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Synthesis of Novel Cobalt(III) Porphyrin−Phosphoryl Complexes

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Novel porphyrinato[phosphoryl] cobalt(III) complexes were synthesized unexpectedly through the reaction of $BrCo^{III}(por)$ (por = porphyrinato dianion) with Me_3SiLi ($MeLi-Me_6Si_2-HMPA$) and MeLi in HMPA at −78 °C. Phosphoryl complexes were also synthesized from HMPA-K and the appropriate organophosphoryl chloride-K. As a result, Me_3SiLi may not always be an appropriate silylating agent for bulky organometallic electrophiles.

Introduction

Transition metal phosphoryl complexes are an important class of compounds due to their relevance to catalytic hydrophosphorylation,[1] catalytic C−P activation,[2] potential chiral Lewis acid catalysts,[3] and enzymatic hydrolysis of phosphodiesters.[4] In the course of attempted syntheses of cobalt porphyrin silyls[5] for the goal of measuring the bond dissociation energy using the kinetic method developed for the coenzyme B-12 and related models,[6] we have discovered an unexpected synthesis of novel cobalt(III) porphyrin−phosphoryl complexes.

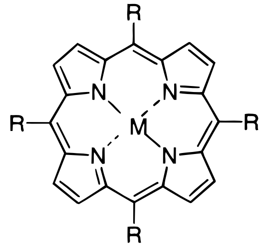
Results and Discussion

The reaction of strongly nucleophilic $[Co^{I}(ttp)]^-$ with Me_3SiCl for the synthesis of a Co−Si complex in a manner similar to the synthesis of cobalt porphyrin−alkyls[7] did not prove to be successful (Chart 1, Table 1). The starting materials, cobalt(II) porphyrins Co^{II}(tpp) (**4**), Co^{II}(ttp) (**5**), and Co^{II}(ttmp) (**6**), were conveniently prepared through the metalation of the corresponding free base porphyrins **1**−**3** with $Co(OAc)_2$ in DMF (eq 1). When a solution of red Co^{II}(ttp) (**5**) in THF or in toluene was reduced with Na/Hg at room temperature under N_2 for 1 day, the brown solution of Co^{I}(ttp)[7] generated was then trapped with Me_3SiCl (eq 2). However, only Co^{II}(ttp) was isolated.

Table 1. Abbreviation for Porphyrin Compounds

	R		
M	Ph	*p*-$CH_3C_6H_4$	3,4,5-$(MeO)_3C_6H_2$
H_2	H_2(tpp), **1**	H_2(ttp), **2**	H_2(ttmp), **3**
Co	Co(tpp), **4**	Co(ttp)**, 5**	Co(ttmp), **6**
CoBr	BrCo(tpp), **7**	BrCo(ttp), **8**	BrCo(ttmp), **9**
CoR, R′ = [P=O(NMe$_2$)$_2$]	RCo(tpp), **10**	RCo(tpp), **11**	RCo(ttmp), **12**

Chart 1



H_2(tpp) **1**, M = H_2, R = Ph
H_2(ttp) **2,** M = H_2, R = *p*-MeC_6H_4
H_2(ttmp) **3**, M = H_2, R = 3, 4, 5-$(MeO)_3C_6H_2$
H_2(por) = a porphyrin

$$H_2(por) \xrightarrow[\text{DMF, reflux, 1h}]{Co(OAc)_2} Co^{II}(por) \quad (1)$$

por =		
tpp	**4**	96 %
ttp	**5**	95 %
ttmp	**6**	98 %

$$Co^{II}(ttp) \cancel{\xrightarrow[\text{2. } Me_3SiCl\text{, } N_2\text{, rt}]{\text{1. Na/ Hg Toluene 2 d}}} Me_3SiCo^{III}(ttp) \quad (2)$$

Synthesis of cobalt porphyrin−silyls was then attempted via the reaction of electrophilic cobalt(III) porphyrin bromides with Me_3SiLi, but the cobalt phosphoryl complexes were unexpectedly formed. The co-

