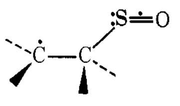

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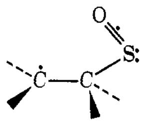

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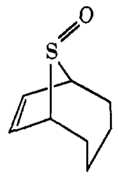

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amination of models, for the C–S transoid conformation in **3d** (but not the cisoid) leads to serious interference between a methyl and the oxygen in the transition state for cyclization.

The retrograde SO-diene reaction is only slightly stereoselective, and interconversion of the thiolene oxides competes effectively against SO extrusion. Together with the fact that diene isomerization accompanies the forward reaction (SO + diene), these observations reveal that the barriers for cleavage of the C–S bonds in the biradical intermediates are similar in magnitude to the rotational barriers discussed above.

If any moral is to be drawn from our study, it is this: the assumption that internal barriers in biradicals are similar to those in stable, closed-shell molecules can be a dangerous oversimplification.[24] The challenging problem of establishing that a particular reaction occurs concertedly is compounded by the possibility that even a rather long-lived intermediate can possess sufficient stereochemical integrity to go undetected.

Our exploration of sulfur monoxide chemistry continues, with the goal, among others, of developing mild methods for generating singlet as well as triplet SO in solution.

Acknowledgment. We are grateful to the U. S. Army Research Office (Durham), the National Science Foundation, and the Petroleum Research Fund, administered by the American Chemical Society, for finanical support of this work. D. M. L. wishes to thank the Alfred P. Sloan Foundation for a Research Fellowship.

(24) Theoretical predictions of rotational barriers in simple biradicals have been made recently by Hoffmann's and Salem's groups: R. Hoffmann, S. Swaminathan, B. G. Odell, and R. Gleiter, *J. Amer. Chem. Soc.*, **92**, 7091 (1970); J. Jean, L. Salem, J. S. Wright, J. A. Horsley, C. Moser, and R. M. Stevens, *Pure Appl. Chem. Suppl.* (23rd Congress), **1**, 197 (1971); J. A. Horsley, Y. Jean, C. Moser, L. Salem, R. M. Stevens, and J. S. Wright, *J. Amer. Chem. Soc.*, **94**, 279 (1972); see also ref 15.

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Received July 12, 1972

Bis(π-cyclopentadienyl)germanium(II)

Sir:

We wish to report the synthesis of the first monomeric germanium(II) compound containing direct carbon–germanium bonds, bis(π-cyclopentadienyl)germanium(II) (germanocene).

Only a few well-characterized compounds of divalent germanium are known.[1] In this respect, germanium lies between carbon and lead. In the former case, all divalent carbon species are highly reactive intermediates (carbenes) whereas the +2 oxidation state of lead is more stable than the +4 state.

Among the organic derivatives of divalent group IVa metals, only dicyclopentadienyltin[2] and dicyclopentadienyllead[3] have been characterized. Attempts to prepare simple alkyl or aryl derivatives of germanium(II) containing direct bonds to carbon led to cyclic oligomers and linear polymers.[4-7] However, divalent germanium species are postulated as fleeting intermediates in several reactions of group IVa compounds,[8] and the dihalides are useful intermediates in syntheses.[9,10]

The reaction of sodium cyclopentadienide (−78°, ethyl ether solvent, 2 hr) or thallium(I) cyclopentadienide (20°, THF, 30 min) with freshly prepared germanium dibromide[9] gave good yields (up to 60%) of germanocene. The use of a solvent in which the cyclopentadienide salt is sparingly soluble is essential to the success of the preparation. No monomeric product can be isolated if THF is used as the solvent for sodium cyclopentadienide. Apparently, a slow, solubility-controlled reaction rate is necessary to minimize polymer formation. The solvents must also be dry and deaerated.

The product was isolated and purified by filtering the cold reaction mixture, removing the solvent under vacuum, and subliming the residue at 20° onto a liquid nitrogen cooled probe. A melting point could not be obtained since germanocene polymerizes rapidly when heated (see below). The resulting polymer does not melt up to 300°. The formula Cp_2Ge was indicated by analysis for both the old (polymerized) and freshly prepared product. *Anal.* Calcd for $C_{10}H_{10}Ge$: C, 59.45; H, 4.79; Ge, 35.76. Found: C, 59.51; H, 5.02; Ge, 35.44. The molecular weight, determined cryoscopically in benzene, was found to be 208 ± 16 ($C_{10}H_{10}Ge$ requires 202.4), thus confirming the monomeric structure. While stannocene is 90% polymerized in 5 days at room temperature,[11] polymerization of solid germanocene to a pale yellow solid, insoluble in common organic solvents, is complete in about 3 hr. Characterization of the polymer was severely hampered by the apparent ease of cleavage of the C_5H_5 groups with halogens and the low solubility, but the yellow color suggests the presence of Ge–Ge bonds in the solid (similar catenates of silicon are yellow[12]). In the presence of air, germanocene is rapidly oxidized through a yellow intermediate to a white, insoluble solid.

