Synthesis of the First Iron Complexes Containing 1,2-Phenylenedioxysilyl Group

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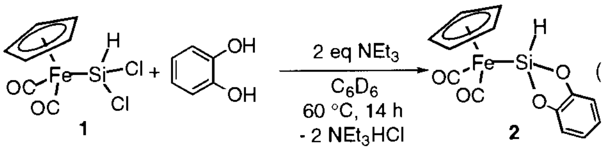
Reaction of $FpSiHCl_2$ (Fp = $(\eta^5\text{-}C_5H_5)Fe(CO)_2$) with catechol in the presence of NEt_3 afforded FpSiH(cat) (**2**: cat = $o\text{-}O_2C_6H_4$). While the reaction in the presence of 1,3-dimethyl-2-imidazolidinone (DMI) gave FpSiCl(cat) (**3**). The NMR investigation of the latter reaction revealed that the hydrosilyl complex **2** is formed as an intermediate which is converted into the chlorosilyl complex **3** via H/Cl exchange between **2** and DMI·HCl.

Silicon compounds containing 1,2-phenylenedioxyl group ($o\text{-}O_2C_6H_4$) show unique features due to the strong electron-withdrawing effect of the 1,2-phenylenedioxyl group and the ring strain of the five membered ring composed of the silicon atom and the 1,2-phenylenedioxyl group. For example, reactions of dichlorosilanes with catechol gave $R_2Si(cat)$ (R = Me or Ph, cat = 1,2-phenylenedioxyl group) which exists as an equilibrium mixture of monomer, $R_2Si(cat)$, and dimer, $R_2Si(cat)_2SiR_2$, in solution.[1] It is also known that the 1,2-phenylenedioxyl group stabilizes hypervalent silicon species.[2] In contrast to the extensive study on the organosilicon compounds with 1,2-phenylenedioxyl group, no transition metal complex with 1,2-phenylenedioxysilyl group has been reported so far. In this paper, we report synthesis of the first (1,2-phenylenedioxysilyl)iron complexes and an unexpected H/Cl substitution reaction on the silicon atom of a (hydro-1,2-phenylenedioxysilyl)iron complex.

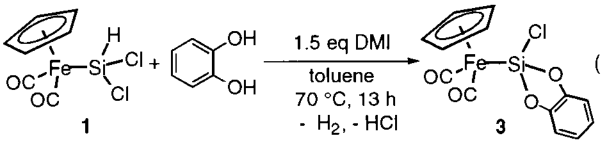
Reaction of $FpSiHCl_2$ (**1**) (Fp = $(\eta^5\text{-}C_5H_5)Fe(CO)_2$) with catechol in the presence of 2 equiv. of triethylamine afforded FpSiH(cat) (**2**)[3] accompanied by the precipitation of triethylammonium chloride (eq 1).



(1)

Complex **2** was characterized by mass and NMR spectroscopy. The mass spectrum of **2** showed peaks at 314, 286, and 257, which are assignable to the molecular ion peak (M^+), M^+-CO, and M^+-2CO-H, respectively. The ^{29}Si NMR of **2** showed a doublet signal at δ 83.6 ppm ($^1J_{Si\text{-}H}$ = 234 Hz), which is downfield-shifted compared to those of typical silyl complexes (-30 ~ +70 ppm).[4] The downfield shift of the ^{29}Si NMR signal is attributable to the deshielding effect caused by the strain of the five membered ring in Si(cat) moiety. The effect has been well documented for various silanes.[5] The ^{1}H NMR signals of the Si-H in **2** appeared at significantly low field (δ 7.32 ppm) compared to those of typical (hydrosilyl)iron complexes such as $FpSiH_3$ (δ 4.10 ppm),[6a] $FpSiH_2{}^tBu$ (δ 4.49 ppm),[6b] and $FpSiHCl_2$ (δ 6.80 ppm).[6a] This downfield shift of the Si-H signal is attributable to the strong electron-withdrawing effect of the 1,2-phenylenedioxyl group and the ring current effect of the aromatic ring in the 1,2-phenylenedioxyl group.

In contrast to the formation of **2** mentioned above, the reaction of **1** with catechol in the presence of 1,3-dimethyl-2-imidazolidinone (DMI) gave FpSiCl(cat) (**3**)[7] as yellow crystals in 72% yield (eq 2).



(2)

The IR spectrum of complex **3** shows two strong ν_{co} bands (2035 cm^{-1} and 1988 cm^{-1}) which are higher by *ca.* 20 cm^{-1} than those of usual silyl-Fp complexes and comparable to those for $FpSiCl_3$ (Table 1). The blue-shift of ν_{co} of **3** indicates that the strong electron-withdrawing effect of the 1,2-phenylenedioxyl and chloro substituents on the silicon atom causes increase of π-back donation from the filled d-orbital of the iron atom to the empty σ*-orbital of Si-O and Si-Cl bonds, which consequently decreases π-back donation from the iron atom to the carbonyl ligands.[9, 10]

