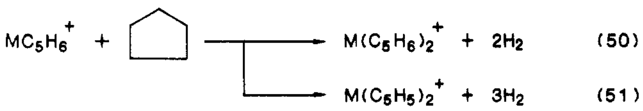
carbon–carbon bond insertion or carbon skeleton rearrangement occurring.

$MC_5H_6^+$ reacts readily as shown in reactions 50 and 51.



The two product ions probably have structures corresponding to dicyclopentadiene and metallocene complexes, respectively. Although Sc^+–benzene and Y^+–benzene ions react further to give dibenzene metal ions,[7,10] this secondary reaction was not observed in their lanthanum counterpart, consistent with the general pattern that secondary reactions are slower as one goes down the group 3 metals.

The $LaC_5H_6^+$ ion structure was confirmed through isotope exchange and CID experiments. No H/D exchange with C_2D_4 was observed, suggesting a lanthanum cyclopentadiene structure, instead of a lanthanum cyclopentadienyl hydride structure. CID at 38 eV gives a predominant $LaC_5H_4^+$ ion as well as two small peaks corresponding to La^+ and $LaC_3H_2^+$. This result is consistent with the cyclopentadiene structure, as opposed to an acyclic structure where CID would produce a great variety of cleavage fragments.

The $LaC_6H_6^+$ CID gives a predominant peak corresponding to the loss of the whole ligand and two minor peaks with the formulae LaC_2^+ and $LaC_6H_4^+$, consistent with a lanthanum–benzene structure.

Conclusion

The reactions of La^+ with alkanes are very similar to that of its first- and second-row congeners, Sc^+ and Y^+. Their similarity in reactivity toward alkanes well demonstrates their similar electronic structures. In analogy with Sc^+ and Y^+, La^+ exhibits very high reactivity toward alkanes. While multiple dehydrogenation is the predominant process for Y^+ and La^+ with small alkanes, abundant carbon–carbon bond and dehydrogenation product ions are formed for acyclic alkanes larger than C_3. Particularly interesting is the formation of dialkyl ions. Only ring-cleaved product ions are formed for Y^+ and La^+ reacting with cyclopropane, while dehydrogenation is predominant for larger cyclic alkanes. Second-row transition-metal ions such as Rh^+,[2] Y^+, and Nb^+[32] display enhanced ability to dehydrogenate, and La^+ seems to further this trend as compared to Sc^+ and Y^+. This suggests a possible generalization that down the periodic table of d-block elements, gas-phase monovalent positive ions tend to exhibit a greater ability to dehydrogenate alkanes. Also interesting is the apparent formation of two distinct $YC_4H_6^+$ and $LaC_4H_6^+$ ions, one believed to have the butadiene structure generated from *n*-butane and the other having the trimethylenemethane structure generated from isobutane or neopentane.

Another interesting trend is the decreased tendency for primary product ions to participate in secondary reactions down the group. While secondary reactions are facile for Sc^+ and Y^+ reactions with alkanes, with the latter being usually slower, only three C_3–C_5 cyclic alkanes react with their lanthanum primary product ions rapidly enough to give secondary product ions observable under our experimental conditions.

Finally, this work has provided preliminary information on a number of reaction mechanisms. Further detailed studies are underway in our laboratory to test the conclusions drawn in this study.

Acknowledgment is made to the Division of Chemical Sciences in the Office of Basic Energy Sciences in the United States Department of Energy (DE-AC02-80ER10689) for supporting this research and to the National Science Foundation (CHE-8310039) for continued support of the FTMS. H.Y. wants to thank the Chinese Government for 1 year of CGP (Chemistry Graduate Program) fellowship support.

Registry No. La^+–CH_2, 105039-61-0; Sc^+, 14336-93-7; Y^+, 14782-34-4; La^+, 14175-57-6; CH_4, 74-82-8; C_2H_6, 74-84-0; C_3H_8, 74-98-6; *n*-C_4H_{10}, 106-97-8; *n*-pentane, 109-66-0; *n*-hexane, 110-54-3; *n*-heptane, 142-82-5; *n*-dodecane, 112-40-3; isobutane, 75-28-5; neopentane, 463-82-1; cyclopropane, 75-19-4; cyclobutane, 287-23-0; cyclopentane, 287-92-3; cyclohexane, 110-82-7; *n*-octane, 111-65-9; *n*-nonane, 111-84-2; *n*-decane, 124-18-5.

