

Synthesis of  $-\{\text{Me}_2\text{Si}-\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})[\text{P}(\text{OR})_3]\text{Me}_2\text{Si}-\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})[\text{P}(\text{OR})_3]\}-$  via selective CO-substitution of  $-\text{[Me}_2\text{Si}-\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2\text{Me}_2\text{Si}-\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2]-$  by  $\text{P}(\text{OR})_3$  ( $\text{R} = \text{Ph}, \text{}^n\text{Bu}, \text{}^n\text{Pr}, \text{Et}, \text{and Me}$ ) under photochemical condition and molecular structure of *trans*- $\{\text{Me}_2\text{Si}-\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})[\text{P}(\text{OMe})_3]\text{Me}_2\text{Si}-\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})[\text{P}(\text{OMe})_3]\}-$

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## Abstract

Ultraviolet irradiation of  $-\text{[Me}_2\text{Si}-\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2\text{Me}_2\text{Si}-\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2]-$  (**2**) in the presence of  $\text{P}(\text{OR})_3$  leads to regioselective substitution of two CO groups at different iron centers to give  $-\{\text{Me}_2\text{Si}-\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})[\text{P}(\text{OR})_3]\text{Me}_2\text{Si}-\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})[\text{P}(\text{OR})_3]\}-$  [ $\text{R} = \text{Ph}$  (**3**);  $^n\text{Bu}$  (**4**);  $^n\text{Pr}$  (**5**); Et (**6**); and Me (**7**)]. Complexes **3–7** are mixtures of *cis* and *trans* isomers in ratios of ca. 1:1.4, as determined by  $^1\text{H-NMR}$  spectra. Both isomers of **3** and **7** were isolated by exploiting their differing solubility while only the *trans* isomers were obtained for **4**, **5** and **6**. The molecular structure of *trans*-**7** has been determined by X-ray diffraction. It is demonstrated that coordination of  $\text{P}(\text{OMe})_3$  at the iron center leads to shortening (0.036 Å) and hence strengthening of the geminal Fe–CO (1.725(3) Å) coordination bond, which is most probably responsible for the regioselectivity of CO-substitution. © 2000 Published by Elsevier Science B.V. All rights reserved.

**Keywords:** Silicon; Iron; Phosphorus; Carbonyl; Substitution; Photochemistry

## 1. Introduction

Intramolecular interactions of Si–Si bonds with transition metal complexes have been demonstrated to occur widely in systems containing the framework  $\text{LnM-Si-Si}$  [1–7] and  $\text{LnM-CH}_2\text{-Si-Si}$  [8], as well as in complexes containing a Si–Si bond linked to  $\eta^4$ -butadiene ligands [9]. This kind of interactions generally leads to cleavage of the Si–Si bonds giving rise to products of silylene extrusion, silyl migration, and migrations of groups at the Si–Si bond [1]. In 1993, we reported that a Si–Si bond linked to two  $\eta^5$ -cyclopentadienyl ligands in the system  $-\text{[Me}_2\text{Si}-\eta^5\text{-C}_5\text{H}_4(\text{CO})\text{Fe}(\text{CO})_2\text{Fe}(\text{CO})-\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2]-$  (**1**) can interact with the intramolecular

Fe–Fe bond [10]. Thus when **1** is heated in refluxing *p*-xylene, a novel reaction between its Si–Si and Fe–Fe bonds takes place to afford a rearranged product  $-\text{[Me}_2\text{Si}-\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2\text{Me}_2\text{Si}-\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2]-$  (**2**) containing two Si–Fe bonds. This reaction is unique in that it involves formally a metathesis process between Si–Si and Fe–Fe bonds. While the mechanistic details of this metathesis reaction is currently the subject of considerable attention [11–15], it is also of interest to explore further the chemistry of the product **2** that has provided a new class of highly stable cyclic structure.

Recently a series of derivatives of **2** with a variety of substituents at the Cp rings [14] or at the silicon atoms [13] have been prepared via this metathesis reaction. Derivatives of **2** that contain a phosphorus ligand at one of the iron centers have also been obtained [12]. In contrast, the introduction of a second phosphorus ligand to prepare complexes with a phosphorus ligand at

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each iron center is not easily achieved via the same reaction. Here we report an alternative method of preparation of the later class of compounds via photochemical CO-substitution of **2** by phosphorus ligands.

