Metal-Tuned Ligand Reactivity Enables CX_2 (X = O, S) Homocoupling with Spectator Cu Centers

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ABSTRACT: Ligand non-innocence is ubiquitous in catalysis with ligands in synthetic complexes contributing as electron reservoirs or co-sites for substrate activation. The latter chemical non-innocence is manifested in H⁺ storage or relay at sites beyond the metal primary coordination sphere. Reaction of a competent CO_2 -to-oxalate reduction catalyst, namely, $[K(THF)_3](Cu_3SL)$, where L^{3-} is a tris(β -diketiminate) cyclophane, with CS₂ affords tetrathiooxalate at long reaction times or at high CS₂ concentrations, where otherwise an equilibrium is established between the starting species and a complex—CS₂ adduct in which the CS₂ is bound to the C atom on the ligand backbone. X-ray diffraction analysis of this adduct reveals no apparent metal participation, suggesting an entirely ligand-based reaction con-



trolled by the charge state of the cluster. Thermodynamic parameters for the formation of the aforementioned $C_{ligand}-CS_2$ bond were experimentally determined, and trends with cation Lewis acidity were studied, where more acidic cations shift the equilibrium toward the adduct. Relevance of such an adduct in the reduction of CO_2 to oxalate by this complex is supported by DFT studies, similar effects of countercation Lewis acidity on product formation, and the homocoupled heterocumulene product speciation as determined by isotopic labeling studies. Taken together, this system extends chemical non-innocence beyond H⁺ to effect catalytic transformations involving C–C bond formation and represents the rarest example of metal–ligand cooperativity, that is, spectator metal ion(s) and the ligand as the reaction center.

INTRODUCTION

Ligand cooperativity is a recurrent theme in metal-catalyzed chemical transformations. This cooperative behavior can be effected through the influence of the secondary coordination sphere, covalent linkages by the supporting ligands to the substrate (or chemical non-innocence/cooperativity), or the redox participation of the ligand (or redox non-innocence). Of the modes of cooperativity, secondary coordination sphere effects and redox non-innocence have been widely explored synthetically and have strong precedent in enzyme systems.¹⁻¹² Classic examples of metal-ligand redox cooperativity rely on a redox-active ligand serving as a reservoir of electrons with the metal center serving as the site of the bondmaking and breaking events.^{3,4} The opposite scenario in which the ligand serves as the reaction site for bonding changes in the substrate with the metal ion(s) as the electron reservoir has a precedent in catalysis only for proton reduction.^{13–17} In this extreme of ligand cooperativity, the redox state of metal species can switch its reactivity on or off by altering the electron density on the reactive ligand site.^{13,18,19} Intermediate cases (i.e., both the metal and ligand cooperate in redox and substrate activation) are well represented in the literature. For instance, seminal work by Milstein and co-workers followed by reports from de Vries and co-workers highlighted the

generality of a de- and rearomatization sequence to effect the functionalization of unsaturated functional groups, particularly nitriles, at tridentate pincer complexes (Figure 1a-c).²⁰⁻²² Recently, Liaw et al. reported that CO₂ reduction to oxalate by an iron nitrosyl complex traverses a C–N bond between a ligand N atom and CO₂ (Figure 1d).²³

Examples of reversible bond formation involving only ligands have been reported but are not in the context of catalytic transformations. For instance, various groups have reported reversible C–C bonds between the *para*-C of aromatic ligands (e.g., pyridine bound to iron(I) β -diketiminate or a perfluorophenylimidocobalt diketimide; Figure S1).^{24,25} This reaction is best described as arising from the radicaloid character on the bound arene. Andersen et al. and Chmielewski et al. similarly reported reversible C–C bonds by a phenanthroline ytterbium complex and a

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Figure 1. Intermediates involved in catalytic cycles where the ligand is covalently supporting a non-H substrate (highlighted in red).

pyrimidine-containing norcorrole nickel complex (Figure S1).^{26,27} Relatedly, β -diketiminates (BDIs) can also react as a nucleophile due to the contribution of the $2p_{\pi}$ orbital of the γ carbon atom to the π -nonbonding HOMO (Figure S17).^{28–30} Reaction at the γ carbon typically affords the addition of unsaturated substrates across the metal and ligand, which is analogous to the Milstein systems (Figure S2).³¹ For example, CO₂ binding to the γ -carbon of BDI complexes is reported for the main group ions Sc³⁺, Mg²⁺, and Li⁺ (Figure 2)^{32–34} with



Figure 2. Structures of the CO₂ adducts involving C_{γ} -CO₂ bond formation with BDI complexes of Sc, Mg, and Li. The fragment derived from CO₂ is depicted in red.

