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Ab Initio Calculations of the Geometries and Bonding Energies of Alkane and Fluoroalkane Complexes with Tungsten Pentacarbonyl

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Ab initio calculations of the bonding energies of alkanes and fluoromethanes to $W(CO)_5$ have been performed in several basis sets and at a variety of different levels of electron correlation. The Møller−Plesset second-order perturbation (MP2) optimized geometries of the complexes show that a variety of coordination modes are available to alkanes and that the fluoromethanes are coordinated through fluorine. The lowest energy geometry has an η^2 agostic bond but two transition states, a second η^2 structure and an η^3 structure, are close in energy. Although the barriers for exchange of H's at one C are low, the barrier for the exchange of C sites is significantly higher. The MP2 bonding energies have been recalculated with diffuse functions on the metal and with polarization functions on the ligands. Basis set superposition errors (BSSE) have been calculated with every basis set. Even before the BSSE corrections, the MP2 bonding energies are in agreement with the experimental trend within each class of complexes (alkanes and fluoromethanes). These results verify that bonding energies increase with increasing alkane size and that CH_3F has the largest bonding energy among fluoroalkane complexes. BSSE corrections play a major role in obtaining good agreement between two classes of complexes because the correction is significantly larger for alkanes in these basis sets. The bonding energy for $W(CO)_6CH_4$ has been calculated at different electron correlation levels such as Møller−Plesset third-order (MP3) and fourth-order (MP4) perturbation and quadratic configuration interaction with singles and doubles (QCISD). Excellent agreement with the experimental data was obtained when the MP2 bonding energies in the largest basis set were corrected for BSSE, zero-point energy (ZPE), temperature, and the difference between the MP2 and QCISD energy.

Introduction

Activation of C−H bonds by transition-metal complexes is an important step in many catalytic cycles and has been studied for some time both experimentally[1] and theoretically.[2] It has been proposed that the precursor in these processes is an adduct between the alkane and metal complex, called an agostic or alkane complex, in which C−H bond(s) coordinate to the metal.[1a−d] Theoretical investigations have established that alkane complexes are intermediates along the reaction pathway for the alkanes C−H bond activation.[2] Understanding the nature of this alkane complex is important for a thorough understanding of the reaction mechanism of C−H activation. For example, the observed increase in binding energies of $W(CO)_5$ alkane with increasing alkane size[3] parallels the increase in the rates for the oxidative addition reaction of alkanes with CpRhCO in the gas phase.[1a]

The alkane complexes have been observed in reactions of alkanes with unsaturated transition-metal carbonyl species, $M(CO)_5$ (M = Cr, Mo, W), where C−H oxidative addition is thermodynamically unfavorable.[3,4] Here, the adduct is the more stable species, unlike cases in which the oxidative addition product is the more stable one. Experimental bonding energies have been measured for these complexes.[3,4] In an extensive gas-phase study, time-resolved infrared spectroscopy was used to determine the bonding enthalpies of alkanes and fluorinated alkanes with $W(CO)_5$.[3] $W(CO)_5$ formed reversible complexes with all alkanes studied, except methane. The bonding energies (reaction 1) increase with increasing alkane size (range 7−11 kcal/mol), but because of the large experimental error (±2 to ±3 kcal/mol), these bonding energies could be nearly equal. A bonding enthalpy of <5 kcal/mol for the complex with methane was inferred by the authors' inability to observe a complex. Fluorinated alkanes showed behavior that depends on the position and degree of substitution. CF_4 and CHF_3 did not form observable complexes, while CH_3F and CH_2F_2 formed complexes with bonding energies of ∼11 and >5 kcal/mol, respectively. Because CF_4 did not produce a stable complex with $W(CO)_5$, Rayner and co-workers assumed that other fluoroalkanes such as CH_3F coordinated to W through a C−H bond.[3] However, the interpretation of recent work on the C−F bond activation assumes precoordination of the fluorocarbon's C−F bond to the metal center.[5]

$$W(CO)_5L \rightarrow W(CO)_5 + L \qquad (1)$$

Because of low stability of the alkane and fluoroalkane complexes, their structures have not been determined experimentally.[1c,3] Ab initio calculations can contribute to an understanding of these structures. There are a number of theoretical studies for methane oxidative addition to different metal complexes,[2] but there is little systematic work on the structures of methane complexes and no previous theoretical work for $W(CO)_5$ alkanes. Likewise, there has been no theoretical work for fluoroalkane complexes of transition metals, so their structures are unknown.

