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Fate of $CH_2{=}CHE$ (E = H, OMe) in the Presence of Unsaturated $Ru(X)(H)L_2{}^{q+}$ (X = Cl, *q* = 0; X = CO, *q* = 1): Highly Sensitive to X and E

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DFT (B3PW91) calculations have been carried out to discuss the role of the ancillary ligand X on the transformations of ethylene and vinyl ether by $RuHX(PH_3)_2{}^{q+}$ (X = Cl, $q = 0$; X = CO, $q = 1$). This study follows the experimental results presented in the preceding paper. The energy of isomerization of the vinyl ether adduct into an alkoxy-stabilized carbene complex is insensitive to the nature of X, whereas the energy of isomerization of the ethylene adduct into the ethylidene complex depends significantly on X. This is interpreted as competing donations from both the metal fragment and the alkoxy group into the empty p orbital of carbene. The insertion of an olefin into the Ru−H bond to make an unsaturated 14-electron alkyl complex is calculated to be strongly endothermic for Cl and much less so for CO. This is shown to be associated with the greater stability of the olefin adduct in the presence of Cl. Insertion of methyl vinyl ether follows the same rules as ethylene. This accounts for the direct (vinyl ether) or indirect (ethylene) experimental observation of alkyl complexes with CO. The regioselectivity of the insertion is discussed, and it is shown that the methoxy group prefers to go to the α carbon of the ethyl skeleton unless a direct $Ru\cdots O_\beta$ interaction forming a four-member ring is possible. An energy decomposition on a model system $Ru(H)(X)(PH_3)_2(OMe_2)^q$ (X = Cl, $q = 0$; X = CO, $q = 1$) is used to evaluate the electrostatic contribution to the $Ru\cdots O$ interaction.

Introduction

It has been shown that an olefin $CH_2{=}CHE$ (E = H, alkyl, alkoxy) can be transformed by $Ru(H)(X)(L)_2{}^{q+}$ (X = Cl, $q = 0$;[1,2] X = CO, $q = 1$;[3,4] L = trialkyl phosphine) into a large variety of products depending on the nature of E (π donor or not), X (π donor or π acceptor), and charge (neutral or cationic). The thermodynamic products are a 1:1 adduct obtained for X = Cl and ethylene, an alkoxy-stabilized cyclic carbene complex for X = CO and 2,3-dihydrofuran, and a β-alkoxy-substituted alkyl complex for X = CO and acyclic vinyl ether. This set of results presents a remarkable opportunity to carry out a computational study to analyze the controlling factors for representative organometallic reactions. We have used DFT calculations to discuss the influence of E and X on the reaction products. We have also used the reduced variational space analysis of the interaction energy between $Ru(Me)XL_2$ and OMe_2 to get some deeper insight into the importance of the electrostatic forces in directing the products of reactions.

Computational Details

The calculations were carried out using the Gaussian 98 set of programs[5] within the framework of DFT at the B3PW91 level.[6,7] LANL2DZ effective core potentials (quasi-relativistic for the metal centers) were used to replace the 28 innermost electrons of Ru and Tc,[8] the 60 innermost electrons of Re,[8] and

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the 10 core electrons of Cl, S, and P.[9] The associated double-ζ basis set was used[8,9] and was augmented by a d polarization function for Cl, S, and P.[10] The other atoms were represented by a 6-31 (d,p) basis set (5d).[11] Full geometry optimization was performed with no symmetry restriction, and the nature of the minima was assigned by analytical frequency calculations. The interaction energy decomposition, which gives access to the electrostatic Es, exchange/steric Ex, polarization of entity A by the electric field generated by entity B and charge-transfer contributions, has been carried out using the reduced variational space (RVS)[12] procedure as implemented in GAMESS[13] with the same basis set but with the six Cartesian d orbitals (instead of five) because of program constraints. Using the RVS algorithm instead of Morokuma's original analysis[14] offers the advantage that the polarization and charge-transfer contributions of each interacting fragment are calculated separately, as proposed earlier for dimers by the constrained space orbital variation (CSOV) method.[15] Because the RVS computations are carried out at the Hartree−Fock level, calculations of the interaction energies between the fragments considered in the RVS computations were carried out at the HF and DFT level to check that the computed quantities were not method- and level-dependent. The absolute values of the binding energies were found to be smaller by about 3 kcal·mol^{-1} at the HF than at the DFT level, a result that shows that in these systems the dispersion forces are of limited importance, and the trend of the interaction energies is found to be very similar at both computational levels (differences smaller than 0.3 kcal·mol^{-1}).

Choosing the Computational Models. The metal fragments were represented as $Ru(X)(H)(PH_3)_2^{q+}$ (X = Cl, q = 0; X = CO, q = 1), in which only structures with trans PH_3 ligands were considered. To save computational time, it is necessary to replace the large phosphine ligands present in the experiments by the model PH_3. This replacement has, however, some consequences on the steric properties of the phosphine ligands in the calculations. Therefore, the agostic interactions observed in $Ru(H)(CO)(P^tBu_2Me)_2^+$ will not be discussed in the present paper.[4] As it was previously shown, the experimentally observed sawhorse coordination around Ru is properly reproduced by $Ru(X)(H)(PH_3)_2$,[1,3] suggesting this model to be well adapted. Olefins have been represented by ethylene and methyl vinyl ether. Our models differ mostly from the real systems through the lack of steric effects from the phosphine ligands and probably also through an approximate representation of the electron-donating ability of the phosphine ligands to the metal. Because of these limitations, all the energy values must be considered with some caution. Therefore, we do not suggest that our calculated relative energies are within chemical accuracy (1−2 kcal·mol^{-1}). Instead, the following strategy is adopted. Two structures should be viewed as highly competitive if the difference in energy ΔE between them is less than 5 kcal·mol^{-1}, a structure is thermally accessible if ΔE is 8−18 kcal·mol^{-1} above the most stable calculated structure, and a structure is probably thermally inaccessible at 25 °C if ΔE > 20 kcal·mol^{-1}.

