The influence of silyl groups on the reactivity and formation of metal–carbon double bonds

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Abstract

In the first part of the article the chemistry of silyl-substituted Fischer-type carbene complexes is reviewed. The presence of a silyl substituent at the carbene carbon considerably changes the properties of complexes of the type $(CO)_5M=C(XR)SiR'_3$ (M = Cr, Mo, W). Depending on the group XR, fragmentation of the carbene ligand (XR = OR or NHR), formation of stable 16-electron carbene complexes $(CO)_4M=C(NR_2)SiR_3$, or formation of ketenes $Ph_3Si(RX)C=C=O$ (X = O, S) is observed.

In the second part two novel methods for the formation of metal–carbon double bonds are discussed, both involving elimination of R_3SiCl: in the first method anionic silyl complexes are used as equivalents of dianionic complexes in the reaction with geminal dihalides, in the second 1-chloro-1-trimethylsilylalkenes are brought into reaction with unsaturated metal fragments.
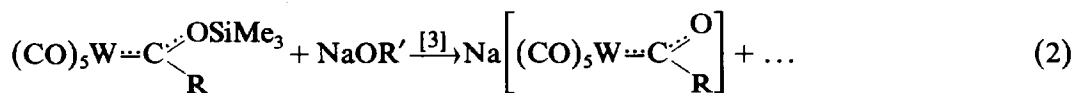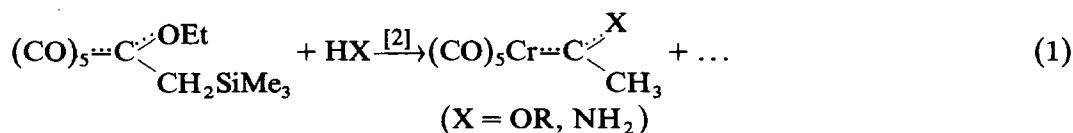
Introduction

Among the hundreds of known carbene complexes [1] there are only a few with silyl substituents. Compared with the rich chemistry of carbene complexes having electron-donating or carbon substituents at the carbene carbon center, virtually nothing was known about the reactions of silyl-substituted carbene complexes. We expected carbene complexes of the type $L_nM=C(XR)SiR'_3$ (XR = OR, SR, NR$_2$ etc.) to be interesting compounds for several reasons viz.: (i) owing to the electrophilic nature of the carbene carbon in Fischer-type complexes, the C(carbene)–Si bond should be labilized, and therefore unusual reactions could be expected. (ii) Despite metal participation in most reactions involving the carbene ligand, there are similarities in the reactions of metal carbene complexes and those of organic carbenes. We therefore hoped that some of the established chemistry of silylcar-

benes would also be found to apply for silylcarbene complexes. (iii) The combination of two substituents with very different properties at the same carbon atom should make the C(XR)SiR'$_3$ entity a very interesting building block for organic compounds.

Although we were disappointed not to find any parallels in the reaction pattern of silyl carbene complexes (CO)$_5$M=C(XR)SiR'$_3$ (M = Cr, Mo, W) and silyl carbenes, our expectations regarding (i) and (iii) turned out to be justified. In the first part of this article the unusual chemistry of silylcarbene complexes of this type is summarized and their potential use in organic reactions is outlined. In the second part we discuss some of our ideas, and their experimental verification, concerning the generation of metal–element double bonds by applying silicon chemistry. Whereas elimination of R$_3$SiX species is frequently used in main-group chemistry for generating multiple bonds, this method has never been employed for the preparation of metal complexes containing M=C double bonds. We will describe two principal ways in which this can be achieved.

Reactions of silyl-substituted Fischer-type carbene complexes

In reactions of Fischer-type carbene complexes with nucleophiles, the base usually adds to the carbene carbon in the first step of the reaction. The resulting adducts may be stable or, more commonly, undergo subsequent reactions. A silicon atom β to the carbene carbon acts as a competitor towards the nucleophile. In both trimethylsilylmethyl- [2] and trimethylsiloxy-substituted [3] carbene complexes the silicon atom and not the carbene carbon atom is attacked by nucleophile (eq. 1 and 2). The enhanced reactivity of the Si–CH$_2$ or Si–O bond is a consequence of the stabilization of the initially formed anion, –CH$_2^-$ or –O$^-$ by delocalization of the lone pair over the carbene system. For (CO)$_5$Cr=C[OSi(SiMe$_3$)$_3$](furyl) even LiBr is sufficiently nucleophilic to cleave the Si–O bond! [4].

$$(CO)_5{=}C\overset{OEt}{\underset{CH_2SiMe_3}{<}} + HX \xrightarrow{[2]} (CO)_5Cr{=}C\overset{X}{\underset{CH_3}{<}} + \ldots \qquad (1)$$

$$(X = OR, NH_2)$$

$$(CO)_5W{=}C\overset{OSiMe_3}{\underset{R}{<}} + NaOR' \xrightarrow{[3]} Na\left[(CO)_5W{=}C\overset{O}{\underset{R}{<}}\right] + \ldots \qquad (2)$$

Such behaviour can no longer be expected if the silyl group is directly bonded to the carbene carbon. The complexes (CO)$_5$M=C(OR)SiR'$_3$ (1), which are prepared by standard methods [5], react with nucleophiles in the conventional way. In particular, with ammonia, primary or secondary amines the corresponding aminocarbene complexes 2 are formed (eq. 3) if the amine is not too bulky [5,6]. With bulky amines (e.g. HNPr$_2^i$, HN(C$_6$H$_{11}$)$_2$) no aminolysis takes place. When the amine is of intermediate size (e.g. HNEt$_2$, NHMeBu^n, HN(Me)CH$_2$Ph) there is loss of one of the organic substituents at nitrogen (eq. 4) [6].

