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Communication

Heterometallic Cu_2Fe and Zn_2Fe_2 Complexes Derived from $[Fe(CO)_4]^{2-}$ and Cu/Fe Bifunctional N_2O Activation Reactivity

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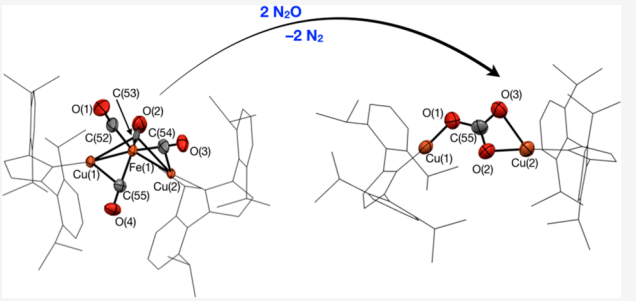
ABSTRACT: The synthesis and characterization of two heterometallic clusters, $[(IPr)Cu]_2Fe(CO)_4$ (**1**) and $[(IPr)ZnFe(CO)_4]_2$ (**2**), derived from Collman's reagent are reported. Methylation of **1** with CH_3I to produce (IPr)CuI and $(IPr)CuFe(Me)(CO)_4$ (**3**) was used to calibrate the relative reactivity of **1** to the previously studied analogue $(IPr)Cu\text{-}FeCp(CO)_2$. Bifunctional N_2O activation by **1** resulted in oxidation of a CO ligand to carbonate rather than the more typically observed CO_2, producing $[(IPr)Cu]_2(\mu\text{-}CO_3)$ (**4**) stoichiometrically along with an iron byproduct that was trapped with PPh_3 as *trans*-$Fe(CO)_3(PPh_3)_2$.



The ongoing effect of climate change motivates the pursuit of technologies that capture[1] greenhouse gases and convert them into useful chemicals or fuels.[2] Achieving such transformations of gaseous small molecules requires catalysts that mediate their efficient activation in order to overcome their thermodynamic stability and/or kinetic inertness.[3] With biological systems as an inspiration, one strategy is to activate inert small molecules using a bifunctional approach, wherein Lewis acidic and basic transition-metal sites cooperate to achieve bond activation. For example, the Ni/Fe cluster of anaerobic carbon monoxide dehydrogenase has been structurally characterized with a bound CO_2 molecule bifunctionally activated by nucleophilic attack at carbon and Lewis acidic stabilization of negative charge accumulation at oxygen.[4] Similarly, N_2O can be converted to N_2 when it is activated by adjacent Cu sites that act in a bifunctional manner, as seen in the Cu_Z cluster of nitrous oxide reductase or the binuclear active sites of Cu-ZSM-5.[5,6] Mimicking this cooperative strategy for small-molecule activation is currently an active area of research.[7−16]

Previously, our group reported the various heterobimetallic catalyst systems (NHC)M-$[M_{co}]$ (NHC = N-heterocyclic carbene; M = Cu, Ag, Au, ZnCl; $[M_{co}]$ = e.g. $FeCp(CO)_2$, $Mn(CO)_5$, $WCp(CO)_3$, $Co(CO)_4$, etc.), which assemble upon mixing (NHC)MCl and $[M_{co}]^-$ precursors.[17−19] These metal−metal bonds feature polarity that we established through computational methods,[19,20] chemical reactivity,[17,19,21] and spectroscopic analysis.[22] For example, we established that the Cu−Fe bond in (NHC)Cu-Fp (Fp = $FeCp(CO_2)$) is polarized: Cu retains positively charged (electrophilic) character, whereas Fe retains negatively charged (nucleophilic) character. This bifunctionality enables cooperative activation of small molecules such as H_2, CS_2, and N_2O under mild conditions.[20,21,23] Additionally, catalyst control over CO_2 reduction selectively was accomplished with (NHC)Cu-[M] catalysts (M = Fe, W, Mo) when they were activated by a H-[B] reductant.[24] However, we still have not succeeded in bimetallic CO_2 activation using this approach, whereas "early−late" heterobinuclear catalysts that do activate CO_2 using early-transition-metal Lewis acids (e.g., Zr^{IV}) are not catalytically active due to the formation of strong metal−oxygen bonds.[7,25,26]

