

A synthetic and structural study on metal cluster complexes of allyl–alkynyl–silanes: Does protonation lead to metal-stabilized silyl cations? ¹

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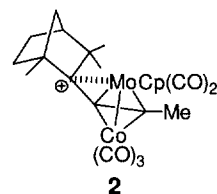
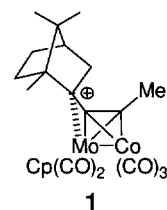
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Abstract

The mono-alkynes $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_2(\text{CH}_2\text{CH}=\text{CH}_2)$ **7** and $(\text{CH}_2=\text{CHCH}_2)\text{Me}_2\text{SiC}\equiv\text{CSiMe}_2(\text{CH}_2\text{CH}=\text{CH}_2)$ **8**, and the di-alkyne $(\text{CH}_2=\text{CHCH}_2)\text{Me}_2\text{SiC}\equiv\text{C}-\text{C}\equiv\text{CSiMe}_2(\text{CH}_2\text{CH}=\text{CH}_2)$ **9**, have been prepared and treated with $\text{Co}_2(\text{CO})_8$ and $\text{Mo}_2(\text{CO})_4\text{Cp}_2$, respectively, to give the corresponding dimetalla-alkyne tetrahedral complexes. Two of the clusters have been structurally characterised: $[\text{Cp}_2\text{Mo}_2(\text{CO})_4][\text{Me}_3\text{SiC}\equiv\text{CSiMe}_2(\text{CH}_2\text{CH}=\text{CH}_2)]$, **11**, crystallised in the space group $C2/c$ with $a = 15.058(3)$ Å, $b = 12.474(2)$ Å, $c = 29.128(6)$ Å, $\beta = 100.12(3)^\circ$, $V = 5386(2)$ Å³, $Z = 8$. $[\text{Co}_2(\text{CO})_6]_2((\text{CH}_2=\text{CHCH}_2)\text{Me}_2\text{SiC}\equiv\text{C}-\text{C}\equiv\text{CSiMe}_2(\text{CH}_2\text{CH}=\text{CH}_2))$, **13**, crystallised in the space group $C2/c$ with $a = 12.604(3)$ Å, $b = 15.447(3)$ Å, $c = 18.382(4)$ Å, $\beta = 107.20(3)^\circ$, $V = 3418(12)$ Å³, $Z = 4$. Treatment of each of these clusters with HBF_4 yielded the corresponding fluorosilane with concomitant formation of propene. It was shown that for $[\text{Co}_2(\text{CO})_6]_2(\text{CH}_2=\text{CHCH}_2)\text{Me}_2\text{SiC}\equiv\text{C}-\text{C}\equiv\text{CSiMe}_2(\text{CH}_2\text{CH}=\text{CH}_2)$ **15**, reaction with only one equivalent of HBF_4 yields the fluorosilane with loss of propene at the non-complexed alkynyl terminus. The relevance of these results to the possible intermediacy of a metal-stabilized silylium ion is discussed. © 1997 Elsevier Science S.A.

1. Introduction

The syntheses, structures, and reactivity of carbocations have played a pivotal role in chemistry for many decades. As shown in Olah's pioneering investigations, such species can be generated in superacid media and studied at leisure [1]. Moreover, as with other short-lived intermediates such as carbynes or cyclobutadienes, transition metal complexes of carbocations, such as **1** or **2**, can be isolated and characterised by X-ray crystallography [2,3].

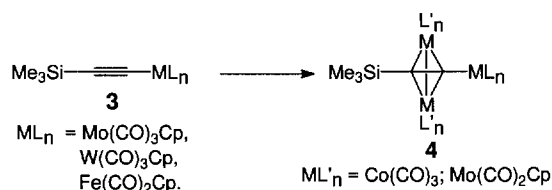
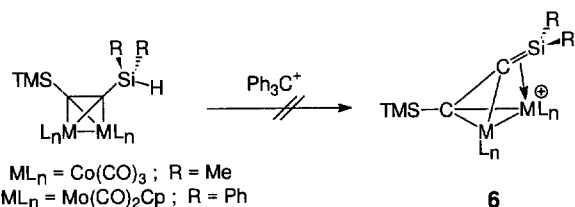


In contrast, the existence of silyl cations continues to attract controversy [4–8]. Silylium ions are thermodynamically stable; they are readily produced in the gas phase and can be conveniently studied by mass spectrometry [9,10]. However, the isolation of (putative

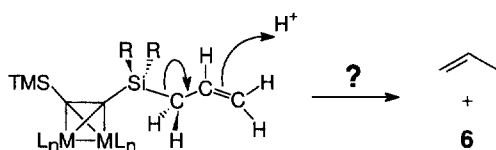
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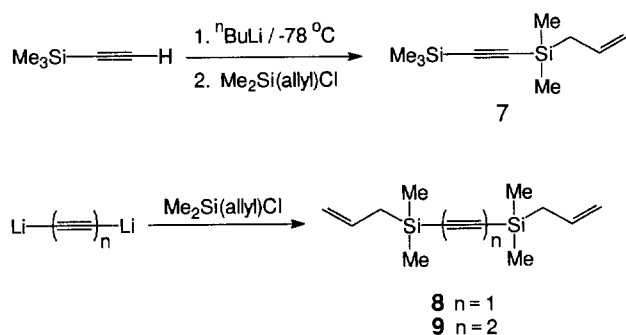
² Also corresponding author.

Scheme 1. Syntheses of clusters possessing $\eta^1\text{-ML}_n$ substituents.

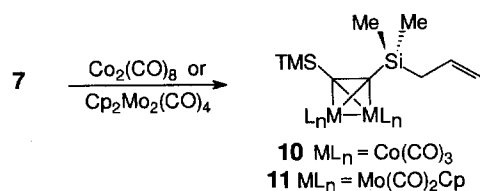
Scheme 2. Silicon hydride clusters do not yield metal-stabilized silyl cations.



Scheme 3. A possible route to metal-stabilized silyl cations from allylsilanes.



Scheme 4. Routes to allylsilyl-ynes and -diynes.



Scheme 5. Synthesis of allylsilyl dimetallic clusters.

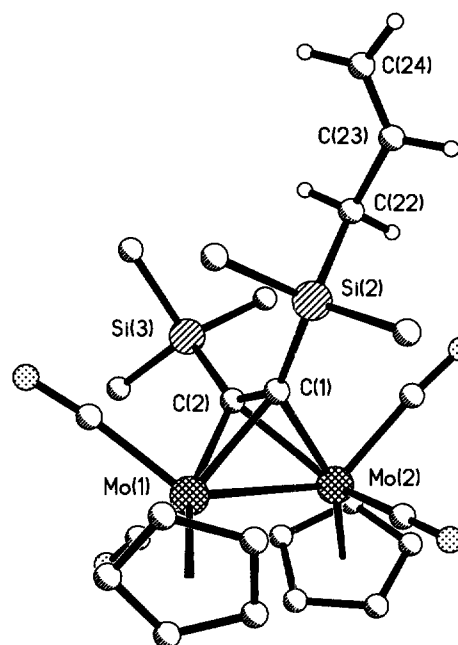
[11,12]) R_3Si^+ salts requires the use of 'least-coordinating' anions [13] as in $[\text{Et}_3\text{Si} \cdot \text{toluene}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ and $[(i\text{-Pr})_3\text{Si}]^+[\text{CB}_{11}\text{H}_6\text{Br}_6]^-$ [14,15].

