

Transition-Metal Silyl Complexes. 37.¹ Reaction of Anionic Silyl, Germyl, and Stannyl Complexes $[(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{CO})_2\text{MnER}_3]^-$ (E = Si, Ge, Sn) with Geminal Organic Dihalides: A Novel Route for the Preparation of Carbene Complexes

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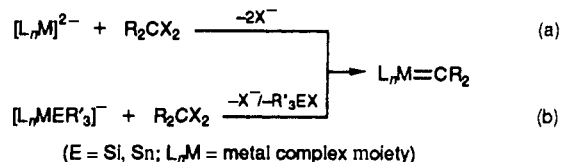
Abstract: The anionic complexes $\text{Na}[\text{MeCp}(\text{CO})_2\text{MnER}_3]$ (E = Si, Ge, Sn) (MeCp = $\eta^5\text{-C}_5\text{H}_4\text{Me}$), obtained by deprotonation of the corresponding hydrido complexes $\text{MeCp}(\text{CO})_2\text{Mn}(\text{H})\text{ER}_3$, react with 3,3-dichlorocyclopropenes to give the cyclopropenyldiene complexes $\text{MeCp}(\text{CO})_2\text{Mn}=\text{C}=\text{CR}=\text{CR}$ (2) by NaCl and R_3ECl elimination. Aminocarbene complexes $\text{MeCp}(\text{CO})_2\text{Mn}=\text{C}(\text{NR}_2)\text{R}'$ (5), including the *N*-methylpyridinylidene complex $\text{MeCp}(\text{CO})_2\text{Mn}=\text{CN}(\text{Me})\text{CHCHCH}$ (5h) and a thiazolinylidene derivative, $\text{MeCp}(\text{CO})_2\text{Mn}=\text{CN}(\text{Me})\text{C}(\text{Me})\text{CHS}$ (5i), were analogously prepared from $[\text{MeCp}(\text{CO})_2\text{MnSiMePh}_2]^-$ and $[\text{R}'_2\text{N}=\text{C}(\text{R}')\text{Cl}]^+$. In these reactions, the anionic complexes $\text{Na}[\text{MeCp}(\text{CO})_2\text{MnER}_3]$ act as preparative equivalents to the dianionic complex $\text{MeCp}(\text{CO})_2\text{Mn}^{2-}$. The X-ray structure analysis of 5i is reported (Mn—C(carbene) 197.0 (3) pm; monoclinic, space group $P2_1/c$ ($Z = 4$), $a = 736.4$ (1) pm, $b = 1418.4$ (3) pm, $c = 1304.6$ (1) pm, $\beta = 95.58$ (1)°).

Introduction

The usefulness of dianionic metal complexes, $[\text{L}_n\text{M}]^{2-}$, for preparative purposes is limited because only a few of them are readily accessible and relatively easy to handle. Furthermore, their ligands can hardly be varied, and therefore there are only a few possibilities to control their reactivity and the properties of the derived products.

The use of anionic silyl, germyl, or stannyl complexes, $[\text{L}_n\text{MER}_3]^-$ (E = Si, Ge, Sn), is a preparative alternative. Anionic complexes of this type not only exhibit the typical properties common to negatively charged metal complexes, such as ion pairing and substitution reactions,²⁻⁵ but also render possible additional preparative applications due to the reactivity of the ER_3 ligand.⁴ Because the ER_3 ligand can be easily removed (formally as a ER_3^+ group) subsequent to substitution reactions, it may be regarded as a "protecting group" for a negative charge. Anionic complexes $[\text{L}_n\text{MER}_3]^-$ are easily prepared by deprotonation of the corresponding hydrido complexes $\text{L}_n\text{M}(\text{H})\text{ER}_3$ or by reaction of metal complexes with ER_3^- . Their high stability even allows for their isolation in many cases although for most preparative applications this is not necessary. As we have shown for complexes of the type $[(\text{CO})_{4-n}\text{L}_n\text{FeER}_3]^-$ ($n = 0-2$; L = PR_3 , $\text{P}(\text{OR})_3$), the steric and electronic properties of the ligands can be varied in a wide range.⁵ Anionic silyl complexes have been reacted with organic halides to prepare complexes containing both an organyl and a silyl ligand.^{2,4,5} Gladysz et al. have demonstrated that the potential of anionic silyl complexes in preparative organometallic chemistry exceeds simple substitution reactions.⁴ They found that on reaction of $[(\text{CO})_4\text{FeSiMe}_3]^-$ with acyl halides initial substitution is followed by a silyl shift to give siloxy-carbene complexes $(\text{CO})_4\text{FeC}(\text{OSiMe}_3)\text{R}$.

