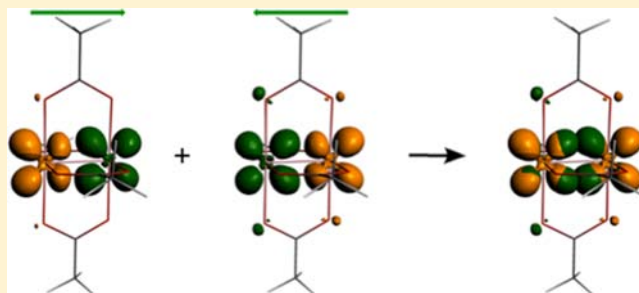


A Theoretical Analysis of Supported Quintuple and Quadruple Chromium–Chromium Bonds

Sylvester Ndambuki and Tom Ziegler*

Department of Chemistry, University of Calgary, Calgary, Alberta Canada, T2N1N4

ABSTRACT: The extended transition state (ETS) energy decomposition scheme has been combined with the natural orbitals for chemical valence (NOCV) density decomposition method (ETS–NOCV) in a study on the shortest, fully supported metal–metal bond ($\text{Cr–Cr} = 1.73 \text{ \AA}$) in $\text{Cr}_2[\text{Ar}'\text{NC}(\text{NMe}_2)\text{NAr}']_2$ [$\text{Ar}' = \text{C}_6\text{H}_3\text{-2,6}(\text{C}_6\text{H}_3\text{-2,6-Pr}^i)_2$]. The scope of the ETS–NOCV method is further demonstrated by a metal–metal bond analysis of the paddlewheel $\text{M}_2(\text{O}_2\text{CCH}_3)_4$ ($\text{M} = \text{Cr, Mo, W}$) complexes. The influence of axial ligands as well as R' groups on the bridging ligands is also analyzed. In addition to the quintuple bonding components ($\sigma^2, \pi^4, \delta^4$) for $\text{Cr}_2[\text{Ar}'\text{NC}(\text{NMe}_2)\text{NAr}']_2$ and quadruple components ($\sigma^2, \pi^4, \delta^2$) for the paddlewheel complexes, we notice additional stability (17–27 kcal/mol) introduced to the metal–metal bond from participation of the lone pairs residing on the π -systems of the bridging X–C–X ($\text{X} = \text{N, O}$) ligand. This is to our knowledge the first time that the strength of the metal–metal bonding components has been determined in a supported metal–metal bond by an energy decomposition scheme.



1. INTRODUCTION

In 2005, Power and co-workers¹ synthesized the first chromium complex $\text{Cr}_2(\text{C}_6\text{H}_3\text{-2,6-Ar}')_2$ ($\text{Ar}' = \text{C}_6\text{H}_3\text{-2,6-Pr}^i$) with a putative quintuple Cr–Cr bond ($R_{\text{Cr–Cr}} = 1.835 \text{ \AA}$) corresponding to the $\sigma^2\pi^4\delta^4$ electronic configuration (see 1 of Figure 1). Since that time, other compounds featuring a formal Cr–Cr quintuple bond have been synthesized and analyzed^{2–4} with different ligand motives. The shortest quintuple metal–metal bond ($\text{Cr–Cr} = 1.729 \text{ \AA}$) was reported in 2009 by Noor and co-workers³ in $\text{Cr}_2[\text{Ar}'\text{NC}(\text{NMe}_2)\text{NAr}']_2$ (**2**), where the Cr–Cr link is bridged by a N–C–N type ligand system (see Figure 1). Thus, in contrast to $\text{Ar}''\text{CrCrAr}''$ (**1**), where Ar'' is bridging through a secondary Cr–aryl bond, compound **2** can unambiguously be considered as containing a supported metal–metal bond.

Until the work by Powers, the highest observed Cr–Cr bond multiplicity was found in the quadruple bonded paddlewheel $\text{Cr}_2\text{L}_4\text{L}'_2$ ($\text{L} =$ bridging ligand, $\text{L}' =$ axial ligand)^{5,6} complexes, where L often is a carboxylate ligand and the Cr–Cr distance varies from 2.2 to 2.5 \AA (see 3 of Figure 1). Paddlewheel complexes (Cr_2L_4) without axial ligands have also been characterized.⁵ The Cr–Cr quadruple bond length for Cr_2L_4 is typically found in the shorter range of 1.8–2.1 \AA . The first Cr_2L_4 complexes had 2,6-dimethoxyphenyl as the bridging ligand⁵ (see 4 of Figure 1). However, Cr_2L_4 complexes have also recently been isolated with bridging carboxylate ligands⁵ (see 5 of Figure 1).

In the first part of this study, we present an extended transition state energy decomposition scheme combined with the natural orbitals for chemical valence (ETS–NOCV)⁷ analysis of the individual contributions from the σ , π , and δ components to the strength of the supported metal–metal

bond in **2** and compare it to the ETS–NOCV analysis obtained previously^{8a} for the unsupported Cr–Cr bond in $\text{Ar}''\text{CrCrAr}''$ (**1**). We shall further examine any influence the Cr–N bridging interaction as well as the isopropyl substituents might have on the stability of the Cr–Cr bond. It was shown^{8a} in the previous study on $\text{Ar}''\text{CrCrAr}''$ that dispersive attractions⁹ between isopropyl groups on different CrAr'' monomers help stabilize the dimer (**1**) compared to two separate CrAr'' units. For the sake of comparison, we shall extend the study to the recently synthesized $\text{Cr}_2(\text{C}_6\text{H}_3\text{-2,6-Ar}'\text{-4-OMe})_2$ complex (**6**) ($\text{Cr–Cr} = 1.816 \text{ \AA}$)¹⁰ with a formal quintuple Cr–Cr bond (see Figure 1). The quintuple bonded systems have previously been analyzed using atoms in molecules (AIM).^{3g,h}

We turn in the second part our attention to the quadruple bonded systems,^{11–15} starting with Cr_2L_4 complexes without an axial ligand.^{14c,d} Here we compare as bridging ligands 2,6-dimethoxyphenyl (**4**) with carboxylates O_2CR (**5**), where the R group varies in its donor and acceptor strength. Comparison will also be given to carboxylate complexes (**5**) $\text{M}_2(\text{O}_2\text{CR})_4$ ($\text{M} = \text{Cr, Mo, W}$)^{6,14} of the heavier group 6 metals. We shall finally assess the influence of the axial ligands in (**3**) $\text{Cr}_2(\text{O}_2\text{CR})_4\text{L}'_2$ on the Cr–Cr bond by comparing the ETS–NOCV analysis of **3** to that of $\text{Cr}_2(\text{O}_2\text{CR})_4$ in **5**.

We have previously applied the ETS–NOCV scheme to metal complexes with unsupported metal–metal bonds.⁸ The present study is the first application to supported metal–metal bonds. Such bonds require special considerations in the definition of the fragments, as it will be discussed shortly.

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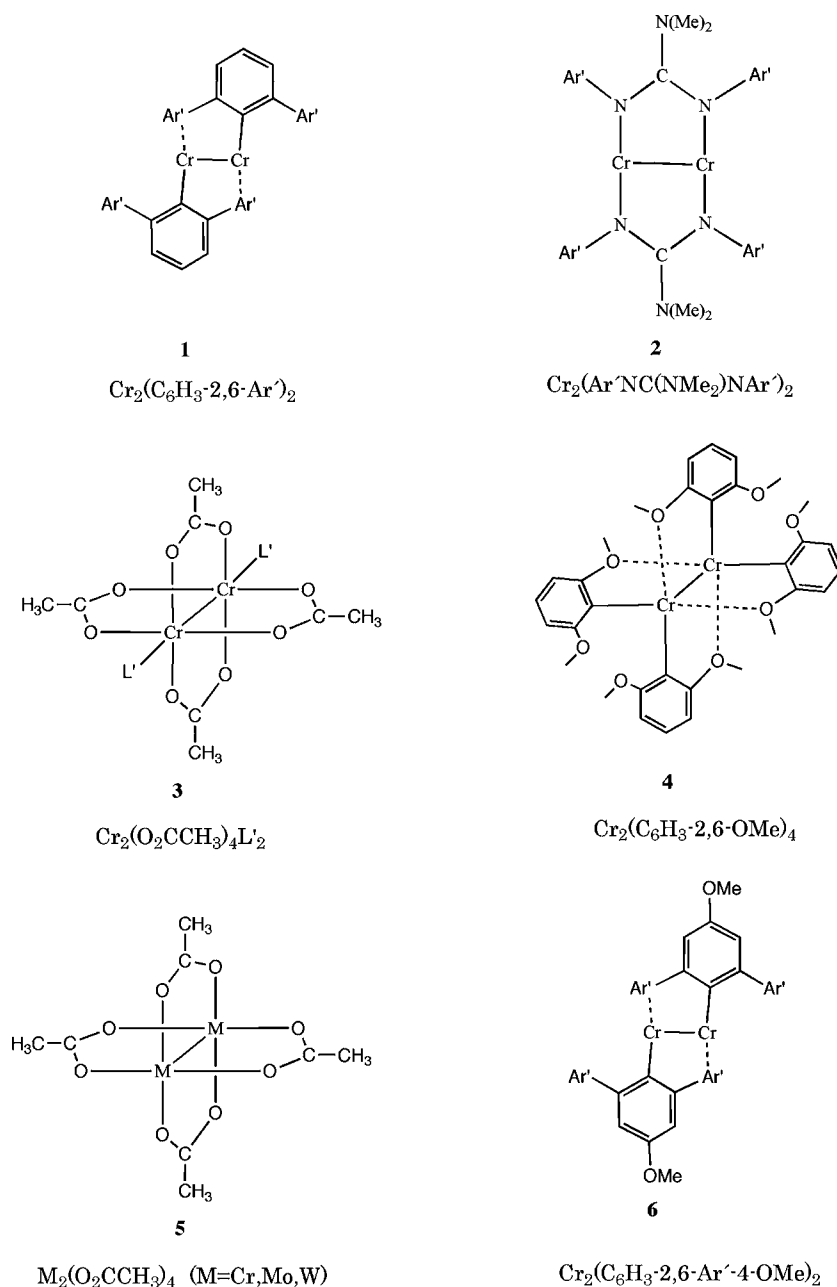


