Tetrakis[(trimethylsilyl)ethynyl] Group 14 metal derivatives: an examination of the electronic interaction between two Group 14 metals connected by an acetylene wire[1]

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This paper is dedicated to Professor Gerald W. King on the occasion of his 65th birthday

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The tetrakis(trimethylsilyl)ethynyl derivatives of Si, Ge, Sn, and Pb were prepared and examined spectroscopically. NMR and Mössbauer spectroscopy and X-ray crystal structure data clearly demonstrate an electronic interaction in the ground state between the distal $SiMe_3$ groups and the central metal atom, leading to a strong shielding of the central metal atom; the respective nmr signals of the central metal are among the most shielded examples reported for a tetrahedral Group 14 metal centre with four carbon ligands. The nature of these electronic interactions is discussed.

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On a préparé les dérivés tétrakis(triméthylsilyl)éthynyles du Si, du Ge, du Sn et du Pb et on a examiné leurs spectres. Les spectres RMN et de Mössbauer et les données relatives aux structures cristallines démontrent clairement l'existence d'une interaction électronique dans l'état fondamental entre les groupes $SiMe_3$ distales et l'atome métallique central; ces interactions donnent lieu à un blindage important de l'atome métallique central et les signaux RMN respectifs de chaque métal central sont parmi les exemples les plus blindés rapportés pour un métal central tétraédrique du groupe 14 portant quatre coordinats carbonés. On discute de la nature de ces interactions électroniques.

[Traduit par la rédaction]

Introduction

Organosilicon chemistry has found extensive application in organic synthesis. This utility results primarily from the ability of silyl groups, usually trimethylsilyl groups, to behave as "super" (1) or "bulky" (2) protons. In essence, a $SiMe_3$ group is more electropositive than a proton and is thus more susceptible to nucleophilic attack on electronic grounds, but is less susceptible to nucleophilic attack for steric reasons. Thus, under conditions with which proton transfer readily takes place, the corresponding silyl groups are stable.

In the case of trimethylsilylalkynes, the materials are higher boiling and much more stable than the corresponding hydrocarbons, particularly in the case of diynes or polyynes (3). Thus, they have been used synthetically as surrogates for acetylenes and related alkynes, notably by Vollhardt (4) (Scheme 1). Polymeric versions of these compounds have also attracted attention recently as materials of potential interest for nonlinear optical applications (5); related materials have been examined as components of membranes (6). In both cases, the properties of interest in the polymers depend upon the presence of silicon in the molecules.

Silylalkynes will, however, react selectively with strong electrophiles. Indeed, under these conditions, the silylacetylenes are more reactive than the parent hydrocarbons. For example, a variety of Lewis acid activated electrophiles add cleanly to silylalkynes, leading to regioselective C—C bond formation (Scheme 2 (7), Scheme 3 (3)).

When compared with a simple alkyne, the origins of the reactivity of a silylalkyne towards electrophiles include the inductive effects of the silyl group, thermodynamic effects (the ultimate cleavage of silicon from the molecule is generally accompanied by the formation of a strong Si—X (X—Br, Cl, F, ≈96–193 kcal/mol) or Si—O bond (≈126–192 kcal/mol) at the expense of a Si—C bond (≈76 kcal/mol) (8), and the stabilization of the intermediate β-silyl vinyl cation via the β-effect.

As part of a program to try to establish the relative importance of these effects, we have been interested in studying the different mechanisms for and extent of electronic transmission from one Group 14 metal to another along an acetylene "wire" in the ground state.

During previous studies of the vinyl β-effect (9) we prepared a series of Group 14 dimetallated alkynes **1**, **2**, **3** and **4** (Fig. 1*a*) that appeared to be potential candidates for this study. The central metal is sensitive to a variety of spectroscopic techniques and can thus reflect the degree of electronic transmission from the distal $SiMe_3$ groups; any such transmission would be amplified by the presence of four distal $SiMe_3$ groups. In this paper, we report our examination of these compounds by different spectroscopic techniques to determine the extent of interaction between the two metals. The magnitude and mechanism of electronic transmission will be discussed.

Results

Preparation of compounds 1–4

The materials for this study can be conveniently prepared starting from lithium trimethylsilylacetylide, which is formed from the reaction of *n*-BuLi with trimethylsilylacetylene. With the exception of lead, the ensuing anion can be quenched by the readily available Group 14 chloro derivatives MCl_4 in THF to give, cleanly in most cases, the corresponding tetrakis(trimethylsilylethylnyl) metals

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[1] Taken from the Ph.D. thesis of C.D., McMaster University, 1991.

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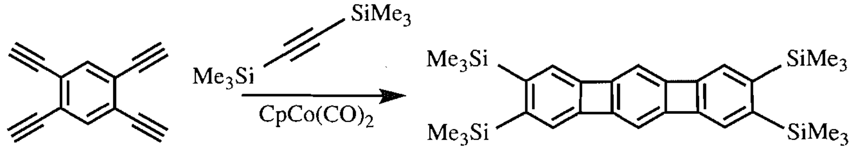
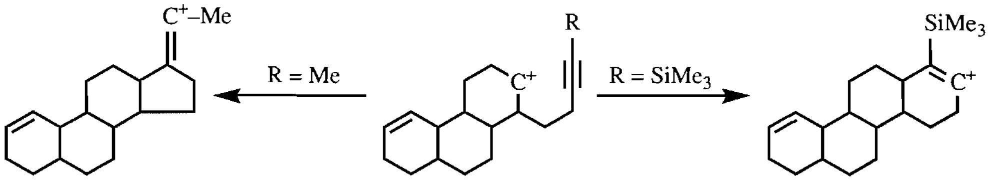
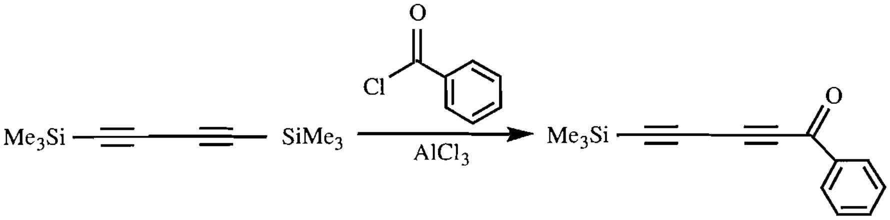


SCHEME 1



SCHEME 2



SCHEME 3

$M(C{\equiv}CSiMe_3)_4$ (M = Si **1**, Ge **2**, Sn **3**). The lead compound **4** was prepared by quenching $Pb(OAc)_4$ with $Me_3SiC{\equiv}CMgBr$ (prepared from $Me_3SiC{\equiv}CH$ and MeMgBr).

