A Journal of the Gesellschaft Deutscher Chemiker

Angewandte Chemie

GDCh

International Edition

www.angewandte.org

Accepted Article

Title: Corroles: The Hitherto Elusive Parent Macrocycle and its Metal Complexes

Authors: Zeev Gross, Amit Kumar, Pinky Yadav, Mahmoud Majdoub, Irena Saltsman, Natalia Fridman, Anil Kumar, Atif Mahammed, and Sachin Kumar

To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.202110964

Link to VoR: https://doi.org/10.1002/anie.202110964

WILEY-VCH

WILEY-VCH

RESEARCH ARTICLE

Corroles: The Hitherto Elusive Parent Macrocycle and its Metal Complexes

Amit Kumar,[a],# Pinky Yadav,[a],# Mahmoud Majdoub,[a],# Irena Saltsman,[a] Natalia Fridman,[a] Sachin Kumar,[a] Anil Kumar, [a],[b] Atif Mahammed,*[a] and Zeev Gross*[a]

[a] Dr. A. Kumar, Dr. P. Yadav, M. Majdoub, Dr. I. Saltsman, Dr. N. Fridman, S. Kumar, Prof. Dr. A. Kumar, Dr. A. Mahammed, Prof. Dr. Z. Gross
Schulich Faculty of Chemistry
Technion – Israel Institute of Technology
Haifa 32000 (Israel)
E-mail: chatif@technion.ac.il; chr10zg@technion.ac.il
[b] Prof. Dr. A. Kumar
Department of Applied Chemistry
Delhi Technological University
Delhi 110042 (India)
[#] These authors contributed equally to this work.

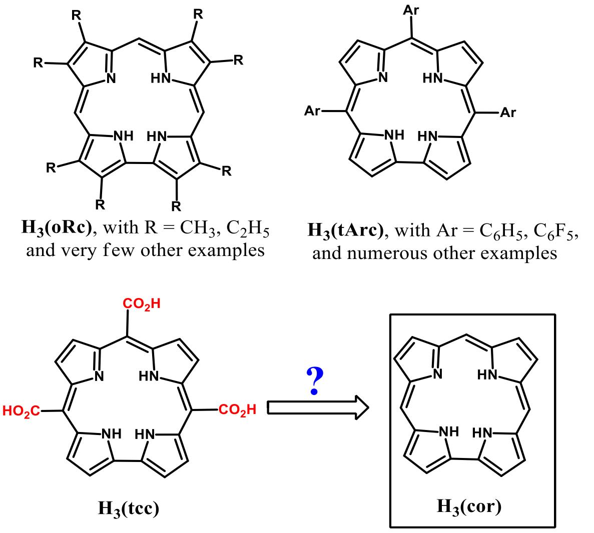
Supporting information for this article is given via a link at the end of the document.

Abstract: The science and technology of corroles, macrocycles that owe their name to the cobalt-chelating prosthetic group of Vitamin B12 and share numerous features with the iron-chelating porphyrin present in heme proteins/enzymes, constantly crosses new boundaries ever since stable derivatives became easily accessible. Particularly important is the increasing utilization of corroles and the corresponding metal complexes for the benefit of mankind, in terms of new drug candidates for treating various diseases and as catalysts for sustainable energy relevant processes. One still unmet challenge is to gain access to the plain macrocycle, as to allow for a full elucidation of the most fundamental properties of corroles. We now report the success in obtaining the substituents-free corrole, by several surprising and conceptually different pathways. Selected features of the corresponding metal complexes are illuminated, for pointing towards unique phenomena that are anticipated to largely expand the horizon regarding their utilization for contemporary catalysis.

Introduction

Corroles were first introduced in the early 1960's, coinciding with Dorothy C. Hodgkin being awarded the Noble Prize that recognized her achievement in determining the structure of Vitamin B12.[1] That raised the interest in corroles, which may be considered the aromatic version of the cobalt-chelating macrocycle corrin that serves as the prosthetic group of this vitamin or, alternatively, as porphyrin analogs with a contracted and tri- rather than di-anionic N4 coordination core. Hodgkin was in fact the person who reported the first X-ray structure determination of a metal-free corrole; and this remained the sole example for more than 30 years.[2] This does not reflect lack of interest in this class of compounds, since there was never any doubt that the photophysical properties of corroles and the unique redox reactions of the corresponding metal complexes are of high relevance for numerous applications. It rather serves as a testimony for how severe obstacles regarding the synthesis of corroles limited development to two annual publications by average, zero patents and no utilization in any practical field. The situation improved dramatically only in 1999, upon the disclosure of facile one-pot syntheses of 5,10,15-triarylcorroles (H_3(tArc), Scheme 1) from obvious building blocks.[3] This initiated worldwide efforts in introducing such molecules and their corresponding metal chelates as key elements for the most urgent needs of modern society. Representative examples are corrole metal complexes for bioimaging and agriculture, as potential drug candidates for many diseases, and as photo- and electro-catalysts for clean and renewable energy processes.[4] Regarding the last aspects, we became increasingly involved in the design of optimally performing corroles by focusing on affecting photophysical and electrochemical properties via hypothesis-driven approaches.[4f, 5] Our current motivation for preparing minimally substituted corroles is that while the *meso*-aryl groups present in the traditionally used derivatives (H_3(tArc) in Scheme 1) are extremely important for homogeneous catalysis, that is not necessarily the case for heterogenous catalysis. This may be exemplified by the procedure required for preparation of metal/nitrogen doped carbon electrodes that are almost as efficient as non-sustainable platinum in catalyzing the oxygen reduction reaction of fuel cells. Both natural and synthetic porphyrins are commonly used as precursors for the pyrolysis process, during which their substituents are removed at about 600 ˚C. Such treatment is obligatory for carbonization, the process upon which the metal-chelating N4 coordination becomes part of the porous carbon material that is used for catalysis.[6] Our hypothesis was that starting with substituent-free corrole would eliminate the need of pyrolysis and eventually allow for a much better control of the number and identity of catalytically active sites. We note that the cobalt(III) complex of plain corrole was reported almost 50 years ago but never used for any application and that surprisingly little has been done with the substituent-free porphyrin (porphine), focusing mainly on electropolymerization.[7] Last, but certainly not least, is the scientific curiosity of studying the fundamental properties of the parent corrole, i.e., with no substituents whatsoever on the macrocycle.

