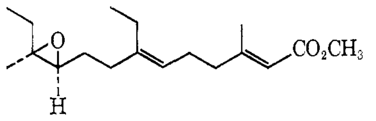
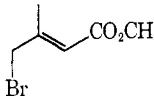
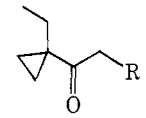


1

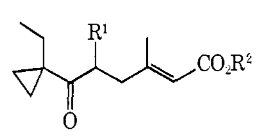
0–23° for 5 hr to give the keto diester **4** ($R^1 = CO_2CH_3$; $R^2 = CH_3$) which, on treatment with barium hydroxide in refluxing aqueous methanol (35 min), underwent hydrolysis and (on acidification) decarboxylation to yield a mixture from which the crystalline keto acid **4** ($R^1 = R^2 = H$), mp 64–65°, was readily isolated in 65% yield. The nmr spectrum (CCl_4) showed a single vinyl methyl absorption at δ 2.18 ppm, characteristic of the *trans* configuration.[1] The keto acid was converted to the methyl ester **4** ($R^1 = H$; $R^2 = CH_3$) with diazomethane. Reduction with sodium borohydride in methanol afforded the carbinol **5** which was transformed, by treatment with phosphorus tribromide and lithium bromide in collidine–ether followed by zinc bromide in ether,[4] into the *trans,trans*-bromodienic ester **6** which proved to contain a maximum of 5% of the *trans,cis* isomer.[7]



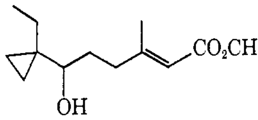
2



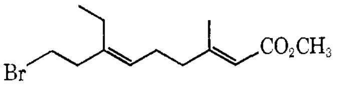
3



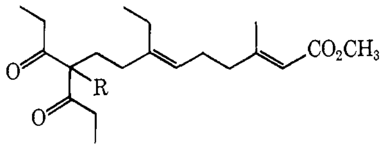
4



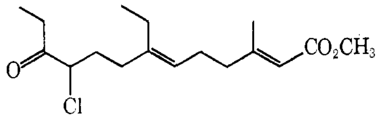
5



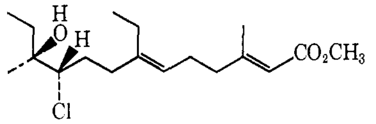
6



7



8



9

The bromo compound **6** was converted, by treatment with sodium iodide in hexamethylphosphoramide for 6 hr at room temperature, into the corresponding iodo compound[8] which, without purification, was allowed to react for 4 days with an excess of the lithium enolate of heptane-3,5-dione in refluxing tetrahydrofuran containing 5% hexamethylphosphoramide. The resulting dione **7** (R = H), which was separated (in 45% yield) by Florisil chromatography from some trienic ester (formed by dehydrohalogenation), was chlorinated by the Kosower method[9] (cupric and lithium chloride in dimethylformamide) to give the chloro dione **7** (R = Cl). This last substance, on treatment at 0° for 25 min with barium hydroxide in ethanol, underwent deacylation to give the chloro ketone **8** which was readily purified by preparative vpc.[10] When the chloro ketone **8** was treated with excess methylmagnesium chloride in tetrahydrofuran at −75° the Grignard reagent reacted only with the keto group to give the racemic chlorohydrin **9**, contaminated with a maximum of 8% of its diastereoisomer (see below).[11] The chlorohydrin, on stirring for 10 min at room temperature with anhydrous potassium carbonate in methanol, was converted into the epoxide **1** (*Anal.* Found: C, 73.3; H, 10.4). The 100-Mc nmr spectrum (CCl_4) of this product was indistinguishable from that of the authentic juvenile hormone[1] except that our specimen showed an additional weak signal at δ 1.17 ppm corresponding to the methyl group at C-11 of the *trans* epoxide.[1] The area under this signal was 5–8% of that under the methyl signal at δ 1.19 ppm for the *cis* isomer.[12] Therefore our product is contaminated with a maximum of 8% of the *trans,trans,trans* isomer[13] and, as shown above, 0–5% of the *trans,cis,cis* isomer. The mass spectrum fragmentation pattern as well as the vpc behavior of our product was indistinguishable from that of the authentic material.

