Multiple Bonds

DOI: 10.1002/ange.200600110

A Quantum Chemical Study of the Quintuple Bond between Two Chromium Centers in [PhCrCrPh]: *trans*-Bent versus Linear Geometry**

Marcin Brynda, Laura Gagliardi,* Per-Olof Widmark, Philip P. Power, and Björn O. Roos*

The recent report of a stable, crystalline compound with a quintuply bonded chromium–chromium core[1] may reopen the debate on the nature of the multiple bonds between transition metals[2] that was initiated by the discovery of a stable, quadruple bond by Cotton et al. in 1964.[3] Although a recent study of a quintuple bond in the uranium dimer[4] U_2 provided strong support for the existence of such bonds, the isolation of the stable [Ar′CrCrAr′] species (Ar′ = 2,6-(2,6-iPr$_2$-C$_6$H$_3$)$_2$-C$_6$H$_3$), which has a planar, *trans*-bent rather than a linear $C_{ipso}Cr{-}CrC_{ipso}$ core and weak temperature-independent paramagnetism, has raised new questions about multiple bonding. Such a *trans*-bent structure was recently predicted for the simple [HCrCrH] dimer by Weinhold and Landis on the basis of DFT calculations and a natural-bond analysis.[5]

The simplest molecule containing a Cr–Cr bond is Cr_2. Its experimental bond length, obtained from laser-induced fluorescence spectroscopy, is 1.679 Å, and this extremely short Cr–Cr bond has a formal bond order of six, although its significance was questioned[6] because of its low dissociation energy (1.53 ± 0.06 eV). According to different theoretical studies, the description of the CrCr interaction in Cr_2 ranges from a sextuple bond,[7–10] through a single bond,[11] to a complete absence of bonding between the chromium atoms.[6] It is now well established that a proper description of the bonding in this species requires a multiconfigurational treatment. A description of the bonding in Cr_2 that is in full agreement with the experimental data was obtained in a recent study.[12] Formally, a sextuple bond is formed, but the effective bond order is only about four because of mixing of excited, less-bonding states into the ground state. Similar behavior was also observed for $[Re_2Cl_8]^{2-}$, in which a formal quadruple bond was found to have a bond order of only about three for similar reasons.[13,14]

The bonding scheme in the [Ar′CrCrAr′] complex resembles that found in the Cr_2 dimer: The interaction of two Cr^I centers with d^5 electron configurations leads to five, rather than six, metal–metal bonding molecular orbitals, along with their antibonding counterparts. The questions that arise are: which electronic configurations dominate the ground-state wave function, and how important is the contribution of the bonding $(\sigma_g)^2(\pi_u)^4(\delta_g)^4$ configuration? The main difference between the bonding in Cr_2 and [Ar′CrCrAr′] lies in the fact that two additional metal–ligand orbital combinations involving the participation of mainly 4s orbitals in the metal–carbon(ligand) bond are present in [Ar′CrCrAr′]. Despite this apparent similarity, the situation in the real complex is more complicated because of the size of the ligands, and also because of the presence of the "indirect" metal–ligand interactions. Because of the presence of the flanking aryl groups in the vicinity of the chromium centers, a weak, but non-negligible interaction occurs.[1] This interaction, along with the large size of the ligand, can lengthen the Cr–Cr bond in the [Ar′CrCrAr′] compound.

We now report the results of a theoretical study of a simplified model compound for [Ar′CrCrAr′], namely [PhCrCrPh] (Ph = phenyl). The complete active space (CAS) self-consistent field (SCF) method[15] was used to generate molecular orbitals and reference functions for subsequent multiconfigurational second-order perturbation calculations of the dynamic correlation energy (CASPT2).[16] Additional DFT calculations were performed on the [PhCrCrPh] model and on the experimentally observed [Ar′CrCrAr′] compound. The results show that the *trans*-bent and linear geometries at the CASPT2 level are essentially degenerate but are separated by an appreciable barrier (Figure 1). Fivefold bonding with filled bonding orbitals $(\sigma_g)^2(\pi_u)^4(\delta_g)^4$ is the predominant configuration in the wave function.

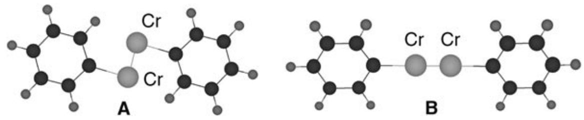

Figure 1. *trans*-Bent (**A**) and linear (**B**) structures of the model [PhCrCrPh] compound optimized at the CASSCF/CASPT2 level.

