

spectral work was done at the Humble Oil and Refining Company in Baytown, Texas and Baton Rouge, La.

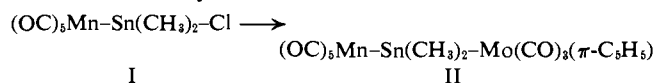
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Metal-Metal Bonding Sequences Involving Three Different Metals

Sir:

A number of compounds have been reported which involve covalent bonds between two different metals in the sequence M-M'-M. A partial listing of some of the more recent would include Fe-Sn-Fe,^{1a} Au-Fe-Au,^{1b} Ge-Pt-Ge,^{1c} Mn-Sn-Mn,^{1d} Mn-Ge-Mn,^{1e} and Ge-Hg-Ge.^{1f} Dighe and Orchin² have now described a compound having a sequence of three different metals, π -C₅H₅Fe(CO)₂HgCo(CO)₄, which is evidently the first example of its type to be reported. We are therefore prompted to communicate a portion of our own work involving sequences M-M'-M''.

We have prepared several compounds of this general type by stepwise replacement of chlorine in dimethyltin dichloride. Thus pentacarbonylmanganesedimethyltin chloride (I) readily forms π -cyclopentadienyltricarbonylmolybdenum(pentacarbonylmanganese)dimethyltin (II) by reaction with π -cyclopentadienylmolybdenumtricarbonyl anion.



Compound II can be isolated from pentane-methylene chloride as yellow crystals, melting without decomposition at 95-96°. *Anal.* Calcd. for C₁₅H₁₁O₈MoSnMn: C, 30.60; H, 1.87; mol. wt., 589. Found: C, 31.2; H, 1.8; mol. wt.,³ 565. The n.m.r. spectrum shows cyclopentadienyl protons at τ 4.65 and methyltin protons centered at τ 9.20; the ratio of areas is 5:6.4 (calcd. 5:6). Infrared carbonyl stretching bands are observed in carbon tetrachloride solution at 2090, 2085, 2056, 2001, 1924, and 1895 cm.⁻¹. These may be compared with the values 1997, 1922, and 1895 cm.⁻¹ observed⁴ in the related compound (CH₃)₃SnMo(CO)₃(π -C₅H₅).

Other compounds which we have prepared are listed in Table I. An aspect of particular interest is the magnitude of spin coupling between methyl protons and the isotopes ¹¹⁷Sn and ¹¹⁹Sn. A progressive decrease in the coupling constant occurs as the methyl groups of tetramethyltin are successively replaced by transition metal atoms.

The trend of coupling constants in relation to bond type can be understood in terms of two concepts applied by Flitcroft and Kaesz⁵ in their study of spin-spin coupling in the methylstannanes: (a) that H₃C-Sn

(1) (a) F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 179 (1964); (b) E. C. Coffey, J. Lewis, and R. S. Nyholm, *ibid.*, 1741 (1964); (c) R. J. Cross and F. Glockling, *Proc. Chem. Soc.*, 143 (1964); (d) R. D. Gorsich, *J. Am. Chem. Soc.*, 84, 2486 (1962); (e) A. G. Massey, A. J. Park, and F. G. A. Stone, *ibid.*, 85, 2021 (1963); (f) N. S. Vyazankin, G. A. Razuvaev, and E. N. Gladyshev, *Dokl. Akad. Nauk SSSR*, 151, 1326 (1963); *Chem. Abstr.*, 59, 14014 (1963).

(2) S. V. Dighe and M. Orchin, *J. Am. Chem. Soc.*, 86, 3895 (1964).
 (3) Mechrolab osmometer in chloroform solution.
 (4) H. R. H. Patil and W. A. G. Graham, to be published.
 (5) N. Flitcroft and H. D. Kaesz, *J. Am. Chem. Soc.*, 85, 1377 (1963).

