ChemComm
Chemical Communications

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Volume 54
Number 1
4 January 2018
Pages 1-112

ChemComm
Chemical Communications
rsc.li/chemcomm

ISSN 1359-7345

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION
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DOI: 10.1039/C9CC03771C

COMMUNICATION

Transition metal-mediated reductive coupling of diazoesters

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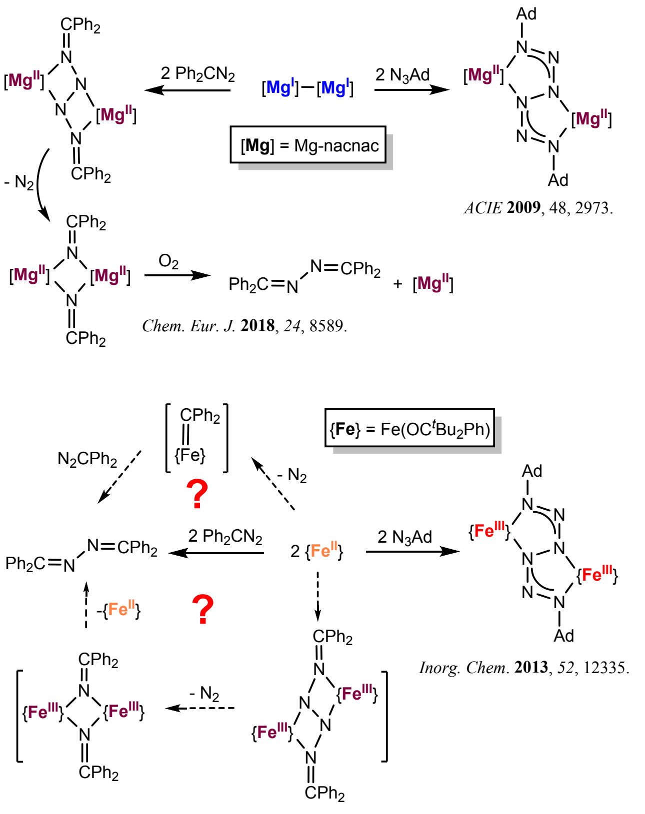
Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

The first transition metal mediated reductive coupling of diazoesters through the terminal nitrogens is reported. The resulting tetrazene-bridged bis(diazenylacetate) serves as a novel dinucleating ligand to iron(III). DFT calculations suggest that the reductive coupling takes place via a κ² intermediate, which induces significant radical character on the terminal nitrogen.

Diazoalkanes [$NNCR^1R^2$] are among the most important nitrogen-containing reactive molecules employed in the transition metal catalysis.[1] The reactivity mode of the coordinated diazoalkane is often determined by the stereoelectronic nature of the transition metal complex.[1] The most common reactivity route exhibited by diazoalkane [$NNCR^1R^2$] is the formation of carbene [CR^1R^2], concurrent with N_2 elimination.[1,2] As a result, diazoalkanes are frequently used as carbene precursors in cyclopropanation, carbene insertion into C-H bonds, and other C-C bond forming reactions.[3] However, coordinated diazoalkane can also follow other reactivity routes, most involving diazoalkane carbon or R^1/R^2 groups, including nucleophilic addition, substitution, and deprotonation.[1] Reductive coupling of diazoalkanes through carbons has been reported as well.[4] In contrast, reductive coupling of diazoalkanes through the terminal nitrogens has not been reported in the transition metal realm, although Stephan and coworkers have very recently described reductive coupling of diphenyldiazomethane using a strongly reducing main group synthon, Mg(I)-nacnac (**Scheme 1**, top).[5, 6] The initially formed product of the reductive coupling of diphenyldiazomethane with Mg(I) synthon (featuring four-membered triazenido chelates) underwent slow decomposition at room temperature to give bridging imido complex ([(nacnac)Mg($NCPh_2$)]$_2$) and dinitrogen; subsequent oxidation produced benzophenone azine $Ph_2CNNCPh_2$. We have recently reported that cobalt(II) bis(alkoxide) complex $Co(OR)_2(THF)_2$[7] (OR = OC^tBu_2Ph) formed isolable high-valent cobalt-carbene $Co(OR)_2(=CPh_2)$ upon reaction with diphenyldiazomethane,[8] while the iron analogue $Fe(OR)_2(THF)_2$[9] yielded benzophenone azine and an unidentified metal product.[8] Whereas formation of benzophenone azine via a



Scheme 1. Top: Mg^I-nacnac-promoted reductive coupling reactions of an organoazide (right) and diphenyldiazoalkane (left). Bottom: $Fe(OR)_2$-promoted reductive coupling of AdN_3 (right) and possible (two-electron and one-electron) mechanisms for the formation of benzophenone azine (left).

