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CrCp*Tp: A High-Spin Cr(II) Sandwich Complex with a Large Structural Distortion

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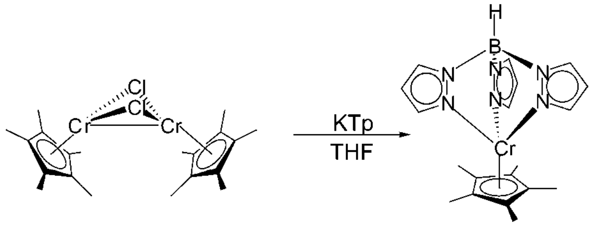
CrCp*Tp was synthesized from the reaction of [CrCp*Cl]$_2$ and KTp. Magnetic measurements indicate it to have a high-spin ($S = 2$) electronic configuration from 5 to 300 K. A single-crystal X-ray study reveals bond lengths typical for a high-spin configuration and a pronounced Jahn–Teller distortion. The nature of this distortion was probed by DFT calculations and the variation in bond lengths successfully reproduced. The metal-based HOMO is significantly antibonding with respect to a single pyrazolyl ring only.

Organometallic Cr(II) complexes of cyclopentadienyl-based ligands with a maximum spin ($S = 2$) ground state are extremely uncommon, with the majority of complexes adopting an $S = 1$ state.[1] Typical examples are found in the metallocene series, in which $CrCp_2$ (Cp = cyclopentadienyl) and its permethylated analogue $CrCp^*_2$ (Cp* = pentamethylcyclopentadienyl) both have two unpaired electrons.[2,3] Use of very bulky Cp ligands can result in high-spin behavior as intramolecular ligand repulsions favor the longer bond lengths associated with the high-spin state. For example, octaisopropylchromocene undergoes a gradual spin transition from a moment of 2.83 μ_B at 2 K to 4.90 μ_B at 300 K.[4] The only example of a chromocene which is high spin at all temperatures studied is bis(1,3-*i*-Pr-indenyl)Cr^{II},[5] but this is believed to be a consequence of the different electronic structure of the indenyl ligand rather than a result of steric effects.[1] We have been interested in the synthesis of mixed-sandwich complexes of Cp^R and hydrotris(pyrazolyl)borate (Tp) ligands, and the investigation of their magnetic and electronic properties. Previous results have shown that, in the case of Co(II), the combination of Cp and Tp ligands gave the first high-spin organometallic Co(II) complex (CoCpTp) whereas its Cp* analogue is low spin.[6] (Methylation of Cp increases the electron-donating ability of the ligand and thus increases ligand-field splittings, further favoring the lower spin state.)[3] Thus one objective of our investigations into mixed Cp/Tp sandwich complexes of 3d metals was to ascertain the spin state of such a complex with Cr(II). $CrTp_2$ is high spin,[7] as are some substituted analogues.[8]

Scheme 1. Synthesis of **1**



Attempts to synthesize CrCpTp by reaction of $CrCp_2$ with 1 equiv of KTp in THF gave as the only isolable products $CrTp_2$, KCp, and unreacted $CrCp_2$. We assume that the desired product is susceptible to displacement of a second Cp ring under these conditions and, therefore, turned our attention to its Cp* analogue, CrCp*Tp, **1**. **1** was successfully synthesized by reaction of [CrCp*Cl]$_2$[9] and KTp in THF, and isolated as a dark purple, oxygen-sensitive crystalline solid by recrystallization from pentane (Scheme 1). The solution magnetic moment was determined by the Evans NMR method ([D$_6$]benzene) to be 4.4 μ_B:[10,11] this is consistent with, but slightly lower than, the spin-only value for a high-spin Cr^{II} ion ($S = 2$, 4.89 μ_B). In the solid state, **1** obeys the Curie−Weiss law over the range 10−300 K, with a moment of 5.02 μ_B ($\theta = -0.4$ K) confirming an $S = 2$ ground state. Thus despite the presence of the strong

