Contra-Binding Rotation in Al⁺−L Complexes (L = C₆H₆, C₄H₄O, C₅H₆, C₄H₄NH): A New Degenerate Rearrangement

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A particular part of the potential-energy surface of Al(L)⁺ complexes (L = benzene, furane, cyclopentadiene, pyrrole, pyridine) has been investigated by means of density functional theory and Hartree−Fock calculations including electron correlation. On the basis of these results, a new kind of degenerate rearrangement will be reported: The barrier for the rotation of the ligand L *toward* the Al⁺−L binding axis can be energetically below the Al(L)⁺ → Al⁺ + L dissociation limit. Thus, such a rotation can occur prior to dissociation. The term *contra-binding rotation* is proposed for this process, which is predicted to take place in the systems Al(C₆H₆)⁺, Al(C₄H₄O)⁺, Al(C₅H₆)⁺, and Al(C₄H₄NH)⁺. The energies of the corresponding transition states (TS_rot) relative to the dissociation products amount to −5 to −14 kcal/mol at 0 K. Concerning Al(C₅H₅N)⁺, a respective TS_rot could not be detected. The aluminum−pyridine complex dissociates instead of a contra-binding rotation. With increasing temperature, the change in free energy of the contra-binding rotation process increases. Under standard conditions (298.15 K and 1013.25 mbar), the G2MP2-calculated ΔG of the contra-binding rotation amount to +0.6 to +0.9 kcal/mol (L = C₄H₄O), −2.8 kcal/mol (L = C₆H₆), −1.4 to −4.8 kcal/mol (L = C₅H₆), and −5.5 to −7.3 kcal/mol (L = C₄H₄NH). A consequence of the present findings is discussed with regard to planar-chiral metal−arene complexes.

Introduction

Cationic aluminum complexes[1] hold a prominent position in homo- and heterogeneous catalysis. Intense effort has been put into identifying active catalyst sites and likely reaction mechanisms. Advanced experimental and theoretical approaches yielded a more detailed picture[2] of the respective processes. For example, the binding characteristics in organometallic Al⁺−L (L = ligand) complexes[3,4] were found to constitute an intermediacy between those of the corresponding alkali ion

and transition metal ion complexes. Two Al⁺-specific aspects are thought to be responsible for this property:[4] the polarizable [Ne] 3s² electron configuration and the energetically low-lying empty 3p orbitals. According to a recent analysis of the binding characteristics in Al⁺−π-L complexes (π-L = benzene, furane, cyclopentadiene, and pyrrole), aluminum's intermediacy with regard to alkali and transition metal ion complexes was confirmed.[5]

π-Bonded M−arene complexes (M = metal atom) have received considerable attention in theoretical[5−7] and experimental[3d,f,8] investigations. Their fluxional behavior represents one highlight of active research. For example, haptotropic rearrangements[9] have been observed by NMR and optical spectroscopy. Albright et al. studied the degenerate η⁶ → η⁶ rearrangement of Cr-

(1) Selected references: (a) Ziegler, K.; Holzkamp, E.; Breil, H.; Martin, H. *Angew. Chem.* **1955**, *67*, 541. (b) Natta, T. *Macromol. Chem.* **1955**, *16*, 213. (c) Sishta, S.; Hathorn, R. M.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 1112. (d) Pellececchia, C.; Grassi, A.; Immirzi, A. *J. Am. Chem. Soc.* **1994**, *116*, 1160, and references therein. (e) Fink, G., Mülhaupt, R., Brintzinger, H. H., Eds. *Ziegler Catalysts: Recent Scientific Innovations and Technological Improvements*; Springer-Verlag: Berlin, 1995.

(2) (a) Uhl, W. *Angew. Chem.* **1993**, *105*, 1449; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1386. (b) Wehmschulte, R. J.; Ruhland-Senge, K.; Olmstead, M. M.; Hope, H.; Sturgeon, B. E.; Power, P. P. *Inorg. Chem.* **1993**, *32*, 2983. (c) Dohmeier, C.; Loos, D.; Schnöckel, H. *Angew. Chem.* **1996**, *108*, 141; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 129. (d) Weiss, J.; Stetzkamp, D.; Nuber, B.; Fischer, R. A.; Boehme, C.; Frenking, G. *Angew. Chem.* **1997**, *109*, 95; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 70. (e) Fischer, R. A.; Schulte, M. M.; Weiss, J.; Zsolnai, L.; Jacobi, A.; Huttner, G.; Frenking, G.; Boehme, C.; Vyboishzchikov, S. F. *J. Am. Chem. Soc.* **1998**, *120*, 1237. (f) Brändle, M.; Sauer, J. *J. Am. Chem. Soc.* **1998**, *120*, 1556.

(3) (a) Hrušák, J.; Stöckigt, D.; Schwarz, H. *Chem. Phys. Lett.* **1994**, *221*, 518. (b) Stöckigt, D.; Hrušák, J. *J. Phys. Chem.* **1994**, *98*, 3675. (c) Stöckigt, D.; Holthausen, M. C.; Koch, W.; Schwarz, H. *J. Phys. Chem.* **1995**, *99*, 5950. (d) Stöckigt, D.; Hrušák, J.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1995**, *149/150*, 1. (e) Stöckigt, D.; Schwarz, J.; Schwarz, H. *J. Phys. Chem.* **1996**, *100*, 8786. (f) Dunbar, R. C.; Klippenstein, S. J.; Hrušák, J.; Stöckigt, D.; Schwarz, H. *J. Am. Chem. Soc.* **1996**, *118*, 5277.
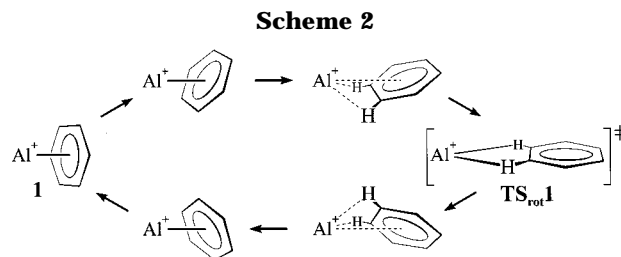
(4) (a) Tortajada, J.; Total, A.; Morizur, J. P.; Alcamí, M.; Mó, M.; Yáñez, M. *J. Phys. Chem.* **1992**, *96*, 8309. (b) Mó, O.; Yáñez, M.; Total, A.; Tortajada, J.; Morizur, J. P. *J. Phys. Chem.* **1993**, *97*, 5553. (c) Kemper, P. R.; Bushnell, J.; Bowers, M. T.; Gellene, G. I. *J. Phys. Chem. A* **1998**, *102*, 8590. (d) Dunbar, R. C. *J. Phys. Chem. A* **1998**, *102*, 8946.

(5) Stöckigt, D. *J. Phys. Chem.* **1997**, *101*, 3800.

(6) (a) Mavri, J.; Koller, J.; Hadzi, D. *J. Mol. Struct. (THEOCHEM)* **1990**, *283*, 305. (b) Zerner, M. C. In *Metal−Ligand Interactions: from Atoms to Clusters, to Surfaces*; Salahub, D. R., Russo, N., Eds.; Kluwer Academic Publisher: New York, 1992. (c) Bauschlicher, C. W., Jr.; Partridge, H.; Langhoff, S. R. *J. Phys. Chem.* **1992**, *96*, 3273. (d) Kumpf, R. A.; Dougherty, D. A. *Science* **1993**, *261*, 1708. (e) Kim, K. S.; Lee, J. Y.; Lee, S. J.; Ha, T.-K.; Kim, D. H. *J. Am. Chem. Soc.* **1994**, *116*, 7399. (f) Lee, J. Y.; Lee, S. J.; Choi, H. S.; Cho, S. J.; Kim, K. S.; Ha, T.-K. *Chem. Phys. Lett.* **1995**, *232*, 67. (g) Basch, H.; Stevens, W. J. *J. Mol. Struct. (THEOCHEM)* **1995**, *338*, 303. (h) Mecozzi, S.; West, Jr., A. P.; Dougherty, D. A. *J. Am. Chem. Soc.* **1996**, *118*, 2307. (i) Caldwell, J. W.; Kollman, P. A. *J. Am. Chem. Soc.* **1996**, *118*, 4177. (j) Chipot, C.; Maigret, B.; Pearlman, D. A.; Kollman, P. A. *J. Am. Chem. Soc.* **1996**, *118*, 2998. (k) Dougherty, D. A. *Science* **1996**, *271*, 163.

