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[17] In several works including our previous communication[11] the gap was determined from the very onset of absorption (see R. D. McCullough, R. D. Lowe, M. Jayaraman, D. L. Anderson, *J. Org. Chem.* **1993**, *58*, 904; T. A. Chen, R. Rieke, *Synth. Met.* **1993**, *60*, 175). Since this procedure leads to rather large uncertainties, extrapolation of the absorption edge to zero was used here, although this procedure leads to larger values.

Deprotonated 2,3:5,6-Dibenzo-7-aza bicyclo[2.2.1]hepta-2,5-diene as a Nitrido Nitrogen Source by Anthracene Elimination: Synthesis of an Iodide(nitride)chromium(VI) Complex**

Daniel J. Mindiola and Christopher C. Cummins*

Nitrides constitute an important class of compounds in both solid-state [1, 2] and solution chemistries.[3] A common synthon for the six valence electron N^- ion, which is isoelectronic to an oxygen atom, is the ubiquitous azide ion.[3] Typifying the formation of a nitride from an azide is the classic synthesis of $[Mo(N)(Cl)_3(bpy)]$.[4] Generation of the nitrido functionality from an azide requires a source of two electrons. Therefore, successful syntheses are typically encountered when a d^n ($n \geq 2$) metal center is employed, and the nitride product has a d^{n-2} configuration. Oxidation of the metal center occurs concomitant with dinitrogen expulsion. However, azide is not always optimal for nitride introduction due to a) the explosive nature of many of its compounds, b) the low solubility in nonpolar solvents of salts such as sodium azide, or c) the lack of steric protection which can lead to multiple or unselective substitutions.

In connection with recent investigations of chromium(VI) organometallic chemistry [5, 6] we required the iodide–nitride complex $[Cr(I)(N)(NRAr_F)_2]$ ($R = C(CD_3)_2CH_3$, $Ar_F = 2,5\text{-}C_6H_3FMe$). Attempts to synthesize the compound from the corresponding azide were unsuccessful. Although the corresponding nitrosyl derivative $[Cr(I)(NO)\text{-}(NRAr_F)_2]$ has been prepared,[7] attempts to deoxygenate it with vanadium(III) [5] have been unsuccessful, a circumstance attributable to the presence of a reactive iodide functionality. Here we describe the successful synthesis of $[Cr(I)(N)(NRAr_F)_2]$ by the reaction of $d^2\text{-}[Cr(I)_2(NRAr_F)_2]$ with $[Li(dbabh)(OEt_2)]$, where Hdbabh is 2,3:5,6-dibenzo-7-azabicyclo[2.2.1]hepta-2,5-diene).[8] This chemistry shows that Hdbabh can be considered an organic analogue of hydrazoic acid in the context of transition metal nitride chemistry.

The amine Hdbabh was prepared by the literature method,[8] and treated with *n*-butyllithium to form $[Li(dbabh)(OEt_2)]$. The chromium(IV) precursor $[Cr(I)_2(NRAr_F)_2]$ was obtained in 82% yield as a black solid following treatment of $[Cr(NRAr_F)_3]$ [5] with iodine. Treatment of $[Cr(I)_2(NRAr_F)_2]$ with of $[Li(dbabh)(OEt_2)]$ in ether elicited a color change to redbrown and ultimately produced diamagnetic [Cr(I)(N)-

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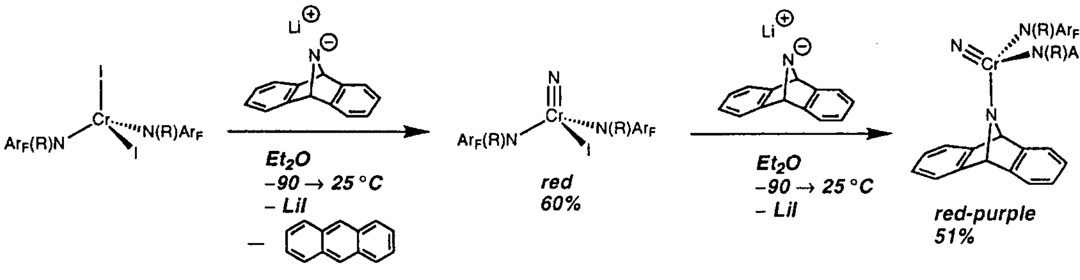


Scheme 1. R = $C(CD_3)_2CH_3$, Ar_F = 2,5-C_6H_3FMe.

