

the homogeneous and heterogeneous cases, we find

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

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 than 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  $r_{HS} \rightarrow \infty$ , 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  $\partial c_A / \partial x = \text{constant}$ , which is possible only for  $c_{a,\infty} \rightarrow \infty$  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

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

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 catalytic 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.

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

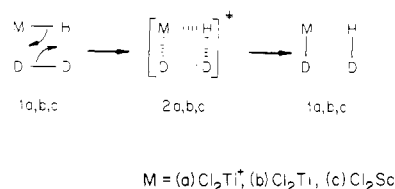
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**Abstract:** With use of ab initio electronic structure theory, activation energies and transition-state geometries have been found for the exchange of the title transition-metal hydrides with  $D_2$ . These calculations indicate that such concerted, 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,<sup>1</sup> but attempts to generalize these rules to organic reactions mediated by transition metals have not led to specific results of comparable utility.<sup>2</sup> 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,<sup>3</sup> 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

### Scheme I



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<sup>4</sup> that allows us to go beyond the simple standards of allowed and forbidden and to begin predicting

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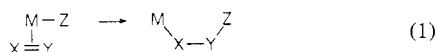
(4) Rappe, A. K.; Goddard, W. A., III, *J. Am. Chem. Soc.*, **1982**, *104*, 297–299, 448–456, 3287–3294.

Table I. Geometries of Cl<sub>2</sub>MH<sup>a,b</sup>

complex	$\theta(\text{ClTiCl})$ , deg	$r(\text{Cl-Ti})$ , Å	$r(\text{TiH})$ , Å	Mulliken populations in M-H bond pair		
				M (valence d)	M (valence s and p)	H
Cl <sub>2</sub> TiH <sup>+</sup>	(140)	(2.328)	1.80 <sup>c</sup>	1.07	0.22	0.71
Cl <sub>2</sub> TiH	(140)	(2.328)	1.70	0.70	0.37	0.87
Cl <sub>2</sub> ScH	(142)	2.35	1.78	0.55	0.44	0.98

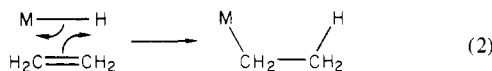
<sup>a</sup> Values in parentheses are not optimized. Other parameters were optimized by using a wave function having a correlated [GV B(1/2)] M-H  $\sigma$  bond. <sup>b</sup> Cl<sub>2</sub>TiH was found to be planar. Cl<sub>2</sub>TiH<sup>+</sup> and Cl<sub>2</sub>ScH were subsequently assumed to be planar. <sup>c</sup> 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.



Our analysis of molecules and their reactions is based on simple valence bond wave functions supplemented by ab initio generalized valence bond (GV B) calculations.<sup>5</sup> Within this description, a chemical bond is formed by the overlap of two one-electron orbitals,<sup>6</sup> and a reaction results from the delocalization of one or more previously localized bonds across several centers and the subsequent relocation 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.<sup>7</sup>

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<sub>s</sub> + 2<sub>s</sub>] 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<sub>2</sub>TiH) on this activation barrier?

## 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<sub>2v</sub> 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 conspicuously 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

Table II. Geometries of Cl<sub>2</sub>M(H)(D)<sub>2</sub><sup>a-c</sup>


complex	$r_1$ , Å	$r_2$ , Å	$\theta$ , deg	$\alpha$ , deg
Cl <sub>2</sub> Ti(H)(D) <sub>2</sub> <sup>+</sup>	1.782	0.992	62	134
	(1.750)	0.993	64	(137)
Cl <sub>2</sub> Ti(H)(D) <sub>2</sub>	1.8459	1.0284	65	148
Cl <sub>2</sub> Sc(H)(D) <sub>2</sub>	1.887	1.014	62	149

<sup>a</sup> In each case the Cl<sub>2</sub>M fragment was held fixed at the values from the Cl<sub>2</sub>MH molecule. <sup>b</sup> C<sub>2v</sub> symmetry was assumed for all complexes. <sup>c</sup> The geometry of Cl<sub>2</sub>Ti(H)(D)<sub>2</sub> and that of Cl<sub>2</sub>Sc(H)(D)<sub>2</sub> 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<sub>2</sub>Ti<sup>+</sup>, this optimization technique could not be used for Cl<sub>2</sub>Ti(H)(D)<sub>2</sub><sup>+</sup>. This reported geometry results from a point-by-point geometry search at the GV B(2/4) level and is therefore only approximate. The geometry in parentheses is the result of this Hartree-Fock gradient optimization.

