Gas-Phase Lewis Acidity of Perfluoroaryl Derivatives of Group 13 Elements

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The gas-phase Lewis acidity of group 13 element aryl and perfluorinated aryl derivatives $E(C_6H_5)_3$, $E(C_6H_4F)_3$, and $E(C_5F_5)_3$ (E = B, Al, Ga) toward different donor molecules (NH_3, H_2O, PH_3, H^-, CH_3^-, F^-) has been theoretically studied at the RI-BP86/def2-TZVPP level of theory. The following order of the acceptor ability has been established: $E(C_6H_5)_3 \approx E(C_6H_4F)_3 < E(C_6F_5)_3 \approx ECl_3$. The acceptor strengths of $E(C_6H_5)_3$ and $E(C_6H_4F)_3$ are comparable to each other but much weaker compared to $E(C_6F_5)_3$, which has a similar acceptor strength to those of the corresponding trihalides ECl_3. The acceptor ability of ER_3 decreases in the order Al > Ga > B. In the gas phase, $Al(C_6F_5)_3$ is found to be a stronger Lewis acid than $B(C_6F_5)_3$ toward all electron donors but H^-. In contrast to $AlCl_3$, which forms stable dimers, $Al(C_6F_3)_3$ is monomeric and therefore has a much higher Lewis acid reactivity . The reactivity of perfluorinated derivatives $E(C_5F_5)_3$ (E = B, Al, Ga) toward ammonolysis and hydrolysis processes and L_2ZrMe_2 (L = Cl, Cp, Cp*) as cocatalysts in olefin polymerization is also discussed.

Introduction

Group 13 perfluoroaryl compounds attracted in the past decade much attention as cocatalysts in olefin polymerization reactions.[1–15] It is believed that the catalytic activity of $E(C_6F_5)_3$ (E = B, Al, Ga) correlates with the strength of their Lewis[3,5] or Brønsted[16] acidity. The Lewis acidity of $E(C_6F_5)_3$ manifests itself in numerous experimental observations. Complexes of $E(C_6F_5)_3$ with different neutral and anionic donor molecules are widely known.[4,6,8,13,16–44] Adducts of $B(C_6F_5)_3$ with nitrogen-containing donors and their activity toward olefin polymerization were the topic of a recent review.[45]

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(1) Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391.

(2) Chen, M.-C.; Roberts, J. A. S.; Marks, T. J. *Organometallics* **2004**, *23*, 932.

(3) Deck, P. A.; Beswick, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 1772.

(4) LaPointe, R. E.; Roof, G. R.; Abboud, K. A.; Klosin, J. *J. Am. Chem. Soc.* **2000**, *122*, 9560.

(5) Chakraborty, D.; Rodriguez, A.; Chen, E. X.-Y. *Macromolecules* **2003**, *36*, 5470.

(6) Bolig, A. D.; Chen, E. X.-Y. *J. Am. Chem. Soc.* **2004**, *126*, 4897.

(7) Chen, E. X.-Y.; Cooney, M. J. *J. Am. Chem. Soc.* **2003**, *125*, 7150.

(8) Mountford, A. J.; Lankaster, S. J.; Coles, S. J.; Horton, P. N.; Hughes, D. L.; Hurthouse, M. B.; Light, M. E. *Inorg. Chem.* **2005**, *44*, 5921.

(9) Chen, E. X.-Y.; Metz, M. V.; Li, L.; Stern, C. L.; Marks, T J *J. Am. Chem. Soc.* **1998**, *120*, 6287.

(10) Chen, E. X.-Y.; Kruper, W. J.; Roof, G.; Wilson, D. R. *J. Am. Chem. Soc.* **2001**, *123*, 745.

(11) Deck, P. A.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 6128.

(12) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 3623.

(13) Liu, Z.; Somsook, E.; Landis, C. R. *J. Am. Chem. Soc.* **2001**, *123*, 2915.

(14) Chen, M.-C.; Roberts, J. A. S.; Marks, T. J. *J. Am. Chem. Soc.* **2004**, *126*, 4605.

(15) Mohammed, M.; Nele, M.; Al-Humydi, A.; Xin, S.; Stapelton, R. A.; Collins, S. *J. Am. Chem. Soc.* **2003**, *125*, 7930.

(16) Bergquist, C.; Bridgewater, B. M.; Harlan, C. J.; Norton, J. R.; Fiesner, R. A.; Parkin, G. *J. Am. Chem. Soc.* **2000**, *122*, 10581.

(17) Stahl, N. G.; Salata, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **2005**, *127*, 10898.

(18) Lee, C. H.; Lee, S. J.; Park, J. W.; Kim, K. H.; Lee, B. Y.; Oh, J. S. *J. Mol. Catal. A: Chem.* **1998**, *132*, 231.

(19) Belgardt, T.; Storre, J.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Inorg. Chem.* **1995**, *34*, 3821.

(20) Ludovici, K.; Tyrra, W.; Naumann, D. *J. Organomet. Chem.* **1992**, *441*, 363.

(21) Tsurugi, H.; Ohno, T.; Yamagata, T.; Mashima, K. *Organometallics* **2006**, *25*, 3179.

(22) Tsurugi, H.; Mashima, K. *Organometallics* **2006**, *25*, 5210.

(23) Bochmann, M.; Sarsfield, M. J. *Organometallics* **1998**, *17*, 5908.

(24) Pohlmann, J. L. W.; Brinckmann, F. E. *Z. Naturforsch. Teil B.* **1965**, *20*, 5.

(25) Bradley, D. C.; Harding, I. S.; Keefe, A. D.; Motevalli, M.; Zheng, D. H. *J. Chem. Soc., Dalton Trans.* **1996**, 3931.

(26) Komon, Z. J. A.; Bu, X.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 1830.

(27) Lee, B. Y.; Bazan, G. C.; Komon, Z. J. A.; Vela, J.; Bu, X. *J. Am. Chem. Soc.* **2001**, *123*, 5352.

(28) Parks, D. J.; Piers, W. E.; Parvez, M.; Atencio, R.; Zaworotko, M. J. *Organometallics* **1998**, *17*, 1369.

(29) Blake, A. J.; Greig, J. A.; Schroeder, M. *J. Chem. Soc., Dalton Trans.* **1988**, 2645.

(30) Siedle, A. R.; Newmark, R. A.; Lamma, W. M.; Huffman, J. C. *Organometallics* **1993**, *12*, 1491.

(31) Cowley, A. H.; Hair, G. S.; McBurnett, B. G.; Jones, R. A. *Chem. Commun.* **1999**, 437.

(32) Hair, G. S.; Cowley, A. H.; Jones, R. A.; McBurnett, B. G.; Voigt, A. *J. Am. Chem. Soc.* **1999**, *121*, 4922.

(33) Cowley, A. H.; MacDonald, C. L. B.; Silverman, J. S.; Gorden, J. D.; Voigt, A. *Chem. Commun.* **2001**, 175.

(34) Kim, Y. H.; Kim, T. H.; Kim, N. Y.; Cho, E. S.; Lee, B. Y.; Shin, D. M.; Chung, Y. K. *Organometallics* **2003**, *22*, 1503.

(35) Focante, F.; Camurati, I.; Resconi, L.; Guidotti, S.; Beringhelli, T.; D'Alfonso, G.; Donghi, D.; Maggioni, D.; Mercandelli, P.; Siron, A. *Inorg. Chem.* **2006**, *45*, 1683.

(36) Kim, Y. H.; Kim, T. H.; Lee, B. Y.; Woodmansee, D.; Bu, X.; Bazan, G. C. *Organometallics* **2002**, *21*, 3082.

(37) Tebbe, K.-F.; Gilles, T.; Conrad, F.; Tyrra, W. *Acta Crystallogr.* **1996**, *C52*, 1663.

(38) Jacobsen, H.; Berke, H.; Doering, S.; Kehr, G.; Erker, G.; Froehlich, R.; Meyer, O. *Organometallics* **1999**, *18*, 1724.

(39) Rodriguez-Delgado, A.; Chen, E. X.-Y. *J. Am. Chem. Soc.* **2005**, *127*, 961.

10.1021/om700798t CCC: $40.75

Despite the large number of experimental studies, the question on the Lewis acidity in the series $B(C_6F_5)_3$, $Al(C_6F_5)_3$, $Ga(C_6F_5)_3$ remains controversial. In some experimental studies[17,18,23] the authors concluded that $B(C_6F_5)_3$ has a significantly higher Lewis acidity compared to $Al(C_6F_5)_3$. For example, Lee et al.[18] concluded on the basis of the CN stretching frequency shift of solid adducts with benzonitrile that "$Al(C_6F_5)_3$ is quite a weaker Lewis acid than $B(C_6F_5)_3$" and that $Al(C_6F_5)_3$ has a similar acidity to $Al(CH_3)_3$. They also stated, that C_6F_5 substituents are only marginally effective in increasing the Lewis acidity.[18] Bochmann and Sarsfield[19] reported that Cp_2ZrMe_2 forms a thermally more stable zwitterionic adduct with $B(C_6F_5)_3$ compared to $Al(C_6F_5)_3$. Stahl, Salata, and Marks concluded on the basis of the calorimetry and NMR studies in solution that $Al(C_6F_5)_3$ has a significantly lower methide affinity than $B(C_6F_5)_3$.[17]