Results

For the sake of convenience, $Ru(H)(Cl)(PH_3)_2$ is denoted as [Ru]HCl, $Ru(H)(CO)(PH_3)_2^+$ as $[Ru]H(CO)^+$, and $Ru(H)(X)(PH_3)_2^{q+}$ as [Ru]HX. In consideration of the very large number of stationary points that have been located, only schematic representations of the minima are given. Only when necessary for the sake of the discussion will the precise geometry of calculated minima be given. The detailed geometry of all located minima are available in the Supporting Information.

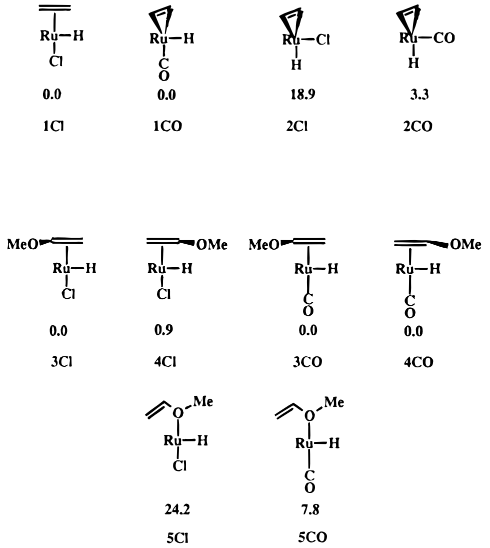

Figure 1. Schematic representations of the optimized structures for C_2H_4 and $CH_2{=}C(H)(OMe)$ adducts to $RuH(X)(PH_3)_2^{q+}$ (X = Cl, q = 0; X = CO, q = 1). The up and down PH_3 ligands have been removed for clarity. Energies (kcal·mol^{-1}) are given with respect to the most stable isomer of each complex.

Ethylene and Vinyl Ether Adducts. It has been shown that all olefins initially form an adduct with [Ru]HX, which is therefore the reactant to be considered for the understanding of the thermodynamics of the reactions. The geometry of [Ru]HX being that of an octahedron with two cis empty sites trans to H and to X, the olefin adds trans or cis to H.

(a) Ethylene with [Ru]H(Cl) and $[Ru]H(CO)^+$. Ethylene coordinates [Ru]HX trans to X to form a square-based pyramid complex with apical hydride (Figure 1). For X = Cl, the C═C bond is parallel to Ru−H, **1Cl**, and for X = CO, it eclipses Ru−P, **1CO**. There is essentially no conformational preference since rotating the olefin by 90° leads to another minimum at very close energy (1.4 kcal·mol^{-1} for CO and 2.1 kcal·mol^{-1} for Cl). The C═C bond is stretched by the coordination to the metal (1.40 Å for Cl, 1.37 Å for CO for any orientation of ethylene in comparison to 1.33 Å for free ethylene), whereas the Ru−C bonds are shorter for Cl (average 2.18 Å) than for CO (average 2.37 Å). These Ru−C and C−C distances suggest that the olefin is less strongly bonded in the case of CO, in agreement with the values of the calculated binding dissociation energies (BDE), which average 38.2 kcal·mol^{-1} for Cl and 29.5 kcal·mol^{-1} for CO. A charge distribution analysis (CDA)[16] shows that the ethylene gives the same amount of electrons to the metal (0.437 for CO and 0.425 for Cl) but receives almost three times more in the case of Cl (0.276) than in the case of CO (0.102) through back-donation, which accounts for the determining influence

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of the latter interaction in the geometry and energy pattern of these olefin complexes.

Additional minima **2X** in which $CH_2{=}CH_2$ is bonded trans to H ($CH_2{=}CH_2$ eclipses Ru−P) were located. In the case of Cl, the secondary minimum **2Cl** is at high energy (18.9 kcal·mol^{-1}) above **1Cl**, whereas coordination cis and trans to H is much more competitive for [Ru]H(CO)$^+$ since **2CO** is only +3.3 kcal·mol^{-1} above **1CO**. The difference in behavior between [Ru]HCl and [Ru]H(CO)$^+$ with respect to the coordination of a π-acceptor ligand is due to the larger π back-donation with X = Cl. Examination of the geometry of **2CO** reveals some structural features that have been observed experimentally. The P−Ru−P angle is strongly bent (158.6°) because the C═C and Ru−P bonds are eclipsed (the small ∠P−Ru−P increases back-bonding into π^*_{CC}). The spectroscopic data on $Ru(H)(CO)(CH_2{=}CH(CH_3))(L)_2^+$ suggest an olefin coordinated trans to H and give a significantly bent P−Ru−P angle.[4] In conclusion, [Ru]HCl has a strongly preferred coordination site for ethylene cis to H, whereas [Ru](H)(CO)$^+$ is more isotropic. This is a key factor for allowing close proximity and thus further reactivity between the olefin and the Ru−H bond.

(b) Methyl Vinyl Ether with [Ru]H(Cl) and [Ru]H(CO)$^+$. On the basis of the results obtained for the $CH_2{=}CH_2$ adduct, only coordination of $CH_2{=}C(H)(OMe)$ trans to X was considered (Figure 1). The unsymmetrically substituted olefin has no preferred orientation for coordination of the C═C bond since the difference in the energies between **3X** and **4X** is less than 1 kcal·mol^{-1}. Adducts **3Cl** and **4Cl**, whose structures are shown as **3Cl$_{ST}$** and **4Cl$_{ST}$** in Figure 2, present no remarkable structural features. In a square-pyramidal geometry with apical hydride, the C═C bond is parallel to Ru−H. In contrast, **3CO** and **4CO** present some remarkable structural features. In **3CO**, shown as **3CO$_{ST}$** in Figure 2, the C═C bond is notably twisted out of the Ru−H−(CO) plane (dihedral angle H−Ru−C−C = 35°), which brings the methoxy oxygen close to Ru (Ru···O = 2.65 Å for CO compared to 2.98 Å for Cl) while keeping the Ru−C distance rather long (average of 2.36 Å for CO vs average of 2.18 Å for Cl). The conformation taken by OCH_3 in the methyl vinyl ether adduct also suggests the presence of an Ru···O interaction for X = CO and not for X = Cl. For CO, OCH_3 is oriented to have a lone pair directed toward the Ru empty coordination site, and for Cl the lone pair points in the opposite direction. The distance between Ru and O is sufficiently short to suggest that $CH_2{=}CH(OMe)$ is bonded like a four-electron three-center ligand. In **4CO** (**4CO$_{ST}$** in Figure 2), $CH_2{=}CH(OMe)$ is mostly bonded through its CH_2 group (Ru−C 2.327 Å), and the bond to the substituted carbon is greatly elongated (2.614 Å), which permits a very short bond to be established between C(sp^2) and the ether oxygen (1.319 Å vs 1.347 in **3CO** and 1.37 in **4Cl**). In **4CO**, the olefin could be viewed as σ bonded to an sp^3 carbon adjacent to a C(H)═O(Me)$^+$ group. A similar distortion has been observed in $CpFe(CO)_2(CH_2{=}CH(NR_2))^+$ with a highly unsymmetrically π-bonded vinylamine group.[17]