Table III. Cl<sub>2</sub>M-H + D<sub>2</sub> → Cl<sub>2</sub>M(H)(D)<sub>2</sub>

reactant	barrier height, kcal/mol	Mulliken populations				
		transition state D···M···H bond			total on H's in MH <sub>3</sub>	
		s	p	d	terminal	central
Cl <sub>2</sub> TiH <sup>+</sup>	2 <sup>a</sup>	0.0	0.06	1.09	0.70	0.82
Cl <sub>2</sub> TiH	21.7	0.0	0.11	0.72	0.93	0.82
Cl <sub>2</sub> ScH	17.4	0.0	0.13	0.61	1.00	0.80

<sup>a</sup> Upper limit; see footnote c, Table II.

Table IV. GV B Pair Overlaps in Active Bonds

system	reactants		transition state	
	M-H	H-H	H···M···D	H···D···D
Cl <sub>2</sub> TiH <sup>+</sup>	0.44	0.80	0.54	0.84
Cl <sub>2</sub> TiH	0.66	0.80	0.72	0.84
Cl <sub>2</sub> ScH	0.74	0.80	0.77	0.84

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 relocate 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.

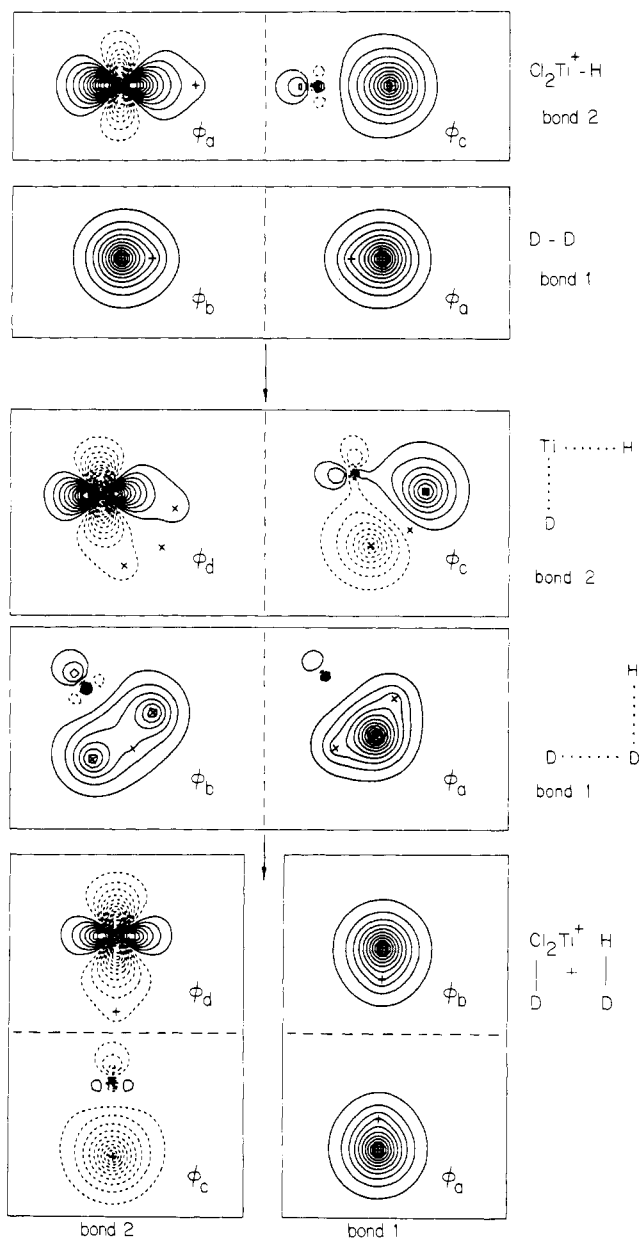
It is critical to note that the two three-center bonds of the transition state are orthogonal to one another, as demanded by the Pauli principle. It is in this ability that transition metals outdo main-group elements. Examining the pericyclic [2<sub>s</sub> + 2<sub>s</sub>] cyclo-dimerization of ethylene (Figure 2), we see that the two active bonds in the reactants (the C-C  $\pi$  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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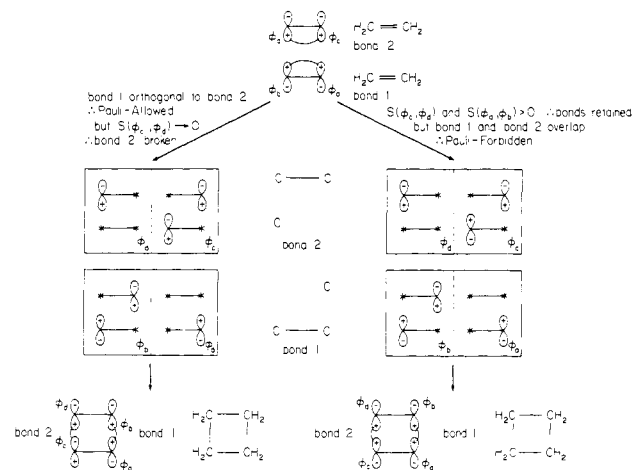


