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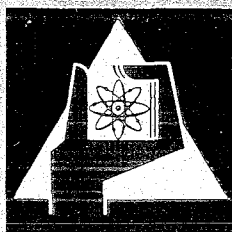
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in Organometallic U(IV)-Compounds

R. v. Ammon, B. Kanellakopulos, R.D. Fischer



GESELLSCHAFT FÜR KERNFORSCHUNG M. B. H.

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NMR EVIDENCE FOR ELECTRON SPIN DELOCALIZATION
IN ORGANOMETALLIC U(IV)-COMPOUNDS

R. VON AMMON and B. KANELLAKOPOLOS

*Institut für Heisse Chemie, Gesellschaft für Kernforschung,
75 Karlsruhe, Germany*

and

R. D. FISCHER

*Anorganisch-Chemisches Laboratorium der Technischen Hochschule München,
8 München, Germany*

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The temperature dependence of the paramagnetic PMR-shifts of $U(C_5H_5)_4$ and $(C_5H_5)_3UBH_4$ has been studied between 165 and 428°K. Both for the ring protons of $U(C_5H_5)_4$ and for the borohydride protons of $(C_5H_5)_3UBH_4$ a remarkably large *indirect* electron spin transfer is indicated. The particularly large average spin transfer to the BH_4 group is best explained by the presence of more than only one U · H · B bridging position.

1. INTRODUCTION

In two previous communications we have reported on the room temperature 1H -NMR (=PMR) spectra of uranium(IV)-tetrakis-cyclopentadienide (UCp_4) [1] and its borohydride derivative Cp_3UBH_4 [2] which in our opinion provide reliable evidence for electron spin delocalization even to the Cp protons of UCp_4 and the BH_4 protons of Cp_3UBH_4 , respectively. Although UCp_4 seems to be a prominent example of a system with an almost isotropic g tensor [3], our interpretation of the UCp_4 spectrum has meanwhile been questioned [4]. The main purpose of the present note is to confirm our initial view by improved arguments involving additional observations on solutions of the two compounds.

2. UCp_4

Unlike that for the tetracyclopentadienides of Nb, Ta [5] and Mo [6] (and most probably also for Ti [7]), the dipole moment of UCp_4 in benzene solution is vanishingly small [3]. This fact should immediately rule out any of the sterically rigid and non-rigid structures $Cp_{4-n}^M UCp_n^C$ to be formulated for $n = 1 - 3$, where Cp^M denotes

a centrally, and Cp^C a non-centrally bonded Cp ligand*. The fact that only one PMR signal is found at room temperature allows all sterically rigid structures to be eliminated. The observation that the PMR spectrum consists of only this one signal at lower temperatures (180 - 325°K) also makes improbable sterically non-rigid structures of this same formulation.

The linewidth of the only detectable signal remains moreover very constant. This behaviour should not be expected for the case of three sterically non-rigid Cp^C ligands as realized best in $MoCp_4$. The presence of only one " σ -Cp-ring" is, on the other hand, very unlikely in view of all so far unsuccessful attempts to prepare the phenyl derivative $Cp_3UC_6H_5$ [10].

If the reciprocal paramagnetic shift $1/\Delta$ is plotted versus the absolute temperature (fig. 1, curve a)**, even the simple Curie law turns out to be satisfactorily valid in so far as the straight line resulting between 185 and 325°K*** after

* Two illustrative examples of sterically non-rigid organometallic complexes with only formally equivalent cyclic ligands, and non-vanishing dipole moments, are $Be(C_5H_5)_2$ [8] and $[C_6(CH_3)_6]_2Ru$ [9].

** The PMR spectra were recorded with a 90 Mc Bruker-Spectrospin spectrometer equipped with a Bruker variable temperature probe.