Like for ethylene, methyl vinyl ether is more strongly bonded to [Ru]HCl (35.6 kcal·mol^{-1}) than to [Ru]H(CO)$^+$ (33.8 kcal·mol^{-1}), but the difference in the BDE is greatly reduced. This comes from the fact that the binding energy of methyl vinyl ether to [Ru]H(CO)$^+$ is 4.3 kcal·mol^{-1} *stronger* than that of ethylene to [Ru]H(CO)$^+$, but the reverse order is calculated for [Ru]HCl (methyl vinyl ether binds 2.6 kcal·mol^{-1} more weakly than ethylene). There is thus a coupled influence of the X ligand and of the substituent on the BDE of olefins. Although several factors could contribute to these variations in binding energies, these results are consistent with the more (less) electron-rich olefin, namely, methyl vinyl ether (ethylene) binds preferentially to the more (less) electrophilic metal fragment, namely, [Ru]H(CO)$^+$ ([Ru]HCl).

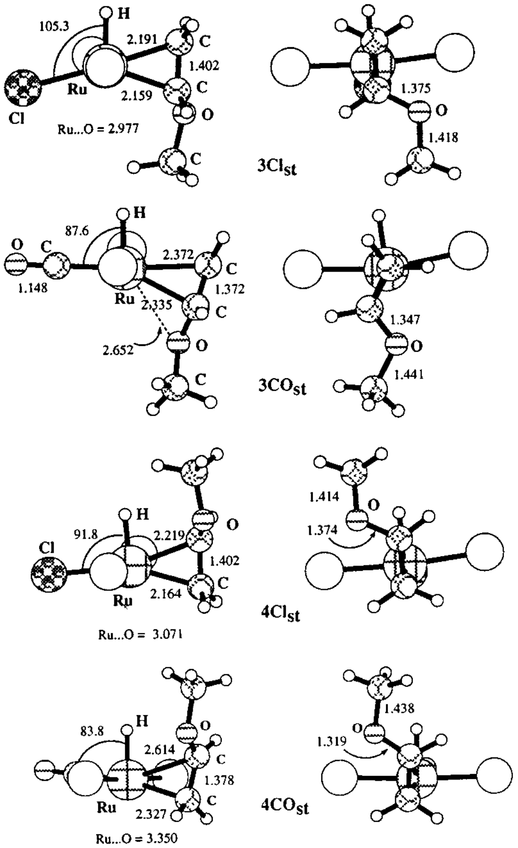

Figure 2. B3PW91 optimized structures for selected complexes. Distances in Å, angles in deg.

The presence of a Ru···O interaction in **3CO** suggests that the oxygen center of the methyl vinyl ether is also a candidate for bonding by itself to the empty sites on the metal. Oxygen-bonded methyl vinyl ethers, **5Cl** and **5CO**, were located as minima 24.2 and 7.8 kcal·mol^{-1} above the most stable corresponding η^2-C═C bonded adduct, respectively. These numbers indicate a large difference in stability with varying X. Despite these energetic differences, the Ru···O distance is remarkably similar in **5Cl** (2.234 Å) and **5CO** (2.233 Å) (see later). In **5CO** (structure **5CO$_{ST}$** in Figure 3), the calculations show that one H of the vinylic CH_2 group approaches the empty coordination site of the metal at a distance, 2.54 Å, characteristic of a weak agostic bonding. For **5Cl**, the longer Ru−CH_2 (Ru−H = 2.82 Å) indicates the absence of an agostic interaction. Thus, oxygen-bonded ether is not to be expected in the case of [Ru]HCl but is a likely competitor in the case of [Ru]H(CO)$^+$, which is

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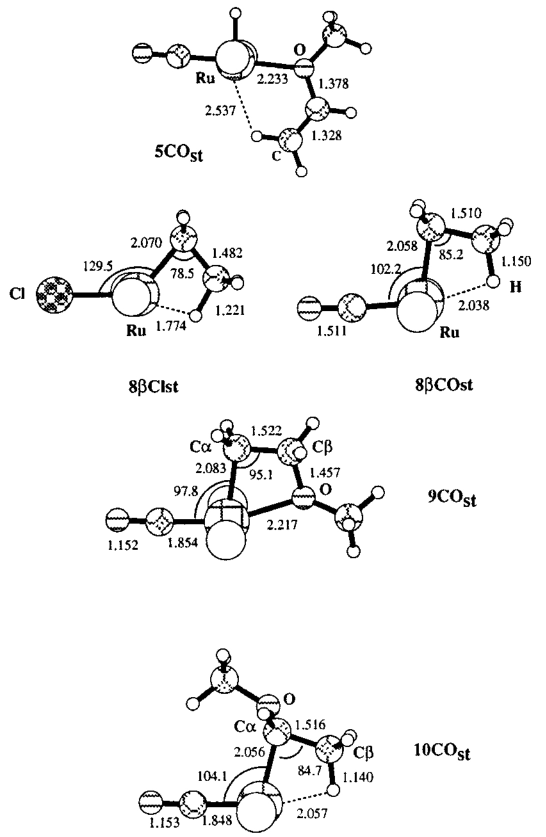

Figure 3. B3PW91 optimized structures for selected complexes. Distances in Å, angles in deg.

consistent with the expected electrophilic character of $[Ru]H(CO)^+$. In the case of methyl vinyl ether, the competition between C═C and O-bonded methyl vinyl ether is probably also influenced by steric factors, which are in favor of O coordination, and thus the two modes of coordination are calculated to be competitive. Experimental results presented in the preceding paper favor the coordination via the oxygen of the alkyl vinyl ether.

