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Mechanisms of Hydride Abstraction from Organometallic Compounds. Effects of Two β-Metal Substituents on the Kinetics of Dehydrometalation[1]

T. G. Traylor* and G. S. Koermer

Department of Chemistry, D-006, University of California, San Diego, La Jolla, California 92093

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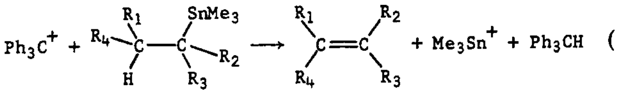
A series of 1,3-dimetallopropanes, $Me_3M(CH_2)_3M'Me_3$, in which M and M' are C, Si, Ge, Sn, and Pb, has been reacted with triphenylcarbenium ion to remove hydride and yield triphenylmethane. The rate constants for these reactions follow the Hammett-type relationship $\log k_2 = \rho\sum\sigma^+ + \text{constant}$, where $\sum\sigma^+$ is the sum of $\sigma^+_{CH_2MPh_3}$ for both metal groups. This relationship leads to the conclusion that both metal groups simultaneously stabilize a carbocation intermediate by vertical stabilization through σ–π conjugation.

In the previous paper[2] we established the anti stereochemistry in the dehydrometalation of alkylstannanes by trityl cation (eq 1). We suggested[2-4] that the transition state for this reaction is stabilized by σ–π conjugation, leading to a vertically stabilized cation. The reaction is accelerated by having electron-donating substituents attached directly at the incipient carbonium ion (R_1R_2, eq 2).[5,6] This result can be explained as arising from a more stable cation in going to a σ–π-conjugated or to a bridged cation or from the formation of a more stable olefin in an E2 process[7] (eq 3-5).



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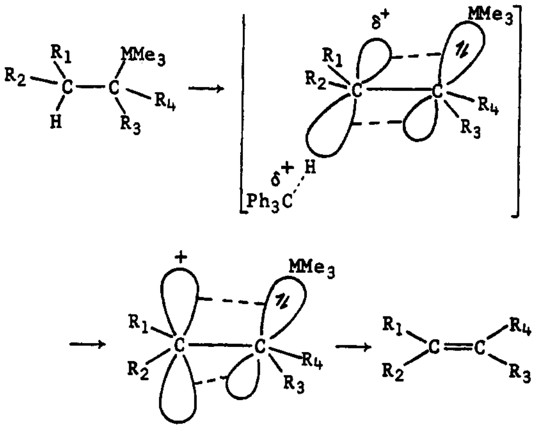

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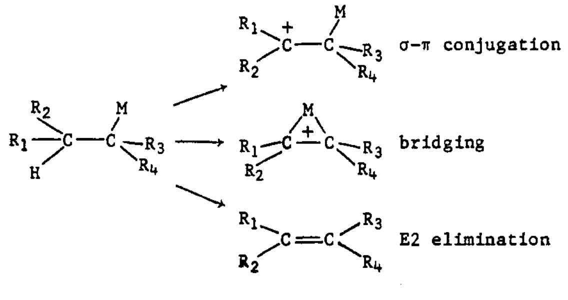

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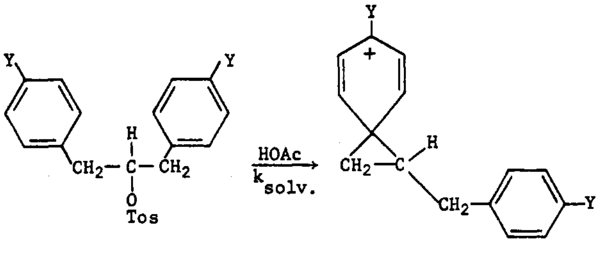
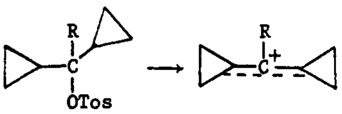
We propose to differentiate these mechanisms by keeping R_2, R_3, and R_4 = H and using as substituents R_1 the isoinductive[8] series CH_2MMe_3 (M = Si, Ge, Sn, Pb) in which the inductive effect and the total effect on olefin stability are either negligibly small[9] (as M changes) or would destabilize the olefin by repulsion.[11] These substituents are very electron-donating to electron-deficient π centers ($\sigma^+_{CH_2MMe_3} = -0.5$ to -1.0 in the above series M = Si to Pb).[9b,10a] We can estimate that the $(Me_3)_3SnCH_2$–CH_2^+ cation would be more resonance stabilized than the $CH_3OCH_2^+$ cation (using $\sigma^+_{OMe} = -0.78$ and $\sigma^+_{CH_2SnMe_3} = -0.81$)[9b,10a] without bridging.

If the reaction derived its driving force from neighboring nucleophilic participation in which a bridged ion is formed, then the result of multiple substitution should be like that observed for phenyl groups which derive their anchimeric assistance from such ion formation.

