

(COOEt)<sub>2</sub>, for excess CH<sub>3</sub>SK gives much CH<sub>3</sub>SSCH<sub>3</sub>; however, reaction of CH<sub>3</sub>Cl with NaCH(COOEt)<sub>2</sub> gives a product highly contaminated with (CH<sub>3</sub>S)<sub>2</sub>C-(COOEt)<sub>2</sub> through a disproportionation of anions. Reduction of the ester by LiAlH<sub>4</sub> gives CH<sub>3</sub>SCH-(CH<sub>2</sub>OH)<sub>2</sub> which, when condensed with isobutyraldehyde,<sup>3</sup> gives a mixture of **1a** and **1b** separated by glpc; configuration is readily assigned by nmr (*J*<sub>4,5</sub>). Oxidation of **1a** and **1b** with the stoichiometric amount of *m*-chloroperbenzoic acid at 0–5° gave **2a** and **2b** whose configurations were unequivocally assigned by dipole measurement: **2a**, 3.50 D, **2b**, 2.46 D. The stereoisomers differ appreciably in their uv absorption: **2a**, λ<sub>max</sub> 202.5 nm (ε 1490); **2b**, λ<sub>max</sub> 208 nm (ε 3400) (both in cyclohexane); the latter absorption is typical of compounds such as cyclohexyl methyl sulfoxides. The ir stretching frequency for S–O differed trivially for **2a** (1060 cm<sup>-1</sup>) and **2b** (1065 cm<sup>-1</sup>) (CCl<sub>4</sub>). Oxidation of **1a** and **1b** with 2 mol of *m*-chloroperbenzoic acid at room temperature gave **3a** and **3b**. All compounds had carbon and hydrogen analyses within 0.3% of the calculated.

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### Hyperconjugation and p–d Homoconjugation in Radicals Containing β Heavy Atom Substituents

Sir:

Following the discovery<sup>1</sup> that certain radicals of type R<sub>2</sub>ĊCR<sub>2</sub>(MR<sub>3</sub>) have a preferred conformation in which the MR<sub>3</sub> group is held out of the radical plane such that the C<sub>β</sub>–M bond has maximum overlap with the p orbital on the radical center, we showed<sup>2</sup> that for such radicals, there was an unusually large isotropic hyperfine coupling to the M nucleus and suggested that this could best be understood in terms of a hyperconjugative delocalization mechanism.

Recently, Kawamura and Kochi<sup>3</sup> have reported some liquid-phase results for <sup>29</sup>Si and <sup>117,119</sup>Sn which strongly support our solid-state data and agree that the large "metal" hyperfine interactions indicate hyperconjugation interaction. Such an interaction is clearly sufficient to explain the hyperfine data and the preferred orientations, but Kawamura and Kochi maintain that in order to explain the g<sub>av</sub> values a considerable amount of delocalization of the unpaired electron into the outer d orbitals of the metal atom is required. We feel that arguments based upon very small differences in g<sub>av</sub> values are unsafe, but that, for these radicals, the deviations from the free-spin value are so small that they constitute evidence against significant d-orbital involvement.

The argument rests upon the g<sub>av</sub> values, some of which are summarized in Table I. Of those used by Kawamura<sup>1</sup> and Kochi,<sup>3</sup> only that for the tin compound need be considered seriously since the differences between the other three values must be close to experimental error. The value of 2.00205 for the tin compound deviates from the free-spin value by ca. –0.00025, which is a shift of ca. 0.4 G at the X band. This must also be quite close to the experimental error involved in its estimate. The issue is, can this really be utilized to prove a 12% delocalization into the tin d-orbital manifold?

The computation given<sup>3</sup> utilizes the g<sub>av</sub> values for the radicals MR<sub>3</sub> in order to estimate the g shift induced by hyperconjugation. For the tin compound, the shift is probably overestimated because no allowance seems to have been made for a spin–polarization contribution to the isotropic coupling to <sup>117,119</sup>Sn.<sup>2</sup> Also, the g<sub>av</sub> value of 2.018 used is that given by Gordy and co-workers<sup>4</sup> for SnH<sub>3</sub>. Our value for Bu<sub>3</sub>Sn radicals is g<sub>av</sub> = 2.007,<sup>5</sup> which would lead to a considerably reduced value for ρ<sub>d</sub> (the d-orbital population).

