Silicon-containing carbene complexes
16*. Intramolecular agostic stabilization versus nucleophilic addition to the 16-electron carbene complex $(CO)_4(L)W{=}C(NMe_2)SiPh_2Me$

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Abstract

The 16-electron complex $(CO)_4W{=}C(NMe_2)SiPh_2Me$ (**1**) was photochemically prepared from $(CO)_5W{=}C(NMe_2)SiPh_2Me$. Reactions with selected nucleophiles, having different ligand properties, were performed to test the strength of the intramolecular agostic interaction of one of the phenyl groups, by which **1** is stabilized. The stable complexes *cis*-$(CO)_4LW{=}C(NMe_2)SiPh_2Me$ were formed with L = $P(OMe)_3$, $P(OEt)_3$ or 2,6-$Me_2C_6H_3NC$. The substituted complexes had no tendency for ligand elimination. Addition of acetonitrile or pyridine to an ether solution of **1** resulted in the formation of *cis*-$(CO)_4(MeCN)W{=}C(NMe_2)SiPh_2Me$ or *cis*-$(CO)_4(C_5H_5N)W{=}C(NMe_2)SiPh_2Me$, respectively. These reactions were reversed on evaporation of the solutions. No reaction was observed with triethylamine.

Key words: Tungsten complexes; Carbene complexes; Silyl complexes

Introduction

Reactions of Fischer-type carbene complexes $(CO)_5MC(XR)R'$ (M = Cr, Mo, W) with organic substrates (L), such as olefins, acetylenes, nitriles, silanes etc., proceed by initial cleavage of a *cis*-CO ligand, followed by addition of L to the vacant coordination site. 16-Electron carbene complexes $(CO)_4MC(XR)R'$ are also postulated as intermediates in other reactions. The two steps, creation of the 16-electron species and addition of L, cannot be separated under the usual reaction conditions. The reaction conditions necessary for CO cleavage therefore inevitably influence the later steps.

The transient species $(CO)_4W{=}C(OMe)Ph$ was identified by time-resolved resonance Raman spectroscopy [2] and matrix photochemistry [3]. The spectra were interpreted in terms of an agostic interaction between a C–H group of the methoxy substituent and the metal. This interaction seemed to be responsible for the geometric stability of the complex, although later reactions with nucleophiles are not inhibited. Reaction with MeCN exclusively yielded the *cis*-substituted complex $(CO)_4(MeCN)W{=}C(OMe)Ph$ [2]. A comparison with the corresponding chromium complex $(CO)_5Cr{=}C(OMe)Ph$ indicated that the agostic interaction only occurs with the tungsten complexes [3]. Unsaturated metal complexes without an agostic interaction were also observed by Poliakoff and Turner [4]. Upon UV or Vis photolysis of $(CO)_5W{=}C(OMe)Ph$ in a solid N_2 matrix, the complexes *cis*- and *trans*-$(CO)_4(N_2)W{=}C(OMe)Ph$ were identified. The N_2 complexes can also be generated by photolysis of $(CO)_5W{=}C(OMe)Ph$ in liquid xenon at −80 °C in the presence of N_2. They are stable under these conditions [4].

We recently prepared stable 16-electron carbene complexes $(CO)_4MC(NR_2)SiR'_3$ (M = Cr, Mo, W) by CO cleavage from the corresponding 18-electron complexes $(CO)_5MC(NR_2)SiR'_3$ [5, 1]. These complexes are intramolecularly stabilized by interaction of one of the silicon substituents with the metal center.

