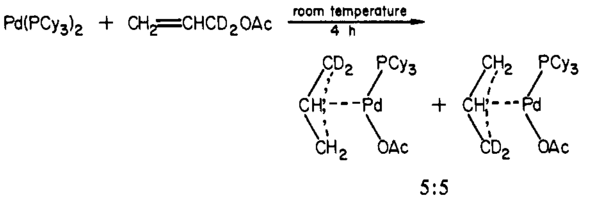
H-D scrambled species such as CHD=CHCHDOAc and CH_2=CDCHDOAc. A small amount of coordinatively unsaturated Pd(0) species such as $Pd(PPh_3)_2$ partly formed seems to be responsible for the catalytic 1,3-shift reaction on interaction with allyl acetate.

Employment of CH_2=$CHCD_2OAc$ in the reaction with $Pd(PCy_3)_2$ affords a mixture of cis and trans isomers of $Pd(\eta^3\text{-}CH_2CHCD_2)(OAc)(PCy_3)$ and a mixture of $[Cy_3P$—CD=$CHCH_2D]^+[OAc]^-$ and $[Cy_3P$—CH=$CHCHD_2]^+[OAc]^-$.



(13)

Allyl-d_2 acetate remaining after the reaction was a mixture of CH_2=$CHCD_2OAc$ and CD_2=$CHCH_2OAc$ in a 6:4 ratio. The reaction of *trans*-$PdEt_2(PEt_3)_2$[11] with allyl acetate at room temperature leads to the C-O bond cleavage to yield $[Pd(\eta^3\text{-}C_3H_5)(PEt_3)_2]^+[OAc]^-$.

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Ultra-High-Field NMR Spectroscopy: Observation of Proton-Proton Dipolar Coupling in Paramagnetic Bis[tolyltris(pyrazolyl)borato]cobalt(II)

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In high-resolution NMR spectra of liquids undergoing rapid molecular tumbling, the observed transition frequencies are averages derived from orientation-dependent local magnetic fields.[2a] Conversely, in solids the motion is quenched, and the spectra contain additional transitions because of orientation-dependent terms in the Hamiltonian,[2b] specifically, dipole-dipole interactions, quadrupole coupling, and chemical shift anisotropy. Spectra obtained in nematic liquid crystal solvents[3] bridge this gap by providing partial orientation in a mobile environment.

The extensive work by Lohman and MacLean[4] on diamagnetic compounds, and our recent study of paramagnetics,[5] show that small partial alignment can also be achieved by application of a strong magnetic field to solutions of magnetically anisotropic molecules containing deuterium. The ensuing order produces a residual deuterium quadrupolar splitting from which magnetic parameters can be deduced. Here we report the first observation of dipole-dipole couplings between *protons* in isotropic solution. This result is significant because of the direct structural information contained in the magnitude of dipolar couplings between $I = {}^1/_2$ spins.

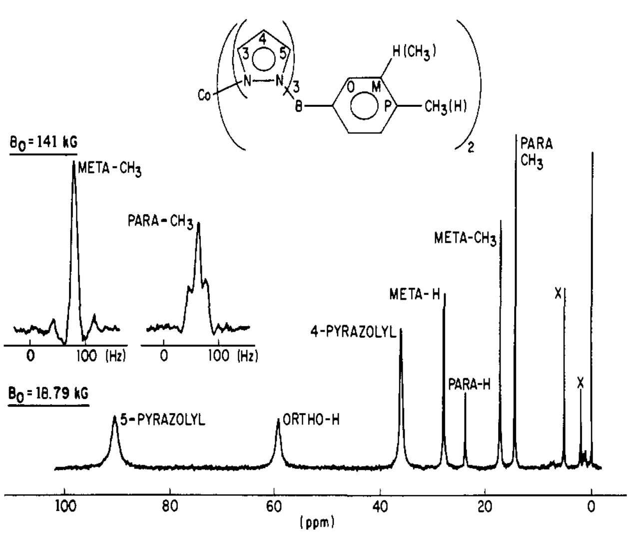

Figure 1. ^1H NMR spectrum of bis[tolyltris(pyrazolyl)borato]cobalt(II) at 80 MHz with the inset showing the methyl resonances at 600 MHz and 293 K. The spectrum is a mixture of *m*-CH_3 and *p*-CH_3 isomers; the para complex is of D_{3d} symmetry. Assignments are shown on the 80-MHz spectrum; the 3-pyrazolyl resonance is approximately 89 ppm upfield of Me_4Si. The 600-MHz spectrum has been resolution enhanced to more clearly reveal the dipolar coupling.

