Cooperative C-O Bond Activation by a Heterobinuclear Al-Fe Complex Operating by a Radical Pair Mechanism

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ABSTRACT: Activation of inert molecules like CO₂ is often mediated by cooperative chemistry between two reactive sites within a catalytic assembly, the most common form of which is Lewis acid/base bifunctionality observed in both natural metalloenzymes and synthetic systems. Here, we disclose a heterobinuclear complex with an Al-Fe bond that instead activates CO₂ and other substrates through cooperative behavior of two radical intermediates. The complex L(Me)Al-Fp (2, L = HC{(CMe)(2,6-Pr₂C₆H₃)N})₃, Fp = FeCp(CO)₃) was found to insert CO₂ and cyclohexene oxide, producing LAI(Me)(µ-κ₂:O-C)Fp (3) and LAl(Me)(µ-OC₆H₅)Fp (4), respectively. Further atom transfer, decarbonylation, and isomerization reactivity was also observed. Detailed mechanistic studies on the CO₂ and epoxide insertion reactions indicate an unusual mechanism in which (i) the Al-Fe bond dissociates homolytically to generate formally AlIII and FeI metalloradicals, then (ii) the metalloradicals add to substrate in a pairwise fashion initiated by O₂ coordination to Al. The accessibility of this unusual mechanism is aided, in part, by the redox non-innocent nature of L that stabilizes formally AlIII intermediates with predominantly AlIII-like character. This “radical pair” pathway represents an unprecedented mechanism for CO₂ activation.

INTRODUCTION

Identifying new reaction pathways for activation of inert substrates enables rational design of catalysts for challenging synthetic transformations. Although historically the activation of inert substrates by coordination complexes has focused on unsaturated mononuclear systems with single-site reactivity, recently there has been a resurgence in cooperative bond activation studies in which reactivity is delocalized over two or more reactive sites within a well-defined system. Examples include frustrated Lewis pairs (FLPs),¹ metal-ligand bifunctional catalysts,² homo- and heterobinuclear metal complexes,³ and multinuclear metal clusters.⁴ As a representative example, one can consider the coordination chemistry of CO₂. While CO₂ activation by mononuclear metal complexes has been mapped extensively,⁵ remaining challenges in catalytic CO₂ fixation have motivated numerous studies on cooperative CO₂ activation.⁶ The dominant paradigm is one of Lewis acid/base bifunctionality (Figure 1a): a Lewis basic reactive site adds a reactive electron pair to the carbon center of CO₂, while the resultant buildup of negative charge on oxygen is simultaneously stabilized by a Lewis acidic reactive site.⁷ Since the seminal work of Floriani on cooperative CO₂ activation by low-valent Co/M bifunctional systems (M = alkali metal),⁸ numerous examples of metal- and non-metal-based systems functioning by this paradigm have been identified.⁹ Moreover, Lewis acid/base bifunctionality is thought to be the operative paradigm in nature, stabilizing CO₂-activated intermediates in both aerobic (Mo/Cu) and anaerobic (Ni/Fe) carbon monoxide dehydrogenase enzymes.¹⁰ Identifying reaction pathways beyond this prevailing CO₂ activation manifold has the potential to open new catalyst design strategies.¹¹

Figure 1. Cooperative CO₂ activation pathways and representative examples: (a) Lewis acid/base bifunctionality, (b) radical pair chemistry (this work).

In this report, we disclose a system that activates CO₂ and other substrates by a radical pair mechanism, which is a novel mechanistic paradigm for cooperative CO₂ reactivity (Figure
In our discovered system, a heterobinuclear complex dissociates homolytically to generate two metalloradical intermediates, which then cooperatively activate CO₂ as a radical pair that donates one electron per metal. Activation of CO₂ by a metalloradical pair is quite rare, and typically generation of the radical pair in those cases requires photochemical or electrochemical activation of a precursor complex.\(^{12}\) The concept of frustrated radical pairs has recently emerged in the field of FLP chemistry,\(^ {12b-c}\) but typically such systems are limited to activation of relatively weak bonds (e.g. H-SnR₃, RO-OR) or substrates possessing radical character of their own (e.g. O₂, TEMPO). On the contrary, here the heterobimetallic radical pair is capable of cooperatively activating not only CO₂ but also the C-O bond of an epoxide as well as Sn and Me₃Si-N₃, all under ambient conditions with no external stimulus.

