PhCH=P(MeNCH$_2$CH$_2$)$_3$N: A Novel Ylide for Quantitative *E* Selectivity in the Wittig Reaction

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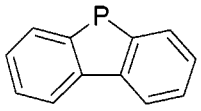
PhCH=P(MeNCH$_2$CH$_2$)$_3$N (**1**), a semi-stabilized ylide prepared from the commercially available nonionic base P(MeNCH$_2$CH$_2$)$_3$N, reacts with aldehydes to give alkenes in high yield with quantitative *E* selectivity. In contrast with other ylides, this *E* selectivity is maintained despite changes in the metal ion of the ionic base used to deprotonate **1**, temperature, and solvent polarity. In conjunction with structural parameters gained from the X-ray molecular structure of **1**, the pathway to *E* selectivity in these reactions is rationalized by the Vedejs model of Wittig reaction stereochemistry.

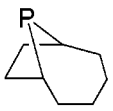
Introduction

The Wittig reaction has long been an important method for the synthesis of alkenes, and it has also attracted considerable attention over the years because it is mechanistically interesting.[1,2] The stereochemistry of the olefination of aldehydes with phosphorus ylides is governed primarily by the nature of the ylide and the reaction conditions. Nonstabilized and stabilized ylides bearing an α-alkyl group tend to give *Z* alkenes, whereas stabilized ylides, which typically bear a π acceptor group on the α carbon, generally react with high selectivity for the *E* olefinic configuration. Semi-stabilized ylides, such as benzyl and allyl ylides, yield mixtures of *Z* and *E* isomers.

Factors that can affect product stereochemistry, such as the structure of the phosphonium salt,[3] the presence of a metal cation,[4] and the reaction conditions,[5] have been extensively investigated. Vedejs' unstablized ylides containing the DBP[6] or BTP[7] moiety react with aldehydes and ketones to afford *E*-alkenes. Lawrence reported that ring-containing semi-stabilized ylides also afford *E*-alkenes with high stereoselectivity.[8] Schlosser reported, however, that semi-stabilized ylides also react with aldehydes to give *Z*-alkenes.[3b,9]

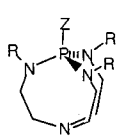


DBP: dibenzophosphole

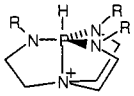


BTP: bridged tetrahydrophosphole

In a preliminary communication,[10] we reported that the novel semi-stabilized ylide **1** obtained from commercially available **2** reacts with aldehydes to give exclusively *E*-alkenes in high yields (reaction 1). To gain insight into the conditions that might affect the reaction stereochemistry of this novel ylide, we have investigated the influence of metal ions, temperature, and solvent polarity using aldehydes as substrates. Our determination of the structure of **1** by X-ray means is of aid in rationalizing the reaction pathway to exclusive *E* selectivity in terms of the Vedejs model.[3c]



	Z	R
1	=CHPh	Me
2	lone pr	Me
3	$^+$CH$_2$Ph	Me
4	=O	Me
5	lone pr	i-Pr
6	$^+$CH$_3$	Me



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$$\mathbf{1} + \text{RCHO} \longrightarrow \textit{E}\text{-PhCH=CHR} + \mathbf{4} \qquad (1)$$

Results and Discussion

Reactions of 1 with Aldehydes. Earlier we reported that commercially available **2**[11] reacts with alkyl halides to give phosphonium salts.[12] Following a similar procedure (using THF as the solvent instead of acetonitrile) the benzyl phosphonium salt **3** was synthesized in high yield and was then deprotonated to form ylide **1** by employing bases such as NaHMDS (sodium hexamethyl disilylamide), LDA and *t*-BuOK. Using NaHMDS, **3** was dehydrohalogenated to form ylide **1** in situ for subsequent

