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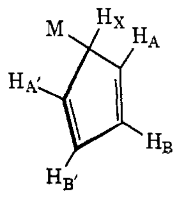
The Interpretation of a Spin-Tickling Experiment on (*Monohapto*cyclopentadienyl)-(methyl)(dichloro)silane

Sir:

It is now well known that *monohapto*cyclopentadienylmetal and metalloid moieties are usually fluxional,[1] and many investigations[2–12] have been conducted to elucidate the rearrangement pathways in these and the related *monohapto*(1-indenyl)metal systems.

In the first mechanistic study of a fluxional *monohapto*cyclopentadienylmetal molecule[2] it was proposed that the rearrangement pathway in $(h^5\text{-}C_5H_5)Fe(CO)_2(h^1\text{-}C_5H_5)$ consists wholly or predominantly of 1,2 shifts. The line of argument, which need not be reviewed here, has as its crucial step the correct assignment of the two parts of the AA′BB′ multiplet due to the olefinic protons in the limiting low-temperature pmr spectrum. While absolutely direct, rigorous proof for that assignment which leads to the conclusion that 1,2 rather than 1,3 shifts are predominant has not been given, an indirect case which we consider to be virtually irrefutable has been built up for several of the transition metal compounds by a variety of data.[3–7]

The principal criteria,[12a] which are quite independent of one another, for the assignment of the AA′BB′ multiplet leading to 1,2 shifts in $(h^5\text{-}C_5H_5)Fe(Ru)(CO)_2(h^1\text{-}C_5H_5)$ are (1) comparison of relative chemical shifts with those in the analogous h^1-1-indenyl compound, where the assignment has been rigorously established by deuteration and multiple resonance experiments,[3,13] (2) correlation of the observed fine structure due to spin–spin coupling with empirically established ranges for magnitudes and signs of such couplings,[4] and (3) inference from the relative sensitivities of the two kinds of olefinic protons in the $h^1\text{-}C_5H_5$ ring of $(C_5H_5)_3MoNO$ to the effects of diamagnetic anisotropies.[5–7] It turns out that for the iron, ruthenium, and molybdenum molecules just discussed, as well as for $(h^5\text{-}C_5H_5)Cr(NO)_2(h^1\text{-}C_5H_5)$,[3] the portion of the AA′BB′ multiplet lying at *lower* field is due to the A protons, as defined in I. However, it was clearly demonstrated[8] that the relative values of the chemical shifts for A and B protons are sensitive to the nature of the group to which the $h^1\text{-}C_5H_5$ or h^1-(1-indenyl) group is attached and that no *general* argument for the constancy of these relative values or even for the constancy of one of them is likely to be tenable or safe.



I

Davison and Rakita[10–12] have studied *monohapto*cyclopentadienyl- and *monohapto*(1-indenyl) derivatives of $(CH_3)_3Si$, $(CH_3)_3Ge$, and $(CH_3)_3Sn$. Employing only the first of the aforementioned criteria, they adopted an assignment for the AA′BB′ multiplet in the $(CH_3)_3M(h^1\text{-}C_5H_5)$ compounds which led to 1,2 shifts. This assignment placed the A protons at *higher* field than the B protons, in contrast to the situation with the transition metal compounds just mentioned. However, as noted in the preceding paragraph, such a reversal is entirely credible and constitutes no cause whatever to doubt Davison and Rakita's conclusion that 1,2 shifts prevail in the nontransition metal (and metalloidal) as well as in the transition metal derivatives. Nevertheless, it rests on only one line of indirect argument.

The recent challenge to the conclusion of 1,2 shifts put forward by Sergeyev, Avramenko, and Ustynyuk[14] on the basis of a spin-tickling experiment[15] on $CH_3Cl_2Si(h^1\text{-}C_5H_5)$ therefore deserved careful scrutiny. These workers report very well-defined experimental results, from which they deduced an assignment opposite to Davison and Rakita's and then, necessarily, a 1,3-shift pathway. We report here that we have scrutinized their interpretation of their spin-tickling experiment and conclude that they are in error. We find that their results nicely confirm 1,2 shifts by confirming Davison and Rakita's assignment.