However, other experimental observations suggest a much stronger Lewis acidity of $Al(C_6F_5)_3$. $Al(C_6F_5)_3$ readily forms complexes with benzene and toluene,[32] while such complexes are not known for $B(C_6F_5)_3$.[43] The adduct of $Al(C_6F_5)_3$ with THF decomposes only at elevated temperature (>200 °C).[18] $Ga(C_6F_5)_3$ forms with Et_2O a stable adduct, which can be purified by sublimation, while $B(C_6F_5)_3 \cdot Et_2O$ dissociates on heating above 60 °C in vacuum, and it partially dissociates in dilute benzene solution.[24] These qualitative observations suggest a stronger Lewis acidity of $Al(C_6F_5)_3$ and $Ga(C_6F_5)_3$ compared to $B(C_6F_5)_3$. Tsurugi and Mashima noted that $Al(C_6F_5)_3$ forms with (2-{*N*-(2,6-diisopropylphenyl)iminomethyl pyrrolyl})Zr-$(CH_2Ph)_3$ a more stable zwitterionic complex than $B(C_6F_5)_3$.[22] It was also reported that $Al(C_6F_5)_3$ alone catalyzes styrene polymerization, while under the same conditions $B(C_6F_5)_3$ was not active. It was assumed that $Al(C_6F_5)_3$–styrene ion pair formation is in part responsible for the polymerization activity.[46] LaPointe et al. examined weakly bonded anions based on the $[(C_6F_5)_3E{-}LN{-}E(C_6F_5)_3]^-$ motif, where E = B, Al and the linking ligand LN = CN^-, azide, dicyanamide, imidazole.[4] They found that both B and Al species are among the best known activators for olefin polymerization reactions, but in contrast to the previous reports, aluminum derivatives exhibit a higher activity as cocatalysts.[4] Early theoretical studies at the BP91/DZP(TZP on Zr) level of theory on the energetics of the metallocene–$E(C_6F_5)_3$ ion pair formation by Ziegler and coworkers also showed that $Al(C_6F_5)_3$ forms much stronger ion pairs compared to $B(C_6F_5)_3$.[47,48]

In light of this controversy and the growing use of $E(C_6F_5)_3$ as catalyst and cocatalyst, we undertook a comparative study of the Lewis acidity of aryl and perflourinated organometallic derivatives ER_3 (E = B, Al, Ga; R = C_6H_5, C_6H_4F, C_6F_5) toward different neutral and anionic Lewis bases: NH_3, H_2O, PH_3, H^-, CH_3^-, F^-, $C_6F_5^-$, THF, toluene, L_2ZrMe_2 (L = Cl, Cp, Cp*). For comparison, we also considered complexes of these donors with group 13 element trichlorides ECl_3. A comparative study of the Lewis acidity of group 13 metal halides was performed.[49,50]

In addition to the Lewis acidity, in the present report we also discuss the reactivity of $E(C_6F_5)_3$. To analyze the Brønsted acidity of $E(C_6F_5)_3$ complexes with water, a comparative theoretical study of the hydrolysis and ammonolysis reactions of $E(C_6F_5)_3$ (E = B, Al, Ga) has been carried out for the first time. Finally, energetic and structural aspects of $E(C_6F_5)_3$ reactions with Zr metallocenes, including catalyst poison reactions, will also be discussed.

Computational Details

All structures were fully optimized using the Gaussian03[51] optimizer together with TurboMole5.7.1[52] energies and gradients at the BP86[53]/def2-TZVPP[54] level of theory. An effective core potential (ECP) with a TZP valence basis set was used for Zr. The resolution-of-identity method[55] has been applied using auxiliary basis sets from the TurboMole library. A fine (multiple) grid m4 was used. Basis set superposition error (BSSE) was estimated by counterpoise method[56a,b] realized in Gaussian03. For complexes of $E(C_6F_5)_3$ with neutral donors BSSE was found to be less than 8 kJ mol^{-1} (Table 2S, Supporting Information). For complexes with anions computed BSSE corrections are significantly larger but strongly dependent on the size of the anion (50–65 kJ mol^{-1} for complexes with H^- and F^-; 31–32 kJ mol^{-1} for complexes with CH_3^-; and only about 11 kJ mol^{-1} for complexes with $C_6F_5^-$). In all cases introduction of the correction does not change the order of the acceptor ability of $E(C_6F_5)_3$. Values for complexes with $E(C_6H_5)_3$ and $E(C_6H_4F)_3$ are expected to be of the same order of magnitude. Given the fact that the counterpoise method generally overestimates BSSE,[56c] in the following discussion we will use reaction energies, uncorrected for BSSE.

Results and Discussion

1. Structural Features of the Donor–Acceptor Complexes and Complex Anions. Major structural characteristics of the monomeric acceptor molecules and donor–acceptor complexes are summarized in Table 1S. With the exception of the asymmetric complexes with water, all optimized adducts possess C_3 symmetry. The optimization of several boron-containing complexes (namely, $B(C_6H_5)_3$ with PH_3 and H_2O; $B(C_6H_4F)_3$ with H_2O; and $B(C_6F_5)_3$ with toluene) resulted only in weakly bonded van der Waals adducts. In contrast, the optimization of the aluminum and gallium analogues resulted in chemically bonded species. This result already points out a stronger acceptor ability of the aluminum and gallium derivatives.

It should be noted that although the optimization of the $B(C_6H_5)_3 \cdot H_2O$ adduct resulted in a weakly bonded van der Waals complex, the adduct was experimentally observed in the solid state structure of $[Re(O)_2(1,4,8,11\text{-tetra-anzacyclotetradecane})]^+Cl^- \cdot 2(B(C_6H_5)_3 \cdot H_2O)$.[29] It is probable that this

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(40) Chakraborty, D.; Chen, E. X.-Y. *Organometallics* **2003**, *22*, 207.

(41) Danopoulos, A. A.; Galsworthy, J. R.; Green, M. L. H.; Cafferkey, S.; Doerrer, L. H.; Hursthouse, M. B. *Chem. Commun.* **1998**, 2529.

(42) Hill, G. S.; Manojlovic-Muir, L.; Muir, K. W.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 525.

(43) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 245.

(44) Doerrer, L. H.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1999**, 4325.

(45) Focante, F.; Mercandelli, P.; Sironi, A.; Resconi, L. *Coord. Chem. Rev.* **2006**, *250*, 170.

(46) Chakraborty, D.; Chen, E. X.-Y. *Macromolecules* **2002**, *35*, 13.

(47) Vanka, K.; Chan, M. S. W.; Pye, C. C.; Ziegler, T. *Organometallics* **2000**, *19*, 1841.

(48) Vanka, K.; Chan, M. S. W.; Pye, C. C.; Ziegler, T. *Macromol. Symp.* **2001**, *173*, 163.

(49) Timoshkin, A. Y.; Suvorov, A. V.; Bettinger, H. F.; Schaefer, H. F. *J. Am. Chem. Soc.* **1999**, *121*, 5687.

(50) Loschen, C.; Voigt, K.; Frunzke, J.; Diefenbach, A.; Diedenhofen, M.; Frenking, G. Z. *Allg. Anorg. Chem.* **2002**, *628*, 1294.

(51) *Gaussian 03*, Rev. D01; Gaussian, Inc.: Wallingford, CT, 2004.

(52) Ahlrichs, R.; Baer, M.; Haeser, M.; Horn, H.; Koelmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165.

(53) (a) Becke, A. D. *Phys. Rev. A.* **1988**, *38*, 3098. (b) Perdew, J. P. *Phys. Rev. B.* **1986**, *33*, 8822.

(54) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.

(55) Eichkorn, K.; Treutler, O.; Ohm, H.; Haeser, M.; Ahlrichs, R. *Chem. Phys. Lett.* **1995**, *242*, 652.

(56) (a) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553. (b) Simon, S.; Duran, M.; Dannenberg, J. J. *J. Chem. Phys.* **1996**, *105*, 11024. (c) Clark, T. *A Handbook of Computational Chemistry*; Wiley: New York, 1985.