Acknowledgment. We wish to express our thanks to Professor B. M. Trost for supplying us with a comparison specimen of the authentic racemic juvenile hormone and for conducting some of the vpc comparisons. We also thank Professor A. Meyer for conducting some preliminary vpc analyses. We are grateful to the U. S. Public Health Service and the National Science Foundation for support of this research.

---

(7) A sample of this bromodienic ester was converted, by treatment with sodium acetate in dimethylformamide (see ref 4), into the corresponding acetoxydienic ester. The 100-Mc nmr spectrum of this material in CCl_4 showed absorption for two protons as a triplet (J = 7 Hz) centered at δ 4.01 ppm corresponding to the protons on the carbon holding the acetoxy group. A weak absorption appeared as a second triplet centered at δ 3.99 ppm due to the *trans,cis* isomer. The relative areas under these two triplets were estimated to be 96 and 4%.

(8) An alternative, more direct approach to the iodo compound involved application of a procedure developed by B. Staskun in our laboratory, *i.e.*, the carbinol **5** was treated with *o*-phenylene phosphorochloridite in pyridine according to E. J. Corey and J. E. Anderson, *J. Org. Chem.* **32**, 4160 (1967), and the resulting crude phosphite ester was in turn treated with zinc iodide in ether giving the iododienic ester in about 75% yield. A sample was converted to the acetate and analyzed as described in ref 7. The results indicated that the product contained only a trace of the *trans,cis* isomer.

(9) E. M. Kosower, W. J. Cole, G.-S. Wu, D. E. Cardy, and G. Meisters, *J. Org. Chem.*, **28**, 630 (1963).

(10) This treatment, which is probably unnecessary, removed a small amount of lower retention time material which we suspect, but have not yet proved, contained the few per cent of unwanted *trans,cis* isomer (see above).

(11) *Cf.* J. W. Cornforth, R. H. Cornforth, and K. K. Mathew, *J. Chem. Soc.*, 112, 2539 (1969).

(12) In benzene solution, a larger (0.04 ppm) separation of the methyl signals was observed, permitting a more accurate estimation of the *cis*:*trans* isomer ratio.

(13) This isomer also has a very high biological activity.[1]

William S. Johnson, Tsung-tee Li
D. John Faulkner, Simon F. Campbell
Department of Chemistry, Stanford University
Stanford, California 94305

Received August 29, 1968

The Nature of the Tin–Transition Metal Bond[1]

Sir:

The discovery of synthetic techniques leading to tin–transition metal compounds has resulted in an

Table I. Nmr Coupling Constants

Compound	$J(Sn^{119}-C-H^1)$, cps	Compound	$J(Sn^{119}-C-H^1)$, cps
$(CH_3)_4Sn$	54.0,[a,b] 54.3[c]	$(CH_3)_2ClSnMn(CO)_5$	45.8[h]
$(CH_3)_3SnC_6H_5$	54.6[d]	$CH_3ClSn[Co(CO)_4]_2$	42.2[f]
$(CH_3)_3SnC_6H_5 \cdot Mo(CO)_3$	57.0[e]	$(CH_3)_2SnBr_2$	66.0[c]
$(CH_3)_3SnCo(CO)_4$	52.6[f]	$CH_3Br_2SnCoCOC_5H_5Br$	56[j]
$(CH_3)_3SnMo(CO)_3C_5H_5$	49.0[g]	$(CH_3Br_2Sn)_2CoCOC_5H_5$	50[j]
$(CH_3)_3SnW(CO)_3C_5H_5$	48.7[g]	$(CH_3)_2Sn[Co(CO)_4]_2$	45.7[f]
$(CH_3)_3SnMn(CO)_5$	48.3[h]	$(CH_3)_2Sn[Mo(CO)_3C_5H_5]_2$	37.4[g]
$(CH_3)_3SnRe(CO)_5$	46.7[h]	$(CH_3)_2Sn[Mn(CO)_5]_2$	36.7[h]
$(CH_3)_3SnCl$	58.5,[b] 60.4[i]	$(CH_3)_2Sn[Re(CO)_5]_2$	36.7[h]
$(CH_3)_2ClSnMo(CO)_3C_5H_5$	47.7[g]	$CH_3Sn[Co(CO)_4]_3$	33.0[f]