$$(CO)_5M{=}C\diagram{OR}{SiR'_3} + HNR_2 \longrightarrow$$

$$\rightarrow (CO)_5M{=}C\diagram{NR_2}{SiR'_3} + ROH \qquad (3)$$

$$(NR_2 = NH_2,\ NHR,\ NMe_2,\ NMeEt,$$

$$NC_4H_8,\ NC_5H_{10})$$

$$\rightarrow (CO)_5M{=}C\diagram{NHR}{SiR'_3} + \dots \qquad (4)$$

(1: M = Cr, Mo, W) $\qquad \left(NR_2 = NEt_2,\ NMeBu^n,\ N(Me)CH_2Ph\right)$

(SiR'$_3$ = SiPh$_{3-n}$Me$_n$, n = 0–2)

In the case of the unsymmetrically substituted amines HNMeR, both $(CO)_5W{=}C(NHMe)SiPh_3$ and $(CO)_5W{=}C(NHR)SiPh_3$ ($R = Bu^n$, CH_2Ph) are formed from $(CO)_5W{=}C(OEt)SiPh_3$ in the latter type of reaction. Since $(CO)_5M{=}C(NEt_2)SiPh_3$ can be prepared by an alternative route (eq. 5) and does not split off an ethylene unit once it is formed, fragmentation of the amino group (eq. 4) must occur during the aminolysis [6].

$$(CO)_5M{=}C\diagram{NHEt}{SiPh_3} + LiBu^n \rightarrow Li\left[(CO)_5M{=}C\diagram{NEt}{SiPh_3}\right] \xrightarrow{[Et_3O]BF_4}$$

$$(CO)_5M{=}C\diagram{NEt_2}{SiPh_3} \qquad (5)$$

Reaction of alkoxycarbene complexes with thiols yields alkylthio-substituted carbene complexes [1], and this method of modifying Fischer carbene complexes can also be applied to silyl-substituted complexes. However, this OR/SR-exchange is less straightforward than previously assumed. We found that **1** does not react with thiols, when they are very pure. Only in the presence of dialkyldisulfides are the alkylthiocarbene complexes **3** formed (eq. 6) [7].

The results of competition experiments suggest **A** as a reasonable transition state. SR/SR'-exchange reactions proceed by the same mechanism. We believe that catalysis by disulfides is not restricted to this example, but may have been overlooked in thiolysis reactions, since thiols generally contain traces of disulfides as a result of air oxidation.

Thermolysis of aryl- or alkyl-substituted alkoxycarbene complexes $(CO)_5M=C-(OR)R'$ ($R' =$ aryl, alkyl) results in organic products originating from the carbene ligand. If $(CO)_5M=C(OMe)R$ ($R =$ Me, Ph) is thermolyzed in the solid state or in aliphatic hydrocarbon solutions, the main product is *cis / trans*-R(MeO)C=C(OMe)R [8,9]. In pyridine, $MeOCH=CH_2$ is formed from $(CO)_5Cr=C(OMe)Me$ by an 1,2-hydrogen shift instead [9]. Several experiments have shown that uncoordinated carbenes are not involved in the formation of these products [8,10]. Aminocarbene complexes $(CO)_5M=C(NR_2)R'$ ($R' =$ aryl, alkyl) are thermally much more robust than their alkoxy analogues. Heating of $(CO)_5Cr=C(NMe_2)Ph$ does not give an olefin, but N,N,N',N'-tetramethyl-α,α'-diphenylethylenediamine coordinated to a $Cr(CO)_4$ fragment [11]. Although thermolyses of $(CO)_5M=C(NR_2)R'$ have not been systematically investigated, this example is consistent with the thermal behaviour of alkoxy carbene complexes in so far as the M=C bond is broken but the carbene ligand is not fragmented.

If R' (alkyl, aryl) is replaced by groups such as $SnPh_3$, $PbPh_3$, SePh, or TePh (Y), a totally different reaction is observed. On heating, the carbene complexes $(CO)_5Cr=C(NR_2)Y$ lose a CO ligand and rearrange to carbyne complexes *trans*-$Y(CO)_4Cr\equiv CNR_2$ [12]. Silyl-substituted carbene complexes $(CO)_5M=C(NR_2)SiR'_3$ (**2a**) occupy an exceptional position between analogous alkyl- or aryl-substituted complexes and the $SnPh_3$-substituted derivative. If the solid complexes $(CO)_5W=C(NR_2)SiR'_3$ are warmed to 100–150°C at about 0.2 torr, a CO ligand is eliminated and stable tetracarbonyl complexes $(CO)_4W=C(NR_2)SiR'_3$ are formed in high yields (eq. 7). The analogous complexes of chromium and molybdenum are obtained to some extent even during the preparation of the pentacarbonyl carbene complexes (eq. 3) [6,13].

$$(CO)_5M\text{---}C\overset{NR_2}{\underset{SiR'_3}{\diagdown}} \quad \overset{T\uparrow}{\rightleftharpoons} \quad CO + (CO)_4M\text{---}C\overset{NR_2}{\underset{SiR'_3}{\diagdown}} \tag{7}$$

$$\textbf{(2a)} \qquad\qquad\qquad \textbf{(4)}$$
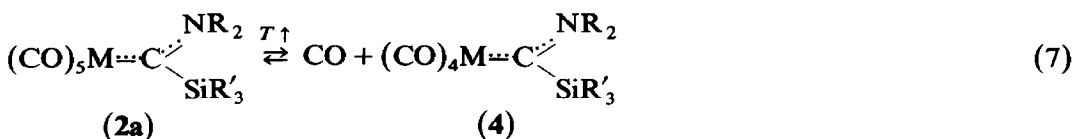
$(NR_2 = NMe_2, NEt_2, NMeEt, NC_4H_8, NC_5H_{10};$

