

Intriguing Chemistry of Molybdenum Corroles

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Supporting Information

ABSTRACT: The development of new methodologies for gaining access to low-valent molybdenum complexes led to spectroscopic identification of mononuclear (oxo)-molybdenum(IV) corroles, as well as the full characterization of a binuclear molybdenum(IV) corrole that is bridged through axial O atoms by a Mg(THF)₄ moiety.

While the capability of corroles (in their trianionic form) to stabilize high-valent metals has and continues to be the traditional focus in metalloporphyrin chemistry,^{1–3} much less research activity has been devoted to the consequential large activity that corroles may impose on low-valent metals. Examples that testify for the above are the aerobic oxidation of chromium(III),^{4a,12} manganese(III),^{4b} and iron(III) corroles,^{4c–f} a phenomenon not shared by the same metal ions in other coordination environments where only the corresponding divalent oxidation states bind and/or activate molecular oxygen.^{5–7} Considering the strong reducing power of early transition metals in general, it is quite surprising that the chemistry of the corresponding corrole chelates remains quite unexplored. Sporadic reports on titanium and vanadium corroles are limited to their most stable oxidation states, (oxo)titanium(IV) and (oxo)vanadium(IV).⁸ The same limitation holds for the heavier congeners of group 6: there are several publications on (oxo)molybdenum(V) corrole,⁹ and a trioxo-bridged binuclear tungsten(VI) corrole has been reported most recently.¹⁰ Only the chemistry of chromium corroles has been developed beyond its most stable (oxo)chromium(V) state.¹¹ This includes crystallographic characterization and reactivity studies of both chromium(III) and (oxo)chromium(V) corroles,¹² as well as spectroscopic investigations of the one-electron-reduction and -oxidation products of the latter: (oxo)chromium(IV) corrole and corrole-oxidized (oxo)chromium(V), respectively.¹³ Considering the very important chemistry of low-valent molybdenum complexes in general,¹⁴ we have now decided to explore that of molybdenum corroles. This was done by first exploring a variety of methodologies for reduction of the (oxo)chromium(V) complex (tpfc)Cr^V(O) [tpfc = trianion of tpfc], followed by looking into their possible adoption for the (oxo)molybdenum(V) corrole (tpfc)Mo^V(O).

The first step was a thorough investigation of the reduction of (tpfc)Cr^V(O), in tetrahydrofuran (THF) under a N₂ atmosphere (Supporting Information, SI). Reaction progress was traced by relying on the fact that the spectroscopic features [UV–vis, NMR, and electron paramagnetic resonance (EPR)] of the 5,10,15-tris(pentafluorophenyl)corrole chromium complexes are well established in all oxidation and coordination states.^{11–13}

Applied reducing agents were NaBH₄, cobaltocene (CoCp₂),^{15a} bis(pentamethylcyclopentadienyl)cobalt(II) (CoCp*₂),^{15b} and trimesitylvanadium(III) [VMes₃(THF)].^{15–17} Employment of the latter led to (tpfc)Cr^{III}, i.e., reductive deoxygenation, while the one-electron-reduction product [(tpfc)Cr^{IV}(O)][–] was obtained with the other reagents. The in situ conversion of [(tpfc)Cr^{IV}(O)][–] to (tpfc)Cr^{III} was enabled by either silylation with chlorotrimethylsilane (TMSCl) or protonation (by MeOH) of the former. The such-formed [(tpfc)Cr^{IV}(OSiTMS)] and [(tpfc)Cr^{IV}(OH)] are apparently easier to reduce, not at least because of the presence of reasonable leaving groups.