Spectroscopic characterization

These Group 14 nuclei are susceptible to examination by several spectroscopic methods; we have focused on NMR, Mössbauer spectroscopy and X-ray crystallography.

Nuclear magnetic resonance

The central metal

The nuclear magnetic resonance spectra of ^1H, ^{13}C, ^{29}Si and the remaining Group 14 elements (^{73}Ge for **2**, ^{119}Sn for **3**, ^{207}Pb for **4**) were measured for compounds **1**–**4**. As the chemical shifts of many Group 14 acetylides have been determined, it is relatively straightforward to evaluate by comparison the additional effect of a second Group 14 element on the alkyne.

Tetraalkynylmetals typically have large negative upfield shifts.[3] The presence of the four distal Me_3Si groups serves to substantially increase the upfield shifts of the central atom (Table 1). The chemical shifts reported here are among the furthest upfield to be reported for tetrahedral Group 14 metals substituted with four carbon ligands.

The distal Me_3Si groups

The central metal also has an effect on the terminal $SiMe_3$ groups. The ^{29}Si NMR chemical shifts show this to be small but observable; the effect of amplification has been lost (Table 2). The differences in the chemical shift correspond to increased shielding by the central atom as Si is substituted with less electronegative and more polarizable metals. The final entry in the table shows, additionally, how the degree of shielding is moderated by the type of carbon ligand on the central metal; less electronegative alkyl sp^3 hybridized carbon ligands, rather than alkyne sp orbital ligands, increase the degree of electronic shielding of the distal $SiMe_3$ by the central metal.

Mössbauer for tin

An additional diagnostic tool for tin compounds is Mössbauer spectroscopy. Regrettably, there are few reported values for alkynyltin compounds. Nevertheless, some general trends may be observed. An increase of *s* electron density is manifested in increased chemical isomer shifts. As *sp* orbitals are more electronegative than sp^2 or sp^3 orbitals, a decrease in chemical isomer shift is expected as sp^3 carbon ligands are sequentially replaced with sp^2 and *sp* hybridized ligands. Similarly, when electronegative groups on the alkyne terminus are replaced by electron-donating groups, an increase in isomer shift value is expected as *s* electron density is increased. However, any π-type interactions will have the effect of shielding the *s* electrons at the tin nucleus, decreasing the observed isomer shift (12). The data shown in Table 3, particular entry 12, demonstrate the latter effect (13, 14).

X-ray

We were unable to obtain suitable crystals for X-ray crystal structure analysis of the lead compound **4**. However, single crystals of compounds **2** and **3** could be readily analyzed; a structure for **1** has previously been reported (15). An ORTEP plot of the structure of **3** is shown in Fig. 1*b*; bond lengths and angles for **2** and **3** are collected in Tables 4, 5 and Tables 6, 7, respectively. A comparison of the C≡C bond lengths, the Me—Si—Me bond angles in the $SiMe_3$ groups,

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[3] For a review of the NMR of the respective elements, see ref. 10*a*; see also, for Si, 10*b*, and for Sn, 10*c*.

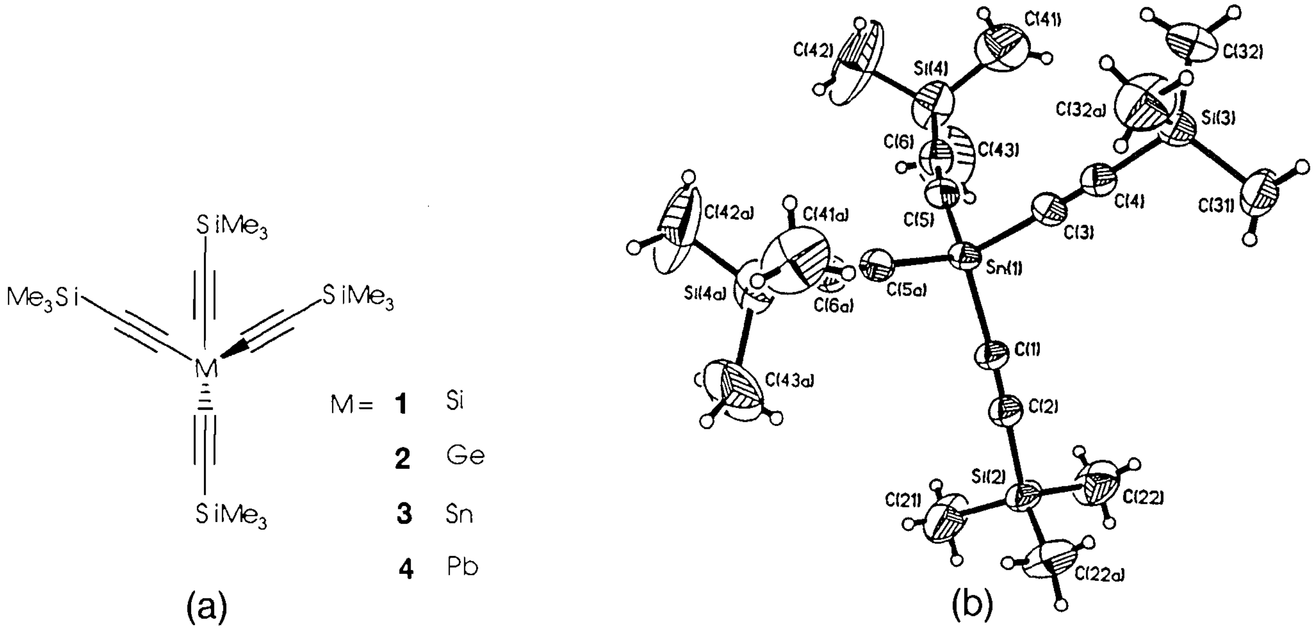

FIG 1. (*a*) The structure of compounds **1–4**; (*b*) ORTEP plot from the X-ray crystal structure of $(Me_3SiC{\equiv}C)_4Sn$ **3**.

TABLE 1. Central metal chemical shifts of the tetrakisacetylides **1–4** and related compounds

Entry	Compound	^{29}Si	^{73}Ge	^{119}Sn	^{207}Pb	Ref.
1	$(Me_3SiC{\equiv}C)_4\mathbf{Si}$	−101.6				
2	$(Me_3SiC{\equiv}C)_4\mathbf{Ge}$		−188.5			
3	$(HC{\equiv}C)_4\mathbf{Sn}$			−356.4		11
4	$(Me_3SiC{\equiv}C)_4\mathbf{Sn}$			−384.5		
5	$(MeC{\equiv}C)_4\mathbf{Pb}$				−687.6	11
6	$(Me_3SiC{\equiv}C)_4\mathbf{Pb}$				−760.7	
7	$(Me_3SiC{\equiv}C)_4\mathbf{Pb}$				−551[a]	

[a] Solid state, non-spinning measurement. The chemical shifts of lead compounds are known to be strongly affected by solvent (10).