Scheme 1

(a) **(b)**
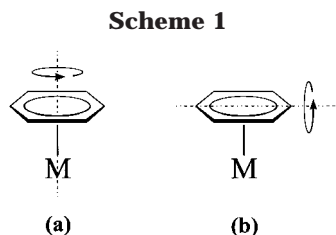
Scheme 2

$(CO)_3(\eta^6$-naphthalene) complexes.[9a] In addition, metal-coordinated arene,[10] butadiene,[11] and fullerene[12] ligands were shown to rotate *about* the M−arene bond ("tripodal rotation", Scheme 1a). Recently, the *endo* to *exo* isomerization of Ru and Os complexes containing tetramethyl-*o*-xylene has been reported.[13]

The issue of the present investigation concerns a new, not yet reported degenerate rearrangement. On the basis of quantum chemical calculations, a *contra-binding* rotation of Al(L)+ complexes will be discussed (Scheme 1b). During this process, the rotation of a ligand L *rectangular* to the Al+−L binding axis (L = benzene, furane, cyclopentadiene, or pyrrole) occurs without Al+−L dissociation.[14] The contra-binding rota-

tion belongs to the class of degenerate concerted reactions. It is a one-step reaction in which reactant and product differ only by the interchange of identical atoms. Rules for predicting the symmetry of a transition state (TS) in degenerate reactions have been introduced.[15] The following points will be raised in the present contribution: (i) the *contra-binding* rotation of a ligand L *toward* the Al+−L axis (for L = C_6H_6, see Scheme 2);[16] (ii) the molecular structures and relative energies of the transition states for contra-binding rotation (TS_rot); (iii) a comparison[17] of pure density functional theory (DFT),[18] DFT/Hartree−Fock-hybrid (DFT/HF),[19,20] and post-Hartree−Fock methods with regard to the PES of contra-binding rotation; (iv) a potential consequence of the contra-binding rotation.

Computational Details

The quantum chemical calculations have been performed by using the Gaussian 94 program package[21] on Digital DEC 3000/300 workstations and on a SGI Power Challenge R8000 with four processors. In the present Kohn−Sham calculations, Slater's local (S)[21] and Becke's gradient-corrected (B)[20f] exchange functionals as well as the correlation functionals reported by Vosko, Wilk, and Nusair (VWN and VWN5),[20a] Lee, Yang, and Parr (LYP),[20d] Perdew (P86),[20c] and Perdew and Wang (PW91)[20g] were employed. The combined abbreviations SVWN, SVWN5, BLYP, BP86, and BPW91 indicate pure DFT approaches. In addition, DFT/HF-hybrid methods such as BHLYP,[19,21] B3LYP,[22] and B3PW91[23] have been applied.[24] In these cases a certain amount of Hartree−Fock exchange is added (50% in BHLYP, 20% in both B3LYP and B3PW91). The

(7) (a) Staley, R. H.; Uppal, J. S. *J. Am. Chem. Soc.* **1975**, *97*, 5920. (b) Hettich, R. L.; Jackson, T. C.; Stanko, E. M.; Freiser, B. S. *J. Am. Chem. Soc.* **1986**, *108*, 5086. (c) Hettich, R. L.; Freiser, B. S. *J. Am. Chem. Soc.* **1987**, *109*, 3537. (d) Bauschlicher, C. W., Jr.; Partridge, H.; Langhoff, S. R. *J. Phys. Chem.* **1992**, *96*, 3273. (e) Willney, K. F.; Yeh, C. S.; Robbins, D. L.; Duncan, M. A. *J. Phys. Chem.* **1992**, *96*, 9106. (f) Meyer, F.; Khan, F. A.; Armentrout, P. B. *J. Am. Chem. Soc.* **1995**, *117*, 9740. (g) Schröder, D.; Hrušák, J.; Hertwig, R. H.; Koch, W.; Schwerdtfeger, P.; Schwarz, H. *Organometallics* **1995**, *14*, 312. (h) Seemeyer, K.; Hertwig, R. H.; Hrušák, J.; Koch, W.; Schwarz, H. *Organometallics* **1995**, *14*, 4409. (i) Schröder, D.; Schwarz, H. *J. Organomet. Chem.* **1995**, *504*, 123.

(8) (a) Sunner, J.; Nishizawa, K.; Kebarle, P. *J. Phys. Chem.* **1981**, *85*, 1814. (b) Meot-Ner (Mautner), M.; Deakyne, C. A. *J. Am. Chem. Soc.* **1985**, *107*, 469. (c) Deakyne, C. A.; Meot-Ner (Mautner), M. *J. Am. Chem. Soc.* **1985**, *107*, 474. (d) Huang, Y.; Freiser, B. S. *J. Am. Chem. Soc.* **1990**, *112*, 5085. (e) Guo, B. C.; Purnell, J. W.; Castleman, A. W., Jr. *Chem. Phys. Lett.* **1990**, *168*, 155. (f) Taft, R. W.; Anvia, F.; Gal, J.-F.; Walsh, S.; Capon, M.; Holmes, M. C.; Hosn, K.; Oloumi, G.; Vasanwala, R.; Yazdani, S. *Pure Appl. Chem.* **1990**, *62*, 17. (g) Dunbar, R. C.; Solooki, D.; Tessier, C. A.; Youngs, W. J. *Organometallics* **1991**, *10*, 52. (h) Afzaal, S.; Freiser, B. S. *Chem. Phys. Lett.* **1994**, *218*, 224. (i) Dunbar, R. C.; Uechi, G. T.; Asamoto, B. *J. Am. Chem. Soc.* **1994**, *116*, 2466. (j) Bock, H.; Gharagozloo-Hubmann, K.; Näther, C.; Nagel, N.; Havlas, Z. *Angew. Chem.* **1996**, *108*, 720; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 631.

(9) (a) Albright, T. A.; Hofman, P.; Hoffmann, R.; Lillya, C. P.; Dobosh, P. A. *J. Am. Chem. Soc.* **1983**, *105*, 3396. (b) Nambu, M.; Mohler, D. L.; Hardcastle, K.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1993**, *115*, 6138. (c) Decken, A.; Britten, J. F.; McGlinchey, M. J. *J. Am. Chem. Soc.* **1993**, *115*, 7275. (d) Zhang, S.; Bordwell, F. G. *Organometallics* **1994**, *13*, 2920.

(10) (a) Merkert, J.; Nielson, R. M.; Weaver, M. J.; Geiger, W. E. *J. Am. Chem. Soc.* **1989**, *111*, 7084. (b) Downton, P. A.; Mailvaganam, B.; Frampton, C. S.; Sayer, B. G.; McGlinchey, M. J. *J. Am. Chem. Soc.* **1990**, *112*, 27. (c) Koefod, R. S.; Mann, K. R. *J. Am. Chem. Soc.* **1990**, *112*, 7287. (d) Kilway, K. V.; Siegel, J. S. *J. Am. Chem. Soc.* **1991**, *113*, 2332. (e) Mailvaganam, B.; Frampton, C. S.; Top, S.; Sayer, B. G.; McGlinchey, M. J. *J. Am. Chem. Soc.* **1991**, *113*, 1177. (f) Braga, D. *Chem. Rev.* **1992**, *92*, 633. (g) McGlinchey, M. J. *Adv. Organometallic Chem.* **1992**, *34*, 285. (h) Singewald, E. T.; Shi, X.; Mirkin, C. A.; Schofer, S. J.; Stern, C. L. *Organometallics* **1996**, *15*, 3062.

(11) (a) Grevels, F.-W.; Jacke, J.; Seevogel, K. *J. Mol. Struct.* **1988**, *174*, 107. (b) Turner, J. J.; Grevels, F.-W.; Howdle, S. M.; Jacke, J.; Haward, M. T.; Klotzbücher, W. E. *J. Am. Chem. Soc.* **1991**, *113*, 8347. (c) González-Blanco, Ò.; Branchadell, V. *Organometallics* **1997**, *16*, 475. (d) Bühl, M.; Thiel, W. *Inorg. Chem.* **1998**, *36*, 22922.

(12) (a) Douthwaite, R. E.; Green, M. L. H.; Stephens, A. H. H.; Turner, J. F. C. *J. Chem. Soc., Chem. Commmun.* **1993**, 1522. (b) Green, M. L. H.; Stephens, A. H. H. *J. Chem. Soc., Chem. Commmun.* **1997**, 793.

(13) (a) Bennett, M. A.; Bown, M.; Hockless, D. C. R.; McGrady, J. E.; Schranz, H. W.; Stranger, R.; Willis, A. C. *Organometallics* **1998**, *17*, 3784. (b) See also the study on *exo* and *endo* forms of Ru(PH_3)_3-{η^4-*o*-(CH_2)_2C_6H_4$}: McGrady, J. E.; Stranger, R.; Bown, M.; Bennett, M. A. *Organometallics* **1996**, *15*, 3109.

(14) However, dissociation of a molecule can be accompanied by rotational diffusion: (a) Longevialle, P.; Botter, R. *J. Chem. Soc., Chem. Commun.* **1980**, 823. (b) Morton, T. H. *Org. Mass Spectrom.* **1992**, *27*, 353. (c) McAdoo, D. J.; Morton, T. H. *Acc. Chem. Res.* **1993**, *6*, 295.

