



Formal chromium–chromium triple bonds and bent rings in the binuclear cycloheptatrienylchromium carbonyls $(C_7H_7)_2Cr_2(CO)_n$ ($n = 6, 5, 4, 3, 2, 1, 0$): A density functional theory study

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ABSTRACT

Binuclear cycloheptatrienylchromium carbonyls of the type $(C_7H_7)_2Cr_2(CO)_n$ ($n = 6, 5, 4, 3, 2, 1, 0$) have been investigated by density functional theory. Energetically competitive structures with fully bonded heptahapto $\eta^7-C_7H_7$ rings are not found for $(C_7H_7)_2Cr_2(CO)_n$ structures having two or more carbonyl groups. This result stands in contrast to the related $(C_nH_n)_2M_2(CO)_n$ ($M = Mn, n = 6; M = Fe, n = 5; M = Co, n = 4$) systems. Most of the predicted $(C_7H_7)_2Cr_2(CO)_n$ structures have bent trihapto or pentahapto C_7H_7 rings and $Cr \equiv Cr$ distances in the range 2.4–2.5 Å suggesting formal triple bonds. In some cases rearrangement of the heptagonal C_7H_7 ring to a tridentate cyclopropyldivinyl or tridentate bis(carbene)alkyl ligand is observed. In addition structures with CO insertion into the C_7H_7-Cr bond are predicted for $(C_7H_7)_2Cr_2(CO)_n$ ($n = 6, 4, 2$). The global minima found for the $(C_7H_7)_2Cr_2(CO)_n$ derivatives for $n = 6, 5$, and 4 are $(\eta^5-C_7H_7)(OC)_2Cr \equiv Cr(CO)_4(\eta^1-C_7H_7)$, $(\eta^3-C_7H_7)(OC)_2Cr \equiv Cr(CO)_3(\eta^{2,1}-C_7H_7)$, and $(\eta^5-C_7H_7)_2Cr_2(CO)_4$, respectively. The global minima for $(C_7H_7)_2Cr_2(CO)_n$ ($n = 3, 2$) have rearranged C_7H_7 groups. Singlet and triplet structures with heptahapto $\eta^7-C_7H_7$ rings are found for the dimetalloenes $(\eta^7-C_7H_7)_2Cr_2(CO)$ and $(\eta^7-C_7H_7)_2Cr_2$, with the singlet structures being of much lower energies in both cases.

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1. Introduction

Cycloheptatrienylmetal carbonyl chemistry dates back to the discovery of the cation $[(\eta^7-C_7H_7)Mo(CO)_3]^+$ (Fig. 1) by Dauben and Honnen [1,2] in 1958. This cation is also historically significant in providing the first example of a cycloheptatrienylmetal complex of any type. Subsequent work led to the discovery of the chromium and tungsten analogues $[(\eta^7-C_7H_7)M(CO)_3]^+$ ($M = Cr$ [3] and W [4]). Furthermore, the other early examples of cycloheptatrienylmetal complexes (Fig. 1), such as $(\eta^7-C_7H_7)V(\eta^5-C_5H_5)$ (Refs. [5,6]) and $(\eta^7-C_7H_7)V(CO)_3$ (Ref. [7]), were also heptahapto derivatives, in which all seven carbon atoms of the C_7H_7 ring are within bonding distance of the metal atom.

Shortly after its discovery, the molybdenum derivative $[(\eta^7-C_7H_7)Mo(CO)_3]^+$ was found to be a useful source of other cycloheptatrienyl derivatives, particularly through the iodide $(\eta^7-C_7H_7)Mo(CO)_2I$, which is readily obtained in good yield from the reaction of $[(\eta^7-C_7H_7)Mo(CO)_3]^+$ with iodide ion [8]. Exploration of the chemical reactivity of $(\eta^7-C_7H_7)Mo(CO)_2I$ soon uncov-

ered another feature of cycloheptatrienylmetal chemistry, namely the ability of the cycloheptatrienyl ring to form stable metal complexes in which not all seven carbon atoms of the C_7H_7 ring are within bonding distance of the metal atom. The first compound of this type to be discovered was the trihapto 18-electron complex $(\eta^3-C_7H_7)Mo(CO)_2(\eta^5-C_5H_5)$ (Fig. 2), which was obtained from the reaction of $(\eta^7-C_7H_7)Mo(CO)_2I$ with sodium cyclopentadienide in preference to the still unknown and presumably unstable 18-electron complex $(\eta^7-C_7H_7)Mo(CO)_2(\eta^1-C_5H_5)$ [9,10]. This observation is a critical one since it indicates that a C_7H_7 ring is more likely than a C_5H_5 ring to bond only partially to a transition metal leaving some uncomplexed carbon atoms. The next $\eta^3-C_7H_7$ derivative to be discovered was the cobalt carbonyl derivative [11] $(\eta^3-C_7H_7)Co(CO)_3$ (Fig. 2), obtained simply from the photolysis of $Co_2(CO)_8$ with cycloheptatriene. The ability of both vanadium and cobalt to form stable $C_7H_7M(CO)_3$ derivatives (Figs. 1 and 2), but with different hapticities of the C_7H_7 rings, indicates the flexibility of such seven-membered rings in adapting their bonding mode to the electronic requirements of the central metal atom.

The analogy between $(\eta^5-C_5H_5)Fe(CO)_2I$ and $(\eta^7-C_7H_7)M(CO)_2I$ ($M = Cr, Mo, W$) suggests similar analogies between the corresponding binuclear derivatives $(\eta^5-C_5H_5)_2Fe_2(CO)_n$ and $(\eta^7-C_7H_7)_2M_2(CO)_n$ ($M = Cr, Mo, W$). For the iron systems both *cis* [12] and *trans* [13–15] isomers of $(\eta^5-C_5H_5)_2Fe_2(CO)_2(\mu-CO)_2$ with

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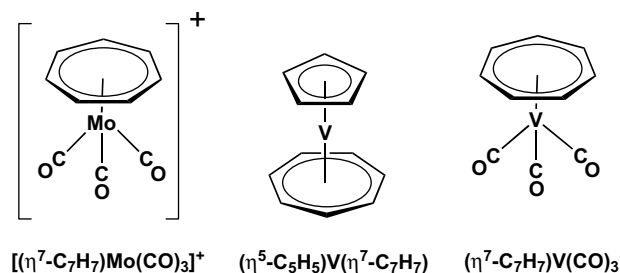


Fig. 1. Some early $\eta^7\text{-C}_7\text{H}_7\text{M}$ derivatives.

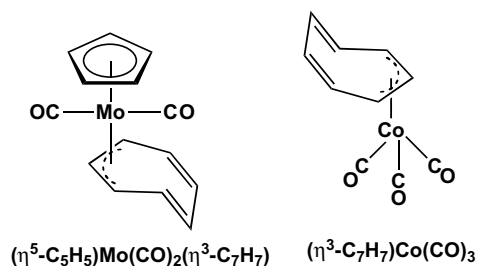


Fig. 2. Some early $\eta^3\text{-C}_7\text{H}_7\text{M}$ derivatives.

formal Fe–Fe single bonds, as well as $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\mu\text{-CO})_3$ with a formal $\sigma + \frac{2}{3}\pi$ Fe=Fe double bond of triplet spin multiplicity, are stable compounds [16–19], characterized structurally by X-ray diffraction. Furthermore, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\mu\text{-CO})_2$, with a formal Fe≡Fe triple bond, is a probable intermediate in the pyrolysis of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2$ to give the tetrahedral Fe_4 cluster [20] $(\eta^5\text{-C}_5\text{H}_5)_4\text{Fe}_4(\mu_3\text{-CO})_4$. However, analogous binuclear $(\text{C}_7\text{H}_7)_2\text{M}_2(\text{CO})_n$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) derivatives have never been synthesized, despite the availability for more than 45 years of possible precursors such as $(\eta^7\text{-C}_7\text{H}_7)\text{M}(\text{CO})_2$.

This paper reports a density functional theory (DFT) study on the binuclear cycloheptatrienylchromium derivatives $(\text{C}_7\text{H}_7)_2\text{Cr}_2(\text{CO})_n$ ($n = 6, 5, 4, 3, 2, 1$). The objective of this research is to determine whether differences between $\text{C}_7\text{H}_7\text{M}$ and $\text{C}_5\text{H}_5\text{M}$ bonding lead to different types of structures than those found in the formally isoelectronic $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_n$ ($n = 4, 3, 2, 1$). A wider range of stoichiometries was chosen than in an earlier DFT study [21] of the apparently isoelectronic iron derivatives $(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_n$ ($n = 4, 3, 2, 1$) in view of the anticipated much greater possibility of a C_7H_7 ring to bond to a metal atom through only a subset of its seven carbon atoms, such as in the trihapto $\eta^3\text{-C}_7\text{H}_7$ derivatives depicted in Fig. 2.

The results from this DFT study turned out to be very striking in that essentially no analogies whatsoever were found between the chemistry of isoelectronic $(\text{C}_7\text{H}_7)_2\text{Cr}_2(\text{CO})_n$ and $(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_n$ derivatives. For the $(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_n$ compounds, including those mentioned above, the five-membered ring always uses all five of its carbon atoms for metal–carbon bonding, thereby forming $\eta^5\text{-C}_5\text{H}_5$ derivatives. The iron–iron distance varies according to the formal bond order required to give the iron atoms the favored 18-electron configuration. However, for the isoelectronic $(\text{C}_7\text{H}_7)_2\text{Cr}_2(\text{CO})_n$ derivatives the Cr≡Cr distance varies little (from 2.4 to 2.5 Å) as the number of carbonyl groups is varied. These predicted Cr≡Cr distances are approximately what might be expected for a formal chromium–chromium triple bond. The hapticities of the C_7H_7 rings range from 1 to 5 as needed to give the chromium atoms reasonable electronic configurations, normally 16- or 18-electron configurations for the singlet structures. Only for the monocar-

bonyl $(\text{C}_7\text{H}_7)_2\text{Cr}_2(\text{CO})$ and the carbonyl-free dimetallocene-like structure $(\text{C}_7\text{H}_7)_2\text{Cr}_2$ are heptahapto structures found to be the global minima. For all of the other $(\text{C}_7\text{H}_7)_2\text{Cr}_2(\text{CO})_n$ systems, the relatively small number of heptahapto structures were all found to be high-energy structures.