TABLE 2. ^{29}Si chemical shifts ($CDCl_3$) of the tetrakisacetylides and related compounds

Entry	Compound	Chemical Shift	Ref.
1	$Me_3SiC{\equiv}CH$	−17.5	11
2	$(Me_3SiC{\equiv}C)_4Si$	−17.5[a]	
3	$(Me_3SiC{\equiv}C)_4Ge$	−17.7	
4	$(Me_3SiC{\equiv}C)_4Sn$	−18.1	
5	$(Me_3SiC{\equiv}C)_4Pb$	−18.0	
6	$Me_3SiC{\equiv}CSiMe_3$	−19.3	11

[a] This study and ref. 11.

and the **C≡C—Si—Me** angles in the compounds we prepared and those to be found in the literature shows only small deviations. However, a comparison of $R_3\mathbf{M}$—**C≡C**—X bond lengths is more intriguing (Table 8); clearly these bond lengths are very dependent upon the nature of the group on the other end of the acetylene wire (X) and the ligands (R) borne by the metal.

Beginning with a consideration of R_3M (R = trialkyl) compounds, a change from X = C to Si/Ge/Sn leads on average to a longer bond (1.84 Å (Table 8 entries 6 and 7) versus 1.83 Å (entries 2–4)). When that distal metal group bears electron-withdrawing ligands such as N*t*Bu or $(C{\equiv}CSiMe_3)_3$, the bond is further lengthened to 1.85 Å (entries 8–11). In contrast, if R = alkynyl, much shorter bond lengths can be seen (entry 12 versus 9–11, entry 16 versus 14 and 15).

Discussion

In all three spectroscopic techniques, we have seen evidence for electronic transmission between the two Group 14 elements linked by an acetylene. In the NMR experiments, this is manifested by significant shielding of the central metal in **1–4** by the four distal $SiMe_3$ groups and to a lesser extent of the $SiMe_3$ groups by the central metal, a significantly smaller Mössbauer isomer shift (I.S.) for the Sn derivatives when the distal $SiMe_3$ groups are present, and shorter bond lengths between the central metal and the adjacent C of the alkyne.

The electronic interaction between the two Group 14 metals could arise strictly from inductive donation through the σ-framework or from a combination of inductive effects and interactions of the π-system including resonance and π-polarization. The $SiMe_3$ group, as judged by Hammett parameters, possesses a very small capacity for σ-electronic donation (26); the parameters are −0.03 and −0.05 for σ_{meta}

TABLE 3. Mössbauer isomer shifts and quadrupole splittings for compound **3** and structurally related compounds

Entry	Compound	Chemical isomer shift[a]	Quadrupole splitting	Ref.
1	$Me_3\mathbf{Sn}CH{=}CH_2$	1.30(5)	1.06(1)	13
2	$Me_3\mathbf{Sn}C{\equiv}C{-}Ph$	1.23(5)	1.17(5)	13
3	$Me_3\mathbf{Sn}C{\equiv}C{-}SiMe_3$	1.21(2)[b]	1.06(1)	
4	$Me_3\mathbf{Sn}C{\equiv}C{-}CH(CH_3)_2$	1.15(5)	1.06(5)	13
5	$Ph_3\mathbf{Sn}C{=}CH_2$	1.28(5)		13
6	$Ph_3\mathbf{Sn}C{\equiv}C{-}SiMe_3$	1.20(4)[b]	0.84(1)	
7	$\mathbf{Sn}(CH_2CH_3)_4$	1.33(8)		13
8	$(CH_3CH_2)_3\mathbf{Sn}C{\equiv}C{-}H$	1.44(5)	1.42(5)	13
9	$(CH_3CH_2)_3\mathbf{Sn}C{\equiv}C{-}CH_3$	1.37(5)	1.22(5)	13
10	$(CH_3CH_2)_3\mathbf{Sn}C{\equiv}C{-}CH_2CH_3$	1.35(5)	1.05(5)	13
11	$\mathbf{Sn}(CH{=}CH_2)_4$	1.22(5)		13
12	$\mathbf{Sn}(C{\equiv}C{-}SiMe_3)_4$	0.82(2)[b]		

[a] Except as otherwise noted, measured against SnO_2 as the source.
[b] This study, measured against $CaSnO_3$ as the source.

TABLE 4. Bond lengths for tetrakis (trimethylsilylalkynyl)germanium **2** (Å)

Ge(1)—C(1)	1.889 (7)	Ge(1)—C(3)	1.894 (6)
Ge(1)—C(5)	1.893 (4)	Ge(1)—C(5A)	1.893 (4)
Si(2)—C(2)	1.851 (7)	Si(2)—C(21)	1.844 (9)
Si(2)—C(22)	1.855 (5)	Si(2)—C(22A)	1.855 (5)
Si(3)—C(4)	1.844 (6)	Si(3)—C(31)	1.862 (7)
Si(3)—C(32)	1.853 (5)	Si(3)—C(32A)	1.853 (5)
Si(4)—C(6)	1.847 (4)	Si(4)—C(41)	1.821 (6)
Si(4)—C(42)	1.852 (8)	Si(4)—C(43)	1.856 (7)
C(1)—C(2)	1.212 (9)	C(3)—C(4)	1.205 (8)
C(5)—C(6)	1.204 (5)		

and σ_{para}, respectively. Thus, the observations described above are better explained by a π-interaction that links the two Group 14 metals through the alkyne.

π-Type electronic interactions (conjugation) between Group 14 metals and adjacent C—C π-systems have previously been invoked for silicon, germanium, and tin compounds (27–30). The inclusion of a fourth atom in the conjugation, a distal Group 14 atom **M**—C≡C—Si, is a natural extension of this. The most compelling example of π-interactions between Group 14 substituted alkynes is in the UV spectra of silyl-terminated polyynes. These are considerably red shifted compared with the H or C terminated polyynes (20, 31).

