ORGANOMETALLICS

Article

CO₂ Activation with Bulky Neutral and Cationic Phenoxyalanes

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Supporting Information

ABSTRACT: The sterically crowded aluminum diphenolate $(2,6-Mes_2C_6H_3O)_2AlEt$ (2; Mes =2,4,6-Me₃C₆H₂-) was converted into the ionic species $[(2,6-Mes_2C_6H_3O)_2Al]^+[CHB_{11}Cl_{11}]^-$ (6) by ethide abstraction with the silylium salt $[Et_3Si][CHB_{11}Cl_{11}]$ or by a combination of β -hydride abstraction and concomitant ethylene elimination with the trityl salt $[Ph_3C][CHB_{11}Cl_{11}]$. Compound 6 consists of solvent-separated ions, and the cation features very short $Al\cdots C$ contacts involving the flanking mesityl groups, leading to an overall distorted-tetrahedral coordination geometry around the aluminum center. Analogous reactions with the diphenolate $(2,6-tBu_2 4-MeC_6H_2O)_2AlEt$ (1) led to *tert*-butyl transfer to the benzene solvent to afford *tert*-butylbenzene as the main product. A 1:1 mixture of the triphenolate $(2,6-Ph_2C_6H_3O)_3Al$ and tri-*tert*-butylphosphine forms a



frustrated Lewis pair, which reacts with CO₂ at room temperature to give the compound $(2,6-Ph_2C_6H_3O)_3AlOC(O)Pt-Bu_3$ (8). The high Lewis acidity of **6** catalyzes the scrambling of the subsituents of Et₃SiH at room temperature to give Et₄Si, Et₂SiH₂, and EtSiH₃ and also the reduction of CO₂ to d_5 -toluene (C₆D₅CH₃) and CH₄ at 82 °C in d_6 -benzene solution.

INTRODUCTION

In addition to being a problematic greenhouse gas, carbon dioxide is also the major C_1 feedstock for photosynthetic organisms, and the chemical industry has been increasing its use as an inexpensive base chemical.^{1,2} Most applications focus on redox-neutral substitutions such as the formation of urea from NH_3 and CO_2 or the synthesis of organic carbonates $OC(OR)_2$.¹ Catalytic reduction to formic acid or methanol with hydrogen as the reducing agent is also of current interest as part of the development of alternative fuels.³⁻⁵ The use of hydrosilanes as more reactive, easy to handle, and rather benign reducing agents has attracted significant interest in recent years.^{6–10} As part of our investigation of very strong Lewis acids, we have shown that the tight ion pairs [Et₂Al]- $[CH_6B_{11}X_6]$ (X = Cl, I) catalyze the reduction of CO₂ to toluene and methane with Et₃SiH as the reducing agent.¹¹ Unfortunately, these systems possess a rather low reactivity, and they suffer from rapid catalyst deactivation. Although the identity of the actual catalytic species is not yet known, it is quite probable that the lability of the Al-C bond contributes to the facile deactivation, especially in the presence of possible protic side products. Considering the high strength and polarity of the Al-O bond, we hypothesized that low-coordinate cationic aluminum alkoxides or phenoxides [(RO)₂Al]⁺ could be more reactive and robust catalysts. In order to prevent aggregation, large substituents were necessary, and the commercially available phenols 2,6-tBu2-4-MeC6H2OH and 2,6-Ph₂C₆H₃OH in addition to the very bulky phenol 2,6- $Mes_2C_6H_3OH$ (Mes = 2,4,6- $Me_3C_6H_2$ -)¹² were selected.

Aluminum phenolate compounds such as MeAl(OC₆H₂-tBu₂-2,6-Me-4)₂ (MAD), MeAl(OC₆H₃-Ph₂-2,6)₂ and Al(OC₆H₃-Ph₂-2,6)₃ have been used as Lewis acid additives in numerous organic transformations, including 1,4-addition to α , β -unsaturated carbonyl compounds or exo-selective Diels–Alder reactions.^{13,14} Several of these compounds have been characterized by X-ray crystallography, which showed that they featured three-coordinate strongly Lewis acidic aluminum centers.^{15–17} Here, we report the synthesis of ethylaluminum diphenolate compounds, the first cationic aluminum diphenolate, and the activation and reduction of CO₂ using some of these species. Ethylaluminum compounds were chosen because methide abstraction is often more difficult in sterically crowded species than formal ethide or alkide abstraction.

RESULTS AND DISCUSSION

While the synthesis of the diphenolates $(2,6-tBu_2-4-MeC_6H_2O)_2AlEt$ (1)¹⁵ and the new compound (2,6-Mes₂C₆H₃O)₂AlEt (2) was readily accomplished according to eq 1, the preparation of $(2,6-Ph_2C_6H_3O)_2AlEt$ (3) proved more difficult, and a pure product has not yet been obtained.

Following Yamomoto's¹⁸ procedure for the synthesis of the related methyl analogue in CH_2Cl_2 led to the isolation of the

