Conclusions

1. Phosphorus–carbon bond strengths in trivalent and pentavalent alkylidenephosphoranes are comparable. Reactivity of the latter species does not arise from weak bonding between the phosphorus and carbon but rather from the zwitterionic character of the bond.

2. The π character of the PC bond in the pentavalent systems can be increased by fluorine substitution at C as evidenced by charge density difference plots. Substitution at phosphorus with electron withdrawing and donating groups does not significantly affect π contributions to the bond.

3. The π bond strength in $HP{=}CH_2$ is calculated to be 107 kcal/mol at MP2/6-31G*//HF/3-21G$^{(*)}$, significantly higher than that in either its nitrogen congener or ethylene.

4. Phosphorus–carbon bonds in the trivalent phosphoranes exhibit the characteristic charge distributions of π bonding. The π orbital is distributed over both centers, in contrast to the pentavalent species.

5. Barriers toward rotation for systems having accessible d orbitals must be interpreted with caution, as they may bear no relationship to bond strength. This has been shown to be the case for pentavalent alkylidenephosphoranes and we show here that it can also occur in the corresponding trivalent species.

Acknowledgment. M.M.F. would like to acknowledge the support of the Chemistry Departments and the Academic Computing Centers at Bryn Mawr and Haverford Colleges for a portion of this work. L.C.A. thanks the National Institutes of Health (GM 26462) and the U.S. Army (ARDEC), Dover, NJ, for furnished support.

Registry No. $HP{=}CH_2$, 61183-53-7; $FP{=}CH_2$, 105801-75-0; $MeP{=}CH_2$, 89149-01-9; $HP{=}CF_2$, 61183-52-6; $H_3P{=}CH_2$, 36429-11-5; $F_3P{=}CH_2$, 110638-16-9; $H_3P{=}CF_2$, 104575-63-5; $Me_3P{=}CH_2$, 14580-91-7.

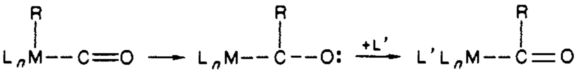
Chemical Origins of Substituent Effects in Alkylpentacarbonylmanganese(I) Group Migration Reactions

Frank U. Axe and Dennis S. Marynick*

Contribution from the Department of Chemistry, The University of Texas at Arlington, Arlington, Texas 76019-0065. *Received May 15, 1987*

Abstract: A molecular orbital study of the effects of different alkyl substituents on the ease of group migration and the stability of the products formed in alkylpentacarbonylmanganese(I) systems ($(CO)_5MnR$, where R = CH_3, CH_2CH_3, $CH_2CH_2CH_3$, $CH(CH_3)_2$, H, $CH_2C_6H_5$, C_6H_5, CH_2F, CF_2H, and CF_3) is presented. Isomerization energies for the group migrating step to an η^1-conformation and an η^2-conformation were calculated for the entire series of substituents. The energies of activation for both of these processes were estimated. The relative overall energy difference for the carbonylation reaction $(CO)_5MnR + CO \rightarrow (CO)_5Mn(COR)$ was also calculated for each derivative. The PRDDO method was used to obtain estimates of the geometries of the germane conformations necessary for a quantitative study of group migration. Ab initio Hartree–Fock calculations at the PRDDO optimized geometries were also carried out to provide an assessment of the calculated energies for a more limited set of the substituents. The calculated results at both levels of theory are compared to available experimental data and are found to be in good qualitative agreement. Localized molecular orbitals are used to analyze the Mn–R bond in the six-coordinate complex. A simple generalized acid–base description of the substituent effects is proposed to rationalize their observed and calculated behavior. This model may be easily extended to predict the qualitative change in migratory aptitude when CO is replaced by some other unsaturated ligand and when the transition-metal moiety is different.

The carbonylation reaction 1 remains a topic[1] of current investigation in organometallic chemistry. This reaction is typically



$$L_nM(R){-}{-}C{\equiv}O \longrightarrow L_nM{-}{-}C(R){-}{-}O{:} \xrightarrow{+L'} L'L_nM{-}{-}C(R){=}O \quad (1)$$

characterized by a topological rearrangement of a σ-bonded anionic group from the transition-metal center to an adjacent carbonyl group. In some transition-metal systems the process of alkyl group migration constitutes the initial step in a two-step process. The newly formed vacancy in the coordination sphere may or may not be followed by the addition of an incoming nucleophile (L′). Although this reaction occurs for a wide variety of transition metals[1b] in a large assortment of d orbital configurations, entering ligands[1a] (L′), and ancilliary ligands[1a] (L), there exists a specific trend in the migratory ability of a wide range of alkyl groups which is common to most of these systems. This basic trend has been attributed to the electron-withdrawing or electron-releasing nature of the substituent. Electron-releasing substituents facilitate the reaction, while electron-withdrawing substituents retard it. These substituent effects have been demonstrated in two ways. First, extensive kinetic studies[2,3] of the effect of the different alkyl substituents on the carbonylation reaction rate have been performed on several systems. Second, thermodynamic data[4,5] for numerous alkyl migratory systems reflect a similar trend in the stability of the products formed. One of the best experimentally

---

[1] (a) Kuhlmann, E. J.; Alexander, J. J. *Coord. Chem. Rev.* **1980**, *33*, 195. (b) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299. (c) Wojcicki, A. *Adv. Organomet. Chem.* **1973**, *11*, 87. (d) Trichel, P. M. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 4, Chapter 29, pp 99–101.

[2] (a) Calderazzo, F.; Cotton, F. A. *Abstr. Int. Conf. Coord. Chem., Stockholm* **1962**, Paper 6H7. (b) Calderazzo, F.; Noack, K. *Coord. Chem. Rev.* **1966**, *1*, 118. (c) Cawse, J. N.; Fiato, R. A.; Pruett, R. L. *J. Organomet. Chem.* **1979**, *172*, 405.

[3] (a) Craig, P. J.; Green, M. *J. Chem. Soc. A* **1968**, 1978. (b) Craig, P. J.; Green, M. *Ibid.* **1969**, 157. (c) Green, M.; Westlake, D. J. *Ibid.* **1971**, 367. (d) Glyde, R. W.; Mawby, R. J. *Inorg. Chim. Acta* **1970**, *4*, 331. (e) Glyde, R. W.; Mawby, R. J. *Inorg. Chem.* **1971**, *10*, 854. (f) Kubota, M.; Blake, D. M.; Smith, S. A. *Ibid.* **1971**, *10*, 1430. (g) Blake, D. M.; Winkelman, A.; Chung, Y. L. *Ibid.* **1975**, *14*, 1326.

[4] Connor, J. A.; Zafarani-Moattar, M. T.; Bickerton, J.; El Saied, N. I.; Suradi, S.; Carson, R.; Al Takhin, G.; Skinner, H. A. *Organometallics* **1982**, *1*, 1166.

[5] (a) Blake, D. M.; Chung, Y. L.; de Faller, J.; Winkelman, A. *J. Am. Chem. Soc.* **1974**, *96*, 5568. (b) Ashcroft, S. J.; Maddock, A. *J. Chem. Soc., Dalton Trans.* **1974**, *462*. (c) Nolan, S. P.; Lopez de la Vega, R.; Mukerjee, S. L.; Hoff, C. D. *Inorg. Chem.* **1986**, *25*, 1160.

