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Reactivity of a Metastable Cobalt(III) Trisulfide Complex: Multiple C–H Functionalization of *p*-Xylene and Disulfides to Afford Photofunctional Cobalt Complexes**

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The chemistry of sterically restricted systems is becoming increasingly important. By protecting otherwise unfavored and unattainable chemical species, sterically restricted systems often give rise to unusual properties and reactivity. Supramolecular cages,[1] frustrated Lewis pairs,[2] and bowl-shaped reaction spaces[3] are types of sterically restricted systems that have been intensively studied. Such systems inside a bowl-shaped η^5-$C_{60}R_5$ ligand[4] are known to effectively perturb the structure and electronic structures of η^5-Cp metal complexes to afford unconventional species (Figure 1).[5] In particular, cobalt trisulfide complex **2**,[5c] which can be synthesized only inside a bowl-shaped $C_{60}Ar_5$ ligand, is of great interest because of the characteristic coexistence of stabilization (6π-aromaticity and strong steric protection) and destabilization (high ring strain and a coordinatively unsaturated metal center). Although a wide range of structures of metal polysulfide complexes have been studied as models of catalysts and enzyme active centers, and this area of research is rather mature,[6] cobalt trisulfide has a rare and unexplored type of structure. Thus, elucidation of its reactivity is promising for gaining new perspectives on novel chemical reactions, such as inert bond activation. Against this background, we herein report on unprecedented reactivity of cobalt trisulfide and demonstrate applications of C–H functionalization reactions to syntheses of a series of photofunctional cobalt complexes.

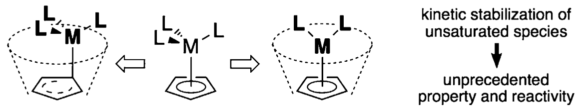
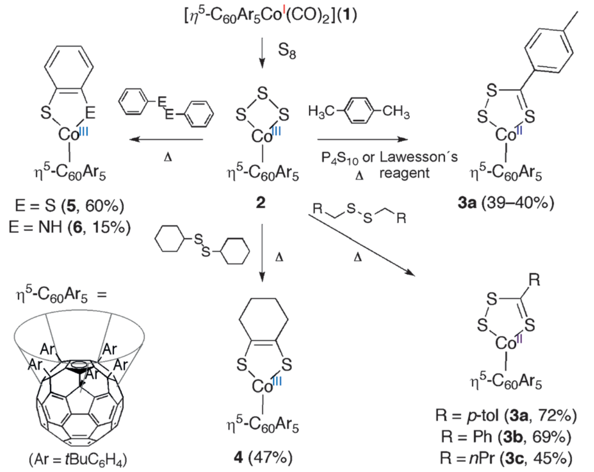


Figure 1. Representation of the effect of bowl-shaped η^5-$C_{60}Ar_5$ ligands.

In the presence of 1 equiv of phosphorus pentasulfide at 100 °C, cobalt trisulfide complex **2** reacted with the *p*-xylene solvent to form, via a formal ring expansion, a five-membered metallacycle, namely cobalt(II) 4-methyl trithioperoxobenzoate (**3a**; Scheme 1). Trithioperoxocarboxylate complexes belong to a rare class of sulfur-rich complexes; only a few examples have been reported to date,[7] for which, however, no cobalt complexes have been successfully synthesized. Triple C–H functionalization of *p*-xylene smoothly proceeded to afford **3a**, giving no detectable amount of singly or doubly C–H-functionalized species. The use of Lawesson's reagent instead of phosphorous pentasulfide also promoted the same C–H functionalization reaction to give **3a** in a similar yield.



Scheme 1. C–H functionalization reactions on cobalt(III) trisulfide complex **2**.

In the search of simpler reactions of cobalt trisulfide, we then investigated on the reactivity of **2** with several sulfur radicals. Sulfur radicals were generated by heating disulfides at 140 °C and were allowed to react with cobalt trisulfide **2**. When primary alkyl disulfides were used, double C–H functionalization proceeded at the geminal position from the sulfur atom to give the corresponding trithioperoxocarboxylate (**3a–c**) in moderate to good yields. The reaction proceeded both for benzylic (**3a** and **3b**) and aliphatic (**3c**) C–H bonds, indicating strong driving forces of the reaction.