Sergeyev, Avramenko, and Ustynyuk first performed an analysis of the pmr spectrum to obtain the magnitudes and *relative* signs[16] of the coupling constants in the AA′BB′ system and the magnitudes of J_{AX} and J_{BX}. This analysis showed that these two constants

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[1] F. A. Cotton, *Accounts Chem. Res.*, **1**, 257 (1968).

[2] M. J. Bennett, F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard, and S. M. Morehouse, *J. Amer. Chem. Soc.*, **88**, 4371 (1966).

[3] F. A. Cotton, A. Musco, and G. Yagupsky, *ibid.*, **89**, 6136 (1967).

[4] F. A. Cotton and T. J. Marks, *ibid.*, **91**, 7523 (1969).

[5] F. A. Cotton and P. Legzdins, *ibid.*, **90**, 6232 (1968).

[6] J. L. Calderon, F. A. Cotton, and P. Legzdins, *ibid.*, **91**, 2528 (1969).

[7] F. A. Cotton, *Discuss. Faraday Soc.*, **No. 47**, 79 (1969).

[8] F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, **91**, 3178 (1969).

[9] P. West, M. C. Woodville, and M. D. Rausch, *ibid.*, **91**, 5649 (1969).

[10] A. Davison and P. E. Rakita, *ibid.*, **90**, 4479 (1968).

[11] A. Davinson and P. E. Rakita, *Inorg. Chem.*, **9**, 289 (1970).

[12] P. E. Rakita and A. Davison, *ibid.*, **8**, 1164 (1969).

[12a] NOTE ADDED IN PROOF.—Very recently another type of evidence has been provided for the assignment which leads to 1,2 shifts: C. H. Campbell and M. L. H. Green, *J. Chem. Soc.*, 1318 (1970).

[13] The fact that the indenyl molecule is not fluxional provides in itself strong support for the 1,2-shift pathway as noted.[3]

[14] N. M. Sergeyev, G. I. Avramenko, and Y. A. Ustynyuk, *J. Organometal. Chem.*, **22**, 79 (1970).

[15] R. A. Hoffman and S. Forsen, *Progr. Nucl. Mag. Resonance Spectrosc.*, **1**, 15 (1966).

[16] D. M. Grant, R. C. Hirst, and H. S. Gutowsky, *J. Chem. Phys.*, **38**, 470 (1963).

were of nearly identical magnitude, *i.e.*, 1.1 and 0.9 Hz.[17] We confirm this analysis (although we believe it could be refined) and using the coupling constants of Sergeyev, Avramenko, and Ustynyuk we calculate[18] the upper spectrum in Figure 1.

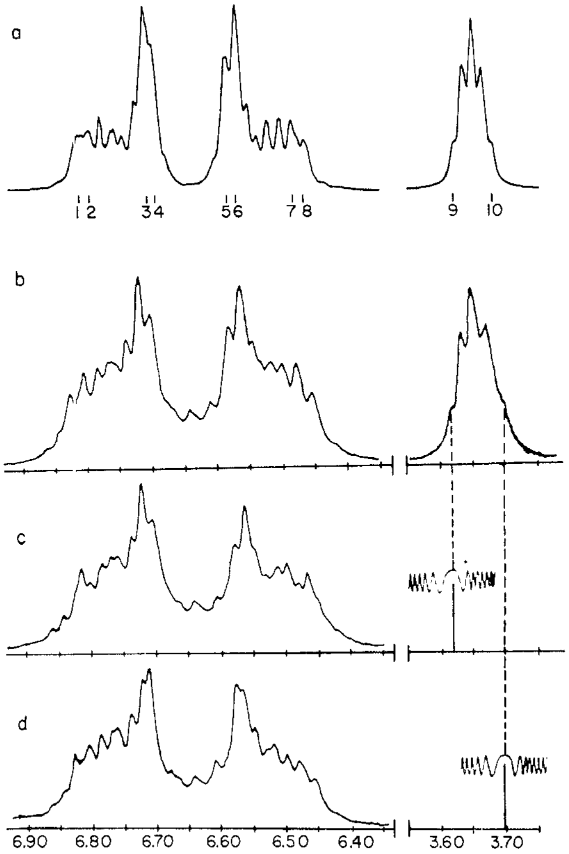

Figure 1.—(a) Computer-simulated spectrum, with J_{AX} = ±1.1 Hz and J_{BX} = ±0.9 Hz. (b) Observed spectrum. (c, d) Spectra recorded with spin tickling of the lines indicated. Spectra b–d are as in ref 14.

