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Electronic Structure of $[(CpCr)\{(CO)_3M\}]\mu$-Cot (M = Cr, Fe): A Theoretical Study

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The electronic structure of two cyclooctatetraene-bridged dinuclear first-row transition metal complexes of the type $[(CpM)\{(CO)_3M'\}]\mu$-Cot (M = Cr; M′ = Fe (**1**), Cr (**2**)) was investigated by complete active space self-consistent field (CASSCF) calculations. In this context the differences in the binding capabilities of the complex fragments CpM and $(CO)_3M$ are discussed on the basis of extended Hückel molecular orbital (MO) calculations. The geometries used for the CASSCF calculations for complex **1** were obtained from the crystal structure. For **2** a model structure was established by geometry optimization using density functional methods. The CASSCF results agree well with the experimental findings and provide insight into the binding situation of the two compounds. Complex **1** can be regarded as being composed of a chromocene-like subunit $CpCr(\eta^5\text{-}C_5H_5)$ and the fragment $(CO)_3Fe(\eta^3\text{-}C_3H_3)$. A direct metal−metal bond is found, involving one initially singly occupied orbital of each fragment, leading to a doublet ground state for **1** with the remaining unpaired electron localized at the chromium center. For **2** no such direct metal−metal bond can be recognized. A very weak direct metal−metal interaction is induced by electron donation from the Cot^{2-} ligand into a formally unoccupied metal−metal binding orbital combination. In the quartet ground state all three unpaired electrons are localized at the chromium center of the formally doubly positive charged CpCr unit, on which complex fragment $[(CO)_3Cr(\eta^5\text{-}Cot)]^{2-}$ acts like a cyclopentadienyl ligand. The coordination sphere of the chromium center of the CpCr unit resembles that of a metallocene metal center and its metal 3d occupation scheme corresponds to that of vanadocene.

Introduction

Dinuclear transition metal compounds are of considerable interest for a number of reasons. The most important one is the ability of these compounds to activate organic and inorganic molecules.[1] In a number of applications dinuclear systems have turned out to be more effective and more selective catalysts than mononuclear species.[2−4] Also, dinuclear transition metal systems play a central role as active sites of enzymes in biological processes.[5] However, little is known about the electronic structure of these compounds, particularly with respect to the interactions between the two metal centers. An understanding of these interactions, however, is essential for a deeper insight into the mechanisms of activation processes. For more complicated complexes, especially for systems in which the metal centers are connected by both direct metal−metal bonds and bridging ligands, simple electron counting rules typically give poor or even qualitatively incorrect descriptions of the bonding situation. Therefore, there is need for more accurate models which are able to describe the bonding in a qualitatively correct manner.

On the basis of a complete active space self-consistent field (CASSCF) study in a recent paper,[6] we introduced a model which describes the electronic structure and properties of the electron-poor synfacial-bridged first-row transition metal systems $[(CpM)(CpM')]\mu$-Cot in a simple way. It has been shown that, structurally and electronically, these systems can generally be considered as combinations of two mononuclear metallocene-like subunits.

In the present paper we discuss the results of a theoretical investigation of the electronic structure of two synfacial-bridged dinuclear compounds of the type $[(CpM)\{(CO)_3M'\}]\mu$-Cot (M = Cr; M′ = Fe (**1**), Cr (**2**)).[7] The properties of these systems are strongly related to those of the bis-cyclopentadienyl compounds. Complex **1**, possessing 33 valence electrons (ve),

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has a doublet ground state, in which the single unpaired electron is localized at the chromium center. Somewhat surprisingly, the ground state of the dichromium system **2** (31 ve) was found to be a quartet. Electron spin resonance (ESR) experiments suggest that all three unpaired electrons are localized at the Cr center of the CpCr unit. For both compounds a direct metal−metal single bond is assumed, although, compared to the [(CpM)(CpM′)]μ-Cot systems containing the same metal centers, the metal−metal distance is increased by about 20 pm for **1** and by about 40 pm for **2**.[8,9] The experimental results for these two complexes showed that this bond lengthening cannot be explained by steric effects alone, but should originate in different electronic interactions between the metals and the ligand fragments Cp$^-$ and (CO)$_3$. A similar increase in the metal−metal distance was found also for other classes of dinuclear systems, when the cyclopentadienyl ligand is replaced by a tricarbonyl unit (for examples, see ref 10).

This effect will be examined in the first part of our discussion by means of extended Hückel molecular orbital (MO) calculations for the complex fragments CpM′ and (CO)$_3$M′. For the dinuclear systems **1** and **2** the results of CASSCF calculations are presented. These results show that the electronic structure and the properties of **1** can be easily explained in the same manner as for the [(CpM)(CpM′)]μ-Cot systems. For complex **2** the electronic structure turns out to be more complicated and, therefore, different assumptions have to be made to explain the binding situation.

