

[Reprinted from the Journal of the American Chemical Society, 82, 558 (1960).]
Copyright 1960 by the American Chemical Society and reprinted by permission of the copyright owner.

[CONTRIBUTION FROM THE INSTITUTE FOR ORGANIC CHEMISTRY T.N.O., UTRECHT, HOLLAND]

Infrared Absorption Spectra of Some IVth Group Organometallic Compounds

BY MALCOLM C. HENRY¹ AND JAN G. NOLTES

RECEIVED APRIL 16, 1959

The infrared absorption spectra of compounds of the type $(C_6H_5)_4M$, $(C_6H_5)_3MCH=CH_2$, $(C_6H_5)_2M(CH=CH_2)_2$, $(C_6H_5)_2MCH_2CH=CH_2$ and $(C_6H_5)_2M(CH_2CH=CH_2)_2$ in which M = Si, Ge, Sn and Pb have been recorded in the region of 3500-680 cm^{-1} . Empirical assignments have been made for specific vibrations. Comparison of the spectra revealed a shift of some characteristic band frequencies to longer wave lengths in the series M = Si, Ge, Sn and Pb. The preparation of triphenylallylsilane, triphenylvinyl-, diphenyldivinyl- and diphenyldiallylgermane, triphenylvinyl- and diphenyldivinyllead, compounds not previously described, is given.²

Although considerable work has been done in the field of infrared spectroscopy of organosilicon compounds, there have been relatively few reports in the literature of the spectra of organometallic compounds of the other IVth main group elements. In connection with a program involving the reactions of organotin hydrides with vinyl- and allyl-substituted IVth group phenylmetal compounds,³ infrared spectra of organometallic derivatives of the type $(C_6H_5)_4M$, $(C_6H_5)_3MCH=CH_2$, $(C_6H_5)_2M(CH=CH_2)_2$, $(C_6H_5)_2MCH_2CH=CH_2$ and $(C_6H_5)_2M(CH_2CH=CH_2)_2$ in which M = Si, Ge, Sn and Pb in the region of 3500-680 cm^{-1} were recorded. This paper deals with tentative band assignments and with characteristic differences in the spectra when passing from Si to Pb as the central metal atom.

Experimental

Preparation of Compounds.—Tetraphenylsilane⁴ was prepared by a Wurtz reaction, tetraphenylgermane,^{5a} tetraphenyltin^{5b} and tetraphenyllead⁶ were prepared by a

Grignard reaction, phenylmagnesium chloride in tetrahydrofuran (THF) being used as the phenylating agent.⁷

These compounds were converted into the corresponding triphenylmetal monohalides $(C_6H_5)_3MX$ and diphenylmetal dihalides $(C_6H_5)_2MX_2$ by published procedures. Triphenylbromosilane $(C_6H_5)_3SiBr$, prepared by Ladenburg⁸ by heating equimolecular amounts of tetraphenylsilane and bromine in a sealed tube, was obtained in an appreciably higher yield (76%) by carrying out the reaction in a high-boiling solvent (ethylene bromide).

The phenylmetal halides were converted into the corresponding vinyl and allyl derivatives by reaction with vinylmagnesium bromide in THF⁹ and with allylmagnesium bromide in diethyl ether.¹⁰ Stock solutions of these reagents were stored in calibrated flasks under nitrogen. Molarities were determined by titrating a hydrolyzed aliquot with standard acid.¹¹ Storage for considerable time did not result in appreciable decrease in reactivity. All reactions were carried out in an atmosphere of dry nitrogen.

Triphenylvinylsilane,^{12,13} triphenylvinyltin,¹⁴ diphenyldivinylsilane,¹⁵ diphenyldivinyltin,¹⁶ triphenylallylgermane,¹⁷ triphenylallyltin,¹⁷ triphenylallyllead,¹⁸ diphenyldi-

(1) U. S. Army Research and Engineering Command, Natick Mass.; work done in Utrecht under the auspices of a Secretary of the Army Research Fellowship.
(2) Juenge and Cook have reported the preparation of triphenylvinyllead and diphenyldivinyllead at the 135th Meeting of the American Chemical Society, April, 1959, Boston, Mass.
(3) M. C. Henry and J. G. Nolttes, *THIS JOURNAL*, **82**, 558 (1960).
(4) A. Polis, *Ber.*, **18**, 1540 (1885).
(5) (a) O. H. Johnson and D. M. Harris, *THIS JOURNAL*, **72**, 5564 (1950); (b) P. Pfeiffer and K. Schuurmann, *Ber.*, **37**, 319 (1904).