The Mo^V/Mo^{IV} redox potential of (tpfc)Mo^V(O) is much more negative than the Cr^V/Cr^{IV} couple in (tpfc)Cr^V(O) (–0.35 and 0.11 V, respectively, vs Ag/AgCl in CH₂Cl₂).^{9,13} This explains the inactivity of (tpfc)Mo^V(O) as an oxygen-transfer reagent, exemplified by the inertness to triphenylphosphine, a reaction that was used to convert (tpfc)Cr^V(O) to (Ph)₃PO-ligated Cr^{III}tpfc.¹³ (tpfc)Mo^V(O) exhibits an intense Soret-like band centered at 434 nm and Q bands centered at 546 and 580 nm (Figure 1, black line), as well as a well-resolved EPR spectrum

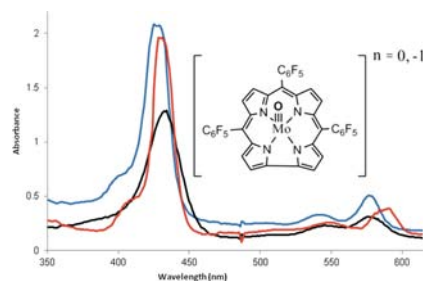


Figure 1. Electronic spectrum of (tpfc)Mo^V(O) (black) and changes upon the addition of CoCp*₂ (red) and [VMes₃(THF)] (blue).

at room temperature.¹³ The addition of either NaBH₄ or CoCp₂ to a N₂-purged THF solution of (tpfc)Mo^V(O) led to the appearance of a sharper and blue-shifted Soret band (from 434 to 426 nm; Figures S6 and S7). The use of the more powerful reducing reagent CoCp*₂ revealed a much more prominent intensity increase of the Soret band and also a new Q band with λ_{max} of 590 nm (Figure 1, red line). These results, together with the disappearance of the EPR signal and appearance of a well-resolved NMR spectrum (Figure 2c, vide infra), are fully consistent with the full and clean formation of [(tpfc)-Mo^{IV}(O)][–]. Identical spectral changes were obtained at longer

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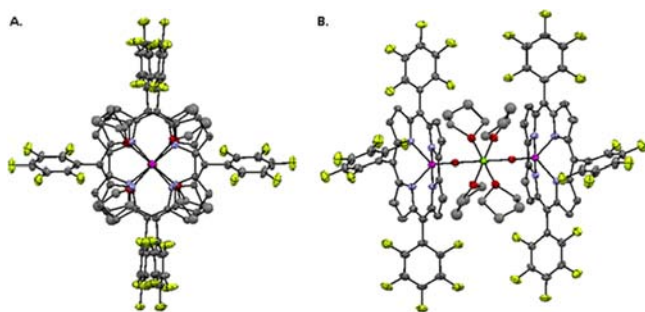


Figure 2. Projection of $[\text{Mo}(\text{tpfc})]_2\text{O}_2\text{Mg}(\text{THF})_4$: (A) top view; (B) side view.

reaction times with CoCp^*_2 , thus indicating that it only reacts slower than CoCp^*_2 because of a smaller thermodynamic driving force. Spectroelectrochemical investigation of the reduction process confirmed this proposal and the spectroscopic characteristics of $[(\text{tpfc})\text{Mo}^{\text{IV}}(\text{O})]^-$. Holding the applied potential at -0.5 V ($E_{1/2} = -0.96$ vs Ag/AgCl for $\text{CoCp}^*_2/[\text{CoCp}^*_2]^+$) led to an intensity increase and a 10 nm blue shift (from 430 to 420 nm) of the Soret band, and the visible band at 580 nm also increased and shifted to 590 nm (Figure S8).

