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Analysing the chromium–chromium multiple bonds using multiconfigurational quantum chemistry

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ABSTRACT

This Letter discusses the nature of the chemical bond between two chromium atoms in different di-chromium complexes with the metal atoms in different oxidation states. Starting with the Cr diatom, with its formally sextuple bond and oxidation number zero, we proceed to analyse the bonding in some Cr(I)–Cr(I) XCrCrX complexes with X varying from F, to Phenyl, and Aryl. The bond distance in these complexes varies over a large range: 1.65–1.83 Å and we suggest explanations for these variations. A number of di-chromium complexes with bond distances around or shorter than 1.80 Å have recently been synthesized and we study one of these complexes, Cr₂(diazadiene)₂ and show how the Cr–Cr bond order is related to the oxidation number and the ligand bonding, factors that are all involved in the determination of the short Cr–Cr bond length: 1.80 Å. The discussion is based on the use of multiconfigurational wave functions, which give a qualitatively correct description of the electronic structure in these multiply bonded systems.

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1. Introduction

Recent advances in the field of the synthetic transition metal complexes exhibiting multiply bonded metal–metal cores [1], have reopened many theoretical questions that have, if not been sent completely *ad-acta*, at least had seen attenuated levels of interest for almost two decades. A major reason for this was the scarcity of new classes of multiple bonded metal–metal compounds appearing in the literature. In fact, not much happened on the synthetic front after the pioneering experimental work of Cotton with the synthesis of the room-temperature stable Re₂Cl₈²⁻ species with a formal quadruple bond [2] even if a large number of other quadruply bonded di-metal compounds have been synthesized and theoretically studied since then. The search for an even higher multiplicity of the metal–metal bond was only recently successful with the synthesis of the first room-temperature stable RCrCrR compound with terphenyl ligands by Power's group [3]. Following the discovery of this first stable quintuply bonded chromium–chromium species and publication of its crystal-structure, several low-valent di-chromium complexes were synthesized in the last three years [4–8]. Not surprisingly, this flurry of experimental activity has been accompanied by a number of theoretical studies, which were undertaken to describe the bonding paradigm in these species [8–16]. However, the effectiveness of rapidly evolving quantum mechanical methods in handling complicated theoretical

descriptions of metal–metal multiple bonding provides ample justification for a reexamination of many of these systems. In this review we shall try to summarize several of these results and see if there is any common pattern which may be used to understand the metal–metal bonding in some of these molecules. In most of the calculations that we refer to, we have used multiconfigurational quantum chemical wave functions because they capture the essentials of the electronic structure in a compact way through the use of the natural orbital concept and effective bond orders. Comparison will also be made with density functional methods because they have frequently been used to analyze the electronic structure of these molecules.

The mother of the multiply bonded Cr₂ species is the Cr diatom itself. Despite the fact that this seemingly simple molecule was first identified and observed more than four decades ago [17,18], the description of its electronic structure remained a longstanding challenge for theoretical chemistry and its bonding is still an area of some debate. We shall therefore start with a short historical perspective of the theoretical efforts to describe the bonding in the Cr₂ and then discuss its recently synthesized derivatives.

2. The chromium–chromium multiple bond – a historical overview

The simplest molecule that exhibits a Cr–Cr bond with multiple character is Cr₂. Based on laser-induced fluorescence spectroscopic studies its experimental bond length was determined to be 1.679 Å [19], and its dissociation energy was calculated to be

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$D_0 = 1.53 \pm 0.06$ eV (35.3 ± 1.4 kcal mol⁻¹) [20]. The experimental potential energy curve is shown in Fig. 1 and the details of the experimental data are discussed in the original reference by Casey and Leopold [21]. As we have recently noted [9], even though this bond is considered extremely short and has a formal bond order of six, its relevance was largely questioned [22] because of its significantly lower dissociation energy, as compared to analogous species involving atoms from the second or third row. Depending on the reported theoretical studies, the description of the bonding in Cr₂ has ranged from a sextuple bond [22–26], through a single bond [27], to an antiferromagnetically coupled diatomic bearing two chromium centers with opposite spins [22].

Before we give a detailed description of the bonding in the Cr–Cr species, it is interesting to recall the electronic structure of Cr₂ and its simplest extension – RCrCrR (where R = H, Me, F, Ph or Ar). Each chromium in the Cr₂ diatom possesses five 3d and one 4s electron and can, in principle, afford a fully sextuple bond between the metal centers. The main difference between Cr₂ and the analogous RCrCrR species lies in the fact that in the latter, a pair of 4s electrons is used to form the M–R bonds with the ligands and therefore only the remaining 3d electrons can be involved in the metal–metal bonding. Then, the ten 3d electrons could result in a fivefold interaction.

With this simple picture in hand we can now consider the development of the chemistry of multiple bonded Cr–Cr species in general. Modern synthetic work in multiple bonded transition metal complexes was initiated by Cotton's quadruply bonded complexes of rhenium [2] and following this discovery, numerous other species with multiply bonded metal–metal cores were synthesized. A large number of chromium complexes exhibiting quadruple Cr–Cr bonds were obtained at that time. Maybe the most famous is the Cotton's Cr₂(2-MeO-5-MeC₆H₃)₄ [28] with two Cr(II) having an experimental Cr–Cr bond length of 1.828 Å. This remained for almost 30 years the shortest metal–metal bond known in an isolable compound, until it was very recently superseded by the quadruply bonded [(Me₃Si)₂NC(NCy)₂CrMe]₂ complex with a very short Cr–Cr bond of 1.773 Å [29]. It should be mentioned, however, that the iconic quadruply bonded chromium acetate Cr₂{OC(O)Me}₄ of Peligot [30,31] had been known since the 1840's, although the nature of the Cr–Cr bond was not recognized until much later.

The break-through discovery, which reinvigorated the concept of multiple bonding in transition metal chemistry, took place in 2005 with the report of the first Cr–Cr complex Ar'CrCrAr' with a

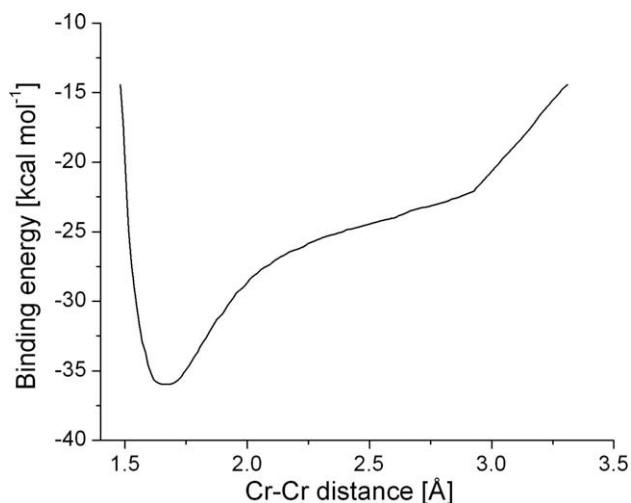


Fig. 1. The experimental potential energy curve for Cr₂ [21].

fivefold Cr–Cr interaction [3]. The Ar'CrCrAr' (Ar' = C₆H₃-2,6-(C₆H₃-2,6-Prⁱ)₂) complex reported by Power's group exhibits a planar trans-bent structure with a very short Cr–Cr bond (1.835 Å) and a Cr–Cr–C angle of 102.8°. As in most of the complexes where terphenyl ligands are used as kinetically stabilizing agents, there is also a relatively short (2.294 Å) secondary Cr–C interaction involving an *ipso*-carbon of one of the flanking aryl rings. Following this experimental work, subsequent synthetic efforts resulted in several other low-valent chromium–chromium species with either modified terphenyl ligands (including electron donating/withdrawing substituents), or with new ligands containing nitrogen. By the substitution of the central phenyl ring of the terphenyl ligand with OMe, SiMe₃ or F, three new variants of the Ar'CrCrAr' were obtained [8] (see Table 1). However, the synthesized structures were strikingly similar to the prototypic Ar'CrCrAr' and only very small effects on the Cr–Cr bond were noticeable. The most important features of these analogous of Ar'CrCrAr' are again the trans-bent solid-state structures with very short Cr–Cr distances that lie in the narrow range of 1.808–1.835 Å. The differences in the Cr–Cr distances could not be correlated with the electron-withdrawing or -donating power of the para substituents and seemed rather to come from crystal-packing effects. Thus, the Cr–Cr bond was shown to be insensitive to the electronic nature of substituent at the para position of the central aryl ring.

