

Diversity of Bonding in Methyl Ate Anions of the First- and Second-Row Elements

Jerzy Cioslowski,^{*,†} Pawel Piskorz,[†] Michael Schimeczek,[‡] and Gernot Boche^{*,‡}

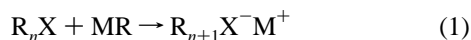
Contribution from the Department of Chemistry and Supercomputer Computations Research Institute, Florida State University, Tallahassee, Florida 32306-3006, and Fachbereich Chemie, Philipps-Universität Marburg, 35032 Marburg, Germany

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Abstract: CCSD/6-311++G(2d,2p) quantum-chemical calculations carried out in conjunction with rigorous analysis of the computed electronic wave functions reveal the existence of four different types of methyl ate anions $(\text{CH}_3)_{n+1}\text{X}^-$, where X is a first- or second-row element. Ate anions with ionic bonds between the central atom and the ligands, formed by elements of the first three main groups, are very stable to the loss of CH_3^- . Hypervalent anions, which obtain from the other second-row elements, possess largely covalent X–C bonding that provides them with (sometimes marginal) stability to the ligand loss. The other two types of ate anions are unique to the first-row elements. The “double-Rydberg” species are derived from nitrogen and oxygen. They are unstable to electron loss and thus most probably not observable in the gas phase. The potentially observable $(\text{CH}_3)_2\text{F}^-$ species is the only member of its class. It has a positive vertical ionization potential, and its dissociation into CH_3F and CH_3^- is predicted to proceed through a small barrier. This anion is found to possess a peculiar electronic structure that involves an entirely new type of bonding, namely, a bypass linkage of the methyl ligands.

Introduction

The term “ate complexes” was coined by Wittig in the late 1950s¹ to describe the products of the reaction



where R is a hydrogen, alkyl, or aryl group, X can be (at least in principle) any element, and M is a monovalent metal such as lithium. Many of these species are believed to constitute key intermediates of the halogen–metal exchange reactions² which are widely employed in syntheses of various organic and organometallic compounds. The relation of some ate anions to the transition states of $\text{S}_\text{N}2$ reactions³ and hypervalent compounds^{4,5} is also worth mentioning.

The stability of ate complexes varies greatly with X. Some of them, such as $\text{Na}^+[(\text{C}_6\text{H}_5)_4\text{B}]^-$, are stable, commonly used reagents,⁶ whereas others, such as $[(\text{TMEDA})_2\text{Li}]^+[(\text{C}_6\text{H}_5)_2\text{I}]^-$ (TMEDA = tetramethylethylenediamine), can be isolated

only at low temperatures.⁷ Although crystal structures of many ate complexes have been determined,⁸ the species with X = Hg, Sn, Se, Te, and I have been characterized only in solution by means of NMR spectroscopy,⁹ the aforementioned $[(\text{TMEDA})_2\text{Li}]^+[(\text{C}_6\text{F}_5)_2\text{I}]^-$ being the only exception. Ate complexes of many elements, such as carbon and chlorine, remain experimentally unknown.

The present study addresses the question of whether the observed large variations in stability of ate anions stem from gradual changes in bond ionicities with the numbers of valence electrons and electronegativities of the central atoms or are manifestations of distinct bonding patterns. With the computed electronic properties of methyl ate anions of the first- and second-row elements clearly pointing to the latter alternative, a systematic classification of all ate anions is obtained. At least three common types of these species are identified, and the remarkable properties of the $(\text{CH}_3)_2\text{F}^-$ anion are uncovered.

