The rule breaking \( \text{Cr}_2(\text{CO})_{10} \). A 17 electron Cr system or a Cr=Cr double bond?

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Density functional theory (DFT) has been used to investigate the conformations and thermochemistry on the singlet and triplet potential energy surfaces (PES) of \( \text{Cr}_2(\text{CO})_{10} \). The global minimum energy structure for the lowest singlet state of \( C_{2h} \) symmetry is consistent with a model of two interacting \( \text{Cr}(\text{CO})_5 \) fragments in which one carbonyl in each fragment acts as an asymmetric four-electron donor bridging carbonyl, with chromium-chromium distances of 2.93 Å (B3LYP) or 2.83 Å (BP86). Avoiding a Cr−Cr bond by incorporating four-electron donor CO groups in this way allows each chromium atom in singlet \( \text{Cr}_2(\text{CO})_{10} \) to attain the favored 18-electron configuration by using, in a simple picture of the bonding, only the six octahedral sp\(^3\)d\(^2\) hybrids. The dissociation energy to two \( \text{Cr}(\text{CO})_5 \) fragments or to \( \text{Cr}(\text{CO})_6 + \text{Cr}(\text{CO})_4 \) fragments is predicted to be 10 kcal mol\(^{-1}\). The lowest triplet state of \( \text{Cr}_2(\text{CO})_{10} \) is predicted to lie \( \sim 10 \) kcal mol\(^{-1}\) above the singlet global minimum. In the case of triplet \( \text{Cr}_2(\text{CO})_{10} \) the lowest energy minima were found to be of \( C_2 \) and \( C_{2h} \) symmetry, with similar energies. The chromium-chromium distances in triplet \( \text{Cr}_2(\text{CO})_{10} \) were found to be shorter than those in the corresponding singlet structures, namely 2.81 Å (B3LYP) or 2.68 Å (BP86) suggesting a \( \sigma + 2(1/2) \pi \) Cr=Cr double bond similar to the O=O bond in \( \text{O}_2 \) or the Fe=Fe bond in the experimentally observed triplet state \( (\text{Me}_3\text{C})_2\text{Fe}_2(\mu-\text{CO})_3 \).

1. Introduction

Recently our group has studied saturated homoleptic binuclear carbonyls of first row transition metals such as nickel,\(^1\) iron,\(^2\) and cobalt\(^3\) using carefully calibrated methods from density functional theory (DFT).\(^4\) The results are in reasonable agreement with available experimental values for geometries and thermodynamic quantities. These theoretical methods have been extended to unsaturated binuclear metal carbonyls. Optimized structures were found exhibiting the following features: (a) Metal−metal multiple bonds with the favored 18-electron rare gas metal electronic configuration such as formal M=M double bonds in \( \text{Ni}_2(\text{CO})_6 \) and \( \text{Fe}_2(\text{CO})_8 \), and formal M=M triple bonds in \( \text{Ni}_3(\text{CO})_6 \), \( \text{Co}_3(\text{CO})_6 \), and \( \text{Fe}_3(\text{CO})_7 \); (b) Four-electron bridging carbonyl groups with the favored 18-electron metal electronic configuration such as in \( C_{2h} \) symmetry \( \text{Fe}_2(\text{CO})_6 \); (c) Metal electron configurations with fewer than 18 electrons, such as the 16-electron configurations for d\(^8\) metal atoms found in unbridged \( \text{Co}_3(\text{CO})_7 \), analogous to the known\(^5\) CoRh(CO)\(_7\).

These results lead to further exploration of structures for as yet undetected unsaturated homoleptic binuclear carbonyls of the first row transition metals by DFT methods. This paper reports our \( \text{Cr}_2(\text{CO})_{10} \) research. Simple electron counting\(^6\) indicates that if all ten CO groups are the...
usual donors of two electrons each, then a Cr=Cr double bond is required to give each chromium atom the favored 18-electron configuration in Cr₂(CO)₁₀.

Our previous results for the saturated homoleptic binuclear chromium carbonyl Cr₂(CO)₁₁ showed this compound to have a flat potential energy surface and to be thermodynamically unstable with respect to dissociation to Cr(CO)₅ and Cr(CO)₆. This accounts for the experimental lack of Cr₂(CO)₁₁ isolation. Substitution of the bridging CO in Cr₂(CO)₁₁ with a hydride produces the stable and well-known HCr₂(CO)₁₀⁻, for which we also predicted the gas phase structure and compared it to two X-ray structures. Deprotonation of HCr₂(CO)₁₀⁻ results in the known Cr₂(CO)₁₀⁻², which has also been structurally characterized. Electrochemical experiments have examined the one-electron oxidation of Cr₂(CO)₁₀⁻² to form Cr₂(CO)₁₀⁻ and the process of Cr–Cr bond cleavage. Two-electron oxidation of Cr₂(CO)₁₀⁻² results in neutral Cr₂(CO)₁₀. Transient (lifetime ~$10^{-3}$ s) Cr₂(CO)₁₀ has been observed in photochemical studies in which Cr(CO)₄ reacts with Cr(CO)₆. These experimental results indicate that Cr₂(CO)₁₀ may have greater stability than the unsaturated Cr₂(CO)₁₁, and thus theoretical investigation of Cr₂(CO)₁₀ has been undertaken to determine the nature of this molecule and reasons for its stability.

