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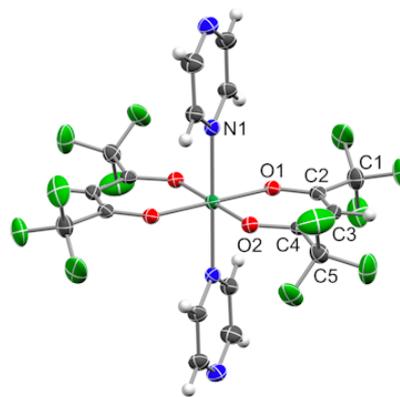
Evidence for Non-Innocence of a  $\beta$ -Diketonate Ligand

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**Abstract:**  $\beta$ -Diketonates, such as acetylacetonate, are amongst the most common bidentate ligands towards elements across the entire periodic table and are considered wholly redox-inactive in their complexes. Herein we show that complexation of 1,1,1,5,5,5-hexafluoroacetylacetonate (hfac<sup>-</sup>) to Cr(II) spontaneously affords Cr(III) and a reduced  $\beta$ -diketonate radical ligand scaffold, as evidenced by crystallographic analysis, magnetic measurements, optical spectroscopy, reactivity studies, and DFT calculations. The possibility of harnessing  $\beta$ -diketonates as electron reservoirs opens up possibilities for new metal-ligand concerted reactivity in the ubiquitous  $\beta$ -diketonate coordination chemistry.

The cooperativity between metal ion-centered and ligand-centered redox events is considered one of the most important strategies to confer noble metal reactivity to base metals, having immense relevance for homogeneous catalysis.<sup>[1]</sup> A plethora of redox-active ligands is now available, although only a handful of the most commonly employed ligands have been shown to exhibit this behavior.<sup>[2]</sup>  $\beta$ -Diketonate ligands are ubiquitous in the coordination chemistry of the s-, d-, p-, and f-blocks of the periodic table. The deprotonated forms of pentane-2,4-dione (acac<sup>-</sup>) and 1,1,1,5,5,5-hexafluoropentane-2,4-dione (hfac<sup>-</sup>), are the most commonly used  $\beta$ -diketonate ligands, with each garnering ~3000 crystallographically characterized compounds.<sup>[3]</sup> Notably, hfac<sup>-</sup> complexes demonstrate highly sought-after properties such as high vapor pressure and high solubility in non-coordinating solvents, making them of interest for wide range of applications, such as chemical vapor deposition,<sup>[4]</sup> homogeneous catalysis,<sup>[5]</sup> and molecule-based magnets.<sup>[6]</sup> Despite being so common, there are no reports of any non-innocence of these ligands.<sup>[7]</sup> In comparison, the related  $\beta$ -diketiminate (NacNac<sup>-</sup>) was reported to be electrochemically oxidizable to the neutral radical form,<sup>[8]</sup> and a similar behavior was observed for the polyaromatic 9-oxidophenalenone.<sup>[9]</sup> although no crystal structures were obtainable for any of these complexes. Likewise, anion-radical formation was reported for  $\alpha$ -diketone ligands,<sup>[10]</sup> but similar reactivity has been elusive for the  $\beta$ -analogues. Even attempts to electrochemically reduce the protonated hfac<sup>-</sup> to its radical anion in solution were unsuccessful and only led to an irreversible