![Diagram of heterobimetallic complexes](image)

**Figure 2.** Previous examples of heterobimetallic Al¹-M or Al³⁻⁻⁻M complexes (M = earth abundant transition metal).

As detailed below, our discovery emerged from studies of an Al-Fe heterobinuclear system. Despite extensive recent work on heterobimetallic chemistry,\(^ {13}\) heterobimetallic complexes combining main group and transition metals are rare in comparison to such complexes pairing two transition metals. Aluminum is the most abundant metal in earth’s crust (7.4%) and finds use in many catalytic transformations.\(^ {14}\) However, heterobimetallic complexes bearing aluminum are not thoroughly studied and their reactivity remains underexplored.\(^ {15}\) especially for heterobimetallic complexes in which aluminum is paired with another earth-abundant metal. The Nöth and Braunschweig groups synthesized Al³⁻⁻⁻Fe heterobimetallic complexes (I and II; Figure 2), but no reactivity was reported.\(^ {16,17}\) Very recently, the Power group reported synthesis of an Al¹-Cu heterobimetallic species (III).\(^ {18}\) Hill, McMullin, and coworkers also prepared Al¹-Cu heterobimetallic complexes and explored their reactivity with CO₂ and carbodiimides.\(^ {19}\) The Lu group prepared a coordination complex containing Ni and Al³⁻⁻⁻ (IV).\(^ {20}\) The Crimmin group synthesized Cr-Al³⁻⁻⁻ complex from the reaction of Al(I) and Cr(CO)₅,\(^ {21}\) although no reactivity was reported.

We became interested in pursuing the chemistry of Al³⁻⁻⁻-Fe complexes. Despite aluminum and iron being the two most abundant metals in earth’s crust (7.4% and 5%, respectively), only a few Al³⁻⁻⁻-Fe heterobimetallic complexes have been reported but their reactivity has never been studied.\(^ {16,17,22}\) Herein we report that the Al³⁻⁻⁻-Fe heterobimetallic complex, L(Me)Al⁻⁻⁻Fe(CO)₂ (L = HC₅(CMe₂)₂,6,7-Pr₃C₆H₃N), is able to insert CO₂ and cyclohexene oxide as well as undergo atom transfer reactions. Moreover, photochemical decarbonylation and isomerization pathways are also reported. All the new complexes were structurally characterized. Using a combined experimental/computational approach, the reaction pathways for CO₂ activation and epoxide ring opening were elucidated to involve (i) homolytic dissociation to formally Al³⁻⁻⁻ and Fe³⁺ metallocradicals, then (ii) pairwise addition to substrate prior to solvent cage escape. This “radical pair” mechanism is a novel mode of cooperative CO₂ activation.

**RESULTS & DISCUSSION**

**Synthesis and thermal reactivity.** To synthesize Al³⁻⁻⁻-Fe heterobimetallic complex LAl(Me)Fp (2, Fp = FeCp(CO)₂), reaction of LAl(Me)I (1) was carried out with KFp in a mixture of toluene and ether for 16 h. Compound 2 was obtained as a colorless solid in moderate yield (66 %) and was found to be soluble in toluene and diethyl ether but to decompose in tetrahydrofuran, chloroform, and dichloromethane.

