DOI: 10.1002/ejic.201000737

Chromium–Chromium Bonding in Binuclear Azulene Chromium Carbonyl Complexes

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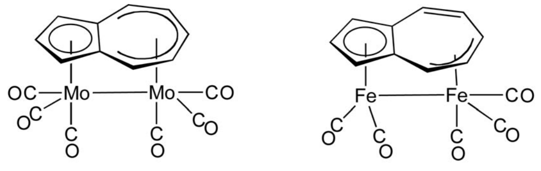
Keywords: Density functional calculations / Chromium / Carbonyl ligands / Metal-metal interactions / Azulene

The experimentally known *cis*-[(η^5,η^5-$C_{10}H_8$)$Cr_2(CO)_6$] structure with a rather long formal Cr–Cr single bond of about 3.3 Å is predicted by density functional theory to be the lowest energy $C_{10}H_8Cr_2(CO)_6$ structure. However, a *trans*-[(η^7,η^5-$C_{10}H_8$)$Cr_2(CO)_6$] structure lies in energy within ca. 4 kcal/mol of this global minimum. The lowest energy structures for the unsaturated derivatives $C_{10}H_8Cr_2(CO)_n$ (n = 5, 4, 3, 2) are all related structures with *cis* stereochemistry of the two chromium atoms, a chromium-chromium bond, and a single bridging carbonyl group. Such structures include singlet *cis*-[(η^5,η^5-$C_{10}H_8$)$Cr_2(CO)_4$ (μ-CO)], singlet *cis*-[(η^7,η^5-$C_{10}H_8$)$Cr_2(CO)_3$(μ-CO)], triplet *cis*-[(η^7,η^5-$C_{10}H_8$)$Cr_2(CO)_2$(μ-CO)], and triplet *cis*-[(η^7,η^5-$C_{10}H_8$)Cr_2(CO)(η^2-μ-CO)], for n = 5, 4, 3, and 2, respectively. The $C_{10}H_8Cr_2(CO)_5$ structure is thermodynamically viable with respect to disproportionation into $C_{10}H_8Cr_2(CO)_6$ and $C_{10}H_8Cr_2(CO)_4$, in contrast to its cyclopentadienyl analogue [(η^5-C_5H_5)$_2Cr_2(CO)_5$]. However, the $C_{10}H_8Cr_2(CO)_4$ structure is thermodynamically unfavorable with respect to disproportionation into $C_{10}H_8Cr_2(CO)_5$ and $C_{10}H_8Cr_2(CO)_3$, in contrast to its very stable and experimentally known cyclopentadienyl analogue [(η^5-C_5H_5)$_2Cr_2(CO)_4$]. The lowest energy structure *cis*-[(η^7,η^5-$C_{10}H_8$)Cr_2(μ-CO)] for the monocarbonyl $C_{10}H_8Cr_2$(CO) is a triplet structure with an unsymmetrical bridging carbonyl group and a Cr≡Cr distance of about 2.4 Å, suggesting a formal triple bond. The qualitatively assigned Cr–Cr formal bond orders (one through five) are remarkably consistent with the Wiberg bond indices obtained from the Weinhold natural bond order analysis.

1. Introduction

The chemistry of azulene metal carbonyls was initiated by Wilkinson and co-workers in 1958[1,2] with the discovery of the thermal reactions of azulene with $Fe(CO)_5$ and $Mo(CO)_6$ to give the stable complexes *cis*-(η^5,η^3-$C_{10}H_8$)-$Fe_2(CO)_5$ and *cis*-(η^5,η^5-$C_{10}H_8$)$Mo_2(CO)_6$ (Figure 1). During the next decade the chemistry of azulene metal carbonyls underwent considerable expansion.[3] A common feature of essentially all of the azulene metal carbonyl derivatives is the bonding of the five-membered ring of azulene to the transition metal as a pentahapto ligand.[3] The involvement of the seven-membered azulene ring in bonding to a transition metal in such complexes is highly variable. Thus in a number of metal carbonyl derivatives of the type [η^5-$C_{10}H_8M(CO)_n$]$_2$ the seven-membered azulene ring is not involved at all in bonding to the metal. Instead the two halves of the binuclear molecule are coupled through a carbon-carbon bond from one seven-membered ring to the other. On the other hand, in the original azulene molybdenum carbonyl *cis*-(η^5,η^5-$C_{10}H_8$)$Mo_2(CO)_6$ the seven-membered ring and the five-membered ring are both bonded to molybdenum atoms as pentahapto ligands so that all ten carbon atoms of the azulene are within bonding distance of one of the metal atoms. The azulene molybdenum carbonyl *cis*-(η^5,η^5-$C_{10}H_8$)$Mo_2(CO)_6$ is thus closely related to the binuclear cyclopentadienylmolybdenum carbonyl (η^5-C_5H_5)$_2$-$Mo_2(CO)_6$ since both complexes have two molybdenum atoms with each bonded to five carbon atoms of a hydrocarbon ligand. Both derivatives are shown by X-ray crystallography to have Mo–Mo bonds of similar lengths, namely 3.235 Å[4] for (η^5-C_5H_5)$_2Mo_2(CO)_6$ and 3.24 Å[5] for *cis*-(η^5,η^5-$C_{10}H_8$)$Mo_2(CO)_6$ (Figure 1).



cis-(η^5,η^5-$C_{10}H_8$)$Mo_2(CO)_6$ *cis*-(η^5,η^3-$C_{10}H_8$)$Fe_2(CO)_5$

Figure 1. The original azulene metal carbonyl complexes synthesized in 1958.

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201000737.

The synthesis of azulene chromium carbonyl derivatives, including a *cis*-[(η^5,η^5-$C_{10}H_8$)$Cr_2(CO)_6$] analogue of the known molybdenum derivative (Figures 1 and 2), turned out to be non-trivial because of the lower reactivity of $Cr(CO)_6$ relative to $Mo(CO)_6$. Thus the thermal reaction of azulene with $Cr(CO)_6$ appears to require temperatures above the decomposition temperatures of any relevant azulene chromium carbonyl derivatives. However, treatment of azulene with the more reactive *fac*-[$(CH_3CN)_3Cr(CO)_3$] under relatively mild conditions results in displacement of the acetonitrile ligands to give a mononuclear derivative [η^5-$C_{10}H_8Cr(CO)_3$] in which the five-membered azulene ring is bonded to the chromium atom as a pentahapto ligand (Figure 2).[6] This leads to a formal zwitterionic structure with a formal negative charge on the chromium atom and a delocalized positive charge on the seven-membered ring. Similar zwitterionic (η^5-$Me_2NC_5H_4$)M(CO)$_3$ (M = Cr, Mo, W) complexes with a formal positive charge on the amine nitrogen are obtained from thermal reactions of metal hexacarbonyls $M(CO)_6$ with 6-(dimethylamino)fulvene.[7,8] A second $Cr(CO)_3$ unit can then be bonded to the azulene ligand by further reaction of the mononuclear [η^5-$C_{10}H_8Cr(CO)_3$] with additional *fac*-[$(CH_3CN)_3Cr(CO)_3$]. The resulting product *cis*-[(η^5,η^5-$C_{10}H_8$)$Cr_2(CO)_6$] (see Figure 2, M = Cr) is a direct analogue of the original molybdenum derivative (Figure 1) and likewise is shown by X-ray crystallography to have a relatively long Cr–Cr bond at 3.26 Å.[9] Again this long Cr–Cr single bond is similar to that found in the corresponding cyclopentadienylchromium carbonyl, namely [(η^5-C_5H_5)$_2Cr_2(CO)_6$] with a Cr–Cr single bond length of 3.281 Å.[10]

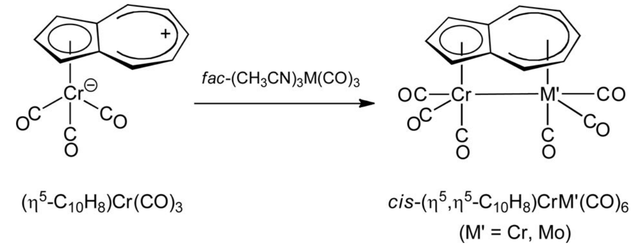


Figure 2. Azulene chromium carbonyl derivatives.

A characteristic feature of the cyclopentadienylmetal carbonyls (η^5-C_5H_5)$_2M_2(CO)_6$ (M = Cr,[11] Mo,[12,13] W) is their thermal decarbonylation to the corresponding (η^5-C_5H_5)$_2M_2(CO)_4$, which are shown by X-ray crystallography to have rather short M≡M distances suggestive of the formal triple bonds needed to give the metal atoms the favored 18-electron configuration (Figure 3). Furthermore, the intermediate chromium derivative [(η^5-C_5H_5)$_2Cr_2(CO)_5$] (which requires a formal Cr=Cr double bond for each chromium atom to have the favored 18-electron configuration) is shown both experimentally and theoretically to be unstable with respect to disproportionation into [(η^5-C_5H_5)$_2$-$Cr_2(CO)_6$] + [(η^5-C_5H_5)$_2Cr_2(CO)_4$].[14]

The analogy discussed above between the binuclear cyclopentadienyl metal carbonyl complexes [(η^5-C_5H_5)$_2Cr_2$-$(CO)_6$] and the binuclear azulene CO-metal compounds *cis*-[(η^5,η^5-$C_{10}H_8$)$Cr_2(CO)_6$] raises the question of the existence of stable unsaturated binuclear azulene chromium carbonyl derivatives. Such derivatives might include *cis*-[(η^5,η^5-$C_{10}H_8$)$Cr_2(CO)_4$] with a formal M≡M triple bond and *cis*-[(η^5,η^5-$C_{10}H_8$)$Cr_2(CO)_5$] with a formal M=M double bond unstable with respect to disproportionation into *cis*-[(η^5,η^5-$C_{10}H_8$)$Cr_2(CO)_6$] + *cis*-[(η^5,η^5-$C_{10}H_8$)$Cr_2(CO)_4$]. This paper reports density functional theory (DFT) studies on the series of binuclear azulene-carbonylchromium complexes of type $C_{10}H_8Cr_2(CO)_n$ (n = 6, 5, 4, 3, 2, 1) in an initial effort to explore this possibility. The more highly unsaturated derivatives (n = 3, 2, 1) were also included for comparison with the corresponding cyclopentadienyl-carbonylchromium derivatives[15] [(η^5-C_5H_5)$_2Cr_2(CO)_n$].

