Molecular Mechanics Model of Ligand Effects. 7. Binding of η^2 Ligands to $Cr(CO)_5$ and CpRh(CO): E_R Values for Olefins

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A molecular mechanics model for the η^2 interaction between olefins and transition metals, utilizing the MMP2 force field, is defined. The model uses a dummy atom displaced from the C═C bond axis with corrections for the changes in connectivity occasioned by the additional atom. Steric sizes for a range of olefins are calculated from this model using the ligand repulsive energy (E_R) methodology. E_R values for 45 olefins in the $Cr(CO)_5$ environment and 38 olefins in the CpRh(CO) environment are calculated and compared with the steric sizes of phosphines, phosphites, amines, and sulfides. There is a good correlation between the calculated E_R values and the second-order rate constant for the coordination of olefins to $HCo[PPh(OEt)_2]_3$.

Introduction

Steric effects influence the roles of alkenes in a variety of transition metal reactions spanning photochemistry,[1] hydralumination,[2] hydrocyanation,[3] hydroboration,[4] hydroformylation,[5] hydrogenation,[6] stereochemistry,[7] kinetics,[8] and thermodynamics.[9] In recent years, highly selective reactions such as alkene isomerization and asymmetric hydroformylation exploited the versatility of transition metal alkene complexes.[10] In many studies the size of the alkene is an important factor in determining physical parameters of the reaction. However, to date no quantitative measures of the steric requirements of bonded olefins have appeared.[11] The shapes of η^2-coordinated olefins are sufficiently far removed from conical to render traditional approaches, e.g. the cone angle methodology,[12] inappropriate as a measure of alkene size.

There have only been a few attempts to model metal–ligand π interactions using molecular mechanics. In this paper we evaluate the different possible approaches and present a method for modeling the η^2-olefinic interaction using an MMP2 type of force field.[13] We also present a measure of the steric demands of a large selection of olefins using the ligand repulsive energy (E_R) methodology.

Molecular Modeling of η^2 Bonding

Few studies are to be found in the current literature involving molecular mechanics modeling of the η^2 interaction between olefins and metals. Those that have been published provide few details regarding the computational model. There are a number of different ways of representing the interaction between a π system and a metal using the MMP2 and related force fields. The first is to bond both olefinic carbon atoms to the metal using single bonds. This approach suffers the disadvantage that the small metallocycles which are thereby defined require extensive parametrization. In addition, this model defines the π system as occupying two coordination sites on the metal rather than one. A second model depicts the ligand as bound to the metal through a dummy atom bonded directly to the metal so as to occupy a single coordination site. A general approach for the modeling of π systems with dummy atoms was proposed by Doman, Landis, and Bosnich.[14] Although η^2 systems were not discussed in detail, the similarities between η^2 and η^n ($n > 2$) systems were presented. The general use of dummy atoms was recently reviewed in the literature.[15] Properly applied, the dummy atom approach can work well for η^3, η^4, η^5, and η^6 ligands;[16] however, its application to η^2 systems can generate problems. One source of difficulty is that in MMP2 the torsion angle terms are defined as 1,4-interactions. Thus, if a dummy atom is placed at the centroid of the C═C bond and if the C═C connectivity is thereby interrupted, the halves of the bond may rotate freely about the dummy–carbon axis because there are no parameters to maintain coplanarity of the sp^2 carbons through the definition of an appropriate torsion angle (Figure 1). If the C═C connectivity is not interrupted by the dummy atom, then

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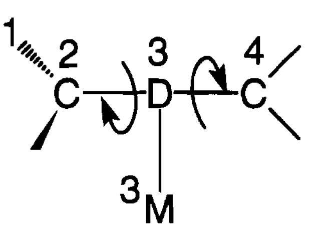

Figure 1. Atom counting if dummy atom D interrupts the C=C connectivity. Note the free rotation of the halves of the olefin with respect to each other. The rotation is prevented if the substituents are in a 1,4-relationship but not when the substituent and olefinic carbon are 1,4 to each other.

the problem of coplanarity of the sp^2 carbons does not arise, but other connectivity problems, described below, do occur. If the olefin is confined to a ring (e.g. norbornadiene), the coplanarity problem may not arise because the parameters which define the ring structure hold the olefin in place. However, it presents a serious source of difficulty for acyclic olefins.

With the exception of the modeling of the approach of norbornene to $[(\eta^5\text{-}C_5Me_5)U(H)\{[(1S)\text{-}endo]\text{-bornoxide}\}]$,[17] all η^2-bonding models in the literature have made use of a pseudo or dummy atom,[14,18] placed at the centroid of the C=C bond without the C=C connectivity being interrupted and bonded directly to the metal.[18,19] The dummy atom is presumably bonded directly to both carbon atoms of the olefin. The published studies have made use of the MM2,[13] Dreiding,[17] and SHAPES[18] force fields.