The effect of TMSCl was found to depend on the reagent applied for the $(\text{tpfc})\text{Mo}^{\text{V}}(\text{O})$ to $[(\text{tpfc})\text{Mo}^{\text{IV}}(\text{O})]^-$ conversion. With NaBH_4 as the reducing agent, the addition of TMSCl initiated a color change from red to orange, a red shift of the Soret band from 420 to 430 nm, and the appearance of two Q bands at 542 and 578 nm. The anaerobically measured ^1H NMR spectrum pointed toward the formation of a diamagnetic complex that is consistent with $(\text{tpfc})\text{Mo}^{\text{IV}}\text{OSi}(\text{CH}_3)_3$: sharp β -pyrrole CH doublets at 9.2–9.7 ppm and a singlet at -1.8 ppm due to coordinated TMS (Figure S14). The conclusion is that applying this reaction sequence on $(\text{tpfc})\text{Mo}^{\text{V}}(\text{O})$, in contrast to the results with $(\text{tpfc})\text{Cr}(\text{O})$, did not lead to the formation of trivalent molybdenum. The addition of TMSCl to a solution of $[(\text{tpfc})\text{Mo}(\text{O})]^-$, obtained via the reduction of $(\text{tpfc})\text{Mo}^{\text{V}}(\text{O})$ by excess CoCp^*_2 , induced the formation of a dark-green (Soret band at 432 nm and Q bands at 550 and 585 nm) complex. While this might indicate a further reduction of the initially formed $(\text{tpfc})\text{Mo}^{\text{IV}}\text{OSi}(\text{CH}_3)_3$, the NMR spectra of that product could not be confidently analyzed. All crystallization attempts of the new complexes did not yield X-ray-quality crystals, and their exposure to air led to the reappearance of $(\text{tpfc})\text{Mo}^{\text{V}}(\text{O})$.

Because of the ambiguity in the results obtained by the stepwise reduction/deoxygenation of $(\text{tpfc})\text{Mo}^{\text{V}}(\text{O})$, the extremely oxophilic $[\text{VMes}_3(\text{THF})]$ was applied next. The addition of $[\text{VMes}_3(\text{THF})]$ to an anaerobic solution of $(\text{tpfc})\text{Mo}^{\text{V}}(\text{O})$ in THF induced immediate changes in the electronic spectra: all bands became more intense and the Soret band maximum shifted from 432 to 428 nm (Figure 1, blue line). More detailed information was obtained from the very informative ^{19}F NMR spectrum of the easily purified product.¹⁸ It revealed very sharp resonances, thus indicative of a new diamagnetic complex rather than the paramagnetic $(\text{tpfc})\text{Mo}^{\text{V}}(\text{O})$ starting material (Figure 2a) and the expected $\text{Mo}^{\text{III}}\text{tpfc}$. Another surprising phenomenon is the similarity of the complexes formed by the treatment of $(\text{tpfc})\text{Mo}^{\text{V}}(\text{O})$ with $[\text{VMes}_3(\text{THF})]$ (Figure 2b) and CoCp^*_2 (Figure 2c), by virtue of their almost identical electronic spectra (Figure 1) and similar ^{19}F NMR spectra.

While the spectroscopic features suggest the formation of molybdenum(IV) corroles (low-spin d^2) in both cases, one

pronounced difference is the separation of ortho- ^{19}F chemical shifts ($\Delta\delta$). The $\Delta\delta$ value of 1 ppm in $[(\text{tpfc})\text{Mo}^{\text{V}}(\text{O})]^-$ (Figure 2c) reflects the differences in the magnetic environments of the *o*-F atoms with syn and anti relationships relative to the Mo–O moiety. The much larger $\Delta\delta$ of 2 ppm in the new complex (Figure 2b) must, however, be of different origin. $\Delta\delta$ values that exceed 1 ppm are characteristic of binuclear corroles where one of the two *o*-F atoms in each C_6F_5 group experiences the diamagnetic ring current effect of the other corrole. Representative examples are the μ -oxo-bridged iron(IV) corrole $[\text{Fe}^{\text{IV}}(\text{tpfc})]_2\text{O}$ and the μ -trioxo-bridged tungsten(VI) corrole $[\text{W}^{\text{VI}}(\text{tpfc})]_2\text{O}_3$.^{19,4b} These spectroscopy-based hints about the formation of a binuclear complex in the reaction between $(\text{tpfc})\text{Mo}^{\text{V}}(\text{O})$ and $[\text{VMes}_3(\text{THF})]$ were verified when high-quality crystals were obtained via crystallization from cold ether (4°C) in the N_2 -purged glovebox (Figure 3).

