# Facile Alkylation of Cobalt(III) Porphyrins by Organosilicon Compounds

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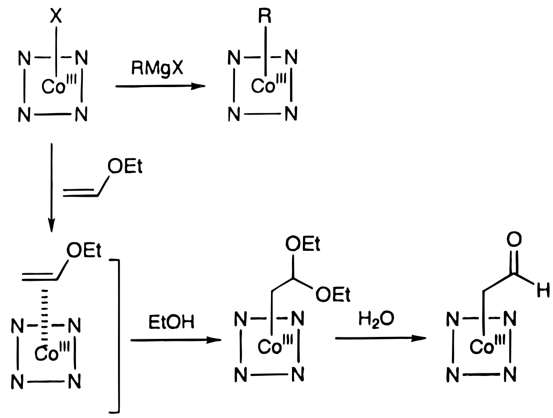
($\sigma$-Alkyl)cobalt(III) porphyrins were easily synthesized and isolated as stable crystalline compounds by the reaction of halogenocobalt(III) porphyrins with silyl enol ethers and ketene silyl acetals. The yields depended on the solvent ($\mathrm{CH_2Cl_2}$ > MeOH), the substituent of the porphyrin periphery (*meso*-tetraphenylporphyrin > octaethylporphyrin), and the axial halogeno ligand of cobalt(III) porphyrins ($\mathrm{F} \geq \mathrm{Cl} \gg \mathrm{Br} \approx \mathrm{I} \approx \mathrm{ClO_4}$). 1-((Trimethylsilyl)oxy)-1,3-butadiene afforded ($\sigma$-4-oxobut-2-enyl)cobalt(III) porphyrins, which showed very broad $^1$H NMR signals at 25 °C. The temperature-dependent dynamic behavior of this complex was explained in terms of the rotation around the C(α)−C($\beta$) bond but not of the $\sigma$−$\pi$ rearrangement in the 4-oxobut-2-enyl ligand.

## Introduction

It has been known that cobalt(III) porphyrins undergo nucleophilic attack by Grignard reagents to generate ($\sigma$-alkyl)cobalt(III) porphyrins (Scheme 1).[1] Vinyl ethers are also nucleophilic enough to be capable of attacking a cobalt(III) center leading to ($\sigma$-formylmethyl)cobalt(III) derivatives via cobalt(III) alkene $\pi$-complex intermediates (Scheme 1).[2] Although the latter method is easily performed even in hydrophilic reaction media, it has never been widely applied, due to the limitation on availability of a variety of vinyl ether derivatives.[3] Silyl enol ethers, ketene silyl acetals, and allylsilanes have recently found wide application as protected carbon nucleophiles in organic synthesis.[4] Since these organosilicon compounds are electron-rich alkenes and thus regarded as analogues of vinyl ethers, they are expected to react with cobalt(III) porphyrins via $\pi$-complex intermediates. Furthermore, since a variety of organosilicon compounds are readily available compared with vinyl ether derivatives, they would extend the scope of the reaction of cobalt(III) porphyrins with electron-rich alkenes as a method for the Co−C bond formation. We now wish to describe the details of the reaction of halogenocobalt(III) porphyrins with organosilicon compounds (Scheme 2).

**Scheme 1**



## Results and Discussion

When TPPCo$^{III}$−Cl (**1a**; 0.030 mmol) (TPP = *meso*-tetraphenylporphyrin dianion) was reacted with 1-phenyl-1-((trimethylsilyl)oxy)ethene (0.20 mmol) in methanol (15 mL) for 50 min, TPPCo$^{III}$−$\mathrm{CH_2COPh}$ **(3a)** was obtained in 72% yield. Table 1 summarizes the result of the reaction of Co(III) porphyrins with various organosilicon compounds. The progress of the reaction was indicated by the formation of a precipitate of ($\sigma$-alkyl)cobalt(III) porphyrins, and thus the use of methanol as a reaction medium makes the product isolation procedure quite simple. The carbonyl stretching mode of **3a** was observed at 1634 cm$^{-1}$ in the IR spectrum. This much lower wavenumber than the ordinary $\nu$(C═O) values is characteristic of ($\sigma$-alkyl)metal(III) complexes with a carbonyl group at the $\beta$-position with respect to the metal and is indicative of the overlap between the filled metal d orbital and the C═O antibonding orbital.[5]