(15) (a) Schaad, L. J.; Hu, J. *J. Am. Chem. Soc.* **1998**, *120*, 1571. (b) Pechukas, P. *J. Chem. Phys.* **1976**, *64*, 1516.

(16) The rotation of a single molecule within a supramolecular bearing has been reported: Gimzewski, J. K.; Joachim, C.; Schlitter, R. R.; Langlais, V.; Tang, H.; Johannsen, I. *Science* **1998**, *281*, 531.

(17) Stöckigt, D. *J. Phys. Chem. A* **1998**, *102*, 10493.

(18) (a) Ziegler, T. *Chem. Rev.* **1991**, *91*, 651. (b) March, N. H. *Electron Density Theory of Atoms and Molecules*; Academic Press: London, 1992.

(19) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372.

(20) (a) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200, and references therein. (b) Colle, R.; Salvetti, O. *J. Chem. Phys.* **1983**, *79*, 1404. (c) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822. (d) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (e) Becke, A. D. *J. Chem. Phys.* **1988**, *88*, 1053. (f) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (g) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244. (h) Baker, J.; Muir, M.; Andzelm, J. *J. Chem. Phys.* **1995**, *102*, 2063.

(21) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision B.3; Gaussian, Inc.: Pittsburgh, PA, 1995.

(22) Hertwig, R. H.; Koch, W. *Chem. Phys. Lett.* **1997**, *268*, 345.

(23) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(24) Stöckigt, D. *Chem. Phys. Lett.* **1996**, *250*, 387.

Table 1. Relative Energies, E_{rel} (in kcal/mol), of the $Al(C_6H_6)^+$ ($^1A_1$) Complex[a] and the Transition State for Contra-Binding Rotation ($TS_{rot}1$) According to Different Levels of Theory. The Relative Energy of the Dissociation Products Is Set to E_{rel} (Al^+ (^1S) + C_6H_6) = 0.0 kcal/mol.[b] The G2MP2-, G1-, or G2-Calculated Data Amount to $E_{rel}(Al(C_6H_6)^+)$ = -35.1, -36.6, or -35.6 kcal/mol, and $E_{rel}(TS_{rot}1)$ = -7.8, -8.3, or -8.0 kcal/mol, Respectively

method	species	3-21G	6-31G(d)	6-311+G(d)	6-311++G(3df,2p)[c]	cc-pVDZ	cc-pVTZ[d]
HF	$Al(C_6H_6)^+$		-28.5	-25.6			
	$TS_{rot}1$		-1.7	-1.1			
MP2(full)	$Al(C_6H_6)^+$		-40.1	-36.5	-39.1	-36.4	-40.1
	$TS_{rot}1$		-7.3	-5.8	-9.2	-8.3	-10.1
QCISD(T)	$Al(C_6H_6)^+$		-36.1[e]	-33.3[e]		-32.6[e]	
	$TS_{rot}1$		-6.1[e]	-4.9[e]		-7.0[e]	
SVWN	$Al(C_6H_6)^+$	-51.9	-49.9	-44.9	-46.1	-46.7	-45.2
	$TS_{rot}1$	-17.2	-19.7	-16.9	-19.8	-18.6	-18.1
SVWN5	$Al(C_6H_6)^+$	-64.7	-49.5	-44.3	-45.4	-46.2	-45.1
	$TS_{rot}1$	-30.2	-19.5	-16.5	-19.3	-18.3	-18.2
BLYP	$Al(C_6H_6)^+$	-36.5	-34.1	-28.3	-28.9	-32.2	-30.3
	$TS_{rot}1$	-8.7	-9.9	-7.0	-9.0	-9.9	-9.3
B3LYP	$Al(C_6H_6)^+$	-36.5	-34.5	-29.6	-30.5	-31.6	-30.8
	$TS_{rot}1$	-7.0	-8.1	-6.0	-7.9	-8.4	-8.2
BHLYP	$Al(C_6H_6)^+$	-35.3	-33.8	-29.8	-31.1	-31.3	-30.8
	$TS_{rot}1$	-4.9	-5.7	-4.2	-6.0	-4.8	-4.9
BPW91	$Al(C_6H_6)^+$	-41.0	-38.7	-34.4	-35.6	-35.9	-35.3
	$TS_{rot}1$	-8.9	-11.1	-8.9	-11.4	-11.4	-11.2
B3PW91	$Al(C_6H_6)^+$	-40.1	-38.3	-34.5	-36.0	-35.6	-35.5
	$TS_{rot}1$	-7.0	-8.9	-7.3	-9.6	-8.1	-8.5

[a] The data on the $Al(C_6H_6)^+$ complex have been taken from ref 5b. [b] Concerning BSSE values, see ref 31. [c] Single-point energy calculation employing the same method but the 6-311+G(d) basis set and ZPVE correction. [d] Single-point energy calculation employing the same method but the cc-pVDZ basis set and ZPVE correction. [e] Single-point energy calculation on MP2(full)/6-311+G(d)-optimized geometry and ZPVE correction.

calculations employed Pople's split-valence basis sets including polarization and diffuse functions (3-21G, 6-31G(d), 6-311+G-(d), and 6-311++G(3df,2p))[25] as well as the correlation-consistent basis sets[26] cc-pVDZ and cc-pVTZ reported from the group of Dunning.[21] Theoretical methods utilized here also involved second-order Møller–Plesset perturbational theory with all electrons correlated (MP2), the quadratic configuration interaction method including single, double, and estimated triple substitutions (QCISD(T)), and G2-calculations.[21,27] The ZPVE values obtained from the DFT and DFT/HF treatments have been scaled by 0.98. In the text, relative energies (E_{rel}) are given in kcal/mol with respect to the dissociation products Al^+(^1S) + L at 0 K. A boldface notation is used to aid in identification of the species in figures, tables, and text.

Results and Discussion

This section is organized as follows. In the beginning, the results concerning contra-binding rotation of the systems $[Al^+,C_6H_6]$, $[Al^+,C_4H_4O]$, $[Al^+,C_5H_6]$, $[Al^+,C_4H_4-NH]$, and $[Al^+,C_5H_5N]$ at 0 K are presented (parts A–E, respectively). In paragraph F, the data from different computational methods will be compared. Thermo-

chemical effects will be considered in part G. Finally (part H), a potential consequence of contra-binding rotation with regard to planar-chiral metal–arene complexes will be discussed.

A. The Al^+–C_6H_6 System. In previous theoretical[3d,5] studies on $Al^+(C_6H_6)$ (**1**), $D_0(Al^+-C_6H_6)$ has been determined to be 35.6 kcal/mol[5] and 39.0 kcal/mol.[3d] The 298 K gas-phase bond dissociation enthalpy amounts to $\Delta H_{diss}^{298 K}(Al^+-C_6H_6)$ = 35(2) kcal/mol as measured via radiative association kinetics.[3f] The present G2 data D_0-$(Al^+-C_6H_6)$ = 35.6 kcal/mol (Table 1) and $\Delta H_{diss}^{298 K}(Al^+-C_6H_6)$ = 35.8 kcal/mol support these findings.

With regard to the contra-binding rotation process depicted in Schemes 1b and 2, a C_{2v}-symmetric transition state structure, **$TS_{rot}1$**, has been located on the $[Al^+,C_6H_6]$ PES. Only one imaginary frequency belongs to **$TS_{rot}1$**. Its vector components indicate the referring contra-binding rotation. In addition, calculations employing the intrinsic reaction coordinate (IRC)[28] following procedure proved the correct assignments of transition state, reactant, and product. Geometrical parameters of **$TS_{rot}1$** are given in Figure 1. An η^1-coordinated Al^+–H–C_6H_5 (C_{2v}) stationary point has also been detected. This species, however, is characterized by *two* imaginary frequencies and will not be discussed in more detail. C–H bond insertion reactions of the $[Al^+,L]$ PES have not been considered in the present context.[29]

The energy of **$TS_{rot}1$** relative to the dissociated products, Al^+ and C_6H_6, has been determined to E_{rel}-(**$TS_{rot}1$**) = -8 to -11 kcal/mol by the MP2, QCISD(T), G1, G2MP2, G2, DFT, and DFT/HF methods (Figure 2 and Table 1). This indicates the benzene rotation toward

(25) (a) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650. (b) Guo, H.; Karplus, M. *J. Chem. Phys.* **1989**, *91*, 1719.

(26) (a) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358. (b) Woon, D. E.; Dunning, Jr., T. H. *J. Chem. Phys.* **1994**, *100*, 2975, and references therein. (c) Basis sets were obtained in part from the Extensible Computational Chemistry Environment Basis Set Database, Version 1.0, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory, which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352, and funded by the U.S. Department of Energy (http://www.emsl.pnl.gov:2080/forms/basisform.html). The Pacific Northwest Laboratory is a multiprogram laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RLO 1830. Contact David Feller, Karen Schuchardt, or Don Jones for further information.