In this case k_{solv} is just twice that observed when only one phenyl group is present (eq 6).[12] Contrasted to this are the results of Hart[13] in the effects of multiple cyclopropyl substitution (eq 7). In this case the second cyclopropyl group accelerates the reaction by about 250 times compared to an isopropyl group. The cyclopropyl group, long regarded as rearranging to a bridged ion with solvo-



$\longrightarrow$ products (6)[12]



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[1] This work was supported by the National Science Foundation, Grant MPS73-08414.

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Table I. NMR and Partial Mass Spectra of Compounds 1-9

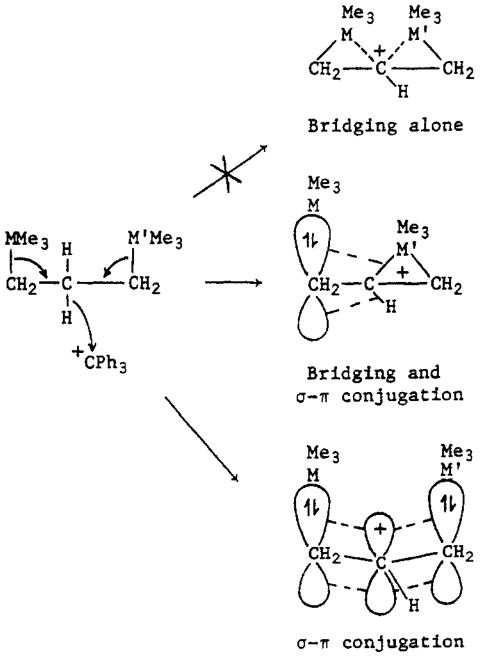
compd	structure	NMR, δ (from Me_4Si)	MS parent peaks,[a] m/e (rel intens)
1	$Me_3Si(CH_2)_3SiMe_3$	0.02 (s, 18 H), 0.62 (m, 4 H), 1.32 (m, 2 H)	188 (9), 189 (2)
2	$Me_3Si(CH_2)_3GeMe_3$	0.2 (s, 9 H), 0.3 (s, 9 H), 1.2-0.5 (m, 6 H)	230 (60), 232 (82), 234 (112)
3	$Me_3Si(CH_2)_3SnMe_3$	0.05 (s, 9 H), 0.15 (s, 9 H, J_{SnCH} = 48 Hz), 1.2-0.4 (m, 6 H)	261 (15.8), 263 (27.5), 265 (36.8)[b]
4	$Me_3Si(CH_2)_3PbMe_3$	0.0 (s, 9 H), 0.6 (s, 9 H), 0.5 (m, 2 H), 1.7 (m, 4 H)	351 (15.5), 352 (16), 353 (35.5)[b]
5	$Me_3Ge(CH_2)_3GeMe_3$	0.05 (s, 18 H), 0.8-0.5 (m, 6 H)	274 (10), 276 (19), 278 (18), 280 (12)[c]
6	$Me_3Ge(CH_2)_3SnMe_3$	0.10 (s, 9 H, J_{SnCH} = 54 Hz), 0.13 (s, 9 H), 1.1-0.6 (m, 6 H)	307 (10.3), 309 (10.7), 311 (8.3)[b]
7	$Me_3Ge(CH_2)_3PbMe_3$	0.2 (s), 0.8 (s), 0.5-1 (m)[d]	d
8	$Me_3Sn(CH_2)_3SnMe_3$	0.1 (s, 18 H), 1.0-0.6 (m, 6 H)	350 (19.3), 351 (16), 352 (43.3), 354 (25), 355 (46.7), 356 (18), 357 (33)[b]
9	$Me_3Sn(CH_2)_3CMe_3$	0.05 (s, 9 H, J_{SnCH} = 52 Hz), 0.96 (s, 9 H), 1.25 (m, 6 H)	245 (16.5), 247 (28), 249 (37)[b]

[a] Only peaks having heights greater than 50% of the largest peaks are shown. See the Experimental Section for discussion of other peaks. [b] $M^+ - 15$ peaks is shown. The parent peak did not appear. [c] Both M^+ and $M^+ - 15$ gave the calculated pattern of intensities. [d] Neither the NMR nor the mass spectra were completely definitive for this compound which was difficult to purify. However, the NMR showed the appropriate pair of singlets for $GeMe_3$ and $PbMe_3$.

lysis, is now commonly accepted to be a simple resonance- (vertical) stabilizing group.[14] Its electron-donating ability is fully realized in vertical ionization processes.[15]

We have applied these same multisubstituent criteria to the dehydrometalation reaction by preparing and studying the rates of dehydrometalation of a series of dimetal compounds, $Me_3MCH_2CH_2CH_2MMe_3$. Having shown that this reaction prefers anti stereochemistry[3] we know in advance that, if both metal groups are to participate, they will do so most effectively from the same side.

