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Redox Chemistry

Nitrene Insertion into C–C and C–H Bonds of Diamide Diimine Ligands Ligated to Chromium and Iron

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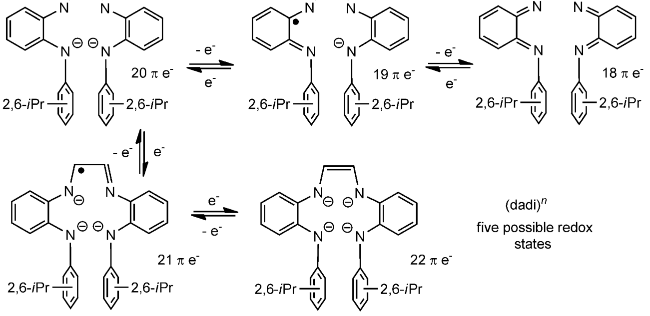
In memory of Gregory L. Hillhouse

Abstract: *The impact of redox non-innocence (RNI) on chemical reactivity is a forefront theme in coordination chemistry. A diamide diimine ligand, [{-CH=N(1,2-C_6H_4)NH(2,6-i$Pr_2C_6H_3$)}$_2$]^n ($n = 0$ to -4), (dadi)^n, chelates Cr and Fe to give [(dadi)M] ([**1**Cr(thf)] and [**1**Fe]). Calculations show [**1**Cr(thf)] (and [**1**Cr]) to have a d^4 Cr configuration antiferromagnetically coupled to (dadi)$^{2-}$*, and [**1**Fe] to be $S = 2$. Treatment with RN_3 provides products where RN is formally inserted into the C–C bond of the diimine or into a C–H bond of the diimine. Calculations on the process support a mechanism in which a transient imide (imidyl) aziridinates the diimine, which subsequently ring opens.*

Reactions of organoazides[1,2] with transition-metal centers provide a historically important[3,4] and useful means to prepare first-row transition-metal imido complexes.[5–19] For certain metals, nitrene-like activity is inferred by the products derived from inter- and intramolecular insertions into C–H bonds,[20–27] aziridinations,[28–31] and related reactions.[32–40] In many instances, imide radical character is inferred from the reactivity and supported by calculations,[41,42] and the chemistry can be related to biological transformations such as the oxygenations by cytochrome P450.[43–49]

During the course of examining chromium and iron complexes chelated by a diamide diimine tetradentate ligand, unusual azide-dependent reactivity featuring C–C and C–H bond activations was discovered in conjunction with redox non-innocence (RNI). RNI is found when ligand and metal d orbitals are close in energy, and electron density can be shuttled back and forth. In principle, ligands with RNI capability can enable reactivity by modulating electron density at the metal.

RNI ligands for first-row transition metals have focused on the diimine[50,51] or imine functionality, mostly in conjunction with pyridine,[6,12,52–54] while amides have been mostly featured in second- and third-row applications.[55,56] In a new thrust targeting the first row,[57] imine and amide functionalities have been combined within a tetradentate framework to afford the [{-CH=N(1,2-C_6H_4)NH(2,6-i$Pr_2C_6H_3$)}$_2$]^n ligand, (dadi)^n. Due to extensive delocalization, (dadi)^n has several potential redox states, five of which are illustrated in Scheme 1. Condensation of glyoxal with two equivalents 1-NH_2,2-N(2,6-i$Pr_2C_6H_3$)C_6H_4 afforded (dadi)H_2 (**1**H_2) in 24% yield, and this can be deprotonated to produce (dadi)^n.



Scheme 1. Five plausible redox states of the (dadi)^n ($n = 0$ to -4) ligand, with the total number of π electrons given for each.

Treatment of (**1**H_2) with [M{N(SiMe_3)$_2$}$_2$(thf)$_n$] (M = Cr, $n = 2$;[58,59] Fe, $n = 1$)[60] in benzene produced 2 equivalents of HN(SiMe_3)$_2$ and [(dadi)M(thf)$_y$] ([**1**M]; for M = {Cr(thf)}, [**1**Cr(thf)]: 76%; for M = Fe, [**1**Fe]: 75%) as maroon and dark green crystals, respectively (Scheme 2). Measurements using Evans' method[61] were consistent with an intermediate spin system ($S = 1$) for [**1**Cr(thf)], while [**1**Fe] is a high-spin ($S = 2$) complex.