0002-7863/88/1510-3728$01.50/0

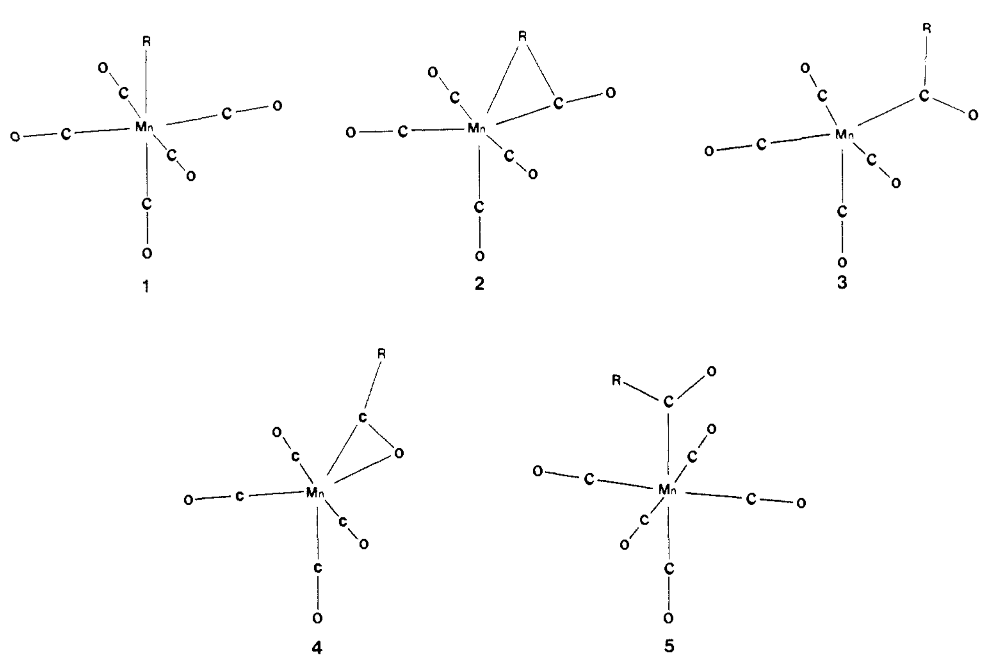


Figure 1. Molecular conformations considered in this study: (1) alkylpentacarbonylmanganese(I); (2) the estimated transition state for alkyl migration; (3) the unsaturated η^1-acyl intermediate; (4) the η^2-acyl intermediate; (5) acylpentacarbonylmanganese(I).

studied examples of an alkyl migratory system is the alkylpentacarbonylmanganese(I) system:

$$(CO)_5MnR + CO \rightarrow (CO)_5Mn(COR) \qquad (2)$$

This system has been extensively studied with respect to its kinetic[2] and thermodynamic[4] behavior for a wide spectrum of different alkyl groups. It is also known[6] to form an acyl intermediate in the course of the carbonylation reaction, and the nature of the intermediary species formed has been of interest,[7] especially with regards to its geometry.

Limited theoretical studies[8,9] of the effects of substituents on the kinetic and thermodynamic behavior of the carbonylation reaction are present in the literature. These studies have employed a wide variety of molecular orbital (MO) methods including extended Hückel,[8c] CNDO,[8e,f] PRDDO,[8a] ab initio Hartree–Fock[8a,d,9] (HF), ab initio Hartree–Fock–Slater[8b] (HFS), and ab initio HF–CI.[8d,g] Unsurprisingly, the (CO)$_5$MnR system has been the subject of prior theoretical[8] investigation,[5] including a recent contribution from this laboratory.[8a] In only two of these prior theoretical studies[8b,9a] emphasis was placed upon the quantitative effects caused by different alkyl groups on the migration process. One study[8b] computed the quantitative effects of methyl and hydride on the migration process in the alkylpentacarbonylmanganese(I) system, while the other study[9a] calculated the quantitative effects of methyl, ethyl, and difluoromethyl on the migration process in a model palladium system. Therefore, a broad range study of substituent effects upon the ease of migration and the thermodynamic stability of carbonylation products remains unaddressed at this time, especially with respect to large alkyl groups like *n*-propyl, isopropyl, trifluoromethyl, phenyl, and benzyl.

In this paper we present an extensive theoretical study of the effects of different substituents on the migratory process in alkylpentacarbonylmanganese(I) systems. We chose this system due to the great wealth of experimental data with which we may compare our calculated results. This study was carried out with the aid of approximate and ab initio MO methods. In order to calculate substituent effects we have chosen three distinct approaches: (1) We calculated the energy of isomerization for the alkyl migration step to form an η^1-acyl complex and an η^2-acyl complex. (2) We calculated the overall exothermicity of the carbonylation reaction (eq 2). (3) We estimated the effects of different substituents upon the activation energy for the migration step. This threefold approach enables us to evaluate both the thermodynamic and kinetic behavior of a wide range of alkyl groups for the (CO)$_5$MnR system. Details of the bonding will be discussed through the aid of localized molecular orbitals (LMO's), overlap populations, degrees of bonding, and atomic charges. A general qualitative rationalization of the calculated trends is also presented.

Calculations and Geometries

The method of partial retention of diatomic differential overlap[10] (PRDDO) is an approximate MO approach which has been shown to mimic well the corresponding minimum basis set ab initio calculation in only a fraction of the time, and without sacrifice of the quantitative accuracy of the ab initio approach. This rapid and quantitative method is ideally suited for a systematic study of substituents in transition-metal systems, especially when large substituents are involved. PRDDO has also been shown[11] to predict metal–ligand bond lengths in transition-metal complexes to a high degree of accuracy, and it works particularly well for determining[11a] equilibrium bond lengths in metal carbonyl complexes. Also, PRDDO has demonstrated[12] its ability to correctly predict conformational preferences in different kinds of organometallic systems. The details of all PRDDO calculations discussed in this work may be found in these early application papers.[11,12] In the present study, we considered five geometric structures to be important. These five geometries are shown in Figure 1. Structure **1** is the six-coordinate alkylpentacarbonylmanganese(I) complex. Structure **3** is the coordinatively unsaturated η^1-acyl intermediate, which is the kinetic product of alkyl migration. Structure **2** is the transition state for the alkyl group migration reaction, which separates **1** from **3**. Structure **4** is the η^2-conformation of the acyl intermediate formed from rearrangement of **3**.

---

(6) Mawby, R. J.; Basolo, F.; Pearson, R. G. *J. Am. Chem. Soc.* **1964**, *86*, 3994.

(7) (a) Flood, T. C.; Jensen, J. E.; Statler, J. A. *J. Am Chem. Soc.* **1981**, *103*, 4410. (b) McHugh, T. M.; Rest, A. J. *J. Chem. Soc., Dalton Trans.* **1980**, 2323.

(8) (a) Axe, F. U.; Marynick, D. S. *Organometallics* **1987**, *6*, 572. (b) Ziegler, T.; Versluis, L.; Tschinke, V. *J. Am. Chem. Soc.* **1986**, *108*, 612. (c) Berke, H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7224. (d) Nakamura, S.; Dedieu, A. *Chem. Phys. Lett.* **1984**, *111*, 243. (e) Saddei, D.; Freund, H. J.; Hohlneicher, *J. Organomet. Chem.* **1980**, *186*, 63. (f) Ruiz, M. E.; Flores-Riveros, A.; Novaro, O. *J. Catal.* **1980**, *64*, 1. (g) Dedieu, A.; Sakaki, S.; Strich, A.; Siegbahn, P. E. M. *Chem. Phys. Lett.* **1987**, *133*, 317.