In this context, we hypothesized that the heterobimetallic catalysts might have higher reactivity if the metal−metal bond polarity were further enhanced by replacing monoanionic $[M_{co}]^-$ with a dianionic metal−carbonyl nucleophile. Collman's reagent, $Na_2Fe(CO)_4$, is a well-known compound for organic and organometallic synthesis.[27] Because Collman's reagent features a highly reduced iron formally in its Fe(2−) oxidation state, we hypothesized that its incorporation into heterobimetallic architectures could increase Cu−Fe bond polarity and perhaps enhance reactivity in comparison to (NHC)Cu-Fp derived from $[Fp]^-$ with a formally Fe(0) center. Herein, we report the synthesis and structural characterization of two new heterometallic complexes, trinuclear $[(IPr)Cu]_2Fe(CO)_4$ (**1**) and tetranuclear $[(IPr)\text{-}ZnFe(CO)_4]_2$ (**2**), and the small-molecule activation chemistry of the Cu derivative which can be compared directly to that of its (IPr)CuFp predecesor (IPr = *N*,*N*′-bis(2,6-diisopropylphenyl)imidazol-2-ylidene). Related complexes

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such as $[(Ph_3P)_2Cu]_2Fe(CO)_4$,[28] $[(PPh_3)Au_2Fe(CO)_4]$,[29] and $[(py)_3ZnFe(CO)_4]$[30] have been characterized before, but reactivity studies were not performed.

Previously, we reported the syntheses of (IPr)CuFp and (IPr)(Cl)ZnFp by reactions between (IPr)CuCl and (IPr)-$ZnCl_2$(THF) synthons and KFp.[17] Analogous preparations were used to synthesize **1** and **2** from $K_2Fe(CO)_4$. The solid-state structure of **1** determined by X-ray crystallography (one of four molecules from the asymmetric unit) is shown in Figure 1a. Unlike $[(Ph_3P)Cu]_2Fe(CO)_4$, which features a *trans*

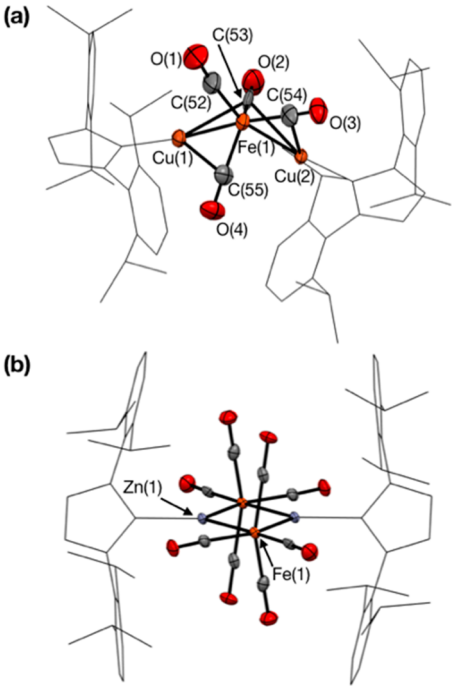


Figure 1. Solid-state structures of (a) $[(IPr)Cu]_2Fe(CO)_4$ (**1**) and (b) $[(IPr)ZnFe(CO)_4]_2$ (**2**) determined by X-ray crystallography. For clarity, hydrogen atoms and cocrystallized solvent molecules are omitted and NHC ligands are shown as wireframes. All other atoms are shown as 50% probability ellipsoids. For **1**, only one of the four molecules from the asymmetric unit is shown.

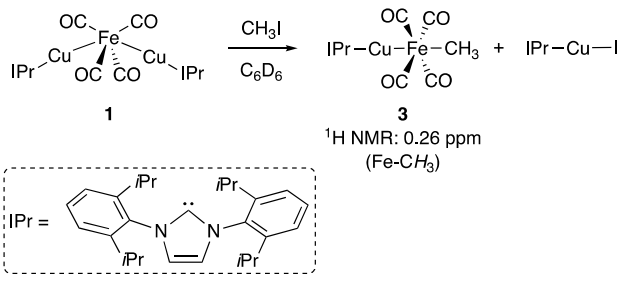
orientation of Cu groups (168.7(2)°) about an octahedral Fe center,[28] complex **1** features a bent Cu−Fe−Cu angle (106.43(5)°) and modestly bent C_{NHC}−Cu−Fe angles (168.1(2) and 172.1(2)°). The Cu−Fe distances (2.348(2) and 2.375(1) Å) are close to the sum of Pyykkö's single-bond covalent radii of Cu and Fe (2.28 Å)[31] and are among the shortest Cu−Fe distances of any type in Cambridge Structural Database (CSD). The Cu−Fe distances of **1** are similar to that of (IPr)Cu−$FeCp(CO)_2$ (2.3462(5) Å) and slightly longer than the shortest known Cu−Fe distance found in (IPr)Cu−$FeCp(CO)(PPh_2Me)$ (2.299(2) Å), which presumably has enhanced dative Fe→Cu donation due to the electron-donating phosphine ligand.[32] The median Cu−Fe distance in the CSD, 2.549 Å, is much longer than the Cu−Fe distances in **1**. The Cu···Cu distance of 3.783(1) Å is too long for a significant interaction. The $[Fe(CO)_4]$ unit contained within **1** has a near-perfect tetrahedral arrangement.