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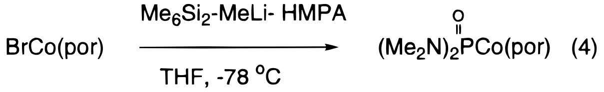
Table 2. Preparation of $Co^{III}(por)[P{=}O(NMe_2)_2]$ 10−12 from Me_6Si_2/MeLi (Eq 4)

por	$Co^{III}(por)$-$[P{=}O(NMe_2)_2]$	$Co^{II}(por)$
tpp	**10**, 62%	**4**, 28%
ttp	**11**, 73%	**5**, 25%
ttmp	**12**, 91% **6** 7%	

balt(III) porphyrin bromides were prepared from the aerobic oxidation of $Co^{II}(por)$ with aqueous HBr (48%) in a solvent mixture of $CHCl_3$/MeOH (1:1 v/v) at room temperature for 2 h in 84−92% yield, respectively (eq 3).[8] An orange solution of Me_3SiLi was generated by the cleavage of $Me_3SiSiMe_3$ with ethereal MeLi in hexamethylphosphoramide (HMPA) at 0 °C under N_2.[9] Following the Goff[10] procedure, BrCo(por) compounds **7**−**9** were reacted with Me_3SiLi in toluene at −78 °C, and the solution was warmed slowly to 0 °C (eq 4, Table 2). The reaction mixture produced two fractions, according to the TLC analysis: one was identified as a $Co^{II}(por)$ and the other was new compounds. After chromatographic separation, the new compounds were isolated.

$$Co^{II}(por)\ \xrightarrow[\text{CHCl}_3\text{/ MeOH, rt, 2 h}]{\text{HBr}}\ BrCo^{III}(por) \qquad (3)$$

por =		
BrCo(tpp)	**7**	92 %
BrCo(ttp)	**8**	86 %
BrCo(ttmp)	**9**	92 %



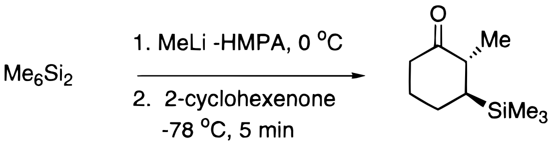
$$BrCo(por)\ \xrightarrow[\text{THF, -78 }^{o}\text{C}]{\text{Me}_6\text{Si}_2\text{-MeLi- HMPA}}\ (Me_2N)_2\overset{O}{\overset{\|}{P}}Co(por) \qquad (4)$$

From the reaction of BrCo(tpp), the product exhibited sharp proton resonances supporting the formation of a diamagnetic Co(III) compound. Two resonances at δ −0.30 and −0.27 ppm appeared with each equal to three hydrogens, suggesting two nonequivalent methyl groups. This was further confirmed by a signal at δ 35.00 ppm in the ^{13}C NMR spectrum. All other Co(por) derivatives also show similar spectral characteristics. Therefore, it seems unlikely the Me_3Si group had been introduced as it would have been a simple singlet.

The structure of **10** was finally elucidated from a single-crystal X-ray diffraction analysis and was shown to be (5,10,15,20-tetraphenylporphyrinato[bis(dimethylamino)phosphoryl]cobalt(III) with the Co atom bounded to a phosphoryl ligand instead of the desired silyl ligand.[3,11] The Co−P bond length is 2.265 Å which lies in the range of reported Co−P bond lengths[12] and is longer by 0.021−0.102 Å compared with those compounds containing a Co−P σ bond, such as the cobalt−phosphinediyl complex[13a] (Co−P bond length = 2.163−2.210 Å) and the cobalt−phosphido complex[13b] (Co−P bond length = 2.244 Å). This lengthening may due to the bonding of the phosphoryl ligand of **9** to a more sterically bulky porphyrin ligand. Both the IR and ^{31}P NMR data are consistent with the proposed structure. The IR spectrum showed a sharp P=O stretching at 1353 cm^{-1} (compared with $\upsilon_{P=O} = 1296\ cm^{-1}$ in HMPA).[14] In the ^{31}P NMR spectrum, a broad singlet appeared at 6.95 ppm, confirming the presence of the phosphorus atom.