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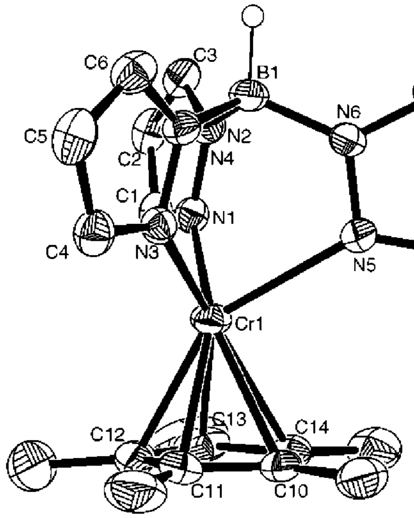

Figure 1. Molecular structure of **1** with thermal ellipsoids at 50% probability. All H atoms (except B−H) are omitted for clarity. Important bond lengths (Å): Cr1−N1 2.092(2), Cr1−N3 2.123(2), Cr1−N5 2.439(2), Cr1−C10 2.372(3), Cr1−C11 2.296(3), Cr1−C12 2.319(3), Cr1−C13 2.317(3), Cr1−C14 2.399(3). Angles (deg) Cp(centroid) = Ct: Ct−Cr1−B1 167.39, Ct−Cr−N1 134.24, Ct−Cr1−N3 132.17, Ct−Cr1−N5 117.11.

electron-donor ligand, Cp*, **1** is a rare example of a Cp^{R}Cr(II) complex with four unpaired electrons. Outside of the two examples from the metallocene series, the 14-electron Cr−carbene complex CrCpCl(1,3-dimesitylimidazoline-2-ylidene) was reported to have an $S = 2$ ground state over the range 5−300 K.[12] Other reported 16-electron Cp*Cr^{II} complexes display moments consistent with $S = 1$ ground states, CrCp*Me(dmpe)[9] and CrCp*Me(bipy).[13,14] Similarly, the dimeric species [(CrCp*)$_2$XY] (where X = Y = Cl, Me, Et, Bu, CH$_2$SiMe$_3$, and Ph; X= Et and Y = Ph) display magnetic behavior consistent with antiferromagnetically coupled $S = 1$ centers,[9] as does [CrCp(O*t*-Bu)]$_2$.[15] We account for our failure to isolate CrCpTp as a consequence of the smaller ligand-field splitting expected for the unmethylated complex and hence increased lability to ligand exchange.

A single-crystal X-ray analysis was performed on **1**,[16] and a view of the structure is given in Figure 1. **1** is considerably distorted from an ideal axially symmetric κ^3-Tp and η^5-Cp* sandwich structure, with the Cr−N5 distance 0.331 Å longer than the average bond length to N1 and N3. The Cr−C10 and Cr−C14 distances are also significantly longer than those to C11, C12, or C13. These structural features can be easily rationalized in terms of a Jahn−Teller distortion for a high-spin d^4 ($S = 2$) configuration, in agreement with the measured magnetic moment for **1**. The three shorter Cr−C bond lengths are similar to the average Cr−C distance in $S = 2$ bis(1,3-isopropylindenyl)chromium(II) (2.32(2) Å),[5] but considerably longer than those for $S = 1$ chromocenes, 2.15−2.20 Å.[17−21] The two short Cr−N bond lengths are similar to the short Cr−N distances in the Jahn−Teller distorted octahedral bis(Tp)Cr^{II} complex, Cr[Tp^{iPr,4Br}]$_2$.[8] The long Cr−N bond length is also similar to those of the more weakly bonded axial pyrazolyl rings in this complex.

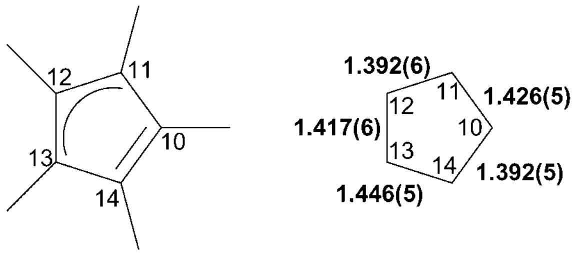

Figure 2. Schematic representation of the ene−allyl distortion in the Cp* ring of **1**. Bond lengths are given in angstroms.

