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THE SYNTHESIS AND CHARACTERIZATION OF TRIS(2,4-DIMETHYLPENTADIENYL)URANIUM, $U(2,4\text{-}C_7H_{11})_3$

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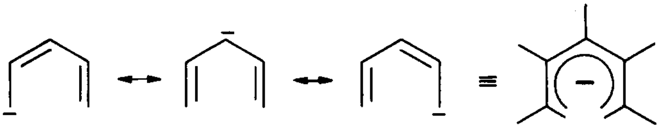
Summary

The reaction of "$UCl_3 \cdot n$THF" with three equivalents of the 2,4-dimethylpentadienyl anion leads to the formation of pyrophoric tris(2,4-dimethylpentadienyl)uranium, a rare example of a homoleptic uranium(III) organometallic compound. The compound has been characterized by infrared and NMR spectroscopy, elemental analysis, and magnetic susceptibility measurements.

Introduction

Metal pentadienyl complexes have been known for some time [1,2]. However, only a relatively few such complexes have been reported, and until recently almost nothing has been known regarding the properties of such systems. The potential advantages of transition metal pentadienyl complexes have recently been described [3], and confirmed somewhat in preliminary work [4]. Certainly a key to these studies have been the reports of convenient synthetic routes to pentadienyl anions [5]. Besides transition metal systems, however, the anionic pentadienyl group can be expected to bond favorably to relatively ionic lanthanide and actinide complexes as well.



Particularly interesting in this regard is the fact that if the three formally anionic carbon atoms (in the 1, 3, and 5 positions) are all simultaneously engaged in bonding to the metal, then the formally uncharged atoms in the 2 and 4 positions will be in close proximity to the metal atom, thus allowing one to gauge the relative responses of these atoms toward the lanthanide or actinide metal ion. Indeed, the complex tris(2,4-dimethylpentadienyl)neodymium, $Nd(2,4\text{-}C_7H_{11})_3$, has recently been synthesized and characterized by single crystal X-ray diffraction, as well as other methods [6]. The structural result did in fact display the neodymium(III) ion in bonding proximity to the uncharged carbon atoms but it was clear that the interaction was repulsive, at least at the observed distance of 2.855(8) Å, since the two uncharged carbon atoms were bent out of the ligand plane in a direction away from the neodymium(III) ion. Since neodymium(III) and uranium(III) species would have identical valences, ligand complements, and even *f* electron configurations, a comparison between $Nd(2,4\text{-}C_7H_{11})_3$ and $U(2,4\text{-}C_7H_{11})_3$ should be particularly direct. It is also worth noting that trivalent uranium organometallic compounds are still quite scarce, and very little is known about them whatsoever. The present study, then should also serve to increase our understanding of this relatively unfamiliar system. For these reasons the synthesis and characterization of the trivalent uranium complex tris(2,4-dimethylpentadienyl)uranium was of interest, and herein are reported the properties of this compound.

Experimental

All operations involving organometallics were carried out under an atmosphere of prepurified nitrogen in Schlenk apparatus or in a glovebox. Nonaqueous solvents were thoroughly dried and deoxygenated in a manner appropriate to each (generally using Na/K with benzophenone indicator) and were distilled under nitrogen immediately prior to use. Carbon and hydrogen analyses were obtained from Dornis and Kolbe Laboratories, and the uranium analysis was obtained from Galbraith Laboratories. 2,4-Dimethyl-1,3-pentadiene was either prepared according to reported procedures [7] or purchased from Wiley Chemicals. It was then converted to the potassium salt of the 2,4-dimethylpentadienyl anion by a reported procedure [5].

Spectroscopic studies. Infrared spectra were recorded on a Perkin–Elmer model 298 spectrophotometer. Mulls were prepared in a glovebox with dry, degassed Nujol. All infrared spectra were calibrated with polystyrene. Magnetic susceptibility measurements were carried out by the Evans method [8] in benzene-d_6.

