

Journal of Organometallic Chemistry, 186 (1980) 241–245
 © Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

SYNTHESES OF EARLY TRANSITION-METAL COMPLEXES CONTAINING METAL–SILICON BONDS

ANA M. CARDOSO, ROBIN J.H. CLARK and STEPHEN MOORHOUSE

*Christopher Ingold Laboratories, University College London, 20 Gordon Street, London
 WC1H OAJ (Great Britain)*

(Received July 16th, 1979)

Summary

The complex $(\eta\text{-C}_5\text{H}_5)_2\text{V}(\text{SiCl}_3)_2$ has been isolated by treatment of $(\eta\text{-C}_5\text{H}_5)_2\text{V}$ with HSiCl_3 in benzene and the complex $(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{H})\text{SiCl}_3$ by similar treatment of $(\eta\text{-C}_5\text{H}_5)_2\text{WH}_2$ with HSiCl_3 . Related reactions between $(\eta\text{-C}_5\text{H}_5)_2\text{MoH}_2$ and HSiCl_3 and between $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2$ and HSiCl_3 led to the formation of yellow and brown products, respectively, but those could not be properly characterised.

Introduction

Since the synthesis of the first silylmetal derivative, $(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SiMe}_3$, there has been increasing interest in attempts to synthesise other transition-metal complexes containing metal–silicon bonds. Much success has been achieved in this respect with Group VI metals, but attempts to extend these syntheses into the realm of Groups V and IV chemistry have been much less successful. Although this situation may in part be brought about by the restricted number of likely starting materials available for elements in these groups, there is also some suggestion that the appropriate metal–silicon overlap integrals are inadequate for effective bonding. Moreover, for Group IV metals no metal–silicon π -back bonding is possible owing to their d^0 configurations, and this further restricts the metal–silicon bond strengths. These considerations are relevant to the very long Zr–Si bond length (2.813 Å) in the only zirconium compound known to contain such a bond viz. $(\eta\text{-C}_5\text{H}_5)_2\text{ZrCl}(\text{SiPh}_3)$ [1,2]. The only titanium and vanadium complexes reported to contain metal–silicon bonds are $\text{Ti}(\text{SiPh}_3)_4$, $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{SiPh}_3)_2$ [3] and $(\text{H}_3\text{Si})\text{V}(\text{CO})_6$ [4]; the authenticity of both of the titanium complexes has been called into question [2]. We report now the syntheses of two new complexes of this sort, $(\eta\text{-C}_5\text{H}_5)_2\text{V}(\text{SiCl}_3)_2$ and $(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{H})\text{SiCl}_3$, and attempts at the syntheses of related titanium and molybdenum complexes.

Experimental

All experiments were carried out using an inert atmosphere or in vacuo. The products were stored in Schlenk tubes. Solvents were dried rigorously by distillation from lithium aluminium hydride.

Reaction of trichlorosilane with dicyclopentadienylvanadium(II)

A mixture of dicyclopentadienylvanadium (1.5 g, 8 mmol) in 20 cm³ of benzene and a large excess of trichlorosilane (3.2 g, 24 mmol) was sealed in an evacuated tube and heated at 80°C for three days. On opening the tube, the yellow-green solid was filtered off, washed with benzene and dried under vacuum, m.p. (dec.) 160°C, yield <50%. Found: C, 26.9; H, 2.34; Cl, 47.1; Si, 12.4; V, 10.9. C₁₀H₁₀Cl₆Si₂V calcd.: C, 26.69; H, 2.24; Cl, 47.27; Si, 12.48, V, 11.32%.

Reaction of trichlorosilane with dicyclopentadienyltungsten(IV) dihydride

A mixture of dicyclopentadienyltungsten dihydride (2.3 g, 7 mmol) in 15 cm³ of benzene and a large excess of trichlorosilane was sealed under vacuum in a glass tube and heated at 120°C for three days. Upon cooling the reaction mixture to room temperature and leaving it for three days, yellow crystals separated from the solution. The tube was opened and the yellow product, (cp)₂W(H)SiCl₃, was isolated by filtration, m.p. (dec.) 170°C, yield <50%. Found: C, 26.7; H, 2.62; Cl, 23.4. C₁₀H₁₁Cl₃SiW calcd.: C, 26.72, H, 2.47, Cl, 23.66%.

