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Reversible Cobalt–Nitrogen Alkyl and Acyl Group Migration in Cobalt Porphyrins

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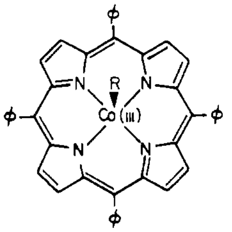
The one-electron electrochemical oxidation of ethyl(5,10,15,20-tetraphenylporphinato)cobalt(III) ($EtCo^{III}TPP$) causes intramolecular rearrangement of the ethyl group to give (*N*-ethyl-5,10,15,20-tetraphenylporphinato)cobalt(II) (N-$EtCo^{II}TPP)^+$. Sodium borohydride reduction of N-$EtCo^{II}TPP^+$ regenerates $EtCo^{III}TPP$ but by an intermolecular rearrangement. Low-temperature studies on (ethoxycarbonyl)(5,10,15,20-tetraphenylporphinato)cobalt(III), which also exhibits (but at a slower rate than that of $EtCo^{III}TPP$) one-electron oxidative rearrangement to (*N*-(ethoxycarbonyl)-5,10,15,20-tetraphenylporphinato)cobalt(II), showed that the initial site of oxidation is at the porphyrin ring to give the corresponding π-cation radical. In this case the cobalt to nitrogen migration occurs upon warming a solution of the π-cation radical.

The redox chemistry of organocobalt compounds is an area of current interest, especially in the context of the chemistry of vitamin B_{12}. Electrochemical parameters have been reported for organo derivatives of cobalamins,[1-4] cobinamides,[1-3] cobaloximes,[5] and cobalt Schiff's bases.[6,7] Chemical and electrochemical reduction of organocobalt complexes usually results in cleavage of the cobalt–carbon bond.[8,9] Oxidation may also cleave this bond, yielding a variety of products; however, in the case of the cobaloximes,[5,10] the initial one-electron oxidation product of the organocobaloximes has been stabilized at low temperatures and EPR measurements indicate that this species is best described as an organocobalt(IV) complex.[5,11-13]

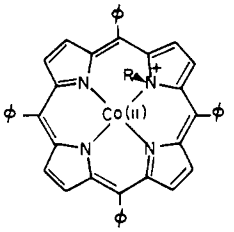
We wish to report that one-electron electrochemical oxidation of organocobalt(III) porphyrins results inter alia in the migration of the organo group from cobalt to a nitrogen of the porphyrin macrocycle. A migration of this type has not, to our knowledge, been previously observed for organocobalt complexes. Moreover, subsequent reduction of the N-substituted cobalt porphyrin results in the re-formation of the cobalt–carbon bond.

Cyclic voltammetry on ethyl(5,10,15,20-tetraphenylporphinato)cobalt(III) ($EtCo^{III}TPP$, **1**) at a platinum electrode in CH_2Cl_2 at 23 °C indicates that the first oxidation ($e_p{}^a$ = 1.08 V) is irreversible as evidenced by the absence of a corresponding cathodic peak in the cyclic voltammogram (Figure 1 (a)). Lowering the temperature increases the cathodic peak current, however, until at −40 °C a quasi-reversible process is observed (Figure 1 (b)) ($e_{1/2}{}^1$ = 0.98 V, Δe_p = 130 mV; $e_{1/2}{}^2$ = 1.19 V, Δe_p = 140 mV; the third wave $e_{1/2}{}^3$ = 1.70 V Δe_p = 130 mV which is present at 23 °C disappears at lower temperatures). Such behavior is characteristic of an oxidation followed by a chemical reaction (ECE), the rate of which is decreased by lowering the temperature. The couples formed at 1.10 and 1.70 V are associated with the product of this reaction while the couples formed at 0.98 and 1.19 V are due to the reversible oxidation of EtCoTPP (at −40 °C).