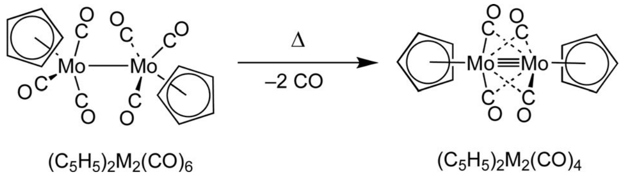


Figure 3. The decarbonylation of (η^5-C_5H_5)$_2M_2(CO)_6$ with a formal M–M single bond to give (η^5-C_5H_5)$_2M_2(CO)_4$ with a formal M≡M triple bond.

2. Theoretical Methods

Electron correlation effects were included by employing density functional theory (DFT) methods, which have evolved as a practical and effective computational tool, especially for organometallic compounds.[16–30] The reliability of such density functional theory (DFT) methods is governed by the quality of the approximate exchange-correlation (XC) energy functional. We chose initially two DFT methods, i.e., the B3LYP and the BP86 methods, which are constructed in very different ways. The B3LYP method is a hybrid HF/DFT method using a combination of the three-parameter Becke functional (B3) with the Lee–Yang–Parr (LYP) generalized gradient correlation functional.[31,32] This method includes exact exchanges and is calibrated by fitting three parameters to a set of experimental results. The BP86 method combines Becke's 1988 exchange functional (B) with Perdew's 1986 gradient-corrected correlation functional method (P86).[33,34] This method does not include exact exchange and is mainly deduced by forcing the functional to satisfy certain exact constraints based on first principles. When these two very different DFT methods agree, confident predictions can be made. However, Reiher and collaborators have found that B3LYP always favors the high-spin state and BP86 favors the low-spin state for a series of the Fe^{II}–S complexes.[35]

For carbon the double-ζ plus polarization (DZP) basis set used here adds one set of pure spherical harmonic d functions with orbital exponents $\alpha_d(C)$ = 0.75 and α_d (O) = 0.85 to the standard Huzinaga–Dunning contracted DZ sets, and is designated (9s5p1d/4s2p1d).[36,37] For H, a set of p polarization functions $\alpha_p(H)$ = 0.75 is added to the

Huzinaga–Dunning DZ sets. For chromium, in our loosely contracted DZP basis set, the Wachters' primitive sets are used, but augmented by two sets of p functions and one set of d functions and contracted following Hood and Pitzer, and designated (14s11p6d/10s8p3d).[38,39]

The geometries of all of the structures were fully optimized using both the DZP B3LYP and DZP BP86 methods. The harmonic vibrational frequencies were determined at the same levels by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates. The corresponding infrared intensities were evaluated analytically as well.

All of the computations were carried out with the Gaussian 03 program, in which the fine grid (75,302) is the default for evaluating integrals numerically, and the tight (10^{-8} hartree) designation is the default for the energy convergence.[40] The finer grid (120,974) was used for more precise resolution of small imaginary vibrational frequencies.[41] Unless otherwise indicated, the structures reported in this paper have only real vibrational frequencies and thus are genuine minima.

3. Results

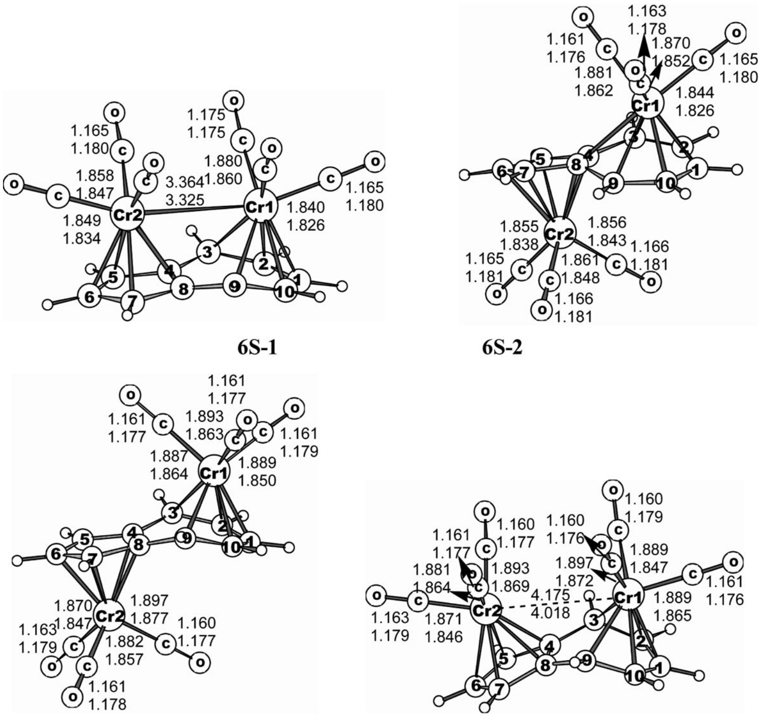
3.1 Molecular Structures

3.1.1 $C_{10}H_8Cr_2(CO)_6$

The *cis* and *trans* singlet and triplet state structures of $C_{10}H_8Cr_2(CO)_6$, consisting of two $Cr(CO)_3$ groups bonded to the azulene molecule, were used as starting points for optimizations with the B3LYP and BP86 methods. Four stable structures of $C_{10}H_8Cr_2(CO)_6$ were obtained without imaginary vibrational frequencies (Figure 4 and Table 1), namely the singlet *cis*-[$C_{10}H_8Cr_2(CO)_6$] structure **6S-1**, the singlet *trans*-[$C_{10}H_8Cr_2(CO)_6$] structure **6S-2**, the triplet *trans*-[$C_{10}H_8Cr_2(CO)_6$] structure **6T-3**, and triplet *cis*-[$C_{10}H_8Cr_2(CO)_6$] structure **6T-4**. All of these structures have exclusively terminal carbonyl groups as indicated by all of the ν(CO) frequencies appearing above 1885 cm^{-1} (BP86 method).

The singlet *cis*-[$C_{10}H_8Cr_2(CO)_6$] structure **6S-1** (Figure 4) is the global minimum. The Cr–C distances in **6S-1** suggest that each of the azulene rings is a pentahapto ligand, which is very similar to the experimentally known structure.[9] The predicted Cr–Cr distance in **6S-1** of 3.364 Å (B3LYP) or 3.325 Å (BP86) is close to the experimental distance of 3.262 Å, determined by X-ray crystallography, and is consistent with the formal single bond required to give both chromium atoms the favored 18-electron configuration.

The singlet *trans*-[$C_{10}H_8Cr_2(CO)_6$] structure **6S-2** (Figure 4) is predicted to lie only 0.9 kcal/mol (B3LYP) or 3.0 kcal/mol (BP86) above the singlet *cis*-[$C_{10}H_8Cr_2(CO)_6$] global minimum **6S-1** structure. In **6S-2** the Cr–C distances suggest that the five-membered and seven-membered azulene rings are pentahapto and heptahapto ligands, respectively. This gives each chromium atom the favored 18-electron configuration in a zwitterionic structure for **6S-2**, with a formal positive charge on the chromium atom bonded to the seven-membered ring and a formal negative charge on the chromium atom bonded to the five-membered ring.



6S-1 6S-2

6T-3 6T-4

Figure 4. The four optimized structures of $C_{10}H_8Cr_2(CO)_6$. In Figs. 4–9 the upper distances were obtained by the B3LYP method and the lower distances by the BP86 method.

Table 1. Bond lengths (Å), total energies (*E*, Hartree), relative energies with zero point correction (Δ*E*, kcal/mol), and spin expectation values ⟨S²⟩ for the $C_{10}H_8Cr_2(CO)_6$ structures.

	cis-[$C_{10}H_8Cr_2(CO)_6$] **6S-1** B3LYP	 BP86	*trans*-[$C_{10}H_8Cr_2(CO)_6$] **6S-2** B3LYP	 BP86	*trans*-[$C_{10}H_8Cr_2(CO)_6$] **6T-3** B3LYP	 BP86	*cis*-[$C_{10}H_8Cr_2(CO)_6$] **6T-4** B3LYP	 BP86
C–C(C_7H_7)	1.43	1.44	1.43	1.44	1.43	1.44	1.43	1.44
C–C(C_5H_5)	1.43	1.44	1.44	1.45	1.43	1.44	1.43	1.44
Cr1–C_7H_7	2.47	2.45	2.39	2.37	2.45	2.42	2.49	2.46
Cr2–C_5H_5	2.24	2.22	2.22	2.21	2.25	2.24	2.24	2.23
Cr1–Cr2	3.364	3.325	4.359	4.320	4.831	4.751	4.175	4.018
–Energy	3155.10752	3155.52068	3155.10503	3155.51485	3155.09629	3155.49396	3155.09374	3155.49008
Zero-point correction	0.20117	0.19584	0.20009	0.19482	0.19823	0.19330	0.19848	0.19338
–*E* (with ZPC)	3154.90635	3155.32484	3154.90494	3155.32004	3154.89806	3155.30066	3154.89527	3155.29670
Δ*E* (with ZPC)	0.0	0.0	0.9	3.0	5.2	15.2	7.0	17.7
⟨S²⟩	0.0	0.0	0.0	0.0	2.05	2.02	2.04	2.02

The triplet *trans*-[$C_{10}H_8Cr_2(CO)_6$] structure **6T-3** and triplet *cis*-[$C_{10}H_8Cr_2(CO)_6$] structure **6T-4** lie 5.2 kcal/mol and 7.0 kcal/mol (B3LYP) or 15.2 kcal/mol and 17.7 kcal/mol (BP86), respectively, higher in energy than the singlet *cis*-[$C_{10}H_8Cr_2(CO)_6$] global minimum **6S-1**. The long Cr–C distances in each of these structures suggest that each of the azulene rings in **6T-3** and **6T-4** structures are pentahapto ligands, thereby giving each chromium atom the favored 17-electron configuration for the triplet. Even in the triplet *cis*-[$C_{10}H_8Cr_2(CO)_6$] structure **6T-4** the long Cr–Cr distance of 4.175 Å (B3LYP) or 4.018 Å (BP86) shows there is no bonding interaction between the metal atoms.