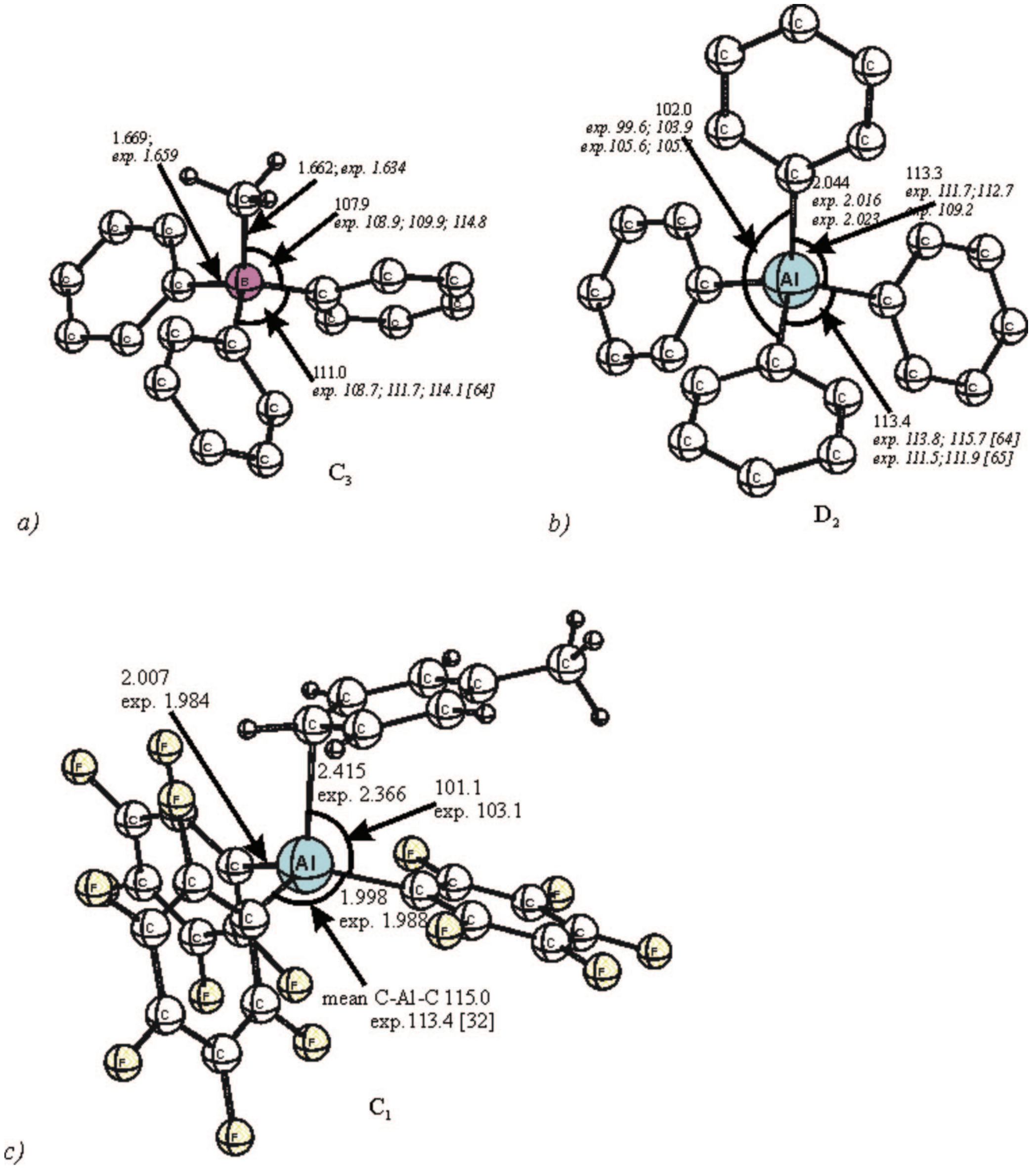

Figure 1. Comparison of the calculated and experimental solid state structures of the some complexes and anions. (a) $[B(C_6F_5)_3CH_3]^-$; (b) $[Al(C_6F_5)_4]^-$; (c) $Al(C_6F_5)_3 \cdot$toluene. In (a) and (b) the fluorine atoms are omitted for clarity. All distances are in Å, angles in deg.

difference is due to significant enhancement of the DA interactions in the solid state, which was observed for many weak or “partially bonded” complexes.[57] In contrast to $B(C_6H_5)_3 \cdot H_2O$, the optimization of the $B(C_6F_5)_3 \cdot H_2O$ adduct results in a DA bonded molecule with a sizable dissociation energy of 37 kJ mol^{-1}.

Our optimized parameters for the gas phase species may be compared with experimental findings for the complexes in the solid state. The comparison for several compounds is given in Figure 1. Our results are generally in good agreement with experiment. As expected, upon complex formation, group 13 alkyls undergo reorganization from the trigonal planar to a tetrahedral geometry. This manifests itself in a decreasing C−E−C angle from 120° in free ER_3 to 113.6−119.1° in the complexes with neutral donors and 107.3−113.4° in the anions. At the same time a lengthening of the E−C bonds is observed. There is a correlation between the M−C bond length increase $\Delta R_{(M\text{-}C)} = R_{M\text{-}C}(ER_3D) - R_{M\text{-}C}(ER_3)$ and the decrease of the C−E−C angle $\Delta\alpha_{C\text{-}E\text{-}C} = 120.0 - \alpha_{C\text{-}E\text{-}C}(ER_3D)$ for all donor and acceptor molecules investigated (Figure 2). Similar bond length−bond angle relationships were observed for the donor–acceptor complexes of group 13 metal halides.[49]

2. Fluorination Effect on the Lewis Acidity of the ER_3 Series (R = C_6H_5, C_6H_4F, C_6F_5). The calculated bond dissociation energies of the complexes are given in Table 1. The adducts with EPh_3 were found to be least stable. Introduction of one fluoro substituent has a very small effect on the dissociation energy. The acceptor strengths of $E(C_6H_5)_3$ and $E(C_6H_4F)_3$ are close to each other and considerably smaller than those of the corresponding trihalides. However, complete substitution of *all* hydrogen atoms by fluorine leads to a considerable enhanced complex stability. Thus, the dissociation enthalpies of $E(C_6F_5)_3$ are comparable (in some cases they are even larger) to those of ECl_3, which indicates a relatively strong acceptor ability. The $E(C_6F_5)_3$ compounds have considerably stronger (by about 100 kJ mol^{-1}) anion affinities than $E(C_6H_5)_3$

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[57] (a) Leopold, K. R.; Canagaratna, M.; Phillips, J. A. *Acc. Chem. Res.* **1997**, *30*, 57. (b) Jonas, V.; Frenking, G.; Reetz, M. T. *J. Am. Chem. Soc.* **1994**, *116*, 8741.

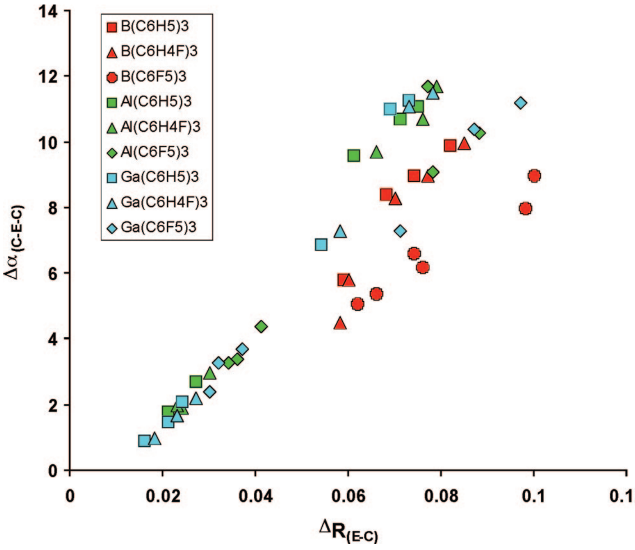

Figure 2. Correlation between increase of the E−C bond distance $\Delta R_{(M\text{-}C)}$ and decrease of the C−E−C angle $\Delta\alpha_{C\text{-}E\text{-}C}$ for the ER_3D complexes. Distances are in Å, angles in deg.

Table 1. Experimetnal and Calculated Dissociation Energies (kJ mol^{-1}) of the Gas Phase Complexes (theoretical values at the RI-BP86/def2-TZVPP level of theory)

	donor					
acceptor	NH_3	H_2O	PH_3	H^-	CH_3^-	F^-
BCl_3	89.3	15.8	13.5	451.2	458.7	426.5
$B(C_6H_5)_3$	45.8	10.1[a]	0.1[a]	383.8	367.7	344.7
$B(C_6H_4F)_3$	40.7	4.8[a]	−12.0	405.2	389.1	366.0
$B(C_6F_5)_3$	97.1	36.5	24.0	528.1	487.5	454.0
$AlCl_3$	143.9 137 ±6[b]	97.4	66.4	482.7	496.8	523.0
$Al(C_6H_5)_3$	94.4	63.8	34.8	395.6	401.1	442.7
$Al(C_6H_4F)_3$	94.6	63.7	34.9	420.2	425.9	467.2
$Al(C_6F_5)_3$	145.5	112.0	63.9	513.6	521.5	552.1
$GaCl_3$	118.3 134 ±3[b]	68.9	56.7	502.4	507.5	456.2
$Ga(C_6H_5)_3$	66.1	23.1	23.1	382.5	376.2	356.1
$Ga(C_6H_4F)_3$	66.3	37.4	22.8	407.5	401.1	379.8
$Ga(C_6F_5)_3$	114.9	74.9	52.9	510.7	506.6	464.7

[a] Optimization resulted in intermolecular interacting fragments. [b] Experimental gas phase dissociation enthalpies taken from ref 49.

and $E(C_6H_4F)_3$. The following order of the acceptor ability can be deduced: $E(C_6H_5)_3 \approx E(C_6H_4F)_3 < E(C_6F_5)_3 \approx ECl_3$.

Our findings are contradictory to the statement by Lee et al.[18] that the C_6F_5 substituent only marginally increases the Lewis acidity and that $Al(C_6F_5)_3$ has a similar acidity to $Al(CH_3)_3$. We find that the introduction of the C_6F_5 group strongly increases the Lewis acidity and that the Lewis acidities of $E(C_6F_5)_3$ are comparable to that of group 13 trihalides ECl_3, which are among the strongest Lewis acids.[58] The failure of the spectral approach of Lee et al.[18] to predict the correct donor strength of $E(C_6F_5)_3$ may come from the fact that the CN frequency shift of the donor molecule may be affected by interactions with the F substituents of the C_6F_5 groups in the solid state (vide infra).

The comparison of the acceptor ability of the group 13 elements shows that the acceptor strength decreases in the order Al > Ga > B. For both aryl and perfluoroaryl substituents the Al derivatives have a larger acceptor ability compared to the B analogues. In particular, the high acceptor ability of $Al(C_6F_5)_3$ should be mentioned. Among all considered acceptors, it has the highest affinity toward NH_3, H_2O, CH_3^-, and F^- and is second toward PH_3 (behind $AlCl_3$) and H^- (behind $B(C_6F_5)_3$). Only with H^- as a Lewis base does $B(C_6F_5)_3$ shows a higher acceptor strength.

Thus, our results show that the complete fluorination of the group 13 aryl derivatives has a very strong effect on the stability of the complexes and that the complexes of $E(C_6F_5)_3$ have dissociation energies that are comparable to those of complexes with ECl_3.