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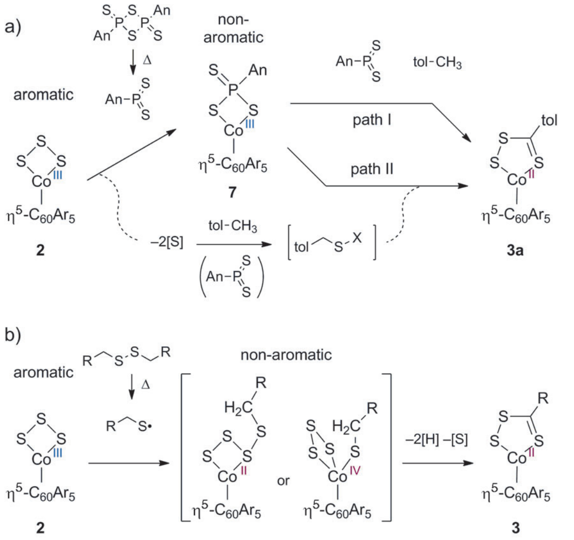
Secondary alkyl and aryl disulfides also underwent C–H functionalization to afford a series of pseudoaromatic[8] cobalt dithiolate complexes under similar conditions. In the case of cyclohexyl disulfide, because there is only one C–H bond at the geminal position, triple C–H functionalization, including two additional C–H bond cleavages at the vicinal position, proceeded to give a conjugated cobalt(III) cyclohexenyl dithiolate **4**. Furthermore, reaction of diphenyl disulfide and **2** gave cobalt(III) benzodithiolate complex **5** through single aryl C–H functionalization. Phenylhydrazine can also be used under these conditions to give a cobalt(III) benzoaminothiolate complex **6**, but the protic nature and lower stability of the radical resulted in a low yield.

For both C–H functionalization of *p*-xylene and disulfides, the reactions start with dearomatization of **2** and end with formation of less-strained five-membered d-π conjugated complexes. In the C–H functionalization reaction of *p*-xylene using Lawesson's reagent, rapid consumption of **2** accompanied by transient formation of cobalt(III) trithiophosphonate complex **7** and eventual formation of the product **3a** was observed (Supporting Information, Figure S1).[9,10] The low stability of **7** prevented its isolation, and thus only allowing HPLC and MALDI-TOF-MS observations, but the good agreement of the characteristic UV/Vis absorption pattern suggested the structure (Supporting Information, Figure S2). The active species **7** is thought to react with another dithiophosphine ylide and *p*-xylene (Scheme 2a, path I) or pre-sulfurized *p*-xylene (path II). In the C–H functionalization reaction of disulfides, dearomaticity of **2** is thought to be caused by an attack of a sulfur radical,[11] followed by abstraction of hydrogen and sulfur (Scheme 2b). No intermediates were observed in these radical reactions, suggesting high reactivity of the radical adducts toward C–H cleavage. Although the details of the reaction mechanisms are unclear in either cases of *p*-xylene or disulfides, disruption of metastable states with thermally activated species is the key to the reactions.



Scheme 2. Possible reaction paths of C–H functionalization reactions. An = anisyl.

The resulting [60]fullerene cobalt complexes were characterized by X-ray crystallography,[12] spectroscopy, electrochemical measurements, and steady-state and time-resolved photophysical techniques. The metallacycle structures were unambiguously determined by X-ray crystallography to reveal 7d-π conjugation in **3**[13,14] and 6π conjugation in **4**–**6**[15,16] (Figure 2a,b; Supporting Information, Figure S3).

