Inorg. Chem. **2000,** *39,* 2704−2705

Coordination Chemistry of the Novel 5,10,15-Tris(pentafluorophenyl)corrole: Synthesis, Spectroscopy, and Structural Characterization of Its Cobalt(III), Rhodium(III), and Iron(IV) Complexes

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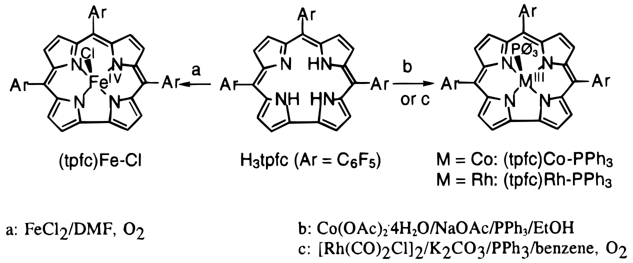
Received November 18, 1999

We have most recently reported the first one-pot synthesis of corroles—macrocycles related to both hemes (porphyrins) and vitamin B$_{12}$ (corrin)—from commercially available precursors.[1,2] In addition, we have demonstrated that the metal complexes of the leading corrole (H$_3$tpfc,[3] Scheme 1) are high-potential catalysts for the activation of hydrocarbons.[4] We now report the synthesis and some spectroscopic features of the cobalt(III), rhodium(III), and iron(IV) complexes of H$_3$tpfc (Scheme 1), together with the X-ray structures of the last two complexes.

The insertion of iron into H$_3$tpfc was achieved by its heating with excess FeCl$_2$ in DMF, evaporation of the solvent, addition of dry benzene, filtration, and repeated evaporation. ^{1}H NMR examination of a benzene-d_6 solution of fresh material revealed the presence of both iron(III) and iron(IV) corrole. The assignment of the iron(III) oxidation state is based on the low-field signals of the pyrrole hydrogens (8.4, 11.2, and 40.0 pmm), which is highly characteristic of complexes with unpaired electrons in the $d_{x^2-y^2}$ orbital.[5] Slow diffusion of *n*-heptane into a benzene solution afforded X-ray quality single crystals of the benzene−solvate of the iron(IV) corrole, (tpfc)Fe−Cl (Figure 1).[6] For preparative purposes, the solid material was dissolved in CH$_2$Cl$_2$, which caused immediate oxidation to the iron(IV) species, as previously observed by Vogel and co-workers for a different iron corrole.[7] Extensive washing with basic water resulted in formation of the μ-oxoiron(IV) corrole dimer (identified by its diamagnetic NMR),[7] which was then treated with HCl/H$_2$O and evaporated to dryness. Recrystallization from solutions of acid washed CH$_2$Cl$_2$ and hexanes affords the pure monomeric (chloro)iron(IV) corrole, whose ^{1}H NMR spectrum is shown in Figure 1.

The insertion of cobalt into H$_3$tpfc was very facile (Scheme 1, path b), as indicated by a fast color change from green (the deprotonated corrole) to red upon the addition of the cobalt salt. The product was isolated in almost quantitative yields and identified as the triphenylphosphine-coordinated cobalt(III) corrole, (tpfc)Co−PPh$_3$. In particular, the NMR spectrum (Figure 1s) is readily indicative of both the diamagnetic Co(III) oxidation state and the coordinated ligand. These are reflected by the sharp NMR signals of the corrole's β-pyrrole hydrogens (8−9 ppm) and the strongly shifted resonances (4.5−7 ppm) of the triphenylphosphine (due to the diamagnetic ring current effect of the corrole).

Scheme 1. Synthesis of the Cobalt(III), Rhodium(III), and Iron(IV) Complexes of H$_3$tpfc



Insertion of rhodium into H$_3$tpfc was achieved by its heating with an excess of [Rh(CO)$_2$Cl]$_2$ in benzene in the presence of triphenylphosphine and K$_2$CO$_3$. The reaction was continued until TLC examination indicated quantitative disappearance of starting material. One main red product was received after chromatography, together with only traces of two yet unidentified green compounds and unreacted corrole. The new red complex was characterized as (tpfc)Rh−PPh$_3$ on the basis of the similarity of its NMR to that of (tpfc)Co−PPh$_3$ and by X-ray crystallography (Figure 2).