3. Dimerization of ER_3 ($R = C_6H_5, C_6H_4F, C_6F_5$). Since we found out that the intrinsic Lewis acidity of $E(C_6F_5)_3$ is close to that of ECl_3, it is of interest to consider the possibility of the dimerization of $E(C_6F_5)_3$. It is well-known, that group 13 metal trihalides exist as dimers in the solid state and in inert solvents, while they undergo reversible thermal dissociation into monomers in the gas phase. $AlCl_3$ and $GaCl_3$ form one of the most stable dimers with gas phase dissociation enthalpies of 122 and 88 kJ mol^{-1} for Al_2Cl_6 and Ga_2Cl_6, respectively.[59] This fact hampers their Lewis acidity, because additional energy is required for the dissociation of the dimer to the monomeric Lewis acid.

To address the question of possible dimerization of ER_3, geometry optimizations of the E_2R_6 dimers were carried out without symmetry constraints. In case of the boron compounds the optimization of the dimers leads to dissociation into monomers. The monomeric nature of boron trihalides and trialkyls is widely known. In contrast, the geometry optimization of Al and Ga analogues resulted in covalently bound dimeric molecules. As an example, the optimized structure of monomeric and dimeric $Al_2(C_6F_5)_6$ is shown in Figure 3, and major structural and thermodynamic characteristics of E_2R_6 dimers are summarized in Table 2. In general, dimers of phenyl and fluorinated phenyl derivatives of Al and Ga have a very low stability. In fact, only $Al_2(C_6H_5)_6$ and $Al_2(C_6H_4F)_6$ have noticeable dissociation energies of about 32 kJ mol^{-1}, while for $Al_2(C_6F_5)_6$ the predicted value is only 3 kJ mol^{-1}. As was shown by Willis and Jensen,[76] DFT methods significantly (by 20–50 kJ mol^{-1}) underestimate the dissociation energy of $Al_2(CH_3)_6$. It is highly probable that absolute dissociation energies of the dimers reported in the present work are also underestimated, but the qualitative trends in the series $E_2(C_6H_5)_6$, $E_2(C_6H_4F)_6$, $E_2(C_6F_5)_6$ are expected to be correct. The structure of $Al_2(C_6H_5)_6$ was determined by X-ray.[61] Our theoretical values are in good agreement with experiment (see Table 2). According to the ^{13}C NMR signals in methylene chloride solution, $Al_2(C_6H_5)_6$ exists as a static bridged dimer at −92 °C, but undergoes rapid intramolecular exchange at 37 °C.[62] In benzene solution $Al_2(C_6H_5)_6$ is partially dissociated.[63] These experimental observations agree with the low dissociation energy of $Al_2(C_6H_5)_6$ computed in the present work. The introduction of fluoro substituents significantly reduces the stability of the dimers. All gallium analogues are predicted to be thermodynamically unstable toward dissociation. This behavior distinguishes $Al(C_6F_5)_3$ and $Ga(C_6F_5)_3$ from corresponding trihalides, which form stable dimers. Our predictions are in accord with the available experimental observations of the monomeric nature of the perfluoroaryl derivatives of B, Al, and Ga.

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(58) Haaland, A. *Angew Chem.* **1989**, *10*, 101;. *Angew Chem. Int. Ed. Engl.* **1989**, *28*, 992.

(59) Internet database “Thermal constants of substances” Version 10. 09. 2006. Yungman, V. S., Ed.; http://www.chem.msu.su/cgi-bin/tkv.pl?-show=welcome.html/welcome.html

(60) Hargittai, M. *Chem. Rev.* **2000**, *100*, 2233.

(61) Malone, J. F.; McDonald, W. S. *J. Chem. Soc., Dalton Trans.* **1972**, 2646.

(62) Olah, G. A.; Prakash, G. K. S.; Liang, G.; Henold, K. L.; Haigh, G. B. *Proc. Natl. Acad. Sci. USA* **1977**, *74*, 5217.

(63) Mole, T. *Aust. J. Chem.* **1963**, *16*, 794.

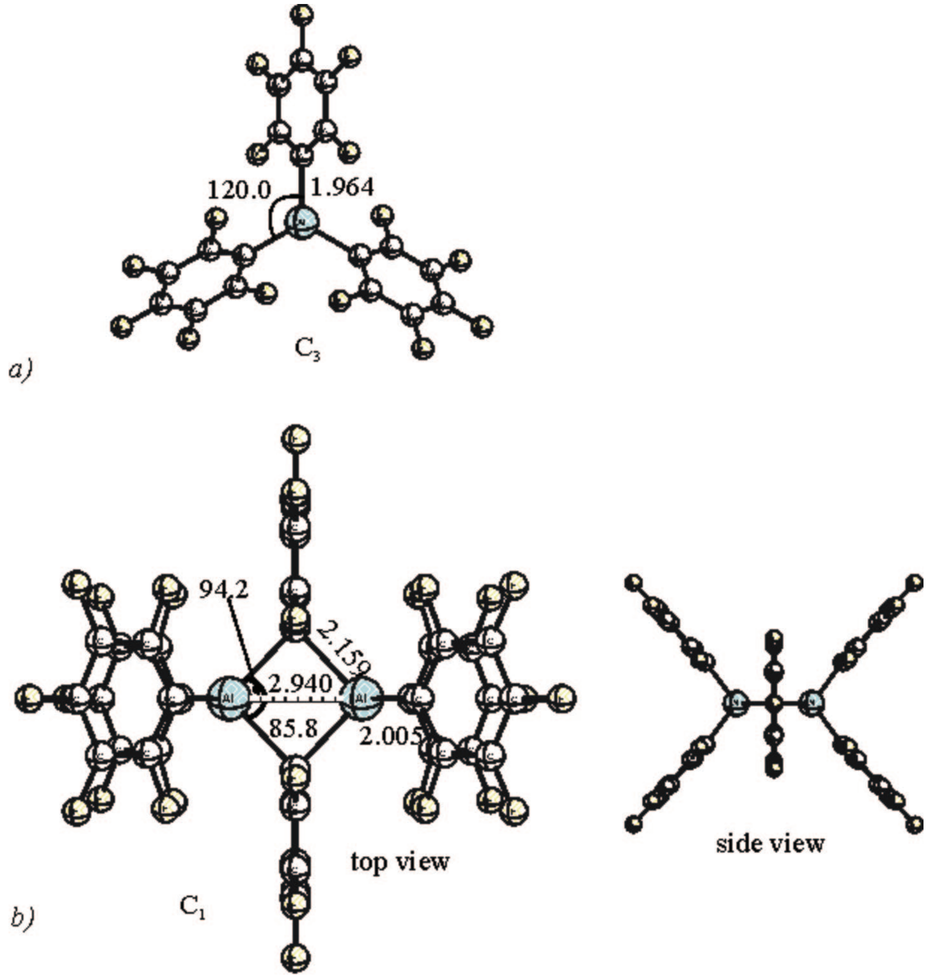


Figure 3. Optimized structures of (a) $Al(C_6F_5)_3$ and (b) its dimer $Al_2(C_6F_5)_6$.

Table 2. Calculated and Experimental Geometry Parameters for E_2R_6 (all distances in Å, all angles in deg, dissociation energies into monomers (per mole of dimer) E^{diss} in kJ mol^{-1}; calculated values at the RI-BP86/def2-TZVPP level of theory; X^t = terminal, X^b = bridging carbon or chlorine atom)

compound	r(M−M)	r(M−X^t)	r(M−X^b)	X^{t}MX^t	X^{b}MX^b	E^{diss}
Al_2Cl_6	3.210	2.093	2.292	121.5	91.1	103.3
Al_2Cl_6 (expt)		2.061(2)[a]	2.250(3)[a]	122.1(31)[a]	90.0(8)[a]	122.2[b]
$Al_2(C_6H_5)_6$	2.728	1.995	2.159	114.5	101.7	31.9
$Al_2(C_6H_5)_6$ (expt)	2.702[c]	1.958[c]	2.182[c]	115.4[c]	103.5[c]	
$Al_2(C_6H_4F)_6$	2.736	1.992	2.158	114.8	101.3	31.2
$Al_2(C_6F_5)_6$	2.940	2.005	2.159	106.9	94.2	3.0
Ga_2Cl_6	3.309	2.137	2.350	122.9	90.5	75.2
Ga_2Cl_6 (expt)		2.116(5)[a]	2.305(6)[a]	124.5(1)[a]	90(1)[a]	87.5[b]
$Ga_2(C_6H_5)_6$	2.726	2.007	2.200	116.0	103.4	−15.2
$Ga_2(C_6H_4F)_6$	2.737	2.004	2.197	116.3	102.9	−16.9
$Ga_2(C_6F_5)_6$	2.977	2.017	2.189	108.3	94.3	−39.0

