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Reversible Heterolytic Methane Activation of Metal-Free Closed-Shell Molecules: A Computational Proof-of-Principle Study

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Utilization of the acid/base effects simultaneously is one of the basic principles used by transition-metal (TM) complexes to activate H–H/C–H σ bonds. In principle, the high reactivity of metal-free FLPs (frustrated Lewis pairs) towards H_2 can also be attributed to these effects. On the basis of our proposed integrated FLPs, we pushed the effects to a higher (if not a limit) level at which the extremely unreactive methane C–H σ bond can be activated by our designed metal-free closed-shell molecules. Three molecules (**M3c**, **M4b**, and **M4c**) among the reported have activation free energies (22.4, 20.0, and 20.2 $\mathrm{kcal\,mol^{-1}}$, respectively) comparable with (or less than) the 22.3 $\mathrm{kcal\,mol^{-1}}$ of a TM model complex that features a Ti=N double bond. The derivative of the TM model has been experimentally shown to be capable of activating methane. Moreover, some of the activation reactions are (or nearly) thermoneutral. For example, the methane activations of **M3c**, **M4b**, and **M4c** are exothermic by –1.9, –4.5, and –5.2 $\mathrm{kcal\,mol^{-1}}$ of free energies, respectively. The kinetics and thermodynamics imply that the molecules could be further developed to realize catalytic methane activation. The electronic structure analyses reveal that, although our metal-free molecules and the TM model complex share the same principle in activating the C–H bond, there are differences as to how they go about maintaining the effective active sites. The reported molecules could be the targets for experimental realizations. The strategy could be applied to the design of similar molecules to realize more general C–H bond activation of alkanes.

Introduction

Functionalization by means of C–H σ-bond activation is a promising strategy to directly and therefore economically transform alkanes (e.g., methane) into more valuable functionalized molecules.[1] Much effort has been devoted to the design and synthesis of new reagents/catalysts that can break the unreactive C–H bond.[2,3] It is known that both transition-metal (TM) complexes[2] (including enzymatic systems[2a,2b]) and TM-free reagents[3] (e.g., ozone,[3a] superacids,[3b] peracids,[3c] and dioxirane[3d]) or species (e.g., free radicals and radical cations,[3e–3l] hydrocarbon ions[3m–3s]) are able to achieve the goal. In the catalog of metal-free methane activation, recent developments include the study of Bettinger's group,[3f] which used the photo-produced in situ triplet borylnitrene to activate methane and a variety of cycloalkanes. Schwarz's group found that the $P_4O_{10}^{\cdot+}$ radical cation can abstract hydrogen atoms from methane,[3i,3l] ethane, and propane.[3j] De Petris's group[3k,3l] showed that the $SO_2^{\cdot+}$ radical cation can also effectively activate methane by means of hydrogen abstraction. However, except for these special metal-free systems mentioned above, there is rarely experimental or computational evidence to show that methane can be activated by "regular" metal-free closed-shell molecules. The unusual reactivity of FLPs recently discovered by Stephan's group[4] and our proposed integrated FLP active sites[5] renewed our early interest[6] in methane activation. We here report a computational proof-of-principle study to show that the C–H σ bond of methane can be cleaved by "regular" closed-shell molecules with experimentally feasible energetics.

Results and Discussion

Both C–H and H–H bond activations involve σ-bond breaking. Although FLPs are very reactive towards H_2 and the principle of using synergic acid/base effects was unveiled by Pápai's and Li's groups,[7] we are interested in whether the principle can be applied to methane activation. The optimized transition state (**FLP-TS** in Scheme 1) for the reaction of an FLP prototype [$P(tBu)_3/B(C_6F_5)_3$[4b]] with methane is shown in Scheme 1. Similar to the TM-mediated C–H versus H–H activations, the FLP is much less reactive towards methane ($\Delta G^{\neq}_{\mathrm{sol}}$ = 38.3 $\mathrm{kcal\,mol^{-1}}$) than towards hydrogen ($\Delta G^{\neq}_{\mathrm{sol}}$ = 13.6 $\mathrm{kcal\,mol^{-1}}$). On the basis of the structure of the transition state, we reasoned that, because the CH_4 moiety lies between the basic and acidic centers, the CH_3 subunit hinders the efficient interactions between the vacant boron orbital and the C–H σ-bonding orbital, which

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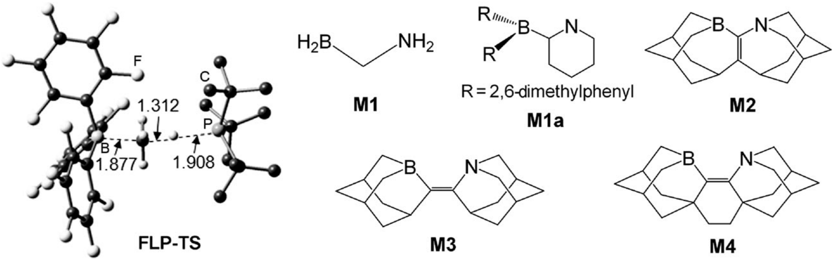


Scheme 1.

weakens the Lewis acid effect of the FLP in breaking the C–H bond of CH_4. We thus hypothesized that a concerted side-on attack via a cyclic transition state could be energetically more favorable. In fact, this attacking pattern is often preferred in TM-mediated methane and hydrogen activations.[2] Note that it has been confirmed by intrinsic reaction coordinate (IRC) calculations that the structure of the transition state of the FLP (**FLP-TS** in Scheme 1) connects to a side-on attacking structure (**FLP-IM** in the Supporting Information, SI1) along the reaction coordinate, which excludes the existence of a side-on attacking transition state for the FLP-mediated methane activation.

