Reductive Alkylation of Cobalt(III) Porphyrin by Tetraalkyltin Compounds and Alkylcobalt(III) Complexes

The chemistry of metal-σ-alkyl derivatives of transition-metal tetraazamacrocyclic complexes, especially of organometallic porphyrin complexes of Co and Fe, has recently attracted significant interest in establishing relations between organometallic chemistry and naturally occurring processes of coenzyme B_{12}[1] as well as cytochrome P450.[2] Organometallic porphyrin complexes can be prepared by the reductive alkylation of metal(III) porphyrins by strong alkylating reagents such as Grignard reagents[3-5] or the oxidation of metal(I) or metal(0) porphyrins, which are formed by electrochemical reactions[6] or by reduction with sodium amalgam or $NaBH_4$, using alkyl halides, olefins, and acetylenes.[7] In both cases, strong reductants are required for the formation of organometallic porphyrins.

This study reports that alkylcobalt(III) porphyrins can be readily prepared by reductive alkylation of $CoTPP^+$ (TPP = dianion of tetraphenylporphyrin) with mild alkylating reagents such as tetraalkyltin compounds and alkylcobalt(III) complexes in acetonitrile and/or chloroform at 298 K. To our knowledge, this is the first example of homogeneous alkylation reactions of metalloporphyrins by alkylmetals that are stable to dioxygen. Such homogeneous systems make it possible to study the kinetics in detail, providing a nice opportunity to elucidate the mechanisms of the reductive alkylation of $CoTPP^+$.

Alkylmetals used as mild alkylating reagents in this study are tetraalkyltin compounds (R_4Sn: R = Me, Et, *n*-Bu, *i*-Pr) and alkylcobalt(III) complexes *cis*-$[R_2Co(bpy)_2]ClO_4$ (R = Me, Et, $PhCH_2$),[9,10] *trans*-$[Me_2Co(DpnH)]$ (DpnH = 11-hydroxy-2,3,9,10-tetramethyl-1,4,8,11-tetraazaundeca-1,3,8,10-tetraen-1-olate),[9,11] and $[RCo(DH)_2py]$ (R = Me, Et, $PhCH_2$; $(DH)_2$ = bis(dimethylglyoximato); py = pyridine).[9,12] These alkylmetals are known to be rather mild reductants, and thus strong oxidants such as $[Fe(N-N)_3]^{3+}$ (N-N = 1,10-phenanthroline and 2,2'-bipyridine) are required for the oxidation of these alkylmetals.[11,13]

Table I. Reductive Alkylation of Co(TPP)Cl (4.0×10^{-2} M) by Alkylmetals (4.0×10^{-2} M) in $CDCl_3/CD_3CN$ (5:1 v/v)

alkylmetal	*T*/K	*t*/min	product (yield/%)
Me_4Sn	298	10	MeCoTPP (38)[a]
Et_4Sn	298	120	EtCoTPP (100)
n-Bu_4Sn	298	180	*n*-BuCoTPP (100)
$[MeCo(DH)_2py]$	298	10	MeCoTPP (33)[a]
$[EtCo(DH)_2py]$	298	120	EtCoTPP (100)
$[PhCH_2Co(DH)_2py]$	323	30	$PhCH_2CoTPP$ (100)
cis-$[Me_2Co(bpy)_2]^+$[b]	298	5	MeCoTPP (24), C_2H_6 (76)
cis-$[Et_2Co(bpy)_2]^+$	298	5	EtCoTPP (60), C_4H_{10} 40)
cis-$[(PhCH_2)_2Co(bpy)_2]^+$	298	5	$PhCH_2CoTPP$ (100)

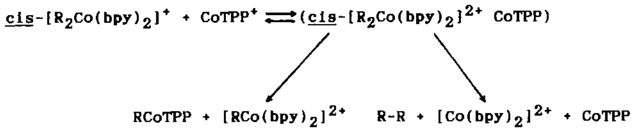
[a] In the prolonged reaction time, MeCoTPP decomposes slowly under the present reaction conditions.[16] [b] The concentrations of Co(TP-P)Cl and *cis*-$[Me_2Co(bpy)_2]^+$ are the same, 2.0×10^{-3} M.

