The Formation of $HAlX_2$ (X = Cl, Br) in the Thermolysis of Intramolecularly Coordinated Alanes $Me_2N(CH_2)_3AlX_2$: A Matrix Isolation Study

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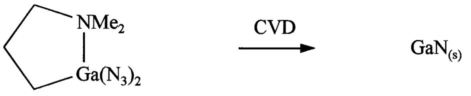
High-vacuum thermolyses of the intramolecularly coordinated alanes $Me_2N(CH_2)_3AlX_2$ with X = Cl, Br (**1**, **2**) were investigated with matrix isolation techniques. Among the products, which were identified with IR spectroscopy, ab initio calculations, and known literature data, are monomeric $HAlCl_2$ and $HAlBr_2$. The experimental vibrational frequencies of these hydrides matches well the calculated harmonic frequencies at the MP2(fc)/6–311G+(2d, p) and B3LYP/6–311G+(2d, p) level of theory. Beside the monomeric $HAlX_2$, the argon matrices of the thermolysis experiments contained CH_4, HCN, $H_2C{=}CH_2$, $H_2C{=}NMe$, $[H_2CCHCH_2]^\bullet$, $H_2C{=}CHCH_3$, and AlX_n (n = 1–3; X = Cl or Br).

Introduction

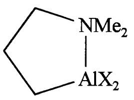
The group-13 nitrides are promising materials for advanced microelectronic and optoelectronic devices.[1][2] Suitable single-source precursors for the chemical vapor deposition of AlN[3], GaN[4], and InN[5] are intramolecularly coordinated group-13 metal azides containing the 3-(dimethylamino)propyl ligand. Recently, we started to investigate these deposition reactions with the matrix isolation technique. We intend to trap reactive intermediates produced by the fragmentation of a single-source precursor on its pathway to the resulting nitride film. By the characterization of these molecules we expect to get insights into the reaction mechanisms of these CVD processes (e.g., Eq. 1), which so far are unknown.



(1)

In order to get first results on the fragmentation pattern of intramolecularly coordinated molecules, we chose model compounds to begin with. In this article we report on gas-phase thermolysis experiments with the chloro- and the bromoalane, **1** and **2**, respectively.

Scheme 1



X = Cl, Br
1, **2**

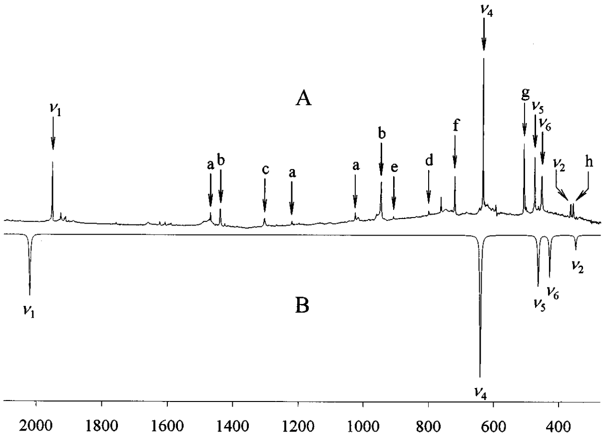
Results and Discussion

The two alanes **1** and **2** are volatile and moisture-sensitive compounds, which can be purified by sublimation in high vacuum. While the dichloro compound was published in 1991[6], no data on the bromide **2** has appeared in the literature.[7] As expected, compound **2** could readily be synthesized from aluminum bromide and $Li(CH_2)_3NMe_2$[8]. The crystal structures of **1** and **2** are unknown, but the ^{27}Al-NMR shift of $\delta = 139$ for **1** and **2** clearly reveals the expected tetra-coordination of aluminum in solution.[3b][9]

We carried out a series of high-vacuum thermolyses of **1** and **2**, respectively (see Experimental Section). Between ambient temperature and oven temperatures of ca. 750°C the IR spectra of the matrix isolated alanes **1** and **2**, respectively, were unchanged. Around ca. 850°C new IR bands appeared, indicating the beginning of fragmentation; above ca. 950°C the typical IR absorptions of the precursors **1** or **2** could no longer be detected in the argon matrices.

