

Assessment of the Bonding in CpRu(PR₃)X (X = F, Cl, OSiH₃, OCH₃)

C. C. Bickford, T. J. Johnson, E. R. Davidson,* and K. G. Caulton*

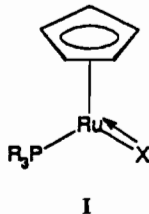
Department of Chemistry, Indiana University, Bloomington, Indiana 47405

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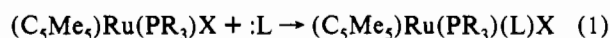
Ab initio SCF calculations were carried out to study the bonding in mirror-symmetric (C₅H₅)Ru(PH₃)X where X = halide, OCH₃, and OSiH₃, with the goal of understanding the effect of X-group lone pairs on the Ru–X bonding. Comparison of these calculations to those where PH₃ has been added, to give mirror-symmetric CpRu(PH₃)₂X (where X = OCH₃), show that the Ru–X π-bonding present in CpRu(PH₃)(OCH₃) is disrupted upon addition of PH₃. Comparison to CpRu(PH₃)₂(CH₃) shows the absence of such changes when the “pure-σ” ligand CH₃ is bound to ruthenium. Comparison to the case CpRu(PH₃)(CO)(OCH₃) reveals how the CO π* orbital stabilizes the otherwise antibonding Ru–OCH₃ molecular orbital and thereby leaves some Ru–O multiple bonding intact. Comparison calculations on mirror-symmetric CpRu(PH₃)(OEH₃) for E = C and Si show the latter to have a longer Ru–O distance and a much flatter energy surface for bending at oxygen.

Introduction

A range of structural and spectroscopic data are consistent with the idea that the Ru–X bond in (η⁵-C₅Me₅)Ru(PR₃)X compounds (X = halide, OR, NR₂) has multiple bond character.¹ Simple electron counting rules (i.e., the 18-electron rule) suggest that a Lewis structure such as I is an appropriate representation



of such molecules.² Nevertheless, such molecules display the chemical reactivity characteristic of Lewis acids (eq 1), thus suggesting that the π donation from a lone pair on X can be eliminated under certain circumstances.



In order to place some of these ideas on a more solid footing, *ab initio* calculations on representative three- and four-ligand molecules have been carried out and analyzed in terms of simple ideas such as multiple bonding and comparative π-donor ability of the group X. We have also investigated the result of varying certain key structural parameters and have sought to identify where possible the orbital interactions which dominate such changes.

Computational Methodology

Due to the complexity of these molecules, we have explored only limited regions of the total energy surface. We benefit here since a considerable number of X-ray structure determinations are available.¹ Since our interest is primarily in the Ru–X bond, as well as deviations in the angle at oxygen in several CpRu(PR₃)(OER')₃ species, we have considered only structures which have a mirror plane of symmetry containing Ru,

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- (1) Johnson, T. J.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1992**, *114*, 2725. Johnson, T. J.; Foltz, K.; Streib, W. E.; Martin, J. D.; Huffman, J. C.; Jackson, S. A.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.*, in press.
- (2) Without the X→Ru π-donation, Ru would have a 16-valence-electron count. Because the 5s and 5p orbitals of ruthenium are found to be ineffective for bonding, the deficiency of valence electrons is less severe than might otherwise be predicted. See below.

P, X (and E), and the center of gravity of the cyclopentadienyl ring. We have reported independently the energy surface for out-of-plane bending and explained there why mirror symmetry gives a minimum energy.¹ Since our interest was more in understanding the atomic orbital interactions which control structural preference, we have not done full geometry optimizations on the Ru–X distance and the Ru–O–E angle, but have instead performed calculations at several points around the experimental values of these parameters. These should represent the general shape of the surface near the experimental equilibrium structure and permit us to identify the changing nature of the atomic orbital composition as one structural parameter is varied. For the halide series, only one point on the energy surface was examined, since the primary interest was in the trends along the series. For the four-ligand molecules (eq 1), only the experimental geometry was examined, since the main interest was the effect of the addition of the fourth ligand.

All calculations were performed using the 6-31G* basis set of Pople³ on all of the atoms except for ruthenium, chlorine, bromine, and iodine. For ruthenium and all halogens except fluorine, we used the pseudopotential of Wadt and Hay.⁴ For ruthenium, their valence (5s, 5p, 5d) basis set was contracted to [2s, 2p, 2d] using atomic SCF calculations. This contraction was performed using the valence ground state (4s²5s²4p⁶4d⁶) to determine the coefficients. The two s-type orbitals were taken directly from this calculation. The first p-type orbital was the 4p orbital from the ground state, while the second was found by taking the 5p orbital from an SCF calculation for the 5s→5p excitation. The d-type orbitals were chosen by contracting the first four primitives in the ground state and leaving the final primitive uncontracted as a radial polarization function. The chlorine, bromine, and iodine contraction was done using the first two canonical s and p orbitals from the anion SCF to go from the Wadt–Hay (3s, 3p) basis to a [2s, 2p] contracted basis. All of the calculations used the MELD programs.⁵

For (C₅H₅)Ru(PH₃)(OCH₃) and (C₅H₅)Ru(PH₃)(OSiH₃), two types of calculations were performed. The first was a simple SCF calculation. Initially, three different electron configurations were considered. These correspond to the six metal d electrons being placed either in an (a')⁶ configuration or in (a')⁴(a'')² or (a'')²(a')⁴. The (a')⁴(a'')² configuration was found to yield the lowest energy with the LUMO being an (a'') orbital. Hence, (a')⁴(a'')² was chosen as the configuration of the ruthenium d electrons for all subsequent calculations.

