Understanding the Preference for the Coplanarity of Alkenyl and Carbonyl Ligands in η^1-Alkenyl Transition-Metal Complexes: A Simple Molecular Orbital Approach and *ab Initio* Calculations

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The preference for coplanarity of alkenyl and carbonyl ligands in η^1-alkenyl transition-metal complexes can be understood in terms of a simple molecular orbital model in which the nonbonding metal t_{2g} orbitals interact with the π^* orbitals of these ligands. Such back-bonding interactions are most favorable when the alkenyl and carbonyl ligands are coplanar, as all three t_{2g} orbitals are utilized by the ligands. Optimized geometries obtained from *ab initio* calculations for a variety of ruthenium alkenyl complexes show the preference for alkenyl−carbonyl planarity when only one or two carbonyl ligands are present in the complex. In these complexes the energy required to rotate the alkenyl ligand is calculated to be approximately 7 kcal/mol, while in complexes with three or more carbonyl ligands this energy decreases due to competition by carbonyl ligands for favorable back-bonding interactions. This competition effectively rules out any preferential alkenyl−carbonyl arrangement, and instead steric interactions dominate. The role of the π-donor chloride ligand in stabilizing the planar alkenyl−carbonyl arrangement was also investigated.

Introduction

Transition-metal alkenyl complexes have attracted considerable interest because of their relevance to organometallic synthesis and catalysis.[1] In particular, it is thought that alkenyl complexes serve as catalytic intermediates in the processes of alkyne polymerization/oligomerization,[2a] hydrogenation,[2b] and hydrosilation.[2c] Numerous transition-metal alkenyl complexes have thus far been synthesized and structurally characterized. Typical examples of alkenyl complexes, all of which have a *pseudo*-octahedral structure, are given in Table 1.

An important structural feature of these complexes is the coplanar orientation of the alkenyl and carbonyl ligands. This is illustrated by **1** and **2**, which show the two preferred configurations of the alkenyl and *cis* carbonyl ligands. The degree of planarity of the alkenyl and *cis* carbonyl ligands is measured by the dihedral

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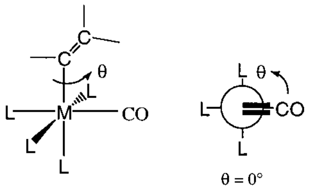
Table 1. Examples of Transition-Metal η^1-Alkenyl Complexes and Their Corresponding Alkenyl−Carbonyl Dihedral Angle θ^a

	complex	dihedral angle θ (deg)	ref
1 CO	$Os(CO)(C_4H_5O_2)Cl\{PMe(t\text{-}Bu)_2\}_2$	2.0	3
	$Ru(CO)(HC{=}CC_3H_8)Cl(C_5N_2H_8)(PPh_3)_2$	2.2	4
	$Ru(CO)\{HPhC{=}C(C{\equiv}CPh)\}(O_2C_2F_3)(PPh_3)_2$	4.3	5
	$Ru(CO)\{HC{=}CH(t\text{-}Bu)\}Cl(C_5N_2H_8)(PPh_3)_2$	6.0	6
	$Ru(CO)(O_2CMe)(HC{=}CHPh)(PPh_3)_2$	6.3	7
	$Fe(CO)(C_{11}H_{11}O)I(PEt_3)_2$	8.3	8
	$Ru(CO)(O_2CH)(HC{=}CHPh)(PPh_3)_2$	9.9	9
	$Ru(CO)\{(MeO_2C)HC{=}C(CO_2Me)\}(CHO_3)(PPh_3)_2$	14.7	6
	$Ir(CO)(C_4O_3H_3)Cl_2(PPh_3)_2$	158.0	10
	$W(CO)(C_{12}H_{19}O_4)(NO)(PMe_3)_2$	176.8	11
	$Ir(CO)(C_{12}H_{12}O_8)(C{\equiv}CPh)(PPh_3)_2$	178.2	12
2 CO	$Ru(CO)_2(HC{=}CHSiMe_2OEt)Cl(PPh_3)_2$	1.8	13
	$Ru(CO)_2\{(MeO_2C)C{=}C(CO_2Me)Cl\}Cl(PPhMe_2)_2$	2.9	14
	$[Fe(CO)_2(C_{15}H_{22}N_2)(PMe_3)_2]^+$	3.9	15
	$Mn(CO)_2(C_{10}H_{12}O_3N_2P)(P_2C_{26}H_{24})$	7.2	16
	$Re(CO)_2(C_{13}H_{15}O)\{P(OC_3H_7)_3\}_2$	12.6	17
	$Ru(CO)_2(C_{11}H_{10}ONS)Cl(P\text{-}n\text{-}Bu_3)$	175.1	18
	$Ru(CO)_2(C_{12}H_{10}O_4)(PPhMe_2)_2$	180.6	19
	$Ru(CO)_2\{H_5C_8C{=}C(Ph)HgCl\}Cl(PMe_2Ph)_2$	184.1	20
3 CO	$Re(CO)_3(C_{15}H_{20}O_4P)$	182.2	21
	$Fe(CO)_3(C_{15}H_{19}O_4P)$	183.8	22
	$Fe(CO)_3(C_{23}H_{32}F_7O_4PS)$	189.3	23
4 CO	$Mn(CO)_4(C_8H_{10}O_4HgBr)$	176.4	24
	$Mn(CO)_4(C_9H_{13}O_3)$	178.3	25
	$Mn(CO)_4(C_6H_5OS)$	178.3	26
	$Re(CO)_4(C_7H_9O_4)$	183.7	21
	$Re(CO)_4(C_8H_{11}O_3)$	188.3	27
	$Mn(CO)_4(C_8H_{12}O_4PS)$	189.6	28
5 CO	$Re(CO)_5(F_6C_2C{=}CC_3F_5)$	30.3	29
	$[(E)\text{-}(EtO_2C)HC{=}C(CO_2Et)]Re(CO)_5$	37.9	30
	$Mn(CO)_5(FC{=}CFH)$	48.0	31

