A Thermally Induced Novel Fragmentation Reaction of Transition Metal Silylcarbene Complexes

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The carbene complexes $(CO)_5WC(OEt)SiPh_3$ (**1**) and $(CO)_5WC(NEt_2)SiPh_3$ (**2**) thermally decompose to give triphenylsilane, ethylene, and $W(CO_6)$ or $(CO)_5WCNEt$, respectively, while in the presence of moist CO, $[Ph_3Si(EtO)CHC(O)]_2O$ is formed, believed to arise *via* the ketene intermediate, $Ph_3Si(EtO)C{=}C{=}O$.

Transition metal carbene complexes can be used as carbene sources in organic syntheses, if the carbene ligand is cleaved from the metal.[1] In the absence of suitable reaction partners aryl- or alkyl-(alkoxy)carbene complexes yield organic products which are equivalent to the dimerized or isomerized former carbene ligand.[2,3] Silylcarbene complexes have not been investigated in this respect. However, if they were to exhibit a similar, 'carbenoid-like' behaviour, organosilicon products derived from silyl carbene intermediates could be expected. The silylcarbenes, $R^1_3Si{-}C{-}R^2$, are particularly interesting species because they can rearrange to silaolefins, $R^1_2Si{=}CR^1R^2$.[4]

When $(CO)_5WC(OEt)SiPh_3$ (**1**)[5] (solid or in decalin solution) was heated to about 125 °C, ethylene was evolved and $W(CO)_6$ and $HSiPh_3$ formed nearly quantitatively [equation (1)]. In this reaction the carbonyl ligand from which the carbene ligand was formed originally is restored. $W(CO)_6$ and $HSiPh_3$ were identified by comparison with authentic materials and ethylene by gas chromatography. Using a combination of differential scanning calorimetry and quadrupole mass spectroscopy we were able to prove that ethylene evolution and thermal decomposition of (**1**) coincide.

$$\underset{(\mathbf{1})}{(CO)_5WC(OEt)SiPh_3} \xrightarrow{125\,^{\circ}C} W(CO)_6 + HSiPh_3 + C_2H_4 \quad (1)$$

$$(\mathbf{1}) \xrightarrow[-EtOH]{+HNEt_2} \underset{(\mathbf{2})}{(CO)_5WC(NEt_2)SiPh_3} \xrightarrow{125\,^{\circ}C} (CO)_5WCNEt + HSiPh_3 + C_2H_4 \quad (2)$$

The fragmentation reaction is not restricted to alkoxysilylcarbene complexes. $(CO)_5WC(NEt_2)SiPh_3$ (**2**)† was prepared in 20% yield by the reaction of (**1**) with neat $HNEt_2$ at room temperature. From the products of the thermal decomposition of (**2**), $(CO)_5WCNEt$ and $HSiPh_3$ were isolated in high yields [equation (2)].

Silanecarboxylic esters, Ph_3SiCO_2R, which are formally similar to (**1**) [$W(CO)_5$ replaced by O], thermally decompose to give carbon monoxide and alkoxytriphenylsilane.[6] However, in the carbene complexes (**1**) and (**2**) the carbene carbon–oxygen or –nitrogen bond was not so easily cleaved owing to the high degree of π-bonding between these atoms. The difference in the thermal behaviour of (**1**) and aryl- or alkyl-(alkoxy)carbene complexes can be explained by weakening of the carbene carbon–silicon bond owing to the carbenium character of the carbene carbon atom. Formation of an isonitrile complex from a carbene complex was also observed, when $(CO)_5CrC(NEt_2)Cl$ was warmed to 30 °C in the solid state (in solution a carbyne complex is formed

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† ^{1}H n.m.r. (CD_3COCD_3, −30 °C, rel. Me_4Si): δ 7.6 (m, C_6H_5, 15H), 4.3 (q, CH_2, 2H), 3.3 (q, CH_2, 2H), 1.4 (t, CH_3, 3H), and 0.8 (t, CH_3, 3H); m.p. 117 °C (decomp.); i.r. (cm^{-1}, pentane): ν_{CO} 2057 m, 1970 w, 1938 vs, 1932 s, and 1921 sh.

$$(\mathbf{1}) + \dot{\mathrm{C}}\mathrm{O} \longrightarrow \mathrm{W(CO)_6} + \underset{(\mathbf{3})}{\mathrm{Ph_3Si(EtO)C{=}C{=}O}} \tag{3}$$

$$2\,(\mathbf{3}) + \mathrm{H_2O} \longrightarrow \underset{(\mathbf{4})}{\mathrm{[Ph_3Si(EtO)CH{-}CO{-}]_2O}} \tag{4}$$

instead).[7] However, in this reaction there are a number of byproducts, and no gaseous products could be identified.

Treatment of a pentane solution of (**1**) with undried carbon monoxide (50 atm pressure, room temperature) yielded the anhydride (**4**) and $W(CO)_6$. Compound (**4**) was characterized by elemental analysis, spectroscopy,‡ and by an *X*-ray structure determination, details of which will be published separately. We believe that a silylketene (**3**) is the primary product [equation (3)], and this is then hydrolysed to (**4**) [equation (4)]. Ketenes are known to be formed in the reactions of CO with other carbene complexes.[8]

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References

1 K. H. Dötz, in 'Transition Metal Carbene Complexes,' Verlag Chemie, Weinheim, 1983, pp. 191—226.

2 E. O. Fischer, *Angew. Chem.*, 1974, **86**, 651; K. H. Dötz, *Naturwissenschaften*, 1975, **62**, 365.

3 E. O. Fischer and U. Schubert, *J. Organomet. Chem.*, 1979, **170**, C13.

4 T. J. Barton and S. K. Hoekman, *J. Am. Chem. Soc.*, 1980, **102**, 1584, and references cited therein.

5 E. O. Fischer, H. Hollfelder, P. Friedrich, F. R. Kreissl, and G. Huttner, *Chem. Ber.*, 1977, **110**, 3467.

6 A. G. Brook and R. J. Mauris, *J. Am. Chem. Soc.*, 1957, **79**, 971.

7 H. Fischer, A. Motsch, and W. Kleine, *Angew. Chem.*, 1978, **90**, 914; *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 842.

8 *E.g.* B. Dorrer and E. O. Fischer, *Chem. Ber.*, 1974, **107**, 2683.

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‡ ^{1}H N.m.r. ($CDCl_3$, rel. Me_4Si): δ 7.32 (m, C_6H_5, 15H), 4.14 (s, CH, 1H), 3.50 (q, CH_2, 1H), 3.18 (q, CH_2, 1H), and 1.06 (t, CH_3, 6H); i.r. (cm^{-1}, CCl_4): ν_{CO} 1803 s and 1743 m; mass: highest observable *m/z* 620 $[M - EtO(H)CCO]^+$; m.p. 185 °C (decomp.).