

DFT Study of Dimethylaluminum Azide Clusters: Structures, Energies, Frequencies and Thermodynamic Properties

XIA, Qi-Ying(夏其英) XIAO, He-Ming*(肖鹤鸣) JU, Xue-Hai(居学海)
GONG, Xue-Dong(贡雪东)

Department of Chemistry, Nanjing University of Science and Technology, Nanjing, Jiangsu 210094, China

DFT/B3LYP method with SDD basis set has been applied to the systems of $(\text{Me}_2\text{AlN}_3)_n$ ($n=1-3$). $(\text{Me}_2\text{AlN}_3)_2$ was found to exhibit the planar Al_2N_2 ring structure. $(\text{Me}_2\text{AlN}_3)_3$ involving a six-membered Al_3N_3 ring was found to exhibit two minima with very similar binding energies (-265.52 and -256.10 $\text{kJ}\cdot\text{mol}^{-1}$). Compared to the monomer, both the structural changes and charge transfers for the clusters are large. Frequency calculations were carried out on each optimized structure and its IR spectra were discussed. Thermodynamic properties reveal that the dimer is the main component in the systems of the $(\text{Me}_2\text{AlN}_3)_n$ ($n=1-3$).

Keywords $(\text{Me}_2\text{AlN}_3)_n$ ($n=1-3$), DFT, IR spectra, thermodynamic property

Introduction

The organoaluminum azide compounds have been widely used in many fields. These compounds are used as the azidating agents,¹⁻³ and the energetic materials which are always used in national defence industry and in space technology, especially to generate thin films of AlN in various chemical vapor deposition (CVD) systems.⁴⁻⁶ Aluminum nitride has useful properties for coatings, especially for optical or optoelectronic devices, acoustic wave devices and electronic microcircuits.⁷

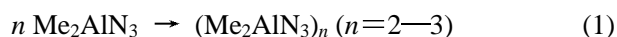
The organoaluminum azide compounds including dimethylaluminum azide (DMAA),^{4,8} diethylaluminum azide (DEAA),^{6,9,10} diethyl(*t*-butylamido)aluminum (DETBA) and diisobutylaluminum azide (DBAA),¹¹ have been synthesized and studied by experimental method. As we know, the behavior of molecular clusters is usually studied between two extremes: the gas phase and the crystal solid phase. Consequently, the valuable knowledge about the transition of these extremes can be obtained by examining the properties of the clusters. Because experimental measurements provide no detailed information about the structures of the clusters, theoretical methods can be used to resolve the problem.

Dimethylaluminum azide (Me_2AlN_3) is the simplest model for organoaluminum azide compounds. In this paper, we firstly employ DFT theory at B3LYP level to predict the characters of the $(\text{Me}_2\text{AlN}_3)_n$ with n up to 3, including the stable optimized geometries, natural atomic charge, binding energies, and IR spectra. Especially the thermodynamic properties can provide useful information for the synthesis of the $(\text{Me}_2\text{AlN}_3)_{2-3}$.

Methods

DFT/B3LYP method with SDD basis set was used to fully optimize the geometries of the clusters formed by two and three Me_2AlN_3 molecules.¹²⁻¹⁴ After stationary points were located, vibrational frequencies were calculated in order to ascertain that each structure was characterized to be the stable one (no imaginary frequencies).

For the following process:



the binding energy (ΔE) of the complex was determined as

$$\Delta E = E_n - nE_1 \quad (n=2-3) \quad (2)$$

where E_n and E_1 are the total energies of the clusters $(\text{Me}_2\text{AlN}_3)_{2-3}$ and the isolated molecule Me_2AlN_3 , respectively.

All calculations were carried out with the Gaussian 98 program¹⁵ on a Pentium IV computer using the default convergence criteria.

Results and discussion

Geometry

Our computational method and basis set reveal the structures of the Me_2AlN_3 monomer and its clusters shown in Figure 1. The partial geometric parameters are summarized in Table 1. The $(\text{Me}_2\text{AlN}_3)_2$ dimer and $(\text{Me}_2\text{AlN}_3)_3$ trimer are formed by two and three Al atoms bridged by the α -nitrogen of the azide groups (connectivity: $\text{Me}_2\text{Al}-\text{N}_\alpha-\text{N}_\beta-\text{N}_\gamma$), respectively. It

* E-mail: xiao@mail.njust.edu.cn; Fax: +86-25-84431622

Received December 11, 2003; revised May 28, 2004; accepted July 1, 2004.