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Electronic Supplementary Information (ESI) available: Experimental procedures, X-ray data collection/refinement details, NMR/IR/UV-is spectra, and computational details. See DOI: 10.1039/x0xx00000x

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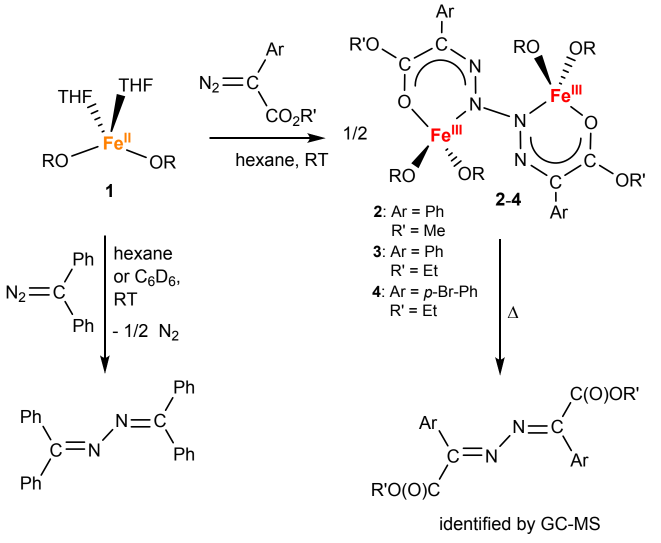
DOI: 10.1039/C9CC03771C



Scheme 2. Reactions of $Fe(OR)_2(THF)_2$ with diphenyl diazomethane and aryl diazoesters described in this manuscript.

metal-carbene intermediate is feasible (particularly given the related Co chemistry), another route to the azine product can also be envisioned, i.e. an Fe^{II}-promoted reductive coupling, followed by an Fe^{III}-promoted oxidation (**Scheme 1**, bottom). This postulate would be consistent with the fact that $Fe(OR)_2(THF)_2$ reductively couples azides to give an hexazene complex,[9a] similarly to Mg^I(nacnac)[6] (**Scheme 1**). We have also described formation of reactive $[Co(OR)_2(CPh(CO_2Me))]$ intermediate via the reaction of $Co(OR)_2(THF)_2$ with diazoester $N_2C(Ph)(CO_2Me)$ (methyl phenyldiazoacetate).[10] Herein we demonstrate that changing the metal in $M(OR)_2(THF)_2$ to Fe leads to a dramatic change in the reactivity of the coordinated diazoester to the reductive coupling. Coupling of the iron-ligated diazoesters through the terminal nitrogens affords a new dinucleating tetrazenediacetate ligand, in which each iron is ligated by the N,O-diazenylacetate chelate. Structural, spectroscopic and computational studies are presented.

The reaction of $Fe(OR)_2(THF)_2$ (**1**) with one equivalent of diphenyldiazomethane produced benzophenone azine in high yield (**Scheme 2**). The reaction of sub-stoichiometric amounts of $Fe(OR)_2(THF)_2$ with diphenyldiazomethane also led to its full conversion to the corresponding azine (see SI for details), suggestive of the catalytic process via an $[Fe^{II}(OR)_2]$ intermediate, albeit we were not able to observe directly any such intermediates. To shed light on the reactivity of iron bis(alkoxide) with diazo compounds, we turned our attention to diazoesters. Treatment of the pale yellow solution of **1** in hexane with the yellow solution of methyl phenyldiazoacetate $N_2C(Ph)(CO_2Me)$ in hexane led to the immediate color change to brown that transitioned to burgundy within 10 minutes; no gas evolution was observed. Subsequent work-up and recrystallization yielded purple crystals of **2**, whose identity is confirmed by X-ray crystallography. Similarly, treatment of **1** with ethyl phenyldiazoacetate or ethyl (4-bromophenyl)diazoacetate yields purple crystals of compounds **3** and **4**. While the crystals of compounds **3** and **4** were too unstable to allow high-quality X-ray structure determination, their identity is strongly supported by the elemental analyses, as well as by the similarity of their IR, UV-vis and Mössbauer spectra to the corresponding spectra of complex **2** (see SI).

