Comparison of complex 4 with the 1:1 adduct of dimethylformamide and the tridentate Lewis acid tris(chloromercury)acetaldehyde (5)[3b] is very informative.

$$(ClHg)_3C\text{-}CHO$$
5

This complex incorporates only two mercury–oxygen interactions with dimethylformamide that are shorter than the sum of their van der Waals radii. One is moderately strong (2.75 (5) Å) and comparable to the bonds in complex 4, but the other is quite weak (3.03 (6) Å). We believe that the symmetrical, cooperative binding of dimethylformamide by dichloro-1,2-phenylenedimercury (1) results from a particularly favorable orientation of the two sites of Lewis acidity. Cooperative binding requires that the complexed oxygen atom be approximately 2.6–2.7 Å from each mercury atom. At the same time, each mercury–oxygen bond should be perpendicular to the primary bonds of the mercury atom. Dichloro-1,2-phenylenedimercury (1) can satisfy these two conditions simultaneously, but tris(chloromercury)acetaldehyde (5) cannot unless the oxygen atom lies close to the plane defined by the atoms Hg–C–Hg. This indicates that bidentate and multidentate Lewis acids derived from 1,2-phenylenedimercury are particularly promising reagents for the binding and activation of carbonyl compounds and related substrates.

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Supplementary Material Available: Tables of mean interatomic distances and bond angles in free and bound dimethylformamide, anisotropic temperature factors, idealized coordinates of the hydrogen atoms, distances to the weighted least-squares planes, and geometry of dimethylformamide in crystal structures (11 pages); a listing of structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

Polar Substituent Effects on NMR Chemical Shifts of Group 14 Elements: Synthesis and NMR (^{13}C, ^{29}Si, ^{119}Sn, and ^{207}Pb) Substituent Chemical Shifts (SCS) of 4-Substituted Bicyclo[2.2.2]oct-1-ylbutanes, -trimethylsilanes, -trimethylstannanes, and -trimethylplumbanes ($M(CH_3)_3$, M = C, Si, Sn, and Pb) and 4-Substituted Bicyclo[2.2.1]hept-1-yltrimethylstannanes[1]

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An extensive series of 4-substituted bicyclo[2.2.2]oct-1-yltrimethylstannanes (**2a**) and 4-substituted bicyclo[2.2.1]hept-1-yltrimethylstannanes (**3a**) has been synthesized and characterized and the ^{119}Sn chemical shifts measured. A remarkably wide range of substituent chemical shifts (SCS; ca. 20 ppm) are obtained for system **2a**, and these have been analyzed in terms of possible substituent–probe interactions. Comparisons have been made between systems **2a** and **3a**, but the signs of the ^{119}Sn substituent chemical shifts (SCS) for the two systems are diametrically opposed, indicating a different blend of "through-space" and "through-bond" effects. Some 4-substituted 1-*tert*-butylbicyclo[2.2.2]octanes (**2b**) as well as more restricted series of trimethylsilanes and trimethylplumbanes (**2c** and **2d**, respectively) have also been acquired and their ^{13}C, ^{29}Si, and ^{207}Pb SCS measured and compared with those of the stannane series. Synthetic approaches that provide efficient access to some 1,4-disubstituted bicyclo[2.2.2]octyl systems are outlined.

Introduction

Organic derivatives of the group 14 elements (silicon, germanium, tin, and lead) have featured prominently in studies of periodicity, and much effort has been devoted to comparisons of spectra, reactivity, etc. In this regard, nuclear magnetic resonance studies, generally utilizing ^1H or ^{13}C nuclei, have provided considerable, if at times conflicting, insights into molecular characteristics and the types of effects that groups incorporating these elements may exert. The increasing ease of acquiring NMR spectra of the group 14 nuclei themselves, i.e., ^{29}Si, ^{119}Sn, and ^{207}Pb in particular, and the recognition that these nuclei respond fairly sensitively to changing molecular characteristics, have resulted in a blossoming interest in such spectra.[2-5]

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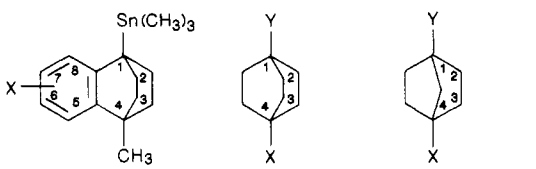
This interest is further nurtured by the availability of more diverse systems incorporating these elements. Although attempts to rationalize the variation of the NMR chemical shifts of these heavy nuclei are generally based on the assumption that the paramagnetic term (σ_p) to the shielding constant is dominant,[2-5] it must be stressed that the theory governing the phenomena is inadequate. Thus, empirical studies involving systematic structural variations on the chemical shifts in model systems are appropriate as this may assist the theoretical approach by delineating some of the important underlying factors.

Generally speaking, with respect to ^{29}Si, ^{119}Sn, and ^{207}Pb NMR chemical shifts, only a few series of compounds incorporating tactical structural changes have been examined so that a proper appreciation of the factors regulating the chemical shifts has not emerged. Substituent effects on ^{29}Si and ^{119}Sn NMR shifts in substituted benzenes have been reported[6-8] and subjected to correlative analysis with substituent constants. Although the range of substituents in the various basis sets of these studies do not permit a precise separation of polar and resonance phenomena by multilinear regression analysis,[9] the results in the main suggest that the shifts respond sensitively to polar influences. In addition, we[8] have observed that remote 6- and 7-substituents in 1-(trimethylstannyl)-4-methyl-1,4-ethano-1,2,3,4-tetrahydronaphthalenes (1), in which direct



1 **2a**, Y = SnMe3 **3a**, Y = Sn(CH3)3
b, Y = C(CH3)3 **b**, Y = F
c, Y = Si(CH3)3
d, Y = Pb(CH3)3
e, Y = F
f, Y = CH3

π-type transmission mechanisms are prohibited, has a surprisingly large influence on the ^{119}Sn chemical shift. However, the interpretation of these polar ^{119}Sn SCS is difficult due to problems associated with disentangling direct field effects from secondary resonance and π-inductive influences. The most suitable model systems for studying polar phenomena in the absence of concomitant π-electron effects are bridgehead–bridgehead disubstituted polycyclic alkanes. These systems, being geometrically rigid, are ideal for providing 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. Since recent synthetic developments[10,11] have made 1,4-disubstituted bicyclo[2.2.2]octanes readily accessible, it appeared that studies of 4-substituted (X) bicyclo[2.2.2]oct-1-yl derivatives of the group 14 elements would be feasible and particularly informative with respect to polar substituent–effect transmission in a saturated system. As will become clear below, important conclusions regarding the "blend" of substituent effects may be based on comparisons of data from the bicyclo[2.2.2]octyl and -[2.2.1]heptyl systems, and hence an examination of the latter system has also been conducted. In this paper we report the synthesis and full characterization of series of 4-substituted bicyclo[2.2.2]octyl- and bicyclo[2.2.1]-heptylstannanes (**2a** and **3a**, respectively) and their ^{13}C and ^{119}Sn NMR spectra and speculate on the mechanisms by which the considerable substituent effects (formally through five bonds) are exerted on the tin nucleus. For comparison, some corresponding butanes, silanes, and plumbanes (**2b**, **2c**, and **2d**, respectively) have been examined also.

Table I. ^{119}Sn Substituent Chemical Shifts (SCS)[a,b] of 4-Substituted Bicyclo[2.2.2]oct-1-yltrimethylstannanes (2a): Polar Field ($\rho_F\sigma_F$) and Residual Contributions

	SCS		$\rho_F\sigma_F$[c]		residual[d]	
X	c-C_6H_{12}	$CDCl_3$	c-C_6H_{12}	$CDCl_3$	c-C_6H_{12}	$CDCl_3$
CN	9.19	10.00	3.16	3.92	6.03	6.08
CF_3	7.07	7.35	2.36	2.80	4.71	4.55
$COCH_3$	5.19	6.16	1.50	2.17	3.69	3.99
$COOCH_3$	5.59	6.48	1.18	1.82	4.41	4.66
$CON(CH_3)_2$	4.54	5.47	1.02	1.75	3.52	3.72
F[e]	10.83	11.67	2.09	2.94	8.74	8.73
Cl	9.66	10.35	2.30	3.01	7.36	7.34
Br	10.95	11.67	2.36	3.08	8.59	8.59
I	13.37	14.08	2.25	2.94	11.12	11.14
OCH_3	7.65	8.76	1.02	1.82	6.63	6.94
$OCOCH_3$	9.02	10.13	1.55	2.31	7.47	7.82
$N(CH_3)_2$	5.11	6.17	0.54	1.26	4.57	4.91
C_6H_5	4.46	4.90	0.80	1.19	3.66	3.71
p-FC_6H_4	5.05	5.32	1.39	1.61	3.66	3.71
p-$CH_3OC_6H_4$	4.21	4.82	0.75	1.05	3.46	3.77
$C{\equiv}CSi(CH_3)_3$	6.02	6.52	1.29	1.68	4.73	4.84
CH_3	3.41	3.40	0.00	0.00	3.41	3.40
$C(CH_3)_3$	1.89	2.04	0.00	0.00	1.89	2.04
$Sn(CH_3)_3$[f]	−5.90	−5.53	0.00	0.00	−5.90	−5.53

[a] Chemical shifts (ppm) relative to parent system **2a**, X = H. Accurate to ±0.04 ppm. [b] Parent system **2a**, X = H, relative to internal $Sn(CH_3)_4$ (TMT): 0.16 (c-C_6H_{12}) and 0.46 ppm ($CDCl_3$). Low-field shifts are positive. [c] See ref 12 for σ_F values. ρ_F values for c-C_6H_{12} and $CDCl_3$ are 5.36 and 7.00 ppm, respectively (see text). [d] (Observed ^{119}Sn SCS) − $\rho_F\sigma_F$ in ppm. [e] $J_{^{119}Sn-^{19}F}$ values (Hz) = 69.58 (c-C_6H_{12}) and 74.47 ($CDCl_3$). [f] $J_{^{119}Sn-^{119}Sn}$ value (Hz) = 120 ($CDCl_3$). ^{119}Sn–^{117}Sn coupling constants were measured from both ^{119}Sn and ^{117}Sn NMR spectra and multipled by 1.046 to obtain $J_{^{119}Sn-^{119}Sn}$.