π-Interactions may arise from either $(n{-}d)\pi$ or $(p{-}d)\pi$ (32) (or $(n{-}\sigma^*)\pi$ or $(p{-}\sigma^*)\pi$) interactions.[4] These would be anticipated to occur through σ*-orbitals in the case of silicon; *d* orbitals are apparently not very important in the interaction with first-row elements (32, 33). There is expected to be an increased propensity for *d* orbital involvement with the lower Group 14 elements. However, as has been noted by Dewar and co-workers (28), Whitesides et al. (29), and others, although *d* orbitals are energetically more available, they are increasingly mismatched in size with the C≡C π-system as one progresses down the periodic table, attenuating the resonance effect.

NMR

The chemical shift reflects the shielding a nucleus experiences. However, with the exception of protons, for which the correlation is reasonably straightforward, the nature of the electronic factors within the molecule that lead to an observed shift remains somewhat contentious. Nevertheless, it may be concluded that the observed magnitude of the change in chemical shift for the central metal is too large to originate, over three bonds, from σ-inductive effects alone. Chemical shifts are more dramatically affected by the presence of heteroatom lone pairs or π-systems on adjacent atoms. The large shift with four distal $SiMe_3$ groups (e.g., entries 3, 4, Table 1) reinforces the suggestion of a π-interaction between the two metals through the alkyne π-system.

Mössbauer

The Mössbauer results are also consistent with the proposed conjugation. Simple inductive effects by the distal $SiMe_3$ group would increase the *s* electron density and would be expected to lead to an *increase* in the Mössbauer I.S. in contrast to our observations. Again, this implies that electronic transmission between the Group 14 metals exists through the π-system of the alkyne.

X-ray

X-ray structures of polyynes and **1**–**3** show alternating single and triple bonds of essentially normal length (20) although some shortening of the single and lengthening of the triple bonds would be expected if π-conjugation was operative. The only significant shortening of single bonds arose with compounds **1**–**3** near the central atom. We attribute this to a π-polarization of the bond when the "spectator ligands" are *sp* ((R-*C*≡*C*)$_3$ **M**—**C**≡C-R') rather than sp^3 hybridized ((R)$_3$ **M**—**C**≡C-R').[5] Such an explanation cannot, however, account for the similarly short bond lengths in $Me_3Si{-}(C{\equiv}C)_4{-}SiMe_3$ (Table 8, entry 5) At the time, it was suggested that 1.20 Å was typical of C—Si bond lengths when the C ligand was *sp* hybridized. However, all crystal structures published since (Table 8) show significantly longer bond lengths (1.84 Å).

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[4] See, however, counter arguments favouring the interaction of σ*-orbitals (33).

[5] We thank a referee for helpful suggestions in clarifying this.

TABLE 5. Bond angles for tetrakis(trimethylsilylalkynyl)germanium **2** (deg)

C(1)—Ge(1)—C(3)	111.0(2)	C(1)—Ge(1)—C(5)	108.9(1)
C(3)—Ge(1)—C(5)	107.8(1)	C(1)—Ge(1)—C(5A)	108.9(1)
C(3)—Ge(1)—C(5A)	107.8(1)	C(5)—Ge(1)—C(5A)	112.5(2)
C(2)—Si(2)—C(21)	106.6(3)	C(2)—Si(2)—C(22)	107.9(2)
C(21)—Si(2)—C(22)	112.0(2)	C(2)—Si(2)—C(22A)	107.9(2)
C(21)—Si(2)—C(22A)	112.0(2)	C(22)—Si(2)—C(22A)	110.2(3)
C(4)—Si(3)—C(31)	107.8(3)	C(4)—Si(3)—C(32)	107.2(2)
C(31)—Si(3)—C(32)	111.8(2)	C(4)—Si(3)—C(32A)	107.2(2)
C(31)—Si(3)—C(32A)	111.8(2)	C(32)—Si(3)—C(32A)	110.6(3)
C(6)—Si(4)—C(41)	108.3(2)	C(6)—Si(4)—C(42)	107.9(2)
C(41)—Si(4)—C(42)	109.8(4)	C(6)—Si(4)—C(43)	107.4(2)
C(41)—Si(4)—C(43)	110.7(3)	C(42)—Si(4)—C(43)	112.6(3)
Ge(1)—C(1)—C(2)	178.7(5)	Si(2)—C(2)—C(1)	179.0(5)
Ge(1)—C(3)—C(4)	176.2(5)	Si(3)—C(4)—C(3)	178.8(6)
Ge(1)—C(5)—C(6)	174.5(3)	Si(4)—C(6)—C(5)	176.7(3)

TABLE 6. Bond lengths for tetrakis(trimethylsilylalkynyl)tin **3** (Å)

Sn(1)—C(1)	2.076 (6)	Sn(1)—C(3)	2.060 (6)
Sn(1)—C(5)	2.060 (5)	Sn(1)—C(5A)	2.060 (5)
Si(2)—C(2)	1.849 (6)	Si(2)—C(21)	1.831 (8)
Si(2)—C(22)	1.848 (8)	Si(2)—C(22A)	1.848 (8)
Si(3)—C(4)	1.855 (7)	Si(3)—C(31)	1.866 (8)
Si(3)—C(32)	1.844 (7)	Si(3)—C(32A)	1.844 (7)
Si(4)—C(6)	1.842 (6)	Si(4)—C(41)	1.818 (10)
Si(4)—C(42)	1.779 (13)	Si(4)—C(43)	1.834 (10)
C(1)—C(2)	1.190 (9)	C(3)—C(4)	1.194 (9)
C(5)—C(6)	1.202 (7)		

Conclusion

Two Group 14 metals, connected by an acetylene wire, interact electronically through π-interactions. The effect is seen in the strong shielding of the central metal in compounds **1–4** and the low isomer shift in the Mössbauer spectrum of **3**. Any effect of π-conjugation is insufficiently strong to affect the $C\equiv C$ bond length, as shown from the X-ray crystal structures of **1–3**; π-polarization is a better explanation of these results.

Experimental

Apparatus, materials, and methods

Due to the hydrolytic instability of the halogen derivatives of the Group 14 metals, all reactions were carried out in dry apparatus under a nitrogen atmosphere using septa and syringes for the transfer of reagents. Methylchlorosilanes were obtained from Dow Corning. Other silicon, germanium, tin, and lead compounds were obtained from Aldrich. All compounds were distilled prior to use. Tetrahydrofuran (THF) and diethyl ether were freshly distilled under a nitrogen atmoshere over benzophenone/potassium. Dichloromethane (CH_2Cl_2) was freshly distilled under a nitrogen atmosphere over calcium hydride (CaH_2) or phosphorus pentoxide (P_2O_5). Chloroform-*d* was obtained from Merck Sharp and Dohme Isotopes, Montreal, and used without further purification. (Trimethylsilyl)acetylene ($Me_3SiC\equiv CH$) was obtained from Aldrich or prepared according to ref. 34, by reaction of $LiC\equiv CH$ with Me_3SiCl.

