Journal of Organometallic Chemistry, 209 (1981) C52—C54
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

BIS(BICYCLOOCTATETRAENYL)DIURANIUM, "BIURANOCENYLENE"

MICHAEL J. MILLER and ANDREW STREITWIESER JR.*
Department of Chemistry, University of California, Berkeley, California 94720 (U.S.A.)

(Received October 7th, 1980)

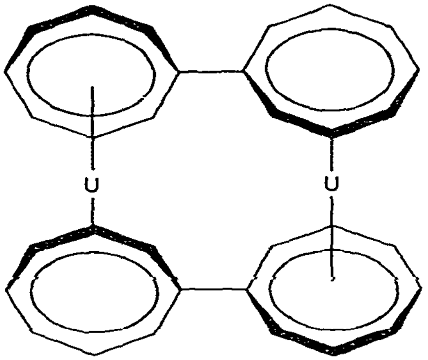
Summary

Bis(bicyclooctatetraenyl)diuranium, (I), was prepared as a byproduct in the preparation of 1,1′-dicyclooctatetraenyluranocene (II) and by reaction of II with colloidal uranium in THF. The ^{1}H NMR spectrum shows a seven-resonance spectrum indicative of a structure in which the joined C_8-rings are twisted with respect to each other. The compound is less thermally stable than uranocene.

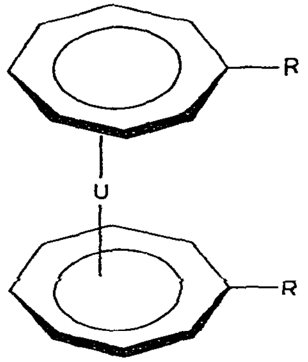
Dinuclear metal sandwich compounds are well known in the transition metal series and are the common products of reaction of conjugated hydrocarbon dianions with transition metal salts [1]; an example is the reaction of fulvalene dianion with $FeCl_2$ to give biferrocenylene [2]. We now report the first analogous such compound for an actinide element, bis(bicyclooctatetraenyl)diuranium (I) which we will refer to as biuranocenylene by analogy.

Cernia and Mazzei [3] mentioned briefly in a review article that uranocene could be prepared by direct reaction of cyclooctatetraene (COT) with colloidal uranium prepared by thermal decomposition of the adduct [4] of UCl_4 and n-butyllithium (BuLi). We confirmed this report but also found that substantially better yields are obtained when the desired COT is added at −78°C to a mixture of UCl_4 and BuLi in tetrahydrofuran (THF) and the combined mixture is allowed to warm to room temperature. In this manner uranocene and 1,1′-di-n-butyluranocene were obtained in yields of 69 and 66%, respectively. This approach was applied to the synthesis of I.

Bicyclooctatetraenyl, obtained in 60% yield by CuCl coupling of cyclooctatetraenylmagnesium bromide, was treated with two equivalents of potassium metal in THF to give the intensely purple solution of the dianion [5]. Addition of a THF solution of UCl_4 resulted in immediate reaction to give a dark green mixture. After stirring for 12 h, solvent removal and Soxhlet extraction with hot hexane, 1,1′-dicyclooctatetraenyluranocene (II), was obtained as a lime green,



(I)



(II, R = C_8H_7)

air sensitive solid in yields ranging from 32—45% [6]. Hot THF extraction of the green residue from the Soxhlet extraction gave I in 45% yield (based on UCl_4). Compound I was obtained as an olive green solid which is only sparingly soluble even in THF. I was also obtained (10—20% yield) by treatment of II with finely divided uranium metal according to the procedure outlined above.

Spectral data for I and II are tabulated below. The fact that I exhibits a large parent ion in its mass spectrum strongly suggests the structure assigned rather than a polymeric structure. Gel filtration studies on Bio Beads, SX-4, also are consistent with the assigned molecular weight of I*. The formation of a dimer rather than a polymer shows that the generalization of Katz and Slusarek [1] concerning such systems with metallocenes extends as well to sandwich compounds of actinides.

The ^1H NMR spectrum of I was particularly interesting. The seven resonances found for the ring protons establish that the structure consists of two uranocene moieties twisted with respect to each other as shown in I to give for each ring three *endo* protons, three *exo* and the unique 5-H. A structure with coplanar joined eight-membered rings would have overlapping 2-hydrogens with large consequent strain energy. The resonance at −97.3 ppm, the highest-field resonance yet observed for a uranocene [7], is undoubtedly that of the *endo*-2 proton which clearly experiences a large pseudocontact shift from both uraniums. The proton resonances show a normal [7] $1/T$ dependence and indicate that the paramagnetism of I results from uraniums that are effectively independent.

The twisted structure of I results in diminished thermal stability. Samples under inert atmosphere at room temperature are seen to decompose over the course of several weeks. Attempted sublimation gave only decomposition products. Nevertheless, a fresh sample gave a good combustion analysis**.

Spectral data: I: VIS (THF) 633, 658, 664, 673, 685, 717 nm; m/e (CEC-103, 70 eV; rel. intensity) 888 (M^+, 23), 675 (0.93), 650 (1.1), 444 (1.1),

---

*Details of this experiment will be given in the full paper.

**Found: C, 43.03; H, 3.44 $C_{32}H_{28}U_2$ calcd.: C, 43.25; H, 3.18% (preparation of H.-K. Wang).