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A Molecular Orbital Study of Methyl Migration in Pentacarbonylmethylmanganese(I)

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Approximate PRDDO calculations and ab initio Hartree–Fock calculations employing a large basis set have been used to study the nature of methyl migration in pentacarbonylmethylmanganese(I). Geometries were determined at the PRDDO level, while energetics were evaluated by using ab initio theory. The optimized geometry of the transition state has been obtained for the first time. The calculated barrier for the closed-shell migration of the methyl group $(CO)_5MnCH_3 \rightarrow (CO)_4Mn(COCH_3)$ is +17 kcal/mol. The coordinatively unsaturated intermediate, which is the kinetic product of methyl migration, is calculated to be 10 kcal/mol less stable than the six-coordinate methyl complex. The geometries and electronic structure of the transition state and the kinetic product are discussed in relation to their possible interaction with solvent and Lewis acids. The potential for the kinetic product, which is found to be a local minimum, to isomerize to other favorable conformations was studied. In-plane bending of the acyl group was found to be relatively easy, and another conformation of the acyl intermediate was found to be 4 kcal/mol more stable than the kinetic product. Also, a η^2 conformation was found to be 11 kcal/mol more stable than the kinetic product. The overall electronic energy difference of the carbonylation reaction $(CO)_5MnCH_3 + CO \rightarrow (CO)_5Mn(COCH_3)$ is calculated to be −8 kcal/mol. Localized molecular orbitals (LMO's) are used to qualitatively examine the bonding present during the migration sequence. The transition-state valence structure is found to be very acyl-like in character. LMO's of the η^2 species indicate that the metal–oxygen bond is predominantly oxygen lone pair like and that the metallacycle formed is highly strained.

Introduction

Migratory insertion[1] of carbon monoxide into a metal–alkyl bond is well-known to be important in homogeneous catalysis[2] and organic synthesis[3] and is thought to be important in heterogeneous catalysis.[4] The carbonylation reaction (eq 1, L = CO) is a classic example of this acylation process.[5]

$$(CO)_5MnCH_3 + L \rightarrow L(CO)_4Mn(COCH_3) \qquad (1)$$

Equation 1 has been extensively studied experimentally with respect to its kinetic and mechanistic behavior,[6,7] stereochemistry,[8,9] thermodynamics,[10] influence by solvents,[7] effect by Lewis acids,[11] and potential intermediate geometries.[8,12] The $(CO)_5MnCH_3$ complex is generally believed[1,7] to initially form a coordinatively unsaturated acyl intermediate (eq 2) via an intramolecular rearrangement (more commonly referred to as a methyl migration).

$$(CO)_5MnCH_3 \rightarrow (CO)_4Mn(COCH_3) \qquad (2)$$

Although the five-coordinate intermediate has never been observed directly in solution, the indirect evidence for its existence is strong.[1,7] Stereochemical studies[8,9] have revealed that the process in eq 2 proceeds by a formal methyl migration (as opposed to carbonyl insertion into the Mn–CH_3 bond), and the incoming nucleophile (L) is found to be cis to the newly formed acyl group. The acyl intermediate is believed[8] to be a square pyramid with the acyl group in a basal position, which is certainly consistent with the cis stereochemistry of the acyl group and L. However, indirect evidence[12] for a trigonal bipyramid, which may contain a η^2-bound acyl group, has been published. The rate of eq 1 has been shown[7] to have a dependence upon the solvent medium used. Polar coordinating solvents seem to have the most profound rate enhancement effects. Finally, a study[11] of the effect of different Lewis acids on the rate has demonstrated that the acidity of the Lewis acid parallels the rate of reaction.

The obvious importance of alkyl group migration reactions in organometallic chemistry has provided the impetus for several theoretical studies.[13–18] Four molecular orbital (MO) studies[13–16] of methyl migration in the $(CO)_5MnCH_3$ system alone have been published. These studies have employed the extended Hückel[13] (EH), the Hartree–Fock–Slater (HFS) ab initio,[14] and the CNDO[15,16] formalisms in an effort to access the qualitative and quantitative nature of methyl migration and related phenomena. Both EH[13] and HFS ab initio[14] were used to give

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quantitative estimates of the methyl migration potential energy surface and conformational preferences of the acyl intermediate. The quantitative findings of these studies[13,14] seem to indicate that the methyl migration step (eq 2) is reasonable; however, their conclusions regarding the stability of the proposed η^2 conformation of the acyl intermediate are in direct disagreement. EH calculations do not predict a stable η^2 intermediate, while the HFS ab initio method does. In addition to the aforementioned work on the $(CO)_5MnCH_3$ system, ab initio calculations,[17] using pseudopotentials on the metal, of methyl migration in the model complex $Ir(CH_3)(F)(CO)(PH_3)_2$ have been reported. This study employed gradient optimization techniques, at different values of the C(methyl)–Ir–C(acyl)angle (which was chosen as the reaction coordinate), in an effort to explore the energetics of the methyl migration potential energy surface in detail. The calculated barriers for methyl migration were much too high when compared to experimental values for real systems; however, the qualitative conclusion of the calculations (methyl migration was predicted to be more facile than carbon monoxide insertion) was consistent with experiment. One other theoretical study[18] of alkyl group migrations has been referenced but, unfortunately, has apparently never been published. Despite the fact that pentacarbonylmethylmanganese(I) is probably the best studied system with respect to its migratory aptitude, it has never been treated in a first principles study.

In this paper we present the results of nonempirical molecular orbital calculations of the complete methyl migration potential energy surface in the $(CO)_5MnCH_3$ complex, and an energetic analysis of several possible conformations of the acyl intermediate, including a η^2 conformer. The great wealth of prior experimental work creates an ideal situation to compare our theoretical results. This work represents the first ab initio study of the complete alkyl migration pathway in any *real* organometallic system, including the first optimized geometry for the transition state.

Pictures of the bonding during the migration sequence are developed with the aid of Mulliken populations and localized molecular orbitals (LMO's). A particular emphasis is placed upon characterizing the bonding in the transition state. The potential influence of solvents and Lewis acids is interpreted through the aid of the calculated geometry and electronic structure of the transition state. Several geometries of the acyl intermediate were studied, and three were found to represent local minima. Finally, the implication of solvent interaction and intramolecular rearrangements are discussed in relation to the possible stereochemistry at the metal.

