J. Am. Chem. Soc. 1992, 114, 3556-3557

Communications to the Editor

Reversible Cleavage of the Cr–Cr Quadruple Bond of [Me$_8$Cr$_2$][Li(THF)]$_4$ via Modification of the Coordination Sphere of the Alkali Cation. Preparation and Crystal Structure of Monomeric [Me$_4$Cr][Li(TMEDA)]$_2$

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Received November 25, 1991

The preparation and crystallographic characterization of [Me$_8$Cr$_2$][Li(THF)]$_4$, reported by Krausse more than 20 years ago,[1] marked a milestone in the development of the chemistry of Cr–Cr quadruple bonds, by posing a puzzling problem for both synthetic and theoretical chemists. This complex is one of the very few cases[2] in which an extremely short Cr–Cr distance (Cr–Cr = 1.980 Å) is formed in the absence of bridging three-center chelating ligands.[3] The distorted coordination geometry (the two chromium atoms are intruded into the coordination polyhedron), the small residual paramagnetism, the *supershort* intermetallic distance, and the absence of bridging ligands all indicate the existence of a Cr–Cr quadruple bond[4] capable of a significant attractive force. By way of contrast, theoretical calculations predicted that the Cr–Cr interaction should be limited, in spite of the very short Cr–Cr distance, to either an efficient antiferromagnetic exchange[5] or a weak Cr–Cr quadruple bond.[6a]

It was initially recognized that the four lithium cations exert a certain stabilizing role on the Cr–Cr quadruple bond.[1] Nevertheless, their interaction is commonly regarded as mainly electrostatic, and it is common belief[6] that the Cr–Cr quadruple bond (either weak or strong) is the primary driving force for the formation of this dimer. However, the observation that Cr–(RO)–Na–(OR)–Cr bridges are capable of holding together a [(RO)$_8$Cr$_2$]$^{4-}$ frame in the absence of a direct Cr–Cr bond [Cr···Cr = 3.6 Å)[7] suggests the possibility that similar Cr–Me–Li–Me–Cr bridges might contribute significantly to stabilizing the dinuclear frame of **1**. The obvious consequence would be that, in spite of the supershort Cr–Cr distance and the efficient magnetic coupling, the Cr–Cr quadruple bond might be not the primary factor for holding together the dimetallic frame.

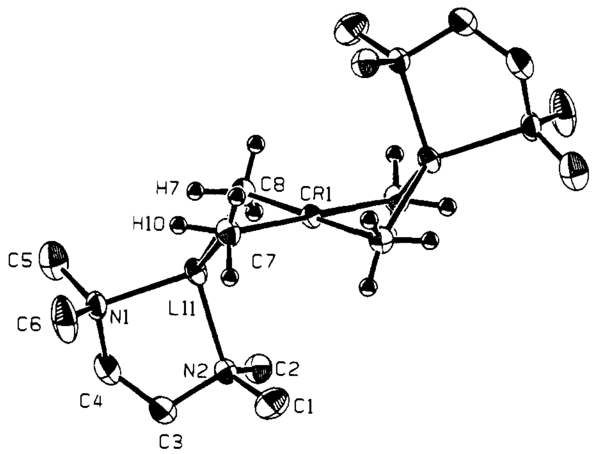
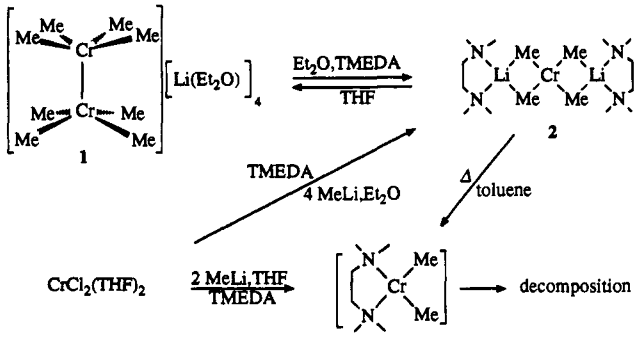


Figure 1. ORTEP drawing of **2** showing the labeling scheme. Thermal ellipsoids are drawn at the 50% probability level. Selected values of bond distances (Å) and angles (deg): Cr(1)–Li(1) = 2.589 (6), Cr(1)–C(7) = 2.204 (5), Cr(1)–C(8) = 2.213 (4), Li(1)–C(7) = 2.176 (7), Li(1)–N(1) = 2.136 (6), Li(1)–H(10) = 2.064, Li(1)–H(7) = 1.992, C(7)–Cr(1)–C(7a) = 180.0 (1), C(7)–Cr(1)–C(8) = 93.8 (2), C(7)–Cr(1)–Li(1)–C(8) = 131.3 (3), [Cr(1)–C(7)–Li(1) = 72.4 (2), Cr(1)–C(8)–Li(1) = 72.6 (2), Li(1)–H(7)–C(8) = 88.67, Li(1)–H(10)–C(7) = 82.27.