1, R = CH_3CH_2–

4, R = $CH_3CH_2O\overset{O}{\overset{\|}{C}}$–



2, R = CH_3CH_2–

5, R = $CH_3CH_2O-\overset{O}{\overset{\|}{C}}-$

So that the oxidation product could be identified, controlled-potential electrolysis at 1.08 V (vs. Ag/AgCl reference) in CH_2Cl_2, 0.1 M (n-$Bu_4N)PF_6$, was carried out which yielded a green solution. Simultaneous coulometry showed that 1.06 e/mol of $EtCo^{III}TPP$ had passed. The optical spectrum of the green solution (λ_{max} = 659, 610, 564, 454 (sh), and 438 nm) was similar to that of metallo-*N*-alkylporphyrins.[14]

Indeed, removal of the cobalt from this complex **2**, purification of the porphyrin by alumina chromatography, and crystallization from dichloromethane–methanol gave a high yield of a product identified as *N*-ethyl-5,10,15,20-tetraphenylporphyrin (*N*-EtTPP). The optical spectrum of *N*-EtTPP is similar to that of the *N*-methyl derivative,[15] and the high-field resonances for the ethyl group in the ^1H NMR (δ −1.72 (3 H, t) and −4.48 (2 H, q)) are consistent with the ethyl group being bonded to nitrogen and experiencing the shielding effect of the porphyrin ring current.[16]

Treatment of *N*-EtTPP with cobalt acetate gave (*N*-ethyl-5,10,15,20-tetraphenylporphinato)cobalt(II) (**2**), identical with that isolated from the one-electron electrochemical oxidation of ethyl(5,10,15,20-tetraphenylporphinato)cobalt(III).

Although the cyclic voltammogram is ***reversible at −40 °C*** (with a sweep rate of 100 mV/s), bulk electrolysis at this temperature did not permit us to observe any reaction intermediates. While the migration of an alkyl group, with its bonding electrons, is a well-documented phenomenon, the corresponding migration of an acyl group is less facile[17] and we anticipated that the reactions of (ethoxycarbonyl)-(5,10,15,20-tetraphenylporphinato)cobalt(III) (**4**) might be slow enough to allow for the observation of reaction intermediates. Cyclic voltammetry on **4** indicates that it is reversibly oxidized at 23 °C (Figure 1 (c)). Nevertheless, while the ester group does not migrate on the time scale of the cyclic

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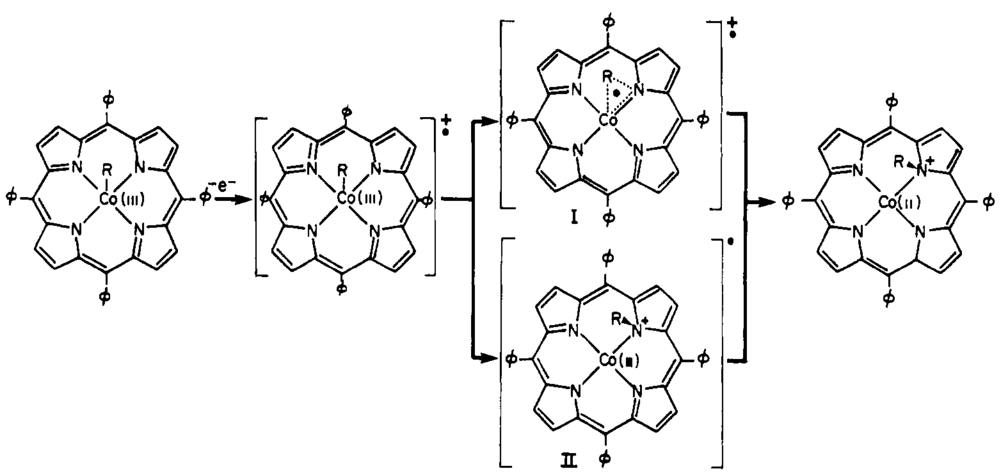
Scheme I



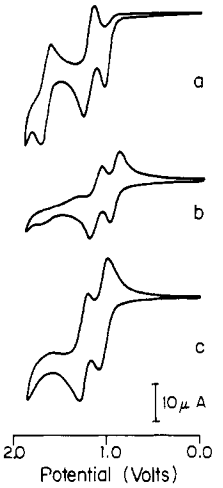


Figure 1. Cyclic voltammograms in dichloromethane, 0.1 M (n-$Bu_4N)PF_6$, measured against Ag/AgCl: (a) compound **1**, 23 °C; (b) compound **1**, -40 °C; (c) compound **4**, 23 °C.

voltammetry, it does migrate when a bulk electrolysis is carried out at room temperature, but at −40 °C the migration is sufficiently slow that the initial one-electron oxidation product can be characterized.