Calculations and Geometries

In the present contribution six structures were considered to be important and are shown in Figure 1. Structures **1** and **3** correspond to the six- and five-coordinate complexes in eq 2, respectively. Structure **2** is the estimated transition state linking conformations **1** and **3**. Structure **4** is the overall product of carbonylation (eq 1 with L = CO). Structure **5** is the η^2 conformation of the acyl intermediate. Finally, structure **6** is the conformation formed by the inplane bending of the acyl group in **3**. All of the geometries were determined by the PRDDO[19,20] method. This minimum basis set approximate molecular orbital treatment has been shown to reproduce to a high

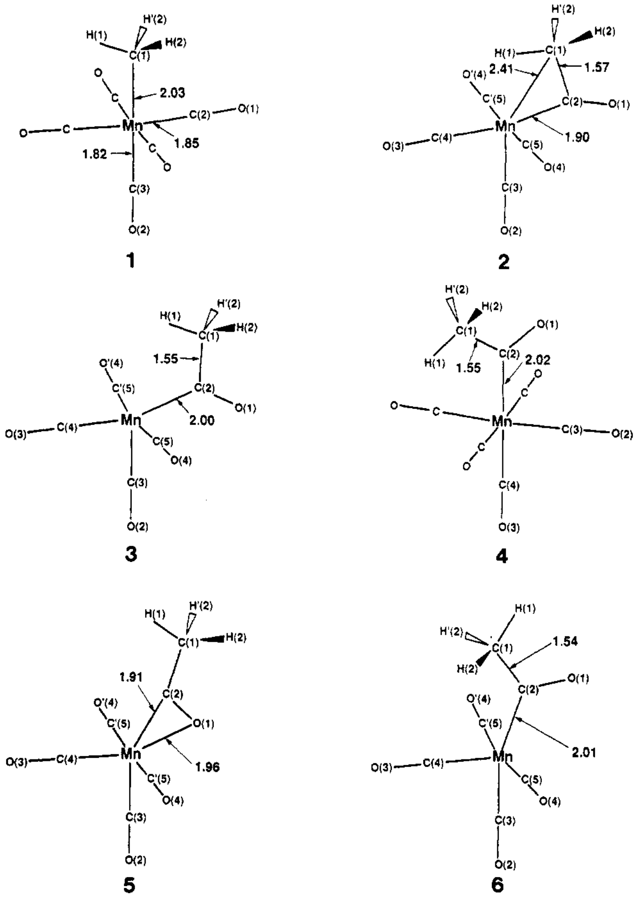

Figure 1. Molecular conformations considered in this study: (1) pentacarbonylmethylmanganese(I); (2) the estimated transition state for methyl migration; (3) the five-coordinate acyl intermediate; (4) pentacarbonylacylmanganese(I); (5) the η^2 conformation of the acyl intermediate; (6) stable isomer of the kinetic product formed by the in-plane bending of the acyl group.

degree of accuracy the results of the corresponding ab initio calculation in a fraction of the time required for the ab initio calculation. We also note that PRDDO yields excellent optimized geometries for a wide range of transition-metal complexes,[21,22] including many closely related to the systems studied in this work. For instance, PRDDO optimized[21] metal–ligand bond lengths for $(CO)_5MnH$, $(CO)_6Cr$, $(CO)_5Fe$, and $(CO)_4Ni$ have an average error of ±0.02 Å, with a maximum error of 0.05 Å in $(CO)_5Fe$. Our approach utilizes the speed and accuracy of PRDDO for computing equilibrium geometries, while the energetics of the geometries are reevaluated with nonempirical MO methods. This amalgam of theoretical methods makes an ambitious study like this computationally feasible.

In conjunction with the PRDDO calculations, we employed the synchronous transit method[23] for determining least energy pathways in chemical reactions (traditional methods for locating transition states require the evaluation of costly second derivatives and are not yet practical for systems of this size). In this approach, an initial estimate of the transition-state geometry is made by the construction of a linear synchronous transit between the Cartesian coordinates of the reactant(s) and product. A path coordinate is defined as

$$P = d_r/(d_r + d_p) \qquad (3)$$

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Table I. Complete Geometries of Structures 1-6 in Angstroms and Degrees

structure	geometrical parameter	calcd	exptl
1	Mn-C(1)	2.03	2.19[a]
	Mn-C(2)	1.85	1.86
	Mn-C(3)	1.82	1.82
	C(2)-Mn-C(3)	92.7	94.7
	H(1)-C(1)-Mn	114.5	
	H(1)-C(1)-H(2)	104.0	
2	Mn-C(1)	2.41	
	Mn-C(2)	1.90	
	C(1)-C(2)	1.57	
	C(2)-O(1)	1.20	
	Mn-C(3)	1.85	
	Mn-C(4)	1.83	
	Mn-C(5)	1.88	
	C(1)-C(2)-O(1)	119.1	
	C(1)-Mn-C(2)	40.5	
	C(1)-C(2)-Mn	87.4	
	C(2)-Mn-C(3)	105.2	
	C(3)-Mn-C(4)	86.4	
	C(3)-Mn-C(5)	95.7	
	C(5)-Mn-C′(5)	168.1	
	H(1)-C(1)-H(2)	106.3	
	H(2)-C(1)-H′(2)	107.2	
	H(1)-C(1)-Mn	56.9	
	H(2)-C(1)-C(2)	113.9	
3	Mn-C(2)	2.00	2.05[b]
	C(1)-C(2)	1.55	1.51
	C(2)-O(1)	1.23	1.20
	Mn-C(3)	1.86	
	Mn-C(4)	1.84	
	Mn-C(5)	1.90	
	C(1)-C(2)-O(1)	117.6	
	C(1)-C(2)-Mn	112.2	
	C(2)-Mn-C(3)	109.0	
	C(2)-Mn-C(4)	161.1	
	C(3)-Mn-C(4)	89.8	
	C(3)-Mn-C(5)	93.2	
	C(5)-Mn-C′(5)	170.5	
	H(1)-C(1)-H(2)	106.8	
	H(2)-C(1)-H′(2)	106.8	
	H(1)-C(1)-C(2)	112.1	
4	Mn-C(2)	2.02	2.05[b]
	C(1)-C(2)	1.55	1.51
	C(2)-O(1)	1.23	1.20
	Mn-C(3)	1.87	
	Mn-C(4)	1.83	
	C(1)-C(2)-O(1)	115.4	
	C(1)-C(2)-Mn	124.2	
	C(3)-Mn-C(4)	92.3	
	H(1)-C(1)-C(2)	112.1	
	H(1)-C(1)-H(2)	106.8	
5	Mn-C(2)	1.91	
	C(1)-C(2)	1.55	
	Mn-O(1)	1.96	
	C(2)-O(1)	1.25	
	Mn-C(3)	1.83	
	Mn-C(4)	1.83	
	Mn-C(5)	1.90	
	C(1)-C(2)-O(1)	119.4	
	C(2)-Mn-O(1)	37.7	
	C(1)-C(2)-Mn	167.2	
	Mn-C(2)-O(1)	73.3	
	Mn-O(1)-C(2)	68.9	
	C(3)-Mn-O(1)	111.5	
	C(3)-Mn-C(4)	92.9	
	C(3)-Mn-C(5)	91.9	
	C(5)-Mn-C′(5)	176.1	
	H(1)-C(1)-H(2)	106.8	
	H(2)-C(1)-H′(2)	106.8	
	H(1)-C(1)-C(2)	112.1	
	H(2)-C(1)-C(2)	112.1	
6	Mn-C(2)	2.01	
	C(1)-C(2)	1.54	
	C(2)-O(1)	1.23	
	Mn-C(3)	1.84	
	Mn-C(4)	1.85	
	Mn-C(5)	1.90	
	C(1)-C(2)-O(1)	117.4	
	C(1)-C(2)-Mn	124.3	
	C(2)-Mn-C(3)	159.4	
	C(2)-Mn-C(4)	110.0	
	C(3)-Mn-C(4)	90.6	
	C(3)-Mn-C(5)	93.2	
	C(5)-Mn-C′(5)	170.7	
	H(1)-C(1)-H(2)	106.8	
	H(2)-C(1)-H′(2)	106.8	
	H(1)-C(1)-C(2)	112.1	