Received: June 28, 2013 **Published:** August 20, 2013

Special Issue: Applications of Electrophilic Main Group Organometallic Molecules



triphenolate $(2,6-Ph_2C_6H_3O)_3Al(4)$,¹⁹ and the mother liquor contained mostly the dimeric monophenolate (2,6- $Ph_2C_6H_3OAlEt_2)_2$ (5)²⁰ and only traces of the target molecule 3. Using hexanes or toluene as solvent gave similar results, and the use of Et₂O resulted in the isolation of the etherate (2,6-Ph₂C₆H₃O)₃Al·OEt₂. Comproportionation of a 1:1 mixture of 4 and 5 in C_6D_6 solution at 80–135 °C in a J. Young type NMR tube for 5 days finally afforded compound 3 in approximately 80% purity. A scale-up of this reaction or comproportionation without solvents did also not lead to pure 3. Interestingly, neither compound $3^{21,22}$ nor the related species $(2,6-Ph_2C_6H_3O)_2AIR$ (R = Me, *i*Bu²²⁻²⁶) have been isolated and characterized completely. Usually, these diphenolates were generated in situ and used as such. In some instances, partial NMR data of $(2,6-Ph_2C_6H_3O)_2AlMe$ $(\delta_H(AlCH_3) -1.75)$ ppm)¹⁸ and (2,6-Ph₂C₆H₃O)₂AliBu ($\delta_{\rm H}({\rm AlCH}_3)$ –1.40 ppm)²⁵ and the adduct (2,6-Ph₂C₆H₃O)₂AlMe·O=C(H)*t*Bu ($\delta_{\rm H}({\rm AlCH}_3)$ = -1.32 ppm)^{18,27} were given, in which the presence of the Al-Me and Al-CH₂ signals at high field supports the composition. It is not quite clear why the synthesis of compound 3 did not work in our hands, but we hypothesize that during its synthesis compound 3, which is most likely a monomer with a three-coordinate Lewis acidic aluminum center, reacts more quickly with the phenol than the primary reaction product, the dimeric phenolate-bridged 5. Thus, the major products are compounds 4 and 5.

The two diphenolates 1 and 2 reacted with the trityl and silylium salts $[Ph_3C][CHB_{11}Cl_{11}]$ and $[Et_3Si][CHB_{11}Cl_{11}]$ (eqs 2 and 3), but only in the reaction with the dimesityl-substituted phenolate 2 was the expected product, the ion- pair $[(2,6-Mes_2C_6H_3O)_2Al][CHB_{11}Cl_{11}]$ (6), obtained.

$$(ArO)_{2}AlEt + [Ph_{3}C][CHB_{11}Cl_{11}]$$

$$\xrightarrow{85 \ ^{\circ}C}{2 \ days} [(ArO)_{2}Al][CHB_{11}Cl_{11}] + Ph_{3}CH + CH_{2}CH_{2}$$
(2)

$$(ArO)_{2}AlEt + [Et_{3}Si][CHB_{11}Cl_{11}]$$

$$\xrightarrow{65-75 \ ^{\circ}C}_{6 h} [(ArO)_{2}Al][CHB_{11}Cl_{11}] + Et_{4}Si$$
(3)

$$Ar = 2,6-Mes_2C_6H_3$$
 -

In contrast to the synthesis of the related species $[2,6-Mes_2C_6H_3GanBu][CHB_{11}Cl_{11}]$, $[2,6-Dipp_2C_6H_3GanBu]-[CHB_{11}Cl_{11}]$,²⁸ and $[2,6-Dipp_2C_6H_3AlEt][CH_6B_{11}Cl_6]^{29}$ the synthesis of **6** through formal ethide abstraction required longer reaction times and significantly higher temperatures. This may be a result of the large size of the two phenolate substituents, which could impede a close contact of the trityl or silylium ion. Alternatively, the higher polarity of the Al–O bond versus the Al–C bond could result in a strengthening of the Al–Et bond.

Compound 6 is partially soluble in benzene or toluene and tends to form a dense oil when the solubility limit is reached. Such liquid clathrates³⁰ are often observed for large solvent-separated ion pairs. A crystalline product has been obtained, when the silylium salt was employed as the ethyl abstracting reagent. Its ¹H and ¹³C{¹H} NMR spectra show broadened signals for the *o*-CH₃ groups and *m*-H(Mes), indicating a fluxional behavior at room temperature. The solid-state structure of 6 consists of separated cations and anions, and one of the two independent cations is depicted in Figure 1.



Figure 1. Thermal ellipsoid plot (30%) of one of the two independent cations in **6**. Hydrogen atoms have been omitted for clarity. Selected distances (Å) and angles (deg): Al(1A)-O(1A) = 1.718(3), Al(1A)-O(2A) = 1.710(3), O(1A)-C(1A) = 1.362(4), O(2A)-C(25A) = 1.358(4), $Al(1A)\cdots C(7A) = 2.430(3)$, $Al(1A)\cdots C(8A) = 2.273(4)$, $Al(1A)\cdots C(31A) = 2.356(3)$, $Al(1A)\cdots C(32A) = 2.358(4)$; O(2A)-Al(1A)-O(1A) = 119.30(14), C(1A)-O(1A)-Al(1A) = 123.8(2), C(25A)-O(2A)-Al(1A) = 122.5(2).

The unit cell contains two independent molecules, whose geometrical features are very similar, so that only one of the two molecules will be discussed here. The aluminum center is four-coordinate in a distorted-tetrahedral fashion by the two phenolate oxygens and two ortho carbons of the flanking mesityl groups. The Al–O distances with values of 1.710(3)and 1.718(3) Å are similar to or slightly longer than those observed for three-coordinate aluminum phenoxides (see e.g. t- $Bu_2Al(O-2,6-t-Bu_2-4-C_6H_2)$ with d(Al-O) = 1.710(2) Å³¹ or $Al(O-2,6-t-Bu_2-4-C_6H_2)_3$ with $d(Al-O) = 1.648(7) Å^{17}$ and are only slightly shorter than those observed in the related terphenylates 2,6-Trip₂C₆H₃OAlMe₂·OEt₂ (Trip = 2,4,6-*i*- $Pr_3C_6H_2-$, d(Al-O) = 1.755(2) Å³² and 2,6- $\text{Dipp}_2C_6H_3OAlH_2\cdot\text{NMe}_3$ (Dipp = 2,6-*i*-Pr₂C₆H₃-, d(Al-O) = 1.745(1) Å³³) with four-coordinate aluminum centers. One of the Al…C distances involving the flanking mesityl groups is shorter (2.273(4) Å) than those reported for the benzene or toluene adducts of the strong Lewis acid $Al(C_6F_5)_3$ with values