Figure 1 provides a molecular view of [**1**Fe], thus revealing its pseudo-square-planar conformation, with a dihedral twist between the diamide-iron and diimine-iron planes of 13.27(10)°. Metric parameters indicate a conventional diamide (dadi)$^{2-}$ ligand with an intact diimine [d(C=N) = 1.294(3) Å (ave), d(CC) = 1.437(3) Å], and Fe–N_{imine} bond lengths of 2.131(4) (ave) Å, which are longer than the

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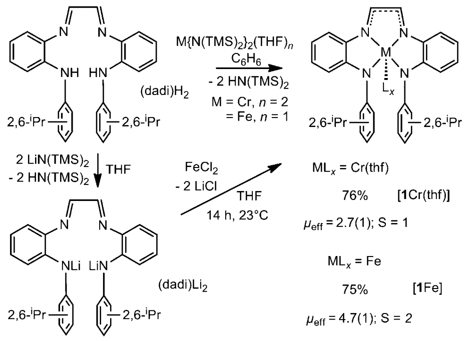


Scheme 2. Syntheses of [(dadi)Fe] ([**1**Fe]) and [(dadi)Cr(thf)] ([**1**Cr(thf)]). thf = tetrahydrofuran.

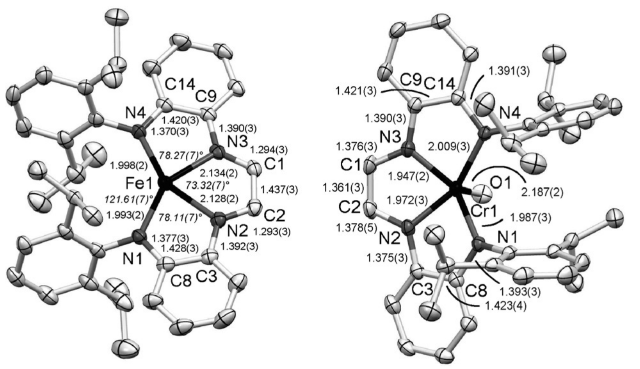
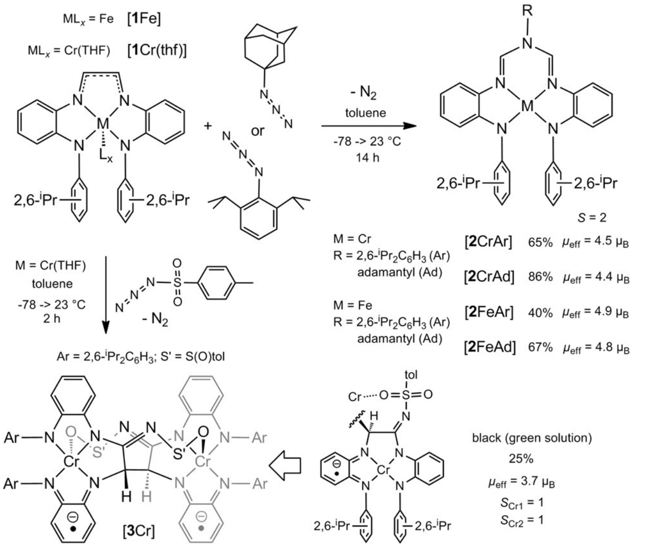


Figure 1. Molecular views obtained from single-crystal X-ray crystallography, with pertinent distances (Å) and angles. Thermal ellipsoids shown at 50% probability. a) [**1**Fe]: ∡N1-Fe-N3, 147.53(7)°; ∡N2-Fe-N4, 151.53(7)°. b) One of two independent [**1**Cr(thf)] molecules (thf methylenes removed for clarity): ∡N1-Cr-N2, 79.55(16)°; ∡N1-Cr-N3, 147.4(18)°; ∡N1-Cr-N4, 119.1(2); ∡N2-Cr-N3, 77.80(7)°; ∡N2-Cr-N4, 157.35(12)°; ∡N3-Cr-N4, 79.83(7)°; ∡N-Cr-O, 98.17(6)° (N1), 90.80(3)° (N2), 105.2(22)° (N3), 98.44(6)° (N4).