3.1.2. $C_{10}H_8Cr_2(CO)_5$

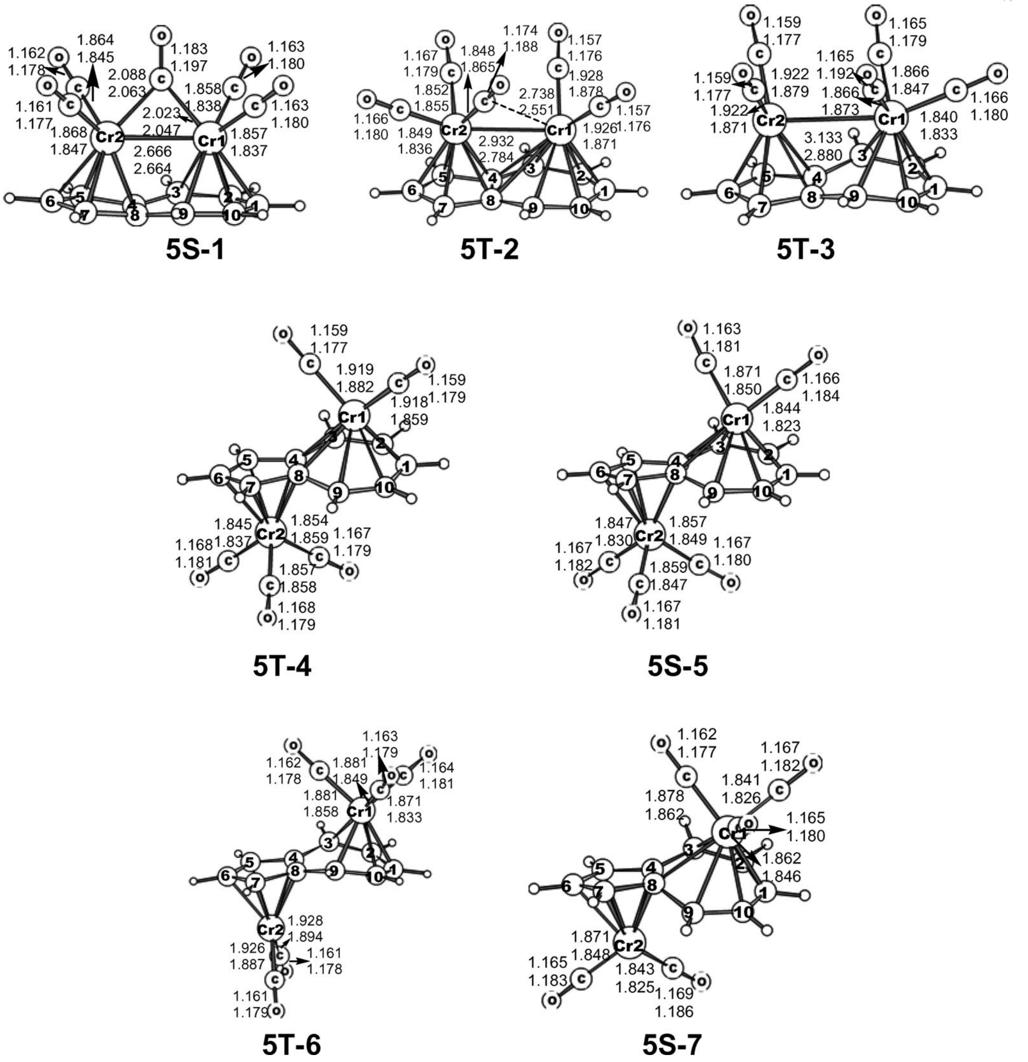
The *cis*- and *trans*-[$C_{10}H_8Cr_2(CO)_5$] structures analogous to the $C_{10}H_8Fe_2(CO)_5$ structures,[42] consisting of one $Cr(CO)_2$ and one $Cr(CO)_3$ group bonded to the azulene molecule, were used as starting points for optimization with the B3LYP and BP86 methods. Three *cis*-[$C_{10}H_8Cr_2(CO)_5$] and four *trans*-[$C_{10}H_8Cr_2(CO)_5$] structures were found (Figure 5 and Tables 2 and 3). The energies of the *cis*-structures are lower than those of the *trans*-structures. The lowest energy of these structures is the singlet bridged *cis*-[$C_{10}H_8Cr_2(CO)_5$] structure **5S-1** with pentahapto coordination of both the five- and seven-membered rings (Figure 5 and Table 2). The predicted Cr=Cr distance of 2.666 Å (B3LYP) or 2.664 Å (BP86) in **5S-1** is about 0.7 Å shorter than the Cr–Cr single bond in the *cis*-[$C_{10}H_8Cr_2(CO)_6$] structure **6S-1** (Figure 4) and is thus consistent with the formal double bond required to give both chromium atoms the favored 18-electron configuration, particularly when the expected shortening of the Cr=Cr double bond by the bridging carbonyl group is considered. This bridging carbonyl group is predicted to exhibit a ν(CO) frequency of 1801 cm^{-1}, which, as expected, is 109 cm^{-1} below the lowest terminal ν(CO) frequency of 1910 cm^{-1} (BP86).

Two triplet *cis*-[$C_{10}H_8Cr_2(CO)_5$] structures were found very close in energy (Figure 5 and Table 2), namely **5T-2** and **5T-3** at 4.5 kcal/mol and 5.4 kcal/mol, respectively, above the global minimum **5S-1** by BP86. Structure **5T-2** has a single semibridging carbonyl group with a short M–C distance of 1.865 Å and a long M–C distance of 2.551 Å by BP86. Both **5T-2** and **5T-3** have the expected pentahapto five-membered ring. However, the Cr–C distances indicate a heptahapto seven-membered ring in **5T-2** but only a pentahapto seven-membered ring in **5T-3**. The Cr–Cr distances of 2.932 Å (B3LYP) or 2.784 Å (BP86) in **5T-2** and 3.133 Å (B3LYP) or 2.880 Å (BP86) in **5T-3** can all be interpreted as the formal single bonds needed to give each chromium atom in a *cis*-[$C_{10}H_8Cr_2(CO)_5$] structure the 17-electron configuration for a binuclear triplet in a structure with only the usual two-electron donor carbonyl groups.

The *trans*-[$C_{10}H_8Cr_2(CO)_5$] structures (Figure 5 and Table 3) are found to lie significantly higher in energy than the corresponding *cis*-structures, particularly when the

Table 2. Bond lengths (Å), total energies (*E*, Hartree), relative energies with zero-point corrections (Δ*E*, kcal/mol), and spin expectation values ⟨S²⟩ for the *cis*-[$C_{10}H_8Cr_2(CO)_5$] structures.

	cis-[$C_{10}H_8Cr_2(CO)_5$] **5S-1** B3LYP	 BP86	*cis*-[$C_{10}H_8Cr_2(CO)_5$] **5T-2** B3LYP	 BP86	*cis*-[$C_{10}H_8Cr_2(CO)_5$] **5T-3** B3LYP	 BP86
C–C(C_7H_7)	1.43	1.43	1.43	1.44	1.43	1.44
C–C(C_5H_5)	1.43	1.44	1.43	1.44	1.43	1.44
Cr1–C_7H_7	2.46	2.45	2.44	2.37	2.48	2.46
Cr2–C_5H_5	2.20	2.19	2.24	2.23	2.24	2.20
Cr1–Cr2	2.666	2.664	2.932	2.784	3.133	2.880
–Energy	3041.72305	3042.13598	3041.73473	3042.12715	3041.73072	3042.12597
Zero-point correction	0.19139	0.18698	0.19050	0.18525	0.19042	0.18563
–*E*(with ZPC)	3041.53166	3041.94900	3041.54424	3041.94190	3041.54031	3041.94034
Δ*E*(with ZPC)	0.0	0.0	–7.9	4.5	–5.4	5.4
⟨S²⟩	0.00	0.00	2.17	2.04	2.31	2.03



5S-1 5T-2 5T-3

5T-4 5S-5

5T-6 5S-7

Figure 5. The seven optimized structures of $C_{10}H_8Cr_2(CO)_5$.