Reactions of 2 with CO₂ and epoxide were carried out since they are useful feedstock for preparation of cyclic or polycarbonate products, often with the involvement of Al catalysts.\(^ {23}\) According to scheme 1, reaction of compound 2 with CO₂ in toluene resulted CO₂-inserted product LAl(Me)(μ:κ₃-O₂C)Fe(CO)₂ (3) as a colorless solid in 81% yield (Scheme 1). Insertion of CO₂ into Al⁻⁻⁻M bonds with κ₃ binding to Al is rare, with previously reported examples involving low valent Al⁻⁻⁻Au and Al⁻⁻⁻Cu complexes rather than Al³⁻⁻⁻ species.\(^ {19,24}\) Compound 3 was stable under heat and vacuum, and we observed no evidence for conversion back to 2 under these conditions. In the \(^ {13}\)C\(^ {1}\)H NMR spectrum of 3, the carbon atom of the κ₃-O₂C moiety resonates at 220.8 ppm, which is shifted downfield compared to the bridging CO₂ unit in [Cp₂ZrCl(μ:κ₃-O₂C)FeCp(CO)₂] (δ =212.6 ppm).\(^ {25}\) Stoichiometric reaction of 2 with cyclohexene oxide was carried out at room temperature, resulting in ring-opened product LAl(Me)(μ-OC₆H₁₅)Fp (4, 57 %, Scheme 1). Ring opening of epoxides using Al/Co heterobimetallic catalysts has been proposed by the Coates group for several carbonylation reactions,\(^ {26}\) but such an intermediate has never been isolated until now. Compound 4 is stable at -25 °C but decomposes slowly at room temperature inside the glove box.
Scheme 1. Thermal and photochemical reactivity studies of an Al$^{III}$-Fe heterobinuclear system, including solid-state structures of complexes 2-7 determined by X-ray crystallography. For clarity, hydrogen atoms and co-crystallized solvent molecules are omitted from the crystal structures; ligand backbones (except nitrogen) are shown as wireframes, and all other atoms are shown as 50% probability ellipsoids.

The molecular structures of 2 and 4 feature four-coordinate aluminum centers with distorted tetrahedral geometries, while 3 has a penta-coordinate aluminum center with distorted square pyramidal geometry, as determined by X-ray crystallography. The Fe-Al bond length [2.478(9) Å] in 2 is comparable to the value of 2.480(1) Å reported for the related compound LAl(Cl)Fp* (Fp* = Cp*Fe(CO)$_2$; Cp* = C$_5$Me$_5$). The Al-O bond lengths in 3 [1.980(1) and 1.897(1) Å] are slightly longer to the corresponding bonds [1.880(5) and 1.861(4) Å] present in (NON)Al(κ$_2$-O$_2$C)AuPMe$_3$ (NON = 4,5-bis(2,6-disopropyl-3-ylidene)-2,7-di-tert-butyl-9,9-dimethylxanthene) reported by the Aldridge group, possibly due to the different aluminum oxidation states. The O-C bond lengths for the Al(κ$_2$-O$_2$C)Fe unit in 3 [1.271(2) and 1.298(2) Å] fall between the typical ranges for C-O single and double bonds. The Fe-C bond [1.933(1) Å] of the Al(κ$_2$-O$_2$C)Fe unit is considerably longer than the Fe-C bond [1.87(1) Å] seen in Ph$_3$Sn(κ$_2$-O$_2$C)FeCl(depe) (depe = 1,2-bis(diethylphosphino)ethane). The molecular structure of 4 reveals that LAl(Me)O and Fp moieties are in trans orientation about the cyclohexane unit. The Al-O bond length [1.728(2) Å] is quite shorter than those
Complex 2 was also found to do sulfur atom abstraction from elemental sulfur, giving product 5 in which sulfur inserted into the Al-Fe bond (64%, Scheme 1). As expected, the Al-S bond length in 5 determined by X-ray crystallography [2.2005(7) Å] is longer than the Al=Si bond length [2.104(1) Å] present in Al=Si(NH) (NH = [(CH₃CN(Pr))₁₂C]) but close to Al-S single bonds in [Al(μ-S):TiC₂ₚ] (2.208(1) and 2.197(1) Å). The Fe-S bond distance (2.316(8) Å) is in the range of those reported in related organoiron-sulfur complexes (2.26-2.35 Å).