In this work, the structures and bonding energies of alkane and fluoromethane complexes with $W(CO)_5$ have been studied with ab initio methods. Our objectives are to determine the structures of the complexes and to verify, if possible, trends in the bonding energies. The optimized geometries for different structures of $W(CO)_5L$ (L = CH_4, C_2H_6, C_3H_8, CH_3F, CH_2F_2, CHF_3, CF_4) at the Møller−Plesset second-order (MP2) level

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are determined. The reliability of MP2 calculation in determining the structures of second- and third-row polyhydride complexes has been verified,[6a] and the MP2 geometry of $W(CO)_6$ is in good agreement with the experimental geometry.[6b] The optimized geometries of alkane and fluoroalkane complexes show the various coordination modes available to alkanes and fluoroalkanes. The bonding energies and basis set superposition error (BSSE) calculated with several different basis sets and the bonding energies at different correlation levels—Møller—Plesset second-order (MP2), third-order (MP3), fourth-order (MP4), and quadratic configuration interaction with singles and doubles (QCISD)—are presented. The calculated binding energies corrected for BSSE, zero-point energy (ZPE), and temperature are compared with the experimental data.[3]

Theoretical Details

Three basis sets were employed in these calculations. In basis set I effective core potentials[7] were used for all atoms except hydrogen. For W a relativistic ECP[7b] was used; the 5s, 6s, 5p, 6p, and 5d orbitals were taken as active. The 541/651/211 contraction (double-ζ) includes the recently proposed valence 6p orbital which has been used successfully in this group.[2e,8] For C, O, and F the double-ζ basis set and effective core potentials of Stevens et al.[7a] were used. For hydrogen a standard double-ζ basis set was used.[9] In basis set II, C, O, F, and H basis sets were expanded to triple-ζ valence basis set.[10] The basis set for W was expanded by the addition of s, p, and d diffuse functions with exponents one-third of the outermost functions. In basis set III, basis function for W were the same as in basis set I, and additional d-polarization functions were added to basis set II for C, O, and F.[9]

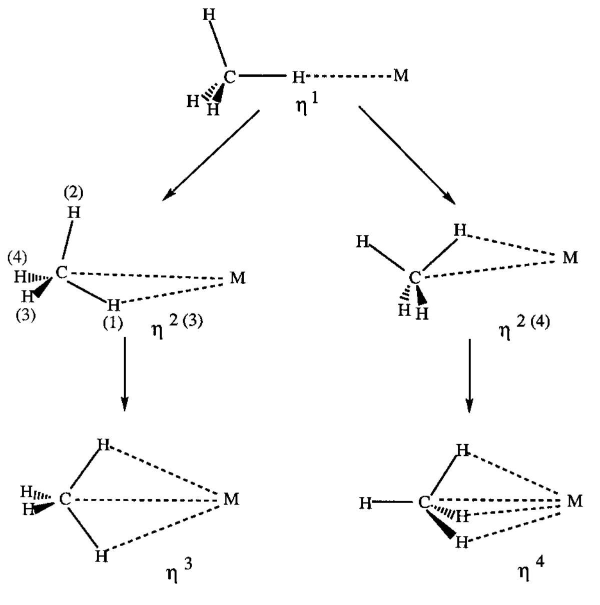
Geometries of $W(CO)_5$, CH_4, and $W(CO)_5CH_4$ with different orientations for CH_4 coordination were optimized at the Hartree—Fock (HF) and at the second-order Møller—Plesset perturbation theory (MP2) level. Geometries of L and $W(CO)_5L$ ($L = C_2H_6, C_3H_8, CH_3F, CH_2F_2, CHF_3, CF_4$) were optimized at the MP2 level. All geometry optimizations were in the basis set I and had O—C—W bond angles fixed at 180° and C_{eq}—W—C_{eq} angles fixed at 90°. Thus, the $W(CO)_5$ fragment had local C_{4v} symmetry. In the η^1 and η^4 structures, the CH_4 fragment had local C_{3v} symmetry, while in $\eta^{2(3)}$ and $\eta^{2(4)}$ it had C_s and in η^3 it had C_{2v} symmetry.

Numerical vibrational frequencies at the HF level were calculated at stationary points to identify them as minima or transition states. For the zero-point energy (ZPE) of reaction 1, frequencies for one structure were recalculated at the MP2 level. It is known that there is only a small difference in the ZPE correction for different alkanes in reactions like (1).[11] The ZPE (MP2) correction for the reaction with CH_4, 1.5 kcal/mol, was used for all reactions.

The bonding energies were calculated as the difference in the energy between products and reactant for reaction 1. The basis set superposition error (BSSE) correction was calculated with a complete counterpoise procedure[12] for each of the basis sets.

The bonding energies for $W(CO)_5CH_4$ were redetermined at the Møller—Plesset third-order (MP3) correlation level with basis sets I and II and at Møller—Plesset fourth-order perturbation (MP4) and quadratic configuration interaction with singles and doubles (QCISD) level with basis set I. The difference between energies at the MP2/I and at the QCISD/I level was used to correct calculated MP2/III energies for all molecules. The calculated bonding energies at the MP2/III level were corrected for BSSE, ZPE, temperature, and difference between MP2 and QCISD levels and then compared with experimental data.

SCHEME 1



Ab initio calculations were performed with GAMESS-UK,[13a] Gaussian 92,[13b] and Gaussian 94[13c] software packages on a Cray SMP-22 at the Chemistry Department, on SGI Indigo and Power Indigo2 workstations in our laboratory, on the IBM-SP2 at the Cornell Theory Center, and on an SGI Power Challenge at the Supercomputer Center of Texas A&M University.

