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Triple Decker Sandwiches and Related Compounds of the First Row Transition Metals with Cyclopentadienyl and Hexafluorobenzene Rings: Remarkable Effects of Fluorine Substitution

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Abstract

The complete series of $\text{Cp}_2\text{M}_2(\mu\text{-C}_6\text{F}_6)$ ($\text{M} = \text{Ti}, \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$) structures have been examined theoretically for comparison with their unsubstituted $\text{Cp}_2\text{M}_2(\mu\text{-C}_6\text{H}_6)$ analogues. The singlet triple decker sandwich titanium complex $\text{Cp}_2\text{Ti}_2(\eta^6, \eta^6\text{-C}_6\text{F}_6)$ with a closed shell electronic structure and a non-planar C_6F_6 ring is preferred energetically by a wide margin (>20 kcal/mol) over other isomers and spin states. This is in contrast to the hydrogen analogue for which related triplet spin state structures are clearly preferred. A similar low-energy triple-decker sandwich $\text{Cp}_2\text{V}_2(\eta^6, \eta^6\text{-C}_6\text{F}_6)$ structure is found for vanadium but with a quintet spin state. The later transition metals from Cr to Ni energetically prefer the so-called “rice-ball” *cis*- $\text{Cp}_2\text{M}_2(\mu\text{-C}_6\text{F}_6)$ structures with varying hapticities of metal-ring bonding, a range of formal orders of metal-metal bonding, and varying spin states depending on the metal atom. Thus the lowest energy $\text{Cp}_2\text{Cr}_2(\mu\text{-C}_6\text{F}_6)$ structures are triplet and quintet structures with pentahapto-trihapto $\eta^5, \eta^3\text{-}\mu\text{-C}_6\text{F}_6$ rings and formal Cr=Cr double bonds. This contrasts with the structure of $\text{Cp}_2\text{Cr}_2(\mu\text{-C}_6\text{H}_6)$ having a bis(tetrahapto) $\eta^4, \eta^4\text{-C}_6\text{H}_6$ ring and a formal Cr-Cr quadruple bond. The lowest energy $\text{Cp}_2\text{Mn}_2(\mu\text{-C}_6\text{F}_6)$ structures are *trans* and *cis* quintet spin state structures. This contrasts with $\text{Cp}_2\text{Mn}_2(\mu\text{-C}_6\text{H}_6)$ for which a closed-shell singlet triple decker sandwich structure is preferred. The lowest energy $\text{Cp}_2\text{Fe}_2(\mu\text{-C}_6\text{F}_6)$ structure is a triplet *cis* structure with a tetrahapto-dihapto $\eta^4, \eta^2\text{-}\mu\text{-C}_6\text{F}_6$ ring and a formal Fe-Fe single bond. The lowest energy $\text{Cp}_2\text{Co}_2(\mu\text{-C}_6\text{F}_6)$ structures are singlet spin state structures with formal M-M single bonds and either bridging bis(trihapto) $\eta^3, \eta^3\text{-C}_6\text{F}_6$ or tetrahapto-dihapto $\eta^4, \eta^2\text{-C}_6\text{F}_6$ rings. For $\text{Cp}_2\text{Ni}_2(\mu\text{-C}_6\text{F}_6)$ low energy singlet *cis* and *trans* structures are both found. The singlet *cis*- $\text{Cp}_2\text{Ni}_2(\mu\text{-C}_6\text{F}_6)$ structure has a Ni-Ni single bond of length ~ 2.5 Å and a bridging bis(dihapto) $\eta^2, \eta^2\text{-C}_6\text{F}_6$ ligand with an uncomplexed C=C double bond. The singlet *trans*- $\text{Cp}_2\text{Ni}_2(\mu\text{-C}_6\text{F}_6)$ structure has a bis(trihapto) $\eta^3, \eta^3\text{-C}_6\text{F}_6$ ligand.

1. Introduction

The serendipitous discovery of sandwich compounds in the 1950s represented a major milestone in the development of transition metal organometallic chemistry and the applications of such organometallic compounds in homogeneous catalysis and organic synthesis. The first such sandwich compound was ferrocene, Cp_2Fe ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$), synthesized independently by two different research groups^{1,2} and shown shortly after the original synthesis to have a then unprecedented structure with the iron atom sandwiched between two planar cyclopentadienyl rings.³ The subsequent 1955 discovery of dibenzenechromium ($\eta^6\text{-C}_6\text{H}_6$)₂Cr showed that transition metals could be sandwiched between a pair of benzene rings as well as a pair of cyclopentadienyl rings.⁴ Later mixed sandwich compounds with two different ring sizes such as $\text{CpMn}(\eta^6\text{-C}_6\text{H}_6)$ ⁵ and $\text{CpV}(\eta^7\text{-C}_7\text{H}_7)$ ⁶ were discovered (Figure 1).

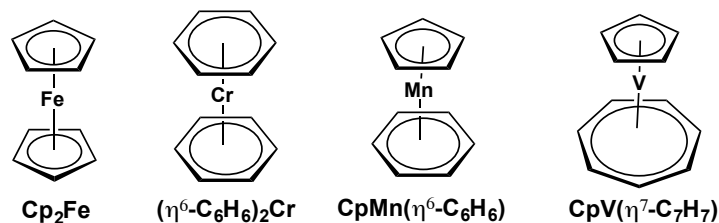


Figure 1. Examples of experimentally known sandwich compounds.

The possibility of extending such sandwich structures to larger molecules including triple-decker sandwich structures was first suggested by the 1964 observation by Schumacher and Taubenest⁷ of Cp_3Ni_2^+ in the mass spectrum of nickelocene. This initial observation was later confirmed by the 1972 synthesis and structural characterization by Werner and Salzer of the stable salt $[\text{Cp}_3\text{Ni}_2][\text{BF}_4]$ (Figure 2).^{8,9,10} The subsequent synthesis and structural characterization of the neutral binuclear mesitylene $(1,3,5\text{-Me}_3\text{C}_6\text{H}_3)_3\text{Cr}_2$ compound by Lamanna¹¹ showed that benzene rings could also be used for the construction of triple decker sandwich structures (Figure 2). In addition the neutral triple-decker sandwich compound $\text{Cp}_2\text{V}_2(\eta^6, \eta^6\text{-}\mu\text{-C}_6\text{H}_6)$ with a central benzene ring and outer cyclopentadienyl rings has been synthesized and structurally characterized by Krüger and coworkers.¹²

Attempts to synthesize triple-decker benzene sandwiches of the type $\text{Cp}_2\text{M}_2(\mu\text{-C}_6\text{H}_6)$ with metals have led to interesting structures of other types (Figure 3). The cobalt compound was found to have a “slipped” triple-decker sandwich $\text{Cp}_2\text{Co}_2(\eta^4, \eta^4\text{-}\mu\text{-C}_6\text{H}_6)$ structure with only four of the six carbons of the central benzene ring bonded to each cobalt atom (Figure 3).¹³ This contrasts with the isoelectronic nickel dication $[\text{Cp}_2\text{Ni}_2(\eta^6, \eta^6\text{-}\mu\text{-C}_6\text{H}_6)]^{2+}$, which has been shown by Green and coworkers¹⁴ to have the central benzene ring symmetrically bonded to each

nickel atom, with all six carbon atoms within bonding distance of each nickel atom. This structure is analogous to and isoelectronic with the Cp_3Ni_2^+ cation structure discussed above (Figure 2).

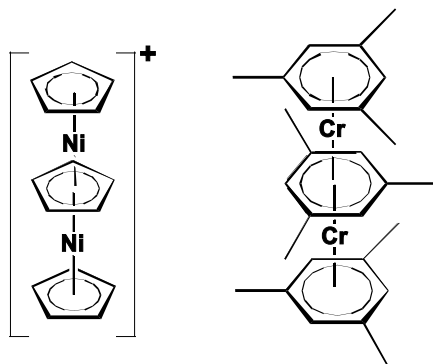


Figure 2. Experimentally known triple-decker sandwich compounds.

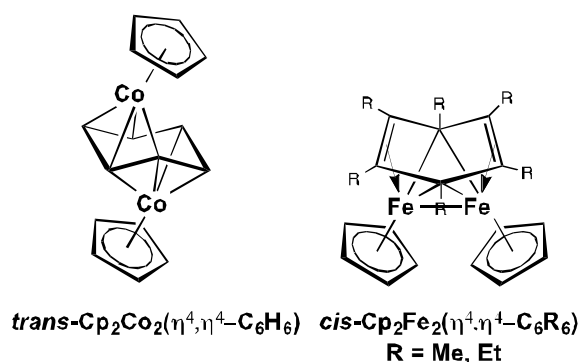


Figure 3. The “slipped” triple decker sandwich *trans*- $\text{Cp}_2\text{Co}_2(\eta^4, \eta^4\text{-C}_6\text{H}_6)$ and the “rice-ball” structure *cis*- $\text{Cp}_2\text{Fe}_2(\eta^4, \eta^4\text{-C}_6\text{R}_6)$ (R = Me, Et).

The triple-decker sandwich structures Cp_3Ni_2^+ , $(1,3,5\text{-Me}_3\text{C}_6\text{H}_3)_3\text{Cr}_2$, and $\text{Cp}_2\text{V}_2(\eta^6, \eta^6\text{-}\mu\text{-C}_6\text{H}_6)$ may be considered to have *trans* stereochemistry with the metal atoms too far apart to form a direct metal-metal bond. This contrasts with the *cis* configuration of the iron atoms in *cis*- $\text{Cp}_2\text{Fe}_2(\eta^4, \eta^4\text{-}\mu\text{-C}_6\text{R}_6)$, which have been synthesized and structurally characterized (Figure 3: R = Me, Et).¹⁵ Such *cis* structures have been called “rice-ball” structures.¹⁶ The experimental and theoretical literature for both the *trans* triple-decker sandwich structures and the *cis* “rice-ball” structures with various bridging carbocyclic and heterocyclic ligands was reviewed in 2004 by Beck and O’Hare.¹⁷ The preferred structures of the complete series of first row transition metal derivatives $\text{Cp}_2\text{M}_2(\mu\text{-C}_6\text{H}_6)$ have been investigated by density functional theory.¹⁸ In general, the early transition metals are found to prefer triple-decker sandwich

structures *trans*-Cp₂M₂(μ-C₆H₆) without direct metal-metal bonds whereas the late transition metals prefer *cis*-Cp₂M₂(μ-C₆H₆) rice-ball structures with direct metal-metal bonds.

The effects of fluorination on the structure, bonding, and chemical reactivity of ligands bound to transition metal centers have been of considerable interest for many years.^{19,20} Particularly interesting synthetic targets are the fluorinated analogues of sandwich compounds such as ferrocene. However, efforts to use the known²¹ pentafluorocyclopentadienide anion, C₅F₅⁻, to synthesize transition metal complexes have proven to be unrewarding.²² Thus, the first transition metal sandwich complex of the C₅F₅ ligand, (η⁵-C₅Me₅)(η⁵-C₅F₅)Ru, was synthesized by Seppelt and coworkers not from the C₅F₅⁻ ligand but instead by extrusion of CO from the pentafluorophenolate Ru(η⁵-C₅Me₅)(η⁵-C₆F₅O) using flash vacuum pyrolysis at 750°C.²² Despite the strong electron-withdrawing properties of the fluorine substituents, the ruthenium complexes (η⁵-C₅X₅)(η⁵-C₅F₅)Ru (X = H, Me) were found to be very stable compounds. However, the difficulty in synthesizing C₅F₅M complexes from the C₅F₅⁻ anion might be a consequence of the strongly electron withdrawing properties of the fluorine atoms. Recently, pentafluoroferrrocene (η⁵-C₅H₅)(η⁵-C₅F₅)Fe was prepared in five steps starting from ferrocene via a one-pot lithiation–electrophilic fluorination sequence.²³

Syntheses of metal complexes of hexafluorobenzene have been more successful, although no stable well-characterized metal complexes with hexahapto η⁶-C₆F₆ ligands have yet been reported. This could also be a consequence of the strong electron-withdrawing properties of the fluorine substituents. However, stable metal hexafluorobenzene complexes include the tetrahapto derivatives CpIr(η⁴-C₆F₆)²⁴ and (η⁶-C₆H₆)Ru(η⁴-C₆F₆)²⁵ (Figure 4).

