

Articles

An Aryllithium Complex with Intramolecular Coordination of an *o*-Diamine Substituent. X-ray and Solution NMR Structures of Dimeric $[\text{Li}\{\text{C}_6\text{H}_4(\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)\text{-2}\}]_2$

Marco H. P. Rietveld,[†] Ingrid C. M. Wehman-Ooyevaar,^{†,‡} G. Marc Kapteijn,[†]
David M. Grove,[†] Wilberth J. J. Smeets,[§] Huub Kooijman,[§]
Anthony L. Spek,^{§,||} and Gerard van Koten^{*,†}

Department of Metal-Mediated Synthesis, Debye Institute, and Department of Crystal and Structural Chemistry, Bijvoet Center for Biomolecular Research, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

Received March 30, 1994[®]

The reaction of 2-bromobenzyl bromide, $\text{BrC}_6\text{H}_4(\text{CH}_2\text{Br})\text{-2}$, with $\text{HN}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2$ affords the diamine $\text{BrC}_6\text{H}_4(\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)\text{-2}$ (**1**). This *o*-diamine aryl bromide reacts quantitatively with *n*-BuLi to give $[\text{Li}\{\text{C}_6\text{H}_4(\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)\text{-2-C,N,N'}\}]_2$ (**2**), which exists as a dimer in benzene (cryoscopy). The structure of **2** in the solid state was determined by X-ray crystallography: space group $P2_1/c$ with $a = 15.7740(13)$ Å, $b = 10.6866(8)$ Å, $c = 18.205(2)$ Å, $\beta = 124.928(9)^\circ$, $Z = 4$, $R = 0.066$, and $R_w = 0.045$ for 1276 observed reflections. In the dimeric structure each lithium atom has a distorted-tetrahedral geometry consisting of coordination by two nitrogens of one ortho substituent and the two C_{ipso} carbons of the aryl rings. Each C_{ipso} is three-center–two-electron bonded to two lithium atoms with characteristic acute $\text{Li}-\text{C}-\text{Li}$ angles of $66.3(4)$ and $66.6(5)^\circ$ and a $\text{Li}\cdots\text{Li}$ distance of $2.444(15)$ Å. ^1H , ^{13}C , and ^7Li NMR spectroscopy of **2** in benzene- d_6 reveal that both nitrogen donor atoms of one ligand coordinate to the same lithium center and that each dimeric molecule (as in the solid state) is one of two enantiomeric pairs in which the two central nitrogen atoms of the *o*-diamine substituents both have the same absolute configuration.

Introduction

Terdentate chelating ligands have proven to be very useful in organometallic chemistry.¹ Such ligands show several specific abilities, including stabilization of a variety of metal oxidation states and control of both reaction and complex stereochemistry as a result of their restricted geometric arrangement. There are now ter-

dentate ligand systems known based on P-donor atoms,^{1a–f} N-donor atoms,^{1g–k} and a combination of P- and N-donor atoms.^{1l,m} We are currently studying the organometallic chemistry of the monoanionic, N,C,N-chelating, aryl ligand system $[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6}]^-$ (*trans*-pincer).² Upon coordination to a metal center two five-membered $\text{M}-\text{C}-\text{C}-\text{C}-\text{N}$ chelate rings are formed which have the $\text{M}-\text{C}$ bond in common; i.e., in trigonal-bipyramidal and octahedral arrangements this ligand either spans axial–equatorial–axial positions or is present in a meridional bonding mode.³ Recently, it has been shown in the tantalum complex $[\text{Ta}(\text{=CH-}t\text{-Bu})\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6-N,C,N'}\}\text{Cl}_2]$ ⁴ that the N-donor

* To whom correspondence should be addressed.

[†] Debye Institute, Utrecht University.

[‡] Present address: Inorganic Chemistry Department, University of Nijmegen, Nijmegen, The Netherlands.

[§] Bijvoet Center for Biomolecular Research, Utrecht University.

^{||} Address correspondence pertaining to crystallographic studies to this author.

[®] Abstract published in *Advance ACS Abstracts*, August 15, 1994.

(1) (a) Ott, J.; Venanzi, L. M.; Ghilardi, C. A.; Midollini, S.; Orlandini, A. *J. Organomet. Chem.* **1985**, *291*, 89. (b) Bianchini, C.; Masi, D.; Meli, A.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1988**, *110*, 6411. (c) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P.; Ramirez, J. A. *Organometallics* **1990**, *9*, 226. (d) Thaler, E. G.; Caulton, K. G. *Organometallics* **1990**, *9*, 1871. (e) Thaler, E. G.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1990**, *112*, 2664. (f) Kiss, G.; Horváth, T. *Organometallics* **1991**, *10*, 3798. (g) Siegl, W. O. *J. Organomet. Chem.* **1976**, *107*, C27. (h) Minghetti, G.; Cinellu, M. A.; Chelucci, G.; Gladiali, S.; Demartin, F.; Manassero, M. *J. Organomet. Chem.* **1986**, *307*, 107. (i) Cinellu, M. A.; Gladiali, S.; Minghetti, G. *J. Organomet. Chem.* **1989**, *363*, 401. (j) Anderson, G. M.; Puddephatt, R. J.; Ferguson, G.; Lough, A. J. *J. Chem. Soc., Chem. Commun.* **1989**, 1297. (k) Canty, A. J.; Honeyman, R. T. *J. Organomet. Chem.* **1990**, *387*, 247. (l) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J. *Organometallics* **1986**, *5*, 2469. (m) Fryzuk, M. D.; Joshi, K. *Organometallics* **1989**, *8*, 722.