[a] Abbreviations used: Me = methyl; Et = ethyl; *n*-Bu = *n*-butyl, *t*-Bu = *tert*-butyl; Ph = phenyl.



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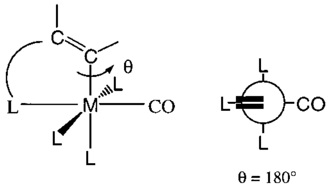

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angle θ, and a Newman projection diagram is shown in **1** for the definition of θ. Experimentally observed values of θ are given in Table 1. Clearly, the majority of complexes exhibit this preference for planarity, with θ values close to either 0 or 180°. There is a general trend for alkenyl complexes containing one or two carbonyl ligands to adopt structures with θ close to 0° unless a chelating ligand is present in the complex, in which case θ is close to 180°. The effect of a chelating alkenyl ligand in complexes with three or four carbonyl ligands restricts the orientation of the alkenyl group so that it is oriented coplanar with a carbonyl group with θ near 180°. In contrast, complexes containing five carbonyl ligands adopt different structures in which θ is close to 45°.

Although this structural preference for alkenyl−carbonyl coplanarity has been noted in previous studies,[32] no explanation for it has yet been given. In this work, we present an orbital interaction model which provides a qualitative explanation for this structural preference. This model is supported by *ab initio* quantum-chemical calculations, which have been used to examine the energetics of alkenyl rotation in these complexes.

Computational Details

Molecular geometries of model complexes have been optimized using both Hartree−Fock (HF) and second-order Møller−Plesset perturbation theory (MP2). Geometries obtained from both methods are similar, and only the results from the MP2 calculations are presented here. The Hay and Wadt effective core potentials (ecp's) with a double-ζ valence basis were used to describe the transition-metal atoms and main-group atoms of period three,[33] while the standard 6-31G basis set was used for all other atoms.[34] In order to simplify calculations, model complexes were used in which alkyl groups have been replaced by hydrogen atoms. Such a substitution is not expected to affect significantly the calculated geometries and relative energies of different conformations.[35]

The energetics of alkenyl rotation have been investigated by calculating the energy of various rotamers corresponding to different values of the alkenyl−carbonyl dihedral angle θ (see **1**). For each value of θ investigated, the rest of the geometry was relaxed, and frequency calculations were performed in order to confirm the existence of minima on the potential energy hypersurfaces.

The effect of including polarization functions in the ligand basis sets was also investigated. Single-point calculations of **3a** at the MP2/6-31G* level based on the optimized MP2/6-31G geometries indicate that the energetics of alkenyl rotation do not change significantly upon inclusion of these extra polarization functions. We conclude from this that the inclusion of polarization functions on the ligand atoms is not necessary to describe the relative energetics of alkenyl rotation.

All calculations were performed using the Gaussian 94 software package[36] on a Silicon Graphics Indigo2 workstation. In an attempt to support the orbital interaction model presented in the following sections, Natural bond order (NBO) analyses were performed using the NBO program[37] as implemented in the Gaussian 94 program.