The continuous wave ^1H NMR spectra were recorded on a Varian EM 390 (90 MHz) spectrometer and the Fourier spectra on a Bruker AM 500 (500 MHz) or Bruker AC 200 (200 MHz) spectrometer. ^{13}C, ^{29}Si, ^{73}Ge ^{119}Sn, and ^{207}Pb NMR measurements were performed on a Bruker WM 250 (at 250 MHz for protons). The ^{207}Pb solid state NMR spectrum was measured on a Bruker MS-100 spectrometer. Unless otherwise specified, the samples were dissolved in chloroform-*d* using tetramethylsilane (TMS) as internal standard ($SnMe_4$ for tin, $PbMe_4$ for lead, and $GeMe_4$ for germanium, respectively). Coupling constants (*J*) are recorded in hertz (Hz). The abbreviations s = singlet, d = doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, and m=multiplet are used in reporting the spectra.

EI mass spectra and chemical ionization (NH_3) mass spectra were recorded at 70 eV with a source temperature of ca. 200°C either on a VG Micromass 7070 F mass spectrometer equipped with a data system comprising a PDP 8A with VG 2000 software or a VG analytical ZAB E mass spectrometer equipped with a VG 11-250 data system. High-resolution mass spectral (HRMS) data were obtained with the VG-ZAB-E instrument by the electron impact (EI) method.

Infrared spectra were run on a Perkin–Elmer 283 spectrometer in $CHCl_3$ solution, $CHCl_3$ film, neat film, or as a KBr pellet.

For ^{119}Sn Mössbauer spectroscopy, thin powdered samples, prepared by grinding the crystalline material to prevent preferred orientation of the crystallites, were pressed into Kel-F sample holders. Mössbauer spectra were recorded at 80 K using an Elscint constant acceleration spectrometer with an MCDPC-IBM AT acquisition system manufactured by CMTE. The samples were cooled in a Technology Systems cryostat. The source was ^{119}Sn (5 mCi, Amersham), in a calcium stannate matrix. The velocity scale was calibrated with a standard iron foil absorber and a $^{57}Co/Rh$ source mounted on the reverse end of the transducer. Calibration spectra were thus recorded without interruption of the drive sequence. The calibration spectra were computer fitted to give a linear velocity scale and folding point. Folded ^{119}Sn spectra were computer fitted using a modified version of the program GMFP (35). All isomer shifts are referenced to a thin absorber of $CaSnO_3$ at room temperature.

Single colourless cubic crystals of $Sn(C\equiv CSiMe_3)_4$ and $Ge(C\equiv CSiMe_3)_4$ were grown from hexane. X-ray diffraction was performed on a Nicolet R3 using MoKα radiation at 183 K. The relevant information is available in Tables 9*a–f* (compound **2**) and Tables 10*a–f* (compound **3**).[6]

General preparative procedure of $(Me_3SiC\equiv C)_4M$

For the silicon species, the tetrakis species **1** and $Cl_3SiC\equiv CSiMe_3$ were prepared simultaneously.

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[6] Tables 9 and 10 can be purchased from: The Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A OS2, Canada.

These tables have also been deposited with the Cambridge Crystallographic Data Centre, and can be obtained on request from The Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, 12 Union Road, Cambridge, CB2 1EZ, U.K.

TABLE 7. Bond angles for tetrakis(trimethylsilylalkynyl)tin **3** (deg)

C(1)—Sn(1)—C(3)	110.8(2)	C(1)—Sn(1)—C(5)	108.9(1)
C(3)—Sn(1)—C(5)	107.9(1)	C(1)—Sn(1)—C(5A)	108.9(1)
C(3)—Sn(1)—C(5A)	107.9(1)	C(5)—Sn(1)—C(5A)	112.4(3)
C(2)—Si(2)—C(21)	105.8(3)	C(2)—Si(2)—C(22)	107.3(2)
C(21)—Si(2)—C(22)	113.9(3)	C(2)—Si(2)—C(22A)	107.3(2)
C(21)—Si(2)—C(22A)	113.9(3)	C(22)—Si(2)—C(22A)	108.1(5)
C(4)—Si(3)—C(31)	106.9(3)	C(4)—Si(3)—C(32)	106.8(3)
C(31)—Si(3)—C(32)	112.2(3)	C(4)—Si(3)—C(32A)	106.8(3)
C(31)—Si(3)—C(32A)	112.2(3)	C(32)—Si(3)—C(32A)	111.5(4)
C(6)—Si(4)—C(41)	107.4(4)	C(6)—Si(4)—C(42)	108.6(4)
C(41)—Si(4)—C(42)	113.1(6)	C(6)—Si(4)—C(43)	107.3(4)
C(41)—Si(4)—C(43)	106.8(4)	C(42)—Si(4)—C(43)	113.3(6)
Sn(1)—C(1)—C(2)	178.3(5)	Si(2)—C(2)—C(1)	178.4(6)
Sn(1)—C(3)—C(4)	178.4(5)	Si(3)—C(4)—C(3)	177.4(6)
Sn(1)—C(5)—C(6)	173.8(4)	Si(4)—C(6)—C(5)	177.2(4)

TABLE 8. Selected bond lengths for compounds **1–4** and related structures[a]

Entry	Compound	R$_3$C-C≡C—M	R$_3$M-C≡**C—M**	(R-C≡C)$_3$**M—C**≡C-M	Ref.
1	Fe$_2$(CO)$_7$[Me$_3$Si-C≡C-C≡**C—SiMe$_3$**]$_2$	1.88(2)			16
2	Steroid-CH(OH)-C≡**C—SiMe$_3$**	1.839			17
3	Me$_3$**Si—C**≡C-complex pyrrole	1.834			18
4	C$_6$(-C≡**C—SiMe$_3$**)$_6$	1.836			19
5	Me$_3$**Si—C**≡C-C≡C-C≡C-C≡**C—SiMe$_3$**		1.821[b]		20
6	[-Me$_2$**Si—C**≡**C—SiMe$_2$**(CH$_2$)$_n$-]$_2$				
	n = 1–4		1.843		21
7	[-(CH$_3$)$_2$**Si—C**≡**C-Si**(CH$_3$)$_2$-]$_2$		1.841		22
8	*t*Bu$_2$(*t*BuNH)**Si—C**≡**C—Si**(*t*BuNH)*t*Bu$_2$		1.851		23
9	(Me$_3$**Si—C**≡C-)$_4$Sn **3**		1.853		
10	(Me$_3$**Si—C**≡C-)$_4$Si **1**		1.854		
11	(Me$_3$**Si—C**≡C-)$_4$Ge **2**		1.865		
12	(Me$_3$Si-C≡**C—**)$_4$**Si 1**			1.824	
13	(Me$_3$Si-C≡**C—**)$_4$**Ge 2**			1.895	
14	*o*-C$_6$H$_4$(-C≡**C—SnMe$_3$**)$_2$	2.09(1)			24
15	Me$_3$**Sn-C**≡C-C≡**C-Sn**Me$_3$		2.136[b]		25
16	(Me$_3$Si-C≡**C—**)$_4$**Sn 3**			2.067	

[a] The values presented are mean values from within a given structure.
[b] Because of the extended conjugation, we include this in the dimetallated group.