(2) (a) van Koten, G.; Timmer, K.; Noltes, J. G.; Spek, A. L. *J. Chem. Soc., Chem. Commun.* **1978**, 250. (b) Grove, D. M.; van Koten, G.; Louwen, J. N.; Noltes, J. G.; Spek, A. L.; Ubbels, H. J. C. *J. Am. Chem. Soc.* **1982**, *104*, 6609. (c) Terheijden, J.; van Koten, G.; Muller, F.; Grove, D. M.; Vrieze, K.; Nielsen, E.; Stam, C. H. *J. Organomet. Chem.* **1986**, *315*, 401. (d) van Koten, G. *Pure Appl. Chem.* **1989**, *61*, 1681; **1990**, *62*, 1155. (e) van der Zeijden, A. A. H.; van Koten, G.; Luijk, R.; Nordemann, R. A.; Spek, A. L. *Organometallics* **1988**, *7*, 1549. (f) van der Zeijden, A. A. H.; van Koten, G.; Nordemann, R. A.; Kojic-Prodic, B.; Spek, A. L. *Organometallics* **1988**, *7*, 1957.

(3) (a) Fraenkel, G.; Fraenkel, A. M.; Geckle, M. J.; Schloss, F. J. *Am. Chem. Soc.* **1979**, *101*, 4745. (b) Jastrzebski, J. T. B. H.; van Koten, G.; Konijn, M.; Stam, C. H. *J. Am. Chem. Soc.* **1982**, *104*, 5490. (c) Seebach, D.; Hässig, R.; Gabriel, J. *Helv. Chim. Acta* **1983**, *66*, 308.

(4) Abbenhuis, H. C. L.; Grove, D. M.; van der Sluis, P.; Spek, A. L.; van Koten, G. *Recl. Trav. Chim. Pays-Bas* **1990**, *109*, 446; *J. Am. Chem. Soc.* **1992**, *114*, 9773.

atoms are present in an unusual cis-coordination mode, affording a *pseudofacial* N,C,N bonding mode of the ligand.

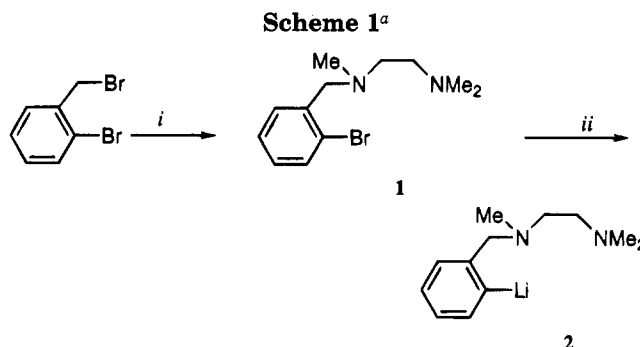
In an extension of our studies into the bonding modes and influences of aryl ligands with substituents containing N-donor atoms in organometallic complexes of the early and late transition metals, we have designed the new monoanionic ligand system $[\text{C}_6\text{H}_4(\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)_2]^-$. This system (*cis*-pincer) is also a potentially terdentate ligand but differs from the *trans*-pincer ligand $[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6}]^-$ in two ways. First, when it is coordinated as a terdentate ligand, it should always give *cis*-coordinated nitrogen atoms. Second, when the $-\text{CH}_2\text{CH}_2\text{NMe}_2$ arm is not coordinating, its flexibility still enables the N-donor atom to approach the metal center closely. In this situation this arm, a Lewis base, may become an active spectator moiety by being involved in an anchimeric type of assistance in metal-centered reactions. With the lithium complexes of this ligand system we have synthesized by transmetalation a series of new metal complexes with the early transition metal tantalum (e.g. $[\text{Ta}(=\text{CH}-t\text{-Bu})\{\text{C}_6\text{H}_4(\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)_2\}\text{X}_2]$ ($\text{X} = \text{Cl}, \text{O}-t\text{-Bu}$) and $[\text{Ta}(\text{CH}_2\text{CH}_2\text{CH}_2)\{\text{C}_6\text{H}_4(\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)_2\}(\text{O}-t\text{-Bu})_2]$)⁵ and also with the late transition metals rhodium, iridium, and platinum (e.g. $[\text{M}\{\text{C}_6\text{H}_4(\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)_2\text{-2-}C,N\}(\text{cod})]$ ($\text{M} = \text{Ir}, \text{Rh}$; *cod* = cycloocta-1,5-diene)⁶ and $[\text{Pt}\{\text{C}_6\text{H}_4(\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)_2\text{-2-}C,N,N'\}\text{Cl}]$).^{6,7} It is also possible to obtain transition-metal complexes stabilized by this ligand *via* oxidative addition, examples being $[\text{Pd}\{\text{C}_6\text{H}_4(\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)_2\text{-2-}C,N,N'\}\text{X}]$ ($\text{X} = \text{Cl}, \text{ONO}_2$)⁸ and $[\text{W}\{\text{C}_6\text{H}_4(\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)_2\}\text{I}(\text{CO})_3]$.⁹

Since we have found that the success of many transmetalation reactions of ortho-substituted diamine aryllithium compounds with transition-metal salts depends on whether the lithium compound is really free from alkyl halides and lithium halides, we have studied the synthesis of pure $[\text{Li}\{\text{C}_6\text{H}_4(\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)\text{-2-}C,N,N'\}]_2$ and its structure in more detail.

Results and Discussion

The *o*-diamine-substituted aryl bromide $\text{BrC}_6\text{H}_4\text{-(CH}_2\text{N(Me)CH}_2\text{CH}_2\text{NMe}_2\text{)-2}$ (**1**) was obtained in 68% yield from a substitution reaction of $\text{BrC}_6\text{H}_4\text{(CH}_2\text{Br)-2}$ with 1 equiv of $\text{HN(Me)CH}_2\text{CH}_2\text{NMe}_2$ in the presence of a large excess of triethylamine as base (see Scheme 1). Pure **1**, which has been characterized by ^1H and ^{13}C NMR, is a pale yellow oil that is somewhat air-sensitive and is best stored at 0°C under a nitrogen atmosphere. Its ^1H NMR spectrum (benzene- d_6 , 200 MHz) shows singlets for the benzylic, $-\text{NMe}$, and NMe_2 groups and two pseudotriplets for the $(\text{CH}_2)_2$ group.

