Metal−Olefin Interactions in $M(CO)_5$(cycloolefin) (M = Cr, Mo, W; Cycloolefin = Cyclopropene to Cyclooctene): Strain Relief and Metal−Olefin Bond Strength

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Density functional theory calculations on the title compounds indicate that metal−olefin bond strengths follow the trend for cyclic olefin strain energies. It was found, however, that the proportionality between metal−olefin bond energy and strain energy is not evenly distributed throughout the olefin series. For instance, cyclopropene and cyclobutene are expected to bind to the metal much more weakly than would be anticipated on the basis of their strain energies. A bond energy decomposition analysis reveals that the metal−olefin interaction is responsible for strain relief in the cycloolefins by means of the rehybridization of the olefinic carbons. However, the geometrical changes accompanying this rehybridization, namely C═C elongation and olefin pyramidalization, involve an energetic cost that is paid at the expense of the bonding interaction energy. Nonpyramidalized strained olefins such as cyclopropene and cyclobutene undergo large conformational changes, to the detriment of their large attractive interaction energies. It was found that a cyclic olefin that is already deformed, such as *trans*-cyclooctene, interacts strongly with a metal to relieve strain but does not suffer much energy-costly reorganizations. This, thus, constitutes an energy benefit to the metal−*trans*-cyclooctene bond strength.

1. Introduction

It is well established that strain relief in both cyclic alkenes and alkanes is the driving force of their reactivity.[1,2] For instance, it is well-known that strain in cyclic alkenes can be relieved by complexation to metals, with a number of examples being reported in the literature.[3−12] These experimental and computational studies indicate that the metal−cyclic olefin bond strength is directly proportional to the amount of strain in the olefin. Past studies have suggested that $sp^2 \rightarrow sp^3$ rehybridization (bond order decrease) of the olefin, as it goes from the free state to the complexed state, is primarily responsible for the relief of the strain energy. Rehybridization is caused by both the reduction of electron density in the HOMO of the olefin, via the σ-type metal−olefin interaction, and the increase of the electron density in the LUMO of the olefin as a result of π back-bonding. Furthermore, it has been suggested that the metal−olefin back-bonding interaction is more important than the σ interaction in the stability of a metal−olefin complex.[13] There are, however, steric and conformational (namely reorganizational) factors that also influence the bond strength between an olefin and a metal complex. Steric interactions may decrease the bond strength, because repulsive orbital interactions force the olefin and metal complex to avoid each other, thereby decreasing the overlap of those orbitals contributing to bonding. It has also been established that rehybridization of the olefin is responsible for a decrease in the metal−olefin bond strength.[14−16] This is due to the elongation of the C−C bond and pyramidalization (i.e. bending of the substituents around the C═C bond out of the plane containing the bond) of the olefin, resulting in an energetic cost at the expense of the energy gained through bonding interactions.

Most of the attention, in the area of metal−cyclic olefin complexes, has been focused on those involving

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[1] Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*, 3rd ed.; Plenum Press: New York, 1993; Part A (Structure and Mechanisms), p 157.

[2] March, J., *Advanced Organic Chemistry. Reactions, Mechanisms, and Structure*, 4th ed., Wiley-Interscience: New York, 1992; p 151.

[3] Traynham, J. G.; Sehnert, M. E. *J. Am. Chem. Soc.* **1956**, *78*, 4024.

[4] Visser, J. P.; Ramakers, J. E. *J. Chem. Soc., Chem. Commun.* **1972**, 178.

[5] Jason, M. E.; McGinnety, J. A.; Wiberg, K. B. *J. Am. Chem. Soc.* **1974**, *96*, 6531.

[6] Evers, J.; Mackor, A. *Tetrahedron Lett.* **1978**, 2317.

[7] Godleski, S. A.; Gundlach, K. B.; Valpey, R. S. *Organometallics* **1985**, *4*, 296.

[8] Klassen, J. K.; Yang, G. K. *Organometallics* **1990**, *9*, 874.

[9] Kumar, A.; Lichtenhan, J. D.; Critchlow, S. C.; Eichinger, B. E.; Borden, W. T. *J. Am. Chem. Soc.* **1990**, *112*, 5633.

[10] Leigh, G. J.; McMahon, C. N. *J. Organomet. Chem.* **1995**, *500*, 219.

[11] Uddin, J.; Dapprich, S.; Frenking, G.; Yates, B. F. *Organometallics* **1999**, *18*, 457.

[12] Yates, B. F. *J. Organomet. Chem.* **2001**, *635*, 142.

[13] Ziegler, T.; Rauk, A. *Inorg. Chem.* **1979**, *18*, 1558.

[14] Cedeño, D. L.; Weitz, E. *J. Am. Chem. Soc.* **2001**, *123*, 12857.

[15] Cedeño, D. L.; Weitz, E.; Bérces, A. *J. Phys. Chem. A* **2001**, *105*, 8077.

[16] Schlappi, D. N.; Cedeño, D. L. *J. Phys. Chem. A* **2003**, *107*, 8763.

10.1021/om050331q CCC: $30.25

cycloalkenes that are highly pyramidalized.[4–7,9–12] It has been found that these olefins bind to metals with a strength that is proportional to the amount of pyramidalization, which is proportional to the amount of strain in the olefin. Preliminary work showed that this occurs because there is a strong interaction between the metal and the olefin that relieves the strain caused by pyramidalization.[11,12] Since pyramidalized cyclic olefins are strained, due both to the presence of the double bond and (more importantly) to the forces keeping the olefin pyramidalized, we consider it important to make a systematic study of the nature of the interaction between the less-studied elemental nonpyramidalized planar monocyclic olefins (cyclopropene, cyclobutene, cyclopentene, cyclohexene, cycloheptene, and *cis*-cyclooctene) and group VI (chromium, molybdenum, and tungsten) metal pentacarbonyls. *trans*-Cyclooctene was included to account for the effects on a nonplanar monocyclic olefin.

Bond energies were calculated and then decomposed into factors that quantify the amount of energy involved in the events leading to both an increase (electrostatic and covalent) and a decrease (steric and reorganizational) in bond strength. Correlations between these factors, molecular orbital populations and energies, and geometrical changes occurring in the olefin and in the metal carbonyl are presented. It was found that the π back-bonding interaction between the metal and the olefin is primarily responsible for the relief of strain, because it induces sp^2 to sp^3 rehybridization of the olefinic carbons.