[a] J. J. Burke and P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 326 (1961). [b] J. R. Holmes and H. D. Kaesz, *ibid.*, **83**, 3903 (1961). [c] E. V. Van den Berghe and G. P. Van der Kelen, *J. Organometal. Chem.*, **6**, 515 (1966). [d] M.-R. Kula, E. Amberger, and K.-K. Mayer, *Chem. Ber.*, **98**, 635 (1965). [e] This work. [f] D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **6**, 981 (1967). [g] H. R. H. Patil and W. A. G. Graham, *ibid.*, **5**, 1401 (1966). [h] W. Jetz, P. B. Simons, J. A. J. Thompson, and W. A. G. Graham, *ibid.*, **5**, 2217 (1966). [i] In nitrobenzene solution: E. Rosenberg and J. J. Zuckerman, unpublished results. [j] R. Kummer and W. A. G. Graham, *Inorg. Chem.*, **7**, 523 (1968).

Table II

Compound	*d*(Sn–M), Å	$\angle$(M–Sn–M), deg	$\angle$(E–Sn–E), deg
$(CH_3)_3SnMn(CO)_5$[a]	2.674	112.2	107.4
$Ph_3SnMn(CO)_5$[b]	2.674	112.7	106.0
$Ph_3Sn[\pi\text{-}C_5H_5Fe(CO)_2]$[c]	2.536	113.4	105.2
$Ph_2Sn[Co(CO)_4Mn(CO)_5]$[d]	2.73 (Sn–Mn) 2.66 (Sn–Co)	114	107.5
$Ph_3SnMn(CO)_4PPh_3$[e]	2.627	114.2	104.3
$(CH_3)_4Sn_3Fe_4(CO)_{16}$[f]	2.747 (Sn^1–Fe)	105.2 (terminal)	106
(Sn^1 = center atom; Sn^2 = terminal atom)	2.625 (Sn^2–Fe)	115.2 (center)	98.8
$ClSn[\pi\text{-}C_5H_5Fe(CO)_2]_2\pi\text{-}C_5H_5Mo(CO)_3$[g]	2.891 (Sn–Mo) 2.59 (Sn–Fe)	115.6 (Fe–Sn–Fe) 115.8 (Fe–Sn–Mo)	97.2 (Fe–Sn–Cl) 98.4 (Mo–Sn–Cl)
$ClSn[Mn(CO)_5]_3$[h]	2.737	116.5	101.0
$Ph_2Sn[Mn(CO)_5]_2$[i]	2.70	117	100
$(CH_3)_2Sn[\pi\text{-}C_5H_5Fe(CO)_2]_2$[j]	2.602	123	104
$(ONO)_2Sn[\pi\text{-}C_5H_5Fe(CO)_2]_2$[k]	2.56	126	67
$Cl_2Sn[\pi\text{-}C_5H_5Fe(CO)_2]_2$[l]	2.492	128.6	94.1
$Sn[Fe(CO)_4]_4$[m]	2.54	133	69

