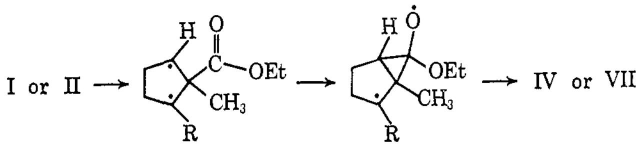
Ester B is assigned structure V on the basis of its distinctive ir and nmr spectra [$\nu(\mathrm{CCl_4})$ 3100 (w), 1740 (s), 1630 (w), and 920 (s) cm^{-1}; $\tau(\mathrm{CCl_4})$ 3.6–4.3 (complex absorption, two protons), 4.7–5.3 (complex absorption, four protons), 5.92 (quartet, two protons), 8.67 (singlet, three protons), and 8.77 (triplet, three protons)].

While the formation of III can be accounted for by a 1,3 hydrogen shift in the diradical E (R = H), the mechanistic origin of IV is less clear. It could arise either *via* a methyl migration, followed by a series of isomerizations, or much more simply by a 1,2 carbethoxyl shift. Decisive information concerning this mechanistic question was gleaned from the thermal rearrangement of the bicyclo[2.1.0]pentane II. Pyrolysis of II gave rise to three isomeric esters, B′, C′, and D′, formed in a ratio of 1:3:4.[4] Ester C′ was identified as VI. Compound VI has been previously reported by us as a photochemical vinylcyclopropyl rearrangement product of ethyl 2-methyl-3-cyclopropyl-2-butenoate;[3] it was also synthesized by an established route.[8] Spectral examination revealed B′ to be VIII. The major product, D′ [$\nu(\mathrm{CCl_4})$ 1740 (s) cm^{-1}; $\tau(\mathrm{CCl_4})$ 5.95 (quartet, two protons), 6.77 (broad triplet, one proton), 7.5–8.3 (complex absorption, four protons), 8.4 (broad singlet, six protons), and 8.77 (triplet, three protons)], was identical with the photochemical vinylcyclopropyl rearrangement product of ethyl 3-(1-methylcyclopropyl)-2-butenoate whose structural designation as VII is secure by analogy.[7]

While the formation of IV from I can be rationalized, albeit deviously, in terms of a methyl shift, the production of VII from II demands a carbethoxyl migration.[9] One possible pathway can be envisaged to proceed *via* a "carbethoxyl participation" mechanism by way of the transition state or intermediate F (R = $\mathrm{CH_3}$).[10]



E F

A comparison of our thermal reactions with those of other bicyclo[2.1.0]pentanes is significant. The parent hydrocarbon affords primarily cyclopentene, with only 0.5% 1,4-pentadiene being detected.[2e] Recently, methyl 3,3-dimethyl-1-bicyclo[2.1.0]pentanecarboxylate has been reported to yield cyclopentene products[2c] also accountable by 1,2 hydrogen migrations from the bridge position. Our bicyclo[2.1.0]pentanes I and II, lacking abstractable hydrogens at the bridge carbon, choose alternate pathways for rearrangement. The formation of large amounts of cyclobutane cleavage products (V and VIII) is novel for a bicyclo[2.1.0]pentane system; 1,3 hydrogen shifts, which account for the formation of III and VI,[11] although not thoroughly substantiated, have been previously invoked in free radical chemistry,[12] while the 1,2 carbethoxyl migration, established here as giving rise to IV and VII, is without analogy in free radical or thermal chemistry.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society for partial support of this research (Grant No. 2445-A1,3). Part of this work was carried out while holding a Special Fellowship, awarded by the National Institutes of General Medical Sciences to M. J. J., at the University of Leiden, The Netherlands, 1967–1968.

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[8] R. Granger and H. Techer, *Compt. Rend.*, **250**, 1282 (1960).

[9] Methyl migration to either radical carbon of E will result in two cyclopentenecarboxylates which are structurally different from VII.

[10] The diradical intermediate E is invoked in this mechanistic scheme solely in analogy with the accepted mechanism which gives rise to cyclopentene from the parent hydrocarbon.[2e] The possibility of a concerted pathway is not ruled out.

[11] It is worth noting that VI can be derived as well from the diradical E by way of a 1,2 carbethoxyl migration to the more stable tertiary position. No such mechanism is possible for the formation of III from I, and a 1,3 hydrogen shift is therefore favored.

[12] R. Kh. Freidlina, *Advan. Free Radical Chem.*, **1**, 211 (1965).

[13] To whom inquiries should be addressed.

[14] Summer visitor from Humboldt State College on a National Science Foundation program for college teachers, 1967.