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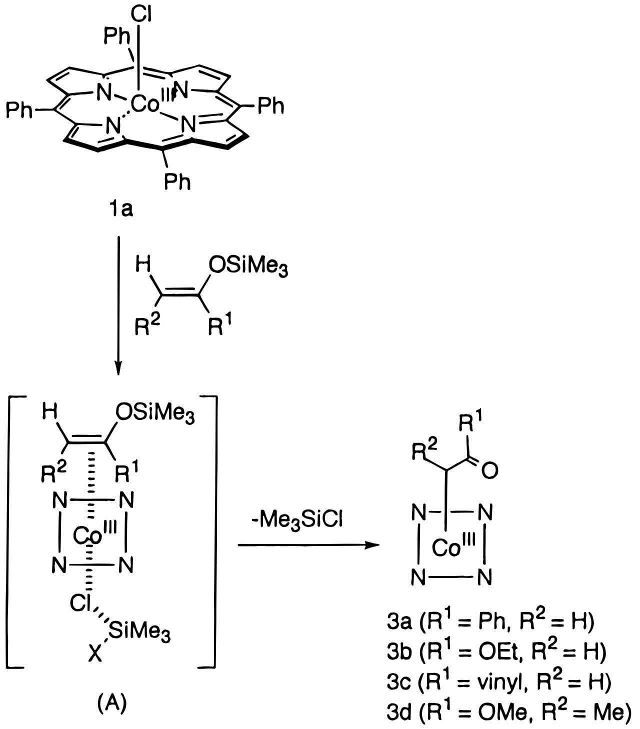
**Table 1. Reaction of (Por)Co$^{III}$−X with R$^2$HC=CR$^1$(OSiMe$_3$)**

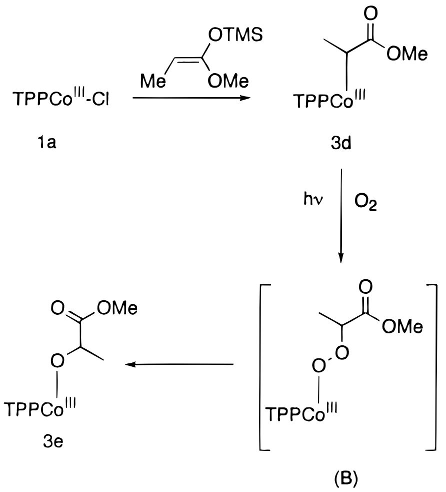
| run no. | Por | X | R$^1$ | R$^2$ | solv | time (min) | prod. | yield (%)[a] |
|---|---|---|---|---|---|---|---|---|
| 1 | TPP | Cl | Ph | H | MeOH | 50 | **3a** | 72 |
| 2 | | Cl | Ph | H | $CH_2Cl_2$ | 2 | **3a** | 85 |
| 3 | | Cl | Ph | H | MeOH | 50 | **3a** | 56 |
| 4 | | $ClO_4^-$ | OEt | H | MeOH | 50 | **3b** | 81 |
| 5 | | Cl | $CH{=}CH_2$ | H | MeOH | 50 | **3c** | 44 |
| 6 | | Cl | $CH{=}CH_2$ | H | $CH_2Cl_2$ | 2 | **3c** | 77 |
| 7 | | Cl | $-CH_2CH_2CH_2-$ | | MeOH | 50 | | 0[b] |
| 8 | | Cl | OMe | Me | MeOH | 50 | **3d** | 39[c] |
| 9 | | Cl | OMe | Me | $CH_2Cl_2$ | 2 | **3d** | 86 |
| 10 | | Cl | H | $CH{=}CH_2$ | MeOH | 10 | **3f** | 67 |
| 11 | | Cl | H | $CH{=}CH_2$ | $CH_2Cl_2$ | 2 | **3f** | 87 |
| 12 | | Cl | $-CH_2CH_2CH{=}CH-$ | | $CH_2Cl_2$ | 2 | | 0[b] |
| 13 | OEP | Cl | Ph | H | MeOH | 50 | | 0 |
| 14 | | Cl | Ph | H | $CH_2Cl_2$ | 2 | **4a** | 71 |
| 15 | | F | Ph | H | $CH_2Cl_2$ | 2 | **4a** | 74 |
| 16 | | Br | Ph | H | $CH_2Cl_2$ | 2 | | 0 |
| 17 | | I | Ph | H | $CH_2Cl_2$ | 2 | | 0 |
| 18 | | $ClO_4^-$ | Ph | H | $CH_2Cl_2$ | 2 | | 0 |
| 19 | | Cl | $CH{=}CH_2$ | H | $CH_2Cl_2$ | 2 | **4c** | 82 |
| 20 | | Cl | H | $CH{=}CH_2$ | $CH_2Cl_2$ | 2 | **4f** | 71 |

[a] Isolated yields, except for run 8. [b] The isolated product was TPPCo$^{II}$. [c] TPPCo$^{III}$−OCH(Me)CO$_2$Me (**3e**) was also obtained in 19% NMR yield.