Reaction of trichlorosilane with dicyclopentadienyltitanium(II) dicarbonyl

A mixture of di-η-cyclopentadienyltitanium dicarbonyl (1.2 g, 5 mmol) in 20 cm³ of cyclohexane and excess of trichlorosilane was sealed under vacuum in a glass tube and heated at 110°C for three days. On opening the tube, which had built up considerable pressure (CO + H₂), an extremely air-sensitive brown solid was isolated by filtration. The product appears to be a mixture of (cp)₂Ti(H)SiCl₃ and (cp)₂Ti(H)(CO)SiCl₃. Found: C, 36.4; H, 3.55; Cl, 30.8%. C₁₀H₁₁Cl₃SiTi calcd.: C, 38.31; H, 3.54; Cl, 33.92%. C₁₁H₁₁Cl₃OSiTi calcd.: C, 38.68; H, 3.25; Cl, 31.14%. C₁₀H₁₀Cl₆Si₂Ti calcd.: C, 26.87; H, 2.25; Cl, 47.59%.

Results and discussion

The reaction of di-η-cyclopentadienylvanadium with trichlorosilane is easy to monitor. The initial deep-purple colouration due to (cp)₂V, changes after several hours at 80°C to royal blue, and yellow-green crystals start to deposit around the walls of the tube. After three days at 80°C the reaction is complete and the product is filtered from the, by now, yellowish green solution. It is believed that this reaction proceeds in two steps: (a) An oxidative-addition reaction of HSiCl₃ to (cp)₂V to afford the royal blue intermediate:

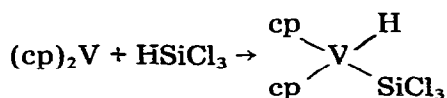
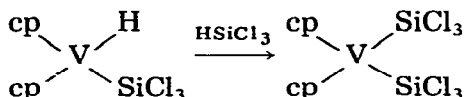


TABLE 1

MAJOR METAL-CONTAINING FRAGMENTS IN THE MASS SPECTRUM OF $(cp)_2V(SiCl_3)_2$

Ion	m/e (<i>I</i>)
$(cp)_2VSiCl_3^+$	314 (34)
$(cp)_2VSiCl_2^+$	279 (15)
$(C_5H_4)VSiCl_3^+$	248 (26)
$(cp)_2VCl^+$	216 (100)
$(cp)_2V^+$	181 (21)
$(C_5H_5)(C_5H_4)V^+$	180 (49)
$(cp)VCl^+$	151 (67)
$(cp)V^+$	116 (52)
V^+	51 (48)

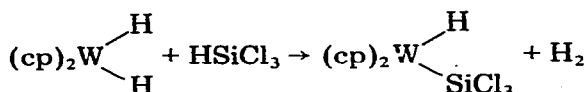
(b) A hydrogen elimination between $(cp)_2V(H)SiCl_3$ and excess of trichlorosilane to yield the final product, di- $(\eta$ -cyclopentadienyl)bis(trichlorosilyl)-vanadium(IV).



Attempts to isolate the intermediate were unsuccessful, owing to its extreme sensitivity to moisture and oxygen.

The bis(trichlorosilyl) derivative, for which complete analytical data were obtained, yields a mass spectrum for which the peak of highest m/e value corresponds to the ion $(cp)_2V(SiCl_3)^+$. The major metal-containing fragments (Table 1) are attributable to the loss of cyclopentadienyl radicals, chlorine and silicon; the formation of the ion $(cp)_2VCl^+$ is noteworthy.