Results and Discussion

CpM versus (CO)$_3$M Fragments. The different binding capabilities of the fragments CpM and (CO)$_3$M result from differences in their frontier orbitals. These orbitals differ in energy as well as in shape and spatial extent. A general study of the binding capabilities of CpM and (CH)$_n$M units was carried out by Hoffmann et al.[10] We focus here on the binding capability with respect to the possibility of formation of direct metal−metal bonds in dinuclear systems such as the [(CpM)(L$_n$M′)]μ-Cot complexes. Figure 1 shows MO correlation diagrams for the subunits CpM (M = Cr) and (CO)$_3$M′ (M′ = Cr, Fe) based on extended Huckel calculations.[11]

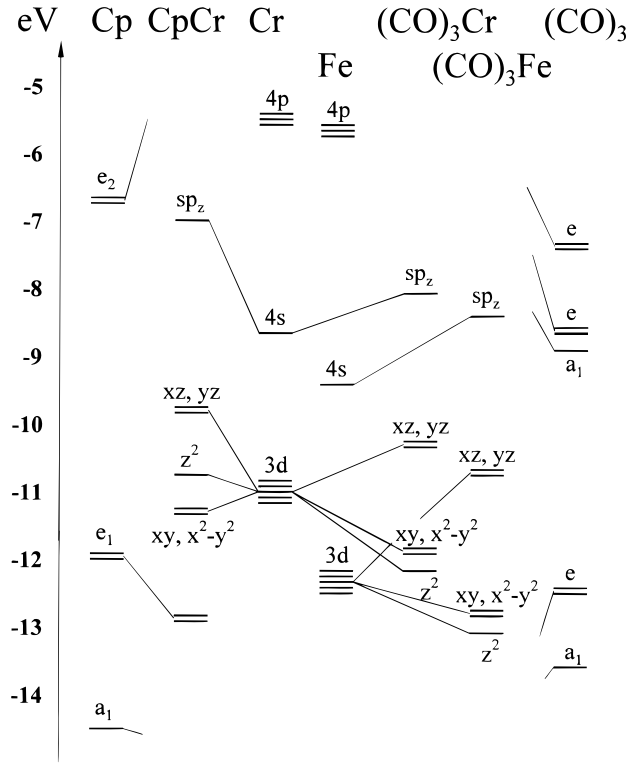

Figure 1. MO correlation diagrams for the fragments CpCr and (CO)$_3$M (M = Cr, Fe) based on extended Hückel calculations.

Table 1. Metal Contributions (in Percent) to the Frontier Orbitals of (CO)$_3$M and CpM

orbital	CpCr	(CO)$_3$Cr	(CO)$_3$Fe
xz	65 d$_{xz}$, 12 p$_x$,	47 d$_{xz}$, 7 d$_{x^2-y^2}$, 19 p$_x$,	40 d$_{xz}$, 7 d$_{x^2-y^2}$, 24 p$_x$,
yz	65 d$_{yz}$, 12 p$_y$,	47 d$_{yz}$, 7 d$_{xy}$, 19 p$_y$	40 d$_{yz}$, 7 d$_{xy}$, 24 p$_y$
z^2	96 d$_{z^2}$, 2 s	63 d$_{z^2}$	71 d$_{z^2}$
$x^2 - y^2$	90 d$_{x^2-y^2}$, 3 p$_z$	51 d$_{x^2-y^2}$, 16 d$_{xz}$	53 d$_{x^2-y^2}$, 20 d$_{xz}$
xy	90 d$_{xy}$, 3 p$_z$	51 d$_{xy}$, 16 d$_{yz}$	53 d$_{xy}$, 20 d$_{yz}$

Because the metal orbitals interact more efficiently with ligand acceptor orbitals, the frontier orbitals z^2, $x^2 - y^2$, and xy of (CO)$_3$M are more stabilized than the corresponding orbitals of the CpM fragment.[12] The most significant difference is in the energy of the z^2 orbitals. In (CO)$_3$M′ the z^2 orbital is stabilized by the interaction of the d$_{z^2}$ orbital with the unoccupied a$_1$ combination of CO π* orbitals. This interaction also significantly reduces its metal character (see Table 1). Because there is no equivalent ligand acceptor orbital in the Cp ligand, a destabilization of the z^2 orbital of the CpM fragment arises from the interaction of the d$_{z^2}$ orbital with filled a$_1$ ligand orbitals. The $x^2 - y^2$ and xy orbitals are slightly stabilized in both fragments. The two orbitals of the tricarbonyl-metal unit show a noticeable mixing of d$_{xz}$ and d$_{yx}$ components with the d$_{x^2-y^2}$ and d$_{z^2}$ orbitals. The energy differences are less significant for the xz and yz orbitals. For (CO)$_3$Cr they are slightly lower and for (CO)$_3$Fe slightly higher than for the corresponding CpM unit (not shown for CpFe). The destabilizing interaction of the d$_{xz}$ and d$_{yz}$ orbitals with filled ligand orbitals of e symmetry leads to an additional mixing of p components to the fragment orbitals which causes the hybrid orbitals of both fragments to point away from the ligands. However, the contribution of p orbitals is much larger in (CO)$_3$M, which makes the xz and yz orbitals more diffuse and extented, which allows, in principle, for longer metal−metal bonds. This explains the experimentally found sequence of metal−metal bond lengths in various dinuclear systems containing different combinations of CpM and (CO)$_3$M fragments.