Table 3. Bond lengths (Å), total energies (E, Hartree), relative energies with zero-point corrections (ΔE, in kcal/mol), and spin expectation values $\langle S^2 \rangle$ for the *trans*-[$C_{10}H_8Cr_2(CO)_5$] structures.

	trans-[$C_{10}H_8Cr_2(CO)_5$] **5T-4**		*trans*-[$C_{10}H_8Cr_2(CO)_5$] **5S-5**		*trans*-[$C_{10}H_8Cr_2(CO)_5$] **5T-6**		*trans*-[$C_{10}H_8Cr_2(CO)_5$] **5S-7**	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
C–C(C_7H_7)	2.23	2.24	2.23	2.22	1.44	1.45	1.44	1.45
C–C(C_5H_5)	2.29	2.24	2.19	2.17	1.43	1.44	1.44	1.45
Cr1–C_7H_7	2.33	2.24	2.29	2.25	1.43	1.44	1.44	1.44
Cr2–C_5H_5	2.44	2.41	2.40	2.38	1.43	1.44	1.44	1.44
Cr1–Cr2	–	–	–	–	–	–	–	–
–Energy	3041.72121	3042.11393	3041.71086	3042.11283	3041.72078	3042.09888	3041.69627	3042.09574
Zero-point correction	0.18952	0.18459	0.19102	0.18586	0.18858	0.18426	0.19092	0.18581
–E (with ZPC)	3041.53169	3041.92934	3041.51984	3041.92697	3041.53220	3041.91462	3041.50535	3041.90993
ΔE (with ZPC)	0.0	12.3	7.4	13.8	–0.3	21.6	16.5	24.5
$\langle S^2 \rangle$	2.22	2.04	0.00	0.00	3.01	2.28	0.00	0.00

more reliable BP86 method is used. The triplet *trans*-[$C_{10}H_8Cr_2(CO)_5$] structure **5T-4** thus is predicted to lie 12.3 kcal/mol (BP86) above the global minimum singlet *cis*-[$C_{10}H_8Cr_2(CO)_5$] structure **5S-1**. The Cr–C distances in **5T-4** indicate the five-membered ring to be pentahapto to a $Cr(CO)_3$ group and the seven-membered ring to be heptahapto towards a $Cr(CO)_2$ group as in **5T-2**. This gives each chromium atom the 17-electron configuration for a binuclear triplet. The corresponding singlet *trans*-[$C_{10}H_8Cr_2(CO)_5$] structure **5S-5** lies 7.4 kcal/mol (B3LYP) or 13.8 kcal/mol (BP86) above the global minimum **5S-1**. The *trans*-[$C_{10}H_8Cr_2(CO)_5$] structures **5T-6** and **5S-7** with a

$Cr(CO)_2$ moiety bonded to the five-membered ring and a $Cr(CO)_3$ moiety bonded to seven-membered ring are predicted by BP86 to lie 21.6 kcal/mol and 24.5 kcal/mol, respectively, above the global minimum **5S-1**. The Cr–C distances suggest that the seven-membered azulene ring is a heptahapto ligand in **5S-7** but only a pentahapto ligand in **5T-6**.

3.1.3. $C_{10}H_8Cr_2(CO)_4$

Four initial structures with two $Cr(CO)_2$ groups bonded to the azulene molecule were optimized for $C_{10}H_8Cr_2(CO)_4$ (see Figure 6 and Tables 4 and 5). The singly bridged singlet and triplet *cis*-$[C_{10}H_8Cr_2(CO)_4]$ structures lie in energy below the corresponding *trans*-$[C_{10}H_8Cr_2(CO)_4]$ structures. The lowest energy structure for $C_{10}H_8Cr_2(CO)_4$ is the singlet *cis*-$[C_{10}H_8Cr_2(CO)_4]$ structure **4S-1**, in which the Cr–C distances to the azulene ligand indicate a pentahapto five-membered ring and a heptahapto seven-membered ring. The Cr≡Cr distance in **4S-1** of 2.455 Å (BP86) is consistent with the formal triple bond in **4S-1** needed to give both chromium atoms the favored 18-electron configuration, assuming that the azulene ring is a formal donor of its ten π-electrons to the pair of chromium atoms. This Cr≡Cr triple bond length in **4S-1** is significantly longer than the experimental Cr≡Cr triple bond length of 2.239 Å in $[(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_4]$ found by X-ray crystallography,[11] probably because of geometric constraints of the azulene ring system.

The triplet *cis*-$[C_{10}H_8Cr_2(CO)_4]$ structure **4T-2** lies 7.0 kcal/mol (B3LYP) or 14.7 kcal/mol (BP86) above the global minimum **4S-1** (Figure 6 and Table 4). Both azulene rings in **4T-2** are pentahapto ligands. The Cr=Cr distance of 2.662 Å (B3LYP) or 2.587 Å (BP86) in **4T-2** can correspond to the formal double bond needed to give both chromium atoms the 17-electron configurations for a binuclear triplet in a $C_{10}H_8Cr_2(CO)_4$ structure with only two-electron donor carbonyl groups and both rings bonded to chromium atoms as pentahapto ligands. The predicted ν(CO) frequencies of 1791 cm^{-1} for **4S-1** and 1774 cm^{-1} for **4T-2** are considerably lower than the other ν(CO) frequencies and thus correspond to the single bridging carbonyl group in each structure.

The energies of the singlet and triplet *trans*-$[C_{10}H_8Cr_2(CO)_4]$ structures **4T-3** and **4S-4** (Figure 6 and Table 5) are predicted by the BP86 method to be considerably higher than the energy of the corresponding *cis* structures. Thus **4T-3** and **4S-4** lie 33.7 kcal/mol and 41.8 kcal/mol, respec-

Table 4. Bond lengths (Å), total energies (*E*, Hartree), relative energies with zero-point corrections (Δ*E*, kcal/mol), spin expectation values $\langle S^2\rangle$, and imaginary vibrational frequencies for the *cis*-$[C_{10}H_8Cr_2(CO)_4]$ structures.

	cis-$[C_{10}H_8Cr_2(CO)_4]$ **4S-1**		*cis*-$[C_{10}H_8Cr_2(CO)_4]$ **4T-2**	
	B3LYP	BP86	B3LYP	BP86
C–C(C_7H_7)	1.43	1.44	1.43	1.44
C–C(C_5H_5)	1.44	1.45	1.44	1.44
Cr1–C_7H_7	2.25	2.24	2.31	2.37
Cr2–C_5H_5	2.22	2.20	2.23	2.19
Cr1–Cr2	2.492	2.455	2.662	2.587
–Energy	2928.36115	2928.76562	2928.34816	2928.74034
Zero-point correction	0.18342	0.17857	0.18160	0.17671
–*E* (with ZPC)	2928.17773	2928.58705	2928.16656	2928.56363
Δ*E* (with ZPC)	0.0	0.0	7.0	14.7
Imaginary frequencies	none	none	15*i*	22*i*
$\langle S^2\rangle$	0.0	0.0	2.34	2.10

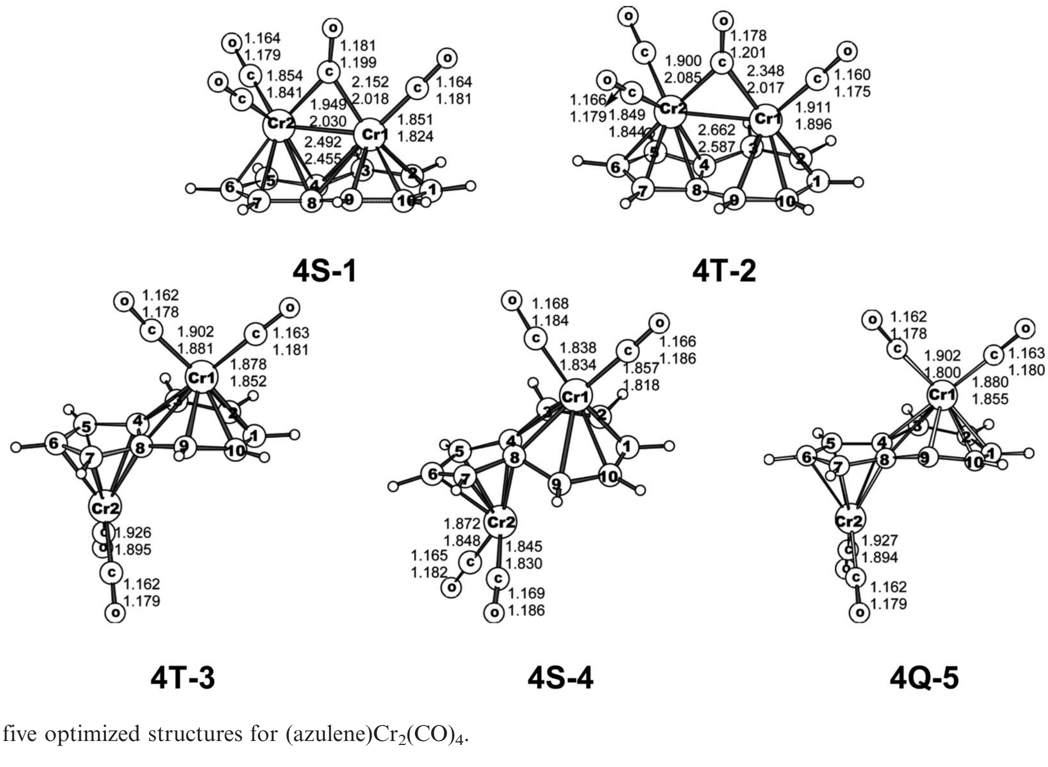


Figure 6. The five optimized structures for (azulene)$Cr_2(CO)_4$.