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 [22–29]. Two DFT methods were used in this study. The first functional is the hybrid B3LYP method, which incorporates Becke's three-parameter exchange 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 (P86) [32,33]. It has been noted that the BP86 method may be somewhat more reliable than the B3LYP method for the types of organometallic systems considered in this paper [34–36].

For carbon and oxygen, the double- ζ plus polarization (DZP) basis set used here (9s5p/4s2p) adds one set of pure spherical harmonic d functions with orbital exponents $\alpha_d(\text{C}) = 0.75$ and $\alpha_d(\text{O}) = 0.85$ to the Huzinaga–Dunning standard contracted DZ sets [37,38]. For Cr, in our loosely contracted DZP basis set, the Wachters' primitive set is used, but augmented by two sets of p functions and one set of d functions and contracted following Hood et al., and designated (14s11p6d/10s8p3d) [39,40]. For the binuclear cycloheptatrienylchromium carbonyls $(\text{C}_7\text{H}_7)_2\text{Cr}_2(\text{CO})_6$, $(\text{C}_7\text{H}_7)_2\text{Cr}_2(\text{CO})_5$, $(\text{C}_7\text{H}_7)_2\text{Cr}_2(\text{CO})_4$, $(\text{C}_7\text{H}_7)_2\text{Cr}_2(\text{CO})_3$, $(\text{C}_7\text{H}_7)_2\text{Cr}_2(\text{CO})_2$, and $(\text{C}_7\text{H}_7)_2\text{Cr}_2(\text{CO})$, there are 548, 518, 488, 458, 428, and 398 contracted Gaussian basis functions, respectively. For $(\text{C}_7\text{H}_7)_2\text{Cr}_2$, there are 368 contracted Gaussian basis functions.

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 are evaluated analytically as well. All of the computations were carried out with the GAUSSIAN 94 program [41] in which the fine grid (75302) is the default for evaluating integrals numerically, and the tight (10^{-8} Hartree) designation is the default for the energy convergence.

Symmetry constraints were used in the initial stages of the optimizations in most cases. Subsequent optimization was carried out by following normal modes corresponding to significant imaginary vibrational frequencies. However, low magnitude imaginary vibrational frequencies are suspect because of significant limitations in the numerical integration procedures used in standard DFT computations. Thus imaginary vibrational frequencies with magnitudes less than $50i \text{ cm}^{-1}$ are considered questionable, and thus were not always pursued in the optimizations [42–44].

3. Results

3.1. Molecular structures

3.1.1. $(\text{C}_7\text{H}_7)_2\text{Cr}_2(\text{CO})_6$

Four energetically low-lying structures were found for $(\text{C}_7\text{H}_7)_2\text{Cr}_2(\text{CO})_6$ (Fig. 3 and Tables 1 and 2) from the initial geometries $(\eta^7\text{-C}_7\text{H}_7)\text{Cr}_2(\text{CO})_6(\eta^3\text{-C}_7\text{H}_7)$ and $(\eta^5\text{-C}_7\text{H}_7)\text{Cr}_2(\text{CO})_6(\eta^5\text{-C}_7\text{H}_7)$. The global minimum of $(\text{C}_7\text{H}_7)_2\text{Cr}_2(\text{CO})_6$ is an unsymmetrical singlet structure $(\eta^5\text{-C}_7\text{H}_7)(\text{OC})_2\text{Cr}\equiv\text{Cr}(\text{CO})_4(\eta^1\text{-C}_7\text{H}_7)$ (**1a-s**) with one pentahapto C_7H_7 ring and one monohapto C_7H_7 ring as indicated by the Cr–C distances. The singlet structure $(\eta^3\text{-C}_7\text{H}_7)(\text{OC})_3\text{Cr}\equiv\text{Cr}$

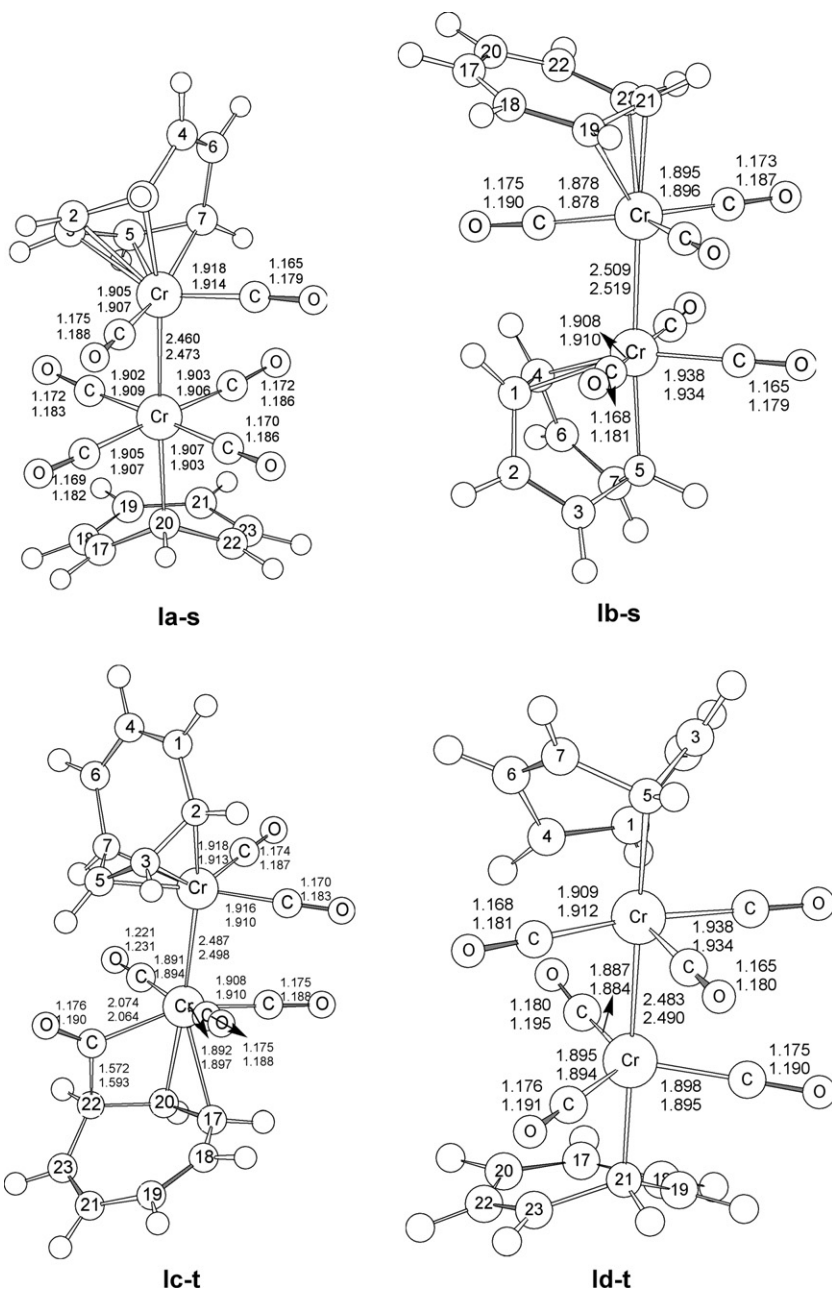


Fig. 3. The optimized structures of $(C_7H_7)_2Cr_2(CO)_6$. All bond distances are in Å.

Table 1

Bond distances (in Å), total energies (E in Hartree), and relative energies (ΔE in kcal/mol) for the $(C_7H_7)_2Cr_2(CO)_6$ structures

	Ia-s (C_1)		Ib-s (C_2)		Ic-t (C_1)		Id-t (C_1)	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Cr–Cr	2.460	2.473	2.509	2.519	2.487	2.498	2.483	2.490
–Energy	3306.524490	3306.83566	3306.48084	3306.79891	3306.47287	3306.78558	3306.46065	3306.76936
ΔE	0.0	0.0	27.4	23.1	32.4	31.4	40.1	41.6
Imaginary frequencies	None	None	None	47i	None	None	None	None
$\langle S^2 \rangle$	0.00	0.00	0.00	0.00	2.03	2.01	2.02	2.01

$(CO)_3(\eta^{2,1}-C_7H_7)$ (**Ib-s**) with two trihapto C_7H_7 rings of different types lies 27.4 kcal/mol (B3LYP) or 23.1 kcal/mol (BP86) above the singlet global minimum **Ia-s**. In structure **Ib-s** the three carbons of one of the trihapto C_7H_7 rings (designated as η^3) are adjacent car-

bons whereas the three carbons of the other trihapto rings are non-adjacent carbons (designated as $\eta^{2,1}$). The triplet structures **Ic-t** and **Id-t** at the relatively high energies of 32.4 kcal/mol (B3LYP)/31.4 kcal/mol (BP86) or 40.1 kcal/mol (B3LYP)/41.6 kcal/

Table 2
Chromium–carbon(cycloheptatrienyl) distances (in Å) for the $(C_7H_7)_2Cr_2(CO)_6$ structures