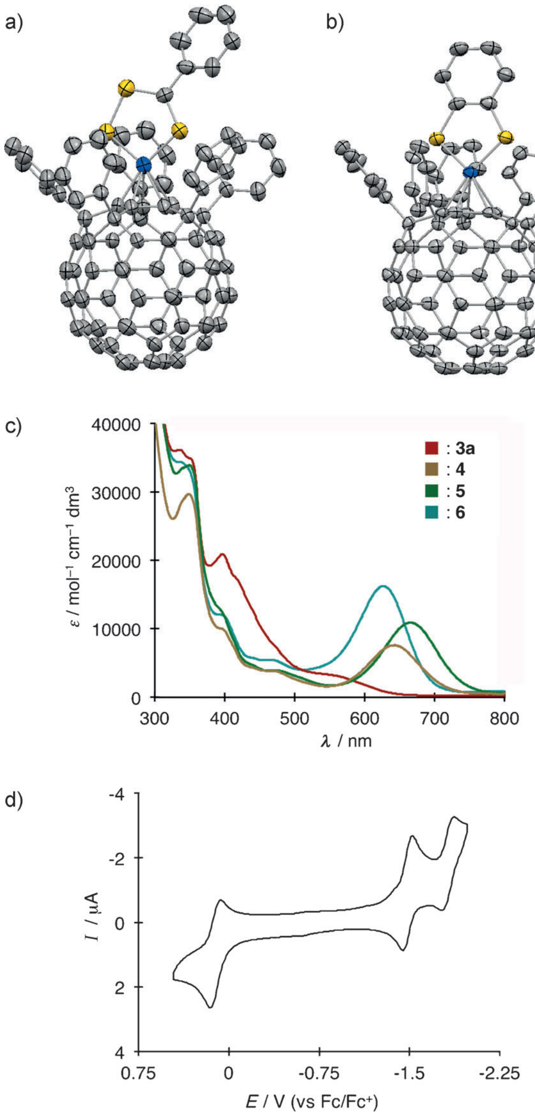


Figure 2. Crystal structures of a) **3b** and b) **5** (ORTEP drawings with ellipsoids set at 50% probability; *t*Bu groups, hydrogen atoms, and solvent molecules are omitted for clarity). c) UV/Vis absorption spectra of **3a**, **4**, **5**, and **6** in CH_2Cl_2. d) Cyclic voltammogram of **3a** in CH_2Cl_2 (tetrabutylammonium perchlorate (TBAP) as supporting electrolyte). $E_1^{ox} = 0.10$ V, $E_1^{red} = -1.48$ V, $E_2^{red} = -1.82$ V (versus Fc/Fc^+).

Bearing electron-accepting C_{60} moieties, all of the [60]fullerene cobalt complexes exhibit unique photofunctionality. While the electronic properties of the C_{60} cores remained similar to a large extent, different electronic structures of the metallacycles brought about diverse photophysical behaviors.

Owing to its electron donor–acceptor structure, **3a** exhibited a weak intramolecular charge-transfer (CT) absorption band involving a redistribution of charge density from the electron-rich cobalt(II) to C_{60} at about 560 nm. On the contrary, **4** and **5** show strong ligand-to-metal charge-transfer absorption (LMCT) from the dithiolate ligands to electron-deficient cobalt(III) at 642 and 666 nm,[17] respectively (Figure 2c).

Electrochemical measurements provided further evidence of the donor–acceptor structure of **3a**, that is, the cobalt(II) and C_{60}, and the donor–acceptor–acceptor structures of **4** and **5**, that is, dithiolate, cobalt(III), and C_{60}. In this regard, the electron-rich cobalt(II) and the electron-accepting C_{60} give rise in **3a** to a reversible oxidation at +0.10 V and reductions at −1.48/−1.82 V, respectively (Figure 2d). Note that **3a** is the first example of a stable paramagnetic [60]fullerene metal complex (Supporting Information, Figure S9). In **4** and **5**, the electron-rich dithiolate ligands, the electron-deficient cobalt(III), and the electron accepting C_{60} underwent dithiolate-centered oxidation at +0.65 V (**4**)/+0.77 V (**5**) (HOMO), cobalt-centered reduction at −1.34 V (**4**)/−0.95 V (**5**) (LUMO), and C_{60}-centered reduction at −1.54 V (**4**)/−1.48 V (**5**) (LUMO+1) (Supporting Information, Figure S4).

As a complement, the photophysical behavior of the [60]fullerene cobalt complexes was characterized (Figure 3 and Supporting Information). Photoexcitation of **3a** by femtosecond pump probe experiments[18] results in a short-lived (ca. 2 ps), non-fluorescent CT state in which charge density is pushed to the electron accepting C_{60} to yield $C_{60}^{\bullet-}$–Co^{III}. Notably, this CT state transforms into energetically lower-lying C_{60} excited states in the form of its singlet excited state with its 920 nm feature (ca. 30 ps) and of a triplet excited state with a 660 nm feature (1.3 ns).[19] This cascade of processes was consistent with fluorescence spectroscopic features of **3a**, which revealed exclusive C_{60} fluorescence at 610 nm after either CT excitation at 564 nm or C_{60} excitation at 350 nm (Supporting Information, Figure S7).[20] Nevertheless, the excitation spectrum of the 610 nm fluorescence maximum largely resembles the absorption spectrum, including the CT absorption around 560 nm. The behavior of **4** and **5** is fundamentally different. In particular, femtosecond pump probe experiments with **4** led to the instantaneous formation and the rapid decay (ca. 5 ps) of the LMCT state, that is, Co^{II}–dithiolate$^{\bullet+}$. The latter is succeeded by an approximately 20% formation of a longer-lived species (ca. 17 ps), which was assigned to a spatially well-separated $C_{60}^{\bullet-}$–dithiolate$^{\bullet+}$ charge-separated state.[21] Such an energetically high-lying state is only accessible because of the closely lying levels of the cobalt-centered LUMO and C_{60}-centered LUMO+1 in **4** (see above). In fact, **5** showed similar dynamics upon photoexcitation, but the larger LUMO to LUMO+1 gap lowers the amplitude of the $C_{60}^{\bullet-}$–dithiolate$^{\bullet+}$ charge-separated state to 10%.[22] The remaining 80% in **4** and 90% in **5** revert directly to the ground state. In the corresponding fluorescence experiments we note, besides C_{60} fluorescence at 610 nm and $C_{60}^{\bullet-}$–dithiolate$^{\bullet+}$ emission, no appreciable LMCT Co^{II}–dithiolate$^{\bullet+}$ emission. Considering the vastly different photophysical features of **3a**, **4**, and **5**, we are currently integrating them into novel photocurrent generation systems by means of self-assembled monolayers.[23,24]