(6) H. Gilman and J. D. Robinson, *THIS JOURNAL*, **49**, 2316 (1927).
(7) H. E. Ramsden, *et al.*, *J. Org. Chem.*, **82**, 1203 (1957).
(8) A. Ladenburg, *Ber.*, **40**, 2274 (1907).
(9) H. Normant, *Compt. rend.*, **239**, 1510 (1954).
(10) H. Gilman and J. H. McClumphy, *Bull. soc. chim. France*, **45**, 1325 (1928).
(11) H. Gilman, *et al.*, *THIS JOURNAL*, **45**, 150 (1923).
(12) L. F. Cason and H. C. Brooks, *ibid.*, **74**, 4582 (1952).
(13) S. D. Rosenberg, *et al.*, *J. Org. Chem.*, **22**, 1200 (1957).
(14) D. Seyferth and F. G. A. Stone, *THIS JOURNAL*, **79**, 515 (1957).
(15) D. Seyferth, *ibid.*, **79**, 2133 (1957).
(16) H. Gilman and C. W. Gerow, *ibid.*, **79**, 342 (1957).
(17) H. Gilman and J. Eisch, *J. Org. Chem.*, **20**, 763 (1955).
(18) P. R. Austin, *THIS JOURNAL*, **53**, 3514 (1931).

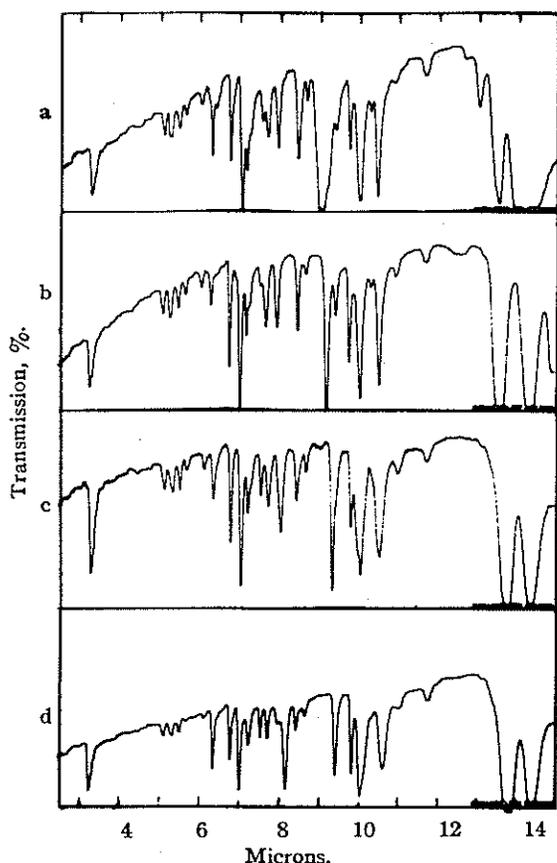


Fig. 1.—Infrared spectra from 3500–680 cm^{-1} of: a, triphenylvinylsilane; b, triphenylvinylgermane; c, triphenylvinyltin; d, triphenylvinyllead.

allylsilane¹⁶ and diphenyldiallyltin¹⁷ have been previously prepared. Triphenylallylsilane, triphenylvinylgermane, diphenyldivinylgermane, diphenyldiallylgermane, triphenylvinyllead and diphenyldivinyllead are new compounds. The attempted isolation of pure diphenyldiallyllead was unsuccessful (compare ref. 17).

