J|A|C|S
ARTICLES

Efficient Chemoselective Carboxylation of Aromatics to Arylcarboxylic Acids with a Superelectrophilically Activated Carbon Dioxide−Al_2Cl_6/Al System

George A. Olah,* Béla Török,† Jens P. Joschek, Imre Bucsi, Pierre M. Esteves,
Golam Rasul, and G. K. Surya Prakash*

*Contribution from the Loker Hydrocarbon Research Institute and Department of Chemistry,
University of Southern California, University Park, Los Angeles, California 90089-1661*

Received June 3, 2002

Abstract: Aromatic carboxylic acids are obtained in good to excellent yield essentially free of diaryl ketones by carboxylation of aromatics with a carbon dioxide−Al_2Cl_6/Al system at moderate temperatures (20−80 °C). To optimize reaction conditions and study the reaction mechanism, experimental variables including temperature, amount of Al_2Cl_6/Al, various Lewis acids, role of metal additive, carbon dioxide pressure, etc. were studied. The carboxylation reaction was found to be stoichiometric rather than catalytic, with aluminum chloride forming a dichloroaluminate of carboxylic acids. Although the carboxylation takes place using $AlCl_3$ itself, the presence of metal additives, especially Al, increased the yield and selectivity of carboxylic acids. Because it was not possible to distinguish between two possible mechanistic pathways of the reaction on the basis of the experimental results, theoretical calculations using density functional theory (DFT) were also carried out. One possible pathway involves an initial complex between benzene and Al_2Cl_6, with subsequent formation of organoaluminum intermediates ($PhAlCl_2$ and $PhAl_2Cl_5$). The other proceeds through the formation of various complexes of CO_2 with aluminum chloride $(AlCl_3)_n$, $n = 1-4$. The calculations have shown that the organometallic pathway, leading eventually through the formation of phenylaluminum dichloride, is endothermic by 33 kcal/mol. In contrast, the preferred CO_2-AlCl_3 complex forms in an exothermic reaction (−6.0 kcal/mol) as does $CO_2AlCl_2^+$. On the basis of both experimental and calculational findings, the most feasible reaction mechanism proposed involves superelectrophilic aluminum chloride activated carbon dioxide reacting with the aromatics in a typical electrophilic substitution.

Introduction

Carbon dioxide as a greenhouse gas contributes significantly to global warming.[1] The Kyoto Treaty of December 1997 intends to restrict the emission of greenhouse gases.[2] Although carbon dioxide is one of these gases, its concentration in the air is only 0.0034%. However, its contribution to the overall greenhouse effect is close to 50%.[3]

The chemical fixation of carbon dioxide is a viable approach to mitigate excessive carbon dioxide preferably by transformation to valuable products. Although several methods are known for the chemical conversion of carbon dioxide, they are generally very energy demanding,[4] limiting the practicality of their use. Developing new methods for CO_2 fixation is thus highly desirable.[5]

One of the most versatile processes for carbon−carbon bond formation is Friedel−Crafts chemistry[6] such as alkylation and acylation. Friedel−Crafts acylation is the preferred method for the preparation of aromatic ketones.[6] Arylcarboxylic acids[7] are involved in important pharmaceuticals belonging to the family of nonsteroidal antiinflammatory drugs (NSAIDs), which are the most widely prescribed medications.[8−10]

---

* To whom correspondence should be addressed. E-mail: olah@usc.edu.

† Present address: Department of Chemistry, Michigan Technological University, 1400 Townsend Drive, Houghton, MI 49931.

(1) Bakker, D.; Watson, A. *Nature* **2001**, *410*, 765. Abelson, P. H. *Science* **2000**, *289*, 1293.

(2) Kyoto Protocol to the United Nations Framework Convention on Climate Change, 1997.

(3) Mintzer, I. M. Energy, Greenhouse Gases Climate Change. In *Annual Reviews of Energy*; Hollander, J. M., Socolow, R. H., Sternlich, D., Eds.; 1990; Vol. 15, p 513.

(4) Stocchi, E. *Industrial Chemistry*; Ellis Horwood: New York, 1990. Inoue, S., Yamazaki, N., Eds. *Organic and Bioorganic Chemistry of Carbon Dioxide*; Kodansha: Tokyo, Wiley: New York, 1982. Halman, M. M. *Chemical Fixation of Carbon Dioxide*; CRC Press: Boca Raton, 1993.

(5) Arakawa, H.; Aresta, M.; Armor, J. N.; Barteau, M. A.; Beckman, E. J.; Bell, A. T.; Bercaw, J. E.; Creutz, C.; Dinjus, E.; Dixon, D. A.; Domen, K.; DuBois, D.; Eckert, J.; Fujita, E.; Gibson, D. H.; Goddard, W. A.; Goodman, D. W.; Keller, J.; Kubas, G. J.; Kung, H. H.; Lyons, J. E.; Manzer, L. E.; Marks, T. J.; Morokuma, K.; Nicholas, K. M.; Periana, R.; Que, L.; Rostrup-Nielson, J.; Sachtler, W. M. H.; Schmidt, L. D.; Sen, A.; Somorjai, G. A.; Stair, P. C.; Stults, B. R.; Tumas, W. *Chem. Rev.* **2001**, *101*, 953.

(6) Olah, G. A., Ed. *Friedel−Crafts and Related Reactions*; Wiley: New York, 1964.

(7) (a) Olah, G. A.; Olah, J. A. In *Friedel−Crafts and Related Reactions*; Olah, G. A., Ed.; Wiley: New York, 1963; Vol. III, Chapter XXXIX, p 1257. (b) Simonetta, M.; Carrá, S. In *The Chemistry of Functional Groups: The Chemistry of Carboxylic Acids and Esters*; Patai, S., Ed.; Wiley: Chichester, New York, 1969; Chapter 1, p 1. Ogliaruso, M.; Wolfe, J. F. In *The Chemistry of Functional Groups: Synthesis of Carboxylic Acids and Their Derivatives*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1991; p 1. (c) Ito, T.; Sugahara, N.; Kindaichi, Y.; Takami, Y. *Nippon Kagaku Kaishi* **1976**, 353. (d) Suzuki, Y.; Hattori, T.; Okuzawa, T.; Miyano, S. *Chem. Lett.* **2002**, 102.

(8) Geis, G. S. *J. Pharmacol.* **1999**, *56*, 31.

(9) (a) Fryers, G. *Aspirin-Towards 2000, Proc. Int. Meeting Sponsored by Eur. Aspirin Foundation*; Royal Society of Medicine: London, 1990. (b) Weissmann, G. *Sci. Am.* **1991**, *264*, 84. Patrono, C. *N. Eng. J. Med.* **1994**, *330*, 1287.

10.1021/ja020787o CCC: $22.00 © 2002 American Chemical Society

The most desirable route for the synthesis of arylcarboxylic acids would be the direct use of carbon dioxide. Friedel and Crafts themselves observed that a minor amount of benzoic acid was formed when carbon dioxide was bubbled through a mixture of aluminum chloride and benzene heated to the boiling point of the latter.[11] A small amount of hydrogen chloride evolved simultaneously. They suggested the following path, involving the initial formation of phenylaluminum dichloride.[11]

$$C_6H_6 + Al_2Cl_6 \rightarrow C_6H_5Al_2Cl_5 + HCl$$

$$C_6H_5Al_2Cl_5 + CO_2 \rightarrow C_6H_5COOAl_2Cl_5$$

$$C_6H_5COOAl_2Cl_5 + H_2O \rightarrow C_6H_5COOH + Al_2Cl_5OH$$

Many previous attempts to make the reaction practical have failed. Pressures of 50−60 bar at 80−150 °C were used in obtaining benzoic acid, *p*-chlorobenzoic acid, *p*-toluic acid, or 2,4-dimethylbenzoic acid from the corresponding aromatics in low yields. In the reactions, however, secondary reaction products such as benzophenones and diphenylmethanes were formed in major amounts.[7a]

Carbon dioxide in the presence of aluminum chloride reacts more readily with the electron-rich oxygenated aromatics. However, complex mixtures are formed. Thus, phenol and carbon dioxide in the presence of aluminum chloride give 2,4- or 4,4′-dihydroxybenzophenone, salicylic acid, aurin, or diphenyl ether by variation of the temperature and pressure. Cresols yield products of similar type. With the more reactive phenols, zinc or ferric chloride can replace aluminum chloride as the catalyst. Dimethylaniline gives tetramethyl-*p*,*p*′-diaminodiphenylmethane and some *p*-dimethylaminobenzoic acid.[7a] The only relatively successful results were achieved with ferrocene derivatives.[7c] Naphthalenes, anthracenes, and phenanthrenes have given the corresponding carboxylic acids in poor yields.[7d]

In our previous work using superacidic conditions, aromatics such as benzene with carbon dioxide gave mainly benzophenone, indicating that any intermediate benzoic acid formed under the reaction conditions reacts further, thus benzoylating excess benzene.[12a]

Despite all attempts,[13−17] no satisfactory conditions were, however, found for the direct carboxylation of aromatics with carbon dioxide to arylcarboxylic acids, and this remained a long-standing challenge.

We now report the first efficient and chemoselective preparation of aromatic carboxylic acids by direct superelectrophilic carboxylation of benzene, and some of its mono-, di-, and trisubstituted derivatives with the carbon dioxide−$AlCl_3$/Al reagent system.

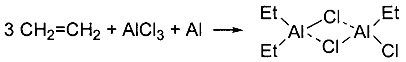
Table 1. Carboxylation of Benzene with CO_2 in the Presence of $AlCl_3$/Al (57 atm CO_2, 18 h)

benzene mL	$AlCl_3$/Al (g/g)	*T* °C	product yield (%) benzoic acid	benzophenone	di-phenyl methane	other[b]
20	10/1.2	120		41		
10	10/1.2	120		15	18	25
10	2.5/0.6	110		35		
10	2.5/0.6	90	9	29		
10	2.5/0.6	80	27	9		
40	2.5/0.6	70	88			
20	2.5/0.6[a]	70	62	6	13	

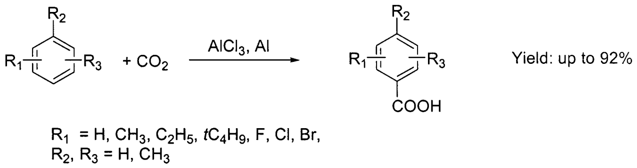
[a] Reaction time: 68 h. [b] Other − unidentified higher M_w products.

