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Preliminary communication

BIS(TETRAMETHYLETHYLCYCLOPENTADIENYL)URANIUM DICHLORIDE

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Summary

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Reaction of tri-n-butyl(tetramethylethylcyclopentadienyl)tin with uranium tetrachloride in toluene results in the red air-sensitive compound bis(tetramethyl-ethylcyclopentadienyl)uranium dichloride.

The only dicyclopentadienyluranium(IV) halides so far reported are those in which the rings are joined by various bridging groups [1]. The known chloro derivatives are complex anions, e.g. $[X(C_5 H_4)_2]_2 U_2 Cl_5 - Li^+$ (THF)₂ where $X = CH_2$, Me₂Si, CH₂ CH₂ CH₂. Although both mono- and tri-cyclopentadienyluranium(IV) halides have been isolated, $(\eta - C_5 H_5)_2 UCl_2$ is unstable.

In a typical preparation $(Me_4 \text{ EtC}_5)(n-C_4 H_9)_3$ Sn was stirred with UCl₄ in a molar ratio of 4/1 in refluxing toluene for 20 h. Toluene was removed from the resulting deep red solution under vacuo and on standing dark red crystals formed. These were very soluble in petrol and toluene. Analyses were consistent with the stoichiometry $C_{22} H_{34} Cl_2 U$ and the mass spectrum showed parent ion peaks indicating the vapour phase species was monomeric. The ¹H NMR in deuterobenzene at room temperature showed broad bands at δ -14.40 (2)s, -5.25 (8)s, +6.0 (4)m, +9.75 (1)s, ppm (relative to $C_6 H_6$). The compound sublimed readily and the gas phase photoelectron spectrum showed the lowest *IE* band at 7.23 eV due to ionization of *f* electrons.

A similar reaction of $(C_5 H_5)(n-C_4 H_9)_3$ Sn with UCl₄ gives $(\eta-C_5 H_5)_3$ UCl as the product [2]. It therefore appears that polyalkyl substitution on the cyclopentadienyl ring stabilizes the dicyclopentadienyluranium dichloride. This is presumably due to steric inhibition of the alternative tricyclopentadienyl product.

References

1 C.A. Secaur, V.W. Day, R.D. Ernst, W.J. Kennelly and T.J. Marks, J. Amer. Chem. Soc., 98 (1976) 3713. 2 J.A. Long, Part II Thesis, Oxford 1977.

Note added in proof. The abstracts of the American Chemical Society Meeting, 1978, report the synthesis of $(Me_sC_s)_2UCl_2$ in a communication given by T.J. Marks.