Table I. Chemical Shifts and Coupling Constants for Methyltin Derivatives^a

Compound	τ_{CH_3}	$\tau_{\text{C}_5\text{H}_5}$	$J(^{119}\text{Sn}-\text{CH}_3)$
(CH ₃) ₄ Sn ^b	9.86		54.0
(CH ₃) ₃ Sn-Mo(CO) ₃ (π -C ₅ H ₅)	9.56	4.59 ^c	48.5
(CH ₃) ₃ Sn-Fe(CO) ₂ (π -C ₅ H ₅) ^{c,d}	9.55	5.11	~49
(CH ₃) ₂ Sn[Mo(CO) ₃ (π -C ₅ H ₅)]-[Mn(CO) ₅]	9.20	4.65 ^c	36.9
(CH ₃) ₂ Sn[W(CO) ₃ (π -C ₅ H ₅)]-[Mn(CO) ₅]	9.18	4.59	37.3

^a Measured in CCl₄ using a Varian HR-100 spectrometer; τ -values relative to tetramethylsilane as internal standard; coupling constant J in c.p.s. ^b From ref. 5. ^c In CHCl₃ solution, using A-60 spectrometer. ^d J. Kenney and W. A. G. Graham, unpublished.

coupling will be proportional to the s-character of the hybrid tin orbital used in the bond to carbon, and (b) the s-character of an atom tends to concentrate in orbitals that are directed toward electropositive groups.⁶ It thus appears that tin orbitals engaged in bonding to transition metals have more than 25% s-character, leaving the methyl-bonded tin orbitals with reduced s-character and diminished coupling constants.

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(6) H. A. Bent, *Can. J. Chem.*, 38, 1235 (1960).

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Hyperconjugative Enhancement of Geminal Coupling Constants

Sir:

Recent symposia^{1,2} have emphasized that use of hyperconjugation for explaining certain molecular properties is a matter of considerable controversy. The disagreement centers on whether electron delocalization involving σ - and π -bonds or hybridizational changes in the connecting C-C σ -bond offers the best means for rationalizing the physical and chemical data. We now wish to present evidence which supports the former.

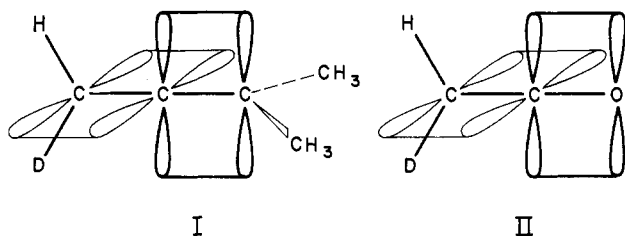
Work by Barfield and Grant³ on π -bond enhancement of geminal coupling constants in adjacent methylene groups has impinged upon the problem by exhibiting the importance of hyperconjugative terms in the transmission of spin-spin couplings in a large number of unsaturated molecules. In this study the symmetry and molecular orientation were shown experimentally and theoretically to affect the degree of delocalization as detected by the modification of the spin-spin coupling constants.

The cumulated systems, allene and ketene, constitute pertinent cases for studying possible hyperconjugative effects. This is illustrated by structures I and II where the methylene group in each compound exhibits an unusually favorable orientation relative to the vicinal π -bond. Not only are these hydrogens locked into the same symmetry plane as the vicinal π -electron systems, but the C=C bond distances between the

(1) "The Conference on Hyperconjugation," Indiana University; *Tetrahedron*, 5, 105 (1959).

(2) "Paper Symposium," *ibid.*, 17, 123 (1962).

(3) M. Barfield and D. M. Grant, *J. Am. Chem. Soc.*, 85, 1899 (1963).



methylene and adjacent carbon atoms are even shorter than for ethylene. These two features, symmetry and bond shortening, would be expected to enhance electron delocalization of the hyperconjugative type.

