TABLE I

REPRESENTATIVE YIELDS OF B_6H_{10} FROM THE REACTION $LiB_5H_8 + B_2H_6$

Solvent	Scale, mmol	B_6H_{10} yield, mmol (%)	$B_{10}H_{14}$ yield, mmol
$(C_2H_5)_2O$	7.2	1.56 (21.7)	0.16
$(C_2H_5)_2O$	30	6.45 (21.5)	Not measd
$(CH_3)_2O$	30	9.20 (30.7)	2.0
$(CH_3)_2O$	30	7.50 (25.0)	1.6
$(CH_3)_2O$	150	37.8 (25.1)	8.96

The identity and purity of the product were established by its molecular weight by vapor density (calcd for B_6H_{10}, 75.95; found, 76.3), vapor pressure,[14] mass spectrum,[15] infrared spectrum,[14] and boron-11 nmr spectrum,[16] all of which were in excellent agreement with published reports.

Decaborane(14) was isolated from the fraction remaining at −45° by warming to room temperature and fractionating through a U trap maintained at −15° (benzyl alcohol slush). Decaborane(14) was identified by its melting point[8] and its boron-11 nmr spectrum.[16]

The preparation of B_6H_{10} can be conveniently scaled up. Typical yields for several scale reactions are given in Table I.

Acknowledgment.—We wish to acknowledge, gratefully, the support of this work by the National Science Foundation. H. D. J. is grateful for support from The Ohio State University Graduate School in the form of a dissertation fellowship.

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[15] I. Shapiro, C. O. Wilson, J. F. Ditter, and W. J. Lehman, *Advan. Chem. Ser.*, **No. 32**, 127 (1961).

[16] T. P. Onak, H. Landesman, R. E. Williams, and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959).

Correspondence

Reply to the Paper by F. A. Cotton and T. J. Marks, "Interpretation of a Spin-Tickling Experiment on(*Monohapto*cyclopentadienyl)-(methyl)(dichloro)silane"[1]

Sir:

The assignment made by Cotton and Marks while analyzing our spin-tickling data for the compound $C_5H_5SiCH_3Cl_2$[2] is absolutely correct. However, 3 months before Cotton and Marks published their paper we published the correction in ref 3, in which this correct assignment was already made. Perhaps Cotton and Marks were not aware of our correction.

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(1) F. A. Cotton and T. J. Marks, *Inorg. Chem.*, **9**, 2802 (1970).

(2) N. M. Sergeyev, G. I. Avramenko, and Yu. A. Ustynyuk, *J. Organometal. Chem.*, **22** (3), 79 (1970).

(3) N. M. Sergeyev, G. I. Avramenko, and Yu. A. Ustynyuk, *ibid.*, **24** (9), C39 (1970).

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The Acidities of Germane and the Phenylgermanes

Sir:

Generally, a phenyl derivative of a nonmetal hydride, $C_6H_5MH_{x-1}$, is more acidic than the parent hydride, MH_x.[1,2] For example, phenylarsine is a stronger acid than arsine, and diphenylarsine is a stronger acid than phenylarsine.[2] However, germane and the phenylgermanes constitute a puzzling exception to this rule. The phenylgermanes are *weaker* acids than germane—the weakness increasing with increasing phenyl substitution.[3,4] Although the exceptional acidities of the phenylgermanes have been cited as evidence for pπ–dπ bonding,[3] no explanation was offered for the implied greater importance of such bonding in the phenylgermanes than in, say, the phenylarsines. The purpose of this communication is to show that the data may be explained in terms of two opposing effects of phenyl substitution: an acid-weakening effect (which we ascribe to pπ–dπ bonding) and an acid-strengthening effect (mainly due to pπ–pπ bonding).

The phenyl group in the molecule $C_6H_5MH_x$ can exert an acid-weakening effect if the atom M has empty valence dπ orbitals which interact with the filled pπ molecular orbitals of the phenyl ring. Such dπ orbitals are available when M is from the second or third row of the periodic table.[5] The acid-weakening effect may

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(1) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Englewood Cliffs, N. J., 1941, p 240 ff; J. B. Hendrickson, D. J. Cram, and G. S. Hammond, "Organic Chemistry," 3rd ed, McGraw-Hill, New York, N. Y., 1970, pp 304–316.

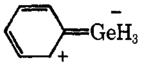
(2) K. Issleib and R. Kümmel, *J. Organometal. Chem.*, **3**, 84 (1965).

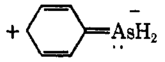
(3) T. Birchall and W. L. Jolly, *Inorg. Chem.*, **5**, 2177 (1966).

(4) T. Birchall and I. Drummond, *J. Chem. Soc. A*, 1401 (1970).