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Table 1. Wittig Reactions with Ylide 1[a]

entry	carbonyl compound	PhCH=CR^{1}R^2 R^1	R^2	yield[b] (%)	E:Z[c] ratio
1	PhCHO	Ph	H	91	*E*
2	*p*-MeOC$_6$H$_4$CHO	*p*-MeC$_6$H$_4$	H	93	*E*
3	*p*-ClC$_6$H$_4$CHO	*p*-ClC$_6$H$_4$	H	93	*E*
4	*trans*-PhCH=CHCHO	*trans*-PhCH=CH	H	94	*E*
5	*c*-C$_6$H$_{11}$CHO	*c*-C$_6$H$_{11}$	H	90	*E*
6	CH$_3$(CH$_2$)$_5$CHO	CH$_3$(CH$_2$)$_5$	H	93	*E*
7	C$_2$H$_5$CH(CH$_3$)CHO	C$_2$H$_5$CH(CH$_3$)	H	86	*E*
8	PhCOMe[d]	Ph	Me	35	56:44
9	(CH$_2$)$_4$C=O[d]	(CH$_2$)$_4$		trace	

[a] All reactions were carried out under argon with the molar ratios of **3**:NaHMDS:aldehyde = 0.6:0.6:0.5 for 15 min at room temperature except where indicated. [b] Isolated yields are based on the aldehyde. [c] The isomer ratios were determined by comparison of ^{1}H NMR spectra of the crude product **4** with those in the literature.[10] [d] Reflux for 12 h in THF.

Table 2. Wittig Reactions with PhCH=P(NMe$_2$)$_3$[a]

entry	carbonyl compound	PhCH=CR^{1}R^2 R^1	R^2	conv[b] (%)	*E*:*Z*[c] ratio
1	PhCHO	Ph	H	98	76:24
2	*p*-MeOC$_6$H$_4$CHO	*p*-MeOC$_6$H$_4$	H	99	74:26
3	*p*-ClC$_6$H$_4$CHO	*p*-ClC$_6$H$_4$	H	100	79:21
4	*trans*-PhCH=CHCHO	*trans*-PhCHCH	H	93	*E*
5	*c*-C$_6$H$_{11}$CHO	*c*-C$_6$H$_{11}$	H	100	*E*
6	CH$_3$(CH$_2$)$_5$CHO	CH$_3$(CH$_2$)$_5$	H	100	83:17
7	C$_2$H$_5$CH(CH$_3$)CHO	C$_2$H$_5$CH(CH$_3$)	H	100	*E*
8	PhCOMe	Ph	Me	41	77:23
9	(CH$_2$)$_4$C=O	(CH$_2$)$_4$		trace	

[a] Reaction conditions were identical to those listed in Table 1 with the molar ratios PhCH$_2$P(NMe$_2$)$_3$Br:NaHMDS:aldehyde = 0.6:0.6:0.5. [b] Based on aldehyde as determined from ^{1}H NMR spectra of the crude alkene. [c] Determined by the same method given in Table 1.

aromatic or aliphatic aldehyde addition that gave exclusively *E*-alkenes in high yields (Table 1).

For aromatic aldehydes, the presence of electron-withdrawing or electron-donating substituents has little influence on the reactivity and selectivity (Table 1, entries 1−3). Aldehydes bearing a bulky group such as cyclohexanecarboxaldehyde (entry 5 in Table 1) also afford exclusively *E*-alkenes in high yields. However, the reaction of **1** with acetophenone (entry 8) is very sluggish, giving a mixture of isomers in low yield even though relatively severe reaction conditions were employed (refluxing for 12 h). Only a trace of product was observed for the reaction of **1** with cyclohexanone.

In contrast to the result in entry 1 of Table 1, benzyltriphenylphosphonium bromide gave *E*- and *Z*-stilbene in a 63:37 ratio (96% conversion) with the same substrate under the same reaction conditions. [PhCH$_2$P(NMe$_2$)$_3$]Br,[13] an acyclic analogue of the tricyclic ylide **1**, was also employed to conduct Wittig reactions under the same conditions as those used for **1** (Table 2). Here the *E* selectivity of the corresponding ylide generated in situ was substantially less in most cases than with **1**, although *E* isomers still predominated.