**Scheme 2**



**Scheme 3**



The $^1$H NMR signals due to the axial organo group of **3a** appear at much higher magnetic fields owing to the ring current effect as shown in Table 2. 1-Ethoxy-1-((trimethylsilyl)oxy)ethene and 2-((trimethylsilyl)oxy)-1,3-butadiene similarly afforded the corresponding ($\sigma$-(2-oxoalkyl)cobalt(III) porphyrins TPPCo$^{III}$−CH$_2$CO$_2$Et (**3b**) and TPPCo$^{III}$−CH$_2$COCH=CH$_2$ (**3c**), in 81% and 44% yields, respectively. These ($\sigma$-alkyl)cobalt(III) porphyrins were thermally stable enough to be purified by column chromatography on silica gel with dichloromethane as an eluent. Reaction of **1a** with 1-methoxy-1-((trimethylsilyl)oxy)-1-propene afforded a mixture of TPPCo$^{III}$−CH(Me)CO$_2$Me (**3d**; 39%) and a cobalt(III) porphyrin byproduct, TPPCoCo$^{III}$−OCH(Me)CO$_2$Me (**3e**; 19%) (Scheme 3). These products could not be separated because they decomposed during column chromatography on silica gel. The $^1$H NMR signals due to the axial alkyl protons of **3d** and **3e** appear as substantially the same splitting pattern but with very different ring current effects, as shown in Table 2. These data are consistent with the structure for **3e**, in which one oxygen atom is inserted into the Co$^{III}$−C bond of **3d**. Although it is well-known that insertion of dioxygen into a M$^{III}$−C bond generates ($\sigma$-alkylperoxo)metal(III) complexes, especially in the cases of secondary and tertiary $\sigma$-alkyl groups,[6] this hypothetical ($\sigma$-1-(carbomethoxyethyl)-peroxo)cobalt(III) structure (B) is not consistent with the $^1$H NMR data observed for **3e**. It is reported that the axial CH$_2$ proton signal shifts from −2.55 ppm to −0.13 ppm upon going from TPPCo$^{III}$−CH$_2$Ph to TPP-Co$^{III}$−OOCH$_2$Ph.[7] Therefore, the observed chemical shift (−3.40 ppm) due to the methine proton of **3e** is consistent not with the Co$^{III}$−OOCH(Me)CO$_2$Me structure but with the Co$^{III}$−OCH(Me)CO$_2$Me structure, taking into account the chemical shift (−3.33 ppm) of the methine proton of **3d**. As for the chemical shift of the methine proton of **3e** in comparison with that of **3d**, the stronger shielding effect due to the porphyrin ring current on the axial $\beta$-position than on the axial

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**Table 2. $^1$H NMR Data for ($\sigma$-alkyl)Co$^{III}$ Porphyrins (3a−f and 4a,c,f)[a]**

| complex | axial alkyl ligand[b] | | | | | |
|---|---|---|---|---|---|---|
| | $\alpha$ | $\beta$ ($\beta'$) | $\gamma$ ($\gamma'$) | $\delta$ | $\epsilon$ | $\zeta$ |
| TPPCo$^{III}$−CH$_2$COPh (**3a**) | −3.13 (s, 2H) | | | 4.59 (d, 2H) | 6.62 (t, 2H) | 7.10 (t, 1H) |
| TPPCo$^{III}$−CH$_2$CO$_2$Et (**3b**) | −3.80 (s, 2H) | | | 1.96 (q, 2H) | 0.21 (t, 3H) | |
| TPPCo$^{III}$−CH$_2$COCH=CH$_2$ (**3c**) | −3.52 (s, 2H) | | 2.25 (dd, 1H) | 3.02 (d, 1H)[c]<br>3.98 (d, 1H)[d] | | |
| TPPCo$^{III}$−CH(Me)CO$_2$Me (**3d**) | −3.33 (q, 1H) | −5.37 (d, 3H) | | 1.73 (s, 3H) | | |
| TPPCo$^{III}$−OCH(Me)CO$_2$Me (**3e**) | | −3.40 (q, 1H) | −0.83 (d, 3H) | | 2.62 (s, 3H) | |
| TPPCo$^{III}$−CH$_2$CH=CHCHO (**3f**) | −2.99 (d, 2H)[e] | 1.10 (dt, 1H)[f] | 3.06 (br, 1H) | 7.37 (br, 1H) | | |
| OEPCo$^{III}$−CH$_2$COPH (**4a**) | −3.72 (s, 2H) | | | 4.33 (d, 2H) | 6.50 (t, 2H) | 6.95 (t, 1H) |
| OEPCo$^{III}$−CH$_2$COCH=CH$_2$ (**4c**) | −4.12 (s, 2H) | | ~2[g] (m, 1H) | 2.65 (dd, 1H)[c]<br>3.70 (dd, 1H)[d] | | |
| OEPCo$^{III}$−CH$_2$CH=CHCHO (**4f**) | −3.65 (d, 2H)[h] | 0.45 (dt, 1H)[i] | 2.57 (dd, 1H) | 7.28 (d, 1H)[j] | | |