Project supported by the National Natural Science Foundation of China (No. 20173028).

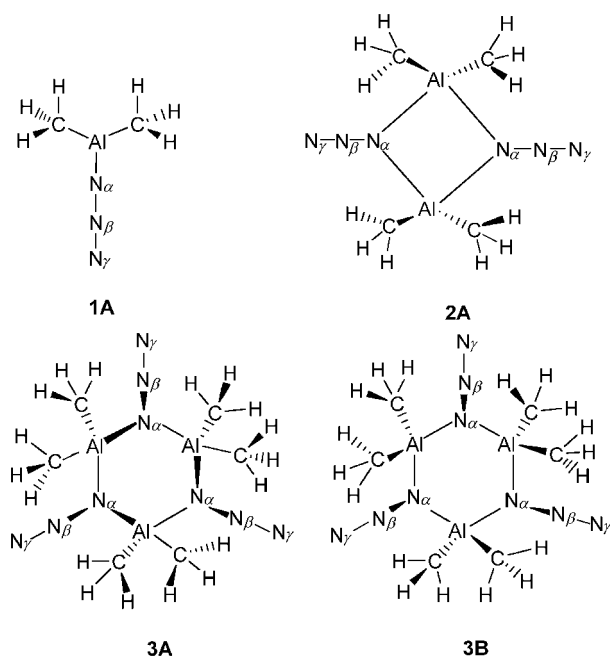


Figure 1 Minima of Me_2AlN_3 monomer and its clusters.

has been established before that in the polymeric I_2GaN_3 ¹⁶ and $[\text{Cl}_2\text{InN}_3(\text{THF})_2]_2$ ¹⁷ (THF=tetrahydrofuran) compounds, cross-linking of the Ga or In atoms occurs both via the α -nitrogen of the N_3 ligand. Our previous computational results also show that $(\text{H}_2\text{AlN}_3)_{2-4}$ ¹⁸ and $(\text{H}_2\text{GaN}_3)_{2-4}$ ¹⁹ clusters are formed by Al or Ga atoms bridged by the α -nitrogen of the azide group. On the other hand, the $\text{N}_3\text{In}[(\text{CH}_2)_3\text{NMe}_2]_2$ ²⁰ compound forms a polymeric structure in which cross-linking of the In atoms occurs via the γ -nitrogen of the N_3 ligand.

The Al_2N_2 tetragonal framework has not been established before in the structures of inorganic and organoaluminum azides except that $(\text{H}_2\text{AlN}_3)_2$ cluster was previously studied by theoretical method.¹⁸ Nevertheless, such a four-membered structure has been proposed for the dimeric azide of indium $[(\text{C}_2\text{H}_5)_2\text{InN}_3]_2$ ⁸ and $[\text{Cl}_2\text{InN}_3(\text{THF})_2]_2$ ¹⁷ and similar Ga_2N_2 ring has been found in the structure of $(\text{H}_2\text{GaN}_3)_2$.¹⁹

Our computation reveals two types of the trimeric $(\text{Me}_2\text{AlN}_3)_3$: a boat-twisting conformation **3A** and a chair-like conformation **3B**. The chair-like structure has been suggested for the trimers $(\text{H}_2\text{AlN}_3)_3$,¹⁸ $(\text{H}_2\text{GaN}_3)_3$,^{19,21,22} and $(\text{Cl}_2\text{GaN}_3)_3$ ²³ in the gas phase, however, $(\text{Me}_2\text{AlN}_3)_3$ in solution is a planar Al—N ring (D_{3h} symmetry).⁸ The Al_3N_3 cyclic core of the structure represents the basic building block. **3A** structure is a newly found one.

