Synthesis and Structural Characterization of a Novel Covalently-Bound Corrole Dimer

Atif Mahammed,[a] Ilona Giladi,[a] Israel Goldberg,*[b] and Zeev Gross*[a]

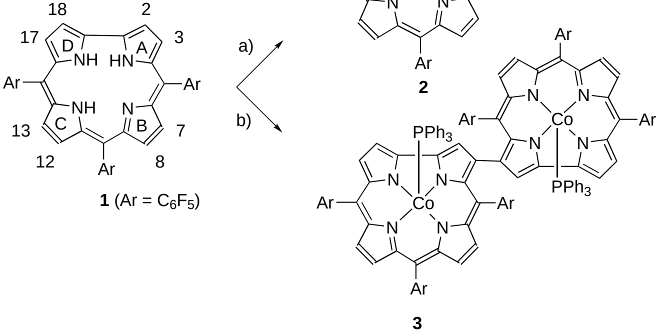
Abstract: The (triphenylphosphine)cobalt(III) complex (**2**) of 5,10,15-tris(pentafluorophenyl)corrole (**1**) is shown to be an valuable precursor to complexes that have not been fully characterized previously. In contrast to other cobalt corroles, aromatic amines can be substituted for the triphenylphosphine in **2** to form six-coordinate bis(amine)cobalt(III) complexes. This is demonstrated by spectroscopic methods and by X-ray crystallography of the bis-pyridine complex **4**, the first of its kind. While **2** and **4** and even their one-electron oxidized complexes are stable, a spontaneous dimerization of the corrole takes place in the absence of strongly bound ligands. The bis-cobalt complex of the novel corrole dimer **6** was fully characterized by spectroscopic methods and X-ray crystallography.

Keywords: cobalt · corroles · dimerization · porphyrinoids · solid-state structures

Introduction

The most important metal in corrole chemistry is cobalt for two main reasons. First, cobalt is the metal bound to the corrin cofactor in Vitamin B_{12}.[1] Second, most synthetic methodologies for the preparation of corroles rely on cobalt and triphenylphosphine, that is, most corroles are isolated as triphenylphosphine-coordinated complexes [Co(cor)PPh_3] (cor = corrole).[2] Still, the coordination chemistry of cobalt(III) corroles is quite undeveloped. For example, only five-coordinate complexes with triphenylphosphine as axial ligand [Co(cor)PPh_3] have been structurally characterized,[3] despite the general tendency of cobalt(III) complexes to be six-coordinate. In addition, the two publications that discuss the reactions of amines with [Co(cor)PPh_3] complexes differ very much in their conclusions (despite the fact that the electronic spectra of the products are virtually identical). While Conlon et al. have reported a substitution reaction as to form mono-amine cobalt(III) corroles,[4a] Adamian et al. analyzed their results as simple addition of the amines to the vacant coordination site of [Co(cor)PPh_3].[5] Using a different synthetic route, Murakami et al. have *isolated* both a four-coordinate cobalt(III) corrole and its mono-pyridine adduct and shown that the six-coordinate bis-pyridine adduct is only formed in solutions that contain excess pyridine.[4b] Another aspect that has been intensively investigated with cobalt corroles is their electrochemistry,[6] with the clear conclusion that in the absence of coordinated PPh_3 their oxidation process is irreversible. Dimeric products were obtained therefrom; however, these have not yet been fully characterized.[7]

We have recently prepared a new corrole with *meso*-pentafluorophenyl substituents (**1** in Scheme 1),[8, 9] shown that its metal complexes are more oxidation resistant than those of the previously used β-pyrrole-substituted corroles,[10] and used them as catalysts for various reactions.[11] In the



Scheme 1. Synthesis of complexes **2** and **3**. a) 1. PPh_3; 2. $Co(OAc)_2$. b) 1. $Co(OAc)_2$; 2. PPh_3.

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current investigation we have focused on the cobalt complexes of **1** with the goal of filling the above-mentioned shortcomings with regard to the reaction mechanism of (triphenylphosphine)cobalt(III) corroles with aromatic amines and the structures of the dimers. The results clearly show that aromatic amines substitute triphenylphosphine and form six-coordinate bis(amine)cobalt(III) corroles. This is demonstrated by spectroscopic methods and by X-ray crystallography of the bis-pyridine complex. The electrochemistry shows that the one-electron-oxidized bis-pyridine and mono-triphenylphosphine cobalt complexes are stable. However, in the absence of strongly bound ligands, a spontaneous dimerization of the corrole occurs and binuclear complexes are obtained. One of these novel derivatives was fully characterized by spectroscopic methods and X-ray crystallography.

Results and Discussion

Synthesis of [Co(tpfc)PPh$_3$] (2) and a dimeric, binuclear complex (3) (tpfc = 5,10,15-tris(pentafluorophenyl)corrole): As may have been expected from the previous literature about cobalt corroles, the insertion of cobalt into **1** is highly facile. Addition of $Co(OAc)_2 \cdot 4H_2O$ to a solution of **1** in ethanol results in a quite fast color change from green to red, and the reaction goes to completion at room temperature (TLC: the highly fluorescent spot of **1** disappears). When triphenylphosphine is present initially, [Co(tpfc)PPh$_3$] (**2**) is isolated in 90% yield (Scheme 1, path a). The diamagnetism of **2** (Co^{III}, low-spin d^6) allows its easy and complete characterization by NMR spectroscopy. Consistent with the C_s symmetry of **2**, there are four β-pyrrole-CH doublets in the ^{1}H NMR spectrum (Figure 1a) and two types of pentafluorophenyl groups in a ratio of 2:1 are apparent in the ^{19}F NMR spectrum. The coordinated triphenylphosphine is also evident in the NMR spectrum at high field, as a result of the diamagnetic current effect of the corrole. However, addition of triphenylphosphine *after* the metallation process is complete results in isolation of an additional product (**3**, Scheme 1, path b). The relative yields of **2** and **3** were quite variable, depending mainly on how late the triphenylphosphine was added (a more reproducible synthesis of **3** is introduced later). According to MS, **3** contains two corroles and two cobalt ions, while its NMR spectrum reveals the presence of two triphenylphosphine ligands. The diamagnetism of **3** allowed the elucidation of additional information about this interesting dimeric and binuclear complex. As may be appreciated from a comparison of the NMR spectra of **2** and **3** (Figure 1b), one β-pyrrole-CH is "missing" in **3**, leaving behind one singlet at $\delta = 8.65$ and six doublets (1H each per corrole, as well as those of the triphenylphosphine protons). This lack of symmetry within each corrole and the identity of the two corroles in **3** are also apparent in its ^{19}F NMR spectrum (not shown), which displays three different pentafluorophenyl groups rather than two as in **2** or six as would be appropriate for a less symmetrical dimer.