Results and Discussion

^{119}Sn SCS for Systems 2a and 3a. The ^{119}Sn SCS for **2a** in c-C_6H_{12} and $CDCl_3$, along with a dissection into polar-field ($\rho_F\sigma_F$) and "residual" contributions (^{119}Sn SCS−$\rho_F\sigma_F$), are assembled in Table I. A cursory examination of these data reveals that all the SCS are *positive* (*downfield* shifts) except for $Sn(CH_3)_3$, which is *negative* (upfield shift). In broad terms, the directions of the shifts accord with the primitive idea that electron-withdrawing polar substituents induce downfield shifts.[2] The SCS cover an impressive range of ca. 20 ppm (between I and $Sn(CH_3)_3$) and confirms our[8] suggestion that ^{119}Sn shifts are surprisingly sensitive to polar substituent influences. Regression analysis revealed that the SCS correlate poorly (r = 0.84 ($CDCl_3$), 0.82 (c-C_6H_{12})) against electric field parameters (σ_F),[12] as was observed with the ^{19}F SCS of

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Table II. ^{119}Sn Substituent Chemical Shifts (SCS)[a,b] of 4-Substituted Bicyclo[2.2.1]hept-1-yltrimethylstannanes (3a)

X	SCS, ppm	
	c-C_6H_{12}	$CDCl_3$
CN	−0.51	−0.22
$COCH_3$	−2.77	−2.49
$CON(CH_3)_2$	−1.53	−0.99
F[c]	−2.33	−1.83
Cl	−0.76	−0.19
Br	−1.57	−0.73
I	−4.20	−3.37
OCH_3	−3.67	−3.10
$N(CH_3)_2$	−3.79	−3.33
C_6H_5	−2.95	−2.96
CH_3	−3.83	−3.91
$C(CH_3)_3$	−3.87	−3.84
$Sn(CH_3)_3$[d]	2.23	2.52

[a] See footnote to Table I. [b] Parent system **3a**, X = H, relative to internal $Sn(CH_3)_4$ (TMT): 4.16 (c-C_6H_{12}) and 4.46 ppm ($CDCl_3$). Low-field shifts are positive. [c] $^1J_{^{119}Sn-^{19}F}$ values (Hz) = 7.33 (c-C_6H_{12}) and 6.60 ($CDCl_3$). [d] $^1J_{^{119}Sn-^{119}Sn}$ value (Hz) = 20.7 ($CDCl_3$). See footnote *f* to Table I.

4-substituted bicyclo[2.2.2]oct-1-yl fluorides (**2e**)[13] and the $^{13}CH_3$ SCS of 4-substitued 1-methylbicyclo[2.2.2]octanes (**2f**).[14] However, unlike the situation for the latter two systems (**2e** and **2f**), the precision of fit of the correlation of the ^{119}Sn SCS for **2a** is not significantly improved by including an electronegativity parameter.[15]

Polar-field susceptibility parameters (ρ_F values; 5.36 for c-C_6H_{12} and 7.00 for $CDCl_3$) may be determined independently by dividing the chemical shift difference between **2a**, X = *p*-FC_6H_4, and **2a**, X = C_6H_5 (Table I; 0.59 (c-C_6H_{12}), 0.42 ($CDCl_3$)), by $\Delta\sigma_F$ for *p*-FC_6H_4 and C_6H_5 (0.11 for c-C_6H_{12}, 0.06 for $CDCl_3$).[12] The validity of this technique is substantiated by the fact that ρ_F values (−4.31, −3.31, and −3.45)[16] obtained by this methodology for α-carbon centers of system 2 where Y = C_6H_5, CN, and $COOCH_3$, respectively, agree reasonably well with those obtained (−4.60, −3.94, and −3.34)[17] for these unsaturated probes by direct correlation of the ^{13}C SCS ($CDCl_3$) against σ_F values. Accepting the idea that the electric field effect on NMR screening constants can be ascribed to differential polarization of the bonds about the magnetic nucleus,[18] the significant ρ_F values for **2a** imply greater polarization of the Sn–C_1 bond vs. Sn–CH_3 bonds. Factorization of the SCS (Table I) clearly demonstrates that although the polar-field term ($\rho_F\sigma_F$) is significant, it is not the dominant factor regulating the ^{119}Sn shifts of **2a**. It is worth noting that the close agreement in "residual" values for both solvents requires that the minor solvent effect (Table I) is embodied in the polar-field term.

Since we suspected that "through-bond" and/or "through-space" electron delocalization mechanisms[19] may be responsible for the large "residual" contributions (Table I) to the ^{119}Sn SCS of **2a**, we decided to carry out a systematic investigation of some of the corresponding 4-substituted bicyclo[2.2.1]heptylstannanes (**3a**). This was prompted by the knowledge that such a structural change (**2a** → **3a**) of the intervening connective bonds affects a significant change in the blend of possible "through-bond" and "through-space" effects underlying appropriate quantum mechanical[19a] and physicochemical parameters.[20] Thus, we were hopeful that some empirical insight into the origins of the residuals for **2a** may evolve from the ^{119}Sn SCS of this new model system (**3a**). These are listed in Table II for c-C_6H_{12} and $CDCl_3$ as solvents. A comparison of the corresponding data for **2a** and **3a** (Tables I and II) reveals a striking contrast between the two systems. Note that the *signs* of the ^{119}Sn SCS of **3a** (Table II) for every substituent are diametrically opposed to those observed for **2a** (Table I). Thus, whereas polar electron-withdrawing groups (e.g., CN, F, Cl, OCH_3, etc.) effect *downfield* shifts in **2a**, *upfield* shifts are observed in **3a** for the corresponding substituents. The converse situation holds for the classical polar σ-electron-donor substituent ($Sn(CH_3)_3$). A further noteworthy difference is the much smaller numerical values of the SCS for **3a** compared to **2a**. In fact the total range of shifts for the former (ca. 6 ppm) is less than a third of that (20 ppm) observed for the latter. The ^{119}Sn SCS for 3a (Table II) were analyzed by multiple regression analysis using polar substituent constants, but no discernible relationship emerged.

Unfortunately, appropriate data is not available (no SCS for a *p*-XC_6H_4 group) to allow factorization of the SCS of **3a** in the same manner as performed for **2a**. However, a consideration of angle and distance factors suggests that the polar-field terms ($\rho_F\sigma_F$) for the two systems should be similar in magnitude and sign. The variations of the one-bond coupling constants (average $^1J_{Sn-CH_3}$ values) for **2a** and **3a** (Tables VI and VII, respectively) strongly supports this conclusion (see correlations later; eq 2 and 3). Thus, the conclusion follows that the residual contributions for **3a** are *opposite* in sign to those for **2a** (Table I). The evidence is that "through-three-bond" delocalization can be antagonistic to both "through-two-bond" (as in **3a**) and "through-space" interactions.[19,20] Accepting that the former is more important in **2a**, the results for the ^{119}Sn shifts are sensible only if the through-space effect is *shielding* and the through-bond effect is *deshielding* for the electronegative substituents. The converse situation must hold for electropositive groups. In contrast, a recent comparison[13,21] for these two bicycloalkanes with the ^{19}F nucleus as the probe (systems **2e** and **3b**) demonstrated *shielding* "through-three-bond" and *deshielding* "through-space" contributions for electronegative substituents and the converse for electropositive groups.

A significant and puzzling distinction between the two probes (^{19}F and ^{119}Sn) is that whereas the residuals for the former in both model systems[13,21] parallel well the elec-

(12) (a) 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 In the main, σ_F values derived from the ^{19}F SCS of 1-X-4-(*p*-fluorophenyl)bicyclo[2.2.2]octanes[13] were employed for the correlations except for the acetylene group (C≡CSiMe$_3$; see ref 24a of ref 12b), *p*-FC_6H_4 and *p*-$CH_3OC_6H_4$. Values for the latter groups were derived from the ^{19}F SCS of 1-fluoro-4-(para-substituted phenyl)bicyclo[2.2.2]octanes.[12c] (b) Adcock, W.; Kok, G. B. *J. Org. Chem.* **1985**, *50*, 1079. (c) Adcock, W.; Abeywickrema, A. N. *J. Org. Chem.* **1982**, *47*, 2945.

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Table III. ^{29}Si Substituent Chemical Shifts (SCS)[a,b] of 4-Substituted Bicyclo[2.2.2]oct-1-yltrimethylsilanes (2c): Polar Field ($\rho_F\sigma_F$) and Residual Contributions

X	SCS		$\rho_F\sigma_F$[c]		residual[d]	
	c-C_6H_{12}	$CDCl_3$	c-C_6H_{12}	$CDCl_3$	c-C_6H_{12}	$CDCl_3$
F[e]	1.13	1.21	0.34	0.47	0.79	0.74
I	1.67	1.78	0.36	0.47	1.31	1.31
C_6H_5	0.63	0.70	0.13	0.18	0.50	0.52
p-FC_6H_4	0.70	0.76	0.22	0.24	0.48	0.52
p-$NO_2C_6H_4$	0.84	0.88	0.34	0.37	0.50	0.51
CH_3	0.51	0.51	0.00	0.00	0.51	0.51

[A] See footnote *a* to Table I. Parent system **2c**, X = H, relative to internal $Si(CH_3)_4$ (TMS): 4.47 (c-C_6H_{12}) and 4.53 ppm ($CDCl_3$). Low-field shifts are positive. [c] ρ_F values for c-C_6H_{12} and $CDCl_3$ are 0.86 and 1.11, respectively (see text). [d] (Observed ^{29}Si SCS) − $\rho_F\sigma_F$ in ppm. [e] $J_{^{29}Si-^{19}F}$ values (Hz) = 6.11 (c-C_6H_{12}) and 6.59 ($CDCl_3$).