"$UCl_3(THF)_n$"

The uranium(III) chloride starting material was prepared in good yield by the method of Andersen [9]. It was isolated with a sodium chloride impurity present which was not removed. To a magnetically stirred solution of 1.62 g (12.6 mmol) naphthalene in 40 ml THF under N_2 at room temperature was added 0.29 g (12.6 mmol) sodium. The resulting green solution was allowed to stir for 12 h at room temperature after which it was added all at once by syringe to a stirred solution of 4.79 g (12.6 mmol) UCl_4 [10] in 30 ml of THF under N_2 at room temperature. After several minutes of stirring a reddish suspension began to appear. The reaction mixture was allowed to stir for 24 h. The resulting red-purple suspension could be isolated either by collection on a medium frit under nitrogen or by stopping the stirring for several hours and subsequent removal of the reddish supernatant by syringe. The crude "$UCl_3 \cdot n$THF" was washed with several portions of ether and pentane to insure removal of all traces of naphthalene and finally dried in vacuo. The product isolated as such contained some sodium chloride (perhaps as $NaUCl_4 \cdot n$THF [11]) but was used in this condition without further purification.

Complete infrared data (Nujol mull): 3068w sh, 1550w, sh, 1510w, sh, 1415w, sh, 1368s, 1260w, 1155w, br, 1060mw, 1028m, sh, 1018m, 890w, 815m, sh, 805m, 760s, 723mw, 677w, sh cm^{-1}.

Tris(2,4-dimethylpentadienyl)uranium, $U(2,4\text{-}C_7H_{11})_3$

To a magnetically stirred suspension of 1.00 g (ca. 2.40 mmol) $UCl_3 \cdot n$THF in 30 ml THF at −78°C was added dropwise a solution of 0.55 g (7.20 mmol) 2,4-dimethylpentadienylpotassium in 20 ml THF. Reaction began immediately with the formation of a deep red-brown color. Upon completion of the addition, the red-brown reaction mixture was allowed to warm to room temperature after which stirring was continued for an additional 15 h. After filtration on a coarse frit the THF was removed in vacuo and the brownish residue was extracted repeatedly with pentane. The pentane extracts were again filtered and concentrated under reduced pressure. Cooling of the red-brown pentane solution to −78°C yielded a dark crystalline product.

Complete infrared data (Nujol mull): 1594w, 1450m, sh, 1260w, 1170w, 1040m, sh, 1015s, 957w, 920w, 877m, sh, 860s, 835m, sh, 792w, 725w cm^{-1}.

Room temperature NMR data (benzene-d_6): 0.96δ (1H), −32.5δ (6H), −36.5δ (2H), −49.3δ (2H).

Magnetic susceptibility (Evans method) 2.4μ_B.

Anal. Found: C, 48.25; H, 6.18; U, 44.03. $C_{21}H_{33}U$ calcd.: C, 48.18; H, 6.35; U, 45.47%.

Results and discussion

The reaction of three equivalents of the 2,4-dimethylpentadienyl anion (2,4-$C_7H_{11}^-$) with the conveniently prepared "$UCl_3 \cdot n$THF" [9] leads directly to the formation of an organouranium product which is slightly to somewhat soluble in noncoordinating organic solvents such as pentane and toluene. After extraction of the product with pentane, purification is achieved by low temperature crystallization to yield the crystalline, pyrophoric compound. Elemental analysis of the product is consistent with the expected formulation $U(2,4\text{-}C_7H_{11})_3$ (see Experimental) and the magnetic susceptibility (by the Evans solution NMR method, μ_{eff} 2.4μ_B), is similar to that obtained for related uranium(III) complexes [11,12]. The preparation of this complex, then, seems to proceed in the straightforward fashion indicated in equation 1.

$$\text{"}UCl_3 \cdot n(\text{THF})\text{"} + 3K(2,4\text{-}C_7H_{11}) \xrightarrow{\text{THF}} U(2,4\text{-}C_7H_{11})_3 + 3KCl \quad (1)$$

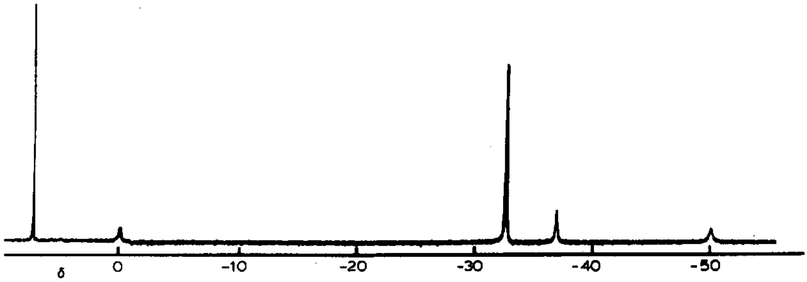
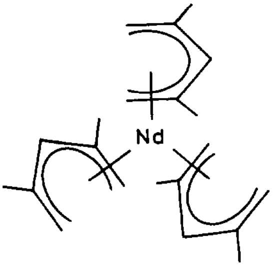


Fig. 1. Room temperature ^{1}H NMR spectrum of $U(2,4\text{-}C_7H_{11})_3$ in benzene-d_6.

