

## Dinitrogen Activation, Partial Reduction, and Formation of Coordinated Imide Promoted by a Chromium Diiminepyridine Complex

Indu Vidyaratne,<sup>†</sup> Jennifer Scott,<sup>†</sup> Sandro Gambarotta,<sup>\*†</sup> and Peter H. M. Budzelaar<sup>\*‡</sup>*Department of Chemistry, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada, and Department of Chemistry, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada*

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Reduction of  $\{2,6\text{-}[2,6\text{-}(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)_2(\text{C}_5\text{H}_3\text{N})]\text{CrCl} \text{ (3)}$  with NaH afforded the dinuclear dinitrogen complex  $\{[2,6\text{-}[2,6\text{-}(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)_2(\text{C}_5\text{H}_3\text{N})]\text{Cr}(\text{THF})_2(\mu\text{-N}_2)]\cdot\text{THF} \text{ (5)}$ . Reaction carried in exclusion of dinitrogen afforded instead deprotonation of the ligand with the formation of  $\{2\text{-}[2,6\text{-}(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)]\text{-6-[2,6-(}i\text{-Pr)}_2\text{PhNC}=\text{CH}_2](\text{C}_5\text{H}_3\text{N})\}\text{Cr}(\text{THF}) \text{ (4)}$ . Further reduction of **5** with NaH yielded a curious dinuclear compound formulated as  $[\{2,6\text{-}[2,6\text{-}(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)_2(\text{C}_5\text{H}_3\text{N})]\text{Cr}(\text{THF})][\{2\text{-}[2,6\text{-}(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)]\text{-6-[2,6-(}i\text{-Pr)}_2\text{PhNC}=\text{CH}_2](\text{C}_5\text{H}_3\text{N})\}\text{Cr}(\text{THF})](\mu\text{-N}_2\text{H})(\mu\text{-Na})_2 \text{ (6)}$  containing two sodium atoms only bound to the dinitrogen unit and the  $\pi$  systems of the two diiminepyridine ligands. Subsequent reduction with NaH triggered a complex series of events, leading to the formation of a species formulated as  $\{2\text{-}[2,6\text{-}(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)]\text{-6-[2,6-(}i\text{-Pr)}_2\text{PhNC}=\text{CH}_2](\text{C}_5\text{H}_3\text{N})\}\text{Cr}(\mu\text{-NH})[\text{Na}(\text{THF})] \text{ (7)}$  on the basis of crystallographic, spectroscopic, isotopic labeling, and chemical degradation experiments.

## Introduction

The continuing saga of dinitrogen activation<sup>1</sup> has steadily developed since the initial discovery of the ability of transition metals to form dinitrogen complexes. As a result of considerable research, the immobilized dinitrogen unit may be guided toward a few diversified stoichiometric transformations.<sup>2</sup> It is only in the past few years, however, that tremendous advances have been made toward understanding the elementary steps by which this exceedingly stable molecule is reduced, cleaved, and protonated.<sup>3</sup> The ingenious design of a catalytic cycle capable of producing ammonia from dinitrogen under very mild conditions<sup>3a,b</sup> can certainly be regarded as the most recent culmination of this chemistry.

Similar to the behavior of the biologically occurring nitrogenase enzyme,<sup>4</sup> the key to the success of the molybdenum-based catalytic cycle relies on the possibility of separating the source of electrons and the source of protons through the judicious use of appropriate reagents. Another possible strategy, suggested by recent results in actinide chemistry,<sup>3d</sup> is to enhance the radical activity of the reduced dinitrogen moiety bound to the metal center, thereby encouraging hydrogen atom extraction from the solvent.

Today, dinitrogen activation is documented with almost all of the metals, but it is trivalent molybdenum<sup>1e,3a,b,5</sup> and tantalum<sup>6</sup> and divalent samarium<sup>7</sup> that provide the largest variety of reduced species. In sharp contrast to the unique versatility of molybdenum, chromium appears to be one of the most reluctant elements to interact with dinitrogen. The only chromium–dinitrogen complexes reported so far are,

\* To whom correspondence should be addressed. E-mail: sgambaro@science.uottawa.ca (S.G.), budzelaar@cc.umanitoba.ca (P.H.M.B.).

<sup>†</sup> University of Ottawa.

<sup>‡</sup> University of Manitoba.

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in fact, less than a handful of Chatt-type zerovalent derivatives containing phosphine<sup>8</sup> or arene ligands.<sup>9</sup> We recently reported the synthesis and characterization of several low-valent chromium complexes of the diiminepyridine ligand.<sup>13h</sup> In the present work, we describe how further reduction of these complexes in the presence of nitrogen leads to a dinitrogen complex and subsequent cleavage of the N–N bond.

The use of the diiminepyridine ligand system for this work was a key to these results. This particular ligand has attracted the attention of researchers for its ability to sustain an exceptional level of activity as an ethylene polymerization catalyst with late transition metals.<sup>10,10</sup> The ability of this ligand to be directly involved in the organometallic chemistry of the metal center has provided mechanistic insight into the variety of processes and transformations accompanying the polymerization.<sup>11,11</sup> Among the several features, there is the possibility of accommodating up to three electrons in the delocalized  $\pi$  system.<sup>12,12</sup> This, in turn, has allowed the formation of complexes that deceptively appear as low-valent but that are, in fact, comprised of a higher-valent metal

coupled to a radical mono- or dianion.<sup>11h,i,13</sup> The electrons stored in the ligand-centered electron reservoir are still available for further chemistry, as is clearly shown by the recurrent dinitrogen activation by these systems.<sup>13d,e</sup> This led us to investigate the possibility of going one step further by adding enough electrons to *cleave* the dinitrogen N–N bond. The use of chromium for this purpose was particularly challenging given its low tendency to form mono- or zerovalent species unless in the presence of highly stabilizing ligands such as cyclopentadienyl anions, carbon monoxide, or phosphines. Thus, chromium complexes of the diiminepyridine ligand<sup>13h</sup> were good candidates for the formation of these “pseudoreduced” complexes, in which the metal actually rests in a higher, stable oxidation state and the electrons for reduction are available in the ligand.

## Experimental Section

All preparations were performed under an inert atmosphere by using standard Schlenk techniques and a nitrogen-atmosphere glovebox.  $\text{CrCl}_2(\text{THF})_2$  was prepared following the standard procedure, and  $\{2,6\text{-}[\text{2,6-}(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)_2(\text{C}_5\text{H}_3\text{N})]\text{CrCl}_3$  (**1**),<sup>11c</sup>  $\{2,6\text{-}[\text{2,6-}(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)_2(\text{C}_5\text{H}_3\text{N})]\text{CrCl}_2$  (**2**),<sup>13h</sup> and  $\{2,6\text{-}[\text{2,6-}(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)_2(\text{C}_5\text{H}_3\text{N})]\text{CrCl}$  (**3**)<sup>13h</sup> were prepared according to published procedures. IR spectra were recorded on Mattson 9000 and Nicolet 750-Magna FT-IR instruments from Nujol mulls prepared in a drybox. Samples for magnetic susceptibility measurements were weighed inside a drybox equipped with an analytical balance and sealed into calibrated tubes. Magnetic measurements were carried out with a Gouy balance (Johnson Matthey) at room temperature and calculated following standard methods and applying corrections for underlying diamagnetism to the data. Elemental analyses were carried out with a Perkin-Elmer 2400 CHN analyzer. Data for X-ray crystal structure determinations were obtained with a Bruker diffractometer equipped with a SMART CCD area detector. NMR spectra were recorded with a Varian AMX-500 spectrometer.