Results and Discussion

Orbital Interaction Model. The complexes listed in Table 1 satisfy the 18-electron rule; thus, each metal

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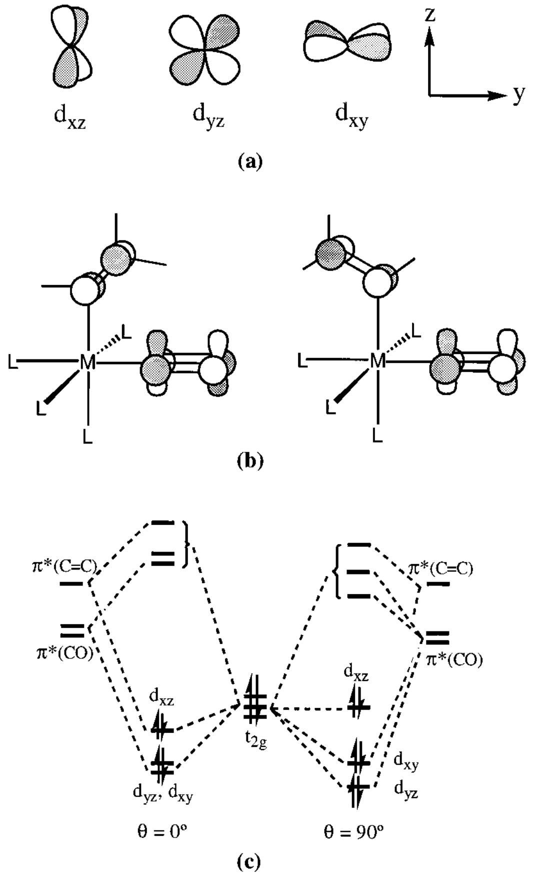


Figure 1. (a) Occupied nonbonding metal t_{2g} orbitals. (b) Orientation of the π* orbitals of the alkenyl and carbonyl ligands relative to the metal atom. (c) Schematic orbital interaction diagram showing the interactions between the metal t_{2g} orbitals and the π* orbitals of both the alkenyl and carbonyl ligands.

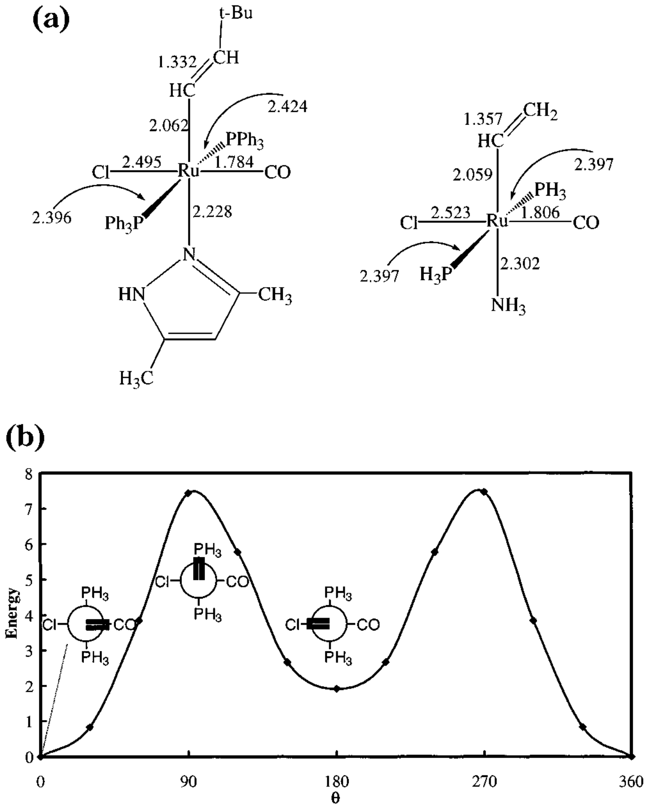
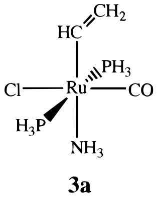


Figure 2. (a) Observed and calculated bond lengths (Å) for [Ru(CO){HC=CH(t-Bu)}Cl($C_5N_2H_8$)(PPh_3)$_2$] and its model complex **3a**. (b) Potential energy surface for **3a** showing the change in relative energy (kcal/mol) with respect to θ (deg). Newman projections showing the relative orientation of the alkenyl ligand within the complex are given on this and subsequent surfaces.

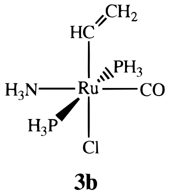
atom has a fully occupied set of t_{2g} orbitals which have π symmetry with respect to the metal–ligand bonds (see Figure 1a). Interaction of these orbitals in the form of back-bonding *via* donation of electron density from these metal t_{2g} orbitals into the π* orbitals of the carbonyl and alkenyl ligands is then possible (Figure 1b), thereby favoring a coplanar arrangement of alkenyl and carbonyl ligands. This qualitative model, based on simple orbital interaction arguments,[38] provides a useful tool for the analysis and interpretation of the results obtained from more detailed *ab initio* calculations.