The bromide–lithium exchange reaction of **1** with 1 equiv of *n*-BuLi in a hexane/diethyl ether mixture at ambient temperature afforded the ortho-lithiated species $[\text{Li}\{\text{C}_6\text{H}_4(\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)\text{-2-}C,N,N'\}]_2$ (**2**)



^a Reagents and conditions: (i) 1 equiv of HN(Me)CH₂CH₂NMe₂, excess of NEt₃, benzene, 1 h; (ii) 1 equiv of *n*-BuLi, diethyl ether, -70 °C, 1.5 h.

quantitatively, and this solvent-free complex was isolated in good yield (see Scheme 1). Recrystallization from hexane affords the aryllithium complex **2** as a white air- and moisture-sensitive microcrystalline solid. It is soluble in benzene, toluene, and diethyl ether, but it is only slightly soluble in pentane. Cryoscopic molecular weight determinations of **2** in benzene (0.05–0.12 M) point to a dimeric aggregation state in this solvent. Deuterolysis of this complex affords a single deuterated organic product that is consistent with **2** existing solely as an ortho-lithiated species.

Although direct lithiation involving hydrogen–lithium exchange of arene substrates containing *o*-amine substituents with an alkyllithium (*n*-BuLi, *sec*-BuLi, or *t*-BuLi) is well-known¹⁰ and is successful for the synthesis of [LiC₆H₃(CH₂NMe₂)_{2-2,6}]₂ (**3**) from C₆H₄(CH₂NMe₂)_{2-1,3} and *n*-BuLi in hexane, this approach is not suitable for the preparation of **2**. In C₆H₅CH₂N(Me)CH₂CH₂NMe₂ there are several reactive C–H groups present that can react with an alkyllithium reagent to afford a mixture of lithiated materials. In particular, in addition to ortho lithiation resulting in **2**, the benzylic protons can also be easily lithiated, leading to the alkyllithium product [Li{CH(Ph)N(Me)CH₂CH₂NMe₂}] in which the C–Li interaction is stabilized by intramolecular Li–N coordination. Attempts to prepare aryllithium **2** *via* reaction of the aryl bromide **1** with metallic lithium also did not lead to a pure product. Accordingly, the preferred synthetic route to **2** is the halide–lithium exchange route, whereby **1** reacts with *n*-BuLi and separation of the aryllithium product from the BuBr byproduct is achieved by crystallization.

Our interest in the structures of organolithium complexes prompted us to characterize **2** as fully as possible; the low solubility of **2** in apolar solvents contrasts with the excellent solubility of the bis-ortho-chelated aryllithium compound $[\text{LiC}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6}]_2$ (**3**; Figure 1) in hexane,^{3b} which had already alerted us to probably significant structural differences between these two complexes.

Structure of [Li{C₆H₄(CH₂N(Me)CH₂CH₂NMe₂-2-*C,N,N'*)}]₂ (2) in the Solid State. The molecular structure of **2** together with the adopted numbering scheme is shown in Figure 2, with bond distances and

(5) Rietveld, M. H. P. Unpublished results.

(6) Wehman-Ooyevaar, I. C. M.; Luitwieler, I. F.; Vatter, K.; Grove, D. M.; Smeets, W. J. J.; Horn, E.; Spek, A. L.; van Koten, G. *J. Chem. Soc., Dalton Trans.* **1994**, 703.

(7) Kapteijn, G. M.; *et al.* Unpublished results.

(8) Alster, P. L.; Boersma, J.; van Koten, G. *Organometallics* **1993**, *12*, 1629.

(9) Kiplinger, J. L.; Richmond, T. G.; Osterberg, C. E. *Chem. Rev.* **1994**, *94*, 373.

(10) (a) Jones, F. N.; Zinn, M. F.; Hauser, C. R. *J. Org. Chem.* **1963**, 28, 663. (b) van der Zeijden, A. A. H.; van Koten, G. *Recl. Trav. Chim. Pays-Bas* **1988**, 107, 431.

(11) (a) Jastrzebski, J. T. B. H.; van Koten, G.; Goubitz, K.; Arlen, C.; Pfeffer, M. *J. Organomet. Chem.* **1985**, 246, C75. (b) Wehman, E.; Jastrzebski, J. T. B. H.; Ernsting, J.-M.; Grove, D. M.; van Koten, G. *J. Organomet. Chem.* **1988**, 353, 145.

