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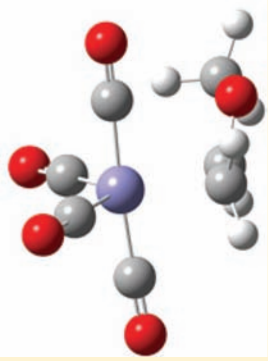
$Fe(CO)_4$ and Related Compounds as Isolobal Fragments

Lisa S. Cunden and R. G. Linck*

Department of Chemistry, Smith College, Northampton, Massachusetts 01063, United States

Supporting Information

ABSTRACT: The $M(CO)_4$ fragment can be assigned to be isolobal with both CH_3^+ and CH_2. In order to investigate this ambiguous isolobal assignment, we report calculations on compounds of the type $M(CO)_4L^n$, where M is Fe ($n = 0$), Mn ($n = -1$), and Co ($n = +1$) and L is an η^2 ligand with a π bond, generally an alkene. The L's are varied in electron-withdrawing ability, and patterns in computed structural parameters are investigated. We report that the equatorial OC−M−CO angle is sensitive to the electron-withdrawing ability of the alkene just as the isolobal prediction suggests. Other structural parameters that vary monotonically with electron-withdrawing ability of the alkene are the "bending back" of the alkene, the metal−ligand bond distances, and carbon−oxygen bond distances. Changing the metal from neutral Fe to a negatively charged Mn or positively charged Co has the result of increasing and decreasing, respectively, the OC−M−CO angle. Several compounds of $Ni(CO)_3L$ are also investigated as a further example of the ability of the isolobal concept to yield chemically useful information.



INTRODUCTION

In December of 1981, Roald Hoffmann gave his Nobel lecture on the relationships between the chemistry of metal complexes, predominately metal carbonyl and related derivatives, and organic molecules.[1] His main purpose was to focus attention on the similarity between metal-containing fragments and simple organic fragments. He proposed: "Two fragments are *isolobal* if the number, symmetry properties, approximate energy and shape of the frontier orbitals and the number of electrons in them are similar—not identical, but similar."[1] The basic relationship had been suggested previously,[2−5] but it was the early work of Hoffman and co-workers[6] that demonstrated how useful the concept could be as an organizing principle for large amounts of data. The basic idea is that removal of a hydrogen atom from CH_4 to give CH_3 (a seven-electron species) yields a substance whose half-filled orbital is similar in energy and symmetry to the orbital produced by removal of a CO from $Cr(CO)_6$ if we provide the $Cr(CO)_5$ fragment with another electron. Doing this in the manner that Hoffman labeled alchemy (we add a nuclear charge along with the electron), we produce $Mn(CO)_5$, a neutral 17-electron fragment. Hoffmann argued that there is an isolobal relationship between the seven-electron CH_3 and the 17-electron $Mn(CO)_5$, and as a result, the chemistry of the two fragments would be similar.

Interestingly, as pointed out by Albright et al.,[7] there is a fascinating ambiguity in this application of the isolobal concept. If the original 18-electron species is $Cr(CO)_6$, and we remove two carbon monoxide ligands and perform "alchemy" twice, then we have an isolobal relationship between the six-electron CH_2 and the 16-electron $Fe(CO)_4$. However, if we use the 18-electron $Fe(CO)_5$ as the starting material, a fragment with the same stoichiometry, $Fe(CO)_4$, is isolobal with CH_3^+. This situation immediately raises the question: Which is it? Viola or Cesario?[8−10] Consider $Fe(CO)_4(H_2CCH_2)$, an approximately trigonal bipyramidal molecule, which has the axis of the alkene in the equatorial plane of the trigonal bipyramidal iron complex. Because the 18-electron materials on which the "two" $Fe(CO)_4$ fragments are based differ, there is a structural feature in the compound, specifically the OC−Fe−CO angle in the equatorial plane, that reflects on the nature of $Fe(CO)_4$: an iron fragment isolobal with CH_2 should have an angle of 90°, whereas a fragment isolobal with the six-electron CH_3^+ should have a 120° angle. Albright et al.[7] noted that some early experimental work reviewed by Ittel and Ibers[11] found angles of about 110°, which indicates that the $Fe(CO)_4$ fragment is a "mixture" of the two isolobal entities, that the bonding pattern is intermediate between the single bond suggested by the isolobal relationship with CH_3^+ and the pair of bonds needed if we treat the $Fe(CO)_4$ fragment as isolobal with CH_2.

The dichotomy can be phrased less severely. The isolobal difference is found in the relative importance of donation from the filled π level of the alkene to the iron center versus back-donation from the d orbitals of the iron atom to the π^* level of the alkene in what is called the Dewar−Chatt−Duncanson model of the bonding of alkenes to transition metal compounds.[12,13] Studies to probe the relative importance of the two bonding modes in metal carbonyls are abundant.[14] Generally, these have focused on some method of dissecting the bonding patterns into σ and π components[14] or have been concerned with net bond energy.[15−17] We were intrigued by the possibility that the OC−Fe−CO angle in the equatorial plane might be used to determine the relative bonding interactions between the iron atom and an alkene ligand. To investigate this, we take advantage of the fact that the electron density of an alkene can be