To a solution of Me$_3$SiC≡CH (7.9 mL, 70.8 mmol) in THF (40 mL) at 0°C was added *n*-BuLi (1.4 in hexanes, 51 mL, 72 mmol). This solution was added slowly over 30 min at 0°C to the metal tetrachloride (e.g., SiCl$_4$; 65 mL, 8 equiv., 567 mmol) in dichloromethane (CH$_2$Cl$_2$; 200 mL) and stirred over 18 h. Then the solvent was removed by simple distillation and the residue was distilled at 55°C/15 Torr (1 Torr = 133.3 Pa) to give 3.5 g of Cl$_3$Si-C≡C-SiMe$_3$ (15.1 mmol, 21% yield). Afterwards, the residue was washed with water, extracted with ether, and recrystallized several times in hexane to give 3 g of **1** (7.1 mmol, 41% yield) (36).

The syntheses of the other metallated (trimethylsilyl) acetylide compounds were performed with some modifications to the procedures reported in the literature. The syntheses were done as described above by the reaction of lithium salt of (trimethylsilyl)acetylide (Me$_3$Si-C≡C-, 4.0 equiv.) with the appropriate silyl, germyl, or stannyl chloride compounds in tetrahydrofuran or ether (37). In these cases, chlorometal derivatives were not obtained as coproducts.

Spectral data

Tetrakis[(trimethylsilyl)ethynyl]silane ((Me$_3$SiC≡C)$_4$Si) 1: mp 154–159°C (from hexane) (lit. (15) mp 160°C (from petroleum ether): IR (CH$_2$Cl$_2$) ν(cm^{-1}): 2965 h, 2900 m, 2010 m, 1950 w, 1875 w, 1400 m, 1250 st, 900-720 st, 700 st, 480 st, 290 st; ^{1}H NMR (CDCl$_3$, 200 MHz): δ(ppm) = 0.21 (s); ^{13}C NMR (CDCl$_3$, 62.9 MHz) δ(ppm): 117.2, 104.2, −0.3; ^{29}Si NMR (CDCl$_3$, 49.69 MHz) δ(ppm): −17.5, −101.6; MS (EI, *m/z*): 416 (M$^+$, 21), 401 (34), 343 (12), 328 (11), 313 (100), 231 (29), 179 (32), 155 (56); HRMS, mass calcd. 416.1669; observed: 416.1663.

Tetrakis[(trimethylsilyl)ethynyl]germane ((Me$_3$SiC≡C)$_4$Ge) 2 (ref. 36): Yield: 94% (lit. (36) yield 58%); mp 175–176°C (from petroleum ether) (lit. (36) mp 176°C); IR (KBr) ν(cm^{-1}) 2970 st, 2900 m, 2105 w, 2000 w, 1955 w, 1870 w, 1450 w, 1410 m, 1315 w, 1255 st, 850 st, 760 st, 820 st, 405 m, 305 m, 300 st; ^{1}H NMR (CDCl$_3$, 200 MHz) δ(ppm): 0.21 (s); ^{13}C NMR (CDCl$_3$, 62.9 MHz) δ(ppm): 114.0, 102.1, −0.3; ^{29}Si NMR (CDCl$_3$, 49.69 MHz) δ(ppm): −17.7; ^{73}Ge NMR (CDCl$_3$, 8.73 MHz) δ(ppm): −188.5 (line width of 125 Hz); MS (EI, *m/z* reported for ^{74}Ge isotope): 447 (41), 389 (18), 359 (25), 253 (10), 229 (12), 201 (53), 155 (18), 119 (100), 97 (32), 73 (95); HRMS; (M$^+$ reported for ^{74}Ge isotope), mass calcd. for M$^+$ + 1:461.1028; observed for M$^+$ + 1:461.1032.

Tetrakis[(trimethylsilyl)ethylnyl]stannane ((Me$_3$Si-C≡C-)$_4$Sn) 3 (ref. 36): Yield: 73% (lit. (36) yield 35%); mp 170–172°C (from petroleum ether or hexane) (lit. (36) mp (dec.) 140°C (from petroleum ether)); IR (KBr) ν(cm^{-1}) 2960 st, 2900 m, 2090 w, 2010 w, 1950 w, 1865 w, 1405 m, 1310 m, 1250 st, 840 st, 755 st, 695 st, 605 m; ^{1}H NMR (CDCl$_3$, 200 MHz) δ(ppm): 0.21 (s); ^{13}C NMR (CDCl$_3$, 62.9 MHz) δ(ppm): 119.5, 103.2, −0.3; ^{29}Si NMR

($\mathrm{CDCl_3}$, 49.69 MHz) δ(ppm): −18.1; ^{119}Sn NMR ($\mathrm{CDCl_3}$, 93.28 MHz) δ(ppm): −384.5; MS (EI, *m/z* reported for ^{119}Sn isotope): 508 ($\mathrm{M^+}$, 15), 493 (17), 405 (16), 314 (72), 247 (83), 217 (35), 179 (80), 165 (86), 119 (30), 97 (100), 73 (79); HRMS ($\mathrm{M^+}$ reported for ^{119}Sn isotope), mass calcd. 508.0916; observed: 508.0915.