The dummy atom approach is not confined to π-olefin interactions. Eckert and co-workers used the same approach in modeling $\eta^2\text{-}H_2$ bonding in $[M(CO)_3(PR_3)_2(\eta^2\text{-}H_2)]$ (M = Mo, W; R = cyclohexyl, *i*-Pr) using MM2.[20]

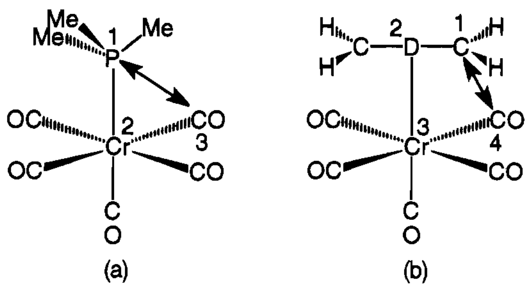

Figure 2. Consequence to E_R with the interruption in C=C connectivity by the dummy. Note in the case of the phosphine (a) the donor atom, P, and basal carbonyl are 1,3 to one another and, thus, the interaction is not included in the calculation of E_R. In the case of the olefin (b) the donor atom and radial carbonyls are 1,4 to each other and the interaction is included in the E_R calculation.

The total molecular mechanics energy for a molecule consists of four components: bond stretch term (for atoms in a 1,2-relationship), angle bend term (for atoms in a 1,3-relationship), torsion angle term (for atoms in a 1,4-relationship), and a van der Waals term (1,4- and higher-interactions). All interactions which have not been considered in the bonded terms (i.e. atoms in 1,2- and 1,3-interactions) are considered in the van der Waals term (within a cutoff radius of typically 8.5 Å). For σ-bonded interactions, application of the connectivity-based algorithm to determine interatomic relationships is straightforward. However, the π-bonded systems, care must be taken in the definition of bonds to ensure that the energy terms employed accurately reflect the atomic connectivity. When the bonding of an olefin to a transition metal center is modeled in terms of a dummy atom, the dummy atom must be anchored to both carbons of the olefin and to the metal. This process artificially adds one atom and three bonds to the molecule and therefore alters the connectivity table. Each olefinic carbon becomes related to the metal via a 1,3-interaction instead of the 1,2-interaction implied by the π bond (Figure 1). In addition, when the dummy atom is interposed between the carbon atoms as in Figure 1, the two olefinic carbons are also in a 1,3-relationship with respect to each other instead of the appropriate 1,2-relationship. This model for olefin bonding has fatal consequences in the calculation of ligand repulsive energies, which are based upon the repulsive van der Waals energy term. To illustrate, consider the calculation of E_R for PMe_3 and ethylene in the $Cr(CO)_5$ environment (Figure 2). For PMe_3, there is a 1,3-relationship between the basal carbonyl carbons and donor atom so there is no van der Waals term for this interaction. It is therefore not included in the calculation of E_R (Figure 2a). With the dummy atom placed between the olefinic carbon atoms and the metal, the relationship between donor atom and basal carbonyls becomes 1,4 with the result that a van der Waals repulsive term is inappropriately included in the E_R calculation (Figure 2b). The problem with 1,3- versus 1,4-interactions is not peculiar to calculation of E_R, since the calculation of the total molecular mechanics energy depends on assigning atoms the correct connectivity.

To avoid the problems just described, we define a molecular mechanics model in which the dummy atom is displaced from the C=C axis by a *small* amount (about 0.02 Å) and two pseudobonds are added, connecting the olefinic carbons directly to the metal (Figure 3). All interactions generated by the pseudobonds are assigned force constants of zero; thus, the bonds merely correct for atom-counting irregularities introduced by the dummy atom. (In most molecular mechanics packages all atoms in a 1,2- or 1,3-relationship are excluded from the van der Waals term. So, atoms which are in both 1,3- and 1,4-relationships are excluded on the basis of the 1,3-relationship.)

Results and Discussion

Calculation of E_R and the Conformational Search. The ligand repulsive energy, E_R, measures the repulsion between a

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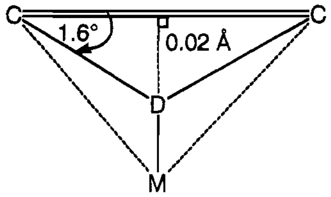

Figure 3. Schematic diagram of the molecular mechanics model for the interaction between an olefin and metal, M. The diagram is greatly exaggerated to show the small displacement of the dummy, D, from the C=C axis. The dashed lines indicate the positions of the pseudobonds which are used to correct for atom counting.

ligand, L, and a prototypical organometallic environment.[21] For an equilibrium metal−ligand distance r_e and van der Waals repulsive energy between a ligand and the entire metal complex to which it is bound, $E_{\mathrm{vdW,repulsive}}$, E_R is defined in terms of the gradient of $E_{\mathrm{vdW,repulsive}}$ as a function of metal−ligand distance, r, scaled by r_e:

$$E_R = -r_e\left(\frac{\partial E_{\mathrm{vdW,repulsive}}}{\partial r}\right)$$

To compute E_R, the best approximation to the global minimum-energy conformation of the organometallic complex is found, using established conformational search methods and an appropriately parametrized MMP2 force field. Then the van der Waals energy term is changed from the attractive-repulsive form

$$E_{\mathrm{vdW}} = D_0\left\{\left[\left(\frac{6}{\gamma - 6}\right)\exp\left[\gamma\left(1 - \frac{r}{r_0}\right)\right]\right] - \left(\frac{\gamma}{\gamma - 6}\right)\left(\frac{r_0}{r}\right)^6\right\}$$

to a purely repulsive one

$$E_{\mathrm{vdW}} = D_0 \exp\left\{\gamma\left(r_0 - \frac{r}{r_0}\right)\right\}$$

and the slope of the plot of $E_{\mathrm{vdW,repulsive}}$ versus r is calculated (D_0 is the potential well depth, γ is a scaling factor, and r is the interatomic distance).[21] This value is then scaled by the equilibrium metal−ligand distance, r_e, to yield E_R. In practice, the plot of $E_{\mathrm{vdW,repulsive}}$ against r is linear over the small range of distances employed. To date, E_R values have been reported for phosphines, phosphites,[21,22] arsines,[21] amines,[23] and S- and O-donor[24] ligands.