Complexes of the cobalt macrocyclic phosphine containing a phosphine-donating Co−P dative bond have been recognized for many years.[15,16] Metalloporphyrin complexes such as (triphenylphosphine)(tetrakis(*p*-chlorophenyl)porphyrinato)cobalt(II) were prepared by addition of PPh_3 to the corresponding cobalt porphyrin in PhCN.[15a,b] Other examples of cobalt−phosphine complexes are (triphenylphosphine)(10-phenyl-2,3,7,8,12,-13,17,18-octamethylcorrolato)cobalt(III)[16] and (triphenylphosphine)-(5,10,15-triphenyl-2,3,7,8,12,13,17,18- octamethylcorrolato)cobalt(III) (Co−P = 2.205 Å).[17] The Co−P bond length resembles that in other cobalt−phosphine compounds.[12a] Ligands of type R−P=O are present in complexes only and attempts at isolating them in the free state result in oligomers.[18] An unusual characteristic of the novel complex **10** is the bonding of a P^V phosphoryl ligand to the cobalt(III) porphyrin which is the only metalloporphyrin containing a covalent cobalt−phosphorus σ bond though other nonporphyrin complexes have been characterized.[3] The yields of the corresponding cobalt(III) porphyrin−phosphoryls **10**−**12** are summarized in Table 2.

This unexpected synthesis of the cobalt(III) porphyrin−phosphoryl raised the question whether the Me_3SiLi had been indeed generated. Me_3SiLi is a versatile silylating agent and can be generated conveniently. To confirm this, $Me_3SiSiMe_3$ was reacted with the ethereal MeLi in HMPA at 0 °C.[9] The precedented reaction of Me_3SiLi with 2-cyclohexen-1-one, followed by trapping with MeI, was repeated to yield the *trans*-3-trimethylsilyl-2-methylcyclohexanone **13**, in 96% (eq 5), which was confirmed by its ^1H NMR and mass spectra after isolation.[9] This firmly supported that Me_3SiLi had indeed been successfully generated.



13 96 % (5)

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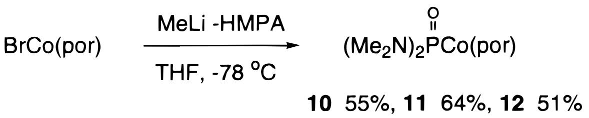
The possibility of the reaction of HMPA with Me_3SiLi was thus suspected. It has been recognized that HMPA is an outstanding solvent for a wide variety of transformations including nucleophilic substitution, β-elimination, Birch-type reduction, and certain oxidations. It has been generally accepted that HMPA is stable to most basic reagenta, and even strongly basic reagents like alkali amides[19] and Grignard[20] reagents have been routinely employed as the metalating agents in HMPA. However, HMPA is not stable toward the organolithium or organopotassium and can be cleaved by *n*-BuLi[21] or metallic K[22] to yield the bis(dimethylamino)phosphoryl anion.

When we followed the procedure of Kaiser,[21] the phosphoryl anion $(Me_2N)_2(O)PLi$ was generated by the reaction of MeLi with HMPA in THF at 0 °C under N_2. BrCo(ttp) (**8**) in THF was then added to the $(Me_2N)_2$-$(O)PLi$ solution at −78 °C (eq 6), and the mixture was warmed to 0 °C in 1 h. After chromatographic purification, the cobalt(III) porphyrin−phosphoryl complex **11** was isolated and was confirmed to be identical in its ^1H NMR spectrum to the complex obtained from the reaction of **6** with Me_3SiLi−HMPA.

