the homogeneous and heterogeneous cases, we find

$$\frac{\Phi^*}{\Phi} = \frac{4\pi D^* R^*(c_{A,\infty} - c_{A,R^*})}{4\pi D R(c_{A,\infty} - c_{A,R})} \approx \frac{r_{HS} r_B}{(r_A + r_B)^2} \qquad (40)$$

since $c_{A,R} = c_{A,R^*} = 0$ and $r_{HS} \gg r_A, r_B$. Clearly, a hard sphere covered with B represents a more effective sink that an individual B, in spite of the much smaller diffusion coefficient of the large particle. Nevertheless, as r_{HS} is increased, the hard-sphere concentration decreases faster (by $1/r_{HS}^2$, from eq 5) than the sink strength increases, leading to the net rate reduction given in (36).

A straightforward extension of the ideas pursued would be to investigate the effect of $r_{HS} \to \infty$, i.e., the localization of B's on a flat surface. In this case, however, one deals with the problem of one-dimensional diffusion described by Fick's laws in Cartesian coordinates, where no steady state is possible for finite bulk concentration $c_{a,\infty}$ and time. This is of course expected, since setting $\partial c_A/\partial t = 0$ implies $\partial c_A/\partial x =$ constant, which is possible only for $c_{a,\infty} \to \infty$ or $\partial c_A/\partial x = 0$. The first case is physically not feasible, and the latter one applies only for slow reactions. Thus no direct comparison can be made.

Summary

The primary, geometric effect of localizing one of the reactants on the surface of large particles (hard spheres) in a bimolecular elementary reaction is the decrease of the rate. We normalized the conditions such that the homogeneous and the interfacial rates could directly be compared by using collision and transition-state theories for the slow and diffusion-control theory for the fast reactions. The essence of the normalization is that the bulk concentration of the reactants is kept constant in the transition from the homogeneous to the heterogeneous case, and the concentrations of the interfacial species are described in the normal bulk number-density units, since the hard spheres are randomly distributed over the space available. In the heterogeneous case, the B molecules and the activated complex X^* bound to the surface lose a major fraction of their degrees of freedom and assume the mobilities of the bulky hard sphere. If the hard spheres were randomly distributed but fixed in space (as in a chromatography or ion-exchange packing), the decrease of the specific rate would be even greater than found in our treatment. In spite of the high local concentrations caused by the clustering of B on the hard spheres, the associated negative geometric effects of the reduction of dimensionality are dominant, leading to a significant rate reduction, especially for diffusion-controlled reactions. Consequently, reactions taking place on the surface of colloidal particles and having a Langmuir–Rideal type mechanism with a rate constant of as small as 10^5–10^4 M^{-1} s may be classified as diffusion controlled. For such a system, the upper limit of the diffusion-controlled rate constant in the usual units can be estimated from

$$k = \frac{2kTL}{3\pi\eta 1000} \frac{r_B^2}{r_A r_{HS}} \ (M^{-1}\ s) \qquad (41)$$

which follows from eq 35, and where L is Avogadro's number.

For "reaction-controlled" rates, the geometric rate reduction is independent of the size of the hard spheres, according to the collision (eq 10) and the transition-state (eq 23) theories. For diffusion-controlled reactions, however, the size of the rate reduction increases with r_{HS} (eq 36).

For slow reactions, it is important to realize that for successful Langmuir–Rideal-type heterogeneous catalitic acceleration, the interfacial reaction needs to have an activation energy at least 10 kJ/mol lower than that of the homogeneous reaction just in order to compensate for the geometric rate reduction, in the absence of surface diffusion.

Acknowledgment. This work was partially supported by the R. A. Welch Foundation, the NATO, and the Organized Research Fund of UTA. The authors thank Prof. H. Hoffmann for his questions concerning our experimental findings on rate reduction at interfaces.