The key to the successful observation of dipolar splitting in our spectra is the 141-kG field currently available[6] for high-resolution NMR spectroscopy. Proton spectra of D_{3d} bis[tolyltris(pyrazolyl)borato]cobalt(II), $Co(TTPB)_2$,[7] are shown in Figure 1 at 80 MHz (B_0 = 18.79 kG) and 600 MHz (B_0 = 141 kG). The para methyl resonance is clearly split into a 1:2:1 triplet ($3D \sim 16$ Hz) at 600 MHz while the meta methyl is unsplit. The corresponding deuterium NMR spectrum of $Co(TTPB\text{-}d_7)_2$ shows all lines split into doublets in the high-field spectrum. The resolving power, or ratio of splitting to line width, is approximately 6 in the deuterium spectrum but near 1 in the proton spectrum. This difference reflects both the increasing difficulty of observing the smaller proton-proton dipolar coupling and a shorter proton T_2.

The deuterium quadrupolar splittings can be measured to give the order parameter S_0 for the alignment at 293 K as previously reported.[4,5]

$$S_0 = (\chi_\parallel - \chi_\perp)B_0^2/15kT = 5.09 \times 10^{-4} \qquad (1)$$

The proton spectrum of the methyl group is easily accounted for with the same alignment (order parameter) and the dipole-dipole interaction term[3,8] to give the dipolar splitting

$$3D_{ij} = \left[\left(\frac{-3\gamma_H^2 h}{4\pi^2}\right)S_0\right]\left(\frac{1}{2}\left\langle\frac{3\cos^2\alpha_{ij} - 1}{R_{ij}^3}\right\rangle\right) \qquad (2)$$

where α_{ij} is the angle between the interproton vector and the principal axis of the susceptibility tensor, R_{ij} is the distance between protons, and the other symbols have their usual meanings. For a standard methyl geometry (R_{CH} = 1.08 Å) the predicted splitting of the para resonance (α = 90°) is 16.7 Hz, in good agreement with the measured value of 16 Hz. The calculated splitting of 4 Hz for the meta resonance (α = 60°) is obscured by the paramagnetic line width.

The observation of dipolar splittings provides an alternative approach to the deuterium quadrupole method[5] for determining the susceptibility anisotropy in paramagnetic complexes. The two

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approaches are complementary because they are applicable to molecules of different size. Deuterium NMR spectroscopy is most appropriate for small paramagnetics because the dominant line-broadening mechanism is quadrupolar relaxation[9] and is minimized by fast rotational correlation times. On the other hand, proton spectra are broadened by electron spin-nuclear spin dipolar relaxation, and the rapid reduction in line width with distance from the metal center (1/r^6)[10] favors this approach for large molecules. In the present example the deuterium quadrupole probe is preferred, particularly since the added mobility of the methyl group increases the deuterium T_2.

It is important to realize that dipolar coupling is inherent in *all* magnetically anisotropic molecules, and proper account of this effect is necessary when interpreting scalar spin-spin couplings. Since the order parameter is quadratic with field strength, observation and reporting of these effects will become more commonplace as superconducting magnet technology achieves higher fields. The value of such observations is clearly the structural information contained in the geometric parameters (α_{ij}, R_{ij}); our trivial example substantiating a methyl group geometry was chosen for simplicity. We expect field dependent studies of dipolar couplings will be applicable to structure determination in larger biological molecules with paramagnetic centers and can be generalized for any interacting $I = {}^1/_2$ nuclei. For example, a typical paramagnetic with an anisotropy of 2000×10^{-6} cgs units mol^{-1} will produce a dipolar coupling of 4.5 Hz between two protons separated by 2 Å in a 600-MHz spectrometer.

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Reduction of Bis(cyclooctatetraene)uranium

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Uranium organometallics have been characterized by five different types of π-bonded ligands, viz., cyclopentadienyl, indenyl, cyclooctatetraene, allyl and arene. So far, of these five, only cyclopentadienyl and indenyl have been shown to occur in complexes of uranium(III).[1,2] A possible route to $\mathrm{U^{III}}$ organometallics with other π-bonded ligands could be by the reduction of allylic derivatives. However, this could be expected to be difficult due to their high instability at room temperature. On the other hand, the synthesis of cyclooctatetraene derivatives (COT = $\mathrm{C_8H_8}$) seems more feasible.

The compound $\mathrm{U^{IV}(COT)_2}$ is thermally stable and soluble in quite a number of organic solvents.[3] Its sandwich structure, analogous to that of ferrocene, is found also in the case of lanthanum(III) as in the anion $\mathrm{Ln^{III}(COT)_2^-}$.[4] In the case of the reduction of $\mathrm{U^{IV}(COT)_2}$ many experiments have been undertaken but were hitherto unsuccessful, due certainly to an excess of reductant leading to an $\mathrm{U^0}$ compound.[5] It is quite probable that the particular stability of $\mathrm{U^{IV}(COT)_2}$ and the reducing power of $\mathrm{U^{III}}$ are responsible for the high fragility of the cyclooctatetraeneuranium(III) compounds.