We have determined the geminal coupling constants, ${}^2J_{\text{HH}'}$, for 1,1-dimethylallene (I) and ketene (II) by deuterium substitution at the methylene carbon. 1,1-Dimethylallene-3-*d* (I) was obtained by treatment⁴ of 3-chloro-3-methyl-1-butyne-1-*d* with lithium aluminum hydride. Ketene-2-*d* (II) was synthesized by pyrolysis of deuterated acetic anhydride at 600°.

Spectra were recorded with a Varian A-60 n.m.r. spectrometer at room temperature for the allene I and -62° for the deuterioketene II. The geminal coupling constants ${}^2J_{\text{HH}'}$ and chemical shift data are given in Table I. Also included is the fairly sizable long-range coupling ${}^5J_{\text{HH}'}$ observed in the substituted allene.

It is possible to construct C-H bonds from carbon orbitals of the following form

$$\Psi(C_i) = [1/(1 + \lambda_i^2)^{1/2}] \{ s + \lambda_i (\cos \theta_i p_z + \sin \theta_i \cos \varphi_i p_x + \sin \theta_i \sin \varphi_i p_y) \} \quad (1)$$

The *z*-axis is taken along the C-C bond, and the *x*-coordinate is selected as the orientation of the vicinal π -bond. Equation 1 is used in a semiempirical approach based on a valence bond perturbation treatment of π -electron delocalization to obtain the expression given in eq. 2 for ${}^2J_{\text{HH}'}$, the vicinal π -bond contribution to the geminal coupling constant. The

$${}^2J_{\text{H}_1\text{H}_2}^\pi = -\eta_1\eta_2AK^2_{p_zp_\pi} \cos^2 \varphi_1 \cos^2 \varphi_2 \quad (2)$$

exchange integral, $K_{p_zp_\pi}$, is between the $2p_z$ orbital used in the C-H bonds and the adjacent $2p_\pi$ orbital, $\eta_i = \lambda_i^2 \sin^2 \theta_i / (1 + \lambda_i^2)$, and A is an empirical constant of proportionality. In an sp^2 carbon with equivalent CH bonds $\eta_1 = \eta_2 = 1/2$, while $\eta_1 = \eta_2 = 2/3$ for the corresponding sp^3 carbon. The parameter A is determinable as follows from the previous work³ on a series of sp^3 geminal couplings where $R_{\text{C-C}}$ was about 1.46 Å.

$$(4/9)AK^2_{p_zp_\pi} (\sim 1.46 \text{ \AA.}) = 8 \text{ c.p.s.} \\ AK^2_{p_zp_\pi}(R) = 18a^2 \text{ c.p.s.} \quad (3)$$

where $a = K_{p_zp_\pi}(R)/K_{p_zp_\pi} (\sim 1.46 \text{ \AA.})$. A value for $a (\sim 1.32 \text{ \AA.})$ equal to 1.71 (3.00 e.v./1.75 e.v.) is obtained for allene and ketene from the graph of the $K_{p_zp_\pi}$ integral given by Coulson and Altmann.⁵ The 1.32 Å. distance was selected as it is a mean of the two literature values for ketene⁶ (1.329 Å.) and allene⁷ (1.311 Å.). The value of $A'K^2_{p_zp_\pi} (\sim 1.32 \text{ \AA.})$ then will equal 52.6 c.p.s. from which a ${}^2J_{\text{H}_1\text{H}_2}^\pi$ contribution of -13.2 c.p.s. is obtained from eq. 2. Estimates of ${}^2J_{\text{H}_1\text{H}_2}^\sigma$,

(4) T. L. Jacobs, E. G. Teach, and D. Weiss, *J. Am. Chem. Soc.*, **77**, 6254 (1955).

(5) C. A. Coulson and S. L. Altmann, *Trans. Faraday Soc.*, **48**, 293 (1952).

(6) W. F. Arendale and W. H. Fletcher, *J. Chem. Phys.*, **21**, 1898 (1953).

(7) B. P. Stoicheff, *Can. J. Phys.*, **33**, 811 (1955).

Table I.