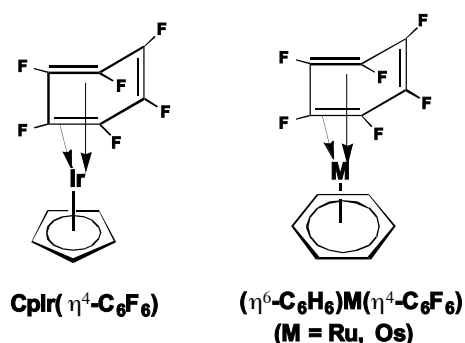


Figure 4. Examples of stable tetrahapto hexafluorobenzene metal sandwich complexes.

No examples of metal complexes with a hexafluorobenzene ligand bridging two metal atoms are known. In view of the stability of the known bridging benzene complexes with terminal cyclopentadienyl rings, namely Cp₂M₂(μ-C₆H₆) (M = V,¹² Fe,¹⁵ Co¹³), the perfluorinated analogues Cp₂M₂(μ-C₆F₆) appear to be possible candidates for experimental realization. We report here density functional theory studies on the complete series of such binuclear

bridging hexafluorobenzene derivatives $\text{Cp}_2\text{M}_2(\mu\text{-C}_6\text{F}_6)$ ($\text{M} = \text{Ti}, \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$) for comparison with their non-fluorinated analogues $\text{Cp}_2\text{M}_2(\mu\text{-C}_6\text{H}_6)$.¹⁸

2. Theoretical Methods

Density functional theory (DFT) methods, which may include electron correlation effects, have evolved as a practical and effective computational tool, especially for organometallic compounds.^{26,27,28,29,30,31,32} The quality of the approximate exchange-correlation (XC) energy functional determines the reliability of such DFT methods. We initially chose two popular DFT methods, the B3LYP and the BP86 methods, which are constructed in very different ways. The well-established B3LYP method combines the three-parameter Becke functional (B3)³³ with the Lee–Yang–Parr (LYP) generalized gradient correlation functional.³⁴ The BP86 method combines Becke's 1988 exchange functional (B)³⁵ with Perdew's 1986 gradient corrected correlation functional (P86).³⁶ Reiher and coworkers have noted that B3LYP favors the high-spin state and BP86 favors the low-spin state for a series of the Fe(II)-S complexes.³⁷ This is also true for the molecules studied in this research so that these two DFT methods may predict global minima in different spin states. For this reason, a new parametrization for the B3LYP functional was proposed by Reiher and coworkers, named B3LYP*, which provides electronic state orderings in agreement with experiment.³⁸ Thus, in order to have a conclusive energy ordering, we discuss the B3LYP* geometries and energies in the text unless otherwise specified. The corresponding results from the B3LYP and BP86 methods are shown in the Supplementary Information. In addition, Slimani et al. proposed in 2004 a similar reparametrization approach for the DFT functionals based on the equilibrium temperature of spin-crossover compounds.³⁹ This new reparametrization approach can provide more accurate amount of exact exchange admixture in DFT functional for certain systems. However, the parameters can be determined only if the experimental equilibrium temperature is known. This is not the case with the molecules discussed in this paper.

DFT methods are less basis set sensitive than higher-level methods, such as coupled cluster theory. In this work, all computations were performed using double- ζ plus polarization (DZP) basis sets. The DZP basis sets used for hydrogen, carbon, and fluorine add one set of pure spherical harmonic polarization functions (p orbitals for H, and d orbitals for C and F) with orbital exponents $\alpha_p(\text{H}) = 0.75$, $\alpha_d(\text{C}) = 0.75$, $\alpha_d(\text{F}) = 1.0$ to the standard Huzinaga–Dunning contracted DZ sets.^{40,41} For the first-row transition metals Ti, V, Cr, Mn, Fe, Co, and Ni, Wachters' primitive sets⁴² were used in our loosely contracted DZP basis set but augmented by two sets of p functions and one set of d functions, with contraction following Hood, Pitzer, and

Schaefer,⁴³ and designated (14s11p6d/10s8p3d). There are 478 contracted Gaussian functions for $\text{Cp}_2\text{M}_2(\mu\text{-C}_6\text{F}_6)$ (M=Ti, V, Cr, Mn, Fe, Co, Ni).

The geometries of all structures were fully optimized. Vibrational frequencies were determined analytically. All of the computations were carried out with the Gaussian 03 program,⁴⁴ exercising the pruned fine grid (75, 302) option for evaluating integrals. The finer grid (120, 974) was used to double check the small imaginary vibrational frequencies. All of the predicted triplet and quintet structures were found to have negligible spin contamination, that is, the values of $S(S+1)$ are very close to the ideal values of 2 and 6, respectively.

The spin-restricted method was used for the closed-shell structures, and the spin-unrestricted method was used for the open-shell structures. We have also tried the unrestricted method for open-shell singlet state structures. However, only four of the *cis*- $\text{Cp}_2\text{M}_2(\mu\text{-C}_6\text{F}_6)$ structures (**Ti-c-2S**, **V-c-1S**, **Cr-c-1S**, and **Mn-c-2S**) in the open-shell singlet state lie at lower energies than the corresponding closed-shell singlet state structures. However, these structures are all higher energy structures than the corresponding triplet or quintet state structures. In addition, the other *cis* structures and all *trans* structures in the open-shell singlet state are predicted to lie at higher energies than the isomeric closed-shell singlet and/or triplet state structures. Therefore the open-shell singlet structures are not discussed in the present paper.

Figures 5 to 11 depict the optimized geometries from the B3LYP*/DZP computations. Tables 1 to 7 report their relative energies and other properties from the three DFT (B3LYP, BP86, and B3LYP*) methods. The structures are designated as **M-a-nX**, where **M** is the metal atom; **a** (= **c** or **t**) for *cis* (rice-ball) or *trans* (triple-decker-sandwich) structures, respectively; **n** orders the structures by their B3LYP* relative energies; and **X** indicates the spin state as **S** (singlet), **T** (triplet), or **Q** (quintet).

3. Results and Discussion

3.1. Molecular Structures

3.1.1. Titanium derivatives. The global minimum $\text{Cp}_2\text{Ti}_2(\mu\text{-C}_6\text{F}_6)$ structure, namely **Ti-t-1S** (Figure 5), is a C_i symmetry triple-decker-sandwich structure. A structure optimized with the constraint of C_{2h} symmetry has two small imaginary vibrational frequencies ($7i$ and $4i$ cm^{-1}) and is slightly higher-lying (0.1 kcal/mol). Following the corresponding normal mode leads to **Ti-t-1S**. The C_6F_6 ring in **Ti-t-1S** is non-planar with alternating Ti-C distances of 2.052 and 2.340 Å to each titanium atom. The non-planarity of the C_6F_6 ring in **Ti-t-1S** contrasts with the planarity of the C_6H_6 ring in predicted structures¹⁸ for the hydrocarbon analogue $\text{Cp}_2\text{Ti}_2(\mu\text{-C}_6\text{H}_6)$. The Ti–Ti distance of 3.252 Å in **Ti-t-1S** suggests a formal single bond, leading to a 16-electron configuration. The corresponding C_s triplet structure **Ti-t-2T**, lying 24.0 kcal/mol in energy

above **Ti-t-1S**, has a longer and presumably non-bonding Ti...Ti distance of ~ 3.5 Å. Structure **Ti-t-2T** has two small imaginary frequencies. However, one of them appears to arise from numerical integration error, since it is removed by using the finer (120, 974) integration grid.

The four *cis* (rice-ball) $\text{Cp}_2\text{Ti}_2(\mu\text{-C}_6\text{F}_6)$ structures are relatively high energy structures, predicted to lie more than 20 kcal/mol above **Ti-t-1S** (Figure 5). The Ti=Ti distances of ~ 2.5 Å are ~ 0.7 Å shorter than that in **Ti-t-1S**, suggesting formal triple bonds. The C_6F_6 rings in both **Ti-c-1T** (C_1) and **Ti-c-2S** (C_1) function as η^5, η^3 ligands, whereas they are η^4, η^4 ligands in **Ti-c-3T** (C_2) and **Ti-c-3S** (C_2). In either case the combination of eight Ti–C bonds from the $\mu\text{-C}_6\text{F}_6$ rings to the titanium atoms, five electrons from the Cp rings, and a formal Ti=Ti triple bond gives each titanium atom a 16-electron configuration. All quintet $\text{Cp}_2\text{Ti}_2(\mu\text{-C}_6\text{F}_6)$ structures are predicted to lie more than 30 kcal/mol above the global minimum and thus are not discussed here.

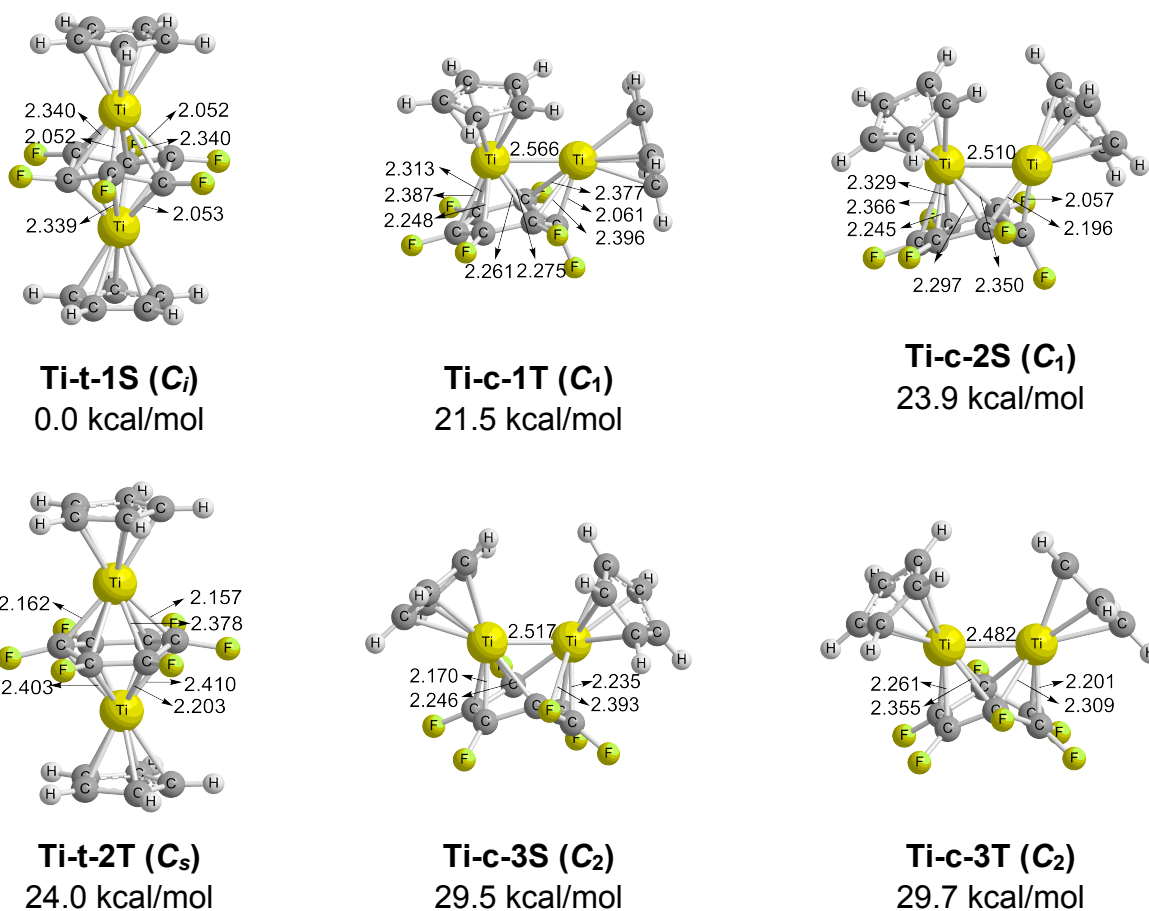


Figure 5. Six $\text{Cp}_2\text{Ti}_2(\mu\text{-C}_6\text{F}_6)$ structures within 30 kcal/mol of the global minimum from the B3LYP* method including their relative energies (kcal/mol).