This study shows that the relief of strain is not the only factor dominating the thermal stability of metal–cycloolefin complexes. Paradoxically, the relief of strain through rehybridization causes large conformational changes in highly strained nonpyramidalized olefins, such as cyclopropene and cyclobutene, to the detriment of the overall metal–olefin bond strength. In contrast, the metal–olefin bond strength of an olefin that is already deformed, such as *trans*-cyclooctene, is not largely influenced by the conformational changes resulting from rehybridization.

2. Computational Methods

The structures of the cyclic alkenes were built using Spartan'02 for Linux.[17] Monte Carlo based conformational searches using the universal MM force field were carried out for the most fluxional alkenes. Geometry optimizations for the alkenes, metal pentacarbonyls, and olefin complexes were carried out using DFT methods with the Jaguar 4.1 computational package[18] under full analytical conditions. The triple-ζ LACV3P** basis set was used. This basis set incorporates Hay and Wadt's relativistic effective core potentials[19] for the inner core electrons and Gaussian type functions for the outermost and valence electrons of the metals. The nonmetals are described by the 6-311G(d,p) basis set.[20]

To decide on a particular DFT method suitable for all three metal complexes, a benchmarking of methods was performed. Bond energies and enthalpies at 298 K were calculated for the reaction

$$\mathrm{M(CO)_5(olefin)\ (g) \rightarrow M(CO)_5\ (g) + olefin\ (g)} \qquad (1)$$

where M = Cr, M, W and olefin = ethene, cyclopropene, cyclobutene, cyclopentene, cyclohexene, cycloheptene, *cis*-cyclooctene, *trans*-cyclooctene. Where available, these were compared to experimental data. A recent benchmarking[21] of group VI metal hexacarbonyls suggested that the B3LYP, BP86, and PWP91 methods would be suitable for the metal complexes studied here.[22] Benchmarking results for the series of complexes are available as Supporting Information. The PWP91 method[23,24] best reproduces the available experimental data for the three-metal series;[8,25–27] thus, it is used preferentially throughout this study. Figure 1 presents both the calculated metal–olefin bond dissociation energies (D_e) and calculated and available experimental enthalpies ($\Delta H°$) at 298 K.

Bond energy decomposition analyses (BEDA) were made using ADF 2004,[28] which incorporates the decomposition scheme of Ziegler and Rauk[13,29] as implemented by Baerends and co-workers.[30] In this analysis (see Scheme 1), the bond energy (D_e) is broken into contributions from four terms:

$$D_e = \Delta E_{oi} + \Delta E_{elect} + \Delta E_{Pauli} + \Delta E_{reorg} \qquad (2)$$

The first term (ΔE_{oi}) is the attractive energy contribution due to the interactions of occupied orbitals of one of the reactants in eq 1 and the empty unoccupied orbitals of the other reactant, as well as those between occupied and empty orbitals within a given reactant. The second term (ΔE_{elect}) is the contribution due to the electrostatic interaction between the two reactants, which is attractive in the systems under study. The third term (ΔE_{Pauli}) is due to the Pauli repulsion between occupied orbitals of both reactants. The final term (ΔE_{reorg}) is the reorganizational energy, the energy involved in the deformation of the reactants from the geometries they adopt in the complex to those they have in their respective isolated ground state. Since D_e is, by definition, a positive number, we have used the following sign convention throughout the paper: repulsive and reorganizational energies are negative, while attractive energies are positive.

The sum of the three first terms in eq 2 will be denoted throughout the paper as the interaction energy (ΔE_{int}):

$$\Delta E_{int} = \Delta E_{oi} + \Delta E_{elect} + \Delta E_{Pauli} \qquad (3)$$

Notice that ΔE_{int} represents the net bonding interaction

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(17) Spartan'02 for Linux; Wavefunction Inc., Irvine, CA, 2002.

(18) Jaguar 4.1; Schrodinger Inc., Portland, OR., 2002.

(19) Hay P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(20) (a) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650. (b) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639. (c) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294. (d) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265.

(21) Sniatynsky R.; Cedeño, D. L. *J. Mol. Struct. (THEOCHEM)* **2004**, *711*, 123.

(22) For a complete description of the DFT methods benchmarked, see Table 1 in ref 21.

(23) For a description of local exchange, see: Slater, J. C. *Quantum Theory of Molecules and Solids*; McGraw-Hill: New York, 1974; Vol. 4.

(24) (a) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, M. R.; Pederson, D. J.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1992**, *46*, 6671. (b) For a description of correlation (local and nonlocal) and nonlocal exchange, see: Perdew, J. P. In *Electronic Structure Theory of Solids*; Ziesche, P., Eschrig, H., Eds.; Akademie Verlag: Berlin, 1991.

(25) (a) McNamara, B.; Becher, D. M.; Towns, M. H.; Grant, E. R. *J. Phys. Chem.* **1994**, *98*, 4622. (b) McNamara, B.; Towns, M. H.; Grant, E. R. *J. Am. Chem. Soc.* **1995**, *117*, 12254.

(26) Wells, J. R.; House, P. G.; Weitz, E. *J. Phys. Chem.* **1994**, *98*, 11256.

(27) M–cyclopentene and M–cyclohexene in hexane solution bond enthalpies were determined using photoacoustic calorimetry: Cedeño, D. L.; Martinez, J.; Robinson, D.; Huftington, C.; Walczack, T. Manuscript in preparation.

(28) (a) ADF2004.01; SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands; http://www.scm.com. (b) te Velde, G.; Bickelhaupt, F. M.; van Gisbergen, S. J. A.; Fonseca Guerra, C.; Baerends, E. J.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931. (c) Fonseca Guerra, C.; Snijders, J. G.; te Velde, G.; Baerends, E. J. *Theor. Chem. Acc.* **1998**, *99*, 391.