10.1002/anie.202110964

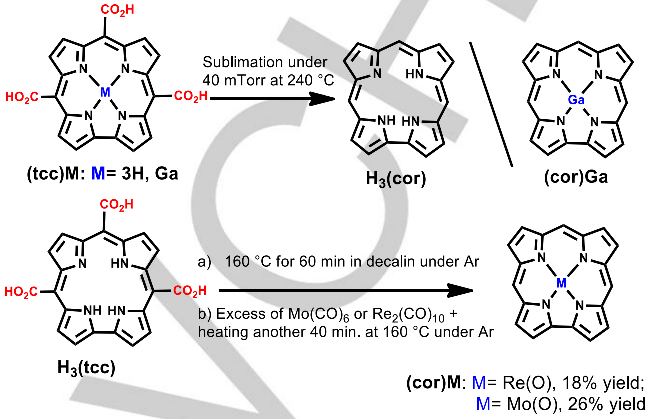


Scheme 1. Structures of the longest known octaalkylcorroles H_3(oRc), the most intensively investigated *meso*-triarylcorroles H_3(tArc), and the most recently introduced tris-carboxylated corrole H_3(tcc) that served as one synthetic precursor for accessing the completely non-substituted corrole H_3(cor) that is reported only now. All these corroles efficiently chelate elements in their +3 or higher oxidation state via their deprotonated N4 coordination core, forming (oRc)M, (tArc)M, (tcc)M) and (cor)M complexes. Representative examples for M are manganese(III), iron(III), cobalt(III), gallium(III), (oxo)molybdenum(V), and (oxo)rhenium(V).

Results and Discussion

We have most recently introduced a largely improved synthesis of the corrole substituted by only CF_3 substituents on the three *meso*-C atoms (5,10,15-tris(trifluoromethyl)corrole, H_3(tfc)),[8] followed by discovering its highly facile hydrolysis to the water-soluble tris-carboxylated derivative H_3(tcc) (Scheme 1).[9] The same route worked equally well for the corresponding manganese(III), iron(III), gallium(III) and phosphorous(V) complexes. Given these developments, we have now decided to check decarboxylation of H_3(tcc) and/or its metal complexes as a viable route to the yet elusive H_3(cor) (Scheme 1) and a large variety of its corresponding metal complexes.

The rather unsophisticated approach of subliming H_3(tcc) for inducing decarboxylation was met with success, as may be appreciated by the UV-vis spectrum of the thus produced H_3(cor) (Figure S7). However, while the good news is that the elusive parent corrole was finally obtained and by a facile pathway, H_3(cor) appeared to be of quite limited stability to ambient humidity and light exposure. This came as no surprise, considering that electron-withdrawing substituents are required for reducing the π-system electron richness of the corrole macrocycle.[4c] Bearing in mind that metal chelation stabilizes corroles very much,[10] the analogous procedure was performed on the gallium(III) complex of H_3(tcc). Sublimation of (tcc)Ga produced (cor)Ga indeed (Scheme 2), which was characterized as the mono-pyridine complex by dissolving the sublimed material in pyridine-containing benzene. Its ^{1}H NMR spectrum (Figure 1A) clearly discloses all CH protons of the corrole: 2 meso-H's at 9.8 and 9.6 ppm in the proper 2:1 respective ratio and the four couples of β-pyrrole H's as doublets with corrole-characteristic *J*-coupling constants of 3.7 – 4.2 Hz.[11] The stability to ambient conditions of (cor)Ga was much larger than that of the free-base H_3(cor), as long as pyridine (or other ligands) are bound to the gallium(III) center. These encouraging achievements also exposed the limitations that must be resolved for gaining access to a large variety of other metal complexes, considering that: a) metallation of preformed H_3(cor) is problematic because of its limited stability; b) performing decarboxylation on the already metallated corroles requires good access to (tcc)M complexes, which is not always the case; and c) both routes rely on two-steps procedures from stable starting compounds (e.g., H_3(tcc) or (tcc)Ga). Of particular relevance regarding the need for an alternative approach is that (tfc)Co and (tfc)Re(O) could actually not be hydrolyzed to (tcc)Co and (tcc)Re(O).[9]



Scheme 2. The synthetic approaches towards the non-substituted corrole H_3(cor) and its corresponding metal complexes (cor)M, wherein M stands for either gallium(III), (oxo)rhenium(V) or (oxo)molybdenum(V). Chemical yields are only reported for the last two metal complexes.