## 2. Experimental

All reactions were performed under a nitrogen atmosphere. Solvents were dried and degassed by refluxing over sodium–diphenylketone under nitrogen and distilled just before use. <sup>1</sup>H-NMR and IR spectra were recorded on a Bruker AC-P200 spectrometer and a Nicolet 560 E.S.P. FT-IR instrument, respectively. Elemental analyses were performed using a Perkin–Elmer 240C spectrometer. Compound **2** was prepared as described previously [10]. Other chemicals were purchased and used as received.

### 2.1. Preparation of $-\{Me_2Si-\eta^5-C_5H_4Fe-(CO)[P(OPh)_3]Me_2Si-\eta^5-C_5H_4Fe(CO)[P(OPh)_3]\}-$ (**3**)

A solution containing 0.234 g (0.5 mmol) of **2**, 0.620 g (2.0 mmol) of P(OPh)<sub>3</sub> and 20 ml of benzene was irradiated with a high-pressure mercury lamp (500 W) in a Pyrex tube for 18 h at room temperature. The solution was then cooled and kept at about 5°C, resulting in the precipitation of a light-yellow solid. Collection of this precipitate gave 0.171 g (33% yield) of *trans*-**3**. The solvent of the mother solution was removed under reduced pressure to give a solid residue, which was dissolved in a small amount of tetrahydrofuran and placed on a column (SiO<sub>2</sub>). Elution with petroleum ether–ether (15:1) and collection of the yellow bands gave 0.102 g (20% yield) of *cis*-**3**.

*trans*-**3**: m.p. 229°C (dec.). Anal. Calc. for C<sub>52</sub>H<sub>50</sub>O<sub>8</sub>P<sub>2</sub>Fe<sub>2</sub>Si<sub>2</sub>: C, 60.47; H, 4.88. Found: C, 60.38; H, 4.96%. <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.99 (s, 6H, SiMe<sub>2</sub>), 1.05 (s, 6H, SiMe<sub>2</sub>), 4.23 (s, 2H, C<sub>5</sub>H<sub>4</sub>), 4.44 (s, 2H, C<sub>5</sub>H<sub>4</sub>), 4.83 (s, 2H, C<sub>5</sub>H<sub>4</sub>), 5.26 (s, 2H, C<sub>5</sub>H<sub>4</sub>), 6.79 (m, 6H, C<sub>6</sub>H<sub>5</sub>), 6.94 (m, 12H, C<sub>6</sub>H<sub>5</sub>), 7.15 (s, 12H, C<sub>6</sub>H<sub>5</sub>). IR (KBr, cm<sup>-1</sup>): ν<sub>CO</sub> 1916 (s).

*cis*-**3**: m.p. 217–219°C. Anal. Calc. for C<sub>52</sub>H<sub>50</sub>O<sub>8</sub>P<sub>2</sub>Fe<sub>2</sub>Si<sub>2</sub>: C, 60.47; H, 4.88. Found: C, 60.44; H, 4.64%. <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.99 (s, 6H, SiMe<sub>2</sub>), 1.10 (s, 6H, SiMe<sub>2</sub>), 4.19 (s, 2H, C<sub>5</sub>H<sub>4</sub>), 4.24 (s, 2H, C<sub>5</sub>H<sub>4</sub>), 4.98 (s, 2H, C<sub>5</sub>H<sub>4</sub>), 5.03 (s, 2H, C<sub>5</sub>H<sub>4</sub>), 6.77 (m, 6H, C<sub>6</sub>H<sub>5</sub>), 6.91 (m, 12H, C<sub>6</sub>H<sub>5</sub>), 7.10 (s, 12H, C<sub>6</sub>H<sub>5</sub>). IR (KBr, cm<sup>-1</sup>): ν<sub>CO</sub> 1917 (s).

### 2.2. Preparation of $-\{Me_2Si-\eta^5-C_5H_4Fe-(CO)[P(O^iBu)_3]Me_2Si-\eta^5-C_5H_4Fe(CO)[P(O^iBu)_3]\}-$ (**4**)

A solution of 0.234 g (0.5 mmol) of **2** and 0.500 g (2.0 mmol) of P(O<sup>i</sup>Bu)<sub>3</sub> in benzene (20 ml) was irradiated by the high-pressure mercury lamp for 10 h. The solvent was

removed under reduced pressure to give a solid residue, which was dissolved in a small amount of benzene and placed on a column (neutral Al<sub>2</sub>O<sub>3</sub>). Elution with petroleum ether–benzene (2:1) gave a yellow band, from which 0.156 g (34% yield) of **4** was obtained as yellow solid. <sup>1</sup>H-NMR analysis of this product showed that it contained a mixture of *cis*-**4** and *trans*-**4** in a ratio of 1:1.4. The mixture was dissolved in *n*-pentane and the solution maintained at –20°C for 24 h, during which time a small amount of pure *trans*-**4** crystallized as yellow crystals.