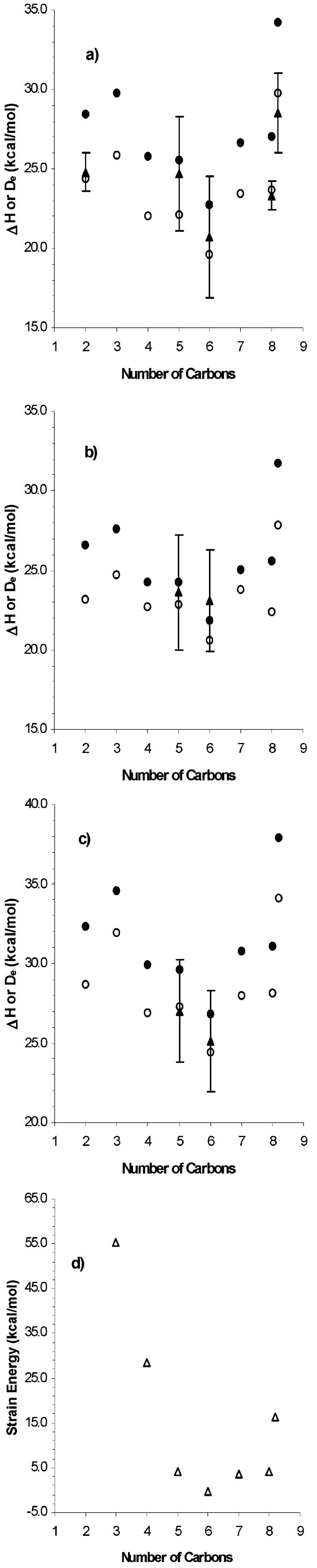

Figure 1. Plots showing the dependence of bond enthalpy ($\Delta H°$: ○, calculated; ▲, experimental) and bond dissociation energy (D_e: ●, calculated) as a function of the number of carbons in the olefin: (a) Cr(CO)$_5$(olefin); (b) Mo(CO)$_5$(olefin); (c) W(CO)$_5$(olefin). Plot d shows calculated strain energies.[35] For clarity, the labels for *trans*-cyclooctene are slightly shifted to the right of those for *cis*-cyclooctene.

between two reactants in a conformation that corresponds to the one they have in the complex. This term can be referred to as the "bond-snap energy".

For the bond energy decomposition analyses, single-point energy calculations for the optimized geometries in Jaguar were carried out using the relativistic ZORA triple-ζ basis set for all atoms.[31] A slightly modified version of the PWP91 method was used in the BEDA analysis. In this version, the VWN[32] local density functional is used instead of that developed by Perdew and co-workers.[24] Utilization of a different basis set and the VWN functional does not alter the trends observed when utilizing Jaguar 4.1. There was a consistent difference of about 2 kcal/mol in the calculated bond energies. In addition to the BEDA analysis, molecular orbital analyses were performed for each system to evaluate the changes in the electron populations occurring when an olefin and a metal pentacarbonyl interact.

3. Results and Discussion

3.1. Calculated Geometries. Chart 1 shows the calculated equilibrium geometries for the tungsten complexes using the PWP91 DFT method. Chromium and molybdenum complexes are not significantly different from the tungsten complexes and are not shown. Relevant geometrical data are, however, summarized for all complexes as well as the free olefins and the metal pentacarbonyls in the Supporting Information.

To our knowledge, there are no known experimental determinations for the geometries of any of the chromium olefin complexes studied here. However, the experimental geometry for the related chromium olefin complex Cr(CO)$_5$(*endo*-6-arylbicyclo[3.1.0]hex-2-ene) is known.[33] This olefin somewhat resembles the Cr(CO)$_5$(cyclopentene) complex in this study and therefore will be compared to it. The average value for the chromium–olefinic carbon (Cr–C$_{ol}$) distance in the bicyclo complex is 229.4 pm, which is relatively close to the value (227.9 pm) for the cyclopentene complex calculated here. The calculated Cr–CO bond lengths for the cyclopentene complex are in good agreement with the calculated values. Experimental values are 184.9, 188.8, and 192.3 pm, and calculated values are 185.7, 189.7, and 190.0 pm for Cr–CO trans to the olefin (Cr–C$_{tr}$) and cis to the olefin (Cr–C$_{\|}$ and Cr–C$_{\perp}$), respectively. The experimental C═C bond length (136.3 pm) is, however, slightly shorter than the calculated 138.9 pm.

In the case of tungsten complexes, there are spectroscopic data for the geometry of W(CO)$_5$(*trans*-cyclooctene).[34] The agreement between the experimental and calculated data is remarkable. The average experimental tungsten–olefinic carbon bond length (W–C$_{ol}$) is 233.8 pm, in good agreement with the calculated 233.3 pm. The experimental W–CO bond lengths are also well reproduced by the calculations: the W–CO experimental bond lengths for the trans CO (W–C$_{tr}$) and the cis

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[29] Ziegler, T.; Rauk, A. *Inorg. Chem.* **1979**, *18*, 1755.

[30] Bickelhaupt, F. M.; Baerends, E. J., In *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; Wiley: New York, 2000; Vol. 15.

[31] (a) van Lenthe, E.; Baerends, E. J.; Snijders, J. G. *J. Chem. Phys.* **1993**, *99*, 4597. (b) van Lenthe, E.; Baerends, E. J.; Snijders, J. G. *J. Chem. Phys.* **1994**, *101*, 9783. (c) van Lenthe, E.; Ehlers, A. E.; Baerends, E. J. *J. Chem. Phys.* **1999**, *110*, 8943.

[32] Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

[33] Fischer, H.; Hoffmann, J. *Chem. Ber.* **1991**, *124*, 981.

[34] Grevels, F.-W.; Jacke, J.; Klotzbücher, W. E.; Mark, F.; Skibbe, V.; Schaffner, K.; Angermund, K.; Krüger, C.; Lehmann, C. W.; Özkar, S. *Organometallics* **1999**, *18*, 3278.