Considering all the above, efforts were first devoted to the preparation the low-spin d^2 (oxo)rhenium(V) and d^6 cobalt(III) corroles. Characterization of such diamagnetic complexes may safely be expected to be easier; and the latter complex is of large relevance for alternative-energy related catalysis. The first approach was to heat H_3(tcc) in the inert and high boiling solvent decalin, in the presence of $Re_2(CO)_{10}$. The hypothesis was that decarboxylation will take place at elevated temperature and that the thus produced H_3(cor) will undergo metalation *in situ*. This was the case indeed, as was first easily evaluated by naked eye. The initially colorless solution, due to insolubility of H_3(tcc) in decalin, started to become colored within 30 minutes at 150 ˚C and $Re_2(CO)_{10}$ was added 1 hour later when all solid material dissolved. The targeted complex, isolated in 18% yield, was easily identified as (cor)Re(O) by its ^{1}H NMR spectrum (Figure 1B) and it appeared to be completely stable when stored at ambient conditions in both the solid state and in solution. Encouraged by the simplicity of that approach, the (oxo)molybdenum(V) corrole (cor)Mo(O) was obtained in a similar fashion (in 26% yield), with $Mo(CO)_6$ as the metal source.

A conceptually different approach was developed for the preparation of the cobalt(III) complex, relying on the quite good access to non-substituted oligopyrromethanes (tri-, tetra- and penta-pyrromethanes) via the microwave-assisted reaction between pyrrole and formalin.[12] While the ultimate goal of those earlier studies was to use these compounds as precursors to H_3(cor), only porphine (the trivial name of the parental (i.e., non-substituted) porphyrin) and a *meso*-pyrrole-substituted porphyrin were obtained.[12] We have now upscaled the reaction conditions of the first step as to obtain the non-substituted tetrapyrromethane (TPM, Scheme 3) in larger amounts (about 1.3 gram per day). This allowed for the renewed efforts of using TPM for the synthesis of the non-substituted corrole, while considering the instability of the target free-base H_3(cor) under the oxidizing conditions that are essential for its formation from TPM. The approach adopted for resolving this synthetic problem was to perform oxidation and metallation in a one-pot fashion. On top of profiting from the much higher stability of metallocorroles towards oxidants, a possible template effect for the cyclization by the cobalt ion was also considered. These investigations started with

10.1002/anie.202110964

cobalt, the perfect match for corroles,[7d] by treating TPM with cobalt acetate in pyridine, which is the best solvent for metallation of corroles and stabilizes metallocorroles by serving as ligand for saturating the coordination sphere of the central metal ion. In terms of chemical yield from very simple and cheap starting material and the amount of isolated material this approach was most rewarding, providing 22 mg (cor)Co(py)$_2$ from 90 mg TPM within a few hours. Cyclization of TPM was performed both with and without adding mild oxidizing agents, revealing that the desired product was formed even in the latter case, albeit in only 3% chemical yield (most of the TPM remained unreacted). Using 3 mol/equivalents of either (diacetoxy)iodobenzene or the fluorinated analog [bis(trifluoroacetoxy)iodo]benzene (PIFA) induced a significant increase in the yields. In the latter case, the target complex was isolated in its 6-coordinate form with two axial pyridine ligands, i.e., (cor)Co(py)$_2$, in a chemical yield of 15%. All the starting TPM was consumed in this reaction, but the many other byproducts were not analyzed yet. The axial pyridines could easily be replaced by triphenylphosphine, either before or after purification of (cor)Co(py)$_2$, leading to the 5-coordinate (cor)Co(PPh$_3$) in 8% yield relative to TPM in the latter case. The ^{1}H NMR spectra of (cor)Co(py)$_2$ and (cor)Co(PPh$_3$) are presented in Figures 1C and 1D, respectively, with a full analysis for the latter complex as described later.

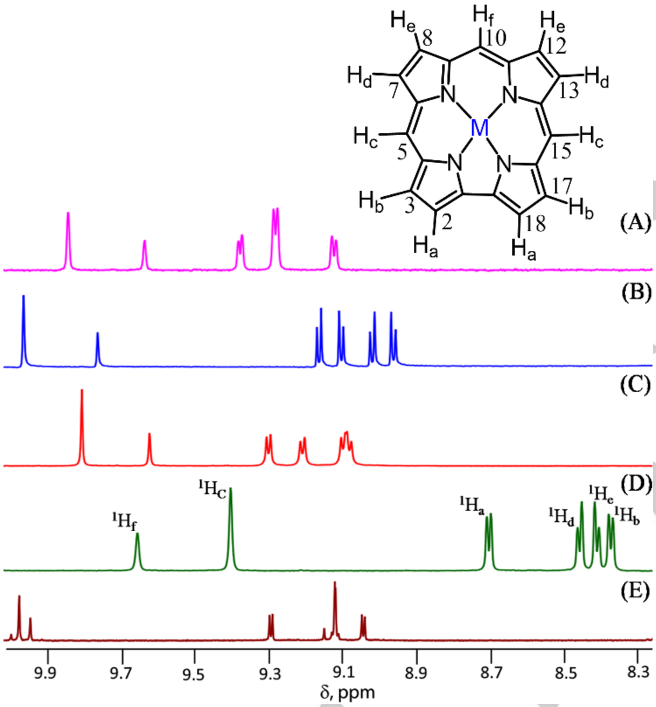
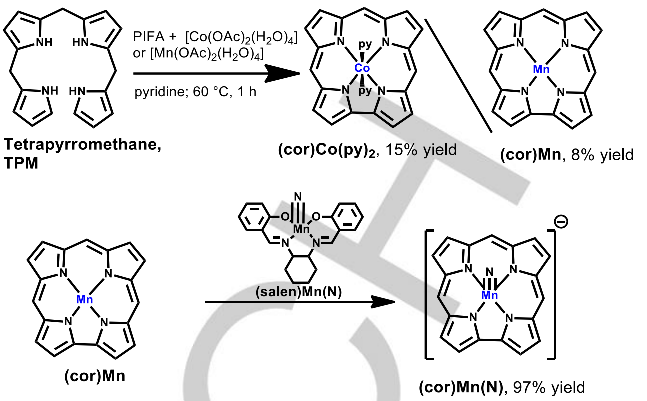
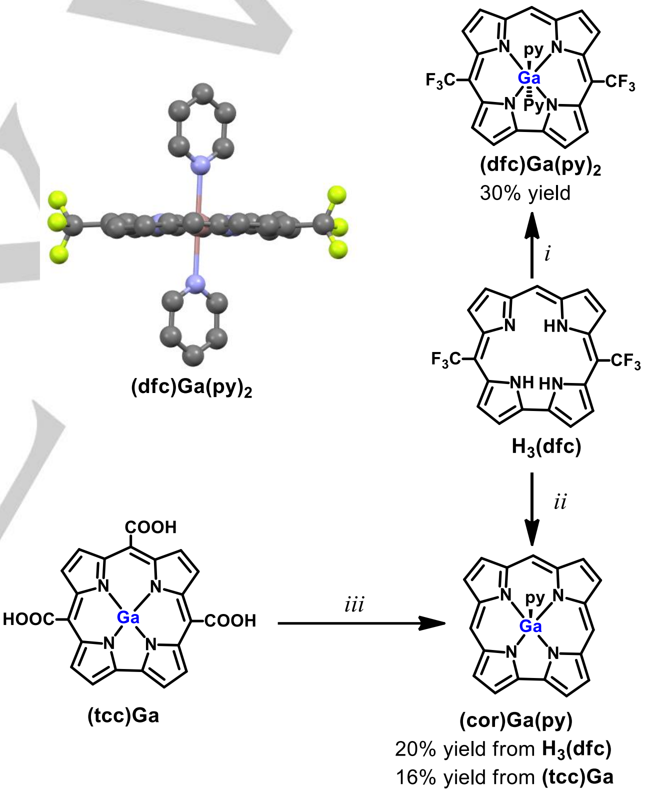