**Preparation of  $\{2\text{-}[\text{2,6-}(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)]\text{-6-}[\text{2,6-}(i\text{-Pr})_2\text{PhNC}=\text{CH}_2](\text{C}_5\text{H}_3\text{N})\}\text{Cr}(\text{THF})$  (**4**).** A solution of **3** (1.138 g, 2.0 mmol) in THF (100 mL) was treated with a suspension of NaH (0.053 g, 2.2 mmol) in tetrahydrofuran (THF; 20 mL) under an argon atmosphere. The resulting green suspension was stirred for 7 days at room temperature, during which the color of the solution changed from green to dark brown. The solvent was evaporated in vacuo, and the dark-brown solid was redissolved in hexane (60 mL) and centrifuged. Dark-green crystals of **4** were isolated upon cooling of the resulting solution (0.967 g, 1.6 mmol, 80% yield). Anal. Calcd (found) for  $\text{C}_{37}\text{H}_{50}\text{CrN}_3\text{O}$  (%): C, 73.48 (73.45); H, 8.33 (8.29); N, 6.95 (6.93). IR (Nujol mull,  $\text{cm}^{-1}$ ):  $\nu$  2900 (s), 2854 (s), 1606 (m), 1574 (s), 1512 (s), 1464 (s), 1433 (s), 1402 (m),

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1379 (s), 1357 (m), 1315 (m), 1300 (s), 1243 (s), 1221 (s), 1195 (m), 1174 (w), 1135 (w), 1091 (m), 1065 (m), 1052 (m), 1017 (m), 1003 (w), 978 (m), 925 (s), 899 (w), 871 (s), 859 (m), 824 (s), 804 (s), 774 (s), 755 (s), 738 (m), 725 (m), 690 (s) [ $\mu_{\text{eff}} = 3.81$ ].

**Preparation of**  $\{[2,6\text{-}[2,6\text{-}(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)_2(\text{C}_5\text{H}_3\text{N})]\text{Cr}(\text{THF})_2(\mu\text{-N}_2)]\}_2\text{ether}$  (**5**). **Method A.** A solution of **2** (1.31 g, 2.0 mmol) in THF (100 mL) was treated with NaH (0.100 g, 4.2 mmol) in THF (20 mL) or metallic sodium (4.1 mmol). The resulting purple mixture was stirred for 7 days at room temperature, during which the color of the solution changed from purple to dark green. The solvent was evaporated in vacuo, and the dark-green solid was redissolved in hexane (80 mL). Dark-green crystals of **5** were isolated upon cooling (0.255 g, 0.19 mmol, 19% yield). Suitable crystals for X-ray diffraction were grown from ether and were found to contain ether of crystallization (vide infra). Anal. Calcd (found) for  $\text{C}_{78}\text{H}_{112}\text{Cr}_2\text{N}_8\text{O}_3$  (%): C, 71.31 (71.27); H, 8.59 (8.55); N, 8.53 (8.48). IR (Nujol mull,  $\text{cm}^{-1}$ ):  $\nu$  2888 (s), 1907 (m), 1850 (m), 1599 (m), 1572 (m), 1540 (w), 1486 (w), 1463 (s), 1426 (s), 1377 (m), 1354 (m), 1338 (m), 1307 (m), 1279 (m), 1232 (m), 1194 (m), 1178 (m), 1155 (w), 1109 (m), 1094 (w), 1004 (w), 985 (w), 951 (w), 930 (w), 880 (s), 862 (m), 793 (m), 787 (m), 756 (s), 728 (s), 694 (w), 665 (w) [ $\mu_{\text{eff}} = 5.72 \mu_{\text{B}}$ ].

**Method B.** A solution of **3** (1.138 g, 2.0 mmol) in THF (100 mL) was treated with either NaH (0.053 g, 2.2 mmol) in THF (20 mL) or metallic sodium (0.048 g, 2.1 mmol). The resulting green solution was stirred for 7 days at room temperature, during which the color of the solution changed from green to dark black-green. The solvent was evaporated in vacuo, and the dark-green solid was redissolved in hexane (80 mL). Dark-green crystals of **5** were obtained upon cooling (0.235 g, 0.179 mmol, 18% yield).

**Preparation of**  $\{[2,6\text{-}[2,6\text{-}(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)_2(\text{C}_5\text{H}_3\text{N})]\text{Cr}(\text{THF})][\{2\text{-}[2,6\text{-}(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)]\text{-}6\text{-}[2,6\text{-}(i\text{-Pr})_2\text{PhNC}=\text{CH}_2\text{-}(\text{C}_5\text{H}_3\text{N})]\text{Cr}(\text{THF})\}(\mu\text{-N}_2\text{H})(\mu\text{-Na})_2]\}$  (**6**). A solution of **5** (0.550 g, 0.42 mmol) was treated with NaH (0.024 g, 1.0 mmol) in toluene (15 mL) under a nitrogen atmosphere. The resulting mixture was stirred for 5 days at room temperature, during which time the color of the solution changed from dark green to dark brown. The excess of NaH was removed by centrifugation, and the resulting solution was evaporated to dryness. The solid residue was redissolved in toluene (25 mL). Dark-brown crystals of **6** were isolated at room temperature after standing for 1 week (0.167 g, 0.13 mmol, 31% yield). Anal. Calcd (found) for  $\text{C}_{74}\text{H}_{102}\text{Cr}_2\text{N}_8\text{Na}_2\text{O}_2$  (%): C, 69.13 (68.92); H, 8.00 (8.11); N, 8.72 (8.66). IR (Nujol mull,  $\text{cm}^{-1}$ ):  $\nu$  3419 (s) {3374 (s) for  $^{15}\text{N}$ ], 2917 (s), 1907 (m), 1850 (m), 1599 (m), 1572 (m), 1540 (w), 1463 (s), 1426 (s), 1377 (s), 1354 (w), 1337 (w), 1306 (m), 1279 (m), 1232 (s), 1194 (m), 1337 (w), 1306 (m), 1279 (m), 1232 (s), 1194 (m), 1178 (m), 1155 (w), 1109 (m), 1094 (m), 1052 (w), 1029 (m), 1004 (w), 984 (m), 975 (m), 951 (w), 930 (w), 879 (s), 862 (s), 793 (m), 787 (m), 756 (s), 727 (s), 694 (m), 666 (w) [ $\mu_{\text{eff}} = 1.92 \mu_{\text{B}}$ ].

**Preparation of**  $\{2\text{-}[2,6\text{-}(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)]\text{-}6\text{-}[2,6\text{-}(i\text{-Pr})_2\text{PhNC}=\text{CH}_2\text{-}(\text{C}_5\text{H}_3\text{N})]\text{Cr}(\mu\text{-NH})[\text{Na}(\text{THF})]\}$  (**7**). **Method A.** A solution of **5** (1.138 g, 0.86 mmol) in THF (100 mL) was treated with a suspension of NaH (0.065 g, 2.7 mmol) in THF (15 mL). The resulting green solution was stirred for 7 days at room temperature, during which the color of the solution changed to dark brown. After centrifugation, the solvent was evaporated in vacuo and the dark-brown solid was redissolved in hexane (65 mL). Dark-brown crystals of **7** were isolated from a concentrated solution upon standing at room temperature for 10 days (0.141 g, 0.22 mmol, 13%). Anal. Calcd (found) for  $\text{C}_{37}\text{H}_{52}\text{CrN}_4\text{NaO}$ : C, 69.02 (68.88); H, 8.14 (8.25); N, 8.70 (8.66). IR (Nujol mull,  $\text{cm}^{-1}$ ):  $\nu$  3413 (m) {3366 (m) for  $^{15}\text{N}$ ], 2855 (s), 1617 (w), 1572 (s), 1512 (s), 1463

(s), 1402 (w), 1378 (m), 1355 (m), 1317 (w), 1261 (w), 1227 (m), 1195 (w), 1164 (w), 1149 (w), 1134 (w), 1092 (m), 1051 (m), 1016 (s), 973 (s), 932 (w), 871 (s), 803 (s), 761 (m), 750 (m), 724 (s), 695 (w), 665 (w), 634 (m).

**Method B.** A solution of **3** (0.750 g, 1.3 mmol) was treated with a suspension of NaH (0.206 g, 8.6 mmol) in THF (15 mL) under a nitrogen atmosphere, and the resulting mixture was stirred for 7 days at room temperature. The color of the solution changed from dark green to dark black-brown. Excess NaH was removed by centrifugation. After evaporation to dryness, the residue was redissolved in hexane (25 mL). Dark-brown crystals of **7** (0.276 g, 0.43 mmol, 33%) were isolated at room temperature after standing for 1 week.

**Method C.** A solution of **6** (0.530 g, 0.41 mmol) was treated with a suspension of NaH (0.042 g, 1.7 mmol) in THF (20 mL) under a nitrogen atmosphere, and the mixture was allowed to stir for 10 days at room temperature. The color of the solution changed from dark brown to dark brown. Excess NaH was removed by centrifugation and evaporated to dryness. The residue was redissolved in hexane (25 mL), and dark-brown crystals of **7** were isolated upon slow cooling at  $-38^\circ\text{C}$  (0.084 g, 0.13 mmol, 16% yield).

