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Article

On the Analysis of the Cr–Cr Multiple Bond in Several Classes of Dichromium Compounds

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Since the discovery of a formal quintuple bond in Ar′CrCrAr′ (CrCr = 1.835 Å) by Power and co-workers in 2005, many efforts have been dedicated to isolating dichromium species featuring quintuple-bond character. In the present study we investigate the electronic configuration of several, recently synthesized dichromium species with ligands using nitrogen to coordinate the metal centers. The bimetallic bond distances of Power's compound and Cr_2-diazadiene (**1**) (CrCr = 1.803 Å) are compared to those found for $Cr_2(\mu\text{-}\eta^2\text{-}ArNC(R)NAr)_2$ (**2**) (CrCr = 1.746 Å; R = H, Ar = 2,6-$Et_2C_6H_3$), $Cr_2(\mu\text{-}\eta^2\text{-}Ar^{Xyl}NC(H)NAr^{Xyl})_3$ (**3**) (CrCr = $1.740^{\mathrm{reduced}}/1.817^{\mathrm{neutral}}$ Å; Ar^{Xyl}= 2,6-C_6H_3-$(CH_3)_2$), $Cr_2(\mu\text{-}\eta^2\text{-}TippPyNMes)_2$ (**4**) (CrCr = 1.749 Å; TippPyNMes = 6-(2,4,6-triisopropylphenyl)pyridin-2-yl (2,4,6-trimethylphenyl)-amide), and $Cr_2(\mu\text{-}\eta^2\text{-}DippNC(NMe_2)N\text{-}Dipp)_2$ (**5**) (CrCr = 1.729 Å, Dipp = 2,6-*i*-$Pr_2C_6H_3$). We show that the correlation between the CrCr bond length and the effective bond order (EBO) is strongly affected by the nature of the ligand, as well as by the steric hindrance due to the ligand structure (e.g., the nature of the coordinating nitrogen). A linear correlation between the EBO and CrCr bond distance is established within the same group of ligands. As a result, the CrCr species based on the amidinate, aminopyridinate, and guanidinate ligands have bond patterns similar to the Ar′CrCrAr′ compound. Unlike these latter species, the dichromium diazadiene complex is characterized by a different bonding pattern involving Cr–Nπ interactions, resulting in a lower bond order associated with the short metal–metal bond distance. In this case the short CrCr distance is most probably the result of the constraints imposed by the diazadiene ligand, implying a Cr_2N_4 core with a closer CrCr interaction.

1. Introduction

The nature of the interactions governing chemical bonds has always fascinated chemists. For quite a long time, transition metal chemistry was ruled by the ideas developed at the end of the 19th century by Alfred Werner.[1] Werner's theory was able to explain, at least partially, the coordination chemistry of these elements, although the metal ion was considered as an isolated unit surrounded by ligands, precluding any direct metal–metal bonding. At best, only indirect transition metal interactions through shared ligands were taken into account. The ability of d-block elements to be involved in direct metal–metal interaction was revealed half a century ago by Cotton and co-workers, giving birth to a new research field of inorganic chemistry: the chemistry of metal–metal multiple-bonded species. In 1963, the first achievement in this area consisted in the isolation of the $[Re_3Cl_{12}]^{3-}$ molecule containing the $Re(III)_3{}^{9+}$ core unit made of three double bonds.[2,3] The second one came in 1964, with the quadruply bonded Re(III)–Re(III) unit in the $K_2[Re_2Cl_8]\cdot 2H_2O$ complex[4–7] featuring a Re–Re distance of 2.24 Å, shorter than the one found in the metallic rhenium (2.75 Å). The surpassing of the triple-bond limit ruled by the p-block elements gave rise to a new challenge: the quest for the multiple bonds with the highest possible order. About one thousand compounds featuring high bond multiplicity have been synthesized and characterized since.[8]

After Cotton's milestone discovery in 1964, no real breakthrough was achieved in this area until the synthesis of

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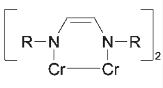
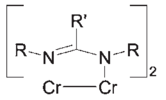
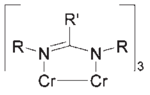
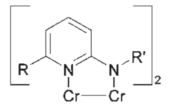
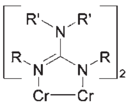
Table 1. Structures of Compounds **1**−**5**[a]

1	**2**	**3**	**4**	**5**
				
diazadiene	amidinate	amidinate (lantern)	aminopyridinate	guanidinate

[a] The nature of the fragments R and R′ is specified in the text.

