I

II → III

$$R_2R'NAlCl_3 \; + \; AlCl_3 \; + \; HCl$$

IV   V

(150 ml; Table I). After evaporation of the solvent and treatment of the residue with water, products were isolated *via* chromatography on activated alumina. The products, usually obtained initially as oils, were crystallized from appropriate solvents (Table I).

This work makes available a new route to silicon compounds of ferrocene and is facile compared to methods previously available for the synthesis of such compounds.[20] The scope of the new process is under further investigation.

(20) E. A. Mailey, C. R. Dickey, G. M. Goodale, and V. E. Matthews, *J. Org. Chem.*, 27, 616 (1962), and references therein.

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Dipole–Dipole Interactions of a Spin-$^1/_2$ Nucleus with a Quadrupole-Coupled Nucleus[1]

Sir:

In recent nmr experiments, the dipolar broadening of the proton resonance in solid $HMn(CO)_5$ and $HCo(CO)_4$ has been used to estimate the metal–hydrogen bond distance.[2,3] The M–H bond distances thus obtained are exceptionally short, 1.28 A for Mn–H and 1.42 A for Co–H. However, the analyses were based on the Van Vleck[4] second moment expression

(2) T. C. Farrer, S. W. Ryan, A. Davison, and J. W. Faller, *J. Am. Chem. Soc.*, 88, 184 (1966).
(3) T. C. Farrar, F. E. Brinkman, T. D. Coyle, A. Davison, and J. W. Faller, *Inorg. Chem.*, 6, 161 (1967).

which assumes that the nuclei are quantized in the direction (z) of the static magnetic field H_0 and which therefore neglects any quadrupole coupling effects at the metal nucleus. This communication describes a theoretical analysis and numerical calculations for a two-spin ($^1/_2$, $^7/_2$) system, having axial symmetry about the internuclear vector **r** and quadrupole coupling at the spin-$^7/_2$ nucleus. It is found that the second moment M_2 of the spin-$^1/_2$ nucleus may be as much as 1.84 times its value in the absence of the quadrupole coupling. Therefore, the M–H bond distances reported previously[2,3] may be as much as 11% too small.

We start with Slichter's expression[5] for the line shape $f(\omega)$ in the vicinity of $\omega_0 = \gamma_I H_0$ when $H_0 \gg \Delta H_{loc}$ and $kT \gg E_a$, for the spin-$^1/_2$ nucleus I. This is

$$f(\omega) = \sum_{E_a > E_b} \delta(E_a - E_b - \hbar\omega) \qquad (1)$$

with E_a and E_b the final and initial Zeeman energies of the eigenstates a and b involved in a transition of nucleus I. The function $\delta(E_a - E_b - \hbar\omega)$ has the value zero or one, respectively, when the argument is nonzero or zero. Equation 1 implies that the transition probabilities near ω_0 are constant; therefore, to find $f(\omega)$ we need only the energy differences $(E_a - E_b)$.

The spin pair is heteronuclear, so the eigenfunctions, ψ_i^+, are the product functions

$$\psi_i^+ = (\pm^1/_2, \phi_i) \qquad (2)$$

and the ϕ_i's are eigenstates of nucleus S. We are concerned only with transitions of nucleus I, which requires that

$$(E_a - E_b)_i = \langle \psi_i^- | \mathcal{H} | \psi_i^- \rangle - \langle \psi_i^+ | \mathcal{H} | \psi_i^+ \rangle \qquad (3)$$

where $\mathcal{H}$ is the Hamiltonian describing spin I. To calculate energies to first order, $\mathcal{H}$ must contain the Zeeman term plus secular perturbations. However, because of the quadrupole interaction, the spin S may be quantized with nonvanishing components away from H_0. Therefore, assuming only dipolar perturbations, we find

$$\mathcal{H} = -\gamma_I \hbar H_0 I_z + \frac{\gamma_I \gamma_S \hbar^2}{r^3} [(1 - 3\cos^2\theta)I_z S_z -$$