The E-Group Dependence for Isomerizing CH_2═CHE into MeC(E) with [Ru]HCl or $[Ru]H(CO)^+$. The energy difference (ΔE, Figure 4) between free C_2H_4 and singlet free $C(CH_3)(H)$ is 79.1 kcal·mol^{-1}. This value is drastically decreased by substituting H by OMe on the carbene carbon (41.6 kcal·mol). The stabilization is even larger if $C(CH_3)(H)$ is bonded to [Ru]HCl (15.9 kcal·mol^{-1}) or $[Ru]H(CO)^+$ (23.4 kcal·mol^{-1}). The stronger Ru═$C(CH_3)$(H) interaction is also evident from the Ru═C distance, shorter for X = Cl (1.84 Å) than for X = CO (1.92 Å). Finally, the joint effect of OMe and the metal fragment makes the transformation essentially thermoneutral (1.5 for X = Cl and 2.2 for X = CO, Figure 4) and thus feasible in the absence of a kinetic barrier or other reaction channels. This set of results fully accounts for the experimental observations[2,4] that 2,3-dihydrofuran isomerizes in the time of mixing to the cyclic O-stabilized carbene complex for $RuHCl(P^iPr_3)_2$ and $RuH(CO)(P^tBu_2Me)_2^+$. In no case was such isomerization observed for ethylene.[2,4]

Why has CO an unfavorable effect in the case of the isomerization of the C_2H_4 adduct into the CH(Me) complex and *not* in the case of the isomerization of the methyl vinyl ether adduct into the methoxycarbene complex (Figure 4)? The π-donor group (OMe) stabilizes the *free* methyl carbene by 37.5 kcal·mol^{-1}, and the coordination to [Ru]HCl lowers the energy of the isomerization by 63.2 kcal·mol^{-1} for C_2H_4. If the stabilizing effects were *additive*, the simultaneous presence of OMe and the metal fragment would have made the isomerization exothermic (stabilization of 37.5 + 63.2 = 100.7 kcal·mol^{-1}). The joint presence of OMe and [Ru]HCl lowers the isomerization energy by only 77.5 kcal·mol^{-1}, a consequence of competition between the two donating groups. Diminishing the electron-donating power of one of the two partners, i.e., [Ru]HCl into $[Ru]H(CO)^+$, can thus be compensated by increased donation from the other group (OMe).

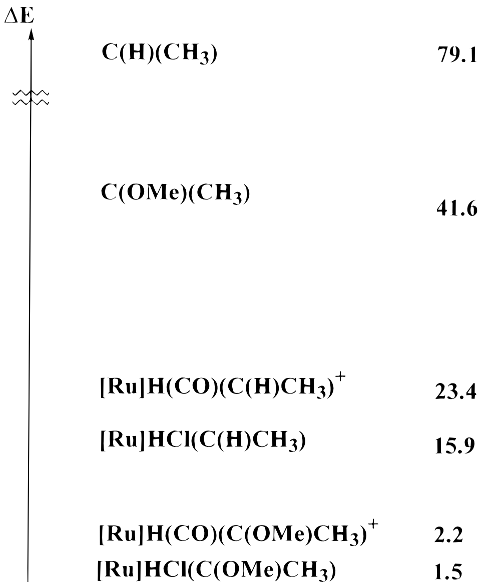

Figure 4. Energies (kcal·mol^{-1}) of carbene species C(E)(Me) relative to their olefin form (CH_2 = CHE) (E = H, OMe) in the presence or absence of $[Ru]HX^{q+}$ (X = Cl, q = 0; X = CO, q = 1).

Only one minimum (a distorted trigonal bipyramid with a small H−Ru−C angle[2]) has been located for [Ru]HCl(═C(Me)(H)), **6Cl**, whereas several minima, **6_{1-3}CO** (with square-pyramidal geometries and the carbene trans to CO or to the empty coordination site) are close in energy (23.4−24.6 kcal·mol^{-1}) for $[Ru]H(CO)({=}C(Me)(H))^+$ (Figure 5). In the case of CO, another minimum, **6_4CO**, with the carbene group trans to H has been located 10 kcal·mol^{-1} higher than the previous group of minima. As in the case of the ethylene complex, [Ru]HCl bonds to carbene in a geometrically preferred manner, whereas $[Ru]H(CO)^+$ has more isotropic bonding capability.

In the case of methyl vinyl ether, several isomeric carbene complexes, all with square-pyramidal coordination at Ru, have with the exception of the higher **7_3Cl** also been located as minima on the potential energy surface for Cl and CO (Figure 6). For all isomers, **7_nX** except **7_6CO**, the plane of the carbene is perpendicular to the Ru−P direction, which would also correspond to the best steric arrangement in the real systems. The Ru═C and C(carbene)−O(Me) distances are influenced by the ancillary ligand at Ru. Keeping in mind that Ru and the oxygen lone pair both give electron density to the empty p orbital of the carbene, an increasing donation from the metal fragment (Cl vs CO) shortens the Ru═C bond (average 1.90 Å for Cl and 2.02 Å for

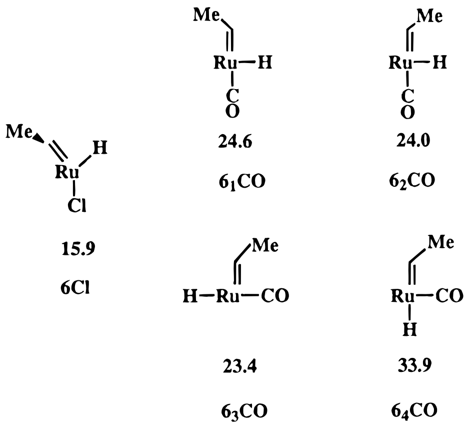

Figure 5. Schematic representation of the optimized structures for $RuH(X)(PH_3)_2(C(H)Me)^{q+}$ (X = Cl, $q = 0$; X = CO, $q = 1$). The up and down PH_3 have been removed for clarity. Energies (kcal·mol^{-1}) are given with respect to the most stable olefin adduct shown in Figure 1.

