

Short Note

[*N,N'*-Di-*tert*-butyl-*P,P*-diphenylphosphinimidic Amidato- $\kappa N, \kappa N'$]chlorosilicon- κSi -tetracarbonyliron

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Abstract: The title complex $\{[\text{Ph}_2\text{P}(t\text{BuN})_2](\text{Cl})\text{Si} \rightarrow \text{Fe}(\text{CO})_4\}$ (**2**) was synthesized via the reaction of chlorosilylene $[\text{Ph}_2\text{P}(t\text{BuN})_2]\text{SiCl}$ (**1**), supported by an iminophosphonamide ligand with $\text{Fe}(\text{CO})_5$ in THF. The molecular structure of **2** was fully characterized by NMR (^1H , ^{13}C , ^{29}Si , and ^{31}P) and IR spectroscopies, as well as single-crystal X-ray diffraction (SCXRD) analysis. In the SCXRD analysis of **2**, the silylene ligand was located in the axial positions of the coordination sphere of the central iron atom and other sites were occupied by carbonyl ligands.

Keywords: iron; silylene; iminophosphonamide; carbonyl complex; single-crystal X-ray diffraction analysis



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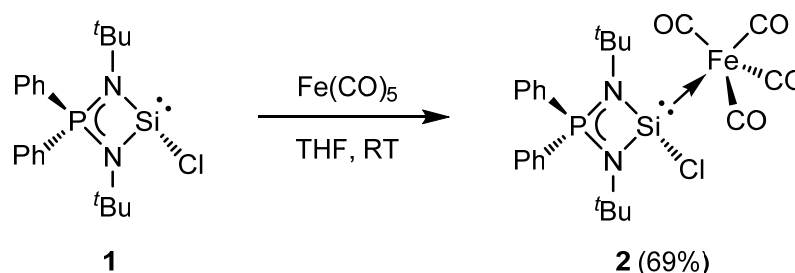
1. Introduction

The chemistry of stable divalent silicon(II) species, silylenes, is currently one of the most intensively researched areas of basic silicon chemistry [1–3]. In this context, a series of Lewis-base-stabilized silylenes can serve as an ancillary ligand in the coordination chemistry because they can behave as a strong nucleophile [4–6]. In particular, the coordination chemistry of silylenes, supported by *N,N'*-chelating amidinate ligands, has developed dramatically over the past few years. Indeed, numerous transition metal complexes utilizing amidinato–silylene ligands have been investigated [7,8]. The resulting complexes were found to be capable of acting as catalysts for transforming organic molecules [5,6] or activating inactive small molecules [9,10]. Among them, amidinato–silylene–iron complexes are particularly attractive candidates for catalysis due to the low cost and high natural abundance of iron, as well as their non-toxic and biocompatible properties [11–20].

Our group has been engaged in the chemistry of p-block elements supported by *N,N'*-chelating iminophosphonamides $[\text{R}_2\text{P}(\text{NR}')_2]$ [21–26]. In particular, chlorosilylenes $[\text{Ph}_2\text{P}(\text{NR})_2\text{SiCl}]$ ($\text{R} = t\text{Bu}$ and $2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$) show the unprecedented complexation ability of transition metals and unique nucleophile behavior due to their strong σ -donating properties [21–23,26]. In this contribution, we present the synthesis and structural characterization of silylene–tetracarbonyliron(0) complex $\{[\text{Ph}_2\text{P}(t\text{BuN})_2](\text{Cl})\text{Si} \rightarrow \text{Fe}(\text{CO})_4\}$, wherein the silylene(II) center is stabilized by an *N,N'*-di-*tert*-butyliminophosphonamide ligand.

2. Results and Discussion

The complexation of chlorosilylene **1** with $\text{Fe}(\text{CO})_5$ proceeded readily at room temperature in THF to afford the corresponding silylene–tetracarbonyliron(0) complex **2** as yellow crystals in 69% yield with the release of a molecule of CO (Scheme 1).



Scheme 1. Synthesis of silylene–tetracarbonyliron(0) complex **2**.

