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Relative magnitude of the .beta.-effect of silyl, germyl, and stannyl groups in the stabilization of vinyl cations

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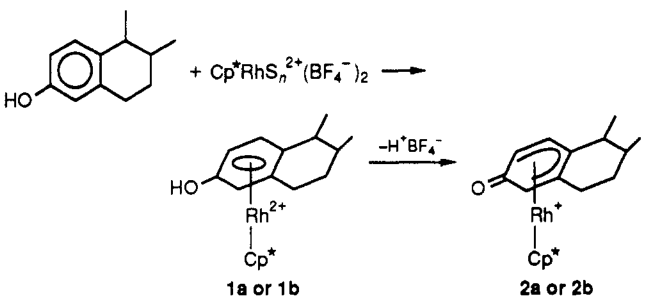
Scheme III



complex [Ru(η^5-2,6-tBu$_2$C$_6$H$_3$O)Cp*] (19.1°).[15]

In order to investigate the solution behavior of the complexes **2a,b**, we have studied their reactivity with HBF$_4$. Treatment of [Cp*Rh(η^5-estradienonyl)]BF$_4$ with HBF$_4$ yielded [Cp*Rh(η^6-estradiol)](BF$_4$)$_2$ (**1a,b**) quantitatively, while in the presence of NEt$_3$ the initial species was regenerated (Scheme II). In addition, we note that in strongly coordinating basic solvents, such as DMSO, compounds **1a,b** were transformed immediately to the conjugated dienonylic form, **2a,b**. In CH$_3$CN, this transformation was slower, occurring over a 10-h period. Due to solubility limitations, other solvents were not studied. It is possible that the driving force for this transformation (**1a,b** → **2a,b**) could be related to the high oxidation state of the rhodium metal in the organometallic moiety Cp*Rh^{III}, which pulls electronic density from the A-ring of β-estradiol and renders the phenol group more acidic.

Repetition of the initial reaction of β-estradiol and RhCp*S$_n^{2+}$(BF$_4^-$)$_2$ (S = acetone, Scheme I), in the presence of HBF$_4$, led to the formation of complex **1a**[16] as the major compound. Upon recrystallization in acetone/ether solution, however, this unstable species gave **2a** in 20% yield. This indicates that a possible route for the synthesis of the species **2a,b** involves initial formation of the kinetically favored species **1a,b**, with subsequent loss of one molecule of HBF$_4$ to give the thermodynamically more stable species, either **2a** or **2b** (Scheme III).

Studies on the reactivity of these complexes and their electrochemical behavior are currently in progress.

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Supplementary Material Available: Tables of positional and thermal parameters and complete bond distances and angles (5 pages); a listing of calculated and observed structure factors (9 pages). Ordering information is given on any current masthead page.

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[16] Anal. Calcd. for C$_{28}$H$_{39}$O$_2$B$_2$F$_8$Rh (**1a**): C, 49.12; H, 5.70. Found: C, 49.70; H, 5.69.

Relative Magnitude of the β-Effect of Silyl, Germyl, and Stannyl Groups in the Stabilization of Vinyl Cations

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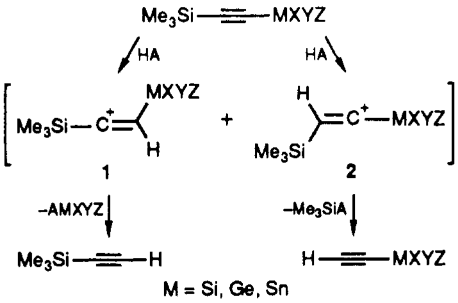
Summary: The competitive addition of acids to 1,2-dimetalated acetylene compounds shows that the relative degree of hyperconjugative stabilization (β-effect) of vinyl cations follows the general trend Sn > Ge > Si but can be altered to a degree by the appropriate modification of the other groups borne by the metal.

The stabilization of vinyl cation intermediates, including hyperconjugative stabilization by a β-silyl group (β-effect), has been reviewed.[1,2] However, examples of the ability of the lower group 14 (group IVA) elements Ge and Sn to stabilize such species have not been reported. We have, therefore, undertaken experiments that allow a comparison of the degree to which the ligands borne by the metal and the metal itself change the magnitude of the β-effect for vinyl cations.

