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Notes

A Bis-[C(trimethylsilyl)-*N*-arylimino]dimethylsilane, $Me_3Si(C{=}NAr)SiMe_2(C{=}NAr)SiMe_3$ (Ar = 2,6-xylyl), as a New β-Diimine Ligand[||]

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Summary: A cobalt complex having bis-[C(trimethylsilyl)-N-arylimino]dimethylsilane, $Me_3Si(C{=}NAr)SiMe_2(C{=}NAr)SiMe_3$ *(Ar = 2,6-xylyl), as a new* β*-diimine ligand was synthesized, and its structure was compared with those of* α*- and* β*-diimine cobalt complexes. Ethylene polymerization catalyzed by these cobalt complexes and their in situ generated nickel homologues was investigated.*

Introduction

Reactivity and selectivity of transition metal catalysts are dependent on the electronic nature and steric environment of the central metal, and the appropriate choice of the ligand is important for catalyst design.[1,2] Among nitrogen donor ligands, which have recently received much attention in organometallic chemistry and catalysis,[3,4] special properties of α-diimine ligands that have bulky aryl substituents on the nitrogen atoms in late transition metal complexes have provided successful and noteworthy examples of efficient catalysts for production of polyolefins (Brookhart's catalysts).[5] In contrast to the conventional nickel catalysts,[6] the α-diimine complexes produce polyethylene with relatively high molecular weight, and the polymer branch is controllable by the ligand design. Stimulated by the success of α-diimine complexes, efforts have been directed to seeking other transition-metal complexes for polyethylene preparation.[3,7] Studies on other diimine catalysts, however, have been limited to β-diimine and *o*-phenylenediimines.[8]

In 1988, Ito and co-workers reported palladium-catalyzed insertion of isonitriles into the Si−Si bonds of trisilanes giving oligo(silylimine) derivatives.[9] The oligo(silylimine) derivatives, $Me_2RSi(C{=}NAr)\{SiMe_2(C{=}NAr)\}_nSiRMe_2$ (n = 1,2,3,4; R = Me, ^{t}Bu, Ph; Ar = 2,6-xylyl, 2,6-diisopropylphenyl), have a structure analogous to β-diimines and potentially ligate with transition metals. In this paper, we report the first synthesis of a cobalt complex having $Me_3Si(C{=}NAr)SiMe_2(C{=}NAr)SiMe_3$ (Ar = 2,6-xylyl) (**1a**) as a bidentate nitrogen ligand. Its structure is compared with those of known α- and β-diimine cobalt complexes. The application of these cobalt complexes and their in situ generated nickel homologues as a catalyst for ethylene polymerization was investigated.

Results and Discussion

Ito and co-workers reported a conformational feature of their oligo(silylimine) derivatives, in which two rotational isomers, syn and anti, exist. The more stable isomer is the anti form, and a significant rotational barrier prevents facile syn−anti interconversion.[9] Although the complexation of **1a** requires the conversion from the anti form to the syn form, the reaction of **1a** with $CoBr_2$ gave the corresponding cobalt complex of **1a** in reasonable yields. Thus, treatment of $Me_3Si(C{=}NAr)SiMe_2(C{=}NAr)SiMe_3$ (Ar = 2,6-xylyl) (**1a**) with $CoBr_2$ in THF at room temperature for 12 h resulted in a significant color change of

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[||] This paper is dedicated to the memory of the late Professor Yoshihiko Ito, Kyoto University.

(1) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Application of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (b) Yamamoto, A. *Organotransition Metal Chemistry*; Wiley: New York, 1986. (c) Crabtree, R. H. *The Organometallic Chemistry of Transition Metals*, Wiley: New York, 1988. (d) Elschenbroich, C.; Salzer, A. *Organometallics*, 2nd ed.; VCH: Weinheim, Germany, 1992; *Organometallchemie*; Teubner: Stuttgart, Germany,-1988. (e) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*; Wiley: New York, 1992.