[a] Reference 24. [b] Reference 25.

where d_r and d_p are the "distances" of the current geometry from the reactant and product, defined as

$$d_r = \frac{1}{N} \sum_{\omega=x,y,z} \sum_{a=1}^{N} [(\omega_a(c) - \omega_a(r))^2]^{1/2} \qquad (4)$$

with a similar definition of d_p. Here the Cartesian coordinates are at "maximum coincidence".[23] This definition of the path coordinate has the distinct advantage of being general for all reactions. Several structures along the linear synchronous transit path are then subjected to a path coordinate constrained geometry optimization. By optimizing selected points along the linear synchronous transit path, one can obtain a complete description of the reaction surface and an estimate (by quadratic interpolation) of the transition-state energy and geometry. Because an essentially continuous series of structures intermediate between the reactant and product is obtained, the highest energy structure found is necessarily an upper bound to the true transition state at the PRDDO level. In this study, structures **1** and **3** were initially chosen as the path limiting structures. Path coordinate constrained geometry optimizations at path coordinates of 0.3 and 0.5 between structures **1** and **3** yielded geometries which lie close in energy to the end points 0.0 and 1.0, respectively. In an effort to exclude these relatively flat portions of the potential energy surface, the optimized geometries at path coordinate values of 0.3 and 0.5 were then chosen as new path limiting structures. The estimated transition-state geometry was found on this abbreviated surface. Additional path coordinate constrained geometry optimizations were performed for a set of structures connecting **3** and **5**. Also path coordinate constrained geometry optimizations were used to study the acyl in-plane bending potential.

The bond distances and angles obtained from PRDDO optimizations on the structures **1**–**5** are presented in Table I, along with experimental values when available. Full geometry optimizations were performed on all structures with the following exceptions: (1) While optimizing

Table II. Values of Orbital Exponents for Manganese Used in the ab Initio Hartree–Fock Calculations

1s	24.396[a]	3d	8.862
2s	8.896[a]	3d′	4.411
2p	10.542[a]	3d″	2.112
3p	4.882	4s, 4p	2.400[b]
3p′	3.020	4s′, 4p′	1.460[b]

[a] See ref 27. [b] Scaled. See ref 30.

structures 1 and 4, the $(CO)_5Mn$ moiety was constrained to retain C_{4v} symmetry, and it was also necessary to stagger the acyl group between the equatorial carbonyls in 4. (2) Structures 3, 5, and 6 were optimized while preserving C_s symmetry. (3) All C–H and noninteracting C–O distances were fixed at values of 1.09 and 1.151 Å, respectively. (4) In the path coordinate constrained geometry optimizations along the methyl migration potential energy surface C_s symmetry was also maintained and the methyl group was oriented such that the in-plane hydrogen trailed the methyl carbon as methyl migration proceeded. It was shown in an earlier study[13] that the constraint of C_s symmetry is reasonable and that the orientation of the in-plane hydrogen was not important. All noninteracting carbonyl–manganese distances were linearly interpolated along the reaction path. (5) C_s symmetry was also preserved in the other potential energy surfaces studied in this work. In most cases the agreement between our theoretically predicted bond distances and experiment[24,25] is excellent. The only major discrepancy is that the predicted manganese–methyl bond length in structure 1 is 0.16 Å shorter than the experimental[24] value reported in an electron diffraction study; however, the reliability of this distance has been questioned.[26] We also note that lengthening the manganese–methyl bond of the PRDDO-optimized geometry to the experimental $Mn–CH_3$ distance lowers the total energy by only 3 kcal/mol at the ab initio level and should therefore not have a major effect on our calculated results.

In all ab initio Hartree–Fock (HF) calculations, the manganese basis set employed was determined by taking Clementi's[27] double-ζ Slater basis for manganese, augmenting the 3s and 3d space by an additional function each and constraining each 3s orbital exponent to be equal to an independent 3d orbital exponent. The valence orbital (3s, 3p, 3d, 4s) exponents for this newly described basis were then reoptimized with respect to the total energy for the $4s^23d^5$ ^6S state of the neutral atom, while leaving the core orbital (1s, 2s, 2p) exponents unchanged. The results of the exponent optimizations are shown in Table II. Constraining the 3s and 3d exponents to be equal allows us to take advantage of the sixth linearly dependent 3d function, which is characteristic of the GAMESS[28] program. The molecular basis set included only the three sets of 3d functions, which were used to describe the 3s and 3d portion of the valence shell of the metal. In our molecular calculations the core orbitals were replaced by a minimal Slater orbital basis.[27] Each core function was then expanded in terms of three primitive Gaussian functions.[29] The 3p and 3d orbitals were expanded in terms of two primitive Gaussians,[29] while the 4s and 4p orbitals were represented by a double-ζ set of single Gaussian[29] orbitals with exponents more properly selected[30] for molecular calculations. Each carbon, oxygen, and hydrogen was represented by a 4-31G[31] split valence basis set. A preliminary study of the reaction, $(CO)_5MnH \rightarrow (CO)_4Mn(COH)$, which has been studied[32] previously, demonstrated that the 4-31G basis produces energetics which are nearly equivalent to those obtained with the Dunning–Hay[33] double-ζ contraction of a 9/5 basis. Additional calculations showed that the energy difference between structures 1 and 3 are similar for the 4-31G basis set on every C, O, and H atom and a basis set which was represented by the Dunning[34] triple-ζ contraction of the 9/5 basis on the C(methyl), C(acyl), and O(acyl) atoms and a 4-31G basis for the rest of the atoms. Attempts were made to use the still smaller 3-21G[35] basis; however, this basis does not appear to describe metal–carbonyl bonding very well (the calculated isomerization energy of 1 to 3 was 14 kcal/mol higher than the corresponding value with a 4-31G basis set). The final ab initio HF calculations employed the above basis with six additional d type polarization functions to supplement the methyl carbons and the interacting carbonyl group's carbon and oxygen with exponents of 0.75 and 0.85 for carbon and oxygen, respectively. We felt that polarization functions on the atoms that are changing their number and type of bonds are imperative to correctly calculate energetics. For $(CO)_5Mn(COCH_3)$ this basis set consisted of 178 independent functions.