*trans*-**4**: m.p. 131–133°C. Anal. Calc. for C<sub>40</sub>H<sub>74</sub>O<sub>8</sub>P<sub>2</sub>Fe<sub>2</sub>Si<sub>2</sub>: C, 52.63; H, 8.17. Found: C, 52.52; H, 7.83%. <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.84 (s, 6H, SiMe<sub>2</sub>), 1.00 (s, 6H, SiMe<sub>2</sub>), 0.84 (t, *J* = 7 Hz, 18H, CMe), 1.37 (m, 12H, OCCCH<sub>2</sub>), 1.49 (m, 12H, OCCH<sub>2</sub>), 3.84 (m, 12H, OCH<sub>2</sub>), 4.37 (s, 2H, C<sub>5</sub>H<sub>4</sub>), 4.65 (s, 2H, C<sub>5</sub>H<sub>4</sub>), 5.27 (s, 2H, C<sub>5</sub>H<sub>4</sub>), 5.38 (s, 2H, C<sub>5</sub>H<sub>4</sub>). IR (KBr, cm<sup>-1</sup>): ν<sub>CO</sub> 1909 (s).

*cis*-**4** [16]: <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.92 (s, 6H, SiMe<sub>2</sub>), 0.95 (s, 6H, SiMe<sub>2</sub>), 0.84 (t, *J* = 7 Hz, 18H, CMe), 1.36 (m, 12H, OCCCH<sub>2</sub>), 1.49 (m, 12H, OCCH<sub>2</sub>), 3.86 (m, 12H, OCH<sub>2</sub>), 4.56 (s, 2H, C<sub>5</sub>H<sub>4</sub>), 4.73 (s, 2H, C<sub>5</sub>H<sub>4</sub>), 4.90 (s, 2H, C<sub>5</sub>H<sub>4</sub>), 5.12 (s, 2H, C<sub>5</sub>H<sub>4</sub>).

### 2.3. Preparation of $-\{Me_2Si-\eta^5-C_5H_4Fe-(CO)[P(O^nPr)_3]Me_2Si-\eta^5-C_5H_4Fe(CO)[P(O^nPr)_3]\}-$ (**5**)

A solution of 0.234 g (0.5 mmol) of **2** and 0.416 g (2.0 mmol) of P(O<sup>n</sup>Pr)<sub>3</sub> in benzene (20 ml) was irradiated in the same way for 12 h. The resulting solution was treated using the procedure detailed in Section 2.2, except that the column was eluted with petroleum ether–ether (25:1). A yellow band was collected, from which 0.248 g (70% yield) of **5** was obtained as yellow solid. The ratio of *cis*-**5** and *trans*-**5** in this solid was determined by <sup>1</sup>H-NMR spectrum to be 1:1.4. A small amount of pure *trans*-**5** was separated out as yellow crystals by dissolving the mixture in *n*-pentane–ether and maintaining the solution at –20°C for 24 h.

*trans*-**5**: m.p. 175–177°C. Anal. Calc. for C<sub>34</sub>H<sub>62</sub>O<sub>8</sub>P<sub>2</sub>Fe<sub>2</sub>Si<sub>2</sub>: C, 49.28; H, 7.54. Found: C, 49.57; H, 7.43%. <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.83 (s, 6H, SiMe<sub>2</sub>), 0.99 (s, 6H, SiMe<sub>2</sub>), 0.85 (t, *J* = 7 Hz, 18H, CMe), 1.49 (m, 12H, CCH<sub>2</sub>C), 3.75 (m, 12H, OCH<sub>2</sub>), 4.36 (s, 2H, C<sub>5</sub>H<sub>4</sub>), 4.64 (s, 2H, C<sub>5</sub>H<sub>4</sub>), 5.19 (s, 2H, C<sub>5</sub>H<sub>4</sub>), 5.36 (s, 2H, C<sub>5</sub>H<sub>4</sub>). IR (KBr, cm<sup>-1</sup>): ν<sub>CO</sub> 1908 (s).

