1985, **107**, 8270.

3 J. M. Ritchey, A. J. Zozulin, D. A. Wroblevski, R. R. Ryan, H. J. Wasserman, D. C. Moody, and R. T. Paine, *J. Am. Chem. Soc.*, 1985, **107**, 501.

4 F. Ossola, G. Rossetto, P. Zanella, G. Paolucci, and R. D. Fischer, *J. Organomet. Chem.*, submitted for publication.

5 Yu. V. Skripkin, O. G. Volkov, A. A. Pasynskii, A. S. Antsyshkina, L. M. Dikareva, V. N. Ostrikova, M. A. Porai-Koshits, S. L. Davydova, and S. G. Sakharov, *J. Organomet. Chem.*, 1984, **263**, 345.

6 R. E. Cramer, R. B. Maynard, J. C. Paw, and J. W. Gilje, *Organometallics*, 1983, **2**, 1336.

7 D. E. Fenton and J. J. Zuckerman, *J. Am. Chem. Soc.*, 1968, **90**, 6226; V. K. Belsky, A. N. Protsky, J. V. Molodnitskaya, B. M. Bulychev, and G. L. Soloveichik, *J. Organomet. Chem.*, 1985, **293**, 69.

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‡ *Crystal data:* $C_{33}H_{30}SnU$, $M = 783.4$, orthorhombic, space group *Pbca*, $a = 19.000(5)$, $b = 18.195(4)$, $c = 16.084(5)$ Å, $U = 5560(2)$ Å^3, $D_c = 1.84$ g cm^{-3} for $Z = 8$. A total of 8857 reflexions were recorded to $\theta = 25°$ on a Philips PW 1100 diffractometer with Mo-K_α radiation (λ 0.71069 Å). The intensities were corrected for Lorentz–polarisation and for absorption. The structure was solved by standard methods and refined to $R = 0.051$ for the 2862 observed reflexions [$I > 3\sigma(I)$]. The ring atoms were refined as rigid bodies.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.