Figure 1 shows a typical IR spectrum recorded after a thermolysis of the alane **2** at ca. 1000°C. The strongest absorption appears at 634.5 cm^{-1} followed by intensive bands at 476.0 and 1952.5 cm^{-1}. The latter lies in the characteristic region of aluminum−hydrogen stretching vibrations, which suggests the formation of a molecule with an AlH bond. Beside the experimental spectrum Figure 1 exhibits a theoretical IR spectrum of $HAlBr_2$ calculated at the B3LYP/6-311G+(2d, p) level of theory. Evidently, there is a good agreement between the major IR absorptions of the experimental spectrum and the theoretical one. In the case of the dichloro compound **1**, the AlH-stretching mode absorbs at 1966.0 cm^{-1}. Even without any calculation, there is no doubt that monomeric $HAlCl_2$ was formed in the pyrolysis of the alane **1**. This species has been synthesized photochemically in argon matrices before (Eq. 2) and was

Figure 1. Experimental and calculated IR spectra: X-axis, 250–2100 cm^{-1}; Y-axis, Absorbance (dimensionless). Spectrum A: products of the thermolysis of compound **2** at ca. 1000°C trapped in argon at 15 K (assignment $\nu_1 - \nu_6$ see Table 1); a: $H_2C{=}NMe$[17] (2900.5[a], 2854.5[a], 1469.5, 1221.0, 1026.5 cm^{-1}), b: $H_2C{=}CH_2$[14a][16] (1440.0, 947.0 cm^{-1}), c: CH_4[14] (1305.0 cm^{-1}), d: $[H_2CCHCH_2]^{\bullet}$ [18] (801.0 cm^{-1}), e: $H_2C{=}CHCH_3$[19] (909.0 cm^{-1}), f: HCN[15] (3305.0[a], 721.0 cm^{-1}), g: $AlBr_3$[20] (508.5 cm^{-1}), h: AlBr[20] (357.5 cm^{-1}). The signal of $AlBr_2$[20] at 458.0 cm^{-1} is too weak to be seen in this spectrum. The strongest among the unassigned bands was found at 763.5 cm^{-1}[b] (see also text). Spectrum B: $HAlBr_2$ calculated at the B3LYP/6−311+G(2d, p) level (half band width of 2 cm^{-1})



[a] Out of the depicted range; [b] For $HAlCl_2$ an unassigned signal was found at 770.0 cm^{-1}

unequivocally characterized by IR spectroscopy and normal coordinate analysis.[10] Within experimental error, the IR frequencies match with the published IR data of $HAlCl_2$ (Table 1, figures in braces).

In Table 1 the experimental and calculated vibrational data of $HAlCl_2$ and $HAlBr_2$ are compiled. The ab initio calculations predict C_{2v}-symmetrical equilibrium geometries for these aluminum hydrides (Table 2); thus, one expects six normal modes belonging to the irreducible representations A_1 (3), B_1 (2), and B_2 (1). In accordance with the calculations (Table 1) only five of the six modes were measured; the calculated frequencies of the XAlX-deformation vibration ν_3 are out of our detectable range of 240–4000 cm^{-1}.

Table 2. Calculated bond length (Å) and angles (deg) of $HAlCl_2$ and $HAlBr_2$[a]

	X = Cl	X = Br
AlH	1.552 (1.557)	1.554 (1.559)
AlX	2.093 (2.096)	2.259 (2.260)
XAlX	118.16 (118.47)	118.65 (119.37)

[a] MP2(fc)/6−311G+(2d, p) and B3LYP/6−311G+(2d, p); results of the B3LYP calculations in parentheses.

For reliable assignments of the IR bands we chose the MP2 and B3LYP methods with the 6-311G+(2d, p) basis set to calculate the harmonic frequencies. As known from the literature[11] MP2 results in higher wavenumbers compared with B3LYP, which is also valid for all of the calculated frequencies in Table 1. Usually, calculated wavenumbers are too large in comparison with the real values, but B3LYP often results in frequencies which are too small for the low energy modes.[12] From that point of view, the two alanes are illustrative examples: the AlH stretch ν_1, the only mode at high energy, is described slightly better by the B3LYP than by the MP2 calculations, while all other detected modes are below 655.0 cm^{-1} (ν_2, ν_4, ν_5, and ν_6) with mean observed/calculated frequency ratios of 0.995 ($HAlCl_2$) and 1.002 ($HAlBr_2$) for the MP2 calculations, whereas the respective ratios are 1.020 and 1.029 for the B3LYP method.