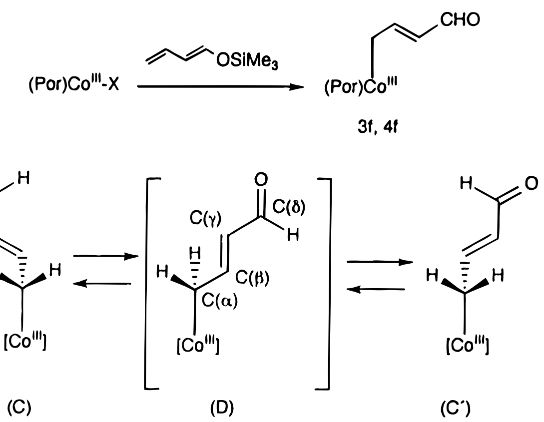
[a] Conditions: 250 MHz, $\delta$ value relative to tetramethylsilane, measured in CDCl$_3$ in 25 °C. [b] $\alpha$, $\beta$, $\gamma$, $\delta$, $\epsilon$, and $\zeta$ are carbon positions relative to the cobalt center. [c] $J_{trans}$ = 17.5 Hz. [d] $J_{cis}$ = 10.5 Hz. [e] $J_{vic}$ = 9.5 Hz. [f] $J_{trans}$ = 15.0 Hz. [g] The chemical shift could not be exactly determined because of the overlapping with signals due to the porphyrin peripheral methyl protons. [h] $J_{vic}$ = 9.3 Hz. [i] $J_{trans}$ = 14.8 Hz.

α-position can cancel out the deshielding effect of the oxygen atom inserted into the Co$^{III}$−C bond. Formation of a similar product has been observed in the reaction of OEPCo$^{II}$ (OEP = octaethylporphyrin dianion) with propionaldehyde in the presence of NaBH$_4$ and O$_2$, which generated a mixture of ($\sigma$-1-formylethyl)cobalt(III) and ($\sigma$-1-formylethoxy)cobalt(III) porphyrins.[5a] The complex **3d** was obtained in a much better yield (86%) in dichloromethane than in methanol (Table 1; runs 8 and 9). Moreover, the byproduct **3e** was not observed in the $^1$H NMR spectrum. The conversion of **3d** to **3e** was promoted when **3d** was allowed to stand in CDCl$_3$ under aerobic conditions. Even if dioxygen was present, the formation of **3e** was greatly suppressed in the dark. Therefore, the oxygenation of **3d** to **3e** takes place by way of the ($\sigma$-1-carbomethoxyethyl)peroxo)cobalt(III) intermediate (B), which is generated through the light-driven O$_2$ insertion into the Co$^{III}$−C bond of **3d**. The generation of **3e** in methanol (Table 1; run 8) would be attributed to the long reaction time. Although the preparation of **3d** was done under aerobic conditions and in room light, a short reaction time (2 min) in dichloromethane precluded the oxygenation of **3d** to **3e**. Although **1a** reacted with 1-((trimethylsilyl)oxy)cyclopentene and 1-((trimethylsilyl)oxy)-1,3-cyclohexadiene, the isolated product was TPPCo$^{II}$. This suggests that the initially formed organocobalt(III) porphyrins would have smaller a Co$^{III}$−C bond dissociation energy due to the steric constraint around the Co$^{III}$−C $\sigma$-bond and thus decomposed rapidly to TPPCo$^{II}$ and an alkyl radical. Reaction of **1a** with allyltrimethylsilane also afforded TPPCo$^{II}$.