	Ia-s (C_1)		Ib-s (C_s)		Ic-t (C_1)		Id-t (C_1)	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
C1Cr	2.108	2.111	2.248	2.244	3.171	3.204	2.242	2.237
C2Cr	2.214	2.211	3.049	3.048	2.129	2.159	3.042	3.039
C3Cr	2.311	2.291	3.011	3.012	2.223	2.154	3.004	3.004
C4Cr	3.061	3.069	2.248	2.244	3.360	3.597	2.258	2.247
C5Cr	2.253	2.237	2.144	2.138	2.213	2.166	2.139	2.132
C6Cr	3.062	3.070	3.049	3.048	3.164	3.191	3.051	3.046
C7Cr	2.126	2.133	3.011	3.012	2.081	2.098	3.008	3.007
C17Cr	3.145	3.148	4.006	4.023	2.385	2.384	4.392	4.424
C18Cr	3.940	3.929	3.357	3.369	3.375	3.380	3.923	3.859
C19Cr	4.276	4.252	2.265	2.274	4.258	4.266	3.045	2.939
C20Cr	2.164	2.160	4.006	4.023	2.193	2.168	4.386	4.419
C21Cr	4.274	4.248	2.099	2.093	4.598	4.592	2.095	2.097
C22Cr	3.141	3.142	3.357	3.369	2.796	2.775	3.911	3.848
C23Cr	3.935	3.922	2.265	2.274	4.103	4.086	3.034	2.928

mol (BP86), respectively, above the global minimum **Ia-s** are related to the corresponding singlet structures. However, in the triplet structure **Ic-t** one of the carbonyl groups on the chromium atom bearing four carbonyl groups (the “bottom” chromium atom in Fig. 3) has inserted into the chromium–carbon bond to give a trihapto $\eta^3-C_7H_7CO$ ligand. The Cr–Cr bond distances for the singlet and triplet structures for $(C_7H_7)_2Cr_2(CO)_6$ fall in the relatively narrow range 2.460–2.509 Å and are interpreted as formal Cr≡Cr triple bonds.

3.1.2. $(C_7H_7)_2Cr_2(CO)_5$

The singlet and triplet structures **Ila-s** and **Ilb-t** (Fig. 4 and Tables 3 and 4) are obtained for $(C_7H_7)_2Cr_2(CO)_5$ upon optimization of singlet and triplet unbridged starting structures. The optimized singlet structure ($\eta^3-C_7H_7$)(OC) $_2$ Cr≡Cr(CO) $_3$ ($\eta^{2,1}-C_7H_7$) (**Ila-s**) is the global minimum with all real vibrational frequencies. This structure (Fig. 4) can be derived from **Ib-s** (Fig. 3) by loss of one carbonyl group from the chromium atom bearing the $\eta^3-C_7H_7$ ring (the “top” chromium atom in the figures). The Cr≡Cr bond

Table 3
Bond distances (in Å), total energies (E in Hartree), and relative energies (ΔE in kcal/mol) for the $(C_7H_7)_2Cr_2(CO)_5$ structures

	Ila-s (C_1)		Ilb-t (C_1)	
	B3LYP	BP86	B3LYP	BP86
Cr–Cr	2.463	2.472	2.508	2.498
–Energy	3193.11429	3193.41936	3193.10044	3193.40575
ΔE	0.0	0.0	8.7	8.5
Imaginary frequencies (S^2)	None	None	None	None
$\langle S^2 \rangle$	0.00	0.00	2.01	2.00

Table 4
Chromium–carbon(cycloheptatrienyl) distances (in Å) for the $(C_7H_7)_2Cr_2(CO)_5$ structures

	Ila-s (C_1)		Ilb-t (C_1)	
	B3LYP	BP86	B3LYP	BP86
C1Cr	3.189	3.235	3.245	3.271
C2Cr	2.043	2.046	2.056	2.067
C3Cr	2.048	2.047	1.943	1.953
C4Cr	3.800	3.846	3.910	3.944
C5Cr	2.109	2.125	2.091	2.140
C6Cr	3.759	3.761	3.903	3.924
C7Cr	3.142	3.117	3.246	3.257
C17Cr	2.274	2.266	2.213	2.209
C18Cr	3.064	3.062	3.050	3.050
C19Cr	3.017	3.017	3.016	3.018
C20Cr	2.247	2.242	2.190	2.192
C21Cr	2.135	2.127	2.124	2.118
C22Cr	3.042	3.039	2.971	2.963
C23Cr	3.000	2.998	2.944	2.935

distance for **Ila-s** is 2.463 Å (B3LYP) or 2.472 Å (BP86), consistent with the triple bond giving one metal atom (the “bottom” one in Fig. 4) the favored 18-electron configuration and the other metal atom (the “top” Cr in Fig. 4) only a 16-electron configuration. The triplet structure **Ilb-t** lying 8.7 kcal/mol (B3LYP) or 8.5 kcal/mol

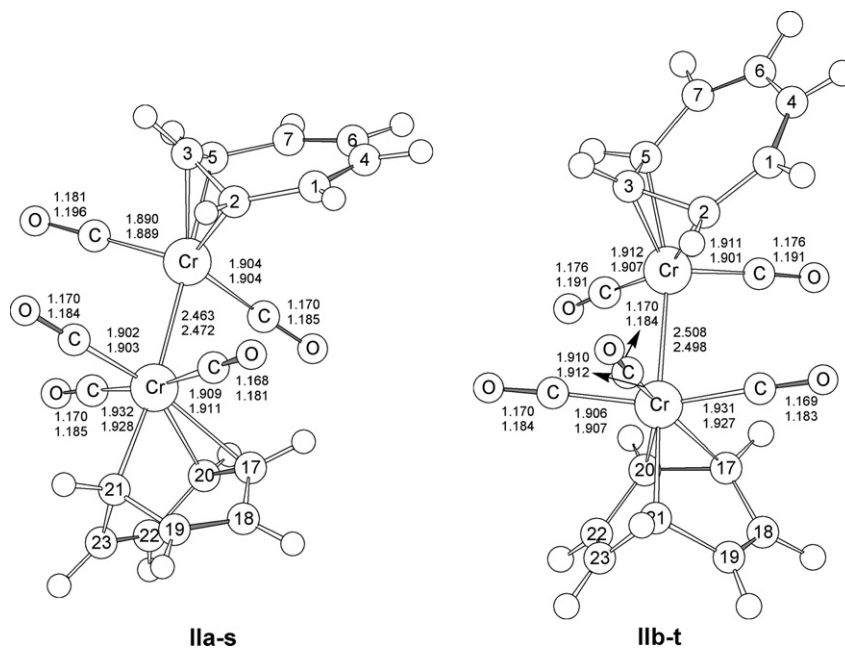


Fig. 4. Optimized structures of $(C_7H_7)_2Cr_2(CO)_5$. All bond distances are in Å.

(BP86) is very similar to the singlet structure **IIa-s**. The Cr–Cr bond distance (2.508 Å by B3LYP or 2.498 Å by BP86) in the triplet structure **IIb-t** is longer than that for the corresponding singlet structure **IIa-s** by 0.043 Å (B3LYP) or 0.026 Å (BP86).

3.1.3. $(C_7H_7)_2Cr_2(CO)_4$

Four starting structures of $(C_7H_7)_2Cr_2(CO)_4$, namely doubly CO-bridged *cis* and *trans* structures as well as unbridged *cis* and *trans* structures, were optimized using the B3LYP and BP86 methods. The global minimum of $(C_7H_7)_2Cr_2(CO)_4$ was found to be the doubly semibridged singlet structure $(\eta^5-C_7H_7)_2Cr_2(CO)_4$ (**IIIa-s**), which has two pentahapto C_7H_7 rings and two semibridging carbonyl groups (Fig. 5 and Tables 5 and 6). This structure is closely related to the structure of the cyclopentadienylchromium carbonyl $(\eta^5-C_5H_5)_2Cr_2(CO)_4$, which has been synthesized and characterized

by X-ray diffraction [45]. The Cr≡Cr distance of 2.421 Å (B3LYP) or 2.433 Å (BP86) can be interpreted to be the formal triple bond needed to give both chromium atoms the favored 18-electron configuration. However, this Cr≡Cr distance in **IIIa-s** is ~ 0.2 Å longer than the experimentally determined [45] distance of 2.23 Å for the likewise formal Cr≡Cr triple bond found in the conventional structure $(\eta^5-C_5H_5)_2Cr_2(CO)_4$. A second singlet structure of $(C_7H_7)_2Cr_2(CO)_4$, namely **IIIc-s** at 22.0 kcal/mol (B3LYP) or 19.9 kcal/mol (BP86) above **IIIa-s**, also has two pentahapto C_7H_7 rings and may be considered to be a high energy stereoisomer of **IIIa-s**. The Cr≡Cr bond distances in **IIIc-s** of 2.456 Å (B3LYP) or 2.466 Å (BP86) are ~ 0.03 Å longer than those in **IIIa-s**, which can be considered to be a minor difference.