The most-significant structural parameters for the *trans*-bent (**A**) and linear (**B**) [PhCrCrPh] structures are reported in Table 1. The computed bond distances for the *trans*-bent structure (Cr–Cr = 1.75 Å, Cr–C = 2.018 Å) are somewhat

---

[*] Dr. M. Brynda, Prof. P. P. Power
Department of Chemistry
University of California, Davis
One Shields Avenue, Davis 95616 CA (USA)
Fax: (+01) 530-752-8995
E-mail: mabrynda@ucdavis.edu
Prof. L. Gagliardi
Département de Chimie Physique
Université de Genève
30, q. E. Ansermet, 1211 Genève (Switzerland)
Fax: (+41) 022-379-6518
E-mail: laura.gagliardi@chiphy.unige.ch
Dr. P.-O. Widmark, Prof. B. O. Roos
Department of Theoretical Chemistry
Chemical Center
P.O. Box 124 S-221 00 Lund (Sweden)

[**] We are grateful to the Petroleum Research Fund administered by the American Chemical Society and the National Science Foundation. B.O.R. and P.-O.W. thank the Swedish Foundation for Strategic Research (SSF) for financial support. L.G. thanks the Swiss National Foundation for financial support.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

Table 1: Bond lengths [Å] and angles [°] of the linear and *trans*-bent structures of [PhCrCrPh] optimized at the CASPT2 level.

[PhCrCrPh]	Cr–Cr	C–Cr	C-Cr-Cr
linear	1.678	2.040	180.0
trans-bent	1.752	2.018	88.4

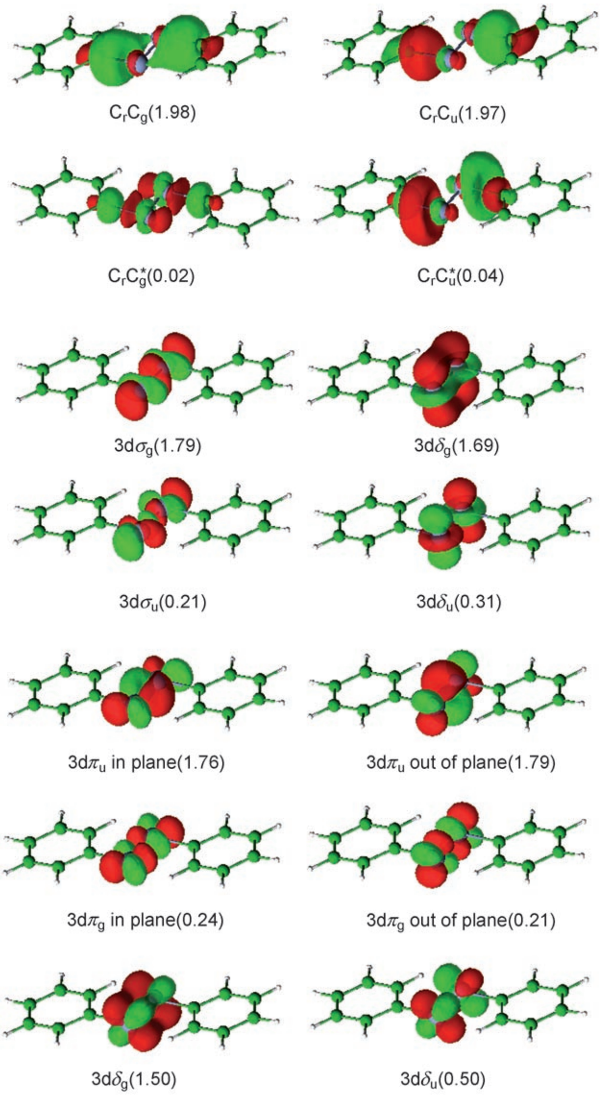

Figure 2. The active molecular orbitals forming the chemical bond between the two chromium centers, and between the chromium centers and the *ipso*-phenyl carbon atoms. The orbital label is given below each orbital, together with the number of electrons occupying the orbital.

shorter than the experimentally determined values (Cr–Cr = 1.83, Cr–C = 2.15 Å).[1] As will be shown below, this difference can be attributed to the extra aryl substituents in [Ar′CrCrAr′], which because of steric and electronic factors as well as the presence of an additional Cr–ring interaction weaken both the Cr–Cr and Cr–C bonds somewhat. The application of the same computational methodology to Cr_2 also affords a shorter Cr–Cr bond (1.662 Å) than the experimental value (1.679 Å). We computed the Cr–Cr bond energy by comparing the energy of the complex with that of two CrPh units (with DFT-optimized geometry) and found it to be 76 kcal mol^{-1}. In comparison, the bond energy of Cr_2 is 36 kcal mol^{-1}. The bond in [PhCrCrPh] is thus twice as strong. The reason is most likely that, in Cr_2, the interaction of the 4s is repulsive at equilibrium geometry.