(9) (a) Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1986**, *108*, 6136. (b) Sakaki, S.; Kitaura, K.; Morokuma, K.; Ohkubo, K. *J. Am. Chem. Soc.* **1983**, *105*, 2280.

(10) (a) Halgren, T. A.; Lipscomb, W. N. *J. Chem. Phys.* **1973**, *58*, 1569. (b) Marynick, D. S.; Lipscomb, W. N. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 1341.

(11) (a) Marynick, D. S.; Axe, F. U.; Kirkpatrick, C. M. *Throckmorton*, L. *Chem. Phys. Lett.* **1982**, *99*, 406. (b) Marynick, D. S.; Reid, R. D. *Ibid.* **1986**, *124*, 17.

(12) (a) Axe, F. U.; Marynick, D. S. *J. Am. Chem. Soc.* **1984**, *106*, 6230. (b) Marynick, D. S. *J. Am. Chem. Soc.* **1984**, *106*, 4064.

Table I. Theoretical and Experimental R–Mn Bond Lengths for $(CO)_5MnR$ (Å)

R	PRDDO	ab initio	exptl
CF_3	2.012	2.126	2.056^a
CF_2H	2.023		
CH_2F	2.022		
$CH_2C_6H_5$	2.024		
CH_3	2.028	2.176	2.185^b
CH_2CH_3	2.033		
$CH_2CH_2CH_3$	2.035		
$CH(CH_3)_2$	2.070		
C_6H_5	2.014		
H	1.560	1.658	1.601^c (1.576) (1.500)

^{a}Reference 21. ^{b}Reference 22. ^{c}Reference 23.

Structure **5** is the overall product of carbonylation (eq 2). The geometries of **1**, **3**, **4**, and **5** were chain-optimized at the PRDDO level. Complete geometry optimizations were performed for these structures, with the following exceptions: All noninteracting C–O distances were set at 1.15 Å. All C–H distances were assumed to be 1.09 Å. In structures **1** and **5** C_{4v} symmetry was maintained for the $(CO)_5Mn$ moiety. All carbon–carbon single bond distances in the ethyl, *n*-propyl, etc., groups were set at 1.54 Å. All of the parameters in the phenyl rings in $(CO)_5Mn(C_6H_5)$ and $(CO)_5Mn(CH_2C_6H_5)$ were taken directly from the geometry for benzene used by Stevens.[13] All C–F distances were optimized once for the parent structure **1** and set at the optimized value of 1.38 Å in all of the remaining structures. Structure **3** was assumed to have C_s symmetry. Structure **2** was obtained for all substituents except H by taking the path coordinate constrained optimized[14] geometry at the PRDDO level of the transition state for the methyl compound reported in our earlier study[8a] and adding the appropriate substituent followed by reoptimization of the geometrical parameters of the new alkyl group, while maintaining the geometry of the $(CO)_4Mn(CCO)$ atoms. The geometry of structure **2** for the hydride species were determined by separate path coordinate constrained geometry optimizations.[14,15] For structures **1**, **3**, and **4**, gradient optimizations were done with a new version of PRDDO. Very minor structural and energetic differences were found, indicating that our optimized geometries are reasonable.

To better assess the energetics of the isomerization and carbonylation reactions, ab initio Hartree–Fock calculations employing a large flexible metal basis set and using the PRDDO optimized geometries were performed. These calculations were performed with the GAMESS[16] program. The details of the metal basis set have been published[8a] previously; however, we note here that this basis set is double-ζ in the 3s, 3p, 4s, and 4p AO's and triple-ζ in the 3d AO's. Two ligand basis sets were used to assess the energetics. Each employed a 4-31G[17] split-valence basis for all carbon, oxygen, and hydrogen atoms (the only exception was for calculations involving $(CO)_5MnC_6H_5$ in which the phenyl hydrogen atoms were represented by a STO-3G[18] basis set). Polarization functions[19] were added to the migrating alkyl group carbon or hydride and to the interacting carbonyl carbon and oxygen atoms. We felt that it was necessary to include polarization functions to accurately calculate conformational energy differences of the types described. Unfortunately, it was not always possible to include polarization functions due to the extreme size of the basis set involved, and so they were omitted for a series of calculations. These two ligand basis sets will be referred to as EBSI and EBSII for the unpolarized and polarized basis sets respectively throughout the remaining text. A more limited set of geometry optimizations was performed at the ab initio HF level of theory. The alkyl–metal bond length in structure **1** was optimized for the methyl, hydride, and trifluoromethyl compounds. In all of these optimizations a 4-31G ligand basis set was used with polarization functions on the alkyl group carbon or the hydride only.

Table II. PRDDO and ab Initio HF Isomerization Energies between (**1**–**3**) and (**1**–**4**) (kcal/mol)

	(1–3)			(1–4)	
R	PRDDO	EBSI^a	EBSII^b	PRDDO	EBSII^b
CF_3	+17	+26	+28	+5	+31
H	+14	+18	+26	−5	+15
CF_2H	+10			−1	
CH_2F	+7			−12	
$CH_2C_6H_5$	+5	0		−17	
C_6H_5	+5^c (−2^d)	−1		−16^c (−20^d)	
CH_3	+1^e	+3	+10^e	−20^e	−1^e
CH_2CH_3	−2	−8		−22	
$CH_2CH_2CH_3$	−2			−22	
$CH(CH_3)_2$	−6			−28	

^{a}4-31G ligand basis set only. ^{b}4-31G ligand basis set plus d-type polarization functions. ^{c}Out-of-plane orientation of the C_6H_5 ring with respect to the C_s plane. ^{d}In-plane orientation of the C_6H_5 ring with respect to the C_s plane. ^{e}Reported in ref 8a.

The crucial results of these geometry optimizations are presented in Table I. These tabulated data consist of the optimized metal–ligand distances for the entire series of substituents for structure **1** at the PRDDO level and in certain instances at the ab initio HF level. Available experimental values are also present in Table I.

Restricted open-shell Hartree–Fock (ROHF) calculations on $CH_3^\bullet$, $CF_3^\bullet$, $CH_2CH_3^\bullet$, $C_6H_5^\bullet$, $CH_2C_6H_5^\bullet$, and $H^\bullet$ were performed. In all cases a 4-31G[17] basis set was used except for the phenyl hydrogens in $C_6H_5^\bullet$ and $CH_2C_6H_5^\bullet$, which were represented by an STO-3G[18] basis set. The geometry for $CH_3^\bullet$ was assumed to be D_{3h} with the C–H distance set at 1.09 Å. The geometry for $CF_3^\bullet$ was the ab initio optimized C_{3v} structure[20] of Benzel et al. The geometry for $CH_2CH_3^\bullet$ was assumed to be the same as that for $CH_3^\bullet$ with a hydrogen atom replaced by a methyl group at a distance of 1.54 Å. The geometry for $C_6H_5^\bullet$ was that assumed by Stevens[13] for benzene with one hydrogen removed. Finally, the geometry for $CH_2C_6H_5^\bullet$ was constructed by substituting an idealized CH_2 group for a hydrogen atom in the Stevens[13] structure for benzene.