Table 5. Bond lengths (Å), total energies (E, Hartree), relative energies with zero-point corrections (ΔE, kcal/mol), and spin expectation values $\langle S^2 \rangle$ for the *trans*-[$C_{10}H_8Cr_2(CO)_4$] structures.

	trans-[$C_{10}H_8Cr_2(CO)_4$]		*trans*-[$C_{10}H_8Cr_2(CO)_4$]		*trans*-[$C_{10}H_8Cr_2(CO)_4$]	
	4T-3		**4S-4**		**4Q-5**	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
C–C(C_7H_7)	1.44	1.44	1.44	1.45	1.44	1.44
C–C(C_5H_5)	1.44	1.45	1.44	1.15	1.44	1.45
Cr1–C_7H_7	2.25	2.24	2.29	2.26	2.29	2.24
Cr2–C_5H_5	2.30	2.26	2.18	2.17	2.30	2.26
Cr1–Cr2	—	—	—	—	—	—
–Energy	2928.34508	2928.70843	2928.30510	2928.69753	2928.34589	2928.70961
Zero-point correction	0.17992	0.17511	0.18214	0.17717	0.17983	0.17516
–E (with ZPC)	2928.16516	2928.53332	2928.12296	2928.52036	2928.16606	2928.53445
ΔE (with ZPC)	7.9	33.7	34.4	41.8	7.3	33.0
$\langle S^2 \rangle$	3.17	3.06	0.0	0.0	6.20	6.08

tively, above the **4S-1** *cis*-[$C_{10}H_8Cr_2(CO)_4$] global minimum. Both *trans*-[$C_{10}H_8Cr_2(CO)_4$] structures **4T-3** and **4S-4** have a pentahapto five-membered ring and an essentially heptahapto seven-membered ring. Because of the significant spin contamination found for **4T-3** by either the B3LYP or BP86 method [$\langle S^2 \rangle = \approx 3.1$ (Table 5) vs. an ideal value of 2], the quintet spin state for *trans*-[$C_{10}H_8Cr_2(CO)_4$] was also optimized. In this connection, the quintet *trans*-[$C_{10}H_8Cr_2(CO)_4$] structure **4Q-5** was found to lie in energy slightly below the singlet and triplet *trans*-[$C_{10}H_8Cr_2(CO)_4$] structures at 7.3 kcal/mol (B3LYP) or 33.0 kcal/mol (BP86) above the global minimum **4S-1.**

3.1.4. $C_{10}H_8Cr_2(CO)_3$

Because of the high degree of unsaturation in the $C_{10}H_8Cr_2(CO)_n$ (n = 3, 2, 1) derivatives, all possible *cis*- and *trans*-structures were optimized for singlet and triplet spin states. Thus four possible $C_{10}H_8Cr_2(CO)_3$ structures were obtained for *cis*- and *trans*-stereochemistry (see Figure 7 and Table 6), including *cis* structures with and without a bridging carbonyl group. We also examined *trans* structures in which the seven-membered ring is bonded either to a $Cr(CO)_2$ group or a Cr(CO) group. The energies of the *trans*-[$C_{10}H_8Cr_2(CO)_3$] structures were found to be significantly higher than the energies of the *cis*-[$C_{10}H_8Cr_2(CO)_3$] structures, consistent with the high unsaturation. Therefore they are not discussed in detail in this paper.

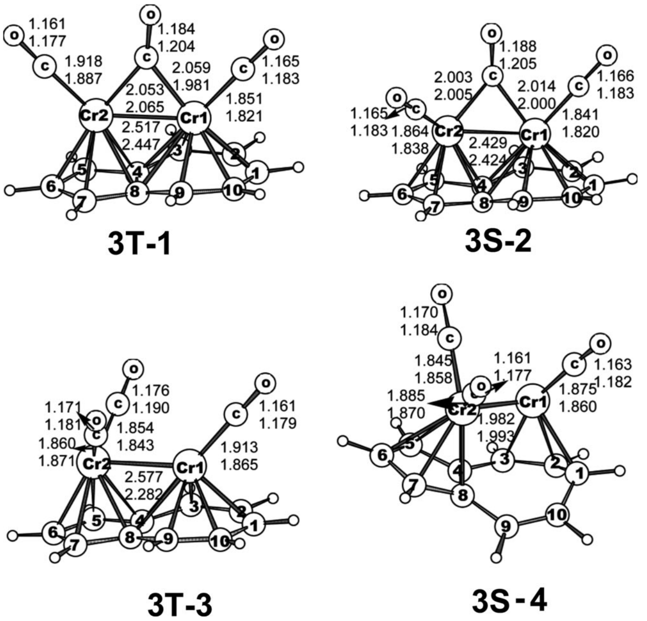


Figure 7. The four optimized structures of *cis*-[$C_{10}H_8Cr_2(CO)_3$].

The global minimum $C_{10}H_8Cr_2(CO)_3$ structure is the triplet **3T-1** with a single bridging carbonyl group as well as a pentahapto five-membered ring and a heptahapto seven-membered ring to the chromium atoms (Figure 7 and

Table 6. Bond lengths (Å), total energies (E, Hartree), relative energies with zero-point corrections (ΔE, kcal/mol), and spin expectation values $\langle S^2 \rangle$ for the *cis*-[$C_{10}H_8Cr_2(CO)_3$] structures.

	cis-[$C_{10}H_8Cr_2(CO)_3$]		*cis*-[$C_{10}H_8Cr_2(CO)_3$]		*cis*-[$C_{10}H_8Cr_2(CO)_3$]		*cis*-[$C_{10}H_8Cr_2(CO)_3$]	
	3T-1		**3S-2**		**3T-3**		**3S-4**	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
C–C(C_7H_7)	1.44	1.44	1.43	1.44	1.43	1.44	1.44	1.44
C–C(C_5H_5)	1.44	1.45	1.44	1.45	1.44	1.45	1.43	1.44
Cr1–C_7H_7	2.27	2.25	2.26	2.25	2.31	2.26	2.74	2.80
Cr2–C_5H_5	2.26	2.21	2.19	2.16	2.24	2.21	2.28	2.28
Cr1–Cr2	2.517	2.447	2.429	2.424	2.577	2.282	1.982	1.993
–Energy	2814.97580	2815.35305	2814.95582	2815.34740	2814.95742	2815.34206	2814.92679	2815.32326
Zero-point correction	0.17259	0.16858	0.17396	0.16914	0.17192	0.16761	0.17267	0.16761
–E (with ZPC)	2814.80321	2815.18447	2814.78186	2815.17826	2814.78550	2815.17445	2814.75412	2815.15565
ΔE	0.0	0.0	12.5	3.6	11.5	6.9	30.8	18.7
ΔE (with ZPC)	0.0	0.0	13.4	3.9	11.1	6.3	30.8	18.1
$\langle S^2 \rangle$	2.33	2.14	0.0	0.0	2.74	2.04	0.0	0.0

Table 6). The predicted Cr≡Cr bond length of 2.517 Å (B3LYP) or 2.447 Å (BP86) in **3T-1** can correspond to a triple bond. This combined with the assumption that the azulene ligand donates all ten of its π electrons to the pair of chromium atoms gives both chromium atoms in **3T-1** the 17-electron configurations associated with a binuclear triplet.

The singlet *cis*-[$C_{10}H_8Cr_2(CO)_3$] structure **3S-2** corresponding structurally to the triplet **3T-1** (Figure 7 and Table 6) is predicted by BP86 to lie 3.9 kcal/mol above **3T-1**. The Cr≡Cr distance of 2.429 Å (B3LYP) or 2.424 Å (BP86) in **3S-2** is very similar to that in **3T-1** and thus is likely also to correspond to a formal triple bond. In **3S-2** this gives one of the chromium atoms an 18-electron configuration but the other chromium atom only a 16-electron configuration.

The other triplet *cis*-[$C_{10}H_8Cr_2(CO)_3$] structure **3T-3** (Figure 7 and Table 6) lies 11.1 kcal/mol (B3LYP) or 6.3 kcal/mol (BP86) above the global minimum **3T-1**. However, significant spin contamination $\langle S^2 \rangle = 2.74$ was found for **3T-3** using the B3LYP method. In **3T-3** the five-membered ring is bonded to a $Cr(CO)_2$ moiety as a pentahapto ligand and the seven-membered ring is bonded to a Cr(CO) moiety as a heptahapto ligand. The very short Cr≡Cr distance of 2.282 Å predicted for **3T-3** corresponds to the formal quadruple bond required to give each chromium atom the favored 18-electron configuration. However, the formal quadruple bond in **3T-3** is not of the usual σ + 2π + δ type, which would lead to a singlet spin state. Instead, the formal quadruple bond in **3T-3** is of the σ + 2π + $^2\!/_2$ δ type with two one-electron δ "half-bonds." This leads to the predicted triplet spin multiplicity. The B3LYP method predicts a significantly longer Cr=Cr distance of 2.577 Å for **3T-3**, which is in the range assigned to Cr=Cr double bonds in the other $C_{10}H_8Cr_2(CO)_n$ complexes. This gives each chromium atom a 16-electron configuration. The triplet spin multiplicity can then arise for the double bond itself, interpreted as a σ + $^2\!/_2$ π bond with two π "half-bonds," each involving a single unpaired electron.

The remaining *cis*-[$C_{10}H_8Cr_2(CO)_3$] structure **3S-4** (Figure 7 and Table 6) is predicted to lie 30.8 kcal/mol (B3LYP) or 18.1 kcal/mol (BP86) above the global minimum **3T-1**. In **3S-4** the five-membered ring is bonded to a $Cr(CO)_2$ moiety as a pentahapto ligand but the seven-membered ring is bonded to the Cr(CO) moiety as only a trihapto ligand. Such a structure requires a dative formal quintuple bond to give each chromium atom the favored 18-electron configuration. This is consistent with the very short Cr–Cr distance of 1.982 Å (B3LYP) or 1.993 Å (BP86), corresponding to a dative quintuple bond. However, the formal quintuple bond found by Power and collaborators[43] in their chromium(I) RCrCrR derivative is even shorter, with a length of 1.835 Å, determined by X-ray diffraction. The presence of the carbonyl groups or the geometric constraints of the azulene ring system could be the cause of a longer chromium–chromium quintuple bond in the *cis*-[$C_{10}H_8Cr_2(CO)_3$] structure **3S-4** than in the chromium(I) RCrCrR derivative of Power and collaborators.[43]

3.1.5. $C_{10}H_8Cr_2(CO)_2$

cis- and *trans*-structures were found for the singlet, triplet and quintet $C_{10}H_8Cr_2(CO)_2$ spin states (Figure 8 and Table 7). The energies of the triplet structures of $C_{10}H_8Cr_2(CO)_2$ are predicted to be lower than those of the corresponding quintet and singlet structures for this highly unsaturated system. The *trans* structures of $C_{10}H_8Cr_2(CO)_2$ lie more than 20 kcal/mol above the *cis* structures are thus are not discussed in detail in this paper.