**Degradation of 6 and Isolation of  $\text{NH}_4\text{BPh}_4$ .** An analytically pure sample of **7** (0.200 g) was treated with a 9% HCl/ $\text{H}_2\text{O}$  solution. After centrifugation of the solution and addition of  $\text{NaBPh}_4$ , a white solid was collected, washed, identified by IR, NMR and MS spectra as  $\text{NH}_4\text{BPh}_4$  (87%), and compared to those spectra of an analytically pure sample. The degradation test was also performed on the  $^{15}\text{N}$  adduct of complex **7**. The IR spectrum displays the characteristic isotopic shift of a NH stretching band from 3218 to 3248  $\text{cm}^{-1}$ . The MS spectrum also exhibits the ammonium ion peak at  $m/z$  19 compared to the  $m/z$  18 peak for the nonisotopically enriched sample. The  $^{15}\text{N}$  NMR resonance was located at 140.1 ppm.

**X-ray Crystallography.** Suitable crystals were selected, mounted on a thin glass fiber with paraffin oil, and cooled to the data collection temperature. Data were collected on a Bruker AXS SMART 1K CCD diffractometer. The crystals consistently diffract very weakly, and the problem was particularly severe for complexes **6** and **7**, which collected only noise above  $2\theta = 20^\circ$ . Nonetheless, the data files gave structures sufficient to demonstrate the heavy atoms' connectivity. For all of the compounds, data collection was performed with three batch runs at  $\varphi = 0.00^\circ$  (650 frames), at  $\varphi = 120.00^\circ$  (650 frames), and at  $\varphi = 240.00^\circ$  (650 frames). Initial unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied. The systematic absences and unit-cell parameters were consistent for the reported space groups. The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on  $F^2$ . A cocrystallized solvent molecule in the structure of **5** was refined isotropically. All of the other non-hydrogen atoms in all of the structures were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. All scattering factors and anomalous dispersion factors are contained in the *SHELXTL 6.12* program library.

Complex **5** has one molecule of diethyl ether per two chromium atoms in the lattice, for which refinement gives the best result when refined with half-occupancy. Relevant crystal data and bond distances and angles are given in Tables 1 and 2, respectively.

Complex **4** is a simple monomeric species (Figure 1) featuring the chromium atom connected to the ligand [Cr1–N1 = 2.020(3) Å, Cr1–N2 = 1.945(3) Å, and Cr1–N3 = 2.019(3) Å] and a



**Table 1.** Crystal Data and Structural Analysis Results of Complexes 4–7

	4	5	6	7
formula	C <sub>37</sub> H <sub>50</sub> CrN <sub>3</sub> O	C <sub>39</sub> H <sub>56</sub> CrN <sub>4</sub> O <sub>1.50</sub>	C <sub>74</sub> H <sub>102</sub> Cr <sub>2</sub> N <sub>8</sub> Na <sub>2</sub> O <sub>2</sub>	C <sub>37</sub> H <sub>52</sub> CrN <sub>4</sub> NaO
<i>M<sub>w</sub></i>	604.81	656.88	1287.63	644.82
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2(1)2(1)2(1)	<i>C</i> 2/ <i>c</i>	<i>P</i> 2/ <i>n</i>	<i>P</i> 2(1)/ <i>c</i>
<i>a</i> (Å)	20.730(4)	25.143(3)	18.148(3)	12.024(3)
<i>b</i> (Å)	8.6418(16)	11.5634(14)	18.561(3)	16.623(5)
<i>c</i> (Å)	19.063(4)	30.241(4)	21.219(3)	18.556(5)
α (deg)	90	90	90	90
β (deg)	90	113.095(2)	103.198(2)	99.425(5)
γ (deg)	90	90	90	90
<i>V</i> (Å <sup>3</sup> )	3415.0(11)	8087.7(17)	6958.6(16)	3658.8(17)
<i>Z</i>	4	8	4	4
radiation (Kα, Å)	0.71073	0.71073	0.71073	0.71073
<i>T</i> (K)	200(2)	213(2)	203(2)	208(2)
<i>D</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	1.178	1.079	1.229	1.171
<i>μ</i> <sub>calcd</sub> (mm <sup>-1</sup> )	0.366	0.316	0.375	0.357
<i>F</i> <sub>000</sub>	1304	2832	2760	1384
<i>R</i> , <i>R<sub>w</sub></i> , <i>2σ</i> <sup>a</sup>	0.0429, 0.1107	0.0674, 0.1757	0.0541, 0.1363	0.0764, 0.1653
GO <sub>F</sub>	1.054	1.086	1.054	1.045

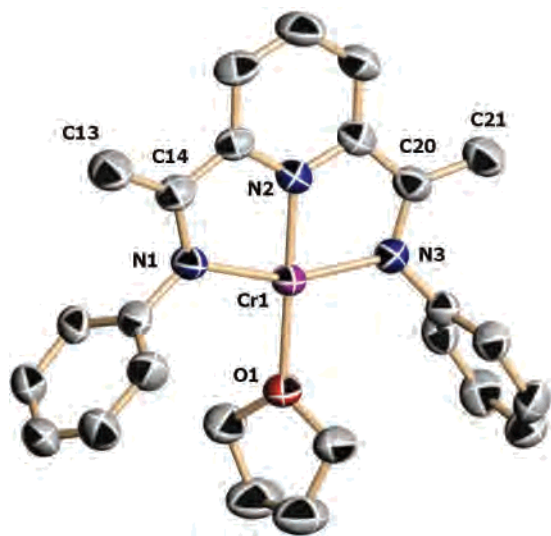
$$^a R = \sum |F_o| - |F_c| / \sum |F_o|. R_w = [\sum (|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}.$$