Once the SCF calculations on the two molecules were completed, two-configuration SCF (TCSCF) calculations were performed in order to determine the best wave function of the form c₁(a')⁴(a'')² + c₂(a'')²(a')⁴. These were undertaken to check for any near-degeneracies in the HOMO. Additionally, as the geometric parameters were changed, it would be possible for the relative importance of the HOMO and the LUMO to change, resulting in a switch of the lowest energy configuration

(3) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 212.

(4) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1982**, *82*, 299.

(5) Developed at the University of Washington by L. McMurchie, S. Elbert, S. Langhoff, and E. R. Davidson; modified by D. Feller and D. Rawlings.

Table 1. Relative Energies of (C₅H₅)Ru(PH₃)(OEH₃) (kcal/mol)

		Ru-O distance	
		1.992 Å	2.028 Å
(Ia) E = C, Ru-O-C = 124.6°			
SCF	0	0	0.44
TCSCF	0	0	0.43
(Ib) E = C, Ru-O-C = 153.4°			
SCF	5.0	5.0	5.4
TCSCF	5.0	5.0	5.4
(IIa) E = Si, Ru-O-Si = 124.6°			
SCF	0.39	0	0
TCSCF	0.40	0	0
(IIb) E = Si, Ru-O-Si = 153.4°			
SCF	0.80	0.66	0.66
TCSCF	0.79	0.64	0.64

of the ruthenium from (a')⁴(a'')² to (a')²(a'')⁴. A TCSCF would verify that there was no significant change in the relative importance of these configurations for changing geometries. For each of the eight calculations (four conformations, each with two substituents (see Table 1)), the second configuration did not contribute more than 4% to the overall wave function. Additionally, the TCSCF and the SCF calculations yielded the same structural predictions for both substituents. As the TCSCF did not contribute any additional insight into the nature of the wave function or the bonding, multiple configurations were not considered in any of the other calculations undertaken.

The geometry was determined using idealized parameters from the experimental structure of (C₅Me₅)Ru(OCH₂CF₃)(PCy₃) where Cy is cyclohexyl.¹ The C-C bond length in C₅H₅ was taken to be the average ring C-C bond length in the C₅Me₅ ring, with an overall D_{5h} symmetry imposed on the C₅H₅ fragment. The distance from the ring to the ruthenium was taken to be the average Ru-C distance in the C₅Me₅ compound. The phosphine hydrogens were placed along the P-C vectors in the experimental structure, while the methoxide hydrogens were placed in a tetrahedral configuration. All other geometric parameters were left unchanged. In another set of calculations, the Ru-O bond length and Ru-O-R angle were changed to the experimental values for (C₅Me₅)Ru(OSiPh₃)(PCy₃).¹ The halide geometries were chosen by using the geometry for (C₅Me₅)Ru(OCH₂CF₃)(PCy₃) but replacing OCH₂CF₃ by halide. The chloride was added at the experimental distance.⁶ For the other halides, the sum of the covalent radii was used.⁷ In the four-ligand cases, the experimental geometry for the CO adduct was used, with the appropriate substitutions on the ligands.⁸ The bis(phosphine) structure was established by symmetrizing the (C₅Me₅)Ru(CO)(OCH₂CF₃)(PCy₃) complex,¹ removing the carbonyl, and inserting another phosphine at the appropriate symmetric geometry.

MO labeling uses the convention that the HOMO is "1", with the deeper occupied orbitals numbered from the top down.

Results and Discussion

General Comments on the Bonding in (C₅H₅)Ru(PH₃)X. The metal coordination geometry of this complex may be regarded as derived from square-planar. In this view, the PH₃ and X groups occupy two sites and the Cp (i.e., C₅H₅) ring sits perpendicular to the plane of the complex and occupies the other two corners of the square. The plane of the Ru, P, O, and the Cp midpoint is a mirror plane of symmetry (the xy plane in II; z is perpendicular to the xy plane). The advantage of recognizing this structural parentage is that the d orbital splitting pattern in the molecule becomes more readily recognizable.

The calculations show that the ligands impose a d orbital occupancy of (d_{xz})²(d_{x²-y²)²(d_{z²})², which allows the six d electrons to avoid the approach direction of the ligand σ electrons as much as possible. In this way, the σ-bonding framework "locks in" the d orbital occupancy, and any π interaction with the group X (or bending of the group OEH₃) will have to adapt to this pattern}

(6) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Chem. Soc., Chem. Commun.* **1988**, 278.

(7) Calculations at Ru-F distances 0.05 Å longer or shorter than the sum of covalent radii gave higher total energies. Additionally, the experimental Ru-Cl distance does equal the sum of covalent radii.

(8) These therefore have no symmetry.