The search for the global minimum-energy conformation needs some attention. Generally, a large number of conformers (typically 1000) is generated using a Monte Carlo search strategy in which individual key torsion angles are randomly varied using BIOGRAF. Each conformer is partially energy-minimized. The 5−10 conformers lowest in energy are then selected, and each is fully energy-minimized. The lowest energy structure is then further refined in Cerius or Cerius^2 by use of simulated annealing.

The molecular dynamics runs take different forms in Cerius and Cerius^2. The goal is to achieve a total of around 3 ps of simulated annealing per run. In Cerius this is achieved by heating the molecule from 300 to 500 K and then cooling back to 300 K in 5 K steps. During each temperature step, 50 anneal steps, each lasting 0.001 ps, are performed. Thus, a total of 3 ps of annealing is achieved. Typically about 6 runs are required to observe a significant decrease in energy.

Table 1. Parameters Added to the MMP2 Force Field

A. Force Constants, k_S (mdyn Å^{-1}), and Strain Free Distances, r_0 (Å), for Bond Stretching

bond	k_S[a]	r_0
D−C(olefin)[b]	10.4	0.728
D−Cr	1.26	1.79
D−Rh	3.00	2.03

B. Force Constants, k_b (mdyn Å rad^{-2}), and Strain-Free Angles, θ_0 (deg), for Bond Angle Deformations

bond	k_b[a]	θ_0
C(olefin)−D−C(olefin)[b]	6.95	176.7
D−C(olefin)−C(olefin)	6.95	1.637
D−C(olefin)−H	0.243	118.4
D−C(olefin)−C(alkyl)	0.550	119.8
D−Cr−CO	0.278	90
D−Rh−Centroid	0.500	135
D−Rh−CO	0.500	90

C. Force Constants, $K_{n,\phi}$ (kcal mol^{-1}), for Torsion Angle Deformations

torsion type	$k_{n,\phi}$	periodicity	phase factor
D−C(olefin)−C(olefin)−D[b]	0	1	−1
C(aryl)−C(olefin)−D−Cr	10	2	1
C(olefin)−C(olefin)−D−Cr	10	2	1
H−C(olefin)−D−Cr	10	2	1
C(alkyl)−C(olefin)−D−Cr	10	2	1

[a] Multiply by 143.88 to convert from mydn Å^{-1} to kcal mol^{-1} Å^2. [b] D = dummy atom at the centroid of the alkene.

In Cerius^2 a different procedure is employed: the molecule is heated from 580 to 600 K and cooled to 580 K in 1 K steps, and the cycle is repeated 17 times. During each temperature step, only 5 steps of dynamics are performed, each lasting 0.0008 ps (yielding a total of 2.88 ps of simulated annealing). Typically, 6−10 of these cycles resulted in a significant decrease in energy.

The combination of a Monte Carlo method and molecular dynamics is designed to prevent a molecule from being trapped in a single locale of local minima throughout the Monte Carlo search. The molecular dynamics run perturbs the molecule differently from the Monte Carlo conformational search. Thus, potentially, several different families of minima can be found. It is important to note that molecular dynamics alone often does not give rise to the lowest energy conformers. The best representation of the global energy minimum conformation was found from a use of the combination of molecular dynamics and Monte Carlo methods.

Modeling of (η^2-olefin)Cr(CO)$_5$ and CpRh(η^2-olefin)(CO) Complexes. The parameters involving the olefin and Cr(CO)$_5$ fragment were based on one crystal structure found in the literature.[25] To maintain the C=C axis at right angles to the metal−olefin bond, the Cr−dummy−C(olefin) bend was assigned an equilibrium angle of 91.6°. This angle differs from 90° to take into account the small displacement of the dummy atom from the C=C axis.

Torsional parameters were derived by analogy to the parameters within MMP2 and are listed in Table 1. There is a good correlation between the relevant distances and angles of the computed and X-ray crystal structure of [(2−3-η^2-*endo*-6-(4-methoxyphenyl)bicyclo[3.1.0]hex-2-ene)Cr(CO)$_5$][25] (Table 2).