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Intramolecular Chlorine–Tin Coordination in an Organotin Derivative of Seven-Coordinate Molybdenum

Sir:

Reaction of tetracarbonylbipyridylmolybdenum with methyltin trichloride has very recently been reported[1] to yield bipy$\mathrm{(OC)_3ClMoSnCH_3Cl_2}$. On the basis of its stoichiometry and low conductivity, the compound was formulated as a seven-coordinate molybdenum derivative in which an electron-pair donating carbonyl group had been replaced by univalent chloride and methyldichlorotin ligands. We now communicate some results of an X-ray diffracton study which establish the coordination geometry about molybdenum and reveal also an unexpected and novel five-coordinate state for the tin atom.

Crystal data are $a = 6.73 \pm 0.02$ Å, $b = 11.14 \pm 0.01$ Å, $c = 24.46 \pm 0.03$ Å, $\beta = 90.5 \pm 0.2°$, space group $P2_1/c$, four molecules per unit cell. Data from seven levels about the a axis were collected on a PAILRED automated diffractometer using crystal monochromatized Mo Kα radiation and a moving-crystal stationary-counter scanning procedure. Within these seven levels 3606 unique reflections were measured, and of these 1924 were considered to be significantly above background ($I \geq 2.6\sigma(I)$ where $\sigma(I)$ was based on counting statistics). The data then extend to a resolution of 1.1 Å in the a direction and 0.7 Å in directions perpendicular to this. The structure was solved by conventional heavy-atom procedures. All nonhydrogen atoms have been located and their coordinates refined by least squares to a present R index (with isotropic thermal motion assumed for all atoms) of 0.098.

The molecular structure is shown in Figure 1, in which the more important bond lengths are indicated. The coordination of molybdenum may be termed a "capped octahedron"[2] comprised of an approximately octahedral bipy$\mathrm{(OC)_3ClMo}$ grouping with the tin atom located over the octahedral face defined by the chlorine atom and two of the carbonyl ligands. This

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[1] R. Kummer and W. A. G. Graham, *Inorg. Chem.*, **7**, 310 (1968).

[2] E. L. Muetterties and C. M. Wright, *Quart. Rev.* (London), **21**, 130 (1967).

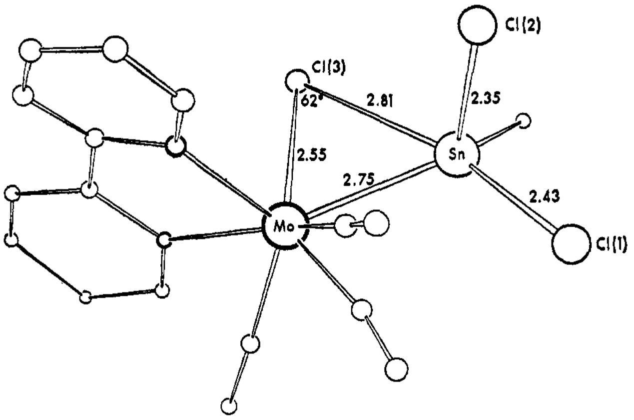

Figure 1. The molecule bipy(OC)$_3$ClMoSnCH$_3$Cl$_2$ as viewed down the *a* axis. Standard errors of all specified bond lengths are less than 0.01 Å, and of the bond angle is 0.3°.

stereochemistry is analogous to that of π-C$_5$H$_5$(OC)$_3$MoCH$_2$CH$_3$,[3] if the π-cyclopentadienyl group in the latter is regarded as a tridendate ligand. The molybdenum-bonded chlorine, Cl(3), is 2.81 Å from the tin atom and clearly bridges the two metal atoms. The tin can be regarded as having a distorted trigonal bipyramidal environment, with Cl(1) and Cl(3) as the axial substituents (angle Cl(1)–Sn–Cl(3) = 168°). The axial bond Sn–Cl(1) is significantly longer (2.43 Å) than the equatorial bond Sn–Cl(2) (2.35 Å). If the values of 1.39 and 1.61 Å are taken as the single-bond covalent radii of tin[4] and molybdenum,[5] respectively, the lengths of all bonds other than the Mo–Sn and the bridging Sn–Cl are close to expected values. The Mo–Sn bond is 0.25 Å short, presumably the result of π bonding, since the halogenotin group is considered to be a strong π acceptor.[8]

Although intramolecular halogen–tin coordination may be a rather general phenomenon, it is not viewed as a determinative structural element. It may operate to the extent permitted by the primary structural features, with consequent wide variation. The effect was first observed in (4-bromo-1,2,3,4-tetraphenyl-*cis*,*cis*-1,3-butadienyl)dimethyltin bromide,[9] where the coordinating bromine–tin distance was greater and distortion from tetrahedral tin less extensive. In cases where two possible coordination geometries have comparable stability, secondary interactions of this type may be decisive. Further structural studies of related molecules are in progress.