reduction event occurring at -1.2 V vs Cp<sub>2</sub>Fe<sup>0/+</sup>.<sup>[11]</sup> The use of reducing metal ions in combination with aromatic  $\pi$ -ligands to form stable charge-transfer complexes is a feature commonly exploited to generate metal-radical complexes.<sup>[12]</sup> We recently reported the reaction of CrCl<sub>2</sub> with pyrazine (pyz) to yield a two-dimensional coordination solid, CrCl<sub>2</sub>(pyz)<sub>2</sub>, in which each pyz is formally reduced by half an electron, and chromium is in oxidation state +III.<sup>[13]</sup> For hfac<sup>-</sup>, binary complexes of the 3d transition series have been reported for V<sup>III</sup>,<sup>[14]</sup> Cr<sup>III</sup>,<sup>[15]</sup> Mn<sup>II,III</sup>,<sup>[16]</sup> Fe<sup>II,III</sup>,<sup>[17]</sup> Co<sup>II</sup>, Ni<sup>II</sup>,<sup>[18]</sup> Cu<sup>II</sup>,<sup>[19]</sup> and Zn<sup>II</sup>,<sup>[20]</sup> none of which are particularly reducing metal ions. We herein report on the spontaneous reduction of hfac<sup>-</sup> by Cr(II) and the characterization of the resulting complexes featuring non-innocent hfac<sup>-</sup> ligands.



**Figure 1.** Thermal ellipsoid plot of **1** drawn at 50% probability level (Cr dark green, F green, O red, N blue, C grey, H white). Selected bond lengths (Å): Cr–O1 1.926(2), Cr–O2 1.931(2), Cr–N1 2.091(2), O1–C2 1.289(4), O2–C4 1.286(4), C1–C2 1.514(4), C2–C3 1.379(5), C3–C4 1.392(4), C4–C5 1.518(4).

The reaction of CrCl<sub>2</sub> in tetrahydrofuran (THF) with hfacH and NEt<sub>3</sub> under strictly anaerobic conditions yields an intensely colored, dark-brown solution. Subsequent addition of pyrazine and concentration of the solution under reduced pressure affords dark-red crystals of *trans*-[Cr(hfac)<sub>2</sub>(pyz)<sub>2</sub>] (**1**, Figure 1) suitable for single crystal X-ray diffraction. **1** crystallizes in the orthorhombic *Pbca* space group and features the Cr site located on an inversion center. The Cr–N distance of 2.091(2) Å and the Cr–O distances of 1.926(2) Å and 1.931(2) Å reveal no clear Jahn-Teller distortion, which, nonetheless, would be partially convoluted with the presence of different ligands. However, for comparison, the isomorphous Cu(II) complex features a Jahn-Teller axis along the Cu–O1 axis with Cu–O1 and Cu–O2 bond lengths of 2.225(4) Å and 1.995(4) Å, respectively.<sup>[21]</sup> Although a number of Cr(II) complexes have been reported to lack the expected Jahn-Teller distortion,<sup>[22]</sup> often attributed to the occurrence of dynamic effects, the absence of a distortion renders the oxidation state assignment of +II ambiguous. Indeed, the Cr–N bond length is typical for Cr(III)-aromatic amine bonds<sup>[23]</sup> and the Cr–O distances are close to those previously reported for [Cr<sup>III</sup>(hfac)<sub>3</sub>] (1.943(5) and 1.955(5) Å).<sup>[24]</sup> In this case, two additional scenarios could be envisioned: (1) electron transfer

