

## Dinitrogen and Acetylide Complexes of Low-Valent Chromium

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Reaction of *trans*-(dmpe)<sub>2</sub>CrCl<sub>2</sub> (dmpe = 1,2-bis(dimethylphosphino)ethane) with one equivalent of LiCCSiMe<sub>3</sub> and one equivalent of *n*BuLi in THF under a dinitrogen atmosphere affords dark orange *trans,trans*-[(Me<sub>3</sub>SiCC)(dmpe)<sub>2</sub>Cr]<sub>2</sub>(μ-N<sub>2</sub>) · hexane (**1**). Under similar conditions but in the absence of acetylide ligand, the reaction of *trans*-(dmpe)<sub>2</sub>CrCl<sub>2</sub> with 2 equivalents of *n*BuLi yields the previously characterized complex *trans*-(dmpe)<sub>2</sub>Cr(N<sub>2</sub>)<sub>2</sub> (**2**), while the reaction of *trans*-(dmpe)<sub>2</sub>CrCl<sub>2</sub> with 2 equivalents of LiCCSiMe<sub>3</sub> in THF yields *trans*-(dmpe)<sub>2</sub>Cr(CCSiMe<sub>3</sub>)<sub>2</sub> (**3**). Compound **3** can also be synthesized by irradiating a mixture of *trans*-(dmpe)<sub>2</sub>CrMe<sub>2</sub> and HCCSiMe<sub>3</sub> or by reduction of HCCSiMe<sub>3</sub> with compound **2**. The magnetic properties, electrochemistry, and crystal structure of *trans,trans*-[(Me<sub>3</sub>SiCC)(dmpe)<sub>2</sub>Cr]<sub>2</sub>(μ-N<sub>2</sub>) are consistent with the complex containing two Cr<sup>I</sup> ions bridged by a neutral N<sub>2</sub> moiety, with a 1.178(10) Å N≡N bond distance. For complex **1** redox processes centered at  $E_{1/2} = -1.69$  V ( $\Delta E_p = 185$  mV) and  $-1.43$  V ( $\Delta E_p = 182$  mV) versus Fe(Cp)<sub>2</sub>/Fe(Cp)<sub>2</sub><sup>+</sup> are assigned to the Cr<sup>I</sup>/Cr<sup>II</sup>/Cr<sup>III</sup> and Cr<sup>I</sup>/Cr<sup>II</sup>/Cr<sup>III</sup> couples, respectively. For *trans*-(dmpe)<sub>2</sub>Cr(CCSiMe<sub>3</sub>)<sub>2</sub> a reversible couple assigned as the Cr<sup>III</sup> couple was observed at  $-1.59$  V ( $\Delta E_p = 242$  mV) versus Fe(Cp)<sub>2</sub>/Fe(Cp)<sub>2</sub><sup>+</sup>. The dinuclear Cr(I)–dinitrogen complex **1** has a room temperature magnetic moment of 2.77 μ<sub>B</sub> while compound **3** displays a moment of 2.55 μ<sub>B</sub>. Density-functional theory calculations performed on a model compound of **1**, namely, *trans,trans*-[(HCC)(dpe)<sub>2</sub>Cr]<sub>2</sub>(μ-N<sub>2</sub>) (dpe = diphosphinoethane), indicate that oxidation of the molecule should result in weakening of the dinitrogen triple bond.

## Introduction

The activation of dinitrogen by end-on, side-on, or bridging coordination to transition metal complexes has been of long-standing interest to chemists.<sup>1</sup> Early transition metal complexes demonstrate rich reactivity with N<sub>2</sub>, for example, with Y,<sup>2</sup> La,<sup>2</sup> Ti,<sup>3</sup> Zr,<sup>4</sup> Hf,<sup>5</sup> V,<sup>6</sup> Nb,<sup>7</sup> Ta,<sup>8</sup> Mo,<sup>9</sup> and W.<sup>10</sup> In particular, many recent advances in dinitrogen chemistry have been achieved with molybdenum complexes including the cleavage of N<sub>2</sub> to form metal nitrido complexes<sup>9a</sup> and the

catalytic conversion of dinitrogen into ammonia.<sup>11</sup> Given the exciting N<sub>2</sub> chemistry available to low valent molybdenum, it seems possible that the lighter congener chromium, in

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- (1) (a) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589. (b) Gambarotta, S. *J. Organomet. Chem.* **1995**, *500*, 117. (c) Hidai, M.; Mizobe, Y. *Chem. Rev.* **1995**, *95*, 1115. (d) Hidai, M. *Coord. Chem. Rev.* **2000**, *200–202*, 379. (e) MacKay, B. A.; Fryzuk, M. D. *Chem. Rev.* **2004**, *43*, 5289. (f) Holland, P. L. *Can. J. Chem.* **2005**, *83*, 296. (g) MacLachlan, E. A.; Fryzuk, M. D. *Organometallics* **2006**, *25*, 1530. (h) Peters, J. C.; Mehn, M. P. *Bio-organometallic Approaches to Nitrogen Fixation Chemistry*. In *Activation of Small Molecules*, Tolman W. B., ed.; Wiley-VCH: Weinheim, Germany, 2006; pp 81–119.
- (2) (a) Evans, W. J.; Lee, D. S.; Ziller, J. W. *J. Am. Chem. Soc.* **2004**, *126*, 454. (b) Evans, W. J.; Lee, D. S.; Lie, C.; Ziller, J. W. *Angew. Chem., Int. Ed.* **2004**, *43*, 5517. (c) Evans, W. J.; Lee, D. S. *Can. J. Chem.* **2005**, *83*, 375.

- (3) (a) Sanner, R. D.; Duggan, D. M.; McKenzie, T. C.; Marsh, R. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 8358. (b) Berry, D. H.; Procoplo, L. J.; Carroll, P. J. *Organometallics* **1988**, *7*, 570. (c) Duchateau, R.; Gambarotta, S.; Beydoun, N.; Bensimon, C. *J. Am. Chem. Soc.* **1991**, *113*, 8986. (d) Beydoun, N.; Duchateau, R.; Gambarotta, S. *Chem. Commun.* **1992**, 244. (e) de Wolf, J. M.; Baaauw, R.; Meetsma, A.; Teuben, J. H.; Gyepes, R.; Varga, V.; Mach, K.; Veldman, N.; Spek, A. L. *Organometallics* **1996**, *15*, 4977. (f) Hagadorn, J. R.; Arnold, J. J. *J. Am. Chem. Soc.* **1996**, *118*, 893. (g) Peters, J. C.; Cherry, J.-P. F.; Thomas, J. C.; Baraldo, L.; Mendiola, D. J.; Davis, W. M.; Cummins, C. C. *J. Am. Chem. Soc.* **1999**, *121*, 10053. (h) Ishino, H.; Nagano, T.; Kuwata, S.; Yokobayashi, Y.; Ishii, Y.; Hidai, M. *Organometallics* **2001**, *20*, 188. (i) Ishino, H.; Takemoto, S.; Hirata, K.; Kanaizuka, Y.; Hidai, M.; Nabika, M.; Seki, Y.; Miyatake, T.; Suzuki, N. *Organometallics* **2004**, *23*, 4554. (j) Hanna, T.; Keresztes, I.; Lobkovsky, E.; Bernskoetter, W. H.; Chirik, P. J. *Organometallics* **2004**, *23*, 3448.
- (4) (a) Sanner, R. D.; Manriquez, J. M.; Marsh, R. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 8351. (b) Fryzuk, M. D.; Love, J. B.; Rettig, S. J.; Young, V. G. *Science* **1997**, *275*, 1445. (f) Morello, L.; Yu, P.; Carmichael, C. D.; Patrick, B. O.; Fryzuk, M. D. *J. Am. Chem. Soc.* **2005**, *127*, 12796. (c) Cohen, J. D.; Fryzuk, M. D.; Loehr, T. M.; Mylvaganam, M.; Rettig, S. J. *Inorg. Chem.* **1998**, *37*, 112. (d) Pool, J. A.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2003**, *125*, 2241. (e) Pool, J. A.; Lobkovsky, E.; Chirik, P. J. *Nature* **2004**, *427*, 527.
- (5) Bernskoetter, W. H.; Olmos, A. V.; Lobkovsky, E.; Chirik, P. J. *Organometallics* **2006**, *25*, 1021.

conjunction with electron-donating ancillary ligands, might also display unique reactivity with dinitrogen. However, few reports have been made focusing on the reactivity between  $N_2$  and Cr,<sup>12–17</sup> and the majority of the previous studies suggest that chromium typically forms highly unstable coordination complexes with  $N_2$ .<sup>13–15</sup>