$$(3 \sin\theta \cos\theta)I_z S_x] \qquad (4)$$

where θ is the angle between H_0 and **r**. Next, we define

$$\Delta\omega_i = -\gamma_I H_0 + (E_a - E_b)\hbar^{-1} \qquad (5)$$

which is a measure of the frequency spread around ω_0 due to dipolar interactions with spin S. Combination of eq 2–5 gives

$$\Delta\omega_i = \frac{\gamma_I \gamma_S \hbar}{r^3} [\langle S_z \rangle_i (3\cos^2\theta - 1) +$$

$$3\langle S_x \rangle_i \sin\theta \cos\theta] \qquad (6)$$

with $\langle S_{x,z} \rangle_i = \langle \phi_i | S_{x,z} | \phi_i \rangle$.

The solutions for $\Delta\omega_i$ require $\langle S_{x,z} \rangle_i$ which in turn depends on ϕ_i. To find the ϕ_i we assumed the quantization axis of nucleus S to be determined by its Zeeman and quadrupole interactions; this approximation is equivalent to $H_0 \gg \Delta H_{loc}$ employed for the I nucleus in

(4) J. H. Van Vleck, *Phys. Rev.*, 74, 1168 (1948).
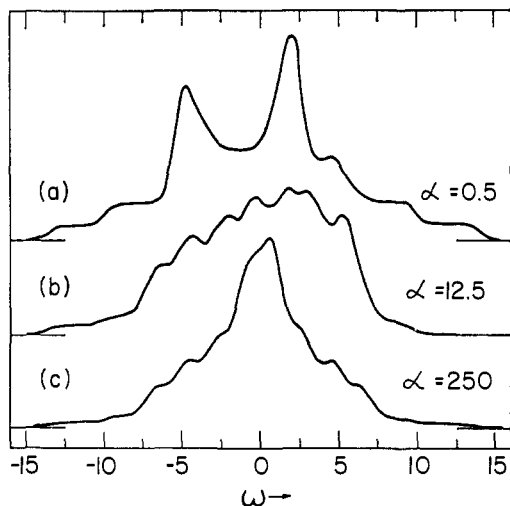(5) C. P. Slichter, "Principles of Magnetic Resonance," Harper and Row Publishers, New York, N. Y., 1963, p 51.

Figure 1. Calculated, Gaussian-broadened, polycrystalline line shapes for a spin-$^1/_2$ nucleus in an axially symmetric two-spin ($^1/_2$, $^7/_2$) system; α is a measure of the relative Zeeman and quadrupolar energies of the spin-$^7/_2$ nucleus; the abscissa units are $\gamma_1\gamma_S\hbar/2r^3 = 1$; the zeros of the spectra occur at $\omega_0 = \gamma_1 H_0$.

eq 1. Therefore, the Hamiltonian, $\mathcal{H}_S$, for nucleus S in the laboratory frame is[6]

$$\mathcal{H}_S = -\gamma_S \hbar H_0 S_z + \frac{e^2 qQ}{4S(2S-1)}\{ {}^1/_2(3S_z^2 - S^2) \times$$

$$(3\cos^2\theta - 1) + {}^3/_2[S_z(S^+ + S^-) +$$

$$(S^+ + S^-)S_z]\sin\theta\cos\theta + {}^3/_4[(S^+)^2 +$$

$$(S^-)^2]\sin^2\theta\} \quad (7)$$

The Zeeman quantized spin functions of S were used as a basis set; the matrix elements of $\mathcal{H}_S$ were calculated, the matrix was diagonalized, and the transformation matrix was obtained. The latter was used to calculate $\langle S_{z,z}\rangle_t$ and thereby $\Delta\omega_t$.