*cis*-**5** [16]: <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.88 (s, 6H, SiMe<sub>2</sub>), 0.92 (s, 6H, SiMe<sub>2</sub>), 0.84 (t, *J* = 7 Hz, 18H, CMe), 1.48 (m, 12H, CCH<sub>2</sub>C), 3.76 (m, 12H, OCH<sub>2</sub>), 4.54 (s, 2H, C<sub>5</sub>H<sub>4</sub>), 4.71 (s, 2H, C<sub>5</sub>H<sub>4</sub>), 4.87 (s, 2H, C<sub>5</sub>H<sub>4</sub>), 5.10 (s, 2H, C<sub>5</sub>H<sub>4</sub>).

### 2.4. Preparation of $-\{Me_2Si-\eta^5-C_5H_4Fe(CO)[P(OEt)_3]Me_2Si-\eta^5-C_5H_4Fe(CO)[P(OEt)_3]\}-$ (**6**)

A solution of 0.234 g (0.5 mmol) of **2** and 0.332 g (2.0 mmol) of P(OEt)<sub>3</sub> in benzene (20 ml) was irradiated for 12 h. The resulting solution was treated using procedures

detailed in Section 2.2 except that elution of the column with petroleum ether–benzene (4:1) was used. Collection of the yellow band afforded 0.237 g (69%) of **6** as yellow solid. <sup>1</sup>H-NMR analysis of this product indicated that it contained *cis*-**6** and *trans*-**6** in a ratio of 1:1.4. *trans*-**6** was obtained as yellow crystals by dissolving the mixture in ether and maintaining the solution at –20°C for 24 h.

*trans*-**6**: m.p. 191–193°C. Anal. Calc. for C<sub>28</sub>H<sub>50</sub>O<sub>8</sub>-P<sub>2</sub>Fe<sub>2</sub>Si<sub>2</sub>: C, 45.17; H, 6.77. Found: C, 45.23; H, 6.68%. <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.82 (s, 6H, SiMe<sub>2</sub>), 0.97 (s, 6H, SiMe<sub>2</sub>), 1.04 (t, *J* = 7 Hz, 18H, CMe), 3.74 (m, 12H, OCH<sub>2</sub>), 4.30 (s, 2H, C<sub>5</sub>H<sub>4</sub>), 4.57 (s, 2H, C<sub>5</sub>H<sub>4</sub>), 5.17 (s, 2H, C<sub>5</sub>H<sub>4</sub>), 5.34 (s, 2H, C<sub>5</sub>H<sub>4</sub>). IR (KBr, cm<sup>-1</sup>): ν<sub>CO</sub> 1910 (s).

*cis*-**6** [16]: <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.89 (s, 6H, SiMe<sub>2</sub>), 1.02 (s, 6H, SiMe<sub>2</sub>), 1.05 (t, *J* = 7 Hz, 18H, CMe), 3.75 (m, 12H, OCH<sub>2</sub>), 4.47 (s, 2H, C<sub>5</sub>H<sub>4</sub>), 4.66 (s, 2H, C<sub>5</sub>H<sub>4</sub>), 4.89 (s, 2H, C<sub>5</sub>H<sub>4</sub>), 5.13 (s, 2H, C<sub>5</sub>H<sub>4</sub>).

### 2.5. Preparation of –{Me<sub>2</sub>Si-η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>Fe(CO)-[P(OMe)<sub>3</sub>Me<sub>2</sub>Si-η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>Fe(CO)[P(OMe)<sub>3</sub>]}– (7)

A solution containing 0.234 g (0.5 mmol) of **2**, 0.248 g (2.0 mmol) of P(OMe)<sub>3</sub> and benzene (20 ml) was irradiated for 16 h and then treated similarly as stated above except that elution of the column with petroleum ether–benzene (3:2) was used. Collection of the yellow band afforded 0.173 g (56% yield) of **7** as yellow solid. <sup>1</sup>H-NMR analysis of this product showed that it was a mixture of *cis*-**7** and *trans*-**7** in the ratio of 1:1.4. Dissolving the mixture in ether and maintaining the solution at –20°C for 24 h gave *trans*-**7** as yellow

crystals. The mother solution, which contained mainly *cis*-**7**, was concentrated to a smaller volume and left at –20°C resulting in a crystalline product. This procedure was repeated several times and finally pure *cis*-**7** was obtained also as yellow crystals.