Table 2. Different Variants of Species **2** and the Corresponding CrCr Bond Distances[a]

a		*b*		*c*		*d*	
R	R′	R	R′	R	R′	R	R′
2,4,6-$Me_3C_6H_2$	H	2,6-$Et_2C_6H_3$	H	2,6-*i*$Pr_2C_6H_3$	H	2,6-*i*$Pr_2C_6H_3$	Me
1.7404(8) Å		1.7454(1) Å		1.7472(10) Å		1.7395(7) Å	

[a] Only the variant ***b*** of species **2** has been investigated in the present work. No relevant changes are expected to occur for the other variants.

Ar′CrCrAr′ (CrCr = 1.835 Å) by Power and co-workers in 2005,[9] bringing to light the first compound featuring a formal quintuple bond. Such accomplishment was possible by making the right choice of transition metal, as well as providing a ligand assuring sufficient kinetic stabilization of the metal−metal bond. In this perspective, the group 6 elements, such as chromium, are *par excellence* the best candidates for the quintuple metal−metal interaction. Five out of their six valence electrons can be used to form the quintuple bond, leaving one electron free to share a bond with the surrounding ligand. The choice of the ligand is the crucial parameter that allows keeping the transition metal in the lowest possible oxidation state, at the same time maximizing the number of valence electrons available for the formation of multiple bonds.

The synthesis of Ar′CrCrAr′ gave new momentum to the chemistry of multiple-bonded metal−metal species and became a new impetus for the isolation of increasingly shorter metal−metal interactions. In this paper we will discuss several such compounds (see Tables 1 and 2 for structural details and numbering). The very short Cr−Cr bond of 1.828 Å measured in solid tetrakis(2-methoxy-5-methylphenyl)-dichromium[10] was challenged in 2007 by Kreisel and co-workers, who isolated the dichromium diazadiene complex (**1**)[11] featuring a Cr−Cr bond distance of 1.803 Å and Cr−N distances of 1.913 and 1.914 Å. The work of Kreisel highlighted the possibility of using a new class of ligands relying on nitrogen that were subsequently used to isolate species featuring short metal−metal bonds with various transition metal elements.[12−15] In 2008, Hsu and co-workers[12] used amidinate ligands to form closely related compounds of the type $[Cr_2(\mu\text{-}\eta^2\text{-}ArNC(R)NAr)_2]$ ($\mathbf{2}_{a-d}$). Their Cr−Cr equilibrium bond distances are close to 1.74 Å (the exact values are reported in Table 2). During the same year, Tsai and co-workers[13] showed that amidinate ligands of the type $Ar^{Xyl}NC(H)NAr^{Xyl}$ (Ar^{Xyl} = 2,6-C_6H_3-$(CH_3)_2$) can be used to achieve very short Cr−Cr bond length within a paddle-wheel-type architecture (**3**). They investigated the paramagnetic neutral species $[Cr_2\text{-}(Ar^{Xyl}NC(H)NAr^{Xyl})_3]$, as well as its reduced form, $[Cr_2\text{-}(Ar^{Xyl}NC(H)NAr^{Xyl})_3]^-$. Both feature short bimetallic distances of 1.817 and 1.740 Å for the neutral and reduced species, respectively. Noor and co-workers[14] investigated a Cr_2 compound based on the aminopyridinate ligand (**4**). This species, unlike compounds **2** and **3**, is composed of a ligand with two nonequivalent coordinated nitrogens, N_{amido} and $N_{pyridine}$. The relevant structural parameters of this complex are the Cr−Cr bond distance of 1.749 Å and the Cr−N_{amido} and Cr−$N_{pyridine}$ bond distances of 1.998 and 2.028 Å, respectively. In 2009, the gap between the bare Cr_2 molecule, having a bond distance of 1.68 Å, and the Cr(I)−Cr(I) unit was bridged by Noor and co-workers.[15] They were able to isolate a compound with a Cr−Cr bond length of 1.729 Å, the shortest metal−metal bond observed to date. It was obtained using guanidinate ligands (**5**), which were shown to ensure a very short Cr(II)−Cr(II) distance of 1.773 Å in $\{(Me_3Si)_2NC(Ncy)_2CrMe\}_2$.[16]