The infrared spectrum of this compound (see Experimental) is devoid of bands attributable to carbon–carbon double bonds and therefore η^1 or η^3 bonding configurations can be ruled out. The ^{1}H NMR spectrum (see Fig. 1) is composed at room temperature of four resonances having relative intensities 1/6/2/2, appearing respectively at 0.96, −32.5, −36.5, and −49.3 ppm (δ)[13] (See Fig. 1). Due to the paramagnetism of the complex, the positions of these resonances vary with temperature. As would be expected, the resonances are also notably broadened compared to the more common uranium(IV) (f^2 configuration) organometallics, for which relatively fast electron relaxation brings about narrow linewidths [14]. The linewidths of the $U(2,4\text{-}C_7H_{11})_3$ resonances, however, are not unlike those observed for $Nd(2,4\text{-}C_7H_{11})_3$ [6], although the relative locations are much different, presumably due to greater paramagnetic contact shift contributions. Chemically this compound behaves similarly to $(C_5(CH_3)_5)_2UCl$ [15], which undergoes extremely rapid halogen abstraction reactions. Thus, addition of CH_2Cl_2 results in immediate decomposition, while both $Nd(2,4\text{-}C_7H_{11})_3$ and $(C_5H_5)UCl_3(THF)_2$ [16] are stable enough to CH_2Cl_2 to allow ^{1}H NMR spectra to be easily obtained.

The information above uniquely defines the composition of the product as tris(2,4-dimethylpentadienyl)uranium and suggests that the three ligands are bound in η^5 fashion as observed in the corresponding C_{3h} neodymium(III) complex [6]:



This seems most reasonable since the uranium(III) ion is ca. 0.05 Å larger in radius than the neodymium(III) ion [17], and the neodymium(III) complex was observed to be sterically crowded in the solid state [6]. Unfortunately, the complex has either not been soluble or stable enough to allow solution molecular weight data to be obtained in noncoordinating solvents. Unlike $U(C_5H_5)_3$, $U(2,4\text{-}C_7H_{11})_3$ does not form base adducts so readily, again suggesting that the monomers are coordinatively saturated. The present complex therefore appears to be one of the simplest and best defined uranium(III) organometallic species as it is homoleptic and probably monomeric [18]. While X-ray diffraction studies have so far been hampered owing to substantial decomposition of the compound in the X-ray beam, further attempts are being made to obtain data through low temperature studies.

Acknowledgements

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References

1 (a) J.E. Mahler and R. Pettit, J. Am. Chem. Soc., 84 (1962) 1511; (b) U. Giannini, E. Pellino, and M.P. Lachi, J. Organomet. Chem., 12 (1968) 551; (c) R. Rienäcker and H. Yoshiura, Angew. Chem., Intl. Ed. Engl., 8 (1969) 677; (d) C. Krüger, ibid., 8 (1969) 678.

2 Some more recent examples: (a) D. Seyferth, E.W. Goldman and J. Pornet, J. Organomet. Chem., 208 (1981) 189; (b) E.W. Abel and S. Moorhouse, J. Chem. Soc., Dalton Trans., (1973) 1706; (c) M.d.l.A. Paz-Sandoval and P. Powell, J. Organomet. Chem., 219 (1981) 81; (d) P. Powell, ibid., 206 (1981) 229, 239, and references therein; (e) C. White, S.J. Thompson, and P.M. Maitlis, ibid., 134 (1977) 319.

3 (a) D.R. Wilson, A.A. DiLullo, and R.D. Ernst, J. Am. Chem. Soc., 102 (1980) 5928; (b) D.R. Wilson, J.-Z. Liu, and R.D. Ernst, ibid., 104 (1982) 1120; (c) J.-Z. Liu and R.D. Ernst, ibid., 104 (1982) 3737; (d) M.C. Böhm, M. Eckert-Maksic', R.D. Ernst, D.R. Wilson, and R. Gleiter, ibid., 104 (1982) 2699; (e) R.D. Ernst, C.F. Campana, D.R. Wilson, and J.-Z. Liu, submitted for publication. (f) D.R. Wilson, R.D. Ernst, and T.H. Cymbaluk, Organometallics, in press.