Details of Calculations

To assure adequate accuracy of the computed electronic properties, relatively high levels of theory were employed in the present study. Geometries of the methyl ate anions $(\text{CH}_3)_{n+1}\text{X}^-$, where X = Li, Be, B, C, N, O, F, Na, Mg, Al, Si, P, S, or Cl, and of the corresponding neutral species $(\text{CH}_3)_n\text{X}$ were initially optimized at the MP2/6-31+G*

* To whom correspondence should be addressed. E-mail addresses: jerzy@kyoko.chem.fsu.edu, boche@ps1515.chemie.uni-marburg.de. Web home pages: <http://www.scri.fsu.edu/~jerzy>, <http://staff-www.uni-marburg.de/~boche>.

[†] Florida State University.

[‡] Philipps-Universität Marburg.

(1) Wittig, G. *Angew. Chem.* **1958**, 70, 65.

(2) Schöllkopf, U. *Methoden der organischen Chemie*; Georg Thieme: Stuttgart, 1970; Vol. 13/1. Beletskaya, I. P.; Artamkina, G. A.; Reutov, O. A. *Russ. Chem. Rev.* **1976**, 45, 330. Wakefield, B. J. *Comprehensive Organic Chemistry*; Pergamon Press: New York, 1979; Vol. 3. Wardell, J. L. In *Inorganic Reactions and Methods*; Zuckermann, J. J., Ed.; VCH: New York, 1988; Vol. 11. Bailey, W. F.; Patricia, J. J. *J. Organomet. Chem.* **1988**, 352, 1. Schlosser, M. In *Organometallics in Synthesis*; Schlosser, M., Ed.; John Wiley & Sons: New York, 1994.

(3) See for example: Shaik, S. S. *Acta Chem. Scand.* **1990**, 44, 205 and references cited therein.

(4) Reed, A. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, 112, 1434 and references cited therein.

(5) Cioslowski, J.; Mixon, S. T. *Inorg. Chem.* **1993**, 32, 3209.

(6) Wittig, G.; Keicher, G.; Rückert, A.; Raff, P. *Liebigs Ann. Chem.* **1949**, 563, 110.

(7) Farnham, W. B.; Calabrese, J. C. *J. Am. Chem. Soc.* **1986**, 108, 2449.

(8) For a recent compilation of crystal structures of ate complexes with X = Li, Be, Mg, Zn, Cd, B, Al, Ga, In, and Tl, see: Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1993**, 32, 1501.

(9) Ogawa, S.; Masutomi, Y.; Erata, T.; Furukawa, N. *Chem. Lett.* **1992**, 2471. Reich, H. J.; Gudmundsson, B. Ö.; Dykstra, R. R. *J. Am. Chem. Soc.* **1992**, 114, 7937. Reich, H. J.; Green, D. P.; Phillips, N. H.; Borst, J. P.; Reich, I. L. *Phosphorus, Sulfur, Silicon* **1992**, 67, 83. Reich, H. J.; Green, D. P.; Phillips, N. H. *J. Am. Chem. Soc.* **1991**, 113, 1414. Reich, H. J.; Green, D. P.; Phillips, N. H. *J. Am. Chem. Soc.* **1989**, 111, 3444. Reich, H. J.; Phillips, N. H. *Pure Appl. Chem.* **1987**, 59, 1021. Reich, H. J.; Phillips, N. H. *J. Am. Chem. Soc.* **1986**, 108, 2102.

Table 1. Calculated Energies of Reaction 2 for Ate Anions with Ionic Bonding^a

X	n	R = CH ₃ ^b	R = H ^c
Li	1	-57.8	-54.0
Na	1	-49.0	-46.9
Be	2	-62.5	-60.1
Mg	2	-64.7	-59.9
B	3	-68.3	-74.1
Al	3	-79.4	-76.2

^a Energies (kcal/mol) at $T = 0$ K, ZPEs included. ^b Present work, CCSD/6-311++G(2d,2p) energies with the MP2/6-311++G(2d,2p) ZPEs and optimized geometries. ^c Reference 17.

level of theory (note that 5d rather than 6d functions were used), and confirmed to be minima by vibrational analysis. Although the large number of readily rotating methyl moieties in some of the anions makes it difficult to guarantee the global nature of these minima, the energy differences between the individual rotamers are small and thus of little significance to the present investigations.