All experimental IR bands of $HAlCl_2$ are found at higher wavenumbers than those of $HAlBr_2$. This is mainly due to the higher molecular mass of bromine compared with chlorine; thus, the effect is strongly pronounced for the two AlX-stretching modes with differences between the chloro and the bromo derivative of 115.5 for ν_2 and 103.5 cm^{-1} for ν_5.

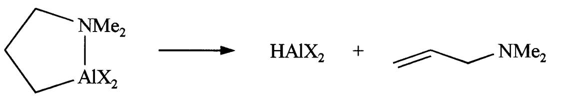
The dihaloalanes are most likely formed by β-hydrogen eliminations (Eq. 3).

There is evidence in the literature that the intramolecularly coordinated 3-(dimethylamino)propyl ligand can be split off by a β-hydrogen elimination pathway;[6a] and, indeed, allyldimethylamine was detected by NMR spec-

Table 1. Experimental and calculated vibrational data for $HAlCl_2$ and $HAlBr_2$. Experimental IR frequencies (cm^{-1}) and observed/calculated frequency ratios (in parentheses for MP2; in square brackets for B3LYP); harmonic frequencies (cm^{-1}) and intensities (in parentheses, km mol^{-1}) calculated at the MP2(fc)/6−311G+(2d, p) and the B3LYP/6−311G+(2d, p) level

				$HAlCl_2$			$HAlBr_2$	
			experimental [a]	MP2	B3LYP	experimental	MP2	B3LYP
A_1:	ν_1	ν(AlH)	1966.0 (0.9415) [0.9677] {1967.6}	2088.1 (110.2)	2031.6 (100.9)	1952.5 (0.9391) [0.9662]	2079.1 (116.2)	2020.9 (108.4)
	ν_2	$\nu_s(AlX_2)$	481.5 (0.9955) [1.0238] {481.3}[b]	483.7 (45.6)	470.3 (44.0)	366.0 (1.0186) [1.0472]	359.3 (29.7)	349.5 (27.6)
	ν_3	$\delta(AlX_2)$		161.9 (10.6)	159.1 (9.4)		107.7 (2.9)	107.2 (2.4)
B_1:	ν_4	δ(XAlH)	654.5 (0.9801) [0.9947] {654.5}	667.8 (334.0)	658.0 (288.7)	634.5 (0.9768) [0.9883]	649.6 (286.0)	642.0 (250.9)
	ν_5	$\nu_{as}(AlX_2)$	579.5 (0.9872) [1.0101] {578.9}[b]	587.0 (43.5)	573.7 (58.7)	476.0 (0.9996) [1.0241]	476.2 (90.6)	464.8 (91.6)
B_2:	ν_6	γ(H)	472.5 (1.0166) [1.0512] {471.8}	464.8 (122.2)	449.5 (102.7)	453.5 (1.0125) [1.0564]	447.9 (92.0)	429.3 (76.3)

[a] Wavenumbers in parentheses were taken from reference[10]. – [b] Listed are the wavenumbers concerning the main isotopomers.



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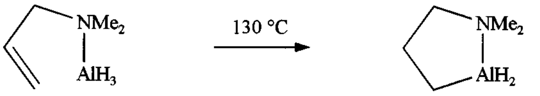
1, 2 X = Cl, Br

troscopy in the exhaust gases of the CVD process as shown by Eq. 1.[4b] The reverse reaction, the hydroalumination, is well known in organic and organometallic syntheses; the synthesis of 3-(dimethylamino)propylalane is given as an example (Eq. 4).[6b]



