

Selectivities of Diels–Alder Reactions Catalyzed by Highly Acidic Boronated Aluminas

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A series of boronated aluminas was prepared by the reaction of BX_3 ($X = F, Cl, Br$) with alumina or by a two-step synthesis involving the reaction of $BH_3 \cdot Me_2S$ with alumina and then with I_2 . The modified aluminas, BX_n/Al_2O_3 , were found to have $n = 3$ (F), $n = 1.5$ (Cl), $n = 1$ (Br), and $n = 1$ (I). The acidity of the solids (indicator dyes) was large and decreased in the order $I \sim Br > Cl > F$. The solids catalyzed the Diels–Alder reactions of methyl acrylate with cyclopentadiene and isoprene with methyl acrylate, both of which occurred in high yield and with high selectivity. The regioselectivity of the isoprene/methyl acrylate reaction in fact is higher than seen previously. The results of the heterogeneous reactions were compared to those catalyzed by *B*-bromo- and *B*-chlorocatecholborane, which serve as models for the boronated aluminas.

Introduction

The Diels–Alder reaction is a concerted $4 + 2$ cycloaddition reaction in which as many as four stereogenic centers are created in a controlled manner. Lewis acids profoundly influence this reaction. They not only greatly accelerate the rate of the reaction¹ but also enhance diastereo- and regioselectivity.² Because of the importance of the Diels–Alder reaction in synthesis, chemists continue to seek out new materials which will enhance selectivities even further.

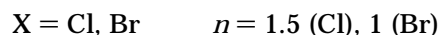
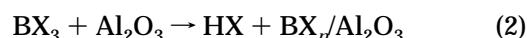
Numerous solids have been found which influence rates and selectivities of the Diels–Alder reaction,³ often in ways that do not have counterparts in solution. Alumina in particular has been shown to be a versatile catalyst for a diverse set of Diels–Alder reactions.³ Selectivities of the alumina-catalyzed reactions often change in synthetically useful ways as the activity of the solid is altered on heating because the nature and number of catalytic sites (partially exposed Al^{3+} ions) change as well. Steric effects induced by the surface of the solid may also influence selectivities.

Solids also serve as supports for Lewis acids. It is possible, for example, to chemisorb $AlCl_3$,⁴ BF_3 ,⁵ and $ZrCl_4$ ⁶ to alumina and silica gel. These new materials have the potential to serve as heterogeneous catalysts of the Diels–Alder reaction. It is the purpose of the present paper to describe the synthesis and characterization of a series of highly acidic boronated aluminas and their use as catalysts in model Diels–Alder reactions.

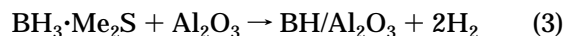
Results and Discussion

Synthesis and Characterization of Catalysts. The syntheses of three of the four boronated aluminas used

in this study were carried out by the direct reaction of BX_3 ($X = F, Cl, Br$; 1 mmol) with unactivated alumina (1 g), which contains about 3.7 mmol of surface hydroxyl groups,⁷ in a hexane slurry at room temperature. In the reaction of $BF_3 \cdot Et_2O$, the ether was displaced but no BF bonds were hydrolyzed (eq 1). In the reactions of BCl_3 and BBr_3 , on the other hand, copious quantities of hydrogen halide were liberated (eq 2). These results are consistent with the known rates of hydrolysis of BX_3 .⁸ Simple analyses of stoichiometry and weight changes of the solids yielded the formulations for the solids shown in eqs 1 and 2. Catalysts with similar characteristics were also prepared by the reaction of the boron halide with alumina which had been activated at 400 °C (400 °C Al_2O_3).