$2_s + 2_s$ Reactions at Transition Metals. 1. The Reactions of D_2 with Cl_2TiH^+, Cl_2TiH, and Cl_2ScH

Michael L. Steigerwald and William A. Goddard III*

Contribution No. 6581 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125. Received May 6, 1983

Abstract: With use of ab initio electronic structure theory, activation energies and transition-state geometries have been found for the exchange of the title transition-metal hydrides with D_2. These calculations indicate that such concerted, suprafacial [2 + 2] reactions proceed at low energy if the M–H bond is nonpolar and covalent, and if this bond uses mostly valence d-orbital character on the metal.

The Woodward–Hoffmann orbital symmetry rules have had a profound effect on the understanding of organic reactions,[1] but attemps to generalize these rules to organic reactions mediated by transition metals have not led to specific results of comparable utility.[2] It is generally assumed that there are no particular reactions that are symmetry forbidden for transition-metal systems. For example, [$2_s + 2_s$] reactions such as migratory insertion pervade organometallic chemistry,[3] whereas analogous reactions are known to be forbidden in strictly organic systems. Our belief (vide infra) is that the detailed nature of the metal–hydrogen and metal–carbon *covalent* bond is critical to the process of these now allowed reactions. An appreciation of the transition-metal–ligand covalent bond is now emerging[4] that allows us to go beyond the simple standards of allowed and forbidden and to begin predicting

Scheme I

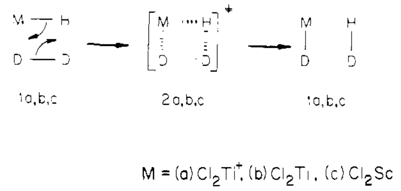

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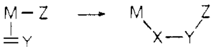
Table I. Geometries of $Cl_2MH^{a,b}$

				Mulliken populations in M–H bond pair		
complex	θ(ClTiCl), deg	r(Cl–Ti), Å	r(TiH), Å	M (valence d)	M (valence s and p)	H
Cl_2TiH^+	(140)	(2.328)	1.80^c	1.07	0.22	0.71
Cl_2TiH	(140)	(2.328)	1.70	0.70	0.37	0.87
Cl_2ScH	(142)	2.35	1.78	0.55	0.44	0.98

[a] Values in parentheses are not optimized. Other parameters were optimized by using a wave function having a correlated [GVB(1/2)] M–H σ bond. [b] Cl_2TiH was found to be planar. Cl_2TiH^+ and Cl_2ScH were subsequently assumed to be planar. [c] When the Ti–H bond length was optimized at the Hartree-Fock level, a value of 1.58 Å was found. Intrapair correlation is critical in this calculation.

relative rates of particular organometallic relations. In this paper we outline some recent studies of concerted reactions of transition metals. We find that low activation barriers for reactions such as (1) will result when the M–Z bond is nonpolar and covalent, involving strictly d character in the metal center.



(1)

Our analysis of molecules and their reactions is based on simple valence bond wave functions supplemented by ab initio generalized valence bond (GVB) calculations.[5] Within this description, a chemical bond is formed by the overlap of two one-electron orbitals,[6] and a reaction results from the delocalization of one or more previously localized bonds across several centers and the subsequent relocalization to give the bonds of the products. The Pauli principle governs the course of these delocalizations, and in so doing provides selection rules for reactivity.[7]

In order to investigate the nature of these reactive orbital delocalizations in the organometallic migratory insertion reaction, we have studied the three reactions shown in Scheme I. These simple exchange reactions are expected to be electronically quite similar to the more traditional $[2_s + 2_s]$ reactions such as insertion of an olefin into a metal–hydrogen bond (eq 2). The study of this sequence was chosen to answer three questions: (1) Does the indicated exchange proceed with a low activation barrier, and, if so, how? (2) What is the effect of the Lewis acidity of the metal center on this activation barrier? (3) What is the effect of spectator electrons (such as the unpaired electron of Cl_2TiH) on this activation barrier?

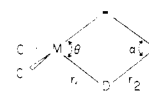
(2)

Results and Discussion

In order to answer these questions, we have determined accurate wave functions for the reactants (**1a–c**) and compared them with analogous wave functions for the indicated transition states (**2a–c**). The geometries of these species were optimized and are reported in Tables I and II. Throughout this study, the chloride ligands, being simple model anionic ligands, were held fixed at the values shown. The four-center transition states were assumed to have C_{2v} symmetry, and the geometries were optimized with this constraint. The activation barriers are quoted in Table III.

