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Reduction of (pddi)Cr reveals redox noninnocence via C–C bond formation amidst competing electrophilicity: [(cpta)CrMe_n][−] (n = 0, 1) and [(pta)Cr]^{−†}

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Reversible cyclopropane formation is probed as a means of redox noninnocence in diimine/diamide chelates via reduction and complex anion formation. Competition from imine attack renders complications in the latter approach, and electrochemical measurements with calculational support provide the rationale.

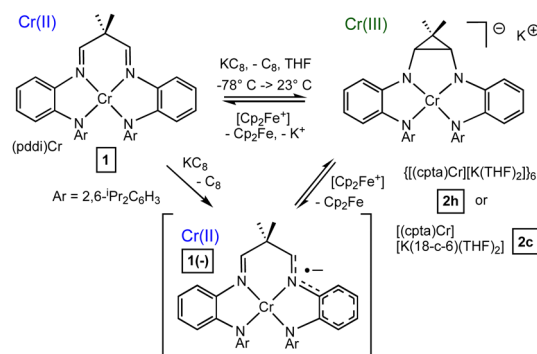
Redox noninnocence (RNI) is a means of expanding the oxidative addition/reductive elimination capability of metal complexes via the shuttling of electrons in and out of peripheral ligands.^{1–7} Previously, these laboratories explored the concept of redox noninnocence in (pddi)Cr (pddi^{2−} = [Me₂C{CH=N(1,2-C₆H₄)N(2,6-ⁱPr₂C₆H₃)₂}]^{2−})⁸ via cyclopropane C–C bond formation in the ligand backbone.^{9–12} Anticipated nitrosylation products containing (cpta)Cr^m (cptaⁿ = [2-Me₂C₃H₂{1,2-N(1,2-C₆H₄)N(2,6-ⁱPr₂C₆H₃)₂}]^{n−}) were unrealized, prompting the design of more direct approaches. Herein are examples of C–C bond-forming RNI with the pddiⁿ ligand, its reversibility, and competing electrophilicity.

Reduction of maroon (pddi)Cr (**1**) with KC₈ in THF, or THF with 1 equiv. 18-crown-6, provided green [(cpta)Cr][K(18-c-6)(THF)₂] (**2c**), or hexamer {[(cpta)Cr][K(THF)₂]}₆ (**2h**) in 76% or 54% yield, respectively. ¹H NMR spectra of **2c** or **2h** in THF-d₈ were the same (2, sol'n), except for the appearance of 18-crown-6 in the former, and Evans' method¹³ measurements were consistent with an *S* = 3/2 core (*μ*(eff) = 3.5(1)*μ*_B). Scheme 1 illustrates a plausible reduction at the ligand (to **1**[−]) rather than at Cr(II), and that subsequent C–C bond formation concomitant with chromium oxidation leads to **2**. Note that K⁰ reduction of **1** causes the formal oxidation of Cr(II) to Cr(III) as both imine carbons are reduced. Ferrocenium oxidation

(1 equiv.) of **2** caused the complete reversion to **1** over a day, and revealed the reversibility of cyclopropane C–C bond formation. Oxidation is likely to occur from either arene-diamide moiety, with accompanying C–C bond-breaking.

The [(cpta)Cr] anion in **2c** is separate from the [K(18-c-6)(THF)₂] cation, and its metrics are clearly those of a tetra-amide. Chromium–nitrogen bonds to the imine in **1** (*S* = 2) average 2.076(9) Å,⁸ while the corresponding amide linkages in **2c** average 1.9401(6) Å, and all of its CrN bond distances are shorter in concert with the change from Cr(II) to Cr(III).¹⁴ The cyclopropane C–N single bond lengths are 1.4316(6) (ave) Å while the related imine distances are 1.289(4) (ave) Å,¹⁵ and the new C–C bond is 1.509(2) Å, a distance whose bond enthalpy is about 101(2) kcal mol^{−1}.¹⁶ Select core distances and angles in **2c** are listed in the caption to Fig. 1 and reflect its *S* = 3/2 ground state. A partial skeletal view of the hexamer, **2h** is also shown, and its core distances are within 0.002 Å and 1° of those in **2c**, except for those involving N1, whose subtle angular changes with connected atoms are features of the hexamer.