The fourth catalyst, a *B*-iodoborate, was prepared indirectly by first treating unactivated alumina (1 g) or [400 °C Al_2O_3] with $BH_3 \cdot Me_2S$ (1 mmol), which liberated 2 equiv of H_2 ,⁹ and then with I_2 (0.5 mmol) (eqs 3 and 4). This reagent, which is similar in structure to BBr/Al_2O_3 , reacted violently with water as is the case for the reaction of BI_3 with water.⁸



Properties of these solids are presented in Table 1. All of the boronated aluminas contain boron–halogen bonds and are highly acidic (H_0),¹⁰ with the acidity increasing as the atomic number of the attached halogen increases.

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(9) As is consistent with the formulation BH/Al_2O_3 , reaction of the solid with water/methanol/glycerol (1:1:1) liberated an equivalent of H_2 .

(10) By comparison unactivated alumina and 400 °C Al_2O_3 have H_0 values of +6.8 and between –3.0 and –8.2, respectively. See: Lee Tan, L. C. Ph.D. Dissertation, University of Tennessee, 1992.

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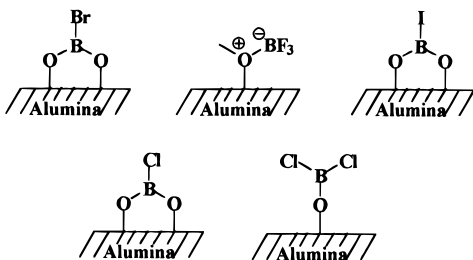
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Table 1. Properties of Boronated Alumina

solid	mode of synthesis	color	¹¹ B NMR chemical shift ^{a,b}	acidity function (<i>H</i> ₀) ^c
BF ₃ /Al ₂ O ₃	BF ₃ ·Et ₂ O + Al ₂ O ₃	white	6.5 (strong), 10.0 (weak)	+0.8 ≤ <i>H</i> ₀ ≤ -3.0 ^d
BCl _{1.5} /Al ₂ O ₃	BCl ₃ + Al ₂ O ₃	light brown	7.0	-3.0 ≤ <i>H</i> ₀ ≤ -8.2 ^e
BBr/Al ₂ O ₃	BBr ₃ + Al ₂ O ₃	reddish brown	7.0	<i>H</i> ₀ ≤ -13.2
BI/Al ₂ O ₃	BI ₃ ·Me ₂ S + Al ₂ O ₃ ; then I ₂	mustard yellow	8.1	<i>H</i> ₀ ≤ -13.2

^a After complexation to pyridine relative to NaB(C₆H₅)₄ at δ = 0. ^b Value for solids prepared with 400 °C Al₂O₃. ^c Determined using indicator dyes. ^d Solid prepared with 400 °C Al₂O₃. ^e Solid prepared with 200 °C Al₂O₃.

This trend is identical to that observed for the Lewis acidities of the boron trihalides.⁸ The bromine- and iodine-containing boronated aluminas, in fact, are among the most acidic solids known; the exact values could not be determined in these two cases because the intense colors of the solids interfered with the colors of the indicators. The BF₃/Al₂O₃, which has a B:F ratio of 1:3, gave two resonances in its solid state ¹¹B NMR spectrum, undoubtedly due to complexed (δ 6.5; strong) and uncomplexed (δ 10.0; weak) BF₃.¹¹ The BCl_{1.5}/Al₂O₃ alumina gave a single resonance in its ¹¹B NMR spectrum. Nonetheless, based on the noninteger ratio of B:Cl, two (or more) chloroboroxy species must be chemisorbed to the surface. On the basis of the single ¹¹B resonance for the bromine- and iodine-containing solids, as well as their unit ratio of boron to halogen, one can formulate a single chemisorbed species in each of these two cases. Structures for the boronated solids are shown below.