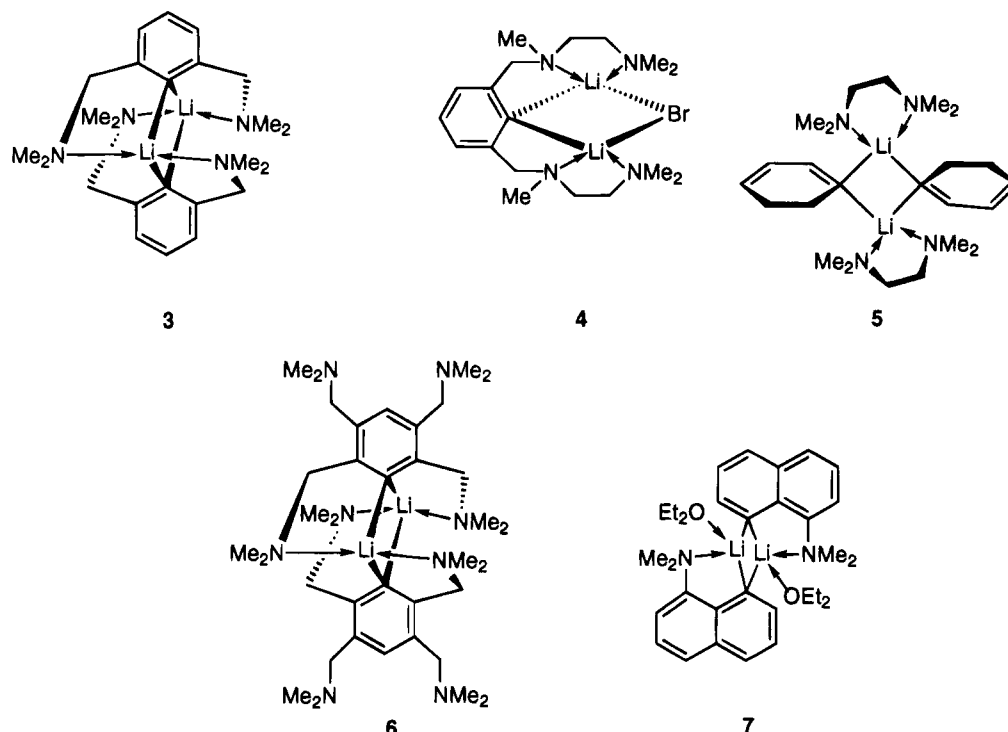


Figure 1. Different aryllithium compounds (3–7) with intramolecular amine–lithium coordination.

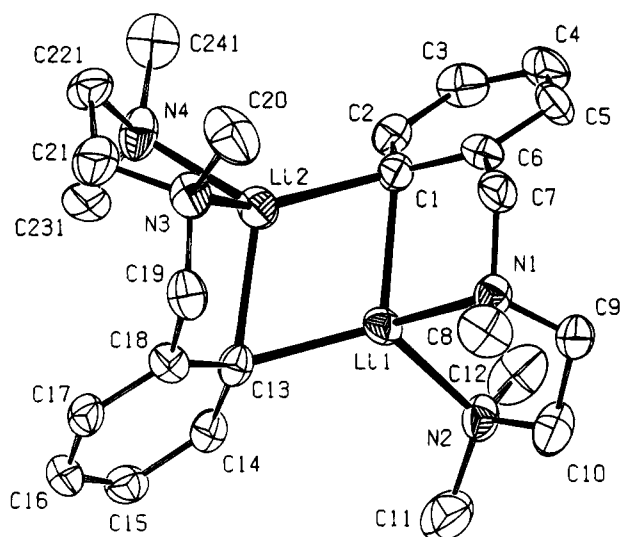


Figure 2. Thermal motion ellipsoid plot (drawn at 50% probability level) of $[\text{Li}(\text{C}_6\text{H}_4\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2-2)]_2$ (**2**) together with adopted numbering scheme.

bond angles being given in Table 1. In the solid state **2** has a dimeric structure that consists of two lithium atoms Li(1) and Li(2) and two monoanionic C,N,N-terdentate-bonded aryl *o*-diamine ligands. The two nitrogen atoms of each ligand coordinate to the same lithium atom, while the C_{ipso} atom of each ligand is bridge-bonded to the lithium pair with characteristically acute Li(1)–C(13)–Li(2) and Li(1)–C(1)–Li(2) angles of 66.6(5) and 66.3(4)°, respectively. M–C–M angles of this magnitude are commonly encountered in polynuclear arylmetal complexes containing two-electron–three-center bridge-bonded aryl anions. In fact this structure of **2** also shows distortions of both the C– C_{ipso} –C angle and C–C distances in the aryl ring that are typical for electron-deficiently bonded aryl groups in arylmetal complexes. For example, the

Table 1. Selected Data for the Geometry of **2**

Bond Distances (Å)			
Li(1)–N(2)	2.143(12)	Li(2)–C(13)	2.266(14)
Li(1)–N(1)	2.149(15)	Li(2)–C(1)	2.176(14)
Li(1)–C(1)	2.288(13)	C(1)–C(2)	1.393(11)
Li(1)–C(13)	2.181(14)	C(1)–C(6)	1.414(2)
Li(1)–Li(2)	2.444(15)	C(13)–C(14)	1.411(12)
Li(2)–N(4)	2.149(14)	C(13)–C(18)	1.413(10)
Li(2)–N(3)	2.130(12)		
Bond Angles (deg)			
N(1)–Li(1)–N(2)	86.8(5)	Li(1)–C(1)–Li(2)	66.3(4)
C(1)–Li(1)–C(13)	111.3(5)	Li(1)–C(13)–Li(2)	66.6(5)
N(4)–Li(2)–N(3)	86.1(5)	C(18)–C(13)–C(14)	110.8(7)
C(13)–Li(2)–C(1)	112.3(5)	C(6)–C(1)–C(2)	111.4(7)
C(13)–Li(1)–N(1)	131.8(6)	C(1)–Li(1)–N(1)	86.2(5)
C(1)–Li(2)–N(3)	135.4(8)	C(13)–Li(2)–N(4)	113.3(7)
C(13)–Li(2)–N(3)	87.5(5)		

C(18)–C(13)–C(14) and C(6)–C(1)–C(2) angles of 110.8(7) and 111.4(7)°, respectively, are less than the 120° expected in a normal aromatic system. These values are somewhat smaller than that found for the C– C_{ipso} –C angle in $[\text{Li}\{\text{C}_6\text{H}_3(\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)_2-2,6\}]\text{LiBr}$ (115.1(3)°; **4**)¹² but are comparable with that in $[\text{LiPh}(\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2)_2]$ (111.8(3)°; **5**)¹³ (Figure 1). These distortions are accompanied by a small, but noticeable, lengthening of the C–C bonds involving C_{ipso} atoms; the average length of these four bonds (C(18)–C(13), C(14)–C(13), C(1)–C(6), and C(5)–C(6)) is 1.408 Å, whereas the average length of the other eight aryl C–C bonds is 1.375 Å.

