α-Organoelement Nitrones: Synthesis, Properties, and IR and ^{13}C NMR Spectral and X-ray Structural Characterization†

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Received September 26, 2006

α-Organoelement-substituted nitrones have been synthesized for the first time through the reaction of the α-lithiated cyclic aldonitrones of 3-imidazoline 3-oxide, pyrroline 1-oxide, 2*H*-imidazole 1-oxide, and 3,4-dihydroisoquinoline 2-oxide series with electrophilic reagents such as $HgCl_2$, $(CH_3)_3SiCl$, $(C_2H_5)_3GeCl$, $(n\text{-}C_4H_9)_3SnBr$, $Ph_2P(O)Cl$, Ph_2PCl, PhSSPh, PhSeSePh, TsCl, and TsF. Aldonitrones of the 3-imidazoline 3-oxide and pyrroline 1-oxide series were shown to readily afford the products of the lithiation−electrophilic substitution reaction. In contrast, aldonitrones of the 2*H*-imidazole 1-oxide and 3,4-dihydroisoquinoline 2-oxide series react smoothly only with halogen-free electrophiles. It was found that an aldonitrone group could be lithiated and selectively reacted with electrophiles even when kinetically more acidic methylene and amino groups are present in the molecule. Characteristic features of IR and ^{13}C NMR spectra of the compounds synthesized are discussed. Selected α-organoelement nitrones are characterized by an X-ray diffraction study.

Introduction

Nitrones are attractive compounds to study for many reasons. It is now well documented that these compounds exhibit a wide spectrum of biological activity[2] and could serve as light-sensitive materials,[3] polymer stabilizers,[4] and useful starting compounds in different synthetic strategies.[5] Due to high synthetic potential and numerous practical applications, considerable efforts have consequently been applied to the preparation of interesting new derivatives, in particular, those containing atoms other than carbon, in an α-position of the nitrone group. However, among all the known nitrones only few bearing a heteroatom adjacent to the nitrone group carbon atom have been reported: aminonitrones,[6] alkoxynitrones,[6b,c,7] mercaptonitrones,[6b,c,8] phosphononitrone,[9] and chloronitrones.[10] Only two synthetic routes toward the above-mentioned nitrones are based on direct transformation of an aldonitrone group.[7,9] Compounds with a metal atom at the α-carbon atom of the nitrone group have never been reported. Although α-germylated hydroxylamines were prepared once,[11] α-germyl nitrones have never been synthesized and described to the best of author's knowledge. As our research interests lie in the application of the lithiation−electrophilic

† Preliminary communication, see ref 1.

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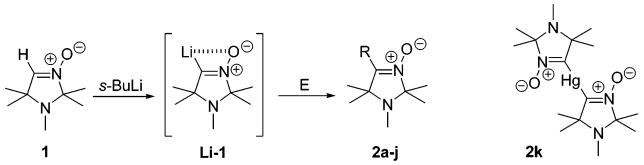
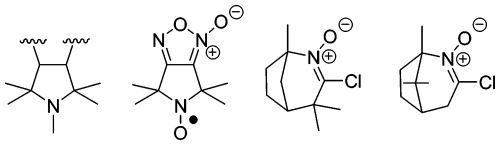
Publication on Web 02/22/2007

Scheme 1



a, E=$(CH_3)_3SiCl$, R=$Si(CH_3)_3$
b, E= $(C_2H_5)_3GeCl$, R=$Ge(C_2H_5)_3$
c, E=$(n\text{-}C_4H_9)_3SnBr$, R=$Sn(n\text{-}C_4H_9)_3$
d, E=$HgCl_2$, R=HgCl
e, E=$Ph_2P(O)Cl$, R=$P(O)Ph_2$
f, E= Ph_2PCl, R=PPh_2
g, E=PhSSPh, R=SPh
h, E= PhSeSePh, R=SePh
i, E=TsF, R= $SO_2C_6H_4$-(p-CH_3)
j, E=TsCl, R=Cl
k, E= $HgCl_2$, 0.5 equiv.

Scheme 2



substitution sequence[12] to the synthesis of α-substituted nitrones, we were interested whether the corresponding α-organoelement-substituted derivatives could be obtained within this approach. Since the synthetic potential of organosilicon,[13] organotin,[14] organomercury,[15] and phenylselenides[16] has already been demonstrated, we focused our initial efforts on the elaboration of synthetic procedures to these derivatives. In our synthetic strategy we rely on our previous report of an original approach to modify the aldonitrone group. The approach comprises α-lithiation of aldonitrones at −70 to −80 °C and subsequent reaction with appropriate electrophilic reagents.[12] Here we report on an extension of the approach[12] to the synthesis of α-organoelement nitrones of 3-imidazoline 3-oxide, pyrroline 1-oxide, 2*H*-imidazole 1-oxide, and 3,4-dihydroisoquinoline 2-oxide series.

Results and Discussion

α-Organoelement-Substituted Derivatives of 3-Imidazoline 3-Oxide and Pyrroline 1-Oxide Series. The metalation of 1,2,2,5,5-pentamethyl-2,5-dihydro-1*H*-imidazole 3-oxide (**1**) with *s*-BuLi readily affords the dipole-stabilized organolithium intermediate **Li-1**.[17] **Li-1** was reacted with $(CH_3)_3SiCl$, $(C_2H_5)_3GeCl$, $(n\text{-}C_4H_9)_3SnBr$, $HgCl_2$, $Ph_2P(O)Cl$, Ph_2PCl, PhSSPh, PhSeSePh, TsF, and TsCl to give nitrones **2a**−**k**, as shown in Scheme 1.

Nitrone **2a** is moisture-sensitive viscous oil that decomposes during one week upon storage in the refrigerator at 2−4 °C.

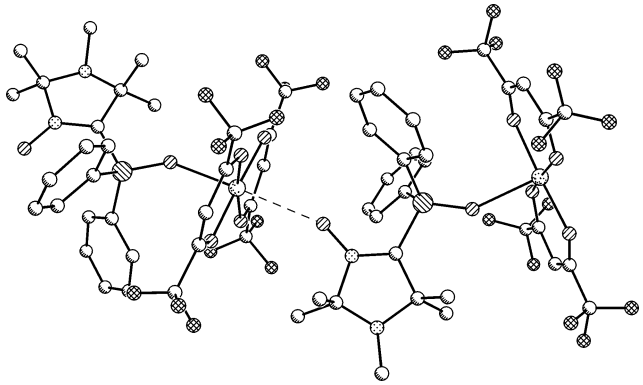
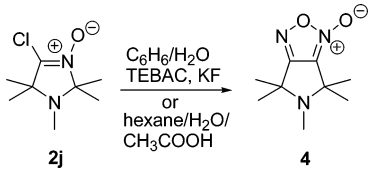


Figure 1. X-ray structure of $[Cu(hfac)_2phln]$. A single unit of the chain-like association is shown; hydrogens are omitted. Crystal data and experimental details for the crystal structure analysis: $C_{29}H_{27}CuF_{12}N_2O_7P$, 838.04, monoclinic, $P2(1)/c$, a = 12.326(2) Å, b = 16.382(1) Å, c = 18.107(2) Å, β = 101.87(1)°, V = 3578.1(7) Å^3, Z = 4, D_{calcd} = 1.556 g/cm^3, transmission coefficient (μ) = 0.763 mm^{-1}, θ range 2.10−24.97°, I_{hkl} measured = 5028, $I_{hkl} > 2\sigma_I$ = 4797 (R_{int} = 0.0121), GOOF for F^2_{hkl} = 0.807, R_1 ($I_{hkl} > 2\sigma_I$) = 0.0484, wR_2 = 0.1129, extinction 0.00000(16).

