

## A Thermally Induced Novel Fragmentation Reaction of Transition Metal Silylcarbene Complexes

Ulrich Schubert,<sup>a</sup> Hannelore Hörnig,<sup>a</sup> Kai-Uwe Erdmann,<sup>a</sup> and Karin Weiss<sup>b</sup>

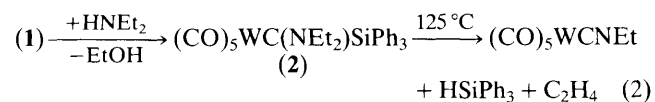
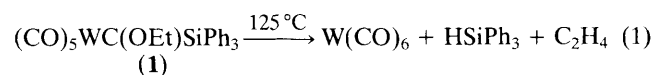
<sup>a</sup> Institut für Anorganische Chemie der Universität, Am Hubland, D-8700 Würzburg, W. Germany

<sup>b</sup> Laboratorium für Anorganische Chemie der Universität, Universitätsstr. 30, D-8580 Bayreuth, W. Germany

The carbene complexes  $(\text{CO})_5\text{WC}(\text{OEt})\text{SiPh}_3$  (**1**) and  $(\text{CO})_5\text{WC}(\text{NEt}_2)\text{SiPh}_3$  (**2**) thermally decompose to give triphenylsilane, ethylene, and  $\text{W}(\text{CO})_6$  or  $(\text{CO})_5\text{WCNEt}$ , respectively, while in the presence of moist  $\text{CO}$ ,  $[\text{Ph}_3\text{Si}(\text{EtO})\text{CHC}(\text{O})]_2\text{O}$  is formed, believed to arise *via* the ketene intermediate,  $\text{Ph}_3\text{Si}(\text{EtO})\text{C}=\text{O}$ .

Transition metal carbene complexes can be used as carbene sources in organic syntheses, if the carbene ligand is cleaved from the metal.<sup>1</sup> 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.<sup>2,3</sup> 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,  $\text{R}_3\text{Si}-\text{C}-\text{R}^2$ , are particularly interesting species because they can rearrange to silaolefins,  $\text{R}_2\text{Si}=\text{CR}^1\text{R}^2$ .<sup>4</sup>

When  $(\text{CO})_5\text{WC}(\text{OEt})\text{SiPh}_3$  (**1**)<sup>5</sup> (solid or in decalin solution) was heated to about 125 °C, ethylene was evolved and  $\text{W}(\text{CO})_6$  and  $\text{HSiPh}_3$  formed nearly quantitatively [equation (1)]. In this reaction the carbonyl ligand from which the carbene ligand was formed originally is restored.  $\text{W}(\text{CO})_6$  and  $\text{HSiPh}_3$  were identified by comparison with authentic materials and ethylene by gas chromatography. Using a

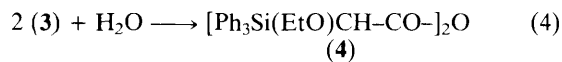
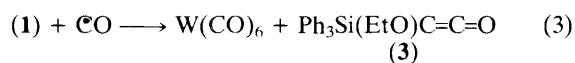


combination of differential scanning calorimetry and quadrupole mass spectroscopy we were able to prove that ethylene evolution and thermal decomposition of (**1**) coincide.

The fragmentation reaction is not restricted to alkoxy-silylcarbene complexes.  $(\text{CO})_5\text{WC}(\text{NEt}_2)\text{SiPh}_3$  (**2**)<sup>†</sup> was prepared in 20% yield by the reaction of (**1**) with neat  $\text{HNEt}_2$  at room temperature. From the products of the thermal decomposition of (**2**),  $(\text{CO})_5\text{WCNEt}$  and  $\text{HSiPh}_3$  were isolated in high yields [equation (2)].

Silanecarboxylic esters,  $\text{Ph}_3\text{SiCO}_2\text{R}$ , which are formally similar to (**1**) [ $\text{W}(\text{CO})_5$  replaced by  $\text{O}$ ], thermally decompose to give carbon monoxide and alkoxytriphenylsilane.<sup>6</sup> 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  $\pi$ -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  $(\text{CO})_5\text{CrC}(\text{NEt}_2)\text{Cl}$  was warmed to 30 °C in the solid state (in solution a carbyne complex is formed

<sup>†</sup> <sup>1</sup>H n.m.r. ( $\text{CD}_3\text{COCD}_3$ , -30 °C, rel.  $\text{Me}_4\text{Si}$ ):  $\delta$  7.6 (m,  $\text{C}_6\text{H}_5$ , 15H), 4.3 (q,  $\text{CH}_2$ , 2H), 3.3 (q,  $\text{CH}_2$ , 2H), 1.4 (t,  $\text{CH}_3$ , 3H), and 0.8 (t,  $\text{CH}_3$ , 3H); m.p. 117 °C (decomp.); i.r. ( $\text{cm}^{-1}$ , pentane):  $\nu_{\text{CO}}$  2057 m, 1970 w, 1938 vs, 1932 s, and 1921 sh.



instead).<sup>7</sup> 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  $\text{W}(\text{CO})_6$ . Compound (4) was characterized by elemental analysis, spectroscopy,<sup>‡</sup> 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)

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<sup>‡</sup> <sup>1</sup>H N.m.r. ( $\text{CDCl}_3$ , rel.  $\text{Me}_4\text{Si}$ ):  $\delta$  7.32 (m,  $\text{C}_6\text{H}_5$ , 15H), 4.14 (s, CH, 1H), 3.50 (q,  $\text{CH}_2$ , 1H), 3.18 (q,  $\text{CH}_2$ , 1H), and 1.06 (t,  $\text{CH}_3$ , 6H); i.r. ( $\text{cm}^{-1}$ ,  $\text{CCl}_4$ ):  $\nu_{\text{CO}}$  1803 s and 1743 m; mass: highest observable  $m/z$  620 [ $M - \text{EtO}(\text{H})\text{CCO}$ ]<sup>+</sup>; m.p. 185 °C (decomp.).

[equation (4)]. Ketenes are known to be formed in the reactions of CO with other carbene complexes.<sup>8</sup>

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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.