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Theoretical and Experimental Evidence for S_N2 Transition States in Oxidative Addition of Methyl Iodide to *cis*-$[M(CO)_2I_2]^-$ (M = Rh, Ir)

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Oxidative addition of organic molecules to unsaturated transition metal complexes is a fundamental process in organometallic chemistry and plays a key role in many important catalytic reactions.[2] An important example is the reaction of methyl iodide with *cis*-$[Rh(CO)_2I_2]^-$, the rate-determining step in the industrial carbonylation of methanol to acetic acid.[3,4] In this communication, we present new theoretical and experimental evidence for the nature of the transition state (TS) in this reaction. *Ab initio* transition structures have been located for nucleophilic attack by *cis*-$[M(CO)_2I_2]^-$ (M = Rh, Ir) on MeI, and computed secondary α-deuterium kinetic isotope effects (KIEs) for the classical S_N2 mechanism are in excellent agreement with experiment.

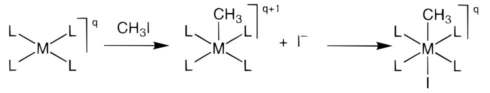
There has been considerable debate concerning the mechanism by which alkyl halides add to square planar complexes.[5] It is widely accepted that, for simple substrates such as MeI, addition occurs via a stepwise mechanism (Scheme 1). The first step is nucleophilic substitution of iodide by the metal complex, presumed to proceed with *inversion* of configuration at carbon. Subsequent coordination of iodide completes the addition to give a six-coordinate alkyl complex.

A wealth of kinetic, stereochemical, and spectroscopic data support this mechanism. However, attempts to probe the stereochemistry at carbon using more complex, chiral substrates have often led to racemization, interpreted as evidence for a radical chain mechanism for substituted alkyl groups.[6] Another pathway which has been considered is concerted, *cis* addition, expected to lead to *retention* of configuration at carbon.[7]

Although there have been a number of theoretical studies on TS geometries for addition of H−H, C−H, and C−C bonds to transition metal complexes,[8] there has been very little computational work on the addition of more polar substrates such as alkyl halides.[9] Here we report *ab initio* molecular orbital calculations for the addition of CH_3I to square planar complexes of Rh and Ir and relate the findings to new experimental data concerning secondary α-deuterium KIEs.

Optimized geometries and frequencies have been obtained at the restricted Hartree−Fock (RHF) level of theory using Gaussian 92.[10] The Los Alamos pseudopotentials and associated Gaussian bases[11] were used throughout with occasional enhancement.[12] The effect of electron correlation on reaction energetics was studied by performing single-point second-order Møller−Plesset (MP2) calculations on the RHF optimized structures. Computed KIEs,[13] (25 °C) correspond to the central barrier (i.e., transformation of the optimized reactant ion−dipole complex into the TS). All frequencies were scaled by a standard factor of 0.89. All optimized transition states had one imaginary frequency; reactant ion−dipole complexes had none.

Scheme 1



We have located two different transition structures, each having C_s symmetry, for nucleophilic attack by *cis*-$[Rh(CO)_2I_2]^-$ on MeI. The first of these (Figure 1a) is a "linear" TS, involving classical backside attack by the transition metal nucleophile and leading to inversion of stereochemistry at carbon. The second (Figure 1b) is a considerably more bent TS which leads to retention of configuration at carbon. The important structural and thermodynamic parameters for these transition states are listed in Table 1. Radical pathways are not considered here, since experimental evidence indicates that single electron transfer processes are important only for higher alkyl substrates.[6,14] Although transition structures have recently been calculated using density functional theory for the model system Pd + MeCl[9] these are the first to be located for nucleophilic attack by a square planar complex.[15]