Triphenylallylsilane.—Triphenylbromosilane (33.9 g., 0.10 mole) dissolved in 50 ml. of THF was added dropwise to 0.10 mole of allylmagnesium bromide in 120 ml. of ether. After being held at room temperature for 4 hours the reaction mixture was decomposed by pouring into cold ammonium chloride solution. The separated ether layer was dried over sodium sulfate and the ether was removed. The residue was recrystallized from ligroin to give 22.0 g. (74%) of colorless crystals with m.p. 84–86°.

Anal. Calcd. for $\text{C}_{21}\text{H}_{20}\text{Si}$: Si, 9.35. Found: Si, 9.43.

Triphenylvinylgermane.—Triphenylbromogermane (11.7 g., 0.03 mole) dissolved in 30 ml. of benzene was added dropwise to 0.07 mole of vinylmagnesium bromide dissolved in 70 ml. of THF. After heating at reflux temperature for 1 hour, the mixture was hydrolyzed in the usual way. Evaporation of the organic layer yielded an oil, a solution of which in hot 96% ethanol upon cooling yielded 8.3 g. (84%) of colorless crystals with m.p. 62–64°.

Anal. Calcd. for $\text{C}_{20}\text{H}_{18}\text{Ge}$: Ge, 21.94. Found: Ge, 21.71.

Diphenyldivinylgermane.—A mixture of 0.09 mole of vinylmagnesium bromide, in 120 ml. of THF and 15.4 g. (0.04 mole) of diphenyldibromosilane was refluxed for 4 hours and thereupon worked up in the usual way. Distillation of the reaction product yielded a colorless liquid with b.p. 111–113° at 0.003 mm., yield 7.3 g. (67%).

Anal. Calcd. for $\text{C}_{16}\text{H}_{16}\text{Ge}$: Ge, 25.85. Found: Ge, 25.92.

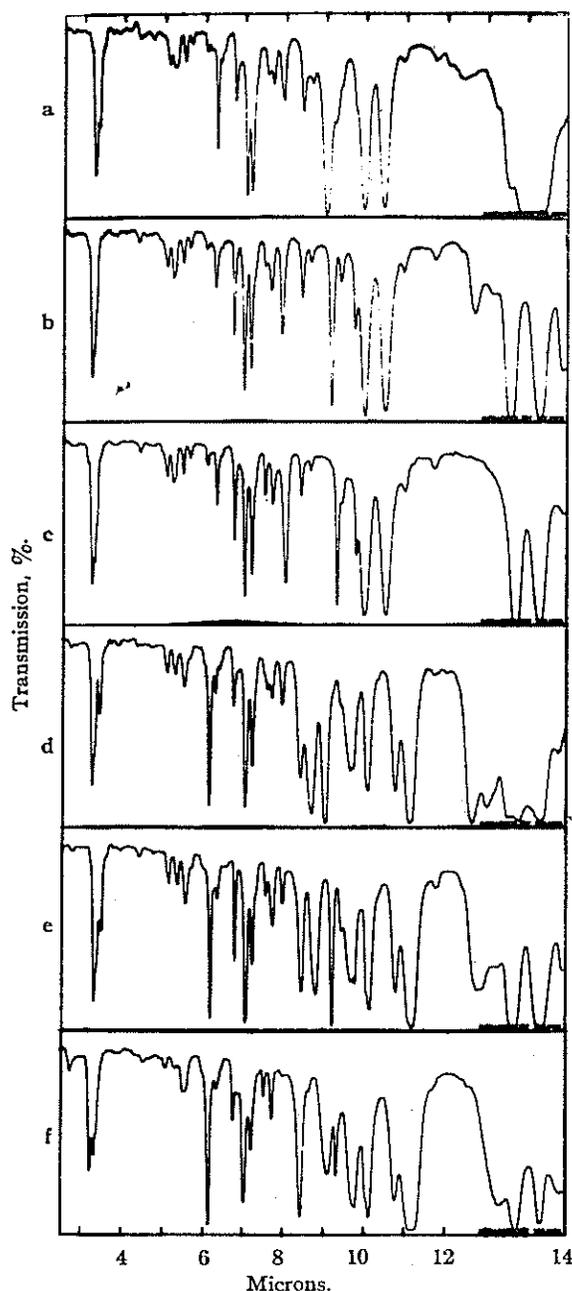


Fig. 2.—Infrared spectra from 3500–680 cm^{-1} of: a, diphenyldivinylsilane; b, diphenyldivinylgermane; c, diphenyldivinyltin; d, diphenyldiallylsilane; e, diphenyldiallylgermane; f, diphenyldiallyltin.