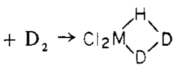
From Table III one sees that these three reactions proceed with low activation barriers (with that of the titanium cation being comspicuously lower), and hence the reactions are allowed. Examination of the active orbitals along the reaction path indicates why this is so. Figure 1 shows the four active one-electron orbitals as they move from reactants to products. We see that the original bond pairs (Ti–H and H–H) are retained throughout the reaction. At the transition state, one of these bonds becomes a three-center bond on the three hydrogens and the other a three-center bond on the titanium and its two neighboring hydrogens. As the reaction proceeds to products, these delocalized bonds relocalize to form the bonds characteristic of the products. The change in bond pair overlaps (Table IV) substantiates our assertion that the two active bonds are retained throughout these reactions.

Table II. Geometries of $Cl_2M(H)(D)_2{}^{a-c}$



complex	r_1, Å	r_2, Å	θ, deg	α, deg
$Cl_2Ti(H)(D)_2{}^+$	1.782	0.992	62	134
	(1.750	0.993	64	137)
$Cl_2Ti(H)(D)_2$	1.8459	1.0284	65	148
$Cl_2Sc(H)(D)_2$	1.887	1.014	62	149

[a] In each case the Cl_2M fragment was held fixed at the values from the Cl_2MH molecule. [b] C_{2v} symmetry was assumed for all complexes. [c] The geometry of $Cl_2Ti(H)(D)_2$ and that of $Cl_2SC(H)(D)_2$ were optimized by using gradient techniques at the Hartree-Fock level. Owing to the inaccuracy of the Hartree-Fock prediction of the Ti–H bond length in Cl_2Ti^+, this optimization technique could not be used for $Cl_2Ti(H)(D)_2{}^+$. This reported geometry results from a point-by-point geometry search at the GVB(2/4) level and is therefore only approximate. The geometry in parentheses is the result of this Hartree–Fock gradient optimization.

Table III. $Cl_2M–H + D_2 \rightarrow$ 

		Mulliken populations				
		transition state D···M···H bond			total on H's in MH_3	
reactant	barrier height, kcal/mol	s	p	d	terminal	central
Cl_2TiH^+	2^a	0.0	0.06	1.09	0.70	0.82
Cl_2TiH	21.7	0.0	0.11	0.72	0.93	0.82
Cl_2ScH	17.4	0.0	0.13	0.61	1.00	0.80

[a] Upper limit; see footnote *c*, Table II.

Table IV. GVB Pair Overlaps in Active Bonds

	reactants		transition state	
system	M–H	H–H	H···M···D	H···D···D
Cl_2TiH^+	0.44	0.80	0.54	0.84
Cl_2TiH	0.66	0.80	0.72	0.84
Cl_2ScH	0.74	0.80	0.77	0.84

It is critical to note that the two three-center bonds of the transition state are orthogonal to one another, as demanded by the Pauli principle. It is in this ability that transition metals outdo main-group elements. Examining the pericyclic $[2_s + 2_s]$ cyclodimerization of ethylene (Figure 2), we see that the two active bonds in the reactants (the C–C π bonds) *cannot* delocalize to give two three-center bonds in the transition state that are mutually orthogonal. Either the two delocalized bonds are not orthogonal (forbidden by the Pauli principle) or one of the bonds is forced to be broken at the transition state (the definition of a forbidden reaction). It is the shape and availability of the transition-metal d orbital that allows the orthogonal delocalization to occur.