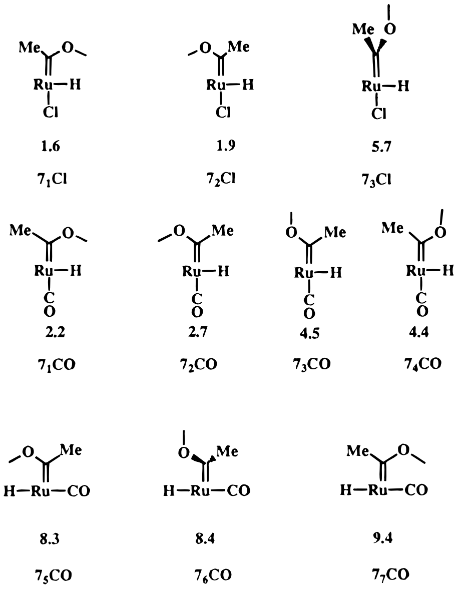

Figure 6. Schematic representation of the optimized structures for $RuH(X)(PH_3)_2(C(OMe)CH_3)^{q+}$ (X = Cl, $q = 0$; X = CO, $q = 1$). The up and down PH_3 have been removed for clarity. Energies (kcal·mol^{-1}) are given with respect to the most stable olefin adduct shown in Figure 1.

CO) and lengthens the C(carbene)−O(alkoxy) bond (1.33 Å for Cl and 1.29 Å for CO). The competition for the metal fragment and OMe substituent to donate electron density into the empty carbene p orbital (already apparent from the ΔE values, Figure 4) accounts for coupled variations of the Ru=C and C−O(Me) bond lengths. Despite the presence of an empty coordination site, the C(Me)(OMe) group was not found to make an additional Ru···O interaction. Thus, **7$_3$CO** has no short Ru···O distance (2.82 Å) and the Ru−C$_\alpha$−O angle is 114°.

The geometry of the complexes was experimentally determined for a large number of alkoxy carbene systems in the case of Cl. The square-based pyramidal geometry with apical hydride suggested by NMR and NOE analysis[2] is in full agreement with the calculated structure of [Ru]HCl(C(CH_3)(OMe)). In the case of CO, the carbene complex results from the isomerization of 2,3-dihydrofuran.[4] The cyclic nature of the carbene is approximated by the Me−C$_\alpha$−O−Me sequence in **7$_4$CO** and **7$_6$CO**. The NMR data suggest a square-pyramidal structure with trans H and CO like **7$_6$CO**, which is less stable than **7$_3$CO**. However, the small differences in energy between all calculated carbene isomers (separated by less than 5 kcal·mol^{-1}) show that the experimentally observed structure is among the group of competing structures.

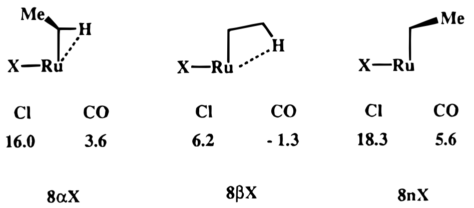

Figure 7. Schematic representation of the optimized structures for $Ru(X)CH_2CH_3^{q+}$. α(β) refers to an α(β) agostic structure. n refers to a nonagostic structure (see text). The up and down PH_3 have been removed for clarity. Energies (kcal·mol^{-1}) are given with respect to the most stable olefin adduct shown in Figure 1.

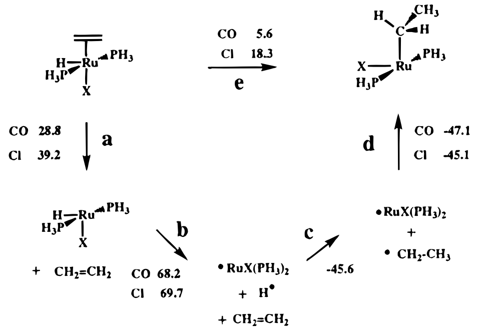

Figure 8. Thermodynamic cycle (energies in kcal·mol^{-1}) for the insertion of C_2H_4 into the RuH bond of RuH(X)-$(PH_3)_2^{q+}$ (X = Cl, $q = 0$; X = CO, $q = 1$).

The Insertion Reaction. Products resulting from the insertion reaction of olefins into the Ru−H bonds have been experimentally observed for X = CO only (proven by production of but-2-ene for ethylene and by Ru η^2-alkoxy alkyl complex for noncyclic vinyl ether).

(a) From Ru(H)(X)(C_2H_4)(PH_3)$_2$ to Ru(X)(CH_2CH_3)-(PH_3)$_2$. A 14-electron four-coordinate ethyl complex results from the insertion of ethylene into the Ru−H bond, which is stabilized by α (**8αX**) or β (**8βX**) agostic interactions, Figure 7. A species deprived of any agostic interaction (**8nX**) has been calculated to be the transition state between **8αX** and **8βX** and can therefore be considered as a "true" 14-electron complex. These species have been calculated to be on the pathway for the isomerization of [Ru](H)(Cl)(CH_2=CH_2) into [Ru](H)(Cl)-(C(H)(CH_3)).[2]

The geometry of **8nX** is analogous to the sawhorse geometry of $RuHX(PH_3)_2$ and does not depend much on X (C$_\alpha$−Ru−Cl = 104.5°, C$_\alpha$−Ru−C = 92.6°), but its energy relative to the ethylene adduct **1X** is much higher for Cl (+18.3 kcal·mol^{-1}) than for CO (+5.6 kcal·mol^{-1}) (Figure 7, Table 1). The stabilization, with respect to **8nX**, via α agostic interaction is small and independent of X (around 2 kcal·mol^{-1} for either Cl or CO) and considerably larger for the β agostic interactions, especially for Cl (6.9 kcal·mol^{-1} for CO and 12.1