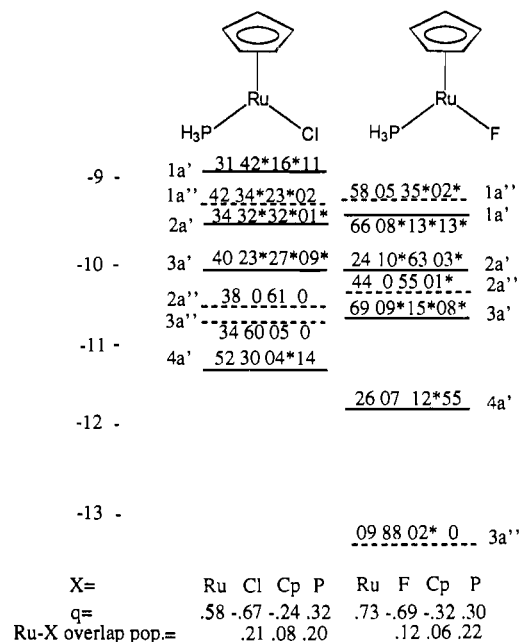
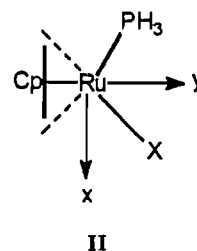


Figure 1. Orbital energies (electronvolts), percent atomic orbital contributions, Mulliken atomic charges (q), and Ru-X overlap populations for mirror-symmetric CpRu(PH₃)X. Solid lines are orbitals of a' symmetry, and dashed lines are a'' orbitals. The order of AO percent composition follows the labels at the bottom of the figure, and asterisk indicates an Ru-X antibonding phase. Thus 4a' is 52% Ru, 30% Cl, 4% Cp, and 14% PH₃ and is Ru-Cp antibonding but bonding between Ru and P and Cl.



of occupied and empty d orbitals. For example, the filled d_{x²-y²} will result in a four-electron destabilization (filled/filled interaction) with the occupied in-plane p orbital on X, π(||). This is a consequence which can be anticipated from the 18-electron rule, since one brings up to the 15-valence electron CpRu(PR₃) fragment a radical X (all considered uncharged) which carries more than one lone pair (for *OR and halogen), rather than the required one (e.g., *NR₂ or *PR₂). The empty d_{yz} is a π-acceptor orbital with respect to the occupied out-of-plane π(⊥) orbital of X and of Cp and thus can lead to charge transfer between X and Cp. The directional character of the filled d_{z²} orbital makes it only minimally metal-ligand antibonding. Finally, the empty d_{xy} orbital can function as a σ acceptor from all ligands.

Halide Compounds. Comparison of the results for two monatomic ligands X is a useful starting point for the analysis of the orbital pattern for CpRu(PR₃)X species and for the effect of varying halide characteristics on the Ru-X bond. The halides F and Cl are compared in Figure 1. In the a' subspace, the empty d_{xy} orbital points toward filled orbitals of all ligands and acts as an acceptor orbital. The d_{x²-y²} orbital points between the ligands and is doubly-occupied. The directional character of the d_{z²} orbital makes it minimally metal-ligand overlapping so the antibonding combination is sufficiently low in energy to contain another of the metal d² electron pairs. In the a'' subspace, there are three electron pairs (one from Cp, one from the metal, and one from X) to distribute. The d_{yz} metal orbital acts as an acceptor orbital for the filled X and Cp orbitals in 3a''. In 3a', the filled X and Cp orbitals enter with a sign pattern that makes them orthogonal

Table 2. Mulliken Parameters upon Stepwise Addition of Halogen to CpRu(PH₃)⁺

	(Cp)RuPH ₃ ⁺ e ^{-a}				
	(Cp)- RuPH ₃ ⁺	(F)	(Cl)	(Cp)- Ru(PH ₃)(F)	(Cp)- Ru(PH ₃)(Cl)
	Charge				
Ru	+0.55	+1.0	+0.89	+0.73	+0.58
Cp	+0.08	-0.31	-0.22	-0.32	-0.24
PH ₃	+0.37	+0.31	+0.33	+0.30	+0.32
halide				-0.69	-0.67
	Overlap Population				
Ru-Cp	0.22	0.20	0.21	0.06	0.08
Ru-P	0.22	0.22	0.23	0.22	0.20
Ru-halide				0.12	0.21

^a This column represents the positive fragment with a point charge added at the distance appropriate to the halide indicated.

to all metal d orbitals so they remain localized on the ligands. The 2a' MO is nominally a metal d² electron pair in d_{xz} with antibonding overlap with X but favorable overlap with the empty Cp e₂ orbital which allows some π back-bonding to Cp. This MO should be most responsive to charge transfer from X to Cp.

The total bond overlap population (bottom of figure) shows that changing from fluoride to chloride nearly doubles the Ru-halide values. Neither the Ru-Cp nor the Ru-P overlap population changes significantly as the halide is varied. The smaller Ru-F overlap population (a gauge of "covalency") suggests greater ionic character for the Ru-F bond. Mulliken atomic charges also change with altered halide. The metal is significantly more positively charged in the fluoro complex, consistent with a more ionic bond for the more electronegative halide. However, it is interesting that the lost charge goes not only to the halide but also to the Cp ring; there appears to be charge transfer, not only in the Ru→F σ sense (based on fluoride electronegativity) but also by π-back-bonding to the Cp ring.

