

Preliminary communication

CYCLOPENTADIENYLURANIUM(IV) COMPLEXES WITH A CHIRAL METALLIC CENTER

I. CHARACTERIZATION OF A PROCHIRAL STRUCTURE BY PMR SPECTROSCOPY

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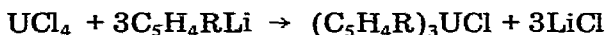
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Summary

A range of compounds $(C_5H_4R)_3UCl$ ($R = \text{alkyl}$) and the two tricyclopentadienyl compounds $(C_5H_5)_2(C_5H_4R)UCl$ and $C_5H_5(C_5H_4R)_2UCl$, ($R = CH(CH_3)_2$) have been isolated and characterized by PMR spectroscopy. For the last compound, the PMR data indicate a magnetic non-equivalence for the cyclopentadienyl protons and for the methyl groups of R ; both are due to the prochirality of the uranium atom.

No cyclopentadienyluranium(IV) complexes with a chiral metallic center have previously been reported. We describe below the synthesis and identification by PMR spectroscopy* of the complex $[C_5H_4CH(CH_3)_2]_2C_5H_5UCl$. In this compound the prochirality of the metal atom must involve a double anisochrony of cyclopentadienyl protons in substituted rings and of the methyl groups in the isopropyl moieties. This identification is supported by the PMR data obtained for a range of substituted tricyclopentadienyl structures.

The substituted tricyclopentadienyl complexes were synthesized by a method similar to that used for $(C_5H_5)_3UCl$ [1]. The cyclopentadienyl anions obtained from methylcyclopentadiene or substituted cyclopentadienes by reduction of the corresponding fulvenes were condensed with UCl_4 in THF.



(I—IV)

(I: $R = CH_3$; II: $R = C(CH_3)_3$; III: $R = Si(CH_3)_3$; IV: $R = CH(CH_3)_2$)

*The PMR signals of uranium(IV) paramagnetic complexes are sharp enough to allow identification of the studied compounds [2].

After centrifugation and evaporation of THF, the crude products are either sublimed or recrystallized at -78°C . The identities were shown by mass spectrometry, in each case, the molecular peak and those of the principal fragments $(M - \text{Cp})^+$, $(M - 2\text{Cp})^+$, $(\text{UCl})^+$ were observed.

The PMR spectra of solutions in deuterobenzene were recorded on a JEOL FX 100 spectrometer. The chemical shifts are given from $\text{C}_6\text{D}_5\text{H}$ used as internal reference, with positive values to high field. The results are presented in Table 1.

TABLE 1
PMR SPECTRA^a OF COMPOUNDS I TO VI

Compound	C_5H_4 protons		C_5H_5 protons	CH proton	CH_3 protons
I, R = CH_3	-4.9(t) (2)	27.8(t) (2)			7.6(s) (3)
II, R = $\text{C}(\text{CH}_3)_3$	-14.0(t) (2)	36.1(t) (2)			11.6(s) (9)
III, R = $\text{Si}(\text{CH}_3)_3$	-9.2(t) (2)	24.3(t) (2)			13.0(s) (9)
IV, R = $\text{CH}(\text{CH}_3)_2$	-10.3(t) (2)	31.5(t) (2)		17.8sept (1)	9.1(d) (6)
V, R = $\text{CH}(\text{CH}_3)_2$	-9.4(t) (2)	26.0(t) (2)	11.4(s) (10)	19.4sept (1)	10.8(d) (6)
VI, R = $\text{CH}(\text{CH}_3)_2$	-11.7(m) (2)	28.3(m) (2)	11.5(s) (5)	18.4sept (2)	9.1(d) (6)
	-7.8(m) (2)	29.9(m) (2)			10.2(d) (6)

^a s, singlet; d, doublet; t, triplet; sept, septet; relative intensities of signals in parentheses.