The aforementioned compounds, based on amidinates, aminopyridinates, and lately on guanidinates, have almost the same $Cr_2(RNC(R)NR)_2$ core unit but differ considerably in the outer architecture. The guanidinates are the latest generation of ligands, which seem to be the most suitable candidates to achieve even shorter Cr−Cr bond lengths. The most interesting feature of these ligands is their possible modification by attaching different groups to the nitrogen

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not involved in the bonding with the metal. Such fine-tuning of the ligand allows the N−C−N fragment to behave as a modifiable pincer, forcing the two transition metals to approach each other to different extents.

As for now, the main target in the dichromium chemistry is the synthesis of the compounds with the Cr−Cr interactions closest to the limit imposed by the Cr_2 molecule.[17] However, the connection between the Cr−Cr bond length and the order of the chemical bond is anything but obvious. Although the nature of the chemical bond can be accurately described using modern quantum chemistry, its quantification in terms of bond order is still a challenge, as it does not refer to any physical observable. Among different methods available to quantify the bond multiplicity, the effective bond order (EBO) is one of the most accurate, reflecting the multiconfigurational character of the electronic configuration of the bond (see Computational Methods). In this work, we investigate the recently synthesized structures with the main goal of establishing a correlation between the EBO and the chromium−chromium bond length in dichromium compounds bearing different classes of stabilizing ligands.

2. Computational Methods

The dichromium compounds discussed in this work were studied using the following scheme based on combined DFT and CASPT2[18,19] approaches. The same strategy was proven to be successful in the study of several metal−metal-containing systems.[20−24] Two degrees of freedom, namely, the Cr−Cr and Cr−N bond distances, were optimized at the CASPT2 level using a numerical procedure (for the lantern species (**3**) only the Cr−Cr bond was studied at the CASPT2 level). For each point of the grid, corresponding to a given set of Cr−Cr and Cr−N bond distances, the rest of the molecule was optimized at the DFT level. The DFT calculations employed DZP basis sets and the B3LYP functional using the TURBOMOLE software.[25] Due to the size of the Cr_2-guanidinate (**5**) complex, geometry optimization employed the PBE functional and resolution-of-the-identity approximation for the evaluation of the Coulomb integrals along with the triple-ζ valence plus polarization (def-TZVP) basis sets on all atoms. For all investigated species, analysis of the electronic structures was performed on the DFT/CASPT2-optimized models. The CASPT2 calculations were performed using the MOLCAS-7.3 package.[26] The ANO-RCC basis set with triple-ζ quality (ANO-RCC-VTZP)[27] was used on chromium, whereas the double-ζ basis set quality (ANO-RCC-VDZP)[28,29] was used on the other atoms. Only for the Cr_2-guanidinate complex were triple-ζ quality basis sets employed on Cr and N, double-ζ quality on C, and minimal basis set (ANO-RCC-MB) on H.[29] C_2 symmetry was imposed for the lantern and the Cr_2-guanidinate species, whereas C_i and C_{2h} symmetry were imposed for aminopyridinate and $Cr_2(\mu\text{-}\eta^2\text{-}ArNC(R)NAr)_2$, respectively. Scalar relativistic effects were included using the Douglas−Kroll−Hess Hamiltonian.[30] The computational costs arising from the two-electron integrals were drastically reduced by employing the Cholesky decomposition technique in all CASSCF/CASPT2 calculations[31,32] combined with the local exchange screening.[33] The decomposition threshold was chosen to be 10^{-4}, as this should correspond to an accuracy in total energies on the order of mhartree or higher. The frozen natural orbital approach with a truncation level of 70% was employed in the CASPT2 (FNO-CASPT2) calculations to reduce disk requirements and computational costs.[34] For all species, orbitals up to and including the 1s for carbon and nitrogen and 2p for chromium were kept frozen.

