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Steric control in the formation of $Co_2(CO)_6$–alkyne complexes from Group 14 tetraalkynes and their reactions with acid

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Abstract

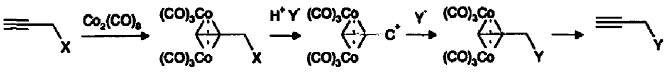
A series of tetrakis(trimethylsilylethyne) derivatives of Group 14 metals (**2–4**) was prepared. $Co_2(CO)_6$ complexes **5–10** were synthesised by the reaction of **2–4** with $Co_2(CO)_8$. From the silyl and germyl based compounds **2** and **3**, either one or two alkynes could be complexed with $Co_2(CO)_6$. In contrast, the tin derived compound **4** could accommodate up to four $Co_2(CO)_6$ complexes. The longest wavelength UV–Vis absorbances of the silicon and germanium-based complexes were consistent with multiple, non-conjugated $Co_2(CO)_6$ chromophores. The tetrakis $Co_2(CO)_6$ complex **10**, however, absorbs at a much longer wavelength suggesting conjugation of $Co_2(CO)_6$ complexes through the tin. The reactivity towards protonolysis of the uncomplexed alkynes **2–4** is a consequence of the hyperconjugative stabilisation of the intermediate β-vinyl cation (the β-effect): $Sn(C{\equiv}CSiMe_3)_3 > SnOTf(C{\equiv}CSiMe_3)_2 > SiMe_3 > Ge(C{\equiv}CSiMe_3)_3 > Si(C{\equiv}CSiMe_3)_3$. The reactivity of the $Co_2(CO)_6$ complexes, however, was quite different from the reactions of **2–4** and from analogous all-carbon systems. Treatment of **5–10** with strong acid led neither to protiodemetallation of the complexed or non-complexed alkynes but to decomplexation of the cobalt. Similarly, ligand metathesis reactions between **10** and Ph_2SiCl_2 were not observed. The normal reactivity of silylalkynes towards electrophiles, which was expected to be enhanced by the presence of the cobalt complex, was diminished by the particular steric environment of the molecules under examination (**5–10**). As a result, the favoured reaction under these conditions was decomplexation of the cobalt.

Keywords: Crystal structures; Cobalt complexes; Carbonyl complexes; Alkyne complexes

1. Introduction

The reaction between $Co_2(CO)_8$ and alkynes leads to the formation of tetrahedral dicobalt hexacarbonyl complexes (Scheme 1) [1]. Such complexes can be effectively used in organic synthesis [2], as the dicobalt complex serves to protect the alkyne from a variety of reagents [3]. With acids, besides the protective role for the alkyne, the α-carbon is activated to nucleophilic substitution through stabilisation of the intermediate carbocation **1** by the transition metals [4]. When the α-carbon of a $Co_2(CO)_6$ alkyne complex is replaced by silicon, Corriu et al. have shown that nucleophilic substitutions of Si–Cl or Si–O groups are not greatly affected by the presence of the cobalt [5]. In contrast, the presence of cobalt serves to activate Si–H bonds to substitution [6,7].

Silyl-substituted alkynes serve as surrogates for alkynyl anions. They react to form new bonds to carbon with subsequent Si–C cleavage under mild, anionic conditions (fluoride [8], Scheme 2A) or via a hyperconjugatively stabilised β-silyl vinyl cation [9] (the β-effect) under electrophilic attack (Scheme 2B) [10,11]. We were interested to learn whether the presence of a dicobalt complex on an adjacent alkyne would facilitate the cleavage of the Si–C bond (bold bond, Scheme 2C) in analogy with the described activation of Si–H bonds [6,7]. It was of further interest to determine: (i) if multiple $Co_2(CO)_6$ groups could be accommodated on a given Group 14 centre and, (ii) the degree to which multiple



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Scheme 1.

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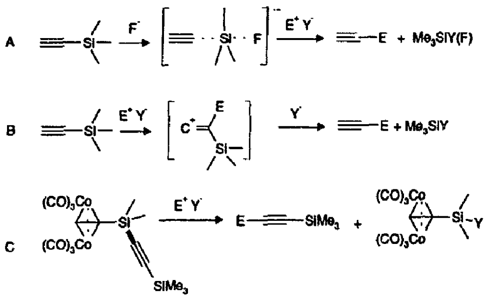


Scheme 2.

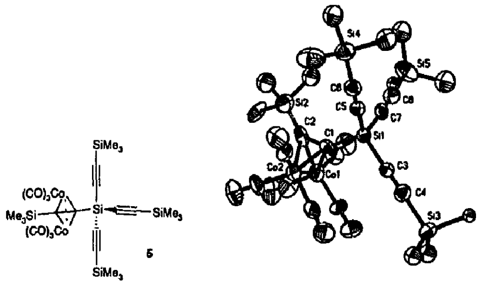


Fig. 1. View of compound 5 showing the atomic numbering scheme (hydrogen atoms are removed for clarity).

groups would cooperate to facilitate Si–C bond cleavage. To examine these questions, we have prepared a series of tetrakis(trimethylsilylalkynyl) Group 14 metal derivatives (**2**–**4**) and examined their reactivity before and after complexation to $Co_2(CO)_8$.