The geometry around the lithium atoms in **2** is distorted tetrahedral; the terdentate bridging of the *o*-diamine aryl ligand results in the formation of two fused, five-membered chelate rings with N(1)–Li(1)–N(2) and N(3)–Li(2)–N(4) bite angles of 86.8(5) and 86.1(5)°, respectively, and in the two rings N(1)–C(7)–C-

(12) Wehman-Ooyevaar, I. C. M.; Kapteijn, G. M.; Grove, D. M.; Spek, A. L.; van Koten, G. *J. Organomet. Chem.* **1993**, 452, C1–C3.
(13) Thoenes, D.; Weiss, E. *Chem. Ber.* **1978**, 111, 31.

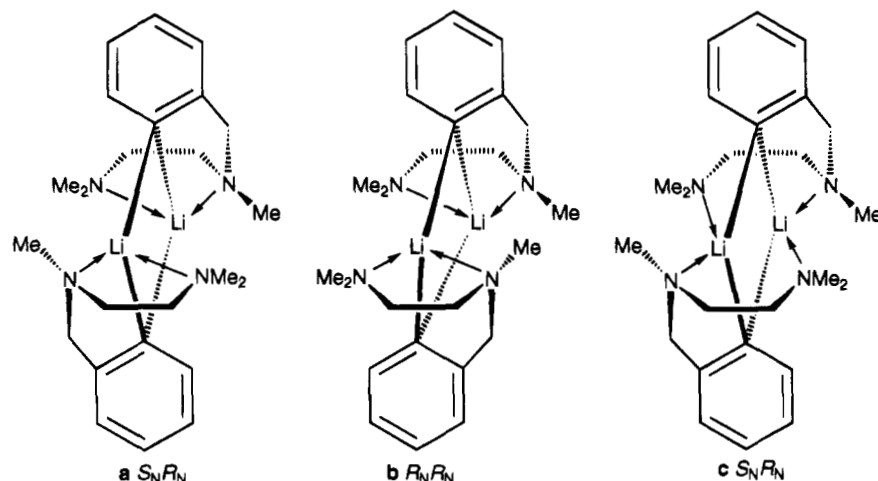


Figure 3. Stereochemical aspects of the dinuclear structure of **2**.

(6)—C(1)—Li(1) and C(18)—C(13)—Li(2)—N(3)—C(19) the values for the bite angles C(1)—Li(1)—N(1) and C(13)—Li(2)—N(3) are 86.2(5) and 87.5(5)°, respectively. These latter values are comparable with that of the C—Li—N angle in the related monomeric compound $[\text{Li}\{\text{C}_6\text{H}_3(\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)_2\cdot 2,6\}]\text{LiBr}$ (**4**),¹² with a value of ca. 87°, and in the dimeric compound $[\text{Li}\{\text{C}_6\text{H}(\text{CH}_2\text{NMe}_2)_4\cdot 2,3,5,6\}]_2$ (**6**), with a value of 86.2(5)° (Figure 1).^{10b} It is worth noting in **2** that because the central N-donor atoms of the aryl *o*-diamine ligand becomes a stable array on coordination to lithium they are consequently stereogenic and dimeric **2** actually crystallizes out as the $S_N S_N$ and $R_N R_N$ enantiomeric pairs (the $S_N S_N$ enantiomer is shown in Figure 2).

In the structure of **2** the angles θ between the planes of the aryl rings and the central plane formed by the lithium atoms and the C_{ipso} atoms Li(1)—C(1)—Li(2)—C(13) are 66.4(5) and 63.3(5)°. Normally in aryllithium complexes without chelate ring restrictions one observes a perpendicular orientation between the aryl plane and the Li—Li axis for a three-center—two-electron bonding mode. In $[\text{Li}\{\text{C}_6\text{H}_3(\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)_2\cdot 2,6\}]\text{LiBr}$ (**4**) and $[\text{Li}\{\text{C}_6\text{H}_2(\text{CH}_2\text{NMe}_2)_4\cdot 2,3,5,6\}]_2$ (**6**) (cf. **3**) the corresponding θ values are 58.0(2) and 58.75(4)°, respectively. These smaller angles presumably result from the fact that the two ortho substituents of each ligand coordinate to different lithium atoms of the lithium pair that is bridged by two C_{ipso} atoms; there is a C_2 symmetry axis running through $\text{C}_{\text{para}}\text{C}_{\text{ipso}}\text{C}_{\text{ipso}}\text{C}_{\text{para}}$ in **6** and through $\text{C}_{\text{para}}\text{C}_{\text{ipso}}\text{Br}$ in **4**. In **2** the N,N-coordination occurs in an asymmetric fashion that leaves the aryl ring more freedom with respect to its orientation relative to the Li—Li vector. It is interesting to compare the structural features of **2** with those of $[\text{LiPh}(\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2)]_2$ (**5**), in which the phenyl rings are nearly coplanar (Figure 1). Actually **2** can also be viewed as a tmeda ligand in which one Me group is substituted by a $\text{CH}_2\text{C}_6\text{H}_4$ anion.

Finally, it is of interest to recall that in **7** (Figure 1) the rigidity of the C,N-chelate causes a nearly coplanar $\text{Li}_2(\text{C}_{\text{ipso}})_2$ arrangement, resulting in the rare structural feature that C_{ipso} is a nearly planar tetracoordinate carbon center ($\theta = 11.1(4)^\circ$);^{11a} in $[\text{LiC}_6\text{H}_3(\text{OMe})_2\cdot 2,6]_4$ this angle has a similar value of ca. 11.1° .¹⁴ The X-ray

structure determination and reactivity studies involving transmetalation reactions with a variety of metal salts and oxidative addition reactions^{5–9} show that, compared to **3**, the lithium core in **2** is less shielded by the unsymmetrically bonded ligand and this gives rise to a more polar structure and a greater reactivity with metal halides (Figure 2).