As Scheme 2 illustrates, treatment of (pddi)Cr (**1**) with MeLi in THF induced formal oxidation of Cr(II) to Cr(IV) concomitant with Me anion adduct formation and 2e[−] reduction of the



Scheme 1 Reduction of (pddi)Cr (**1**) and oxidation of [(cpta)Cr][K(18-c-6)(THF)₂] (**2**) showing reversible cyclopropane C–C bond formation.

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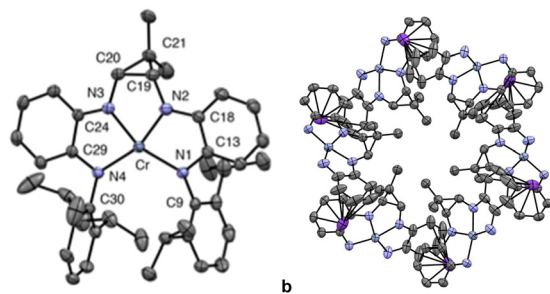


Fig. 1 (a) Molecular view of the [(cpta)Cr] anion of (**2c**). Selected distances (Å) and angles (°): CrN1, 2.0016(12); CrN2, 1.9405(13); CrN3, 1.9396(13); CrN4, 1.9976(12); N1C13, 1.3928(18); N2C18, 1.366(2); N2–C19, 1.4311(19); C19C20, 1.509(2); N3C20, 1.432(2); N3C24, 1.3634(19); N4C29, 1.3864(17); N1CrN2, 80.38(5); N1CrN3, 159.43(5); N1CrN4, 119.49(5); N2CrN3, 80.94(5); N2CrN4, 159.75(5); N3CrN4, 79.91(5); N2C19C20, 110.73(13); N2C19C21, 119.70(15); N3C20C19, 110.57(13); N3C20C21, 120.84(15). (b) K[arene-diamide]₆ connectivity of **2h**; THFs and 2,6-*i*-Pr₂C₆H₃ groups removed for clarity.

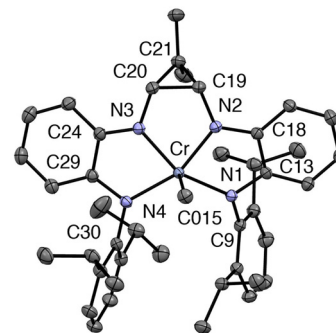
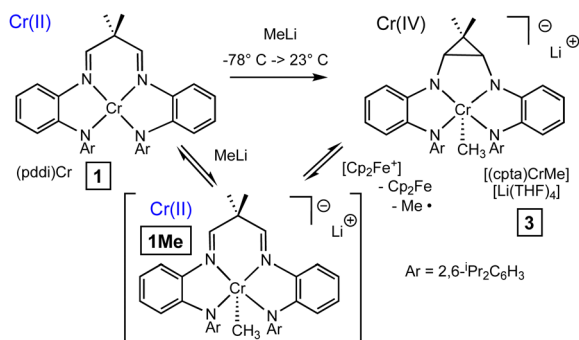


Fig. 2 Molecular view of the [(cpta)CrMe] anion of (**3**). Selected distances (Å) and angles (°): CrN1, 1.9968(12); CrN2, 1.9382(12); CrN3, 1.9285(13); CrN4, 2.0398(12); CrC015, 2.0766(15); N1C13, 1.3931(18); N2C18, 1.3582(19); N2–C19, 1.4251(18); C19C20, 1.502(2); N3C20, 1.4269(18); N3C24, 1.3618(19); N4C29, 1.3804(19); N1CrN2, 80.35(5); N1CrN3, 150.83(5); N1CrN4, 114.37(5); N2CrN3, 79.81(5); N2CrN4, 157.13(5); N3CrN4, 79.60(5); N1CrC015, 97.16(6); N2CrC015, 92.31(6); N3CrC015, 104.80(6); N4CrC015, 102.50(6); N2C19C20, 109.68(12); N2C19C21, 117.87(12); N3C20C19, 110.46(12); N3C20C21, 119.48(13).

