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Binuclear Carbonylheptalenechromium Complexes: Partition of Heptalene into a Complexed Heptafulvene Subunit and an Uncomplexed 1,3-Diene Subunit for Coordination to a Multiply Bonded Pair of Chromium Atoms

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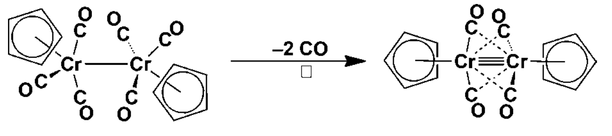
The possibility of extending carbonylchromium chemistry of the bicyclic non-benzenoid aromatic hydrocarbon heptalene from the known mononuclear (η^6-$C_{12}H_{10}$)Cr(CO)$_3$ to binuclear derivatives of the type $C_{12}H_{10}Cr_2(CO)_n$ (n = 6, 5, 4, 3) is examined by density functional theory. The lowest energy $C_{12}H_{10}Cr_2(CO)_6$ structures have each heptalene ring bonded to an independent Cr(CO)$_3$ unit as a hexahapto or heptahapto ligand with Cr···Cr distances too long (4.4 to 6.0 Å) for direct bonding. The lowest energy $C_{12}H_{10}Cr_2(CO)_5$ structure has an eight-carbon heptafulvene subunit of the heptalene unit coordinated to a carbonyl-bridged $Cr_2(CO)_4$(μ-CO) unit as an octahapto ligand leaving an uncomplexed *cis*-1,3-diene subunit in the heptalene ligand. The short Cr≡Cr distance in this structure of ca. 2.36 Å suggests the formal triple bond required to give each chromium atom the favored 18-electron configuration. A slightly higher energy $C_{12}H_{10}Cr_2(CO)_5$ structure by ca. 3 kcal/mol has all 12 heptalene carbon atoms bonded to an unbridged $Cr_2(CO)_5$ with a Cr–Cr distance of ca. 3.3 Å corresponding to the formal single bond required to give each chromium atom the favored 18-electron configuration. The global minima for the more highly unsaturated $C_{12}H_{10}Cr_2(CO)_n$ (n = 4, 3) complexes are predicted to have a four-electron donor bridging η^2-μ-CO group as indicated by short Cr–O distances consistent with a direct bond and a low ν(CO) frequency consistent with a low formal C–O formal bond order.

1. Introduction

The first example of a stable metal carbonyl derivative containing a metal-metal multiple bond was the binuclear pentamethylcyclopentadienylmolybdenum derivative $(Me_5C_5)_2Mo_2(CO)_4$, first reported by King and Bisnette in 1967.[1] The analogous chromium compound $(Me_5C_5)_2Cr_2(CO)_4$ was subsequently synthesized in 1973.[2] Shortly thereafter $(Me_5C_5)_2Cr_2(CO)_4$ was shown by X-ray diffraction[3] to have an unusually short Cr≡Cr distance of 2.24 Å, as compared with a much longer Cr–Cr single bond length[4] of 3.281 Å in $(C_5H_5)_2Cr_2(CO)_6$ (Figure 1). The short Cr≡Cr distance in $(Me_5C_5)_2Cr_2(CO)_4$ suggests the formal triple bond required to give each chromium atom the favored 18-electron configuration. The stability of such Cr≡Cr triple bonds in these binuclear carbonyl-cyclopentadienylchromium derivatives is indicated by the recently discovered[5] instability of $(C_5H_5)_2Cr_2(CO)_5$ with respect to disproportionation into $(C_5H_5)_2Cr_2(CO)_6$ with a Cr–Cr single bond and $(C_5H_5)_2Cr_2(CO)_4$ with a Cr≡Cr triple bond. This reaction is an unusual example of the disproportionation of a M=M double bonded derivative into a M–M single bonded derivative and the corresponding M≡M triple bonded derivative.



$(C_5H_5)_2Cr_2(CO)_6$ $(C_5H_5)_2Cr_2(CO)_4$

Figure 1. Binuclear carbonyl-cyclopentadienylchromium complexes with Cr–Cr single bonds and Cr≡Cr triple bonds.

A question of interest is whether related binuclear carbonylchromium complexes of bicyclic non-benzenoid aromatic hydrocarbons can be synthesized containing chromium–chromium multiple bonds. Azulene is the most readily available of such hydrocarbons and thus has been studied the most extensively.[6] Both a mononuclear azulene-tricarbonylchromium[7] (η^5-$C_{10}H_8$)Cr(CO)$_3$ and a binuclear azulene dichromium hexacarbonyl[8] (η^5,η^5-$C_{10}H_8$)$Cr_2(CO)_6$ have been synthesized (Figure 2). X-ray diffraction shows the latter to have a Cr–Cr single bond length of

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3.26 Å, which is very close to the Cr–Cr single-bond length of 3.28 Å in $(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_6$, discussed above.[2,3] However, efforts to synthesize unsaturated binuclear azulene carbonylchromium derivatives $C_{10}H_8Cr_2(CO)_n$ ($n < 6$) have been unsuccessful; such species might be candidates for structures with chromium–chromium multiple bonds. Recent theoretical studies[9] predict a tetracarbonyl structure $(\eta^5,\eta^5\text{-}C_{10}H_8)Cr_2(CO)_3(\mu\text{-}CO)$ with one bridging carbonyl group and a short enough ca. 2.47 Å Cr≡Cr distance to be interpreted as the formal triple bond required to give both chromium atoms the favored 18-electron configuration. However, this formal Cr≡Cr triple bond is ca. 0.2 Å longer than the Cr≡Cr triple bond in $(Me_5C_5)_2Cr_2(CO)_4$, discussed above. In addition, $(\eta^5,\eta^5\text{-}C_{10}H_8)Cr_2(CO)_3(\mu\text{-}CO)$ is predicted theoretically to be disfavored with respect to disproportionation into $C_{10}H_8Cr_2(CO)_5 + C_{10}H_8Cr_2(CO)_3$ in contrast to the very stable $(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_4$.

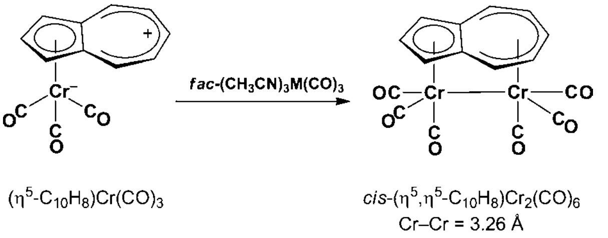


Figure 2. Mononuclear and binuclear azulene-carbonylchromium complexes.

Another bicyclic non-benzenoid hydrocarbon of interest is heptalene, which was first synthesized by Dauben and Bertelli in 1961.[10] A mononuclear tricarbonyl-heptalenechromium derivative $(\eta^6\text{-}C_{12}H_{10})Cr(CO)_3$ has been reported (**3a** in Figure 3).[11,12] In addition some binuclear carbonylchromium derivatives of substituted heptalenes have been synthesized, such as the two tetramethylheptalene dichromium hexacarbonyl isomers **3b** and **3c** (Figure 3).[13,14] This paper explores theoretically the possibility of synthesizing binuclear carbonyl-heptalenechromium derivatives $C_{12}H_{10}Cr_2(CO)_n$ (n = 6, 5, 4, 3) with particular emphasis on such derivatives with chromium–chromium multiple bonds. This research has led to the discovery of an unusual relatively low energy Cr≡Cr triply bonded $C_{12}H_{10}Cr_2(CO)_5$ structure in which four carbon atoms of the heptalene ligand are bonded to one chromium atom as a tetrahapto *cisoid* 1,3-diene unit and another four carbon atoms of the heptalene unit are bonded to the other chromium atom as a Y-shaped tetrahapto trimethylenemethane unit. This mode of bonding partitions the 12 carbon atoms of the heptalene ligand into an eight-carbon heptafulvene unit bonded to the two chromium atoms and a four-carbon uncomplexed 1,3-diene unit. This unusual bis(tetrahapto) bonding mode using only eight of the 12 carbon atoms of the heptalene unit to two chromium atoms in this Cr≡Cr triply bonded $C_{12}H_{10}Cr_2(CO)_5$ structure is an interesting demonstration of the stability of metal–metal triple bonds in such binuclear carbonylchromium structures.