Stereochemical Aspects of the Structure of $[\text{Li}\{\text{C}_6\text{H}_4(\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)_2\cdot 2\text{-C,N,N'}\}]_2$ (2**) in Solution.** The structure of **2** in solution has been studied by cryoscopy and ^1H , ^{13}C , and ^7Li NMR spectroscopy (see Experimental Section). The cryoscopic molecular weight data obtained in benzene (0.05–0.12 M) show that **2** exists as a dimer in solution. Furthermore, it is often possible by detection of the multiplicity of the C_{ipso} atom NMR resonance in aryllithium species to gain information about the aggregation state. For example, for **3** ^{13}C NMR data for C_{ipso} (seven lines with $^1J(^{13}\text{C}, ^7\text{Li})$; 1:2:3:4:3:2:1 intensity) confirm a dinuclear structure in which C_{ipso} is equivalently bonded to two isochronic Li nuclei.^{11b} Unfortunately, for **2** this multiplicity was not resolved even at low temperature (toluene- d_8 , 253 K, 50 MHz: the two Li atoms are isochronic, as indicated by the observation of a single ^7Li resonance at 2.08 ppm).

The further assignment of the solution structural features of dimeric **2** concerning the binding of the diamine substituents is based on both the chirality of the NMe groups and the different possible orientations of the aryl ring; the three structures **a–c** can be proposed (Figure 3). In structures **a** and **b** both nitrogen atoms of one $-\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2$ moiety are coordinating to the same lithium atom, but they differ in the orientation of the aryl ring. In structure **c** one nitrogen atom of a $-\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2$ moiety coordinates to one lithium atom, while the second N atom of the same moiety coordinates to the other lithium center. The Li—Li distance is too long in **c** to be bridged by the $-\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2$ unit; this structure for **2** seems therefore highly unlikely and only **a** and **b** have been considered further as possible structures. In **2** the central $-\text{NMe}-$ grouping becomes a stereogenic center upon coordination. In structure **a** (that has an inversion center in which the pairs of bridging C_{ipso} and lithium atoms are centers of chirality with opposite configurations) the two stereogenic nitrogen centers give rise to a single diastereoisomer with an $S_N R_N$ configuration.

(14) Harder, S.; Boersma, J.; Brandsma, L.; van Heteren, A.; Kanters, J. A.; Bauer, W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1988**, *110*, 7802–7806.

In contrast, structure **b** consists of one pair of enantiomers ($R_N R_N$ and $S_N S_N$). The alternative $R_N S_N$ configuration for **b** as well as the enantiomeric pair $R_N R_N$, $S_N S_N$ for **a** are not possible for geometrical reasons.

On this basis, when all nitrogen donor atoms are coordinated, then the NMR spectrum of **2** should afford just one resonance pattern for either structure **a** or structure **b**; these two patterns are expected to be different, but it would not be easy, given a single pattern, to make a decision regarding which of these two structures it represents. The X-ray structure (Figure 2) showed possibility **b** to represent the structure of **2** in the solid state, and the ^1H and ^{13}C NMR spectra are consistent with this structure. It is worth noting here that the bonding mode in $[\text{Li}\{\text{C}_6\text{H}_3(\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)_2\cdot 2,6\}]\cdot\text{LiBr}$ (**4**) is like that in structure **a** (see Figure 1) and the bonding mode in structure **b** resembles that of the dimer $[\text{LiPh}(\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2)]_2$ (**5**). In the ^1H spectrum of **2** (benzene- d_6 , 298 K, 200 MHz) there is a characteristic low-field doublet resonance at 8.32 ppm that is indicative of an aromatic proton positioned ortho to a metal atom.¹² The coordination of the $-\text{NMe}-$ moiety to lithium is clear from the anisochronism of the benzylic protons (AB pattern) as well as from the low-field shift of the $-\text{NMe}-$ protons at 2.49 ppm (in free $\text{C}_6\text{H}_5\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2$ they resonate at 2.08 ppm). The $-\text{NMe}_2$ unit affords a broad resonance at 1.5 ppm, and this, in combination with broadened methylene resonances, is evidence for fluxional behavior between coordinated and noncoordinated NMe_2 situations ("arm-off"/"arm-on" process). This fluxionality was clearly shown in a series of variable-temperature ^{13}C NMR experiments. At 253 K (toluene- d_8 , 50 MHz) the Me groups of the $-\text{NMe}_2$ substituent are diastereotopic (two resonances at 44.3 and 47.8 ppm), consistent with coordination of the $-\text{NMe}_2$ unit to a lithium center. At ca. 288 K the Me signals for the $-\text{NMe}_2$ unit coalesce ($\Delta G \approx 13.9$ kcal mol $^{-1}$), and at 333 K there is one sharp resonance at 45.7 ppm. The latter value is very close to that of the Me groups of the $-\text{NMe}_2$ unit in free $\text{C}_6\text{H}_5\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2$ (45.9 ppm); i.e., at ambient temperature the $-\text{NMe}_2$ group of **2** is (on average) noncoordinating. The $-\text{NMe}-$ resonance of **2** is at 44.8 ppm at all temperatures. This is 2.2 ppm to lower field than in free $\text{C}_6\text{H}_5\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2$, and it can be concluded that the $-\text{NMe}-$ groups in **2** are always coordinated to the lithium centers.

Conclusions

A convenient route for the preparation of pure, halide-free **2** involves the substitution reaction of $\text{BrC}_6\text{H}_4\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2$ with 1 equiv of $n\text{-BuLi}$ in Et_2O at -70°C . In solution and in the solid state **2** exists as a dimer. The central N-donor centers are stereogenic upon coordination to lithium with a unique stereochemistry ($R_N R_N$, $S_N S_N$ enantiomeric pair); the aryl groups each bridge *via* C_{ipso} between two lithium atoms, while both nitrogen atoms of each *o*-diamine substituent coordinate to the same lithium center. With this organolithium compound new metal complexes with early and late transition metals are accessible *via* transmetalation reactions with the corresponding metal salts.

