o-anisylboron dichloride forms a resin at room temperature, but the *para* compound only after prolonged heating at 290–300°, and the *ortho* boronic acid eliminates methanol under mild conditions while this behavior has not been observed for the *para* acid. It is probable that there is a direct "through space" effect in the *ortho* case which is absent in the other. In accord with this suggestion it is found that the Slater 2p orbital overlap integrals between the *ortho* substituent atoms and the adjacent boron atom are small but not negligible ($S_{B_\sigma-O_\sigma} \simeq 0.04$; $S_{B_\sigma-C_\sigma} \simeq 0.17$–$0.01$).

Experimental Section

Attempted Preparation of *o*-Anisylboron Dichloride.—*o*-Anisylmercuric chloride was prepared by the action of mercuric chloride (85.0 g) on *o*-anisylmagnesium chloride, prepared from magnesium (7.1 g) and *o*-anisyl chloride (55.0 g) in tetrahydrofuran (200 ml) under nitrogen. The product of the reaction with mercuric chloride was poured into water and the solid extracted with and recrystallized from chloroform. A yield of 65 g of *o*-anisylmercuric chloride was obtained.

o-Anisylmercuric chloride (20.0 g) was shaken for 5 hr at room temperature in a large stoppered flask with a large excess of boron trichloride in dry benzene (100 ml). At the end of the reaction excess boron trichloride was removed *in vacuo*. The fact that mercuric chloride was precipitated, identified by qualitative tests, indicated that reaction had occurred. Removal of the benzene *in vacuo* gave a brown tar which did not fume in air and gave an nmr spectrum in which the methyl proton resonance was only about one-tenth of the expected intensity and was therefore not *o*-anisylboron dichloride. As its formation was not anticipated no attempt was made to collect the methyl chloride presumably evolved.

Preparation of I.—Reaction after the method of Bean and Johnson[3] of *o*-anisyl bromide (100.0 g) with magnesium (12.8 g) in tetrahydrofuran (250 ml) under nitrogen and subsequent reaction of this Grignard reagent at −78° with tri-*n*-butyl borate (123.0 g) and hydrolysis gave 41.89% *o*-anisylboronic acid, which was recrystallized from water. *Anal.* Calcd for $C_7H_9O_3B$: C, 55.3; H, 6.0. Found: C, 55.2; H, 6.1. Heated *in vacuo* at 40–50° *o*-anisylboronic acid (24.0 g) gave a hard brown resin, I (*ca.* 18 g). The starting material showed the expected methoxy proton resonance at 3.86 ppm, but this was absent in that of the resin, although in the aromatic proton region the two spectra were very similar.

Preparation of II.—The resin I (15.0 g) was refluxed with excess boron trichloride in benzene for 3 hr from water and Drikold condensers fitted in series, after allowing the initial reaction to subside. The solvent was removed *in vacuo* and the product sublimed at 88° (0.05 mm). The product, obtained in about 20% yield as a white powder which hydrolyzed rapidly on exposure to air, was *o*-(oxyboron dichloride)phenylboron dichloride. *Anal.* Calcd for $C_6H_4B_2OCl_4$: C, 28.1; H, 1.6. Found: C, 29.2; H, 2.2. The ^{11}B magnetic resonance spectrum of II recorded in CCl_4 at 20 Mcps showed two peaks of essentially equal intensity, a fairly sharp one at 7 ppm and a broad one at *ca.* 21 ppm downfield of an external trimethyl borate reference. The sharp peak is probably to be associated with the boron of the $OBCl_2$ group and the broad peak with that of the $CBCl_2$ group. This assignment is based on the fact that of 15 $ArBCl_2$ (Ar = substituted aryl) compounds we have studied, 14 have boron resonances between 36 and 38 ppm downfield of trimethyl borate (the exception is Ar = *p*-anisyl at 35.6 ppm), while $ArBF_2$ compounds have resonances in the range 6–7.5 ppm.[6] Our assignments then follow from simple electronegativity comparisons.

