Serendipitous synthesis of a novel cobalt(III) porphyrin phosphoryl complex

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A novel complex [bis(dimethylamino)phosphoryl](5,10,15,20-tetraphenylporphyrinato)cobalt(III) 1 is synthesized serendipitously by the reaction of [Co^{III}(tpp)Br] with Me_3SiLi ($MeLi–Si_2Me_6$–HMPA) at −78 °C in thf and its structure is characterized by a single-crystal X-ray study.

Transition-metal silyls are important intermediates in hydrosilylation reactions[1] and silane polymerization.[2] In order to gain a better understanding of their roles in these catalytic processes, we have initiated measurement of bond dissociation energies of metal–silyl complexes.[3] In the course of the attempted preparation of cobalt porphyrin silyls, we have discovered a serendipitous synthesis of a novel cobalt(III) porphyrin phosphoryl complex.

Our first attempt to prepare a silyl complex, by treating the strongly nucleophilic [Co^{I}(tpp)]$^-$ anion with Me_3SiCl in a manner similar to the synthesis of cobalt porphyrin alkyl compounds[4] did not prove to be successful. Only [Co^{II}(tpp)] was isolated (both in thf and toluene).[4] On the other hand, when [Co^{III}(tpp)Br] was silylated with Me_3SiLi ($MeLi–Si_2Me_6$–HMPA) (HMPA = hexamethylphosphoramide) at −78 °C in thf, adapting the Goff procedure,[5] the reduction product [Co^{II}(tpp)] (28%) and a new product **1** (62%)† were isolated. Compound **1** showed sharp proton resonances supporting the formation of a diamagnetic cobalt(III) compound. Two resonances at δ −0.30 and −0.27 appeared, each of intensity 6 H suggesting two non-equivalent methyl groups which however appeared as a singlet at δ 35.02 in the ^{13}C NMR spectrum. It is unlikely, therefore that the Me_3Si group had been introduced.

The structure of **1** was revealed by a single-crystal X-ray diffraction analysis [eqn. (1), Fig. 1] and was shown to

$$Me_3Si{-}SiMe_3 + MeLi \xrightarrow[\text{HMPA–THF, −78 °C}]{[Co(tpp)Br]} \underset{\mathbf{1}\ \ 62\%}{[Co(tpp)\{PO(NMe_2)_2\}]} \quad (1)$$

be [bis(dimethylamino)phosphoryl)](5,10,15,20-tetraphenylporphyrinato)cobalt(III) [Co^{III}(tpp){$PO(NMe_2)_2$}].‡ The coordination sphere of the cobalt atom shows square-pyramidal geometry with four porphyrinato nitrogen atoms occupying the basal sites and the phosphorus atom of bis(dimethylamino)phosphoryl group residing at the axial site. The Co–N bond length is 1.972 Å in accord with five-coordinate organocobalt(III) porphyrins.[6] The Co–P bond length is 2.265 Å which lies in the range of the relatively few reported Co–P bond lengths[7] and is longer by 0.021–0.102 Å compared with compounds containing Co–P σ bonds, such as in a cobalt–phosphinediyl complex[8a] (Co–P 2.163–2.210 Å) and a cobalt–phosphido complex[8b] (Co–P 2.244 Å). This slight lengthening may be due to the bonding of the phosphoryl ligand of **1** to a bulky cobalt–porphyrin moiety. The porphyrin ring is close to planar with a mean deviation of 0.12 Å from the basal plane for four *meso* carbons whereas the nitrogen atoms deviate alternatively above and below it by 0.10 Å. The IR spectrum showed a sharp P=O stretch at 1352 cm^{-1} (compared with $\upsilon_{P=O}$ 1295.6 cm^{-1} in HMPA).[9] In the ^{31}P NMR spectrum, a broad singlet appeared at δ 6.95 confirming the presence of a phosphorus atom and the line broadening is probably due to the quadrupolar effect of cobalt ($\omega_{\frac{1}{2}}$ = 1096 Hz).[10]