*** Footnote see next page.

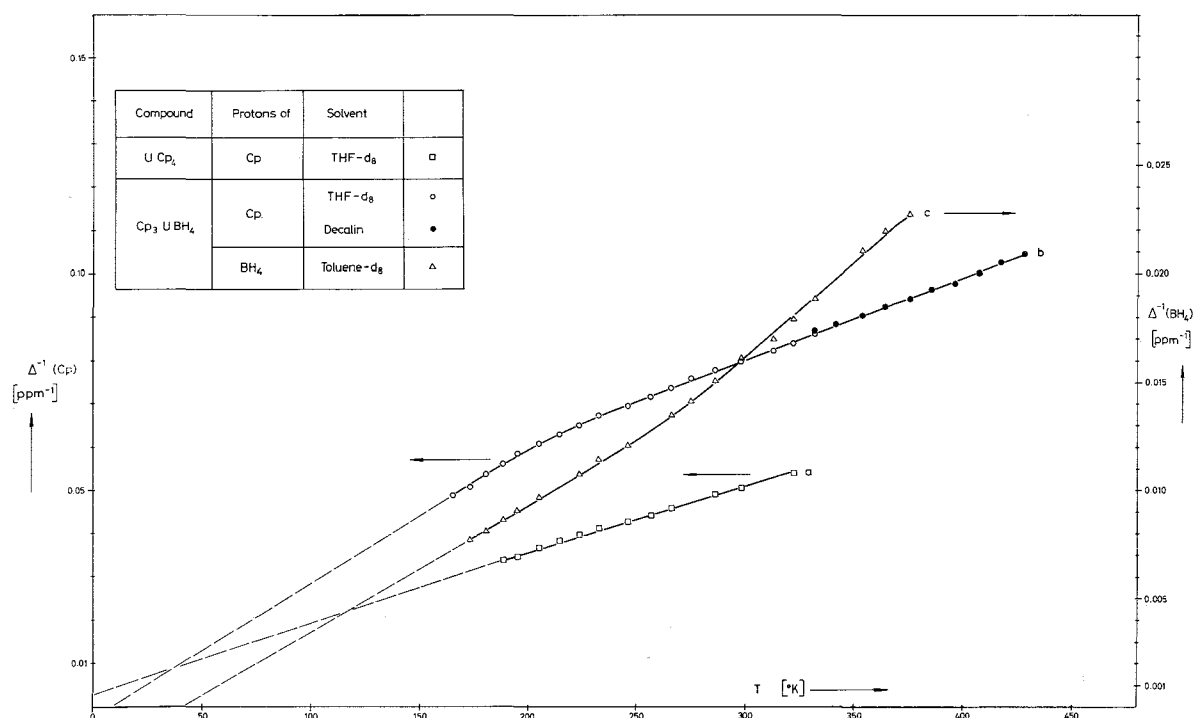


Fig. 2. Reciprocal paramagnetic shift as a function of the absolute temperature [$\Delta = \Delta U(T) - \Delta U(300^\circ\text{K})$].

extrapolation toward $T = 0$ intersects the $1/\Delta$ axis quite close to the coordinate origin.

Apart from providing thus additional confirmation for the absence of sterically non-rigid species $\text{Cp}_{4-n}^M \text{UCp}_n^C$ for $n \neq 0$, and likewise for the absence of excited crystal field levels at ca. 128 to 226 cm^{-1} above the electronic ground state, this important result also justifies *a posteriori* the applicability of eq. (1) as adopted in ref. [1].

For sterically non-rigid molecules eventually occurring for $n = 0$ it should be expected that during each NMR event a large number of steric rearrangements will take place most probably from one equilibrium structure into other equivalent ones. Thus, the average g values due to the effective crystal field produced by this dynamic process should approach tetrahedral conditions even better than the values for one of the equilibrium structures. Considering furthermore that for trigonal distortion the steric factor

$$\bar{K}(\text{Cp}) = \frac{(3\cos^2\theta - 1)/r^3}{UH}$$

determining the dipolar interaction term for the three equivalent Cp ligands apart from the g factor anisotropy amounts to ca. $-5.49 \times 10^{21} \text{ cm}^{-3}$ [11], the reduced g factor anisotropy actually surviving should exceed the rather high value of $g_{\parallel} - g_{\perp} \approx 1.4$ to contribute more than 10% to the total shift (of e.g. +18.6 ppm at 322°K).

3. Cp₃UBH₄

After the replacement of one Cp ligand in UCp₄ by the BH₄ group more favourable conditions for a larger g factor anisotropy will undoubtedly arise. Apart from the observation of quite different Cp proton shifts for these two complexes, evidence for noticeable differences in the U(IV) crystal field splitting patterns is also provided by the pronounced non-linearity of the $1/\Delta$ versus T curves for the Cp and BH₄ protons of Cp₃UBH₄ between 165 and 428°K (fig. 1, curves b and c). Since, on the other hand, both curves approach linearity above ca. 310°K , and are very likely to become also linear below ca.

*** Above ca. 350°K , the formation of insoluble decomposition products of UCp₄ causes appreciable uncertainty in the measurements.