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[3] M. J. Bennett and R. Mason, *Proc. Chem. Soc.*, 273 (1963).

[4] Calculated as half the Sn–Sn distance in diphenyltin hexamer, as reported by D. H. Olson and R. E. Rundle, *Inorg. Chem.*, **2**, 1310 (1963); this value agrees well with that derived from the C–Sn distance in methyltin compounds.

[5] Although the single-bond radius appropriate for the transition metal in carbonyl derivatives is open to discussion, three starting points give essentially this value: the Mo–CH$_2$ distance in π-C$_5$H$_5$(OC)$_3$MoCH$_2$CH$_3$;[3] the Mo–N distance in *cis*-diethylenetriaminemolybdenum tricarbonyl;[6] and the Mo–Mo distance in [π-C$_5$H$_5$(OC)$_3$Mo]$_2$.[7]

[6] F. A. Cotton and D. C. Richardson, *Inorg. Chem.*, **5**, 1851 (1966).

[7] F. C. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, **27**, 809 (1957); R. J. Doedens and L. F. Dahl, *J. Am. Chem. Soc.*, **87**, 2576 (1965), footnote 21.

[8] W. Jetz, P. B. Simons, J. A. J. Thompson, and W. A. G. Graham, *Inorg. Chem.*, **5**, 2217 (1966); W. A. G. Graham *ibid.*, **7**, 315 (1968).

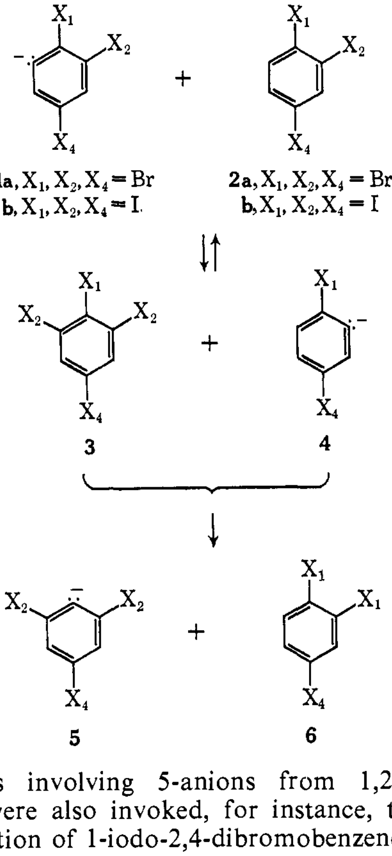
[9] F. P. Boer, J. J. Flynn, H. H. Freedman, S. V. McKinley, and V. R. Sandel, *J. Am. Chem. Soc.*, **89**, 5068 (1967); F. P. Boer and H. H. Freedman, personal communication.

Iodine Scrambling Accompanying Base-Catalyzed Isomerization of 1,2,4-Triiodobenzene

Sir:

The base-catalyzed isomerization and disproportionation of oligohalobenzenes was rationalized by Moyer and Bunnett[1,2] in terms of a sequence of nucleophilic displacements *on halogen*, in which an aryl anion nucleophile displaces an aryl anion leaving group. For example, the isomerization of 1,2,4- to 1,3,5-tribromobenzene, catalyzed by potassium anilide in liquid ammonia, was postulated to involve attack of 6-anion **1a** on the 2-Br of **2a**, forming the product pair **3** and **4** (probably as a complex), quickly followed by attack of anion **4** on X$_1$ of **3** to form **6** and **5**, which is the conjugate base of the observed isomerization product (Scheme I).

Scheme I



Pathways involving 5-anions from 1,2,4-trihalobenzenes were also invoked, for instance, to explain transformation of 1-iodo-2,4-dibromobenzene to 1,2,4-tribromobenzene (Scheme II, with **7a** and **8a**).

An intriguing observation was that 1,2,4-triiodobenzene afforded very little of its 1,3,5 isomer[3] under

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[1] C. E. Moyer, Jr., and J. F. Bunnett, *J. Am. Chem. Soc.*, **85**, 1891 (1963).

[2] C. E. Moyer, Jr., Ph.D. Thesis, Brown University, 1964; *Dissertation Abstr.*, **25**, 4412 (1965).

[3] 1,2,4-Triiodobenzene was initially reported[1] not to isomerize, but subsequently Moyer[2] obtained a trace of its 1,3,5 isomer from one run. In the present work, under slightly different conditions, yields of the 1,3,5 isomer as high as 5% have been obtained.