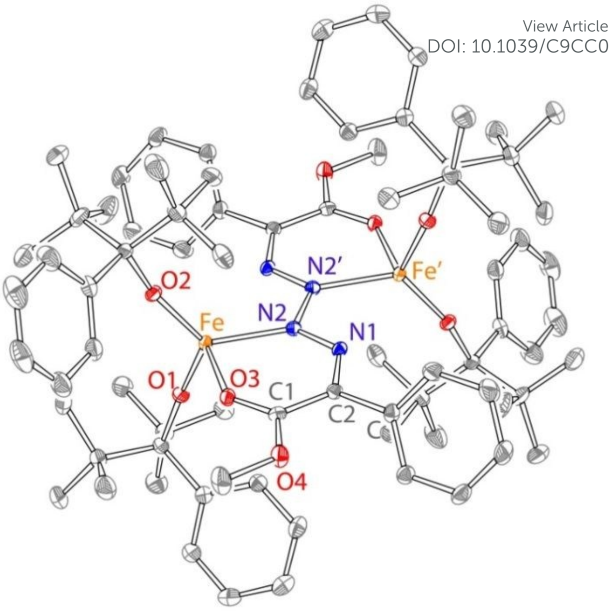


Figure 1. Structure of complex **2**, $[Fe_2(\mu\text{-}\kappa2{:}\kappa2\text{-}MeO_2CC(Ph)NNNNC(Ph)CO_2Me)(OR)_4]$, 50% probability ellipsoids.[19] H atoms and co-crystallized ether molecule are omitted for clarity. Selected bond distances (Å) and angles (º): Fe – O1 1.785(1); Fe – O2 1.783(1), Fe – O3 2.002(1), 2.034(1), O3 – C1 1.249(2), C1 – C2 1.436(2), C2 – N1 1.333(2), N1 – N2 1.308(2), N2 – N2' 1.394(2), O2 Fe O1 119.29(5), O2 – Fe – N1 114.71(5), O1 – Fe1 – N1 123.36(5), O3 – Fe – N2 82.01, O3 – Fe – O2 102.90(5), O3 – Fe – O1 100.89(5).

X-ray structure determination of **2** revealed a di-iron complex bridged by a tetrazene-linked dinucleating ligand $[\mu\text{-}\kappa^2{:}\kappa^2\text{-}MeO_2CC(Ph)NNNNC(Ph)CO_2Me]$ (**Figure 1**), that results from the reductive coupling of diazoesters via terminal nitrogens. The coordination environment around each iron is distorted trigonal monopyramidal, featuring two monodentate alkoxides, and the N,O-diazenylacetate chelate. The structure is centrosymmetric, with half a molecule occupying the asymmetric unit. Iron-oxygen bond distances suggest an iron(III) oxidation state, indicating that the $[MeO_2CC(Ph)NNNNC(Ph)CO_2Me]$ ligand is a dianion. Comparison of the intraligand [ONNNNO] bond distances (see **Figure 1**) with the corresponding bond distances in free diazoalkane[11] points to significant electron delocalization within the chelate rings. Whereas the central N-N bond distance (1.394(2) Å) appears close to a single bond, the planarity of the ligand suggests electron delocalization between the O,N-chelates. We also note that while the overall ligand structure, resulting from the reductive coupling of the diazoester, is new,[12] it is related to the dinucleating hexazene ligand, which results from the reductive coupling of organoazides.[6, 9, 13, 14]

The IR spectra of the compounds **2-4** are similar, demonstrating prominent signals around 1555, 1260, 1150 and 1005 cm^{-1}, suggestive of the C=O ester, tetrazene N-C/N-N, and alkoxide C-O stretching vibrations (**Figure S1-S4**). This

DOI: 10.1039/C9CC03771C

assignment relies on previously reported IR spectra of tetrazene complexes,[15] and the recent combined spectroscopic and computational investigation of the IR spectra of related hexazene complexes.[16] DFT calculations[17] support these assignments, with calculated stretches at 1570, 1335, 1224, and 1060 cm^{-1} for these motions that have significant intensity (**Figure S21**). The UV-vis spectra for **2**-**4** (see SI) all demonstrate a peak at 516 nm.

