

# Transition Metal Silyl Complexes. 53.<sup>1</sup> Magnitude of the Chelate Effect in the Oxidative Addition of Si–H Bonds

Ulrich Schubert\* and Hilmar Gilges

Institut für Anorganische Chemie, Technische Universität Wien,  
Getreidemarkt 9, A-1060 Wien, Austria

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The chelate complexes  $(\text{CO})_4\text{W}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{SiHR}_2)$  ( $\text{R} = \text{Me}, \text{Ph}$ ), containing W,H,Si three-center two-electron bonds, were photochemically prepared from  $\text{W}(\text{CO})_6$  and  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{SiR}_2\text{H}$ . The phosphine complexes  $(\text{CO})_5\text{W}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{SiR}_2\text{H})$  are intermediates in this reaction. The high NMR coupling constants  $J_{\text{SiWH}}$  in the chelate complexes (98.1 and 95.2 Hz) indicate that due to the chelating situation an earlier stage of the oxidative addition of the Si–H bond is frozen than in the corresponding nonchelated complexes. The stabilization brought about by the chelating (phosphinoethyl)silyl ligand is slightly larger than the electronic effect caused by substituting another CO ligand by  $\text{PR}_3$  or by replacing  $\text{SiR}_3$  ( $\text{R} = \text{alkyl}, \text{aryl}$ ) for  $\text{SiCl}_3$  in nonchelated complexes.

## Introduction

Oxidative addition of an A–B bond to a transition-metal center can be promoted by its incorporation into a chelate system.<sup>2</sup> “Chelate assistance” sometimes allows addition of A–B bonds to metal centers which otherwise would not undergo this type of reaction. For example, while the Sn–C bonds of tetraalkyl- or tetra-arylstannanes cannot be added to iron carbonyl moieties to give stable complexes, one of the Sn–R bonds ( $\text{R} = \text{methyl}, \text{phenyl}$ ) in  $(\text{CO})_4\text{Fe}(\text{R}'_2\text{PCH}_2\text{CH}_2\text{SnR}_3)$  readily adds to the iron center.<sup>3</sup> The resulting complex  $(\text{CO})_3(\text{R})\text{Fe}(\text{R}'_2\text{PCH}_2\text{CH}_2\text{SnR}_2)$  is stabilized by formation of the five-membered Fe–Sn–C–C–P ring.

Oxidative addition/reductive elimination reactions are very much influenced by the electronic and steric properties of the reactants. For example, small and electron-donating coligands at the metal or electro-negative substituents at the A–B bond promote the oxidative addition. We have previously shown that these factors can be studied in much detail by investigating the  $\text{E}\cdots\text{H}$  interaction ( $\text{E} = \text{Si}, \text{Sn}$ ) in complexes containing M,E,H three-center two-electron bonds.<sup>4</sup> Complexes of this type can be considered “frozen intermediates” in the oxidative addition (or reductive elimination) of E–H bonds. We have shown that the contribution of the various factors influencing oxidative addition (reductive elimination) can be correlated with the magnitude of the  $\text{E}\cdots\text{H}$  interaction, which can be determined by monitoring the changes in structural or spectroscopic parameters.<sup>5</sup> The goal of the present work was to get an estimate on the magnitude of the chelate

effect compared with other factors promoting oxidative addition reactions.

In complexes of a given type, there is a good correlation of the stage of the oxidative addition reaction with the NMR coupling constants, which are between  $^1J_{\text{EH}}$  and  $^2J_{\text{EMH}}$ .  $^1J_{\text{SiH}}$  is typically in the range of 200 Hz, while  $^2J_{\text{SiMH}}$  in hydrido silyl complexes without a Si,H interaction is below 20 Hz. The SiMH coupling constants in the complexes of the type  $(\pi\text{-arene})\text{L}_2\text{M}(\text{H})\text{SiR}_3$ , in which the three-center bonds were confirmed by structure analyses, are in the range 40–70 Hz.<sup>4</sup>