We have obtained the reduction of $\mathrm{U^{IV}(COT)_2}$ to a $\mathrm{U^{III}}$ compound by controlling the amount of reducing agent used. The reaction was followed by observing the optical spectra, and the products were characterized by their ^{1}H NMR signals. We have also obtained the same compound in solution by a second method using the reaction of $\mathrm{U^{III}Cl_3{\cdot}THF}$ with $\mathrm{K_2COT}$.

The two methods mentioned above are as follows:

(1) An aliquot volume of lithium naphthalenide in THF was gradually added to the $\mathrm{U^{IV}(COT)_2}$ solution. The progress of the reduction was followed spectrophotometrically by observing the decrease of the four peaks of $\mathrm{U^{IV}(COT)_2}$ (613, 639, 657, and 675 nm). The final clear brown solution had a spectrum which did not show any well-defined maxima in the visible range but presented a small band in the near infrared range (~1700 nm) (Figure 1). It is worthwhile to note that the four bands of the initial $\mathrm{U^{IV}(COT)_2}$ completely disappeared when we employed a $\mathrm{C_{10}H_8^-/U^{IV}}$ ratio of about 1. In such a case ESR measurements showed that no naphthalenide was left over after the reduction. This was also confirmed by the disappearance of the $\mathrm{C_{10}H_8^-}$ optical spectrum [$\lambda_{\max}$ ~800 nm (ϵ 2.25×10^3 L mol^{-1}/cm^{-1})] and the appearance of the UV spectrum of naphthalene (310, 285 nm). The ^{1}H NMR spectrum of this solution presents a single broad (40 Hz) line at 37 ppm high field relative to $\mathrm{C_6H_6}$ at room temperature.

It was possible to obtain crystals when a very pure solution of $\mathrm{U(COT)_2}$ was reduced by $\mathrm{Li^+C_{10}H_8^-}$ and kept overnight. The brown needles were extremely sensitive to air (pyrophoric) and are insoluble in toluene.

Elementary analysis did not provide valid results owing to the high instability of the solid. (The C/Li ratio found was ~23 and C/H ~ 1; the amount of product was insufficient to allow uranium analysis.) Mass spectra present peaks which were assigned as follows: 446, $\mathrm{U(COT)_2^+}$; 151, Li·2THF; 78, Li·THF; 72, THF; 104, $\mathrm{C_8H_8^+}$. Peaks at 135 ($\mathrm{C_{10}H_8Li}$), 128 ($\mathrm{C_{10}H_8}$), 1107, and 862 were also detected. The ^{1}H NMR signal of these crystals, very soluble in THF-d_8, is identical with that obtained with the original solution (37 ppm; see above). This single NMR signal, of the same order of magnitude as that for $\mathrm{U(COT)_2}$, requires a sandwich structure in which the two COT rings are equivalent. The NMR and mass spectra strongly suggest the formula $\mathrm{U(C_8H_8)_2^-Li_n^+{\cdot}THF}$.

(2) The same compound can also be obtained directly from $\mathrm{U^{III}}$. To a solution of $\mathrm{UCl_4}$[6] in THF, an excess of NaH or LiH was added so as to obtain $\mathrm{UCl_3}$. THF[6] identified by its visible spectrum (450, 475, 510, and 540 nm). To this solution was then added $\mathrm{K_2(COT)}$, and the ^{1}H NMR signal of the resulting brown solution was identical with that obtained by method 1.

That the uranium is trivalent has been well established as follows:

(a) Figure 2 shows the ESR spectrum of a frozen solution cooled to 6 K. The similarity of this spectrum with those of other $\mathrm{U^{III}}$ compounds[7] which are very broad and asymmetric as well as the fact that $\mathrm{U^{VI}}$ and $\mathrm{U^{IV}}$ do not give ESR spectra and $\mathrm{U^{V}}$ does, but something quite different, leads us to assign our spectrum to $\mathrm{U^{III}}$. This signal disappears at higher temperature or when the solution is oxidized.

(b) The ^{1}H NMR spectra show that the protons of the ligands COT undergo a paramagnetic shift of the order of 40 ppm at room temperature. Although the paramagnetic shifts induced by $\mathrm{U^{III}}$ are very close to those of $\mathrm{U^{IV}}$, at least in the case of cyclopentadienyls,[8] the effect of temperature on this shift shows a behavior quite different from that of $\mathrm{U^{IV}}$ which follows the Curie-Weiss law (Figure 3).

(c) Addition of this trivalent compound (obtained by using the first method) to a solution of $\mathrm{Ti^{IV}(\mathit{i}\text{-}OC_3H_7)_4}$ in THF leads to $\mathrm{Ti^{III}}$

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