 CO_2 capture being reversible for the Sc^{3+} and Mg^{2+} compounds. Both C_{γ} -X bond formation and cleavage must readily occur to activate substrates and release products in any catalytic cycle. Contrasting the tridentate meridional chelating ligands, no catalytic transformations are reported to harness the non-innocence of BDI ligands in substrate activation.

Among a series of reports of CO₂ reduction to oxalate, we noted that systems that achieve the catalytic turnover feature coordinatively saturated metal centers (Figure 3),³⁵ while coordinatively unsaturated copper centers bind to the formed oxalate and arrest after a single turnover.^{36,37} In this context, our group previously reported kinetic studies of CO₂ reduction to oxalate by tricopper sulfide and selenide clusters (Cu₃SL⁻ and Cu₃SeL⁻, where $L^{3-} = \text{tris-}\beta$ -(diketiminate), namely, 1⁻ and 2^- , respectively; Figure 3). These two catalysts display a cation and solvent dependence of the observed rate constant, wherein more Lewis acidic cations and less coordinating solvents favor the kinetics for the formation of oxalate. Additionally, 2^- reacts faster than 1^- , which can be explained by the stronger reducing power of the former ($E_{1/2}$ of -1.44 V and -1.58 V vs the ferrocene couple for 1 and 2, respectively).^{39,40} Herein, we report the reactivity of 1^- with



Figure 3. Cu-based molecular catalysts for the reduction of CO_2 to oxalate.

the related heterocumulene carbon disulfide, which results in a hemilabile C–C bond between the substrate and ligand with no apparent interaction between the metal center and substrate. In contrast to other examples of CS₂ homocoupling to $C_2S_4^{2-}$, which are proposed to occur by a transient with CS₂ bound to the redox active metal,^{41–45} we provide evidence in support of a ligand-centered mechanism for the homocoupling of both CS₂ and CO₂. As a consequence, this constitutes the first report of a functional ligand with spectator redox-active metal centers capable of catalyzing C–C coupling, which is a unique example of the last type of metal–ligand chemical cooperativity.

RESULTS AND DISCUSSION

Addition of 22 equiv of ${}^{13}\text{CS}_2$ to a 4.9 mM solution of $[\mathbf{K}(\mathbf{THF})_3]\cdot\mathbf{1}$ at an ambient temperature in THF- d_8 afforded a green solution and a brown precipitate upon mixing. No ${}^{13}\text{C}$ labeled products were observed in the ${}^{13}\text{C}$ NMR spectrum of the THF soluble fraction (Figure S14). However, dissolution of the nonvolatiles of this reaction in MeOH- d_4 and analysis by ${}^{13}\text{C}$ NMR spectroscopy reveal a signal at 270.1 ppm and support the formation of tetrathiooxalate as the only ${}^{13}\text{C}$ labeled species (Figures S15 and S16).⁴⁶ A similar ${}^{13}\text{C}$ NMR experiment performed at -80 °C with 4.0 mM [$\mathbf{K}(\mathbf{THF})_3$]·1, and 2.3 equiv ${}^{13}\text{CS}_2$ revealed a signal at 231.9 ppm, which is suggestive of the formation of a dithiocarboxylate (Figure S12).⁴⁷⁻⁵¹

At ambient temperature, 0.05 mM $[K(THF)_3]\cdot 1$, and 1 equiv of CS₂, minimal to no reaction is observed. Upon cooling to -55 °C, a color change from blue to turquoise. Warming this reaction mixture to ambient temperature reverses this color change (Figure S4), suggesting that the low-temperature species is in equilibrium with $[K(THF)_3]\cdot 1$.

Single-crystal X-ray diffraction on blue crystals of the lowtemperature species, $[K(THF)_2]$ ·3, were grown at -35 °C from slow diffusion of pentane into a saturated THF solution containing excess CS₂. This structure revealed CS₂ bound to the γ -C of one BDI arm of the ligand (Figure 4 and Scheme 1). The bond lengths and angles around the γ -C bound to CS₂ and the loss of planarity of the chelate arm match prior structures in which the γ -C of BDI metal complexes acts as a nucleophile and support a neutral diimine chelate.³⁰ The K⁺ interacts with the installed dithiocarboxylate, two THF molecules, and a η^{5} -



Figure 4. Geometry-optimized structures for $[K(THF)_3]$ ·3 (left) and $[K(THF)_3]$ ·4 (right).