Scheme 3



Nitrone **2b** is a low-melting (about 28 °C) crystalline compound, while **2c** is a fluid liquid (at room temperature). Since **2c** undergoes decomposition when in contact with water, the latter was excluded from the workup procedure. When $(C_2H_5)_3SnCl$ was used instead of $(n\text{-}C_4H_9)_3SnBr$, the reaction afforded a product that underwent decomposition so rapidly that it could not be isolated and characterized. Nitrones **2b** and **2c** can be stored at −5 °C for weeks without any trace of decomposition. Nitrones **2d**−**i** are stable crystalline solids. When 0.5 equiv of $HgCl_2$ was introduced into the reaction, the disubstituted mercuric derivative **2k** was obtained. α-Chloronitrone **2j**, when purified by recrystallization, is stable at −5 °C for a long time, without a trace of decomposition. However, when dissolved in organic solvent, the compound completely decomposes within 24 h.

On the basis of the literature data, it has been assumed that derivative **2e** could be a ligand with regard to transition metal ions (cf. ref 18). Indeed, phosphinoylnitrone **2e** (phln) forms a crystalline complex with Cu(II)-hexafluoroacetylacetonate [Cu(hfac)$_2$]. The structure of the molecular complex $[Cu(hfac)_2phln]$ was determined by a single-crystal X-ray diffraction study. The square-pyramidal environment of the copper atom is made by the four oxygen atoms of the hfac ligands in the basal plane (average Cu−O distance is 1.93 Å), and the phosphine oxide oxygen atom is in the apical position (Cu−O distance is 2.260(2) Å, Figure 1). At the opposite side the copper atom makes an additional contact to the N-oxide oxygen of the neighboring ligand at a distance of 2.790(2) Å. Bond lengths of the C═N and P═O groups of the phln ligand (1.287(1) and 1.485(1) Å, correspondingly) coincide with that of the corresponding

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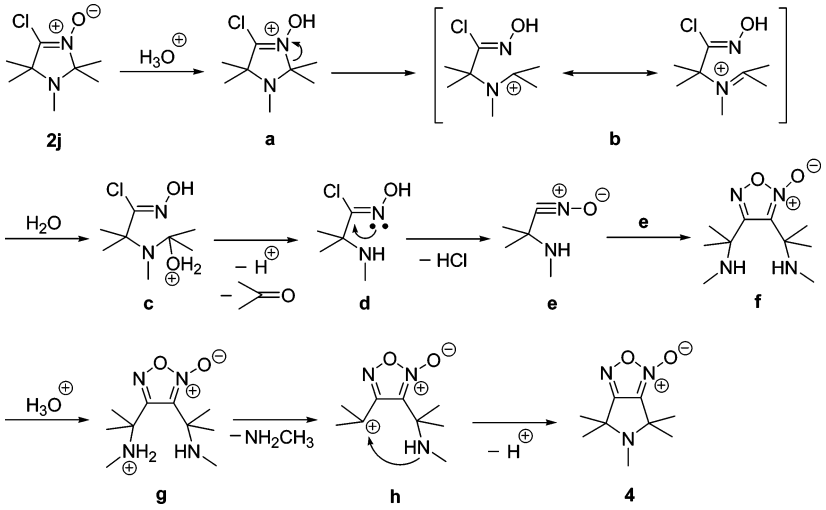
Scheme 4

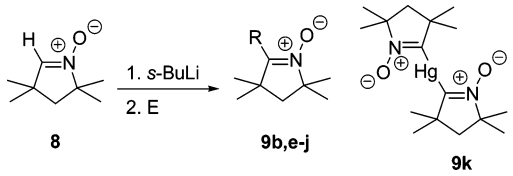


uncoordinated organic moieties (CSDB ver. 5.24[19]) within the standard deviation. Thus, these bond lengths are not affected by the coordination. Other bond lengths and angles in the molecule also have typical values. Due to the additional contact made by the copper atom to the N-oxide oxygen of the neighboring molecule, the molecules are associated into weakly bound chains running along the *c*-axis.

An attempt to substitute the chlorine atom in the α-chloronitrone **2j** was undertaken. Under phase-transfer catalysis conditions [benzene/H_2O, benzyltriethylammonium chloride (TEBAC), KF] a weak polar compound was obtained, whose ^{13}C NMR spectrum did not reveal the resonances inherent in the 3-imidazoline 3-oxide heterocycle. The same compound was obtained in an 80% yield when **2j** was treated with a mixture of hexane and 2% aqueous acetic acid. Surprisingly, the reaction does not proceed in dry hexane in the presence of glacial acetic acid.

The ^{13}C NMR spectrum of the resulting compound showed, in addition to resonances characteristic for aliphatic carbon atoms at δ 22.41, 24.33, and 25.54 ppm, the resonances at δ 58.57, 59.21, 168.54, and 117.13 ppm. The signals in the region δ 55−70 ppm are typical of resonances of quaternary carbon atoms adjacent to nitrogen atoms.[20] The appearance of these signals in the spectrum suggests that the fragment **3** has to be present in the structure of the molecule (Scheme 2). Thus, we assigned the signal at δ 168.54 ppm to the carbon atom resonance of the C═N group and the signal at δ 117.13 ppm to the resonance of the carbon atom of the C═N→O group. A mass spectrum of the resulting compound reveals the peak of a molecular ion (M^+) at 197.11648 Da corresponding to the elemental composition $C_9H_{15}N_3O_2$. The spectral data obtained allowed us to assign the resulting compound the structure of 4,4,5,6,6-pentamethyl-5,6-dihydro-4*H*-pyrrolo[3,4-*c*][1,2,5]-oxadiazole 1-oxide (**4**) (Scheme 3). ^{13}C resonances at δ 117.13 and 168.54 ppm fit rather well into the range reported for corresponding signals in furoxane derivatives.[21a] The set of vibrations in the IR spectrum of **4** is very similar to that of

Scheme 5



b, E= $(C_2H_5)_3GeCl$, R=$Ge(C_2H_5)_3$
e, E=$Ph_2P(O)Cl$, R=$P(O)Ph_2$
f, E= Ph_2PCl, R=PPh_2
g, E=PhSSPh, R=SPh
h, E= PhSeSePh, R=SePh
i, E=TsF, R=$SO_2C_6H_4$-(*p*-CH_3)
j, E=TsCl, R=Cl
k, E= $HgCl_2$, 0.5 equiv.

furoxane derivative **5** (Scheme 2).[22] Specifically, the characteristic feature of both spectra is the presence of the intense vibration band of the C═N→O group at 1666 cm^{-1}.[23]

As previously reported the azabicyclo[3.2.1]oct-2-ene heterocycle in chloronitrones **6** and **7** (Scheme 2) is stable even when boiling in dilute sulfuric acid.[24] The formation of furoxane derivative **4** obviously results from the low hydrolytic stability of the imidazoline heterocycle. A plausible scheme of transformations of the chloronitrone **2j** is shown in Scheme 4. At the first stage, the hydrolytic cleavage of α-chloronitrone **2j** results in the α-chlorooxime **d** formation. The elimination of HCl from the α-chlorooxime molecule affords the nitrile oxide **e**, dimerization of which produces the furoxane heterocyclic system.[21b] The protonation of the methyl amino group followed by methylamine elimination results in generation of tertiary carbocation **h**. Further nucleophilic attack of the lone electron pair of the $NHCH_3$ group on the cation center and a subsequent deprotonation step yield the final product **4**.