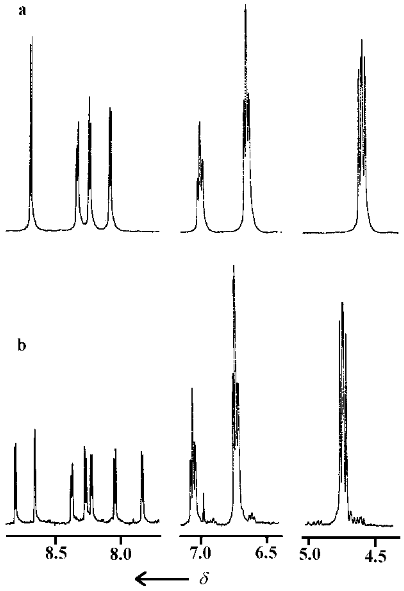


Figure 1. ^{1}H NMR spectra of the (triphenylphosphine)cobalt(III) complexes of the monomeric and dimeric corroles, **2** (a) and **3** (b), respectively.

These observations and the MS data clearly indicate that a covalent C–C bond, utilizing the same carbon from each of the monomeric subunits, attaches the two corroles to each other. In fact, two out of four possible structures can be ruled out by analyzing the coupling constants in **2** and **3**. First note that the four β-pyrrole-CH doublets (2H each) in **2** can be classified in two groups, two doublets with a large coupling constant ($J = 5.0$ Hz) and two with a small one ($J = 4.6$ Hz), while there are four doublets with $J = 5.0$ Hz and only two with $J = 4.6$ Hz in **3**. Since we have found that the size of the J values may serve for differentiation between protons on the porphyrin-like pyrrole rings B and C (large J) and the bipyrrole-like A and D rings (smaller J),[12] the fact that a smaller coupling constant is "missing" in **3** serves to indicate that the two corroles are attached to each other through either C2 or C3 (Scheme 1). However, differentiation between these two possibilities is not trivial. Fortunately, this task was achieved by X-ray crystallography as explained in a later section.

Abstract in Hebrew:

במסגרת עבודה זו הראינו שהקומפלקס של (טריפנילפוספין)קובלט(III) עם טריס(פנטאפלואורופניל)קורול (**2**) מהווה חומר מוצא מצוין לקומפלקסים שלא אופיינו בצורה מושלמת עד כה. בניגוד לקומפלקסי קובלט קורולים אחרים, אמינים ארומטיים מחליפים את הטריפנילפוספין ב- **2** ליצירת קומפלקסי ביס-אמין שש-קואורדינטיביים. ענין זה הוכח באמצעות שיטות ספקטרוסקופיות וגם כן ע"י קריסטלוגרפיה של קרני X לקומפלקס קובלט ביס-פרידין (**4**), שהוא הראשון מסוגו. בעוד ש- **2** ו- **4** ואפילו תוצרי החמצון החד-אלקטרוניים שלהם הם יציבים, מתרחשת דימריזציה ספונטנית של הקורול בהעדר ליגנדות הקשורות חזק לקובלט. הקומפלקס ביס-קובלט של הקורול הדימרי (**6**) אופיין בצורה מושלמת ע"י שיטות ספקטרוסקופיות ובקריסטלוגרפיית קרני X.

Reaction of [Co(tpfc)PPh$_3$] (2) with aromatic amines: Similar to previous observations with other cobalt corroles, gradual addition of various amines to **2** resulted in pronounced changes in the electronic spectra (Figure 2). The final spectrum was quite insensitive to the identity of the amine and excellent isosbestic points were obtained with all amines, indicating a clean transformation (no *observable* intermediates) from **2** (split Soret band: 376 and 408 nm) to the products (single Soret band at 440–444 nm and two pronounced Q-bands around 600 nm). In addition, the required amount (mol %) for completing the spectral changes was very sensitive to the particular amine. Quantitative analysis of the data for pyridine, 4-methylpyridine, and imidazole clearly revealed that the reaction is second order with respect to the amine, that is, compound **2** is transformed into bis(amine)cobalt(III) corroles, such as [Co(tpfc)(py)$_2$] (**4** in Scheme 2). Interestingly, the equilibrium constant for imidazole (29000 M^{-1}) was found to be more than three orders of magnitudes larger than that for pyridine (11.4 M^{-1}) and there is also a significant electronic effect ($K = 72.5$ M^{-1} for 4-methylpyridine). An extremely large steric effect exists for both type of amines, reducing the equilibrium constants for 2-methylpyridine and 2-methylimidazole to such an extent that prohibited reliable measurements.

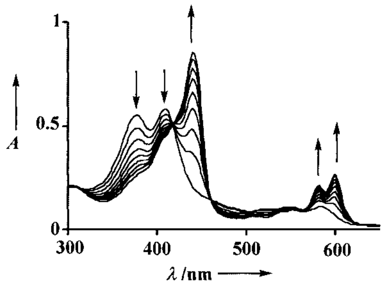


Figure 2. Changes in the electronic spectra upon the addition of increasing amounts of pyridine to a solution of **2** in CH_2Cl_2, due to its transformation into **4**.