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Table 1. Structural Parameters for $Fe(CO)_4$(Alkene)

compound	charge on Fe fragment	$OC_{eq}FeCO_{eq}$ angle	C=C bond length	$Fe-C_{alkene}$[a] bond length	$C-O_{eq}$[a] bond length
1	−0.21	111.8	1.4009	2.3083	1.1484
2	−0.20	115.7	1.3944	2.2880	1.1480
3	−0.11	114.9	1.3957	2.1968	1.1466
4	−0.08	110.7	1.4026	2.1704	1.1460
5	−0.07	113.3	1.3976	2.1610	1.1456
6	−0.07	112.9	1.3944	2.1528, 2.2226	1.1445, 1.1469
7	−0.03	114.6	1.3981	2.1583, 2.2086	1.1438, 1.1460
8	−0.05	115.3	1.3988	2.1889	1.1455
9	−0.02	113.5	1.3994	2.1456, 2.2180	1.1443, 1.1427
10	−0.03	114.0	1.3986	2.1483, 2.2394	1.1439, 1.1443
11	−0.06	114.0	1.3926	2.1545, 2.2008	1.1444, 1.1465
12	0.02	113.1	1.4034	2.1403, 2.1646	1.1428, 1.1440
13	0.10	112.7	1.4167	2.0868	1.1406
14	0.13	111.4	1.4134	2.0701	1.1398
15	0.00	113.0	1.4001	2.1514	1.1440
16	0.11	111.4	1.4101	2.1253, 2.1499	1.1420, 1.1415
17	0.14	111.4	1.4206	2.1068, 2.1287	1.1414, 1.1399
18	0.25	109.7	1.4407	2.0954	1.1377
19	0.25	110.4	1.4416	2.0716, 2,1301	1.1394, 1.1367
20	0.17	110.7	1.4195	2.1094	1.1400
21	0.34	108.8	1.4561	2.0710, 2.1081	1.1361, 1.1350
22	0.42	107.8	1.4824	2.0876	1.1337

[a] For asymmetric alkenes, the less substituted side is given first.

manipulated by changing the substituents, that it can be made electron-poor by the presence of withdrawing groups, such as cyano groups, or electron-rich by incorporation of an oxygen atom or nitrogen atom whose lone pairs are in conjugation with the double bond. For some alkenes, a rough measure of these changes in electron density is available in the ionization energies of the alkenes.[18]

The hypothesis is that electron-withdrawing substituents on the alkene will induce the $Fe(CO)_4$ fragment to release electrons to the alkene via back-bonding; this release of electrons by the $Fe(CO)_4$ fragment will cause it to resemble the isolobal CH_2— and form one ligand to metal bond and one metal to ligand bond—and thereby have a $OC_{eq}-Fe-CO_{eq}$ angle closer to 90°. Contrarily, if the alkene is electron-rich, the $Fe(CO)_4$ fragment will favor the isolobal CH_3^+, and the $OC_{eq}-Fe-CO_{eq}$ angle will be closer to 120°. In this paper, we present the results of our computations on a series of $Fe(CO)_4$(alkene) complexes, as well as some isoelectronic species, to test if the electronic properties of alkenes affect the $OC_{eq}-Fe-CO_{eq}$ angles as predicted.

CALCULATIONAL METHODS

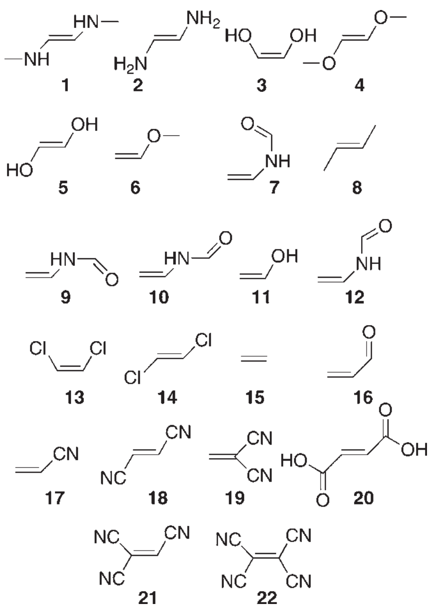
Calculations were performed using the Gaussian 09 package[19] as well as the ADF2009[20−22] program. In the former, the DFT functional B3LYP[23] was used with the VTZP basis set of Schaefer et al.[24,25] Although all the structural variables that we report are based on B3LYP/VTZP calculations, we obtained the same *relative* values using HF calculations with the 6-31+G* basis set. We also used Grimme's B97-D functional[26] to test the role, if any, of dispersive forces in our results. The geometry was optimized under the OPT=tight criterion, and the integration grid was ultrafine. Frequency calculations were used to verify that minima were obtained. Hirshfeld[27] charges were calculated and were used to describe charge flow. The basis set for the ADF calculations was the Slater type functions with triple-ζ, TZP. The local density part of the functional was that of Vosko, Wilk, and Nusair,[28] and the gradient approximation was that of Becke[29] and Perdew.[30]

RESULTS AND DISCUSSION

If we treat the alkene as a single ligand, the $Fe(CO)_4$(alkene) complexes are trigonal bipyramidal in shape with the alkene occupying one of the equatorial positions; the C=C axis of the alkene is in the trigonal plane. This arrangement has been found experimentally for ethylene[31] as well as several other alkenes.[32−35] Albright et al.[6d] have discussed the factors important in causing this orientation of the ethylene ligand. We verified that our basis set and functional gave answers consistent with the previous extended-Hückel calculations by doing several simple calculations with ethylene as the ligand. We twisted the axis of the carbon—carbon double bond of the alkene until it was perpendicular to the trigonal plane and left all other parameters fixed; the energy increased by about 30 kcal/mol, similar to the result found by Albright et al.[6d] When allowed to relax with the $C_{alkene}-C_{alkene}-Fe-C_{ax}$ dihedral angle frozen at 0°, we found the molecule underwent a pseudorotation of the carbon monoxide ligands such that those carbon monoxide ligands originally axial became equatorial. However, there is at least one report in the literature with the axis of the alkene partially rotated about the axis from the iron atom to the center of the carbon—carbon double bond;[34] we discuss this phenomenon below.