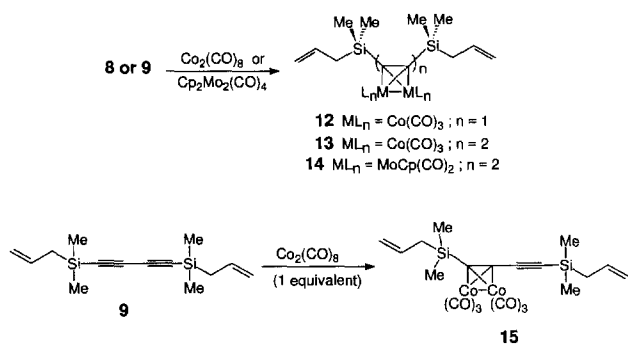
Transition metal cluster complexes of silyl poly-ynes have been the subject of several recent studies owing to their potential applications in materials science. Lang and co-workers have shown that η^1 -metalloalkynes **3** are precursors to the mixed-metal clusters **4** which, when pyrolyzed, yield metal carbide ceramics, as depicted in Scheme 1 [16–18].

Cobalt, nickel, molybdenum or tungsten clusters have also been prepared from diynes and tetraynes [19–23]. Perhaps the most fascinating molecule in this series of poly-yne derivatives is $\text{C}_{18}[\text{Co}_2(\text{CO})_4\text{dppm}]_3$, the tris-cluster complex derived from the nonayne cyclo[18]carbon [24]. Such clusters are also able to stabilize α -carbocations. We were interested to establish if they could also stabilize analogous silicon cations.

We have previously reported the syntheses of a series of metal cluster complexes **5**, which possess an Si–H unit [25]. However, attempts to generate a metal-stabilized silyl cation **6**, from this compound by using the Ph_3C^+ cation to abstract a hydride moiety were unsuccessful. Indeed, the X-ray crystal structure of **5b** suggests that steric hindrance precludes the approach of the bulky trityl cation to the Si–H bond, as seen in Scheme 2.

We describe herein the syntheses and reactivity of a series of allylsilane derivatives of metal clusters. These compounds should be subject to protonation at the γ -carbon with generation of a β -silyl-stabilized cation [26,27]. Cleavage of the silicon α -carbon bond and subsequent loss of propene could then lead to a silyl

Fig. 1. X-ray crystal structure of **11**.



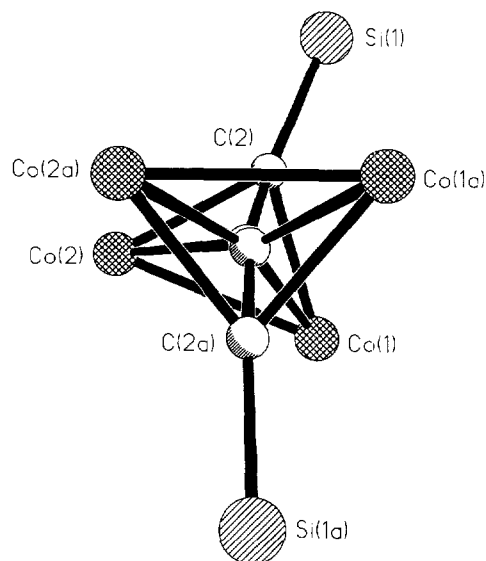
Scheme 6. Routes to allylsilane metal clusters.

cation, as depicted in Scheme 3. This process will occur via an S_E2' mechanism, as shown by Hosomi and Sakurai [28] and Fleming et al. [29]. Protonation at the terminal allylic carbon should alleviate the steric problems associated with direct electrophilic attack at the silicon center. In the carbocation series, McClain et al. [30] have reported the X-ray crystal structure of the dimolybdenum dication $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{CH}_2\text{-C}\equiv\text{C-CH}_2)]^{2+}$, and one can envisage the possibility of preparing a disilylium analogue.

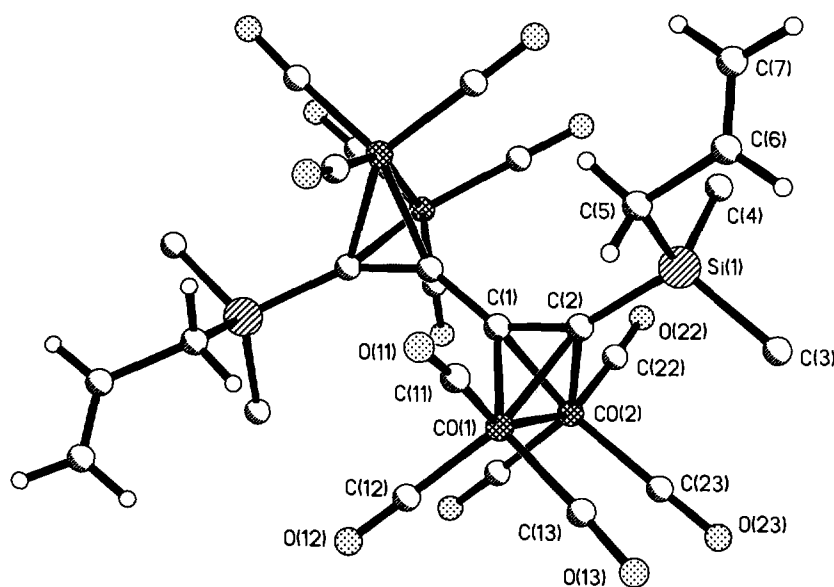
2. Results and discussion

2.1. Synthetic and structural aspects

As a prelude to the syntheses of a series of alkynylsilane clusters, the mono- and di-alkynyl silanes **7**, **8**, and **9** were prepared by treatment of the appropriate lithio-alkyne with allyldimethylchlorosilane, as shown in Scheme 4.

Fig. 3. View along the C(1a)–C(1) bond in **13** showing the staggered conformation of the two cluster cores.