Bulk electrolysis of **4**, at room temperature, in CH_2Cl_2 and 1.08 V yielded a green solution, and coulometry indicated that a one-electron oxidation had occurred. Removal of the cobalt from the complex **5** and subsequent purification gave a 74% yield of N-(ethoxycarbonyl)-5,10,15,20-tetraphenylporphyrin (**6**) which exhibited ^1H NMR resonances at δ 0.88 (2 H, q) and −1.22 (3 H, t) and had spectral (UV, mass spectra) and analytical properties consistent with the assigned structure. Electrolysis of **4** at −40 °C, in a cell designed so that electronic spectra can be monitored as the electrolysis proceeds,[18] was carried out at 1.08 V. During the one-electron oxidation, the initial optical spectrum of **4** changed to that shown in Figure 2. During the reaction, clean isosbestic points were observed, suggesting only two species were present. The optical spectrum of the one-electron oxidized product of **4** (at −40 °C) exhibited maxima at 409, 426, 535, 590, and 654 nm. These spectral changes are similar to those reported for the one-electron oxidation of $Co^{III}TPP^+$ to $Co^{III}TPP^{2+}\cdot$, where it has been established[19] that the $Co^{III}TPP^{2+}\cdot$ is a porphyrin radical. Indeed the optical spectra of both $Co^{III}TPP^{2+}\cdot$ and the one-electron oxidation product of **4** at −40 °C show that both of these species are cobaltic porphyrin *π-cation radicals*.[20] The potential for the oxidation of $Co^{III}TPP^+$ to $Co^{III}TPP^{2+}\cdot$ of 1.19 V in benzonitrile[19] is close to what we observe (1.10 V) for the same oxidation in dichloromethane. Since the potentials for the oxidation of $RCo^{III}TPP$ (R = Et, $e_{1/2}{}^1$ = 0.98 V[21] and R = EtO_2C, $e_{1/2}{}^1$ = 1.04 V) are close to those of $Co^{III}TPP^+$, it is reasonable to assume that the same electrode process is taking place in each case. Moreover the constancy of $\Delta E_{Ox} = E_{1/2}{}^2 - E_{1/2}{}^1$ for $Co^{III}TPP^+$ (ΔE_{Ox} = 230 mV), $EtCo^{III}TPP$ (**1**) (ΔE_{Ox} = 210 mV) and $EtO(O)CCo^{III}TPP$ (**4**) (ΔE_{Ox} = 230 mV) shows that both events are ring oxidations.

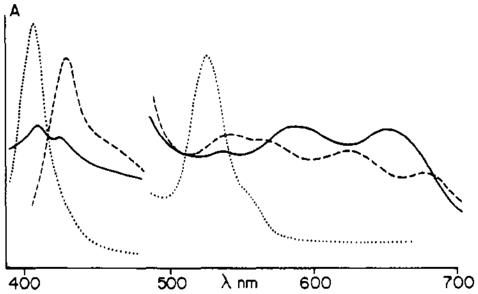


Figure 2. Optical spectra in CH_2Cl_2-(n-$Bu_4)PF_6$: (ethoxycarbonyl)(5,10,15,20-tetraphenylporphinato)cobalt(III) (**4**) (⋯); the one-electron oxidation product of **4** at −40 °C (—), warmed to 23 °C (- - -) to give **5**.

Thus *before* rearrangement, the one-electron oxidation products are the cobaltic π-cation radicals (the optical spectrum of oxidized **4** at −40 °C confirms this). It should be noted that these observations are in contrast to the one-electron oxidations of organocobalt Schiff's bases[11] and organocobaloximes[5,13] where the oxidation takes place to give Co(IV) derivatives.

Warming a solution of the π-cation radical $EtO(O)CCo^{III}TPP^+\cdot$ (the one-electron oxidation product **4**) from −40 to 25 °C results in an immediate change in the optical spectrum (Figure 2) which is characterized by an increase in intensity and red shifting of the Soret band. The resulting optical spectrum is identical with that after the room-temperature bulk electrolysis of **4** which produced (N-(ethoxycarbonyl)-5,10,15,20-tetraphenylporphinato)cobalt(II) (**5**).