Diphenyldiallylgermane.—The mixture obtained on dropwise addition of 15.4 g. (0.04 mole) of diphenyldibromogermane to 0.08 mole of allylmagnesium bromide in 100 ml. of ether was refluxed for 4 hours and thereupon worked up in the usual way. Distillation of the reaction product yielded a colorless liquid with b.p. 117–120° at 0.007 mm., yield 9.4 g. (77%).

Anal. Calcd. for $\text{C}_{18}\text{H}_{20}\text{Ge}$: Ge, 23.50. Found: Ge, 23.64.

Triphenylvinyllead.—A suspension of 19.0 g. (0.04 mole) of triphenyllead chloride in 50 ml. of THF was added dropwise to 0.052 mole of vinylmagnesium bromide in 75 ml. of THF. After heating at 50° for 15 minutes the reaction mixture was worked up in the usual way. Evaporation of the dried organic layer yielded an oil which failed to crystallize. Distillation was accompanied by considerable decom-

(19) R. H. Meen and H. Gilman, *J. Org. Chem.*, **22**, 684 (1957).

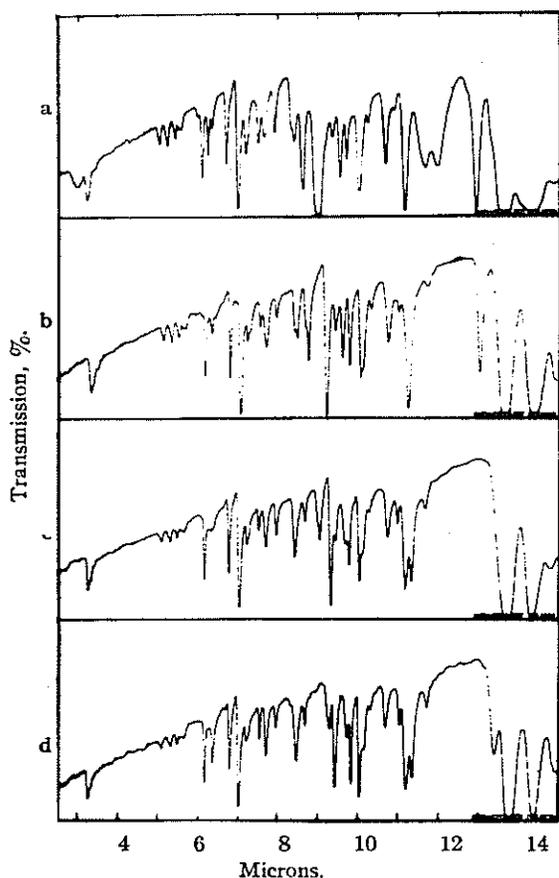


Fig. 3.—Infrared spectra from 3500–680 cm^{-1} of: a, triphenylallylsilane; b, triphenylallylgermane; c, triphenylallyltin; d, triphenylallyllead.

position and gave a fraction with b.p. 150–154° at 0.002 mm. which solidified on cooling, m.p. 32–35°, yield 2.7 g. (14%). An analytical sample recrystallized from ethanol melted at 35–36°.

Anal. Calcd. for $\text{C}_{20}\text{H}_{18}\text{Pb}$: Pb, 44.51. Found: Pb, 44.58.

Diphenyldivinyllead.—When 25.0 g. (0.058 mole) of diphenyllead dichloride was added portionwise to 0.117 mole of vinylmagnesium bromide in 150 ml. of THF the solid went gradually into solution and a muddy-green color developed. Warming the mixture at 50° resulted in deposition of metallic lead. Working up of the reaction mixture in the usual way yielded a yellow oil which was distilled with much decomposition. A colorless liquid with b.p. 111–114° at 0.002 mm., 9.8 g. (41%), was collected. Once pure, this compound can be kept for considerable time without decomposition.

