

# Synthesis and structure of tetrakis(isopropylimino)bis-[tris(dimethylamino)silylamino]alane

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Received 13 October 2004; accepted 15 November 2004

## Abstract

A novel cage-type compound tetrakis(isopropylimino)bis[tris(dimethylamino)silylamino]alane,  $H_6Al_6(N^iPr)_4[NSi(NMe_2)_3]_2$ , (**1**), was prepared by reaction of tris(dimethylamino)silylamine  $H_2NSi(NMe_2)_3$  with poly(isopropyliminoalane)  $(HAIN^iPr)_6$ . The molecular structure of **1** was determined and discussed on the basis of FTIR, NMR and X-ray crystallographic analysis.

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*Keywords:* Dimethylamino; Silylamino; Alane; Synthesis; Structure

## 1. Introduction

Synthesis and characterization of organometallic compounds containing Al–N–Si backbones are of current interest due to their potential applications as single-source precursors for the preparation of silicon aluminum nitride materials with a defined shape, e.g., as coating or fibres [1–3]. We recently reported for the first time the preparation of tris(dimethylamino)silylamine,  $[(CH_3)_2N]_3SiNH_2$  TDSA, by ammonolysis of tris(dimethylamino)chlorosilane  $[(CH_3)_2N]_3SiCl$ , an intermediate prepared from the reaction of silicon tetrachloride with dimethylamine [4]. A mesoporous silicon diimide gel, which is a precursor for high surface area mesoporous silicon nitride, [5] was prepared from TDSA via a non-aqueous ammonolytic sol–gel method [4]. We are now actively seeking to prepare novel ternary Si–Al–N precursor molecules, using tris(dimethylamino)silylamine as a

starting material. The synthetic strategy we have adopted is to use tris(dimethylamino)silylamine or its lithium salt as reagents to assemble precursor molecules containing, in addition to  $Si(NMe_2)_3$  groups,  $Al(NHSiN_3)_n$  backbones. These precursor materials should be convertible into high-surface-area silicon aluminum diimide gels by a similar sol–gel process, and hence to mesoporous Si–Al–N ceramics. A single-source precursor molecule  $(C_4H_8O)Al[(NHSi(NMe_2)_3)]_3$  was successfully prepared by a reaction of lithium tris(dimethylamino)silylamide  $[(CH_3)_2N]_3SiNHLi$  with aluminium chloride [6].

Poly(isopropyliminoalane)  $(HAIN^iPr)_6$  is a well known cage-type compound possessing an  $(AlN)_6$  skeleton and has been shown to be a potentially useful soluble precursor for aluminum nitride [7]. Since AlH groups are capable of hydrogen elimination reactions with NH groups, a hybrid pre-ceramic precursor for Al–Si–C–N nanocomposites has been prepared by the reaction of  $(HAIN^iPr)_6$  with a ring-type  $[Me-Si(H)NH]_n$ , but no structure of the precursor molecule was reported. [3] Although many cage-type compounds containing the  $(AlN)_6$  skeleton such as  $(HAl-NCH_2R)_6$  ( $R = Ph, p-MeC_6H_4$  and  $p-CF_3C_6H_4$ ) and