**Figure 1.** GVB orbitals for the  $\text{Cl}_2\text{Ti}^+-\text{H} + \text{D}_2 \rightarrow \text{Cl}_2\text{Ti}^4-\text{D} + \text{HD}$  reaction: (i) reactants; (ii) transition state; (iii) products. Solid lines indicate positive amplitude and dashed lines indicate negative amplitude. The spacing between contours is 0.05 au.

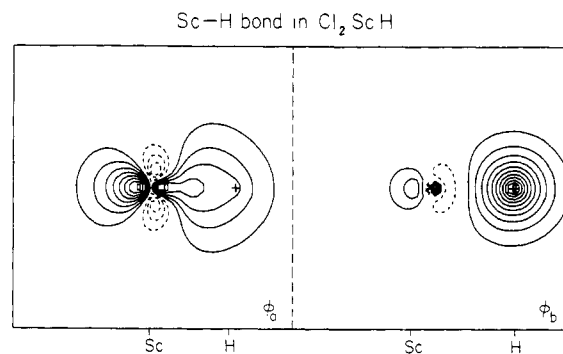
( $\text{Cl}_2\text{TiH}$ )<sup>+</sup> system. The metal orbital in this Ti-H bond is ~90% d in character, whereas in the other two cases, the corresponding metal orbital is only 50–70% d (Table I, Figures 1, 3, and 4).

In comparing the reaction of ( $\text{Cl}_2\text{TiH}$ )<sup>+</sup> with that of the isoelectronic  $\text{Cl}_2\text{ScH}$ , 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,<sup>8</sup> and therefore the lower energy of the transition

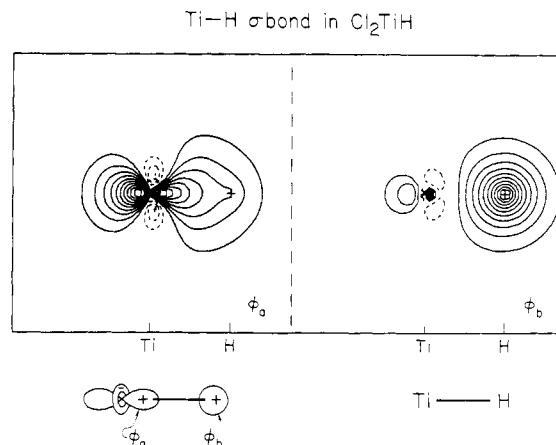
(8) In almost all transition-metal atoms, single ionization results in the removal of an electron from the valence s orbital rather than from the valence d orbital (Moore, C. E. "Atomic Energy Levels"; U. S. Government Printing Office: Washington, DC, 1971; National Standard Reference Data Series, NBS 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 electroegative substituents (e.g., H) to use in bonding. In general, higher positive charge on the metal (due either to electroegative 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 electroegativity at M, and hence our statement in the text.



**Figure 2.** Valence bond orbitals for the  $\text{C}_2\text{H}_4 + \text{C}_2\text{H}_4 \rightarrow \text{cyclobutane}$  reaction: (i) reactants; (ii) transition state; (iii) products.



**Figure 3.** GVB orbitals describing the Sc-H bond of  $\text{Cl}_2\text{ScH}$ . The spacing between contours is 0.05 au.