Scheme I



In this article we show that anionic silyl and stannyl complexes can substitute dianionic complexes in the reaction with organic geminal dihalides to give carbene complexes (Scheme I). Preliminary results⁶ and the extension of this method to the preparation of phosphinidene complexes⁷ were already reported. By a related approach, a cationic cyclopropenyldiene complex has already been prepared by reaction of $\text{Cp}(\text{CO})_2\text{FeSiMe}_3$ with 1-chloro-2,3-diphenylcyclopropenylium tetrafluoroborate.⁸

Carbene complexes have been prepared by reaction of dianionic complexes, such as $[(\text{CO})_5\text{Cr}]^{2-}$, $[(\text{CO})_4\text{Fe}]^{2-}$, or $[\text{Cp}(\text{CO})_3\text{V}]^{2-}$, with 3,3-dichloro-1,2-diphenylcyclopropene⁹ or amide halides, $[\text{Me}_2\text{N}=\text{C}(\text{R})\text{Cl}]\text{Cl}$,¹⁰ according to Scheme Ia. To make both preparative routes (Scheme I) comparable, we used the same type of geminal dihalides for the $\text{R}'_3\text{EX}$ elimination route discussed in this article. The scope of the reaction was investigated for the complexes $[\text{MeCp}(\text{CO})_2\text{MnER}_3]^-$ (E = Si, Ge, Sn) (1). The corresponding dianionic complex, $\text{MeCp}(\text{CO})_2\text{Mn}^{2-}$ was only recently described,¹¹ but, according to our experience, its synthesis is less straightforward than it appears from that reference. Reactions of this dianionic complex with geminal dihalides were not reported.

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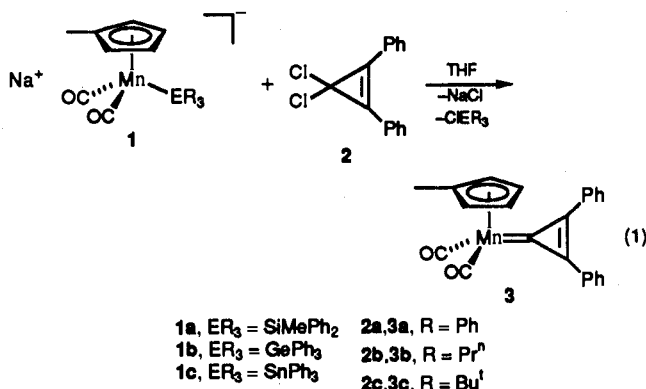
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Results and Discussion

Reaction of the anionic silyl complex **1a**, which is prepared by deprotonation of $\text{MeCp}(\text{CO})_2\text{Mn}(\text{H})\text{SiMePh}_2$ with NaH ,³ with the 3,3-dichlorocyclopropenes **2a-c** in THF at room temperature results in the anticipated carbene complexes **3a-c** in reasonable yields.



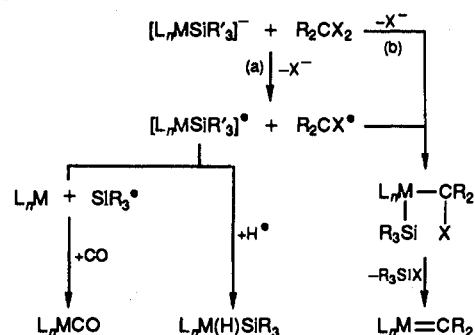
The method is not restricted to the use of anionic silyl complexes. Reaction of the anionic germyl complex **1b** or stannyl complex **1c** (analogously prepared from the corresponding hydrido complexes¹²) with 3,3-dichloro-1,2-diphenylcyclopropene (**2a**) gave the carbene complex **3a** in about the same yield. The chlorosilane and chlorogermane formed according to eq 1 were identified by GC.

After separation of the byproducts $\text{MeCp}(\text{CO})_3\text{Mn}$ and $\text{MeCp}(\text{CO})_2\text{Mn}(\text{H})\text{ER}_3$, the carbene complexes are obtained as yellow (**3b,c**) or red (**3a**) solids (**3a,c**) or oils (**3b**) which are soluble in benzene or THF but only sparingly soluble in saturated hydrocarbons. The red color of the phenyl derivative **3a** is probably due to delocalization of π -electron density from the phenyl groups into the cyclopropenylidene ring.

For the formation of the carbene complexes **3** we postulate a mechanism, the first step of which consists of substitution of one chlorine atom of **2** by the anionic complex. Although we were not able to observe the postulated intermediates $\text{MeCp}(\text{CO})_2\text{Mn}(\text{ER}_3)\text{C}(\text{Cl})\text{R}_2$ (**A**) spectroscopically, even at low temperatures, they appear reasonable in light of other substitution products derived from **1a**.³ Subsequent elimination of R_3ECl from **A** would result in the formation of the carbene complexes. An alternative mechanism, in which the order of the two steps (elimination of Cl^- and R_3ECl) is reversed, appears rather unlikely. If R_3ECl elimination is the preliminary step of the reaction, $\text{MeCp}(\text{CO})_2\text{Mn}(\text{SnPh}_3)_2$ ¹² should also react with **2a** to give a carbene complex. However, there is no reaction between both compounds.

The nature of the byproducts formed in the reaction of **1** with geminal organic dihalides suggests that the mechanism of this reaction is actually more complicated. Generally, when anionic silyl complexes are reacted with halogen compounds, the corresponding hydrido silyl complexes are often formed as byproducts, in some cases even as the only products instead of the substitution products (vide infra). The byproducts strongly suggest the importance of electron-transfer reactions to give radical intermediates. A possible mechanism, which explains all the observed products, is given in Scheme IIa ($\text{L}_n\text{M} = \text{MeCp}(\text{CO})_2\text{Mn}$). Once the $[\text{MeCp}(\text{CO})_2\text{MnSiR}_3]^\bullet$ radical has been formed it can take up a hydrogen atom from the solvent to give the hydrido silyl complex, or it can decompose to give the 16-electron $\text{MeCp}(\text{CO})_2\text{Mn}$ species. The formation of $\text{MeCp}(\text{CO})_3\text{Mn}$ and $\text{MeCp}(\text{CO})_2\text{Mn}(\text{H})\text{SiMePh}_2$ upon oxidation of **1a** is clearly confirmed by reaction of the anionic silyl complex with $[\text{Cp}_2\text{Fe}]\text{PF}_6$ in THF. Immediately after addition of the oxidant, both products are IR spectroscopically observed in addition to $\text{MeCp}(\text{CO})_2\text{Mn}(\text{THF})$,