For species **2**, **4**, and **5**, the complete active space (CAS) contains 12 electrons distributed in 12 orbitals (12, 12). This space comprises all the 3d orbitals forming the Cr−Cr multiple bond as well as one bonding and one antibonding orbital, describing the Cr−N interactions. The Cr−N bonding and antibonding orbitals are lying lower and higher in energy, respectively, and therefore their occupation numbers are either 2 or 0. For species **3**, only the orbitals describing the Cr−Cr multiple bond were included, resulting in 10 and 9 electrons distributed in 10 orbitals, for the reduced and neutral compound, respectively. Species **1** was investigated in our previous study.[23] The natural orbital occupation numbers were used for the evaluation of the effective bond order (EBO),[24,35,36] which is defined as half the difference between the sum of the occupation numbers of the bonding orbitals minus the sum of the occupation numbers of the antibonding orbitals of the Cr−Cr multiple bond.

3. Results

3.1. Cr_2 and Amidinate Ligands. Following the successful synthesis of the dimolybdenum complex with each metal center coordinated to two nitrogen donors,[37] Tsai and co-workers extended the same concept to the dichromium species using sterically cumbersome amidinates. In the present study we have investigated the bonding situation in $Cr_2(\mu\text{-}\eta^2\text{-}ArNC(R)NAr)_2$ (R = H, Ar = 2,6-$Et_2C_6H_3$) (**2**) at the combined DFT/CASPT2 level of theory. The Cr−Cr and the Cr−N bond lengths optimized at the CASPT2 level of theory are 1.764

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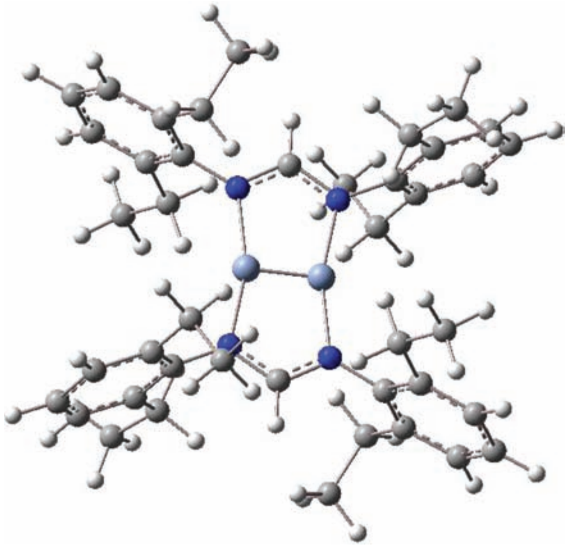

Figure 1. Cr_2-amidinate complex (**2**). Cr is depicted in light blue, N in dark blue, C in gray, and H in white.

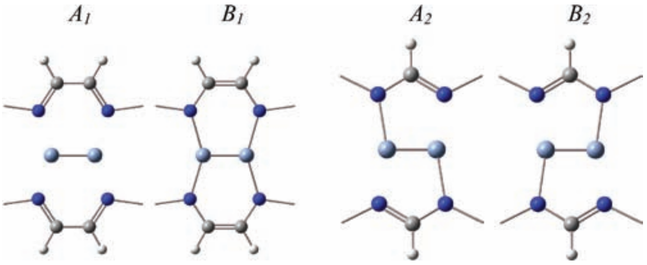

Figure 2. Resonance forms for species **1** (left) and **2** (right).

and 1.991 Å, respectively, in good agreement with the experimental values of 1.746 and 2.014 Å. The associated EBO of 3.80 is obtained using the natural orbital occupation numbers (Figure S1, Supporting Information). The charge distribution within this compound can be depicted as a combination of two negatively charged ligands stabilizing the central dichromium unit with a formal charge of +2. Although the CrCr core unit is interacting with four equivalent nitrogens (in contrast to the two equivalent carbon atoms in PhCrCrPh), the two structures have similar bonding patterns, leading to the formation of a formal quintuple bond. An interesting feature characterizing the bonding is the complete absence of the Cr−Nπ interaction, which is present in compound **1**. This situation can be explained on the basis of the charge distribution within each ligand. The electron is delocalized over the $N_1C(R)N_2$ fragment, and therefore N_1 can be the N_{amido} nitrogen involved in the bonding with the CrCr, whereas N_2 can be the N_{imino} involved in the π bond with the central carbon atom. Two resonance forms can be drawn, shown as A_2 and B_2 in Figure 2.