These changes arise both from addition of a charge to the (Cp)RuPR₃⁺ fragment and from the donation of electrons from the halide to the metal. These two effects are seen most clearly by calculating them in a stepwise fashion. Table 2 shows that the Ru-P bond in the positively-charged Ru(Cp)PH₃⁺ fragment already has the overlap population of that in CpRu(PH₃)X. The Cp, however, carries a positive charge and compensates for the lost electron density (and lost ionic bonding) with a stronger covalent bond (note larger Ru-Cp overlap population in CpRuPH₃⁺ compared to that in CpRu(PH₃)X). Upon addition of a negative point charge at the fluoride site in the complex, the electrons on the ruthenium are repelled toward the Cp ring. This results in the ruthenium carrying a large positive charge and the Cp a negative charge (roughly equal to that carried in the actual fluoride complex), creating an ionic bond between Ru and Cp. There is a corresponding 10% decrease in the Ru-Cp overlap population. Replacement of the point charge by the fluoride (i.e., with orbitals) then results in some donation from fluoride to the metal. The chloride shows similar effects. Additionally, the metal center is not as highly charged for Ru-Cl since the chlorine is less electronegative, resulting in a more covalent bond (as reflected in the larger Ru-Cl overlap population compared to that of Ru-F).

The ionic character deduced for the Ru-F bond from overlap populations is also supported by the Mulliken atomic charges. The ionic contribution to the Ru-X bond strength ($q_{Ru}q_X/R_{Ru-X}$) is larger for X = F not only because both charges are larger but especially because the bond length is a full 0.5 Å (~25%) shorter.

The dependence of orbital energies on halide identity (Figure 1) can also be rationalized to some extent on the basis of the atomic orbital energies for the free anion of each halide (Table 3). The point is clearest for those MO's which have large halide participation. Thus, the deeper-lying fluoride causes 3a'', 5a', and 6a' to drop on moving from chloride to fluoride. Note that,

Table 3. Halogen Atomic Orbital Energies (eV), Overlap Integrals, and Mulliken Charges

	E(ns) ^d	E(np) ^d	pσ	pπ	Mulliken charge ^c	
			overlap ^a	overlap ^b	halogen	ruthenium
fluorine	-40.22	-28.17	0.124	0.080	-0.69	+0.73
chlorine	-27.74	-19.20	0.100	0.065	-0.67	+0.58
bromine	-25.62	-16.95	0.097	0.070	-0.50	+0.41
iodine	-22.70	-14.97	0.084	0.061	-0.52	+0.35

^a $\langle p\sigma|d_{x^2-y^2} \rangle = 3^{1/2}\langle p\sigma|d_{z^2} \rangle$ using halide anion orbital. ^b $\langle p_{\perp}|d_{xz} \rangle = \langle p_{\parallel}|d_{xy} \rangle$ using halide anion orbital. ^c In CpRu(PH₃)X. ^d Neutral-atom orbital energies (using uncontracted (3s, 3p) basis for chlorine, bromine, and iodine).

in each of these cases, the halide character in these MO's increases on going from chloride to fluoride. This is another reflection of increased ionic character in the wave functions.

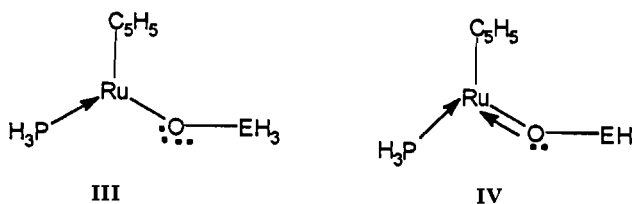
The 4a' orbital also drops in energy from Cl to F, but it does not gain increased halogen character. It loses halogen character and becomes dominated by phosphorus character. This localization is a reflection of the general trend for less mixing in every MO when X = F compared to X = Cl.

The orbitals 1a', 2a', 3a', and 1a'' have much more equal participation by Ru and X when X is chlorine, due to the better energy match of the Ru and Cl orbitals. Because of the presence of more than 18 valence electrons (i.e., several halide lone pairs), these orbitals also exhibit a fundamental feature anticipated in the 18-electron rule: interactions between filled d and filled halide p_r orbitals yield frontier orbitals which are Ru-X antibonding. This is especially evident for the more covalent chloride. Finally, for both halides, the orbitals 2a'' and 4a'' have negligible halide character; they are, respectively, Ru-Cp bonding and Cp localized. Both the 2a'' and 4a'' reverse the above trend in which orbitals lie lower in energy for the fluoride. These two orbitals rise in energy from Cl to F since the Cp is more negative for the fluoride, and the Cp character of these MO's thus controls the energy rise.

In the a'' space, where Ru-X π-bonding is easiest to identify, there is strong mixing for the chloro compound but only very weak mixing for the fluoro case. By this criterion, covalent π-bonding (π-donation) is greater with chlorine than with fluorine. This indicates that the smaller energy gap for chlorine is more important than the overlap integral.

Examination of the overlap integrals and Mulliken charges for the full series of four halides (Table 3) shows a regular decrease in positive charge on ruthenium and a decrease in negative charge on halide from F to I. These trends reflect the energy gap between the metal and the halide orbitals. (Note, however, that the σ and π Ru-X overlap integrals all decrease down the halide group, reflecting the fact that Ru-X bond lengthening is more important than X-orbital expansion in determining the overlap trend.) Ruthenium-phosphorus bonding remains relatively unaffected as halide is changed, as judged both from phosphorus Mulliken charge and Ru-P overlap population.