Fe$-$N$_{\text{amide}}$ [1.996(4) (ave) Å] distances. In contrast, the pseudo-square-pyramidal [**1**Cr(thf)] displays an apparently reduced diimine fragment with $d(\text{CC})_{\text{ave}} = 1.361(3)$ Å, and $d(\text{CN})_{\text{ave}}$ of 1.376(3) and 1.378(5) Å, which are about 0.08 Å longer and shorter, respectively, than the corresponding distances in [**1**Fe]. The diamide portion of the ligand is normal, but now the Cr$-$N$_{\text{amide}}$ bond lengths of 1.998(16) (ave) Å are longer than those of the Cr$-$N$_{\text{imine}}$ bonds [1.960(17) (ave) Å]. The dihedral twist angle of 13.2(4)° is similar, despite the Cr residing slightly above the ligand plane, as ∡N-Cr-O = 98(6)°(ave).

Calculations on [**1**Fe] (DFT and MCSCF) support the (dadi)$^{2-}$ quintet d^6 electronic structure implicated by its crystal structure and magnetism, but two plausible descriptions exist for [**1**Cr(thf)]: a) antiferromagnetic (AF) coupling between an $S = 1$ excited state of [(dadi)$^{2-}$]*, containing electrons in π and π* orbitals, and a high-spin chromous center, and b) AF coupling of Cr$^{\text{III}}$ and (dadi)$^{3-}$. Since the computed spin density on the Cr center in [**1**Cr(thf)] is 3 $^3/_4$ e$^-$, (a) is the dominant description of the complex, albeit with a significant admixture of (b).

Precedent suggested that the imido derivatives of [**1**Cr(thf)][12] and [**1**Fe][5–9] could be prepared from organoazides, but surprising results ensued from such attempts. Treatment of [**1**Cr(thf)] with RN_3 [R = adamantyl (Ad), or 2,6-iPr$_2$C$_6$H$_3$ (Ar)] afforded products derived from formal insertion of a nitrene into the C$-$C bond of the diimine unit. Purple and blue [{RN(-CH=N(1,2-C$_6$H$_4$)NH(2,6-iPr$_2$C$_6$H$_3$))}$_2$Cr] (R = Ad, [**2**CrAd]; R = Ar, [**2**CrAr]) are synthesized in good yields as illustrated in Scheme 3. Related maroon iron species, [{RN(-CH=N(1,2-C$_6$H$_4$)NH(2,6-iPr$_2$C$_6$H$_3$))}$_2$Fe] (R = Ad, [**2**FeAd]; R = Ar, [**2**FeAr]) were prepared from [**1**Fe] in slightly lower yields.



Scheme 3. Azide-derived nitrene insertions into C$-$C and C$-$H bonds.

Use of an electron-withdrawing azide, tosyl azide, generated a product consistent with initial nitrene insertion into a C$-$H bond of the diamine (Scheme 3). A dimer, [**3**Cr] (ca. 60% crude; 25% isolated), results from C$-$C bond formation at one side of the original diimide unit, as the adjacent carbon atom has lost its hydrogen to the formation of a C=N bond within an η^1-amidinate. Dinitrogen (1.0 equiv) was detected by Toepler pump, but no evidence of dihydrogen was noted. No NH absorption is observed in its IR spectrum and a C$-$NH$-$S unit is ruled out because of spatial H overlap with the coplanar arene C$-$H, hence the hydrogen is likely to be found in byproducts of the reaction. A μ_{eff} of 3.7 μ_B for the dimer is consistent with two non-interacting $S = 1$ centers.