The *trans*-bent planar structure is only 1 kcal mol^{-1} higher in energy than the linear structure. However, the compound [Ar′CrCrAr′] has a *trans*-bent structure, and we presume that this preference is a result of the secondary interaction between the chromium and the flanking ring of the ligand. This behavior is not possible in our model compound. A reaction path between **A** and **B** was determined by interpolating the extreme values of the Cr–Cr bond length, Cr–C bond length, and C-Cr-Cr angle. A barrier of 20 kcal mol^{-1} with respect to the linear structure **B** exists for a Ph-Cr-Cr angle of 131°.

The electronic structures of **A** and **B** were analyzed. The major configuration in both forms has all the bonding orbitals occupied: $(\sigma_g)^2(\pi_u)^4(\delta_g)^4$ with a total weight of 45 % in the CASSCF wave function for **A**, which corresponds to a formal quintuple bond. The second dominating configuration has a weight of 9 % and corresponds to a double excitation $(\delta_g)^2(\delta_u)^2$. The effective bond order is smaller than five as a result of the large occupation of the antibonding orbitals. It can be estimated as the sum of the occupation numbers of the bonding orbitals, minus the corresponding sum for the antibonding orbitals, divided by two. For the form **A**, we obtained the following occupation numbers (Figure 2): $\sigma_g(1.79)$, $\sigma_u(0.21)$, $\pi_u(3.54)$, $\pi_g(0.46)$, $\delta_g(3.19)$, $\delta_u(0.81)$. These values yield an effective bond order of 3.52. The corresponding number for the linear form **B** is 3.69. The larger number is a reflection of the shorter Cr–Cr bond (see the Supporting Information for a picture of the orbitals of **B** along with the occupation numbers). Although the calculated bond order is less than five, the bond is formally quintuple, because five orbitals and five electrons on each atom are involved in the bonding.

The geometry optimizations of the model [PhCrCrPh] compound were also performed at the DFT level of theory, and yielded a minimum for the linear optimized geometry with a Cr–Cr bond length of 1.560 Å. The single configurational DFT approach typically underestimates the Cr–Cr bond lengths. Optimization of a planar *trans*-bent structure with constrained C_{2h} symmetry led to a second-order transition point with the Cr–Cr bond length of 1.658 Å and a Cr-Cr-C angle of 95.0°. A considerable change in the C-Cr-Cr-C core geometry is observed in the DFT-optimized structure of the [Ar′CrCrAr′] molecule. A wider C-Cr-Cr angle (102.7°) and a net elongation of the Cr–Cr bond (by 0.049 Å relative to the [PhCrCrPh] model) clearly indicate that the bulky terphenyl substituents are responsible for these structural changes. Analysis of the DFT results reveals that two different interactions contribute to such behavior: a repulsive interaction between aryl groups in the terphenyl ligands, and a very weak, bonding interaction of the flanking aryl groups with the chromium atoms.

We conclude that a quintuple bond is formed between the Cr atoms in the model compound [PhCrCrPh]. This description is consistent with the pairing of five electrons from each CrPh moiety. The bonding also seems to be stronger than in the formally sixfold bonded chromium dimer Cr_2, which we attribute to the absence of the 4s orbital in the Cr−Cr bond. The geometry of the model compound used in this study is close but not identical to that of the experimentally observed [Ar′CrCrAr′] species. The Cr−Cr bond in [Ar′CrCrAr′] is almost 0.05 Å longer than that in [PhCrCrPh]. When this difference is added to the value of 1.75 Å calculated for [PhCrCrPh] at the CASSCF/CASPT2 level, a Cr−Cr bond length of 1.80 Å results, which is quite close to the experimental value of 1.83 Å. Furthermore, the C-Cr-Cr angle obtained from the DFT-optimized structure (102.7°) of [Ar′CrCrAr′] is identical to the C-Cr-Cr angle determined experimentally in the X-ray structure of this compound. The computed difference in the Cr−Cr bond lengths in [PhCrCrPh] and [Ar′CrCrAr′] is therefore the result of steric repulsion and the extra Cr–ligand bonding that occurs between the metal centers and the flanking aryl groups in the experimental compound. This bonding, even though it is weak, has a significant influence on the structure; it weakens both the Cr−Cr and the Cr−Ph bond.