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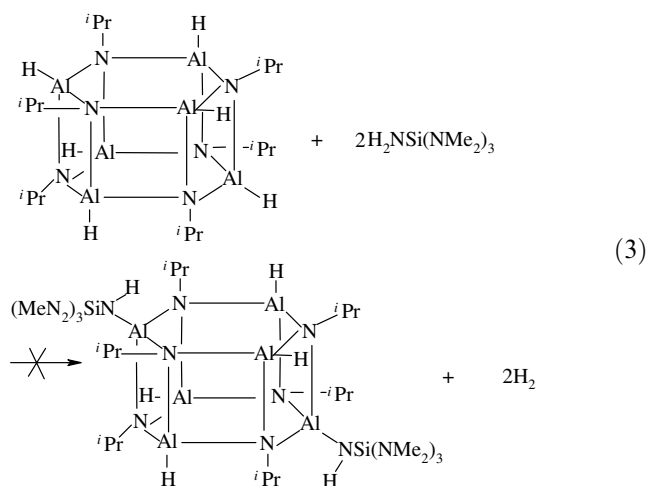
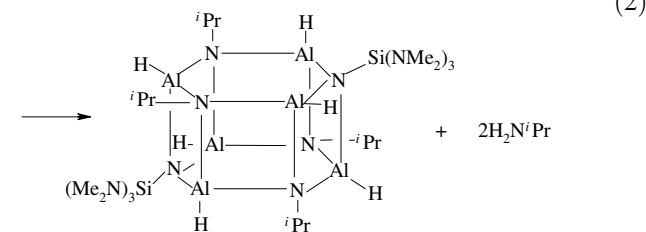
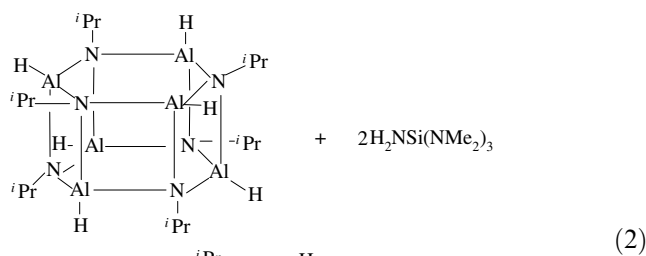
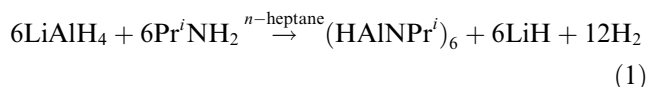
E-mail address: [f.cheng@hull.ac.uk](mailto:f.cheng@hull.ac.uk) (F. Cheng).

(RAINR')<sub>6</sub> (R' = C<sub>2</sub>H<sub>4</sub>NMe<sub>2</sub>) have been prepared [8,9] no cage-type molecule containing (AlN)<sub>6</sub> skeleton coordinated with silylamino groups has been reported to date.

In this paper we report the preparation and structure of a novel cage-type molecule tetrakis(isopropylimino)bis[tris(dimethylamino)silylamino]alane H<sub>6</sub>Al<sub>6</sub>(N<sup>*i*</sup>Pr)<sub>4</sub>[NSi(NMe<sub>2</sub>)<sub>3</sub>]<sub>2</sub> (**1**), by a reaction between TDSA and poly(isopropyliminoalane) (HAIN<sup>*i*</sup>Pr)<sub>6</sub>. The molecular structure of **1** was determined on the basis of its FTIR, NMR, MS and X-ray crystallographic spectra. The sol-gel processing of **1** will be discussed separately.

## 2. Results and discussion

Poly(isopropyliminoalane) (HAIN<sup>*i*</sup>Pr)<sub>6</sub> was prepared by a modification of a previous report according to reaction (1). [10]



The compound **1** was prepared by a reaction between TDSA and (HAIN<sup>*i*</sup>Pr)<sub>6</sub> according to reaction (2). Based on a previous result [3] compound **2**, a cage-type molecule [(Me<sub>2</sub>N)<sub>3</sub>SiNH]<sub>2</sub>H<sub>4</sub>Al<sub>6</sub>(N<sup>*i*</sup>Pr)<sub>6</sub> produced by a hydrogen elimination reaction (Eq. (3)), would be expected. However, a remarkable reaction took place at two nitrogen sites to replace two isopropyl chains with the tris(dimethylamino)silane groups (Eq. (2)).

When a TDSA–pentane solution was added to a (HAIN<sup>*i*</sup>Pr)<sub>6</sub>–pentane solution, evolution of a small amount of gas, probably hydrogen, was observed arising from a reaction between AlH groups of (HAIN<sup>*i*</sup>Pr)<sub>6</sub> with NH<sub>2</sub> groups of TDSA in an undesired site. After further reaction for 18 h at room temperature a white paste was obtained. <sup>1</sup>H NMR analysis showed that the paste was a mixture of materials including compound **1** but not including [(Me<sub>2</sub>N)<sub>3</sub>SiNH]<sub>2</sub>H<sub>4</sub>Al<sub>6</sub>(N<sup>*i*</sup>Pr)<sub>6</sub>. Compound **1** was separated by recrystallisation from pentane at –80 °C.