Our previously proposed integrated FLPs,[5] exemplified by models **M1** and **M2** (Scheme 1), are suitable for such a side-on attack and were used as starting points. As shown in Table 1, the calculations on the **M1** methane activation gave a barrier ($\Delta G^{\neq}_{\text{sol}}$) of 33.6 kcal mol^{-1} and on the more experimentally practicable molecule (**M1a**) gave a barrier of 46.8 kcal mol^{-1}. The high barriers of **M1** and **M1a** can be attributed to the following two factors: (i) the active sites are not reactive enough to activate methane because methane is much more difficult to activate than H_2[1a] and (ii) the steric effect of the bulky dimethylphenyl groups of **M1a** also disfavor the reaction. Previously, we[5b] proposed tuning the relative orientation of the two critical orbitals (i.e., the vacant boron orbital and nitrogen lone pair) of **M1** into a face-to-face arrangement like that in **M2** to enhance the reactivity of the active site. Based on **M2**, we designed more experimentally practicable molecules that reach the kind of reactivity towards H_2 that is comparable with the well-known metal–ligand bifunctional hydrogenation catalysts.[8] Indeed, **M2** is more reactive towards methane than **M1** and has a lower activation barrier of around 2.0 kcal mol^{-1} (Table 1). To further improve the reactivity of the active site, **M3** and **M4** were designed in this study. In agreement with our assumption that because methane is larger than hydrogen molecules, an enlarged active site could benefit methane activation, **M3** and **M4** are more reactive towards methane than **M2** by around 4.0 kcal mol^{-1} (Table 1). Taking **M2** and **M3** as examples, we also investigated the ability of methane activation of their counterparts by replacing the N centers with P centers (see SI2 in the Supporting Information). The counterparts of **M2** and **M3** have much higher barriers (49.5 and 46.0 kcal mol^{-1} in SI3, respectively). The high barriers can be mainly ascribed to the repulsive electrostatic interactions between the positive P center (+0.82 e and +0.84 e for the counterparts of **M2** and **M3**, respectively) and the positive H–(CH_3) atom. In contrast, the nitrogen atoms in **M2** and **M3**, as well as others reported in this paper, all bear negative charges [e.g., –0.59 e (**M2**) and –0.57 e (**M3**)].

Table 1. Relative enthalpies and free energies (in kcal mol^{-1}) in cyclohexane solvent,[a] HOMO–LUMO gap (in eV), and the distortion energies[b] (in kcal mol^{-1}) of the molecules (E_{mol}) and CH_4 moieties (E_{CH_4}) in the transition states.

Molecule	Transition state		Product		Gap	E_{mol}	E_{CH_4}
	$\Delta H^{\neq}$	$\Delta G^{\neq}$	ΔH	ΔG			
M1	22.5	33.6	1.2	11.8	8.2	18.3	42.1
M2	20.4	31.2	0.8	13.4	7.5	14.0	37.0
M3	15.5	27.0	0.3	11.5	7.9	13.2	36.3
M4	16.2	27.5	–0.9	10.3	7.8	13.8	38.8
M1a	31.9	46.8	8.5	23.2	7.0	19.7	40.8
M2a	21.5	33.0	2.3	12.9	7.5	16.1	38.4
M3a	17.1	30.0	–0.6	11.4	7.7	15.1	38.5
M4a	16.3	28.1	–2.4	9.6	7.6	14.9	40.1
M2b	14.7	26.5	–10.0	2.1	7.1	16.2	32.5
M3b	17.3	28.3	–5.8	4.8	7.9	24.1	31.9
M4b	7.7	20.0	–16.7	–4.5	7.2	14.3	34.2
M2c	13.6	25.4	–12.0	–0.7	6.9	16.5	31.3
M3c	10.4	22.4	–13.6	–1.9	7.6	17.2	30.5
M4c	8.1	20.2	–17.4	–5.2	7.2	15.8	32.3
5	11.3	22.3	–21.4	–11.4	7.0	2.5	38.9
P/B[c]	28.9	38.3	–6.1	3.2	4.7	36.5	33.9

[a] Gas-phase results are given in SI3 in the Supporting Information. [b] See ref.[5b] [c] P/B = P(tBu)$_3$/B(C_6F_5)$_3$.