The most unusual singlet structure of $(C_7H_7)_2Cr_2(CO)_4$ is **IIIb-s** (Fig. 5 and Tables 5 and 6), which lies 3.2 kcal/mol (B3LYP) or

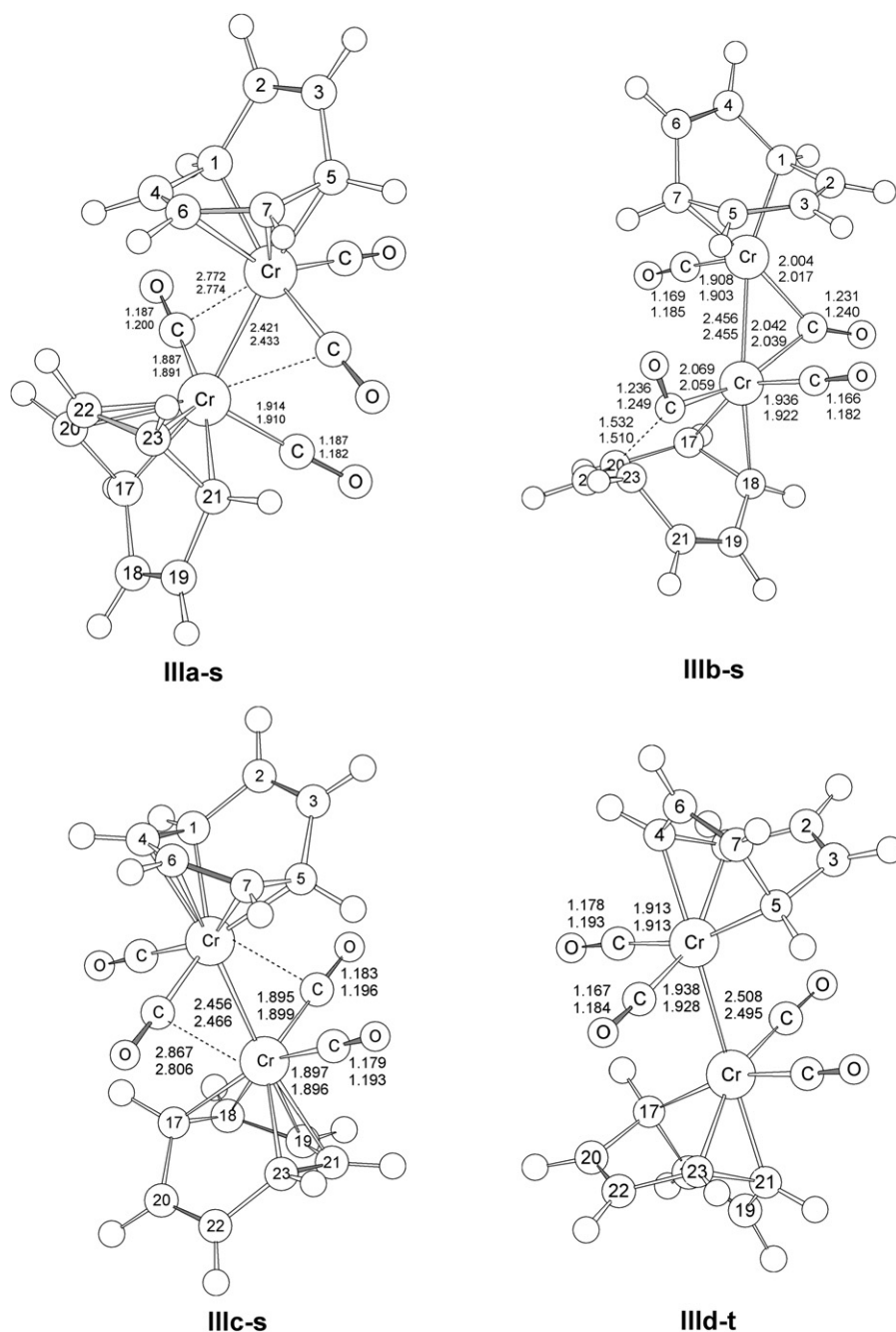


Fig. 5. Optimized structures of $(C_7H_7)_2Cr_2(CO)_4$. All bond distances are in Å.

Table 5
Bond distances (in Å), total energies (E in Hartree), and relative energies (ΔE in kcal/mol) for the $(C_7H_7)_2Cr_2(CO)_4$ structures

	<i>cis</i> -(C_7H_7) ₂ Cr ₂ (CO) ₂ (μ -CO) ₂ IIIa-s (C ₁)		(C_7H_7) ₂ Cr ₂ (CO) ₃ (μ -CO) IIIb-s (C ₁)		<i>trans</i> -(C_7H_7) ₂ Cr ₂ (CO) ₂ (μ -CO) ₂ IIIc-s (C ₁)		<i>trans</i> -(C_7H_7) ₂ Cr ₂ (CO) ₄ IIId-t (C _i)	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Cr–Cr	2.421	2.433	2.456	2.455	2.456	2.466	2.508	2.495
Cr–C(bridge)	1.887/2.772	1.891/2.774	2.004	2.017	1.895/2.867	1.899/2.806	–	–
Cr–C(terminal)	1.914	1.910	1.908	1.903	1.897	1.896	1.913/1.938	1.913/1.928
			1.936	1.922				
			2.069	2.059				
C–O(bridge)	1.187	1.200	1.231	1.240	1.183	1.196	–	–
C–O(terminal)	1.167	1.182	1.169	1.185	1.179	1.193	1.178/1.167	1.193/1.184
			1.166	1.182				
			1.236	1.249				
–Energy	3079.77955	3080.08382	3079.77452	3080.06053	3079.74457	3080.05214	3079.74358	3080.03747
ΔE	0.0	0.0	3.2	14.6	22.0	19.9	22.6	29.1
Imaginary frequencies	None	None	None	None	None	None	44i	11i

Table 6
Chromium–carbon(cycloheptatrienyl) distances (in Å) for the $(C_7H_7)_2Cr_2(CO)_4$ structures

	IIIa-s (C ₂)		IIIb-s (C _s)		IIIc-s (C ₁)		IIId-t (C _i)	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
C1Cr	2.118	2.124	2.049	2.054	2.152	2.157	2.023	2.047
C2Cr	3.056	3.065	2.180	2.184	3.107	3.119	2.919	2.913
C3Cr	3.056	3.064	2.300	2.282	3.093	3.105	2.942	2.931
C4Cr	2.256	2.239	2.948	2.947	2.196	2.188	2.030	2.043
C5Cr	2.098	2.102	2.259	2.247	2.108	2.117	2.108	2.109
C6Cr	2.327	2.306	2.943	2.941	2.326	2.301	2.907	2.921
C7Cr	2.221	2.218	2.052	2.054	2.245	2.228	2.916	2.930
C17Cr	2.098	2.102	1.999	2.006	2.108	2.117	2.108	2.109
C18Cr	3.056	3.064	2.003	2.019	2.245	2.228	2.916	2.930
C19Cr	3.056	3.065	3.083	3.101	2.326	2.301	2.907	2.921
C20Cr	2.221	2.218	3.096	3.097	3.093	3.105	2.942	2.931
C21Cr	2.118	2.124	3.481	3.496	2.196	2.188	2.030	2.043
C22Cr	2.327	2.306	3.509	3.510	3.107	3.119	2.919	2.913
C23Cr	2.256	2.239	3.125	3.126	2.152	2.157	2.023	2.047

14.6 kcal/mol (BP86) above **IIIa-s**. The most conspicuous structural feature in **IIIb-s** is the carbonyl insertion into the M–C₇H₇ bond (the bottom ring of **IIIb-s** in Fig. 5) to give a trihapto η^3 -C₇H₇CO group.

The other C₇H₇ ring is clearly a pentahapto ring (see distances in Table 6). Each chromium atom in **IIIb-s** has a terminal carbonyl group. The remaining carbonyl group bridges the chromium–chromium bond. The Cr=Cr distance of 2.456 Å (B3LYP) or 2.455 Å (BP86) in **IIIb-s** is in the typical range found in most of the $(C_7H_7)_2Cr_2(CO)_n$ derivatives discussed in this paper and can be interpreted as a formal triple bond.

One triplet structure (Fig. 5 and Tables 5 and 6) was also found for $(C_7H_7)_2Cr_2(CO)_4$ within 30 kcal/mol of the global minimum, namely **IIId-t** at 22.6 kcal/mol (B3LYP) or 29.1 kcal/mol (BP86) above **IIIa-s**. Structure **IIId-t** is a *trans* unbridged structure with two tetrahapto η^4 -C₇H₇ rings, which means that the unpaired electrons must lie on the rings, at least formally. The Cr=Cr distance of 2.508 Å (B3LYP) or 2.495 Å (BP86) is somewhat longer than that in **IIIa-s**. This might mean that **IIId-t** has a formal Cr=Cr double bond, which would give both chromium atoms the 16-electron configuration with unpaired electrons on each η^4 -C₇H₇ ring leading to the triplet spin state.

3.1.4. $(C_7H_7)_2Cr_2(CO)_3$

Initial structures of $(C_7H_7)_2Cr_2(CO)_3$ having three, two, or one bridging CO groups were optimized leading to one singlet structure

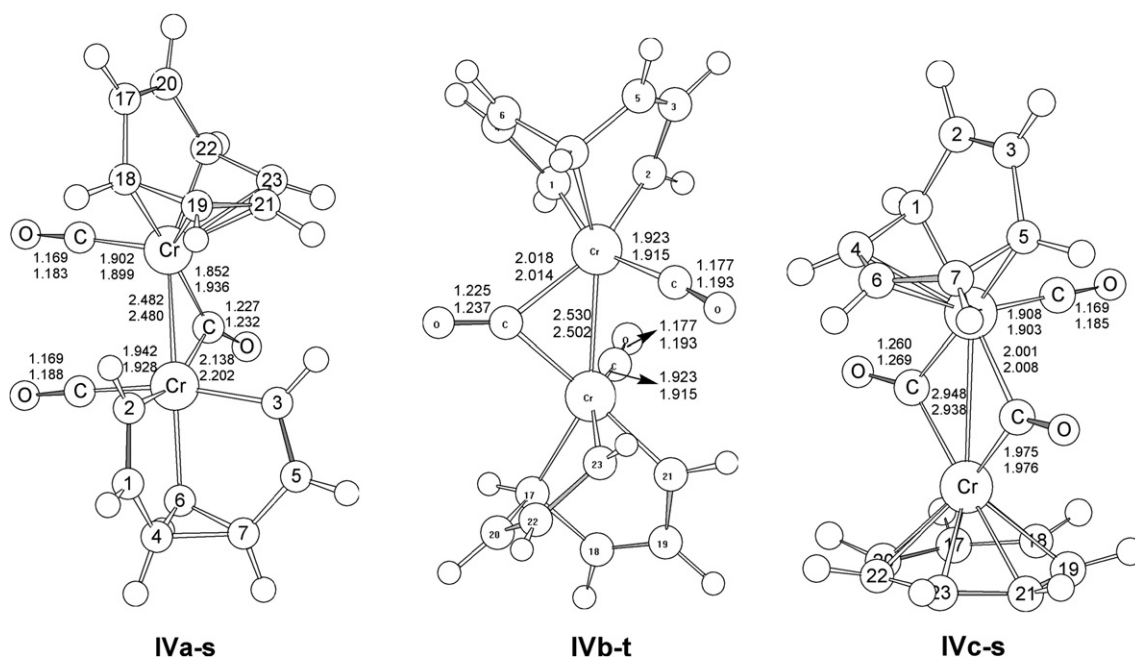
**Fig. 6.** Optimized structures of $(C_7H_7)_2Cr_2(CO)_3$. All bond distances are in Å.