When equimolar amounts of **1** and ethyl-d_5-(5,10,15,20-tetraphenyl-d_8-porphyrinato)cobalt(III) (**7**) were electrolyzed

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(21) This is $e_{1/2}{}^1$ at −40 °C. The anodic peak of this couple exhibits a small (~40 mV) cathodic shift as the temperature is lowered from 23 to −40 °C.

at 1.08 V, the rearrangement was shown to be intramolecular since there was no scrambling of the alkyl groups in the products (**2** and **8**). Two alternate pathways suggest themselves where the alkyl or acyl group (R; Scheme I) migrates with either one electron (intermediate I) or two electrons (intermediate II). Reduction of **2**, with sodium borohydride or with electrochemistry, causes a *net* reversal of the reaction since **1** is regenerated. However, in this case, the reaction is intermolecular. Compound **2** shows, after demetalation, a parent peak in the mass spectrum at m/e 642 which is also the base peak and no fragmentation peaks until a weak peak (10%) at 614 (TPP). The *N*-ethyl-d_5-tetraphenyl-d_8-porphyrin analogue exhibits the same features with the parent peak now at 655. When a mixture of **1** and its deuterated analogue were electrochemically oxidized to **2** and then demetalated, the mass spectrum of the product showed peaks at only 642 and 655. This mixture of deuterated and nondeuterated *N*-ethyl-5,10,15,20-tetraphenylporphyrin was metalated to give **2** and **8**. Mass spectroscopy at this stage showed that no scrambling of the deuterated and nondeuterated ethyl groups had occurred. Reduction of this mixture using the conditions described by Ogoshi et al.[22] gave **1**. The mass spectrum of this mixture contained peaks at 700 and 713, but in addition comparably intense peaks at 705 and 708 were also present, showing that scrambling of the deuterated and nondeuterated ethyl groups between the deuterated and nondeuterated cobalt porphyrins had occurred.

Ogoshi et al.[22] have observed that the reduction of (*N*-methyloctaethylporphyrinato)cobalt(II) with sodium borohydride gives, in analogy to the reactions described above, the methylcobalt(III) octaethylporphyrin. They suggest, with no supporting evidence, that the reaction can be considered to be an intramolecular oxidative addition through the C–N bond to a Co(I) ion. While we have not studied these reactions in the octaethylporphyrin (OEP) series, it is reasonable to expect that the OEP and TPP series will behave in a similar fashion and that the rearrangement observed by Ogoshi et al. is in fact intermolecular. This is indeed what one would predict if the reductive rearrangement does proceed via a cobalt(I) species. There are many examples, especially in vitamin B_{12} and related chemistry, of cobalt(I) species behaving as powerful nucleophiles in S_N2 reactions at a tetrahedral carbon center.[23] With S_N2 reactions in general, there is a strict requirement for collinearity between nucleophile–carbon–leaving group in the transition state.[24] There is no reason to expect that this is not the case in the borohydride-induced rearrangement of **2** → **1**. This being the case, there is no way the nucleophilic Co(I) (after reduction of **2**) can bring about an S_N2 mediated oxidative addition by intramolecularly attacking the *N*-alkyl group. This steric restriction does not obtain in an intermolecular reaction, which we expect accounts for the intermolecularity we observe in the migration of alkyl from nitrogen to cobalt when initiated by borohydride reduction.

Experimental Section

Materials. Tetrahydrofuran (THF) was distilled from $LiAlH_4$ and methylene dichloride from CaH_2. The supporting electrolyte, tetra-*n*-butylammonium hexafluorophosphate (n-Bu_4NPF_6), was prepared by mixing tetra-*n*-butylammonium iodide with ammonium hexfluorophosphate in acetone. After NH_4I was removed by filtration, the product was precipitated with water and collected by filtration, recrystallized three times from ethanol–water, and dried under high vacuum. NMR spectra were measured on a Varian XL100 spectrometer and mass spectra on a AEIMS-902 spectrometer (direct probe inlet at 70 eV). Ultraviolet and visible spectra were recorded with the use of a Cary Model 17 spectrophotometer.

Cyclic voltammetric studies were carried out at a platinum electrode in CH_2Cl_2. A Ag/AgCl couple was used as reference. Standard 3 electrode operational amplifier circuitry was used as described previously.[25] Bulk controlled-potential electrolyses were performed in CH_2Cl_2 at platinum using a PAR Model 173 potentiostat. Since Co–C bonds are readily photolysed, all operations on such complexes were carried out in subdued light.

