The sample was removed from the cell and analyzed for H_2O content 6.1×10^{-3} M). A sample of NBS (0.0866 g) was weighed into a Pyrex reaction ampule which was protected from light. An aliquot of the dichloromethane (2 mL) was added, and the vessel was attached to a high vacuum system. The volatile material was transferred under vacuum to a second vessel and was analyzed for its H_2O content and found to be 1.1×10^{-2} M.

Registry No. NBS, 128-08-5; cyclopentane, 287-92-3; cyclohexane, 110-82-7; succinimidyl radical, 24344-83-0.

Fluorine-19 Nuclear Magnetic Resonance Studies of 4-Substituted Bicyclo[2.2.2]oct-1-yl Fluorides: Resonance Effects of Some Group 14 Substituents Attached to Saturated Carbon Centers[†]

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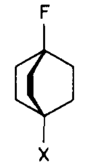
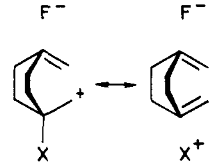
Recent studies[1,2] have revealed that the ^{19}F chemical shifts of 4-substituted bicyclo[2.2.2]oct-1-yl fluorides **1** respond sensitively and systematically to the polar electronic effects of remote substituents. The resulting ^{19}F substituent chemical shifts (SCS), which reflect primarily changes in the fluorine σ-electron density,[1,3] are dominated by the polar field (σ_F effect) and electronegativity (σ_X effect) influences of the substituent. The former factor has its origin in the polarization of the CF σ bond and, thus, depends on the component of the electric field along the CF bond (E_z) as well as on the longitudinal polarizability of the CF bond. The latter substituent factor, which pertains to the polarity of the substituent–substrate bond (σ-inductive effect), is transmitted chiefly by a "through-three-bond" electron delocalization mechanism (a σ-resonance or σ–σ hyperconjugative effect.[4] In valence bond terminology, the σ-resonance effect in **1** may be denoted by canonical structures **2** and **3** (depicted for only one of the three ethano bonds). Thus, the dependence of the ^{19}F SCS of **1** on substituent electronegativity may be understood on the basis of the relative importance of these contributing resonance canonical structures. It should be noted that these structures are analogous to the resonance structures commonly drawn to represent hyperconjugative interactions (σ–π) between the C–F bond (and C–X bond) and the π-system in CH_2X derivatives of benzyl fluoride. Within the framework of PMO theory,[5] the resonance effect in **1** is proportional to $c^2\beta^2/\Delta E$, where c is the coefficient at the carbon atom of attachment (or site of substitution), β is the resonance integral associated with the appropriate orbitals, and ΔE is the orbital energy gap between the orbitals. The former parameter dominates the numerator of the expression for three-center donor–acceptor orbital interactions of the type C---C–X.[6] Hence, an alternative means of rationalizing the aforementioned electronegativity effect in **1** centers around the magnitude of c and ΔE for the appropriate bond MOs (σ_{CX} and σ_{CX}*).[6]



1



2 **3**

Table I. ^{19}F Substituent Chemical Shifts (SCS)[a] of System 1 for Some Group 14 Substituents: Polar Field ($\rho_F\sigma_F$)[b,c] and Electronegativity ($\rho_X\sigma_X$)[d] or Resonance Contributions

	SCS, ppm		$\rho_F\sigma_F$, ppm		$\rho_X\sigma_X$, ppm	
	c-C_6H_{12}	$CDCl_3$	c-C_6H_{12}	$CDCl_3$	c-C_6H_{12}	$CDCl_3$
CMe_3	−3.11[e]	−3.20[e]	−0.03	−0.11	−3.08	−3.09
$SiMe_3$[f]	1.54	1.61	0.00	−0.05	1.54	1.66
$GeMe_3$	1.63	1.69	−0.03	−0.11	1.66	1.80
$SnMe_3$	3.67[e]	3.83[e]	−0.03	−0.11	3.70	3.94
$PbMe_3$[g]	2.87	3.00	−0.16	−0.26	3.03	3.26