The Cr_2-ligand interaction exhibited by species **1** is different, and one of its resonance forms is of the diamido type (B_1 in Figure 2). The associated bonding pattern is featured by two metal centers, each coordinated to two nitrogens. However, in this case it is not obvious how to assign the oxidation state to the dichromium unit, which can be considered in the range from +1 to +2, as reported in our previous work.[23] In order to understand how the bond multiplicity is affected by the type of nitrogen present in the ligands, it is interesting to look at two closely related ligands, namely, $RNSi(Me_2)NR$ and $RNC(R')NR$, used to stabilize the Mo−Mo unit.[37,38] The difference resides in the number of amido nitrogens within the ligands: one and two for $RNC(R')NR$ and $RNSi(Me_2)NR$, respectively. The difference, even though small, is enough to result in a decrease of the bond order, going from a quintuple to a quadruple bond.

3.2. Cr_2 and Lantern Amidinate Ligands. Amidinate molecules proved to be efficient stabilizing ligands for dichromium species, resulting in a paddlewheel-type architecture with the dichromium unit residing inside the cage created by $[Ar^{Xyl}NC(H)NAr^{Xyl}]_3$ (Ar^{Xyl} = 2,6-C_6H_3-$(CH_3)_2$). In the present model, the 2,6-C_6H_3 methyl groups were replaced by hydrogens. The structural parameters obtained from the CASPT2 optimization, the Cr−Cr and the Cr−N bond lengths, are 1.777 (1.817) and 1.982 (2.044) Å for the neutral paramagnetic species (**3**) and 1.738 (1.740) and 2.017 (2.092) Å for the reduced one (**3**). (The experimental bond lengths are reported in parentheses.) Both theory and experiment confirm a shortening of the Cr−Cr bond when going from the neutral to the reduced species. Such a trend arises from the change of the number of electrons involved in the chemical bond. In the case of the neutral paramagnetic species, the ${Cr_2}^{3+}$ unit has a $\sigma^2\pi^4\delta^3$ electronic configuration, whereas the ${Cr_2}^{2+}$ in the reduced compound has a $\sigma^2\pi^4\delta^4$ electronic configuration. The presence of one extra electron in the δ bonding orbital in the latter case increases the corresponding bond order. The EBO values calculated for these compounds are 3.46 and 3.91 for the neutral and the reduced species, respectively (natural orbital occupation numbers in the Supporting Informations, Figures S2 and S3). Note that there are no changes in the EBO contribution from the σ and π orbitals (Table 3). The nature of the chemical bond for the neutral species **3** can be viewed as an intermediate situation between species **1** and **2**, as one of the 3dδ molecular orbitals is neither empty (**1**) nor doubly occupied (**2**). The resulting difference in the EBO values caused by the single occupation of the 3dδ orbitals is interesting, as it shows the important role played by these orbitals in the Cr−Cr bond, even though they are characterized by smaller overlap compared to the other metal−metal orbitals.

3.3. Cr_2 and Aminopyridinate Ligands. The calculations were performed on a simplified model, where the cumbersome 2,4,6-triisopropylphenyl (TIP) and 2,4,6-trimethylphenyl (Mes) flanking aryls were replaced by phenyl groups (**4**). The compound has two types of nitrogen atoms, namely, the N_{amido} and $N_{pyridine}$. Species **4** can be described by two resonance forms, where the electron can be localized either on the N_{amido} (resonance form 1) or on the $N_{pyridine}$ (resonance form 2). Both nitrogens are involved with the same weight in the interaction with the CrCr core, as indicated by the shape of the Cr−N molecular orbitals (Figure S4, Supporting Information) as well as their charge obtained from the Mulliken population analysis ($N_{pyridine}$: −0.6294, N_{amido}: −0.7156). As a consequence, the two resonance forms exhibit a single

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Table 3. EBO Values for Species **2**−**5**: σ, π, δ Contributions and Total EBO[a]

σ, π, and δ Contributions											
2			**3**			**4**			**5**		
σ	π	δ	σ	π	δ	σ	π	δ	σ	π	δ
0.83	1.62	1.36	0.81(0.81)	1.66(1.61)	1.44(1.04)	0.82	1.57	1.27	0.83	1.62	1.35
Total EBO											
3.80			3.91 (3.46)			3.65			3.79		

[a] The total EBOs were calculated using the natural orbital occupation numbers reported in the Supporting Information (S1 to S5). For species **3**, the values reported in parentheses refer to the paramagnetic neutral compound.