(C₅H₅)Ru(PH₃)(OEH₃) Compounds (E = C, Si). Conventional electron counting would assign 16- and 18-valence-electron counts to the Lewis structures III and IV. The preference for 18 valence



electrons is based on the idea of full utilization of the bonding (and nonbonding) orbitals which originate from 4d, 5s, and 5p valence orbitals (nine in all). Since the calculations reported here reveal rather little use of the 5s and 5p orbitals,⁹ the (ligand-metal bonding)¹⁰(metal-ligand antibonding)⁶ configuration leaves

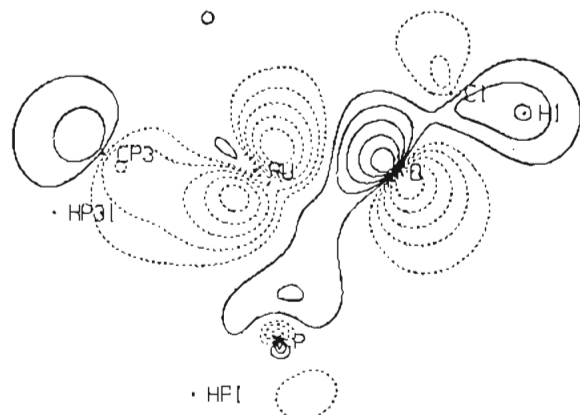
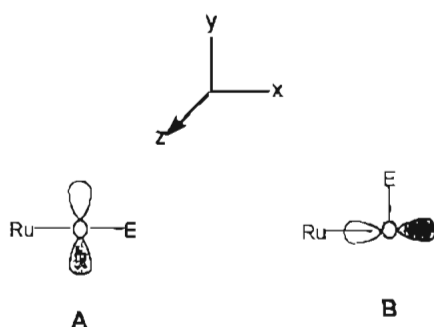


Figure 4. Plot of the $1a'$ orbital of $\text{CpRu}(\text{PH}_3)(\text{OCH}_3)$ in the plane of symmetry, defined by the Ru, P, and O atoms.

Ru–O bond. At an Ru–O–E angle of 180° , the $\pi(\parallel)$ orbital overlaps the metal d_{xy} orbital in a π manner (A) and is orthogonal



to $d_{x^2-y^2}$ and d_{z^2} . At 90° it has purely σ (B) overlap with $d_{x^2-y^2}$ and d_{z^2} and is orthogonal to d_{xy} . For filled d_{xy} and d_{z^2} orbital and empty $d_{x^2-y^2}$ orbital, configuration B is favored. At intermediate angles, the alteration of these roles will strongly influence certain of the resulting molecular orbital energies. Because the (variable) angular parameter lies in the nodal plane of all a'' orbitals, these orbitals will generally be less perturbed as the Ru–O–E angle changes. Figure 3 confirms this point for all a'' (dashed) orbitals of both the methoxide and the siloxide. Figure 4 shows a typical $1a'$ orbital. In this case, the orbital is the antibonding combination of $d_{z^2}-d_{x^2-y^2}$ with the $\pi(\parallel)$ orbital of oxygen.

For both E = C and Si, the major change on decreasing angle Ru–O–E is to alter the energies of $1a'$, $2a'$, and $3a'$. The HOMO, $1a'$, and $3a'$ are mostly metal d orbiting to oxygen and are stabilized on going from A toward B. In both cases, the energy change is less for the siloxide than for the methoxide. This is because the bond between ruthenium and the methoxide is more covalent than that with the siloxide, as judged by Ru–O overlap populations (+0.04 (C) and –0.04 (Si) at 124.6°).¹² Overlap is thus more influential for the more covalent methoxide, and the more ionic compound has a softer energy surface. The siloxide compensates, however, by having a larger overlap population between Ru and Cp (0.08 (E = C) vs 0.16 (E = Si)). It is this smaller influence of bending on siloxide orbital energies which leads to the “softer” (i.e., shallower) total energy surface (Table 1). In general, however, a larger angle (A) weakens the σ component of the Ru–O bond and thus weakens the net bonding. This is tied to the fact (see above) that the oxygen 2s orbital lies so deep in energy that it is ineffective for covalent bonding. Indeed, the siloxide compound has a slightly antibonding Ru–O overlap population at both angles. At the same time, the rise in the $1a'$ energy upon opening the Ru–O–E angle is a result of the energetic

(12) Mulliken overlap populations reflect trends in wave function between analogous molecules, but their absolute values must be interpreted with considerable caution.

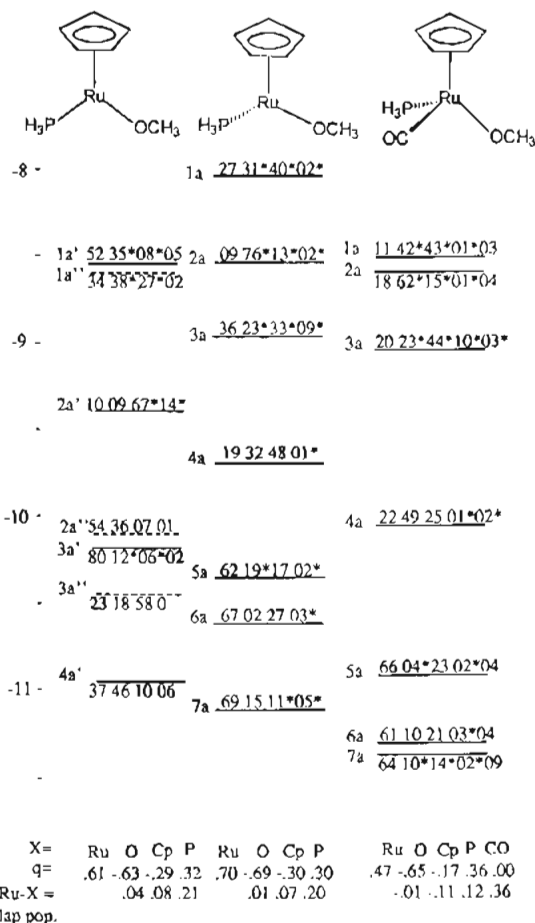


Figure 5. Energies (ev), AO composition, and Mulliken parameters for mirror-symmetric and pyramidal $\text{CpRu}(\text{PH}_3)(\text{OCH}_3)$ and its CO adduct.

remoteness of the 5p metal orbital and thus of its failure to stabilize the HOMO as the angle opens.