Structure of 1. Crystals of **1** suitable for X-ray crystallography were obtained by treating **3** with freshly prepared NaNH$_2$. After the reaction, the mixture was extracted with pentane and then filtered. The solvent was removed by vacuum-drying to afford crude ylide **1**. Crystals were obtained by slow sublimation of this residue under vacuum. The main features of the molecular structure are the nearly planar stereochemistry of N(4) [bond angle sum around N(4) = 359.24(12)°] and the transannular P−N(4) distance of 3.1947(13) Å. These metrics are consistent with a lack of P−N(4) transannular interaction, since the latter distance is close to the sum of the van der Waals radii.[11]

Table 3. Metal Ion Effects on Wittig Reactions with Ylide 1[a]

entry	base	aldehyde	yield[b] (%)	*E*/*Z*[d]
1	KHMDS	PhCHO	93	*E*
2	KHMDS	CH$_3$(CH$_2$)$_5$CHO	84	*E*
3	*t*-BuOK	PhCHO	91	*E*
4	*t*-BuOK	CH$_3$(CH$_2$)$_5$CHO	88	*E*
5	LiHMDS	PhCHO	88	*E*
6	LiHMDS	CH$_3$(CH$_2$)$_5$CHO	89	*E*
7	LDA	PhCHO	90	*E*
8	LDA	CH$_3$(CH$_2$)$_5$CHO	82	*E*
9	metal ion free	PhCHO	96[c]	*E*
10	metal ion free	CH$_3$(CH$_2$)$_5$CHO	41[c]	*E*

[a] Reaction conditions were identical to those listed in Table 1, with the molar ratios **1**:base:aldehyde = 0.30:0.30:0.25. [b] Isolated yields are based on the aldehyde. [c] Conversions were determined from ^{1}H NMR spectra of the crude alkene based on the aldehyde. [d] Determined by the same method given in Table 1.

Metal Ion Effect. Metal ions play an important role in the stereochemistry of the Wittig reaction. McEwen investigated the reaction of benzylidenediphenylmethylphosphorane with aldehydes in the presence of Na^+, K^+, and Li^+ [4] and found that the product mixture was enriched with *Z*-alkene when lithium ion was present (*E*/*Z* = 36/54 to 26/74), while the *E* isomer predominates in the presence of sodium or potassium ions. Lawrence also found that the reaction of a cyclophosphorinanium salt[8] with aldehydes gave predominately *E*-alkenes (*E*/*Z* = 97/3) when KHMDS was used as a base, although the selectivity decreased (*E*/*Z* = 67/33) when butyllithium was used. For allylic phosphorus ylides,[14] the lithium salt effect on the stereochemistry of the Wittig reaction depended on the type of aldehyde and phosphorus moiety. Thus for the triphenylphosphine ylide, for example, lithium ion favored the *Z*-alkene, while *E*-alkene predominated for the reaction of tributylphosphorus ylide with sterically congested aldehydes.

To evaluate the effect of metal ions on the stereoselectivity of **1** with aldehydes, sodium, potassium, and lithium bases were chosen to deprotonate **3** to form ylide **1**. When ylide **1** so generated was reacted with aldehydes in situ, exclusively *E*-alkenes were produced (Table 3). Thus the reaction is insensitive to an observable lithium ion effect. For comparison, the reactions of [PhCH$_2$P(NMe$_2$)$_3$]Br with aldehydes in the presence of potassium and lithium bases were carried out under the same conditions. The data listed in Table 4 (entries 1−4) show that the results of using a potassium base are similar to those produced with NaHMDS (Table 2, entries 2 and 6). Both *E* and *Z* isomers were observed, although the *E* isomer again dominates. However, the lithium base produced variable effects. Thus the reaction of PhCH$_2$P(NMe$_2$)$_3$Br with benzaldehyde in the presence of lithium ion afforded the corresponding alkene with high *E* selectivity, but with heptaldehyde it led to a 24% decrease in *E* selectivity (Table 3, entries 7 and 8). Interestingly, the reactions of PhCH=P(NMe$_2$)$_3$ with PhCHO and

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Table 4. Metal Ion Effects on Wittig Reactions with PhCH=P(NMe$_2$)$_3$[a]

entry	base	aldehyde	conversion[b] (%)	E/Z[c]
1	KHMDS	PhCHO	95	76/24
2	KHMDS	$CH_3(CH_2)_5CHO$	98	81/19
3	*t*-BuOK	PhCHO	97	76/24
4	*t*-BuOK	$CH_3(CH_2)_5CHO$	100	77/23
5	LiHMDS	PhCHO	100	91/9
6	LiHMDS	$CH_3(CH_2)_5CHO$	100	67/33
7	LDA	PhCHO	100	93/7
8	LDA	$CH_3(CH_2)_5CHO$	100	69/31
9	metal ion free	PhCHO	96	81/19
10	metal ion free	$CH_3(CH_2)_5CHO$	97	84/16