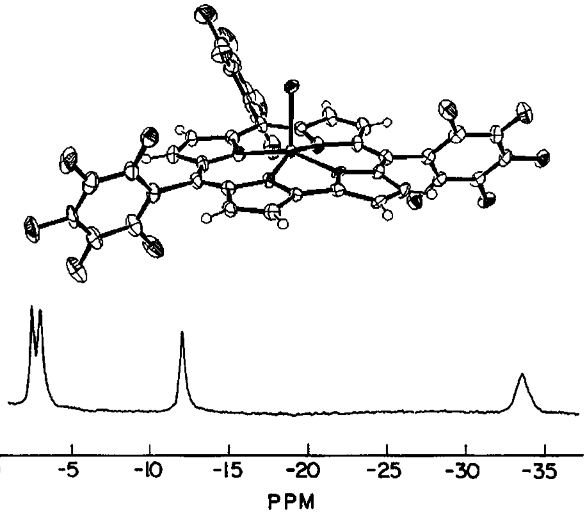


Figure 1. ^{1}H NMR spectrum (in benzene-d_6 at room temperature) and an ORTEP view of the X-ray crystal structure of the (chloro)iron(IV) corrole, (tpfc)Fe−Cl.

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(1) Gross, Z.; Galili, N.; Saltsman, I. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1427.

(2) For an excellent recent review about corroles, see the following. Sessler, J. L.; Weghorn, S. J. *Expanded, Contracted, & Isomeric Porphyrins*; Pergamon: Oxford, 1997; Chapter 1.

(3) (a) H$_3$tpfc is now commercially available from Strem Chemicals (Illinois). (b) Patent pending application no.126426 (Gross, Z.; Technion).

(4) Gross, Z.; Simkhovich, L.; Galili, N. *J. Chem. Soc., Chem. Commun.* **1999**, 599.

(5) La Mar, G. N.; Walker, F. A. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. IV, Chapter 2, pp 61−157.

(6) Crystal data for (tpfc)Fe−Cl: $C_{37}H_8ClF_{15}FeN_4 \cdot C_6H_6$, $M_r = 962.88$, monoclinic, space group $P2_1/c$, $a = 17.889(1)$ Å, $b = 14.130(1)$ Å, $c = 15.276(1)$ Å, $\beta = 99.65(1)°$, $V = 3806.7(4)$ Å^3, $Z = 4$, $T = 117$ K, $D_{calc} = 1.680$ g cm^{-3}, $F(000) = 1912$, μ(Mo Kα) = 0.58 mm^{-1}, crystal size ∼0.30 mm × 0.25 mm × 0.10 mm, $2\theta_{max} = 46.5°$, 5446 unique reflections, 577 refined parameters, R1 = 0.091 for 4388 observations with $F_o > 4\sigma(F_o)$, R1 = 0.109 (wR2 = 0.249) for all unique data. A number of residual electron density peaks (>1.0 e Å^{-3}) were found near the Fe ion in the corrole center.

(7) Vogel, E.; Will, S.; Tilling, A. S.; Neumann, L.; Lex, J.; Bill, E.; Trautwein, A. X.; Wieghardt, K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 731.

10.1021/ic991342c CCC: $19.00

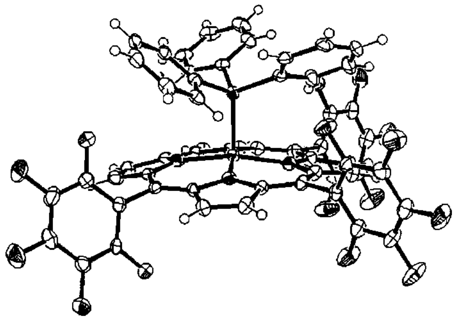

Figure 2. ORTEP view of the X-ray crystal structure of the triphenylphosphine-coordinated rhodium(III) corrole, (tpfc)Rh−PPh_3.

