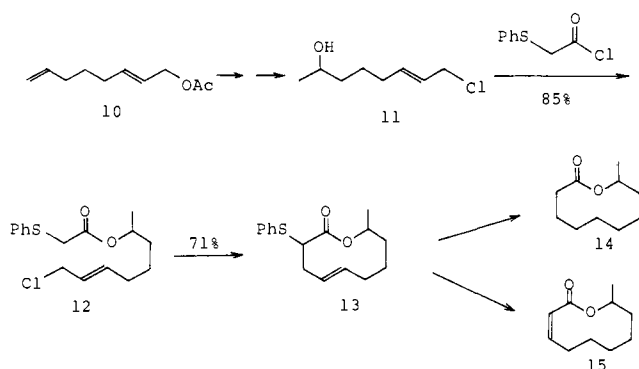


from the butadiene telomer **5**.¹³ The alcohol **6** was acylated with phenylthioacetyl chloride to give the ester **7** in 82% yield: IR 1730 cm⁻¹; NMR (CCl₄) δ 5.3 (2 H, m, olefinic), 4.5–5.05 (1 H, m, CHOCO), 3.5 (2 H, s, CH₂SPh), 3.1 (2 H, t, *J* = 7 Hz, CH₂I). The ester **7** (0.93 mmol in 15 mL of THF) was added to a THF solution (35 mL) of potassium hexamethyldisilazane (1.4 mmol) at 60 °C in 3.5 h. The cyclized product **8** was obtained in 75% yield after chromatography: IR 1730 cm⁻¹; NMR (CCl₄) δ 4.7–5.5 (3 H, m, olefinic and CHOCO), 3.3–3.8 (1 H, m, CHSPh). The high yield of the cyclization seems to be due to the presence of the double bond in **7**. The cyclization of the corresponding saturated 12-membered ring gave the lactone in 51% yield. Reductive elimination of the phenylthio group with deactivated Raney nickel¹⁵ gave recifeiolide (**9**) as an oil in 80% yield: IR 1730 cm⁻¹; NMR (CCl₄) δ 4.7–6.0 (3 H, m, olefinic and CHOCO), 1.9–2.4 (6 H, m, =CCH₂ and CH₂CO), 1.2 (3 H, d, *J* = 6.2 Hz, CH₃); mass spectrum *m/e* 196 (M⁺). Anal. Calcd: C, 73.43; H, 10.27. Found: C, 73.54; H, 10.36.

The 10-membered lactone **13** was then prepared from the telomer **10**, readily obtained by the palladium catalyzed telomerization of butadiene with acetic acid.¹⁶ The acylation of the alcohol **11**^{9c} with phenylthioacetyl chloride afforded the desired ester **12**. The cyclization proceeded smoothly to give



the 10-membered lactone **13** in 71% yield. The treatment of **13** with Raney nickel afforded 9-decanolide (**14**) in 90% yield, which is a natural product isolated from *Phoracantha synonyma* by Moore and Brown:¹⁷ IR 1725 cm⁻¹; NMR (CCl₄) δ 4.6–5.1 (1 H, br, CHOCO), 2.0–2.8 (2 H, br, CH₂CO); mass spectrum *m/e* 170 (M⁺). The double bond in **13** was hydrogenated by using PtO₂ and the subsequent oxidative removal¹⁰ of the phenylsulfonyl group produced the unsaturated lactone **15** in 91% yield, which was prepared by Wakamatsu et al. as a precursor of (±)-diploidalide C:¹⁸ IR 1710 cm⁻¹; NMR (CCl₄) δ 6.23 (1 H, dt, *J* = 7 and 11 Hz, olefinic), 5.75 (1 H, d, *J* = 11 Hz, olefinic), 4.8–5.5 (1 H, m, CHOCO), 2.4–3.2 (2 H, m, =CCH₂), 1.3 (3 H, d, *J* = 6 Hz, CH₃); mass spectrum *m/e* 168 (M⁺).

