60.0 (C7″), 107.3, (C4′), 107.6 (C5), 108.8 (C3), 118.5 (C3″), 126.8 (C5′), 129.6 (C3a″), 140.9 (C4), 142.1 (C3′), 170.2 (C7a″); HRMS calcd for $C_{19}H_{21}N_5$ $M^{\bullet+}$ 319.1797, found $M^{\bullet+}$ 319.1800.

2-(3,5-Dimethyl-*N*-pyrazolyl)-6-[(4*S*,7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2-indazolyl]pyridine (9): yield method A, 11%, method C, 60%; mp 132.5–134 °C; ν_{max} (KBr) 2900, 1590, 1440, 1360, 1290, 940, 780 cm^{-1}; ^1H NMR (300 MHz) δ_H 0.73 (s, 3 H, *syn*-8″-CH_3), 1.00 (s, 3 H, *anti*-8″-CH_3), 1.24 (m, 1 H, *endo*-H5″), 1.35 (s, 3 H, 7″-CH_3), 1.43 (m, 1 H, *endo*-H6″), 1.90 (m, 1 H, *exo*-H6″), 2.13 (m, 1 H, *exo*-H5″), 2.31 (s, 3 H, 3′-CH_3), 2.74 (s, 3 H, 5′-CH_3), 2.83 (d, 1 H, H4″), 6.01 (s, 1 H, H4′), 7.62 (dd, 1 H), 7.68 (dd, 1 H, H3 and H5) 7.80 (dd, 1 H, H4), 7.98 (s, 1 H, H3″); ^{13}C NMR δ_C 10.6 (7″-CH_3), 13.6 (3′-CH_3), 15.1 (5′-CH_3), 19.0 (*anti*-8″-CH_3), 20.7 (*syn*-8″-CH_3), 27.5 (C5″), 33.7 (C6″), 47.1 (C4″), 50.3 (C8″), 60.0 (C7″), 107.8 (C5), 109.2 (C4′), 110.4 (C3), 118.6 (C3″), 129.4 (C3a″), 140.5 (C4), 141.2 (C5′), 149.8 (C3′), 170.0 (C7a″). Anal. Calcd for $C_{21}H_{25}N_5$: C, 72.6; H, 7.3; N, 20.2. Found: C, 72.0; H, 7.3; N, 19.9.

2-Bromo-6-(3,5-dimethyl-*N*-pyrazolyl)pyridine (10): yield method A, 52%; mp 75.5–76.5 °C ν_{max} (KBr) 1570, 1420, 1400, 1110, 970, 780, 710 cm^{-1}; ^1H NMR (300 MHz) δ_H 2.28 (s, 3 H, 3′-CH_3), 2.65 (s, 3 H, 5′-CH_3), 5.99 (s, 1 H, H4′), 7.29 (d, 1 H, H3), 7.60 (t, 1 H, H4), 7.84 (d, 1 H, H5); ^{13}C NMR δ_C 13.6 (3′-CH_3), 14.7 (5′-CH_3), 109.7 (C4′), 113.5 (C5), 124.2 (C3), 138.8 (C2), 140.2 (C4), 142.2 (C5′), 150.5 (C3′). Anal. Calcd for $C_{10}H_{10}BrN_3$: C, 47.6; H, 4.0; N, 16.7. Found: C, 47.8; H, 3.8; N, 16.9.

Supplementary Material Available: ^1H and ^{13}C NMR spectra of all new ligands. Preparations, elemental analyses and IR spectra of the copper complexes of the ligands (15 pages). Ordering information is given on any current masthead page.

Three-Center Transition Structures for Alkene Hydroboration and Alkylborane Rearrangement

Nicolaas J. R. van Eikema Hommes and Paul von Ragué Schleyer*

Institut für Organische Chemie der Friedrich-Alexander Universität Erlangen-Nürnberg, Henkestrasse 42, D-8520 Erlangen, Germany

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The mechanistic details of alkene hydroboration,[1] one of the basic reactions in modern organic chemistry,[2] have intrigued both experimental and theoretical chemists for more than three decades.[3-7] Several basic questions remain unanswered, which we will address in this paper using high-level ab initio theory: (1) Is there a π-complex intermediate in the hydroboration reaction? (2) What is the structure of the transition state? Does it have four-center[4-6] or three-center[7] character? (3) Does the alkylborane rearrangement occur intramolecularly, or does it proceed intermolecularly, by Brown's[2] dissociation/recombination mechanism? We also emphasize the importance of including electron correlation in the geometry optimizations.