Table 7Bond distances (in Å), total energies (E in Hartree), and relative energies (ΔE in kcal/mol) for the singlet $(C_7H_7)_2Cr_2(CO)_3$ structures

	$(C_7H_7)_2Cr_2(CO)_2(\mu-CO)$ IVa-s (C_1)		$(C_7H_7)_2Cr_2(\mu-CO)_3$ IVb-t (C_2)		$(C_7H_7)_2Cr_2(CO)(\mu-CO)_2$ IVc-s (C_1)	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Cr–Cr	2.482	2.480	2.530	2.502	2.948	2.938
Cr–C(bridge)	1.952/2.138	1.936/2.202	2.018	2.014	2.001/1.975	2.008/1.976
Cr–C(terminal)	1.902/1.942	1.899/1.928	1.923	1.915	1.908	1.903
C–O(bridge)	1.227	1.232	1.225	1.237	1.260	1.269
C–O(terminal)	1.169/1.169	1.183/1.188	10.177	1.193	1.169	1.185
–Energy	2966.43565	2966.71776	2966.38177	2966.66056	2966.36811	2966.65991
ΔE	0.0	0.0	33.8	35.9	42.4	36.3
Imaginary frequencies	None	None	None	None	None	None

Table 8Chromium–carbon(cycloheptatrienyl) distances (in Å) for the $(C_7H_7)_2Cr_2(CO)_3$ structures

	IVa-s (C_1)		IVb-t (C_2)		IVc-s (C_1)	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
C1Cr	2.832	2.837	1.994	2.016	2.063	2.067
C2Cr	1.991	1.985	1.992	2.007	2.968	2.973
C3Cr	2.008	2.003	2.858	2.863	2.968	2.973
C4Cr	2.899	2.900	2.876	2.878	2.213	2.214
C5Cr	2.884	2.893	2.865	2.866	2.063	2.067
C6Cr	2.063	2.063	2.887	2.880	2.270	2.261
C7Cr	2.952	2.960	2.066	2.061	2.214	2.215
C17Cr	2.969	2.987	2.066	2.061	2.209	2.197
C18Cr	2.065	2.075	2.865	2.867	2.096	2.112
C19Cr	2.271	2.248	2.858	2.863	2.187	2.197
C20Cr	2.972	2.990	2.887	2.880	2.224	2.221
C21Cr	2.320	2.301	1.992	2.007	2.226	2.221
C22Cr	2.072	2.086	2.876	2.878	2.114	2.140
C23Cr	2.218	2.226	1.994	2.016	2.148	2.141

(IVa-s) more than 30 kcal/mol below any other $(C_7H_7)_2Cr_2(CO)_3$ structure (Fig. 6 and Tables 7 and 8). The triply bridged structure $(C_7H_7)_2Cr_2(\mu-CO)_3$ was found to collapse to the singly bridged structure $(C_7H_7)_2Cr_2(CO)_2(\mu-CO)$ (**IVa-s**).

The obviously favorable $(C_7H_7)_2Cr_2(CO)_3$ structure **IVa-s** (Fig. 6 and Tables 7 and 8) has a number of unusual features. One of its C_7H_7 rings (the “lower” one in Fig. 6) has undergone a transannular rearrangement to give a tridentate cyclopropyl divinyl ligand similar to that predicted in previous work [46] to be present in the lowest energy structure of $(C_7H_7)_2Cr$. The other C_7H_7 ring (the “upper” one in Fig. 6) remains intact and bonds to the chromium atom as a $\eta^5-C_7H_7$ pentahapto ligand. Each chromium atom bears a terminal carbonyl group. The remaining carbonyl group bridges the $Cr\equiv Cr$ bond, which has the typical 2.482 Å (B3LYP) or 2.480 Å (BP86) distance interpreted to be a formal triple bond.

Two high energy structures were also found for $(C_7H_7)_2Cr_2(CO)_3$ (Fig. 6 and Tables 7 and 8). The triplet structure **IVb-t**, at 33.8 kcal/mol (B3LYP) or 35.9 kcal/mol (BP86) above **IVa-s**, has two trihapto C_7H_7 ligands, two terminal carbonyl groups, and a carbonyl group bridging the chromium–chromium bond. The trihapto C_7H_7 ligands are rather unusual ones, since one of the C–C bonds of the C_7H_7 ring has been broken, making a bis(carbene)alkyl ligand donating a total of five electrons through three metal–carbon bonds. If the $Cr\equiv Cr$ bond distance of 2.530 Å (B3LYP) or 2.502 Å (BP86) is still considered to be within the range of a formal metal–metal triple bond, then each chromium atom has the 17–electron configuration expected for a triplet spin state, since it receives five electrons from

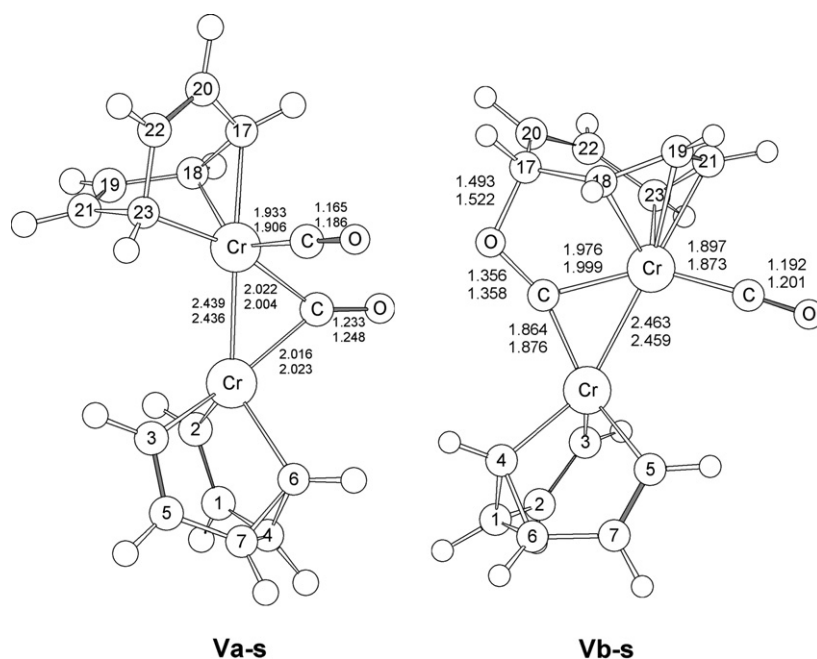
**Fig. 7.** Optimized structures of $(C_7H_7)_2Cr_2(CO)_2$. All bond distances are in Å.

Table 9

Bond distances (in Å), total energies (E in Hartree), and relative energies (ΔE in kcal/mol) for the $(C_7H_7)_2Cr_2(CO)_2$ structures

	Va-s (C_1)		Vb-s (C_1)	
	B3LYP	BP86	B3LYP	BP86
Cr–Cr	2.439	2.436	2.463	2.459
Cr–C(bridge)	2.022 2.016	2.004 2.023	1.976 1.864	1.999 1.876
Cr–C(terminal)	1.933	1.906	1.897	1.873
C–O(bridge)	1.233	1.248	1.356	1.358
C–O(terminal)	1.165	1.186	1.192	1.201
–Energy	2853.07782	2853.34199	2853.06412	2853.32487
ΔE	0.0	0.0	8.6	10.7
Imaginary frequencies (S^2)	None	None	None	None

Table 10

Chromium–carbon (in cycloheptatrienyl rings) distances (in Å) for the $(C_7H_7)_2Cr_2(CO)_2$ structures

	Va-s (C_1)		Vb-s (C_1)	
	B3LYP	BP86	B3LYP	BP86
C1Cr	2.807	2.820	2.897	2.900
C2Cr	1.985	1.985	2.832	2.839
C3Cr	1.991	1.991	1.989	1.986
C4Cr	2.864	2.873	2.048	2.049
C5Cr	2.837	2.851	1.992	1.990
C6Cr	2.031	2.032	2.927	2.936
C7Cr	2.896	2.908	2.857	2.869
C17Cr	2.049	2.071	2.889	2.904
C18Cr	2.033	2.166	2.050	2.053
C19Cr	2.728	2.352	2.253	2.210
C20Cr	2.946	2.983	3.404	3.420
C21Cr	2.730	2.336	2.227	2.184
C22Cr	2.944	2.976	3.099	3.110
C23Cr	2.057	2.062	2.036	2.038

the C_7H_7 ligand, two electrons from the terminal carbonyl group, one electron from the shared bridging carbonyl group, and three electrons from the formal $Cr=Cr$ triple bond.