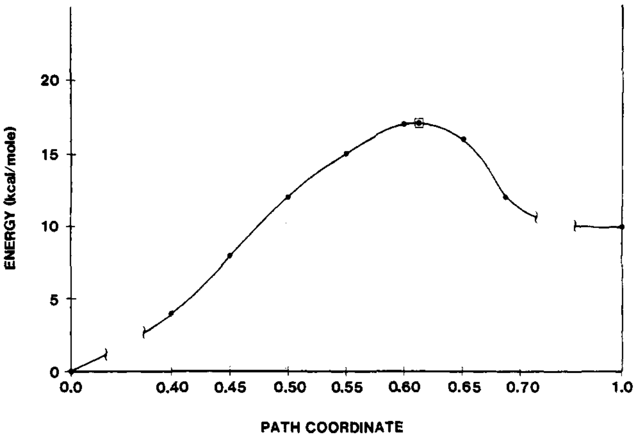

Figure 2. A plot of the methyl migration potential energy surface. Structure 1 corresponds to a path coordinate value of 0.0 and structure 3 to a path coordinate value of 1.0. All of the remaining data points correspond to path coordinate values on the abbreviated surface. The zero of energy is structure 1.

Selected geometries along the PRDDO-generated potential energy surface for methyl migration were used in subsequent ab initio HF calculations, employing the basis set described above. The transition-state geometry was determined from the quadratic interpolation of the ab initio HF total energies at the PRDDO-optimized geom-

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(30) Similar atomic orbital optimizations were carried out for chromium(0) and titanium(0). The atomic 4s and 4s′ orbital exponents were multiplied by a scaling factor that was determined by energy optimizing this scaling factor in the molecules $(CO)_6Cr$ and $[Ti(H)_2(C_3H_7)]^+$. In both cases a value of ~1.57 was obtained for these very different systems. This scaling factor was used without change for the Mn systems reported here, resulting in the scaled 4s/4p exponents listed in Table II.

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Table III. Mulliken Population Analysis for the HOMO in $(CO)_5MnCH_3$ from the ab Initio Hartree-Fock Calculations

path coordinate	0.0	0.40[a]	0.45[a]	0.50[a]	0.55[a]	0.60[a]	0.617[a,b]	0.65[a]	0.70[a]	1.0
C(methyl)	1.22	1.13	1.13	0.91	0.77	0.33	0.37	0.34	0.32	0.23
C(acyl)	0.00	0.04	0.04	0.16	0.35	0.49	0.47	0.49	0.49	0.53
O(acyl)	0.02	0.03	0.03	0.23	0.37	0.73	0.72	0.72	0.73	0.74
Mn	0.54	0.56	0.59	0.50	0.38	0.32	0.33	0.32	0.36	0.33
eigenvalue	−0.373	−0.381	−0.368	−0.339	−0.333	−0.312	−0.315	−0.314	−0.318	−0.309

[a] Path coordinates on the abbreviated linear synchronous transit surface. [b] Estimated transition state by ab initio Hartree–Fock theory.

etries in the region of the transition state. A graph of these results appears in Figure 2. A similar procedure was used to determine the ab initio barrier for the isomerization of **3** to **5**.

Discussion

Energetics. The calculated isomerization energy between structures **1** and **3** at the ab initio HF level is +10 kcal/mol, which certainly lends credence to the notion that the five-coordinate acyl intermediate is rather stable relative to the reactant $(CO)_5MnCH_3$. Although the stability of the acyl intermediate is a necessary condition for a methyl migration to occur, it is not a sufficient condition—a moderate barrier for the isomerization of **1** to **3** must also exist. The energy profile for methyl migration at the ab initio HF level predicts an activation energy of +17 kcal/mol. Experimental estimates[6,7] of the activation energy for methyl migration in $(CO)_5MnCH_3$ define a range between 14–17 kcal/mol. The PRDDO value for the same isomerization energy between **1** and **3** is much smaller, at +1 kcal/mol. The barrier for methyl migration predicted by PRDDO is +18 kcal/mol, and is found[36] to occur at a somewhat less advanced value of the path coordinate than the transition state found at the ab initio HF level. The overall energy difference for the carbonylation reaction (eq 1, L = CO) was computed to be −8 kcal/mol at the ab initio HF level. Experimental enthalpy measurements for the same reaction are in the neighborhood of −8 and −13 kcal/mol. The ΔE calculated by PRDDO for eq 1 is too negative for reasons we feel we understand.[37] The results of our ab initio HF calculations and previous theoretical studies are quantitatively and qualitatively similar although differences between the calculations exist. For instance, EH[13] predicts a barrier of +20 kcal/mol for methyl migration, but the five-coordinate intermediate (**3**) is only slightly more stable than the transition state. HFS ab initio[14] calculations estimated the barrier for methyl migration to be +21 kcal/mol, while the isomerization energy for eq 2 was calculated to be +18 kcal/mol. Both the EH[13] and the HFS ab initio[14] studies have reported calculated activation energies close to our value, but the stability of **3** in these prior studies is underestimated relative to our calculations. We also must point out that the geometries used in the EH[13] and HFS ab initio[14] studies were arrived at by using the experimental[24] geometry for **1** and logical assumptions along with partial optimization of certain critical geometrical parameters for **2** and **3**. Much more thorough geometry optimizations were performed in the present study. None of the foregoing theoretical studies attempted to compute the energy difference for eq 1.

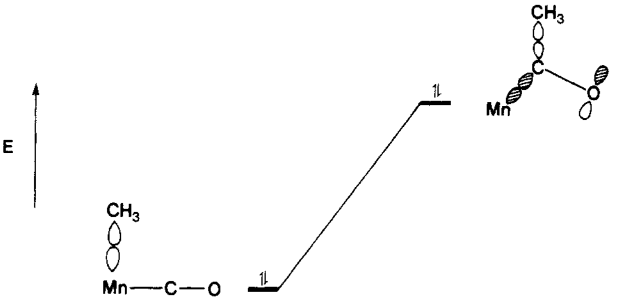

Figure 3. Schematic depiction of the evolution of the HOMO which is dominantly methyl lone pair MO in the reactant (**1**) and a π-type acyl MO in the product (**3**).