In all cases, the initial geometries were subsequently reoptimized at the MP2/6-311++G(2d,2p) level of theory. At the same time, vibrational frequencies, properties of atoms in molecules (AIMs),¹⁰ covalent bond orders,¹¹ and AOM-localized natural orbitals¹² were obtained. Single-point CCSD/6-311++G(2d,2p) energies were computed at the optimized MP2/6-311++G(2d,2p) geometries for all the systems but (CH₃)₃C⁻ and (CH₃)₅Si⁻. In addition, *G*₂ calculations¹³ were carried out for the fluorine species. All calculations were performed with the GAUSSIAN 94¹⁴ and TURBOMOLE¹⁵ suites of programs.

Results and Discussion

In agreement with the experimental observations, the predicted energies of the reaction

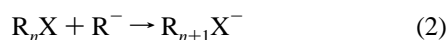


exhibit large variations (Tables 1 and 2). Analysis of the computed electronic wave functions in terms of localized natural orbitals, covalent bond orders, and atomic charges makes it possible to divide the ate anions under study into four distinct categories. These categories are discussed separately in the following text.

Ate Anions with Ionic Bonding. This category encompasses the (CH₃)₂Li⁻, (CH₃)₂Na⁻, (CH₃)₃Be⁻, (CH₃)₃Mg⁻, (CH₃)₄B⁻, and (CH₃)₄Al⁻ species. Among these, the (CH₃)₄B⁻ and (CH₃)₄Al⁻ anions, which one might view as covalent compounds satisfying the octet rule, are least ionic. However, even

(10) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Clarendon Press: Oxford, 1994.

(11) Cioslowski, J.; Mixon, S. T. *J. Am. Chem. Soc.* **1991**, *113*, 4142.

(12) Cioslowski, J. *Int. J. Quantum Chem.* **1990**, *S24*, 15. Cioslowski, J. *J. Math. Chem.* **1991**, *8*, 169.

(13) Curtiss, A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221. Curtiss, L. A.; Carpenter, J. E.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1992**, *96*, 9030.

(14) GAUSSIAN 94: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; 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. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A., Gaussian, Inc., Pittsburgh, PA, 1995.

(15) TURBOMOLE: Ahlrichs, R., Universität Karlsruhe, Deutschland, 1991. Häser, M.; Ahlrichs, R. *J. Comput. Chem.* **1989**, *10*, 104. Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. M. *Chem. Phys. Lett.* **1989**, *162*, 165. Horn, H.; Weiss, H.; Häser, M.; Ehrig, M.; Ahlrichs, R. *J. Comput. Chem.* **1991**, *12*, 1058. Häser, M.; Almlöf, J.; Feyereisen, M. W. *Theor. Chim. Acta* **1991**, *79*, 115. Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571. Häser, M.; Ahlrichs, R.; Baron, H. P.; Weis, P.; Horn, H. *Theor. Chim. Acta* **1992**, *83*, 455.

Table 2. Calculated Energies of Reaction 2 for Ate Anions of the Other Types^a

X	n	MP2/	MP2/	CCSD/
		6-31+G ^b	6-311++G(2d,2p)	6-311++G(2d,2p) ^c
N	3	46.1	28.8	30.4
O	2	85.2	68.6	68.0
F	1	24.7	26.3	42.5 ^d
Si	4	-22.0	-25.2	n/a
P	3	-9.1	-13.1	-8.3
S	2	-0.1	-5.8	0.5
Cl	1	-1.3	-6.6	2.1

^a Energies (kcal/mol) at $T = 0$ K, ZPEs included. ^b 5d rather than 6d polarization functions used. ^c CCSD/6-311++G(2d,2p) energies with the MP2/6-311++G(2d,2p) ZPEs and optimized geometries. ^d The corresponding *G*₂ value is 32.8 kcal/mol.