The solid-state structure of **1** contains four independent molecules in the asymmetric unit; only one molecule is discussed here but is representative of the isostructural set. Four short Cu···CO distances are evident: Cu(1)···C(55), 2.373(7) Å; Cu(1)···C(53), 2.442(6) Å; Cu(2)···C(54), 2.47(1) Å; Cu(2)···C(53), 2.404(8) Å. The corresponding asymmetry parameters[33] indicate that all are in the semi-bridging regime.[34] The C(53)−O(2) unit can be considered a semibridging μ_3-CO between Fe(1) and both Cu(1) and Cu(2); the C(53)−O(2) distance of 1.25(1) Å indicates significant CO activation. The C(54)−O(3) and C(55)−O(4) units can be considered semibridging μ_2-CO ligands between Fe(1) and Cu(2) or Cu(1), respectively; the corresponding C−O distances of 1.194(8) and 1.183(9) Å, respectively, indicate weaker activation. The fourth C(52)−O(1) unit is a terminal carbonyl group with a correspondingly short C−O distance of 1.15(1) Å. The solid-state IR spectrum of **1** has a feature at 1952 cm^{-1} assigned to the terminal CO ligand, features at 1874 and 1833 cm^{-1} assigned to the semibridging μ_2-CO ligands, and a feature at 1814 cm^{-1} assigned to the more activated μ_3-CO semibridging carbonyl. The $^{13}C\{^1H\}$ NMR spectrum exhibits a single CO resonance at 216.5 ppm, indicating that the semibridging interactions are fluxional such that the four CO sites exchange with each other in solution on the NMR time scale.

The solid-state structure of **2** is shown in Figure 1b. Unlike coordinatively saturated, binuclear $L_3ZnFe(CO)_4$ complexes,[30] the unsaturated "$(IPr)ZnFe(CO)_4$" species in **2** apparently dimerizes to form tetranuclear $[(IPr)ZnFe(CO)_4]_2$. The Zn−Fe distances in **2** of 2.5221(7) and 2.5293(8) Å are much longer than that in (IPr)(Cl)Zn−$FeCp(CO)_2$ (2.3714(4) Å).[17] To compare the M−Fe distances, Cotton's formal shortness ratio (FSR) calculations can be used to correct for metal sizes.[35] The average FSR value for Cu−Fe in **1** (1.004) is smaller than that for Zn−Fe in **2** (1.048), which might be due to the differences in Pauling's atomic radii for Cu (1.173 Å) and Zn (1.249 Å).[36] The Fe centers in **2** have nearly ideal octahedral environments, possibly due to the lack of any close Zn···CO contacts to create structural distortions as in **1**. The cross-cluster Fe···Fe (4.196(1) Å) and Zn···Zn (2.8124(5) Å) distances are too long for any significant interaction.

We have begun to benchmark the reactivity of these new clusters using reactions for which **1** can be compared directly to its (IPr)CuFp analogue. We initially established the Cu−Fe bond polarity of (IPr)CuFp through its reactivity with methyl iodide.[17,22] Similarly, here complex **1** was exposed to equimolar CH_3I. An analysis of the product mixture by ^1H NMR indicated quantitative formation of (IPr)CuI and a second species assigned as $(IPr)CuFe(Me)(CO)_4$ (**3**) (Scheme 1). No evidence for $(IPr)CuCH_3$ or $I_2Fe(CO)_4$ was detected, consistent with the proposed Cu−Fe bond polarity of formally Cu(I) Lewis acidic and Fe(2−) Lewis basic sites. Exposure of the product mixture to additional CH_3I did not result in any further conversion of **3** to (IPr)CuI. Because we initially