The results for compound **2**—substitution plus addition—are quite different from the earlier mentioned conflicting reports about the reactions of other (triphenylphosphine)cobalt(III) corroles with amines: addition only versus substitution only.[4a, 5] In order to resolve these apparent contradictions and to substantiate our results, the reaction product formed from **2** and pyridine was isolated and fully characterized.

Characterization of [Co(tpfc)(py)$_2$] (4): The required bis-pyridine complex was most conveniently prepared directly from **1**, through its reaction with Co(OAc)$_2$ · 4 H$_2$O in pyridine as solvent. [Co(tpfc)(py)$_2$] (**4**) was isolated in 81 % yield, as long as small amounts of pyridine are present throughout the workup process. All spectroscopic features of **4** were identical with those obtained from the reaction of **2** with pyridine, clearly indicating substitution of the triphenylphosphine by pyridine. The presence of two pyridines per cobalt in **4** is easily determined by ^{1}H NMR spectroscopy, in which the resonances of the coordinated pyridines are located at high field due to the diamagnetic current effect of the corrole (Figure 3). Since the electronic spectra of the reaction products of **2** with the other amines are very similar to that of **4**, they may be assigned with reasonable confidence as bis(amine)cobalt(III) corroles as well.

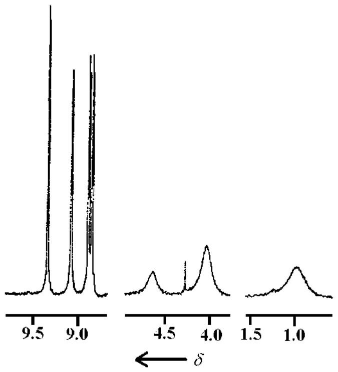


Figure 3. ^{1}H NMR spectrum of the bis(pyridine)cobalt(III) complex **4**.

More details about the structure of **4** were obtained from X-ray crystallographic analysis. The molecular structure is presented in Figure 4, showing the flatness of the corrole macrocycle and the nearly coplanar mutual alignment of the

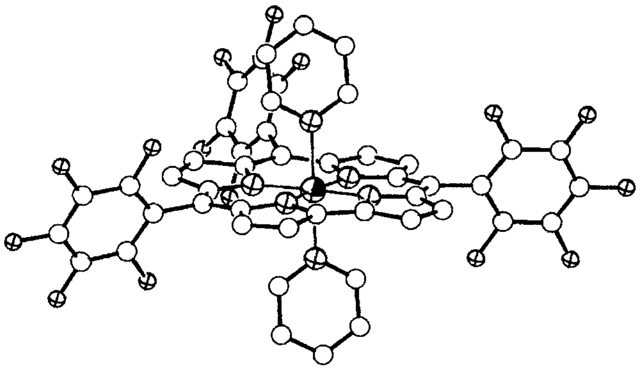
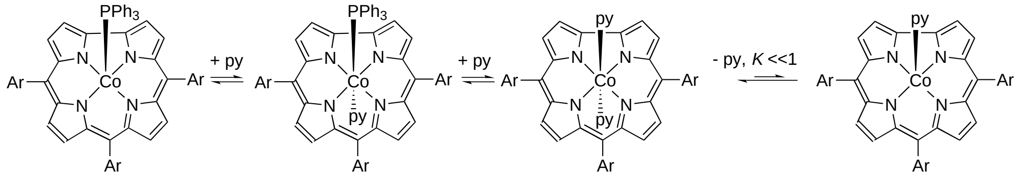


Figure 4. Molecular structure of **4**. The Co–N(pyrrole) and Co–N(pyridine) bond lengths are 1.873(4)–1.900(4) Å and 1.994(4)–1.995(4) Å, respectively. Note the nearly coplanar alignement of the two pyridyl axial ligands.



2 (not observed) **4** **5**

Scheme 2. Transformation of complex **2** into **4** and **5**.

two coordinated pyridines. The largest deviation from the mean plane defined by all the corrole atoms is as small as 0.14 Å, and the cobalt is located perfectly in the plane defined by the four inner nitrogen atoms. Both features are very similar to the recently obtained crystal structure of the bis(pyridine)iron(III) complex of **1**,[11c] but quite different from that of the previously characterized five-coordinate corrole complexes.[3] Still, the Co–N(pyrrole) bond lengths in all corrole complexes are very similar and shorter by about 0.1 Å than in porphyrins (Table 1), suggesting that corroles provide an ideal coordination core for cobalt(III). An alternative explanation could rely on the higher oxidation state of cobalt in corroles, but note that the (non-restricted) Co–N(pyridine) bond in **4** is actually somewhat longer than in [Co(oep)(py)$_2$] (oep = octaethylporphyrin).

Table 1. Comparison of selected structural parameters in **4**, **6**, and related compounds.

Compound	M–N(pyrrole) bond length range [Å]	M–X(axial ligand) bond lengths [Å]	M deviation [Å] from the N$_4$(corrole) plane	reference
4[a]	1.873–1.900	1.994, 1.994	0.002	this work
6[a]	1.868–1.899	1.989, 2.000	0.006	this work
Co(cor)PPh$_3$[b]	1.835–1.889	2.210	0.280	[3a]
	1.878–1.900	2.206	0.281	[3b]
	1.863–1.891	2.201	0.280	[3c]
Co(oec)Ph[c]	1.844–1.870	1.937	0.185	[14]
Co(tpyp)[d]	1.988–2.002	2.290	0.000	[15]
Co(oep)(py)$_2$[e]	1.948–1.968	1.956, 1.970	0.002	[16]
Fe(tpfc)(py)$_2$[f]	1.865–1.923	2.028, 2.032	0.001	[11c]

[a] M refers to a six-coordinate Co^{III} in [Co(tpfc)(py)$_2$]. [b] M refers to a five-coordinate Co^{III}. [c] M refers to a five-coordinate Co^{IV}. [d] M refers to a six-coordinate Co^{II} in a self-assembled coordination polymer of tetrapyridylporphyrin. [e] M refers to a six-coordinate Co^{II} in an octaethylporphyrin system. [f] M refers to a six-coordinate Fe^{III}.