In the "linear" TS the MeI substrate approaches an axial site of the square planar complex, with the iodine atom directed away from the metal. The MeI unit is tilted slightly toward the carbonyl ligands with a deviation from Rh−C−I linearity of $\theta \approx 10°$. The C−I distance (R_I) is significantly longer than those found in transition states for other nucleophilic substitutions on MeI,[16] indicating a late TS. RHF optimizations with an extended basis[12] lead to a more linear ($\theta \approx 5°$) and slightly earlier TS. The main contribution to Rh−C bonding in the linear TS comes from the overlap of an occupied Rh d_{z^2} orbital with the C−I σ^* LUMO of MeI. The corresponding TS for the iridium system is similar but with a larger metal−carbon distance (R_{Nu}) and a smaller value of R_I, corresponding to a somewhat earlier TS. The deviation from Ir−C−I linearity ($\theta \approx 3°$) is smaller than for rhodium. The thermodynamic barrier heights computed at the RHF level (Table 1) are substantially larger than experimental values ($\Delta H^{\ddagger}_{EXP}$ 50−60 kJ mol^{-1}).[4,14] However, single-point MP2 calculations on the RHF optimized structures give activation energies much closer to experiment.[17] The large correlation energy can be attributed to changes in covalency on $M-CH_3$ bond formation.

Retention of configuration in the bent TS (Figure 1b) results from a side-on approach of MeI toward the metal complex. Apart from the large Rh−C−I angle ($\theta \approx 95°$), the other major structural difference is the long Rh−C distance, ca. 0.6 Å greater than for the linear TS. Intrinsic reaction coordinate (IRC)

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(1) (a) University of Sheffield. (b) BP Chemicals, Hull.

(2) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(3) Forster, D. *Adv. Organomet. Chem.* **1979**, *17*, 255. Dekleva, T. W.; Forster, D. *Adv. Catal.* **1986**, *34*, 81. Howard, M. J.; Jones, M. D.; Roberts, M. S.; Taylor, S. A. *Catal. Today* **1993**, *18*, 325.

(4) Haynes, A.; Mann, B. E.; Morris, G. E.; Maitlis, P. M. *J. Am. Chem. Soc.* **1993**, *115*, 4093. Haynes, A.; Mann, B. E.; Morris, G. E.; Maitlis, P. M. *J. Am. Chem. Soc.* **1993**, *115*, 4093.

(5) Henderson, S.; Henderson, R. A. *Adv. Phys. Org. Chem.* **1987**, *23*, 1.

(6) Labinger, J. A.; Osborn, J. A. *Inorg. Chem.* **1980**, *19*, 3230.

(7) Pearson, R. G.; Muir, W. R. *J. Am. Chem. Soc.* **1970**, *92*, 5519.

(8) Koga, N.; Morokuma, K. *Chem. Rev.* **1991**, *91*, 823. Ziegler, T.; Tschinke, V.; Fan, L.; Becke, A. D. *J. Am. Chem. Soc.* **1989**, *111*, 9177.

(9) Bickelhaupt, F. M.; Ziegler, T.; Schleyer, P. v. R. *Organometallics* **1995**, *14*, 2288.

(10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Wong, M. W.; Foresman, J. B.; Robb, M. A.; Head-Gordon, M.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92/DFT*; Gaussian, Inc.: Pittsburgh, PA, 1993.

(11) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270.

(12) The extended basis is described in the supporting information.

(13) Bigeleisen, J.; Mayer, M. G. *J. Chem. Phys.* **1947**, *15*, 261.

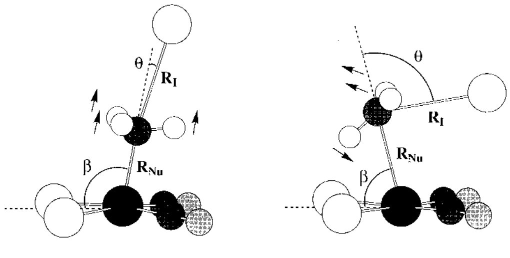
(14) Ellis, P. R.; Pearson, J. M.; Haynes, A.; Adams, H.; Bailey, N. A.; Maitlis, P. M. *Organometallics* **1994**, *13*, 3215.

(15) A comparison with density functional theory for our systems will be reported elsewhere.

(16) Leaving-group distances of 3.0−3.2 Å compared to 2.5−2.9 Å for nucleophiles, Cl^-, Br^-, I^-, NH_3. Shaik, S.; Ioffe, A.; Reddy, A. C.; Pross, A. *J. Am. Chem. Soc.* **1994**, *116*, 262.

(17) Electron correlation effects are similar for addition of CH_4 to $RhCl(PH_3)_2$. Koga, N.; Morokuma, K. *J. Phys. Chem.* **1990**, *94*, 5454.

