

The situations i and iii have already been explored computationally in some detail.⁴ Presently we deal with a prototype of the less well-documented situation ii, in which nearly degenerate S_1 and T_1 states are expected to be of "charge-transfer-biradical" nature and to lie high above the nonpolar S_0 state. Figure 2 shows the state energies of aminoborane calculated as a function of the twist angle θ by an ab initio method using a Dunning (3s, 2p, d, R) basis set⁵ and the multireference CI⁶ with about 10 000 configurations.

At planarity, several Rydberg states of aminoborane lie below the valence states. As θ increases, the state order changes in a manner familiar from calculations on alkenes.⁷ At orthogonality, the lowest four states are of valence character. The wave functions of the S_0 , S_1 , and T_1 states are those expected from the above discussion: in S_0 , $^1A^2$ enters with 92% weight; in S_1 , 1AB enters with 92% weight; in T_1 , 3AB enters with 92% weight. Thus, in S_0 , the N atom carries a lone pair and the excitations into S_1 and T_1 involve a transfer of one of its electrons onto the B atom, producing charge-transfer-biradical states. Their calculated dipole moments are 4.8 D.

At orthogonality, where both S_1 and T_1 exhibit the expected minimum, S_1 actually lies a few kilocalories per mole below T_1 . We are not aware of any other singlet ground state molecule for which such a "negative" S_1 - T_1 splitting has been observed or calculated.

According to the simple four-configuration model outlined above, T_1 should lie below S_1 by a small amount ($2K_{AB}$). Introduction of additional CI preferentially stabilizes S_1 and brings it below T_1 . This is due to the "dynamic spin polarization" effect,⁸ already well understood from the case of 90° twisted ethylene. Since this should be quite general, it is likely that a negative S_1 - T_1 splitting will be found for other charge-transfer biradicals as well.

As far as we know, charge-transfer-biradical states of the type calculated here have not been observed for species as simple as our example, i.e., case II where A and B can each be well represented by a single AO. We believe that our calculations are sufficiently reliable for a prediction of photochemical events along the cis-trans isomerization path of aminoborane (in reality, other paths may be followed). After initial excitation of planar aminoborane into a S_1 or T_1 state of predominantly Rydberg nature, localized on the amino group, collisions should relax the molecule to orthogonal geometry where S_1 and T_1 are of charge-transfer-biradical nature and highly polar. Emission from the twisted state will have a large Stokes shift and will be quite sensitive to environmental effects.

Strongly Stokes-shifted emission from excited states of molecules twisted along a bond linking an acceptor to a donor has been reported in the gas phase,⁹ nonpolar solvents,¹⁰ and, above all, polar^{11,12} solvents. These states are commonly referred to as "twisted internal charge transfer" (TICT) states.¹³ In this sense,

at their orthogonal minima, the S_1 and T_1 states of aminoborane are TICT states, and its Rydberg states play a role analogous to that of the locally excited states of the usual TICT species, in which A and/or B reside on large conjugated moieties.

Aminoborane represents a particularly simple example of the TICT phenomenon and can be viewed as a prototype.¹⁴ Not only does its simplicity permit an ab initio calculation with a high degree of reliability, it also offers clear insight into the physical origin of the preferred orthogonality of the A and B orbitals in the S_1 and T_1 states (cf. the previously empirical "minimum overlap rule"¹¹).

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(13) Since our model considerations do not demand that the orthogonality of A and B be reached by twisting, we view the concept of charge-transfer-biradical excited states as more general than the TICT concept. For instance, an aromatic radical cation linked by a saturated chain to an aromatic radical anion represents a charge-transfer-biradical excited state but not a TICT state. In this case, A is the HOMO of one and B the LUMO of the other aromatic moiety.

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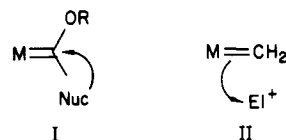
Reaction of Cp₂Ti=CH₂ with Organic Halides: Evidence for a Radical Mechanism