One last important finding about **4** was obtained during attempted measurements of its absorption coefficient. As shown in Figure 5, the response to dilution was not identical at all wavelengths, most easily seen by comparing the relative heights of the maxima at 390 and 440 nm. Addition of pyridine or triphenylphosphine at any stage induced spectral changes corresponding to transformation to **4** and **2**, respectively; this strongly indicates that **4** dissociates to the mono-pyridine complex **5** (+ pyridine) at high dilution (Scheme 2, right part). We also note the spectral similarity of the developing band at 390 nm to the mono-pyridine cobalt corrole isolated by Murakami et al. (λ_{max} = 383 nm).[4b] The dilution data was further used for determination of the dissociation constant of six-coordinate **4** to five-coordinate **5** (+ pyridine) as 3.3×10^{-5} M in CH_2Cl_2. This low value is in contrast to observations with octaalkyl corrole complexes of cobalt(III) and iron(III), in which six-coordinate complexes are only obtained in the presence of very large excess of ligands (the dissociation constant of [Co(oec)(py)$_2$] is 2.6×10^{-2} M).[4b] Therefore, it may be concluded that the metal complexes of the electron-poor **1** are much more Lewis-acidic than those of the electron-rich complexes of octaalkyl corroles.

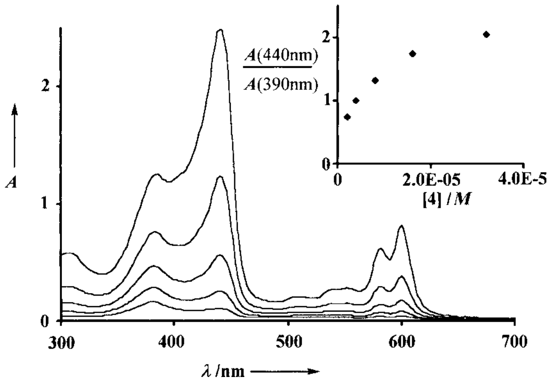


Figure 5. The nonlinear effect of dilution on the electronic spectrum of the isolated bis(pyridine)cobalt(III) complex **4**, due to its equilibrium with **5**.

Electrochemistry of [Co(tpfc)PPh$_3$] (2) and [Co(tpfc)(py)$_2$] (4): The cyclic voltammogram (CV) of **2** reveals that its first oxidation ($E_{1/2}$ = 0.70 V) and second reduction ($E_{1/2}$ = −1.28 V) processes are reversible, while the first reduction is not (Figure 6). The latter observation is analogous to previous findings with triphenylphosphine-coordinated cobalt complexes of other corroles.[6] Based on the analysis of Kadish and co-workers,[5] we assign the first reduction of **2** to a Co^{III}/Co^{II} couple and the irreversibility of the process to dissociation of triphenylphosphine from the cobalt(II) complex ($[Co(tpfc)PPh_3]^- \rightarrow [Co(tpfc)]^- + PPh_3$). The first oxidation ($E_{1/2}$ = 0.58 V) and second reduction ($E_{1/2}$ = −1.25 V) processes are also reversible for the bis-pyridine complex **4**. However, the first reduction peak (irreversible process, E_{pa}) of **4** is strongly affected by the addition pyridine moving gradually from −0.2 V with no external pyridine to −0.7 V with 0.5 M pyridine. This observation is in excellent agreement with the earlier discussed dissociation of pyridine from **4**. The virtually identical second reduction potentials of **4** and **2** further suggest that upon one-electron reduction of **4** the affinity to pyridine coordination is very much reduced. The most evident explanation is that identical species are involved therein, that is, *both* pyridines are dissociated from the one-electron reduced **4** (and PPh$_3$ from one-electron reduced **2**) to form

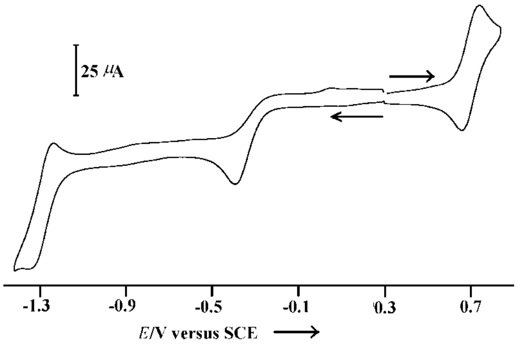
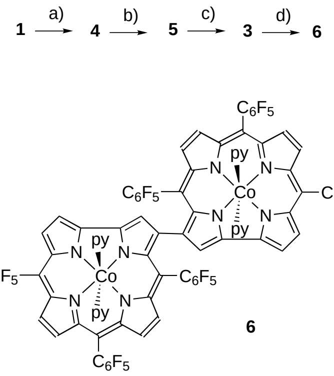


Figure 6. The cyclic voltammogram of the (triphenylphosphine)cobalt(III) corrole **2**, in 0.1 M TBAP/CH_3CN solution at a scan rate of 0.1 V s^{-1}.

square planar [Co(tpfc)]$^-$. Within the current investigations no efforts were devoted to identify the reduction site (metal vs corrole) of the second reduction process, but in order to corroborate the electrochemical analyses we decided to isolate also the mono-pyridine complex **5**. This resulted in the novel observation discussed in the next section.

Preparation of dimeric, binuclear cobalt corroles 3 and 6: Inspired by the above-mentioned results for the bis(pyridine)cobalt(III) corrole **4**, we considered that its treatment by column chromatography in the absence of coordinating ligands in the elution mixture should be a facile methodology for preparation of the mono-pyridine complex **5** (Scheme 3). This was indeed true, but upon standing for recrystallization (with no coordinating ligand in the solvent mixture) we noticed that **5** was transformed to other species (TLC). Addition of triphenylphosphine after complete disappearance of **5**, resulted in isolation (in 65 % relative to **1**) of the dimer **3**. Since we were not successful in growing X-ray quality crystals of **3**, its coordinated triphenylphosphine groups were substituted by pyridine in a fashion similar to the transformation of **2** to **4**. This resulted in isolation of **6** (78 % yield), whose ^{1}H NMR spectrum (Figure 7) is similar to that of **3** (Figure 1), but with four coordinated pyridines instead of the two triphenylphosphines in **3**. The other structural details of **6** were elucidated by X-ray crystallography.



