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Calculations of the Effects of Methyl Groups on the Energy Differences between Cyclooctatetraene and Bicyclo[4.2.0]octa-2,4,7-triene and between Their Iron Tricarbonyl Complexes

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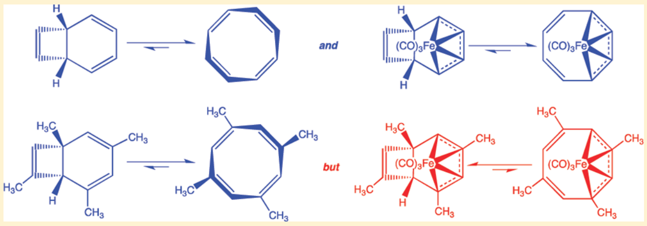
Ⓢ *Supporting Information*

ABSTRACT: In accord with experiment, DFT calculations find that cyclooctatetraene (COT, **1a**) is lower in energy than its valence isomer, bicyclo[4.2.0]octa-2,4,7-triene (BCOT, **3a**) and that the iron tricarbonyl complex of COT [COT-Fe(CO)$_3$, **2a**] is lower in energy than the iron tricarbonyl complex of BCOT [BCOT-Fe(CO)$_3$, **4a**]. Also in agreement with experiment are the DFT findings that 1,3,5,7-tetramethylCOT (TMCOT, **1b**) is lower in energy than 1,3,5,7-tetramethylBCOT (TMBCOT, **3b**), but that the iron tricarbonyl complex of TMCOT [TMCOT-Fe(CO)$_3$, **2b**] is higher in energy than the iron tricarbonyl complex of TMBCOT [TMBCOT-Fe(CO)$_3$, **4b**]. Calculations of the energies of isodesmic reactions allow the effect of each of the four methyl groups in **1b**−**4b** to be analyzed in terms of its additive contribution to the relative energies of TMCOT (**1b**) and TMBCOT (**3b**) and to the Fe(CO)$_3$ binding energies in TMCOT-Fe(CO)$_3$ (**2b**) and TMBCOT-Fe(CO)$_3$ (**4b**). Our calculations also predict that the eight methyl groups in octamethylCOT-Fe(CO)$_3$ [OMCOT-Fe(CO)$_3$, **2c**] should have much more than twice the effect of the four methyl groups in TMCOT-Fe(CO)$_3$ (**2b**) on raising the energy of OMCOT-Fe(CO)$_3$ (**2c**), relative to that of OMBCOT-Fe(CO)$_3$ (**4c**). The effects of the interactions between the methyl groups in OMCOT-Fe(CO)$_3$ (**2c**) and OMBCOT-Fe(CO)$_3$ (**4c**) are dissected and discussed.

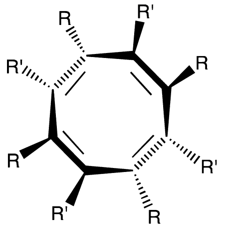


■ INTRODUCTION

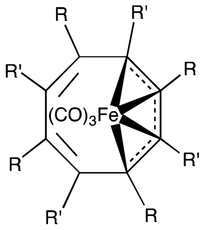
Iron tricarbonyl complexes are certainly the best studied and most useful transition metal complexes of conjugated dienes.[1] For example, Fe(CO)$_3$, has been widely applied in organic synthesis as a protecting group for conjugated dienes,[2] and the steric bulk of the Fe(CO)$_3$ group has been used to control the diastereoselectivity of product formation.[3] The electronic structures of diene-Fe(CO)$_3$ complexes have been the subject of numerous calculations.[4]

Fe(CO)$_3$ has been found to coordinate to two of the double bonds in cyclooctatetraene (COT, **1a**), producing cyclooctatetraeneiron tricarbonyl [COT-Fe(CO)$_3$, **2a**].[5] The crystal structure of **2a**[6] indicates Fe(CO)$_3$ complexation flattens the tub-shaped equilibrium geometry of **1a**, so that in **2a** Fe(CO)$_3$ is bonded to a planar, conjugated, butadiene-like residue. However, the NMR spectrum of **2a** shows that, even at very low temperatures, the Fe(CO)$_3$ group moves rapidly around the nearly planar, eight-membered ring.[7]

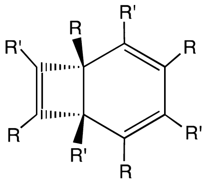
COT (**1a**) is known to be in rapid equilibrium with bicyclo[4.2.0]-2,4,7-octatriene (BCOT, **3a**).[8] Since **3a** contains a planar, conjugated, cyclohexadiene ring, **3a** too might have been expected to form a complex with Fe(CO)$_3$. However, bicyclo[4.2.0]-2,4,7-octatrieneiron tricarbonyl [BCOT-Fe-(CO)$_3$, **4a**)] was not reported to have been found in the reaction of **1a** with Fe(CO)$_5$, which forms **2a**.[5] Nevertheless, **4a** was subsequently prepared by an alternative method.[9]



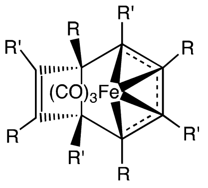
1a, R = R' = H
b, R = CH$_3$, R' = H
c, R = R' = CH$_3$



2a, R = R' = H
b, R = CH$_3$, R' = H
c, R = R' = CH$_3$



3a, R = R' = H
b, R = CH$_3$, R' = H
c, R = R' = CH$_3$



4a, R = R' = H
b, R = CH$_3$, R' = H
c, R = R' = CH$_3$

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To try to gain more insight into the fluxional behavior of **2a**,[7] Cotton and Musco attempted to synthesize **2b**, the 1,3,5,7-tetramethyl derivative of **2a**, by reaction of 1,3,5,7-tetramethylcyclooctatetraene (TMCOT, **1b**) with $Fe_2(CO)_9$. However, this reaction did not produce the expected TMCOT-$Fe(CO)_3$ complex (**2b**). Instead, 1,3,5,7-tetramethylbicyclo[4.2.0]-2,4,7-octatrieneiron tricarbonyl [TMBCOT-$Fe(CO)_3$, **4b**] was isolated.[10] This result is very surprising because, without the $Fe(CO)_3$ group, TMCOT (**1b**) is so heavily favored over 1,3,5,7-tetramethylbicyclo[4.2.0]-2,4,7-octatriene (TMBCOT, **3b**) that **3b** has not been detected to be in equilibrium with **1b**.[11]

Although TMBCOT-$Fe(CO)_3$ (**4b**) was isolated more than 40 years ago, the reason why **4b**, rather than the monocyclic isomer, TMCOT-$Fe(CO)_3$ (**2b**), is formed in the reaction of **1b** with $Fe_2(CO)_9$ has apparently not been investigated. In this paper, we provide a detailed computational study of why the four methyl groups in **1b** favor the formation of **4b**, rather than **2b**,[10] whereas as already noted, without the four methyl groups, COT-$Fe(CO)_3$ (**2a**) rather than BCOT-$Fe(CO)_3$ (**4a**) is formed from **1a**.[5]

Our calculations systematically address the following questions about the energy differences between COT derivatives **1** and **2** and their respective bicyclic isomers **3** and **4**: (i) What is the effect of the $Fe(CO)_3$ complexation in COT-$Fe(CO)_3$ (**2a**) and BCOT-$Fe(CO)_3$ (**4a**) on modifying the energy difference between COT (**1a**) and BCOT (**3a**)? (ii) Do the four methyl groups in TMCOT (**1b**) and TMBCOT (**3b**) make the energy difference between these two isomers significantly different than the energy difference between COT (**1a**) and BCOT (**3a**)? (iii) As suggested by the isolation of TMBCOT-$Fe(CO)_3$ (**4b**), rather than TMCOT-$Fe(CO)_3$ (**2b**),[10] does $Fe(CO)_3$ complexation make **4b** lower in energy than **2b**? (iv) What is the energetic effect of each of the four different types of methyl groups in **2b**−**4b** on the energy differences between COTs **1b** and **2b** and their bicyclic isomers, **3b** and **4b**, respectively? (v) Are the individual methyl substituent effects on the energy differences between **1b** and **3b** and between **2b** and **4b** additive?

Octamethyl (OM)COT (**1c**) has been prepared, and it was found to be greatly favored at equilibrium over OMBCOT (**3c**).[15] However, the reaction of **1c** with $Fe_2(CO)_9$ has not been reported. In this paper we describe the results of calculations on (vi) the effect of the eight methyl groups in **1c** on the energy difference between it and **3c**, and (vii) we predict that OMBCOT-$Fe(CO)_3$ (**4c**) will be found to be much lower in energy than its isomer, OMCOT-$Fe(CO)_3$ (**2c**). Finally, comparisons of the calculated energy differences between OMCOT (**1c**) and OMBCOT (**3c**) and between OMCOT-$Fe(CO)_3$ (**2c**) and OMBCOT-$Fe(CO)_3$ (**4c**) with the calculated energy differences between TMCOT (**1b**) and TMBCOT (**3b**) and between TMCOT-$Fe(CO)_3$ (**2b**) and TMBCOT-$Fe(CO)_3$ (**4b**) allow us to compute (viii) the energetic effects of the interactions between the methyl groups on adjacent ring carbons in **1c**−**4c**.