Photochemical reactivity: Complexes 2 and 3 are stable thermally (up to 60 °C) in Cd₄ for at least for 12 h but were found to react further upon irradiation with UV light. Irradiation of a Cd₄, solution of 2 for 5 h at room temperature resulted in yellow crystals of new complex 6 in low yield (Scheme 1). The solid-state IR spectrum of 6 does not show any intense bands in the 2100-1800 cm⁻¹ region characteristic of terminal carbonyl groups, but a new band indicative of bridging carbonyl groups was observed at 1524 cm⁻¹. Due to poor solubility in common organic solvents, we could not characterize complex 6 in the solution state, but the identity of the product was confirmed by single-crystal XRD studies. The molecular structure consists of two [LAl(Me)] and one [CpFeCO₂] motifs. It is worth mentioning here that the [CpFeCO₂] motif was not characterized structurally in any complex to date, despite the long history of [CpFe(CO)₂] chemistry. The Fe-Fe distance in 6 is 2.3543(5) Å, which is significantly shorter than the Fe single bond of the classical [Fe₂(CO)₅] [2.523(1) Å] or in [CpFe(CO)₂] [2.5389(3) Å] and can thus be calculated as a Fe=Fe double bond. The C-O bond length in 6 [1.292(3) Å] is longer than the terminal C-O bonds [1.157(4) Å] present in 2.

Subsequently, a Cd₄, solution of 3 was irradiated at ambient temperature for 5 h. The ¹H NMR spectrum reveals complete conversion of 3 to 7 (Scheme 1). In the ¹H NMR spectrum of compound 3, the methyl protons bonded to the aluminum center appear as a singlet at -0.20 ppm but are shifted downfield to 1.71 ppm in 7, indicating methyl migration from the aluminum center to the ligand backbone. The crystal structure of 7 revealed that its aluminum center is tetra-coordinate with two nitrogen and two oxygen atoms in its immediate environment. It also confirmed that the methyl group migrated from aluminum to the β-diketiminate backbone as anticipated from ¹H NMR spectroscopy. The methyl migration to the β-diketiminate ligand transforms it into a dianionic ligand. Although the M-C bond migration phenomenon is common in transition metal β-diketiminate chemistry, this is first report involving an aluminum β-diketinate. The C₄NAlSix membered ring is puckered with both Al-N bonds being almost equal in distance 1.774(3) Å and 1.808(3)). The Al-O bond lengths [1.862(2) Å and 1.848(2)] are shorter than in 3 due to change in coordination number at the aluminum center.

Computational analysis of atomic charges & bonding. To better understand the origins of reactivity of our Al³⁺-Fe heterobimetallic complex LAl(Me)Fp (2), we decided to study the charge distribution using NBO 36 (Figure S19) and QTAIM 37 (Figure 3) analysis methods on pre-optimized geometries for complex 2 and, for modelling purposes, its simplified counterparts with methyl (Me) 8 and phenyl (Ph) 9 substituents in place of 2,6-disopropylphenyl (dipp) in 2. QTAIM charges, being origin-independent 38 and more “chemically intuitive”, are consistent with representation of complexes 2, 8 and 9 as featuring strongly polarized covalent Al³⁺-Fe⁶⁺ bonds. For comparison, we also calculated NBO and QTAIM charges for a well-studied heterobimetallic system 39. Al³⁺MesCuFp 10 (MesIsMes= 1,3-bis(2,4,6-trimethylphenyl)-4,5-dimethylimidazol-2-ylidine, Figures S19 and 3). Just like for Al-Fe complexes, QTAIM charges are much closer to traditional ideas of valences, with Cu being in the oxidation state of (almost) one and Fe being in the oxidation state of zero.

Figure 3. Calculated QTAIM charges for selected atoms in 2 and 8-10, with M-Fe Wiberg bond indices indicated below the structures.

To further confirm the presence of the covalent bond between two metals, we calculated Wiberg Bond Indices (WBI) in Löwdin orthogonalized basis 36 (Figure 3 and Table S1). From the obtained data we can conclude that the Al-Fe bond in 2 is almost twice as covalent as the Cu-Fe bond in 10.