4 S.H. Severson, D.R. Wilson, T.H. Cymbaluk, J. Higashi, R.W. Parry, and R.D. Ernst, work in progress.

5 (a) H. Yasuda, Y. Ohnuma, M. Yamauchi, H. Tani, and A. Nakamura, Bull. Chem. Soc. Jpn., 52 (1979) 2036; (b) J. Hartmann and M. Schlosser, Helv. Chim. Acta., 59 (1976) 453.

6 R.D. Ernst and T.H. Cymbaluk, Organometallics, 1 (1982) 708.

7 (a) O.N. Jitkow and M.T. Bogert, J. Am. Chem. Soc., 63 (1941) 1979; (b) Replacement of the methyl Grignard reagent by methyllithium seems to improve the product purity somewhat.

8 D.F. Evans, J. Chem. Soc., (1959) 2003.

9 (a) R.A. Andersen, Inorg. Chem., 18 (1979) 1507; (b) see also D.C. Moody, A.J. Zozulin, and K.V. Salazar, Inorg. Chem., 21 (1982) 3856.

10 J.A. Hermann and J.F. Suttle, Inorg. Syn., 5 (1957) 143.

11 Note the existence of $NaUCl_4 \cdot 5H_2O$ [11a] and other complex species. (a) R. Barnard, J.I. Bullock, B.J. Gellatly, and L.F. Larkworthy, J. Chem. Soc., Dalton Trans., (1972) 1932; (b) M.E. Hendricks, E.R. Jones, Jr., J.A. Stone, and D.G. Karraker, J. Chem. Phys., 60 (1974) 2095.

12 (a) Two other reported uranium(III) organometallic compounds apparently have effective room temperature moments of ca. $2.0-2.3\mu_B$, even though uranium(III) coordination compounds generally feature a moment of ca. $2.9-3.4\mu_B$ and $U(C_5(CH_3)_5)_2$(dmpe)H is reported as having a magnetic moment of ca. $3.5\mu_B$ [12d]. It is not clear how these differences should be reconciled. (b) B. Kanellakopulos, E.O. Fischer, E. Dornberger and F. Baumgärtner, J. Organomet. Chem., 24 (1970) 507; (c) B. Kanellakopulos, E. Dornberger, and H. Billich, ibid., 76 (1974) C42. (d) M.R. Duttera, P.J. Fagan, T.J. Marks, and V.W. Day, J. Am. Chem. Soc., 104 (1982) 865.

13 Note that the four line ^1H NMR pattern argues against η^2 (acac-like) coordination as all four protons on the C(1) and C(5) atoms should be equivalent.

14 P.J. Fagan, J.M. Manriquez, T.J. Marks, C.S. Day, S.H. Vollmer, and V.W. Day, Organometallics, 1 (1982) 170, and references therein.

15 (a) R.G. Finke, Y. Hirose, and G. Gaughan, J. Chem. Soc., Chem. Commun., (1981) 232; (b) R.G. Finke, D.A. Schiraldi, and Y. Hirose, J. Am. Chem. Soc., 103 (1981) 1875.

16 R.D. Ernst, W.J. Kennelly, C.S. Day, V.W. Day, and T.J. Marks, J. Am. Chem. Soc., 101 (1979) 2656.

17 R.D. Shannon, Acta. Cryst., A32 (1976) 751.

18 (a) One can note that $Nd(indenyl)_3$ [18b] and $U(indenyl)_3$ [18c] are both monomeric, despite the fact that the bonded portion of the indenyl ligand is considerably smaller than the bonded pentadienyl portion. Thus, $U(2,4\text{-}C_7H_{11})_3$ is also expected to be monomeric. (b) J.L. Atwood, J.H. Burns, and P.G. Laubereau, J. Am. Chem. Soc., 95 (1973) 1830. (c) J. Meunier-Piret, J.P. Declercq, G. Germain, and M. Van Meerssche, Bull. Soc. Chim. Belg., 89 (1980) 121.