Figure 1. ^{1}H NMR spectra (400 MHz, in C_6D_6) of the *meso* and β-pyrrole protons of A) (cor)Ga(py); B) (cor)Re(O); C) (cor)Co(py)$_2$; D) (cor)Co(PPh$_3$), including the complete assignment of the ^{1}H chemical shifts of the corrole macrocycle; and E) (cor)Mn(N).

Similar success was obtained in the oxidative cyclization of TPM in the presence of manganese(II) acetate in pyridine, affording (cor)Mn in 8% yield (Scheme 3). Its electronic spectrum revealed the characteristic of Mn^{III} corroles: strongly split near UV (Soret) bands and a charge-transfer band at 478 nm (in EtOAc, Fig. S14). Considering the difficulties in characterization of the d^4 (cor)Mn complex[13], it was converted to the Mn^V (low-spin d^2) oxidation state via treatment with (salen)Mn(N) in methanol solution (Scheme 3).[14] This very effective nitrogen atom transfer reaction yielded the diamagnetic (nitrido)Mn(V) corrole, (cor)Mn(N), characterized by ^{1}H NMR spectroscopy [(Figure 1E).



Scheme 3. One-pot synthesis of (cor)Co and (cor)Mn via one-pot oxidative cyclization of TPM and metalation by cobalt(II) or manganese(II) acetate tetrahydrate; and the preparation of the diamagnetic (cor)Mn(N) by nitrogen atom transfer from (salen)Mn(N) to the paramagnetic (cor)Mn.



Scheme 4. Preparation of (dfc)Ga(py)$_2$ by metalation of H$_3$(dfc) with a reasonable excess of GaCl$_3$ (route *i*) and of (cor)Ga(py) by either treating H$_3$(dfc) with large excess of GaCl$_3$ (route *ii*) or by heating a pyridine solution of (tcc)Ga (route *iii*). The X-ray crystal structure of (dfc)Ga(py)$_2$ is also presented (all H atoms have been omitted for clarity).

10.1002/anie.202110964

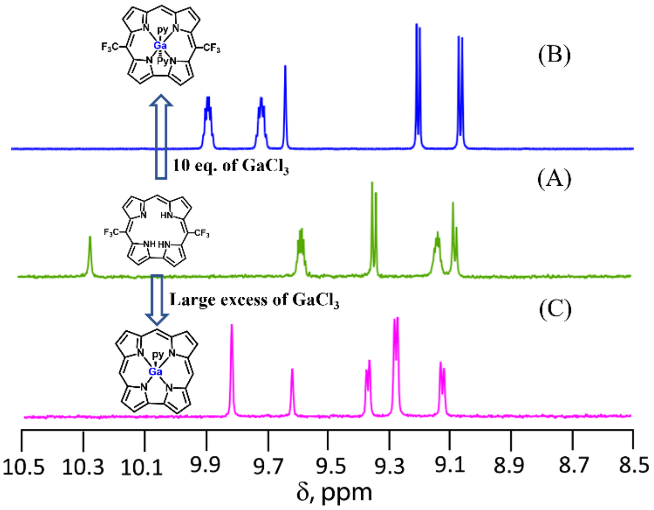


Figure 2. ^1H NMR spectra (400 MHz, in C_6D_6) of the *meso* and β-pyrrole protons of A) H_3(dfc); B) (dfc)Ga(py)$_2$, which was obtained by reacting H_3(dfc) with *small* excess of $GaCl_3$; and C) (cor)Ga(py), which was obtained by reacting H_3(dfc) with *large* excess of $GaCl_3$.