Participation of the empty π* orbitals of the alkenyl ligand in back-bonding interactions will result in a strengthened metal–carbon bond.[39] When an alkenyl complex contains other π-acceptor ligands (*e.g.*, the CO ligand), competition for back-donation, and therefore the relative orientation of the alkenyl ligand, will affect the stability of the complex. Figure 1b shows the orientation of π* orbitals in an alkenyl complex when the alkenyl and carbonyl ligands are both *cis* and coplanar. The metal d_{xz} orbital interacts with the alkenyl π* orbital, while the metal d_{yz} and d_{xy} orbitals are free to interact with the π* orbitals of the carbonyl ligand. Thus, a coplanar arrangement of alkenyl and carbonyl ligands results in maximal back-donation with a concomitant increase in the stability of the complex. This argument can also be used to explain the θ = 180° arrangement of alkenyl and carbonyl ligands, since the metal t_{2g} and ligand π* orbitals are also aligned favorably in this orientation. This simple orbital interaction model suggests that the preference for ligand coplanarity exhibited in these complexes is electronic in origin. The relevant orbital interaction diagram for both θ = 0° (or 180°) and θ = 90° is illustrated in Figure 1c.

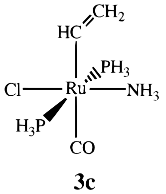
Complexes with One Carbonyl Ligand. The model complex **3a** was used to study the energetics of alkenyl rotation. The optimized geometry of **3a** in Figure 2a along with the experimentally observed structure of [Ru(CO){HC=CH(t-Bu)}Cl($C_5N_2H_8$)(PPh_3)$_2$][6] shows relatively good agreement between the calculated and experimental geometries.



3a



3b



3c

The potential energy surface corresponding to rotation of the alkenyl ligand in **3a** is shown in Figure 2b. The barrier to rotation is approximately 7.4 kcal/mol, which is significantly higher than the values found in simple

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Table 2. NBO π^* Occupancies for the Alkenyl and Carbonyl Ligands in 3a and 5

			5		
	3a			π^*(CO)	
θ	π^*(C=C)	π^*(CO)	π^*(C=C)	*cis*	*trans*
0	0.090	0.727	0.074	0.600	0.402
30	0.089	0.716	0.074	0.590	0.406
60	0.086	0.698	0.072	0.572	0.415
90	0.082	0.696	0.070	0.566	0.422
120	0.086	0.712	0.072	0.585	0.410
150	0.088	0.716	0.075	0.591	0.409
180	0.088	0.716	0.075	0.596	0.408

organic alkene molecules, where alkenyl rotation is often less than 2 kcal/mol.[40] The surface shows two minima corresponding to both coplanar conformations, and frequency calculations confirmed that these minima are real. The optimized geometry is consistent with the observed complex, for which θ is 6.0°.

These calculations for the model Ru−alkenyl complex show that the $\theta = 0°$ conformation is preferred over the $\theta = 180°$ geometry by about 1.9 kcal/mol. The orbital interaction model presented here, however, does not differentiate between geometries with $\theta = 0°$ or $\theta = 180°$, though Table 1 shows that complexes containing chelating ligands tend to adopt the $\theta = 180°$ conformation. Nevertheless, coplanarity is preserved even when the alkenyl group is part of a chelating ligand, which further suggests that orbital interactions are a dominant factor in determining molecular geometry.

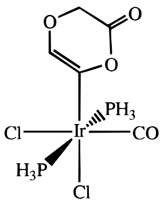
This preference for a planar orientation of alkenyl and carbonyl ligands results in a significant energy barrier for rotation of the alkenyl ligand about the metal−alkenyl bond. This barrier can be attributed to competition for π back-donation with the carbonyl ligand, which is a strong π acceptor. Detailed NBO analyses (Table 2) show that when $\theta = 0$ and 180° the occupancies of the π^* orbitals for both the carbonyl and alkenyl ligands are largest, indicating that maximum metal(d)−π^* back-donation has occurred. Although small, these occupancies correlate well with the potential energies. When $\theta = 90°$ (and 270°), the occupancies of these π^* orbitals are smallest, resulting from competition for back-donation.

This rotational barrier is significantly lowered when the positions of the Cl and NH_3 ligands are exchanged (**3b**); *i.e.*, the Cl ligand is no longer *trans* to the carbonyl group. Complex **3b** is less stable than the model complex **3a** by 4.1 kcal/mol. The alkenyl rotation barrier in **3b** is lowered to 2.7 kcal/mol, probably because the π-donor properties of the Cl ligand enhance the strength of the Ru−CO bond in **3a**. This change in ligand arrangement does not, however, affect the preference for coplanarity of the alkenyl and carbonyl ligands.