In the conditions analogous to that given above for 3-imidazoline 3-oxide derivatives, 2,2,4,4-tetramethyl-3,4-dihydro-2*H*-pyrrole 1-oxide (**8**) was reacted with $(C_2H_5)_3GeCl$, $HgCl_2$, $Ph_2P(O)Cl$, Ph_2PCl, PhSSPh, PhSePh, TsF, and TsCl, affording the α-organoelement nitrones **9b**,**e**−**k** in good yields (Scheme 5).

The approach we describe here is even applicable to the compounds containing other reactive groups along with the

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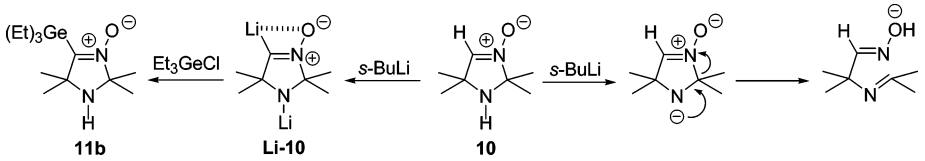
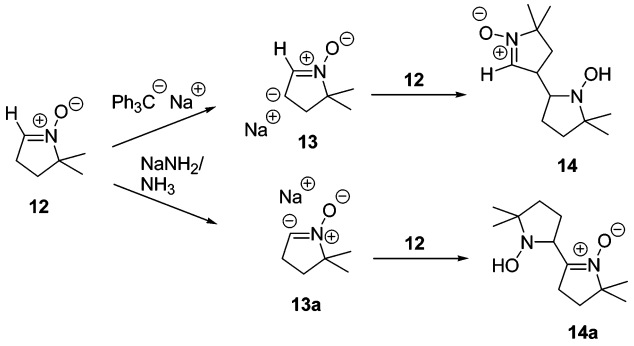
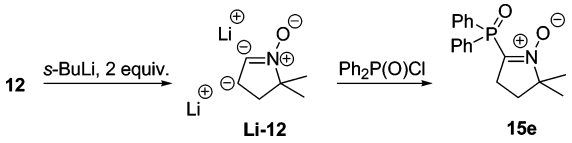
Scheme 6



Scheme 7



Scheme 8



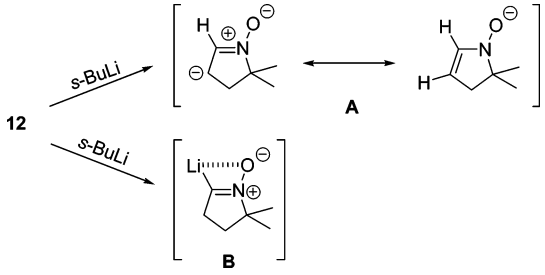
aldonitrone functionality. Thus, the 3-imidazoline derivative **10** containing an "acidic" secondary amino functionality was also introduced into an α-lithiation−electrophilic substitution sequence. The reaction of **Li-10** with $(C_2H_5)_3GeCl$ affords a 30% yield of the α-germanylnitrone **11b** (Scheme 6). In this case the length of the lithiation step was extended to 30 min and 2 equiv of *s*-BuLi was introduced into the reaction. One of the likely reasons for a poor yield of only 30% is the secondary reaction arising from the imidazoline heterocycle cleavage triggered by the amine hydrogen abstraction (Scheme 6).

As it has been reported, 2,2-dimethyl-3,4-dihydro-2*H*-pyrrole 1-oxide (DMPO) (**12**), containing an active methylene group in position 4 of the heterocycle, yields compound **14** upon treatment with triphenylmethyl sodium (Scheme 7).[25] The reaction obviously proceeds through methylene hydrogen abstraction and further nucleophilic attack of the resulting carbanion **13** onto the aldonitrone group of the next DMPO molecule. When sodamide in liquid ammonia was used as a base, an isomeric product, **14a**, was obtained. The product **14a** most likely results from the deprotonation of the aldonitrone group and an attack of the carbanion **13a** formed on the free aldonitrone group of the DMPO molecule (Scheme 7).[25]

We have found that reaction of **12** with $Ph_2P(O)Cl$ under conditions described in the typical procedure (see Experimental Section) results in a complex mixture of products. As for the nitrone **10**, using 2 equiv of *s*-BuLi and elongating the lithiation time to 40 min followed by reaction with electrophile allowed us to obtain the product of phosphorylation of the aldonitrone group, 5-(diphenylphosphinoyl)-2,2-dimethyl-3,4-dihydro-2*H*-pyrrole 1-oxide (**15e**), in a 60% yield (Scheme 8).

In principle, the lithiation of DMPO could proceed by two different pathways. In the first pathway, the abstraction of the methylene hydrogen would lead to resonance-stabilized carbanion **A**, while the methyne hydrogen abstraction pathway would result in the formation of dipole-stabilized organolithium intermediate **B** (Scheme 9).

Scheme 9



Metalation of DMPO with triphenylmethyl sodium reported in ref 25 is apparently evidence of a higher kinetic acidity of the methylene hydrogens in the position 4 as compared with that of the methyne one. This is in line with our own kinetic measurements. In the experiment on CD_3ONa-catalyzed H−D exchange in DMPO monitored by ^1H NMR we have found that in 4 h the multiplet in the region δ 2.6−2.8 ppm, corresponding to the resonance of methylene hydrogens in position 4 of the pyrroline heterocycle, reveals only 33% of the initial integral intensity, meanwhile the intensity of the triplet signal at δ = 7.1 ppm, corresponding to the resonance of the methyne hydrogen, decreases only 5% within the same time.

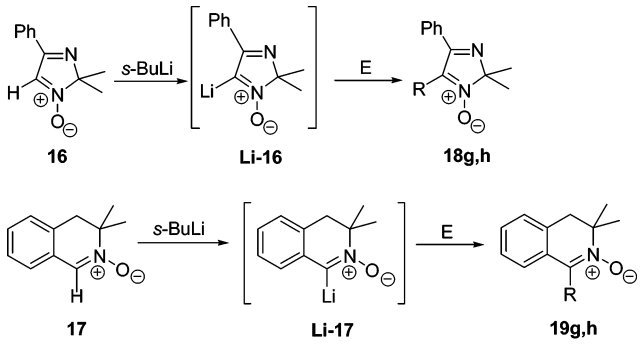
We speculate that using 2 equiv of *s*-BuLi and elongating the lithiation time favor the formation of the dianion **Li-12** (Scheme 8). When **Li-12** reacts with $Ph_2P(O)Cl$, the reaction occurs at the nitrone group, the site of the least acidic proton in **12** and the more nucleophilic carbon in **Li-12**.

Lithiation−Electrophilic Substitution in the Aldonitrones of 2*H*-Imidazole 1-Oxide and 3,4-Dihydroisoquinoline 2-Oxide Series. The lithiation of 2*H*-imidazole 1-oxide **16** (λ_{max} = 280 nm) and 3,4-dihydroisoquinoline 2-oxide **17** (λ_{max} = 309 nm) affords deep purple-violet solutions that imply shifts in λ_{max} to the region of 390−455 nm. Such bathochromic shifts in the electron absorption spectra were not observed in the lithiation of aldonitrones **1**, **8**, **10**, and **12** bearing, in contrast to **16** and **17**, the isolated aldonitrone functions. These bathochromic shifts may be evidence of delocalized character of the electrons of a carbanion lone pair in the organolithium species **Li-16** and **Li-17**. The deprotonation of carbon acids that give rise to delocalized carbanions is well known to result in the pronounced bathochromic shift in their electron absorption spectra relative to the conjugate acids. For example, the ionization of triphenylmethane, $Ph_3CH \rightarrow Ph_3C^-(K^+, THF)$, is accompanied by a shift in λ_{max} from 254 to 486 nm.[26] The true nature of the bathochromic shifts in the species **Li-16** and **Li-17** remains to be discovered. The purple-violet color vanished when solutions of **Li-16** and **Li-17** were reacted with PhSSPh and PhSeSePh; α-substituted nitrones **18g**,**h** and **19g**,**h**, respectively (Scheme 10), were obtained in good yields. This finding provides additional evidence that the color of the reaction mixtures arises due to formation of the organolithium species. Earlier we showed that reaction of **Li-17** with benzaldehyde is also

(25) Brown, R. F. S.; Clark, V. M.; Lamchen, M.; Sir Todd, A. *J. Chem. Soc.* **1959**, *6*, 2116−2122.