Single crystals of **2** were obtained from a saturated THF solution at $-10\text{ }^{\circ}\text{C}$. The molecular structure of **2** was unequivocally determined using single-crystal X-ray diffraction (SCXRD) analysis. The ORTEP is depicted in Figure 1, and selected bond lengths and angles are summarized in Table 1. Complex **2** crystallized in the monoclinic space group $P2_1/c$ with a molecule of THF per unit cell. The solvate THF molecules in **2** were disordered in two positions with the relative occupancy of 0.722(8) and 0.278(8). The SCXRD analysis of **2** reveals that the silylene ligand was located in the axial positions of the coordination sphere of the central iron atom and other sites were occupied by carbonyl ligands. The chlorine atom on the silicon atom and an equatorial carbonyl ligand were *trans* to one another with respect to the Si–Fe bond. The geometry of five-coordinated compounds can be evaluated using the angular structure parameter τ [$\tau = (\beta - \alpha)/60$] [27]. This parameter can be readily calculated using the two largest basal angles (α and β) around the central atom in the five-coordinated compound (Figure 2). Thus, $\tau = 1$ had a trigonal bipyramidal structure with D_{3h} symmetry, while the square pyramidal structure with C_{4v} symmetry had $\tau = 0$. The calculated τ value for **2** was 0.78, indicating that the iron atom is defined as the somewhat distorted trigonal bipyramidal geometry. The silicon atom exhibited a distorted tetrahedral geometry; the sum of the bond angles around the Si1 atom (362.36°) was within the range of those of the corresponding silylene-ligated tetracarbonyliron(0) complexes [$353.92\text{--}362.64^{\circ}$] [17–19]. Despite the strong σ -donor ability of **1**, the Si1–Fe1 bond length [$2.2675(6)\text{ \AA}$] was slightly longer than that of the related amidinato–silylene–iron(0) complexes [$2.237(7)\text{--}2.2777(5)\text{ \AA}$] [17–19], probably due to the steric repulsion between the phenyl group on the phosphorus atom and the carbonyl ligand. Two Si–N bond lengths [$1.8001(15)$ and $1.8078(15)\text{ \AA}$] in the four-membered ring fell in the same range as those of the reported three-coordinated silylenes [$1.8291(19)\text{--}1.8750(16)\text{ \AA}$] [17–19]. The Si–Cl bond length in **2** was $2.1161(7)\text{ \AA}$, which is slightly shorter than the corresponding bond length in the starting **1** [$2.2291(11)\text{ \AA}$] [21].

Table 1. Selected bond lengths [$\text{\AA}$] and bond angles [$^{\circ}$].

Bond Lengths	[$\text{\AA}$]	Bond Angles	[$^{\circ}$]
Si1–Fe1	2.2675(6)	Si1–Fe1–C21	174.28(6)
Si1–Cl1	2.1161(7)	Si1–Fe1–C22	86.99(6)
Si1–N1	1.8001(15)	Si1–Fe1–C23	86.12(6)
Si1–N2	1.8078(15)	Si1–Fe1–C24	91.12(6)
Fe1–C21	1.791(2)	C22–Fe1–C23	127.39(9)
Fe1–C22	1.784(2)	C23–Fe1–C24	111.64(9)
Fe1–C23	1.774(2)	C22–Fe1–C24	120.59(9)
Fe1–C24	1.788(2)	Cl1–Si1–N1	104.37(6)
		Cl1–Si1–N2	104.82(5)
		N1–Si1–N2	80.31(7)