Results and Discussion

Geometries of Alkane Complexes. Crystal structures for complexes with the BH_4^- ligand show that this ligand can be coordinated by 1, 2, or 3 hydrogen atoms,[14] and ab initio calculations show that these structures are minima[14] and that there are only small differences in energy among different structures. Isoelectronic methane can show a similar variety of coordination modes (Scheme 1).

In this work five possible structures for the $W(CO)_5CH_4$ complex—η^1, $\eta^{2(3)}$, η^3, and η^4—have been studied (shown in Scheme 1 and Figure 1). There are two different η^2 structures: one, $\eta^{2(3)}$, is connected with the η^3 structure, and the other, $\eta^{2(4)}$, is connected with the η^4 structure. For the three nonbonding hydrogens in the $\eta^{2(3)}$ structure two equivalent ones are farther and the third is closer to metal, but in the $\eta^{2(4)}$ structure the two equivalent ones are closer to metal and the third is farther.

All possible structures were optimized at the HF/I level and at the MP2/I level. In geometries optimized at the HF/I level, as expected from results on the $W(CO)_6$ complex,[6b] W—C bonds are longer and C—O bonds are shorter than those at MP2/I level. W—H and W—C bonds are longer at the HF/I level, and C—H bonds are shorter. Thus, the HF level underestimates the agostic interaction between methane and $W(CO)_5$. Bonding energies at the HF level are also too small. The HF level calculations are not adequate for either the geometry or energy of this system.

At the HF/I level η^1 and η^4 stationary structures do not exist, and of the other structures, the $\eta^{2(3)}$ structure has the lowest energy. Frequency calculations at the HF level show that the $\eta^{2(3)}$ structure is a true minimum and that the $\eta^{2(4)}$ and η^3 structures are transition states. For structures optimized at MP2/I level stationary points for all structures exist. Again, the $\eta^{2(3)}$ structure has the lowest energy on the MP2 potential surface (without the correction for BSSE), and the $\eta^{2(4)}$ and η^3 structures appear to be transition states. However, the MP2/I energy difference between $\eta^{2(3)}$, $\eta^{2(4)}$, and η^3 is only about 1 kcal/mol (with or without BSSE correction), and the order of

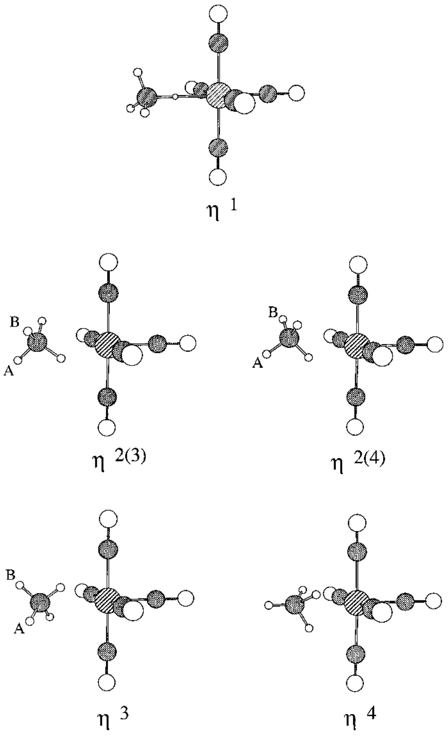


Figure 1. Geometries for η^1, $\eta^{2(3)}$, $\eta^{2(4)}$, η^3, and η^4 structure of W(CO)$_5$-alkane complexes. For methane complex A and B are H. For ethane A is CH and B is H. For propane bonded with secondary carbon ((CH$_3$)$_2$CH$_2$), A and B are CH$_3$; for propane bonded with primary carbon (CH$_3$CH$_2$CH$_3$), A is CH$_3$CH$_2$ and B is H. The most important geometrical parameters are given in Table 1.

TABLE 1: Geometrical Data[a] for Different Structures[b] of W(CO)$_5$−Alkanes

alkane	structure	W−C	W−H	C−H
CH$_4$	η^1	2.945	1.797	1.148
	$\eta^{2(4)}$	2.859	2.058	1.150
	$\eta^{2(3)}$	2.804	2.096	1.147
	η^3	2.764	2.350	1.129
	η^4	2.597	2.212	1.148
CH$_3$CH$_3$	$\eta^{2(4)}$	2.872	2.017	1.154
	$\eta^{2(3)}$	2.8141	2.047	1.153
	η^3	2.756	2.326	1.131
(CH$_3$)$_2$CH$_2$[c]	$\eta^{2(4)}$	2.986	1.982	1.155
	$\eta^{2(3)}$	2.815	2.012	1.157
	η^3	2.746	2.304	1.132
CH$_3$CH$_2$CH$_3$[d]	$\eta^{2(4)})$	2.866	2.00	1.155
	$\eta^{2(3)}$	2.805	2.047	1.153
	η^3	2.749	2.322	1.132

[a] MP2/I geometries, all distances in Å. [b] For different structures see Figure 1. [c] Secondary carbon coordinated. [d] Primary carbon coordinated.