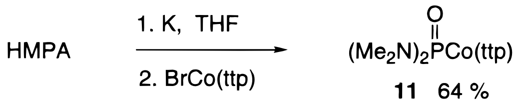


$$\text{BrCo(por)} \xrightarrow[\text{THF, -78 °C}]{\text{MeLi -HMPA}} (Me_2N)_2\overset{O}{\overset{\|}{P}}Co(por) \qquad (6)$$

10 55%, **11** 64%, **12** 51%

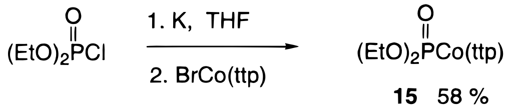
The reason for successful reaction of Me_3SiLi with organic electrophiles such as cyclohexenone but not with organometallic electrophiles such as cobalt porphyrin bromides presumably has both steric and electronic origins. Cyclohexenone is sterically less hindered and harder to reduce than cobalt porphyrin bromides in which the cobalt atom has easily accessible oxidation states of Co^I, Co^{II}, and Co^{III}.

HMPA was also cleaved by metallic K in THF to give a yellow solution of $(Me_2N)_2(O)PK$, which reacted with BrCo(ttp) **6** at −78 °C (eq 7) giving **10** in 64% yield (eq 6). Generation of phosphoryl anions was also successful via the reaction of $(EtO)_2(O)PCl$ (**14**) with potassium metal. Reaction of the resulting $(EtO)_2(O)P^-$ anions with BrCo(ttp) (**8**) at −78 °C yielded complex **15** in 58% yield (eq 8). According to the above evidence, HMPA is cleaved by RLi (Me_3SiLi or MeLi) to give $(Me_2N)_2(O)PLi$. The mechanism of this reaction is an 1,2-elimination of the α-amino proton of HMPA by RLi to give gaesous methane and *N*-methylimine and the phosphoryl anion (eq 9).[21]



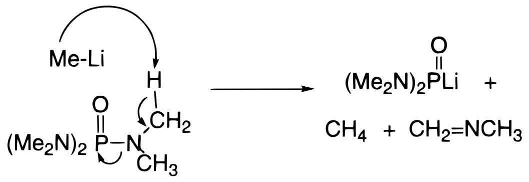
$$\text{HMPA} \xrightarrow[\text{2. BrCo(ttp)}]{\text{1. K, THF}} (Me_2N)_2\overset{O}{\overset{\|}{P}}Co(ttp) \qquad (7)$$

11 64 %



$$(EtO)_2\overset{O}{\overset{\|}{P}}Cl \xrightarrow[\text{2. BrCo(ttp)}]{\text{1. K, THF}} (EtO)_2\overset{O}{\overset{\|}{P}}Co(ttp) \qquad (8)$$

15 58 %



(9)

It is instructive to gain some insight into these novel cobalt(III) porphyrin−phosphoryls **10**−**12**. According to the ^1H NMR spectra the two distinctive signals at around zero ppm correspond to the bis(dimethylamino) protons with spin-splitting by a phopshorus atom ($J \sim$ 8 Hz).[23] Magnetical nonequivalence due to hindered rotation about the P−N bond is unlikely because the chemical shifts of the two signals of **11** in benzene-d_6 remained the same from 298 to 333K. Compared with the proton resonance of the HMPA (2.38 ppm), it is high-field shifted by about 2.5 ppm, mainly due to the porphyrin ring current effect. The carbon chemical shifts of the bis(dimethylamino) group show a singlet which indicates these carbons are magnetically equivalent. The chemical shifts of the bis(dimethylamino) carbons in **10**, **11**, and **12** are nearly the same, ranging from δ 35.00 to 35.09 ppm and shifted slightly upfield by 1.60 ppm compared with that of HMPA (δ 36.60 ppm).

The IR stretching frequency of P═O bond in **10**−**12** and **15** appears at 1352−1360 cm^{-1} ($\upsilon_{P=O} = 1296$ cm^{-1} in HMPA).[14] It is possible that the bond order of the P−O bond in cobalt(III) porphyrin−phosphoryls is higher than that in HMPA since the phosphorus atom bonds to a more electron-deficient cobalt(III) resulting in less resonance stabilization than that of HMPA.

