Regioselective silylphosphination of methyl vinyl ketone with complexes containing cyclic and linear iron–silicon–phosphorus reacting sites†

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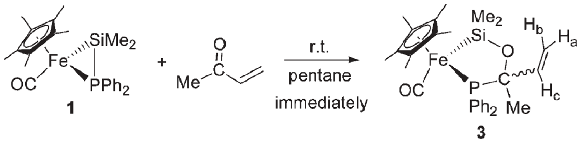
Treatment of Cp*(CO)Fe{κ^2(*Si,P*)-$SiMe_2PPh_2$} with methyl vinyl ketone gave a 1,2-addition product, Cp*(CO)Fe{κ^2(*Si,P*)-$SiMe_2OCMe(CH{=}CH_2)PPh_2$}. A linear-type $Cp^*(CO)_2FeSiMe_2PPh_2$ also reacted with the ketone to yield a 1,4-addition product, $Cp^*(CO)_2Fe$\{κ^1(*Si*)-$SiMe_2OC(Me){=}CHCH_2PPh_2$\}, which was further converted to a seven-membered metallacycle, Cp*(CO)Fe{κ^2(*Si,P*)-$SiMe_2OC(Me){=}CHCH_2PPh_2$}, upon photolysis.

The formation of phosphametallacyclopropanes by cyclometallation is well established for coordinatively unsaturated complexes with a $PMeR_2$ ligand.[1] However, little effort has been made to synthesize the silicon analogs. The first phosphasilametallacyclopropane was reported by Paine *et al.*, who utilized the reaction of a tungsten phosphenium complex with silylenoid reagents for the synthesis.[2] Recently, our group succeeded in the generation and observation of Cp(CO)Fe{κ^2(*Si,P*)-$SiMe_2PPh_2$}, which dimerized at room temperature to form $Cp_2Fe_2(CO)_2[\mu_2$–{κ^2(*Si,P*)-$SiMe_2PPh_2$}$]_2$.[3] The introduction of the bulkier Cp* ligand permitted the isolation of a three-membered metallacycle Cp*(CO)Fe{κ^2(*Si,P*)-$SiMe_2PPh_2$} (**1**), which reacted with nucleophiles to give insertion products.[4] The high reactivity of these phosphasilametallacyclopropanes, in sharp contrast with the carbon analogs, seems to reflect the highly polarized Si(δ+)–P(δ−) bond in the three-membered ring. Here, the reactions of **1** and a linear-type $Cp^*(CO)_2FeSiMe_2PPh_2$ (**2**) with methyl vinyl ketone are reported, and the molecular structures and properties of the resulting insertion products are discussed.

Complex **1** reacted with methyl vinyl ketone to give the insertion product **3** in 75% isolated yield (eqn. (1)). The ^1H NMR spectrum of the residue after evaporation of the reaction mixture indicated the presence of isomers **3a** and **3b** in a 2 : 1 molar ratio as geometric isomers, the generation of which is dependent on the relationships between the groups on the iron and carbon atoms in the five-membered ring. Although the assignment of **3a** and **3b** is unclear at present, one of the isomers has been uniquely determined by X-ray diffraction study (Fig. 1).§ The P–Fe–Si bite angle is 81.95(3)°. The C–O double bond of the ketone is inserted into the silicon–phosphorus bond, with the oxygen atom bound to the silicon atom and the carbon atom bound to the phosphorus atom. The O2–C4 bond distance (1.418(3) Å) lies in the normal range expected for the single bond and is similar to that in a previously reported Cp*(CO)Fe{κ^2(*Si,P*)-$SiMe_2OCMe_2PPh_2$}.[4] In this isomer, the vinyl group and the carbonyl ligand are located on the same side with respect to the five-membered ring defined by Fe, Si, O2, C4, and P.



(1)

^1H NMR analysis of the crystals of **3**, obtained by recrystallization and dissolved in benzene-d_6, indicated a molar ratio of 1 : 2 (**3a** : **3b**), differing from the ratio for **3** obtained by evaporation of the reaction mixture. Furthermore, this ratio remained unchanged at room temperature, clearly indicating that interconversion between the two isomers does not occur at room temperature. In the ^1H NMR spectrum, signals of the vinyl group were observed at δ 5.00 (a), 5.63 (b), and 6.05 (c) for **3a**, and δ 4.94 (a), 5.38 (c), and 5.56 (b) for **3b** with appropriate coupling patterns (letters in parentheses denote positions, see eqn. (1)).

The formation of **3** can be rationalized by assuming the transient formation of the ketone-stabilized phosphido(silylene) complex (Scheme 1).[5,6] The lone pair on the phosphorus atom attacks the carbonyl carbon of the ketone to give the product.