$(NRAr_F)_2$] along with anthracene in essentially quantitative yields, according to ^{1}H NMR spectra of crude reaction mixtures (Scheme 1). Following removal of anthracene, [Cr(I)(N)$(NRAr_F)_2$] was isolated in about 60% yield. A ^{2}H NMR signal at $\delta = 14.8$ ($\Delta\nu_{1/2} = 28$ Hz) attributable to the presumed intermediate chromium(IV) compound [Cr(dbabh)(I)$(NRAr_F)_2$] was observed to grow in and decay during the reaction of [Cr$(I)_2(NRAr_F)_2$] with [Li(dbabh)(OEt_2)].

[Cr(I)(N)$(NRAr_F)_2$] was characterized by elemental analysis, and by ^{1}H, ^{2}H, ^{19}F, ^{13}C NMR, and UV/Vis spectroscopies. X-ray crystallography also confirmed the formulation of [Cr(I)(N)$(NRAr_F)_2$] as a terminal nitride complex; the Cr–N bond length is 1.541(5) Å (Figure 1). The structure of [Cr(I)(N)$(NRAr_F)_2$] is characterized by coparallel stacking of the 2,5-C_6H_3FMe residues. The amido lone pairs are oriented perpendicular to the chromium nitrido functionality, which in turn is protected by the proximal *tert*-butyl groups. Such a conformation was seen previously for [V(I)$(N_3Mes)(NRAr_F)_2$];[9] in the present case a pseudo mirror plane renders the complex pseudo-C_s-symmetric and relates two parallel, π-stacked aryl rings.

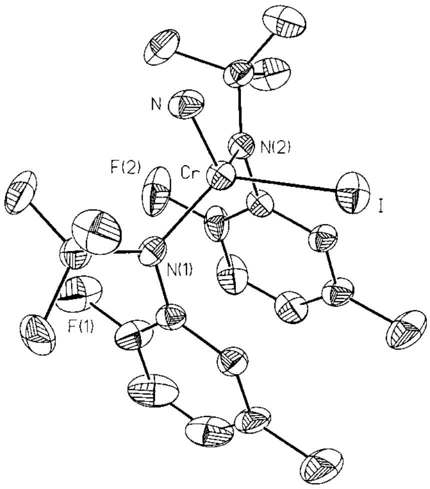


Figure 1. Structure of [Cr(I)(N)$(NRAr_F)_2$] with thermal ellipsoids at the 35% probability level. Selected bond lengths [Å]: Cr–N 1.541(5), Cr–N(1) 1.823(5), Cr–N(2) 1.835(5), Cr–I 2.5995(11).