■ COMPUTATIONAL METHODOLOGY

The B3LYP density functional method, which is a combination of Becke's 3-parameter hybrid functional[16] with the electron correlation functional of Lee, Yang, and Parr (LYP),[17] was employed to carry out all the calculations described in this paper. The 6-31G(d) basis set[18] was used for carbon, oxygen, and hydrogen atoms. The LANL2DZ basis set, in conjunction with the LANL2DZ pseudo potential,[19] was used for the iron atom in $Fe(CO)_3$. Vibrational analyses were performed on all optimized geometries, to ensure that the optimized structures corresponded to local minima and to obtain zero-point energy (ZPE) corrections. The ZPE-corrected relative energies are given in this paper, but they are the same to within a few tenths of a kcal/mol as the uncorrected relative energies.[20] At constrained geometries, the latter are used, since the vibrational analyses are not physically meaningful at such geometries. The Gaussian 09 suite of programs[21] was used for all of the calculations reported in this paper.

■ RESULTS AND DISCUSSION

Energy Differences between COT (1a) and BCOT (3a) and between Their $Fe(CO)_3$ Complexes (2a and 4a). As shown in eq 1, COT (**1a**) is calculated to be lower in energy that BCOT (**3a**) by 9.4 kcal/mol.[22a]

$$\text{BCOT } (\mathbf{3a}) \rightarrow \text{COT } (\mathbf{1a}) \quad \Delta E = -9.4 \text{ kcal/mol} \tag{1}$$

Similarly, COT-$Fe(CO)_3$ (**2a**) is computed to be lower in energy than BCOT-$Fe(CO)_3$ (**4a**) by 5.8 kcal/mol.[22b]

$$\text{BCOT-Fe(CO)}_3 \ (\mathbf{4a}) \rightarrow \text{COT-Fe(CO)}_3 \ (\mathbf{2a}) \quad \Delta E = -5.8 \text{ kcal/mol} \tag{2}$$

Combining eqs 1 and 2 into the isodesmic reaction in eq 3 shows that complexation of $Fe(CO)_3$ is calculated to make the energy difference between **2a** and **4a** 3.6 kcal/mol smaller than the energy difference between **1a** and **3a**.[22c]

$$\text{BCOT } (\mathbf{3a}) + \text{COT-Fe(CO)}_3 \ (\mathbf{2a}) \rightarrow \text{COT } (\mathbf{1a}) + \text{BCOT-Fe(CO)}_3 \ (\mathbf{4a}) \quad \Delta E = -3.6 \text{ kcal/mol} \tag{3}$$

This is the amount by which the adiabatic $Fe(CO)_3$ binding energy is larger in BCOT-$Fe(CO)_3$ (**4a**) than in COT-$Fe(CO)_3$ (**2a**).

The 3.6 kcal/mol larger $Fe(CO)_3$ binding energy in **4a** than in **2a** is due, at least in part, to the necessity for the puckered eight-membered ring in COT (**1a**) to partially planarize, in order to bind $Fe(CO)_3$ in **2a**, whereas much smaller geometry changes are necessary for BCOT (**3a**) to bind $Fe(CO)_3$ in **4a**. In fact, if the $Fe(CO)_3$ group is removed from **2a** and **4a**, with the geometries of the COT and BCOT rings frozen at the geometries that they have in **2a** and **4a**, the isodesmic reaction in eq 4 gives the difference between the energies necessary to distort COT (**1a**) and BCOT (**3a**) to the geometries that they have in, respectively, COT-$Fe(CO)_3$ (**2a**) and BCOT-$Fe(CO)_3$ (**4a**).

$$\text{BCOT } (\mathbf{3a}) + \text{COT@}\mathbf{2a} \rightarrow \text{COT } (\mathbf{1a}) + \text{BCOT@}\mathbf{4a} \quad \Delta E = -13.4 \text{ kcal/mol} \tag{4}$$

Since the energy required to distort COT (**1a**) to the geometry it has in COT-$Fe(CO)_3$ (**2a**) is 13.4 kcal/mol larger than the energy required to distort BCOT (**3a**) to the geometry it has in BCOT-$Fe(CO)_3$ (**4a**), why is the difference between the adiabatic $Fe(CO)_3$ binding energies in **2a** and **4a** only 3.6 kcal/mol? The answer can be obtained by subtracting eq 3 from eq 4, which results in

$$\begin{gathered}\text{BCOT-Fe(CO)}_3\ (\mathbf{4a}) + \text{COT@}\mathbf{2a} \rightarrow \\ \text{COT-Fe(CO)}_3\ (\mathbf{2a}) + \text{BCOT@}\mathbf{4a} \\ \Delta E = -9.8\ \text{kcal/mol}\end{gathered} \tag{5}$$

Equation 5 gives the difference between the "vertical" $Fe(CO)_3$ binding energies in COT-$Fe(CO)_3$ (**2a**) and BCOT-$Fe(CO)_3$ (**4a**). The energy difference of −9.8 kcal/mol between eqs 3 and 4 means that COT, when constrained to the optimized geometry that it has in COT-$Fe(CO)_3$ (**2a**), binds $Fe(CO)_3$ 9.8 kcal/mol more strongly than BCOT does, when BCOT is also constrained to the optimized geometry it has in BCOT-$Fe(CO)_3$ (**4a**).

The reason why partially planarized COT binds $Fe(CO)_3$ 9.8 kcal/mol more strongly than BCOT is that the energy difference between the HOMO and LUMO is much smaller in COT (**1a**), at the geometry of COT-$Fe(CO)_3$ (**2a**), than in BCOT (**3a**), at the geometry of BCOT-$Fe(CO)_3$ (**4a**).[25] At the nearly planar geometry of COT-$Fe(CO)_3$ (**2a**), the HOMO of COT (**1a**) is higher in energy than the HOMO of BCOT (**3a**) is, at the geometry of BCOT-$Fe(CO)_3$ (**4a**). This makes the HOMO of **1a@2a** much better than the HOMO of **3a@4a** at donating electron density to the LUMO of $Fe(CO)_3$. Similarly, at the geometry of COT-$Fe(CO)_3$ (**2a**), the LUMO of COT (**1a**) is lower in energy than the LUMO of BCOT (**3a**), at the geometry of BCOT-$Fe(CO)_3$ (**4a**). This makes the LUMO of **1a@2a** much better than the LUMO of **3a@4a** at accepting electron density from the HOMO of $Fe(CO)_3$. The stronger HOMO−LUMO and LUMO−HOMO interactions of **1a@2a** than of **3a@4a** with $Fe(CO)_3$ is what makes the vertical $Fe(CO)_3$ binding energy of **1a@2a** 9.8 kcal/mol larger than that of **3a@4a**.[4]

Effect of Tetramethylation on the Energy Differences between TMCOT (1b) and TMBCOT (3b) and between Their $Fe(CO)_3$ Complexes (2b and 4b). For TMCOT (**1b**) and TMBCOT (**3b**) the analogue of eq 1 is

$$\begin{gathered}\text{TMBCOT}\ (\mathbf{3b}) \rightarrow \text{TMCOT}\ (\mathbf{1b}) \\ \Delta E = -7.0\ \text{kcal/mol}\end{gathered} \tag{6}$$

Comparison of eq 6 with eq 1 shows that tetramethylation reduces the magnitude of the energy difference between COT and BCOT by 2.4 kcal/mol.[26a] However, in agreement with experiment,[11] 1,3,5,7-TMCOT (**1b**) is still calculated to be much lower in energy than the corresponding 1,3,5,7-TMBCOT (**3b**).