of 2.342(6) and 2.366(2) Å³⁴ or the intramolecular Al···C contact in $[(2,6-Mes_2C_6H_3)_2Al][B(C_6F_5)_4]$ with a value of 2.353(1) Å, 35 whereas the other Al···C contact is very similar to these (2.356(3) Å). As the Al…C distances to the neighboring carbons are only slightly longer (2.430(3) and 2.358(4) Å), the interactions may also be viewed as η^2 coordinations. Previously observed η^2 -Al···C contacts range from 2.485(1) to 2.619(1) Å in one of the structures of $[(2,6-Mes_2C_6H_3)_2Al][B(C_6F_5)_4]^{35}$ and from 2.471(2) to 2.540(2) Å in the cyclohexene adduct $(C_6F_5)_3 Al \cdot (\eta^2 \text{-cyclo-}C_6H_{10})^{.36}$ As a result of the strong Al···C contacts the O-Al-O angle is reduced to 119.3(1)° from the expected 180° for a two-coordinate species. Similarly, the same Al...C contacts are also responsible for the rather long Al-O distances. There are no cation---anion interactions other than van der Waals contacts. The shortest H(cation)…Cl(anion) distance is 2.828 Å (Cl12···H27B), which is close to the sum of the van der Waals radii of H and Cl (2.85 Å).³⁷ The closest Al… Cl distance is 5.647 Å (Al1B···Cl8C). This is in stark contrast with e.g. $[Et_2Al][CH_6B_{11}Cl_6]$, which features rather short Al... Cl contacts (2.429 and 2.440 Å) and should be considered a tight ion pair.³⁸ Currently, no other donor-free monomeric main-group-metal phenolates bearing *m*-terphenyl groups are known. The related and isoelectronic alkaline-earth compounds $\{(2,6-Ph_2C_6H_3O)_2M\}_2$ (M = Mg, Ca, Sr, Ba) are dimeric with bridging phenolates, ArOM(μ -OAr)₂MOAr.³⁹ The large metals Ca, Sr, and Ba also feature secondary $M \cdots C(\pi)$ interactions involving the flanking phenyl groups, similar to the case for 6.

Attempts to obtain $[(2,6-tBu_2-4-MeC_6H_2O)_2Al][CHB_{11}Cl_{11}]$ (7) according to eqs 2 and 3 were unsuccessful. Only a small amount of Ph₃CH or Et₄Si was formed, and the main product was d_5 -tert-butylbenzene, t-BuC₆D₅. The small amounts of Ph₃CH and Et₄Si suggest that some 7 may have formed, which then initiated the *tert*-butyl transfer from 1 (or 7) to the solvent $(C_6H_6 \text{ or } C_6D_6)$. The resulting H⁺ or D⁺ could regenerate 7 to continue the cycle. However, despite numerous attempts we have not been able to identify the aluminum product(s). Attempted methyl abstraction from the related compounds $(2,6-tBu_2-4-MeC_6H_2O)_2$ AlMe and $(2,4,6-tBu_3C_6H_2O)_2$ AlMe with $[Ph_3C][B(C_6F_5)_4]$ also did not lead to the desired cationic species but to various unidentified products.⁴⁰ Although tert-butyl transfer was not observed in this case, it has been observed previously that tert-butyl phenols are sensitive to strong Lewis acids.^{27,41} In this context, it should also be mentioned that the ionic compound 6 experiences slow H/D exchange in C_6D_6 solution involving the aromatic hydrogens of the phenolate substituents. Residual toluene is also converted into C6D5CH3. These findings and the short intramolecular Al···C contacts in 6 are a testament to the high Lewis acidity of low-coordinate cationic aluminum diphenolates.

Reaction with CO₂. Although numerous coordination compounds of CO₂ are known,⁴² coordination through one of the weakly Lewis basic oxygens to form a linear η^1 complex such as L_nM-O=C=O is rare.⁴³ One example is an

electrophilic uranium(III) complex, in which the bulky ligand only allows end-on coordination of CO_2 .⁴⁴ As the diphenolate **2**, the triphenolate **4**, and the ionic species **6** possess similar characteristics, solutions of these compounds were exposed to an excess of CO_2 . However, no reaction was observed by ¹H and ¹³C{¹H} NMR spectroscopy. Addition of the bulky phosphine tBu_3P to these solutions led to the formation of new sets of signals in the case of **4** and **6**, whereas no reaction was observed for **2**. The combination of a bulky Lewis acid and a bulky Lewis base can lead to the formation of a frustrated Lewis pair (FLP).⁴⁵ Such species can possess remarkable properties, including the activation of dihydrogen at room temperature.⁴⁶

Addition of CO_2 to a solution of a 1:1 mixture of 4 and the bulky phosphine tBu_3P afforded the CO_2 adduct (2,6-Ph₂C₆H₃O)₃AlOC(O)PtBu (8) as a colorless crystalline solid in 55% yield. Compound 8 is stable up to its melting point of 137 °C in its solid form, but it partially dissociates into its starting materials upon dissolution into C_6D_6 or $CDCl_3$. Increase of the CO_2 partial pressure to about 1 atm increases the amount of dissolved 8 to approximately 50%. The relatively low yield for 8 is most likely due to the equilibrium detailed in eq 4. Compound 8 possesses the lowest solubility in the system and precipitates from the reaction mixture (toluene) in the presence of excess CO_2 .

$$(2,6-Ph_2C_6H_3O)_3AI + PtBu_3 + CO_2$$

4

$$(2,6-Ph_2C_6H_3O)_3AI-O \xrightarrow{O} PtBu_3$$

$$8$$
(4)

Since the first example of a CO₂ adduct derived from an FLP, $(C_6F_5)_3BOC(O)PtBu_3$,⁴⁷ a few examples of aluminum-based adducts have been described, including $(C_6F_5)_3AIOC(O)PtBu_3$ (A),⁴⁸ Me₂AICH₂PMe₂(μ -CO₂) (B),⁴⁹ and PhCH= CPMes₂(AltBu₂)(μ -CO₂) (C)⁵⁰ and the doubly substituted Mes₃PC(OAIX₃)₂ (D; X = Cl, Br, I)^{51,52} (Scheme 1).

