

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

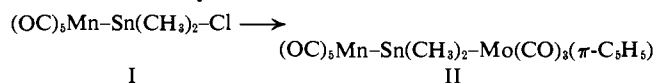
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Metal-Metal Bonding Sequences Involving Three Different Metals

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}	$\tau_{\text{C}_5\text{H}_5}$	$J(^{119}\text{Sn-CH}_3)$
(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).