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However, in none of the thermolysis experiments of compound **1** or **2** did we detect allyldimethylamine in argon matrices.[13] Beside the two dihaloalanes, we identified CH_4,[14] HCN,[15] $H_2C{=}CH_2$,[14a][16] $H_2C{=}NMe$,[17] $[H_2CCHCH_2]^\bullet$,[18] and $H_2C{=}CHCH_3$[19] (see Figure 1). One might believe that allyldimethylamine is produced by the thermolyses according to Eq. 3, and because the temperatures are so high that it is further pyrolyzed. In order to prove this speculation, we conducted thermolysis experiments with amine/argon mixtures (1:500). The fragmentation of the amine begins around 800°C, and at ca. 1150°C we could not detect any allyldimethylamine in argon matrices. All the mentioned above molecules were found, but they were produced in different ratios than for the thermolysis experiments of compound **1** and **2**, respectively. Furthermore, there were new, unidentified IR bands, which we have not identified so far. As mentioned before, allyldimethylamine was detected in the exhaust gases of the deposition reaction Eq. 1, and with increasing deposition temperatures increasing amounts of $H_2C{=}CH_2$ and NMe_3 were found; however, we did not find NMe_3 amoung the thermolyses products of compound **1** and **2**.

Among the pyrolysis products, the aluminum halide species AlX [X = Cl: 455.0 ($Al^{35}Cl$) and 450.0 ($Al^{37}Cl$) cm^{-1}; X = Br: 357.5 cm^{-1}], AlX_2 [X = Cl: 564.0 ($Al^{35}Cl_2$) and 561.5 ($Al^{35}Cl^{37}Cl$) cm^{-1}; X = Br: 458.0 cm^{-1}], and AlX_3 [X = Cl: 619.0 ($Al^{35}Cl_3$) and 615.0 ($Al^{35}Cl_2{}^{37}Cl$) cm^{-1}; X = Br: 508.5 cm^{-1}] could be unequivocally identified by comparison with known literature data.[20] At this point we will not suggest various reaction pathways which explain the AlX_n species, because they would be purely speculative; obviously, further experiments are necessary.

Conclusion

Up to date, only two monomeric aluminum hydrides of the type H_nAlX_{3-n} (n = 1−3) have been characterized, i.e., AlH_3[21] and $HAlCl_2$[10]; with $HAlBr_2$ we examined a third example. However, it is surprising that the hydrides $HAlX_2$ withstand the rather harsh thermolyses conditions. We hope to expand the method described in this paper to get access to new, reactive group-13 molecules. As mentioned in the introduction, **1** and **2** were chosen as model compounds for intramolecularly coordinated group-13 metal azides in order to get first insights into the fragmentation mechanism of these types of substances. The results reported here demonstrate that the fragmentation of the compounds **1** and **2** are not as simple as it seems at first glance. Further investigations are in progress and we will report on this outcome shortly.

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Experimental Section

General Remarks: All procedures for syntheses were carried out under a dry nitrogen atmosphere with standard Schlenk techniques. Solvents were dried by standard procedures, distilled, and stored under nitrogen and molecular sieves (4 Å). The reagents $Me_2N(CH_2)_3AlCl_2$ (**1**)[6b] and $Li(CH_2)_3NMe_2$[8] were prepared according to the literature procedures. − NMR: Varian Unity 500 (ambient temp.; 499.843, 130.195, and 125.639 MHz for ^1H, ^{27}Al, and ^{13}C, respectively); calibrated against residual protons of the deuterated solvents. ^1H- and ^{13}C-chemical shift are reported relative to TMS and ^{27}Al-NMR values relative to the external standard $[Al(acac)_3]$ in C_6D_6. As a result of the electric quadrupole moment of the ^{27}Al nucleus the carbon atoms bound to aluminum could not be detected in the ^{13}C-NMR measurement. − Elemental analyses (C, H, N): Carlo-Erba elemental analyzer, Model 1106. − MS: Finnigan MAT 95.