[a] Chemical shifts (ppm) relative to parent system (1, X = H). A positive sign implies deshielding (downfield shift). Accurate to ±0.01 ppm. [b] ρ_F values for system 1 in c-C_6H_{12} and $CDCl_3$ are −3.13 and −5.25, respectively (see ref 1). [c] σ_F values derived from the ^{19}F SCS of 1-X-4-(*p*-fluorophenyl)bicyclo[2.2.2]octanes (ρ_F values for c-C_6H_{12} and $CDCl_3$ are 2.70 and 2.57, respectively (see ref 1)). ^{19}F SCS of this system in c-C_6H_{12} for MMe_3 groups (see ref 9b) lead to the following σ_F parameters: 0.01 (CMe_3), 0.00 ($SiMe_3$), 0.01 ($GeMe_3$), 0.01 ($SnMe_3$), 0.05 ($PbMe_3$). ^{19}F SCS (ppm) for $CDCl_3$ (this study) are as follows: 0.05 (CMe_3), 0.03 ($SiMe_3$), 0.06 ($GeMe_3$), 0.04 ($SnMe_3$), 0.14 ($PbMe_3$). These SCS lead to similar σ_F values: 0.02 (CMe_3), 0.01 ($SiMe_3$), 0.02 ($GeMe_3$), 0.02 ($SnMe_3$), 0.05 ($PbMe_3$). [d] ^{19}F SCS (obsd) $-\rho_F\sigma_F$ (ppm). [e] Taken from ref 1. [f] $J_{^{29}Si-^{19}F}$ not observed. [g] $J_{^{207}Pb-^{19}F}$ values (Hz): 134.5 (c-C_6H_{12}), 143.8 ($CDCl_3$).

[†] In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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(2) Adcock, W.; Abeywickrema, A. N.; Kok, G. B. *Tetrahedron Lett.* **1982**, *23*, 3615. Adcock, W.; Abeywickrema, A. N.; Kok, G. B. *J. Org. Chem.* **1984**, *49*, 1387.

(3) (a) A *decrease* in σ-electron density leads to *negative* ^{19}F SCS (*upfield* shift) in system 1.[3b] The converse situation holds for an *increase* in σ-electron density.[3c] (b) Adcock, W.; Abeywickrema, A. N. *J. Org. Chem.* **1982**, *47*, 2945. (c) On the basis of theoretical studies, it has been suggested that an *increase* in the total electronic population is accompanied by a downfield shift (sp^3C, carbonyl C, and dialkyl ether O atoms) when the increase in charge is dictated by that of the σ population (Fliszár, S.; Cardinal, G.; Bêraldin, M. T. *J. Am. Chem. Soc.* **1982**, *104*, 5287).

(4) (a) We have proposed[1,2] that the electronegativity dependent "through-three-bond" effect (TB-3 effect) in 1 is governed predominantly by the hyperconjugative interaction between the bridging ethano bonds and the C–F bond, i.e., σ_{CC}–σ_{CF}*, the dominant donor–acceptor interaction (represented in valence bond terms by structure **2**). This conjugative interaction may be enhanced or decreased (relative to X = H) depending on the net result of the hyperconjugative interactions between σ_{CC} and the substrate–substituent bond molecular orbitals (σ_{CX} and σ_{CX}*). (b) It is of interest to note that Grob et al.[4c] have invoked a similar resonance effect (called twofold hyperconjugation) to account for the fact that certain 4-substituted (X) bicyclo[2.2.2]octyl nisylates (X = H, COO^-, $CONH_2$, CH_2OH, and CH_2NH_2) appear to solvolyze faster than expectations based on σ_I^q values (derived from the pK_a values of 4-substituted *quinuclidium perchlorates*). Subsequently, calculations were presented[4d] which did not support the concept. However, odd electron delocalization onto the remote C–H bond in the bicyclo[2.2.2]octan-1-yl radical[4e] is further strong experimental evidence for the resonance idea. It is important to bear in mind that, in general, "through-bond" effects cannot compete with direct polar field interactions ($\rho_F\sigma_F$) in the case of chemical reactivity.[2] (c) Grob, C. A.; Rich, R. *Tetrahedron Lett.* **1978**, 663. Grob, C. A.; Rich, R. *Helv. Chim. Acta* **1979**, *62*, 2793. (d) Wenke, G.; Lenoir, D. *Tetrahedron Lett.* **1979**, 2823. (e) Kawamura, T.; Matsunaga, M.; Yonezawa, T. *J. Am. Chem. Soc.* **1978**, *100*, 92 and references cited therein.