A handful of chromium dinitrogen complexes exist: of the mononuclear complexes, only *trans*-(dmpe)<sub>2</sub>Cr(N<sub>2</sub>)<sub>2</sub> (dmpe = 1,2-bis(dimethylphosphino)ethane), in which two dinitrogen moieties are terminally *trans*-bound to a Cr(0) center, is stable at room temperature and has been structurally characterized.<sup>12</sup> In this case, the complex is generated by reducing *trans*-(dmpe)<sub>2</sub>CrCl<sub>2</sub> with Na/Hg. Analogues of this compound, namely, *trans*-(Me<sub>3</sub>P)<sub>4</sub>Cr(N<sub>2</sub>)<sub>2</sub> and *trans*-(dppe)<sub>2</sub>-Cr(N<sub>2</sub>)<sub>2</sub><sup>14</sup> (dppe = 1,2-bis(diphenylphosphino)ethane, are less stable and lose dinitrogen and phosphine ligands when warmed to room temperature, and hence, they have not been structurally characterized. Dinuclear complexes of chromium have also been reported, and of these, three have been structurally characterized: [(CO)<sub>2</sub>(η<sup>6</sup>-C<sub>6</sub>Et<sub>6</sub>)Cr]<sub>2</sub>(μ-N<sub>2</sub>),<sup>15</sup> which is unstable to recrystallization above 0 °C, {[{2,6-[2,6-(*i*-Pr)<sub>2</sub>PhN=C(CH<sub>3</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>3</sub>N)]<sub>2</sub>Cr(THF)]<sub>2</sub>(μ-N<sub>2</sub>)}·THF,<sup>16</sup> which can activate and reduce dinitrogen, and [(*i*-Pr<sub>2</sub>Ph)<sub>2</sub>nacnacCr]<sub>2</sub>(μ-N<sub>2</sub>)<sup>17</sup> (nacnac = β-diketiminato) in which the bridging

dinitrogen ligand is bound side-on to the Cr(I) centers. Several other Cr(0) compounds containing π-bonded cyclic hydrocarbon ligands, [(CO)<sub>2</sub>(η<sup>6</sup>-Ar)Cr]<sub>2</sub>(μ-N<sub>2</sub>) (where Ar = C<sub>6</sub>H<sub>6</sub>, C<sub>6</sub>Me<sub>6</sub>, or C<sub>6</sub>H<sub>3</sub>Me<sub>3</sub>), were also reported but have not yet been structurally characterized.<sup>13</sup>

Although few stable Cr/N<sub>2</sub> complexes exist, those that have been reported recently are stabilized by their anionic or π-accepting nitrogen based ancillary ligand sets; diiminepyridine,<sup>16</sup> and β-diketiminato.<sup>17</sup> It has been demonstrated that acetylide ligands possess strong π-donor character with early first row transition metals and that the bond is of a highly covalent nature.<sup>18</sup> We have previously shown that (C≡CR)<sup>1-</sup> ligands are capable of providing highly stable mononuclear chromium compounds, and<sup>19</sup> given the experimental observations reported herein, we believe that the ancillary acetylide ligand is important to the stabilization of *trans,trans*-[(Me<sub>3</sub>SiCC)(dmpe)<sub>2</sub>Cr]<sub>2</sub>(μ-N<sub>2</sub>). We also demonstrate that the synthetic approach that afforded **1** can be extended to provide an alternate, mercury-free method for synthesis of the known compound *trans*-(dmpe)<sub>2</sub>Cr(N<sub>2</sub>)<sub>2</sub> (**2**).<sup>12</sup> To our knowledge, these complexes, along with *trans*-(dmpe)<sub>2</sub>Cr(CCSiMe<sub>3</sub>)<sub>2</sub> (**3**), represent the first examples of end-bound acetylide ligands with monovalent and divalent octahedral chromium.<sup>20</sup>

## Experimental Section

**Preparation of Compounds.** All manipulations were performed under a nitrogen atmosphere using standard Schlenk line and glovebox techniques. Syntheses of *trans*-(dmpe)<sub>2</sub>CrCl<sub>2</sub> and *trans*-(dmpe)<sub>2</sub>CrMe<sub>2</sub> were carried out as reported previously.<sup>21</sup> Diethyl ether and toluene were passed over alumina, tetrahydrofuran was distilled from Na/benzophenone, and hexanes were purchased in Sure/Seal bottles. All solvents were degassed prior to use and stored over 3 Å molecular sieves. Trimethylsilylthyne was degassed by three freeze–pump–thaw cycles and stored over 3 Å molecular sieves. All other reagents were used without further purification.

***trans,trans*-[(Me<sub>3</sub>SiCC)(dmpe)<sub>2</sub>Cr]<sub>2</sub>(μ-N<sub>2</sub>)·Hexane (**1**).** To a 40 mL tetrahydrofuran (THF) solution of *trans*-(dmpe)<sub>2</sub>CrCl<sub>2</sub> (1.0 g, 2.4 mmol) and Me<sub>3</sub>SiCCH (0.29 g, 3.0 mmol) chilled at –78 °C, *n*BuLi (2.4 mL, 5.9 mmol, 2.5 M hexanes solution) was added via syringe, and the mixture was stirred at –78 °C for 3 h. Upon

- (6) (a) Song, J.-I.; Berno, P.; Gambarotta, S. *J. Am. Chem. Soc.* **1994**, *116*, 6927. (b) Buijink, J.-K. F.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 2004. (c) Berno, P.; Hao, S.; Minhas, R.; Gambarotta, S. *J. Am. Chem. Soc.* **1994**, *116*, 7417. (d) Ferguson, R.; Solari, E.; Floriani, C.; Osella, D.; Ravera, M.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1997**, *119*, 10104.
- (7) Fryzuk, M. D.; Kozak, C. M.; Bowdridge, M. R.; Patrick, B. O.; Rettig, S. J. *J. Am. Chem. Soc.* **2002**, *124*, 8389.
- (8) (a) Fryzuk, M. D.; Johnson, S. A.; Rettig, S. J. *J. Am. Chem. Soc.* **1998**, *120*, 11024. (b) Fryzuk, M. D.; Johnson, S. A.; Koetzle, T. F. *J. Am. Chem. Soc.* **2001**, *123*, 3960. (c) Fryzuk, M. D.; MacKay, B. A.; Johnson, S. A.; Patrick, B. O. *Angew. Chem., Int. Ed.* **2002**, *41*, 3709. (d) Fryzuk, M. D.; MacKay, B. A.; Patrick, B. O. *J. Am. Chem. Soc.* **2003**, *125*, 3234. (e) MacKay, B. A.; Patrick, B. O.; Fryzuk, M. D. *Organometallics* **2005**, *24*, 3836.
- (9) (a) Laplaza, C. E.; Cummins, C. C. *Science* **1995**, *268*, 861. (b) Laplaza, C. E.; Johnson, M. J. A.; Peters, J. C.; Odom, A. L.; Kim, E.; Cummins, C. C.; George, G. N.; Pickering, I. J. *J. Am. Chem. Soc.* **1996**, *118*, 8623. (c) Mindiola, D. J.; Meyer, K.; Cherry, J.-P. F.; Baker, T. A.; Cummins, C. C. *Organometallics* **2000**, *19*, 1622. (d) Solari, E.; Da Silva, C.; Iacono, B.; Hesschenbrouck, J.; Rizzoli, C.; Scopelli, R.; Floriani, C. *Angew. Chem., Int. Ed.* **2001**, *40*, 3907. (e) Yandulov, D. V.; Schrock, R. R. *J. Am. Chem. Soc.* **2002**, *124*, 6252.
- (10) (a) Anderson, S. N.; Richards, R. L.; Hughes, D. L. *Chem. Commun.* **1982**, 1291. (b) Carmona, E.; Marin, J. M.; Poveda, M. L.; Atwood, J. L.; Rogers, R. D. *Polyhedron* **1983**, *2*, 185. (c) Murray, R. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 4557. (d) Anderson, S. N.; Richards, R. L.; Hughes, D. L. *J. Chem. Soc., Dalton Trans.* **1986**, 245. (e) Hu, C.; Hodgeman, W. C.; Bennett, D. W. *Inorg. Chem.* **1996**, *35*, 1621. (f) Butts, M. D.; Bryan, J. C.; Luo, X.-L.; Kubas, G. J. *Inorg. Chem.* **1997**, *36*, 3341. (g) Habeck, C. M.; Lehnert, N.; Nather, C.; Tuzcek, F. *Inorg. Chim. Acta* **2002**, *337*, 11.
- (11) (a) Yandulov, D. V.; Schrock, R. R. *Science* **2003**, *301*, 76. (b) Schrock, R. R. *Acc. Chem. Res.* **2005**, *38*, 955.
- (12) (a) Girolami, G. S.; Salt, J. E.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Am. Chem. Soc.* **1983**, *105*, 5954. (b) Salt, J. E.; Girolami, G. S.; Wilkinson, G.; Montevalli, M.; Thornton-Pett, M.; Hursthouse, M. B. *Dalton Trans.* **1985**, 685.
- (13) Sellman, D.; Maisell, G. Z. *Naturforsch.* **1972**, *27B*, 465.
- (14) (a) Karsch, H. H. *Angew. Chem., Int. Ed. Engl.* **1977**, *17*, 56. (b) Sobota, P.; Jezowski-Trzebiatowska, B. *J. Organomet. Chem.* **1977**, *131*, 341.
- (15) Denholm, S.; Hunter, G.; Weakley, T. J. R. *Dalton Trans.* **1987**, 2789.
- (16) Vidyaratne, I.; Scott, J.; Gambarotta, S.; Budzelaar, P. H. M. *Inorg. Chem.* **2007**, *46*, 7040.
- (17) Monilla, W. H.; Yap, G. P. A.; MacAdams, L. A.; Theopold, K. H. *J. Am. Chem. Soc.* **2007**, *129*, 8090.
- (18) (a) Lichtenberger, D. L.; Renshaw, S. K.; Bullock, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 3276. (b) Lichtenberger, D. L.; Renshaw, S. K. *Organometallics* **1993**, *12*, 3522. (c) Manna, J.; John, K. D.; Hopkins, M. D. *Adv. Organomet. Chem.* **1995**, *38*, 79, and references therein. (d) Belanzoni, P.; Re, N.; Sgamellotti, A.; Floriani, C. *Dalton Trans.* **1997**, 4773. (e) Berben, L. A.; Long, J. R. *Inorg. Chem.* **2005**, *44*, 8459.
- (19) (a) Nast, R.; Sirtl, E. *Chem. Ber.* **1955**, *88*, 1723. (b) *Z. Anorg. Allg. Chem.* **1963**, *320*, 135. (c) Schlientz, W. J.; Ruff, J. K. *J. Chem. Soc. A* **1971**, 1139. (d) Nast, R. *Coord. Chem. Rev.* **1982**, *47*, 89, and references therein. (e) Berben, L. A.; Long, J. R. *J. Am. Chem. Soc.* **2002**, *124*, 11588.
- (20) (a) Some examples of non-octahedral monovalent and divalent chromium acetylide complexes include Schlientz, W. J.; Ruff, J. K. *J. Chem. Soc. A* **1971**, *9*, 1131. (b) Nesmeyanov, A. N.; Makarova, L. G.; Vinogradova, V. N.; Korneva, V. N.; Ustynyuk, N. A. *J. Organomet. Chem.* **1979**, *166*, 217. (c) Cotton, F. A.; Daniels, L. M.; Murillo, C. A.; Pascual, I. *Inorg. Chem.* **1988**, *1*, 1. (d) Ustynyuk, N. A.; Filatova, T. V.; Vinogradova, V. N.; Leont'eva, L. I.; Semeikin, O. V.; Epshtein, L. M.; Shubina, E. S.; Saitkulova, L. N.; Bakhmutova, E. V.; Chistyakov, A. L.; Stankevich, I. V. *Russ. Chem. Bull.* **1999**, *48*, 1165. (e) Berry, J. F.; Cotton, F. A.; Lu, T.; Murillo, C. A.; Roberts, B. K.; Wang, X. *J. Am. Chem. Soc.* **2004**, *126*, 7082.
- (21) Girolami, G. S.; Wilkinson, G.; Galas, A. M. R.; Thornton-Pett, M.; Hursthouse, M. B. *Dalton Trans.* **1985**, 1339.