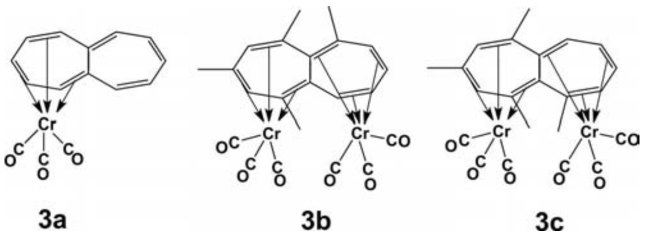

3a 3b 3c

Figure 3. The known tricarbonyl-heptalenechromium $(\eta^6\text{-}C_{12}H_{10})$-$Cr(CO)_3$ and two known isomers of hexacarbonyl-tetramethylheptalenedichromium.

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.[15–29] Three DFT methods were used in this study. The first functional is the popular hybrid B3LYP method, which incorporates Becke's three-parameter functional (B3) with the Lee, Yang, and Parr (LYP) correlation functional.[30,31] The second approach is the BP86 method, which marries Becke's 1988 exchange functional (B) with Perdew's 1986 correlation functional.[32,33] The BP86 method method usually provides better vibrational frequencies. The third functional used in this work is a hybrid *meta*-GGA DFT method, M06L, developed by Truhlar's group.[34] This functional reflects considerable progress by Truhlar's group toward the development of improved exchange-correlation functional that are essential for expanding the applicability of Kohn–Sham DFT. The M06L functional was constructed using three strategies, namely constraint satisfaction, modeling the exchange-correlation hole, and empirical testing. The studies in Truhlar's group suggest that M06L is one of the best functionals for the study of organometallic and inorganic thermochemistry, and may be the best functional for transition metal energetics. Reiher and collaborators[35] found that the B3LYP method overestimates the energies of the high-spin states. However, the BP86 method overestimates the energies of the low-spin states. The M06L method typically predicts an energy between the B3LYP and BP86 predictions. When these three very different DFT methods agree, confident predictions can be made. For most of the structures studied in the present work, the methods agree quite well.

For carbon and oxygen atoms, the double-ζ plus polarization (DZP) basis set used here adds one set of pure spherical harmonic d functions with orbital exponents $a_d(C) = 0.75$ and $a_d(O) = 0.85$ to the standard Huzinaga–Dunning contracted DZ sets, and is designated (9s5p1d/4s2p1d).[36,37] For H, a set of p polarization functions $a_p(H) = 0.75$ 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, DZP BP86, and DZP M06L 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. The reported ν(CO) frequencies are those determined by the BP86 method, which has been shown to be more reliable than the B3LYP method for this purpose.[40] In this work, the reported ν(CO) frequencies predicted by the BP86 method are also found to be closer to the experimental values than those determined by the M06L method.

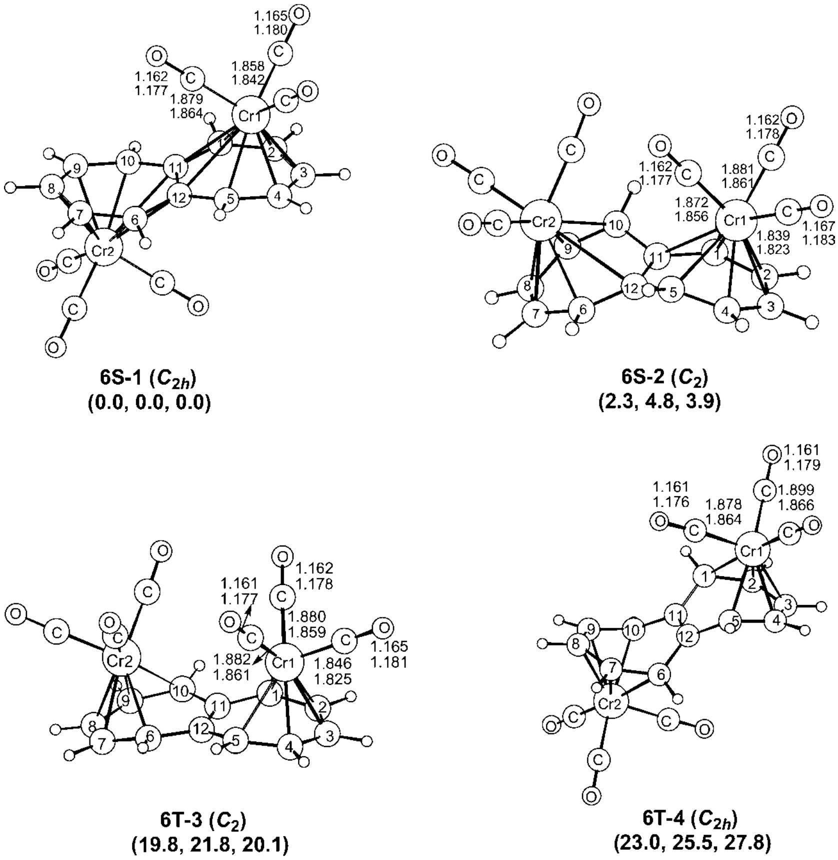
All of the computations were carried out with the Gaussian 09 program,[34] in which the fine grid (75,302) is the default for evaluating integrals numerically, and the tight designation is the default for the energy convergence.[41] The finer (120, 974) grid was used for more precise resolution of small imaginary vibrational frequencies.[42] 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 $C_{12}H_{10}Cr_2(CO)_6$. Four low-lying $C_{12}H_{10}Cr_2(CO)_6$ structures, namely two singlet structures (**6S-1** and **6S-2**) and two triplet structures (**6T-3** and **6T-4**) were obtained (Figure 4 and Table S1 in the Supporting Information). The global minimum is the C_{2h} *trans*-$C_{12}H_{10}Cr_2(CO)_6$ structure **6S-1**. The BP86 method predicts all real frequencies for **6S-1**. However, a very small imaginary vibrational frequency of $16i\,cm^{-1}$ is predicted by the B3LYP method, which becomes real using the finer (120, 974) grid. The Cr–C distances indicate that each heptalene ring is a heptahapto ligand towards one of the chromium atoms with C11 and C12 within a relatively long bonding distance (ca. 2.77 Å) of both chromium atoms. Dividing the 12 π electrons of the heptalene system equally between the two chromium atoms gives each chromium atom the favored 18-electron configuration.