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In this paper we report the synthesis and ^{19}F SCS of three new derivatives of system 1 (X = $SiMe_3$, $GeMe_3$, and $PbMe_3$) which, together with the previously published data for two other compounds (1, X = CMe_3 and $SnMe_3$),[1] provide results for a complete series of Group 14 substituents (MMe_3: M = C, Si, Ge, Sn, and Pb). Since a lack of appropriate experimental parameters has prevented unequivocal testing of theoretical predictions of the relative group electronegativities of these substituents,[7,8] in particular, NMR chemical shift information unencumbered by various phenomena (proximity, magnetic anisotropic, and stereochemical effects) which are well-known to obscure chemical shift/electron density relationships, we were hopeful that the shift parameters from 1 would help to shed new light on this much debated question.[7] Model system 1 provides a unique opportunity in this regard since the charge density monitor (^{19}F SCS) is relatively free of the aforementioned complicating factors.

The ^{19}F SCS of system 1 for the MMe_3 substituents (M = C, Si, Ge, Sn, and Pb) along with a dissection into polar field and resonance (or electronegativity) contributions are presented in Table I. An examination of the results for both solvents reveals several salient features. Firstly, the large resonance influence for each substituent is the dominant if not exclusive factor in most instances and that the field effect contributions ($\rho_F\sigma_F$) are effectively negligible except for the $PbMe_3$ group.[9] Secondly, the *negative* resonance contribution for the CMe_3 group implies that this substituent is a *σ-electron withdrawing* (*or attracting*) group relative to hydrogen when attached to a sp^3 hybridized carbon atom. Although this result is not in accord with the current dominant viewpoint,[10] it is in agreement with group electronegativity scales[7,8,11] and recent theoretical considerations.[12,13] Thirdly, as anticipated, it is clearly evident that the resonance contributions for the other congeneric groups are *positive* implying *σ-electron donation*. Now since the C_{sp^3}–M bond MO energies (M = Si, Ge, Sn, and Pb) are reliably estimated from the ionization potentials of suitable model compounds on the basis of Koopman's theorem[14] and, in addition, their relative magnitude readily inferred from bond strengths,[15,16] the resonance effect for these metalloidal groups should increase in the order Pb > Sn > Ge > Si based on ΔE (vide supra), which decreases as M changes from Si to Pb. Clearly, the observed order Sn > Pb > Ge ~ Si must be due to c^2 (vide supra) offsetting the order firmly dictated by ΔE. Thus, the following relative group electronegativity scale is suggested from the results: C > H > Ge > Si > Pb > Sn. This order clearly supports those scales, of which there are several (group and element electronegativities),[7,8,17] which have Ge more electronegative than Si. However, the most notable discrepancy is the position of Pb which is indicated by available group and element electronegativities to be either the most or least electropositive of the metalloids. Fourthly, it is of interest to note that the order of electron release by σ-resonance for the MMe_3 groups in system 1 virtually parallels the order of hyperconjugative electron release (Pb ~ Sn > Ge ~ Si > H > C)[18] for CH_2MR_3 substituents (R = Me or C_6H_5) attached to neutral aromatic systems. The only significant discrepancy is the position of Pb and this is probably attributable to a significant redistribution of the hybrid orbitals around this metalloid when directly attached to the bicyclooctane group.[9a] The parallel between both types of resonance (σ–σ and σ–π) exemplifies that similar factors ($c^2/\Delta E$) are governing both interactions.[19] However, the more pronounced effects for the σ–σ interaction is probably a manifestation of the better energy matching of the appropriate interacting orbitals in 1 as well as the stereochemical rigidity of this system.

Finally, we should like to draw attention to the fact that an attempt to extend the present study of 1 to other metalloidal substituents (SiH_3, GeH_3, etc.) by established synthetic procedures[9b] was thwarted by the remarkable instability of (4-fluorobicyclo[2.2.2]oct-1-yl)lithium (1, X = Li). This compound was found to undergo Grob fragmentation[20] completely in less than 10 min at −80 °C (see Experimental Section). Such a facile internal displacement of fluoride from a fluoroalkane in the absence of strong

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(7) Huheey, J. E. "Inorganic Chemistry"; Harper and Row: New York, 1983; pp 144–160, pp 845–848, and references cited therein.

(8) (a) Inamoto, N.; Masuda, S. *Tetrahedron Lett.* **1977**, 3287. (b) Inamoto, N.; Masuda, S. *Chem. Lett.* **1982**, 1003, 1007, and references cited therein.