Ethyl(5,10,15,20-tetraphenylporphinato)cobalt(III) ($EtCo^{III}TPP$ (1)). (5,10,15,20-Tetraphenylporphinato)cobalt(II)[26] (1.06 g, 1.5 mmol) in THF (250 mL) was reduced for 1 h under an argon atmosphere, with 1% sodium amalgam, to Co^ITPP. (From this point on all solutions were protected from light to prevent photolysis of cobalt–carbon bonds, by covering flasks with aluminum foil and working in a darkened room.) Ethyl iodide was purged with argon for 15 min, and then 10 mL (0.12 mol) of ethyl iodide was added with a syringe to the porphyrin mixture. The solution was stirred for 5 min and filtered to remove the amalgam. The filtrate was taken to dryness by rotary evaporation and the residue triturated with chloroform. The mixture was filtered and the solid discarded. The product was precipitated from the chloroform solution by the addition of petroleum ether. The solid was collected by filtration and twice recrystallized from chloroform–petroleum ether to give 680 mg (65%) of **1**: mass spectrum (relative intensity) 700 (M^+, 10), 671 (100); λ_{max} (CH_2Cl_2) 407, 524 nm; ^1H NMR ($CDCl_3$) δ –4.94 (t, 3 H, CH_3CH_2Co), –3.46 (q, 2 H, CH_3CH_2Co), 7.63–7.76 and 8.06–8.18 (m, 20 H, phenyl), 8.80 (s, 8 H, β-pyrrole). Anal. Calcd for $C_{46}H_{33}N_4Co$: C, 78.84; H, 4.75; N, 7.99. Found: C, 78.97; H, 4.71; N, 8.04.

(*N*-Ethyl-5,10,15,20-tetraphenylporphinato)cobalt(II) (2). Ethyl(5,10,15,20-tetraphenylporphinato)cobalt(III) (**1**) (11.8 mg, 0.017 mmol) was dissolved in methylene dichloride (8 mL containing 0.05 M n-Bu_4NPF_6) and oxidized at 1.08 V at room temperature while passing argon through the solution. When 1.1 e/mol had been passed, the current had essentially stopped flowing. The solution was taken to dryness and dissolved in a minimum volume of methylene chloride. Petroleum ether was added which caused precipitation of the supporting electrolyte. This process was repeated to remove more electrolyte, and the porphyrin mixture was then chromatographed on a thin layer of silica gel with use of CH_2Cl_2–CH_3OH. The product was removed from the plate and crystallized from CH_2Cl_2–petroleum ether to give 4.8 mg (~40%) of **2**: λ_{max} (nm) (CH_2Cl_2) 438, 454 (sh), 564, 610, 659; mass spectrum 700 (M^+, 2), 671 (100).

***N*-Ethyl-5,10,15,20-tetraphenylporphyrin (3).** Ethyl(5,10,15,20-tetraphenylporphinato)cobalt(III) (**1**; 53 mg) in 7 mL of CH_2Cl_2 containing 0.05 M n-Bu_4NPF_6 was oxidized and converted to (*N*-ethyl-5,10,15,20-tetraphenylporphinato)cobalt(II) (**2**) as described above. Cobalt was removed from the oxidation product by treating the electrolyte solution with trifluoroacetic acid and then water (10 mL). The organic phase was washed with water (2 × 10 mL) and then 1 M NH OH (10 mL, to deprotonate the porphyrin). The organic phase was diluted to 20 mL with CH_2Cl_2. Methanol (20 mL) and 0.1 M NH_4OH (9 mL) were added, the mixture was stirred and separated, and the organic phase was brought to 20 mL by the addition of CH_2Cl_2. The process was repeated, and the combined aqueous phases were extracted with CH_2Cl_2 (3 mL). The combined organic phases were taken down to dryness. The residue was dissolved in a small volume of methylene dichloride. Methanol (10 mL) and water (2 mL) were added, and the methylene chloride was removed on a rotary evaporator. The precipitated product was collected by filtration and washed with aqueous methanol. The product was then chromatographed on neutral alumina (grade II) with the use of methylene dichloride and crystallized from CH_2Cl_2–MeOH to give 37 mg of **3** (76%) (an analytical sample was recrystallized from CH_2Cl_2–MeOH): mass spectrum 642 (M^+, 100), 627 (2), 614 (4); λ_{max} (nm) (CH_2Cl_2) 433, 500 (sh), 533, 576, 613, 677; ^1H NMR ($CDCl_3$) δ –4.48 (q, 2 H, $CH_3CH_2N^+$), –1.72 (t, 3 H, $CH_3CH_2N^+$), 7.50 (s, 2 H, β-pyrrole), 7.76 and 8.1–8.4 (m, 20 H, phenyl), 8.46 (d, 2 H, β-pyrrole), 8.66 (d, 2 H, β-pyrrole), 8.78 (s, 2 H, β-pyrrole). Anal. Calcd for $C_{46}H_{34}N_4$: C, 85.95; H, 5.33; N, 8.72. Found: C, 85.60; H, 5.14; N, 8.70.