Discussion

Optimized Geometries. The PRDDO optimized metal–ligand bond lengths appear to be somewhat short compared to experiment, while the ab initio HF optimized metal–ligand distances are somewhat long[21-23] (Table I). The experimental difference between the Mn–CH_3[22] and the Mn–CF_3[21] bond lengths is ~0.13 Å. Our theoretical values for the same difference calculated by the ab initio and PRDDO methods are ~0.05 and ~0.02 Å, respectively. Although it is well-known[24] that transition-metal alkyl linkages are typically longer than their perfluoro counterparts, the difference between the two is more typically[24] 0.05–0.08 Å, not 0.13 Å. Therefore, it is not surprising to find that the accuracy of the experimental[22] Mn–CH_3 distance has been scrutinized.[25] A more reasonable estimate of the actual Mn–CH_3 distance based upon the experimental Mn–CF_3 distance and our theoretical Mn–CH_3/Mn–CF_3 relative differences is in a range from 2.08 to 2.11 Å. The remaining geometrical parameters for the entire series, although they were optimized, did not vary substantially from the structures of **3**, **4**, and **5** of the methyl system, which has already been reported in great detail.[8a] Finally, we note that

---

(13) Stevens, R. M.; switkes, E.; Laws, E. A.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1971**, *93*, 2603.

(14) Halgren, T. A.; Lipscomb, W. N. *Chem. Phys. Lett.* **1977**, *49*, 225.

(15) The PRDDO optimized geometry of **2** for the $(CO)_5MnH$ species is the following: Mn–H = 1.938 Å, H–C(formyl) = 1.218 Å, Mn–C(formyl) = 1.887 Å, C(formyl)–O(formyl) = 1.206 Å, Mn–C(formyl)–O(formyl) = 171.1°. Compared to the optimized geometry of **2** for the $(CO)_5MnCH_3$ species which is as follows: Mn–C(methyl) = 2.209 Å, C(methyl)–C(acyl) = 1.850 Å, Mn–C(acyl) = 1.869 Å, C(acyl)–O(acyl) = 1.186 Å, Mn–C(aryl)–O(acyl) = 174.2°.

(16) Dupuis, M.; Spangler, D.; Wendoloski, J. J. *General Atomic and Molecular Electronic Structure System*, National Resources for Computations in Chemistry, as modified by: Schmidt, M. W., North Dakota State University; Elbert, S. T., Iowa State University.

(17) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724.

(18) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

(19) The values of the exponents for each primitive set of Gaussian functions was 0.75, 0.85, and 1.00 for carbon, oxygen, and hydrogen, respectively.

(20) Benzel, M. A.; Maurice, A. M.; Belford, R. L. Dykstra, C. E. *J. Am. Chem. Soc.* **1983**, *105*, 3802.

(21) Beagley, B.; Young, G. G. *J. Mol. Struct.* **1977**, *40*, 295.

(22) Seip, H. M.; Seip, R. *Acta Chem. Scand.* **1970**, *24*, 3431.

(23) (a) La Placa, S. J.; Hamilton, W. C.; Ibers, J. A.; Davison, A. *Inorg. Chem.* **1969**, *8*, 1928. (b) McNeill, E. A.; Scholer, F. R. *J. Am. Chem. Soc.* **1977**, *99*, 6243. (c) Robiette, A. G.; Sheldrick, G. M.; Simpson, R. N. F. *J. Mol. Struct.* **1969**, *4*, 221.

(24) (a) Bennett, M. A.; Chee, H. K.; Robertson, G. B. *Inorg. Chem.* **1979**, *18*, 1061. (b) Bennett, M. A.; Chee, H. K.; Jeffery, J. C.; Robertson, G. B. *Inorg. Chem.* **1979**, *18*, 1071.

(25) Andrews, M. A.; Eckert, J.; Goldstone, J. A.; Passell, L.; Swanson, B. *J. Am. Chem. Soc.* **1983**, *105*, 2262.

lengthening of the Mn–CH$_3$ distance from the PRDDO optimized value to the experimental value results in an energy lowering of only 3 kcal/mol at the ab initio level. This will, of course, affect all of our results in the same manner and have no net effect on the trends discussed here.

Isomerization Energies. We have calculated the energy difference between structures **1** and **3** and **1** and **4** at the PRDDO level for the entire series of substituents considered in this work. We also calculated the same two energy differences at the ab initio HF level using the two ligand basis sets previously described for a more limited set of the substituents. These calculated results are presented in Table II. An immediate trend in the calculated data is apparent at both the PRDDO and ab initio HF levels of theory. The relative stability of the isomerization products relative to **1** decreases as the electron-withdrawing ability of the substituent increases. This is consistent with experiment.[1-5] The ab initio HF results spread the calculated substituent effects over a larger energy range than does PRDDO. The inclusion of polarization functions in the ligand basis set (EBSII) has a significant effect on the absolute values of the calculated isomerization energies compared to the unpolarized ligand basis set (EBSI) HF and PRDDO calculations. However, the relative energy differences calculated with the two ligand basis sets remain essentially unchanged. The isomerization of **1** to **4** follows the same trend calculated for the isomerization of **1** to **3**, only this isomerization yields an acyl product that is appreciably more stable than **3**. The η^2-conformations are all predicted to be ~19 kcal/mol more stable than the corresponding kinetic product at the PRDDO level, while extended basis ab initio HF calculations yield ~10 kcal/mol stabilizations of the η^2-conformation for the methyl and hydride compounds. The η^2-form of the trifluoro complex is predicted to be slightly less stable than the corresponding η^1-conformation at the extended basis set ab initio HF level.

Although no direct experimental thermochemical data for (CO)$_5$MnR systems exists for the two isomerizations described, thermodynamic data on some related platinum systems is available. Blake et al.[3g] measured the enthalpies of carbonylation for the following reaction

$$CF_nH_{3-n}IrCl_2[P(C_6H_5)]_2CO \rightarrow (CF_nH_{3-n}CO)IrCl_2[P(C_6H_5)]_2 \quad (3)$$