The *cis*-$C_{12}H_{10}Cr_2(CO)_6$ structure **6S-2** (C_2 symmetry) lies only 2.3 kcal/mol (B3LYP), 4.8 kcal/mol (BP86), or 3.9 kcal/mol (M06L) in energy above the global minimum **6S-1** (Figure 4 and Table S1). The Cr–Cr distance of 4.781 Å (B3LYP) or 4.761 Å (BP86) in **6S-2** suggests no direct inter-



6S-1 (C_{2h})
(0.0, 0.0, 0.0)

6S-2 (C_2)
(2.3, 4.8, 3.9)

6T-3 (C_2)
(19.8, 21.8, 20.1)

6T-4 (C_{2h})
(23.0, 25.5, 27.8)

Figure 4. The four optimized $C_{12}H_{10}Cr_2(CO)_6$ structures. In Figures 4, 5, 6, and 7 the upper distances were obtained by the B3LYP method and the lower distances by the BP86 method. The numbers in parentheses are the relative energies (ΔE in kcal/mol) predicted by the B3LYP, BP86, and M06L methods.

Table 1. The ν(CO) frequencies (in cm^{-1}) predicted for **6S-2** by the BP86 method, and a comparison of the experimental ν(CO) frequencies[13] of the tetramethylheptalene $Cr_2(CO)_6$ derivatives **3b** and **3c** (Figure 3) with those predicted by the BP86, B3LYP, and the M06L methods. Infrared intensities (km/mol) are in parentheses.

6S-2	BP86		1991 (1357)	1960 (1667)	1930 (1080)	1909 (1132)
	Exp.	CH_2Cl_2	1987	1960	1916	1890
		THF	1995	1970	–	1890
3b	BP86		1977 (1030)	1957 (1735)	1910 (815)	1908 (712)
	B3LYP		2054 (1286)	2030 (2095)	1988 (1043)	1981 (718)
	M06L		2061 (1232)	2036 (1875)	1987 (1991)	1981 (1837)
	Exp.	CH_2Cl_2	1989	1961	1923	1893
		THF	1995	1970	–	1890
3c	BP86		1980 (1163)	1959 (1580)	1912 (1480)	1910 (605)
	B3LYP		2058 (1450)	2032 (1903)	1988 (1308)	1985 (716)
	M06L		2065 (1341)	2037 (1788)	1990 (1062)	1985 (785)

action between the two chromium atoms. The Cr–C distances suggest that each seven-membered ring functions as a hexahapto ligand, thereby giving each chromium atom the favored 18-electron configuration.

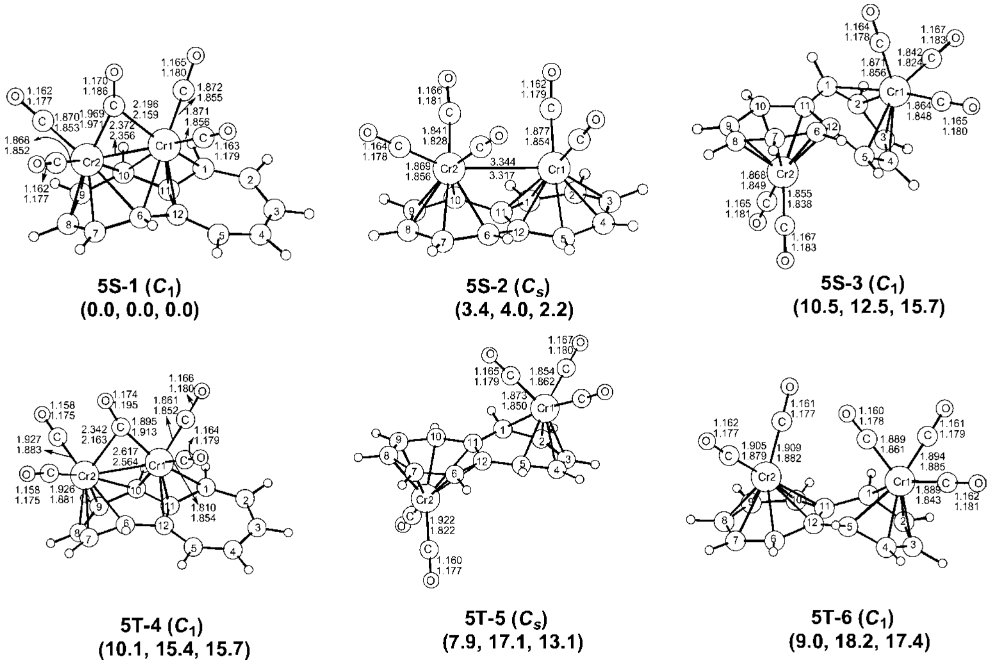
Binuclear carbonylchromium complexes of unsubstituted heptalene have not yet been synthesized. However, two isomers of tetramethylheptalene dichromium hexacarbonyl have been synthesized. One of these isomers has been shown by X-ray crystallography to have structure **3c** essentially equivalent to **6S-2** (Figure 3).[13] The ν(CO) frequencies predicted by the BP86 method for **6S-2** are comparable to those observed in the experimental structures **3b** and **3c** in Figure 3 (Table 1). However, frequencies predicted by the B3LYP or the M06L method are not as close to the experimental values as those predicted by the BP86 method. The predicted energy for the structure **3c** is only 1.2 kcal/mol (B3LYP), 0.6 kcal/mol (BP86), or 1.2 kcal/mol (M06L) higher than the experimental synthesized structure **3b**.

The two triplet $C_{12}H_{10}Cr_2(CO)_6$ structures **6T-3** and **6T-4** are predicted to have significantly higher energies than the corresponding singlet states (Figure 4 and Table S1). Thus the C_2 triplet *cis*-$C_{12}H_{10}Cr_2(CO)_6$ structure **6T-3** lies 19.8 kcal/mol (B3LYP), 21.8 kcal/mol (BP86), or 20.1 kcal/mol (M06L) in energy above the global minimum **6S-1**. The Cr···Cr distances in **6T-3** of 4.437 Å (B3LYP) or 4.443 Å (BP86) indicate no direct chromium–chromium bonding. The Cr–C distances in **6T-3** suggest that each seven-membered ring of the heptalene system functions as a pentahapto ligand, thereby giving each chromium atom the 17-electron configuration for a binuclear triplet. The C_{2h} triplet *trans*-$C_{12}H_{10}Cr_2(CO)_6$ structure **6T-4** lies 23.0 kcal/mol (B3LYP), 25.5 kcal/mol (BP86), or 27.8 kcal/mol (M06L) in energy above the global minimum **6S-1**. Just like **6T-3**, each heptalene ring in **6T-4** functions as a pentahapto ligand, again giving each chromium atom a 17-electron configuration, consistent with a binuclear triplet. A small imaginary frequency of 31*i* cm^{-1} (B3LYP) or 42*i* cm^{-1} (BP86) is predicted for structure **6T-4**. This small imaginary frequency was not removed by using the finer (120, 974) integration grid.