200°K, it seems reasonable to expect here at least one excited crystal field level at ca. $175 \pm 50 \text{ cm}^{-1}$ above the ground state. To avoid additional complications to be expected as long as the excited level(s) around 175 cm^{-1} are noticeably populated, we shall for a first tentative discussion of the origin of the paramagnetic shifts of Cp_3UBH_4 confine ourselves only to its magnetic properties somewhat below room temperature ($\approx 50^\circ\text{K} \leq T \leq \approx 200^\circ\text{K}$) as best represented by the slopes of the two extrapolated curve sections b and c in fig. 1. Ignoring here also the experimental consequences of additional $^{11}\text{B}-^1\text{H}$ nuclear spin-spin coupling [2]*, the observation of the constant intensity ratio of 15:4 of the overall Cp and BH_4 signals over the entire temperature range confirms our initial assumption [2] of a strong BH_4 proton delocalization.

Adopting here for a moment the convenient view that the four BH_4 protons move almost freely on the surface of a sphere with radius r_{BH} around the boron atom the sign of the effective steric factor $3\cos^2\theta(\text{HUB}) - 1$, averaged over all possible proton positions, should turn out unambiguously positive if for the largest possible angle $\theta(\text{HUB})_{\text{max}}$ (as arising for $\angle\text{UHB} = 90^\circ$, see fig. 2) holds: $\cos^2(\text{HUB})_{\text{max}} \geq \frac{1}{3}$. This condition can be reformulated in terms of interatomic distances: $2r_{\text{UB}}^2 \geq 3r_{\text{BH}}^2$. By inspection of

some representative B-H and U-X distances from the literature** the validity of the latter inequality is readily confirmed and it follows that, for the axially symmetric f^2 system in question, any pseudocontact contribution to Δ must be negative, causing a low field shift. The strongly positive experimental shift $\Delta(\text{BH}_4)$ is thus exclusively due to genuine spin transfer and can be expressed approximately by the effective hyperfine coupling parameter $A(\text{BH}_4)_{\text{min}}$, if eqs. (5) and (6) of ref. [11] are solved for $\Delta(\text{BH}_4)$ and a reasonable mean value \bar{g}_\parallel at a distinct temperature. However, as long as the (negative) pseudocontact contribution does not vanish completely, this average $A(\text{BH}_4)_{\text{min}}$ over all possible proton positions and also over all thermally populated crystal field levels signifies only a possible lower limit.

A somewhat more realistic estimate

* The effective coupling parameter $|J_{\text{BH}}|$ decreases from the room temperature value of ca. 86 cps [2] down to approximately zero at 210°K . This phenomenon is presently under closer investigation.

** For $\text{Be}(\text{BH}_4)_2$ and $\text{Al}(\text{BH}_4)_3$: $r_{\text{BH}} \approx 1.2 - 1.4 \text{ \AA}$; $r_{\text{BeB}} = 1.8 \text{ \AA}$; $r_{\text{AlB}} = 2.19 \text{ \AA}$ [12-14].

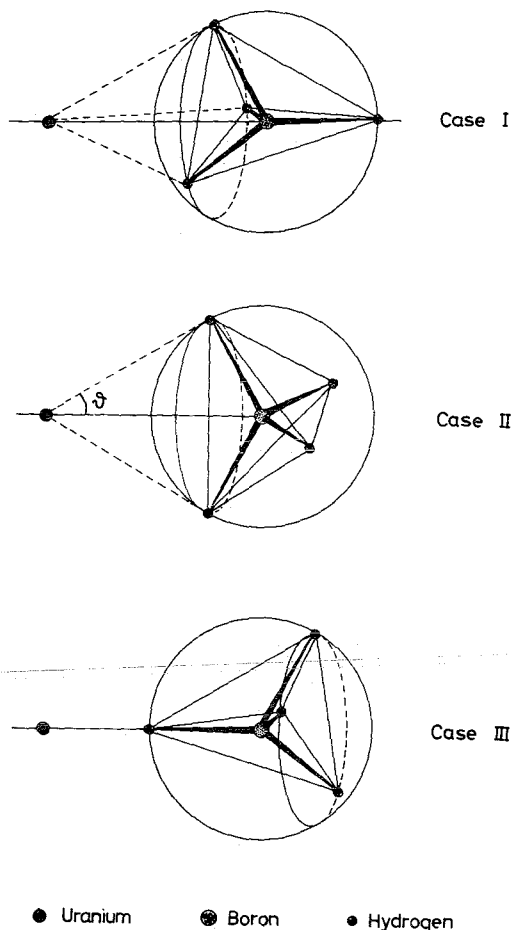


Fig. 2. Schematic representation of three possible model assumptions for the positions of the BH_4 protons relative to the neighbouring $\text{U}(\text{IV})$ ion in Cp_3UBH_4 .