(26) Buncel, E.; Menon, B. C. *J. Org. Chem.* **1979**, *44*, 317−320.

Scheme 10



18, **19**: **g**, E= PhSSPh, R=SPh
18, **19**: **h**, E= PhSeSePh, R=SePh

accompanied with the disappearance of the color, affording (3,3-dimethyl-3,4-dihydroisoquinoline-2-oxide-1-yl)phenylmethanol.[27] In striking contrast to the reaction with PhSSPh and PhSeSePh, aldonitrones **16** and **17** yielded inseparable mixtures of products when they were reacted with halogen-containing electrophilic reagents such as $(CH_3)_3SiCl$, $(C_2H_5)_3GeCl$, $HgCl_2$, Ph_2PCl, TsCl, and TsF. In principle, in the systems under study a standard carbanion mechanism could compete with a single-electron transfer (SET) process. An electron transfer from a carbanion to an electrophile substrate could result in an R−Hal bond cleavage and formation of reactive/unstable radicals (cf. ref 28). Meyers et al. have found that in the reaction of organolithium compounds with alkyl halides the SET process could be at least partially suppressed by addition of HMPA or pentynylcopper.[29] For **Li-16** and **Li-17** neither HMPA nor hexynylcopper affected the selectivity of the reaction; in both cases complex mixtures of products were observed. Recently, Adam et al. encountered a similar problem in the lithiation−electrophilic substitution reaction in a series of tetrahydroisoquinoline gulonic amides. The reaction resulted in a moderate yield (less than 50%) with recovery of ca. 30% of the starting material.[30] Neither use of other bases (*s*-BuLi, LiHMDS (lithium hexamethyldisilazide), LDA) nor addition of additives (HMPA, TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine), DMPU (1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone or *N*,*N*′-dimethylpropyleneurea)) led to an increase in the yields.[30] We have found that reactivity of both 2*H*-imidazole 1-oxide **16** and 3,4-dihydroisoquinoline 2-oxide **17** is also unaffected by such additives as HMPA, TMEDA, and DMPU. These findings might evidence that the SET process is hardly involved into the reactions of **Li-16** and **Li-17** with electrophiles, although this reaction pathway cannot be ruled out yet.

Organoelement nitrones **2**, **9**, **11**, **15**, **18**, and **19** were characterized by IR, UV, ^1H and ^{13}C NMR, mass spectrometry (M^+), and elemental analysis (see Experimental Section). Detailed discussion of the characteristic features of the IR and ^{13}C NMR spectra of the organoelement nitrones synthesized in this work is included as Supporting Information. The crystal structures of selected nitrones were determined by X-ray diffraction studies (see Figures 2−9, Table 1, and the Supporting Information). Thermal ellipsoids in Figures 2−9 are drawn at the 30% probability level.

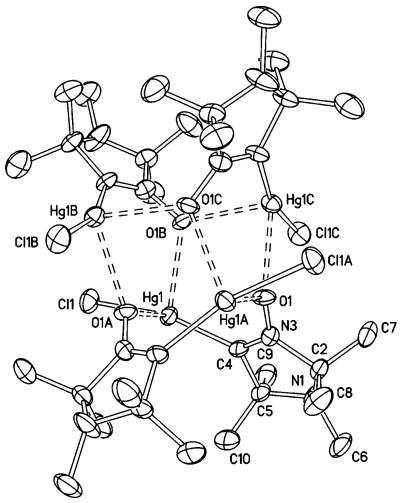


Figure 2. X-ray structure of **2d** (tetrameric unit, hydrogens omitted). Selected bond distances (Å) and angles (deg): Hg(1)−Cl(1) 2.335(3), Hg(1)−C(4) 2.05(1), Hg(1)−O(1A) 2.536(8), Hg(1)−O(1B) 2.509(8), N(3)−O(1) 1.30(1), N(3)−C(4) 1.262(15), C(4)−Hg(1)−Cl(1) 162.7(3), C(4)−Hg(1)−O(1A) 103.0(4), C(4)−Hg(1)−O(1B) 104.5(3).

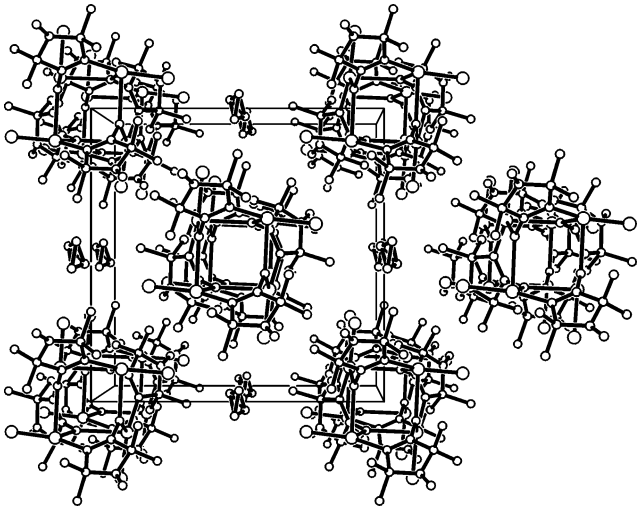


Figure 3. Discrete molecular complexes composed of four monomeric units of **2d**: supermolecules are packed into nanotubular stacks oriented along the *c*-axis. View down the stacking axis of the tetrameric unit is shown; hydrogens are omitted.

Summary

A series of α-organoelement-substituted nitrones, bearing the ClHg-, $(CH_3)_3Si$-, $(C_2H_5)_3Ge$-, $(n\text{-}C_4H_9)_3Sn$-, $Ph_2P(O)$-, Ph_2P-, PhS-, PhSe-, Cl-, and $p\text{-}CH_3(C_6H_4)SO_2$-substituents at the α-carbon atom of the nitrone group, were synthesized. ClHg-, $(CH_3)_3Si$-, $(C_2H_5)_3Ge$-, $(n\text{-}C_4H_9)_3Sn$-, $Ph_2P(O)$-, Ph_2P-, PhSe-, and $p\text{-}CH_3(C_6H_4)SO_2$-substituted nitrones were synthesized for the first time. To access these compounds, we designed an original approach combining (1) α-lithiation of cyclic aldonitrones of 3-imidazoline 3-oxide, pyrroline 1-oxide, 2*H*-imidazole 1-oxide, and 3,4-dihydroisoquinoline 2-oxide series with *s*-BuLi and (2) further reaction of the resulting organolithium derivatives

(27) Voinov, M. A.; Grigor'ev, I. A. *Russ. Chem. Bull. Int. Ed. Engl.* **2002**, *51* (2), 297−305.

(28) See, for instance: (a) Szwarc, M. *Acc. Chem. Res.* **1972**, *5*, 169−176. (b) Andrieux, C. P.; Merz, A.; Savéant, J.-M. *J. Am. Chem. Soc.* **1985**, *107*, 6097−6103. (c) Lund, H.; Daasbjerg, K.; Lund, T.; Pedersen, S. U. *Acc. Chem. Res.* **1995**, *28*, 313−319. (d) Pause, L.; Robert, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **2000**, *122*, 9829−9835. Buncel, E.; Dust, J. M. In *Carbanion Chemistry. Structure and Mechanisms*; Oxford University Press: Oxford, New York, 2003; Chapter 2, pp 105−118.