M2–**M4** are just the models for our strategic development and not experimentally operable because they can be dimerized, thereby disabling their activation ability. Therefore, dimerizations must be avoided. Moreover, because our goal is to achieve methane activation and the C–H σ bond is more difficult to activate than the H–H σ bond, the designed candidates would have higher reactivity than those for H_2 activation, which raises the concern that the candidates could be destroyed by reacting with each other (referred to hereafter as self-destruction) because the candidates also contain C–H σ bonds. This concern exerts more strict restrictions on the design of bulky substituents to overcome dimerizations. The molecules we reported previously have exposed methyl groups and were found to be unsuitable (see SI4 in the Supporting Information for details). As shown by **M*X*a** (X = 2–4) in Figure 1, we were able to overcome the dimerization and self-destruction issues by means of the concave active sites, by adding two

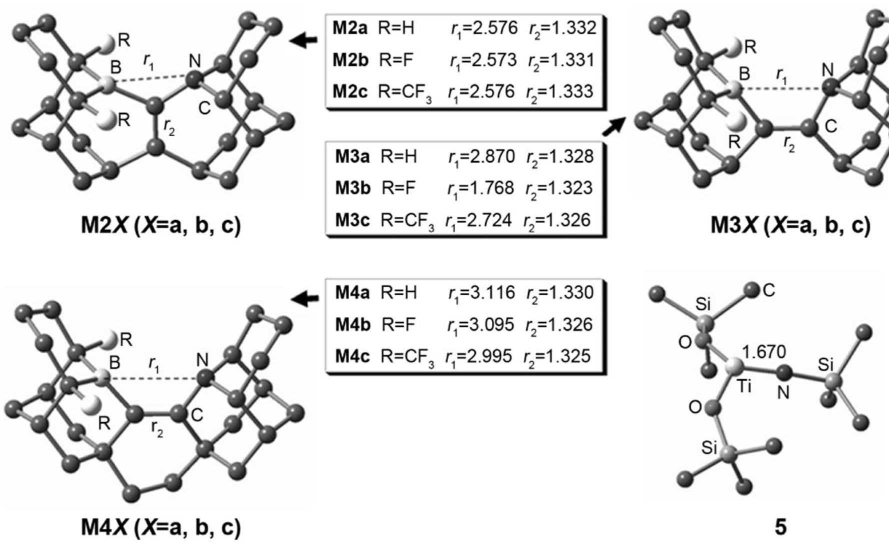


Figure 1. M05-2X/6-31G(d,p)-optimized structures of the designed candidates and the model of the experimental TM complex. Some trivial hydrogen atoms are omitted for clarity.

cyclohexane-like rings to **M2**–**M4**. By using F atoms in **M*X*b** and CF_3 groups in **M*X*c** (X = 2–4) (Figure 1), we intended to lower the barriers through the enhancement of the Lewis acidities of the B centers. As listed in Table 1, the large HOMO–LUMO gaps (6.9–8.2 eV) of these molecules exclude their diradical characters.

Before we report the kinetics and thermodynamics of the methane activations of **M*X*a**, **M*X*b**, and **M*X*c** (X = 2–4), we need to confirm whether they can overcome dimerization and self-destruction issues. For brevity, the detailed energetic and geometric results are provided in SI4 in the Supporting Information, and we summarize the major results below. By using the same procedure as we used previously,[5a–5c] we attempted to locate the possible dimers. The optimization for the dimers of **M2a** gave two separated monomers due to severe steric congestion. We could locate one type of dimer for **M3a** and **M4a**, but they are highly strained and lie 113.0 and 123.0 kcal mol^{-1} above **M3a** + **M3a** and **M4a** + **M4a**, respectively. The other type of dimers for **M3a** and **M4a** also went to the separated monomers, respectively. Because **M*X*b** and **M*X*c** have steric effects close to those of **M*X*a** (X = 2–4), it should be safe to conclude that they are also able to avoid the dimerization issue. We then checked whether they can self-destruct. Using cyclohexane (which is also used as a solvent in TM-mediated methane activation experiments[9b]) to mimic the chemical features of our designed molecules, we calculated the barriers for activating the C–H bond of cyclohexane. The barriers ($\Delta G^{\neq}_{\mathrm{gas}}$) are in the range of 42.3–44.0 (**M*X*a**), 33.3–41.7 (**M*X*b**), and 40.6–50.1 kcal mol^{-1} (**M*X*c**), which are at least 9.0 (**M*X*a**), 6.9 (**M*X*b**), and 20.4 kcal mol^{-1} (**M*X*c**, X = 2–4) larger than those for methane activation, respectively, though the C–H bond of cyclohexane is weaker than the C–H bond of methane. This is reasonable because the concave active sites of the designed molecules spatially prevent the proximity of cyclohexane to the active sites. Because **M*X*b** and **M*X*c** (X = 2–4) contain C–F bonds, we further checked the possible self-destruction by means of C–F bond activations. Using CH_3F as a probe molecule, the predicted barriers for activating the C–F bond range from 30.3 to 42.1 kcal mol^{-1}, which are 7.5–17.4 kcal mol^{-1} higher than those for methane activation. Because the designed molecules are more sterically bulky than the probe molecules (cyclohexane and CH_3F), it can be expected that the barriers for self-destructions by means of C–H or C–F bond activations should be higher than the values estimated on the basis of the activation of probe molecules. It is possible to control the experimental conditions to avoid self-destruction.

The reactions of **M*X*a**, **M*X*b**, and **M*X*c** (X = 2–4) with methane have been studied. Figure 2 only presents the structures for the three best reactions (**M3c**, **M4b**, and **M4c**) and the rest are given in SI3 in the Supporting Information. The energetic results in the solvent are compiled in Table 1. Experimentally, it has been found that a variety of early TM complexes can break C–H bond of alkanes by means of 1,2-addition to the TM–imido double bond.[9] As a reference to examine whether our molecules are reactive enough to activate methane, the reaction of the TM complex model (**5**) with methane was also studied at the current levels and the energetic and geometric results are included in Table 1 and Figure 1, respectively. Sakaki's group[10] recently used **5** as a model to gain insight into the mechanism of the experimental methane 1,2-addition to the TM complex $[(t\mathrm{Bu}_3\mathrm{SiO})_2\mathrm{Ti} = \mathrm{NSi}t\mathrm{Bu}_3{}^{[9b]}]$.

