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Diverse Thermal and Photochemical Reactivity of an Al−Fe Bonded Heterobimetallic Complex

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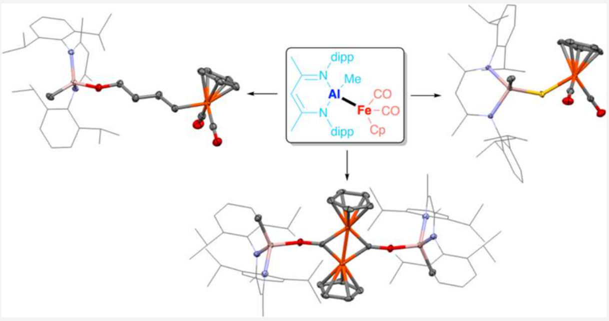
ABSTRACT: A heterobimetallic Al−Fe complex, LAl(Me)Fp (Fp = $FeCp(CO)_2$, L is a β-diketiminate), was found to have diverse reaction chemistry including cooperative ring-opening of tetrahydrofuran to form $LAl(Me)O(CH_2)_4Fp$, atom transfer with propylene sulfide and elemental sulfur to form LAl(Me)(μ-S)Fp, and group transfer with trimethylsilyl azide to form $LAl(Me)N_3$. Photodecarbonylation formed $[LAl(Me)]_2(CpFe{=}FeCp)(\mu_3{:}\eta^2\text{-}CO)_2$, which features the Fe═Fe bonded $[CpFe(CO)]_2$ unit that is the unsaturated analogue of well-known Fp_2. Despite Al and Fe being the two most earth-abundant metals, this report represents one of the only surveys of the reactivity behavior of an Al/Fe heterobinuclear complex.



Heterobimetallic complexes can involve any two metals from the periodic table, and significant efforts have been spent to determine combinations in which there are potentially beneficial differences between the two metal centers.[1,2] As the field continues to expand, many applications of heterobimetallic complexes have been discovered in bond activation and catalysis.[3−8] The two most abundant metals on earth are aluminum (7.4%) and iron (5%), and so it is surprising that the reaction chemistry of Al/Fe heterobimetallic complexes is underdeveloped in this context. The groups of Nöth, Braunschweig, Aldridge, Crimmin, and Fischer synthesized different Al−Fe bonded heterobimetallic complexes during 1996−2021 (**I-VI**; Figure 1a), but in none of these cases were reactivity studies reported.[9−13] Very recently we synthesized the heterobimetallic Al−Fe complex **1** and studied its reactivity with CO_2, cyclohexene oxide, and benzophenone (Figure 1b).[14] Our study revealed unique reaction mechanisms in which the Al−Fe bond in **1** dissociates homolytically to in situ generate two radical intermediates, which then cooperatively activate substrates upon their *O*-coordination to Al. Subsequently, Crimmin's group reported detailed mechanistic investigation of pyridine C(sp^2)−H activation by an Al/Fe heterobinuclear system.[15] While our study focused on activation of specific C—O/C═O bonds and Crimmin's focused specifically on pyridine *ortho*-metalation, there has not yet been a wide-ranging reactivity survey of any Al/Fe system. Here, we report further reactivity studies of complex **1** that showcase the diverse range of transformations accessible to this system.

We previously observed cooperative ring-opening of cyclohexene oxide by **1** (Figure 1b).[14] Given that epoxides possess significant ring strain on the order of 26 kcal/mol,[16] we wondered whether complex **1** would be sufficiently reactive to open a less strained cyclic ether. To probe this question, we chose to examine tetrahydrofuran (THF), whose ring strain energy is only 5.4 kcal/mol.[16] Stoichiometric reaction of **1** with THF (1 equiv) in toluene at room temperature for 24 h resulted in clean formation of ring-opened complex LAl(Me)(μ-OC_4H_8)Fp (**2**) (61%; Scheme 1). Yellow crystals of **2** suitable for X-ray crystallography were obtained from pentane at −25 °C after a week. The molecular structure confirmed that the THF ring had been opened: [LAl(Me)O] and [Fp] moieties were found to be connected by a linear four-carbon chain. The Al−O and Fe−C_{alkyl} bond lengths [1.714(1) and 2.065(2) Å, respectively] are similar to those in the cyclohexene oxide ring-opened product, LAl(Me)(μ-OC_6H_{10})-Fp.[14] The solid-state IR spectrum of **2** shows intense ν_{CO} bands at 1939 and 1996 cm^{-1}, which also are quite close to those in the cyclohexene oxide ring-opened complex. Ring opening reactions of THF by both Al[17−19] and Fe[20,21] compounds have been observed previously but, invariably, involve cationic mechanisms. Given that generation of cationic intermediates can be ruled out in this case,[14] the observed reaction is a novel example of THF opening by a radical pathway. There are only a few previous reports of crystallographically characterized compounds showing ring-opened THF captured between two metal centers,[22−25] none of which resulted from reactions of THF with well-defined