To our knowledge there are no crystal structure data for complexes of the type [CpRh(CO)(η^2-vinyl)]. Therefore, the molecular mechanics model for this system was based on a combination of crystal structure data for [CpRh(CO)L] (L =

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Table 2. Comparison of the Key Bond Distances (Å) and Angles (deg) between Crystal Structure and Computed Structure of (2–3-η^2-*endo*-6-(4-methoxyphenyl)bicyclo[3.1.0]hex-2-ene)$Cr(CO)_5$

bond distance or angle	X-ray	computed	bond distance or angle	X-ray	computed
Cr–C6(7)[a]	2.3925	2.393	C6–Cr–C7	33.1	33.5
Cr–CO	1.8938	1.883	Cr–C6–C7	74.5	73.9
Cr–C8	3.308	3.232	Cr–C7–C8	112.5	109.8
Cr–C11	3.239	3.211	Cr–C6–C11	111.3	109.4

[a] Numbering scheme is the same as in ref 25.

Table 3. E_R (kcal mol^{-1}), Solid Angles, Ω° (deg), Cr–D Distances (Å), and Total Molecular Mechanics Energies, E_{tot} (kcal mol^{-1}), for Alkenes η^2hBonded to $Cr(CO)_5$

ligand	E_r	Ω°	r_e	E_{tot}
ethene	37	107	2.265	6.862
1-propene	57	115	2.280	7.987
1-butene	58	118	2.281	8.789
1-pentene	58	121	2.280	9.284
(*E*)-1,3-butadiene[a]	62	115	2.282	5.347
(trimethylsilyl)ethene	64	132	2.283	5.838
(*Z*)-1,3-butadiene[a]	66	113	2.283	8.950
3-methyl-1-butene	69	126	2.290	11.49
bicyclo[3.1.0]hex-2-ene	71	124	2.287	130.3
endo-6-(4-methoxyphenyl)-bicyclo[3.1.0]hex-2-ene	71	131	2.287	144.8
endo-6-phenylbicyclo[3.1.0]hex-2-ene	71	131	2.287	134.4
styrene	71	121	2.287	9.305
1-hexene	72	119	2.278	9.974
cis-1,3-pentadiene	73	124	2.287	18.02
bicyclo[2.2.0]hex-2-ene	74	119	2.296	106.2
cyclopentene	74	126	2.292	19.30
allylbenzene	75	124	2.280	11.03
cis-2-butene	75	124	2.290	10.80
cyclopentadiene	76	116	2.294	17.498
cis-2-pentene	77	127	2.291	11.04
cis-3-hexene	79	130	2.292	11.83
trans-1,3-pentadiene	79	125	2.294	16.96
trans-2-butene	79	124	2.298	9.996
2-methyl-1-propene	80	125	2.296	9.002
trans-2-pentene	80	133	2.299	10.85
trans-3-hexene	81	130	2.299	11.60
3,3-dimethyl-1-butene	83	135	2.294	16.26
1,4-cyclohexadiene	85	123	2.296	13.24
bicyclo[2.2.2]oct-2-ene	86	133	2.303	38.25
bicyclo[2.2.1]hept-2-ene	88	129	2.306	50.39
cyclohexene	88	132	2.297	15.08
bicyclo[2.2.1]-1,3-hexadiene	90	121	2.302	53.43
cis-1,2-bis(trimethylsilyl)ethene	91	157	2.293	10.52
cis-2-hexene	91	130	2.290	11.46
trans-1,2-bis(trimethylsilyl)ethene	96	153	2.301	8.907
2-methyl-2-butene	97	134	2.309	12.42
2-methyl-1-pentene	98	134	2.298	11.38
trans-2-hexene	99	131	2.297	11.55
cis-β-methylstyrene	101	130	2.295	17.53
1,4-cyclooctadiene	103	131	2.313	34.73
trans-β-methylstryene	113	131	2.307	11.99
2,3-dimethyl-2-butene	115	142	2.321	16.68
trans-stilbene	116	137	2.312	14.45
cis-stilbene	119	137	2.317	28.99
1,1-diphenylethene	132	138	2.324	27.36

[a] Butadiene exists as *E* and *Z* isomers with respect to the C–C σ bond.

phosphine),[22] [CpRh(η^2-vinyl)$_2$],[26] and [(indenyl)Rh(η^2-vinyl)$_2$][27] complexes. As described previously, the cyclopentadienyl ligand is bound to the metal center by use of a dummy atom located at the position of the centroid of the cyclopentadienyl ring. The parameters for this interaction were not modified from our previous study.[22] The Rh–vinyl interaction was modeled analogously to the Cr–ethylene interaction. Relevant parameters are summarized in Table 1. There is good agreement between the computed and X-ray geometries for the relevant interactions (average Rh–C(olefin) distance 2.153 Å;[26,27] calculated Rh–C(olefin) distance 2.153 Å).