Anal. Calcd. for $\text{C}_{16}\text{H}_{16}\text{Pb}$: Pb, 49.87. Found: Pb, 49.61, 49.82.

Apparatus and Technique.—The infrared spectra were obtained with a Perkin-Elmer Infracord spectrophotometer equipped with a sodium chloride prism. The solid samples were recorded using the potassium bromide pressed disk method; the liquid samples were recorded in a 0.025-mm. cell with sodium chloride windows.

Results and Discussion

The spectra of the phenylmetal compounds presented in Figs. 1, 2 and 3 show the usual absorptions associated with aromatic compounds at 3058, at 1075, in the region of 730–750 and at 690 cm^{-1} .²⁰ The latter vibrations are all evidence for

(20) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1954.

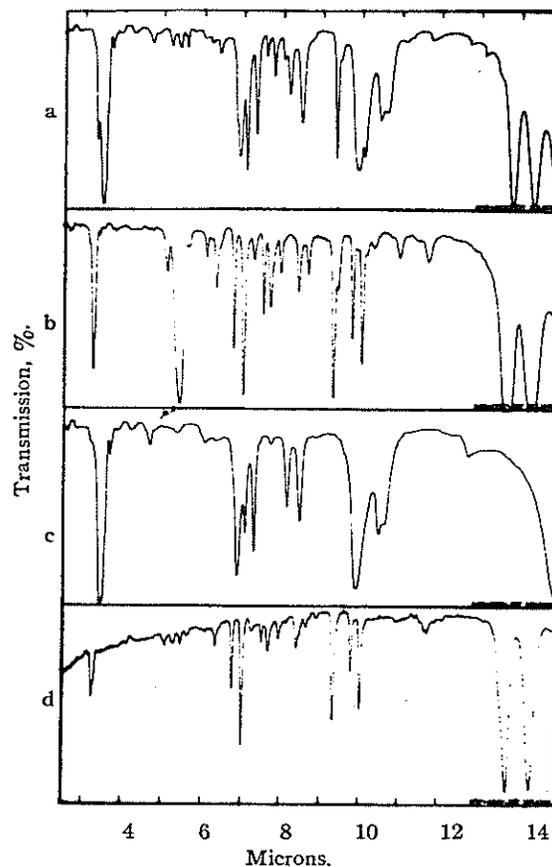


Fig. 4.—Infrared spectra from 3500–680 cm^{-1} of: a, phenyltriethyltin; b, triphenyltin hydride; c, tetraethyltin; d, hexaphenyldistannane.

the presence of monosubstituted phenyl groups as are the absorption frequencies between 1600 and 2000 cm^{-1} . These above-mentioned absorptions show no shift as the central metal atom changes and are absent in the spectra of molecules containing only aliphatic groups (see, e.g., the spectrum of tetraethyltin, Fig. 4).

One of the most interesting areas of the spectra occurs in the region 1050 to 1120 cm^{-1} . In a preliminary communication²¹ the occurrence of a sizable band shift in the spectra of a series of IVth group tetraphenylmetal compounds has been noted. The following band shift was observed: tetraphenylsilane 1100 cm^{-1} , tetraphenylgermane 1080 cm^{-1} , tetraphenyltin 1065 cm^{-1} and tetraphenyllead 1052 cm^{-1} . A corresponding band is absent in the spectrum of tetraphenylmethane. The same shift also occurs in each series of the mixed phenyl compounds, i.e., the monovinyl, the divinyl, the monoallyl and the diallyl series (Figs. 1, 2 and 3). The band at 1065 cm^{-1} is also present in the spectrum of hexaphenyldistannane, triphenyltin hydride and phenyltriethyltin, while it is noticeably absent in the spectrum of tetraethyltin (Fig. 4). As it is clear that frequencies of vibrations directly involving metal atoms are well beyond the rock salt region, this band is believed to be a perturbed phenyl vibrational absorption, probably a C–H

(21) J. G. Noltes, M. C. Henry and M. J. Janssen, *Chemistry & Industry*, 298 (1959).