In contrast to compound 8, species A-D are stable toward CO_2 loss in solution, although compound C loses CO_2 when heated at 135 °C under vacuum in the solid state. The crystal structure of 8 (Figure 2) shows a four-coordinate aluminum center surrounded by three phenolate ligands in a typical propeller-like fashion.

The fourth coordination site is occupied by the $tBu_3PC(O)$ -O- group. The Al-O_{phenol} distances with an average value of 1.710 Å are close to those reported for $(2,6-Ph_2C_6H_3O)_3Al\cdot L$ (L = Lewis base) compounds.^{53–55} The Al-OC(O)- distance is 1.819(2) Å, the O-C(O) distance is 1.287(4) Å, the C==O distance is 1.206(4) Å, and the (O)C-P distance is 1.906(3) Å. Despite the bulk of the phenolate substituents these values are very close to those observed for A (1.828, 1.289, 1.209, and 1.884 Å, respectively) and C (1.859, 1.280, 1.206, and 1.919 Å, respectively). The C==O stretching frequency for **8** (1708



Figure 2. Thermal ellipsoid plot (30%) of 8. Hydrogen atoms and the *o*-phenyl substituents have been omitted for clarity. Selected distances (Å) and angles (deg): Al(1)–O(1) = 1.716(3), Al(1)–O(2) = 1.707(3), Al(1)–O(3) = 1.708(2), Al(1)–O(4) = 1.819(2), O(1)–C(1) = 1.343(4), O(4)–C(55) = 1.287(4), O(5)–C(55) = 1.206(4), P(1)–C(55) = 1.906(3), P(1)–C(56) = 1.880(4), P(1)–C(60) = 1.873(4), P(1)–C(64) = 1.892(4); O(2)–Al(1)–O(1) = 113.37(13), O(3)–Al(1)–O(1) = 109.67(13), O(2)–Al(1)–O(4) = 105.42(13), O(1)–Al(1)–O(4) = 109.45(12), O(2)–Al(1)–O(4) = 102.42(13), O(3)–Al(1)–O(4) = 109.45(12), C(55)–O(4)–Al(1) = 112.6(2), O(5)–C(55)–O(4) = 128.9(3).

cm⁻¹) is higher than that for A (1686 cm⁻¹), which may account for the more facile CO_2 loss for 8.

Although a reaction was observed when tBu_3P was added to a solution of **6** and CO_2 in C_6D_6 , no product could be isolated, and this reaction is under current investigation.

Reduction of CO₂. We have shown previously that the strong Lewis acids $[Et_2Al][CH_6B_{11}X_6]$ (X = Cl, I) catalyzed the reduction of CO2 with Et3SiH, albeit rather slowly. We hypothesized that strong Lewis acids with robust Al-O bonds should be better catalysts. Although no interaction between the ionic species 6 and CO_2 could be detected, benzene solutions of 6 catalyzed the reduction of CO₂ with Et₃SiH. As we hoped, the reduction was faster, and the reaction mixture remained homogeneous. A solution of 6 and Et₃SiH (1/33) in C₆D₆ was exposed to excess CO₂ (ca. 1.3 atm), and the progress of the reaction was monitored by ${}^{1}H$ and ${}^{13}C{}^{1}H$ NMR spectroscopy. The addition of CO₂ led to a broadening and splitting of the o-Me signals of the phenoxy substituents in the ¹H NMR spectrum, indicating a chemical change. After 19 h at room temperature the methyl signals of 6 sharpened, and a small amount of C₆D₅CH₃ formed. Subsequent heating at 85 °C for 4 h resulted in the formation of more toluene as well as the appearance of Et₂SiH₂ (see below). More than 90% of Et₃SiH was consumed after 25 h at 85 °C, and the reaction was complete after another 24 h at 85 °C. The main product was $C_6D_5CH_3$ (60% of the silane hydrogen), followed by CH_4 (ca. 18%) and traces of $(C_6D_5)_2CH_2$ (ca. 2%). The formation of HD was also confirmed (ca. 14%). The silane products consisted of Et_4Si and various polysiloxanes, similar to the reductions catalyzed by $[Et_2Al][CH_6B_{11}X_6]$.¹¹ The reactions are summarized in Scheme 2, which is based on previous observations by Piers and us.^{8,11} The formation of Et_3SiOD has



not been observed directly, but it is implied by the formation of diphenylmethane and toluene. Furthermore, the alcoholysis of hydrosilanes with Lewis acid catalysis is well-known,⁵⁶ and the observation of HD can be traced back to the reaction of Et_3SiH with Et_3SiOD .

For comparison, the reductions catalyzed by $[Et_2A]$ - $[CH_6B_{11}X_6]$ required 10% catalyst loading (vs 3% for 6), 2.5 days (vs 2 days for 6), and CH₄ was the main product (70% of the silane hydrogen) followed by $C_6D_5CH_3$ (26%) and $(C_6D_5)_2CH_2$ (4%).