(27) (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968. (c) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221. (d) Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 1293.

(28) The intrinsic reaction coordinate can be qualitatively thought of as the lowest energy pathway in mass-weighted coordinates: (a) Gonzales, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154. (b) Gonzales, C.; Schlegel, H. B. *J. Chem. Phys.* **1990**, *94*, 5523. (c) Deng, L.; Ziegler, T. *Int. J. Quantum Chem.* **1994**, *52*, 731.
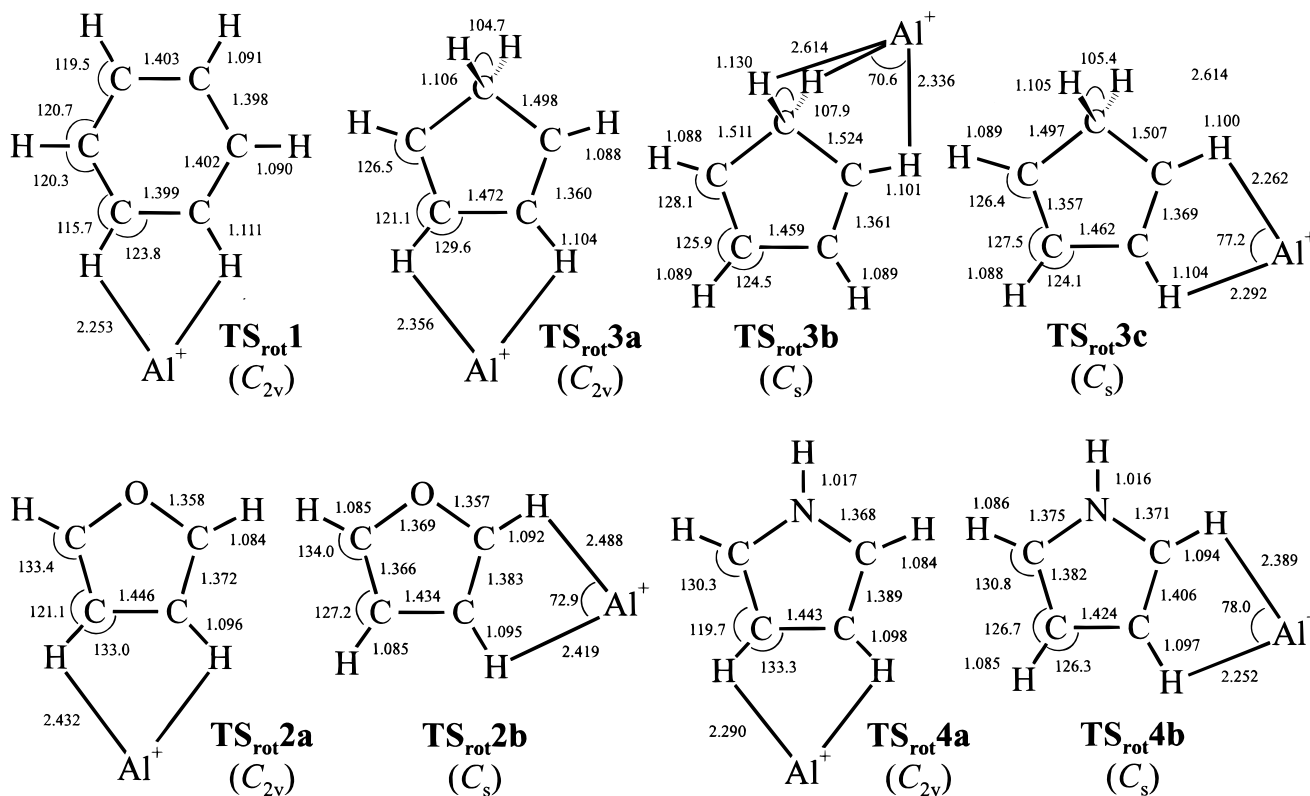
(29) Stöckigt, D. To be published.

Figure 1. Selected geometrical parameters of transition states for contra-binding rotation (TS$_{rot}$) as obtained with the BPW91/6-311+G(d) level of computation.
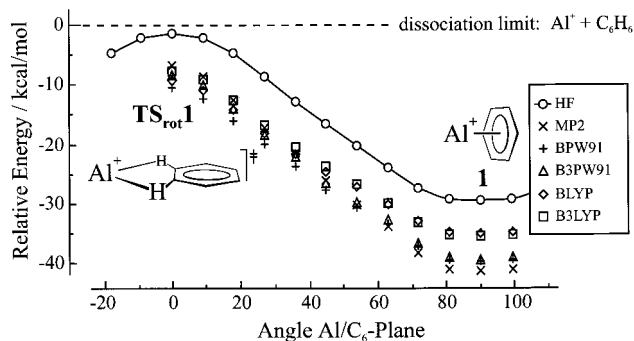

Figure 2. Schematic PES of the contra-binding rotation pathway in the case of the Al(C$_6$H$_6$)$^+$ system. The data points indicate that a 360° rotation of the benzene ligand can occur without Al$^+$−C$_6$H$_6^+$ dissociation (dotted line). The 6-31G(d) basis set was employed throughout. The structure at each point has been optimized with a frozen Al/C$_6$ angle. Data are given without ZPVE correction (cf. Table 1).

the Al$^+$−C$_6$H$_6$ bond to be energetically *more favorable* as compared to the Al$^+$−C$_6$H$_6$ dissociation. The barrier for the contra-binding rotation **1** ⇌ **1** amounts to ca. 27 kcal/mol via **TS$_{rot}$1**. The estimated basis set superposition error (BSSE) according to the counterpoise correction[30] indicates a revision of E_{rel}(**TS$_{rot}$1**) of less than 1 kcal/mol.[31]

In Figure 2, a part of the calculated [Al$^+$,C$_6$H$_6$] PES related to the contra-binding rotation process is pre-

(30) (a) van Duijneveldt, F. B.; van Duijneveldt-van de Rijdt, J. G. C. M.; van Lenthe, J. H. *Chem. Rev.* **1994**, *94*, 1873. (b) Xantheas, S. S. *J. Chem. Phys.* **1996**, *104*, 8821. (c) Dargel, T. K.; Hertwig, R. H.; Koch, W. *J. Chem. Phys.* **1998**, *108*, 3876.

(31) In the case of **TS$_{rot}$1**, the BSSEs have been computed to be 0.0 kcal/mol (B3LYP/6-31G(d)), 0.6 kcal/mol (B3LYP/6-311+G(d)), 0.4 kcal/mol (BPW91/6-31G(d)), 0.9 kcal/mol (BPW91/6-311+G(d)), 0.8 kcal/mol (MP2(full)/6-31G(d)), and 0.1 kcal/mol (MP2(full)/6-311+G(d)).

sented. The depicted data points have been obtained by calculating the relative energies (*y*-axis) without constrained geometrical parameters except a fixed angle between Al$^+$ and the midpoint of benzene's C$_6$ plane (*x*-axis, angle Al/C$_6$-plane). The corresponding intrinsic reaction coordinate belongs to the C_s symmetry point group. Therefore, six identical ways to reach **TS$_{rot}$1** from **1** are possible. The part of the PES depicted in Figure 2 describes one-fourth of a complete 360° rotation of Al$^+$ vs benzene.

B. The Al$^+$−C$_4$H$_4$O System. Recently, two Al-(C$_4$H$_4$O)$^+$ isomers were identified as minima on the [Al$^+$,C$_4$H$_4$O] PES, i.e., an Al$^+$−oxygen-coordinated complex with C_{2v} symmetry (**2a**) and a ca. 7 kcal/mol more stable complex in which Al$^+$'s empty p orbitals and furane's π MOs interact (**2b**, C_s).[5] A transition state, **TS2ab**, for the conversion **2a** ⇌ **2b** has been found. Its barrier height with regard to the minimum complexes **2a** and **2b** is ca. 1 and 8 kcal/mol, respectively. Two additional transition state structures, **TS$_{rot}$2a** (C_{2v}) and **TS$_{rot}$2b** (C_s), have been detected. In each case, one imaginary frequency was computed. The related vector components and IRC investigations indicate the referring contra-binding rotation. Geometrical parameters of **TS$_{rot}$2a** and **TS$_{rot}$2b** are given in Figure 1. The relative energies of **TS$_{rot}$2a**, **TS$_{rot}$2b**, and Al(C$_4$H$_4$O)$^+$ (**2a**) are summarized in Table 2.