The reaction is much faster in dichloromethane than in methanol to give better yields of ($\sigma$-2-oxoalkyl)cobalt(III) porphyrins (Table 1; runs (1, 2), (5, 6), (8, 9), (10, 11), (13, 14)). This is probably because methanol competes with alkenes for the axial coordination site of Co(III). A TPP ligand is superior to an OEP ligand in this reaction, probably because the electron-withdrawing effect of the former makes the cobalt center more reactive toward nucleophilic reagents. Thus, OEPCo$^{III}$−Cl (**2a**) did not react with 1-phenyl-1-((trimethylsilyl)oxy)ethylene in methanol, in contrast to the case of **1a** (Table 1, runs 1 and 13). When dichloromethane was used as a solvent in this reaction, however, OEPCo$^{III}$−CH$_2$COPh (**4a**) was obtained in 71% yield.

The axial anionic ligand of cobalt(III) porphyrins plays a key role in this reaction. The yield of **4a** decreased in the order F ≥ Cl ≫ Br ≈ I ≈ ClO$_4$ (Table 1; runs 14−18). This trend suggests that the reaction is driven by the bonding energy of a Si−X bond (X = F > Cl > Br > I > ClO$_4$) of Me$_3$Si−X generated in the reaction.

**Scheme 4**



The above observations point to the dual role of an organosilicon compound, that is, the nucleophilic attack on the cobalt as an electron-rich olefin and the abstraction of the axial halide ion as a Lewis acid. Scheme 2 illustrates such a push−pull intermediate (A).

Interestingly, the reaction of **1a** with 1-((trimethylsilyl)oxy)-1,3-butadiene gave a good yield of TPPCo$^{III}$−CH$_2$CH=CHCHO **(3f)** with no indication of the formation of TPPCo$^{III}$−CH(CH=CH$_2$)CHO (Scheme 4). The ($\sigma$-allyl)cobalt(III) complex **3f** could not be purified by chromatography because of its labile nature, and thus small signals derived from some impurities are seen in the $^1$H NMR spectrum (see Figure 1). The $^1$H NMR signals due to the axial organo group of **3f** were assigned according to the H−H COSY experiment as summarized in Table 2. The spin−spin coupling constant ($J$ = 15 Hz) between two olefinic protons is consistent with the trans-olefinic structure of the axial organo group. The complex **3f** showed temperature-dependent $^1$H NMR spectra, as shown in Figure 1. While signals due to the porphyrin peripheral protons (7−9 ppm) are extremely broad and are unresolved at room temperature, they sharpen with lowering temperature to give an ordinary spectral pattern of ($\sigma$-alkyl)cobalt(III) porphyrins at −60 °C. This temperature-dependency is not attributed to paramagnetism, because the chemical shifts for the protons in the axial organo group are characteristic of the diamagnetic Co(III) complexes and do not change throughout the temperature range examined (+40 to −60 °C). It has been known that allylcobaloximes show

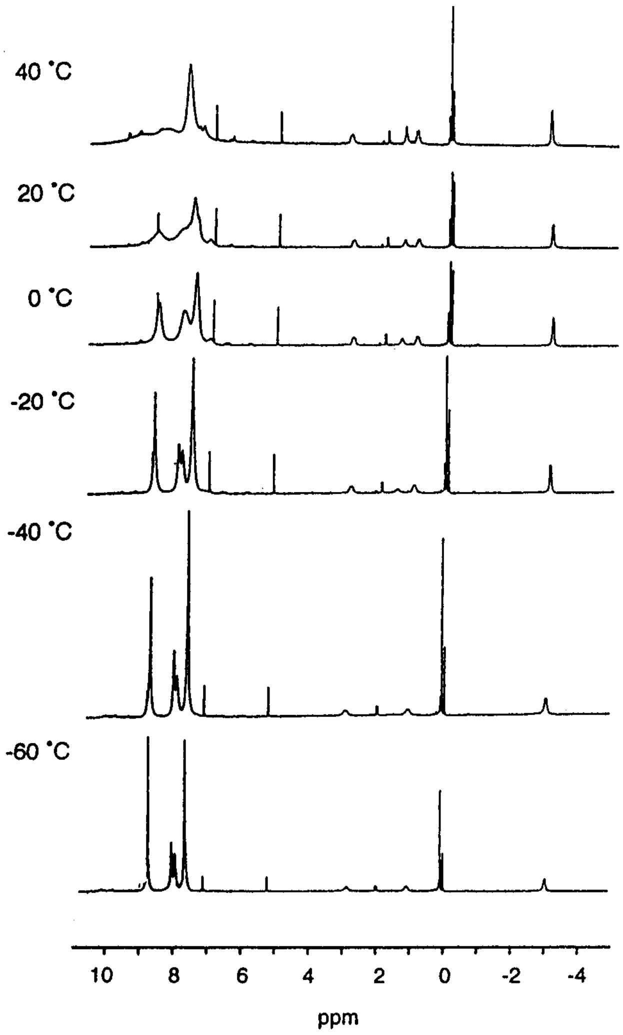
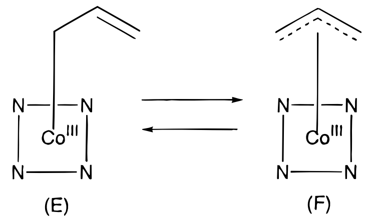