In comparison with the models **M2**–**M4**, the activations of **M2a**–**M4a** are only slightly kinetically less favorable (Table 1). In comparison with the large barrier difference (13.2 kcal mol^{-1}) between **M1** and **M1a**, the slightly higher barriers indicate that the active sites with additional protection constructions are still structurally and electronically optimal for methane activation. This encouraged us to use electron-withdrawing F substituents in **M2b**–**M4b** and CF_3 groups in **M2c**–**M4c** to further lower the barriers. As seen

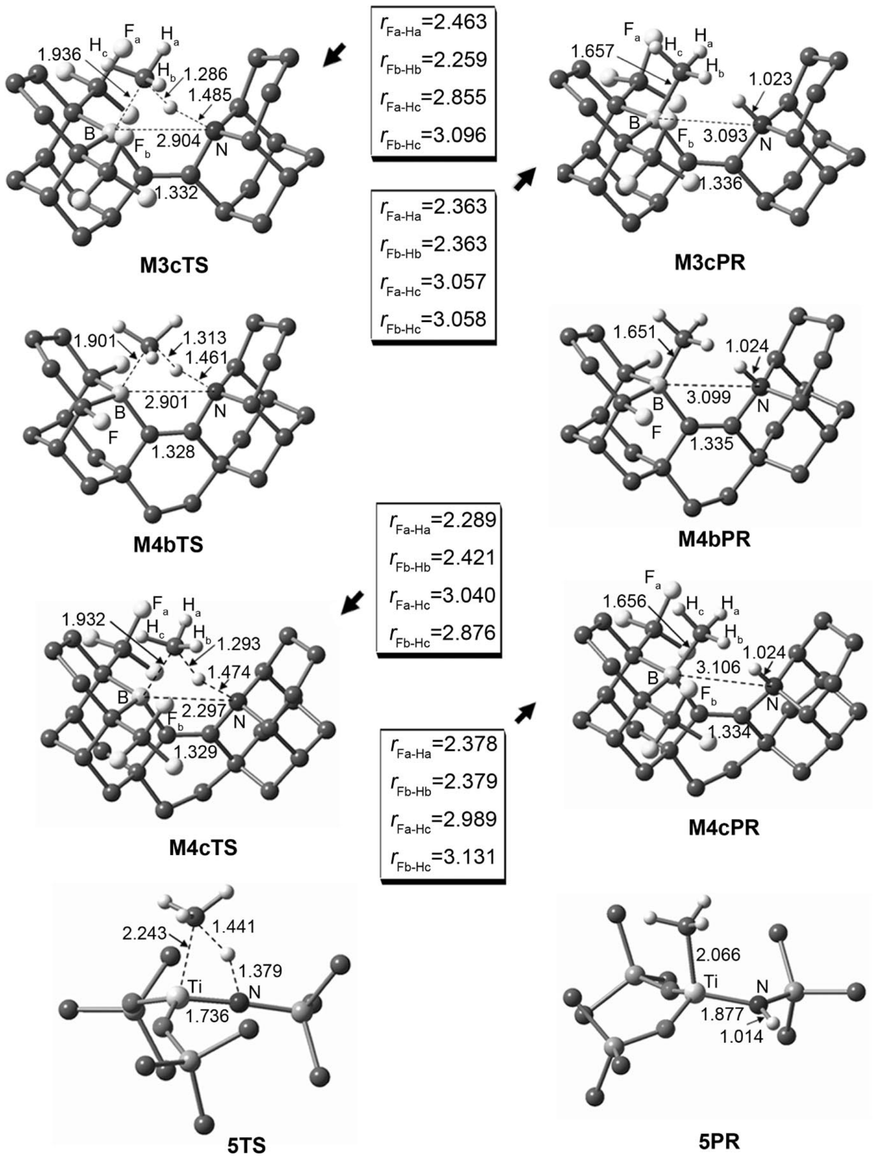


Figure 2. M05-2X/6-31G(d,p)-optimized structures of transition states and products of **M3c**, **M4b**, **M4c**, and **5**. Some trivial hydrogen atoms are omitted for clarity.

in Table 1, the improvements are substantial. Remarkably, the barriers of **M4b** (20.0 kcal mol^{-1}) and **M4c** (20.2 kcal mol^{-1}) are smaller than the 22.3 kcal mol^{-1} of **5** and the barrier of **M3c** (22.4 kcal mol^{-1}) is also comparable with that of **5**. Note that the TM complex [(tBu$_3$SiO)$_2$Ti = NSitBu$_3$] modeled by **5** has been experimentally demonstrated to be capable of activating methane by means of 1,2-addition,[9b] and should have a barrier higher than that of **5** because the simplified model does not account for the more crowded steric effects due to the bulky tBu groups.