$[=A(\text{BH}_4)_{\text{corr}}]$ may be obtained if the corresponding dipolar interactions are also taken into account. In order to avoid an exaggerated steric factor $\bar{K}(\text{BH}_4)$ (which would arise particularly from the spherical model) the smallest value $\bar{K}(\text{BH}_4)_I$ of the three different equilibrium structures I-III as shown in fig. 2 was adopted, assuming $r_{\text{UB}} = r_{\text{UC1}} = 2.5 \text{ \AA}$ for $\text{Cp}_3\text{UC1}$ [15], $r_{\text{BH}} = 1.3 \text{ \AA}$ and all angles $\angle\text{HBH}$ being exactly tetrahedral. Since the exact \bar{g}_\parallel value is not known for $T \approx 100^\circ\text{K}$, a number of reasonable values for this quantity were considered which will result if the experimental $\Delta(\text{Cp})$ value of Cp_3UBH_4 is assumed to contain various plausible amounts of pseudocontact contribution.

Guided by the previous experience that the pseudocontact contribution to $\Delta(\text{Cp})$ of $\text{Cp}_3\text{UOC}_2\text{H}_5$ amounts to ca. 60% [11], the interval of plausible contact contributions to $\Delta(\text{Cp})$ of Cp_3UBH_4 was limited to 0 - 60%.

From the data in table 1 is seen that for varying g_{\parallel}^2 values the parameter $A(\text{Cp})$ changes considerably while $A(\text{BH}_4)_{\text{corr}}$ remains comparatively constant. The absolute values of $A(\text{BH}_4)_{\text{corr}}$ are larger by almost two orders of magnitude than, for instance, the mean isotropic value \bar{A} (-2.75×10^5 cps) of UCp_4 [1]. This considerable difference in actual spin transfer suggests strongly that the total average $A(\text{BH}_4)_{\text{corr}}$ arises largely from the bridging protons ($\text{U} \cdot \text{H} \cdot \text{B}$) which, unlike the Cp protons, are immediate neighbouring atoms of the paramagnetic centre.

One consequence of this view is that equilibrium structures I and II are to be preferred over III with its single $\text{U} \cdot \text{H} \cdot \text{B}$ bridging proton. Since, moreover, according to a series of recent observations on paramagnetic 3d transition metal complexes, nuclei directly attached to the paramagnetic centre uniquely show strong low field shifts [16], the reverse sign of the BH_4 proton shift suggests that in these two cases in fact different spin transfer mechanisms should predominate. For transition metal complexes, most frequently a direct spin transfer basing upon metal-to-ligand orbital overlapping ($A > 0$) is postulated. However, the spin transfer from the U(IV) ion to the protons in its immediate neighbourhood should most sensibly be considered indirect, i.e. dominated by spin polarization ($A < 0$). This latter deduction, which is valid primarily for the UHB bridging protons, appears to be also in fair accord with our previous inter-

pretation [1] of the $\Delta(\text{Cp})$ value of UCp_4 in view of the apparent inconsistencies with McConnell's theory for indirect C-H spin transfer in cyclic π electron systems. Likewise the U(IV)-to-ring-carbon spin transfer step will most probably be indirect.

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Table 1
Comparison of hyperfine splitting parameters at $T \leq 200^\circ\text{K}$ for the Cp ring protons and BH_4 protons of Cp_3UBH_4 resulting for some reasonable model assumptions (see text) a)

| Fermi contact contribution [%] to ring proton shift | Pseudocontact contribution $\Delta[\text{ppm}]$ ($T=195^\circ\text{K}$) | \bar{g}_{\parallel}^2 b) | $A(\text{Cp}) \times 10^{-5}$ [cps] | $A(\text{BH}_4)_{\text{min}} \times 10^{-5}$ [cps] | $A(\text{BH}_4)_{\text{corr}} \times 10^{-5}$ [cps] |
|---|---|----------------------------|-------------------------------------|--|---|
| 0 | 17.2 | 11.76 | 0 | 47.9 | 178.3 |
| 20 | 13.8 | 9.44 | 1.66 | 53.9 | 171.7 |
| 40 | 10.3 | 7.04 | 3.86 | 61.8 | 162.6 |
| 60 | 6.9 | 4.72 | 7.04 | 75.5 | 158.0 |

a) Any possible improvement of the model assumption used for the evaluation of the data in table 1 is not expected to affect the general deductions actually drawn in the text.

b) For the determination of the A -values the additional approximation was adopted: $\sqrt{g_{\parallel}^2} \approx \bar{g}_{\parallel}$.

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