

# Breaking the 1.80 Å Barrier of the Cr–Cr Multiple Bond Between Cr<sup>II</sup> Atoms\*\*

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Since the discovery of Cr–Cr bonds of unusual shortness,<sup>[1]</sup> this functionality has attracted considerable interest from both the experimental and theoretical point of view.<sup>[2]</sup> The remarkable shortness of these contacts had initially led workers to believe that a strong Cr–Cr interaction exists in these systems.<sup>[3]</sup> Therefore, the initial difficulties of *ab initio* techniques to calculate meaningful energy profiles were ascribed to the crudeness of the theoretical methods.<sup>[4]</sup> However, experimental work has clearly demonstrated the surprising weakness of these bonds.<sup>[5,6]</sup> The paradoxical dichotomy of supershort, superweak quadruple bonds<sup>[7]</sup> can only be reconciled if we regard the Cr–Cr interaction not as a multiple chemical bond in its classical sense, but as a ligand artifact instead.<sup>[8]</sup> In fact, the short contacts have been exclusively detected, among the several dozens of Cr–Cr “multiple bonds”, only in the presence of bridging metal–ligand interactions, with only one exception.<sup>[9]</sup> This rule holds true at least in complexes where the Cr–Cr distance remains in the range of 1.90 Å and higher. The recent discovery of Cr<sup>I</sup>–Cr<sup>I</sup> formally quintuple-bonded systems of variable shortness (1.74–1.83 Å) has marked a new milestone in this field.<sup>[10]</sup> The monovalent state and the consequent presence of only one counteranion makes these systems ideal for the occurrence of exceedingly short Cr–Cr contacts. Still the ligand seemingly plays a decisive role in determining the existence of short Cr–Cr contacts.<sup>[11]</sup> The divalent state remains more challenging, and obtaining Cr<sup>II</sup>–Cr<sup>II</sup> quadruple bond lengths below the level of 1.87 Å was traditionally regarded as an impossible task. The ingenious use of a diimine ligand has recently enabled the preparation of a divalent species with only one ligand system per metal, and set a new record of 1.80 Å for the Cr≡Cr quadruple bond.<sup>[12]</sup> The characterization of this species and its successful quantum-chemical treatment, demonstrated that it is not only possible to achieve such short Cr–Cr distances, but also to form a genuine quadruple Cr–Cr bond. Closed-shell density functional (DFT) calculations, carried out on the quadruple-bonded complex  $[(\text{ArN}=\text{CH}-\text{CH}=\text{NAr})\text{Cr}]_2$ , with a higher-than-expected Cr–Cr bond

order (4.28)<sup>[13]</sup>, also predicted a Cr–Cr distance (1.764 Å) appreciably shorter than the experimental value. Thus, we investigated whether even shorter Cr≡Cr bond lengths were possible, provided that the bridging bonding interactions were appropriately optimized. The present work was aimed at testing the possibility of obtaining Cr≡Cr bond lengths below the current limit of 1.80 Å.

In the search for very short contacts and following the Hein principle<sup>[14]</sup> for the optimization of metal–ligand interactions in three-center chelating geometries, two previously described phenomena are, in our opinion, particularly informative. Firstly, a structural study carried out on a series of chromium<sup>[15]</sup> and vanadium<sup>[16]</sup> amidinate systems has shown that the deformation of the NCN ligand backbone, as determined by the steric contacts between the groups attached to the C and N atoms, determines the extent of M–M separation and even the formation of monomeric versus dimeric structures. Secondly, a more accurate reassessment of the structure of  $[\text{Me}_8\text{Cr}_2\text{Li}_4(\text{thf})_4]$ ,<sup>[17]</sup> initially believed to incorporate a quadruple Cr≡Cr bond without bridging interactions,<sup>[18]</sup> has shown that a network of Cr–Me–Li–Me–Cr agostic interactions is in fact responsible for holding the dimeric structure and causing such short Cr–Cr distances.<sup>[5d,19]</sup>

