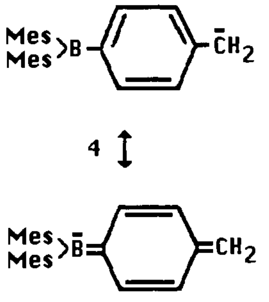
Cl and boron atom is 360°. Despite the bulky substituents at the B–C1 bond, the dihedral angle between the BC5C14 and the Cl Si P planes is only 31.5°, which is much smaller than that found for Mes_3B (50°)[15] but comparable to the value observed for **4** (25.8°).[2d] These results as a whole suggest that, in the solid state, compound **3a** has partial boron–carbon double bond character.



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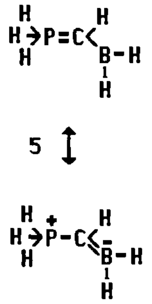

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In solution, a similar picture emerges from NMR spectroscopy.[16] The ^{11}B chemical shift for **3a** of +63.5 lies between the shifts observed for $MeBMes_2$ (+82.0)[17] and $H_2C{=}BMes_2^-$ (+35.0).[2c] Compared to the ^{11}B NMR data of previously reported C-borylated phosphorus ylides,[8a] the ^{11}B nucleus in **3a** is slightly deshielded, probably due to the presence of bulky substituents at the PCB skeleton. The ^{13}C NMR signal for the C1 atom is observed at +54.4, showing a strongly deshielded ylidic carbon atom compared to those in nonstabilized phosphorus ylides (e.g., +7.3 in $(iPr_2N)_2PF{=}C(SiMe_3)_2$[18]). In the ^1H and ^{13}C NMR spectra of **3a**, separate signals are observed for the two mesityl groups. Even at 110 °C, rotation about the B–C1 bond is slow relative to the NMR time scale, giving a rotation barrier $\Delta G^{\ddagger} > 90$ kJ mol^{-1}.[19,20] For the parent system **5**, the planar conformation has been calculated to be 120 kJ mol^{-1} more stable than the perpendicular one.[21,22]

On the other hand, for **3b**, the two methoxy groups at the boron atom are equivalent even at −80 °C, and therefore, no rotational barrier could be determined. At low temperature, the molecule probably adopts a conformation with a perpendicular orientation of the bonding planes of the boron and carbon atoms, meaning that B–C π-interactions are negligible. In addition, the ^{11}B chemical shift of +30.6 is almost identical with that of $MeB(OMe)_2$.[23] Obviously, the dimethoxyboron group cannot compete with the σ^* orbital of the phosphorus moiety for the electron density at the ylidic carbon atom.

Acknowledgment. Thanks are due to the CNRS for financial support of this work and to the Alexander von Humboldt Foundation and Conseil Régional Midi-Pyrénées for a postdoctoral fellowship (K.H.v.L.).

Supplementary Material Available: Tables of bond distances, angles, dihedral angles with estimated standard deviations, atomic coordinates and equivalent isotropic displacement factors, and anisotropic atomic displacement factors and H atom coordinates (5 pages). Ordering information is given on any current masthead page.

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(16) NMR data in C_6D_6 at 25 °C, with chemical shifts δ relative to external TMS (^1H, ^{13}C, ^{29}Si), $BF_3{\cdot}OEt_2$ (^{11}B), 85% phosphorus acid (^{31}P), $^nJ(^{31}PX)$ in parentheses and $^nJ(^{19}FX)$ in braces, in hertz, are as follows. **3a**: ^1H NMR (200 MHz) 6.76 (s), 6.70 (s) (each 2 H, aryl H), 4.04 (9.4) (d sept) (4 H, NCH), 2.50 (s), 2.47 (s) (each 6 H, *o*-CH_3), 2.17 (s) (6 H, *p*-CH_3), 1.16 (d), 1.00 (d) (each 12 H, $NC(CH_3)_2$), 0.23 (s) (9 H, $Si(CH_3)_3$); ^{11}B NMR (96.3 MHz, C_7D_8, 75 °C) 63.5 ($\nu_{1/2}$ = 410 Hz); ^{13}C NMR (50.3 MHz) 147.3 (<4) (br), 146.1 (27.1) (br) (ipso C), 141.0, 139.8, (<1) (*o*-C), 136.0, 135.4 (*p*-C), 128.7, 128.3 (*m*-C), 54.4 (127.7) {<3} (br) (PC), 48.4 (5.5) {1.8} (NC), 25.0, 24.7 (*o*-CH_3), 24.7 (4.0) {1.4}, 24.5 (4.8) {1.1} (NC*C*), 21.2, 21.1 (*p*-CH_3), 4.8 (3.6) {1.8} ($SiCH_3$); ^{29}Si NMR (39.7 MHz) −10.9 (20.0) {0.7}; ^{31}P NMR (32.4 MHz) 72.9 {1006.9}. **3b**: ^1H NMR (200 MHz) 4.03 (12.3) (d sept) (4 H, NCH), 3.63 (s) (6 H, $B(OCH_3)_2$), 3.53 (11.9) (d) (3 H, $POCH_3$), 1.20 (d), 1.18 (d) (each 12 H, $NC(CH_3)_2$), 0.31 (0.3) (9 H, $Si(CH_3)_3$); ^{11}B NMR (25.7 MHz) 30.6 ($\nu_{1/2}$ = 290 Hz); ^{13}C NMR (50.3 MHz) 52.4 (4.8) (POC), 52.0 (BOC), 47.5 (6.8) (NC), 24.9 (2.1), 24.2 (4.1) (NC*C*), 4.3 (4.7) ($SiCH_3$), BC not observed; ^{29}Si NMR (15.9 MHz) −12.4 (6.6); ^{31}P NMR (32.4 MHz) 69.2.