The spin-tickling experiment must next be used to resolve the sign ambiguities. Basically such an experiment consists of irradiating certain transitions within one spin multiplet with a weak radiofrequency field and observing which lines within the same or other multiplets are perturbed. Ideally, only transitions which share energy levels with the irradiated transition will be affected, and lines corresponding to these transitions should be split or at least perturbed. The ordering of the transitions and energy levels depends on the signs of J_{AX} and J_{BX} relative to the signs for the AA'BB' system. One may therefore predict the results of the spin-tickling experiment for each combination of signs and compare with experiment. Such predictions can be made in three independent ways: (1) qualitatively by extrapolation from simpler systems (*e.g.*, an ABX system), (2) by examining how an AA'BB' system is perturbed by coupling to X, and (3) by direct computation of the AA'BB'X system.[18–20] We have used each of these methods and in each case we arrive at the same qualitative predictions shown in the upper part of Table I. The fact that each independent line of reasoning gives the same qualitative result makes it virtually impossible that there is a qualitative logical error in any of them. Only the + − and − + sign combinations are considered in Table I since purely qualitative reasoning shows that the combinations + + and − − would lead to unsymmetrical effects on the AA'BB' multiplet in the experiment performed, whereas the observed effects are such as to preserve the symmetry of the multiplet. Our predictions are quite different from those of Sergeyev, Avramenko, and Ustynyuk, given in the lower part of the table.[21] Figure 1, the lower part of which reproduces the experimental results of Sergeyev, Avramenko, and Ustynyuk, shows that the tickling experiment validates case A. From this point on, empirical arguments, *i.e.*, that J_{AX} must be >0 while J_{BX} must be ≤0, which Sergeyev, Avramenko, and Ustynyuk themselves used and which indeed seem quite secure[4,22,23] lead to the assignment of the upfield portion of the multiplet to the A protons and thus, finally, to the conclusion that 1,2 shifts predominate.

TABLE I

PREDICTED RESULTS OF CERTAIN TICKLING EXPERIMENTS

	Assumed signs of coupling constants, Hz				
Case	J_{AX} (= ±1.1)	J_{BX} (= ±0.9)	Transition tickled	Transition to be perturbed	Source
A	+	−	9	1,2,7,8	This work
	+	−	10	3,4,5,6	
B	−	+	9	3,4,5,6	This work
	−	+	10	1,2,7,8	
C	−	+	9	1,2,5,6	SAU[14]
	−	+	10	3,4,7,8	
D	+	−	9	3,4,7,8	SAU[14]
	+	−	10	1,2,5,6	

This result is very satisfying because, in addition to confirming the occurrence of 1,2 shifts, it indicates that in all of the systems of type I as well as the analogous indenyl systems, where the metal or metalloidal group is nontransitional (*e.g.*, a group IV element, Hg, or H) the relative chemical shifts of the A and B protons are consistent, with A being upfield from B. In the transition metal systems, the large diamagnetic anisotropies due to additional ligands such as h^5-C_5H_5, CO, and NO

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[17] The significant difference here from the cases of $(h^5\text{-}C_5H_5)Fe(CO)_2\text{-}(h^1\text{-}C_5H_5)$ and its Ru analog[4] lies in the near equality of the magnitudes of the constants and the symmetrical appearance of the multiplet in this case, whereas for the Fe and Ru compounds, fortuitously (and felicitously) one coupling constant was *ca.* 0.0 Hz while the other was ±1.2 Hz; this led directly to the assignment.

[18] NMRPLOT, a modified version of the computer program LAOCN3 by A. A. Bothner-By and S. M. Castellano, was kindly supplied by Professor G. M. Whitesides of this department. We thank Mrs. Jeanne Krieger for advice concerning its use.