2. Results and discussion

2.1. *Preparation and complexation with $Co_2(CO)_8$ of alkynes 2–4 with acid*

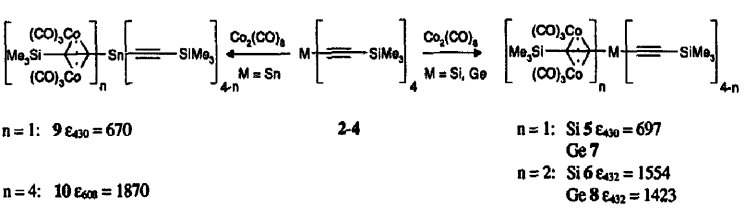
The tetrakis(trimethylsilylalkynyl) Group 14 metals derivatives (**2**–**4**) could be readily prepared from $LiC{\equiv}CSiMe_3$ and the appropriate MCl_4 compound [12,13]. The reaction of compounds **2**–**4** with $Co_2(CO)_8$ was straightforward. In the cases of **2** and **3** it was possible to isolate the complexes with one (**5**) (Si), (**7**) (Ge) [2] or two (**6**) (Si), (**8**) (Ge) of the alkynes complexed, respectively (Scheme 3, $n = 1,2$). It was also possible to obtain suitable crystals for an X-ray structure analysis of **5** (Fig. 1, Tables 1–3) [3]. Attempts to force the reaction thermally, in the hope of complexing three or all four of the alkynes, however, led only to decomposition of the products. In contrast, with compound **4**, the use of 4 equiv. of $Co_2(CO)_8$ led to the tetrakis(dicobalt hexacarbonyl) derivative **10** (Scheme 3, $n = 4$); stoichiometric amounts of $Co_2(CO)_8$ led primarily to the monocomplexed derivative **9** (Scheme 3). Although in both reactions with **4** there were compounds with intermediate polarity between those of **9** and **10** (from thin layer chromatography, the putative bis- and tris-$Co_2(CO)_6$ complexes), it proved impossible to purify them.

The inability to prepare tris- and tetrakis-$Co_2(CO)_6$ complexes of **2** (or analogously of **3**) is a consequence of steric constraints. With the shorter M–C bond lengths (Si or Ge), more than two of the dicobalt complexes cannot be accommodated; with its longer bond to carbon, the tin compound is not similarly constrained.

Corriu et al. have reported the preparation of the tris-$Co_2(CO)_6$ complex of $(MeC{\equiv}C)_3SiH$ [7]. Presumably, differences between these results and ours lie in the lower steric bulk of the methyl group, when compared to $SiMe_3$, at the alkyne termini and, more importantly, the very small fourth ligand on Si, the hydrogen, which leaves one quadrant of the compound essentially empty.

The dicobalt complexes **5**–**10** showed interesting differences in their UV spectra. Compounds **5** and **9** bearing a single dicobalt hexacarbonyl complex had similar absorbances (≈432 nm) and extinction coefficients (≈700) indicating that the dicobalt hexacarbonyl complex chromophore is not perturbed by the presence of Si, Ge or Sn, respectively. The bis(dicobalt hexacarbonyl) complexes **6** and **8** also had similar absorbances (≈432 nm) with approximately double the extinction coefficient, again suggesting that the contributions for two isolated cobalt chromophores to the observed absorbance are additive.

The tetrakis complex **10** had both a different colour and an extinction coefficient which was inconsistent with the additive effects of four isolated $Co_2(CO)_6$ chromophores. It is



Scheme 3.

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[2] This compound was characterized only by ¹H NMR. While the data are consistent with this structure, the assignment is not conclusive at this point in time.

[3] Packing disorder in all four $SiMe_3$ groups was evident. The disorders were modelled by defining three to four rigid $SiMe_3$ groups on each terminal silicon site. Common carbon temperature factors for each rigid group were refined by least-squares analysis. An ORTEP showing the disorder is included in the supplementary material.

reasonable to ascribe the different colour of **10** to a conjugative interaction between $Co_2(CO)_6$ groups through tin [13]. Consistent with this interpretation is the colour of compounds, bearing adjacent $Co_2(CO)_6$ groups, prepared from 1,3-diynes. They are typically green rather than red compounds[4] [14,15], although not exclusively [16]. Theoretical calculations support the proposition that, in the case of adjacent complexes, conjugation is involved [17]. Conjugation between $Co_2(CO)_6$ groups through an intervening alkene group has, moreover, been reported [18]. The possibility of the colour difference between **9** and **10** arising from other sources must, however, be noted. In particular, shifts in geometry of the cobalt complex as a result of steric compression could be important.

2.2. *Reactivity of the uncomplexed alkynes towards strong protic acids*

Upon protonation of a silylmetalalkyne, an internal competition can occur between two regioisomeric β-metal vinyl cations. If protonation is rate determining, as has been observed in related examples [12], the product ratio allows the assignment of the relative β-effect of the groups involved; the group that ultimately leaves was better able to stabilise the intermediate β-vinyl cation. For instance, if $SiMe_3$ has a stronger β-effect than $M(C{\equiv}CSiMe_3)_3$ (**11**) (Scheme 4A, **11** more stable than **12**), the products of the protonolysis will be Me_3SiOTf and $H{-}C{\equiv}C{-}M(C{\equiv}CSiMe_3)_3$.

Alkynes **2–4** were demetallated (Table 4) using strong protic acids (F_3CSO_3H(TfOH), CH_3SO_3H(MsOH) and F_3CCO_2H(TFA)). Strong acids were used to minimise any contribution to the reaction rate from nucleophilic attack of the counterion [13,19]. It is possible to show from the results in Table 4 that, similar to examples reported elsewhere [19,20], the predominant factor in the β-effect of Group 14 groups for vinyl cations is the polarisability of the metal Sn > Ge > Si[5]. Thus, tin is preferentially cleaved from the alkyne **4** upon the addition of triflic or trifluoroacetic acid as $Sn(C{\equiv}CSiMe_3)_3$. This order, however, can be perturbed in the case of Si and Ge by the ligands on the metal. Clearly, Me_3Si has a better β-effect than $Ge(C{\equiv}CSiMe_3)_3$ as can be seen by the fact that it wins the internal competition (Table 4, entries 3–5 and 7, 8). In this case, the increase in polarisability on going from Si to Ge is more than compensated for by the increased electronegativity of the alkynyl sp orbitals. These reduce the electron density in the M–C sp^2 bond involved in the hyperconjugative stabilisation of the cationic intermediate. The relative β-effect of the following groups can thus be assigned [21]: $Sn(C{\equiv}CSiMe_3)_3$ > $SnOTf(C{\equiv}CSiMe_3)_2$ > $SiMe_3$ > $Ge(C{\equiv}CSiMe_3)_3$ > $Si(C{\equiv}CSiMe_3)_3$.