Scheme 3. Synthesis of complex **6**. a) Co(OAc)$_2$, pyridine; b) column chromatography; c) air, PPh$_3$ (65 % yield from **1**); d) pyridine (78 % yield from **3**).

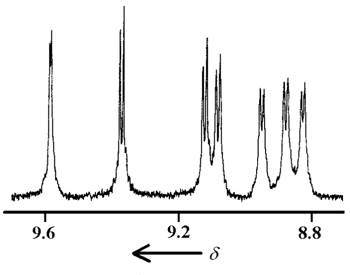


Figure 7. Partial ^{1}H NMR spectrum of **6**, the pyridine-coordinated cobalt(III) complex of the dimeric corrole.

Characterization of the dimeric, binuclear cobalt corrole 6: X-ray quality crystals of **6** were obtained by recrystallization from a heptane/benzene mixture, and its molecular structure is shown in Figure 8. First note that it has a C_2 symmetry axis. The two corroles are attached to each other by a 1.48 Å C–C bond, utilizing the same carbon on each corrole (C3), and the dihedral angle between them is 45°.

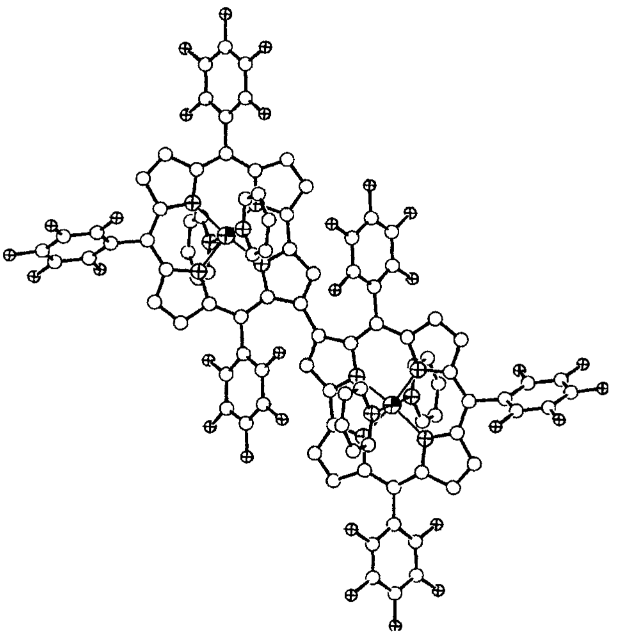


Figure 8. Molecular structure of **6**. The Co–N(pyrrole) and Co–N(pyridine) bond lengths are within 1.868(6)–1.899(5) Å and 1.989(6)–2.000(6) Å, respectively. The C(sp^2)–C(sp^2) link between the two parts of the dimer is 1.479(13) Å, while the twist angle between the two corrole rings is 45.0(2)°.

This is in excellent agreement with the earlier discussed NMR analysis, which could not be used to differentiate between the attachment through C2 or C3. Interestingly, the structural aspects of each cobalt corrole subunit are remarkably similar to that of the monomeric complex **4**. This includes the almost perfect in-plane location of the metal, the mutually parallel arrangement of the two pyridines, and all the Co–N bond lengths (Figure 8 and Table 1).

The cobalt corrole dimer with the 45° twist about the connecting bond has a compact, yet sterically unhindered structure, in which the pentafluorobenzene ring of one corrole is aligned along the missing-carbon C1–C19 side of the other corrole ring. It is conceivable that the two rings cannot be similarly attached to each other through the porphyrin-like C7 or C8 carbon atoms due to prohibitive hindrance between the C$_6$F$_5$ substituents. However, the preferred binding through C3 rather than through C2 (which appears to be the least constrained option) is intriguing and requires an explanation that is not based on structural arguments. Fortunately, we have recently carried out DFT calculations on the gallium complex of **1** (**7**), as well as on its one-electron oxidation product (**7**$^+$, a gallium corrole π radical cation).[10d] The calculated gross atomic spin populations on C3 were found to be much larger than those on C2, in the HOMO of both **7** and **7**$^+$. As far as these calculations are relevant to the cobalt complexes of **1**, the exclusive C3–C3 bond formation suggests that electronic factors are responsible for the selectivity. As for the mechanism of the dimerization, we note that **3** is only obtained in the absence of coordinating ligands. Accordingly, we suspect that the four-coordinate cobalt complex is not stable with regard to corrole oxidation, and that the thus obtained π radical cation complex is attacked by the electron-rich corrole of non-oxidized material. This hypothesis is in agreement with the observations of Kadish et al. on [Co(oec)], in which oxidative dimerization is only obtained in the absence of coordinating ligands.[7]

As mentioned earlier, dimeric products were also reported with metal complexes (cobalt, nickel, and copper) of β-pyrrole-alkylated corroles, but their structures have not been fully elucidated.[7] Other dimeric and binuclear complexes include the recently reported metal–metal bound ruthenium complex and spacer-bridged corroles.[13] However, the herein described compounds **3** and **6** are substantially different from all these complexes by means of their direct carbon–carbon bond. The electronic spectrum of **6** suggests strong electronic interactions between its corroles, manifested in a 40 nm red-shift and large intensification of the lowest energy absorption band relative to the monomeric bis(pyridine)cobalt corrole **4** (Figure 9). These indications will be addressed in future studies, in which the emphasis will be devoted to the fundamental physical properties of these intriguing complexes.

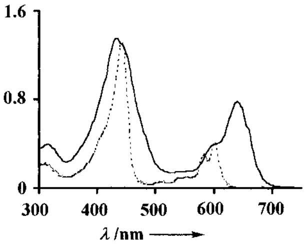


Figure 9. The electronic spectra of the bis(pyridine)cobalt(III) complexes of the monomeric (**4**, dashed line) and dimeric (**6**, full line) corroles, at identical concentrations in 1 % pyridine/CH_2Cl_2 solutions.