The π-donor properties of the Cl ligand in **3a** were examined by studying the analogous complex in which the Cl ligand was replaced by H. This replacement lowers the barrier to 6.1 kcal/mol, a reduction of 1.3 kcal/mol, and further suggests the importance of the strengthening of the Ru−CO interaction by the π-donor properties of the Cl ligand.

Complex **3c**, in which the alkenyl and carbonyl ligands are in a *trans* arrangement, was used to further confirm that the observed preference for a coplanar orientation of alkenyl and carbonyl ligands is electronic in nature. The orbital interaction model presented here predicts that no orientation of the alkenyl and carbonyl ligands results in favorable back-donation because of their *trans* arrangement. The orientation of the alkenyl ligand is therefore likely to be decided by steric interactions. A *trans* arrangement of carbonyl and alkenyl ligands is not favored energetically, however, and **3c** is 19.6 kcal/mol higher in energy than **3a**. This finding emphasizes the importance of the favorable orbital interactions that occur when the alkenyl and carbonyl ligands are arranged in a *cis* manner.

An exception to the orbital interaction model is the complex $[Ir(CO)Cl_2(C_4H_3O_3)(PPh_3)_2]$[10] (**4**), in which the dihedral angle is 158.0° even though the alkenyl ligand is unidentate. In this molecule, it is likely that competing interactions between the oxygen lone pairs and the π^* orbitals of the alkenyl group predominate resulting in a non-coplanar arrangement of ligands.



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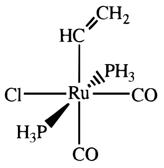

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Complexes with Two Carbonyl Ligands. Alkenyl complexes containing two carbonyl ligands also tend to adopt a conformation in which the alkenyl and carbonyl ligands are coplanar (see Table 1). The model complex **5** was used to study the energetics of alkenyl rotation in molecules with two *cis* carbonyl ligands. The potential energy curve, shown in Figure 3, is similar to that obtained for the single carbonyl molecule and shows that coplanarity of alkenyl and carbonyl ligands is preferred. The conformation with $\theta = 0°$ is most stable, which is also the case for the observed complex $[Ru(CO)_2(CH{=}CHSiMe_2OEt)Cl(PPh_3)_2]$.[13] The barrier to rotation in the dicarbonyl complex is approximately 7.1 kcal/mol, and the difference in energy between the minima at $\theta = 0°$ and $\theta = 180°$ is 1.3 kcal/mol.

The similarity between the potential curves for the carbonyl− and dicarbonyl−alkenyl complexes can be explained in terms of the orbital interaction model. In complex **5** the carbonyl ligands are *cis* to each other, although the additional carbonyl is *trans* to the alkenyl ligand. The latter *trans* carbonyl ligand exerts the same metal(d)−carbonyl (π^*) interaction, irrespective of the alkenyl position, and the orientation of the alkenyl ligand in these molecules is thus determined only by the *cis* carbonyl ligand.

The occupancies of the carbonyl and alkenyl π^* orbitals derived from NBO analysis (Table 2) are consistent with this picture, although the presence of the additional carbonyl ligand in **5** results in occupancies that are generally smaller than those obtained for complex **3a**. In particular, the *trans* carbonyl has smaller occupancies because of the weakened interaction with the metal due to the presence of the alkenyl

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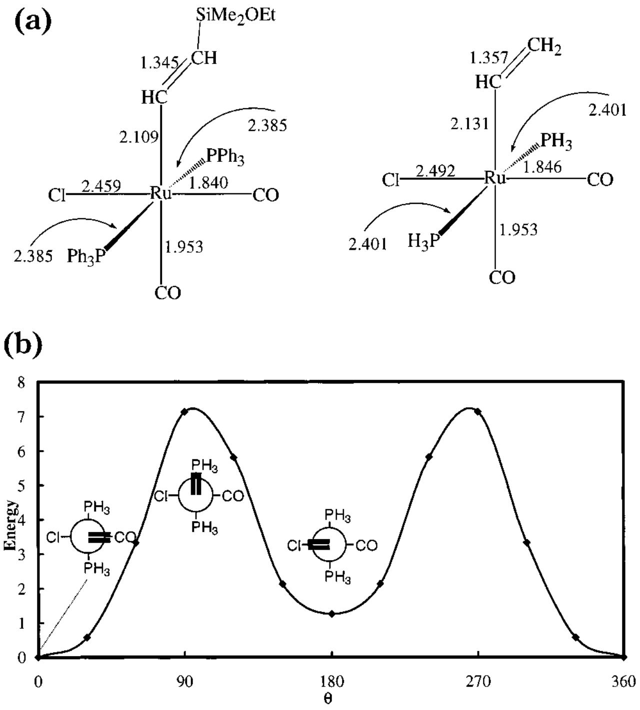
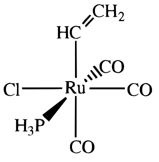