Table 1
X-ray structure summary for compound **5**

Empirical formula	$C_{26}H_{36}Co_2O_6Si_5$
Formula weight	702.86
Temperature (K)	83(2)
Wavelength (Å)	0.71073
Crystal system	tetragonal
Space group	$I4_1/a$
Unit cell dimensions	
a (Å)	27.873(2)
b (Å)	27.873(2)
c (Å)	20.458(3)
α (°)	90
β (°)	90
γ (°)	90
Volume ($Å^3$)	15894(3)
Z	16
Density (calc.) ($Mg\ m^{-3}$)	1.175
Absorption coefficient (mm^{-1})	1.015
$F(000)$	5824
Crystal size (mm)	0.05 × 0.15 × 0.11
θ Range data collection (°)	2.07–22.51
Index ranges	$-1 \leq h \leq 30$, $-1 \leq k \leq 30$, $-1 \leq l \leq 22$
Reflections collected	6355
Independent reflections	5190 (R(int) = 0.0665)
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	5188/284/484
Goodness-of-fit on F^2	1.018
Final R indices ($I > 2\sigma(I)$)	
R_1	0.0857
wR_2	0.1438
R indices (all data)	
R_1	0.2555
wR_2	0.2217
Largest diff. peak, hole ($e\ Å^{-3}$)	312, −0.237

2.3. *Reactivity of the dicobalt complexes*

2.3.1. *Reactivity towards protic acids*

The reaction of **2** with triflic acid (or methanesulfonic acid (MsOH)), as noted above, led to the sequential loss of $SiMe_3$ groups. In contrast, the reaction of the bis(dicobalt) species **6** under the same conditions led neither to protiodesilylation of the $SiMe_3$ group on a complexed nor uncomplexed alkyne. Instead, loss of cobalt from the alkyne to regenerate **2** was accompanied by the formation of a pink material that, based on the colour and the broadened ^1H NMR signals, is likely paramagnetic Co^{II}. **5**, **8** and **9** similarly underwent decomplexation of the cobalt without any observed reaction at the silylalkyne. The reaction of **10** with excess MsOH overnight led to formation of the monocomplexed **9** and other unidentified species with concomitant formation of the Co^{II} precipitate.

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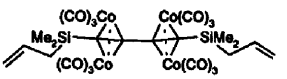
[4] We have prepared compound **14** and related compounds [14]; compound **14** had a ϵ_{612} of 885.



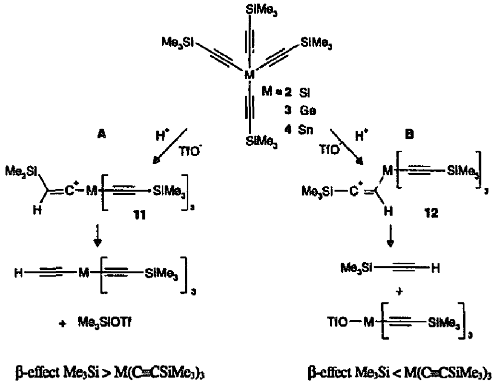
[5] The reaction rate upon going from Ge to Si (entries 3–5 → 7,8 → 9) was observed to decrease. As loss of Me_3Si was observed in both cases, we are unable to say from these experiments what the relative β-effect is for the $(Me_3SiC{\equiv}C)_3M$ (M = Ge, Si) groups. We therefore rely on previous work in assigning the order shown [12,13,19].

Table 2
Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for 5 [a]

	x	y	z	U_{eq} [b]
Co(1)	837(1)	1594(1)	2597(1)	91(1)
Co(2)	981(1)	698(1)	2608(1)	79(1)
Si(1)	1694(1)	1279(1)	3766(2)	65(1)
Si(2)	203(2)	1055(2)	3854(3)	114(2)
Si(3)	3070(2)	1579(2)	2378(2)	106(2)
Si(4)	1787(2)	−43(2)	5295(2)	100(2)
Si(5)	1426(2)	2582(2)	5297(3)	147(2)
O(1)	−25(5)	1652(5)	1804(8)	175(6)
O(2)	694(5)	2492(5)	3277(7)	155(5)
O(3)	1612(5)	1851(4)	1706(6)	138(5)
O(4)	165(4)	406(5)	1811(6)	146(5)
O(5)	1131(5)	−189(4)	3328(6)	127(4)
O(6)	1830(5)	655(5)	1755(6)	137(5)
C(1)	1143(5)	1187(4)	3281(6)	62(4)
C(2)	661(5)	1107(5)	3309(7)	83(5)
C(3)	2213(5)	1380(5)	3246(6)	65(4)
C(4)	2549(5)	1445(5)	2906(7)	82(5)
C(5)	1769(4)	753(5)	4286(6)	59(4)
C(6)	1784(5)	426(5)	4664(7)	79(4)
C(7)	1609(5)	1790(5)	4320(7)	73(4)
C(8)	1535(6)	2110(5)	4693(7)	91(5)
C(21)	321(6)	1621(7)	2085(10)	140(8)
C(22)	752(7)	2130(7)	3011(9)	113(6)
C(23)	1311(6)	1770(7)	2055(7)	107(6)
C(24)	481(6)	516(6)	2114(8)	101(6)
C(25)	1081(6)	160(6)	3035(7)	90(5)
C(26)	1507(6)	674(6)	2074(8)	86(5)

[a] Me groups (C, H) are not included in this listing but may be found in the Supplementary material (see Section 5).

[b] U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.



Scheme 4.

2.3.2. Ligand metathesis of 10

Unlike carbon, tin compounds readily undergo ligand metathesis, particularly if electronegative groups are involved [22]. Thus, the mixture of Me_4Sn and $SnCl_4$ readily leads to the formation of 2 equiv. of Me_2SnCl_2. However, as with acids, the exposure of **10** to other tin compounds did not lead to the expected reaction: with excess $SnCl_4$ an intractable tar was formed, the use of a less reactive compound, Ph_2SnCl_2, led to no reaction. Heating the mixture led only to decomplexation of the cobalt cluster.