Although our calculated energetics are in good agreement with experiment, other ab initio work on related systems has produced much higher barriers.[17,32] This is the case for the energies reported by Sakaki[17] et al. for $Ir(CH_3)(F)(CO)(PH_3)_2$. Their high barriers are probably attributable to the use of 3-21G basis set for the ligands and the use of PH_3 and F as models for PPh_3 and I. We have found that the 3-21G basis set does not describe metal–carbonyl bonding well (the calculated ΔE for reaction 2 is overestimated by ~14 kcal/mol relative to the 4-31G basis set). Similar calculations by Nakamura and Dedieu[32] on hydride migration in $(CO)_5MnH$ suffer from the lack of polarization functions in the basis set and employ an approximate CI treatment, the effects of which are hard to estimate.

The Transition State. In order to demonstrate that our calculated methyl migration potential energy surface is reasonable, we analyzed the evolution of the dominant MO interaction along the calculated reaction sequence, which has been discussed in previous studies.[13,16] This interaction (Figure 3) is best described as the initial donation of the methyl lone pair orbital in the $Mn–CH_3$ bond into the vacant π-antibonding orbital of the interacting carbonyl group. As the methyl group migrates, the orbital energy rises and the MO evolves into what is dominantly an acyl oxygen "π-type" lone pair orbital. This is evidenced in our calculations from a Mulliken population analysis of this molecular orbital. The total atomic populations for C(methyl), C(acyl), O(acyl), and Mn for the orbital interaction shown in Figure 3 has been tabulated for the entire potential energy surface. The results of these tabulations are presented in Table III. A gradual depopulation of the C(methyl) and Mn orbitals occurs, accompanied by build-up of electron density on the C(acyl) and O(acyl) atoms. A dramatic switch in the orbital character takes place in the neighborhood of the estimated transition-state geometry. It turns out that in our calculations this evolving orbital is the highest occupied molecular orbital (HOMO) throughout the transformation from reactants to products. One naturally expects the HOMO in **3** to be the acyl "π-type" lone pair in analogy to aldehydes and ketones. Close inspection of the atomic populations of the HOMO in **2** and **3** reveal that sizeable non-

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(36) The value of the path coordinate for the ab initio transition state on the abbreviated surface was 0.617. The path coordinate for the PRDDO transition state was 0.568 and yielded calculated Mn–C(methyl) and C(methyl)–C(acyl) distances of 2.21 and 1.85 Å, respectively.

(37) PRDDO's energies are generally systematically low compared to the corresponding ab initio values; however, for certain molecules such as CO, which was included in the initial parameterizations, the PRDDO energy is much closer to the "correct" ab initio value. This has the effect of making the calculated ΔE for eq 1 with L = CO too negative. (The actual value obtained at the PRDDO level is −39 kcal/mol.) See also: (a) Throckmorton, L.; Marynick, D. S. *J. Comput. Chem.* **1985**, *6*, 652. (b) Throckmorton, L.; Marynick, D. S., manuscript in preparation.

local contributions to the MO exist. The delocalized nature of the HOMO can be attributed to the mixing of the "π-type" oxygen lone pair with the C(methyl)–C(acyl), the Mn–C(acyl), and the C(acyl)–O(acyl) bonds, which only serves to destabilize this formally nonbonding MO. It does not seem surprising to find that Lewis acids accelerate the reaction since they have been shown[38] to react at the acyl oxygen, and coordinate the lone pair orbital. Since the lone pair orbital is present in the transition state and already significantly raised in energy, interaction of the lone-pair orbital in the transition state with a Lewis acid would only stabilize it, thus, the rate should increase.

The geometry of the estimated transition state is rather interesting. The Mn–C(methyl) and C(methyl)–C(acyl) distances are 2.41 and 1.57 Å, respectively. Thus, the carbon–carbon bond is nearly formed, and the manganese-carbon bond is essentially broken in the region of the transition state. Sakaki et al.[17] also found a rather short carbon–carbon distance (1.63 Å) and long metal–carbon (2.57 Å) distance in their gradient optimized transition-state geometry for $Ir(CH_3)(F)(CO)(PH_3)_2$. This result is indicative of a general conclusion in several experimental[39,40] and theoretical[13,17] studies which is the transition states for alkyl group migrations are very acyl-like in character, meaning the electronic structure and geometry of **2** should bear a close resemblance to that of **3**. This result is even more pronounced when viewed in terms of the localized molecular orbitals (see LMO section). The geometry of **2** offers insight into the manner in which polar coordinating solvents may influence the stability of the transition state. The sizeable vacancy left in the coordination sphere by the departing methyl group creates an ideal situation for the coordinating lone pair(s) of the solvent to bind the metal. Any kind of stabilization of **2** would result in a rate increase. A solvent-assisted migration in $(CO)_5MnCH_3$ was previously noted[7] and suggested to be related to the solvent-assisted dissociation mechanism[41] believed to be common for many octahedral complexes. A kinetic study[42] of migratory insertion in $(\eta^5\text{-}C_5H_5)Mo(CO)_3CH_3$ concluded that methyl migrations are catalyzed by direct attack of the solvent at the transition-metal center while methyl migration occurs. A very recent kinetic study[43] on $(CO)_5Mn(p\text{-}CH_3OC_6H_4CH_2)$ demonstrated that nucleophilic reagents (e.g., donating solvents) catalyze the formation of the unsaturated acyl intermediate and that substitution of coordinated nucleophiles by stronger ligands occurs via a dissociative pathway. The open nature of our calculated transition state is entirely consistent with the idea that nucleophilic solvents should catalyze its formation.

Conformational Analysis. The calculated structure of the kinetic product closely resembles a square pyramid with the acyl group occupying a basal position in the coordination sphere. The carbonyl group in **3**, which was formerly the axial carbonyl in **1**, forms essentially 90° angles with the remaining carbonyl groups and a somewhat larger angle of 109° with the acyl group. Recently, ^{13}C NMR experiments by Flood et al.[8] have demonstrated that methyl migration in $(CO)_5MnCH_3$ proceeds through a square-pyramidal intermediate with the acyl group in a basal position. A basal-substituted square-pyramidal intermediate is also consistent with the observation that the stereochemistry of the incoming nucleophile (L in eq 1) is cis to the acyl group. During the geometry optimizations for **3** a suitable set of geometrical modes was designated such that interconversion of **3** and **5** was possible, suggesting that **3** is at least a local minimum on the pseudorotational potential energy surface at the PRDDO level. The openness of the square-based structure strongly suggests that interaction with coordinating solvents is inevitable. Therefore, in the presence of coordinating solvents eq 2 should proceed with the formation of a solvent-bound six-coordinate complex. The solvent complex and the nucleophile (L) can then undergo a dissociative interchange reaction,[41] provided the solvent is labile. Trapping of the acyl intermediate **3** (which must certainly occur as early as the transition state (**2**)) by coordinating solvents ensures that the product of methyl migration is stable.