On the basis of these considerations, we believe that the more metal d character in the M–Z bond (eq 1) the lower the activation barrier for the exchange reaction and analogous insertions. This is because any metal s or p character in the active bond must be removed on going to the X...M...Z three-center bond in the symmetrical transition state, leading to increased activation energy (see Table IV), and this change in optimal orbital hybridization about the metal will be energetically costly. This contributes to the explanation for the very low barrier for exchange in the

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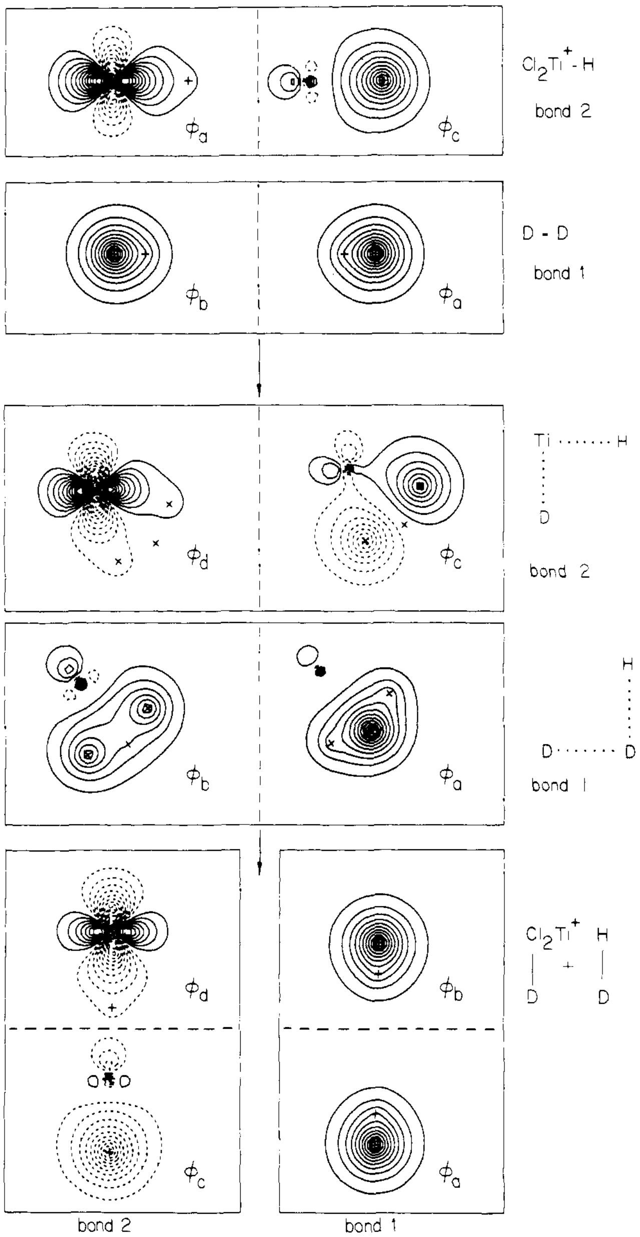

Figure 1. GVB orbitals for the $Cl_2Ti^+-H + D_2 \rightarrow Cl_2Ti^+-D + HD$ reaction: (i) reactants; (ii) transition state; (iii) products. Solid lines indicate positive amplitude and dashed lines indicate negative amplitude. The spacing between contours is 0.05 au.

$(Cl_2TiH)^+$ system. The metal orbital in this Ti-H bond is ~90% d in character, whereas in the other two cases, the corresponding metal orbital is only 50-70% d (Table I, Figures 1, 3, and 4).

In comparing the reaction of $(Cl_2TiH)^+$ with that of the isoelectronic Cl_2ScH, we see that the effect of increasing the intrinsic Lewis acidity of the metal center is to decrease the barrier height for the exchange reaction. One explanation for this is given above. The more electroegative the metal center, the more d character in the active bond,[8] and therefore the lower energy of the transition state. A second point is that the overlap of the two bonding orbitals in $(Cl_2TiH)^+$ is quite low (0.44) compared with that in Cl_2ScH (0.74). This indicates that the TiH bond in $(Cl_2TiH)^+$ is significantly weaker than the Sc-H bond in Cl_2ScH. This would imply a correspondingly lower barrier for the exchange reaction. Finally, even though H_2 is not a particularly good Lewis base, a donor/acceptor interaction (to the extent of an additional transfer of 0.21 electron from the new H_2 to the Cl_2TiH fragment) stabilizes the cationic transition state.