Table 3. MP2/6-311++G(2d,2p) Strongly Occupied Localized Orbitals of the (CH₃)₃Be⁻ Anion

LNO	occup	<i>T</i> (au) ^a	description
1–3	2.000	16.048	core orbitals of C (100% localized)
4	2.000	6.839	core orbital of B (99.5% localized)
5–7	1.962	1.116	lone pairs of C (91.8% localized on the CH ₃ fragments)
8–10	1.967	0.953	C–H bonds (3.5% ionic, 96.9% localized)
11–16	1.966	0.940	C–H bonds (3.0% ionic, 96.8% localized)

^a The orbital kinetic energy.

these species possess covalent bond orders of only 0.402 and 0.263, respectively, indicating a high degree of ionicity. This considerable ionicity is reflected in the charges of the central atoms which equal 1.942 for boron and 2.389 for aluminum. Although the ionicities of the X–C bonds in the other four anions vary somewhat with the electronegativities of X, they remain high in all cases. The central atoms in these species possess large positive charges (Li, 0.880; Na, 0.806; Be, 1.683; Mg, 1.642), and the X–C covalent bond orders are small (Li–C, 0.120; Na–C, 0.185; Be–C, 0.182; Mg–C, 0.220).

Analysis of bonding in terms of localized natural orbitals (LNOs) has been proved to provide valuable insight into electronic structures of a wide variety of chemical systems.^{5,16} Applied to (CH₃)₃Be⁻, it produces a clear picture of bonding in all ate anions of the ionic type (Table 3). There are only five symmetry-unique LNOs that describe the core orbitals of the three carbons and the beryllium (LNOs 1–4), the lone pairs of the carbons (LNOs 5–7), and the C–H bonds (LNOs 8–16). Covalent Be–C bonding is absent, in agreement with the aforementioned magnitudes of atomic charges and bond orders.

The absence of covalent bonding is further confirmed by the patterns observed in the computed energies of reaction 2 (Table 1) and the X–C bond lengths (Table 4). The energies, which follow roughly the charges on the central atoms, are strikingly similar to those obtained previously for the H_{*n*+1}X⁻ ate anions,¹⁷ and are quite insensitive to the level of theory employed in their calculations—exactly as expected for highly ionic compounds. Moreover, even in the systems with monovalent metals, where steric repulsion can be easily ruled out, the attachment of the methyl anion to the neutral CH₃X species brings about an increase in the X–C bond length (Table 4), implying strong electrostatic repulsions among the ligands within the

(16) Cioslowski, J.; McKee, M. L. *J. Phys. Chem.* **1992**, *96*, 9264. Cioslowski, J. *J. Am. Chem. Soc.* **1993**, *115*, 5177. Boche, G.; Lohrenz, J. C. W.; Cioslowski, J.; Koch, W. In *The Chemistry of Sulfur Containing Functional Groups*; Patai, S., Rappoport, Z., Eds.; John Wiley and Sons: New York, 1993. Cioslowski, J. *Int. J. Quantum Chem.* **1993**, *S27*, 309. Cioslowski, J.; Liu, G.; Martinov, M.; Piskorz, P.; Moncrieff, D. *J. Am. Chem. Soc.* **1996**, *118*, 5261. Cioslowski, J.; Liu, G.; Moncrieff, D. *J. Org. Chem.* **1996**, *61*, 4111.

(17) Boldyrev, A. I.; Simons, J. *J. Chem. Phys.* **1993**, *99*, 4628.

Table 4. Calculated X–C Bond Lengths in the (CH₃)_nX and (CH₃)_{n+1}X[−] Species with Ionic Bonding^a

X	n	R _{X–C} (Å)		ΔR _{X–C}	
		(CH ₃) _n X	(CH ₃) _{n+1} X [−]	(Å)	(%)
Li	1	1.990	2.121	0.131	6.6
Na	1	2.343	2.503	0.160	6.8
Be	2	1.688	1.795	0.107	6.3
Mg	2	2.104	2.202	0.099	4.7
B	3	1.574	1.648	0.074	4.7
Al	3	1.967	2.035	0.068	3.4

^a The MP2/6-311++G(2d,2p) optimized geometries.