Prior semiempirical[4] and Hartree Fock ab initio[5,8] calculations on model olefin hydroboration reactions indicate the formation of weakly bound π-complexes, four-center transition states, and activation barriers between 6 and 12 kcal/mol. However, the barriers decrease when electron correlation is taken into account.[6,8] Indeed, for the parent reaction of borane and ethylene, no transition structure

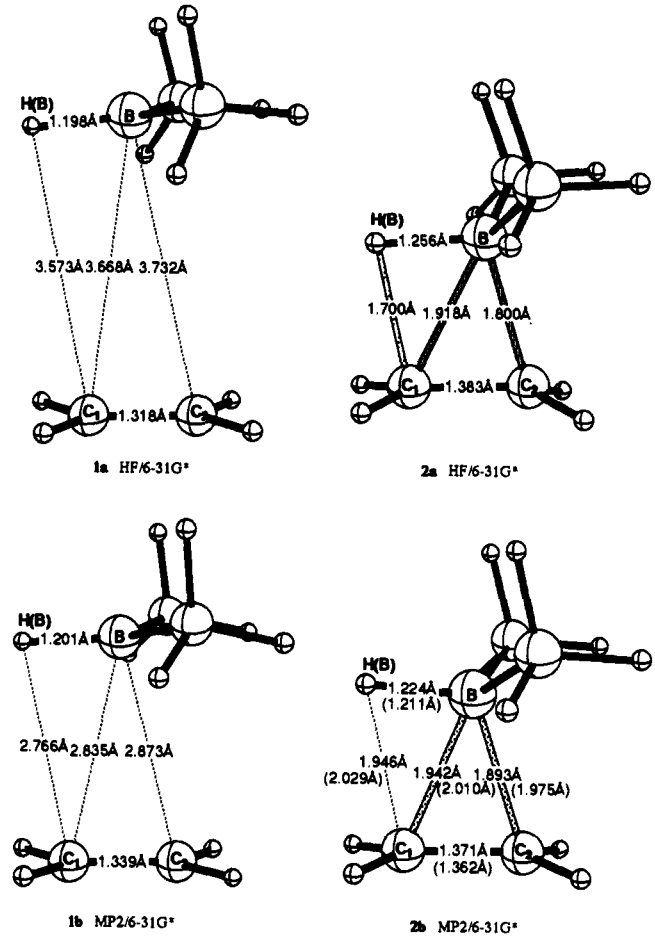

Figure 1. HF/6-31G* and MP2/6-31G* optimized structures for the π-complex of dimethylborane and ethylene and the transition structure for hydroboration.

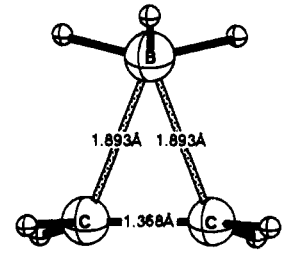

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Figure 2. MP2/6-31G** optimized transition structure for intramolecular rearrangement of ethylborane.

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Table I. Absolute Energies (-au)

compound	3-21G	6-31G*	MP2fu/6-31G*	MP2fc	MP3	MP4SDTQ
$H_2C{=}CH_2$	77.600 99	78.031 72	78.294 86	78.285 03	78.305 97	78.319 80
$HB(CH_3)_2$	103.918 85	104.492 63	104.843 09	104.828 92	104.864 53	104.879 84
$C_2H_4 + C_2H_7B$	181.519 84	182.524 35	183.137 95	183.113 95	183.170 50	183.199 64
π-complex 1	181.522 50	182.525 80	183.143 03	183.119 30	183.174 80	183.294 36
TS 2	181.484 31	182.491 42	183.140 17	183.115 91	183.166 15	183.197 74

Table II. Relative Energies (kcal/mol)

compound	3-21G	6-31G*	MP2fu/6-31G*	MP2fc	MP3	MP4SDTQ
$C_2H_4 + C_2H_7B$	1.7	0.9	3.4	3.4	2.7	3.0
π-complex 1	0.0	0.0	0.0	0.0	0.0	0.0
TS 2	20.3	21.6	1.8	2.1	5.4	4.2

Table III. NAO Charges and NAO-Wiberg Bond Indexes[a]

	$C_2H_4 + C_2H_7B$		π-complex 1		TS 2		TS 3
	HF	corr	HF	corr	HF	corr	corr
C(1)	-0.416	-0.426	-0.412	-0.415	-0.248	-0.334 (-0.340)	-0.394
C(2)	-0.416	-0.426	-0.415	-0.425	-0.596	-0.474 (-0.448)	-0.394
B	0.779	0.716	0.784	0.669	0.330	0.270 (0.322)	-0.259
H(B)	-0.118	-0.097	-0.122	-0.091	0.059	0.037 (-0.003)	0.021
"HBR_2"			-0.007	-0.054			-0.252
C(1)-C(2)	2.034	1.885	2.028	1.849	1.370	1.456 (1.526)	1.463
C(1)-B			0.007	0.047	0.357	0.325 (0.287)	0.377
C(2)-B			0.007	0.047	0.571	0.403 (0.341)	0.377
C(1)-H(B)			0.000	0.001	0.192	0.071 (0.045)	0.036
B-H	0.966	0.933	0.966	0.933	0.709	0.799 (0.840)	0.876