Preparation of *o*-(Oxydihydroxyboron)boronic Acid (III).—Addition of water to II resulted in immediate hydrolysis. The white product, recrystallized from water, was *o*-(oxydihydroxyboron)boronic acid. *Anal.* Calcd for $C_6H_8B_2O_5$: C, 39.5; H, 4.8. Found: C, 39.6; H, 4.4. An attempt was made to dehydrate this acid to give I. Dehydration *in vacuo* at 100° was accompanied by some darkening, and the infrared spectrum of the product indicated that although I, or some closely related material, was a major product, the dehydration had not proceeded cleanly.

Nmr Spectra.—Proton magnetic resonance spectra were recorded on a Varian A60 spectrometer, deuteriochloroform being used as solvent. Boron resonance spectra were recorded at 14,700 gauss on a modified AEI RS2 spectrometer.

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(6) C. A. Eggers and S. F. A. Kettle, to be published.

CONTRIBUTION FROM THE INORGANIC CHEMISTRY SECTION,
NATIONAL BUREAU OF STANDARDS, WASHINGTON, D. C.,
AND THE DEPARTMENT OF CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
CAMBRIDGE, MASSACHUSETTS

A Broad-Line Proton Magnetic Resonance Study of Cobalt Tetracarbonyl Hydride

BY T. C. FARRAR,[1] F. E. BRINCKMAN,[1] T. D. COYLE,[1]
A. DAVISON,[2a] AND J. W. FALLER[2b]

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A recent publication from these laboratories[3] reported the determination of the metal–hydrogen bond distance in manganese carbonyl hydride, $HMn(CO)_5$, the first such measurement in this class of compounds. In that investigation, the bond length was determined from the second moment of the broad-line proton magnetic resonance spectrum. The contribution of intermolecular dipole–dipole interactions was evaluated on the basis of a crystal structure determination by other workers[4] from which the heavy-atom positions were known. We have now measured the broad-line spectrum of polycrystalline cobalt tetracarbonyl hydride, $HCo(CO)_4$. Although no information is available on the crystal structure of this material, the fine structure observed in the nmr spectrum allows one to estimate the magnitude of intermolecular dipole–dipole interactions. Further, line separations provide an independent measure of the cobalt–hydrogen bond distance. In this note we report a semiquantitative determination of the Co–H distance (1.2 ± 0.1 A) and comment briefly on the use of the nmr method for structural investigation of polycrystalline samples of compounds providing examples of two-spin systems. Some sources of error in the broad-line technique are also discussed.

(1) National Bureau of Standards.

(2) (a) Department of Chemistry, Massachusetts Institute of Technology; (b) National Science Foundation Graduate Fellow, 1953–1966.

(3) T. C. Farrar, W. Ryan, A. Davison, and J. W. Faller, *J. Am. Chem. Soc.*, **88**, 184 (1966).

(4) S. J. LaPlaca, W. C. Hamilton, and J. A. Ibers, *Inorg. Chem.*, **3**, 1491 (1964).

Experimental Section

The samples of $HCo(CO)_4$ were prepared by modification of the $[(C_5H_5N)_6Co][Co(CO)_4]_2$-intermediate route described by Sternberg, *et al.*[5] The initially colorless crystalline hydride was collected at −80° and subsequently recondensed under a carbon monoxide atmosphere into a 10-mm o.d. Pyrex nmr sample tube; thus cocondensation of liquid CO was avoided. The final samples, which were pale to dark yellow, were pumped at −80° to remove traces of hydrogen and carbon monoxide and sealed off.

Proton broad-line nmr spectra were recorded at 29.9 MHz from −80 to −180°. With the instrumental parameters used, no saturation of the proton resonance signal was observed. From −80° to about −135° only a single sharp line (the line width was less than 200 mgauss (10^4 gauss = 1 Tesla) was observed for the solid $[HCo(CO)_4$ melts at about −26°]. From −140 to −180° a complex eight-line proton spectrum $[I(^{59}Co) = {}^7/_2]$ was observed. A typical spectrum, recorded at −145°, is shown in Figure 1. The second moment of the proton spectrum of $HCo(CO)_4$ is 22.5 ± 1.0 gauss^2;[6] it is constant from about −145 to −180° for the three different samples used in this study.