[a] Reaction conditions were identical to those listed in Table 1, with the molar ratios [PhCH$_2$P(NMe$_2$)$_3$:base:aldehyde = 0.30:0.30:0.25. [b] Conversions were determined from ^{1}H NMR spectra of the crude alkene based on aldehyde. [c] Determined by the same method given in Table 1.

Table 5. Wittig Reactions of 1 with Aldehydes in THF at −78 °C[a]

entry	base	aldehyde	conversion[b] (%)	*E*/*Z*[c]
1	NaHMDS	PhCHO	100	*E*
2	NaHMDS	$CH_3(CH_2)_5CHO$	94	*E*
3	KHMDS	PhCHO	100	*E*
4	KHMDS	$CH_3(CH_2)_5CHO$	90	*E*
5	LiHMDS	PhCHO	99	*E*
6	LiHMDS	$CH_3(CH_2)_5CHO$	88	*E*

[a] Reaction conditions were identical to those listed in Table 1, with the molar ratios **1**:base:aldehyde = 0.30:0.30:0.25. [b] Conversion determined by ^{1}H NMR spectra of the crude alkene based on aldehyde. [c] Determined by the same method given in Table 1.

Table 6. Solvent Effects on Wittig Reaction with Ylide 1[a]

entry	solvent	aldehyde	conversion[b] (%)	*E*/*Z*[c]
1	pentane	PhCHO	96	*E*
2	pentane	$CH_3(CH_2)_5CHO$	90	*E*
3	toluene	PhCHO	100	*E*
4	toluene	$CH_3(CH_2)_5CHO$	95	*E*
5	acetonitrile	PhCHO	100	*E*
6	acetonitrile	$CH_3(CH_2)_5CHO$	92	*E*

[a] Reaction conditions were identical to those listed in Table 1, with the mmolar ratios **1**:NaHMDS:aldehyde = 0.30:0.30:0.25. [b] Conversion determined by ^{1}H NMR spectra of the crude alkene based on aldehyde. [c] Determined by the same method given in Table 1.

$Me(CH_2)_5CHO$ in the absence of metal ion produced more than 80% *E* product in each case (Table 4) while the same reactions with ylide **1** produced exclusively *E* products (Table 3).

Reaction Temperature and Solvent Effect. The effect of temperature on the stereochemistry of Wittig reactions of semi-stabilized benzyltriphenylphosphorus ylide showed that the *Z*/*E* ratio of the alkene product increased moderately with decreasing temperature.[15] For ylide **1**, the use of NaHMDS, KHMDS, and LiHMDS as bases in reactions conducted at −78 °C and at room temperature again gave exclusively *E*-alkenes (Table 5).

All the aforementioned reactions were carried out in THF. Other solvents such as acetonitrile, toluene, and pentane were also examined as solvents using NaHMDS as a base. All the reactions of ylide **1** with aldehydes in these solvents also gave exclusively *E*-alkenes (Table 6).

Mechanistic Considerations. Because the quantitative stereoselectivity of the reactions we report here for

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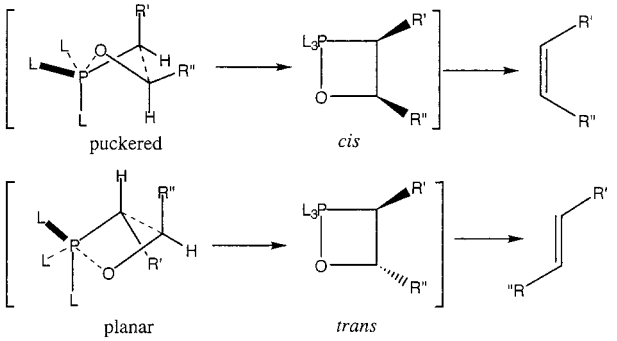
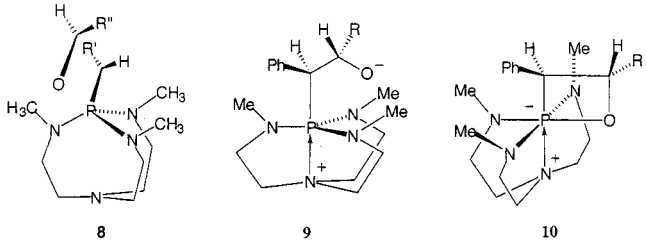
Scheme 1