In an attempt to combine these two features, we prepared a  $[\{(\text{guanidinate})\text{CrMe}\}_2]$  complex. The  $(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2$  guanidinate monoanion has the same three-center chelating geometry of an amidinate. As such, it is suitable for accommodating short Cr–Cr contacts. In addition, the ligand deformation, arising from the steric repulsion between the trimethylsilyl (TMS) groups and the *ipso* H atoms of the cyclohexyl (Cy) groups, was estimated to be only slightly larger than that in formamidinate dimeric complexes. Therefore, we reasoned that, should a dimeric structure still be possible, an exceedingly short Cr<sup>II</sup>–Cr<sup>II</sup> distance could result. The presence of the Cr–Me function was also deemed necessary for two reasons. It allows the presence of only one bulky guanidinate ligand per chromium center, thus preventing prohibitive steric congestion. Also, it may play a possible role in accommodating short Cr–Cr distances, as in the case of  $[\text{Me}_8\text{Cr}_2\text{Li}_4(\text{thf})_4]$ .<sup>[19]</sup>

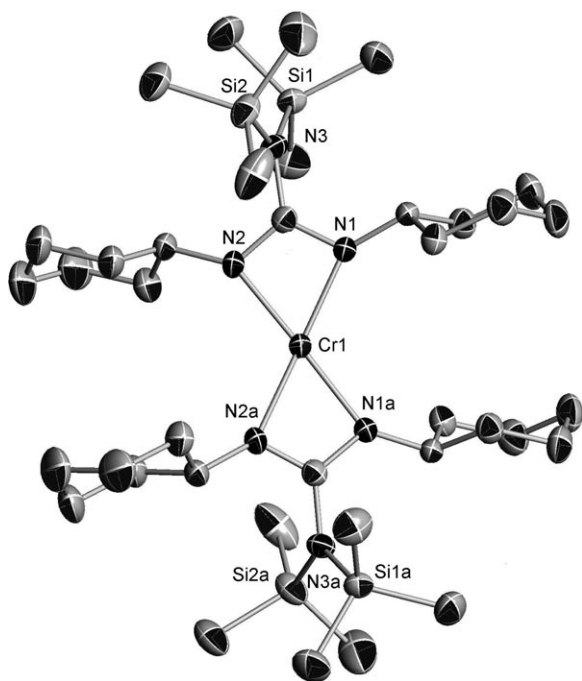
Accordingly, the reaction of  $[\text{CrCl}_2(\text{thf})_2]$  with  $(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2\text{Li}$  gave the expected monomeric complex  $[\{(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2\}_2\text{Cr}]$  (**1**), with the two anions coordinating to the Cr center with a predictable distorted square-planar coordination geometry (Figure 1).

Unsurprisingly, the magnetic moment ( $\mu_{\text{eff}} = 4.77 \mu_{\text{B}}$ ) was as expected for a Cr<sup>II</sup> monomeric complex in a square-planar ligand field. An inspection of the nonbonding contacts between the *ipso* C–H and the TMS groups (2.4 Å) indicated that there was indeed room for widening the bite angle of the

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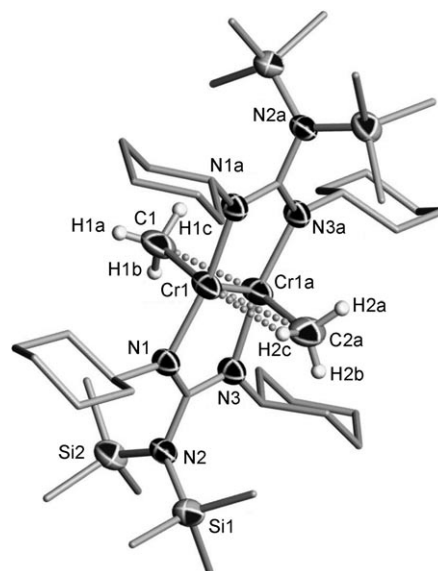
**Figure 1.** ORTEP representation of **1**, with thermal ellipsoids set at 50% probability and hydrogen atoms omitted for clarity. Atoms labeled with "a" are generated by the symmetry operation. Selected bond lengths [Å]: Cr–N1 2.084(3), Cr–N2 2.077(3).

two N donor atoms of the NCN skeleton to accommodate a dimeric structure. For that purpose, one guanidinate anion had to be replaced by a small ligand.