in plane deformation vibration,²² which shifts to lower frequencies as the weight of the metal atom increases. As this shift is relative to the central metal atom, this band is useful as a characteristic vibration frequency. A corresponding band shift has been observed in the infrared spectra of the phenyl halides.²³

Young, *et al.*,²⁴ have described phenyl-silicon vibrations at 1429 and 1110 cm^{-1} . These authors regard the absorption at 1429 cm^{-1} to be characteristic of the phenyl-silicon structure. This band, which is also present in phenyl compounds of the other IVth group elements, does, however, not shift as it should were it indeed characteristic of a specific phenyl-metal structure. Moreover, the band at 1429 cm^{-1} is situated in the region where aliphatic vibrations occur, which is apparent upon comparison of the spectra of tetraethyltin and phenyltriethyltin (Fig. 4). Since there are no interfering vibrations around 1100 cm^{-1} and as has already been noted the frequency of the absorption in this region is specifically dependent on the nature of the metal atom, the perturbed phenyl vibrations in the area between 1050 and 1120 cm^{-1} may be successfully used for the characterization of molecules containing different phenyl-IVth group metal bonds.^{1,2}

A corresponding picture is presented by the compounds containing vinyl groups where the $=\text{CH}_2$ out-of-plane bending vibration is perturbed by the adjacent metal atom. This results in a characteristic band shift in the region of 940 to 960 cm^{-1} (Figs. 1 and 2). The following values are tabulated: triphenylvinylsilane 960 cm^{-1} , diphenyldivinylsilane 960 cm^{-1} , triphenylvinylgermane

952 cm^{-1} , diphenyldivinylgermane 952 cm^{-1} , triphenylvinyltin 950 cm^{-1} , diphenyldivinyltin 950 cm^{-1} and triphenylvinyllead 942 cm^{-1} . Since the position of this band is relative to the central metal atom it is useful as a characteristic vibration frequency.

In the compounds containing allyl groups the out-of-plane hydrogen deformation absorptions are noticed at 894 and 930 cm^{-1} characteristic of $\text{CH}_2=\text{CHR}$ where R must contain at least one carbon. No shift is noticed going from one metal atom to another.

The C-H stretching vibration for triphenylmethane has been proposed by Fox and Martin²⁵ to occur at 2890 cm^{-1} , that of Si-H in the case of triphenylsilane has been reported at about 2135 cm^{-1} ,²⁶ a shift of 755 cm^{-1} . The corresponding Ge-H frequency is reported to be about 2040 cm^{-1} ²⁷ while the Sn-H frequency as observed in aliphatic tin hydrides is about 1820 cm^{-1} .²⁸ The spectrum of triphenyltin hydride which shows the tin-hydrogen absorption occurring at 1825 cm^{-1} is presented in Fig. 4. In all cases the absorption is strong. Because the hydrogen atom is so light relative to the attached atom, it is obvious that as the weight of the adjacent atom increases the vibrational shift should decrease markedly.

Acknowledgment.—The authors are indebted: to Prof. Dr. G. J. M. van der Kerk, Director of this Institute, for encouragement; to Dr. E. S. Hedges, Director of the International Tin Research Council, for his supporting interest; to Dr. M. J. Janssen for discussions; to Miss F. I. van den Hoek Ostende and Mr. H. A. Budding for experimental help.

(25) J. J. Fox and A. E. Martin, *Proc. Royal Soc. (London)*, **A175**, 208, 234 (1940).

(26) A. Kaplan, *THIS JOURNAL* **76**, 5580 (1954).

(27) R. West, *ibid.*, **75**, 6080 (1953).

(28) D. R. Lide, Jr., *J. Chem. Phys.*, **19**, 1605 (1951); R. Mathis Noel, *et al.*, *Compt. rend.*, **243**, 251 (1956).

(22) D. H. Whiffen, *J. Chem. Soc.*, 1350 (1956).

(23) R. R. Randle and D. H. Whiffen, *Trans. Faraday Soc.*, **52**, 9 (1956); A. R. Katritzky and J. M. Lagoniski, *J. Chem. Soc.*, 4155 (1958).

(24) C. W. Young, *et al.*, *THIS JOURNAL*, **70**, 3758 (1948).