Figure 1. Molecular structures of metal–metal bonding complexes.

2. COMPUTATIONAL METHODS AND DETAILS

We shall first briefly introduce the basic principles of the energy decomposition scheme, ETS, and the density decomposition scheme, NOCV.

2.1. Extended Transition State Method (ETS).¹⁶ In the ETS approach, one analyzes the energy (E_{AB}) of a molecule AB as formed from two fragments A and B. The energy (E_{AB}) is usually represented as a sum of four chemically meaningful terms given in eq 1.¹⁶

$$\Delta E_{\text{int}} = \Delta E_{\text{prep}} + \Delta E_{\text{elst}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{disp}} + \Delta E_{\text{orb}} \quad (1)$$

Here ΔE_{prep} represents the preparation energy required to modify fragments A and B from their original geometries to the ones they have in AB. This energy is destabilizing. The term ΔE_{elst} denotes the electrostatic interaction^{7,16} between the two distorted fragments (A' and B') as they are brought from infinite separation to their final positions in the combined molecule (AB) without any change in density. This term is stabilizing for neutral fragments. Further, ΔE_{Pauli} represents the destabilizing⁷ interaction between the occupied orbitals

on A' and B', respectively. It is customary^{7,16} to combine ΔE_{elst} and ΔE_{Pauli} into the steric interaction energy $\Delta E_{\text{steric}} = \Delta E_{\text{elst}} + \Delta E_{\text{Pauli}}$. Further, ΔE_{disp} is the stabilizing van der Waals dispersion interactions⁹ between the two fragments A' and B' in AB. Finally, the last term, ΔE_{orb} , represents the stabilizing interactions between occupied molecular orbitals on one fragment and unoccupied molecular orbitals on the other, as well as mixing of occupied and virtual orbitals on the same fragment. Participation of the virtual orbitals gives rise to a change in density¹⁶ expressed as

$$\Delta \rho = \sum_{\lambda} \sum_{\mu} \Delta P_{\mu\lambda} \psi_{\lambda}(1) \psi_{\mu}(1) \quad (2)$$

where the sum is over all occupied and virtual molecular orbitals of the two fragments A and B, orthogonalized on each other.⁷ We can write the energy^{16–18} associated with the orbital interaction as

$$\Delta E_{\text{orb}} = \sum_{\lambda} \sum_{\mu} \Delta P_{\mu\lambda} F_{\lambda\mu}^{\text{TS}} \quad (3)$$

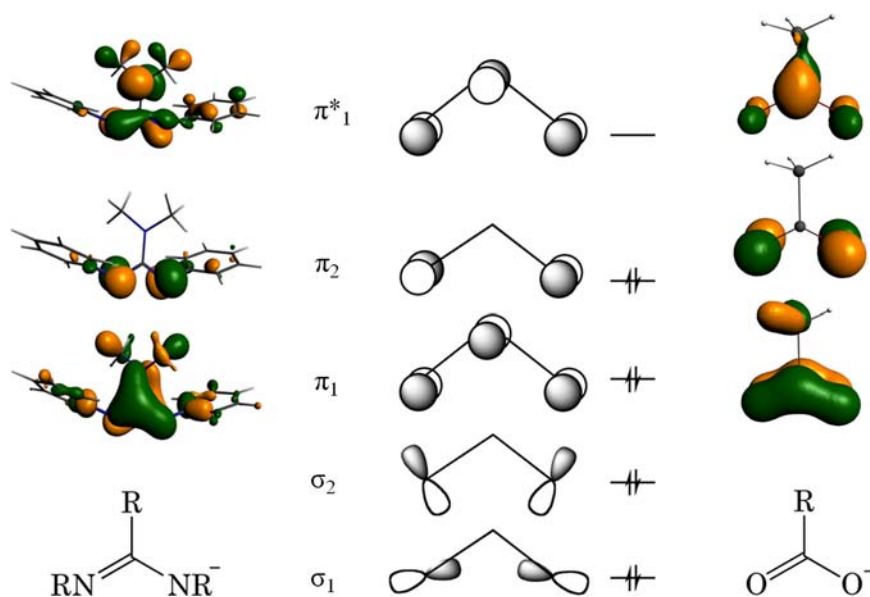


Figure 2. Frontier orbitals of $[X-C(R)-X]^-$ ($X = NR, O$).

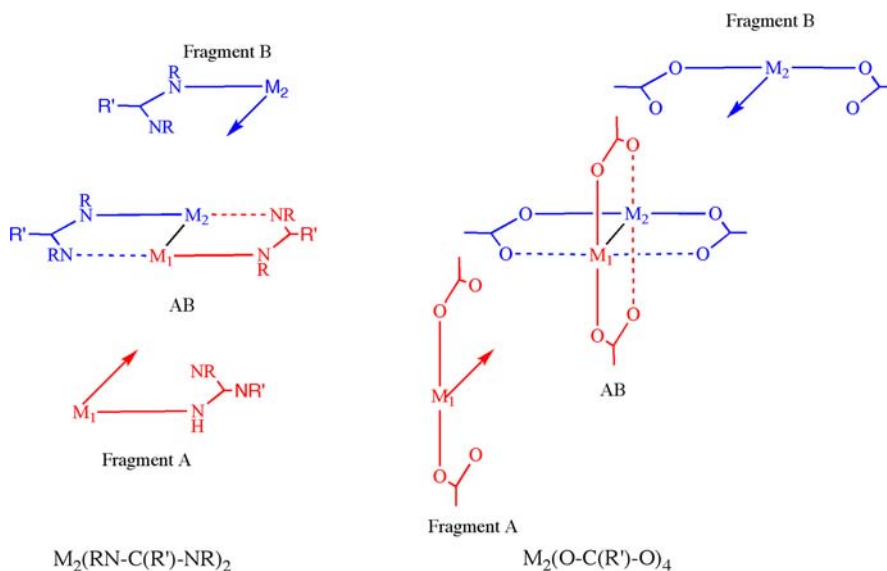


Figure 3. Fragmentation of $M_2[RN-C(R')-NR]_2$ and $M_2[O-C(R')-O]_2$.

Here $F_{\lambda\mu}^{TS}$ is a Kohn–Sham Fock matrix element that is defined in terms of a transition state potential at the midpoint between the combined fragments and the final molecule, hence the term extended transition state (ETS) method.^{7,16}

2.2. Natural Orbitals for Chemical Valence (NOCV). In the NOCV approach the deformation density matrix ΔP is diagonalized.^{7,19} Thus,

$$\Delta P C_i = v_i C_i; \quad i = 1, M \quad (4)$$

where M denotes the total number of fragment molecular orbitals and C_i is a column vector containing the eigenvectors to ΔP . The eigenvectors, also called natural orbitals for chemical valency (NOCV),^{20,21} are given as

$$\varphi_i(1) = \sum_{\lambda} C_{i\lambda} \psi_{\lambda}(1) \quad (5)$$

In the NOCV representation, the deformation density can be written as a sum of pairs of complementary eigenfunctions (φ_k, φ_{-k})

corresponding to the eigenvalues v_k and v_{-k} with the same absolute value but opposite signs.^{7,19}

$$\Delta\rho(1) = \sum_{k=1}^{M/2} v_k [-\varphi_{-k}^2(1) + \varphi_k^2(1)] = \sum_{k=1}^{M/2} \Delta\rho_k(1) \quad (6)$$