warming to room temperature with vigorous stirring, a dark orange solution formed, which was stirred for an additional 2 h before removal of the solvent in vacuo. The orange-brown product was extracted into hexanes (ca. 10 mL), filtered to remove LiCl, and stored at  $-25\text{ }^{\circ}\text{C}$ . After 2 days, 0.25 g of orange plate-shaped crystals of product were collected by filtration and dried under  $\text{N}_2$ . Concentration of the solution to about 3 mL and cooling to  $-25\text{ }^{\circ}\text{C}$  yielded further crops, to give **1** (0.38 g) in 29% crystalline yield. Absorption spectrum (MeCN):  $\lambda_{\text{max}}$  ( $\epsilon_{\text{M}}$ ) 264 (sh, 15390), 291 (16740), 352 (15320), 426 (58860), 942 (25340  $\text{L mol}^{-1}\text{cm}^{-1}$ ) nm. IR(solid, ATR):  $\lambda_{\text{CC}}$  2011 (w),  $\lambda_{\text{CSi}}$  836 (s)  $\text{cm}^{-1}$ .  $\mu_{\text{eff}} = 2.77\ \mu_{\text{B}}$  at 295 K. ES<sup>+</sup>-MS (MeCN/THF):  $m/z$  546 ([**1**]<sup>+</sup>). Anal. Calcd for  $\text{C}_{40}\text{H}_{96}\text{Cr}_2\text{N}_2\text{P}_8\text{Si}_2$ : C, 47.42; H, 9.55; N, 2.77. Found: C, 47.50; H, 9.82; N, 2.61. <sup>1</sup>H-NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  5.10 (br, 18H, SiMe<sub>3</sub>), 2.18 (br, 8H, PCH<sub>2</sub>), -2.85 (br, 24H, PCH<sub>3</sub>), -4.35 (br, 8H, PCH<sub>2</sub>), -20.17 (br, 24H, PCH<sub>3</sub>).

**trans-(dmpe)<sub>2</sub>Cr(N<sub>2</sub>)<sub>2</sub> (2).** A green solution of *trans*-(dmpe)<sub>2</sub>CrCl<sub>2</sub> (0.55 g, 1.3 mmol) in THF (10 mL) was cooled to  $-73\text{ }^{\circ}\text{C}$ , and *n*BuLi (1.0 mL, 2.5 mmol, 2.5 M hexanes solution) was added. The reaction was allowed to warm to room temperature, and the color of the solution changed to dark red. After stirring for 10 h, the solvent was removed in vacuo, toluene (10 mL) was added, and a yellow solid was separated from a red solution by filtration through celite. The toluene was removed in vacuo to afford **2** as a red solid (0.45 g, 85%) which was crystallized from a saturated solution of toluene (5 mL) to give 0.25 g (47%) of product. The unit cell parameters and <sup>1</sup>H NMR and IR spectra of this compound were consistent with previous reports.<sup>12</sup>

**trans-(dmpe)<sub>2</sub>Cr(CCSiMe<sub>3</sub>)<sub>2</sub> (3) from trans-(dmpe)<sub>2</sub>CrCl<sub>2</sub>.** A solution of Me<sub>3</sub>SiCCH (45 mg, 0.46 mmol) in THF (5 mL) was cooled to  $-78\text{ }^{\circ}\text{C}$ , and *n*BuLi (0.22 mL, 0.55 mmol) was added. After stirring the colorless solution for 1 h at room temperature, a green solution of *trans*-(dmpe)<sub>2</sub>CrCl<sub>2</sub> (99 mg, 0.23 mmol) in THF (5 mL) was added dropwise, inducing an immediate color change to red. The solution was stirred for 12 h, and the solvent was removed under reduced pressure. Toluene was added, and a white precipitate was removed by filtration. The solvent was removed under reduced pressure to give 120 mg (94%) of **3** as a dark orange powder. X-ray quality crystals of **3** were obtained from concentrated solutions of toluene cooled to  $-25\text{ }^{\circ}\text{C}$ . Absorption spectrum (THF):  $\lambda_{\text{max}}$  ( $\epsilon_{\text{M}}$ ) 255 (11300), 269 (sh, 7560), 281 (sh, 6220), 351 (4790), 365 (5030), 395 (3510  $\text{L mol}^{-1}\text{cm}^{-1}$ ) nm. IR (solid, ATR):  $\lambda_{\text{CC}}$  1973 (m), 1932 (w),  $\lambda_{\text{CSi}}$  836 (s)  $\text{cm}^{-1}$ .  $\mu_{\text{eff}} = 2.55\ \mu_{\text{B}}$  at 295 K. ES<sup>+</sup>-MS (MeCN/THF):  $m/z$  546 ([**3**]<sup>+</sup>). Anal. Calcd for  $\text{C}_{22}\text{H}_{50}\text{P}_4\text{Si}_2\text{Cr}$ : C, 48.37; H, 9.15. Found: C, 48.56; H, 9.27. <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  -27.6 (s, 24H, PCH<sub>3</sub>), -3.9 (s, 8H, PCH<sub>2</sub>) 9.05 (s, 18H, SiMe<sub>3</sub>).

**trans-(dmpe)<sub>2</sub>Cr(CCSiMe<sub>3</sub>)<sub>2</sub> (3) from trans-(dmpe)<sub>2</sub>Cr(N<sub>2</sub>)<sub>2</sub>.** To a red solution of *trans*-(dmpe)<sub>2</sub>Cr(N<sub>2</sub>)<sub>2</sub> (27 mg, 0.066 mmol) in toluene (5 mL) was added Me<sub>3</sub>SiCCH (16 mg, 0.16 mmol). The reaction mixture was heated for 12 h at  $80\text{ }^{\circ}\text{C}$  and then filtered through Celite. The solvent was removed under reduced pressure to afford 36 mg (97%) of **3** as an orange solid. When this reaction was carried out in a sealed NMR tube, a <sup>1</sup>H resonance at 4.47 ppm attributable to H<sub>2</sub> was observed.