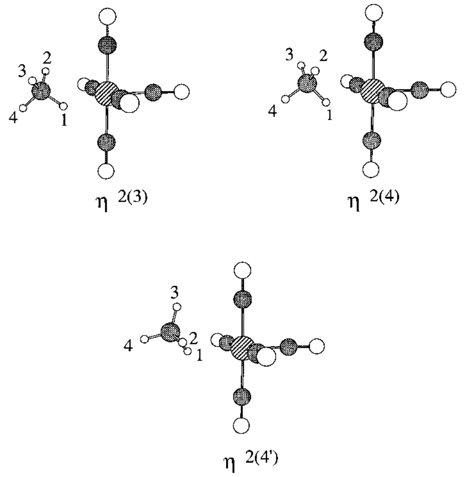


Figure 2. Geometries for structures $\eta^{2(3)}$, $\eta^{2(4)}$, and $\eta^{2(4')}$ of W(CO)$_5$-fluoromethanes. The most important geometrical parameters are given in Table 2.

their stabilities depends on the basis set (as will be discussed later, see Table 3). These results are in agreement with previous studies of other methane complexes.[2] These studies also show small energy difference among different methane structures and variations in the most stable structure depending on the system (complex)[2b] and on the method and basis set.[2c,d,h] Different relative stabilities of isomers with and without BSSE correction are known for other molecules.[15]

Because of the small energy differences between the $\eta^{2(3)}$, $\eta^{2(4)}$, and η^3 structures of the methane complex, geometries of W(CO)$_5$C$_2$H$_6$ and W(CO)$_5$C$_3$H$_8$ were optimized for all three coordination modes at the MP2/I level. For ethane the $\eta^{2(3)}$ structure has the lowest energy on MP2/I potential surface, but again all three structures have similar energies and the order of stability depends on the basis set and BSSE.

Propane can coordinate to a metal at the primary carbon (CH$_3$CH$_2$CH$_3$) or at the secondary carbon ((CH$_3$)$_2$CH$_2$), so six structures were optimized for W(CO)$_5$C$_3$H$_8$ (Tables 1 and 3). The structures, in which the secondary carbon is coordinated, are more stable than those in which the primary carbon is coordinated (Table 3). Among structures coordinated through the primary carbon, the $\eta^{2(3)}$ structure is the most stable on the MP2/I potential surface before correction for BSSE, but again the $\eta^{2(4)}$ and η^3 structures are close in energy. However, among structures coordinated through the secondary carbon, the $\eta^{2(3)}$ is the most stable both with and without corrections for BSSE.

The $\eta^{2(3)}$ structures are the most stable on the MP2/I potential surface before correction for BSSE for all complexes with alkanes, and they are the most stable in the larger basis sets after BSSE corrections (Table 3). For these complexes the $\eta^{2(4)}$ structure has the longest W−C bond and the shortest W−H bond length; the η^3 has the shortest W−C and the longest W−H bonds (Table 1). The $\eta^{2(3)}$ structure has intermediate W−C and W−H bond lengths (Table 1). However, the distance between the midpoint of the C−H bond and W is the shortest for the $\eta^{2(3)}$ structure (2.408 Å) compared to the η^3 (2.503 Å) and the $\eta^{2(4)}$ (2.424 Å) structures. Comparing the η^3 structure of complexes with CH$_4$, C$_2$H$_6$, and C$_3$H$_8$ shows that W−C bond length decreases with increasing alkane size. This is consistent with increasing stability of these complexes. Comparing the W−C bond length in the $\eta^{2(3)}$ and the $\eta^{2(4)}$ structures is not so straightforward, because of lower symmetry of these structures with ethane and propane.

Geometries of Fluoromethane Complexes. Geometries for W(CO)$_5$L (L = CH$_3$F, CH$_2$F$_2$, CHF$_3$, and CF$_4$) were also optimized at the MP2/I level. There are clearly more isomers of fluoromethane complexes than of methane complexes. Optimizations were started with $\eta^{2(3)}$, $\eta^{2(4)}$, and η^3 structures for the methane complex replacing hydrogen(s) with fluorine(s). In many cases different initial structures converged to the same final structure. All optimized structures belong to three types: $\eta^{2(3)}$, $\eta^{2(4)}$, and $\eta^{2(4')}$ (Figure 2). This notation is similar to the notation for the alkane complexes, but structure $\eta^{2(4')}$ does not exist for alkane complexes and for fluoromethanes appears only for CH$_2$F$_2$ and CHF$_3$ complexes with F bonded to the W and with F in position 2 and H in position 3 (Figure 2). In this structure the dihedral C−W−F−C angle is about 45°, while in the $\eta^{2(4)}$ structure this angle is about 0°. Although we continue to use the notation η^2, in cases where F is coordinated to metal, the C is much further from W (3.5 Å) than in the cases where H is coordinated (2.9 Å). We continued with this name to have a uniform notation for all isomers and because the C−F−W