Conclusion

This study has revealed the following quite fundamental aspects of cobalt corroles. The reactions of aromatic amines with the triphenylphosphine-coordinated cobalt corrole **2** was proven to be a substitution reaction, through the isolation and full characterization of one such complex (**4**, the first of its kind). The relatively short Co–N(corrole) bond lengths and their insensitivity to other structural aspects strongly implies that corroles are ideally suited for cobalt chelation. However, stable complexes are only obtained when the cobalt(III) ion is coordinated by either one triphenylphosphine or two amines (in addition to coordination to the four nitrogen atoms of the corrole). In the absence of the above-mentioned ligands, the cobalt complex of **1** undergoes a highly selective C–C dimerization. One of these novel complexes (**6**) was fully characterized and will serve as starting material for investigating its properties in various advanced applications.

Experimental Section

All the standard experimental details are reported in one of our most recent publication.[11c]

Synthesis of 2: A solution of **1** (20 mg, 25 μmol) and dry NaOAc (30 mg, 366 μmol) in EtOH (10 mL) was stirred for 5 min, after which $Co(OAc)_2 \cdot 4H_2O$ (30 mg, 120 μmol) and PPh_3 (50 mg, 191 μmol) were added. After stirring for 1.5 h at 25 °C, the solvent was evaporated and the residue was passed through a column of silica with CH_2Cl_2/hexane (1:8) as eluent. Following recrystallization from CH_2Cl_2/hexane, **2** was obtained in 90 % yield (25 mg, 22.5 μmol). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 8.68$ (d, ^3J(H,H) = 4.6 Hz, 2H; β-pyrrole H), 8.33 (d, ^3J(H,H) = 5.0 Hz, 2H; β-pyrrole H), 8.24 (d, ^3J(H,H) = 5.0 Hz, 2H; β-pyrrole H), 8.08 (d, ^3J(H,H) = 4.6 Hz, 2H; β-pyrrole H), 7.00 (t, ^3J(H,H) = 8 Hz, 3H; *para*-H of PPh_3), 6.65 (t, ^3J(H,H) = 8 Hz, 6H; *meta*-H of PPh_3), 4.58 (d, ^3J(H,H) = 8 Hz, ^3J(P,H) = 12 Hz, 6H; *ortho*-H of PPh_3); ^{19}F NMR (188 MHz, $CDCl_3$, 25 °C): $\delta = -137.2$ (dd, ^3J(F,F) = 23 Hz, ^4J(F,F) = 9 Hz, 2F; *ortho*-F), −137.5 (dd, ^3J(F,F) = 23 Hz, ^4J(F,F) = 9 Hz, 1F; *ortho*-F), −138.5 (dd, ^3J(F,F) = 23 Hz, ^4J(F,F) = 9 Hz, 2F; *ortho*-F), −138.8 (dd, ^3J(F,F) = 23 Hz, ^4J(F,F) = 9 Hz, 1F; *ortho*-F), −154.1 (t, ^3J(F,F) = 23 Hz, 3F; *para*-F), −162.4 (m, 6F; *meta*-F); UV/Vis (CH_2Cl_2): λ_{max} ($\varepsilon \times 10^{-4}$) = 376 (6.3), 408 (6.7), 548 (1.1), 584 nm (1.2 $mol^{-1}dm^3cm^{-1}$); MS (DCI^+): *m*/*z* (%): 1115.2 (16) $[M+H]^+$, 852.5 (100) $[M+H-PPh_3]^+$; MS (DCI^-): *m*/*z* (%): 850.5 (100) $[M-PPh_3]^-$.

Synthesis of 3: A solution of **1** (20 mg, 25 μmol) and $Co(OAc)_2 \cdot 4H_2O$ (30 mg, 120 μmol) in pyridine (5 mL) was heated at 100 °C for 15 min. The solvent was evaporated and the residue was passed through a column of silica with CH_2Cl_2/hexane (1:8) as eluent. During chromatography, the green bis-pyridine product **4** turns red, due to formation of the mono-pyridine cobalt corrole **5**. Compound **5** was isolated and left in a 10 mL solution of hexane/CH_2Cl_2 for two days, during which the color changed from red to green. At this stage, PPh_3 (50 mg, 191 μmol) was added and the residue was passed through a column of silica with CH_2Cl_2/hexane (1:4) as eluent, providing **3** in 65 % yield (18 mg, 8.1 μmol). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 8.80$ (d, ^3J(H,H) = 4.6 Hz, 2H; β-pyrrole H), 8.65 (s, 2H; β-pyrrole H), 8.37 (d, ^3J(H,H) = 5.0 Hz, 2H; β-pyrrole H), 8.26 (d, ^3J(H,H) = 5.0 Hz, 2H; β-pyrrole H), 8.22 (d, ^3J(H,H) = 4.6 Hz, 2H; β-pyrrole H), 8.04 (d, ^3J(H,H) = 5.0 Hz, 2H; β-pyrrole H), 7.83 (d, ^3J(H,H) = 5.0 Hz, 2H; β-pyrrole H), 7.05 (t, ^3J(H,H) = 7.3 Hz, 6H; *para*-H of PPh_3), 6.72 (t, ^3J(H,H) = 8 Hz, 12H; *meta*-H of PPh_3), 4.73 (d, ^3J(H,H) = 8 Hz, ^3J(P,H) = 12 Hz, 12H; *ortho*-H of PPh_3); ^{19}F NMR (188 MHz, $CDCl_3$, 25 °C): $\delta = -136.7$ (m, 4F; *ortho*-F), −137.3 (dd, ^3J(F,F) = 25 Hz, ^4J(F,F) = 7 Hz, 2F; *ortho*-F), −138.2 (m, 4F; *ortho*-F), −139.0 (dd, ^3J(F,F) = 25 Hz, ^4J(F,F) = 7 Hz, 1F; *ortho*-F), −154.1 (m, 4F; *para*-F), −155.6 (t, ^3J(F,F) = 23 Hz, 2F; *para*-F), −162.1 (m, 4F; *meta*-F), −162.8 (m, 4F; *meta*-F), −163.8 (m, 2F; *meta*-F), −165.2 (m, 2F; *meta*-F); UV/Vis (CH_2Cl_2): λ_{max} ($\varepsilon \times 10^{-4}$) = 380 (7.9), 416 (8.3), 566 (2.2), 610 nm (2.6 $mol^{-1}dm^3cm^{-1}$); MS (DCI^-): *m*/*z* (%): 1703.4 (50) $[M-2PPh_3]^-$, 851.9 (100) $[(M-2PPh_3)/2]^-$.