In contrast, eq 7 shows that the tetramethylated, bicyclic complex, TMBCOT-$Fe(CO)_3$ (**4b**), is computed to be lower in energy than the tetramethylated, COT complex, TMCOT-$Fe(CO)_3$ (**2b**), by 2.6 kcal/mol.[26b]

$$\begin{gathered}\text{TMBCOT-Fe(CO)}_3\ (\mathbf{4b}) \rightarrow \text{TMCOT-Fe(CO)}_3\ (\mathbf{2b}) \\ \Delta E = 2.6\ \text{kcal/mol}\end{gathered} \tag{7}$$

This computational finding is in agreement with the isolation of TMBCOT-$Fe(CO)_3$ (**4b**), rather than TMCOT-$Fe(CO)_3$ (**2b**), as the major product from the reaction of TMCOT (**1b**) with $Fe_2(CO)_9$ at 125 °C.[10] Although it is certainly possible that kinetics contribute to the formation of **4b**, rather than **2b**, the lower energy calculated for **4b** is sufficient to provide an explanation for the isolation of **4b**.[26c]

Comparing eq 7 with eq 2 shows that tetramethylation results in a change of 2.6 − (−5.8) = 8.4 kcal/mol in the relative energies of the monocyclic and bicyclic $Fe(CO)_3$ complexes. Comparison of eq 6 with eq 1 shows that 2.4 kcal/mol of this change comes from the effect of tetramethylation on reducing the 9.4 kcal/mol energy difference between BCOT (**3a**) and COT (**1a**) to the 7.0 kcal/mol energy difference between TMBCOT (**3b**) and TMCOT (**1b**). The remainder of the 8.4 kcal/mol energy change in the relative energies of the monocyclic and bicyclic $Fe(CO)_3$ complexes must come from the effect of the four methyl groups on making the difference between the $Fe(CO)_3$ binding energies in TMCOT-$Fe(CO)_3$ (**2b**) and TMBCOT-$Fe(CO)_3$ (**4b**) 6.0 kcal/mol larger than the difference between the $Fe(CO)_3$ binding energies in COT-$Fe(CO)_3$ (**2a**) and BCOT-$Fe(CO)_3$ (**4a**).

This can be verified by subtracting eq 7 from eq 6 to afford eq 8

$$\begin{gathered}\text{TMBCOT}\ (\mathbf{3b}) + \text{TMCOT-Fe(CO)}_3\ (\mathbf{2b}) \\ \rightarrow \text{TMCOT}\ (\mathbf{1b}) + \text{TMBCOT-Fe(CO)}_3\ (\mathbf{4b}) \\ \Delta E = -9.6\ \text{kcal/mol}\end{gathered} \tag{8}$$

which shows that $Fe(CO)_3$ in **4b** is bound to TMBCOT (**3b**) 9.6 kcal/mol more strongly than $Fe(CO)_3$ in **2b** is bound to TMCOT (**1b**). Comparison of eq 8 with eq 3 confirms that tetramethylation does, indeed, increase the difference between the adiabatic $Fe(CO)_3$ binding energies in the BCOT and COT complexes by 6.0 kcal/mol, from 3.6 kcal/mol between BCOT-$Fe(CO)_3$ (**4a**) and COT-$Fe(CO)_3$ (**2a**) to 9.6 kcal/mol between TMBCOT-$Fe(CO)_3$ (**4b**) and TMCOT-$Fe(CO)_3$ (**2b**).

Does tetramethylation increase the $Fe(CO)_3$ binding energy in TMBCOT-$Fe(CO)_3$ (**4b**) relative to that in BCOT-$Fe(CO)_3$ (**4a**)? Or does tetramethylation decrease the $Fe(CO)_3$ binding energy in TMCOT-$Fe(CO)_3$ (**2b**) relative to that in COT-$Fe(CO)_3$ (**2a**)? The energies calculated for another pair of isodesmic reactions can be used to answer these two questions.

The isodesmic reaction that compares the $Fe(CO)_3$ binding energies in TMCOT-$Fe(CO)_3$ (**2b**) and COT-$Fe(CO)_3$ (**2a**) is

$$\begin{gathered}\text{COT-Fe(CO)}_3\ (\mathbf{2a}) + \text{TMCOT}\ (\mathbf{1b}) \\ \rightarrow \text{TMCOT-Fe(CO)}_3\ (\mathbf{2b}) + \text{COT}\ (\mathbf{1a}) \\ \Delta E = 11.3\ \text{kcal/mol}\end{gathered} \tag{9}$$

The isodesmic reaction that compares the $Fe(CO)_3$ binding energies in TMBCOT-$Fe(CO)_3$ (**4b**) and BCOT-$Fe(CO)_3$ (**4a**) is

$$\begin{gathered}\text{BCOT-Fe(CO)}_3\ (\mathbf{4a}) + \text{TMBCOT}\ (\mathbf{3b}) \\ \rightarrow \text{TMBCOT-Fe(CO)}_3\ (\mathbf{4b}) + \text{BCOT}\ (\mathbf{3a}) \\ \Delta E = 5.3\ \text{kcal/mol}\end{gathered} \tag{10}$$

Thus, our calculations find that tetramethylation decreases the $Fe(CO)_3$ binding energy in *both* TMCOT-$Fe(CO)_3$ (**2b**) relative to COT-$Fe(CO)_3$ (**2a**) and TMBCOT-$Fe(CO)_3$ (**4b**) relative to BCOT-$Fe(CO)_3$ (**4a**). However, the reduction in

$Fe(CO)_3$ binding energy on tetramethylation is 11.3 − 5.3 = 6.0 kcal/mol larger in TMCOT-$Fe(CO)_3$ (**2b**) than in TMBCOT-$Fe(CO)_3$ (**4b**).

The energy changes that occur on tetramethylation of **1a**−**4a**, to form **1b**−**4b**, are shown graphically in Figure 1.

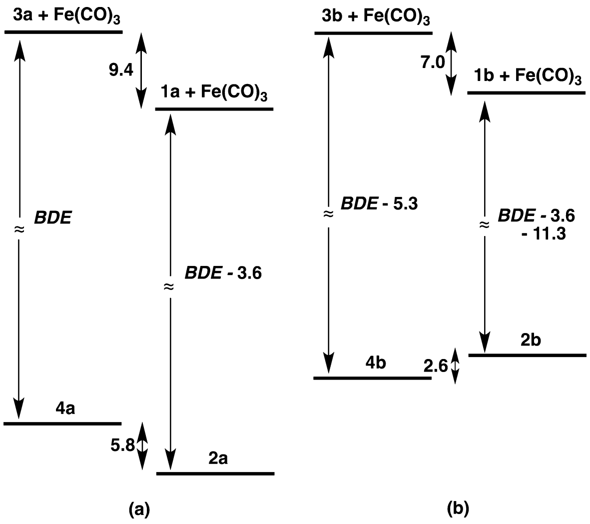
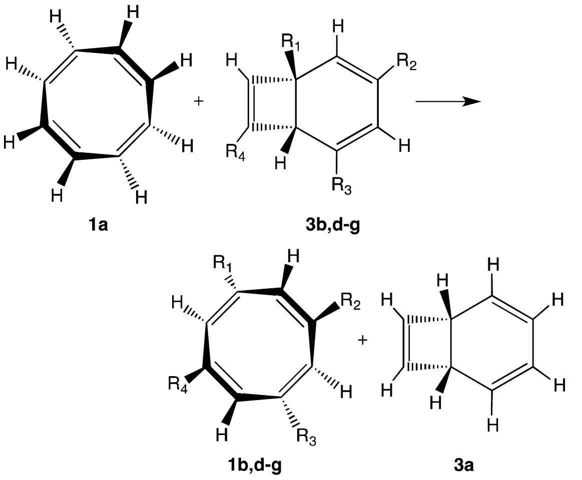


Figure 1. Diagrams, showing schematically how (a) the energy difference of 9.4 kcal/mol between COT (**1a**) and BCOT (**3a**), plus the 3.6 kcal/mol lower $Fe(CO)_3$ binding energy (BDE) of **1a** compared with that of **3a**, make COT-$Fe(CO)_3$ (**2a**) 5.8 kcal/mol lower in energy than BCOT-$Fe(CO)_3$ (**4a**); (b) the energy difference of 7.0 kcal/mol between TMCOT (**1b**) and TMBCOT (**3b**), plus the effects of tetramethylation on making the $Fe(CO)_3$ binding energies of **1b** and **3b** lower than those of **1a** and **3a** by, respectively, 11.3 and 5.3 kcal/mol, combine to make TMCOT-$Fe(CO)_3$ (**2b**) 2.6 kcal/mol higher in energy than TMBCOT-$Fe(CO)_3$ (**4b**).