Table II. Comparison of the Observed Second-Order Rate Constants (k_{obs}) for the Reduction of $Co(TPP)ClO_4$ by Alkylmetals in MeCN at 298 K with Those (k_{calc}) Calculated for the Outer-Sphere Electron-Transfer Reactions

alkylmetal	k_{obs}[a]/M^{-1} s^{-1}	k_{calc}[b]/M^{-1} s^{-1}
$[MeCo(DH)_2py]$	1.5×10^{-1}	2×10^{-1}
$[EtCo(DH)_2py]$	1.5×10^{-2}	8×10^{-1}
cis-$[Me_2Co(bpy)_2]^+$	1.2×10^{2}	1×10^{3}
cis-$[Et_2Co(bpy)_2]^\bullet$	1.0×10^{2}	4×10^{3}
cis-$[(PhCH_2)_2Co(bpy)_2]^+$	2.1×10^{2}	5×10^{2}
trans-$[Me_2Co(DpnH)]$	2.9×10^{4}	7×10^{3}
Me_4Sn	1.1	1×10^{-13}
Et_4Sn	4.0×10^{-1}	1×10^{-8}
n-Bu_4Sn	3.1×10^{-1}	9×10^{-8}
i-Pr_4Sn	3.4×10^{-4}	4×10^{-6}

[a] The experimental errors are ±10%. [b] Calculated by using the Marcus theory;[18] see text.

Scheme I



To our surprise, however, Co(TPP)Cl is readily reduced by R_4Sn as well as alkylcobalt(III) complexes in chloroform/acetonitrile (5:1 v/v)[14] to yield the alkylcobalt(III) porphyrins, as shown in eq 1 (in the case of R_4Sn). The formation of RCoTPP is readily

$$R_4Sn + Co(TPP)Cl \rightarrow RCoTPP + R_3SnCl \qquad (1)$$

identified by the characteristic ^1H NMR signals in the high-field regions due to the alkyl group bound to Co.[15] Yields of RCoTPP in the formal carbanion transfer from R_4Sn and alkylcobalt(III) complexes are listed in Table I.[16]

When *cis*-$[R_2Co(bpy)_2]^+$ (R = Me and Et) is used as alkylating reagents, the alkylation of $CoTPP^+$ is accompanied by formation of the coupling products of the alkyl groups (R-R). Such formation of the coupling products, which could arise via the corresponding dialkylcobalt(IV) complexes,[9] demonstrates the involvement of an electron-transfer process in the reductive alkylation of $CoTPP^+$ by *cis*-$[R_2Co(bpy)_2]^+$, as shown in Scheme I.[17] In

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(14) The solubility of Co(TPP)Cl is increased in chloroform/acetonitrile (5:1 v/v) as compared with that in chloroform or acetonitrile.

(15) ^1H NMR ($CDCl_3/CD_3CN$ 5:1 v/v, 298 K, JEOL JNM-GSX-400 instrument operating at 400 MHz), δ (Me_4Si) of coordinated alkyl ligand (ppm): MeCoTPP, -4.41 (s, 3 H); EtCoTPP, -4.95 (t, 3 H), -3.47 (q, 2 H); *n*-BuCoTPP, -4.78 (m, 2 H), -3.65 (t, 2 H), -1.47 (m, 2 H), -0.84 (t, 3 H); $PhCH_2CoTPP$, -2.58 (s, 2 H), 3.24 (d, 2 H), 5.70 (t, 2 H), 6.64 (t, 1 H). Porphyrin ligand proton resonances were found at 7.71 (m, 12 H), 8.06 (m, 8 H), and 8.76 ppm (s, 8 H).

(16) The yields of MeCoTPP in the reactions of CoTPP with Me_4Sn and $[MeCo(DH)_2py]$ become smaller in the prolonged reaction time because of the concomitant decomposition of MeCoTPP under the present reaction conditions to give unidentified products.