Figure 2 illustrates [{2,6-iPr$_2$C$_6$H$_3$-N(-CH=N(1,2-C$_6$H$_4$)-NH(2,6-iPr$_2$C$_6$H$_3$))}$_2$Cr] [**2**CrAd] and [{AdN(-CH=N(1,2-C$_6$H$_4$)NH(2,6-iPr$_2$C$_6$H$_3$))}$_2$Fe] [**2**FeAd], thus showing their pseudo-square-planar geometries.[62] The 26.5° twist in the latter is substantially greater than the 10.3° distortion in the {CrN$_4$} frame, a distortion that is also evident in the core angles listed. Elongated Fe$-$N$_{\text{imine}}$ distances [2.129(4) Å (ave)] relative to 1.993(6) Å (ave) Fe$-$N$_{\text{amide}}$ bond lengths are in contrast to the 2.030(14) Å (ave) Cr–N distances. Occupation of the M$-$N σ* orbital (d$_{xy}$, x-axis defined by Fe1–N5) in the

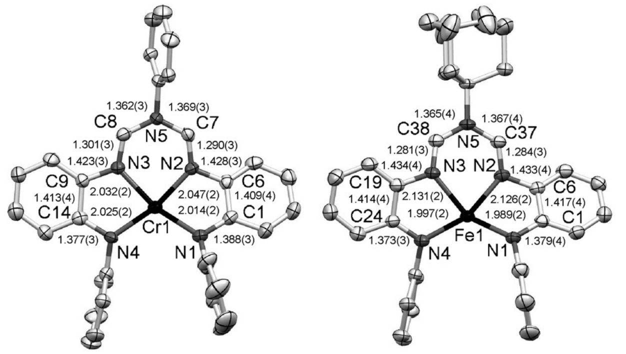


Figure 2. Molecular views obtained from single-crystal X-ray crystallography (*i*Pr groups have been removed for clarity), with pertinent distances [Å] and core angles [°] listed. Thermal ellipsoids shown at 50% probability. a) One of two independent [{2,6-$i\mathrm{Pr_2C_6H_3}$-N(-CH=N(1,2-$\mathrm{C_6H_4}$)NH(2,6-$i\mathrm{Pr_2C_6H_3}$)}$_2$Cr] [**2**CrAr] molecules: ∡N1-Cr-N2, 80.22(13); ∡N1-Cr-N3, 163.82(13); ∡N1-Cr-N4, 113.28(13); ∡N2-Cr-N3, 86.75(13); ∡N2-Cr-N4, 164.64(12); ∡N3-Cr-N4, 81.02(13). b) {AdN(-CH=N(1,2-$\mathrm{C_6H_4}$)NH(2,6-$i\mathrm{Pr_2C_6H_3}$)}$_2$Fe (**2**-FeAd): ∡N1-Fe-N2, 79.94(9)°; ∡N1-Fe-N3, 149.39(9)°; ∡N1-Fe-N4, 127.03(9); ∡N2-Fe-N3, 80.77(8)°; ∡N2-Fe-N4, 148.03(9)°; ∡N3-Fe-N4, 79.85(8)°. [**2**CrAd] is not illustrated (see the Supporting Information).

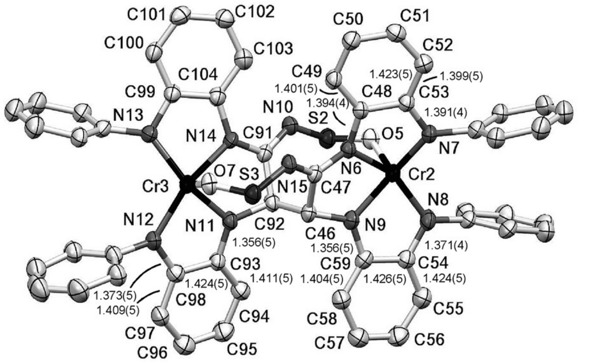


Figure 3. A molecular view of the dimer [**3**Cr] (an additional 1/2 dimer in the asymmetric unit is not shown) obtained from a single crystal X-ray study, with *i*Pr groups, tolyl, and sulfoxide oxygen removed for clarity. Thermal ellipsoids shown at 50% probability.

case of [**2**FeAd], but not in [**2**CrAr], undoubtedly contributes to the angular and bond distortions in the former.