Still another route was discovered when the recently reported 5,15-bis-CF_3-substituted corrole H_3(dfc)[9] was treated with $GaCl_3$. The expected (dfc)Ga(py)$_2$ (^1H NMR and X-ray structure displayed in Figure 2 and Scheme 4) was obtained when a reasonable excess (10 equivalents) of $GaCl_3$ was used, but (cor)Ga(py) was formed when a very large excess of the metal salt was utilized (Scheme 4, routes *i* and *ii*, respectively). Clues for the origin of this surprising phenomenon were obtained by the following experiments: a) heating of the gallium complex of the tris-carboxylated corrole (tcc)Ga in pyridine or decalin did provide (cor)Ga(py) even in the absence of $GaCl_3$ (Scheme 4, route *iii*); treatment of either H_3(tfc) or (tfc)Ga with excess $GaCl_3$ in hot pyridine did not lead to (cor)Ga(py); and c) the same holds true when already isolated (dfc)Ga(py)$_2$ was treated under the same conditions that were successful for the free-base H_3(dfc) (Scheme 4, route *ii*). These results suggest that the one-pot C-CF_3 to C-H transformation requires hydrolysis to proceed prior to metalation. This is apparently more facile for the bis-CF_3 substituted corrole, likely because its non-substituted C10 position increases the chance for hydrolysis via attack on the remote (from CF_3) carbon atom.[9]

Bearing in mind that porphyrins are considered as the pigments of life, and also that corroles are actually more fluorescent than porphyrins, raised the interest in examining the effect of H *vs.* CF_3 *vs.* C_6F_5 *meso*-C-substituents on the absorption and emission spectra of (cor)Ga, (tfc)Ga and (tpfc)Ga. These comparisons, performed in pyridine as solvent for assuring that all complexes will be 6-coordinate with two *trans*-pyridine ligands (Fig. S16), uncovered that: a) the largest differences appear in the near-UV absorbances (termed Soret bands), which appear at highest energy (λ_{max} = 407 nm) for (cor)Ga, followed by (tfc)Ga and (tpfc)Ga which are significantly more red-shifted (λ_{max} = 426 and 428 nm, respectively); b) the differences are smaller regarding the lowest-energy electronic transitions (termed Q bands), with λ_{max} = 596, 594, and 610 nm for (cor)Ga, (tfc)Ga and (tpfc)Ga, respectively; c) the maximum fluorescence wavelengths of (cor)Ga and (tfc)Ga are almost identical (longer by 2 nm for the former) and shorter by about 20 nm relative to (tpfc)Ga; and d) the relative fluorescence quantum yields are 1.00, 0.38, and 0.50 for (tpfc)Ga, (tfc)Ga and (cor)Ga, respectively (Fig. S16 and Table S1). This data allows for the conclusion that the HOMO-LUMO gap in (cor)Ga is higher than that of (tpfc)Ga and similar to that of (tfc)Ga; and that, quite surprisingly, the ratio of radiative vs. non-radiative decay rates of the singlet-excited state is less large for (tpfc)Ga.

One outstanding feature of the new complexes is that all the ^1H NMR resonances could be assigned with full confidences, as exemplified for (cor)Co(PPh$_3$) (Figure 1D and S23). In short, the C10-H atom (H_f) experiences long range ^4J coupling with the C8-H/C12-H (H_e) atoms, which are strongly coupled to their vicinal C7-H/C13-H (H_d) atoms. All other resonances were similarly assigned to specific H atoms, an achievement for which is hardly any prior art in the field and none for corroles with a C_2 symmetry axis.[15]

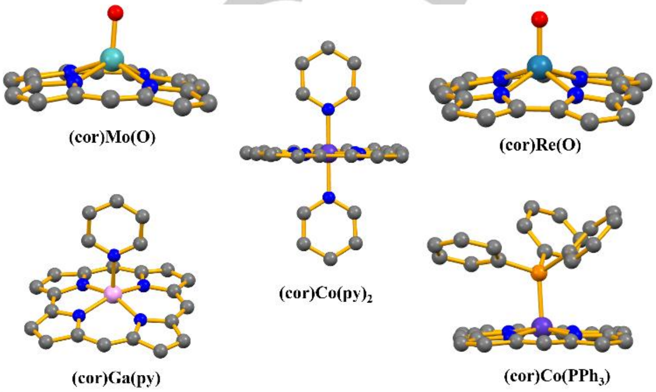


Figure 3. The X-ray structures of the (oxo)molybdenum(V), (oxo)rhenium(V), (pyridine)gallium(III), (bis-pyridine)cobalt(III) and (triphenylphosphine)cobalt(III) complexes of the *completely non-substituted* corrole (All H atoms have been omitted for clarity).[16]

The stability of the (cor)M complexes allowed for their full characterization by X-ray crystallography (Figure 3 and Table S2). The *trans*-bis-pyridine coordinated (cor)Co(py)$_2$ displays a practically planar corrole, in which the cobalt ion deviates only 0.003 and 0.002 Å from the planes defined by the four chelating nitrogen atoms and by the 23-core atoms, respectively. This is distinctively different from the 5-coordinate (cor)Co(PPh$_3$), (cor)Ga(py), (cor)Re(O) and (cor)Mo(O) complexes wherein the corrole is domed and the out of the N4 plane displacements of the metal ion towards the single axial ligand are 0.278, 0.391, 0.688 and 0.736 Å, respectively. Inspection of Table S3, wherein data from the same metal ions chelated by the corroles with either CF_3, C_6F_5, or H on the *meso*-C atoms is compiled, does disclose similar structural features for all of them. That comparison also reveals that the average metal-$N_{pyrrole}$ bond lengths in (cor)M are shorter by 0.002 - 0.024 Å, relative to those present in the CF_3- and C_6F_5-substituted corroles. This finding testifies for stronger metal chelation by the less electron-withdrawing corrole. Supporting and independent evidence for the last conclusion is provided by cyclic voltammetry, exemplified by the redox potentials of (cor)Co(PPh$_3$), (tpfc)Co(PPh$_3$) (tfc)Co(PPh$_3$) being -2.04, -1.74, and -1.55 V *vs.* Fc/Fc$^+$, respectively. This data is not of pure scientific interest only, but also of large potential relevance for electrocatalysis.