A part of the [Al$^+$,C$_4$H$_4$O] PES related to contra-binding rotation is shown in Figure 3. The depicted data points have been obtained by calculating the relative energies (*y*-axis) with relaxed geometrical parameters except a fixed angle between Al$^+$ and the plane formed by furane's O and the two adjacent C atoms (*x*-axis, angle Al/OC$_2$). The respective intrinsic reaction coordi-

Table 2. Energies (in kcal/mol) of the Singlet Al(L)$^+$ Complexes (L = Furane, Cyclopentadiene, and Pyrrole) and the Transition States for Contra-Binding Rotation (TS$_{rot}$2−TS$_{rot}$4) Relative to the Dissociated Products, i.e., E_{rel} (Al$^+$ (^{1}S) + L) = 0.0 kcal/mol According to Different Levels of Theory[a]

method	Al(C$_4$H$_4$O)$^{+b}$	TS$_{rot}$2a	TS$_{rot}$2b	Al(C$_5$H$_6$)$^+$	TS$_{rot}$3a	TS$_{rot}$3b	TS$_{rot}$3c	Al(C$_4$H$_4$NH)$^+$	TS$_{rot}$4a	TS$_{rot}$4b
HF/6-31G(d)	−20.6	−0.1	+0.6	−23.6	−2.1	−1.8	−3.6	−34.5	−6.8	−4.5
HF/6-311+G(d)	−18.5	+0.5	+0.8	−21.1	−1.7	−1.3	−3.0	−31.0	−5.8	−3.6
B3LYP/6-31G(d)	−24.9	−4.9	−4.6	−31.9	−8.0	−7.9	−11.8	−41.8	−14.5	−12.6
B3LYP/6-311+G(d)	−21.9	−2.5	−2.3	−27.2	−6.0	−5.8	−9.1	−36.1	−11.2	−9.4
B3LYP/6-311++G(3df,2p)^c	−22.2	−4.2	−4.2	−28.0	−7.5	−7.4	−11.2	−36.3	−13.2	−11.4
B3LYP/cc-pVDZ	−23.8	−5.3	−5.1	−29.4	−8.3	−8.1	−12.0	−38.8	−14.8	−12.9
B3LYP/cc-pVTZ^d	−22.6	−4.8	−4.7	−28.1	−7.9	−7.8	−11.5	−37.0	−13.9	−12.1
BPW91/6-31G(d)	−24.7	−7.5	−7.2	−37.0	−11.0	−11.2	−15.5	−46.3	−17.9	−16.0
BPW91/6-311+G(d)	−21.9	−5.0	−4.7	−32.7	−8.9	−9.0	−12.8	−41.2	−14.6	−12.8
BPW91/6-311++G(3df,2p)^c	−22.2	−7.2	−7.2	−33.9	−10.8	−10.9	−15.1	−41.6	−16.9	−15.1
BPW91/cc-pVDZ	−23.5	−7.9	−7.7	−34.4	−11.2	−11.3	−15.6	−43.2	−18.0	−16.1
BPW91/cc-pVTZ^d	−22.6	−7.7	−7.6	−33.7	−11.2	−11.3	−15.5	−42.0	−17.6	−15.7
B3PW91/6-31G(d)	−24.2	−5.7	−5.2	−35.9	−9.0	−9.1	−13.1	−45.5	−15.8	−13.7
B3PW91/6-311+G(d)	−21.8	−3.8	−3.3	−32.2	−7.4	−7.4	−11.0	−41.1	−13.2	−11.1
B3PW91/6-311++G(3df,2p)^c	−22.2	−5.9	−5.8	−33.4	−9.3	−9.4	−13.4	−41.7	−15.5	−13.6
MP2(full)/6-31G(d)	−25.8	−4.3	−3.5	−35.9	−7.1	−7.1	−10.8	−47.4	−14.3	−11.9
MP2(full)/6-311+G(d)^e	−21.6	−3.2	−2.4	−32.4	−6.1	−6.0	−9.0	−42.4	−12.0	−9.5
MP2(full)/cc-pVDZ^e	−23.0	−5.8	−5.0	−32.6	−7.8	−8.1	−11.7	−43.1	−15.5	−13.1
G2MP2(0 K)	−23.8	−4.9	−4.4	−30.5	−7.4	−8.2	−11.0	−40.9	−13.9	−11.6

^{a} For estimated BSSE values, see ref 31. ^{b} Data of the ^{1}A$_1$ complex, see ref 5. ^{c} Single-point calculation on the optimized geometry employing the 6-311+G(d) basis set and the same method. ^{d} Single-point calculation on the optimized geometry employing the cc-pVDZ basis set and the same method. ^{e} ZPVE data taken from the MP2(full)/6-31G(d) calculation.
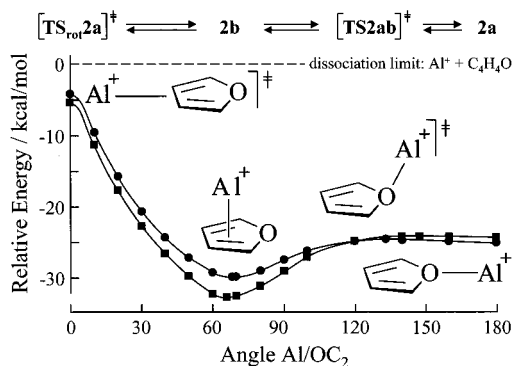

Figure 3. Schematic PES of the contra-binding rotation pathway in the case of the Al(C$_4$H$_4$O)$^+$ system. The data points indicate that a 360° rotation of the furane ligand can occur without Al$^+$−C$_4$H$_4$O dissociation (dotted line). The results obtained with the B3LYP (●) and the BPW91 (■) functionals and the 6-31G(d) basis set are displayed. The structure at each point has been optimized with a frozen angle between Al and the plane formed by furane's oxygen and the two adjacent carbons (angle Al/OC$_2$). Data are given without ZPVE correction (cf. Table 2).

Scheme 3
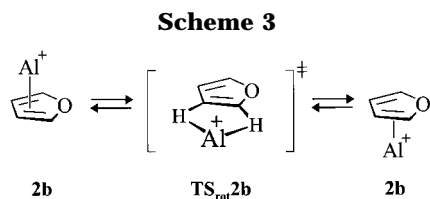
nate[28] is characterized by C_s symmetry; that is, the aluminum cation moves in furane's C_s plane (**2a** → **TS$_{rot}$2ab** → **2b** → **TS$_{rot}$2a** in Figure 3). Two rotations according to the PES shown in Figure 3 yield the identical complex **2a**. The G2MP2 method provides E_{rel}-(**TS$_{rot}$2a**) = −4.9 kcal/mol.

An additional reaction path for contra-binding rotation of the [Al$^+$,C$_4$H$_4$O] PES must be taken into consideration (Scheme 3): the process **2b** → **TS$_{rot}$2b** → **2b**. The relative energy of **TS$_{rot}$2b** (C_s) is below the dissociation limit, i.e., E_{rel}(**TS$_{rot}$2b**) = −4.4 kcal/mol
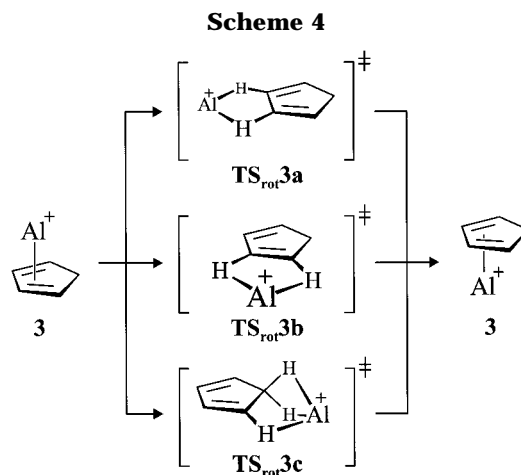
Scheme 4

(G2MP2). The corresponding IRC is characterized by the C_1 symmetry point group. The barrier heights for the degenerate rearrangements **2b** ⇌ **2b** amount to 19.0 kcal/mol via **TS$_{rot}$2a** (Figure 3) and 19.4 kcal/mol via **TS$_{rot}$2b** (Scheme 3).