Scheme I



We have now found that [Me$_8$Cr$_2$][Li(L)]$_4$ [L = THF, Et$_2$O] can be reversibly cleaved to form an unprecedented monomeric high-spin Me$_4$CrLi$_2$ species via simple replacement of the Lewis base coordinated to the alkali cation. The reaction of [Me$_8$Cr$_2$][Li(Et$_2$O)]$_4$ (**1**) with TMEDA in ether solution proceeds rapidly at room temperature to form extremely air-sensitive orange-yellow crystals of [Me$_4$Cr][Li(TMEDA)]$_2$ (**2**) (Scheme I).[8] The same compound can be conveniently prepared on a large scale and in analytically pure form by reaction of CrCl$_2$(THF)$_2$ with 4 equiv of MeLi in Et$_2$O containing an excess of TMEDA followed by further recrystallization from pure TMEDA. Complex **2** is surprisingly stable in neat TMEDA, from which it can be recrystallized at about 80 °C, without appreciable signs of decom-

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(8) Method A: A light-yellow solution of **1** (0.8 g, 1.5 mmol) in Et$_2$O (200 mL) was treated with neat TMEDA (20 mL). The resulting orange solution was concentrated to small volume, and the small amount of insoluble material separated during the concentration was removed by filtration. Extremely air-sensitive orange-yellow crystals of **2** (0.6 g, 1.7 mmol, 57% yield) were obtained upon standing overnight at −30 °C. Satisfactory analytical results were obtained. IR (Nujol mull, cm^{-1}, KBr): ν 1360 (s), 1295 (s), 260 (m), 1180 (m), 1160 (s), 1135 (s), 1100 (m), 1070 (s), 1040 (s), 1020 (s), 950 (s), 840 (w), 790 (s), 770 (s), 720 (w), 615 (s), 590 (sh). Method B: A suspension of CrCl$_2$(THF)$_2$ (12.4 g, 46 mmol) in neat TMEDA (400 mL) was refluxed overnight, resulting in a blue insoluble solid. The resulting mixture was cooled at −50 °C, and a solution of MeLi in Et$_2$O (130 mL, 1.4 M) was added dropwise by syringe. The green solid that initially formed disappeared upon stirring at room temperature, resulting in an orange suspension. The solid was isolated by filtration and recrystallized from neat TMEDA (80 °C), yielding bright-orange octahedral crystals (10 g, 28 mmol, 61% yield).

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position. Conversely, decomposition and formation of black tarry material was observed in hot toluene. Similar decomposition products were observed upon treating $CrCl_2(THF)_2$ with 2 equiv of MeLi in the presence of TMEDA. The formation of **2** can be reversed and complex **1** can be reformed just by dissolving **2** in THF, evaporating the solvent to dryness, and recrystallizing the residual solid from ether. Complex **2** is paramagnetic with a magnetic moment consistent with a monomeric square-planar d^4 Cr(II) complex ($\mu_{eff} = 4.98\ \mu_B$).

The monomeric structure of **2** has been demonstrated by X-ray analysis.[9] The molecule is composed of a square-planar central monomeric Me_4Cr core [C(7)–Cr(1)–C(7a) = 180.0 (1)°, C(7)–Cr(1)–C(8) = 93.8 (2)°] connected to each of the two LiTMEDA fragments through two bridging methyl groups (Figure 1). The two identical $CrLiMe_2$ moieties are folded in a butterfly conformation with the lithium atom elevated above the Me_4Cr plane [C(7)–Cr(1)–Li(1)–Cr(8) = 131.3 (3)°]. The angles subtended at the bridging carbon atoms [Cr(1)–C(7)–Li(1) = 72.4 (2)°, Cr(1)–C(8)–Li(1) = 72.6 (2)°] are considerably narrow and, together with the short Cr–Li distances [Cr(1)–Li(1) = 2.589 (6) Å], might suggest some extent of Cr→Li bonding interaction. The Cr–C distances are elongated [Cr(1)–C(7) = 2.204 (5) Å, Cr(1)–C(8) = 2.213 (4) Å] with respect to other neutral Cr(II) alkyls[10] and are comparable to those found in complex **1** and other bridged Cr(II) aryls.[11] The lithium atoms possess a normal tetrahedral geometry with the coordination tetrahedron defined by two carbon and two TMEDA nitrogen atoms [Li(1)–C(7) = 2.176 (7) Å, Li(1)–N(1) = 2.136 (6) Å].