Finally, the orbital interaction energy (ΔE_{orb}) is expressed in terms of the NOCV's as

$$\Delta E_{\text{orb}} = \sum_{k=1}^{M/2} v_k [-F_{-k,-k}^{TS} + F_{k,k}^{TS}] = \sum_{k=1}^{M/2} \Delta E_k^{\text{orb}} \quad (7)$$

where $F_{-k,-k}^{TS}$ and $F_{k,k}^{TS}$ are diagonal Kohn–Sham matrix elements defined over NOCV's with respect to the transition state (TS) intermediate between the density of the final molecule AB and the superimposed fragment densities of A' and B'.⁷ The advantage of the expression in eq 7 for ΔE_{orb} over that of eq 3 is that only a few complementary NOCV pairs normally contribute significantly to ΔE_{orb} . It is clear from eqs 6 and 7 that, for each complementary NOCV pair representing one of the charge deformations $\Delta\rho_k$ we have as well the corresponding bond energy contribution ΔE_k^{orb} .⁷ The

deformation density $\Delta\rho$ contributions can usually be interpreted in terms of interactions that correspond to σ, π, δ -bonding or σ -donation and π -back-donation, even when the molecule AB lacks symmetry.⁷

2.3. Computational Details. All DFT calculations presented here were based on the Amsterdam density functional program version 2010.01 in which ETS–NOCV was implemented.²² Use was made of the Becke–Perdew exchange–correlation functional (BP86)^{23,24} and a standard triple- ζ STO basis with one set of polarization functions for all atoms. Relativistic effects for Cr, Mo, and W atoms were included at the scalar relativistic ZORA level of approximations as implemented in the ADF program.²² The fragment and molecular orbitals, as well as contours of deformation densities, were plotted using the ADF-GUI interface.²² The crystal structures of the systems studied, unless stated otherwise, were obtained from the crystal database.^{3,10,14} All hydrogen coordinates were optimized while all the other atoms were kept at frozen positions. The dispersion term ΔE_{disp} of eq 1 was taken from the dispersion-corrected DFT scheme by Grimme et al.⁹ as implemented in ADF.

3. RESULTS AND DISCUSSION

3.1. Frontier Orbitals of the Bridging Ligand $[X-C(R)-X]^-$ and Fragmentation of $Cr_2(X-C(R)-X)_n$. The bridging ligands $[X-C(R)-X]^-$ in **2** ($X = NR$) as well as **3** ($X = O$) have each two σ -donor orbitals σ_1, σ_2 , in addition to two π -donor orbitals π_1, π_2 and one π -acceptor orbital π_1^* . These frontier orbitals, as shown in Figure 2, are well-positioned for interactions with metal combinations on the Cr–Cr link in $Cr_2[X-C(R)-X]_n$.

In analyzing the Cr–Cr bonding in $Cr_2[X-C(R)-X]_n$ we shall split it into two $Cr[X-C(R)-X]_{n/2}$ fragments as illustrated for **2** ($X = NR$) as well as **3** ($X = O$) in Figure 3. In both cases we have to break not only the Cr–Cr link but also some Cr–X bonds. For $Ar''CrCrAr''$ (**1**) and the $Cr_2(C_6H_3-2,6-Ar'-4-OMe)_2$ complex (**6**), the two fragments are formed by breaking the secondary aryl–chromium bonds, whereas the fragmentation in (**4**) $Cr_2(C_6H_3-2,6-OMe)_4$ was carried out by cleaving the Cr–O bonds.

3.2. Chromium–Chromium Bonding in $Cr_2[Ar'NC(NMe_2)NAr']_2$ and $Cr_2(C_6H_3-2,6-Ar'-4-OMe)_2$. We shall begin our discussion of the metal–metal bonding in $Cr[Ar'NC(NMe_2)NAr']$ (**2**) by using the model system $Cr[Ar^*NC(NMe_2)NAr^*]$ (**2***), where we temporarily have removed the Pr^i groups for clarity. Figure 4 displays the metal-based singly occupied fragment orbitals of $Cr[Ar^*NC(NMe_2)NAr^*]$ and the doubly occupied metal–metal bonding orbitals of $Cr_2[Ar^*NC(NMe_2)NAr^*]_2$. Of lowest energy are two π -type metal–metal bonding molecular orbitals π_1 and π_2 of $Cr_2[Ar^*NC(NMe_2)NAr^*]_2$. They are in-phase combinations of the d_{xy} and d_{yz} singly occupied metal fragment orbitals, respectively. Here the fragments carry a local coordinate system with the z -axis along the Cr–N bond and the y -axis along the metal–metal bond. Next in Figure 4 is the Cr–Cr σ -bonding orbital. It combines two hybrid fragment orbitals that each is predominantly $d_{x^2-y^2}$ (45.1%) and d_{z^2} (17.6%) in character. The first δ -bonding orbital is shown as δ' in Figure 4. It is predominantly Cr-4s (49.8%) with substantial involvement of d_z (24.8%). The HOMO can also be characterized as δ -bonding. It is an in-phase combination of the corresponding d_{xz} Cr-fragment orbital (see Figure 4). The metal–metal bonding orbitals of $Cr_2(C_6H_3-2,6-Ar'-4-OMe)_2$ (**6**) are quite similar to those displayed in Figure 4 and will not be shown here.

Table 1 affords the ETS analysis according to eq 1 for the interaction energy ΔE_{int} between the two $Cr[Ar'NC(NMe_2)NAr']$ hextet fragments of opposite high spin-polarization as

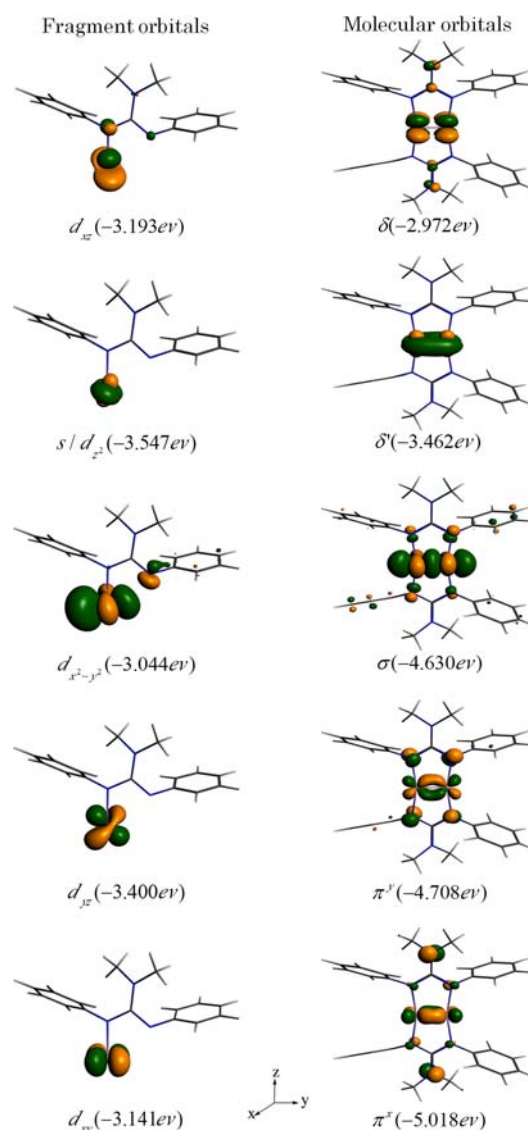


Figure 4. The metal-based singly occupied fragment orbitals of $Cr[Ar^*NC(NMe_2)NAr^*]$ and the doubly occupied metal–metal bonding orbitals of $Cr_2[Ar^*NC(NMe_2)NAr^*]_2$.