We selected complexes of the type  $(\text{CO})_{5-n}(\text{PR}'_3)_n\text{W}(\text{H})\text{SiR}_3$  for the present study, because the deliberate tuning of the W,H,Si three-center interaction by the electronic influence of the coligands L and the substituents at silicon was previously demonstrated by us for nonchelated complexes of this type (including the molybdenum and stannyl derivatives).<sup>5,6</sup> In the present study we prepared the corresponding complexes in which  $\text{PR}'_3$  and  $\text{SiR}_3$  are part of an undistorted chelate ligand. By comparison of the relevant spectroscopic data we were able to quantify the stabilizing effect of the chelating situation relative to the previously investigated electronic factors.

## Experimental Section

All manipulations were carried out under an atmosphere of dry and oxygen-free argon, using standard Schlenk tube techniques. All solvents were dried by standard procedures. Silica was dried *in vacuo* for 4 h and flushed with Ar. A medium-pressure mercury lamp type Heraeus TQ150 (150 W) was used for UV irradiation.

Infrared spectra were recorded on a Perkin-Elmer IR 1310 spectrometer using  $\text{CaF}_2$  cuvettes. NMR spectra were recorded on a Bruker AC 250 spectrometer.  $^{31}\text{P}$  NMR spectra are referenced against external  $\text{H}_3\text{PO}_4$ . DSC measurements were performed on a Shimadzu DSC-50 analyzer in an Ar atmosphere.

**Preparation of  $(\text{CO})_5\text{W}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{SiPh}_2\text{H})$  (1a).** A 0.41 g (1.15 mmol) amount of  $\text{W}(\text{CO})_6$  was dissolved in 110

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mL of Et<sub>2</sub>O. The solution was irradiated at -20 °C until the IR spectrum showed complete conversion to (CO)<sub>5</sub>W(OEt<sub>2</sub>) [bands at 1930 cm<sup>-1</sup> (vs) and 1890 cm<sup>-1</sup> (s)] after about 1 h. Then 0.43 g (1.09 mmol) of Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>SiPh<sub>2</sub>H<sup>7</sup> was added in the dark to the deep yellow solution. After being warmed to room temperature and stirred for an additional 2 h, the solution was filtered through glass wool/Celite. Then all volatiles were removed *in vacuo*. The light brown residue was dissolved in 10 mL of petroleum ether and the solution filtered through 10 cm of silica. During this procedure, the product is adsorbed on silica (brown zone). After washing with 50 mL of petroleum ether, the product was eluted with 60 mL toluene/petroleum ether (1:4). After removal of the solvent, the remaining yellow oil was washed three times with 8 mL of petroleum ether each at -70 °C. After drying *in vacuo* **1a** is obtained as a yellow powder: Yield 0.33 g (42%); mp 86 °C; IR (petroleum ether) ν(SiH) = 2120 (w, br), ν(CO) = 2070 (m), 1985 (w), 1940 (vs) cm<sup>-1</sup>; <sup>1</sup>H NMR (250.13 MHz, C<sub>6</sub>D<sub>6</sub>) δ 1.19–1.28 (m, 2 H, SiCH<sub>2</sub>), 2.48–2.58 (m, 2 H, PCH<sub>2</sub>), 5.03 (t, 1 H, <sup>3</sup>J<sub>HCSiH</sub> = 3.10 Hz, <sup>1</sup>J<sub>SiH</sub> = 196.5 Hz, SiH), 6.89–7.62 (m, 20 H, Ph); <sup>31</sup>P NMR (101.25 MHz, C<sub>6</sub>D<sub>6</sub>) δ 16.40 (<sup>1</sup>J<sub>WP</sub> = 239.2 Hz); <sup>13</sup>C NMR (62.90 MHz, C<sub>6</sub>D<sub>6</sub>) δ 6.76 (s br, SiCH<sub>2</sub>), 28.47 (d, <sup>1</sup>J<sub>PC</sub> = 22.2 Hz, PCH<sub>2</sub>), 127.0–137.5 (Ph), 197.4 (d, cis-<sup>2</sup>J<sub>PWC</sub> = 6.92 Hz, CO), 199.4 (d, trans-<sup>2</sup>J<sub>PWC</sub> = 21.3 Hz, CO). Anal. Calc for C<sub>31</sub>H<sub>25</sub>O<sub>5</sub>PSiW: C, 51.86; H, 3.49. Found: C, 51.24; H, 3.61.