Table 1. Nonagostic 8_nX and Agostic Structures $8_{\alpha}X$ and $8_{\beta}X$ for $[Ru](X)(CH_2CH_3)^q$ ($X = Cl$, $q = 0$; $X = CO$, $q = 1$)[a]

	8αCO	**8βCO**	**8nCO**	**8αCl**	**8βCl**	**8nCl**
ΔE	3.6	−1.3	5.6	16.0	6.2	18.3
dE	−2.0	−6.9	0.0	−2.3	−12.1	0.0
C−H agostic	1.10	1.15	1.10	1.13	1.22	1.10
C−C	1.51	1.51	1.51	1.51	1.48	1.51
Ru···H	2.45	2.04	>2.59	2.33	1.77	>2.60
$X-Ru-C_{\alpha}$	95.4	102.2	92.6	122.3	129.5	104.5
$Ru-C_{\alpha}-H_{\alpha}$	95.7		103.2−109.1	91.2		105.9−107.4
$Ru-C_{\alpha}-C_{\beta}$		85.1	113.1		78.5	116.2
ν_{na}(CH)	3043−3178	3108−3197	3033−3148	3025−3192	3095−3197	2988−3116
ν_{a}(CH)	2947	2546		2779	1923	

[a] Distances in Å, angles in deg, and vibrational frequencies in cm^{-1}. ΔE (kcal·mol-1) is the energy relative to the ethylene adducts **1X**, dE is the energy relative to **8nX**. ν_a is the calculated frequency (cm^{-1}) for the agostic CH bonds and ν_{na} (CH) for the nonagostic CH bonds on the same carbon center.

kcal·mol^{-1} for Cl). Consequently, the β agostic ethyl complex **8βX** is 1.3 kcal·mol^{-1} *below* the ethylene adduct for CO and remains 6.2 kcal·mol^{-1} *above* the ethylene adduct for Cl.

Replacing Cl by CO is thus energetically beneficial for the intrinsic stability of the 14-electron complex **8nX** relative to the ethylene adduct **1X** since **8nCO** is close, although higher, in energy to **1CO** whereas **8nCl** is far above in energy from **1Cl**. A thermodynamic cycle was designed (Figure 8) to provide an interpretation for the calculated trend. The CO ligand diminishes the bond dissociation energy (BDE) of ethylene to [Ru]HX (step a) most likely because of diminished π-back-donation. Step b (or d) corresponds to the homolytic cleavage (or reverse reaction) of Ru−H (or Ru−ethyl) bonds. This agrees with previous studies that have shown that an M−H bond is stronger than an M−C bond for late transition metal complexes.[18] It also appears that these binding energies do not vary much with X. The major contributor to the different energies of step e for Cl and CO is thus step a, namely, in the binding energy of ethylene.

The larger stabilization associated with the β in comparison to the α agostic interaction is well documented in various species and deserves no additional comments.[19,20] Focusing on the β agostic interaction, the influence of X is somewhat surprising. It has been stated that agostic interactions are favored by positive charge on the metal.[21] Our results contradict this statement since the interaction energy is twice as large for the neutral **8βCl** than for the cationic **8βCO** (Figure 7). This suggests that agostic interaction is not entirely determined by the alkyl group acting as an electron donor to the Lewis acidic electron-deficient complex. The elongation of the β agostic C−H (1.22 Å) (**8βCl**$_{\mathbf{ST}}$, Figure 3, Table 1) is the highest reported through calculations and contrasts with the elongation calculated in **8βCO** (1.15 Å) (**8βCO**$_{\mathbf{ST}}$, Figure 3, Table 1), which is more typical of an agostic bond.[19,20] These geometrical features are fully supported by calculations of the C−H frequencies (Table 1), which show that the β C−H bond vibrational frequency is significantly lowered with respect to the nonagostic C−H bond in the same structure and is more lowered for Cl than for CO (2546 cm^{-1} vs 3108−3197 cm^{-1} in **8βCO**; 1923 vs 3095−3197 cm^{-1} in **8βCl**). While quantitative aspects of these agostic interactions may vary with the level of calculation, the significant difference between the CO and Cl^{-} analogues should still appear.[22]

(b) From the Ru−Vinyl Ether Adduct to the OMe-Substituted Alkyl Complex. After insertion of the methyl vinyl ether into the Ru−H bond, the OMe group can be on C_{α} or C_{β} in the ethyl ligand depending on the regioselectivity of the insertion. The methoxy oxygen atom is itself a likely candidate for coordinating to Ru in place of a C−H bond. Two reference 14-electron complexes deprived of either C−H agostic or Ru···O interaction with OMe at the α or β carbon have been obtained by constraining the $X-Ru-C_{\alpha}-H$ dihedral angle to 0°. The energies of the resulting eight structures are given in Figure 9. The reference 14-electron species, as well as the agostic complexes, are at higher energy for Cl than for CO, which thus reproduces some of the trends found in the case of ethylene.

(i) X = CO: Thermodynamic and Kinetic Isomers. The calculated most stable alkyl isomer, **9CO** (Figure 9), whose structure is **9CO**$_{\mathbf{ST}}$ in Figure 3, has a Ru···O bond and OMe on C_{β} and corresponds to the complex $Ru(CO)(\eta^2\text{-}CH_2CH_2OMe)(P^tBu_2Me)_2^+$ characterized in the solid state. Experimental and calculated geometrical parameters are in excellent agreement, especially for the Ru···O distance (calc 2.22 Å vs expt 2.226(8) Å). Two other isomers with OMe on C_{α} are close in energy to **9CO**. Complex **10CO** (with structure **10CO**$_{\mathbf{ST}}$ in Figure 3), stabilized by a β C−H agostic interaction, only 2.2 kcal·mol^{-1} above **9CO** corresponds to the kinetic intermediate characterized by low-temperature NMR spectroscopies at −60 °C. This result is also consistent with the nature of the primary insertion product calculated for [Ru]HCl plus C_2H_4.[2]

(ii) Regioselectivity of the Insertion into the Ru−H Bond. The OMe group has a marked preference to be on C_{α} of the substituted alkyl chain in the true 14-electron complexes for X = Cl and CO. A thermodynamic cycle (Figure 10) was designed to understand this regioselectivity. Step d compares OMe on C_{α} vs C_{β} in the alkyl complexes and can be decomposed in the homolytic cleavage (step a) and formation (step c) of the

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[22] The factors responsible for this especially large agostic interaction in **8βCl** are under study.