The global minimum $C_{10}H_8Cr_2(CO)_2$ structure **2T-1** is predicted to be triplet *cis*-[$C_{10}H_8Cr_2(CO)_2$] (Figure 8 and Table 7) with a four-electron donor η^2-μ-CO group, as indicated by a short Cr–O distance of 2.163 Å and a very low ν(CO) frequency of 1578 cm^{-1} (BP86). Both the five-membered and seven-membered azulene rings in **2T-1** are bonded to chromium atoms as pentahapto ligands. The Cr=Cr distance in **2T-1** is predicted to be 2.690 (B3LYP) or 2.606 Å (BP86), corresponding to a formal double bond. This gives each chromium atom a 15-electron configuration. Two chromium atoms, each with 15-electron configurations, can lead to a binuclear triplet.

The lowest lying quintet *cis*-[$C_{10}H_8Cr_2(CO)_2$] structure is **2Q-2** (Figure 8 and Table 7) at only 1.7 kcal/mol (BP86) above the **2T-1** global minimum. In **2Q-2** the five-membered ring as a pentahapto ligand whereas the seven-membered ring is a trihapto ligand. The Cr=Cr distance of 2.738 Å (B3LYP) or 2.708 Å (BP86) corresponds to a formal double bond.

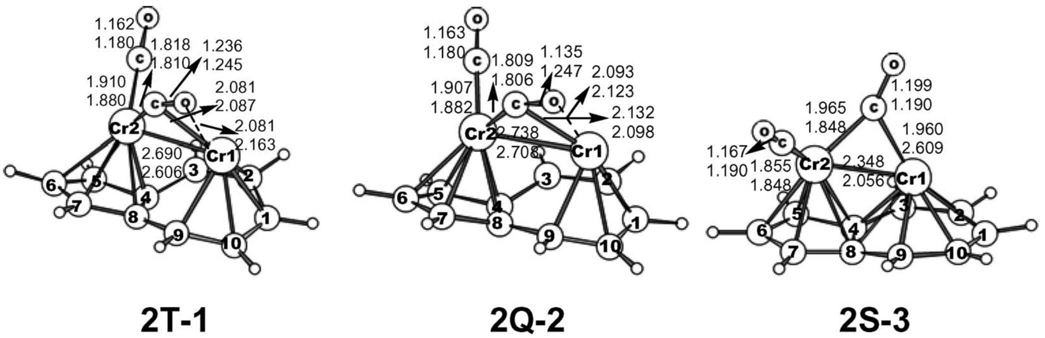


Figure 8. The three optimized structures of *cis*-[$C_{10}H_8Cr_2(CO)_2$].

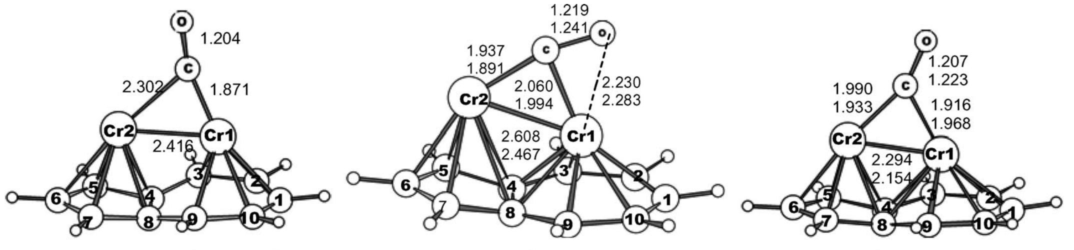
Table 7. Bond lengths (Å), total energies (*E*, Hartree), relative energies with zero-point corrections (Δ*E*, kcal/mol), and spin expectation values ⟨S²⟩ for the *cis*-[$C_{10}H_8Cr_2(CO)_2$] structures.

	cis-[$C_{10}H_8Cr_2(CO)_2$]		*cis*-[$C_{10}H_8Cr_2(CO)_2$]		*cis*-[$C_{10}H_8Cr_2(CO)_2$]	
	2T-1		**2Q-2**		**2S-3**	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
C–C(C_7H_7)	1.44	1.45	1.44	1.45	1.43	1.44
C–C(C_5H_5)	1.44	1.45	1.44	1.45	1.44	1.46
Cr1–C_7H_7	2.46	2.43	2.46	2.43	2.19	2.19
Cr2–C_5H_5	2.20	2.19	2.20	2.19	2.22	2.32
Cr1–Cr2	2.690	2.606	2.738	2.708	2.348	2.056
–Energy	2701.58463	2701.96645	2701.61219	2701.96398	2701.55647	2701.94474
Zero-point correction	0.16429	0.15948	0.16394	0.15964	0.16477	0.15972
–*E* (with ZPC)	2701.42035	2701.80697	2701.44825	2701.80434	2701.39170	2701.78502
Δ*E* (with ZPC)	0.0	0.0	–17.5	1.7	18.0	13.8
⟨S²⟩	3.05	3.01	6.37	6.12	0.0	0.0

The singlet *cis*-[$C_{10}H_8Cr_2(CO)_2$] structure **2S-3** (Figure 8 and Table 7) lies 18.0 kcal/mol (B3LYP) or 13.8 kcal/mol (BP86) above the **2T-1** global minimum. The very short Cr–Cr distance of 2.056 Å (BP86) in **2S-3** predicted by the BP86 method is consistent with the formal quintuple bond required to give each chromium atom the favored 18-electron configuration. However, the B3LYP method predicts a significantly longer Cr≡Cr distance of 2.348 Å in **2S-3** corresponding to a formal triple bond. The latter structure gives each chromium atom a 16-electron configuration.

3.1.6. $C_{10}H_8Cr_2(CO)$

The singly bridged structures **1T-1**, **1Q-2**, and **1S-3** are found for triplet, quintet, and singlet *cis*-[$C_{10}H_8Cr_2(CO)$], respectively, using the more reliable BP86 method (Figure 9 and Table 8). The triplet *cis*-[$C_{10}H_8Cr_2(CO)$] structure **1T-1** lies below the corresponding quintet **1Q-2** and singlet **1S-3** structures by 8.8 kcal/mol and 20.2 kcal/mol (BP86), respectively. The spin contaminations in **1T-1** are significant even using BP86 methods with an ⟨S²⟩ value of 4.11 relative to the ideal value of 2 for a triplet. Both azulene rings in **1T-1** function as pentahapto ligands towards a chromium atom. The Cr≡Cr bond of 2.416 Å (BP86) in the triplet **1T-1** can correspond to a formal triple bond, thereby giving each chromium atom a 15-electron configuration. The unpaired electrons from two chromium atoms with a 15-electron configuration can lead to a binuclear triplet. The quintet *cis*-[$C_{10}H_8Cr_2(CO)$] structure **1Q-2** has a four-electron donor η²-μ-CO group, as indicated by a short Cr–O dis-



1T-1 (BP86) **1Q-2** **1S-3**

Figure 9. The three optimized structures of $C_{10}H_8Cr_2(CO)$.

Table 8. Bond lengths (Å), total energies (*E*, Hartree), relative energies with zero-point corrections (Δ*E*, kcal/mol), spin expectation values ⟨S²⟩, and infrared ν(CO) frequencies (cm⁻¹) for the $C_{10}H_8Cr_2(CO)$ structures.

	[*cis*-$C_{10}H_8Cr_2(CO)$]	*cis*-[$C_{10}H_8Cr_2(CO)$]		*cis*-[$C_{10}H_8Cr_2(CO)$]	
	1T-1	**1Q-2**		**1S-3**	
	BP86	B3LYP	BP86	B3LYP	BP86
C–C(C_7H_7)	1.44	1.436571	1.443714	1.44	1.44
C–C(C_5H_5)	1.45	1.4432	1.4564	1.45	1.46
Cr1–C_7H_7	2.34	2.182571	2.165429	2.20	2.20
Cr2–C_5H_5	2.28	2.471	2.3978	2.18	2.21
Cr1–Cr2	2.416	2.608	2.467	2.294	2.151
–Energy	2588.55111	2588.19614	2588.53810	2588.15157	2588.51977
Zero-point correction	0.14961	0.15375	0.15063	0.15592	0.15042
–*E* (with ZPC)	2588.40150	2588.04239	2588.38747	2587.99565	2588.36935
Δ*E* (with ZPC)	0.0	0.0	8.8	28.7	20.2
⟨S²⟩	4.11	7.25	6.41	0.0	0.0
ν(CO)	1793	1666	1585	1860	1793

Table 9. Energies (kcal/mol) with zero-point corrections for carbonyl dissociation and disproportionation of *cis*-[$C_{10}H_8Cr_2(CO)_n$] derivatives. These results are based on the global minima for each structure.