**Preparation of (CO)<sub>5</sub>W(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>SiMe<sub>2</sub>H) (1b).** A 0.89 g (2.53 mmol) amount of W(CO)<sub>6</sub> was irradiated as described for **1a**, and then 0.60 g (2.53 mmol) of Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>SiMe<sub>2</sub>H<sup>7</sup> was added. The mixture was warmed to room temperature in 1 h and stirred for an additional 2 h, during which the color faded to pale yellow and the IR band at 1890 cm<sup>-1</sup> disappeared. After filtration of the solution through glass wool, all volatiles were removed *in vacuo*. The light brown oil was extracted 3 times with 20 mL of petroleum ether, leaving a brown residue. The solvent was removed from the combined solution. The residue was purified by column chromatography on silica. Some (phosphinoalkyl)silane and traces of W(CO)<sub>6</sub> were first extracted with petroleum ether, and then the complex was eluted with 1:1 toluene/petroleum ether. After removal of all volatiles *in vacuo*, the light yellow powder was twice washed with 5 mL of pentane at -30 °C and dried *in vacuo*. Yield 0.49 g (37%); mp 74 °C; IR (toluene) ν(SiH) = 2105 (br), ν(CO) = 2060 (m), 1980 (w), 1935 (vs) cm<sup>-1</sup>; <sup>1</sup>H NMR (250.13 MHz, C<sub>6</sub>D<sub>6</sub>) δ 0.13 (d, 3H, <sup>3</sup>J<sub>HSiCH</sub> = 3.80 Hz, Si-CH<sub>3</sub>), 0.50–0.65 (m, 2 H, SiCH<sub>2</sub>), 2.35–2.42 (m, 2 H, PCH<sub>2</sub>), 3.97 (sep, 1 H, <sup>3</sup>J<sub>HCSiH</sub> = 3.85 Hz, SiH), 7.25–7.69 (m, 10 H, Ph); <sup>31</sup>P NMR (101.25 MHz, C<sub>6</sub>D<sub>6</sub>) δ 16.1 (<sup>1</sup>J<sub>WP</sub> = 239.2 Hz). Anal. Calc for C<sub>21</sub>H<sub>21</sub>O<sub>5</sub>PSiW: C, 42.30; H, 3.55. Found: C, 42.53; H, 3.77.