Since in some unsaturated binuclear metal compounds, the triplet state may lie lower in energy than the singlet, both electronic states are investigated for Cr₂(CO)₁₀. The computed optimized structures for both the singlet and triplet states of the neutral Cr₂(CO)₁₀ molecule are presented in Fig. 1 (singlet) and Fig. 2 (triplet). Analysis of the relationships between the geometries, harmonic vibrational frequencies and thermodynamic stabilities of the structures in each electronic state illustrate how the loss of two electrons perturbs the highly symmetric $D_{4h}$ dianion Cr₂(CO)₁₀⁻². These analyses also provide some insight into the nature of this unsaturated Cr–Cr bond as well as the difference in predictions between the B3LYP and BP86 functionals.

![Fig. 1](image-url)  
Three singlet Cr₂(CO)₁₀ structures predicted with the B3LYP and BP86 functionals. The energetic relationship of the structures is $E(C_{2h}) < E(C_{2v}) < E(D_{2h})$. Significant geometric differences exist between the B3LYP and BP86 methods for the $C_{2v}$ structure.

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2. Theoretical methods

Our basis set for C and O begins with Dunning’s standard double-$\zeta$ contraction\textsuperscript{15} of Huzinaga’s primitive sets\textsuperscript{16} and is designated (9s5p/4s2p). The double-$\zeta$ plus polarization (DZP) basis set used here adds one set of pure spherical harmonic d functions with orbital exponents $\alpha_{d}(C) = 0.75$ and $\alpha_{d}(O) = 0.85$ to the DZ basis set. For Cr, our loosely contracted DZP basis set, the Wachters primitive set,\textsuperscript{17} is used, but augmented by two sets of p functions and one set of d functions, contracted following Hood, Pitzer and Schaefer\textsuperscript{18} and designated (14s11p6d/10s8p3d). For Cr$_2$(CO)$_{10}$, there are 398 contracted Gaussian functions in the present flexible DZP basis set.

Electron correlation effects were included employing DFT methods, which are acknowledged to be a practical and effective computational tool, especially for organometallic compounds.\textsuperscript{19} Among density functional procedures, the most reliable approximation is often thought to be the hybrid Hartree–Fock (HF)/DFT method, B3LYP, which uses the combination of the three-parameter Becke exchange functional with the Lee–Yang–Parr correlation functional.\textsuperscript{20,21} However, another DFT method, which combines Becke’s 1988 exchange functional\textsuperscript{22} with Perdew’s 1986 nonlocal correlation functional method (BP86),\textsuperscript{23} has proven effective\textsuperscript{24} and is also used in this research.

We fully optimized the geometries of all structures with the DZP B3LYP and DZP BP86 methods. At the same levels we also computed the vibrational frequencies by analytically evaluating 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,\textsuperscript{25} exercising the fine grid (75 302) option for evaluating integrals numerically, and the tight ($10^{-5} E_{h}$) designation is the default for the self-consistent field (SCF) convergence. Cases for which finer integration grids were used are addressed below.

In the search for minima using all currently implemented DFT methods, low magnitude imaginary vibrational frequencies are suspect because of significant limitations in the numerical

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Fig. 2 Six triplet Cr$_2$(CO)$_{10}$ structures predicted with the B3LYP and BP86 functionals. The energetic relationship of the structures is $E(C_{2}) < E(C_{2h}) < E(C_{2v}) < E(D_{2h}) < E(D_{4d}) < E(D_{4h})$ for the B3LYP functional, while it is $E(C_{2h}) < E(C_{2}) < E(D_{2h}) < E(C_{2v}) < E(D_{4d}) < E(D_{4h})$ for BP86.
integration procedures used. Thus, for an imaginary vibrational frequency with a magnitude less than 100 cm\(^{-1}\), there is an energy minimum identical to or very close to the structure of the stationary point in question. Therefore, we generally do not follow such low imaginary vibrational frequencies. However, we reevaluated the \(D_{4h}\) structure of \(\text{Cr}_2\text{(CO)}_{10}\) with finer integration grids, but the small imaginary vibrational frequencies persisted. For low harmonic vibrational frequencies, the DFT methodology requires further development to yield rock solid predictions. However, continued efforts to discover and document patterns within systems which display these discrepancies will provide both direction in the development of DFT and insight into “unusual” bonding situations.