Results and Discussion

The impetus for the use of the $AlCl_3$/Al system came by the early work of Hall and Nash in the late 1930s, who found that ethylene when reacted with $AlCl_3$/Al gave ethylaluminum sesquichloride.[18] In our studies of such organoaluminum systems, reaction with carbon dioxide gave carboxylic acids, including methyl malonic acid.[12]



After screening many carbon dioxide−Lewis acid halide systems, we pursued the carboxylation of benzene by the aluminum trichloride−aluminum system in detail.



We systematically investigated a number of experimental variables such as reaction temperature, time, and catalyst−reactant ratio. Representative results are tabulated in Table 1.

It was found that, at more elevated temperatures (studied up to 120 °C), no benzoic acid could be observed, and benzophenone and diphenylmethane were the only isolable products. Benzoic acid initially formed clearly is further transformed by its Friedel−Crafts benzoylation of excess benzene to benzophenone and then by an ionic hydrogenation pathway to diphenylmethane (Table 1). However, lower temperatures resulted in a gradual increase in yield of the benzoic acid. Benzoic acid became significant at 90 °C and was formed exclusively at 70 °C. According to these results, several benzene derivatives were studied in detail in their carboxylation reaction. The optimized results are summarized in Table 2.

The results show that the direct carboxylation could be carried out at moderate temperatures in good to excellent yields, without the formation of a significant amount of diaryl ketones, which are readily formed at higher temperatures. It is also important to note that with more active substrates such as mesitylene, carboxylation to the corresponding acid (80% yield) takes place even at 20 °C.

---

(10) (a) Ito, Y.; Kato, H.; Yasuda, S.; Kato, N.; Yoshida, T.; Yamamoto, Y. Y. Japanese Patent, JP 92-279165 19920925; *Chem. Abstr.* **1994**, *121*, 255669. (b) Ito, Y.; Kato, H.; Yasuda, S.; Kato, N.; Yoshida, T.; Ueshima, M. Japanese Patent, JP 92-216666 19920723; *Chem. Abstr.* **1994**, *121*, 133985.

(11) (a) Friedel, C.; Crafts, J. M. *Compt. Rend.* **1878**, *86*, 1368. (b) Friedel, C.; Crafts, J. M. *Ann. Chim. Phys.* **1883**, *14*, 433.

(12) (a) Olah, G. A.; Farooq, O.; Farnia, S. M. F.; Bruce, M. R.; Clouet, F. L.; Morton, P. R.; Prakash, G. K. S.; Stevens, R. S.; Bau, R.; Lammertsma, K.; Suzer, S.; Andrews, L. *J. Am. Chem. Soc.* **1988**, *110*, 3231. (b) Olah, G. A.; Prakash, G. K. S.; Rasul, G. *Arkivoc* **2002**, 7.

(13) Morgan, G. T.; Pratt, D. D. *Br. Pat.* **1930**, *353*, 464.

(14) Fumasoni, S.; Collepardi, M. *Ann. Chim.* **1964**, *54*, 1122.

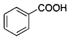
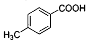
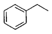
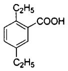
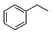
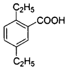
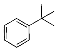
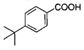
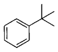
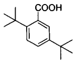
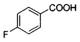
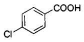
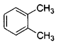
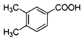
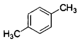
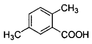
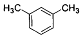
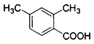
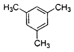
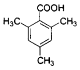
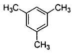
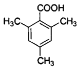
(15) Lebedev, B. L.; Pastuhova, I. V.; Eiduc, Y. T. *Izv. Akad. Nauk, Ser. Khim.* **1972**, *4*, 967.

(16) Bottacio, G.; Chiusoli, G. P.; Felicioli, M. G. *Gazz. Chim. Ital.* **1973**, *103*, 105.

(17) Kouwenhoven, H. W.; van Bekkum, H. In *Handbook of Heterogeneous Catalysis*; Ertl, G., Knözinger, H., Weitkamp, J., Eds.; Wiley-VCH: New York-Weinheim, 1997; Vol. 5, p 2358.

(18) (a) Hall, F. C.; Nash, A. W. *J. Inst. Pet. Technol.* **1937**, *23*, 679. (b) Hall, F. C.; Nash, A. W. *J. Inst. Pet. Technol.* **1938**, *24*, 471.

Table 2. Carboxylation of Benzene and Substituted Aromatics with a $CO_2/AlCl_3/Al$ System (57 atm CO_2 and 18 h Reaction Time)

Reactant	T °C	Major Product	Yield[a] %	Selectivity (%)
	70		88	-
	60		69	*o*/*m*/*p* 7/3/90
	40		79	see Scheme 1
	20		40[b]	see Scheme 1
	40		46	see Scheme 1
	20		25[b]	see Scheme 1
	40		47	*o*/*m*/*p* 1/1/98
	60		45	*o*/*m*/*p* 3/2/95
	40		89	11/89[c]
	40		85	91
	40		92	-
	40		83	-
	20		80[b]	-

[a] Isolated yields. [b] 68 h reaction time. [c] 2,3-Dimethylbenzene carboxylic acid/3,4-dimethylbenzene carboxylic acid.

The amount of the acid formed in the carboxylation reaction was found to be dependent on the amount of Al_2Cl_6/Al used. Although carboxylic acid formation was also observed without the added Al metal, addition of Al powder to the system increased the yield of the carboxylic acids significantly. Deactivated aromatics such as halobenzenes gave lower yields, whereas nitrobenzene gave only some byproducts but no carboxylic acid.

Alkylbenzenes tend to isomerize (disproportionate) when treated with anhydrous aluminum chloride, decreasing the yield of the expected carboxylic acids. In some cases, when the starting aromatic compound underwent isomerization or disproportionation, the formation of derived substituted aromatic carboxylic acids was observed (Scheme 1). In the case of bromobenzene, only exclusive disproportionation took place.[19] The product distribution in the reaction of *tert*-butylbenzene indicates that disproportionation and the formation of di-*tert*-butylbenzene are faster than carboxylation. Di-*tert*-butylbenzene is more reactive than the monosubstituted compound. The reactivity difference between the mono- and di-*tert*-butylbenzene is the determining factor for the product distribution (Scheme 1).

To learn more about the carboxylation reaction and to find optimized conditions, we extended the study to several other variables such as the nature and amount of the acid, role of metal additives, etc. First, the effects of several Lewis and Brønsted acids were tested. The results are tabulated in Table 3.

Scheme 1

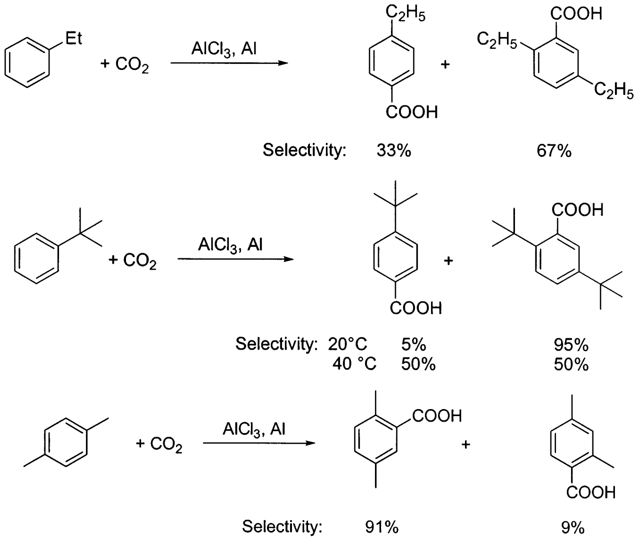
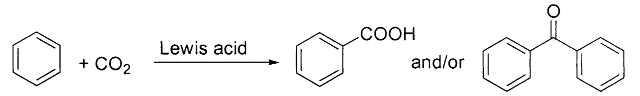


Table 3. Effect of Different Lewis and Brønsted Acids on the Carboxylation of Benzene with CO_2 (57 atm CO_2)



acid	*T* (°C)	yield[a] (%)	product selectivity acid	ketone	other products
$AlCl_3$	80	50	100	0	
$AlBr_3$	80	57	85	15	
SbF_5	40				phenol (5%)

[a] For acid, based on 1:1 $AlCl_3$:product ratio.

Despite the wide range of solid and liquid Lewis and Brønsted acids tested, it was found that except for aluminum halides none of the other acids ($TiCl_4$, $FeCl_3$, $FeBr_3$, $GaCl_3$, $Ga(OTf)_3$, CF_3SO_3H, K-10, Nafion-H) were able to promote the effective carboxylation reaction. A small amount of phenol was isolated in the reaction with SbF_5 most likely as a result of oxidation. Using $TiCl_4$ at higher temperature (150 °C), we obtained a small amount of diphenylmethane derivatives, while the other acids were inactive. Except for the isomerization and the cracking reactions, no carboxylic acid formation was observed. Because aluminum chloride itself is also inactive in its hydrated forms ($AlCl_3{\cdot}H_2O$ to $AlCl_3{\cdot}6H_2O$), it became clear that the optimum range of acid catalysts for the reaction is very narrow.

The effects of reaction time and the amount of Al_2Cl_6/Al were also studied to learn more about the nature of the reaction. The carboxylation of toluene, which can be carried out at lower temperature due to the more active nature of toluene, was selected to test the reaction. The results are shown in Figures 1 and 2.

The yield of *p*-toluic acid continuously increases with the reaction time; after 12 h, however, the increase becomes very slow, and after 18 h the curve turns to saturation. This indicates that the reaction reached its maximum yield, and further extension in reaction time does not result in further enhancement of the yield. On the basis of this, the effect of the amount of $AlCl_3/Al$ was studied in 18 h long reactions. As Figure 2 demonstrates, the amount of carboxylic acid produced approximately linearly increases with the amount of aluminum chloride. This observation strongly suggests that the reaction

---

(19) Olah, G. A.; Tolgyesi, W. S.; Dear, R. E. A. *J. Org. Chem.* **1962**, *27*, 3441.