$SiR'_3 = SiPh_3, SiPh_2Me, SiPhMe_2)$

The stabilities of the 16-electron carbene complexes **4** decrease in the order W > Mo ≈ Cr for a given SiR'_3 group, and in the order $SiPh_3 > SiPh_2Me > SiPhMe_2$ for a given metal. An explanation for both the formation and the stability of the unique complexes **4** can be found in the solid-state structure of $(CO)_4W=C(N_5H_{10})SiPh_3$ (Fig. 1) [13]. The coordination around the metal atom is not greatly influenced by the loss of one CO ligand: the bond distances around the carbene carbon are not different from those in comparable 18-electron carbene complexes, and the bond angles within the $(CO)_4W$ moiety are hardly distorted. One of the phenyl groups of the $SiPh_3$ moiety screens the empty coordination site at tungsten, which is *cis* to the carbene ligand. Since all except one of the W–C(phenyl) distances exceed 300 pm, and since the shortest W–C(phenyl) distance (268.8(8) pm) is much longer than the

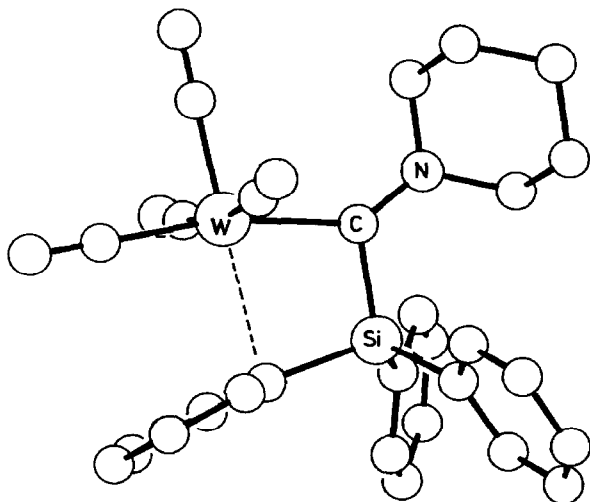Fig. 1. Molecular structure of $(CO)_4W=C(NC_5H_{10})SiPh_3$. W–C(carbene) 214.7(9), C(carbene)–Si 187.7 (9), W–C(carbene–N 138.0(7) pm, W–C(carbene)–Si 101.2(4)°, N–C(carbene)–Si 120.8 (7)°, C(carbene)–Si–C(phenyl) 101.7, 112.3, 113.9(4)°.

W–C(olefin) distances in *cis*-$(CO)_4$(olefin)W(carbene) complexes (238–252 pm), there can be only a very weak π-interaction between the phenyl group and the metal. The main structural difference between analogous 18-electron (**2a**) and 16-electron complexes (**4**) is the presence of a sterically unstrained carbene ligand in the latter. Since the (planar) amino group is forced into the carbene plane by the π-interaction between the carbene carbon and the nitrogen atom, severe steric interactions between the groups R at nitrogen and both the metal carbonyl moiety and the SiR'_3 group result in **2a**. We believe that relief of the steric strain within the carbene ligand is the driving force for the formation of **4** from **2a**. Optimal bond angles at the carbene carbon (the magnitude of which can be derived by comparison with a series of octahedral rhenium complexes containing the $C(OR)SiRh_3$ ligand [14]) are only possible for the 16-electron complexes **4**, and are impossible for **2a**.

The pseudo-octahedral geometry of **4** is also maintained in solution. Compared with *cis*-substituted complexes $(CO)_4LM=C(OR)R'$, the $\nu(CO)$ bands of **4** are shifted to lower wavenumbers, but the pattern remains the same. In the ^{13}C NMR spectra of **4** only two CO resonances are observed, indicating that the molecules are fluxional on the NMR time scale. We attribute this behaviour to the very weak interaction between the phenyl ring and the metal atom.

Dissociative loss of a carbonyl ligand has been postulated as the initial step in many reactions of Fischer-type carbene complexes $(CO)_5M=C(XR)R'$, but in no case have the 16-electron $(CO)_4M=C(XR)R'$ intermediates been observed directly. The fact that the complexes **4** are stable and in most cases can be isolated seems to be due to a balance between steric and electronic effects. The $SiPh_3$ substituent (and to a lesser extent the $SiPh_2Me$ and $SiPhMe_2$ substituents) favours CO elimination because of its steric bulk, and stabilizes the electron-deficient complexes by screening the empty coordination site. On the other hand, the C(carbene)–Si bond is just strong enough to prevent migration of the SiR_3 group from C(carbene) to the metal

and formation of silyl-substituted carbyne complexes (such as occurs in the case of $(CO)_5Cr\!\!=\!\!C(NEt_2)SnPh_3$).

The notion that the 16-electron complexes **4** are related to the intermediates in reactions of Fischer-type carbene complexes is supported by their reaction pattern. Donor molecules such as CO, MeCN or PR_3 stereospecifically add to the empty coordination site *cis* to the carbene ligand even at room temperature (eq. 8). This is

$$(CO)_4W\!\!=\!\!C\!\!\diagup^{NMe_2}_{\diagdown SiPh_3} + L \rightarrow cis\text{-}(CO)_4LW\!\!=\!\!C\!\!\diagup^{NMe_2}_{\diagdown SiPh_3} \qquad (8)$$

$$(L = CO, MeCN, PTol_3, PPh_2Me, PEt_3)$$
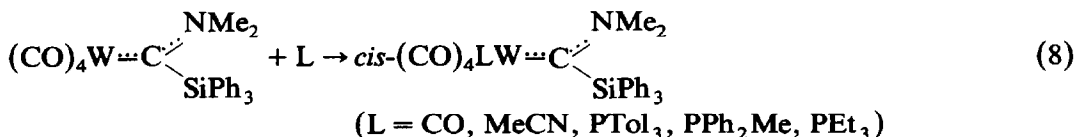
in contrast to substitution reactions of pentacarbonyl carbene complexes, which require higher temperatures or photochemical conditions (to split off a CO ligand). At these conditions isomerisation to the *trans* compound and decomposition cannot be prevented [1].