Scheme 1

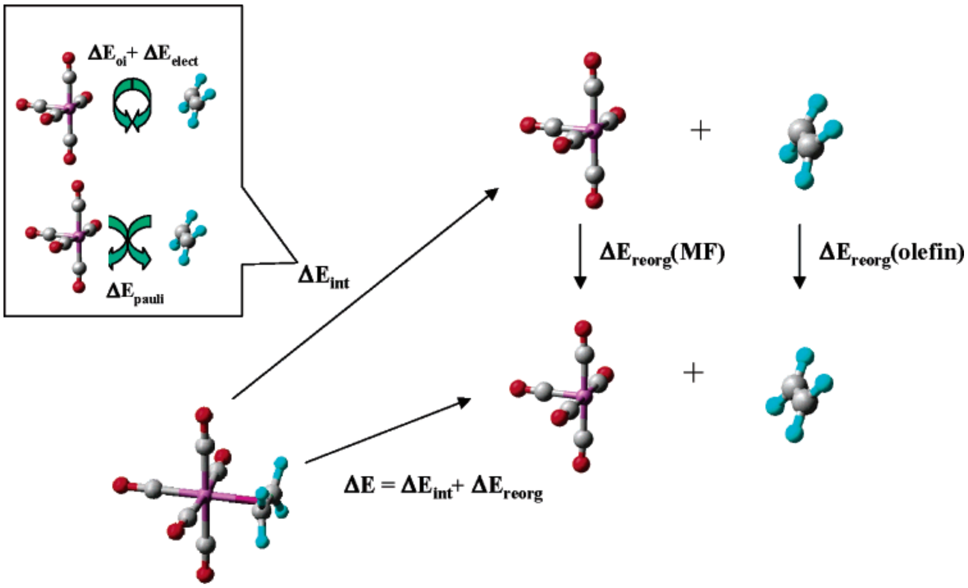
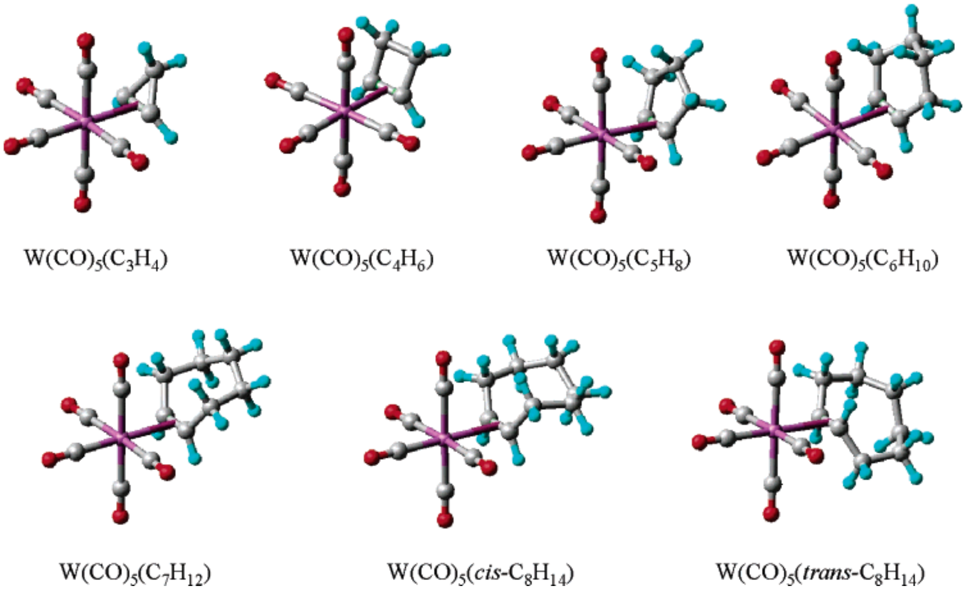


Chart 1


W(CO)$_5$(C$_3$H$_4$) W(CO)$_5$(C$_4$H$_6$) W(CO)$_5$(C$_5$H$_8$) W(CO)$_5$(C$_6$H$_{10}$)

W(CO)$_5$(C$_7$H$_{12}$) W(CO)$_5$(*cis*-C$_8$H$_{14}$) W(CO)$_5$(*trans*-C$_8$H$_{14}$)

COs of 201.1 and 204.9 pm compare well to the calculated 201.4 and 205.1 pm, respectively. The experimental C═C bond length (138.4 pm) is also in good agreement, although similar to the chromium example above, it is slightly shorter than the calculated value (140.2 pm). OC−W−CO bond angles are also well reproduced by the calculations, being 179.4 and 175.7° in comparison to the experimental values of 177.0 and 175.4°, respectively. Finally, the agreement with the torsional angle C−C═C−C, which defines the out-of-plane angle (Ω_{RR}), is also excellent. The experimental out-of-plane angle is 24.3°, while the calculated value is 25.6°. To our knowledge there are no experimental determinations of molybdenum pentacarbonyl olefin complexes that relate closely to those studied here. Despite this, the excellent agreement between the calculations and experimental determinations for the chromium and tungsten complexes allow us to say that the calculations for molybdenum complexes are also very reliable.

As expected, the calculations reflect the lengthening of the C═C bond and the pyramidalization (i.e. bending of the substituents out of the C═C plane) of the olefin when the olefin bonds to the metal pentacarbonyl. The changes in these geometrical features of the olefin will be discussed later in the context of the energetics of the metal−olefin interaction.

3.2. Metal−Olefin Bond Energies. As illustrated in Figure 1, DFT calculations with the PWP91 method agree well with known experimental bond enthalpies throughout the transition-metal group. In general, bond enthalpies are consistently calculated to be approximately 2−4 kcal/mol below bond dissociation energies (D_e). Figure 1 also includes estimated strain energies obtained from the literature.[35] It is evident from the figure that the metal−olefin bond energies follow a U-shaped trend that resembles the trend in the amount of strain for these olefins. However, relative differences

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[35] Wiberg, K. B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 312.

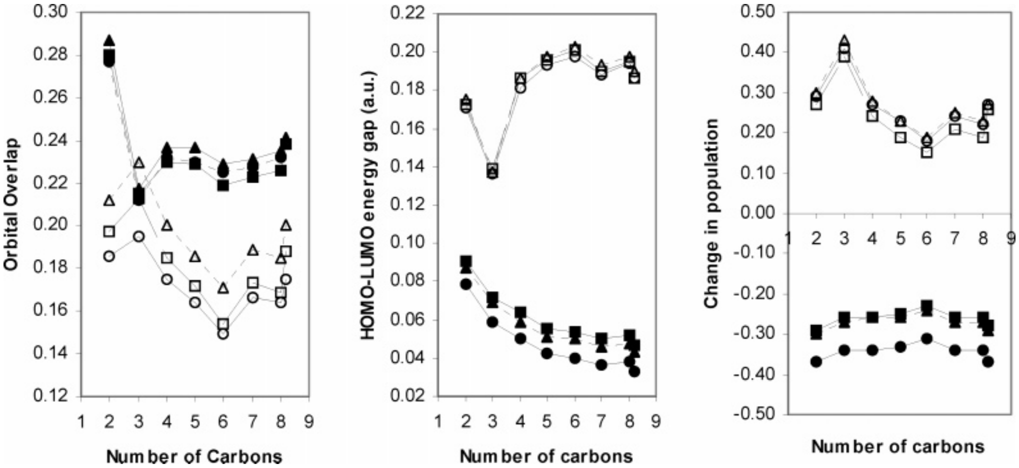

Figure 2. Plots showing the dependence of (from left to right) HOMO−LUMO orbital overlaps, HOMO−LUMO energy gaps, and changes in the olefin's HOMO and LUMO electron populations on the number of carbons in the olefin of $M(CO)_5$-(cycloolefin) complexes. Open symbols are used for orbitals involved in the π back-bonding and filled symbols for orbitals involved in the σ interaction. Circles denote M = Cr, squares denote M = Mo, and triangles denote M = W. For clarity, the labels for *trans*-cyclooctene are slightly shifted to the right of those for *cis*-cyclooctene.

in strain are much larger than relative differences in metal−olefin bond strength. In other words, if one were to correlate strain energies and metal−olefin bond strengths there would be a strong deviation between cyclopropene and cyclobutene and the other olefins.