The high energy singlet structure **IVc-s** at 42.4 kcal/mol (B3LYP) or 36.3 kcal/mol (BP86) above **IVa-s** (Fig. 6 and Table 7) is the structure with the largest number of carbonyl groups found in this research having a heptahapto $\eta^7-C_7H_7$ ring using all of its carbon atoms to bond to one of the metal atoms. The other C_7H_7 ring is a pentahapto $\eta^5-C_7H_7$ ring. The Cr–Cr distance of 2.948 Å (B3LYP) or 2.938 Å (BP86) in **IVc-s** is the longest such distance found in this work and may be considered to correspond to a for-

Table 11

Bond distances (in Å), total energies (E in Hartree), and relative energies (ΔE in kcal/mol) for the singlet $(C_7H_7)_2Cr_2(CO)$ structures

	$(C_7H_7)_2Cr_2$ ($\mu-CO$) Vla-s (C_{2v})		$(C_7H_7)_2Cr_2$ ($\mu-CO$) Vlb-t (C_s)	
	B3LYP	BP86	B3LYP	BP86
Cr–Cr	2.403	2.408	2.363	2.356
Cr–C(bridge)	1.995	2.004	1.967	1.992
C–O(bridge)	1.240	1.248	1.243	1.244
–Energy	2739.59020	2739.87181	2739.52274	2739.81122
ΔE	0.0	0.0	42.3	38.0
Imaginary frequencies	None	None	None	14i

Table 12

Chromium–carbon(cycloheptatrienyl) distances (in Å) for the $(C_7H_7)_2Cr_2(CO)$ structures

	Vla-s (C_{2v})		Vlb-t (C_s)	
	B3LYP	BP86	B3LYP	BP86
C1Cr	2.205	2.194	2.205	2.183
C2Cr	2.186	2.136	2.121	2.162
C3Cr	2.123	2.224	2.189	2.166
C4Cr	2.186	2.205	2.211	2.185
C5Cr	2.231	2.224	2.240	2.210
C6Cr	2.123	2.194	2.150	2.171
C7Cr	2.231	2.136	2.144	2.153
C17Cr	2.205	2.194	2.205	2.183
C18Cr	2.186	2.136	2.121	2.162
C19Cr	2.123	2.224	2.189	2.166
C20Cr	2.186	2.205	2.211	2.185
C21Cr	2.231	2.224	2.240	2.210
C22Cr	2.123	2.194	2.150	2.171
C23Cr	2.231	2.136	2.144	2.153

mal single bond. This gives each chromium atom in **IVc-s** a 16-electron configuration. The interpretation of a Cr–Cr distance of ~ 2.9 Å as a formal single bond supports our interpretation of $Cr=Cr$ distances in the range 2.4–2.5 Å (found throughout this work) as formal triple bonds.

3.1.5. $(C_7H_7)_2Cr_2(CO)_2$

Six starting structures were optimized for $(C_7H_7)_2Cr_2(CO)_2$, including doubly bridged structures as well as *trans*- and *cis*-unbridged structures of both singlet and triplet spin multiplicities. This led to only two singlet structures, namely **Va-s** and **Vb-s** (Fig. 7 and Tables 9 and 10) within 70 kcal/mol of the global minimum.

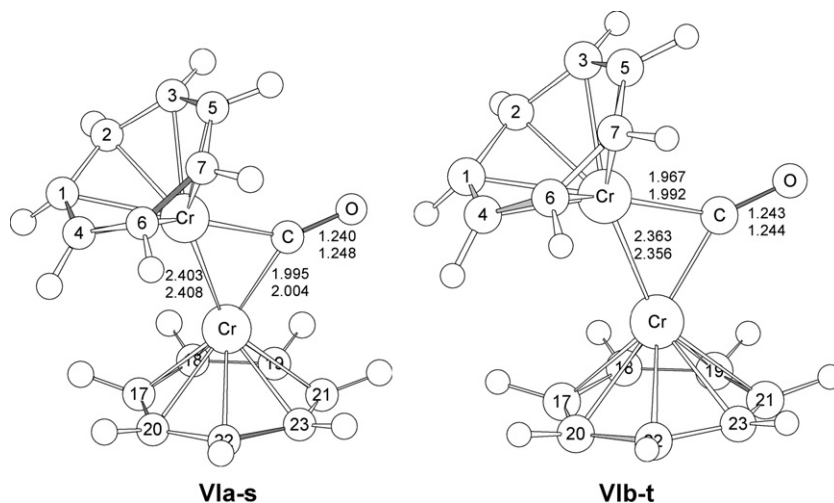


Fig. 8. Optimized geometries for the $(C_7H_7)_2Cr_2(CO)$ structures. All bond distances are in Å.

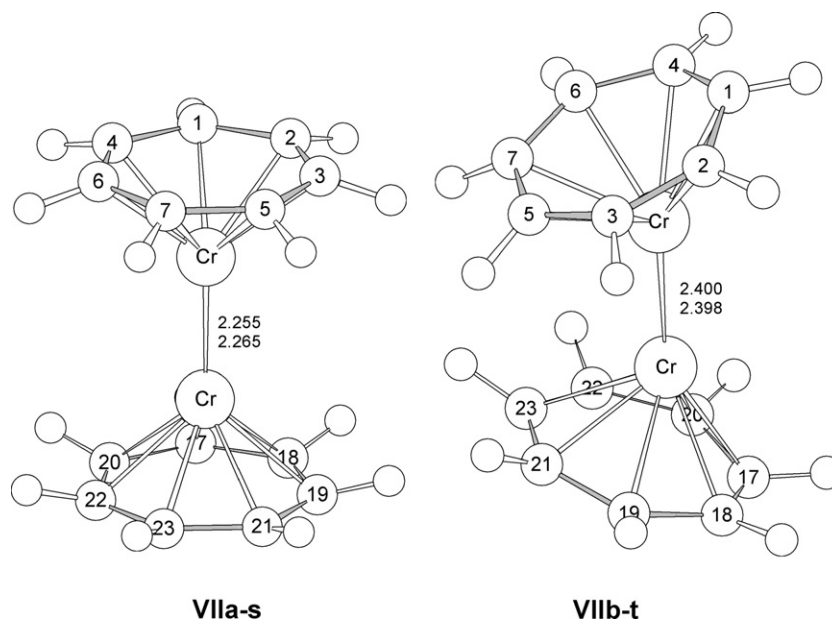


Fig. 9. Optimized geometries for the $(C_7H_7)_2Cr_2$ structures. All bond distances are in Å.

Table 13

Bond distances (in Å), total energies (E in Hartree), and relative energies (ΔE in kcal/mol) for the singlet $(C_7H_7)_2Cr_2$ structures

	VIIa-s (C_{2v})		VIIb-t (C_{2v})	
	B3LYP	BP86	B3LYP	BP86
Cr–Cr	2.255	2.265	2.400	2.398
Cr–C ₇ H ₇	2.163	2.166	2.200	2.200
–Energy	2626.14608	2626.41287	2626.08937	2626.36345
ΔE	0.0	0.0	35.6	31.0
Imaginary frequencies	None	None	None	None

Table 14

Chromium–carbon (in cycloheptatrienyl rings) distances (in Å) for the $(C_7H_7)_2Cr_2$ structures

	VIIa-s (C_{2v})		VIIb-t (C_{2v})	
	B3LYP	BP86	B3LYP	BP86
C1Cr	2.162	2.164	2.223	2.217
C2Cr	2.162	2.165	2.167	2.172
C3Cr	2.163	2.166	2.215	2.218
C4Cr	2.162	2.165	2.223	2.217
C5Cr	2.163	2.166	2.189	2.187
C6Cr	2.163	2.166	2.215	2.218
C7Cr	2.163	2.166	2.167	2.172
C17Cr	2.162	2.164	2.223	2.217
C18Cr	2.162	2.165	2.167	2.172
C19Cr	2.163	2.166	2.215	2.218
C20Cr	2.162	2.165	2.223	2.217
C21Cr	2.163	2.166	2.189	2.187
C22Cr	2.163	2.166	2.167	2.172
C23Cr	2.163	2.166	2.215	2.218

In the global minimum $(C_7H_7)_2Cr_2(CO)_2$ structure **Va-s** one of the C_7H_7 rings (the “lower” one in Fig. 7) has rearranged to a tridentate cyclopropyldivinyl ligand similar to that found in **IVa-s**. The other C_7H_7 ring remains intact as a 1,2,5-trihapto $\eta^{2,1}-C_7H_7$ ligand with two separated uncomplexed C=C double bonds.

The second singlet structure of $(C_7H_7)_2Cr_2(CO)_2$, namely **Vb-s** at 8.6 kcal/mol (B3LYP) or 10.7 kcal/mol (BP86) above **Va-s**, also has a tridentate cyclopropyldivinyl ligand (the “bottom” ring in Fig. 7). In addition, the carbonyl group bridging the two chromium atoms in

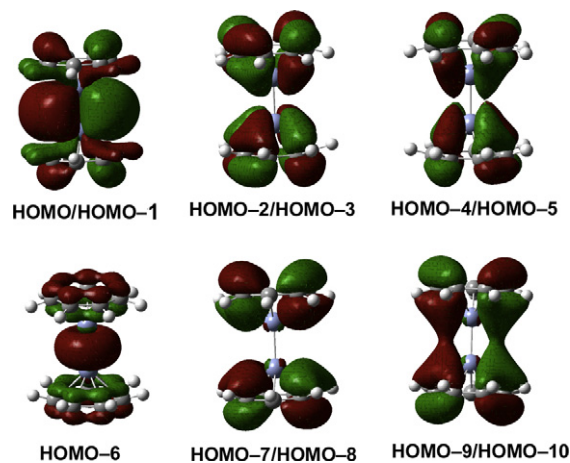


Fig. 10. The 11 highest lying filled orbitals in $(\eta^7-C_7H_7)_2Cr_2$.