TABLE 2: Geometrical Data[a] for Different Structures[b] of $W(CO)_5$−Fluoromethanes

fluoromethane	structure	W−C	W−F	C−F
CH_3F	coordinated F			
	$\eta^{2(3)}$ (FHHH)	3.509	2.349	1.508
	$\eta^{2(4)}$ (FHHH)	3.487	2.349	1.507
	coordinated H			
	$\eta^{2(3)}$ (HHFH)	2.772	2.376	1.124
	$\eta^{2(4)}$ (HHHF)	2.924	2.046	1.145
	$\eta^{2(3)}$ (HFHH)	2.819	2.076	1.145
CH_2F_2	coordinated F			
	$\eta^{2(3)}$ (FFHH)	3.614	2.405	1.478
	$\eta^{2(4)}$ (FHHF)	3.474	2.377	1.483
	$\eta^{2(4')}$ (FFHH)	3.500	2.383	1.478
CHF_3	coordinated F			
	$\eta^{2(3)}$ (FHFF)	3.508	2.400	1.456
	$\eta^{2(4')}$ (FFHF)	3.503	2.414	1.455
	$\eta^{2(4)}$ (FFFH)	3.572	2.438	1.451
	coordinated H			
	$\eta^{2(4)}$ (HFFF)	3.215	2.306	1.124
CF_4	$\eta^{2(3)}$	3.592	2.469	1.432

[a] All distances in Å. [b] For different structures see Figure 2.

angle is similar to the C−H−W angle. In Figure 2 the closest atom to the metal is labeled 1 and the farthest is 4. In the naming of the different isomers we begin with the structural symbol and then the symbols of F and H; the first symbol is the closest atom, and the last symbol is the farthest atom. For example, in the $\eta^{2(3)}$(HHFH) isomer of the CH_3F complex, the F atom is in position 3 in the $\eta^{2(3)}$ structure (Figure 2). The most important geometrical parameters for the optimized structures are given in Table 2.

Results for complexes with CH_3F and CHF_3 show that structures with coordinated F are much more stable than those with agostic C−H bonds (Table 3). Thus, the latter structures were not optimized for the CH_2F_2 complex (Tables 2 and 3).

Although we will discuss the bonding energies in more detail later, the difference in stability between structures with coordinated F and those with an agostic C−H bond (Table 3) is so large that we are confident that in these complexes F is coordinated to the metal. To the best of our knowledge, this is the first theoretical result to show that in fluorinated alkanes F coordinates the transition metal. Rayner and co-workers[3] expected that F was not coordinated to W because CF_4 did not make a stable complex with $W(CO)_5$.[3] However, as we will discuss, our results show that CH_3F makes a strong complex with $W(CO)_5$ and CF_4 bonds only weakly. Prompted by our calculations, Dobson et al. observed that 1-fluorohexane is coordinated to $W(CO)_5$ though the F.[16]

Additional evidence that structures with F coordinated were observed in the experiment comes from the experimental IR spectra.[3] The C−O stretching frequencies in the time-resolved infrared spectra of fluoroalkane complexes are shifted by ∼10 cm^{-1} to low energy compared to the case of the alkane complexes.[3] This shift is not easy to explain, if one assumes, as the authors did, that fluoroalkanes are coordinated by an agostic C−H bond. We believe that the correct explanation results from F coordinating to the W. In the MP2/I optimized geometries the CO bonds in CH_3F complexes, in which F is bonded to W, are about 0.001 Å longer than those in alkane complexes. Using a relationship between CO bond length and force constant,[17] one can show that this difference in bond distances is in agreement with shift of ∼10 cm^{-1} to lower energy in the C−O stretching frequency. In contrast, when CH_3F is coordinated to W though an agostic C−H bond, the CO bonds are shorter than those in the alkane complexes, a result would predict behavior of the stretching frequencies in the wrong direction. Thus, we are now certain that the fluoroalkanes coordinate to $W(CO)_5$ through F.

With increasing numbers of F in fluorinated methanes (CH_3F, CH_2F_2, CHF_3, and CF_4) the bonding energies of the $W(CO)_5$ complexes decrease (Table 3). This decrease parallels the decrease in the calculated negative charge on F: −0.411 in CH_3F, −0.334 in CH_2F_2, −0.254 in CHF_3, and −0.179 in CF_4. Bonding energy for the CH_3CH_2F complex was not calculated, but the experimentally observed bonding energy for this complex is the largest[3] and the calculated negative charge on F is larger for this molecule (−0.423).

There are also some parallel changes in geometrical parameters. With increasing numbers of F, the C−F bonds are shorter and the W−C and the W−F distances are mostly longer (Table 2), although there are some overlapping values. For the most stable isomers there is a clear increase in W−F bond length in going from the CH_3F complex to the CF_4 complex.

Although there are only small differences in geometrical parameters between bonded methane and fluorinated methane bonded by an agostic bond (Tables 1 and 2), the fluoroalkane complexes are less stable than the alkane complexes. The difference in stability can again be correlated with the electron density this time in the C−H bond. Methane has C and H charges of −0.26 and +0.06, respectively, and is bound to $W(CO)_5$ by 7.26 kcal/mol, while CH_3F has C and H charges of +0.09 and +0.11, respectively, and is bound by 2.14 kcal/mol. The bonding energy for CHF_3, with C−H agostic, is totally repulsive (−5.24 kcal/mol), and the C and H charges are correspondingly more positive (+0.58 and +0.18, respectively). Thus, even simple alkanes may have a substantial electrostatic component to the agostic bond.