Metric parameters affiliated with [**3**Cr] reflect a subtle difference between the amide amidinate arene and the diamide arene, as Figure 3 reveals. The average C–N, C(N)–C(N), and C–C distances affiliated with the latter are 1.364(9), 1.428(5), and 1.411(10) Å, respectively, while the corresponding distances of the former average 1.408(12), 1.410(11), and 1.397(5) Å, thus suggesting 1 e^- reduction of the diamide arene.[63] Calculations suggest that each chromium is best considered to be Cr^{III} ligated by amide, amidinate, and an AF coupled arene diimine radical anion, thus resulting in two $S = 1$ centers. The new C46–C92 bond is a lengthy 1.60(2) Å (ave), thus hinting at possible reversible formation such as those seen in reversible 2-azaallyl couplings.[62] C–N distances for the η^1-amidinate average 1.323(2) Å, and the square-pyramidal cores, shown in Figure 4, have varied d(CrN) bond lengths which support a Cr^{III} formulation. The sulfur bond distances are consistent with S–N, S–C, and S=O bonds.[63]

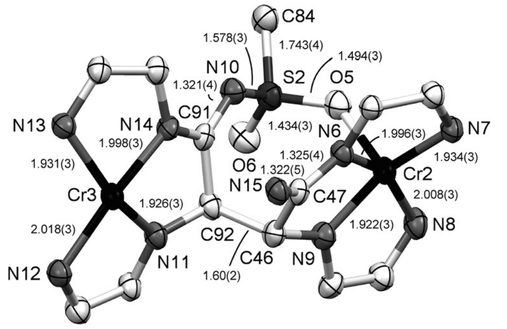
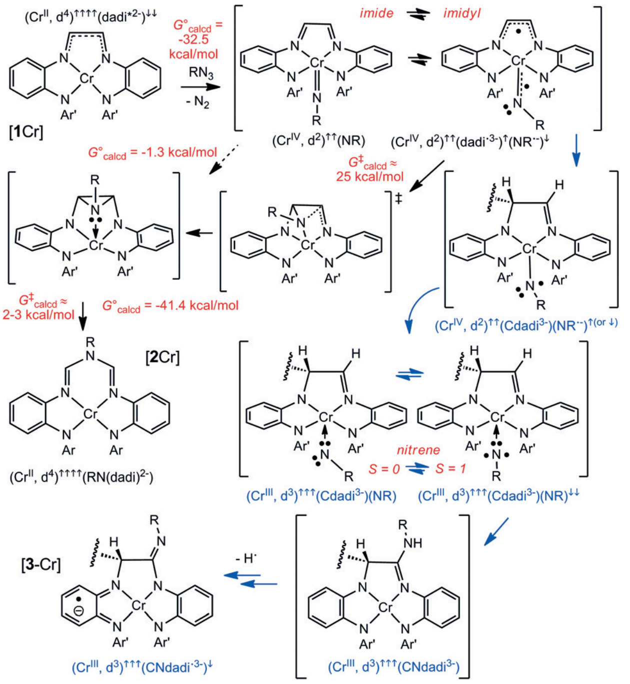


Figure 4. A core view of [**3**Cr] and selected metric parameters [°]: ∡N6-Cr2-N7, 80.60(12); ∡N6-Cr2-N8, 155.92(13); ∡N6-Cr2-N9, 78.40(12); ∡N7-Cr2-N8, 111.99(12); ∡N7-Cr2-N9, 146.24(13); ∡N8-Cr-N9, 80.52(12); ∡O5-Cr2-N6, 93.32(11); ∡O5-Cr2-N7, 106.70(12); ∡O5-Cr2-N8, 101.92(12); ∡O5-Cr2-N9, 100.65(12); similar angles describe Cr3. Thermal ellipsoids shown at 50% probability.



Scheme 4. Proposed imidyl (aziridination ring opening to [**2**Cr], black; calculated free energies shown in red) and nitrene reactivity (to give [**3**Cr]; blue) from [**1**Cr].