3.1.2. *Vanadium Derivatives.* Five $\text{Cp}_2\text{V}_2(\mu\text{-C}_6\text{F}_6)$ structures, including two quintet structures, two triplet structures, and one singlet structure, were optimized (Figure 6). The global minimum structure **V-t-1Q** (C_1) is a quintet with all real vibrational frequencies when the finer (120, 974) integration grid is used. The predicted V...V distance in **V-t-1Q** of 3.496 Å is too long to form a direct chemical bond. The hexafluorobenzene ring in **V-t-1Q** is nearly planar with a dihedral angle of $\sim 20^\circ$. The six V-C bonding distances between the carbon atoms in the C_6F_6 ring and the “upper” vanadium atom (Figure 6) range from 2.16 to 2.37 Å (Figure 2), thereby giving that vanadium atom a 16-electron configuration. For the other vanadium atom, only four V-C distances fall within bonding distance, suggesting for that vanadium atom only a 14-electron configuration. In contrast, in another *trans* structure, namely the C_{2h} triplet **V-t-1T**, lying 17.7 kcal/mol in energy above **V-t-1Q**, all twelve V-C bonds are within the bonding range of ~ 2.1 to 2.3 Å. The V–V distance in **V-t-1T** of 3.202 Å can be interpreted as a formal single bond. This gives each vanadium atom a 17-electron configuration consistent with a binuclear triplet. Structure **V-t-1T** has two small imaginary frequencies, $28i$ and $26i$ cm^{-1} , which are removed by using the finer integration grid (120, 974).

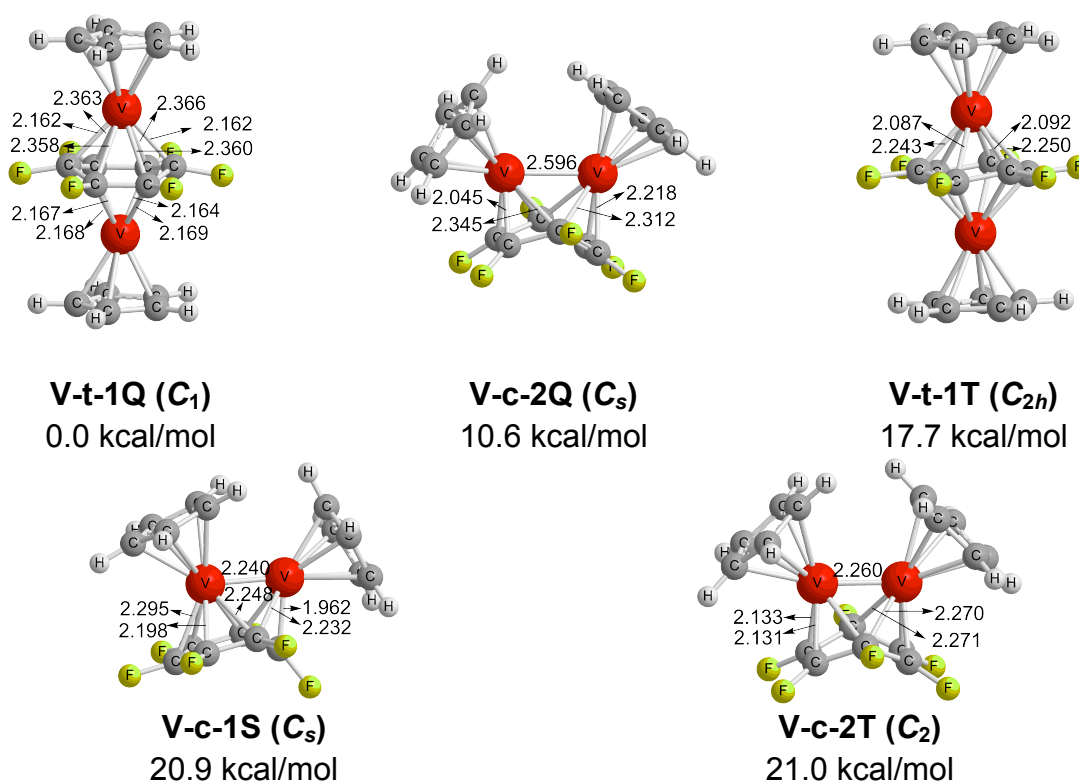


Figure 6. Five $\text{Cp}_2\text{V}_2(\mu\text{-C}_6\text{F}_6)$ structures within 30 kcal/mol of the global minimum from the B3LYP* method including their relative energies (kcal/mol).

The quintet *cis* Cp₂V₂(μ-C₆F₆) structure **V-c-2Q** (C_s), lying ~11 kcal/mol in energy above **V-t-1Q**, has a bridging bis(tetrahapto) η⁴,η⁴-C₆F₆ ring (Figure 6). The V=V distance of 2.596 Å can be interpreted as a formal double bond, thereby giving each vanadium atom a 16-electron configuration consistent with a high-spin quintet state. The other two *cis* (rice-ball) structures, namely singlet **V-c-1S** (C_s) and triplet **V-c-2T** (C₂), are close in energy and lie ~21 kcal/mol above the quintet structure **V-c-1Q**. The hexafluorobenzene ligands in **V-c-2T** and **V-c-1S** are η⁴,η⁴-C₆F₆ and η⁵,η³-C₆F₆, respectively, with a total of eight V–C bonding interactions in both cases to the two vanadium atoms. The short V–V distances of 2.260 Å and 2.240 Å for **V-c-2T** and **V-c-1S**, respectively, suggest formal quadruple bonds giving each vanadium atom the favored 18-electron configuration. In the singlet **V-c-1S** the formal V–V quadruple bond is a σ + 2π + δ bond containing four electron pairs. However, in the triplet **V-c-2T** the formal V–V quadruple bond corresponds to a σ + 2π + ½δ arrangement with two δ single electron “half bonds” providing the two unpaired electrons for the triplet spin state.

3.1.3. Chromium Derivatives. Seven Cp₂Cr₂(μ-C₆F₆) structures were found within 30 kcal/mol of the global minimum using the B3LYP* method (Figure 7). The lowest energy structure is the triplet *cis* structure **Cr-c-1T**, in which the distorted hexafluorobenzene ring is a pentahapto-trihapto η⁵,η³-μ-C₆F₆ ligand. One of the trihapto carbon atoms lies outside the C₆F₆ ring plane. The trihapto Cr–C bonding distances are 2.031, 2.457, and 2.457 Å, respectively, while the pentahapto Cr–C bond distances fall in the narrow range of 2.16 to 2.20 Å. The Cr=Cr distance of ~2.5 Å can be interpreted as a formal double bond, providing each chromium a 17-electron configuration for a binuclear triplet if the chromium atoms bonded to five and three carbon atoms of the η⁵,η³-μ-C₆F₆ ligand have formal positive and negative charges, respectively.

Three low energy quintet Cp₂Cr₂(μ-C₆F₆) structures **Cr-c-1Q** (C_s), **Cr-c-2Q** (C₂), and **Cr-t-3Q** (C_{2h}) were found within 20 kcal/mol of **Cr-c-1T** (Figure 7). Structure **Cr-c-1Q** is a *cis* (rice-ball) structure, lying 3.7 kcal/mol in energy above **Cr-c-1T**. The geometry of **Cr-c-1Q** is similar to that of **Cr-c-1T** with a pentahapto-trihapto η⁵,η³-μ-C₆F₆ ligand. The Cr=Cr distance in **Cr-c-1Q** of 2.542 Å (B3LYP*) is also similar to that in **Cr-c-1T**, thus suggesting a formal double bond. This gives each chromium atom a 17-electron configuration if the chromium atoms bonded to five and three carbon atoms of the η⁵,η³-μ-C₆F₆ ligand have formal positive and negative charges, respectively. This accounts for two of the unpaired electrons of the quintet spin state. The remaining two unpaired electrons can come from the formal Cr=Cr double bond, which is of the σ + ½π type with two orthogonal π single-electron “half-bonds”. Thus the Cr=Cr double bond is similar to the O=O double bond in dioxygen or the Fe=Fe double bond in the triplet spin state organometallic (Me₅C₅)₂Fe₂(μ-CO)₃, which has been structurally characterized by X-ray crystallography.^{45,46}