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Metal carbenes have been demonstrated in such important catalytic processes as olefin metathesis² and Fischer-Tropsch CO³ reduction and suggested as intermediates in Ziegler-Natta polymerization⁴ and hydrocarbon cracking.⁵ The reactivity patterns exhibited by isolated metal carbenes are divided into two classes—electrophilic carbenes I,⁶ which add nucleophiles at the



carbene carbon, and nucleophilic carbenes II,⁷ which add elec-

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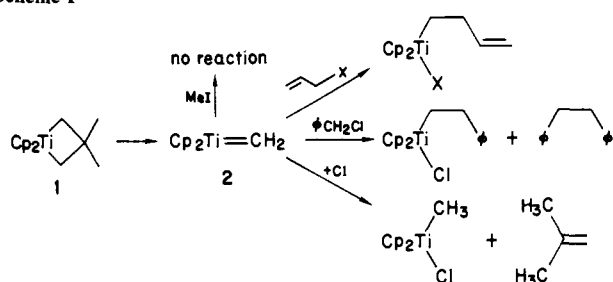
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Scheme I



trophiles at the carbene carbon. We now report evidence which demonstrates a different type of reactivity pattern for a metal carbene—reaction by electron transfer.

We have previously shown that titanocene metallocyclobutanes such as **1** can function as reagents for a variety of synthetically useful transformations, presumably through the carbene **2**.⁸ To further characterize the reactivity of **2**, its reactions with alkyl halides were explored. Treatment of **1** with allylic chloride (1.1 equiv, room temperature, C_6D_6 , 12 h) produced a quantitative yield (^1H NMR) of butenyltitanocene chloride instead of a stable metallacycle resulting from reaction with the olefin. Further study of reactions of **1** with alkyl halides gave the results shown in Scheme I. Most interesting, while **1** reacts readily with activated alkyl halides, slowly with *tert*-butyl chloride, no reaction is observed with excess methyl iodide, even after prolonged reaction times. Such a reactivity pattern is contrary to that expected for a $\text{S}_{\text{N}}2$ -type displacement, the pathway that **2** would be expected to follow in reactions with alkyl halides.^{7,9} Since nucleophilic displacement did not explain the observed reactivity, we decided to study this reaction in detail, choosing benzyl chloride as substrate.

The reaction of **1** with benzyl chloride (1.2 equiv) gave the known phenethyl titanocene chloride^{9a} and bibenzyl in a ratio of 90:10. The reaction exhibited second-order kinetics in C_6D_6 ($k = 9.3 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$, $\tau_{1/2} = \sim 59 \text{ min}$, room temperature, first order in both **1** and PhCH_2Cl) and showed little sensitivity to para substitution of the aromatic ring. For example, relative rates of *p*-methoxybenzyl, *p*-phenylbenzyl, *p*-chlorobenzyl, *p*-methylbenzyl, and benzyl chloride were 2.64, 2.99, 2.45, 1.33, and 1.0.^{9b} Seeking to support our assumption that **2** was actually an intermediate in this reaction, we exposed the crystalline trimethylphosphine¹⁰ adduct **3** to benzyl chloride (Scheme II). This reaction gave a 95:5 ratio of phenethyltitanocene chloride and bibenzyl and was essentially instantaneous. This suggested that the ligated carbene was more reactive than free carbene. In confirmation, addition of 10 mol % (dimethylamino)pyridine (DMAP)⁶ revealed a significant rate enhancement ($\tau_{1/2} = 8 \text{ min}$, room temperature) over the reaction without added DMAP.¹¹ Moreover, essentially no bibenzyl (<5%) was formed in the reaction. In addition, the reaction of **1** with benzyl chloride showed a linear dependence on DMAP concentration and the reaction became zero order in benzyl chloride concentration; consistent with the reaction proceeding via **4** (Scheme II).

The details of the carbon–carbon bond-forming process in the reaction of **4** (and **3**) with PhCH_2Cl were investigated by examining the stereochemical course of this process. Treatment of **1** in the presence of 10 mol % DMAP with an excess of optically active PhCHDCl (80% ee)¹² gave, after $(\text{CH}_3)_3\text{COOH}$ oxidation¹³