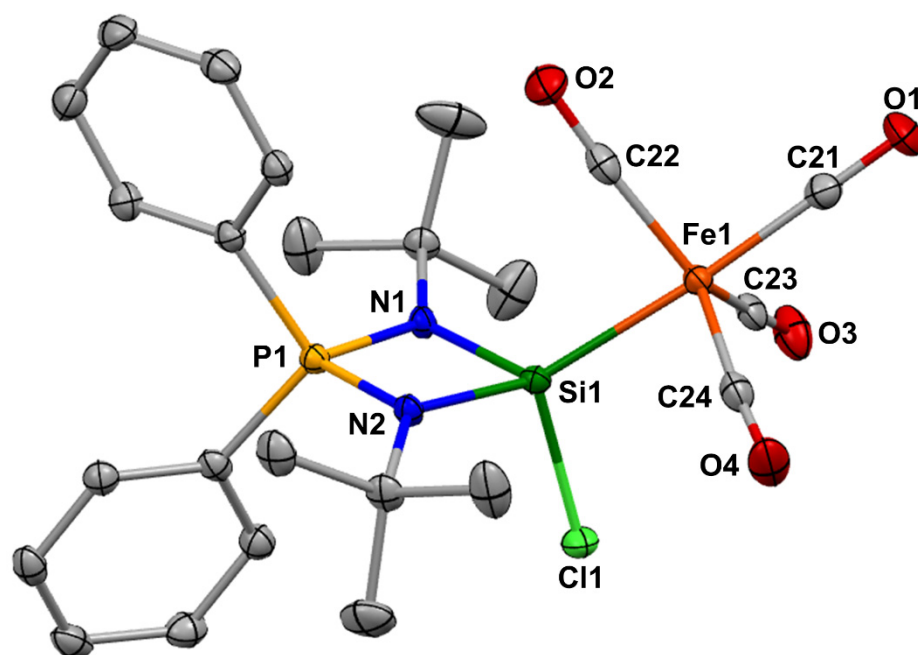


Figure 1. ORTEP [28] of **2** with thermal ellipsoids at a 50% probability. All hydrogen atoms and a molecule of THF in the unit cell were omitted for clarity.

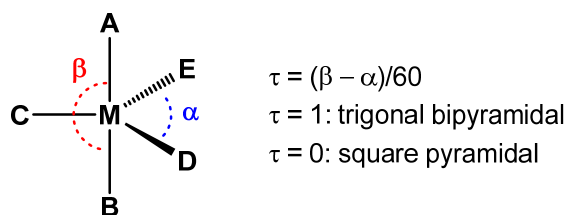


Figure 2. The trigonal bipyramidal geometry with basal angles α and β , and angular structure parameter τ .

The structure of **2** was also confirmed following spectroscopic analyses. The ^1H NMR spectrum of **2** in C_6D_6 displayed a singlet signal assigned to the $t\text{Bu}$ groups at 1.22 ppm. The aromatic protons were observed as broad signals at 7.07 and 8.03 ppm. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2**, the carbonyl ligands binding to the iron center were resonated at 217.0 ppm, which is comparable to those of the related amidinato–silylene– $\text{Fe}(\text{CO})_4$ complexes (213.1–217.2 ppm) [17–20]. In the $^{31}\text{P}\{^1\text{H}\}$ NMR of **2**, a sharp singlet signal appeared at 46.8 ppm, which is quite similar to that of the starting **1** (46.6 ppm) [21]. The $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **2** showed a doublet signal via the ^{31}P coupling of 11.9 Hz at 74.6 ppm, and shifts to a lower field compared to that of the starting **1** (59.8 ppm) [21] and falls in the range of those in the related amidinato–silylene– $\text{Fe}(\text{CO})_4$ complexes (40.3–112.8 ppm) [17–20]. The absorptions due to carbonyl stretching vibrations in the IR spectrum were observed at 2029, 1944, and 1913 cm^{-1} , consistent with the results of SCXRD analysis exhibiting local C_3v symmetry on the iron(0) site. All NMR (Figures S1–S4) and IR (Figure S5) spectra are in the Supplementary Materials.

3. Materials and Methods

3.1. General Considerations

Unless otherwise noted, all experiments were carried out under an argon atmosphere using standard Schlenk-line techniques or a UNICO glovebox. ^1H , ^{13}C , ^{29}Si , and ^{31}P NMR spectra were recorded on Bruker Avance-500 (500 MHz for ^1H , 126 MHz for ^{13}C , 99 MHz for ^{29}Si , and 202 MHz for ^{31}P) and Bruker Avance-400 (400 MHz for ^1H , 101 MHz for ^{13}C , and 162 MHz for ^{31}P) spectrometers, with C_6D_6 as the solvent at room temperature.

The IR spectrum was recorded on a TENSOR II. All melting points were determined on a Mel-Temp capillary tube apparatus and were uncorrected. Elemental analyses were carried out at the Molecular Analysis and Life Science Center of Saitama University. All solvents were dried over 4A molecular sieves or potassium mirror before use. All materials were obtained from commercial suppliers and were used without further purification, except **1** [21], which was prepared according to the corresponding literature procedure.