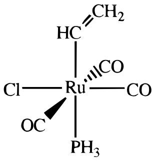
Figure 3. (a) Observed and calculated bond lengths (Å) for $[Ru(CO)_2Cl(HC{=}CHSiMe_2OEt)(PPh_3)_2]$ and its model complex **5**. (b) Potential energy surface for **5** showing the change in relative energy (kcal/mol) with respect to θ (deg). The surface shows two minima corresponding to coplanar alkenyl and carbonyl ligands.

ligand, which exerts a strong *trans* influence. This is also reflected in the Ru−C(O) bond length, which is 1.846 Å for the *cis* carbonyl but is 1.953 Å for the *trans* carbonyl. When $\theta = 0$ and 180°, the π^* occupancies of both the *cis* carbonyl and alkenyl ligands are largest, and as found for the single carbonyl case above, the π^* occupancies are lowest when $\theta = 90°$ (and 270°). The opposite situation is found for the *trans* carbonyl ligand, where the π^* occupancies are highest when $\theta = 90°$ (and 270°). These results can be understood in terms of the competition for back-donation of metal d electrons by the three π-acceptor ligands.

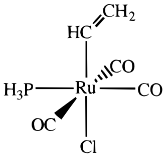
Complexes with Three Carbonyl Ligands. Observed alkenyl complexes containing three carbonyl ligands adopt structures of type **2**, in which the alkenyl ligand is coplanar with the carbonyl ligand and $\theta = 180°$, since the alkenyl group is part of a chelating ligand which prevents a conformation with $\theta = 0°$. Facial (**6a**) and meridional (**6b**) model complexes were used to investigate the energetics of alkenyl rotation, and the corresponding potential energy surfaces are shown in Figures 4 and 5 for **6a** and **6b**, respectively.



6a



6b



6c

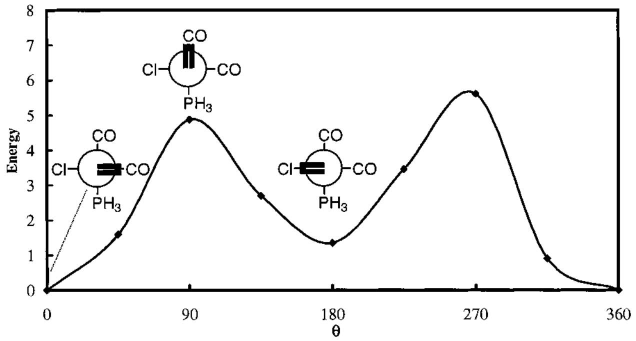


Figure 4. Potential energy surface for **6a** showing the change in relative energy (kcal/mol) with respect to θ (deg). Note that minimum energy geometries correspond to orientations in which the alkenyl ligand is coplanar with both a carbonyl and a chloride ligand.

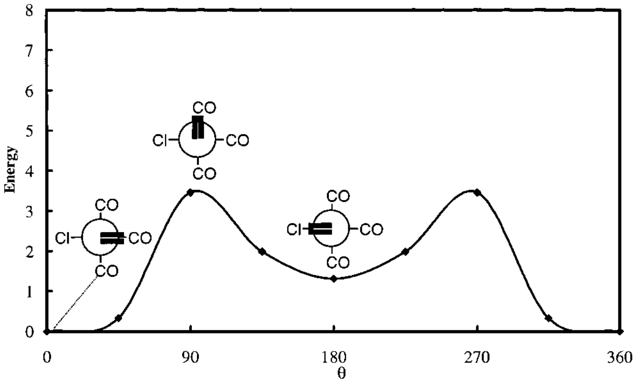


Figure 5. Potential energy surface for **6b** showing the change in relative energy (kcal/mol) with respect to θ (deg). As in the potential energy surface for **6a**, minimum energy geometries correspond to orientations in which the alkenyl ligand is coplanar with both a carbonyl and a chloride ligand.