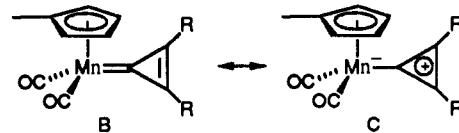
Scheme II



which gradually decomposes. Cyclic voltammetric investigation of a THF solution of **1a** showed that the redox process is approximately reversible ($E_{1/2} = -0.28$ V, $E_{pa} = -0.17$ V). At present it is unclear whether all reactions of anionic silyl (germyl, stannyl) complexes with geminal dihalides involve an electron-transfer step (Scheme IIa) or whether a substitution mechanism (Scheme IIb) is also operative for certain combinations of starting compounds.

Formation of carbene complexes according to Scheme II is thermodynamically favored, if the sum of bond energies of the new bonds, i.e., the E-X bond, the M-C(carbene) bond, and the lattice energy of the eliminated salt, exceeds the sum of the bond energies of the broken bonds, i.e., the M-E bond and two C-X bonds. The driving force for the reaction certainly is the formation of the salt and the stable E-X bond of the eliminated R_3EX molecule. However, the question arises as to what extent stabilization of the resulting carbene complex is important for the progress of the reaction. Since substituents which stabilize the carbene carbon (which is partially positively charged) also activate the C-Cl bonds in the organic dihalide, the answer to this question also provides information on how general this route to carbene complexes is in respect to the organic dihalide.

From the X-ray structure analysis of **3a**⁵ and other cyclopropenylidene complexes it is known that carbene complexes of this type are stabilized due to electron withdrawal from the cyclopropene unit, according to C.



Reaction of **1a** with 7,7-dichlorobicyclo[4.1.0]heptane at room temperature only yields $\text{MeCp}(\text{CO})_3\text{Mn}$ and $\text{MeCp}(\text{CO})_2\text{Mn}(\text{H})\text{SiMePh}_2$, and reaction of **1a** with 7,7-dichlorocycloheptatriene mainly $\text{MeCp}(\text{CO})_3\text{Mn}$ with only a very small amount of the hydrido silyl complex. These dichloro derivatives obviously are reasonably good oxidants and therefore no carbene complexes are obtained, although cycloheptatrienylidene complexes would also be stabilized. By analogy, reaction of $\text{Na}_2[(\text{CO})_5\text{Cr}]$ or $\text{Na}_2[(\text{CO})_4\text{Fe}]$ with 7,7-dichlorocycloheptatriene also resulted in redox reactions instead of formation of cycloheptatrienylidene complexes.¹³ While **1a** reacts with MeI within a few minutes to give the substitution product $\text{MeCp}(\text{CO})_2\text{Mn}(\text{Me})\text{SiMePh}_2$, no reaction is observed with Ph_2CCl_2 at room temperature within an hour. These results indicate that synthesis of carbene complexes according to Scheme Ib requires dihalogen compounds which are not easily reduced and have reasonably activated C-Cl bonds.

These requirements are met by amide chlorides of the type $[\text{R}_2\text{N}=\text{C}(\text{R}')\text{Cl}]\text{Cl}$ (**4**), which are ionic due to electronic stabilization of the carbon atom by the NR_2 group. Their reactivity is determined by the electrophilic carbon atom. As a matter of fact, the amide chlorides **4** react at room temperature with the

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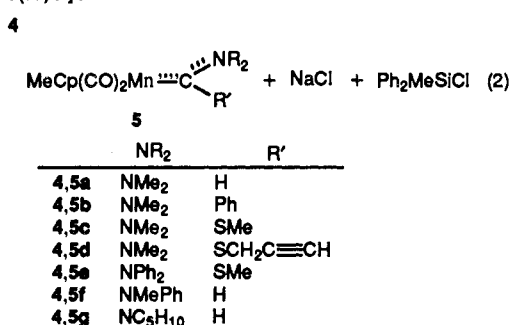
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Table I. IR (Toluene) and ^{13}C NMR Data (C_6D_6) of the Carbene Complexes **3** and **5**