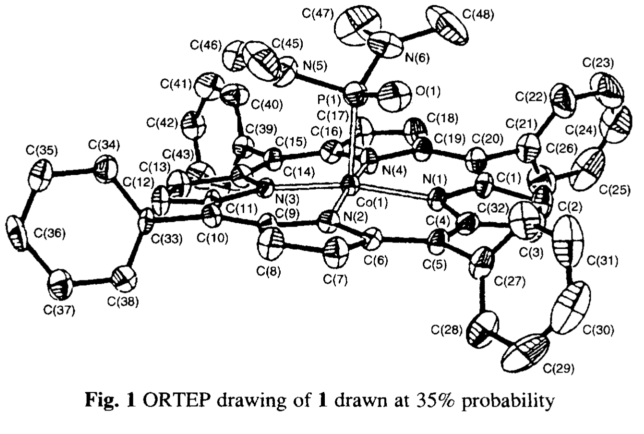
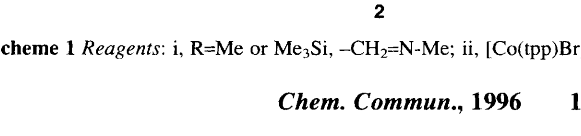


Fig. 1 ORTEP drawing of **1** drawn at 35% probability

In order to confirm the successful generation of Me_3SiLi under the employed reaction conditions, the well precedented reaction of Me_3SiLi with cyclohex-2-en-1-one, followed by trapping with MeI was repeated.[11] The expected product, *trans*-3-trimethylsilyl-2-methylcyclohexanone, was obtained in 96% yield, this experiment confirming that Me_3SiLi was successfully generated.

Complex **1** is likely to be obtained from the reaction of [Co^{III}(tpp)Br] and $(Me_2N)_2P(O)^-$ **2**, generated from the reaction of organolithiums with HMPA.[12] Anion **2**[12] was independently generated from MeLi–HMPA and successfully trapped with [Co^{III}(tpp)Br] to give **1** in 55% yield (Scheme 1) and its spectral characteristics were identical with the complex generated from Me_3SiLi–HMPA–[Co^{III}Br(tpp)]. It is of note that the reaction of [Co^{I}(tpp)]$^-$ with $(Me_2N)_2P(O)Cl$ did not produce complex **1** but only gave [Co^{II}(tpp)] in 43% yield, demonstrating the unique synthesis of the cobalt(III) porphyrin phosphoryl complex.

Since organocobalt complexes have been routinely prepared from [Co^{III}(tpp)Br],[13] this serendipitious synthesis of complex **1** may be accounted for by the reaction of Me_3SiLi with HMPA to give $(Me_2N)_2P(O)^-$ **2**. Even though Me_3SiLi reacts with an organic electrophile, cyclohex-2-en-1-one, its reaction towards a bulky organometallic electrophile, [Co^{I}II(tpp)Br], may be slower and instead Me_3SiLi preferably abstracted a proton from HMPA to give a more stabilized phosphoryl anion **2**, and then complex **1** after reaction with [Co^{III}(tpp)Br]. This observation indicated that the use of Me_3SiLi–HMPA as a silylating agent for a bulky organometallic electrophile may not always be appropriate.



Scheme 1 *Reagents*: i, R=Me or Me_3Si, $-CH_2{=}N{-}Me$; ii, [Co(tpp)Br]

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Footnotes

† [Bis(dimethylamino)phosphoryl](5,10,15,20-tetraphenylporphyrinato)-cobalt(III): $C_{48}H_{40}CoN_6OP$: 62% yield. *Selected characterization data*: ^1H NMR ($CDCl_3$, 250 MHz) δ −0.30 (s, 6 H), −0.27 (s, 6 H), 7.72 (s, 12 H), 8.10 (br s, 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) 6.95 ($\omega_{\frac{1}{2}}$ = 1096 Hz); UV–VIS (CH_2Cl_2), λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}) 408 (5.22), 530 (4.17); IR (thin film) 1352 cm^{-1}; FABMS, *m/z* 806 (M^+); Anal. Calc. 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%.

‡ *Crystal data* for **1**·Ch_2Cl_2: grown from dichloromethane–hexane: $C_{48}H_{40}CoN_6OP \cdot CH_2Cl_2$ crystallizes in the space group $P\bar{1}$ (no. 2) with a = 11.179(2), b = 13.034(3), c = 15.877(3) Å, α = 110.44(3) β = 95.43(3), γ = 94.79(3), U = 2141.1(7) Å^3, Z = 2, D_c = 1.383 g cm^{-3}. Refinement converged to R = 0.074, R' = 0.072.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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