Thermolysis of dialkylamino-substituted carbene complexes **2a** results exclusively in the loss of a CO ligand and formation of **4**. If one alkyl group is replaced by hydrogen, an alternative pathway becomes more favourable. When solid monoalkylaminocarbene complexes $(CO)_5M\!\!=\!\!C(NHR)SiR'_3$ (**2b**) are heated above their melting points, $HSiR_3$ elimination with formation of the isonitrile complexes $(CO)_5MCNR'$ and $(CO)_4M(CNR')_2$ and $M(CO)_6$ takes place quantitatively (eq. 9) [15]. We found no indication of the formation of a 16-electron complex for any monoalkylamino carbene complex **2b**.

$$(CO)_5M\!\!=\!\!C\!\!\diagup^{NHR}_{\diagdown SiR'_3} \xrightarrow{T\uparrow} HSiR'_3 + (CO)_5MCNR' \qquad (9)$$
$$\textbf{(2b)} \qquad\qquad \downarrow$$
$$(CO)_4M(CNR')_2 + M(CO)_6$$
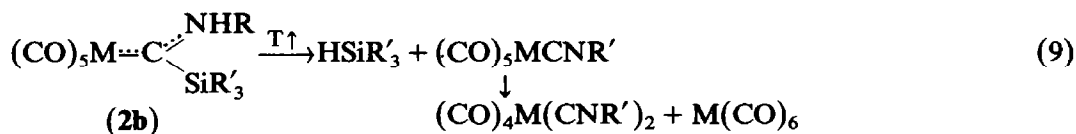
Since only $DSiPh_2Me$ and no $HSiPh_2Me$ is obtained from $(CO)_5W\!\!=\!\!C(NDEt)SiPh_2Me$, the silane hydrogen atom must come from the NH group. Joint thermolysis of the deuterated and non-deuterated complexes **2b** additionally gives the crossover products, e.g. from a mixture of $(CO)_5W\!\!=\!\!C(NHEt)SiPh_3$ and $(CO)_5W\!\!=\!\!C(NDEt)SiPh_2Me$ not only $HSiPh_3$ and $DSiPh_2Me$ but also $DSiPh_3$ and $HSiPh_2Me$ are formed. Through control experiments we were able to exclude preceding or subsequent exchange reactions. From these results we conclude that fragmentation of monoalkylamino-substituted complexes **2b** proceeds intermolecularly.

Elimination of HX from $L_nM\!\!=\!\!C(NHR)X$ has occasionally been observed for groups X having a lone pair [16]. In the case of pentacarbonyl carbene complexes of Cr, Mo and W mention must be made mainly of complexes of the type $(CO)_5M\!\!=\!\!C(NHR')SR$, which are formed on reaction of $(CO)_5M\!\!=\!\!C(SR)_2$ or $(CO)_5MCS$ with primary amines, and spontaneously decompose by HSR (H_2S) elimination to give the corresponding isonitrile complexes [17].

The products obtained on thermolysis of alkoxy(silyl)carbene complexes **1** are less uniform than in the case of amino(silyl)carbene complexes. Depending on the metal and on the reaction conditions, various amounts of $HSiPh_3$, $EtC(O)SiPh_3$, and $EtSiPh_3$ are formed from $(CO)_5M\!\!=\!\!C(OEt)SiPh_3$ (eq. 10), and these add up to at least 95% of the silicon-containing products [18]. Some of the ketone is π-coordi-

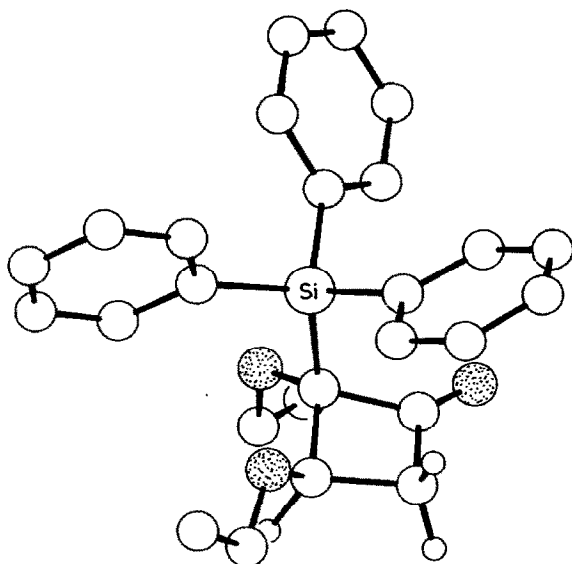nated to a M(CO)$_3$ moiety via one of its phenyl substituents [19].

$$\text{(CO)}_5\text{M}{\cdots}\text{C}{\overset{\text{OEt}}{\underset{\text{SiPh}_3}{}}} \quad \begin{cases} \rightarrow \text{HSiPh}_3 + \text{C}_2\text{H}_4 + \text{M(CO)}_6 & \text{(10a)} \\ \rightarrow \text{Et-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-SiPh}_3 + \text{Et-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-SiPh}_2[\text{C}_6\text{H}_5\text{M(CO)}_3] + \dots & \text{(10b)} \\ \rightarrow \text{EtSiPh}_3 + \text{M(CO)}_6 & \text{(10c)} \end{cases}$$

(1: M = Cr, Mo, W)

The product ratio strongly depends on the metal: thermolysis of the tungsten complex in the solid state or in octane solution gives only HSiPh$_3$, ethylene and W(CO)$_6$ (eq. 10a), whereas from the chromium complex both HSiPh$_3$ and EtC(O)SiPh$_3$ are obtained, and from the molybdenum complex all three types of organosilicon products are formed. Dioxane as a solvent promotes reaction pathways (eq. 10c and eq. 10b) for M = W and increases the relative amounts of EtC(O)SiPh$_3$ and EtSiPh$_3$ for M = Cr and Mo. When the corresponding methoxy-substituted complexes (CO)$_5$M=C(OMe)SiPh$_3$ are thermolyzed, MeSiPh$_3$ is the main product in all cases and only traces of MeC(O)SiPh$_3$ are observed.