(Ethoxycarbonyl)(5,10,15,20-tetraphenylporphinato)cobalt(III) (4). This was prepared from (5,10,15,20-tetraphenylporphinato)cobalt(II)[26]

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[25] D. C. Borg, J. Fajer, R. H. Felton, and D. Dolphin, *Proc. Natl. Acad. Sci. U.S.A.*, **67**, 813 (1970).

(1.0 g, 1.5 mmol) and redistilled deoxygenated ethyl chloroformate (5 mL, 0.051 mol) in a manner identical with that described for **1** above to give 425 mg (38%) (an analytical sample was prepared by two recrystallizations from chloroform–petroleum ether): mass spectrum (relative intensities) 744 (M^+, 12), 700 (1), 680 (1), 671 (100); λ_{max} (CH_2Cl_2) 408, 527; ^1H NMR ($CDCl_3$, 100 MHz) δ –0.83 (t, 3 H, CH_3CH_2O), 1.40 (q, 2 H, CH_3CH_2O), 7.5–7.7 and 7.9–8.15 (m, 20 H, phenyl), 8.80 (s, 8 H, β-pyrrole). Anal. Calcd for $C_{47}H_{33}N_4O_2Co$: C, 75.80; H, 4.47; N, 7.52. Found: C, 75.61; H, 4.51; N, 7.44.

(*N*-(Ethoxycarbonyl)-5,10,15,20-tetraphenylporphinato)cobalt(II) (5). (Ethoxycarbonyl)(5,10,15,20-tetraphenylporphinato)cobalt(III) (**4**) (12.7 mg) was oxidized at 1.08 V and worked up as described above for the preparation of **2** from **1** to give 8.2 mg (~65%) of **5**: mass spectrum 744 (M^+, 5), 700 (1), 671 (100).

***N*-(Ethoxycarbonyl)-5,10,15,20-tetraphenylporphyrin (6).** Ethoxycarbonyl(5,10,15,20-tetraphenylporphinato)cobalt(III) (**4**) (39.6 mg, 0.053 mmol) in CH_2Cl_2 (10 mL containing 0.05 M *n*-Bu_4NPF_6) was electrolyzed at 1.08 V until 1.1 e/mol had been consumed. Trifluoroacetic acid was added to the solution to remove the cobalt. Supporting electrolyte was removed as described above for the preparation of **2**. The product was purified by chromatography in neutral alumina (grade II) and crystallized from CH_2Cl_2–MeOH to give **6** (27 mg, 80%) (an analytical sample was recrystallized from CH_2Cl_2–MeOH): mass spectrum 686 (M^+, 100) 642 (7), 614 (32); λ_{max} (CH_2Cl_2) 437, 493 (sh), 524, 566, 646, 714; ^1H NMR ($CDCl_3$) δ –1.22 (t, 3 H, ester CH_3), 0.88 (q, 2 H, ester CH_2), 7.44 and 8.1–8.34 (m, 20 H, phenyl), 8.02 (s, 2 H, β-pyrrole), 8.44 (s, 2 H, β-pyrrole), 8.47 (s, 2 H, β-pyrrole), 8.67 (s, 2 H, β-pyrrole). Anal. Calcd for $C_{47}H_{34}N_4O_2$: C, 82.19; H, 4.99; N, 8.16. Found: C, 81.47; H, 4.61; N, 8.34.