The <sup>1</sup>H NMR spectrum of compound **1** showed that the molar ratio of –Si(NMe<sub>2</sub>)<sub>3</sub> groups to –<sup>*i*</sup>Pr was 1:2, see Section 4. The broad signal centred at 131 ppm in the <sup>27</sup>Al NMR spectrum was consistent with an HAIN<sub>3</sub> environment [11]. The FTIR analysis confirmed the absence of NH groups as well as the presence of AlH groups with different environments [11]. The combination of the <sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si and <sup>27</sup>Al NMR spectra, FTIR spectrum and the mass spectrum indicate that tetrakis(isopropylimino)bis[tris(dimethylamino)silylamino]alane H<sub>6</sub>Al<sub>6</sub>(N<sup>*i*</sup>Pr)<sub>4</sub>[NSi(NMe<sub>2</sub>)<sub>3</sub>]<sub>2</sub> had indeed been obtained.

The molecular structure of compound **1** was determined by single-crystal X-ray diffraction analysis (Table 1). A view of the molecule is shown in Fig. 1 and selected bond lengths and angles are collected in Table 2. Partial decomposition occurred prior to data collection due to

Table 1  
Crystal data for compound **1**

Formula	C <sub>24</sub> H <sub>70</sub> Al <sub>6</sub> N <sub>12</sub> Si <sub>2</sub>
Formula weight	744.4
Crystal system	Orthorhombic
Space group	Pbca
<i>a</i> (Å)	16.982(2)
<i>b</i> (Å)	13.228(2)
<i>c</i> (Å)	18.797(5)
<i>α</i> (°)	90
<i>β</i> (°)	90
<i>γ</i> (°)	90
<i>V</i> (Å <sup>3</sup> )	4222.7(14)
<i>Z</i>	4
Temperature (K)	150(2)
<i>λ</i> (Å)	0.71073
No. of reflection collected	13,922
No. of independent reflections	3705 [ <i>R</i> <sub>int</sub> = 0.2129]
No. of data/restraints/parameters	3705/0/199
<i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0545, <i>wR</i> <sub>2</sub> = 0.0762
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.1583, <i>wR</i> <sub>2</sub> = 0.0996
Largest different peak and hole (e <sup>−</sup> Å <sup>−3</sup> )	0.558 and −0.278

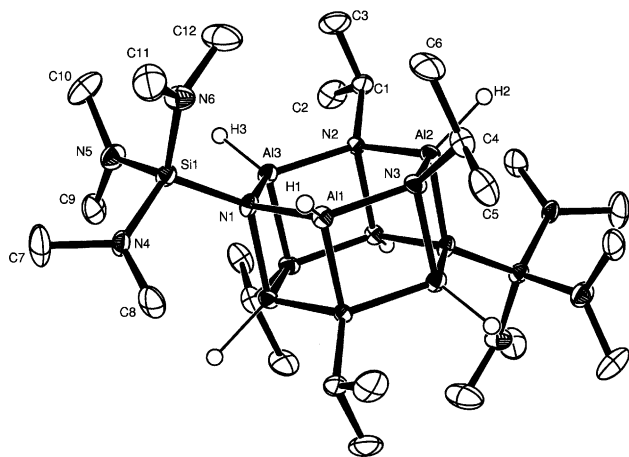


Fig. 1. ORTEP plot of the molecular structure of compound **1** [12]. Hydrogen atoms in the dimethylamino groups are omitted for clarity. Equivalent positions are generated by the symmetry operator:  $-x + 1, -y, -z$ .