1 is quite insensitive to a lithium salt effect, to temperature, and to changes in solvent, we suggest that the tricyclic cage structure of this reagent plays a pivotal role in the stereochemical outcome of the reaction. According to the Vedejs model,[3c] the reaction of an ylide with an aldehyde occurs through a cycloaddition that gives an oxaphosphetane intermediate whose stereochemistry is determined by the interplay of 1,2 and 1,3 steric interactions in a four-center transition state set up for the formation of *cis*- or *trans*-oxaphosphetanes, thus leading to *Z*- or *E*-olefins, respectively (Scheme 1). If a 1,3-interaction between a phosphorus substituent and a carbonyl substituent dominates, a *cis*-oxaphosphetane will be formed by the puckered four-centered transition state in order to avoid the 1,3-interaction. However the *trans*-oxaphosphetane will be formed by the planar four-centered transition state to relieve a dominating 1,2-interaction between R′ on the ylide and R″ on the aldehyde.

In contrast to flexible ylides, such as those derived from triphenyl and tris(dimethylamino)phosphine, ylide **1** incorporates a bicyclic phosphine whose compact and relatively rigid cage moiety apparently dramatically reduces the 1,3-interaction between a phosphorus substituent and a carbonyl substituent in the process of forming an oxaphosphetane. Consequently, a 1,2-interaction between R′ and R″ dominates, favoring formation of a four-centered *trans*-oxaphosphetane transition state that leads to *E*-alkene. Whereas a trigonal bypyramidal (TBP) phosphorus stereochemistry is likely in oxaphosphetane transition states derived from acyclic phosphines as shown in Scheme 1, bicyclic **1** is more likely to form a distorted TBP stereochemistry at phosphorus as is roughly depicted in **8**. From this structure it is seen that R′ and R″ that are well away from the CH_3 groups in the cage. Any steric interactions experienced by the phosphetane substituents and the methyl groups on the cage are further minimized by the twisting of the bridging groups along the C_3 axis of the cage in **8** which pulls the CH_3 groups downward from the planar oxaphosphetane moiety. Intermediate structures of types **9** and **10** cannot be ruled out.



The Vedejs model also rationalizes the poor stereoselectivity observed when ketones react with ylide **1**. When an H substituent in an aldehyde is replaced by a carbon-containing group, the increase in steric hindrance intensifies 1,3-interactions, thus allowing both 1,2- and 1,3-interactions to play a role in the development of the oxaphosphetane transition states, consequently leading to a mixture of *trans* and *cis* oxaphosphetanes and hence to a mixture of *E*- and *Z*-alkenes. Although a higher product *E:Z* ratio might have been expected in the reaction of acetophenone with **1** (Table 1, entry 8) than with $PhCH{=}P(NMe_2)_3$ (Table 2, entry 8) it is noteworthy that it was necessary to reflux the former reaction but not the latter. More steric congestion in the former reaction owing to the greater rigidity of ylide **1** may have played a role in this somewhat unexpected result.

Experimental Section

THF, ether, *n*-pentane, and toluene were distilled from Na and benzophenone and stored over 4 Å molecular sieves. Acetonitrile was distilled from P_4O_{10}. All the reactions were conducted under argon. Elemental analysis were carried out in the Instrument Services Laboratory of the Chemistry Department at Iowa State University.

$[PhCH_2P(MeNCH_2CH_2)_3N]Br$ (3). To a solution of **2** (1.40 g, 6.48 mmol) in THF (10 mL) was added benzyl bromide (1.33 g 7.78 mmol) by syringe at 0 °C. The white solid precipitated several minutes later. The mixture was stirred at room temperature for 12 h, and the precipitate was filtered, washed with ether (50 mL), and then dried under vacuum to give a white solid (2.38 g, 94%). The yield was only 75% when acetonitrile was used as the solvent.