Whereas mixtures of $[Et_2AI][CH_6B_{11}X_6]$ and Et_3SiH remained unchanged at room temperature, mixtures of **6** and Et_3SiH (1/24.5) led to scrambling of the silane substituents to afford Et_4Si , Et_2SiH_2 , and even small amounts of $EtSiH_3$ after 7 days at room temperature. This may be an expression of the higher Lewis acidity of the cation in **6**, which is π coordinated to arenes but does not display the close cation…anion interactions of $[Et_2AI][CH_6B_{11}X_6]$. Furthermore, the ³*J* H– Si–CH₂ coupling in mixtures of **6** and Et_3SiH is lost, whereas the Et_3SiH ¹H NMR signal is unaffected by the presence of $[Et_2AI][CH_6B_{11}X_6]$. A similar loss of Si–H coupling was observed for mixtures of Et_3SiH and $B(C_6F_5)_3$ and was attributed to the equilibrium expressed in eq 5.⁵⁷ The analogous equilibrium involving **6** and Et_3SiH is given in eq 6. Et_3SiH + $B(C_6F_5)_3$ — Et_3SiH -B($C_6F_5)_3$

$$---$$
 [Et₃Si]⁺[HB(C₆F₅)₃]⁻ (5)

 $Et_3SiH + [Al(OAr^*)_2]^+ - [Et_3Si-H-Al(OAr^*)_2]^+$

$$\underbrace{} [Et_3Si]^+ + HAI(OAr^*)_2 \qquad (6)$$

The solution that was obtained after **6** and Et₃SiH were reacting with each other for 7 days was exposed to CO₂ as described previously, and broadening and splitting of the *o*-Me signals were observed after 21 h at room temperature. Heating at 82 °C for 1 h afforded some C₆D₅CH₃ and CH₄, and the reaction was practically complete after 10 h at 82–83 °C to give mainly C₆D₅CH₃ (50% of the silane hydrogen), followed by CH₄ (ca. 16%) and traces of (C₆D₅)₂CH₂ (1%) similar to the distribution using pure Et₃SiH as before. The silanes EtSiH₃ and Et₂SiH₂ were consumed before Et₃SiH, suggesting a higher reactivity for the former. The reduction of a second charge of CO₂ with Et₃SiH in this solution required twice as much time (23 h), possibly an indication of catalyst degradation.

Attempts to reduce CO_2 with Et₃SiH using the triphenolate 4, the CO_2 adduct 8, or combinations of 4 with 2,6-di-*tert*-

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butylpyridine or 2,6-lutidine (potential FLP's) as catalysts were unsuccessful.

CONCLUSIONS

Compound 6 is the first example of a donor solvent free cationic aluminum diphenolate, and the stabilizing intramolecular Al…C interactions are among the shortest ones that have been reported to date. The resulting high Lewis acidity of the aluminum center leads to the facile catalyzed scrambling of the Et₃SiH substituents at room temperature, and 6 is a more reactive catalyst than the previously reported tight ion pairs $[Et_2Al][CH_6B_{11}X_6]^{11}$ for the reduction of CO₂ with Et₃SiH to d_5 -toluene and CH₄. Unfortunately, catalyst 6 also suffers from deactivation during the CO₂ reduction, despite the large protecting phenolate substituents and the strong Al-O bonds. Potential improvements could be the use of even larger phenols such as 2,6-Dipp₂C₆H₃OH (Dipp = 2,6-*i*Pr₂C₆H₃-)⁵⁸ and the employment of a very bulky diprotic bidentate phenol based on the binaphthol or VAPOL⁵⁹ framework. The formation of the CO₂ adduct 8 is a testament to the high Lewis acidity of the $Al-O_3$ core in 4. On the other hand the failure of both 4 and 8 to catalyze the reduction of CO₂ with Et₃SiH may point toward the mechanism of this reaction. In one scenario, the Lewis acid will coordinate CO₂, and the base will attack the activated carbon to give the presumed primary product, $Et_3SiOC(O)H$. In the other scenario, one which is at work in the $B(C_6F_5)_3$ -catalyzed hydrosilylation of aldehydes and ketones, 57,60 the substrate activates the silane leading to hydride transfer to the Lewis acid, and this hydride reduces the substrate. On the basis of the observations that compound 6 catalyzes the scrambling of the substituents on Et₃SiH and that triphenolate 4 does not, possibly due to a combination of steric repulsion and lower Lewis acidity, it seems likely that the second scenario is at work. In the case of 6, the neutral aluminum hydride (2,6-Mes₂C₆H₃O)₂AlH would be the active intermediate during the CO_2 reduction (see eq 6). Future work will focus on the synthesis of this compound and the investigation of its chemistry.

EXPERIMENTAL SECTION

General Procedures. All work was performed under anaerobic and anhydrous conditions by using either modified Schlenk techniques or a Vacuum Atmospheres drybox. Solvents were freshly distilled under $N_{\rm 2}$ from sodium, potassium, or sodium/potassium alloy and degassed twice prior to use or they were dispensed from a commercial solvent purification system. The compounds 2,6-Mes $_2C_6H_3OH$, ¹² (2,6-*t*Bu $_2$ -4-MeC $_6H_2O$) $_2AlEt$ (1),¹⁵ and [Ph $_3C$][CHB $_{11}Cl_{11}$]⁶¹ were prepared according to literature procedures. All other reagents were obtained from commercial suppliers and used as received. NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. ¹H NMR chemical shift values were determined relative to the residual protons in C_6D_6 or $CDCl_3$ as internal reference (δ 7.16 or 7.26 ppm). ¹³C NMR spectra were referenced to the solvent signal (δ 128.39 or 77.0 ppm), ¹¹B NMR spectra to a solution of F_3B ·OEt₂ in C₆D₆ as external standard (δ 0 ppm), and ³¹P NMR spectra to a solution of Ph₃P in C₆D₆ as external standard (δ –6 ppm). The ATR-FTIR spectrum of 8 was collected on a Nicolet IR200 FT-IR spectrometer with ATR attachment (ATR = attenuated total reflection). GC/MS spectra were collected on an HP G1800GCD gas chromatograph. Melting points were determined in Pyrex capillary tubes sealed under nitrogen with a Mel-Temp apparatus and are uncorrected.