Another feature of the methane activations of **M*X*b** and **M*X*c** (X = 2–4) worthy of emphasis is that they are (or nearly) reversible. The free energies of the products, relative to their corresponding reactants, are in the range of –5.2–4.8 kcal mol^{-1}. In terms of the reversibility, the designed metal-free molecules are better than **5**, for which the methane activation is exothermic by 11.4 kcal mol^{-1}. Reversibility is important to realize catalytic reactions. For instance, both TM and TM-free hydrogenation catalysts have the kinetics and thermodynamics for reversible hydrogen activation.[8,11] In addition, the activated H and CH_3 in the products lie closely on the same side, which could facilitate the transfer of H and CH_3 to other substrates to complete catalytic cycles, which is similar to the hydrogen activation of metal–ligand bifunctional hydrogenation catalysts.[8]

It has been revealed that the synergistic acid/base effects are crucial for the facile H–H bond cleavages of FLPs. The basic principle is applicable to our predicted methane activations. However, the methane activation of the typical P(tBu)$_3$/B(C_6F_5)$_3$ FLP has a much higher barrier ($\Delta G^{\neq}_{\text{sol}}$ = 38.3 kcal mol^{-1}). On the basis of the present study, in addition to the side-on attacking pattern mentioned above, we can add the following factors that are responsible for the higher reactivity of our molecules relative to typical FLPs:

(i) The fine-tuned active sites enhance the synergistic acid/base effect. (ii) The side-on attack causes less distortion. In the transition state of $P(tBu)_3/B(C_6F_5)_3$ FLP methane activation, the distortion energy[5b] (the energy difference between the B/P pair moiety fixed in the structure of the transition state and the free B/P pair) of the FLP is 36.5 kcal mol^{-1}, whereas the values in the present cases are in the range of 13.2 to 19.7 kcal mol^{-1}, except for **M3b** that has a distortion energy of 24.1 kcal mol^{-1} due to the formed weak B–N dative bond (r_{B-N} = 1.768 Å; see Figure 1). However, the distortion energies of the CH_4 moiety (the energy difference between the moiety fixed in the structure of the transition state and the free methane) are relatively more comparable (see Table 1), which indicates that C–H bond breaking starts at a similar degree of distortion of CH_4. (iii) The electron-withdrawing effect of F and CF_3 groups in **M*X*b** and **M*X*c** (X = 2–4) further contributes to lower the energy barriers. (iv) As indicated by the C–H···F distances (Figure 2), C–H···F hydrogen bonding exists in the transition states of **M*X*c** (X = 2–4), which is also helpful in lowering the barriers.

In terms of electronic structure, our molecules are similar to the TM model complex **5**. Each of the active sites contains an electron-deficient center (B or Ti) and an electron-rich center (i.e., N) to serve as electron acceptor and donor for operation of the synergistic acidic/basic effects, which results in a similar activation mechanism (heterolytic cleavage). However, comparing our molecules with **5** raises an intriguing question. Although the Ti and N centers in **5** can be bound together directly, the N and B centers in our molecules have to be separated by linkage(s). The NH_2BH_2 (without the linkage) has a H_2 activation energy barrier of 43.2 kcal mol^{-1}, which is significantly larger than the 10.2 kcal mol^{-1} of CH_2-separated **M1** at the CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ+ZPE(MP2) level.[5a] To gain insight into this issue, we compared the two critical orbitals of **5** with those of BH_2NH_2 and **M3** in Figure 3. It can be observed that the LUMO of **5** is dominated by the Ti d_{z^2} atomic orbital and the HOMO–1 is occupied by the nitrogen p_π lone pair. Due to the unmatched symmetries of the two orbitals, the nitrogen lone-pair electrons cannot be donated to the electron-deficient Ti center. In contrast, the vacant boron orbital and nitrogen lone-pair orbital have the same orbital (p_π) symmetries to interact with each other, which results in electron donation and a weakening of the acidity of B and the basicity of the N centers. When the B and N centers are separated by linkages as exemplified by **M3**, the interaction between the vacant boron orbital and nitrogen lone pair is spatially prohibited. Therefore, the acidic and basic centers are well maintained and the synergistic acid/base effects can operate as desired. Put briefly, the activation principles of the TM complex (e.g., **5**) and our metal-free molecules are the same, but the ways to preserve the effective acid/base active sites are different.

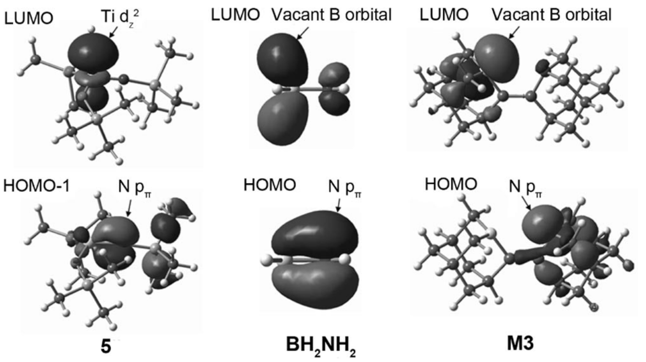
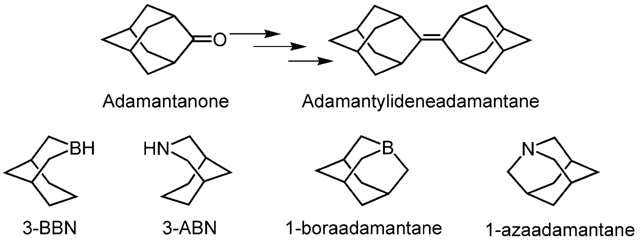


Figure 3. Two critical orbitals of **5**, BH_2NH_2, and **M3**.