We emphasize, as in earlier work in this series, that the intent is not to model precisely any particular structure but to create a molecular mechanics model that yields minimum-energy structures close to those observed and that remains constant throughout a series of related calculations. To compare the ligand repulsive energy values for olefins with phosphines, amines, and sulfides, the same prototypical fragments ($Cr(CO)_5$ and CpRhCO) need to be used. Just as important, the force field parameters controlling the geometry of the fragment need to remain constant for the comparisons of E_R to be meaningful. Therefore, the Cr–C≡O, C≡O–lone pair, and related parameters were retained from previous studies.[21–24,28]

Ligand Repulsive Energy Values in the $Cr(CO)_5$ Environment. The ligand repulsive energy values for 45 olefins bonded to $Cr(CO)_5$ are listed in Table 3. To our knowledge there are no quantitative measures of steric size for η^2-bonded ligands in the literature.[11] The olefins are, on average, similar in size to P-donor ligands and larger than amines or sulfides. The trend in ligand repulsive energies can be illustrated with the cone angle, θ:[12] ethylene ($\theta = 117°$ [29]) is similar in size to PMe_3 ($\theta = 118°$ [12]) and to NH_2Cy, a relatively large amine ($\theta = 115°$ [30]). As a rough comparative measure, the confidence interval[31] for the E_R values for olefins is 83 ± 7 kcal mol^{-1} as compared with 76 ± 7 kcal mol^{-1} for P-donor ligands,[21] 71 ± 15 kcal mol^{-1} for N-donor ligands,[23] and 61 ± 3 kcal mol^{-1} for S-donor[24] ligands. The olefins have large E_R values because the groups bonded to the olefinic carbons lie in the plane of the C=C bond. Thus, the olefin–metal interaction brings a large number of atoms into proximity to the basal CO groups. Therefore, there is a greater repulsion between basal carbonyl groups and the ligand than encountered with other ligands.

In the energy-minimized structure for the $Cr(CO)_5(\eta^2\text{-olefin})$ complexes, the C=C bond eclipses the OC–Cr–CO axis (Figure 4). This places the olefinic substituents between the arms of the basal carbonyl ligands of the $Cr(CO)_5$ fragment. To minimize the steric repulsion between these groups and the basal carbonyl ligands, the substituents should be located at 45° with respect to the carbonyl ligands. In the energy-minimized structure, the olefinic substituents are located about 30° from one of the basal CO groups, implying that one pair of CO groups is always affected by the olefin to a greater extent than the other. Repulsions between groups attached to the olefinic carbons and the basal CO groups are manifested in out-of-plane displacements of the olefinic substituents and angles between axial Cr–CO and basal Cr–CO bonds. The two different types of radial

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(31) The confidence interval interval is calculated from

$$\mu = \bar{x} \pm \frac{ts}{\sqrt{n}}$$

where μ is the population mean (i.e. the mean calculated with infinite data), $\bar{x}$ is the observed mean, s is the standard deviation, n is the number of observations, and t is Student's t value. All confidence intervals were calculated at the 95% confidence level.

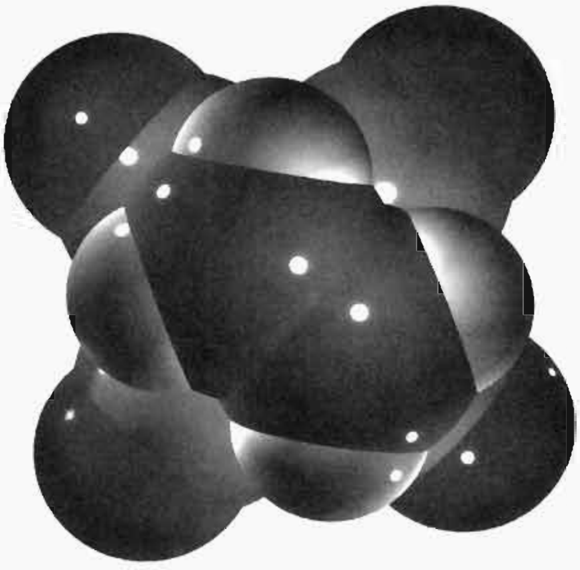

Figure 4. Space-filling model of the $Cr(CO)_5(\eta^2\text{-ethylene})$ complex. Notice how the olefin substituents (in this case H atoms) straddle the basal CO groups.

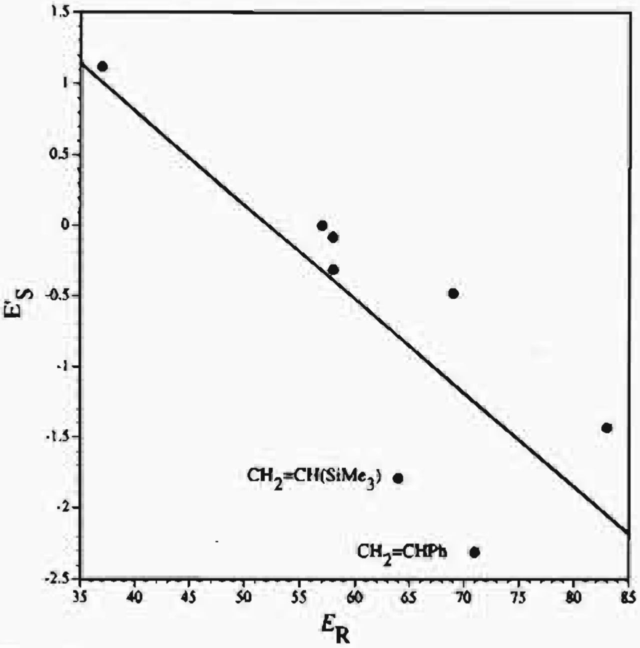

Figure 5. Plot of the Taft steric parameter, E'_S, for the alky group R versus E'_R for $Cr(CO)_5(\eta^2\text{-}CH_2CHR)$ before removal of outliers.