Table 3
Selected bond lengths (Å) and angles (°) for 5

Bond	Length	Bond	Angle
Co(1)–C(1)	1.994(11)	C(3)–Si(1)–C(1)	111.6(6)
Co(1)–C(2)	2.05(2)	C(3)–Si(1)–C(5)	112.0(6)
Co(2)–C(1)	1.990(12)	C(4)–C(3)–Si(1)	179.7(14)
Co(2)–C(2)	2.04(2)	C(2)–C(1)–Si(1)	145.0(11)
Co(1)–C(21)	1.78(2)	Si(1)–C(1)–Co(2)	131.1(7)
Co(1)–C(22)	1.73(2)	C(2)–C(1)–Co(1)	72.6(8)
Co(1)–C(23)	1.79(2)	Co(2)–C(1)–Co(1)	78.9(4)
Co(1)–Co(2)	2.531(3)	C(1)–C(2)–Si(2)	141.4(11)
Co(2)–C(24)	1.79(2)	C(1)–C(2)–Co(1)	68.1(9)
Co(2)–C(25)	1.76(2)	Si(2)–C(2)–Co(2)	137.9(9)
Co(2)–C(26)	1.83(2)	C(21)–Co(1)–C(1)	141.4(8)
Si(1)–C(1)	1.846(13)	C(22)–Co(1)–C(1)	101.9(7)
Si(1)–C(3)	1.817(14)	C(22)–Co(1)–C(2)	100.9(7)
Si(2)–C(2)	1.70(2)	C(22)–Co(1)–C(21)	98.1(9)
Si(2)–C(9A)	1.90(2)	C(23)–Co(1)–C(1)	105.9(7)
Si(2)–C(10A)	1.89(2)	C(1)–Co(1)–C(2)	39.4(4)
Si(2)–C(11A)	1.89(2)	C(22)–Co(1)–Co(2)	150.2(6)
Si(3)–C(4)	1.85(2)	C(21)–Co(1)–Co(2)	100.1(7)
Si(3)–C(12A)	1.84(2)	C(1)–Co(1)–Co(2)	50.5(3)
Si(3)–C(13A)	1.90(2)	C(25)–Co(2)–C(24)	99.4(7)
Si(3)–C(14A)	1.89(3)	C(25)–Co(2)–C(1)	101.8(6)
C(1)–C(2)	1.36(2)	C(24)–Co(2)–C(1)	139.5(7)
C(3)–C(4)	1.18(2)	C(1)–Co(2)–C(2)	39.5(4)
		C(25)–Co(2)–Co(1)	150.7(5)
		C(24)–Co(2)–Co(1)	98.7(5)
		C(1)–Co(2)–Co(1)	50.6(3)
		C(2)–Co(2)–Co(1)	52.0(4)
		C(2)–Si(2)–C(9A)	110(2)
		C(10A)–Si(2)–C(9A)	107(2)
		C(11A)–Si(2)–C(9A)	108(2)
		C(3)–C(4)–Si(3)	177(2)
		C(4)–Si(3)–C(13A)	107(2)
		C(12A)–Si(3)–C(4)	107(2)
		C(12A)–Si(3)–C(13A)	111(2)

2.4. Comparison with all-carbon systems

It has been clearly demonstrated that the presence of a $Co_2(CO)_6$–alkyne complex serves to stabilise adjacent carbocations [4,23]. A series of stable, isolable cationic complexes has been isolated which can further react with a series of nucleophiles (Scheme 1) [24]. Clearly, however, unlike the all-carbon dicobalt alkynyl complexes, complexes described in this report bearing Group 14 elements adjacent to the cobalt are much more susceptible to acid attack. Although such sensitivity towards acid is not unknown [25], it is rather unusual [6].

In considering the origin of this sensitivity, it is necessary to consider the steric environment of the central metal. As has been described above, with Si or Ge as the central atom,

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[6] Corriu et al. observed that related compounds were fragile [6].