(9) (a) The σ_F values for the MMe_3 groups (except M = Pb) are effectively *zero* because vectorial summation of the $M^{\delta+}$–$C^{\delta-}$ bond moments essentially cancel out (based on T_d symmetry about M) and, therefore, the net group moment must approximate the small $C^{\delta-}$–$H^{\delta+}$ bond moment. The significant *positive* σ_F value (0.05) for $PbMe_3$ implies that the group moment of the substituent is dominated by the $Pb^{\delta+}$–$CH_3{}^{\delta-}$ bond moment. This is confirmed by the $^1J_{C-Pb}$ values in $CDCl_3$ ($^1J_{CH_3-Pb}$ = 140.38 Hz and $^1J_{C-Pb}$ = 505.36 Hz) for the model system 1-X-4-(*p*-fluorophenyl)bicyclo[2.2.2]octane, X = $PbMe_3$) from which the σ_F parameters are derived.[1,9b,c] Accepting that the Fermi contact term is the dominant determinant of the one-bond coupling, these $^1J_{C-Pb}$ values compared to that for $PbMe_4$ in $CDCl_3$ ($^1J_{CH_3-Pb}$ = 249 Hz) are consistent with a major redistribution of s character in the binding hybrid orbitals directed toward the Me groups and the bridgehead carbon of the bicyclooctane (BCO) ring, in response to the strong donor characteristics of the latter ring system relative to Me. Consequently, there is considerably more s character in the Pb hybrid directed toward the BCO ring than those binding the Me groups. (b) Adcock, W.; Aldous, G. L.; Kitching, W. *J. Organomet. Chem.* **1980**, *202*, 385. (c) The symbol σ_F is employed in place of σ_I in view of the overwhelming evidence that σ_I is a manifestation of polar field effects.

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(17) Boyd, R. J.; Markus, G. E. *J. Chem. Phys.* **1981**, *75*, 5385.

(18) (a) Adcock, W.; Cox, D. P.; Kitching, W. *J. Organomet. Chem.* **1977**, *133*, 393. (b) The order of hyperconjugative electron release of CH_2MR_3 substituents (M = Si, Ge, Sn, and Pb; R = Me and C_6H_5 (≡ Ph)) is formalized in terms of the relative magnitude of their $\sigma_R{}^\circ$ values:[18a]: −0.20 (CH_2SiMe_3), −0.20 (CH_2GeMe_3), −0.24 (CH_2SnMe_3), −0.24 (CH_2PbMe_3); −0.17 (CH_2SiPh_3), −0.17 (CH_2GePh_3), −0.21 (CH_2SnPh), −0.21 (CH_2PbPh_3). These are averaged values (±0.01) determined from appropriate ^{19}F and ^{13}C SCS data from the benzene and naphthalene ring system. A similar set of statistically refined values have been obtained for these groups and appropriate alkyl substituents from ^{1}H and ^{13}C NMR data of 4-substituted styrenes[18c] (Private communication, Professor W. F. Reynolds): −0.124 (Me), −0.105 (CH_2CMe_3), −0.186 (CH_2SiMe_3), −0.191 (CH_2GeMe_3), −0.226 (CH_2SnMe_3), −0.228 (CH_2PbMe_3). (c) Reynolds, W. F.; Gomes, A.; Maron, A.; MacIntyre, D. W.; Tanin, A.; Hamer, G. K.; Peat, I. R. *Can. J. Chem.* **1983**, *61*, 2376 and references cited therein.

(19) (a) The clear demonstration from this study that resonance effects in 1 parallel those in the benzylic system strongly suggests that the factor responsible for the anomalous ^{19}F chemical shift for certain CH_2X substituents (X = NMe_2, CN, F, and CH_3) in the latter substrate[19b] are conjugative in origin[19c] and, therefore, dependent on electronegativity which is not necessarily proportional to σ_F.[1,2] The *relative* conjugative (or electronegativity) effects of NMe_2, CN, F, and CH_3 in 1[1] are not in accord with expectations based on their σ_F values. This is the "anomaly" observed in the benzylic system.[19b] (b) Happer, D. A. R.; Steenson, B. E. *Org. Magn. Reson.* **1983**, *21*, 252. (c) Adcock, W.; Abeywickrema, A. N. *J. Org. Chem.* **1982**, *47*, 779.