BDI of a proximal complex to give a 1D-chain structure (Figure S3). The structure here evokes those of the main group complexes as the Cu remains bound to the two N atom donors, contrasting the metal ion dissociation from the diimine chelate observed by Hayton and co-workers in the reaction product of a BDI nickel complex and CS₂ (Figure S2).⁵² The Cu center in the neutral diimine arm is disordered over two positions with 46 and 54% occupancy or Cu_{46%} and Cu_{54%}, respectively (Figure 4 and Figure S2). Cu_{54%} is displaced from the chelate plane by 0.571 Å (vs 0.0511 Å at the unaffected arm), whereas Cu_{46%} is displaced by 0.200 Å. The Cu–SCS distance (2.698(9) Å for Cu_{54%} and 3.11(1) for Cu_{46%}) is much greater than the sum of the covalent radii (viz. 2.37 Å),⁵³ suggesting a minimal Cu–SCS interaction in the solid state. The C_γ–CS₂ bond length in [K(THF)₂]·3 (Table 1) is within

Table 1. $C_{BDI}-CX_2$ (X = S, O) Bond Lengths for M·3 (M = $[K(THF)_2]^+$ and $[K(THF)_3]^+$), $[K(THF)_3]$ ·4 and the BDI-CS₂ Adduct Reported by Hayton and Co-workers, and Corresponding Calculated Mayer Bond Orders for $[K(THF)_3]$ ·3 and $[K(THF)_3]$ ·4

	d (Å)	Mayer BO
C _{BDI} -CS ₂ Hayton	1.54(1)	
C_{BDI} - CS_2 experimental	1.565(4)	
C _{BDI} -CS ₂ calculated	1.5475	0.6500
C_{BDI} - CO_2 calculated	1.6164	0.8942

range of reported C–C single bonds and comparable to Hayton et al.'s Ni complex.⁵² For comparison, the average C–C bond length of the ethyl groups on the phenyl caps is 1.528(5) Å, and the labile C–C bond in the Gomberg's dimer is 1.597(4) Å.⁵⁴

Given the observed reversibility of the reaction of $[K-(THF)_3]\cdot 1$ with CS₂ arising from the formation of a labile C–C bond in $[K(THF)_2]\cdot 3$ (Scheme 1), we monitored this reaction with a large excess of CS₂ (i.e., 165 equiv) by variable temperature UV-visible spectroscopy (VT UV-vis). At

ambient temperature, new bands at 608 and 736 nm are observed, together with those for the reduced complex at 695 nm. The new bands increase in intensity with a concomitant decrease in those at 695 nm upon cooling to -35 °C, whereas the new bands disappear completely upon warming to 55 °C (Figure 5 and Figure S3). Values of K_{eq} at various temperatures



Figure 5. Single-crystal structure of $[K(THF)_2]$ ·3 at 50% thermal ellipsoid depicting only Cu_{54%}. For clarity, atoms in the structure are partially transparent, except for the Cu₃S cluster with the primary coordination sphere and the BDI arm bonded to CS₂. Solvent molecules of crystallization and H atoms are omitted for clarity with Cu, K, S, N, and C atoms depicted as bronze, pink, yellow, blue, and gray ellipsoids, respectively.

were calculated by varying the equivalents of CS_2 and deconvoluting the mixture as a composite of the reduced complex and the presumed CS_2 adduct (Figures S5, S6, and S8). Thermodynamic parameters determined from a van't Hoff analysis are consistent with an entropically disfavored exothermic reaction (Table 2 and Figure S9). The obtained

Table 2. Thermodynamic Parameters for the Formation of 3^- with $[K(THF)_2]^+$ and $[Cp*_2Co]^+$ as Counterions

	$[K(THF)_2] \cdot 3$	[Cp* ₂ Co]·3
$\Delta H \; (\text{kJ} \cdot \text{mol}^{-1})$	$-28(2)^{a}$	$-38(1)^{c}$
$\Delta S (J \cdot mol^{-1} \cdot K^{-1})$	$-49(9)^{a}$	$-130(5)^{c}$
$\Delta G \; (\mathrm{kJ} \cdot \mathrm{mol}^{-1})$	$-14(3)^{b}$	$-6(2)^{d}$
^a Temperature range: 248–278	K. ^b Temperature:	278 K. ^c Tempe

ature range: 178–248 K. ^dTemperature: 248 K.