However, very recent reports provide evidence that the chemistry of Cr–Cr complexes is not limited to the use of the bulky terphenyl moieties, but can easily be extended to other types of supporting ligands. In particular, chemical entities containing nitrogen are an emerging ligand class that can stabilize multiple bonded metal–metal species. For example, two derivatives of diimines ligands where each chromium atom interacts with two nearby nitrogens have recently been described. Kreisel et al. synthesized a di-chromium compound (μ - η^2 -HⁱLiPr)₂Cr₂, HⁱLiPr = *N,N'*-bis(2,6-diisopropylphenyl)-1,4-diazadiene, where the Cr–Cr core is coordinated by two diazadienes [5]. In this compound, the geometry around each Cr atom is trigonal planar, with each metal coordinated to two N atoms from two bridging diazadiene ligands, as well as by the neighboring Cr atom. The interesting feature of this complex is the very short Cr–Cr distance of 1.803 Å (shorter by ~0.03 Å than the previously reported Ar'CrCrAr'), making it one of the shortest metal–metal distances reported to date. It is also important to mention that due to the particular nature of the N₂CrCrN₂ core (close to planar arrangement around Cr₂) in this complex, no secondary interactions of Cr with other parts of the ligands are involved. A similar compound, L₂Cr₂, L = [6-(2,4,6-triisopropylphenyl)pyridin-2-yl](2,4,6-trimethylphenyl)amide, with a slightly different ligand containing two nonequivalent nitrogens (one pyridino and one imino) was recently reported by Noor et al. [6]. This compound is characterized by an exceptionally short Cr–Cr distance of 1.749 Å and a rather short Cr–N_{amido} bond length (1.998 Å). Unlike in the previous compound, two different types of nitrogens are involved in the bonding with the chromium core.

In addition, a further report shows that the fivefold Cr–Cr bond does not necessarily imply planar (or close to planar) structures as in the case of the RCrCrR or RN₂CrCrN₂R species, but can also be stabilized by somehow unexpected arrangement of the ligands. Tsai et al. have synthesized a paramagnetic molecule containing three diimine ligands forming a cage (lantern) that hosts a Cr–Cr core with a Cr–Cr interaction of 1.817 Å [7]. Reduction of this molecule afforded its diamagnetic congener, which is a stable entity and exhibits the shortest Cr–Cr bond known to date of (1.740 Å) for anything other than the Cr diatom itself.

Last but not least in the saga of the low-valent chromium–chromium complexes, four new molecules with Cr–Cr cores using modified bis(amidinate) ligands with short N–N distances were reported, while we were submitting this review by Hsu et al. These

Table 1

Recently synthesized low-valent Cr–Cr species with a fivefold interaction between the chromium atoms. Experimental CrCr distances are reported from the available X-ray structures. BO DFT – Bond order represented by Wiberg bond indices from DFT calculations; EBO – Effective Bond Order from CASPT2 calculations as defined in paragraph 4.

CrCr species	CrCr distance (Å)	BO DFT	EBO CASPT2
Cr ₂	1.679	CS-6.03 ^c , BS-3.46 ^c	4.51 [16], this work
PhCrCrPh ^a Linear	1.687 ^b	CS-4.82 ^c , BS-3.79 ^c	3.52 [9]
PhCrCrPh ^a Trans-bent	1.750 ^b		
FCrCrF ^a	1.650 ^b	CS-4.88 ^c , BS-2.87 ^c	3.83
Ar ^c CrCrAr ^c Ar ^c = C ₆ H ₃ -2,6-(C ₆ H ₃ -2,6-Pr ₂) ₂ [3]	1.835	CS-4.12, BS-1.79	3.43 [13]
Ar [*] CrCrAr [*] Ar [*] = 4-SiMe ₃ -Ar ^c [8]	1.808		
Ar ^y CrCrAr ^y Ar ^y = 4-OMe-Ar ^c [8]	1.816		
Ar ^δ CrCrAr ^δ Ar ^δ = 4-F-Ar ^c [8]	1.831		
[Cr ₂ -(Ar ^{Xyl} NC(H)NAr ^{Xyl}) ₃] ⁻ [7]	1.740	CS-3.45, BS-2.48	
(Ar ^{Xyl} =2,6-C ₆ H ₃ -(CH ₃) ₂)			
[Cr ₂ -(Ar ^{Xyl} NC(H)NAr ^{Xyl}) ₃] [7]	1.817	OS-2.82	
(Ar ^{Xyl} =2,6-C ₆ H ₃ -(CH ₃) ₂)			
(μ-η ² -H ₁ L ^{iPr}) ₂ Cr ₂ , H ₁ L ^{iPr} = N,N'-bis(2,6-diisopropylphenyl)-1,4-diazadiene [6]	1.803	CS-4.02, BS-2.58	
	1.799 ^b		
[Cr ₂ {ArNCHNAr} ₂] Ar = 2,4,6-Me ₃ C ₆ H ₂ [4]	1.740	CS-4.49, BS-2.79	
[Cr ₂ {ArNCHNAr} ₂] Ar = 2,6-Et ₂ C ₆ H ₃ [4]	1.745		
[Cr ₂ {ArNCHNAr} ₂] Ar = 2,6- ⁱ Pr ₂ C ₆ H ₃ [4]	1.747		
[Cr ₂ {ArNCMeNAr} ₂] Ar = 2,6- ⁱ Pr ₂ C ₆ H ₃ [4]	1.740		

^a Model species used in the quantum computations.

^b Optimized Cr–Cr distances obtained from CASPT2 calculations.

^c DFT BO's computed at CASPT2 optimized CrCr distances.

complexes are characterized by the extremely short metal–metal bonds of 1.74 Å, which were stated to be independent of the steric hindrance of the ligands [4].

3. A historical overview of the theoretical methods

In this short prospective we have no aim to provide a complete overview of all the theoretical efforts that have been devoted to the understanding of the bonding in Cr–Cr complexes. Several excellent reviews exist on this topic [21,27,32–35] and the reader is invited to consult these Letters as well as the references therein. Instead, we now present an account of the important steps in the theoretical development of the description of the multiply bonded Cr–Cr species over the last three decades.

The first attempts to address theoretically the multiple metal–metal bond in the chromium diatom are due to the work of Klotzbucher and Ozin [36] who used the extended Hückel (EH) and SCF-X α -SW molecular orbital techniques to investigate the spectroscopic data and bonding in Cr₂ obtained experimentally at low-temperatures in an Argon matrix. As pertinently noticed by Politzer et al. [27] in his 1999 review discussing these early results, 'ironically, but prophetically, one of the more successful treatments of Cr₂ was one of the earliest, and used the semi-empirical extended Hückel technique'.