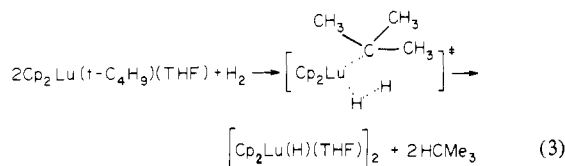
**Figure 4.** GVB orbitals describing the Ti-H bond of  $\text{Cl}_2\text{TiH}$ . The spacing between contours is 0.05 au.

state. A second point is that the overlap of the two bonding orbitals in ( $\text{Cl}_2\text{TiH}$ )<sup>+</sup> is quite low (0.44) compared with that in  $\text{Cl}_2\text{ScH}$  (0.74). This indicates that the TiH bond in ( $\text{Cl}_2\text{TiH}$ )<sup>+</sup> is significantly weaker than the Sc-H bond in  $\text{Cl}_2\text{ScH}$ . This would imply a correspondingly lower barrier for the exchange reaction. Finally, even though  $\text{H}_2$  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  $\text{H}_2$  to the  $\text{Cl}_2\text{TiH}$  fragment) stabilizes the cationic transition state.

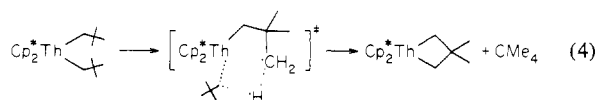
Comparison of the exchange reactions of  $\text{Cl}_2\text{ScH}$  and  $\text{Cl}_2\text{TiH}$  shows the effect of the odd electron on titanium. In order to transform from the metal bonding orbital in the reactant to that at the transition state, the reactant orbital must mix with some

of the d orbital which is singly occupied in the case of  $\text{Cl}_2\text{TiH}$  but empty in the case of  $\text{Cl}_2\text{ScH}$ . Equivalently, the odd electron in  $\text{Cl}_2\text{Ti}(\text{H})(\text{D})_2$  must be in an orbital that is orthogonal to the  $\text{H}\cdots\text{Ti}\cdots\text{D}$  and  $\text{H}\cdots\text{D}\cdots\text{D}$  bonds. This orthogonality requirement results in energetic destabilization and is absent in the case of  $\text{Cl}_2\text{Sc}(\text{H})(\text{D})_2$ . 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  $\text{Cl}_2\text{TiH}$  to -0.5153 hartree in  $\text{Cl}_2\text{TiH}_3$ , 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  $\text{Cp}_2^*\text{ZrH}_2$  and  $\text{D}_2^9$  the direct hydrogenolysis of lanthanide alkyl complexes,<sup>10</sup> and the ther-



molysis of  $\text{Cp}_2^*\text{Th}(\text{CH}_2\text{CMe}_3)_2$ ,<sup>11</sup> proceeds by a direct four-center



concerted mechanism, as in our model studies. Furthermore, these results suggest that the titanium site in Ziegler-Natta polymerization<sup>12</sup> 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  $\text{Cl}^-$  from the sphere of the metal.<sup>13</sup>

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### 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- $\zeta$  basis sets were used on the metals and unscaled triple- $\zeta$  sets on each hydrogen atom.<sup>14</sup> The chlorine atoms were described by valence minimum basis sets that were optimized for  $\text{Cl}_2\text{TiH}_2$ , and the chlorine core electrons were described by an ab initio effective potential.<sup>15</sup> The geometries of the  $\text{Cl}_2\text{MH}_3$  species were optimized by using the GVB gradient program of Low and Goddard.<sup>16</sup>

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 function (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  $\text{H}_2$  plus the following wave function on  $\text{Cl}_2\text{MH}$ : 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  $\text{Cl}_2\text{ScH}$  and  $\text{Cl}_2\text{TiH}^+$ , this reduces to GVB-PP, but for  $\text{Cl}_3\text{TiH}$  there are additional spin-coupling terms arising from the extra electron.

As a control, we calculated the barrier for the exchange reaction of  $\text{H} + \text{D}_2 \rightarrow \text{HD} + \text{D}$ . 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.<sup>17</sup> These comparisons indicate that our calculations should yield barriers that are systematically  $\sim 5$  kcal/mol high.

**Registry No.**  $\text{H}_2$ , 1333-74-0;  $\text{D}_2$ , 7782-39-0;  $\text{TiCl}_2\text{H}^+$ , 87803-85-8;  $\text{TiCl}_2\text{H}$ , 87803-86-9;  $\text{ScCl}_2\text{H}$ , 87803-87-0.

(14) The metal basis sets are from: Rappé, A. K.; Smedley, T. A.; Goddard, W. A. III *J. Phys. Chem.*, **1981**, 85, 2607-2611. The hydrogen basis used is a triple- $\zeta$  contraction of the Huzinaga (unscaled) six primitive basis. See: Dunning, T. H., Jr.; Hay, P. J. In "Modern Theoretical Chemistry: Methods of Electronic Structure Theory", Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; Vol. 3 and references therein.

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