Compared to the monomer, the bond lengths $\text{N}_\alpha\text{—Al}$ in the dimer and trimer structures increase by 20.7 and 20.7—22.4 pm, respectively. The $\text{N}_\alpha\text{—N}_\beta$ bond lengths of the dimer and trimers increase by 3.0 and 4.2—4.5 pm, respectively, however, the $\text{N}_\beta\text{—N}_\gamma$ bond lengths decrease by 0.9 and 1.0—1.4 pm. The Al—C bond lengths increase by 1.0 and 0.6—1.5 pm for the dimer

and trimer, respectively. Obviously, the bond length changes are in the following orders: trimer > dimer, $\text{N}_\alpha\text{—Al} > \text{N}_\alpha\text{—N}_\beta > \text{N}_\beta\text{—N}_\gamma \approx \text{Al—C}$. The $\text{N}_\alpha\text{—N}_\beta$ and Al—C bond length increases show that it could easily eliminate N_2 ($\text{N}_\beta\text{—N}_\gamma$) and CH_3 groups to yield AlN material. The $\text{N}_\alpha\text{—N}_\beta\text{—N}_\gamma$ bond angles are about 180.0° for all the structures, which is typical of those reported for other crystalline group 13 covalent azides. The average bond angles $\text{N}_\beta\text{—N}_\alpha\text{—Al}$ are *ca.* 129.6° , 118.7° and 117.3° in the structures **2A**, **3A** and **3B**. The average bond angles $\text{N}_\alpha\text{—Al—N}_\alpha$ are *ca.* 79.2° , 95.4° and 97.2° in the corresponding structures. The average bond angles $\text{Al—N}_\alpha\text{—Al}$ are about 100.7° , 122.7° and 125.0° .

Natural atomic charge

The computational natural atomic charges are listed in Table 2. Here we only consider the charges occurring on Al and N_α atoms in the four- and six-membered ring structures in the polymerization progress. Compared to the monomer, the N_α atoms acquire 0.0792 e and 0.0787 e in **2A**; the N_α atoms in **3A** acquire 0.0911 e, 0.0915 e and 0.0769 e; the N_α atoms in **3B** acquire 0.0803 e, 0.0806 e and 0.0805 e. By the similar analysis, the charges on Al atoms change little, and the highest value is 0.0065 e. Obviously, charge changes are in the following order for the dimer and trimers: $\text{N}_\alpha > \text{Al}$ atoms.

Energy

Table 3 reports the total energies, zero point energies (ZPE), and ZPE corrections for the binding energies of the $(\text{Me}_2\text{AlN}_3)_{2-3}$ clusters. The uncorrected and corrected binding energies are both in the orders: **3A** > **3B** > **2A**. The proportions of ZPE corrections to their binding energies ΔE_{ZPEC} are 3.43%, 4.40% and 5.00% for **2A**, **3A** and **3B**, respectively, which indicates that the ZPE corrections for the binding energies are small. After the corrections of the ZPE, the binding energies are -173.28 , -265.52 and -256.10 $\text{kJ}\cdot\text{mol}^{-1}$ for **2A**, **3A**, and **3B**, respectively. Obviously, the binding energies of two trimers are very similar and the binding energy of the most attractive trimer is about 9.42 $\text{kJ}\cdot\text{mol}^{-1}$ lower than that of the other trimer.

IR spectrum

The simulated infrared (IR) spectra for the Me_2AlN_3 monomer and the clusters are shown in Figure 2, where the intensity is plotted against the harmonic vibrational frequencies (the scale factor is 0.96^{24}). For the complexity of vibrational modes, it is difficult to attribute all bands, so we have only analyzed some vibrational frequencies that facilitate assignment of the observed peaks. For the monomer **1A**, it was found that the asymmetric stretching vibration for the azide group has the highest intensity at 2118.7 and the symmetric stretching vibration of the azide group appears at 1407.4 cm^{-1} . The two peaks at 1265.3 and 802.6 cm^{-1} were

Table 1 Geometries of Me₂AlN₃ monomer and its clusters (bond lengths in angstroms, angles in degrees)