The most successful description of the multiple Cr–Cr bonding was achieved, however, using the multiconfigurational quantum chemistry methods. As far as these multiconfigurational methods are concerned, the chromium diatom is 'by excellence' the golden case to be probed, since its electronic ground state is highly multiconfigurational in character, as demonstrated by the weight of the closed-shell Hartree–Fock configuration in the total wave function, which is only 45% at the equilibrium geometry [37]. First multireference study of the Cr₂ diatomic comes from Goodgame and Goddard [22], who used the spin-optimized generalized valence bond (GVB) method including inter-pair correlations and van der Waals interactions with 6000 configurations. They described the ground state of the Cr₂ as an antiferromagnetic dimer with very low lying electronic states and noticed an absence of multiple bonding between the metal centers. In subsequent Letters with the modified generalized valence bond (MGVB) method [38,39] they have also predicted the double minimum for the potential energy curve of Cr₂ with short bond at 1.61 Å and a longer bond at >3.0 Å. The long

bond was described as a bearing a single 4s–4s interaction with the *d* shells antiferromagnetically coupled into a net singlet state, whereas to the short bond form were assigned five covalent bonds from the chromium *d*–*d* orbitals. One of the most extensive studies concerning the Cr₂ diatom was undertaken by Dachsel et al. [40] who reported a MRACPF calculation that used more than a billion configurations, yielding a bond distance of 1.72 Å and a largely underestimated bond energy of only 25.1 kcal mol⁻¹ (experimental = 35.3 kcal mol⁻¹). Early work involving a CASPT2 treatment to account for the large dynamic correlation effects resulted in a very reasonable description of Cr₂, showing the utility of the multiconfigurational approach for the study of such highly correlated system [41–43]. After the removal of a number of intruder states that have appeared in the wave function deteriorating severely the result, a highly accurate dissociation energy of 35.7 kcal mol⁻¹ and a slightly overestimated Cr–Cr distance of 1.71 Å (exp. 1.68 Å) were obtained. This work was further extended by Andersson, who used a modified form of the zeroth-order Hamiltonian in the CASPT2 method providing a detailed description of a large number of Cr₂ excited states [44].

However, these early studies are afflicted by errors due to the choice of the basis set and the treatment of relativistic effects. A large BSSE correction to the binding energy was obtained with the basis set used in the work of Roos and Andersson's, even if an attempt was made to enlarge the basis set in the 3s, 3p region. Scalar relativistic effects were introduced only at the lowest level using perturbation theory with a non-relativistic basis set. The problem was finally resolved in a Letter by Roos published in 2003 [37], where accurate spectroscopic constants and bond length, as well as bond energy were obtained. This work was done with a basis set of the atomic natural orbital type (ANO) [45] using the Douglas–Kroll Hamiltonian [46] to account for scalar relativistic effects. The semi-core electrons were included in the correlation treatment (3s, 3p for first row transition metals). The problem with intruder states was solved with the aid of a modified zeroth-order Hamiltonian (the IPEA shift [47]) and an extended active space.

In parallel to more demanding multiconfigurational treatments, other methods have also been employed to describe these systems. The earliest attempts to describe the Cr–Cr bond using the HFS (or X α) theory, which is an approximation to the Kohn–Sham DFT formulation, gave Cr–Cr bond and force constants, which were in a reasonably good agreement with experimental values, however

the bond energies suffered notoriously from large errors. In addition these calculations were unable to predict accurately the shelf region of the potential. The calculations using the local spin-density approximation by Delley et al. [48] and later on by Baykara et al. [49] yielded a potential curve for Cr₂ with a single minimum and a highly anharmonic shape. The calculations using a modified non-local density functional theory reported by Ziegler, Tschinke and Becke gave better results [50], with a Cr–Cr distance of 1.65 Å and slightly overestimated dissociation energy to 40.4 kcal mol⁻¹. However, as shown in Fig. 1 in the first paragraph, the characteristic feature of the experimental potential energy curve for the Cr₂ is that it has a shoulder at longer Cr–Cr separation around 3.0–4.0 Å. Such a shoulder (which arises from the interaction of the 4s orbitals and will be discussed in more detail later) should also be reflected in the calculated potential energy curves. In 1994 Bauschlicher and Partridge [32] calculated the potential energy curves for Cr₂ using three popular functionals, commonly used for the calculations of the multiply bonded transition metal complexes, namely pure BLYP and hybrid B3LYP and B3P86. In his report he drew attention to the fact that only the BLYP curve displayed a slight shoulder between 2.5 and 3.0 Å, in agreement with experiment, unlike the analogous curves obtained with the two other functionals. This work suggested that use of the hybrid functionals (e.g. B3LYP, B3P86) is not appropriate in the case of strongly correlated electrons and provides a very poor description of the Cr₂ potential energy curve. Several years later, Edgecombe and Becke analyzed this issue by performing calculations on the ground state potential energy curve of Cr₂ using three different DFT approaches: SVWN, BLYP, and B3P86. These calculations performed within the broken symmetry approach with the spin projection method proposed by Noodleman to correct the ground state energy [51,52] used a large basis set (uncontracted Huzinaga 14s9p5d2f appended with two 4f functions). Very interestingly, only the potential energy curve obtained with the hybrid B3P86 functional showed a double well with a first minimum at 1.59 Å and a second one at 2.40 Å. The corresponding dissociation energies were calculated to be 31.8 and 26.3 kcal mol⁻¹ respectively [53]. More recently, the DFT calculations have been also used to probe the electronic structure of other Cr–Cr species. In 2001 Weinhold and Landis predicted a trans-bent structure for the quintuply bonded HCrCrH species [54], several years before the synthesis of the Ar'CrCrAr' was achieved.

After the report of the experimental results on the Ar'CrCrAr', a multitude of DFT studies were published, mainly with the aim of characterizing the extent of multiple bonding in the experimentally reported Cr–Cr core, as well as to determine the geometrical features in the synthetic Cr–Cr complexes. Yet, all of these reported studies are based on the assumption that the DFT can be used in its monodeterminantal formulation to probe the Cr–Cr bonding by treating the chromium–chromium interaction as a unique closed-shell spin configuration. This assumption might be considered legitimate, because of the largest apparent weight of this configuration in a CASSCF wave function. Such an approach gives, no doubt, a very simplified picture of the bonding situation; however, there is a qualitative agreement between the molecular orbitals involved in the Cr–Cr bonding obtained from multiconfigurational methods and those obtained from DFT.

4. The theoretical approach

The discussion of the electronic structure and the chemical bond in the molecules studied in this Letter will be based on multiconfigurational wave functions, in particular, the Complete Active Space (CAS) SCF method [45], as well as Density Functional Theory (DFT) [55]. The CASSCF method constructs a wave function as a full

CI in a subspace of the molecular orbitals, the active space. This orbital space has to be chosen such that it reflects the multiconfigurational character of the wave function during the chemical process under study. In addition, a number of inactive orbitals will be doubly occupied. They are assumed to be unaffected by the changes in the electronic structures that may take place. The choice of these orbital spaces is the key to a successful CASSCF calculation.