Table 2  
Selected bond distances (Å) and angles (°) for compound **1**

Bond distances		Bond angles	
Al(1)–N(1)	1.918(4)	N(3)–Al(1)–N(1)	117.44(18)
Al(1)–N(3)	1.904(4)	N(3)–Al(1)–N(2) <sup>a</sup>	91.13(17)
Al(1)–N(2) <sup>a</sup>	1.970(4)	N(1)–Al(1)–N(2) <sup>a</sup>	90.62(18)
Al(2)–N(2)	1.891(4)	N(2)–Al(2)–N(3)	119.02(18)
Al(2)–N(3)	1.904(4)	N(2)–Al(2)–N(1) <sup>a</sup>	92.18(18)
Al(2)–N(1) <sup>a</sup>	1.946(4)	N(3)–Al(2)–N(1) <sup>a</sup>	92.10(15)
Al(3)–N(1)	1.914(4)	N(2)–Al(3)–N(1)	115.71(18)
Al(3)–N(2)	1.908(4)	N(2)–Al(3)–N(3) <sup>a</sup>	91.10(18)
Al(3)–N(3) <sup>a</sup>	1.966(4)	N(1)–Al(3)–N(3) <sup>a</sup>	91.20(18)
		Al(3)–N(1)–Al(1)	123.40(2)
		Al(3)–N(1)–Al(2) <sup>a</sup>	88.48(17)
		Al(1)–N(1)–Al(2) <sup>a</sup>	88.51(17)
		Al(2)–N(2)–Al(3)	122.80(2)
		Al(2)–N(2)–Al(1) <sup>a</sup>	88.60(17)
		Al(3)–N(2)–Al(1) <sup>a</sup>	88.68(17)
		Al(2)–N(3)–Al(1)	120.80(2)
		Al(2)–N(3)–Al(3) <sup>a</sup>	88.16(17)
		Al(1)–N(3)–Al(3) <sup>a</sup>	88.92(18)

<sup>a</sup> Equivalent positions are generated by the symmetry operator:  $-x + 1, -y, -z$ .

its highly air sensitive nature. However a satisfactory refinement of this sample was achieved. Compound **1** consists of an hexagonal prism of the (AlN)<sub>6</sub> cage with top and bottom faces, which are made of two almost planar six-membered (AlN)<sub>3</sub> rings related by inversion symmetry. These six-membered rings are linked together by six transverse Al–N bonds forming six rectangular side faces of the prism. Each aluminum atom is tetrahedrally bonded to three nitrogen atoms and one hydrogen atom. Two *trans*-(Me<sub>2</sub>N)<sub>3</sub>Si groups and four *trans*-<sup>*i*</sup>Pr groups are situated on six nitrogen atoms away from the cage. As with the structure of the parent (HAIN<sup>*i*</sup>Pr)<sub>6</sub> [13] the Al–N bonds in the six-membered rings [1.907(4) Å (average)] are significantly shorter than the transverse

bonds [1.961(3) Å (average)]. The Al–N–Al bond angles in the six-membered rings [122.33 (8)° average] are wider than the corresponding N–Al–N bond angles [117.39 (17)° average], while in the four-membered rings the former is 88.56(16)° average, which is slightly smaller than the latter of 91.39 (17)° average. All of these general structural features are similar to those observed for (HAIN<sup>*i*</sup>Pr)<sub>6</sub> as well as other hexameric iminoalanes such as (HAIN<sup>*n*</sup>Pr)<sub>6</sub> [14] and (ClAIN<sup>*i*</sup>Pr)<sub>6</sub> [15].

The mechanism for the formation of **1** in this synthetic procedure has not yet been established. The evolution of H<sub>2</sub> gas and the decrease of the relative intensity of Al–H band in the IR spectrum of the paste product compared to that of compound **1** indicated that reaction (**3**) did occur when TDSA was added to (HAIN<sup>*i*</sup>Pr)<sub>6</sub> solution. However, the presence of a number of doublets at 1.1–1.7 ppm (due to (CH<sub>3</sub>)<sub>2</sub>CH) in the <sup>1</sup>H NMR of the oil obtained after separation of **1** from the paste suggests that the cage has been broken during the further reaction. Compound **1** might form with the cleavage of Al–N bonds and subsequent rearrangement of the molecular structure [16].

### 3. Conclusion

A first example of a stable cage-type silylaminoalane H<sub>6</sub>Al<sub>6</sub>(N<sup>*i*</sup>Pr)<sub>4</sub>[NSi(NMe<sub>2</sub>)<sub>3</sub>]<sub>2</sub> with two different substituents was prepared by a reaction between tris(dimethylamino)silylamine H<sub>2</sub>NSi(NMe<sub>2</sub>)<sub>3</sub> and poly(isopropyliminoalane) (HAIN<sup>*i*</sup>Pr)<sub>6</sub>. The symmetric nature of this substitution should make it possible to use the proven ammonolytic chemistry of TDSA to develop a novel silicon aluminum imido gel in which Al and Si atoms are interdispersed at the atomic level. The conversion of this novel compound into silicon aluminum imido gel is being carried out and will be reported separately.