**Table 2.** Selected Bond Distances (Å) and Angles (deg) of Complexes 4–7

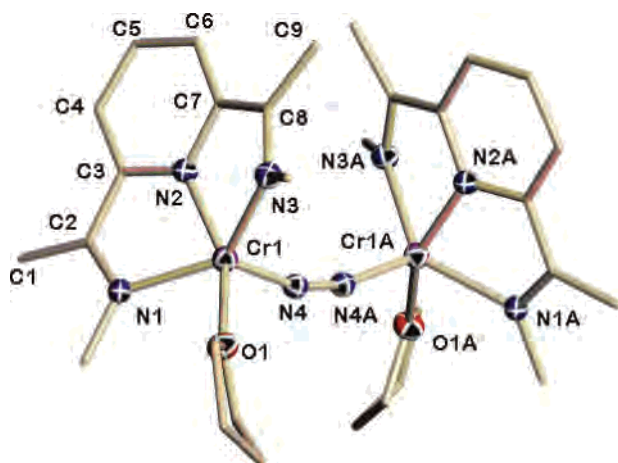
4	5	6	7
Cr1–N1 = 2.020(3)	Cr1–N1 = 2.141(3)	Cr1–N1 = 2.054(4)	Cr1–N1 = 2.010(6)
Cr1–N2 = 1.945(3)	Cr1–N2 = 1.940(3)	Cr1–N2 = 1.953(4)	Cr1–N2 = 1.958(6)
Cr1–N3 = 2.019(3)	Cr1–N3 = 2.083(3)	Cr1–N3 = 2.086(4)	Cr1–N3 = 2.010(6)
Cr1–O1 = 2.084(2)	Cr1–N4 = 1.781(3)	Cr1–N7 = 1.770(4)	Cr1–N4 = 1.911(10)
N1–C14 = 1.379(4)	Cr1–O1 = 2.182(3)	Cr1–O1 = 2.124(3)	Na1–N4 = 2.157(10)
N3–C20 = 1.383(4)	N4–N4a = 1.241(6)	Cr2–N4 = 2.079(3)	Na1–O1 = 2.239(7)
C13–C14 = 1.425(5)	N1–C2 = 1.338(5)	Cr2–N5 = 1.944(4)	Na1–C22 = 2.962(8)
C20–C21 = 1.445(5)	N3–C8 = 1.366(5)	Cr2–N6 = 2.060(3)	Na1–C23 = 2.991(8)
C14–C15 = 1.436(5)	C1–C2 = 1.512(5)	Cr2–N8 = 1.765(4)	Na1–C24 = 3.021(8)
C19–C20 = 1.425(5)	C8–C9 = 1.505(6)	Cr2–O2 = 2.147(3)	Na1–C25 = 3.041(8)
N2–C15 = 1.361(4)	C2–C3 = 1.424(5)	N1–C2 = 1.400(6)	Na1–C26 = 2.989(8)
N2–C19 = 1.383(4)	C7–C8 = 1.406(5)	N3–C8 = 1.426(6)	Na1–C27 = 2.936(8)
N1–Cr1–N2 = 79.04(11)	N2–C3 = 1.372(5)	N2–C3 = 1.387(6)	Na1–C5A = 2.951(9)
N1–Cr1–N3 = 157.85(11)	N2–C7 = 1.404(5)	N2–C7 = 1.396(6)	Na1–C6A = 2.879(8)
N1–Cr1–O1 = 101.18(11)	N1–Cr1–N2 = 75.33(12)	C1–C2 = 1.465(6)	N1–C2 = 1.377(9)
N2–Cr1–N3 = 78.86(11)	N1–Cr1–N3 = 137.88(12)	C2–C3 = 1.405(7)	N3–C8 = 1.373(9)
N2–Cr1–O1 = 178.50(12)	N1–Cr1–N4 = 109.51(12)	C3–C4 = 1.415(7)	N2–C3 = 1.366(9)
N3–Cr1–O1 = 100.95(11)	N1–Cr1–O1 = 91.84(11)	C4–C5 = 1.352(7)	N2–C7 = 1.378(9)
	N2–Cr1–N3 = 76.61(12)	C5–C6 = 1.437(7)	C1–C2 = 1.484(10)
	N2–Cr1–N4 = 103.46(13)	C6–C7 = 1.470(7)	C2–C3 = 1.408(10)
	N2–Cr1–O1 = 151.88(12)	C7–C8 = 1.383(6)	C7–C8 = 1.434(10)
	N3–Cr1–N4 = 107.13(13)	C8–C9 = 1.470(7)	C8–C9 = 1.452(10)
	N3–Cr1–O1 = 98.56(11)	N1–Cr1–N2 = 77.62(15)	N1–Cr1–N2 = 78.1(3)
	N4–Cr1–O1 = 104.41(12)	N1–Cr1–N3 = 138.31(15)	N1–Cr1–N3 = 156.0(3)
	Cr1–N4–N4a = 161.95(15)	N1–Cr1–N7 = 109.52(15)	N1–Cr1–N4 = 102.6(3)
		N1–Cr1–O1 = 95.04(14)	N2–Cr1–N3 = 77.8(3)
		N2–Cr1–N3 = 77.93(15)	N2–Cr1–N4 = 178.9(4)
		N2–Cr1–N7 = 101.55(15)	N3–Cr1–N4 = 101.4(3)
		N2–Cr1–O1 = 155.28(13)	Cr1–N4–Na1 = 128.7(5)
		N3–Cr1–N7 = 108.12(15)	
		N3–Cr1–O1 = 93.31(13)	
		N7–Cr1–O1 = 103.15(14)	
		Cr1–N7–N8 = 163.5(3)	
		Cr2–N8–N7 = 159.7(3)	

molecule of THF [Cr1–O1 = 2.084(2) Å] in a distorted square-planar geometry [N1–Cr1–N2 = 79.04(11)°, N1–Cr1–N3 = 157.85(11)°, N1–Cr1–O1 = 101.18(11)°, N2–Cr1–N3 = 78.86(11)°, N2–Cr1–O1 = 178.50(12)°, and N3–Cr1–O1 = 100.95(11)°]. The metal shows virtually no deviation from the plane identified by the four donor atoms. The bond distances formed by the methyl groups with the imine carbon atoms are shorter than expected for C–C single bonds [C13–C14 = 1.425(5) Å and C20–C21 = 1.445(5) Å]. This is indicative of deprotonation of one of the two methyl groups and which, by being disordered over the two equivalent positions, provide distances somewhat intermediate between the values expected for single and double bonds.

**Complex 5.** The structure consists of a symmetry-generated dimer with two identical {2,6-(*i*-Pr)<sub>2</sub>PhN=C(Me)}<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>N)}-Cr(THF) units connected by one bridging end-on-ligated dinitrogen unit (Figure 2). The coordination geometry around the metal center can best be described as distorted square-pyramidal ( $\tau = 0.23$ ). The basal plane is comprised of the three nitrogen atoms of the ligand system [Cr1–N1 = 2.141(3) Å, Cr1–N2 = 1.940(3) Å, and Cr1–N3 = 2.083(3) Å] and the coordinated THF oxygen atom [Cr1–O1 = 2.182(3) Å, N1–Cr1–N2 = 75.33(12)°, N1–Cr1–N3 = 137.88(12)°, N1–Cr1–O1 = 91.84(11)°, N2–Cr1–N3 = 76.61(12)°, N2–Cr1–O1 = 151.88(12)°, and N3–Cr1–O1 = 98.56(11)°]. The bridging dinitrogen unit is located on the apical



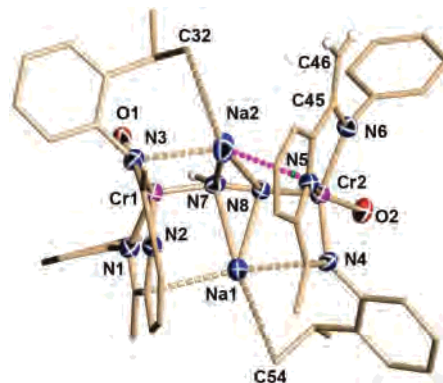
**Figure 1.** Partial thermal ellipsoid plot of **4** with ellipsoids drawn at the 30% probability level. Isopropyl substituents on the aryl groups have been omitted for clarity.



**Figure 2.** Partial thermal ellipsoid plot of **5** with ellipsoids drawn at the 30% probability level. Aryl groups on the imine nitrogen atoms have been omitted for clarity.

position [ $\text{Cr1-N4} = 1.781(3) \text{ \AA}$ ,  $\text{N4-Cr1-N1} = 109.51(12)^\circ$ ,  $\text{N4-Cr1-N2} = 103.46(13)^\circ$ ,  $\text{N4-Cr1-N3} = 107.13(13)^\circ$ , and  $\text{N4-Cr1-O1} = 104.41(12)^\circ$ ]. The N–N distance is longer than that in free dinitrogen [ $\text{N4-N4a} = 1.241(6) \text{ \AA}$ ], and the geometry about the  $\text{Cr}_2\text{N}_2$  unit deviates substantially from linearity [ $\text{Cr1-N4-N4a} = 161.95(15)^\circ$ ]. The long bonding distance formed by the two methyl groups with the imine carbon atoms [ $\text{C1-C2} = 1.512(5) \text{ \AA}$  and  $\text{C8-C9} = 1.505(6) \text{ \AA}$ ] is consistent with the presence of C–C single bonds. However, the bond lengths of the imine functions have been lengthened with respect to the neutral ligand [ $\text{N1-C2} = 1.338(5) \text{ \AA}$  and  $\text{N3-C8} = 1.366(5) \text{ \AA}$ ], which is also paralleled by a shortening in the  $\text{C}_{\text{imine}}\text{-C}_{\text{ortho}}$  bond distances [ $\text{C2-C3} = 1.424(5) \text{ \AA}$  and  $\text{C7-C8} = 1.406(5) \text{ \AA}$ ] and a lengthening in the  $\text{N}_{\text{pyr}}\text{-C}_{\text{ortho}}$  bond distances [ $\text{N2-C3} = 1.372(5) \text{ \AA}$  and  $\text{N2-C7} = 1.404(5) \text{ \AA}$ ].

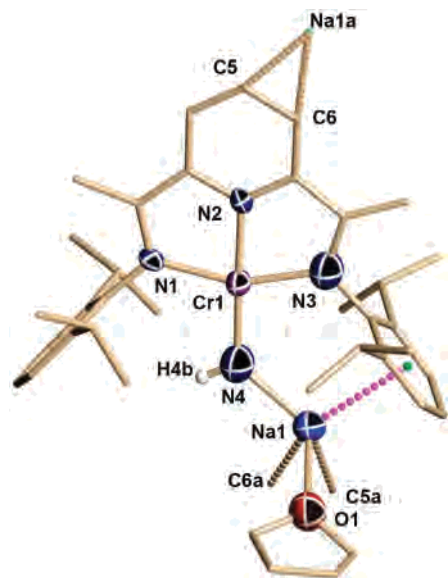
**Complex 6.** The molecular structure of **6** is closely related to that of **5**, featuring a chromium dimer bridged by a dinitrogen unit (Figure 3). Each chromium center adopts a severely distorted trigonal-bipyramidal geometry in which the two imine nitrogen donor atoms of the ligand and the nitrogen atom of the dinitrogen residue are bound in the equatorial plane [ $\text{Cr1-N1} = 2.054(4) \text{ \AA}$ ,  $\text{Cr1-N3} = 2.086(4) \text{ \AA}$ ,  $\text{Cr1-N7} = 1.770(4) \text{ \AA}$ ,  $\text{N1-Cr1-N3} =$



**Figure 3.** Partial thermal ellipsoid plot with ellipsoids of **6** drawn at the 30% probability level. Some of the isopropyl groups and THF carbon atoms have been omitted for clarity.