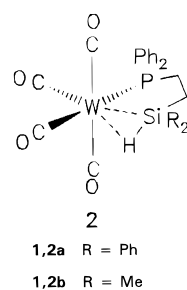
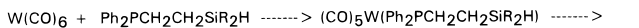
**Preparation of (CO)<sub>4</sub>W(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>SiHPh<sub>2</sub>) (2a).** A 0.67 g (1.91 mmol) amount of W(CO)<sub>6</sub> and 0.76 g (1.91 mmol) of Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>SiPh<sub>2</sub>H were dissolved in 120 mL of toluene, and the solution was irradiated at -20 °C. Ar was bubbled through the solution during irradiation. The reaction was monitored by IR spectroscopy. After the IR band at 2070 cm<sup>-1</sup> typical for the intermediate (CO)<sub>5</sub>W(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>SiPh<sub>2</sub>H) has almost completely disappeared (after about 2 h), the yellow solution was warmed to room temperature and filtered through glass wool. After removal of all volatiles *in vacuo*, the remaining light brown oil was treated with 10 mL of Et<sub>2</sub>O and stirred for about 0.5 h. The brown solution was separated from the pale yellow precipitate, which was washed twice with 3 mL of ether each. After drying *in vacuo*, 0.61 g (0.88 mmol) of **2a** (46%) was obtained as a pale yellow powder: Mp 47 °C (dec); IR (toluene) ν(CO) = 2035 (m), 1980 (s), 1920 (vs), 1890 (s) cm<sup>-1</sup>; <sup>1</sup>H NMR (250.13 MHz, C<sub>6</sub>D<sub>6</sub>) δ -6.90 (d) (1 H, <sup>2</sup>J<sub>PWH</sub> = 2.15 Hz, <sup>1</sup>J<sub>WH</sub> = 37.0 Hz, <sup>1</sup>J<sub>SiWH</sub> = 98.1 Hz, W-H), 1.43–1.60 (m, 2 H, SiCH<sub>2</sub>), 2.19–2.28 (m, 2 H, PCH<sub>2</sub>), 7.03–7.73 (m, 20 H, Ph); <sup>31</sup>P NMR (101.25 MHz, C<sub>6</sub>D<sub>6</sub>) δ 42.8 (<sup>1</sup>J<sub>WP</sub> =

254.0 Hz); <sup>13</sup>C NMR (62.90 MHz, C<sub>6</sub>D<sub>6</sub>) δ 16.3 (d, <sup>2</sup>J<sub>PCC</sub> = 22.4 Hz, SiCH<sub>2</sub>), 28.7 (d, <sup>1</sup>J<sub>PC</sub> = 27.1 Hz, PCH<sub>2</sub>), 128–137 (Ph), 200.2 (d, cis-<sup>2</sup>J<sub>PWC</sub> = 6.92 Hz, CO), 202.8 (d, trans-<sup>2</sup>J<sub>PWC</sub> = 22.6 Hz, CO), 205.9 (d, cis-<sup>2</sup>J<sub>PWC</sub> = 6.51 Hz, CO); <sup>29</sup>Si NMR (49.7 MHz, C<sub>6</sub>D<sub>6</sub>) δ 11.4 (s, br). Anal. Calc for C<sub>30</sub>H<sub>25</sub>O<sub>4</sub>PSiW: C, 52.04; H, 3.64. Found: C, 52.61; H, 3.80.

**Preparation of (CO)<sub>4</sub>W(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>SiHMe<sub>2</sub>) (2b).** A 1.24 g (2.07 mmol) amount of **1b** was irradiated in 120 mL of toluene at -20 °C, bubbling Ar through the solution. The reaction was monitored by IR spectroscopy. After 1.5 h of irradiation, all **1b** was consumed, and there were only ν(CO) bands of **2b** in the IR spectrum. Then the brown reaction mixture was filtered through glasswool/Celite at -20 °C to separate insoluble decomposition products. After removal of all volatiles *in vacuo*, the remaining brown oil was dissolved in 25 mL of petroleum ether/toluene (4:1) and filtered through 10 cm of silica. The adsorbed complexes (brown zone) were washed with 20 mL of petroleum ether to remove organic byproducts (particularly Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>SiR<sub>2</sub>H). Then a yellow solution was eluted with 40 mL of toluene. Their concentration *in vacuo* yielded a yellow oil, consisting of a mixture of mostly **2b** and some **1b**. During the workup procedure **1b** is regenerated from **2b**, even at low temperatures. Attempts to separate both complexes by chromatography were unsuccessful; pure **1b** can be eluted, but the zone of **2b** always contains some **1b** due to decomposition during chromatography. Fractional crystallization was unsuccessful due to the very similar solubility of both compounds. IR (toluene): ν(CO) = 2020 (m) 1985 (w) 1930 (vs) 1885 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (250.13 MHz, C<sub>6</sub>D<sub>6</sub>): δ -8.18 (s, br, 1 H, <sup>1</sup>J<sub>SiWH</sub> = 95.2 Hz, <sup>1</sup>J<sub>WH</sub> = 36.4 Hz, WH), 0.35 (s, br, 6 H, SiCH<sub>3</sub>), 0.85–0.96 (m, 2 H, SiCH<sub>2</sub>), 2.52–2.60 (m, 2 H, PCH<sub>2</sub>), 7.19–7.80 (m, 20 H, Ph). <sup>31</sup>P NMR (101.25 MHz, C<sub>6</sub>D<sub>6</sub>): δ 40.0 (<sup>1</sup>J<sub>WP</sub> = 256.7 Hz).