Although the used methods gave quite differing charge values, trends between structures in question are consistent. This allowed us to (initially) simplify our model and study Me-substituted complex 8 in lieu of complex 2 to study its reactivity in silico towards CO₂ insertion and epoxide ring opening at a lower computational cost.

Combined computational/experimental investigation of reaction mechanisms. We decided to begin with calculating energies for two dissociation pathways (Scheme 2a), homolytic and heterolytic, for truncated model complexes 8 and 9. However, dissociation energies for both 8 and 9 proved to be too high, even when including effects of the toluene solvent. It is worth noting that Gibbs free energies and enthalpies are significantly (>20 kcal/mol) lower for homolytic rather than heterolytic dissociation. Steric bulkiness of substituents (i.e. Me vs Ph) appeared rather irrelevant: for homolytic dissociation both ∆Gₜ and ∆Hₜ were just ~6 kcal/mol lower for significantly bulkier Ph (9), and for heterolytic dissociation Gibbs free energies and enthalpies for Ph were even higher than for Me (8). Therefore, we decided not to proceed with dissociation calculations.

in compound 3. The Fe-C₃ bond length is 2.111(3) Å, which is in range of reported Fe-C₃alkyl bonds.
for complex 2 \((R = \text{dipp})\), a decision that later proved imprudent.

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\begin{align*}
\text{Homolytic dissociation} & \quad \Delta G_\text{d} = +48.3 \text{ kcal/mol for 8 (R = Me)} \\
& \quad \Delta G_\text{d} = +42.5 \text{ kcal/mol for 9 (R = Ph)}
\end{align*}
\]

\[
\begin{align*}
\text{Heterolytic dissociation} & \quad \Delta G_\text{h} = +74.0 \text{ kcal/mol for 8 (R = Me)} \\
& \quad \Delta G_\text{h} = +74.2 \text{ kcal/mol for 9 (R = Ph)}
\end{align*}
\]

**Scheme 2.** Unscaled Gibbs free energies (PBE1PBE) for (a) Al-Fe bond dissociation and (b) concerted CO\textsubscript{2} insertion pathways.

Since calculated dissociation energies turned out to be too high for reactions that occur readily at ambient conditions, we decided to explore possible mechanistic pathways beginning with the concerted CO\textsubscript{2} insertion (Scheme 2b) via the corresponding transition state (TS). Obtained Gibbs free energies (all relative to 8) indicated that while the CO\textsubscript{2} insertion per se is thermodynamically favorable, the concerted pathway’s high activation barrier is inconsistent with a reaction that occurs with reasonable rate at room temperature, which is what was observed experimentally. To make sure the obtained TS energy was not some sort of a functional artifact, we recalculated the transition state energy using several DFT functionals (Figure S16), as well as the TS energy of CO\textsubscript{2} insertion for complex 9. Obtained Gibbs free energies are generally consistent among all employed functionals, which indicates that such a high obtained value is not an error of the chosen functional.

However, it is commonly accepted\(^{41}\) that translational entropies for reactions in solution should be corrected (scaled) since the loss of molar entropy when two or more molecules in solution interact is not accounted by solvation free energies. Thus, we applied one of the most used correction methods,\(^{42}\) which effectively calls for neglecting the contribution of translational entropy altogether. Since such an approach introduces an unknown degree of uncertainty to the Gibbs energies, we limited ourselves only to qualitative comparison of the calculated activation barriers. The scaled TS Gibbs energies (Figure S16) were found to be in the desired range \((-25 \pm 1 \text{ kcal/mol})\) for some functionals. Nevertheless, the activation barrier for this reaction would be higher since the real translational entropy term is not zero.