As depicted in Scheme 5, the mono-allyl system **7** reacts with $\text{Co}_2(\text{CO})_8$ or $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ to yield the dimetallatetrahedranes **10** or **11**, respectively. These clusters were identified by the use of ^1H , ^{13}C , and ^{29}Si NMR, infrared spectroscopy and mass spectrometry; the dimolybdenum cluster **11**, was additionally characterised by X-ray crystallography. The structure of **11** appears in Fig. 1 and the overall molecular geometry closely resembles those previously reported [25,31] for the related systems $[\text{Cp}_2\text{Mo}_2(\text{CO})_4](\text{Me}_3\text{Si-C}\equiv\text{C-SiPh}_2\text{H})$, **5b** and $[\text{Cp}_2\text{Mo}_2(\text{CO})_4](\text{Me}_3\text{Si-C}\equiv\text{C-SiMe}_3)$. For our present purposes, however, we note that the allyl fragment is oriented so as to leave the terminal

Fig. 2. X-ray crystal structure of **13**.

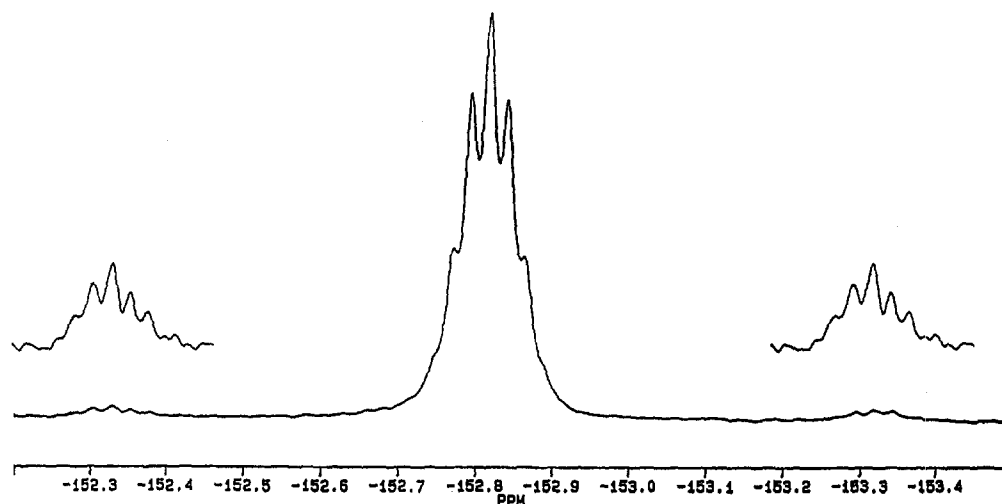
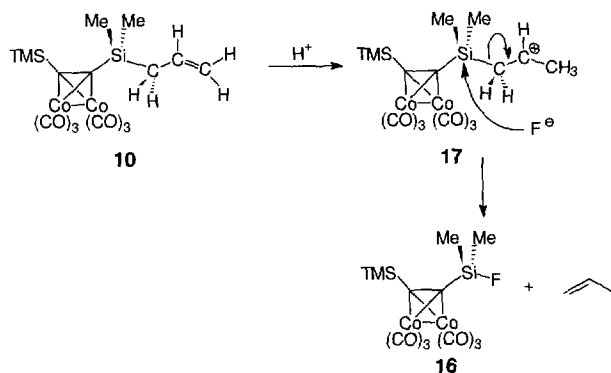


Fig. 4. 282.42 MHz ^{19}F NMR spectrum of $(\text{Me}_3\text{Si-C}\equiv\text{C-SiMe}_2\text{F})\text{Co}_2(\text{CO})_6$, **16**, showing the ^{29}Si satellite peaks.

methylene group entirely exposed and readily accessible to an incoming electrophile.

Treatment of the diallyl-monoalkyne and -dialkyne, **8** and **9**, respectively, with excess $\text{Co}_2(\text{CO})_8$ or $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ yielded the clusters **12**, **13** and **14**. The reaction of **9** with one equivalent of $\text{Co}_2(\text{CO})_8$ led to the unsymmetrical product **15** which possesses both a free and complexed triple bond, as depicted in Scheme 6. The X-ray crystal structure of the diallyl double cluster **13** is shown in Fig. 2. As with the bis-trimethylsilyl analogue, $(\text{Me}_3\text{Si-C}\equiv\text{C-C}\equiv\text{C-SiMe}_3)[\text{Co}_2(\text{CO})_6]_2$, previously reported by Magnus and Becker [21], the cluster core adopts the 'staggered ethane' conformation illustrated in Fig. 3. The torsion angle $\text{C}(2)\text{-C}(1)\text{-C}(1\text{A})\text{-C}(2\text{A})$ is 162° .

In contrast to the normal linear arrangement of the $\text{C-C}\equiv\text{C-C}$ linkage in free alkynes, complexation of the triple bond to a dimetallic fragment brings about a $\text{C-C}\equiv\text{C}$ bond angle in the range 136° to 145° as also seen in the structure of **13**. Thus, $\text{Co}_2(\text{CO})_6$ moieties have been used not only as protecting groups [32], but also to allow geometrically disfavored cyclization reactions [33–35], or to stabilize strained alkynes such as (hexafluorocyclohexa-3-ene-1-yne)[$\text{Co}_2(\text{CO})_6$] [36].

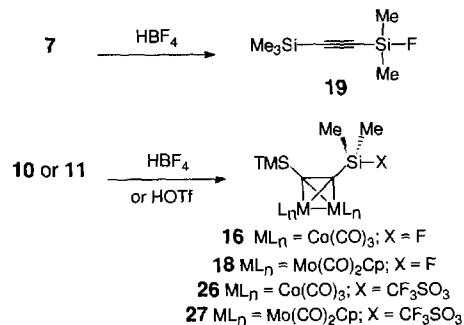


Scheme 7. Proposed mechanism for the formation of **16**.

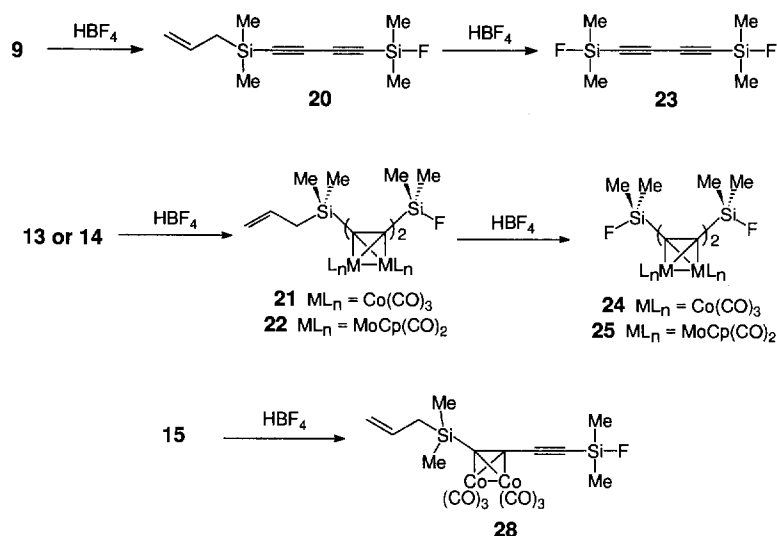
One could envisage the incorporation of the diyne cluster **13** into a cyclodiallykyne, perhaps via successive hydrosilylations [37]. However, the steric bulk of the double cluster hinders rotation about the central carbon-carbon bond and forces the two allyl substituents to maintain their approximate anti-periplanar orientation, a conformation from which cyclization could not readily be envisaged.