**Figure 1.** Variable-temperature $^1$H NMR (250 MHz) spectra of TPPCo$^{III}$−CH$_2$CH=CHCHO (**3f**) in CDCl$_3$ at 40, 20, 0, −20, −40, and −60 °C. Signals due to some impurities: $\delta$ 9.5, 6.9, 6.1, 2.0 (CH$_3$CH=CHCHO), 7.23 (CHCl$_3$) 5.24 (CH$_2$Cl$_2$), 1.51 (H$_2$O) 0.15, 0.10 (Me$_3$Si).

**Scheme 5**



temperature-dependent NMR spectra in solution.[8] Significant changes in the $^1$H NMR signals due to the axial allyl group have been observed to provide evidence in support for the occurrence of $\sigma$−$\pi$ rearrangement between a ($\sigma$-allyl)cobaloxime (E) and a ($\pi$-allyl)cobaloxime (F) (Scheme 5).[9] In contrast, the signals due to the axial alkyl ligand of **3f** are almost unchanged over the temperature range, except that the formyl proton at $\delta$ 7.37 (25 °C) shifts to higher fields and gets broader as the temperature goes down. The observed $^1$H chemical shifts due to the axial organo group of **3f** are consistent with those expected on the basis of the ring current term in a $\sigma$-allyl structure, but not with those in a $\pi$-allyl structure. Thus, interconversion between a $\sigma$-allyl and a $\pi$-allyl structure is unlikely to occur with temperature change in the present case.

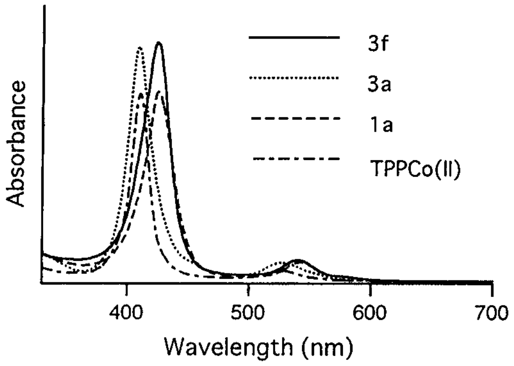


**Figure 2.** UV−vis spectra of **3f**, **3a**, **1a**, and TPPCo$^{II}$ in CH$_2$Cl$_2$.

The $\nu$(C=O) frequency at 1672 cm$^{-1}$ observed for **3f** is lower than that of crotonaldehyde (1700 cm$^{-1}$).[10] The UV−vis spectra of **3f** and **4f** are similar to those of halogenocobalt(III) porphyrins **1a** and **2a** (see Figure 2), whereas the UV−vis spectra of **3a**−**d**, and **4a,c** are identical with those of the corresponding Co(II) porphyrins as is the case with ordinary ($\sigma$-alkyl)cobalt(III) porphyrins. This indicates that the ligand field supplied by the axial organo group is weaker in **3f** and **4f** than in ordinary ($\sigma$-alkyl)cobalt(III) porphyrins. These spectroscopic properties are suggestive of the charge transfer from the Co−C(α) $\sigma$-bond to the carbonyl group through the $\sigma$−$\pi$ conjugation in the axial organo group of **3f** and **4f**. In order for this $\sigma$−$\pi$ conjugation to work well, the parallel conformation (C) is preferred to the perpendicular conformation (D) as depicted in Scheme 4, because overlap of the $\sigma$-orbital of the Co−C(α) bond and the $\pi$-orbitals of the enone moiety is maximal in the former conformation. The dihedral angle, $\angle$Co−C(α)−C($\beta$)−C($\gamma$) is ca. 90 and 270° with the enone moiety being kept planar in the parallel conformations C and C′, and 180° in the perpendicular conformation D in Scheme 4.[11]

The unusual dynamic behavior observed in the $^1$H NMR is explainable in terms of a hypothetical equilibrium process between C and C′. At low temperatures, the axial organo group is confined to either of the two parallel conformations, C and C′, while the porphyrin ring is rotating around the Co−C(α) bond quickly on the NMR time scale. In fact, eight $\beta$-pyrrole protons of the porphyrin ring are identical at −60 °C (see Figure 1). As the temperature rises, the enone moiety begins to rotate around the C(α)−C($\beta$) bond, changing its position between two parallel conformations, C and C′. When the equilibrium process between C and C′ is occurring as fast as the rotation of the porphyrin ring, the enone moiety appears to move slowly with respect to the position of the porphyrin protons. In this case,