0002-7863/96/1518-3029$12.00/0



(a) Linear TS‡ **(b) Bent TS‡**

Figure 1. Linear (a) and bent (b) transition states for nucleophilic attack by *cis*-$[Rh(CO)_2I_2]^-$ on methyl iodide. Geometrical parameters, R_{Nu}, R_I, θ, and β are listed in Table 1. The arrows indicate the C−H(D) bending modes of principal importance in determining the α-D KIEs.

Table 1. Optimized Geometrical Parameters for Transition States in the Reactions of *cis*-$[M(CO)_2I_2]^-$ and I^- with MeI[a]

nucleophile	R_{Nu} (Å)	R_I (Å)	θ (deg)	β (deg)	$\Delta E^{‡\,b}$ kJ mol^{-1}	$\Delta E_{sub}{}^b$ kJ mol^{-1}	$\Delta E_{add}{}^b$ kJ mol^{-1}
			"Linear" TS‡				
$[Rh(CO)_2I_2]^-$	2.190	3.202	9.7	99.2	+146.0	+98.2	+37.3
					+71.2[c]	+59.6[c]	−41.4[c]
$[Ir(CO)_2I_2]^-$	2.430	2.939	2.6	94.3	+92.2	+20.3	−43.5
					+43.2[c]	+29.6[c]	−75.3[c]
I^-	2.788	2.788	0		+30.5	0	
			"Bent" TS‡				
$[Rh(CO)_2I_2]^-$	2.801	3.195	94.7	84.6	+234.7		
					+254.6[c]		

[a] Full geometric details and absolute energies of optimized structures (RHF, LANL1DZ basis) are given in the supporting information. [b] The barrier height for nucleophilic substitution, $\Delta E^‡$, and reaction energies, ΔE_{sub} and ΔE_{add}, are calculated with respect to the reactant ion−dipole complexes. [c] MP2 single-point calculations using extended LANL1DZ basis.[12]

calculations show that both transition states lead to the same products: a neutral, five-coordinate methyl complex, $[CH_3Rh(CO)_2I_2]$, and a free iodide ion. Both mechanisms are therefore properly described as S_N2 processes; the bent TS *does not* correspond to a concerted addition of MeI to the metal center. The values of $\Delta E^‡$ indicate that the linear TS is strongly favored over the bent TS at both the RHF and MP2 levels.

The nucleophilic substitution process is found to be endothermic (ΔE_{sub}, Table 1) for both metals, but less so for iridium. The overall oxidative addition process (ΔE_{add}, Table 1) is endothermic for rhodium but exothermic for iridium,[18] at the RHF level. The results are in qualitative agreement with experiment; salts of $[CH_3Ir(CO)_2I_3]^-$ are isolable, whereas the analogous Rh complex is unstable with respect to loss of MeI.[4,14] Correlation leads to product stabilization for both metals.

Secondary α-D KIEs have been widely used to probe TS structure for S_N2 reactions. Computed secondary α-D KIEs, together with experimental values,[19] are presented in Table 2 for the reactions of *cis*-$[M(CO)_2I_2]^-$ and I^- with $CH(D)_3I$. Also included are values of Wolfe's looseness parameter,[20] Westaway's R_{TS} parameter,[21] and the contributions of C−H(D) bending and stretching vibrations to the computed KIEs.[22]

Table 2. Calculated Secondary α-D KIEs, $(k_H/k_D)_{TOT}$ (Hartree−Fock, LANL1DZ Level), Contributions from C−H(D) Bending and Stretching Vibrations,[22] and Values of L_{TS}[20] and R_{TS}[21]

nucleophile	$(k_H/k_D)_{TOT}$	$(k_H/k_D)_B$	$(k_H/k_D)_S$	L_{TS}	R_{TS}	$(k_H/k_D)_{EXP}{}^a$
			"Linear" TS‡			
$[Rh(CO)_2I_2]^-$	1.15	1.23	0.92	53.57	5.39	1.16 ± 0.03
$[Ir(CO)_2I_2]^-$	1.09	1.27	0.85	47.08	5.37	1.06 ± 0.03
$[I^-]$	1.07	1.26	0.83	49.30	5.57	1.05, 1.10[b]
			"Bent" TS‡			
$[Rh(CO)_2I_2]^-$	1.92	1.51	0.88		6.00	