2.2. Reactions of allyl clusters with HBF_4

The protonation of $(\text{Me}_3\text{Si-C}\equiv\text{C-SiMe}_2\text{-CH}_2\text{-CH=CH}_2)\text{Co}_2(\text{CO})_6$, **10**, with HBF_4 in an NMR tube at -90°C was monitored by ^{13}C , ^{19}F and ^{29}Si NMR spectroscopy. At that temperature, the formation of the fluorosilane **16** was readily observable via the appearance of a 269 Hz silicon-coupled doublet in the ^{19}F spectrum, as shown in Fig. 4. Concomitantly, the ^{13}C NMR spectrum revealed peaks at 133.8, 115.1 and 74.7 ppm, characteristic for propene [38]. There was no evidence for the production of either a β -stabilized silyl cation, **17**, nor for a silylium ion. We note that Lambert has very recently reported NMR data for a β -stabilized silyl cation [26,27]. If either of these species are produced, their lifetime must be very short under these



Scheme 8. Reactions of allyldisilaalkynes with HBF_4 or triflic acid.

Scheme 9. Reactions of diallyldisilaalkynes with HBF_4 .

reaction conditions. The most probable scenario involves protonation of the allyl unit with subsequent rapid, nucleophilic attack by fluoride ion at silicon, as depicted in Scheme 7.

Analogously, the dimolybdenum allyl cluster **11**, and the free ligand **7**, both behave similarly with HBF_4 to give the corresponding fluorosilanes, **18** and **19**, respectively as depicted in Scheme 8. Treatment of the bis-allyl compounds **9**, **13** and **14** with one equivalent of HBF_4 gives the monofluorosilane products, **20**, **21** and **22**, respectively. Addition of a further equivalent of HBF_4 yielded the corresponding di-fluorosilanes, **23**, **24** and **25**, respectively, as shown by ^{29}Si NMR (see Scheme 9). In a similar experiment, treatment of **10** and **11** with triflic acid yields the analogous silyl triflates, **26** and **27**, as in Scheme 8.

We have shown previously, by means of molecular orbital calculations at the extended Hückel level, that dimetallic clusters should provide some modest stabilization to alkynyl-silylium ions [25]. However, if the propene elimination process were to occur by the mechanism depicted in Scheme 7, one would not necessarily expect enhanced reactivity for the Co or Mo clusters relative to the free ligands: the metal is too far removed from the intermediate β -silyl cation to participate in its stabilization. To examine this question, a series of competitive protonation experiments were run on the NMR-tube scale; equimolar quantities of **7** vs. **10**, **7** vs. **11**, and **10** vs. **11**, were each treated with somewhat less than one equivalent of HBF_4 at $-80^\circ C$, and the progress of the reaction was monitored by ^{19}F NMR. The NMR data (see Section 3) showed that, within the error limits, the free ligand and the Co or Mo complexes proved to be equally susceptible to protonation of the allyl substituents, with subsequent formation of the appropriate fluorosilane.

However, these experiments are open to the criticism that the free silyl-alkyne and its cluster complexes may not be equally soluble in the medium. To counter this argument, the mono-complexed diyne **15** was also allowed to react with HBF_4 at -80° , in this case, the ^{29}Si NMR spectrum of the product indicated that the major product, **28** was derived from attack on the allyl-silane at the uncomplexed triple bond, as seen in Scheme 9.

It is apparent from the above studies that if free silylium ions are produced in these protodesilylation reactions, they are insufficiently stabilized by the transition metals to have reasonable lifetimes. This may be a consequence of poor stabilisation but may be more likely attributed to the facility with which triflate, and particularly fluoride, attack silicon nuclei. Thus, to achieve the preparation of a transition metal stabilized silylium ion, we too will have to resort to the use of non-nucleophilic counter-ions.

2.3. Conclusions

The complexation of monoallyl- and diallyl-disilaalkynes and diallyl-disiladialkynes with $Co_2(CO)_6$ or $Mo_2(CO)_4Cp_2$ fragments readily occurs. It has been clearly demonstrated that protonation at the methylene terminus of an alkynylallylsilane (free or metal complexed alkyne) with either HBF_4 or triflic acid readily occurs with elimination of propene and formation of the corresponding silyl fluoride or triflate. There is, as yet, no evidence of an isolable metal-stabilized silyl cationic intermediate. It is evident that these electrophilic attacks on the allyl-silanes must avoid the use of any counterions that could form covalent bonds with silicon. Future manuscripts will describe our endeavors in this area.

3. Experimental

3.1. Instrumentation

All experiments were carried out under an atmosphere of dry nitrogen, using standard Schlenk techniques. ^1H , ^{13}C , ^{19}F , and ^{29}Si NMR spectra were recorded on a Bruker AC-200, AC-300, or an Avance DRX-500 spectrometer. Proton spectra on the latter instrument were acquired using a 5 mm broadband inverse probe with triple axis gradient capability. Spectra were obtained with 8 scans in 32K data points over a 3.788 kHz spectral width (4.325 s acquisition time). The sample temperature was maintained at 30°C by a Bruker Eurotherm variable-temperature unit. The free induction decay (FID) was processed using exponential multiplication (line broadening: 0.2 Hz) and was zero-filled to 64K before Fourier transformation.

Infrared spectra were obtained on a Bio-Rad FTS-40 spectrometer, using NaCl windows. Electron impact (EI) and chemical ionization (CI, NH_3) mass spectra were recorded at 70 eV with a source temperature of 200°C on a VG analytical ZAB-E mass spectrometer equipped with a VG 11-250 data system.

3.2. Materials

Tetrahydrofuran (Caledon), acetonitrile (Caledon) and di-*n*-butyl ether (Aldrich) were distilled from potassium/benzophenone. CH_2Cl_2 (Caledon) was distilled prior to use from P_2O_5 . Hexane (Caledon) and toluene (Caledon) were distilled prior to use. Only distilled water was used. Allyldimethylchlorosilane (Aldrich) was distilled prior to use. Otherwise, the compounds from Aldrich: *n*-butyllithium, dibutylether, trimethylsilylethyne, trichloroethylene, hexachlorobutadiene, triflic acid, and HBF_4 -etherate complex were used without further purification. $\text{Co}_2(\text{CO})_8$, and $\text{Mo}_2\text{Cp}_2(\text{CO})_6$ were obtained from Strem Chemicals, and were used as supplied without further purification. The $\text{Mo}_2\text{Cp}_2(\text{CO})_6$ was heated under reflux in toluene for 24 h in order to form the more reactive $\text{Cp}(\text{CO})_2\text{Mo}\equiv\text{Mo}(\text{CO})_2\text{Cp}$ [39], which was subsequently used in situ for the preparations detailed below.