The cleavage of the Cr–Cr quadruple bond, obtained by replacing a Lewis base coordinated to the alkali cation, without altering the coordination environment of the transition metal, is surprising. It demonstrates that (i) the role of the alkali cation is vital to the stability of the Cr–Cr interaction of complex **1** and (ii) the Cr–Cr interaction (if any) cannot hold together the dinuclear frame in the absence of Cr–Me–Li–Me–Cr bridges. Therefore, the question again arises as to whether or not the definition of chemical bond is appropriate for the Cr–Cr interaction[12] in complex **1**, in spite of the very short intermetallic distance and the efficient magnetic coupling. Interestingly, we have found that the isostructural $Me_8Mo_2Li_4(THF)_4$[13] cannot be cleaved in similar or harder reaction conditions, in agreement with theoretical calculations which predict the existence of a significant Mo–Mo quadruple bond.[14] Another fascinating question arises from the nature of bonding in the Cr–Me–Li–Me–Cr bridges, thus expected to be responsible for holding together the dinuclear frame of **1**.[1] Although indication of the nature of this interaction cannot be provided by the poor quality structure of **1**, it might be suggested by the bonding mode of lithium with the Me_4Cr moiety of **2**. The data set of **2** was of sufficient quality to locate and refine the hydrogen atoms. The hydrogens of each bridging methyl group define a slightly distorted tetrahedron centered on carbon with the fourth position occupied by chromium. Each lithium atom is placed side-on and perpendicularly with respect to one of the three C–H bonds of each of two bridging methyl groups [Li(1)–H(7)–C(8) = 88.67°, Li(1)–H(10)–C(7) = 82.27°], forming considerably short Li···H distances [Li(1)–H(10) = 2.064 Å, Li(1)–H(7) = 1.992 Å]. These geometrical features suggest, as long as we consider the hydrogen atom positions as significant, that the sp^3 orbital of the bridging carbon atom is oriented mainly toward the transition metal. Thus, the short Cr–Li distance of **2**, the folding of the Me_2CrLi core, and the narrow angle subtended at the carbon atom might be regarded as the optimal distance imposed by the two Li–H agostic interactions, rather than as an improbably strong Cr→Li bond.

We are currently exploring the chemical reactivity and the possible catalytic features of complex **2**.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Research Council of Canada (operating grant) and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Supplementary Material Available: Tables listing atomic positional parameters, anisotropic thermal parameters, and complete bond distances and angles for **2** (14 pages); listing of observed and calculated structure factors for **2** (10 pages). Ordering information is given on any current masthead page.

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[9] Crystal data for **2**: orthorhombic, *Pcab*, $a = 12.707$ (5) Å, $b = 15.600$ (6) Å, $c = 11.829$ (6) Å, $V = 2345$ (3) Å^3, $Z = 4$, $R = 0.049$ ($R_w = 0.047$) for 191 parameters and 1411 significant reflections out of 2382 collected at $T = 100$ K. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in difference Fourier maps and refined isotropically in the last cycle of full-matrix refinement.

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Determination of Absolute Stereochemistry of Acyclic 1,3-Polyols by a Difference CD Method

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Received December 4, 1991

Determination of the absolute configuration of acyclic 1,3-polyols by a spectroscopic method remains a difficult task. Over 200 1,3-polyhydroxylated polyene macrolides are known,[1] but the stereochemistry is established in only a handful of cases.[2–7] In these stereochemical studies, ^1H NMR analysis has been used for the assignment of relative stereochemistry. Recently, ^{13}C NMR analysis of 1,3-diol acetonides has proved to be a simple and reliable method for determining the relative configurations of *syn*- and *anti*-1,3-diols.[8,9] On the other hand, the CD exciton chirality method has played an important role in determining the absolute configuration of rigid molecules.[10] However, the method is rarely applied to acyclic polyols because regioselective introduction of chromophores to the polyols is difficult and the conformation of an acyclic system is more complex than that of a cyclic system. Application of the method to acyclic 1,2-polyols has been extensively studied by Nakanishi,[11] but the extension to skipped

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