Inorganic Chemistry
Communication
pubs.acs.org/IC

Direct Synthesis of Ligand-Based Radicals by the Addition of Bipyridine to Chromium(II) Compounds

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Ⓢ *Supporting Information*

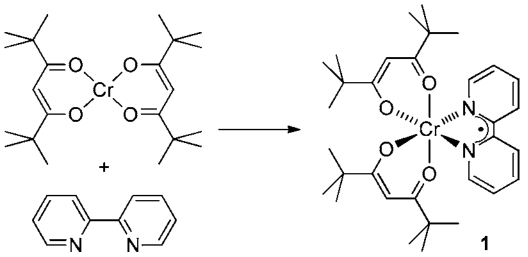
ABSTRACT: The reaction of 2,2′-bipyridine (bpy) with monomeric chromium(II) precursors was used to prepare the $S = 1$ complexes Cr(tBu-acac)$_2$(bpy) (**1**) and (η^5-Cp)(η^1-Cp)Cr(bpy) (**3**), as well as the $S = 2$ compound Cr[N(SiMe$_3$)$_2$]$_2$(bpy) (**4**). The crystallographically determined bond lengths indicate that the bpy ligands in **1** and **3** are best regarded as radical anions, while **4** shows no structural evidence for electron transfer from Cr^{II} to the neutral bpy ligand.

Over the past 15 years, several remarkably effective first-row transition-metal catalysts have employed chelating ancillary ligands with conjugated pyridine and/or imine donors.[1] While the ability of diimine-based ligands to accept an electron to form anionic ligand radicals has long been recognized,[2] the connection between the electronic structure and reactivity remains to be fully understood.[3] Substituted 2,2′-bipyridine (bpy) ligands have been used in situ to generate first-row metal catalysts for organic synthesis.[4] However, compared to pyridinediimine and related tridentate ligands,[5] general synthetic methods to prepare well-defined complexes with only a single bidentate redox-active diimine ligand have yet to be developed.

In this paper, we report new chromium(III) complexes with radical-anionic ligands prepared by the addition of neutral bpy to known monomeric chromium(II) precursors. This synthetic strategy, previously employed by Theopold, Wieghardt, and Mu with diimine ligands and CrCl$_2$,[6−8] relies on the characteristic single-electron-transfer reactivity[9] of Cr^{II} to produce inert octahedral chromium(III) complexes antiferromagnetically coupled to the ligand-based radical. Recent studies by Wieghardt and co-workers have demonstrated the ubiquity of these interactions in what were previously considered to be low-spin chromium(II) complexes[7] and the remarkable correlation between the crystallographically determined C$_{py}$−C$_{py}$ bond length and the bpy oxidation level revealed through detailed spectroscopic, magnetic, and computational studies.[10] Interestingly, we have found that electron transfer to the bpy lowest unoccupied molecular orbital (LUMO) π* is dictated not only by the reducing ability of the Cr^{II} d^4 precursor but also by the geometry of the product.

As shown in Scheme 1, our synthesis employed Cr(tBu-acac)$_2$ (tBu-acac = 2,2,6,6-tetramethylheptane-3,5-dionate) because it is soluble in Et$_2$O or hydrocarbon solvents,[11] unlike the polymeric Cr(acac)$_2$.[12] The reaction of Cr(tBu-acac)$_2$ with bpy results in a rapid color change from light orange-brown to dark green. Isolated Cr(tBu-acac)$_2$(bpy) (**1**) has $\mu_{eff} = 2.74\ \mu_B$ in solution (Evans, C$_6$D$_6$), consistent with an electronic structure with $S = 1$. The UV−vis spectrum of **1** has multiple intense features between 700 and 400 nm, with ε values ranging from 2000 to 4500 M^{-1} cm^{-1}. The corresponding Cr(tBu-acac)$_2$(tBu-bpy) complex, **1a**, was also prepared by the same procedure using 4,4′-di-*tert*-butyl-2,2′-bipyridine (tBu-bpy). A related Cr(acac)$_2$(diimine) complex was reported by Wieghardt and co-workers.[13]

Scheme 1. Synthesis of a Neutral tBu-acac Complex 1



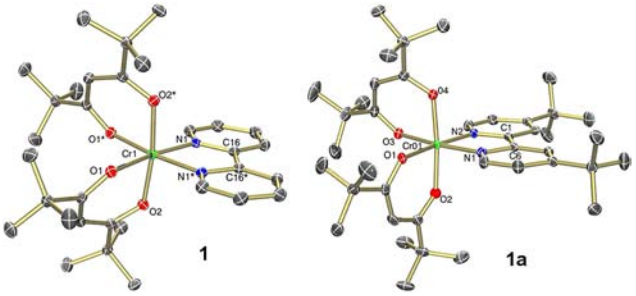


Figure 1. Thermal ellipsoid diagrams (50%) of **1** (left) and **1a** (right). All H atoms have been omitted for clarity.