$138.31(15)^\circ$ ,  $\text{N1-Cr1-N7} = 109.52(15)^\circ$ , and  $\text{N7-Cr1-N3} = 108.12(15)^\circ$ ]. The THF oxygen atom and pyridine nitrogen atom occupy the axial positions [ $\text{Cr1-N2} = 1.953(4) \text{ \AA}$ ,  $\text{Cr1-O1} = 2.124(3) \text{ \AA}$ ,  $\text{N2-Cr1-O1} = 155.28(13)^\circ$ ,  $\text{N1-Cr1-O1} = 95.04(14)^\circ$ ,  $\text{N1-Cr1-N2} = 77.62(15)^\circ$ ,  $\text{N2-Cr1-N3} = 77.93(15)^\circ$ ,  $\text{N3-Cr1-O1} = 93.31(13)^\circ$ ,  $\text{N7-Cr1-N2} = 101.55(15)^\circ$ , and  $\text{N7-Cr1-O1} = 103.15(14)^\circ$ ]. The  $\text{Cr}_2\text{N}_2$  unit shows a folding comparable to that of **5** [ $\text{Cr1-N7-N8} = 163.5(3)^\circ$  and  $\text{Cr2-N8-N7} = 159.7(3)^\circ$ ], and the N–N distance [ $\text{N7-N8} = 1.288(5) \text{ \AA}$ ] seems to be in agreement with the presence of a double bond, similar to that seen in complex **5**. The folding along the N–N vector could be the result of the presence of hydrogen atoms on one or both of two nitrogen atoms, although the large Cr–N–N angles make this rather unlikely. The precise nature of the bridging dinitrogen unit will be discussed in more detail later on. Different from **5**, two sodium atoms are side-on-bonded to the dinitrogen unit [ $\text{Na1-N7} = 2.618(4) \text{ \AA}$  and  $\text{Na1-N8} = 2.478(4) \text{ \AA}$ ], forming a puckered  $\text{Na}_2\text{N}_2$  moiety. Each of the two sodium atoms is bonded to one imine nitrogen atom [ $\text{Na1-N4} = 2.587(4) \text{ \AA}$ ] as well as weakly  $\pi$ -bonded to the pyridine ring of the opposite ligand. The coordination geometry of each sodium atom is completed by an agostic interaction with the methyl unit of one isopropyl group of one aromatic ring [ $\text{Na1}\cdots\text{C54} = 3.079(6) \text{ \AA}$ ]. The imine methyl groups show C–C distances [1.465(6), 1.470(7), and 1.486(6)  $\text{ \AA}$  with  $\text{C45-C46} = 1.435(6) \text{ \AA}$ ; average 1.464  $\text{ \AA}$ ] that are shorter than expected for  $\text{C}_{\text{sp}^2}\text{-C}_{\text{sp}^3}$  single bonds (usually around 1.50  $\text{ \AA}$ , as found in **1–3**) but not short enough for the typical scenario of one deprotonated methyl group equally disordered over two positions (around 1.43  $\text{ \AA}$ , as found in **4**). In this particular case, it suggests that a single deprotonation may have occurred in the dimer: one double bond disordered over four positions may well account for the observed C–C distances.

**Complex 7.** The structure of complex **7** (Figure 4) is comprised of a mononuclear square-planar chromium center, surrounded by the ligand system [ $\text{Cr1-N1} = 2.010(6) \text{ \AA}$ ,  $\text{Cr1-N2} = 1.958(6) \text{ \AA}$ , and  $\text{Cr1-N3} = 2.010(6) \text{ \AA}$ ]. An NH or  $\text{NH}_2$  group occupies the fourth coordination site [ $\text{Cr1-N4} = 1.911(10) \text{ \AA}$ ,  $\text{N1-Cr1-N2} = 78.1(3)^\circ$ ,  $\text{N1-Cr1-N3} = 156.0(3)^\circ$ ,  $\text{N1-Cr1-N4} = 102.6(3)^\circ$ ,  $\text{N2-Cr1-N3} = 77.8(3)^\circ$ ,  $\text{N2-Cr1-N4} = 178.9(4)^\circ$ , and  $\text{N3-Cr1-N4} = 101.4(3)^\circ$ ], forming a bridge to a sodium atom [ $\text{N4-Na1} = 2.157(10) \text{ \AA}$ ]. In turn, the sodium cation carries one molecule of THF and is  $\pi$ -bonded to one aryl ring of the ligand [ $\text{Na1-O1} = 2.239(7) \text{ \AA}$ ], assembling an infinite array via bonding to the meta and para carbon atoms of an identical unit [ $\text{Na1-C5a} = 2.951(9) \text{ \AA}$  and  $\text{Na1-C6a} = 2.879(8) \text{ \AA}$ ]. The  $\text{C}_{\text{methyl}}\text{-C}_{\text{imine}}$  bonds are rather short for C–C single bonds and suggest that one of the two methyl groups might, in fact, have undergone deprotonation with conse-



**Figure 4.** Partial thermal ellipsoid plot with ellipsoids of **7** drawn at the 30% probability level.

quent formation of a double bond. The other bond distance alterations are characteristic of reduction by two electrons [N1–C2 = 1.377(9) Å, N3–C8 = 1.373(9) Å, N2–C3 = 1.366(9) Å, N2–C7 = 1.378(9) Å, C2–C3 = 1.408(10) Å, and C7–C8 = 1.434(10) Å].

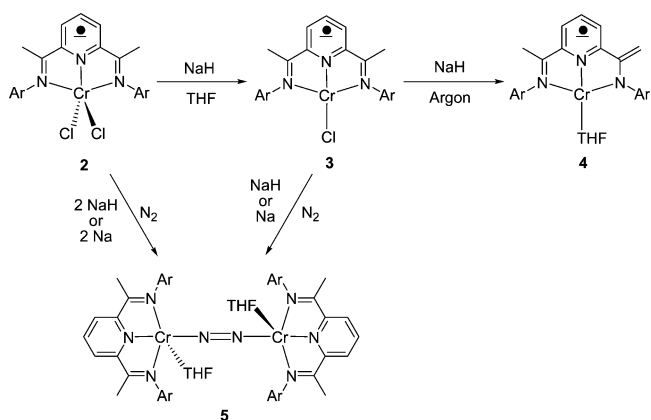
**Calculations.** In calculations on mononuclear model systems, the 2,6-(*i*-Pr)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> groups were replaced by methyl groups and THF was replaced by Me<sub>2</sub>O. Spin states up to  $S = 5/2$  were considered for each species, and geometries were fully optimized for each individual spin state. The full system was then optimized, assuming the spin state that was lowest for the model system. Vibrational analyses were not feasible for these large open-shell systems.

All calculations were carried out with the *Turbomole* program<sup>14</sup> coupled to the PQS Baker optimizer.<sup>15</sup> All calculations used the spin-unrestricted formalism; even for “ $S = 0$ ” systems, spin-unrestricted calculations gave significantly lower energies than spin-restricted calculations. Geometries were fully optimized at the b3-lyp level<sup>16</sup> using the Turbomole SV(P) basis set<sup>14a,c</sup> on all atoms. Orbital drawings were created using Molden.<sup>17</sup> The Supporting Information shows relevant orbitals for the most stable spin states of model systems (orbitals for the full systems are roughly similar but are much more difficult to interpret because of mixing with the arene  $\pi$  orbitals).