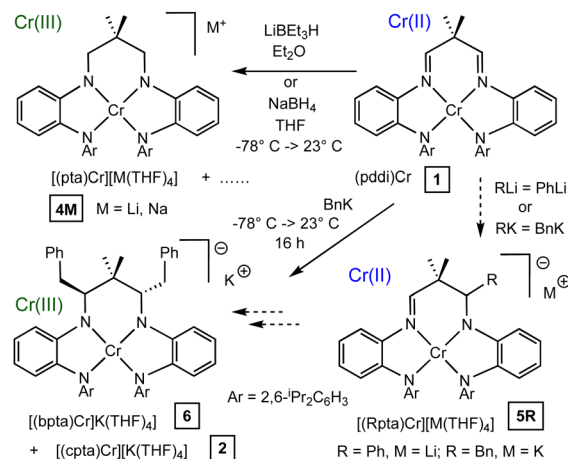


Scheme 2 Reduction of (pddi)Cr (**1**) with MeLi to afford [(cpta)CrMe][Li(THF)₄] (**3**).

chelate. Cyclopropanated product [(cpta)CrMe][Li(THF)₄] (**3**) is paramagnetic ($S = 1$; $\mu(\text{eff}) = 2.7(1)\mu_{\text{B}}$)¹³ and was isolated in 63% yield. It is likely that adduct formation to Cr(II) incurs only a modest electronic change, and the added electron density induces the $2e^-$ diimine coupling to generate the formal Cr(IV) tetraamide π -Pr-containing chelate, cpta.

With an Addison parameter of $\tau = 0.11$,¹⁷ the [(cpta)CrMe] anion of **3** is clearly pseudo square pyramidal, with core N–Cr–C angles varying from $92.31(6)^\circ$ to $104.80(6)^\circ$. The average deviation of N(amide)Cr distances between **2** and **3** is 0.006 \AA , with the greatest 0.0422 \AA , hence the formal oxidation state change is not metrically evident.¹⁸ Pertinent bond distances and angles are listed in the Fig. 2 caption.

Many reagents that can be construed as nucleophiles were unreactive with (pddi)Cr (**1**), e.g. PMe_3 or N_3^- , and others manifested alternative paths to adduct formation. Evidence of $1e^-$ reduction was observed for NaNH_2 , and the pddi proved susceptible to attack by hydride and other alkyl anion sources. As Scheme 3 reveals, addition to the electrophilic imines was observed with LiBET_3H or NaBH_4 to afford tetraamide [(pta)Cr][M(THF)₄] (**4M**, $M = \text{Li, Na}$) in 68% or 46% yield.



Scheme 3 Hydride and benzyl anion addition to (pddi)Cr (**1**).

Unidentifiable disproportionation product(s) are likely to balance the double hydride addition to **1**.

The molecular view of the [(pta)Cr] anion of **4Li** is pseudo square planar (Fig. 3), with core Cr–N distances consistent with an $S = 3/2$ ($\mu(\text{eff}) = 3.9(1)\mu_{\text{B}}$)¹³ tetraamide, and within 0.03 \AA of those of **2** and **3**. Carbon–nitrogen bond lengths of $1.458(2)$ and $1.457(2) \text{ \AA}$ in the propyl ligand backbone are clearly those of single bonds,¹⁵ and related angles of the methylenes are those of strained sp^3 -carbons: $115.81(14)^\circ$ and $113.32(14)^\circ$.

In concert with hydride addition, exposure of (pddi)Cr (**1**) to BnK afforded the analogous double addition product [(bpta)Cr][K(THF)₄] (**6**), and in this case, crystallization with 18-c-6 present afforded a 1:1 mixture of **6**:**2**, which eluded separation. The reaction of **1** and PhLi revealed Ph addition to one imine, consistent with the triamide [(Rpta)Cr][M(THF)₄] (**5R**; $R = \text{Ph}$, $M = \text{Li}$; $R = \text{Bn}$, $M = \text{K}$), according to a partial X-ray structure determination that provided the connectivity. A related benzyl



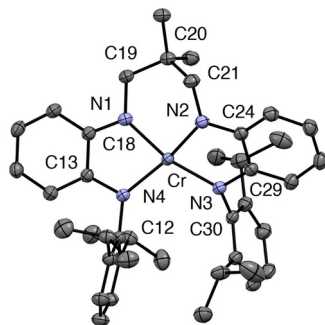


Fig. 3 Molecular view of the [(pta)Cr] anion of (**4Li**). Selected distances (Å) and angles (°): CrN1, 1.9594(14); CrN2, 1.9663(14); CrN3, 1.9928(14); CrN4, 2.0089(14); N4C13, 1.391(2); N1C18, 1.369(2); N1–C19, 1.458(2); N2C21, 1.457(2); N2C24, 1.374(2); N3C29, 1.388(2); N1CrN2, 92.39(6); N1CrN3, 162.74(6); N1CrN4, 81.14(6); N2CrN3, 80.72(6); N2CrN4, 164.57(6); N3CrN4, 109.19(6); N1C19C20, 115.81(14); N2C21C20, 113.32(14).