It is also noteworthy to mention that the calculations indicate that, for a given olefin, tungsten forms a stronger bond to the olefin than do the other two metals and that molybdenum and chromium will bind to a given olefin similarly (with some olefins favoring molybdenum). Experimental evidence clearly confirms this observation for tungsten, and although available experimental values do not allow us to make conclusions about any specific differences between molybdenum−olefin and chromium−olefin bond energies, they seem to suggest that such bond energies for a given olefin are not significantly different.

3.3. The Metal−Cycloolefin Interaction from a Molecular Orbital Perspective. As already mentioned above, although the general trend of metal−olefin bond energies follow the U-shaped trend of the cyclic olefin strain energy, there is an important question that arises: *If cyclopropene and cyclobutene have so much strain energy (56 and 29 kcal/mol, respectively), why are their metal−olefin bond strengths not significantly larger than those for the other olefins*?

It is also noticeable that, for the three metal series of complexes, *trans*-cyclooctene is predicted to bind more strongly than either of these small cyclic olefins. In terms of the qualitative Dewar−Chatt−Duncanson (DCD) model[36,37] and previous studies,[11,12] the strain relief that occurs in olefins with highly deformed π-electron systems is greatly due to the back-bonding interaction. Since *trans*-cyclooctene is the only olefin in the series that shows a π system that is deformed (by twisting) in the free state, one may formulate a second question: *Is the back-bonding interaction in cyclopropene and cyclobutene relatively weaker than it is in* trans-*cyclooctene?*

Figure 2 presents orbital overlaps and energy gaps for the frontier molecular orbitals involved in the HOMO−LUMO interactions between the olefin and the $M(CO)_5$ fragment.

As can be seen, the σ overlap for the cyclic olefins is smaller than that of ethylene and does not change much with an increase in the number of carbons, except in the case of cyclopropene. On the other hand, the π overlap is more dependent on the number of carbons and follows the U-shaped trend observed for strain energy and metal−olefin bond energies. In general, the σ interaction involves an orbital overlap that is larger than that for a π or back-bonding interaction. In the cyclopropene complexes, however, the π overlap is close in magnitude to the σ overlap and it, indeed, becomes larger for the tungsten complex. Orbital overlaps support the role of the back-bonding in the relief of strain. The olefin with the most strain seems to adopt a state in which the LUMO becomes more available to interact with the metal pentacarbonyl.

From the perspective of the HOMO−LUMO gaps, the energy gap for the σ interaction shows a monotonic decrease that levels off at the larger olefins. This trend may suggest an improvement in the σ interaction as the number of carbons in the ring increases. The energy gap for the π interaction shows an inverted U-shaped trend, in which the metal−cyclopropene complex has the smallest gap and, therefore, the most favorable back-bonding interaction. It is obvious that the combination of both HOMO−LUMO overlaps and energy gaps define the capability of the olefin as a σ and π bonder. This capability correlates to the change in the electron populations of the olefin's HOMO and LUMO (Figure 2).

The change in the electron population of the HOMO of the olefins is almost the same for all of them, with subtle differences that follow the trend in orbital overlap better than the trend in the σ interaction energy gap. The change in the electron population of the LUMO reflects the effects of both the overlap and the energy gap of the π interaction. It is clear that both of these reinforce each other to produce the U-shaped trend, in which cyclopropene distinguishes itself as the best back-

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(36) Dewar, M. J. S. *Bull. Chem. Soc. Fr.* **1951**, *18*, C71.
(37) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939.

Table 1. Results (in kcal/mol) of a Bond Energy Decomposition Analysis for M(CO)$_5$(cycloolefin) Complexes

	C2	C3	C4	C5	C6	C7	*c*-C8	*t*-C8
				M = Cr				
$\Delta E_{\mathrm{Pauli}}$	−82.6	−107.2	−85.9	−75.3	−66.9	−80.4	−76.3	−90.1
$\Delta E_{\mathrm{elect}}$	60.9	75.3	63.8	57.6	51.7	61.9	59.2	69.4
ΔE_{oi}	55.2	75.4	55.2	48.8	43.1	51.7	48.9	57.8
ΔE_{int}	33.5	43.5	33.1	31.1	27.9	33.2	31.8	37.1
$\Delta E_{\mathrm{reorg}}$-(olefin)	−5.6	−13.8	−8.4	−6.7	−6.7	−8.2	−6.1	−4.0
$\Delta E_{\mathrm{reorg}}$-(MF)	−0.9	−1.2	−0.8	−0.8	−0.7	−0.6	−0.7	−0.7
D_{e}	27.0	28.5	23.6	23.6	20.5	24.4	25.0	32.4
				M = Mo				
$\Delta E_{\mathrm{Pauli}}$	−72.6	−96.2	−72.8	−64.4	−57.5	−71.0	−67.3	−82.6
$\Delta E_{\mathrm{elect}}$	55.8	70.5	57.3	52.4	47.1	57.6	55.1	67.0
ΔE_{oi}	46.9	65.8	44.8	39.7	35.3	43.2	41.0	50.0
ΔE_{int}	30.1	40.1	29.3	27.7	24.9	29.8	28.8	34.4
$\Delta E_{\mathrm{reorg}}$-(olefin)	−4.4	−12.5	−6.4	−5.1	−4.9	−6.4	−4.7	−3.4
$\Delta E_{\mathrm{reorg}}$-(MF)	−1.0	−1.5	−0.8	−0.6	−0.5	−0.7	−0.8	−1.0
D_{e}	24.7	26.1	22.1	22.0	19.5	22.7	23.3	30.0
				M = W				
$\Delta E_{\mathrm{Pauli}}$	−95.7	−125.2	−98.2	−87.5	−80.3	−95.0	−91.3	−104.8
$\Delta E_{\mathrm{elect}}$	72.3	90.9	75.8	69.7	64.2	75.8	73.0	83.8
ΔE_{oi}	59.4	85.2	59.9	53.6	49.8	57.9	56.1	64.7
ΔE_{int}	36.0	50.9	37.5	35.8	33.7	38.7	37.8	43.7
$\Delta E_{\mathrm{reorg}}$-(olefin)	−6.0	−15.4	−8.7	−7.0	−7.1	−8.5	−6.5	−4.2
$\Delta E_{\mathrm{reorg}}$-(MF)	−1.1	−1.5	−0.9	−0.7	−0.7	−0.9	−1.0	−1.1
D_{e}	28.9	34.0	27.9	28.1	25.9	29.3	30.3	38.4