The equation used to relate the Δg values to ρ<sub>d</sub>, namely<sup>3</sup>

$$\Delta g_d = 4\xi_d \rho_d (E_0 - E_d)$$

depends strongly upon the magnitude of E<sub>0</sub> – E<sub>d</sub>, the energy gap between the carbon 2p orbital and the outer metal d orbital. (The d orbitals were assumed to be nearly degenerate.<sup>3</sup>) This gap was estimated to be about 6.9 eV,<sup>3</sup> and it is this very large value that enables the authors to reconcile a very small g shift with a large d-orbital population. It seems to me that this energy gap is so large that no appreciable delocalization of the type envisaged could possibly occur. If, then, the gap is reduced (as a result, say, of d-orbital contraction) to a value that would accord with a 12% delocalization, then the equation would predict a negligible ρ<sub>d</sub> value.

One has only to recall the known situation for first-row transition metal complexes<sup>6</sup> to appreciate that, for systems involving nearly degenerate, magnetically coupled d orbitals, g shifts are very large indeed, and, even if the spin population is reduced to 10%, by delocalization onto ligands, g shifts of the order of 0.1 or more are to be expected. In other words, one would need to postulate a very large splitting of the d levels in order to accommodate the very small change in g<sub>av</sub> with even a 1% delocalization into the d manifold.

The main point of this note, however, is to show that results for several other radicals in this class, all of which exhibit the required preferred conformation and, where measured, a large isotropic coupling to the metal nucleus, have g values which, when analyzed by the method of Kawamura and Kochi,<sup>3</sup> give quite different results.

(i) The best documented radical of this class is MeĊHCH<sub>2</sub>AsO<sub>3</sub>H, which has g-tensor components (corrected using the full Breit–Rahi equation) of 2.008, 2.002, and 2.012, giving g<sub>av</sub> = 2.0073.<sup>2</sup> In order to

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(2) A. R. Lyons and M. C. R. Symons, *Chem. Commun.*, 1068 (1971); *J. Chem. Soc., Faraday Trans. 2*, 622 (1972).

(3) T. Kawamura and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 648 (1972).

(4) R. L. Morehouse, J. J. Christiansen, and W. Gordy, *J. Chem. Phys.*, **45**, 1751 (1966).

(5) Unpublished result.

(6) This comparison is valid, since the spin–orbit coupling constants are of similar magnitude to that for tin.

**Table I.** Values of  $g_{av}$  for Some of the Radicals Discussed in the Text<sup>a</sup>

Radical	$H_2\dot{C}CH_2C(Me)_3$	$H_2\dot{C}CH_2Si(Me)_3$	$H_2\dot{C}CH_2Ge(Me)_3$	$H_2\dot{C}CH_2Sn(Me)_3$			
$g_{av}$	2.00268	2.00265	2.00255	2.00205			
Radical	$Me\dot{C}HCH_2AsO_3H^b$	$H_2\dot{C}C(OH)MePO(OMe)_2^c$	$HOCH_2\dot{C}HCH_2SO_3^-$	$H_2\dot{C}CH(Me)PPh_3^{+b}$			
$g_{av}$	2.0073	2.00273	2.0026 <sup>d</sup>	2.003			
Radical	$H_2\dot{C}CH_2AsEt_3$	$Me_3Si\dot{C}$	$Me_3Ge\dot{C}$	$H_3Sn^e$	$Bu_3Sn^f$		
$g_{av}$	~2.01 <sup>b</sup>	2.0031	2.0100	2.018	2.007		
Radical	$PH_3^{+b}$	$PEt_3^{+b}$	$AsEt_3^{+b}$	$SO_3^{2-g}$	$PO_3^{2-h}$	$AsO_3^{2-i}$	
$g_{av}$	~2.007	~2.007	~2.01	2.0036	2.001	1.997	

<sup>a</sup> Data from ref 3 unless otherwise stated. <sup>b</sup> Reference 2. <sup>c</sup> Reference 10. <sup>d</sup> Reference 11. <sup>e</sup> Reference 4. <sup>f</sup> Unpublished results. <sup>g</sup> G. W. Chantry, A. Horsfield, J. R. Morton, and D. H. Whiffen, *Mol. Phys.*, **5**, 233 (1962). <sup>h</sup> A. Horsfield, J. R. Morton, and D. H. Whiffen, *ibid.*, **4**, 475 (1961). <sup>i</sup> Reference 8.

allow for the effect of hyperconjugation delocalization, we need  $\rho\sigma$ , which is *ca.* 15.7%<sup>2</sup> and  $g_{av}$  for the  $\beta$ -group radical,  $HAO_3$ . For the radical  $AsO_3^{2-}$ ,  $g_{av}$  is reported to be 2.005 in one environment,<sup>7</sup> and 1.997 in another,<sup>8,9</sup> and our unpublished results for this radical favor the latter value. Thus, the  $\rho\sigma$  correction makes the  $g$  shift even more positive, whereas any delocalization into the outer d manifold for arsenic must require a negative shift.