(2) (a) Tolman, C. A. *J. Am. Chem. Soc*. **1970**, *92*, 2953−2956. (b) van Leeuwen, P. W. N. M.; Kamer, P. C. J.; Reek, J. N. H.; Dierkes, P. *Chem. Rev.* **2000**, *100*, 2741−2769.

(3) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169−1203.

(4) (a) Lersch, M.; Tilset, M. *Chem. Rev.* **2005**, *105*, 2471−2526. (b) Van Koten, G.; Vrieze, K. *Adv. Organomet. Chem*. **1982**, *21*, 151−239. (c) Van Koten, G.; Jastrzebski, J. T. B. H.; Vrieze, K. *J. Organomet. Chem*. **1983**, *250*, 49−61. (d) Vrieze, K.; Van Koten, G. *Inorg. Chem. Acta* **1985**, *100*, 79−96. (e) Rendina, L. M.; Puddephatt, R. J. *Chem. Rev.* **1997**, *97*, 1735−1753. (f) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689−3745. (g) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921−2990.

(5) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc*. **1995**, *117*, 6414−6415.

(6) Keim, W. *Angew. Chem., Int. Ed. Engl.* **1999**, *29*, 235−244.

(7) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* 2003, **103**, 283−315.

(8) (a) Feldman, J.; McLain, S. J.; Partharathy, A.; Marshall, W. J.; Calabrese, J. C.; Arther, S. D. *Organometallics.* **1997**, *16*, 1514−1516. (b) Stirany, R. T.; Matturo, M. G.; Zushma, S.; Patil, A. O. PCT Int. Appl. WO0174743, 2001; *Chem. Abstr*. **2001**, 135, 289188.

(9) (a) Ito, Y.; Nishimura, S.; Ishikawa, M. *Tetrahedron Lett.* **1987**, *28*, 1293−1294. (b) Ito, Y.; Matsuura T.; Murakami, M. *J. Am. Chem. Soc.* **1988**, *110*, 3692−3693. (c) Ito, Y.; Suginome, M.; Matsuura, T.; Murakami, M. *J. Am. Chem. Soc.* **1991**, *113*, 8899−8908.

10.1021/om700711r CCC: $37.00

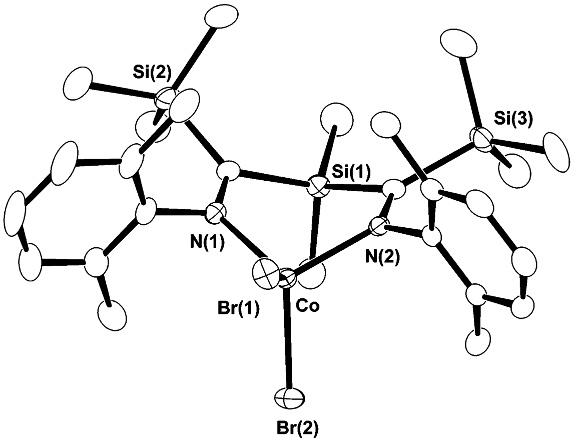
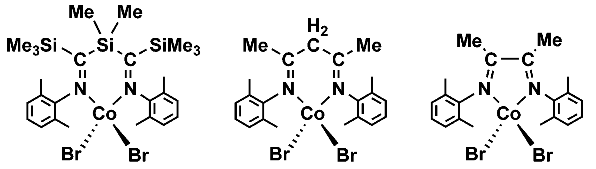


Figure 1. Molecular structure of **2a** showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. The ORTEP drawings of **2b** and **2c** are depicted in the Supporting Information.