Discussion

We interpret the fine structure observed in the broad-line nmr spectrum below −145° as arising from the dipole–dipole interaction between the proton and the ^{59}Co nucleus and associate the eight principal peaks discernible in the spectrum with the contribution from those molecules whose Co–H internuclear vector is perpendicular, or nearly so, to the applied field. On this basis, both the second moment and the peak separations may be related to the internuclear distance. If we represent the distance between the two outermost peaks in the spectrum in Figure 1 by Ξ, then it is easy to show that the Co–H bond distance, r, is given by $r = [(2I_{Co} \cdot \gamma_{Co}\hbar)/\Xi]^{1/3}$ where I_{Co} $(= {}^7/_2)$ is the spin of the ^{59}Co nucleus and the γ_{Co} is the cobalt magnetogyric ratio.

If one assumes that the Co–H dipole–dipole interaction is the only interaction contributing significantly to the second moment of the proton spectrum,[7] then the Co–H bond distance can be obtained from the value of the second moment by using the well-known Van Vleck equation[8] which relates the second moment, $\Delta H_2{}^2$, of a polycrystalline sample spectrum to the internuclear distance: $\Delta H_2{}^2 = (4/15)\hbar^2\gamma_H{}^2\gamma_{Co}{}^2 I_{Co}(I_{Co} + 1)r^{-6}$. From the second moment we obtain a value of 1.42 ± 0.05 A^6 for the Co–H bond distance; from the line shape data we obtain a distance of 1.2 ± 0.1 A. Although the precision of the line shape measurements is fair, the accuracy is poor owing to the uncertainty in relating the "real" position of the "perpendicular" lines to the outermost peaks in the spectrum envelope. The error given for the line shape determination of r includes this uncertainty.

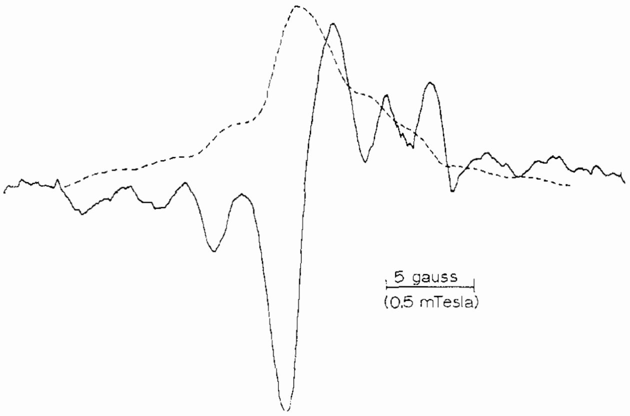

Figure 1.—Proton magnetic resonance spectrum of $HCo(CO)_4$. The solid curve is the derivative spectrum as recorded; the dashed line is the absorption spectrum calculated therefrom. Spectrometer frequency, 29.95 MHz; temperature, −145°; modulation amplitude, 1.5 gauss; modulation frequency, 200 Hz.

The reason for the discrepancy between the bond distance determined by the two different methods is very probably that part of the proton spectrum cannot be recovered from the noise. This unobservable portion of the spectrum arises from molecules whose Co–H internuclear vector is parallel (or nearly so) to the large applied magnetic field, H_0. Although this part of the spectrum is weak, it contributes significantly to the second moment since it occurs far out in the wings.[9]

For $HCo(CO)_4$, then, the second-moment data place an upper limit on the Co–H bond distance, since only the "perpendicular" part of the proton spectrum can be, at present, observed. This is, of course, true in general whenever the "parallel" part of the spectrum cannot be observed, and great care must be exercised when using second-moment data to obtain structural information about high-spin ($I \geq 1$) systems.[10]

It should be noted that the constancy of the observed second moment below −145° implies that thermal motions are effectively "frozen out." Any residual motion would, of course, have the effect of increasing the inferred Co–H bond length.

At present, all available evidence, including field dependence of the line shape and field and temperature dependence of the spin–lattice and spin–spin relaxation times, strongly suggests that the asymmetric shape of the spectrum is due to the chemial shift anisotropy of the proton. This interaction also affects the second moment of the spectrum $[\Delta H_2{}^2 \text{(total)} = \Delta H_2{}^2 \text{(dipole–dipole)} + {}^4/_{45}\,(\sigma_\perp - \sigma_{||})^2 H_0{}^2]$,[11] but here the effect is

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(5) H. W. Sternberg, I. Wender, and M. Orchin, *Inorg. Syn.*, **5**, 192 (1957).