CO are evidenced by the differing OC(axial)−Cr−CO(radial) angles of 87.6 and 84.8° for the two sets. These angles are substantially less than the strain-free angle of 90°.

The E_R values for $H_2C{=}CHR$ ligands show the expected increase from R = H (E_R = 37 kcal mol^{-1}) to R = *t*-Bu (E_R = 83 kcal mol^{-1}; Table 3). In fact the relationship between E_R and E'_S, the Taft−Dubois steric parameter,[32] is linear over the range of these ligands (r = 0.80; Figure 5). There are two outliers in this relationship: R = SiMe$_3$ and R = Ph. Phenyl rings often prove anomalous in correlations involving steric size, because of variations in the barriers to free rotation of the phenyl group.[11] If these outliers are removed, the correlation improves significantly (r = 0.986; 6 data points).

Successive substitutions of hydrogens for methyl groups in ethylene result in a linear increase in E_R value of about 20 kcal mol^{-1} per methyl group ($H_2C{=}CH_2$, E_R = 37 kcal mol^{-1}; $MeHC{=}CH_2$, E_R = 57 kcal mol^{-1}; $Me_2C{=}CH_2$, E_R = 80 kcal mol^{-1}; $Me_2C{=}CHMe$, E_R = 97 kcal mol^{-1}; $Me_2C{=}CMe_2$, E_R = 115 kcal mol^{-1}).

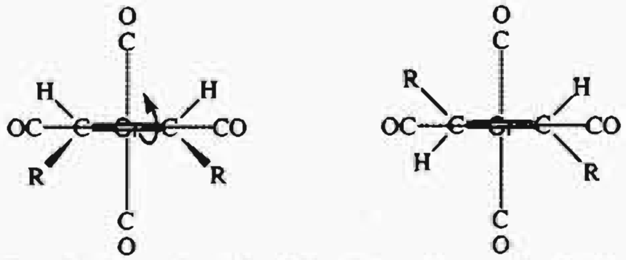

Figure 6. Illustration of the tilting of the olefin from the $Cr(CO)_5$ fragment. In the case of the *cis* isomer, the two substituents can tilt from the basal CO groups to alleviate steric repulsion. In the case of the *trans* isomer, any tilting for one substituent forces the other substituent closer to the basal CO groups.

In all cases except for phenyl-substituted olefins, the *cis* isomer shows a lower E_R value than the *trans*. To relieve the steric strain imposed by the substituents, the radical carbonyls need to bend away from the closest substituent on the olefin. In the case of the *cis* isomer, two carbonyl groups bend toward a third radial carbonyl, whereas in the *trans* isomer, two basal carbonyl groups bend toward the other two (Figure 6). The lower values for E_R for the *cis*-substituted olefins may arise from their ability to tilt with respect to the metal−olefin bond axis to relieve the unequal repulsion at the two ends. To test the prediction that *cis* isomers are smaller than *trans* η^2-bonded olefins and to illustrate the application to olefin E_R values in linear free-energy correlations, we examined the correlation between E_R and the second-order rate constants for coordination of a variety of olefins to $HCo[PPh(OEt)_2]_3$.[33] The relationship tested is of the form $\ln k = a\mathcal{F} + bE_R + c$, where $\mathcal{F}$ is a measure of the electron-releasing character of the olefin and E_R measures the steric requirement.[28b] The quantity $\mathcal{F}$ is taken as the sum of the field parameters for the four groups bound to the two olefinic carbons.[34] (The field parameter is essentially a measure of relative inductive effects operating through the σ-bond system.)

The plot illustrated in Figure 7 yields a correlation r of 0.95, with a = 8.79, b = −0.15, and c = 30.5. As expected, the negative sign for b indicates that the rate constant is negatively correlated with increased steric demand of the olefin. In agreement with the comparative E_R values, the rate constants are larger for *cis* olefins than for their *trans* isomers. The positive value for a connotes that the rate constant increases as the groups attached to the olefinic carbons become more electron withdrawing.

The effect of adding carbons between the bridgehead carbons in norbornyl systems is interesting. There is a large increase in E_R on going from bicyclo[2.2.0]hex-2-ene (E_R = 74 kcal mol^{-1}) to bicyclo[2.2.1]hept-2-ene (E_R = 88 kcal mol^{-1}). However, there is no significant change in going to bicyclo[2.2.2]oct-2-ene (E_R = 86 kcal mol^{-1}). The effect relates to the positions of the tertiary bridgehead carbons (positions 1 and 4). In the case of bicyclo[2.2.0]hex-2-ene, these carbon atoms are pulled into each other and are kept a constant distance from the basal carbonyl groups and, hence, show a small repulsion between tertiary carbons and radial CO. In the case of the other two ligands, the presence of the carbon between the bridgehead carbon atoms allows C1 and C4 to move further apart and get