For both **6a** and **6b**, the minimum energy geometries occur when the alkenyl ligand is coplanar with both the CO and Cl ligands. This is an interesting result, as it again suggests that the Cl ligand also plays a role in determining the alkenyl−carbonyl arrangement. Using the orbital interaction model described here, coplanarity of the alkenyl ligand with either carbonyl ligand in **6a** should be possible, with the expected outcome being that the alkenyl might prefer to be midway between both carbonyl ligands. Instead, the alkenyl ligand adopts a position in which it is coplanar with both the CO and Cl ligands, and the energy is a maximum when the alkenyl ligand is coplanar with the other carbonyl ligand (see Figure 4). The situation is similar also for **6b**, which also prefers a geometry in which the carbonyl, chloride, and alkenyl ligands are coplanar. This can be rationalized by considering the π-donor properties of the Cl ligand, which effectively "push" electron density onto the metal atom, which in turn allows for more back-donation of metal electron density to the carbonyl and alkenyl ligands. Bond lengths support this, where Ru−C(O) and Ru−C(alkenyl) are 1.840 and 2.131 Å, respectively, in the minimum energy geometry, while in the $\theta = 90°$ geometry the values are 1.849 and 2.143 Å. The potential energy curves for the *fac* (**6a**) and *mer* (**6b**) complexes are thus quite similar to those calculated for complexes **3a** and **5**, indicating that the Cl ligand does play a role in determining the structure and stability of these complexes.

Model complex **6c**, in which the positions of Cl and PH_3 ligands in **6b** are exchanged, was used to investi-

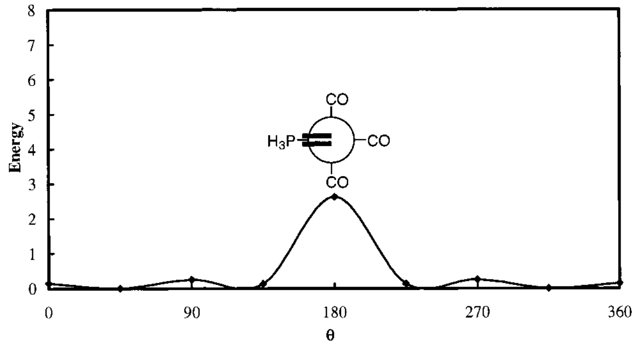
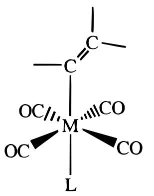


Figure 6. Potential energy surface for **6c** showing the change in relative energy (kcal/mol) with respect to θ (deg). The energy is a maximum when the alkenyl ligand eclipses the other ligands, indicating that steric interactions dominate in complexes of this type.

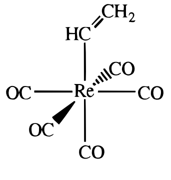
gate further the importance of a *trans* CO−Cl arrangement in these complexes. The potential energy surface (Figure 6) shows that the minimum energy conformations occur when the alkenyl ligand is situated between two proximate carbonyls at $\theta = \pm 45°$. This preference may be explained by the fact that the three carbonyl ligands compete equally for favorable back-bonding, which rules out any preference for the coplanarity of the alkenyl ligand with any single carbonyl ligand. Instead, the orientation is dictated by steric interactions, and Figure 6 shows that the energy is a maximum when the alkenyl ligand eclipses the sterically larger phosphine group. Finally, the energy of **6c** is 9.0 kcal/mol higher than that of **6a**, again indicative of unfavorable interactions between *trans* CO ligands and the positive influence of the Cl ligand in enhancing back-donation.

It is also worth noting that the rotational barrier becomes smaller as the number of carbonyl ligands in the complex is increased. The alkenyl rotation barriers for **6a** and **6b** are smaller than the corresponding values for the one- and two-carbonyl molecules and differ by approximately 2 kcal/mol. These results suggest that electronic effects dominate the one- and two-carbonyl molecules. In **6c**, the minimum-energy conformations are largely dictated by steric factors, as no favorable arrangement of ligands that enhances bonding interactions is possible.

Complexes with Five Carbonyl Ligands. The alkenyl complexes containing five carbonyl ligands given in Table 1 adopt structure **7**, in which the alkenyl ligand is not coplanar with any CO ligand; *i.e.*, $\theta = 30-48°$. The calculated minimum energy geometry is in good agreement with the observed complex, $[(E)\text{-}(EtO_2C)HC{=}C(CO_2Et)]Re(CO)_5$.[30]



7



8

The potential energy surface for model complex **8** (Figure 7) shows four degenerate minimum-energy conformations with the alkenyl group staggered with respect to the proximate carbonyl ligands. It is also worth noting that the barrier to rotation for **8** is very low, on the order of 0.5 kcal/mol, indicating essentially free rotation of the alkenyl ligand. This is explained using the same reasoning discussed above for the tricarbonyl−alkenyl complexes: no electronic preference for alkenyl−carbonyl coplanarity exists because of the competition for metal−carbonyl back-bonding; therefore, the alkenyl orientation is dominated only by steric interactions.