 $(2,6-Mes_2C_6H_3O)_2AIEt$ (2). A solution of AIEt₃ (0.10 g, 0.9 mmol) in hexanes (10 mL) was added dropwise to a suspension of 2,6-Mes₂C₆H₃OH (0.56 g, 1.7 mmol) in hexanes (20 mL) with cooling in an ice bath. A clear pale yellow solution was obtained after a few

minutes after the end of the alane addition. The mixture was warmed to room temperature and stirred for another 2 h. Concentration to 5-10 mL under reduced pressure afforded a fine colorless precipitate, which was redissolved by brief warming with a heat gun. After ca. 30 min at room temperature a crystalline solid began to separate. Cooling to -20 °C for 1 week afforded the product as a mixture of colorless very small and several large well-shaped crystals. Yield: 0.42 g, 69% based on 2,6-Mes₂C₆H₃OH. Mp: 254-258 °C. ¹H NMR (C₆D₆, 400.13 MHz): δ 6.89 (Å part of A₂B system, J = 7.8 Hz, m-H, 4H), 6.84 (B part of A₂B system, J = 7.8 Hz, p-H, 2H), 7.75 (s, m-H(Mes), 8H), 2.24 (s, p-CH₃, 12 H), 2.05 (s, o-CH₃, 24 H), 0.47 (t, J = 8.0 Hz, CH₂CH₃, 3H), -1.01 (q, J = 8.0 Hz, CH₂CH₃, 2H). ¹³C{¹H} NMR $(C_6 D_{6'} 100.61 \text{ MHz}): \delta 153.49 (i-C), 137.80 (o-C(Mes)), 137.53,$ 137.23, 130.59 (o-C), 130.38 (m-C), 130.30 (m-C(Mes)), 120.01 (p-C), 21.42 (p-CH₃), 21.03 (o-CH₃), 9.34 (CH₂CH₃), -5.40 (br, CH₂CH₃).

Reaction of Et₃Al with 2 equiv of 2,6-Ph₂C₆H₃OH. *Procedure* A. A solution of AlEt₃ (0.23 g, 2.0 mmol) in hexanes (6 mL) was added to a solution of 2,6-Ph₂C₆H₃OH (0.99 g, 4.0 mmol) in CH₂Cl₂ (20 mL) with cooling in an ice bath. After 30 min the ice bath was removed; the pale yellow solution was warmed to room temperature and after an additional 2 h concentrated to ca. 10 mL under reduced pressure. As no crystals formed after 4 days at -20 °C, the solution was concentrated further (ca. 5 mL), and a small amount of colorless crystals began to form after 2 h. Cooling at -20 °C for 5 days afforded a yellow crystalline solid, which was identified by NMR spectroscopy as $4 \cdot 1.8$ CH₂Cl₂. Yield 0.77 g, 0.89 mmol, 89% based on eq 7.

$$4\text{ArOH} + 2\text{AlEt}_{3} \rightarrow (\text{ArO})_{3}\text{Al} + \frac{1}{2}(\text{Et}_{2}\text{AlOAr})_{2}$$
$$+ 2\text{EtH}\uparrow$$
(7)

Removal of the volatiles from the mother liquor gave a foamy solid, which after crystallization from hot hexanes afforded a 1:9 mixture of 3 and $5.^{20}$

Procedure B. A solution of AlEt₃ (0.24 g, 2.0 mmol) in toluene (5 mL) was added to a solution of 2,6-Ph₂C₆H₃OH (1.01 g, 4.1 mmol) in toluene (10 mL) with cooling in an ice bath. After 30 min the ice bath was removed; the pale yellow solution was warmed to room temperature and after an additional 3 h concentrated to ca. 2 mL under reduced pressure. As no crystals formed overnight, hexanes (4 mL) was added, and pale yellow crystals of 4 began to form within 1 h at room temperature. Over a period of 4 weeks at room temperature a second batch of large (2 mm) colorless crystals appeared, which were identified as compound 5.²⁰ Combined yield: 0.83 g.

Comproportionation of 4 and 5. Solutions of 4 (23 mg, 30 μ mol) and 5 (11 mg, 16 μ mol) in C₆D₆ (0.5 mL each) were combined in a J. Young type NMR tube and heated at 86–87 °C in an oil bath for a combined 31 h followed by an additional 88 h at 133–136 °C. The reaction was essentially complete after the first 18 h at 135 °C. The solution was a mixture of mainly 3 (78%) and small amounts of unreacted 4 (6%) and 5 (15%) (see the Supporting Information). ¹H NMR (C₆D₆, 400.13 MHz) data for 3: δ 7.66 (d, *J* = 5.8 Hz, *o*-H(Ph), 8H), 7.23 (d, *J* = 7.6 Hz, *m*-H(C₆H₃), 4H), 6.99 (m, *m*- and *p*-H(Ph), 12H), 6.90 (t, *J* = 7.6 Hz, *p*-H(C₆H₃), 2H), 0.19 (t, *J* = 8.0 Hz, AlCH₂CH₃, 3H), -1.57 (q, *J* = 8.0 Hz, AlCH₂CH₃, 2H).

[(2,6-Mes₂C₆H₃O)₂AI][CHB₁₁Cl₁₁] (6). Procedure A. [Ph₃C]-[CHB₁₁Cl₁₁] (16 mg, 21 μ mol) was added to a solution of 2 (15 mg, 21 μ mol) in C₆D₆ (0.5 mL) inside a J. Young type NMR tube. The mixture was shaken briefly to afford a yellow-orange emulsion, from which a red-orange oil, [Ph₃C][CHB₁₁Cl₁₁], separated within minutes. The ¹H NMR spectrum of the colorless supernatant showed only traces of the expected side products Ph₃CH and ethane after 2 h. The reaction mixture was agitated by fastening the NMR tube to a horizontally aligned overhead stirrer and slowly rotating the tube. As after 21 h rotation only a very slight increase in the side products was observed, the reaction mixture was heated at 85 °C for 2 days in an oil bath. During this time the dense orange phase faded to pale yellow. The top layer was pipetted off, and the bottom layer was washed with

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 $C_6D_6~(0.2~mL)$ and dissolved in a $C_6D_6/C_6D_5Br~2/1$ mixture (0.5 mL).

