

Preliminary communication

THE INTERACTION OF TRICYCLOPENTADIENYL DERIVATIVES OF URANIUM(IV) AND TRIALKYLALUMINIUM

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Summary

It has been found by ^1H NMR that on interaction between $(\eta^5\text{-C}_5\text{H}_5)_3\text{UR}$ and AlR_3 the exchange of alkyl radicals takes place.

Previously, we have studied the interaction between tricyclopentadienyl-uranium chloride Cp_3UCl ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$), and triethylaluminium [1]. It has been shown that the interaction results in the formation of a stable complex of the $\text{Cp}_3\text{UCl} \cdot \text{Al}(\text{C}_2\text{H}_5)_3$ type.

Using ^1H NMR, we have now studied the interaction of Cp_3UR (where $\text{R} =$ ethyl, n-butyl, allyl, phenyl or $-\text{O}-\text{C}_2\text{H}_5$), and AlR'_3 (where $\text{R}' =$ methyl, ethyl or isobutyl). NMR spectra were recorded on Tesla BS-487C and Bruker HW-90 instruments at 80 and 90 MHz, respectively.

A typical spectrum of the systems investigated is shown in Fig. 1, where the original $\text{Cp}_3\text{U}(\text{n-C}_4\text{H}_9)$ (Table 1) and organoaluminium compound signals are seen together with some other signals. The ratio of the areas under unknown signals to those under $\text{Cp}_3\text{U}(\text{n-C}_4\text{H}_9)$ signals depends on the initial $\text{Cp}_3\text{UR}/\text{AlR}'_3$ ratio. These new signals correspond to those of $\text{Cp}_3\text{UR}'$ by spin-spin coupling and chemical shifts. The formation of $\text{Cp}_3\text{UR}'$ is possible only in the case of exchange of alkyl radicals in the reaction



where $\text{R} =$ ethyl, n-butyl, allyl, phenyl or $-\text{O}-\text{C}_2\text{H}_5$, and $\text{R}' =$ methyl, ethyl or isobutyl.

This is indicated in particular by the agreement between the data on chemical shifts due to Cp_3UCH_3 prepared by reaction (1) and the results given for it in [2]. In order to make the fact of $\text{Cp}_3\text{U}(\text{C}_2\text{H}_5)$ and $\text{Cp}_3\text{U}(\text{iso-C}_4\text{H}_9)$ formation more convincing we have prepared them by another method [2]. Chemical shifts for the compounds prepared by us by this method were in agreement with those for the products obtained by reaction (1). ^1H NMR data for tricyclopentadienyl

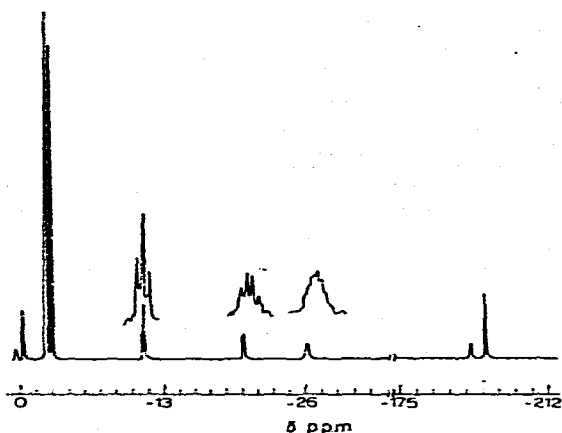


Fig.1. Typical NMR spectrum of a $\text{Cp}_3\text{UR}/\text{AIR}_3$ system.

derivatives of uranium prepared by reaction (1) and original tricyclopentadienyl-butyluranium are listed in Table 1.

The fact that there is no exchange in systems of the type $\text{Cp}_3\text{UR} + \text{Cp}_3\text{UR}'$ even at 413 K [2] enables the associative route of reaction (1) to be chosen (from the two possible routes, dissociative and associative), as is often proposed in similar reactions of *d*-transition metals. Unlike $\text{Cp}_3\text{UCl} \cdot \text{AIR}_3$, the complex

proposed in [1], the intermediate complex of the type $\text{Cp}_3\text{U} \begin{array}{c} \text{R} \\ \diagdown \quad \diagup \\ \text{AIR}'_2 \\ \diagup \quad \diagdown \\ \text{R}' \end{array}$

TABLE 1

^1H NMR DATA FOR Cp_3UR COMPOUNDS AT 293 K ^a

R	Chemical shifts δ (ppm.)				
	H(C ₅ H ₅)	H(C ₁)	H(C ₂)	H(C ₃)	H(C ₄)
CH ₃	-2.6 s	-196 s			
C ₂ H ₅	-2.9 s	-190 q	-12.2 t		
H-C ₄ H ₉	-3.0 s	-192 m	-26.4 m	-20.5 m	-11.5 t
iso-C ₄ H ₉	-3.2 s	-187 m	-18.8 m	-17.4 d	

^a All spectra measured in toluene-*d*₆; benzene used as internal standard, chemical shifts recalculated relative to tetramethylsilane ($\delta = +7.3$ ppm); minus sign indicating upfield shift; s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

formed in reaction (1) seems to be very unstable. Its lifetime is short and its concentration low, and therefore it could not be recorded by ^1H NMR.

References

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