3.1.2 $C_{12}H_{10}Cr_2(CO)_5$. Six structures were optimized for $C_{12}H_{10}Cr_2(CO)_5$, namely three singlet structures (**5S-1**, **5S-2**, and **5S-3**) and three triplet structures (**5T-4**, **5T-5**, and **5T-6**) (Figure 5 and Table S2). The global minimum is the singlet *cis*-$C_{12}H_{10}Cr_2(CO)_5$ structure **5S-1** with a single bridging carbonyl exhibiting a relatively low vibrational frequency of 1866 cm^{-1} (BP86). The Cr–C distances in **5S-1** indicate five carbon atoms within bonding distance for each chromium atom. However, the two carbon atoms C6 and C10 are shared by the two chromium atoms so that eight rather than 10 of the 12 carbon atoms of the heptalene system are within bonding distance of at least one of the chromium atoms. These eight complexed carbon atoms of the heptalene unit form a heptafulvene subunit. This leaves an uncomplexed 1,3-diene subunit in the heptalene system of **5S-1** with relatively short uncomplexed C=C double bond lengths of 1.38 Å (B3LYP) or 1.39 Å (BP86). The predicted Cr≡Cr distance of 2.372 Å (B3LYP) or 2.355 Å (BP86) in **5S-1**, although somewhat longer than the experimental Cr≡Cr triple bond of 2.24 Å in $(\eta^5\text{-}Me_5C_5)_2Cr_2(CO)_4$,[3] is still short enough to be considered as a formal triple bond. This gives each chromium atom the favored 18-electron configuration, assuming that the eight complexed carbons of the heptafulvene submit in **5S-1** donate their eight π electrons to the Cr_2 system.

The second singlet *cis*-$C_{12}H_{10}Cr_2(CO)_5$ structure **5S-2** is a C_s structure lying only 3.4 kcal/mol(B3LYP), 3.0 kcal/mol (BP86) or 2.2 kcal/mol (M06L) above the global minimum **5S-1** (Figure 5 and Table S2). Structure **5S-2**, unlike **5S-1**, has exclusively terminal carbonyls. The Cr–C distances suggest that one heptalene ring functions as a pentahapto ligand to one chromium atom, and the other heptalene ring functions as a heptahapto ligand to the other chromium atom so that all 12 π electrons of the heptalene system are bonded to the Cr_2 unit. The Cr–Cr distance of 3.344 Å (B3LYP) or 3.317 Å (BP86) in **5S-2** is rather long but nevertheless only ca. 0.05 Å longer than the experimental 3.28 Å Cr–Cr single bond length in $(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_6$.[4] Interpreting this Cr–Cr interaction as a formal Cr–Cr single bond gives each chromium atom in **5S-2** the favored 18-electron configuration. A small imaginary frequency of 13*i* cm^{-1} was predicted by the M06L method, but the B3LYP method and the BP86 method predicted all real ones.

The third singlet $C_{12}H_{10}Cr_2(CO)_5$ structure is a *trans* structure **5S-3** lying 10.5 kcal/mol (B3LYP), 12.5 kcal/mol (BP86), or 15.7 kcal/mol (M06L) above the global minimum **5S-1** (Figure 5 and Table S2). The Cr–C distances in



5S-1 (C_1)
(0.0, 0.0, 0.0)

5S-2 (C_s)
(3.4, 4.0, 2.2)

5S-3 (C_1)
(10.5, 12.5, 15.7)

5T-4 (C_1)
(10.1, 15.4, 15.7)

5T-5 (C_s)
(7.9, 17.1, 13.1)

5T-6 (C_1)
(9.0, 18.2, 17.4)

Figure 5. The six optimized $C_{12}H_{10}Cr_2(CO)_5$ structures.

5S-3 indicate that one of the heptalene seven-membered rings functions as a pentahapto ligand to the $Cr(CO)_3$ group, and the other heptalene seven-membered ring as a heptahapto ligand to the $Cr(CO)_2$ group. Considering the singlet **5S-3** as a zwitterion with a positive charge on one of the chromium atoms and a negative charge on the other chromium atom gives the chromium atom with the negative charge the favored 18-electron configuration and the chromium atom with the positive charge only a 16-electron configuration.

Singlet $C_{12}H_{10}Cr_2(CO)_5$ structures are seen to be favored over triplet structures by the three DFT methods. Thus the lowest energy triplet $C_{12}H_{10}Cr_2(CO)_5$ structure **5T-4** lies 10.1 kcal/mol (B3LYP), 15.4 kcal/mol (BP86), or 15.7 kcal/mol (M06L) in energy above the singlet global minimum **5S-1** (Figure 5 and Table S2). Structure **5T-4** has a single semibridging carbonyl group exhibiting a relatively low ν(CO) frequency at 1803 cm^{-1}. The short Cr–C distance to this semibridging carbonyl group is 1.895 Å (B3LYP) or 1.913 Å (BP86) and the long Cr–C distance to this semibridging carbonyl group is 2.342 Å (B3LYP) or 2.163 Å (BP86). Similar to **5S-1**, five carbon atoms of the heptalene system in **5T-4** lie within bonding distance for each chromium atom with two of them shared by the two chromium atoms leading to a complexed heptafulvene subunit. This leaves an uncomplexed *cis* 1,3-diene subunit in one of the heptalene rings with relatively short uncomplexed C=C distances of 1.38 Å (B3LYP) or 1.40 Å (BP86). The Cr=Cr distance of 2.617 Å (B3LYP) or 2.566 Å (BP86) in **5T-4** can correspond to a formal double bond, thereby giving each chromium a 17-electron configuration consistent with a binuclear triplet.

The second triplet $C_{12}H_{10}Cr_2(CO)_5$ structure **5T-5** is a C_s *trans* structure, lying 7.9 kcal/mol (B3LYP), 17.1 kcal/mol (BP86), or 13.1 kcal/mol (M06L) above **5S-1** (Figure 5 and Table S2). A small imaginary vibrational frequency of $7i$ cm^{-1} is predicted for **5T-5** by both methods. The Cr–C distances indicate that one heptalene ring is bonded to the $Cr(CO)_3$ group as a pentahapto ligand and the other heptalene ring is bonded to the $Cr(CO)_2$ group as a heptahapto ligand. This gives each chromium atom the 17-electron configuration for a binuclear triplet.

The remaining triplet $C_{12}H_{10}Cr_2(CO)_5$ structure is the *cis* structure **5T-6**, lying 9.0 kcal/mol (B3LYP), 18.2 kcal/mol (BP86), or 17.4 kcal/mol (M06L) in energy above the global minimum **5S-1**. Despite the *cis* geometry in **5T-6**, the very long Cr···Cr distance of 4.358 Å (B3LYP) or 4.418 Å (BP86) indicates no direct metal-metal bond. The Cr–C distances in **5T-6** indicate that one heptalene ring is a pentahapto ligand to the $Cr(CO)_3$ group and the other heptalene ring is a heptahapto ligand to the $Cr(CO)_2$ group. This gives each chromium atom in **5T-6** the 17-electron configuration for a binuclear triplet.

3.1.3 $C_{12}H_{10}Cr_2(CO)_4$. Six structures were optimized for $C_{12}H_{10}Cr_2(CO)_4$, namely four *cis* structures (**4S-1**, **4T-2**, **4T-3**, and **4T-6**) and two *trans* structures (**4T-4** and **4S-5**) (Figure 6 and Table S3). The global minimum is the singlet *cis*-$C_{12}H_{10}Cr_2(CO)_3(\eta^2\text{-}\mu\text{-}CO)$ structure **4S-1**. In **4S-1**, there is a four-electron donor carbonyl suggested by the short Cr–O distance of 2.273 Å (B3LYP) or 2.264 Å (BP86) and the relatively low ν(CO) frequency of 1704 cm^{-1} (BP86). The Cr–C distances in **4S-1** suggest one pentahapto heptalene ring and one heptahapto heptalene ring so that all 12 heptalene π electrons are donated to the Cr_2 system. The

Cr–Cr distance of 3.097 Å (B3LYP) or 3.060 Å (BP86) in **4S-1** can be interpreted as a formal single bond, thereby giving each chromium atom the favored 18-electron configuration in a *cis*-$C_{12}H_{10}Cr_2(CO)_3(\eta^2$-μ-CO) structure with one four-electron donor bridging carbonyl group.