Starting from adamantanone (Scheme 2), Schaap et al.[12] succeeded in joining two adamantanone molecules to give adamantylideneadamantane, which is structurally very similar to our model **M3**. Furthermore, the experimentally accessible compounds[13] such as 3-borabicyclo[3.3.1]-nonane (3-BBN), 3-azabicyclo[3.3.1]nonane (3-ABN), 1-boraadamantane, and 1-azaadamantane also have the structural elements that are embedded in our designed molecules. The decisive coupling steps of two adamantanone molecules may provide clues for the experimental realization of our designed molecules. If these molecules can be synthesized, we will have quite a different approach to activate methane according to our predicted kinetics and thermodynamics. Concerning the important issue of how to convert methane (or other alkanes) into functionalized high-value chemicals and the benefits that the TM-free way could bring to our environment, efforts to see if the proposed strategy works experimentally could prove to be worthwhile.



Scheme 2.

Conclusion

C–H σ-bond activation of methane has attracted extensive research effort because it is not only a promising approach to directly functionalize the inert and abundant molecule but also because it lies at the heart of our understanding of chemical reactivity. Although utilization of the synergistic acid/base effects is one of the basic principles for TM-mediated hydrogen and methane activations, we have pushed the effects to a higher (if not a limit) level in the metal-free domain, at which the extremely unreactive C–H bond can be activated by our designed metal-free closed-shell molecules. We have TM complexes for both H–H and C–H bond activations, but there has been no experimental or computational evidence for FLP-based C–H activation. In principle, our computational study demonstrates that, if properly constructed, FLP-based metal-free systems can also reach the high reactivity of TM complexes. The reported examples could be the target of experimental realizations. The strategy could be extended to similar molecules for methane activation or more general C–H σ-bond activation of alkanes.

Computational Methods

All structures reported in this work were optimized and then characterized to be energy minima (no imaginary frequency) or transition states (only one imaginary frequency) at the M05-2X/6-31G(d,p) level in the gas phase. The M05-2X functional[14] has proven to be suitable for studying similar reactions by others[15] and us.[5a–5c] Using cyclohexane as a solvent representative, the solvent effects were accounted by the IEFPCM model[16] in combination with the UFF atomic radii with explicit radius for hydrogen atoms. The IEFPCM calculations were performed at the M05-2X/6-311++G(2d,p) level with the gas-phase M05-2X/6-31G(d,p) structures. The M05-2X/6-31G(d,p) harmonic frequencies were used for thermal and entropic corrections at 297.15 K and 1 atm. The activations are entropically unfavorable processes. It should be noted that the ideal gas-phase model overestimates the entropic penalties of the reactions because the suppressing effect of the solvent on the freedom of the transitional and vibrational motions are not properly accounted for by the ideal gas-phase model. Our reported free-energy barriers should therefore be considered conservative estimations. All these calculations were carried out by using the Gaussian 03 program.[17]

Supporting Information (see footnote on the first page of this article): Optimized geometries of the reaction of $P(tBu)_3/B(C_6F_5)_3$ with methane, B/P counterparts, energetic and geometric results of the reported systems, and verification of self-destruction issues.

Acknowledgments

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[1] a) G. J. Kubas, *Metal Dihydrogen and σ-Bond Complexes*, Kluwer Academic/Plenum Publishers, New York, **2001**; b) K. I. Goldberg, A. S. Goldman, *Activation and Functionalization of C–H Bonds*, Oxford University Press, Washington, DC, **2004**; c) W. B. Tolman, *Activation of Small Molecules*, Wiley-VCH, Weinheim, **2006**; d) R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, 4th ed., Wiley-Interscience, New Jersey, **2005**.

[2] For examples: a) A. E. Shilov, G. B. Shul'pin, *Chem. Rev.* **1997**, *97*, 2879; b) S. Ye, F. Neese, *Curr. Opin. Chem. Biol.* **2009**, *13*, 89; c) H. Y. Chen, S. Schlecht, T. C. Semple, J. F. Hartwig, *Science* **2000**, *287*, 1995; d) J. A. Labinger, J. E. Bercaw, *Nature* **2002**, *417*, 507; e) K. Godula, D. Sames, *Science* **2006**, *312*, 67; f) R. G. Bergman, *Nature* **2007**, *446*, 391; g) H. M. L. Davies, J. R. Manning, *Nature* **2008**, *451*, 417; h) B. A. Vastine, M. B. Hall, *Coord. Chem. Rev.* **2009**, *253*, 1202; i) I. A. I. Mkhalid, J. H. Barnard, T. B. Marder, J. M. Murphy, J. F. Hartwig, *Chem. Rev.* **2010**, *110*, 890; j) D. Balcells, E. Clot, O. Eisenstein, *Chem. Rev.* **2010**, *110*, 749; k) J. Roithová, D. Schröder, *Chem. Rev.* **2010**, *110*, 1170; l) M. M. Díaz-Requejo, P. J. Pérez, *Chem. Rev.* **2008**, *108*, 3379; m) C. Copéret, *Chem. Rev.* **2010**, *110*, 656; n) M. Schlangen, H. Schwarz, *Dalton Trans.* **2009**, 10155; o) M. P. Doyle, R. Duffy, M. Ratnikov, L. Zhou, *Chem. Rev.* **2010**, *110*, 704; p) D. Wang, E. R. Farquhar, A. Stubna, E. Münck, L. Que Jr., *Nature Chem.* **2009**, *1*, 145; q) A. S. Goldman, *Nature Chem.* **2009**, *1*, 109.