Table 4
Reaction products of **2**–**4** upon protonation

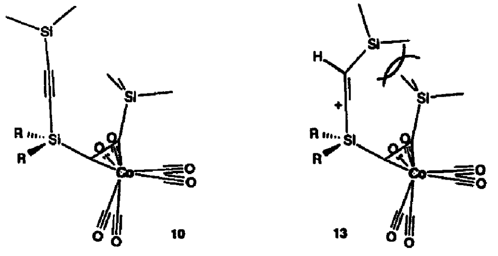
Entry	Starting material	Acid	Equiv. acid	Time (min)	Products	Conversion[a] (%)
1	$\mathrm{Sn(C{\equiv}CSiMe_3)_4}$ (**4**)	TfOH	1	2	$\mathrm{TfOSn(C{\equiv}CSiMe_3)_3, Me_3SiC{\equiv}CH}$	100
2			2	2	$\mathrm{TfOSn(C{\equiv}CSiMe_3)_3, Me_3SiC{\equiv}CH}$	88
					($\mathrm{HC{\equiv}CH}$[b] $\mathrm{Me_3SiOTf}$)	13
3	$\mathrm{Ge(C{\equiv}CSiMe_3)_4}$ (**3**)	TfOH	2	2	$\mathrm{(Me_3SiC{\equiv}C)_3Ge(C{\equiv}CH), Me_3SiOTf}$	31
					$\mathrm{(Me_3SiC{\equiv}C)_2Ge(C{\equiv}CH)_2, Me_3SiOTf}$	20
					$\mathrm{(Me_3SiC{\equiv}C)Ge(C{\equiv}CH)_3, Me_3SiOTf}$	14
					$\mathrm{Ge(C{\equiv}CH)_4, Me_3SiOTf}$	9
4			3	2	$\mathrm{(Me_3SiC{\equiv}C)_3Ge(C{\equiv}CH), Me_3SiOTf}$	17
					$\mathrm{(Me_3SiC{\equiv}C)_2Ge(C{\equiv}CH)_2, Me_3SiOTf}$	26
					$\mathrm{(Me_3SiC{\equiv}C)Ge(C{\equiv}CH)_3, Me_3SiOTf}$	13
					$\mathrm{Ge(C{\equiv}CH)_4, Me_3SiOTf}$	30
5			4	2	$\mathrm{(Me_3SiC{\equiv}C)_2Ge(C{\equiv}CH)_2, Me_3SiOTf}$	23
					$\mathrm{(Me_3SiC{\equiv}C)Ge(C{\equiv}CH)_3, Me_3SiOTf}$	8
					$\mathrm{Ge(C{\equiv}CH)_4, Me_3SiOTf}$	69
6	$\mathrm{Si(C{\equiv}CSiMe_3)_4}$ (**2**)	TfOH	4	2	$\mathrm{Si(C{\equiv}CH)_4, Me_3SiOTf}$	100
7	$\mathrm{Ge(C{\equiv}CSiMe_3)_4}$ (**3**)	MsOH	2	120	$\mathrm{(Me_3SiC{\equiv}C)_3Ge(C{\equiv}CH), Me_3SiOMs}$	50
					$\mathrm{(Me_3SiC{\equiv}C)_2Ge(C{\equiv}CH)_2, Me_3SiOMs}$	13
					$\mathrm{(Me_3SiC{\equiv}C)Ge(C{\equiv}CH)_3, Me_3SiOMs}$	6
8	$\mathrm{Ge(C{\equiv}CSiMe_3)_4}$ (**3**)	MsOH	2	960	$\mathrm{(Me_3SiC{\equiv}C)_3Ge(C{\equiv}CH), Me_3SiOMs}$	33
					$\mathrm{(Me_3SiC{\equiv}C)_2Ge(C{\equiv}CH)_2, Me_3SiOMs}$	42
					$\mathrm{(Me_3SiC{\equiv}C)Ge(C{\equiv}CH)_3, Me_3SiOMs}$	9
					$\mathrm{Ge(C{\equiv}CH)_4, Me_3SiOMs}$	6
9	$\mathrm{Si(C{\equiv}CSiMe_3)_4}$ (**2**)	MsOH	1	45	no reaction	6
10			5	300	$\mathrm{(Me_3SiC{\equiv}C)_3SiC{\equiv}CH, Me_3SiOMs}$	25
11	$\mathrm{Sn(C{\equiv}CSiMe_3)_4}$ (**4**)	$\mathrm{F_3CCOOH}$	1	2.5	$\mathrm{F_3CCO_2Sn(C{\equiv}CSiMe_3)_3, Me_3SiC{\equiv}CH}$	20

[a] Based on $\mathrm{Me_3SiX}$ (X = OTf, OMs, $\mathrm{OCOCF_3}$) or $\mathrm{Me_3Si{-}C{\equiv}CH}$ for which relative concentrations could be unequivocally measured. Starting material was the residual material in the product mixture.

[b] Other products were also present in small amounts which are tentatively identified as $\mathrm{(Me_3SiC{\equiv}C)_2Sn(OTf)_2}$.

only two of four alkynes undergo complexation with $\mathrm{Co_2(CO)_6}$ whereas the Sn-centred compound can undergo complete complexation. In the first two cases, significant steric encumbrance of the central metal exists in the complexed materials. In order for any of these complexes to react with acid, significant reorganisation of the complex is required. The uncomplexed alkyne in **6** must rehybridise from sp to sp^2 with a concomitant development of additional unfavourable steric interactions (**13**) (Scheme 5). Thus, the competing decomplexation of the $\mathrm{Co_2(CO)_6}$–alkyne may be more favourable than direct proton attack at an alkyne. Similarly, the reorganisation of **10** necessary to interact with $\mathrm{Ph_2SnCl_2}$ may be sufficiently unfavourable such that decomplexation and other decomposition pathways are preferentially followed.

As a result of the sensitivity of the cobalt complexes to Lewis and protic acids, for the steric reasons noted, it has not been possible to determine to what extent a $\mathrm{Co_2(CO)_6}$ complex facilitates the cleavage of an adjacent Group 14 alkyne. The determination of this and the extent, if any, to which the transmission of electron density is affected by the intervening Group 14 element will require the utilisation of less hindered complexes.



Scheme 5.

3. Conclusions

When multiple silylalkynes are bound to a single Group 14 metal centre, the reactivity of a given alkynyl group is not especially affected by the proximity of the other alkynyl groups; upon protic challenge, the alkynyl groups underwent protiodemetallation. The prevalent reaction, protiodemetallation of the group with the best β-effect, followed the order of polarisability (Sn > Ge > Si), but the relative order of Ge and Si was perturbed by the electron-donating ability of the spectator ligands.

The proximity of multiple alkynes does, however, affect the facility with which $\mathrm{Co_2(CO)_6}$ complexes are formed and react. Thus, with the compounds containing shorter Ge–C and Si–C bond lengths, a maximum of two $Co_2(CO)_6$ complexes can form. In contrast, with the longer Sn–C bonds, **4** can undergo cobalt complexation four times over to give **10**. The complexes of the Si and Ge alkynes have UV absorbances consistent with multiple, isolated $Co_2(CO)_6$ complexes ($\epsilon_{432} = \approx 700/Co_2(CO)_6$ complex), the tetrakis-$Co_2(CO)_6$ complex of tin compound **10** has a longer wavelength absorbance suggesting conjugation through tin ($\epsilon_{608} = 1870$).

When compared with all carbon-based $Co_2(CO)_6$ complexes, the Group 14 substituted species were very susceptible to acid attack. For steric reasons, rather than undergoing protiodesilylation as was observed in the uncomplexed species **2–4**, the complexes underwent loss of cobalt.