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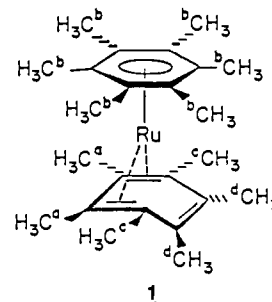
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Arene-Transition Metal Complexes. 1. Site Exchange and Chemical Characteristics of $\eta^6\text{-C}_6(\text{CH}_3)_6\text{Ru-}\eta^4\text{-C}_6(\text{CH}_3)_6$

Sir:

The implication of η^4 -arene-metal complexes as intermediates^{1–3} in coordination catalysis of arene hydrogenation has raised a number of basic questions about arene-metal complexes such as what factors affect $\eta^6 \rightleftharpoons \eta^4$ interconversions, intermolecular arene (η^6 or η^4) exchange, and hydrogen-deuterium exchange between D₂ and the C–H bonds in the arene complexes. Bis(hexamethylbenzene)ruthenium(0), **1**, is an excellent model for study—first and foremost because it is a catalyst precursor for arene hydrogenation,² second because the ground-state structure in the solid⁴ and solution⁵ states has both η^4 -arene and η^6 -arene ligands, and third because the molecule is fluxional. We describe here spectroscopic and chemical studies for the ruthenium complex that resolve some of the dynamic issues and also establish a unique alane catalysis of a new fluxional process. The exchange studies have implicated alkyl alanes as possible promoters for the ruthenium-catalyzed arene hydrogenation reaction, and such a pro-



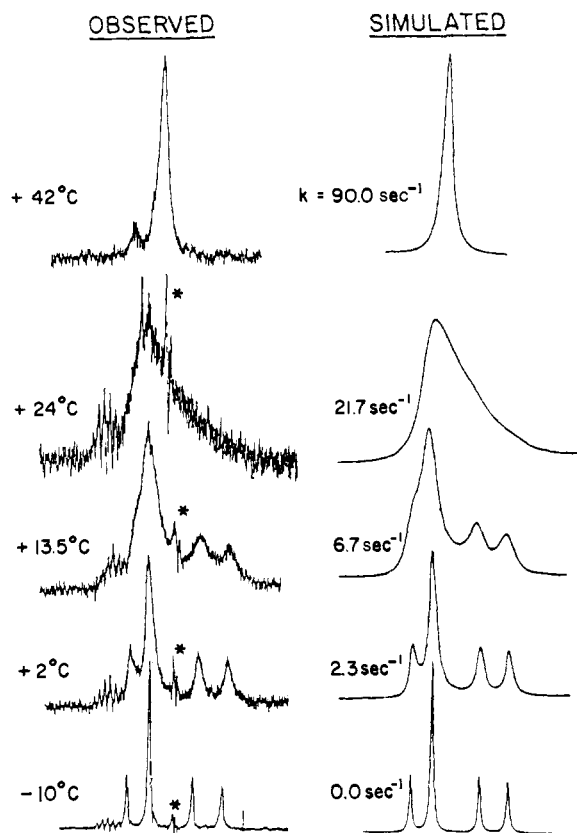


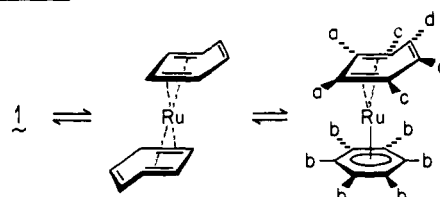
Figure 1. The variable-temperature ^1H NMR spectra (60 MHz) and simulated spectra of $\eta^6\text{-C}_6(\text{CH}_3)_6\text{Ru-}\eta^4\text{-C}_6(\text{CH}_3)_6$ in toluene- d_8 . Spectral sweep widths are 250 Hz except for the $+42^\circ\text{C}$ spectrum which is 500 Hz. The asterisk marks the position of a noninteracting impurity and the low-field multiplet represents the trace CD_2H impurity resonance of the toluene- d_8 solvent. Chemical shift values at -10°C are 1.92, 1.77, 1.47, and 1.27 ppm. The rate constants, cited for the simulated spectra, are for $k_{b\rightarrow a}$.

motion effect was demonstrated in catalytic studies with **1** and trimethylaluminum.

We have reexamined the fluxionality of bis(hexamethylbenzene)ruthenium(0) which was originally reported by Fischer and Elschenbroich.⁵ Consistent with the solid-state structure, **1**, the ^1H NMR spectrum below 5°C had four methyl resonances of relative intensity 2:6:2:2. Assignments of these resonances to sites labeled a through d as shown in **1** are in order of increasing shift to higher fields.⁶ The resonances assigned to the methyl groups (d) of the "nonbonded" olefin in the η^4 -arene ring had a half-height line width of 1.50 Hz which was slightly larger than that of the others (1.36 Hz) at -10°C .