In $(CO)_4W{=}C(NMe_2)SiHMes_2$ (Mes = 2,4,6-$C_6H_2Me_3$), the SiH group being in β-position with respect to the metal center interacts with the tungsten atom [1], and in $(CO)_4W{=}C(NC_5H_{10})SiPh_3$ with one of the phenyl groups [5]. Due to the agostic W,H,Si or W,Ph,Si interaction, the carbene ligands are quite distorted. The W–C(carbene)–Si angle in $(CO)_4W{=}C(NMe_2)$-

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$SiHMes_2$ is only 87.6(6)°, compared with 113.1(4)° in $(CO)_5W{=}C(NC_4H_8)SiHMes_2$, and the sum of the C–Si–C angles is 351.1°. The agostic β-Si–C interaction in $(CO)_4W{=}C(NC_5H_{10})SiPh_3$ is weaker; there is only a small tilt of the phenyl plane relative to the C_{ipso}–Si vector (8°), and the W–C(carbene)–Si angle is 101.2(4)°.

A similar agostic interaction in a carbene complex was found in $[Tp'(CO)_2W{=}C(Ph)CH_2R]BF_4$ (Tp' = hydridotris(3,5-dimethylpyrazolyl); R = H, Me), where the β-*C–H* group interacts with the metal [6]. This results in a similar distortion (W–C(carbene)–CH_3 91(1)°) as in $(CO)_4W{=}C(NMe_2)SiHMes_2$.

The agostic interactions in the silyl-substituted complexes are weak enough to allow access to the empty coordination site by nucleophiles. Upon reaction of $(CO)_4W{=}C(NMe_2)SiPh_3$ with CO the 18-electron complexes were quantitatively re-formed, and reaction with MeCN or phosphines exclusively yielded *cis*-$(CO)_4LW{=}C(NMe_2)SiPh_3$ (L = MeNC, PR_3) [5]. This is in contrast to the reactions of 18-electron Fischer-carbene complexes with PR_3, which always give mixtures of *cis* and *trans* isomers, due to the necessary reaction conditions for CO cleavage. Reactions of the 16-electron complexes proceed at low temperatures and are therefore not complicated by side reactions.

In this paper we report reactions of the 16-electron complex $(CO)_4W{=}C(NMe_2)SiPh_2Me$ (**1**) with a selection of nucleophiles of different basicity and steric bulk. These investigations were performed to get information on the strengths of the agostic interaction of the phenyl group.

Experimental

All operations were performed in an atmosphere of dry and oxygen-free N_2, using dried and nitrogen-saturated solvents. A high pressure Hg lamp (Heraeus TQ 150) was used for the photochemical reactions. Column chromatography was performed with silica (Woelm, 0.063–0.200 mm mesh) as the stationary phase, from which oxygen was removed by heating *in vacuo* and storage under N_2. IR spectra: Perkin-Elmer 283, CaF_2 cuvettes. ^1H NMR and ^{13}C NMR spectra: Bruker AC 200 (200.1, and 50.3 MHz, respectively). ^{29}Si NMR spectra: Bruker AMX 400 (79.5 MHz). ^{31}P NMR spectra: Jeol FX 90Q (36.2 MHz).

Photochemical preparation of $(CO)_4W{=}C(NMe_2)SiPh_2Me$ (1)

A solution of 340 mg (0.59 mmol) $(CO)_5W{=}C(NMe_2)SiPh_2Me$ [5] in 150 ml ether is irradiated with UV light at −20 °C. A weak stream of N_2 is bubbled through the solution to expel CO. The reaction is stopped when the ν(CO) bands of the starting compound have disappeared. The solution is filtered, and the solvent is removed *in vacuo*. The residue is chromatographed at −20 °C with a 1:2 mixture of ether and petroleum ether. The first, yellow zone contains unreacted $(CO)_5W{=}C(NMe_2)SiPh_2Me$, and the second, red zone compound **1**. Removal of the solvent results in 289 mg (86%) or analytically pure **1**. The spectroscopic data are identical with those reported earlier [5].

Preparation of cis-$(CO)_4[P(OR)_3]W{=}C(NMe_2)SiPh_2Me$ (2)

A 1.1–1.8-fold excess of $P(OR)_3$ was added under stirring to a solution of about 0.2 mmol of **1** in 30 ml ether at room temperature. After 1 h all volatiles were removed *in vacuo*. The residue was dissolved in the minimum amount of ether. Upon addition of pentane the complexes **2** precipitated at −30 °C. The orange–red complexes were washed three times with 5 ml pentane each and dried *in vacuo*.