Both **1** and **1a** have been characterized by single-crystal X-ray diffraction (Figure 1). In both structures, the Cr center displays a relatively undistorted geometry, with Cr−O bond lengths between 1.962 and 1.976 Å and Cr−N bond lengths of 2.0015(10) Å for **1** and 1.9883(14) and 1.9927(13) Å for **1a**. The interpyridine C−C distances of 1.427(2) Å for **1** and 1.419(2) Å for **1a** lie in the range exhibited for bpy ligands that have been reduced by a single electron.[10] In the absence of

Received: November 27, 2012
Published: February 18, 2013

dx.doi.org/10.1021/ic302590g | *Inorg. Chem.* 2013, 52, 2271−2273

detailed spectroscopic, magnetic, and computational studies, the precise electronic structures of **1** and **1a** cannot be definitively assigned. Nevertheless, the crystallographic data suggest that the bpy ligands in both **1** and **1a** can be considered as radical anions, with the observed $S = 1$ spin state being attributable to antiferromagnetic coupling between the ligand-based radical and the three unpaired electrons of the Cr^{III} center.

Single-electron oxidation of **1** with iodine followed by anion metathesis with NaBPh$_4$ gives the cationic complex [Cr(tBu-acac)$_2$(bpy)][BPh$_4$] (**2**). The UV−vis spectrum of **2** displays only a single band at 550 nm in EtOH with a greatly reduced extinction coefficient of 90 M^{-1} cm^{-1}, and its μ_{eff} = 3.88 μ_B in solution (Evans, C$_6$D$_6$) is consistent with a $S = {}^3/_2$ spin state. Complex **2** can also be independently synthesized via [Cr(tBu-acac)$_2$(H$_2$O)$_2$]$^+$ following the procedure of Kaizaki and co-workers.[14] The molecular structure of **2** was determined crystallographically (see the Supporting Information, SI). The coordination geometry at Cr remains octahedral, with the somewhat shorter Cr−O bond lengths between 1.925 and 1.948 Å being attributable to a change in the overall charge from neutral **1** to cationic **2**. Significantly, the Cr−N bond lengths of 2.0683(10) and 2.0664(11) Å in **2** are longer than those in **1**, and the C_{py}−C_{py} bond length has extended by over 0.05 Å to 1.4787(17) Å, consistent with oxidation of the bpy ligand from a radical anion to neutral.[10]

The similarity in the coordination geometry at Cr^{III} between neutral **1** and cationic **2** should facilitate outer-sphere single-electron-transfer reactions. Consistent with this expectation, cyclic voltammetry (CV) of cationic **2** in tetrahydrofuran (THF)/0.1 M [NBu$_4$][PF$_6$] shows a reversible reduction at −1.53 V versus [Cp$_2$Fe]$^{+/0}$. UV−vis spectroelectrochemistry demonstrates that the reduction of **2** results in the clean formation of **1**. A second reversible reduction at −2.63 V versus [Cp$_2$Fe]$^{+/0}$ may be due to a further reduction of **1** to anionic [Cr(tBu-acac)$_2$(bpy)]$^-$, although we have not yet been able to prepare this complex synthetically. Complex **1** also reacts rapidly with Ph$_3$CBr to give [Cr(tBu-acac)$_2$(bpy)]$^+$ and trityl radical,[15] as identified by UV−vis spectroscopy (see the SI).

The direct addition of bpy to chromocene at room temperature generates Cp$_2$Cr(bpy) (**3**). Unlike its highly reactive heavier group 6 congeners, chromocene typically only forms weak bonds with neutral donor ligands because of the relative stability of the $S = 1$ state for Cp$_2$Cr.[16] The stability of **3** can be attributed to single electron transfer from Cr^{II} to bpy to generate an inert chromium(III) complex antiferromagnetically coupled to a bpy radical anion while retaining the $S = 1$ state with μ_{eff} = 2.92 μ_B in solution (Evans, C$_6$D$_6$). As shown in Figure 2, complex **3** has an (η^5-Cp)(η^1-Cp)Cr(bpy) structure[17] with short C_{py}−C_{py} [1.425(2) Å] and Cr−N [1.9825(13) Å and 1.9684(12) Å] bond lengths consistent with the bpy ligand in the radical-anionic oxidation level.[10] The structure of **3** is similar to that of Cp*Cr(bpy)(CH$_2$Ph), an $S = 1$ complex prepared by Theopold and co-workers by bpy-induced alkyl radical loss from Cp*Cr^{III}(benzyl)$_2$ precursors.[18] Although Cp$_2$Cr typically requires elevated temperatures for protonolysis reactions with alcohols,[19] **3** reacts readily under ambient conditions with 2 equiv of (tBu-acac)H to generate **1**, as identified by UV−vis spectroscopy.