(CH₃)_{n+1}Xⁿ⁺ bonding environment. Accordingly, the methyl moieties are located as far as possible from each other, conferring *D*_{3h}/*D*_{3d}, *C*_{3h}, and *T*_d symmetries upon the anions with *n* = 1, 2, and 3, respectively.

“Double-Rydberg” Ate Anions of the First-Row Elements.

Attachment of an R[−] anion to a R_nX neutral that obeys the octet rule affords a 10-electron system. The fate of the extraneous electron pair depends strongly on the central atom X. In the case of first-row elements, the two electrons are usually expelled to the exterior of the anion, giving rise to a system composed of a cationic core with an octet of electrons surrounded by a weakly bound (or unbound) electron pair. These double-Rydberg anions¹⁸ are often stable with respect to electron loss but not to the loss of the ligand anion.^{19,20}

At the PUMP2/6-31++G(2d,2p) level of theory, both the (CH₃)₃O[−] and (CH₃)₄N[−] species are found to possess negative vertical ionization potentials of −1.2 and −0.6 eV, respectively. Therefore, unlike their H₃O[−] and H₄N[−] counterparts,^{18–20} these anions are not expected to be experimentally observable in the gas phase. Consequently, although the electronic properties computed with basis sets devoid of unnormalizable functions describing infinitely diffuse Rydberg orbitals may have some relevance to studies of the behavior of the (CH₃)₃O[−] and (CH₃)₄N[−] anions in condensed phases, they are necessarily of approximate nature. The (CH₃)₅C[−] species is not even a minimum on the potential energy hypersurface, which is not surprising in light of the similar property of H₅C[−]^{19,20} and the fact that this ate anion is an analog of transition states of S_N2 reactions.³

The *C*_{3v} (CH₃)₃O[−] and *T*_d (CH₃)₄N[−] anions have singlet ground states with rather narrow (several kcal/mol) singlet–triplet energy gaps. Their central atoms bear sizable negative charges (O, −1.018; N, −0.870). The large X–C covalent bond orders (O–C, 0.748; N–C, 0.866) indicate considerable electron sharing between the central atoms and the ligands. These X–C bonds are only slightly longer than those in the corresponding (CH₃)_nX parent compounds (Table 5).

The presence of the Rydberg electron pair is conspicuous in the LNOs of (CH₃)₃O[−] (Table 6). LNOs 1–17 are essentially those of the corresponding cation with highly ionic O–C interactions and weakly ionic C–H bonds. Among them, the lone pair of oxygen (LNO 5) is readily recognizable. LNO 18, which possesses very low kinetic energy indicative of great spatial delocalization, describes the Rydberg pair. The electronic structure of (CH₃)₄N[−] is very similar.

Hypervalent Ate Anions of the Second-Row Elements.

Whereas geometry optimizations of (CH₃)₃O[−] and (CH₃)₄N[−] invariably converge to the highly symmetrical structures de-

(18) Simons, J.; Gutowski, M. *Chem. Rev.* **1991**, *91*, 669 and references cited therein.(19) Gutowski, M.; Simons, J. *J. Chem. Phys.* **1990**, *93*, 3874.(20) Ortiz, J. V. *J. Chem. Phys.* **1987**, *87*, 3557. Ortiz, J. V. *J. Phys. Chem.* **1990**, *94*, 4762.**Table 5.** Calculated X–C Bond Lengths in the (CH₃)_nX and (CH₃)_{n+1}X[−] Species of the Other Types^a