2a: yield 72%, m.p. 94 °C (dec.). IR (ether): ν(CO) 2005(m), 1914(s), 1891(vs). ^1H NMR (C_6D_6): δ 1.41 (s, 3H, $SiCH_3$), 2.65 (d, *E*-NCH_3, ^5J(PWCNCH) 1.2 Hz), 3.28 (d, 9H, $POCH_3$, ^3J(POCH) 11.2 Hz), 3.46 (s, *Z*-NCH_3), 7.48–7.53 (m, 10H, Ph). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 7.73 (s, $SiCH_3$), 51.58 (d, $POCH_3$, ^2J(POC) 2.0 Hz), 54.20 (s, *E*-NCH_3), 58.92 (s, *Z*-NCH_3), 128.52, 129.40, 134.88, 137.77 (C_6H_5), 203.80 (d, ^2J(PWC) 9.8 Hz), 204.80 (d, ^2J(PWC) 9.2 Hz), 209.56 (d, ^2J(PWC) 7.6 Hz) (CO), 293.26 (s, C(carbene)). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 146.76, ^1J(WP) 376.59 Hz. $^{29}Si\{^1H\}$ NMR (C_6D_6): δ −14.69, ^3J(SiCWP) 3.2 Hz. *Anal.* Found: C, 40.76; H, 4.24; N, 2.15. Calc. for $C_{23}H_{28}NO_7PSiW$ (673.4): C, 41.02; H, 4.19; N, 2.08%.

2b: yield 76%, m.p. 106 °C (dec.). IR (ether): ν(CO) 2005(m), 1913(s), 1889(vs). ^1H NMR (C_6D_6): δ 1.03 (t, 9H, CCH_3, ^3J(HCCH) 7.1 Hz), 1.47 (s, 3H, $SiCH_3$), 2.68 (d, *E*-NCH_3, ^5J(PWCNCH) 1.3 Hz), 3.52 (s, *Z*-NCH_3), 3.86 (quint, 6H, $POCH_2$, ^3J(HCCH) and ^3J(POCH) 7.4 Hz), 7.52–7.56 (m, 10H, Ph). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 8.03 (s, $SiCH_3$), 16.20 (d, ^3J(POCC) 5.8 Hz, CCH_3), 54.33 (s, *E*-NCH_3), 58.83 (s, *Z*-NCH_3), 60.82 (d, ^2J(POC) 3.3 Hz), 129.36, 134.89, 137.89 (C_6H_5). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 140.99, ^1J(WP) 370.73 Hz. $^{29}Si\{^1H\}$ NMR (C_6D_6): δ −14.73, ^3J(SiCWP) 1.9 Hz. *Anal.* Found: C, 43.59; H, 4.92; N, 2.04. Calc. for $C_{26}H_{34}NO_7PSiW$ (715.5): C, 43.65; H, 4.79; N, 1.96%.

Preparation of cis-$(CO)_4(2,6\text{-}Me_2C_6H_3NC)W{=}C(NMe_2)SiPh_2Me$ (3)

19 mg (0.14 mmol) 2,6-$Me_2C_6H_3NC$ were added under stirring to a solution of 81 mg (0.14 mmol) of **1** in 25 ml ether at room temperature. After 1 h all volatiles were removed *in vacuo*. The orange–red residue was washed four times with 5 ml pentane each and dried *in vacuo*. Yield 73 mg (77%), m.p. 167 °C (dec.). IR

(pentane): ν(CN) 2087(m), ν(CO) 1989(m), 1916(s), 1900(vs). ^{1}H NMR (C_6D_6): δ 1.41 (s, 3H, $SiCH_3$), 2.04 (s, 6H, $C_6H_3CH_3$), 2.60 (s, *E*-NCH_3), 3.51 (s, *Z*-NCH_3), 7.48–7.53 (m, 13H, C_6H_5 and C_6H_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 8.18 (s, $SiCH_3$), 18.69 (s, $C_6H_3CH_3$), 53.93 (s, *E*-NCH_3), 58.78 (s, *Z*-NCH_3), 127.84–137.32 (C_6H_5 and C_6H_3), 202.76, 205.76, 208.67 (CO), 293.82 (s, C(carbene)). $^{29}Si\{^1H\}$ NMR (C_6D_6): δ −15.81. *Anal.* Found: C, 50.91; H, 4.19; N, 4.26. Calc. for $C_{29}H_{28}N_2O_4SiW$ (680.5): C, 50.19; H, 4.15; N, 4.12%.