 ΔH value is within the range seen for the homolytic dissociation of other labile σ C–C bonds, which span values between 26 and 84 kJ/mol, including that for Gomberg's dimer (46 kJ/mol).^{26,27} Enthalpy changes are available for some of Milstein's and Fedushkin's systems,^{20,22,55} but deconvoluting the contribution of the metal–ligand bond is not trivial and precludes a direct comparison.

Previously, our group reported that the single turnover pseudo-first-order rate constants for oxalate formation from CO_2 by 1^- and 2^- increase with more Lewis acidic counterions.³⁸ Given that tetrathiooxalate formation observed here parallels that of CO_2 to oxalate reduction by 1^- and $2^{-,38}$ we were curious if the equilibrium observed for CS_2 capture by 1^- was similarly sensitive to countercation identity. Therefore, we determined the equilibrium constant (K_{eq}) for the formation of adduct 3^- with $[Cp*_2Co]^+$ (Cp* = 1,2,3,4,5pentamethylcyclopentadienyl) as a counterion using VT UV– vis spectroscopy. Treatment of $[Cp*_2Co]\cdot 1$ with 40 equiv CS_2 at ambient temperature results in no significant changes with respect to the spectrum of 1^- . As for $[K(THF)_3]\cdot 1$, lowering the temperature results in the appearance of two new bands at 613 and 729 nm; however, these bands are discernible only at temperatures below $-65 \,^{\circ}$ C for $[Cp*_2Co]\cdot 1$ and conversions comparable to those observed for $[K(THF)_3]\cdot 1$ required substantially lower temperatures (Figure 6 and Figure S7). The



Figure 6. VT-UV-visible spectra in the range from 55 to -35 °C for a reaction between [**K**(**THF**)₃]·1 at 0.05 mM and 165 equiv CS₂ in THF.

corresponding thermodynamic parameters highlight that the contribution of entropy dominates the effect of changing the counterion on the equilibrium constants (Table 2 and Figure S10). We hypothesize that the differences in enthalpy and entropy change for $[Cp^*_2Co]^+$ versus K⁺ as the countercation correlate with the energetic cost to reorganize the cation–complex interaction from the reactant to product; that is, dissociation of K⁺ from $[K(THF)_3]$ ·1 in the starting material costs more versus the less tightly bound $[Cp^*_2Co]^+$, whereas the more localized negative charge on the dithiocarboxylate versus 1⁻ affords a tighter cation–anion pair (Figure S11).

Given these results with CS₂ activation and homocoupling to $C_2S_4^{2-}$, we probed whether the reduction of CO₂ to oxalate proceeded by a similar ligand-based pathway. Indeed, a nucleophilic attack by supporting ligands was proposed in other systems as the first step toward CO₂ reduction to oxalate, 23,56 and CO₂ adducts at BDI are known (Figure 2). However, these adducts have not exhibited further reactivity beyond reversible binding; in those cases, a lack of available reducing equivalents likely precludes reductive coupling. By comparison, reversible binding to CS_2 by 1^- hints at the propensity for Cu to participate in bonding similar to p-block elements, supporting the covalency previously reported for the tricopper-chalcogen core⁴⁰ and the growing evidence of Cu complexes having inverted ligand fields.^{57–61} Notably, CX_2 (X = S, O) binding by 1^{-} can be viewed as stimulus-responsive; whether the effect arises from the redox load of the complex or the change in overall charge remains to be determined.

A lack of observable intermediates and coincident pseudofirst-order rate constants for the formation of 1 and decay of 1⁻ in single turnover experiments with CO₂ have limited mechanistic studies; however, the formation of tetrathiooxalate, the countercation dependence, and the precedent in other BDI complexes support parallel reactivities for CS₂ and CO₂ with 1⁻. We reasoned then that coupling CS₂ to CO₂ could provide additional support for a common mechanism. Unfortunately, the addition of CO₂ to [K(THF)₂]·3 generated in situ with excess CS₂ affords oxalate as the only CO₂-derived product based on ¹³C NMR spectra (Figure S13). The reaction rate of $[K(THF)_3]$ ·1 with CO₂ and subsequent downstream steps to oxalate and 1 must be faster than the reaction of $[K(THF)_2]$ ·3 with CO₂ or with the analogous CO₂ adduct $[K(THF)_2]$ ·4, which disturbs the equilibrium involving CS₂ and $[K(THF)_3]$ ·1 (Scheme 1).