[a] R. F. Bryan, *Chem. Commun.*, 355, (1967). [b] H. P. Weber and R. F. Bryan, *ibid.*, 443 (1966). [c] R. F. Bryan, *J. Chem. Soc., A*, 192 (1967). [d] B. P. Bir'yukov, Yu. T. Struchkov, K. N. Anisimov, N. E. Kolobova, O. P. Osipova, and M. Ya. Zakharov, *Chem. Commun.*, 749 (1967). [e] R. F. Bryan, *J. Chem. Soc., A*, 172 (1967). [f] R. M. Sweet, C. J. Fritchie, Jr., and R. A. Schunn, *Inorg. Chem.*, **6**, 749 (1967). [g] J. E. O'Connor and E. R. Corey, *J. Am. Chem. Soc.*, **89**, 3930 (1967). [h] J. H. Tsai, J. J. Flynn, and J. P. Boer, *Chem. Commun.*, 702 (1967). [i] B. T. Kilbourn and H. M. Powell, *Chem. Ind.* (London), 1578 (1964). [j] B. P. Bir'yukov, Yu. T. Struchkov, K. N. Anisimov, N. E. Kolobova, and V. V. Skripkin, *Chem. Commun.*, 159 (1968). [k] B. P. Bir'yukov, Yu. T. Struchkov, K. N. Anisimov, N. E. Kolobova, and V. V. Skripkin, *ibid.*, 750 (1967). [l] J. E. O'Connor and E. R. Corey, *Inorg. Chem.*, **6**, 968 (1967). [m] P. F. Lindley and P. Woodward, *J. Chem. Soc., A*, 382 (1967).

enormous amount of effort being focused recently on these interesting systems, and many examples are now known. We report in this communication some Sn^{119m} Mössbauer and proton nmr data and offer an interpretation of these and other spectroscopic and structural data in terms of the nature of the tin-metal bond.

It is readily apparent from Figure 1 that the Mössbauer isomer shift (IS) increases monotonically with the substitution of transition metal atoms in either $R_{4-n}SnM_n$ or $X_{4-n}SnM_n$. This corresponds in the theory of the Sn^{119m} IS to an increase in $|\psi_{ns}(0)|^2$ viewed presumably isotropically from the tin nucleus. The nmr $J(Sn^{119}-C-H^1)$ in the methyltin derivatives is also related in the Fermi contact mechanism to the s distribution at the tin atom, in this case directed along the bonding axes to carbon. The nmr data in Table I indicate that the increase in $|\psi_{ns}(0)|^2$ at the tin nucleus is accompanied by a balancing decrease in the s character of the tin-carbon bond with metal substitution in $(H_3C)_{4-n}SnM_n$. Given a fixed amount of tin 5s character to distribute, these observations dictate a parallel concentration of s character in the tin-transition metal bond.[2] The enhanced s character in the tin-metal bond is reflected in the larger than tetrahedral $\angle$M–Sn–M and smaller than tetrahedral $\angle$C–Sn–C and $\angle$X–Sn–X, and also in the tendency for short *d*(Sn–M) and long *d*(Sn–C) and *d*(Sn–X) as listed in Table II as compared with the sums of the appropriate radii.[3]

An alternative explanation for the structural data mentioned above involves interactions between electron pairs from the filled d orbitals of the transition metal and the empty tin 5d orbitals.[4] Indeed, quadrupole

(1) A preliminary report of this work was given at the International Symposium on Valence and Reactivity, Oxford, England, Jan 1968.

(2) This is in accord with the predictions of isovalent hybridization: H. Bent, *Chem. Rev.*, **61**, 275 (1961).

(3) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

(4) (d → d)–π bonding in group IV transition metal compounds has been discussed on the basis of chemical [A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, **87**, 1133 (1965)], infrared [B. J. Aylett and J. M. Campbell, *Chem. Commun.*, 217 (1965); W. Jetz, P. B. Simons, J. A. J. Thompson, and W. A. G. Graham, *Inorg. Chem.*, **5**, 2217 (1966); A. P. Hagen and A. G. McDiarmid, *ibid.*, **6**, 686 (1967); D. J. Patmore and W. A. G. Graham, *ibid.*, **6**, 981 (1967); N. Flitcroft, D. A. Harbourne, I. Paul, P. M. Tucker, and F. G. A. Stone, *J. Chem. Soc., A*, 1130 (1966); R. Ugo, S. Cenini, and F. Bonati, *Inorg. Chim. Acta*, **1**, 451 (1967)], nmr [R. V. Lindsay, Jr., G. W. Parshall, and U. G. Stolberg,