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Oxidative Addition of SiH_4 to $Pt(PH_3)_2$. An ab Initio MO/MP4 Study

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The C–H oxidative addition is one of the important processes in catalytic reactions of transition-metal complexes.[2,3] The Si–H oxidative addition is also expected to be important in reactions of various Si compounds with transition-metal complexes.[4,5] In this regard, knowledge of the factors determining the Si–H oxidative addition is fundamental to understanding reactions of Si compounds with transition-metal complexes. However, a theoretical study of Si–H oxidative addition to transition metals has not been reported, to our knowledge, while coordination of SiH_4 and $HSiCl_3$ with $CpMn(CO)_2$[6] and α-H abstraction in Cp_2Ti-

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(1) Visiting professor from Kumamoto University.

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0002-7863/91/1513-5063$02.50/0

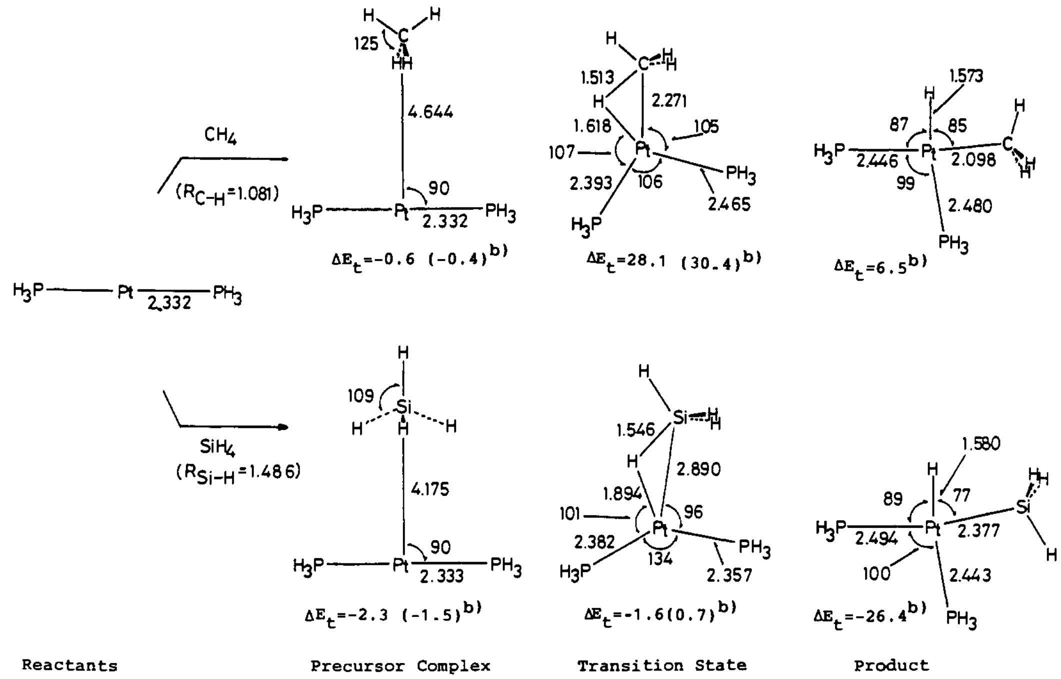

Figure 1. Optimized geometries (a) and total energies (b) of the reactant, the precursor complex, the transition state, and the product (a) Distances in Å and angles in deg. Optimization carried out at the Hartree–Fock level with the BS-I set. (b) At the MP4(SDQ) level (kcal/mol unit). Positive values mean destabilization in energy relative to the reactants, $Pt(PH_3)_2 + EH_4$ (E = C or Si). Values in parentheses—after correction of basis set super position error by the Boys method.[15]

$(H)(SiH_3)$[7] have been theoretically investigated.