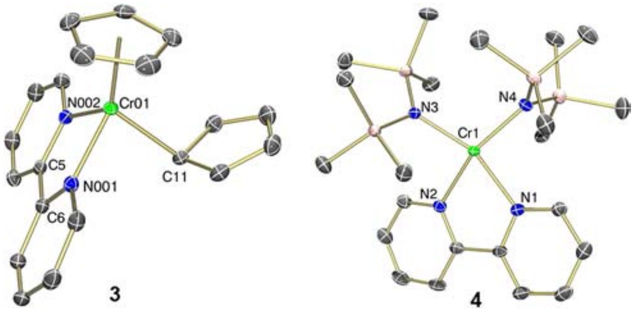
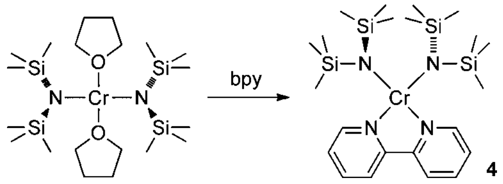


Figure 2. Thermal ellipsoid diagrams (50%) of **3** (left) and **4** (right). All H atoms have been omitted for clarity, and only one of the two independent molecules present in the unit cell is shown for **4**.

The reaction of Cr[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ with bpy results in the dark-purple complex Cr[N(SiMe$_3$)$_2$]$_2$(bpy) (**4**; Scheme 2), which has two intense absorbances at 509 and 372 nm in Et$_2$O, each with $\varepsilon \approx 1300$ M^{-1} cm^{-1}.[20] In contrast to the $S = 1$ spin state observed for **1**, **1a**, and **3**, complex **4** has μ_{eff} = 4.62 μ_B in solution (Evans, C$_6$D$_6$) consistent with an $S = 2$ spin state. As shown in Figure 2, **4** exhibits a distorted square-planar geometry in the solid state, with N_{py}−N_{py}−N_{Si}−N_{Si} dihedral angles of 20.0° and 20.7° for the two independent molecules of **4** in the unit cell. The relatively long C_{py}−C_{py} [1.481(3) Å and 1.485(3) Å] and Cr−N_{py} (between 2.14 and 2.16 Å) distances are consistent with a *neutral* bpy ligand.[10] Like **3**, the bis(amido)bipyridine complex **4** is also converted to **2** when treated with 2 equiv of (tBu-acac)H, as demonstrated by UV−vis spectroscopy and CV (see the SI).

Scheme 2. Synthesis of 4



For **4**, the absence of single electron transfer from Cr^{II} upon bpy coordination can be accounted for using concepts from ligand-field theory. Because of the steric bulk of the N(SiMe$_3$)$_2$ ligands, **4** is stable as a monomeric complex with a coordination number of 4. This allows the compound to adopt the electronically favorable (albeit sterically distorted) square-planar geometry shown in Figure 2 while retaining a high-spin Cr^{II} $S = 2$ spin state.[21] The same electronic structure is observed for Cr(Mes)$_2$(bpy), where Mes (mesityl) = 2,4,6-Me$_3$C$_6$H$_2$, which also has a slightly distorted square-planar geometry, an $S = 2$ spin state, and a neutral bpy ligand.[22] This is in contrast to *octahedral* complexes such as **1**, where electron transfer to the bpy LUMO π^* is energetically favorable compared to either the high-spin ($S = 2$, $t_{2g}{}^3e_g{}^1$) or low-spin ($S = 1$, $t_{2g}{}^4e_g{}^0$) electron configurations for Cr^{II}.[6−8,23] Although both **4** and Cr(Mes)$_2$(bpy) would be expected to have very electron-rich Cr^{II} centers, neither complex exhibits any structural evidence for bpy acting as a π-acceptor ligand.

New paramagnetic chromium bipyridine complexes have been prepared by the addition of the neutral ligand to well-defined monomeric chromium(II) precursors. For Cr(tBu-acac)$_2$ and Cp$_2$Cr, the $S = 1$ products **1** and **3** are best regarded not as low-spin Cr^{II} but as Cr^{III} antiferromagnetically coupled to an unpaired electron on the bpy ligand.[7,10] The geometry of the octahedral or three-legged-piano-stool products appears to play a significant role in electron transfer from Cr^{II} to bpy LUMO π^*, as the four-coordinate complex **4** remains $S = 2$, and displays the bond lengths expected for a neutral bpy ligand. The protonolysis reactions of **3**, **4**, and related complexes, as well as their outer-sphere reactivity with organic halides,[24] are currently under investigation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files, tables and text giving crystallographic data for **1**, **1a**, **2**, **3**, and **4**, complete experimental details, and UV−vis spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful to the Natural Sciences and Engineering Research Council of Canada (NSERC), the Canadian Foundation for Innovation, and the University of British Columbia for financial support. K.M.S. thanks Anita Lam for collecting X-ray diffraction data for complexes **1**, **1a**, **2**, and **4**.

■ DEDICATION

This paper is dedicated to Prof. Peter Legzdins on the occasion of his 70th birthday.

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