4. Experimental

Due to the instability of dicobalt octacarbonyl and the alkynyl cobalt complexes and the hydrolytic instability of the Group 14 metal chlorides, all reactions were carried out under a nitrogen atmosphere in a dry apparatus using septa and syringes for reagent transfer. All liquids were distilled prior to use. Solvents were dried by distillation from potassium/benzophenone under a N_2 atmosphere. Trifluoromethanesulfonic acid, methanesulfonic acid, cesium fluoride, tetrachloro-silane, tetrachloro-germane and tetrachloro-stannane, n-butyl lithium and trimethylsilylacetylene were obtained from Aldrich and used without further purification. Chlorotrimethylsilane was obtained from Dow Corning, Canada, and distilled prior to use. Dicobalt octacarbonyl was obtained from Strem Chemicals. Chloroform-d was obtained from Merck, Sharp and Dohme. Silica gel and TLC plates were obtained from Merck, Darmstadt.

Radial chromatography was performed on a Harrison Research Chromatotron (model 7924T). Hexane was used as a solvent on plates prepared using silica gel 60 PF-254 containing $CaSO_4$ from Merck.

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 and ^{29}Si NMR were performed on a Bruker AC-200 (at 50.3 MHz for carbon) and Bruker WM-250 (at 62.9 MHz for carbon and 49.7 MHz for silicon) spectrometer. ^{59}Co, ^{73}Ge and ^{119}Sn NMR were also attempted on the WM-250, but no signals were observed. Chemical shifts are reported with respect to tetramethylsilane, as standard, set to 0 ppm. Coupling constants (J) are recorded in hertz (Hz).

Electron impact (EI) and chemical ionization (CI, NH_3) mass spectra were recorded at 70 eV with a source temperature of ~200 °C and a VG analytical ZAB-E mass spectrometer equipped with a VG 11-250 data system. Fast Atom Bombardment (FAB) spectra were obtained on the ZAB-E instrument using 3-nitrobenzyl alcohol as the matrix. High resolution mass spectral (HRMS) data were obtained with the VG-ZAB-E instrument by the EI method. IR spectra of KBr pellets were obtained using a Perkin Elmer 283 spectrometer and Fourier spectra on a BIO RAD FTS-40 spectrometer. The abbreviations s = strong, m = medium and w = weak are used. UV–Vis spectra were recorded on a Hewlett Packard HP 8451 A diode array spectrometer.

Crystals of $(Me_3SiC{\equiv}C)_3Si(C{\equiv}CSiMe_3)\cdot(Co_2(CO)_6)$ (**5**) suitable for X-ray diffraction were grown from hexane. X-ray crystallographic data for **5** were collected at −190 °C on a Siemens P4 diffractometer equipped with a rotating anode and using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The background measurements were obtained by using a stationary crystal and stationary counter at the beginning and end of the scan time [26]. The compound structure was solved by using the Patterson method routine contained in the SHELXTL-Plus program library.

Elemental analyses were performed by Guelph Chemical Laboratories, Guelph, Canada.

4.1. General preparative procedure for metalated alkynes 2–4

The previously reported method [13] was used for the syntheses of tetrakis(trimethylsilylalkynyl) derivatives of silicon (**2**), germanium (**3**) and tin (**4**).

To a solution of $Me_3SiC{\equiv}CH$ (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_2Cl_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 mm Hg to give 3.5 g of $Cl_3Si{-}C{\equiv}C{-}SiMe_3$ (15.1 mmol, 21% yield). Afterwards, the residue was washed with water, extracted with ether and recrystallised several times in hexane to give 3 g of **2** (7.1 mmol, 41% yield) [27].

The syntheses of the other metallated (trimethylsilyl)acetylide compounds were performed with some modifications to the procedure reported in the literature. The syntheses were done as described above by the reaction of lithium salt of (trimethylsilyl)acetylide ($Me_3Si{-}C{\equiv}C{-}Li^+$, 4.0 equiv.) with the appropriate silyl, germyl or stannyl chloride compounds in tetrahydrofuran or ether [28]. In these cases, chlorometal derivatives were not obtained as coproducts.

4.1.1. Spectral data

4.1.1.1. Tetrakis[(trimethylsilyl)ethynyl]silane ($(Me_3SiC{\equiv}C)_4Si$ (2)) [29]

M.p.: 154–159 °C (from hexane); lit. [29]: 160 °C (from petroleum ether). ^1H NMR ($CDCl_3$, 200 MHz): δ 0.21 (s). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ 117.2, 104.2, −0.3. ^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ −17.5, −101.6. IR (CH_2Cl_2): ν 2965s, 2900m, 2010m, 1950w, 1875w, 1400m, 1250s, 900–720s, 700s, 480s and 290s cm^{-1}. MS (EI, m/z):

416 (M^+, 21), 401 (34), 343 (12), 328 (11), 313 (100), 231 (29), 179 (32), 155 (56). HRMS: mass observed: 416.1663; mass calculated: 416.1669.

4.1.1.2. Tetrakis[(trimethylsilyl)ethynyl]germane ((Me$_3$SiC≡C)$_4$Ge (3)) [27]

Yield: 94%; lit. [27]: 58%. M.p.: 175–176 °C (from petroleum ether); lit.: 176 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.21 (s). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ 114.0, 102.1, −0.3. ^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ −17.7. ^{73}Ge NMR ($CDCl_3$, 8.73 MHz): δ −188.5 (line width of 125 Hz). IR (KBr): ν 2970s, 2900m, 2105w, 2000w, 1955w, 1870w, 1450w, 1410m, 1315w, 1255s, 850s, 760s, 820s, 405m, 305m and 300s cm^{-1}. 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 fro ^{74}Ge isotope) mass observed for $M^+ + 1$: 461.1032; mass calculated for $M^+ + 1$: 461.1028.