(29) Meyers, A. I.; Edwards, P. D.; Rieker, W. F.; Bailey, T. R. *J. Am. Chem. Soc.* **1984**, *106*, 3270−3276.

(30) Adam, S.; Pannecoucke, X.; Combret, J.-C.; Quirion, J.-Ch. *J. Org. Chem.* **2001**, *66*, 8744−8750.

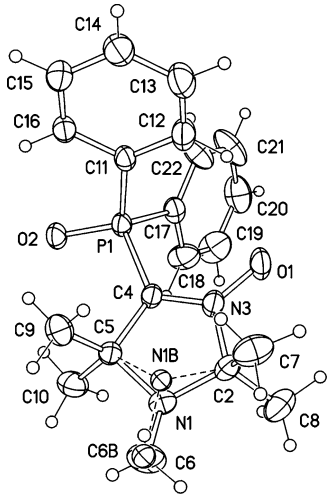


Figure 4. X-ray structure of **2e**. Selected bond distances (Å) and angles (deg): P(1)−O(2) 1.481(1), P(1)−C(4) 1.806(2), P(1)−C(11) 1.802(2), P(1)−C(16) 1.792(2), N(3)−C(4) 1.298(3), N(3)−O(1) 1.281(2), N(3)−C(4)−P(1)−O(2) 170.6(2), N(3)−C(4)−P(1)−C(11) −69.0(2), N(3)−C(4)−P(1)−C(17) 48.2(2).

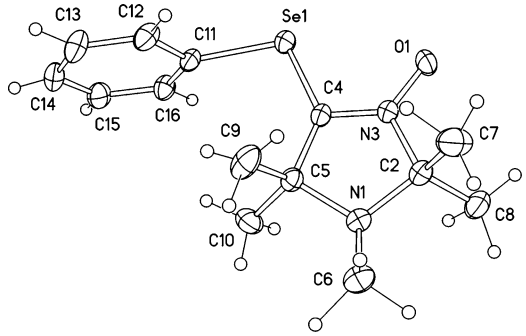


Figure 5. X-ray structure of **2h**. Selected bond distances (Å) and angles (deg): Se(1)−C(4) 1.893(4), Se(1)−C(11) 1.929(5), N(3)−C(4) 1.291(6), N(3)−O(1) 1.299(5), C(4)−Se(1)−C(11) 102.2(2), N(3)−C(4)−Se(1)−C(11) −177.8(3).

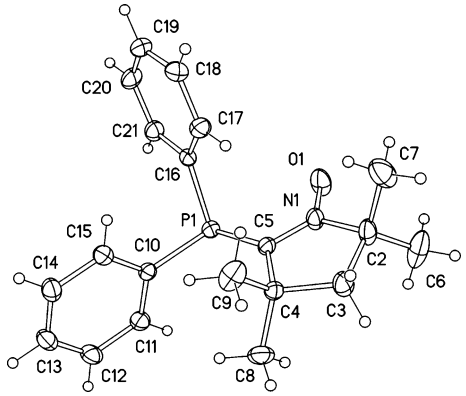


Figure 6. X-ray structure of **9f**. Selected bond distances (Å) and angles (deg): P(1)−C(5) 1.826(3), P(1)−C(10) 1.846(3), P(1)−C(16) 1.833(3), N(1)−C(5) 1.299(3), N(1)−O(1) 1.286(3), N(1)−C(5)−P(1)−C(10) 180.0(3), N(1)−C(5)−P(1)−C(16) 75.7(3).

with electrophilic reagents. Aldonitrones of 3-imidazoline 3-oxide and pyrroline 1-oxide series were found to readily afford the products in a high yield in the lithiation−electrophilic substitution sequence. In contrast, aldonitrones of the 2*H*-imidazole 1-oxide and 3,4-dihydroisoquinoline 2-oxide series react smoothly only with halogen-free electrophiles. An aldonitrone group could be selectively lithiated and reacted with electrophiles even when kinetically more acidic methylene and

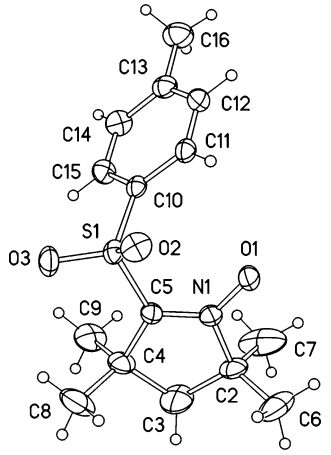


Figure 7. X-ray structure of **9i**. Selected bond distances (Å) and angles (deg): S(1)−C(5) 1.761(2), S(1)−O(2) 1.429(2), S(1)−O(3) 1.433(2), S(1)−C(10) 1.758(2), N(1)−C(5) 1.296(3), N(1)−O(1) 1.264(2), N(1)−C(5)−S(1)−O(3) 178.0(2), C(5)−S(1)−C(10)−C(15) 87.7(2).

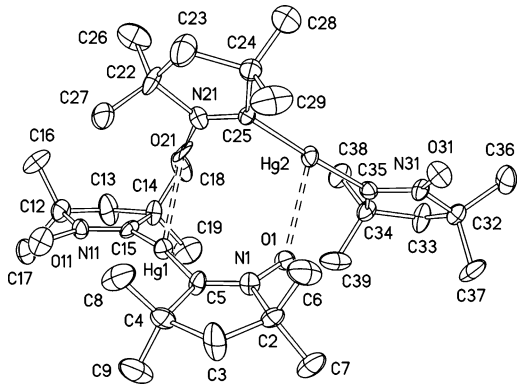


Figure 8. X-ray structure of **9k** (dimeric unit, hydrogens omitted). Selected bond distances (Å) and angles (deg): O(1)−N(1) 1.36-(2), N(1)−C(5) 1.24(2), O(11)−N(11) 1.43(2), N(11)−C(15) 1.27-(3), O(21)−N(21) 1.46(3), N(21)−C(25) 1.25(3), O(31)−N(31) 1.33(2), N(31)−C(35) 1.34(2), Hg(1)−C(5) 2.10(2), Hg(1)−C(15) 2.08(2), Hg(1)−O(21) 2.45(3), Hg(2)−C(25) 2.050(15), Hg(2)−C(35) 2.06(2), Hg(2)−O(1) 2.60(2), O(21)−Hg(1)−C(5) 104.9-(8), O(21)−Hg(1)−C(15) 83.5(7), O(1)−Hg(2)−C(25) 101.8(6), O(1)−Hg(2)−C(35) 81.7(6).

amino groups are present in the molecule, as were observed with 2,2-dimethyl-3,4-dihydro-2*H*-pyrrole 1-oxide and 2,2,5,5-tetramethyl-2,5-dihydro-1*H*-imidazole 3-oxide, respectively. The compounds synthesized in the work were characterized by IR, UV, ^{1}H and ^{13}C NMR, mass spectrometry, and elemental analysis; the crystal structures of several compounds were determined by X-ray diffraction analysis. Characteristic spectral (IR and ^{13}C NMR) and structural features of the synthesized α-organoelement nitrones were discussed. The authors believe that the reaction sequence described here would be of a general interest in the synthesis of cyclic α-heteroatom-substituted nitrones.