Table 15

Energies (kcal/mol) for carbonyl dissociation and disproportionation of $(C_7H_7)_2Cr_2(CO)_n$ derivatives

	B3LYP	BP86
$(C_7H_7)_2Cr_2(CO)_6$ (Ia-s) \rightarrow $(C_7H_7)_2Cr_2(CO)_5$ (Ila-s) + CO	47.3	52.3
$(C_7H_7)_2Cr_2(CO)_5$ (Ila-s) \rightarrow $(C_7H_7)_2Cr_2(CO)_4$ (IIla-s) + CO	–0.1	1.6
$(C_7H_7)_2Cr_2(CO)_4$ (IIla-s) \rightarrow $(C_7H_7)_2Cr_2(CO)_3$ (IVa-s) + CO	5.7	20.8
$(C_7H_7)_2Cr_2(CO)_3$ (IVa-s) \rightarrow $(C_7H_7)_2Cr_2(CO)_2$ (Va-s) + CO	14.4	26.9
$(C_7H_7)_2Cr_2(CO)_2$ (Va-s) \rightarrow $(C_7H_7)_2Cr_2(CO)$ (Vla-s) + CO	95.9	86.2
$(C_7H_7)_2Cr_2(CO)$ (Vla-s) \rightarrow $(C_7H_7)_2Cr_2$ (VIIa-s) + CO	68.5	79.0
$2(C_7H_7)_2Cr_2(CO)_5$ (Ila-s) \rightarrow $(C_7H_7)_2Cr_2(CO)_6$ (Ia-s) + $(C_7H_7)_2Cr_2(CO)_4$ (IIla-s)	–47.3	–50.7
$2(C_7H_7)_2Cr_2(CO)_4$ (IIla-s) \rightarrow $(C_7H_7)_2Cr_2(CO)_5$ (Ila-s) + $(C_7H_7)_2Cr_2(CO)_3$ (IVa-s)	5.8	19.2
$2(C_7H_7)_2Cr_2(CO)_3$ (IVa-s) \rightarrow $(C_7H_7)_2Cr_2(CO)_4$ (IIla-s) + $(C_7H_7)_2Cr_2(CO)_2$ (Va-s)	8.7	6.1
$2(C_7H_7)_2Cr_2(CO)_2$ (Va-s) \rightarrow $(C_7H_7)_2Cr_2(CO)_3$ (IVa-s) + $(C_7H_7)_2Cr_2(CO)$ (Vla-s)	81.5	59.3
$2(C_7H_7)_2Cr_2(CO)$ (Vla-s) \rightarrow $(C_7H_7)_2Cr_2(CO)_2$ (Va-s) + $(C_7H_7)_2Cr_2$ (VIIa-s)	27.4	7.1

Vb-s has inserted into the metal–ring bond to the other C_7H_7 ring to form a bridging C_7H_7OC oxycarbene ligand, which functions

formally as a five-electron donor to the “top” chromium atom and a two-electron donor to the “bottom” chromium atom. In both **Va-s** and **Vb-s** the Cr=Cr distances fall in the typical 2.43–2.47 Å range found in this chemistry, and are tentatively assigned as formal triple bonds.

3.1.6. $(C_7H_7)_2Cr_2(CO)$

Optimizations have been carried out on singlet and triplet $(C_7H_7)_2Cr_2(CO)$ structures in which the single CO group is either bridging or terminal. The structures of $(C_7H_7)_2Cr_2(CO)$ with terminal carbonyl groups are not stationary points but collapse to the bridged stable isomers **Vla-s** and **Vlb-t** (Fig. 8 and Tables 11 and 12) upon optimization, for both the singlet and triplet spin states. The predicted global minimum for $(C_7H_7)_2Cr_2(CO)$ is the singlet C_{2v} structure **Vla-s**, which was found to have a small imaginary vibrational frequency of $13i\text{ cm}^{-1}$ (B3LYP) or $14i\text{ cm}^{-1}$ (BP86). The corresponding very similar triplet structure **Vlb-t** is much higher in energy lying 42.3 kcal/mol (B3LYP) or 38.0 kcal/mol (BP86) above **Vla-s**. The Cr=Cr distances in both **Vla-s** and **Vlb-t** fall in the range 2.36–2.41 Å consistent with formal triple bonds giving the metal atoms 17-electron configurations.

3.1.7. $(C_7H_7)_2Cr_2$

Bis(heptahapto) dimetallocene-type structures are found for both singlet and triplet $(\eta^7-C_7H_7)_2Cr_2$ (Fig. 9 and Tables 13 and 14). The C–C bond lengths in the C_7H_7 rings are 1.438 Å (B3LYP) or 1.447 Å (BP86) for the singlet structure **VIIa-s** having D_{7h} symmetry within 0.001 Å (Table 14) and parallel C_7H_7 rings. The bent C_s triplet structure $(\eta^7-C_7H_7)_2Cr_2$ (**VIIb-t**) is of considerably higher energy at 35.6 kcal/mol (B3LYP) or 31.0 kcal/mol (BP86) above **VIIa-s**.

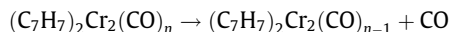
The Cr=Cr distance in **VIIa-s** at 2.255 Å (B3LYP) or 2.265 Å (BP86) is consistent with the triple bond required to give the Cr atoms 16-electron configurations. This interpretation of the chromium–chromium bonding in **VIIa-s** is supported by an analysis of its frontier bonding molecular orbitals (Fig. 10). Because of the sevenfold symmetry of the dimetallocene $(\eta^7-C_7H_7)_2Cr_2$, all except one of the highest lying 11 bonding MOs appear as degenerate pairs, of which only one member of each degenerate pair is shown in Fig. 10. The bonding MOs for the Cr=Cr triple bond in **VIIa-s** are seen to be the non-degenerate HOMO–6 for the σ bond and the degenerate pair HOMO and HOMO–1 for the two orthogonal π -bonds. The remaining four degenerate pairs of MOs for $(\eta^7-C_7H_7)_2Cr_2$ in Fig. 10 do not correspond to significant metal–metal bonding but instead are mainly localized on the rings. Most significantly, no MOs are seen corresponding to the δ bonding components that would be required for a chromium–chromium quintuple bond.

The significantly shorter Cr=Cr triple bond distance in singlet $(\eta^7-C_7H_7)_2Cr_2$ than in the singlet metal carbonyls $(\eta^7-C_7H_7)_2Cr_2(CO)_n$ may relate to the lack of carbonyl groups in $(\eta^7-C_7H_7)_2Cr_2$ to draw electrons from the metal–metal multiple bond through back-bonding. The bonding in singlet $(\eta^7-C_7H_7)_2Cr_2$ (**VIIa-s**) uses eight of the nine orbitals of the sp^3d^5 manifolds of each chromium atom, namely five orbitals for the $\sigma + 2\pi + 2\delta$ fivefold bonding of the chromium atom to the $\eta^7-C_7H_7$ ring and three additional orbitals for the Cr=Cr triple bond. The nine chromium valence orbitals in the sp^3d^5 valence orbital manifold are not sufficient to form both a fivefold $\sigma + 2\pi + 2\delta$ bond to the $\eta^7-C_7H_7$ ring (as a formal 10π -electron $C_7H_7^{3-}$ trianion) and the chromium–chromium quintuple bond necessary to give the chromium atoms the normally favored 18-electron configuration. In the bent triplet $(\eta^7-C_7H_7)_2Cr_2$ structure **VIIb-t** the Cr=Cr distance is about 0.13 Å longer than the presumed Cr=Cr triple bond in the corresponding singlet structure **VIIa-s**, consistent with a presumed double bond. The single non-bonding electrons on each chromium atom in triplet **VIIb-t** are

apparently stereochemically active, leading to a bent rather than parallel arrangement of the $\eta^7-C_7H_7$ rings.

3.2. Dissociation energies

Table 15 reports the energies of the following single carbonyl dissociation steps:



In determining these dissociation energies, the fragments were allowed to relax. The predicted dissociation energy of one CO group from $(C_7H_7)_2Cr_2(CO)_6$ (Table 15) is 47.3 kcal/mol (B3LYP) or 52.3 kcal/mol (BP86). However further dissociation of a CO group from $(C_7H_7)_2Cr_2(CO)_5$ to give $(C_7H_7)_2Cr_2(CO)_4$ is almost thermoneutral with a miniscule dissociation energy of 0.1 kcal/mol (B3LYP) or 1.6 kcal/mol (BP86). Thus $(C_7H_7)_2Cr_2(CO)_5$ appears to be evanescent with respect to extrusion of a carbonyl ligand. The next CO dissociation process, namely $(C_7H_7)_2Cr_2(CO)_4$ dissociation to $(C_7H_7)_2Cr_2(CO)_3 + CO$, requires 5.7 kcal/mol (B3LYP) or 20.8 kcal/mol (BP86). Further dissociation of $(C_7H_7)_2Cr_2(CO)_2$ to

Table 16

Metal carbonyl $\nu(CO)$ frequencies (in cm^{-1}) predicted by the BP86 method for the $(C_7H_7)_2Cr_2(CO)_n$ ($n = 6, 5, 4, 3, 2, 1$) structures