In conclusion, we have discovered a convenient method of synthesizing cobalt porphyrin−phosphoryl complexes from the reactions of alkyl lithium−HMPA with cobalt porphyrin bromides. The observation indicated that the use of Me_3SiLi−HMPA as a silylating agent for a bulky organometallic electrophile may not always be appropriate.

Experimental Section

UV−vis spectra were recorded on a Hitachi U-3300 spectrophotometer using CH_2Cl_2 as the solvent. IR spectra were recorded on a Perkin Elmer 1600 FT-IR spectrometer as a neat film on NaBr plates. ^1H NMR spectra were recorded on a Bruker WM 250 (250 MHz) or a Bruker AMX 500 (500 MHz) spectrometer. Chemical shifts (δ) are reported with reference to the residual $CHCl_3$ (δ 7.24 ppm) in $CDCl_3$, and the coupling constants (J) are reported in Hertz (Hz). ^{13}C NMR spectra were obtained on either a Bruker WM 250 (62.9 MHz) or Bruker AMX 500 (125 MHz) spectrometer and referenced to the residual $CHCl_3$ (δ 77.00 ppm) in $CDCl_3$. ^{31}P NMR spectra were recorded on a Bruker AMX 500 (202 MHz) spectrometer, and the chemical shift (δ) was referenced to the external standard H_3PO_4 (0 ppm). FABMS spectra were recorded on a Joel JMS-HX 110 mass spectrometer using *m*-nitrobenzyl alcohol (NBA) as the matrix at National Tsing-Hua University,

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Taiwan. Elemental Analyses were performed by Medac Ltd., Department of Chemistry, Brunel University, United Kingdom.

Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. Tetrahydrofuran (THF) and toluene were distilled from the sodium benzophenone ketyl and sodium, respectively, immediately prior to use. HMPA was distilled from CaH_2. Me_3SiCl was distilled from CaH_2, stored in a Telfon-stoppered round-bottomed flask, and degassed by the freeze−pump−thaw method (three cycles) immediately prior to use. Silica gel (70−230 mesh) was used for column chromatography. Thin-layer chromatography (TLC) was performed on Merck precoated silica 60F254 plates.

Cobalt(III) Tetraphenylporphyrin Bromide BrCo(tpp) (7).[8a] To a solution of the Co(tpp) (**4**, 0.30 g, 0.44 mmol) in $CHCl_3$/MeOH (200 mL, 1:1) was added aq HBr (48%, 2 mL). The mixture was stirred at room temperature for 2 h to give a red solution. $CHCl_3$ (50 mL) was added, and the mixture was washed with water (100 mL) and dried ($MgSO_4$). The mixture was evaporated to dryness to give a purple residue. The residue was recrystallized from $CHCl_3$ and petroleum ether (bp 40−60 °C) to yield a purple solid (0.31 g, 92%). $R_f = 0.30$ (5% MeOH in $CHCl_3$ v/v).

Cobalt(III) Tetratolylporphyrin Bromide BrCo(ttp) (8).[8b,c] Co(ttp) (**5**, 0.30 g, 0.41 mmol) and aqueous HBr (48%, 2 mL) were stirred in $CHCl_3$/MeOH for 2 h to give a purple solid **6** (0.28 g, 0.35 mmol, 86%). $R_f = 0.25$ (5% MeOH in $CHCl_3$ v/v). ^1H NMR ($CDCl_3$, 250 MHz) δ 2.63 (s, 12 H), 7.50 (brs, 8 H), 8.04 (brs, 8 H), 8.74 (s, 8 H).