The structure of germanocene is presumably similar to those of stannocene and plumbocene which have been found to be angular in the gas phase.[13] The pmr spec-

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(1) O. H. Johnson, *Chem. Rev.*, **51**, 431 (1952); F. Glockling, "The Chemistry of Germanium," Academic Press, New York, N. Y., 1969.

(2) E. O. Fischer and H. Grubert, *Z. Naturforsch. B*, **11**, 423 (1956).

(3) E. O. Fischer and H. Grubert, *Z. Anorg. Chem.*, **286**, 237 (1956).

(4) H. Gilman and G. L. Schwebke, *Advan. Organometal. Chem.*, **1**, 90 (1964).

(5) O. M. Nefedov and S. P. Kolesnikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 201 (1966).

(6) W. P. Neumann and E. K. Konig, *Justus Liebigs Ann. Chem.*, **677**, 1 (1964).

(7) L. C. Willemsens and G. J. M. van der Kerk, *J. Organometal. Chem.*, **2**, 271 (1964).

(8) O. M. Nevedov and M. N. Manakov, *Angew. Chem., Int. Ed. Engl.*, **5**, 1021 (1966); further literature cited there.

(9) M. D. Curtis and P. Wolber, *Inorg. Chem.*, **11**, 431 (1972).

(10) J. V. Scibelli and M. D. Curtis, *J. Organometal. Chem.*, **40**, 317 (1972).

(11) P. G. Harrison and J. J. Zuckerman, *J. Amer. Chem. Soc.*, **91**, 6885 (1969).

(12) C. G. Pitt, M. M. Bursey, and P. F. Rogerson, *ibid.*, **92**, 519 (1970), and references therein.

(13) (a) A. Almenningen, A. Haaland, and T. Motzfeldt, *J. Organometal. Chem.*, 7, 97 (1967); (b) Cp_2Pb contains bridging Cp groups in the solid: C. Panattoni, G. Bombieri, and U. Croatto, *Acta Crystallogr.*, **21**, 823 (1966).

Table I. Infrared Frequencies of Selected Dicyclopentadienyl Metal Complexes (cm^{-1})

Complex	i (ν_{CH})	ii (ν_{CH})	iii (ν_{CC})	iv (ν_{CC})	v (δ_{CH})	vi (π_{CH})	vii (π_{CH})
Ca(Cp)$_2$	3049		1499		1006		760
Sn(Cp)$_2$	3065	2924	1428	1114	1004	788	758
Pb(Cp)$_2$	3021	2914	1416	1112	1007	752	740
Fe(Cp)$_2$	3086	2909	1408	1104	1001	854	814
Cr(Cp)$_2$	3076	?	1404	1098	987	829	766
Ge(Cp)$_2$	3088 (m)	2945 (m)	1429 (m)	1112 (ms)	1005 (ms)	811 (ms)	759 (s)

trum consists of a sharp singlet at δ 5.96 ppm compared with δ 5.81 and 6.25 (*vs.* TMS) for Cp$_2$Sn and Cp$_2$Pb,[14] respectively. The chemical shifts thus show an alternation similar to that found for the tetramethyl derivatives.[15] The mass spectrum of a freshly prepared sample was obtained with an inlet temperature of 37° and with ionizing energies of 20, 50, and 70 eV. There were no significant differences in these spectra. The 50-eV spectrum showed a parent ion peak (Ge^{74}) at m/e 204 (rel intensity 2.4) which had the correct isotope distribution for Ge$_1$. Peaks corresponding to CpGe$^+$ (m/e 139), C$_3$H$_3$Ge$^+$ (m/e 113), and C$_2$HGe$^+$ (m/e 99) were also observed. This fragmentation behavior is similar to that shown by stannocene,[11] vanadocene, and nickelocene but differs from that of *monohapto*cyclopentadienyls.[16]