3.3. Preparation of $\text{Me}_3\text{SiC}\equiv\text{C-SiMe}_2(\text{allyl})$, (7)

n-Butyllithium (96 ml, 2.5 M in hexane, 0.25 mol) was added dropwise to a solution of trimethylsilylethyne (25 g, 0.25 mol) in diethyl ether (100 ml) at -78°C via syringe over a 30-min period, and the solution was then allowed to warm to room temperature. After stirring for 2 h, the solution was cooled to -78°C and allyldimethylchlorosilane (36 ml, 0.25 mol) in diethyl ether (15 ml) was added dropwise. The solution was allowed to warm to room temperature and

stirred for 24 h. The product was extracted into diethyl ether, and the separated organic phase was dried over MgSO_4 for 2 h. Removal of the volatile organic solvents by rotary evaporation yielded the product **7** as a clear oil (44.8 g, 0.24 mol, 96%).

7: ^1H NMR (CDCl_3 , 500.13 MHz) δ 5.77 (m, 1H, $\text{CH}_2=\text{CHCH}_2$), 4.89 (m, 2H, $\text{CH}_2=\text{CHCH}_2$), 1.60 (m, 2H, $\text{CH}_2=\text{CHCH}_2$), 0.14 (s, 6H, $\text{Si}(\text{CH}_3)_2$), 0.12 (s, 9H, $\text{Si}(\text{CH}_3)_3$); ^{13}C NMR (CDCl_3 , 75.03 MHz) δ 133.8 ($\text{CH}_2=\text{CHCH}_2$), 114.8 ($\text{CH}_2=\text{CHCH}_2$), 113.9, 112.0 ($\text{C}\equiv\text{C}$), 24.0 ($\text{CH}_2=\text{CHCH}_2$), -0.1 (SiMe_2), -2.3 (SiMe_3); ^{29}Si NMR (CH_2Cl_2 , 59.6 MHz) δ -19.0 , -19.2 . Mass spectrum (DEI, m/z (%)): 181 (76) $[\text{M}-\text{CH}_3]^+$, 166 (87) $[\text{M}-2\times\text{CH}_3]^+$, 155 (100) $[\text{M}-\text{CH}_2=\text{CHCH}_2]^+$, 73 (65) $[\text{TMS}]^+$; (CI, NH_3 , m/z (%)): 214 (78) $[\text{M}]^+$, 197 (41) $[\text{M}+1]^+$; (high resolution, DEI): calculated mass for $^{12}\text{C}_9\text{H}_{17}\text{Si}_2$ $[\text{M}-\text{Me}]^+$, 181.0869, observed, 181.0866 amu.

3.4. Preparation of bis-allyl ligands $(\text{allyl})\text{Me}_2\text{Si}(\text{C}\equiv\text{C})_n\text{-SiMe}_2(\text{allyl})$; $n = 1$, (8), and $n = 2$ (9)

n-Butyllithium (3 equivalents for **8**, 4 equivalents for **9**) was added dropwise to a solution of chlorohydrocarbon (trichloroethylene (6.9 g, 0.053 mol) for **8**, hexachlorobutadiene (15.7 g, 61 mmol) for **9**) in diethyl ether (30 ml) at -78°C via cannula over a 30 min period. After stirring for 2 h, the solution was cooled to -78°C and allyldimethylchlorosilane (for **8**: 16.6 ml, 14.8 g, 0.12 mol; for **9**: 18 ml, 15.7 g, 0.13 mol) in diethyl ether (5 ml) was added dropwise; the solution was allowed to warm to room temperature and stirred for 24 h. The product was extracted with water. After removal of volatile components by rotary evaporation, the organic phase yielded (**8**: 85%, or **9**: 80%) as an oil.

8: ^1H NMR (CDCl_3 , 300.13 MHz) δ 5.75 (m, 1H, $\text{CH}_2=\text{CHCH}_2$), 4.84 (m, 2H, $\text{CH}_2=\text{CHCH}_2$), 1.59 (m, 2H, $\text{CH}_2=\text{CHCH}_2$), 0.13 (s, 6H, $\text{Si}(\text{CH}_3)_2$); ^{13}C NMR (CDCl_3 , 50.03 MHz) δ 133.6 ($\text{CH}_2=\text{CHCH}_2$), 113.8 ($\text{CH}_2=\text{CHCH}_2$), 80.0 ($\text{C}\equiv\text{C}$), 23.9 ($\text{CH}_2=\text{CHCH}_2$), -2.4 ($\text{Si}(\text{CH}_3)_2$); ^{29}Si NMR (CH_2Cl_2 , 59.6 MHz) δ -19.4 . Mass spectrum (DEI, m/z (%)): 207 (16) $[\text{M}-\text{CH}_3]^+$, 181 (24) $[\text{M}-\text{CH}_2=\text{CHCH}_2]^+$, 99 (14) $[\text{CH}_2=\text{CHCH}_2\text{SiMe}_2]^+$; (CI, NH_3 , m/z (%)): 240 (19) $[\text{M}+18]^+$, 223 (65) $[\text{M}+\text{H}]^+$; (high resolution, DEI): calculated mass for $^{12}\text{C}_{11}\text{H}_{19}\text{Si}_2$ $[\text{M}-\text{Me}]^+$, 207.1025, observed, 207.1016 amu.

9 [40]: ^1H NMR (CDCl_3 , 500.13 MHz) δ 5.75 (m, 1H, $\text{CH}_2=\text{CHCH}_2$), 4.88 (m, 2H, $\text{CH}_2=\text{CHCH}_2$), 1.61 (m, 2H, $\text{CH}_2=\text{CHCH}_2$), 0.15 (s, 6H, $\text{Si}(\text{CH}_3)_2$); ^{13}C NMR (CDCl_3 , 125.03 MHz) δ 133.0 ($\text{CH}_2=\text{CHCH}_2$), 114.6 ($\text{CH}_2=\text{CHCH}_2$), 88.8, 84.3 ($\text{C}=\text{C}$), 23.3 ($\text{CH}_2=\text{CHCH}_2$), -2.8 ($\text{Si}(\text{CH}_3)_2$); ^{29}Si NMR (CH_2Cl_2 , 59.6 MHz) δ -16.5 . Mass spectrum (DEI, m/z (%)): 231 (17) $[\text{M}-\text{CH}_3]^+$, 205 (100) $[\text{M}-$

$\text{CH}_2=\text{CHCH}_2]^+$, 164 (51) $[\text{M}-2 \times (\text{CH}_2=\text{CHCH}_2)]^+$; (Cl, NH_3 , m/z (%)): 264 (100) $[\text{M}+18]^+$, 247 (27) $[\text{M}+H]^+$; (high resolution, DEI): calculated mass for $^{12}\text{C}_{13}\text{H}_{19}\text{Si}_2$ $[\text{M}-\text{Me}]^+$, 231.1025, observed, 231.1023 amu.