3.2. Synthesis of Complex 2

In a Schlenk tube, to a THF (2 mL) solution of chlorosilylene **1** (140 mg, 0.36 mmol), $\text{Fe}(\text{CO})_5$ (0.05 mL, 0.37 mmol) was added at ambient temperature. After stirring for 1 h, the reaction mixture was concentrated under reduced pressure, and the crude product was crystallized from a saturated THF solution at -10°C to give **2** (138 mg, 69%) as yellow crystals. Mp. 141–142 $^\circ\text{C}$ (decomp.). ^1H NMR (400 MHz, 25°C C_6D_6): δ = 1.22 (s, 18H, CH_3tBu), 7.07 (br, 6H, CH_{Ar}), 8.03 (br, 4H, CH_{Ar}). $^{13}\text{C}\{^1\text{H}\}$ (100 MHz, 25°C , C_6D_6): δ = 32.0 (d, J_{CP} = 5.6 Hz, CH_3tBu), 55.3 (C_{tBu}), 126.2 (d, J_{CP} = 99.3 Hz, C_{Ar}), 129.1 (d, J_{CP} = 11.3 Hz, CH_{Ar}), 129.1 (d, J_{CP} = 11.0 Hz, CH_{Ar}), 134.3 (d, J_{CP} = 2.9 Hz, CH_{Ar}), 134.5 (d, J_{CP} = 2.9 Hz, CH_{Ar}), 134.7 (d, J_{CP} = 12.1 Hz, CH_{Ar}), 134.8 (d, J_{CP} = 12.2 Hz, CH_{Ar}), 217.0 (CO). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, 25°C , C_6D_6): δ = 46.6. $^{29}\text{Si}\{^1\text{H}\}$ NMR (99 MHz, 25°C , C_6D_6): δ = 74.6 (d, J_{SiP} = 11.9 Hz). IR(KBr): ν_{CO} = 2029, 1944, 1913 cm^{-1} . Anal. Calculated for $\text{C}_{24}\text{H}_{28}\text{ClFeN}_2\text{O}_4\text{PSi}$: C, 51.58; H, 5.05; N, 5.01. Found: C, 51.84; H, 5.07; N, 4.90.

3.3. SCXRD Analysis of 2

A yellow single crystal of **2** was grown from a saturated THF solution at -10°C . The intensity data were collected at 100 K on a Bruker SMART APEX II diffractometer employing graphite-monochromated $\text{MoK}\alpha$ radiation (λ = 0.71073 Å). The structure was solved using direct methods (SHELXT) [29] and refined with full-matrix least-squares procedures on F^2 for all reflections (SHELXL) [30]. Hydrogen atoms were located by assuming the ideal geometry and were included in the structure calculations without any further refinement of the parameters. The structures of overlapped and disordered THF molecules were restrained to be identical to each other using DFIX (σ = 0.01), SAME (σ_1 = 0.01, σ_2 = 0.02), and DELU (σ_1 = 0.01, σ_2 = 0.02) instructions.

Crystal data for $\text{C}_{28}\text{H}_{36}\text{ClFeN}_2\text{O}_5\text{PSi}$ (**2**): M = 630.95 g mol^{-1} , monoclinic, $P2_1/c$, a = 9.3227(7), b = 27.786(2), c = 11.5041(9) Å, β = $94.5030(10)^\circ$, V = 2970.9(4) Å³, Z = 4, D_x = 1.411 g cm^{-3} , $F(000)$ = 1320, and μ = 0.732 mm^{-1} . CCDC deposition number: 2192007.

4. Conclusions

We demonstrated the synthesis and spectroscopic characterization of the novel silylene-tetracarbonyliron(0) complex $\{[\text{Ph}_2\text{P}(\text{tBuN})_2](\text{Cl})\text{Si} \rightarrow \text{Fe}(\text{CO})_4\}$. Further applications of N,N' -chelating silylenes are currently under investigation in our laboratory.

Supplementary Materials: The following are available online. All NMR (Figures S1–S4) and IR (Figure S5) spectra, and crystallographic data for **2** in Crystallographic Information File (CIF) format. CCDC 2192007 also contains the supplementary crystallographic data for this paper.

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Data Availability Statement: CCDC 2192007 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif (accessed on 31 July 2022), or by emailing data_request@ccdc.cam.ac.uk or contacting The Cambridge

Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

Conflicts of Interest: The authors declare no conflict of interest.

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