Effect of an Added Ligand on the Electronic Configuration at Ruthenium. While studying the changes in the Ru–O–E angle in $\text{CpRu}(\text{PH}_3)(\text{OEH}_3)$, we carried out a TCSCF calculation to determine if other configurations of the ruthenium contributed significantly to the overall wave function as the geometry was varied. It was found that this was not the case. However, a change in configuration is seen in forming the CO adduct $\text{CpRu}(\text{PH}_3)(\text{CO})(\text{OEH}_3)$. The filled–filled repulsion which develops on approach of the CO lone pair to the metal d_{z^2} electrons of mirror-symmetric $\text{CpRu}(\text{PH}_3)(\text{OEH}_3)$ is relieved by moving the d_{z^2} pair into the low-lying d_{yz} orbital of mirror-symmetric $\text{CpRu}(\text{PH}_3)\text{X}$. The d_{yz} orbital is thereby rendered unavailable for π -bonding with Cp and with OR. This change of configuration also occurs simply upon bending back the Cp ring (essentially around the x axis¹³) even before forming a bond to CO (Figure 5).

As a result of this change, the Cp ring in II is no longer able to bond effectively to the d_{yz} orbital and instead bonds to some combination of d_{xz} and $d_{x^2-y^2}$. Since d_{z^2} is now nominally empty, this results in an effective bond, but the back-donation of the d_{xz} orbital to the Cp π^* orbital is disrupted by this change in geometry. This results in little net effect on the magnitude of the overlap population on distortion. Filling of d_{yz} and d_{xz} also results in the Ru–O π -bond being weakened, since no d_x orbitals remain empty to accept the oxygen π electrons. In Figure 5, this effect is seen by following orbital energies, with the destabilization of $2a''$ (going to $2a$ in the distorted complex) as opposed to the stabilization of

(13) The angular parameter P–Ru–Cp(centroid) is relatively unaffected (138° vs 132°). The O–Ru–Cp(centroid) angle, however, goes from 140° to 121° upon carbonylation.

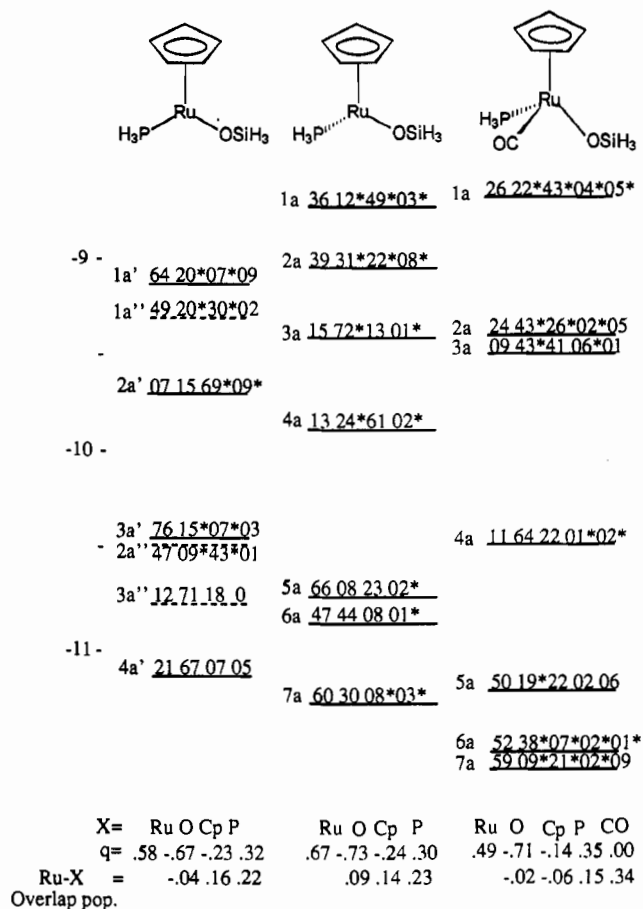


Figure 6. Energies (eV), AO composition, and Mulliken parameters for mirror-symmetric and pyramidal CpRu(PH₃)(OSiH₃) and its CO adduct.