(ii) Similarly, for the radical  $H_2\dot{C}C(OH)MePO(OMe)_2$ ,  $g_{av} = 2.00273$ ,<sup>10</sup> while those for  $PO_3^{2-}$  and related radicals are usually slightly less than 2.000. Thus again, the  $g_a$  value is positive rather than negative.

(iii) The radical  $HOCH_2\dot{C}HCH_2SO_3^-$  has  $g_{av} = 2.0026$ ,<sup>11</sup> while that for  $SO_3^{2-}$  is generally reported to be *ca.* 2.00345.

Our results for many other radicals in this class are generally insufficiently accurate to enable us to deduce  $g$  values to better than *ca.*  $\pm 0.002$ , but, in all cases, values close to that of the free spin were found, which leads us to conclude that d-orbital participation is of trivial significance (compare data in Table I).

Finally, one can estimate the extent of delocalization with fair accuracy from the values of the isotropic coupling to the  $\alpha$  protons. For the tin compound mainly considered herein, Kawamura<sup>1</sup> and Kochi find  $a(\alpha H) = 19.69$  G, whereas the corresponding carbon compound had  $a(\alpha H) = 22.06$  G. This gives a 10.7% total delocalization of the spin. Since it is agreed that the  $\sigma$  delocalization corresponds to *ca.* 13% delocalization,<sup>3</sup> one must surely conclude that there is no other major delocalization mechanism.

Our results for many similar radicals<sup>2</sup> give good agreement between the delocalization estimated for the  $\alpha$ -proton coupling and that estimated for the metal coupling.

It is interesting to note that a very similar criticism can be made of the arguments presented by Mackey and Wood,<sup>12</sup> as modified by Kawamura<sup>1</sup> and Kochi,<sup>3</sup> upon which much of this work<sup>3</sup> was based. These workers found very small negative shifts in  $g_{av}$  for the series  $H_2\dot{C}CMe_3$ ,  $H_2\dot{C}SiMe_3$ ,  $H_2\dot{C}GeMe_3$ , and  $H_2\dot{C}SnMe_3$  and hence argued in favor of d-orbital partici-

pation. While their value of *ca.* 1% was too small to affect the  $\alpha$ -proton coupling constants appreciably, the revised value<sup>3</sup> of *ca.* 10% is; since, in fact, the  $\alpha$ -proton coupling constants are almost invariant through the series, it is unlikely that such a large delocalization is occurring. Furthermore,  $g_{av}$  values for isostructural radicals derived from group V elements, such as  $R_2\dot{C}PR_3^+$  and  $R_2\dot{C}AsR_3^+$ , are in fact clearly greater than that of the corresponding carbon radicals,<sup>13</sup> which again seems to nullify the argument.

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### The Formation of Tin-Group III Metal-Metal Bonded Derivatives and Their Nuclear Magnetic Resonance Spectra

Sir:

The formation of mixed metal-metal bonded compounds has been of interest for many years because of the information which may be gained from study of the bonding interactions and varied chemical reactivity of these species. Major efforts have been placed on obtaining metal group III derivatives but these have failed to yield significant results for other than boron derivatives. We now wish to report preliminary data on the formation of Sn-Al, Sn-Ga, Sn-In, and Sn-Tl bonded derivatives. Data on the Sn-<sup>1</sup>H coupling across these metals as well as Tl-<sup>1</sup>H coupling in these species are also included.

$Li[Sn(CH_3)_3]$  was prepared by reaction of  $Sn_2(CH_3)_6$  (0.25 ml) with lithium metal in 4 ml of dimethoxyethane (DME) at  $-10$  to  $-5^\circ$  for 4 hr. At  $0^\circ$   $J_{SnCH} = 10.0$  Hz and  $\delta$  1.925 ppm above cyclopentane for this compound. Wells and Brown<sup>1</sup> reported  $J_{SnCH} = 5.2$  Hz when the compound was prepared in THF, as described by Tamborski, *et al.*<sup>2</sup> These results and those in Table I show that  $J_{Sn-H}$  in  $LiSn(CH_3)_3$  varies substantially both as a function of solvent and temperature due to ion pair and complex formation and will be discussed elsewhere.<sup>3</sup>

The  $Li[B(CH_3)_4]$  was obtained from the reaction of  $LiCH_3$  and  $B(CH_3)_3$  in ethyl ether<sup>4</sup> while  $Li[Al(CH_3)_4]$

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