4.1.1.3. Tetrakis[(trimethylsilyl)ethynyl]stannane ((Me$_3$Si–C≡C–)$_4$Sn (4)) [27]

Yield: 73%; lit. [27]: 35%. M.p.: 170–172 °C (from petroleum ether or hexane); lit. [27]: decomposition at 140 °C (from petroleum ether). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.21 (s). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ 119.5, 103.2, −0.3. ^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ −18.1. ^{119}Sn NMR ($CDCl_3$, 93.28 MHz): δ −384.5. IR (KBr): ν 2960s, 2900m, 2090w, 2010w, 1950w, 1865w, 1405m, 1310m, 1250s, 840s, 755s, 695s and 605m cm^{-1}. MS (EI, m/z reported for ^{119}Sn isotope): 508 (M^+, 15), 493 (17), 405 (16), 314 (72), 247 (83), 217 (35), 179 (80), 165 (86), 119 (30), 97 (100), 73 (79). HRMS: (M^+ reported for ^{119}Sn isotope) mass observed: 508.0915; mass calculated: 508.0916.

4.2. Preparation of dicobalt hexacarbonyl-η^2-alkynyl complexes

From the ^{1}H NMR spectra of the reaction mixtures described below, conversion to reaction products was quite high in all cases; very little starting material remained. However, during isolation and particularly chromatography, significant degradation occurred with the starting material as a major product. This is ascribed to the acidic decomplexation of $Co_2(CO)_6$ caused by the silica gel.

4.2.1. Preparation of 5, the dicobalt hexacarbonyl derivative of 2

To a solution of $Co_2(CO)_8$ (178 mg, 0.47 mmol) in THF (25 ml) was added **2** (194 mg, 0.47 mmol) in hexane (25 ml). After 36 h at 50 °C, the solvents were evaporated under reduced pressure and the residue (mostly starting material) was purified by radial chromatography (hexane eluent) to give 25 mg (8%) of **5**.

M.p. 109 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.16 (s, 27H), 0.35 (s, 9H). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ −0.8, 0.5, 116.7, 200.1. IR (KBr): ν 2960m, 2900w, 2090s, 2050s, 2020s, 1530s, 1405m, 1250s, 840s, 795s, 755s, 695m, 615w, 600w, 520s and 495s cm^{-1}. UV (hexane): ϵ_{430} (l mol^{-1} cm^{-1}) = 697, ϵ_{352} = 4602. MS (FAB, m/z): 647 ($M^+ + 1 - 2CO$).

4.2.2. Preparation of 6, the bis(dicobalt hexacarbonyl) derivative of 2

To a solution of $Co_2(CO)_8$ (880.0 mg, 2.32 mmol) in THF (25 ml) was added **2** (200.0 mg, 0.48 mmol) in hexane (25 ml). The mixture was heated to 50 °C for 24 h and stirred a further 24 h at r.t. After removal of the organic solvents under reduced pressure, the residue was chromatographed (radial chromatography, hexane) to give 70 mg (14.7%) of **6** as a dark red solid.

M.p. 96 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.10 (s, 18H), 0.39 (s, 18H). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ −1.0, 1.1, 94.6, 98.8, 108.4, 116.6, 200.4. ^{29}Si NMR ($CDCl_3$): δ −17.7, 0.9, 56.7. IR (KBr): ν 2970m, 2960m, 2090s, 2040s, 2020s, 1550m, 1490m, 1410m, 1250s, 840s, 780s, 750m, 695w, 655w, 605w, 520s, 495s and 460m cm^{-1}. UV (hexane): ϵ_{432} (l mol^{-1} cm^{-1}) = 1554, ϵ_{348} = 9990. MS (FAB, m/z): 960 ($M^+ - CO$).

Attempts were made to force the reaction, in an attempt to prepare tris- and tetrakis-(dicobalt hexacarbonyl) derivatives. Thus, $Co_2(CO)_8$ (700 mg, 1.845 mmol) and **2** (150 mg, 0.32 mmol) were combined in THF:hexane (1:1, 40 ml). The mixture was heated at 80 °C for 36 h. TLC and ^{1}H NMR monitoring of the mixture showed no indication of new cobalt complexes.

4.2.3. Preparation of 7 and 8, the dicobalt hexacarbonyl derivatives of 3

To $Co_2(CO)_8$ (2.88 g, 8.42 mmol) in THF (35 ml) was added **3** (333 mg, 0.72 mmol) in hexane (25 ml). The mixture was heated to 40 °C for 51 h and following removai of the solvents under reduced pressure, radial chromatography in hexane led to two fractions, the bis(dicobalt hexacarbonyl derivative) **8** (340 mg, 46%) and **7** (10 mg, 2%).

7: ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.06 (s, 27H), 0.36 (s, 9H), (see also Footnote [2]).

8: M.p. 104 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.10 (s, 18H), 0.39 (s, 18H). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ −0.9, 1.0, 88.5, 91.8, 106.1, 115.0, 109.2, 200.1. ^{29}Si NMR ($CDCl_3$, 49.7 MHz): δ −17.9, 0.8. IR (KBr): ν 2960w, 2920w, 2080s, 2050s, 2020s, 1545m, 1490m, 1410m, 1250s, 840s, 755m, 720s, 695w, 600w, 520s and 495s cm^{-1}. UV (hexane): ϵ_{430} (l mol^{-1} cm^{-1}) = 1423, ϵ_{350} = 8197. MS (FAB, m/z): 950 ($M^+ + 1 - 3CO$).

Forcing conditions (80–100 °C for 43 and 6 h, respectively) led to new spots on the TLC which could not be isolated. The yields of **7** and **8** under these conditions were dramatically reduced.

*4.2.4. Preparation of **9**, the dicobalt hexacarbonyl derivative of **4***

To a solution of $Co_2(CO)_8$ (74 mg, 0.2 mmol) in THF (25 ml) was added **4** (100 mg, 0.2 mmol) in hexane (25 ml). After 25.5 h at r.t., the solvents were evaporated under reduced pressure and the residue (mostly starting material) was purified by radial chromatography (hexane eluent) to give 20 mg (13%) of **9**.

M.p. 90 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.16 (s, 27H), 0.34 (s, 9H). ^{13}C NMR ($CDCl_3$, 200 MHz): δ −0.5, 0.7, 103.4, 120.3, 199.9. IR (KBr): ν 2960m, 2900w, 2090s, 2050s, 2020s, 1530s, 1405m, 1250s, 840s, 795s, 755s, 695m, 615w, 600w, 520s and 495s cm^{-1}. UV (hexane): ϵ_{430} (l mol^{-1} cm^{-1}) = 670, ϵ_{352} = 4314. MS (FAB, m/z): 647 ($M^+ + 1 - 2CO$).