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electrophilic catalysis[21] is a very rare phenomenon indeed. The result provides compelling justification for the notion[1,2] that a "through-three-bond" electron delocalization mechanism (represented by canonical structures 2 and 3 is a strong regulator of the ^{19}F SCS of system 1.

Experimental Section

General Methods. Melting and boiling points are uncorrected. All distillations were performed on a Kugelrohr apparatus (Büchi GKR-50).

1-Fluoro-4-(trimethylsilyl)bicyclo[2.2.2]octane (1, X = Si(CH$_3$)$_3$). By use of a procedure outlined by Shippey and Dervan,[23] a solution of 1-fluoro-4-iodobicyclo[2.2.2]octane (1, X = I[22]; 1.0 g, 0.004 mol) in dry hexamethylphosphoric triamide (HMPA; 10 mL) containing freshly prepared sodium methoxide (0.7 g, 0.013 mol) was treated dropwise with hexamethyldisilane (1.7 g, 0.012 mol) at 0 °C under a nitrogen atmosphere. After addition was complete the reaction mixture was allowed to warm to room temperature and then stirred for 24 h. A standard workup followed by Kugelrohr distillation of the crude product afforded the silicon compound (1, X = SiMe$_3$) as a white solid which recrystallized from methanol as needles (0.2 g, 33%): mp 72–73 °C; ^{1}H NMR (CDCl$_3$) δ –0.13 (9 H, s, Si(CH$_3$)$_3$), 1.80–1.83 (12 H, m, CH$_2$CH$_2$); ^{13}C NMR (CDCl$_3$, relative to Me$_4$Si) δ 95.21 (J_{CF} = 181.64 Hz; C1), 31.30 (J_{CF} = 17.21 Hz; C2), 28.09 (J_{CF} = 8.42 Hz; C3), 16.77 (J_{CF} = 1.83 Hz; C4), –4.64 (J_{CSi} = 50.17 Hz; SiCH$_3$). Anal. Calcd for C$_{11}$H$_{21}$FSi: C, 65.95; H, 10.55. Found: C, 65.81; H, 10.60.

1-Fluoro-4-(trimethylgermyl)bicyclo[2.2.2]octane (1, X = Ge(CH$_3$)$_3$). A HMPA solution of the fluoro iodide (1, X = I[22]; 1.0 g, 0.004 mol) was added to (trimethylgermyl)lithium (prepared from Me$_3$GeBr (0.8 g, 0.004 mol) and lithium (0.1 g, 0.0142 mol) as described in the literature[24]) in HMPA (15 mL). The reaction mixture was allowed to stir for 2 h at room temperature before being worked up in the usual manner. Kugelrohr distillation (100 °C/2 mm) of the crude product and then recrystallization from methanol afforded a white solid (0.2 g, 42%): mp 71 °C; ^{1}H NMR (CDCl$_3$) δ 0.10 (9 H, s, GeCH$_3$), 1.73–1.80 (12 H, m, CH$_2$CH$_2$); ^{13}C NMR (CDCl$_3$, relative to Me$_4$Si) δ 94.82 (J_{CF} = 181.27 Hz; C1), 31.73 (J_{CF} = 16.84 Hz; C2), 29.13 (J_{CF} = 8.79; C3), 20.45 (J_{CF} = 2.20; C4), –5.48 (GeCH$_3$). Anal. Calcd for C$_{11}$H$_{21}$FGe: C, 53.94; H, 8.66. Found: C, 54.16; H, 8.89.