bonding olefin of all and cyclohexene the worst. This molecular orbital analysis clearly shows that, just on the basis of the strength of the back-bonding interaction, cyclopropene should be the olefin with the largest metal−olefin bond energy. They also indicate that cyclobutene does not differ much from *trans*-cyclooctene. These stand-alone molecular orbital arguments *provide an answer to the second question posed above but are not sufficient to provide an answer to the first question.*

3.4. Bond Energy Decomposition Analysis of the Metal−Olefin Interaction. Table 1 summarizes the results of the BEDA according to the terms defined in eqs 2 and 3. The reorganizational energy ($\Delta E_{\mathrm{reorg}}$) has been further broken into two terms, one corresponding to the olefin, $\Delta E_{\mathrm{reorg}}$(olefin), and one to M(CO)$_5$, $\Delta E_{\mathrm{reorg}}$(MF).

The BEDA shows that there are certain differences when the interaction terms of an olefin with a given metal are compared. However, further analysis indicates that when such values are considered relative to each other, the three metal series are very similar. For example, if the magnitude of attractive interactions ($\Delta E_{\mathrm{elect}} + \Delta E_{\mathrm{oi}}$) between the metal and the olefin is compared to the magnitude of the Pauli repulsion energy ($\Delta E_{\mathrm{Pauli}}$), it is found that the attractive forces are ~8% larger than are the repulsive interactions. Another interesting aspect is that, for most complexes, covalent interactions (ΔE_{oi}) are responsible for about 44−46% of the attractive interaction. However, for the cyclopropene complex the covalent interaction contributes slightly more (48−50%). This clearly shows the effect of back-bonding on the interaction of this particular olefin with the metals, and it supports the results obtained above when the molecular orbitals were considered. The BEDA also shows that the magnitude of most of the energy terms follows a U-shaped trend similar to those found in the bond energies and strain energies (Figure 1).

The similarity between the trends in the BEDA terms and the strain energy seems to suggest that strain relief is the driving force of the metal−olefin interaction and that such force impinges its effect upon both repulsive and attractive interactions. However, close analysis shows that the overall bond strength (D_{e} or $\Delta H°$) is largely influenced by the extent of reorganization ($\Delta E_{\mathrm{reorg}}$) that the olefin undergoes as it is bonded to the M(CO)$_5$ fragment, as illustrated in Figure 3. In this graph the total height of the column corresponds to ΔE_{int} (see eq 3). It is evident that, if reorganization is not considered, cyclopropene would interact with M(CO)$_5$ more favorably than does any other olefin. However, the reorganizational energy (14−17 kcal/mol) in the cyclopropene complex is the highest. It reduces the interaction energy by about 33−35%. On the other hand, the *trans*-cyclooctene complex requires the least reorganization (4−5 kcal/mol), lowering the interaction energy by only 12−13%. Interestingly, cyclobutene is predicted to interact more weakly than *trans*-cyclooctene does, similar to the way cycloheptene and *cis*-cyclooctene and ethylene do.

As can be observed in Table 1, most of the reorganizational term (~80−90%) is due to reorganization of the olefin. In all cases reorganization of the M(CO)$_5$ fragment only takes about 1 kcal/mol. Thus, overall reorganizational effects could be attributed to the reorganization in the olefin as it bonds to the metal. It can then be stated that *reorganization of cyclopropene is mostly responsible for a metal−olefin bond energy that is predicted to be lower than that expected if the trend in strain energy were to be followed.*

3.5. Strength of the Interaction and Olefin Reorganization: A Molecular Paradox. So far the molecular orbital and BEDA analyses have reinforced the notion of the importance of strain relief and its influence in the metal−olefin bond strength and thermodynamic stability of metal−cycloolefin complexes. Strain relief is achieved by both elongation of the C=C bond and bending of the substituents in the olefin (pyramidalization). These are consequences of the sp^3-like rehybridization of the sp^2 olefinic carbons through their interaction with the metal. Chart 2 illustrates the geometrical changes each olefin undergoes upon bonding to M(CO)$_5$ (shown are results for W(CO)$_5$(olefin) complexes).

Figure 4 shows a correlation between the number of carbons in the olefin and the elongation of the C=C bond, as well as the change in the out-of-planarity angle (Ω). Notice that the trend is U-shaped and resembles that of the strain energy and metal−olefin bond strengths. Cyclopropene is the olefin that rehybridizes the most, as evidenced by the largest change in both the C=C bond length and out-of-planarity angle. In terms of C=C bond elongation, cyclobutene and *trans*-cyclooctene are next to cyclopropene. This is somewhat expected because, in terms of strain energy, they come next to cyclopropene. In terms of the change in the out-of-planarity angle (Ω), cyclobutene is next to cyclopropene, as expected, but *trans*-cyclooctene is the olefin with the smallest change in such angle. This is not