Dibromo[3-(dimethylamino)propyl]aluminum (**2**): 2.60 g (27.95 mmol) of $Li(CH_2)_3NMe_2$ were added to a solution of 7.45 g of $AlBr_3$ (27.95 mmol) in 50 ml of toluene, and the reaction mixture was stirred overnight. The suspension was filtered, and the solid was washed with two 10-ml portions of toluene. After removal of the solvent in high vacuum, sublimation (50−75°C, 10^{-3} mbar) gave 5.51 g of **2** (72%) as a colorless solid, m.p. 98−101°C. − ^1H NMR (C_6D_6): δ = 0.35 (t, ^3J = 7.78 Hz, 2 H, $AlCH_2$), 1.16 (pseudo quintet, ^3J = 6.71 Hz, 2 H, $AlCH_2CH_2$), 1.68 (t, ^3J = 6.41 Hz, 2 H, NCH_2), 1.70 (s, 6 H, CH_3). − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 20.02 ($AlCH_2CH_2$), 45.51 (CH_3), 62.12 (NCH_2). − ^{27}Al NMR (C_6D_6): δ = 139 ($h_{1/2}$ = 750 Hz). − MS (70 eV), m/z (%): 273 (100) $[M^+]$, 245 (45) $[M^+ - C_2H_4]$, 230 (76) $[M^+ - C_2H_5N]$, 192 $[M^+ - Br]$, 187 (41) $[M^+ - (CH_2)_3N(CH_3)_2]$. − $C_5H_{12}AlBr_2N$ (272.95): calcd. C 22.00, H 4.43, N 5.13; found C 21.66, H 4.50, N 5.11.

Matrix Isolation: The matrix apparatus consists of a vacuum line (Leybold Turbovac 151; Leybold Trivac D4B) and a Displex CSW 202 cryogenic closed-cycle system (APD Cryogenics Inc.) fitted with CsI windows. In a typical experiment the starting compound was kept in a small metal container in high vacuum at constant temperature (10^{-6} to 10^{-7} mbar; compound **1**: 35−50°C; compound **2**: 50−60°C), while a flow of argon was conducted over the sample (Linde 6.0; flow = 1.0 sccm; MKS mass flow controller type 1179). Subsequently, this gaseous mixture was passed through an Al_2O_3 tube (inner diameter of 1 mm; heated by tungsten wire coiled around the last 10 mm). The hot end of the pyrolysis tube was just 25 mm away from the cooled CsI window to assure that a maximum amount of volatile fragments emerging from the oven were trapped in the matrix. For the temperature determination of the pyrolysis oven a current-to-temperature relation was measured with a thermocouple (Thermocoax: NiCr/NiAl) inside of the Al_2O_3 tube.

The concentrations of the samples in the matrices are unknown. Therefore, several experiments under various conditions were carried out to insure that the molecules were indeed matrix-isolated. The concentration of the samples decreases significantly at lower sublimation temperatures (20°C for **1** and 35°C for **2**), but no differences in the IR spectra were observed. At higher concentrations the half band widths of IR bands increased and new broad IR bands appeared indicating that notable parts of the molecule are no longer matrix-isolated under these conditions.

The IR spectra of the matrices (15 K) were recorded on a Perkin-Elmer FTIR 1720x from 240 to 4000 cm^{-1} with a resolution of 1 cm^{-1}.

Ab initio Calculations: The GAUSSIAN 94 package[22], run on a cluster of workstations (*Rechenzentrum der RWTH Aachen*), was applied for all ab initio calculations. The total energies E_h (in Hartrees) and the ZPVE (in kJ mol^{-1}; in parentheses) are as follows: − $HAlCl_2$: −1162.046298 (26.64) for MP2(fc)/6−311+G(2d, p); −1163.649857 (25.97) for B3LYP/6−311+G(2d, p). − $HAlBr_2$: −5387.697127 (24.64) for MP2(fc)/6−311+G(2d, p); −5391.474382 (24.01) for B3LYP/6−311+G(2d, p).

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[1] D. A. Neumayer, J. G. Ekerdt, *Chem. Mater.* **1996**, *8*, 9−25, and references therein.

[2] A. C. Jones, P. O′Brien, *CVD of Compound Semiconductors*; VCH: Weinheim, **1997**.

[3] [3a] R. A. Fischer, A. Miehr, H. Sussek, H. Pritzkow, E. Herdtweck, J. Müller, O. Ambacher, T. Metzger, *J. Chem. Soc., Chem. Commun.* **1996**, 2685−2686. − [3b] J. Müller, R. A. Fischer, H. Sussek, P. Pilgram, R. Wang, H. Pritzkow, E. Herdtweck, *Organometallics* **1998**, *17*, 161−166.