In addition to the possible kinetic schemes that would allow for the accumulation of 3^- but not the CO₂ congener 4^- , another possible reason could be a difference in the equilibrium position for the reaction of $[K(THF)_3]$ ·1 with \overline{CS}_2 versus \overline{CO}_2 , that is, in the energies of $[K(THF)_2]$ ·3 and its CO_2 analog ([K(THF)₂]·4) as compared to complexes lacking the $C_v - CX_2$ bond. To that end, we turned to density functional methods. Our calculations were benchmarked with our experimental results with CS₂. First, we optimized the geometry of the crystallographic coordinates of $[K(THF)_2]$ ·3 in which the η^5 -BDI coordination to K⁺ was replaced by one or two THF molecules (abbreviated as $[K(THF)_n]$ ·3 and n = 3 or 4). Second, we optimized only the H-atom positions for $[K(THF)_3]$ ·1 starting from the reported crystallographic coordinates. Third, we optimized a structure in which a CS₂ molecule was placed in close proximity to the K⁺ ion and the $[Cu_3S]^{2+}$ core in $[K(THF)_3] \cdot 1$ (abbreviated $[K(THF)_3] \cdot 1$ $1+CS_2$). For comparison, we computed the CO₂ congeners of $[K(THF)_n]$ ·3 (abbreviated $[K(THF)_3]$ ·4) and $[K(THF)_3]$ · 1+CO₂ (Tables S5–S10).

The optimized geometries for $[K(THF)_n]$ ·3 with 3 or 4 THF molecules are comparable, and both reproduce the main features of the crystal structure of $[K(THF)_2]$. with respect to the C_{γ} -CS₂ bond lengths (Table 1). One notable deviation, however, is that the computed Cu-SCS contacts are shorter than the X-ray structure (by approximately 0.5 Å) and suggestive of a coordination bond. This result is independent of the number of THF molecules bound to K⁺ and the method used (i.e., BP86, TPSSh, or B3LYP). Somewhat surprisingly, optimized geometries for [K- $(THF)_3$]·1+CS₂ afforded structures in which the K⁺ remains bound to one BDI arm and that lacks the C-C bond between C_{γ} and CS_2 , with a CS_2 interacting with a Cu center and the K⁺ ion. Setting all calculated species relative to $[K(THF)_3]$ ·1 and free CS2, [K(THF)3]·3 (-93.41 kJ/mol) is the lowest energy species followed by $[K(THF)_3]$ ·1+CS₂ (-52.50 kJ/mol). Gratifyingly, these results agree with the experiment as $[K(THF)_2]$ ·3 is an observable intermediate upon a reaction of $[K(THF)_3]$ ·1 with CS₂ and with the computed and experimental C_{γ} -CS₂ bond energies being comparable (-40.9 kJ/mol vs -38.1 kJ/mol). We posit that the energetic cost to displace $[K(THF)_3]^+$ from a BDI arm to interact with the dithiocarboxylate effectively makes [K(THF)₃]·1+CS₂ a local minimum. Additionally, calculations on $[K(THF)_3]$ ·1 support the fact that the unpaired α electron occupies an orbital of metal-BDI σ^* and Cu–S π^* character, which is consistent with prior calculations on the LUMO for neutral 1.³⁹ Occupying this orbital conceivably leads to greater electron density on the BDI arms and enhanced nucleophilicity. Indeed, more negative Mulliken charges are observed on all C_{y} atoms in $[K(THF)_3]$ ·1 as compared to 1 (Table S3). In prior calculations on 1, we also noted minimal mixing of the π -type nonbonding orbitals on the BDI arms with those of the cluster; for example, the three highest occupied orbitals on 1 were a pseudo e' and a_2' molecular orbitals almost exclusively derived from linear combinations of the BDI nonbonding π -type orbitals. By contrast, we observe substantial mixing of the cluster-based

orbitals with the nonbonding π -type orbitals on the BDI arms in $[K(THF)_3]$ ·1. This greater mixing upon reduction may serve to enhance the delocalization of the electron density of the metal cluster onto C_{γ} of the BDI arms, thereby increasing the nucleophilicity and activating the complex for a reaction with CS₂ (Figure S18).³⁰