## Results and Discussion

The divalent **2** is readily formed via a straightforward reaction of the neutral ligand with CrCl<sub>2</sub>(THF)<sub>2</sub>.<sup>13h</sup> Its

**Scheme 1**



reduction with NaH in THF (Scheme 1) afforded the reduced species **3**, which forms a potent ethylene polymerization catalyst upon activation with monoamine oxidase.<sup>13h</sup> In spite of the connectivity suggesting a rare case of the monovalent non-cyclopentadienylchromium complex, the fairly regular square-planar coordination geometry around the metal center strongly suggests that, similar to the cases of the recently reported aluminum and iron complexes,<sup>11i,13d,f,g</sup> the complex contains a *higher valent* metal center magnetically coupled to one or more ligand-centered unpaired electrons. This observation prompted further attempts to reduce both **2** and **3**.

Treatment of **3** with NaH under argon (with careful exclusion of dinitrogen from the reaction medium) afforded a complex formulated as **4** (Scheme 1). The mononuclear structure (Figure 1) contains a formally Cr<sup>I</sup> atom surrounded by the monodeprotonated form of the ligand and one molecule of THF in an overall square-planar geometry. The formation of **4** arises from the deprotonation of one of the two methyl groups attached to the imine function, implying that, in the absence of dinitrogen, NaH acted as a base. The oxidation state of **4** is most likely the same as that in the starting complex **3**, as is strongly suggested by the similar square-planar coordination geometry and very comparable values of the magnetic moment. Although the magnetic values are not completely in agreement with the d<sup>4</sup> electronic configuration of divalent chromium, they can be reasonably explained in terms of a divalent chromium atom coupled to a ligand radical dianion.<sup>11h,13f</sup>

**Electronic Structure of Mononuclear Chromium Complexes.** Density functional theory calculations were performed for various spin states of simplified models of **1–4**. For the lowest-energy spin state, geometry optimizations were then performed for the complete molecule. Calculated geometrical parameters are collected and compared with experimental values in Table 3. The agreement was generally satisfactory, although calculated bond lengths to chromium are systematically long. Orbital pictures (for the simplified models) are given in the Supporting Information.

The trivalent **1** prefers the expected high-spin ( $S = 3/2$ ) ground state. It has an approximately octahedral metal

- (14) (a) Ahlrichs, R.; et al. *Turbomole*, version 5; Theoretical Chemistry Group, University of Karlsruhe, Jan 2002. (b) Treutler, O.; Ahlrichs, R. *J. Chem. Phys.* **1995**, *102*, 346–354. (c) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571–2577. (d) Schäfer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829–5835. (e) Andrae, D.; Haeussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123–141.
- (15) (a) *PQS*, version 2.4; Parallel Quantum Solutions: Fayetteville, AK, 2001 (the Baker optimizer is available separately from PQS upon request). (b) Baker, J. J. *Comput. Chem.* **1986**, *7*, 385–395.
- (16) (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372–1377. (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652. (d) All calculations were performed using the *Turbomole* functional “b3 lyp”, which is not identical to the *Gaussian* “B3LYP” functional.

- (17) Schaftenaar, G.; Noordik, J. H. *J. Comput.-Aided Mol. Des.* **2000**, *14*, 123–134.



**Table 3.** Calculated and Observed Bond Lengths for Mononuclear Chromium Complexes

bond <sup>a</sup>	1		2		3		4	
	calcd	exp <sup>b</sup>	calcd	exp <sup>c</sup>	calcd	exp <sup>c</sup>	calcd	exp
Cr–N	2.211	2.142	2.120	2.118	2.131	2.077	2.067	2.020
	2.026	1.991	1.931	1.993	1.964	1.934	1.974	1.945
C=N	1.292	1.301	1.318	1.296	1.323	1.321	1.377	1.381
C <sub>im</sub> –C <sub>py</sub>	1.495	1.468	1.452	1.484	1.450	1.438	1.457	1.431
C <sub>im</sub> –“Me”	1.505	1.489	1.506	1.477	1.508	1.501	1.436	1.435
Cr–Cl/O	2.358	2.314	2.266	2.299	2.307	2.287	2.134	2.084
	2.265	2.282	2.269	2.416				

<sup>a</sup> Averaged where appropriate. <sup>b</sup> Reference 19. <sup>c</sup> Reference 13h.

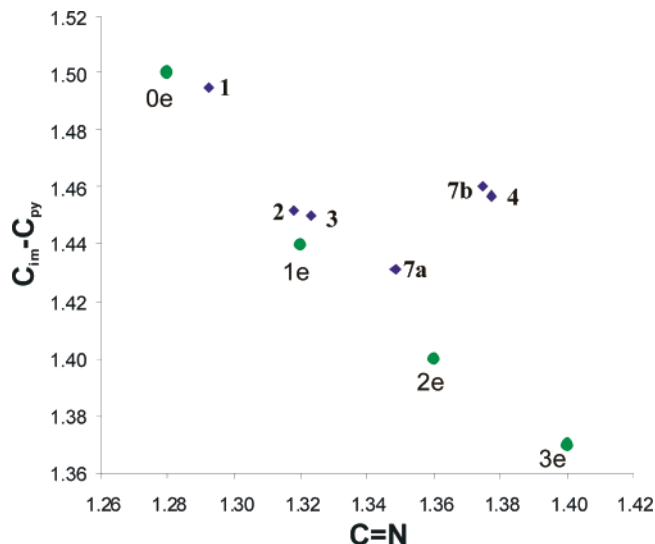
environment, with the apical chloride atoms bent backward toward the pyridine ring. The calculated ligand C=N and C<sub>im</sub>–C<sub>py</sub> distances are close to those of the free ligand and, as expected, indicate that there is no significant electron transfer to ligand  $\pi^*$  orbitals.

Complex **2** prefers a triplet ( $S = 1$ ) ground state by a small margin (ca. 0.5 kcal mol<sup>-1</sup> for the simplified model). This preference already indicates that the complex is *not* an ordinary Cr<sup>II</sup> complex (which would normally prefer a high-spin  $S = 2$  ground state).<sup>18</sup> Rather, the orbital analysis of the triplet state shows occupied  $d_{xz}$ ,  $d_{yz}$ , and  $d_{xy}$  orbitals in the  $\alpha$  manifold but a mostly ligand  $\pi^*$ -type occupied orbital of  $\beta$  spin (of the same symmetry as  $d_{xz}$ ). Thus, this complex is best described as having Cr<sup>III</sup> coupled to a ligand radical anion. In agreement with this description, it shows elongated C=N bonds and shortened C<sub>im</sub>–C<sub>py</sub> bonds.

Interestingly, calculations indicate that complex **3** contains Cr<sup>II</sup> coupled to a ligand radical anion. Thus, whereas the reduction of the trivalent precursor to the divalent **2** is ligand-centered, further reduction to **3** is metal-centered. The  $\alpha$  manifold of **3** contains occupied  $d_{xz}$ ,  $d_{yz}$ ,  $d_{xy}$ , and  $d_z^2$  orbitals, whereas a single occupied ligand  $\pi^*$ -like orbital is found in the  $\beta$  manifold.

The deprotonated complex **4** also features Cr<sup>II</sup> coupled to a ligand-centered unpaired electron mainly located in the intact imine–pyridine portion of the monodeprotonated ligand. In earlier work, we observed easy dimerization of similar monodeprotonated ligand complexes through coupling of the terminal methylene groups.<sup>11c,e</sup> Dimerization might be made more difficult here by the presence of the additional unpaired electron on the ligand: the hypothetical dimer would contain two formally zerovalent chromium atoms.

The ligand C=N and C<sub>im</sub>–C<sub>py</sub> distances can be used to estimate the amount of metal-to-ligand electron transfer.<sup>13b</sup> Because of the small changes in the bond lengths involved, this requires either highly accurate X-ray data or the use of calculated distances (which suffer much less from random errors). Figure 5 shows calculated average distances for the above complexes (and for **7**, discussed later on), together with the “standard values” for transfer of zero to three



**Figure 5.** Calculated ( $\blacklozenge$ ) C=N and C<sub>im</sub>–C<sub>py</sub> distances for complexes **1–4** and **7a/7b**, compared to reference values ( $\bullet$ ) for the transfer of zero to three electrons.<sup>13i</sup>

electrons.<sup>13i</sup> The positions of complexes **1–3** in the graph are indeed consistent with the transfer of zero, one, and one electrons, respectively. Complexes **4** and **7b** do not follow the trend of the other points, which is to be expected because they contain a deprotonated ligand.