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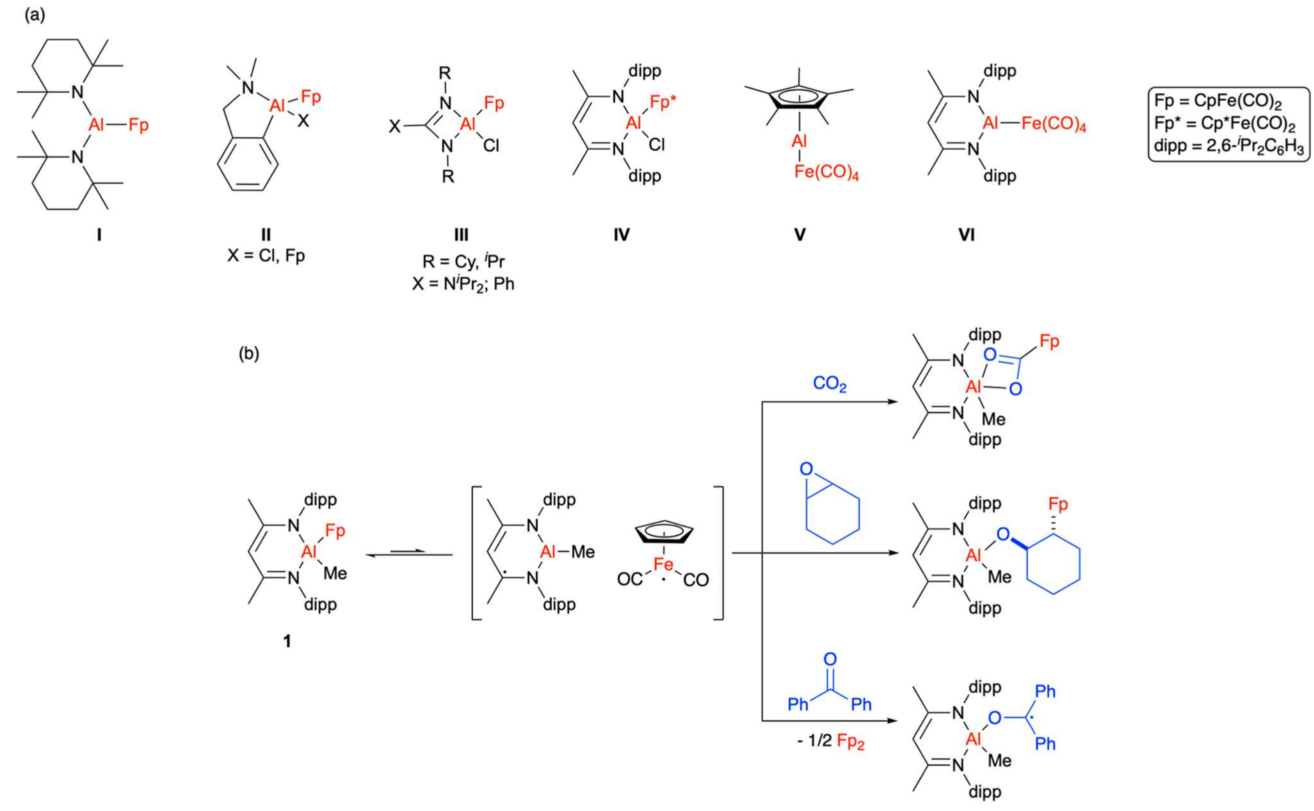
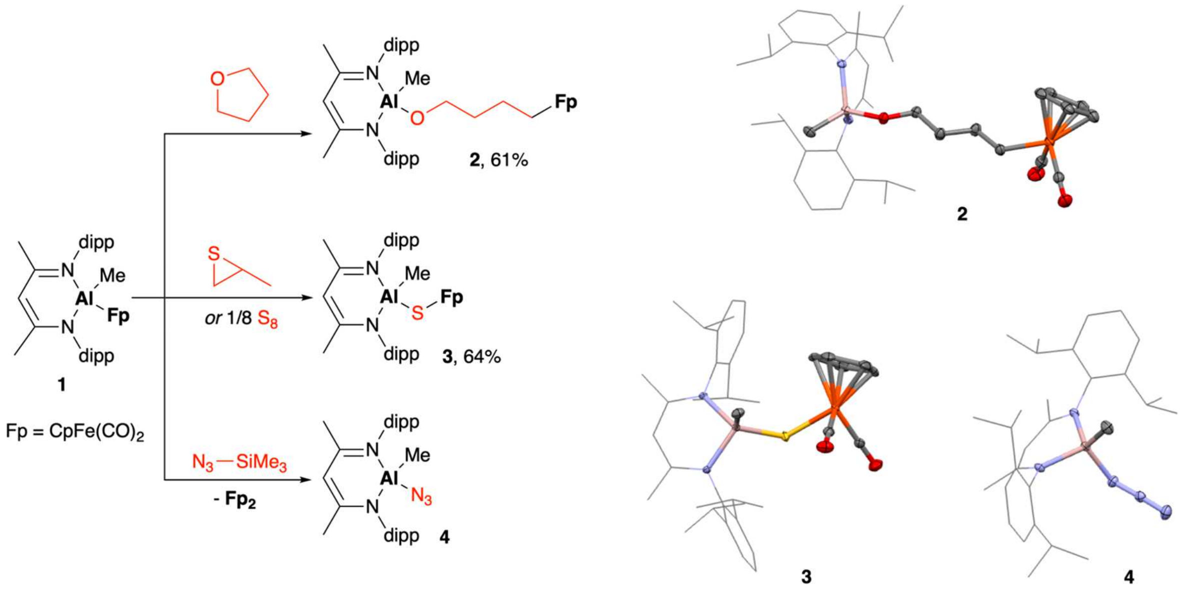