Owing to the stability of [Li(dbabh)(OEt_2)] at 25 °C, it was presaged that a d^0 complex of dbabh would be resistant to anthracene elimination. Accordingly, treatment of the precursor [Cr$(I)_2(NRAr_F)_2$] with two equivalents of [Li(dbabh)(OEt_2)] led to formation of one equivalent of anthracene along with the new nitrido complex [Cr(N)(dbabh)$(NRAr_F)_2$] (Scheme 1). The yield of isolated dark red [Cr(N)(dbabh)$(NRAr_F)_2$] subsequent to separation from antracene was 51%. [Cr(N)(dbabh)$(NRAr_F)_2$] was characterized by X-ray crystallography in addition to elemental analysis and a battery of spectroscopies. The Cr–$N_{nitrido}$ bond length is 1.536(3) Å, and the appreciable steric crowding in the molecule is evident upon inspection of Figure 2. An interesting aspect of the structure of [Cr(N)(dbabh)$(NRAr_F)_2$] is the near planarity at the nitrogen atom in the complexed dbabh ligand; planarity at this nitrogen atom is disfavored by virtue of strain.[8] In addition, the Cr–N_{dbabh} bond length of 1.814(3) Å compares well with the distances between chromium and the $NRAr_F$ nitrogen atoms. (1.856(3) and 1.863(3) Å). Extended Hückel calculations[10] performed on [Cr(N)(dbabh)-$(NRAr_F)_2$] indicate dbabh to be similar to $NRAr_F$ in terms of π-donor ability, inasmuch as the three amide lone pairs all contribute substantially to the HOMO. In fact, examination of the Cr–N overlap populations (o.p.) indicates the dbabh nitrogen atom to interact with the chromium atom more strongly (o.p. 0.74) than the two $NRAr_F$ nitrogen atoms (o.p. 0.65, 0.66); the Cr–$N_{nitrido}$ o.p. is 1.18. Two isomers of [Cr(N)(dbabh)$(NRAr_F)_2$] are observed by solution ^{19}F and ^{1}H NMR spectroscopies. The major isomer exhibits inequivalent $NRAr_F$ ligands, which is consistent with the solid-state structure (Figure 2). The observed quivalence of the $NRAr_F$

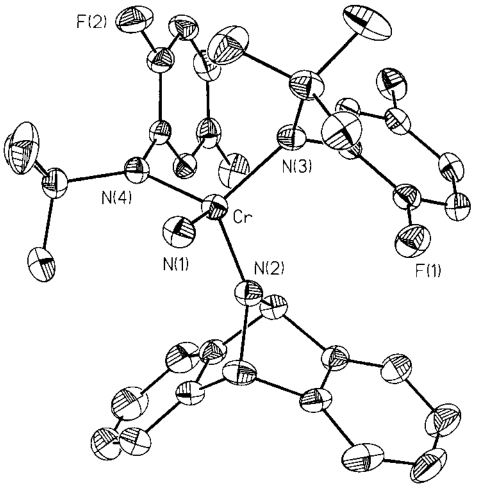


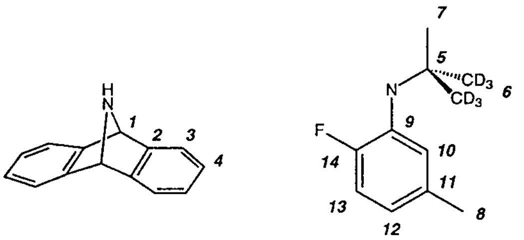
Figure 2. Structure of [Cr(N)(dbabh)$(NRAr_F)_2$] with thermal ellipsoids at the 35% probability level. Selected bond lengths [Å]: Cr–N(1) 1.536(3), Cr–N(2) 1.814(3), Cr–N(3) 1.863(3), Cr–N(4) 1.856(3).

ligands for the minor isomer is indicative of a pseudo mirror symmetry, as observed for $[Cr(I)(N)(NRAr_F)_2]$.

In summary, the anion derived from deprotonation of Hdbabh has been demonstrated to serve as an organic analogue of azide ion in the context of nitride chemistry. Further applications of this approach to other molecular and solid-state nitrides will be described in due course.

Experimental Section

All manipulations were carried out under an atmosphere of purified nitrogen using standard glovebox or Schlenk techniques, unless stated otherwise. All solvents were dried and deoxygenated prior to use. NMR assignments are with reference to the numbering shown in Scheme 2.



Scheme 2. Numbering for the assignments for the NMR signals.