The calculations that we did on $Fe(CO)_4(H_2CCH_2)$, as those of others before us,[16,31,36−40] produced an $Fe-CO_{ax}$ distance that was longer than the $Fe-CO_{eq}$ one; this is in contrast to the early,[32] and oft-quoted, experimental data for $Fe(CO)_4(H_2CCH_2)$. However, a careful microwave study[31] has found values for these bond distances that agree with modern DFT

Scheme 1



calculations, with Fe$-$CO$_{ax}$ and Fe$-$CO$_{eq}$ equal to 1.815 Å and 1.806 Å, respectively. For those 10 compounds with a C_2 symmetry axis (and hence unique Fe$-$CO$_{ax}$ and Fe$-$CO$_{eq}$ distances), we have found the axial bond is consistently longer, on average by 0.011 ± 0.003 Å, independent of the other structural differences that we do find among the various Fe(CO)$_4$(alkene) compounds. It has been suggested for the osmium analogue,[31,41] and by implication here, that the back-bonding to the equatorial carbon monoxide ligands should be greater than that to the axial, leading to the shorter Fe$-$CO$_{eq}$ bond. If this is true, it should be reflected in the carbon atom$-$oxygen atom bond distances as well. We find for the 10 compounds with a C_2 axis that the ratio of the CO$_{eq}$/CO$_{ax}$ bond lengths is greater than one, averaging 1.004 ± 0.001. In contrast to these constant structural features, the absolute values of both the Fe$-$C distances and the C$-$O distances, as well as the OC$_{eq}-$Fe$-$CO$_{eq}$ angles are very sensitive to the nature of the alkene. We now turn to a discussion of these other parameters.

We give in Table 1 some of the calculated structural parameters for the Fe(CO)$_4$L complexes, where L is an alkene, that we have studied. The alkenes, which are defined in Scheme 1, have been arranged in order of the decreasing energy of the HOMO calculated at the HF/6-311+G(d) on compounds whose geometry was minimized at the B3LYP/6-311+G(d) level, following the procedure of Düfert and Werz.[42] For the compounds where there is available data, the energy of the HOMO and the ionization energy obtained by physical methods[17,42] are in reasonable agreement with each other. Because the presence of heteroatoms attached to the alkene delocalize the HOMO from the carbon$-$carbon double bond region, we desired another method of following the electron acceptor/donor properties of the alkenes. We decided to adopt the charge transfer from the alkene to the Fe(CO)$_4$ fragment, as measured by the total charge on the Fe(CO)$_4$ fragment, determined using Hirshfeld charges. In column two of Table 1, we list the charge on the Fe(CO)$_4$ fragments. These data with a few exceptions parallel the HOMO energy data. We use this second measure of electron flow in the analyses that follow.

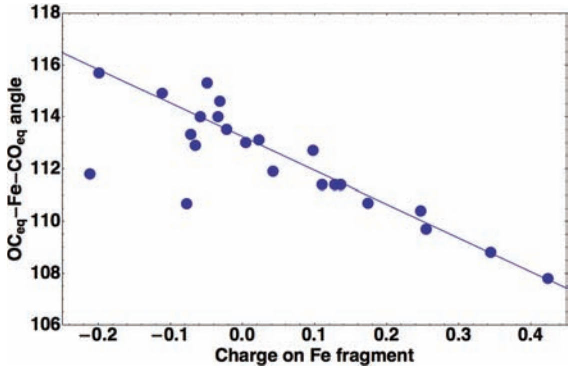


Figure 1. The correlation between the OC$_{eq}-$Fe$-$CO$_{eq}$ angle (in degrees) and the Hirshfeld charge on the Fe(CO)$_4$ fragment for various alkenes. The line is the least-squares fit to the data minus the points for *trans*-1,2-dimethoxyethene, L = **1**, and *trans*-1,2-di-N-methylaminoethene, L = **4**, which are the two points well below the line. See the text for a justification of the rejection of these points from the fit. The equation for the line is angle = 113.2$-$12.9Z_{Fe}, where Z_{Fe} is the charge on the Fe(CO)$_4$ fragment; the correlation coefficient is $-$0.96.

Several features are immediately apparent from our data. There is a significant change in the OC$_{eq}-$Fe$-$CO$_{eq}$ angle, ranging from 115.7° for **2**, a strongly electron-donating alkene, to 107.8° for tetracyanoethene, an electron-withdrawing alkene. In Figure 1, we give a plot of the angle versus the charge on the Fe(CO)$_4$ fragment. The trend in this figure is obvious, and with some scattered points removed, it approaches a straight line relationship. Does some special effect cause the scatter? The points most deviant give us a clue to the origin. These points are found for the compounds of alkenes **1** and **4**. In these cases, there are methyl groups on the substituents of the alkene, one hydrogen atom of which is pointed at an equatorial carbon monoxide, only 2.86 and 2.84 Å away, respectively. (If the OC$_{eq}-$Fe$-$CO$_{eq}$ angle for L = **1** was the same value as that found for L = **2**, an alkene with similar electronic properties, the distance between the methyl hydrogen atom and the carbon of the equatorial CO would be 2.80 Å.) Given that the OC$_{eq}-$Fe$-$CO$_{eq}$ bending motion is on a flat potential energy surface—it occurs at approximately 60 cm^{-1} in the calculated vibrational spectra—a compression of the OC$_{eq}-$Fe$-$CO$_{eq}$ bond angle by steric interactions seems very reasonable. The two compounds with L = **1** and L= **4** can be compared with the compounds with L = **2** and L = **5**, respectively, which have similar energies for their HOMOs and similar charge transfers to the Fe(CO)$_4$ fragment but lack the steric interaction of a methyl group: the compounds with L = **2** and L = **5** fall in the region of the general line in Figure 1. At a reviewer's request, we repeated these calculations on compounds with L = **1**, **2**, **4**, **5**, **14**, **17**, and **22** using the B97-D functional of Grimme.[26] A plot very similar to that shown in Figure 1 results, with the points for the compounds with L = **1** and **4** displaced from the line to smaller angles. Thus, the inclusion of dispersive forces does not change our observations.