The potential for the kinetic product (**3**) to rearrange to more favorable conformations has been a subject in a number of papers.[8,12–14] The tendency for five-coordinate transition-metal complexes to undergo intramolecular rearrangements is well-known[44,45] and strongly suggests that other conformations of the acyl intermediate may be energetically close to **3** or even stationary positions on the pseudorotational potential energy surface. One of the most promising conformations to which **3** could transform would be a η^2-acyl complex (**5**). Precedence for this type of ligand binding in 16-electron transition-metal complexes of molybdenum[46] and ruthenium[47] exists. In addition, an infrared study[12] of the photolysis products of $(CO)_5Mn(COCH_3)$ reported that the $(CO)_4Mn(COCH_3)$ intermediate formed by this process has a pseudo-C_{2v} structure, which is consistent with an equatorially substituted trigonal-bipyramid or an η^2-acyl-bound structure in which the acyl group behaves much like a bidentate ligand. Further observations in the same study[12] showed that the frequency corresponding to the acyl carbonyl C–O bond stretch was much lower than normal C–O stretching frequencies and could be taken as direct evidence for a η^2-bound acyl group.

Our ab initio HF calculations predict an 11 kcal/mol stabilization of the η^2 structure (**5**) over the coordinatively unsaturated intermediate (**3**). A similar energy difference between **3** and **5** was predicted by HFS ab initio theory.[14] Thus, both methods overestimate slightly the stability of **5**, since they predict **5** to be the global minimum on the potential energy surface. However, these calculations strongly suggest that **5** is the preferred structure of the intermediate in the absence of solvent. The η^2 structure **5** is apparently not a minimum on the EH potential energy surface. The energy difference between **3** and **5** calculated by PRDDO is −20 kcal/mol. The PRDDO-optimized geometry for **5** is somewhat different from those determined experimentally and by the HFS ab initio method for d^6 metals. Calculated Mn–C and Mn–O distances are 1.91 and 1.96 Å, respectively. Experimental[46,47] values for d^6 transition-metal complexes show an average difference between the two distances of ~0.2 Å, while complexes of early transition metals show[48] an average difference of

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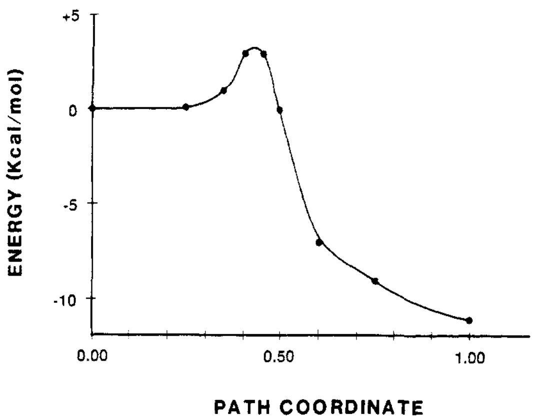

Figure 4. The calculated potential energy surface between structures **3** and **5** in which the zero of energy is structure **3**.

~0.1 Å. The optimized η^2 structure by Ziegler et al.[14] has a ~0.4 Å difference between the Mn–C and Mn–O distances. However, we must point out that the near equivalent Mn–C and Mn–O distances predicted by PRDDO is more consistent with the C_{2v} assignment[12] of the structure of $(CO)_4Mn(COCH_3)$. An X-ray structure[49] on a related manganese(I) complex containing an acyl fragment bonded through the oxygen reported a Mn–O distance of 2.06 Å. The stability of the η^2 interaction is due primarily to the interaction of the highly destabilized "π-type" oxygen lone pair of **3** with vacant metal orbitals. This is demonstrated by the Mulliken population analysis of the HOMO, which shows atomic contributions of 0.74/0.33 and 0.38/0.66 for O/Mn in **3** and **5**, respectively (and represents a net transfer of ~0.3e from the oxygen to the metal). Also the eigenvalue for the HOMO is lowered by ~0.05 au in going from **3** to **5**, indicating that the lone pair orbital is stabilized. The calculated potential energy surface by the synchronous transit method is shown in Figure 4. A 3 kcal/mol barrier for the isomerization of **3** to **5** was found at both the ab initio HF and PRDDO levels of theory. Although the kinetic product **3** is predicted to be a local minimum by PRDDO, it is clear that the capacity for facile rearrangement to **5** is present. If interaction between the solvent and **3** is significant, then **5** may be precluded altogether; otherwise **5** is most likely the global minimum for the acyl intermediate.

It is important to analyze conformations of the acyl intermediate that could potentially change the stereochemistry of the product. The bending of the acyl group in **3** along an in-plane path can generate other possible stationary conformations of the acyl intermediate. Structure **6** corresponds to such a conformation formed by the in-plane bending of the acyl group and a 180° rotation of the methyl group. PRDDO optimization of structure **6** demonstrates that it is a stationary point. The relative energy difference of **3** and **6** is –4 and ~0 kcal/mol at the ab initio HF and PRDDO levels, respectively. Preliminary linear synchronous transit calculations between **3** and the isomer of **6** in which the methyl group was not rotated indicated that the potential energy surface for the intraconversion of **3** to **6** was extremely flat. An estimate of the barrier for the in-plane bend by PRDDO is +3 kcal/mol. A similar result was found by Ziegler et al.[14] using HFS ab initio MO theory. Additionally, a preliminary examination of the linear synchronous transit connecting **5** and **6** indicated a barrier of less than 1 kcal/mol. Again, this suggests that **5** will be the dominate form of the unsaturated intermediate of the unsolvated complex. In order to rationalize the product stereochemistry found in Flood's[8] labeling experiments, Ziegler[14] invoked that solvent participation must occur in order to maintain the stereochemical integrity of the kinetic product (**3**), leading to highly specific products. However, the recent evidence[43] that ligand substitution reactions in the $L(CO)_4Mn(COCH_3)$ system occur via a dissociative pathway implies that an unsolvated five-coordinate intermediate must exist. The presence of unsolvated **3** or **6** will almost certainly provide the opportunity for the rearrangement to **5**. It may be that solvent participation is an important feature of this system, as suggested by Ziegler et al.[14] Alternatively, the reaction of an incoming nucleophile with **5** may be stereospecific, thus preserving the stereochemistry of the products. Further exploration of these possibilities is beyond the scope of the present study, but it is worth noting that PRDDO studies of the rotation of the acyl group in **5**, which *would* result in nonstereospecific products, showed that this process has a rather high barrier associated with it (ca. 44 kcal/mol).