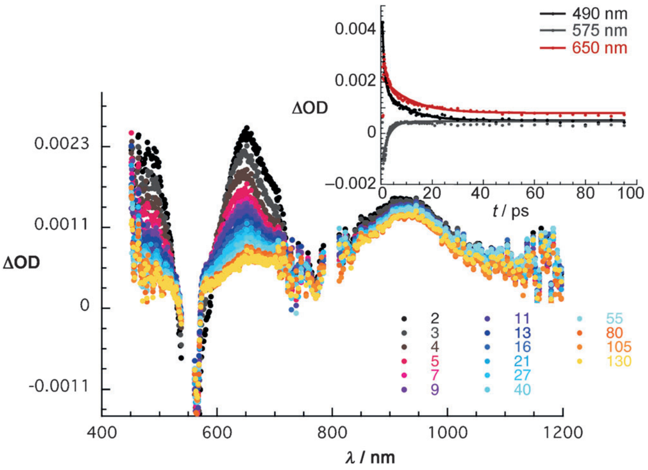


Figure 3. Differential absorption spectra of **3a** upon femtosecond pump probe experiments with time delays of between 2.1 and 210 ps (see figure for details) in argon-saturated toluene. Inset: Time-absorption profiles of **3a** upon femtosecond pump probe experiments at 550 nm in argon-saturated toluene.

In summary, we have elucidated the unprecedented reactivity of a metastable cobalt trisulfide complex by developing a variety of multiple C−H functionalization reactions of *p*-xylene and disulfides. The key to the reactions is the disruption of the metastability of cobalt trisulfide by thermally activated species to generate reactive intermediates. By taking advantages of these direct C−S bond formation reactions, several photofunctional cobalt complexes were synthesized and their photophysical properties were investigated. The $C_{60}Ar_5$ moieties worked as bowl-shaped steric protecting groups, as well as electron acceptors in photophysical processes.

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[9] To date, several trithiophosphonate complexes have been reported to show unique reactivity (Ref. [10]), but no cobalt complexes are known.

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[11] The reaction of **2** with thiol is very slow, but combination of thiol and elemental sulfur (a weak oxidizing reagent for thiol) give the corresponding C–H functionalization products. This observation indicates that the active species is a sulfur radical.

[12] CCDC 895454 (**3a**), 895455 (**3b**), 895656 (**4**), 895457 (**5**), and 895456 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[13] The Co–S bond length of 2.13 Å is shorter than the typical Co–S single bond of 2.23–2.25 Å, and C–S bond lengths of 1.65 and 1.69 Å are within the range of a C=S bond.

[14] Metal trithioperoxocarboxylates can be roughly classified into a nonplanar unconjugated type (for example, Ref. [7b]) and a planar d-π conjugated type (for example, Ref. [7c]). Complex **3** belongs to the latter, judging from the planarity of the five-membered ring and small bond alternations in the two C–S bonds and two Co–S bonds.

[15] The Co–S, C–S, and C–C bond lengths are identical to those in reported Cp and Cp* analogues (Ref. [16]; $Cp = C_5H_5$, $Cp^* = C_5Me_5$).

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[17] Note that this absorption is substantially red-shifted from the absorptions of $[CpCoS_2C_6H_4]$ (566 nm) and $[Cp^*CoS_2C_6H_4]$ (574 nm) because of the electron-withdrawing effect of C_{60} through homoconjugation (see also Ref. [19]). The same tendency can also be found in **4** and **6**.

[18] The excitation wavelength was 387 nm, which mainly excites C_{60}; however, the same result was obtained when the metallacycle was excited. The same is true for **4** and **5**.

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[20] Excitation of the metallacycle (564 nm) and C_{60} core (350 and 398 nm) gave similar emission efficiencies on the order of 10^{-4}.

[21] Ground-state bleaching is a characteristic feature of the pump-probe absorption measurements.

[22] The first and second reduction potentials of **4** differ only by 0.20 eV, while those of **5** differ by 0.53 eV.

[23] Derivatives with donor–acceptor structure (for example, **3**) are expected to generate cathodic photocurrent (see also Ref. [24a,b]), derivatives with donor–donor–acceptor structure without long-range CT (for example, **5**) are expected to generate anodic photocurrent (see Ref. [24c]), and derivatives with donor–donor–acceptor structure with long-range CT (for example, **4**) are expected to generate amphiphilic photocurrent.

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