Lithiation of Hdbabh: To a thawing solution of Hdbabh[8] (5.88 g, 30.42 mmol) in ether (90 mL) was added *n*-butyllithium (32.0 mmol, 20 mL of a 1.6 M) drowpise with a pipet. On warming to room temperature the lithium amide (light salmonpink in color) began to precipitate. After partial removal of solvent the colorless solid was collected by filtration, washed with cold pentane, and dried (6.24 g, 22.8 mmol, 75.1%). Integration of the compound's ^1H NMR spectrum indicated one molecule of ether per lithium atom. ^1H NMR ($[D_8]THF$): $\delta = 4.99(1), 6.46-6.87\ (3, 4)$; ^{13}C NMR ($[D_8]THF$): $\delta = 71.24(1), 158.22(2), 115.81, 120.00\ (3, 4)$.

$[Cr(I)_2(NRAr_F)_2]$: To a solution of $[Cr(NRAr_F)_3]$[5] (1.1805 g, 1.97 mmol) in benzene (30 mL) was added dropwise iodine (0.505 g, 1.99 mmol) as a solution in benzene (10 mL). ^2H NMR spectroscopic monitoring indicated complete consumption of $[Cr(NRAr_F)_3]$ after 2 h at 28 °C. Subsequent to removal of benzene, $[Cr(I)_2(NRAr_F)_2]$ was obtained as black needles (1.096 g, 82%) by recrystallization (ether, – 35 °C); m.p. 146–147 °C. ^2H NMR (C_6D_6): $\delta = 16.6$ ($\delta\nu_{1/2}$, 14.5 Hz); magnetic susceptibility (benzene, 25 °C): 2.83 μ_B; EI-MS: $m/z = 678$ (M^+); elemental analysis calcd for $C_{22}H_{18}D_{12}CrF_2I_2N_2$: C 43.00, H 5.41, N 4.18; found: C 42.55, H 5.25, N 4.01.

$[Cr(I)(N)(NRAr_F)_2]$: To a thawing solution of $[Cr(I)_2(NRAr_F)_2]$ (1.002 g, 1.477 mmol) in ether (75 mL) was added dropwise a cold solution of $[Li(dbabh)(OEt_2)]$ (0.388 g, 1.420 mmol) in ether (15 mL). The mixture was stirred and allowed to warm to 25 °C. The mixture was stirred for 16 h, during which time the color changed from brown-black to red-brown. Subsequent to removal of solvent in vacuo the residue was extracted with pentane, and the extract was filtered through celite. Solvent was removed from the extract in vacuo. The residue was extracted with THF and the extract was filtered through activated charcoal to remove anthracene. Removal of and lyophilization from benzene afforded a red-brown powder (0.505 g, 0.894 mmol, 60.54%). Recrystallization from CH_3CN gave red crystals (0.301 g, 0.532 mmol, 36%); m.p. 188–190 °C. ^1H NMR (C_6D_6): $\delta = 7.504(10), 6.314 - 6.222(12,13), 1.873(8), 1.721(7)$. ^{13}C NMR (C_6D_6): $\delta = 19.96(8), 33.14(6), 33.88(7), 72.03(5), 116.5, 130.5, 132.9, 134.1, 148.7\ (9-13), 150.7(14)$; ^{19}F NMR (C_6D_6): $\delta = -113.7$ (major), -109.7, -115.1 (minor); UV/Vis (CH_3CN): 365 nm (ε 1951), 283 nm (ε 2699); elemental analysis calcd for $C_{22}H_{18}D_{12}CrF_2IN_3$: C 46.73, H 4.95, N 7.43; found: C 46.73, H 5.35, N 7.23.

