New entry to dimetal sandwich complexes, including a radical anion

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New entry to dimetal sandwich complexes, including a radical anion

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Nicholas S. Labrum,[a] Yaroslav Losovyj,[a] and Kenneth G. Caulton*[a]

Amide is displaced from $Cr[N(SiMe_3)_2]_2(THF)_2$ by equimolar [K(18-crown-6)][naphthalene] to form the dimetal sandwich $Cr_2(naphthalene)_2^-$ as a radical anion paired with $[K(18\text{-crown-}6)]^+$. Two Cr in the sandwich do not form any multiple Cr/Cr bond, and instead each interacts with one naphthalene in an η^6 fashion and with the second naphthalene in an η^4 connectivity. The naphthalene C/C distances show the effect of back donation from two chromium to a greater extent than simply by 1 electron ring reduction, by comparison to the naphthalene radical anion. The SOMO of the product was established by variable temperature EPR spectroscopy, and atom ratios and elemental purity, were supported by XPS. The possible generality of the displacement of $N(SiMe_3)_2^-$ from low valent metal is discussed.

The multiple rings in polycyclic aromatic hydrocarbons (PAH) *appear* to have the potential to bind *several* metals, and on the same side of the PAH.[1] Binding a second PAH to those same two metals, to make a sandwich, is a challenge[1b, 2] since often the low valent metal source carries its own ligands (very often CO or PR_3), which are retained; “leaving groups” are rarely available in such syntheses. The solution to this is to use elemental metal as the source, which was the motivation behind metal atom vaporization chemistry,[3] as well as the matrix isolation method.[4] Alternative synthetic approaches were authoritatively reviewed[5] where it was shown that Li and Na naphthalenides react with $MCl_3(THF)_3$ to give $M(C_{10}H_8)_2$, where M = V, Cr, and Mo. These species are very different from the new product reported here, showing perhaps the difference with potassium as cation.

We report here on a discovery which can be evaluated to illustrate a potentially useful addition to the available synthetic methods. It begins with reaction of an already somewhat low valent metal source, $Cr[N(SiMe_3)_2]_2(THF)_2$, together with a reductant chosen to be soluble and readily weighed, hence amenable to more accurate control of stoichiometry: [K(18-crown-6)][$C_{10}H_8$].[6] While this reagent was intended to deliver reducing equivalents, the naphthalene *electron carrier* is found to play an active role in product identity, and its scarcity here helps control the production of a dimetal sandwich, rather than simply form monometal $M(naphthalene)_2$.

Reaction of $Cr[N(SiMe_3)_2]_2(THF)_2$ with equimolar [K(18-crown-6)][$C_{10}H_8$] in THF at room temperature proceeded in time of mixing with color change from violet to dark red. This isolated product shows no ^1H NMR signal (other than crown ether singlet), consistent with ring protons in radical species relaxing very fast. Needle shaped crystals suitable for an X-ray diffraction study were grown by pentane diffusion into a concentrated THF solution of the crude reaction mixture at room temperature over 24 hours. The solid state structure was revealed as a 1D polymer of the repeating unit, [K(18-crown-6)][$Cr_2(C_{10}H_8)_2$], Figure 1, which crystallized in space group $P\overline{1}$ with rigorous crystallographic centers of symmetry located on both K2 and the Cr3/Cr3’ vector. There are 1.5 formula units in the asymmetric unit. The homoleptic bis(naphthalene) dichromium sandwich complex displays both η^4/η^6 coordination of naphthalene to chromium atoms. The C_6 ring centroid to centroid distances are 2.500, 2.497, and 2.499 Å, respectively. Given the Cr1-Cr2 and Cr3-Cr3’ distances (2.8704(4) and 2.8757(6) Å) are greater than centroid to centroid distances, no multiple Cr/Cr bond exists here. The anionic [$Cr_2(C_{10}H_8)_2$] moiety is compensated by [K(18-crown-6)] cation with K1-C2 and K1-C3 distances ranging from 3.186 to 3.374 Å; every K binds to two carbons of two different naphthalenes, as well as to one crown to create a polymeric connectivity (Fig. 1). The naphthalene rings are all “stepped,” such that the carbons of the η^4 fragment are 0.161 - 0.290 Å from the η^6 plane, towards Cr, strengthening the butadiene/Cr binding.