Table IV. ^{207}Pb Substituent Chemical Shifts (SCS)[a,b] of 4-Substituted Bicyclo[2.2.2]oct-1-yltrimethylplumbanes (2d): Polar Field ($\rho_F\sigma_F$) and Residual Contributions

X	SCS		$\rho_F\sigma_F$[c]		residual[d]	
	c-C_6D_{12}	$CDCl_3$	c-C_6D_{12}	$CDCl_3$	c-C_6D_{12}	$CDCl_3$
F[e]	19.11	19.67	3.41	3.92	15.70	15.75
C_6H_5	7.88	8.56	1.31	1.59	6.57	6.97
p-FC_6H_4	8.84	9.12	2.27	2.15	6.57	6.97
CH_3	5.91	6.02	0.00	0.00	5.91	6.02

[a] See footnote *a* to Table I. [b] Parent system **2d**, X = H, relative to external $Pb(CH_3)_4$ in toluene (80% v/v): 54.49 (c-C_6D_{12}) and 57.08 ppm ($CDCl_3$). Low-field shifts are positive. [c] ρ_F values for c-C_6D_{12} and $CDCl_3$ are 8.73 and 9.33, respectively (see text). [d] (Observed ^{207}Pb SCS) − $\rho_F\sigma_F$ in ppm. [e] $J_{^{207}Pb-^{19}F}$ values (Hz) = 135.49 (c-C_6D_{12}) and 143.74 ($CDCl_3$).

tronegativity influences of the substituents, the corresponding contributions for the latter display no such obvious relationship. For the ^{119}Sn probe, the unusual order and dislocating trends of the SCS for the halogen substituents (similar σ_F values but vastly different electronegativities) in both system (Tables I and II) is worth noting. The aforementioned distinction between the two probes probably reflects the different nature of the orbital interactions underlying the electron-delocalization mechanisms for each particular nucleus as well as their mix. In our earlier communication[1] we offered some tentative speculation concerning the likely dominant orbital interactions governing the coupling of the appropriate bond MOs (CF or CSn and CX). However, in view of the complexity of the situation and, in particular, the lack of knowledge concerning the effects of the through-bond and through-space electron-delocalization mechanism on the tensorial components of the chemical shifts, it would seem wise not to rehash our previous brief comments here or to speculate further on the likely pertinent molecular parameters responsible for the puzzling shift variations.

^{13}C, ^{29}Si, and ^{207}Pb SCS for Systems 2b, 2c, and 2d. The ^{29}Si and ^{207}Pb SCS for **2c** and **2d**, together with a dissection into polar-field and residual contributions, are set out in Tables III and IV, respectively. Although the range of substituents is clearly limited, a comparison of these shift parameters with the corresponding ^{119}Sn SCS for **2a** (Table I) reveals a similar pattern. Bearing in mind the relative chemical shift dispersions of the Si, Sn, and Pb nuclides,[2,5] it appears that the various shifts respond fairly similarly to polar substituent electronic influences. In striking contrast, the ^{13}C SCS for **2b** (listed in Table V) are not only very small by comparison (in many instances, practically negligible) but, in general, where significant, (e.g., X = F) they are of *opposite* sign to those of the heavier group 14 probes. The latter response to electronic effects is reminiscent of the *reverse* $^{13}CH_3$ SCS

Table V. ^{13}C Substituent Chemical Shifts (SCS)[a-c] for the Quaternary Carbon in the *tert*-Butyl Group of 4-Substituted 1-*tert*-Butylbicyclo[2.2.2]octanes (2b)

X	SCS	$\rho_F\sigma_F$[d]	residual[e]
COOH	−0.16[f]	0.00	−0.16
F	−0.39[f]	0.00	−0.39
Cl	−0.30	0.00	−0.30
Br	−0.13	0.00	−0.13
I	0.24[f]	0.00	0.24
OCH_3	−0.30[f,g]	0.00	−0.30
C_6H_5	−0.08[f]	0.00	−0.08
p-$NO_2C_6H_4$	−0.08	0.00	−0.08
CH_3	−0.10	0.00	−0.10
$Sn(CH_3)_3$	−0.03	0.00	−0.03

[a] See footnote *a* to Table I. [b] Solvent, $CDCl_3$. Parent system **2b**, X = H: 34.32 ppm (relative to internal Me_4Si). [c] Accurate to ±0.04 ppm. [d] ρ_F is zero (see text). [e] (Observed ^{13}C SCS) − $\rho_F\sigma_F$ in ppm. [f] Compounds available from other studies. [g] X = OCH_3: ^{13}C NMR ($CDCl_3$, relative to Me_4Si) δ 73.46 (C1), 29.45 (C2), 26.48 (C3), 34.93 (C4), 34.02 ($C(CH_3)_3$), 25.31 ($C(CH_3)_3$).

reported for the β-carbon of para-substituted ethylbenzenes[22] and the methyl group of system **2f**;[14] i.e., net electron-withdrawal leads to *upfield* shifts. The much smaller range of residual shifts for **2b** compared to **2f**[14] is surprising and is probably related to the respective shift/charge density ratios of the two different carbon centers rather than the degree of "through-three-bond" coupling of the CX and CY (Y = CH_3 and $C(CH_3)_3$) bonds.

Utilizing the same methodology employed above for the $Sn(CH_3)_3$ group in **2a**, polar-field susceptibility parameters (ρ_F values) may be derived for the other $M(CH_3)_3$ groupings ($\rho_F(CDCl_3)$ = 0.00, 1.11, and 9.33 for M = C, Si, and Pb, respectively; ρ_F(c-C_6H_{12}) = 0.86 and 8.73 for M = Si and Pb, respectively). The determination of the values for M = C and Si involved the respective chemical shift differences between *p*-$NO_2C_6H_4$ and C_6H_5 and the appropriate $\Delta\sigma_F$ values (0.24 for c-C_6H_{12} and 0.16 for $CDCl_3$).[13] Clearly, the relative magnitude of the ρ_F values for the $M(CH_3)_3$ groups (M = Pb > Sn >> Si >>> C) is in line with intuitive expectations that the mode of action of the electric field is to essentially distort the electron cloud of the nucleus (M), and, hence, the perturbation should increase with polarizability (descension of group 14). It is of interest to note that the *zero* value for the quaternary carbon center is in complete accord with a prediction by Batchelor.[23]

Finally, it should be emphasized that attempts to rationalize variations in the chemical shifts of the group 14 nuclei usually involve the assumption that the local paramagnetic contribution, which is generally expressed in a simplified form (eq 1), is dominant[2-5] (where r = mean

$$\sigma_A^p \propto \langle r^{-3}\rangle_{np}\Delta E^{-1}\sum Q_{AB} \quad (1)$$

orbital radius term (related to effective nuclear charge), ΔE = mean excitation energy, and Q_{AB} = bond-order electron density matrix term). For a series of structurally similar compounds, it is generally assumed that ΔE remains constant and, therefore, the charge dependence of chemical shifts results from either the $\langle r^{-3}\rangle_{np}$ or $\sum Q_{AB}$ terms, or both. The residual contributions (c-C_6H_{12}) to the ^{29}Si, ^{119}Sn, and ^{207}Pb SCS for *fluorine* as substituent (0.79, 8.74, and 15.70 ppm, respectively) in the bicyclooctane

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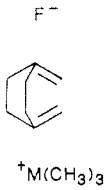
(23) Batchelor, J. G. *J. Am. Chem. Soc.* **1975**, *97*, 3410.

system (see Tables I, II, and IV) offer a means of testing these theoretical ideas. If it is assumed that these residuals are manifestations of a decrease in the electron population at the various heavy nuclei as a result of the "through-three-bond" electron-delocalization mechanism (in valence bond terms, this may be denoted by canonical structure **4**; depicted for only one of the three ethano bonds)[24] and,



4

moreover, if it is also assumed that the relative magnitude of this σ-conjugative electronic effect for the $M(CH_3)_3$ groupings is reflected by the appropriate residual ^{19}F SCS (c-C_6H_{12} (ppm): 1.54, 3.70, and 3.03 for $SiMe_3$, $SnMe_3$, and $PbMe_3$, respectively),[24] then *relative* shift/charge density ratios can be calculated for the element pairs (Pb/Sn = 2.2 and Sn/Si = 4.6). Most significantly, these experimentally determined ratios are in remarkably good agreement with the corresponding ratios determined from the $\langle r^{-3}\rangle_{np}$ values given by Jameson and Gutowsky[25] (Pb/Sn = 1.9 and Sn/Si = 4.5).[5] We believe this is compelling evidence for believing that the charge dependence of the chemical shifts (induced by remote substituents) of the heavy group 14 nuclides residues exclusively in the $\langle r^{-3}\rangle_{np}$ term. On the other hand, the small *reverse* ^{13}C SCS noted above for the quaternary carbon of the $C(CH_3)_3$ group, and other saturated carbon probe centers, suggests that the situation for ^{13}C chemical shifts is apparently more obscure. It is possible that the shift/charge dependency relationship for the latter shifts may have its origin in more than one factor ($\langle r^{-3}\rangle_{np}$ and $\sum Q_{AB}$). Where these factors are finely balanced, it is possible that the relationship breaks down even for remote substituents.

Coupling Constants. Several features of some of the coupling constants are worthy of note. Firstly, it can be seen that the one-bond $^{13}CH_3$–$^{117,119}Sn$ and $^{13}CH_3$–^{207}Pb coupling constants for **2a** and **2d** (X = H; Table VI; 297, 283, and 126 Hz, respectively) are considerably less than the values for $Sn(CH_3)_4$ and $Pb(CH_3)_4$ (336, 322, and 249 Hz, respectively).[26] Note, however, that the corresponding values of $^1J_{Sn-Cl}$ and $^1J_{Pb-Cl}$ for **2a** and **2d** (X = H; Table VI; 474, 453, and 530 Hz, respectively) are substantially increased and that $\sum J$ about Sn and Pb is fairly similar for each set of compounds (**2a** and $Sn(CH_3)_4$; **2d** and $Pb(CH_3)_4$). Accepting that the Fermi contact term is the dominant determinant of one-bond coupling,[2] these variations are consistent with a major redistribution of s character in the Sn and Pb binding hybrid orbitals directed toward the CH_3 groups and the bridgehead carbon of the bicyclooctane (BCO) ring, in response to the much stronger σ-donor characteristics of the latter ring system relative to CH_3. Thus, there is considerably more s character in the hybrid orbitals directed toward the BCO ring than those binding the CH_3 groups. The significantly larger $^1J_{Sn-CH_3}$ values for **3a** (X = H; Table VII; 313 and 299 Hz) compared to **2a** (X = H; see above) confirms the known relative σ-donor characteristics of the two saturated ring systems (more s character in the exocyclic orbital at the bridgehead of the bicycloheptane system than the corresponding hybrid orbital for the BCO ring).[27] In contrast to the situation described for Sn and Pb, it is of interest to note that $^1J_{Si-CH_3}$ for **2c** (X = H; 49.81 Hz; see footnote *c* of Table VI) is not dramatically different from the corresponding value for $Si(CH_3)_4$ ($^1J_{Si-CH_3}$ = 50.3 Hz ($CDCl_3$)).[26a] These observations emphasize further the consequences of the relative polarizabilities of the valence electrons of the group 14 elements.