Table 1. ETS Analysis^c for $Cr_2[Ar'NC(NMe_2)NAr']_2$ (**2**) and $Cr_2(C_6H_3-2,6-Ar'-4-OMe)_2$ (**6**)

	Cr–Cr = 1.729 Å		Cr–Cr = 1.816 Å	
	2	2* ^d	6	6* ^e
ΔE_{elst}	−469.2	−432.7	−418.5	−398.2
ΔE_{Pauli}	648.2	600.9	610.0	584.6
$\Delta E_{\text{steric}}^a$	179.0	168.2	191.5	186.4
ΔE_{orb}	−311.5	−299.7	−261.9	−259.7
ΔE_{disp}	−34.1	−8.8	−39.5	−18.5
ΔE_{int}^b	−166.6	−140.3	−109.9	−91.8

^aSteric interaction: $\Delta E_{\text{steric}} = \Delta E_{\text{Pauli}} + \Delta E_{\text{elst}}$. ^bTotal bonding energy: $\Delta E_{\text{int}} = \Delta E_{\text{steric}} + \Delta E_{\text{orb}} + \Delta E_{\text{disp}}$. ^cEnergies in kcal/mol. ^dComplex **2*** without isopropyl groups. ^eComplex **6*** without isopropyl groups.

they are combined according to Figure 3 (left) to form $Cr_2[Ar'NC(NMe_2)NAr']_2$ (**2**). Dimerization of the two $Cr[Ar'NC(NMe_2)NAr']$ fragments leads to a destabilizing Pauli term (ΔE_{Pauli}) of 648.2 kcal/mol due to the repulsive interaction between same-spin occupied orbitals on different

fragments. This destabilization is countered by a stabilizing electrostatic term (ΔE_{elst}) of -469.2 kcal/mol due to the interpenetration of electron densities from the two fragments as they come together to form the final molecule. The sum of these two terms is the steric interaction ($\Delta E_{\text{steric}} = \Delta E_{\text{elst}} + \Delta E_{\text{Pauli}}$). It amounts to $\Delta E_{\text{steric}} = 179.0$ kcal/mol. The steric term is finally offset by the orbital interaction $\Delta E_{\text{orb}} = -311.5$ kcal/mol and the van der Waals stabilization energy $\Delta E_{\text{disp}} = -34.1$ kcal/mol. The total dimerization energy amounts to $\Delta E_{\text{int}} = -166.6$ kcal/mol (Table 1). We have for comparison also considered the model system $\text{Cr}_2[\text{Ar}^*\text{NC}(\text{NMe}_2)\text{NAr}^*]_2$ (2^*) without isopropyl groups. The interaction energy is now reduced in absolute terms by 26.3 kcal/mol to $\Delta E_{\text{int}} = -140.3$ kcal/mol. This reduction is very close to the corresponding absolute drop in the van der Waals stabilization energy ΔE_{disp} by 25.3 kcal/mol to -8.8 kcal/mol (Table 1). Also shown in Table 1 is the ETS analysis for the formation of $\text{Cr}_2(\text{C}_6\text{H}_3-2,6\text{-Ar}'-4\text{-OMe})_2$ (6). The dimerization energy of 6 , $\Delta E_{\text{int}} = -109.9$ kcal/mol, is in absolute terms much lower than in the case of 2 with $\Delta E_{\text{int}} = -166.6$ kcal/mol. Removing the isopropyl groups in 6^* reduces $-\Delta E_{\text{int}}$ by 18.1 kcal/mol to 91.8 kcal/mol, mostly as a result of the drop in ΔE_{disp} by 21.0 kcal/mol. It is thus clear that the presence of isopropyl groups in 2 and 6 increases the dimerization energy by ~ 20 kcal/mol compared to 2^* and 6^*). A similar stabilization^{8a} of 21 kcal/mol was found for Powers compound 1 compared to 1^* , where the isopropyl groups were removed.

It follows from Table 1 that the dimerization energy ΔE_{int} for 2 is 56.7 kcal/mol larger than for 6 in absolute terms. Here $\Delta E_{\text{disp}} + \Delta E_{\text{steric}}$ contributes with only 7.1 kcal/mol, whereas ΔE_{orb} adds 49.4 kcal/mol. While ΔE_{orb} clearly is responsible for the greater dimer stability of 2 compared to 6 , it is not clear whether this is due to a stronger Cr–Cr interaction or the formation of more stable Cr–N bonds in 2 compared to the Cr–O links generated in 6 .

We have addressed this question by performing a NOCV analysis of ΔE_{orb} according to eq 7 for 2 and 6 as well as 2^* and 6^* . The results are reported in Table 2. We plot in addition for 2 the NOCV deformation density components $\Delta\rho_k(1)$ of eq 6 along with the corresponding energy contributions ΔE_k^{orb} from eq 7 in Figures 5 and 6. It follows from the figures that the NOCV analysis clearly separates contributions from the Cr–Cr

Table 2. NOCV^b Contributions to ΔE_{orb} in $\text{Cr}_2[\text{Ar}'\text{NC}(\text{Me}_2)\text{NAr}']_2$ (2) and $\text{Cr}_2(\text{C}_6\text{H}_3-2,6\text{-Ar}'-4\text{-OMe})_2$ (6)

	Cr–Cr = 1.729 Å		Cr–Cr = 1.816 Å	
	2	$2^*{}^c$	6	$6^*{}^d$
$\Delta\rho_{\text{orb}}^\sigma$	-101.0	-98.3	-82.0	-80.7
$\Delta\rho_{\text{orb}}^{\pi_1}$	-60.8	-60.5	-51.2	-49.9
$\Delta\rho_{\text{orb}}^{\pi_2}$	-60.8	-60.5	-51.2	-49.9
$\Delta\rho_{\text{orb}}^\delta$	-14.1	-13.0	-13.4	-12.3
$\Delta\rho_{\text{orb}}^{\delta'}$	-40.2	-37.5	-33.2	-33.0
$\Delta\rho_{\text{orb}}^{\text{sec}}$	-17.6	-16.5	-11.1	-17.7
$\Delta\rho_{\text{orb}}^{\text{sec}'}$	-6.6	-6.6	-4.7	-4.7
$\Delta\rho_{\text{orb}}^{\text{rest}}$	-10.4	-6.8	-15.1	-11.5
$\Delta\rho_{\text{orb}}^a$	-311.5	-299.7	-261.9	-259.7

^a $\Delta\rho_{\text{orb}}^\sigma = \Delta\rho_{\text{orb}}^\sigma + \Delta\rho_{\text{orb}}^{\pi_1} + \Delta\rho_{\text{orb}}^{\pi_2} + \Delta\rho_{\text{orb}}^\delta + \Delta\rho_{\text{orb}}^{\delta'} + \Delta\rho_{\text{orb}}^{\text{sec}} + \Delta\rho_{\text{orb}}^{\text{sec}'}$ + $\Delta\rho_{\text{orb}}^{\text{rest}}$. ^bEnergies in kcal/mol ^cComplex 2 without isopropyl groups. ^dComplex 6 without isopropyl groups.

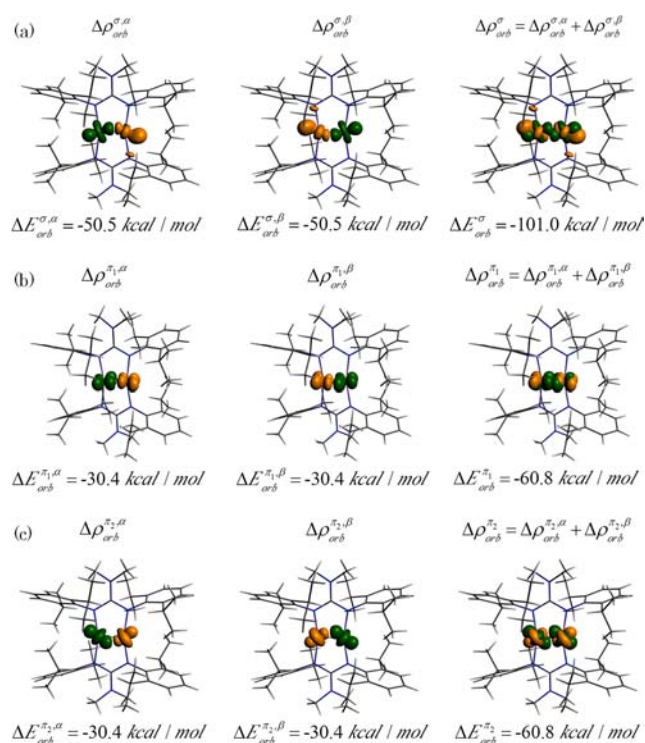


Figure 5. The NOCV deformation densities and associated energy contributions representing σ, π -bonding in $\text{Cr}_2[\text{Ar}^*\text{NC}(\text{NMe}_2)\text{NAr}^*]_2$. The contour values are 0.006 au. Green represents positive and orange negative.

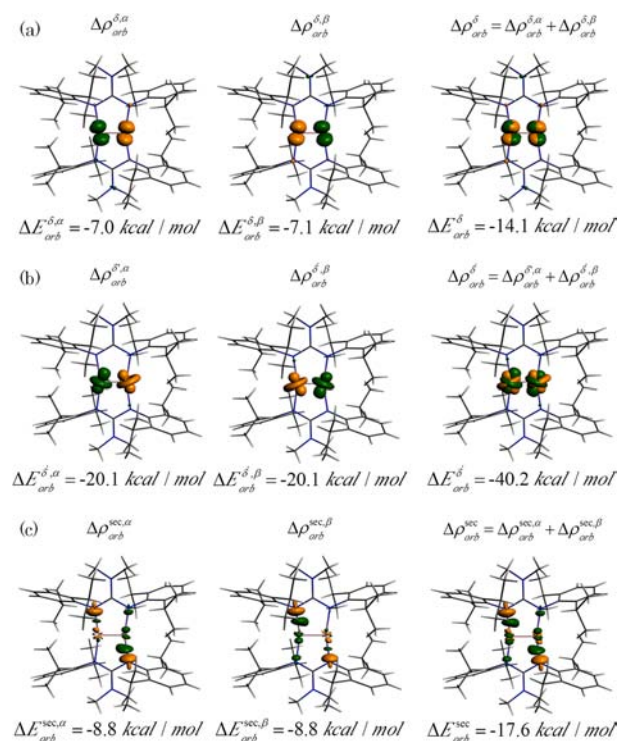


Figure 6. Contours of the NOCV deformation densities in $\text{Cr}_2[\text{Ar}^*\text{NC}(\text{NMe}_2)\text{NAr}^*]_2$. (a) δ' - and (b) δ -bonding. Contour values are 0.006 au. (c) Contours of the NOCV deformation densities $\Delta\rho_{\text{orb}}^{\text{sec}}$ for the Cr–N bonding interactions. The contour values are 0.001 au. Green represents positive and orange negative.

bond formation and the Cr–N interaction. We shall thus be able to decompose ΔE_{orb} accordingly.