Replacement of one of the two guanidinate groups by a methyl group afforded analytically pure, diamagnetic  $[(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2\text{CrMe}]_2$  (**2**) in crystalline form. For this transformation,  $\text{Me}_3\text{Al}$  proved to be the best alkylating agent. The crystal structure for **2** reveals a dinuclear compound incorporating the shortest  $\text{Cr}^{\text{II}}\text{--Cr}^{\text{II}}$  quadruple bond reported to date (Cr1–Cr1a 1.773(2) Å), longer only than two recently reported  $\text{Cr}^{\text{I}}\text{--Cr}^{\text{I}}$  quintuple bonds.<sup>[10a,b]</sup> Two guanidinate ligands adopt the classical three-center chelating geometry. Each methyl group is placed in a terminal position and disordered with equal occupancy on the two sides of each metal (Figure 2). Although terminally bonded, the methyl groups show a curious orientation towards the second chromium atom, possibly suggesting the presence of a four-center agostic,  $\text{Cr}(\text{CH}_2\text{--H})\text{--Cr}$  interaction. Difference Fourier maps positioned the hydrogen atoms as expected. A half-occupancy interstitial toluene molecule was squeezed out from the refinement.

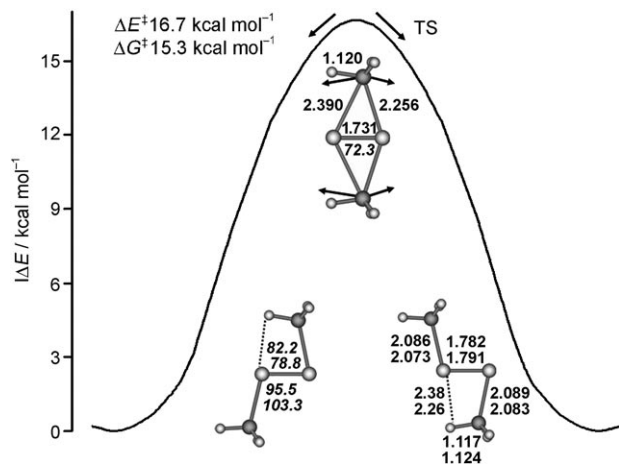
Variable-temperature NMR spectroscopy detected no decoalescence of the methyl resonance at  $\delta = -0.782$  ppm at the freezing-point temperature of the solvent, indicating that, should these agostic interactions truly exist, they do not prevent fast rotation of the  $\text{Cr}\text{--Me}$  bond. Different from the vast majority of paddle-wheel  $\text{Cr}_2$  complexes, with Cr–Cr distances above 1.9 Å, we found no evidence that **2** could be cleaved upon treatment with Lewis bases.<sup>[5,6]</sup>

DFT calculations (see the Supporting Information) on both the nontruncated and truncated models, where the Cy