Procedure B. A Teflon-capped Schlenk vial was charged with [Ph₃C][CHB₁₁Cl₁₁] (75 mg, 98 µmol), C₆D₆ (1.5 mL), and Et₃SiH (103 mg, 0.88 mmol), and the mixture was stirred for 22 h. During this time the yellow-orange trityl salt phase faded to almost colorless. The colorless top layer was pipetted off, and the oily bottom layer was washed with hexanes (1.5 mL) to afford the silvlium salt [Et₃Si]-[CHB₁₁Cl₁₁] as a yellowish sticky solid. A solution of 2 (70 mg, 98 μ mol) in toluene (1.5 mL) was added to the silvlium salt to give a twophase system as before. After the system was stirred overnight the bottom phase turned cloudy yellow-ocher. The mixture was heated at 65-75 °C for 6 h. The top layer was pipetted off, and the bottom layer was washed with C_6D_6 (0.8 mL). After 3 days at room temperature colorless thin plates of $6.2C_6H_6$ formed in both the oily layer and the washing. C_6D_6 (0.6 mL) was added to the crystals from the oily layer, and the mixture was heated at 80 °C for 3 h followed by crystallization for 2 days at room temperature. These crystals were used for the X-ray structure determination. The crystals obtained from the washing were used for the NMR spectroscopic analysis. They contained ca. 5.5 equiv of C₆D₅CH₃. ¹H NMR (C₆D₆, 400.13 MHz): δ 6.76 (m), 6.66 (s, m-H(Mes)), 2.63 (s, CHB₁₁Cl₁₁, 1H), 2.20 (s, p-CH₃, 12H), 1.60 (s, br, o-CH₃, 24H). The aromatic hydrogen signals could not be integrated because the hydrogens were partially replaced by deuterium. ¹³C{¹H} NMR (C₆D₆, 100.61 MHz): δ 149.30 (*i*-C), 143.38, 39.36, 21.65 (*p*- CH_3), 20.66 (br, o-CH₃). ¹¹B NMR (C₆D₆, 100.38 MHz): δ -2.21 (p-B, 1B), -9.67 (o- or m-B, 5B), -12.85 (o- or m-B, 5B).

Attempted Synthesis of $[(2,6-tBu_2-4-MeC_6H_2O)_2A]$ -[CHB₁₁Cl₁₁] (7). *Procedure A*. A J. Young type NMR tube was charged with [Ph₃C][CHB₁₁Cl₁₁] (10 mg, 13 µmol), C₆D₆ (ca. 0.5 mL), and 1 (7 mg, 14 µmol) inside a drybox. The mixture was shaken briefly to afford a yellow-orange emulsion, from which a red-orange oil, [Ph₃C][CHB₁₁Cl₁₁], separated within minutes. The reaction mixture was then sonicated for 2 h in an ultrasound bath. Since no visible change was observed, the NMR tube was stirred horizontally overnight with no visible change. NMR and GC-MS spectra showed the formation of d_5 -tert-butylbenzene (t-BuC₆D₅)⁶² and trace amounts of triphenylmethane. There were no NMR signals from the starting material, 1.

Procedure B. A J. Young type NMR tube was charged with [Ph₃C][CHB₁₁Cl₁₁] (20 mg, 26 μ mol), benzene (0.4 mL), and Et₃SiH (15 mg, 129 μ mol) inside a drybox. The reaction mixture was stirred horizontally for 1 h, giving a colorless oily phase. The mother liquor was pipetted off, and the silylium compound was washed with hexanes (2 × 0.3 mL) and benzene (0.5 mL). C₆D₆ (0.5 mL) and 1 (7 mg, 14 μ mol) were added, and the reaction mixture was rotated horizontally overnight, forming an insoluble colorless solid. NMR and GC-MS spectra of the supernatant showed the formation of *tert*-butylbenzene and tetraethylsilane. There were no NMR signals from the starting material, 1. Attempts to dissolve the solid residue in bromobenzene were not successful.

(2,6-Ph₂C₆H₃O)₃AlO(CO)PtBu₃ (8). A solution of 2,6-Ph₂C₆H₃OH (0.87 g, 3.5 mmol) in toluene (10 mL) was added dropwise to a solution of AlEt₃ (0.14 g, 1.2 mmol) in toluene (5 mL) at room temperature, leading to immediate gas evolution and a slight warming. After 1.5 h the pale yellow solution of 4 was added to solid tBu₃P to give a clear pale yellow solution. The reaction flask was evacuated and back-filled with dry CO2. After 15 min a fine colorless precipitate formed, and after another 1 h the CO2 uptake was complete. The stopcock was closed, and the precipitate was dissolved by brief heating with a heat gun. Within 2 h colorless crystals began to form (0.52 g). Concentration of the mother liquor to ca. 5 mL, followed by CO₂ addition and successive dissolution of the precipitate by brief heating, afforded another 0.13 g. Yield: 0.65 g, 55%, based on 2,6-Ph₂C₆H₃OH. Mp: 137–150 °C with gas evolution. ATR-FTIR: 1708 cm⁻¹ (st, $\nu_{C=0}$). Dissolution in C₆D₆ or CDCl₃ led to partial decomposition into 4, tBu₃P, and CO₂. Increase of the partial CO₂ pressure to ca. 1 atm increased the amount of dissolved 8 to approximately 50%. The NMR data for 8 are extracted from the spectra of the latter solution. ¹H NMR (C_6D_6 , 400.13 MHz): δ 7.70