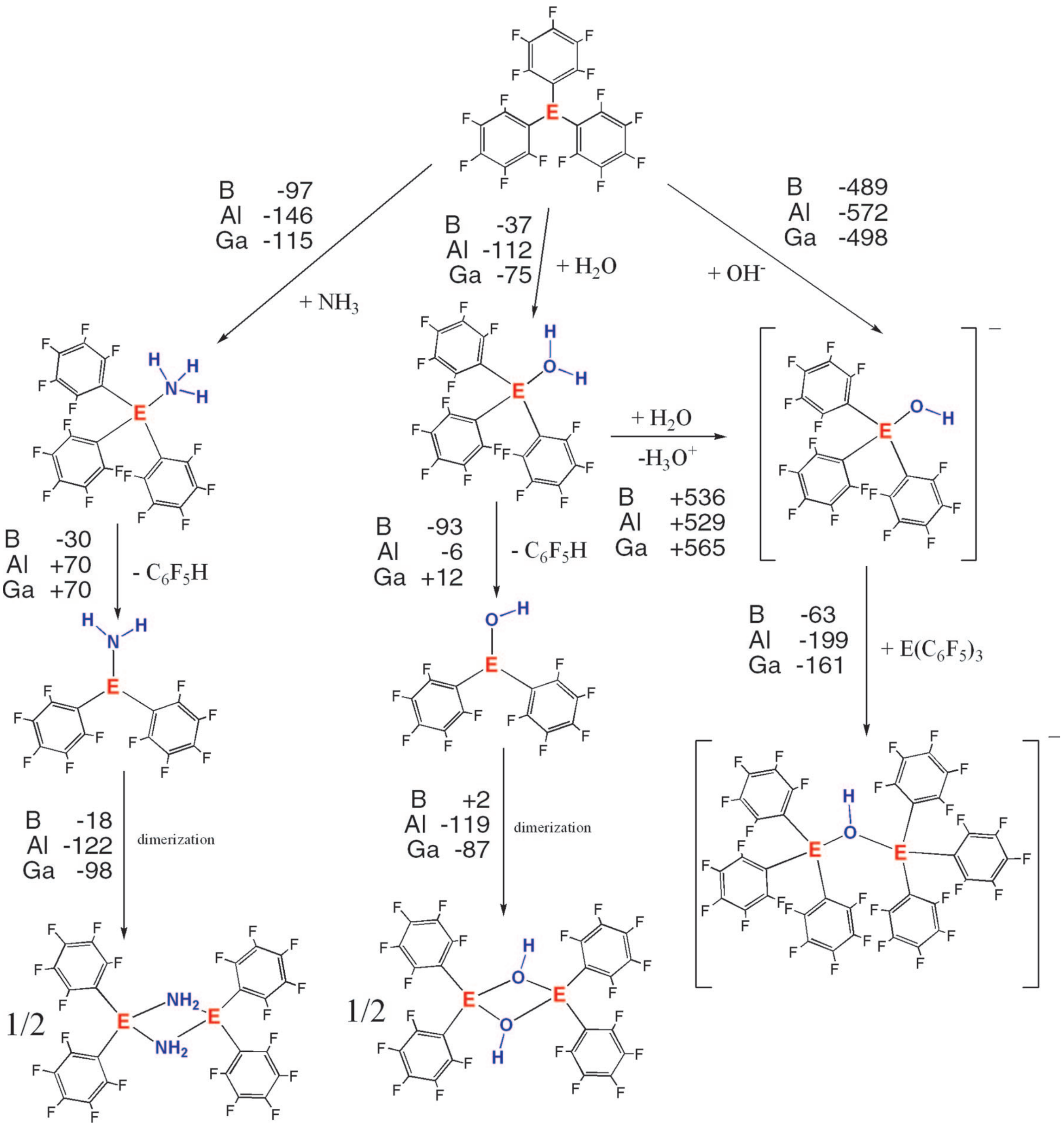
[a] Gas phase electron diffraction data taken from ref 60. [b] Standard gas phase dissociation enthalpies from ref 59. [c] Experimental X-ray data from ref 61.

4. Lewis Acidity of $E(C_6F_5)_3$ toward Weak Lewis Bases and Complex Anions. The fact that $E(C_6F_5)_3$ are monomeric places them among the strongest Lewis acids. Since there is no endothermicity associated with dissociation of the dimer, the "real" Lewis acidity of $E(C_6F_5)_3$ is much higher compared to ECl_3, as can be deduced from the exothermicity of the following ammonia displacement reaction: $ECl_3NH_3 + E(C_6F_5)_3 = E(C_6F_5)_3NH_3 + ½ E_2Cl_6$.

The reaction energies are *exothermic* by 53 and 34 kJ mol^{-1} for Al and Ga compounds, respectively. The analogous reaction between BCl_3NH_3 and $B(C_6F_5)_3$ with formation of monomeric BCl_3 is exothermic by only 8 kJ mol^{-1}.

In contrast to Al_2Cl_6, the monomeric nature of $Al(C_6F_5)_3$ allows it to participate in DA interactions with very weak Lewis bases. Experimentally, σ-complexes with benzene and toluene are reported only for $Al(C_6F_5)_3$.[32] The structural parameters of the $Al(C_6F_5)_3\cdot$arene complexes indicate η^1-coordination of the arene, which indicates a similarity of these complexes to $Al(C_6F_5)_3\cdot$THF.[19] Our computational results also show that only $Al(C_6F_5)_3$ forms with toluene a DA complex with a small dissociation energy of 14 kJ mol^{-1}. Our optimized gas phase geometry is in satisfactory agreement with the solid state X-ray data[19] (see Figure 1c). The optimization of the boron analogue resulted in a weakly bonded van der Waals complex. In the

Scheme 1. Theoretzically Predicted Energies (kJ mol^{-1}) of the Gas Phase Reactions of $E(C_6F_5)_3$ with Ammonia, Water, and Hydroxyl Anion



case of gallium, the dissociation energy of the complex is predicted to be less than 2 kJ mol^{-1}.

In addition to the complexes with neutral donors, we optimized the $[E(C_6F_5)_4]^-$ anions with D_2 symmetry constraint. Major structural parameters are given in Table1S. The affinity toward $C_6F_5^-$ also decreases in the order Al (-300 kJ mol^{-1}) > Ga (-279 kJ mol^{-1}) > B (-242 kJ mol^{-1}). Our predicted geometrical parameters of C_3 symmetric $[B(C_6F_5)_3Me]^-$ (Figure 1a) and D_2 symmetric $[Al(C_6F_5)_4]^-$ (Figure 1b) are in reasonable agreement with the respective experimental geometries of the asymmetric anions found by X-ray diffraction in the solid state.[64]

The high Lewis acidity of $E(C_6F_5)_3$ manifests itself in so-called "double" activation of the metallocenes $L_2Zr\{Me\text{-}Al(C_6F_5)_3\}_2$[10] and in the formation of stable multiple ions such as $(C_6F_5)_3E{-}A{-}E(C_5F_5)_3$, where A = F^-,[2,65] CH_3^-,[10] and OH^-.[41,44] Marks and co-workers[2] noted an improved catalytic activity of polynuclear complexes bridged by a F^- ligand, such as $[F\{Ga(C_6F_5)_3\}_2]^-$ and $[F_2\{Al(C_6F_5)_3\}_3]^{2-}$, which were employed as cocatalysts for olefin polymerization. A more detailed report on the structures and reactivity of the similar ions has recently appeared.[65] We considered the formation of such ions with F^- and OH^- bridges. While F^--bridged compounds show a linear E−F−E arrangement, structures with an OH^- bridging group possess E−O−E angles of about 140°. The affinity of $E(C_6F_5)_3$ toward $[FE(C_6F_5)_3]^-$ was calculated to be 15 kJ mol^{-1} *endothermic* for boron and 150 and 126 kJ mol^{-1} *exothermic* for Al and Ga, respectively. The analogous affinity of $E(C_6F_5)_3$ toward $[E(C_6F_5)_3(OH)]^-$ is exothermic by 63, 199, and 161 kJ mol^{-1} for B, Al, and Ga, respectively. Our predictions qualitatively agree with experimental observations of $[(OH)\{B(C_6F_5)_3\}_2]^-$ anions. $Al(C_6F_5)_3$ once again shows a greater affinity compared to its group 13 neighbors.

We conclude that due to its very strong acceptor ability and monomeric nature $Al(C_6F_5)_3$ is one of the strongest Lewis acids.

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(64) Mariott, W. R.; Gustafson, L. O.; Chen, E. X.-Y. *Organometallics* **2006**, *25*, 3721.

(65) Chen, M.-C.; Roberts, J. A. S.; Seyam, A. M.; Li, L.; Zuccaccia, C.; Stahl, N. G.; Marks, T. J. *Organometallics* **2006**, *25*, 2833.

Table 3. Calculated Reaction Energies (kJ mol^{-1}) of Gas Phase Reactions of $E(C_6F_5)_3$ toward Different Donor Molecules at RI-BP86/def2-TZVPP

process	E = B	E = Al	E = Ga
$E(C_6F_5)_3 + NH_3 = E(C_6F_5)_3 \cdot NH_3$	−97.1	−145.5	−114.9
$E(C_6F_5)_3 + NH_3 = E(C_6F_5)_2NH_2 + C_6F_5H$	−127.4	−75.8	−45.13
$E(C_6F_5)_3 + NH_3 = \frac{1}{2}[E(C_6F_5)_2NH_2]_2 + C_6F_5H$	−145.0	−197.5	−143.1
$E(C_6F_5)_3 + H_2O = E(C_6F_5)_3 \cdot H_2O$	−36.5	−112.0	−74.9
$E(C_6F_5)_3 + H_2O = E(C_6F_5)_2OH + C_6F_5H$	−129.7	−117.6	−63.0
$E(C_6F_5)_3 + H_2O = \frac{1}{2}[E(C_6F_5)_2OH]_2 + C_6F_5H$	−127.6	−236.8	−150.2
$E(C_6F_5)_3 + C_6H_5CH_3 = E(C_6F_5)_3 \cdot C_6H_5CH_3$	−0.3	−13.8	−1.3
$E(C_6F_5)_3 + THF = E(C_6F_5)_3 \cdot THF$	−4.0	−104.0	−63.8
$E(C_6F_5)_3 + 3HCl = ECl_3 + 3C_6F_5H$	−221.6	−400.8	−323.7
$E(C_6F_5)_3 + C_6F_5^- = [E(C_6F_5)_4]^-$	−241.9	−300.4	−279.2
$E(C_6F_5)_3 + [FE(C_6F_5)_3]^- = [E(C_6F_5)_3FE(C_6F_5)_3]^-$	−15.3	−149.7	−125.7
$E(C_6F_5)_3 + [(OH)E(C_6F_5)_3]^- = [E(C_6F_5)_3(OH)E(C_6F_5)_3]^-$	−63.4	−198.6	−161.2
$ZrCl_2(CH_3)_2 + E(C_6F_5)_3 = [ZrCl_2(CH_3)]^+[E(C_6F_5)_3(CH_3)]^-$	40.4	−21.2	−9.0
$ZrCp_2(CH_3)_2 + E(C_6F_5)_3 = [ZrCp_2(CH_3)]^+[E(C_6F_5)_3(CH_3)]^-$	−17.8	−65.2	−44.3
$ZrCp^*_2(CH_3)_2 + E(C_6F_5)_3 = [ZrCp^*_2(CH_3)]^+[E(C_6F_5)_3(CH_3)]^-$	−14.4	−73.6	−52.8
$ZrCl_2(CH_3)_2 + E(C_6F_5)_3 = ZrCl_2(CH_3)(C_6F_5) + E(C_6F_5)_2(CH_3)$	−20.3	−9.2	−13.7
$ZrCp_2(CH_3)_2 + E(C_6F_5)_3 = ZrCp_2(CH_3)(C_6F_5) + E(C_6F_5)_2(CH_3)$	−38.1	−27.0	−31.5
$ZrCp^*_2(CH_3)_2 + E(C_6F_5)_3 = ZrCp^*_2(CH_3)(C_6F_5) + E(C_6F_5)_2(CH_3)$	−31.8	−20.6	−25.1
$Cl_2ZrMe^+ + THF = Cl_2ZrMeTHF^+$	−259.1		
$Cp_2ZrMe^+ + THF = Cp_2ZrMeTHF^+$	−151.5		
$Cp^*_2ZrMe^+ + THF = Cp^*_2ZrMeTHF^+$	−91.6		