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(11) According to the semiempirical MO calculation (see Experimental Section), an energy minimum was observed at the conformation where the dihedral angle $\angle$Co−C(α)−C($\beta$)−C($\gamma$) is 96.8°. This parallel conformation E is more stable by 5 kcal/mol than the perpendicular conformation F.

the magnetic environment of the protons at the porphyrin periphery fluctuates, owing to the conformational change between C and C′. This fluctuation would not be averaged out when the equilibrium process between C and C′ is occurring as fast as the rotation of the porphyrin ring, because the enone moiety appears to move slowly with respect to the position of the protons at the porphyrin periphery. This explains the broadening of the proton signals due to the porphyrin periphery with increasing temperature. On the other hand, the magnetic environment of the axial organo group does not change so much before and after the conformational change of the enone group, because of the symmetrical disklike shape of the porphyrin ring. Thus, the conformational change between C and C′ makes no difference in the magnetic environment of the axial ligand protons, even if the porphyrin ring appears to rotate slowly with respect to the rate of the conformational change. This is also because of the symmetrical disklike shape of the porphyrin ring. Therefore, the $^1$H signals due to the axial organo group are thought to be almost independent of the temperature.

In conclusion ($\sigma$-alkyl)cobalt(III) porphyrins with a carbonyl group at the $\beta$-position of the alkyl ligand have been prepared conveniently through the reaction of halogenocobalt(III) porphyrins with organosilicon reagents. On the basis of the effects, on the reactivity, of solvents, axial halogeno ligands, and substituents of the porphyrin periphery, a push−pull mechanism as shown in Scheme 2 is favored. This reaction may alternatively be explained in terms of the coupling reaction of Co(II) and an alkyl radical induced by the single electron transfer from an organosilicon compound to cobalt(III) porphyrin. The redox potentials of cobalt(III) porphyrins (∼0.7 V vs. SCE for TPPCo in dichloromethane)[2b] and these organosilicon compounds (∼1.3 V vs. SCE in acetonitrile),[12] however, would be inconsistent with this mechanism.

## Experimental Section

$^1$H NMR spectra were measured on a Bruker AC-250 (250 MHz) spectrometer, and the chemical shifts are referenced to tetramethylsilane as an internal standard. UV−vis spectra were measured on a Shimazu UV-2400PC instrument. IR spectra were obtained as KBr disks on a Hitachi I-2000 spectrometer. Dichloromethane was dried by distilling from calcium hydride and stored over 4 Å molecular sieves. Methanol was simply distilled before use.

**General Method.** A mixture of TPPCo(III)−Cl (0.030 mmol), an organosilicon compound (0.20 mmol), and methanol (15 mL) was stirred in a 100 mL Erlenmeyer flask. Then, ($\sigma$-alkyl)cobalt(III) porphyrin began precipitating within 10 min. After the solution was stirred for 50 min, the solid was collected by filtration and washed with methanol. When dichloromethane (7 mL) was used as a solvent for this reaction, the reaction mixture was evaporated with a rotary evaporator, and the residue was washed with methanol. Except for **3d**−**f** and **4f**, the product was purified by column chromatography on silica gel with dichloromethane as an eluent and recrystallized from dichloromethane−methanol.

**3a**: $^1$H NMR (CDCl$_3$) $\delta$ 8.80 (s, 8H, $\beta$-PyH), 8.07 (br, 8H, *o*-PhH), 7.68−7.78 (m, 12H, *m*- and *p*-PhH), see Table 2 for the axial alkyl protons; UV−vis (CH$_2$Cl$_2$) 525.5, 410.0 nm; IR (KBr) 1634 cm$^{-1}$ [$\nu$(C=O)]. Anal. Calcd for $C_{52}H_{35}N_4OCo$: C, 78.98; H, 4.46; N, 7.08. Found: C, 78.93; H, 4.47; N, 7.10.

**3b**: $^1$H NMR (CDCl$_3$) $\delta$ 8.88 (s, 8H, $\beta$-PyH), 8.13 (br, 8H, *o*-PhH), 7.69−7.78 (m, 12H, *m*- and *p*-PhH), see Table 2 for the axial alkyl protons; UV−vis (CH$_2$Cl$_2$) 527.0, 408.0 nm; IR (KBr) 1696 cm$^{-1}$ [$\nu$(C=O)]. Anal. Calcd for $C_{48}H_{35}N_4O_2Co$: C, 75.98; H, 4.65; N, 7.39. Found: C, 75.79; H, 4.50; N, 7.50.