3. Results

3.1 The reliability of DFT for chromium carbonyls

Our previous work has shown that geometries and vibrational frequencies predicted using B3LYP and BP86 DFT functionals were in reasonable agreement (~0.02 Å for bond distances) with experimental and higher level theoretical results for \(\text{Cr(CO)}_6\), \(\text{Cr(CO)}_5\), \([\text{Cr(CO)}_3\text{H}]^+\), and \([\text{Cr(CO)}_4\text{H}]^+\). In that work similar agreement was also found for \([\mu\text{-H}]\text{Cr}_2\text{(CO)}_{10}]^+\), for which an experimental geometry is known. The prediction for the bridged species is similar to that for the solid crystal owing to the Cr–H interaction and the stabilizing nature of the bridging species. This is in contrast to the \([\text{Cr}_2\text{(CO)}_{10}]^{2-}\) dianion which is predicted to have a somewhat longer Cr–Cr distance, (3.30 Å, both functionals) than the experimental distances (2.98–3.00 Å) for Cr–Cr in \([\text{Cr}_2\text{(CO)}_{10}]^{2-}\) crystals\(^\text{26,27}\). The difference between the isolated gas phase species, in which some bond lengthening is possible, and the constrained environment of the solid crystal may account for this difference in the dianion geometry. With only the dianion differing significantly from experimentally determined geometry (explainable by the effects of excess charge) these results would seem to indicate at least a qualitative reliability of DFT for these molecules.

3.2 Singlet \(\text{Cr}_2\text{(CO)}_{10}\)

The fully optimized structures for the singlet electronic state of \(\text{Cr}_2\text{(CO)}_{10}\) (sketches in Fig. 1) are displayed in Figs. 3, 4, and 5. The relative energies of the structures and corresponding imaginary harmonic vibrational frequencies are listed in Table 1.

Fig. 3 shows the dibridged \(C_{2h}\) structure having all real harmonic vibrational frequencies; the electronic state is \(^1\text{A}_g\). This structure is a genuine minimum with both the B3LYP and BP86 functionals and has the lowest energy among all nine neutral \(\text{Cr}_2\text{(CO)}_{10}\) structures examined here. In addition, the energy of the \(C_{2h}\) conformer is lower than that of two \(\text{Cr(CO)}_5\) fragments by 8.6

![Fig. 3 The asymmetrically bridging \(C_{2h}\) global minimum energy structure for singlet \(\text{Cr}_2\text{(CO)}_{10}\) (all real harmonic vibrational frequencies) from the B3LYP and BP86 methods. Distances are reported in Å.](image)
(B3LYP) or 16.6 kcal mol$^{-1}$ (BP86), respectively. For fragmentation to Cr(CO)$_6$ and Cr(CO)$_4$ the energy differences are 7.9 kcal mol$^{-1}$ (B3LYP) and 15.1 kcal mol$^{-1}$ (BP86).

The relatively long Cr–Cr distance (B3LYP, 2.928 Å; BP86, 2.832 Å) in the Cr$_2$(CO)$_{10}$ structure of $C_{2h}$ symmetry suggests that the Cr···Cr interaction takes place primarily through the π bonds of the bridging CO groups rather than through multiple bonding between the two chromium atoms.

Fig. 4 The second lowest energy singlet structure for Cr$_2$(CO)$_{10}$, with $C_{2v}$ symmetry, all real harmonic vibrational frequencies (B3LYP) and one large imaginary harmonic vibrational frequency (BP86). Distances are reported in Å.

(B3LYP) or 16.6 kcal mol$^{-1}$ (BP86), respectively. For fragmentation to Cr(CO)$_6$ and Cr(CO)$_4$ the energy differences are 7.9 kcal mol$^{-1}$ (B3LYP) and 15.1 kcal mol$^{-1}$ (BP86).

The relatively long Cr–Cr distance (B3LYP, 2.928 Å; BP86, 2.832 Å) in the Cr$_2$(CO)$_{10}$ structure of $C_{2h}$ symmetry suggests that the Cr···Cr interaction takes place primarily through the π bonds of the bridging CO groups rather than through multiple bonding between the two chromium atoms.