Ethyl-d_5-(5,10,15,20-tetraphenyl-d_8-porphinato)cobalt(III) (7). (5,10,15,20-Tetraphenyl-d_8-porphinato)cobalt(II) (prepared from 5,10,15,20-tetraphenyl-d_8-porphyrin[27]) (200 mg, 0.3 mmol) was reacted with ethyl-d_5 bromide (3 g, 37 mmol; Merck Sharp and Dohme of Canada Ltd., Isotopes Division) as described above for the preparation of **1** to give 110 mg (53%) of **7**: mass spectrum 713 (M^+, 8), 679 (100). During this reaction the deuterium content of the ethyl group (>95%) and that of the porphyrin (>92% at *o*-phenyls) were maintained.

(*N*-Ethyl-d_5-5,10,15,20-tetraphenyl-d_8-porphinato)cobalt(II) (8). Ethyl-d_5-(5,10,15,20-tetraphenyl-d_8-porphinato)cobalt(III) (**7**) (50 mg) was oxidized at 1.08 V as described in the preparation of **2** to give the product **8** (32 mg, 64%): mass spectrum 713 (M^+, 3), 679 (100).

Conversion of 8 to 7 by Reduction with Sodium Borohydride. (*N*-Ethyl-d_5-5,10,15,20-tetraphenyl-d_8-porphinato)cobalt(II) (**8**; 10 mg) in tetrahydrofuran (35 mL) was treated at room temperature with sodium borohydride (10 mg) under argon. The mixture was stirred for 0.5 h then and taken down to dryness at room temperature. The product was extracted into methylene dichloride and purified as described above for the preparation of **1** to give 6.8 mg (~65%) of a product identical with **7**: mass spectrum 713 (3), 708 (3), 705 (2), 700 (3), 671 (100).

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Registry No. **1**, 61730-43-6; **2**, 78638-41-2; **3**, 73568-09-9; **4**, 78638-40-1; **5**, 78638-42-3; **6**, 78656-78-7; **7**, 78638-43-4; **8**, 78638-44-5; $Co^{II}TPP$, 14172-90-8; $Co^{II}TPP$-d_8, 78638-45-6.

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Contribution from le Laboratoire de Chimie des Organométalliques, ERA du CNRS No. 477, et le Laboratoire de Chimie du Solide et Inorganique Moléculaire associé au CNRS No. 254, Université de Rennes, Campus de Beaulieu, 35042 Rennes Cedex, France

A New Bridging Ligand in Dinuclear Iron Carbonyl Species. Synthesis, Properties, and X-ray Structure Determination of Xanthate–$Fe_2(CO)_6$ Complexes

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The complexes μ-(alkoxymethanethione-*C*,*S*)-μ-(alkylthio)-1,1,1,2,2,2-hexacarbonyldiiron are obtained in good yield by reaction of *O*-alkyl *S*-alkyl dithiocarbonates (or xanthates) with diiron nonacarbonyl. These compounds were characterized by microanalysis and IR, ^1H and ^{13}C NMR, and mass spectroscopies. The structure of the complex obtained from *O*-(adamantylmethyl) *S*-methyl dithiocarbonate has been determined by single-crystal X-ray diffraction. The crystals are triclinic, space group $P\bar{1}$, with $Z = 2$ and $a = 7.765$ (3) Å, $b = 11.025$ (2) Å, $c = 14.155$ (2) Å, $\alpha = 106.24$ (4)°, $\beta = 104.56$ (4)°, and $\gamma = 90.37$ (2)°. A full-matrix least-squares method refined the structure to $R = 0.033$ from 2715 nonzero independent reflections. The structure shows that fragmentation of the ligand has occurred and that one iron atom has inserted into the carbon–sulfur single bond, giving rise to two orthogonal bridges made from the thiocarbonyl function and by the *S*-alkyl group. This unexpected behavior of the xanthate ligand provides a convenient route to dissymmetrically bridged diiron hexacarbonyl species where the carbon of the bridge presents a carbenic character in agreement with the ^{13}C and X-ray data. Displacement of one or two carbonyls or removal of the *O*-alkyl group by a phosphorus ligand is also described, and the mass spectra of the complexes are discussed.

Introduction

In the course of our investigations concerning the design of organometallic combinations which can be used as templates[1] either in a chemical or photochemical manner, we have studied the behavior of new ligands toward metal carbonyls. Electron-rich sulfur-containing functional groups have been chosen for their well-known propensity to coordinate with transition metals, and we have already described complexation of trithiocarbonates[2] by $Fe_2(CO)_9$ and desulfurization of xanthates

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