Figure 1. (a) Previously synthesized complexes with Al−Fe bonds. (b) Preliminary reactivity studies of Al−Fe bonded complex **1**.

Scheme 1. Diverse Reaction Chemistry of Heterobimetallic Al−Fe Complex 1[a]



[a] Fp = CpFe(CO)$_2$, dipp = 2,6-di-isopropylphenyl, isolated yields shown. Formation of **2**−**3** was performed in toluene solution at room temperature, and formation of **4** was performed in benzene-d_6 solution at room temperature. Molecular structures of **2**−**4** determined by X-ray crystallography are shown as 50% probability ellipsoids except for β-diketiminate carbons, which are shown as wire frames; hydrogen atoms are omitted for clarity.

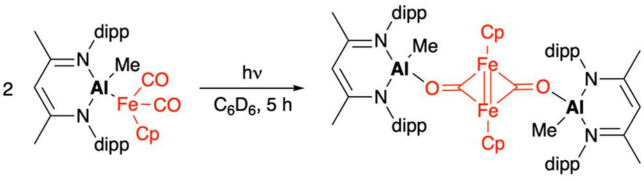
binuclear complexes. In this case, our results show that C−O activation chemistry of **1** is not restricted only to weak C−O bonds. This behavior complements behavior of other bimetallic systems toward THF[26−28] and expands the diversity of outcomes available from binuclear mechanisms.

We also sought to explore the reactivity of **1** toward an episulfide. Rather than forming a ring-opened product, the reaction of **1** with propylene sulfide resulted in sulfur atom insertion into the Al−Fe bond with extrusion of propylene. The resulting complex, LAl(Me)(μ-S)Fp (**3**), was isolated in 68% yield (Scheme 1). Yellow crystals of **3** suitable for X-ray crystallography were obtained from a mixture of toluene and pentane at −25 °C. The molecular structure of **3** features a four-coordinate aluminum center with distorted tetrahedral geometry. As expected, the Al–S bond [2.2005(7) Å] is longer than the Al═S bond [2.104(1) Å] in LAl═S(NHC) (NHC = [{(CH$_2$)CN(^{i}Pr)}$_2$C:])[29] but is close to Al–S single bond lengths in [LAl(μ-S)$_2$TiCp$_2$] [2.208(1) and 2.197(1) Å].[30] The Fe–S bond distance in **3** [2.3161(8) Å] is in the range of those reported in related Fp-SR complexes (2.26–2.35 Å).[31] The same product **3** was isolated from the reaction of **1** with elemental sulfur in 64% yield (Scheme 1).

Given that **1** is known to react as a biradical toward various substrates, one might expect it to do group abstraction from reactants with homolytically weak bonds. Accordingly, reaction of **1** with Me$_3$SiN$_3$ produced 1/2 Fp$_2$, which is indicative of Fp· dimerization (as seen previously with benzophenone, Figure 1b), along with a new LAl(Me)X product. Single crystals of this product were grown from a mixture of toluene and pentane at −25 °C, allowing us to identify it as the monoazide derivative, LAl(Me)N$_3$ (**4**; Scheme 1). Unfortunately, we have been unable to obtain pure samples of **4**, and so the only available spectroscopic data involves characterization of the crude reaction mixture with an internal ^{1}H NMR integration standard.