In order to corroborate the surface structures of the boronated aluminas, one of them, BBr/Al₂O₃, was subject to further characterization. Transmission IR spectra taken on alumina before and after treatment with BBr₃ confirmed, as expected, that the surface hydroxyl groups were consumed in the reaction. Hydrolysis of the solid and appropriate titrations of the aqueous phase with OH⁻ and Ag⁺ demonstrated that 1 mmol of BBr was initially chemisorbed to the surface.¹² Fast atom bombardment mass spectrometry on the surface of the solid gave negative results, consistent with BBr being covalently bonded to the surface. ESCA was difficult to carry out because of the nonconducting nature of the solid but did nonetheless reveal the presence of O, Al, B and Br on the surface. All of these results reinforce the proposed structure of this solid and lend credence to the other structures as well.

Because the dienophile must complex to the chemisorbed Lewis acid, which is in a fairly congested environment, before the catalyzed Diels–Alder reaction will occur, two qualitative experiments, one kinetic and the other thermodynamic, were performed on BBr/Al₂O₃ to show that its acid sites were accessible to base. In the

Table 2. Selectivities in the Reactions of Methyl Acrylate with Cyclopentadiene and Isoprene^a

catalyst	MA + CP		MA + IP	
	N:X	(% yield)	para:meta	(% yield)
BF ₃ /Al ₂ O ₃ –toluene	24	(31) ^b	5.8	(0.8) ^c
BCl _{1.5} /Al ₂ O ₃ –toluene	12	(78) ^b	35	(80) ^c
BBr/Al ₂ O ₃ –toluene	13	(88) ^b	49	(76) ^c
BBr/Al ₂ O ₃ –no solvent	8	(18) ^d	56	(62) ^c
BI/Al ₂ O ₃ –toluene	16	(47) ^b	23	(56) ^c
uncatalyzed	4.9 ^e		2.5 ^f	
Al ₂ O ₃ , unactivated	5.8 ^g		2.5 ^h	
Al ₂ O ₃ , 400 °C-activated	52 ^g		5.2 ^h	
<i>B</i> -chlorocatecholborane–CH ₂ Cl ₂	19	(47) ⁱ	23	(94) ^c
<i>B</i> -bromocatecholborane–CH ₂ Cl ₂	19	(49) ⁱ	25	(63) ^c
AlCl ₃ –benzene	99 ^j		20	(84) ^c
LiClO ₄ –ether	8 ^{k,l}		3.4 ^{k,l}	

^a All reactions were run at ambient temperature. ^b 1 h reaction time. ^c 3 h reaction time. ^d 4 h reaction time. ^e In CH₃CN. ^f Neat. ^g Reference 3a. ^h Jennifer Wilson, unpublished results. ⁱ 1.5 h reaction time. ^j Isaacs, N. S. *Physical Organic Chemistry*; Wiley: New York, 1987; p 705. ^k Pagni, R. M.; Kabalka, G. W.; Bains, S.; Plesco, M.; Wilson, J.; Bartmess, J. *J. Org. Chem.* **1993**, *58*, 3130. ^l 6 M LiClO₄.

first, the solid was treated with an excess of CH₃Li/ether. The initial broad ¹¹B resonance at δ = ~10 ppm was replaced with a very sharp one at δ = -0.8 ppm, due the presence of the chemisorbed bromomethyl borate complex. Thus, all of the BBr units are available for reaction with CH₃Li. In the second experiment, dilute solutions of pyridine (4.26 × 10⁻⁴ M) in cyclohexane were equilibrated with varying quantities of BBr/Al₂O₃ (0.016–0.053 g), and the amount of pyridine adsorbed was determined spectrophotometrically. Under these conditions 40–53% of the pyridine was adsorbed (on a per BBr basis). Since the bromoborate units cover the majority of the surface of the solid, a significant fraction of the pyridine adsorption must be due to its complexation to BBr. In any event, the results described in the next section on Diels–Alder reactions demonstrate that sufficient acid sites are available to the dienophile to ensure that the entirety of each Diels–Alder reaction is catalyzed.