	B3LYP (with ZPC)	BP86 (with ZPC)
cis-[$C_{10}H_8Cr_2(CO)_6$] (**6S-1**) → *cis*-[$C_{10}H_8Cr_2(CO)_5$] (**5S-1**) + CO	32.0	33.5
cis-[$C_{10}H_8Cr_2(CO)_5$] (**5S-1**) → *cis*-[$C_{10}H_8Cr_2(CO)_4$] (**4S-1**) + CO	19.0	24.8
cis-[$C_{10}H_8Cr_2(CO)_4$] (**4S-1**) → *cis*-[$C_{10}H_8Cr_2(CO)_3$] (**3T-1**) + CO	31.9	50.3
cis-[$C_{10}H_8Cr_2(CO)_3$] (**3T-1**) → *cis*-[$C_{10}H_8Cr_2(CO)_2$] (**2T-1**) + CO	37.1	34.5
cis-[$C_{10}H_8Cr_2(CO)_2$] (**2T-1**) → *cis*-[$C_{10}H_8Cr_2(CO)$] (**1T-1**) + CO	–	52.1
2 *cis*-[$C_{10}H_8Cr_2(CO)_5$] (**5S-1**) → *cis*-[$C_{10}H_8Cr_2(CO)_6$] (**6S-1**) + *cis*-[$C_{10}H_8Cr_2(CO)_4$] (**4S-1**)	13.0	8.7
2 *cis*-[$C_{10}H_8Cr_2(CO)_4$] (**4S-1**) → *cis*-[$C_{10}H_8Cr_2(CO)_5$] (**5S-1**) + *cis*-[$C_{10}H_8Cr_2(CO)_3$] (**3T-1**)	–12.9	–25.5
2 *cis*-[$C_{10}H_8Cr_2(CO)_3$] (**3T-1**) → *cis*-[$C_{10}H_8Cr_2(CO)_4$] (**4S-1**) + *cis*-[$C_{10}H_8Cr_2(CO)_2$] (**2T-1**)	–5.2	15.7
2 *cis*-[$C_{10}H_8Cr_2(CO)_2$] (**2T-1**) → *cis*-[$C_{10}H_8Cr_2(CO)_3$] (**3T-1**) + *cis*-[$C_{10}H_8Cr_2(CO)$] (**1T-1**)	–	–17.6

tance of 2.230 Å (Figure 9) as well as a low ν(CO) frequency of 1585 cm^{-1}. The Cr≡Cr distance of 2.467 Å in **1Q-2** by the BP86 method can correspond to a formal triple bond giving each chromium atom a 16-electron configuration, which could lead to a quintet spin state. In the singlet *cis*-[$C_{10}H_8Cr_2(CO)$] structure **1S-3** the azulene seven-membered ring is bonded to a chromium atom as a heptahapto ligand and the five-membered ring is bonded to the other chromium atom as a pentahapto ligand. The carbonyl group in **1S-3** is a normal two-electron donor carbonyl group. The very short Cr≣Cr bond lengths of 2.294 Å (B3LYP) or 2.154 Å (BP86) in **1S-3** can correspond to a formal quadruple bond. This gives each chromium atom a 16-electron configuration, assuming that the azulene ligand donates all of its ten π-electrons to the dichromium system.

3.2 Thermochemistry

Table 9 reports the energies of the single carbonyl dissociation reactions

[$C_{10}H_8Cr_2(CO)_n$] → [$C_{10}H_8Cr_2(CO)_{n-1}$] + CO

In determining these dissociation energies, the fragments were allowed to relax.

The predicted dissociation energy of one CO group from *cis*-[$C_{10}H_8Cr_2(CO)_6$] (**6S-1**) (Table 9) to give *cis*-[$C_{10}H_8Cr_2(CO)_5$] is 32.0 kcal/mol (B3LYP) or 33.5 kcal/mol (BP86) consistent with the experimental observation of its formation from reactions of suitable chromium carbonyl derivatives with azulene. Further dissociation of a CO group from *cis*-[$C_{10}H_8Cr_2(CO)_5$] (**5S-1**) to give *cis*-[$C_{10}H_8Cr_2(CO)_4$] (**4S-1**) requires a somewhat lower energy of 19.0 kcal/mol (B3LYP) or 24.8 kcal/mol (BP86). These carbonyl dissociation energies as well as the other carbonyl dissociation energies are similar to the related experimental BDEs[44] of 27 kcal/mol, 41 kcal/mol, and 37 kcal/mol for $Ni(CO)_4$, $Fe(CO)_5$, and $Cr(CO)_6$, respectively.

Table 9 also lists the energies for the disproportionation reactions 2 *cis*-[$C_{10}H_8Cr_2(CO)_n$] → *cis*-[$C_{10}H_8Cr_2(CO)_{n+1}$] + *cis*-[$C_{10}H_8Cr_2(CO)_{n-1}$]. The pentacarbonyl *cis*-[$C_{10}H_8Cr_2(CO)_5$] is seen to be thermodynamically favorable with respect to such disproportionation whereas the tetracarbonyl *cis*-[$C_{10}H_8Cr_2(CO)_4$] is thermodynamically disfavored with respect to such disproportionation. This is the opposite of the energetics for the corresponding cyclopentadienylchromium carbonyls, where $(C_5H_5)_2Cr_2(CO)_5$ is endothermic with respect to such disproportionation and the tetracarbonyl $(C_5H_5)_2Cr_2(CO)_4$ is exothermic with respect to disproportionation.[14]

3.3. Atomic Population, Natural Bonding Orbital (NBO) Analyses, and Chromium–Chromium Bonding

Table 10 lists the Wiberg bond indices (WBIs) and bond lengths for the Cr–Cr bonds in the *cis*-[$C_{10}H_8Cr_2(CO)_n$] de-

Table 10. Atomic charges and Wiberg bond indices for the *cis*-[$C_{10}H_8Cr_2(CO)_n$] structures by the BP86 method.

	Natural charge on Cr1/Cr2	Wiberg bond index	Cr–Cr distance [Å]	Formal Cr–Cr bond order
cis-[$C_{10}H_8Cr_2(CO)_6$] (**6S-1**)	–1.50/–1.41	0.24	3.325	1
cis-[$C_{10}H_8Cr_2(CO)_6$] (**6T-4**)	–1.33/–1.38	0.04	4.018	0
cis-[$C_{10}H_8Cr_2(CO)_5$] (**5S-1**)	–1.10/–1.19	0.59	2.664	2
cis-[$C_{10}H_8Cr_2(CO)_5$] (**5T-2**)	–0.77/–1.48	0.32	2.784	1
cis-[$C_{10}H_8Cr_2(CO)_5$] (**5T-3**)	–1.36/–0.80	0.28	2.880	1
cis-[$C_{10}H_8Cr_2(CO)_4$] (**4S-1**)	–0.56/–1.36	0.78	2.455	3
cis-[$C_{10}H_8Cr_2(CO)_4$] (**4T-2**)	–0.19/–1.28	0.60	2.587	2
cis-[$C_{10}H_8Cr_2(CO)_3$] (**3T-1**)	–0.70/–0.25	0.75	2.447	3
cis-[$C_{10}H_8Cr_2(CO)_3$] (**3S-2**)	–0.63/–0.42	0.85	2.424	3
cis-[$C_{10}H_8Cr_2(CO)_3$] (**3T-3**)	–0.24/–0.86	1.02	2.282	4
cis-[$C_{10}H_8Cr_2(CO)_3$] (**3S-4**)	+0.03/–0.86	2.15	1.993	5
cis-[$C_{10}H_8Cr_2(CO)_2$] (**2T-1**)	+0.60/–0.89	0.46	2.606	2
cis-[$C_{10}H_8Cr_2(CO)_2$] (**2Q-2**)	+0.59/–0.85	0.33	2.708	1
cis-[$C_{10}H_8Cr_2(CO)_2$] (**2S-3**)	+0.26/–0.61	2.00	2.056	5
cis-[$C_{10}H_8Cr_2(CO)$] (**1T-1**)	–0.08/–0.52	0.76	2.416	3
cis-[$C_{10}H_8Cr_2(CO)$] (**1Q-2**)	–0.04/+0.40	0.79	2.467	3
cis-[$C_{10}H_8Cr_2(CO)$] (**1S-3**)	+0.02/+0.17	1.71	2.154	4

rivatives. The results from the BP86 method are used, since less spin contamination was found in the triplet and quintet structures, relative to the B3LYP method. The lengths of Cr–Cr single bonds fall in the range 2.71 to 2.88 Å except for the unusually long Cr–Cr single bond of 3.325 Å in the *cis*-[$C_{10}H_8Cr_2(CO)_6$] structure **6S-1**, probably arising from steric hindrance between the two $Cr(CO)_3$ moieties. The WBIs of these Cr–Cr single bonds fall in the range 0.24 to 0.33. For the formal Cr=Cr double bonds the WBIs fall in the range 0.46 to 0.60, which are about twice the values of the WBIs for Cr–Cr single bonds. The Cr=Cr double bonds in these azulene complexes are also consistently shorter at 2.58 to 2.66 Å. The Cr≡Cr triple bonds continue the trend by having WBIs in the range 0.75 to 0.85, about three times the Wiberg bond indices for Cr–Cr single bonds. The Cr≡Cr triple bonds are also significantly shorter with predicted lengths in the rather narrow range of 2.41 to 2.47 Å.