3.5. Preparation of di-metallic clusters of general type $(\text{Me}_3\text{Si}-\text{C}\equiv\text{CSiMe}_2(\text{allyl}))[\text{ML}_n]_2$ (**10**) and (**11**)

The appropriate metal carbonyl was dissolved in THF (30 ml), and solution of **7** in THF (10 ml) was added dropwise over a period of 30 min at 25°C. The reaction mixture was allowed to stir overnight at room temperature. The solvent was removed by rotary evaporation, and the mixture was then subjected to flash chromatography on silica gel, which gave the desired compound.

For **10**: $\text{Co}_2(\text{CO})_8$ (2.33 g, 6.8 mmol) and **7** (1.33 g, 6.8 mmol) yielded **10** as a red oil (2.05 g, 5.8 mmol; 88%). ^1H NMR (CD_2Cl_2 , 200 MHz) δ 5.88 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 4.98 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 1.84 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 0.36 (s, 9H, SiMe_3), 0.37 (s, 6H, SiMe_2); ^{13}C NMR (CD_2Cl_2 , 50.3 MHz) δ 203.3 ($\text{C}\equiv\text{O}$), 135.9 ($\text{CH}_2\text{CH}=\text{CH}_2$), 116.4 ($\text{CH}_2\text{CH}=\text{CH}_2$), 95.4, 92.9 ($\text{C}\equiv\text{C}$), 27.3 ($\text{CH}_2\text{CH}=\text{CH}_2$), 2.9 (SiMe_3), -0.49 ($\text{SiMe}_2(\text{allyl})$); ^{29}Si NMR (CH_2Cl_2 , 59.6 MHz) δ 0.64 (SiMe_3), -0.81 ($\text{SiMe}_2(\text{allyl})$). IR (neat) ν_{CO} at 2048 and 2017 cm^{-1} . Mass spectrum (DEI, m/z (%)): 426 (40) $[\text{M}-2\text{CO}]^+$, 398 (30) $[\text{M}-3\text{CO}]^+$, 370 (75) $[\text{M}-4\text{CO}]^+$, 342 (70) $[\text{M}-5\text{CO}]^+$, 314 (100) $[\text{M}-6\text{CO}]^+$.

For **11**: $\text{Mo}_2\text{Cp}_2(\text{CO})_6$ (1.73 g, 3.5 mmol) and **7** (0.69 g, 3.5 mmol) yielded **11** as red crystals (1.8 g, 2.8 mmol; 80%). ^1H NMR (CD_2Cl_2 , 200 MHz) δ 5.78 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.19 (s, 10H, Cp-H's), 4.87 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 1.72 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 0.20 (s, 9H, SiMe_3), 0.12 (s, 6H, SiMe_2); ^{13}C NMR (CD_2Cl_2 , 50.3 MHz) δ 229.6 ($\text{C}\equiv\text{O}$), 135.8 ($\text{CH}_2\text{CH}=\text{CH}_2$), 113.5 ($\text{CH}_2\text{CH}=\text{CH}_2$), 92.7, 92.5 ($\text{C}\equiv\text{C}$), 88.9 (Cp's), 27.3 ($\text{CH}_2\text{CH}=\text{CH}_2$), 3.5 (SiMe_3), 0.6 ($\text{SiMe}_2(\text{allyl})$); ^{29}Si NMR (CH_2Cl_2 , 59.6 MHz) δ -7.1 (SiMe_3), -10.9 ($\text{SiMe}_2(\text{allyl})$). IR (neat) ν_{CO} at 2066 and 1998 cm^{-1} . Analysis: Found: C, 45.81; H, 4.72; $\text{C}_{24}\text{H}_{30}\text{Mo}_2\text{O}_4\text{Si}_2$ Calc.: C, 45.72; H, 4.80.

3.6. Preparation of di-metallic clusters of general type $(\text{allyl})\text{Me}_2\text{Si}-(\text{C}\equiv\text{C})_n-\text{SiMe}_2(\text{allyl})[\text{ML}_n]_2$; (**12**), (**13**), (**14**), and (**15**)

The appropriate metal carbonyl was dissolved in THF (30 ml), and solution of the alkynyl ligand in THF (10 ml) was added dropwise over a period of 30 min at 25°C. The reaction mixture was allowed to stir overnight at room temperature. The solvent was removed by rotary evaporation, and the mixture was then subjected

to flash chromatography on silica gel, which gave the desired compound.

For **12**: $\text{Co}_2(\text{CO})_8$ (1.71 g, 5.0 mmol) and **8** (1.11 g, 5.0 mmol) yielded **12** as a red oil (2.2 g, 4.4 mmol; 87%). ^1H NMR (CD_2Cl_2 , 200.13 MHz) δ 5.78 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 4.95 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 1.63 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 0.29 (s, 6H, SiMe_2); ^{13}C NMR (CD_2Cl_2 , 75.03 MHz) δ 201.6 ($\text{C}\equiv\text{O}$), 133.6 ($\text{CH}_2\text{CH}=\text{CH}_2$), 114.6 ($\text{CH}_2\text{CH}=\text{CH}_2$), 25.2 ($\text{CH}_2\text{CH}=\text{CH}_2$), -1.0 (SiMe_2); ^{29}Si NMR (CH_2Cl_2 , 59.6 MHz) δ -0.8 (SiMe_2). IR (neat) ν_{CO} at 2018, 2046, and 2085 cm^{-1} . Mass spectrum (DEI, m/z (%)): 467 (15) $[\text{M}-(\text{CH}_2\text{CH}=\text{CH}_2)]^+$, 424 (60) $[\text{M}-3(\text{CO})]^+$, 396 (50) $[\text{M}-4(\text{CO})]^+$, 368 (45) $[\text{M}-5(\text{CO})]^+$, 340 (100) $[\text{M}-6(\text{CO})]^+$.

For **13**: $\text{Co}_2(\text{CO})_8$ (4.2 g, 12.3 mmol) and **9** (1.2 g, 4.9 mmol) yielded **13** as green crystals (2.7 g, 3.3 mmol; 67%). ^1H NMR (CD_2Cl_2 , 200 MHz) δ 5.87 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 4.93 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 1.91 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 0.32 (s, 6H, SiMe_2); ^{13}C NMR (CD_2Cl_2 , 50.3 MHz) δ 200.0 ($\text{C}\equiv\text{O}$), 134.0 ($\text{CH}_2\text{CH}=\text{CH}_2$), 114.7 ($\text{CH}_2\text{CH}=\text{CH}_2$), 25.0 ($\text{CH}_2\text{CH}=\text{CH}_2$), -1.4 ($\text{SiMe}_2(\text{allyl})$); ^{29}Si NMR (CH_2Cl_2 , 59.6 MHz) δ -0.9. IR (neat) ν_{CO} at 2077, 2057 and 2029 cm^{-1} . Analysis: Found: C, 38.30; H, 2.58; $\text{C}_{26}\text{H}_{22}\text{Co}_4\text{O}_{12}\text{Si}_2$ Calc.: C, 38.15; H, 2.71.