Diels–Alder Reactions

Because a variety of chiral and achiral dienes and dienophiles have been used in the Diels–Alder reactions, a diverse number of selectivities are known for the uncatalyzed and catalyzed 4 + 2 cycloaddition reaction. In this study, the effect of the boronated aluminas on the diastereoselectivity and regioselectivity of two classic Diels–Alder reactions, cyclopentadiene (CP) plus methyl acrylate (MA) and isoprene (IP) + MA, which have been widely studied in other contexts, has been examined. The reaction of CP with MA, which yields endo (N) and exo (X) adducts (eq 5), has been examined in numerous solvents^{13,14} and has been used to determine Ω [log(N:

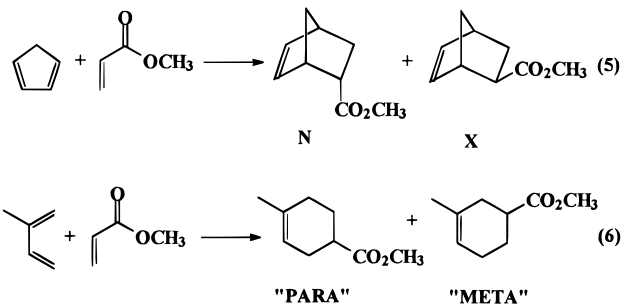
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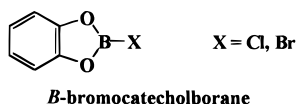
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X)], Berson's solvent polarity parameter.¹⁵ The Lewis acid-catalyzed reaction of CP with MA yields enhanced N:X selectivity.¹⁶ The reaction of IP with MA, on the other hand, yields the "para" and "meta" regioisomers (eq 6) whose para:meta selectivity is enhanced by Lewis acids.¹⁷



The results of the boronated-alumina-catalyzed Diels–Alder reactions are shown in Table 2. Also reported are results obtained using the Lewis acids *B*-chloro- and *B*-bromocatecholborane which have structural features



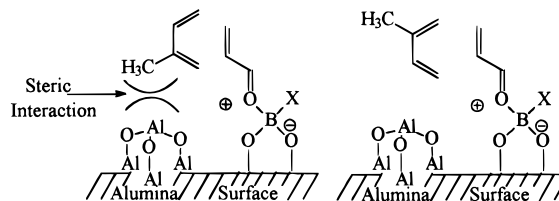
similar to those of the boronated aluminas, unactivated and activated aluminas which have some surface characteristics in common with the boronated aluminas, aluminum trichloride which is a classic Lewis acid widely used in organic synthesis, and LiClO_4 in ether which is a Lewis acid of current interest that is used to catalyze Diels–Alder and other reactions.¹⁸ To put these data into perspective, the results for the uncatalyzed reactions are reported as well. Although a few of the catalyzed Diels–Alder reactions have been reported by others, with one exception the results in Table 2 were obtained in this laboratory.

The best results for the boronated-alumina-catalyzed reactions were obtained when the reactions were carried out in a slurry with toluene which provided a conduit for the rapid transport of the reactants from one place on the surface to another. Although the Diels–Alder reactions could have occurred in toluene, this was not the case because the observed selectivities were far larger than for the uncatalyzed reactions.²³ These Diels–Alder reactions could also be carried out in the absence of solvent, but the rates were significantly slower. For the reaction of CP with MA on $\text{BBr}/\text{Al}_2\text{O}_3$, for example, an 88% yield of adducts was generated in toluene after 1 h, but only an 18% yield was obtained in the absence of toluene after 4 h. For the three other boronated aluminas, no more than a 1% yield of products was obtained for the solvent-free reactions after 4 h. The boronated-alumina-catalyzed reactions were run for relatively short times because the reactions were fast and the adducts slowly degraded ($\sim 1\%$ per hour) on standing in the presence of the solids; interestingly, the selectivities did not change. Although it is not clear how the esters

degrade, it is noteworthy that, when methyl phenylacetate was first treated with $\text{BBr}/\text{Al}_2\text{O}_3$ in benzene for 1 h at room temperature and the resulting slurry then treated with aniline, *N*-phenylphenylacetamide was produced in 10% yield. By contrast, methyl benzoate was unreactive under the same conditions.¹⁹