[a] HF: RHF-NAO charges and bond indexes for RHF-optimized structures. Corr: Correlated (MP4) NBO charges and bond indexes at MP2-optimized structures. Values for 6-31G* augmented with p-type polarization functions on H(B) are given in parentheses.

exists at the MP2/6-31G* level.[6] The experimental data are sparse. Fehlner[9] reported a *free energy* of activation of 2 ± 3 kcal/mol for this reaction in the gas phase, but this has been attributed to the entropy contribution.[6] Higher barriers are expected with alkylboranes, due to substituent stabilization and steric effects. Hence, we have now examined the reaction of dimethylborane and ethylene at correlated levels and have optimized the π-complex and the transition structure at MP2/6-31G*.[10] Furthermore, we investigated a structural alternative for the π-complex of ethylene and borane, which might be involved in alkylborane rearrangements.

The HF/6-31G* and MP2/6-31G* structures for the dimethylborane–ethylene π-complex 1 and the transition structure 2 are compared in Figure 1. Absolute and relative energies are given in Tables I and II, respectively. The HF/6-31G* complexation energy for dimethylborane with ethylene is only -0.9 kcal/mol, but this increases with correlation to -3.0 kcal/mol (MP4SDTQ/6-31G*//MP2/6-31G*). As a consequence of the greater binding energy at correlated levels, the borane becomes considerably more pyramidal and the distance to the C–C double bond decreases by more than 0.8 Å (see Figure 1). Changes due to correlation also are apparent from the NBO charges[10f] and Wiberg bond indexes[10g] listed in Table III. π-Donation from ethylene into the empty boron p orbital

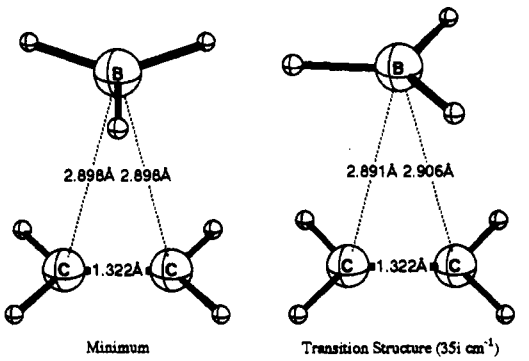

Figure 3. HF/6-31G** optimized structures for the π-complex of ethylene and borane.

amounts to 0.054 e in the MP2-optimized complex; a C–B bond index of about 0.05 results. In contrast, these interactions in the RHF complex are almost neglegible.

Electron correlation changes the interpretation of the nature of the transition structure (TS). At HF/6-31G*, the TS **2a** (which resembles that described by Houk et al.[6]) appears to involve four centers: H(B) is only 1.7 Å away from C(1), and the two C–B distances differ by 0.12 Å in length. In contrast, the MP2-optimized TS **2b** has three-center character! The H(B) is farther away from C(1), and the two C–B distances are nearly the same. This conclusion is supported by the bond orders in Table III. Use of p-type polarization functions on the migrating hydrogen increases the C(1)–H(B) distance even further and leads to even weaker bonding (Figure 1, Table III, values in parentheses). At MP2, the transition structure comes earlier along the addition path than that located at the RHF level. At MP4SDTQ/6-31G*, the overall activation barrier from the separated reactants is 1.2 kcal/mol, and 4.2 kcal/mol from the complex.

These differences between RHF- and MP2-optimized transition structures for the hydroboration reaction may have some important consequences: RHF-optimized structures have been used for the analysis of endo vs exo

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additions to norbornene[5d] and for the development of molecular mechanics force fields for the study of regioselectivity.[5c] It would be desirable to ascertain if the MP2 geometries give significantly different results.

We also investigated a new structure **3** for the complex of borane and ethylene, in which the unique B–H is perpendicular rather than parallel to the C–C double bond (Figure 2). Indeed, **3** is the only minimum for the complex at the RHF level (the B–H parallel form, studied by earlier investigators,[5,6] is a transition structure at RHF; see Figure 3). However, **3** is a transition structure when optimized at MP2. The imaginary vibration corresponds to rotation of the BH_3 unit; the reaction path then leads directly to ethylborane.[6] Hence, complex **3** represents the transition structure for degenerate rearrangement of ethylborane, $H_2BCH_2CH_3 \rightleftarrows$ **3** $\rightleftarrows CH_3CH_2BH_2$. The three-center bonding in transition structure **3** is characterized by a substantial π-donation, 0.252 e, from ethylene to boron and by C–B and C–C bond indexes comparable to those found in the transition structure for addition, **2b** (Table III). Such intramolecular boron migrations occur stereospecifically, as was found experimentally, e.g., with cyclic substrates under mild reaction conditions.[11] At higher temperatures, mixtures are obtained, as expected from Brown's alternative dehydroboration/hydroboration mechanism.[2] Our results agree nicely. We calculate the migration barrier (ΔE_a) in ethylborane to be 23 kcal/mol (MP4SDTQ/6-31G**//MP2/6-31G**), whereas dissociation into ethylene and borane requires 31.5 kcal/mol. The latter process, however, is favored by entropy. For this model reaction, we calculate the free energies of activation to be nearly equal at 300 K, 22.5 kcal/mol. The dissociation mechanism prevails at higher temperatures, while intramolecular rearrangement is favored below this temperature.