The Me_3M groups are large and, like phenyl groups, could not participate at the same time. On the other hand, a combined σ–π conjugated bridged intermediate could be formed (see eq 8–10). This would also involve considerable repulsion between methyl groups. It therefore seems most likely that, with bridging, only a factor of 2 (or less) would result from this double substitution as was observed for phenyl groups.[12]



(8)

Bridging alone

(9)

Bridging and σ-π conjugation

(10)

σ-π conjugation

Results

Compound Characterization. The 1,3-dimetallopropanes used in this work were prepared by several methods, including catalyzed addition of M–H to the double bond, reactions of Grignard or lithium alkyl reagents with trimethylmetal halides, or nucleophilic displacement by trimethylmetal anions, as described in the Experimental Section. All of these compounds display high-field singlets for the MMe_3, characteristic for each metal. The mass spectra are also characteristic for each compound as a result of the presence of several stable isotopes of some metals. For example, the compound $Me_3Si(CH_2)_3SnMe_3$, containing several Sn isotopes, displays a distribution of parent mass peaks which is definitive for the molecular formula.

The compounds were purified, and their purity was determined by gas–liquid chromatography except for $Me_3Ge(CH_2)_3PbMe_3$, which decomposed upon injection into the gas–liquid chromatography instrument. It was purified by column chromatography. Table I presents the NMR and pertinent mass spectral peaks of the dimetal compounds.

Kinetics. The reaction is first order in each reagent, producing triphenylmethane and the allyltrimethylmetal derivative (eq 11). However a very fast reaction of the

$$Ph_3C^+ + Me_3MCH_2CH_2CH_2M'Me_3 \xrightarrow{k_2} H_2C{=}CHCH_2M'Me_3 + {}^+MMe_3 + Ph_3CH \quad (11)$$

allyltrimethylmetal compound with triphenylcarbenium ion ensues,[16] resulting in the consumption of 2 mol of trityl cation for each mole of dimetal compound (eq 12).

$$H_2C{=}CHCH_2MMe_3 + Ph_3C^+ \rightarrow Ph_3CCH_2CH{=}CH_2 + {}^+MMe_3 \quad (12)$$

Reactions were followed by observing the disappearance of trityl fluoborate absorbance at 431 nm under pseudo-first-order conditions with an excess of the organometallic compounds. Under these conditions, where 2 moles of trityl cation are consumed for each dehydrometalation, eq 13 holds, where b_0 is the initial concentration of trityl

$$\ln (b_0/b_0 - 2x) = k_{obsd}\, t \quad (13)$$

cation and x is the amount of each reagent consumed by

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Table II. Rate Constants for the Reaction of Triphenylmethyl Fluoborate with Alkyl Metal Compounds of Group 4 in Acetonitrile at 30 °C[a]

compd	structure	mol of alkyl metal/ mol of $Ph_3C^+BF_4^-$	k_2/H,[f] L M^{-1} s^{-1}	$-\log k_2/H$	$-\Sigma\sigma^+{}_{CH_2MPh_3}$[b]
1	$Me_3Si(CH_2)_3SiMe_3$	0.5	6.2×10^{-6} [c,d]	5.21	1.08
2	$Me_3Si(CH_2)_3GeMe_3$	>20	1.9×10^{-5}	4.72	1.17
3	$Me_3Si(CH_2)_3SnMe_3$	>20	5.9×10^{-4}	3.23	1.35
4	$Me_3Si(CH_2)_3PbMe_3$	>12	1.3×10^{-1}	0.89	1.57
5	$Me_3Ge(CH_2)_3GeMe_3$	>20	1.8×10^{-4} [e]	3.74	1.26
6	$Me_3Ge(CH_2)_3SnMe_3$	>20	7.1×10^{-3}	2.15	1.44
7	$Me_3Ge(CH_2)_3PbMe_3$	>10	2×10^{-1}	0.7	1.66
8	$Me_3Sn(CH_2)_3SnMe_3$	>20	4×10^{-2}	1.4	1.62
9	$Me_3Sn(CH_2)_3CMe_3$	1	2×10^{-4} [c,d]	3.7	1.14

[a] All rate constants except those for 9 were averages of two or more runs. [b] From ref 10a. [c] Solvent 50% CD_3CN in CH_2Cl_2. [d] Determined by NMR at 25 °C and corrected to 30 °C by using the $\Delta H^{\ddagger}$ of ref 5. [e] A value of 1.75×10^{-4} was obtained by the NMR method. [f] The bimolecular rate constant per hydrogen.

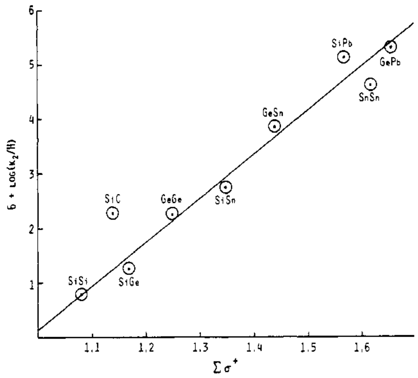


Figure 1. Plots of log k_2/H for rates of hydride abstraction from $Me_3M(CH_2)_3MMe_3$ vs. the sum of the two $\sigma^+{}_{CH_2MMe_3}$ values for each compound. Data are from Table II.

the dehydrometalation. Then, $b_0 - 2x$ is proportional to absorbance, and $k_{obsd} = 2k_1$, k_1 being the pseudo-first-order rate for the dehydrometalation. The bimolecular rate constant, k_2 of eq 11, is obtained by dividing k_1 by the concentration of organometallic reagent. Division of k_2 by 2 for the two equivalent hydrogens available for abstraction gives k_2/H, the bimolecular rate constant per hydrogen.