An examination of the variable-temperature spectra shown in Figure 1 clearly shows a simultaneous broadening of resonances representing all four sites. Coalescence into one symmetrical peak at 1.67 ppm occurred at temperatures above 35°C with a line width of <3 Hz above 60°C . Spectra measured at ten different temperatures between $+2$ and 42°C were simulated by the density matrix procedure of Kaplan^{7a} and Alexander^{7b} for the various mutual and nonmutual exchange processes. The best fit for a single basic permutational mechanism is shown in Figure 1. This process allows interchange of site b with sites a, c, and d, and vice versa, and interchange of sites a, c, and d only through site b (assuming a rapid rotation of the η^6 ring on the NMR time scale). An Arrhenius plot yielded an activation energy of 16.1 ± 1.3 kcal/mol with $\Delta H^\ddagger = 15.6 \pm 1.3$ kcal/mol and $\Delta S^\ddagger = -3 \pm 5$ eu. A plausible physical representation of this basic permutational mechanism may be predicated on a 16-electron $\text{Ru}[\eta^4\text{-C}_6(\text{CH}_3)_6]_2$ inter-

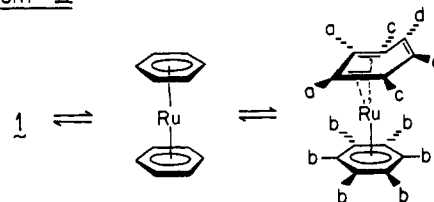
Mechanism I



mediate as shown in Mechanism I. For d^8 metals, such a 16-electron complex should be close in energy to the η^6 -arene- $\text{M-}\eta^4$ -arene state; actually we suggest that with a third row metal, Os(0) or Ir(1), isolation of a quasi square planar bis(η^4 -arene)-metal complex may be feasible. This bis(η^4 -arene)ruthenium intermediate earlier was invoked² for the catalytic reactions to allow for an oxidative addition of hydrogen to the complex.

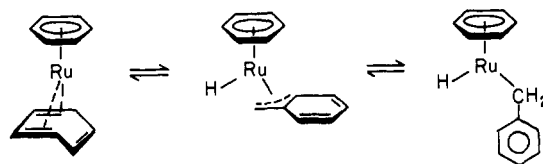
A conceivable though electronically less likely mechanism involving a bis(η^6 -arene)ruthenium (20-electron) intermediate, **II**, can be distinguished from the 16-electron intermediate in Mechanism I. For Mechanism II, the equal facility with which sites a, c, and d are converted into each other and into site b leads to a set of simulated spectra that do not fit the observed spectra.⁸

Mechanism II



Earlier we postulated that the observed H-D exchange that occurs in all methyl groups for the catalytic systems based on **1** with methylarene- d_2 mixtures might proceed through the formation of a benzylruthenium hydride intermediate shown in Mechanism III. Formation of such intermediates cannot solely account for the observed site exchange in **1**. However, Tebbe had suggested to us that the concentration of such a

Mechanism III



benzylruthenium hydride species might be raised through complexation with alanes⁹ in accordance with his observations on the stabilizing effect of aluminum alkyls or hydrides on transition metal hydride or methylene complexes.¹⁰ In fact, we have found that trimethylaluminum and also dimethylaluminum chloride exert a profound influence on the dynamics of site exchange in **1** and on the chemistry of **1**.

Although trimethylaluminum and **1** do not detectably form a complex,¹¹ the DNMR spectra for solutions of **1** with 7, 10, or 100 molar % of trimethylaluminum were grossly different from those for solutions of **1** only. In the presence of trimethylaluminum ($[\text{Al}(\text{CH}_3)_3] \approx 0.07[\mathbf{1}]$), the well-resolved four-line pattern for **1** was not observed (90 MHz) until temperatures of -30°C (-40°C at 60 MHz) were attained. The character of line-shape changes above -30°C in no fashion corresponded to those for pure **1**. By inspection of Figure 2, it can be seen that site exchange fully localized in the η^4 -arene ligand occurred first, and then, at higher temperatures, site exchange between the η^4 and η^6 configurations occurred. Rates for these two distinct processes were both dependent upon the trimethylaluminum concentration. The full reversibility of the