Experimental Section

Typical Procedure. An *s*-BuLi hexane solution (2.3×10^{-3} mol) was placed under argon in a three-necked flat-bottomed flask fitted with a magnetic stirrer, dropping funnel, and thermometer and cooled to −70 °C. Then, a solution of **1** (1.9×10^{-3} mol in 3 mL of THF) was added dropwise over 15 min upon vigorous stirring. After this, the solution of electrophile (2.1×10^{-3} mol in 3 mL of THF) was added at once, and the reaction mixture was stirred for

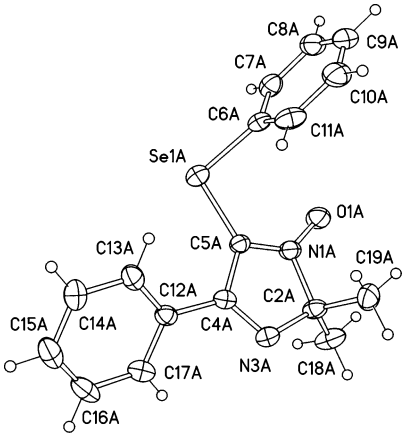


Figure 9. X-ray structure of **18h**. The structure of one of two crystallographically independent molecules is shown. Selected bond distances (Å) and angles (deg): Se(1)−C(5) 1.880(5), 1.892(6), Se(1)−C(6) 1.922(7), 1.911(6), O(1)−N(1) 1.275(7), 1.278(7), N(1)−C(5) 1.293(8), 1.307(8), C(5)−Se(1)−C(6) 97.7(2), 97.2(3), N(1)−C(5)−Se(1)−C(6) −44.5(6), 60.6(5), C(5)−C(4)−C(12)−C(13) −45.7(9), 18(1).

5 min at −70 °C and allowed to warm to 0 °C. In the case of nitrones **2a**,**b**,**d** and **9b** the reaction mixture was quenched with 2 mL of H_2O, the organic layer was quickly separated, and the aqueous phase was extracted with $CHCl_3$. The combined organic layers were dried ($MgSO_4$) over 40 min, and the solvent was evaporated under reduced pressure. The solid precipitate of **2d** was washed with ether, collected on the filter, and recrystallized. In the cases of **2c**, **2j**, and **9j** the reaction mixture was allowed to warm to 0 °C and evaporated under reduced pressure. In the case of **2c** hexane (20 mL) was added to the residue, the precipitate was filtered off and discarded, and the clear hexane solution was evaporated to give the chromatographically pure product. The nitrones **2j** and **9j** were purified by chromatography on Al_2O_3 (hexane/EtOAc, 1:1). In the rest of the cases the residues were purified by chromatography; the conditions are given in each particular case. The synthesized compounds were characterized with IR, UV, NMR, mass spectrometry (M^+), and microanalyses. Characteristics of compounds **2a**−**e**,**j** were given in our preliminary communication.[1]

4-Diphenylphosphanyl-1,2,2,5,5-pentamethyl-2,5-dihydro-1*H*-imidazole 3-oxide, 2f. Separation by preparative thin-layer chromatography (Al_2O_3, hexane/EtOAc, 1:1) gives **2f** as colorless crystals (0.5 g, 77%): mp 93−95 °C (from hexane). IR (KBr, cm^{-1}): 1527 (C═N); UV (EtOH, λ_{max}) 256 nm (ϵ = 9290). ^{1}H NMR ($(CD_3)_2CO$) δ (ppm): 1.18, 1.38 (each s, 6H, CH_3), 2.39 (s, 3H, NCH_3), 7.3−7.5 (m, 10H, arom). ^{13}C NMR ($(CD_3)_2CO$) δ (ppm): 24.60, (CH_3), 25.26 (CH_3, d, $^3J_{C-P}$ = 3 Hz), 27.44 (NCH_3), 66.49 (C5, d, $^2J_{C-P}$ = 14 Hz), 91.21 (C2), 129.07 (d, $^3J_{C-P}$ = 8 Hz, *m*-arom), 129.75 (s, *p*-arom), 134.13 (d, $^1J_{C-P}$ = 7 Hz, *i*-arom), 134.55 (d, $^2J_{C-P}$ = 21 Hz, *o*-arom), 141.32 (d, $^1J_{C-P}$ = 37 Hz, C═N). Anal. Calcd for $C_{20}H_{25}N_2OP$: C, 70,57; H, 7,40; N, 8,23; P, 9,10. Found: C, 70,70; H, 7,30; N, 8,15; P, 9,43. MS (M^+): calcd for $C_{20}H_{25}N_2O$: 340.17045, found 340.17090.

1,2,2,5,5-Pentamethyl-4-phenylsulfanyl-2,5-dihydro-1*H*-imidazole 3-oxide, 2g. The reaction mixture was quenched with 5% aqueous NaOH solution (20 mL), and the organic phase was dried over $MgSO_4$. The residue, obtained after solvent evaporation, solidified after trituration with hexane to give product **2g** as a white powder (0.26 g, 52%): mp 50−52 °C (from hexane). IR (KBr, cm^{-1}): 1538 (C═N). UV (EtOH, λ_{max}): 252 nm (ϵ = 7480). ^{1}H NMR ($CDCl_3$) δ (ppm): 1.26, 1.46 (each s, 6H, CH_3), 2.39 (s, 3H, NCH_3), 7.2−7.4 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$) δ (ppm): 23.98, 24.24 (CH_3), 27.30 (NCH_3), 65.07 (C5), 90.44 (C2), 127.65 (*p*-Ph), 128.88 (*o*-Ph), 130.87 (*m*-Ph), 129.41 (*i*-Ph), 134.85 (C═N). Anal. Calcd for $C_{14}H_{20}N_2OS$: C, 63.63; H, 7.62; N, 10.60; S, 12.13. Found: C, 63.60; H, 7.50; N, 10.33; S, 12,42. MS (M^+): calcd for $C_{14}H_{20}N_2OS$ 264.12963, found 264.12931.

1,2,2,5,5-Pentamethyl-4-phenylselenyl-2,5-dihydro-1*H*-imidazole 3-oxide, 2h. The reaction mixture was quenched with 5% aqueous NaOH solution (20 mL), and the organic phase was dried over $MgSO_4$. The residue, obtained after solvent evaporation, solidified after trituration with hexane to give product **2h** as a white powder (0.41 g, 70%): mp 108−110 °C (from hexane). IR (KBr, cm^{-1}): 1562 (C═N). UV (EtOH, λ_{max}): 259 nm (ϵ = 9830). ^{1}H NMR ($CDCl_3$) δ (ppm): 1.06, 1.40 (each s, 6H, CH_3), 2.28 (s, 3H, NCH_3), 7.2−7.34 (m, 3H, Ph), 7.55−7.7 (m, 2H, Ph). ^{13}C NMR ($CDCl_3$) δ (ppm): 23.92, 24.25 (CH_3), 27.13 (NCH_3), 65.91 (C5), 89.71 (C2), 124.61 (*i*-Ph), 128.66 (*p*-Ph), 128.98 (*m*-Ph), 135.29 (*o*-Ph), 139.42 (C═N). Anal. Calcd for $C_{14}H_{20}N_2OSe$: C, 54.02; H, 6.48; N, 9.00. Found: C, 54.22; H, 6.35; N, 8.80. MS (M^+): calcd for $C_{14}H_{20}N_2OSe$ 264.12963, found 264.12931.