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[32] Buckner, S.; MacMahan, T.; Freiser, B. S., unpublished results.

Theoretical Study of the Hydrogenation of Metal–Ligand π Bonds: Reaction of Cl_2TiCH_2 with H_2 To Form Cl_2TiHCH_3

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Correlated ab initio theoretical calculations at the valence double ζ plus polarization level are used to study the addition of dihydrogen across a titanium–carbon π bond. We find the reaction occurs with a small activation energy (ΔH^{*}_{300K} = 10.5 kcal/mol) from a weakly bound H_2 adduct complex (ΔH_{300K} = 3.8 kcal/mol). The reaction is also fairly exothermic (ΔH_{300K} = 21.5 kcal/mol). The explanation for the small barrier is precisely the same as for previously studied four-center 2 + 2 reactions. The geometry of the transition state for this reaction (and related four-center 2 + 2 reactions) is quite similar to related organic radical plus bond reactions.

Introduction

There are few documented examples of the hydrogenation of metal–ligand multiple bonds (eq 1a–c),[1–3] despite the analogy to other more common metal–ligand four-center 2 + 2 reactions. This paucity is due to either

$$M{=}CR_2 + H_2 \rightarrow M(H)(CHR_2) \quad (1a)$$

$$M{=}NX + H_2 \rightarrow M(H)(NHX) \quad (1b)$$

$$M{=}O + H_2 \rightarrow M(H)(OH) \quad (1c)$$

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[1] Schrock, R. R. *Science (Washington, D.C.)* **1983**, *219*, 13–18.

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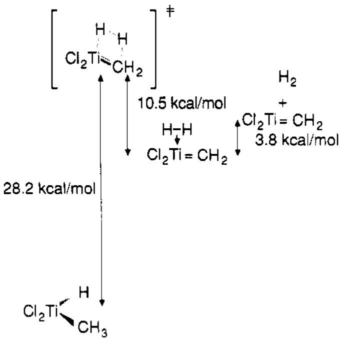
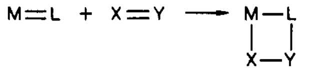


Figure 1. The reaction energy diagram for addition of H_2 across the π bond of Cl_2TiCH_2. The energies are $\Delta\Delta H_{300K}$ obtained from the CI calculations and computed vibrational frequencies and moments of inertia.

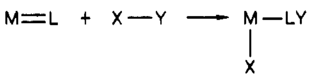
prohibitively high activation energetics or an inherent endothermicity for these reactions. Theoretical study will help clarify the energetics of this reaction type as well as provide data for transition-state geometric and energetic comparisons with the other subsets of the general class of metal–ligand four-center 2 + 2 reactions (eq 2a–d). An example of the first reaction (2a) is olefin metathesis.[4] The second (2b) is exemplified by olefin insertion and polymerization.[5] The third (2c) is less common, but, recently, alkane exchange involving Sc and Lu complexes has been reported.[6] The fourth member has only recently been documented.[7-9] Casey and Neumann[7] have observed that low-valent carbenes can be reduced by dihydrogen, though this reaction might occur through the prior oxidative addition of H_2 (eq 3). Schrock and Wengrovius have demonstrated the addition of H_2 across a high-valent alkylidyne π bond (eq 4), and Rothwell and co-workers[9] have described the intramolecular addition of C–H bonds across metal–carbon π bonds (eq 5). The reverse α abstraction or elimination reaction is more common.[10]



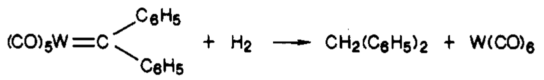
$$M{=}L + X{=}Y \longrightarrow \begin{array}{c}M{-}L\\ |\quad|\\ X{-}Y\end{array} \qquad (2a)$$

$$M{-}L + X{=}Y \longrightarrow M{-}X{-}Y{-}L \qquad (2b)$$

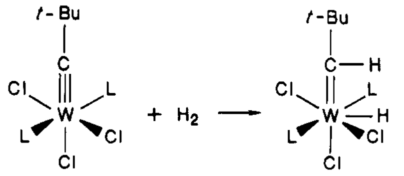
$$M{-}L + X{-}Y \longrightarrow M{-}X + L{-}Y \qquad (2c)$$