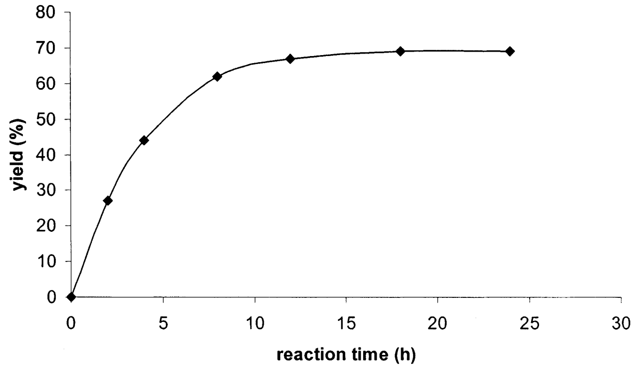


Figure 1. Effect of reaction time on carboxylation of toluene to *p*-toluic acid with CO_2 in the presence of $AlCl_3$/Al (56 atm CO_2, 20 mL of toluene, $T = 60$ °C).

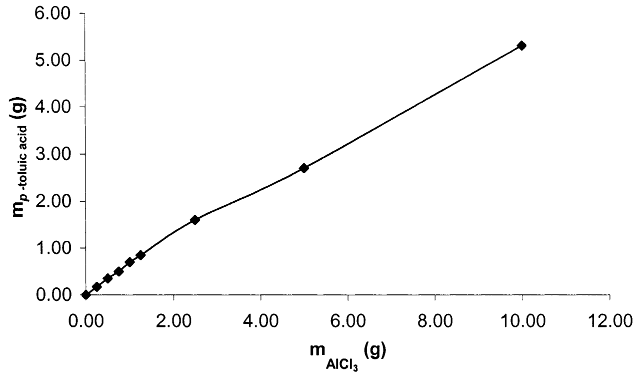


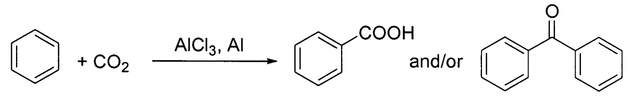
Figure 2. Effect of amount of $AlCl_3$/Al on carboxylation of toluene to *p*-toluic acid with CO_2 (57 atm CO_2, 20 mL of toluene, $T = 60$ °C, $AlCl_3$/Al molar ratio = 1).

similar to most Friedel–Crafts acylation reactions is of stoichiometric nature. Another observation, that the yields calculated on the basis of the reactant:$AlCl_3$ = 1:1 ratio never exceed the theoretical 100% (the yield is usually ~80%), also supports the above suggestion. Therefore, the $AlCl_3$/Al system is considered to be a reagent in this system rather than a catalyst. Consequently, the yields of carboxylic acids were calculated on the basis of the 1:1 $AlCl_3$:product ratio.

Screening various solvents for the reaction, we found that the best solvents are an excess of the aromatic compounds themselves. Efforts to increase the yields and the selectivity toward carboxylic acid formation using other solvents, however, failed. Benzophenone is formed selectively but in low yield (9%) in supercritical CO_2. Common organic hydrocarbons underwent transformations such as isomerization or disproportionation and were not found to be inert under the reaction conditions. Because it is known that $AlCl_3$ even at relatively modest temperatures initiates isomerization and cracking of common solvents, these observations were expected.[19]

The effect of the pressure of carbon dioxide on the reaction was, however, significant. The reactions were carried out under the usual experimental conditions with only the CO_2 pressure changed. Significant changes were observed both in yield and in selectivity. The data are summarized in Table 4.

Table 4. Effect of CO_2 Pressure on the Yield and Selectivity of Carboxylation of Benzene with CO_2 in the Presence of a $AlCl_3$/Al System



m_{AlCl_3} (g)	m_{Al} (g)	T (°C)	benzene (mL)	CO_2 (atm)	product	yield (g)	yield[a] (%)
1.25	0.3	80	20	7	benzophenone	0.9	53
1.25	0.3	80	20	14	acid/ketone 65/35	0.72	~60
1.25	0.3	80	20	29	acid/ketone 85/15	0.75	~65
1.25	0.3	80	20	57	benzoic acid	1.0	88

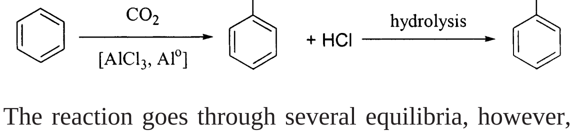
[a] Based on 1:1 $AlCl_3$:product ratio.

The results unambiguously show that a gradual increase in initial carbon dioxide pressure (measured at room temperature, before reaction) resulted in significant enhancement both in overall yield and in selectivity of benzoic acid. At an initial CO_2 pressure (57 atm), pure benzoic acid could be isolated in good yield. In contrast, at the lowest CO_2 pressure (7 atm) studied, benzophenone was isolated in only a moderate yield.

The Al-halides/Al system appears to be very important in initiating the reaction. As mentioned earlier (Table 3), aluminum halides ($AlCl_3$, $AlBr_3$) themselves are able to initiate the carboxylation of aromatics, albeit in lower yields and selectivities. In view of our earlier study on superelectrophilic ":$AlCl_2$" species generated from $AlCl_3$ and Al,[12] it was decided to study the role of aluminum and other added metals in the case of the carboxylation of *m*-xylene. The results are summarized in Table 5.

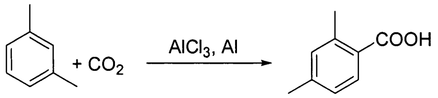
As shown, $AlCl_3$ itself produced the 2,4-dimethylbenzoic acid in only moderate yield. Addition of metallic Mg in a 1:1 molar ratio slightly increased the yield. However, in contrast with the metal-free reaction, wherein the product was obtained as a brown oil and needed further purification, Mg addition into the system resulted in a pure product. In the case of addition of Zn to $AlCl_3$, similar observations were made; however, the yields are considerably higher. The most significant effect was observed using metallic aluminum as an additive. Adding aluminum in a 1:1 molar ratio greatly increased the systems' efficiency; the product was formed in a very high yield and chemoselectivity. Gradually increasing the Al/$AlCl_3$ ratio to 2 and eventually 3, we obtained yields exceeding 100% (based on $AlCl_3$). Thus, added metallic aluminum has a significant role including leaching HCl formed in the system to form an excess of aluminum chloride in situ.

The overall reaction can be described as follows:



The reaction goes through several equilibria, however, and involves HCl formation. The role of Mg and Zn is to shift these equilibria into the product formation by binding the HCl formed. However, unlike $AlCl_3$, Mg or Zn halides are not able to initiate the carboxylation reaction. In contrast, with the added aluminum, the metal reacts with the HCl to form aluminum chloride in situ that is able to initiate further carboxylation. One cannot distinguish between the yield-enhancing effect and HCl binding. However, yields higher than 100% strongly suggest that formation of aluminum chloride from metallic aluminum takes place, giving unexpectedly high yields of carboxylic acids.

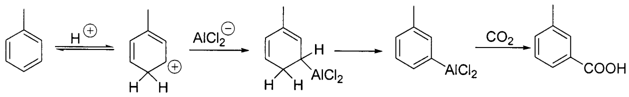
Table 5. Effect of Metal Additives on the Yield of Carboxylation of *m*-Xylene with CO_2 in the Presence of a $AlCl_3$/Metal System (57 atm CO_2)



metal	$AlCl_3$/metal mole ratio	*T* (°C)	*m*-xylene (mL)	time (h)	yield[a] (%)
	N/A	40	20	20	42
Mg	1:1	40	20	20	46
Zn	1:1	40	20	20	69
Zn	1:3	40	20	20	59
Al	1:1	40	20	20	92
Al	1:2	40	20	20	104
Al	1:3	40	20	20	111

[a] Based on 1:1 $AlCl_3$:product ratio.

Scheme 2



Furthermore, the effect of HCl itself on the system was determined by adding up to 21 atm of HCl gas. No carboxylation was observed. When air or oxygen (21 atm) was added, no benzoic acid was formed; however, a small amount of phenol was isolated. In experiments under 6 and 2 atm of air pressure, benzoic acid was obtained in 28 and 32% yields, respectively. This indicates that, although the added gas (air or O_2) decreased the yields, they were not able to suppress the carboxylation reaction. The $AlBr_3$/Al system shows similar features to the $AlCl_3$/Al system.

The mechanism of the $AlCl_3$-initiated direct carboxylation reaction of aromatics is open for discussion since the first original explanation offered by Friedel and Crafts 120 years ago. There are alternate pathways to be considered to account for the observed reaction of aromatics with carbon dioxide.

A possible reaction path would involve protonation of the aromatic hydrocarbon by the $HCl-AlCl_3$ (formed from H_2O impurities and $AlCl_3$) superacidic system and subsequent quenching of the arenium ion by $AlCl_3OH^-$ anion as an $AlCl_2^-$ equivalent. This is similar to Kovacic's amination reaction using ClN_3-AlCl_3[20] (Scheme 2).

According to this reaction path, *m*-toluic acid should be formed from toluene. However, this is not the case. Our experimental data clearly show (Table 2) that *p*-toluic acid is formed with high selectivity. In addition, the reaction does not occur in the presence of excess HCl gas. As a result, the protolytic benzene activation by the superacidic $HCl-AlCl_3$ system as a pathway can be clearly ruled out.

The other alternative routes are (i) the formation of an organoaluminum compound ($PhAlCl_2$ and its $AlCl_3$ complexes) and its subsequent reaction with CO_2 and (ii) activation of carbon dioxide by aluminum chloride and its electrophilic attack on the aromatic ring.

In their original paper,[11] Friedel and Crafts already proposed the possibility of an organometallic pathway, the formation of phenylaluminum dichloride as an intermediate.[11] We carefully studied the behavior of arylaluminum species such as triphenyaluminum and its derivatives, phenylaluminum dichloride and phenylaluminum dibromide, as possible intermediates under the reaction conditions. The results are summarized in Table 6.