Chart 1



2a **2b** **2c**

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 2a−2c

	2a	2b	2c
ring size	6	6	5
θ	118.4	135.5	168.5
d	1.319	1.361	1.579
γ	21.96	16.19	
l	0.493	0.380	
δ	41.60	26.27	
m	0.742	0.323	
	Bond Lengths		
C=N	1.300(2) 1.299(2)	1.277(5)	1.275(4) 1.285(4)
E−C	1.932(2) 1.939(2)	1.507(7)	
Co−N	2.039(2) 2.056(2)	2.020(3)	2.052(2) 2.054(2)
Co−Br	2.361(2) 2.382(2)	2.378(2) 2.374(2)	2.356(6) 2.357(6)
	Bond Angles		
N−Co−N	99.75(7)	95.3(2)	79.52(11)
C-E-C	109.39(9)	122.1(6)	
E−C−N	115.4(2) 114.5(2)	123.2(4)	
C−N−Co	126.6(2) 127.8(2)	122.8(3)	114.6(2) 114.8(2)
Sum of the angle in the metallacycle	693.4	709.4	539.9

the solution from blue to green. Removal of volatiles followed by extraction with CH_2Cl_2 gave a solution containing the desired Co(II) complex (**2a**) (Chart 1). Although the paramagnetism of **2a** complicated the detailed structural analyses by NMR spectroscopy, elemental analysis and X-ray crystallography supported the formation of **2a**. The molecular structure of **2a** is depicted in Figure 1, and selected bond lengths and angles are summarized in Table 1. For comparison, structural parameters of cobalt complexes of β-diimine and α-diimine, **2b**, and **2c** synthesized are also listed in Table 1 (Details are described in the Supporting Information).

The cobalt center of **2a** is bound to two nitrogen and two bromine atoms with Co−N = 2.039(2), 2.056(2) Å, and Co−Br = 2.361(2), 2.382(2) Å, assuming a tetrahedral coordination geometry. The complex **2a** has a six-membered 1,4-silacobaltacyclic structure, which adopts a boat conformation. The Co and Si atoms are out of the plane defined by two C=N moieties by 0.493 and 0.742 Å, respectively. The dihedral angles defined by the plane that includes the two C=N moieties and a phenyl plane connected to the nitrogen atoms are 79.93 and 84.28°. The bond lengths of C=N(1.300(2), 1.299(2) Å) and C−Si-(1.932(2), 1.939(2) Å) are comparable to those of the known oligo(silylimine) derivatives.[9]

Similarly, the cobalt centers of **2b** and **2c** adopt a tetrahedral coordination geometry with two nitrogen atoms and two Br atoms, and the Co−N and Co−Br bond lengths are comparable to those of the other related complexes.[10] The cobalt atom of **2b** is out of the plane defined by two imino groups by 0.380 Å, while the five-membered cobaltacycle ring of **2c** is almost planar and the sum of the internal angles of the ring (539.9°) is close to the theoretical value of 540°. Interesting structural features of **2a**∼**c** are seen in the angle θ and the distance d defined in Figure 2; θ decreases in the order **2c** (168.5 °) > **2b** (135.5 °) > **2a** (118.4 °), whereas d decreases in the order **2c** (1.579 Å) > **2b** (1.361 Å) > **2a** (1.319 Å). The θ and d determine the space volume available for coordination of the other ligands to the cobalt center. In the cases of **2a**∼**c**, larger θ and d provide a larger space for the bromine coordination. In other words, **2a** is structurally similar to **2b** in that both complexes have a six-membered, nonplanar, boat-form conformation, but **2a** has a smaller coordination site for other ligands than **2b** or **2c**. These structural features of **2a** are derived from the presence of two Si−C bonds in the cobaltacycle. The *Si*−*C*(=NR) distances in **2a** are longer than the corresponding *C*−*C*(=NR) distances of **2b** and **2c**. The longer C=N bonds are also the origin of the structural features of **2a**. In the cobalt complexes, the C=N bond lengths of **2a** (1.300(2), 1.299(2) Å) are longer than those of **2b** and **2c** (1.27∼1.28 Å).