5. Reactivity of $E(C_6F_5)_3$: Hydrolysis and Ammonolysis. Since the first reports on the synthesis and identification of group 13 perfluoroaryl derivatives $E(C_6F_5)_3$ were published, their reactivity toward water has become a subject of numerous experimental studies.[16,20,25,29,33,40–43,66] Generally, the evolution of pentafluorobenzene C_6F_5H was observed, but in controlled conditions complexes with one, two, or three water molecules have been detected.

Reactions with water are of interest for practical purposes, since Ishihara et al.[67] report a high activity of bis(perfluorophenyl)borinic acid $HOB(C_6F_5)_2$ as an effective Oppenauer oxidation catalyst for allylic and benzylic alcohols. $B(C_6F_5)_3$ was also found to be an active catalyst in this reaction. However, the authors suggest that it reacts with water to form the active species $HOB(C_6F_5)_2$. Interestingly, (perfluorophenyl)boronic acid $(HO)_2B(C_6F_5)$ was found to be inert.

The considered reactions between $E(C_6F_5)_3$ and water are summarized in Scheme 1. The energetic characteristics of the processes with respect to separated $E(C_6F_5)_3$ and H_2O are presented in Table 3, while the energies of the intermediate steps are shown in Scheme 1.

The formation of the adduct with water is exothermic, with the trend of the $E(C_6F_5)_3 \cdot H_2O$ complex formation energies being Al > Ga > B. The evolution of C_6F_5H from the adduct with formation of monomeric $HOE(C_6F_5)_2$ is strongly exothermic for boron (−93), only slightly exothermic for aluminum (−6), and endothermic for Ga (+12). However, dimerization of $HOE(C_6F_5)_2$ is strongly exothermic for Al and Ga but slightly endothermic for boron. The overall energies (kJ mol^{-1}) of the first step of the hydrolysis of the adduct $E(C_6F_5)_3 \cdot H_2O$ are −91 (B), −125 (Al), and −75 (Ga), indicating a high exothermicity of the hydrolysis processes for all adducts. We conclude that all $E(C_6F_5)_3 \cdot H_2O$ complexes are not stable with respect to hydrolysis with concomitant C_6F_5H elimination.

Our conclusions are in agreement with experimental observations. The adduct $B(C_6F_5)_3 \cdot H_2O$ is thermally unstable; the formation of C_6F_5H and $HOB(C_6F_5)_2$ was proven by ^1H NMR at 70 °C. $HOB(C_6F_5)_2$ is susceptible to further hydrolysis with formation of monomeric $(HO)_2B(C_6F_5)$.[25] $Al(C_6F_5)_3 \cdot H_2O$ has a half-life of $t_{1/2} = 33$ h in toluene solution at room temperature while slowly eliminating C_6F_5H.[40] After 7 days $Al(C_6F_5)_3 \cdot H_2O$ completely converts to $[Al(C_6F_5)_2OH]_n$ (n most probably 2) and C_6F_5H. $[Al(C_6F_5)_2OH]_n$ is stable at room temperature, but it completely hydrolyzes on heating.[40] The adduct $Ga(C_6F_5)_3 \cdot OEt_2$ is completely hydrolyzed within a few minutes in acidic and basic aqueous solutions to give $Ga(OH)_3$ and C_6F_5H without any evidence of intermediates.[20] This behavior is also observed for gallium trihalides, while unfluorinated organogallium derivatives are partially hydrolyzed to form diorganogallium ions.[68] In contrast to fully hydrolyzable ECl_3, complexes with water are isolated and structurally characterized for $E(C_6F_5)_3$. It is assumed that the high Lewis acidity and additional intra- and intermolecular H···F hydrogen bonding stabilizes such adducts.

H···F intramolecular interactions are an interesting structural feature of all $E(C_6F_5)_3 \cdot H_2O$ adducts. In solid $Al(C_6F_5)_3 \cdot H_2O$, two hydrogen atoms of H_2O molecule are involved in H···F hydrogen bonding, one in intramolecular and the second one in intermolecular interactions.[40] Interestingly, the intermolecular contact of 2.13(2) Å is slightly shorter compared to the intramolecular distance of 2.32(3) Å. Weak bifurcated H···F hydrogen bonds were experimentally observed in the solid anion $[E(OH)(C_6F_5)_3]^-$, which is coordinated to $[PtMe(bu_2\text{-}bpy)]^+$ via the oxygen atom.[42] The authors noted that the H···F interactions slightly elongate the corresponding C−F bonds, which is in agreement with our theoretical observations (Figure 4d). Similar interactions also play a role in complexes of $M(C_6F_5)_3$ (M = B, Al) with nitrogen-containing donors, where weak N−H···F−C hydrogen bonding interactions lead to significantly more acute values for one of the C−M−C angles.[8] One can speculate that intramolecular interactions will also be present in the solid nitrile adducts studied by Lee,[18] which would affect the CN stretching mode and therefore change the derived order of the acceptor ability of $E(C_6F_5)_3$.

In our optimized gas phase structures of $E(C_6F_5)_3 \cdot H_2O$, both hydrogen atoms of water are involved in intramolecular H···F bonds. The distances are 1.735 and 1.750 Å for B, 1.813 and 1.816 Å for Al, and 1.886 and 1.890 Å for gallium. The E−C

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(66) Schaffer, W. P.; Quan, R. W.; Bercaw, J. E. *Acta Crystallogr.* **1993**, *C49*, 881.

(67) Ishihara, K.; Kurihara, H.; Yamamoto, H. *J. Org. Chem.* **1997**, *62*, 5664.

(68) Elschenbroich, C.; Salzer, A.; Organometallchemie, B. G. *Teubner Verlag, Stuttgart, 1 Auflage* **1986**, 98 ff., as cited in ref 20.