Because larger differences in the energies of the relevant fragment orbitals tend to interfere with the formation of a metal−metal bond, the metal−metal interactions should be generally weaker for homodinuclear complexes if the metal centers have different ligand spheres. Thus, the metal−metal bond in complex fragments such as CpM−MCp or (CO)$_3$M−M(CO)$_3$ should be stronger than in a CpM−M(CO)$_3$ fragment. The same effect has been found for the heteronuclear system **1** compared to [(CpCr)(CpFe)]μ-Cot.[7] However, there is no general trend for heteronuclear complexes, because the effect

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(12) To avoid confusion it should be mentioned that throughout our discussion we distinguish between the fragment frontier orbitals labeled xy, $x^2 - y^2$, z^2, xz, yz, and the pure metal d functions.

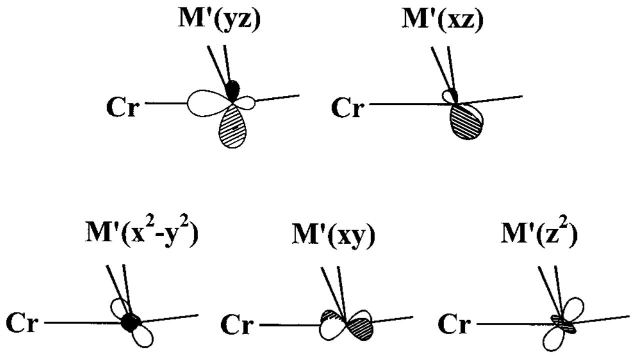
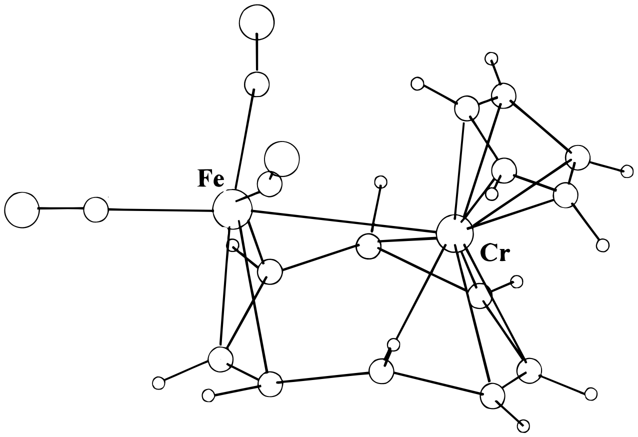


Figure 2. Frontier orbitals of the (CO)$_3$M′ fragment relative to the Cr center of the CpCr unit of the dinuclear systems [(CpCr){(CO)$_3$M′}]μ-Cot.

Scheme 1



depends on whether the shift of the orbitals, resulting from the metal−ligand interactions, brings the fragment orbitals closer together or splits them further.

The qualitative shape of the metal contributions to the frontier orbitals of a (CO)$_3$M′ fragment with respect to the position of the second metal center in the systems [(CpCr){(CO)$_3$M′}]μ-Cot is shown in Figure 2. The diffuse M′(*yz*) orbital is best suited for the formation of a longer metal−metal σ bond, since it points directly toward the second metal center. An orientation relevant for metal−metal π bonding is found for the M′(*xy*) orbital. However, this orbital is less diffuse than the M′(*yz*) orbital and an effective metal−metal π interaction could occur only at smaller metal−metal distances. Therefore, it is not possible to form a strong σ and a π bond at once. Accordingly, it should be more favorable to form a strong metal−metal σ bond, resulting in a relatively large metal−metal distance, rather than a weak σ and a π bond.

The [(CpCr){(CO)$_3$Fe}]μ-Cot System. The heteronuclear Cr−Fe system[7] possesses 33 valence electrons and has a doublet ground state. ESR experiments suggest that the single unpaired electron is localized at the chromium center. X-ray crystal structure analysis shows an η^5 and η^3 coordination of the Cot ligand at the Cr and the Fe centers, respectively (Scheme 1).