Inspection of the zero-field ^{57}Fe Mössbauer spectrum recorded at 80 K of a neat powder sample of **2** reveals a well-defined quadrupole doublet that accounts for ~97% of the iron present in the sample. This doublet has parameters, δ = 0.55(1) mm/s and ΔE_Q = 2.52(3) mm/s, that are very similar to those observed for Fe(OR')(ArNNNNAr), δ = 0.49 mm/s and ΔE_Q = 2.20 mm/s (where R' = C^{t}Bu$_2$(3,5-Ph$_2$Ph) and Ar = MeOPh, 3,5-Me$_2$Ph).[18] The latter values were shown to originate from high-spin iron(III) ions of complexes for which the S = 5/2 iron spin is antiferromagnetically coupled to the S = 1/2 of an anionic tetrazene ligand. Thus, this similarity clearly indicates that the two iron sites of **2** also adopt a high-spin ferric configuration. However, the resonances observed for **2** are considerably broader than those of Fe(OR')(ArNNNNAr) ($\Gamma_{L/R}$ = 0.68/0.75 mm/s vs Γ = 0.33 mm/s). The spectra of **3** and **4** (SI) exhibit very similar spectral parameters to the spectrum of **2** (Table S8). While the increased linewidth might be indicative of structural heterogeneities, it might also originate from unresolved magnetic hyperfine splitting. Further studies are being undertaken to delineate these effects.

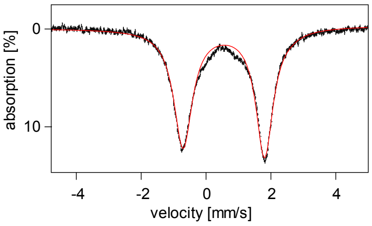


Figure 2. ^{57}Fe Mössbauer spectrum recorded in zero field at 80 K for **2** and simulation (red trace).

The stability of complex **2** was investigated. A stirred solution of **2** (0.178 mM) slowly decayed at room temperature, demonstrating a color change from purple to dark-brown. Monitoring the decomposition reaction by UV-vis showed gradual disappearance of the peak at 516 nm (**2**), while a new peak at 378 nm grows in (see SI for details); approximately 20% of **2** remains after 5 days. The decomposition reaction followed first order, with $k = 4\times10^{-6}$ s^{-1}. Heating the solution of **2** to 50 °C overnight led to full decomposition, producing a yellow-brown solution. Whereas ^{1}H NMR of the resulting solution contains only broad resonances, the GC-MS spectrum contains the corresponding azine, free diazoalkane, and the alkoxide ligand. No olefin was observed in GC, suggesting, albeit indirectly, that no carbene forms in the reaction.[10] These results are consistent with the eventual decomposition of the tetrazene-bridged bis(diazenylacetate) species to produce azine, as could be proposed by the Fe(OR)$_2$-catalyzed reaction with diphenyldiazoalkane; we hypothesize that the reaction of the diazoester is significantly slower due to the chelating nature of the intermediate.

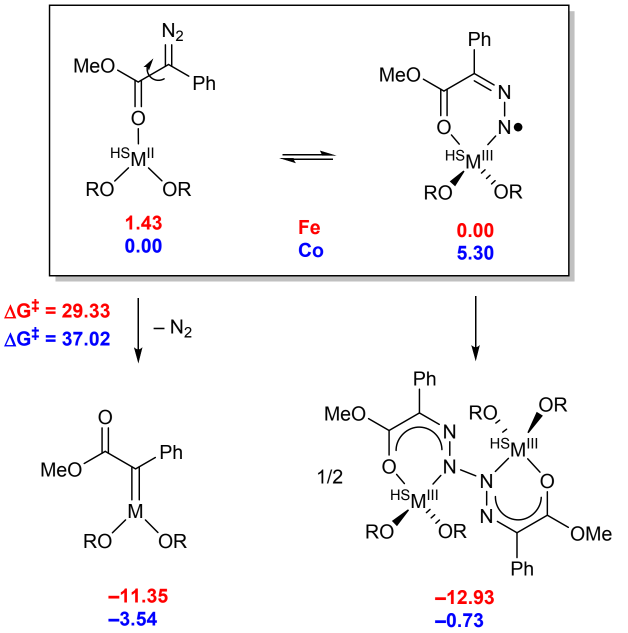


Figure 3. Summary of Gibbs free energies (kcal/mol) for N2 loss vs. reductive coupling pathways for iron (red) and cobalt (blue). The energy for the reductively coupled product is presented per metal equivalent.