**trans-(dmpe)<sub>2</sub>Cr(CCSiMe<sub>3</sub>)<sub>2</sub> (3) from trans-(dmpe)<sub>2</sub>CrMe<sub>2</sub>.** A solution of *trans*-(dmpe)<sub>2</sub>CrMe<sub>2</sub> (20 mg, 0.052 mmol) and Me<sub>3</sub>SiCCH (21 mg, 0.21 mmol) in toluene-*d*<sub>8</sub> was sealed in a quartz NMR tube fitted with a J. Young cap and then irradiated with 320 nm radiation in a Rayonet apparatus. After 18 h, the solution had become dark orange, and the <sup>1</sup>H NMR spectrum indicated that complete conversion to **3** had occurred with no formation of side products.

**Table 1.** Crystallographic Data<sup>a</sup> for the Complexes *trans,trans*-[(Me<sub>3</sub>SiCC)(dmpe)<sub>2</sub>Cr]<sub>2</sub>( $\mu$ -N<sub>2</sub>)·Hexane (**1**) and *trans*-(dmpe)<sub>2</sub>Cr(CCSiMe<sub>3</sub>)<sub>2</sub> (**3**)

	<b>1</b>	<b>3</b>
formula	C <sub>40</sub> H <sub>96</sub> Cr <sub>2</sub> N <sub>2</sub> P <sub>8</sub> Si <sub>2</sub>	C <sub>16</sub> H <sub>50</sub> CrP <sub>4</sub> Si <sub>2</sub>
fw	1013.11	546.68
T, K	124	165
space group	C2/c	P $\bar{1}$
Z	8	1
a, Å	37.302(8)	9.349(3)
b, Å	20.407(4)	9.985(3)
c, Å	16.971(3)	10.209(4)
$\alpha$ , deg		70.405(5)
$\beta$ , deg	116.85(3)	64.705(5)
$\gamma$ , deg		72.222(5)
V, Å <sup>3</sup>	11526(4)	797.0(5)
$d_{\text{calc}}$ , g/cm <sup>3</sup>	1.673	1.139
$R_1(wR_2)$ , %	9.45 (27.88)	4.58 (11.11)

<sup>a</sup> Obtained with graphite-monochromated Mo K $\alpha$  ( $\lambda = 0.71073\text{ \AA}$ ) radiation. <sup>b</sup>  $R_1 = \sum \Delta F_o / \sum |F_o|$ ,  $wR_2 = \{\sum [w(F_o^2 - F_c^2)]^2 / \sum [w(F_o^2)^2]\}^{1/2}$ .

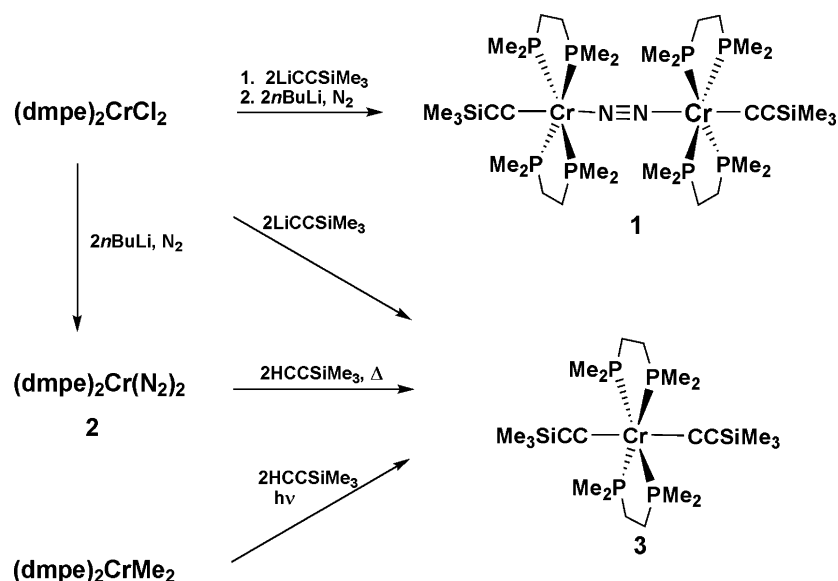
**X-ray Structure Determinations.** Single crystal X-ray structure determinations were performed for compounds **1** and **3** (see Table 1).<sup>22</sup> Crystals were quickly coated in Paratone-N oil under a nitrogen atmosphere, mounted on Kapton loops, transferred to a Siemens APEX diffractometer, and cooled in a nitrogen stream. Initial lattice parameters were obtained from a least-squares analysis of more than 30 centered reflections; these parameters were later refined against all data. A full hemisphere of data was collected for all compounds. Data were integrated and corrected for Lorentz polarization effects using SAINT<sup>22b</sup> and were corrected for absorption effects using SADABS 2.3.<sup>22c</sup>

Space group assignments were based upon systematic absences, *E* statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps and were refined against all data using the SHELXL 5.0 software package.<sup>22d</sup> Thermal parameters for all non-hydrogen atoms were refined anisotropically, except for the disordered dmpe ligands and hexane solvate molecules in **1**. Refinement of the N atoms in **1** as either C or O atoms resulted in unreasonable thermal parameters. Hydrogen atoms, where added, were assigned to ideal positions and refined using a riding model with an isotropic thermal parameter 1.2 times that of the attached carbon atom (1.5 times for methyl hydrogens).

**Other Physical Measurements.** Absorption spectra were measured with a Hewlett-Packard 8453 spectrophotometer. Infrared spectra were recorded on a Nicolet Avatar 360 FTIR spectrometer equipped with a horizontal attenuated total reflectance (ATR) accessory. Cyclic voltammetry was performed in a 0.1 M solution of (Bu<sub>4</sub>N)ClO<sub>4</sub> in THF using a Bioanalytical systems CV-50W voltammograph, a platinum disk working electrode, a platinum wire supporting electrode, and a silver wire reference electrode. Reported potentials are all referenced to the [Fe(Cp)<sub>2</sub>]<sup>0/+</sup> couple and were determined using decamethylferrocene as an internal standard ( $-0.58\text{ V}$  versus [Fe(Cp)<sub>2</sub>]<sup>0/+</sup> for this system). Magnetic susceptibility data were measured on a Quantum Design MPMS-XL SQUID magnetometer for compound **1** with the sample sealed in a polycarbonate capsule and a heat-sealable plastic bag. Diamagnetic

(22) (a) *SMART Software Users Guide*, Version 5.1; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 1999. (b) *SAINT Software Users Guide*, Version 7.0; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 1999. (c) Sheldrick, G. M. *SADABS*, Version 2.03; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 2000. (d) Sheldrick, G. M. *SHELXL*, Version 6.12; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 1999. (e) *International Tables for X-Ray Crystallography*; Kluwer Academic Publishers: Dordrecht, 1992; Vol. C.

Scheme 1



corrections were obtained from Pascal's constants and for the sample holder by subtraction of the measured susceptibility of an empty holder. The Evans method was used for determining the room temperature susceptibility of compound **3**.<sup>23</sup> Mass spectrometric measurements were performed on VG Quattro (Micromass) spectrometer equipped with an analytical electrospray ion source instrument. NMR spectra were measured with a Bruker AVB 400 MHz instrument. Elemental analyses were performed by the UC Berkeley, Department of Chemistry Analytical Facility.

**Electronic Structure Calculations.** Density-functional theory (DFT) calculations were performed using Jaguar version 6.5<sup>24</sup> with a spin-unrestricted formalism for compound **1**; a small amount of spin contamination was observed (12%). Electronic structure calculations were performed on *trans,trans*-[(HCC)(dpe)<sub>2</sub>Cr]<sub>2</sub>(μ-N<sub>2</sub>) (dpe = diphosphinoethane) as a model for complex **1**. Complex geometries were taken from the crystal structure of **1** and optimized using the B3LYP functional.<sup>25</sup> The bond lengths and angles for the optimized structure deviated from those observed in the crystal structure by less than 4%. Effective core potentials were employed for Cr and Si (LACVP\*\*) together with the corresponding Gaussian basis sets.<sup>26</sup> The 6-31+G\* basis set was used for C, P, N, and H.<sup>27</sup>

## Results and Discussion

**Synthesis of *trans,trans*-[(Me<sub>3</sub>SiCC)(dmpe)<sub>2</sub>Cr]<sub>2</sub>(μ-N<sub>2</sub>) (**1**).** Our entry into chromium dinitrogen chemistry arose when the reaction of LiCCSiMe<sub>3</sub> with *trans*-(dmpe)<sub>2</sub>CrCl<sub>2</sub> yielded a small amount of crystalline *trans,trans*-[(Me<sub>3</sub>-SiCC)(dmpe)<sub>2</sub>Cr]<sub>2</sub>(μ-N<sub>2</sub>) (**1**) in addition to the targeted product, *trans*-(dmpe)<sub>2</sub>Cr(CCSiMe<sub>3</sub>)<sub>2</sub> (**3**). Optimization of the stoichiometry and the reaction times enabled compounds **1** and **3** to be exclusively synthesized (Scheme 1). In the first step of the optimized synthesis of **1**, two equivalents of *n*BuLi were added to a 1:1 solution of *trans*-(dmpe)<sub>2</sub>CrCl<sub>2</sub> and HCCSiMe<sub>3</sub> in THF held at -78 °C. Stirring this solution for 3 h at low temperature enabled all of the HCCSiMe<sub>3</sub> to be converted to LiCCSiMe<sub>3</sub>; the solution remained bright green during this time. Upon removal of the cooling bath and with rapid stirring of the reaction mixture to ensure saturation with N<sub>2</sub>, the color of the solution quickly turned to dark orange. Removal of the solvent under vacuum after no more than 1 h, followed by extraction of the product into hexane, and cooling of the solution to -25 °C for over 1 week allowed **1** to be isolated in high purity as small, plate-shaped crystals in 29% crystalline yield.