**Dinitrogen Activation.** Complex **4** does not react with nitrogen. However, the reaction of both **2** and **3** with an appropriate amount of either metallic sodium or sodium hydride in THF and under a nitrogen atmosphere afforded the corresponding dinuclear dinitrogen complex **5**.

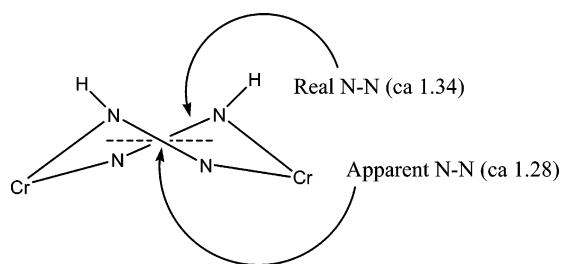
The connectivity of **5**, as established by an X-ray crystal structure (Figure 2), showed a dinuclear complex with the two square-pyramidal chromium atoms bridged by one end-on-bonded dinitrogen unit and each surrounded by one ligand and one molecule of coordinated THF. The complex is basically isostructural with the vanadium analogue.<sup>13e</sup> The N–N distance [N4–N4a = 1.241 Å] of the coordinated dinitrogen unit also compares well with that of the vanadium complex, possibly suggesting that the dinitrogen unit has undergone a two-electron reduction. Dinitrogen-bridged dichromium complexes are rare, and the bridging bonding mode of dinitrogen between two chromium atoms has never been observed before.<sup>9</sup> The partial reduction of dinitrogen suggests the possibility of regarding the complex as bearing two divalent (or trivalent) chromium centers bound to monoanionic (or dianionic) ligands and bridged by an N<sub>2</sub><sup>2-</sup> unit. Complex **5** is paramagnetic and displays a room-temperature magnetic moment per molecule of  $\mu_{\text{eff}} = 5.72 \mu_{\text{B}}$ . This value is certainly lower than that expected for two high-spin Cr<sup>II</sup> d<sup>4</sup> centers. On the other hand, the internal coupling between the metal center and the ligand radical anion, as is normally observed in the reduced species of this ligand system,<sup>11h,i</sup> as well as the possible coupling between the two metal centers, may well result in a rather nondiagnostic value of the magnetic moment.

Regardless of how we consider the metal oxidation state in **5**, its formation can be easily rationalized in terms of reduction of the metal center followed by intramolecular

(18) For example, see: (a) O'Connor, C. J. *Magnetochemistry—Advances in Theory and Experimentation. Progress in Inorganic Chemistry*; John Wiley & Sons: New York, 1982; pp 203–283. (b) Gambarotta, S. *Comments Inorg. Chem.* **1991**, *4*, 195.

(19) Esteruelas, M. A.; López, A. M.; Méndez, L.; Oliván, M.; Oñate, E. *Organometallics* **2003**, *22*, 395.

Scheme 2



reoxidation at the expense of both the coordinated dinitrogen unit and the ligand system.

The partial reduction of the dinitrogen unit in **5** is intriguing and suggests that further reduction of the dinitrogen moiety may be possible. Accordingly, the reaction of **5** with NaH afforded dark-brown paramagnetic crystals of a complex formulated as **6** on the basis of the X-ray crystal structure (Figure 3) and spectroscopic evidence. The yield, although low, was well reproducible. The dinuclear structure of the complex is surprisingly similar to that of **5**, with each chromium center surrounded by the ligand and a molecule of THF and the two chromium entities apparently bridged through an end-on-bonded dinitrogen moiety. Different from complex **5**, however, is the presence of two sodium atoms bonded to each side of the dinitrogen unit, forming a folded  $N_2Na_2$  unit. In addition, each sodium atom is  $\pi$ -bound to one pyridine ring and forms an agostic contact with one of the four methylisopropyl groups of one aryl substituent. The severe puckering of the  $N_2Na_2$  moiety and consequent pyramidalization of the nitrogen atom suggested that perhaps hydrogenation may have occurred. Accordingly, the IR spectrum of complex **6** did show one single medium/weak resonance at  $3419\text{ cm}^{-1}$  that shifted to  $3374\text{ cm}^{-1}$  in the sample prepared with  $^{15}N_2$ . This clearly indicates the presence of one N–H function. The room-temperature magnetic moment is surprisingly low [ $\mu_{\text{eff}} = 1.92\ \mu_B$ ]. In spite of having been generated in THF and crystallized from toluene, the complex, once crystallized, shows no solubility in any solvent that it does not react with, thus regrettably preventing spectroscopic investigations in solution.

The formation of **6** from **5** implies from the formal point of view a two-electron reduction followed by one hydrogen atom transferred from one of the four imine methyl group to the dinitrogen moiety. Calculations on these structures could only be reconciled with the observed structure if it was assumed that the crystal shows disorder between Cr–NH=N–Cr and Cr–N=NH–Cr orientations of the  $N_2H$  bridge: an ordered bridge would be sharply angled at the NH moiety (ca  $130^\circ$ ) and much closer to linear at the other nitrogen atom (Scheme 2). If the structure is indeed disordered, the observed N–N distance may not be meaningful. The large Cr–N–N angles appear to rule out the possibility of having a  $\mu\text{-}N_2H_2$  unit in the structure.

**Electronic Structure of Dinuclear Chromium Complexes.** In view of the uncertainties surrounding the formulation of **6**, we considered both  $N_2H$ -bridged (**6a**:  $\{[2,6\text{-}[2,6\text{-}(i\text{-}Pr)_2\text{PhN}=\text{C}(\text{CH}_3)_2(\text{C}_5\text{H}_3\text{N})]\text{Cr}(\text{THF})\}_2(\mu\text{-}N_2H)(\mu\text{-}Na)_2$ ) and dinitrogen-bridged (**6b**:  $\{[2,6\text{-}[2,6\text{-}(i\text{-}Pr)_2\text{PhN}=\text{C}(\text{CH}_3)_2(\text{C}_5\text{H}_3\text{N})]\text{Cr}(\text{THF})\}_2(\mu\text{-}N_2)(\mu\text{-}Na)_2$ ) structures. Structure **6a**, assumed above for complex **6**, seems the most likely in view of the observation of an N–H stretch vibration in the IR spectrum. Structure **6b** corresponds to simple two-electron reduction of **5** and is of interest in itself even if it would not correspond to the actual structure of complex **6**.

Constructing satisfactory theoretical descriptions of dinuclear complexes **5** and **6b** turned out to be surprisingly difficult. Several spin states, differing mainly in the coupling between the electrons on different chromium atoms, are close in energy. It seems likely that the methods we are using (several functionals were tried) do not describe the balance between the donation to the highly delocalized ligand  $\pi^*$  system and to the rather compact dinitrogen  $\pi^*$  orbitals and the occupation of metal 3d orbitals very well.<sup>20</sup> In order to arrive at some sort of theoretical description, nonetheless, we constrained both Cr– $N_2$  bonds to their experimental (X-ray) values.

For complex **5**, this produces an electronic structure in which each chromium center is essentially  $\text{Cr}^{\text{III}}$ ; each ligand has one  $\pi^*$  orbital doubly occupied and one 3d electron coupled to an electron in a dinitrogen  $\pi^*$  orbital; i.e., we have a doubly reduced dinitrogen molecule, isoelectronic with dioxygen. Other spin states show different couplings between the chromium centers and ligand  $\pi^*$  orbitals and also sometimes occupation of two different ligand  $\pi^*$  orbitals. In view of the problems mentioned above, we think that our results, in particular as regards coupling between chromium and ligand orbitals, should be treated with caution. However, a description as  $[L^{2-}\text{Cr}^{\text{III}}(\text{THF})_2(N_2^{2-})]$  seems reasonable based on the results mentioned earlier for mononuclear complexes. The alternative  $[L^-\text{Cr}^{\text{II}}(\text{THF})_2(N_2^{2-})]$  description seems less likely because the  $\text{Cr}^{\text{II}}$  centers in such a complex would have their  $d_z^2$  orbitals occupied and hence should not bind ligands in apical positions.<sup>21</sup>

For hypothetical structure **6b**, the tendency to eliminate dinitrogen is strong. Calculations with Cr–N distances constrained to their experimental values produce an electronic structure that still is most easily described as containing two  $\text{Cr}^{\text{III}}$ , each bound to a ligand trianion (one  $\pi^*$  orbital doubly and the other one singly occupied) and to  $N_2^{2-}$ . The role of the sodium atoms is just to provide electrons to the  $\pi^*$  systems of the diiminepyridine ligands. Dissociation of dinitrogen allows rearrangement and occupation of the Cr  $d_z^2$  orbitals, which (as for **5**) is the driving force for expulsion of dinitrogen.