Cobalt(III) Tetrakis(3,4,5-trimethoxyphenyl)porphyrin Bromide BrCo(ttmp) (9).[8d] Co(ttmp) (**3**, 0.30 g, 0.29 mmol) and aqueous HBr (48%, 2 mL) were stirred in (1:1 v/v) $CHCl_3$/MeOH for 2 h to give **7** as a purple solid (0.29 g, 0.27 mmol, 92%). $R_f = 0.21$ (5% MeOH in $CHCl_3$). ^1H NMR ($CDCl_3$, 250 MHz) δ 3.94 (s, 24 H), 4.14 (s, 12 H), 7.42 (d, 8 H), 8.87 (s, 8 H).

5,10,15,20-Tetraphenylporphyrinato[bis(dimethylamino)phosphoryl]cobalt(III) $(Me_2N)_2P(O)Co(tpp)$ (10). To a solution of hexamethyldisilane (0.36 g, 2.5 mmol) in HMPA (2.0 mL) at 0 °C under N_2 was added an ethereal solution of MeLi (1.6 M, 1.43 mL, 1.5 mmol) was added via a syringe to give an orange solution, and the reaction was stirred for 15 min. Freshly distilled THF (10 mL) was then added, and the solution was cooled to −78 °C. A solution of BrCo(tpp) (**7** 0.10 g, 0.13 mmol) in freshly distilled THF (10 mL) was added dropwise via a cannula. The mixture was allowed to warm to 0 °C slowly for 1 h and was poured into pentane (50 mL). It was then washed with water (50 mL × 2) and dried ($MgSO_4$). After removal of the solvent, the red residue was chromatographed over silica gel using CH_2Cl_2 as the eluent to give the Co(tpp) **4** (28%) and 5% MeOH in CH_2Cl_2 (v/v) as eluent to elute the red product fraction. The solvent was removed to give a red solid. The solid was recrystallized by a mixture of CH_2Cl_2/hexane to give the pure red crystals of **10** (0.067 g, 62%). $R_f = 0.24$ (3:1 CH_2Cl_2/acetone. ^1H NMR ($CDCl_3$, 250 MHz) δ −0.28 (d, 12 H, $J = 7.9$ Hz), 8.10 (brs, 8 H), 8.85 (s, 8 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 35.02, 122.09, 126.84, 127.71, 127.93, 132.71, 132.25, 141.77, 146.26; ^{31}P NMR ($CDCl_3$, 202 MHz) δ 6.95 (line width = 1096 Hz); UV−vis (CH_2Cl_2), λ_{max}, nm (log ϵ) 408 (5.22), 530 (4.17); IR (thin film) 3054, 2923, 1352, 752 cm^{-1}; FABMS *m/z* 806 (M^+). Anal. Calcd for $C_{48}H_{40}CoN_6OP{\cdot}CH_2Cl_2$: C, 66.05; H, 4.76; N, 9.44; P, 3.84. Found: C, 66.48; H, 4.87; N, 9.23; P, 3.35.

5,10,15,20-Tetratolylporphyrinato[bis(dimethylamino)phosphoryl]cobalt(III) $(Me_2N)_2P(O)Co(ttp)$ (11). A solution of BrCo(ttp) (**8**, 0.10 g, 0.128 mmol) in THF (10 mL) was added to the Me_3SiLi [Me_6Si_2 (0.36 g, 2.5 mmol)−HMPA (2 mL)−MeLi (1.6 M, 1.43 mL, 1.5 mmol)] in THF (10 mL) at −78 °C under N_2, and the solution was then warmed slowly to 0 °C for 1 h. After workup and chromatographic separation, **11** was obtained as a red solid (0.081 g, 73%). $R_f = 0.08$ (3:1 CH_2Cl_2:acetone. ^1H NMR ($CDCl_3$, 250 MHz) δ −0.34 (d, 12 H, $J = 8.6$ Hz), 2.64 (s, 12 H), 7.48 (d, 8 H, $J = 7.8$ Hz), 7.95 (d, 8 H, $J = 7.8$ Hz), 8.82 (s, 8 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 21.48, 35.01, 122.09, 127.61, 132.65, 133.23, 137.31, 138.91, 146.38; gate decoupling ^{13}C NMR (C_6D_6, 125.8 MHz) δ 22.15 ($J_{C-H} = 126.4$ Hz), 36.06 (q, $J_{C-H} = 136.7$ Hz), 123.30 (d, $J_{C-H} = 156.6$ Hz), 133.65 (d, $J_{C-H} = 133.7$ Hz), 134.30 (d, $J_{C-H} = 173.9$ Hz), 138.07, 140.31, 145.68; ^{31}P NMR ($CDCl_3$, 202 MHz) 11.47; UV−vis (CH_2Cl_2), λ_{max}, nm (log ϵ) 410 (5.18), 531 (4.14); IR (thin film) 3022, 2921, 1352, 780 cm^{-1}; FABMS *m/z* 863 ($M^+ + 1$). Anal. Calcd for $C_{52}H_{48}CoN_6OP{\cdot}H_2O$: C, 70.90; H, 5.72; N, 9.54; P, 3.52. Found: C, 71.29; H, 5.69; N, 9.46; P, 3.98.