Although ketone formation has already been observed in one case [20], decomposition routes 10a and 10c are without precedent in the chemistry of Fischer-type carbene complexes and must therefore be attributed to the presence of a silyl group. The kind of products and the influence of the metal, the alkoxy group and the solvent on the product ratio can be understood, if alkylsilyl complexes (CO)$_5$M(R)SiPh$_3$ (D) are assumed to be the common intermediate, from which the observed organosilicon products would be formed by standard organometallic reactions (reductive elimination, alkyl/acyl rearrangement, β-elimination) [18]. Equation 11 shows how D might be formed from 1.

$$\underset{\text{(1)}}{\text{(CO)}_5\text{M}{\cdots}\text{C}{\overset{\text{OR}}{\underset{\text{SiPh}_3}{}}}} \xrightarrow{-\text{CO}} \underset{\text{(B)}}{\text{(CO)}_4\text{M}{\cdots}\text{C}{\overset{\text{OR}}{\underset{\text{SiPh}_3}{}}}} \xrightarrow{} \underset{\text{(C)}}{\text{(CO)}_4(\text{Ph}_3\text{Si})\text{M}{\equiv}\text{COR}} \xrightarrow{} \underset{\text{D}}{\text{(CO)}_5\text{M}{\overset{\text{R}}{\underset{\text{SiPh}_3}{}}}} \quad \text{(11)}$$

By analogy with the behaviour of dialkylamino(silyl)carbene complexes (CO)$_5$M=C(NR$_2$)SiR$'_3$, elimination of CO and formation of the 16-electron complexes B appears to be a reasonable initial step. Because π-overlap between the carbene carbon and the adjacent donor group is more effective in aminocarbene complexes than in alkoxycarbene complexes, the carbene carbon atom in alkoxycarbene complexes bears a higher positive charge. Therefore the C(carbene)–Si bond in B should be more labile than in 4, and migration of the silyl group from the carbene carbon to the metal atom is facilitated. A similar situation is found with stannyl- or plumbyl-substituted carbene complexes (CO)$_5$Cr=C(NEt$_2$)EPh$_3$ (E = Sn, Pb), which thermally rearrange to carbyne complexes trans-(CO)$_4$(Ph$_3$E)Cr≡CNEt$_2$ with loss of CO [12]. Formation of D from C requires migration of the group R from oxygen to the metal atom. Since calkoxycarbyne complexes are unknown, this step must remain without precedent for the time being *.

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* See Note added in proof [32].

Fragmentation of $(CO)_5W=C(OEt)SiPh_3$ (eq. 10) can be suppressed by treating the complex with CO under moderate pressure. Under these conditions the entire carbene ligand is cleaved from the metal and ethoxy(triphenylsilyl)ketene (5a) is quantitatively formed (eq. 12) [21].

$$(CO)_5W=C(OEt)SiPh_3 + 2\ CO \xrightarrow[20\,°C]{50\ atm} W(CO)_6 + \underset{EtO}{\overset{Ph_3Si}{>}}C=C=O \qquad (12)$$

$$(5a)$$

Because of its high reactivity, ketene 5a could not be isolated, but it was unequivocally identified from its ν(CCO) band and by its hydrolysis product $(Ph_3Si(EtO)CHCOOH)$. For preparative use (vide infra), in situ generation of 4a is sufficient.

While generation of 5a requires moderate CO pressure, the corresponding ethyl-thio-substituted ketene 5b and its metal complex 6 are formed even on decomposition of the very labile ethylthio(silyl)carbene complex $(CO)_5W=C(SEt)SiPh_3$ (3) at ambient temperature (eq. 13). The yield of 5b and 6 can be increased by bubbling CO through a pentane solution of 3. The ketene complex 6 is rather labile, and readily splits off the ketene ligand. This can be achieved in a quantitative way by treating 6 with tetraethylammonium chloride or with 50 atm of carbon monoxide at 80–100 °C. Compared to 5a, the thio analogue 5b is less reactive, and is fairly stable.

$$(CO)_5W\!\cdots\!C\!\!\underset{SiPh_3}{\overset{SEt}{<}} + CO \rightarrow \underset{EtS}{\overset{Ph_3Si}{>}}C=C=O + \underset{Et-S}{\overset{Ph_3Si}{>}}C=C=O \qquad (13)$$

$$(3) \qquad\qquad (5b) \qquad\qquad \underset{W(CO)_5}{\big\downarrow}$$

$$(6)$$

$$\underset{\text{50 atm CO/80-100 °C}}{\underline{\qquad NEt_4Cl\ or \qquad}}$$

Formation of ketenes or ketene complexes by carbonylation of carbene complexes has been confirmed in several cases, in both stoichiometric and catalytic reactions [1]. The ketenes $Ph_3Si(EtX)C=C=O$ (5a: X = O, 5b: X = S) are mainly of interest from a preparative point of view, because of the presence of a silyl group and an alkoxy or alkylthio substituent on the same carbon atom. Known silylke-tenes, such as $Me_3SiCH=C=O$, react only with very activated olefins to give cyclobutanone derivatives [22]. The presence of an alkoxy group in 5a causes an increase in reactivity. If $(CO)_5W=C(OEt)SiPh_3$ is treated with 50 atm of CO in the presence of 2,3-dihydrofurane, the cyclobutanone 7 is obtained (89% yield) by [2 + 2]cycloaddition of in situ-generated ketene 5a (eq. 145). The stereoselectivity of this reaction is high: the isomers 7a and 7b are formed in a 16/1 ratio [21].

$$5a\ +\ \text{(furan)} \longrightarrow \text{(7a)} \quad \text{(7b)} \qquad (14)$$

Ethyl vinyl ether reacts similarly (eq. 15). The stereochemistry of the main isomer 8a has been elucidated by an X-ray structure determination (Fig. 2). Besides the two

Fig. 2. Molecular structure of the cyclobutanone **8a**; *trans*-orientation of the two ethoxy groups is to be expected for the major isomer from stereochemical considerations [24].