It will be seen that the equivalent protons H_α and H_β of the substituted cyclopentadienyl rings are split into two triplets ($J \simeq 2.4$ Hz), the first at about -10 ppm and the second at about $+30$ ppm. The large differences of chemical shifts compared with those for diamagnetic cyclopentadienyl complexes, do not allow the triplets to be attributed to the α or β protons of the substituted groups [3]. The protons of the substituents of the rings appear as sharp singlets from 13 – 7 ppm for the compounds I and III, while the isopropyl groups of IV are assigned to one doublet, and one clearly resolved septet (ΔH 1/2 1.7 Hz) (J 6.7 Hz).

The compound $\text{C}_5\text{H}_5[\text{C}_5\text{H}_4\text{CH}(\text{CH}_3)_2]_2\text{UCl}$ (V) was made by adding two equivalents of the anion $[(\text{C}_5\text{H}_4\text{CH}(\text{CH}_3)_2)^-]$ to one equivalent of $\text{C}_5\text{H}_5\text{UCl}_3$ in THF [4]. Even after recrystallization, whatever conditions are used for the preparation in addition to the compound V, small quantities of $[\text{C}_5\text{H}_4\text{CH}(\text{CH}_3)_2]_3\text{UCl}$ (IV) and $(\text{C}_5\text{H}_5)_2[\text{C}_5\text{H}_4\text{CH}(\text{CH}_3)_2]\text{UCl}$ (VI) are always obtained. They come from the redistribution of the cyclopentadienyl ligands during the condensation [5]. The three components of the mixture were identified by PMR and mass spectrometry; the expected three molecular peaks are observed along with fragments corresponding to the loss of one or two cyclopentadienyl ligands.

Compound VI was made by the method used for V, the $[\text{C}_5\text{H}_4\text{CH}(\text{CH}_3)_2]\text{UCl}_3$ being prepared in situ in THF and then added to two equivalents of the cyclopentadienyl anion. During the reaction redistribution of the cyclopentadienyl rings also occurred. In addition to VI, small quantities of V and of $(\text{C}_5\text{H}_5)_3\text{UCl}$ were identified by mass and PMR spectrometry. The PMR spectrum of compound VI (Table 1) shows features similar to those of the complexes $(\text{C}_5\text{H}_4\text{R})_3\text{UCl}$: viz. two triplets ($J \simeq 2.4$ Hz) for the substituted cyclopentadienyl protons, one singlet for the C_5H_5 ring, and one doublet and one septet for the isopropyl group.

A large anisochrony of the substituted cyclopentadienyl protons is apparent in

the spectrum of compound V (see Table 1) which shows two groups of two undifferentiated multiplets, the first two at -11.7 and -7.8 ppm, the second two at 28.3 and 29.9 ppm. The non-equivalence of the methyl groups is also strongly enhanced. They split into two doublets at 9.1 and 10.2 ppm. Such double non-equivalence unambiguously points to the prochirality of the uranium atom. The enhancement of anisochrony in those compounds compared with that in analogous diamagnetic structures makes the cyclopentadienyl complexes of uranium especially suitable for stereochemical study by PMR spectroscopy.

We are extending this study to diastereoisomeric pairs, obtained from chiral bridged dicyclopentadienyl anions.

References

- 1 H.L. Anderson and L.R. Crisler, *J. Organometal. Chem.*, **17** (1969) 345.
- 2 T.J. Marks, A.H. Seyam and J.R. Kolb, *J. Amer. Chem. Soc.*, **95** (1973) 5529; J.M. Manriquez, P.J. Fagan and T.J. Marks, *J. Amer. Chem. Soc.*, **100** (1978) 3939.
- 3 D.H. Slocum and C.R. Ernst, *Advan. Organometal. Chem.*, **10** (1972) 79.
- 4 K.W. Bagnall and J.D. Edwards, *J. Organometal. Chem.*, **80** (1974) C14; K.W. Bagnall, J. Edwards and A.C. Tempest, *J. Chem. Soc. Dalton*, (1978) 295.
- 5 Ou Khan, A. Dormond and J.P. Letourneux, *J. Organometal. Chem.*, **132** (1977) 149.