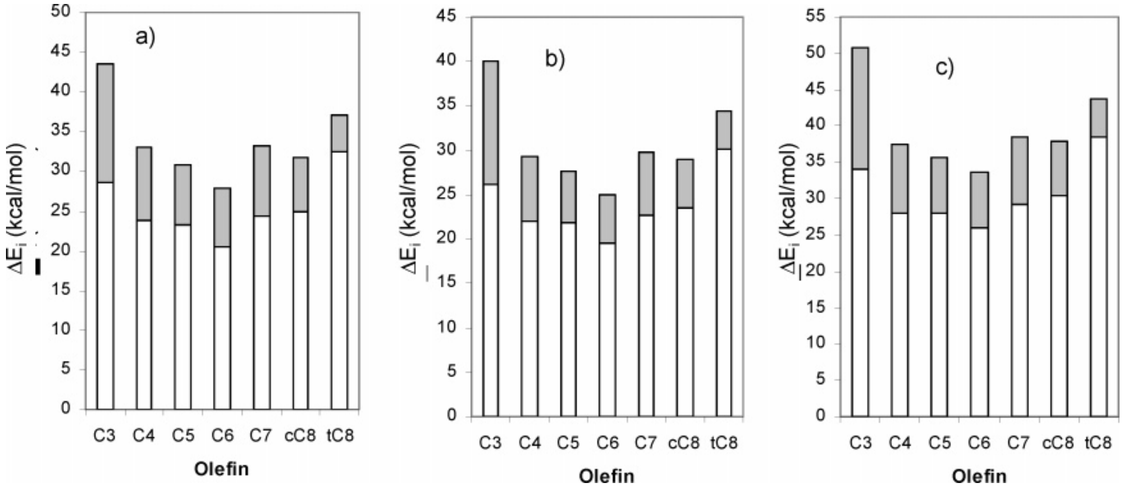
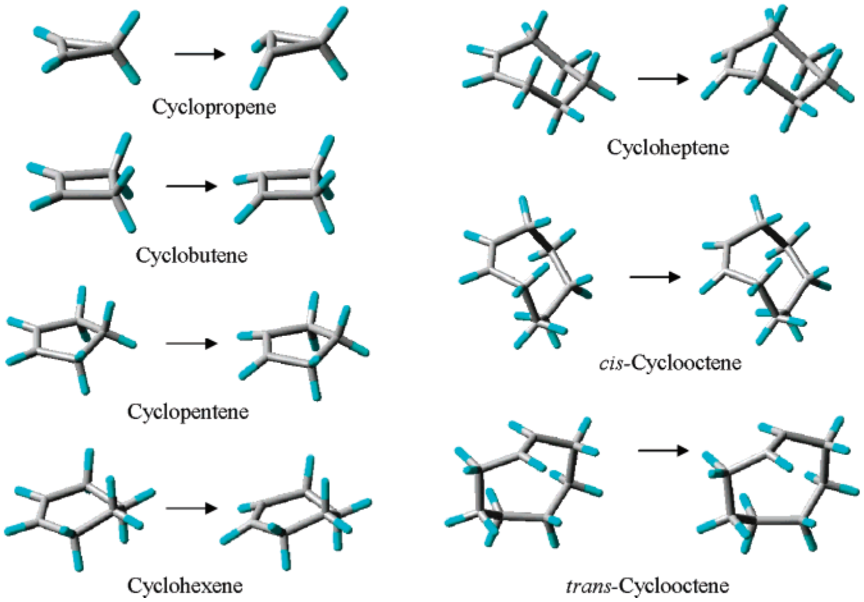


Figure 3. Bar graphs showing the trend in the "bond snap energy" (ΔE_{int}, total column height) and the magnitude of reorganizational energy ($\Delta E_{\mathrm{reorg}}$, shaded area) as a function of the olefin size. The white area of the bar corresponds to the bond dissociation energy (D_e). Labels on the horizontal axes denote each olefin by the number of carbons it contains (cC8 = *cis*-cyclooctene, tC8 = *trans*-cyclooctene).

Chart 2



surprising, since *trans*-cyclooctene is already nonplanar (i.e. deformed) before it even bonds to the metal. While all the other olefins are nearly flat (with out-of-plane angles between 0 and 1°) around the double bond, *trans*-cyclooctene is nonplanar with an out-of-plane angle of 21° as measured relative to the C−C=C−C plane.

As seen in Figure 4, the out-of-plane angle of planar olefins, especially cyclopropene, changes dramatically upon complexation to the metal, while this angle in *trans*-cyclooctene increases by a small amount (~5°). It is interesting to add that, in the case of *trans*-cyclooctene, the out-of-plane angle relative to the H−C=C−H plane is actually very close to 1° and changes to about 8° upon binding. This is very close to the out-of-plane angle change experienced by ethylene (~10°).

Thus, in *trans*-cyclooctene strain relief occurs mainly thru C=C bond elongation concomitant with small out-of-plane deformation. In contrast, cyclopropene relieves strain by undergoing both a large bond C=C elongation and bending of the substituents out of the C=C plane (pyramidalization). This is achieved by a strong π back-bonding interaction, which is facilitated by a favorable HOMO−LUMO energy gap and overlap. Cyclohexene is the least strained olefin and thus does not require strong interactions with the metal. Hence, its HOMO−LUMO energy gaps and overlaps are the least favorable. The problem with rehybridizations involving large changes in both C=C lengths and pyramidalization angles is that the accompanying conformational changes are energetically costly. The geometrical changes occurring upon rehybridization correlate well with the olefin reorganizational energy, $\Delta E_{\mathrm{reorg}}$, as shown in Figure 5. The energetic cost of reorganization is compensated by utilizing energy that results from the highly favorable net interaction energy (ΔE_{int}), mainly through attractive electrostatic and covalent interactions.

It is quite paradoxical that the factor that contributes to strain relief of a cyclic olefin upon binding is, at the