For **14**: $\text{Mo}_2\text{Cp}_2(\text{CO})_6$ (7.4 g, 15.2 mmol) and **9** (1.5 g, 6.1 mmol) yielded **14** as a red oil (4.9 g, 4.4 mmol; 72%). ^1H NMR (CD_2Cl_2 , 200 MHz) δ 5.79 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.37 (s, 20H, Cp-H's), 5.00 (m, 4H, $\text{CH}_2\text{CH}=\text{CH}_2$), 1.69 (s, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 0.14 (s, 12H, SiMe_2); ^{13}C NMR (CD_2Cl_2 , 50.3 MHz) δ 135.3 ($\text{CH}_2\text{CH}=\text{CH}_2$), 113.4 ($\text{CH}_2\text{CH}=\text{CH}_2$), 92.7 (Cp's), 25.3 ($\text{CH}_2\text{CH}=\text{CH}_2$), -1.2 ($\text{SiMe}_2(\text{allyl})$); ^{29}Si NMR (CH_2Cl_2 , 59.6 MHz) δ -22.2. IR (neat) ν_{CO} at 1998, 1957 and 1935 cm^{-1} .

For **15**: $\text{Co}_2(\text{CO})_8$ (1.9 g, 5.5 mmol) and **9** (1.5 g, 6.1 mmol) yielded **15** as a dark red oil (1.81 g, 3.4 mmol; 62%). ^1H NMR (CD_2Cl_2 , 200 MHz) δ 5.79 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 4.89 (m, 4H, $\text{CH}_2\text{CH}=\text{CH}_2$), 1.65 (m, 4H, $\text{CH}_2\text{CH}=\text{CH}_2$), 0.30, 0.19 (s, 12H, SiMe_2). ^{13}C NMR (CD_2Cl_2 , 50.3 MHz) δ 199.8 ($\text{C}\equiv\text{O}$), 134.3, 133.7 ($\text{CH}_2\text{CH}=\text{CH}_2$), 114.6, 114.0 ($\text{CH}_2\text{CH}=\text{CH}_2$), 103.8, 102.1 (cluster carbons), 89.0, 85.2 ($\text{C}\equiv\text{C}$), 24.2, 23.7 ($\text{CH}_2\text{CH}=\text{CH}_2$), -1.5, -2.3 ($\text{SiMe}_2(\text{allyl})$); ^{29}Si NMR (CH_2Cl_2 , 59.6 MHz) δ 0.9, -15.4. IR (hexane) ν_{CO} at 2092, 2058 and 2032 cm^{-1} .

3.7. Reaction of $\text{Me}_3\text{Si}-\text{C}\equiv\text{C}-\text{SiMe}_2(\text{allyl})[\text{ML}_n]_2$ with HBF_4

To a solution of the compound in CH_2Cl_2 (0.5 ml of a 0.05 M solution) in a 5 mm NMR tube was added HBF_4 -etherate complex (0.9 equiv.) at -80°C. The 282.42 MHz ^{19}F spectra were acquired at this temperature. **7** gave **19**: δ -156.8 (septet, $^1J_{\text{Si}-\text{F}} = 269$ Hz;

$^3J_{F-H} = 7$ Hz). **10** gave **16**: $\delta -152.8$ (septet, $^1J_{Si-F} = 279$ Hz; $^3J_{F-H} = 6$ Hz). **11** gave **18**: $\delta -132.2$ (septet, $^1J_{Si-F} = 269$ Hz; $^3J_{F-H} = 7$ Hz).

3.8. Reaction of (allyl)Me₂Si-C≡C-C≡C-SiMe₂(allyl)[ML_n]_m (m = 2 or 4) with HBF₄

To a solution of the compound in CH₂Cl₂ (1.5 ml of a 0.05 M solution) in a 10 mm NMR tube was added HBF₄-etherate complex (0.9 equiv.) at -80°C . The 59.6 MHz ²⁹Si NMR spectra were acquired at this temperature. The sample was then removed from the probe and kept at -80°C in a dry ice/isopropanol bath where a second equivalent of HBF₄ was added, and the ²⁹Si NMR spectrum was obtained at -80°C . **9** gave **20**: $\delta -6.1$ (d, $^1J_{Si-F} = 278$ Hz), -15.7 (s); and then **23**: $\delta 4.1$ (d, $^1J_{Si-F} = 271$ Hz). **13** gave **21**: $\delta 17.1$ (d, $^1J_{Si-F} = 278$ Hz), 5.9 (s); and then **24**: $\delta 17.1$ (d, $^1J_{Si-F} = 278$ Hz). **14** gave **22**: $\delta 3.6$ (d, $^1J_{Si-F} = 270$ Hz), -15.8 (s); and then **25**: $\delta 3.9$ (d, $^1J_{Si-F} = 271$ Hz).

Table 1
Crystal data and structure refinement for **11** and **13**

	11	13
Empirical formula	C ₂₄ H ₃₀ Mo ₂ O ₄ Si ₂	C ₂₆ H ₂₂ Co ₄ O ₁₂ Si ₂
Molecular weight	630.54	818.34
Description	parallelepiped	plate
Dimensions, mm	0.3 × 0.2 × 0.2	0.3 × 0.2 × 0.35
Temperature, K	293(2)	293(2)
Wavelength, Å	0.71073	0.56086
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	C2/c
Z	8	4
a, Å	15.058(3)	12.604(3)
b, Å	12.474(2)	15.447(3)
c, Å	29.128(6)	18.382(4)
β, deg	100.12(3)	107.20(3)
Volume, Å ³	5386(2)	3418.8(12)
Calc. Density, g/cm ³	1.555	1.590
Abs coeff., mm ⁻¹	1.046	1.055
F(000)	2544	1640
θ-range for collection, deg.	2.13 to 29.98	1.69 to 16.05
Index ranges	-19 ≤ h ≤ 19 0 ≤ k ≤ 17 0 ≤ l ≤ 40	-1 ≤ h ≤ 12 -1 ≤ k ≤ 15 -18 ≤ l ≤ 17
No. Reflections collected	6630	2212
No. Independent reflection	6630	1708
R(int)	0.0470	0.0665
Refinement method	Full-matrix least-squares on F ²	
Data/restraints/parameter	6595/0/289	1708/0/199
Goodness-of-fit on F ²	1.059	0.594
Final R indices (I > 2σ(I)) ^a	R ₁ = 0.0433 wR ₂ = 0.0932	R ₁ = 0.0387 wR ₂ = 0.0460
R indices (all data) ^a	R ₁ = 0.0751 wR ₂ = 0.1250	R ₁ = 0.1713 wR ₂ = 0.0673
Largest diff. Peak, e/Å ³	0.722	0.257
Largest diff. Hole, e/Å ³	-0.390	-0.258

^a $R_1 = \sum (|F_o| - |F_c|) / \sum |F_o|$; $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{0.5}$.