[3] For examples: a) H. Varkony, S. Pass, Y. Mazur, *J. Chem. Soc., Chem. Commun.* **1974**, 437; b) G. A. Olah, G. K. S. Prakash, J. Sommer, *Science* **1979**, *206*, 13; c) H. J. Schneider, W. Müller, *J. Org. Chem.* **1985**, *50*, 4609; d) R. Mello, M. Fiorentino, C. Fusco, R. Curci, *J. Am. Chem. Soc.* **1989**, *111*, 6749; e) A. A. Fokin, P. R. Schreiner, *Chem. Rev.* **2002**, *102*, 1551; f) H. F. Bettinger, M. Filthaus, H. Bornemann, I. M. Oppel, *Angew. Chem. Int. Ed.* **2008**, *47*, 4744; g) U. H. Brinker, *Advances in Carbene Chemistry*, Jai Press, Greenwich, CT, **1994**; h) J. Vignolle, X. Cattoën, D. Bourissou, *Chem. Rev.* **2009**, *109*, 3333; i) N. Dietl, M. Engeser, H. Schwarz, *Angew. Chem. Int. Ed.* **2009**, *48*, 4861; j) N. Dietl, M. Engeser, H. Schwarz, *Chem. Eur. J.* **2009**, *15*, 11100; k) G. de Petris, A. Troiani, M. Rosi, G. Angelini, O. Ursini, *Chem. Eur. J.* **2009**, *15*, 4248; l) R. H. Crabtree, *Nature Chem.* **2009**, *1*, 348; m) V. G. Anicich, P. F. Wilson, M. J. McEwan, *J. Am. Chem. Soc. Mass Spectrom.* **2006**, *17*, 544; n) D. Schröder, H. Schwarz, P. Milko, J. Roithová, *J. Phys. Chem. A* **2006**, *110*, 8346; o) D. Ascenzi, N. Cont, G. Guella, P. Franceschi, P. Tosi, *J. Phys. Chem. A* **2007**, *111*, 12513; p) J. Žabka, M. Polášek, D. Ascenzi, P. Tosi, J. Roithová, D. Schröder, *J. Phys. Chem. A* **2009**, *113*, 11153; q) J. Roithová, C. L. Ricketts, D. Schröder, *Collect. Czech. Chem. Commun.* **2008**, *73*, 811; r) C. L. Ricketts, D. Schröder, C. Alcaraz, J. Roithová, *Chem. Eur. J.* **2008**, *14*, 4779; s) J. Roithová, C. L. Ricketts, D. Schröder, *Int. J. Mass Spectrom.* **2009**, *280*, 32.

[4] For examples, see: a) G. C. Welch, R. R. S. Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, *314*, 1124; b) G. C. Welch, D. W. Stephan, *J. Am. Chem. Soc.* **2007**, *129*, 1880; c) D. W. Stephan, *Org. Biomol. Chem.* **2008**, *6*, 1535; d) D. W. Stephan, *Dalton Trans.* **2009**, 3129; e) D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2009**, *48*, 46.

[5] a) Z.-X. Wang, G. Lu, H. Li, L. Zhao, *Chin. Sci. Bull.* **2010**, *55*, 239; b) G. Lu, H. Li, L. Zhao, F. Huang, Z.-X. Wang, *Inorg. Chem.* **2010**, *49*, 295; c) L. Zhao, H. Li, G. Lu, Z.-X. Wang, *Dalton Trans.* **2010**, DOI: 10.1039/b921941b. d) The integrated FLPs mean the incorporation of the acidic/basic centers, which are separated by proper linkages (e.g., CH_2 linkage), into one molecular framework.

[6] a) Z.-X. Wang, M.-B. Huang, *J. Am. Chem. Soc.* **1998**, *120*, 6758; b) Z.-X. Wang, M.-B. Huang, R.-Z. Liu, *Can. J. Chem.* **1997**, *75*, 996; c) Z.-X. Wang, M.-B. Huang, *J. Chem. Soc. Faraday Trans.* **1998**, *94*, 635.

[7] For examples, see: a) T. A. Rokob, A. Hamza, A. Stirling, T. Soós, I. Pápai, *Angew. Chem. Int. Ed.* **2008**, *47*, 2435; b) Y. Guo, S. Li, *Inorg. Chem.* **2008**, *47*, 6212.

[8] For examples, see: a) R. Noyori, T. Ohkuma, *Angew. Chem. Int. Ed.* **2001**, *40*, 40; b) R. Noyori, *Angew. Chem. Int. Ed.* **2002**, *41*, 2008; c) K. Abdur-Rashid, S. E. Clapham, A. Hadzovic, J. N. Harvey, A. J. Lough, R. H. Morris, *J. Am. Chem. Soc.* **2002**, *124*, 15104; d) S. E. Clapham, A. Hadzovic, R. H. Morris, *Coord. Chem. Rev.* **2004**, *248*, 2201; e) T. Ikariya, K. Murata, R. Noyori, *Org. Biomol. Chem.* **2006**, *4*, 393; f) M. Z. de Iuliis, R. H. Morris, *J. Am. Chem. Soc.* **2009**, *131*, 11263.