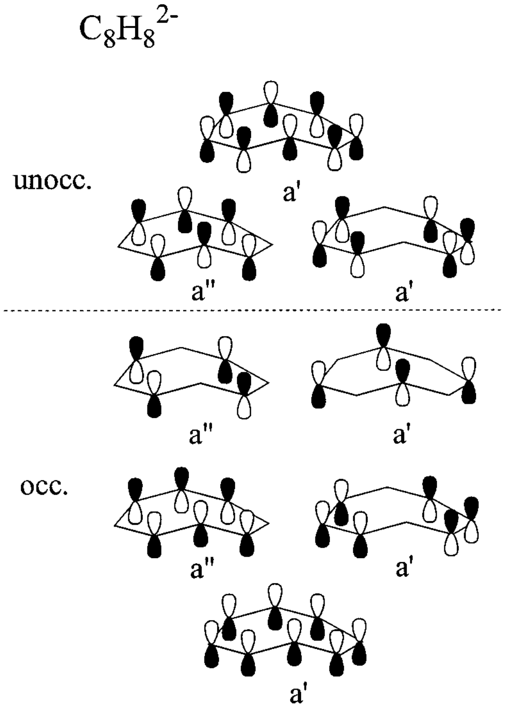


Figure 3. Structure of the π orbitals of the Cot^{2-} ligand. Because of the bend structure of the Cot ring in the dinuclear systems there are no degenerate π orbitals. The orbitals are labeled according to the C_s symmetry of the complexes.

The metal−metal distance was determined to be 294 pm, which is about 20 pm longer than in the [(CpCr)(CpFe)]μ-Cot[9] system (32 ve). Nevertheless, a direct metal−metal single bond is assumed, which yields a valence bond description with the iron and the chromium centers having 18 and 17 ve, respectively (see ref 7). To refine this description and combine with the above analysis, the complex can be formally subdivided into the fragments CpCr$^+$, (CO)$_3$Fe$^+$, and Cot^{2-}. Because of the structural similarity between the chromocene-like complex fragments CpCrC$_5$H$_5$ of **1** and of (CpCr)$_2\mu$-Cot,[8] it can further be assumed that the occupation of the chromium d orbitals in the CpCr$^+$ fragment corresponds to that of the triplet ground state of chromocene,[13] which has turned out to be the case in the [(CpM)(CpM′)]μ-Cot complexes. Of course, the energetic ordering of the occupied frontier orbitals (z^2, $x^2 - y^2$, xy; one of them is doubly occupied) can be different from that of the mononuclear metallocene due to the slightly bent structure of the chromocene-like complex half and the interaction with the (CO)$_3$Fe$^+$ fragment.[14] In the (CO)$_3$Fe$^+$ fragment the three frontier orbitals z^2, $x^2 - y^2$, and xy are formally doubly occupied and the orbital yz is singly occupied. In this way, a direct metal−metal bond can be formed by the overlap of the orbitals Cr($x^2 - y^2$) and Fe(yz). The Cot^{2-} fragment is assumed not to affect the occupation and structure of the metal orbitals essentially. Because the conjugation of the π system of the Cot ligand is disconnected, it is possible to divide it formally into two separate π systems (Figures 3 and 4). Thus, the Cot ligand should act as a C$_5$H$_5^-$ (or Cp$^-$) and a C$_3$H$_3^-$ ligand coordinated to the CpCr$^+$ and (CO)$_3$Fe$^+$ fragments, respectively.

The above considerations were used to construct a model wave function, which can describe the binding situation of **1** in a qualitatively correct manner. It must be emphasized that for this purpose a multiconfigurational approach is needed, which is not only because of the presumed weak metal−metal bond. The metal−ligand interactions of bridged dinuclear systems can be a source of large nondynamical correlation effects as well. As in our previous work,[6] we applied the CASSCF method[15−17] to the problem. The active space was defined initially to contain the singly occupied Cr(z^2) orbital, the metal−metal bonding and

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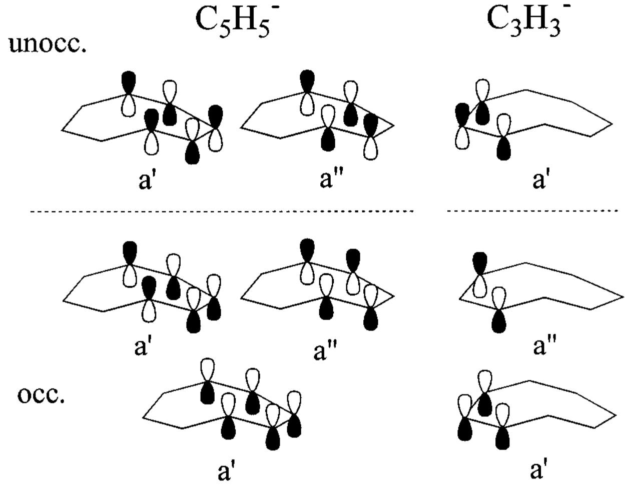


Figure 4. Cot^{2-} π system separated into a $C_5H_5^-$ and a $C_3H_3^-$ π subsystem.

corresponding antibonding orbitals, and the orbitals Cr(xy), Fe(xy), and Fe($x^2 - y^2$). To each of the latter three orbitals one correlation partner of the same symmetry, which usually represents the metal−ligand antibonding combination, was included which resulted in an active space of nine electrons in nine orbitals (5a′4a″). In principle it would be desirable to include at least another six orbitals in the active space, namely the Fe(z^2) orbital and the two highest occupied Cot^{2-} π orbitals (see Figure 3) plus their three metal−ligand antibonding counterparts. This would lead to a CAS(15/15) wave function, which is not feasible for calculation.