Compound **1** is very soluble in common organic solvents and was analyzed by a variety of spectroscopic techniques. The UV-vis absorption spectrum of **1** is dominated by intense metal-to-ligand charge-transfer (MLCT) and ligand-to-metal charge transfer (LMCT) bands at high energy, which obscure any d-d transitions that may otherwise have been observed. The nature of the intense low energy band at 942 nm (25340 L mol<sup>-1</sup> cm<sup>-1</sup>) is unknown; however, it is most likely because of a d-d transition to which the highly covalent bonding nature imparts significant ligand character or a LMCT absorption.<sup>28</sup> Although **1** is paramagnetic, with a magnetic moment of 2.77 μ<sub>B</sub> at 298 K, the <sup>1</sup>H NMR

(23) (a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003. (b) Beccoals, J. K. *Mol. Phys.* **1968**, *15*, 129.

(24) *Jaguar*, Version 6.5; Schrödinger, LLC: New York, NY, 2005.

(25) Zheng, K. C.; Wang, J. P.; Peng, W. L.; Liu, X. W.; Yun, F. C. *J. Phys. Chem. A* **2001**, *105*, 10899.

(26) (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270. (b) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284. (c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299. (d) Dunning, T. H., Jr.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., Ed.; Plenum: New York, 1976; Vol. 3, p 1. (e) Check, C. E.; Faust, T. O.; Bailey, J. M.; Wright, B. J.; Gilbert, T. M.; Sunderlin, L. S. *J. Phys. Chem. A* **2001**, *105*, 8111.

(27) (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. (b) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. (c) Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 4233. (d) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (e) Binkley, J. S.; Pople, J. A. *J. Chem. Phys.* **1977**, *66*, 879. (f) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; DeFrees, D. J.; Pople, J. A.; Gordon, M. S. *J. Chem. Phys.* **1982**, *77*, 3654.

(28) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, 1984.

spectrum is informative and contains five paramagnetically shifted resonances that have peak areas in a ratio of 12:12:9:4:4. Resonances attributable to the methyl (−2.84 and −20.2 ppm) and methylene (2.18 and −4.37 ppm) protons of the dmpe ligands were resolved, and the resonance for the SiMe<sub>3</sub> group is shifted downfield to 5.10 ppm. The IR spectrum displays just one peak in the region 1800–2100 cm<sup>−1</sup> that is attributed to the C≡C stretching mode (2011 cm<sup>−1</sup>). As for the [(CO)<sub>2</sub>(η<sup>6</sup>-C<sub>6</sub>Et<sub>6</sub>)Cr]<sub>2</sub>(μ-N<sub>2</sub>) complex,<sup>15</sup> there is no peak in the IR spectrum of **1** that is attributable to a N≡N stretching mode, which is consistent with the centrosymmetric geometry.

Compound **1** is remarkably stable when compared to many of the known mono- and dinuclear chromium dinitrogen complexes. Heating a toluene-*d*<sub>8</sub> solution of **1** at 90 °C under vacuum, under a dinitrogen atmosphere, or in the presence of HCCSiMe<sub>3</sub> for 48 h yielded no appreciable change to the <sup>1</sup>H NMR spectrum. Additionally, when compound **1** was photolysed with 320 nm radiation in a Rayonet apparatus for 48 h, no decomposition was apparent by <sup>1</sup>H NMR spectroscopy. In contrast to the (dmpe)<sub>2</sub>Cr(N<sub>2</sub>)<sub>2</sub> (**2**) complex, which reacts with HCCSiMe<sub>3</sub> (vide infra), the Cr–N<sub>2</sub>–Cr bonds remain intact after heating **1** as high as 90 °C in the presence of HCCSiMe<sub>3</sub> which suggests that the stability of **1** might be related to the presence of the π-donating acetylide ligands. In addition, it appears that **1** represents a rare example of an octahedral chromium(I) complex which is not of the form (CO)<sub>5</sub>CrX (where X = a monoanionic ligand).<sup>29</sup>

**Synthesis of *trans*-(dmpe)<sub>2</sub>Cr(N<sub>2</sub>)<sub>2</sub> (**2**).** In the reaction to form compound **1**, reduction of the chromium center is occurring to yield a Cr(I) species from the Cr(II) starting material. It seemed possible that this synthetic procedure should be extendable to other systems and provide a convenient approach for the synthesis of other Cr/N<sub>2</sub> compounds. In an effort to further probe this idea, reactions between *n*BuLi and *trans*-(dmpe)<sub>2</sub>CrCl<sub>2</sub> were investigated. Previously, it has been established that *trans*-(dmpe)<sub>2</sub>CrCl<sub>2</sub> reacted with *n*BuLi under H<sub>2</sub> or Ar atmospheres to form (dmpe)<sub>2</sub>Cr(H)<sub>4</sub>.<sup>12</sup> However, when one equivalent of *n*BuLi was reacted with *trans*-(dmpe)<sub>2</sub>CrCl<sub>2</sub> under an atmosphere of N<sub>2</sub>, the crude reaction mixture analyzed by <sup>1</sup>H NMR spectroscopy to contain both *trans*-(dmpe)<sub>2</sub>CrCl<sub>2</sub> and *trans*-(dmpe)<sub>2</sub>Cr(N<sub>2</sub>)<sub>2</sub> (**2**) as the major components of a mixture of products. Compound **2** was cleanly synthesized by reacting two equivalents of *n*BuLi with (dmpe)<sub>2</sub>CrCl<sub>2</sub> under an atmosphere of N<sub>2</sub> (Scheme 1), and characterized by comparison of the <sup>1</sup>H NMR and IR spectra and the unit cell parameters with the previously reported data.<sup>12</sup> This synthesis of **2** represents a useful alternative to the previously reported procedure<sup>12</sup> because it avoids the use of mercury yet provides synthetically useful quantities of *trans*-(dmpe)<sub>2</sub>Cr(N<sub>2</sub>)<sub>2</sub>.

**Synthesis of *trans*-(dmpe)<sub>2</sub>Cr(CCSiMe<sub>3</sub>)<sub>2</sub> (**3**).** The synthesis of **3** could be achieved by reacting *trans*-(dmpe)<sub>2</sub>CrCl<sub>2</sub> with two equivalents of LiCCSiMe<sub>3</sub>. Precise control over reaction stoichiometry, achieved by titrating the hexane

**Table 2.** Selected Average Interatomic Distances (Å) and Angles (deg) for the Complexes *trans,trans*-[(Me<sub>3</sub>SiCC)(dmpe)<sub>2</sub>Cr]<sub>2</sub>(μ-N<sub>2</sub>)·Hexane (**1**) and *trans*-(dmpe)<sub>2</sub>Cr(CCSiMe<sub>3</sub>)<sub>2</sub> (**3**)

	<b>1</b>	<b>3</b>
Cr–P	2.315(4)	2.334(6)
Cr–N	1.870(10)	
Cr–C	2.007(10)	2.043(3)
N≡N <sup>a</sup>	1.177(10)	
C≡C	1.24(1)	1.207(4)
C–Si	1.810(10)	1.815(3)
P–Cr–P	81.9(2), 96.9(2), 167.7(2)	83.07(4), 96.92(4), 180
P–Cr–N	96.1(3)	
P–Cr–C	84.9(4)	90.0(3)
C–Cr–N	177.8(4)	
Cr–N≡N	177.1(8)	
Cr–C≡C	177.4(1)	176.4(2)
C≡C–Si	178.5(8)	173.5(3)

<sup>a</sup> bond-length from one measurement only, not an average.

solution of *n*BuLi, and longer reaction times (12 h) than employed in the synthesis of **1** were required to obtain a pure product. The C≡C stretching frequency in the IR spectrum of **3** occurs at a lower frequency (1969 cm<sup>−1</sup>) than in the case of **1**, and the identity of this product was confirmed by single crystal X-ray diffraction. As in the case of compound **1**, the <sup>1</sup>H NMR spectrum of the paramagnetic compound **3** is informative and contains three paramagnetically shifted resonances that have peak areas in a ratio of 12:9:4. There is one distinct chemical shift for each of the methyl and methylene resonances of dmpe at −27.6 and −3.9 ppm, respectively, indicating that the complex favors the *trans* configuration in solution.