Table 6. Reaction of Phenylaluminum Compounds with Carbon Dioxide

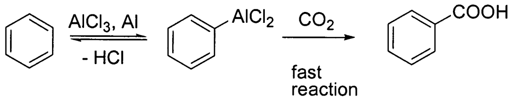
reactant	solvent	*T* °C	products (%)[a] benzoic acid	biphenyl	phenol
Ph_3Al	benzene	80	25	23	1
Ph_3Al	hexane	80	65		
$PhAlCl_2$	benzene	80	35		
$PhAlCl_2$	ether	80	traces		5
$PhAlCl_2$	hexane	80	92		2
$PhAlCl_2$	hexane	RT	57		
$PhAlBr_2$	benzene	80	41		
$PhAlBr_2$	hexane	80	93		2
$PhAlBr_2$	hexane	RT	59		

[a] Isolated yields.

As shown, Ph_3Al readily reacts with CO_2 to form benzoic acid in both benzene and hexane solution, although the yields are only moderate. As a major byproduct, biphenyl was obtained in benzene. It is, most likely, the product of a side reaction between the reactant and solvent. In hexane solvent, no biphenyl was formed. These data are in agreement with the literature reports.[21] We prepared the proposed intermediate $PhAlCl_2$ (obtained as a dimer)[22] and treated it with CO_2 in different solvents. Using benzene as a solvent, we found that the question arises that $PhAlCl_2$ still may act as a Lewis acid and react with excess benzene under the experimental conditions. This was avoided by carrying out the reaction in hexane. In hexane, an excellent yield of benzoic acid was obtained (92%). In this case, the solvent cannot react with the Lewis acid; the product acid is formed as a result of CO_2 insertion into the C$-$Al bond.

According to the above-mentioned results, we cannot, however, entirely rule out the intermediacy of $PhAlCl_2$ in the carboxylation reaction. Therefore, experiments were carried out to detect the presence of $PhAlCl_2$ in the reaction mixture. First, $AlCl_3$ and then $AlCl_3$/Al were heated in benzene at 80 °C for 20 h under argon pressure. After cooling, the remaining solid was filtered off under an inert atmosphere, and the liquid sample was studied. After removal of benzene, a small amount of solid was obtained that was dissolved in C_6D_6, and its ^1H NMR spectrum was recorded. None of these samples, however, showed any evidence for the presence of $PhAlCl_2$ in the reaction mixtures. Unlike the formation of ethylaluminum-sesquichloride reported by Hall and Nash,[18] benzene does not react with $AlCl_3$/Al mixtures to produce phenylaluminum derivatives.

We were not able to detect $PhAlCl_2$ or $PhAlBr_2$ as an intermediate in the reaction by NMR; however, its concentration could be very low in equilibria. The sensitivity of NMR is generally low, and therefore it may not be possible to observe species in very low concentrations. Experimental results obtained with $PhAlCl_2$ and $PhAlBr_2$ show that the reaction of CO_2 with these organoaluminum compounds is a fast reaction. Thus, the failure to observe the intermediate by NMR in the reaction mixture is not sufficient to rule out this path.



---

(20) (a) Kovacic, P.; Levisky, J. A. *J. Am. Chem. Soc.* **1966**, *88*, 100. (b) Kovacic, P.; Levisky, J. A. *J. Am. Chem. Soc.* **1966**, *88*, 1000. (c) Kovacic, P.; Lowery, M.; Field, K. W. *Chem. Rev.* **1970**, *70*, 639. (d) Strand, J. W.; Kovacic, P. *J. Am. Chem. Soc.* **1973**, *95*, 2977.

Some of the experimental data seem to support this pathway as the reaction does not take place in the presence of excess HCl, and air (or oxygen) has some detrimental effect on it (organoaluminum compounds are known to be air sensitive[21]).

The second pathway would involve the activation of carbon dioxide by complexation with the acid (either by a Lewis or a Brønsted acid). The linear O═C═O molecule, however, has to bend significantly to develop an empty p-orbital on the carbon. A weak, Lewis acid complexation would leave CO_2 still mostly linear. As compared to NO_2^+, which is also linear, but more polarizable, CO_2A^+ would not be an efficient carboxylating agent in its own right.[23] However, the formation of a rearranged $CO_2-Al_2Cl_6$ complex or the superelectrophilic activation of carbon dioxide by Al_2Cl_6 could result in a reasonably active carbon dioxide-aluminum chloride species to react with aromatic hydrocarbons. To study these possibilities, density functional theory (DFT) studies on the activation process were carried out. Both possible pathways were computed using the density functional theory (DFT) method.

Aluminum chloride is known to dimerize in noncoordinating solvents[24] and in the gas phase[25] up to temperatures of 440 °C. At temperatures between 440 and 800 °C, it is a mixture of the monomer and the dimer. On the basis of this behavior, $AlCl_3$ is expected to be a dimer in the benzene solution. By the method of isothermal distillation, aluminum chloride was found to be present as a dimer (Al_2Cl_6) in a saturated solution in benzene at room temperature.[26] Nevertheless, it is known that the interaction of benzene with aluminum chloride could lead to the formation of a weak π-complex between benzene and monomer $AlCl_3$.[27] Support for this claim comes especially from the solubility measurements of aluminum chloride in aromatic solvents.[28] Kim et al. have shown, by ab initio calculations, that the benzene−$AlCl_3$ complex is a minimum on the potential energy surface (PES), thus being a possible (stable) intermediate in this media.[27] Their calculations indicate that this species consists of an oriented π-complex, where one of the carbon atoms of benzene interacts with the aluminum atom of the $AlCl_3$. π-Complexes of aromatics were not considered to be intermediates in the Friedel−Crafts reactions.[7a] However, there is increasing evidence that in certain electrophilic aromatic substitutions of the Friedel−Crafts type, the transition state may be represented as an oriented π-complex.[29]

Nevertheless, the above-mentioned ab initio studies on this system considered the interaction of the only monomeric $AlCl_3$ with a single benzene molecule, and this may not be a realistic model for processes in solution.

To represent a more probable situation, the complexes of benzene with the monomeric as well as dimeric aluminum chloride were calculated at the DFT B3LYP/6-311+G*//B3LYP/6-31+G* level. Further solvation by a second benzene molecule was also taken into account in the cases where solvation effects could be significant (Figure 3).

Figure 3 illustrates the optimized geometries of the structures found as minima on the PES of benzene and $AlCl_3$ and Al_2Cl_6. Species **1** is the oriented π-complex, similar to the one predicted by Kim et al.,[27] but with a second benzene molecule solvating the system. Structures **2** and **3** represent, respectively, the complexes of Al_2Cl_6 with benzene, while structures **4** and **5** correspond to the organoaluminum compounds hypothetically formed as intermediates in the reaction.

Structure **2** represents the bridged Al_2Cl_6 solvated by two benzene molecules. This species keeps basically the same structure of the isolated bridged Al_2Cl_6 (Figure 4), as expressed by the small changes in the geometric parameters.

This indicates that the solvation of the bridged Al_2Cl_6 in benzene is due mainly to dispersive (van der Waals) forces. It is known that aluminum chloride, in the absence of HCl, does not react with aromatic hydrocarbons.[30] However, complexes of benzene and Al_2Br_6 are formed and can even be crystallized.[31] Crystal structure obtained by X-ray diffraction for the benzene−Al_2Br_6 complex[31] is similar to our computed complex **2** by the present DFT calculations.

Structure **3** is also predicted to be a minimum on the PES, corresponding to the complex formed between benzene and the monobridged Al_2Cl_6. In this complex, the aluminum chloride dimer acts as an activated Lewis acid, interacting with the π-system of benzene. The second benzene molecule solvates the complex essentially by long-range interactions, as expressed by the interatomic distances of this molecule to the benzene−Al_2Cl_6 complex, roughly 3.3 Å (Figure 3). This is essentially complex **1**, which is further complexed by a second $AlCl_3$ molecule (forming the monobridged structure). The further complexation of the π-complex (structure **1**) by another $AlCl_3$ molecule giving **3** promotes a stronger interaction of the electrophilic aluminum atom with the π-system, as expressed by the shorter interatomic distance Al−C of this complex (2.273 Å). The analogous interatomic distance in structure **1** is 2.420 Å. This indicates that the $AlCl_3$ is being superelectrophilically activated by the second $AlCl_3$ molecule.[34] This species is predicted to be an oriented π-complex, because the electrophilic center, which coincides with the aluminum atom in $AlCl_3$, lies on the top of a carbon atom in the benzene molecule. The π-complex between benzene and a monobridged Al_2Br_6 was previously proposed by Brown et al.[32] to explain the instability of the intermediate Al_2Br_6:C_6H_6 observed by several experimental methods. The relative enthalpies of the complexes **1**−**5** and other isomeric systems of interest are shown in Table 7.

It can be seen that the most stable species is the Al_2Cl_6 sandwiched by two benzene molecules, that is, structure **2**. Such

---

[21] (a) Eisch, J. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 1, p 555. (b) Eisch, J. J. In *Comprehensive Organometallic Chemistry*, 2nd ed.; Abel, E. W., Wilkinson, G., Stone, F. G. A., Eds.; Pergamon Press: Oxford, 1995; Vol. 1, p 431.

[22] Grosse, A. V.; Mavity, J. M. *J. Org. Chem.* **1940**, *5*, 106.

[23] Olah, G. A.; Rasul, G.; Aniszfeld, R.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1992**, *114*, 5608.

[24] (a) Norris, J. F.; Rubinstein, D. *J. Am. Chem. Soc.* **1939**, *61*, 1163. (b) Mao, X.; Xu, G. *Huaxue Wuli Xuebao* **1988**, *1*, 347. (c) Smirnov, V. V.; Perlovskaya, O. R. *Zh. Fiz. Khim.* **1998**, *72*, 1092. (d) Mains, G. J.; Nantsis, E. A.; Carper, W. R. *J. Phys. Chem. A* **2001**, *105*, 4371.

[25] Aarset, K.; Shen, Q.; Thomassem, H.; Richardson, A. D.; Hedberg, K. *J. Phys. Chem. A* **1999**, *103*, 1644.

[26] Nagy, F.; Dobis, O.; Litvan, G.; Telcs, I. *Acta Chim. Acad. Sci. Hung.* **1959**, *21*, 397.