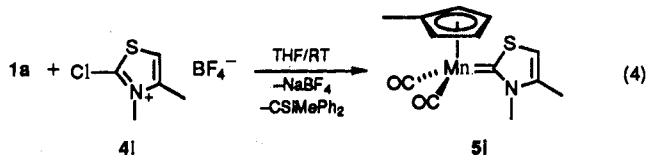
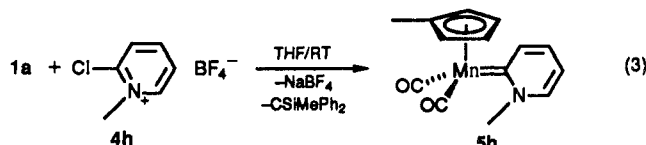
compd	$\nu(\text{CO})$ (cm^{-1})	δ C(carbene)	$\delta\text{C}(\text{CO})$	δ NR ₂	others
3a	1935, 1867	243.1	233.5		178.9 (C(ring))
3b	1933, 1864	240.4	234.7		191.7 (C(ring))
3c	1931, 1862	238.9	235.2		196.1 (C(ring))
5a	1930, 1861	269.4	235.4	43.8, ^b 52.7 ^a	
5b	1920, 1854	282.3	235.3	44.9, ^a 48.9 ^b	134.7–120.8 (Ph)
5c	1917, 1852	276.5	233.1	45.1, ^a 52.7 ^b	23.6 (SMe)
5d	1919, 1855	272.8	232.7	47.1, ^a 52.3 ^b	30.8 (SCH ₂), 73.1 (≡CH), ^c 80.2 (—C≡)
5f	1928, 1860				
5g	1933, 1866	274.6	234.4	44.1 (Me), 151.3–121.2 (Ph)	
5h	1930, 1859	265.0	235.2	54.6, ^b 64.7 ^a (α -CH ₂)	27.1, ^b 27.8 ^a (β -CH ₂), 24.5 (γ -CH ₂)
5i	1909, 1842	241.5	235.5	148.5, 143.7, 125.0, 116.7 (NC ₄ H ₄), 53.3 (NMe)	
5j	1922, 1854	241.1	235.3	145.6 (N—C≡), 39.6 (Me)	117.8 (S—CH=), ^c 14.9 (≡C—Me)

^a Cis. ^b Trans. ^c Doublet in the proton-doupled spectrum.

anionic silyl complex **1a**, and the carbene complexes **5** are obtained in good yields (eq 2).



The heterocyclic compounds **4h** and **4i** can be equally employed to yield the pyridinylidene complex **5h** or the thiazolynylidene complex **5i**, respectively (eqs 3 and 4).



Because the amide chlorides are only sparingly soluble in THF, an excess of **4** was employed. In all reactions, MeCp(CO)₃Mn and MeCp(CO)₂Mn(H)SiMePh₂ are observed as byproducts. All carbene complexes **5**, except **5e**, were obtained analytically pure by column chromatography. The diphenylamino derivative **5e** is only formed in low yields and was only spectroscopically detected. Reaction of **4e** is obviously a borderline case: the phenyl groups decrease the electrophilicity of the carbon atom and probably also induce some steric hindrance.

The carbene complexes **5a**, **5c**, **5d**, **5f**, **5g**, and **5i** are yellow to ochre solids, and **5b** and **5h** are red oils. They are rather stable compounds which are readily dissolved in toluene or THF but are only sparingly soluble in saturated hydrocarbons.

Aminocarbene complexes of the type Cp(CO)₂MnC(R')NR₂ were thus far only obtained by reaction of the acetylene complex Cp(CO)₂Mn(η^2 -C₂H₂) with ammonia, MeNH₂, or Me₂NH.¹⁴ Fischer's method for the preparation of aminocarbene complexes, i.e., aminolysis of alkoxy carbene complexes, is not successful for Cp(CO)₂MnC(R')OR.¹⁵ Thus, reaction of the anionic silyl

complex **1a** according to eqs 2–4 provides a new and very easy access to these complexes.

Surprisingly, reaction of **1a** with [Me₂N=CCl₂]Cl does not give the anticipated carbene complex MeCp(CO)₂MnCl(NMe₂) but instead gives the hydrogen-substituted complex MeCp(CO)₂MnC(H)NMe₂ (**5a**). If this reaction is carried out in THF-*d*₈, the deuterated complex MeCp(CO)₂MnC(D)NMe₂ is obtained. Thus the solvent is identified as the source of the hydrogen. Presently we do not know in what stage of the reaction Cl/H exchange occurs. However, chlorocarbene complexes are known to have rather labile C(carbene)–Cl bonds. Complexes (CO)₅MC(Cl)NR₂, for instance, easily rearrange to carbyne complexes *trans*-Cl(CO)₄MCNR₂.¹⁶

Fischer-type carbene complexes can be regarded as carbenium ions, which are stabilized by π -interaction of the carbenium center with its substituents (one of them being the metal complex moiety).¹⁸ The π -interaction of a particular substituent with the carbene carbon depends not only on its own π -donor ability but also on the relative π -donor ability of the other substituents at the same carbene carbon atom. The Cp(CO)₂Mn moiety is a very good π -donating group and therefore the carbene carbon in complexes such as Cp(CO)₂MnCPh₂ or Cp(CO)₂MnC(OEt)Ph is mainly stabilized by the metal moiety.¹⁹

Both the $\nu(\text{CO})$ bands in the infrared spectra and the chemical shifts of the carbene carbon atoms in the ^{13}C NMR spectra of the new carbene complexes **3** and **5** (Table I) show that the carbene ligands in these complexes are highly stabilized by their organic substituents, leaving a high electron density at the manganese atom. For comparison, the $\nu(\text{CO})$ bands in Cp(CO)₂MnCPh₂²⁰ and Cp(CO)₂MnC(OEt)Ph²¹ are considerably higher (1977, 1919 and 1969, 1898 cm^{-1} , respectively), and the resonances of the carbene carbon atoms appear at a much lower field (363.7 and 372.7 ppm in Cp(CO)₂MnC(Me)R [R = Ph, Me]²²). In the cyclopropenylidene complexes **3** stabilization occurs by partial aromatization of the cyclopropene unit (C). According to the spectroscopic data, there is little influence of the cyclopropene substituents on the electron distribution. The X-ray structure analysis of **3a** has been discussed elsewhere.⁵