(where n = 0–3). The experimental values are +21, +17, +12, and +7 kcal/mol for n = 3, 2, 1, and 0, respectively. These data compare very well with our corresponding PRDDO calculated values of +17, +10, +7, and +1 kcal/mol for the (CO)$_5$MnR system. In addition to these experimental ΔH's, the literature contains some theoretically calculated isomerization energies for the manganese system and related complexes. For instance, ab initio HFS calculations[8b] predict the isomerization energy of **1** to **3** to be +19 and +40 kcal/mol for the methyl and hydride species, respectively, while our EBSII calculations yielded +10 and +25 kcal/mol for the same isomerizations. Although these calculated ΔE's are larger than our corresponding values, they still reflect the same qualitative difference between the two substituents. Ab initio HF calculations[8d] with a Dunning 9/5[26] split valence basis for the ligands yielded a predicted value of +11 kcal/mol for the isomerization of **1** to **3** for (CO)$_5$MnH. This result compares well with our ab initio HF calculations using the comparable 4-31G ligand basis (EBSI), which yielded +18 kcal/mol. Configuration interaction calculations in the same study[8d,g] predict a larger value of +30 kcal/mol for the isomerization energy (**1**–**3**). Our calculations indicate that most of the increase in the **1** to **3** isomerization energy may be attributed to the presence of polarization functions, and not electron correlation effects. A more detailed study of basis set effects on the energetics of group migration has appeared elsewhere.[27] In a more recent theoretical paper,[9a] Koga and Morokuma calculated isomerization energies for the reaction Pd(R)(H)(CO)(PH$_3$) → Pd(RCO)(H)(PH$_3$) (where R = CH$_3$, CH$_2$CH$_3$, and CHF$_2$, with values of +19, +15, and +31 kcal/mol respectively). These results parallel our PRDDO (+1, −2, +10 kcal/mol) and ab initio HF values (+3 and −8 kcal/mol). In the case of the phenyl species, two different conformations for structures **3** and **4** were examined. One conformation has the phenyl ring perpendicular to the mirror plane of the molecule, and the other conformation has the phenyl ring in the symmetry plane of the molecule. In both structures **3** and **4** the in-plane orientation of the phenyl ring was found to be the energetically preferred conformation at the PRDDO level. These results are consistent with the experimental structures of ruthenium[28a] and molybdenum[28b] η^2-benzoyl complexes, which both have the in-plane phenyl ring orientation.

Table III. Calculated Relative Bond Energies for the R–Mn Bond (kcal/mol)

R	EBSI[a]	EBSII[b]	exptl[c]
CH$_2$CH$_3$	−10		
CH$_3$[d]	0	0	0
C$_6$H$_5$	+11		+4
H	+20	+19 (+17[e])	+14
CF$_3$	+39	+30	+4
CH$_2$C$_6$H$_5$	−10		−16

[a] 4-31G ligand basis set only. [b] 4-31G ligand basis set plus d-type polarization functions. [c] Reference 4. [d] The bond energy of the Mn–CH$_3$ bond was arbitrarily set at zero. [e] Reference 28.

The most commonly invoked explanation[1] of the origins of substituent effects in transition-metal alkyl migration reactions is related to the relative strengths of the metal–alkyl bond. We have calculated a series of relative energy differences for the following reaction:

$$(CO)_5MnR + CH_3^\bullet \rightarrow (CO)_5MnCH_3) + R^\bullet \quad (4)$$

By calculating the relative energy differences for a series of alkyl groups, we are able to expose the predicted trend in metal–alkyl bond strengths. This objective was achieved by taking the energy of the alkyl free radical directly from ROHF calculations. The relative calculated metal–alkyl bond energies are reported in Table III at the EBSI and EBSII levels of theory. This method predicts that the metal–ligand bond strength increases in the order CH$_3$ < H < CF$_3$, which parallels the **1** to **3** and **1** to **4** isomerization energies. The experimental[4] gas-phase values of the bond enthalpies vary as CH$_3$ < H > CF$_3$. In a recent theoretical paper[29] the Mn–H and the Mn–CH$_3$ bond energies were calculated, and the relative CH$_3$/H bond energy was found to be +17 kcal/mol in good agreement with our values of +20 and +19 kcal/mol. However, a serious discrepancy exists between the calculated and experimental relative bond energy for the Mn–CF$_3$ bond.

The Mn–R bond strength has proven to be a useful indicator of the migratory aptitude of a particular alkyl group. Our calculations are entirely consistent with this idea for CH$_3$, CH$_2$CH$_3$, H, and CF$_3$. However, we point out that this rationale does not hold true for CH$_2$C$_6$H$_5$ or C$_6$H$_5$. Both the experimental and calculated relative bond energies (Table III) predict that the Mn–CH$_2$C$_6$H$_5$ bond is weaker than the Mn–CH$_3$ bond. Experimentally, it is known that a benzyl group has a poorer migratory ability than a methyl group in the alkylpentacarbonylmanganese(I) system and other related systems.[1] The anomalously low Mn–CH$_2$C$_6$H$_5$ bond energy may be attributed to resonance stabilization of the unpaired electron by the π system of the phenyl ring. Conversely, a phenyl group is known[2a] experimentally to migrate more easily than a methyl group. Yet, both theory and experiment indicate that the Mn–C$_6$H$_5$ bond is stronger or at least on par with a methyl group. This suggests that the π system must be important in stabilizing the transition state during phenyl migration. Also, the π accepting ability of the phenyl ring may be responsible for the stronger Mn–C$_6$H$_5$ bond. In conclusion we feel that metal–

---

(26) Dunning, T. H.; Hay, P. J. *Modern Theoretical Chemistry*; Schaefer, H. F., Ed.; Plenum: New York, 1977; Vol. 3, pp 1–27.

(27) Axe, F. U.; Marynick, D. S. *Chem. Phys. Lett.*, in press.

(28) (a) Roper, W. R.; Taylor, G. E.; Waters, J. M.; Wright, L. J. *J. Organomet. Chem.* **1979**, *182*, C46. (b) Curtis, M. D.; Shiu, K. B.; Butler, W. M. *J. Am. Chem. Soc.* **1986**, *108*, 1550.

(29) Ziegler, T.; Tschinke, V.; Becke, A. *J. Am. Chem. Soc.* **1987**, *109*, 1351.

Table IV. Relative PRDDO and ab Initio HF Carbonylation Reaction ΔE's and Relative Experimental $\Delta H_{(g)}$'s (kcal/mol)

R	PRDDO	EBSI[a]	EBSII[b]	exptl[c]
CF_3	+18	+35	+29	+5
H	+11	+14	+14	+13[d]
CF_2H	+9			
$CH_2C_6H_5$	+6	+4		
C_6H_5	+5[d] (+14[e])	+3[d]		+2
CH_2F	+2			
CH_3[f]	0	0	0	0
CH_2CH_3	−2	−6		
$CH_2CH_2CH_3$	−3			
$CH(CH_3)_2$	+1			

[a] 4-31G ligand basis set only. [b] 4-31G ligand basis plus polarization functions. [c] Reference 4. [d] Out-of-plane orientation of the C_6H_5 ring with respect to the C_s plane. [e] In-plane orientation of the C_6H_5 ring with respect to the C_s plane. [f] All values for this substituent were arbitrarily set to zero. Reference 29. The actual values are −39 (PRDDO), −14 (EBSI), −8 (EBSII), and −8 (exptl) kcal/mol.

alkyl bond strengths are an important factor in determining the ease of alkyl migration, but one must exercise caution in applying this notion in a general sense.

The Carbonylation Reaction. We have calculated relative[30] ΔE's for the carbonylation of the entire series of substituents considered in this work at the PRDDO level and for a more limited selection of the substituents at the ab initio HF level. These calculated results are presented in Table IV. The relative reaction ΔE's calculated by PRDDO are qualitatively similar to those calculated by ab initio HF theory. The absolute values of the PRDDO calculated reaction ΔE's appear to be too negative for reasons we have already expressed in our earlier work[8a] on methyl migration. Comparison of these reaction ΔE's with the isomerization energies already presented (Table II) shows that the relative trends predicted by the two separate sets of data parallel one another very well at both levels of theory. It should also be noted that from the calculated data already reported, we may ascertain estimates of the energy of Mn–CO bond cleavage in $(CO)_5Mn(RCO)$. One obtains essentially constant values of ~40 and ~17 kcal/mol at the PRDDO and ab initio levels of theory for the entire spectrum of substituents studied. Therefore, it seems reasonable to say that the predicted trend in the reaction ΔE's depends on the energetics of the alkyl migration step almost exclusively. These results are consistent with the finding[1d] that the rate of decarbonylation is much less dependent on the migrating substituent, owing the rate-determining step primarily to metal–carbonyl bond cleavage.