The second *cis*-$C_{12}H_{10}Cr_2(CO)_4$ structure is the C_s triplet structure **4T-2**, lying 1.5 kcal/mol (B3LYP), 8.7 kcal/mol (BP86), or 3.3 kcal/mol (M06L) in energy above the global minimum **4S-1** (Figure 6 and Table S3). In **4T-2** one heptalene ring is bonded to a $Cr(CO)_3$ fragment as a pentahapto ligand and the other heptalene ring is bonded to a Cr(CO) fragment as a heptahapto ligand. The Cr→Cr distance of 3.190 Å (B3LYP) or 3.053 Å (BP86) can be interpreted as a dative single bond from the $Cr(CO)_3$ group to the Cr(CO) group thereby giving each chromium atom a 17-electron configuration for a binuclear triplet. A small imaginary frequency of 13*i* cm^{-1} is predicted for **4T-2** by the B3LYP method, which can be eliminated by using the finer integration grid (120, 974). However, the B86 method predicts all real frequencies.

The third *cis*-$C_{12}H_{10}Cr_2(CO)_4$ structure **4T-3** is a C_2 triplet state structure lying 6.5 kcal/mol (B3LYP) or 10.7 kcal/mol (BP86) in energy above the global minimum **4S-1** (Figure 6 and Table S3). An imaginary vibrational frequency of 91*i* cm^{-1} is predicted for **4T-3** by the B3LYP method, but the BP86 method predicts all real frequencies. In **4T-3** each heptalene ring is bonded to a $Cr(CO)_2$ group as a heptahapto ligand so that all 12 π electrons of the heptalene system are donated to the Cr_2 unit. The predicted Cr=Cr distance of 2.786 Å (B3LYP) or 2.771 Å (BP86) in **4T-3** corresponds to a formal double bond, thereby giving each chromium atom the favored 18-electron configuration. The triplet spin state of **4T-3** arises from two unpaired electrons within the Cr=Cr double bond, which is a $\sigma + {}^2/_2\,\pi$ bond similar to the O=O double bond in dioxygen or the Fe=Fe double bond in the stable organometallic $(\eta^5\text{-}C_5H_5)_2Fe_2(\mu\text{-}CO)_3$.[43–45] Following the normal mode of the 91*i* cm^{-1} imaginary frequency of **4T-3** predicted by the B3LYP method leads to the C_1 structure **4T-6** lying 5.7 kcal/mol above the global minimum **4S-1**. In **4T-6**, one of the heptalene rings bonds to a $Cr(CO)_2$ group as a heptahapto ligand whereas the other heptalene ring bonds to the other $Cr(CO)_2$ group as a pentahapto ligand. The predicted Cr→Cr distance of 2.922 Å in **4T-6** can correspond to a formal dative single bond from the Cr atom bonded to the heptahapto heptalene ring to the Cr atom bonded to the pentahapto heptalene ring. This gives each chromium atom in **4T-6** the 17-electron configuration for a binuclear triplet. Attempts to optimize a $C_{12}H_{10}Cr_2(CO)_4$ structure analogous to **4T-6** by the BP86 method led instead to structure **4T-3**.

The *trans*-$C_{12}H_{10}Cr_2(CO)_4$ structures **4T-4** and **4S-5** were found to have energies much higher than those of the related *cis* structures (Figure 6 and Table S3). Thus the C_s structure **4T-4** lies 14.0 kcal/mol (B3LYP) or 19.8 kcal/mol (BP86) above **4S-1**. The Cr–C distances indicate a pentahapto heptalene ring bonded to one $Cr(CO)_2$ unit and a heptahapto heptalene ring bonded to the other $Cr(CO)_2$ unit. In this way one chromium atom obtains a 17-electron configuration and the other a 15-electron configuration, which can correspond to a binuclear triplet. The second *trans*-$C_{12}H_{10}Cr_2(CO)_4$ structure is a C_i singlet **4S-5**, lying at the relatively high energy of 22.2 kcal/mol (B3LYP) or 22.5 kcal/mol (BP86) above **4S-1**. The Cr–C distances in **4S-5** indicate that each heptalene ring functions as a heptahapto ligand to one of the $Cr(CO)_2$ units. Dividing the 12 π electrons equally between the two $Cr(CO)_2$ units gives each chromium atom a 16-electron configuration.

3.1.4 $C_{12}H_{10}Cr_2(CO)_3$. Five structures were optimized for $C_{12}H_{10}Cr_2(CO)_3$ including three *cis* structures (**3T-1**, **3S-2**, and **3S-3**) and two *trans* structures (**3T-4** and **3S-5**) (Figure 7 and Table S4). The global minimum predicted by

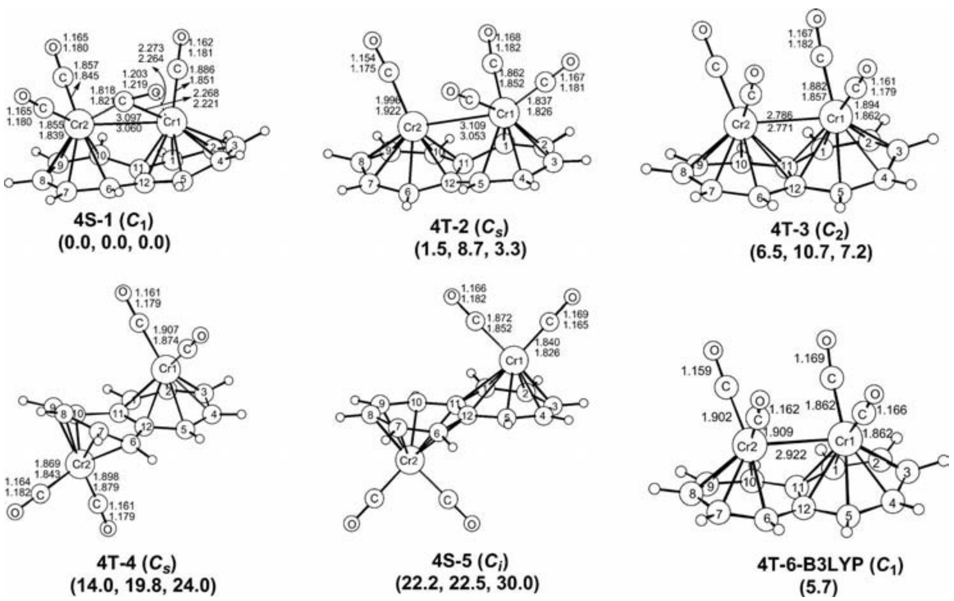


Figure 6. The six optimized $C_{12}H_{10}Cr_2(CO)_4$ structures.

the B3LYP method is the triplet *cis*-$C_{12}H_{10}Cr_2(CO)_2(\eta^2$-μ-CO) structure **3T-1** with the four-electron donor bridging carbonyl indicated by the short Cr–O distance of 2.244 Å (B3LYP) or 2.238 Å (BP86) and the low ν(CO) frequency of 1671 cm^{-1} (BP86). The Cr–C distances predicted for **3T-1** indicate one pentahapto heptalene ring and one heptahapto heptalene ring so that all 12 π electrons of the heptalene system are bonded to the Cr_2 unit. The Cr–Cr distance of 2.971 Å (B3LYP) or 2.900 Å (BP86) is consistent with the formal single bond, thereby giving each chromium atom the 17-electron configuration for a binuclear triplet.