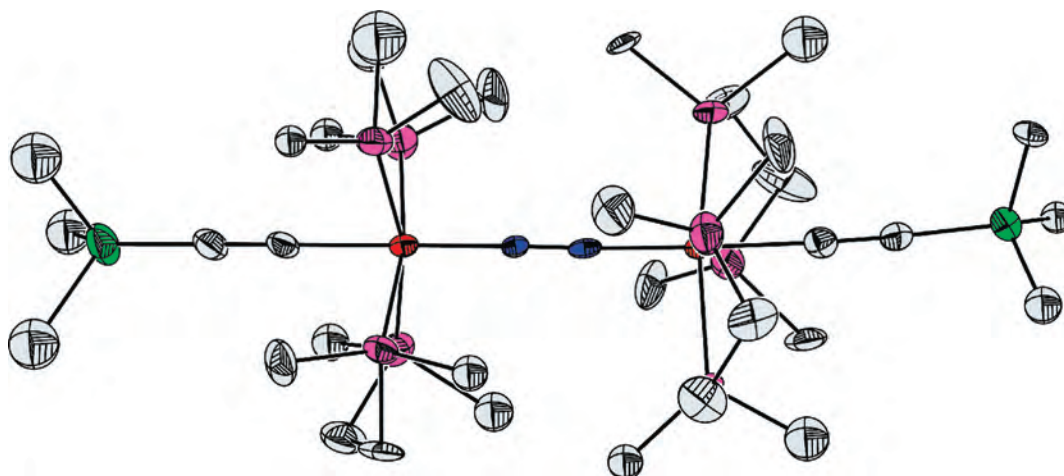
Compound **3** can also be synthesized from *trans*-(dmpe)<sub>2</sub>Cr(N<sub>2</sub>)<sub>2</sub> (**2**) by reduction of HCCSiMe<sub>3</sub> to (CCSiMe<sub>3</sub>)<sup>1−</sup> and H<sub>2</sub> (Scheme 1). In contrast to **1**, which showed no reactivity with HCCSiMe<sub>3</sub>, the reaction between **2** and HCCSiMe<sub>3</sub> proceeds in an NMR tube that was flame sealed under vacuum, and the formation of H<sub>2</sub> was observed by <sup>1</sup>H NMR spectroscopy. This reaction also proceeds under dinitrogen atmospheres when heated at 60 °C for 12 h. In contrast, it has been shown previously that the reaction of **2** with PhCCPh under thermal conditions leads to formation of *cis*-(dmpe)<sub>2</sub>Cr(PhCCPh)<sub>2</sub>, and it has also been reported that complex **2** does not react with HCCPh to form an analogue of **3** under photolysis conditions; this reaction was not investigated at elevated temperatures.<sup>12</sup>

A third method for the synthesis of **3** was also developed. When HCCSiMe<sub>3</sub> was added to a solution of *trans*-(dmpe)<sub>2</sub>CrMe<sub>2</sub> in THF and the mixture was photolyzed (320 nm) for 18 h, the <sup>1</sup>H NMR spectrum indicated complete consumption of the reactants and quantitative formation of **3** (Scheme 1). Photolysis has previously been employed in the synthesis of similar compounds such as *trans*-(dmpe)<sub>2</sub>-Fe(CPh)<sub>2</sub> from (dmpe)<sub>2</sub>FeMe<sub>2</sub> and HCCPh.<sup>30</sup>

**Crystal Structures.** Orange plate-shaped crystals of **1** suitable for X-ray analysis were obtained by cooling a concentrated hexane solution at −25 °C for several days (see Tables 1 and 2). The diffraction data for **1** was of high enough quality to determine connectivity. However, factors such as loss of

(29) A search of the Cambridge Structural database revealed no octahedral chromium(I) complexes, other than those of the form (CO)<sub>5</sub>CrX (where X = monoanionic ligand).

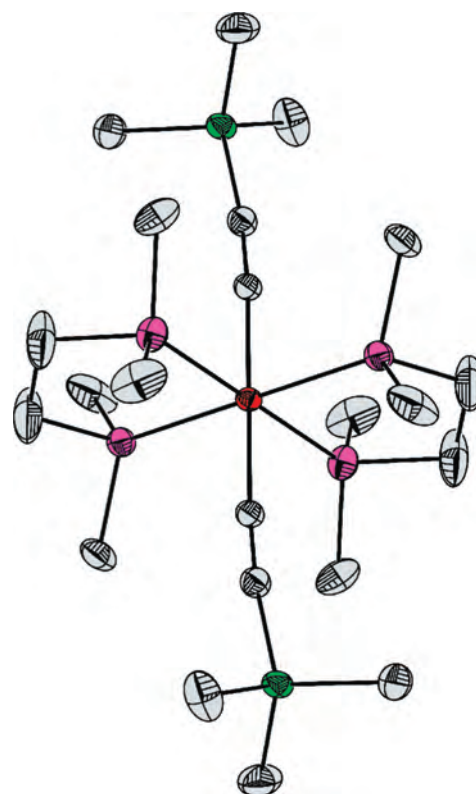
(30) Field, L. D.; Turbull, A. J.; Turner, P. *J. Am. Chem. Soc.* **2002**, *124*, 3692.



**Figure 1.** Structure of the dinitrogen complex *trans,trans*-[(Me<sub>3</sub>SiCC)(dmpe)<sub>2</sub>Cr]<sub>2</sub>( $\mu$ -N<sub>2</sub>) (**1**). Red, green, gray, pink, and blue ellipsoids represent Cr, Si, C, P, and N atoms, respectively; ellipsoids are shown at the 30% probability level, and H atoms are omitted for clarity.

solvate hexane molecules and the extremely narrow width of the plate-shaped crystal contributed to low resolution of the diffraction data, and large errors are associated with the distances and angles listed in Table 2. As shown in Figure 1, the ligand geometry around the chromium atoms is approximately octahedral. The dmpe ligands are slightly splayed out from the center of the molecule most likely because of steric interactions with the dmpe ligands on the opposite Cr center. The entire Si–C≡C–Cr–N≡N–Cr–C≡C–Si backbone of compound **1** is quite linear, as illustrated by the angles of the C≡C–Si, Cr–C≡C, C–Cr–N, and Cr–N≡N units which all deviate from 180° by only 3° at most. The 1.178(3) Å N≡N distance is slightly longer than the 1.0987 Å distance in free dinitrogen<sup>31</sup> suggesting that some small reduction of the N≡N triple bond has occurred.<sup>32</sup> Given the quality of the X-ray crystallographic data, caution must be taken when drawing conclusions based on the N≡N bond distance, however; the additional physical measurements described below are consistent with the formulation that **1** contains two Cr(I) ions bridged by neutral N<sub>2</sub>.

Compound **3** readily crystallizes from solutions of hexanes cooled to –25 °C as orange block-shaped crystals. As observed for **1**, the ligands adopt an octahedral geometry around the chromium center (Figure 2). The 2.043(3) Å Cr–C distance for the divalent **3** is comparable to the analogous 2.057(3) and 2.077(3) distances observed in trivalent [(Me<sub>3</sub>tacn)Cr(CCH)<sub>3</sub>]<sup>19</sup> (Me<sub>3</sub>tacn = *N, N', N''*-trimethyl-1,4,7-triazacyclononane) and Li<sub>3</sub>[Cr(CCSiMe<sub>3</sub>)<sub>6</sub>]·6THF complexes,<sup>18c</sup> respectively. Consistent with the expected triple bond character, the 1.207(4) Å acetylide C≡C distance is comparable to the 1.2033(2) Å distance in acetylene.<sup>34</sup> The C≡C–Si and Cr–C≡C angles deviate only slightly from 180° at 173.5(3)° and 176.4(3)°, respectively.



**Figure 2.** Structure of *trans*-(dmpe)<sub>2</sub>Cr(CCSiMe<sub>3</sub>)<sub>2</sub> (**3**). Red, green, pink, and gray spheres represent Cr, Si, P and C atoms, respectively; ellipsoids are shown at the 30% probability level, and H atoms are omitted for clarity.