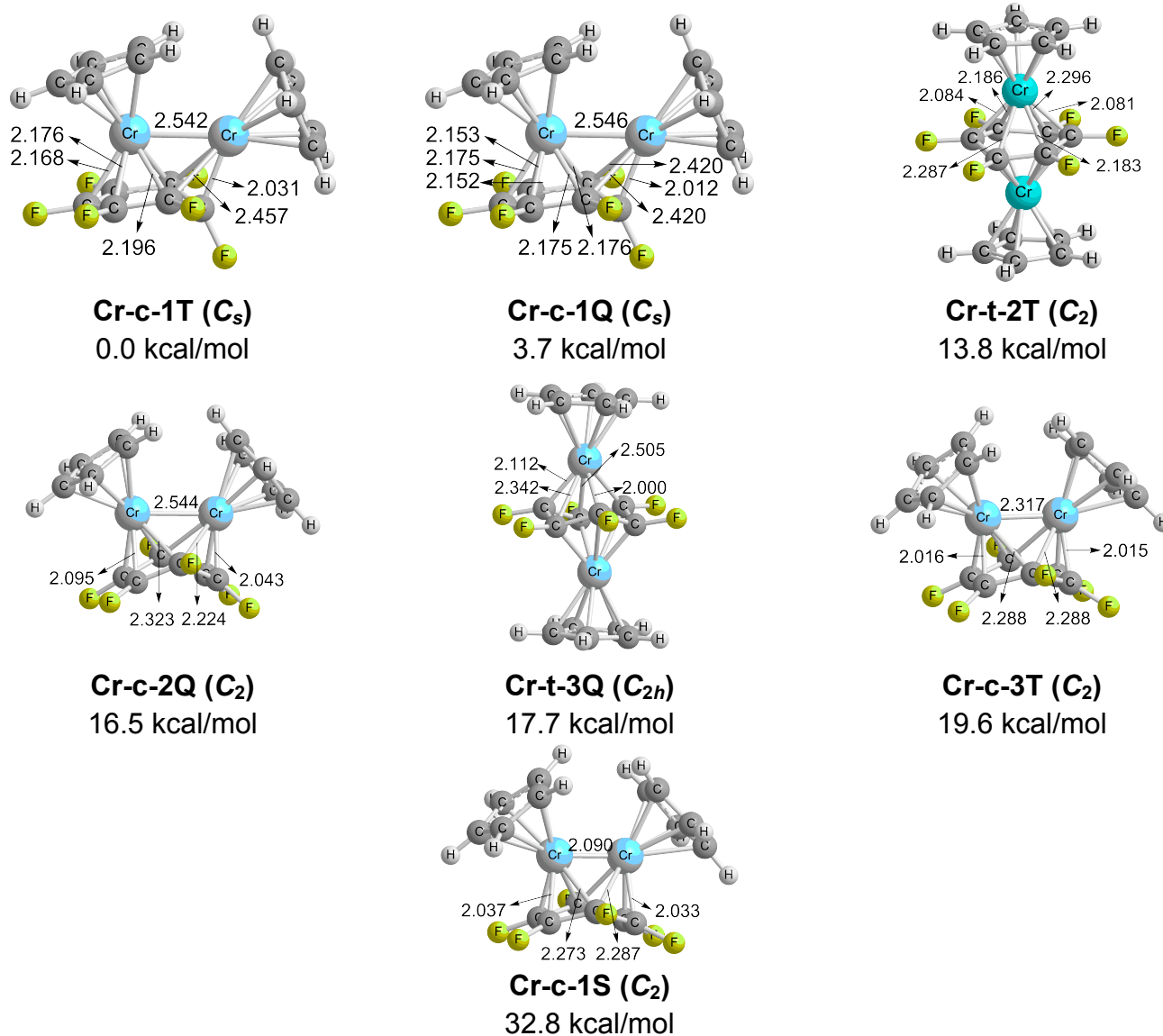


Figure 7. Seven Cp₂Cr₂(μ-C₆F₆) structures within 30 kcal/mol of the global minimum from the B3LYP* method including their relative energies (kcal/mol).

The second Cp₂Cr₂(μ-C₆F₆) structure is the *cis* structure **Cr-c-2Q**, lying 12.8 kcal/mol in energy above **Cr-c-1Q** (Figure 7). In **Cr-c-2Q**, the hexafluorobenzene ring is a symmetrical folded bridging η⁴,η⁴-C₆F₆ ligand bonding as a tetrahapto ligand to each chromium atom. The Cr=Cr distance of 2.544 Å is similar to that in **Cr-c-1Q**, suggesting a formal double bond and similar electron bookkeeping scheme to that described above for **Cr-c-1Q**. A quintet triple-decker sandwich structure **Cr-t-3Q** is also found with an energy close to that in **Cr-c-2Q**. Each chromium atom is linked to the distorted C₆F₆ ring, with Cr-C distances ranging from 2.00 to 2.51 Å (Figure 7). Structure **Cr-t-3Q** is predicted to have two small imaginary frequencies

using the default (75, 302) integration grid. However, they are removed with the finer (120, 974) integration grid.

As for the other two triplet $\text{Cp}_2\text{Cr}_2(\mu\text{-C}_6\text{F}_6)$ structures, the *trans* triple-decker sandwich structure **Cr-t-2T** (C_2), lying 13.8 kcal/mol above **Cr-c-1T**, has a slightly distorted C_6F_6 ring and an antipodal $\text{Cr}\cdots\text{Cr}$ distance of 3.299 Å (Figure 7). Structure **Cr-t-2T** has a small imaginary frequency of $33i\text{ cm}^{-1}$, which can be reduced to $8i\text{ cm}^{-1}$ by using the finer (120, 974) integration grid. The C_2 *cis* (rice-ball) structure **Cr-c-3T**, lying 19.6 kcal/mol in energy above **Cr-c-1T**, has a similar geometry to **Cr-c-2Q** except for the shorter $\text{Cr}=\text{Cr}$ distance of 2.317 Å.

The lowest energy singlet $\text{Cp}_2\text{Cr}_2(\mu\text{-C}_6\text{F}_6)$ structure **Cr-c-1S** is a high-energy structure, lying 32.8 kcal/mol in energy above **Cr-c-1T** (Figure 7). The hexafluorobenzene ring is a folded η^4, η^4 -ligand bonding as a tetrahapto ligand to each chromium atom. The $\text{Cr}=\text{Cr}$ distance of 2.090 Å is ~ 0.5 Å shorter than the ~ 2.5 Å $\text{Cr}=\text{Cr}$ distances interpreted above as formal double bonds. Formulating the $\text{Cr}=\text{Cr}$ bond in **Cr-c-1S** as a formal triple bond gives each chromium atom in **Cr-c-1S** the favored 18-electron configuration.

3.1.4. Manganese Derivatives. Five low-lying $\text{Cp}_2\text{Mn}_2(\mu\text{-C}_6\text{F}_6)$ structures (two quintets, two singlets, and one triplet) were obtained within 20 kcal/mol of the global minimum by the B3LYP* method (Figure 8). The $\text{Cp}_2\text{Mn}_2(\mu\text{-C}_6\text{F}_6)$ global minimum is a C_1 quintet spin state triple-decker sandwich structure **Mn-t-1Q**, with a long $\text{Mn}\cdots\text{Mn}$ distance of 3.930 Å and a nearly planar hexahapto-dihapto η^6, η^2 - C_6F_6 ring. The manganese atom bonded to all six carbon atoms of the η^6, η^2 - C_6F_6 ring has Mn-C bond distances ranging from 1.98 to 2.28 Å. This manganese atom has the favored 18-electron configuration. The other manganese atom, bonded to only two carbon atoms with Mn-C bond lengths of ~ 2.07 Å, has only a 14-electron configuration, accounting for the quintet spin state. The C_s *cis* (rice-ball) quintet structure **Mn-c-2Q** is energetically close to **Mn-t-1Q** (0.2 kcal/mol, Figure 8) with a tetrahapto-dihapto bridging η^4, η^2 - C_6F_6 ring and an Mn-Mn distance of 2.589 Å. Interpreting this Mn-Mn interaction as a formal single bond gives one manganese atom in **Mn-c-2Q** a 17-electron configuration and the other manganese atom a 15-electron configuration. This is consistent with the predicted quintet spin state.

The C_{2v} singlet triple-decker sandwich $\text{Cp}_2\text{Mn}_2(\mu\text{-C}_6\text{F}_6)$ structure **Mn-t-1S**, lying 9.3 kcal/mol in energy above **Mn-t-1Q**, has an antipodal $\text{Mn}\cdots\text{Mn}$ distance of 3.211 Å and a planar bis(hexahapto) η^6, η^6 - C_6F_6 ring, thereby giving each Mn atom the favored 18-electron configuration (Figure 8). The C_2 *cis* (“rice-ball”) structure **Mn-c-2S**, lying 15.5 kcal/mol in energy above **Mn-t-1Q**, has a folded bis(tetrahapto) η^4, η^4 - C_6F_6 ring. The Mn=Mn distance of 2.276 Å in **Mn-c-2S** is ~ 0.1 Å longer than the experimental Mn=Mn triple bond distance of 2.17 Å found by X-ray crystallography⁴⁷ for $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Mn}_2(\mu\text{-CO})_3$. Interpreting the Mn=Mn

interaction in **Mn-c-2S** as a formal double bond gives each manganese atom the favored 18-electron configuration.

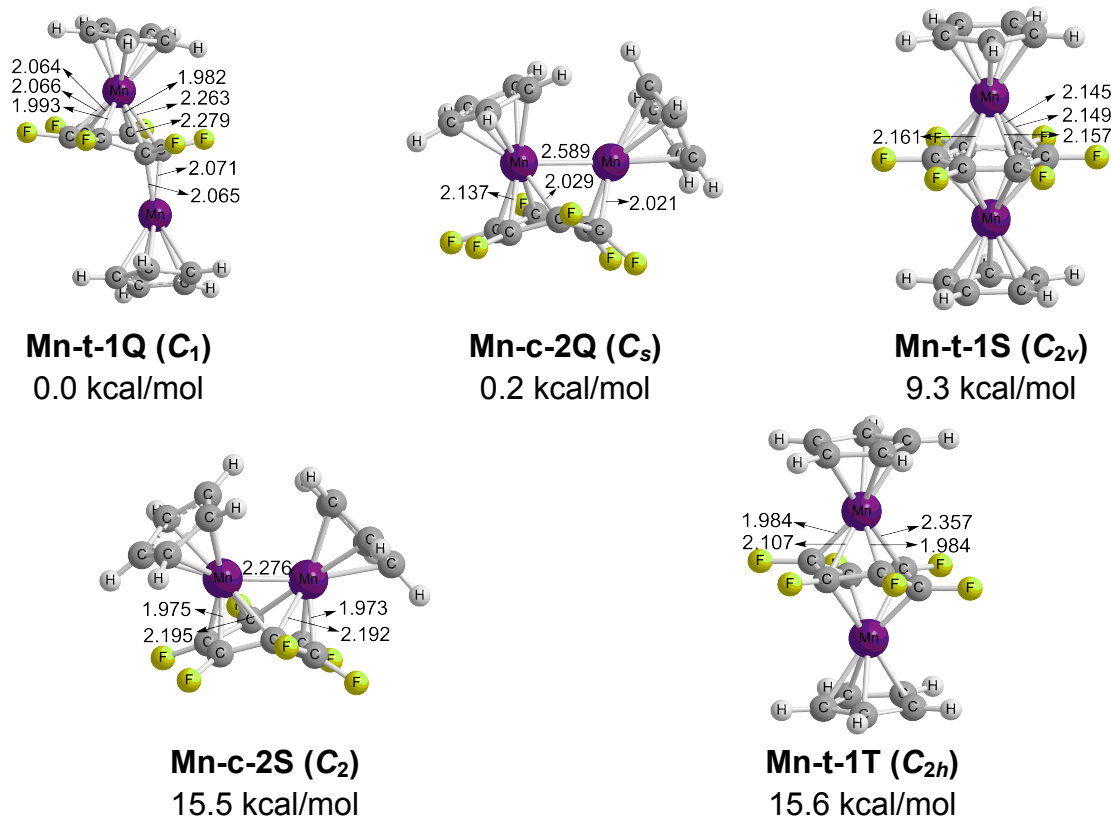


Figure 8. Five $Cp_2Mn_2(\mu-C_6F_6)$ structures within 20 kcal/mol of the global minimum by the B3LYP* method including their relative energies (kcal/mol).

The only triplet $Cp_2Mn_2(\mu-C_6F_6)$ structure is the C_{2h} triple-decker sandwich **Mn-t-1T**, lying 15.6 kcal/mol in energy above **Mn-t-1Q** (Figure 8). The central C_6F_6 ring in **Mn-t-1T** is bonded to each manganese atom as a tetrahapto $\eta^4, \eta^4-C_6F_6$ ligand. This gives each manganese atom in **Mn-t-1T** a 16-electron configuration.