*trans*-**7**: m.p. 187°C (dec.). Anal. Calc. for C<sub>22</sub>H<sub>38</sub>O<sub>8</sub>-P<sub>2</sub>Fe<sub>2</sub>Si<sub>2</sub>: C, 40.01; H, 5.80. Found: C, 39.81; H, 5.84%. <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.78 (s, 6H, SiMe<sub>2</sub>), 0.92 (s, 6H, SiMe<sub>2</sub>), 3.21 (d, *J* = 11 Hz, 18H, OMe), 4.29 (s, 2H, C<sub>5</sub>H<sub>4</sub>), 4.49 (s, 2H, C<sub>5</sub>H<sub>4</sub>), 5.14 (s, 2H, C<sub>5</sub>H<sub>4</sub>), 5.29 (s, 2H, C<sub>5</sub>H<sub>4</sub>). IR (KBr, cm<sup>-1</sup>): ν<sub>CO</sub> 1913 (s).

*cis*-**7**: m.p. 139–141°C. Anal. Calc. for C<sub>22</sub>H<sub>38</sub>O<sub>8</sub>-P<sub>2</sub>Fe<sub>2</sub>Si<sub>2</sub>: C, 40.01; H, 5.80. Found: C, 39.77; H, 5.59%. <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.82 (s, 6H, SiMe<sub>2</sub>), 0.83 (s, 6H, SiMe<sub>2</sub>), 3.25 (d, *J* = 11 Hz, 18H, OMe), 4.44 (s, 2H, C<sub>5</sub>H<sub>4</sub>), 4.56 (s, 2H, C<sub>5</sub>H<sub>4</sub>), 4.84 (s, 2H, C<sub>5</sub>H<sub>4</sub>), 5.14 (s, 2H, C<sub>5</sub>H<sub>4</sub>). IR (KBr, cm<sup>-1</sup>): ν<sub>CO</sub> 1921 (s), 1908 (s).

### 2.6. Crystal and molecular structure of *trans*-**7**

Yellow crystals of *trans*-**7** suitable for X-ray diffraction analysis were obtained from an ether solution. A crystal having approximate dimensions of 0.1 × 0.22 × 0.29 mm was mounted on a glass fiber. Data collection was performed on a BRUCKER SMART 1000 diffractometer at room temperature using a 2θ–ω scan technique with Mo–K<sub>α</sub> radiation (λ = 0.71073 Å). The structure was solved by the direct methods using SHELX-90 program and refined by least square methods on *F*<sup>2</sup>. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added theoretically and included in the refinement process in an isotropic manner. Crystal data and selected experimental information are listed in Table 1. Selected bond lengths and angles are shown in Table 2.

Table 1  
Crystal data and structure refinement for *trans*-**7**

Empirical formula	C <sub>22</sub> H <sub>38</sub> Fe <sub>2</sub> O <sub>8</sub> P <sub>2</sub> Si <sub>2</sub>
Formula weight	660.34
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>C</i> 2/ <i>c</i>
Unit cell dimensions	
<i>a</i> (Å)	13.1529(13)
<i>b</i> (Å)	9.8092(10)
<i>c</i> (Å)	23.457
α (°)	90
β (°)	100.963(2)
γ (°)	90
<i>V</i> (Å <sup>3</sup> )	2971.1(5)
<i>Z</i>	4
<i>D</i> <sub>calc</sub> (mg m <sup>-3</sup> )	1.476
θ Range for data collection	1.77 to 25.68°
Reflections collected	6401
Independent reflections	2812 [ <i>R</i> <sub>int</sub> = 0.0467]
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	2812/0/239
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.039
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0357, <i>wR</i> <sub>2</sub> = 0.0831
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0494, <i>wR</i> <sub>2</sub> = 0.0891