$(C_7H_7)_2Cr_2(CO)_6$	
Ia-s (C_1)	1912(a, 195), 1931(a, 245), 1943(a, 468), 1958(a, 1357), 1980(a, 1500), 2035(a, 511)
Ib-s (C_s)	1922(a', 250), 1936(a', 342), 1958(a', 448), 2026(a', 925), 1917(a'', 72), 1977(a'', 1619)
Ic-t (C_1)	1674(a, 249) , 1903(a, 186), 1911(a, 384), 1935(a, 941), 1940(a, 1066), 1994(a, 1136)
Id-t (C_1)	1881(a, 452), 1890(a, 252), 1915(a, 390), 1953(a, 319), 1972(a, 1513), 2016(a, 971)
$(C_7H_7)_2Cr_2(CO)_5$	
Ila-s (C_1)	1889(a, 568), 1929(a, 258), 1940(a, 474), 1962(a, 242), 2006(a, 774)
Ilb-t (C_1)	1888(a, 264), 1927(a, 20), 1945(a, 1475), 1953(a, 1428), 1993(a, 216)
$(C_7H_7)_2Cr_2(CO)_4$	
IIla-s (C_1)	1932(a, 21), 2071(a, 1670), 1927(b, 1527), 2019(b, 452)
IIlb-s (C_1)	1617(a, 212) , 1623(a, 62) , 1950(a, 1601), 1968(a, 24)
IIlc-s (C_1)	1885(a _g , 0), 1941(a _g , 0), 1888(a _u , 1364), 1911(a _u , 1337)
IIId-t (C_1)	1879(a _g , 0), 1961(a _g , 0), 1883(a _u , 1251), 1931(a _u , 1496)
$(C_7H_7)_2Cr_2(CO)_3$	
IVa-s (C_1)	1684(a, 459) , 1914(a, 519), 1987(a, 1104)
IVb-s (C_2)	1594(a, 184) , 1922(a, 375), 1878(b, 1060)
IVc-s (C_1)	1542(a, 42) , 1625(a, 33) , 1961(a, 870)
$(C_7H_7)_2Cr_2(CO)_2$	
Va-s (C_1)	1619(a, 30) , 1956(a, 973)
Vb-s (C_1)	1636(a, 24) , 1904(a, 781)
$(C_7H_7)_2Cr_2(CO)$	
Vla-s (C_{2v})	1603(a₁, 387)
Vlb-t (C_s)	1547(a', 224)

Bridging $\nu(CO)$ frequencies are given in **bold**.

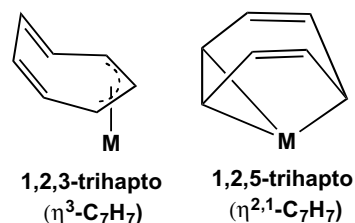


Fig. 11. The two types of trihapto C_7H_7 rings.

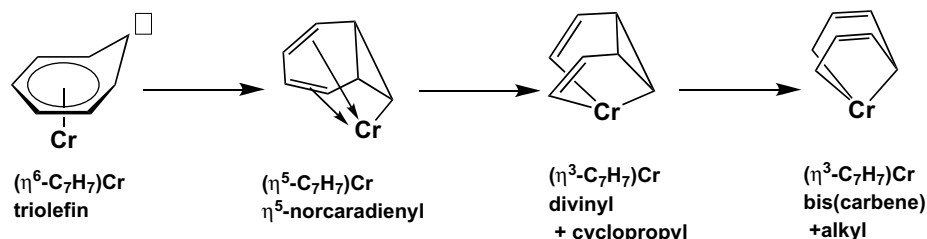


Fig. 12. Some rearrangements of the C_7H_7 ligand.

$(\text{C}_7\text{H}_7)_2\text{Cr}_2(\text{CO}) + \text{CO}$, requires the very high energy of 95.9 kcal/mol (B3LYP) or 86.2 kcal/mol (BP86). Thus $(\text{C}_7\text{H}_7)_2\text{Cr}_2(\text{CO})_2$ appears to be quite resistant to carbonyl dissociation.

The disproportionation reactions $2(\text{C}_7\text{H}_7)_2\text{Cr}_2(\text{CO})_n \rightarrow (\text{C}_7\text{H}_7)_2\text{Cr}_2(\text{CO})_{n+1} + (\text{C}_7\text{H}_7)_2\text{Cr}_2(\text{CO})_{n-1}$ were also investigated (Table 15). The disproportionation of $(\text{C}_7\text{H}_7)_2\text{Cr}_2(\text{CO})_5$ to $(\text{C}_7\text{H}_7)_2\text{Cr}_2(\text{CO})_6 + (\text{C}_7\text{H}_7)_2\text{Cr}_2(\text{CO})_4$ is seen to be highly exothermic at -47.3 kcal/mol (B3LYP) or -50.7 kcal/mol (BP86) indicating the at best fleeting nature of this pentacarbonyl. The other $(\text{C}_7\text{H}_7)_2\text{Cr}_2(\text{CO})_n$ derivatives ($n = 4, 3, 2, 1$) are seen to be energetically favored with respect to disproportionation.

3.3. Infrared spectra

Table 16 summarizes the $\nu(\text{CO})$ frequencies of the $(\text{C}_7\text{H}_7)_2\text{Cr}_2(\text{CO})_n$ derivatives using the BP86 functional, which has been found to be more reliable for $\nu(\text{CO})$ frequencies than the B3LYP method [47,48]. As expected, the bridging $\nu(\text{CO})$ frequencies appear ~ 300 cm^{-1} below the terminal $\nu(\text{CO})$ frequencies in similar compounds and thus typically around 1600 cm^{-1} . The $\nu(\text{CO})$ frequencies of the carbonyl groups inserted into the $\text{C}_7\text{H}_7\text{-M}$ bonds in structures **1c-t** of $(\text{C}_7\text{H}_7)_2\text{Cr}_2(\text{CO})_6$, **111b-s** of $(\text{C}_7\text{H}_7)_2\text{Cr}_2(\text{CO})_4$, and **1Vb-s** of $(\text{C}_7\text{H}_7)_2\text{Cr}_2(\text{CO})_2$ also appears in a similar region.

4. Discussion

This study has as its point of departure the isoelectronic series $(\eta^n\text{-C}_n\text{H}_n)_2\text{M}_2(\text{CO})_n$ ($\text{M} = \text{Co}$, $n = 4$ [49]; $\text{M} = \text{Fe}$, $n = 5$ [21]; $\text{M} = \text{Mn}$, $n = 6$), where all of the optimized structures were found to have intact $\eta^n\text{-C}_n\text{H}_n$ rings, which bond to the metal atoms using all of their carbon atoms. The next members of this isoelectronic series are the $(\text{C}_7\text{H}_7)_2\text{Cr}_2(\text{CO})_n$ derivatives discussed in this paper. To our surprise, no examples of energetically competitive heptahapto $\eta^7\text{-C}_7\text{H}_7$ structures were found in this work other than the monocarbonyls $(\eta^7\text{-C}_7\text{H}_7)_2\text{Cr}_2(\mu\text{-CO})$ (**1Va-s** and **1Vb-t** in Fig. 8) and the carbonyl-free dimetalloenes $(\eta^7\text{-C}_7\text{H}_7)_2\text{Cr}_2$ (**1VIIa-s** and **1VIIb-t** in Fig. 9). Instead bent trihapto and pentahapto C_7H_7 rings were frequently found. The bent trihapto C_7H_7 rings are of the following two types (Fig. 11):

- (1) The 1,2,3-trihapto derivatives ($\eta^3\text{-C}_7\text{H}_7$) in which three adjacent carbons of the C_7H_7 ring are bonded to the metal atom with an uncomplexed conjugated 1,3 diene unit.
- (2) The 1,2,5-trihapto derivatives (literally $\eta^{2,1}\text{-C}_7\text{H}_7$) in which an adjacent pair of carbon atoms and an "isolated" carbon atom are bonded to the metal atom leaving two isolated uncomplexed $\text{C}=\text{C}$ double bonds.

Structures with 1,2,3-trihapto $\eta^3\text{-C}_7\text{H}_7$ rings are known in a number of stable compounds including those depicted in Fig. 2, whereas structures with 1,2,5-trihapto $\eta^{2,1}\text{-C}_7\text{H}_7$ rings are apparently not known experimentally. Of interest is structure **1b-s** for $(\text{C}_7\text{H}_7)_2\text{Cr}_2(\text{CO})_6$ (Fig. 3) with an example of each type of trihapto C_7H_7 ring.

Examples were found in this work where the heptagonal C_7H_7 ring rearranges to other types of isomeric C_7H_7 ligands. The tridentate cyclopropyldivinylyl ligand found in structures **1Va-s**, **1Va-s**, and **1Vb-s** (Figs. 6 and 7) can be obtained from a hexahapto $\eta^6\text{-C}_7\text{H}_7$ ligand through a norcaradienyl rearrangement (Fig. 12). This process can also lead to the tridentate five-electron donor bis(carbene)alkyl ligand, as found in structure **1Vb-t** (Fig. 6) if the two olefin-Cr bonds in the intermediate η^5 -norcaradienyl structure rearrange to a chelating bis(carbene) unit by rupture of the C-C single bond of the cyclopropane separating the two vinyl groups.

Another interesting feature of the structures found in this work is the near constancy of the chromium-chromium distances in the range 2.4–2.5 Å regardless of the number of carbonyl groups or the nature of the C_7H_7 ligand. Interpreting $\text{Cr}=\text{Cr}$ bonds of such length as formal triple bonds leads to reasonable electron counts in most cases. In this connection it is interesting that the first examples of formal metal-metal triple bonds in metal carbonyl chemistry were found in cyclopentadienylmetal carbonyl derivatives of the type $(\eta^5\text{-R}_5\text{C}_5)_2\text{M}_2(\text{CO})_4$ ($\text{M} = \text{Cr}$, [45,50,51] Mo [52,53]; $\text{R} = \text{H}$, Me) having structures similar to the $(\eta^5\text{-C}_7\text{H}_7)_2\text{Cr}_2(\text{CO})_4$ global minimum **1IIIa-s** (Fig. 5) found for $(\text{C}_7\text{H}_7)_2\text{Cr}_2(\text{CO})_4$.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.06.036.

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