(d, br, J = 6.4 Hz, o- or m-H, (Ph), 12H), 7.32 (m, obscured by 4), 7.13 (m, partially obscured by C_6D_5H), 6.88 (m, obscured by 4), 0.42 (d, $J_{HP} = 14.0$ Hz, $C(CH_3)_3$, 27H). $^{13}C\{^{1}H\}$ NMR (C_6D_6 , 100.61 MHz): δ 155.87 (d, $^{1}J_{CP} = 92.4$ Hz, PCO), 153.86 (*i*-C), 142.43 (quaternary C), 138.62 (quaternary C), 133.64 (quaternary C), 132.18, 130.72, 126.31, 119.09, 38.42 (d, $^{1}J_{CP} = 20.0$ Hz, $PC(CH_3)_3$), 30.13 (PC(CH₃)₃). $^{31}P\{^{1}H\}$ NMR (C_6D_6 , 161.97 MHz): δ 41.3. **Catalytic Reduction of CO₂.** A J. Young type NMR tube

containing 6 (3 μ mol, from procedure A), Ph₃CH (5 μ mol), Et₃SiH (16 μ L, 12 mg, 100 μ mol), and C₆D₆ (0.6 mL) was degassed by two freeze-pump-thaw cycles and filled with CO₂ at atmospheric pressure, with the bottom half of the NMR tube being cooled at ca. -60 °C. After 19 h at room temperature the ¹H NMR spectrum showed a change in the appearance of the o-Me signals (one sharp signal on top of a broad signal) and a weak signal at 4.85 ppm, which could be due to $H_2C(OSiEt_3)_2$ (5.01 ppm in $C_6D_5Br^8$). Heating at 83 °C for 4 h led to the formation of $C_6D_5CH_3$ (7 μ mol) and Et_2SiH_2 (12 μ mol). A small amount of methane (0.15 ppm) and a trace of HD (4.43 ppm, t, J_{HD} = 42.6 Hz) were also detected. After 25 h at 82–83 °C 90% of Et₃SiH was consumed, and after an additional 24 h at 82-83 °C the reaction was judged complete (99% Et₃SiH consumed). The reaction products were $C_6D_5CH_3$ (20 μ mol, 60% of silane hydrogen), $(C_6D_5)_2CH_2$ (1 µmol, 2% of silane hydrogen), CH₄ (4 µmol, 16% of silane hydrogen), and HD (14 μ mol, 14% of silane hydrogen). The amounts of both gases have been estimated using the Henry constants for solutions of both gases ($k_{\rm H}(\rm CH_4) = 0.021$ M/atm,⁶³ $k_{\rm H}(\rm H_2) =$ 0.0028 M/atm⁶⁴) in benzene and a gas volume of approximately 2 mL.

Catalytic Scrambling of Et₃SiH and Reduction of CO₂. A J. Young type NMR tube containing 6 (4 μ mol, from procedure B), Et₃SiH (16 μ L, 12 mg, 100 μ mol), and a 2/1 mixture of C₆D₆ and C₆D₅Br (0.6 mL) was monitored by multinuclear NMR spectroscopy over a period of 7 days. Within 5 h at room temperature the formation of Et₂SiH₂ and Et₄Si was detected, and after 19 h a small amount of EtSiH₃ formed. The mixture changed little over the 6 days at room temperature, and its composition was approximately EtSiH₃/Et₂SiH₂/ Et₃SiH/Et₄Si = 2.5/18/49/30.5.

CO₂ was added to the degassed sample as before, and the progress of the reaction was monitored by ¹H and ¹³C{¹H} NMR spectroscopy. The hydrosilanes were consumed (97%) after 11 h at 82–84 °C, and the products were C₆D₅CH₃ (17 μ mol, 51% of silane hydrogen), (C₆D₅)₂CH₂ (0.2 μ mol, 0.5%), CH₄ (4 μ mol, 16%), and HD (10 μ mol, 10% of silane hydrogen). More Et₃SiH (16 μ L, 12 mg, 100 μ mol) and CO₂ were added, and the mixture was heated at 83–87 °C. After 23 h 96% of the hydrosilane was consumed, and after an additional 24 h no more hydrosilane was detectable.

X-ray Crystallography. Crystals of 6.2C₆D₆ and 8 were grown as described above. The data were collected using a diffractometer with a Bruker APEX CCD area detector and graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å) at 100(2) K. The data were corrected for absorption by the empirical method,⁶⁵ and the structures were solved and refined using the SHELXS and SHELXL packages.⁶⁶ There were two formula units per asymmetric unit of the cell for $6.2C_6D_6$. The sample exhibited racemic twinning with a refined twin ratio of 0.41(3), as shown by the refined Flack parameter. The C-H location in one anion was disordered. The occupancies of atoms C1D, B4D, and Cl4D were refined to 0.860(4) and 0.140(4). Restraints on the positional parameters of the disordered atoms were required. The three tert-butyl groups on the phosphorus in 8 were disordered and refined with split occupancies. The occupancies for C57, C58, and C59 refined to 0.684(7) and 0.316(7), those for C61, C62, and C63 refined to 0.708(11) and 0.292(11), and those for C65, C66, and C67 refined to 0.761(12) and 0.239(12). Restraints on the positional and displacement parameters of the disordered atoms were required.

ASSOCIATED CONTENT

Supporting Information

Figures giving NMR data for compounds **2**, **3**, **6**, and **8** and the reduction of CO_2 catalyzed by **6**, X-ray tables, additional images of the structures of $6\cdot 2C_6D_6$ and **8**, and CIF files for $6\cdot 2C_6D_6$

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and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This paper is dedicated to Prof. Dr. Werner Uhl on the occasion of his 60th birthday. Financial support from the National Science Foundation (Grant CHE 0718446) is gratefully acknowledged.

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