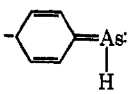
(5) M. D. Curtis and A. L. Allred, *J. Amer. Chem. Soc.*, **87**, 2554 (1965); J. A. Bedford, J. R. Bolton, A. Carrington, and R. H. Prince, *Trans. Faraday Soc.*, **59**, 53 (1963); C. Glidewell, D. W. H. Rankin, and A. G. Robiette, *J. Chem. Soc.*, 2935 (1970).

be ascribed to a stabilization of the acid, relative to its conjugate base. There is little such stabilization of the conjugate base because the pπ–dπ interaction would cause a shift of electron density toward an atom with a formal charge of 1 −. For the cases of phenylgermane[6] and phenylarsine, the effect probably has a similar magnitude, and contributing resonance structures of the following type can be written





The acid-strengthening effect of the phenyl group in $C_6H_5MH_x$ is due (in addition to a relatively weak σ inductive effect) to a stabilization of the anion by interaction of an empty pπ molecular orbital of the phenyl ring with a filled pπ "nonbonding" orbital of the M atom. The effect is operative in the phenyl derivatives of methane and of the hydrides of elements of groups V and VI.[7] For example, in the case of phenylarsine, resonance structures of the following type can be written for the anion



We assume that the valence orbitals of the arsenic atom in the anion are involved in bonding as follows: one pσ orbital in the As–H bond, a pσ orbital and a pπ orbital in the As–C bond, and an s orbital for the completely nonbonding lone pair. On this basis the ion should be completely planar, with a 90° C–As–H bond angle. Presumably there is little such pπ–pπ stabilization of phenylarsine; the long-pair orbital on the arsenic atom in phenylarsine probably has very little p character because of the high s^2p^3–sp^4 promotion energy.[8] (The H–As–H bond angle of 91.8° in arsine[9] is structural evidence of the "inertness" of the lone pair).

The acid-strengthening effect is inoperative in phenylgermane[10] because the lone-pair orbital on the germanium atom of the $C_6H_5GeH_2^-$ ion (like that on the arsenic atom of the isoelectronic $C_6H_5AsH_2$) has little p character. Consequently there can be no significant pπ–pπ interaction between the phenyl ring and the germanium atom in the anion without an energetically unfavorable hybridization of the germanium orbitals. These conclusions are consistent with the facts that no compound is known containing a pπ–pπ bond between carbon and germanium and that the germacyclopentadienide ion shows no aromatic character.[11]

Apparently whenever the π acid-strengthening effect of a phenyl group is operative, it overpowers any possible acid-weakening effect. The latter effect wins by default in the case of phenylgermanes; it probably will be found to do likewise in the case of phenylsilanes—and perhaps in the case of phenylstannanes. It should be pointed out that possibly the acid-weakening effect of a phenyl group can be ascribed partly or completely to a cause other than pπ-dπ bonding; whatever the cause, the explanation of the weak acidity of the phenylgermanes remains intact.

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[6] Birchall and Drummond[4] have observed slight downfield nmr shifts for the ortho and para hydrogens of phenylgermane, relative to benzene. Because various complicated factors can influence the chemical shifts of ring protons, these results are difficult to interpret in terms of pπ–dπ bonding. Indeed, it is not even known whether pπ–dπ bonding sufficient to account for the observed acidity effects would involve enough electron withdrawal from the phenyl ring to cause a significant chemical shift in the nmr of the phenyl protons.

[7] The nonbonding electrons of the conjugate bases of these hydrides have considerable p character. This feature is a prerequisite for the π acid-strengthening effect.

[8] C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory," W. A. Benjamin, New York, N. Y., 1964, p 122.

[9] W. L. Jolly, "The Chemistry of the Non-Metals," Prentice-Hall, Englewood Cliffs, N. J., 1966, p 91.

[10] Birchall and Drummond[4] have observed a slight *downfield* nmr shift for the ortho hydrogens of the phenylgermane anion. They have interpreted the nmr spectrum as evidence for the absence of conjugation between germanium and the ring.

[11] M. D. Curtis, *J. Amer. Chem. Soc.*, **91**, 6011 (1969).

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Fundamental Nature of the Correlation of ΔH *vs.* ΔS. Lanthanide Fluoride Complexes

Sir:

In a recent communication, Fay and Purdie[1] discussed the "correlation of ΔH and ΔS for a series of analogous metal complexes" with respect to "common structure throughout the series" and illustrated the confusion which has evolved in this subject. Their stated intent was "to point out the incorrect reasoning of this interpretation—in order to prevent any later misguidance in the interpretation of these approximately linear relationships." By examining two linear relations between ΔH and ΔS constructed from measured values for several lanthanide and alkaline earth complexes, they suggested that either a linear least-squares fit or a linear fit with $d\Delta H/d\Delta S = 0.298$ (*i.e.*, corresponding to the temperatures of the measurements) is satisfactory. Accordingly they concluded with two statements: (1) "Since the linear correlation is contingent upon a certain restriction on ΔG and since ΔG tells us nothing about the structure of the complexes in solution, then conversely the linear dependence of ΔH–ΔS should be independent of the structural properties of the complexes." (2) "The reason for the correlation is more fundamental than one of structure."

In this communication we shall attempt to indicate the significance of the "fundamental" part of the second conclusion by Fay and Purdie (FP) but at the same time try to demonstrate the fallacy of accepting without qualification the second part (*i.e.*, "one of structure") and the last part of the first conclusion (*i.e.*, "ΔH–ΔS should be independent of the structural properties. . ."). In fact, the potential rationale and theory underlying the correlation is a fundamental one which if investigated and understood in this perspective is intimately

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[1] D. P. Fay and N. Purdie, *Inorg. Chem.*, **9**, 195 (1970).