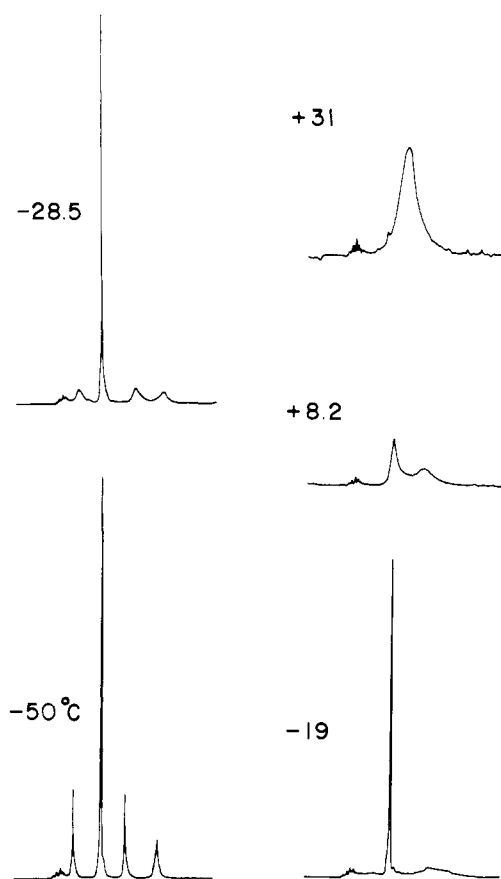


Figure 2. The DNMR spectra of $\eta^6\text{-C}_6(\text{CH}_3)_6\text{Ru-}\eta^4\text{-C}_6(\text{CH}_3)_6$ in the presence of 7 molar % of $\text{Al}(\text{CH}_3)_3$, recorded on a Bruker HX 90 in toluene- d_8 at a sweep width of 1000 Hz. Chemical shift values at -50°C are 1.95, 1.74, 1.55, and 1.32 ppm. There is a difference in the half-height bandwidth of the high-field resonance as compared with the other resonances and with that of the -10°C spectrum in Figure 1 which is a temperature (enhanced viscosity broadening—with respect to the reference solvent resonance) effect observed both here and in solutions of pure **1**. Note that there is a slight chemical-shift dependence on temperature.

alane interaction was demonstrated by vacuum removal of the alane to give **1** that yielded DNMR spectra indistinguishable from those of samples of **1** that had never been in contact with the alane.

The NMR data indicate that there is no direct interaction between the $\eta^6\text{-C}_6(\text{CH}_3)_6\text{Ru-}\eta^4\text{-C}_6(\text{CH}_3)_6$ structure itself and either the trimethylaluminum monomer or dimer. At -65°C , the solution of a 1:1 molar mixture of ruthenium complex and trimethylaluminum showed the characteristic limiting ^1H spectrum for the alane dimer wherein the separate resonances for the bridging and terminal methyl groups were all resolved as reported by Brown and Williams¹² for pure trimethylaluminum. Furthermore, the DNMR ^1H resonances of the alane in admixture with the ruthenium complex follow the very same line-shape changes, characteristic of bridge-terminal methyl group site exchange, reported (and reproduced by us) for the pure compound. Nevertheless, at -65°C and below, the catalyzed site exchange in the η^4 -arene ring was still fast on the NMR time scale in the 1:1 mixture. Clearly then the alane must be interacting with a low concentration ruthenium species, perhaps a hydride, and this interaction is not significantly perturbing the characteristic alane spectrum.

We submit that this interactive effect of alanes is of substantial scientific and chemical significance. The low-temperature exchange process seems to be best simulated by a permutation that has as its *simplest* physical representation a 1,3 shift in the η^4 -arene ligand. This specific process could be occurring in pure **1** at rates not greater than $\sim 1/5$ that of the

basic permutational process physically depicted in Mechanism I. Mechanism I involves a postulated² intermediate in the catalytic reactions of **1**. An essential point here is that both of these processes are catalyzed by the alane with the localized η^4 -arene ring site exchange more profoundly rate enhanced. In terms of feasible physical processes, both a 1,3 ring shift and an elaboration of Mechanism III¹³ possess the appropriate permutational character to account for the DNMR spectra of the catalyzed low-temperature process. Further mechanistic comment is deferred until a detailed kinetic analysis has been completed for the alane catalyzed reaction. The important chemical observation at this stage of the research is that we have found the addition of trimethylaluminum to the catalytic system² based on **1** to raise the rate (factor of 4–5) of arene hydrogenation. The production of cyclohexenes in this reaction was totally suppressed by the alane. Furthermore, this alane appears to stabilize the ruthenium complex in the catalytic reaction as indicated by the complete suppression of solution discoloration in long-term catalytic reactions. Thus, the presence of the alane qualitatively alters the character of the hydrogenation reaction catalyzed by the ruthenium complex. We are now broadly examining the effect of alanes in fluxional processes of arene-metal complexes and in catalytic hydrogenation reactions.^{14–16}