Tetramethylation is calculated to make the energy difference between TMBCOT (**3b**) and TMCOT (**1b**) 2.4 kcal/mol smaller than the 9.4 kcal/mol energy difference between BCOT (**3a**) and COT (**1a**). Tetramethylation is also calculated to make the difference between the $Fe(CO)_3$ binding energies of TMBCOT-$Fe(CO)_3$ (**4b**) and TMCOT-$Fe(CO)_3$ (**2b**) 6.0 kcal/mol larger than the difference between the $Fe(CO)_3$ binding energies of BCOT-$Fe(CO)_3$ (**4a**) and COT-$Fe(CO)_3$ (**2a**). The net effect of tetramethylation is thus to make the energy difference between TMBCOT-$Fe(CO)_3$ (**4b**) and TMCOT-$Fe(CO)_3$ (**2b**) 8.4 kcal/mol smaller than the 5.8 kcal/mol energy difference between BCOT-$Fe(CO)_3$ (**4a**) and COT-$Fe(CO)_3$ (**2a**). As shown graphically in Figure 1, the change of 8.4 kcal/mol in the relative energies of BCOT-$Fe(CO)_3$ (**4a**) and COT-$Fe(CO)_3$ (**2a**), caused by tetramethylation, results in the calculated energy of TMBCOT-$Fe(CO)_3$ (**4b**) being 2.6 kcal/mol lower than that of TMCOT-$Fe(CO)_3$ (**2b**).[26c]

Contribution of the Individual Methyl Groups to the Energetic Effects of Tetramethylation. What are the contributions of each of the four unique methyl groups in **4b** and **2b** to the 8.4 kcal/mol change in the relative energies of BCOT-$Fe(CO)_3$ (**4a**) and COT-$Fe(CO)_3$ (**2a**) on tetramethylation? We begin with the effects of four methyl groups on reducing the 9.4 kcal/mol calculated energy difference between BCOT (**3a**) and COT (**1a**) to the 7.0 kcal/mol calculated energy difference between TMBCOT (**3b**) and TMCOT (**1b**). The effect of each of the four different methyl groups in TMBCOT (**3b**) is given by one of the isodesmic reactions for the four methylBCOTs (MBCOTs) **3d**−**g** in eq 11. The energy of each of these reactions is given in Table 1.



(11)

Table 1. Energies (kcal/mol) Computed for the Isodesmic Reaction in Equation 11

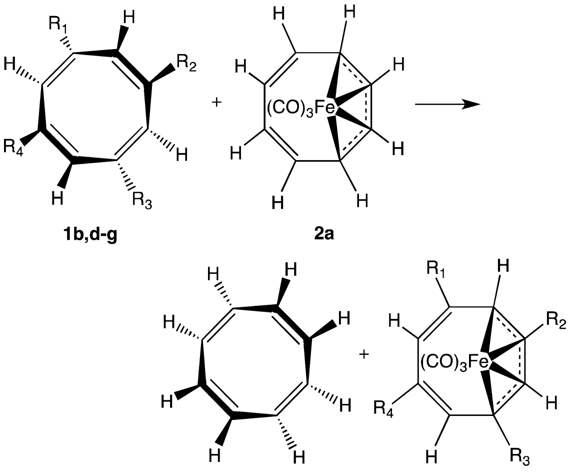
compounds	R_1	R_2	R_3	R_4	Δ*E*
b	CH_3	CH_3	CH_3	CH_3	2.4
d	CH_3	H	H	H	−1.2
e	H	CH_3	H	H	0.1
f	H	H	CH_3	H	0.8
g	H	H	H	CH_3	2.7

Table 1 shows that the effects of the four different methyl groups in MBCOTs **3d**−**g** are additive in TMBCOT (**3b**). Table 1 also reveals that the methyl group on the double bond of the four-membered ring of 7-MBCOT (**3g**) is entirely responsible for the net effect of the four methyl groups in **3b** on reducing the energy difference between **1a** and **3a** by 2.4 kcal/mol. Why does the methyl group in 7-MBCOT (**3g**) make the calculated energy difference between **3g** and MCOT (**1d**) 2.7 kcal/mol lower than the calculated energy difference between BCOT (**3a**) and COT (**1a**)?

Since **1d**−**g** in eq 11 are all different designations for the same molecule, MCOT, and since **1a** and **3a** appear in all four reactions, the energy difference between any pair of the isomers, **3d**−**g**, is equal to the difference between their Δ*E* values in Table 1. Therefore, one can also ask, why is 7-MBCOT (**3g**), in which a methyl group is attached to the double bond of the cyclobutene ring of BCOT (**3a**), lower in energy than MBCOTs **3e** and **3f**, in both of which a methyl group is attached to a double bond of the six-membered ring?

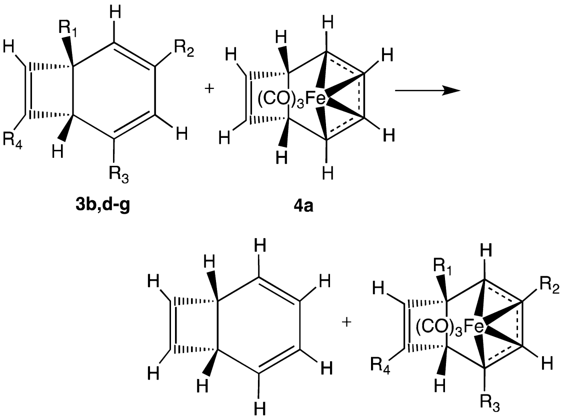
We attribute the lower energy of **3g** to the fact that the four-membered ring makes the $H_3C-C{=}C$ bond angle of 135.1° in **3g** 13−14° larger than the $H_3C-C{=}C$ bond angles of 122.4° in **3e**, 122.9° in **3f**, and 121.0° in **1d**. The larger the $H_3C-C{=}C$ bond angle, the greater the distance between the methyl proton that eclipses the double bond and the proton attached to the distal carbon of the double bond. This $H_2C-H\cdots H$ distance is calculated to be 2.982 Å in **3g**, which is 0.6−0.7 Å larger than the $H_2C-H\cdots H$ distances of 2.385 Å in **3e**, 2.391 Å in **3f**, and 2.296 Å in **1d**. Table S1 of the Supporting Information gives the energies of methyl transfer reactions between cyclobutene and a variety of 1-methylcycloalkenes, and as shown in Table S1, there is a good correlation between the energies of these isodesmic reactions and the $H_2C-H\cdots H$ distances in the 1-methylcycloalkenes.

Tetramethylation also increases the 3.6 kcal/mol difference between the $Fe(CO)_3$ binding energies in BCOT-$Fe(CO)_3$ (**4a**) and COT-$Fe(CO)_3$ (**2a**) by 6.0 kcal/mol in TMCOT-$Fe(CO)_3$ (**2b**) and TMBCOT-$Fe(CO)_3$ (**4b**). Figure 1 shows that the four methyl groups make the $Fe(CO)_3$ binding energy in TMCOT-$Fe(CO)_3$ (**2b**) 11.3 kcal/mol smaller than in COT-$Fe(CO)_3$ (**2a**) and 5.3 kcal/mol smaller in TMBCOT-$Fe(CO)_3$ (**4b**) than in BCOT-$Fe(CO)_3$ (**4a**). The effects of each of the four different methyl groups in **2b** and in **4b** on the $Fe(CO)_3$ binding energies are given by the isodesmic reactions in eqs 12 and 13, respectively. The energies of these reactions are given in Tables 2 and 3.



1b,d-g **2a** **1a** **2b,d-g**

(12)



3b,d-g **4a** **3a** **4b,d-g**

(13)

Table 2. Energies (kcal/mol) Computed for the Isodesmic Reaction in Equation 12, Which Gives the Difference between the $Fe(CO)_3$ Binding Energies in 2b,d–g and 2a

compounds	R$_1$	R$_2$	R$_3$	R$_4$	ΔE
b	CH_3	CH_3	CH_3	CH_3	11.3
d	CH_3	H	H	H	2.1
e	H	CH_3	H	H	1.2
f	H	H	CH_3	H	5.4
g	H	H	H	CH_3	2.2

Table 3. Energies (kcal/mol) Computed for the Isodesmic Reaction in Equation 13, Which Gives the Difference between the $Fe(CO)_3$ Binding Energies in 4b,d–g and 4a

compounds	R$_1$	R$_2$	R$_3$	R$_4$	ΔE
b	CH_3	CH_3	CH_3	CH_3	5.3
d	CH_3	H	H	H	1.7
e	H	CH_3	H	H	0.5
f	H	H	CH_3	H	2.6
g	H	H	H	CH_3	0.3

Comparison of the results in these two tables shows that the methyl group at R$_3$ in MCOT-$Fe(CO)_3$ **2f** has a 2.8 kcal/mol greater effect on weakening the $Fe(CO)_3$ binding energy than the methyl group at R$_3$ in MBCOT-$Fe(CO)_3$ **4f**, and the methyl group at R$_4$ in MCOT-$Fe(CO)_3$ **2g** has a 1.9 kcal/mol greater effect on weakening the $Fe(CO)_3$ binding energy than the methyl group at R$_4$ in MBCOT-$Fe(CO)_3$ **4g**. The 4.7 kcal/mol net effect of these two methyl groups accounts for nearly 80% of the 6.0 kcal/mol lower $Fe(CO)_3$ binding energy in TMCOT-$Fe(CO)_3$ (**2b**) than in TMBCOT-$Fe(CO)_3$ (**4b**).