0020-1669/90/1329-2558$02.50/0

the case of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$, however, $PhCH_2CoTPP$ is obtained exclusively (Table I). Such selective formation of $PhCH_2CoTPP$ may be ascribed to the slow reductive elimination of two benzyl ligands as compared with the other alkyl ligands of *cis*-$[R_2Co(bpy)_2]^{2+}$ (R = Me and Et), as reported previously.[9]

A quantitative evaluation of the contribution of such electron-transfer processes in the reductive alkylation of $CoTPP^+$ by alkylcobalt(III) complexes may be achieved by comparing the observed rate constants with those predicted by the Marcus theory for the rates of outer-sphere electron-transfer reactions.[18] The second-order rate constants for the reduction of $Co(TPP)ClO_4$ by alkylmetals in MeCN at 298 K were determined by monitoring the disappearance and rise of the absorption bands at 434 and 407 nm due to the decay of $CoTPP^+$ and the formation of RCoTPP, respectively.[19,20] The reported values of self-exchange rate constants of alkylcobalt(IV/III) complexes[9] and a cobalt(III/II) porphyrin[21] together with the electron-transfer equilibrium constants, obtained from the one-electron oxidation potentials of the alkylcobalt(III) complexes[9] and the one-electron reduction potential of $CoTPP^+$ in MeCN,[21] constitute a satisfactory basis for accounting for the k_{obs} values in light of the Marcus relation.[18] The calculated electron-transfer rate constants k_{calc} and the observed second-order rate constants are listed in Table II. The k_{calc} values are about the same order of magnitude as the corresponding k_{obs} values, although most k_{obs} values are somewhat smaller than the k_{calc} values.[22] Such agreement indicates that the rate-determining step for the reductive alkylation of $CoTPP^+$ by alkylcobalt(III) complexes mainly consists of the electron-transfer process, as shown in Scheme I.[22]

The k_{calc} values of R_4Sn are also evaluated by the same manner as the case of alkylcobalt(III) complexes, using the reported values of self-exchange rate constants and the one-electron-oxidation potentials of R_4Sn,[13] and are listed in Table I, together with the k_{obs} values for the reduction of $CoTPP^+$ by R_4Sn. In contrast with the case of alkylcobalt(III) complexes, the k_{calc} values of R_4Sn are 10^2–10^{13} times smaller than the k_{obs} values, as shown in Table II. A close scrutiny of the data reveals that the deviation from the calculated values of outer-sphere electron transfer is the most pronounced with the least hindered tetraalkyltin, i.e., Me_4Sn. The magnitude of the deviation decreases with increasing the size of the alkyl group (Table II). Such a trend must reflect steric effects that perturb the inner-sphere coordination of R_4Sn to $CoTPP^+$ in the transition state for the reductive alkylation, which is clearly distinguished from the outer-sphere electron-transfer processes involved in the corresponding reactions of alkylcobalt(III) complexes.[23]

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[17] The bis complex $[Co(bpy)_2]^{2+}$ shown in Scheme I may be converted to the tris complex $[Co(bpy)_3]^{3+}$, which was identified by ^1H NMR spectroscopy, since thermodynamic considerations indicate that the tris complex is more stable than the bis complex: Fukuzumi, S.; Ishikawa, K.; Tanaka, T. *Organometallics* **1987**, *6*, 358.

[18] The Marcus relation for the rate constant of the electron transfer from the reductant (1) to the oxidant (2), k_{12}, is given by $k_{12} = (k_{11}k_{22}K_{12}f)^{1/2}$, where k_{11} and k_{22} are the rate constants of the corresponding self-exchanges and K_{12} is the equilibrium constant for the electron-transfer reaction. The K_{12} value is obtained from the oxidation potential of the reductant, $E°_{ox}$, and the reduction potential of the oxidant, $E°_{red}$ by using the following equation: $\log K_{12} = (-2.3RT/F)^{-1}(E°_{ox} - E°_{red})$. The parameter f is given by $\log f = (\log K_{12})^2/[4 \log (k_{11}k_{22}/Z^2)]$, where Z, the frequency factor, is taken to be 1×10^{11} M^{-1} s^{-1}: Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

[19] Kinetic measurements were carried out by using a Union RA-103 stopped-flow spectrophotometer and a Union SM-401 spectrophotometer under the pseudo-first-order conditions where the concentrations of alkylmetals were maintained at >10-fold excess of the $CoTPP^+$ concentration with half-lives shorter than 10 s and much longer than 10 s, respectively. The second-order rate constants were determined with $Co(TPP)ClO_4$ in MeCN instead of Co(TPP)Cl in $CHCl_3$/MeCN (5:1 v/v), since the thermodynamic parameters required for calculation of the electron-transfer rate constants have been obtained in MeCN.[9,13,21]

[20] The absorption maximum of RCoTPP (λ_{max} = 407 nm)[7b] is different from λ_{max} of CoTPP (412 nm).[19]