In this work, SiH_4 oxidative addition to $Pt(PH_3)_2$ is studied with the ab initio MO/MP4 method. $Pt(PH_3)_2$ is selected here because similar Si–H (X=H, Si, or halogen) oxidative addition to $Pt(PR_3)_2$ has been reported.[4c,5] One of the interesting results is that the SiH_4 oxidative addition is significantly exothermic and proceeds very easily, while the CH_4 oxidative addition is endothermic and proceeds with a substantially high activation barrier.

Ab initio MO/MP4(SDQ) calculations were carried out with the Gaussian 82 program.[8] Geometry optimization was performed at the Hartree–Fock (HF) level, using the BS-I set.[10] In MP4(SDQ) calculations, all core orbitals were excluded from the active space, where the BS-II set[11] was used.

A precursor complex, $Pt(PH_3)_2(CH_4)$, has the $Pt–CH_4$ moiety of C_{2v} symmetry (Figure 1),[12] whereas $Pt(PH_3)_2(SiH_4)$ has the $Pt–SiH_4$ moiety of C_{3v} symmetry.[13] The latter structure resembles silane–ammonia adducts.[14] CH_4, SiH_4, and $Pt(PH_3)_2$ moieties are little distorted in both precursors. Stabilization energies of both precursor complexes are very small but they do not disappear after correcting the basis set super position error (see values given in Figure 1). Their small stabilization energies are in contrast to a considerably large stabilization energy of d^8 $RhCl(PH_3)_2(CH_4)$.[3j] Because of very small stabilization energies and negligibly small charge transfer,[16] $Pt(PH_3)_2(SiH_4)$ and $Pt(PH_3)_2(CH_4)$ can be viewed as a van der Waals complex.

At the transition state, both SiH_4 and CH_4 approach Pt with the H atom in the lead (Figure 1). Several interesting differences are found between SiH_4 and CH_4 oxidative addition: (1) The $Pt(PH_3)_2$ moiety distorts more in the CH_4 reaction than in the SiH_4 reaction. (2) The C–H bond significantly lengthens but the Si–H bond slightly lengthens. (3) The Pt–H distance is longer in the SiH_4 oxidative addition than in the CH_4 oxidative addition. These results suggest that the SiH_4 oxidative addition reaches a transition state earlier than the CH_4 oxidative addition.

The CH_4 oxidative addition is endothermic and requires a considerably high activation barrier (Figure 1), as has been reported previously.[3b] On the other hand, the SiH_4 oxidative addition is significantly exothermic, and its activation barrier is much smaller than that of the CH_4 oxidative addition. This small activation barrier accords with the result that the transition state is reached relatively early in the SiH_4 oxidative addition.

The Si–H bond energy of SiH_4 is estimated to be smaller than the C–H bond energy of CH_4 by 15.4 kcal/mol at the MP4(SDQ) level.[17] By considering an assumed reaction, eq 1, the $Pt–SiH_3$ bond is estimated to be more stable than the $Pt–CH_3$ bond by 16.4

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(12) The C_{3v} structure of the $Pt–CH_4$ moiety has a minimum at $R(Pt–C)$ = 4.7 Å and its stabilization energy is only 0.2 kcal/mol, being less than the C_{2v} structure by 0.2 kcal/mol at the HF level with the BS-I set.

(13) The C_{2v} structure of the $Pt–SiH_4$ moiety has a minimum at $R(Pt–Si)$ = 4.83 Å, and its stabilization energy is less than that of the C_{3v} structure by 0.1 kcal/mol at the Hartree–Fock level and by 1.0 kcal/mol at the MP4(SDQ) level.

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(17) (a) CH_3 and SiH_3 radicals were calculated with the UMP4(SDQ) method by using the BS-II set, where their geometries were optimized with the UHF-MO method by using the BS-I set. (b) This difference agrees well with the experimental value. Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.

$$\mathrm{Pt(H)(SiH_3)(PH_3)_2 + {}^{\bullet}CH_3 \rightarrow Pt(H)(CH_3)(PH_3)_2 + {}^{\bullet}SiH_3} \quad (1)$$

kcal/mol at the MP4(SDQ) level.[18] Therefore, the Si-H bond which is weaker than the C-H bond and the Pt-SiH_3 bond which is stronger than the Pt-CH_3 bond are considered the main reasons for the larger exothermicity and the smaller activation barrier of the SiH_4 oxidative addition than those of the CH_4 oxidative addition.