[27] (a) Tarakeshwar, P.; Lee, J. Y.; Kim, K. S. *J. Phys. Chem. A* **1998**, *102*, 2253. (b) Tarakeshwar, P.; Kim, K. S. *J. Phys. Chem. A* **1999**, *103*, 9116. (c) Tarakeshwar, P.; Kim, K. S. *J. Phys. Chem. A* **1999**, *103*, 11486.

[28] Fairbrother, F.; Scott, N.; Prophet, H. *J. Chem. Soc.* **1956**, 1164.

[29] (a) Olah, G. A.; Kuhn, S. J.; Flood, S. H. *J. Am. Chem. Soc.* **1961**, *83*, 4571. (b) Olah, G. A.; Kuhn, S. J.; Flood, S. H. *J. Am. Chem. Soc.* **1961**, *83*, 4581.

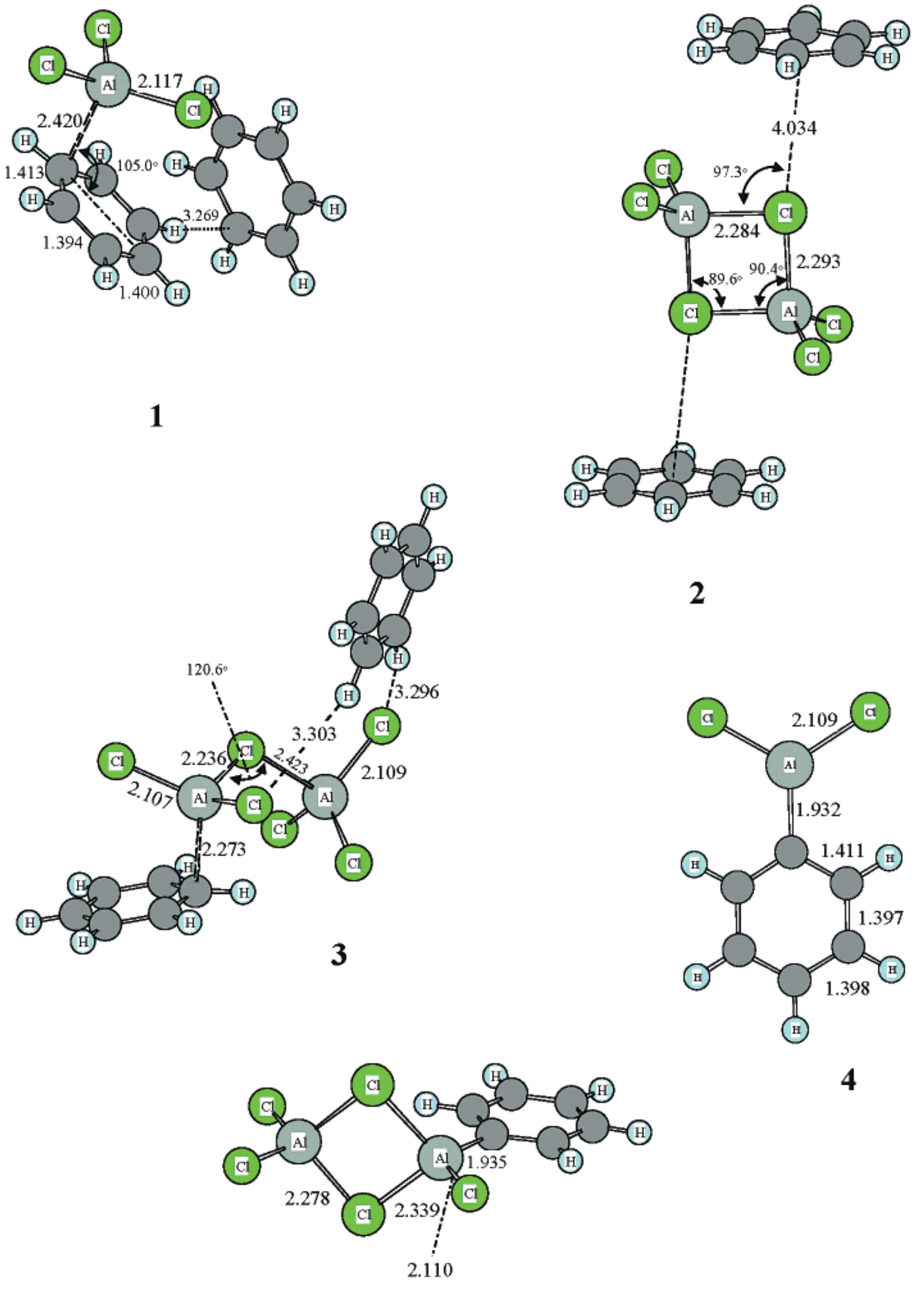
[30] Brown, H. C.; Pearsall, H. W.; Eddy, L. P.; Wallace, W. J.; Grayson, M.; Nelson, K. L. *Ind. Eng. Chem.* **1953**, *45*, 1462.

[31] Eley, D. D.; Taylor, J. H.; Wallwork, S. C. *J. Chem. Soc.* **1961**, 3867.

[32] Brown, H. C.; Wallace, W. J. *J. Am. Chem. Soc.* **1953**, *75*, 6265.

[33] Ryzhva, G. L.; Zibareva, L. N.; Bratchikov, A. V.; Slizhov, Y. G.; Nekhoroshev, V. P. *Zh. Fiz. Khim.* **1980**, *54*, 3275.

[34] Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 767.



1

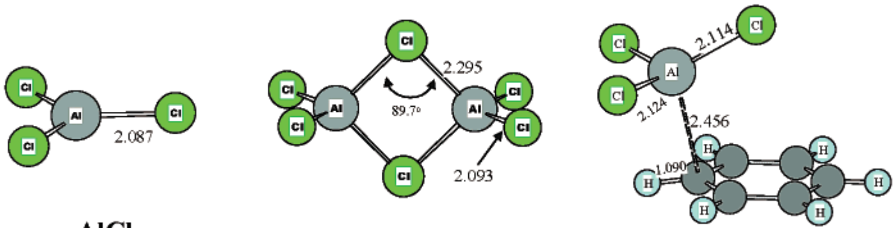
2

3

4

5

Figure 3. Optimized geometries of **1**−**5** at the B3LYP/6-31+G* level.



$AlCl_3$

Al_2Cl_6

C_6H_6:$AlCl_3$

Figure 4. Optimized geometries, at B3LYP/6-31+G* level, for monomeric and dimeric aluminum chloride, and for the π-complex 1:1 with benzene.

species were previously identified by X-ray structure determination of crystals formed from $AlBr_3$ and benzene.[31] Equilibria data of benzene with $AlCl_3$ indicate that the ΔH and ΔS of complex formation are −3.23 kcal/mol and −6.41 cal/mol K,

Table 7. Reaction Enthalpies (298.15 K and 1 atm) for the Equilibria Involving Aluminum Chloride and Benzene, Calculated at B3LYP/6-311+G*//B3LYP/6-31+G* + ZPE Level

reaction	ΔH_o (298.15 K) (kcal/mol)
$Al_2Cl_6 + 4C_6H_6 = (2) + 2C_6H_6$	−2.4
$Al_2Cl_6 + 4C_6H_6 = 2\ (1)$	8.6
$Al_2Cl_6 + 4C_6H_6 = (3) + 2C_6H_6$	5.4
$Al_2Cl_6 + 4C_6H_6 = (4) + (1) + HCl + C_6H_6$	48.7
$Al_2Cl_6 + 4C_6H_6 = (5) + HCl + 3C_6H_6$	35.2
$Al_2Cl_6 = 2AlCl_3$	20.5

Table 8. Relative Energies (298.15 K and 1 atm) for the Complexes Involving Aluminum Chloride and Benzene, Calculated at B3LYP/6-311+G*//B3LYP/6-31+G* + ZPE Level

isomer	relative energy ($\delta\Delta H_o$ 298.15 K) (kcal/mol)
$Al_2Cl_6 + 4C_6H_6$	2.4
2 (1)	11.0
$(2) + 2C_6H_6$	0.0
$(3) + 2C_6H_6$	7.8
$(4) + (1) + HCl + C_6H_6$	51.1
$(5) + HCl + 3C_6H_6$	37.6

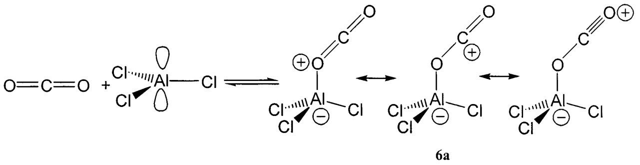
respectively.[33] Our calculations for the enthalpy of interaction between aluminum chloride with benzene giving **2** gave a value of −2.4 kcal/mol, thus being in good agreement with the experimental value of −3.23 kcal/mol. Interaction energies of various structural possibilities are given in Table 8.

It is shown that the interaction of benzene with monomeric $AlCl_3$ giving **1** is endothermic by 8.6 kcal/mol, significantly higher than the experimental value. Nevertheless, **2** is not expected to be an effective Lewis acid to react with CO_2 because the π-orbital of aluminum atoms is involved in bonding with the chlorine atoms. This led us to conclude that this species is significantly involved in the media, due to its high stability. However, its involvement in the reaction is unlikely; there are possible preequilibria involving other species. This species could be either the monobridged species **3** (as the nonionized or intimate pair of $AlCl_2^+{\cdot}AlCl_4^-$) or the organometallic complex **4**. Our DFT results indicate that a thermodynamically favorable species, the monobridged cluster **3**, could be involved in a preequilibrium and is 7.8 kcal/mol less stable than species **2**. The organometallic complex **5** ($PhAl_2Cl_5$) is 37.6 kcal/mol higher in energy than **2**, which suggests that this pathway is energetically unfavorable.