(6) All of the errors reported here are standard deviations: see, for example, H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," 2nd ed, D. Van Nostrand Co., Inc., New York, N. Y., 1956, p 511.

(7) An independent theoretical calculation of the proton line shape including the effects of chemical shift anisotropy and line broadening has been carried out by workers in another laboratory (D. Vanderhart and H. S. Gutowsky, private communication). The line shapes obtained are in substantial agreement with the significant features of the observed eight-line spectrum including the occurrence of the strong central line and the multiplet separations. A discussion of chemical shift anisotropy in transition metal hydrides is given by A. D. Buckingham and P. J. Stephens in "Nuclear Magnetic Resonance in Chemistry," Academic Press Inc., New York, N. Y., 1965, pp 35–43, and references cited therein. A more complete discussion of this and related points will be given in a subsequent publication.

(8) J. H. Van Vleck, *Phys. Rev.*, **74**, 1168 (1948).

(9) An experimental demonstration of the importance of this factor has been obtained in the case of $H^{11}B(OCD_3)_2$ [T. C. Farrar, J. Cooper, and T. D. Coyle, *Chem. Commun.*, 610 (1966)], which is also effectively a two-spin system, and for which the "parallel" portion of the proton spectrum can be resolved. The total second moment is 21.9 gauss^2, corresponding to a B–H distance of 1.25 A. Neglect of the contribution of the outer lines in the "parallel" spectrum leads to an apparent second moment of 14.2 gauss^2 and a B–H distance of 1.34 A.

(10) It is likely that in the case of $HMn(CO)_5$ the distance reported[3] is an upper limit. This and related molecules are being further investigated using an instrument of higher sensitivity.

(11) E. R. Andrew and D. P. Tunstall, *Proc. Phys. Soc.* (London), **81**, 986 (1963).

small enough that it should not invalidate the qualitative comments above concerning the upper limit placed on the Co–H bond distance.

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CONTRIBUTION FROM THE BAKER LABORATORY,
CORNELL UNIVERSITY, ITHACA, NEW YORK

Donor–Acceptor Complexes of Bis(*o*-phenylenedioxy)silane and -germane

BY C. M. SILCOX YODER AND J. J. ZUCKERMAN

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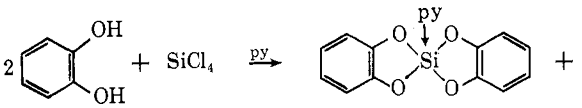
Use of bases to facilitate esterification of organosilicon, -germanium, and -tin halides is well known. While chlorosilanes react vigorously with diols to liberate hydrogen chloride, the reaction of organochlorogermanes is sluggish, requiring tertiary amines for good yields,[1] and organotin halides fail to esterify at all in the absence of base.[2] The action of base in these systems is not straightforward, however, since, apart from taking up hydrogen halide formed in the esterification reaction,[3] molecular bases may also form adducts.

This publication describes the effect of tertiary amines on the synthesis of spiro-(silicon- and germanium-) oxygen heterocycles from the tetrachlorides.

Results and Discussion

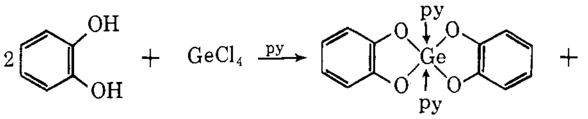
Attempts to prepare bis(*o*-phenylenedioxy)silane and -germane in the presence of tertiary amines lead to the isolation of adducts of these compounds. Addition of silicon tetrachloride to catechol in excess pyridine gives the 1 : 1 pyridine complex of bis(*o*-phenylenedioxy)silane (mp 265° dec). The previously elusive[4] bis(*o*-phenylenedioxy)germane forms as a 1 : 2 complex with pyridine (mp 215–235° dec). Both adducts sublime unchanged. Reversed addition (pyridine first mixed with the tetrachloride, followed by catechol) gives the identical 1 : 1 and 1 : 2 products