Secondly, it can be seen that the one-bond $^{13}CH_3$–$^{117,119}Sn$ and $^{13}CH_3$–^{207}Pb couplings (Table VI and VII) display significant variations on changing the substituent. In fact, for systems **2a** and **3a**, for which there is a substantial basis set of polar substituents, linear regression analysis indicates that there is a fair linear correlation between $^1J_{Sn-CH_3}$ (average values) and σ_F[12] (eq 2 and 3; nonpolar groups (X = H, CH_3, $C(CH_3)_3$, and $Sn(CH_3)_3$) excluded from the analysis). These trends in the ^1J values (Sn and Pb) are again consistent with a redistribution of s character in the binding hybrid orbitals. An increase in the polar-field influence of the substituent effectively reduces the donor ability of the bicycloalkane ring system. Hence, an increase in s character in the bonding orbital to CH_3 occurs, with a corresponding increase in $^1J_{M-CH_3}$ and a consequential reduction in $^1J_{M-Cl}$ (M = Sn or Pb) on increasing the σ_F value of the substituent.

$$^1J_{Sn-CH_3} = 30.76\sigma_F + 288 \text{ (system 2a; } r = 0.96,\ n = 14) \quad (2)$$

$$^1J_{Sn-CH_3} = 32.74\sigma_F + 302 \text{ (system 3a; } r = 0.93,\ n = 9) \quad (3)$$

Finally, the large unprecedented five-bond long-range coupling constants observed in the BCO ring ($CDCl_3$ (Hz): $^5J_{^{29}Si-^{19}F} = 6.59$, $^5J_{^{119}Sn-^{19}F} = 74.47$, $^5J_{^{207}Pb-^{19}F} = 143.74$, and $^5J_{^{119}Sn-^{119}Sn} = 120$; see footnotes *e* and *f* to Table I and footnote *e* to Tables III and IV)[28] dramatically exemplify the extent to which the bridgehead bonds are coupled by the "through-three-bond" electronic mechanism in this model substrate. The five-bond couplings in the BCO ring system are to be compared with the much smaller values observed in the benzene ring where these elements are similarly disposed ($CDCl_3$ (Hz): $^5J_{^{29}Si-^{19}F}$ is not observed;[3] $^5J_{^{119}Sn-^{19}F} = 9.27$; $^5J_{^{207}Pb-^{19}F} = 18.6$).[29] It should be noted that the corresponding $^5J_{^{119}Sn-^{19}F}$ and $^5J_{^{119}Sn-^{119}Sn}$ couplings are much reduced in the bicycloheptane (BCH) system (6.6 and 20.7 Hz, respectively; see footnotes *c* and *d* to Table II)[28] compared to those observed in the BCO ring. This latter result is another striking manifestation of the change in "mix" of "through-bond" and "through-space" effects in these caged saturated systems. However, it should be borne in mind that the "through-bond" component to the long-range couplings in the BCH system has a ^4J component as well as ^5J contributions (the latter are much reduced because the bridgehead bonds, and the ethano connectivities are not optimally aligned for five-bond transmission as is the case in the BCO ring). Thus a sign difference between these two "through-bond" components (^4J and ^5J) could also contribute to the observed large

(24) (a) Adcock, W.; Iyer, S. V. *J. Org. Chem.* **1985**, *50*, 1538. (b) The "through-three-bond" effect in these $M(CH_3)_3$-substituted bicyclo[2.2.2]oct-1-yl fluorides has been ascribed[24a] predominantly to the coupling of the σ_{CM} and σ^*_{CF} bond MOs by the bridging ethano bonds.
(25) Jameson, C. J.; Gutowsky, H. S. *J. Chem. Phys.* **1964**, *40*, 1714.
(26) (a) This study. (b) See also ref 2.
(27) Della, E. W.; Cotsaris, E.; Hine, P. T. *J. Am. Chem. Soc.* **1981**, *103*, 4131 and references therein.
(28) Average $^{117,119}Sn$–^{19}F and ^{207}Pb–^{19}F coupling constants in the BCO ring have been obtained from the ^{19}F NMR spectra.[13,21,24a] However, the corresponding ^{29}Si–^{19}F coupling was not observed in the latter.[24a]
(29) (a) This study. The compound was available from another investigation.[29b] (b) Adcock, W.; Cox, D. P.; Kitching, W. *J. Organomet. Chem.* **1977**, *133*, 393.

differential between the long-range couplings for these two bicyclic systems.

Experimental Section

General Data. Melting and boiling points are uncorrected. Analytical vapor-phase chromatographic (VPC) analyses were performed on a Varian 1740 gas chromatograph using a 10-ft column of 5% SE-30 on 100/120 Chromosorb W. Combined gas chromatography–mass spectrometry (GC–MS) was performed on a Hewlett-Packard 5992B instrument, fitted with an OV101 capillary column. Some mass spectra were recorded on AEI-MS30 or AEI-MS902 spectrometers generally operating at an ionizing potential of 70 eV. Distillations were generally carried out with a Kugelrohr apparatus (Buchi:GKR-50). Hence, boiling points quoted below pertain to the latter equipment.

NMR Spectra. The broad-band proton-decoupled ^{13}C NMR spectra were recorded in the pulse Fourier transform mode on JEOL FX-90Q or FX-100 spectrometers operating at 22.53 and 25.05 MHz, respectively. Assignments for the various compounds described in the text below as well as those listed in Tables VI and VII followed unambiguously from chemical shift, intensity, and substituent-effects considerations.[11,21] Various coupling constants ($^{117,119}Sn$–^{13}C, ^{207}Pb–^{13}C, and ^{19}F–^{13}C) in many instances were helpful in confirming assignments. It should be noted that the assignments of C1 and C4 previously reported for one of the plumbanes (**2d**, X = C_6H_5) are incorrect.[30] In addition, the chemical shift for the methyl groups of one of the bicyclo[2.2.1]heptyl-1-stannanes (**3a**, X = F) was inadvertently reported in error.[21]

^{119}Sn spectra were recorded at 37.08 and 33.34 MHz on JEOL FX-100 and JEOL FX-90Q spectrometers, respectively. ^{207}Pb and ^{29}Si spectra were recorded at 18.70 and 17.76 MHz, respectively, on a JEOL FX-90Q spectrometer. Gated incoherent proton decoupling was used in order to suppress the nuclear Overhauser effect when recording the Si and Sn spectra. Routine ^1H NMR spectra were measured with a Varian EM-360(60 MHz).

Synthesis of Compounds. Some of the compounds were available from previous studies (**2a**, X = I;[31] **3a**, X = F;[21] **2c**, X = I,[31] C_6H_5,[30] and *p*-FC_6H_4[30]). Several others were prepared as previously described (**2a**, X = F,[11] C_6H_5,[32] *p*-FC_6H_4,[32] and CH_3;[14] **2d**, C_6H_5,[30] and *p*-FC_6H_4[30]). Many of the precursor 4-substituted bicyclo[2.2.2]oct-1-yl iodides were available from other work (X = CF_3[12b] $OCOCH_3$,[33] $C{\equiv}CSiMe_3$,[12b] CH_3,[14] and $C(CH_3)_3$[12b]). Others were prepared as previously described (X = F,[11] C_6H_5,[32] and *p*-FC_6H_4[32]). Literature procedures were followed in the preparation of 1-chlorobicyclo[2.2.1]heptane[34] and 1,4-diiodobicyclo[2.2.1]heptane.[35] All the other precursor 4-substituted bicyclo[2.2.1]heptyl-1-iodides were available from another study.[36]

1-Iodobicyclo[2.2.2]octane. A solution of 1-methoxybicyclo[2.2.2]octane (10.0 g, 0.065 mol; prepared in the manner previously indicated)[11] in acetic anhydride (113 mL) at 0 °C under nitrogen was treated carefully with freshly distilled 55% aqueous hydroiodic acid (113 mL). The resulting reaction mixture was then heated under reflux, in the dark, for 36 h. After cooling, the reaction mixture was poured onto ice/water and, after neutralization with 10% aqueous sodium hydroxide, was extracted (3×) thoroughly with ether. The combined ether extract was washed successively with 10% aqueous sodium thiosulfate and sodium bicarbonate solutions and then dried. Removal of the solvent afforded a very viscous liquid, which, on attempted distillation, became deeply colored (orange-red). Column chromatography (alkaline alumina; pentane as eluant) of the crude product afforded the title compound as a white solid: 13.7 g (81%); mp 27–28 °C (lit.[37] mp 27–28 °C).

4-Iodobicyclo[2.2.2]octane-1-carbonitrile. By use of the procedures outlined by Adcock et al.[11] for the conversion of 4-fluorobicyclo[2.2.2]octane-1-carboxylic acid to the corresponding fluoronitrile, 4-iodobicyclo[2.2.2]octane-1-carboxylic acid (3g, 10.5 mmol) was converted via the amide to the title compound, which was obtained as fine white crystals after sublimation and then recrystallization from a hexane/ethanol mixture (1:1): mp 198–199 °C (lit.[38] mp 186 °C); ^{13}C NMR ($CDCl_3$, relative to Me_4Si) δ 24.83 (C1), 32.76 (C2), 38.88 (C3), 37.88 (C4), 124.12 (CN). Anal. Calcd for $C_9H_{12}IN$: C, 41.40; H, 4.63. Found: C, 41.19; H, 4.64.

4-Iodobicyclo[2.2.2]octan-1-amine. By use of the procedures outlined by Adcock et al.[11] for the conversion of 4-fluorobicyclo[2.2.2]octane-1-carboxylic acid to the corresponding fluoroamine, 4-iodobicyclo[2.2.2]octane-1-carboxylic acid (5.0 g, 17.9 mmol) was converted via the acid chloride to the title compound, which was obtained as a white solid (3.7g, 83%) after sublimation; mp 53–57 °C. Recrystallization of a sample from pentane gave white plates: mp 56–59 °C (lit.[38] 164 °C); mass spectrum, *m/e* 251 (M^+), 124 ($M^+ - 127$); ^1H NMR ($CDCl_3$) δ 1.35 (2 H, s, NH_2), 1.47–2.77 (12 H, m, CH_2CH_2). Anal. Calcd for $C_8H_{14}IN$: C, 38.26; H, 5.58; I, 50.58; N, 5.58. Found: C, 38.42; H, 5.63; I, 50.00; N, 5.50.