C. The Al$^+$−C$_5$H$_6$ System. Concerning the contra-binding rotation process of the [Al$^+$,C$_5$H$_6$] PES, three transition state structures, **TS$_{rot}$3a** (C_{2v}), **TS$_{rot}$3b** (C_s), and **TS$_{rot}$3c** (C_s), have been identified. Therefore, three different contra-binding rotation pathways can be considered (Scheme 4). Only one imaginary frequency resulted for each transition state. The vector components point to the referring degenerate rearrangement. Geometrical parameters of **TS$_{rot}$3a**, **TS$_{rot}$3b**, and **TS$_{rot}$3c** are given in Figure 1. The relative energies of **TS$_{rot}$3a**, **TS$_{rot}$3b**, **TS$_{rot}$3c**, and Al(C$_5$H$_6$)$^+$ (**3**) are summarized in Table 2. The G2MP2 method provides E_{rel}(**TS$_{rot}$3a**) = −7.4 kcal/mol, E_{rel}(**TS$_{rot}$3b**) = −8.2 kcal/mol, and E_{rel}-(**TS$_{rot}$3c**) = −11.0 kcal/mol. The barrier heights of the conversion **3** ⇌ **3** amount to 23.1 kcal/mol via **TS$_{rot}$3a**, 22.4 kcal/mol via **TS$_{rot}$3b**, and 19.6 kcal/mol via **TS$_{rot}$3c** (Scheme 4). However, a competing process is the C−H bond insertion process resulting in H−Al(C$_5$H$_5$)$^+$.[29]

Scheme 5
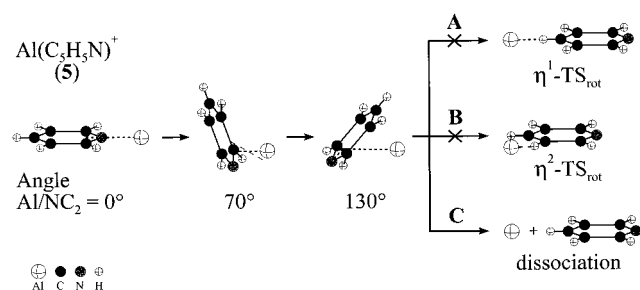
D. The Al^{+}−C$_4$H$_4$NH System. Concerning the contra-binding rotation process of the [Al^{+},C$_4$H$_4$NH] PES, two transition state structures, **TS$_{rot}$4a** (C_{2v}) and **TS$_{rot}$4b** (C_s), have been detected. Each of them is characterized by only one imaginary frequency, which is connected with vector components indicating the referring contra-binding rotation. A TS$_{rot}$ corresponding to **TS$_{rot}$3c** has not been found for the [Al[+],C$_4$H$_4$NH] PES. Geometrical parameters of **TS$_{rot}$4a** and **TS$_{rot}$4b** are given in Figure 1. The relative energies of **TS$_{rot}$4a**, **TS$_{rot}$4b**, and Al-(C$_4$H$_4$NH)[+] (**4**) are summarized in Table 2. The G2MP2-method provides E_{rel}(**TS$_{rot}$4a**) = −13.9 kcal/mol and E_{rel}(**TS$_{rot}$4b**) = −11.6 kcal/mol. The barrier heights for the degenerate rearrangement **4** ⇌ **4** amount to 32.8 kcal/mol via **TS$_{rot}$4a** and 35.1 kcal/mol via **TS$_{rot}$4b**.

E. The Al^{+}−C$_5$H$_5$N System. A completely different scenario is operative in the [Al^{+},C$_5$H$_5$N] PES. Applying various methods and levels of calculation, we were not able to locate a transition state for contra-binding rotation, i.e., a potential **TS$_{rot}$5**. The dissociation channel yielding Al[+] + C$_5$H$_5$N turns out to be energetically preferred over any contra-binding rotation process. This result is summarized in Scheme 5. Up to the angle Al/NC$_2$ ≈ 130°, the interaction between Al^{+} and pyridine's π-system results in a relative energy below the dissociation limit. Further movement of the metal center induces strong increase in relative energy due to (i) repulsion between aluminum's 3s^2 orbital and pyridine's hydrogen atoms, (ii) diminished charge−dipole moment attraction, and (iii) decrease of charge−polarization attraction. Finally, dissociation of the Al^{+}−C$_5$H$_5$N complex takes place (path **C**). An η^1-coordinated TS (path **A**) turns out to be higher in energy as compared to the dissociation limit. It is further characterized by two imaginary frequencies. An η^2-coordinated TS in analogy with the cases discussed for the other Al(L)[+] systems (cf. Figure 1) is not even a stationary point on the respective PES (path **B**).

F. Discussion of Computed Data. Considering the systems Al(L)[+] (L = benzene, furane, cyclopentadiene, and pyrrole), a transition state for contra-binding rotation is energetically *below* the dissociation limit, as predicted by the applied methods at 0 K.[32] In the case of Al(pyridine)[+], however, dissociation occurs prior to contra-binding rotation. The accuracy of the computed 0 K relative energies are expected[17] to be below ±5 kcal/

mol with G2MP2 and ±2 kcal/mol with G2. Accordingly, **TS$_{rot}$2a** and **TS$_{rot}$2b** are the only candidates whose E_{rel} data are close to the dissociation limit at 0 K (cf. Table 2 and part G).

The stability of TS$_{rot}$ relative to the dissociation products, Al^{+} + L, can be rationalized from the sum of attractive dispersion and charge-induced polarization effects. The components from charge−ligand dipole and charge−ligand quadrupole forces contribute to a much less significant but repulsive manner. The MO analysis of the Al^{+}−L binding characteristics of TS$_{rot}$ reveals small π-type interactions between Al's empty p$_z$ orbitals and the ligands' HOMOs. Therefore, stabilization of TS$_{rot}$ relative to the dissociation products might be achieved by increasing the corresponding charge−dipole and charge−quadrupole attraction.[29]

Concerning geometric data of the species under investigation, the following trends have been observed. DFT- and DFT/HF-predicted bond lengths and angles agree closely with MP2/6-31G(d) ones. In comparison with the geometric data of Al(C$_6$H$_6$)[+] and C$_6$H$_6$, the C−H and C−C bond lengths remain almost constant in **TS$_{rot}$1**. The H,C,C angles in **TS$_{rot}$1** match the 120.0° value of **1** and C$_6$H$_6$, except for those hydrogens which are coordinated to aluminum (H,C,C = 123.8°). They are bent away from the cationic aluminum center. Similar trends apply to the other Al^{+}−L transition states for contra-binding rotation.

Employing various levels of theory, the imaginary frequencies of the transition states of contra-binding rotation have been computed. They amount to ca. i100−i200 cm^{−1} depending on methods and systems. As expected, the HF-calculated imaginary frequencies are the lowest. The values from MP2, BPW91, BLYP, and DFT/HF approaches are quite similar to each other. Compared to the pure density functionals BPW91 and BLYP, admixing of 20% exact HF exchange (B3PW91 and B3LYP) results in deviations of <20%. Basis set dependencies of the imaginary frequency within a given method are found to be rather small. The 3-21G-predicted DFT and DFT/HF values are similar within 5−10%. The 3-21G and 6-31G(d) calculated ones are the highest throughout, and those from 6-311+G(d) are slightly below the 6-31G(d)-computed ones. The imaginary frequencies computed with cc-pVDZ[26] appear to be lower than or similar to those computed with Pople's basis sets.[25]

As pointed out previously,[5] the LYP-containing functionals seem to underestimate D_0(Al^{+}−π-L) of the complexes **1**, **2b**, **3**, and **4** by ca. 5 kcal/mol. This was attributed to the fact that the LYP correlation functional does not reach the uniform electron gas limit in contrast to P86 and PW91.[5] The reported discrepancy is further corroborated by the present G2, G2MP2, and G1 data[27c,d] (vide supra). The relative energy of the transition state[33] **TS$_{rot}$1**, however, is almost independent of the applied correlation functional, i.e., LYP vs PW91 (cf. Table 1).

(32) The gas-phase scenario under investigation can be altered significantly by solvent effects. Concerning respective examples, see: (a) Bohme, D. K.; Mackay, G. I. *J. Am. Chem. Soc.* **1981**, *103*, 978. (b) Jayaraman, C.; Smith, S. F.; Jorgensen, W. *J. Am. Chem. Soc.* **1985**, *107*, 154. (c) Zipse, H. *J. Am. Chem. Soc.* **1994**, *116*, 10773. (d) Zipse, H.; Apaydin, G.; Houk, K. N. *J. Am. Chem. Soc.* **1995**, *117*, 8608. (e) Zipse, H. *J. Am. Chem. Soc.* **1995**, *117*, 11798.

(33) Repeatedly, the relative energies of transition states have been found to be underestimated by DFT methods. See for example: (a) Fan, L.; Ziegler, T. *J. Chem. Phys.* **1990**, *92*, 3645. (b) Stanton, R. V.; Merz, K. M., Jr. *J. Chem. Phys.* **1994**, *100*, 434. (c) Baker, J.; Andzelm, J.; Muir, M.; Taylor, P. R. *Chem. Phys. Lett.* **1995**, *237*, 53. (d) Baker, J.; Muir, M.; Andzelm, J. *J. Chem. Phys.* **1995**, *102*, 2063. (e) Nguyen, M. T.; Creve, S.; Vanquickenborne, L. G. *J. Phys. Chem.* **1996**, *100*, 18422. (f) Jursic, B. S. *Chem. Phys. Lett.* **1996**, *156*, 213. (g) Basch, H.; Hoz, S. *J. Phys. Chem. A* **1997**, *101*, 4416.
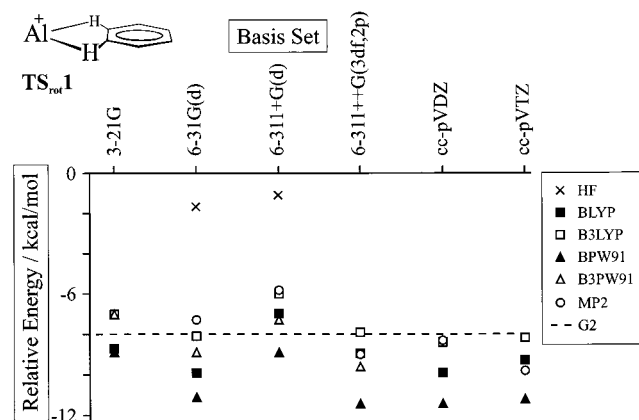
Figure 4. Basis set dependencies of the energy of $TS_{rot}1$ relative to the dissociation channel $Al^+ + C_6H_6$ (0.0 kcal/mol) by employing different quantum chemical models.