Cr(II) complex (**5Bn**) is a plausible intermediate that can transfer an electron to (pddi)Cr (**1**) to afford **2**. The resulting neutral Cr(III) benzylated complex is likely susceptible to attack by a second BnK to provide **6**.

Fig. 4 illustrates the dibenzylated anion of [(bpta)Cr][K(18-c-6)(THF)₂] (**6**) that cocrystallized with **2c**. Chromium–nitrogen bond distances listed in the caption are consistent with amide linkages, and the backbone CC- and CN-distances possess C(sp³)–C(sp³), and the N–C(sp³) values.¹⁵ The pseudo square-planar coordination manifests greater distortion ($\Sigma \angle \text{NCrN} = 375.9^\circ$) than **1** (360.8°),⁸ **2c** (360.7°), and **4** (362.9°), presumably due to the tetraamide core in combination with the added sterics of the anti-arrangement of the benzylated backbone.

Free energy calculations pertinent to Schemes 1 and 2 are given in Scheme 4. While reduction of (pddi)Cr (**1**) to [(cpta)Cr]K(THF)_n (**2**) was suggested to occur *via* a 1e[−]-reduced intermediate (**1(−)**), it is surprising that thermal formation of the neutral (cpta)Cr (**1CC**) complex is only 11.8 kcal mol^{−1} endoergic, providing an alternative path, one that is common to Scheme 2. Adduct formation of MeLi and **1** to **1Me** is exoergic by −7.2 kcal mol^{−1}, and the ensuing CC-bond formation to [(cpta)CrMe][Li(THF)_n] (**3**) is also favorable by

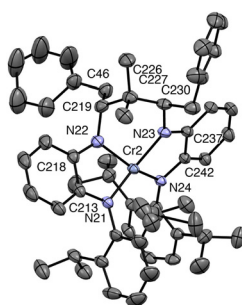
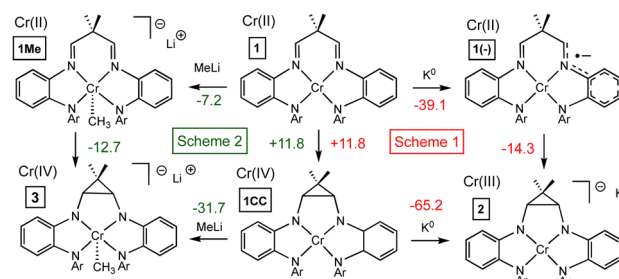


Fig. 4 Molecular view of the [(bpta)Cr] anion of (**6**). Selected distances (Å) and angles (°): CrN21, 1.9786(15); CrN22, 1.9345(17); CrN23, 1.9643(15); CrN24, 1.9673(15); N22C219, 1.463(3); N23C227, 1.469(2); C219C226, 1.561(3); C219C46, 1.541(3); C226C227, 1.556(3); C227C230, 1.562(3); N21CrN22, 81.62(7); N21CrN23, 149.04(7); N21CrN24, 120.22(6); N22CrN23, 92.34(7); N22CrN24, 144.00(7); N23CrN24, 81.66(6).



Scheme 4 Calculated free energies (kcal mol^{−1}) of paths pertinent to Scheme 1 (red) and Scheme 2 (green) relative to (pddi)Cr (**1**) at 0.0 kcal mol^{−1}.

−12.7 kcal mol^{−1}. While the likely path, barriers to even these simple paths involving charged species are difficult to assess, and while formation of **1CC** is endoergic by +11.8 kcal mol^{−1}, the adduct might form *via* an empty d_{z²} orbital on the Cr(IV) species.¹⁹

The cyclic voltammogram of (pddi)Cr (**1**) in Fig. 5 shows a reduction at −2.50 V (rel. to Fc/Fc⁺), followed by a second at −2.76 V. An oxidation wave at −2.53 V and another at much more positive potential (−0.99 V) are also observed. If the potential is cycled immediately after the first reduction wave, only the oxidation at −0.99 V is observed, consistent with reduction to [(pddi)Cr][−] (**1(−)**), followed by rapid CC bond formation to **2**, and oxidation back to **1**, with $\Delta E_p = 1.51$ V. The second reduction and corresponding oxidation likely correspond to a reversible [(cpta)Cr][−] (**2**) to [(cpta)Cr]^{2−} couple.