In aminocarbene complexes of the type (π -C₅R₅)(CO)₂MnC(R')NR'₂, such as **5**, π -interaction between the carbene carbon and the nitrogen appears to be the major way of stabilization (in **5h** aromatization may also play a role). This is not only supported by the spectroscopic data of **5** but also by the structural data of the known aminocarbene complexes (π -C₅Me₅)(CO)₂MnC-

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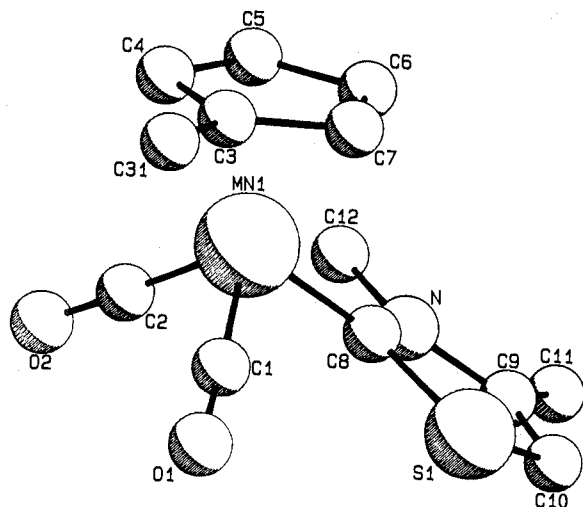
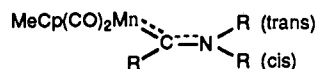


Figure 1. A PLUTO drawing of the carbene complex **5i**. Hydrogen atoms are omitted for clarity.

(Me)NR₂ (NR₂ = NH₂, NMe₂) and (π-C₅H₄Me)(CO)₂MnC(Me)NH₂,¹⁵ in which the Mn–C(carbene) distances (199.1 (4), 194.1 (3), and 193.9 (9) pm, respectively) are distinctly longer than in MeCp(CO)₂MnC(OEt)Ph (186.5 (14) pm) and other Cp(CO)₂MnCR₂ complexes with less π-donating substituents.¹⁹ Because of the high π-donor ability of the NR₂ substituent, the alkylthio substituents in **5c,d** provide no additional stabilization and cannot compete with the amino group and the MeCp(CO)₂Mn moiety for π-bonding with the carbene carbon. The small low-field shift of the carbene carbon atoms in the ¹³C NMR spectra of **5b**, **5c**, and **5d** compared with **5a** is probably due to the deshielding effect of the phenyl group or the sulfur atom.²³

Because of the C(carbene)–N π-interaction, the two methyl groups in the NMe₂ derivatives are not chemically equivalent. The NR₂ signals in the ¹H and ¹³C NMR spectra of the complexes **5** were tentatively assigned to the cis and trans substituents assuming that the order of the signals (which depends on the substituent R') is the same as in the well-investigated complexes (CO)₅MC(NR₂)R' (M = Cr, Mo, W).²⁴



For (π-C₅Me₅)(CO)₂MnC(Me)NHMe two isomers were observed (methyl groups cis or trans relative to C(carbene)–N).¹⁴ Contrary to this, the spectra of **5f**, also having two different substituents at nitrogen, only show one methyl group signal in the ¹H NMR spectrum and one C(carbene) signal in the ¹³C NMR spectrum. The occurrence of only one isomer for **5f** is probably due to the steric bulk of the phenyl group. By comparison of δ(NMe) with that of **5a**, this isomer should have the methyl group in the trans position. This assignment is also reasonable from a stereochemical point of view, because the cis position is less hindered and is therefore occupied by the bulkier phenyl group.

The X-ray structure analysis (Figure 1, Tables II and III) of **5i** supports the conclusions concerning bonding drawn from the spectroscopic data. The bond lengths around the carbene carbon [C(8)] support the notion that π-interaction between C(8) and N is dominating: the Mn–C(8) distance (197.0 (3) pm) is one of the longest Mn–C(carbene) distances observed so far,¹⁹ while C(8)–N (134.6 (4) pm) is considerably shorter in comparison to a C(sp²)–N single bond. π-Interaction of the sulfur atom or aromatization of the thiazoline ring does not play a role for the stabilization of the carbene ligand: the C(9)–C(10) and C(9)–N

Table II. Selected Bond Lengths (pm) and Angles (deg) with Their Standard Deviations of **5i**