1,2,2,5,5-Pentamethyl-4-(toluene-4-sulfonyl)-2,5-dihydro-1*H*-imidazole 3-oxide, 2i. Separation by preparative thin-layer chromatography (Al_2O_3, hexane/EtOAc, 2:1) gives **2i** as colorless crystals (0.26 g, 43%): mp 193−194 °C (from hexane/EtOAc, 1:3). IR (KBr, cm^{-1}): 1542 (C═N), 1331 (S═O asym.), 1154 (S═O sym.). UV (EtOH, λ_{max}): 231 nm (ϵ = 11147), 267 nm (ϵ = 9336). ^{1}H NMR ($CDCl_3$) δ (ppm): 1.33, 1.57 (each s, 6H, CH_3), 2.41 (s, 3H, NCH_3), 2.32 (s, 3H, *p*-CH_3), 7.31 (d, 2H, J_{HH} = 8 Hz), 7.97 (d, 2H, J_{HH} = 8 Hz). ^{13}C NMR ($CDCl_3$) δ (ppm): 21.63 (CH_3−Ar), 23.92, 24.27 (CH_3), 26.60 (NCH_3), 64.73 (C2), 92.73 (C5), 129.13 (arom), 129.23 (arom), 135.21 (*i*-1-arom), 142.67 (C═N), 145.39 (*i*-4-arom). Anal. Calcd for $C_{15}H_{22}N_2O_3S$: C, 58.04; H, 7.14; N, 9.02; S, 10.33. Found: C, 58.19; H, 7.30; N, 9.18; S, 10.16. MS (M^+): calcd for $C_{15}H_{22}N_2O_3S$ 310.13511, found 310.13482.

Bis(1,2,2,5,5-Penthamethyl-2,5-dihydro-1*H*-imidazole-3-oxide-4-yl)mercury, 2k. An oily product obtained after solvent removal was chromatographed on silica gel with $CHCl_3$ + 5% CH_3OH as eluent to give **2k** as colorless crystals (0.19 g, 40%); mp 185−188 °C (from hexane). IR (KBr, cm^{-1}): 1558 (C═N). UV (EtOH, λ_{max}) 263 nm (ϵ = 8900). ^{1}H NMR ($CDCl_3$) δ (ppm): 1.28, 1.44 (each s, 6H, CH_3), 2.33 (s, 3H, NCH_3). ^{13}C NMR ($CDCl_3$) δ (ppm): 24.36, 25.00 (CH_3), 27.63 (NCH_3), 66.44 (C5), 91.61 (C2), 179.82 (C═N). Anal. Calcd for $C_{16}H_{30}HgN_4O_2$: C, 37.60; H, 5.92; N, 10.97. Found: C, 37.88; H, 5.91; N, 10.84. MS (M^+): calcd for $C_{16}H_{30}HgN_4O_2$ 512.20749, found 512.20765.

4,4,5,6,6-Pentamethyl-5,6-dihydro-4*H*-pyrrolo[3,4-*c*][1,2,5]-oxadiazole 1-oxide, 4. Method A. The chloronitrone **2j** (0.2 g, 0.001 mol), BTEAC (0.04 g, 1.75 × 10^{-4} mol), and KF × $2H_2O$ (0.5 g, 0.005 mol) were added to a mixture of benzene and water (1:1, 10 mL) and refluxed upon vigorous stirring for 5 days. The organic layer was separated, the aqueous phase was extracted with $CHCl_3$ (1 × 10 mL), and the combined organic extracts were dried over $MgSO_4$. Solvents were removed under reduced pressure; the residue was chromatographed on Al_2O_3 (petroleum ether + 7% EtOAc, fraction with R_f = 0.5 was collected), to give **4** (0.045 g, 43%).

Method B. A solution of the chloronitrone **2j** (0.2 g) in a mixture of hexane and 2% aqueous acetic acid (5 mL, 1:1) was vigorously stirred for 30 min. The hexane solution was washed with 5% aqueous $NaHCO_3$ solution, dried over $MgSO_4$, and chromatographed as specified above. Compound **4** was obtained as colorless crystals (0.085 g, 80%), mp 95−97 °C (from hexane). IR (KBr, cm^{-1}): 1660 (C═N→O). UV (EtOH, λ_{max}) 263 (4677). ^{1}H NMR ($CDCl_3$, δ, ppm): 1.40 (s, 6H, $2CH_3$), 1.45 (s, 6H, $2CH_3$), 2.32 (s, 3H, N−CH_3). ^{13}C NMR ($CDCl_3$, δ, ppm): 22.41, 24.30 (CH_3), 25.51(NCH_3), 58.57, 59.21 (C−C═N), 118.54 (*C*═N→O), 168.55 (*C*═N). Anal. Calcd for $C_9H_{15}N_3O_2$: C, 54.81; H, 7.67; N, 21.30. Found: C, 54.98; H, 7.73; N, 21.23. MS (M^+): calcd for $C_9H_{15}N_3O_2$ 197.11643, found 197.11655.

2,2,4,4-Tetramethyl-5-triethylgermanyl-3,4-dihydro-2*H*-pyrrole 1-oxide, 9b. The product was purified by chromatography

Table 1. Crystal Data and Experimental Parameters for the Crystal Structure Analyses of 2d, 2e, 2h, 9f, 9i, 9k, and 18h

	2d	2e	2h	9f	9i	9k	18h
Brutto formula	$C_8H_{15}ClHgN_2O$ + 0.5 CH_3OH	$C_{20}H_{25}N_2O_2P$	$C_{14}H_{20}N_2OSe$	$C_{20}H_{24}NOP$	$C_{15}H_{21}NO_3S$	$C_{16}H_{28}HgN_2O_2$	$C_{17}H_{16}N_2OSe$
M	407.28	356.39	311.28	325.37	295.39	480.99	343.28
cryst size (mm^3)	0.5 × 0.28 × 0.16	0.8 × 0.44 ×+ 0.14	1.08 × 0.30 × 0.10	0.93 × 0.2 × 0.2	1.0 × 0.17 × 0.17	1.0 × 0.5 × 0.4	0.9 × 0.5 × 0.2
cryst syst	tetragonal	monoclinic	orthorhombic	orthorhombic	monoclinic	monoclinic	orthorhombic
space group	$I\bar{4}$	$P2_1/c$	$Pna2_1$	$P2_12_12_1$	$P2_1/n$	$P2_1$	$P2_12_12_1$
a (Å)	14.521(1)	12.4029(8)	23.007(2)	6.0014(6)	6.5914(9)	11.862(4)	5.5666(5)
b (Å)	14.521(1)	8.9187(5)	6.2670(6)	12.545(1)	27.895(4)	11.552(3)	9.0518(7)
c (Å)	12.388(1)	17.793(1)	10.081(1)	23.887(3)	8.802(1)	13.875(5)	61.911(6)
β (deg)	90	90.994(6)	90	90	92.128(15)	102.19(3)	90
volume ($Å^3$)	2611.8(3)	1967.9(2)	1453.6(3)	1798.4(3)	1617.3(4)	1858(1)	3119.6(5)
Z, ρ_{calc} (Mg/m^3)	8, 2.071	4, 1.203	4, 1.422	4, 1.202	4, 1.213	4, 1.719	8, 1.462
μ (mm^{-1})	11.968	0.154	2.574	0.157	0.206	8.288	2.407
F(000) (e)	1528	760	640	696	632	936	1392
scan mode, θ_{max} (deg)	$\theta/2\theta$, 30.00	$\theta/2\theta$, 25.00	$\theta/2\theta$, 24.99	$\theta/2\theta$, 27.5	$\theta/2\theta$, 25.00	$\theta/2\theta$, 27.52	ω, 21.98
no. of unique reflns (R_{int})	2130(0.0184)	3468(0.0152)	1350 (0.045)	2390(0.0)	2817(0.015)	4447(0.0345)	2932(0.0525)
abs corr	empirical	integration	integration	integration	integration	integration	empirical
T_{min}/T_{max}	0.4247/0.9256	0.9394/0.9797	0.4470/0.7983	0.9642/9782	0.9222/0.9760	0.0627/0.2218	0.5199/0.9980
goodness-of-fit on F^2	1.034	1.021	1.128	1.062	1.047	1.095	1.059
R_1, wR_2 [$I > 2\sigma(I)$]	0.0400, 0.0934	0.0456, 0.1104	0.0316, 0.0807	0.0455,0.1136	0.0494, 0.1346	0.0574, 0.1642	0.0416, 0.1119
no. of reflns [$I > 2\sigma(I)$]	1877	2653	1245	2000	2338	4116	2712
R_1, wR_2 (all data)	0.0490, 0.0987	0.0650, 0.1230	0.0358, 0.0838	0.0574, 0.1243	0.0593, 0.1436	0.0619, 0.1679	0.0458, 0.1170