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[22] The rate of cleavage of the cobalt–carbon bond following the electron transfer may also be involved partially in the rate-determining step, when the k_{obs} values of the overall reactions become smaller than the k_{calc} values of the electron-transfer processes. In the case of *trans*-$[Me_2Co(DpnH)]$, the k_{obs} value is somewhat larger than the k_{calc} value, indicating contribution of an inner-sphere process.[13,21,23]

[23] For comparison between outer-sphere and inner-sphere electron-transfer processes, see: Reference 13. Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 5839. Kochi, J. K. *Angew. Chem.* **1988**, *100*, 1331. Haim, A. *Prog. Inorg. Chem.* **1983**, *30*, 273. Seaman, G. C.; Haim, A. *J. Am. Chem. Soc.* **1984**, *106*, 1319.

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Facile α/β Diastereomerism in (2,2,2-Trifluoroethyl)cobalt Corrins

In a recent publication,[1] unequivocal evidence was presented that reductive alkylation of cobinamides (Cbi's) with $^{13}CH_3I$ leads essentially exclusively to formation of the β-alkylcobinamide (i.e., CH_3 in the "upper" axial position). We now wish to report a startlingly different result upon reductive alkylation of cobinamide with CF_3CH_2I.

When Factor B[2,3] was reduced with zinc/acetic acid and alkylated with CF_3CH_2I,[4] the monocationic alkylcobinamide fraction from cation-exchange chromatography showed two bands by HPLC[5] (mobility relative to CNCbl, R_{CN} = 1.23 and 1.48), both of which were readily converted to diaquocobinamide ($(H_2O)_2Cbi$, R_{CN} = 0.77) upon aerobic photolysis. The two compounds were readily separated by semipreparative HPLC. The more slowly migrating compound had a UV–visible spectrum (Figure 1A, dashed line) essentially identical, above 300 nm, with that of the base-off species of the previously characterized[6] CF_3CH_2Cbl (Figure 1B, dashed line). Moreover, its ^{19}F NMR spectrum consisted of a triplet at 57.38 ppm (Table I), J = 13.9 Hz, again essentially identical with that of the base-off CF_3CH_2Cbl (Table I). We conclude that this compound is the β-diastereomer of CF_3CH_2Cbi, i.e. α-(H_2O)-β-(CF_3CH_2)Cbi (hereafter β-CF_3CH_2Cbi). The other compound (R_{CN} = 1.23) had a UV–visible spectrum (Figure 1A, solid line) quite similar to that of β-CF_3CH_2Cbi, except that its longest wavelength band (i.e. the α-band) is red-shifted 27 nm (Table I). Its spectrum was cleanly converted to that of $(H_2O)_2Cbi$[7] upon aerobic photolysis and to that of $(CN)_2Cbi$[8] upon aerobic photolysis in excess cyanide. Its ^{19}F NMR resonance (δ = 59.52 ppm, J = 14.7 Hz) was distinctly downfield from those of base-off CF_3CH_2Cbl and base-on CF_3CH_2Cbl (Table I). Both compounds were also characterized by FAB-MS (glycerol matrix). The positive-ion mass spectra were virtually identical, with a parent ion mass 1072.8 for β-CF_3CH_2Cbi and 1072.9 for the other compound (calculated for $M^+ - H_2O$[9]

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[1] Brown, K. L.; Peck-Siler, S. *Inorg. Chem.* **1988**, *27*, 3548–3555.

[2] Factor B is a mixture of the diastereomeric cyanoaquocobinamides α-(CN)-β-(H_2O)Cbi and α-(H_2O)-β-(CN)Cbi.

[3] Renz, P. *Methods Enzymol.* **1971**, *18*, 82–92.

[4] Typical preparative-scale conditions: 100 mg of Factor B (0.09 mmol) in 25 mL of 10% acetic acid was purged with argon for 1 h. Zinc wool, 2.0 g (briefly freshed by swirling in 1.0 N HCl), was introduced and reduction allowed to proceed for 30 min under argon. A 1.0-mL aliquot of CF_3CH_2I (10 mmol) was injected, and after 2 min the reaction mixture was desalted by either passage through an Amberlite XAD-2 column or extraction through phenol. Purification of the alkylcobinamides was effected by ion-exchange chromatography on SP-Sephadex, Na^+ form, the RCbi's eluting in 0.1 M sodium acetate, pH 5.0.

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