Close inspection of the Cp* intra-ring C−C distances reveals the presence of an ene−allyl distortion; the variation in bond lengths is shown in Figure 2. The angle between the plane defined by C11, C12, C13 and that defined by C10, C11, C13, C14 gives the fold angle, ω, of the ring and is found to be 4.30(46)°. These features are typical of Cp*-containing complexes with ene−allyl distortions and are of a magnitude similar to those previously reported.[22]

We performed DFT (density functional theory) calculations to trace the origin of the unusual structural features arising from this Jahn−Teller distortion.[23] Geometry optimizations were performed starting from an undistorted structure containing a mirror plane symmetry element. The spin of the Cr center was fixed to be $S = 2$, and the initial optimization was simplified by using an unsubstituted Cp ring. The calculation was then further refined by the addition of methyl groups to the Cp ring.

The calculations for CrCp*Tp were found to predict two Cr−N bond lengths of 2.02 Å and a third longer bond of 2.43 Å. These are in good agreement with the crystallographically determined distances: the calculated short bonds

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(16) Crystal structure data for **1** (150 K): Mo Kα radiation ($\lambda = 0.71073$ Å), crystal dimensions 0.6 × 0.2 × 0.1 mm, orthorhombic space group *Pcab* (No. 61), $a = 13.7972(5)$ Å, $b = 14.3138(5)$ Å, $c = 20.4916(7)$ Å, $V = 4046.9(2)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.314$ Mg m^{-3}, $\mu = 0.581$ mm^{-1}, $2\theta_{max} = 27.61°$, 8221 measured reflections, 4265 independent of which $3371 > 2\sigma(I)$, R1 = 0.0586, wR2 = 0.1394, GOF = 1.103, min/max electron density = −1.00/0.83 e Å^{-3}.

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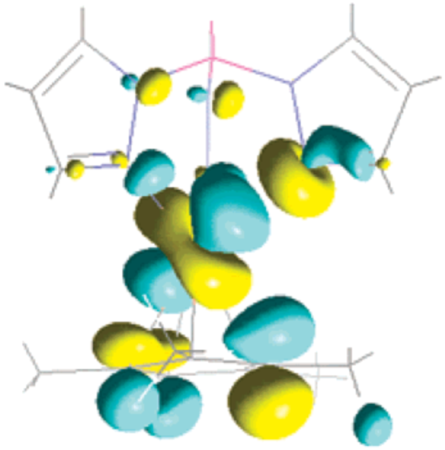

Figure 3. Calculated isosurface for the HOMO of **1**.

are slightly shorter than those actually observed, but the longer bond length is almost identical. Variation in the Cr−C distances is also reproduced with short Cr−C distances of 2.26 Å and a long distance of 2.35 Å. The long Cr−C distance is found to lie to a carbon on the same side of the molecule as the long Cr−N distance, in agreement with the observed structure. In a symmetrically bound MCpTp complex, with effective C_{3v} symmetry, the d orbitals split as $a_1 < 1e < 2e$. The two d orbitals of highest energy are antibonding orbitals of π symmetry with respect to the principal axis (equivalent to the metal-based e_{1g} orbitals in a D_{5d} metallocene, or the $2e_g$ orbitals in a D_{3d} MTp_2 complex). In a d^4 high-spin complex one electron occupies these 2e orbitals giving rise to a ^5E ground state subject to Jahn−Teller distortion. The removal of the electronic degeneracy leads to an energy splitting between the former 2e levels of 1.49 eV; hence there is substantial stabilization of the HOMO. The more stable occupied orbital, of a′ symmetry, is shown in Figure 3.

It has 58% metal d character and is strongly antibonding between Cr and a σ orbital on a N donor atom on one of the pyrazolyl rings, but shows less interaction with the other two pyrazolyl rings. As a consequence there is a single lengthened Cr−N bond. The a_1 HOMO is also antibonding between Cr and the e_1 π orbitals of the Cp* ring (Figure 3). Unequal occupancy of the ring e_1 π levels generates the crystallographically observed ene−allyl distortion of the Cp* ring.

In conclusion, **1** is a rare example of a high-spin $Cp^RCr(II)$ complex with a large structural distortion. Other $[MCp^RTp]^+$ complexes we have synthesized also show a similar sensitivity of molecular structure to electronic configuration which can be partly attributed to the flexibility of the Tp ligand. We will report on these further examples in due course.

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Supporting Information Available: Full experimental details and characterizing data for **1** and calculated orbital energies for **1** and CrCpTp. This material is available free of charge via the Internet at http://pubs.acs.org.

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