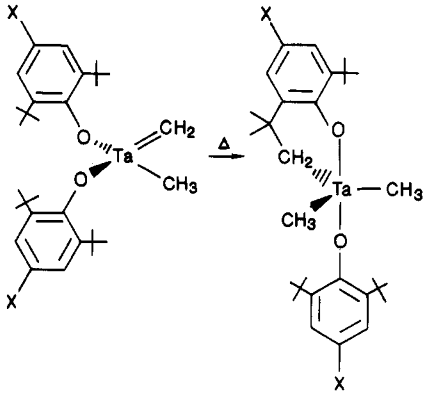
$$M{=}L + X{-}Y \longrightarrow \begin{array}{c}M{-}LY\\ |\\ X\end{array} \qquad (2d)$$



$$(CO)_5W{=}C(C_6H_5)_2 + H_2 \longrightarrow CH_2(C_6H_5)_2 + W(CO)_6 \qquad (3)$$



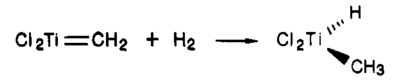
(4)



(5)

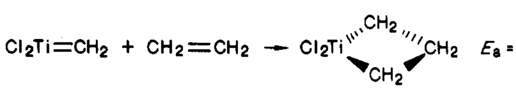
Results and Discussion

In this paper we present a study on the hydrogenation of a titanium–carbon π bond (reaction 6). The dichloro ligand set was used to retain maximal consistency with previous theoretical work.[11-14] The methodology used is described in the theoretical details section below.



$$Cl_2Ti{=}CH_2 + H_2 \longrightarrow Cl_2Ti(H)(CH_3) \qquad (6)$$

The barrier for reaction 6 in the forward direction is small, $\Delta H^{\ddagger}_{300K}$ = 6.7 kcal/mol relative to free H_2 and 10.5 kcal/mol relative to complexed H_2 (see Figure 1). This is similar to the previously calculated barriers[11-13] (eq 7–9).



$$Cl_2Ti{=}CH_2 + CH_2{=}CH_2 \longrightarrow Cl_2Ti(CH_2)_3 \quad E_a = 6\ \text{kcal/mol} \qquad (7)$$

$$Cl_2Ti{-}H^+ + D_2 \rightarrow Cl_2Ti{-}D^+ + HD \quad E_a = 2\ \text{kcal/mol} \qquad (8)$$

$$Cl_2Ti{-}CH_3^+ + CH{=}CH_2 \rightarrow Cl_2Ti{-}C_3H_7^+ \quad E_a = 10\ \text{kcal/mol} \qquad (9)$$

For reaction 6, we also find a small binding energy for H_2 to the Lewis acidic $Cl_2Ti{=}CH_2$ fragment (ΔH_{300K} = 3.8 kcal/mol). This interaction is simply Lewis acid–base in nature and is substantially weaker than that found for reaction of ethylene with this fragment.[11] In fact, when entropy is considered,[15] the equilibrium favors dissociated H_2 (ΔG_{300K} = +3.6 kcal/mol). This can be contrasted to

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(2) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123–175. Dehnicke, K.; Strahle, J. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 413–486.

(3) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic: New York, 1981.

(4) Grubbs, R. H. *Prog. Inorg. Chem.*, **1978**, *24*, 1–50. Calderon, N.; Lawrence, J. P.; Ofstead, E. A. *Adv. Organomet. Chem.* **1979**, *17*, 449–492. Ivin, *Olefin, Metathesis*; Academic: New York, 1983.

(5) Pino, P.; Mulhaupt, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 857–875.

(6) Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 337–339. Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1983**, 276–277. Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491–6493. Thompson, M. E.; Bercaw, J. E. *Pure Appl. Chem.* **1984**, *56*, 1–11. Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51–56. Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T. *Organometallics* **1986**, 5, 443–450.