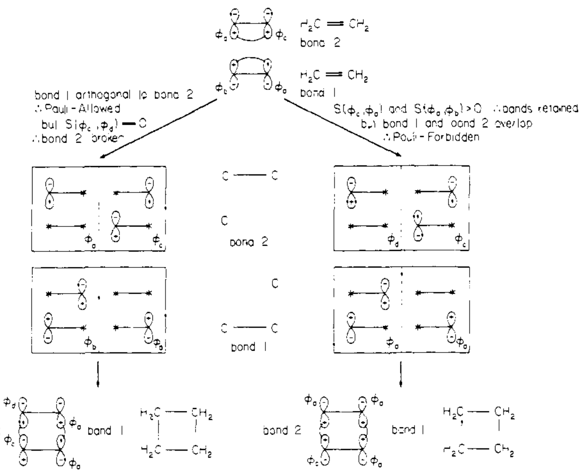

Figure 2. Valence bond orbitals for the $C_2H_4 + C_2H_4 \rightarrow$ cyclobutane reaction: (i) reactants; (ii) transition state; (iii) products.

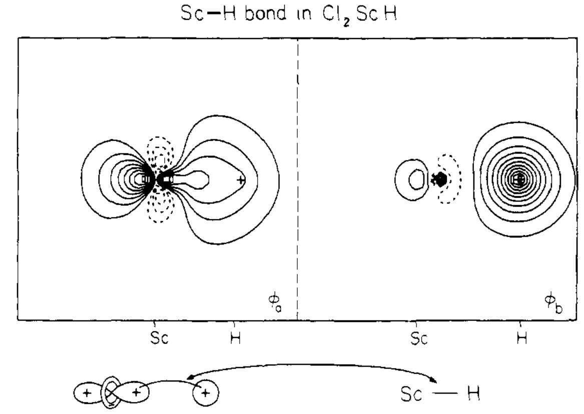

Figure 3. GVB orbitals describing the Sc-H bond of Cl_2ScH. The spacing between contours is 0.05 au.

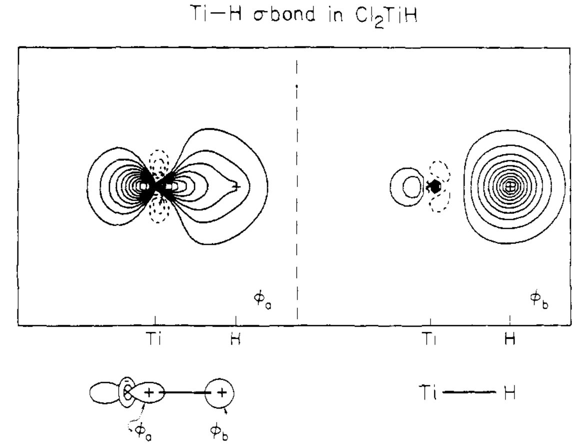

Figure 4. GVB orbitals describing the Ti-H bond of Cl_2TiH. The spacing between contours is 0.05 au.

Comparison of the exchange reactions of Cl_2ScH and Cl_2TiH shows the effect of the odd electron on titanium. In order to transform from the metal bonding orbital in the reactant to that at the transition state, the reactant orbital must mix with some

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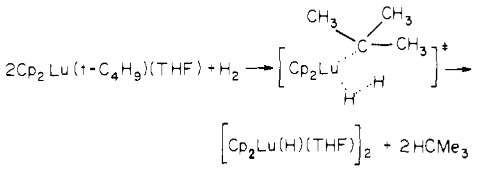
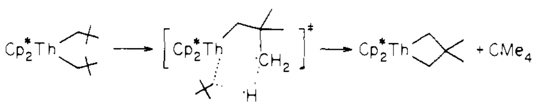
[8] In almost all transition-metal atoms, single ionization results in the removal of an electron from the valence s orbital rather than from the valence d orbital (Moore, C. E. "Atomic Energy Levels"; U. S. Government Printing Office: Washington, DC, 1971; National Standard Reference Data Series, NBS 35). Therefore, electroegative substituents (e.g., Cl) will bond to a transition metal using the more easily ionized valence s orbital of the metal, thereby making a more polar (and stronger) bond. This will have less valence s space (and, consequently, relatively more valence d space) for the electronegative substituents (e.g., H) to use in bonding. In general, higher positive charge on the metal (due either to electronegative substituents or to ionization) will indicate that less valence s and more valence d space will be available for subsequent bonding. Higher positive charge on M also indicates a higher electronegativity at M, and hence our statement in the text.