X	n	R _{X–C} (Å)		ΔR _{X–C}	
		(CH ₃) _n X	(CH ₃) _{n+1} X [−]	(Å)	(%)
N	3	1.455	1.494	0.040	2.7
O	2	1.415	1.473	0.058	4.1
F	1	1.393	2.012	0.619	44.4
Si	4	1.880	2.043 (ax)	0.163	8.7
			1.944 (eq)	0.064	3.4
P	3	1.848	2.087 (ax)	0.238	12.9
			1.871 (eq)	0.023	1.2
S	2	1.812	2.149 (ax)	0.337	18.6
			1.821 (eq)	0.009	0.5
Cl	1	1.792	2.221	0.429	23.9

^a The MP2/6-311++G(2d,2p) optimized geometries.**Table 6.** MP2/6-311++G(2d,2p) Strongly Occupied Localized Orbitals of the (CH₃)₃O[−] Anion

LNO	occup	T (au) ^a	description
1	2.000	29.206	core orbital of O (100% localized)
2–4	2.000	16.059	core orbitals of C (100% localized)
5	1.974	2.747	lone pair of O (96.5% localized)
6–8	1.955	2.222	O–C bonds (62.7% ionic, 96.8% localized)
9–14	1.970	1.105	C–H bonds (10.8% ionic, 95.9% localized)
15–17	1.970	1.105	C–H bonds (10.8% ionic, 96.1% localized)
18	1.873	0.178	Rydberg orbital

^a The orbital kinetic energy.

scribed above, for methyl ate anions with X = Si, P, S, and Cl it is possible to locate low-symmetry global minima that correspond to geometries conventionally ascribed to hypervalent species. At the highest level of theory employed in the present study, the *C*_s (CH₃)₃S[−] and *D*_{3h} (CH₃)₂Cl[−] species are unstable with respect to the loss of the methyl anion (Table 2), but the *C*_{2v} (CH₃)₄P[−] anion is stable (and so is its H₄P[−] prototype²¹). Unlike its carbon analog (see above), the *C*_{3h} (CH₃)₅Si[−] species is found to lie well below the (CH₃)₄Si + CH₃[−] dissociation products (Table 2), in line with the theoretically predicted²² and experimentally observed²³ stability of H₅Si[−].

The equilibrium geometries of the hypervalent ate anions are characterized by the presence of two types of X–C bonds. The two axial bonds are longer than their equatorial counterparts [Table 5; note that only axial X–C bonds are present in (CH₃)₂Cl[−]]. The C_{ax}–X–C_{ax} bond angles in the phosphorus and sulfur species are less than 180°, amounting to 171.3° and 175.6°, respectively, at the MP2/6-311++G(2d,2p) level of theory, whereas a collinear C_{ax}–X–C_{ax} atom arrangement is found in (CH₃)₅Si[−] and (CH₃)₂Cl[−]. The C_{eq}–X–C_{eq} bond angle in (CH₃)₄P[−] is 106.4°.

The electronic structure of (CH₃)₂Cl[−] is typical of the hypervalent ate anions. The chlorine atom bears a charge of −0.345, and the Cl–C covalent bond order is 0.860. Even by the recently published highly restrictive criteria,⁵ this anion is clearly a genuine hypervalent system. Analysis of the computed LNOs (Table 7) leads to the same conclusion. In addition to core orbitals (LNOs 1–7) and the LNOs describing the C–H