(7) Casey, C. P.; Neumann, S. M. *J. Am. Chem. Soc.* **1977**, *99*, 1651–1652.

(8) Wengrovius, J. H.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1982**, *104*, 1739–1740.

(9) Chamberlain, L. R.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 7338–7340. Chamberlain, L. R.; Rothwell, A. P.; Rothwell, I. P. *Ibid.* **1984**, *106*, 1847–1848. Chamberlain, L. R.; Rothwell, I. P.; Huffman, J. C. *Ibid.* **1986**, *108*, 1502–1509.

(10) Pu, L. S.; Yamamoto, A. *J. Chem. Soc., Chem. Commun.* **1974**, 9–10. Cooper, N. J.; Green, M. L. H. *Ibid.* 761–762. Schrock, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 6577–6578. Schrock, R. R.; Sharp, P. R. *Ibid.* **1978**, *100*, 2389–2399. Malatesta, V.; Ingold, K. U.; Schrock, R. R. *J. Organomet. Chem.* **1978**, *152*, C53–C56. Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3210–3222. Cooper, N. J.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1979**, 1121–1127.

(11) Rappé, A. K.; Upton, T. H. *Organometallics* **1984**, *3*, 1440–1442. Upton, T. H.; Rappé, A. K. *J. Am. Chem. Soc.* **1985**, *107*, 1206–1218.

(12) fujimoto, H.; Yamasaki, T.; Mizutani, H.; Koga, N. *J. Am. Chem. Soc.* **1985**, *107*, 6157–6161.

(13) Steigerwald, M. L.; Goddard III, W. A. *J. Am. Chem. Soc.* **1984**, *106*, 308–311; Rabaâ, H.; Saillard, J.-Y.; Haffmann, R. *J. Am. Chem. Soc.* **1986**, *108*, 4327–4333.

(14) Koga, N.; Obara, S.; Kitaura, K.; Morokuma, K. *J. Am. Chem. Soc.* **1985**, *107*, 7109–7116.

(15) The calculated moments of inertia, vibrational frequencies, and symmetry factors are used to determine the temperature dependence of the Δ*H* and *S* for each of the species along the reaction coordinate. The dominant entropic difference between free H_2 and the complexed form is the loss of translational degrees of freedom.

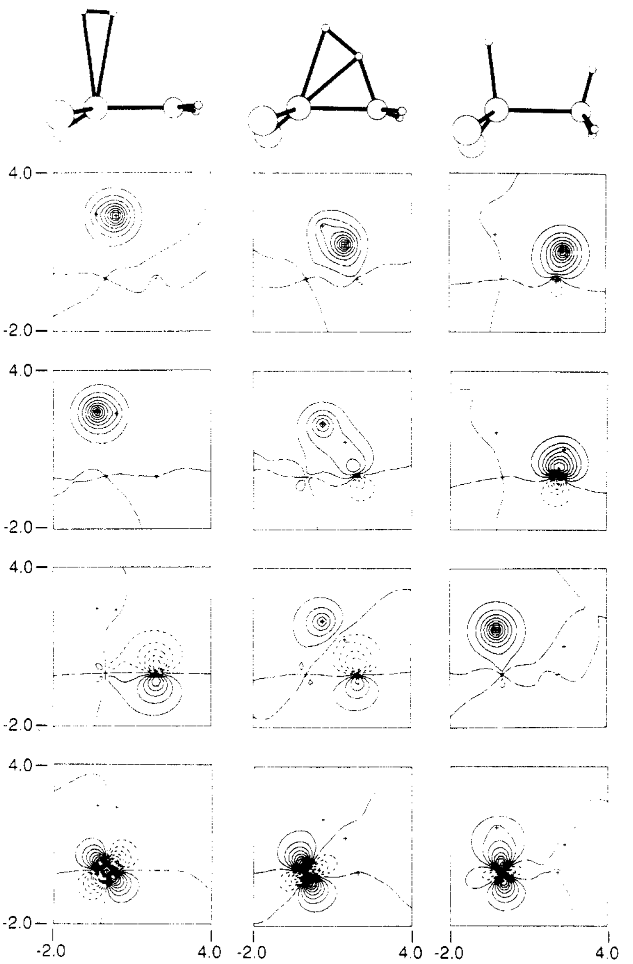
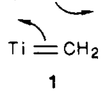