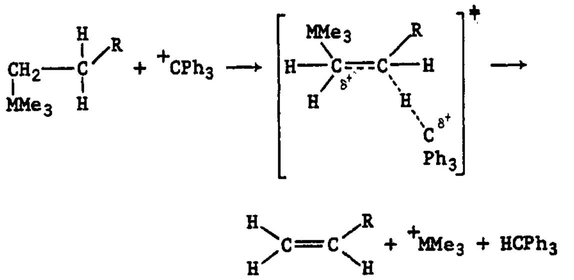
As a confirming, or sometimes more convenient, method we measured some of the rates by NMR, observing the rate of decrease of the high-field proton resonance of one of the MMe_3 groups. These rates were measured at equal initial concentrations of trityl fluoborate and organometallic compound 9 but at twice the original concentration of the organometallic with dimetal compounds, for reasons discussed above. Kinetic constants for the series of compounds 1–9 are given in Table II.

Discussion

The reaction of triphenylmethyl fluoborate with alkylmetal compounds could proceed by either electron transfer[17] or by hydride abstraction.[4,18] Electron transfer has been observed with organometallic compounds having low ionization potentials, e.g., allyltrimethyltin and electronegatively substituted trityl cations. However, trityl cation itself does not react by electron transfer with simple alkyltin compounds.[16] We have observed that 1,2-dimetalloalkanes have lowered ionization potentials as a result of σ–σ conjugation.[19] However, 1,3-dimetalloalkanes have ionization potentials which are very similar to those of the simple alkylmetal compounds.[19] Therefore, there is very little likelihood that these compounds would undergo electron transfer. Product studies of both types of reactions are also inconsistent with electron transfer from alkyl metal compounds of group 4B.[3,20]

There remain the three possibilities for elimination, i.e., concerted elimination, carbonium ion formation with bridging, and carbonium ion formation without bridging.

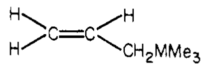
The driving forces which have been established for concerted eliminations (eq 14) are olefin stability and the



(14)

stabilities of the leaving groups.[7] The $^+MMe_3$ group becomes more stable as the electronegativity of M decreases. Therefore it is expected and found that the reaction rate increases greatly in the series Si < Ge < Sn < Pb.[4,21,22]

As regards the stability of the olefin, we must compare thermodynamic stabilities of the olefins of the type shown below. The π bond and the CH_2–M σ bond interact



strongly, splitting these two orbitals by about 2.20 eV.[11,23] However, this does not result in stabilizing the olefin. The CH_2MMe_3 groups have an inductive effect which is very similar to that of a methyl group and which is very little dependent upon the nature of M.[9b,24] We therefore conclude that, if this reaction were concerted, the second metal (the one which remains) should have little effect on the rate. No positive charge would be generated there because the positive charge, being related to C–M bond breaking, is found on the leaving metal.

A plot of log k_2/H vs. the sum of the two $\sigma^+{}_{CH_2MMe_3}$ values[10a] for all of the compounds studied is shown in Figure 1. Although there is considerable scatter, the

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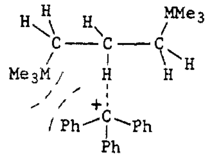
conclusion that both metals simultaneously participate in accelerating the rate is quite clear. The correlation with the vertical $\sigma^+_{CH_2MMe_3}$ values (i.e., determined from vertical ionization potentials) suggests simultaneous vertical stabilization.

A comparison of the ρ slope for a series in which the leaving group changes (the SiSi, SiGe, SiSn series) with one in which the leaving group remains the same (SnC, SnSi, SnGe, SnSn) is instructive. If the leaving group were dominating the reaction, as it would in concerted elimination, then the sensitivity to changes in the leaving group (SiSi to SiPb) should be much larger than sensitivity to changes in the remaining metal group (the series SnSi to SnSn). However, rate constants for both series fall on the same $\rho\sigma$ line within our experimental accuracy (Figure 1). This result is consistent with vertical stabilization of the cation by both CH_2MMe_3 groups.

This comparison of the effect of changing the leaving metal vs. changing the remaining metal is clearly seen in the series $Me_3Si(CH_2)_3SiMe_3$, $Me_3Si(CH_2)_3SnMe_3$, and $Me_3Sn(CH_2)_3SnMe_3$, where the first Sn for Si substitution (leaving group) increases the rate by a factor of 95 and the second (nonleaving group) by 68. We conclude that the metal, M′, which remains behind in reaction 11, has just as much effect on the rate of reaction of these dimetal compounds as does the metal, M, which leaves.