### 4. Experimental

#### 4.1. General

All procedures were performed under a protective nitrogen atmosphere using standard Schlenk techniques or in a nitrogen filled glove box. The solvents pentane and heptane were freshly distilled from sodium/benzophenone prior to use. Tris(dimethylamino)silylamine (Me<sub>2</sub>N)<sub>3</sub>SiNH<sub>2</sub> TDSA was prepared according to our previous report [4]. Lithium aluminum hydride, isopropylamine and aluminium chloride were obtained from Aldrich. The NMR spectra were obtained on a JEOL JNM-LA400FT NMR spectrometer using C<sub>6</sub>D<sub>6</sub> as solvent. IR spectrum was recorded on a Nicolet Magna-500 FTIR spectrometer. MS spectra were recorded on a SHIMADZU GC MS – QP 5050 spectrometer. Single

crystal X-ray diffraction data were collected on a STOE IPDS II diffractometer.

#### 4.2. Preparation of poly(isopropyliminoalane) ( $\text{HAIN}^i\text{Pr}$ )<sub>6</sub>

Preparation of ( $\text{HAIN}^i\text{Pr}$ )<sub>6</sub> was modified from a previous report [10]. To a rapidly stirred suspension of  $\text{LiAlH}_4$  (2.52 g, 66.4 mmol) in heptane (50 mL) at 0 °C was added a solution of  $(\text{CH}_3)_2\text{CHNH}_2$  (3.44 g, 58.2 mmol) in heptane (15 mL). The mixture was stirred at 0 °C for 2 h and then at reflux for 20 h. After filtration, the filtrate was reduced to 20 mL and cooled at –40 °C to yield the product as white crystalline solid. <sup>1</sup>H NMR:  $\delta$  = 1.40 (d, 6H,  $-\text{CH}(\text{CH}_3)_2$ ), 3.61 (m, 1H,  $-\text{CH}(\text{CH}_3)_2$ ); <sup>13</sup>C NMR:  $\delta$  = 27.1 (s,  $\text{CH}(\text{CH}_3)_2$ ), 48.7 (s,  $-\text{CH}(\text{CH}_3)_2$ ); <sup>27</sup>Al NMR:  $\delta$  = 128.6 (s,  $\text{HAIN}_3$ ); IR (Nujol film,  $\text{cm}^{-1}$ ): 1860 (s,  $\nu(\text{AlH})$ ).

#### 4.3. Preparation of tetrakis(isopropylimino)bis[tris(dimethyl amino)silylamino]alane

A solution of TDSA (2.47 g, 14 mmol) in dry pentane (30 mL) was added to a solution of poly(isopropyliminoalane) ( $\text{HAIN}^i\text{Pr}$ )<sub>6</sub> (3.48 g, 6.8 mmol) in dry pentane (60 mL). The mixture was stirred at room temperature for 36 h. After removal approximately half of the pentane under reduced pressure, the solution was cooled to –80 °C and left for three days to give a white crystal. The solvent was decanted off and the crystals washed with cold ( $\approx -80$  °C) pentane and then dried under vacuum. Yield (1.06 g, 21%). <sup>1</sup>H NMR (ppm):  $\delta$  = 2.63 (s, 18H,  $\text{Si}[(\text{N}(\text{CH}_3)_2)_3]$ ), 1.60 and 1.39 (s, 6H,  $-\text{CH}(\text{CH}_3)_2$ ), 3.61 (m, 1H,  $-\text{CH}(\text{CH}_3)_2$ ); <sup>13</sup>C NMR (ppm):  $\delta$  = 38.7 (s,  $\text{Si}[(\text{N}(\text{CH}_3)_2)_3]$ ), 28.4 and 25.4 (s,  $-\text{CH}(\text{CH}_3)_2$ ), 49.2 (s,  $-\text{CH}(\text{CH}_3)_2$ ); <sup>29</sup>Si NMR (ppm):  $\delta$  = –34.4 (s,  $\text{Si}[(\text{N}(\text{CH}_3)_2)_3]$ ); <sup>27</sup>Al NMR (ppm):  $\delta$  = 131.0 (s,  $\text{HAIN}_3$ ); IR (Nujol,  $\text{cm}^{-1}$ ): 2955 (vs), 2929 (vs), 2850 (vs), 2792 (vs), 1882/1873 (s) ( $\nu(\text{AlH})$ ), 1465 (s), 1386 (m), 1366 (m), 1285 (vs), 1182 (vs), 1117 (s), 1071 (s), 985 (vs), 920 (s), 821 (m), 749 (vs), 735 (vs), 709 (vs), 670 (s), 618 (m), 460 (m)  $\text{cm}^{-1}$ ; MS ( $m/z$ , EI): 744[1]<sup>+</sup>.