Figure 2. Contour plots of the GVB orbitals defining the reactive space for the addition of H_2 across the π bond of Cl_2TiCH_2 along the reaction coordinate. The plotting plane contains titanium, carbon, and both hydrogens that originate from H_2. The first column represents the π complex, the second column the transition state, and the final column the product methyl hydride. The first two rows are the one-electron orbitals for the H_2 bond pair, which turns into a C–H bond pair. The third row starts as the p orbital on carbon π bonded to titanium and ends up as an s orbital on hydrogen. The final row is paired to the third row, initially as a Ti–C π bond, ultimately as a Ti–H σ bond.

the recently observed group 6–8 H_2 adduct complexes where the bound H_2 unit is stable.[16] For these systems the metal can participate in back-bonding to the σ^* orbital of the H_2[16b] though the interaction is dominantly σ donor.

The small barrier for reaction 6 is due to the ease with which the Ti dπ orbital originally bonded to methylene can rehybridize. Because this d orbital can change its shape during the reaction, it can retain overlap with the methylene p orbital as it moves from carbon to H^a. This orbital motion along the reaction coordinate is indicated in 1.



1

The GVB orbital contour plots demonstrating this orbital motion are shown in Figure 2. The d orbital involved in covalent π bonding to the p orbital of the methylene ligand (row 4 of Figure 2) rehybridizes along the reaction coordinate permitting it to retain substantial overlap with the p orbital (row 3 of Figure 2) which moves from the methylidene carbon to H^a. The Ti–C π bond is transformed into a Ti–H^a σ bond. This orbital motion and rehybridization occur in response to the delocalization of the H_2 σ bond pair from the H^a–H^b bonding region to the C–H^b bonding region where a σ bond is formed between carbon and H^b in the product methyl hydride (rows 1 and 2 of Figure 2).

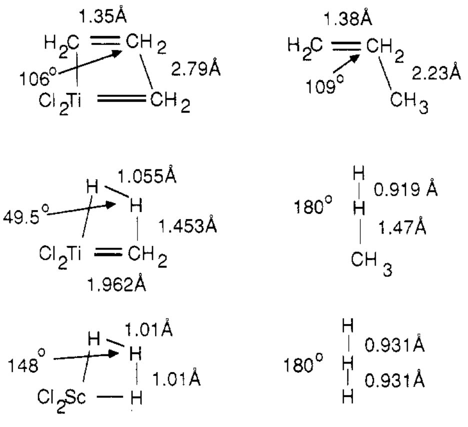
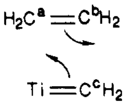
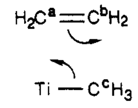


Figure 3. Relevant geometric coordinates for the transition states of three examples of analogous transition-metal-containing four-center reactions and organic three-center reactions.

The same orbital motion was observed to occur for **2**[11] and **4**[13] and is not inconsistent with the published description of **3**.[12] As previously discussed[11] for **2**, the π bond between C^a and C^b is converted into a σ bond between C^b and C^c. In response to this, the π bond between Ti and C^c transforms into a σ bond between Ti and C^a. For **3**, Fujimoto and co-workers used paired interacting orbitals[12] to indicate that the π bond between C^a and C^b does become a σ bond between C^b and C^c and the σ bond between Ti and C^c does change into a σ bond between Ti and C^a. For **4**, Steigerwald and Goddard[13a] showed that the σ bond between H^a and H^b turns into a σ bond between H^b and H^c. In response to this, the σ bond between Ti and H^c rearranges into a σ bond between Ti and H^a. In each case, the orbital originally on center C necessarily builds in the orthogonality constraints to the bond pair moving from between centers A and B to be between centers B and C. Thus, all four subsets of four-center metal containing 2 + 2 reactions occur with small barriers for precisely the same electronic reasons.