The longer C=N distances of oligo(silylimine) derivatives, which are typically seen in the C=N distances in Me$_3$Si[{C=N(2,6-xylyl)}SiMe$_2$]$_2${C=N(2,6-xylyl)}SiMe$_3$ (1.27∼1.32 Å), are due to the $\sigma_{Si-C}-\pi^*_{C=N}$ interaction.[9] The $\sigma_{Si-C}-\pi^*_{C=N}$ interaction also contributes to reducing the force constant of C=N bonds; IR absorption bands at 1536−1552 cm^{-1} seen in Ito's oligosilylimine derivatives (**1a**; 1549 cm^{-1}) are significantly lower than the $\nu_{C=N}$ of ordinary imines (1610−1680 cm^{-1}: Me{C=N(2,6-xylyl)}CH$_2${C=N(2,6-xylyl)}Me (**1b**), 1624 cm^{-1}; Me{C=N(2,6-xylyl)}Me){C(=N2,6-xylyl)}Me (**1c**), 1643 cm^{-1}). These features are also seen in the cobalt complexes; the $\nu_{C=N}$ absorptions decrease in the order **2b** (1654 cm^{-1}) > **2c** (1643 cm^{-1}) ≫ **2a** (1523 cm^{-1}). Although another special electronic property of **1a** due to the $\sigma_{Si-C}-\pi^*_{C=N}$ interaction is the bathochromic shift of UV−vis absorptions, there are few characteristic differences in UV−vis absorptions of the cobalt complexes among **2a**, **2b**, and **2c**.

Application of the bis-[C(trimethylsilyl)-*N*-arylimino]dimethylsilane ligand to homogeneous catalysis was examined in methyl aluminoxane (MAO)-assisted polymerization of ethylene. Ethylene polymerization was carried out in a 100 mL stainless steel autoclave fitted with a Teflon inner tube. MAO was used as the activator. Under 0.8 MPa of ethylene, the α-diimine cobalt complex **2c** showed some activity to form

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(10) (a) Laine, T. V.; Kinga, M.; Maaninen, A.; Aitola, E.; Leskela, M. *Acta Chem. Scand.* **1999**, *53*, 968−973. (b) Tanabiki, M.; Tsuchiya, K.; Motoyama, Y.; Nagashima, H. *Chem. Commun.* **2005**, 3409−3411.

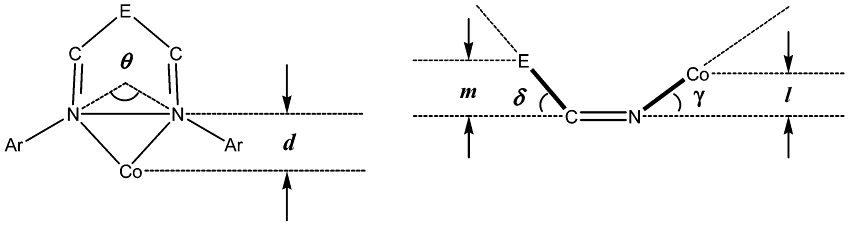

Figure 2. Definition of the distances *d*, *m*, *l*, and the angles θ, δ, and γ.

Table 2. Polymerization of Ethylene[a]

entry	catalyst	mol of catalyst μmol	yield g	activity g/(mmol·h)	[η]	T_m °C
1	**3c**	5	36.62	7324	3.0	125.8
2	**3b**	100	0.70	7	19.0	120.0
3	**3a**	100	8.54	85.4	3.6	129.8

[a] Conditions: cocatalyst: MAO (200 equiv), ethylene 0.8 MPa, toluene 500 mL, 30 °C, 60 min.

polyethylene (2.0 g/(mmolCo·h)). Under the same conditions, the β-diimine complex and the silylimine complex did not give polyethylene. Although attempts to isolate the bis-[C(trimethylsilyl)-*N*-arylimino]dimethylsilane complex of nickel were unsuccessful because of the instability of the product, the nickel homologue of **2a** was generated in situ by treatment of $NiBr_2$(dme) with **1a**. As summarized in Table 2, the α-diimine nickel catalyst **3c** exhibited high catalytic activity (over 7 kg/(mmolNi·h)), whereas the β-diimine catalyst **3b** showed almost no activity. These are in accord with the results reported in the literature.[8a] Interestingly, the silylimine nickel catalyst **3a** is moderately active. The order of activity, a complex having a five membered ring (**3c**) > complexes having a six-membered ring (**3a** and **3b**), suggests a primary factor of the active nickel catalyst to be rigidity of the structure[11] and a space for coordination of the polymer chain and ethylene, which is related to θ and *d* (vide supra). Although detailed investigations of the facets of coordination chemistry and homogeneous catalysis are required to clarify the ligand effect of bis-[C(trimethylsilyl)-*N*-arylimino]dimethylsilanes, the present results clearly demonstrate that this is a new class of the bidentate nitrogen ligands.[12,13]