The CASSCF wave function may be analyzed in terms of its natural orbitals and their occupation numbers, which describe different correlation effects. If the active space includes the important orbitals, they will remain stable when the active space is increased, ultimately to the full CI limit. They are therefore useful tools to discuss the electronic structure of the studied molecules. In multiconfigurational quantum chemistry, a single chemical bond is described by a pair of orbitals, a bonding and an antibonding one. Usually, their occupation numbers add up to 2.0. Thus, two electrons reside in these two orbitals. If the occupation number of the bonding orbital, η_b , is close to two and the corresponding antibonding orbital has a small occupation number, η_{ab} , there is a fully developed chemical bond with a bond order equal to one. This is the situation for the chemical bonds in most normal molecules at their equilibrium geometry. However, in transition metal compounds with multiple metal–metal bonds, one often sees occupation numbers η_b , which are smaller than two. If the two occupation numbers η_b and η_{ab} are both close to one, we have no chemical bond, but two antiferromagnetically coupled unpaired electrons. We can therefore define a quantity, the effective bond order, EBO, which quantifies the formation of a chemical bond [16]. For a single bond it is defined as

$$\text{EBO} = (\eta_b - \eta_{ab})/2$$

The EBO will be close to one for a fully developed single bond and close to zero when the bond is dissociated. In multiply bonded systems, one has to add up the individual values for each pair of bonding and antibonding orbitals to obtain the total EBO. At transition states on an energy surface, one often finds half broken bonds where the EBO is somewhere between the two limits. This also often happens in multiply bonded systems that include orbital pairs with weak overlap, for example, the δ orbitals along a metal–metal bond. We shall encounter such examples below. The EBO gives us a means of quantifying the bond order concept for accurate wave functions. It is meaningless for Hartree–Fock wave functions or for closed-shell DFT, but could be useful in a broken symmetry UHF situation if a natural orbital analysis is carried out.

The CASSCF wave function is used to analyze the bonding in a given complex. In order to obtain accurate energies, one has to add an estimate of the dynamic correlation effects. This will be done here using multiconfigurational second-order perturbation theory, CASPT2 [42]. Details of the calculations will be given for each of the systems to be discussed. All calculations have been performed using the MOLCAS program system [45].

The DFT calculations reported here were carried out using the B3LYP hybrid approximation to the exact exchange–correlation energy functional as implemented in the GAUSSIAN 03 program [56]. Preparation of the guess wave functions for the broken symmetry approach was performed using the AOMIX program [57] by Gorelsky (see the Ref. [57] for details). The potential energy curves of Cr₂ and the parent PhCrCrPh molecules were obtained by single point calculations at increasing Cr–Cr separation between 1.3 and 5.0 Å. The basis set used for the description of Cr₂ was the contracted (7s6p4d2f1g) cc-pVTZ that accounts for the correlation of the 4s3d electrons [58]; the basis set used for the description of the PhCrCrPh was the (5s3p2d) DGAUSS DGDZVP [59,60] internally stored in GAUSSIAN 03.

The broken symmetry (BS) approach for the calculation of the electronic structure of the transition-metal diatoms due to Noodleman's work [51,52] has been discussed in several Letters [61,62], and here we report only the most important elements of this DFT ansatz. The approach for the transition-metal diatoms is based on the Dirac-van Vleck Hamiltonian, which accounts for the exchange-coupling between the two metal centers:

$$\hat{H}_{HDVV} = -2J\hat{S}_A\hat{S}_B$$

Here J stands for the exchange-coupling parameter and \hat{S}_A and \hat{S}_B define the local spin operators for centres A and B , respectively. In case of DFT, the BS energy is obtained by a standard SCF procedure using an unrestricted calculation with the appropriate guess wave function, which leads to the BS solution with different orbitals for different spin. To calculate J it is also necessary to compute the high-spin (HS) state with $M_S = S_A + S_B = (S_{\max})$. With these quantities in hand, the J can be evaluated based on Noodleman's equation as:

$$J = \frac{E_{HS} - E_{BS}}{S_{\max}^2}$$

An alternative approach was proposed by Yamaguchi et al. [63,64], where J is computed as:

$$J = \frac{E_{HS} - E_{BS}}{\langle \hat{S}^2 \rangle_{HS} - \langle \hat{S}^2 \rangle_{BS}}$$

Note that the Yamaguchi equation is valid for the entire range of coupling strengths and reduces to the Noodleman equation only in the weak coupling limit [61]. The energy of the ground state is then obtained using the following equation:

$$E_{GS} = E_{BS} + S_{\max}J$$

In case of the Cr–Cr species, the $3d$ electrons are assumed to be antiferromagnetically coupled and $S_A = S_B = 5/2$. Therefore, $S_{\max} = 5$ and the ground state energy is obtained as:

$$E_{GS} = E_{BS} + 5J$$

For all DFT calculations reported in the recent Letters on Cr–Cr species and discussed in the following paragraphs, the level of theory used by the authors of the original experimental or theoretical Letters is described in the corresponding references and it is omitted here.

The bond orders (BO) calculated with DFT using A_{OMIX} [57] are represented by Wiberg bond indices defined as

$$B_{AB} = \sum_{a \in A} \sum_{b \in B} (PS)_{ba} (PS)_{ab}$$

where P is the total density matrix and S is the overlap integral matrix.

5. The chromium diatom and other Cr–Cr species studied with the CASSCF/CASPT2 method

We shall start this exploration of the chromium–chromium multiple bond with a discussion of the bond between two Cr(0) atoms, the Cr₂ diatom. Very recently, this diatom has been used to illustrate the ability of the DFT method to compute potential curves for multiply bonded systems [65]. Below we shall perform a comparison between results obtained with the CASPT2 and DFT but first we shall take closer look at its electronic structure. This will be helpful when we try to understand the Cr–Cr bond in more complex systems.

The Cr–Cr bond is formed from the six unpaired electrons on each of the atoms that have the ground state $(3d)^5(4s)^1, ^7S$. Thus, in principle, a sextuple bond can be formed between the two chromium atoms. It is not surprising that such a bond is difficult to

quantify theoretically because of the strong correlation effects that occur due to the crowdedness of electrons in the bonding region. CASPT2 calculations [37] have, however, yielded spectroscopic constants and a potential curve in good agreement with experiment. We can thus conclude that its electronic structure is also well described at this level of theory. In Fig. 2 are shown the most important active orbitals obtained from the CASPT2 calculation. There are six bonding orbitals ($4s\sigma_g$, $3d\sigma_g$, $3d\pi_u$, and $3d\delta_g$) and six corresponding antibonding orbitals ($4s\sigma_u$, $3d\sigma_u$, $3d\pi_g$, $3d\delta_u$). Bonding and antibonding orbitals are paired together. One notices that in each pair the two occupation numbers add up to 2.00, which makes it possible to attach an EBO to each pair. The first pair is formed from the $4s$ atomic orbitals forming a σ bond with an EBO of 0.90. It has been argued that this orbital is more to be regarded as a Rydberg orbital (see for example Ref. [21]) than as a truly bonding orbital. It is true that at the equilibrium bond distance (1.68 Å), the $4s$ – $4s$ interaction is repulsive because of the much larger size of the $4s$ orbitals compared to the $3d$'s. The $4s\sigma_g$ orbital is, however, doubly occupied with only a small occupation of the corresponding antibonding orbital $4s\sigma_u$. These two orbitals will not play any role in the description of the Cr–Cr multiple bond in the complexes to be described below. The two electrons will move to the ligands, leaving a Cr–Cr moiety with at most five electron pairs.

These five pairs form the $3d$ bonds in the Cr–Cr complexes. As can be seen in the figure, their binding power differs substantially. The $3d\sigma$ -orbital pair makes a bond with an EBO of 0.77, while the $3d\pi$ bonds exhibit an EBO of 0.81 each, and the $3d\delta$ bonds an EBO of 0.58 each. The total EBO is therefore 4.45. So, is the bond in the Cr–Cr diatom a sextuple, quintuple, or even only a quadruple bond? The last conclusion could be derived from the fact the δ bonds are very weak and could also be considered as two pairs of antiferromagnetically coupled $3d\delta$ atomic orbitals. This observation will be useful in the discussion of the bonding in some of the complexes presented later, keeping in mind that these orbitals can instead form bonds with the ligands.