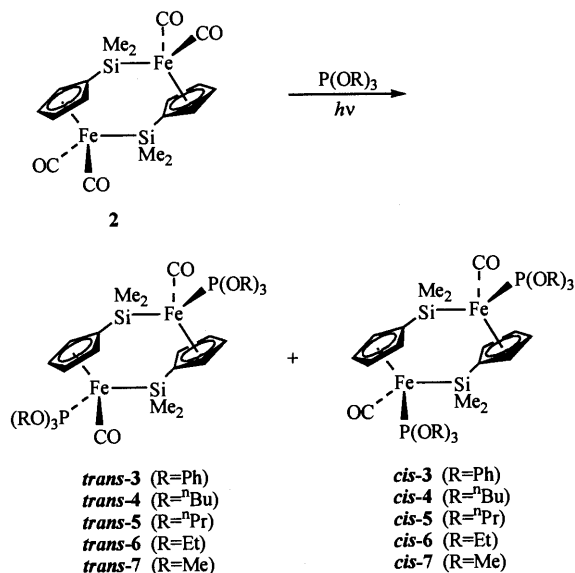
## 3. Results and discussion

We have reported in a previous paper that CO-substitution for phosphorus ligands in **2** is insignificant under thermal condition [12]. However, when **2** is irradiated with a high-pressure mercury lamp in the presence of phosphorus ligands, two CO groups of **2** can easily be substituted by the phosphorus ligands. Thus, reaction of **2** with an excess of P(OPh)<sub>3</sub> in benzene under irradiation leads to isolation of *cis*-**3** and *trans*-**3** in 20 and 33% yields, respectively (Scheme 1). It is found that *trans*-**3** is sparingly soluble in common organic solvents. The complex precipitates from the reaction system as a yellow solid at the end of the reaction upon cooling. On the other hand, the *cis*-**3** is much more soluble in benzene and can be obtained from the solution after filtration of the solid product. The poor solubility of *trans*-**3** can be improved by use of P(O<sup>*n*</sup>Bu)<sub>3</sub> in place of P(OPh)<sub>3</sub> in above reaction. The product obtained in this case is a mixture of *cis*-**4** and *trans*-**4** as a yellow solid (Scheme 1). The ratio of the

Table 2  
Bond lengths (Å) and angles (°) for *trans*-7<sup>a</sup>

Bond lengths			
Fe(1)–Si(1)	2.3093(8)	Fe(1)–P(1)	2.1139(8)
Fe(1)–C(1)	1.725(3)	Si(1)–C(15)	1.891(3)
Si(1)–C(5)	1.887(4)	Si(1)–C(6)	1.893(4)
Fe(1)–C(11)	2.107(3)	C(11)–C(15)	1.444(4)
Fe(1)–C(12)	2.110(3)	C(12)–C(11)	1.390(5)
Fe(1)–C(13)	2.106(3)	C(13)–C(12)	1.410(6)
Fe(1)–C(14)	2.094(3)	C(14)–C(13)	1.422(5)
Fe(1)–C(15)	2.121(3)	C(15)–C(14)	1.417(4)
Bond angles			
Si(1A)–C(15)–Fe(1)	134.30(13)	C(15)–Fe(1)–Si(1)	97.76(7)
C(15A)–Si(1)–Fe(1)	112.20(8)	C(14)–C(15)–Si(1A)	127.7(2)
P(1)–Fe(1)–Si(1)	90.05(3)	P(1)–Fe(1)–C(15)	161.47(8)

<sup>a</sup> Symmetry:  $-x+3/2, -y+1/2, -z+1$ .



Scheme 1.

two isomers in this mixture is determined by <sup>1</sup>H-NMR spectra to be 1:1.4. Both isomers appear to be very soluble in common organic solvents, including *n*-pentane. Pure *trans*-4 is obtained as yellow crystals via partial crystallization of the mixture in *n*-pentane at  $-20^{\circ}\text{C}$ ; however, *cis*-4 is not isolated out in pure state due to its similar solubility to *trans*-4. To facilitate separation of both isomers, other phosphorus ligands, i.e. P(O<sup>n</sup>Pr)<sub>3</sub>, P(OEt)<sub>3</sub>, and P(OMe)<sub>3</sub>, were trialed and found to give the products 5–7 as mixtures of their respective *cis* and *trans* isomers in the same ratio of 1:1.4 (Scheme 1). Of the three phosphites only the last [P(OMe)<sub>3</sub>] produced the *cis* and *trans* products with sufficiently different solubility characteristics to allow isolation of the pure *cis* isomer. The complex *trans*-7 was found to be less soluble in diethylether compared to *cis*-7. Thus, *trans*-7 was obtained by recrystallization

of the mixture at  $-20^{\circ}\text{C}$ , and pure *cis*-7 was obtained from the mother solution after careful crystallization.

It is noteworthy that ratios of the *cis* to the *trans* isomers for 3–7 are almost the same in each case (ca. 1:1.4), with the *trans* isomers produced predominantly over the *cis* isomers. This phenomenon can be rationalized according to the mechanism that involves photochemical elimination of the CO groups from the iron centers as an initial step, followed by addition of the phosphorus ligands to the vacant coordination sites. Noting that the six-membered cyclic structures in these compounds generally take a chair conformation, the phosphorus ligands, which are bulkier than the CO groups, will preferentially occupy the equatorial positions [10,12] (see below). Therefore, formation of the *trans* isomer with two phosphorus ligands both occupying the equatorial positions will involve a less crowded approach for the phosphorus ligands to attack the iron center, as compared to the case of *cis* isomers in which one of the phosphorus ligands has to be in an axial position of the chair conformed ring. Of particular significance is the fact that the two phosphorus ligands have been introduced to different iron centers rather than to the same one. This regioselectivity implies that coordination of the phosphorus ligand to the iron center strengthens the Fe–CO bond and consequently prevents the second CO group from being substituted. This stabilization of the geminal CO coordination bond on the introduction of phosphorus ligands is confirmed through IR spectra and analysis of the molecular structure (see below).