During the course of the reactivity study of **1**, the linear-type phosphinosilyl complex **2**, a precursor of **1**, was also found to react with methyl vinyl ketone to give complex **4** in 65% isolated yield (eqn. (2)). The X-ray crystal structure analysis of **4** (Fig. 2) clearly shows that the methyl vinyl ketone was inserted into the silicon–phosphorus bond, with the silicon atom bonded to the O1 atom and the phosphorus atom bonded to the C6 atom.§ The C3–C5

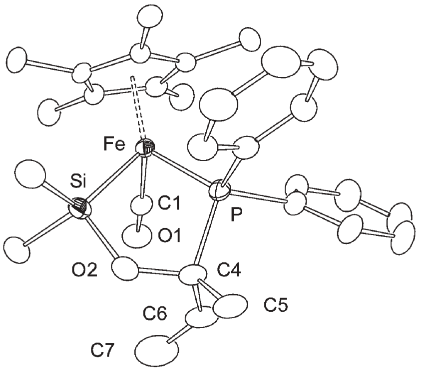


Fig. 1 Molecular structure of an isomer of **3**. Selected bond distances (Å) and angles (°): Fe–Si 2.2982(8), Fe–P 2.1808(7), Si–O2 1.711(2), O2–C4 1.418(3), P–C4 1.927(3), P–Fe–Si 81.95(3).

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† Electronic supplementary information (ESI) available: synthesis details. See http://www.rsc.org/suppdata/cc/b4/b413861a/

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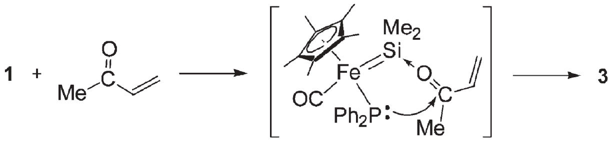


Scheme 1

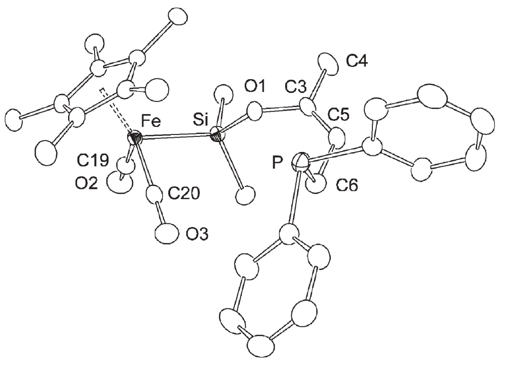
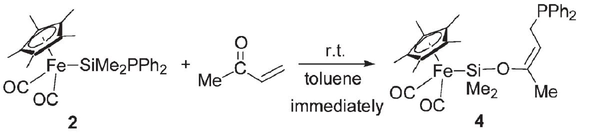


Fig. 2 Molecular structure of **4**. Selected bond distances (Å): Fe–Si 2.3010(6), Si–O1 1.6792(13), P–C6 1.861(2), O1–C3 1.378(2), C3–C4 1.498(3), C3–C5 1.332(3), C5–C6 1.501(3).

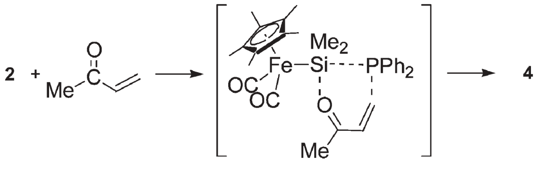
bond distance of 1.332(3) Å is significantly shorter than the distances of both C3–C4 (1.498(3) Å) and C5–C6 (1.501(3) Å), and lies in the normal range expected for the double bond. Based on the structural features, complex **4** can be described as a product of 1,4-addition of **2** to methyl vinyl ketone at the silicon–phosphorus bond.



(2)

The $^{29}Si\{^1H\}$ NMR spectrum of **4** shows a singlet signal at δ 68.2. The lack of coupling with the ^{31}P nucleus supports the formation of the 1,4-addition product. The ^{31}P NMR spectrum includes a signal at δ −14.3, the chemical shift of which is in the range for the free tertiary phosphines of the type PPh_2(alkyl).

Couret *et al.* reported the reaction of germyl- and silylphosphines $R_3EPR'_2$ (E = Ge, Si) with α,β-unsaturated ketones to form a 1,4-*Z*-adduct.[7,8] The stereochemistry was explained by a mechanism involving the nucleophilic attack of the β-carbon by the phosphorus atom and the transient formation of a six-membered cyclic transition state. The present reaction of **2** with methyl vinyl ketone also gave the 1,4-*Z*-adduct exclusively, which can be explained analogously as illustrated in Scheme 2.



Scheme 2

Irradiation of **4** in pentane for 30 min using a 450 W medium-pressure Hg lamp gave complex **5** as yellow crystals in 60% isolated yield. In accordance with the formation of the seven-membered cyclic structure, the two methyl groups on the silicon atom became chemically inequivalent, with signals at δ 0.92 and 1.15 in the ^1H NMR spectrum. The $^{31}P\{^1H\}$ NMR spectrum revealed a signal at δ 65.9, indicating the complexation of the phosphine part with the iron center. In the $^{29}Si\{^1H\}$ NMR spectrum, a doublet signal was observed at δ 79.3, indicating coupling with the ^{31}P nuclei (J_{PSi} = 43.5 Hz). The infrared spectrum exhibited only one band for ν_{CO} at 1896 cm^{-1}, indicating the dissociation of one CO ligand from **4**.