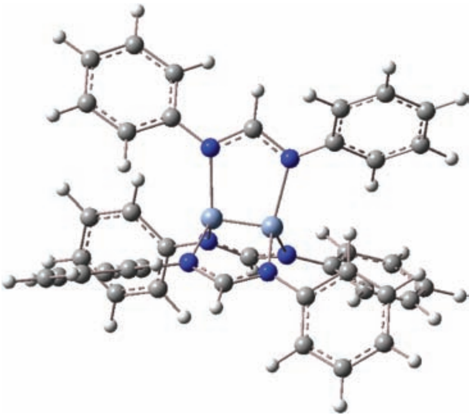

Figure 3. Lantern Cr_2-amidinate complex (**3**). See Figure 1 for color coding.

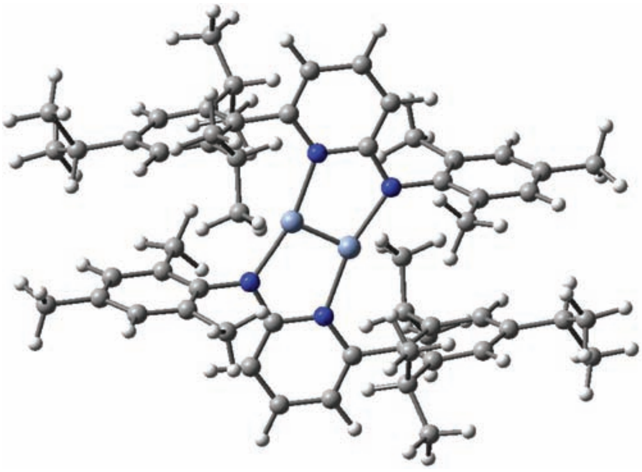

Figure 4. Cr_2-aminopyridinate complex (**4**). See Figure 1 for color coding.

Cr−Nσ interaction, which involves either the N_{amido} or the $N_{pyridine}$ atom. The most relevant parameters obtained from the CASPT2 optimization, the Cr−Cr, Cr−N_{amido}, and Cr−$N_{pyridine}$ bond distances, are respectively 1.806 (1.749), 1.990 (1.998), and 2.010 (2.028) Å. (The experimental bond lengths are reported in parentheses.) The difference of about 0.06 Å between experiment and theory in the case of the Cr−Cr bond distance might be due to the less pronounced steric hindrance when replacing TIP and Mes groups by the smaller phenyl groups. The effective bond order exhibits a value of 3.65 at the computed equilibrium bond distance.

3.4. Cr_2 and Guanidinate Ligands. The potential of guanidinates to stabilize short metal−metal distances was shown by Horvath and co-workers.[16] Very recently Kempe and co-workers succeeded in synthesizing a new homobimetallic chromium complex with guanidinate ligands,[15] which is visualized in Figure 5. The Cr−Cr bond length is 1.729 Å and is the shortest metal−metal distance reported for a stable compound. A specific feature of this structure is the planar arrangement of the three nitrogen atoms and their residues, which are frozen between two bulky 2,6-isopropyl phenyls. Such ligand architecture excludes any out-of-plane arrangement of the methyl groups attached to the noncoordinating nitrogen atom. The methyl groups push the two 2,6-isopropylphenyl groups further down, resulting in a shortening of the metal−metal bond. We have performed two sets of calculations: one on the experimentally synthesized complex (**5**) and one on a model system, in which the isopropyl substituents were replaced by methyl groups.