[4] [4a] A. Miehr, M. R. Mattner, R. A. Fischer, *Organometallics*, **1996**, *15*, 2053−2059. − [4b] A. Miehr, O. Ambacher, W. Rieger, T. Metzger, E. Born, R. A. Fischer, *Chem. Vap. Deposition* **1996**, *2*, 51−55. − [4c] R. A. Fischer, A. Miehr, E. Herdtweck, M. R. Mattner, O. Ambacher, T. Metzger, E. Born, S. Weinkauf, C. R. Pulham, S. Parsons, *Chem. Eur. J.* **1996**, *2*, 1353−1358.

[5] R. A. Fischer, A. Miehr, T. Metzger, E. Born, O. Ambacher, H. Angerer, R. Dimitrov, *Chem. Mater.* **1996**, *8*, 1356−1359.

[6] [6a] H. Schumann, U. Hartmann, W. Wassermann, O. Just, A. Dietrich, L. Pohl, M. Hostalek, M. Lokai, *Chem. Ber.* **1991**, *124*, c 1113−1119. − [6b] U. Dümichen, K.-H. Thiele, T. Gelbrich, J. Sieler, *J. Organomet. Chem.* **1995**, *495*, 71−75.

[7] Compound **2** is mentioned in: R. A. Fischer, T. Priermeier, *Organometallics*, **1994**, *13*, 4306−4314.

[8] K.-H. Thiele, E. Langguth, G. E. Müller, *Z. Anorg. Allg. Chem.* **1980**, *462*, 152−158.

[9] J. Müller, U. Englert, *Chem. Ber.* **1995**, *128*, 493−497, and references therein.

[10] H. Schnöckel, *J. Mol. Struct.* **1978**, *50*, 275−280.

[11] [11a] A. P. Scott, L. Radom, *J. Phys. Chem.* **1996**, *100*, 16502−16513. − [11b] G. Rauhut, P. Pulay, *J. Phys. Chem.* **1995**, *99*, 3093−3100.

[12] A. Y. Timoshkin, H. F. Bettinger, H. F. Schaefer III, *J. Am. Chem. Soc.* **1997**, *119*, 5668−5678.

[13] For comparison with IR spectra of thermolysis experiments, we measured the IR spectrum of matrix isolated allyldimethylamine in argon (amine:argon ratio 1:500).

[14] [14a] G. Herzberg, *Molecular Spectra and Structure*, 1st ed., D. Van Nostrand Reinhold Company, Inc., Princeton, NJ, **1945**, Vol. II. − [14b] J. Müller, *J. Am. Chem. Soc.* **1996**, *118*, 6370−6376.

[15] [15a] D. E. Milligan, E. M. Jacox, *J. Chem. Phys.* **1963**, *39*, 712−715. − [15b] D. V. Lanzisera, L. Andrews, *J. Phys. Chem. A* **1997**, *101*, 824−830.

[16] L. Andrews, G. L. Johnson, B. J. Kelsall, *J Chem. Phys.* **1982**, *76*, 5767−5773.

[17] [17a] J. Hinze, R. F. Curl, Jr., *J. Am. Chem. Soc.* **1964**, *86*, 5068−5070. − [17b] I. Stolkin, T.-K. Ha, Hs. H. Günthard, *Chem. Phys.* **1977**, *21*, 327−347.

[18] [18a] G. Maier, H. P. Reisenauer, B. Rohde, K. Dehnicke, *Chem. Ber.* **1983**, *116*, 732−740. − [18b] J. W. Huang, W. R. M. Graham, *J. Phys, Chem.* **1990**, *93*, 1583−1596.

[19] L. Andrews, G. L. Johnson, B. J. Kelsall, *J. Am. Chem. Soc.* **1982**, *104*, 6180−6186.

[20] P. Hassanzadeh, A. Citra, L. Andrews, M. Neurock, *J. Phys. Chem.* **1996**, *100*, 7317−7325, and references therein.

[21] [21a] F. A. Kurth, R. A. Eberlein, H. Schnöckel, A. J. Downs, C. R. Pulham, *J. Chem. Soc., Chem. Commun.* **1993**, 1302−1304. − [21b] P. Pullumbi, Y. Bouteiller, L. Manceron, C. Mijoule, *Chem. Phys.* **1994**, *185*, 25−37.

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

[98228]