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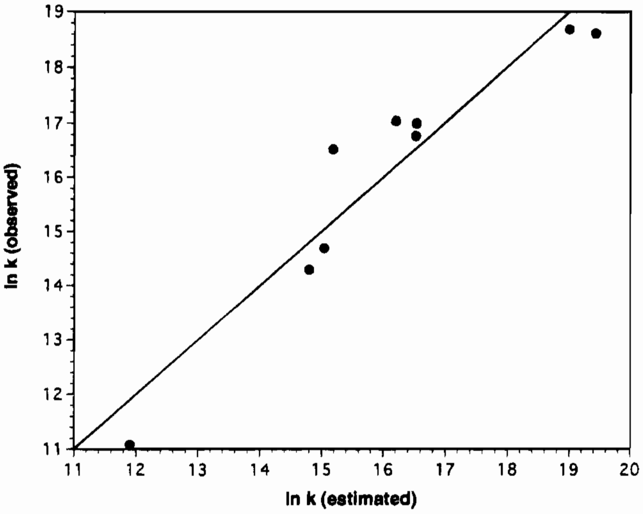

Figure 7. Least-squares fit of rate constants for addition of olefins to $HCo[PPh(OEt)_2]_3$ to $\ln k = a\mathscr{F} + bE_R + c$.

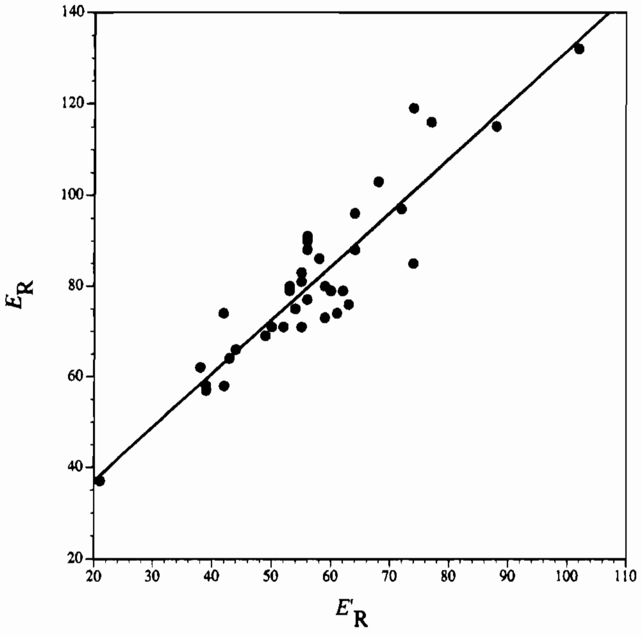

Figure 8. Plot of E_R for $Cr(CO)_5(\eta^2\text{-vinyl})$ versus E'_R for $CpRh(CO)(\eta^2\text{-vinyl})$.

closer to the carbonyl groups, thereby increasing the repulsion between tertiary carbons and carbonyls. The number of carbon atoms between the bridgehead does not affect the positions of these two carbon atoms, and therefore, the E_R values remain constant after the ring strain is relieved.

Ligand Repulsive Energy Values in the CpRhCO Environment. There is a good correlation between E_R, measured in the $Cr(CO)_5$ environment, and E'_R, measured in the CpRhCO environment ($r = 0.92$; Figure 8; Table 4). The regression equation is $E_R = 1.18E'_R + 13.4$. The slope of 1.18 indicates that the CpRhCO environment is less sterically congested than the $Cr(CO)_5$ environment.[21] The olefins again turn out to be similar in size to the phosphine ligands (confidence intervals:[31] $E'_R = 57 \pm 5$ kcal mol^{-1} for olefins (Table 4) and 53 ± 6 kcal mol^{-1} for phosphines[22]). It is important to note that even though the absolute values of E_R are different from E'_R, the general *trends* are the same. Therefore, a ligand with a large E_R also has a relatively large E'_R. All the trends in E_R values discussed above also apply to the E'_R values. For example, addition of methyl groups to the ethylene fragment gives rise to an average of a 17 kcal mol^{-1} increase in E'_R per methyl group (Table 4). In addition, there is a linear relationship between E'_R and E'_S[32] ($r = 0.98$; 6 data after removal of outliers).

Table 4. E'_R (kcal mol^{-1}), Rh–D Distances (Å), and Total Molecular Mechanics Energies, E_{tot} (kcal mol^{-1}), for Alkenes η^2-Bonded to CpRhCO

ligand	E'_R	r_e	E_{tot}
ethene	21	2.035	−18.52
(*E*)-1,3-butadiene[a]	38	2.045	−20.98
1-butene	39	2.045	−17.23
1-propene	39	2.046	−17.80
1-pentene	42	2.046	−16.28
bicyclo[2.2.0]hex-2-ene	42	2.057	96.12
(trimethylsilyl)ethene	43	2.046	−21.23
(*Z*)-1,3-butadiene[a]	44	2.047	−17.90
3-methyl-1-butene	49	2.048	−14.81
styrene	50	2.046	−20.17
bicyclo[3.1.0]hex-2-ene	52	2.053	106.6
trans-2-butene	53	2.060	−16.38
trans-2-pentene	53	2.058	−15.84
cis-2-butene	54	2.056	−15.53
3,3-dimethyl-1-butene	55	2.051	−11.72
endo-6-(4-methoxyphenyl)-bicyclo[3.1.0]hex-2-ene	55	2.053	113.8
endo-6-phenylbicyclo[3.1.0]hex-2-ene	55	2.055	106.4
trans-3-hexene	55	2.058	−14.96
bicyclo[2.2.1]-1,3-hexadiene	56	2.065	27.01
bicyclo[2.2.1]hept-2-ene	56	2.065	21.13
cis-1,2-bis(trimethylsilyl)ethene	56	2.052	−15.36
cis-2-pentene	56	2.056	−15.06
bicyclo[2.2.2]oct-2-ene	58	2.065	8.689
2-methyl-1-propene	59	2.061	−16.37
cis-1,3-pentadiene	59	2.058	−10.34
trans-1,3-pentadiene	60	2.062	−16.38
cyclopentene	61	2.070	−3.299
cis-3-hexene	62	2.059	−13.62
cyclopentadiene	63	2.070	−5.907
cyclohexene	64	2.067	−3.339
trans-1,2-bis(trimethylsilyl)ethene	64	2.056	−23.94
1,4-cyclooctadiene	68	2.068	1.624
2-methyl-2-butene	72	2.072	−13.50
1,4-cyclohexadiene	74	2.075	−9.224
cis-stilbene	74	2.065	−5.860
trans-stilbene	77	2.063	−20.85
2,3-dimethyl-2-butene	88	2.092	−8.836
1,1-diphenylethene	102	2.076	−0.1000