No attempt to theoretically compute the energy change for the carbonylation reaction (eq 2) or any related systems has appeared, except for one isolated instance.[8d] In that study the relative effect of substituents was not assessed. Experimental[4] gas-phase enthalpies for the carbonylation reaction (eq 2) are also reported in Table IV. The relative[30] experimentally measured[4] ΔH values for the carbonylation of $(CO)_5MnCH_3$, $(CO)_5MnH$, and $(CO)_5MnC_6H_5$ are in very good agreement with the computed relative ab initio HF values. Poorer agreement is found for $(CO)_5MnCF_3$. However, it should be mentioned that experimentally the carbonylation of the trifluoromethyl species is less exothermic than the methyl species, which is certainly qualitatively consistent with our calculations. The PRDDO calculated ΔE's are qualitatively similar to the ab initio HF values and therefore compare with the experimental data in much the same way. More recently, thermochemical data[5c] on the $RMo(CO)_3Cp$ system ($R = H, CH_3, C_2H_5$ and $Cp = C_5H_5^-$) have been published. In this study a series of different phosphine and phosphite ligands were reacted with $RMo(CO)_3Cp$ to produce the corresponding acyl phosphine or phosphite. The general conclusion was that CO insertion into the $Mo–CH_2CH_3$ bond is ~2 kcal/mol more favorable than that into the $Mo–CH_3$ bond and that CO insertion into the $Mo–CH_3$ bond is ~13 kcal/mol more favorable than that into the Mo–H bond. These results are in very good agreement with our calculations.

Table V. PRDDO Estimated Energies of Activation for the Alkyl Migration Step (kcal/mol)

R	ΔE^*	R	ΔE^*
CF_3	+33	H[a]	+20
CF_2H	+35	CH_3	+18
CH_2F	+26	CH_2CH_3	+15
C_6H_5	+22	$CH_2CH_2CH_3$	+15
$CH_2C_6H_5$	+22	$CH(CH_3)_2$	+12

[a] Determined by independent orthogonal optimizations. Reference 15.

The Transition State. The estimated energies of the transition state (**2**) between **1** and **3** relative to **1** at the PRDDO level only are reported in Table V for all substituents considered in this study. The more electron withdrawing groups have higher calculated energies of activation and should retard or even prevent the migration process entirely. Electron releasing groups have the opposite effect. The order of the activation energies are consistent with the experimentally known[2] relative reaction rates for the $(CO)_5MnR$ system and other related transition-metal systems. The experimentally measured[3c] enthalpies of activation for carbonylation in $RFe(CO)_2Cp$ (R = methyl, ethyl, and isopropyl) are +18, +14, and +13 kcal/mol, respectively. These values are in excellent agreement with our theoretically calculated values for the same set of alkyl groups in the manganese system, which are +18, +15, and +12 kcal/mol. The only qualitative difference between our theoretically estimated activation energies and the experimentally observed reaction rates is for the phenyl compound, which is known to lie experimentally between an ethyl and a methyl group in reaction rate. The use of the methyl transition-state geometry may not be optimal for this unique alkyl group. One very interesting facet of phenyl migration obtained from this approximate transition-state geometry is that the energetically preferred orientation of the phenyl ring is perpendicular to the mirror plane of the molecule in much the same way that phenyl bridging occurs in beryllium compounds[31] and in the phenonium ion postulated[32] in organic substitution reactions. The kinetic stability of structure **3** (i.e., the height of the barrier for the decarbonylation of **3** to **1**) for all substituents studied (except for hydride) is ~17 kcal/mol. The kinetic stability of structure **3** for the hydride is much smaller, at only ~6 kcal/mol. This explains why the thermodynamically unstable perfluoro acyls are isolatable, although they gradually decarbonylate to **1**, while formal complexes are not. The calculated ordering between the CF_3 and CF_2H group may seem inverted; however, experimentally measured[3g] activation energies for alkyl migration in the previously cited platinum study show a similar relationship between these two groups.

Acid–Base Considerations. A more simplified view of the substituent effects in group migratory reactions is as follows. We restrict ourselves to pure σ donors and, therefore, exclude the phenyl group, which has been discussed above. Consider the $(CO)_5Mn$ moiety to possess two different kinds of acidic sites (in the Lewis sense), namely the transition-metal center and a carbonyl carbon. These correspond to a hybrid of metal 3d, 4s, and 4p AO's for the manganese center and a CO $2\pi^*$ at the carbonyl carbon. The qualitative ordering of these two vacant MO's places the antibonding orbital of the carbonyl groups above the energy of the vacant metal hybrid orbital. Weakly basic alkyl groups like CF_3 will have a very stable lone pair orbital and will interact unfavorably with the higher energy CO $2\pi^*$ orbital. More basic alkyl groups have more energetic lone pair orbitals, which are closer in energy to the unoccupied $2\pi^*$ orbitals. They will tend to interact better with the $2\pi^*$ orbitals than weakly basic alkyl

---

[30] The actual calculated values for the ΔE for $(CO)_5MnCH_3 + CO \rightarrow (CO)_5Mn(COCH_3)$ are −39, −14, and −8 kcal/mol at the PRDDO, EBSI, and EBSII levels of theory, respectively. The actual experimental value is −8 kcal/mol. These reaction energies, both theoretical and experimental, were all arbitrarily set to zero, and the remaining theoretical and experimental reaction energies were then shifted accordingly.

[31] Marynick, D. S. *J. Am. Chem. Soc.* **1981**, *103*, 1328.

[32] Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 2nd ed.; Harper and Row: New York, 1981.

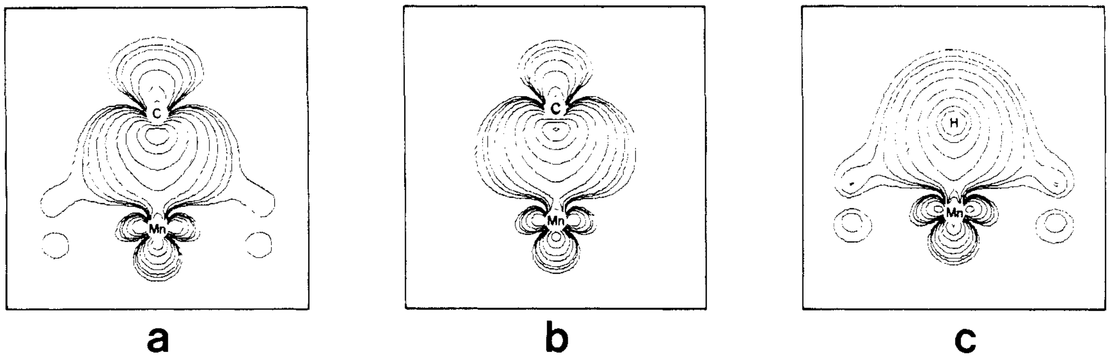


Figure 2. Localized molecular orbital contour plots of the R–Mn bond in **1**: (a) $(CO)_5MnCH_3$; (b) $(CO)_5MnCF_3$; (c) $(CO)_5MnH$. (Contour values: 0.5, 0.4, 0.3, 0.2, 0.1, 0.05, 0.02, 0.01, 0.005, 0.0035, 0.002 e/au^3.)