Trimethylstannyl(trimethylsilyl)acetylene ($\mathrm{Me_3Si\text{-}C{\equiv}C\text{-}SnMe_3}$) *(ref. 38)*: Yield: 71% (lit. (38) yield 68%) bp ~25°C at 1 Torr; IR (neat) ν(cm^{-1}): 2965 st, 2920 st, 2905 st, 2370 w, 2075 w, 1450 m, 1405 m, 1305 w, 1245 st, 1190 w, 830 st, 750 st, 690 st; ^{1}H NMR ($\mathrm{CDCl_3}$, 200 MHz) δ(ppm): 0.28 (s, 9H), 0.16 (s, 9H); ^{13}C NMR ($\mathrm{CDCl_3}$, 62.9 MHz) δ(ppm): 117.6, 113.2, 0.5, −7.4; ^{29}Si NMR ($\mathrm{CDCl_3}$, 49.69 MHz) δ(ppm): −20.9; ^{119}Sn NMR ($\mathrm{CDCl_3}$, 93.28 MHz) δ(ppm): −73.6; MS (EI, *m/z* reported for ^{119}Sn isotope): 247 ($\mathrm{M^+ - CH_3}$, 100), 217 (12), 185 (6); HRMS ($\mathrm{M^+}$ reported for ^{119}Sn isotope), mass calcd. for $\mathrm{M^+ - CH_3}$: 246.9965; observed for $\mathrm{M^+ - CH_3}$: 246.9984.

Triphenylstannyl(trimethylsilyl)acetylene ($\mathrm{Me_3SiC{\equiv}CSnPh_3}$) *(ref. 39)*: Yield: 92% (lit. (39) yield 61%); mp 73–74°C (lit. (39) mp 74–76°C); ^{1}H NMR ($\mathrm{CDCl_3}$, 200 MHz) δ(ppm): 7.75–7.65 (m, 6H), 7.5–7.4 (m, 9H), 0.3 (s, 9H); ^{13}C NMR ($\mathrm{CDCl_3}$, 62.9 MHz) δ(ppm): 139.9, 136.7, 129.5, 129.2, 121.4, 108.7, 0.17; ^{29}Si NMR ($\mathrm{CDCl_3}$, 49.69 MHz) δ(ppm): −19.5; ^{119}Sn NMR ($\mathrm{CDCl_3}$, 93.28 MHz) δ(ppm): −175.4; MS (EI, *m/z* reported for ^{119}Sn isotope): 448 ($\mathrm{M^+}$, 3), 433 (5), 371 (39), 341 (4), 294 (3), 274 (35), 221 (27), 197 (37), 159 (50), 135 (32), 120 (100), 97 (18); HRMS ($\mathrm{M^+}$ reported for ^{119}Sn isotope), mass calcd.: 448.0669; observed: 448.0677.

Tetrakis[(trimethylsilyl)ethynyl]plumbane
($\mathrm{(Me_3Si\text{-}C{\equiv}C)_4Pb}$) ***4***

A solution of methylmagnesium bromide (3 M in ether, 5.9 mL, 17.7 mmol) was added slowly to a solution of (trimethylsilyl)acetylene ($\mathrm{Me_3Si\text{-}C{\equiv}C\text{-}MgBr}$, 2.5 mL, 17.7 mmol) in tetrahydrofuran (20 mL) at 0°C. The solution was stirred 1 h at 0°C and about 1.5 h at room temperature until no more bubbles were observed. After cooling at 0°C, lead tetraacetate (0.8 g, 1.8 mmol) was added through glass tubing under a nitrogen atmosphere over 30 min. The mixture was stirred 1 h at 0°C and 4.5 h at room temperature (brown solution). After work-up with 1% aqueous HCl and water, the product was extracted with diethyl ether and the solution dried over magnesium sulfate. The crude compound was recrystallized in hexane. Yield: 37% (lit. (36) yield 47%); mp 155°C (dec.) (lit. (36) mp 108°C (from petroleum ether)); ^{1}H NMR ($\mathrm{CDCl_3}$, 200 MHz) δ(ppm): 0.21 (s); ^{13}C NMR ($\mathrm{CDCl_3}$, 62.9 MHz), δ(ppm): 117.4, 111.7, −0.3; ^{29}Si NMR ($\mathrm{CDCl_3}$, 49.69 MHz) δ(ppm): −18.0; ^{207}Pb NMR ($\mathrm{CDCl_3}$, 52.33 MHz) δ(ppm): −760.7 (line width of 40 Hz); ^{207}Pb NMR (solid state without spinning, 20.93 MHz) δ(ppm): −551 (line width of 100 Hz); MS (EI, *m/z* reported for ^{208}Pb isotope): 581 ($\mathrm{M^+ - CH_3}$, 11), 551 (4), 493 (41), 402 (20), 335 (13), 305 (100), 290 (95), 261 (23).