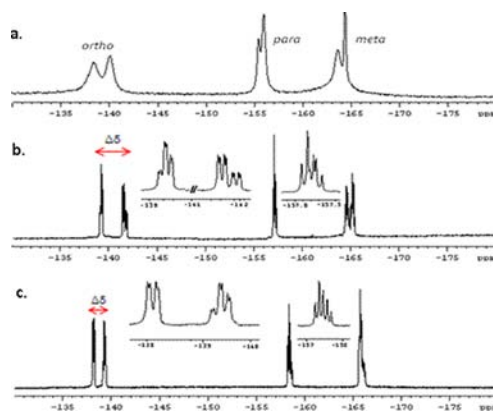


Figure 3. ^{19}F NMR spectra (under N_2 , in $\text{THF}-d_8$, relative to CFCl_3 , $\delta = 0.00$) of $(\text{tpfc})\text{Mo}^{\text{V}}(\text{O})$ (a). Complex obtained upon the addition of $[\text{VMes}_3(\text{THF})]$ to $(\text{tpfc})\text{Mo}^{\text{V}}(\text{O})$ (b). Complex obtained upon the addition of CoCp^*_2 to $(\text{tpfc})\text{Mo}^{\text{V}}(\text{O})$ (c).

The crystal data are as follows (excluding additional severely disordered diethyl ether solvent in the crystal lattice, eight molecules per unit cell, which could not be modeled by discrete atoms): $\text{C}_{90}\text{H}_{64}\text{F}_{30}\text{MgMo}_2\text{N}_8\text{O}_6 \cdot 2\text{C}_4\text{H}_8\text{O}$, $M = 2267.76$, monoclinic, space group $P2_1/n$, $a = 15.0152(7)$ Å, $b = 15.6890(6)$ Å, $c = 24.8277(12)$ Å, $\beta = 102.512(2)^\circ$, $V = 5709.8(4)$ Å³, $Z = 2$, $T = 110(2)$ K, $\rho_{\text{calcd}} = 1.319$ g cm⁻³, 25490 reflections measured, 10006 unique ($R_{\text{int}} = 0.061$; $2\theta_{\text{max}} = 50.1^\circ$), final $R = 0.079$ ($R_w = 0.189$) for 5984 reflections with $I > 2\sigma(I)$ and $R = 0.126$ ($R_w = 0.207$) for all data.

The dinuclear complex is located on crystallographic centers of inversion, with two of the four magnesium-bound THF ligands revealing conformational disorder. The individual $(\text{Mo}^{\text{IV}}-\text{O})(\text{tpfc})$ units on opposite sites of the inversion have a domed structure with a square-pyramidal coordination environment around the Mo center, similar to that observed in the monomeric $\text{Mo}^{\text{V}}(\text{O})$ complex.^{9a} The Mo ion is located 0.78 Å above the plane of the four pyrrole N atoms and 1.0 Å above the mean plane of the 19-atom carbon macrocycle. All of the equatorial Mo–N(pyrrole) bonds of the five-coordinate Mo ion are within 2.03–2.05 Å. The axial Mo–O bond length is 1.714(4) Å, significantly longer than that of 1.684(2) Å observed for $(\text{tpfc})\text{Mo}^{\text{V}}(\text{O})$.^{9a} The Mg ion in the center of the corrole dimer is six-coordinate, with four THF ligands occupying the equatorial positions at $\text{Mg}-\text{O}_{\text{THF}}$ distances of 2.085 and 2.086(4) Å and two Mo-linked O sites at the axial positions

with $\text{Mg}-\text{O} = 2.010(4) \text{ \AA}$. The observed coordination geometry around the Mg ion is very similar to that reported recently for the six-coordinate $\text{Mg}(\text{THF})_6$ complex.²⁰ The earlier mentioned additional molecules of the diethyl ether solvent are located in a disordered manner in the interstitial/intermolecular channel voids spanning along the *b* axis of the crystal.