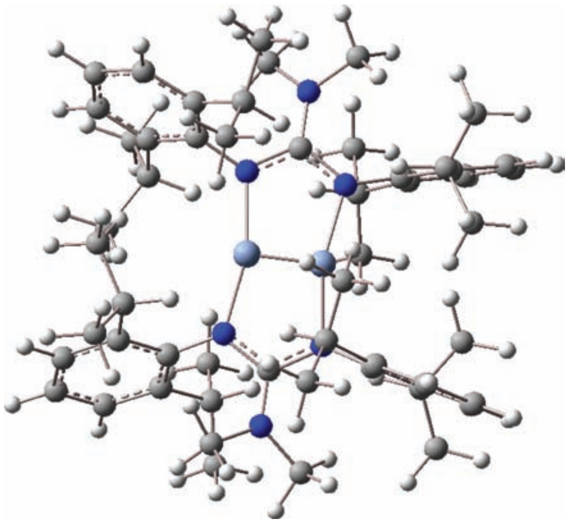

Figure 5. Cr_2-guanidinate complex. See Figure 1 for color coding.

The Cr−Cr and Cr−N bond lengths optimized at the CASPT2 level of theory are 1.752 and 1.990 Å, respectively, in good agreement with the experimental values of 1.729 and 2.022/2.013 Å.[15] Since the difference between the two Cr−N distances is small, an averaged value was used in the calculations. In the simplified model, the corresponding optimized bond lengths are 1.772 and 2.002 Å. Thus, having less bulky substituents (and consequently a weaker steric hindrance) affects significantly the

Cr—Cr bond length, which increases by about 0.02 Å. This is compatible with the N—C—N fragment acting as a pincer and therefore forcing the two metals to approach each other. The formal charge of each Cr atom is +1. The bonding scheme in the Cr_2-guanidinate complex (**5**) is virtually the same as that in the Cr_2-amidinate (**2**) (Supporting Information, Figure S5). The values for the computed effective bond order for structure **5** and its simplified model are 3.79 and 3.72, respectively. The result shows that they are identical in terms of their electronic structure, $\sigma^2\pi^4\delta^4$, which supports the assumption that the observed bond lengths are primarily determined by the structural pressure of the ligands rather that changes in the electronic structure.

Table 4. Most Important Structural Parameters and EBOs of Different Cr_2 Compounds[a]

LCrCrL	*d*(Cr—Cr), Å	*d*(Cr—L), Å	EBO
Cr_2	1.66		4.46
lantern reduced (**3**)	1.738	2.017	3.91
PhCrCrPh	1.752	2.018	3.52
Cr_2-amidinate (**2**)	1.764	1.991	3.80
lantern neutral (**3**)	1.777	1.982	3.46
Cr_2-diazadiene (**1**)	1.799	1.909	3.43
Cr_2-aminopyridinate (**4**)	1.806	1.990 2.010	3.65
Cr_2-guanidinate (**5**)	1.752	1.990	3.79
Ar′CrCrAr′	1.836	2.132	3.43

[a] Cr—Cr, Cr—ligand bond distances (Å) are computed at the CASPT2 level for different species containing the dichromium unit. EBOs are based on the natural occupation numbers of the molecular orbitals localized on the bimetallic unit. The Ar′CrCrAr′ structure was taken from experimental X-ray crystallographic data.

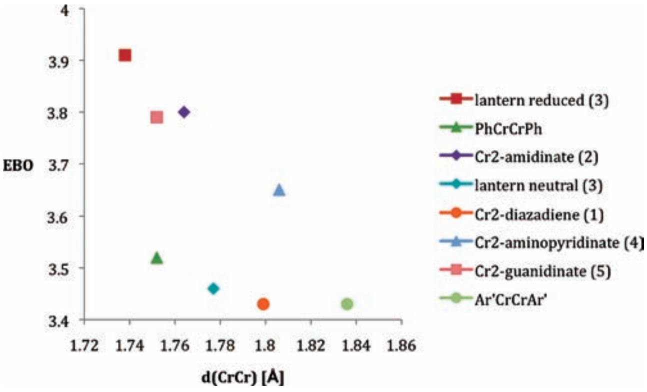

Figure 6. Effective bond order as a function of Cr—Cr distance for different compounds.