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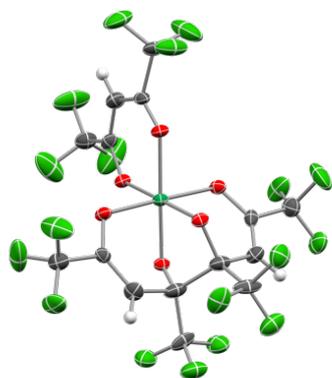
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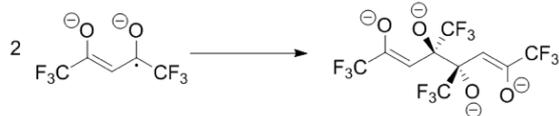
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from Cr(II) to pyrazine to form  $\{\text{Cr}^{\text{III}}(\text{pyz})_2\}^{+}$ , or (2) electron transfer from Cr(II) to the  $\text{hfac}^-$  to yield  $\{\text{Cr}^{\text{III}}(\text{hfac})_2\}^{3-}$ . In order to compare the metrics of the  $\text{pyz}$  and  $\text{hfac}^-$  ligands with the vast number of published crystal structures containing these ligands ( $\sim 1300$  and  $\sim 3000$ , respectively),<sup>[3]</sup> we screened the Cambridge Structural Database for C–N and C–C bond lengths of  $\text{pyz}$  and for the C–O, C–CF<sub>3</sub>, and C–CH bond lengths of  $\text{hfac}^-$  (Figure S3-4). In **1**, the average  $\text{pyz}$  bond lengths amount to C–N 1.337 Å and C–C 1.383 Å which both coincide almost perfectly with the estimated gaussian mean for all reported pyrazine structures (C–N 1.335 Å, C–C 1.380 Å). For  $\text{hfac}^-$  complexes, the average C–O distance in **1** of 1.288 Å is amongst the longest 1.5% of all structures, whilst the average C–CF<sub>3</sub> and C–CH distances are close to the mean values (Figure S4). DFT geometry optimization of  $\text{hfac}^-$  and the mono-radical  $\text{hfac}^{\bullet-}$  (Figure S10) reveal that, upon a one-electron reduction, the C–O bond elongates by  $\sim 5\%$  Å, whereas the C–CF<sub>3</sub> bond contracts slightly by  $\sim 3\%$ , and the C–CH bond length is virtually unaffected. The experimental bond lengths of the  $\text{hfac}^-$  echo this trend (Figure S4) whereas the bond lengths of the  $\text{pyz}$  ligands are entirely unaffected as expected for the non-reduced case (Figure S3). These observations point towards the redox-activity of the  $\text{hfac}^-$  ligands dominating over that of the  $\text{pyz}$  ligands. To corroborate this hypothesis, the closely related complex, *trans*-[Cr( $\text{hfac}$ )<sub>2</sub>(THF)<sub>2</sub>] (**2**), previously assigned as a Cr(II) complex, was studied. The synthesis and the structural characterization at 198 K were reported by Harada and Girolami.<sup>[15]</sup> Attempts to synthesize **2** (see SI) using a modified procedure in which  $\text{CrCl}_2$  was treated with  $\text{hfacH}$ , followed by deprotonation with triethylamine, were unsuccessful and only led to the isolation of red crystals of **3**. The crystal structure of **3** is shown in Figure 2 and features an octahedrally coordinated Cr bound to one  $\text{hfac}^-$  ligand and a quadruply deprotonated (*R,R*)

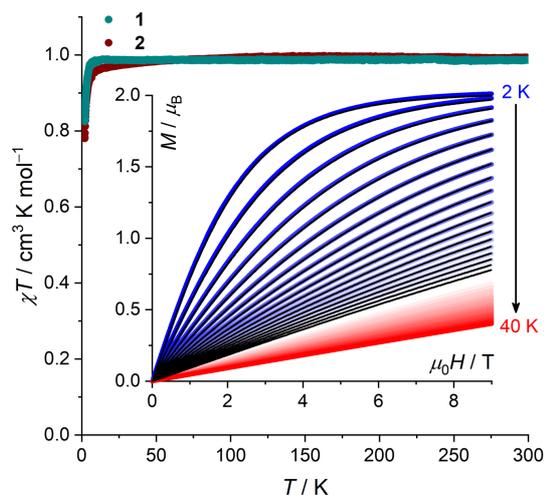


**Figure 2.** Thermal ellipsoid plot of one of the enantiomeric Cr complexes of **3** drawn at 50% probability level (Cr dark green, F green, O red, C grey, H white). Triethylammonium counter-ions and co-crystallized diethyl ether molecules have been omitted for clarity.