isomers of the cyclobutanone **8** (**8a/8b** 20/1), small amounts of the cyclopropane derivative **9** were detected [23].
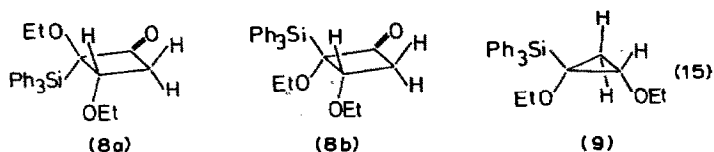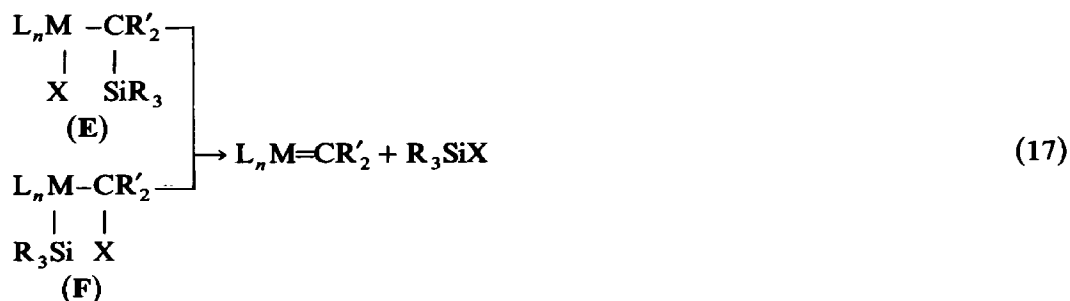

While **8a**, **8b** arise from [2 + 2]cycloaddition between ketene **5a** and ethyl vinyl ether, compound **9** is formed by direct attack of the olefin to the carbene complex [25]. Reasonable yields of **9** can be obtained by reaction of the carbene complex with an excess of ethyl vinyl ether at 50°C in the absence of CO [23]. Under these conditions no ketene (and hence no **8**) is formed, and decomposition of the carbene complex (eq. 10) does not play a major role. Assignment of the configuration of **9** was made on stereochemical grounds. The second isomer is obviously formed only in minute amounts.

Ketene **5a** is reactive enough to give [2 + 2]cycloadducts even with less activated olefins. With cyclopentadiene the bicyclic ketone **10** (**10a/10b** 5/1) can be obtained in 68% yield (eq. 16) [23].
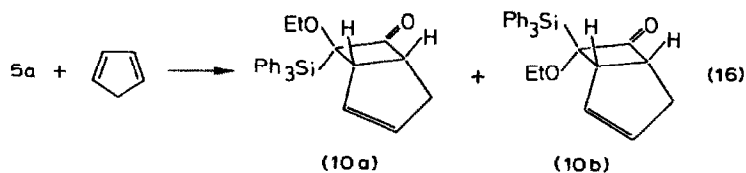
Formation of M=C double bonds by R_3SiX elimination

There is a marked difference between main-group and transition-metal chemistry in respect of methods of double bond generation. Whereas with main groups species, 1,2-eliminations, rearrangements and retro-cycloadditions are employed, a variety of other methods has been applied to the synthesis of transition-metal complexes containing metal–carbon multiple bonds. We became interested in the question of whether 1,2-elimination of silane derivatives, R_3SiX, which is frequently used in main group chemistry, could provide a preparative route to carbene or vinylidene complexes. R_3SiX elimination could occur from two different types of intermediates (eq. 17), which differ in respect of the relative position of the groups to be eliminated.

$$
\left.
\begin{array}{c}
L_nM \;\; -CR'_2 \\
\;\; | \quad\;\; | \\
X \quad SiR_3 \\
\textbf{(E)} \\
\\
L_nM - CR'_2 \\
\;\; | \quad\;\; | \\
R_3Si \;\; X \\
\textbf{(F)}
\end{array}
\right\} \rightarrow L_nM{=}CR'_2 + R_3SiX
\tag{17}
$$

Our work on the reactions of anionic silyl complexes with metal halides and metal complex halides [26] prompted us to investigate the possibility of generating intermediates of the type **F** by treating anionic silyl complexes with geminal dihalides. We started with 3,3-dichloro-1,2-diphenylcyclopropene, because this compound is known to form a cyclopropenylidene complex with $[(CO)_5Cr]^{2-}$ [27]. Reaction of $[MeCp(CO)_2MnSiMePh_2]^-$ or $[(Ph_3P)(CO)_3FeSiMePh_2]^-$ with the dihalide in fact results in the expected carbene complexes (eq. 18). The corresponding anionic germyl- or stannyl-substituted complexes can be used analogously [28].

$$
\left[L_nM{-}ER \right]^- \; + \; \underset{Cl}{\overset{Cl}{\diagup}}{\Big\langle}{\underset{Ph}{\overset{Ph}{\diagup}}} \longrightarrow L_nM{=}C{\underset{Ph}{\overset{Ph}{\diagup}}} \; + \; R_3ECl \; + \; Cl^- \tag{18}
$$
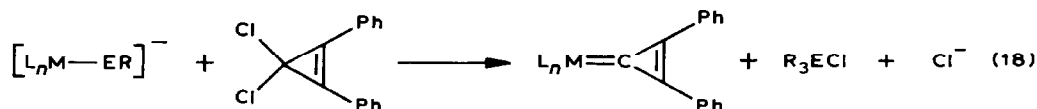
$(L_nM \; = \; MeCp(CO)_2Mn \; , \; (Ph_3P)(CO)_3Fe \; ; \; E \; = \; Si, Ge, Sn)$

In these reactions, the anionic silyl, germyl or stannyl complexes $[L_nM{-}ER_3]^-$ act as equivalents of L_nM^{2-}. Since they can be prepared for a variety of metals and ligand environments, and since they are usually not difficult to handle, they should be applicable to syntheses like eq. 18 more widely than is possible with L_nM^{2-}. In particular, they could supplement the preparative use of L_nM^{2-} when these latter complexes are unknown or too unstable.