2



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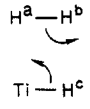

4

Comparison of the geometries of the transition states for all four subsets of this class of reaction with the transition states for the analogous radical plus bond reactions[17-19] (see Figure 3) leads us[20] to the following observation: addition of the metal orbital and the fourth electron provides only a modest perturbation to the transition state for the analogous three-electron radical plus bond reaction. The major feature ascribed to the metal

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(16) (a) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. *J. Am. Chem. Soc.* **1984**, *106*, 451–452. (b) Hay, P. J. *Chem. Phys. Lett.* **1984**, *103*, 466–469. (c) Morris, R. H.; Sawyer, J. F.; Shiralian, M.; Zubkowski, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5581–5582. (d) Crabtree, R. H.; Lavin, M. *J. Chem. Soc., Chem. Commun.* **1985**, 794–795.

(17) Arnaud, R.; Barone, V.; Olivella, S.; Sole, A. *Chem. Phys. Lett.* **1985**, *118*, 573–579.

(18) Walch, S. P. *J. Chem. Phys.* **1980**, *72*, 4932–4940.

(19) Liu, B. *J. Chem. Phys.* **1984**, *80*, 581.

(20) Upton, T. H.; Rappé, A. K., unpublished results.

is the capacity for its participating orbital (the fourth orbital in the 2 + 2 reaction) to rehybridize through the participation of an additional, empty d orbital, retaining overlap with the third or radical orbital of the bond plus radical reaction.

Summary

We have found the addition of dihydrogen across a titanium–carbon π bond occurs with a small activation energy. The explanation for this small barrier is precisely the same as for previously studied four-center 2 + 2 reactions.[11-14] The geometry of the transition state for this reaction (and related 2 + 2 reactions) is observed to be quite similar to related organic radical plus bond reactions. Reaction 6 is decidedly exothermic.

Calculational Details

A. Basis Sets and Effective Potentials. All of the calculations reported here were carried out by using Cartesian Gaussian basis sets. For both Cl[21] and Ti,[11] an effective potential was used to replace the core electrons allowing self-consistent orbital optimization to be carried out only for the valence electrons. For geometry optimization, a (7s,4p/3s,2p) basis was used for carbon,[22] and a (5s/2s) basis, scaled by 1.2, was used for the hydrogens.[23] The carbon basis was augmented with a single set of d Gaussians ($\zeta = 0.75$) for a final set of calculations at the optimum geometries. The H_2 hydrogen basis was augmented with a single set of p Gaussians ($\zeta = 0.425$) for the final set of calculations at the optimum geometries. For chlorine a valence minimum basis (3s,3p/1s,1p)[21] was used. For Ti, a valence double-ζ (3s,2p,4d/2s,2p,2d) basis[24] was used.

B. Wave Functions. The geometries of the reactant, transition state, and product were each determined by using GVB(2/4) wave functions and analytic gradients (discussed below). For the reactant and transition state, the Ti–C π and H–H σ bonds were explicitly correlated. For the product, the Ti–H and Ti–C σ bonds were correlated. For the final optimized geometries, GVB(3/6) wave functions were obtained and CI calculations were performed consisting of RCI quandruples plus all single and double excitations from the GVB orbitals to the entire virtual space. For the reactant and transition state, the Ti–C σ and π H–H σ bonds were explicitly correlated. For the product, the Ti–H, Ti–C, and one of the C–H σ bonds were correlated.

C. Geometry Optimizations. As mentioned above, the geometries of the reactant, transition state, and product were determined by using analytic derivatives of the form

$$d_h = \partial E(\Psi_{\mathrm{GVB}})/\partial q_i$$

for all Cartesian coordinates q of each atom i in the molecule, using the numerical procedure of Dupuis and King[25] and the expression for the energy derivative of a GVB "perfect pairing" wave function defined by Morikuma et al.[26] Second derivatives $k_{li,mj}$ were estimated by using Badger's rules[27] and updated with finite difference of the first derivatives at each geometry by using a procedure implemented by Upton and Rappé.[20] With the assumption of the total potential near the minimum to be of the form

$$V(r) = V_0 + dr + \tfrac{1}{2}kr^2$$

the global minimum in the potential was found by using successive Newton–Raphson steps,[28] $\Delta r = -d/k$ to define new test geometries. To locate the transition state, the lagrange multiplier technique of Simons and co-workers[29] was used. At the optimized transition-state structure, steps were taken along the reaction coordinate with the above described CI wave function to obtain the final transition-state geometry (the CI geometry only differed by 0.0497 Å from the GVB-PP geometry). The final geometries and CI total energies are collected in Table I.