	1,1-Dimethylallene	Ketene
	Experimental values	
δ (CH ₂), p.p.m.	4.44 (neat)	2.47 (neat), 2.43 (85% in TMS), 2.20 (9% in TMS)
δ (CHD), p.p.m.	4.42 (neat)	2.40 (85% in TMS), 2.17 (9% in TMS)
δ (CH ₃), p.p.m.	1.63 (neat)	
${}^2J_{\text{HD}}$, c.p.s.	$\pm 1.38 \pm 0.05$	$\pm 2.42 \pm 0.06$
${}^2J_{\text{HH}'}$, c.p.s.	$\pm 9.0 \pm 0.3$	$\pm 15.8 \pm 0.4$
${}^5J_{\text{HH}'}$, c.p.s.	$\pm 3.10 \pm 0.05$	
	Predicted values	
${}^2J_{\text{HH}'}$, c.p.s.	+2.2 ^a	-2.1 ^b
${}^2J_{\text{HH}'}$, c.p.s.	-13.2	-13.2
${}^2J_{\text{HH}'} = {}^2J_{\text{HH}'}^\sigma + {}^2J_{\text{HH}'}^\pi$	-11.0	-15.3

^a Average of ethylene, +2.3 c.p.s. [D. M. Graham and C. E. Holloway, *Can. J. Chem.*, **41**, 2114(1963)], and propene, +2.1 c.p.s. [A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **83**, 231 (1961)]. ^b Average of four vinyl compounds with a strongly electronegative vicinal group: vinyl fluoride -3.2 c.p.s. [C. N. Banwell and N. Sheppard, *Proc. Roy. Soc. (London)*, **A263**, 136 (1961)], vinyl chloride -1.4 c.p.s. [C. N. Banwell, N. Sheppard, and J. J. Turner, *Spectrochim. Acta*, **16**, 794 (1960)], vinyl bromide -1.8 c.p.s. [H. S. Gutowsky, M. Karplus, and D. M. Grant, *J. Chem. Phys.*, **31**, 1278 (1959)], methyl vinyl ether -2.0 c.p.s. [R. T. Hobgood, Jr., G. S. Reddy, and J. H. Goldstein, *J. Phys. Chem.*, **67**, 110 (1963)].

the σ contribution to the couplings, can be rationalized from work on vinyl and ethylenic derivatives as indicated in Table I. Considering the many approximations involved, the comparison of predicted vs. experimental values for ${}^2J_{\text{HH}'}$ is remarkable. While estimates for ${}^2J_{\text{H}_1\text{H}_2}^\sigma$ are admittedly coarse, this term is considerably smaller than ${}^2J_{\text{H}_1\text{H}_2}^\pi$, which will account for the magnitude of the observed geminal coupling constants. It should be indicated that the success of this interpretation rests on the experimental coupling constants being of a negative sign.

Using an equation identical in form with eq. 2, ${}^5J_{\text{HH}'}$ for 1,1-dimethylallene is calculated to be +5.3 c.p.s. Using the parameters $\eta_1 = 1/2$, $\eta_2 = 2/3$, $\cos^2 \varphi_1 = 1$, $(\cos^2 \varphi_2)_{\text{av}} = 1/2$, $a_1 = 1.7$, and $a_2 = 1.0$, a value of 30.6 c.p.s. is obtained for $AK^2_{p_zp_\pi}(\text{CH}_2) \cdot K_{p_zp_\pi}(\text{CH}_3)$. As values for the other contributions to the long-range ${}^5J_{\text{HH}'}$ coupling are not available, it is not possible to compare directly the predicted ${}^5J_{\text{HH}'}$ with the experimental value of ${}^5J_{\text{HH}'} = \pm 3.1$ c.p.s. It is reasonable, however, to infer that the sizable ± 3.1 coupling constant over five bonds is due primarily to a hyperconjugative term involving electron delocalization. While the above interpretation is semiempirical, the results based on the hyperconjugative model are in reasonable agreement with experiment, and as such are preferred to explanations based upon changes in hybridization.

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