of the d orbital which is singly occupied in the case of Cl_2TiH but empty in the case of the Cl_2ScH. Equivalently, the odd electron in $Cl_2Ti(H)(D)_2$ must be in an orbital that is orthogonal to the H···Ti···D and H···D···D bonds. This orthogonality requirement results in energetic destabilization and is absent in the case of $Cl_2Sc(H)(D)_2$. In this case our calculations indicate that this mixing is of moderate energetic cost, 4.3 kcal (even though the orbital energy of the singly-occupied orbital changes from -0.5314 hartree in Cl_2TiH to -0.5153 hartree in Cl_2TiH_3, a destabilization of 10.1 kcal/mol). We expect that such spectator d electrons may have even greater effect upon reaction barriers in other systems.

These results may have distinct implications for our appreciation of known organometallic processes. For example, we expect that the exchange of H for D between $Cp_2{}^*ZrH_2$ and D_2[9] the direct hydrogenolysis of lanthanide alkyl complexes, [10] and the thermolysis of $Cp_2{}^*Th(CH_2CMe_3)_2$,[11] proceeds by a direct four-center concerted mechanism, as in our model studies. Furthermore, these results sugest that the titanium site in Ziegler–Natta polymerization [12] is more active if it is a *cationic* Ti(IV) rather than a neutral Ti(III). In this way, our work underscores the suggestion that one of the functions of the Lewis acidic cocatalysts used in Ziegler–Natta polymerization is to remove an anionic ligand such as Cl^- from the sphere of the metal.[13]



(3)



(4)

Acknowledgment. One of the authors (M.L.S.) gratefully acknowledges financial support in the form of Predoctoral Fellowships from the National Science Foundation (1978–1981) and the Sun Oil Co. (1982–1983). This work was partially supported by a grant (No. CHE80-17774) from the National Science Foundation.

Appendix: Details of the Calculations

These calculations were performed at the fully ab initio level. All titanium, scandium, and hydrogen orbitals (core as well as valence) were optimized explicitly. Geometries were optimized at the calculational levels outlined in Tables I and II. Valence double-ζ basis sets were used on the metals and unscaled triple-ζ sets on each hydrogen atom.[14] The chlorine atoms were described by valence minimum basis sets that were optimized for Cl_2TiH_2, and the chlorine core electrons were described by an ab initio effective potential.[15] The geometries of the Cl_2MH_3 species wre optimized by using the GVB gradient program of Low and Goddard.[16]

In determining the barrier height (Table III) we calculated the GVB–PP(2/4) wave function at the saddle point, included the two additional spin eigenfunctions characteristic of a full GVB wave funtion (i.e., GVB–RCI), and then carried out a CI calculation allowing all single excitations from the six GVB–RCI configurations to all virtual orbitals. This procedure relaxes all orbital orthogonality and spin-coupling restrictions involved in interactions of the orbitals and is expected to yield accurate barriers. In the limits of the reactant and product species, the above wave function reduces to a GVB(1/2) wave function on H_2 plus the following wave function on Cl_2MH: starting with GVB–PP(1/2) and including the third configuration of the RCI, we include all single excitations into the full virtual space. For Cl_2ScH and Cl_2TiH^+, this reduces to GVB–PP, but for Cl_3TiH there are additional spin-coupling terms arising from the extra electron.

As a control, we calculated the barrier for the exchange reaction of $H + D_2 \rightarrow HD + D$. Using our method, we calculate a barrier of 14.6 kcal/mol for this reaction. The most accurate calculations available show this barrier to be 9.90 kcal/mol.[17] These comparisons indicate that our calculations should yield barriers that are systematically ~5 kcal/mol high.

Registry No. H_2, 1333-74-0; D_2, 7782-39-0; $TiCl_2H^+$, 87803-85-8; $TiCl_2H$, 87803-86-9; $ScCl_2H$, 87803-87-0.

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