Reaction of 1 with acetonitrile

When 7 mg (0.25 mmol) MeCN were added to a solution of 93 mg (0.17 mmol) **1** in 25 ml ether at room temperature under stirring, the red solution instantaneously became orange–red. The IR spectrum showed new ν(CO) bands at 1995(m), 1913(vs) and 1880(s). After 2 h, all volatiles were removed *in vacuo*. The remaining orange solid was identified by IR and NMR spectroscopy as **1**.

Reaction of 1 with pyridine

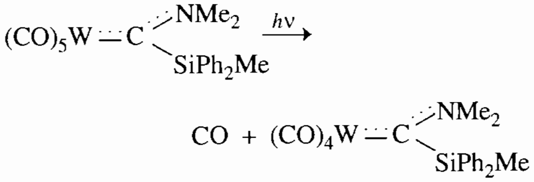
When 14 mg (0.18 mmol) pyridine were added to a solution of 85 mg (0.15 mmol) **1** in 25 ml ether at room temperature under stirring, the color of the red solution became lighter. After 10 min, the IR spectrum showed new ν(CO) bands at 1998(m) and 1874(s) (assigned to complex **4b**) in addition to those of **1** (the third band is probably hidden below the band of **1** at 1906 cm^{-1}). After 1 h, additional 14 mg (0.18 mmol) were added, resulting in an increase in intensity of the new ν(CO) bands. After 1 h all volatiles were removed *in vacuo*. The remaining orange solid was identified by IR and NMR spectroscopy as **1**.

Reaction of 1 with triethylamine

To a suspension of 150 mg (0.27 mmol) **1** in 40 ml heptane, 30 mg (0.30 mmol) NEt_3 were added at room temperature under stirring. Since there was no change in the ν(CO) bands of the IR spectrum, additional 30 mg NEt_3 were added after 6 h. After 6 days all volatiles were removed *in vacuo*. The remaining orange solid was identified by IR and NMR spectroscopy as a mixture of **1** and its decomposition products ($(CO)_5W{=}C(NMe_2)SiPh_2Me$ and $W(CO)_6$).

Results and discussion

We have previously reported the synthesis of the 16-electron complex $(CO)_4W{=}C(NMe_2)SiPh_2Me$ (**1**) and related carbene complexes by controlled thermolysis of the corresponding 18-electron complexes [5]. Since the 16-electron carbene complexes are thermally labile too, this method requires much care and inevitably results in partial decomposition. Laser photochemical studies suggested that $(CO)_4W{=}C(NC_4H_8)SiPh_3$ is also formed by irradiation of $(CO)_5W{=}C(NC_4H_8)SiPh_3$ within the ligand field absorption [7]. We have now found that photolysis is indeed much more efficient than thermolysis as a preparative method. Irradiation of an ether solution of $(CO)_5W{=}C(NMe_2)SiPh_2Me$ results in the nearly quantitative formation of **1** (eqn. (1)), which was isolated in 86% yield.



$$(CO)_5W{=}C\begin{matrix}NMe_2\\SiPh_2Me\end{matrix}\xrightarrow{h\nu} CO + (CO)_4W{=}C\begin{matrix}NMe_2\\SiPh_2Me\end{matrix}$$

1

When an excess of a phosphite was added to an ether solution of **1**, there was a clean reaction leading exclusively to the *cis*-substituted carbene complexes **2** (eqn. (2)). There was no spectroscopic indication of a byproduct or another isomer. The same is true for the reaction of **1** with the bulky isonitrile 2,6-$Me_2C_6H_3NC$ (eqn. (3)).