The CASSCF/CASPT2 results presented above [37] yield a bond distance of 1.66 (1.68) Å and a bond energy (D_0) of 38.0 (35.3) kcal mol^{−1} where the experimental values are given within parentheses. The potential curve is shown in Fig. 5 together with the experimental curve from the work of Casey and Leopold [21] and the corresponding curves obtained from DFT calculations that will be described in the DFT section.

The bonding situation described above (with, as noticed, the exception of the $4s$ electrons) is also valid for the analogous

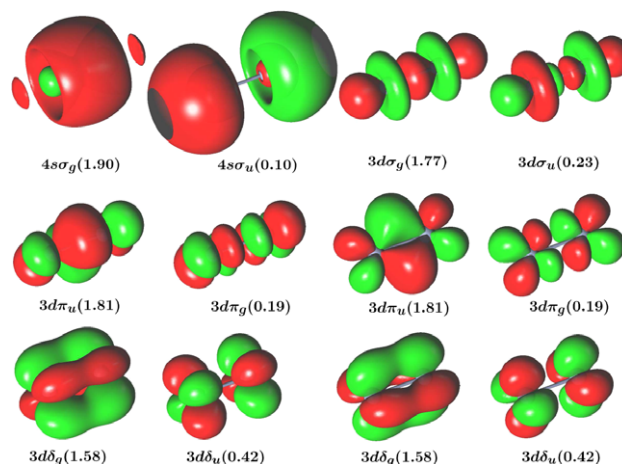


Fig. 2. The natural orbitals for the chromium diatom. Orbital labels and occupation numbers are given below each orbital (contour lines at the density 0.07 e/au³).

Cr–Cr species, where the chromium atoms are attached to the *ipso-carbon* (the ring carbon atom bearing the substituent at position 1) of a neighboring aryl ligand. Such species are represented by the room-temperature stable $\text{Ar}'\text{CrCrAr}'$ complex (cf. Fig. 3) as well as its synthetic analogues with modified substituents on the terphenyl ligand.

The Cr–Cr bonding in $\text{Ar}'\text{CrCrAr}'$ was first analyzed using a simplified model [9] where the ligands were replaced by two phenyl rings, the PhCrCrPh . The interaction of the two chromium atoms leads in this case to five, rather than six, metal–metal bonding molecular orbitals, along with their antibonding counterparts. The CASPT2 optimization results in two structures. The first one is trans-bent, with the computed Cr–Cr and Cr–C distances of Cr–Cr = 1.75 Å and Cr–C = 2.02 Å respectively. Note that these distances are slightly shorter than the experimentally determined values in the case of the corresponding $\text{Ar}'\text{CrCrAr}'$ (Cr–Cr = 1.83 Å, Cr–C = 2.15 Å) and this discrepancy is believed to arise from additional weak interactions with the ligands. Such an interaction is attributed to the extra aryl substituents in $\text{Ar}'\text{CrCrAr}'$, which because of steric and electronic factors as well as the presence of an additional Cr–Phenyl ring interaction weaken both the Cr–Cr and Cr–C bonds somewhat. The second structure is linear, with a short Cr–Cr bond of 1.678 Å and Cr–C bond of 2.040 Å. It lies only 1 kcal mol⁻¹ lower in energy than the trans-bent structure. The Cr–Cr bond energy, obtained by comparing the energy of the CAS-

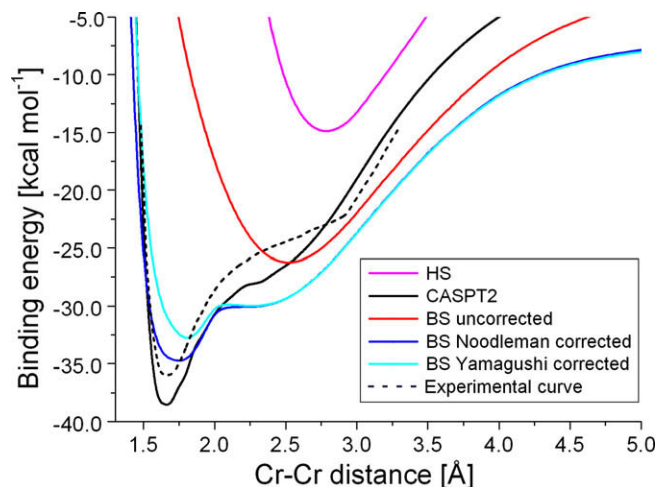


Fig. 5. The potential energy curve for the chromium diatom obtained with the DFT calculations using a B3LYP functional and an acc-pTZVP basis set (see text for details). The CASPT2 curve (black solid line) and the experimental curve [21] (black dashed line) are provided for comparison. HS – high-spin curve ($S=5$), BS uncorrected – broken symmetry open singlet curve without energy correction; BS Noodleman corrected – broken symmetry open singlet curve with energy correction according to Noodleman's equation; BS Yamagushi corrected – broken symmetry open singlet curve with energy correction according to Yamagushi's equation.

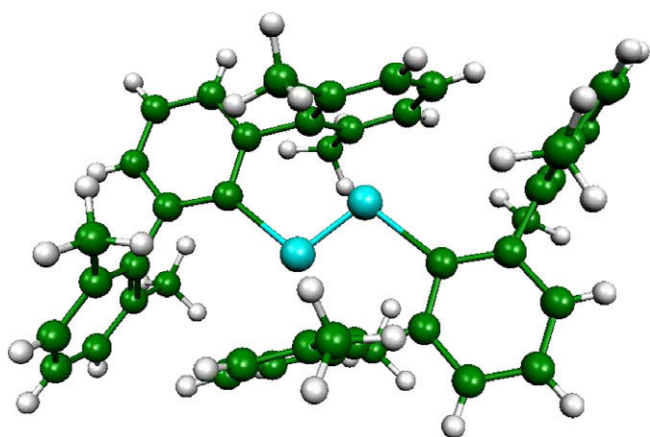


Fig. 3. Molecular structure of the model species for the $\text{Ar}'\text{CrCrAr}'$ recently synthesized by Power's group [3], where isopropyl groups were replaced with methyls.

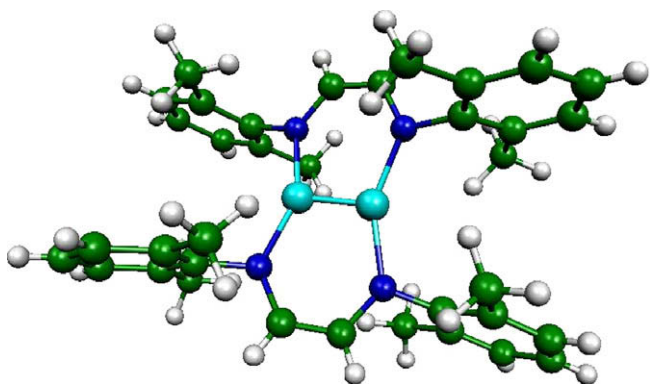


Fig. 4. Molecular structure of model species for the Cr_2 diazene recently synthesized by Kreisel et al. [5], where the isopropyl groups were replaced with methyls.

PT2 optimized PhCrCrPh complex with that of two CrPh units (with DFT-optimized geometry), yields a value of 76 kcal mol⁻¹. This is almost twice the bond energy found for Cr_2 (36 kcal mol⁻¹). As discussed in the case of Cr_2 , the interaction of the 4s electrons is repulsive at equilibrium geometry, causing an important weakening of the Cr–Cr bond. Such weakening does not occur in the RCrCrR structures because of the direct involvement of the 4s electrons in the Cr–C bond with the ligand (see however the discussion below on possible remaining effect of the 4s orbital on the Cr–Cr bond distance).