Fig. 5 The symmetrically dibridged singlet Cr$_2$(CO)$_{10}$ structure with $D_{2h}$ symmetry and one large imaginary harmonic vibrational frequency for both B3LYP and BP86. Distances are reported in Å.
<table>
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<tr>
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<th>State</th>
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<th>Relative energy/kcal mol$^{-1}$</th>
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<td>$^1A_g$</td>
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<td>(none)</td>
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<td>$^1A_1$, $^1A_g$</td>
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</table>
The Cr–C distances of the four symmetry equivalent perpendicular terminal carbonyls are 1.925 Å (B3LYP) or 1.909 Å (BP86). The four unique Cr–C distances in the C–Cr–Cr–C plane are 1.923 Å for the shorter bridging Cr–C and 1.931 Å for the terminal Cr–C opposite to the shorter bridging Cr–C. Similarly, the distances are 2.589 Å for the longer bridging Cr–C and 1.865 Å for the terminal Cr–C opposite to the longer bridging Cr–C with the B3LYP method. With the BP86 functional the respective distances are 1.920 Å, 1.905 Å, 2.463 Å and 1.848 Å. The first two Cr–C distances in Cr₃(CO)₁₀ are very close to the analogous computed Cr–C distances in Cr(CO)₅ (1.923 Å B3LYP and 1.905 Å BP86), specifically the ¹A₂ state of C₄ symmetry. However, the Cr–C distances for the remaining bridging carbonyls are much longer. The increased distance reflects the significantly weaker interaction in the bridging Cr–C compared to the terminal Cr–C distance computed for the Cr(CO)₅ fragment. The corresponding C–O distances are as follows: 1.155 Å, 1.159 Å, 1.162 Å and 1.152 Å with B3LYP and 1.169 Å, 1.173 Å, 1.178 Å and 1.167 Å with BP86, which are again nearly the same as the computed C–O distances in Cr(CO)₅ (1.162 Å with B3LYP and 1.171 with BP86). These distances also compare favorably with the experimentally known values in Cr(CO)₆ of 1.916 ± 0.002 Å (rCr–C) and 1.140 ± 0.003 Å (rC–O).㉘

Finally, consideration of the Cr–C–O angles for the shorter bridging carbonyl shows significant deviation from linearity at 165.7° (B3LYP) and 164.8° (BP86). This deviation is in accord with the proposed π-bonding from the C–O bond of this carbonyl to a chromium atom. The other four Cr–C–O angles do remain close to 180°. The C–Cr–C angles are also computed to be close to 90°, as shown in Fig. 3. Thus it is logical to conclude that the lowest energy structure for Cr₃(CO)₁₀ is an 18-electron species, in which the longer bridging carbonyls contribute two π electrons to complete the 18 electron configuration for each chromium atom.

Imposing C₂ᵥ symmetry forces the bridging carbonyls to produce the C₂ᵥ structure with an ¹A₁ electronic wavefunction. The two structures thus produced are shown in Fig. 4a (B3LYP) and 4b (BP86). With the B3LYP method this structure has no imaginary harmonic vibrational frequencies and is only 1.6 kcal mol⁻¹ higher than the C₂ᵥ structure. However, with the BP86 method this structure has one significantly large imaginary harmonic vibrational frequency of b₂ symmetry at 348i cm⁻¹ and two small imaginary vibrational frequencies at 50i (a₁) and 40i cm⁻¹ (b₁). The larger BP86 imaginary vibrational frequency corresponds to a return to the lower energy C₂ᵥ structure that lies 7.9 kcal mol⁻¹ lower. As discussed above, we only consider imaginary vibrational frequencies with magnitudes over 100 cm⁻¹ to be indisputable. This is another example showing that the B3LYP and BP86 are sometimes inconsistent in predicting the number of the imaginary frequencies for these metal dimers. In either case we conclude that the C₂ᵥ structure is not a genuine minimum but rather a higher order stationary point on the energy surface for BP86.

The geometric differences between the B3LYP and BP86 C₂ᵥ structures for singlet Cr₃(CO)₁₀ (Fig. 4) are also striking. Unexpectedly, the chromium-chromium distance is a very long 4.311 Å with the B3LYP functional. It appears that a loosely associated complex of Cr(CO)₄ and Cr(CO)₆ forms with a bridging Cr⋯O distance of 2.545 Å (B3LYP), implying that the two fragments have a very weak connection. However, with BP86 the Cr–Cr bond distance is 2.834 Å, which is essentially the same as the Cr–Cr bond distance in C₂ᵥ symmetry (2.832 Å, BP86). This C₂ᵥ structure behaves similarly to other binary homoleptic transition metal carbonyls where the B3LYP and BP86 methods sometimes lead to widely different structural predictions³,⁵ and so direct comparison cannot be made. However, in previous work the BP86 functional performed better for the prediction of the [(μ-H)Cr₃(CO)₁₀]⁻ structure, and similar confidence may be warranted here since the HF component without electron correlation can lead to the errors in B3LYP.