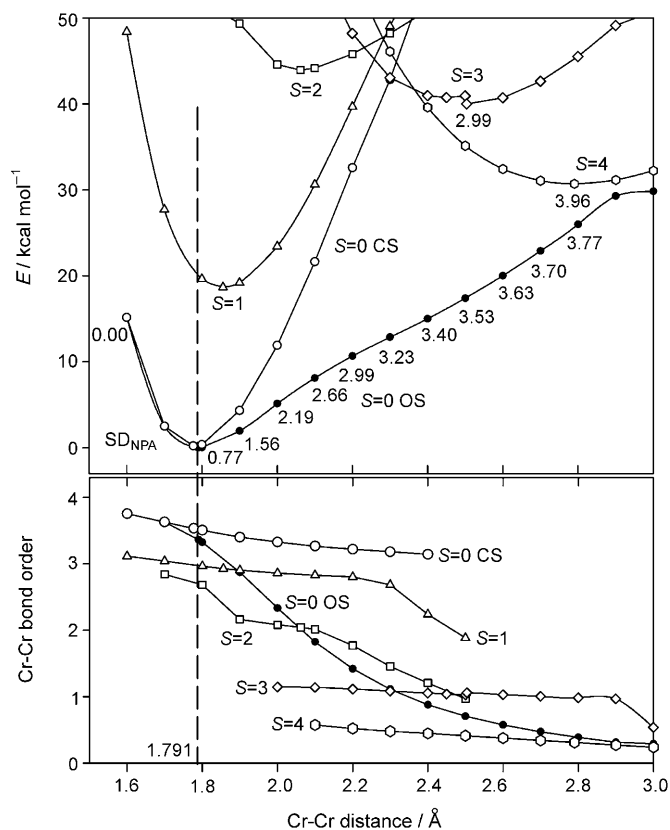


**Figure 2.** ORTEP representation of **2**, with thermal ellipsoids set at 50% probability and selected hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Cr1–Cr1a 1.773(1), Cr1–N1 2.019(3), Cr1–C1 2.192(7), Cr1a–C1 2.521(8), Cr1–C2a 2.181(7), Cr1...H2c 1.15; C1–Cr1–Cr1a 78.2(2), N1–Cr1–Cr1a 96.51(9), C1–Cr1–N1 91.2(4), N1–Cr1–N1a 166.0(1).

and  $\text{Me}_3\text{Si}$  groups in **2** were replaced by the Me and  $\text{H}_3\text{Si}$  groups, respectively (see Figure S1 in the Supporting Information), yielded geometrical parameters in good agreement with the experimental values. The calculated Cr–Cr distance for the nontruncated model (1.782 Å) is in excellent agreement (0.009 Å) with the experimental value (1.773 Å). The predicted Cr–Cr distance in the truncated model (1.791 Å) is only slightly longer. DFT calculations also predicted the presence of a four-center agostic interaction and the inward orientation of the two methyl groups. The results are summarized in Figure 3, and show that symmetrization to regular bridging methyl groups, as expected during the Me exchange between the two Cr atoms, would require a significant amount of energy ( $\Delta G^\ddagger = 15.3$  kcal mol<sup>−1</sup>). Among the possible spin states which have been used for calculation (Figure 4), the singlet states, both open- and closed-shell, displayed the lowest energies with a difference of only 0.5 kcal mol<sup>−1</sup> in favor of the open-shell, broken-symmetry configuration<sup>[20]</sup>. The lowest excited state (approximately 20 kcal mol<sup>−1</sup> above the ground state), in both truncated and nontruncated models, is a triplet state with a slightly longer Cr–Cr bond (Figure 4). In comparison, the similar triplet excited state of the  $\text{Cr}^{\text{II}}\text{--Cr}^{\text{II}}$  complexes with a weaker Cr–Cr interaction lies at a much lower energy (1–3 kcal mol<sup>−1</sup>), thus accounting for their ubiquitously detected temperature-dependent paramagnetism.<sup>[2a,g]</sup> Consistent with this indication of stronger a Cr–Cr interaction in **2**, the potential energy profile shows a well-defined minimum, corresponding to a Cr–Cr bond energy of at least 40 kcal mol<sup>−1</sup>. As can be expected for the  $\text{Cr}^{\text{II}}$  dimers, the open-shell distances at the singlet and the nonet state ( $S=4$ ) become degenerate at the long Cr–Cr limit of the dimer dissociation



**Figure 3.** The DFT optimized structures of truncated and full models (only the Cr<sub>2</sub>Me<sub>2</sub> fragments are shown for clarity) and their relative energies. Of the interatomic distances [Å] and bond angles [°] shown in pairs, the upper values apply to the nontruncated model, and the lower values to the truncated model. Bond angles are shown in italics. For the transition state (TS) structure, the bonds and angles are only presented for the truncated model. Arrows indicate forward and backward movement along the potential energy surface at the TS.



**Figure 4.** Potential energy surfaces (top) and Cr–Cr bond orders (bottom) for different spin states (*S*=0 OS: open-shell singlet, filled circles; *S*=0 CS: closed-shell singlet, open circles; *S*=1: triplet, triangles; *S*=2: pentet, squares; *S*=3: septet, diamonds; *S*=4: nonet, hexagons) of the truncated model complex as a function of the Cr–Cr internuclear distance [Å]. The NPA-derived atomic spin density of the broken-symmetry wave function for the open-shell singlet state is indicated (NPA=natural population analysis). The vertical dashed line indicates the position of the energy minimum for the ground state.