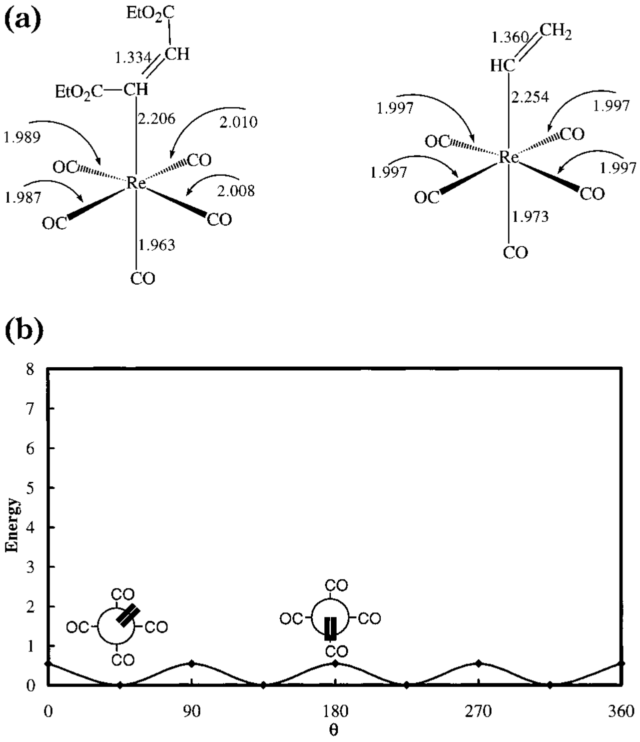


Figure 7. (a) Observed and calculated bond lengths (Å) for $[(E)\text{-}(EtO_2C)HC{=}C(CO_2Et)]Re(CO)_5$ and its model complex **8**. (b) Potential energy surface for **8** showing the change in relative energy (kcal/mol) with respect to θ (deg). Minima correspond to orientations where the alkenyl ligand is staggered with respect to the proximate carbonyl ligands.

It may be argued that the arrangement of the carbonyl ligands in **8** is the dominant factor affecting the alkenyl orientation, *i.e.*, that electronic and not steric factors are important in this complex. This was tested by replacing all of the equatorial carbonyl ligands in **8** by ammonia ligands. The potential energy surface calculated for this model complex is similar to that obtained for **8**, and the rotational barrier is only slightly larger (1.6 kcal/mol). The similarity between these potential energy surfaces suggests that steric factors are indeed most important in determining the rotational barrier for **8**. The slightly larger rotational barrier is a result of the fact that the ammonia ligand is sterically larger than the carbonyl ligand.

Summary

A simple orbital interaction model is presented which explains the preference for alkenyl−carbonyl coplanarity in transition-metal alkenyl complexes. This model is based on interactions between the set of occupied t_{2g} orbitals of the central metal atom and the π^* orbitals belonging to both the alkenyl and carbonyl ligands. *Ab*

Table 3. Summary of the Relative Energies (kcal/mol) Calculated for the Important Rotational Isomers of the Various Complexes

structure	minima	maxima	minima	barrier
3a[a]	0.0 ($\theta = 0°$)	7.4 ($\theta = \pm 90°$)	1.9 ($\theta = 180°$)	7.4
4	0.0 ($\theta = 0°$)	7.1 ($\theta = \pm 90°$)	1.3 ($\theta = 180°$)	7.1
6a	0.0 ($\theta = 0°$)	5.6 ($\theta = \pm 90°$)	1.4 ($\theta = 180°$)	5.6
6b[b]	0.0 ($\theta = 0°$)	3.5 ($\theta = \pm 90°$)	1.3 ($\theta = 180°$)	3.5
6c[b]	0.0 ($\theta = \pm 45°$)	2.6 ($\theta = 180°$)	0.1 ($\theta = \pm 135°$)	2.6
8	0.0 ($\theta = \pm 45°$)	0.5 ($\theta = 0, \pm 90, 180°$)	0.0 ($\theta = \pm 135°$)	0.5

[a] Isomers **3b** and **3c** are 4.1 and 19.6 kcal/mol higher in energy than **3a**, respectively. [b] Isomers **6b** and **6c** are 2.7 and 9.0 kcal/mol higher in energy than **6a**, respectively.

initio calculations for a variety of metal–alkenyl complexes suggest that this simple model can be used to understand the distinct preference for alkenyl–carbonyl planarity, and the energetics of alkenyl rotation studied here are summarized in Table 3.

The preference for coplanarity is largest when the complex contains only one or two carbonyl ligands, where barriers to rotation of approximately 7 kcal/mol were calculated. Our calculations also suggest that the π-donor properties of the chloride ligand enhance metal–carbonyl and metal–alkenyl back-bonding and provide extra inducement for these ligands to be coplanar. As the number of carbonyl ligands is increased, no orientation of the alkenyl ligand results in overall favorable interactions, as the carbonyl ligands essentially compete with each other for the metal t_{2g} orbitals. In these complexes steric factors dominate and the alkenyl ligand adopts a position which results in minimized steric interactions with other ligands.

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