**Scheme 1.** Dimerization of  $\text{hfac}^{2-}$ .

or (*S,S*)-1,1,1,8,8,8-hexafluoro-4,5-bis(trifluoromethyl)-4,5-dihydroxooctane-2,7-dione. Its formation is hypothesized to proceed via a pinacol coupling-type reaction of two  $\text{hfac}^{2-}$  radical dianions (Scheme 1). Notably, this reactivity contrasts that of manganese(III)-mediated radical reactions of ketones which lead to  $\alpha$ -oxoalkyl radical intermediates.<sup>[27]</sup> Following the published procedure,<sup>[26]</sup> using  $\text{Na}(\text{hfac})$  as a starting material, revealed a crystalline sample of **2**. A redetermination of the crystal structure at 120 K reveals only minor differences to the published 198 K structure. Notably, the Cr–O<sub>hfac</sub> distances (1.923(3) Å) and the metrics of the  $\text{hfac}^-$  ligands in **2** are close to those determined for **1** suggesting a common oxidation state for the Cr centers in the two compounds (see Figure S1, S4).



**Figure 3.** Temperature dependence of the  $\chi T$  product ( $\chi = M/\mu_0 H$ ,  $\mu_0 H = 1$  T) for polycrystalline **1** and **2** between 1.7 K and 300 K. Inset:  $M$  vs  $\mu_0 H$  data for **1** at selected low temperatures (2 to 40 K in 1 K steps).  $M$  vs  $H$  data for **2** are shown in Figure S6. The black lines are fits to the experimental data as described in the main text.

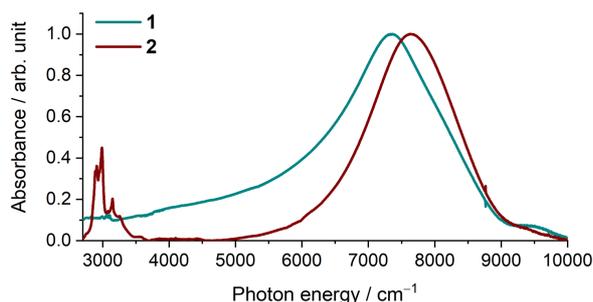
The temperature dependence of the susceptibility-temperature product,  $\chi T$ , of **1** and **2** is shown in Figure 3. The 300 K value amounts to  $0.98 \text{ cm}^3 \text{ K mol}^{-1}$  (**1**) and  $0.99 \text{ cm}^3 \text{ K mol}^{-1}$  (**2**) which are far from the  $3.0 \text{ cm}^3 \text{ K mol}^{-1}$  expected for a high-spin Cr(II) ion with an  $S = 2$  ground state. Indeed, the experimental value is reminiscent of an  $S_T = 1$  ground state with a  $g$ -factor close to 2. Such a situation could be found in low-spin Cr(II), which, however, is only found with the most extreme strong-field ligands and thus irrelevant for the present ligand sphere of **1** and **2**.<sup>[28]</sup> On the contrary, electron transfer from the initially present Cr(II) to one of the ligands may give rise to an  $S_T = 1$  if the antiferromagnetic interaction between the resulting Cr(III) ( $S = 3/2$ ) and the radical ( $S = 1/2$ ) is on the order of the thermal energy at room temperature or larger. On lowering temperature, the  $\chi T$  products of **1** and **2** remain roughly constant until  $\sim 8$  K where they decrease abruptly, a behavior that can be attributed to concerted effects of magnetic anisotropy and weak antiferromagnetic interactions between adjacent molecules in the solid. Attempts to observe any curvature in the  $\chi T$  product of **1** and **2** at temperatures higher than room temperature were unsuccessful and hence an experimental estimation of the magnitude of a super-exchange interaction was

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impossible. Both **1** and **2** exhibit irreversible increases in the  $\chi T$  product indicative of thermal decomposition at high temperatures (Figure S5). The magnetization vs magnetic field data are shown in the inset of Figure 3. The magnetization saturates only at large magnetic fields indicative of a significant magnetic anisotropy. The data were modelled using the spin-Hamiltonian:

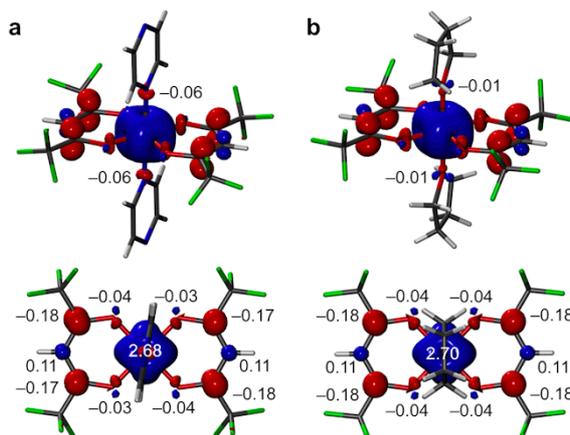
$$\widehat{H} = g\mu_B\mu_0 \mathbf{H} \cdot \widehat{\mathbf{S}}_T + D(\widehat{S}_{T,z}^2 - S_T(S_T + 1)/3)$$

where  $S_T = 1$  is the coupled spin state arising from the antiferromagnetic coupling of an  $S = 3/2$  spin with an  $S = 1/2$  spin. The magnetic anisotropy is reflected in the zero-field splitting parameter,  $D$ . The fit to the  $M$  vs  $H$  data affords for both **1** and **2**:  $g = 2.0$  and  $D$  of  $+2.2 \text{ cm}^{-1}$ . The  $D$  is related to the single-ion Cr(III)  $D_{Cr}$  parameter value through  $D_{Cr} = 2/3 \times D_{S_T=1} = +1.5 \text{ cm}^{-1}$ .<sup>[29]</sup> Notably, the magnitude of  $D_{Cr}$  is almost one order of magnitude larger than those commonly found for tetragonal Werner-type Cr(III) complexes,<sup>[30]</sup> although organometallic Cr(III) complexes frequently have even larger  $D_{Cr}$  values.<sup>[31]</sup> Reasonable fits to the  $M$  vs  $H$  data can also be obtained with a negative  $D_{S_T=1}$  parameter but were excluded due to a larger statistical  $\chi^2$  value. Alternating current (ac) susceptibility measurements at 1.8 K reveal no indications of slow relaxation of the magnetization (time scale  $10^1$ – $10^4$  Hz), with or without the application of a static magnetic field. This observation is coherent with an  $m_{S_T=1} = 0$  ground state.



**Figure 4.** Attenuated total reflectance (ATR) NIR-spectra obtained at room temperature of polycrystalline **1** and **2**. The spectra were normalized to unity at the absorption maximum.

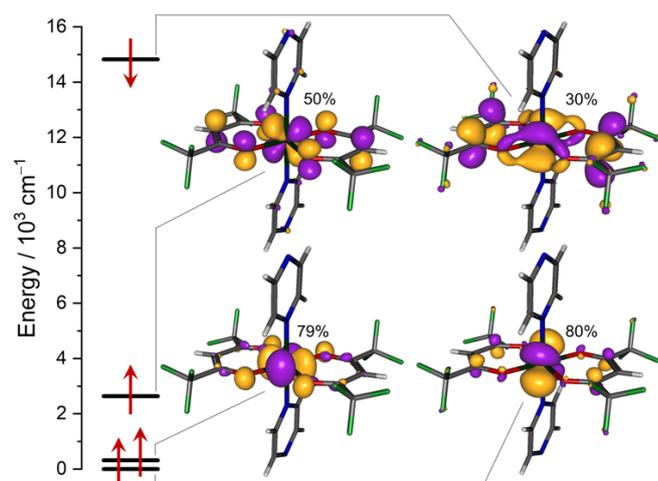
The optical ultraviolet-visible spectra of **1** and **2** feature several bands which are too intense ( $\epsilon > 1000 \text{ M}^{-1} \text{ cm}^{-1}$ ) to be classified as d-d transitions and are attributed to charge-transfer transitions (Figure S7). The spectra are remarkably similar suggesting a comparable electronic structure of **1** and **2**. The attenuated total reflectance spectra in the near-IR region of **1** and **2** are shown in Figure 4. For both compounds, an intense, broad (fwhm  $1 \sim 1900 \text{ cm}^{-1}$ ,  $2 \sim 1500 \text{ cm}^{-1}$ ) absorption band is observed, which is a typical fingerprint of mixed-valency,<sup>[32,33]</sup> and is attributed to the  $\text{hfac}^{+2}/\text{hfac}^-$  IVCT. Cyclic voltammetry affords a single reversible oxidation of **1** at a largely negative potential of  $-1.7 \text{ V}$  vs  $\text{Cp}_2\text{Fe}^{0/+}$  (Figure S8), assigned to the formation of  $\{\text{Cr(III)}(\text{hfac})_2\}^+$ . This species could not be isolated (see SI), but its formulation is corroborated by DFT calculations (see Figure S13). We were unable to observe any reversibility in the oxidation process for **2**. To obtain further insight into the electronic structures of **1** and **2**,