The rates of reaction of dimetalalkyl compounds do not correlate with the rates of reaction of the $Et_3MCH_2CH_3$ series. The ρ slope for the dimetal series is −8 compared to −14 for the Et_4M series.[4,10b] Furthermore, $Me_3SnCH_2CH_2CH_2C(CH_3)_3$ should react about 10^4 times faster than the $Et_3SnCH_2CH_3$ compound if we accept a σ^+ value of −0.33 for the neopentyl group and $\rho = -14$ for the $Me_3SnCH_2CH_2R$ monometal series. (The σ^+ values of Et_3SnCH_2 and Me_3SnCH_2 are the same.[10a]) However, $Me_3SnCH_2CH_2CH_2$-*t*-Bu reacts 13 times *slower* than does Et_4Sn, suggesting that a 10^5-fold rate reduction results from something other than electronic effects. The decreased rates of the neopentyl-type compounds are explicable as a steric interaction between the neopentyl-type group and the triphenylmethyl cation or the second CH_2MMe_3 group (A or B). We have no way of correcting for changes in this steric effect with M in CH_2MMe_3 and have assumed that it changes very little. In A both the steric interaction and slower *cis*-hydride removal are involved, whereas in B the σ–π overlap would be greatly reduced by the methyl group repulsions which would tend to rotate the groups around bond a.



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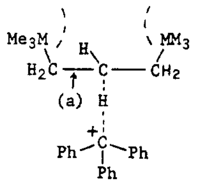
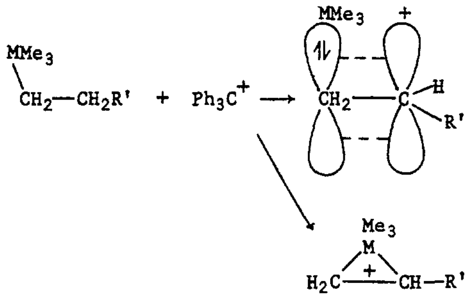


(A) (B)

The decreased ρ slope with the dimetal compounds probably arises as a result of the great stabilization of the first group. Thus, by the reactivity–selectivity principle,[25] the series $Me_3Si(CH_2)_3SiMe_3$ to $Me_3Si(CH_2)_3SnMe_3$ should display a lower ρ slope than the series $Me_3SiCH_2CH_3$ to $Me_3SnCH_2CH_3$, as is found. These observations are not consistent with either E2 elimination or neighboring-group participation by the MMe_3 group.

These quantitative treatments do not establish a two-step mechanism. But the failure to trap an intermediate $Me_3SnCH_2CH_2^+$ reported by Uglova et al.[18] is also not proof that there is no such intermediate. Such a metal-location might be expected to have a very short lifetime.

The $Me_3SiCH_2CH_2^+$ ion has been demonstrated as an intermediate by Cook, Eaborn, and Walton.[26] Notice that the plot of log k_2/H vs. $\sigma^+_{CH_2M'Me_3}$ (Figure 1) includes $Me_3Si(CH_2)_3SiMe_3$, which must have a cationic intermediate. If a change in mechanism occurred upon changing Si to Ge and Sn, then the correlation should not hold. These results lead us to conclude that the reaction is not concerted in those reactions following the $\rho\sigma^+$ relationship. The two-step reaction proceeds through a carbonium ion, and this ion might be stabilized by one or both of the C–M bonds by either vertical stabilization as σ–π conjugation[9b,11] or by neighboring nucleophilic participation,[26,27] forming the metallonium ion (eq 15 and 16). However, the steric bulk of the MMe_3 group is even greater than that of a phenyl substituent. Because the smaller phenyl groups do not simultaneously participate, the bulkier MMe_3 groups would clearly be prevented from such simultaneous participation (eq 17). Therefore neighboring-group participation is not the source of stabilization provided by the second MMe_3 group.



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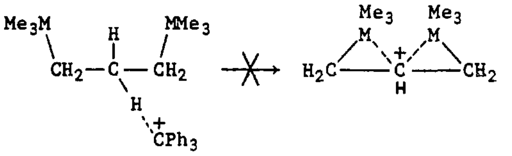
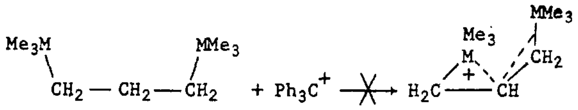


(17)

The combination of neighboring nucleophilic participation and resonance stabilization (eq 18) also has problems. The substitution of a resonance-stabilizing group on a cationic center has the effect of canceling the k_Δ, or participation term, in solvolyses (eq 19). The substitution of R = *p*-anisyl so stabilizes the cation that the k_Δ disappears.[27] But a group such as CH_2SnMe_3 is more stabilizing to a cation than is the *p*-anisyl group.