I

4py·HCl (1)

$$SiCl_4 + 2py \longrightarrow [SiCl_4 \cdot 2py] \xrightarrow{diol} I + 4py \cdot HCl$$



II

4py·HCl (2)

$$GeCl_4 + 2py \longrightarrow [GeCl_4 \cdot 2py] \xrightarrow{2diol} II + 4py \cdot HCl$$

Triethylamine has larger steric requirements than pyridine, although it is a stronger base toward the proton. In our system triethylamine behaves exactly like pyridine, giving the 1 : 1 and 1 : 2 adducts independent of the order of addition. N,N-Dimethylformamide (DMF) has no observable effect. No DMF adducts of silicon[5] or germanium tetrachlorides are known.

The complexes of tin tetrachloride with pyridine, triethylamine, and DMF are insoluble white solids impervious to further reaction with diol, in accord with reported behavior on alcoholysis.[6]

The Sn^{119m} Mössbauer spectrum of bis(N,N-dimethylformamide)tetrachlorostannane[7] contains a singlet resonance at $0.00 + 0.06$ mm/sec with respect to an $Sn^{119m}O_2$ source, identical with that reported for the bis-pyridine adduct.[8]

1,8-Dihydroxynaphthalene and 2,2′-dihydroxybiphenyl give the spiro esters bis(1,8-naphthalenedioxy)silane[9] and -germane (a novel ring system[10]) and bis(2,2′-diphenylenedioxy)silane[11,12] and -germane,[4,12,13] free of associated base and independent of the order of addition. As well as failing to form adducts, these six- and seven-membered heterocycles are not so susceptible to hydrolysis or polymerization as the five-membered systems.

The thermodynamic stability of fourth-group amine adducts increases $Si < Ge \ll Sn$ as does the tendency for higher coordination.[14] The tetrachloride–base adducts formed as a first step in our syntheses are apparently sufficiently labile to suffer further reaction with the diol.

Heating the dipyridine complex of bis(*o*-phenylenedioxy)germane in DMF precipitates a new complex whose infrared spectrum shows the strong carbonyl and other bands characteristic of DMF.[15]

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[1] D. C. Bradley, L. Kay, and W. Wardlow, *Chem. Ind.* (London), 746 (1953).

[2] H. J. Emeléus and J. J. Zuckerman, *J. Organometal. Chem.* (Amsterdam), **1**, 328 (1964).

[3] Hydrogen chloride acceptors such as sodium carbonate or sodium metal which are not also molecular bases are not effective in promoting reaction of organotin chlorides with dihydric phenols.[2]

[4] J. J. Zuckerman, *J. Chem. Soc.*, 1322 (1963).

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[6] J.-Cl. Marie, *Ann. Chim.* (Paris), **6**, 969 (1961).

[7] R. C. Aggarwal and P. P. Singh, *Z. Anorg. Allgem. Chem.*, **332**, 103 (1964).

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[9] C. M. Silcox and J. J. Zuckerman, *J. Organometal. Chem.* (Amsterdam), **5**, 483 (1966).

[10] The Ring Index recommendation for this system is either naphtho[1,8-*de*]-2-germa-*m*-dioxin or naphtho[1,8-*de*]-1,3,2-dioxagermine. In conformity with our previous reports, we name these heterocycles as derivatives of silane and germane in this communication.

[11] R. Schwartz and W. Kuchen, *Z. Anorg. Allgem. Chem.*, **279**, 84 (1955); J. J. Zuckerman, *J. Chem. Soc.*, 873 (1962).

[12] C. M. Silcox and J. J. Zuckerman, *J. Am. Chem. Soc.*, **88**, 168 (1966).

[13] R. Müller and L. Heinrich, *Chem. Ber.*, **95**, 2276 (1962).

[14] I. R. Beattie, *Quart. Rev.* (London), **17**, 383 (1963).

[15] Our study of the changes in the infrared absorption frequencies of DMF on complexation is the subject of a separate communication: E. W. Randall, C. M. S. Yoder, and J. J. Zuckerman, *Inorg. Chem.*, **5**, 2240 (1966).