Imposition of further symmetry constraints produces the dibridged D₂h structure, the last of the singlet structures considered (Fig. 5). Both the B3LYP and BP86 functionals yield several imaginary vibrational frequencies above 100 cm⁻¹ for this structure, including the b₃u frequency at 404i cm⁻¹ (B3LYP) or 438i cm⁻¹ (BP86) and the b₃u frequency at 153i cm⁻¹ (B3LYP). These normal modes correspond to motions that reduce the symmetry to the lower energy C₂ᵥ and C₄h structures. Also, the D₂h structure is higher by 9.2 kcal mol⁻¹ (B3LYP) or 8.4 kcal mol⁻¹ (BP86) than the C₂ᵥ global minimum. Clearly, this symmetric dibridged Cr₅(CO)₁₀ structure is not a minimum. However, the predicted chromium–chromium distance for this structure is the shortest among the three singlet structures, namely 2.724 Å (B3LYP) or 2.678 Å (BP86) but obviously still in the range of a single bond. The dibridging Cr–C distance is 2.170 Å (B3LYP) or 2.135 Å (BP86) which is longer than the Cr–C distance in the Cr(CO)₅ fragment (1.923 Å B3LYP and 1.905 Å
BP86) and also longer than the experimental Cr(CO)₅ distance of 1.916 Å. Thus we conclude that there is a Cr–Cr single bond in this structure.

### 3.3 Triplet Cr₂(CO)₁₀

For singlet Cr₂(CO)₁₀, stationary points were found for three symmetries, all lying close in energy. However, for triplet Cr₂(CO)₁₀, structures were found of six different symmetries, all lying about 10 kcal mol⁻¹ above the singlet structures in energy. Thus the singlet C₂ₙh structure is the global energy minimum among all of the Cr₂(CO)₁₀ structures studied. The relative energies of the triplet Cr₂(CO)₁₀ structures and their imaginary harmonic vibrational frequencies are listed in Table 2. For triplet Cr₂(CO)₁₀ (Fig. 2) the fully optimized structures are shown in Figs. 6–11.

Fig. 6 shows the unbridged staggered C₂ structure of the lowest energy B3LYP triplet electronic state, ³B, which is a genuine minimum with both the B3LYP and BP86 methods. However, using the BP86 functional the doubly bridged C₂ₙh structure shown in Fig. 7 lies lower than the C₂ structure by 0.1 kcal mol⁻¹. Remarkably, the C₂ and the C₂ₙh structures differ considerably in geometry. Furthermore, the C₂ triplet Cr₂(CO)₁₀ is higher in energy than its two constituent singlet fragments of Cr(CO)₅ by 4.1 kcal mol⁻¹ with B3LYP and lower by 3.4 kcal mol⁻¹ with BP86. In order to explore the accommodation of electrons around Cr in terms of the 18-electron rule, the Cr–Cr distance, the Cr–C distances, and the Cr–Cr–C angles in this triplet Cr₂(CO)₁₀ isomer are compared with those in Cr₂(CO)₁₀⁺²⁻, which is a saturated compound where the Cr–Cr single bond gives each chromium atom the favored 18-electron noble gas configuration. The Cr–Cr distance in Cr₂(CO)₁₀ is computed to be 2.805 Å (B3LYP) and 2.726 Å (BP86), which is significantly shorter than the theoretical Cr–Cr distance of 3.30 Å in the Cr₂(CO)₁₀⁺²⁻ dianion. This might suggest the existence of a weak Cr=Cr double bond, similar to the oxygen–oxygen double bond in O₂ in which a single Cr–Cr s bond is complemented by “half bonds” involving a single bonding electron in each of the two perpendicular p orbitals. An organometallic example of a similar triplet metal–metal double bond is the Fe=Fe double bond in (η⁵-Me₅C₅)₂Fe₂(μ-CO)₃ (I), which has been characterized structurally (Fe=Fe of 2.27 Å) and which has been determined experimentally by magnetic measurements to have a magnetic moment of 2.5 ± 0.1 μB, corresponding to a triplet ground state.²⁹

![Image](image.png)