To gain additional insights on the mechanism, we next conducted an Eyring analysis by obtaining experimental, pseudo-first order (excess CO\textsubscript{2}) rate constants for CO\textsubscript{2} activation by 2 across the temperature range 263-303 K (Figure 4). Fitting the data to the Eyring equation provided the experimentally determined activation parameters for CO\textsubscript{2} insertion by complex 2: \(\Delta H^\circ = 24.9 \text{ kcal/mol}, \Delta S^\circ = 20.5 \text{ kcal/mol}^{\circ}\text{K}, \Delta G^\circ_{298K} = 18.8 \text{ kcal/mol}\). The activation entropy for this reaction is large and positive, which indicates a dissociative rate-determining step and is therefore inconsistent with the concerted mechanism shown in Scheme 2b (which should give \(\Delta S^\circ < 0\)). Moreover, the trans-stereochemistry of the ring-opened product 4 evident by X-ray crystallography indicates anti-addition of the two metals to the epoxide and thus also testifies against any similar concerted mechanisms.

**Figure 4.** Eyring analysis to extract activation parameters for the CO\textsubscript{2} activation reaction by 2.

With these considerations in mind, we decided to revisit the dissociation pathways, this time with the model for 2 with full-sized dipp-substituted ligands (Scheme 3). To our surprise, the dissociation Gibbs free energies and enthalpies were ~15...
kcal/mol lower than for closest counterpart 9. This brought the activation barrier down, closer to the experimental value and within the expected range for a room-temperature reaction. Therefore, relying on models with truncated substituents, a common approach in computational organometallic chemistry, is not always justified. It is curious that addition of just two isopropyl groups to each phenyl ring had such drastic effect on dissociation energies, which we attribute solely to significantly higher steric tension in complex 2 relative to 8 and 9, given their similar electronic structures. Collectively, these observations also reinforce the critical importance of calibrating computed mechanisms with experimental (preferably kinetics) data.

Scheme 3. Gibbs free energies (PBE1PBE) for Al-Fe bond dissociation of 2.

With more evidence towards homolytic dissociation of complex 2 as the origin of its reactivity and having ruled out several alternatives (Figure S18), we calculated the Gibbs free energies of interactions of both Al and Fe metalloradicals with both CO₂ and cyclohexene oxide. As follows from the obtained Gibbs energies, it is clear that both CO₂ and cyclohexene oxide prefer to react with the Al radical 13 (Al(dipp)) first rather than with Fe radical 14 (Fp), as indicated in Scheme 4. In the first case, for CO₂ insertion, we could not localize a minimum corresponding to the radical Fe-CO₂ complex 15 (however, we were able to localize a minimum for a similar anionic complex, which has been observed experimentally⁵¹, see SI for more details). Instead, the localized minimum was some sort of a supramolecular complex of Fp radical 14 and CO₂ held together by weak non-covalent bonds (as shown by QTAIM diagrams and calculated WBIs; Figure 5a). However, we localized a minimum for the complex 16 where a linear CO₂ molecule is coordinated on the Al center of complex 13, giving a quite strong covalent bond (also Figure 5a). Such coordination is endothermic, but the subsequent interception of Fp radical 14 makes CO₂ insertion a thermodynamically favorable process.

Scheme 4. Gibbs free energy diagram for calculated pathways of CO₂ activation mediated by 2.

Epoxide ring opening is also an exothermic process even for initiation with the Al radical 13, while initiation by Fe radical 14 has a very high barrier (Scheme 5). Subsequent recombination of Al-epoxide complex 18 with Fp 14 to give the observed product 4 is energetically very favorable.

Scheme 5. Gibbs free energy diagrams for calculated pathways of cyclohexene oxide ring opening mediated by 2.

Scheme 6. Reaction of 2 and Me₃SiN₃, including solid-state structures of complex 19 determined by X-ray crystallography. For clarity, hydrogen atoms and co-crystallized solvent molecules are omitted from the crystal structures; ligand backbones (except nitrogen) are shown as wireframes, and all other atoms are shown as 50% probability ellipsoids.