Further information on this weak interaction can be obtained from DFT calculations, which, because of their monodeterminantal character, cannot properly describe the bonding between the two chromium centers, but can yield important information about the chromium–aryl interaction. The weak chromium–aryl interaction involves mainly chromium centers and the *ipso*-carbon atoms of the flanking aryl groups. This situation bears some resemblance to that observed in chromocene (bis(cyclopentadienyl)chromium(II)) and related derivatives, which have chromium–aryl(centroid) bond lengths in the range 1.60–1.65 Å.[17] In [Ar′CrCrAr′], however, the chromium–aryl(centroid) bond is much longer (2.23 Å). Also, the analysis of the orbital overlaps shows that the chromium–aryl interaction is different and concerns mainly the *ipso*-carbon atom of the flanking aryl group, rather than the whole aryl ring. This situation is a result of the relative positions of the phenyl rings and the Cr center. The "twist" of the flanking aryl group, which causes a pronounced asymmetry, as well as the different orientation of the chromium d orbitals make this interaction weaker than the η^5 complexation observed in chromocene. The DFT calculations suggest that the $Cr-C_{ipso}$ interaction is quite weak and has a value of approximately 1–2 kcal mol^{-1}.

Finally, inspection of the potential-energy surface (PES) scans of the [PhCrCrPh] model (see the Supporting Information) clearly indicates that a *trans*-bent structure is not a minimum but rather a transition point on the PES. Although the size of the bulky terphenyl ligands precluded frequency analysis of the DFT-optimized structure of [Ar′CrCrAr′], we believe that the sterically bulky terphenyl ligands can stabilize the *trans*-bent geometry, and turn a transition point into a minimum in a fashion analogous to that observed in [Ar*PbPbAr*] (Ar* = 2,6-$Ph_2C_6H_3$).[18]

In summary, the number of singly occupied orbitals available for Cr−Cr bonding determines uniquely the formal bond order: six in the chromium dimer, five in the present Cr^I compound, and four in Cr^{II} compounds such as $[Cr_2(O_2CMe)_4]$ (Cr−Cr = 1.97 Å,[19] calculated bond length = 1.94 Å).[20]

Experimental Section

Computational details: The CASSCF/CASPT2 calculations were performed by using the software MOLCAS-6.2.[21] The active orbitals were formed by 14 electrons in 14 molecular orbitals (MOs). These orbitals are the two bonding and two antibonding Cr−C MOs and the five bonding and five antibonding Cr−Cr MOs arising as linear combinations of Cr 3d and 4s as well as the phenyl radical orbitals.

Basis sets of the atomic natural-orbital type were used for all atoms. For chromium a basis set developed for relativistic calculations with the Douglas–Kroll–Hess (DKH) Hamiltonian[22,23] was employed. A primitive set 21s15p10d6f4g2h was contracted to 6s5p3d2f1g,[24] whereas basis sets of DZP quality were used for H (7s3p contracted to 2s1p) and C (10s6p3d contracted to 3s2p1d).[25] Scalar relativistic effects were thus included at all levels of theory. Spin-orbit (SO) coupling was not included in the present study. It will have only minor effects on the computed structure for the singlet electronic ground state of the molecule. The CASSCF/CASPT2 method and the basis sets used here have been successful in a number of studies on dimetal compounds such as $[Re_2Cl_8]^{2-}$[14] and the octamethyldimetalates of Cr^{II}, Mo^{II}, and Re^{III}.[13]

An initial geometry optimization was performed both for the planar linear structure (D_{2h} symmetry; Figure 1 **A**) and the planar bent structure (C_{2h} symmetry; Figure 1 **B**) at the DFT level. In the subsequent CASPT2 calculations, only three parameters were reoptimized, namely the Cr−Cr and Cr−Ph bond lengths and the Cr-Cr-Ph angle both for the D_{2h} and C_{2h} structures. The phenyl ring DFT parameters were kept fixed.

DFT calculations were performed by using the zero-order relativistic approximation (ZORA) relativistic Hamiltonian.[26] The geometry optimizations of the model [PhCrCrPh] species were performed with the ADF program[27] in which the ZORA Hamiltonian is combined with Kohn–Sham formalism by using the Becke–Lee–Yang–Paar (BLYP) approximation to the exchange-correlation functional and Slater type orbitals of TZ2P quality. A basis set of TZP quality was used for the optimization of the whole [Ar′CrCrAr′] molecule and the corresponding [PhCrCrPh] model. Vibrational frequencies were analyzed for the minima and the stationary points. The PES scans were performed with fully relaxed geometry (except for the imposed point-group symmetry with a fixed *trans*-bent angle) at each step of the scan. Additional details of DFT calculations are reported in the Supporting Information.