(19) D. D. Elleman and S. L. Manatt, *J. Chem. Phys.*, **36**, 2346 (1962).

(20) M. A. Cooper, D. D. Elleman, C. D. Pearce, and S. L. Manatt, *ibid.*, in press. We thank Dr. Manatt for showing us his results in advance of publication.

(21) There would appear to be certain purely typographical errors in Sergeyev, Avramenko, and Ustynyuk's labeling which further confuse their argument.

(22) H. Gunther, *Z. Naturforsch. B*, **24**, 680 (1969).

(23) M. Karplus, *J. Amer. Chem. Soc.*, **85**, 2870 (1963).

are presumably responsible for reversing this situation, as we have already suggested.[8]

(24) NSF Predoctoral Fellow, 1966–1970.
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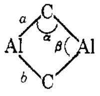
The Molecular Structure and Bonding in Hexamethyldialuminum

Sir:

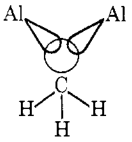
In the past few months a lively controversy has developed over the nature of the methyl bridge bonding in $Al_2(CH_3)_6$. This author wishes to point out that *on the basis of the published structural data there is no basis for controversy.* Disputation has been engendered solely by incomplete analysis of the available data.

In 1967 Vranka and Amma[1] carried out an X-ray structural study of crystalline $Al_2(CH_3)_6$. They found the distances and angles shown in I and concluded that each bridge bond could best be understood as a two-electron, three-center (2e-3c) interaction employing an orbital on each Al atom and a quasi-tetrahedral orbital on the carbon atom as previously proposed by Longuet-Higgins[2] and depicted schematically in II.



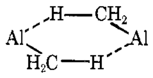
$a = b = 2.14 \pm 0.01$ Å
$\alpha = 74.7°$
$\beta = 105.3°$

I

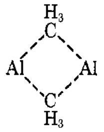


II

More recently, Byram, *et al.*,[3] have claimed that their further refinement of the structure, using Vranka and Amma's own data, led to the conclusions that (a) the Al and C positions as given by Vranka and Amma are correct, but (b) one of the hydrogen atoms of the bridging methyl group is located in or near the central Al–C–Al–C ring plane at distances of 1.08 (12) Å from C and 1.78 (13) Å from Al, the figures in parentheses being the (rather large) estimated standard deviations for these distances. From this they concluded that the structure contains two two-electron hydrogen bridge bonds, such as might be represented by III. Dewar and Patterson[4] have recently depicted structures III and IV (which is simply a schematic representation of Vranka and Amma's structure) as alternatives and reported nqr data which they believe favors IV.

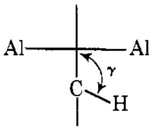


III



IV

When the available structural information is considered *in full*, one finds that III does not depict a viable structural alternative to IV. It is simply an unjustified, incorrect, and misleading drawing. From the C–H and H···Al distances given by Byram, *et al.*, and the *essentially equal* pair of Al–C distances,[5] simple trigonometry shows that the angle γ in V is 93° with an uncertainty of at least 12° due to the esd's of the C–H and H···Al distances. This is entirely compatible with the 2e-3c Al–C–Al bonding situation symbolized by IV and does not require the acceptance of the situation represented by III. The only justifiable conclusion would seem to be that rotation of the bridging methyl groups in IV about their threefold axes may be somewhat restricted with a preference for the rotamer having one H atom in the central ring plane.



V

In conclusion, the work of Byram, *et al.*, does not, contrary to their claim, raise any real question about the previously accepted view of the structure and bonding of the bridge system in $Al_2(CH_3)_6$; it most certainly provides no palpable grounds for rejecting this picture.

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(1) R. G. Vranka and E. L. Amma, *J. Amer. Chem. Soc.*, **89**, 312 (1967).
(2) H. C. Longuet-Higgins, *J. Chem. Soc.*, 139 (1946).
(3) S. K. Byram, J. K. Fawcett, S. C. Nyburg, and R. J. O'Brien, *Chem. Commun.*, 16 (1970).
(4) M. J. S. Dewar and D. B. Patterson, *ibid.*, 544 (1970).
(5) Note that III depicts these as being very unequal, which is a gross misrepresentation.

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