Mn–C(1)	176.6 (3)	N–C(8)	134.6 (4)
Mn–C(2)	175.9 (3)	N–C(9)	140.5 (4)
Mn–C(3)	214.0 (4)	N–C(12)	146.6 (4)
Mn–C(4)	212.7 (4)	C(9)–C(10)	133.3 (5)
Mn–C(5)	214.8 (4)	C(9)–C(11)	149.1 (5)
Mn–C(6)	215.5 (4)	C(3)–C(4)	141.8 (5)
Mn–C(7)	215.0 (4)	C(4)–C(5)	141.2 (6)
Mn–C(8)	197.0 (3)	C(5)–C(6)	140.3 (5)
S–C(8)	172.0 (3)	C(6)–C(7)	139.8 (6)
S–C(10)	172.6 (4)	C(7)–C(3)	143.6 (5)
O(1)–C(1)	115.9 (4)	O(2)–C(2)	116.4 (4)
C(1)–Mn–C(2)	91.4 (2)	C(8)–N–C(9)	117.2 (3)
C(1)–Mn–C(8)	93.8 (1)	C(8)–N–C(12)	122.0 (3)
C(2)–Mn–C(8)	94.0 (1)	C(9)–N–C(12)	120.7 (3)
Mn–C(8)–S	120.8 (2)	N–C(9)–C(10)	112.1 (3)
Mn–C(8)–N	132.5 (2)	S–C(10)–C(9)	109.9 (3)
S–C(8)–N	106.6 (2)	C(8)–S–C(10)	94.1 (2)

Table III. Positional Parameters of the Non-Hydrogen Atoms of **5i**

atom	x	y	z	B (eq)
Mn	0.26834 (6)	0.24169 (3)	0.04619 (4)	3.022 (9)
S	0.1679 (1)	0.43256 (6)	–0.07993 (7)	3.87 (2)
O1	0.0100 (3)	0.3463 (2)	0.1571 (2)	5.06 (6)
O2	0.5630 (4)	0.2756 (2)	0.2120 (2)	5.65 (7)
N	0.4830 (3)	0.3730 (2)	–0.0800 (2)	2.95 (5)
C1	0.1133 (4)	0.3070 (2)	0.1118 (3)	3.51 (7)
C2	0.4473 (5)	0.2636 (2)	0.1447 (3)	3.72 (7)
C3	0.0925 (5)	0.1214 (2)	0.0434 (3)	4.02 (7)
C4	0.2771 (5)	0.0931 (3)	0.0681 (3)	4.43 (8)
C5	0.3732 (5)	0.1155 (3)	–0.0164 (3)	4.69 (8)
C6	0.2497 (6)	0.1580 (3)	–0.0925 (3)	4.59 (8)
C7	0.0774 (5)	0.1629 (3)	–0.0576 (3)	4.23 (8)
C8	0.3302 (4)	0.3496 (2)	–0.0383 (2)	2.97 (6)
C9	0.4746 (4)	0.4527 (2)	–0.1443 (2)	3.30 (6)
C10	0.3110 (5)	0.4940 (2)	–0.1519 (3)	3.83 (7)
C11	0.6343 (5)	0.4810 (3)	–0.1979 (3)	4.53 (8)
C12	0.6532 (4)	0.3194 (3)	–0.0583 (3)	3.89 (7)
C31	–0.0594 (6)	0.1048 (3)	0.1085 (4)	5.9 (1)

distances are typical for a localized C=C bond, and both C(sp²)–S bond lengths (C(8)–S 172.0 (3) pm and C(10)–S 172.6 (4) pm) are equal within the standard deviations. In thiocarbene complexes with a significant C(carbene)–S π-interaction the C–S distance is shortened to about 165–169 pm.¹⁸

For carbene complexes of the type Cp(CO)₂MnCR₂ the conformation in which the carbene plane coincides with the mirror plane of the Cp(CO)₂Mn fragment is electronically favored. This conformation is indeed found in most complexes of this type, if the organic substituents at the carbene carbon are not too bulky.¹⁹ However, the relative energy of other conformations is not much higher, and therefore rotation of the carbene ligand is possible to adjust the conformation to steric requirements. In **5i** the angle between the plane of the planar carbene ligand and the mirror plane of the Cp(CO)₂Mn fragment is 78°. This is probably not only caused by steric effects but also facilitated by the low Mn–C(carbene) bond order.

Conclusions

The anionic silyl, germyl, or stannyl complexes **1** react with activated geminal organic dihalides or related compounds to give carbene complexes by a substitution/R₃ECl elimination pathway. The outcome of these reactions is the same as for dianionic complexes. Therefore, anionic silyl, germyl, or stannyl complexes [L_nMER₃][–] (E = Si, Ge, Sn) generally can be used as substitutes for the corresponding dianionic complexes [L_nM]^{2–}, particularly if the latter are difficult to handle or unknown. In addition to the comparatively easy preparation and handling of the complexes [L_nMER₃][–], the reactivity of the complexes may be controlled to some extent by the nature of the element E and the substituents R. Although redox reactions impair the generality of their applications (the same is true for most anionic metal carbonyl derivatives), the results reported in this article show that anionic

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silyl, germyl, or stannyl complexes are valuable new reagents for organometallic syntheses.

Experimental Section

All operations were performed in an atmosphere of dry and oxygen-free nitrogen, with use of dried and nitrogen-saturated solvents. Melting points were determined by differential thermoanalysis (DuPont Thermal Analyzer); IR spectra, Perkin-Elmer 283, CaF₂ cuvettes; ¹H NMR spectra, Varian T60, Jeol FX 90 Q, and Bruker AC 200; ¹³C NMR spectra, Bruker AC 200 (50.3 MHz) and Bruker WM 400 (100 MHz).

Preparation of the Cyclopropenylidene Complexes 3. To a solution of 2 mmol of **1** (in situ prepared according to ref 3) from MeCp(CO)₂Mn(H)ER₃ in 30 mL of THF was added a solution of 2.5 mmol of **2** in 10 mL of THF at room temperature, resulting in an immediate color change to red (**3a**) or orange red (**3b,c**). The reaction mixture was filtered and concentrated to 3–5 mL.