3a'' (going to 7a). The overall energy of the complex increases by 18.9 kcal/mol upon distortion (*without* addition of CO), consistent with the mirror-symmetric form of CpRu(PH₃)(OCH₃) being the overall minimum.¹

The actual addition of the carbonyl (Figure 5) results in the electron density being pulled away from the Cp and onto the ruthenium. This is seen both in the Mulliken charges and in the overlap populations. The spatial character of the d orbitals changes negligibly on addition of carbonyl, relative to the pyramidal complex. The σ -donation of the carbonyl is offset exactly by π -back donation; the carbonyl remains uncharged. The change in the electron density, however, has a large effect on the bonding in the complex. The π -back-donation indirectly removes density from the Ru-Cp bond and Ru-O bond and places it in the Ru-CO bond, by changing the polarization of the predominantly d_{xy} molecular orbital. The addition of the carbonyl results in a stabilization of the distorted (i.e., pyramidal) complex by 19.7 kcal/mol, yielding a net stabilization (bond dissociation energy, BDE) of 0.8 kcal/mol for distortion and addition.¹⁴

As the siloxide is deformed from mirror symmetry (Figure 6), the molecular orbital containing the oxygen p π orbital rises in energy, to a position above the Cp π molecular orbital, similar to the methoxide case. However, there are quantitative differences. The total energy increase (Figure 6) for distortion of the siloxide (which places Cp electron density in the Ru d orbital that mixes with the oxygen p π orbital, thereby destabilizing the d π -p π bond to the alkoxide) is only 13.3 kcal/mol (compared to 18.9 kcal/mol for the methoxide). Additionally, the rise in orbital energy of the d π -p π molecular orbital is less extreme. Both of

(14) While this number is small, calculations on Cr(CO)₆ consistently show BDE's to be underestimated with an SCF wave function. More accurate calculations give better BDE's without changing the qualitative picture of bonding. See: Machado, F. B. C.; Davidson, E. R. *J. Phys. Chem.* 1993, 97, 4397.

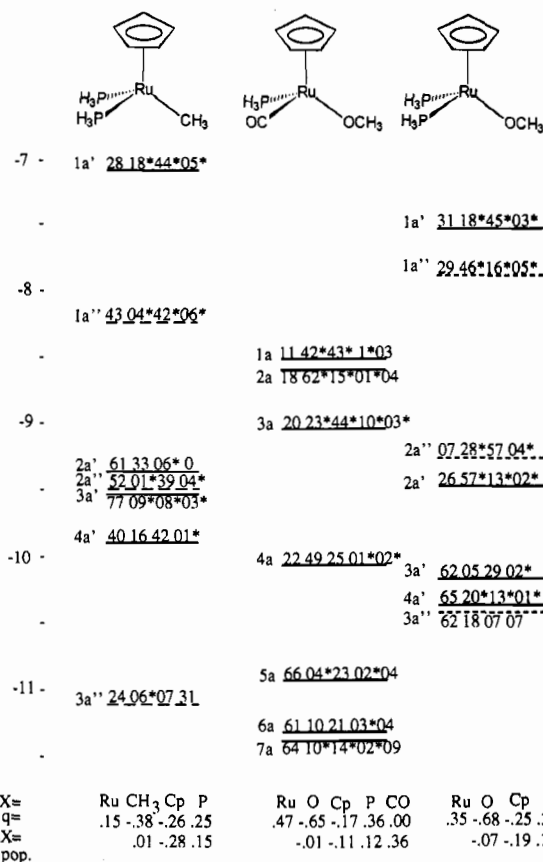


Figure 7. Orbital energies and AO composition for CpRu(PH₃)(L)X species.

these effects are consistent with the fact that the siloxide is a weaker bonding partner than OCH₃.

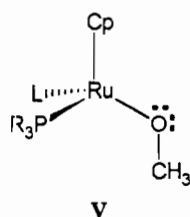
The difference in total energy for CpRu(PH₃)(OEH₃) + CO relative to that of CpRu(PH₃)(CO)(OEH₃) is the bond dissociation energy (BDE) for CO. This calculation gives BDEs of 5.6 kcal/mol for E = Si and 0.8 kcal/mol for E = C. This is consistent with the idea of less CO-induced disruption of O→Ru π -bonding in CpRu(PH₃)(OEH₃) when E = Si. The compound CpRu(PH₃)(OSiH₃) is thus the stronger Lewis acid, or the "more unsaturated".

(C₂H₅)Ru(PH₃)(OCH₃)L Species. To the extent that there is O→Ru π bonding in CpRu(PH₃)(OR), the bonding within adducts CpRu(PH₃)(OR)L should show the disruption of that π interaction in order to allow formation of the Ru-L bond. Such adducts thus serve as useful benchmarks to better understand the orbital pattern of CpRu(PH₃)(OR) itself. We consider first the case where L is a pure- σ donor. The case L = PH₃ approaches this ideal.

(a) Comparison of CpRu(PH₃)₂X (X = CH₃, OCH₃). In assessing the orbital pattern and composition of CpRu(PH₃)₂(OCH₃), a useful and relevant comparison compound is CpRu(PH₃)₂(CH₃). The latter lacks the oxygen lone pairs which are expected to produce filled-filled destabilization in the methoxide. As shown in Figure 7 (far left and right), the HOMO in the a' space changes little in AO composition from OCH₃ to CH₃. This follows since the main change occurs by introduction of the O π orbital, which is of a'' symmetry. The HOMO for both OCH₃ and CH₃ is metal-ligand antibonding. A large change occurs in the a'' HOMO, which takes on much more X ligand character for methoxide than for methyl; this shows the O π charge buildup and, being Ru-O antibonding, is one site where the filled-filled interaction is evident. The overall result of these changes is to make the Ru-X overlap population significantly less antibonding for CH₃ than for OCH₃ and to transfer a major amount of Mulliken charge from Ru to OCH₃ (relative to CH₃).