The second *cis*-$C_{12}H_{10}Cr_2(CO)_3$ structure **3S-2** is the singly bridged C_{2v} singlet *cis*-$C_{12}H_{10}Cr_2(CO)_2$(μ-CO), lying in energy 11.3 kcal/mol above (B3LYP), 6.7 kcal/mol below (BP86), or only 0.7 kcal/mol (M06L) above the global minimum **3T-1** (Figure 7 and Table S4). This tendency of the B3LYP method to favor triplet spin state structures relative to the BP86 method has been previously noted by Reiher et al.[35] The bridging carbonyl group in **3S-2** exhibits a ν(CO) frequency at 1735 cm^{-1} (BP86), which, as expected, is significantly lower than the ν(CO) frequencies of the terminal carbonyl groups. The Cr–C distances in **3S-2** suggest two heptahapto heptalene rings so that all 12 carbon atoms are within bonding distance of at least one chromium atom. A Cr≡Cr triple bond is then required to give each chromium atom in **3S-2** the favored 18-electron configuration, assuming that the heptalene ligand contributes half of its 12 π electrons to each chromium atom. However, the predicted Cr≡Cr distance of 2.627 Å (B3LYP) or 2.611 Å (BP86) in **3S-2** is much longer than the experimentally determined Cr≡Cr triple bond length of 2.24 Å in $(\eta^5\text{-}Me_5C_5)_2Cr_2(CO)_4$ or even the theoretical Cr≡Cr triple bond length of 2.36 Å predicted above for **5S-1** (Figure 5 and Table S2). It thus appears that for **3S-2** the constraints of the heptalene geometry appear to override other considerations in determining the effective chromium–chromium bond order.

The third *cis*-$C_{12}H_{10}Cr_2(CO)_3$ structure **3S-3** lies 11.5 kcal/mol (B3LYP) or 6.4 kcal/mol (BP86) above the global minimum **3T-1** (Figure 7 and Table S4). Structure **3S-3** has a four-electron donor bridging η^2-μ-CO group as suggested by the short Cr–O distance of 2.228 Å (B3LYP) or 2.223 Å (BP86) and the low ν(CO) frequency of 1666 cm^{-1} (BP86). The coordination environment for **3S-3** is very similar to that of the global minimum **3T-1**. The predicted Cr–Cr distance of 3.069 Å (B3LYP) or 3.029 Å (BP86) can correspond to a formal single bond, thereby giving Cr1 the favored 18-electron configuration but Cr2 only a 16-electron configuration.

The two *trans*-$C_{12}H_{10}Cr_2(CO)_3$ structures (**3T-4** and **3S-5**) lie much higher in energy (Figure 7 and Table S4). Thus the triplet **3T-4** lies 16.6 kcal/mol (B3LYP) or 18.9 kcal/mol (BP86) above the global minimum **3T-1**. The C_1 singlet structure **3S-5** lies even higher in energy 32.9 kcal/mol (B3LYP) or 24.9 kcal/mol (BP86) above **3T-1**. In **3T-4**, one heptalene ring functions as a pentahapto ligand to a $Cr(CO)_2$ unit and the other heptalene ring functions as a heptahapto ligand to a Cr(CO) unit. Both chromium atoms have 15-electron configurations, which can correspond to a binuclear triplet. However, in **3S-5** each heptalene ring functions as a heptahapto ligand. If one chromium atom in **3S-5** has a formal negative charge and the other chromium atom has a formal positive charge then the chromium atom with the formal negative charge has a 16-electron configuration and the chromium atom with the formal positive charge has only a 14-electron configuration. The large deviations of the electron configurations of both

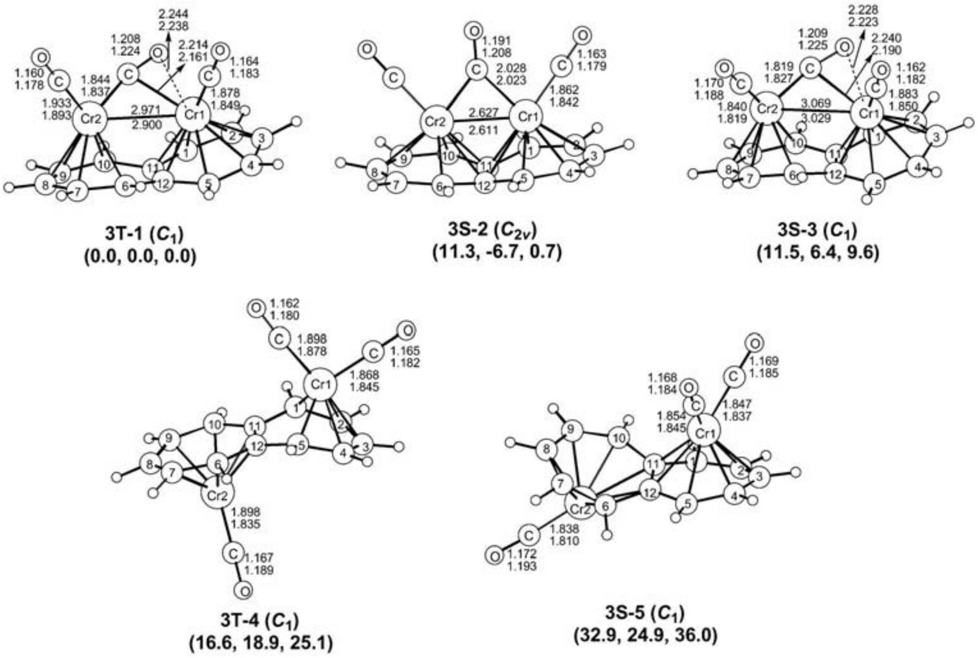


Figure 7. The five optimized $C_{12}H_{10}Cr_2(CO)_3$ structures.

chromium atoms in **3S-5** from the favored 18-electron configuration might account for the relatively high energy of this structure.

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

Table 2 lists the Wiberg bond indices (WBIs) and bond lengths for the Cr–Cr bonds in the *cis*-$C_{12}H_{10}Cr_2(CO)_n$ derivatives (n = 6, 5, 4, 3) using the BP86 method. The WBIs are seen to follow a consistent pattern with Cr–Cr single bonds in the range 0.29 to 0.36, Cr=Cr double bonds in the range 0.39 to 0.52, and Cr≡Cr triple bonds in the range 0.78–0.84. The WBIs for the Cr···Cr interactions at clearly non-bonding distances are close to zero, namely in the range 0.04 to 0.07. These WBI values for the chromium–chromium bonds in the *cis*-$C_{12}H_{10}Cr_2(CO)_n$ derivatives are consistent with previous studies[46] on metal-metal bonded derivatives, which suggest typical WBI values of 0.2 to 0.3 for unbridged formal metal-metal single bonds. In addition, for all of the *cis*-$C_{12}H_{10}Cr_2(CO)_n$ derivatives (n = 6, 5, 4, 3), the WBI values support the metal-metal bond order assignments based on metal-metal distances and electron counting discussed above.