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[a] Department of Chemistry, Indiana University, Bloomington IN.
E-mail: caulton@indiana.edu

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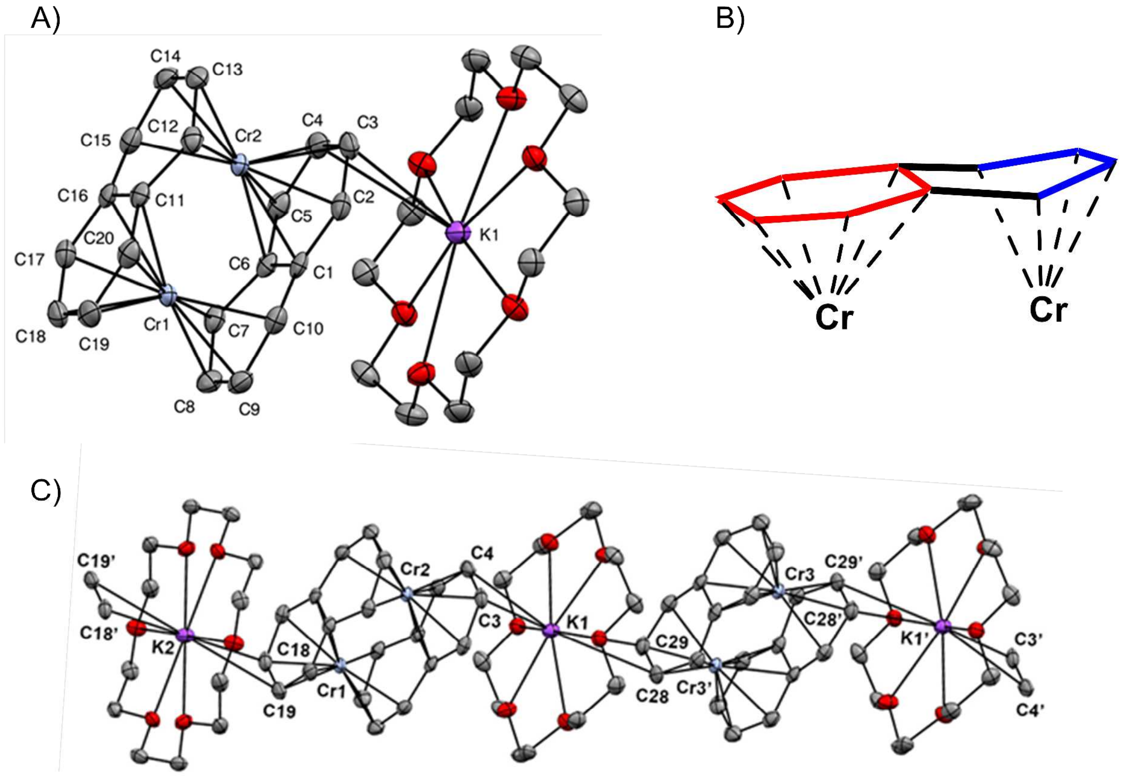

Figure 1. A) Mercury diagram of the nonhydrogen atoms of one repeat unit [K(18-crown-6)][$Cr_2(C_{10}H_8)_2$] with thermal ellipsoids shown at 50% probability. Carbon and oxygen atoms (unlabeled) are shown in grey and red, respectively. Selected structural parameters (Å): Cr1-C18: 2.1030(19); Cr1-C19: 2.1032(18); Cr2-C3: 2.0997(19); Cr2-C4: 2.1002(18); Cr3-C28: 2.1407(19); Cr3-C29: 2.1464(18); K1-C3: 3.186; K1-C4: 3.156; K2-C18: 3.272; K2-C19: 3.267; K3-C28: 3.350; K3-C29: 3.374. **B)** Line drawing of ring "stepping" resulting from η^6 and η^4 coordination modes. **C)** Chain polymer is also illustrated.

To confirm the presence of chromium, a crystalline sample was also interrogated using X-ray photoelectron spectroscopy, sampling the face of a single crystal (see ESI). This revealed the presence of K, Cr, O and C, with negligible Cl, N and Si.

To further characterize this compound, its EPR spectrum was recorded at 298 K in THF and revealed (Fig. 2) a strong signal, characteristic of an S equal 1/2 species and with a g value of 1.987. With a linewidth of 49 G, no hyperfine coupling was resolved. Overall this contributes to the conclusion that the spin is strongly localized in the aromatic pi system, but the g value deviation from 2.00 suggests some small metal contribution. The EPR spectrum of a species assigned as the mono-metal ion $[Cr(C_{10}H_8)_2]^-$ shows a g value of 1.995.[7]

The EPR spectrum recorded at 77K (ESI, Figure S2) can be simulated with three g values, showing anisotropy too large for a purely organic radical. The resolution of one g value from the other two is enough to show that there is significant participation by the metal orbitals in the SOMO. The similarity of two of the g values indicates approximate axial symmetry and, thus, the second metal does not significantly perturb the otherwise axial symmetry of the two rings around a given chromium. This supports the conclusion that there is no strong Cr-Cr interaction.

The sandwich Cr_2(naphthalene)$_2$ is unknown, and there are no M_2(naphthalene)$_2$ sandwiches of any metal; in general, metals prefer being "anti," on opposite sides of different rings of a single polycyclic aromatic.[2a] Searching more generally for M_2(polycyclic aromatic hydrocarbons)$_2$, M_2(pentalenes)$_2$ are known for M = Ti, V,Cr, Mn, Fe, Mo, Rh and Pd.[8] Finally single metal Cr(PAH)$_2$ have demonstrated redox chemistry.[2b, c, 9] See Electronic Supporting Information for an analysis of the pattern of naphthalene C/C bond length *changes* as a consequence of back donation and the additional one electron reduction in $[Cr_2(\text{naphthalene})_2]^-$.