Figure 5a depicts $\Delta\rho_{\text{orb}}^{\sigma\alpha}$ representing the flow of electron density from the occupied $d_{x^2-y^2}$ σ -orbital on the right-hand fragment of α -spin to the empty $d_{x^2-y^2}$ σ -orbital on the left-hand fragment of the same spin. Also shown is $\Delta\rho_{\text{orb}}^{\sigma\beta}$, which represents the reverse flow of electrons with β -spin. We finally have $\Delta\rho_{\text{orb}}^{\sigma} = \Delta\rho_{\text{orb}}^{\sigma\alpha} + \Delta\rho_{\text{orb}}^{\sigma\beta}$. In total, we get a contribution of $\Delta E_{\text{orb}}^{\sigma} = -101.0$ kcal/mol to ΔE_{orb} from the σ -component of the Cr–Cr bond formation corresponding to the creation of the σ -molecular orbital in Figure 4. In parts b and c of Figure 5 are depicted the two π -components π_1 and π_2 as $\Delta\rho_{\text{orb}}^{\pi_1}$ and $\Delta\rho_{\text{orb}}^{\pi_2}$, respectively, along with the corresponding energy contributions $\Delta E_{\text{orb}}^{\pi_1}$ and $\Delta E_{\text{orb}}^{\pi_2}$ of -60.8 and -60.8 kcal/mol, respectively. Thus, each of the π -bonds are somewhat weaker than the σ -bond, although the sum of their strength exceeds that of the σ -component. We note that $\Delta\rho_{\text{orb}}^{\pi_1}$ and $\Delta\rho_{\text{orb}}^{\pi_2}$ correlate well with the two bonding orbitals π_1 and π_2 of Figure 4.

Figure 6a,b depicts the deformation densities $\Delta\rho_{\text{orb}}^{\delta}$ and $\Delta\rho_{\text{orb}}^{\delta'}$ and related energies $\Delta E_{\text{orb}}^{\delta}$ and $\Delta E_{\text{orb}}^{\delta'}$ corresponding to the two δ -bonding orbitals δ and δ' of Figure 4. They contribute $\Delta E_{\text{orb}}^{\delta} = -14.1$ kcal/mol and $\Delta E_{\text{orb}}^{\delta'} = -40.2$ kcal/mol, respectively. Thus, the first component (δ) corresponding to the δ -HOMO of Figure 4 must be considered weak. Nevertheless, our NOCV analysis is consistent with the presence of a quintuple Cr–Cr bond in **2** with a total Cr–Cr bonding interaction of $\Delta E_{\text{orb}}^{\sigma} + \Delta E_{\text{orb}}^{\pi_1} + \Delta E_{\text{orb}}^{\pi_2} + \Delta E_{\text{orb}}^{\delta} + \Delta E_{\text{orb}}^{\delta'} = -276.9$ kcal/mol. The remaining part of ΔE_{orb} (-34.6 kcal/mol) is due to the Cr–N interactions.

We display in Figure 6c the largest NOCV contribution to the Cr–N bonding in terms of $\Delta\rho_{\text{orb}}^{\text{sec}}$ and the corresponding energy $\Delta E_{\text{orb}}^{\text{sec}} = -17.7$ kcal/mol. We see from $\Delta\rho_{\text{orb}}^{\text{sec}}$ that density is moved from the aryl carbons to the two nitrogens involved in new Cr–N bond formation as a result of the dimerization process. The other two terms $\Delta\rho_{\text{orb}}^{\text{sec}'}$ and $\Delta\rho_{\text{orb}}^{\text{rest}}$ can also primarily be seen as involving Cr–N bond formation. Also shown in Table 2 are the bonding components for **2*** without the isopropyl groups. It follows from Table 2 that the removal of the isopropyl groups in **2*** reduces the Cr–Cr bonding contribution to $-\Delta E_{\text{orb}}$ by 7.1 kcal/mol, whereas the reduction in the Cr–N bonding contribution is 4.7 kcal/mol.

Turning next to **6**, we note that the contour plots of the Cr–Cr bonding deformation densities $\Delta\rho_{\text{orb}}^{\sigma}$, $\Delta\rho_{\text{orb}}^{\pi_1}$, $\Delta\rho_{\text{orb}}^{\pi_2}$, $\Delta\rho_{\text{orb}}^{\delta}$, and $\Delta\rho_{\text{orb}}^{\delta'}$ on the one hand and the Cr–C_{ipso} bonding deformations densities $\Delta\rho_{\text{orb}}^{\text{sec}}$, $\Delta\rho_{\text{orb}}^{\text{sec}'}$, and $\Delta\rho_{\text{orb}}^{\text{rest}}$ on the other hand are quite similar to those already shown for **2**. They will as a consequence not be shown here. The contribution from the Cr–Cr bond formation to $-\Delta E_{\text{orb}}$ is reduced from 276.9 kcal/mol in **2** to 231.0 kcal/mol in **6**, whereas the corresponding reduction in the Cr–C_{ipso} bonding interaction only amounts to 3.7 kcal/mol. It is thus clear that the reduction in the dimerization energy in absolute terms for **6** compared to **2** comes from the Cr–Cr bonding interaction. The stronger Cr–Cr bond in **2** compared to **6** has the following contributions from the different components: σ (-19.0 kcal/mol), π_1 (-9.6 kcal/mol), π_2 (-9.6 kcal/mol), δ' (-7.0 kcal/mol), and δ (-0.7 kcal/mol).

We note that the steric interaction in **2** is smaller (179.1 kcal/mol) than in **6** (191.5 kcal/mol) although the Cr–Cr distance in **2** is shorter (1.729 Å) than in **6** (1.816 Å). Thus, **2** owes its stronger Cr–Cr bond to the fact that the Cr–Cr atoms

can come closer together to form stronger Cr–Cr interactions without paying a higher steric cost.

It is gratifying to see that the ETS–NOCV scheme is able to distinguish between contributions from metal–metal and metal–ligand interactions. It is further able to resolve the metal–metal interaction into its σ -, π -, and δ -components, in spite of the fact that the two complexes **2** and **6** have little or no symmetry. Perhaps even more encouraging is the fact that this analysis can be carried out for supported metal–metal bonds with bridges between the metal centers.

3.3. Metal–Metal Bonding in $M_2(O_2CR')_4$ ($M = \text{Cr, Mo, W}$), $\text{Cr}_2(\text{C}_6\text{H}_3\text{-2,6-OME})_4$, and $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$. We shall now in the first place analyze the metal–metal bonding in $M_2(O_2CR')_4$, where $M = \text{Cr, Mo, W}$ (**5**) and $R' = \text{CH}_3$. A discussion will further be given of the Cr–Cr bond strength in **5** for various R' groups (F, Cl, H, CF_3 , CMe_3) with different donor/acceptor abilities. Here the Cr–Cr distances will be constrained to that in $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$ of distance 1.97 Å^{14c} for comparison purposes. The Cr–Cr metal bonding will also be analyzed in $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$ (**3**), where in addition to the bridging tetracarboxylate groups, the Cr metal centers are coordinating to axial ligands (H_2O), as is the case for a vast majority of tetracarboxylate bridged systems where the axial positions on the metal centers are filled by donor ligands (L') (**3**) or coordinating oxygen atoms of other $M_2(O_2CR')_4$ molecules.⁵ In this case, the Cr–Cr distance was 2.29 Å.⁵ The choice of fragments for our analysis of $M_2(O_2CR')_4$ is shown in Figure 3 (right) as the two interacting species A [$M_2(O_2CR')_2\downarrow\downarrow\downarrow\downarrow$] and B [$\uparrow\uparrow\uparrow M_2(O_2CR')_2$] of opposite spin polarization with a C_{2v} or C_2 geometry. Finally, we shall present a Cr–Cr bond analysis in $\text{Cr}_2(\text{C}_6\text{H}_3\text{-2,6-OME})_4$ (**4**) with the fragment choice presented in Figure 3 (left), where we cleave the “secondary” Cr–O bond in addition to the Cr–Cr link to form the two $\text{Cr}_2(\text{C}_6\text{H}_3\text{-2,6-OME})_2$ monomers.