1-(Dimethylamino)-4-iodobicyclo[2.2.2]octane. Following the procedure of Meiners et al.[39] as described by Adcock et al.[11] for the methylation of 4-fluorobicyclo[2.2.2]octan-1-amine, the aforementioned iodoamine (1.5 g, 6.0 mmol) was converted to the title compound. Sublimation (1.65 g, 90%) and recrystallization from hexane afforded colorless plates: mp 101–103.5 °C (lit.[38] 94 °C); ^1H NMR ($CDCl_3$) δ 1.57–2.77 (12 H, m, CH_2CH_2), 2.18 (6 H, s, $N(CH_3)_2$); ^{13}C NMR ($CDCl_3$, relative to Me_4Si) δ 50.7 (C1), 38.1 (C2), 41.1 (C3), 43.9 (C4), 30.4 ($N(CH_3)_2$). Anal. Calcd for $C_{10}H_{18}IN$: C, 43.03; H, 6.45; N, 5.02. Found: C, 42.68; H, 6.79; N, 4.95.

4-Iodo-*N*,*N*-dimethylbicyclo[2.2.2]octane-1-carboxamide. 4-Iodobicyclo[2.2.2]octane-1-carboxylic acid (0.5g, 1.79 mmol) was treated with thionyl chloride in a standard manner to give the acid chloride. An ethereal solution of the latter compound was treated with dry dimethylamine to afford the title compound. Sublimation afforded a white solid (0.4, 73%), mp 116–118 °C (lit.[38] 126 °C).

1-Acetyl-4-iodobicyclo[2.2.2]octane. By use of the procedure of Rubottom et al.[40] an ethereal solution of methyllithium (6 mL of 1.5 M solution, 0.0072 mol; prepared from chloromethane) was added quickly to a well-stirred solution of 4-iodobicyclo[2.2.2]-octane-1-carboxylic acid[12b] (1 g, 0.0072 mol) in ether (25 mL) kept at 0 °C under an atmosphere of nitrogen. After the reaction mixture was stirred at this temperature for a further 2 h, freshly distilled chlorotrimethylsilane (12 mL, 0.01 mol) was added to the solution and the mixture was then allowed to warm up to room temperature. A standard workup followed by Kugelrohr distillation and then recrystallization from a hexane/ethanol mixture (1:1) afforded a white solid (0.9 g, 90.6%): mp 71–72 °C; ^1H NMR ($CDCl_3$) δ 1.6–2.06 (6 H, m, CH_2CH_2), 2.1 (3 H, s, $COCH_3$), 2.43–2.70 (6 H, m, CH_2CH_2); ^{13}C NMR ($CDCl_3$, relative to Me_4Si) δ 41.36 (C1), 31.12 (C2), 39.74 (C3), 42.92 (C4), 25.04 (CH_3), 212.52 (CO). Anal. Calcd for $C_{10}H_{15}IO$: C, 43.19; H, 5.44. Found: C, 42.88; H, 5.85.

1-Iodo-4-methoxybicyclo[2.2.2]octane. By use of the procedure of Abeywickrema and Della[41] as described by Adcock et al.[11] for the conversion of 4-fluorobicyclo[2.2.2]octane-1-carboxylic acid to the corresponding fluoroiodide, 4-methoxybicyclo[2.2.2]octane-1-carboxylic acid[11] (3 g, 16.3 mmol) was treated with *tert*-butyl hypoiodite and then irradiated to afford the title compound.

Sublimation of the very crude residue followed by recrystallization from a hexane/ethanol mixture (1:1) afforded fine white crystals (1.1 g, 25%): mp 71–72 °C (lit.[42] 79.6–79.8 °C); ^1H NMR

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Table VI. ^{13}C Chemical Shifts[a,b] of 4-Substituted Bicyclo[2.2.2]oct-1-yltrimethylsilanes (2c), -stannanes (2a), and -plumbanes (2d)

X	chemical shift, ppm					
	C1	C2	C3	C4	$M(CH_3)_3$	others
				Silanes (**2c**)[c]		
H	15.62	26.01	25.83	23.89	−4.76	
F[d]	16.77	28.10	31.30	95.23	−4.65	
	(1.83)	(8.79)	(17.21)	(181.65)		
C_6H_5[e]	16.51	26.75	32.10	34.41	−4.71	150.74 (i), 125.58 (o), 127.99 (m), 125.34 (p)
p-FC_6H_4[d,e]	16.47	26.71	32.26	34.10	−4.74	146.48 (i), 127.0 (o), 114.58 (m), 160.87 (3.05), (7.94), (20.75), (243.22)
p-$NO_2C_6H_4$[e]	16.49	26.50	31.92	35.41	−4.75	158.60 (i), 126.55 (o), 123.24 (m), 145.82 (p)
CH_3	16.24	26.69	33.16	27.26	−4.70	28.78 (CH_3)
				Stannanes (**2a**)[f]		
H	21.71	30.12	27.32	23.50	−12.68	
	[453]	[n.o.]	[52.7]	[n.o.]	[283]	
	[474]		[55.3]		[297]	
CN	18.84	28.74	30.23	26.48	−12.50	125.16 (CN)
	[424]	[n.o.]	[50.9]	[6.23]	[296]	
	[444]		[53.5]		[311]	
CF_3[d]	20.59	28.82	24.95	36.53	−12.55	128.98 (CF_3)
	[433]	[n.o.]	[av 53.2]		[293]	(279.3)
	[453]		(1.46)	(24.9)	[307]	
$COOCH_3$	20.75	29.01	29.58	37.84	−12.51	51.49 (CH_3), 178.29 (CO)
	[n.o.]	[n.o.]	[52.5]	[n.o.]	[290]	
			[54.9]		[303]	
$CON(CH_3)_2$	21.00	29.82	28.91	38.89	−12.52	38.51 (CH_3), 176.75 (CO)
	[n.o.]	[n.o.]	[n.o.]	[n.o.]	[289]	
					[303]	
F[d]	21.62	31.77	32.48	94.20	−12.33	
	[421]	[n.o.]	[54.7]	[9.8]	[294]	
	[441]		[56.1]		[308]	
	(1.47)	(7.8)	(16.6)	(181.6)		
Cl	20.35	32.42	37.21	68.03	−12.40	
	[424]	[n.o.]	[53.2]	[n.o.]	[294]	
	[443]		[55.7]		[308]	
Br	20.02	33.24	38.53	65.53	−12.44	
	[n.o.]	[n.o.]	[52.7]	[n.o.]	[296]	
			[54.7]		[310]	
I	19.29	33.85	41.49	48.74	−12.55	
	[424]	[n.o.]	[51.8]	[9.5]	[294]	
	[444]		[53.7]		[309]	
OCH_3	21.78	31.24	30.56	72.67	−12.45	48.27 (CH_3)
	[431]	[n.o.]	[55.0]	[9.2]	[290]	
	[450]		[57.0]		[304]	
$N(CH_3)_2$	21.23	37.84	27.41	53.30	−12.60	30.60 (CH_3)
	[437]	[n.o.]	[av 54.20]	[8.8]	[288]	
	[457]				[301]	
C_6H_5[e]	22.02	30.73	33.13	33.65	−12.55	150.62 (i), 125.54 (o), 127.99 (m), 125.35 (p)
	[443]	[n.o.]	[53.2]	[5.4]	[284]	
	[464]		[55.7]		[297]	
p-FC_6H_4[d,e]	21.91	30.72	33.34	33.18	−12.51	146.37 (i), 126.97 (o), 114.58 (m), 160.86 (p)
	[442]	[n.o.]	[av 54.9]	[n.o.]	[287]	(3.1), (7.9), (20.8), (243.5)
	[463]				[301]	
p-$CH_3OC_6H_4$[e]	22.05	30.77	33.35	33.02	−12.54	142.86 (i), 126.39 (o), 113.34 (m), 157.27 (p), 55.1 (CH_3)
	[n.o.]	[n.o.]	[av 55]	[n.o.]	[286]	
					[300]	
$C{\equiv}CSi(CH_3)_3$	20.35	32.87	29.75	31.96	−12.57	115.07 ($C{\equiv}CSi$)
	[440]	[n.o.]	[53.2]	[n.o.]	[289]	82.85 ($C{\equiv}CSi$)
	[461]		[55.2]		[303]	0.37 (CH_3)
CH_3	22.11	30.75	34.21	26.59	−12.61	28.92 (CH_3)
	[449]	[n.o.]	[54.9]	[n.o.]	[284]	[13.6]
	[470]		[57.5]		[297]	
$C(CH_3)_3$	21.45	30.54	26.20	34.29	−12.64	34.29 (C), 25.14 (CH_3)
	[450]	[n.o.]	[52.0]	[n.o.]	[284]	[6.6]
	[471]		[54.0]		[297]	
$Sn(CH_3)_3$	21.39	31.42	31.42	21.39	−12.77	
	[456]	[50.5, 52.7]		[456]	[283]	
	[478]	[5.9]		[478]	[297]	
				Plumbanes (**2d**)[f]		
H	36.83	33.03	29.00	23.23	−5.27	
	[530]	[n.o.]	[100.3]	[8.4]	[126]	
F[d]	34.34	34.05	33.77	92.94	−4.79	
	[458]	[n.o.]	[102.7]	[21.6]	[162]	
	(2.2)	(8.06)	(16.48)	(182.38)		

Table VI (Continued)

X	chemical shift, ppm					
	C1	C2	C3	C4	$M(CH_3)_3$	others
C_6H_5[e]	36.64	33.44	34.74	33.34	-5.11	150.2 (i), 125.54 (o), 127.99 (m), 125.39 (p)
	[509]	[6.6]	[101.1]	[13.2]	[137]	[18.6], [n.o.]
p-FC_6H_4[d,e]	36.32	33.37	34.92	33.05	-5.09	145.91 (i), 126.96 (o), 114.55 (m), 160.86 (p)
	[505]	[7.3]	[100.7]	[n.o.]	[140]	(3.05), (7.32), (20.75), (243.53)
CH_3	37.04	33.45	35.76	26.25	-5.27	28.56 (CH_3)
	[523]	[4.4]	[105.5]	[10.3]	[130]	[31.5]

[a] Chemical shifts for $CDCl_3$ solution relative to $Si(CH_3)_4$. n.o. = not observed. Accurate to ±0.04 ppm. Low-field shifts are positive. [b] The carbon numbering system is as shown on the structural formulae in the introduction. [c] $^1J_{^{13}C-^{29}Si}$ values (Hz): H, 49.81; F, 50.17; C_6H_5, 49.87; p-FC_6H_4, 50.66; p-$NO_2C_6H_4$, 50.78; CH_3, 49.81. [d] $^{13}C-^{19}F$ coupling constants (in Hz) are listed in parentheses. [e] The aromatic carbons are designated ipso (i), ortho (o), meta (m), and para (p) with respect to the bicyclooctyl group. [f] $^{13}C-^{117,119}Sn$ and $^{13}C-^{207}Pb$ coupling constants (Hz) are given in brackets.