For the crystal structure determination of compound **1** a single crystal was mounted on a glass fibre using perfluoropolyether oil and transferred to a Stöe IPDS II imaging plate diffractometer equipped with an Oxford Cryosystems 700 series cooling system. The data were collected using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71073) at 150 K. Absorption correction was not applied. The structure was solved by direct methods (SHELXS-97) [17] and refined by full-matrix least-squares on  $F^2$  using SHELXL-97 [18]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions.

## 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference number 244045 for compound **1**. Copies of the information may be obtained from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

## Acknowledgements

Part of this work was carried out as part of the EU project NANOSENSEOFLEX. We also thank the Engineering and Physical Sciences Research Council (EPSRC) for financial support.

## References

- [1] E. Kroke, Y.-L. Li, C. Konetschny, E. Lecomte, C. Fasel, A. Riedel, *Mater. Sci. Eng.* 26 (2000) 97.
- [2] J. Löffelholz, M. Jansen, *Adv. Mater.* 7 (1995) 289.
- [3] S. Kolyma, H. Nakashima, Y. Sugahara, K. Kuroda, *Chem. Lett.* (1998) 191.
- [4] R. Rovai, C.W. Lehmann, J.S. Bradley, *Angew. Chem. Int. Ed.* 38 (1999) 2036.
- [5] F. Cheng, S. Clark, S.M. Kelly, J.S. Bradley, F. Lefebvre, *J. Am. Ceram. Soc.* 87 (2004) 1413.
- [6] J.S. Bradley, F. Cheng, S.J. Archibald, R. Supplit, R. Rovai, C.W. Lehmann, C. Kruger, F. Lefebvre, *J. Chem. Soc. Dalton Trans.* (2003) 1846.
- [7] Y. Sato, S. Koyama, Y. Sugahara, K. Koruda, *J. Ceram. Soc. Jpn.* 104 (1996) 143.
- [8] N.D. Reddy, H.W. Roesky, M. Noltemeyer, H.G. Schmidt, *Inorg. Chem.* 41 (2002) 2374.
- [9] J.E. Park, B.J. Bae, Y. Kim, J.T. Park, H. Suh, *Organometal* 18 (1999) 1059, and references therein.
- [10] S. Cucinella, G. Dozzi, A. Mazzei, T. Salvatori, *J. Organomet. Chem.* 90 (1975) 257.
- [11] Y. Sugahara, T. Onuma, O. Tanegashima, K. Kuroda, C. Kato, *J. Ceram. Soc. Jpn.* 100 (1992) 101.
- [12] Ortep-3 for Windows L.J. Farrugia, *J. Appl. Crystallogr.* 30 (1997) 565.
- [13] M. Cesari, G. Perego, G.D. Piero, S. Cucinella, E. Cernia, *J. Organomet. Chem.* 78 (1974) 203.
- [14] G.D. Piero, M. Cesari, G. Perego, S. Cucinella, E. Cernia, *J. Organomet. Chem.* 129 (1977) 289.
- [15] G.D. Piero, G. Perego, S. Cucinella, M. Cesari, A.J. Mazzei, *J. Organomet. Chem.* 136 (1977) 13.
- [16] M. Cesari, S. Cucinella, in: I. Iaiduc, D.B. Sowerby (Eds.), *The Chemistry of Inorganic Homo- and Heterocycles*, Academic Press, London, 1987, p. 167.
- [17] G.M. Sheldrick, SHELXS-97, Program for structure solution, University of Göttingen, Göttingen, Germany, 1997.
- [18] G.M. Sheldrick, SHELXL-97: Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen, Germany, 1997.