<sup>1</sup>H-NMR spectra of 3–7 generally show two singlets due to Si–Me protons, four singlets due to the C<sub>5</sub>H<sub>4</sub> groups and a number of signals due to the phosphorus ligands P(OR)<sub>3</sub>. While both *cis* and *trans* isomers show the same numbers of signals, it is found that their chemical shifts are significantly different. For example, two singlets due to Si–Me groups appear at 0.83 and 0.82 ppm with a difference of 0.01 ppm for *cis*-7, while they are at 0.78 and 0.92 ppm with a difference of 0.14 ppm for *trans*-7. Signals due to C<sub>5</sub>H<sub>4</sub> groups for *cis*-7 (5.14, 4.84, 4.56 and 4.44 ppm) are also obviously different from those for *trans*-7 (5.29, 5.14, 4.49 and 4.29 ppm). Even for the signals due to the P(OMe) groups, there are slight differences between *cis*-7 (3.27 and 3.22 ppm) and *trans*-7 (3.23 and 3.18 ppm). These differences provide an easy way to distinguish between the *cis* and *trans* isomers.

IR spectra of *trans* isomers of 3–7 are very similar to each other and each show a strong absorption band in the region of CO stretching vibrations, e.g. at 1916 cm<sup>-1</sup> for *trans* 3 and 1913 cm<sup>-1</sup> for *trans*-7. This band is closely related to the corresponding ones observed for  $-\text{[Me}_2\text{Si} - \eta^5 - \text{C}_5\text{H}_4\text{Fe(CO)}_2\text{Me}_2\text{Si} - \eta^5 - \text{C}_5\text{H}_4\text{Fe(CO)P(OR)}_3\text{]-}$  [8 (R = Ph): 1911 cm<sup>-1</sup>; 9 (R = Me): 1901 cm<sup>-1</sup>] [12], whereas it is much lower than the bands for

the moiety  $\text{Fe}(\text{CO})_2$  of **2** ( $1926$  and  $1975\text{ cm}^{-1}$ ) [10], of **8** ( $1921$  and  $1977\text{ cm}^{-1}$ ) and of **9** ( $1921$  and  $1984\text{ cm}^{-1}$ ) [12]. On the other hand, IR spectra of the *cis* isomers are significantly different from one another. Although it can be expected that the IR spectra for the *cis* isomers should give rise to two absorption bands, due to CO groups at equatorial and axial positions, this phenomenon is not observed in the spectrum of *cis*-**3**. In this spectrum only one slightly broadened band at  $1917\text{ cm}^{-1}$  is found, presumably due to the fact that the chair conformation of the cyclic structure has been twisted by the very bulky group  $\text{P}(\text{OPh})_3$ . However, it is found that *cis*-**7** gives rise to the expected two absorption bands at  $1921$  and  $1908\text{ cm}^{-1}$ . These absorption bands of the *cis* isomers are close to those of the *trans* isomers, whereas all the absorption bands of both *cis* and *trans* isomers have much lower frequencies than those of the unsubstituted  $\text{Fe}(\text{CO})_2$  moieties. The fact that a carbonyl group geminal to a phosphorus ligand gives rise to the absorption band at lower frequency than that of carbonyl groups on an iron center without phosphorus ligands has been attributed to the electron donating effect of the phosphorus ligands [12]. This effect can strongly enhance back donation of electrons from the iron atom to vacant  $\pi^*$ -orbitals of the carbonyl group, leading to strengthening of the Fe–CO bond and hence weakening of the C–O multiple bond. This observation is in accord with the fact that the CO group geminal to a phosphorus ligand is not easily substituted (see above).