One puzzle regarding the novel structure is the source of Mg therein, for which the only reasonable candidate is the bromo(mesityl)magnesium bromide, used for the preparation of $[\text{VMes}_3(\text{THF})]$ according to the procedure introduced by Floriani et al.¹⁷ Indeed, repetitive solvation of the intensively blue $[\text{VMes}_3(\text{THF})]$ revealed residual white solid therein, and the purest reagent reacted much more slowly with $(\text{tpfc})\text{Mo}^{\text{V}}(\text{O})$. This further suggested that residual bromo(mesityl)magnesium and not $[\text{VMes}_3(\text{THF})]$ is responsible for the reduction process. The reaction of bromo(mesityl)magnesium with $(\text{tpfc})\text{Mo}^{\text{V}}(\text{O})$ confirmed this hypothesis, as it led to a complex with an identical electronic spectrum and a ¹⁹F NMR spectrum very similar to that in the reaction with $[\text{VMes}_3(\text{THF})]$.

We provide fresh insight into the chemistry of molybdenum corroles, achieved via the development of new methodologies for reduction of the very stable (oxo)molybdenum(V) complex. This led to the spectroscopic identification of what appears to be mononuclear $(\text{tpfc})\text{Mo}^{\text{IV}}(\text{O})^-$ and $(\text{tpfc})\text{Mo}^{\text{IV}}\text{OSi}(\text{CH}_3)_3$, as well as the full characterization of a binuclear molybdenum(IV) corrole. The latter case is apparently novel, displaying a structure in which each of the two metal ions is chelated by a trianionic corrolate and one axial O atom and these subunits are bridged by a $\text{Mg}(\text{THF})_4$ moiety.

■ ASSOCIATED CONTENT

■ Supporting Information

Reduction of $(\text{tpfc})\text{Cr}^{\text{V}}(\text{O})$ by NaBH_4 , CoCp_2 , CoCp^*_2 , and $[\text{VMes}_3(\text{THF})]$, proposed mechanism of the deoxygenative reduction of $(\text{tpfc})\text{Cr}^{\text{V}}(\text{O})$, and crystallographic data for $[\text{Mo}(\text{tpfc})_2\text{O}_2\text{Mg}(\text{THF})_4]$ in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ Notes

The authors declare no competing financial interest.

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(18) Synthesis of $[\text{Mo}(\text{tpfc})_2\text{O}_2\text{Mg}(\text{THF})_4]$: A 20 mL THF solution of $(\text{tpfc})\text{Mo}^{\text{V}}(\text{O})$ (50 mg, 0.125 mmol) was stirred with excess of $[\text{VMes}_3(\text{THF})]$ at room temperature in a glovebox under N_2 . After 10 min, the color of the mixture changed from blood red (reactant) to light purple (product). THF was evaporated and replaced by diethyl ether, in which unreacted $[\text{VMes}_3(\text{THF})]$ was not soluble. The solution was filtered and evaporated. Crystallization from a minimum amount of diethyl ether yielded 70 mg (69%) of purple X-ray-quality crystals. ¹⁹F NMR (188 MHz, $\text{THF}-d_8$): δ -139.33 (dt, *J* = 26.59 and 8.08 Hz, 6F; *o*-F), -141.69 (dd, *J* = 24.51 and 7.4 Hz, 4F; *o*-F), -141.92 (dd, *J* = 20.98 and 7.6 Hz, 2F; *o*-F), -157.19 (t, *J* = 20.73 Hz, 4F; *p*-F), -157.34 (t, *J* = 21.02 Hz, 2F; *p*-F), -164.85 (m, 6F; *m*-F), -165.28 (m, 6F; *m*-F). ¹H NMR (200 MHz, $\text{THF}-d_8$): δ 9.08 (d, 4H), 8.72 (d, 4H), 8.64 (d, 4H), 8.55 (d, 4H). UV-vis (CH_2Cl_2 ; λ_{max} [nm] ($\epsilon \times 10^{-3}$ [$\text{M}^{-1} \text{cm}^{-1}$]): 424 (185.3), 577 (37.6).

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