The analysis of the corresponding CASSCF wave function shows that the major configuration has a total weight of 45% and all the bonding orbitals occupied ($\sigma_g^2(\pi_u)^4(\delta_g)^4$). The second dominating configuration has a weight of 9% and corresponds to a double excitation ($\delta_g^2 \rightarrow (\delta_u)^2$) showing the weakness of the 3d δ bond. The analysis of the occupation numbers in a manner analogous to the Cr_2 case, shows the following: The computed values for the Cr–Cr bonding orbitals and their antibonding counterparts in PhCrCrPh are $\sigma_g(1.79)$, $\sigma_u(0.21)$, $\pi_u(1.76)$, $\pi_g(0.24)$, $\pi_u(1.79)$, $\pi_g(0.21)$, $\delta_g(1.69)$, $\delta_u(0.31)$, $\delta_g(1.50)$, $\delta_u(0.50)$, yielding a total EBO of 3.52. The fractional EBO's for σ , π and δ bonds are $\sigma = 0.79$, two π bonds of 0.76, 0.79 and two δ bonds of 0.69 and 0.50. Thus we see that the fractional EBO's for the CrCr bond are almost identical with the ones obtained for the Cr_2 and the difference between the total EBO's calculated for these species (3.52 vs. 4.45) is due only to the remaining single bond (with fractional EBO of 0.90) formed by the 4s electrons in the additional Cr–C bond with the ligand. Finally we can now have a quick look at the entire $\text{Ar}'\text{CrCrAr}'$ species where the ligands were kept to include the secondary interaction of the chromium atoms with the π system of the ligand [13]. The total EBO is 3.43, in fact almost identical to the one obtained for PhCrCrPh [9].

When the terphenyl moieties are replaced with the ligands containing nitrogen such as the diimines, the situation changes. Even if the total EBO is similar in the case of the RCrCrR and $\text{RN}_2\text{CrCrN}_2\text{R}$ species, the bonding situation and the interactions involved are somewhat different. We have recently described such a bonding in a model compound [12] based on the X-ray structure of the corresponding experimental species reported by Kreisel et al. [5] (see Fig. 4).

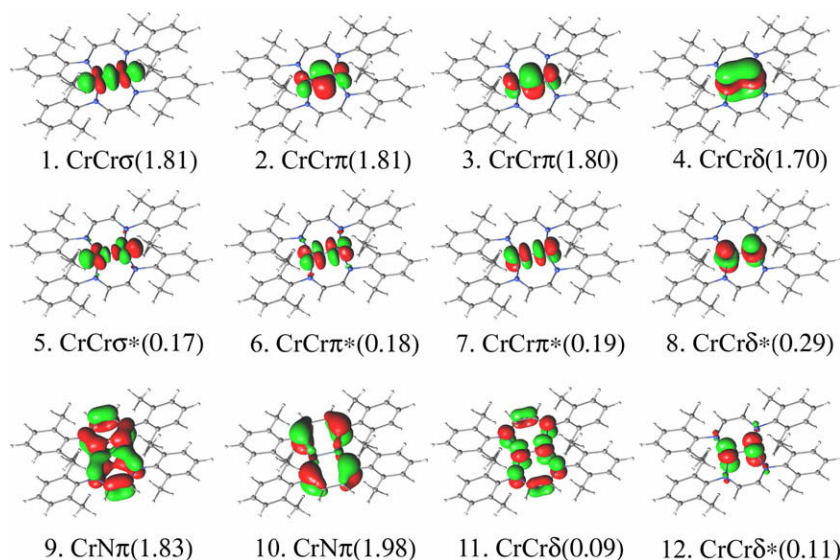


Fig. 6. The 12 CASSCF natural orbitals with their occupation numbers in the $\text{Cr}_2(\text{diazadiene})_2$ complex. Orbitals 9–12 shows the combined Cr–Cr δ bond and Cr–N π bond. The contour line used is $0.05 e/\text{au}^3$.

The leading configuration in the CASSCF wave function is, in a manner, identical to all the other compounds studied here, since it is the closed-shell configuration $(\text{Cr}-\text{Cr})\sigma^2(\text{Cr}-\text{Cr})\pi^4(\text{Cr}-\text{Cr})\delta^2(\text{Cr}-\text{N})\pi^4$, with a weight of 60%. It is interesting to notice that all the other configurations contribute to the wave function with weights lower than 5%. Since additional atoms (nitrogens) are present in the ligands, one has to include these atoms in the active space. By using 12 electrons in 13 orbitals we have obtained 10 molecular orbitals, which are almost completely localized on the Cr–Cr moiety, and two more delocalized orbitals which extend to the nitrogen atoms through bonds to the imine π orbitals. The presence of such delocalized orbitals in the active space makes the evaluation of the EBO less straightforward, for the evident reason that their contribution to the Cr–Cr bond cannot be directly assigned. It is, however, possible to carry out a localization of the orbitals such that the orbitals located at the Cr–Cr moiety are clearly defined. These orbitals are no longer eigenfunctions of the density matrix, but the effect of the off-diagonal elements is small and may be neglected in the calculation of the EBO [12]. Such a procedure was applied and yielded a total EBO of 3.43. The fractional EBO's obtained from the localized orbitals, which can now be simply assigned as being involved in the CrCr bonding only without any ambiguity, are quite interesting. The occupation numbers for the Cr–Cr bonding orbitals and their antibonding counterparts are $\sigma_g(1.81)$, $\sigma_u(0.17)$, $\pi_u(1.81)$, $\pi_g(0.18)$, $\pi_u(1.80)$, $\pi_g(0.19)$, $\delta_g(1.70)$, $\delta_u(0.29)$, $\delta_g(0.75)$, $\delta_u(0.19)$, yielding a total EBO of 3.43. The fractional EBO's are again very similar to the other compounds for all the orbitals, except for the δ interaction, for which the occupation numbers are much smaller. This is due to the fact that this localized orbital was obtained through a localization procedure from the orbital, in which initially an important part of the bonding occurred with the neighboring nitrogen atoms in the form of a Cr-imine π bond [12] (cf. Fig. 6).

6. The chromium diatom and other Cr–Cr species studied with DFT

Since we have already discussed in details the bonding in Cr_2 and in several larger molecules containing the Cr–Cr core in the multiconfigurational methods section, here we would rather present shortly the analogous DFT results and later on, discuss the sim-

ilarity and the differences between the two theoretical descriptions. The DFT in its monodeterminantal formulation, which is commonly used by most of the inorganic chemists and more generally by the experimentalists, can only describe the bonding in a Cr–Cr moiety either as a closed-shell system, or as an open shell determinant with $M_S = 0$, in which all or a fraction of the unpaired electrons on both metal centers are antiferromagnetically coupled. The DFT 'wave function' is in the latter case not an eigenfunction of spin and symmetry and is commonly referred to as a broken symmetry (BS) wave function. The spin symmetry can be approximately restored using the Noodleman spin Hamiltonian, as described in the theoretical section.

The present calculations were performed with the hybrid functional B3LYP, because of its widespread use in the majority of the DFT studies describing the above mentioned experimental results. It is, no doubt, possible to look into the same problem with other functionals but this is not the point here. It is important to recall that within the B3LYP approximation to the exact exchange-correlation functional, the Cr_2 (as well as PhCrCrPh or in general RCrCrR species) remain unbound if computed in the closed-shell singlet state (CS). If we compare now the potential curves for the Cr_2 molecule (Fig. 5) with the analogous potential curves obtained with the CASPT2 method, several things are striking. First, let consider the closed-shell potential. It is not surprising that the DFT description of the closed-singlet state is not appropriate in describing the experimental curve for Cr_2 . The energy is too high and the obtained minimum corresponds to a Cr–Cr bond length of 1.56 \AA , 0.1 \AA smaller than experiment. It is worth noting that such an underestimation of the Cr–Cr bond distance arises with most of the popular DFT functionals not only in the optimized structures of Cr_2 but also of the analogous RCrCrR species [3,9,13].