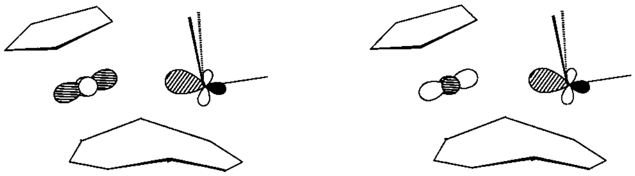
To confirm the reliability of our final results, on account of the limitations according to the active space, a number of CAS(9/9) calculations were carried out in which the composition of the active space was systematically varied (7a′2a″, 6a′3a″, 5a′4a″, 4a′5a″, 3a′6a″). For each active space, we tried to calculate the lowest quartet and doublet states. In addition, because the results of CASSCF calculations are usually sensitive to the initial guess, different doublet, quartet, and sextet RHF wave functions were tested as starting orbitals for each active space.

The lowest energy by far was obtained for a $^2A'$ state with the 5a′4a″ active space. The corresponding wave function also yielded the only physically reasonable description of the electronic ground state of the system among all wave functions tested. Therefore, we conclude that it is indeed the best possible CAS(9/9) wave function (for the given one-particle basis) representing the ground-state electronic structure of complex **1**. The resulting occupation numbers and characters of the active orbitals are given in Table 2.

Table 2. Population and Character of the Active Orbitals of the Doublet Ground State of [(CpCr){(CO)$_3$Fe}]μ-Cot (1)

orbital	occ. no.	character	
32a″	0.07	Cot $\pi \rightarrow$ Cr(xz)	(M−Cot)*
53a′	0.10	Cot $\pi \rightarrow$ Cr(yz)	(M−Cot)*
31a″	0.15	Cr(xy) $\rightarrow$ Cot π	(M−Cot)*
52a′	0.49	Cr($x^2 - y^2$) − Fe(yz)	(M−M′)*
51a′	1.00	Cr(z^2)	M
50a′	1.51	Cr($x^2 - y^2$) − Fe(yz)	(M−M′)
30a″	1.85	Cr(xy) $\rightarrow$ Cot π	(M−Cot)
49a′	1.90	Cot $\pi \rightarrow$ Cr(yz)	(M−Cot)
29a″	1.93	Cot $\pi \rightarrow$ Cr(xz)	(M−Cot)
48a′ inactive	2.00	Fe(yz)	M−CO
28a″ inactive	2.00	Fe(xz)	M−CO
47a′ inactive	2.00	Fe(z^2)	M−CO

Scheme 2



50a’ **52a’**

From the orbital populations and structures it can be concluded that the calculated electronic structure essentially agrees with our assumptions. The unpaired electron is localized at the chromium center, occupying the Cr(z^2) orbital. Thus, it should be only slightly affected by interaction with the second metal center. The orbital pair 50a′/52a′ describes a direct metal−metal bond. As assumed, it is formed by the overlap of the two formally singly occupied fragment orbitals Cr($x^2 - y^2$) and Fe(yz) (Scheme 2).

Because of the position of the fragments CpCr$^+$ and (CO)$_3$Fe$^+$ relative to one another, the bond has mainly σ character. The formal bond order, obtained as the difference of the population of the bonding and the antibonding orbital divided by two, is only 0.5, which suggests a rather weak metal−metal bond. Note, however, that the inclusion of dynamical correlation effects, e.g., by means of a subsequent CASPT2 or MRCI calculation, would, in general, reduce somewhat the weight of the metal−metal antibonding configurations in the wave function and, therefore, predict a stronger metal−metal bond.[18]

Orbital 30a″ can be identified as the metal−ligand bonding combination of Cr(xy). Together with its corresponding antibonding counterpart 31a″ it describes an electron pair mainly localized at the chromium center, confirming the assumption that the electronic structure of the complex fragment CpCr(η^5-C_5H_5) of **1** is essentially equivalent to that of chromocene. However, this orbital pair exhibits a stronger interaction between the metal and the $C_5H_5^-$ part of the π system of the Cot ligand than is found between the d_{xy} orbital (or equivalently $d_{x^2-y^2}$) and the Cp π orbitals in the mononuclear metallocene complex. The same can be concluded for the other four active orbitals 49/53a′ and 29/32a″. They represent not the metal−ligand bonding and antibonding combinations of Fe(xy) and Fe($x^2 - y^2$), but the two highest occupied Cot^{2-} π orbitals, again from the $C_5H_5^-$ part of the Cot π system. Within these orbitals a considerable charge transfer takes place from the Cot π into the formally unoccupied xz and yz orbitals of the chromium center. The Fe(xy) and Fe($x^2 - y^2$) orbitals as well as the Fe(z^2) orbital can be found among the inactive orbitals. Their structures essentially match those for the (CO)$_3$M fragment shown in Figure 1.