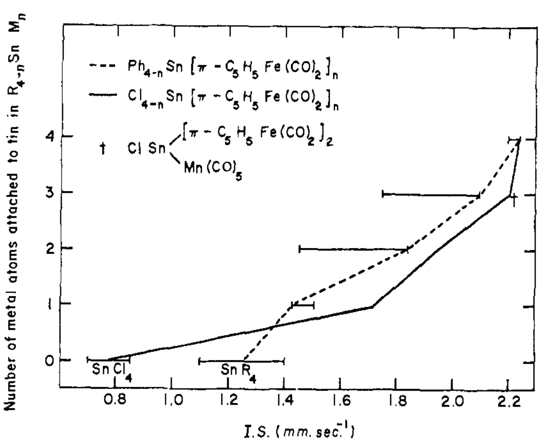
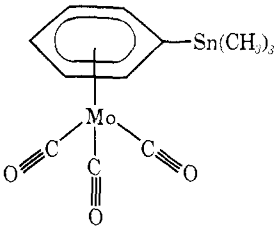


Figure 1. Sn^{119m} Mössbauer isomer shift *vs.* transition metal substitution at tin in $R_{4-n}SnM_n$ and $X_{4-n}SnM_n$. Horozontal bars represent the range of values reported.

splittings (QS) in the range 1.15–1.43 mm/sec are resolved in the Sn^{119m} Mössbauer spectra of several organotin derivatives of the type $R_{4-n}SnM_n$ (values in mm/sec): $PhSn[Co(CO)_4]_3$ (1.28 ± 0.12),[5a] $Ph_2Sn[Co(CO)_4]_2$ (1.43 ± 0.12[5a] and 1.15 ± 0.07[5b]), $Ph_2Sn[Co(CO)_4][Mn(CO)_5]$ (1.15 ± 0.07),[5b] $Ph_3Sn[Co(CO)_4]$ (1.0 ± 0.07),[5b] $(CH_3)_2Sn[Fe(CO)_4]_2Sn[Fe(CO)_4]_2Sn(CH_3)_2$ (1.24 ± 0.10),[5c] $(CH_3)_2Sn[Fe(CO)_4]_2Sn(CH_3)_2$ (1.22 ± 0.10),[5c] $(n\text{-}Bu)_2Sn[Fe(CO)_4]_2Sn(n\text{-}Bu)_2$ (1.26).[5d] According to one accepted view, resolvable QS in asymmetric organotin(IV) compounds arises only when population of empty tin 5d orbitals by electron pairs from adjacent atoms can take place.[6,7] Thus the observation of resolvable QS in these compounds is *prima facie* evidence for (d → d)-π bonding.

However, in systems of the type $R_{4-n}SnX_n$, where X = halogen or a ligand containing nitrogen, oxygen, or sulfur, $|\psi_{ns}(0)|^2$ and IS decrease generally with increasing *n*. The consequence of populating the tin 5d orbitals by (p → d)-π bonding in these systems would be the further reduction of $|\psi_{ns}(0)|^2$ by shielding. Thus both effects change IS in the same direction. In the tin–transition metal systems, on the other hand, IS would be expected to increase with the substitution of metal atoms in $R_{4-n}SnM_n$ or $X_{4-n}SnM_n$, but decrease as a result of the shielding introduced by π bonding with the transition metal. It is clear from the data presented in Figure 1 that if (d → d)-π interactions are present at all they do not predominate over the other factors responsible for the distribution of electrons at the tin atom.[8]

We have recently examined another type of tin-containing, transition metal compound, trimethyltinphenylmolybdenum tricarbonyl, which is monomeric [calcd for $C_{12}H_{14}O_3MoSn$: mol wt, 424; found: 431, 433 (osmometry in benzene),[9] 424 (mass spectrometry)] and which gives evidence of a small QS (<1.0 ± 0.12 mm/sec). One explanation of the appearance of this QS is based upon a (d → d)-π interaction between molybdenum and tin as has been postulated in the analogous silicon-containing ferrocenes.[10] If such an interaction led to five-coordination at the tin atom with concomitant changes in the symmetry of the trimethyltin group, these changes would be reflected in the infrared $\nu(SnC_3)$ and nmr $J(Sn^{119}\text{-}C\text{-}H^1)$.[11] However, infrared and nmr spectra show no significant differences from the trimethylphenyltin ligand itself,[12] and we conclude that the QS arises from an enhanced electric field gradient in the tin–phenyl bond brought about by the metal complexation.