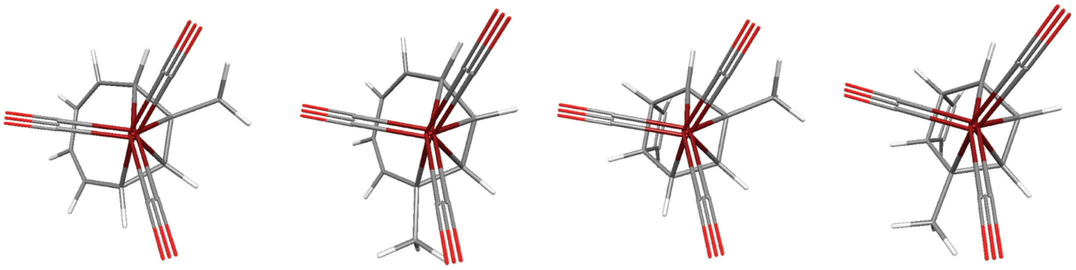
The very small (0.3 kcal/mol) effect of the methyl group at R$_4$ on the $Fe(CO)_3$ binding energy in **4g** (Table 3) is easy to understand, because the methyl group is far away from the $Fe(CO)_3$ group. However, the same would appear to be true of the methyl group at R$_4$ in **2g**. Why is this methyl group in **2g** computed to weaken the $Fe(CO)_3$ binding energy by 2.2 kcal/mol (Table 2) relative to that in COT-$Fe(CO)_3$ (**2a**)?

At least part of the answer is that bonding of the $Fe(CO)_3$ group in COT complexes **2a**–**g** requires significant flattening of the eight-membered ring, so that the four carbons of each of the two butadiene groups in **2a**–**g** become essentially coplanar. Complete planarization of the eight-membered ring is calculated to extract a 1.3 kcal/mol larger energetic penalty from MCOT (**1d** $\equiv$ **1e**–**g**) than from COT (**1a**), because in planar **1d** the methyl group interacts with the hydrogens at both adjacent carbons, whereas at the tub-shaped equilibrium geometry of **1d** the methyl group interacts strongly with only the hydrogen on the same C–C double bond.[27]

The greater energetic cost of planarizing MCOT (**1d**) than COT (**1a**) contributes to the effect of methylation on lowering the adiabatic $Fe(CO)_3$ binding energies in all four of the MCOT-$Fe(CO)_3$ complexes (**2d**–**g**). In fact, the difference between the energies for *partially* planarizing the eight-membered rings in TMCOT (**1b**) and COT (**1a**), compared to the geometries that they have in, respectively, TMCOT-$Fe(CO)_3$ (**2b**) and COT-$Fe(CO)_3$ (**2a**) is 3.6 kcal/mol, which is about three times larger than the difference between the *complete* planarization energies of MCOT (**1d**) and COT (**1a**). Therefore, the greater energetic cost of partially planarizing the eight-membered ring in TMCOT (**1b**) than in COT (**1a**) is a major contributor to the 6.0 kcal/mol lower $Fe(CO)_3$ binding energy in TMCOT-$Fe(CO)_3$ (**2b**) than in TMBCOT-$Fe(CO)_3$ (**4b**).[28]

The methyl group at R$_3$ in MCOT-$Fe(CO)_3$ **2f** has by far the largest effect on reducing the $Fe(CO)_3$ binding energy, relative to that in COT-$Fe(CO)_3$ (**2a**). The ΔE = 5.4 kcal/mol reduction of the $Fe(CO)_3$ binding energy in **2f**, relative to **2a**, (Table 2) is 2.8 kcal/mol larger than the ΔE = 2.6 kcal/mol reduction of the $Fe(CO)_3$ binding energy in MBCOT-$Fe(CO)_3$ **4f**, relative to that in BCOT-$Fe(CO)_3$ (**4a**) (Table 3).

One contributor to the 2.8 kcal/mol larger value of ΔE for **2f** in Table 2 than for **4f** in Table 3 is, again, the greater energetic cost of partially planarizing the eight-membered ring in MCOT (**1d**) than in COT (**1a**). However, as discussed above, the size of this effect is only on the order of 3.6/4 = 0.9 kcal/mol.



2e **2f** **4e** **4f**

Figure 2. Optimized geometries for MCOT-Fe$(CO)_3$ complexes **2e** and **2f** and for MBCOT-Fe$(CO)_3$ complexes **4e** and **4f**. The H_3C−C−Fe−CO dihedral angles in these complexes are **2e**, 33.8°; **2f**, 4.5°; **4e**, 28.3°; and **4f**, 19.8°.

Therefore, there must be another substantial contributor to the 2.8 kcal/mol larger ΔE value for **2f** than for **4f**.

Evidence that the methyl group at R_3 of **2f** weakens the Fe$(CO)_3$ binding in this MCOT complex can be found in the Fe−C bond lengths in **2f**. The length of the bond between iron and the methylated carbon in MCOT-Fe$(CO)_3$ complex **2f** is 2.328 Å, which is 0.104 Å longer than the bond between iron and the unmethylated terminal carbon of the butadiene group. In fact, except for the Fe−C bond to the methylated carbon in **2f**, the lengths of all the bonds between iron and the terminal butadiene carbons in COT-Fe$(CO)_3$ **2a** and MCOT-Fe$(CO)_3$ complexes **2d−g** range from 2.197 to 2.234 Å.[29]

One might also expect the bond between iron and the methylated terminal carbon of the butadiene group in MBCOT-Fe$(CO)_3$ **4f** to be unusually long, and it is, indeed, longer than the bond between iron and the unmethylated terminal carbon of the butadiene group in **4f**. These Fe−C bond lengths are, respectively, 2.210 and 2.146 Å. However, the difference of 0.064 Å between these Fe−C bond lengths in MBCOT-Fe$(CO)_3$ **4f** is 0.040 Å less than the difference of 0.104 Å between the two corresponding Fe−C bond lengths in MCOT-Fe$(CO)_3$ **2f**. The 0.040 Å larger difference between these pairs of Fe−C bond lengths in MCOT-Fe$(CO)_3$ complex **2f** than in MBCOT-Fe$(CO)_3$ complex **4f** is consistent with the substantially larger ΔE value for MCOT-Fe$(CO)_3$ **2f** (Table 2) than for MBCOT-Fe$(CO)_3$ **4f** (Table 3).

It might be argued that for $R_3 = CH_3$ the greater decrease in the Fe$(CO)_3$ binding energy in MCOT-Fe$(CO)_3$ **2f** than in MBCOT-Fe$(CO)_3$ **4f** must be related to ring size, eight carbons in the case of **2f** and six carbons in the case of **4f**. However, for $R_2 = CH_3$ the effect of the methyl group on reducing the Fe$(CO)_3$ binding energy is only $\Delta E = 1.2$ kcal/mol for the eight-membered ring in MCOT-Fe$(CO)_3$ complex **2e**, which is just 0.7 kcal/mol greater than $\Delta E = 0.5$ kcal/mol for the six-membered ring in MBCOT-Fe$(CO)_3$ complex **4e**.

Moreover, the calculated lengths of the Fe−C bonds to the two internal carbons of the butadiene groups are 2.086 and 2.068 Å in MCOT-Fe$(CO)_3$ complex **2e** and 2.098 and 2.076 Å in MBCOT-Fe$(CO)_3$ complex **4e**. In both complexes, the calculated lengths of the Fe−C bonds to the two internal carbons of the butadiene groups differ by only about 0.02 Å. Therefore, neither the Fe$(CO)_3$ binding energies nor the Fe−C bond lengths in **2e** and in **4e** give any indication that the difference between the size of the ring in each of these two complexes results in a significantly larger effect of the methyl group at R_2 on destabilizing MCOT-Fe$(CO)_3$ complex **2e** than MBCOT-Fe$(CO)_3$ complex **4e**.

The calculated effects of methyl group substitution on the Fe$(CO)_3$ binding energies in Tables 2 and 3 lead to three questions. First, why is ΔE substantially (2.8 kcal/mol) larger for $R_3 = CH_3$ in MCOT-Fe$(CO)_3$ complex **2f** than in MBCOT-Fe$(CO)_3$ complex **4f**? Second, why is ΔE only 0.7 kcal/mol larger for $R_2 = CH_3$ in MCOT-Fe$(CO)_3$ complex **2e** than in MBCOT-Fe$(CO)_3$ complex **4e**? Third, why are the values of ΔE for $R_3 = CH_3$ in complexes **2f** and **4f** each 4−5 times larger than the values of ΔE for $R_2 = CH_3$ in complexes **2e** and **4e**? The optimized geometries of **2e**, **2f**, **4e**, and **4f**, which are shown in Figure 2, provide the answers to all three questions.