Let us now switch to the high-spin curve. As expected, due to the energetically unfavorable ferromagnetic coupling between the electrons on both chromium centers with two $M_S = 5/2$ (note that the total spin is $S = 5$ and the multiplicity $2S + 1 = 11$), the curve presents a minimum only at a very large separation of 2.8 \AA , which corresponds to the $4s-4s$ bond. The curve obtained with the uncorrected low spin BS solution alone gives a minimum at about 2.5 \AA . However, as can be seen from the Fig. 5, the spin projection technique performed either via the Noodleman or the Yamaguchi correction results immediately in a better agreement

with the experimental parameters, yielding minima at 1.73 Å and 1.80 Å, respectively. In addition, the shoulder on the curve that arises at about 2.30 Å is also reproduced. This is in line with the previous finding by Becke, who obtained the spin projected broken symmetry solutions for Cr₂ diatom with a very similar shape [53]. The shape of the curves depends of course on the functional and the basis set used, and one has to be careful in selecting the proper basis set. Here we have used a large basis set with two *f* and one *g* functions. The presence of the *f* functions has been reported to be very important in the proper description of the strongly correlated systems such as the multiply bonded chromium diatom [66–68]. However the use of a smaller basis set (DGDZVP, data not shown) fortuitously results in a slightly better agreement for the equilibrium Cr–Cr bond distance (1.69 Å).

The dissociation energy of 32.7 kcal mol⁻¹ calculated at the equilibrium distance as the difference between the energy the two Cr fragments minus the energy of the Cr₂ molecule (with Noodleman's energy correction) is slightly lower than the experimental one (36.0 kcal mol⁻¹), and also as compared to 38.0 kcal mol⁻¹ obtained from the CASPT2 calculations [37].

Analogous calculations were also performed on the PhCrCrPh model (data not shown). In this case, the dissociation curve as obtained from DFT is similar to the one obtained for Cr₂. The major difference is the equilibrium distance of 1.70 Å (as compared to 1.75 obtained from the CASPT2 optimization). A characteristic feature of the spin-projected BS curve is also the absence of the shoulder in the vicinity of 2.5 Å, which was observed in the spin-projected BS curve of Cr₂. This is easily explained by the absence of the 4s electrons, which are now being involved in the Cr–C bond with the phenyl rings. The calculated dissociation energy (36 kcal mol⁻¹) is however much lower than the energy obtained from the CASPT2 calculations

After this more detailed description of the two model species, we shall discuss other DFT studies, which concern synthetic Cr–Cr compounds. The already mentioned Ar'CrCrAr' was recently investigated with DFT within a closed-shell description. The DFT computed bond order was 4.12 and the molecular orbitals obtained from the closed-shell description are similar to the ones obtained from the CASSCF wave function [3,13]. An additional difficulty in this compound is the secondary interaction of chromium with the flanking aryl, which is the origin of the slight elongation of the Cr–Cr bond length as compared to the PhCrCrPh model. DFT is useful in analyzing such a secondary interaction. Unlike the chromium–chromium bonding that cannot be analyzed properly with the closed-shell DFT, in the case of the secondary interactions of the metal with the ligands, DFT performs relatively well. Our calculations on both restrained models for Ar'CrCrAr' and on the simplified Cr–Benzene species indicate that the interaction between the Cr atom and the arene system is weak (as compared to much stronger interaction that occurs for example in the case of the corresponding Fe and Co species [13]).

The DFT closed-shell studies performed on the Cr₂(diazadiene)₂ complex by Kreisel et al. [5] result in reasonable agreement of the optimized geometries with the geometrical features of the experimental X-ray structure. There are six molecular orbitals involved in the bonding, of which five are localized on the Cr–Cr fragment and the additional one is a π type Cr–N interaction. This is also consistent with the MO picture obtained from the CASPT2 study, however the DFT computed BO is as usual too high (4.28) as compared to the one obtained from the CASSCF wave function (3.43).

Since we have been discussing the differences between the DFT and CASSCF pictures of the bonding in Cr–Cr species, an important problem that arises when the computed bond orders are compared between the two approaches should be briefly discussed. Inspection of Table 1, shows that the computed bond orders at experimental Cr–Cr distances using DFT in both, the closed-shell

and broken symmetry approach are different from the EBO's computed with the CASPT2. Clearly, the closed-shell DFT calculations always overestimate the Cr–Cr bond order, while in the broken symmetry approach, the inverse effect is observed. For example, for the PhCrCrPh at the equilibrium distance the CASPT2 computed EBO is 3.5 while the DFT calculations result in a BO of 4.2 for the CS state and 2.8 for the BS state. Quite surprisingly, the CASPT2 computed EBO is in this case the average of the BO values computed for CS and BS states. Similar behavior is observed for the other species including the complexes with the nitrogen containing ligands.

7. Discussion

The ultimate goal of the theoretical studies focused on the multiple metal–metal bonds is to understand the bonding pattern in terms of the corresponding electronic structure. Such understanding can help us to answer several questions, e.g. why is one bond shorter than the other, or how the bond order is related to the bond length. As far as the multiple Cr–Cr bond is concerned, several topics are of interest. The first one is the effective bond order of the Cr–Cr bond. It is important to understand how it is influenced by the ligands, or more precisely, how the electronic structure of the ligand affects the bonding between the chromium atoms.

How long is therefore the 'natural' bond length for the quintuple Cr(I)–Cr(I) interaction? We have seen that the bond length in Cr₂ is 1.68 Å and one might think that this is a lower limit, considering the formation of a sextuple bond in this case. However, we also know that the 4s–4s interaction is repulsive at this distance. What happens if we remove the 4s electrons? This can be done by adding an electronegative ligand to each Cr atom, as for example in the hypothetical compound FCrCrF. Optimization of the geometry of this molecule at the CASPT2 level of theory with ANO-RCC-VTZP basis sets gives a Cr–Cr distance of 1.65 Å, 0.03 Å shorter than in the Cr diatom. The 4s electrons are effectively removed by the electronegative ligand and we may thus consider 1.65 Å as the 'unbiased' Cr(I)–Cr(I) bond length. This may sound somewhat surprising, considering that all the measured (and computed) Cr–Cr distances are longer than 1.70 Å. The only exception so far is the value computed for the linear PhCrCrPh, which is 1.68 Å. The difference compared to FCrCrF can be attributed to the more covalent bond formed between Cr and the phenyl group. At the trans-bent equilibrium geometry of this system however, the computed bond length is 1.75 Å, causing a lengthening of 0.07 Å (the experimental value for the Ar'CrCrAr' complex is 1.83 Å, but this difference, as we mentioned, can be attributed to the extra Cr–Aryl interaction [13]). It seems that the bond length depends mainly on two factors, the effectiveness in the removal of the 4s electrons and the involvement of the 3d orbitals in the Cr–L bonding. In trans-bent PhCrCrPh this second factor is certainly important.

As demonstrated by the experimental findings and the CASPT2 calculations, the Cr–Cr bond seems to be fairly insensitive to the modification of the ligands, even if different classes of ligands are compared. For all the complexes that we have studied, with the fivefold Cr–Cr interaction, the EBO ranges between 3.3 and 3.8. This range is much narrower if only one class of ligands is taken into account (e.g. for the terphenyl ligands the EBO's are 3.4–3.5). The second observation is that there is no simple relation between the Cr–Cr bond length and the bond order. Moreover, there even seems to be no simple relation between the type of the ligand and the same bond length.