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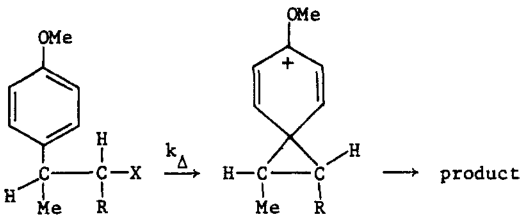

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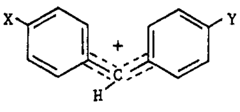
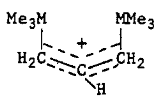
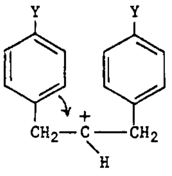
Because $^+CH_2MMe_3$ is capable of very large vertical stabilization, as demonstrated by photoelectron spectroscopy[11,23] and charge-transfer spectroscopy,[9] and because the other mechanisms are very unlikely, we conclude that this hydride abstraction occurs with the formation of a short-lived intermediate which enjoys vertical stabilization from σ–π conjugation by the two C–metal bonds. This MCH_2–C^+H–CH_2M system (B) is therefore to be compared to the diphenylcarbenium ion system[27] (A) rather than the dibenzylcarbenium ion (C).[13]



(A)

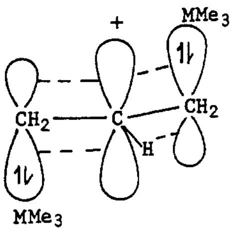


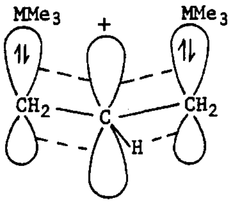
(B)



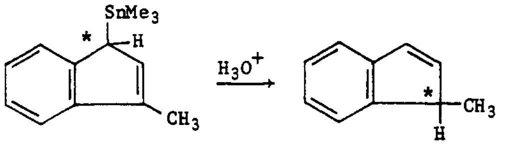
(C)

The cation could be syn or anti.



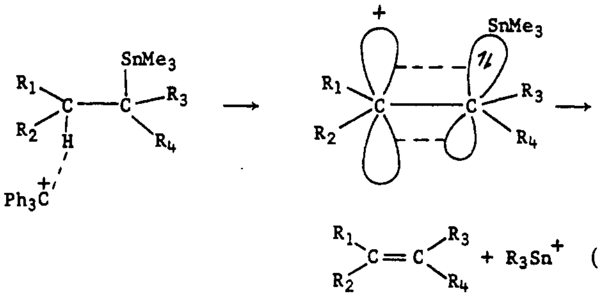


The reaction of allylmetal compounds with electrophiles, e.g., H_3O^+, follows an anti pathway[28] (eq 20).



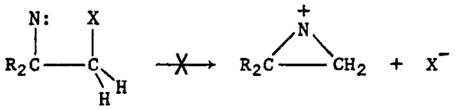
(20)

If the dimetallocation is a model for this transition state, then the anti configuration is preferred. However, hydride abstraction in organotin compounds favors anti arrangement of the leaving group and metal group by factors of 20–100[2,3] (eq 21).

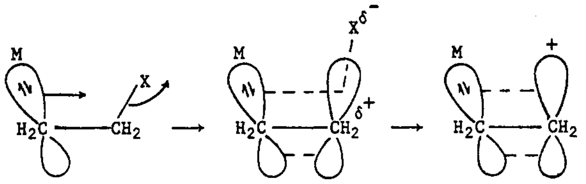


(21)

Contrasted to neighboring nucleophilic participation, which encounters severe steric repulsion with the leaving group in front-side participation (eq 22), σ–π conjugation can afford π overlap without such repulsion (eq 23). The syn vs. anti ratio is 20–100 compared to $>10^6$ for neighboring nucleophilic participation leading to the rate acceleration of the magnitude reported here.

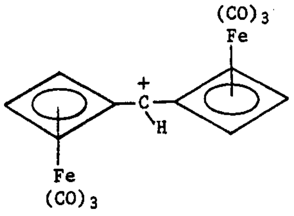


(22)

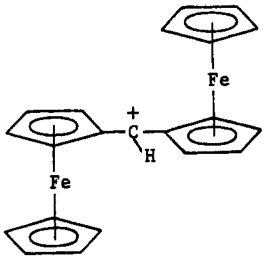


(23)

Crystal structures of the analogous bis(β-metalloalkyl)carbenium ions **10** and **11** have shown an anti stereochemistry.[29] These compounds, like ours, show considerable enhancement of stability with addition of the second metallocene group.[30]



10[29]



11[29,30]

The weight of evidence, although not conclusive, seems to favor the anti stereochemistry of two such metals. This would then account for the lowered slope observed for the nonleaving metal because trans elimination is preferred in this dehydrometalation, and thus one of the metals would contribute more to cation stabilization than does the other. The steric effect encountered by the trityl cation would favor the syn arrangement of the two trimethylmetal groups. But this geometrical question is not answered by our results.

After submission of this paper a rather similar study by Davis and Jacocks[10b] appeared. They found that rates of acid-catalyzed elimination of Me_3SiOH from a series of compounds $Me_3SiCH_2C(R_1)(R_2)(OH)(R_1 = R_2 = H; R_1 = R_2 = Me; R_1 = Me_3SiCH_2, R_2 = H)$ followed the $\rho\sum\sigma^+$ relationship just as reported in the present work. They also concluded that both Me_3Si groups provided vertical stabilization.