The interacting singly occupied metal fragment orbitals and the corresponding molecular orbitals that constitute the quadruple bond in the paddlewheel $M_2(O_2CR')_4$ ($M = \text{Cr, R}' = \text{H}$) systems with a d_{4h} geometry are shown in Figure 7, alongside the interacting C_{2v} fragments with the z -axis along the metal–metal bond. The metal atoms of the metal–metal quadruple bond are formally in the +2 oxidation state. The interaction between the singly occupied d_{z^2} , d_{xy} , d_{xz} , and d_{yz} fragment components on each metal center make up the quadruple bond with the electronic configuration $\sigma^2\pi^4\delta^2$, while the metal s , p , and $d_{x^2-y^2}$ hybrid orbitals participate in the metal–O bonding. Lowest in energy among the occupied metal–metal bonding orbitals is the σ -component a_{1g} made up of the in-phase combination of metal d_{z^2} orbitals on each fragment. Next in energy are the two degenerate π -orbitals from the interaction of the d_{xz} , d_{yz} type metal fragment components. Highest in energy is the metal δ -orbital that arises from the d_{xy} fragment metal–metal orbital overlap. We note that the fragment and molecular orbitals featuring the $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$ and $\text{Cr}_2(\text{C}_6\text{H}_3\text{-2,6-OME})_2$ systems are quite similar to those shown for $M_2(O_2CR')_4$ in Figure 7. They will as a consequence not be discussed separately here.

It follows from Table 3 for the tetracarboxylate bridged systems $M_2(O_2CR')_4$ ($M = \text{Cr, Mo, W}$; $R' = \text{CH}_3$) that the quadruple bond ($-\Delta E_{\text{int}}$) follows the trend $\text{Cr} \ll \text{Mo} < \text{W}$ ($202 \ll 311 < 326$ kcal/mol) as expected and previously discussed.^{8b} The weaker Cr–Cr bond primarily reflects a less favorable orbital interaction of -315.5 kcal/mol compared to -379.9 kcal/mol for $M = \text{Mo}$ and -469.3 kcal/mol for $M = \text{W}$.

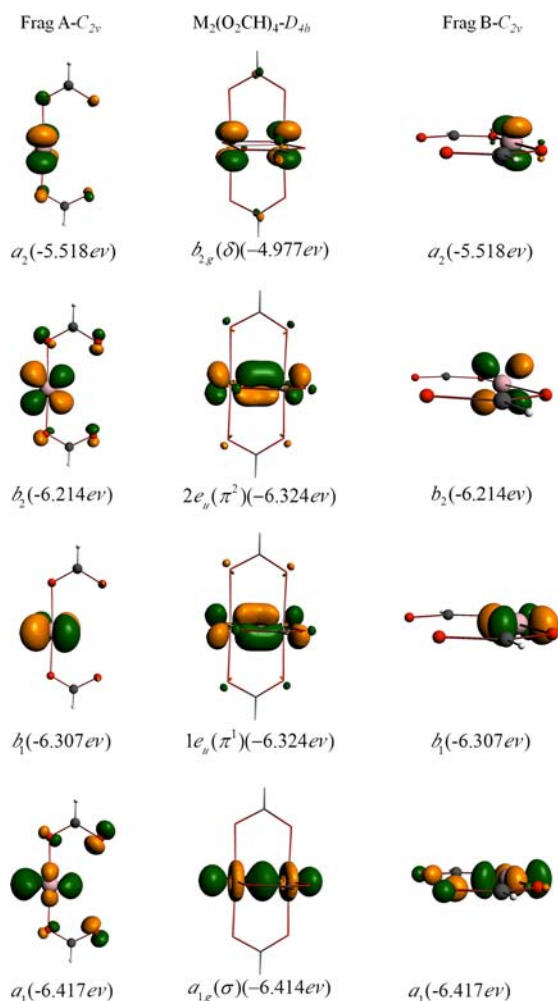


Figure 7. Metal fragment and molecular orbitals for the paddlewheel systems.

The orbital interactions would indicate a stronger M–M bond for M = Mo compared to M = W. However, this trend is reversed for the total M–M energy by the steric interactions that are larger by 25.9 kcal/mol for M = Mo. The lower steric interactions for 5d compared to 4d elements are a general trend that originates from the relativistic destabilization and expansion of 5d orbitals as explained elsewhere.^{8b} It is in general responsible for ligands L bound to 4d elements being more labile than ligands bound to 5d elements.

The orbital interaction ($-\Delta E_{\text{orb}}$) decomposition (NOCV) for $M_2(O_2CR')_4$ (M = Cr, Mo, W; R' = CH₃) show a σ -bond represented by ΔE_{orb} of Table 4 and depicted as (d) $\Delta\rho_{\text{orb}}^{\sigma}$ in Figures 8, 9, and 10 for the Cr, Mo, and W systems, respectively. The σ -bond ($-\Delta E_{\text{orb}}^{\sigma}$) strength increases significantly from 125.6 kcal/mol for Cr to 206.4 kcal/mol for Mo and only slightly to 214.3 kcal/mol for W. The degenerate π -orbital interaction terms are shown for the deformation densities (c) $\Delta\rho_{\text{orb}}^{\pi_1}$ and (d) $\Delta\rho_{\text{orb}}^{\pi_2}$ in Figures 8, 9, and 10. The energies $-\Delta E_{\text{orb}}^{\pi_1}$ and $-\Delta E_{\text{orb}}^{\pi_2}$ increase from M = Cr with 56.8 kcal/mol to M = Mo with 76.3 kcal/mol and decrease slightly for M = W with 72.7 kcal/mol. The δ -bonding component ($-\Delta E_{\text{orb}}^{\delta}$) increases as 11.3 kcal/mol (Cr), 36.4 kcal/mol (Mo), and 42.7 kcal/mol (W) and constitutes the weakest of the M–M bonding components. The corresponding deformation densities are shown in part a of Figures 8–10. We present in Table 4 energy terms $\Delta E_{\text{orb}}^{\text{sec}}$, $\Delta E_{\text{orb}}^{\text{sec}'}$, and $\Delta E_{\text{orb}}^{\text{rest}}$ representing the formation of the metal–X (X = O) bond that is cleaved during fragmentation and recombined during dimerization. The first term is $\Delta E_{\text{orb}}^{\text{sec}}$. It represents density flow from the bridging ligand to the bonding metal–X (X = O) region as depicted in (e) $\Delta\rho_{\text{orb}}^{\text{sec}}$ in Figures 8–10. Other contributions to the orbital interaction term that are part of the metal–X (X = O) bonding are referred to as $\Delta E_{\text{orb}}^{\text{sec}'}$ and $\Delta E_{\text{orb}}^{\text{rest}}$. In total, only 20% ΔE_{orb} comes from the M–X interaction. We have so far demonstrated the ability of our decomposition scheme to separate major bonding components between metal centers into individual contributions such as σ , π , and δ even for systems characterized by multiple bridging ligands. We shall next discuss the influence of different R' groups in X–CR'–X (X = O; R' = F, Cl, H, CF₃, CH₃, and CMe₃) on the strength of the Cr–Cr bond.

Presented in Table 3 are ETS results for $Cr_2(O_2CR')_4$, where methyl group in $Cr_2(O_2CCH_3)_4$ has been replaced with F, Cl, H, CF₃, CH₃, and CMe₃ groups. Trends in the observed $R_{\text{Cr-Cr}}$ distances for different R' seem to suggest that the Cr–Cr bond strength increases with the donor ability of R'. For the single atoms, F, Cl, and H, we calculate an increase in bonding strength ($-\Delta E_{\text{int}}$) of about 10 kcal/mol on moving from the weak donor F to the more electron donating H atom. The trend here can be attributed to the orbital interaction term ($-\Delta E_{\text{orb}}$) that increases by about 12 kcal/mol from F to H. The terms ΔE_{steric} and ΔE_{disp} vary only by 3 kcal/mol.