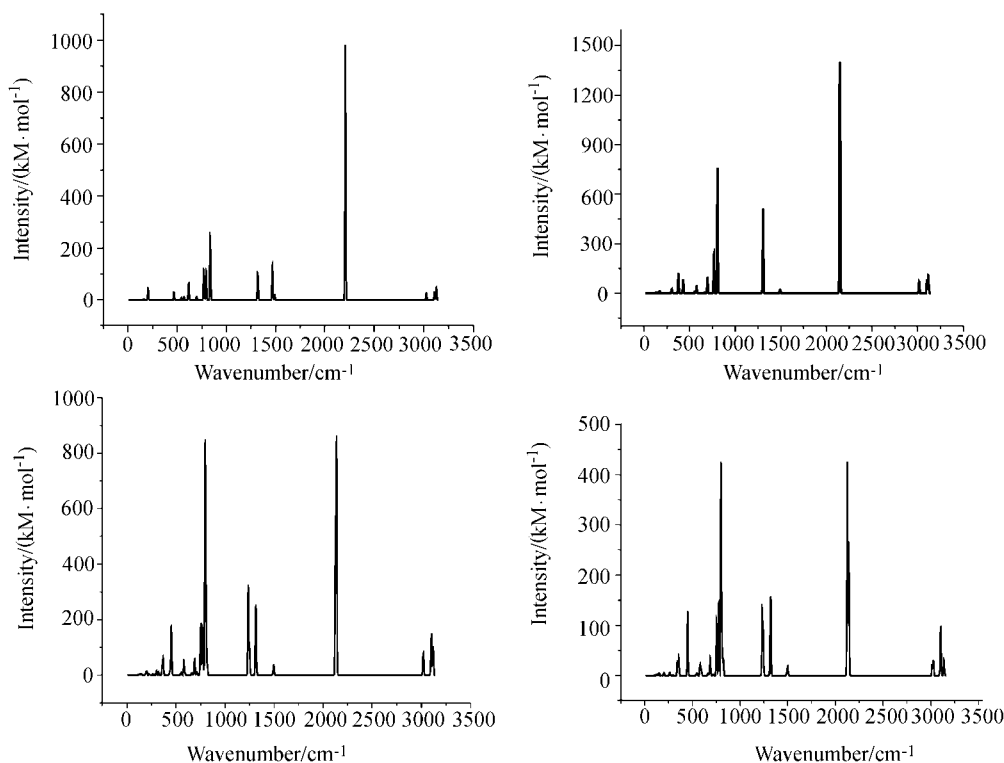
	1A	2A	3A	3B
N _β —N _γ	1.177	1.168	1.163	1.164
		1.168	1.163	1.164
			1.167	1.164
N _α —N _β	1.222	1.252	1.267	1.267
		1.252	1.267	1.267
			1.264	1.267
Al—N _α	1.796	2.003	2.009	2.020
		2.002	2.003	2.018
		2.002	2.010	2.016
		2.004	2.003	2.018
			2.020	2.018
			2.018	2.019
Al—C	1.958	1.968	1.964	1.968
	1.958	1.968	1.972	1.968
		1.968	1.967	1.965
		1.968	1.971	1.972
			1.971	1.965
			1.967	1.973
N _α —N _β —N _γ	180.0	180.0	179.7	179.4
		179.7	179.7	179.5
			180.0	179.5
N _β —N _α —Al	179.7	129.5	118.8	117.2
		129.7	118.5	117.3
		130.1	118.6	117.5
		129.2	118.3	117.3
			118.8	117.5
			119.0	117.2
N _α —Al—N _α		79.3	92.5	97.2
		79.2	97.0	96.9
			96.8	97.4
Al—N _α —Al		100.8	122.8	125.2
		100.7	123.0	124.8
			122.2	125.0

Table 2 The natural atomic charges obtained from NBO analysis (e)

	1A	2A	3A	3B
N _α	−0.7868	−0.8660	−0.8779	−0.8671
		−0.8655	−0.8783	−0.8674
			−0.8637	−0.8673
Al	1.8513	1.8510	1.8492	1.8448
		1.8512	1.8513	1.8449
			1.8507	1.8455

Table 3 Energies of the Me_2AlN_3 monomer and its clusters ($\text{kJ}\cdot\text{mol}^{-1}$)

	E	ΔE	ZPE	ΔE_{ZPEC}
1A	-1277220.63		224.28	
2A	-2554620.49	-179.23	454.76	-173.28
3A	-3831939.09	-277.20	685.01	-265.52
3B	-3831930.80	-268.91	686.18	-256.10