The natural charge on a given chromium atom appears to be related mainly to the number of the carbonyl groups to which it is bonded with an increasing number of Cr–CO bonds leading to an increased natural negative charge. This suggests that the negative charge on the chromium atom from OC→Cr forward bonding is not completely counterbalanced by the concurrent Cr→CO π→π* back-bonding. Thus the Cr atoms bonded to three CO groups have natural charges of –1.3 to –1.5 (Table 2), the Cr atoms bonded to two CO groups have negative charges of –0.8 to –0.9, and the Cr atoms bonded to a single CO group are nearly neutral (ca. 0.0). The Cr–O interaction in a four-electron donor bridging η^2-μ-CO group removes a significant amount of negative charge. This leads to natural charges around –0.5 for such chromium atoms bonded to the oxygen side of a four-electron donor bridging η^2-μ-CO group as well as a single terminal CO group, e.g., Cr1 in **4S-1**, **3T-1**, and **3S-3.**

3.3 Thermochemistry

Table 3 reports the energies of the single carbonyl dissociation reactions

$$C_{12}H_{10}Cr_2(CO)_n \rightarrow C_{12}H_{10}Cr_2(CO)_{n-1} + CO$$

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

All of the CO dissociation energies of the $C_{12}H_{10}Cr_2(CO)_n$ derivatives (n = 6, 5, 4) are reasonably high and comparable to the experimental CO dissociation energy[47] of 37 kcal/mol for $Cr(CO)_6$. Thus the predicted dissociation energy of one CO group from *trans*-$C_{12}H_{10}Cr_2(CO)_6$ (**6S-1**) (Table 3) to give *cis*-$C_{12}H_{10}Cr_2(CO)_5$ (**5S-1**) is 31.1 kcal/mol (B3LYP) or 33.1 kcal/mol (BP86). Further dissociation of a CO group from *cis*-$C_{12}H_{10}Cr_2(CO)_5$ (**5S-1**) to give *cis*-$C_{12}H_{10}Cr_2(CO)_4$ (**4S-1**) requires 31.9 kcal/mol (B3LYP) or 41.0 kcal/mol (BP86). Subsequent CO dissociation from *cis*-$C_{12}H_{10}Cr_2(CO)_4$ (**4S-1**) to give *cis*-$C_{12}H_{10}Cr_2(CO)_3$ (**3T-1**) requires 35.1 kcal/mol (B3LYP) or 48.5 kcal/mol (BP86).

Table 2. Atomic charges and Wiberg bond indices for the *cis*-$C_{12}H_{10}Cr_2(CO)_n$ structures by the BP86 method.

	Natural charge on Cr1/Cr2	Wiberg bond index	Cr–Cr distance (Å)	Formal Cr–Cr bond order
cis-$C_{12}H_{10}Cr_2(CO)_6$ (**6S-2**)	–1.484/–1.484	0.04	4.716	0
cis-$C_{12}H_{10}Cr_2(CO)_6$ (**6T-3**)	–1.330/–1.330	0.04	4.443	0
cis-$C_{12}H_{10}Cr_2(CO)_5$ (**5S-1**)	–1.304/–1.367	0.78	2.355	3
cis-$C_{12}H_{10}Cr_2(CO)_5$ (**5S-2**)	–0.894/–1.486	0.29	3.317	1
cis-$C_{12}H_{10}Cr_2(CO)_5$ (**5T-4**)	–1.236/–0.960	0.52	2.566	2
cis-$C_{12}H_{10}Cr_2(CO)_5$ (**5T-6**)	–1.462/–0.772	0.07	4.148	0
cis-$C_{12}H_{10}Cr_2(CO)_4$ (**4S-1**)	–0.460/–1.428	0.31	3.060	1
cis-$C_{12}H_{10}Cr_2(CO)_4$ (**4T-2**)	–1.521/–0.064	0.31	3.053	1
cis-$C_{12}H_{10}Cr_2(CO)_4$ (**4T-3**)	–0.826/–0.826	0.39	2.771	2
cis-$C_{12}H_{10}Cr_2(CO)_3$ (**3T-1**)	–0.537/–0.518	0.36	2.900	1
cis-$C_{12}H_{10}Cr_2(CO)_3$ (**3S-2**)	–0.623/–0.623	0.84	2.611	3
cis-$C_{12}H_{10}Cr_2(CO)_3$ (**3S-3**)	–0.483/–0.564	0.43	3.029	1

Table 3. Energies (kcal/mol) for carbonyl dissociation and disproportionation of $C_{12}H_{10}Cr_2(CO)_n$ derivatives. These results are based on the global minima for each structure.

	B3LYP	BP86	M06L
cis-$C_{12}H_{10}Cr_2(CO)_6$ (**6S-1**) → *cis*-$C_{12}H_{10}Cr_2(CO)_5$ (**5S-1**) + CO	31.1	34.0	29.6
cis-$C_{12}H_{10}Cr_2(CO)_5$ (**5S-1**) → *cis*-$C_{12}H_{10}Cr_2(CO)_4$ (**4S-1**) + CO	31.9	39.9	35.8
cis-$C_{12}H_{10}Cr_2(CO)_4$ (**4S-1**) → *cis*-$C_{12}H_{10}Cr_2(CO)_3$ (**3T-1**) + CO	35.1	48.5	42.5
2*cis*-$C_{12}H_{10}Cr_2(CO)_5$ (**5S-1**) → *cis*-$C_{12}H_{10}Cr_2(CO)_6$ (**6S-1**) + *cis*-$C_{12}H_{10}Cr_2(CO)_4$ (**4S-1**)	0.7	5.8	6.2
2*cis*-$C_{12}H_{10}Cr_2(CO)_4$ (**4S-1**) → *cis*-$C_{12}H_{10}Cr_2(CO)_5$ (**5S-1**) + *cis*-$C_{12}H_{10}Cr_2(CO)_3$ (**3T-1**)	3.2	8.6	6.7

Table 3 also shows the energies for the disproportionation reactions 2 *cis*-$C_{12}H_{10}Cr_2(CO)_n$ → *cis*-$C_{12}H_{10}Cr_2(CO)_{n+1}$ + *cis*-$C_{12}H_{10}Cr_2(CO)_{n-1}$. Such disproportionation reactions for both the pentacarbonyl *cis*-$C_{12}H_{10}Cr_2(CO)_5$ and the tetracarbonyl *cis*-$C_{12}H_{10}Cr_2(CO)_4$ require energies less than 10 kcal/mol indicating only modest viability of such species towards disproportionation.

4. Discussion

The global minimum predicted for $C_{12}H_{10}Cr_2(CO)_6$ is the C_{2h} *trans*-(heptalene)$Cr_2(CO)_6$ structure **6S-1**, in which each heptalene ring bonds as a heptahapto ligand to a $Cr(CO)_3$ group (Figure 4 and Table S1). The two carbon atoms common to the two seven-membered rings in **6S-1**, namely C11 and C12, are within bonding distance of both chromium atoms, albeit a rather long bonding distance of ca. 2.77 Å. The 12 π electrons of the heptalene unit can be partitioned equally between the chromium atoms leading to the favored 18-electron configuration for each chromium atom. A C_2 *cis*-$C_{12}H_{10}Cr_2(CO)_6$ structure **6S-2** lies only 2.3 kcal/mol (B3LYP) or 4.8 kcal/mol (BP86) above the global minimum **6S-1**. The Cr–C distances indicate that each heptalene ring in **6S-2** functions as a hexahapto ligand in contrast to the heptahapto bonding of each heptalene ring to a chromium atom in **6S-1**. The binuclear *cis*-tetramethylheptalene dichromium hexacarbonyl **3c** (Figure 3), which has been characterized structurally by X-ray crystallography, has been optimized using the three different density functional methods. The predicted Cr–C distances are comparable to the experimental ones (Table S5). The most intense ν(CO) frequencies calculated by the BP86 method are also close to the experimental values.