The few examples of Cr–Cr bonds of formal orders of four and five in the highly unsaturated *cis*-[$C_{10}H_8Cr_2(CO)_n$] (n = 3, 2, 1) complexes continue this trend but with a less regular increase in the WBI values (Table 10). The two examples of formal quadruple bonds found in this research are of distinctly different types. The triplet spin state in the *cis*-[$C_{10}H_8Cr_2(CO)_3$] structure **3T-3** (Figure 7) with a predicted Cr≣Cr distance of 2.282 Å (BP86) and a WBI of 1.02 arises from the quadruple bond itself, which is of the $\sigma + 2\pi + {}^2\!/_2\delta$ type with two δ "half-bonds" containing the unpaired electrons. However, the quadruple bond in the singlet *cis*-[$C_{10}H_8Cr_2(CO)$] structure **1S-3** (Figure 9) is a more usual $\sigma + 2\pi + \delta$ type with one usual two-electron δ bond and no unpaired electrons. In this case the Cr≣Cr distance is predicted to be significantly shorter at 2.154 Å with a much higher WBI of 1.71. The single example of a formal Cr–Cr quintuple-bonded *cis*-$C_{10}H_8Cr_2(CO)_n$ structure, namely the *cis*-$C_{10}H_8Cr_2(CO)_3$ structure **3S-4**, has an even shorter chromium–chromium distance of 1.99 Å and an even higher WBI of 2.15.

The main factor in determining the natural charges on a given chromium atom is the number of Cr–C bonds to carbonyl groups (Table 10). The more such Cr–C bonds, the more negative the natural charge. This suggests that the negative charge on the chromium atom from the C→Cr forward bonding is not completely removed by the concurrent Cr→C π→π* back-bonding. Thus Cr atoms bonded to three CO groups have natural charges of –1.0 to –1.5, while Cr atoms bonded to two CO groups have negative charges of –0.8 to –0.9, and Cr atoms bonded to a CO group are close to neutral (≈ 0.0). A Cr–O interaction with a four-electron donor bridging η^2-μ-CO group removes a significant amount of negative charge, leading to natural charges of ca. +0.6 on such chromium atoms (e.g., Cr1 in **2T-1** and Cr1 in **2Q-2**).

4. Discussion

The predicted structure for [$C_{10}H_8Cr_2(CO)_6$] is the *cis* structure **6S-1** (Figure 4) with both azulene rings functioning as pentahapto ligands to chromium atoms. This structure is very similar to that of the cyclopentadienyl derivative [$(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_6$], except that in the latter the two pentahapto rings are not joined as they are not parts of a single azulene ligand. Even the Cr–Cr single bond lengths in *cis*-[$(\eta^5,\eta^5\text{-}C_{10}H_8)Cr_2(CO)_6$] and [$(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_6$] are very similar at a relatively large distance of ca. 3.3 Å.

For [$C_{10}H_8Cr_2(CO)_6$] a low energy *trans* structure **6S-2** lies within about 4 kcal/mol of the *cis*-[$(\eta^5,\eta^5\text{-}C_{10}H_8)Cr_2(CO)_6$] (**6S-1**) global minimum (Figure 4 and Table 1). In **6S-2** the seven-membered azulene ring is a heptahapto rather than a pentahapto ligand so that both chromium atoms can attain the favored 18-electron configuration in a zwitterionic structure (Figure 10) without any need for sterically implausible direct metal-metal bonding for a *trans* structure. For the more unsaturated [$C_{10}H_8Cr_2(CO)_n$] ($n \leq 5$) derivatives the *trans* structures always lie significantly higher in energy than the lowest lying *cis* isomers, since there is no way for the *trans* structures to have the direct chromium-chromium bonding that is necessary for the metals to obtain the favored 18-electron configuration. This energy difference between the *cis* and *trans* structures increase as the unsaturation in the [$C_{10}H_8Cr_2(CO)_n$] derivatives increases by decreasing the numbers of carbonyl groups.

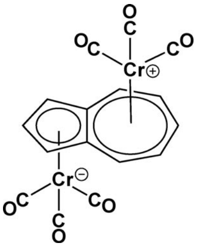


Figure 10. A zwitterionic structure for *trans*-[$(\eta^7,\eta^5\text{-}C_{10}H_8)Cr_2(CO)_6$] (**6S-2**) with the favored 18-electron configuration for both chromium atoms and no metal–metal bond.

The lowest energy structures for the unsaturated derivatives [$C_{10}H_8Cr_2(CO)_n$] (n = 5, 4, 3, 2, 1) are all related, since they are *cis* structures containing a chromium–chromium bond bridged by a single carbonyl group. In the pentacarbonyl structure of this type, namely singlet *cis*-[$(\eta^5,\eta^5\text{-}C_{10}H_8)Cr_2(CO)_5$] (**5S-1** in Figure 5), each azulene ring is a pentahapto ligand to a chromium atom, which also bears two carbonyl groups. The predicted Cr=Cr distance of about 2.66 Å in **5S-1** corresponds to the formal double bond needed to give both chromium atoms the favored 18-electron configuration. The lowest energy [$C_{10}H_8Cr_2(CO)_5$] structure **5S-1** is thermodynamically viable with respect to disproportionation into [$C_{10}H_8Cr_2(CO)_6$] + [$C_{10}H_8Cr_2(CO)_4$]. This is different from the cyclopentadienyl analogue [$(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_5$], which has been shown both experimentally and theoretically[14] to be thermodynamically unstable with respect to disproportionation into [$(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_6$] + [$(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_4$], both of which are known stable compounds.

The lowest energy tetracarbonyl structure, namely singlet *cis*-[$(\eta^7,\eta^5\text{-}C_{10}H_8)Cr_2(CO)_4$] (**4S-1** in Figure 7), can be derived from the lowest energy pentacarbonyl structure **5S-1** by loss of a terminal carbonyl group and conversion of the seven-membered azulene ring from a pentahapto to a heptahapto ligand. The Cr≡Cr distance shortens to 2.47 ± 0.02 Å, corresponding to a formal triple bond. This gives each chromium atom the favored 18-electron configuration, assuming that the azulene ligand donates all ten of its π-electrons to the dichromium system. Also, the structure of *cis*-[(η^7,η^5-$C_{10}H_8$)$Cr_2(CO)_4$] (**4S-1**), with a heptahapto-coordinated seven-membered azulene ring, is different from that of the cyclopentadienyl analogue [(η^5-C_5H_5)$_2$$Cr_2(CO)_4$], in which both rings are necessarily pentahapto ligands. The known cyclopentadienyl-carbonylchromium [(η^5-C_5H_5)$_2$$Cr_2(CO)_4$] is stable, whereas the azulene analogue *cis*-[(η^7,η^5-$C_{10}H_8$)$Cr_2(CO)_3$(μ-CO)] (**4S-1**) is predicted to be thermodynamically disfavored with respect to dissociation into the lowest energy singlet $C_{10}H_8Cr_2(CO)_5$ + $C_{10}H_8Cr_2(CO)_3$ structures.

The lowest energy tricarbonyl structure, namely triplet *cis*-[(η^7,η^5-$C_{10}H_8$)$Cr_2(CO)_3$] (**3T-1** in Figure 7), may be derived from the tetracarbonyl structure **4S-1**, by loss of one of the two terminal carbonyl groups from the $Cr(CO)_2$ unit. This leads to a more symmetrical arrangement of carbonyl groups in **3T-1** than in **4S-1** but the Cr≡Cr distance remains about the same at 2.47 ± 0.02 Å, suggesting retention of the formal triple bond. This leads to 17-electron configurations for each of the chromium atoms in the tricarbonyl *cis*-[(η^7,η^5-$C_{10}H_8$)$Cr_2(CO)_3$] (**3T-1**), consistent with its triplet spin multiplicity.

The lowest energy structure for the dicarbonyl, namely triplet *cis*-[(η^7,η^5-$C_{10}H_8$)Cr_2(CO)(η^2-μ-CO)] (**2T-1** in Figure 8), may be derived from the tricarbonyl structure **3T-1** by a loss of one of the terminal carbonyl groups. This is balanced by the conversion of the bridging carbonyl group in **2T-1** from a normal terminal carbonyl group to a four-electron donor η^2-μ-CO bridging carbonyl group as indicated by a short Cr–O distance of 2.12 ± 0.04 Å and an unusually low ν(CO) frequency of 1578 cm^{-1} (BP86). The Cr=Cr distance in **2T-1** lengthens to 2.65 ± 0.05 Å, which is about the same as the formal Cr=Cr double bond in the pentacarbonyl structure *cis*-[η^5,η^5-$C_{10}H_8Cr_2(CO)_5$] (**5S-1** in Figure 5) discussed above.

The lowest energy structure for the monocarbonyl is triplet *cis*-[(η^5,η^5-$C_{10}H_8$)Cr_2(CO)] (**1T-1** in Figure 9) in which the carbonyl is a two-electron donor semibridging carbonyl group and both azulene rings are pentahapto ligands. Here the Cr≡Cr distance of 2.416 Å can be interpreted as a formal triple bond giving each chromium atom a 15-electron configuration. The single unpaired electrons on each chromium atom with a 15-electron configuration in a binuclear complex can lead to a triplet spin state.

Supporting Information (see also the footnote on the first page of this article): Chromium–carbon and carbon–carbon distances (in Å) for the $C_{10}H_8Cr_2(CO)_n$ (n = 6, 5, 4, 3, 2, 1) structures (Tables S1 to S7); complete tables of harmonic vibrational frequencies and infrared ν(CO) frequencies (in cm^{-1}) for the $C_{10}H_8Cr_2(CO)_n$ (n = 6, 5, 4, 3, 2, 1) structures (Tables S8 to S33); for the complete Gaussian reference (ref.[40]).

Acknowledgments

We are grateful to the China National Science Foundation (Grant 10774104 and 10974161) and the Fundamental Research Funds for the Central Universities (SWJTU09CX079 and SWJTU09ZT39) as well as the U.S. National Science Foundation (Grant CHE-0749868 and CHE-0716718) for support of this work. H. W. thanks the Faculty of Chemistry and Chemical Engineering of Babeş-Bolyai University in Cluj-Napoca, Romania, for providing CPU time.

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Received: July 6, 2010