Table VII. ^{13}C Chemical Shifts[a] of 4-Substituted Bicyclo[2.2.1]heptyl-1-trimethylstannanes (3a)

X	chemical shift, ppm						
	C1	C2	C3	C4	C7	$Sn(CH_3)_3$	others
H	33.85	34.38	30.75	36.43	42.45	-11.75	
	[n.o.]	[16.9]	[51.3]	[65.2]	[13.2]	[299]	
						[313]	
CN	35.13	34.43	35.71	36.95	48.09	-11.64	123.72 (CN)
	[n.o.]	[14.2]	[43.9]	[n.o.]	[15.6]	[314]	
			[46.9]			[329]	
$COCH_3$	35.82	35.06	33.91	61.09	46.21	-11.70	27.41 (CH_3)
	[n.o.]	[17.1]	[47.9]	[n.o.]	[14.2]	[306]	212.88 (CO)
			[49.8]			[320]	
$CON(CH_3)_2$	32.87	35.50	33.85	55.28	47.91	-11.79	37.4 (CH_3)
	[n.o.]	[16.6]	[48.8]	[64]	[14.7]	[305]	176.05 (CO)
						[319]	
F	31.30	34.32	33.24	104.68	44.51	-12.03	
	[n.o.]	[10.3]	[39.1]	[75.2]	[6.4]	[307]	
				[78.1]		[321]	
	(4.4)	(9.3)	(20.5)	(210.5)	(16.6)		
Cl	34.74	35.56	39.38	70.15	50.69	-11.80	
	[n.o.]	[11.7]	[41.5]	[n.o.]	[8.8]	[308]	
						[321]	
Br	[n.o.]	36.04	40.64	62.07	51.95	-11.76	
		[n.o.]	[n.o.]	[n.o.]	[9.8]	[n.o.]	
I	34.35	36.46	43.60	38.15	54.8	-11.60	
	[n.o.]	[13.7]	[43.0]	[n.o.]	[10.7]	[307]	
			[44.9]			[321]	
OCH_3	34.05	34.68	32.30	88.94	43.67	-11.98	53.04 (CH_3)
	[n.o.]	[11.7]	[40.7]	[70.3]	[7.7]	[303]	
			[42.5]			[317]	
$N(CH_3)_2$	33.44	35.17	29.82	72.47	45.18	-11.90	41.22 (CH_3)
	[n.o.]	[13.7]	[44.0]	[65.9]	[11.2]	[302]	
			[45.9]			[316]	
C_6H_5	35.65	35.78	38.47	52.25	47.30	-11.76	146.30 (i)
	[n.o.]	[15.3]	[47.0]	[61.0]	[12.8]	[300]	126.58 (o)
			[49.4]	[64.1]		[315]	127.94 (m)
							125.50 (p)
CH_3	36.40	36.02	37.99	44.36	49.5	-11.83	20.48 (CH_3)
	[n.o.]	[16.1]	[48.3]	[65.9]	[9.8]	[297]	
			[50.3]			[312]	
$C(CH_3)_3$	35.17	35.69	31.42	55.48	42.52	-11.83	27.46 (CH_3)
	[n.o.]	[15.6]	[47.4]	[n.o.]	[12.2]	[296]	32.03 (C)
			[50.3]			[310]	[4.88]
$Sn(CH_3)_3$	33.44	35.22	35.22	33.44	46.53	-11.54	
	[n.o.]	[21.0]	[21.0]	[n.o.]	[13.7]	[297]	
		[54.2]	[54.2]			[311]	
		[56.2]	[56.2]				

[a] See footnotes *a*, *b*, and *d–f* to Table VI.

($CDCl_3$) δ 1.6–1.93 (6 H, m, CH_2CH_2), 2.46–2.76 (6 H, m, CH_2CH_2), 3.23 (3 H, s, OCH_3); ^{13}C NMR ($CDCl_3$, relative to Me_4Si) δ 42.52 (C1), 41.52 (C2), 33.11 (C3), 69.13 (C4), 49.02 (OCH_3).

1,4-Diiodobicyclo[2.2.2]octane. Prepared from 1-iodo-4-methoxybicyclo[2.2.2]octane (1.0 g, 37.6 mmol) by treatment with aqueous HI in the manner described above for the preparation of 1-iodobicyclo[2.2.2]octane. After the reaction mixture had been heated under reflux for 72 h in the dark under a nitrogen atmosphere, it was quenched by pouring onto ice and the precipitate collected by vacuum filtration. Sublimation afforded the diiodide as a white solid (1.22 g, 90%) which was recrystallized from a hexane/ethanol mixture: mp 239–240 °C (lit.[42] 239–240.5 °C); ^1H NMR ($CDCl_3$) δ 2.56 (12 H, s, CH_2CH_2); ^{13}C NMR ($CDCl_3$, relative to Me_4Si) δ 39.01 (C1,4), 44.01 (C2,3).

1-Bromo-4-methoxybicyclo[2.2.2]octane. By use of the procedure of Cristol and Firth[43] as described by Adcock et al.[11] for the conversion of 4-fluorobicyclo[2.2.2]octane-1-carboxylic acid

(42) Zimmerman, H. E.; Goldman, T. D.; Hirzel, T. K.; Schmidt, S. P. *J. Org. Chem.* **1980**, *45*, 3933.

(43) Cristol, S. J.; Firth, W. C. *J. Org. Chem.* **1961**, *26*, 280.

to the corresponding fluorobromide, 4-methoxybicyclo[2.2.2]octane-1-carboxylic acid[11] (10 g, 0.05 mol) was treated with red mercuric oxide and then bromine in dichloromethane as solvent. After a standard workup, the very crude residue (viscous orange liquid) was slowly sublimed to afford the title compound as a white solid (4.5 g, 38%): mp 41–43 °C; ^{13}C NMR ($CDCl_3$, relative to Me_4Si) δ 61.27 (C1), 38.30 (C2), 32.07 (C3), 70.37 (C4), 49.24 (OCH_3). Anal. Calcd for $C_9H_{15}BrO$: C, 49.32; H, 6.85. Found: C, 49.54; H, 6.61.

1-Bromo-4-iodobicyclo[2.2.2]octane. 1-Bromo-4-methoxybicyclo[2.2.2]octane (2.2 g, 0.01 mol) was treated with 55% aqueous HI in the manner described above for the preparation of 1-iodobicyclo[2.2.2]octane. After the reaction mixture had been heated under reflux for 24 h in the dark under a nitrogen atmosphere, it was quenched by pouring onto ice and the precipitate was extracted into ether. Removal of the solvent afforded a residue which gave a white solid on sublimation. ^{13}C NMR and VPC analyses indicated the product was a mixture of the title compound (40%) and 4-bromobicyclo[2.2.2]octan-1-ol (60%). The mixture was separated by column chromatography (silica gel; pentane as eluant). 1-Bromo-4-iodobicyclo[2.2.2]octane was obtained as a white solid (1.1 g, 35%): mp 230–232 °C; ^1H NMR ($CDCl_3$) δ 2.4–2.5 (12 H, m, CH_2CH_2); ^{13}C NMR ($CDCl_3$, relative to Me_4Si) δ 58.27 (C1), 41.01 (C2), 43.30 (C3), 39.28 (C4). Anal. Calcd for $C_8H_{12}BrI$: C, 30.50; H, 3.81. Found: C, 30.68; H, 3.92.

4-Bromobicyclo[2.2.2]octan-1-ol was also obtained as a white solid: mp 163–164 °C (lit.[44] 163–165 °C); ^{13}C NMR ($CDCl_3$, relative to Me_4Si) δ 66.46 (C1), 36.42 (C2), 38.50 (C3), 61.34 (C4).

A repeat experiment in which the bromo–methoxy precursor was placed under reflux for 72 h with aqueous HI and acetic anhydride afforded a mixture of the title compound (≃70%) and 1,4-diiodobicyclo[2.2.2]octane (≃30%). An attempt to separate the mixture was unsuccessful.

Subsequently, we found that the preferred method for synthesizing 1-bromo-4-iodobicyclo[2.2.2]octane is treatment of 4-bromobicyclo[2.2.2]octane-1-carboxylic acid[12b] (3 g, 0.013 mol) with *tert*-butyl hypoiodite followed by irradiation in the same manner as previously described for the preparation of 1-fluoro-4-iodobicyclo[2.2.2]octane[11] from the corresponding acid. After a standard workup, the product was chromatographed (silica gel; pentane as eluant) and sublimed to afford the title compound as a white solid (2.5 g, 61%).

1-Chloro-4-iodobicyclo[2.2.2]octane. 4-Chlorobicyclo[2.2.2]octane-1-carboxylic acid[12b] (2.5 g, 13.2 mmol) was treated with *tert*-butyl hypoiodite and then irradiated in the same manner as previously described for the preparation of 1-fluoro-4-iodobicyclo[2.2.2]octane from the corresponding acid.[11] After a standard workup, sublimation (2.8 g, 78%), and then recrystallization from hexane afforded the title compound as needles: mp 209–210 °C; ^1H NMR ($CDCl_3$) δ 2.1–2.6 (12 H, m, CH_2CH_2); ^{13}C NMR ($CDCl_3$, relative to Me_4Si) δ 62.59 (C1), 39.64 (C2), 42.48 (C3), 37.84 (C4). Anal. Calcd for $C_8H_{12}ClI$: C, 35.49; H, 4.44. Found: C, 35.76; H, 4.54.

1-Iodo-4-(*p*-methoxyphenyl)bicyclo[2.2.2]octane. By use of the procedure of Deulsfeu and Guerrero[45] for the demethylation of *N*-methyl-(3-methoxy-4-hydroxyphenyl)alanine, 1-(*p*-(2-hydroxyethoxy)ethoxy)phenyl)-4-methoxybicyclo[2.2.2]octane (obtained as a byproduct from the Wolff–Kishner reduction of 1-methoxy-4-(*p*-fluorophenyl)bicyclo[2.2.2]octan-2-one)[32] was treated with a mixture of red phosphorus, 55% aqueous HI, and acetic anhydride. After workup, some of the crude sublimed 1-iodo-4-(*p*-hydroxyphenyl)bicyclo[2.2.2]octane (13.15 g, 34 mmol) product was dissolved in dry acetone (40 mL) and placed under reflux for 40 h with iodomethane (4.8 g) and anhydrous potassium carbonate (4.7 g) as described by Allen and Gates.[46] After standard workup, the title compound (11.0 g, 82%) was obtained as a white solid on sublimation and recrystallization from a hexane/ethanol mixture (1:1): mp 122–125 °C; ^{13}C NMR ($CDCl_3$, relative to Me_4Si) δ 46.29 (C1), 41.15 (C2), 36.15 (C3), 31.01 (C4), 140.79 (para), 126.14 (meta), 113.51 (ortho), 157.65 (ipso), 55.21 (OCH_3). Anal. Calcd for $C_{15}H_{15}IO$: C, 52.65; H, 5.60. Found: C, 52.32; H, 6.04.