Synthesis of 4: A solution of **1** (20 mg, 25 μmol) and $Co(OAc)_2 \cdot 4H_2O$ (30 mg, 120 μmol) in pyridine (5 mL) was heated at 100 °C for 15 min. The solvent was evaporated, and the green residue was passed through a column of silica with CH_2Cl_2/hexane/pyridine (1:4:0.01) as eluent. After recrystallization from CH_2Cl_2/hexane/pyridine (1:1:0.01), **4** was obtained in 81 % yield (20.5 mg, 20.3 μmol). ^1H NMR (400 MHz, $[D_6]$benzene, 25 °C) $\delta = 9.32$ (d, ^3J(H,H) = 4.4 Hz, 2H; β-pyrrole H), 9.06 (d, ^3J(H,H) = 4.8 Hz, 2H; β-pyrrole H), 8.87 (d, ^3J(H,H) = 4.8 Hz, 2H; β-pyrrole H), 8.83 (d, ^3J(H,H) = 4.4 Hz, 2H; β-pyrrole H), 4.63 (brs, 2H; *para*-H of pyridine), 4.03 (brs, 4H; *meta*-H of pyridine), 0.97 (brs, 4H; *ortho*-H of pyridine); ^{19}F NMR (188 MHz, $[D_6]$benzene, 25 °C): $\delta = -139.2$ (m, 6F; *ortho*-F), −153.8 (t, ^3J(F,F) = 23 Hz, 3F; *para*-F), −163.0 (m, 4F; *meta*-F), −163.4 (m, 2F; *meta*-F); UV/Vis (CH_2Cl_2, 1 % pyridine): λ_{max} ($\varepsilon \times 10^{-4}$) = 440 (10.8), 582 (2.6), 600 nm (3.4 $mol^{-1}dm^3cm^{-1}$); MS (DCI^+): *m*/*z* (%): 854.9 (100) $[MH-2py]^+$; MS (DCI^-): *m*/*z* (%): 852.9 (100) $[M-2py]^-$.

Synthesis of 6: Pyridine (1 mL) and **3** (15 mg, 6.7 μmol) were dissolved in CH_2Cl_2 (3 mL) and stirred for 5 min. The solvent was passed through a column of silica with CH_2Cl_2/hexane/pyridine (1:4:0.01) as eluent. Compound **6** was obtained in 78 % yield (10.5 mg, 5.2 μmol) after recrystallization from CH_2Cl_2/hexane/pyridine (1:1:0.01). ^1H NMR (400 MHz, $[D_6]$benzene, 25 °C): $\delta = 9.58$ (d, 2.3 Hz, 2H; β-pyrrole H), 9.37 (d, ^3J(H,H) = 4.2 Hz, 2H; β-pyrrole H), 9.12 (d, ^3J(H,H) = 4.6 Hz, 2H; β-pyrrole H), 9.08 (d, ^3J(H,H) = 4.8 Hz, 2H; β-pyrrole H), 8.95 (d, ^3J(H,H) = 4.4 Hz, 2H; β-pyrrole H), 8.87 (d, ^3J(H,H) = 4.9 Hz, 2H; β-pyrrole H), 8.82 (d, ^3J(H,H) = 4.0 Hz, 2H; β-pyrrole H), 5.16 (brs, 2H; *para*-H of pyridine), 4.71 (brs, 2H; *para*-H of pyridine), 4.56 (brs, 4H; *meta*-H of pyridine), 4.16 (brs, 4H; *meta*-H of pyridine), 1.33 (brs, 8H; *ortho*-H of pyridine); ^{19}F NMR (188 MHz, $[D_6]$benzene, 25 °C): $\delta = -136.1$ (dd, ^3J(F,F) = 34 Hz, ^4J(F,F) = 7 Hz, 2F; *ortho*-F), −139.0 (m, 10F; *ortho*-F), −153.6 (t, ^3J(F,F) = 23 Hz, 2F; *para*-F), −153.8 (t, ^3J(F,F) = 23 Hz, 2F; *para*-F), −156.0 (t, ^3J(F,F) = 23 Hz, 2F; *para*-F), −163.0 (m, 8F; *meta*-F), −164.4 (m, 2F; *meta*-F), −165.0 (t, ^3J(F,F) = 25 Hz, 2F; *meta*-F); UV/Vis (CH_2Cl_2, 1 % pyridine): λ_{max} ($\varepsilon \times 10^{-4}$) = 314 (3.1), 432 (10.8), 600 (3.1), 640 nm (6.3 $mol^{-1}dm^3cm^{-1}$); MS (DCI^-): *m*/*z* (%): 1702.2 (50) $[M-4py]^-$, 851.9 (100) $[(M-4py)/2]^-$.

X-ray crystallography of 4 and 6: X-ray quality crystals of **4** and **6** were obtained by slow recrystallization from mixtures of benzene/heptane/pyridine (1:1:0.01).

Crystal structure analyses: Corroles **4** and **6** yielded tiny single crystals (mostly twinned) that contained disordered solvent and diffracted poorly. Therefore, their diffraction data were measured on a Nonius KappaCCD diffractometer at low temperature (ca. 110 K) in order to minimize atomic thermal displacements and to increase the signal-to-noise ratio. The crystal structures were solved and refined by standard crystallographic techniques.