From a purely qualitative point of view, one would expect a smaller bond order for a longer bond, based on the intuitive notion of the overlapping molecular orbitals between the metal atoms. However many different other factors can influence the bond

length. For example, in the case of the diimine ligands, the strain in the NCCN ligand moieties is most probably the key factor that holds the two Cr atoms in place and severely limits the variations in the Cr–Cr bond distance.

This brings us to an interesting property that relates to the (relatively moderate) strength of the Cr–Cr quintuple bond, which we have recently described as its apparent ‘robustness’. In a recent theoretical Letter we have addressed this Cr–Cr distinctiveness [13], which, while not relevant to the di-chromium molecule, becomes very important in the case of the bulky ligands used for the stabilization of the Cr–Cr bond, namely the secondary interactions with the arene part of the ligand. Such interaction could, in principle, be responsible for large variations in the Cr–Cr bond length. However, recent reports of the species where Cr–Cr core is attached to very different ligands, where such interaction is absent, seems to contradict this hypothesis. On the other hand, dramatic differences between species where the atoms forming the metal–metal cores are different from chromium seem to elucidate this problem. Recently, we have demonstrated that, for example, the Co–Co and Fe–Fe dimers synthesized with the same ligand as the ones used in $Ar'CrCrAr'$ are not formed. This is because the metal ions themselves interact strongly with the arene parts of the ligands, precluding a significant multiple bonding between the metal centers. Instead ‘half-metalloenes’ are obtained with the metal ions complexed in the ${}^6\eta$ fashion to the arene moiety of the ligand. The DFT calculations performed on simplified molecular models to probe the extent of this arene–metal interaction, suggest that at least two factors contribute to the structural differences observed between the quintuply bonded chromium dimer and its cobalt and iron congeners. Our conclusion is that the robustness of the Cr–Cr quintuple bond is related to the special character of the $RCr(I)$ species, whose electronic (d^5) structure seems to preclude strong interactions with the nearby arenes, such as benzene or phenyl fragments. This is most probably due to the fact that Cr(I) is particularly stable due to the half-filled d -shell, which results in a large number of favorable intra-atomic exchange interactions that reduce Coulomb repulsion. Therefore Cr(I) is reluctant to lose these favorable interactions, which greatly diminish its affinity to interact with other ligands. This apparent reluctance to interact more strongly with the surrounding π system of the ligand is an important factor that contributes to the stability of the quintuple Cr–Cr bond. The second factor is related to the most important attribute of the Cr(I)–Cr(I) bond, which is the presence of a high number (10) of valence electrons that exactly match the number of bonding molecular orbitals. The additional experimental evidence comes from the fact that the monomeric Ar–Co and Ar–Fe congeners of monomeric Ar–Cr form easily direct adducts with the benzene molecule, while in the analogous monomeric Ar–Cr species the Cr atom is complexed rather by PMe_3 or THF molecules [69].

Another interesting aspect of the chromium–chromium interactions studied here is the oxidation state of the chromium atoms in different Cr–Cr bonds. Is this oxidation state always the same? In the simplest case of the $RCrCrR$ species, the answer is trivial. The oxidation state of Cr is +1. However, when the N -containing ligands enter the game, the determination of the formal oxidation state is not straightforward anymore. First, the diimine ligands can be considered either as entities with -2 , -1 , or even 0 charge. Such a redox ambiguity is typical of diimines, where several resonance structures can in principle be considered. In the case of the Cr_2 (diazadiene) $_2$ compound reported by Kresiel et al. [5], the bond lengths in the ligand suggest a reduced form, e.g. an oxidation state between -1 and -2 . Therefore the oxidation state of the Cr ions should be between +1 and +2. We have argued that Cr atoms lose the 4s electrons, which in this case would participate in the bond of Cr atom with the ligands. In addition, π bonds are formed between Cr and N, half a bond per Cr–N pair. This gives a formal ox-

idation number of +1.5. The situation is even more confusing with the ‘lantern’ compound reported by Tsai et al. [7]. Here the three diimine ligands forming the cage should have a total charge of -3 , bringing the formal oxidation state to somewhere between 1.5 and 2.0 and this should result in a formation of a quadruple bond. Still, the bond distance is shorter, 1.74 Å.

In order to test if we could also obtain an unbiased bond length for the Cr(II)–Cr(II) interaction, we also performed CASPT2 calculations on F_2CrCrF_2 . The optimization of this species did, however, not lead to any bound species. Our conclusion is that two Cr(II) ions will not form a bond due to the increased Coulomb repulsion and the decreased bond order as compared to Cr(I). Instead, the short bond lengths observed in the synthesized Cr(II)–Cr(II) compounds have to be explained by the nature of the supporting ligands that are always bi-dentate and hold the Cr(II) ions in place. Some examples of such compounds were given above.

8. Conclusions and perspectives

The present study has analyzed the Cr–Cr multiple bond as it occurs in Cr_2 , as well as in different recently synthesized low-valent Cr–Cr complexes. This multiple bond is characterized by one feature that is invariant and does not change with the nature of the ligand or with the oxidation state of the Cr atom: that is, the $(3d\sigma)^2(3d\pi)^4$ triple bond. This bond is fully formed in all the species studied here and exhibits always an EBO close to 2.3. The remaining δ bonds are however much weaker. Depending on the ligand attached to the metal center, a competition between the Cr–Cr bonding and the Cr–ligand bonding involving the orbitals participating in the δ bonds occurs. For example in the case of the imine ligands, Cr–N π bonds are formed instead of Cr–Cr δ bonds. Formation of Cr–N π bonds in turn lowers the bond order and should in principle also lead to longer bond lengths. However this is not always the case, due to the steric influence of the dentate ligands, which lead to bond lengths that maximizes the Cr ligand interaction at the expense of the small changes in the Cr–Cr bond energy. We can therefore conclude that the weakness of the δ bonds is the most important factor that makes the Cr–Cr bond length flexible and strongly dependent on the nature of the ligands.

The molecules discussed here have also been studied using DFT with the B3LYP functional. This approach has several shortcomings for the wave functions with such a strong multiconfigurational nature as those describing the Cr–Cr multiple bond. Normally, the closed-shell DFT wave function is not stable but degrades to a broken symmetry solution if allowed to do so. The closed-shell solution can be then useful for the optimization of the general structural features of the low-valent Cr–Cr complex, but the Cr–Cr bond length is underestimated by about 0.1 Å and need to be re-optimized at a higher level of theory. The broken symmetry solution is even less useful. It gives much too long Cr–Cr bond distances and the electronic structure is severely distorted with the S^2 values different from zero. Energy wise, it is possible to correct approximately for these shortcomings in the broken symmetry approach using the Noodleman or Yamaguchi techniques, as described above, but this approach will not correct other properties and is difficult to use, for example, for the commonly performed tasks such as the geometry optimizations.

The final conclusion is that in order to describe properly the electronic structure of the compounds studied here, we need the multiconfigurational wave function approach. This approach can today be applied for increasingly bulky systems, making it available for the real chemical complexes that are studied experimentally. And clearly, the number of experimental reports concerning multiply bonded species with large ligands is growing very fast. For such large molecules, DFT can be useful as a helping hand because the

CASSCF/CASPT2 approach has not yet reached the stage where full geometry optimizations for system with about 100 atoms are possible. A careful combination of DFT and the wave function approach becomes therefore quite useful in many cases. However, this may change in the near future due to the development of the Cholesky decomposed gradient techniques [70] that will allow geometry optimizations of large molecular systems at the CASSCF level.

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