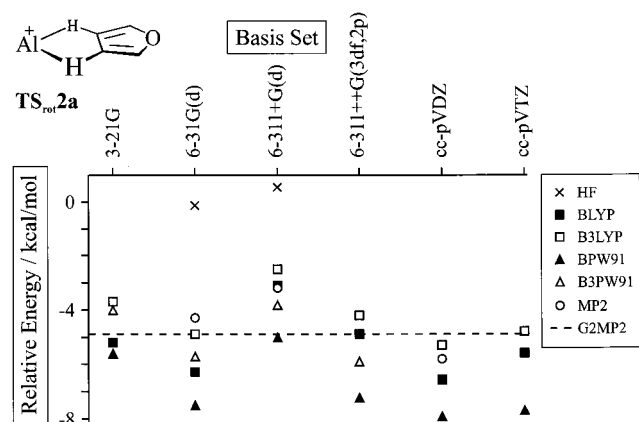**Figure 5.** Basis set dependencies of the energy of $TS_{rot}2a$ relative to the dissociation channel $Al^+ + C_4H_4O$ (0.0 kcal/mol) by employing different quantum chemical models.

However, a similar trend is observed as reported in the recent investigation of the $[Al^+, C_2H_5OH]$ PES:[17] The best agreement between the G2-computed data of E_{rel}-($TS_{rot}1$) = −8.0 kcal/mol and the DFT data has been obtained with the B3LYP method and the 6-311++G-(3df,2p) ($E_{rel}(TS_{rot}1)$ = −7.9 kcal/mol) or cc-pVTZ (E_{rel}-($TS_{rot}1$) = −8.2 kcal/mol) basis sets. The relative energy of $TS_{rot}1$ according to B3PW91/6-311++G(3df,2p) amounts to −9.6 kcal/mol.[24]

The following trend can be noted with regard to basis set dependencies of TS_{rot}s' relative energies (cf. Figures 4 and 5). Using basis sets of triple-ζ quality, the DFT- and DFT/HF-computed relative energies of the transition states for contra-binding rotation are lower compared to G2MP2 data, by less than 1 kcal/mol for B3LYP, ca. 1−2 kcal/mol for BLYP, B3PW91, and 3−4 kcal/mol for BHLYP, BPW91. Compared to G2MP2, the 6-311+G(d) basis set results in slightly lower relative energies, 6-31G(d) and cc-pVDZ yield similar E_{rel} data, and even 3-21G can yield quite good estimates. Thus, a similar trend as in the $[Al^+, C_2H_5OH]$ system is present.[17]

G. Thermochemistry. The relative energy (E_{rel}) data of $Al(L)^+$ complexes and TS_{rot}'s in Tables 1 and 2 refer to gas-phase conditions at 0 K. The G2MP2-calculated internal energy (U and $U°$), enthalpy ($H°$), and free energy ($G°$) of stationary points at 298.15 K and 1013.25 mbar are given in Table 3. The changes of the internal energy ($\Delta U°$), enthalpy ($\Delta H°$), and free energy ($\Delta G°$) of

Table 3. Thermodynamic Data of Stationary Points Calculated at the G2MP2 Level in Hartrees (U, Internal Energy; H, Enthalpy; G, Free Energy; T = 298.150 K; p = 1013.25 mbar)

species	$U(0\,K)$	$U(T)$	$H(T,p)$	$G(T,p)$
Al^+	−241.713810	−241.712394	−241.711450	−241.728466
C_6H_6	−231.776253	−231.771748	−231.770804	−231.801394
C_4H_4O	−229.627845	−229.624093	−229.623149	−229.653443
C_5H_6	−193.703701	−193.699462	−193.698517	−193.729669
C_4H_4NH	−209.774336	−209.770284	−209.769340	−209.800091
C_5H_5N	−247.816378	−247.812017	−247.811073	−247.843127
$Al(C_6H_6)^+$	−473.546042	−473.539539	−473.538595	−473.575155
$Al(C_4H_4O)^+$ $[C_{2v}]$	−471.379644	−471.373704	−471.372760	−471.409709
$Al(C_4H_4O)^+$ $[C_s]$	−471.387233	−471.381466	−471.380521	−471.417329
$Al(C_5H_6)^+$	−435.466181	−435.459949	−435.459005	−435.496499
$Al(C_4H_4NH)^+$	−451.553312	−451.547592	−451.546648	−451.582901
$Al(C_5H_5N)^+$	−489.604608	−489.598365	−489.597421	−489.634781
$TS_{rot}1$	−473.502560	−473.496330	−473.495385	−473.534245
$TS_{rot}2a$	−471.349427	−471.343952	−471.343008	−471.380420
$TS_{rot}2b$	−471.348722	−471.343206	−471.342262	−471.380943
$TS_{rot}3a$	−435.429336	−435.423370	−435.422425	−435.460426
$TS_{rot}3b$	−435.430550	−435.424619	−435.423675	−435.462173
$TS_{rot}3c$	−435.434992	−435.429146	−435.428202	−435.465842
$TS_{rot}4a$	−451.510349	−451.504796	−451.503852	−451.540208
$TS_{rot}4b$	−451.506688	−451.501080	−451.500136	−451.537381

these processes at 298.15 K and 1013.25 mbar are given in Table 4. As shown above for the relative energy data of the $Al(C_6H_6)^+$ system at 0 K, also the $\Delta U°$, $\Delta H°$, and $\Delta G°$ quantities of the $Al(C_6H_6)^+$ formation have been obtained from G1, G2, and G2MP2. The latter two methods provide values that are similar within ≤3%. The difference from the G1-calculated data is slightly higher (ca. 5−7%).

$$Al^+ + L \rightarrow Al(L)^+ \qquad (1)$$

$$Al(L)^+ \rightarrow TS_{rot} \qquad (2)$$

$$Al(L)^+ \rightarrow Al^+ + L \qquad (3)$$
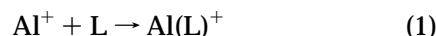
The following trends in thermochemistry can be extracted from the data in Tables 3 and 4. (i) The increase of temperature (0 K vs 298.15 K) is negligible for the change of the internal energy (E_{rel} vs $\Delta U°$) of both processes, the complex formation reactions (eq 1), and the contra-binding rotation (eq 2). (ii) The influence of $T\Delta S$ term is much higher. Accordingly, the difference between the change of enthalpy ($\Delta H°$) and the change of free energy ($\Delta G°$) for the two processes depicted in eqs 1 and 2 amounts to ca. 6−7 kcal/mol. The transition state for contra-binding rotation becomes less favorable for all systems under investigation by increasing temperature compared to the dissociation (eq 3). Concerning $TS_{rot}2a$ and $TS_{rot}2b$, $\Delta G°$ of eq 2 (L = C_4H_4O) is even positive; that is, dissociation will occur *prior* to contra-binding rotation. Concerning $TS_{rot}1$, $TS_{rot}3a$, and $TS_{rot}3b$, $\Delta G°$ of eq 2 appears to be slightly below or close to zero. In the case of the $Al(C_4H_4NH)^+$ system, however, $\Delta G°$ for the contra-binding rotation is negative, i.e., −7.3 kcal/mol ($TS_{rot}4a$) and −5.5 kcal/mol ($TS_{rot}4b$).