However, they pointed out that in coordinating solvents elimination of the more reactive $Me_3MCH_2CH_2OH$ compounds (M = Sn, Pb) changes from the carbenium mechanism, which we describe here, to a more concerted E2-like mechanism. Our hydride-abstraction studies are carried out in noncoordinating solvents, and the $\rho\sigma^+$ behavior which we observe suggests that, in this reaction, all the MMe_3 groups provide vertical stabilization and proceed through the same two-step mechanism.

Conclusion

Application of the multiple-substitution method of Kohnstam, Hart, and Schleyer to the question of carbonium ion stabilization by metallomethyl groups (the β effect of metals) shows that this stabilization is provided by resonance (vertical stabilization) and not by neighboring nucleophilic participation.

Experimental Section

NMR spectra were obtained with Varian T-60, EM-360, or HR-220 spectrometers. Visible spectra and spectrophotometric

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[28] Kashin, A. N.; Bakunin, V. N.; Khutoryanski, V. A.; Beletskaya, I. P.; Reutov, O. A. *J. Organomet. Chem.* **1979**, *171*, 309–319.

[29] Davis, R. E.; Simpson, H. D.; Grice, N.; Pettit, R. *J. Am. Chem. Soc.* **1971**, *93*, 6688–6690.

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kinetics were obtained by using a Cary 15 instrument equipped with a Cary automatic sample changer and a LO-Temprol 154 temperature bath. Mass spectra were run on an LKB 4000 instrument. The mass spectra of the parent peak or the M$^+$ - 15 peak in each of the compounds **1**–**9** (except for **7**) were accurately simulated by a computer program[31] designed to calculate parent peaks of compounds having multiple isotopes of several elements.

Methylene chloride was distilled and stored over molecular sieves. Acetonitrile was stirred over calcium hydride and distilled from phosphorus pentoxide. Trideuterioacetonitrile was distilled from calcium hydride and stored over molecular sieves. Other reagents were used as received.

(γ-Bromopropyl)trimethylsilane was prepared by the method of Sommer, Van Strien, and Whitmore:[32] bp 70–80 °C (25 mm) [lit. 70 °C (25 mm)]; NMR δ 0.0 (s, 9 H), 0.6 (m, 2 H), 1.8 (m, 2 H), 3.3 (t, 2 H).

(γ-Bromopropyl)trimethylgermane was prepared from (γ-hydroxypropyl)trimethylgermane[33] [NMR δ 0.2 (s, 9 H), 0.8 (m, 2 H), 1.7 (m, 2 H), 3.6 (t, 2 H), 5.0 (s, 1 H)] by the method of Sommer et al.:[32] NMR δ 0.2 (s, 9 H), 0.8 (m, 2 H), 2.0 (m, 2 H), 3.3 (t, 2 H).

(γ-Bromopropyl)trimethylstannane. (Trimethylstannyl)lithium was prepared from 7 g of trimethyltin chloride (35 mM) and 0.80 g of lithium wire (112 mM) in 40 mL of dry tetrahydrofuran. The lithium reagent was filtered under argon into a dropping funnel above an argon-flushed, 100-mL, round-bottomed flask containing 25 g (~125 mM) of 1,3-dibromopropane (freshly distilled and dried over calcium sulfate). The lithium trimethyltin was added slowly with vigorous stirring. The reaction turned gray immediately, and a Gilman test showed no lithium reagent present. Stirring continued for 3 h. The reaction was poured into a saturated ammonium chloride–ice–ether mixture with stirring. The aqueous layer was separated and extracted with ether. The ether extracts were combined, washed with brine, and dried (MgSO$_4$), and the solvent was removed. Distillation at reduced pressure gave unreacted 1,3-dibromopropane and (γ-bromopropyl)trimethylstannane: bp 55–60 °C (~5 mm); yields of 10–40%; NMR δ 0.1 (s, 9 H), 0.8 (m, 2 H), 2.0 (m, 2 H), 3.25 (t, 2 H).

1,3-Bis(trimethylsilyl)propane (1). (γ-Bromopropyl)trimethylsilane (1 g, 5 mM) was added with vigorous stirring to 0.3 g of magnesium in 100 mL of ether. The reaction was covered with argon and protected with a drying tube. A crystal of iodine along with gentle heating was used to initiate the reaction. Presence of the Grignard reagent was ascertained by a Gilman test.[34] The reagent was filtered under argon before use to remove excess magnesium. Alternatively (γ-bromopropyl)trimethylsilane could be treated with excess lithium wire to give the corresponding lithium reagent. This reaction was carried out in anhydrous ether at ice-bath temperatures. Addition of 1 equiv of freshly distilled trimethylsilyl chloride in ether afforded **1** which was purified by gas–liquid chromatography (yield 60%). The NMR and mass spectral data are shown in Table I.

1-(Trimethylsilyl)-3-(trimethylgermyl)propane (2). To 1.0 g (8.4 mM) of trimethylgermyl hydride[35] were added 4 drops of 0.01 M chloroplatinic acid in 2-propanol.[33] A red-brown color resulted. After the reaction mixture was cooled in an ice bath, allyltrimethylsilane (0.7 g, 6.1 mM) was added slowly. The reaction was stirred for 24 h. The reaction mixture was taken up in pentane and washed twice with water to remove chloroplatinic acid. The product was purified by gas–liquid chromatography (yield 70%). NMR and mass spectra are shown in Table I. The compound was also prepared from (γ-bromopropyl)trimethylgermane.