Further evidence of the steric interaction can be found by examining the details of the structure of the complex with alkene **6**. This asymmetric compound has an OC$_{eq}-$Fe$-$CO$_{eq}$ angle about where we expect it on the basis of the energy of the HOMO or the charge flow; it escapes the steric interaction found in the compound of alkene **4** even though the compound with L = **6** also has a methyl group. The iron complex of **6** achieves its

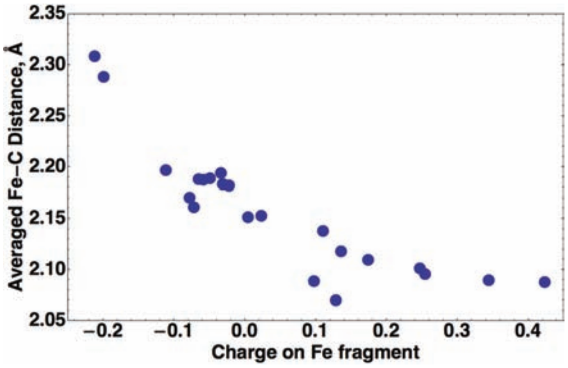


Figure 2. The dependence of the iron–alkene carbon bond distance (averaged in the asymmetrical cases) upon the charge on the Fe(CO)$_4$ fragment. The two points near a charge of 0.1 that deviate on the low side of the trend are for the two isomers of 1,2-dichloroethene. If this deviation is meaningful, it is for reasons not apparent to us.

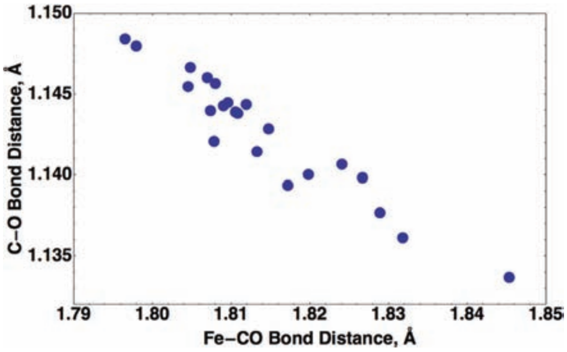


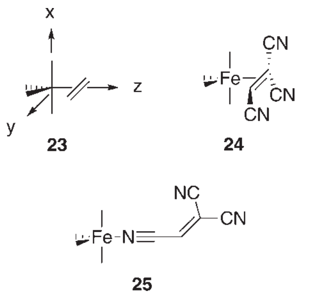
Figure 3. A plot illustrating typical correlation behavior between various distances and angles in the Fe(CO)$_4$L, L an alkene: Dependence of the carbon–oxygen bond distance for an equatorial carbon monoxide versus the corresponding iron–carbon distance for that same carbon monoxide. In the case of asymmetric molecules, the relevant carbon monoxide is on the same side of the molecule as the least substituted side of the alkene, i.e., *cis* to the least substituted side of the alkene.

normal angle by two small distortions that yield rich results. First, the alkene double bond is not perpendicular to the iron atom but rather is tilted at an angle of about 93°,[44] such that the substituted side of the alkene moves away from the Fe(CO)$_4$ fragment. Second, the center of the alkene bond slides along the perpendicular to the iron atom by a small amount. Both of these small adjustments to the geometry of the bonding are leveraged by the distance between the double bond and the methyl group to move the methyl group significantly away from an equatorial carbon monoxide ligand, increasing the distance between the carbon atom of the equatorial CO ligand and the methyl hydrogen atom to 2.95 Å. A second kind of twisting of the alkene to avoid steric hindrance is seen most strikingly in the iron complex of fumaric acid, L = **20**. In the X-ray determination of this structure, there are three different environments for the fumaric acid.[34] In two of these, the alkene has rotated about the vector from the iron atom to the center of the alkene double bond by about 17°. Because the compounds in this crystal are hydrogen-bonded to each other, it is not clear whether the origin of this twist involves these hydrogen bonds or some steric issue. In our calculation, the hydrogen-bonding issue is eliminated, yet we find a rotation of the alkene about the iron–alkene bond center, a rotation of about 10°. This rotation increases the distance between the carbonyl oxygen atom of the acid and the axial carbon monoxide ligand. One further example of the strong role that steric interactions play in the details of the structure is to be found in the N-vinylformamide compounds, **7**, **9**, **10**, and **12**. These four compounds are conformers of each other and have relative energies of 2.2, 0.0, 0.2, and 2.8 kcal/mol, respectively. Rotations about the amide bond go over transition states on the order of 20 kcal/mol; those around the nitrogen–alkene carbon bond are lower, about 6 kcal/mol. The last three are all planar as free alkenes. Compound **7** has a $C-C_{alkene}-N-C_{amide}$ dihedral angle in the free alkene of about 24°. All of the compounds distort slightly upon coordination, but the modification in **7** is extensive: the $C-C_{alkene}-N-C_{amide}$ dihedral angle expands to more than 42° in the coordinated alkene in order to keep the –CHO group from being too close to one of the axial carbon monoxide ligands of the iron atom.

There are numerous other parameters that also depend, not unexpectedly, on how tightly the alkene holds on to electrons. For instance, the length of the bond between the iron atom and the carbon atoms of the alkene, averaged between the two different lengths for molecules lacking a symmetry element, show a systematic trend with the charge on the Fe(CO)$_4$ fragment, as shown in Figure 2. The argument for this correlation is that electron-withdrawing alkenes have more back-bonding, which is the dominant bonding interaction in such compounds,[14,31,41] and hence shorter bonds between the iron atom and the alkene. This donation of charge to the electron-withdrawing alkenes also affects the bond lengths of the C–O bonds, both axial and equatorial, as well as the Fe–CO bond lengths. Greater positive charge, lower electron density, on the metal center leads to lower back-donation to the carbon monoxide ligands, and hence shorter C–O bonds and longer Fe–CO bonds with electron-withdrawing ligands—see Table 1. A large number of correlations exist between the various structural parameters. We illustrate in Figure 3 one of these, the inverse relationship between the equatorial C–O bond length and the corresponding Fe–C bond length. (Note that these data are, for compounds that do not have a plane of symmetry, from the side of the molecule in which the alkene is least substituted.)