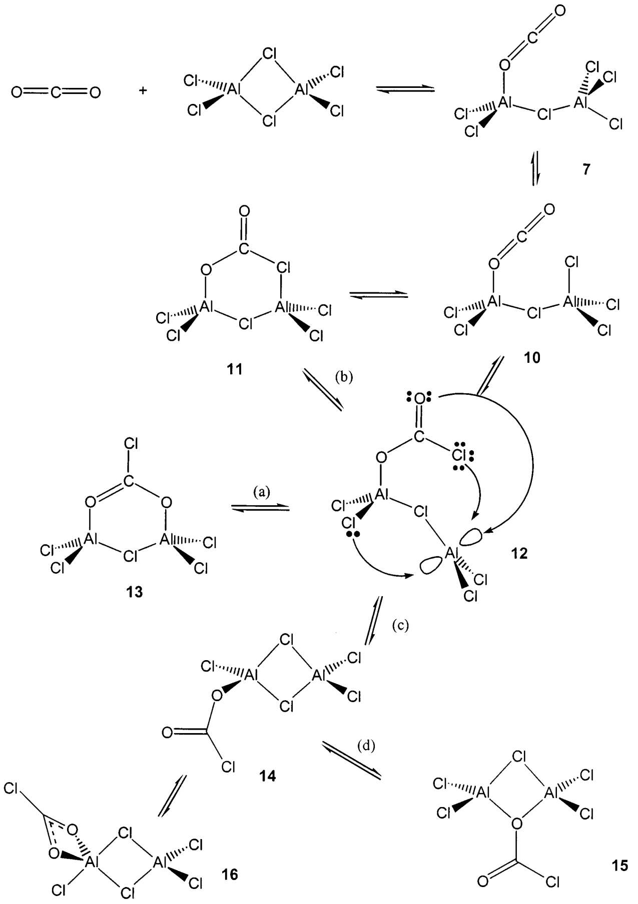
Besides the benzene−$AlCl_3$ interaction, aluminum chloride complexation with CO_2 in aromatics could also lead to an activated intermediate, which could react with the aromatic hydrocarbons. To obtain better insight into the activation process, the possible interactions of CO_2 with aluminum chloride were studied at the B3LYP/6-311+G*//B3LYP/6-311+G* level. As a first approach, we investigated the interactions of CO_2 with the $(AlCl_3)_n$ species ($n = 1-4$). We focused, however, on the interaction of CO_2 with the monomeric ($AlCl_3$) and the dimeric (Al_2Cl_6) aluminum chloride, because these species are known to exist in these solutions.

The study of the system indicates that the equilibria involving CO_2 and the monomer ($AlCl_3$) and the dimer (Al_2Cl_6) of aluminum chloride, shown respectively in Schemes 1 and 2, are feasible. The first possibility deals only with the complex formation between monomeric aluminum chloride with CO_2 (Scheme 3)

Scheme 3. Complex Formation by the Interaction of CO_2 with Monomeric $AlCl_3$



Scheme 4. Equilibria Involving CO_2 and Al_2Cl_6 Dimer



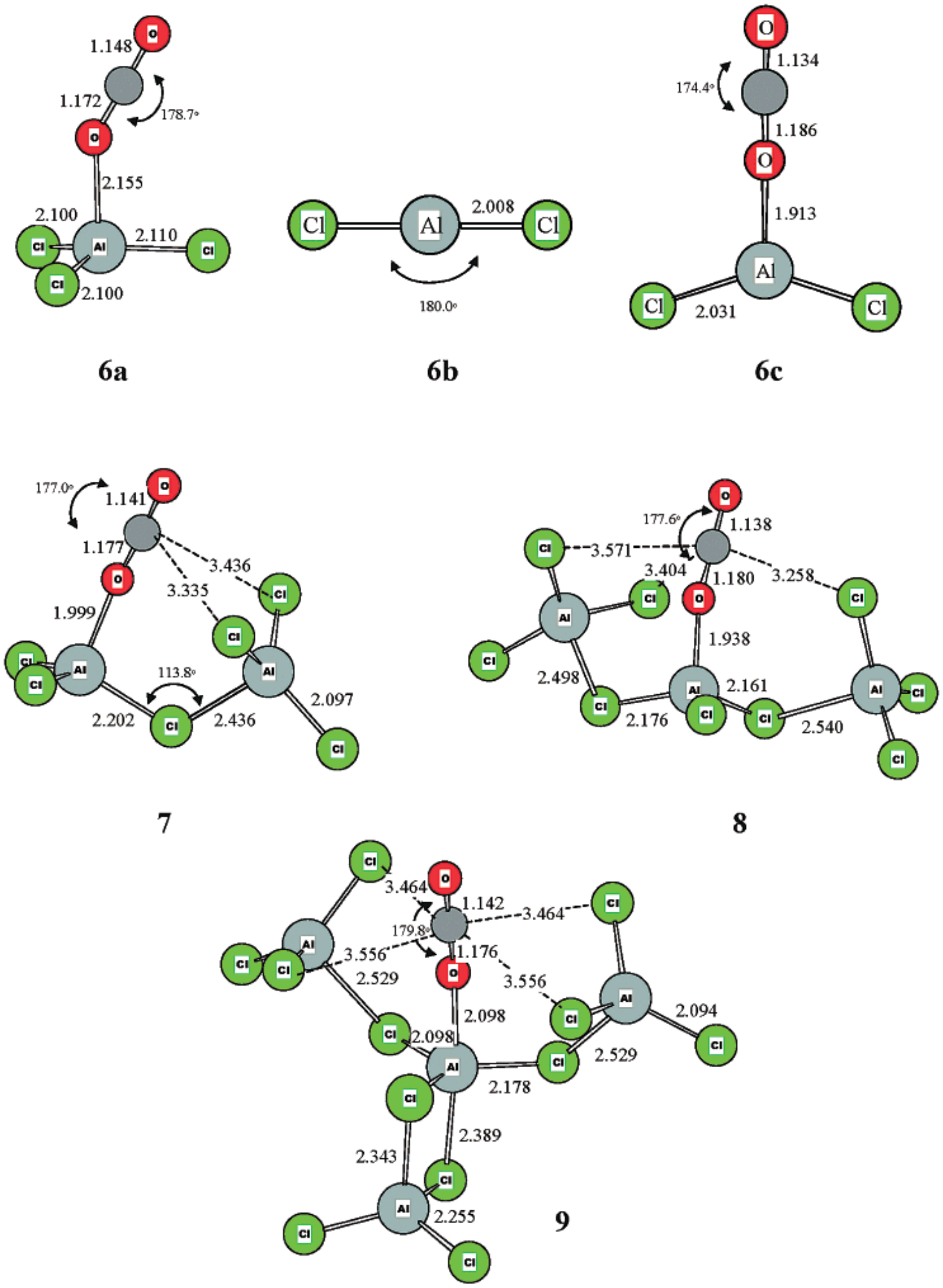
The interaction of CO_2 with the dimeric Al_2Cl_6 shows a more complex picture, with the formation of different possible intermediates (Scheme 4).

Complexation of CO_2 with $AlCl_3$ leads to the O-coordinated structure $Cl_3Al{-}O{=}C{=}O$ (**6a**), which was found to be a stable minimum (Figure 5).

Linear CO_2 becomes slightly bent in complex **6a**, with the bond angle of 178.7°. The Al−O bond distance in structure **6a** is 2.155 Å. The C−O ($AlCl_3$) and C−O bond distances are 1.172 and 1.147 Å, respectively, only 0.011 Å longer and 0.014 Å shorter than C−O bond length in CO_2. Enthalpy of complex formation for this case was found to be exothermic by 6.0 kcal/mol (Table 9).

Superelectrophilic activation[34] of the complex **6a** by aluminum chloride is possible. To investigate this possibility, calculations of **6a** further complexed with one or two $AlCl_3$ molecules were investigated. This would decrease the back-donation (Scheme 5) of the nonbonded electron pairs of the chlorine atoms to the aluminum, increasing the electron deficiency of the empty p-orbital on the carbon.

This would enhance the electrophilicity of the carbon atom, leading to superelectrophilic activation (Scheme 6).



6a **6b** **6c**

7 **8**

9

Figure 5. Optimized geometries of complexes formed by interaction of $(AlCl_3)_n$, $n = 1-4$, with CO_2 at the B3LYP/6-311+G* level.

Table 9. Calculated Enthalpies of Complexation of CO_2 with $(AlCl_3)_n$, $n = 1-4$, and $^+AlCl_2$ at 298 K (B3LYP/6-311+G*//B3LYP/6-311+G* + ZPE level)

reaction	ΔH_{rel} (298 K) (kcal/mol)	$\nu_{CO,terminal}$ (cm^{-1})	$\nu_{CO,complexed}$ (cm^{-1})
$CO_2 + AlCl_3 \rightarrow CO_2{\cdot}AlCl_3$ (**6a**)	−6.0	2448	1383
$CO_2 + {}^+AlCl_2 \rightarrow CO_2{\cdot}AlCl_2^+$ (**6c**)	−27.5	2488	1397
$CO_2 + Al_2Cl_6 \rightarrow CO_2{\cdot}Al_2Cl_6$ (**7**)	+5.9	2468	1397
$CO_2 + Al_3Cl_9 \rightarrow CO_2{\cdot}Al_3Cl_9$ (**10**)	+6.8	2476	1388
$CO_2 + Al_4Cl_{12} \rightarrow CO_2{\cdot}Al_4Cl_{12}$ (**11**)	+2.4	2464	1373
CO_2	-*x*-	2464	1373

Figure 6 shows the optimized geometries of the $(AlCl_3)_n$ ($n = 1-4$) aluminum chloride clusters.

Geometries of these complexes show interesting features. In all of the $CO_2{\cdot}(AlCl_3)_n$ ($n = 1-4$) complexes, the Al−O bond length does not change significantly. In all of the cases, the CO_2 molecule is just slightly bent in the complexes, as expressed by the O═C═O bond angle of 178.7°, 177.0°, 177.6°, and 179.8°, respectively, for species **6a**, **7**, **8**, and **9**. The structure of the $CO_2{\cdot}(AlCl_3)_4$ complex is interesting, because the aluminum atom expands its valence to accommodate one extra pair of electrons from one of the chlorine atoms, becoming pentacoordinated. Pentacoordinated aluminum is also a feature predicted for the $(AlCl_3)_3$ and $(AlCl_3)_4$ clusters (Figure 6).