Table I. Molecular Coordinates and Cl Total Energies[a]

atom	x	y	z
(a) $Cl_2Ti{=}CH_2$ CI Total Energy = −1806.064 573			
Ti	0.0	0.0	0.0
Cl1	−2.189 733 8	0.0	−0.832 370 4
Cl2	2.189 733 8	0.0	−0.832 370 4
C	0.0	0.0	1.935
H1	−0.910 406 0	0.0	2.521 188 3
H2	0.910 406 0	0.0	2.521 188 3
(b) $Cl_2Ti{=}CH_2{\cdot}H_2$ CI Total Energy = −1807.233 537			
Ti	0.0	0.0	0.0
Cl1	−2.163 241 0	−0.345 070 2	−0.835 208 5
Cl2	2.163 241 0	−0.345 070 2	−0.835 208 5
C	0.0	0.0	1.932 82
H1	−0.910 980 1	−0.007 578 0	2.518 824 9
H2	0.910 980 1	−0.007 578 0	2.518 824 9
H3	0.0	2.428 060 3	−0.337 759 2
H4	0.0	2.384 273 4	0.399 251 5
(c) $Cl_2Ti{=}CH_2{\cdot}H_2$ Transition-State CI Total Energy = −1807.209 767			
Ti	0.0	0.0	0.0
Cl1	−2.149 646 8	−0.512 669 3	−0.791 545 3
Cl2	2.149 646 8	−0.512 669 3	−0.791 545 3
C	0.0	0.0	1.962 3
H1	−0.904 246 1	−0.088 644 7	2.545 980 9
H2	−0.904 346 1	−0.088 644 7	2.545 980 9
H3	0.0	2.025 767 5	0.635 578 7
H4	0.0	1.361 485 9	1.454 778 1
(d) Cl_2TiHCH_3 CI Total Energy = −1807.258375			
Ti	0.0	0.0	0.0
Cl1	−2.114 928 0	−0.695 966 5	−0.666 795 3
Cl2	2.114 928 0	−0.695 966 5	−0.666 795 3
C	0.0	0.0	2.112 6
H1	−0.903 105 2	−0.500 869 4	2.430 422 3
H2	0.903 105 2	−0.500 869 4	2.430 422 3
H3	0.0	1.694 475 2	−0.235 049 5
H4	0.0	1.052 523 5	2.372 344 2

[a] Coordinates are in angstroms and energies in hartrees.

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Note Added in Proof. Bercaw and co-workers have reported the addition of dihydrogen across the metal–nitrogen π bond in the complex $Cp_2{}^*ScNHPh$.[30]

Registry No. Cl_2TiCH_2, 79899-81-3; Cl_2TiHCH_3, 105930-82-3.

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(21) Rappé, A. K.; Smedley, T. A.; Goddard III, W. A. *J. Phys. Chem.* **1981**, *85*, 1662–1666.

(22) Rappé, A. K.; Goddard III, W. A., unpublished results.

(23) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293–1302.

(24) Rappé, A. K.; Smedley, T. A.; Goddard III, W. A. *J. Phys. Chem.* **1981**, *85*, 2607–2611.

(25) Dupuis, M.; and King, H. F. *J. Chem. Phys.* **1978**, *68*, 3998–4004.

(26) Kato, S.; Morokuma, K. *Chem. Phys. Lett.* **1979**, *65*, 19–25. Goddard, J. D.; Handy, N. C.; Schaefer III, H. F. *J. Chem. Phys.* **1979**, *71*, 1525–1530.

(27) Badger, R. M. *J. Chem. Phys.* **1934**, *2*, 128–131; **1935**, *3*, 710–714.

(28) Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214–218.

(29) Simons, J.; Jorgensen, P.; taylor, H.; Ozment, J. J. *Phys. Chem.* **1983**, *87*, 2745–2753.

(30) Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T. *Organometallics* **1986**, *5*, 443–450.