Geometry optimizations for the proposed CO_2 adduct $[K(THF)_3]$ ·4 yield a comparable structure to the CS_2 congener except that the CO_2 carboxylate is rotated away from the copper cluster to afford Cu–O distances greater than expected for a coordination bond (Figure 7).⁶² The absence of



Figure 7. UV–visible spectra at -35 °C for $[K(THF)_3]\cdot 1$ (red trace) and $[Cp*_2Co]\cdot 1$ (blue trace) both at 0.05 mM with 40 equiv CS₂ in THF.

a Cu–OCO interaction suggests that the role of the $[Cu_3S]^{2+}$ core is to tune the electronic structure of the ligand to trigger CO₂ capture by nucleophilic attack with subsequent nethomolytic C₇–CO₂ bond cleavage to yield oxalate. Contrasting the CS₂ series, the optimized structure $[K(THF)_3]$ ·1+CO₂ (i.e., no C–C bond) is lower in energy (-41.6 kJ/mol) than $[K(THF)_3]$ ·4 (-36.8 kJ/mol) as referenced to the sum of the energies of $[K(THF)_3]$ ·1 and CO₂. In $[K(THF)_3]$ ·1+CO₂, CO₂ is held within the pocket between K⁺ and the $[Cu_3S]^{2+}$ cluster and interacts with only the K⁺ center. These calculated energies agree with our inability to observe $[K(THF)_3]$ ·4 in kinetic experiments (Scheme 2). Taken together with the CS₂ calculations, K⁺ coordination to the CX₂ fragment in $[K(THF)_3]$ ·3 and $[K(THF)_3]$ ·4 is consistent with the cation and solvent dependence of the reaction rates and prior reports





of CO_2 ligation to BDI complexes wherein Lewis acid coordination to the CO_2 derived carboxylate is observed.^{33,38}

Forming labile C–C bonds with the ligand, which is controlled by electronic fine-tuning of the $[Cu_3S]^{2+}$ core upon reduction, evokes that reported for the release of Michael-type products from reversible coordination of nitriles to pincer ligands upon the addition of Michael acceptors,^{20–22} suggesting that the labile C–C bond is instrumental for productive coupling chemistry. Reaction of 1^- with heterocumulenes constitutes a rare example of a functional ligand— one extreme of metal–ligand cooperativity— and in which a net one-electron reaction is initiated by a two-electron step (nucleophilic attack).¹³

CONCLUSIONS

Reversible coordination of CS_2 to the γ -C of a BDI ligand in a $[Cu_3-\mu^3-S]^{2+}$ cyclophanate complex 3⁻ is reported. The formation of this labile C-C bond was studied by VT-UVvisible spectroscopy, and the product was characterized by single-crystal X-ray diffraction and NMR methods. DFT calculations performed on the CS₂ adduct agree with experimental data, with 3^- being lower in energy than the reactants, 1^- and CS₂. Similar calculations on a CO₂ analogue of 3^- reveal that a comparable structure, namely, 4^- , is energetically accessible, albeit destabilized versus the outer sphere CO₂ associated complex by 4.8 kJ/mol. In the CO₂ adduct 4⁻, the CO₂ fragment is twisted away from the copper cluster, suggesting no active involvement of the [Cu₃S]²⁺ core in the CO_2 trapping. In light of these results, we infer that the CO2 adduct is an intermediate in the reduction of carbon dioxide to oxalate by 1^- and 2^- . To gauge the relevance of the computationally observed CO_2 adduct 4⁻ in the mechanism to form oxalate, we searched for and successfully identified tetrathiooxalate by ¹³C NMR in reactions with ¹³CS₂, further supporting analogous mechanisms in play for the reduction of both heterocumulenes. These results therefore highlight the relevance of ligand cooperativity in catalysis and in particular of the underrepresented extreme of functional ligands with spectator metals.

ASSOCIATED CONTENT

3 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.3c11928.

Experimental details, VT UV–vis data, detailed thermodynamic calculations, ¹³C NMR data, Mulliken charges, calculated MO representations, crystallographic data, and DFT optimized coordinates (PDF)

Accession Codes

CCDC 2300148 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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Captions for Figures 4–7 were corrected on January 10, 2024.