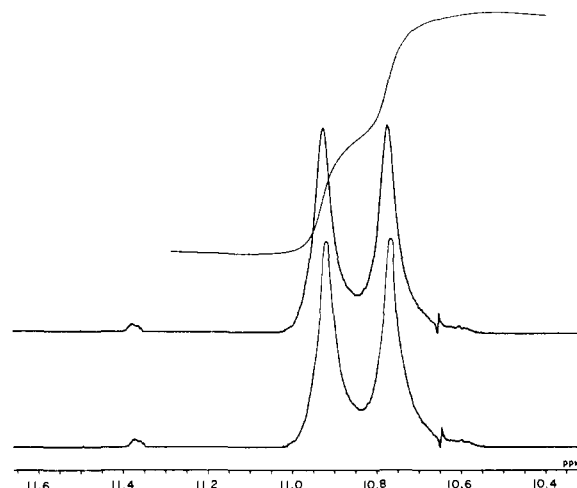
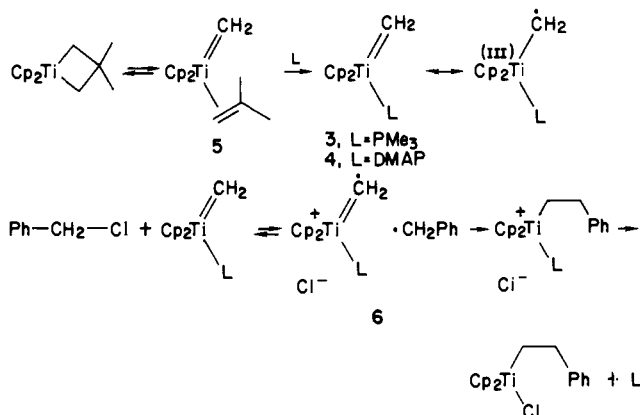
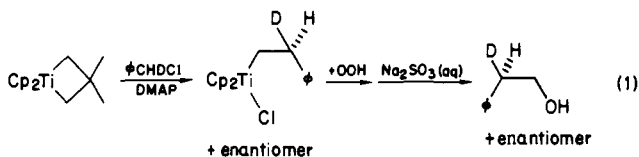


Figure 1. ^1H NMR (α carbon protons decoupled), 400-MHz, showing ratio of enantiomers of $\text{PhCHDCH}_2\text{OH}$ to be 1:1.

Scheme II



and Na_2SO_3 workup, a quantitative yield of the β -chiral 2-phenethyl alcohol (eq 1). Determination of the stereochemistry



at the β -carbon was achieved by using ^1H NMR at 400 MHz and confirmed with ^2H NMR at 77.6 MHz (proton decoupled) in the presence of 50 mol % $\text{Eu}(\text{dcm})$ ¹⁴ in a method similar to that of Stille.¹² The results shown in Figure 1 indicate that a complete loss of stereochemistry has occurred in the carbon–carbon bond-forming event.¹⁵ Racemization occurred during product formation, since recovered unreacted benzyl chloride showed complete retention of optical activity.

Taken together, the results are most readily explained by the mechanism shown in Scheme II. In the proposed mechanism **L** traps out the carbene–olefin complex **5** to form a carbon ligand complex. This complex either induces radical character on the carbene carbon, making it more reactive, or at least increases the lifetime of the methylidene, increasing its chance to react with a benzyl chloride. At this point, the complex transfers an electron to the substrate (e.g., benzyl chloride) to give **6** which, by radical coupling and ligand exchange, yields phenethyltitanocene chloride.

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Bibenzyl is produced by benzyl radicals escaping from the cage and dimerizing.

In short, the reaction of methylenetitanocene (**2**) with alkyl halides exhibits behavior contrary to that expected for either of the two previously defined classes of metal carbenes and to that predicted from reactions with olefins or organic carbonyls. The results presented are best explained by invoking one-electron steps for both the cleavage of the carbon-halogen bond and the formation of the carbon-carbon bond and suggest that instead of two distinct classes of metal carbenes, metal carbenes manifesting a continuum of reactivity behavior may exist. The pathway followed in a particular reaction is dictated by the combination of the characteristics of the metal carbene and the nature of the substrate.

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Registry No. **1**, 80122-07-2; **3**, 95044-99-8; DMAP, 57951-36-7; $\text{Cp}_2\text{Ti}(\text{Cl})\text{CH}_2\text{CH}=\text{CH}_2$, 90076-38-3; $\text{Cp}_2\text{Ti}(\text{Cl})\text{CH}_2\text{CH}_2\text{Ph}$, 12663-68-2; $\text{Cp}_2\text{Ti}(\text{Cl})\text{CH}_3$, 1278-83-7; PhCH_2Cl , 100-44-7; PhCHDCl , 79449-94-8; $\text{C}_6\text{H}_5\text{CHDCH}_2\text{OH}$, 10606-75-4; allylic chloride, 107-05-1; *tert*-butyl chloride, 507-20-0; methyl iodide, 74-88-4; bibenzyl, 103-29-7; 2-methyl-1-propene, 115-11-7; *p*-methoxybenzyl chloride, 824-94-2; *p*-phenylbenzyl chloride, 1667-11-4; *p*-chlorobenzyl chloride, 104-83-6; *p*-methylbenzyl chloride, 104-82-5.