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From the preceding discussion we conclude that complex **1** can be considered, in a manner similar to the [(CpM)(CpM′)]μ-Cot systems, as a combination of the two mononuclear subunits CpCr(η^5-C_5H_5) and $(CO)_3$Fe(η^3-C_3H_3). The first fragment has an electronic structure equivalent to chromocene, containing two unpaired electrons. The second fragment possesses a single unpaired electron. The overall electron deficiency of the metal centers in the two separated fragments is balanced in the dinuclear complex by the formation of a direct metal−metal bond and by metal−ligand donor−acceptor interactions. This results in a doublet ground state for complex **1**, where the remaining single unpaired electron is localized at the chromium center.

The [(CpCr){(CO)$_3$Cr}]μ-Cot System. For the dichromium system the situation is more complicated than for **1**. The complex possesses 31 valence electrons and the ground state is a quartet, in which all three unpaired electrons are localized at the chromium center of the CpCr unit (Cr1). The ESR spectrum is quite similar to that of vanadocene, suggesting that the unpaired electrons occupy the same orbitals (z^2, $x^2 - y^2$, and xy) in both systems and are not substantially affected by interactions with the chromium center of the $(CO)_3$Cr unit (Cr2) in **2**. Considering the experimental results and the conclusions drawn from the analysis of the binding capabilities of the CpM and $(CO)_3$M fragments, the assumption of a direct metal−metal bond in **2** is not well supported. To recognize a direct metal−metal bond one would have to start by assuming the presence of four unpaired electrons in the $CpCr^+$ fragment, which, considering the orbital energies (see Figure 1), is quite unlikely. Furthermore, this would imply that the Cr−Cr bond is formed by the interaction of the $x^2 - y^2$ orbitals of both metal centers, since, in contrast to **1,** the more diffuse Cr2(yz) orbital is unoccupied in the fragment $(CO)_3Cr^+$. The metal−metal bond would then be similar to the Cr−Cr bond in the complex $(CpCr)_2\mu$-Cot, which is about 40 pm shorter than in **2** (239 vs 279−285 pm). Of course, when different assumptions are made about the electron distribution in the complex fragments, other formal descriptions of the bonding situation are conceivable. For example, one could start by assuming a d^3 configuration for Cr1 and a d^6 configuration for Cr2, which corresponds to the ionic resonance structure proposed by Hermans et al.[7] This leads to the possibility of a two-electron donor bond formed by the doubly occupied Cr2($x^2 - y^2$) orbital donating electrons into the empty orbital Cr1(yz), similar to the metal−metal binding mechanism suggested by Bieri et al.[19] for the [(C_7H_8Rh)(CpRh)]μ-Cot and [(CpCo){(CO)$_3$Mo}]μ-Cot systems. However, this argument does not seem feasible due to the large metal−metal distance.

To resolve the issues mentioned above concerning the electronic structure of complex **2**, we have to establish a reasonable molecular geometry. The experimentally determined structure shows a relatively large deviation from C_s symmetry. The Cot ligand coordinates with four carbon atoms to Cr1 and with five carbon atoms to Cr2 (Scheme 3). Four slightly different molecules were found in the unit cell, which points to a structure which is not very rigid. For that reason, it is not entirely clear whether the distortion of the molecule results from packing effects or is determined by forces inherent in the system.[20]

To obtain a reasonable molecular geometry for the investigation of the electronic structure we optimized complex **2** at the density functional theory (DFT) B3LYP[21] level. During the optimization procedure C_s symmetry was enforced. The most important structural parameters are summarized in Table 3. With the exception of the distance between Cr1 and the bridging carbon atom C1 (see Scheme 3), all optimized structural parameters are in the range of the experimental values. The excellent agreement of the metal−metal distances indicates that the intermetallic interactions are not significantly affected by the symmetry restriction.[22−24]

The CASSCF investigation of the electronic structure of the dichromium system follows a very similar strategy to that performed for **1**, including the calculation of the lowest doublet and quartet state for a variety of CAS(9/9) wave functions as well as the testing of different sets of starting orbitals. Again it should be emphasized that a wave function with a larger active