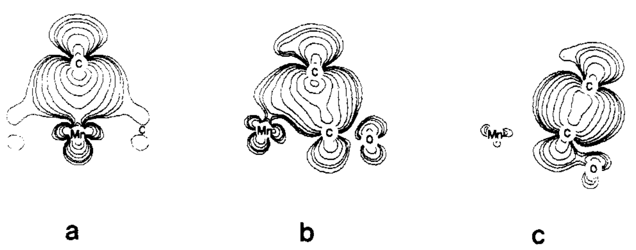

Figure 5. Contour plots of the three key LMO's and their atomic populations in structures **1**–**3**: (a) manganese–methyl bond in structure **1**; (b) acyl-like carbon–carbon bond in the PRDDO-estimated transition-state structure **2**; (c) Carbon(methyl)–carbon(acyl) bond in structure **3** (contour values: 0.5, 0.4, 0.3, 0.2, 0.1, 0.05, 0.02, 0.01, 0.005, 0.0035, 0.002 e/au^3). The atomic populations for C(methyl), C(acyl), and manganese respectively are (a) 1.33, 0.02, 0.40, (b) 1.37, 0.52, 0.11, and (c) 1.17, 0.86, 0.00.

Localized Molecular Orbitals. Localized molecular orbitals provide a useful means of obtaining qualitative information about the valence structure of molecules from the highly delocalized canonical MO's, which are the output of a HF-type calculation. A simple criterion for a unitary transform from canonical MO's to localized counterparts was defined by Boys[50] and was used to localize the PRDDO wave functions. In Figure 5 the important LMO's in structure **1**–**3** are presented along with the total populations for the C(methyl), C(acyl), and Mn atoms in each LMO. Figure 5a is the LMO representing the methyl–manganese bond in structure **1**. Perhaps the most striking feature is the delocalization of the dominantly methyl lone pair into the neighboring carbonyl π-antibonding orbitals. This result is characteristic[51] of metal–carbonyl systems with formally anionic ligands and is highly suggestive of the inherent tendency of the methyl group to migrate. The acyl nature of the transition state is further evidenced by Figure 5b, which is the acyl-like carbon–carbon bond LMO of the transition state at the PRDDO-estimated geometry. The calculated hybridization[52] of this orbital at the methyl carbon is $sp^{1.8}$, which represents a substantial enhancement of the s character of this hybrid relative to the idealized sp^3 hybridization

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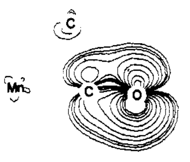

Figure 6. Contour plot of the oxygen "π-type" lone pair LMO in the PRDDO transition state. (The contour values in this plot are the same as those reported for Figure 5.)

expected for a fully saturated carbon. This increased s character probably allows for better simultaneous overlap between the methyl hybrid and the two other atoms involved in the migration; however, the dominant interaction is between C(methyl) and C(acyl). This is clear from atomic populations of this orbital, which are as follows: C(methyl), 1.37e; C(acyl), 0.52e; Mn, 0.11e. In addition, the C(methyl) hybrid points more toward the C(acyl) than the Mn. The angular deviation of this hybrid is 19° with respect to the C(methyl)–C(acyl) internuclear axis and 35° with respect to the C(methyl)–Mn axis. The LMO in Figure 5c corresponds to the C(methyl)–C(acyl) bond in structure **3**. Comparison of the LMO in Figure 5c with Figure 5a shows the greater covalency of the C(methyl)–C(acyl) bond vs. the C(methyl)–Mn bond. Since the transition state is found to be acyl-like in character, it is not surprising to find an LMO corresponding to an oxygen π-type lone pair. Figure 6 illustrates the presence of the π lone pair on the oxygen atom at the PRDDO estimate of the transition-state geometry. The significant atomic populations are 1.77 for O(acyl) and 0.22 for C(acyl) which indicates that the majority of the electron density resides on the acyl oxygen. The calculated hybridization at the oxygen is $s^{1.0}p^{4.3}$, reflecting the dominant role of oxygen p orbital character in this LMO. The bond angle deviation of the oxygen contribution to the LMO is 89.9° with respect to the C–O bond axis. The essentially orthogonal bond angle deviation is typical of an LMO possessing local π-symmetry. On the basis of earlier observations and the LMO's in Figures 5 and 6, we are in a position to conjecture that the migrating methyl group causes the nucleophilic displacement of a π-bond in the unsaturated ligand. This idea is more easily realized when viewed in terms of Lewis structures as follows:

$$L_nM(R){-}A{=}B \longrightarrow L_nM{-}A(R){-}B: \quad (5)$$

We further surmise that the migration of alkyl groups to unsaturated cis ligands in transition-metal complexes represents the dissociation of the alkyl group, which does not occur in the more conventional sense. Figure 7 shows the LMO's of the C(acyl)–Mn (Figure 7a) and O(acyl)–Mn (Figure 7b) bonds in structure **5** along with the total atomic populations. Comparing Figure 7a to Figure 7b, one can see that the C(acyl)–Mn bond (Figure 7a) shows a greater amount of delocalization onto the manganese center than the O(acyl)–Mn bond (Figure 7b). This observation is further emphasized by the atomic populations of these two LMO's which are 1.71e for C(methyl) and 0.27e for Mn in the C(acyl)–Mn bond and 1.82e for O(acyl) and 0.19e for Mn in the O(acyl)–Mn bond. The hybridization calculated for the O(acyl)–Mn bond is $sp^{2.2}$. The calculated hybridization at the acyl carbon for the C(acyl)–Mn LMO is $sp^{1.0}$, while the hybridization at the metal is $sp^{2.0}d^{4.7}$. The metal hybridization for the same interaction in **3** is $sp^{1.1}d^{2.2}$, which represents a large increase in the utilization of d orbitals to provide extra flexibility in the highly strained metallacycle **5**. The calculated bond angle deviations for the C(acyl)–Mn bond relative to the bond axis in **3** and **5** are 3.6° and 46.1°, respectively. The large increase in the bond angle deviations for the C(acyl)–Mn bond in going from **3** to **5** is a further indication of the strained nature of the η^2-acyl structure. The appreciable ring strain present in **5** is in direct opposition to what appears to be a very favorable coordinating interaction. The ring strain therefore diminishes the full capacity for the oxygen lone pair to fill the vacancy in the coordinate sphere of the acyl intermediate, thus ensuring that the carbonyl oxygen will remain relatively labile.