The ir spectrum of germanocene is inconsistent with ionic or monohapto[17] bonding. Tsutsui[18] has classified metal cyclopentadienyls into three categories based on their ir spectra. Table I contains the infrared bands observed[18] for calcium dicyclopentadienide ("ionically bonded"), stannocene and plumbocene ("centrally σ-bonded"), ferrocene and chromocene ("centrally π-bonded"), as well as those for germanocene.[19]

In ionically bonded complexes only four infrared active fundamentals of the C$_5$H$_5$ ring are observed in accordance with the effective symmetry of D_{5h}. The effective symmetry of the C$_5$H$_5$ ring in "centrally σ-bonded" and "centrally π-bonded" complexes is C_{5v} and seven bands are infrared active. Bands vi and vii of the centrally π-bonded complexes are at much higher frequencies than those of the centrally σ-bonded complexes,[18] band vi never being observed above 800 cm^{-1} for the σ complexes. The spectrum of germanocene does not fall neatly into either the "π" or "σ" category, which suggests that these labels are not descriptive of the actual bonding pattern in these cyclopentadienyl compounds.

The Raman spectrum (Ar$^+$, 4880-Å excitation) of solid germanocene at −100° has been obtained. Six prominent bands (one possibly split into a doublet) are observed in the regions 100–600 cm^{-1}: 110 w, 158–165 mw, 202 m, 225 m, 270 ms, 298 w. On the basis of a C_{2v} structure, one would expect up to eight bands in this region corresponding to metal–ring vibrations. The Raman spectrum is consistent with either angular Cp$_2$Ge or a more complicated arrangement with bridging C$_5$H$_5$ groups as found in solid Cp$_2$Pb.[13b] In the absence of isotopic labeling and depolarization measurements on solution spectra, it is impossible to make definitive assignments of these low frequency vibrations at this time.

Bands in Cp$_2$Ge which can readily be associated with C–C stretches and CCC deformations occur at higher energies than the corresponding bands in Cp$_2$Fe.[20] In ferrocene, the iron withdraws ring π density into the empty xz and yz orbitals, and populates the ring π^* orbitals by backbonding *via* the filled $x^2 - y^2$ and xy orbitals. Both effects decrease the C–C bond order leading to a decrease in the frequencies of vibrations involving these bonds. In the case of germanocene, there can be no back-donation into the ring π^* orbitals (since the d orbitals are empty) leaving only the π bonding to the Ge p orbitals as a mechanism of withdrawing π density from the ring.

Aside from its high reactivity toward oxygen and its tendency to polymerize, germanocene is surprisingly unreactive compared to the germanium dihalides and other "carbenoids."[21] Germanium dibromide reacts rapidly with dienes[9,22] and alkynes, and "inserts" into carbon halogen bonds.[22] The two requirements for a compound to exhibit carbene-type behavior are an empty acceptor orbital of π symmetry and a lone electron pair.[21] As discussed above, the p_y orbital of germanium is probably involved in π bonding to the C$_5$H$_5$ rings and is thus "occupied," leading to a drastic decrease in electrophilic carbenoid reactivity. On the other hand, it is anticipated that germanocene should exhibit enhanced nucleophilic character, and these aspects of its reactivity are under study. A full comparison of the structure and reactivity of germanocene is expected to aid in the general understanding of main group cyclopentadienyls.

Acknowledgments. The authors wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for a grant in support of this research, and the National Science Foundation for funds used in the purchase of the mass spectrometer.

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Received September 16, 1972

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(14) L. D. Dave, D. F. Evans, and G. Wilkinson, *J. Chem. Soc.*, 3684 (1959).

(15) C. R. McCoy and A. L. Allred, *J. Inorg. Nucl. Chem.*, **25**, 1219 (1963).

(16) M. I. Bruice, *Advan. Organometal. Chem.*, **6**, 273 (1968).

(17) E. Maslowsky, Jr., and K. Nakamoto, *Inorg. Chem.*, **8**, 1108 (1969).

(18) M. Tsutsui, "Characterization of Organometallic Compounds," Part 1, Interscience, New York, N. Y., 1969.

(19) Bands i, ii, vi, and vii in benzene-d_6 solution; iii, iv, and v in methylene chloride solution.

(20) E. R. Lippencott and R. D. Nelson, *Spectrochim. Acta*, **10**, 307 (1958).

(21) M. E. Volpin, Y. D. Koreshkov, V. G. Dulova, and D. N. Kursanov, *Tetrahedron*, **18**, 107 (1962).

(22) T. K. Gar and V. F. Mironov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 855 (1965).