(21) Bachrach, S. M.; Mulhearn, D. C. *J. Phys. Chem.* **1993**, *97*, 12229. Moc, J.; Morokuma, K. *Inorg. Chem.* **1994**, *33*, 551.(22) Maitre, P.; Volatron, F.; Hiberty, P. C.; Shaik, S. S. *Inorg. Chem.* **1990**, *29*, 3047. Sini, G.; Ohanessian, G.; Hiberty, P. C.; Shaik, S. S. *J. Am. Chem. Soc.* **1990**, *112*, 1407. Gordon, M. S.; Windus, T. L.; Burggraf, L. W.; Davis, L. P. *J. Am. Chem. Soc.* **1990**, *112*, 7167. Sini, G.; Hiberty, P. C.; Shaik, S. S. *J. Chem. Soc., Chem. Commun.* **1989**, 772. Kalcher, J. *J. Mol. Struct.: THEOCHEM* **1988**, *167*, 235. Reed, A. E.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1987**, *133*, 553. Brandemark, U.; Siegbahn, P. E. M. *Theor. Chim. Acta* **1984**, *66*, 233. Keil, F.; Ahlrichs, R. *Chem. Phys.* **1975**, *8*, 384. Wilhite, D. L.; Spialter, L. *J. Am. Chem. Soc.* **1973**, *95*, 2100.(23) Hajdasz, D. J.; Squires, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 3139.

Table 7. MP2/6-311++G(2d,2p) Strongly Occupied Localized Orbitals of the $(\text{CH}_3)_2\text{Cl}^-$ Anion^a

LNO	occup	<i>T</i> (au) ^b	description
8	1.979	3.094	σ lone pair of Cl (98.7% localized)
9–10	1.959	2.030	π lone pairs of Cl (97.3% localized)
11–12	1.918	1.421	Cl–C bonds (22.0% ionic, 88.5% localized)
13–18	1.966	1.013	C–H bonds (0.9% ionic, 97.3% localized)

^a Only the valence LNOs are listed. ^b The orbital kinetic energy.

Table 8. MP2/6-311++G(2d,2p) Strongly Occupied Localized Orbitals of the $(\text{CH}_3)_2\text{F}^-$ Anion

LNO	occup	<i>T</i> (au) ^a	description
1	2.000	37.281	core orbital of F (100% localized)
2–3	2.000	16.048	core orbitals of C (100% localized)
4	1.985	4.002	2s-like lone pair of F (99.3% localized)
5–6	1.970	3.040	π lone pairs of F (98.1% localized)
7	1.883	2.590	C–F–C tricentric bond (78.7% on F, 9.8% on each C)
8	1.854	1.145	C–C bypass bond (38.9% on each C, 6.5% on F)
9–14	1.967	1.027	C–H bonds (1.7% ionic, 97.7% localized)

^a The orbital kinetic energy.

bonds (LNOs 13–18), there are three lone pairs located at the chlorine atom (LNOs 8–10) and two Cl–C bonds (LNOs 11 and 12) that are somewhat ionic. In other words, 10 electrons are ascribed to the central atom, making it hypervalent. The bonding patterns in the other three species are essentially identical, the lone pairs being gradually replaced by X–C bonds as the number of the methyl ligands increases from two to five.

$(\text{CH}_3)_2\text{F}^-$ Anion. Thanks to its highly unusual electronic structure, the $(\text{CH}_3)_2\text{F}^-$ species occupies a unique place among methyl ate anions. Unlike its $(\text{CH}_3)_4\text{N}^-$ and $(\text{CH}_3)_3\text{O}^-$ counterparts, the $(\text{CH}_3)_2\text{F}^-$ anion is stable with respect to electron loss ($\text{IP}_{\text{vert}} = 1.0$ and 1.4 eV at the PUMP2/6-311++G(2d,2p) and *G2* levels of theory, respectively). Although it lies well above the separated $\text{CH}_3\text{F} + \text{CH}_3^-$ pair (see Table 2; also note that the *G2* standard enthalpy of dissociation is -32.5 kcal/mol), a barrier to dissociation that is 3.5 kcal/mol high (ZPEs not included) is predicted by MP2/6-31+G* calculations. As expected, the corresponding transition state is very early, possessing the F–C bond lengths of 1.716 and 2.171 Å. These results indicate that, unlike H_2F^- ,^{18–20} $(\text{CH}_3)_2\text{F}^-$ may be experimentally observable.