1-Fluoro-4-(trimethylplumbyl)bicyclo[2.2.2]octane (1, X = Pb(CH$_3$)$_3$). By use of the procedure of Williams,[25] a solution of (trimethylplumbyl)magnesium chloride (TPMC) was prepared by adding dry powdered lead chloride (1.49 g, 0.005 mol) to a well-stirred THF solution of methylmagnesium chloride (20 mL of 0.02 M solution, 0.02 mol) at 0 °C under an atmosphere of nitrogen. After the reagent mixture was stirred at 0 °C for 2 h, a THF solution of the fluoro iodide (1, X = I[22]; 1.5 g, 0.0059 mol) was then added slowly while maintaining the temperature at 0 °C. The mixture was then stirred at that temperature for 5 h and then an additional 16 h at room temperature before quenching with a saturated aqueous solution of ammonium chloride. A standard workup followed by two careful Kugelrohr distillations (100 °C/1 mm) of the crude product afforded the lead compound 1 (X = Pb(CH$_3$)$_3$ as a colorless liquid (0.8 g, 35.7%): ^{1}H NMR (CDCl$_3$) δ 0.53 (9 H, s, PbCH$_3$; J_{Pb-H} = 48 Hz), 2.17 (12 H, m, CH$_2$CH$_2$); ^{13}C NMR (CDCl$_3$, relative to Me$_4$Si) δ 92.94 (J_{CF} = 182.38 Hz, J_{CPb} = 21.61 Hz; C1), 33.77 (J_{CF} = 16.48 Hz, J_{CPb} = 102.73 Hz; C2), 34.05 (J_{CF} = 8.06 Hz; C3), 34.34 (J_{CF} = 2.2 Hz, J_{CPb} = 458.13 Hz; C4), –4.79 (J_{CPb} = 161.87 Hz; PbCH$_3$). An elemental analysis was not sought. The compound slowly disproportionated over a period of 3 months.

Treatment of 1-Fluoro-4-iodobicyclo[2.2.2]octane (1, X = I) with *tert*-Butyllithium. A solution of the iodide (1 (X = I[22]; 0.7 g, 2.8 mmol) in dry diethyl ether (7 mL) was cooled to –80 °C and treated with 6 mL of 1.5 M *tert*-butyllithium (9 mmol) in pentane. After 10 min, a solution of 4.3 g of bromine in diethyl ether (19 mL) was slowly added and the reaction mixture allowed to warm to room temperature. After a standard workup, almost quantitative amounts of 1,4-bis(bromomethyl)-1,4-dibromocyclohexane was obtained as a brown solid. A sample was recrystallized from hexane/diethyl ether (2:1) to afford prisms: mp 129–132 °C (lit.[26] mp 134–136 °C; ^{1}H NMR (CDCl$_3$) δ 1.86–2.66 (8 H, m, CH$_2$CH$_2$), 4.00 (4 H, s, CH$_2$Br); ^{13}C NMR (CDCl$_3$, relative to Me$_4$Si) δ 35.25 (C2, 3, 5, and 6), 43.43 (CH$_2$Br), 69.12 (C1 and 4). No 1,4-dibromobicyclo[2.2.2]octane, indicative of the formation of [2.2.2]propellane,[27] was detected in the crude reaction product either by ^{1}H and ^{13}C NMR or GLPC. Furthermore, no 1-bromo-4-fluorobicyclo[2.2.2]octane was detected, indicating that lithiation and decomposition was complete. The former conclusion follows from recent studies which showed that the replacement of I by Br in the bicyclo[2.2.2]octane ring system is facile even at low temperature.[27]

An experiment was also performed in which, after lithiation (10 min), the reaction mixture at –80 °C was quenched quickly with excess dry CO$_2$ gas. No 4-fluorobicyclo[2.2.2]octane-1-carboxylic acid[22] was isolated from the reaction, confirming the rapid and complete decomposition of the lithium derivative (1, X = Li).

NMR Spectra. The ^{13}C and ^{19}F NMR spectra were obtained as described in previous papers.[1,2,3b] ^{1}H NMR spectra were measured with a Varian EM-360 (60 MHz) spectrometer on CDCl$_3$ solutions.

Registry No. 1 (X = CMe$_3$), 81687-86-7; 1 (X = SiMe$_3$), 95552-61-7; 1 (X = GeMe$_3$), 95552-62-8; 1 (X = SnMe$_3$), 78385-88-3; 1 (X = PbMe$_3$), 95552-63-9; 1 (X = I), 78385-89-4; TPMC, 51258-94-7; 1,4-bis(bromomethyl)-1,4-dibromocyclohexane, 62947-52-8.

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Delocalized Carbanions: The Facile Synthesis of Disubstituted Butadienes and Diols

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The synthetic utility of delocalized carbanions resulting from the abstraction of a proton α to a double bond has been established[1] by using strong metalating agents such as *n*-butyllithium/tetramethylethylenediamine (*n*-BuLi/TMEDA)[2,3] or Lochmann's base system (*n*-BuLi/potassium *tert*-butoxide in pentane).[4–6] Lochmann's base system has been shown to cause allylic metalation of conjugated dienes, with the notable exception of isoprene

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