*4.2.5. Preparation of **10**, the tetrakis(dicobalt hexacarbonyl) derivative of **4***

To a solution of $Co_2(CO)_8$ (1.20 g, 3.51 mmol) in THF (25 ml) was added **4** (200 mg, 0.39 mmol) in hexane (25 ml). After 21 h at 50 °C the solvents were evaporated under reduced pressure and the residue (mostly starting material) was purified by radial chromatography (hexane eluent) to give 310 mg (48%) of **10**.

M.p. > 290 °C (decomp.). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.41 (s, 36H). ^{13}C NMR ($CDCl_3$, 200 MHz): δ 0.9, 114.5, 200.5. ^{29}Si NMR ($CDCl_3$, 250 MHz): δ 0.7. IR (KBr): ν 2960w, 2900w, 2070s, 2050s, 2030s, 2000s, 1475s, 1410w, 1260w, 1250s, 835s, 750w, 685w, 620w, 540w, 520s and 490s cm^{-1}. UV (hexane): ϵ_{608} (l mol^{-1} cm^{-1}) = 1870, ϵ_{352} = 4602. *Anal.* Calc. for $C_{44}H_{36}Co_8O_{24}Si_4Sn$: C, 32.00; H, 2.20. Found: C, 31.69; H, 2.40%.

4.3. Reaction of tetrakis(trimethylsilylalkynyl) Group 14 metal derivatives with strong protic acids

Triflic acid (TfOH) was used neat. The reactions were started by the addition of TfOH (2.2 μl, 0.025 mmol) to a solution of the compound (0.50 ml, 0.05 M, 0.025 mol) in a 5 mm NMR tube. For all studies using methanesulfonic acid (MsOH), the reactions were started by the addition of a MsOH solution (0.10 ml of different concentrations in $CDCl_3$) to a solution of the compound in a 5 mm NMR tube (0.40 ml, 0.0625 M, 0.025 mmol). The adjustment of the NMR spectrometer typically required 90 s, after which the spectra were recorded. The reactions were followed on Bruker AC-200 (200 MHz) at r.t. (the temperature was maintained at 23 °C) and the time was recorded at the end of each spectrum of four scans. The spectral features of the biproducts are given here. The product ratios may be found in Table 4.

4.4. Reactions with triflic acid (TfOH)

4.4.1. From 2

$Me_3SiOSO_2CF_3$: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.53 (s, 4 × 9H).

$Si(C{\equiv}CH)_4$ [30]: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.64 (s, 4H).

4.4.2. From 3

$(Me_3SiC{\equiv}C)_3Ge(C{\equiv}CH)$: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.21 (s, 27H), 2.60 (s, 1H).

$(Me_3SiC{\equiv}C)_2Ge(C{\equiv}CH)_2$: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.25 (s, 18H), 2.52 (s, 2H).

$(Me_3SiC{\equiv}C)Ge(C{\equiv}CH)_3$: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.33 (s, 9H), 2.54 (s, 3H).

$Ge(C{\equiv}CH)_4$: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.54 (s, 4H).

4.4.3. From 4

$Me_3SiC{\equiv}CH$: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.20 (s, 9H), 2.33 (s, 1H).

$TfOSn(C{\equiv}CSiMe_3)_3$: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.26 (s, 27H).

4.5. Reactions with methane sulfonic acid

4.5.1. From 2

$MeSO_3SiMe_3$: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.53 (s, 9H), 3.08 (s, 3H).

4.6. Reaction with trifluoroacetic acid (TFA)

No reaction was observed between **2** or **3** and TFA over 12 h. Trifluoroacetic acid reacted with **4** to give initially (< 1 equiv.) $Me_3SiC{\equiv}CH$ and $F_3CCO_2Sn(C{\equiv}CSiMe_3)_3$. As the number of equivalents was increased, a complex reaction mixture resulted.

$(Me_3SiC{\equiv}C)_3SnO_2CCF_3$: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.23 (s, 27H).

4.7. Reaction of tetrakis(trimethylsilylalkynyl)($Co_2(CO)_6$ Group 14 metal derivatives with methanesulfonic acid (MsOH)

To a solution of the cobalt complex (≈ 10 mg) in $CDCl_3$ (0.5 ml) was added MsOH (≈ 2 equiv.). The ^{1}H NMR was followed over several hours. The only notable changes involved decomplexation of the cobalt and concomitant formation of a pink precipitate.

6: 10.8 mg (10 μmol), MsOH (1 drop).

^{1}H NMR 12 h, **6**:**5**:**2** 53:39:7. There were no $HC{\equiv}C$ peaks observed.

10: 10.0 mg (6.0 μmol), MsOH (3 drops, excess).

^{1}H NMR 12 h, **10**:**9** 95:5. There were no $HC{\equiv}C$ peaks observed. Some other peaks, possibly the bis- or tris-($Co_2(CO)_6$) compounds were observed: 0.25 (s, relative ratio 3), 0.06 (s, relative ratio 1).

*4.8. Reaction of **10** with tin compounds*

To a solution of **10** (10.0 mg, 6.0 μmol) in $CDCl_3$ (0.5 ml) was added $SnCl_4$ (5 drops, excess). Within 20 min, all starting material had disappeared leading to an intractable mixture.

To a solution of **10** (10.0 mg, 6.0 μmol) in $CDCl_3$ (0.5 ml) was added Ph_2SnCl_2 (prepared by the reaction of $SnPh_4$ with $SnCl_4$, [31,32], 2.1 mg, 6.0 μmol). After one week at r.t., there was no visible change in the solution by ^{1}H NMR.

5. Supplementary material

Tables listing bond lengths, bond angles, positional parameters, an ORTEP including full disorder, and displacement coefficients for **5** (25 pages) have been deposited with the Cambridge Crystallographic Data Center.

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