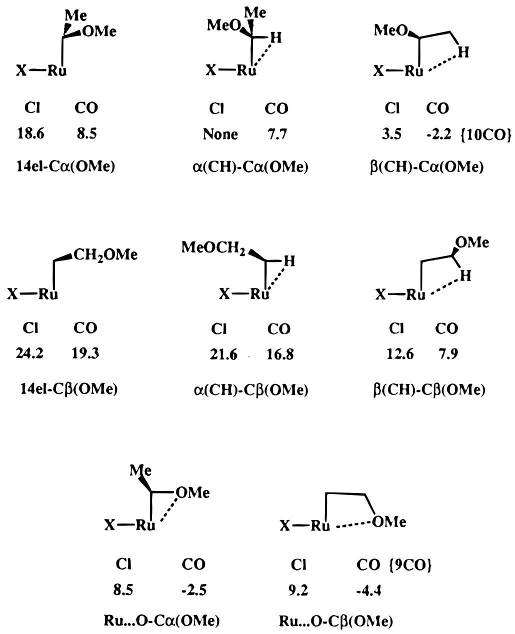

Figure 9. Schematic representation of the optimized structures for the methoxy-substituted ethyl complex of $RuH(X)(PH_3)_2{}^{q+}$ (X = Cl, $q = 0$; X = CO, $q = 1$). The up and down PH_3 have been removed for clarity. Energies (kcal·mol^{-1}) are given with respect to the most stable olefin adduct shown in Figure 1.

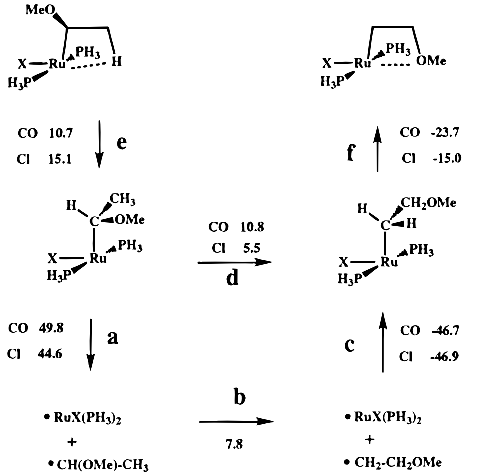

Figure 10. Thermodynamic cycle (energies in kcal·mol^{-1} associated with the α/β OMe substitution in the ethyl complex of $RuH(X)(PH_3)_2{}^{q+}$ (X = Cl, $q = 0$; X = CO, $q = 1$).

Ru−C bond and the OMe transfer from C_α to C_β in the free substituted alkyl radical (step b). The Ru−C BDE depends only little on the position of the OMe group and is close to the value calculated for the nonsubstituted ethyl group (47 kcal·mol^{-1}; X = CO). The major contributor to the regioselectivity of the OMe group seems to be associated with its preference to be on the radical carbon in the substituted ethyl chain (step b). The stabilization of a radical by diverse heteroatomic groups (such as OH, OMe, F) is well documented.[23-27] The β C−H agostic structures have the same regio preference for OMe to be on C_α for either Cl or CO (Figure 9). As obtained for the ethyl complex, the β C−H agostic interaction is larger for Cl than CO (step e in Figure 10).

Table 2. Olefin Bond Dissociation Energy (BDE) in kcal·mol^{-1} and M···O Distance in Å for $[M](CH_3)(X)(OMe_2)^{q+}$ (11X, M = Ru, X = CO, $q = 1$; X = H, Cl, CN, $q = 0$; M = Tc, X = CO, $q = 0$; M = Re, X = CO, $q = 0$)

metal fragment	BDE	M···O
11Cl	14.1	2.25
11CO	22.0	2.25
11CN	7.2	2.33
11H	6.7	2.42
$[Tc](CH_3)(CO)$	12.3	2.37
$[Re](CH_3)(CO)$	10.3	2.33

(iii) X Group Dependence of the Ru···O Interaction. One of the alkoxy oxygen lone pairs could be a good candidate for binding to Ru and thus can modify the C_α/C_β substitution preference. The Ru···O interaction within a three-membered ring gives less stabilizing energy, 11.0 kcal·mol^{-1} (CO) and 10.1 kcal·mol^{-1} (Cl), than that within a four-membered ring (respectively 23.7 and 15.0 kcal·mol^{-1}, step f in Figure 10) due to cyclic constraint. This large stabilization energy associated with the Ru···O interaction in the four-membered ring geometry increases the preference for OMe to be on C_β. In the case of Cl, the two isomers have almost the same energy with still a slight preference by 0.7 kcal·mol^{-1} for OMe to be on C_α (compare Ru···O−C_α (OMe) to Ru···O−C_β (OMe) for Cl in Figure 9). In the case of CO, the preference for OMe to be on C_β is achieved (compare Ru···O−C_α (OMe) to Ru···O−C_β (OMe) for CO in Figure 9), although substitution on C_β is preferred over C_α by only 1.9 kcal·mol^{-1}.