Considering the vast knowledge accumulated in the last two decades regarding the advantages of (much larger) porphyrinoids as molecular catalysts, whose activity is boosted by annealing them onto carbon material by very high temperature pyrolysis, we predicted that the current synthetic breakthrough might be transformative regarding electrocatalysis and related applications. Preliminary results supportive of these expectations were obtained by adsorbing the (cor)M complexes, with M= Co(PPh$_3$), Co(py)$_2$, Re(O), or Mo(O), onto Vulcan XC72R carbon by adding the latter to isopropanol solutions of the former. In all cases, the (cor)M complexes were adsorbed faster and to much larger degree compared to the C_6F_5- and CF_3- reported corroles (Figure 4 for M = Mo(O) and Figs. S17-S19 for other metal complexes). The adsorbed amounts of the catalysts were calculated by comparing the UV-Vis spectra of their original solutions before and after the addition of the carbon, revealing that all the (cor)M were totally adsorbed on the Vulcan XC72R carbon. In fact, the intensively colored (cor)M solutions became completely colorless within < 30 minutes after the addition of the carbon nanoparticles.

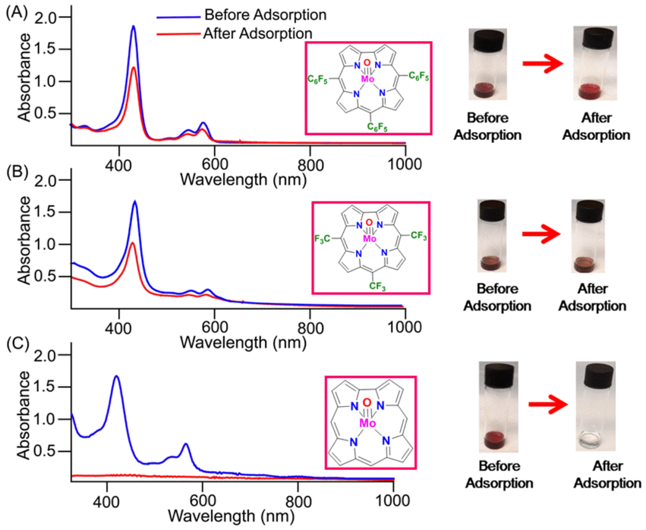


Figure 4. Results obtained by spontaneous adsorption (examined after 30 min for (cor)(Mo(O), and after 12 hr. for the others) from solutions of (tfc)Mo(O), (tpfc)Mo(O), or (cor)Mo(O) (0.8 mg each, in 1 mL isopropanol), checked by recording the UV-vis spectra of the solutions before (blue) and after (red) the addition of a Vulcan XC72R carbon (10 mg) (A-C).

The carbon modified by (cor)Mo(O) was adsorbed on the surface of glassy carbon electrodes in order to check its ability to reduce protons to hydrogen. Figure 5A shows the performance of Vulcan XC72R carbon only (red) relative to (cor)Mo(O) and 20% Pt adsorbed onto XC72R (blue and pink, respectively) as the solid support, in 0.5 M H_2SO_4 solution and under nitrogen. (cor)Mo(O) shows very good catalytic activity with only a 280 mV overpotential (Figure 5A), and electrocatalytic stability for more than 15 hours (Figure 5B). Clearly visible bubbles of H_2 gas were generated on the surface of the electrode upon bulk electrolysis at applied potential of -0.8 V (vs. Ag/AgCl) (Figure 5C). Quantification of the thus generated hydrogen gas was performed by gas chromatography, leading to the conclusion that (cor)Mo(O) is a very effective catalysts for proton reduction with a Faradaic efficiency (FE) of 92%.

Another aspect, which is predicted to become important in future utilization of (cor)M complexes for electrocatalysis and many other purposes, was briefly addressed by heating solid (cor)Co(PPh)$_3$ in a simple Kugelrohr apparatus under the quite weak vacuum of 40 mTorr. This revealed that it was sublimed without decomposition at 220 ℃, in sharp contrast with both porphyrins and phthalocyanines for which much higher temperatures and ultrahigh vacuum (10^{-5}-10^{-9} Torr) are normally applied.[17] The combination of low molecular weight and absence of macrocycle substituents in (cor)M complexes are the apparent reasons for this feature; and this paves the way for introducing such complexes for many advanced applications.