3.1.5. Iron Derivatives. Five $Cp_2Fe_2(\mu-C_6F_6)$ structures are found within 20 kcal/mol of the global minimum using the B3LYP* method (Figure 9). The three *cis* (“rice-ball”) structures (one triplet, one singlet, and one quintet) are lower in energy than the two *trans* (triple-decker sandwich) structures. The $Cp_2Fe_2(\mu-C_6F_6)$ global minimum is a C_s triplet rice-ball structure **Fe-c-1T** with a bridging tetrahapto-dihapto $\eta^4, \eta^2-\mu-C_6F_6$ ligand, based on Fe-C distances of 1.996, 1.996, 2.076, and 2.076 Å for the “left” iron atom and those of 1.983, 1.983, 2.594, and 2.594 Å for the “right” iron atom (Figure 9). Interpreting the Fe-Fe distance of 2.538 Å as a formal Fe-Fe single bond gives the “left” iron atom the favored 18-electron configuration but the

“right” iron atom only a 16-electron configuration. The 16-electron configuration on the “right” iron atom can be responsible for the triplet spin state.

The *cis* (“rice-ball”) structures **Fe-c-1S** (C_2) and **Fe-c-1Q** (C_s) have similar energies, namely ~ 5 kcal/mol above **Fe-c-1T**, and similar Fe–Fe distances of ~ 2.5 Å, interpreted as formal single bonds (Figure 9). In **Fe-c-1S** the hexafluorobenzene ring is a folded bis(tetrahapto) η^4, η^2 - μ - C_6F_6 ligand, thereby giving both the Fe atoms the favored 18-electron configurations. The geometry of the quintet structure **Fe-c-1Q** is very similar to that of the triplet structure **Fe-c-1T** discussed above.

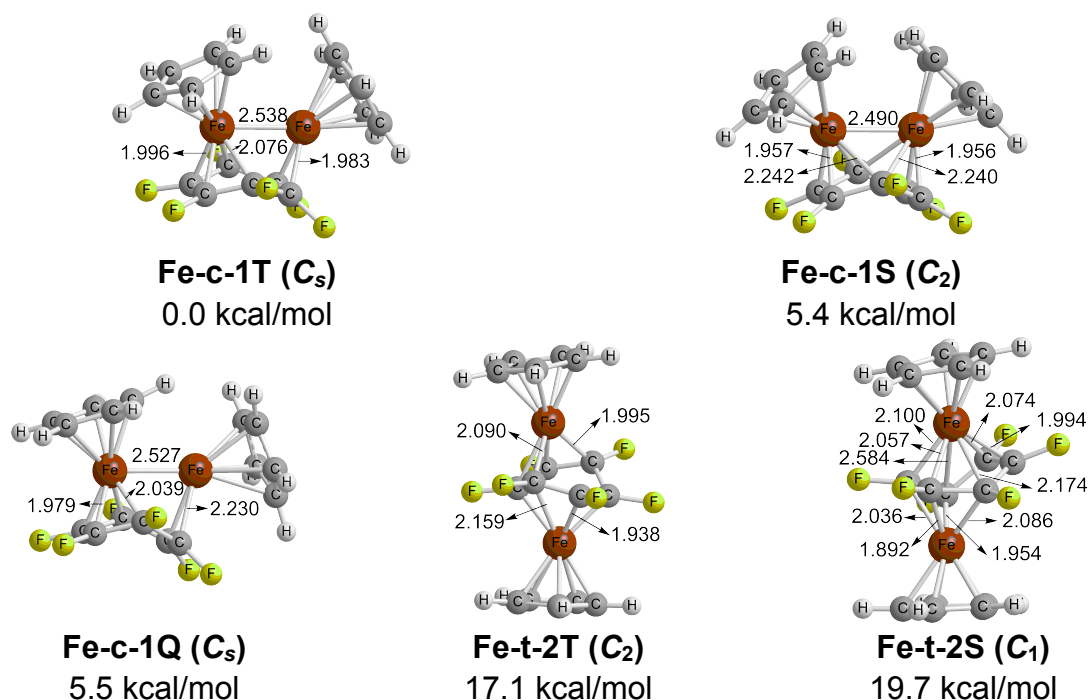


Figure 9. Five Cp₂Fe₂(μ -C₆F₆) structures within 20 kcal/mol of the global minimum by the B3LYP* method including their relative energies (kcal/mol).

3.1.6. Cobalt Derivatives. Three singlet and two triplet optimized Cp₂Co₂(μ -C₆F₆) structures were found (Figure 10). The C_2 singlet structure **Co-c-1S** is predicted to be the lowest energy structure. The distorted hexafluorobenzene ring symmetrically bonds to the central Co₂ unit as a bis(trihapto) η^3, η^3 -C₆F₆ ligand. The Co–C bond lengths are predicted to be 1.919, 2.001, and 2.005 Å. The Co–Co distance of 2.560 Å in **Co-c-1S** can be regarded as a formal single bond, providing each cobalt atom with the favored 18-electron configuration. The related unsymmetrical C_1 singlet Cp₂Co₂(η^4, η^2 - μ -C₆F₆) structure **Co-c-2S**, lying only 1.9 kcal/mol in energy above **Co-c-1S**, is similar to **Co-c-1S** except the bridging η^4, η^2 - μ -C₆F₆ ligand is a

tetrahapto-dihapto rather than a bis(trihapto) ligand. The Co→Co distance of 2.862 Å in **Co-c-2S** is ~0.3 Å longer than the Co–Co single bond distance in **Co-c-1S**, but it still can correspond to a direct cobalt-cobalt interaction. In this case, however, a Co→Co dative bond from the cobalt atom bonded to four carbon atoms of the η^4, η^2 -C₆F₆ ligand to the cobalt atom bonded to only two carbon atoms is what is required to give each cobalt atom in **Co-c-2S** the favored 18-electron configuration. The C₂ triplet structure **Co-c-1T**, lying 6.6 kcal/mol in energy above **Co-c-1S**, has a geometry similar to that of **Co-c-1S** with a Co–Co distance of 2.508 Å. The spin densities are ~0.9 on each cobalt atom of **Co-c-1T** consistent with 17-electron cobalt configurations and the triplet spin state.

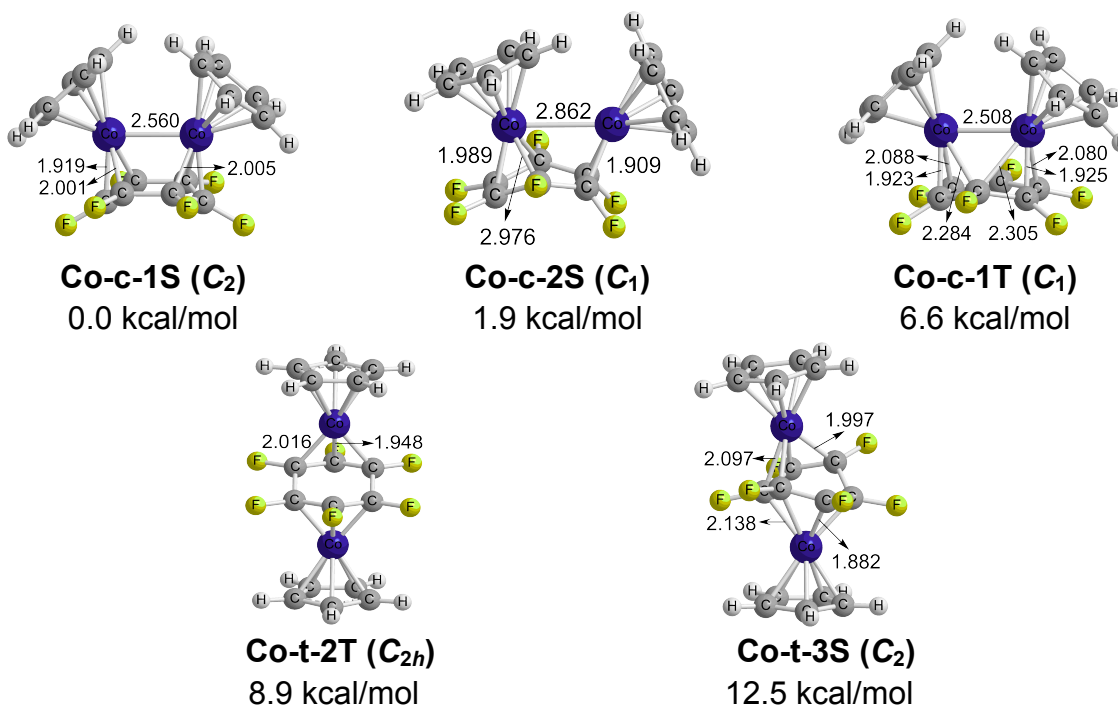


Figure 10. Five Cp₂Co₂(μ-C₆F₆) structures within 20 kcal/mol of the global minimum by the B3LYP* method including their relative energies (kcal/mol).

The C_{2h} triplet triple-decker-sandwich structure **Co-t-2T**, lying 8.9 kcal/mol in energy above **Co-c-1S**, has a bis(trihapto) bridging η^3, η^3 -C₆F₆ ring with Co–C bond distances of 2.016, 1.948, and 2.016 Å (Figure 10). This gives each cobalt atom in **Co-t-2T** a 17-electron configuration, consistent with a triplet state. The C₂ singlet structure **Co-t-3S**, lying 12.5 kcal/mol in energy above **Co-c-1S**, is also a triple-decker sandwich structure with a clearly non-bonding Co··Co distance of 3.625 Å. The bridging hexafluorobenzene ring in **Co-t-3S** is a bis(tetrahapto) η^4, η^4 -C₆F₆ ligand, giving each cobalt atom the canonical 18-electron configuration.

3.1.7 Nickel Derivatives. For the nickel derivative $\text{Cp}_2\text{Ni}_2(\mu\text{-C}_6\text{F}_6)$, three singlet and two triplet structures are obtained within 20 kcal/mol (Figure 11). None of the five structures has any imaginary vibrational frequencies using the B3LYP* method with the finer (120, 974) integration grid. The global minimum predicted by the B3LYP* method is a C_1 singlet structure **Ni-c-1S**. The bridging hexafluorobenzene ligand in **Ni-c-1S** is a bis(dihapto) $\eta^2, \eta^2\text{-C}_6\text{F}_6$ ligand with Ni-C distances ranging from 1.950 to 1.983 Å and an uncomplexed C=C double bond distance of 1.361 Å. The predicted Ni-Ni distance in **Ni-c-1S** of 2.504 Å corresponds to a formal single bond, yielding for each nickel atom the standard 18-electron configuration.

The singlet triple-decker sandwich structure **Ni-t-2S**, lying only 0.8 kcal/mol in energy (B3LYP*) above **Ni-c-1S**, has a bridging bis(trihapto) $\eta^3, \eta^3\text{-C}_6\text{F}_6$ ligand with bonding Ni-C distances of 1.9 to 2.0 Å (Figure 11). This gives each nickel atom the favored 18-electron configuration. The C_2 triplet triple-decker sandwich structure **Ni-t-1T**, lying 4.5 kcal/mol in energy above **Ni-c-1S**, has a bridging bis(dihapto) $\eta^2, \eta^2\text{-C}_6\text{F}_6$ ligand with Ni-C bonding distances of 1.9 to 2.0 Å and an uncomplexed C=C double bond of length 1.366 Å. This gives each nickel atom in **Ni-t-1T** a 17-electron configuration consistent with a binuclear triplet.