Scheme 3

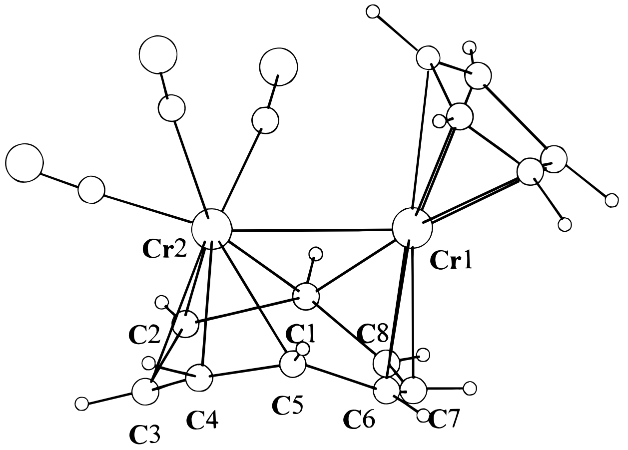

Table 3. Most Important Structural Parameters of [(CpCr){(CO)$_3$Cr}]μ-Cot (2) (Distances in pm)

bond	opt.[a]	exp.
Cr1−Cr2	284.2	279−285
Cr1−C7	217.8	207−226
Cr1−C6/C8	224.1	216−240/204−220
Cr1−C1/C5	282.6	233−247/273−287
Cr2−C1/C5	246.6	239−241/238−248
Cr2−C2/C4	225.4	220−235/221−236
Cr2−C3	223.2	215−236

[a] Method: DFT (B3LYP); basis sets: C,O,H 6-31G**; Cr ECPs from Dolg et al.[27]

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(20) The recently determined structure for [(Cp*Cr){(CO)$_3$Cr}]μ-Cot (Cp* = C_5Me_5) has turned out to be very similar to the experimental geometry of **2**, particularly with respect to the Cr−Cr distance and the M−Cot−M coordination mode. This gives some evidence that the distorted structure of **2** is indeed determined by inherent forces. Heck, J.; Brussard, H. C. Unpublished work.

(21) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(22) Note that the presently available DFT methods are not always capable of describing accurately the properties of first-row transition metal compounds, particularly in the case of dinuclear systems. In the course of our study of the Cot-bridged dinuclear complexes, geometry optimizations were attempted also for **1** and for a number of complexes of the type [(CpM)(CpM′)]μ-Cot, using different functionals and basis sets. Although the optimizations gave results in very good agreement with the experimental structure for the dichromium complex $(CpCr)_2\mu$-Cot, they gave very poor results for the other systems in this study, generally yielding intermetallic distances much larger than the experimental values. Other authors have reported similar results for geometry optimizations of dinuclear first-row transition metal compounds (see refs 23, 24).

(23) Cotton, F. A.; Feng, X. *J. Am. Chem. Soc.* **1997**, *119*, 7514.

(24) Andersson, K.; Bauschlicher, C. W., Jr.; Persson, B. J.; Roos, B. O. *Chem. Phys. Lett.* **1996**, *257*, 238.

Table 4. Population and Character of the Active Orbitals of the Ground State of [(CpCr){(CO)$_3$Cr}]μ-Cot (2)

orbital	occ. no.	character	
53a′	0.09	Cr2 (z^2)	(M−CO)*
52a′	0.10	Cr2 ($x^2 - y^2$)	(M−CO)*
32a″	0.10	Cr2 (xy)	(M−CO)*
51a′	1.00	Cr1 ($x^2 - y^2$)	M
50a′	1.00	Cr1 (z^2)	M
31a″	1.00	Cr1 (xy)	M
30a″	1.90	Cr2 (xy)	(M−CO)
49a′	1.90	Cr2 ($x^2 - y^2$)	(M−CO)
48a′	1.91	Cr2 (z^2)	(M−CO)
47a′ (inactive)	2.00	Cot $\pi \rightarrow$ Cr1,2 (yz)	(M−Cot)
29a″ (inactive)	2.00	Cot $\pi \rightarrow$ Cr1 (xz)	(M−Cot)

space would be desirable. The active space should be composed of the three singly occupied orbitals Cr1(z^2), Cr1($x^2 - y^2$), and Cr1(xy), a metal−metal bonding orbital and the corresponding antibonding counterpart, the formally doubly occupied orbitals Cr2(z^2) and Cr2(xy), and the two highest occupied Cot^{2-} π orbitals as well as the four corresponding metal−ligand antibonding combinations, leading in all to 13 electrons in 13 active orbitals.

The lowest energy was obtained for a ^{4}A″ state, which is considered to represent the best possible description of the ground state of **2** by means of a CAS(9/9) wave function in the given one-particle basis. The character and population of the corresponding active orbitals (6a′3a″) are shown in Table 4. The three unpaired electrons are indeed localized at chromium center of the CpCr unit, occupying the orbitals z^2, $x^2 - y^2$, and xy, which, as in vanadocene, essentially represent the three formally nonbonding metal d orbitals. The other six active orbitals can be identified as the z^2, $x^2 - y^2$, and xy orbitals of the (CO)$_3$Cr fragment (see Figure 2**)** and their metal−carbonyl antibonding counterparts. Within the active orbital set there is no indication of a direct metal−metal bond.