Scheme 4 illustrates a plausible sequence of reactions rationalizing the azide chemistry of [**1**Cr] or [**1**Cr(thf)], and by inference, [**1**Fe]. Azide treatment of [**1**Cr] affords a Cr^{IV} center ligated by a dadi^{3-} ligand containing an azaallyl radical AF coupled to an imidyl radical,[41] that is, [(Cr^{IV})$^{\uparrow\uparrow}$(dadi$^{\bullet 3-}$)$^{\uparrow}$(NR$^{\bullet -}$)$^{\downarrow}$] ($\Delta G^{\circ}_{\mathrm{calcd}} = -32.5\ \mathrm{kcal\,mol^{-1}}$). This assignment is based on calculations of the truncated model {(dadi′)CrNMe} (H in place of 2,6-$i\mathrm{Pr_2C_6H_3}$) illustrated in Figure 5. Lying 3 $\mathrm{kcal\,mol^{-1}}$ above the triplet is an $S = 0$ broken symmetry solution with like-spin imidyl and dadi^{3-} ligands, AF coupled to d^2 Cr^{IV}. Both solutions stand in contrast to Wieghardt's

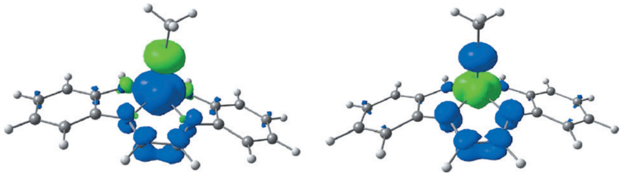


Figure 5. Spin density (IsoValue = 0.01) of triplet (left) and singlet (right) [(dadi′)Cr=NMe]. Note for the triplet the positive spin density on the metal ($\rho_{spin} \approx +2\,e^-$) and dadi ligand ($\rho_{spin} \approx +1\,e^-$), and the negative spin density on the imidyl nitrogen ($\rho_{spin} \approx -1\,e^-$). For the broken-symmetry singlet, the spin density on the imidyl ($\rho_{spin} \approx +1\,e^-$) and dadi ($\rho_{spin} \approx +1\,e^-$) ligand are positive, while the Cr has negative spin density ($\rho_{spin} \approx -2\,e^-$).

$S = 0$ [(py-imine)$_2$Cr=NR] complex,[12] which contains a normal imide and AF coupled pyridine imine ligands, perhaps accounting for the observed reactivity differences.

Transition states (TSs) proved difficult to locate, but a truncated model with -NCH=CHN- in place of the phenylene groups permitted a more efficient search of the reaction space for the each TS (Scheme 4). A TS for nitrene transfer was located at about 25 kcal mol^{-1} (ΔG) above that of the imidyl species en route to a transient aziridine, which is only -1.3 kcal mol^{-1} below that of the imidyl. The reaction does not occur stepwise, but the TS is asymmetric, as if coupling of the imidyl and azaallyl radical occurs while the RN: is in alignment to undergo nucleophilic attack at the remaining imine. The subsequent aziridine ring opening has a modest barrier (ca. 5 kcal mol^{-1}) to afford [**2**Cr] in a process that is substantially exoergic ($\Delta G = -41.4$ kcal mol^{-1}).

As illustrated in Scheme 4, possible stabilization of CrNR in the case of the electron-deficient tosyl–N fragment may allow the azaallyl radical to couple intermolecularly.[64,65] Reduction to Cr^{III} by the imidyl ligand leads to a nitrene, a group capable of inserting into C–H bonds. These steps, and ensuing chemistry involving a formal loss of H$^\bullet$, presumably to byproducts, have not been investigated computationally because of the modest yield of [**3**Cr] and the complexity of its formation.

The reactivity and chemistry herein dovetails with transient imido species of the first row, but here the RNI of the (dadi)$^{n-}$ ligand clearly plays a role in the conversion of [**1**M] into [**2**M] (M = Cr, Fe) and [**3**Cr]. It is notable that the (dadi)$^{2-}$ redox state is 20 e$^-$, or 4n, and has some anti-aromatic character,[66] a factor that can be construed as critical for RNI to be productive in terms of reactivity.[54] As a ligand prone to reduction, it effectively competes with the R–N moiety for electrons from the Fe and Cr, thus resulting in radical character on both ligands, and subsequent C–N and C–C bond-forming events. The nitrene insertion products, [**2**Cr] and [**2**Fe], possess 22 e$^-$ macrocyclic ligands, and can be construed as stable $4n+2$ systems because of the inclusion of the NR lone pair in the π system. They are unreactive when treated with RN$_3$, and are quite thermally stable.

Additional synthetic, reactivity, and computational studies on [**1**M] [M = Ti(thf), Ti(Cl$^-$), V, Cr, Mn, and Fe] are ongoing.

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