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[18] (a) The p orbital of Si lies higher in energy than that of C, which would favor an interaction between SiH_3 and Pt. (b) The relative strength of M-SiH_3 and M-CH_3 (M = Ti, Zr, or Co) has been theoretically discussed: Ziegler, T.; Tschinke, V.; Versluis, L. *Polyhedron* **1988**, *7*, 1625.

"Living" Titanium(IV) Catalyzed Coordination Polymerizations of Isocyanates

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Polyisocyanates[1,2] have received a great deal of attention in recent years due to their chiral helical structure,[3] stiff-chain solution characteristics,[4] liquid crystalline properties,[5] induced optical activities,[6] and molecular weight dependent chain dimensions in solution.[7] Despite this impressive list of unusual properties, the full development of polyisocyanates has been hindered by the lack of efficient synthetic routes.[8] Highly sensitive, low-temperature, anionic isocyanate polymerizations introduced over 30 years ago are not "living", give low yields at low monomer to initiator ratios, and are plagued by a side reaction, namely, back-biting of the active end-group along the polymer chain to form cyclic trimers.[1]

We report that $TiCl_3(OCH_2CF_3)$ (I) and $TiCl_3(OCH_2CF_3)(THF)_2$[9] (II) can *quantitatively* polymerize alkyl isocyanates at room temperature with no detectable formation of cyclic trimer (eq 1). Furthermore, our experimental evidence strongly indicates that these polymerizations are, in fact, "living", and this feature allows for the formation of polyisocyanates of controlled molecular weight and block copolymers.

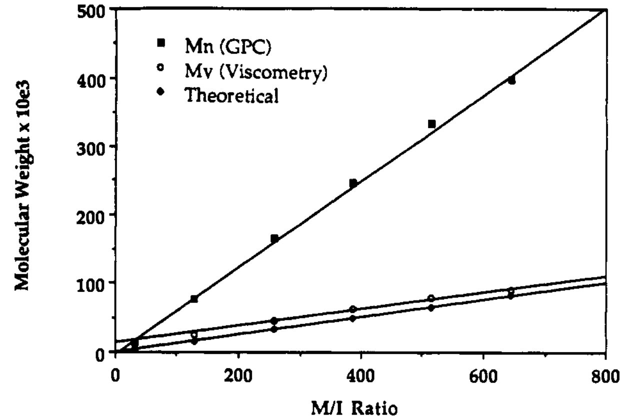


Figure 1. Variation in the molecular weight as a function of the monomer to initiator ratio of a typical solution polymerization. M_n: determined by GPC relative to polystyrene standards. M_v: determined by Ubbelohde type capillary viscometry.

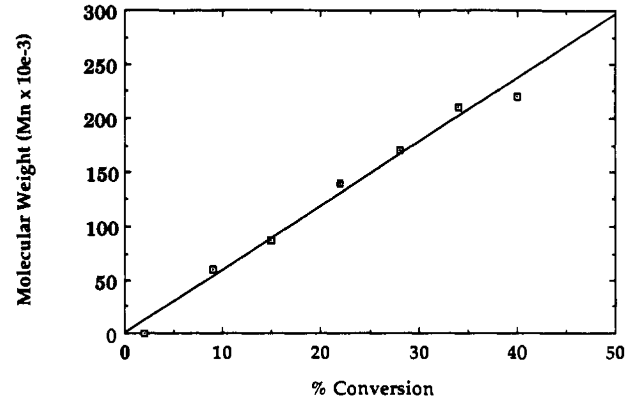
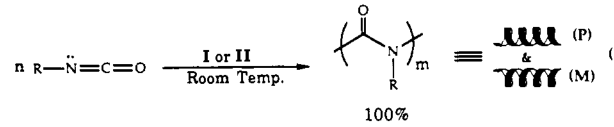


Figure 2. Variation in the molecular weight (M_n) as a function of the percent conversion of a typical solution polymerization. M_n: determined by GPC relative to polystyrene standards. Percent conversion: assessed by correlating the reaction time with kinetic data.

 (1)

During initial studies, the yield of polymer systematically varied from 0% to 100% depending upon the initial monomer concentration. Further polymerization-kinetics studies on *n*-hexyl isocyanate revealed that termination processes were not occurring and that these concentration-dependent yields were due to the fact that *polymerizations using I and II are fully reversible between isocyanate polymer and monomer.* This is the first definitive confirmation of ceiling temperature effects in isocyanate polymerizations. Previously, monomer/polymer to trimer transformations were observed.[10] Eromosele and Pepper observed that anionic isocyanate polymerizations displayed ceiling temperature effects; however, it was shown that in this case depolymerization occurred irreversibly to trimer, so it was not a true monomer-polymer equilibrium.[11]

Another unusual feature of polymerizations using I and II is that the polymer can be isolated with the active titanium end-

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