3a: Pentane was added to the THF solution. After 5 min of stirring at room temperature the dark red precipitate was separated and recrystallized from toluene/pentane. The resulting solid was washed with pentane to remove traces of MeCp(CO)₂Mn and dried in vacuo: mp 131 °C, yield 0.18 g (24%) from **1a**, 27% from **1b**, and 25% from **1c** (the reaction of **1c** with **2a** is done at –20 °C): ¹H NMR (200 MHz, C₆D₆, δ) 2.0 (s, 3 H, C₅H₄Me), 4.71 (m, 2 H, C₅H₄), 4.84 (m, 2 H, C₅H₄), 7.2–8.1 (m, 10 H, C₆H₅). Anal. Found (Calcd): C, 73.06 (72.63); H, 4.50 (4.50).

3b: the solvent was completely removed, and the oily residue was dissolved in 5 mL of toluene. Upon column chromatography on SiO₂ at 5 °C (column 50 × 1 cm) with toluene the first zone contained MeCp(CO)₂Mn and MeCp(CO)₂Mn(H)SiMePh₂, and the second zone contained **3b**. The product-containing zone was eluted, and the solvent was removed in vacuo. The product was recrystallized from pentane at –78 °C. On warming to room temperature the yellow solid melted to give an orange red oil: yield 0.25 g (41%); ¹H NMR (200 MHz, C₆D₆, δ) 0.85 (s, br, 6 H, CH₂Me), 1.58 (m, 4 H, CH₂Me), 1.99 (s, 3 H, C₅H₄Me), 2.48 (s, br, 4 H, CH₂CH₂Me), 4.57 (m, 2 H, C₅H₄), 4.65 (m, 2 H, C₅H₄). Anal. Found (Calcd): C, 65.10 (65.38); H, 6.86 (6.73).

3c: The same workup procedure was applied as for **3b**: yellow solid, mp 40 °C; yield 0.26 g (38%); ¹H NMR (200 MHz, C₆D₆, δ) 1.2 (s, 18 H, CMe), 2.0 (s, 3 H, C₅H₄Me), 4.53 (m, 2 H, C₅H₄), 4.64 (m, 2 H, C₅H₄). Anal. Found (Calcd): C, 67.19 (67.05); H, 7.51 (7.40).

Preparation of the Carbene Complexes 5a–h. To a solution of 2 mmol of **1a** in 20 mL of THF was added 3 mmol of the amide chloride **4**, while the solution was stirred. On addition of **4**, the color of the solution changed to orange red (**4a,b,g,h**) or green (**4c,e,f**). After filtration, the solvent was removed from the solution in vacuo. The residue was dissolved in 3–5 mL of toluene and chromatographed at 5 °C, as described for **3b**. Isolation of the products was done as for **3b**. Some of the carbene complexes, particularly **5c** and **5e**, were chromatographed twice or even three times to get analytically pure samples.

5a: yield 0.21 g (37%); mp 52 °C; ochre solid; ¹H NMR (200 MHz, C₆D₆, δ) 1.8 (s, 3 H, C₅H₄Me), 2.4 (s, 3 H, NMe trans), 3.1 (s, 3 H, NMe cis), 4.3 (m, 2 H, C₅H₄), 4.5 (m, 2 H, C₅H₄), 10.4 (s, 1 H, CH). Anal. Found (Calcd): C, 53.53 (53.45); H, 5.84 (5.71); N, 5.40 (5.47); Mn, 21.83 (22.23).

5b: yield 0.25 g (39%); orange red oil; ¹H NMR (200 MHz, C₆D₆, δ) 2.1 (s, 3 H, C₅H₄Me), 2.6 (s, 3 H, NMe cis), 3.0 (s, 3 H, NMe trans), 4.3 (m, 2 H, C₅H₄), 4.8 (m, 2 H, C₅H₄), 7.6–8.4 (m, 5 H, C₆H₅). Anal. Found (Calcd): C, 63.00 (63.16); H, 5.99 (5.61); N, 4.13 (4.33).

5c: yield 0.28 g (38%); mp 42 °C, yellow solid; ¹H NMR (200 MHz, C₆D₆, δ) 1.7 (s, 3 H, C₅H₄Me), 2.7 (s, 3 H, NMe cis), 3.5 (s, 3 H, NMe trans), 2.7 (s, 3 H, SMe), 4.0 (m, 2 H, C₅H₄), 4.2 (m, 2 H, C₅H₄). Anal. Found (Calcd): C, 48.86 (49.15); H, 5.27 (5.50); N, 4.53 (4.78); Mn, 18.68 (18.73).

5d: yield 0.27 g (43%); mp 52 °C (dec), yellow solid; ¹H NMR (200 MHz, C₆D₆, δ) 1.7 (s, 3 H, C₅H₄Me), 1.9–3.8 (m, 9 H, NMe, SCH₃, and ≡CH), 4.2 (m, 4 H, C₅H₄). Anal. Found (Calcd): C, 52.91 (53.00); H, 5.05 (5.08); N, 4.48 (4.41).