[a] Butadiene exists as *E* and *Z* isomers with respect to the C–C σ bond.

Although the trends in E_R and E'_R values are the generally same, there are some differences due to the differences in molecular geometries of the systems. For example, the E'_R values are generally slightly larger for *cis*-CHR=CHR than for *trans*-CHR=CHR ligands. The *trans* isomers have one R group located near the cyclopentadienyl ring and one near the CO group, whereas the *cis* isomers have both R groups located near the cyclopentadienyl ring.

Methods

All calculations were performed on a Silicon Graphics Iris Indigo R3000 or Silicon Graphics Iris Indigo^2 R4400 workstation using BIOGRAF 3.2.1s, Cerius 3.2, Cerius^2 1.0, and Cerius^2 1.5, comprehensive molecular mechanics modeling packages supplied by Molecular Simulations Inc., Burlington, MA. The MMP2 force field[13] was employed with modifications listed in Table 1 and previous publications in this series.[21–24,28]

The parameters of the molecular mechanics model for $Cr(CO)_5(\eta^2\text{-vinyl})$ were based in part on the crystal structure of $(2\text{–}3\text{-}\eta^2\text{-}endo\text{-}6\text{-}(4\text{-methoxyphenyl})bicyclo[3.1.0]hex\text{-}2\text{-ene})Cr(CO)_5$[25] as well as previous publications in this series.[28] The η^2 interaction between Cr and vinyl was expressed in terms of a single bond from Cr to a dummy atom, D, centered between the carbon atoms of the C=C bond. This atom was bonded to both carbons of the vinyl but removed from the

C=C axis by 0.02 Å. All bond stretch and angle terms were adjusted to take this displacement into account. The Cr−D force constant was based on the Cr−CO force constant. The dissociation energy of (η^2-ethene)−Cr is approximately 65% of the value for Cr−CO;[35] the Cr−D bond was therefore assigned a stretching constant of 1.36 mdyn Å^{-1}, 65% of the Cr−CO stretching constant. The dummy atom was firmly anchored to the vinyl carbons by means of high stretching and bending force constants (10.4 mdyn Å^{-1} and 6.95 mdyn Å rad^{-2}, respectively; Table 1). The remaining parameters for the vinyl carbon and dummy atoms, listed in Table 1, were derived from reasonable analogy to the organic systems.

The Rh−vinyl interaction was modeled in an analogously to the Cr−ethylene interaction. The Rh−vinyl force constant was set to 3.70 mdyn Å^{-1} (the same value as the Rh−Cp force constant). All parameters added to the MMP2 parameter set are summarized in Table 1.

Energy minimization was carried out using the conjugate gradient 200 minimizer with a step size of 2.00 Å and a termination criterion of 0.100 kcal mol^{-1} Å^{-1}. Once the complexes were energy-minimized, they were submitted to a Monte Carlo conformational search in BIOGRAF 3.2.1s. Typically 500−1000 conformers were generated by Monte Carlo variation of any one of several designated key dihedral angles, and each conformer was fully minimized. The lone pairs were removed from the lowest energy conformer and $Cr(CO)_5(\eta^2$-vinyl) complexes submitted to Cerius and the CpRh(CO)(η^2-vinyl) complexes submitted to Cerius^2 for molecular simulated annealing. (The lone pairs must be removed because the molecular dynamics algorithm is appropriate to the motions of nuclear masses. After the molecular dynamics cycles were complete, the lone pairs were replaced.) In Cerius, single cycles of anneal dynamics were performed with the temperature ramped from 300 to 600 K in 5 K steps. During each temperature interval, 50 molecular dynamics steps were performed, each lasting 0.001 ps. The final structure was energy-minimized and the total molecular mechanics energy compared to that of the starting structure. Up to 8 cycles were performed in order to get the best representation of the global minimum-energy conformation. In Cerius^2 1.0, 18 anneal cycles were performed with the temperature ramped from 580 to 600 K in 1 K steps. During each temperature interval, 5 molecular dynamics steps of 0.000 80 ps were performed. Up to two sets of 18 cycles were performed to obtain the best representation of the global minimum-energy conformation.

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