Crystal data for ***4***: $C_{47}H_{18}CoF_{15}N_6 \cdot 0.5\,C_7H_{16}$, $M_r = 1060.7$, orthorhombic, space group $P2_12_12_1$ (No. 19), $a = 8.420(1)$, $b = 16.468(1)$, $c = 32.929(1)$ Å, $V = 4566.0(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.543\ \mathrm{g\,cm^{-3}}$, $2\theta_{max} = 50.7°$, 8093 unique reflections. Final $R1 = 0.060$ for 6162 reflections with $F > 4\sigma(F)$, $R1 = 0.090$ and $wR2 = 0.152$ for all data. The crystalline compound represents a racemic twin, and the heptane solvent is severely disordered in the lattice.

Crystal data for ***6***: $C_{47}H_{17}CoF_{15}N_6 \cdot 0.5\,C_6H_6 \cdot 2\,H_2O$, $M_r = 1084.7$, monoclinic, space group $C2/c$ (No. 15), $a = 28.348(1)$, $b = 8.953(1)$, $c = 35.960(1)$ Å, $\beta = 93.90(1)°$, $V = 9105.5(9)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.582\ \mathrm{g\,cm^{-3}}$, $2\theta_{max} = 50.2°$, 6302 unique reflections. Final $R1 = 0.066$ for 3392 reflections with $F > 6\sigma(F)$, $R1 = 0.160$ and $wR2 = 0.154$ for all data. Molecules of the dimeric cobalt corrole were located on symmetry axes of twofold rotation. The benzene solvent was positioned on centers of inversion; molecules of water appeared to be disordered within the intermolecular voids.

In both structures the pentafluorophenyl substituents exhibited a large-amplitude wagging motion, which reflects on their partial rotational disorder that could not be resolved. This disorder, particularly in the structure of **6**, caused a relatively large percentage of very weak reflections that could be accurately measured. As a result, the *R* factor for the data set that contains the weak reflections buried in the intensity background is relatively high. The considerably lower *R* factor for the significant data (above the intensity threshold) confirms the correctness of the structure.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 162497 (**4**) and 162498 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

The equilibrium constants (*K*): The equilibrium constants (*K*) for the reactions of [Co(tpfc)PPh$_3$] (**2**) with amines [Eq. (1), Am = amine] were measured at 25 °C in CH_2Cl_2 with the following initial concentrations: **2**, $\sim 10^{-5}$ M; pyridine and γ-picoline, in the range of 10^{-3}–10^{-4} M; imidazole, in the range of 10^{-5}–10^{-6} M. The concentrations of [Co(tpfc)(amine)$_2$] ([AD]) as a function of the amine concentration were calculated from Equation (2), in which OD_0 is the initial absorption (of **2**) and OD is the absorption measured at any given amine concentration.

$$[\mathrm{Co(tpfc)PPh_3}]\ (\mathbf{2}) + 2\,\mathrm{amine\ (A)} \rightleftharpoons [\mathrm{Co(tpfc)(Am)_2}]\ (\mathrm{AD}) + \mathrm{PPh_3} \qquad (1)$$

$$K = [\mathrm{AD}][\mathrm{PPh_3}]/[\mathbf{2}][\mathrm{A}]^2 = [\mathrm{AD}]^2/([\mathbf{2}]_0 - [\mathrm{AD}])([\mathrm{A}]_0 - 2[\mathrm{AD}])^2 \qquad (1a)$$

$$[\mathrm{AD}] = (\mathrm{OD_0} - \mathrm{OD})/(\varepsilon(\mathbf{2}) - \varepsilon(\mathrm{AD})) = \Delta\mathrm{OD}/\Delta\varepsilon \qquad (2)$$

At 440 nm, $\varepsilon(\mathbf{2}) = 27000\ \mathrm{M^{-1}cm^{-1}}$ and the ε(AD) for [Co(tpfc)(py)$_2$], [Co(tpfc)(imidazole)$_2$], and [Co(tpfc)(γ-picoline)$_2$] are 108000, 114000, and 116000 $\mathrm{M^{-1}cm^{-1}}$, respectively. The ε(AD) were measured by adding enough amine to **2**, as to assure its full conversion to the bis-amine complex.

The dissociation constant (K_{diss}): The dissociation constant (K_{diss}) of [Co(tpfc)(py)$_2$] (**4**) to [Co(tpfc)(py)] (**5**) [Eq. (3)] was measured by

$$[\mathrm{Co(tpfc)(py)_2}] \rightleftharpoons [\mathrm{Co(tpfc)(py)}] + \mathrm{py} \qquad (3)$$

monitoring the changes in the absorption at 440 nm as a function of the initial concentration of **4** ([**4**]$_0$) [Eqs. (4)–(7)]. OD_0 is the calculated absorption that would have been obtained if there was no dissociation of **4** ($\varepsilon(\mathbf{4}) = 108000\ \mathrm{M^{-1}cm^{-1}}$) to **5** and OD is the experimental value at given initial concentrations of **4**. The value for $\varepsilon(\mathbf{5})$ is not known, but can be resolved by the utilization of the linear Equation (7). From the data at 25 °C in CH_2Cl_2, $K_{diss} = 3.33 \times 10^{-5}$ M was obtained.

$$K_{diss} = [\mathrm{py}][\mathbf{5}]/[\mathbf{4}] \qquad (4)$$

$$[\mathbf{5}] = [\mathrm{py}] = (\mathrm{OD_0} - \mathrm{OD})/(\varepsilon(\mathbf{5}) - \varepsilon(\mathbf{4})) = \Delta\mathrm{OD}/\Delta\varepsilon \qquad (5)$$

$$[\mathbf{4}] = [\mathbf{4}]_0 - [\mathbf{5}] = [\mathbf{4}]_0 - \Delta\mathrm{OD}/\Delta\varepsilon \qquad (6)$$

$$[\mathbf{4}]_0/\Delta\mathrm{OD} = \Delta\mathrm{OD}/(K_{diss}\Delta\varepsilon^2) + 1/(\Delta\varepsilon) \qquad (7)$$

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