The structures of the iron and rhodium complexes are quite different, despite the fact that both complexes are pentacoordinated.[8] While the corrole ring is quite planar in (tpfc)Fe−Cl (the largest deviation out of the 23-atom plane is ≤0.17 Å, see Figure 3a), it is clearly domed in (tpfc)Rh−PPh_3. This can easily be seen in the latter complex from the negative deviations of the N atoms and the Rh ion from the 23-atom plane, while most of the ring C atoms display positive (i.e., in the opposite direction) deviations from this plane (Figure 3b). Further indication of this effect is provided by comparing the out-of-plane displacements of the metal ions with respect to the entire corrole ring and with the plane defined by the four pyrrole nitrogens. The respective displacements of Fe from these two planes are nearly the same, 0.4034(11) and 0.3670(11) Å, while that of Rh is 0.4693(5) Å from the corrole but only 0.2763(5) Å from the N_4 plane. The metal−nitrogen bonds are very long in (tpfc)Rh−PPh_3, the average Rh−N bond length of 1.968 Å being longer than for any other structurally characterized metallocorrole.[2,9] On the other hand, both Fe−Cl (2.238 Å) and Fe−N (average) (1.901 Å) bond lengths are quite short in (tpfc)Fe−Cl, even when compared to the only previously characterized iron(IV) corrole, (oec)Fe−Cl (Fe−Cl 2.256 Å, Fe−N (average) 1.906 Å).[7] The short Fe−N bonds, together with the quite large dihedral angles of the aryl groups with the corrole (62.7(2)°, 64.4(2)°, and 73.1(2)° for the three C_6F_5 rings), are all consistent with the Fe(IV) formulation. In the alternative formulation of $(\text{tpfc}^{\bullet+})\text{Fe}^{\text{III}}$−Cl, the expectations would be of larger Fe−N bonds and smaller dihedral angles.[10] Also, a comparison of the C−C bond lengths in the crystal structures of H_3(tpfc),[11] (tpfc)Rh−PPh_3, and (tpfc)Fe−Cl reveals no major differences (which might have been expected if the corrole ring in (tpfc)Fe−Cl is oxidized). In all complexes the average C−C bond lengths are similar (1.404, 1.410, and 1.405 Å, respectively), which may be further divided into short $C_{\beta\text{-pyrrole}}-C_{\beta\text{-pyrrole}}$ bonds (1.36 ± 0.02, 1.36 ± 0.01, and 1.356 ± 0.01, respectively) and long bonds (1.415 ± 0.04, 1.423 ± 0.026, and 1.418 ± 0.043, respectively).