Consider first the results of the reaction of CP with MA. The boronated-alumina-catalyzed reactions in toluene gave excellent N:X selectivity, being higher, for example, than those obtained in CH_3CN , on unactivated alumina, and even in $\text{LiClO}_4/\text{ether}$. With the exception of the reaction with $\text{BF}_3/\text{Al}_2\text{O}_3$, the yields were good. However, the selectivities obtained using the model Lewis acids, *B*-chloro- and *B*-bromocatecholborane, were, with one exception, higher than observed using the boronated aluminas. The selectivities were even larger with AlCl_3 and 400 °C-activated alumina, where defect sites catalyze the reaction.³ There are no obvious trends in the boronated alumina data, and there is no correlation between selectivity of the reaction and Lewis acidity of the catalyst. For example, $\text{BBr}/\text{Al}_2\text{O}_3$ and $\text{BI}/\text{Al}_2\text{O}_3$, with $H_0 \leq -13.2$, afforded far lower N:X selectivities than did 400 °C-activated alumina with H_0 no larger than -8.2 .

Unlike the reactions of CP with MA which gave good, but not outstanding, selectivities on the boronated aluminas, the reaction of IP with MA gave, with one exception, superior selectivities on the boronated aluminas. In fact the yields were far higher than ever observed before. The reaction using $\text{BF}_3/\text{Al}_2\text{O}_3$ afforded poor results (selectivity; yield); this may be a consequence of the fact that this material is a Brønsted acid. As was the case with the CP + MA reaction, there is no apparent correlation between selectivity and Lewis acidity. The superior results of the IP + MA reaction on boronated alumina may be due to a steric effect of the methyl group on IP with the alumina surface in the transition state leading to the meta product which does not exist in the transition state leading to the para product. This cannot be the whole picture, however, because the para:meta selectivity is low on 400 °C-activated alumina where steric effects should also be important.



Conclusions

A series of boronated aluminas has been prepared, characterized, and used to catalyze two model Diels–Alder reactions: CP + MA and IP + MA. Good N:X selectivity was found for the first reaction and superior para:meta selectivity for the second. Although Lewis acidity should play a role in selectivity by modifying the magnitude of the LUMO coefficients of the complexed dienophile, no correlation between Lewis acidity and selectivity was found. Other features of the complexed dienophile and the transition state such as conformational preferences (*cisoid* versus *transoid*; *syn* versus *anti*) and steric effects also play important roles in

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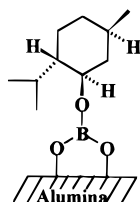
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determining selectivity. Steric effects, in fact, seem to be important in explaining the very high para:meta selectivity of the IP + MA reaction on boronated alumina.

These results and those reported earlier by Mayoral²⁰ and by us²¹ show that Lewis acid-modified solids are useful Diels–Alder catalysts. Because the halogen in these solids can be displaced by achiral and chiral alkyl and alkoxy groups, new solids with even more interesting catalytic properties are possible. In fact the menthyl derivative of $\text{BBr}/\text{Al}_2\text{O}_3$, prepared by the reaction of menthol and $\text{BBr}/\text{Al}_2\text{O}_3$, is an effective catalyst for the asymmetric Diels–Alder reaction of CP with menthyl acrylate.²¹