[a] Experimental KIEs. [b] 20 °C in MeOH and H_2O, respectively.[25]

The calculated KIEs for the "linear" transition states are small and normal (>1), consistent with classical S_N2 reactions, which typically exhibit inverse (<1) or small normal values of k_H/k_D. By contrast, a much larger KIE is computed for the bent TS in the Rh system. Our theoretical KIEs for the linear transition states are in excellent agreement with experiment, giving overwhelming evidence for an S_N2 *inversion* mechanism in these reactions. Secondary α-D KIEs of a similar magnitude (0.94−1.17) have previously been reported for the reactions of Vaska's complex, $[Ir(CO)Cl(PPh_3)_2]$, with MeI.[23]

Our analysis of the origins of the computed KIEs shows that they are dominated by large, normal contributions from C−H(D) bending vibrations. The biggest contribution comes from the "umbrella" bending mode (Figure 1a) which is sterically unhindered in the large available space between nucleophile and leaving group. The considerably larger normal KIE for the bent transition state originates principally from a rocking motion about the C−I axis (Figure 1b). The C−H(D) stretching contribution to the total KIE is inverse in all cases, in agreement with recent theoretical treatments of S_N2 reactions.[21,24]

The smaller observed KIE for the iridium nucleophile is correctly predicted by theory. This decrease correlates with smaller values of both L_{TS} and R_{TS}, indicating a tighter transition state than for rhodium. The KIE for the identity reaction between MeI and I^- is in good agreement with reported experimental data,[25] providing valuable support for the reliability of our methods. The observed and calculated KIEs for *cis*-$[Ir(CO)_2I_2]^-$ are similar to those for I^-, as are the respective contributions from C−H(D) bending and stretching vibrations. Normal bending contributions are again dominant, but larger inverse stretching contributions bring the total KIEs below that for the rhodium nucleophile. Previous data have shown the nucleophilicity of *cis*-$[Ir(CO)_2I_2]^-$ to be ca. 2 orders of magnitude greater than that of *cis*-$[Rh(CO)_2I_2]^-$ and similar to that of iodide,[14] suggesting a correlation between KIE and nucleophilicity for both transition metal and other nucleophiles.

In conclusion, we have located transition states for nucleophilic attack by *cis*-$[M(CO)_2I_2]^-$ on MeI, leading to either inversion or retention of configuration at carbon. The former is energetically preferred and gives computed KIEs in excellent agreement with experiment for both Rh and Ir complexes.

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Supporting Information Available: Experimental details for kinetic measurements, results of additional calculations, and full geometric details of optimized structures (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(18) Full details of optimized geometries for the metal alkyl intermediates and oxidative addition products will be published elsewhere.

(19) Procedures for kinetic measurements are described in refs 4 and 14. Full rate data (25 °C) are given in the supporting information.

(20) The looseness parameter, L_{TS}, is defined in: Shaik, S. S.; Schlegel, H. B.; Wolfe, S. *J. Chem. Soc., Chem. Commun.* **1988**, 1322.

(21) $R_{TS} = R_{Nu} + R_I$. Poirier, R. A.; Wang, W.; Westaway, K. C. *J. Am. Chem. Soc.* **1994**, *116*, 2526.

(22) The vibrational KIE, $(k_H/k_D)_{VIB} \approx (k_H/k_D)_B(k_H/k_D)_S$, where $(k_H/k_D)_B$ is the contribution from C−H(D) bending vibrations and $(k_H/k_D)_S$ is the contribution from the C−H(D) stretching vibrations.

(23) Stang, P. J.; Schiavelli, M. D.; Chenault, H. K.; Breidegam, J. L. *Organometallics* **1984**, *3*, 1133.

(24) Wolfe, S.; Kim, C.-K. *J. Am. Chem. Soc.* **1991**, *113*, 8056. Barnes, J. A.; Williams, I. H. *J. Chem. Soc., Chem. Commun.* **1993**, 1286.

(25) Seltzer, S.; Zavitsas, A. A. *Can. J. Chem.* **1967**, *45*, 2023.