The crystal and molecular structure of *trans*-**7** has been determined by X-ray diffraction. The molecule, as shown in Fig. 1, has  $C_i$  symmetry. The six-membered cyclic structure, consisting of two silicon, two iron and two Cp-carbon atoms adopts a precise chair conformation similar to that of **2** [10]. The two trimethylphosphite ligands coordinate to different iron atoms in a *trans* arrangement, and both occupy the equatorial positions at the chair conformed ring, while the CO groups prefer the axial positions. This is as expected since the trimethylphosphite groups are much bulkier than the

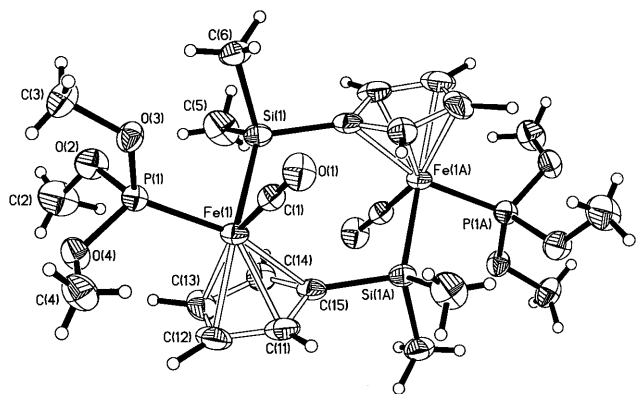


Fig. 1. ORTEP drawing (30% probability level) of *trans*-**7**.

CO groups. It is found that length of the Si–Fe bond ( $2.3093(8)\text{ \AA}$ ) is slightly shorter than that of **2** ( $2.315(2)\text{ \AA}$ ) [10]. This phenomenon has also been observed in the molecular structure of **9** [12], in which the lengths of the two Si–Fe bonds are  $2.305(2)$  and  $2.313(2)\text{ \AA}$ . This change of the lengths of Si–Fe bonds caused by coordination of trimethylphosphite to the iron atom of **9** has been attributed to the electron-donating effect of the phosphorus ligands, which enhance back donation of electrons from the iron center to the vacant 3d-orbitals of the silicon atoms [12]. As a result, the Si–Fe bond is strengthened on coordination of the phosphorus ligand. The Fe–CO bond length is also effected by the introduction of a phosphorus ligand. The length of Fe–CO bond in *trans*-**7** is found to be  $1.725(3)\text{ \AA}$ , which is obviously shorter than that in **2** ( $1.751(6)$  and  $1.761(7)\text{ \AA}$  for the two CO groups in equatorial and axial positions, respectively) [10]. This phenomenon has also been observed in complex **9**, in which the Fe–CO bond ( $1.713(7)\text{ \AA}$ ) geminal to the  $\text{P}(\text{OMe})_3$  ligand is obviously shorter than the other two Fe–CO bonds ( $1.752(10)\text{ \AA}$  and  $1.742(8)\text{ \AA}$ , respectively) [12]. All the observations demonstrate that the coordinative bond of a CO group to the iron atom has been stabilized by the introduction of a geminal phosphorus ligand, which provides a direct evidence for the postulations of this stabilization based on the phenomenon observed in the photochemical reaction and the IR spectra analyses (see above).

It is noted that the CO-substitution of **2** studied in the present paper is similar to that of its acyclic analogue  $\text{Cp}(\text{CO})_2\text{Fe-SiMe}_3$ , which has been reported to react with  $\text{PR}_3$  under photochemical conditions leading to CO-substitution [17], but differing from that of the Fe–C analogue  $\text{Cp}(\text{CO})_2\text{Fe-CH}_3$ , which reacts with  $\text{PR}_3$  under the same conditions leading to insertion of a CO group into the Fe–C bond to give  $\text{Cp}(\text{PR}_3)(\text{CO})\text{Fe-COCH}_3$ . This difference between the Fe–Si and Fe–C systems is due to the fact that the Fe–Si bond is much more stable compared to the Fe–C bond [17]. The high stability of the Fe–Si linkage may result from both the  $\sigma$  interaction between the two atoms and back donation of electrons from the iron center to the vacant 3d-orbitals of the silicon atom [18]. The stabilization of the Fe–CO coordination bond by a geminal  $\text{P}(\text{OR})_3$  ligand, which is most probably responsible for the regioselectivity of the CO-substitution observed in the present study, can only result from the enhanced back-donation of electrons from the iron center to the vacant  $\pi^*$ -orbitals of the CO ligand, caused by coordination of  $\text{P}(\text{OR})_3$ .

#### 4. Supplementary material

Details of structural determination, including atomic coordinates and thermal parameters, a full list of bond

lengths and angles, have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 136843. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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