**Figure 5.** Broken-symmetry DFT-calculated spin-density plots for **1** (a) and **2** (b) (isosurface value =  $0.005 a_0^{-3}$ ,  $a_0$  being the Bohr length). Selected Mulliken spin populations are indicated. Non-indicated spin populations are below 0.01.

broken-symmetry DFT calculations at the TPSSh/def2-TZVP-ZORA level were performed. For **1**, the energy difference between the broken symmetry (BS(3,1),  $S_T = 1$ ) ground state and the high-spin (HS,  $S = 2$ ) excited state amounts to  $5488 \text{ cm}^{-1}$ , which, following the convention by Yamaguchi, results in a superexchange coupling constant of  $J = 3032 \text{ cm}^{-1}$  (Hamiltonian definition  $\widehat{H} = J \widehat{\mathbf{S}}_{Cr} \cdot \widehat{\mathbf{S}}_{\text{radical}}$ ). The DFT-calculated spin densities are shown in Figure 5. Notably, the spin-density in **1** is vanishing on the pyz ligands, but is substantial on the  $\text{hfac}^-$  ligands. The integrated Mulliken spin populations suggest the presence of an  $S = 3/2$  Cr(III) (spin population: 2.68) and one unpaired electron smeared over two crystallographically identical  $\text{hfac}^-$  ligands (see Figure 5a). The analogous calculations performed for **2** are highly similar to those of **1** (see Figure 5b,  $J = 2993 \text{ cm}^{-1}$ ) emphasizing the absence of participation of the pyz and THF ligands in the redox event. The qualitative frontier MO diagram for **1** (**2**) is shown in Figure 6 (S12) and features three singly occupied Cr-based orbitals reminiscent of a  $(d_{xy})^1(d_{zx})^1(d_{xy})^1$  electronic configuration, and one singly occupied orbital of predominant ligand character. The structural characterization of the closely related  $[\text{Cr}(\text{acac})_2]$  was reported by Cotton et al. and features a square-planar Cr ion with, presumably, very weak Cr...C interactions ( $> 3 \text{ \AA}$ ).<sup>[34]</sup> The bulk effective magnetic moment was determined to  $4.99 \mu_B$  (corresponding to a  $\chi T$  product of  $3.1 \text{ cm}^3 \text{ K mol}^{-1}$ ), in good agreement with expectations for a high-spin  $d^4$  complex. DFT calculations were performed on  $[\text{Cr}(\text{acac})_2]$ , which yields a high-spin,  $S = 2$  ground state stabilized by  $9455 \text{ cm}^{-1}$  from the BS state. Both the HS and BS state exhibit little spin density (Figure S14) on the  $\text{acac}^-$  ligands. Furthermore, the Mulliken spin population of Cr in the ground state amounts to 4.10 which corroborates the presence of Cr(II) in  $[\text{Cr}(\text{acac})_2]$ . Attempts to synthesize the analogous  $[\text{Cr}(\text{hfac})_2]$  by sublimation of **2** *in vacuo* were unsuccessful and yielded  $[\text{Cr}(\text{hfac})_3]$  as the only crystalline product. Synthesis attempts in non-coordinating solvents (see SI) systematically yielded the C–C coupled product as found in **3**. DFT geometry optimization of the hypothetical  $[\text{Cr}(\text{hfac})_2]$  predicts a square planar geometry similar to  $[\text{Cr}(\text{acac})_2]$  and a HS ground state with a Cr Mulliken spin population of 4.04 (Figure S15).