Table 1. Position of ν_{co} bands of silyliron complexes [a]

complex	$\tilde{\nu}$ / cm^{-1}	Ref.
complex **3**	2035, 1988	This work
$FpSiH_3$	2008, 1959	8a
$FpSiPh_3$	2004, 1954	8b
$FpSi(OMe)_3$	2011, 1952	8c
$FpSiCl(OMe)_2$	2019, 1969	8c
$FpSiCl_3$	2043, 1999	8d

[a] in cyclohaxane solution

To elucidate the formation mechanism of **3**, the reaction of **1** with catechol in the presence of DMI was monitored by ^{1}H and ^{29}Si NMR spectroscopy. Upon heating a benzene-d_6 solution of **1**, catechol, and 2 equiv. of DMI, formation of **2** was first observed at the early stage of the reaction, followed by formation of **3**. Complex **2** disappeared completely at the end of the reaction. This result indicates that the hydrosilyl complex **2** is an intermediate for the formation of **3**.

The possible formation mechanism of **3** is outlined in Scheme 1: (i) Reation of **1** with catechol in the presence of DMI afforded complex **2** and HCl, and (ii) the Si-H group of **2** undergoes chlorination by the reaction of **2** with the generated DMI·HCl adduct to form the final complex **3**.

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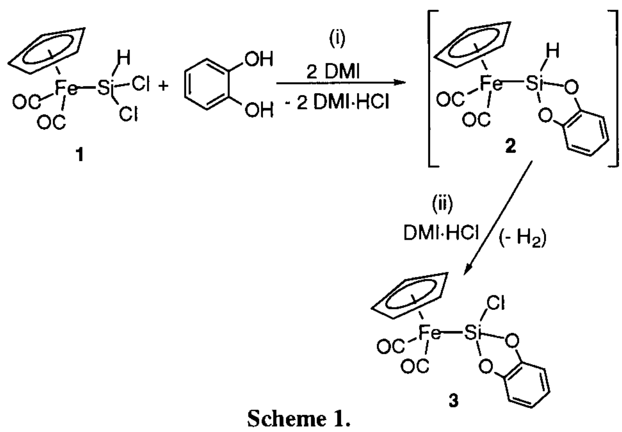

Scheme 1.

The step (i) requires a base to trap the generated HCl and shifts the reaction to the right since **1** did not react with catechol in the absence of a base. When NEt_3 is used as the base, the generated HCl is effectively removed from the reaction system as an insoluble precipitate of triethylammonium chloride. On the other hand, the DMI·HCl adduct is soluble in toluene and benzene-d_6. Thus, the DMI·HCl adduct attacks **2** efficiently to give H/Cl substitution product **3**.

Interestingly, reaction of the (hydrodichlorosilyl)iron complex **1** with DMI·HCl did not afford $FpSiCl_3$ at all under conditions similar to those employed for the synthesis of the (chlorosilyl)iron complex **3**. This clearly indicates that the Si-H bond in **2** is activated by the phenylenedioxyl group on the silicon atom.

References and notes

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3 Although complex **2** was formed in good yield (74%) which was confirmed by the ^{1}H NMR spectrum, isolation of **2** was unsuccessful because this was highly air sensitive. Data for **2**: ^{1}H NMR (300 MHz, C_6D_6) δ 3.94 (s, 5H, C_5H_5), 6.76 (dd, J_{HH} = 5.58, 3.48 Hz, 2H, *o*-$O_2C_6H_4$), 7.13 (dd, J_{HH} = 5.58, 3.48 Hz, 2H, *o*-$O_2C_6H_4$), 7.32 (s, 1H, SiH). ^{13}C NMR (75.5 MHz, C_6D_6) δ 83.7 (C_5H_5), 113.6, 121.2, 149.9 (*o*-$O_2C_6H_4$), 211.4 (CO). ^{29}Si NMR (59.6 MHz, C_6D_6) δ 83.6 (d, $^1J_{SiH}$ = 234 Hz). MS (EI, 70 eV) *m/z* 314 (M^+, 18.6), 286 (M^+-CO, 41.4), 257 (M^+-2CO-H, 11.8).

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7 Data for **3**: ^{1}H NMR (300 MHz, C_6D_6) δ 3.98 (s, 5H, C_5H_5), 6.75 (dd, J_{HH} = 5.79, 3.48 Hz, 2H, *o*-$O_2C_6H_4$), 7.12 (dd, J_{HH} = 5.79, 3.48 Hz, 2H, *o*-$O_2C_6H_4$). ^{13}C NMR (75.5 MHz, C_6D_6) δ 84.1 (C_5H_5), δ 113.7, 121.7, 149.2 (*o*-$O_2C_6H_4$), δ 210.5 (CO). ^{29}Si NMR (59.6 MHz, C_6D_6) δ 59.5. MS (EI, 70 eV) *m/z* 348 (M^+, 73.5), 314 (M^+-CO, 11.9), 292 (M^+-2CO, 100). IR (cyclohexane) 1988, 2035 cm^{-1} (ν_{CO}). Anal. Found: C, 44.99; H, 2.73%. Calcd for $C_{13}H_9O_4ClSiFe$: C, 44.79; H, 2.60%.

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