The R' = CF₃, CH₃, and CMe₃ series displays a similar trend with an increase in bonding ($-\Delta E_{\text{int}}$) by about 21 kcal/mol from CF₃ to CMe₃ (Table 3), a trend that largely can be attributed to $-\Delta E_{\text{orb}}$ increasing by about 46 kcal/mol. The

Table 3. ETS Analysis^a of the Quadruple M–M Compounds

complex	R'	ΔE_{elst}	ΔE_{Pauli}	$\Delta E_{\text{steric}}^b$	ΔE_{orb}	ΔE_{disp}	ΔE_{int}^c
3		−356.1	495.8	139.7	−273.6	−14.1	−148.0
4		−361.1	504.1	143.0	−254.2	−24.2	−135.4
5 (M = Cr)	F	−322.9	519.9	197.0	−326.6	−10.0	−139.6
5 (M = Cr)	Cl	−326.6	525.8	199.2	−337.6	−12.3	−150.7
5 (M = Cr)	H	−354.9	551.1	196.2	−338.5	−9.7	−152.0
5 (M = Cr)	CF ₃	−332.4	468.6	136.2	−319.7	−11.6	−195.1
5 (M = Cr)	CH ₃	−371.4	495.6	124.2	−315.5	−11.4	−202.7
5 (M = Cr)	CMe ₃	−399.3	565.1	165.8	−365.9	−16.5	−216.6
5 (M = Mo)	CH ₃	−526.7	705.3	178.6	−479.9	−10.4	−311.7
5 (M = W)	CH ₃	−598.8	751.5	152.7	−469.3	−10.0	−326.6

^aEnergies in kcal/mol. ^bSteric interaction: $\Delta E_{\text{steric}} = \Delta E_{\text{Pauli}} + \Delta E_{\text{elst}}$. ^cTotal bonding energy: $\Delta E_{\text{int}} = \Delta E_{\text{steric}} + \Delta E_{\text{orb}} + \Delta E_{\text{disp}}$.

Table 4. NOCV Contributions^a to ΔE_{orb}^b of the Quadruple M–M Compounds

complex	R	$\Delta E_{\text{orb}}^{\sigma}$ ^b	$\Delta E_{\text{orb}}^{\pi_1}$ ^b	$\Delta E_{\text{orb}}^{\pi_2}$ ^b	$\Delta E_{\text{orb}}^{\delta}$ ^b	$\Delta E_{\text{orb}}^{\text{sec}}$	$\Delta E_{\text{orb}}^{\text{sec'}}$	$\Delta E_{\text{orb}}^{\text{rest}}$	ΔE_{orb}^b
3		-146.1	-27.6	-27.6	-4.2	-28.0	-27.2	-12.9	-273.6
4		-95.6	-54.6	-54.6	-10.0	-16.1	-12.9	-10.4	-254.2
5 (M = Cr)	F	-170.2	-44.6	-44.6	-6.4	-30.5	-20.9	-9.4	-326.6
5 (M = Cr)	Cl	-171.4	-46.7	-46.7	-8.7	-30.3	-24.0	-9.8	-337.6
5 (M = Cr)	H	-173.2	-45.4	-45.4	-10.6	-30.6	-23.0	-10.3	-338.5
5 (M = Cr)	CF ₃	-127.7	-59.3	-59.3	-11.0	26.7	-24.2	-11.5	-319.7
5 (M = Cr)	CH ₃	-125.6	-56.8	-56.8	-11.3	-27.5	-25.1	-12.4	-315.5
5 (M = Cr)	CMe ₃	-168.1	-58.9	-58.9	-14.2	-28.3	-25.9	-11.6	-365.9
5 (M = Mo)	CH ₃	-206.4	-76.3	-76.3	-36.4	-40.3	-32.2	-12.0	-479.9
5 (M = W)	CH ₃	-214.3	-72.7	-72.7	-42.7	-30.6	-25.0	-11.3	-469.3

^aEnergies in kcal/mol. ^b $\Delta E_{\text{orb}} = \Delta E_{\text{orb}}^{\sigma} + \Delta E_{\text{orb}}^{\pi_1} + \Delta E_{\text{orb}}^{\pi_2} + \Delta E_{\text{orb}}^{\delta} + \dots + \Delta E_{\text{orb}}^{\text{rest}}$

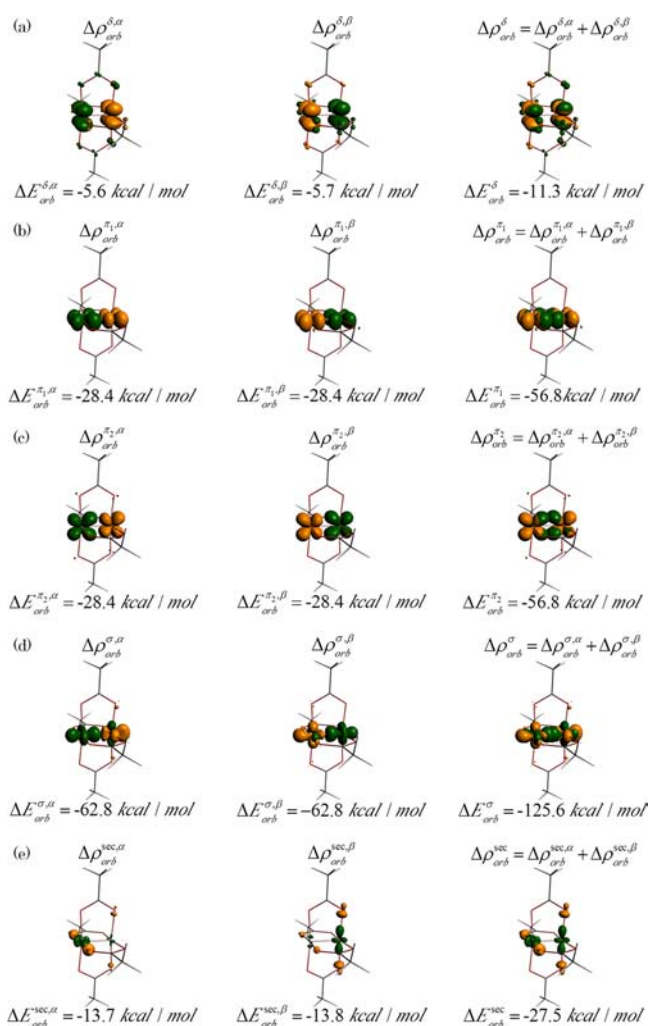


Figure 8. Contours of the NOCV deformation densities representing σ, π, δ -bonding and the corresponding orbital interaction energies in $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$. The contour values are 0.006 au. Green represents positive and orange negative.

sizable increase in $-\Delta E_{\text{int}}$ of about 14 kcal/mol on moving from CH_3 to CMe_3 compared to about 8 kcal/mol on moving from CF_3 to CH_3 is partly due to the $-\Delta E_{\text{disp}}$ term that becomes more stabilizing with the extra methyl groups on CMe_3 .

It is apparent from Table 3 that the axial H_2O ligand in $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$ (**3**) weakens the Cr–Cr bond by 54.7 kcal/mol compared to the $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$ system. This is in

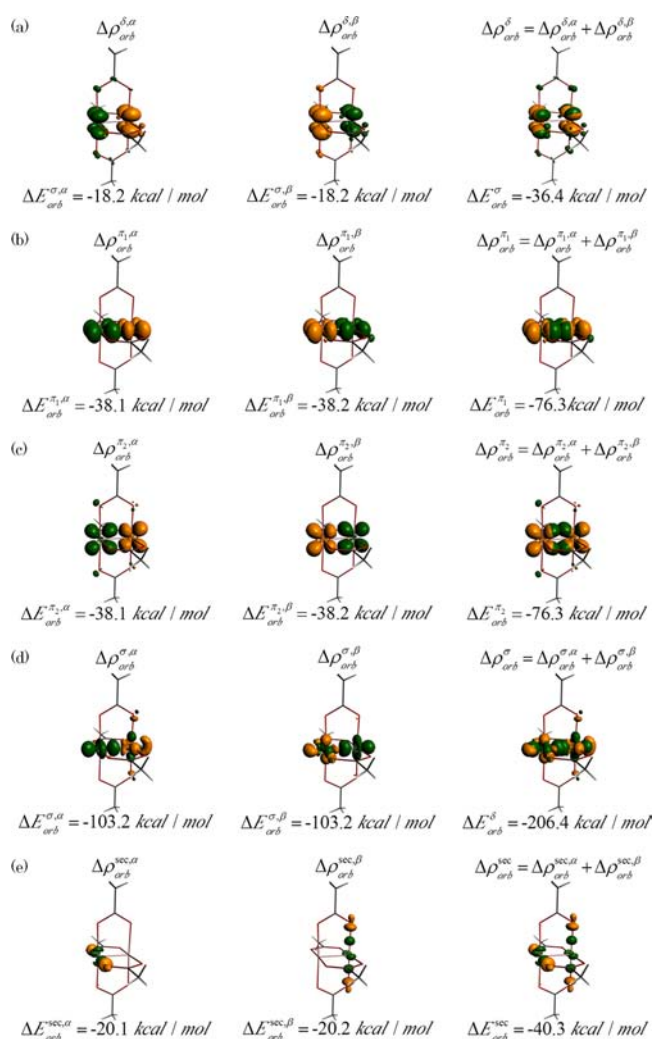


Figure 9. Contours of the NOCV deformation densities representing σ, π, δ -bonding and the corresponding orbital interaction energies in $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$. The contour values are 0.006 au. Green represents positive and orange negative.