The 1:2 K:Cr product stoichiometry indicates that, compared to the 1:1 stoichiometry employed, some K has been lost, but 2 amides per Cr are also missing. A possible fate of those would be to form $Cr[N(SiMe_3)_2]_3^-$. This could be explained by either eq. 1 or 2, with the latter being closer to the K:Cr stoichiometry employed here.

In the hypothesis of eq. 2, all reduction comes from [K(18-crown-6)][$C_{10}H_8$], and two-thirds of the chromium serves as

$$5\,K[C_{10}H_8] + 2\,Cr[N(SiMe_3)_2]_2 \longrightarrow KCr_2(C_{10}H_8)_2 + 4\,K[N(SiMe_3)_2] + 3\,C_{10}H_8 \quad (1)$$

$$5\,K[C_{10}H_8] + 6\,Cr[N(SiMe_3)_2]_2 \longrightarrow KCr_2(C_{10}H_8)_2 + 4\,KCr[N(SiMe_3)_2]_3 + 3\,C_{10}H_8 \quad (2)$$

Lewis acid, not being reduced. $Cr[N(SiMe_3)_2]_2$ is established[10] to accept a third amide, yielding unreduced chromium in $NaCr[N(SiMe_3)_2]_3$. In addition, several $K(crown)Cr[N(SiMe_3)_2]_2$ complexes containing Cr(I) are demonstrated[11] to be linear two-coordinate monomers. The ^1H NMR chemical shifts of these amides are consistently about +28 ppm, regardless of the cation crown or crypt present. Indeed, ^1H NMR spectra (see ESI, Figure S1) of the $Cr[N(SiMe_3)_2]_2(THF)_2$:[K(18-crown-6)][$C_{10}H_8$] reaction solution using 1:1 stoichiometry in $THFd_8$ shows $SiMe_3$ signals with a chemical shift of 28.2 ppm, consistent with a paramagnetic chromium product, and inconsistent with purely $K[N(SiMe_3)_2]$.

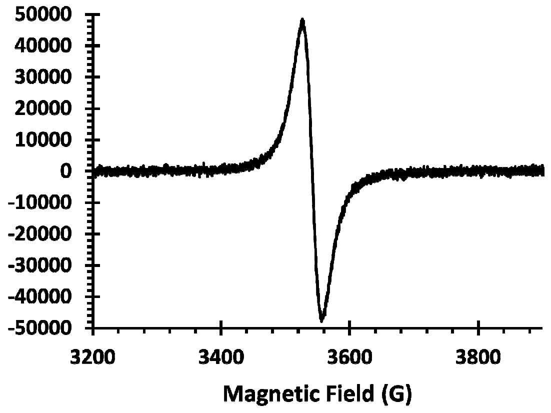

Figure 2. EPR spectrum of a 3.75 mM of [K(18-crown-6)][$Cr_2(C_{10}H_8)_2$] in THF at 298 K (modulation amplitude = 2 G); g_{iso} = 1.987.

Thus, the *bis*-silylamide serves as a cooperative *leaving group* in this chemistry and provides Cr in a conveniently reactive form. While reductive displacement of amide is a rare reaction, there is precedent for something similar: potassium reacts[12] with the already electron-excessive 19 valence electron Cp_2Co in the presence of ethylene to form $CpCo(C_2H_4)_2$ (85% yield), and KCp. This method was subsequently applied[13] with complete removal of both Cp^- ligands from Cp_2Fe with Li metal, ethylene, and TMEDA base to produce $[Li(TMEDA)]_2Fe(C_2H_4)_4$.

Similar discoveries have been reported[14] in a very different context: lanthanides $Ln[N(SiMe_3)_2]_3$ react with alkali metal M to form $N_2[Ln[N(SiMe_3)_2]_2(THF)]_2$, with co-product $K[N(SiMe_3)_2]$ trapped by additional reagent, forming $MLn[N(SiMe_3)_2]_4$. While those results have been interpreted primarily in terms of lanthanide size, it could be equally well viewed as showing that the silylamide is a cooperative leaving group when a suitable replacement ligand, here N_2, is available for the reduced metal. The emerging general principle of alleviating excess charge build-up by expelling anionic amide by neutral N_2, or polycyclic aromatic hydrocarbon or even ethylene appears promising.

The need to scavenge silylamide requires reagent $M[NR_2]_n$ to be sterically able to add more silylamide, so success with this synthetic approach may favor lower valent metal amides. Alternatively, the leaving group ability of the amide can be tuned by employing the still bulkier amides introduced in more recent times. [15]

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Conflicts of interest

There are no conflicts to declare

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Graphical abstract:

A new approach to the synthesis of low valent metal sandwich complexes showing the unanticipated ease with which silylamides can function as leaving groups resulting a 1D polymer of the repeating unit, [K(18-crown-6)][$Cr_2(C_{10}H_8)_2$].