Table VI. Degrees of Bonding and Overlap Populations for the Mn–R Bond in Structure **1**

R	DOB	OP	R	DOB	OP
CF_3	0.696	0.313	CH_3	0.716	0.346
CF_2H	0.707	0.331	CH_2CH_3	0.717	0.354
CH_2F	0.713	0.334	$CH_2CH_2CH_3$	0.716	0.357
$CH_2C_6H_5$	0.693	0.339	$CH(CH_3)_2$	0.705	0.368

groups like CF_3 and lower the energy required for isomerization. Indirect quantitative evidence for the proposed acid–base relationship may be seen in the degrees of bonding and overlap populations for the Mn–R interaction in structure **1** (Table VI). Both the overlap populations and the degrees of bonding[33] between the metal and the alkyl group increase as the basicity of the alkyl group increases. Also, the optimized manganese–alkyl distances in Table I reflect the relative basicity of the alkyl groups. The relative positioning of the $2\pi^*$ orbitals would lead one to expect that replacing the unsaturated carbonyl ligand with a ligand that has a lower π^* orbital would increase the acidity of the ligand site, and thereby better promote the migration of alkyl groups. The thiocarbonyl ligand, which is known[34] to accept both methyl and hydride transfer, is a likely candidate and has been the subject of a prior theoretical study.[8b] PRDDO calculations[35] of the analogous **1** to **3** isomerization energies for $(CO)_4Mn(CS)CH_3$ and $(CO)_4Mn(CS)H$ yielded −11 and −1 kcal/mol, respectively. These values are in good qualitative agreement with those calculated by Ziegler and co-workers.[8b] The lowest unoccupied molecular orbitals (LUMO's) in free CS and in structure **1** of the $(CO)_4Mn(CS)R$ complexes lie below those of the LUMO's in free CO and the $(CO)_5MnR$ complexes. Additionally, the relative energy difference for the isomerization of **1** to **3** for the thiocarbonyl complexes is ~3 kcal/mol less than in the pure carbonyl complexes, which is consistent with the idea that the two acidic sets of orbitals are closer together in energy in the thiocarbonyl complexes than in the pure carbonyl complexes. This result is also consistent with the theoretical prediction of ab initio HFS calculations. If the energy of the metal orbitals is perturbed then changes in the absolute and relative **1** to **3** isomerization energies should occur. As an example we chose to examine the $(CO)_4CoR$ system, which has been studied extensively experimentally[36] and theoretically.[37] The $(CO)_4Co^+$ moiety is found to be a weaker acid than $(CO)_5Mn^+$ (i.e., the energy of the metal hybrid is higher for $(CO)_4Co^+$ than it is for $(CO)_5Mn^+$). This is substantiated by PRDDO calculations[35] on the $(CO)_4CoR$ complexes. Both the PRDDO calculated degrees of bonding and group charges indicate that less donation occurs in the Co–R bonds than in the corresponding Mn–R bonds (also, this behavior is more apparent from the LMO's, see LMO's section). Therefore, it is not surprising that the calculated **1** to **3** isomerization energies for $(CO)_4CoCH_3$ and $(CO)_4CoH$ are −16 and −12 kcal/mol, respectively. This is also consistent with the fact that the rates of carbonylation in these systems are significantly faster[38] than in the manganese system. The $(CO)_4CoCH_2C_6H_5$ species is found to insert CO with ease, while the analogous manganese compound does not readily submit to carbonylation. Furthermore, the formyl complex for the isoelectronic anionic system $(CO)_4Fe(COH)^-$ is kinetically stable[39] for a finite amount of time.

Table VII. LMO Atomic Populations and Hybridizations for the R–Mn Bond in Structure **1**

R	Mn	C	hybridization
CF_3	0.35	1.61	$sp^{1.2}$
CF_2H	0.37	1.59	$sp^{1.5}$
CH_2F	0.39	1.56	$sp^{1.6}$
$CH_2C_6H_5$	0.39	1.52	$sp^{1.7}$
CH_3	0.40	1.53	$sp^{1.6}$
CH_2CH_3	0.41	1.52	$sp^{1.6}$
$CH_2CH_2CH_3$	0.41	1.52	$sp^{1.6}$
$CH(CH_3)_2$	0.41	1.54	$sp^{1.6}$
C_6H_5	0.39	1.55	$sp^{1.3}$
H	0.48	1.38	s

Localized Molecular Orbitals. Localized molecular orbitals provide a convenient means of qualitatively analyzing the valence structure of molecules. The Boy's method[40] was used to localize the PRDDO wave functions. The first area of interest is the Mn–R bond in structure **1**. Atomic populations and hybridizations[41] for the Mn atom and the atom of the R group bonded to the metal for the entire series are presented in Table VII. The electron distribution of the Mn–R bond is mainly centered on the R group atom. Closer inspection of these populations reveals a significant difference in the polarity of the Mn–R bond as a function of the R group. The Mn–CF_3 LMO is considerably more polar than the Mn–CH_3 LMO, and the degree of polarity increases in the order $CH_3 > CH_2F > CF_2H > CF_3$. This is entirely consistent with accepted ideas regarding the electron-withdrawing nature of perfluoro alkyl groups. An opposite effect occurs, although not as profound as for the perfluoroalkyls, for more electron-releasing groups. A parallel relationship between the hybridization at the alkyl group atom and the electron-withdrawing ability of the alkyl group also exists. The exchange of hydrogen atoms for fluorine atoms increases the amount of s character in the alkyl hybrid (Table VI). This enhancement of s character in the perfluoro alkyl hybrid may be responsible for the shorter metal–alkyl distances usually observed for perfluoro alkyl groups compared to alkyl groups. Increasing the s contribution tends to decrease the radial maximum of the alkyl group hybrid pair of electrons, thereby reducing the metal–alkyl distance. No noticeable change in the hybridization between the remaining alkyl

---

[33] Armstrong, D. R.; Perkins, P. G.; Stewart, J. P. *J. Chem. Soc., Dalton Trans.* **1973**, 838.

[34] Collins, T.; Roper, W. R. *J. Organomet. Chem.* **1978**, *73*, 159.

[35] Axe, F. U. Ph.D. Thesis, The University of Texas at Arlington, 1987.

[36] Heck, R. F. *Adv. Organomet. Chem.* **1966**, *4*, 243.

[37] Antolovic, D.; Davidson, E. R. *J. Am. Chem. Soc.* **1987**, *109*, 977 and references therein.

[38] Nagy-Magos, Z.; Bor, G.; Marko, L. *J. Organomet. Chem.* **1968**, *14*, 205.

[39] Collmann, J. P.; Winter, S. R. *J. Am. Chem. Soc.* **1973**, *95*, 4089.

[40] Boys, S. F. *Quantum Theory of Atoms, Molecules, and the Solid State*, Lowdin, P. O., Ed.; Academic: New York, 1966; pp 253–262.