Experimental Section

¹H and ¹³C NMR spectra were recorded on Jeolco FX 90Q and Bruker AC-250 and AC-400 instruments. Solid state ¹¹B NMR spectra were recorded on a Nicolet NT 200 instrument in a Doty rotor with $\text{NaB}(\text{C}_6\text{H}_5)_4$ as standard ($\delta = 0$); samples were complexed with pyridine prior to analysis. IR spectra were recorded on a Biorad Spec 3200 FTG-60 instrument. FAB mass spectra spectra were recorded on a VG ZAB-EQ hybrid spectrometer, while ESCA were obtained using a Perkin-Elmer I #5100 instrument. Gas chromatography was carried out on Varian Model 3700 and Hewlett-Packard HP 5890 instruments, and GC/MS on a Hewlett-Packard HP 98785A instrument. Acidity function (H_0) measurements were carried out by standard procedures.²²

Synthesis of $\text{BF}_3/\text{Al}_2\text{O}_3$. In a 250-mL, round-bottomed flask equipped with a septum-sealed side arm and a magnetic stir bar was placed 50 g of unactivated Brockmann grade I neutral alumina. The flask was then fitted with a vacuum adapter, flushed with argon, and flame-dried. The flask was allowed to cool while maintaining the argon purge. After the flask was charged with hexanes (30 mL) to make a slurry, $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (7.1 g; 6.1 mL, 50 mmol) was added via syringe. The slurry was allowed to stir for 3 h. The solvent was removed *in vacuo*. Heat was applied to the flask, while still under vacuum, until the solid was completely dry. The solid was transferred, under argon, to a flame-dried, septum-sealed Erlenmeyer flask for later use.

Synthesis of $\text{BCl}_{1.5}/\text{Al}_2\text{O}_3$ and $\text{BBr}/\text{Al}_2\text{O}_3$. In a 250-mL, round-bottomed flask equipped with a septum-sealed side arm and a magnetic stir bar was placed 50 g of unactivated Brockmann grade I neutral alumina. The flask was then fitted with a vacuum adapter, flushed with argon, and flame-dried. The flask was allowed to cool while the argon purge was maintained. After the flask was charged with hexanes (30 mL)

to make a slurry, BX_3 (50 mmol; 50 mL of 1 M solution in hexanes) was then added via a double-ended needle dropwise over 10–15 min. Copious quantities of HX were liberated during the reaction. The slurry was then allowed to stir for 3 h. The solvent was removed *in vacuo*, and solid was transferred, under argon, to a flame-dried, septum-sealed Erlenmeyer flask for later use.

Synthesis of $\text{BI}/\text{Al}_2\text{O}_3$. In a 250-mL, round-bottomed flask equipped with a septum-sealed side arm and a magnetic stir bar was placed 50 g of unactivated Brockmann grade I neutral alumina. The flask was then fitted with a vacuum adapter, flushed with argon, and flame-dried. The flask was allowed to cool while the argon purge was maintained. After the flask was charged with hexanes (30 mL) to make a slurry, $\text{BH}_3 \cdot \text{Me}_2\text{S}$ (3.8 g; 4.7 mL; 50 mmol) was added via syringe. After the slurry was stirred for 3 h, iodine (25 mmol; 6.3 g) in hexanes (50 mL) was added via a double-ended needle. The solvent was removed *in vacuo*. The solid was transferred, under argon, to a flame-dried, septum-sealed Erlenmeyer flask for later use.

Reaction of Methyl Acrylate with Isoprene and Cyclopentadiene on Boronated Alumina. To a flame-dried 250-mL, round-bottomed flask equipped with a septum-sealed side arm and a magnetic stir bar was transferred, under argon, $\text{BX}_3/\text{Al}_2\text{O}_3$ (5 g). The flask was sealed with a septum and charged with toluene (10 mL). Methyl acrylate (0.43 g; 5.0 mmol) was then added via syringe and the reaction flask allowed to stir for 5 min. Isoprene (1.0 g; 1.5 mmol) was then added via syringe. After the reaction mixture was stirred at room temperature for 3 h, methanol (15 mL) was added and the mixture allowed to stir for 15 min. The product was then removed from the alumina by washing with methanol (2×15 mL) and then ether (2×15 mL). After the solution was filtered through a glass-fritted filter packed with Celite, the mixture was concentrated *in vacuo* and decane (0.2 g; 1.4 mmol) was added as an internal standard for GC analysis.