For $C_{12}H_{10}Cr_2(CO)_5$, the global minimum is predicted to be an unusual singlet *cis*-$C_{12}H_{10}Cr_2(CO)_5$ structure **5S-1** with a single bridging carbonyl group and a very short Cr≡Cr distance of ca. 2.36 Å consistent with a formal triple bond (Figure 5 and Table S2). The eight carbon atoms of a heptafulvene subunit within the heptalene ligand in **5S-1** are bonded to the Cr_2 unit leaving an uncomplexed *cis*-1,3-diene subunit (Figure 8). Heptafulvene itself, as a free hydrocarbon not complexed to a metal atom, decomposes above –60 °C.[48] However, its iron tricarbonyl complex, synthesized by indirect methods not requiring free heptafulvene, is stable and has been structurally characterized by X-ray crystallography (Figure 9).[49]

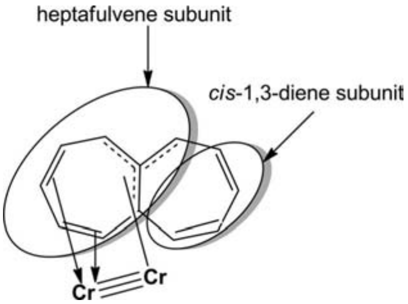


Figure 8. The bonding of the heptalene ligand to the Cr_2 unit in the $C_{12}H_{10}Cr_2(CO)_5$ structure **5S-1**. In this structure eight of the 12 heptalene carbon atoms are bonded to the triply bonded pair of chromium atoms as a heptafulvene subunit leaving an uncomplexed four-carbon *cis* 1,3-diene subunit. The five carbonyl groups are omitted for clarity.

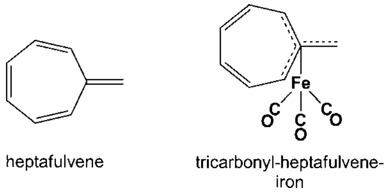


Figure 9. Heptafulvene and its tricarbonyliron complex.

A second singlet $C_{12}H_{10}Cr_2(CO)_5$ structure **5S-2** with all terminal carbonyls lies only ca. 3 kcal/mol in energy above **5S-1**. In **5S-2** all 12 heptalene carbon atoms are bonded to the Cr_2 unit so that the Cr_2 unit receives all 12 heptalene π electrons. The relatively long Cr–Cr distance of 3.344 Å (B3LYP) or 3.317 Å (BP86) in **5S-2** can be interpreted as a formal single bond, thereby giving each chromium atom the favored 18-electron configuration. The Wiberg bond index of 0.78 for the formal Cr≡Cr triple bond in **5S-1** (BP86) is approximately three times that of 0.29 for the Cr–Cr single bond in **5S-2**. This provides further support for the postulation of a formal Cr≡Cr triple bond in **5S-1**. This leads to the favored 18-electron configuration for both chromium atoms even though only eight of the heptalene π electrons are donated to the Cr_2 unit through its heptafulvene subunit.

All of the global minima for the more highly unsaturated $C_{12}H_{10}Cr_2(CO)_n$ (n = 4, 3) complexes by the B3LYP method are predicted to have a four-electron donor bridging η^2-μ-CO group as indicated by short Cr–O distances consistent with a direct bond and a low ν(CO) frequency consistent with a low formal C–O formal bond order. Thus the $C_{12}H_{10}Cr_2(CO)_4$ global minimum **4S-1** is the singlet *cis*-$C_{12}H_{10}Cr_2(CO)_3(\eta^2$-μ-CO) in which the Cr–C distances suggest one pentahapto heptalene ring and one heptahapto heptalene ring with all 12 heptalene carbon atoms within bonding distance of at least one chromium atom. The Cr–Cr distance of 3.097 Å (B3LYP) or 3.060 Å (BP86) can be interpreted as a formal single bond consistent with its WBI of 0.31 (BP86). This gives each chromium atom in **4S-1** the favored 18-electron configuration. The $C_{12}H_{10}Cr_2(CO)_3$ global minimum by the B3LYP method is the triplet *cis*-$C_{12}H_{10}Cr_2(CO)_2(\eta^2$-μ-CO) structure **3T-1**, also with a four-electron donor η^2-μ-CO group. The Cr–C distances predicted for **3T-1** indicate one pentahapto heptalene ring and one heptahapto heptalene ring with all 12 heptalene carbon atoms within bonding distance of at least one chromium atom. The Cr–Cr distance of ca. 2.9 Å in **3T-1** is consistent with the formal single bond, thereby giving each chromium atom the 17-electron configuration for a binuclear triplet.

The global minimum for $C_{12}H_{10}Cr_2(CO)_3$ by the BP86 method is the singlet *cis*-$C_{12}H_{10}Cr_2(CO)_2(\eta^2$-μ-CO) structure **3S-2** in contrast to the triplet **3T-1** global minimum by the B3LYP method. This is consistent with the tendency for the B3LYP method to favor higher spin states, as discussed by Reiher et al.[35] In such cases, the M06L functional always predicts an intermediate energy between the energies predicted by B3LYP and BP86. The Cr–C distances in **3S-2** indicate that each heptalene ring functions as a heptahapto ligand to a chromium atom so all 12 heptalene carbon atoms are within bonding distance of at least one chromium atom. Thus the Cr_2 unit in **3S-2** receives all 12 π electrons of the heptalene system. The chromium–chromium distance of ca. 2.6 Å is rather long for the formal Cr≡Cr triple bond required to give both chromium atoms in **3S-2** the favored 18-electron configuration. However, the high WBI of 0.84 for this Cr≡Cr bond is approximately three times the typical value for a Cr–Cr single bond (Table 2), so it is reasonable to consider the chromium–chromium interaction in **3S-2** to be a triple bond, at least in the formal sense. In this case the constraints of the heptalene geometry appear to prevent the Cr≡Cr triple bond length from being the usual short value of 2.2 to 2.4 Å.

Supporting Information (see footnote on the first page of this article): Tables S1 to S4: Total energies (E in hartree), relative energies (ΔE in kcal/mol), Cr–Cr bond lengths (in Å), numbers of imaginary vibrational frequencies (Nimg), and spin expectation values $\langle S^2 \rangle$ for the (heptalene)$Cr_2(CO)_n$ (n = 6, 5, 4, 3) structures; Table S5: The chromium–carbon distances and the carbon-carbon distances for the X-ray confirmed structure **3c** (Figure 3); Tables S6 to S7: Optimized coordinates of the **3b** and **3c** structures (Figure 3); Tables S8 to S11: Cr–C(heptalene) distances in the $C_{12}H_{10}Cr_2(CO)_n$ (n = 6, 5, 4, 3) structures; Tables S12 to S15: C–C(heptalene) distances in the $C_{12}H_{10}Cr_2(CO)_n$ (n = 6, 5, 4, 3) structures; Tables S16 to S35: Atomic coordinates of the optimized structures for the $C_{12}H_{10}Cr_2(CO)_n$ (n = 6, 5, 4, 3) structures; Tables S36 to S55: Harmonic vibrational frequencies (cm^{-1}) and infrared intensities (in parentheses in km/mol) for the $C_{12}H_{10}Cr_2(CO)_n$ (n = 6, 5, 4, 3) structures.

Acknowledgments

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