[41] Switkes, E.; Stevens, R. M.; Lipscomb, W. N.; Newton, M. D. *J. Chem. Phys.* **1969**, *51*, 2085.

group exists, with the exception of the phenyl group, which naturally has a greater s character since it is already considered to be sp^2 hybridized. Density plots of the Mn–R bond in **1** for $(CO)_5MnCH_3$, $(CO)_5MnCF_3$, and $(CO)_5MnH$ appear in Figure 2, plots a, b, and c, respectively. An immediate contrast between parts a and b of Figure 2 is apparent. First, the $Mn-CH_3$ LMO (2a) is noticeably more delocalized toward the Mn atom than is the $Mn-CF_3$ LMO (2b). Second, delocalization of the alkyl lone pair into neighboring carbonyl $2\pi^*$ antibonding orbitals is clearly present in the $Mn-CH_3$ LMO, but absent in the $Mn-CH_3$ LMO. The delocalization of the methyl lone pair into the carbonyl $2\pi^*$ orbital, while the trifluoromethyl group does not, is a manifestation of the greater basicity of the methyl group. The qualitative difference between the $Mn-CH_3$ and the $Mn-CF_3$ bonds is in complete agreement with the conclusions[42] reached by Hall and Fenske. The Mn–H LMO (2c) shows both greater delocalization to the metal and the carbonyl $2\pi^*$ orbitals than the methyl group (2a). This is probably due to the shorter Mn–H distance and the greater angular flexibility of the hydrogen s orbital, compared to the sp hybrid of the methyl lone pair.

The LMO's of $(CO)_4CoCH_3$ were also calculated. The atomic populations for Co and C(methyl) in the $Co-CH_3$ LMO are 0.37 e and 1.60 e, respectively. The corresponding Mn and C(methyl) atomic populations in the $Mn-CH_3LMO$ are 0.40 e and 1.53 e. This comparison further exemplifies the greater acidity of the $(CO)_5Mn$ moiety compared to $(CO)_4Co$. The calculated hybridizations at the metal in these two LMO's are $s^{1.0}p^{1.3}d^{3.5}$ and $s^{1.0}p^{1.2}d^{1.0}$ for the $Mn-CH_3$ and $Co-CH_3$ LMO's, respectively. These results provide insight as to why the $(CO)_4Co^+$ moiety is a weaker base than $(CO)_5Mn^+$. The smaller amount of metal 3d character in the $Co-CH_3$ LMO requires greater utilization of the less energetically favorable 4s and 4p AO's in forming the metal–alkyl bond. The decrease in the participation of the Co 3d AO's in the $Co-CH_3$ LMO relative to the $Mn-CH_3$ LMO is a direct result of the d^8 configuration of $(CO)_4CoCH_3$ versus the d^6 configuration of $(CO)_5MnCH_3$.

Conclusions

We have presented a theoretical study of the effects of a large set of different substituents upon the kinetic and thermodynamic behavior of the group migration reaction in alkylpentacarbonylmanganese(I) systems. This study was accomplished by first performing appropriate geometry optimizations of the relevant conformations (**1**–**5**) for each substituent at the PRDDO level of theory. In most instances the PRDDO optimized geometries agreed very well with experiment. More limited geometry optimizations were carried out at the ab initio HF level of theory. The relative energetics obtained at the PRDDO level were then reevaluated by ab initio HF theory and were found to agree qualitatively well with the ab initio calculations. These calculated energetic quantities included the following: the energy of isomerization of **1** to **3** and **1** to **4**, the estimated barrier for the two isomerizations, and the relative energy change for the carbonylation reaction (eq 2). It was found that electron-releasing alkyl groups should facilitate group migration and stabilize the product formed, while electron-withdrawing alkyl groups should retard the migratory step and destabilize the product formed. Traditionally, the observed trends in these substituent effects have often been rationalized in terms of metal–alkyl bond strengths; however, we have presented an alternative and more general rationale, which employs simple Lewis acid–base arguments. More basic alkyl groups tend to interact more favorably with the CO $2\pi^*$ orbitals, while less basic alkyl groups interact to a lesser extent with CO $2\pi^*$ orbitals. This leads to a reduced tendency for electron-withdrawing alkyls to migrate relative to electron-releasing alkyls. This acid–base picture is supported by our calculations of the overlap populations, degrees of bonding, group charges, optimized metal–alkyl bond lengths, and localized molecular orbitals. The kinetic stability of the formyl complex **3** is found to be much less than that of the corresponding acyl complexes.

Acknowledgment. We thank the Robert A. Welch Foundation (Grant Y-743), Cray Research Inc., and the Organized Research Fund of the University of Texas at Arlington for their support of this work. We also thank the University of Texas System Center for High Performance Computing for the use of their computational facilities.

Registry No. **1** (R = CF_3), 13601-14-4; **1** (R = CF_2H), 15022-34-1; **1** (R = CH_2F), 15337-23-2; **1** (R = $CH_2C_6H_5$), 14049-86-6; **1** (R = CH_3), 13601-24-6; **1** (R = CH_2CH_3), 15694-83-4; **1** (R = $CH_2CH_2CH_3$), 15628-53-2; **1** (R = $CH(CH_3)_2$), 113686-65-0; **1** (R = C_6H_5), 13985-77-8; **1** (R = H), 16972-33-1.

---

(42) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768.

Calculation of the Free Energy of Association of Nucleic Acid Bases in Vacuo and Water Solution[1]

Piotr Cieplak[†] and Peter A. Kollman*

Contribution from the Department of Pharmaceutical Chemistry, School of Pharmacy, University of California, San Francisco, California 94143. *Received July 27, 1987*

Abstract: The free energy perturbation/molecular dynamics (FEP/MD) method has been applied to study the solvation effect on the association of the nucleic acid bases in vacuo and in water solution. Five complexes were considered: the adenine–thymine Watson–Crick H-bonded pair, an adenine–thymine stacked pair, an adenine–adenine stacked pair, the guanine–cytosine Watson–Crick H-bonded pair, and a guanine–cytosine stacked pair. The stacked complexes were calculated to be slightly more stable than the H-bonded complexes in water, whereas in vacuo the H-bonded complexes are favored, which is consistent with available experiments.[1] Furthermore, the magnitude of the calculated free energies of nucleic acid base association in water (ΔG = 0 to −2 kcal/mol) is consistent with the magnitude found experimentally. This shows that it is now possible to calculate ab initio the free energies of noncovalent association of complex molecules in solution.

It is well-known that two of the main factors responsible for the stabilization of the DNA double helix are the hydrogen bond and stacking interactions between nucleic acid bases. Several lines of experimental evidence confirm the importance of these types of interactions. Among them are the studies on the analysis of the dependence of melting temperature[2] on base content of helices as well as recent studies on the influence of dangling (unpaired) nucleotide ends and terminal base pairs on stability and helix

---

[†] Permanent address: Quantum Chemistry Laboratory, Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland.

(1) Nakano, N. I.; Igarashi, S. J. *Biochemistry* **1970**, *9*, 577.

(2) Crothers, D. M.; Zimm, B. H. *J. Mol. Biol.* **1964**, *9*, 1.

0002-7863/88/1510-3734$01.50/0