In the case of tungsten, the corresponding starting material, $(cp)_2W$, is unknown, and hence $(cp)_2WH_2$ was used instead in the reaction with trichlorosilane. The reaction proceeds smoothly with elimination of molecular hydrogen:



The reaction stopped with the formation of $cp_2W(H)SiCl_3$, and the use of more forcing conditions (130°C/10 days) in an attempt to promote the formation and isolation of $(cp)_2W(SiCl_3)_2$ was unsuccessful. The yellow compound had extremely low solubility in all the deuterated solvents tried, and this precluded the recording of its 1H NMR spectrum. Hence evidence for the presence of a W-H linkage in the molecule had to be obtained by chemical means. If di- η -cyclopentadienyltrichlorosilyltungsten hydride is stirred in carbon tetrachloride, the 1H NMR spectrum of the solution shows a peak at τ 2.76 ppm, indicating the formation of chloroform. Such a result could only be obtained if the tungsten complex were a hydride. Thus:

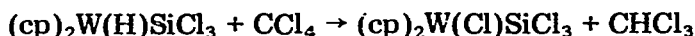


TABLE 2
MAJOR METAL-CONTAINING FRAGMENTS IN THE MASS SPECTRUM OF $(cp)_2W(H)SiCl_3$

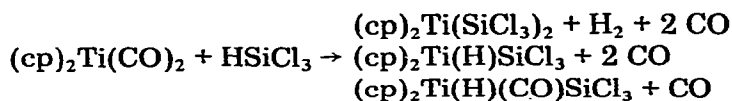
Ion	<i>m/e</i> (<i>I</i>)
$(cp)_2WSiCl_3^+$	449 (7)
$(cp)_2WSiCl_2^+$	414 (2)
$(cp)WSiCl_2^+$	349 (8)
$(cp)WSiCl^+$	314 (100)
$(cp)WSiCl_2^{2+}$	157 (24)
$(cp)WCl^+$	286 (24)
$(cp)WCl_2^{2+}$	143 (11)
$C_3H_3WCl^+$	260 (12)
$C_2H_2WCl^+$	247 (5)
WCl^+	221 (8)

Such replacement of hydride by halide is a well-known reaction of metal hydrides [5].

The mass spectrum (Table 2) shows the highest peak at *m/e* 449 corresponding to the ion $(cp)_2W(SiCl_3)^+$. As in the spectrum of $(cp)_2V(SiCl_3)_2$, the major metal-containing fragments are due to the loss of cyclopentadienyl radicals, successive loss of halogen atoms and also elimination of acetylene; this feature is characteristic of the mass spectra of many cyclopentadienyl transition-metal complexes [6]. The doubly charged ions $(cp)WCl_2^{2+}$ and $(cp)WSiCl_2^{2+}$ were also observed in the spectrum, as well as other W—Cl containing species.

Attempts to carry out the analogous reaction between $HSiCl_3$ and $(cp)_2MoH_2$ led to the isolation of a yellow complex, which could not be characterised.

The reaction of di- η -cyclopentadienyltitanium(IV) dichloride with trichlorosilane was also attempted in a similar way at temperatures up to 250°C, but without success. Similar lack of success occurred with $(cp)_2VCl_2$. Since $(cp)_2TiCl_2$ failed to afford the desired product in its reaction with trichlorosilane, dicyclopentadienyltitanium dicarbonyl [7] was used instead as starting material. This oxidative addition type reaction is believed to proceed in one or more of the following ways:



However, the brown product obtained, being extremely air-sensitive, was difficult to identify for certain. The analytical data seem to indicate that the product is a mixture of $(cp)_2Ti(H)SiCl_3$ and $(cp)_2Ti(H)(CO)SiCl_3$. Unfortunately its low solubility and rapid decomposition in suitable solvents precluded NMR studies as an assistance to its characterisation.

In conclusion it is clear that, although metal—silicon bonded species involving the early transition metals can be formed, they are either insufficiently stable, or too labile in many cases, for full characterisation to be feasible.

References

- 1 K.W. Muir, *J. Chem. Soc. A*, (1971) 2663.
- 2 B.M. Kingston and M.F. Lappert, *J. Chem. Soc. (Dalton)*, (1972) 69.
- 3 E. Hengge and H. Zimmermann, *Angew. Chem. Internat. Ed.*, 7 (1968) 142.
- 4 J.S. Allinson, B.J. Aylett and H.M. Colquhoun, *J. Organometal. Chem.*, 112 (1976) C7.
- 5 M.L.H. Green and D.J. Jones, *Advan. Inorg. Chem. Radiochem.*, 7 (1965) 115.
- 6 M.I. Bruce, *Advan. Organometal. Chem.*, 6 (1968) 273.
- 7 B. Demerseman, G. Rouquet and M. Bigorgne, *J. Organometal. Chem.*, 101 (1975) C24.