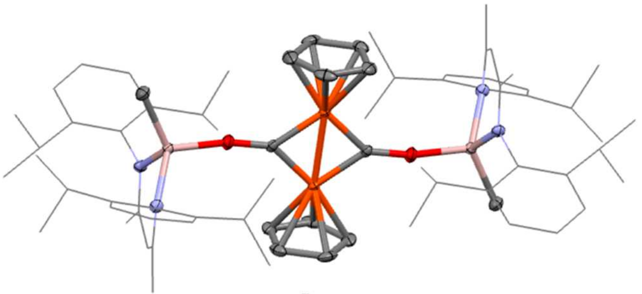
After successfully carrying out various thermal reactions, we were also interested in photochemical reactivity of **1**. Complex **1** is stable thermally (up to 80 °C) in C$_6$D$_6$ for at least 12 h but was found to react further upon irradiation with UV light. Irradiation of a C$_6$D$_6$ solution of **1** for 5 h at room temperature resulted in precipitation of yellow crystals of a new complex (**5**) in low yield (Scheme 2). The solid-state IR spectrum of **5** 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}. This frequency value is unusually low even for classical μ_3-CO ligands but is in range for previous cases in which μ_3:η^2-CO ligands were *C*-bound to two transition metals and *O*-bound to a Lewis acid (1351–1650 cm^{-1}).[32−34] Complex **5** was found to be insoluble in benzene, chloroform, and dichloromethane. The ^{1}H NMR spectrum of **5** was recorded in THF-d_8, although gradual decomposition was observed in that solvent. The identity of the product was determined by X-ray crystallography and elemental analysis. The tetrametallic structure consists of two [LAl(Me)] units bridged by one [(CpFeCO)$_2$] unit, with the carbonyl groups acting as μ_3:η^2-CO ligands that are *C*-bound to Fe and *O*-bound to Al. It is noteworthy that the [(CpFeCO)$_2$] motif has never been structurally characterized in any complex to date, despite the long history of [CpFe(CO)$_2$]$_2$ chemistry.[35] The diiron distance in **5** is 2.3543(5) Å, which is significantly shorter than the Fe–Fe single bond of the classical [Fe$_2$(CO)$_9$] [2.523(1) Å] or in [CpFe(CO)$_2$]$_2$ [2.5389(3) Å].[36,37] Thus, complex **5** can be formulated as having a Fe═Fe double bond. The C–O bond length in **5** [1.292(3) Å] is longer than the terminal C–O bonds [1.157(4) Å] present in **1** and falls between the typical C–O single and double bond ranges. The Al–O bond lengths in **5** [1.739(2) and 1.743(2) Å] are shorter than the corresponding bonds [1.980(1) and 1.897(1) Å] present in LAl(Me)(μ:κ^2-O$_2$C)Fp[14] but comparable to the Al–O bond [1.714(1) Å] present in complex **2**. Thus, the lengthening of C–O bonds and correspondingly low υ_{CO} value are attributed to strong Al–O interactions.

Scheme 2. Decarbonylative Dimerization of 1 to Produce Tetrametallic 5 upon Irradiation with UV Light[a]



1

5, 38%



5

[a]dipp = 2,6-di-isopropylphenyl. The molecular structure of **5** determined by X-ray crystallography is shown as 50% probability ellipsoids except for β-diketiminate carbons, which are shown as wire frames; hydrogen atoms, cocrystallized solvent molecules, and a second molecule of **5** from the asymmetric unit are omitted for clarity.

In conclusion, a series of reactivity studies were carried out on heterobimetallic Al–Fe complex **1**, with all resulting products being successfully characterized crystallographically. Uncovered reaction profiles include cooperative ring opening of THF, sulfur atom transfer from propylene sulfide and S$_8$, radical azide abstraction from N$_3$SiMe$_3$, and decarbonylative dimerization to produce an unusual [(CpFeCO)$_2$] moiety stabilized by Al coordination. Collectively, these observations expand upon previously reported reactivity studies and showcase the diverse range of transformations available to **1**, the first Al–Fe heterobimetallic complex whose reaction chemistry has been extensively mapped.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.2c00280.

Experimental procedures and characterization data (PDF)

Accession Codes

CCDC 2100521–2100522, 2100524, and 2166714 contain 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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