5,10,15,20-Tetrakis(3,4,5-trimethoxyphenyl)porphyrinato[bis(dimethylamino)phosphoryl]cobalt(III) $(Me_2N)_2P(O)Co(ttmp)$ (12). A solution of BrCo(ttmp) (**7**, 0.10 g, 0.09 mmol) in THF (10 mL) was added to the Me_3SiLi [HMDS (0.36 g, 2.5 mmol)/HMPA (2 mL)/MeLi (1.43 mL, 1.5 mmol)] at −78 °C in THF (10 mL) under N_2 and was warmed slowly to 0 °C to give **12** as a red solid (0.96 g, 91%). $R_f = 0.22$ (3:1 CH_2Cl_2/acetone. ^1H NMR ($CDCl_3$, 250 MHz) δ −0.27 (s, 12 H, $J = 8.9$ Hz), 3.92 (s, 24 H), 4.12 (s, 12 H), 7.31 (s, 8 H), 8.94 (s, 8 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 35.09, 56.55, 61.32, 111.98, 122.09, 132.99, 137.21, 138.20, 146.43, 151.97; ^{31}P NMR ($CDCl_3$, 202 MHz) 8.76; UV−vis (CH_2Cl_2), λ_{max}, nm (log ϵ) 413(5.15), 531 (4.07); IR (thin film) 2936, 2836, 1361, 762 cm^{-1}; FABMS *m/z* 1166 (M^+). Anal. Calcd for $C_{60}H_{66}CoN_6O_{13}P{\cdot}H_2O$: C, 60.09; H, 5.78; N, 7.08; P, 2.61. Found: C, 60.56;H, 5.48; N, 6.59; P, 2.52.

Preparation of *trans*-3-Trimethylsilyl-2-methylcyclohexanone (13).[9] A solution of Me_6Si_2 (0.50 mL, 2.50 mmol) in anhydrous HMPA (2 mL) was cooled to 0 °C under N_2. Ethereal MeLi (1.25 mL, 2 mmol) was added via syringe, and the resulting orange solution was stirred for 15 min. THF (10 mL) was added, and the solution was immediately cooled to −78 °C. A solution of cyclohexenone (0.144 g, 1.50 mmol) in THF (1 mL) was then added dropwise. After stirring an additional 15 min, MeI (0.50 mL) was injected and the mixture was poured into pentane (50 mL) and thoroughly washed with water (2 × 25 mL) to remove HMPA. The organic fraction was dried (MgSO4), and after removal of the solvent, a light yellow oil of **13** was isolated (0.265 g, 96%). ^1H NMR ($CDCl_3$, 250 MHz) δ 0.13 (s, 9H), 1.04 (d, 3 H, $J = 6.7$ Hz), 1.03−2.40 (m, 8 H); MS (70 eV) 184 (1), 183 (11), 155 (30), 75 (100), 74 (19), 73 (100), 67 (12).