For the generation of type **E** intermediates we developed another approach. Reaction of vinylsilanes $R_3Si(X)C{=}CR'_2$ with $MeCp(CO)_2Mn$, which is generated by the usual methods, results in π-coordination of the olefin. We obtained a number of such olefin complexes **11** as isolable compounds (eq. 19) [29].

$$[MeCp(CO)_2Mn] \ + \ \underset{X}{\overset{R_3Si}{>}}C=C\underset{R'}{\overset{R'}{<}} \ \longrightarrow \ MeCp(CO)_2Mn - \overset{\overset{\overset{R'}{\underset{|}{C}}R'}{\|}}{\underset{\underset{X}{\overset{|}{C}}SiR_3}{}} \qquad (19)$$

$$(X = H , Cl , Br) \qquad\qquad\qquad (11)$$

$$MeCp(CO)_2Mn - \overset{\overset{\overset{Me \quad Me}{\underset{|}{C}}}{\|}}{\underset{\underset{X}{\overset{|}{C}}SiMe_3}{}} \ \rightleftharpoons \ \left[MeCp(CO)_2Mn \underset{Me_3Si}{\overset{X}{<}} C=CMe_2 \right] \ \longrightarrow$$

$$(11: X = Cl , Br) \qquad\qquad\qquad (G)$$

$$\longrightarrow MeCp(CO)_2Mn = C = CMe_2 \ + \ Me_3SiCl \qquad (20a)$$

$$(12)$$

$$\underset{Me_3Si(Cl)C=CMe_2}{\overset{excess}{\longrightarrow}} MeCp(CO)_2Mn - \overset{\overset{\overset{\overset{Me \quad Me}{\underset{\|}{C}}}{\underset{\|}{C}}}{\|}}{\underset{\underset{\underset{Me \quad Me}{C}}{\|}}{}} \ + \ 2 \ Me_3SiCl \qquad (20b)$$

$$(13)$$
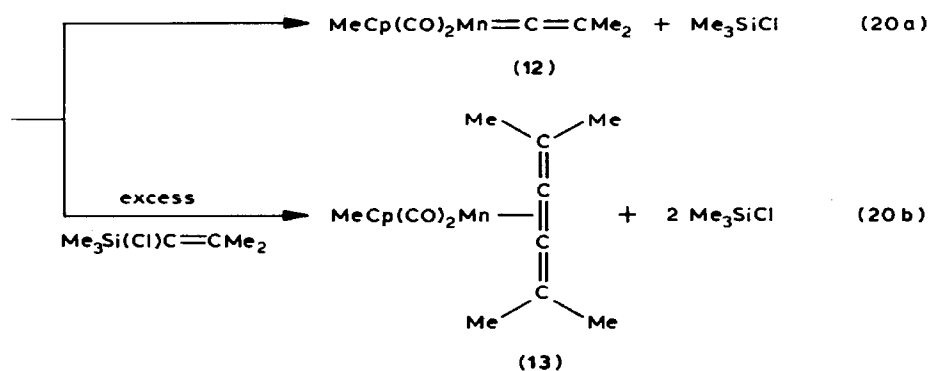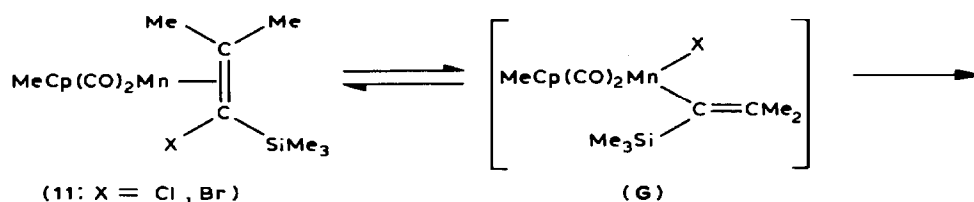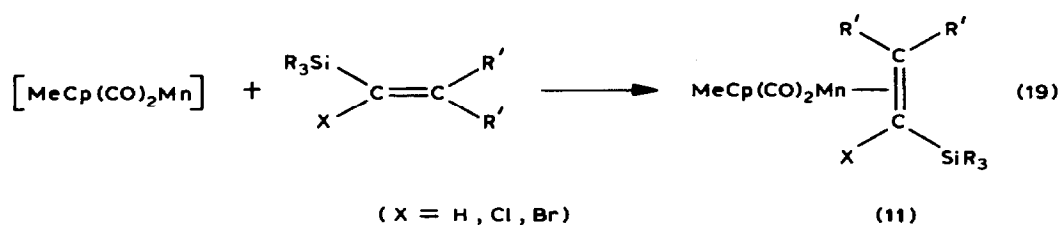
However, some of the olefin complexes undergo subsequent reactions. Thus when a pentane solution of 11 (X = Br, R_3Si = Me_3Si, R' = Me) is allowed to stand for some days at room temperature the olefin complex is converted to the vinylidene complex 12 (eq. 20a).

Irridiation of $MeCp(CO)_3Mn$ and $Me_3Si(Cl)C=CMe_2$ with UV light for 2 h at room temperature gives 12 directly in good yields. If at least a 10-fold excess of the vinylsilane is used in this reaction, the outcome is different (eq. 20b); in the butatriene complex 13 obtained two vinylidene units are coupled to the metal center. Complex 13 is also formed on reaction of $Me_3Si(Cl)C=CMe_2$ with a stoichiometric amount of $MeCp(CO)_2Mn(THF)$ [29]. Since this reaction takes two days for completion and no olefin complex can be spectroscopically observed, the stationary concentration of the π-olefin intermediate 11 is so small that 11 finds itself surrounded by a large local excess of the vinyl silane and therefore gives the butatriene complex 13 instead of the vinylidene complex 12.