Experimental Section

General Considerations. Syntheses were carried out using standard Schlenk techniques under an atmosphere of purified nitrogen. All solvents were dried and distilled under nitrogen prior to use. N,N,N' -trimethylethylenediamine and 2-bromobenzyl bromide are commercially available and were used as received. ^1H , ^{13}C , and ^7Li NMR spectra were recorded on Bruker AC 200 and AC 300 spectrometers. ^1H and ^{13}C NMR data are in ppm relative to TMS, with a positive sign indicating a downfield shift. The ^7Li NMR data were obtained at a temperature of 0°C with chemical shifts referenced to external 1.0 M LiCl in H_2O . Coupling constants (J) are in hertz. ^1H and ^{13}C spectra were obtained in benzene- d_6 at 25°C unless stated otherwise. Elemental analyses were performed by Dornis und Kolbe Microanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany.

Synthesis of $\text{C}_6\text{H}_4\text{Br}(\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)_2$ (1**).** To a solution of N,N,N' -trimethylethylenediamine (13.3 mL, 102 mmol) and NEt_3 (40 mL) in C_6H_6 (100 mL) was added dropwise a solution of 2-bromobenzyl bromide (25.3 g, 101 mmol) in C_6H_6 (110 mL). After 1 h the resulting white suspension ($\text{HNEt}_3\cdot\text{Br}$) was filtered and washed with C_6H_6 (25 mL). The filtrate was concentrated by removing the solvent *in vacuo*. This resulted in a light yellow oily residue, which was purified by bulb-to-bulb distillation to yield **1** as a colorless oil (17.0 g, 68%). ^1H NMR (200 MHz, CDCl_3): δ 7.56 (d, 1 H, $^3J_{\text{H,H}} = 7$, H_{aryl}), 7.44 (d, 1 H, $^3J_{\text{H,H}} = 7$, H_{aryl}), 7.04 (t, 1H, $^3J_{\text{H,H}} = 7$, H_{aryl}), 6.76 (t, 1 H, $^3J_{\text{H,H}} = 7$, H_{aryl}), 3.59 (s, 2 H, $\text{Ar}-\text{CH}_2-\text{N}$), 2.52 (t, 2 H, $^3J_{\text{H,H}} = 7$, CH_2), 2.38 (t, 2 H, $^3J_{\text{H,H}} = 7$, CH_2), 2.15 (s, 3 H, NCH_3), 2.10 (s, 6 H, $\text{N}(\text{CH}_3)_2$). ^{13}C NMR (50 MHz, CDCl_3): δ 139.1 (C_{aryl}), 132.7 (C_{aryl}), 130.8 (C_{aryl}), 128.2 (C_{aryl}), 127.2 (C_{aryl}), 124.5 (C_{aryl}), 61.9 ($\text{Ar}-\text{CH}_2-\text{N}$), 58.0 (CH_2), 56.1 (CH_2), 45.8 ($\text{N}(\text{CH}_3)_2$), 42.5 (NCH_3). Anal. Calcd for $\text{C}_{12}\text{H}_{19}\text{BrN}_2$: C, 53.14; H, 7.06; N, 10.33. Found: C, 53.16; H, 7.07; N, 10.42.

Synthesis of $[\text{Li}\{\text{C}_6\text{H}_4(\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)_2\cdot\text{C}_6\text{H}_4\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2\cdot 2\}]\cdot 2$ (2**).** To a solution of $\text{BrC}_6\text{H}_4\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2$ (7.74 g; 28.5 mmol) in Et_2O (25 mL) was added slowly at -70°C $n\text{-butyllithium}$ (20 mL of a 1.5 M solution in hexane; 30 mmol), which resulted in immediate precipitation of a white solid. The reaction mixture was stirred for 1.5 h, during which time the temperature was raised to room temperature. The resulting suspension was centrifuged and the supernatant removed by decantation. The solid obtained was washed with pentane (3×10 mL) (following a workup procedure similar to that described above for **1**) and then dried *in vacuo* to afford **2** as a white powder (5.4 g, 97% yield). Recrystallization from toluene at -20°C afforded small, colorless crystals suitable for a molecular weight determination. Molecular weight (cryoscopy in benzene): 340 ($c = 0.05$), 346 ($c = 0.07$), 352 ($c = 0.12$); calcd for a dimeric unit 396. Crystals suitable for an X-ray analysis were obtained by cooling down a saturated solution of **2** in Et_2O . ^1H NMR (300 MHz, C_6D_6): δ 8.32 (d, 1 H, $^3J_{\text{H,H}} = 7$, $\text{H}_{\text{aryl}}(6)$), 7.37 (t, 1 H, $^3J_{\text{H,H}} = 7$, $\text{H}_{\text{aryl}}(4)$), 7.26 (t, 1 H, $^3J_{\text{H,H}} = 7$, $\text{H}_{\text{aryl}}(5)$), 7.18 (d, 1 H, $^3J_{\text{H,H}} = 7$, $\text{H}_{\text{aryl}}(3)$), 4.22 (d, 1 H, $\text{Ar}-\text{CH}_2-\text{N}$), 3.28 (d, 1 H, $^2J_{\text{H,H}} = 12$, $\text{Ar}-\text{CH}_2-\text{N}$), 2.75 (m, 1 H, $\text{NCH}_2\text{CH}_2\text{NMe}_2$), 2.49 (s, 3 H, $-\text{NCH}_3-$), 2.1 (m, 1 H, $\text{NCH}_2\text{CH}_2\text{NMe}_2$), 1.70 (m, 1 H, $\text{NCH}_2\text{CH}_2\text{NMe}_2$), 1.55 (m, 1 H, $\text{NCH}_2\text{CH}_2\text{NMe}_2$), 1.53 (br s, 6 H, $-\text{N}(\text{CH}_3)_2$). ^{13}C NMR (C_6D_6 , 75 MHz): δ 150.5 ($\text{ArC}(2)$), 142.6 ($\text{ArC}(6)$), 125.6, 124.3, 124.0 ($\text{ArC}(3)-(5)$), 71.5 ($\text{Ar}-\text{CH}_2-\text{N}$), 57.6, 52.1 ($\text{NCH}_2\text{CH}_2\text{NMe}_2$), 46 (br, $-\text{N}(\text{CH}_3)_2$), 44.8 (br, $-\text{NCH}_3-$), C_{ipso} not observed. ^7Li NMR (toluene- d_8 , 0°C , 77.77 MHz): δ 2.08.