The identification of the O-bound CO₂ adduct 16 along the reaction pathway is notable, as this coordination mode has rarely been observed experimentally⁶⁰ and is typically proposed
during (1-electron) reductive coupling of CO$_2$ to form oxalate\(^{45}\) (rather than for 2-electron CO$_2$ reduction). Moreover, it is a rare example of a formally Al$^3$ species playing an important role in reactivity.\(^{46}\) Thus, we chose to analyze the electronic structure of 16 and its precursor complex 13 further. Calculated Mulliken spin densities for selected atoms (Figure 5b) of these complexes indicate that the unpaired electron is mostly delocalized through the conjugated β-diketiminate ligand but not on Al itself for either complex, nor on the CO$_2$ moiety in the case of 16. In other words, although 13 is formally a [(L)Al$^3$(Me)] species, it is perhaps better formulated as [(L$^2$)Al$^{13}$(Me)] and thus possess a vacant Al-centered 3$p$ orbital for substrate coordination.

Given these computational results indicating an unusual radical-pair mechanism for the cooperative bond activation chemistry of 2, we sought experimental evidence for formation of metalloradicals 13 and/or 14 under relevant conditions. One observation we can report is the reaction of 2 with excess Me$_2$SiN$_2$, which resulted LAI(Me)N$_2$ (19) and Fp$_2$ as major products (Scheme 6). The formation of Fp$_2$ as the dominant Fe-containing product in this reaction can be viewed as experimental validation of metalloradical 14 forming in situ. Further evaluation of the radical-pair reactivity of 2 is currently underway in our laboratory.

CONCLUSIONS

A series of reactivity studies were carried out on a heterobimetallic Al-Fe complex, 2. Most notably, complex 2 reacts cleanly with CO$_2$ and cyclohexene oxide, giving CO$_2$ inserted product 3 and epoxide ring opening product 4, respectively. Detailed kinetic and theoretical studies were performed on these two reactions and indicated an unusual radical-pair mechanism in which Al-Fe homolytic dissociation precedes pairwise metalloradical addition to substrate. Particularly novel aspects of this study include:

- Unexpected involvement of formally Al$^3$ reactive intermediates
- An unprecedented mechanism for CO$_2$ activation
- An instructive interplay between theory and experiment that emphasizes the importance in computational organometallic chemistry of (i) validating calculated reaction pathways with kinetics measurements, and (ii) modeling complete (as opposed to truncated) ligand substituents

METHODS

Experimental methods. All experimental manipulations were carried out under inert dinitrogen atmosphere using standard Schlenk line and glovebox techniques. All new compounds were characterized by $^1$H and $^{13}$C($^1$H) NMR spectroscopy, solid-state IR spectroscopy, and single-crystal X-ray diffraction. Detailed experimental procedures and spectral data are available as Supplementary Information, and supporting crystallographic data in the form of CIF files are available upon request from the Cambridge Crystallographic Data Centre using deposition numbers 2100519-2100528.

Computational methods. Density Functional Theory calculations (at the PBE0\(^{76}\)-G3B\(^{77}\)/def2-TZVP\(^{78}\) level of theory; SMD\(^{79}\) solvation model with toluene parameters), as implemented in the Gaussian 16 (Revision B.01)\(^{80}\) code, were employed to optimize molecular geometries and determine bonding energies, Mulliken spin densities and NBO charges (using NBO version 3.1,\(^{49}\) as implemented in Gaussian 16). The open-source MultiWFN\(^{90}\) (version 3.8) program was employed to calculate and visualize Wiberg bond indices, QTAIM charges, critical points and paths (using data derived from Gaussian DFT calculations). For more details on comprehensive computational methods please see Supplementary Information.

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures, spectral data, computational data (PDF)

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ACKNOWLEDGMENT
This material is based upon work supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences (BES), under Award Number DE-SC0021055. Computational resources and services were provided by the Advanced Cyberinfrastructure for Education and Research (ACER) group at UIC. Instrumentation for X-ray crystallography at UIC was funded, in part, by the National Institutes of Health under grant ROI GM116820. The structure of complex 7 was obtained using NSF’s ChemMatCARS Sector 15 supported by the Divisions of Chemistry (CHE) and Materials Research (DMR), National Science Foundation, under grant number NSF/CHE-1834750. Use of the Advanced Photon Source, an Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357.

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