Scheme 5. Valence Bond Representation of Back-Donation of Nonbonded Electrons of Chlorine to the Aluminum Atom

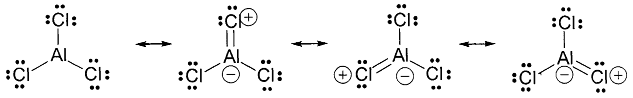


Table 9 shows the enthalpies of complex formation between CO_2 and $AlCl_3$, Al_2Cl_6, Al_3Cl_9, and Al_4Cl_{12} at 298.15 K and C═O vibrational bands for each complex.

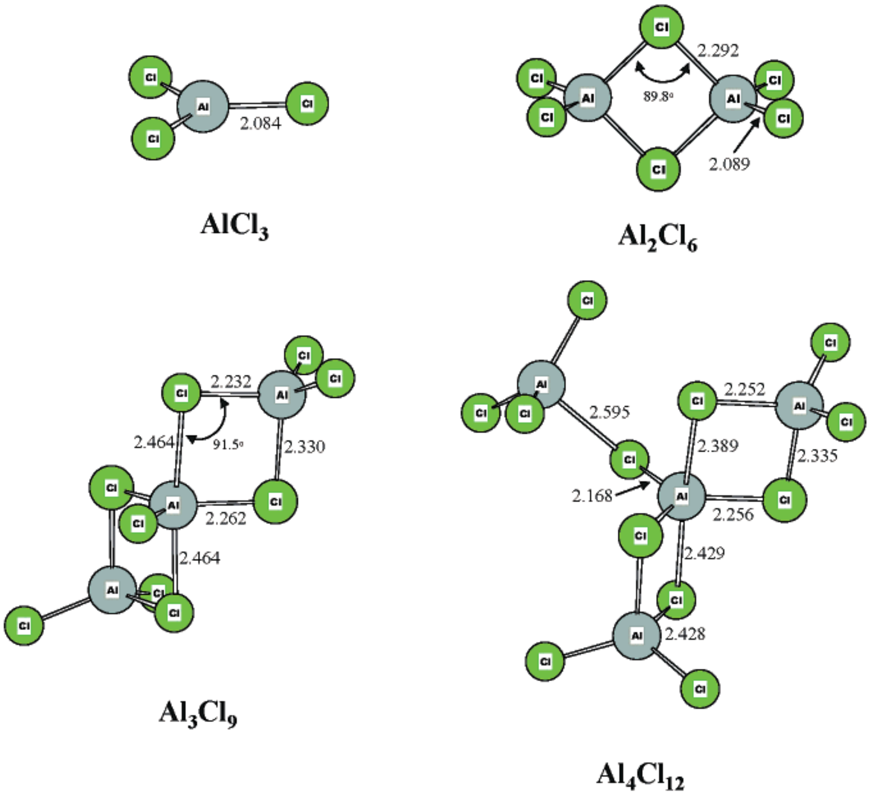
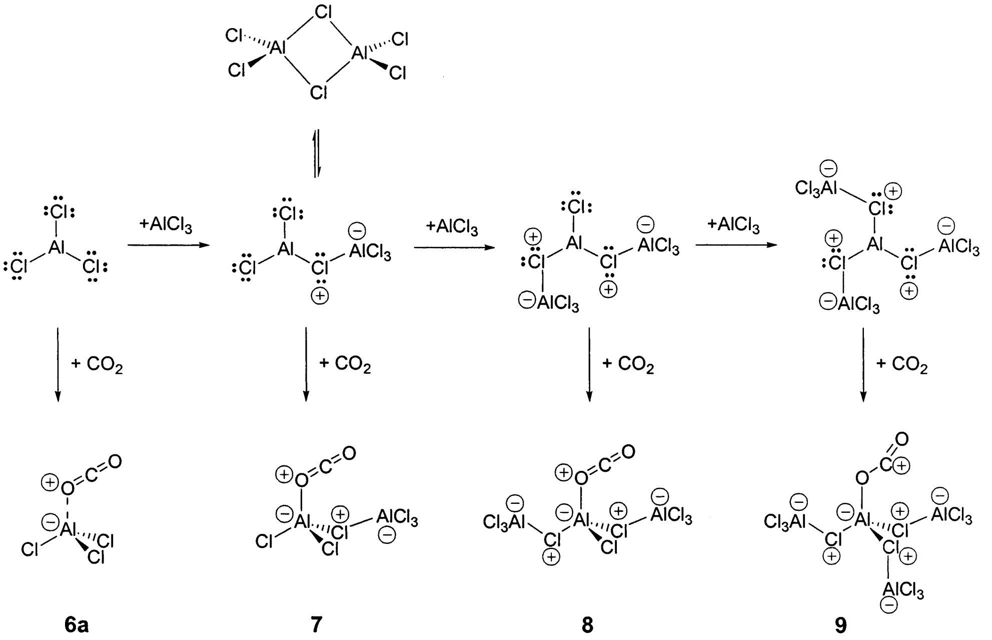


Figure 6. Optimized geometries of $AlCl_3$, Al_2Cl_6, Al_3Cl_9, and Al_4Cl_{12} at the B3LYP/6-311+G* level.

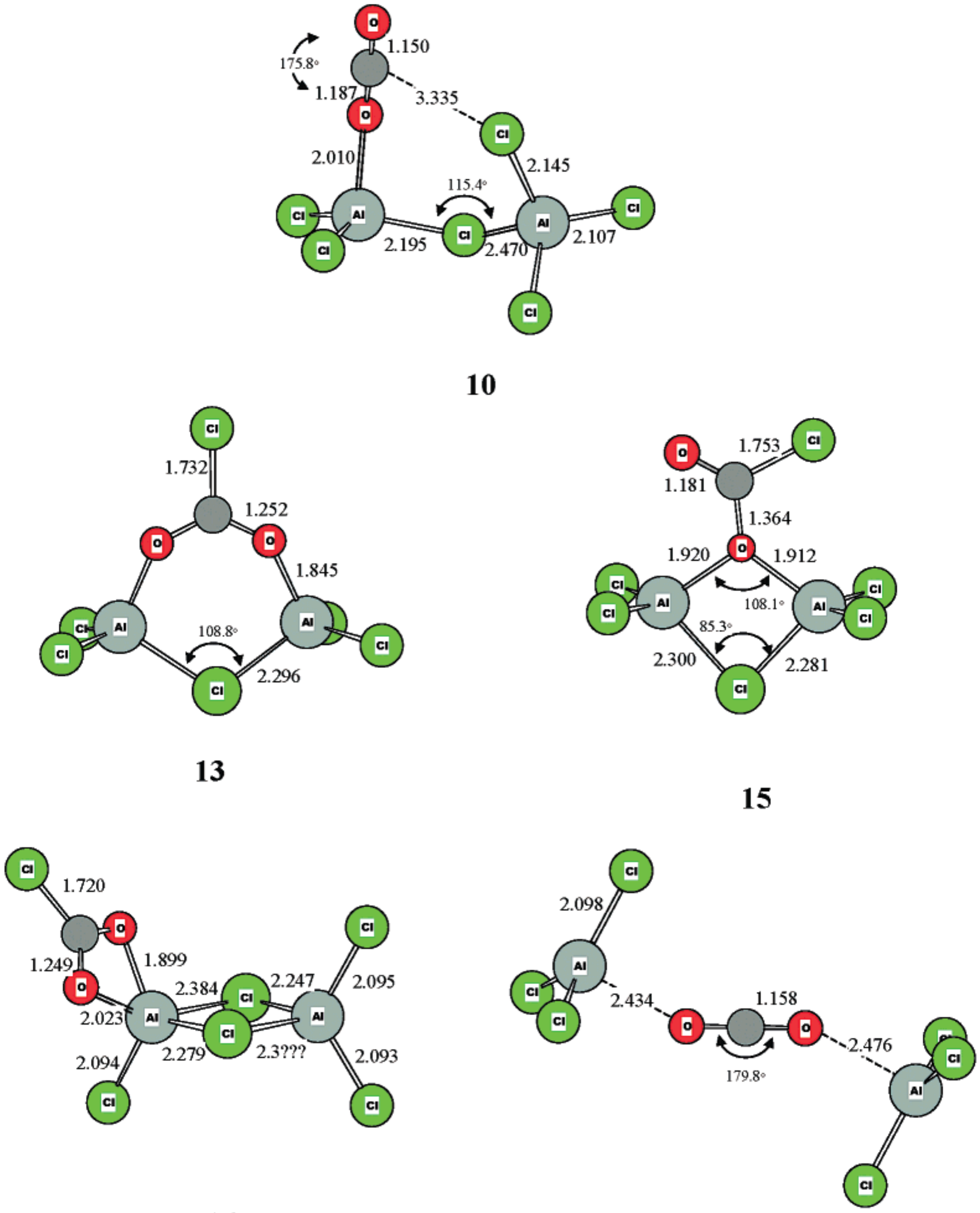
Scheme 6. Possible Activation of CO_2 by Superelectrophilic Aluminum Chloride



It can be seen that the CO_2 complexation is an endothermic reaction in all cases, except the reaction involving monomeric $AlCl_3$ or $^+AlCl_2$ species. Dimeric aluminum chloride, however, is also capable of ionizing under suitable conditions.

$$Al_2Cl_6 \rightleftharpoons {}^+AlCl_2 + AlCl_4^-$$

$^+AlCl_2$ is a doubly electron-deficient superelectrophile, and its interaction with carbon dioxide was also calculated. The Al−Cl bond distance in optimized structure **6b** is 2.008 Å. Complexation of CO_2 with **6b** leads to O-coordinated structure **6c**, which was found to be a minimum. Carbon dioxide remains linear in the C_{2v} symmetric complex **6c**. The Al−O bond distance in **6c** is 1.913 Å. This is much shorter than the Al−O distance in **6a** (2.155 Å) (Figure 5). Enthalpy of complex formation from CO_2 and **6b** was found to be exothermic by 27.5 kcal/mol. The complex formation between neutral $(AlCl_2)_2$ and CO_2 was also calculated; however, no minimum was found on the PES.



10

13

15

16

17

Figure 7. Geometries of the complexes formed by interaction of Al_2Cl_6 with CO_2 at the B3LYP/6-311+G* level.