$$1 + P(OR)_3 \longrightarrow$$

$$cis\text{-}(CO)_4[P(OR)_3]W{=}C(NMe_2)SiPh_2Me \quad (2)$$

2a: R = Me
2b: R = Et

$$1 + 2,6\text{-}Me_2C_6H_3NC \longrightarrow$$

$$cis\text{-}(CO)_4(2,6\text{-}Me_2C_6H_3NC)W{=}C(NMe_2)SiPh_2Me$$

3

(3)

Reaction of **1** with the trialkylphosphites or 2,6-$Me_2C_6H_3NC$ proceeds as previously found for the reaction of $(CO)_4W{=}C(NMe_2)SiPh_3$ with P(*p*-tolyl)$_3$, PPh_2Me, $PPhMe_2$, PMe_3, PEt_3 or the smaller MeNC. The phosphine-, phosphite-, or isonitrile-substituted carbene complexes *cis*-$(CO)_4LW{=}C(NMe_2)SiR_3$ are very stable and show no tendency for eliminating either these ligands or one of the CO ligands. The spectroscopic data are as expected for this type of complex.

When **1** was analogously reacted with acetonitrile in ether, the red solution immediately turned yellow, and the IR spectrum showed the characteristic ν(CO) bands of a complex of the type *cis*-$(CO)_4ML_2$, assigned to *cis*-$(CO)_4(MeCN)W{=}C(NMe_2)SiPh_2Me$ (**4a**) (eqn. (4)). A similar observation was made when pyridine was added. After addition of about one equivalent of pyridine the ν(CO) bands of both **1** and a complex of the type *cis*-$(CO)_4ML_2$ were observed in about a 1:1 ratio. When another equivalent of pyridine was added, the ratio shifted to 3:1 in favor of the product, which presumably is *cis*-$\mathrm{(CO)_4(C_5H_5N)W{=}C(NMe_2)SiPh_2Me}$ (**4b**) (eqn. (4)).

$$1+\mathrm{L} \rightleftharpoons cis\text{-}\mathrm{(CO)_4LW{=}C(NMe_2)SiPh_2Me} \qquad (4)$$

4a: $\mathrm{L{=}MeCN}$
4b: $\mathrm{L{=}C_5H_5N}$

When the reaction mixtures were concentrated *in vacuo*, an orange-red solid was obtained, identified as pure **1** by IR and NMR spectroscopy. The reaction of **1** with acetonitrile or pyridine is obviously reversed if MeCN or pyridine are removed from the mixture.

Addition of $\mathrm{NEt_3}$ to ether or heptane solutions of **1** (in the latter solvent the complex is more stable) did not result in new ν(CO) bands in the IR spectrum, even if an excess of $\mathrm{NEt_3}$ was employed. After a few days, only the known decomposition reaction was observed, leading to $\mathrm{(CO)_5W{=}C(NMe_2)SiPh_2Me}$, $\mathrm{W(CO)_6}$ and $\mathrm{MePh_2SiSiPh_2Me}$.

These experiments show that the stability of the substitution products *cis*-$\mathrm{(CO)_4LW{=}C(NMe_2)SiPh_2Me}$ with regard to the elimination of L depends to a very high degree on the kind of L. Although there is no clear correlation with the ligand properties yet, the experimental results indicate that a low σ-donor/π-acceptor ratio is required for binding a ligand L *cis* to the carbene ligand. Steric factors seemingly do not play an important role. In the usual Fischer-type carbene complexes the easy elimination of L would lead to decomposition, because the resulting 16-electron complexes are not stable. In the case of *cis*-$\mathrm{(CO)_4LW{=}C(NR_2)SiR'_3}$, elimination of L gives the stable 16-electron carbene complexes $\mathrm{(CO)_4W{=}C(NR_2)SiR'_3}$, and therefore reversible reactions, such as eqn. (4) can be studied at ambient conditions.

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