The premise of the experiment is that competitive protonation of a dimetalated acetylene will proceed via the most stable β-carbocation (stronger β-effect) and lead, after loss of the better stabilizing group, to a monometalated acetylene (Scheme I).

Scheme I



We chose to use the SiMe$_3$ group as a reference point. A series of metalated (trimethylsilyl)acetylenes was prepared by the reaction of lithium (trimethylsilyl)acetylide (1.1 equiv) with the appropriate silyl/germyl/stannyl chloride (1.0 equiv, 1-5 M, THF or ether, 0-25 °C, nitrogen atmosphere). The protonations were carried out in CDCl$_3$ solution with several acids, including F$_3$CSO$_3$H, MeSO$_3$H, F$_3$CCOOH, Cl$_3$CCOOH, Cl$_2$HCCOOH, and ClCH$_2$COOH.

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Table I. Reaction Products of the Protonation of Dimetalated Acetylenes Presented in Order of Decreasing β-Effect

$$\mathrm{Me_3SiC{\equiv}CMXYZ} \xrightarrow{\mathrm{H^+}} \mathrm{HC{\equiv}CSiMe_3}$$

entry no.	M	XYZ	acid	k, 10^4 s^{-1} M^{-1}	ref[a]
1	Sn	Me_3	$ClCH_2COOH$	10.1 ± 0.3	14
2	Sn	Bu_3	$ClCH_2COOH$	3.6 ± 0.2	15
3	Sn	Ph_3	Cl_3CCOOH	91.0 ± 7	8
4	Sn	Ph_3	F_3CCOOH		
5	Sn	$(-C{\equiv}CSiMe_3)_3$	F_3CCOOH		7
6	Ge	Me_3	F_3CCOOH	0.40 ± 0.03	16
7	Si	t-$BuMe_2$	H_3CSO_3H		17

[a] Reference for the preparation of the starting materials.

The reaction was followed with ^1H NMR (200 MHz) spectroscopy, with the signals of $Me_3SiC{\equiv}CH$ or the trimethylsilyl ester of the acid being used in particular to gauge the degree of completion. Thus, a 2.5 M solution of the acid in $CDCl_3$ (F_3CSO_3H, triflic acid, was added neat) was added to a 0.05 M solution of the compound in $CDCl_3$ in an NMR tube (5 mm, nitrogen atmosphere).

We use two factors to assess the relative β-effect of a given group.[3] First, for each compound there is the internal competition between groups on the acetylene. The group with the better β-effect of the two will be lost via the most stabilized vinyl cation. For example, with $Bu_3SnC{\equiv}CSiMe_3$ the production of $HC{\equiv}CSiMe_3$ and loss of the Bu_3Sn group from intermediate 1 (Scheme I) shows the tin to have a better β-effect than $SiMe_3$. Second, for those groups with a better effect than $SiMe_3$, the groups may be ordered by the relative rate at which the group is lost with a given acid:[6] the faster the reaction, the better the β-effect. The reaction rates covered a very large range, and it was impossible to determine the rates for all compounds with a single acid. However, in all cases, the rate of product formation was faster with stronger acids and it was, therefore, possible to establish an overall order by comparing the absolute reaction rates of compounds with different acids. The largest β-effect was assigned to the group that reacted fastest with the weakest acid, Me_3Sn and $ClCH_2COOH$, respectively.

Other groups were examined that had a poorer β-effect than $SiMe_3$ ($SiMe_3$ was lost from the acetylene). These included $Ge(-C{\equiv}CSiMe_3)_3$,[7] $SiPh_3$,[8] and $Si(-C{\equiv}CSiMe_3)_3$:[7] $GePh_3$[9] was approximately the same as $SiMe_3$. The relative rates (via **2**, Scheme I) of these reactions would show the importance of inductive effects on the basicity of the alkyne but provide no further information about the β-effect. In addition, we examined $SiCl_3$,[10] $SiMe_2Cl$,[11] $SiMe(OMe)_2$,[12] $SiMe(OMe)_2$,[13] $Si(NMe_2)_2Me$, and $Si(NMe_2)_3$. The chlorosilanes and methoxysilanes underwent competitive nucleophilic substition with the acid counterion; the amino compounds were protonated and did not react further.