Table VIII. Physical and Analytical Properties of 4-Substituted Bicyclo[2.2.2]oct-1-yltrimethylstannanes (2a) and Bicyclo[2.2.1]hept-1-yltrimethylstannanes (3a)

system	(X)	bp (*p*, mm) or mp, °C	elemental anal. calcd C	calcd H	found C	found H
2a	H	<30 (31–32)[48]				
2a	CN	53.5–54.5	48.37	7.05	47.47	7.10
2a	CF_3	83.5–85	42.27	6.20	42.56	6.13
2a	$CON(CH_3)_2$	54–56	48.87	7.90	49.74	7.95
2a	OCH_3	135–145 (3)	47.57	7.98	47.13	7.84
2a	$N(CH_3)_2$	160 (3), <30	49.41	8.55	49.53	8.72
2a	Cl[a]	50–54	42.98	6.89	42.90	6.78
2a	p-$CH_3OC_6H_4$	88–90	57.64	6.44	57.93	6.51
2a	$C{\equiv}CSi(CH_3)_3$	110–113	52.05	8.19	51.05	8.83
2a	$C(CH_3)_3$	103–104	54.76	9.13	54.85	9.22
2a	$Sn(CH_3)_3$	128–130	38.59	6.89	39.20	7.00
3a	H[b]	68–70 (8) [67–68 °C (8)][48]				
3a	CN[b]	105 (0.5), <30	46.53	6.74	45.04	6.63
3a	$COCH_3$[b,c]	115 (0.05)				
3a	$CON(CH_3)_2$[b,c]	130 (0.05), <20				
3a	OCH_3[b]	70 (10)	45.72	7.62	45.46	7.60
3a	$N(CH_3)_2$[b,c]	100 (0.8)				
3a	C_6H_5[b]	105 (0.02)	59.14	7.35	57.90	7.25
3a	CH_3[b,c]	90 (3)				
3a	$C(CH_3)_3$[b]	100 (0.7)	53.37	8.96	54.49	8.98
3a	$Sn(CH_3)_3$[b]	90 (0.01), 73–75	37.02	6.69	37.36	6.76

[a] GC–MS indicated approximately 95% purity. Contaminated with **2a** (X = $Sn(CH_3)_3$). [b] Homogeneous with respect to VPC (SE-30 and OV-17). [c] Elemental analyses not sought.

Preparation of Bicyclo[2.2.2]oct-1-yl- and Bicyclo[2.2.1]-hept-1-yltrimethylstannanes (2a and 3a). Except for bicyclo[2.2.1]*hept-1-yltrimethylstannane* (**3a**, X = H), which was prepared by adding trimethyltin chloride to a filtered solution of bicyclo[2.2.1]hept-1-yllithium (prepared from 1-chlorobicyclo[2.2.1]heptane (1.0 g, 7.7 mmol) and lithium chips (0.74 g, 107.8 mmol) in cyclohexane under argon at room temperature for 90 min), most of the compounds were prepared by adding dropwise a tetrahydrofuran (THF) solution of the appropriate 4-substituted bicyclo[2.2.2]oct-1-yl or bicyclo[2.2.1]hept-1-yl iodide to an excess of (trimethylstannyl)lithium (3–4 equiv) in THF at 0 °C under an atmosphere of dry nitrogen. The latter reagent was prepared in a standard way.[47] After keeping the well-stirred reaction mixture at 0 °C for approximately 10 h, the reaction was quenched with a saturated aqueous ammonium chloride solution and extracted with ether. The extract was dried over anhydrous magnesium sulfate, filtered, and the solvent evaporated to afford the product which was either sublimed or distilled. Yields varied between 40 and 70%. All these compounds were characterized by ^{13}C NMR (Tables VI and VII). The spectrum for the acetoxytin derivative (**2a**, X = $OCOCH_3$) is not listed because impurities prevented unambiguous assignments for some of the resonances. Two other compounds (**2a**, X = $COOCH_3$ and $COCH_3$) were also not obtained analytically pure. However, the assignments of the ^{13}C NMR spectra of these compounds were unequivocal. Physical and elemental data (where obtained) of the stannanes **2a** and **3a** are listed in Table VIII.

It can be seen (Table VIII) that some of the tin compounds have elemental analyses outside the generally accepted limits. However, this is not an uncommon occurrence in organotin chemistry. Their structures are unequivocally supported by their ^{13}C NMR spectra (Tables VI and VII).

For several of the halo iodides (1-chloro- and 1-bromo-4-iodobicyclo[2.2.2]octane and 1-chloro- and 1-iodo-4-iodobicyclo[2.2.1]heptane) as well as two halo bromides (1-bromo-4-chlorobicyclo[2.2.1]heptane and 1,4-dibromobicyclo[2.2.1]heptane) in-

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(48) Della, E. W.; Patney, H. K. *Aust. J. Chem.* **1979**, *32*, 2243.

Table IX. Physical and Analytical Properties of 4-Substituted 1-*tert*-Butylbicyclo[2.2.2]octanes (2b)

X	mp, °C	^{1}H NMR data ($CDCl_3$), δ (Me_4Si)	^{13}C NMR data ($CDCl_3$), δ (Me_4Si)	elemental anal. calcd C	calcd H	found C	found H
H	70–72	0.77 (9 H, s, $C(CH_3)_3$), 1.46 (13 H, s, CH_2CH_2 and CH)	34.69 (C1), 25.29 (C2), 26.20 (C3), 23.66 (C4), 34.32 ($C(CH_3)_3$), 25.03 ($C(CH_3)_3$)	86.66	13.33	87.07	12.90
Cl	73–75	0.80 (9 H, s, $C(CH_3)_3$), 1.60–1.76 (6 H, m, CH_2CH_2), 1.93–2.22 (6 H, m, CH_2CH_2)	34.22 (C1), 27.78 (C2), 36.47 (C3), 67.76 (C4), 34.02 ($C(CH_3)_3$), 25.22 ($C(CH_3)_3$)	71.79	10.54	71.45	10.52
Br	104–106	0.76 (9 H, s, $C(CH_3)_3$), 1.50–1.83 (6 H, m, CH_2CH_2), 2.03–2.36 (6 H, m, CH_2CH_2)	33.52 (C1), 28.71 (C2), 37.92 (C3), 64.86 (C4), 34.19 ($C(CH_3)_3$), 25.16 ($C(CH_3)_3$)	58.78	8.63	59.13	8.33
CH_3	40–42	0.77 (12 H, s, $C(CH_3)_3$ and CH_3), 1.37 (12 H, s, CH_2CH_2)	35.26 (C1), 25.90 (C2), 33.61 (C3), 27.11 (C4), 34.22 ($C(CH_3)_3$), 25.35 ($C(CH_3)_3$), 28.13 (CH_3)	86.58	13.41	86.62	13.30
p-$NO_2C_6H_4$[a]	200	0.86 (9 H, s, $C(CH_3)_3$), 1.73 (12 H, s, CH_2CH_2), 7.46–8.33 (4 H, m, aromatic)	35.69 (C1), 25.77 (C2), 32.46 (C3), 35.19 (C4), 34.24 ($C(CH_3)_3$), 25.29 ($C(CH_3)_3$), 158.41 (i), 126.46 (o), 123.24 (m), 145.86 (p)[b]				

[a] Elemental analysis not sought. [b] See footnote *e* to Table VI.

verse addition with a deficient amount of (trimethylstannyl)lithium (1.3 equiv) was effected in order to avoid complete substitution. ^{13}C and ^{119}Sn NMR coupled with combined GC–MS techniques were employed to unambiguously characterize the resulting product mixtures. 1-Chloro- and 1-bromo-4-iodobicyclo[2.2.2]octane both gave mixtures containing the unreacted precursor iodide (ca. 50%) plus three stannanes (**2a**, X = Cl, I, and $Sn(CH_3)_3$, and **2a**, X = I, Br, and $Sn(CH_3)_3$, respectively) in the ratio of 7.2:1.4:1 and 4:2:1, respectively. The mechanistic details and implications of these reactions have been dealt with separately elsewhere.[49] Treatment of the product mixture from the chloro iodide with excess (trimethylstannyl)lithium afforded a mixture containing **2a**, X = Cl (55%), and **2a**, X = $Sn(CH_3)_3$ (45%). Differential sublimation of the mixture provided a fairly pure sample of the chlorotin derivative, mp 50–54 °C (GC–MS indicated approximately 95% purity). It should be noted that, in connection with another study,[31] the iodotin compound (**2a**, X = I) has been obtained analytically pure by treating the fluorotin compound (**2a**, X = F) with iodotrimethylsilane.

Full details of the trimethylstannylation mixtures from 1,4-dihalobicyclo[2.2.1]heptanes will be presented elsewhere in due course.[50]

Bicyclo[2.2.2]oct-1-yltrimethylsilane (2c, X = H) and (4-Methylbicyclo[2.2.2]oct-1-yl)trimethylsilane (2c, X = CH_3). Both compounds were obtained by trimethylsilylation of the appropriate iodides according to a procedure recently outlined for the preparation of the fluorosilicon derivative **2c**, X = F.[24a] The parent compound **2c**, X = H, was obtained as a white microcrystalline solid (39%) after recrystallisation from methanol: mp 67–68 °C; ^{1}H NMR ($CDCl_3$) δ −0.13 (9 H, s, $Si(CH_3)_3$), 1.15 (13 H, s, CH_2CH_2 and CH); ^{13}C NMR (see Table VI). Anal. Calcd for $C_{11}H_{22}Si$: C, 72.13; H, 12.56. Found: C, 72.25; H, 12.40.