4. Discussion

With the most relevant parameters in hand for the different species containing the dichromium unit, we can now attempt to rationalize the results, by establishing a trend between the effective bond order and the Cr—Cr bond length. A quick glance at Table 4 does not lead to any immediate conclusion, since bond length and EBO do not seem to be correlated. However, a more detailed analysis of the plot (Figure 6) of the EBO versus CrCr bond distance allows us to find a linear correlation between these two parameters within the same group of ligands. At this point, one has to recall that the EBO value is a function of the orbital's overlap, which is tightly correlated to their shape and to the effect of the ligands. Therefore, in order to correlate EBOs with observable CrCr bond lengths, the examined compounds have to be divided into subgroups according to the class of ligands.

On the basis of the nature of the ligands two groups of compounds can be defined. The first one includes Ar′CrCrAr′ and PhCrCrPh, in which the element coordinating the metal center is a carbon atom. In this case, the involved ligands, namely, phenyl and terphenyl, are not able to impose any constraints on the diatomic unit. The second group encompasses species **1** to **5**, in which nitrogen is the element coordinating the metal center. In contrast to the first group, these are bridging ligands, and therefore the two nitrogens of a single ligand are able to interact with Cr_2. Such differences have important effects on the dichromium bond distance. Indeed, in the Ar′CrCrAr′ species, the role of the ligand seems to be more protective: it acts as a shield against interactions of Cr with the surroundings rather than a pincer meant to allow the two Cr atoms to approach each other. In our previous work,[21] we have shown that the bulky terphenyl ligand has only a very small effect on the chromium—chromium interaction since replacing it by a phenyl group does not significantly affect the optimized CrCr bond length. In addition to their ability to protect the Cr_2 unit, bridging ligands such as amidinates, aminopyridinates, and guanidinates can have a direct effect on the Cr—Cr bond length by tuning the size of the residues in the outer part of the bulky ligands. Moreover, they tend to avoid short Cr—N bond lengths since even a small decrease of the Cr—N distance is associated with a lengthening of the bimetallic unit. The importance of these features is demonstrated by the calculations performed on the modified aminopyridinate compound. Indeed, replacing the bulky TIP and Mes residues by smaller groups such as phenyl results in a CrCr bond length longer than the experimental one. The simplification of the ligand is also associated with an increase of about one degree of the angle enclosed by the $N_{pyridine}CN_{amido}$ fragment. Such a trend is also observed for the guanidinate species when the isopropyl groups were replaced by methyls.

Closer inspection of Figure 6 shows that two of the molecules under examination, **1** and the neutral form of **3**, do not agree with the general linear trend between EBO and dichromium bond distance. The case of complex **1** has been discussed before,[23] and its unusual behavior is the consequence of the Cr—Nπ interaction, which is not present in the other compounds. The neutral form of species **3** is also an exception, connected with its electronic configuration, characterized by a singly occupied δ orbital. Indeed, the reduction of this compound leads to the reduced lantern species, whose behavior is in agreement with the established linear correlation trend.

5. Conclusions

We demonstrated that a linear correlation exists between the Cr—Cr bond length and the effective bond order in dichromium compounds belonging to the same class of supporting ligands. The shortening of the Cr—Cr bond length is a result of the stabilization of the bimetallic unit as well as the structural constraints imposed by the ligand on the CrCr core. The latter point is clearly demonstrated by species **1**, which features a short CrCr bond distance associated with a small EBO value. The stability of a chemical bond is related to the strength of the interaction between two atoms, which, in turn, can be measured in terms of the dissociation energy. This quantity, often regarded as the most accurate gauge of the chemical bond stability, experimentally can be obtained only for very simple molecules. The concept of bond order, on the other hand, is intuitive for chemists and can be related to the reactivity of the species being studied. The reactivity depends on the degree of overlap between the orbitals forming the bond. The δ orbitals are good candidates for such a purpose, as their overlap is lower than the one featured by σ and π orbitals. Thus, in the cases presented here, a low EBO can be associated with weak δ bonds and the possibility of reactivity with external compounds or with the ligand itself. The former situation was highlighted very recently,[17] by the direct carboalumination of a dichromium multiple bond, whereas the latter one was reported in 2007[39] and was based on metal−ligand charge transfer involving the δ orbital.

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Supporting Information Available: This material including the *xyz* coordinates of the different compounds is available free of charge via the Internet at http://pubs.acs.org.

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(39) Chisholm, M. H. *Proc. Natl. Acad. Sci. U. S. A* **2007**, *104*(8), 2563–2570.