**Magnetic Measurements.** Consistent with the X-ray structural characterization and elemental analysis data which formulate **1** as two  $S = 1/2$  Cr<sup>I</sup> ions bridged by a neutral N<sub>2</sub> ligand, values for  $\chi_{MT}$  of 0.96 cm<sup>3</sup> K/mol per dimer and a  $g$  value of 2.25 at 300 K were obtained (Figure 3). These values indicate that the chromium centers are essentially magnetically isolated.<sup>35</sup> The slight drop in  $\chi_{MT}$  at low temperature can be attributed to inter- or intramolecular antiferromagnetic

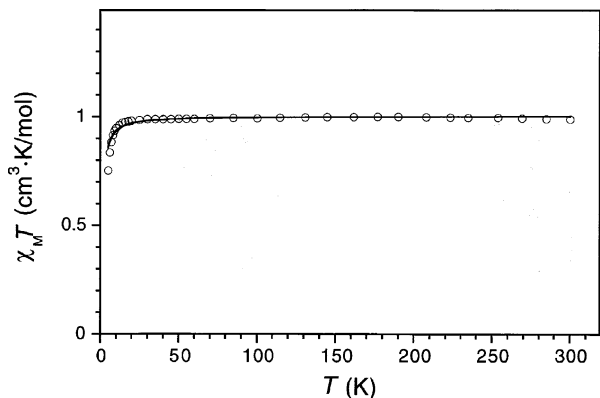
(31) Wilkinson, P. G.; Houk, N. B. *J. Chem. Phys.* **1956**, *24*, 528.

(32) Assignment of this molecule as a Cr(II)-diimide suggested would require an N–N single bond. Although the crystal structure is not of high quality, the N–N distance is clearly not a single bond. (NN triple bond = 1.0999 Å,<sup>31</sup> NN double bond = 1.22 Å, NN single bond = 1.45 Å,<sup>33</sup> observed here = 1.177(10) Å).

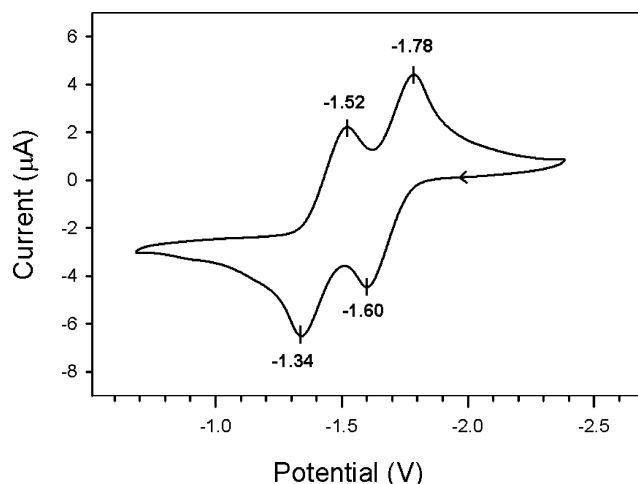
(33) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Butterworth Heinemann: Boston, 1997.

(34) Fast, H.; Welsh, H. L. *J. Mol. Spectrosc.* **1972**, *41*, 203.

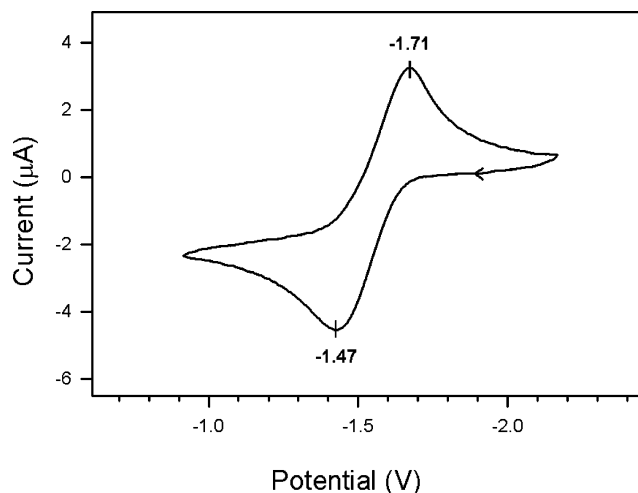
(35) (a) Kanamori, K. *Coord. Chem. Rev.* **2003**, *237*, 147. (b) Lukens, W. W., Jr.; Andersen, R. A. *Inorg. Chem.* **1995**, *34*, 3440. (c) Ren, Q.; Chen, Z.; Ren, J.; Wei, H.; Feng, W.; Zhang, L. *J. Phys. Chem. A* **2002**, *106*, 6161.



**Figure 3.** Magnetic behavior of *trans,trans*-[(Me<sub>3</sub>SiCC)(dmpe)<sub>2</sub>Cr]<sub>2</sub>(μ-N<sub>2</sub>) (**1**) (circles) in an applied field of 10 kG. The solid line represents a calculated fit to the data.



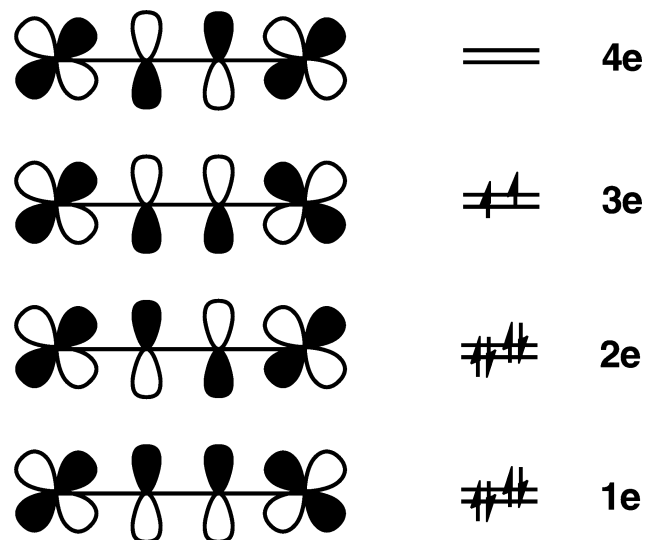
**Figure 4.** Cyclic voltammogram of *trans,trans*-[(Me<sub>3</sub>SiCC)(dmpe)<sub>2</sub>Cr]<sub>2</sub>(μ-N<sub>2</sub>) (**1**) in THF. The measurements were performed on a platinum electrode at a scan rate of 100 mV/s with 0.1 M (Bu<sub>4</sub>N)ClO<sub>4</sub> as the supporting electrolyte. Potentials are referenced to Fe(Cp)<sub>2</sub>/Fe(Cp)<sub>2</sub><sup>+</sup>.



**Figure 5.** Cyclic voltammogram of *trans*-(dmpe)<sub>2</sub>Cr(CCSiMe<sub>3</sub>)<sub>2</sub> (**3**) in THF. The measurements were performed on a platinum electrode at a scan rate of 100 mV/s with 0.1 M (Bu<sub>4</sub>N)ClO<sub>4</sub> as the supporting electrolyte. Potentials are referenced to Fe(Cp)<sub>2</sub>/Fe(Cp)<sub>2</sub><sup>+</sup>.

interactions. The data for **1** were fit using an exchange Hamiltonian of the form  $\hat{H} = -2J\hat{S}_{Cr(1)} \cdot \hat{S}_{Cr(2)}$ , to give  $J =$

**Scheme 2**



$-0.91 \text{ cm}^{-1}$ .<sup>36</sup> The small magnitude of this magnetic coupling is in agreement with that observed in other dinitrogen bridged complexes of early first-row transition metals such as  $[\{K(\text{diglyme})_3(\mu\text{-mesitylene})_2(3,5\text{-Me}_2\text{C}_6\text{H}_3\text{V})_2(\mu\text{-N}_2)\}]$  at  $J = -0.65 \text{ cm}^{-1}$ .<sup>6d</sup> Magnetic susceptibility measurements performed on compound **3** revealed a magnetic moment of  $2.55 \mu_B$ . This value is in close agreement with those reported for *trans*-(dmpe)<sub>2</sub>CrCl<sub>2</sub> and *trans*-(dmpe)<sub>2</sub>CrMe<sub>2</sub> at 2.76 and  $2.70 \mu_B$ , respectively.<sup>21</sup>

**Electrochemical Measurements.** Evidence for the existence of electron delocalization between the Cr(I) centers of **1** is seen in the cyclic voltammogram (Figure 4). The experiment was performed in a 1 mM solution of **1** in THF with 0.1 M Bu<sub>4</sub>NClO<sub>4</sub> as the supporting electrolyte. Two distinct oxidation events are evident at  $E_{1/2} = -1.69 \text{ V}$  ( $\Delta E_p = 185 \text{ mV}$ ) and  $-1.43 \text{ V}$  ( $\Delta E_p = 182 \text{ mV}$ ) versus Fe(Cp)<sub>2</sub>/Fe(Cp)<sub>2</sub><sup>+</sup>. The oxidation waves are each one-electron in nature and are assigned to the Cr<sup>I</sup><sub>2</sub>/Cr<sup>II</sup> and Cr<sup>I</sup>Cr<sup>II</sup>/Cr<sup>II</sup> couples, respectively. The separation between these two couples in the cyclic voltammogram of **1** indicates a comproportionation constant of  $K_c = 10^{4.5}$  associated with the following equilibrium (eq 1).