The $(\text{CH}_3)_2\text{F}^-$ anion has D_{3h} symmetry and a singlet ground state, the singlet–triplet energy difference amounting to ca. 19 kcal/mol at the PUMP2/6-31+G* level of theory. The uniqueness of its electronic structure stems from the presence of an unprecedented bypass bond between the carbon atoms of the two methyl groups (Table 8). Out of the total of ten electrons, the central fluorine atom takes eight, leaving only two electrons for the ligands. Accordingly, in addition to core orbitals (LNOs 1–3), and the C–H bonds (LNOs 9–14), there are three lone pairs on fluorine (LNOs 4–6). LNO 7 is essentially yet another lone pair with some residual tricentric bonding to the two ligands. It is only because of this bonding that the $(\text{CH}_3)_2\text{F}^-$ anion does not collapse to CH_3CH_3 and F^- . The remaining LNO 8 describes a peculiar C–C bypass bond that, the central atom notwithstanding, directly links the methyl groups. Consequently, the fluorine atom bears a charge of -0.591 , and the C–C covalent bond order is greater than its F–C counterpart (0.565 vs 0.455). Thus, to the first degree of approximation, $(\text{CH}_3)_2\text{F}^-$ has the structure of $\text{H}_3\text{C}\cdots\text{F}^-\cdots\text{CH}_3$. As unexpected as it may seem, this picture of bonding is consistent with the computed geometry and vibrational frequencies. The F–C bonds are unusually long (Table 5), and the force constant for

C–F–C bending is very low. In addition, the presence of an octet of electrons on the fluorine atom explains the predicted stability with respect to electron loss.

Conclusions

High-level quantum-chemical calculations carried out in conjunction with rigorous analysis of the computed electronic wave functions reveal the existence of four different types of ate anions R_{n+1}X^- . The anions with ionic bonding between the central atom and the ligands are formed by elements of the first three main groups. These species are very stable with respect to the loss of the ligand anion and possess positive vertical ionization potentials. Their X–C bonds, which are only slightly longer than those in the corresponding neutral systems R_nX , are almost completely ionic. Consequently, their central atoms are positively charged and their ligands bear negative charges. The resulting electrostatic repulsion among the ligands determines the geometries of these anions.

Many other elements, including silicon, phosphorus, sulfur, and chlorine, are capable of forming hypervalent ate anions. The X–C bonding in these species is largely covalent, imparting (sometimes marginal) stability with respect to the loss of R^- . Lower-symmetry geometries, accounted for by the hypervalency of the central atom, are a rule. The axial X–C bonds are longer than their equatorial counterparts.

There are two other types of ate anions that are unique to the first-row elements. The double-Rydberg anions contain either nitrogen or oxygen as the central atom. They are unstable to electron loss and thus most probably not observable in the gas phase. Their electronic structures are best described in terms of a cationic core surrounded by a Rydberg electron pair with one unbound electron.

The $(\text{CH}_3)_2\text{F}^-$ species is the only member of the fourth class of ate anions. It possesses a positive vertical ionization potential, and its dissociation into CH_3F and CH_3^- is predicted to proceed through a small barrier. This potentially observable anion has a peculiar electronic structure that involves an entirely new type of bonding, i.e., a bypass linkage of the methyl ligands. This unusual bonding accounts for the long F–C distances and the low vibrational frequency of the C–F–C bending.

Carbon is found incapable of forming a methyl ate anion.

Although the results of electronic structure studies reported in this paper pertain to methyl ate anions, the conclusions they lead to can be safely carried over to species with ligands of similar sizes and electronegativities, i.e., other alkyl and aryl groups. The classification of ate anions presented here is expected to aid future experimental and theoretical research on these important systems.

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Supporting Information Available: Tables listing the total energies of the species under study of different levels of theory (with and without ZPEs) (4 pages). See any current masthead page for ordering information and Web access instructions.