Line shapes for a polycrystalline sample were obtained from numerical values for $\Delta\omega_i$ in 400 divisions of the interval $0 \leq \theta \leq \pi$, such that each line consisted of 3200 points, each point being weighted by its probability, $\sin\theta$. The lines were then folded with a rather narrow Gaussian function. In this way line shapes were calculated for the entire range of the parameter

$$\alpha = |\gamma_S \hbar H_0 [e^2 qQ/4S(2S-1)]^{-1}| \quad (8)$$

with $S = {}^7/_2$. Figure 1 shows lines calculated for three values of α. The parameter α gives the relative magnitudes of the Zeeman and quadrupole interactions for the S nucleus. It is seen that as the quadrupole interaction becomes larger, or the Zeeman smaller, the extremities of the spectrum do not broaden; however, the intensity is redistributed toward the wings. Also, the line shapes for intermediate α are very asymmetric. This reflects the fact that the Zeeman and quadrupole terms in $\mathcal{H}_S$ depend differently on S_z so that the $+m_z$ and $-m_z$ states are affected differently. However, in spite of the asymmetry, the zero of the first moment remains at ω_0 for the entire range of α. The asymmetry in Figure 1 corresponds to Zeeman and quadrupole interactions of the same sign in eq 8. The asymmetry is reversed if they are of opposite sign, so it can, in

(6) A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, London, England, 1961, p 233.
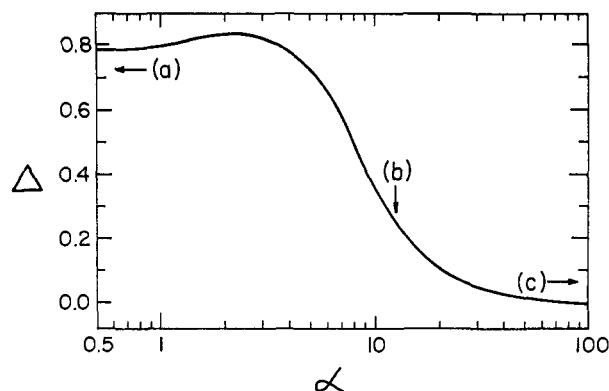

Figure 2. Variation in the second moment of the spin-$^1/_2$ nucleus in the two-spin ($^1/_2$, $^7/_2$) system as a function of α; $\Delta = (M_2 - M^0_2)/M^0_2$ where M_2 is the second moment and M^0_2 is the second moment in the absence of quadrupolar effects.

principle, be used to establish the sign of the quadrupole coupling constant.

The second moment can be a sensitive function of α as shown by the results in Figure 2 for the unbroadened line. The sharpest changes occur in the region $30 > \alpha > 3$, so line-shape and M_2 observations as a function of H_0 in this region might enable one to establish the magnitude of the quadrupole coupling constant in addition to its sign. Beyond the range of α given in Figure 2, M_2 does not change noticeably; there are, however, discernible changes in the line shape. The asymptotic value of M_2 for large quadrupole interactions[7] is 1.79 times its value in their absence. Therefore, if such effects were neglected for $\alpha \gtrsim 0.3$, and the observed value of M_2 used to evaluate the internuclear distance r, the true value of r would be 1.10 times the apparent value. Thus, our treatment gives a corrected, upper limit of 1.57 A on the H–Co bond distance of $HCo(CO)_4$ and an upper-limit estimate of 1.42 A for the H–Mn bond in $HMn(CO)_5$. These bond distances should be quite feasible because of the large quadrupole moments of ^{51}Co and ^{55}Mn and the resultant probably small values of α.

At present, we are trying to fit the $HCo(CO)_4$ proton spectrum as a function of H_0. Whether or not this is successful will depend on the complications introduced by the scalar coupling and the anisotropy of the proton chemical shift. Similar line-shape and second-moment analyses are planned for the spin-$^3/_2$ and -$^5/_2$ cases.

(7) An approximate analysis of this limiting case has been made independently by G. M. Sheldrick, with results similar to ours. We thank him for sending us a preprint of his work.

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The Chemistry of Bisiminium Cations. I.
A Synthesis of 1-Deuterio Aldehydes

Sir:

Bisiminium cations (*e.g.*, I and II) are described by Kröhnke[1] as reasonably stable crystalline solids easily

(1) F. Kröhnke and H. Leister, *Chem. Ber.*, **91**, 1295 (1958).