The Cr–C bond lengths of the five nonequivalent carbonyls in the triplet C₂ symmetry Cr₂(CO)₁₀ are in the range: 1.903 Å–1.946 Å (B3LYP) or 1.873 Å–1.925 Å (BP86). The two methods both show that the axial Cr–C bond lengths are shorter than those of the Cr–C (1.923 Å B3LYP and 1.905 Å BP86) in the constituent Cr(CO)₅ fragments or in Cr(CO)₆ with the experimentally known 1.916 ± 0.002 Å (r_Cr–C). This suggests an increased interaction between the chromium and the carbon atoms (along the C₄ axis in the Cr(CO)₅ fragment) leading to formation of the Cr=Cr bond. The corresponding C–O distances remain nearly the same compared to the C–O bond length in the Cr(CO)₅ fragment. In similar fashion to the singlet, the terminal Cr–C–O bond angle closes up from 180° to 172.5° with B3LYP and to 166.5° with BP86. However, these two corresponding carbonyls are no longer in the same plane and have very long distances (2.892 Å B3LYP and 2.628 Å BP86) to the opposite chromium atom. These distances are even longer than the Cr–C long-bridging distance (2.589 Å B3LYP and 2.463 Å BP86) in the singlet C₂ₙh minimum. Also, the Cr–Cr–C angles (with the axial carbonyls) are 159.4° (B3LYP) and 150.8° (BP86). This implies a much weaker interaction between the bridging Cr–C in the triplet C₂ structure, providing further indication of greater bond strength than in the three previously discussed singlet structures. Finally, both the Cr–C–O and the C–Cr–C angles remain nearly unchanged compared to the corresponding angles in the Cr(CO)₅ fragments.

Lying close in energy to the C₂ structure but with two bridging carbonyls is the ³B₉ electronic state of C₂ₙh symmetry shown in Fig. 7. With the BP86 functional it lies the lowest energetically (by about 0.1 kcal mol⁻¹) among the six triplet structures and has all real harmonic vibrational
Table 2  Energies and stationary point characteristics of triplet Cr$_2$(CO)$_{10}$. Relative energies refer to the $C_{2h}$ symmetry $^1A_g$ ground state of Cr$_2$(CO)$_{10}$

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<th>Sym.</th>
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frequencies. However, with the B3LYP functional it has one very small imaginary vibrational
frequency of a1u symmetry at 18i cm⁻¹ and an energy 2 kcal mol⁻¹ higher than the C2 minimum,
indicating that this structure is either a minimum or very close to one. The C2h structures of the
singlet and the triplet electronic states differ in three parameters: the Cr–Cr distance, the difference
in bridging lengths, and the different Cr–C–O angle. Firstly, the Cr–Cr distance is shortened from
2.928 Å to 2.818 Å (B3LYP) and from 2.832 Å to 2.677 Å (BP86). Secondly, for the longer bridging
carbonyl, the B3LYP functional predicts lengthening from 2.589 Å to 2.652 Å whereas BP86
suggests shortening from 2.463 Å to 2.258 Å. Lastly, B3LYP computes the Cr–C–O angle to be
165°, which is nearly the same as in the singlet C2h structure, while BP86 computes the value of
152°, which is much more bent than in the singlet C2h structure, 164°. This not only provides
evidence that a double bond for the triplet structure may exist with B3LYP, like the triplet C2
structure, but also that bridging π interactions may occur similar to those in the singlet C2h
structure for BP86.

Fig. 6  The unbridged C2 symmetry B3LYP minimum energy structure for triplet Cr₂(CO)₁₀ predicted from
B3LYP and BP86 methods. Distances are reported in Å.

Fig. 7  The dibridged BP86 minimum energy structure for triplet Cr₂(CO)₁₀ with C2h symmetry. This structure
has one small imaginary harmonic vibrational frequency for B3LYP and is a genuine minimum with the BP86
method. Distances are reported in Å.
The further geometric constraint of forcing the bridging carbonyls to be symmetric leads to the $C_{2v}$ dibridged structure (the $^3A_2$ electronic state lies lower with B3LYP, and the $^3B_2$ electronic state lies lower with BP86) shown in Fig. 8. This structure is higher lying energetically by 2.5 kcal mol$^{-1}$ and 5.7 kcal mol$^{-1}$ above the triplet minima, namely the $C_2$ structure, with B3LYP and the $C_{2h}$ structure, with BP86, respectively. The $C_{2v}$ structure has only one imaginary vibrational frequency at 74i cm$^{-1}$ (b$_2$ symmetry, B3LYP) and at 119i cm$^{-1}$ (b$_1$ symmetry, BP86). This imaginary vibrational frequency shows that the structure is not a minima, since it leads back to the staggered $C_2$ minimum. Similarly, for BP86, the frequencies lead back to the eclipsed $C_{2h}$ minimum.