**Figure 2** IR spectra of the title compounds.

assigned to CH_3 symmetric and asymmetric deformation vibrations, respectively. As for the dimer **2A**, the peak at 2062.1 cm^{-1} was assigned to the N_3 asymmetric stretching vibrational mode. CH_3 symmetric and asymmetric deformation vibrations were located at 1253.8 and 773.8 cm^{-1} , respectively. The N_3 asymmetric, symmetric stretching and twisting, CH_3 symmetric and asymmetric deformation vibrations for **3A** were located at 2050.6 , 1187.5 , 433.0 , 1262.4 and 766.1 cm^{-1} , respectively. The corresponding modes for the trimer **3B** are 2040.0 , 1183.7 , 431.0 , 1268.2 and 768.0 cm^{-1} . For all the structures, C—H stretching vibration modes appear around 3000.0 cm^{-1} .

Thermodynamic property

Table 4 gives the values of thermodynamic properties of Me_2AlN_3 clusters. The magnitudes of heat capacities (C_p^0) for clusters with the same number of molecules (n) are approximately the same at each temperature, and larger than $n \times C_p^0$ (**1A**) by 11.40 – 17.08 and 23.24 – $32.77\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ for $n=2$ and 3 respectively. The dimerization and trimerization entropies (ΔS_T) and enthalpies (ΔH_T) decrease at any temperature

from 298.2 to 700.0 K . The dimerization and trimerization processes are therefore exothermic ones accompanied by a decrease in the disordered degree, and the dimerization and trimerization become weak as temperature increases.

The dimerization and trimerization enthalpies for the dimer and trimers at 298.2 K and $1.01 \times 10^5\text{ Pa}$ are -175.52 , -269.53 and $-260.74\text{ kJ}\cdot\text{mol}^{-1}$, respectively. From the $\Delta G_T = \Delta H_T - T\Delta S_T$ equation, we can obtain the change of Gibbs free energy (ΔG_T). Judged by the value of ΔG_T , the dimerization and trimerization processes can occur spontaneously at low temperature. Both the values of ΔH_T and ΔG_T imply that the stability sequence is **3A** > **3B**, which is consistent with the results from the corrected binding energies. The absolute values of the calculated ΔG_T for the more stable dimer and trimer at 298.2 K are large, which shows that there is no monomer existing. Based on the equation $\Delta G = -RT \ln K_p$, the proportion for **2A** : **3A** is equal to $128630 : 1$ at 298.2 K , which reveals that the dimer is the main component of the $(\text{Me}_2\text{AlN}_3)_{1-3}$ clusters.

Table 4 Thermodynamic properties of Me₂AlN₃ monomer and its clusters at different temperatures^a

	T/K	C _p ⁰ /(J•mol ⁻¹ •K ⁻¹)	S _T ⁰ /(J•mol ⁻¹ •K ⁻¹)	H _T ⁰ /(kJ•mol ⁻¹)	ΔS _T ⁰ /(J•mol ⁻¹ •K ⁻¹)	ΔH _T ⁰ /(kJ•mol ⁻¹)	ΔG _T ⁰ /(kJ•mol ⁻¹)
1A	298.2	129.63	421.45	27.20			
	500.0	167.19	497.94	57.39			
	700.0	193.31	558.58	93.58			
2A	298.2	270.66	604.50	52.16	-238.40	-175.52	-104.43
	500.0	350.29	764.71	115.40	-231.17	-172.66	-57.08
	700.0	403.70	891.57	191.11	-225.59	-169.33	-11.42
3A	298.2	412.67	787.98	77.59	-476.37	-269.53	-127.48
	500.0	533.36	1032.15	173.97	-461.67	-263.72	-32.89
	700.0	612.70	1225.02	289.06	-450.72	-257.20	58.30
3B	298.2	412.13	777.25	76.96	-487.10	-260.74	-115.49
	500.0	533.06	1021.22	173.26	-472.60	-255.01	-18.71
	700.0	612.51	1214.01	288.30	-461.73	-248.54	74.67

Conclusion

The computational results predict that the clusters all possess cycle-like structures formed by two and three Al atoms bridged by the α -nitrogen of the azide groups. Both the structural changes and charge transfers of each cluster are great compared to the monomer. The trimer occurs as two structures that correspond to minima with similar binding energies (-265.52 and -256.10 kJ•mol⁻¹). The ZPE correction is less significant in all cases. For the dimer and trimer, the N₃ asymmetric and symmetric stretching, CH₃ symmetric and asymmetric deformation vibrations are located at 2100.0, 1200.0, 1260.0 and 770.0 cm⁻¹, respectively. The ratio for **2A** : **3A** is equal to 128630 : 1 at 298.2 K, which shows that the dimer is the main component of the (Me₂AlN₃)₁₋₃ clusters.