Bonding Energies for Alkanes and Fluoroalkanes. With geometries optimized at the MP2/I level, bonding energies were recalculated at the MP2 level with basis set II for all structures, and with basis set III for all structures for methane and ethane, and the most stable structures for propane and fluorinated methanes. The BSSE for all three basis sets were calculated. The calculated bonding energies, with different basis sets, without and with BSSE correction are shown in Table 3. Every column in this table, regardless of basis set and BSSE correction, shows that the bonding energy increases with increasing alkane size, as was observed experimentally.[3] A large part of this increase is connected to the degree of substitution at the C−H agostic bond. Thus, propane bound at a primary C−H is only 0.26 kcal/mol more stable than the ethane complex, while that bound to the secondary C−H is 1.63 kcal/mol more stable. Experimental results for fluoroalkanes, which show only CH_3F and CH_2F_2 making complexes with $W(CO)_5$,[3] are consistent with our results that the bonding energy of fluoromethanes, regardless of basis set and BSSE correction, decreases with increasing numbers of F.

Comparing binding energies for complexes with propane and CH_3F shows that the BSSE correction is essential to obtain relative energy differences in agreement with experimental data (Tables 3 and 5). Experimentally, the bonding energy for the most stable CH_3F complex is larger than that for the most stable propane complex. Before correction for BSSE, the MP2/I bonding energies for propane and CH_3F are very similar, and the MP2/II bonding energy for propane is even larger than that for CH_3F. However, after the BSSE correction the bonding energies for the CH_3F complex are consistently larger in all three basis sets. Thus, to compare the bonding energies of alkanes and fluoroalkanes complexes, one must correct for the BSSE, even though the trends are correct within each class of complexes, without BSSE corrections.

TABLE 3: Bonding Eneries (ΔE) and Bonding Energies Corrected for BSSE (ΔE-BSSE) for Different Structures of W(CO)L[a] for Three Different Basis Sets[b] in kcal/mol

		BS I		BS II		BS III	
L	structure	ΔE	ΔE-BSSE	ΔE	ΔE-BSSE	ΔE	ΔE-BSSE
CH_4	η^3	15.21	6.09	16.32	7.43	16.85	8.51
	$\eta^{2(4)}$	15.00	7.26	15.40	7.89	15.63	8.56
	$\eta^{2(3)}$	15.67	7.07	16.43	8.07	16.75	8.88
CH_3CH_3	η^3	18.03	7.25	19.41	8.93	19.24	10.25
	$\eta^{2(4)}$	17.56	8.88	18.05	9.71	18.05	10.34
	$\eta^{2(3)}$	18.83	8.79	19.71	10.07	19.89	11.02
$(CH_3)_2CH_2$	η^3	20.95	8.06	22.53	10.01		
	$\eta^{2(4)}$	19.79	9.13	20.73	10.45		
	$\eta^{2(3)}$	22.08	10.18	22.97	11.66	22.89	12.65
$CH_3CH_2CH_3$	η^3	18.99	7.62	20.49	9.467		
	$\eta^{2(4)}$	19.29	9.48	19.75	10.48	19.83	11.28
	$\eta^{2(3)}$	19.72	9.12	20.70	10.40		
CH_3F	$\eta^{2(3)}$(HHFH)	10.51	0.97	11.29	2.46		
	$\eta^{2(4)}$(HHHF)	9.73	2.14	9.57	2.78		
	$\eta^{2(4)}$(HFHH)	11.43	2.53	11.82	3.54		
	$\eta^{2(3)}$(FHHH)	22.20	13.82	21.54	14.12		
	$\eta^{2(4)}$(FHHH)	22.40	14.06	21.62	14.38	20.78	13.77
CH_2F_2	$\eta^{2(3)}$(FFHH)	17.33	9.44	16.79.	9.70		
	$\eta^{2(4)}$(FHHF)	17.36	9.52	16.93	10.00		
	$\eta^{2(4')}$(FFHH)	18.03	9.76	17.61	10.20	17.36	10.22
CHF_3	$\eta^{2(3)}$(FHHF)	13.49	5.71	13.47	6.37		
	$\eta^{2(4')}$(FFHF)	13.79	5.79	13.50	6.53	13.84	7.22
	$\eta^{2(4)}$(FFFH)	13.84	5.93	13.49	6.52		
	$\eta^{2(4)}$(HFFF)	1.18	−5.24	1.38	−4.75		
CF_4	$\eta^{2(3)}$	10.42	2.44			10.75	4.34

[a] Geometries are given in Figures 1 and 2 and in Tables 1 and 2. [b] Basis set are described in the text.

TABLE 4: Bonding Energies (kcal/mol) for η^2 Structure[a] of $W(CO)_5CH_4$ for Different Methods and Basis Sets[b]

	BS I	BS II
HF	2.15	
MP2	15.00	15.40
MP3	11.25	11.31
MP4(SDQ)	13.41	
MP4(SDTQ)	15.57	
QCISD	11.63	

[a] Geometry optimized at the MP2/I level. [b] Basis sets are described in the text.