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **11**

	x	y	z	U _{eq}
Mo(1)	2597(1)	3594(1)	1870(1)	43(1)
Mo(2)	1916(1)	2688(1)	948(1)	43(1)
Si(3)	70(1)	3960(1)	1404(1)	47(1)
Si(2)	2100(1)	5765(1)	1032(1)	52(1)
C(1)	1942(3)	4376(3)	1234(1)	39(1)
C(2)	1279(3)	3793(3)	1373(1)	38(1)
C(3)	3893(4)	2764(5)	2260(2)	81(2)
C(4)	3762(4)	3704(6)	2497(2)	84(2)
C(5)	3874(3)	4572(5)	2199(2)	74(2)
C(6)	4071(3)	4142(4)	1789(2)	62(1)
C(7)	4083(3)	3026(5)	1829(2)	68(2)
C(8)	1686(5)	1200(4)	478(2)	81(2)
C(9)	2375(5)	934(4)	845(2)	79(2)
C(10)	2012(4)	926(4)	1249(2)	77(2)
C(11)	1090(4)	1184(4)	1139(2)	73(2)
C(12)	883(4)	1355(4)	659(2)	82(2)
C(13)	3098(3)	3121(5)	819(2)	64(1)
C(14)	1429(3)	3476(4)	372(2)	55(1)
C(15)	1951(3)	4510(4)	2256(2)	55(1)
C(16)	1916(4)	2427(4)	2089(2)	63(1)
C(17)	-335(4)	2970(5)	1792(2)	83(2)
C(18)	-143(4)	5318(5)	1633(2)	81(2)
C(19)	-604(3)	3840(5)	808(2)	67(1)
O(13)	3788(3)	3299(4)	721(2)	95(2)
O(14)	1180(3)	3873(4)	19(1)	87(1)
O(15)	1630(3)	4999(4)	2517(1)	87(1)
O(16)	1562(3)	1728(4)	2245(1)	90(1)
C(20)	2202(4)	6696(4)	1536(2)	76(2)
C(21)	3116(4)	5885(5)	752(2)	92(2)
C(22)	1101(4)	6232(4)	592(2)	78(2)
C(23A)	932(17)	7400(19)	596(9)	80(2)
C(23B)	1311(7)	7323(8)	395(4)	80(2)
C(24)	1020(7)	8194(7)	478(4)	153(4)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

3.9. Reaction of Me₃Si-C≡C-SiMe₂(allyl)[ML_n]₂ with HOTf

To a solution of the compound in acetonitrile (1.5 ml of a 0.05 M solution) in a 10 mm NMR tube was added triflic acid (0.9 equiv.) at -80°C . The 59.6 MHz ²⁹Si spectra were acquired at this temperature. **10** gave **16**: $\delta -0.3$ (SiMe₃), -4.9 (SiMe₂). **11** gave **18**: $\delta -6.2$ (SiMe₃), -11.2 (SiMe₂).

3.10. Competitive reactions

HBF₄-etherate (0.9 equiv.) was added at -80°C to a 10-mm NMR tube containing equimolar amounts of the two compounds in CH₂Cl₂ (1.5 ml of a 0.05 M solution of each). The 282.42 MHz ¹⁹F spectra were acquired at this temperature, and the 59.6 MHz ²⁹Si spectrum of **15** was also acquired at this temperature. **7** vs. **10**: gave **16** (47%) and **19** (53%). **7** vs. **11**: gave **18** (48%) and **19** (52%). **10** vs. **11**: gave **16** (52%) and **18** (48%). **15**

gave **28**: δ 4.1 (doublet, $^1J_{\text{Si-F}} = 271$ Hz), 0.8(s). $[\text{Co}_2(\text{CO})_8](\text{CH}_2=\text{CHCH}_2\text{-SiMe}_2\text{-C}\equiv\text{C-C}\equiv\text{C-SiMe}_2\text{F})$.

4. X-ray crystallography

X-ray crystallographic data for **11** were collected from a single crystal which was mounted on a glass fibre and transferred to a P4 Siemens diffractometer, equipped with a rotating anode and graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). X-ray crystallographic data for **13** were collected from a single crystals which was mounted on a glass fibre and transferred to a P3 Siemens diffractometer, using an graphite-monochromated Ag-K α radiation ($\lambda = 0.56086$ Å). Three standard reflections, that were measured after every 97 reflections, showed neither instrument instability nor crystal decay. Data were corrected for absorption using an empirical Ψ -scan method. The structures were solved by using the direct methods procedure in the Siemens SHELXTL program library [41,42], and refined by full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms except for the C(1) of structure **13** which was left isotropic. Crystallographic data collection parameters for **11** and **13** are summarized in Table 1, while atomic coordinates for **11** and **13** are presented in Tables 2 and 3, respectively.

For **11**, the final refined structure was based on a disordered model in which the allyl could exist in one

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **13**

	x	y	z	U_{eq}
Co(1)	6720(2)	6684(2)	3070(1)	60(1)
Co(2)	6774(1)	8244(2)	3346(1)	55(1)
Si(1)	7006(3)	7874(3)	1531(2)	62(1)
C(1)	5606(8)	7570(9)	2613(6)	42(3)
C(2)	6458(10)	7639(9)	2328(6)	46(4)
C(3)	8539(8)	7767(10)	1846(5)	117(7)
C(4)	6411(9)	7124(7)	743(6)	82(5)
C(5)	6600(15)	9014(9)	1249(8)	107(7)
C(6)	7081(19)	9274(13)	610(12)	139(9)
C(7)	6515(21)	9416(14)	-21(11)	178(11)
C(21)	6434(13)	9311(11)	3068(8)	71(5)
O(21)	6219(10)	10034(6)	2936(6)	97(4)
C(22)	6439(10)	8186(11)	4229(7)	61(4)
O(22)	6228(8)	8156(8)	4791(4)	94(4)
C(23)	8267(13)	8381(11)	3676(7)	72(5)
O(23)	9216(8)	8458(8)	3915(5)	98(4)
C(11)	6335(13)	6281(9)	3865(8)	72(5)
O(11)	6070(9)	6045(6)	4382(6)	93(4)
C(12)	6332(15)	5811(11)	2463(9)	80(6)
O(12)	6036(10)	5258(7)	2033(6)	110(4)
C(13)	8175(13)	6479(10)	3350(7)	70(5)
O(13)	9113(9)	6357(7)	3526(6)	104(4)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

of two conformations. Based on the observed thermal displacement ellipsoids, it was assumed that only the positions of the β carbon atoms of the ring were significantly affected by this disorder. The occupancy of the two conformations was allowed to refine as a free variable (the final ratio of approximately 71:29), and then hydrogen atoms for each unique component of the disorder were placed in calculated positions and allowed to refine based on the carbon atom to which they were attached.

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