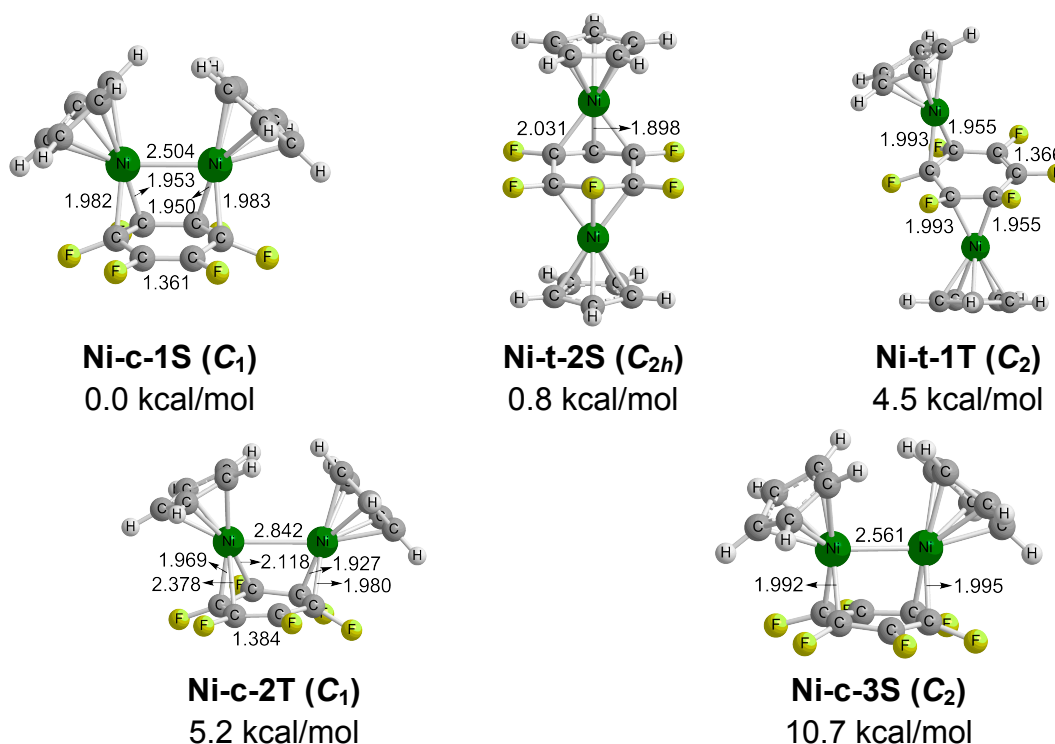


Figure 11. Five $\text{Cp}_2\text{Ni}_2(\mu\text{-C}_6\text{F}_6)$ structures within 20 kcal/mol of the global minimum by the B3LYP* method including their relative energies (kcal/mol).

The C_1 triplet rice-ball $\text{Cp}_2\text{Ni}_2(\mu\text{-C}_6\text{F}_6)$ structure **Ni-c-2T**, predicted to lie 5.2 kcal/mol above **Ni-c-1S**, has a bridging bis(dihapto) $\eta^2, \eta^2\text{-C}_6\text{F}_6$ ligand similar to that in **Ni-c-1S** (Figure 11). The Ni \cdots Ni distance of 2.842 Å in **Ni-c-2T** is more than 0.3 Å longer than that in **Ni-c-1S** suggesting no direct Ni-Ni bond. This then gives each nickel atom in **Ni-c-2T** a 17-electron configuration characteristic of a binuclear triplet. The 17-electron configurations of the nickel atoms in **Ni-c-2T** are consistent with their Mulliken atomic spin densities of 0.63 and 0.78. The other singlet rice-ball structure **Ni-c-3S**, lying 10.7 kcal/mol in energy above **Ni-c-1S**, has a bridging bis(dihapto) $\eta^2, \eta^2\text{-}\mu\text{-C}_6\text{F}_6$ ring and an Ni–Ni single bond of length 2.561 Å. This gives each nickel atom in **Ni-c-3S** the favored 18-electron configuration. The tetrahapto hexafluorobenzene ring in **Ni-c-3S** is different from those in **Ni-c-1S** and **Ni-c-2T**, with the two uncoordinated carbon atoms in para (opposite) rather than ortho (adjacent) positions.

3.2 Molecular Orbital (MO) Schemes of the Triple-Decker *trans*- $\text{Cp}_2\text{M}_2(\mu\text{-C}_6\text{F}_6)$ Sandwiches

Chesky and Hall⁴⁸ first studied the MOs of triple-decker sandwich compounds related to those discussed in this paper in order to analyze the photoelectron spectra of the vanadium derivatives *trans*- $\text{Cp}_2\text{V}_2(\mu\text{-arene})$ (arene = benzene or mesitylene). Their computations, reported in 1984, used Fenske-Hall methods.⁴⁹ In our previous paper,¹⁸ we found that the M–M distances in the triple-decker sandwiches *trans*- $\text{Cp}_2\text{M}_2(\mu\text{-C}_6\text{H}_6)$ (M = Ti, V, Cr, Mn) can be related specifically to the occupancy of the σ_g MO, which consists of a symmetric overlap of the $d(z^2)$ orbitals of the two metal atoms. When the critical σ_g orbital is fully occupied, the M–M distances are around 3.2 Å, whereas when the σ_g orbital has only a single electron in it, the M–M distances increase to about 3.4 Å. Other frontier molecular orbitals make little contribution to the M \cdots M distances.

The situation in the fluorine substituted triple-decker sandwiches *trans*- $\text{Cp}_2\text{M}_2(\mu\text{-C}_6\text{F}_6)$ (M = Ti, V, Cr, Mn), appears to be more complicated than that in their hydrogen analogues. Figure 12 depicts the frontier MOs arising from our DFT methods for the singlet *trans*- $\text{Cp}_2\text{Mn}_2(\eta^6, \eta^6\text{-}\mu\text{-C}_6\text{F}_6)$ structure (**Mn-t-1S** in Figure 8). This can be considered to be a “closed-shell” structure since each manganese atom has the favored 18-electron configuration. The frontier orbitals for the corresponding chromium, vanadium, and titanium derivatives are essentially the same, though the energy orderings may be different. The labels used in Figure 12 are in accord with those in our previous work.¹⁸ Figure 12 shows that the LUMO and LUMO+1 are a pair of essentially degenerate π_u orbitals, the HOMO and HOMO-1 are a pair of essentially degenerate δ_g orbitals, followed by a σ_u orbital as HOMO-2, a pair of degenerate δ_u orbitals as HOMO-3 and HOMO-4, and a σ_g orbital as HOMO-5. This energy order differs from that by the Fenske-Hall method, which places the σ_u and σ_g MOs at higher energies than the degenerate δ_g

MOs. It also differs from the energy order of *trans*-Cp₂Mn₂(μ-C₆H₆),¹⁸ in which the σ_g MO lies above the degenerate δ_u MOs.

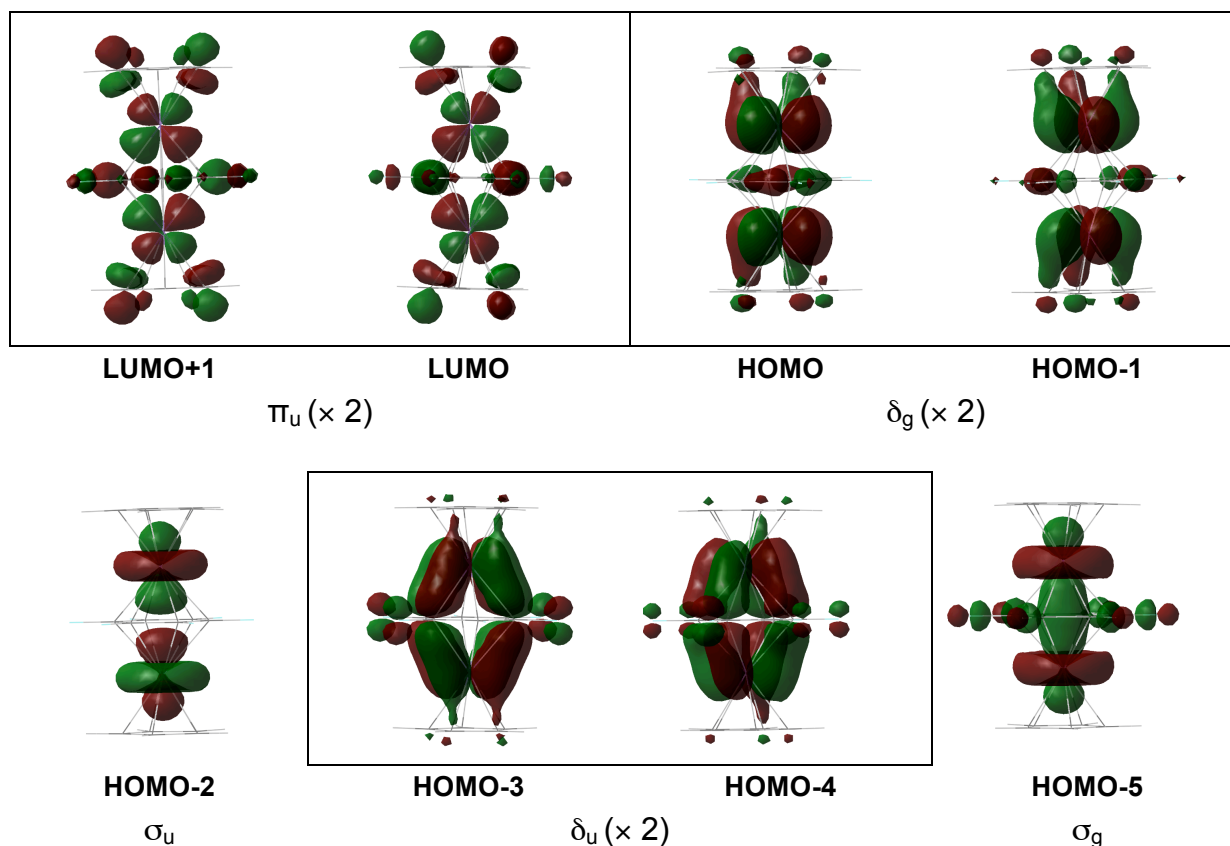


Figure 12. The frontier molecular orbitals listed in order from LUMO+1 to HOMO-5 for **Mn-t-1S**. The other *trans*-Cp₂M₂(μ-C₆F₆) (M= Ti, V, Cr, Mn) structures have essentially the same orbitals, though in different energy orders.

In the singlet *trans*-Cp₂Mn₂(μ-C₆F₆) structure (**Mn-t-1S**) these six MOs (HOMO down to HOMO-5) are all filled, i.e., σ_g²δ_u⁴σ_u²δ_g⁴, with the higher lying π_u orbitals (LUMO and LUMO+1) unoccupied (Table 1). The triplet *trans*-Cp₂Cr₂(μ-C₆F₆) (**Cr-t-2T**) has two less electrons in the two degenerate δ_g orbitals, so the occupancy becomes σ_g²δ_u⁴σ_u²δ_g² with the two unpaired electrons in the degenerate δ_g orbitals. The triplet **V-t-1T** structure has two electrons less than **Cr-t-2T**; these two electrons are taken from the σ_u orbital leading to the occupancy σ_g²δ_u⁴δ_g², with the two unpaired electrons still in the degenerate δ_g orbitals. The two electrons lost in going from the triplet **V-t-1T** to the singlet **Ti-t-1S** are the two unpaired electrons in the two δ_g orbitals, leading to the occupancy σ_g²δ_u⁴ and a singlet spin state (Table 1). Thus **Ti-t-1S** has a closed shell electronic configuration consistent with its being the lowest energy Cp₂Ti₂(μ-C₆F₆) structure by more than 20 kcal/mol.

Table 1. Occupancy of the frontier MOs; Wiberg bond indices (WBIs), formal bond orders (BO), distances between the two metals (d_{M-M} , Å), twice covalent radius⁵⁰ (r_{cov}^M , Å) and van der Waals radius⁵¹ (r_{vdW}^M , Å) for the two metal atoms, spin densities on the metal atoms (ρ_s^M , the left/right values for the upper/lower metal atoms in figures), and spin densities on the C₆F₆ ring (ρ_s^R) for the *trans*-Cp₂M₂(C₆F₆) (M = Mn, Cr, V, Ti) structures.