Nevertheless, the more superelectrophilically activated aluminum chloride seems to favor complexation with CO_2, which behaves as a weak nucleophile. This suggests that the surface of aluminum chloride, which can be regarded as the $(AlCl_3)_4$ expanded in two dimensions, can work as a superelectrophilic surface, favoring the complexation of CO_2. This result also points out the low basicity of the CO_2 molecule, because the chlorine in aluminum chloride is predicted to be more basic than CO_2, leading to a slightly endothermic enthalpy of complex formation of this molecule in this system.

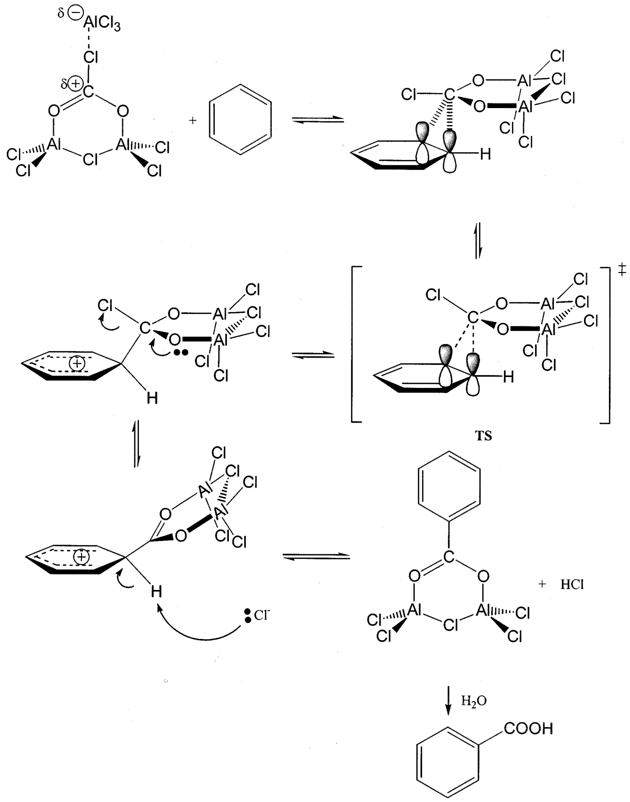
Optimization of all structures shown in Scheme 4 was attempted, but some of the species did not appear to be minima on the PES. Figure 7 shows the optimized structures of species **10**, **13**, **15**, **16**, and **17**, which were found as minima on the PES.

Table 10. Relative Enthalpies at 298 K and C=O Vibrational Frequencies for the $CO_2{\cdot}Al_2Cl_6$ Complex Isomers (B3LYP/6-311+G*//B3LYP/6-311+G* Level)

species	ΔH_{rel} (298 K) (kcal/mol)	$\nu_{CO,asym}$ (cm^{-1})	$\nu_{CO,sym}$ (cm^{-1})
$CO_2{\cdot}Al_2Cl_6$ (**7**)	1.55	2468	1393
$CO_2{\cdot}Al_2Cl_6$ (**10**)	2.16	2458	1385
$CO_2{\cdot}Al_2Cl_6$ (**13**)	0.0	1661	1385
$CO_2{\cdot}Al_2Cl_6$ (**15**)	17.91	1871	1073
$CO_2{\cdot}Al_2Cl_6$ (**16**)	11.11	1579	1376
$Cl_3Al{-}O{=}C{=}O{-}AlCl_3$ (**17**)	9.6	2448	1390
$CO_2 + Al_2Cl_6$	7.45		

Table 10 contains the relative enthalpies (ΔH) for the species **7** and those shown in Figure 7. The most stable species found for this system was species **13**. This species is similar to the chloroformate aluminum salt with internal coordination with

Scheme 7. Mechanistic Pathway for the Reaction of Benzene with CO_2 Activated by $AlCl_3$



the other aluminum atom in the dimer. Nevertheless, structures **7** and **10** are close in energy as compared to **13**, 1.6 and 2.2 kcal/mol higher in energy, respectively.

Geometric parameters of structures **13**−**16** clearly show that these species contain a typical sp^2 carbonyl functional group. This is supported by the characteristic sp^2 C═O vibrational modes around 1660 cm^{-1}. Structure **17** can be considered as di-*O*-($AlCl_3$) complexes of CO_2.

The possibility of species **13** (a six-member ring) as the more stable intermediate among the structures proposed in Scheme 4 raises the mechanistic possibility of its involvement in the reaction of benzene with CO_2 and $AlCl_3$. This mechanistic possibility is delineated in more detail in Scheme 7.

In the above mechanistic proposal, an initial activation of CO_2 by two molecules of aluminum chloride affording the intermediate **13** should be expected. After this species is formed in the reaction media, it would react with benzene (similar to a chloroformic species). Nevertheless, this mechanism does not exclude the possibility of other competing pathways, involving species **7** and **10** or even an organometallic like $PhAlCl_2$ intermediate.

On the basis of both the experimental and the theoretical data, a differentiation of possible mechanistic pathways can be proposed. There is a significant energy difference between the organometallic path and that involving carbon dioxide activation. Considering the formation of the most preferable intermediate, we found that calculations suggest that the CO_2-AlCl_3 complex is the least energy demanding process. Although several isomeric structures can be assumed and calculated for CO_2-AlCl_3 (or Al_2Cl_6) complexes, the energy requirement for their formation is significantly (38−28 kcal/mol) lower than that for the formation of $PhAlCl_2$. Consequently, on the basis of the presently available data, direct CO_2 activation appears to be the preferred pathway.

Conclusions

In conclusion, the direct carboxylation of aromatic compounds was achieved in high yields with the CO_2-AlCl_3/Al reagent system. A variety of substituted benzenes were carboxylated, giving their corresponding carboxylic acids. Added aluminum metal plays a significant role in the reaction. Although it may not necessarily actively contribute to the activation of carbon dioxide, its binding of HCl formed in the reaction impedes side reactions and the formation of byproducts. As it also forms additional aluminum chloride, it leads to an increase of the yields of carboxylic acids. To evaluate the mechanistic aspects of the reaction, the effect of several experimental variables was also studied, including the reaction of organoaluminum compounds with carbon dioxide. Density functional theoretical calculations were also carried out to probe the energy requirements for various possible activation processes and pathways. In accordance with the experimental and computational results, superelectrophilic activation of carbon dioxide by aluminum chloride complexation and its reaction with aromatics is proposed as the most viable pathway for the studied carboxylations.

Experimental Section and Calculations

In this study, $AlCl_3$ and Al as well as the aromatic reactants were purchased either from Fluka or from Aldrich. The high purity carbon dioxide (Coleman grade, 99.995% purity) was purchased from Matheson. Triphenylaluminum was commercially available from Organometallic, Inc., while phenylaluminum dichloride and phenylaluminum dibromide were synthesized according to the literature reports.[22] The carboxylation reactions were carried out in a Parr monel autoclave, following a general procedure. The product identification was carried out by GC-MS (HP 5890 GC coupled with a HP-5971 mass selective detector) using a 30m long DB-5 column; ^1H and ^{13}C NMR spectra were obtained on a 300 MHz superconducting NMR spectrometer in $CDCl_3$ solvent with tetramethylsilane as the internal standard.

The General Procedure for the Carboxylation of Aromatic Compounds. Preparation of Mesitylene Carboxylic Acid. First, 2.5 g (18.75 mmol) of $AlCl_3$ and 0.6 g (22.2 mmol) of Al were placed into a magnetically stirred Parr autoclave under argon atmosphere, and then 40 mL of mesitylene was added. After closing the autoclave, it was pressurized by CO_2 up to 57 bar pressure, and the mixture was heated to 40 °C and allowed to react for 18 h (external oil bath) under continuous stirring (1000 rpm). The reaction was then stopped by cooling and depressurizing, and water was added to the reaction mixture. The products were extracted with ether, and the acid was transferred to the aqueous phase by extraction with 10% NaOH. The pH of the collected NaOH extract was adjusted to pH = 1 by adding aqueous HCl and placed into an ice bath. Precipitated white crystals were filtered and dried. Finally, 2.55 g (83%) of 2,4,6-trimethyl-benzoic acid was obtained.

It should be noted that, during our studies, aluminum chloride samples from different batches (same catalog number and grade and each from Aldrich) were used. We observed that different samples showed different activities. These changes in activity could be taken into account, and the reaction temperature was adjusted to the individual samples.

Phenylaluminum Dichloride ($PhAlCl_2$). A mixture of triphenylaluminum (1.0 g, 3.75 mmol) and anhydrous aluminum chloride (1.0 g, 7.5 mmol) was placed into a high pressure Carins tube under argon atmosphere. The tube was closed, and the mixture melted at 180 °C for 1 h. The reaction mixture was then cooled slowly, and a white crystalline solid was obtained upon filtration. mp 93−94 °C, lit. 94−95 °C.[22]

Phenylaluminum Dibromide ($PhAlBr_2$). A mixture of triphenylaluminum (1.0 g, 3.75 mmol) and anhydrous aluminum bromide (2.0 g, 7.5 mmol) was reacted according to the preparation of $PhAlCl_2$. A white solid was obtained.

Calculations. Density functional theory (DFT)[35] calculations were performed with the Gaussian 98[36] package of programs. Optimized geometries were obtained at the B3LYP[37]/6-311+G*//B3LYP/6-311+G* levels.[38] Vibrational frequencies at the B3LYP/6-31+G* level were used to characterize stationary points as minima (number of imaginary frequencies (NIMAG) = 0) and to evaluate zero-point vibrational energies (ZPE), which were scaled by a factor of 0.98. Energies were obtained at the B3LYP/6-311+G*//B3LYP/6-311+G* + ZPE and B3LYP/6-311+G*//B3LYP/6-31+G* + ZPE levels. Calculated energies are given as Supporting Information.

Acknowledgment. Support of our work by the Loker Hydrocarbon Research Institute and National Science Foundation is gratefully acknowledged.

Supporting Information Available: Computational data concerning the absolute energies, zero-point energies, and thermal corrections for the calculated species (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA020787O

---

(35) Ziegler, T. *Chem. Rev.* **1991**, *91*, 651.

(36) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(37) Becke's Three Parameter Hybrid Method Using the LYP Correlation Functional: Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(38) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986.