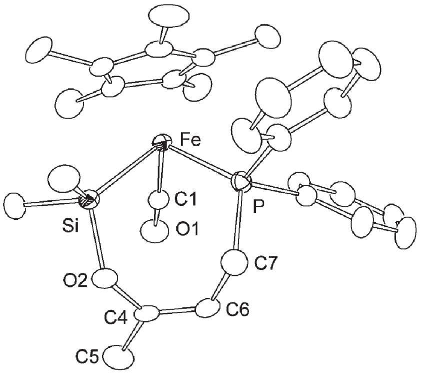
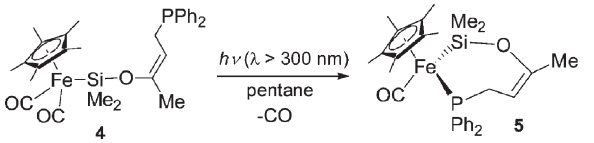


Fig. 3 Molecular structure of **5**. Selected bond distances (Å) and angles (°): Fe–Si 2.2944(8), Fe–P 2.1931(7), Si–O2 1.7053(18), O2–C4 1.358(3), C4–C5 1.497(3), C4–C6 1.324(3), C6–C7 1.490(4), P–C7 1.853(3), P–Fe–Si 93.72(3).

The molecular structure of **5** was unequivocally determined by an X-ray diffraction study (Fig. 3).§ The molecule contains a seven-membered ring, formed through the dissociation of one carbonyl ligand followed by coordination of the phosphine part to the iron center (eqn. (3)). The P–Fe–Si bite angle is 93.72(3)°. It should be noted that complex **5** can be regarded as a 1,4-addition product in the reaction of **1** with methyl vinyl ketone, although such a product was not detected at all in that reaction. This result also demonstrates that the isomerization between **3** and **5**, through the cleavage and formation of P–C bonds, does not occur at room temperature.



(3)

The insertion of unsaturated organic molecules into metal–silicon bonds has been widely investigated so far.[9] In contrast, the cyclic Fe–Si–P reacting site in **1** and the linear site in **2** were found to add to methyl vinyl ketone through Si–P bond cleavage in different reaction modes; 1,2-addition for the former, and 1,4-addition for the latter. These regioselective silylphosphination reactions of α,β-unsaturated ketones may be applicable in organic syntheses, and such trials are currently in progress.

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Notes and references

§ *Crystal data.* For **3**: $C_{29}H_{37}FeO_2PSi$, M = 532.50, monoclinic, $P2_1/c$ (no. 14), a = 9.7874(6), b = 11.2168(7), c = 25.7032(18) Å, β = 97.956(4)°,

V = 2794.6(3) Å^3, D_c = 1.266 g cm^{-3}, Z = 4, T = 150 K, MoKα (λ = 0.71069 Å), μ = 6.63 cm^{-1}, 23548 collected reflections, 6373 unique reflections (R_{int} = 0.040), $R1$ = 0.033 and $wR2$ = 0.123 ($I > 2.0\ \sigma(I)$). For **4**: $C_{30}H_{37}FeO_3PSi$, M = 560.51, triclinic, $P\bar{1}$ (no. 2), a = 9.6625(7), b = 12.0795(7), c = 12.8947(7) Å, α = 99.7325(14), β = 94.253(4), γ = 100.4248(17)°, V = 1450.36(16) Å^3, D_c = 1.283 g cm^{-3}, Z = 2, T = 150 K, MoKα (λ = 0.71069 Å), μ = 6.45 cm^{-1}, 14208 collected reflections, 6605 unique reflections (R_{int} = 0.020), $R1$ = 0.0370 and $wR2$ = 0.0868 ($I > 2.0\ \sigma(I)$). For **5**: $C_{29}H_{37}FeO_2PSi$, M = 532.50, monoclinic, $P2_1/n$ (no. 14), a = 9.1251(16), b = 15.172(2), c = 19.699(2) Å, β = 97.714(6)°, V = 2702.6(7) Å^3, D_c = 1.309 g cm^{-3}, Z = 4, T = 150 K, MoKα (λ = 0.71069 Å), μ = 6.86 cm^{-1}, 25257 collected reflections, 6163 unique reflections (R_{int} = 0.062), $R1$ = 0.049 and $wR2$ = 0.088 ($I > 2.0\ \sigma(I)$). Sheldrick, G. M. *SHELXS-97, Programs for Solving X-ray Crystal Structures*, University of Göttingen, 1997; Sheldrick, G. M. *SHELXL-97, Programs for Refining X-ray Crystal Structures*, University of Göttingen, 1997. CCDC 250453–250455. See http://www.rsc.org/suppdata/cc/b4/b413861a/ for crystallographic data in .cif or other electronic format.

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