H. A Potential Consequence of Contra-Binding Rotation. In the previous sections, a new degenerate rearrangement of the complexes $Al^+-C_6H_6$, $Al^+-C_4H_4O$, $Al^+-C_5H_6$, and $Al^+-C_4H_4NH$ has been introduced. On the basis of quantum chemical computations a contra-binding rotation process has been uncovered.[14,32] At 0 K, its barrier has been found to be close to but below

Table 4. Change of Thermodynamic Quantities (Internal Energy ΔU°, Enthalpy ΔH°, and Free Energy ΔG°, T = 298.15 K, p = 1013.25 Mbar) Relative to the Dissociation Products Al+ + L in Kcal/Mol According to Different Levels of Theory

species		ΔU°			ΔH°			ΔG°		
		G1	G2	G2MP2	G1	G2	G2MP2	G1	G2	G2MP2
C_6H_6	**1**	−36.2	−35.2	−34.8	−36.8	−35.8	−35.4	−29.9	−28.9	−28.4
	TS$_{rot}$1	−8.1	−7.8	−7.6	−8.7	−8.4	−8.2	−3.2	−2.9	−2.8
C_4H_4O	**2**			−23.3			−23.9			−17.4
	TS$_{rot}$2a			−4.7			−5.3			0.9
	TS$_{rot}$2b			−4.2			−4.8			0.6
C_5H_6	**3**			−30.2			−30.8			−24.1
	TS$_{rot}$3a			−7.2			−7.8			−1.4
	TS$_{rot}$3b			−8.0			−8.6			−2.5
	TS$_{rot}$3c			−10.8			−11.4			−4.8
C_4H_4NH	**4**			−40.7			−41.3			−34.1
	TS$_{rot}$4a			−13.9			−14.5			−7.3
	TS$_{rot}$4b			−11.5			−12.1			−5.5

Scheme 6

(6)   **(7)**
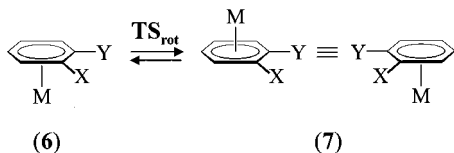
the dissociation channel. A concomitant $\eta^6 \rightarrow \eta^4 \rightarrow \eta^2$ isomerization[10a] has not been observed for these Al(L)+ complexes. As it is characteristic for degenerate rearrangements, the products and reactants of the respective contra-binding rotation processes are identical. With increasing temperature, the transition state for contra-binding rotation becomes less probable for the systems under investigation (cf. part G). Therefore, matrix-isolation or jet-expansion experiments might be suited for studying this kind of rearrangement experimentally. The most promising system for detecting contra-binding rotation seems to be Al(C₄H₄NH)+.[29]

Contra-binding rotation can be operative in planar-chiral metal−arene complexes,[29,34] which are applied to enantioselective catalytic reactions.[35] Consider a metal complex **6** with a central atom M and a 1,2-substituted benzene ligand (Scheme 6). If a degenerate rearrangement via TS$_{rot}$ is energetically below the dissociation process—yielding M + o-C₆H₄XY—the metal atom can migrate from the bottom of the ring (**6**) toward its top

(**7**). As a consequence, racemization of the starting compound **6** can occur, i.e., **6** ⇌ **7**! Assume the chiral, enantiomerically pure metal−arene complex **6** is used in enantioselective catalysis;[35] racemization (**6** ⇌ **7**) will lower the enantiomeric excess of the catalytic reaction! This scenario can be present also in planar-chiral metal complexes[29] with (i) a 1,3-substituted benzene ligand and (ii) a pyrrole or pyridine ligand substituted in position 1 or 2.[35]

Conclusions

A particular part of the potential-energy surface of Al(L)+ complexes (L = benzene, furane, cyclopentadiene, pyrrole, and pyridine) has been examined by means of ab initio molecular orbital and density functional theory. The present density functionals were shown to perform as well as high-level ab initio MO approaches if basis sets of at least double-ζ quality are employed.[5,17,24]

A new degenerate rearrangement has been uncovered, which is termed *contra-binding rotation*. Concerning L = benzene, furane, cyclopentadiene, or pyrrole, at least one transition state for the contra-binding rotation (TS$_{rot}$) in Al+−L complexes has been found to be energetically *below* the dissociation channel at 0 K, which would yield Al+ + L. Therefore, the rotation of the ligand L *toward* the Al+−L bond is thermodynamically feasible without dissociation in the gas phase[32] (Schemes 1 and 2). The 0 K relative energies of the TS$_{rot}$ have been calculated to amount to ca. 8 kcal/mol (L = benzene), ca. 4−5 kcal/mol (furane), 7−11 kcal/mol (cyclopentadiene), and 12−14 kcal/mol (pyrrole) *below* the dissociation limit. The corresponding barrier heights amount to ca. 27 kcal/mol (L = benzene), ca. 19−20 kcal/mol (furane), 19−23 kcal/mol (cyclopentadiene), and 33−35 kcal/mol (pyrrole). With regard to the Al+−furane, Al+−cyclopentadiene, and Al+−pyrrole cases, two, three, and two different transition states and reaction coordinates for the contra-binding rotation have been obtained, respectively. Concerning Al+−C₅H₅N, the dissociation process is energetically more favorable compared with the contra-binding rotation process. An $\eta^6 \rightarrow \eta^4 \rightarrow \eta^2$ isomerization[10a] prior to the contra-binding rotation has not been observed in any case.[5]

On increasing temperature, however, the change in free energy of the contra-binding rotation process increases. Under standard conditions (298.15 K and 1013.25 mbar), ΔG is slightly *positive* for the contra-binding rotation in Al(C₄H₄O)+, slightly *negative* for the

(34) (a) Marquarding, D.; Klusacek, H.; Gokel, G. W.; Hoffmann, P.; Ugi, K. *J. Am. Chem. Soc.* **1970**, *92*, 5389. (b) Hayashi, T.; Kumada, M. *Acc. Chem. Res.* **1982**, *15*, 395. (c) Riant, O.; Samuel, O.; Kagan, H. B. *J. Am. Chem. Soc.* **1993**, *115*, 5835. (d) Jones, G. B.; Heaton, S. B. *Tetrahedron Asymmetry* **1993**, *4*, 261. (e) Baldoli, C.; Maiorana, S.; Carrea, G.; Riva, S. *Tetrahedron Asymmetry* **1993**, *4*, 767. (f) Griffiths, S. L.; Perrio, S.; Thomas, S. E. *Tetrahedron Asymmetry* **1994**, *5*, 1847. (g) Uemura, M.; Nishimura, H.; Yamada, S.; Hayashi, Y. *Tetrahedron Asymmetry* **1994**, *5*, 1673. (h) Kündig, E. P.; Xu, L. H.; Schnell, B. *Synlett* **1994**, 413. (i) Tsukazi, M.; Tinkl, M.; Roglans, A.; Chapell, B. J.; Taylor, N. J.; Snieckus, V. *J. Am. Chem. Soc.* **1996**, *118*, 685. (j) Togni, A. *Angew. Chem.* **1996**, *108*, 1581; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1475. (k) Siegel, S.; Schmalz, H.-G *Angew. Chem.* **1997**, *109*, 2569; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2456.
(35) (a) Ruble, J. C.; Fu, G. C. *J. Org. Chem.* **1996**, *61*, 7230. (b) Ruble, J. C.; Latham, H. A.; Fu, G. C. *J. Am. Chem. Soc.* **1996**, *61*, 7230. (c) Pasch, R.; Kölle, U.; Ganter, B.; Englert, U. *Organometallics* **1997**, *16*, 3950. (d) Dosa, P. I.; Ruble, J. C.; Fu, G. C. *J. Org. Chem.* **1997**, *62*, 444. (e) Nishibayashi, Y.; Takei, I.; Uemura, S.; Hidai, M. *Organometallics* **1998**, *17*, 3420. (f) Garrett, C. E.; Fu, G. C. *J. Org. Chem.* **1998**, *63*, 1370. (g) Ruble, J. C.; Tweddell, J.; Fu, G. C. *J. Org. Chem.* **1998**, *63*, 2794. (h) Liang, J.; Ruble, J. C.; Fu, G. C. *J. Org. Chem.* **1998**, *63*, 3154. (i) Qiao, S.; Fu, G. C. *J. Org. Chem.* **1998**, *63*, 4168. (j) Garrett, C. E.; Fu, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 7479. (k) Crousse, B.; Xu, L.-H.; Bernardinelli, G.; Kündig, E. P. *Synlett* **1998**, 658. (l) Ryabov, A. D.; Firsova, Y. N.; Goral, V. N.; Ryabova, E. S.; Shevelkova, A. N.; Troitskaya, L. L.; Demeschik, T. V.; Sokolov, V. I. *Chem. Eur. J.* **1998**, *4*, 806.

contra-binding rotation in $Al(C_6H_6)^+$ and $Al(C_5H_6)^+$, but clearly negative for the contra-binding rotation in $Al(C_4H_4NH)^+$. Further computational studies on planar-chiral Al^+ complexes are under way aimed at further investigating possible racemization via contra-binding rotation.[29]

Supporting Information Available: Table 5 (basis set dependencies of the imaginary frequencies), an extended version of Table 2, and the molecular structures (*z* matrixes) of the transition states for contra-binding rotation (**TS$_{rot}$1**, **TS$_{rot}$2a**, **TS$_{rot}$2b**, **TS$_{rot}$3a**, **TS$_{rot}$3b**, **TS$_{rot}$3c**, **TS$_{rot}$4a**, and **TS$_{rot}$4b**). This material is available free of charge via the Internet at http://pubs.acs.org. The *z* matrixes of the $Al(L)^+$ complexes have been published previously.[5]

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