Figure 2 shows that the H_3C−C−Fe−CO dihedral angle in **2f** is only 4.5°, so that the CH_3−C and one Fe−CO bond are almost eclipsed. This accounts for the much larger value of $\Delta E = 5.4$ kcal/mol in Table 2 for MCOT-Fe$(CO)_3$ complex **2f**, compared to $\Delta E = 1.2$ kcal/mol in MCOT-Fe$(CO)_3$ complex **2e**, where the H_3C−C−Fe−CO dihedral angle is 33.8°.

Fe$(CO)_3$ complexes of dienes have a strong preference for adopting the conformations shown in Figure 2, with one carbonyl group *anti* to the diene.[4] Consequently, the orientation of the Fe$(CO)_3$ group, relative to the six-membered ring in MBCOT-Fe$(CO)_3$ complexes **4e** and **4f**, is very similar to the orientation of the Fe$(CO)_3$ group, relative to the eight-membered ring, in MCOT-Fe$(CO)_3$ complexes **2e** and **2f**. However, the smaller bond angles in the six- than in the eight-membered ring make the H_3C−C−Fe−CO dihedral angle of 19.8° in **4f** 15.3° larger than that of 4.5° in MCOT-Fe$(CO)_3$ complexes **2f**. The larger H_3C−C−Fe−CO dihedral angle in **4f** than in **2f** helps to make the value of $\Delta E = 2.6$ kcal/mol for **4f** in Table 3 smaller by 2.8 kcal/mol than the value of $\Delta E = 5.4$ kcal/mol for **2f** in Table 2.

For a methyl group that is attached to an internal carbon of the complexed diene, ring size makes a smaller difference in the H_3C−C−Fe−CO dihedral angle than when a methyl group is attached to a terminal carbon of the complexed diene. Consequently, the H_3C−C−Fe−CO dihedral angle of 33.8° in MCOT-Fe$(CO)_3$ complex **2e** is only larger by 5.5° than the H_3C−C−Fe−CO dihedral angle of 28.3° in MBCOT-Fe$(CO)_3$ complex **4e**. As a result of the large H_3C−C−Fe−CO dihedral angles in **2e** and **4e** and the small difference between these angles, the respective values of $\Delta E = 1.2$ kcal/mol and $\Delta E = 0.5$ kcal/mol for these two complexes differ only by 0.7 kcal/mol.

It may at first seem surprising that MCOT-Fe$(CO)_3$ complex **2e** has a 5.5° larger H_3C−C−Fe−CO dihedral angle than MBCOT-Fe$(CO)_3$ complex **4e**, but also a 0.7 kcal/mol larger value of ΔE than **4e**. However, it should be recalled that ca. 1 kcal/mol more energy is required to planarize MCOT (**1d**), in forming MCOT-Fe$(CO)_3$ complexes **2d**−**g**, than to planarize COT (**1a**) in forming MCOT-Fe$(CO)_3$ complex (**2a**). This difference in planarization energies contributes to reducing the Fe$(CO)_3$ binding energies in MCOT-Fe$(CO)_3$ complexes **2d**−**g** and thus to raising each of the ΔE values for the isodesmic reaction in eq 12 by roughly 1 kcal/mol. Thus, the fact that ΔE for MCOT-Fe$(CO)_3$ **2e** in eq 12 is a little less than 1 kcal/mol larger than ΔE for MBCOT-Fe$(CO)_3$ **4e** in eq 13 is actually quite consistent with the fact that the H_3C−C−Fe−CO dihedral angle is calculated to be 5.5° larger in **2e** than in **4e**.

Energy Difference between OMCOT (1c) and OMBCOT (3c) and between Their Fe$(CO)_3$ Complexes (2c and 4c). Although octamethylCOT (OMCOT, **1c**) was initially thought to rearrange to OMBCOT (**3c**),[15a] the rearrangement product was subsequently shown to be octamethysemibullvalene.[15b] Askani succeeded in preparing **3c** and found that on warming it undergoes ring opening to **1c**.[15c] Therefore, there is no doubt that, as is the case for COT (**1a**)[7] and for TMCOT (**1b**),[11] OMCOT (**1c**) is lower in energy than its bicyclic isomer, OMBCOT (**3c**).

To the best of our knowledge, the product of the reaction of **1c** with Fe$(CO)_5$, $Fe_2(CO)_9$, or any other source of Fe$(CO)_3$ has not been reported. Therefore, we decided to use calculations to predict whether the eight methyl groups in OMCOT-Fe$(CO)_3$ (**2c**) will, like the four methyl groups in TMCOT-Fe$(CO)_3$ (**2b**),[10] result in the bicyclic isomer, OMBCOT-Fe$(CO)_3$ (**4c**), being lower in energy than OMCOT-Fe$(CO)_3$ **2c**.

First we computed the energy difference between OMCOT (**1c**) and OMBCOT (**3c**), uncomplexed with Fe$(CO)_3$. Our calculations found the ring-opening reaction of **3c** to **1c** in eq 14 to be energetically favorable by 3.1 kcal/mol.

$$\text{OMBCOT } (\mathbf{3c}) \rightarrow \text{OMCOT } (\mathbf{1c}) \quad \Delta E = -3.1 \text{ kcal/mol} \tag{14}$$

The four methyl groups in TMCOT (**1b**) reduce the energy of $\Delta E = -9.4$ kcal/mol for BCOT (**3a**) → COT (**1a**) in eq 1 to $\Delta E = -7.0$ kcal/mol for **3b** → **1b** in eq 6. Thus, if the energetic effect of two sets of four methyl groups in OMCOT (**1c**) and OMBCOT (**3c**) was strictly additive, the energy of the reaction in eq 14 would be $\Delta E = -9.4 - 2[-9.4 - (-7.0)] = -4.6$ kcal/mol. The difference of 1.5 kcal/mol between this estimate of −4.6 kcal/mol, based on additivity, and the actual value of $\Delta E = -3.1$ kcal/mol for the reaction in eq 14 is the size of the effect of interaction of the four methyl groups at C1, C3, C5, and C7 with the four methyl groups at C2, C4, C6, and C8 on reducing the energy difference between OMCOT (**1c**) and OMBCOT (**3c**).

It seems quite likely that the origin of some or all of the 1.5 kcal/mol smaller interaction between the methyl groups in OMBCOT (**3c**) than in OMCOT (**1c**) is the smaller repulsion between the two methyl groups attached to C7 and C8 of the cyclobutene ring in **3c**, compared to two methyl groups on the same double bond of **1c**. The first of these methyl−methyl repulsion energies can be computed from the disproportionation reaction

$$2(\text{7-MBCOT}) \ (\mathbf{3g}) \rightarrow \text{7,8-DMBCOT} + \text{BCOT } (\mathbf{3a}) \quad \Delta E = 0.5 \text{ kcal/mol} \tag{15}$$

The second can be computed from the disproportionation reaction

$$2\text{MCOT } (\mathbf{1d}) \rightarrow \text{1,2-DMCOT} + \text{COT } (\mathbf{1a}) \quad \Delta E = 3.1 \text{ kcal/mol} \tag{16}$$

The difference of 2.6 kcal/mol between these two isodesmic reactions represents the amount of energy by which the methyl−methyl repulsion energy in 1,2-DMCOT is greater than that between the methyl groups on the double bond of the cyclobutene ring in 7,8-DMBCOT.[28] This difference is more than sufficient to account for the 1.5 kcal/mol net contribution of the smaller methyl−methyl interactions in OMBCOT (**3c**) than in OMCOT (**1c**) to reducing the 7.0 kcal/mol energy difference between TMBCOT (**3b**) and TMCOT (**1b**) to the 3.1 kcal/mol energy difference between OMBCOT (**3c**) and OMCOT (**1c**).

In contrast to the modest energy difference of 3.1 kcal/mol between OMBCOT (**3c**) and OMCOT (**1c**) in eq 14, there is a very large difference between the energies computed for OMBCOT-Fe$(CO)_3$ (**4c**) and OMCOT-Fe$(CO)_3$ (**2c**).

$$\text{OMBCOT-Fe(CO)}_3 \ (\mathbf{4c}) \rightarrow \text{OMCOT-Fe(CO)}_3 \ (\mathbf{2c}) \quad \Delta E = 32.0 \text{ kcal/mol} \tag{17}$$

Obviously, the ring opening of **4c** to **2c** is calculated to be highly unfavorable energetically. It is much more unfavorable than the ring opening of TMBCOT-Fe$(CO)_3$ (**4b**) to TMCOT-Fe$(CO)_3$ (**2b**), which is computed only to have $\Delta E = 2.6$ kcal/mol. Thus, the results of our calculations lead us to predict unequivocally that reaction of OMCOT (**1c**) with $Fe_2(CO)_9$ will produce OMBCOT-Fe$(CO)_3$ (**4c**), rather than OMCOT-Fe$(CO)_3$ (**2c**), as the product.