(b) **Comparison of $\text{CpRu}(\text{PH}_3)(\text{CO})(\text{OCH}_3)$ with $\text{CpRu}(\text{PH}_3)(\text{OCH}_3)$.** The calculation on $(\text{C}_5\text{H}_5)\text{Ru}(\text{OCH}_3)(\text{PH}_3)\text{CO}$ was carried out using the experimental structure for $(\text{C}_5\text{Me}_5)\text{Ru}(\text{P}^i\text{-Pr}_2\text{Ph})(\text{OCH}_2\text{CF}_3)\text{CO}$. Important structural changes implicit in this choice include lengthenings of the Ru–C distance by 0.1–0.2 Å and of the Ru–O distance by 0.1 Å. The results (Figure 5, left and right) show negligible change in O and P atomic charge on coordination of CO. Moreover, the CO assumes zero net charge as a result of net cancellation of σ -donation and π -acceptance. Coordination of CO has the effect of removing 0.12e of charge from the Cp ring and reducing the positive charge on Ru by 0.14e. The overlap populations show greatest covalency for the Ru–CO bond and a reduction in overlap population from Ru to methoxide, PH_3 , and C_5H_5 . The Ru–Cp overlap population is significantly negative (–0.11) in the CO adduct, consistent with the experimentally determined lengthening of the Ru–Cp distances on carbonylation.

Carbonylation takes the Ru–O overlap population from slightly positive (0.04) to slightly negative (–0.01), consistent with bond weakening and lengthening (by 0.1 Å). Application of the 18-electron rule to any $\text{CpRu}(\text{PR}_3)\text{L}(\text{OR})$ molecule (L = Lewis base) suggests localization of two lone pairs on oxygen (V), with



the consequence of two four-electron destabilizations between these lone pairs and two occupied d_π orbitals. This translates into antibonding Ru–O interactions, analogous to the formation of (destabilized) n_A-n_B combinations of lone-pair orbitals in $\text{H}_2\text{N}_A-\text{N}_B\text{H}_2$ or $\text{HO}_A-\text{O}_B\text{H}$. This is evident in Figure 5, which shows the highest (three) occupied orbitals to have Ru–O antibonding character; they are also Ru–Cp antibonding. Also noteworthy is the fact that the highest four orbitals have only moderate metal character but have rather much more OR (and Cp) ligand character. This corresponds to our conclusions from reactivity studies¹ of the increased electron density of alkoxide oxygen upon binding of L to $\text{Cp}^*\text{Ru}(\text{PR}_3)(\text{OR})$.

(c) **Comparison of $\text{CpRu}(\text{PH}_3)_2(\text{OCH}_3)$ with $\text{CpRu}(\text{PH}_3)(\text{CO})(\text{OCH}_3)$.** This pair of compounds permits evaluation of the extent

to which the $\text{CO}(\pi^*)$ orbital can remedy the filled–filled destabilization between $\text{Ru}(d_\pi)$ and O_π orbitals. This would also be called a push–pull delocalization of the four-electron repulsion,¹⁵ which has the consequence of stabilizing the filled π^* Ru–OMe orbital and thus making it less antibonding. Figure 7 (center and right) shows that replacing PH_3 by CO stabilizes every orbital and makes the Ru–O overlap population less antibonding via the dominant Ru–CO interaction. The ruthenium Mulliken charge becomes more positive as a result of replacement of PH_3 by CO.¹⁶ All of these confirm the results expected from simple principles upon introduction of a ligand with a low-lying empty orbital of π -symmetry along the Ru–L bonds. Note that these consequences are possible even from small CO participation precisely because there is so much oxygen character in the four highest MO's and these MO's are significantly Ru– OCH_3 antibonding. Taken together, these calculations show that significant Ru– OCH_3 π -bonding persists in the carbonyl compound because of an effective push–pull interaction through Ru to CO.

Conclusion

By a variety of criteria, there is $\text{X}\rightarrow\text{Ru}$ π -donation in $\text{CpRu}(\text{PH}_3)\text{X}$ species for X = halide, OCH_3 , and OSiH_3 , which is absent when X = CH_3 . In spite of this π -donation, the halide examples present an excess of lone pairs to the metal valence orbitals, and thus the frontier orbitals of these species are Ru–X antibonding in character. Binding of a second PH_3 to $\text{CpRu}(\text{PH}_3)\text{X}$ diminishes the $\text{X}\rightarrow\text{Ru}$ π -donation, while the corresponding binding of CO diminishes such π -donation to a lesser extent due to a push–pull interaction between the CO π^* orbital and the filled Ru–X antibonding frontier orbital. Comparison of $\text{CpRu}(\text{PH}_3)(\text{OEH}_3)$ shows that Ru–O π -bonding and the Ru–O–E angle are both influenced by diminished oxygen lone pair donor power when E = Si.

Acknowledgment. This work was supported by NSF Grants CHE 91 03915 and CHE-9007393.

Supplementary Material Available: A table showing metal orbital participation for $\text{CpRu}(\text{OCH}_3)\text{PH}_3$ and $\text{CpRu}(\text{OCH}_3)(\text{CO})\text{PH}_3$ (1 page). Ordering information is given on any current masthead page.

- (15) Poulton, J. T.; Folting, K.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1992**, *31*, 3190.
- (16) Comparison calculations on $\text{CpRu}(\text{PH}_3)(\text{L})\text{CH}_3$ for L = PH_3 and CO show that the introduction of CO drains only half the Mulliken charge from Ru (0.07e) in comparison to the effect (0.12e) when methoxide is present. The methoxide lone pairs thus dominate the changes on introducing a π -acid ligand.