The Ru···O distance does not reflect the Ru···O BDE since the Ru···O distances are calculated to be equal for X = Cl and CO (2.22 Å) despite the 8.7 kcal·mol^{-1} difference in Ru···O binding energy. To probe the role of the cyclic constraint on the Ru···O distance and interaction energy in $[Ru]X(\eta^2\text{-}CH_2CH_2OMe)$, **9X**, the acyclic model complex $[Ru]X(CH_3)(OMe_2)$, **11X**, was studied. The Ru···O distances and BDE of OMe_2 to $[Ru]X(CH_3)$ are within 0.02 Å and 1 kcal·mol^{-1} of that in the cyclic systems (Table 2). The close equivalence between the cyclic and acyclic systems shows that neither the geometrical nor the energetic pattern found in the four-membered species is due to cyclic strain. A similar pattern (equal Ru···O distances and very different binding energies) was also shown in [Ru]H(X) (O-bonded methyl vinyl ether) complexes. The large BDE in the CO case is in agreement with the characterization of an OEt_2 adduct of $RuH(CO)(P^tBu_2Me)_2{}^+$. The short Ru···O bond obtained for X = CO and Cl, which contrasts with the significant difference in BDE, is paradoxical. The large BDE for CO could be associated with the π-accepting capability of CO, which induces a push/pull effect with the oxygen lone pair of OMe_2[28] or with the positive charge of the complex. To study the

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Table 3. RVS Decomposition Analysis for $[Ru](CH_3)(X)(OMe_2)^{q+}$, 11X (X = CO, $q = 1$; X = Cl, $q = 0$)

energy	11CO	11Cl	E(11CO) − E(11Cl)
E_{INT}	−26.8	−13.8	−13
Es	−36.8	−30.7	−6.1
Ex	29.1	32.1	−3.0
Es+Ex	−7.6	1.5	−9.1
POL1	−2.0	−2.1	0.1
POL2	−6.4	−2.9	−3.5
CT1	−1.3	−1.9	0.6
CT2	−6.7	−6.2	−0.5
BSSE1	−0.3	−0.4	0.1
BSSE2	−0.8	−0.9	0.1
TOTAL	−24.4	−11.6	−12. 8
FULL WITH BSSE	−25.7	−12.6	−13.1

relative importance of these two factors in **11X**, two approaches were used. The cationic $[Ru](CH_3)(CO)^+$ species was replaced by neutral isoelectronic fragments bearing no π-donor ligands. Replacing CO by CN^- or H^- or replacing [Ru] by [Tc] or [Re] diminishes the BDE of OMe_2 to the metal fragment by more than 10 kcal·mol^{-1} and lengthens the Ru···O bond by an average of 0.2 Å (Table 2). Consequently, the large OC−Ru$^+$···O interaction seems to be associated with its cationic character. The BDE of OMe_2 in the neutral **11Cl** is larger than in the neutral analogues with non π-donor X ligands probably due to the larger σ-donating ability of CO, H^-, and CN^- vs Cl^-. The same trans influence accounts for the longer Ru···O distance.

A RVS decomposition of the interaction energy between the $\{Ru(Me)(X)(PH_3)_2\}^{q+}$ and OMe_2 fragments was carried out, as an alternative analysis, for X = Cl ($q = 0$) and X = CO ($q = 1$). These computations are carried out between the fragments frozen in the optimized geometry of the whole complex (Table 3). The interaction energies first calculated at the HF level (see Computational Details) are similar to the previously given values and can be thus used for analyzing the origin of the larger stabilization energy for **11CO** than for **11Cl**. Both Es, which describes the electrostatic interaction between the two fragments, and Ex, which is related to the steric repulsion between the two fragments (determined by the overlap between their occupied orbitals), favor the cationic metal fragment with X = CO by 6.09 and 3.02 kcal·mol^{-1}, respectively. Thus, Es + Ex, which depends only on the interacting fragment unperturbed wave functions, strongly (9.11 kcal·mol^{-1}) favors the cationic system with X = CO. The presence of a positive charge is also responsible for the polarization contribution (POL2) of the OMe_2 favoring X = CO over X = Cl by 3.50 kcal·mol^{-1}. The other terms contribute in a negligible manner (less than 1 kcal·mol^{-1}) to the difference between total interaction energies. The results of these computations show clearly the primary importance of the electrostatic forces in the stability of the complexes considered here.

Conclusions

The theoretical studies have shown why olefins can be transformed to a large variety of products by the 14-electron $[Ru]HXL_2$ unsaturated species. Although this study was exclusively concerned with the thermodynamic aspects of the transformations, the availability of the hydride to react with the olefin is implicitly at the hearts of the transformations. A full reaction path study in the case of $[Ru]HCl(PH_3)_2$ and C_2H_4[2] has shown how the hydride is involved in the transformation of the ethylene adduct in the ethyl and carbene complexes. A cis coordination of H and the olefin is therefore a favorable criteria for further reactions. The same arrangement has been calculated to be easily accessible for $RuH(CO)(PH_3)_2(\eta^2\text{-}C_2H_4)^+$. Our results should extend to any olefin since calculations on methyl vinyl ether have shown that the substituent on the olefin plays little role on the starting reactant, the η^2-olefin complex.

The 14-electron alkyl species is calculated to be more energetically accessible with respect to the 16-electron η^2-olefin adduct for X = CO than for X = Cl. The binding energy of the olefin is found to be the controlling factor. Stabilizing the olefin adduct through back-donation (case of Cl) stabilizes the reactant and thus increases the energy difference between the reactant and the more saturated alkyl species. This result is nicely related to the well-known ability for d^0 Cp_2MR^+ complexes to catalyze olefin polymerization.[29] The experimental results presented in the accompanying paper have shown that alkoxy-substituted ethyl complexes with Ru···O interaction could be isolated from reaction of alkyl vinyl ether with $RuH(CO)L_2^+$. Calculations have shown that a strong Ru···O interaction is required to make the ethyl complex energetically competitive with the olefin adduct. Strong Ru···O interaction is shown to be associated with the presence of a CO ligand and a total positive charge on the complex. The presence of a large electrostatic contribution has been shown to be a major component of the stabilization interaction.

In contrast to the formation of the ethyl complex, the formation of the carbene complex is favored by back-donation of the metal fragment to stabilize the methyl carbene group. The stabilizing influence of the metal is nevertheless not sufficient, and the presence of an additional stabilizing interaction from a π-donor substituent on the carbene is required. The presence of these two joined-but-competing stabilizing effects has the paradoxical result to permit the electron-donating power of the metal to vary via change of ligand and charge (from π-donor Cl to π-acceptor CO) without changing the energy of reaction for the transformation of the η^2-olefin adduct into the carbene complex. This suggests that other 14-electron metal hydrido fragments should be able to achieve the same transformation.

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Supporting Information Available: Tables of coordinates for all located maxima. This material is available free of charge via the Internet at http://pubs.acs.org.

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