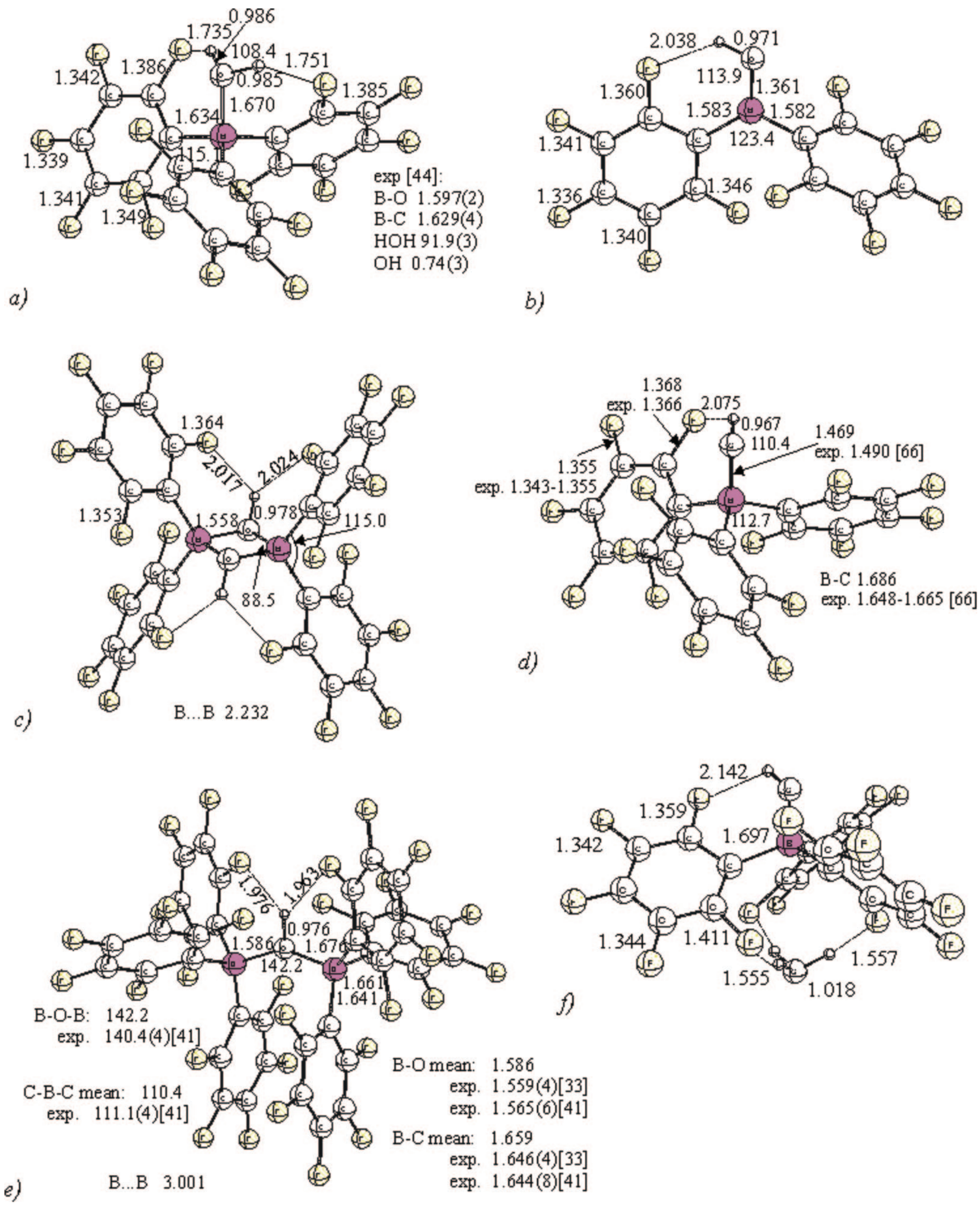
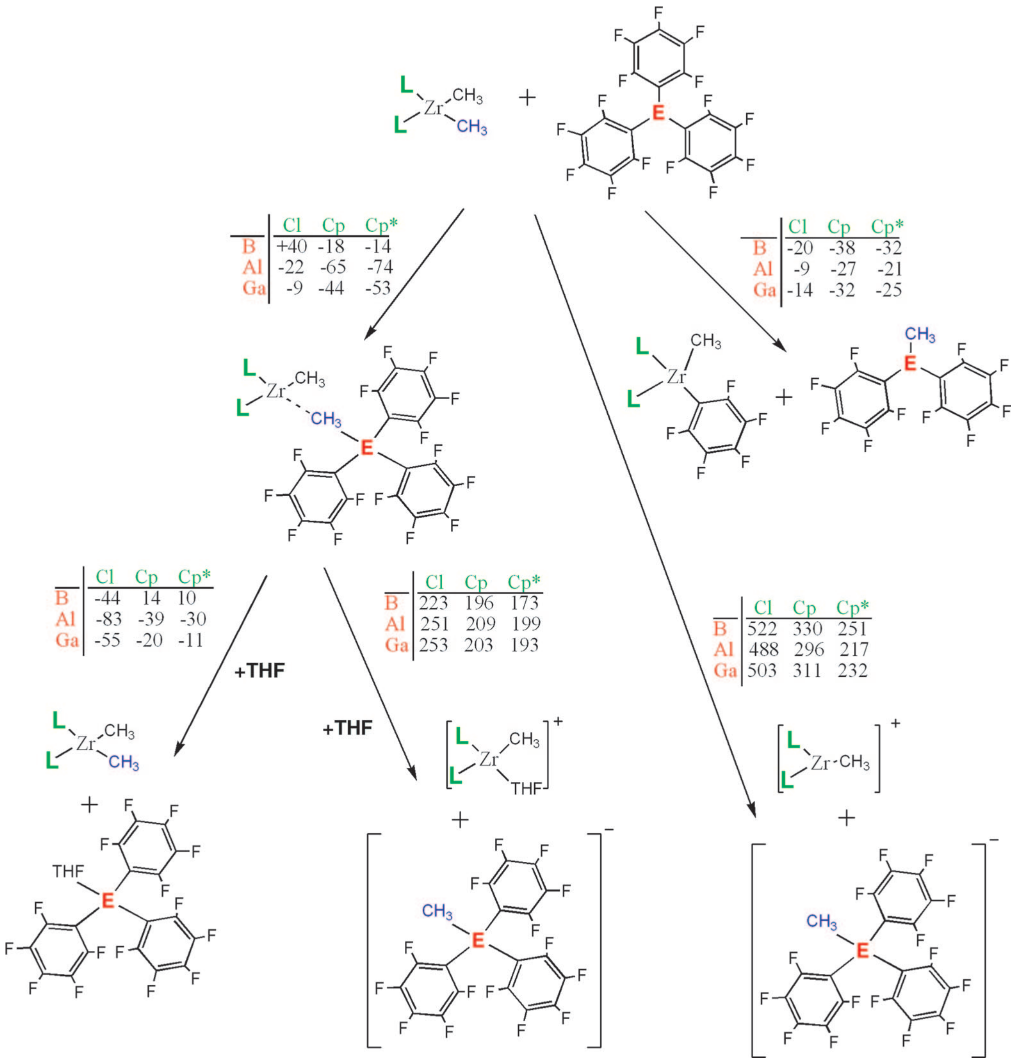


Figure 4. Optimized structures of the $B(C_6F_5)_3$ adduct with water (a) and initial stage hydrolysis products: (b) monomeric $B(C_6F_5)_2OH$; (c) dimer $[B(C_6F_5)_2OH]_2$; (d) monomeric anion $[B(C_6F_5)_3OH]^-$; (e) dimeric anion $[B(C_6F_5)_3(\mu\text{-}OH)B(C_6F_5)_3]^-$; (f) ion pair formed by H_3O^+ and $[E(OH)(C_6F_5)_3]^-$. Distances are in Å, angles in deg.

bond distance increases along the series B, Al, Ga, which pushes the fluorine atoms of the C_6F_5 group away from the hydrogen atoms of the water molecule. Thus, boron compounds have a better stabilization due to shorter H•••F intermolecular contacts. Such short contacts result in a noticeable lengthening of the O−H bond of the water molecule (as compared to both free H_2O and bonded water in the $AlPh_3 \cdot H_2O$ complex). This activation of the coordinated water molecule is closely related to the Brønsted acidity of the water complexes.[16] We computed the values for the protonation of a water molecule yielding the formation of the anion. $[E(OH)(C_6F_5)_3]^-$. $E(C_6F_5)_3 \cdot H_2O + H_2O = H_3O^+ + [E(OH)(C_6F_5)_3]^-$.

For the separated ions in the gas phase this reaction is very endothermic (530–565 kJ mol^{-1}). We also considered the possibility of the formation of ion pairs between H_3O^+ and $[E(OH)(C_6F_5)_3]^-$. The optimization of an ion pair in which the H_3O^+ cation is coordinated to the $[E(OH)(C_6F_5)_3]^-$ anion via an O−H bond resulted in proton transfer, yielding the more stable neutral complex with two water molecules, $E(C_6F_5)_3 \cdot 2H_2O$. The optimization of an alternative structure with H_3O^+ placed above the C_6F_5 groups resulted in an ion pair (Figure 4f) with three close intramolecular H•••F contacts. The energy of such an ion pair is 135 (B), 136 (Al), and 170 (Ga) kJ mol^{-1} higher compared to the neutral complex $E(C_6F_5)_3 \cdot 2H_2O$. The formation of the $H_3O^+ \cdots [E(OH)(C_6F_5)_3]^-$ gaseous ion pair from $E(C_6F_5)_3 \cdot H_2O$ and H_2O is endothermic by 95, 85, and 126 kJ mol^{-1} for B, Al, and Ga, respectively. However, there is a strong possibility that in solution the solvatation energy will overcome the unfavorable ion pair generation and rather lead to dissociation of the $E(C_6F_5)_3 \cdot 2H_2O$ complex into solvated $[E(OH)(C_6F_5)_3]^-$ and H_3O^+ ($H_{2n+1}O_n^{\ +}$). We note that according to our results, the Al derivatives show the least endothermic values, indicating a higher Brønsted acidity of Al-containing compounds.

Scheme 2. Theoretically Predicted Energies (kJ mol^{-1}) of the Gas Phase Activation of L_2ZrMe_2 by $E(C_6F_5)_3$



Analogous to water, we also addressed ammonolysis reactions of $E(C_6F_5)_3$ (Scheme 1). The complexation with ammonia is much stronger compared to water. The complex formation energies are −97, −146, and −115 kJ mol^{-1} for B, Al, and Ga, respectively. The ammonolysis of such strongly bonded complexes (elimination of pentafluorobenzene with formation of monomeric amido derivative $NH_2E(C_6F_5)_2$) is much less favorable compared to hydrolysis. The reaction is only slightly exothermic for boron (−30), while for Al and Ga it is endothermic by 70 kJ mol^{-1}. However, taking into account the exothermic dimerization energies of the amides, the overall energies of the ammonolysis are exothermic by −48, −52, and −28 kJ mol^{-1} for B, Al, and Ga, respectively. These energies are substantially lower compared to the corresponding hydrolysis process. Nevertheless, the exothermicity of the reaction suggest that all $E(C_6F_5)_3$ species should be unstable toward ammonolysis.

Reactivity of $E(C_6F_5)_3$ with Zr Metallocenes. Because of the important role of $E(C_6F_5)_3$ as cocatalysts in olefin polymerization reactions, it is of interest to compare the trends in the reactivity of $E(C_6F_5)_3$ toward Zr metallocenes. As model compounds, we chose a series of L_2ZrMe_2 (L = Cl, C_5H_5, C_5Me_5) species. The calculations showed that the difference in energetics of ion pair formation with $B(C_6F_5)_3$ in the gas phase and in solution (computed by COSMO model) is less than 1 kcal mol^{-1}.[48] Our theoretical gas phase results are presented in Scheme 2 and Table 3. The theoretically predicted geometries for Cp_2ZrMe_2 and the $[Cp^*_2ZrMe]^+[MeB(C_6F_5)_3]^-$ ion pair agree reasonably well with experimental findings in the solid state[69,70] (Figure 5).