$[PhCH_2P(NMe_2)_3]Br$.[14] To a solution of HMPT (1.63 g, 10.0 mmol) in ether (30 mL) was added benzyl bromide (1.71 g, 10.0 mmol) by syringe. The reaction solution was stirred at room temperature for 12 h. The resulting precipitate was filtered, washed with ether (30 mL), and dried under vacuum to give a white solid (2.16 g, 65%). Mp: 224−225 °C; ^{1}H NMR ($CDCl_3$): δ 2.76 (d, J = 9.6 Hz), 4.34 (d, 2 H, J = 15.9 Hz), 7.26−7.43 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 30.5 (d, J = 101.3 Hz), 38.1, 128.2, 129.0, 129.2, 130.7 (d, J = 5.3 Hz). ^{31}P NMR ($CDCl_3$): δ 59.70.

$PhCH{=}P(MeNCH_2CH_2)_3N$ (1). To a solution of freshly prepared $NaNH_2$ (3.40 g, 87.0 mmol) prepared in situ in liquid NH_3 (60 mL) was carefully added **3** (0.39 g, 1.0 mmol) at −78 °C. The mixture was stirred at this temperature for 4 h, then the NH_3 was allowed to evaporate slowly, and pentane (60 mL) was added. The solution was then stirred at room temperature for an additional 12 h. The solid was removed by filtration, followed by removal of the pentane under vacuum to give the crude product, which was vacuum sublimed (100 °C at 0.5 mmHg) to afford pure product (267 mg, 87%). A single crystal suitable for X-ray crystallography was obtained by slow sublimation (85−90 °C at 0.5 mmHg). ^{1}H NMR (C_6D_6): δ 2.21−2.24 (m, 6 H), 2.31−2.39 (m 6H), 2.49 (d, H, J = 9 Hz), 6.68−6.73 (m, 1H), 7.04−7.31 (m, 5H). ^{31}P NMR (C_6D_6): δ 51.60.

Typical Procedure for the Reaction Shown in Eq 1. A solution of sodium bis(trimethylsilyl)amide (NaHMDS, 0.6 mmol) in THF (1.5 mL) at 0 °C was added to a suspension of **3** (0.6 mmol) in THF (1.5 mL). After the reaction solution was stirred at room temperature for 8 h, the aldehyde (0.5 mmol) was added. The reaction mixture was then stirred under the reaction conditions stated in Table 1 followed by quenching with saturated aqueous $NaHCO_3$ (5 mL). The phases were separated, and the water layer was washed with ether (3 × 10 mL). The organic layers were combined and dried over $MgSO_4$. The solvent was removed with a rotary evaporator and then under vacuum to give the crude product, which was purified by flash chromatography (hexane/ethyl acetate = 80:1) to give the alkene. The aqueous layer was extracted with toluene (3 × 10 mL) to give **4**, whose ^{31}P and ^{1}H NMR spectra are consistent with those in the literature.[16]

Metal-Free Procedure. A solution of NaHMDS (0.3 mmol) in THF (0.75 mL) at 0 °C was added to a suspension of **3** (0.3 mmol) in THF (0.75 mL). After the solution was stirred at room temperature for 8 h, the solvent was removed under vacuum. Pentane (30 mL) was added to the dry residue, and the mixture was stirred at room temperature for 1 h. The mixture was filtered, and then pentane was removed from the filtrate to afford **1**. THF (1.5 mL) was added with stirring for an additional 5 min, and then the aldehyde (0.25 mmol) was added. The mixture was stirred at room temperature for 15 min followed by quenching with saturated aqueous $NaHCO_3$ (5 mL). The phases were separated, and the water layer was washed with ether (2 × 5 mL). The organic layers were combined and dried over $MgSO_4$. The solvent was removed with a rotary evaporator and then with a vacuum pump to afford the crude product. The yield and stereochemistry were determined by ^{1}H NMR spectroscopy (Tables 3 and 4).

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Supporting Information Available: NMR data for Wittig products reported, computer drawing of the molecular structure of **1**, and crystal data, atomic coordinates, bond lengths, bond angles, anisotropic displacement parameters, hydrogen coordinates for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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