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**Figure 6.** Frontier Kohn-Sham SOMO energy level diagram for **1** plotted on a relative energy scale and with the percental contribution of the Cr atomic orbitals to the SOMOs indicated (cf. Figure S12 for **2**).

These computational results suggest that the electron transfer is imposed by the presence of axial ligands. Pictorially, one can imagine that the axial ligands destabilize the singly occupied  $d_{z^2}$  orbital of Cr(II), thereby favoring electron transfer to the  $hfac^-$  ligands. It is remarkable that the presence of a weak-field ligand as THF is sufficient to promote the electron-transfer. However, this result is paralleled by that of the {Cr(II)-bpy} (bpy = 2,2'-bipyridine) redox-couple, which is always found as {Cr(III)-bpy $^{+}$ } in octahedral complexes,<sup>[35]</sup> but as {Cr(II)-bpy $^0$ } when the coordination geometry of Cr is square planar.<sup>[36]</sup> While one may speculate if the apparent non-innocence of the  $hfac^-$  ligand has led to incorrectly assigned metal ion oxidation states in previously

reported complexes, it is noteworthy to consider the electronic structure situation of **1** and **2**. Indeed, the combination of a high-spin  $d^4$  configuration and a moderate reducing power leading to a half-filled, high-energy  $d_{z^2}$  orbital renders Cr(II) almost unique. Thus, it seems possible that **1** and **2** are the only examples of non-innocence of simple  $\beta$ -diketonates in transition metal complexes.

In conclusion, we have demonstrated the existence of redox non-innocence of  $hfac^-$  through the spontaneous reduction by Cr(II). Cr(II) complexes are well-known to be highly efficient catalysts for e.g. the arylation<sup>[37]</sup> and hydrosilylation<sup>[38]</sup> of ketones, hydrogenation of polycyclic aromatic hydrocarbons,<sup>[39]</sup> and C–C cross-couplings.<sup>[40]</sup> Unfortunately, the unknown exact chemical nature of most of these catalyst complexes and the intermediates preclude an evaluation of their electronic structures. Given that a simple ligand as  $hfac^-$  becomes non-innocent under the influence of moderately reducing Cr(II), it is tempting to speculate that Cr $^{II-L} \leftrightarrow$  Cr $^{III-L^+}$  valence tautomerism, in general, could be of relevance for purported Cr(II) catalysis.

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### Conflict of interest

The authors declare no conflict of interest.

**Keywords:** non-innocent ligands • chromium • bidentate ligands • magnetic properties

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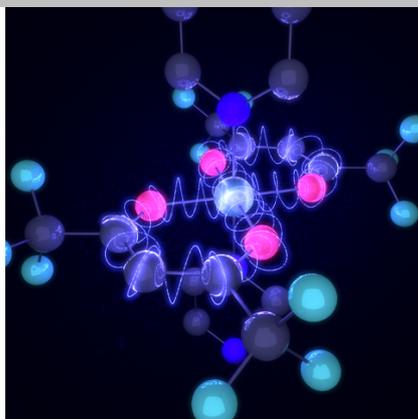
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$\beta$ -Diketonates are amongst the most common ligands towards elements across the periodic table and are wholly redox-inactive in their complexes. We provide experimental and computation evidence for the first complexes incorporating  $\beta$ -diketonate radicals. The possibility of dumping electrons into ubiquitous  $\beta$ -diketonates may open up new perspectives for concerted metal-ligand reactivity.



*Morten Gotthold Vinum, Laura Voigt, Colby Bell, Dmytro Mihrin, René Wugt Larsen, Kensha Marie Clark, Kasper S. Pedersen\**

**Evidence for Non-Innocence of a  $\beta$ -Diketonate Ligand**