Finally, a compelling case has been made that the "bending back" of the alkenes should increase; the more the back-bonding, the more the Fe(CO)$_4$ fragment appears isolobal with CH_2. We tried several methods of quantitatively measuring the degree of "bending back". It is only with *trans*-disubstituted or tetrasubstituted alkenes that these methods work, as only in these compounds does the alkene remain symmetrical. First, we examined the dihedral angle suggested by Cedeno et al.[15] We define Θ_{XX} as the angle (180°–XCCX dihedral), where the X groups are trans to each other in the alkene; for a planar alkene, Θ_{XX} is zero, so the larger the value of Θ_{XX}, the greater the distortion. The value of Θ_{HH} showed a rough correlation with charge transfer to the iron. We also attempted to use the pyramidalization angle of Hrovat and Borden[45] as well as measure the distance between the plane defined by the vector between the two hydrogen atoms and the normal to the iron–alkene vector, and the corresponding plane defined by the carbon atoms of the alkene. All of these measures give some agreement with the charge transferred, but none is as impressive as that given by the $OC_{eq}-Fe-CO_{eq}$ angles.

Scheme 2



In order to verify that the important factor in the variation in the $OC_{eq}-Fe-CO_{eq}$ angle is the conversion from dominant σ interaction (isolobal with CH_3^+) to both σ and π interaction through back-bonding (isolobal with CH_2), we have performed a Morokuma/Zeigler[46−49] analysis of the bonding between the $Fe(CO)_4$ fragment and some of the alkenes using the ADF calculational package.[22] For the purposes of these calculations, we define the axes as shown in **23** (Scheme 2). For tetracyanoethene, with C_{2v} symmetry, the empty $19a_1$ orbital (LUMO) is a mixture of d_{z^2}, $d_{x^2-y^2}$, and $4p_z$. This orbital can interact with the π bonding orbital of the alkene. The other important orbital on the metal fragment is the HOMO, $10b_2$, a mixture of d_{yz} and $4p_y$; this orbital is of the correct symmetry to interact with the empty π^* orbital of the alkene. These orbitals are substantially the same as those found by Albright et al.[6d] in their extended Hückel treatment of $Fe(CO)_4(C_2H_4)$. For tetracyanoethene, the bonding interaction between the $Fe(CO)_4$ fragment and the alkene in a_1 symmetry is 24 kcal/mol, whereas the b_2 contribution is 83 kcal/mol. The dominant contribution of these two interactions are what the Dewar−Chatt−Duncanson model predicts: donation of the π orbital of the alkene into the metal-based a_1 and back-donation from the metal-based b_2 into the π^* of the alkene. There are small contributions from a_2 orbitals (about 2 kcal) and b_1 orbitals (6 kcal/mol). If the alkene is changed from the electron-withdrawing tetracyanoethene to ethene itself, the magnitudes of the a_1 and b_2 interactions change. For ethene, we obtain a_1, 34 kcal/mol, and b_2, 41 kcal/mol (and 1 and 3 kcal/mol for a_2 and b_1, respectively), whereas Nechaev et al.[39] report 35 and 41 kcal/mol, respectively. This change is exactly what we would anticipate: better donation from the π bond of the ethene and poorer acceptance of electron density into the π^*.

To examine this further in the set of compounds we have studied, we need to consider compounds of lower symmetry. Those with any symmetry operation at all have C_2 symmetry. In these compounds, the a_2 and b_1 interactions mix into the a_1 and b_2, respectively. Since the former interactions are small, and we are looking for general trends, we will assume that the a and b interactions in compounds of C_2 symmetry are the proper comparisons. Given this premise, consistency demands we also lump the a_2 interaction of tetracyanoethene and ethene into the a_1 interaction, and similarly with the b_1 and b_2. Given this approximation, we show in Figure 4 plots of the magnitude of the interactions versus the charge on the iron center. As the electron-withdrawing ability of the alkene increases, the bonding interaction between the π orbital of the alkene and the iron center decreases. In contrast, the interaction of the filled b_2 orbital on the iron center with the π^* of the alkene increases. The sensitivity to the electron-withdrawing ability of the alkene of the b/π^* interaction is about 5 times that of the a/π interaction.

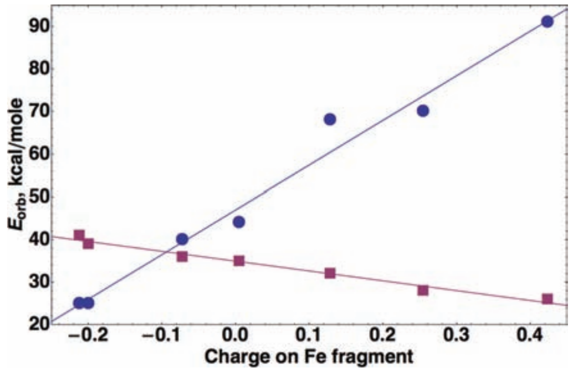


Figure 4. The a (sum of a_1 and a_2 for systems of C_{2v} symmetry) orbital interaction energies (squares) and the b (sum of b_1 and b_2 for C_{2v} symmetry) orbital interaction energies (circles) as a function of the charge on the $Fe(CO)_4$ fragment from Morokuma/Zeigler analysis of the bonding in $Fe(CO)_4L$ compounds. The equation for the least-squares fit to the a symmetry interaction is $E_a = 34.9 - 23.1Z_{Fe}$ with a correlation coefficient of −0.99, and that for the b symmetry interaction is $E_b = 46.9 + 104.9Z_{Fe}$ with a correlation coefficient of 0.99.

Isostructural Analogues to $Fe(CO)_4$. We have also examined two systems that are isostructural and isoelectronic with the $Fe(CO)_4$ fragment to verify the arguments presented. The $Mn(CO)_4^-$ fragment can also be isolobal with both CH_3^+ and CH_2; we would expect, on the basis of the charge, that the resemblance should be closer to CH_2. Hence the $OC_{eq}-Mn-CO_{eq}$ angle should be closer to 90°. The data in Table 2 show that this expectation is met. The $OC_{eq}-Mn-CO_{eq}$ angle varies from 102.4° with L = **22** to only about 111° for L = **2**; both values are smaller than in the corresponding iron compounds, as expected. We also note that the alkene carbon−carbon bonds are longer, consistent with moving the isolobal behavior toward that of CH_2 with concomitant formation of the isolobal equivalent of cyclopropane.