(Figure 4). The calculated Cr–Cr bond order for the ground electronic state of **2** is 3.25. As expected, the frontier molecular orbitals of **2** are mainly centered on Cr, with a high level of 3d character (see Tables S1 and S2 in the Supporting Information). The HOMO–LUMO gap (1.8 eV or 42 kcal mol<sup>-1</sup>) is substantial, and accounts well for the diamagnetism. One Me group generates a four-center agostic Cr–(CH<sub>2</sub>–H)–Cr interaction with the second Cr atom (C–H 1.117–1.124 Å, Cr–H 2.26–2.38 Å, Figure 3) therefore narrowing the Me–Cr–Cr bond angle to 82.2° and 78.8°, in nontruncated and truncated models, respectively (experimental value 78.2(2)°). The red-shifted methyl C–H stretch at 2830 cm<sup>-1</sup> in the IR spectrum of **2**, which was predicted by the DFT calculation to be at 2768 cm<sup>-1</sup> in the truncated model, provides evidence for this interaction. A frequency calculation for the nontruncated model was not attempted owing to the large size of the complex.

In summary, by the judicious choice of ligand systems, we have obtained the shortest Cr<sup>II</sup>–Cr<sup>II</sup> multiple bond detected to date. Interestingly, preliminary DFT calculations on the hypothetical {(guanidinate)Cr<sup>I</sup>} dimer predicted a diamagnetic dinuclear complex with a Cr–Cr bond length of 1.71 Å. Work towards the preparation of such a complex is currently underway.

## Experimental Section

[(Me<sub>3</sub>Si)<sub>2</sub>NC(NCy)<sub>2</sub>Cr] (**1**): (Me<sub>3</sub>Si)<sub>2</sub>NC(NCy)<sub>2</sub>Li (786 mg, 2 mmol) was added to a suspension of [CrCl<sub>2</sub>(thf)<sub>2</sub>] (266 mg, 1 mmol) in toluene (20 mL). The color of the solution changed from purple to red over 30 min. The reaction mixture was stirred at room temperature for 24 h and centrifuged to remove LiCl. The supernatant liquid was stored at –30 °C two days and the product crystallized out as red needles (350 mg, 0.45 mmol, 45 %). Crystals suitable for single-crystal X-ray diffraction were obtained by recrystallization from hot toluene. Additional product may be obtained by removal of solvent from the mother liquor under reduced pressure. IR (Nujol):  $\tilde{\nu}$  = 1464, 1404, 1354, 1344, 1304, 1252, 1193, 1141, 1077, 1007, 964, 946, 886, 864, 839 cm<sup>-1</sup>. Elemental analysis calcd for C<sub>38</sub>H<sub>80</sub>CrN<sub>6</sub>Si<sub>4</sub>: C 58.11, H 10.27, N 10.70; found: C 58.09, H 10.23, N 10.68.

[(Me<sub>3</sub>Si)<sub>2</sub>NC(NCy)<sub>2</sub>CrMe]<sub>2</sub>·(C<sub>7</sub>H<sub>8</sub>)<sub>0.5</sub> (**2**): Trimethylaluminum (36 mg, 0.50 mmol) was added to a solution of **1** (200 mg, 0.25 mmol) in toluene (20 mL). The solution turned dark red in color upon addition of trimethylaluminum. The reaction mixture was stirred at room temperature for 8 h. The resultant solution was stored at –30 °C for 3 days, and complex **2** crystallized out as green blocks, suitable for X-ray diffraction, alongside red needle-shaped crystals of **1**. Crystals of **2** were isolated manually. <sup>1</sup>H NMR ([D<sub>8</sub>]THF):  $\delta$  = –0.782 (s, 6H, Cr–CH<sub>3</sub>), 0.506 (s, 36H, Si–CH<sub>3</sub>), 1.0–1.8 (br m, 40H, CH<sub>2</sub>), 3.972 ppm (m, 4H, CH). IR (Nujol):  $\tilde{\nu}$  = 2921, 2855, 2830, 1451, 1344, 1297, 1253, 1174, 1136, 1076, 1009, 935, 840 cm<sup>-1</sup>. Elemental analysis (after removal of the interstitial toluene) calcd for C<sub>40</sub>H<sub>88</sub>Cr<sub>2</sub>N<sub>6</sub>Si<sub>4</sub>: C 55.38, H 9.99, N 9.69; found: C 55.03, H 9.86, N 9.70.

CCDC 698753 (**1**) and 698754 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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