Received: January 11, 2006
Revised: March 15, 2006

Keywords: ab initio calculations · chromium · density functional calculations · metal–metal interactions · multiple bonds

---

[1] T. Nguyen, A. D. Sutton, M. Brynda, J. C. Fettinger, G. J. Long, P. P. Power, *Science* **2005**, *310*, 844.

[2] F. A. Cotton, C. A. Murillo, R. A. Walton, *Multiple Bonds between Metal Atoms*, 3rd ed. (Eds.: F. A. Cotton, C. A. Murillo, R. A. Walton), Springer, New York, **2005**.

[3] F. A. Cotton, N. F. Curtis, C. B. Harris, B. F. G. Johnson, S. J. Lippard, J. T. Mague, W. R. Robinson, J. S. Wood, *Science* **1964**, *145*, 1305.

[4] L. Gagliardi, B. O. Roos, *Nature* **2005**, *433*, 848.

[5] F. Weinhold, C. R. Landis, *Valency and Bonding. A Natural Bond Orbital Donor–Acceptor Perspective*, Cambridge University Press, Cambridge, **2005**, p. 556.
[6] M. M. Goodgame, W. A. Goddard III, *J. Phys. Chem.* **1981**, *85*, 215.
[7] C. J. Barden, J. C. Rienstra-Kiracofe, H. F. Schaefer III, *J. Chem. Phys.* **2000**, *113*, 690.
[8] E. A. Boudreaux, E. Baxter, *Int. J. Quantum Chem.* **2001**, *85*, 509.
[9] E. A. Boudreaux, E. Baxter, *Int. J. Quantum Chem.* **2004**, *100*, 1170.
[10] E. A. Boudreaux, E. Baxter, *Int. J. Quantum Chem.* **2005**, *105*, 199.
[11] E. J. Thomas, J. S. Murray, C. J. O'Connor, P. Politzer, *Theochem* **1999**, *487*, 177.
[12] B. O. Roos, *Collect. Czech. Chem. Commun.* **2003**, *68*, 265.
[13] F. Ferrante, L. Gagliardi, B. E. Bursten, A. P. Sattelberger, *Inorg. Chem.* **2005**, *44*, 8476.
[14] L. Gagliardi, B. O. Roos, *Inorg. Chem.* **2003**, *42*, 1599.
[15] B. O. Roos, *Adv. Chem. Phys.* **1987**, 399.
[16] K. Andersson, P. A. Malmqvist, B. O. Roos, A. J. Sadlej, K. Wolinski, *J. Phys. Chem.* **1990**, *94*, 5483.
[17] V. M. Rayon, G. Frenking, *Organometallics* **2003**, *22*, 3304.
[18] Y. Chen, M. Hartmann, M. Diedenhofen, G. Frenking, *Angew. Chem.* **2001**, *113*, 2107; *Angew. Chem. Int. Ed.* **2001**, *40*, 2051.
[19] S. N. Ketkar, M. Fink, *J. Am. Chem. Soc.* **1985**, *107*, 338.
[20] K. Andersson, C. W. Bauschlicher, Jr., B. J. Persson, B. O. Roos, *Chem. Phys. Lett.* **1996**, *257*, 238.
[21] G. Karlstroem, R. Lindh, P.-A. Malmqvist, B. O. Roos, U. Ryde, V. Veryazov, P.-O. Widmark, M. Cossi, B. Schimmelpfennig, P. Neogrady, L. Seijo, *Comput. Mater. Sci.* **2003**, *28*, 222.
[22] M. Douglas, N. M. Kroll, *Ann. Phys.* **1974**, *82*, 89.
[23] B. A. Hess, *Phys. Rev. A* **1986**, *33*, 3742.
[24] B. O. Roos, R. Lindh, P.-A. Malmqvist, V. Veryazov, P.-O. Widmark, *J. Phys. Chem. A* **2005**, *109*, 6575.
[25] K. Pierloot, B. Dumez, P.-O. Widmark, B. O. Roos, *Theor. Chim. Acta* **1995**, *90*, 87.
[26] E. van Lenthe, P. E. S. Wormer, A. van der Avoird, *J. Chem. Phys.* **1997**, *107*, 2488.
[27] ADF-2005.01, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com. For full reference details, see the Supporting Information.