The calculated BSSE depends on both basis set and geometry, as can be expected from the nature of this error. For all geometries with alkanes, except for secondary bonded propane, the BSSE is largest for the η^3 structure, in which the alkane molecule is the "closest" to $W(CO)_5$. The BSSE increases slightly with increasing alkane size. For every geometry the BSSE is smaller for larger basis set, although these differences are small. Thus, BSSE is still large even with basis sets which are larger than those typically used on metal complexes. (Our preliminary results with cc-pVDZ basis sets[18] on all ligand atoms show that BSSE for ligands is smaller for this large basis set: BSSE for CH_4 fragment is 2.73 with basis set III and 1.37 with cc-pVDZ. Unfortunately, lack of cc-pVDZ basis set with EPC's for W prevented complete calculation with this basis set). The calculated BSSE is much larger at the MP2 level than at the HF level, because of the "configuration set superposition error."[15a] Our calculations show that BSSE for the η^2 structure of $W(CO)_5$ ethane is very similar for different correlation methods: for the CH_3CH_3 fragment at the MP2 level BSSE is 4.847 kcal/mol, at the MP3 it is 4.851 kcal/mol, at the MP4 it is 5.012 kcal/mol, and at the CSID it is 4.334 kcal/mol. Overall, the BSSE remains disconcertingly large even in our largest basis set. However, the internal consistency of our results gives us some confidence that the counterpoise correction[12a] accounts for most of the error.

The bonding energies for an η^2 structure of $W(CO)_5CH_4$ were calculated at different correlation levels (Table 4), using geometries optimized at the MP2 level. The bonding energies at the HF/I level are very small (2.15 kcal/mol) (Table 4) as one would expect from results for other CH_4 complexes.[2h,d,f,g] Higher levels of theory show larger bonding energies, but the perturbation theory is not converging as well as one might expect for a weak complex of a third-row transition metal. The MP2 and MP4 (SDTQ) bonding energies are somewhat larger than the QCISD energy, while the MP3 is similar to the QCISD, a result that has been noted before.[8,19] The difference between MP2 and QCISD energies is 3.37 kcal/mol. This difference should be similar for larger basis sets (the difference between MP2/I and MP3/I is very close to the difference between MP2/II and MP3/II, (Table 4), and for energies corrected for BSSE (BSSE is very similar for different correlation methods). Assuming that the QCISD energies are the most accurate and that this difference will be almost the same for other alkane and fluoroalkane complexes, we used this value (3.37) to correct the calculated MP2/III bonding energies for the most stable structures of the complexes.

To compare these bonding energies with experimental data (ΔH values), they must be converted to bonding enthalpies. So, the bonding energies (MP2/III corrected for BSSE and for the difference between MP2 and QCISD energies) were then corrected for ZPE and temperature.[20] These theoretical ΔH^{300} values for the most stable structures of alkanes and fluoroalkanes with $W(CO)_5$ are shown together with experimental data in Table 5. The agreement between the experimental and the calculated bonding enthalpies is excellent. All the differences between the experimental and theoretical data are within the experimental error range, where it is given. Only the calculated value for methane still seems a little too high. As one would expect from the data's qualitative appearance, an excellent correlation exists between the calculated and experimental bonding enthalpies (Figure 3) for ethane, propane, and CH_3F complexes. This least-squares plot can be used to correct for the remaining systematic error in the theoretical data, a procedure which assumes that the experimental data have only random error. When the least-squares correlation was used to

TABLE 5: Calculated, Experimental, and Predicted Bonding Eneriges for $W(CO)_5L^a$

L	calcd	exptl[b]	predicted[c]
CH_4	6.39	<5	4.17
C_2H_6	8.53	7.4 ± 2	6.99
C_3H_8	10.16	8.1 ± 2	9.12
CH_3F	11.28	11.2 ± 3	10.59
CH_2F_2	7.73	>5	5.90
CHF_3	4.73	<5	1.99
CF_4	1.85	<5	−1.81

[a] In kcal/mol. [b] From reference (Br90). [c] From linear regression.

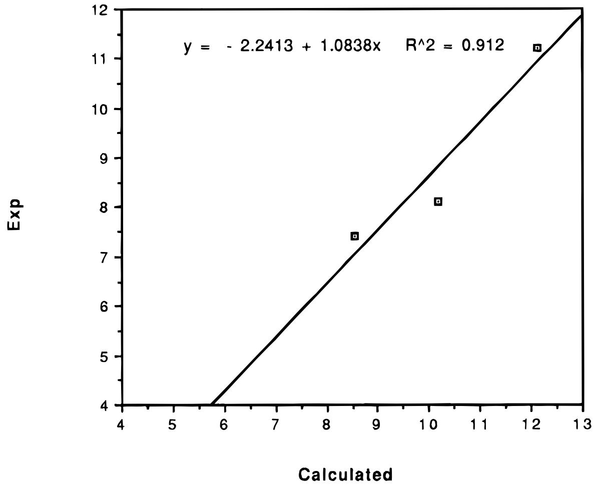


Figure 3. Relationship between experimental and computed bonding energies for $W(CO)_5$ complexes with ethane, propane, and CH_3F.

correct bonding enthalpies, the predicted values are shown in the last column of Table 5. These values are in excellent agreement with experimental data. This excellent correlation suggests that the relative bonding enthalpies of these systems are more accurate than what one might infer from the absolute error.