Compounds formed from the $Co(CO)_4^+$ fragment and alkenes should also be isolobal with both CH_3^+ and CH_2; in this case, the positive charge should nudge the isolobal character toward that of CH_3^+. Thus the $OC_{eq}-Co-CO_{eq}$ angle should be larger than that found for the corresponding iron carbonyl compounds. Our data, in Table 3, clearly support the contention. All of the angles found were between 117° and 120°, the latter the ideal angle for isolobal association with the methyl cation. Several peculiar features of the data for the $Co(CO)_4^+$ fragment are worth noting. First, for L = **6**, the angle is quite large, even though the charge on the cobalt fragment is not extensively negative. This is because the alkene is shifted as described above for the iron carbonyl analogue. In the case of this cobalt fragment, the angle of the tilt of the alkene double bond with respect to the perpendicular of the axis from the cobalt atom to the double bond is 14°, and the shift of the center of the double bond along this perpendicular is nearly 0.06 Å. This is clearly seen in the disparate bond distances from the Co to the two alkene carbon atoms. In the limit of this argument, the alkene is bonded to the cobalt atom through the unsubstituted carbon of the alkene, so the ligand is becoming η^1 instead of η^2, which removes the back-bonding characteristics. The molecule is approaching a five coordinate metal complex; the compound is essentially like $Co(CO)_4NH_3^+$. This result reminds us of the Eisenstein and Hoffmann analysis of the inducement of nucleophilic reactivity of an alkene by slippage of the alkene along the perpendicular to the

Table 2. Structural Parameters for $Mn(CO)_4(alkene)^-$

compound	charge on Mn fragment	$OC_{eq}MnCO_{eq}$ angle	C=C bond length	$Mn-C_{alkene}$[a] bond length	$C-O_{eq}$[a] bond length
2	−0.87	110.7	1.4100	2.2004	1.1666
5	−0.76	108.9	1.4138	2.1332	1.1645
6	−0.76	107.9	1.4175	2.1534, 2.1514	1.1636, 1.1661
15	−0.77	108.2	1.4220	2.1625	1.1649
17	−0.58	106.3	1.4486	2.1121, 2.1493	1.1610, 1.1588
18	−0.43	104.6	1.4696	2.1155	1.1557
21	−0.31	103.4	1.4915	2.0898, 2.1457	1.1535, 1.1519
22	−0.21	102.4	1.5119	2.1237	1.1500

[a] For asymmetric alkenes, the less substituted side is given first.

Table 3. Structural Parameters for $Co(CO)_4(alkene)^+$

compound	charge on Co fragment	$OC_{eq}CoCO_{eq}$ angle	C=C bond length	$Co-C_{alkene}$ bond length[a]	$C-O_{eq}$ bond length[a]
2	0.39	118.1	1.4053	2.5072	1.1316
5	0.59	117.1	1.3871	2.2959	1.1291
6	0.59	119.1	1.3850	2.2084, 2.5502	1.1283, 1.1309
15	0.75	117.3	1.3780	2.2127	1.1252
17	0.81	117.8	1.3868	2.1969, 2.2284	1.1245, 1.1227
18	0.86	117.6	1.3987	2.2084	1.1240

[a] For asymmetric alkenes, the less substituted side is given first.

metal double bond vector.[50] Second, we were unable to locate a minimum on the potential energy surface for η^2 bonding of the alkene to the cobalt atom for L = **21** or L = **22**. The potential energy surface seems to favor a square planar, 16-electron, $Co(CO)_4^+$ species and a loosely associated, undistorted, alkene. We did find a minimum in energy for L = **21** that involved bonding of the alkene through the nitrogen atom of one of the cyano groups. To understand this result, we built similar compounds for the $Fe(CO)_4$ fragment. The electronic energy difference (η^2 alkene, **24**, minus η^1 nitrile, **25**) was 0.9 kcal/mol: there is relatively little energy difference between the two forms in the $Fe(CO)_4L$ case for L = **21**. When we change to $Co(CO)_4^+$, the electron-withdrawing alkene, positively polarized at the alkene carbons atoms, and the positively charged cobalt center are repulsive. This would account for our failure to find an η^2 alkene minimum for these highly electron-withdrawing alkenes.

The bending back of the alkenes, as measured by the angle Θ_{HH}, discussed above, provides another way of viewing the difference in the isolobal behavior of the charged complexes. Back-bonding in the complexes isolobal with CH_2 should cause an increase in Θ_{HH}; therefore we anticipate that the value of Θ_{HH} will be larger for complexes with the $Mn(CO)_4^-$ fragment than for those with the $Co(CO)_4^+$ fragment. We find Θ_{HH} for the complexes with ethene as the alkene have values of 32°, 27°, and 20° for the Mn, Fe, and Co compounds, respectively; for L = **5**, the values are 36°, 29°, and 22°, and for L = **18** they are 34°, 31°, and 22°, respectively, for the three metals. These data establish that the "bending-back" angle of the alkene, at least when compared to compounds with similar steric interactions, as well as the $OC_{eq}-M-CO_{eq}$ angle, follow the patterns expected from the isolobal model. We conclude from our study of these charged tetracarbonyl metal fragments that we can control the bonding characteristics from approximately isolobal with the methyl cation to approximately isolobal with CH_2 by changing the alkene as well as the charge on the metal atom. A similar model for the role of charge has been suggested often before. The following are two examples: a study of $M(CO)_6^n$, where n runs from −2 to +3,[51] and a study of MCO and MCO^+ complexes, in which Nakashima and co-workers[52] postulated that both σ donation and π back-bonding are important in the neutral molecules, whereas in the positively charged species, σ donation dominates.