Imposing further symmetry constraints on the triplet structure leads to the dibridged $D_{2h}$ structure ($^3B_{3g}$ electronic state) which is shown in Fig. 9. Similar to the singlet $D_{2h}$ structure (Fig. 5), the dibridged Cr$_2$(CO)$_{10}$ has the shortest Cr–Cr distance (2.679 Å B3LYP and 2.648 Å BP86) among the nine structures considered here. The bridging Cr–C distances (2.110 Å B3LYP and 2.098 Å BP86) for this structure are longer than the Cr–C bond distance in Cr(CO)$_5$ (1.923 Å B3LYP and 1.905 Å BP86). Thus we assign to this structure a four-center six π electron bond. For the B3LYP method the dibridged $D_{2h}$ Cr$_2$(CO)$_{10}$ has two imaginary vibrational frequencies: one at 105i cm$^{-1}$ (b$_{2g}$ symmetry) that corresponds to the $C_{2h}$ structure and one at 80i cm$^{-1}$ (b$_{3u}$ symmetry).
that corresponds to the $C_{2v}$ structure. The one imaginary frequency of the BP86 functional, namely a $b_{2g}$ mode, is predicted at 95i cm$^{-1}$. The energy is 2.9 kcal mol$^{-1}$ above the triplet minimum $C_3$ with B3LYP and 0.2 kcal mol$^{-1}$ above the triplet minimum $C_{2h}$ with BP86. Therefore we conclude that the $D_{2h}$ structure is not a genuine minimum, but energetically very close to the $C_{2h}$ minimum.

Our highest symmetry structures that might formally possess a Cr=Cr double bond are the unbridged $D_{4d}$ ($^3A_1$ electronic state) and $D_{4h}$ ($^3A_{2g}$ electronic state) structures of Cr$_2$(CO)$_{10}$ shown in Figs. 10 and 11. Unexpectedly, both the $D_{4d}$ and $D_{4h}$ structures have quite long chromium–chromium distances, for the former 2.731 Å (B3LYP) and 2.704 Å (BP86), and 2.827 Å (B3LYP) or 2.795 Å (BP86) for the latter. The staggered $D_{4d}$ structure (Fig. 10) is qualitatively similar to the eclipsed $D_{4h}$ structure (Fig. 11). However, the latter has a chromium–chromium distance, that is longer by 0.096 Å (B3LYP) and 0.091 Å (BP86), consistent with simple steric repulsion arguments. For the $D_{4d}$ structure the two equatorial and one axial Cr–C bond distances are predicted to be 1.937 Å and 1.941 Å (B3LYP), respectively or 1.921 Å and 1.910 Å (BP86), which are quite similar

![Fig. 10](image1.png) The staggered nonbridging structure for triplet Cr$_2$(CO)$_{10}$ with $D_{4d}$ symmetry. This conformer has one small imaginary harmonic vibrational frequency with B3LYP and two large imaginary harmonic vibrational frequencies with BP86 method. Distances are reported in Å.

![Fig. 11](image2.png) The eclipsed nonbridging structure for triplet Cr$_2$(CO)$_{10}$ with $D_{4h}$ symmetry and one large imaginary harmonic vibrational frequency with both the B3LYP and BP86 methods. Distances are reported in Å.

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to the corresponding bond lengths of Cr(CO)$_3$ and to the experimental Cr(CO)$_6$ distance of 1.916 Å. The axial C–O distances are interesting in that these are identical to the B3LYP and BP86 results for Cr(CO)$_3$ and the experimental result for Cr(CO)$_6$. However, the Cr–C distances are slightly longer. This lengthening suggests a very weak interaction between the two equivalent Cr(CO)$_3$ fragments.

From vibrational frequency analyses neither the $D_{4d}$ nor $D_{4h}$ structure is a true minimum on the potential energy surface. For the $D_{4d}$ structure, both methods yield a degenerate harmonic vibrational frequency, $\epsilon_3$, at 509i cm$^{-1}$ (B3LYP) and 235i cm$^{-1}$ (BP86). For the $D_{4h}$ structure B3LYP yields one harmonic imaginary vibrational frequency of 22i cm$^{-1}$ ($a_{1u}$), while BP86 yields three harmonic imaginary vibrational frequencies of 363i cm$^{-1}$ ($e_g$) and 20i cm$^{-1}$ ($a_{1u}$). The $a_{1u}$ mode (for both B3LYP and BP86) corresponds to an internal rotation changing the symmetry to $D_{4d}$. Similarly, the BP86 $e_g$ symmetry normal modes lead to the lower symmetry $C_{2h}$ structure.