	Mn-t-1T	Mn-t-1S	Cr-t-3Q	Cr-t-2T	V-t-1Q	V-t-1T	Ti-t-2T	Ti-t-1S
π_u								
δ_g								
σ_u								
δ_u								
σ_g								
BO	0	0	0.5	0	0	1	0.5	1
WBI	0.11	0.10	0.19	0.09	0.05	0.60	0.32	0.71
d_{M-M}	3.47	3.21	3.43	3.30	3.50	3.20	3.52	3.25
$2r_{cov}^M$	2.78 (low spin)		2.78		3.06		3.20	
$2r_{vdW}^M$	4.92		4.84		4.90		4.90	
ρ_s^M	1.16/1.16	—	2.54/2.54	1.29/1.29	2.46/2.14	1.28/1.28	0.42/1.48	—
ρ_s^R	-0.26	—	-0.98	-0.51	-0.52	-0.56	0.08	—

Table 1 also shows four higher spin *trans*-Cp₂M₂(μ -C₆F₆) structures. For the triplet *trans*-Cp₂Mn₂(μ -C₆F₆) (**Mn-t-1T**), compared with **Mn-t-1S**, one electron is excited from the HOMO δ_g orbital to the LUMO π_u orbital, leading to the electronic configuration $\sigma_g^2 \delta_u^4 \sigma_u^2 \delta_g^3 \pi_u^1$. The two electrons lost in going from the triplet **Mn-t-1T** to the quintet **Cr-t-3Q** come from the δ_g and σ_u orbitals, leading to the $\sigma_g^2 \delta_u^4 \sigma_u^1 \delta_g^2 \pi_u^1$ electronic configuration. Similarly the electronic configurations for **V-t-1Q** and **Ti-t-2T** are $\sigma_g^1 \delta_u^4 \sigma_u^1 \delta_g^2$ and $\sigma_g^1 \delta_u^4 \delta_g^1$, respectively.

For all eight *trans* structures listed in Table 1, the σ_g orbital is associated with the M-M bonding orbital, while the σ_u orbital is the M-M antibonding orbital. The formal M-M bond order in the *trans*-Cp₂M₂(C₆F₆) derivatives is mainly related to the occupancies of the σ_g and σ_u orbitals. When both bonding and anti-bonding orbitals are fully occupied, namely $\sigma_g^2 \sigma_u^2$, the formal M-M bond order equals zero such as in the singlet **Mn-t-1S**, the triplet **Mn-t-1T**, and the triplet **Cr-t-2T**. The M-M bond order for the quintet **V-t-1Q** is also zero, since both the σ_g and σ_u orbitals are half-occupied. The M-M bond orders of the quintet **Cr-t-3Q** and triplet **Ti-t-2T** are 0.5 with the configurations of $\sigma_g^2 \sigma_u^1$ and $\sigma_g^1 \sigma_u^0$, respectively. When the configuration of the *trans*-Cp₂M₂(μ -C₆F₆) structure is $\sigma_g^2 \sigma_u^0$, such as the triplet **V-t-1T** and singlet **Ti-t-1S**, the corresponding bond order is of 1. Our theoretical M-M Wiberg bond index (WBI) values,

obtained with the NBO 5.0 program,⁵² are in excellent agreement with these M-M bond orders. Thus, the WBI values for M-M bond orders of zero are less than 0.11, those for M-M bond orders of one are larger than 0.60, and those for the intermediate bond order of half are 0.19 and 0.32 (Table 1).

In Table 1, the formal metal-metal bond orders show obvious correlations with the M-M distances. Thus the M-M distances of the structures with the bond orders of 1, such as **V-t-1T** and **Ti-t-1S**, are within 0.14 Å of the sum of two covalent radii of M, i. e., $2r_{\text{cov}}^{\text{M}}$. For the four structures where the bond orders are of zero, the corresponding M-M distances are longer by at least 0.43 Å from $2r_{\text{cov}}^{\text{M}}$. For the two structures with bond order of 0.5, and the corresponding M-M distance for **Ti-t-1S** is longer than $2r_{\text{cov}}^{\text{M}}$ by 0.32 Å. However, the corresponding M-M distance for **Cr-t-3Q** seems too long (longer than $2r_{\text{cov}}^{\text{M}}$ by 0.65 Å). This may relate to the π_{u} orbitals, which correspond to the interaction of the $d_{\text{xz}}/d_{\text{yz}}$ orbitals of the metal atoms with the $e_{1\text{g}}$ orbitals of the C_6F_6 ring. These π_{u} orbitals have antibonding character, owing to the nodes between the metal $d_{\text{xz}}/d_{\text{yz}}$ orbitals and the C_6F_6 ring $e_{1\text{g}}$ orbitals. Therefore, if the π_{u} orbitals are occupied, the M-M distances become longer. Thus when the configuration of the *trans*- $\text{Cp}_2\text{M}_2(\mu\text{-C}_6\text{F}_6)$ (M= Ti, V, Cr, Mn) structure is $\sigma_{\text{g}}^2\pi_{\text{u}}^0$, such as **Mn-t-1S**, **Cr-t-2T**, **V-t-1T**, **Ti-t-1S**, the M...M distances behave normal. When one of the π_{u} orbitals is occupied with the $\sigma_{\text{g}}^2\pi_{\text{u}}^1$ configuration, such as in **Cr-t-3Q**, the M-M distances become much longer. Similarly, the M-M distance in **Mn-t-1T** with the $\sigma_{\text{g}}^2\pi_{\text{u}}^1$ configuration is also exceptionally long (longer than $2r_{\text{cov}}^{\text{M}}$ by 0.69 Å).

In order to investigate spin delocalization in the paramagnetic structures, the Mulliken spin densities on the metal atoms ($\rho_{\text{s}}^{\text{M}}$) and on the C_6F_6 ligand ring ($\rho_{\text{s}}^{\text{R}}$) were obtained. Our theoretical spin density values shown in Table 1 indicate that the unpaired electrons are localized mainly on the metal atoms with only small spin densities on the C_6F_6 rings. For example, the spin densities on each metal atom ($\rho_{\text{s}}^{\text{M}}$) for the triplet structures **Mn-t-1S**, **Cr-t-2T**, and **V-t-1T** are slightly larger than 1 (Table 1), suggesting that each metal atom has roughly one unpaired electron, while the total spin density (absolute value) on the C_6F_6 ring is less than 0.6. For the triplet **Ti-t-2T**, the spin densities are not evenly distributed on the two Ti atoms owing to the quite different Ti-C distances between the upper and lower Ti atoms, but there is still no spin delocalization to the C_6F_6 ligand (with $\rho_{\text{s}}^{\text{R}} < 0.1$). Similarly, for the two quintet structures **Cr-t-3Q** and **V-t-1Q**, the spin densities on the metal atoms are also slightly larger than 2, suggesting that each metal atom has roughly 2 unpaired electrons, whereas the total spin densities (absolute values) on the C_6F_6 ring are less than 1. In summary, there is only very small spin delocalization observed between the metal atoms and the ring ligands for our high spin *trans*- $\text{Cp}_2\text{M}_2(\mu\text{-C}_6\text{F}_6)$ (M= Ti, V, Cr, Mn) structures.

4. Discussion

The titanium and vanadium systems are characterized by triple decker sandwich $\text{Cp}_2\text{M}_2(\eta^6, \eta^6\text{-C}_6\text{F}_6)$ structures with fully bonded bis(hexahapto) bridging benzene rings as the lowest energy structures. The singlet titanium derivative $\text{Cp}_2\text{Ti}_2(\eta^6, \eta^6\text{-}\mu\text{-C}_6\text{F}_6)$ structure **Ti-t-1S** has a closed shell $\sigma_g^2\delta_u^4$ configuration (Table 1) and is the lowest energy $\text{Cp}_2\text{Ti}_2(\mu\text{-C}_6\text{F}_6)$ structure by a substantial margin of more than 20 kcal/mol. This differs significantly from the hydrogen analogue $\text{Cp}_2\text{Ti}_2(\mu\text{-C}_6\text{H}_6)$ for which a triplet spin state triple decker sandwich structure is the lowest energy structure.¹⁸ Another feature of interest in the singlet $\text{Cp}_2\text{Ti}_2(\eta^6, \eta^6\text{-}\mu\text{-C}_6\text{F}_6)$ structure **Ti-t-1S** is the alternation of the Ti–C(benzene) distances from each titanium atom between ~ 2.05 and ~ 2.34 Å. If the shorter of these Ti–C distances is considered a bonding distance and the longer of these distances is considered a non-bonding distance, then the local environments around the titanium atoms in **Ti-t-1S** are very similar to those in the long-known titanium alkyls and aryls CpTiR_3 ($\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$).

In contrast to $\text{Cp}_2\text{Ti}_2(\eta^6, \eta^6\text{-}\mu\text{-C}_6\text{F}_6)$ the lowest energy $\text{Cp}_2\text{V}_2(\eta^6, \eta^6\text{-}\mu\text{-C}_6\text{F}_6)$ structure is the quintet spin state triple decker sandwich structure **V-t-1Q**, at least by the B3LYP and B3LYP* methods. However, the BP86 method predicts the triplet spin state structure **V-t-1T** to be the lowest energy structure. For the hydrogen analogue $\text{Cp}_2\text{V}_2(\eta^6, \eta^6\text{-}\mu\text{-C}_6\text{H}_6)$ the corresponding quintet spin state triple decker sandwich structure is the lowest energy structure, even by the BP86 method.¹⁸

The chromium system $\text{Cp}_2\text{Cr}_2(\mu\text{-C}_6\text{F}_6)$ differs from the corresponding titanium and vanadium systems in having the *cis* “rice-ball” structures **Cr-c-1T** and **Cr-c-1Q** rather than triple decker sandwich structures as the lowest energy structures. In this sense the $\text{Cp}_2\text{Cr}_2(\mu\text{-C}_6\text{X}_6)$ ($\text{X} = \text{F}, \text{H}$) systems resemble each other. However, substituting hydrogen with fluorine leads to a major change in these structures. Thus the lowest energy $\text{Cp}_2\text{Cr}_2(\mu\text{-C}_6\text{H}_6)$ structure is a singlet state with the bridging benzene ring bonded to each chromium atom as a tetrahapto $\eta^4, \eta^4\text{-C}_6\text{H}_6$ ligand with an ultrashort $\text{Cr}=\text{Cr}$ distance of ~ 2.05 Å, suggesting a formal triple or quadruple bond. However, the two lowest energy $\text{Cp}_2\text{Cr}_2(\mu\text{-C}_6\text{F}_6)$ structures **Cr-c-1T** and **Cr-c-1Q** likewise have eight Cr–C bonds, but unsymmetrically distributed so that the bridging $\eta^5, \eta^3\text{-C}_6\text{F}_6$ is a pentahapto-trihapto ligand rather than a bis(tetrahapto) ligand, such as in the hydrogen analogue $\text{Cp}_2\text{Cr}_2(\eta^4, \eta^4\text{-}\mu\text{-C}_6\text{H}_6)$. The $\text{Cr}=\text{Cr}$ distances in **Cr-c-1T** and **Cr-c-1Q** of ~ 2.54 Å are essentially independent of the spin state and are ~ 0.5 Å longer than the $\text{Cr}=\text{Cr}$ distance in the hydrogen analogue $\text{Cp}_2\text{Cr}_2(\eta^4, \eta^4\text{-}\mu\text{-C}_6\text{H}_6)$. It appears reasonable to consider the $\text{Cr}=\text{Cr}$ interactions in **Cr-c-1T** and **Cr-c-1Q** as formal double bonds, thereby giving each chromium atom a 17-electron configuration. In **Cr-c-1T** this accounts for the two unpaired electrons of the triplet spin state assuming a $\sigma + \pi$ $\text{Cr}=\text{Cr}$ double bond similar to that in ethylene. For the quintet **Cr-c-1Q** the $\text{Cr}=\text{Cr}$ double bond can be considered to be a $\sigma + \frac{1}{2}\pi$ double bond with two