Non-Alkene Compounds of $Fe(CO)_4$. During the course of this work, we also investigated several nonalkene double bonded species. Our results are complementary to those of Chen et al.,[10] who looked at some of the same compounds bonded (mostly) in an η^1 fashion. Our aim was to examine how these compounds with π bonds of various sorts affect the $OC_{eq}-Fe-CO_{eq}$ angle. We anticipated the behavior of these compounds would be considerably less regular than that of the alkenes because the nature of the double bond between the two atoms varies significantly, as does the oxidizing ability of the ligand. The compounds that we investigated vary from relatively minor perturbations of an alkene—for instance, to an imine—to compounds which we would expect to deviate strongly from the alkene model, singlet oxygen bonded η^2 to the iron center. Needless to say, we were pleasantly surprised when the isolobal model accounted for the data in a very satisfactory manner. The data we obtained are given in Table 4, and a plot of the $OC_{eq}-Fe-CO_{eq}$ bond angle versus the charge on the $Fe(CO)_4$ fragment is given in Figure 5. Over almost the full range of possible angles (102−120°), the $OC_{eq}-Fe-CO_{eq}$ angle is easily estimated by reference to the charge on the $Fe(CO)_4$ fragment. The complex with O_2 should be thought of as an organometallic analogue of a dioxirane. A significant amount of charge flows from the iron fragment to the oxygen atoms, and the O−O bond length is 1.403 Å. At the other extreme, the η^2 complex with dinitrogen has a N−N bond length of 1.115 Å, which is nearly the

Table 4. Structural Parameters for $Fe(CO)_4(L)$ Compounds

compound	charge on Fe fragment	$OC_{eq}FeCO_{eq}$ angle	X=Y bond length	Fe–X bond length[a]	CO_{eq} bond length[a]
formaldehyde	0.16	110.2	1.2880	2.1146, 2.0236	1.1432, 1.1394
imine of formaldehyde	0.04	111.9	1.3385	2.1558, 2.1027	1.1440, 1.1422
dinitrogen	−0.03	119.7	1.1146	2.2800	1.1443
cis-diimide	0.12	109.7	1.3334	2.0690	1.1412
trans-diimide	0.09	109.5	1.3291	2.0800	1.1400
dioxygen	0.42	102.1	1.4032	1.9200	1.1300

[a] For asymmetric compounds, the less substituted side is given first.

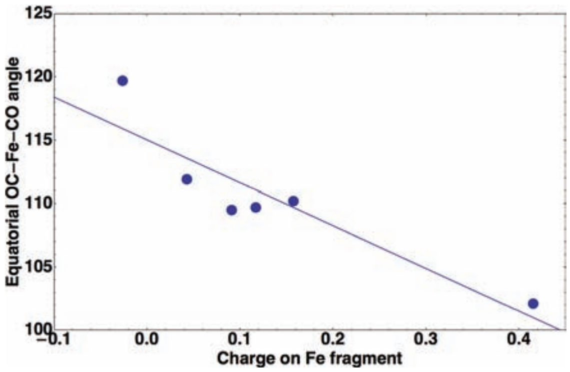


Figure 5. The OC_{eq}–Fe–CO_{eq} angle for $Fe(CO)_4L$, where L are compounds with double bonds which are attached to the iron atom in an η^2 fashion, versus the charge on the $Fe(CO)_4$ fragment. The line is to draw attention to the trend rather than to imply a linear relationship. The point most scattered from the line (120° angle) is for N_2.

same length as that found in the η^1 compounds investigated by Chen et al.[10]

Does the Model Work with $Ni(CO)_3$? Although the $Fe(CO)_4L$ compounds are useful for this study of dual isolobal relationships, there are other possibilities. Compounds of the stoichiometry $Ni(CO)_3L$ are one such case. The $Ni(CO)_3$ fragment, "derived" from $Ni(CO)_4$ by removal of a CO, is a 16-electron system that could (with proper orbital shape and energy) be isolobal with the methyl cation and should have tetrahedral bond angles. The same fragment obtained from $Fe(CO)_5$ by removal of two carbon monoxide ligands followed by the addition of two nuclei and two electrons is also a 16-electron fragment, but now isolobal with CH_2; the bond angles in this material are mixed, two at 90° and one at 120°. The change in angle between the two extremes in the case of the $Ni(CO)_3$ fragment is much less obvious than it is in the $Fe(CO)_4$ fragment, but we thought it would be amusing to determine if the model we have presented above is valid for the $Ni(CO)_3$ fragment. If the model is valid, the electron-withdrawing alkenes should have smaller angles than the electron-donating ones.

The structures of the $Ni(CO)_3L$, where L is an alkene, have a roughly trigonal pyramidal nickel-tricarbonyl fragment attached to the alkene along the pseudo-3-fold axis of the $Ni(CO)_3$ fragment, an axis that we define as the z axis. Looking down this z axis, the carbon–carbon double bond of the alkene appears approximately perpendicular (the angles vary from 77° to 85°—see below) to one of the Ni–CO directions. We define the direction of that Ni–C bond as x and the direction perpendicular to it (roughly the direction of the carbon–carbon double bond under normal conditions) as y. For L = ethene, we had difficulty obtaining an optimized minimum in energy. We obtained a satisfactory optimization (at tight convergence) at two geometries (with energies differing by about 0.001 kcal/mol) in which $C-C_{alkene}-Ni-C$ dihedral angles differed by over 7°. Indeed, for L = **5**, we found that with a basis set without polarization functions, TZV, that the axis of the double bond was rotated nearly 90° so that is was along the x axis; adding the polarization function caused the double bond to rotate back to the y axis. These results are completely consistent with a frequency analysis on the $Ni(CO)_3L$ compounds: The lowest energy vibrational motion in the $Ni(CO)_3L$ is a twisting motion around the z axis that ranges between 8 and 21 cm^{-1} in energy.[53] Although we have not investigated the energy barrier for rotation in detail, it is clear from an analysis of the steps taken during a geometry convergence run that it is small.