With B3LYP, we have pursued the possibility that the small imaginary vibrational frequency (22i cm$^{-1}$, $a_{1u}$) is fictitious for the $D_{4h}$ structure. As discussed in the Theoretical Methods section, these results are obtained with the (75 302) grid. For the $D_{4h}$ structure of Fig. 11, we reoptimized the B3LYP geometry with the (99 590) numerical integration grid. The B3LYP structure is essentially unchanged, with the Cr–Cr distance decreasing insignificantly from 2.827 Å to 2.826 Å. With the tighter grid the $a_{1u}$ vibrational frequency increases slightly to 24i cm$^{-1}$. Therefore, we conclude that this imaginary $a_{1u}$ vibrational frequency is genuine and that this structure is extremely close to a structure of slightly lower symmetry.

4. Discussion

The optimized structures for Cr$_2$(CO)$_{10}$ may be related to resonance between (a) structure IIa with no direct Cr—Cr bond and two special bridging carbonyls donating four electrons each; and (b) structure IIb with a Cr=Cr double bond and only terminal CO groups donating two electrons each.

In structure IIa, which is favored for singlet Cr$_2$(CO)$_{10}$ (Fig. 3), each of the bridging CO groups thus donates a lone pair to one chromium atom through a Cr–C two-electron two-center bond. The latter is similar to the usual bonds between metal atoms and terminal CO groups in most metal carbonyls including Cr(CO)$_6$. In addition these bridging CO groups donate a second electron pair to the other chromium atom through a longer $\pi$-bond from the multiple carbon–oxygen bond. These two bridging carbonyl groups in structure IIa are thus similar to the unique bridging carbonyl group in the binuclear manganese carbonyl complex (Ph$_2$PCH$_2$PPh$_2$)$_2$–Mn$_2$(CO)$_4$(μ-CO) (III), which has been isolated$^{30}$ and its structure determined by X-ray diffraction.$^{31}$ Each chromium atom in structure IIa for Cr$_2$(CO)$_{10}$ uses octahedral sp$^3$d$^2$ hybridization to form six bonds to carbonyl groups, sufficient to give each chromium atom the favored 18-electron rare gas configuration, since the two bridging CO groups
each form bonds with such a hybrid from each chromium atom. The pervasive tendency of zerovalent chromium to form such octahedral hybrid orbitals is reflected first in the high stability of octahedral Cr(CO)₆. However, this tendency is also seen in the preference of H₂Cr(CO)₅, which has been characterized spectroscopically at low temperatures, for the structure of a dihydrogen complex (H₂)Cr(CO)₅ (IVa). The latter uses six octahedral hybrid orbitals rather than the dihydride (H)₂Cr(CO)₅ (IVb), which requires a less favorable set of seven hybrid orbitals, presumably some type of sp³d³ hybrid.

The lowest energy structure for triplet Cr₂(CO)₁₀ (Fig. 6) is a Cr–Cr doubly bonded structure (IIb) having only terminal CO groups. In this structure the Cr–Cr double bond consists of two perpendicular one-electron π “half-bonds” (designated 2/2 π here and in our abstract) similar to the O=O bond in O₂ or the Fe=Fe bond in (η⁵-Me₅C₅)₂Fe₂(μ-CO)₃ (I). Assuming that the metal–metal bond axis is the z-axis, these perpendicular one-electron π-half-bonds use the metal dₓz and dᵧz orbitals, which are not involved in the sp³d³(z²-x²-y²) octahedral hybridization of each chromium atom required for the six σ bonds (i.e., the bonds to the five terminal CO groups and the Cr–Cr σ-bond). In the symmetry point group for the lowest energy triplet Cr₂(CO)₁₀ structure (C₂), the metal dₓz and dᵧz orbitals are not strictly degenerate since the C₂ point group has only non-degenerate irreducible representations. This differs from both the Dₘₘ point group of O₂ and the Dₘₘₘ local symmetry of the Fe–Fe bond in (η⁵-Me₅C₅)₂Fe₂(μ-CO)₃ (I) in which the metal dₓz and dᵧz orbitals belong to the two-fold degenerate irreducible representations eᵣ and π₂, respectively. However, the analysis of the imaginary vibrational frequencies for Dₘₘₘₘ triplet Cr₂(CO)₁₀ discussed above suggests that the lowest energy C₂ structure for triplet Cr₂(CO)₁₀ (Fig. 6) may be very close to the Dₘₘₘₘ structure (Fig. 11), differing only by tilting the Cr(CO)₅ “halves” of local C₄ symmetry. If this is the case, then the energy difference between the metal dₓz and dᵧz orbitals in the C₂ structure of triplet Cr₂(CO)₁₀ may be smaller than the pairing energy of the two electrons so that a triplet rather than a singlet structure is preferred. Note that in the Dₘₘₘₘ point group the metal dₓz and dᵧz orbitals belong to the two-fold degenerate irreducible representation E₉.

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References