## Results and Discussion

The complexes **2** were prepared by UV-irradiating a toluene solution of W(CO)<sub>6</sub> and Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>SiR<sub>2</sub>H at -20 °C (eq 1). IR spectroscopic monitoring of the reaction showed the phosphine complexes **1** to be intermediates.



The phosphine complexes **1** were independently prepared by thermal reaction of the corresponding (phosphinoalkyl)silane with the photochemically generated solvent complex (CO)<sub>5</sub>W(OEt<sub>2</sub>). The complexes **1** can be converted to **2** by UV irradiation, although this procedure has no preparative advantage.

The phenyl derivative **2a** was obtained analytically pure, while **2b** could not be isolated free of the phosphine complex **1b**. Attempts to purify **2b** always resulted in partial decomposition regenerating **1b**. The fact that **2b** readily decomposes by elimination of the Si-H bond indicates that the complexes **2** are at the borderline of stability at room temperature with regard to reductive elimination.

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**Table 1. Comparison of NMR Coupling Constants  $J_{\text{SiH}}$  in Complexes of the Type  $(\text{CO})_{5-n}(\text{L})\text{W}(\text{SiHR}_3)$** 

compd	$J_{\text{SiH}}$ (Hz)
Uncoordinated	
$(\text{CO})_5\text{W}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{SiPh}_2\text{H})$ ( <b>1a</b> )	196.5
Chelating	
$(\text{CO})_4\text{W}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{SiHPh}_2)$ ( <b>2a</b> )	98.1
$(\text{CO})_4\text{W}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{SiHMe}_2)$ ( <b>2b</b> )	95.2
Nonchelating <sup>a</sup>	
$(\text{CO})_4(\text{Ph}_3\text{P})\text{W}(\text{SiHPh}_3)$	n.s.
$(\text{CO})_3(\text{dppe})\text{W}(\text{SiHTolCl}_2)$	34.8
$(\text{CO})_3(\text{dppe})\text{W}(\text{SiHCl}_3)$	19.9

<sup>a</sup> From ref 5. "n.s." = not stable at room temperature due to reductive elimination. See text for the discussion of the electronic influence of the substituents at silicon.

The  $\nu(\text{CO})$  bands in the IR spectrum of **2a** are typical for an octahedral complex of the type *cis*-( $\text{CO})_4\text{WLL}'$ . The three chemically nonequivalent CO ligands cause three separate doublets in the  $^{13}\text{C}$  NMR spectrum with the corresponding *cis*- or *trans*- $^2J_{\text{PWC}}$  couplings. Due to coupling with the phosphorus atom, the hydride resonance at  $-6.90$  ppm is also a doublet with the typical *cis*- $^2J_{\text{PWH}}$  of 2.5 Hz. The singlet resonance in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum shows a significant downfield shift of about 25 ppm, compared to **1**. This is a well-documented phenomena for phosphorus atoms incorporated into a five-membered ring.<sup>8</sup> Combining these data, we conclude that the structures of the complexes **2** are almost undistorted octahedral. This is typical for complexes containing M,H,Si three-center bonds, where the Si-H bond occupies *one* coordination site.