The two highest occupied Cot^{2-} π orbitals (see Figure 3) are found within the inactive orbital space. As a consequence of the electron deficiency in the CpCr^{2+} fragment, the π orbital of a″ symmetry, which formally interacts with the unoccupied xz orbitals of both metal centers, donates electrons primarily to the xz orbital of Cr1. The a′ π orbital, however, donates electrons into the yz orbitals ($d_{yz} + p_y$) of both metal centers, which produces some electron density between the two metal centers. Thus, orbital 47a′ gives rise to a direct metal−metal binding interaction. However, because the metal contributions to this orbital are very small, this interaction has to be considered as extremely weak, which is in agreement with the very small zero field splitting seen in ESR experiments as well as with the very high reactivity of complex **2** in general.

Because of the population and structure of the active orbitals, the complex can be formally subdivided into the fragments CpCr^{2+}, (CO)$_3$Cr, and Cot^{2-}. The Cot ligand coordinates with five carbon atoms to Cr2. Combination of the fragments (CO)$_3$Cr and Cot^{2-} thus leads to the complex fragment [(CO)$_3$Cr(η^5-Cot)]$^{2-}$, in which Cr2 possesses 18 valence electrons. Taking into account the direct metal−metal binding interaction mentioned above, for the optimized structure, in which the Cot ligand is coordinated to Cr1 with only three carbon atoms, this fragment acts on the CpCr^{2+} unit similar to a cyclobutadiene ligand, in which one carbon atom is replaced by Cr2.

The fact that in the experimental structure of **2** the Cot ligand is found to coordinate with four carbon atoms to Cr1 suggests, however, that [(CO)$_3$Cr(η^5-Cot)]$^{2-}$ can be considered to act like a cyclopentadienyl ligand on CpCr^{2+}. This results in 15 valence electrons for Cr1 corresponding to the metal 3d population in vanadocene.

Concluding Remarks

The different binding capabilities of the complex fragments CpM and (CO)$_3$M have turned out to be the main reasons for the differences in the properties of **1** and **2** compared to their [(CpM)(CpM′)]μ-Cot analogues. The CASSCF calculations provide considerable insight into the binding situation of the two compounds. The heteronuclear Fe−Cr system can be regarded, much in the same way as the [(CpM)(CpM′)]μ-Cot complexes, as being composed of a chromocene-like subunit CpCrC$_5$H$_5$, which, like chromocene, initially contains two unpaired electrons, and the fragment (CO)$_3$Fe(η^3-C$_3$H$_3$) with initially one unpaired electron at the iron center. To compensate for the overall electron deficiency in the dinuclear system a direct metal−metal bond is formed, involving one initially singly occupied orbital of each fragment. This leads to a doublet ground state for **1** with the remaining unpaired electron localized at the chromium center. In contrast, for the homonuclear system **2** no such direct metal−metal bond was found. In the quartet ground state the three unpaired electrons are localized at the chromium center of the doubly positive charged CpCr unit (Cr1). For this subunit the complex fragment [(CO)$_3$Cr(η^5-Cot)]$^{2-}$, in which the chromium center has 18 valence electrons, acts like a cyclopentadienyl ligand, resulting in 15 valence electrons for Cr1 and a metal 3d occupation scheme like in vanadocene.

Methods

The extended Hückel MO analyses were performed with the weighted modified Wolfsberg−Helmholtz formula[25] as programmed in the package CACAO.[26] The atomic parameters were used as given in the package. The bond lengths and angles for the fragments (CO)$_3$M and CpM were obtained from the crystal structures of **1** and **2**. They were modified to yield C_{3v} and C_{5v} symmetry for (CO)$_3$M and CpM, respectively. To allow more orbital mixing, calculations with slightly distorted structures were carried out as well. These calculations, however, gave, results almost identical to those for the symmetric fragments.

For the investigation of the electronic structure of **1** the geometry was taken from the crystal structure with only minor changes to yield C_s symmetry. For complex **2** a structure feasible for a CASSCF study was established by geometry optimizations using density functional methods. Several functionals and basis sets were tested. The best structure in comparison to the experimental geometry was obtained with the hybrid functional B3LYP[21] using the standard 6-31G** basis set for the ligands and effective core potentials and the corresponding valence basis set of Dolg et al.[27] for the metal atoms. This structure was used throughout the CASSCF calculations for the dichromium system. During the optimization C_s symmetry was enforced. Optimizations starting from distorted geometries were attempted, but they tended to yield the structure with C_s symmetry as well. Vibrational frequencies were not calculated for the optimized symmetric structure. Therefore, it is not entirely clear whether the structure corresponds to a real minimum or to a saddle point (transition state) between equivalently distorted structures. This is, however, of no concern for this work, because the optimized

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geometry bears the main structural features of **2**, in particular the metal−metal distance.

As in our previous study,[6] for the CASSCF calculations the standard 3-21G basis set for the ligands and effective core potentials and the corresponding valence basis sets of Hay and Wadt[28] for the metals were used. This basis was proven to be sufficiently flexible to give a qualitatively correct description of the electronic structure of the dinuclear Cot-bridged transition metal complexes. All CASSCF and DFT calculations were carried out with the program package GAUSSIAN 94.[17]

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