orthogonal single-electron π “half-bonds” similar to the double bond in dioxygen or the Fe=Fe double bond in the organometallics^{45,46} $(\eta^5\text{-C}_5\text{X}_5)_2\text{Fe}_2(\mu\text{-CO})_3$. Thus for **Cr-c-1Q** two of the four unpaired electrons for the quintet spin state come from the 17-electron configurations for the chromium atoms, and the other two unpaired electrons come from the single electrons in the two π “half bonds”. The lower Cr-Cr formal bond orders of two as well as higher spin states in the fluorinated *cis*-Cp₂Cr₂(η^5, η^3 -C₆F₆) complexes **Cr-c-1T** and **Cr-c-1Q** relative to the Cr-Cr triple or quadruple bond in the lowest energy hydrogen analogue *cis*-Cp₂Cr₂(η^4, η^4 -C₆H₆) may relate to the stronger back-bonding of the metal into the δ^* antibonding orbitals of the C₆F₆ rings because of the electron-withdrawing properties of the fluorine atoms. Such increased back-bonding can remove electron density that is needed for formal Cr-Cr bond orders greater than two.

The singlet manganese triple-decker sandwiches *cis*-Cp₂Mn₂(η^6, η^6 -C₆X₆) (X = H, F) clearly have closed shell $\sigma_g^2 \delta_u^4 \sigma_u^2 \delta_g^4$ configurations for their frontier molecular orbitals (Table 1). This structure for the hydrogen species is demonstrably the lowest energy structure with both the B3LYP and BP86 methods.¹⁸ However, for the perfluorinated Cp₂Mn₂(μ -C₆F₆) two quintet spin state structures **Mn-t-1Q** and **Mn-c-2Q** are clearly the lowest energy structures by both the B3LYP and B3LYP* methods. Structure **Mn-t-1Q** has the central μ -C₆F₆ ring fully bonded to one manganese atom as a hexahapto ligand, hence giving that manganese atom the favored 18-electron configuration similar to the manganese atom in the long-known sandwich compound CpMn(η^6 -C₆H₆).^{5,53} However, the μ -C₆F₆ ring is bonded to the other manganese atom only as a dihapto ligand, thereby giving that manganese atom only a 14-electron configuration. The resulting four “holes” in this 14-electron configuration relative to a closed-shell 18-electron configuration in a high-spin system can account for the four unpaired electrons of the quintet spin state of **Mn-t-1Q**. The hydrogen analogue *trans*-Cp₂Mn₂(η^6, η^2 -C₆H₆) is also found, but it is a higher energy structure by the BP86 method. Structure **Mn-c-2Q** has a bridging tetrahapto-dihapto η^4, η^2 -C₆F₆ ring donating six electrons to the central Mn₂ unit. The Mn=Mn distance of ~ 2.6 Å is close to that of the Cr=Cr double bonds in the related “rice-ball” *cis*-Cp₂Cr₂(μ -C₆F₆) structures **Cr-c-1T** and **Cr-c-1Q** and likewise can be interpreted as a formal single bond. This gives one manganese atom in **Mn-c-2Q** a 17-electron configuration and the other one 15-electron configuration accounting for the four unpaired electrons in this quintet spin state structure.

The lowest energy Cp₂M₂(μ -C₆F₆) structures of the later transition metals iron, cobalt, and nickel are singlet *cis* structures with ~ 2.5 Å M–M distances suggesting formal single bonds with the hapticities of the bridging μ -C₆F₆ ligand adjusted to give both metal atoms the favored 18-electron configuration. Thus the singlet Cp₂Fe₂(η^4, η^4 -C₆F₆) structure **Fe-c-1S** resembles the lowest energy structure of its hydrogen analogue with a bridging bis(tetrahapto) η^4, η^4 -C₆F₆ ring. The triplet structure **Fe-c-1T** has an η^4, η^2 -C₆F₆ ring unsymmetrically bonded to the central Fe₂

unit as a tetrahapto ligand to one iron atom and a dihapto ligand to the other iron atom with an Fe–Fe distance of 2.538 Å interpreted as a formal single bond. The total of six Fe–C bonds to the central Fe₂ unit can be interpreted as either giving one iron atom an 18-electron configuration and the other iron a 16-electron configuration or as giving each iron atom a 17-electron configuration depending on whether formal charges are placed on the iron atoms. Either interpretation can rationalize the triplet spin state of **Fe-c-1T**.

The lowest energy Cp₂M₂(μ-C₆F₆) (M = Co, Ni) structures follow a similar pattern. Thus the lowest energy Cp₂Co₂(μ-C₆F₆) structure **Co-c-1S** has a bis(trihapto) η³,η³-C₆F₆ ring bonded to the Co₂ unit with a Co–Co single bond distance of ~2.56 Å. Similarly, the lowest energy Cp₂Ni₂(μ-C₆F₆) structure **Ni-c-1S** has a bis(dihapto) η²,η²-C₆F₆ ligand with an uncomplexed C=C double bond of length ~1.36 Å bonding to the Ni₂ unit with an Ni–Ni single bond distance of ~2.50 Å. In both **Co-c-1S** and **Ni-c-1S** each metal atom has the favored 18-electron configuration. The Cp₂Co₂(η³,η³-μ-C₆F₆) structure **Co-c-1S** is essentially identical to the lowest energy predicted structure of the hydrogen analogue, which has a similar Co–Co distance of ~2.58 Å. However, the singlet Cp₂Ni₂(η²,η²-C₆F₆) structure **Ni-c-1S** is very different from the two lowest energy structures of the hydrogen analogue, which are both triplet spin state *cis*-Cp₂Ni₂(η³,η³-μ-C₆H₆) structures with longer ~2.7 Å Ni–Ni bonds and 19-electron nickel configurations. The nickel/hexafluorobenzene system also forms a low-energy singlet *trans*-Cp₂Ni₂(η³,η³-C₆F₆) structure **Ni-t-2S** with a central bis(trihapto) η³,η³-C₆F₆ ligand. The *trans* stereochemistry of **Ni-t-2S** keeps the nickel atoms far apart at a non-bonding distance of ~4.2 Å. Nevertheless, the nickel atoms in **Ni-t-2S** have the favored 18-electron configuration. Structure **Ni-t-2S** has a low energy hydrogen analogue *trans*-Cp₂Ni₂(η³,η³-C₆H₆).

5. Summary

The singlet triple decker sandwich titanium complex Cp₂Ti₂(η⁶,η⁶-C₆F₆) with a closed shell electronic structure is preferred energetically by a wide margin (>20 kcal/mol) over other isomers and spin states. This differs from the hydrogen analogue for which related triplet spin state structures are clearly preferred. A similar low-energy quintet triple decker sandwich Cp₂V₂(η⁶,η⁶-C₆F₆) structure is found for vanadium similar to the hydrogen analogue Cp₂V₂(η⁶,η⁶-C₆H₆) for which the quintet spin state structure is energetically preferred by a significant margin.

The later transition metals from Cr to Ni energetically prefer the so-called “rice-ball” *cis*-Cp₂M₂(μ-C₆F₆) structures with varying hapticities of metal-ring bonding, varying formal metal-metal bond orders, and different spin states depending on the metal atom. Thus the lowest energy Cp₂Cr₂(μ-C₆F₆) structures are triplet and quintet structures with

pentahapto-trihapto η^5, η^3 - μ -C₆F₆ rings and formal Cr=Cr double bonds. This contrasts with the lowest energy Cp₂Cr₂(μ -C₆H₆) structure with a bis(tetrahapto) η^4, η^4 -C₆H₆ ring and a formal Cr-Cr quadruple bond. The lowest energy Cp₂Mn₂(μ -C₆F₆) structures are *trans* and *cis* quintet spin state structures. This contrasts with Cp₂Mn₂(μ -C₆H₆) for which a closed-shell singlet triple-decker sandwich structure is the lowest energy structure.

The lowest energy Cp₂Fe₂(μ -C₆F₆) structure is a triplet *cis* structure with a tetrahapto-dihapto η^4, η^2 - μ -C₆F₆ ring and a formal Fe-Fe single bond. This contrasts with the hydrogen analogue Cp₂Fe₂(μ -C₆H₆) for which singlet and triplet structures with more symmetrical bis(tetrahapto) η^4, η^4 -C₆H₆ bonding of the central ring to the iron atoms are energetically preferred. The lowest energy Cp₂Co₂(μ -C₆F₆) structures are singlet spin state structures with formal M-M single bonds and either bridging bis(trihapto) η^3, η^3 -C₆F₆ or tetrahapto-dihapto η^4, η^2 -C₆F₆ rings. The former structure is closely related to the lowest energy Cp₂Co₂(μ -C₆H₆) structure. For Cp₂Ni₂(μ -C₆F₆) low energy singlet *cis* and *trans* structures are both found. The singlet *cis*-Cp₂Ni₂(μ -C₆F₆) structure has a Ni-Ni single bond of length ~ 2.5 Å and a bridging bis(dihapto) η^2, η^2 -C₆F₆ ligand with an uncomplexed C=C double bond. The singlet *trans*-Cp₂Ni₂(μ -C₆F₆) structure has a bis(trihapto) η^3, η^3 -C₆F₆ ligand. This latter structure has a low-energy hydrogen analogue *trans*-Cp₂Ni₂(η^3, η^3 - μ -C₆H₆). However, the low-energy hydrogen analogues *cis*-Cp₂Ni₂(μ -C₆H₆) have bis(trihapto) bridging η^3, η^3 -C₆H₆ rings and triplet spin states along with formal Ni-Ni single bonds of length ~ 2.7 Å.

Supplementary Information. Tables S1-S7. Relative energies (ΔE , in kcal/mol), numbers of imaginary vibrational frequencies with the finer (120, 974) integration grid (N_{imag}), M-M distances (Å), and spin $\langle S^2 \rangle$ values for the Cp₂M₂(μ -C₆F₆) (M = Ti, V, Cr, Mn, Fe, Co, Ni) structures. Tables S8 to S45: Electronic energies and Cartesian coordinates of the optimized Cp₂M₂(μ -C₆F₆) (M = Ti, V, Cr, Mn, Fe, Co, Ni) structures by the B3LYP*, B3LYP, and BP86 methods; complete Gaussian 03 reference (Reference 44).

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Triple Decker Sandwiches and Related Compounds of the First Row Transition Metals with Cyclopentadienyl and Hexafluorobenzene Rings: Remarkable Effects of Fluorine Substitution

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The early transition metals Ti and V energetically prefer the triple decker sandwich structures *trans*-Cp₂M₂(η⁶,η⁶-μ-C₆F₆) structures. However, the later transition metals from Cr to Ni energetically prefer the so-called “rice-ball” *cis*-Cp₂M₂(μ-C₆F₆) structures with varying hapticities of metal-ring bonding, a range of formal orders of metal-metal bonding, and varying spin states depending on the metal atom.