Note Added in Proof. After this note was submitted, we located the TS for reaction of borane and ethylene at the RQCISD/6-31G** level, which also exhibits three-center character. The activation barrier, relative to the π-complex, is 0.05 kcal/mol at RQCISD(T)/6-311+G**//RQCISD/6-31G**.

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Facile One-Pot Amidation of Carboxylic Acids by Amines Catalyzed by Triphenylstibine Oxide/Tetraphosphorus Decasulfide (Ph_3SbO/P_4S_{10})

Ryôki Nomura,* Takahiro Nakano, Yasuhiro Yamada, and Haruo Matsuda

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamada-Oka, Suita, Osaka 565 Japan

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Although thiocarboxylic acids are useful acylating reagents for the synthesis of amides and peptides,[1,2] their popularity is markedly lower than that of acyl chlorides, anhydrides, and such active esters as thiol esters.[3] This has much to do with their limited availability,[4] higher susceptibility to autoxidation,[5] and unpleasant odor. In our continuing studies on the utilization of organoantimony compounds in organic synthesis, triphenylstibine oxide (Ph_3SbO) was found to catalyze several condensation reactions,[6] including the aminolysis of thiocarboxylic acids by amines to give amides.[2] It was also found that, in the presence of tetraphosphorus decasulfide (P_4S_{10}), Ph_3SbO accelerated the thiolation of carboxylic acids to the corresponding thiocarboxylic acids **4**.[7] Thus, we deduced that

Scheme I

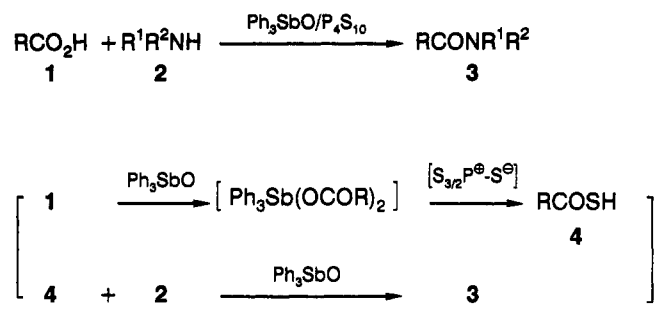

Table I. Ph_3SbO/P_4S_{10}-Catalyzed Amidation of Carboxylic Acids[a]

amides	method[c]	T (°C)	t (h)	yields[b] (%)
AcNH-*n*-Hex[d]	A	40	5	90
	A[e]	80	12	0
	A[f]	80	12	0
	A[g]	80	24	0
AcNH-*t*-Bu	A	40	6	80
$AcNEt_2$	A	60	12	75
AcNHPh	A	60	5	69
$AcNHCH_2CH_2OH$	B	50	1	95[h]
$AcNHCH_2CH{=}CH_2$	B	40	0.5	90[h]
$Cl_2CHCONHPr$	A[i]	60	8	96
$CH_2{=}CHCONH$-*i*-Pr	A	50	6	56
t-BuCONH-*t*-Bu	B	80	12	88[h]
t-BuCONHPh	A	80	5	87
$(CH_2CH_2CO)_2(NHPr)_2$	A	80	6	65
BzNH-*t*-Bu	A	80	24	65
BzNHPh	A	80	5	75
Z-Gly-Gly-OEt	C	30	0.5	83
Z-Phe-Leu-OEt	C	30	2	75
Z-Leu-Phe-OMe	C	30	2	73
Z-Ser-Gly-OEt	C	30	2	71
Z-Tyr-Gly-OEt	C	30	2	79

[a] Reaction conditions: $1/2/Ph_3SbO/P_4S_{10}$ = 5/5/0.25/0.75; 20 mL of solvent. [b] Isolated yield. [c] Details of methods A, B, and C are given in the Experimental Section. [d] *n*-Hex denotes *n*-C_6H_{13}. [e] No P_4S_{10} was present. [f] No Ph_3SbO was present. [g] Neither Ph_3SbO nor P_4S_{10} was present. [h] Yield based on 1. [i] $CHCl_3$ was the solvent.

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