The reaction of methyl acrylate with cyclopentadiene, prepared by cracking the dimer, was run and analyzed in a manner similar to that described above except for the reaction time.

***B*-Halocatecholborane-Catalyzed Reaction of Methyl Acrylate with Isoprene and Cyclopentadiene.** *B*-Halocatecholborane (0.25 g) (halogen = chlorine or bromine) was transferred, under argon, to a flame-dried 100-mL, round-bottomed flask equipped with a septum-sealed side arm and a magnetic stir bar. After the flask was sealed with a septum, it was charged first with methylene chloride (20 mL) and then with methyl acrylate (3.0 g; 35 mmol). After the mixture was stirred for 5 min, isoprene (7.1 g; 1.1×10^2 mmol) was added. After 3 h at room temperature, 10 mL of cold 50% aqueous methanol was added to the reaction mixture. The reaction mixture was extracted with methylene chloride (3×15 mL). The combined organic phase was dried over anhydrous MgSO_4 (5 g) and filtered (through a glass-fritted filter packed with Celite). The mixture was concentrated *in vacuo*, and decane (0.20 g; 1.4 mmol) was added as an internal standard for GC analysis.

The reaction of methyl acrylate and cyclopentadiene was run and analyzed in a manner similar to that described above.

Aminolysis of Methyl Phenylacetate on $\text{BBr}/\text{Al}_2\text{O}_3$. To a flame-dried 250-mL, round-bottomed flask equipped with a septum-sealed side arm and a magnetic stir bar was transferred, under argon, $\text{BBr}/\text{Al}_2\text{O}_3$ (5 g). The flask was sealed with a septum and charged with 10 mL of benzene. Methyl phenylacetate (0.8 g; 5 mmol) was then added via syringe and the reaction mixture in the flask allowed to stir for 1 h at room temperature. Aniline (0.50 g; 5.0 mmol) was then added via syringe. After the reaction mixture was stirred for 3 h, a saturated solution of NaHCO_3 in water (15 mL) was added and the mixture allowed to stir for 15 min. The product was then removed from the alumina by extraction with ethyl acetate (4×15 mL). After the solution was filtered, the solvent was removed *in vacuo* and the residue purified via flash chromatography (15% ethyl acetate in hexanes). The product, *N*-phenylphenylacetamide, was identical to an authentic sample.

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(23) The catalytic sites retain their activity throughout the reaction. A reaction of 111 mmol each of MA and CP in 10.0 mL of toluene on 2.22 g of $\text{BBr}/\text{Al}_2\text{O}_3$ for 3 h gave 40 mmol of Diels–Alder adducts. This corresponds to a turnover of 6 mmol of each reactant per mmol of BBr per hour.

Attempted Aminolysis of Methyl Benzoate with BBr/Al₂O₃. To a flame-dried 250-mL, round-bottomed flask equipped with a septum-sealed side arm and a magnetic stir bar was transferred, under argon, BBr/Al₂O₃ (5 g). The flask was sealed with a septum and charged with 10 mL of benzene. Methyl benzoate (0.7 g; 0.6 mL; 5 mmol) was then added via syringe and the reaction flask allowed to stir for 1 h at room temperature. Aniline (5.0 mL) was then added via syringe. After the reaction mixture was stirred for 3 h, a saturated solution of NaHCO₃ in water (15 mL) was added and the mixture allowed to stir for 15 min. The product was then removed from the alumina by extraction with ether (4 × 15 mL). After the organic phase was filtered through a glass-fritted filter packed with Celite, the organic phase was dried over anhydrous MgSO₄ (5 g) and filtered through a glass-fritted

filter packed with Celite. TLC indicated that no benzanilide was formed in the reaction.

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