Since 12 does not react with $Me_3Si(Cl)C=CMe_2$ in THF at room temperature, 12 cannot be a precursor of 13. It seems reasonable to assume that 12 and 13 are formed from a common precursor. We postulate that the intermediate in question is G, formed from 11 by thermal or photochemical oxidative addition of the C–Cl or
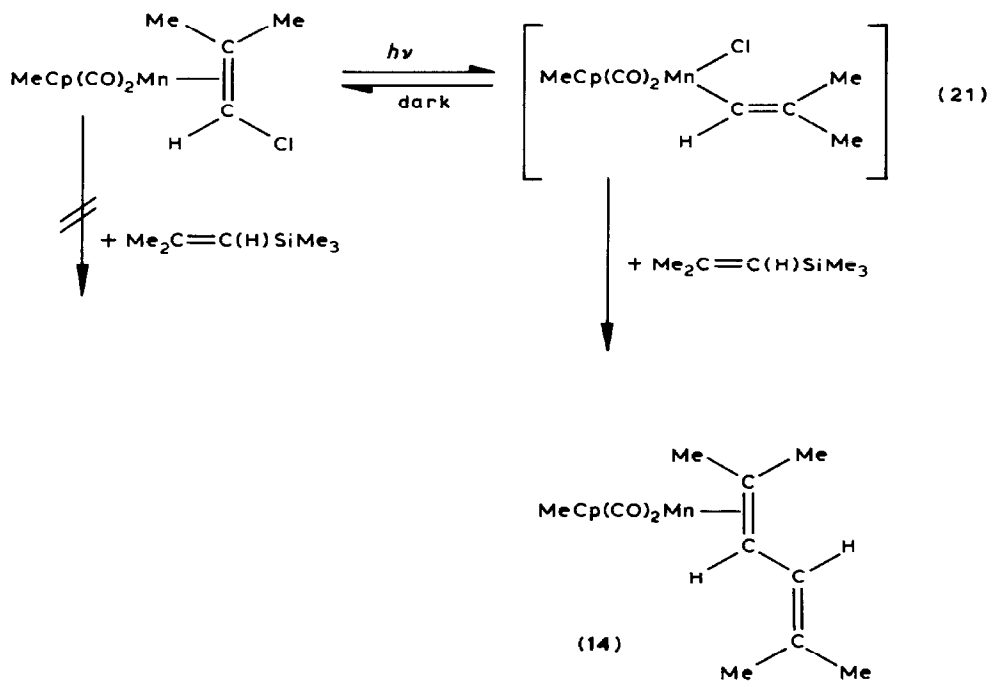
C–Br bond to the metal (the hypothetical possibility that the C–Si rather than the C–X bond is oxidatively added can be excluded, since **11**, X = H, is a stable compound). Not surprisingly, the rate of the conversion of **11** into **G** depends on both the SiR_3 substituent and the halogen. For instance, photochemical reaction of $MeCp(CO)_3Mn$ with $Ph_2MeSi(Cl)C=CMe_2$ in pentane gives the π-complex as a major and **12** as a minor product, while **12** is exclusively formed under the same conditions when the Me_3Si derivative is used.

Intramolecular 1,2-elimination of Me_3SiX from **G** gives the vinylidene complex **12**. A strong hint as to how the butatriene complex could be formed from **G** was obtained in the following way. When $MeCp(CO)_3Mn$ was irradiated with $Me_2C=CHCl$ in pentane, a yellow solution was obtained ($\nu(CO)$ 1970, 1920 cm^{-1}). The solution turns red in the dark and the π-complex $MeCp(CO)_2Mn(Me_2C=CHCl)$ ($\nu(CO)$ 1960, 1900 cm^{-1}) can be isolated. We believe that the yellow solution contains $MeCp(CO)_2Mn(Cl)CH=CMe_2$, which in contrast to **G** cannot undergo a 1,2-elimination reaction and thermally reverts to the π-olefin complex. The isomerization can be reversed by switching on the lamp again. To find out whether the butatriene complex **13** is formed from **11** or from **G** we added $Me_2C=CHSiMe_3$ to both the yellow and the red solution. Whereas no reaction was observed between the olefin and the π-complex (red solution), the diene complex **14** was formed, when $Me_2C=CHSiMe_3$ is added to the yellow solution, presumably containing $MeCp(CO)_2Mn(Cl)CH=CMe_2$ (eq. 21).

If an analogous mechanism is assumed for the formation of **13**, a substituted butadiene ligand, $Me_2C=C(SiMe_3)C(Cl)=CMe$ would be expected and would subsequently undergo Me_3SiCl elimination to give tetramethylbutatriene.

The coupling of two vinylidene units at the metal is only possible if the substituents at the β-carbon of the vinyl derivative have certain properties. We were

unable to prepare the corresponding tetraphenylbutatriene complex from 1-chloro-1-(trimethylsilyl)-2,2-diphenylethene. In this case intramolecular elimination of Me_3SiCl predominates and the vinylidene complex $MeCp(CO)_2Mn=C=CPh_2$ is exclusively formed.

Whereas monosubstituted vinylidene ligands (C=CHR) are readily obtained from 1-alkynes [30], preparative routes to complexes containing disubstituted vinylidene ligands (C=CR$_2$) are less general. The previously known compound $Cp(CO)_2Mn=C=CMe_2$, was synthesized by a multistep procedure [31]. In contrast, our method (eq. 20a) is rather simple and uses readily available precursors for the vinylidene unit. Successful synthesis of $Ar(CO)_2Cr=C=CR_2$ (Ar = C_6H_6, $C_6H_3Me_3$, C_6Me_6; R = Me, Ph) and $(R'_3P)(CO)_3Fe=C=CR_2$ [29] indicates that vinylidene complexes of other metals can probably also be prepared by this route.

Whether this method of generating metal carbon double bonds is also applicable to the synthesis of carbene complexes has yet to be investigated.

Acknowledgements

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