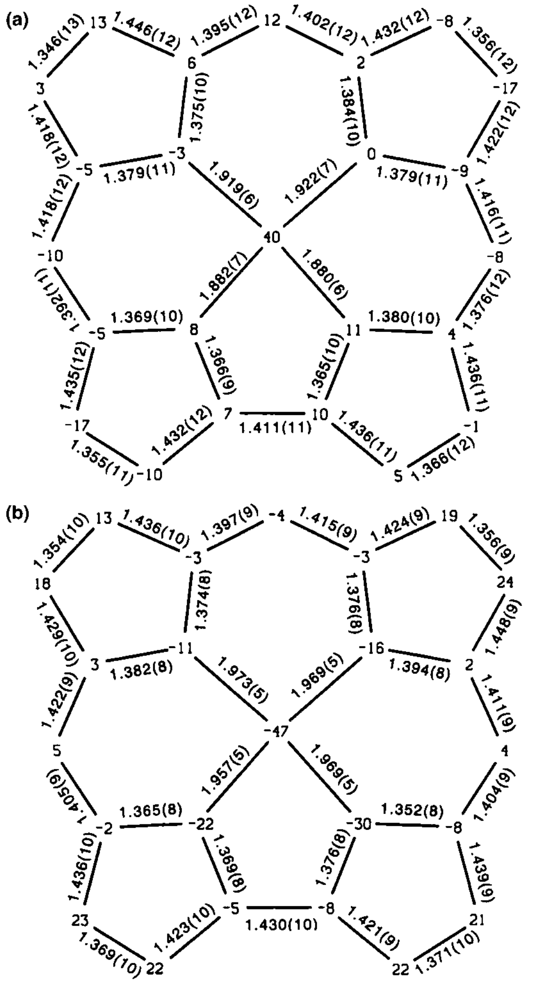

Figure 3. Formal diagrams of the corrole cores in (a) (tpfc)Fe−Cl and (b) (tpfc)Rh−PPh_3 displaying the perpendicular displacement of the individual atoms (in units of 0.01 Å) from the mean plane of the 23-atom core, as well as all bond distances (Å).

Concluding, we report now three metal complexes of the first readily available corrole whose rhodium(III) and iron(IV) derivatives have been found to be potent catalysts. On the basis of the solid-state structures of these complexes, we are currently preparing rhodium(III) corroles with bulkier phosphines for their utilization as catalysts for cyclopropanation of olefins.

Acknowledgment. Partial support of this research by “The Fund for the Promotion of the Research at the TechnionTechnion” (Z.G.) and “The Israel Science Foundation” (I.G.) is greatly acknowledged.

Supporting Information Available: Crystallographic data in CIF format and Figure 1s. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Crystal data for tpfc)Rh−PPh_3 (excluding solvent): $C_{55}H_{23}F_{15}N_4PRh$, M_r = 1158.65, triclinic, space group $P\bar{1}$, a = 8.413(1) Å, b = 15.397(1) Å, c = 20.356(1) Å, α = 91.80(1)°, β = 101.51(1)°, γ = 91.90(1)°, V = 2580.4(4) Å^3, Z = 2, T = 117 K, D_{calc} = 1.491 g cm^{-3}, $F(000)$ = 1152, μ(Mo Kα) = 0.46 mm^{-1}, crystal size ~0.25 mm × 0.20 mm × 0.15 mm, $2\theta_{\max}$ = 46.5°, 685 refined parameters, 6669 unique reflections, R1 = 0.060 for 6016 observations with $F_o > 4\sigma(F_o)$, R1 = 0.067 (wR2 = 0.181) for all unique data, $|\Delta\rho| \leq 1.2$ e Å^{-3}, the highest residual peaks of 1.1 and 1.2 e Å^{-3} being located near the rhodium cation. A number of additional peaks (0.8−1.1 e Å^{-3}) located around the inversion centers represent a disordered solvent included in the lattice (possibly a molecule of *n*-hexane) that could not be reliably identified. Correspondingly, the solvent content has not been included in the above data.

(9) This appears to be the first structure for any Rh(III)−PPh_3 corrole. For the structures of Co(III)−PPh_3 and Rh(III)−$AsPh_3$ corroles, see the following. Paolesse, R.; Jaquinod, L.; Nurco, D. J.; Mini, S.; Sagone, F.; Boschi, T.; Smith, K. M. *J. Chem. Soc., Chem. Commun.* **1999**, 1307. Paolesse, R.; Licoccia, S.; Bandoli, G.; Dolmella, A.; Boschi, T. *Inorg. Chem.* **1994**, *33*, 1171. Boschi, T.; Licoccia, S.; Paolesse, R.; Tagliatesta, P.; Azarnia, M. *J. Chem. Soc., Dalton Trans.* **1990**, 463.

(10) (a) Ehlinger, N.; Scheidt, W. R. *Inorg. Chem.* **1999**, *38*, 1316 and references therein. (b) Note that there is no steric restriction for smaller dihedral angles between the C_6F_5 rings and the corrole, as is indeed observed in the crystal structure of H_3(tpfc).[11]

(11) Gross, Z.; Galili, N.; Simkhovich, L.; Saltsman, I.; Botoshansky, M.; Bläser, D.; Boese, R.; Goldberg, I. *Org. Lett.* **1999**, *1*, 599.