Calculations using ADF indicate that the HOMO of the $Ni(CO)_3$ fragment is an a'' orbital which is a mixture of d_{yz} and d_{xy} with some $4p_y$ mixed in. This a'' orbital is capable of interacting with the π^* orbital of the double bond. The energy of this orbital is −6.04 eV compared to −5.4 eV for the HOMO in the $Fe(CO)_4$ fragment. The LUMO in the nickel compound is an a' orbital, composed mostly of the metal $4p_z$ orbital, that is of the correct symmetry and spatial location to accept electrons from the π bond of the alkene. The energy of this orbital is −3.75 eV compared to −4.73 in the corresponding Fe fragment. Because of the inverse energy difference term in a perturbation approach, we anticipate that the energy of the interaction in the $Ni(CO)_3L$ compounds should be less than that in the $Fe(CO)_4L$ compounds. For the ethene compound, the ADF analysis of net bonding energy (including Pauli, electrostatic, and orbital interactions[49]) gives a value of −46.7 kcal/mol for $Fe(CO)_4(H_2CCH_2)$ and a value of only −25.9 kcal/mol for $Ni(CO)_3(H_2CCH_2)$.

There are several difficulties in analyzing the $Ni(CO)_3L$ data: (1) Instead of one angle to measure, we have three. (2) Because of the low symmetry, there is reason to suspect that those angles will all differ. And, (3) the total change between the two limits of the angle is small. To avoid the first two of these difficulties, our strategy is simply to look at the sum of the three OC–Ni–CO angles. We anticipate in an ideal world that these would vary from 300° to about 330°, with the largest angles being those with electron-donating alkenes. We have examined seven compounds. We present the results in Table 5 and show a plot of the sum of the three angles versus the charge on the $Ni(CO)_3$ fragment in Figure 6. Surprisingly, the latter plot shows a strong correlation between the charge and the sum of the three C–Ni–C angles, an almost perfectly linear relationship. This remarkable correlation may be purely coincidental, but we point out that the structure of the nickel compounds should obviate steric interactions that are to be found in the $M(CO)_4L$ compounds.

Table 5. Structural Parameters for the $Ni(CO)_3L$ Complexes

alkene	charge on Ni fragment	twist angle	C−Ni−C angles	Ni−C bond length	Ni−CO bond length
1	−0.19	85.2	114.4, 109.8, 107.3	2.3927, 2.4076	1.8221, 1.8136, 1.8194
5	−0.13	84.8	112.7, 112.0, 110.2	2.3173, 2.3288	1.8374, 1.8158, 1.8181
6	−0.13	80.4	112.8, 111.4, 110.5	2.4205, 2.2569	1.8365, 1.8135, 1.8209
15	−0.07	82.0	110.8, 111.0, 109.7	2.2318, 2.2318	1.8468, 1.8206, 1.8206
17	0.04	77.4	108.8, 110.9, 107.9	2.1885, 2.1689	1.8686, 1.8308, 1.8311
18	0.14	86.8	108.8, 107.9, 105.7	2.1319, 2.1361	1.8990, 1.8367, 1.8451
21	0.23	84.3	109.4, 105.5, 104.6	2.0899, 2.1231	1.9269, 1.8451, 1.8549

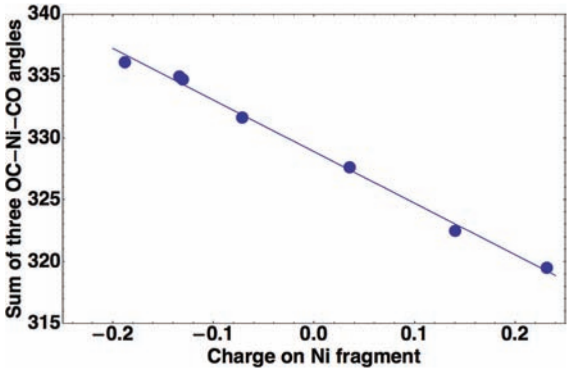


Figure 6. Dependence of the sum of the three OC−Ni−CO angles on the charge found on the $Ni(CO)_3$ fragment for various alkenes. The individual points can be assigned from the data in Table 5. The straight line function that fits the data is given by the expression $329 - 41.7Z_{Ni}$, where Z_{Ni} is the charge on the nickel fragment with a correlation coefficient of 0.997.

CONCLUSIONS

This study establishes that there is an isolobal relationship between the $Fe(CO)_4$ fragment and *both* CH_2 and CH_3^+. Which one depends upon the bonding characteristics of the alkene—electron-donating or -withdrawing. The $Fe(CO)_4$ fragment behaves more like CH_2 in the latter case and more like the methyl cation in the former. We have established that the $OC_{eq}-Fe-CO_{eq}$ angle is a reasonable structural indicator of the nature of the isolobal relationship. We find it impressive that this correlation between the $OC_{eq}-Fe-CO_{eq}$ angle and the nature of the alkene holds at all. The potential energy surface of the CO bending motions in these molecules is so flat that it is striking that any trend remains after consideration of all the small energy perturbations that could change the angle. For instance, the flatness of the bending surface implies that any steric energy interactions should easily be able to cause a shift in the angle. We have pointed out above how this does occur in several of the $M(CO)_4L$ compounds that we studied. Nevertheless, with the removal of compounds with obvious steric interactions, there is a clear trend in the $OC_{eq}-Fe-CO_{eq}$ angle with the electronic properties of the alkene, and if we use the charge flow as a measure of the electron attracting ability of the ligand, for other η^2 compounds, such as formaldehyde, dioxygen, diimide, as well. The beauty of Hoffmann's isolobal argument is that it seems to not only give a rough correlation between properties of main group and transition metals but is also able to predict some of the finer structural relationships in these molecules.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Tables of atomic coordinates and the energies of all compounds studied in this paper are available. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: rlinck@smith.edu.

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