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- (8) Mechanisms I and II are literally distinguished in the reverse reaction wherein I yields the initial (identical) configuration and II may exchange sites a, c, and d.
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- (10) F. N. Tebbe, *J. Am. Chem. Soc.*, **95**, 5412 (1973).
- (11) No new ^1H NMR resonances were observed for **1** in the presence of $\text{Al}(\text{CH}_3)_3$ except those of $\text{Al}(\text{CH}_3)_3$ itself. Furthermore the resolved low-temperature (-50°C) spectrum of **1** in the presence of 7 molar % $\text{Al}(\text{CH}_3)_3$ shows essentially the same chemical shifts as did pure **1** at that temperature.
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- (15) A titanium(II)-arene complex containing complexed aluminum trichloride, $\text{C}_6\text{H}_6\text{TiAl}_2\text{Cl}_6$, is a catalyst for arene hydrogenation: R. I. Mink, M. Y. Darenbourg, E. L. Muetterties, T. Groshens, and K. J. Klabunde, submitted for publication.
- (16) The presence of an alane is neither a necessary nor a sufficient condition for catalytic activity in an arene-transition metal complex. For example,

bis(arene) complexes of ruthenium(0) are active catalysts in the absence of an alane² and bis(arene) complexes of molybdenum(0) are inactive at 140 °C in the presence and absence of trimethylaluminum (M. Millar and E. L. Muetterties, unpublished results).

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Naphthalene-Butadiene Exciplex. An Extended Hückel Calculation

Sir:

In 1966 Hammond¹ reported the quenching of the excited singlet state of naphthalene by conjugated dienes. Since that time a large body of evidence has been gathered to support the contention that weakly bound excited-state complexes, exciplexes, mediate the acceleration of naphthalene radiationless decay during the quenching act. However, the electronic nature of the forces which stabilize the exciplex intermediate remains controversial. Weller² and Evans³ have argued that charge-transfer interactions are the most important contributors to exciplex stabilization, while Hammond and co-workers⁴ have suggested that, although charge transfer can be important, it need not be, and that excitation resonance and/or vibronic mixing can dominate in some systems. In support of this latter view, Weiss has presented evidence in the system triphenylphosphine-substituted anthracene⁵ to show that the electronic nature of the exciplex intermediate can be systematically altered by substitution in the aromatic portion.

We present results of extended Hückel (EHT) calculations on the electronic states of the system naphthalene-butadiene which clearly indicate the importance of excitation resonance in stabilization of this exciplex pair. We also wish to suggest that relatively simple calculational approaches such as EHT can provide valuable insights into the nature of electronic interactions in exciplex models which quite closely parallel true experimental systems.⁶

We have used the EHT program of Hoffmann⁷ as modified by Anderson⁸ to include two-centered repulsions. Within the supermolecule approach we have searched for energy minima on the ground state and the four formal excited singlet surfaces of the system naphthalene (N)-*s-cis*-butadiene (B) with partial geometry optimization⁹ programs developed at Du Pont.¹⁰ State parameters have been calculated at various points on the surfaces in order to ascertain contributions from both charge and electronic mixing.