Acknowledgments. Some tin–transition metal compounds were donated by Professors W. A. G. Graham of the University of Alberta, Edmonton, Alberta, Canada, and B. R. Willeford of Bucknell University, Lewisburg, Pa. Mössbauer spectra were recorded with the assistance of N. W. G. Debye. This work was supported by the Advanced Research Projects Agency and the National Science Foundation under Grants GP-5025 and GP-9249.

J. Am. Chem. Soc., **87**, 658 (1965); G. W. Parshall, *ibid.*, **88**, 704 (1966)], structural [W. T. Robinson and J. A. Ibers, *Inorg. Chem.*, **6**, 1208 (1967); P. F. Lindley and P. Woodward, *J. Chem. Soc., A*, 382 (1967); M. Elder, W. A. G. Graham, D. Hall, and R. Kummer, *J. Am. Chem. Soc.*, **90**, 2189 (1968)], and theoretical [O. Kahn and M. Birgorgne, *J. Organometal. Chem.*, **10**, 137 (1967), and references cited therein] grounds.

(5) (a) This work; (b) A. N. Karasev, N. E. Kolobova, L. S. Polak, V. S. Shpinel, and K. N. Anisimov, *Teor. Eksperim Khim.*, **2**, 126 (1966); (c) M. T. Jones, *Inorg. Chem.*, **6**, 1249 (1967); (d) R. H. Herber, *Progr. Inorg. Chem.*, **8**, 1 (1967).

(6) T. C. Gibb and N. N. Greenwood, *J. Chem. Soc., A*, 43 (1966); N. N. Greenwood and J. N. R. Ruddick, *ibid.*, 1679 (1967).

(7) This point has recently been reexamined in the light of SCMO calculations: N. N. Greenwood, P. G. Perkins, and D. H. Wall, Proceedings of the Symposium on the Mössbauer Effect, London, Dec 1967; Symposium of the Faraday Society, *No. 1, in press.*

(8) This conclusion is supported by a recent theoretical analysis of the Sn^{119m} Mössbauer IS: V. I. Goldanskii, E. F. Makarov, and R. A. Stukan, *J. Chem. Phys.*, 47, 4048 (1967).

(9) B. R. Willeford, personal communication, 1968.

(10) M. Kumada, *Pure Appl. Chem.*, **13**, 167 (1967).

(11) R. Okawara and M. Wada, *Advan. Organometal. Chem.*, **5**, 137 (1967).

(12) QS/IS = ρ < 1.8, which is suggestive of four-coordination: R. H. Herber, H. A. Stöckler, and W. T. Reichle, *J. Chem. Phys.*, **42**, 2447 (1965); W. T. Reichle, *Inorg. Chem.*, **5**, 87 (1966).

D. E. Fenton, J. J. Zuckerman
Department of Chemistry, State University of New York at Albany
Albany, New York 12203

Received July 1, 1968

The Energetics of Dissymmetric Interactions. Differential Solubility of *d*- and *l*- and *dl-cis*-$[Co(en)_2Cl_2]ClO_4$ and the Enantiomerization in (−)-2,3-Butanediol

Sir:

In principle the interactions of the enantiomeric forms of a dissymmetric molecule with a dissymmetric environment must be different.[1] Provided that the dissymmetric discrimination is sufficiently large, the effects known as asymmetric transformations and asymmetric syntheses are observed.[2–10] In all these cases

---

(1) C. Mavroyanis and M. J. Stephen, *Mol. Phys.*, **5**, 629 (1962).

(2) R. Kuhn, *Ber.*, **65**, 49 (1932).

(3) H. Leuchs and J. Wutke, *ibid.*, **46**, 2420 (1913).

(4) E. E. Turner and M. M. Harris, *Quart. Rev.* (London), **1**, 299 (1947).