Preparation of 11 from Reaction of HMPA and MeLi. To a solution of HMPA (0.41 g, 2.3 mmol) in THF (5 mL) at 0 °C was added MeLi in hexane (1.6 M, 1.44 mL, 2.3 mmol) via a syringe under N_2. The solution was stirred for 30 min to give a yellow solution and was cooled to −78 °C. A solution of BrCo(ttp) (**8**) in THF (10 mL) was added via cannula under N_2. It was then warmed up to 0 °C and poured into pentane (50 mL). The mixture was thoroughly washed with H_2O (50 mL × 2) and dried ($MgSO_4$). After removal of the solvent, the red residue was chromatographed over silica gel with CH_2Cl_2 as eluent to give the Co(ttp) (15%) and then with a solvent mixture of CH_2Cl_2/MeOH (95:5) as the eluent to obtain the red fraction. The solvent was removed to give **11** as a red solid (0.057 g, 52%). $R_f = 0.08$ (3:1 CH_2Cl_2/acetone. It was identical in spectral characteristics and R_f with that prepared from Me_6Si_2/MeLi/HMPA.

Preparation of 11 from the Reaction of 8 with $(Me_2N)_2(O)PK$.[22] To a suspension of K (0.25 g, 0.633 mmol) in THF (10 mL) at room temperature, $(Me_2N)_2(O)PCl$ (0.098 g, 0.575 mmol) was added via a syringe under N_2. The yellow mixture was stirred at room temperature for 24 h and was chilled to −78 °C. A solution of BrCo(ttp) **8** in THF (10 mL) was added via a cannula, and the mixture was warmed up to 0 °C slowly. The red mixture was then poured into pentane (50 mL), washed thoroughly with H_2O (50 mL × 2), and dried

($MgSO_4$). After removal of the solvent, the red residue was chromatographed over silica gel using CH_2Cl_2 as the eluent to give the Co(ttp) (20%) and then a solvent mixture of CH_2Cl_2/MeOH (95:5) as eluent to give **11** as a red solid (0.042 g, 38%). $R_f = 0.08$ (3:1 CH_2Cl_2:/acetone). It was identical in spectral characteristics and R_f with that prepared from Me_6Si_2/MeLi/HMPA.

5,10,15,20-Tetratolylporphyrinato(diethoxyphosphoryl)cobalt(III) $(EtO)_2(O)PCo(ttp)$ (15). To a suspension of K (0.099 g, 2.53 mmol) in THF (10 mL) at room temperature was added $(EtO)_2(O)PCl$ (0.397 g, 2.30 mmol) via syringe under N_2. The yellow mixture was stirred at room temperature for 24 h and was cooled to −78 °C. A solution of BrCoTTP (**6**) in THF (10 mL) was added via a cannula, and the mixture was warmed up to 0 °C slowly. After chromatographic purification, **15** was isolated as a red solid (0.062 g, 58%). $R_f = 0.62$ (5% MeOH in CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 250 MHz) δ −0.21 (t, 6 H, $J = 7.0$ Hz), 0.64 (q, 2 H, $J = 3.3$ Hz), 1.03 (q, 2 H, $J = 3.3$ Hz), 2.68 (s, 12 H), 7.53 (d, 8 H, $J = 7.5$ Hz), 7.99 (d, 8 H, $J = 7.5$ Hz), 8.94 (s, 8 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 14.85, 21.45, 58.52, 122.38, 127.61, 132.70, 133.33, 137.41, 138.76, 146.01; ^{31}P NMR ($CDCl_3$, 202 MHz) 6.13; UV−vis (CH_2Cl_2), λ_{max}, nm (log ϵ) 410 (4.51), 526 (3.33); IR (thin film) 3024 2922, 1353, 733 cm^{-1}; FABMS M$^+$ m/z 864. The sample for analysis was dried in high vacuum (0.15 Torr) at room temperature overnight. Anal. Calcd for $C_{52}H_{46}CoN_4O_3P \cdot H_2O$: C, 70.74; H, 5.48; N, 6.35; P, 3.51. Found: C, 71.56; H, 5.25; N, 6.36; P, 3.52.

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