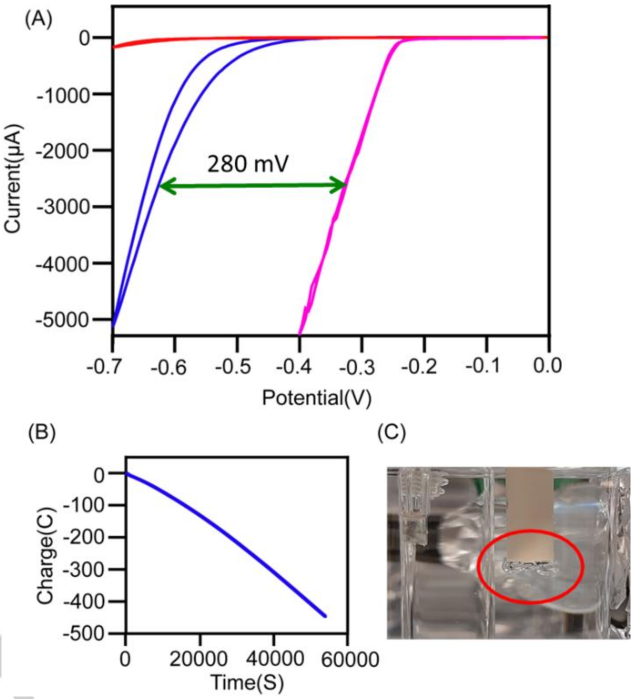


Figure 5. A) Cyclic voltammograms of Vulcan XC72R carbon only (red), (cor)Mo(O) adsorbed onto Vulcan XC72R carbon (blue), and 20% Pt adsorbed onto Vulcan XC72R carbon (pink) as the solid support, in 0.5 M H_2SO_4 solution and under nitrogen. Scan rate: 50 mV/s, Ag/AgCl and Pt wire were used as reference and counter electrodes, respectively. B) Charge curve of (cor)Mo(O) adsorbed onto Vulcan XC72R carbon during 15 hr of bulk electrolysis at applied potential of −0.8 V. C) H_2 generation in the form of bubbles on the surface of glassy carbon electrode modified by (cor)Mo(O) after 10 min of bulk electrolysis at applied potential -0.8 V.

Conclusion

We introduce the parent corrole with no substituents whatsoever, as well as several elemental ions chelated by it. This dream come true triumph became permissible due to a combination of several novel discoveries that include -CF_3 hydrolysis, facile decarboxylation reactions, and metal-assisted cyclization. Also presented are some of the many predictable advantages of these compounds/complexes: extremely strong bonding to solid surfaces, excellent performance as electrocatalysts for proton to hydrogen reduction, and the facile sublimation of the metal complexes of unsubstituted corrole.

Acknowledgements

This research was supported by the Israel Science Foundation (to Z.G.).

Conflict of interest

The authors declare no conflict of interest.

Keywords: corroles • molybdenum • cobalt • one-put-synthesis • hydrogen-evolution-reaction

10.1002/anie.202110964

[1] a) A. W. Johnson, I. T. Kay, *J. Chem. Soc.* **1965**, 1620-1629; b) D. C. Hodgkin, J. Pickworth, J. H. Robertson, K. N. Trueblood, R. J. Prosen, J. G. White, *Nature* **1955**, *176*, 325-328.

[2] B. F. Anderson, T. J. Bartczak, D. C. Hodgkin, *J. Chem. Soc., Perkin Trans. 2* **1974**, 977-980.

[3] a) Z. Gross, N. Galili, I. Saltsman, *Angew. Chem. Int. Ed.* **1999**, *38*, 1427-1429; b) R. Paolesse, S. Mini, F. Sagone, T. Boschi, L. Jaquinod, D. J. Nurco, K. M. Smith, *Chem. Commun.* **1999**, 1307-1308.

[4] a) J. F. B. Barata, M. G. P. M. S. Neves, M. A. F. Faustino, A. C. Tomé, J. A. S. Cavaleiro, *Chem. Rev.* **2017**, *117*, 3192-3253; b) R. D. Teo, J. Y. Hwang, J. Termini, Z. Gross, H. B. Gray, *Chem. Rev.* **2017**, *117*, 2711-2729; c) I. Aviv, Z. Gross, *Chem. Commun.* **2007**, 1987-1999; d) Y. Fang, Z. Ou, K. M. Kadish, *Chem. Rev.* **2017**, *117*, 3377-3419; e) S. M. M. Lopes, M. Pineiro, T. M. V. D. Pinho e Melo, *Molecules* **2020**, *25*, 3450; f) A. Mahammed, K. Chen, J. Vestfrid, J. Zhao, Z. Gross, *Chem. Sci.* **2019**, *10*, 7091-7103; g) R. De, S. Gonglach, S. Paul, M. Haas, S. S. Sreejith, P. Gerschel, U.-P. Apfel, T. H. Vuong, J. Rabeah, S. Roy, W. Schöfberger, *Angew. Chem. Int. Ed.* **2020**, *59*, 10527-10534; h) X. Liang, J. Mack, L.-M. Zheng, Z. Shen, N. Kobayashi, *Inorg. Chem.* **2014**, *53*, 2797-2802; i) L. Flamigni, D. T. Gryko, *Chem. Soc. Rev.* **2009**, *38*, 1635-1646.

[5] a) X. Zhan, S. Kolanu, S. Fite, Q.-C. Chen, W. Lee, D. G. Churchill, Z. Gross, *Photoch. Photobio. Sci.* **2020**, *19*, 996-1000; b) K. Sudhakar, A. Mahammed, Q.-C. Chen, N. Fridman, B. Tumanskii, Z. Gross, *ACS Appl. Energy Mater.* **2020**, *3*, 2828-2836; c) W. Sinha, A. Mahammed, N. Fridman, Y. Diskin-Posner, L. J. W. Shimon, Z. Gross, *Chem. Commun.* **2019**, *55*, 11912-11915; d) Q.-C. Chen, Z.-Y. Xiao, S. Fite, A. Mizrahi, N. Fridman, X. Zhan, O. Keisar, Y. Cohen, Z. Gross, *Chem. Eur. J.* **2019**, *25*, 11383-11388; e) X. Zhan, P. Yadav, Y. Diskin-Posner, N. Fridman, M. Sundararajan, Z. Ullah, Q.-C. Chen, L. J. W. Shimon, A. Mahammed, D. G. Churchill, M.-H. Baik, Z. Gross, *Dalton Trans.* **2019**, *48*, 12279-12286; f) X. Zhan, P. Teplitzky, Y. Diskin-Posner, M. Sundararajan, Z. Ullah, Q.-C. Chen, L. J. W. Shimon, I. Saltsman, A. Mahammed, M. Kosa, M.-H. Baik, D. G. Churchill, Z. Gross, *Inorg. Chem.* **2019**, *58*, 6184-6198; g) K. Sudhakar, A. Mahammed, N. Fridman, Z. Gross, *Dalton Trans.* **2019**, *48*, 4798-4810.