X-ray structure analysis: Crystals were grown from at – 30 °C. A red plate of approximate dimensions 0.79 × 0.35 × 0.09 mm was selected. Data collection was carried out on a Siemens platform goniometer equipped with a CCD detector. The structure was solved by direct methods in conjunction with difference Fourier techniques. All non-hydrogen atoms were refined anisotropically.[11] Crystal and refinement data: $C_{22}H_{30}CrF_2IN_3$, space group $P2_1/n$, $\alpha = 9.269(2)$, $b = 28.634(8)$, $c = 9.443(2)$ Å, $\alpha = 90$, $\beta = 97.09(3)$, $\gamma = 90°$, $Z = 4$, $V = 2487.2(11)$ Å^3, $\varrho_{cacld} = 1.478\ g\,cm^{-3}$, $T = 183(2)$ K, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $\mu(MO_{K\alpha}) = 1.728\ mm^{-1}$, $F(000) = 1112$, total reflections = 9945, independent reflections = 3578, data/parameter ratio = 3574/263, $R_1 = 0.0474$, $wR_2 = 0.0980$, GOF = 1.062, residuals based on $I > 2\sigma(I)$.

$[Cr(N)(dbabh)(NRAr_F)_2]$: To a thawing solution of $[Cr(I)_2(NRAr_F)_2]$ (0.200 g, 0.295 mmol) in ether (20 mL) was added dropwise a cold solution of $[Li(dbabh)(OEt_2)]$ (0.164 g, 0.600 mmol) in ether (15 mL). After the mixture was warmed to 25 °C and stirred for 12 h, solvent was removed in vacuo. The residue was extracted with pentane, the extract was filtered through celite, and the solvent was removed in vacuo from the extract. The residue was dissolved in THF, and the solution filtered through activated charcoal and concentrated in vacuo. Recrystallization from CH_3CN gave $[Cr(N)(dbabh)(NRAr_F)_2]$ as a beet-red solid (0.094 g, 0.149 mmol, 51%); m.p. 170 °C (decomp.). ^1H NMR (C_6D_6): $\delta = 1.48-1.57\ (7, 8), 1.98-2.09\ (7, 8), 5.70-5.86\ (1), 6.51-7.00\ (3, 4, 9-14)$; ^{13}C NMR (C_6D_6): $\delta = 21.0, 32.91(6, 7), 64-66(1), 81.13(5), 116.5, 121.9, 126.2, 133.1, (9-13, 3, 4)\ 140.7, 150.0\,14)$; ^{19}F NMR (C_6D_6): $\delta = -110.5, 117.7$ (major), -113.5 (minor); UV/Vis (CH_3CN): 249 nm (ε 15, 146), 353 nm (ε 9709), 505 nm (ε 8932); elemental analysis calcd for $C_{36}H_{28}D_{12}CrF_2N_4$: C 68.55, H 6.39, N 8.88; found: C 68.55, H 6.08, N 7.85.

X-ray structure of $[Cr(N)(dbabh)(NRAr_F)_2] \cdot 0.5\,MeCN$: Crystals were gronw from CH_3CN at – 30 °C. A red plate of approximate dimensions 0.70 × 0.41 × 0.22 mm was selected. Data collection was carried out on a Siemens platform goniometer equipped with a CCD detector. The structure was solved by direct methods in conjunction with difference Fourier techniques. All non-hydrogen atoms were refined anisotropically.[11] Crystal and refinement data: $C_{37}H_{40}CrF_2N_{4.5}$, space group $P\bar{1}$, $a = 9.5207(3)$, $b = 11.0757(3)$, $c = 17.9577(5)$ Å, $\alpha = 83.3100(10)$, $\beta = 89.8710(10)$, $\gamma = 71.4340(10)°$, $Z = 2$, $V = 1781.62(9)$ Å^3, $\delta = {}_{calcd} = 1.189\ g\,cm^{-3}$, 188(2) K, $Mo_{K\alpha}$ radiation, ($\lambda = 0.71073$ Å), $\mu(Mo_{K\alpha}) = 0.362\ mm^{-1}$, $F(000) = 671$, total reflections = 7324, independent reflections = 5002, data/parameter ratio = 4992/405, $R_1 = 0.0611$, $w\mathrm{R}_2 = 0.1757$, GOF = 1.084, residuals based on $I > 2\sigma(I)$.

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