This value is comparable to that usually associated with class II mixed-valent compounds<sup>37</sup> and is significantly smaller than the value of  $K_c = 10^{9.9}$  calculated for the mixed-valent state of  $[\text{K}(\text{diglyme})_3][(\text{3,5-Me}_2\text{C}_6\text{H}_3\text{V})_2(\mu\text{-N}_2)]$  in which the dinitrogen bridge has been significantly reduced.<sup>6d</sup> The voltammogram for **3** displays one reversible wave at  $-1.59 \text{ V}$  ( $\Delta E_p = 242 \text{ mV}$ ) versus Fe(Cp)<sub>2</sub>/Fe(Cp)<sub>2</sub><sup>+</sup>, which is assigned to the Cr<sup>II</sup>/Cr<sup>III</sup> couple (Figure 5).

**Electronic Structure Considerations.** Electronic structure calculations were performed on the model complex *trans*-

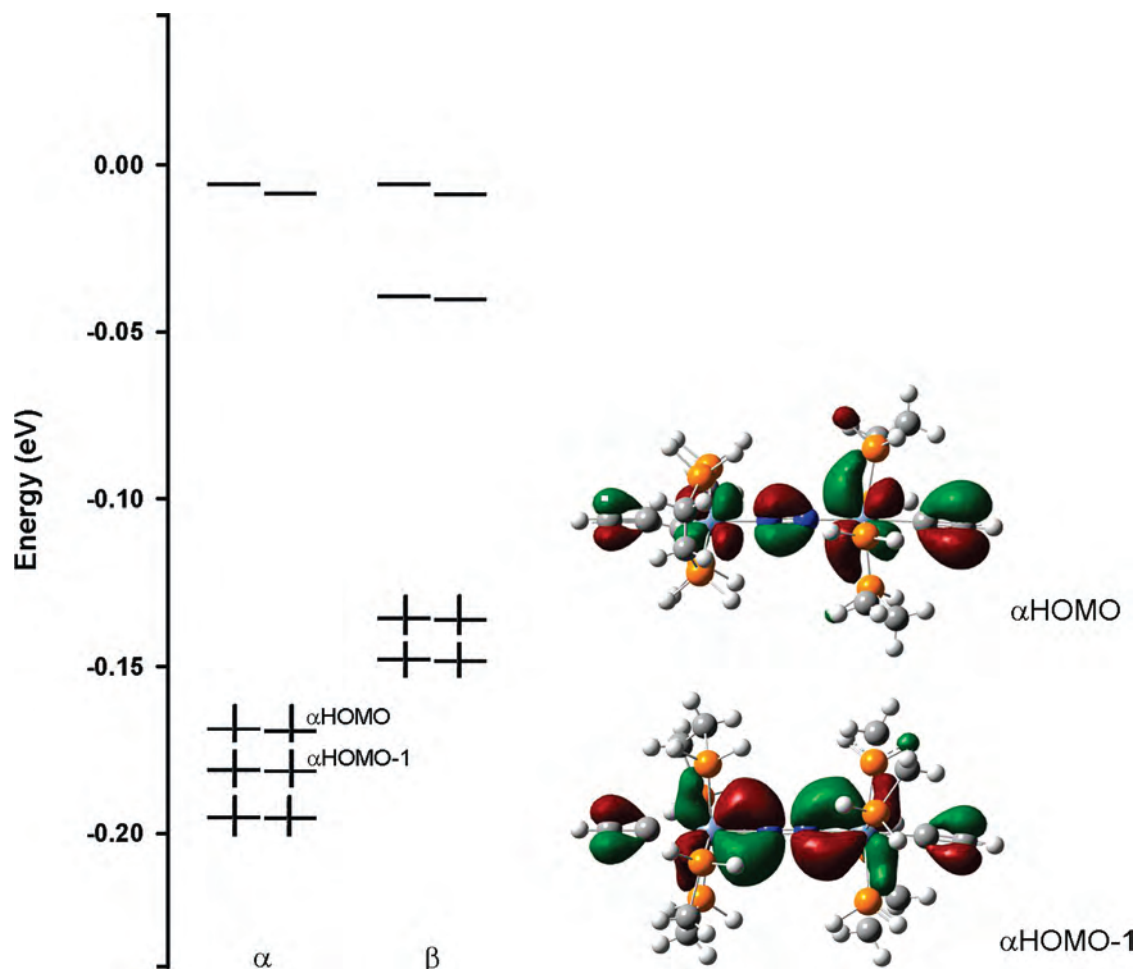
(36) Schmitt, E. A., Ph. D. Thesis, University of Illinois at Urbana-Champaign, 1995.

(37) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247.

(38) (a) Chatt, J.; Fay, R. C.; Richards, R. L. *J. Chem. Soc. A* **1971**, 2399.

(b) Treitel, J. M.; Flood, M. T.; March, R. E.; Gray, H. B. *J. Am. Chem. Soc.* **1969**, *91*, 6512. (c) Treitel, J. M.; Flood, M. T.; March,

R. E.; Gray, H. B. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 639.



**Figure 6.** Frontier portion of the energy level diagram calculated for *trans,trans*-[(HCC)(dpe)<sub>2</sub>Cr]<sub>2</sub>( $\mu$ -N<sub>2</sub>). One each of the degenerate  $\alpha$  HOMO and  $\alpha$  HOMO-1 molecular orbitals are shown.

*s,trans*-[(HCC)(dpe)<sub>2</sub>Cr]<sub>2</sub>( $\mu$ -N<sub>2</sub>). As expected for a complex consisting of two dinitrogen-bridged octahedral metal centers, the frontier molecular orbitals comprise a series of four doubly degenerate energy levels whose energies increase with increasing nodal number (Scheme 2).<sup>38,6d</sup> The nature of the metal nitrogen and metal acetylide interactions in the highest occupied molecular orbital (HOMO) are similar, both are antibonding with respect to the Cr–N bond because of contributions from the dinitrogen and acetylide  $\pi$ -bonding orbitals (Figure 6). One observation regards the apparent stability of the Cr(I) dimer reported here as compared with the Cr(0) dimers that have been reported previously. In the d<sup>6</sup> Cr(0) compounds an extra pair of d electrons would be placed into the  $\beta$  molecular orbitals resulting in greater N–N bond strength but lower Cr–N bond strength. Experimental results agree with this statement in that many known Cr(0) dinitrogen-bridged dimers decompose above room temperature liberating dinitrogen,<sup>15,13</sup> while compound **1** is remarkably stable even at elevated temperatures.

The most striking insight available from the molecular orbital depiction is that, upon removal of the two unpaired electrons from the HOMO (which has N–N  $\pi$  and Cr–N  $\pi^*$  character), the bond strength of the dinitrogen bridge should be reduced concomitant with the strengthening of the metal–nitrogen bond. This suggests that oxidation of the

compound could represent a method for cleaving the bound dinitrogen ligand. Although the Cr–N bond would be strengthened, molecular orbital considerations imply that formation of an octahedral chromium–nitride species would be unfavorable because of the trans influence of the  $\pi$ -donating Me<sub>3</sub>SiC≡C<sup>−</sup> ligand and the relatively high d-electron count of the chromium center. Oxidative cleavage of dinitrogen was documented for the molybdenum–trisanilide system in which the C<sub>3v</sub> symmetry imparts large stabilization to, and hence facilitates the isolation of, the terminal nitride complex {N[C(CD<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>][3,5-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>]}<sub>3</sub>MoN.<sup>9a,b</sup>

### Outlook

The foregoing results demonstrate that *n*BuLi can be used as a convenient reagent for the formation of low-valent chromium dinitrogen complexes such as *trans,trans*-[(Me<sub>3</sub>SiCC)(dmpe)<sub>2</sub>Cr]<sub>2</sub>( $\mu$ -N<sub>2</sub>) and *trans*-(dmpe)<sub>2</sub>Cr(N<sub>2</sub>)<sub>2</sub>. In contrast to many of the previously reported Cr–N<sub>2</sub> complexes, these results indicate that compound **1** is unusually stable even at elevated temperatures, demonstrating a synthetic application of the covalent and  $\pi$ -donating nature of the (C≡CSiMe<sub>3</sub>)<sup>1−</sup> ancillary ligand positioned trans to the N<sub>2</sub> ligand. Molecular orbital considerations suggest that oxidation of the dimer should weaken the N≡N bond and activate the N<sub>2</sub> ligand toward further reduction. Given that



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the electrochemical studies imply that oxidation of compound **1** will lead to stable Cr(II) containing complexes, continuing studies should focus on the use of chemical oxidants to activate the N<sub>2</sub> unit of the *trans,trans*-[(Me<sub>3</sub>SiCC)(dmpe)<sub>2</sub>Cr]<sub>2</sub>(μ-N<sub>2</sub>) complex and extend the synthetic approaches implemented in this study toward the formation of more reactive chromium dinitrogen complexes.

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**Supporting Information Available:** X-ray crystallographic files (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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