[6] a) J. M. Ziegelbauer, T. S. Olson, S. Pylypenko, F. Alamgir, C. Jaye, P. Atanassov, S. Mukerjee, *J. Phys. Chem. C* **2008**, *112*, 8839-8849; b) A. Li, S. A. Nicolae, M. Qiao, K. Preuss, P. A. Szilágyi, A. Moores, M.-M. Titirici, *ChemCatChem* **2019**, *11*, 3602-3625; c) K. Ojha, E. M. Farber, T. Y. Burshtein, D. Eisenberg, *Angew. Chem. Int. Ed.* **2018**, *57*, 17168-17172; d) D. Eisenberg, P. Prinsen, N. J. Geels, W. Stroek, N. Yan, B. Hua, J.-L. Luo, G. Rothenberg, *RSC Adv.* **2016**, *6*, 80398-80407.

[7] a) M. O. Senge, M. Davis, *J. Porphyrins Phthalocyanines* **2010**, *14*, 557-567; b) D. V. Konev, C. H. Devillers, K. V. Lizgina, V. E. Baulin, M. A. Vorotyntsev, *J. Electroanal. Chem.* **2015**, *737*, 235-242; c) M. A. Vorotyntsev, D. V. Konev, C. H. Devillers, I. Bezverkhyy, O. Heintz, *Electrochim. Acta* **2010**, *55*, 6703-6714; d) M. Conlon, A. W. Johnson, W. R. Overend, D. Rajapaksa, C. M. Elson, *J. Chem. Soc., Perkin Trans. 1* **1973**, 2281-2288.

[8] P. Yadav, S. Khoury, A. Mahammed, M. Morales, S. C. Virgil, H. B. Gray, Z. Gross, *Org. Lett.* **2020**, *22*, 3119-3122.

[9] P. Yadav, S. Khoury, N. Fridman, V. K. Sharma, A. Kumar, M. Majdoub, A. Kumar, Y. Diskin-Posner, A. Mahammed, Z. Gross, *Angew. Chem. Int. Ed.* **2021**, *60*, 12829-12834.

[10] X. Jiang, G. Pomarico, M. Bischetti, P. Galloni, D. O. Cicero, Y. Cui, K. M. Kadish, R. Paolesse, *New J. Chem.* **2018**, *42*, 8207-8219.

[11] Y. S. Balazs, I. Saltsman, A. Mahammed, E. Tkachenko, G. Golubkov, J. Levine, Z. Gross, *Magn. Reson. Chem.* **2004**, *42*, 624-635.

[12] I. Saltsman, Z. Gross, *Tetrahedron Lett.* **2008**, *49*, 247-249.

[13] J. Bendix, H. B. Gray, G. Golubkov, Z. Gross, *Chem. Commun.* **2000**, 1957-1958.

[14] G. Golubkov, Z. Gross, *J. Am. Chem. Soc.* **2005**, *127*, 3258-3259.

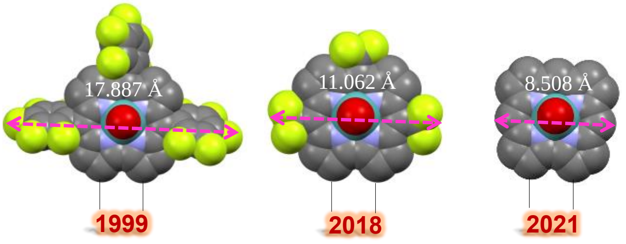
[15] D. Ren, O. Smaga, X. Fu, X. Li, M. Pawlicki, S. Koniarz, P. J. Chmielewski, *Org. Lett.* **2021**, *23*, 1032-1037.

[16] Deposition Numbers 2058437 (for (cor)Co(PPh$_3$)), 2058438 (for (cor)Co(py)$_2$), 2058439 (for (cor)Ga(py)), 2058440 (for (cor)Mo(O)), 2058441 (for (cor)Re(O)), 2058442 (for (dfc)Ga(py)$_2$) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

[17] a) X.-L. Zhang, J.-W. Jiang, Y.-T. Liu, S.-T. Lou, C.-L. Gao, Q.-Y. Jin, *Sci. Rep.* **2016**, *6*, 22756; b) S. Toru, I. Taira, F. Masatoshi, *Chem. Lett.* **1988**, *17*, 257-260; c) P. P. Semyannikov, T. V. Basova, V. M. Grankin, I. K. Igumenov, *J. Porphyrins Phthalocyanines* **2000**, *04*, 271-277.

10.1002/anie.202110964

Entry for the Table of Contents



Following the impact of the previous century's latest year discovery of triarylcorroles and the more recently described CF_3-substituted corroles, is the now described development of three synthetic routes to the completely unsubstituted corrole. This already allowed for the introduction of five fully characterized metal complexes chelated by this corrole, which were used for starting to uncover unique beneficial features that are relevant to clean energy catalysis and many other purposes.