**3c**: $^1$H NMR (CDCl$_3$) $\delta$ 8.86 (s, 8H, $\beta$-PyH), 8.14 (br, 8H, *o*-PhH), 7.74 (m, 12H, *m*- and *p*-PhH), see Table 2 for the axial alkyl protons; UV−vis (CH$_2$Cl$_2$) 526.0, 409.0; IR (KBr) 1656 cm$^{-1}$ [$\nu$(C=O)]. Anal. Calcd for $C_{48}H_{33}N_4OCo{\cdot}H_2O$: C, 75.98; H, 4.65; N, 7.39. Found: C, 76.44; H, 4.61; N, 7.43.

**3d**: $^1$H NMR (degassed CDCl$_3$) $\delta$ 9.02 (s, 8H, $\beta$-PyH), 8.87 (m, 8H, *o*-PhH), 7.73 (m, 12H, *m*- and *p*-PhH), see Table 2 for the axial alkyl protons; UV−vis (CH$_2$Cl$_2$) 527.0, 409.0 nm; IR (KBr) 1704 cm$^{-1}$ [$\nu$(C=O)]. Anal. Calcd for $C_{48}H_{35}N_4O_2Co$: C, 75.98; H, 4.65; N, 7.39. Found: C, 76.15; H, 4.63; N, 7.40.

**3f**: $^1$H NMR (CDCl$_3$) $\delta$ 9.4−8.7 (br, 8H, $\beta$-PyH), 8.7−7.6 (br, 20H, PhH), see Table 2 for the axial alkyl protons; UV−vis (CH$_2$Cl$_2$) 538.5, 423.0 nm; IR (KBr) 1672 cm$^{-1}$ [$\nu$(C=O)]. Anal. Calcd for $C_{48}H_{33}N_4OCo{\cdot}H_2O$: C, 75.98; H, 4.65; N, 7.39. Found: C, 76.46; H, 4.63; N, 7.49.

**4a**: $^1$H NMR (CDCl$_3$) $\delta$ 10.08 (s, 4H, meso H), 3.98 (m, 16H, Et), 1.87 (t, 24H, Et), see Table 2 for the axial alkyl protons; UV−vis (CH$_2$Cl$_2$) 551.0, 516.0, 393.5 nm; IR (KBr) 1638 cm$^{-1}$ [$\nu$(C=O)]. Anal. Calcd for $C_{44}H_{51}N_4OCo$: C, 74.35; H, 7.23; N, 7.88. Found: C, 74.82; H, 7.32; N, 7.81.

**4c**: $^1$H NMR (CDCl$_3$) $\delta$ 10.20 (s, 4H, meso H), 4.03 (m, 16H, Et), 1.88 (t, 24H, Et), see Table 2 for the axial alkyl protons; UV−vis (CH$_2$Cl$_2$) 550.0, 517.0, 392.5. IR (KBr), cm$^{-1}$: 1658 [$\nu$(C=O)]. Anal. Calcd for $C_{40}H_{49}N_4OCo$: C, 72.71; H, 7.47; N, 8.48. Found: C, 73.25; H, 7.70; N, 8.56.

**4f**: $^1$H NMR (CDCl$_3$) $\delta$ 10.5−9.5 (br, 4H, meso H), 5.0−3.0 (br, 16H, Et), 2.5−1.5 (br, 24H, Et), see Table 2 for the axial alkyl protons; UV−vis (CH$_2$Cl$_2$) 555.5, 523.5, 405.5 nm; IR (KBr) 1706 cm$^{-1}$ [$\nu$(C=O)]. Anal. Calcd for $C_{40}H_{49}N_4OCo{\cdot}H_2O$: C, 70.77; H, 7.57; N, 8.26. Found: C, 71.54; H, 7.25; N, 8.34.

**Semiempirical MO Calculation.** Theoretical calculations were performed with the SPARTAN package version 4.0 (Wavefunction, Inc., Irvine, CA). A preliminary structure refinement using molecular mechanics based on the SYBYL force field was applied to a model in which peripheral substituents of the complex **3f** were replaced by hydrogens. Geometry optimization by the MNDO/d MO calculation using a PM3 (tm) MO method[13] generated the conformation C as an energy minimum structure (heat of formation −1518 kcal/mol). After the dihedral angle $\angle$Co−C($\alpha$)−C($\beta$)−C($\gamma$) of the conformation C was constrained to 180°, optimization was similarly carried out to afford the conformation D (heat of formation −1513 kcal/mol.

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