Molecular orbitals corresponding to (pddi)Cr (**1**) and [(cpta)Cr][K(THF)_n] (**2**) reveal the consequences of low symmetry and unpaired spins (Fig. 6); virtually all are admixtures of ligand and Cr(3d). A 1e[−] reduction of **1** is likely to be in the β -LUMO (L π^* , −1.35 eV) resulting in an $S = 3/2$ configuration due to antiferromagnetic (AF) coupling. The ensuing formation of **2** *via* C–C bond formation is spin-allowed, and likely to occur immediately to attenuate electron density near and at the Cr. This is supported by the calculated favorable free energy (−14.3 kcal mol^{−1}, Scheme 4) for **1(−)** → **2**, and the MO of **2**, which manifests a low-lying α -LUMO at −1.39 eV. It can accept an

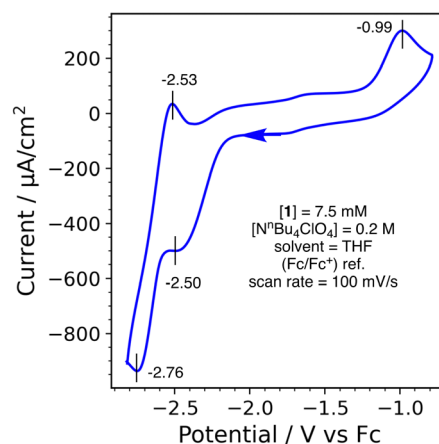


Fig. 5 Cyclic voltammogram of (pddi)Cr (**1**).

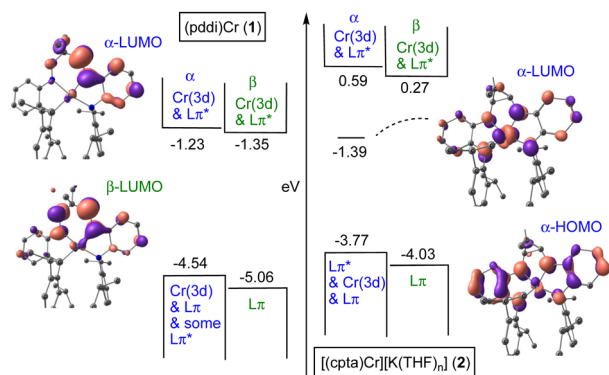


Fig. 6 Respective relative α (blue) and β (green) molecular orbitals of (pddi)Cr (**1**) and [(cpta)Cr][K(THF)₆] (**2**); details are found in the ESI.†

electron consistent with the aforementioned reversible reduction at -2.76 V. The low-lying β -LUMO ($L\pi^*$) MO of **1** is also a site that invites nucleophilic attack, as observed for the hydride, Ph(–) and Bn(–) chemistry in Scheme 3.

Formation of [(cpta)CrMe][Li(THF)_n] (**3**) is less well rationalized. Empty Cr(3d) orbitals and ligand ($L\pi^*$) orbitals of (pddi)Cr (**1**) are positioned similarly according to energy, but d_{22} is half-occupied, affording some e^-e^- repulsion upon an axial nucleophilic attack. It is intriguing that cyclopropane formation (**1** \rightarrow **1CC**, Scheme 4) is calculated to be only 11.8 kcal mol^{–1} endoergic, perhaps suggesting a means of allowing attack at an empty d_{22} orbital. MOs of **3** are admixed to the extent that identifying α - and β -orbitals as primarily Cr(d)- or ligand-based is not appropriate. Consequently, while formal oxidation states (FOSS) are used to classify these complexes, the similar structural metrics of **1**, **2c**, **3**, **4Li**, and **6** show that the variance upon oxidation is modest.¹⁸ It is clear that storing electrons in a C–C bond can be incorporated into a ligand for RNI applications.

All synthetic and most spectroscopic work was conducted by AAD; MRK performed the cyclic voltammetry; TRC is responsible for calculations, and SNM is the crystallographer. Conception of the project and management is the purview of PTW.

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Conflicts of interest

There are no conflicts to declare.

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