Experimental

General. Manipulation of air and moisture sensitive organometallic compounds was carried out under a dry argon atmosphere using standard Schlenk-tube techniques associated with a high-vacuum line. All solvents were distilled over appropriate drying reagents prior to use (THF, hexane; Ph_2CO/Na, CH_2Cl_2; CaH_2, acetone; MS 4A). ^1H, ^{13}C NMR spectra were recorded on a JEOL Lambda 600 or a Lambda 400 spectrometer at ambient temperature unless otherwise noted. ^1H, ^{13}C NMR chemical shifts (δ values) were given in ppm relative to the solvent signal (^1H, ^{13}C). Melting points were measured on a Yanaco SMP3 micromelting point apparatus. Elemental analyses were performed by a Perkin-Elmer 2400II/CHN analyzer. Melting temperature of polymer (T_m) was measured by a differential scanning calorimeter (DSC). Analysis of the polymer branch was performed by ^{13}C NMR measured in 1,2-dichlorobenzene at 120 °C. Diimine ligands, 2,2,4,4,6,6-hexamethyl-3,5-bis(2,6-dimethylphenylimino)-2,4,6-trisilaheptane-(**1a**),[9c] 2,4-bis(2,6-dimethylphenylimino)pentane (**1b**),[14] and 2,3-bis(2,6-dimethylphenylimino)butane (**1c**) were synthesized by the methods reported in the literature.

Preparation of 2a, 2b, and 2c. In a typical example, $CoBr_2$ (0.689 g, 3.15 mmol) and **1a** (1.534 g, 3.29 mmol) were dissolved in THF (40 mL). The mixture was stirred at room temperature for 12 h during which time the color of the solution changed from blue to green. The solvent was evaporated and the residue extracted with CH_2Cl_2. Removal of volatiles followed by washing with hexane gave desired Co(II) complex (**2a**) as a green powder (1.14 g, 92%). Single crystals of **2a** were grown from CH_2Cl_2/pentane; mp 118 °C. Anal. Calcd for $C_{26}H_{42}Br_2CoN_2Si_3$: C, 45.55; H, 6.17; N, 4.09. Found: C, 45.42; H, 6.15; N, 4.19%. IR 1523 cm^{-1} ($\nu_{C=N}$). UV−vis (THF; λ_{max}, nm; ϵ, M^{-1} cm^{-1}) 684 (381), 596 (sh) (163).

Using similar procedures, **2b** and **2c** were synthesized. **2b:** mp 256 °C. Anal. Calcd for $C_{21}H_{26}Br_2CoN_2$: C, 48.03; H, 4.99; N, 5.33. Found: C, 47.90; H, 4.96; N, 5.26%. IR 1654 cm^{-1}($\nu_{C=N}$). UV−vis (THF; λ_{max}, nm; ϵ, M^{-1} cm^{-1}) 687 (268), 615 (sh) (159). **2c:** mp >290 °C. Anal. Calcd for $C_{20}H_{24}Br_2CoN_2$: C, 46.99; H, 4.73; N, 5.48. Found: C, 47.33; H, 4.94; N, 5.10%. IR 1643 cm^{-1}($\nu_{C=N}$). UV−vis (THF; λ_{max}, nm; ϵ, M^{-1} cm^{-1}) 684 (328), 594 (sh) (130).