5f: yield 0.26 g (42%); mp 31 °C, yellow solid; ¹H NMR (200 MHz, C₆D₆, δ) 2.0 (s, 3 H, C₅H₄Me), 2.8 (s, 3 H, NMe), 4.6 (m, 4 H, C₅H₄), 6.9–7.7 (m, 5 H, C₆H₅), 9.7 (s, 1 H, CH). Anal. Found (Calcd): C, 62.44 (62.14); H, 5.23 (5.22); N, 4.78 (4.53).

5g: yield 0.22 g (38%); mp 41 °C, yellow solid; ¹H NMR (200 MHz, C₆D₆, δ) 1.1 (m, 2 H, δ-CH₂), 1.2 (m, 2 H, β-CH₂ trans), 1.6 (m, 2 H, β-CH₂ cis), 1.9 (s, 3 H, C₅H₄Me), 2.9 (t, 2 H, α-CH₂ trans), 3.8 (t, 2 H, α-CH₂ cis), 4.38 (m, 2 H, C₅H₄), 4.52 (m, 2 H, C₅H₄). Anal. Found (Calcd): C, 59.02 (58.54); H, 6.54 (6.32); N, 4.42 (4.88).

Preparation of 5h. To a solution of 2 mmol of **1a** in 20 mL of THF was added 0.54 g (2.5 mmol) of 1-methyl-2-chloropyridinium tetrafluoroborate (**4h**), while the solution was vigorously stirred. The color of the solution changed to dark red. **5h** was isolated in 37% yield (0.21 g) as a red, viscous oil as described for **5a–g**: ¹H NMR (200 MHz, C₆D₆, δ) 1.69 (s, 3 H, C₅H₄Me), 3.82 (s, 3 H, NMe), 4.17 (m, 2 H, MeC₅H₄), 4.26 (m, 2 H, MeC₅H₄), 5.9, 6.1, 6.8, 8.4 (m, 4 H, NC₅H₄). Anal. Found (Calcd): C, 59.83 (59.37); H, 5.32 (4.98); N, 4.65 (4.95).

Preparation of 5i. To a solution of 2 mmol of **1a** in 20 mL of THF was added 0.66 g (3 mmol) of 2-chloro-3,4-dimethylthiazolium tetrafluoroborate (**4j**), while the solution was vigorously stirred. The color of the solution changed to light red. Complex **5i** was isolated in 34% yield (0.20 g) as an ochre solid, mp 68 °C dec, as described for **5a–g**: ¹H NMR (200 MHz, C₆D₆, δ) 1.43 (s, 3 H, CMe), 1.79 (s, 3 H, C₅H₄Me), 3.44 (s, 3 H, NMe), 4.3 (m, 2 H, C₅H₄), 4.42 (m, 2 H, C₅H₄), 5.90 (s, 1 H, CH). Anal. Found (Calcd): C, 51.51 (51.49); H, 4.70 (4.65); N, 4.53 (4.62); Mn, 18.00 (18.12).

Reaction of 1a with [Me₂N=CCl₂]Cl in THF-d₈. From a solution of 0.5 mmol of **1a** in THF the solvent was completely removed. The oily residue was suspended in pentane until it solidified. The solid (**1a**) was filtered off, washed with pentane, and dried in vacuo. The pyrophoric powder was redissolved in 7 mL of THF-d₈ and reacted with 0.13 g (0.8 mmol) [Me₂N=CCl₂]Cl at room temperature. After filtration and removal of the solvents from the solution, the residue was ¹H and ¹³C NMR spectroscopically identified as deuterated **5a**.

Cyclovoltammetry: working and counter electrode, Pt; reference electrode, calomel. A 10^{–3} M solution of **1a** in THF was investigated at room temperature, with 10^{–1} M NBu₄PF₆ as supporting electrolyte: scan range, 100 mV s^{–1}; E_{pa} –0.17 V; E_{pc} –0.38 V (E_{1/2} of ferrocene as a reference was 0.57 V).

X-ray Structure Analysis of 5i. Crystals were obtained by cooling a solution of **5i** in toluene/pentane (1:1) to –30 °C. A crystal (0.3 × 0.2 × 0.15 mm) was mounted on a Enraf-Nonius CAD4 four-circle diffractometer in a sealed tube. Mo Kα radiation (λ = 71.069 pm, graphite monochromator) was used for all measurements. Crystal data: monoclinic, P2₁/c, a = 736.4 (1) pm, b = 1418.4 (3) pm, c = 1304.6 (1) pm, β = 95.58 (1)°, V = 1354 × 10⁶ pm³, Z = 4, D_{calc} = 1.49 g cm^{–3}, μ = 10.8 cm^{–1}. Cell dimensions were determined from 25 reflections with high diffraction angles from different parts of the reciprocal space. The 2773 unique reflections were measured between 4° ≤ 2θ ≤ 52° by the ω/θ method. The reflections were corrected for polarization and Lorentz effects and by an empirical absorption correction. The structure was solved by the Patterson method. The positions of the hydrogen atoms were calculated according to an idealized geometry. Refinement was performed by the full-matrix least-squares method (Enraf-Nonius SDP) with anisotropic thermal parameters for all non-hydrogen atoms. The parameters of the hydrogen atoms were not refined. The final R was 0.038 and R_w was 0.041 (w = 4F_o²/σ²(F_o²)), with use of 2398 observed reflections with F_o ≥ 2σ(F_o).

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft.

Supplementary Material Available: Listings of the final atomic coordinates, thermal parameters, bond lengths, bond angles, and torsional angles (8 pages); listings of observed and calculated structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.