The results are presented in Table I in order to relative rate of reaction and, therefore, in order of decreasing β-effect. With the exception of $Me_3SiC{\equiv}CGePh_3$ all reactions involved the clean loss of only one of the metals.

The trend for a larger β-effect[5] in the order Sn > Ge > Si generally holds, although it can be seen that, with appropriate substitution, Ge has a poorer β-effect than Si (t-$BuMe_2Si > Ph_3Ge \approx Me_3Si > (Me_3SiC{\equiv}C)_3Ge$). From these studies we can conclude that ligands reduce the β-effect of a vinyl cation for a given metal in the order $sp^3 > sp^2 > sp$, a trend that parallels their relative electronegativity as expected.[18]

These experiments demonstrate that the relative β-effect of group 14 metals depends on both the metal and the ligands and follows the order

$$\begin{aligned}&\mathrm{Me_3Sn > Bu_3Sn > Ph_3Sn >}\\ &\quad \mathrm{(Me_3SiC{\equiv}C)_3}\mathit{Sn} \mathrm{> Me_3Ge >} t\text{-}\mathrm{BuMe_2Si > Ph_3Ge \approx}\\ &\qquad \mathrm{Me_3Si > (Me_3SiC{\equiv}C)_3}\mathit{Ge}\mathrm{, Ph_3Si, (Me_3SiC{\equiv}C)_3}\mathit{Si}\end{aligned}$$

We are currently examining in more detail the kinetics of these reactions to allow a quantitative β-effect scale to be established.

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[3] The protonation of the acetylene can be controlled by inductive effects alone (basicity of the alkyne)[4] or by the inductive and β-effects acting cooperatively. We believe that the latter situation is relevant particularly because the inductive effects of $SiMe_3$, $GeMe_3$, and $SnMe_3$, for example, should be similar on the basis of the electronegativity difference of the metals. However, the rates of reaction of the three disubstituted acetylenes differed dramatically (Table I), more than could be accounted for by inductive effects alone, as has also been found to be the case in alkyl β-carbocation stabilization.[5]

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[6] We conclude that protonation is the rate-determining step, given that the kinetics of the reaction are first order in both the acid and the acetylene and that the rate of the reaction follows the order of acidity of the acids used, not the order of nucleophilicity of the acid counterions.

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[9] $Ph_3GeC{\equiv}CSiMe_3$ was prepared in the following manner: To a solution of (trimethylsilyl)acetylene (Aldrich, 98%, 1.81 mmol, 0.26 mL) in THF (dried from potassium benzophenone ketyl, 10 mL) at −78 °C under a nitrogen atmosphere was added n-BuLi (2.32 M in hexane, 1.80 mmol, 0.78 mL) via syringe. The solution was warmed to 0 °C over 30 min. After the mixture was cooled to −78 °C, a solution of Ph_3GeCl (Aldrich, 97%, 0.623 g, 1.75 mmol) in dry THF (5 mL) was added slowly (10 min). The reaction mixture was stirred for 30 min at −78 °C and overnight at 25 °C. The reaction mixture was quenched with water and extracted three times with ether. The combined organic layers were dried with $MgSO_4$ and filtered, and the solvent was removed under reduced pressure to give a yellow-white solid. Recrystallization from 2-propanol at −5 °C gave 0.57 g (1.42 mmol, 81%) of white crystals. The compound was air-stable for months; mp 68–69 °C. ^1H NMR (200 MHz, $CDCl_3$): δ 0.30 (s, 9 H), 7.35–7.50 (m, 9 H), 7.60–7.75 (m, 6 H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 0.01, 107.3, 117.2, 128.4, 129.5, 134.5, 135.1. ^{29}Si NMR (49.69 MHz, $CDCl_3$): δ −18.9. IR ($CHCl_3$): ν 3060, 3010, 2970, 1960, 1890, 1820, 1770, 1480, 1435, 1245, 1200, 1085, 840 cm^{-1}. MS (m/z, reported for ^{74}Ge isotope): 402 (M^+, 20), 387 (62), 325 (46), 228 (100), 159 (12), 135 (11). Anal. Calcd for $C_{23}H_{24}GeSi$: C, 68.87; H, 6.03; Si, 7.00. Found: 68.74; 6.30; 7.25.

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