References

- Rawal, V. H.; Zhong, H. M. *Tetrahedron Lett.* **1994**, 35, 4947.
- Mereyala, H. B.; Frei, B. *Helv. Chim. Acta* **1986**, 69, 415.
- Chung, B. Y.; Park, Y. S.; Cho, I. S. *Bull. Korean. Chem. Soc.* **1988**, 9, 269.
- Boyd, D. C.; Haasch, R. T.; Mantell, D. R.; Schulze, R. K.; Evans, J. F.; Gladfelter, W. L. *Chem. Mater.* **1989**, 1, 119.
- Schulze, R. K.; Boyd, D. C.; Evans, J. F.; Gladfelter, W. L. *J. Vac. Sci. Technol. A* **1990**, 8, 2338.
- Boo, J. H.; Lee, S. B.; Kim, Y. S.; Park, J. T.; Yu, K. S.; Kim, Y. *Phys. Stat. Sol. A* **1999**, 176, 711.
- Sheppard, L. M. *Am. Ceram. Soc. Bull.* **1990**, 69, 1801.
- Müller, J.; Dehnicke, K. *J. Organomet. Chem.* **1968**, 12, 37.
- Dehnicke, K. *J. Organomet. Chem.* **1966**, 6, 298.
- Gao, Z. X.; Zhang, X. H.; Feng, L. C. *Chin. J. Inorg. Chem.* **2002**, 18, 654 (in Chinese).
- Zhang, X. H.; Gao, Z. X. *Chin. J. Inorg. Chem.* **2001**, 17, 819 (in Chinese).
- Fletcher, R.; Powell, M. J. D. *Comput. J.* **1963**, 6, 163.
- Schlegel, H. B. *J. Comput. Chem.* **1982**, 3, 214.
- Peng, C. Y.; Ayala, P. Y.; Schlegel, H. B.; Frisch, M. J. *J. Comput. Chem.* **1996**, 17, 49.
- Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A. 7; Gaussian Inc., Pittsburgh, PA, **1998**.
- Dehnicke, K.; Kruger, N. *Z. Anorg. Allg. Chem.* **1978**, 444, 71.
- Steffek, C.; McMurrin, J.; Pleune, B.; Kouvetakis, J. *Inorg. Chem.* **2000**, 39, 1615.
- Xia, Q. Y.; Xiao, H. M.; Ju, X. H.; Gong, X. D. *J. Phys. Chem. A* **2004**, 108, 2780.
- Xia, Q. Y.; Xiao, H. M.; Ju, X. H.; Gong, X. D. *Int. J. Quantum Chem.* **2004**, 100, 301.
- Fischer, R. A.; Sussek, H.; Miehr, A.; Pritzkow, H.; Herdtweck, E. *J. Organomet. Chem.* **1997**, 548, 73.
- McMurrin, J.; Dai, D.; Balasubramanian, K.; Steffek, C.; Kouvetakis, J.; Hubbard, J. L. *Inorg. Chem.* **1998**, 37, 6638.
- McMurrin, J.; Kouvetakis, J.; Smith, D. J. *Appl. Phys. Lett.* **1999**, 74, 883.
- McMurrin, J.; Todd, M.; Kouvetakis, J.; Smith, D. J. *Appl. Phys. Lett.* **1996**, 69, 203.
- Pople, J. A.; Schlegel, H. B.; Krishnan, R.; Defrees, D. J.; Binkley, J. S.; Frisch, M. J.; Whiteside, R. A.; Hout, R. F.; Hehre, W. J. *Int. J. Quantum Chem. Quantum Chem. Symp.* **1981**, 15, 269.