Equation 14 shows that the ring opening of OMBCOT (**3c**) to OMCOT (**1c**) is calculated to be favorable by 3.1 kcal/mol. Therefore, subtraction of eq 17 from eq 14 gives

$$\text{OMBCOT } (\mathbf{3c}) + \text{OMCOT-Fe(CO)}_3 \ (\mathbf{2c}) \rightarrow \text{OMCOT } (\mathbf{1c}) + \text{OMBCOT-Fe(CO)}_3 \ (\mathbf{4c}) \quad \Delta E = -35.1 \text{ kcal/mol} \tag{18}$$

as the greater Fe$(CO)_3$ binding energy in OMBCOT-Fe$(CO)_3$ (**4c**), relative to OMCOT-Fe$(CO)_3$ (**2c**). Comparison of eq 18 with eq 3 shows that the eight methyl groups in **1c**−**4c** make the 35.1 kcal/mol difference in the Fe$(CO)_3$ binding energies between OMBCOT-Fe$(CO)_3$ (**4c**) and OMCOT-Fe$(CO)_3$ (**2c**) 31.5 kcal/mol larger than the 3.6 kcal/mol difference in Fe$(CO)_3$ binding energies between BCOT-Fe$(CO)_3$ (**4a**) and COT-Fe$(CO)_3$ (**2a**).

Equation 9 shows that the four methyl groups in TMCOT (**1b**) make the Fe$(CO)_3$ binding energy in TMCOT-Fe$(CO)_3$ (**2b**) 11.3 kcal/mol lower than in COT-Fe$(CO)_3$ (**2a**), and eq 10 shows that the four methyl groups in TMBCOT (**3b**) make the Fe$(CO)_3$ binding energy in TMBCOT-Fe$(CO)_3$ (**4b**) 5.3 kcal/mol lower than in BCOT-Fe$(CO)_3$ (**4a**). [These effects of the four methyl groups in **1b**−**4b** are shown graphically in Figure 1.] Therefore, it is easy to guess that the eight methyl groups in **1c**−**4c** decrease the Fe$(CO)_3$ binding energies in both OMCOT-Fe$(CO)_3$ (**2c**) and OMBCOT-Fe$(CO)_3$ (**4c**) but decrease the Fe$(CO)_3$ binding energy in **2c**, relative to COT-Fe$(CO)_3$ (**2a**), by 31.5 kcal/mol more than in **4c**, relative to BCOT-Fe$(CO)_3$ (**4a**).

This conjecture is easily verified by comparing the Fe$(CO)_3$ binding energies for the octamethylated and unmethylated monocyclic and bicyclic Fe$(CO)_3$ complexes.

$$\text{COT-Fe(CO)}_3\ (\mathbf{2a}) + \text{OMCOT}\ (\mathbf{1c}) \rightarrow \text{OMCOT-Fe(CO)}_3\ (\mathbf{2c}) + \text{COT}\ (\mathbf{1a}) \quad \Delta E = 37.5\ \text{kcal/mol} \tag{19}$$

and

$$\text{BCOT-Fe(CO)}_3\ (\mathbf{4a}) + \text{OMBCOT}\ (\mathbf{3c}) \rightarrow \text{OMBCOT-Fe(CO)}_3\ (\mathbf{4c}) + \text{BCOT}\ (\mathbf{3a}) \quad \Delta E = 6.0\ \text{kcal/mol} \tag{20}$$

If additivity were followed, eq 9 shows that the four methyl groups at each of the two sets of nonadjacent carbons in **1c** and **2c** would be expected to reduce the Fe(CO)$_3$ binding energy in OMCOT-Fe(CO)$_3$ (**2c**) by 2 × 11.3 = 22.6 kcal/mol, relative to COT-Fe(CO)$_3$ (**2a**). According to eq 19, the actual reduction in Fe(CO)$_3$ binding energy, caused by the eight methyl groups in OMCOT-Fe(CO)$_3$ (**2c**), is 37.5 − 22.6 = 14.9 kcal/mol more than the reduction expected from additivity of the effect of four methyl groups on the Fe(CO)$_3$ binding energy in TMCOT-Fe(CO)$_3$ (**2b**).[31a] This large deviation from additivity is due to the destabilizing effects of interactions between the eight pairs of methyl groups at adjacent carbons being larger in OMCOT-Fe(CO)$_3$ (**2c**) than in OMCOT (**1c**) by 14.9 kcal/mol.[30]

Similarly, using eq 10, additivity of the effect of four methyl groups on the Fe(CO)$_3$ binding energy in TMBCOT-Fe(CO)$_3$ (**4b**) would predict a 2 × 5.3 = 10.6 kcal/mol reduction in the Fe(CO)$_3$ binding energy, relative to BCOT-Fe(CO)$_3$ (**4a**), caused by the eight methyl groups in OMBCOT-Fe(CO)$_3$ (**4c**). According to eq 20, the actual reduction in Fe(CO)$_3$ binding is 6.0 − 10.6 = −4.6 kcal/mol less than that expected from additivity.[31b] The −4.6 kcal/mol deviation from additivity represents the amount by which the destabilizing effects of interactions between the eight pairs of methyl groups at adjacent carbons are smaller in OMBCOT-Fe(CO)$_3$ (**4c**) than in OMBCOT (**3c**).[30]

Both the large (14.9 kcal/mol) calculated effect of the interactions between the eight pairs of methyl groups on adjacent carbons in reducing the Fe(CO)$_3$ binding energy in OMCOT-Fe(CO)$_3$ (**2c**) and the smaller calculated effect (−4.6 kcal/mol) of methyl−methyl interactions on *enhancing* the Fe(CO)$_3$ binding energy in OMBCOT-Fe(CO)$_3$ (**4c**) are readily explicable. However, even without these effects of methyl−methyl interactions, additivity of the effects of the four methyl groups on Fe(CO)$_3$ bonding in TMCOT-Fe(CO)$_3$ (**2b**) and in TMBCOT-Fe(CO)$_3$ (**4b**) leads to the prediction of a much higher [2(11.3 − 5.3) = 12.0 kcal/mol] Fe(CO)$_3$ binding energy in OMBCOT-Fe(CO)$_3$ (**4c**) than in OMCOT-Fe(CO)$_3$ (**2c**). Therefore, we have relegated the detailed analysis of the effects of the 14.9 − (−4.6) = 19.5 kcal/mol difference between the methyl−methyl interactions in these two compounds to Section S1 of the Supporting Information for this manuscript.

CONCLUSIONS

In agreement with the experimental observations, our calculations find that COT (**1a**) is lower in energy than BCOT (**3a**); COT-Fe(CO)$_3$ (**2a**) is lower in energy than BCOT-Fe(CO)$_3$ (**4a**); TMCOT (**1b**) is lower in energy than TMBCOT (**3b**); but TMCOT-Fe(CO)$_3$ (**2b**) is higher in energy than TMBCOT-Fe(CO)$_3$ (**4b**). Of the calculated change of 8.4 kcal/mol in the relative energies of Fe(CO)$_3$ complexes **2a** and **4a**, caused by the addition of the four methyl groups in complexes **2b** and **4b**, 2.4 kcal/mol is computed to come from a reduction of the energy difference between COT (**1a**) and BCOT (**3a**). The remainder of the change in relative energies comes from the four methyl groups effecting a 6.0 kcal/mol greater reduction in the Fe(CO)$_3$ binding energy in TMCOT-Fe(CO)$_3$ (**2b**), relative to COT-Fe(CO)$_3$ (**2a**), than in TMBCOT-Fe(CO)$_3$ (**4b**), relative to BCOT-Fe(CO)$_3$ (**4a**).

The major part of this 6.0 kcal/mol difference between the effects of tetramethylation on Fe(CO)$_3$ binding energies comes from the change in the ring geometry of COT, but not BCOT, on Fe(CO)$_3$ complexation. Partial planarization of the tub-shaped eight-membered ring, which is required for Fe(CO)$_3$ complexation, results in a 3.6 kcal/mol larger increase in energy in TMCOT (**1b**) than in COT (**1a**) due to an increase in the interaction between each of the four methyl groups and the hydrogen on the double bond that is closest to the methyl group in TMCOT (**1b**).