Ethylene Polymerization. In a 100 mL stainless steel autoclave fitted with a Teflon inner-tube was placed the precatalyst **2a**−**c** (100 μmol) and toluene (43 mL). A toluene solution of MAO (PMAO-S available from TOSOH-FINECHEM Corp. 2.85 M in toluene) was added via syringe (7 mL, 200 equiv for precursor **2a**−**c**), and the mixture was stirred for 1 h at room temperature. Then ethylene (0.8 MPa) was introduced, and the mixture was stirred at room temperature for 40 min. Unreacted ethylene was released, and methanol (5 mL) was added to stop the polymerization. Polyethylene was precipitated when the reaction mixture was poured into a methanol solution of HCl. The polymer was collected by filtration and dried in vacuo.

X-ray Diffraction Experiments. Single crystals of all complexes were grown from CH_2Cl_2/pentane. X-ray crystallography was performed on a Rigaku Saturn CCD area detector with graphite monochromated Mo Kα radiation ($\lambda = 0.71070$A). The data were collected at 123(2) K using ω scan in the θ range of $3.0 \leq \theta \leq 27.5°$ (**2a**), $3.0 \leq \theta \leq 27.5°$ (**2b**), $3.1 \leq \theta \leq 27.5°$ (**2c**). The data obtained were processed using Crystal-Clear (Rigaku) on a Pentium computer and were corrected for Lorentz and polarization effects. The structures were solved by direct methods[15] for **2a**, **2b**, and **2c**

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[11] Keim, W.; Schulz, R. P. *J. Mol. Catal.* **1994**, *92*, 21−33.

[12] In the literature, the low activity of **3b** is explained by abstraction of a methylene proton by MAO during the polymerization, which gives inactive Ni(nacnac) complexes (see ref 13). The bis-[C(trimethylsilyl)-*N*-arylimino]dimethylsilane complex **2a** has no proton which can react with MAO.

[13] (a) Cope-Eatough, E. K.; Mair, F. S.; Pritchard, R. G.; Warren, J. E.; Woods, R. J. *Polyhedron* **2003**, *22*, 1447−1454. (b) Radzewich, C. E.; Guzei, L. A.; Jordan. R. F. *J. Am. Chem. Soc.* **1999**, *121*, 8673−8674.

[14] Budzelaar, P. H. M.; Moonen, N. N. P.; de Gelder, R.; Smits, J. M. M.; Gal, A. W. *Eur. J. Inorg. Chem.* **2000**, 753−769.

[15] (a) Sheldrick, G.M. *SHELX97*; Universitat Göttingen, Göttingen, Germany, 1997. (b) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Guagliardi, A.; Moliterni, A.; Polidori, G.; Spagna, R. SIR97. *J. Appl. Cryst.* **1999**, *32*, 115−119.

and expanded using Fourier techniques.[16] The non-hydrogen atoms were refined anisotropically except for the solvent atoms (THF for **2b** and acetone for **2c**). Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 7297 observed reflections and 349 variable parameters for **2a**, 3050 observed reflections and 155 variable parameters for **2b**, and 5127 observed reflections and 266 variable parameters for **2c**. Neutral atom scattering factors were taken from Cromer and Waber.[17] All calculations were performed using the CrystalStructure[18,19] crystallographic software package. Details of final refinement as well as the bond lengths and angles are summarized in the Supporting Information, and the numbering scheme employed is also shown in the Supporting Information, and were drawn with ORTEP at 50% probability ellipsoid.

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Supporting Information Available: The molecular structures of **2a**, **2b**, and **2c** and details of crystallographic studies (**2a, 2b, 2c**). This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. *The DIRDIF-99 Program System;* Technical Report of the Crystallography Laboratory; University of Nijmegen: Nijmegen, The Netherlands, 1999.

(17) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. 4.

(18) *CrystalStructure 3.8.0: Crystal Structure Analysis Package*; Rigaku and Rigaku/MSC: The Woodlands, TX, 2000−2006.

(19) Carruthers, J. R.; Rollett, J. S.; Betteridge, P. W.; Kinna, D.; Pearce, L.; Larsen, A.; Gabe, E. *CRYSTALS;* Chemical Crystallography Laboratory: Oxford, U.K., 1999; Issue 11.