[9] a) P. J. Walsh, F. J. Hollander, R. G. Bergman, *J. Am. Chem. Soc.* **1988**, *110*, 8729; b) C. C. Cummins, S. M. Baxter, P. T. Wolczanski, *J. Am. Chem. Soc.* **1988**, *110*, 8731; c) C. C. Cummins, C. P. Schaller, G. D. Vanduyne, P. T. Wolczanski, A. W. E. Chan, R. Hoffmann, *J. Am. Chem. Soc.* **1991**, *113*, 2985; d) P. J. Walsh, F. J. Hollander, R. G. Bergman, *Organometallics* **1993**, *12*, 3705; e) C. P. Schaller, P. T. Wolczanski, *Inorg. Chem.* **1993**, *32*, 131; f) J. de With, A. D. Horton, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 903; g) J. L. Bennett, P. T. Wolczanski, *J. Am. Chem. Soc.* **1994**, *116*, 2179; h) C. P. Schaller, J. B. Bonanno, P. T. Wolczanski, *J. Am. Chem. Soc.* **1994**, *116*, 4133; i) Y. L. Sun, R. G. Bergman, *J. Am. Chem. Soc.* **1995**, *117*, 5877; j) C. P. Schaller, C. C. Cummins, P. T. Wolczanski, *J. Am. Chem. Soc.* **1996**, *118*, 591; k) J. L. Bennett, P. T. Wolczanski,

J. Am. Chem. Soc. **1997**, *119*, 10696; l) D. F. Schafer II, P. T. Wolczanski, *J. Am. Chem. Soc.* **1998**, *120*, 4881; m) P. Royo, J. Sánchez-Nieves, *J. Organomet. Chem.* **2000**, *597*, 61; n) A. P. Duncan, R. G. Bergman, *Chem. Rec.* **2002**, *2*, 431; o) H. M. Hoyt, F. E. Michael, R. G. Bergman, *J. Am. Chem. Soc.* **2004**, *126*, 1018; p) H. M. Hoyt, R. G. Bergman, *Angew. Chem. Int. Ed.* **2007**, *46*, 5580; q) Y. Boutadla, D. L. Davies, S. A. Macgregor, A. I. Poblador-Bahamonde, *Dalton Trans.* **2009**, 5820; r) P. T. Wolczanski, *Chem. Commun.* **2009**, 740.

[10] N. Ochi, Y. Nakao, H. Sato, S. Sakaki, *J. Am. Chem. Soc.* **2007**, *129*, 8615.

[11] For examples, see: a) P. A. Chase, G. C. Welch, T. Jurca, D. W. Stephan, *Angew. Chem. Int. Ed.* **2007**, *46*, 8050; b) H. D. Wang, R. Fröhlich, G. Kehr, G. Erker, *Chem. Commun.* **2008**, 5966; c) V. Sumerin, F. Schulz, M. Atsumi, C. Wang, M. Nieger, M. Leskela, T. Repo, P. Pyykko, B. Rieger, *J. Am. Chem. Soc.* **2008**, *130*, 14117.

[12] A. P. Schaap, G. R. Faler, *J. Org. Chem.* **1973**, *38*, 3061.

[13] a) Y. N. Bubnov, M. E. Gursky, D. G. Pershin, *J. Organomet. Chem.* **1991**, *412*, 1; b) Y. N. Bubnov, N. Y. Kuznetsov, M. E. Gurskii, A. L. Semenova, G. D. Kolomnikova, T. V. Potapova, *Pure Appl. Chem.* **2006**, *78*, 1357; c) M. E. Gurskii, K. A. Lyssenko, A. L. Karionova, P. A. Belyakov, T. V. Potapova, M. Y. Antipin, Y. N. Bubnov, *Russ. Chem. Bull.* **2004**, *53*, 1963; d) M. E. Gurskii, S. Y. Erdyakov, T. V. Potapova, Y. N. Bubnov, *Russ. Chem. Bull.* **2008**, *57*, 802.

[14] a) Y. Zhao, N. E. Schultz, D. G. Truhlar, *J. Chem. Theory Comput.* **2006**, *2*, 364; b) Y. Zhao, D. G. Truhlar, *Acc. Chem. Res.* **2008**, *41*, 157.

[15] a) T. A. Rokob, A. Hamza, A. Stirling, I. Pápai, *J. Am. Chem. Soc.* **2009**, *131*, 2029; b) A. Hamza, A. Stirling, T. A. Rokob, I. Pápai, *Int. J. Quantum Chem.* **2009**, *109*, 2416; c) T. A. Rokob, A. Hamza, I. Pápai, *J. Am. Chem. Soc.* **2009**, *131*, 10701.

[16] J. Tomasi, B. Mennucci, E. Cances, *J. Mol. Struct.* **1999**, *464*, 211.

[17] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, *Gaussian 03*, Revision E.01, Gaussian, Inc., Wallingford, CT, **2004**.

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