Computational studies were conducted to understand the origins of the divergent reactivity between Fe (reductive coupling) and Co (carbene formation); key results are presented in **Figure 3**. DFT calculations on the methyl phenyldiazoacetate adduct suggest the quintet state is lowest in energy and corresponds to a high-spin Fe^{III} ion antiferromagnetically coupled to a diazoester anion radical (**Figure S18**); the κ^2-adduct is slightly more stable than the κ^1-adduct for Fe. Reduction of the diazoester, which occupies an N–N π^* orbital, and formation of the six-membered metallacycle stabilizes this species toward N$_2$ expulsion. The barrier to N$_2$ expulsion is calculated to be 29.3 kcal/mol and the reaction to form the quintet iron carbene is exergonic by 11.4 kcal/mol. Reductive coupling to form **2** from two of these adducts is exergonic by –25.9 kcal/mol. This species is calculated to be a ferromagnetically coupled S = 5 state with two high-spin Fe^{III} ions (see **Table S4** for alternative spin states). Coupling of the diazoester radicals is predicted to have no enthalpic barrier on both surfaces (**Figure S19**). Using the entropy loss for formation of **2** from two diazo adducts places an upper limit on the entropic barrier of ~17 kcal/mol, much lower than the calculated barrier for N$_2$ loss. A comparison to cobalt (**Figure 3**) illuminates why we did not observe this coupled product for that metal.[10] Formation of the κ^2 product, which has reduced diazoester and ^{HS}Co^{III} is disfavored, as compared to Fe, due to the lower reducing potential of Co(OR)$_2$.[7] We hypothesize that this unfavorable equilibrium, which must be overcome for two equivalents before reductive coupling can occur, makes N$_2$ loss and carbene formation

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competitive as compared to iron. Unlike iron, cobalt is also predicted to favor carbene formation over reductive coupling.

In conclusion, we have demonstrated that iron(II) bis(alkoxide) complex $Fe(OR)_2(THF)_2$ reductively couples methyl phenyldiazoacetate through the terminal nitrogens to afford a dinuclear product featuring dinucleating tetrazene-bridged bis(diazenylacetate) ligand. Spectroscopic, structural, and computational studies indicate two high-spin iron(III) centers coordinated by a monoanionic 2-diazenylacetate chelate each. DFT suggests that reductive coupling takes place via a κ^2-bound diazoester that develops significant radical character at the terminal nitrogen. This behavior stands in contrast to the related cobalt complex that undergoes N_2 expulsion and carbene formation, in part due to the preferred κ^1-bound diazoester. This work provides insight into the reactivity of $Fe(OR)_2(THF)_2$ with diazoalkanes, and gives another example of the unique “metalloradical” nature of $[Fe(OR)_2]$. Our future studies will focus on the exploration of the reductive coupling of additional substrates using uniquely mild yet powerful one-electron reagent $Fe(OR)_2(THF)_2$.

Acknowledgements

S.A.S acknowledges partial support from the University of Idaho. We thank Dr. Andrew Ozarowski at NHMFL and Prof. Yisong Guo at CMU for recording the Mössbauer data. NHMFL is supported by the NSF Cooperative Agreement No. DMR-1157490 and the State of Florida. S.G. and R.L.L. are grateful to the National Science Foundation (NSF) for current support under grant number CHE-1855681. A.G. is a Rumble fellow.

Conflicts of interest

There are no conflicts to declare.

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19 CCDC 1915378 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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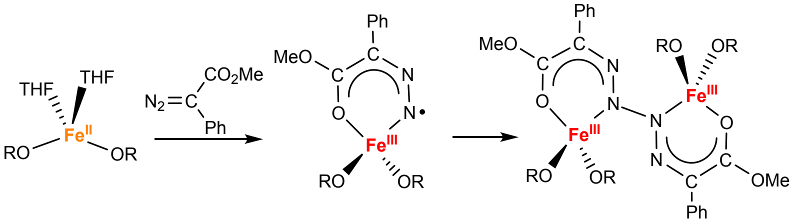
TOC graphic and abstract



The first transition-metal mediated reductive coupling of diazoesters is reported. The reaction proceeds via a κ^2-coordinated intermediate, featuring significant radical character on the terminal nitrogen.