line with the observation⁵ that the Cr–Cr bond distance in **3** is 2.29 Å⁵ compared to 1.97 Å^{14c} for $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$. However, the net destabilization is the combined effect of several opposing factors. Thus, adding an axial water molecule to one of the metal fragments will modify the mostly d_z^2 type orbital holding a single electron as $4s/4p_z$ character is added to reduce the emerging antibonding interaction with the incoming

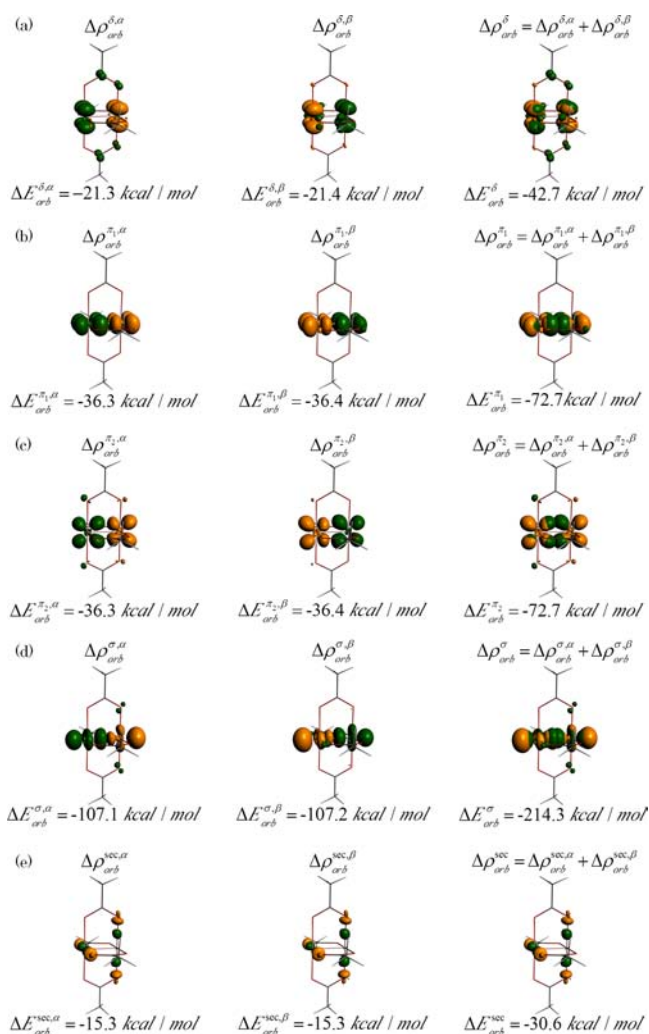


Figure 10. Contours of the NOCV deformation densities representing σ, π, δ -bonding and the corresponding orbital interaction energies in $W_2(O_2CCH_3)_4$. The contour values are 0.006 au. Green represents positive and orange negative.

water lone-pair. The result is an orbital pointing in the direction trans to the Cr–OH₂ bond. As the two fragments next approach each other, the singly occupied directional hybrid orbital on one fragment will interact more repulsively with occupied orbitals on the other fragment than a pure d_{z^2} component. The result is an increase in the Pauli repulsion and the steric interaction (15.5 kcal/mol), leading to a longer Cr–Cr bond distance. The longer Cr–Cr bond will in turn weaken the π - and δ -bonding by about 58 and 7 kcal/mol, respectively (Table 4) as the bonding π - and δ -overlaps are reduced by the longer Cr–Cr vector. Finally, the directional character of the two singly occupied fragment hybrid orbitals results in a σ -bond that is 20 kcal/mol stronger than in the corresponding complex without axial water ligands.

Complexes of the type $Cr_2(C_6H_3-2,6-OMe)_4$ (4) were the first example of quadruple bonded chromium systems without axial ligands. We shall analyze 4 here in terms of two $Cr(C_6H_3-2,6-OMe)_2$ fragments formed by breaking the Cr–O bond. It is clear from Figure 11a–d that 4 exhibits the four quadruple bond components. The strongest in energy is $\Delta E_{orb}^{\sigma} = -95.6$ kcal/mol due to the σ -bonding interaction. Next comes $\Delta \rho_{orb}^{\pi_1}$ and $\Delta \rho_{orb}^{\pi_2}$ with the combined contribution of $\Delta E_{orb}^{\pi} = -109.2$

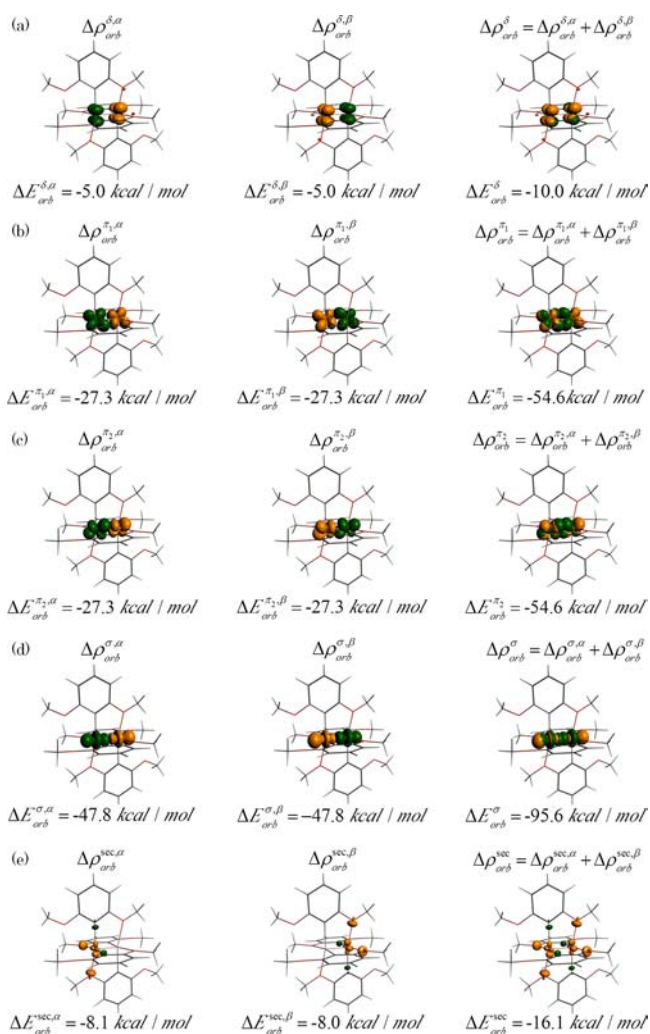


Figure 11. Contours of the NOCV deformation densities representing σ, π, δ -bonding and the corresponding orbital interaction energies in $Cr_2(C_6H_3-2,6-OMe)_4$. The contour values are 0.006 au. Green represents positive and orange negative.

kcal/mol describing the π -bonding. Finally, we have $\Delta \rho_{orb}^{\delta}$ due to a weak δ -bonding component with $\Delta E_{orb}^{\delta} = -10$ kcal/mol. The Cr–O bond contributes -50 kcal/mol to ΔE_{orb} with the largest component given by ΔE_{orb}^{sec} (Table 4). The Cr–Cr bond strength is weaker in 4 than in $Cr_2(O_2CCH_3)_4$.

4. CONCLUDING REMARKS

We have now by the help of the ETS–NOCV scheme analyzed the bonding in $Cr_2[Ar'NC(Me)_2NAr']_2$ (2) with the shortest Cr–Cr (1.729 Å) distance and compared the bonding to that of the very similar $Cr_2(C_6H_3-2,6-Ar'-4-OMe)_2$ complex (6) with Cr–Cr = 1.816 Å. The ETS–NOCV method finds for both systems a quintuple bond, as was the case in a previous study on the complex 1 first synthesized by Power. The Cr–Cr bond in 2 was found to be stronger and shorter than in 6 and 1 because the steric interaction between the two constituting fragments in 2 is smaller than in 6 and 1. For all three systems, dispersion is seen to strengthen the stability of the complexes by ~ 20 kcal/mol due to van der Waals interactions between isopropyl groups on aryl groups attached to different metal centers.

Our ETS–NOCV study was extended to studies on complexes of group 6 metals with a supported quadruple bond where the influence of the metal, donating substituents on the bridging ligands, and additional axial ligands on the metal–metal bond strength was discussed and compared to experimental findings. We have in this study clearly demonstrated that the ETS–NOCV scheme can be used to study the metal–metal bond in supported systems with a ligand bridge. The ETS–NOCV method is not only able to separate M–L and M–M contributions to the stability of the bridge bond but it is also able to break down the M–M bond into its σ -, π -, and δ -components.

AUTHOR INFORMATION

Corresponding Author

*E-mail: Ziegler@ucalgary.ca.

Notes

The authors declare no competing financial interest.

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