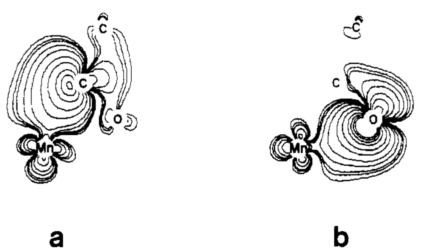

Figure 7. Contour plots of the LMO's of the C(acyl)–Mn bond (a) and the O(acyl)–Mn bond (b) in the η^2 structure **5**. The atomic populations for C(acyl) and Mn in (a) are 1.71 and 0.27, respectively. The atomic populations for O(acyl) and Mn in (b) are 1.82 and 0.19, respectively. (The contour values in these plots are the same as those reported for Figure 5.)

Conclusion

We have presented a full reaction surface for methyl migration in $(CO)_5MnCH_3$ and a conformational analysis of the acyl intermediate. Geometries for the reactant (**1**), product (**3**), and transition state (**2**) structures were obtained with the PRDDO method. The energetics of these geometries were then reevaluated with large basis set ab initio HF calculations. The calculated energy difference between structures **1** and **3** is +10 kcal/mol at the ab initio level. The overall energy difference for eq 1 is calculated to be −8 kcal/mol at the ab initio HF level. The calculated energy of activation by ab initio HF theory is +17 kcal/mol. The transition state (**2**) geometry and electronic structure was found to closely resemble that of the unsaturated pentacoordinate acyl intermediate (**3**). The coordinative unsaturation present in the transition-state geometry implies that coordinating solvents could interact with the vacancy, thereby stabilizing the transition state and accelerating the rate of reaction. The similarity between the electronic structure of **2** and **3** is evidenced by the presence of the "π-type" oxygen lone pair orbital in the transition state. Interaction of this highly destabilized MO with the vacant orbitals of Lewis acids would stabilize the transition state and hence accelerate the reaction. In addition to the kinetic product (**3**) a η^2 conformation (**5**) of the acyl intermediate was found to be a minimum on the potential energy surface. A facile intraconversion between **3** and **5** is possible with a +3 kcal/mol barrier in going from **3** to **5**. A similarly facile interconversion between **5** and **6** exists. On the basis of our calculations, if solvent coordinates **2** and **3**, it can form a stable complex and might preclude **5**. If **3** or **6** is essentially free of intimate solvent interaction, intraconversion to **5** is allowed and would be expected. Stereochemical specificity may be retained by invoking solvent participation with **3** or by assuming that the incoming nucleophile reacts stereospecifically with **5**. The LMO's of the transition state revealed that the transition state has significant acyl character. This was evidenced by the two-center LMO between the methyl carbon and the acyl carbon (Figure 5b), and the existence of the oxygen "π-type" lone pair LMO (Figure 6). The LMO plots for the migration sequence suggest that the migrating methyl group behaves as a nucleophile and displaces a π-bond in the interacting carbonyl group. LMO plots of the η^2-acyl bonds exhibit the true bidentate nature of this mode of bonding. The manganese–oxygen interaction is best described as the σ donation of the "π-type" lone pair orbital on the oxygen with vacant atomic orbitals on the metal. Although the η^2 interaction seems to be electronically favorable, the apparent strain present in the metallacycle works to diminish the stabilization.

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A Theoretical Study of the Bonding and XPS Spectra of Chromium Interacting with a Polyimide Model Compound

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Molecular orbital calculations have been performed on a complex of chromium with *N,N′*-diphenylpyromellitimide, a compound structurally similar to the PMDA part of the PMDA–ODA polyimide repeat unit. The PMDA/Cr complex investigated involving chromium located above the central benzene ring is one of several possible complexes formed under the experimental conditions of clean surfaces and ultrahigh vacuum. The calculated C 1s core levels, together with Koopmans' approximation, provide a reasonable fit to the carbon 1s XPS data, if it is assumed that the observed spectrum reflects a portion of both reacted and unreacted molecular species.

Introduction

Polymers such as PMDA–ODA polyimide, shown in Figure 1, have been the focus of recent interest motivated by technological applications that require thin film insulators with high thermal and mechanical stability.[1] Studies of the interface formed between such polymers and various metals have been performed to gain fundamental information about the interfacial metal–polymer bonding in an attempt to optimize relevant properties, e.g., adhesion.

The interpretation, at the molecular level, of data derived from spectroscopic studies such as XPS (X-ray photoelectron spectroscopy), is complicated by the presence of several different types of functional groups composing the PMDA–ODA polyimide polymer. It would be useful to distinguish the extent to which each of these groups interacts with the deposited metallic layer. To achieve a better understanding of metal–polymer interactions, we have studied the interaction of metal atoms with model compounds containing functional groups found in the polyimide polymer.

To investigate how the polymer might interact with deposited metal atoms, we have computationally investigated the interaction of a single metal atom with a fragment of the polyimide repeat unit. The present work will compare experimental XPS results and theoretical ab initio calculations of a PMDA model compound (*N,N′*-diphenylpyromellitimide) shown in Figure 1 (bottom). The PMDA model compound represents an excellent model for one part of the PMDA–ODA polyimide, Figure 1 (top), since it is structurally similar to the segment of the polymer that is found between two adjacent ether oxygens on a polymeric strand. By studying the PMDA model compound, information about one building block of PMDA–ODA polyimide is obtained, and certain details concerning the nature of metal–polymer interactions are revealed.

The approach that we will use is one in which the transition-metal–PMDA model compound is treated as an organometallic complex. We will look for analogies between the orbital interactions of the PMDA model compound with the transition-metal atom and similar orbital interactions in stable organometallic complexes that have been previously investigated.

Computational Methods

All calculations performed are ab initio and carried out with the GAMESS series of programs.[2] For first- and second-row atoms, an STO-3G basis set[3] was employed. Since it is well-known that the 3d orbitals of transition-metal atoms cannot be represented by a single exponent, an STO-3G expansion[4] for each of the two Slater orbitals obtained by Clementi[5] for the Cr atom was used. This had the effect of allowing the 3d orbitals of Cr to have a double-ζ expansion. The 4s and 4p orbitals of chromium were also expanded in an STO-3G basis with exponents taken from Pietro et al.[4]

For the present work, bond lengths, bond angles, and dihedral angles for the PMDA model compound were chosen from the X-ray structure of 4,4′-bis(phthalalimide) diphenyl ether.[6] The dihedral angle between the phenyl

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