The methylsilicon compound **2c**, X = CH_3 was obtained as a white microcrystalline solid (33%) after recrystallization from methanol: mp 41–42 °C; ^{1}H NMR ($CDCl_3$) δ −0.13 (9 H, s, $Si(CH_3)_3$), 0.83 (3 H, s, CH_3), 1.5 (12 H, s, CH_2CH_2); ^{13}C NMR (see Table VI). Anal. Calcd for $C_{12}H_{24}Si$: C, 73.36; H, 12.34. Found: C, 72.92; H, 12.48.

Bicyclo[2.2.2]oct-1-yltrimethylplumbane (2d, X = H), (4-Methylbicyclo[2.2.2]oct-1-yl)trimethylplumbane (2d, X = CH_3), and (4-(*p*-Fluorophenyl)bicyclo[2.2.2]oct-1-yl)trimethylplumbane (2d, X = *p*-FC_6H_4). These compounds were prepared by treating the appropriate iodide (0.005 mol) in dry diethyl ether (10 mL) at −80 °C with 8 mL of 1.5 M *tert*-butyllithium (0.01 mol) in pentane followed quickly, after 30 min, by the addition of a suspension of trimethyllead chloride (2.87 g, 0.01 mol) in anhydrous ether (6 mL) to the well-stirred reaction mixture, which was then allowed to warm to room temperature. After a standard workup, the compounds were purified by sublimation and recrystallization from methanol to afford white microcrystalline solids in fair yields (45–52%). Physical properties (mp and ^{1}H NMR) of the compounds prepared are as follows. **2d**, X = H): mp 71–72 °C; ^{1}H NMR ($CDCl_3$) δ 0.57 (9 H, s, $Pb(CH_3)_3$, $^2J_{Pb-H}$ 48 Hz), 1.63 (13 H, s, CH_2CH_2 and CH); ^{13}C NMR (see Table VI). **2d**, X = CH_3: mp 57–58 °C; ^{1}H NMR ($CDCl_3$) δ 0.53 (9 H, s, $Pb(CH_3)_3$, $^2J_{Pb-H}$ = 48 Hz), 0.63 (3 H, s, CH_3), 1.43–1.73 (12 H, m, CH_2CH_2); ^{13}C NMR (see Table VI). **2d**, X = *p*-FC_6H_4: mp 79–79.5 °C; ^{1}H NMR ($CDCl_3$) δ 0.60 (9 H, s, $Pb(CH_3)_3$, $^2J_{Pb-H}$ = 48 Hz), 2.27–2.33 (12 H, m, CH_2CH_2), 7.33–7.66 (4 H, m, aromatic); ^{13}C NMR (see Table VI).

Elemental analyses were not sought for these compounds. All the lead compounds slowly disporportionated over a period of several months.

(4-(*p*-Nitrophenyl)bicyclo[2.2.2]oct-1-yl)trimethylsilane (2c, X = *p*-$NO_2C_6H_4$). A solution of (4-phenylbicyclo[2.2.2]-oct-1-yl)trimethylsilane[30] (**6**, X = C_6H_5; 86.6 mg, 0.34 mmol) in acetic anhydride (0.7 mL) was treated with nitric acid and the reaction worked up as previously described for the preparation of 1-fluoro-4-(*p*-nitrophenyl)bicyclo[2.2.2]octane.[51] Recrystallization from methanol afforded the title compound as colorless needles (57.2 mg, 55%): mp 150–152 °C; ^{13}C NMR (see Table VI).

Preparation of 4-Substituted 1-*tert*-Butylbicyclo[2.2.2]-octanes (2b, X = H, CH_3, Cl, Br, and *p*-$NO_2C_6H_4$). Following literature procedures, 1-*tert*-butyl-4-iodobicyclo[2.2.2]octane[12b] was treated appropriately with Li/*t*-BuOH/THF,[52] ICl,[53] or Br_2[54] in order to prepare the parent system (X = H) and the two halogen

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compounds (X = Cl and Br). The methyl derivative (X = CH_3) was obtained by treating a sample of the chloro compound with trimethylaluminium as previously described.[55] A solution of 1-*tert*-butyl-4-phenylbicyclo[2.2.2]octane[55] (**2b**, X = C_6H_5) (0.283 g, 0.0012 mol) in acetic anhydride (3 mL) was nitrated as above for the preparation of **2c** (X = *p*-$NO_2C_6H_4$). Recrystallization from methanol afforded 1-*tert*-butyl-4-(*p*-nitrophenyl)bicyclo-[2.2.2]octane (**2b**, X = *p*-$NO_2C_6H_4$) as fine colorless needles (0.21 g, 62%). Physical and elemental analytical data for these systems (**2b**) are given in Table IX.

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Registry No. **2a** (X = CN), 84010-79-7; **2a** (X = CF_3), 105253-17-6; **2a** (X = $COCH_3$), 105253-18-7; **2a** (X = $COOCH_3$), 105253-19-8; **2a** (X = $CON(CH_3)_2$), 105253-20-1; **2a** (X = F), 78385-88-3; **2a** (X = Cl), 84010-80-0; **2a** (X = Br), 84010-81-1; **2a** (X = I), 84010-82-2; **2a** (X = OCH_3), 84010-84-4; **2a** (X = $OCOCH_3$), 105253-21-2; **2a** (X = $N(CH_3)_2$), 84010-83-3; **2a** (X = C_6H_5), 68756-27-4; **2a** (X = *p*-FC_6H_4), 68756-25-2; **2a** (X = *p*-$CH_3OC_6H_4$), 105253-22-3; **2a** (X = $C{\equiv}CSi(CH_3)_3$), 105253-23-4; **2a** (X = CH_3), 84010-85-5; **2a** (X = $C(CH_3)_3$), 84010-86-6; **2a** (X = $Sn(CH_3)_3$), 84010-87-7; **2a** (X = H), 73075-71-5; **2b** (X = COOH), 5605-13-0; **2b** (X = F), 81687-86-7; **2b** (X = Cl), 105253-35-8; **2b** (X = Br), 105253-36-9; **2b** (X = I), 94994-05-5; **2b** (X = OCH_3), 81687-94-7; **2b** (X = C_6H_5), 64872-46-4; **2b** (X = *p*-$NO_2C_6H_4$), 105253-37-0; **2b** (X = CH_3), 105253-38-1; **2b** (X = H), 49576-45-6; **2c** (X = F), 95552-61-7; **2c** (X = I), 99631-74-0; **2c** (X = C_6H_5), 76889-41-3; **2c** (X = *p*-FC_6H_4), 76889-50-4; **2c** (X = *P*-$NO_2C_6H_4$), 105253-33-6; **2c** (X = CH_3), 105176-60-1; **2c** (X = H), 105253-32-5; **2d** (X = F), 95552-63-9; **2d** (X = C_6H_5), 76889-43-5; **2d** (X = *p*-FC_6H_4), 76889-52-6; **2d** (X = CH_3), 105176-62-3; **2d** (X = H), 105253-34-7; **3a** (X = CN), 105253-40-5; **3a** (X = $COCH_3$), 105253-24-5; **3a** (X = $CON(CH_3)_2$), 105253-25-6; **3a** (X = F), 84010-89-9; **3a** (X = Cl), 105253-26-7; **3a** (X = Br), 105253-27-8; **3a** (X = I), 84010-90-2; **3a** (X = OCH_3), 84010-88-8; **3a** (X = $N(CH_3)_2$), 105253-28-9; **3a** (X = C_6H_5), 105253-29-0; **3a** (X = CH_3), 105253-30-3; **3a** (X = $C(CH_3)_3$), 105253-31-4; **3a** (X = $Sn(CH_3)_3$), 84010-91-3; **3a** (X = H), 42204-95-5; 1-iodobicyclo[2.2.2]octane, 931-98-6; 1-methoxybicyclo[2.2.2]octane, 7697-14-5; 4-iodobicyclo[2.2.2]octane-1-carboxylic acid, 80745-61-5; (trimethylstannyl)lithium, 17946-71-3; 1-iodo-4-methylbicyclo[2.2.2]octane, 55044-63-8; trimethyllead chloride, 1520-78-1; 1-iodo-4-(*p*-fluorophenyl)bicyclo[2.2.2]octane, 61541-35-3; tin-119, 14314-35-3; lead-207, 14119-29-0.

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$PdCl_2$–$NaHCO_3$ Catalyzed Phenylation of Acyclic Allylic Alcohols. 3.[1] 1,2-Chirality Transfer in a Heck Reaction via a Wacker-Type Intermediate

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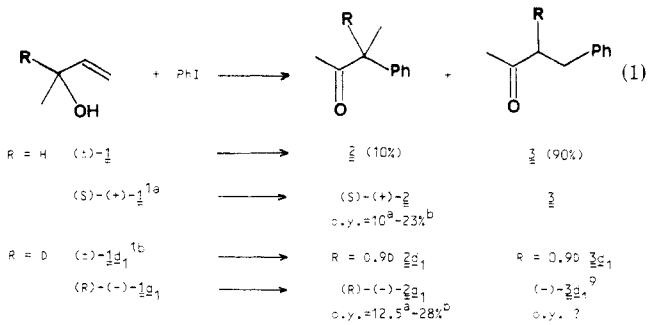
$PdCl_2$–$NaHCO_3$ catalyzed γ-phenylation of chiral 3-methylbut-3-en-2-ol with aryl iodides, a Heck-type reaction, affords chiral 3-benzylbutanone with up to 27% optical yield. The configuration of this ketone is clearly related to that of the unstable (β-hydroxyalkyl)palladium σ-complex, which is a key feature in the Wacker process. Different stereoselectivities were observed for *cis*- and *trans*-pent-3-en-2-ols.

Introduction

Stereoselective transition-metal-catalyzed formation of carbon–carbon bonds in acyclic molecules is a challenging objective. In previous work,[1a] we have shown that a measure of stereocontrol could be achieved in applying the Heck reaction[2] to chiral but-3-en-2-ol (eq 1). Although



[a] Optical yield calculated from the maximum specific rotation-$[\alpha]_D^{20}$ 866° (cyclohexane).[1] [b] Calculated from $[\alpha]_D^{20}$ 368° (*c* 1.6, cyclohexane).[11] o.y. = optical yield.

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the observed chirality transfer was only moderate, we decided that our usual mechanistic probes,[3] namely, the use of chiral acyclic allylic alcohols, could be valuable for the further stereochemical study of this reaction.

We report here our results on the stereochemistry of the phenylation of several such substrates under catalytic conditions[1] similar to those previously reported[4-7] ($PdCl_2$; $NaHCO_3$; DMF).

Results and Discussion

Since the phenylation of chiral butenol 1[1a] affords the achiral **3** as a major product, we decided to extend our

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