1-(Trimethylsilyl)-3-(trimethylstannyl)propane (3). This compound was prepared by reacting the Grignard reagent of (γ-bromopropyl)trimethylsilane with trimethyltin chloride (Alfa) as described above. Alternatively, (γ-bromopropyl)trimethylsilane was treated with lithium trimethyltin in tetrahydrofuran. By both procedures the yield of product was 60–65% (see Table I).

1-(Trimethylsilyl)-3-(trimethylplumbyl)propane (4). This compound was prepared by reacting the lithium reagent derived from (γ-bromopropyl)trimethylsilane with trimethylplumbyl acetate as describe above (see Table I).

1,3-Bis(trimethylgermyl)propane (5).[36] Hexamethylphosphoramide (HMPA) was purified by distillation at reduced pressure [80 °C (10 mm)] from lithium wire. The distillate was stored over molecular sieves. In a three-necked, 100-mL round-bottomed flask equipped with an argon inlet, a magnetic stirrer, and an addition funnel were placed ~10 mL of HMPA and 0.4 g of lithium wire (10 mM). Then 1 g of trimethylgermyl bromide (5 mM) in an equal volume of HMPA was slowly added with vigorous stirring.[37] The blue color disappeared, and the solution turned bright yellow. Then 0.4 g of 1,3-dibromopropane (2 mM) was added; the reaction turned white. After the mixture was stirred overnight, water and pentane were added, and the solution became clear. The water layer was separated and extracted with pentane. Pentane extracts were washed twice with water and dried (MgSO$_4$). The solvent was removed at reduced pressure, and 0.4 g of clear liquid remained (yield 60%). See Table I for the properties after purification by gas–liquid chromatography.

1-(Trimethylgermyl)-3-(trimethylstannyl)propane (6). This material was best prepared by reacting the lithium reagent prepared from (γ-bromopropyl)trimethylgermane with trimethyltin chloride (Alfa) in ether as described above (yield 63%). The product was purified by gas–liquid chromatography (see Table I).

1-(Trimethylgermyl)-3-(trimethylplumbyl)propane (7). Reacting the lithium reagent prepared from (γ-bromopropyl)trimethylgermane with trimethylplumbyl acetate (Alfa) in ether, as described above, yielded 30% of this compound. It could not be purified by GLC due to decomposition. It was partially purified by liquid chromatography on alumina.

1,3-Bis(trimethylstannyl)propane (8).[2] This compound was prepared by treating 1,3-dibromopropane (3.1 g, 15 mM) with lithium trimethyltin prepared from 8 g of trimethyltin chloride (4 mM) and excess lithium wire in tetrahydrofuran by the method described above: yield 48% (based on bromide); bp 79–82 °C (0.7 mm); see Table I.

(4,4-Dimethylpentyl)trimethylstannane (9). 4,4-Dimethyl-1-bromopentane, prepared by radical addition of HBr to the corresponding olefin[37] (1.5 g, 8.4 × 10^{-3} M) in 1 mL of ether, was added to 0.6 g of lithium wire (0.1 M) in 10 mL of dry ether under an argon blanket. After being stirred for 0.5 h, the reaction mixture was filtered under argon to remove excess lithium. Then 1.7 g (8.6 × 10^{-3} M) of trimethyltin chloride in 1 mL of ether was added. A vigorous reaction occurred with formation of a white precipitate. After the mixture stirred overnight, 15 mL of water was added. The aqueous layer was separated and extracted twice with ether. The organic extracts were combined and dried (MgSO$_4$), and the ether was distilled off to yield 1.9 g of crude product (86%) which was purified by gas–liquid chromatography.

Kinetic Methods. Solutions for kinetics were prepared under argon in dry solvents. Aliquots of the tritylfluoborate solution (~3 × 10^{-2} M) were mixed by using argon-flushed syringes with aliquots of the organometallic reagent in a capped cuvette, and these were thermostated at 30.00 ± 0.02 °C (or at 25.00 ± 0.02 °C) in the Cary 15 spectrophotometer. Some absorbing byproduct was produced slowly, causing the infinity value to drift slightly. Therefore infinity points were chosen for the best pseudo-first-order fit for the early part of the reaction. The rates so obtained were in accurate agreement with those determined by NMR, where this color problem is absent. The observed and calculated infinity values differed by about 10%.

Registry No. **1**, 2295-05-8; **2**, 77882-70-3; **3**, 77882-71-4; **4**, 77882-72-5; **5**, 77882-73-6; **6**, 77882-74-7; **7**, 77882-75-8; **8**, 35434-81-2.

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[31] This program was written and kindly supplied by B. D. Dombee, J. Lowther, and E. Carberry, Southwest Minnesota State College, Marshall, MN. For modifications to include Sn isotopes, see: Hannon, S. J. Thesis, University of California, San Diego, 1975, pp 203–214.

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