Scheme 1. Methyl Iodide Reactivity of 1



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hypothesized that **1** would have more reactive Cu−Fe bonds than (IPr)CuFp, we sought to measure rate constants under pseudo-first-order conditions (excess CH_3I), using ^1H NMR to monitor the appearance of Fe−CH_3 resonances. The observed rate constants at room temperature for **1** and (IPr)CuFp were 0.028 and 0.041 s^{-1}, respectively. In other words, in contrast to our initial hypothesis, the two complexes are about equally reactive toward CH_3I within error. This result highlights the limitations of formal oxidation states in predicting reactivity behavior.[37]

We previously reported that exposure of (NHC)CuFp derivatives to N_2O results in Cp^- migration from Fe to Cu, producing (NHC)CuCp products quantitatively with precipitation of an amorphous $Fe_xC_yO_z$ material.[21] Thus, we were curious to examine the behavior toward N_2O of complex **1**, which lacks a Cp^- group. Stirring a solution of **1** in toluene under N_2O (1 atm) at room temperature caused rapid precipitation of a dark brown material. Analysis of the soluble fraction by ^1H NMR spectroscopy indicated the formation of a single product, which was determined to be the carbonate complex $[(IPr)Cu]_2(\mu\text{-}CO_3)$ (**4**) by X-ray crystallography. The solid-state structure of **4** (Figure 2) shows a bridging μ-

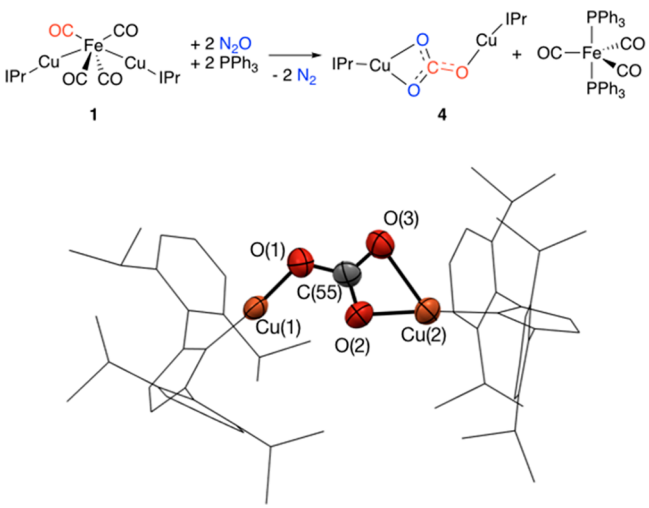

Figure 2. Stoichiometry of N_2O activation by **1** (top) and solid-state structure of $[(IPr)Cu]_2(\mu\text{-}CO_3)$ (**4**; bottom).

carbonate ligand that binds in a κ^1 mode through O(1) to Cu(1) and a κ^2 mode through O(2) and O(3) to Cu(2). The dark brown precipitate forming alongside **4** did not dissolve in any common organic solvents, but on the basis of the reaction stoichiometry it is expected to be $1/n[Fe(CO)_3]_n$. Accordingly, this byproduct could be solubilized by trapping with a phosphine ligand. Exposure of **1** to N_2O (1 atm) in the presence of PPh_3 (3 equiv) produced *trans*-$Fe(CO)_3(PPh_3)_2$ along with $OPPh_3$ (0.04 equiv). The generation of *trans*-$Fe(CO)_3(PPh_3)_2$ was confirmed by ^{31}P NMR spectroscopy as well as comparison of X-ray diffraction data to literature reports.[38] Independently, triphenylphosphine was found to be unreactive toward both **1** and N_2O individually under these conditions. The overall balanced reaction (Figure 2) involves a single CO ligand being oxidized to $[CO_3]^{2-}$ by 2 equiv of N_2O. Although metal catalysts are known to mediate oxygen atom transfer from N_2O to CO to generate CO_2,[39,40] including in automobile catalytic converters,[41] to our knowledge the production of $[CO_3]^{2-}$ has not been reported before.

No reaction between **1** and CO_2 (1 atm) in C_6D_6 at room temperature was observed from ^1H NMR spectral data. Use of isotopically enriched $^{13}CO_2$ further indicated that no equilibration was occurring between carbon dioxide and the carbonyl groups, as has been observed in some early−late heterobimetallic systems.[25] Further work on activation of CO_2 and other small molecules by **1** and **2** is ongoing in our laboratories.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00212.

Experimental procedures and spectral data (PDF)

Accession Codes

CCDC 1985380−1985382 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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