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1. I. Fleming. Organosilicon compounds. *In* Comprehensive organic chemistry. *Edited by* D.H.R. Barton and W.D. Ollis. Pergamon, New York. 1979. Vol. 3, Chap. 13, p. 544.
2. J.R. Hwu and N. Wang. Chem. Rev. **89**, 1599 (1989); J.R. Hwu and J.M. Wetzel. J. Org. Chem. **50**, 3946 (1985).
3. D.R.M. Walton and F. Waugh. J. Organomet. Chem. **37**, 45 (1972), and references cited therein.
4. K.P.C. Vollhardt. Angew. Chem. Int. Ed. Engl. **23**, 539 (1984), and references cited therein.
5. R. Bortolin, S.S.D. Brown, and B. Parbhoo. Macromolecules, **23**, 2465 (1990); T.J. Barton and S. Ijadi-Maghsoodi. Macromolecules, **24**, 1257 (1991); Macromolecules, **23**, 4485 (1990); T.J. Barton, Y. Pang, and S. Ijadi-Maghsoodi. J. Polym. Sci. Part A: Polym. Chem. **28**, 935 (1990).
6. T. Masuda and T. Higashimura. *In* Silicon-based polymer Science. *Edited by* J.M. Ziegler and F.W.G. Fearon. Adv. Chem. Ser. 224, Washington, D.C. 1990. Chap. 35, pp. 641–661; T. Masuda, T. Hamano, K. Tsuchihara, and T. Higashimura. Macromolecules, **23**, 1374 (1990); T. Masuda, M. Takatsuka, B.Z. Tang, and T. Higashimura. J. Membr. Sci. **49**, 69 (1990).
7. W.S. Johnson, T.M. Yarell, R.F. Myers, D.R. Morton, and S.G. Boots. J. Org. Chem. **45**, 1254 (1980).
8. E. Colvin. Silicon in organic synthesis. Butterworths, London 1981. p. 4.
9. M.A. Brook and C. Dallaire. Organometallics, **9**, 2873 (1990); C. Dallaire and M.A. Brook. Organometallics, **12**, 2332 (1993).
10. (*a*) R.K. Harris and B.E. Mann *Editors* NMR and the periodic table. Academic, London. 1978; (*b*) R.B. Taylor, B. Parbhoo, and D.M. Fillmore. *In* The analytical chemistry of silicones. *Edited by* A.L. Smith. Wiley, New York. 1991; (*c*) P.J. Smith and A.P. Tupciauskas. Annu. Rep. NMR Spectrosc. **8**, 291 (1978); V.S. Petroxyan. Prog. NMR Spectrosc. **11**, 115 (1977).
11. S. Kerschl, A. Sebald, and B. Wrackmeyer. Magn. Reson. Chem. **23**, 514 (1985).
12. K. Schlosser, E. Hoyer, and D. Arnold. Spectrochim. Acta, Part A: **30A**, 1431 (1974); W.R. Cullen, J.R. Sams, and J.A. Thompson. Inorg. Chem. **10**, 843 (1971); D.E. Williams and C.W. Kocher. J. Chem. Phys. **52**, 1480 (1970).
13. J.J.Zuckerman. Adv. Organomet. Chem. **9**, 22 (1971).
14. P.J. Smith. Organomet. Chem. Rev. A, **5**, 373 (1970); T.C. Gibb. Principles of Mössbauer spectroscopy. Chapman and Hall, London. 1976; P.A. Flinn. *In* Mössbauer isomer shifts. *Edited by* G.K. Shenoy and F.E. Wagner. North Holland, Amsterdam. 1978.
15. H. Schmidbaur, J. Ebenhoch, and G. Müller. Z. Naturforsch. B: Chem. Sci. **43**, 49 (1988).
16. R.C. Pettersen and G.G. Cash. Inorg. Chim. Acta, **34**, 261 (1979).
17. F.H. Allen, W.B.T. Cruse, and O. Kennard. Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem. **B36**, 2337 (1980).
18. T. Kusumoto, T. Hiyama, and K. Ogata. Tetrahedron Lett. **35**, 4197 (1986).
19. R. Diercks. J.C. Armstrong, R. Boese, and K.P.C. Vollhardt. Angew. Chem. Int. Ed. Engl. **25**, 268 (1986).
20. B.F. Coles, P.B. Hitchcock, and D.R.M. Walton. J. Chem. Soc. Dalton Trans. 445 (1975).
21. G.Å. Eliassen, E. Kloster-Jensen, and C. Rømming. Acta Chem. Scand. Ser. B: **40**, 574 (1986).
22. H. Sakurai, Y. Nakadaira, A. Hosomi, Y. Eriyama, and C. Kabuto. J. Am. Chem. Soc. **105**, 3359 (1983).
23. W. Clegg, W. Klingebiel, J. Neemann, G.M. Sheldrick, and N. Vater. Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem. **B37**, 987 (1981).
24. G. Adiwidjaja and G. Grouhi-Witte. J. Organomet. Chem. **188**, 91 (1980).
25. C. Brouty, P. Spinal, and P. Whuler. Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem. **B36**, 2624 (1980).
26. A.R. Bassindale and P.G. Taylor. *In* The chemistry of organic silicon compounds. *Edited by* S. Patai and Z. Rappoport. Wiley, Chichester. 1989. Chap. 13, pp. 893–963.
27. Yu.V. Kolodyazhnyi, N.I. Sizova, I.G. Lorents, L.I. Kuznetsova, A.P. Sadimenko, L.I. Ol'khovskaya, and N.V. Komarov. Zh. Obshch. Khim. **52**, 1855 (1982); Yu. V. Kolodyazhnyi, I.G. Lorents, S.B. Bulgarevich, A.P. Sadimenko, L.I. Ol'khovskaya, N.V. Komarov, and O.A. Osipov. Zh. Obshch. Khim. **54**, 2594 (1984).
28. P.K. Bischof, M.J.S. Dewar, D.W. Goodman, and T.B. Jones. J. Organomet. Chem. **82**, 89 (1974).

29. G.M. Whitesides, J.G. Segestad, S.P. Thomas, D.W. Andrews, B.A. Morrison, E.J. Panek, and J. san Filippio, Jr. J. Organomet. Chem. **22**, 365 (1970); G. Eng and C.R. Dillard. Inorg. Chim. Acta, **31**, 227 (1978); Inorg. Chim. Acta, **28**, 99 (1978); N.W. Alcock, M. Pierce-Butler, G.R. Willey, and K. Wade. J. Chem. Soc. Chem. Commun. 183 (1975); D.R. Eaton and W.R. McClellan. Inorg. Chem. **6**, 2134 (1967).
30. C. Cauletti, C. Furlani, G. Granozzi, A. Sebald, and B. Wrackmeyer. Organometallics, **4**, 290 (1985).
31. R. Eastmond, T.R. Johnson, and D.R.M. Walton. Tetrahedron, **28**, 4601 (1972).
32. W. Adcock and G.L. Aldous. Tetrahedron Lett. **28**, 3387 (1970); H. Janes and E. Oldfield. J. Am. Chem. Soc. **108**, 5743 (1986); E. Kupce, E. Liepin, E. Zicmane, and E. Lukevics. J. Chem. Soc. Chem. Commun. 819 (1989).
33. B.T. Luke, J.A. Pople, M.-B. Krogh-Jespersen, Y. Apeloig, J. Chandrasekhar, and P. von R. Schleyer. J. Am. Chem. Soc. **108**, 260 (1986); E.R. Reed, C. Schade, P. von R. Schleyer, P.V. Kamath, and J. Chandrasekhar. J. Chem. Soc. Chem. Commun. 67 (1988); B. Rempfer, H. Oberhammer, and N. Auner. J. Am. Chem. Soc. **108**, 3893 (1986).
34. L. Brandsma and H.D. Verkruijsse. Synthesis of acetylenes, allenes and cumulenes. *In* Study in organic chemistry. Vol. 8. Elsevier, New York. 1981. p. 55.
35. K. Ruebenbauer and T. Birchall. Hyperfine Interact. **7**, 125 (1979).
36. (*a*) N.V. Komarov and O.G. Yarosh. J. Gen. Chem. USSR (Engl. Transl.), **37**, 260 (1967); (*b*) M.F. Shostakovskii, N.V. Komarov, and O.G. Yarosh. Bull. Acad. Sci. URSS Div. Chem. Sci. 2458 (1967).
37. N.J. Fitzmaurice, R. Jackson, and P. Perlmutter. J. Organomet. Chem. **285**, 375 (1985).
38. W. Findeiss, W.E. Davidsohn, and M.C. Henry. J. Organomet. Chem. **9**, 435 (1967).
39. C.S. Kraihanzel and M.L. Losee. J. Organomet. Chem. **10**, 427 (1967).