Quenching of a solution of **2** in C_6D_6 with an excess of D_2O gave $\text{C}_6\text{H}_4\text{-D-1}-(\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)_2$ according to ^1H and ^{13}C NMR data. ^1H NMR (C_6D_6 , 300 MHz): δ 7.33 (d, 1 H, $^3J_{\text{H,H}} = 7$, $\text{H}_{\text{aryl}}(6)$), 7.18–7.12 (m, 3 H, $\text{H}_{\text{aryl}}(3,4,5)$), 3.36 (s, 2 H, $\text{Ar}-\text{CH}_2-\text{N}$), 2.4 (m, 4 H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2$), 2.08 (s, 3 H, $-\text{NCH}_3-$), 2.06 (s, 6 H, $-\text{N}(\text{CH}_3)_2$). ^{13}C NMR (C_6D_6 , 75 MHz): δ 140 ($\text{C}_{\text{aryl}}(2)$), 128.8 (t, $^1J_{\text{D,C}} = 24$, C_{ipso}), 129.1, 128.5, 128.3, 127.1 ($\text{C}_{\text{aryl}}(3,4,5,6)$), 63.0 ($\text{Ar}-\text{CH}_2-\text{N}$), 58.2, 58.0 ($\text{NCH}_2\text{CH}_2\text{NMe}_2$), 45.9 ($-\text{N}(\text{CH}_3)_2$), 42.6 ($-\text{NCH}_3-$).

Table 2. Crystallographic Data for **2**

Crystal Data	
formula	C ₂₄ H ₃₈ Li ₂ N ₄
mol wt	396.47
cryst syst	monoclinic
space group	P2 ₁ /c (No. 14)
Z	4
a, b, c (Å)	15.7740(13), 10.6866(8), 18.205(2)
β (deg)	124.928(9)
V (Å ³)	2516.0(5)
D _{calcd} (g cm ⁻³)	1.047
F(000)	864
μ _{calcd} (cm ⁻¹)	0.6
cryst size (mm)	0.25 × 0.25 × 1.0
Data Collection	
T, K	298
θ _{min} , θ _{max} (deg)	1.37, 22.92
radiation (Mo Kα) (Å)	0.710 73 (Zr filtered)
scan type	ω/2θ
Δω (deg)	0.53 + 0.35 tan θ
horiz, vert aperture (mm)	3.00, 4.00
ref refls	215, 122, 321
data set	-17 to +17, -11 to 0, -17 to +17
total no. of data	7649
total no. of unique data	3447 (R _{int} = 0.0211)
no. of obsd data	1276 (I > 2.5σ(I))
Refinement	
no. of refined params	301
weighting scheme	[σ ² (F) + 0.000114F ²] ⁻¹
final R, R _w , S ^a	0.066, 0.045, 1.15
(Δ/σ) _{av} , (Δ/σ) _{max} in final cycle	0.022, 0.21
min, max residual density (e Å ⁻³)	-0.18, 0.22

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|; R_w = [\sum [w(|F_o| - |F_c|)^2] / \sum [w(F_o^2)]]^{1/2}.$$

Crystal Structure Determination and Refinement of **2.** A clear, rod-shaped crystal was sealed in a Lindemann-glass capillary and transferred to an Enraf-Nonius CAD4-F diffractometer. Accurate unit-cell parameters and an orientation matrix were determined by least-squares refinement of 25 well-centered reflections (SET4) the range 4.7° < θ < 11.1°. The unit-cell parameters were checked for the presence of higher lattice symmetry.¹⁵ Crystal data and details on data

collection and refinement are presented in Table 2. Data were corrected for Lp effects but not for absorption. Three periodically measured reference reflections showed no significant linear decay (<1%) during 85 h of X-ray exposure time. The structure was solved by automated direct methods (SHELXS86¹⁶). Refinement on F was carried out by full-matrix least-squares techniques (SHELX76¹⁷). Hydrogen atoms were included in the refinement on calculated positions (C-H = 0.98 Å) riding on their carrier atoms. In the five-membered chelate ring containing N(3)-Li(2)-N(4) there is conformational disorder, i.e. ring pucker up and down based on C(22), and atoms C(22), C(23), and C(24) are disordered over two positions. The site occupation factor of the major component of the disorder model was refined to a value of 0.52(2). All non-hydrogen atoms were refined with anisotropic thermal parameters; the hydrogen atoms were refined with two overall isotropic thermal parameters with values of 0.058(6) and 0.125(7) Å². Weights were introduced in the final refinement cycles. Neutral atom scattering factors were taken from Cromer and Mann¹⁸ and anomalous dispersion corrections from Cromer and Liberman.¹⁹ Geometrical calculations and illustrations were performed with PLATON.²⁰ All calculations were performed on a DECstation 5000/125.

Acknowledgment. This work was supported in part (A.L.S. and W.J.J.S.) by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

Supplementary Material Available: Further details of the structure determinations, including tables of atomic coordinates, thermal parameters, bond lengths and angles, and torsion angles for **2** (10 pages). Ordering information is given on any current masthead page.

OM940248V

(16) Sheldrick, G. M. SHELXS86 Program for Crystal Structure Determination; University of Göttingen, Göttingen, Germany, 1986.

(17) Sheldrick, G. M. SHELX76 Program for Crystal Structure Determination; University of Cambridge, Cambridge, U.K., 1976.

(18) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, A24, 321.

(19) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, 53, 1891.

(20) Spek, A. L. *Acta Crystallogr.* **1990**, A46, C34.

(15) Spek, A. L. *J. Appl. Crystallogr.* **1988**, 21, 578.