Transition States. As mentioned above, there are only small energy differences between the $\eta^{2(3)}$, $\eta^{2(4)}$, and η^3 structures of the methane complex. The $\eta^{2(3)}$ structure is the minimum, and the $\eta^{2(4)}$ and η^3 structures are transition states. The η^3 structure is a transition state for a rocking motion between two $\eta^{2(3)}$ minima: one with H(1) bonded to the metal and the other with H(2) bonded to the metal (Scheme 1). The $\eta^{2(4)}$ structure is a transition state for methane rotation about the C−H(1) bond, in which H(2) and H(4) exchange places. Thus, through these two transition state, $\eta^{2(4)}$ and η^3, all four hydrogens can be exchanged.

Ethane can coordinate through two different carbons, and there are several different possibilities for a transition state between these two minima. It could be a structure directly connecting two $\eta^{2(3)}$ minima (one at each C), one connecting $\eta^{2(3)}$ (at one C) with the η^3 transition state (at the other C), or one connecting two η^3 transition states (one at each C). These structures were first optimized as transition states at the HF level. The optimization of the one connecting $\eta^{2(3)}$ and η^3 structures finished as an $\eta^{2(3)}$ structure. The apparent transition state connecting two η^3 structures has an energy of −187.132 972 4 au, while the structure connecting two $\eta^{2(3)}$ structures (with two equivalent ethane carbons) has a lower energy (−187.137 109 7 au). This latter structure has C_2 symmetry with W−C bond distances of 4.178 Å and W−H (the closest) of 3.480 Å. Numerical frequencies were calculated for this structure, and there are two imaginary frequencies: 63.9i and 10.3i cm^{-1}. The normal coordinate for the first frequency shows that the motion is toward $\eta^{2(3)}$ structures and that for the second shows that the motion rolls the whole ethane. This approximate transition state was reoptimized at HF level, removing C_2 symmetry. A true transition state with lower symmetry was obtained (Figure 4). Calculated numerical frequencies show that only one imaginary frequency at 61.6i cm^{-1} remained. The energy of this transition state (−187.137 112 7 au) is almost the same as the energy of symmetric one. The W−C bond distances are 4.154 and 4.222 Å. For the closer C, two H are oriented toward W with W−H bond distances of 3.557 and 4.166 Å. For the other C, one H is oriented toward W with a W−H distance of 3.454 Å. The QST2 method[21] with $\eta^{2(3)}$ and η^3 input structures gave the same transition state. To calculate the bonding energy and barrier, the transition state was reoptimized at the MP2 level. Because of the similar energies and geometries of the true and approximate transition state with C_2 symmetry, a symmetric structure was maintained. At the MP2 level the W−C and the W−H bonding distances are 3.317 and 2.668 Å, respectively. The bonding energy at the MP2 level, corrected for BSSE and ZPE, is 1.52 kcal/mol, and the barrier, corrected for BSSE and ZPE, is 6.59 kcal/mol. Because of the large BSSE for the transition state, a structure with W−C bonds longer by 10% has a smaller BSSE and a lower total energy after the corrections. For this structure, the bonding energy is 2.80 kcal/mol and the barrier is 5.33 kcal/mol.

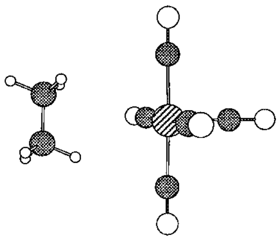


Figure 4. Geometry for transition state of carbon exchange in ethane.

Conclusion

The theoretical results reported here resolved a number of questions about structures and bonding energies of $W(CO)_5$alkane and $W(CO)_5$fluoroalkane complexes. In general, η^2 structures are the most stable for the alkane complexes. However, other structures with different H positions on the same C are so close in energy and the barriers so small that complexes will be fluxional, but the exchange of C atoms has a significantly higher barrier. The results clearly support the experimental trend, which was somewhat ambiguous, that the bonding energies increase with increasing alkane size. The results also show that much of this increase is due to increasing substitution on the C of the C−H agostic bond. Optimized geometries and calculated bonding energies for $W(CO)_5$fluoromethane complexes show that fluorine is bonded to tungsten. The results also explain the decrease in bonding energies with increasing F substitution through a decreasing charge on F. Overall, the trend in the relative bonding energies, increasing with alkane size, secondary C−H greater than primary, CH_3F greater than CH_4, and CH_3F greater than CF_4, points to a major electrostatic component to both the R_3CF- - -$W(CO)_5$ and the R_3CH- - -$W(CO)_5$ bonds.

The calculated bonding energies demonstrate that relative energies at the MP2 level, even without BSSE correction, are in good agreement with the experimental data within the same class of complexes. However, BSSE corrections are essential for getting agreement in the relative energies between complexes with alkanes and fluoroalkanes.

In general, MP2 bonding energies seem to be too large even after BSSE correction. Excellent agreement with experimental data was obtained when the BSSE corrected MP2/III bonding energies were corrected to QCISD energies and for temperature and ZPE. The differences between calculated enthalpies for alkane and fluoroalkane complexes of $W(CO)_5$ and experimental data are less than experimental error.

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