A lesser part of the 6.0 kcal/mol difference between the effects of tetramethylation on Fe(CO)$_3$ binding energies comes from a much smaller $H_3C{-}C{-}Fe{-}CO$ dihedral angle, involving the methyl group at a terminal carbon of the coordinated butadiene group, in TMCOT-Fe(CO)$_3$ (**2b**) than in TMBCOT-Fe(CO)$_3$ (**4b**). The smaller dihedral angle results in a greater destabilizing interaction in **2b** than in **4b** between this methyl group and a CO ligand. The energetic destabilization is manifested in a significantly longer Fe−C distance in **2b** than in **4b** to the terminal butadiene carbon that is methylated.

Addition of four more methyl groups to TMCOT (**1b**), to form OMCOT (**1c**), makes the calculated energy difference between **1c** and OMBCOT (**3c**) even smaller than the energy difference between **1b** and TMBCOT (**3b**). However, in agreement with experiment, OMCOT (**1c**) is still calculated to be favored energetically over OMBCOT (**3c**).

On the other hand, the eight methyl groups in OMCOT-Fe(CO)$_3$ (**2c**) are calculated to weaken Fe(CO)$_3$ binding in this complex far more than eight methyl groups weaken Fe(CO)$_3$ binding in OMBCOT-Fe(CO)$_3$ (**4c**). The very large reduction in Fe(CO)$_3$ binding energy in **2c**, relative to that in COT-Fe(CO)$_3$ (**2a**), is largely a consequence of destabilizing interactions between pairs of methyl groups on adjacent C═C bonds, when the tub-shaped equilibrium geometry of OMCOT (**1c**) is forced to become partially planar by coordination of the Fe(CO)$_3$ group in OMCOT-Fe(CO)$_3$ (**2c**). In contrast, Fe(CO)$_3$ coordination does not require a large geometry change in OMBCOT (**3c**), and the methyl−methyl repulsion energy in OMBCOT-Fe(CO)$_3$ (**4c**) is less than that in OMBCOT (**3c**).

As a consequence of the small energy difference between OMCOT (**1c**) and OMBCOT (**3c**) and the very large reduction in Fe(CO)$_3$ binding energy in OMCOT-Fe(CO)$_3$ (**2c**), relative to OMBCOT-Fe(CO)$_3$ (**4c**), **4c** is calculated to be far lower in energy than **2c**. This prediction awaits experimental verification.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The energies of methyl transfer reactions between cyclobutene and a variety of 1-methylcycloalkenes, an analysis of the effects of methyl−methyl interactions on the Fe(CO)$_3$ binding energies in OMCOT-Fe(CO)$_3$ (**2c**) and in OMBCOT-

$Fe(CO)_3$ (**4c**), and optimized geometries and energies for **1a**–**4a** and their monomethyl (**1d**–**g**, **4d**–**g**), tetramethyl (**1b**–**4b**), and octamethyl (**1c**–**4c**) derivatives. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) (a) To determine the effect of changing the functional and the basis set on the energies computed for the reactions in eqs 1–3, we recomputed these energies with Truhlar's M06-L functional,[23] using both the 6-31G(d)[18] and the 6-311++G(d,p)[24] basis sets. COT (**1a**) is calculated to be lower in energy than BCOT (**3a**) by 6.8 and 7.9 kcal/mol at, respectively, the M06-L/6-31G(d) and M06-L/6-311++G(d,p) levels of theory. These energies can be compared with the B3LYP/6-31G(d) value of $\Delta E = -9.4$ kcal/mol for **3a** → **1a** in eq 1. (b) COT-$Fe(CO)_3$ (**2a**) is calculated to be lower in energy than BCOT-$Fe(CO)_3$ (**4a**) by 4.0 and 4.3 kcal/mol at, respectively, the M06-L/6-31G(d)+LANL2DZ and M06-L/6-311++G(d,p)+LANL2DZ levels of theory. B3LYP/6-31G(d) gives $\Delta E = -5.8$ kcal/mol for **4a** → **2a** in eq 2. (c) B3LYP/6-31G(d) finds ring opening of **3a** to **1a** and of **4a** to **2a** to be more favorable than M06-L/6-31G(d) does by, respectively, 2.6 and 1.8 kcal/mol and more favorable than M06-L/6-311++G(d,p) does by 1.5 kcal/mol for both reactions. The effect of the $Fe(CO)_3$ binding in **2a** and **4a** on reducing the energy difference between **1a** and **3a** is 2.8 and 3.6 kcal/mol at, respectively, the M06-L/6-31G(d)+LANL2DZ and M06-L/6-311++G(d,p)+LANL2DZ levels of theory. The latter value is in exact agreement with the B3LYP/6-31G(d) value for the energy of the reaction in eq 3.

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(25) One indication that the HOMO–LUMO gap in COT (**1a**) at the geometry of COT-$Fe(CO)_3$ (**2a**) is much smaller than the HOMO–LUMO gap in BCOT (**3a**) at the geometry of BCOT-$Fe(CO)_3$ (**4a**) is that the (U)B3LYP singlet–triplet energy difference is 39.8 kcal/mol lower in **1a** at the geometry of **2a** than in **3a** at the geometry of **4a**. Of course, if the COT ring in **2a** were perfectly planar and the C–C bonds all had the same length, the HOMO and LUMO of **1a** at this geometry would be degenerate by symmetry and have exactly the same energy.

(26) (a) TMCOT (**1b**) is calculated to be lower in energy than TMBCOT (**3b**) by 3.9 and 4.7 kcal/mol at M06-L/6-31G(d) and M06-L/6-311++G(d,p) level of theory, respectively. These energy differences between the mono- and bicyclic isomers are 2–3 kcal/mol smaller in magnitude than the B3LYP/6-31G(d) value of $\Delta E = -7.0$ kcal/mol for the reaction in eq 6. (b) TMBCOT-$Fe(CO)_3$ (**4b**) is calculated to be lower in energy than TMCOT-$Fe(CO)_3$ (**2b**) by 4.5 and 4.7 kcal/mol at M06-L/6-31G(d)+LANL2DZ and M06-L/6-311++G(d,p)+LANL2DZ levels of theory, respectively. These M06-L energy differences between the mono- and bicyclic $Fe(CO)_3$ complexes favor the bicyclic isomer by about 2 kcal/mol more than

the B3LYP/6-31G(d) value of ΔE = 2.6 kcal/mol for the reaction in eq 7. (c) In the reactions in eqs 1, 2, 6, and 7, M06-L finds ring opening to be less favorable (and in the case of eq 7, more unfavorable) by 2−3 kcal/mol more than B3LYP does. Consequently, the M06-L results strongly support the qualitative B3LYP finding that **4b** is lower in energy than **2b**, thus explaining why **4b**, rather than **2b**, is isolated from the reaction of TMCOT (**1b**) with $Fe_2(CO)_9$.[10]

(27) Since planarization is calculated to extract only a 1.3 kcal/mol larger energetic penalty from MCOT (**1d**) than from COT (**1a**), there are presumably other smaller effects that contribute to making the $Fe(CO)_3$ binding energy in MCOT-$Fe(CO)_3$ (**2g**) 2.2 kcal/mol lower than that in COT-$Fe(CO)_3$ (**2a**).

(28) The energetic cost of MCOT planarization presumably also contributes to the 2.1 kcal/mol reduction in the $Fe(CO)_3$ binding energy in MCOT-$Fe(CO)_3$ complex **2d**. The reason that the ΔE values for $R_1 = CH_3$ in MCOT-$Fe(CO)_3$ complex **2d** (Table 2) and in MBCOT-$Fe(CO)_3$ complex **4d** (Table 3) are nearly the same is almost certainly that the methyl group at R_1 in **4d** interacts with and destabilizes the $Fe(CO)_3$ group, which is *syn* to this methyl group in MBCOT-$Fe(CO)_3$ complex **4d**.

(29) All of the Fe−C bond lengths in **2a**−**g** and in **4a**−**g** are provided in the Supporting Information for this paper, which gives the optimized geometries of all the molecules discussed.

(30) Each of the energies in the text that is attributed to methyl−methyl repulsions is actually computed from the energy of an octamethyl compound, plus the energy of the unmethylated compound, minus twice the energy of the tetramethyl compound. This energy difference is dominated by the methyl−methyl repulsion energy in the octamethyl compound. Therefore, for the sake of simplicity, we refer to such an energy difference as the "methyl−methyl repulsion energy" in the octamethyl compound.

(31) (a) The difference between eq 19 and twice eq 9 gives an isodesmic reaction that compares the disproportionation energies of 2(**2b**) → **2c** + **2a** and 2(**1b**) → **1c** + **1a**. (b) The difference between eq 20 and twice eq 10 gives an isodesmic reaction that compares the disproportionation energies of 2(**4b**) → **4c** + **4a** and 2(**3b**) → **3c** + **3a**.