The presence of a W,H,Si three-center bond was confirmed by the  $J_{\text{SiWH}}$  coupling constants (Table 1). While the Si,H coupling constant in **1a** (196.5 Hz) is in the normal range for  $^1J_{\text{SiH}}$ , the absolute values of  $J_{\text{SiWH}}$  for **2a** (98.1 Hz) and **2b** (95.2 Hz) are typical for three-center bonds. Their magnitude indicates that the oxidative addition of the Si-H bond in **2** is arrested in an earlier stage than in the nonchelated complexes  $(\text{CO})_{5-n}(\text{PR}'_3)_n\text{M}(\text{H})\text{SiR}_3$  ( $\text{M} = \text{Mo}, \text{W}$ ).

A comparison of complexes containing M,H,C three-center bonds with those containing M,H,Si or M,H,*Sn* three-center bonds shows that in most organyl complexes oxidative addition of the C-H bond is in an earlier stage than that of E-H in the corresponding silyl or stannyl complexes. We have pointed out earlier that this may be a coincidence, because in nearly all organyl complexes the relevant C-H bond is tethered to the metal center by another interaction (i.e. there is a chelating situation).<sup>4</sup> We have postulated that incorporating Si-H bonds into chelate systems allows one to arrest the oxidative addition of the Si-H bond in an earlier stage than in corresponding nonchelated complexes.

As a matter of fact, a few complexes were prepared in the meantime with  $J_{\text{SiMH}}$  coupling constants larger than 90 Hz. In all of them the silicon atom involved in three-center bonding has an additional link to the metal.<sup>9-12</sup> However, the complexes **2** are the first where the corresponding nonchelated complexes are available for a direct comparison.

## Conclusions

We have previously shown that addition of  $\text{HSiR}_3$  to the photochemically generated 16-electron complexes  $[(\text{CO})_5\text{M}]$  or  $[(\text{CO})_4(\text{R}_3\text{P})\text{M}]$  does not result in hydrido silyl complexes stable at ambient conditions, because the complexes readily decompose by reductive elimination of the silane. When the parameters favoring oxidative addition were successively changed, complexes not undergoing reductive elimination of the silane at room temperature were only obtained with at least *two* electron-donating ligands *and* two electronegative substituents at silicon.<sup>5,6</sup> The stable complex with the least electronic stabilization was  $(\text{CO})_3(\text{dppe})\text{W}(\text{H})\text{SiTolCl}_2$ , for which the coupling constant  $J_{\text{SiWH}}$  of 34.8 Hz clearly showed the presence of a W,H,Si three-center bond. In the complex  $(\text{CO})_3(\text{dppe})\text{W}(\text{H})\text{SiCl}_3$ , with a third chloride substituent (i.e. where oxidative addition was pushed one step further) the Si-H bond was fully added to the tungsten center ( $J_{\text{SiWH}} = 19.9$  Hz) (Table 1).

While the complexes **2** are stable at room temperature, the electronically equivalent nonchelated complexes  $(\text{CO})_4(\text{R}'_3\text{P})\text{W}(\text{H})\text{SiR}_3$  ( $\text{R}, \text{R}' = \text{alkyl, aryl}$ ) instantaneously decompose by reductive elimination of the silane. Since the chelating  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{SiR}_2$  ligand does not distort an octahedral complex significantly, geometric distortion of the metal fragment, observed in other types of complexes,<sup>13</sup> cannot be the source of the stabilization in **2**. The sterically less demanding situation (the  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{SiR}_2$  ligand requires less space than the electronic equivalent  $\text{Ph}_2\text{PCH}_3 + \text{CH}_3\text{SiR}_2$ ) probably has only a minor influence on the stabilization. The major source of stabilization therefore is the chelate effect. By comparison with nonchelated complexes of this type, we find that the stabilization brought about by the chelating (phosphinoethyl)silyl ligand is slightly larger than the electronic effect caused by substituting a CO ligand by  $\text{PR}_3$  or by replacing  $\text{SiR}_3$  ( $\text{R} = \text{alkyl, aryl}$ ) for  $\text{SiCl}_3$  in nonchelated complexes.

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