The formation of ion pairs with Cp_2ZrMe_2 and $Cp^*_2ZrMe_2$ in the gas phase is found to be exothermic. This observation qualitatively agrees with experimental studies in toluene using batch titration calorimetry by Marks.[3] The formation of contact ion pairs $Cp_2ZrMe^+MeB(C_6F_5)_3^-$ was measured to be exothermic by −96.7 kJ mol^{-1}, and the methyl substitution yielding Me_2Cp and Me_5Cp increased the reaction enthalpy up to −101.7 and −153.6 kJ mol^{-1}, respectively. Our predicted values reproduce this trend, but the calculated values are substantially lower compared to both the experiment and previous theoretical values at the BP91/DZP(TZP on Zr) level reported by Ziegler.[47,48,71]

The structures of the ion pairs indicate that the methyl moiety is transferred from Zr to the group 13 element. A dynamic NMR study revealed that the activation barriers for the methyde abstraction are small (8–25 kJ mol^{-1}) and relatively insensitive to the nature of the borane.[3] The experimental value for the activation barrier is close to the planarization energy computed in the present work of CH_3^- (24 kJ mol^{-1} at BP86/def2-TZVPP and 11.6 kJ mol^{-1} at CCSD(T)/aug-cc-pVTZ). This fact indicates that the formation of the ion pair is

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(69) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015.

(70) Hunter, W. E.; Hrncir, D. C.; Bynum, R. V.; Penttila, R. A.; Atwood, J. L. *Organometallics* **1983**, *2*, 750.

(71) Chan, M. S. W.; Vanka, K.; Pye, C. C.; Ziegler, T. *Organometallics* **1999**, *18*, 4624.

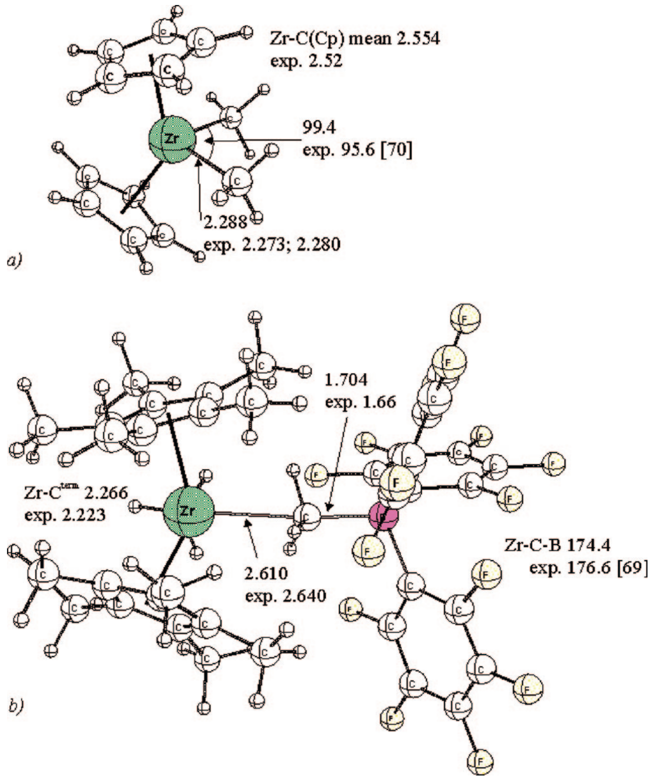

Figure 5. Comparison of the computed and experimental solid state structures of (a) Cp_2ZrMe_2 and (b) ion pair $[Cp^*{}_2ZrMe]^+[MeB(C_6F_5)_3]^-$. All distances are in Å, angles in deg.

primarily determined by the CH_3^- planarization energy and therefore does not depend on the counterion. We conclude that ion pair formation is thermodynamically favorable and should not be kinetically prohibited.

Marks et al.[17] noted a different reactivity between the $L_2ZrMe_2B(C_6F_5)_3$ and $L_2ZrMe_2Al(C_6F_5)_3$ ion pairs with THF. For the boron compounds, THF is coordinated to Zr and separated ions $[MeB(C_6F_5)_3]^-$ and $L_2ZrMeTHF^+$ are obtained, while in the case of Al, neutral $Al(C_6F_5)_3 \cdot THF$ and L_2ZrMe_2 are formed.[17] Our theoretical computations of the two reaction pathways (Scheme 2) show that for B displacement of the ion pair with THF with formation of $E(C_6F_5)_3 \cdot THF$ is predicted to be *endothermic*, but the reaction is *exothermic* for Al and Ga (Scheme 2). This comes from much stronger bonding between $Al(C_6F_5)_3$ and THF (104 kJ mol^{-1}) compared to the bonding between $B(C_6F_5)_3$ and THF (only 4 kJ mol^{-1}). The alternative pathway with generation of separated ions $L_2ZrMeTHF^+$ and $[MeB(C_6F_5)_3]^-$ is highly endothermic in the gas phase, but one can argue that such ions may become stabilized in solution.

We also considered CH_3/C_6F_5 exchange reactions between L_2ZrMe_2 and $E(C_6F_5)_3$, which are believed to lead to the catalyst degradation.[23,72] We find that for all $L_2ZrMe_2/E(C_6F_5)_3$ combinations such exchange reactions are *exothermic* in the gas phase (Scheme 2). We predict that for boron compounds the exchange reactions are slightly more favorable compared to the ion pair formation in the gas phase, while for Al and Ga the situation is reversed. Thus, the experimentally observed[23,72] more facile redistribution of C_6F_5 ligands from $Al(C_6F_5)_3$ to Zr (with formation of $Cp_2ZrMeC_6F_5$) compared to $B(C_6F_5)_3$ may be kinetically controlled.

Previous computational results of Ziegler[48] showed very small (less than 5 kJ mol^{-1}) difference between ion pair formation energies in the gas phase and in solution using the COSMO model. Influence of the solvent on the ligand redistribution processes is also expected to be very small. Therefore, our conclusions about energetics of the ion pair formation and ligand exchange reactions are expected to hold for the processes in solutions as well.

We point out that $E(C_6F_5)_3$ compounds in general have a very high tendency toward exchange reactions. A facile CH_3/C_6F_5) exchange between group 13 derivatives was reported by Klosin[73] and by Cowley.[74]

The high tendency for the Cl/C_6F_5 exchange for E = Al manifests itself in the experimentally found reaction between $Al(C_6F_5)_3$ with CH_2Cl_2, which yields dimeric $[ClAl(C_6F_5)_2]_2$.[75] The reaction of $Ga(C_6F_5)_3OEt_2$ with HCl yields $GaCl_3$ and HC_6F_5 (without evidence for the intermediates $Ga(C_6F_5)_2Cl$ and $Ga(C_6F_5)Cl_2$).[20] We find that the Cl/C_6F_5 exchange reactions $E(C_6F_5)_3 + 3HCl = ECl_3 + 3C_6F_5H$ are highly exothermic for all elements E (−222, −401, – 324 kJ mol^{-1} for B, Al, Ga, respectively). Therefore it is not surprising that there are no observed intermediates for the reaction with HCl.[20]

Thus, in addition to the strong Lewis acidity, $E(C_6F_5)_3$ are quite active species that have a tendency to undergo hydrolysis/ammonolysis reactions and they participate in ligand redistribution reactions. These side processes are thermodynamically favorable and must be taken into account when applying strong Lewis acids $E(C_6F_5)_3$ as catalysts and cocatalysts.

Conclusions

The acceptor properties of the perfluoroaryl compounds of group 13 elements in the gas phase were theoretically studied at the RI-BP86/def2-TZVPP level of theory. The following orders of the acceptor ability have been established: $E(C_6H_5)_3 \approx E(C_6H_4F)_3 \approx E(C_6F_5)_3 \approx ECl_3$; Al > Ga > B.

In contrast to previous statements,[17,18,23] we find that fluorination significantly enhances the Lewis acidity and that $Al(C_6F_5)_3$ is one of the strongest Lewis acids. In contrast to dimeric Al_2Cl_6, the monomeric nature of $Al(C_6F_5)_3$ allows it to form stable complexes with very weak Lewis bases.

Along with its strong Lewis acidity, $E(C_6F_5)_3$ compounds are potentially active species as catalysts that should undergo hydrolysis/ammonolysis reactions and participate in ligand redistribution reactions. These side processes are thermodynamically favorable and could considerably affect the reactivity of the $E(C_6F_5)_3$ species as catalysts and cocatalysts.

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Supporting Information Available: Table with major structural and energetic parameters (dissociation energies and total energies) for investigated complexes and table with BSSE corrections for $E(C_6F_5)_3$ complexes computed by counterpoise method. This material is available free of charge via the Internet at http://pubs.acs.org.

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(72) Siedle, A. R.; Newmark, R. A. J. *Organomet. Chem.* **1995**, *497*, 119.

(73) Klosin, J.; Roof, G. R.; Chen, E. X.-Y.; Abboud, K. A. *Organometallics* **2000**, *19*, 4684.

(74) Hair, G. S.; Cowley, A. H.; Gorden, J. D.; Jones, J. N.; Jones, R. A.; Macdonald, C. L. B. *Chem. Commun.* **2003**, 424.

(75) Chakraborty, D.; Chen, E. X.-Y. *Inorg. Chem. Commun.* **2002**, *5*, 698.

(76) Willis, B. G.; Jensen, K. F. *J. Phys. Chem. A* **1998**, *102*, 2613.