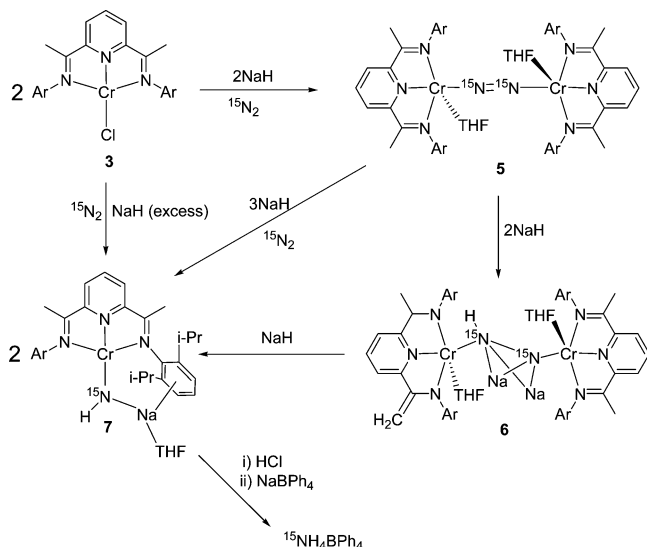
Our preferred model **6a** does not dissociate in the calculation. The pronounced asymmetry of the complex makes unambiguous interpretation of the orbital occupation pattern difficult. The structure, like **5** and **6b**, appears to contain two  $\text{Cr}^{\text{III}}$  centers, one bound to a ligand trianion

(20) The alternative possibility that the actual structure of **5** differs from the one we tried to model in having fewer or more hydrogen atoms cannot be entirely excluded at this stage.

(21) In fact, upon elongation of the Cr– $N_2$  distance, the  $d_z^2$  orbital becomes occupied, and this seems to cause dissociation of the dinitrogen molecule in the calculation.



Scheme 3



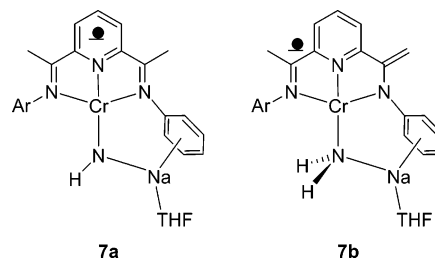
monoradical (as in **6b**) and the other one to the monodeprotonated closed-shell ligand trianion. The bridging  $\text{N}_a=\text{N}_b\text{H}$  fragment is effectively  $1^-$  and is nearly linear around  $\text{N}_a$  but sharply angled around  $\text{N}_b$ . This structure is well reconciled with the observed structure of **6** if we assume disorder in the  $\text{N}_2\text{H}$  bridge (and possibly also in the ligand deprotonation site), as explained above.

**Cleavage of Dinitrogen.** Further treatment of **6**, or more conveniently of either **5** or **3**, with NaH in appropriate amounts (Scheme 3) afforded a new paramagnetic [ $\mu_{\text{eff}} = 3.60 \mu_{\text{B}}$ ] complex formulated as **7** on the basis of the X-ray crystal structure, spectroscopic data, and chemical degradation experiments. The yield was very low but always reproducible.

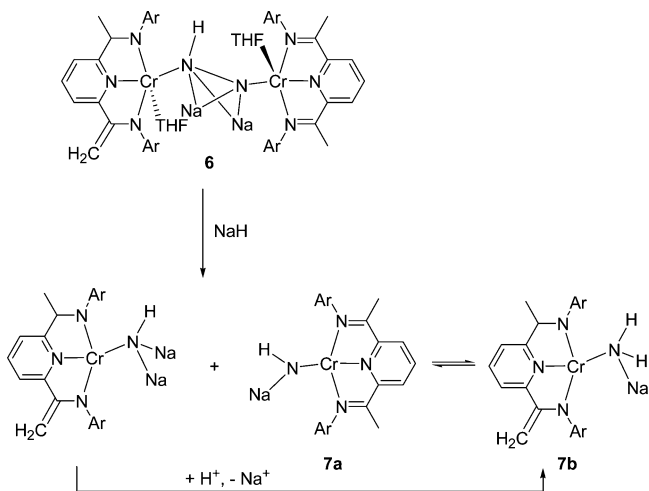
The structure revealed a chromium center in a square-planar environment defined by the three donor atoms of the ligand system and a non-hydrogen light atom. This atom, in turn, bridges a sodium atom,  $\pi$ -bonded to one of the aryl substituents (Figure 4). The thermal parameters of the bridging atom could be satisfactorily refined as either carbon or nitrogen. The hydrogen atom(s) at nitrogen could not be located, but the IR spectrum of **7** displays one sharp peak at  $3413 \text{ cm}^{-1}$ , in the area typical for NH stretching bands. Crystalline samples with identical cell parameters obtained by carrying out the same reaction under  $^{15}\text{N}_2$  displayed an isotopic shift to  $3366 \text{ cm}^{-1}$ . In addition, chemical degradation with diluted HCl followed by precipitation with  $\text{NaBPh}_4$  afforded analytically pure samples of  $^{15}\text{NH}_4\text{BPh}_4$ , therefore conclusively demonstrating that the bridging atom is nitrogen and its origin is dinitrogen gas.

The isotope enrichment demonstrates that the formation of **7** is the result of dinitrogen cleavage. The fact that **7** could be obtained from **3**, **5**, or **6** suggests that **5** and **6** may be regarded as intermediates in the formation of **7**, with **6** being the immediate precursor. The square-planar geometry of the chromium center is very comparable to that of **3** and **4**, thus indicating that even in this case the metal center is present in the divalent state; i.e., reduction of **6** has taken place at nitrogen, *not* at the metal center. The low magnetic moment

Scheme 4



Scheme 5



of [ $\mu_{\text{eff}} = 3.60 \mu_{\text{B}}$ ] is not compatible with plain  $\text{Cr}^{\text{II}}$  but rather suggests that the complex contains high-spin  $\text{Cr}^{\text{II}}$  coupled to a ligand-centered unpaired electron. There are two tautomeric formulations that together would account for the above observations (Scheme 4). The first is a complex containing a nondeprotonated ligand (as a radical anion) and a uninegative  $\text{NHNa}(\text{THF})$  fragment. Electronically, this variation (**7a**) would be similar to complex **3**. As a second possibility, the complex may contain a monodeprotonated ligand (as a radical dianion) and a neutral  $\text{NH}_2\text{Na}(\text{THF})$  fragment. Electronically, the formulation **7b** would be similar to complex **4**. However, the fact that the IR spectrum shows only one slightly broad band for the N–H stretching possibly indicates that the structure **7a** is the dominant one in the tautomeric equilibrium.

A possible rationalization for the formation of **7** could start with **5** reacting with an additional 1 equiv of NaH and resulting in cleavage of the N–N bond, producing one monosodium amide and one disodium amide complex (Scheme 5). The latter is likely to be basic enough to deprotonate any solvent and form a monosodium amide.

## Conclusions

In this paper, we have reported the formation of a bridging chromium–dinitrogen complex, its partial reduction and hydrogenation, and eventual cleavage to an imide product. Given the unusual paucity of dinitrogen chemistry among chromium complexes, it seems plausible that the electron-storage capabilities of the diminepyridine ligand play an important role in this sequence of reactions. The chemistry is complex, with several reactions occurring in parallel. Given

### *Chromium Diiminepyridine Complex*

that chromium seems to have no inclination for dinitrogen fixation/activation, these transformations, which have been otherwise observed only in molybdenum chemistry,<sup>3a,b,5</sup> can only be ascribed to the remarkable ability of the diiminepyridine ligand to act as an electron reservoir in multistep reductive transformations.

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and acknowledgment is given to I. Korobkov for solving crystal structures and to M. Renade for technical assistance with the preparation of **3**.

**Supporting Information Available:** Complete crystallographic data (CIF) for the complexes reported in this paper and orbital plots [b3-lyp/SV(P) level] for models of complexes **1–7**. This material is available free of charge via the Internet at <http://pubs.acs.org>. IC700810F