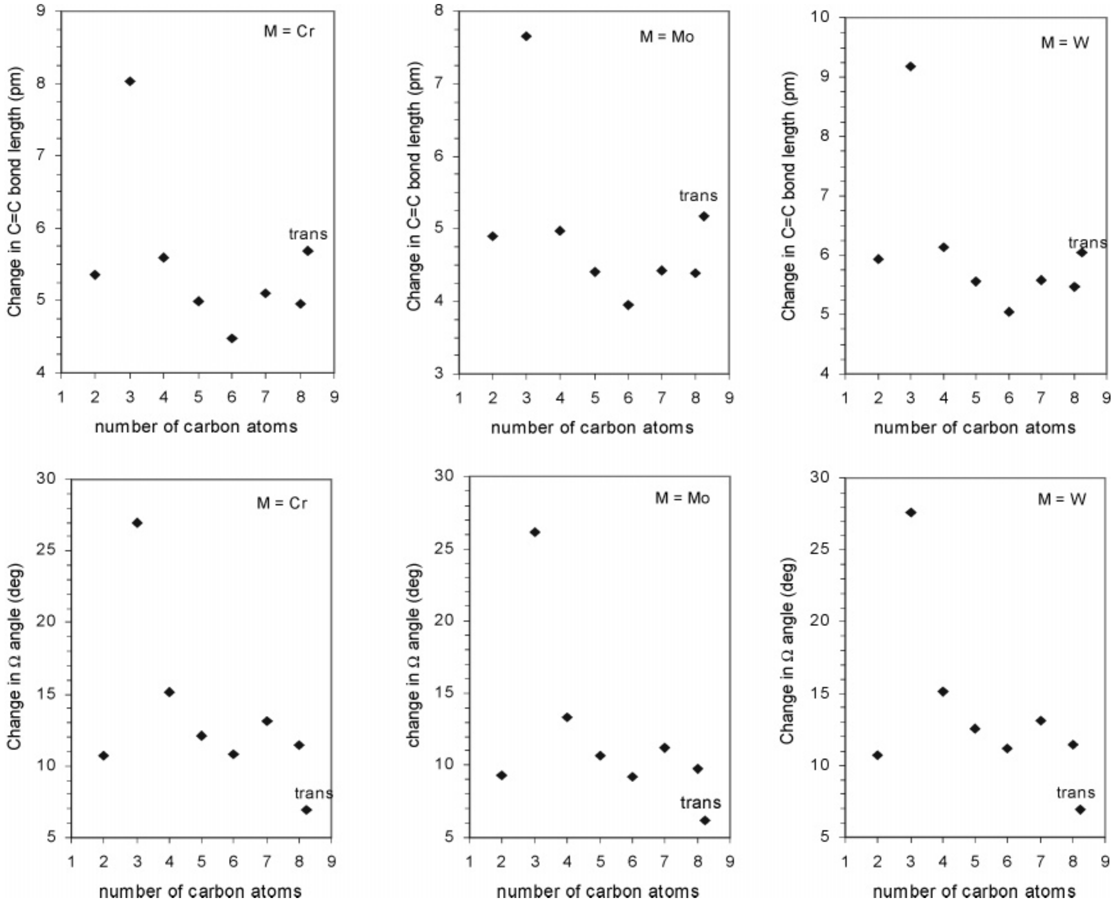


Figure 4. Plots showing the dependence of changes in geometrical parameters of the bonded olefin in M(CO)$_5$(cycloolefin) complexes relative to free olefin as a function of the number of carbons in the olefin: (top plots) C═C bond length; (bottom plots) out-of-plane angle (Ω).

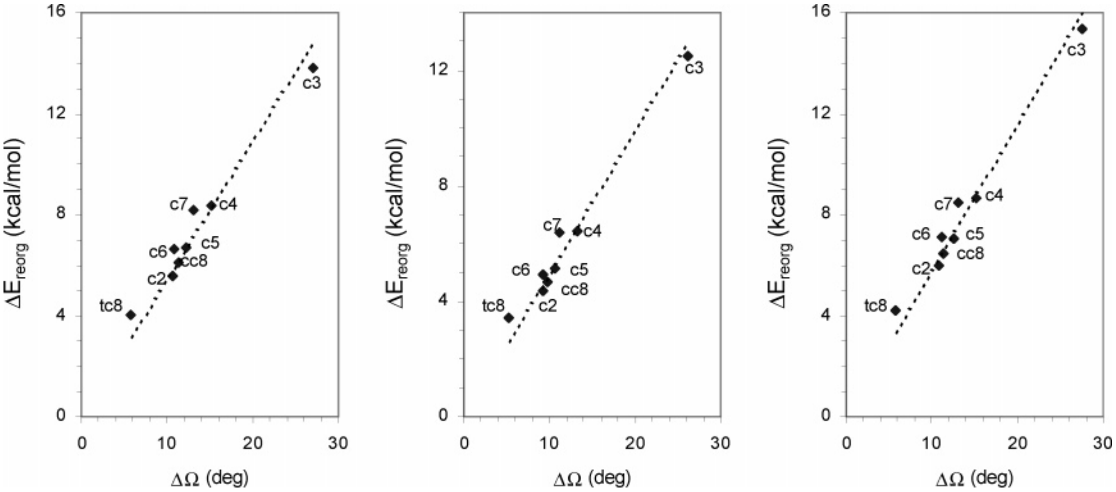


Figure 5. Plots showing the correlation between the change in the out-of-plane angle (Ω) and reorganizational energy for M(CO)$_5$(cycloolefin). From left to right, M = Cr, Mo, W. Each label represents a cycloolefin according to the number of carbons in it (tc8 = *trans*-cyclooctene, cc8 = *cis*-cyclooctene).

same time, a factor that contributes to a net decrease of the overall metal−olefin bond energy.

4. Conclusions

The trend in metal−olefin bond energies was found to correlate well with the trend in strain energies. However, if the relative amount of strain were taken as a parameter to predict relative metal−cycloolefin bond strengths, one would anticipate that M−cyclopropene and M−cyclobutene bond strengths would be significantly larger than the M−*trans*-cyclooctene bond strength. The calculated metal−olefin bond energies demonstrate that this is not the case, and, indeed, the *M−cyclopropene and M−cyclobutene bond energies are predicted to be smaller than the M−*trans*-cyclooctene bond energy*. From the point of view of molecular orbital interactions, the π back-bonding interaction is the electronic factor that makes certain cyclic olefins bind to metals differently. The trend in HOMO−LUMO energy gaps, overlaps, and electron populations for back-bonding resemble the trends in strain energy and metal−olefin bond energy.

Since cyclopropene is the olefin with the largest back-bonding interaction, and both cyclobutene and *trans*-cyclooctene behave quite similarly, single molecular orbital interpretations (such as those prescribed by the Dewar−Chatt−Duncanson model) are not enough to explain the predicted differences in metal−olefin bond strengths. However, such back-bonding is quite necessary to relieve the strain, because this is a result of the C═C bond elongation and pyramidalization ($sp^2 \rightarrow sp^3$ rehybridization). Thus, cyclopropene, which is the most strained olefin, undergoes the strongest metal−olefin interaction in order to relieve its strain. Paradoxically, the conformational changes resulting from rehybridization are energetically costly and occur at the expense of the interaction energy resulting from favorable electrostatic and covalent attractions. The *energetic cost of rehybridizing cyclopropene and cyclobutene is large enough to counteract their interaction energy to the extent that the overall bond energy is below that of strained deformed olefins*. For instance, *trans*-cyclooctene does not undergo considerable reorganization, since it is already deformed before it is bonded to the metal.

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Supporting Information Available: Tables giving benchmarking results and geometries. This material is available free of charge via the Internet at http://pubs.acs.org.

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