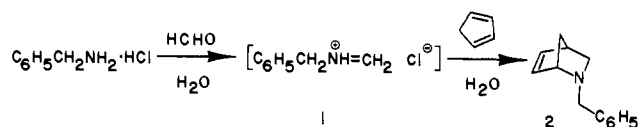
Aza Diels-Alder Reactions in Aqueous Solution: Cyclocondensation of Dienes with Simple Iminium Salts Generated under Mannich Conditions

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Compared to the all-carbon Diels-Alder reaction, the imino variation has received only scant attention, despite the enormous potential it holds for alkaloid synthesis.^{1,2} The vast majority of aza cycloadditions recorded in the literature have employed imines substituted with one or more electron-withdrawing activating groups; however, a few successful examples have been reported that utilize dialkyliminium salts.³ Although simple imines are unreactive toward electron-rich dienes, Danishefsky has recently demonstrated that Lewis acid catalysis is sufficient to promote reaction with a highly reactive diene.⁴ We now wish to report that simple unactivated iminium salts, generated *in situ* under Mannich-like conditions, react with dienes in an exceptionally mild and convenient aqueous aza Diels-Alder reaction.

Preliminary studies focused on the reaction of a variety of dienes with the benzyliminium ion **1** derived from formaldehyde and benzylamine. Addition of neat cyclopentadiene (2.0 equiv) to a 2.5 M aqueous solution of benzylamine hydrochloride (1.0 equiv) and 37% aqueous formaldehyde (1.4 equiv) gave rise to a heterogeneous reaction mixture which was vigorously stirred for 3 h at room temperature. Workup^{5a} provided a near quantitative yield of bicyclic amine **2**. This procedure is applicable to a number



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Table I. Reaction of Iminium Ions with Dienes^a

entry	diene	amine	temp, °C	time	product	% yield ^b
1		BnNH ₂ ·HCl	55	42 h		35 (41)
2		BnNH ₂ ·HCl	35	48 h		64 (69)
3		BnNH ₂ ·HCl	35	70 h		(59)
4		BnNH ₂ ·HCl	55	96 h		62
5		BnNH ₂ ·HCl	25	23 h		45 (49)
6 ^c		MeNH ₂ ·HCl	25	3 h		82
7 ^d		NH ₄ Cl	25	6 h		44
8 ^d		NH ₄ Cl	35	96 h		(40)

^aAll reactions were run with 1.3 equiv of amine hydrochloride and 1.3 equiv of 37% aqueous formaldehyde solution unless otherwise stated. The aqueous solutions were ca. 2.85 M in amine hydrochloride.
^bIsolated yields. Yields in parentheses are based on ¹H NMR.
^cReaction was carried out in 2.6 M monomethylamine hydrochloride with 2.0 equiv of cyclopentadiene and 1.4 equiv of 37% formaldehyde.
^dReaction was conducted in a saturated ammonium chloride solution.

of other dienes (Table I).^{5b} As can be seen from the table, reaction times and temperatures vary according to the reactivity of the diene. With the exception of entry 6, all condensation reactions were carried out in sealed ampules. Yields varied from modest to good. Use of alcoholic solvents inevitably led to a decrease in the reaction rate, however, aqueous tetrahydrofuran mixtures could be employed without any noticeable effect in reaction rate and yield. Entries 3 and 5 address the regioselectivity question. The results shown in Table I are consistent with those reported in previous work on iminium salts.^{3b,d} The formation of a single diastereomer in the reaction of (*E,E*)-2,4-hexadiene with iminium ion **1** (entry 4) is mechanistically significant. The high stereospecificity observed for this reaction is characteristic of a truly concerted cycloaddition rather than an ionic, stepwise process.

The recent surge of interest in asymmetric Diels-Alder cycloaddition reactions⁶ using chiral dienophiles and dienes prompted us to explore the potential for chiral induction employing an optically active iminium ion. In a preliminary study, aqueous formaldehyde was treated at 0 °C with (-)- α -methylbenzylamine hydrochloride in the presence of cyclopentadiene. After 20 h at 0 °C, a 4:1 mixture of separable diastereomers (cf. **3** and **4**) were isolated in 86% yield.



To date use of acetaldehyde in place of formaldehyde has met with only limited success. Reaction of cyclopentadiene with benzylamine hydrochloride and acetaldehyde afforded a 47% isolated yield of a mixture of the *exo* and *endo* adducts **5** and **6**



in a 1.5:1 ratio, respectively. The reaction rate was substantially