Figure 1 shows a projection of the $E_{\text{tot}}(r,d)$ surfaces for B approaching N from above in a restricted coplanar fashion, i.e., **1**. The ground configuration ($N^0 \cdots B^0$) is repulsive for $r < 3.6$ Å for all values of d . The lowest excited singlet state E_1 is weakly bound, minimizing at $r = 2.90$ Å, $d = 2.51$ Å, at an energy 0.17 eV (3.9 kcal/mol) below that of the separated species (and 0.19 eV (4.4 kcal/mol) below the separated configuration $N^* \cdots B^0$). For large values of r , this state exhibits substantial charge transfer (0.996 e^- at 5-Å separation), consistent with the configuration $N^+ \cdots B^-$.¹¹ However, at the minimum charge transfer is nearly absent (0.071 e^- excess on B). Analysis of the calculated wave function coefficients in the vicinity of the minimum reveals substantial orbital interaction between the N and B subunits when compared with the localized MO's calculated for the separated (5 Å) species (Table I). The $N \cdots B$ local symmetry (C_s) permits mixing of the N and B HOMO's and of their LUMO's. At distances r less than ~ 4 Å, the system can only be viewed as a supermolecule whose

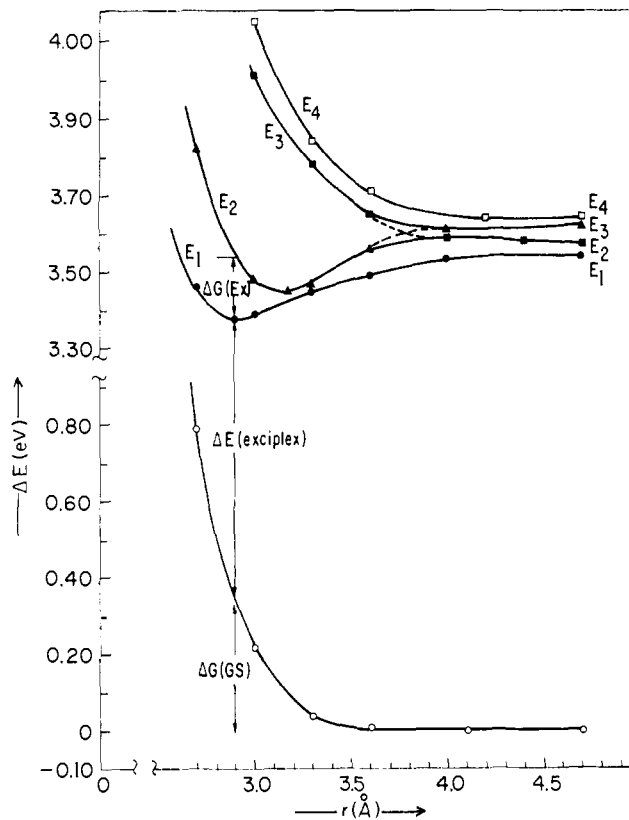
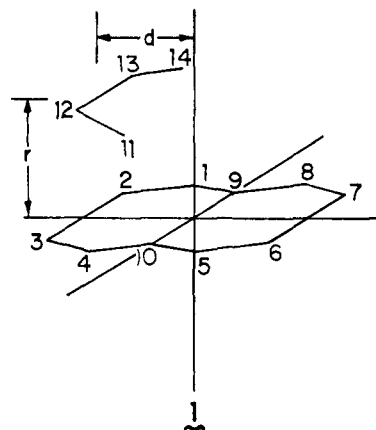


Figure 1. Calculated energies for the $N \cdots B$ electronic states as a function of interplanar separation, r (see **1**) at $d = 2.51$ Å. Symbols refer to calculated points: ○ (GS, ground state); ● (E_1 : excitation MO 36 → 35); ■ ($E_{2,3}$: MO 37 → 35); ▲ ($E_{3,2}$: MO 36 → 34); □ (E_4 : MO 37 → 34). See note 12.



HOMO (MO 36¹²) is an antibonding composite of N- and B-localized HOMO's and whose LUMO (MO 35) is a bonding combination of the localized LUMO's. As a direct consequence of this mixing, the lowest excited state E_1 is stabilized by removal of an electron from a HOMO having antibonding interactions between N and B and placement into an N-B bonding LUMO. This stabilization is reflected in positive overlap populations (C_1-C_{14} , 0.027; C_2-C_{13} , 0.005) between the N and B units in the excited state E_1 at the minimum. Moreover, the analysis shows that the E_1 state is best described as an excitation resonance state which exhibits considerable $B^* \cdots N^0$ (38%) and $B^0 \cdots N^*$ (55%) character and only a 7% charge-transfer component ($B^- \cdots N^+$).

The approach of B^0 to N^* , the experimentally observed quenching act, is considered by reference to calculated surface E_2 of Figure 1. We find that E_2 is very slightly repulsive (~ 0.02 eV) at $r \approx 4$ Å, at which point an attempted surface crossing