(Al_2O_3, $CHCl_3$/hexane, 9:1) to give **9b** as a colorless oil (0.45 g, 80%). IR (neat, cm^{-1}): 1523 (C═N). UV (EtOH, λ_{max}): 259 (ϵ = 4677). ^{1}H NMR ($CDCl_3$, δ, ppm): 0.9−1.07 (M, 15H, Ge−Et_3), 1.13, 1.37 (both s, 6H, CH_3), 1.70 (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$, δ, ppm): 3.75 (Ge−CH_3CH_2); 9.00 (Ge−CH_3CH_2), 28.06, 29.16 (both CH_3), 42.53 (C4), 50.69 (CH_2), 74.46 (C2), 154.69 (C═N). Anal. Calcd for $C_{14}H_{29}GeNO$: C, 56.05; H, 9.74; N, 4.67. Found: C, 56.30; H, 9.97; N, 4.44.

5-(Diphenylphosphinoyl)-2,2,4,4-tetramethyl-3,4-dihydro-2*H*-pyrrole 1-oxide, 9e, was isolated as colorless crystals (0.47 g, 73%): mp 177−178 °C (from hexane/benzene, 1:1). IR (KBr, cm^{-1}): 1527 (C═N). UV (EtOH, λ_{max}): 224 nm (ϵ = 16730), 265 nm (ϵ = 7995). ^{1}H NMR ($CDCl_3$) δ (ppm): 1.33, 1.55 (each s, 6H, CH_3), 2.05 (s, 2H, CH_2), 7.3−7.5 (m, 6H, arom), 7.7−7.9 (m, 4H, arom). ^{13}C NMR ($CDCl_3$) δ (ppm): 27.53, 29.19 (CH_3), 43.10 (d, $^2J_{C-P}$ = 9 Hz, C4), 50.48 (d, $^3J_{C-P}$ = 7 Hz, CH_2), 75.30 (d, $^3J_{C-P}$ = 6 Hz, C2), 128.07 (d, $^2J_{C-P}$ = 13 Hz, *o*-arom), 130.98 (d, $^1J_{C-P}$ = 120 Hz, *i*-arom), 131.27 (d, $^3J_{C-P}$ = 11 Hz, *m*-arom), 131.81 (d, $^4J_{C-P}$ = 2 Hz, *p*-arom), 142.62 (d, $^1J_{C-P}$ = 102 Hz, C═N). Anal. Calcd for $C_{20}H_{24}NO_2P$: C, 70.36; H, 7.09; N, 4.10; P, 9.07. Found: C, 70.30; H, 7.13; N, 4.13; P, 8.72.

5-(Diphenylphosphanyl)-2,2,4,4-tetramethyl-3,4-dihydro-2*H*-pyrrole 1-oxide, 9f, was isolated as colorless crystals (0.44 g, 71%); mp 136−138 °C (from hexane/EtOAc, 15:1). IR (KBr, cm^{-1}): 1510 (C═N). UV (EtOH, λ_{max}): 257 nm (ϵ = 8640). ^{1}H NMR ((CD_3)$_2$CO) δ (ppm): 1.13, 1.37 (each s, 6H, CH_3), 2.11 (s, 2H, CH_2), 7.2−7.6 (m, 10H, arom). ^{13}C NMR ((CD_3)$_2$CO) δ (ppm): 28.11 (CH_3), 29.97 (d, $^3J_{C-P}$ = 3 Hz, CH_3), 43.47 (d, $^2J_{C-P}$ = 10.5 Hz, C4), 50.85 (d, $^3J_{C-P}$ = 2 Hz, CH_2), 74.19 (C2), 128.99 (d, $^3J_{C-P}$ = 8 Hz, *m*-arom), 129.60 (s, *p*-arom), 134.75 (d, $^2J_{C-P}$ = 22 Hz, *o*-arom), 134.75 (d, $^1J_{C-P}$ = 7 Hz, *i*-arom), 132.33 (d, $^1J_{C-P}$ = 11 Hz, C═N). Anal. Calcd for $C_{20}H_{24}NOP$: C, 73.82; H, 7.43; N, 4.30; P, 9.52. Found: C, 73.56; H, 7.44; N, 4.35; P, 9.51. MS (M^+): calcd for $C_{20}H_{24}NOP$ 325.15954, found 325.15952.

2,2,4,4-Tetramethyl-5-phenylsulfanyl-3,4-dihydro-2*H*-pyrrole 1-oxide, 9g. The reaction mixture was quenched with 5% aqueous NaOH solution (20 mL), 15 mL of ether was added, and the organic layer was separated from the aqueous phase, washed once with 5% aqueous NaOH solution (10 mL), and dried over $MgSO_4$. **9g** was isolated as colorless crystals (0.31 g, 67%): mp 72−74 °C (from hexane/EtOAc, 4:1). IR (KBr, cm^{-1}): 1530 (C═N). UV (EtOH, λ_{max}): 256 nm (ϵ = 8550). ^{1}H NMR ((CD_3)$_2$CO) δ (ppm): 1.22, 1.39 (each s, 6H, CH_3), 2.14 (s, 2H, CH_2), 7.2−7.35 (m, 5H, Ph). ^{13}C NMR ((CD_3)$_2$CO) δ (ppm): 27.94, 28.92 (CH_3), 42.42 (C4), 48.54 (CH_2), 74.03 (C2), 127.61 (*p*-Ph), 129.62 (*o*-Ph), 130.50 (*m*-Ph), 132.04 (*i*-Ph),139.65 (C═N). Anal. Calcd for $C_{14}H_{19}NOS$: C, 67.43; H, 7.68; N, 5.62; S, 12.85. Found: 67.47; H, 7.70; N, 5.38; S, 12.67. MS (M^+): calcd for $C_{14}H_{19}NOS$ 249.11873, found 249.11906.

2,2,4,4-Tetramethyl-5-phenylselenyl-3,4-dihydro-2*H*-pyrrole 1-oxide, 9h. The reaction mixture was quenched with 5% aqueous NaOH solution (20 mL), 15 mL of ether was added, and the organic layer was separated from the aqueous phase, washed once with 5% aqueous NaOH solution (10 mL), and dried over $MgSO_4$. The residue obtained after removal of solvents was triturated with hexane/*tert*-butyl methyl ether (7:1) to give **9h** as colorless crystals (0.4 g, 73%): mp 98−100 °C (from hexane). IR (KBr, cm^{-1}): 1540 (C═N). UV (EtOH, λ_{max}): 261 nm (ϵ = 10530). ^{1}H NMR ($CDCl_3$) δ (ppm): 0.98, 1.38 (each s, 6H, CH_3), 1.97 (s, 2H, CH_2), 7.2−7.4 (m, 3H, Ph), 7.6−7.75 (m, 2H, Ph). ^{13}C NMR ($CDCl_3$) δ (ppm): 27.65, 29.06 (CH_3), 43.68 (C4), 50.53 (CH_2), 72.16 (C2), 124.48 (*i*-Ph), 129.14 (*o*,*m*-Ph), 136.52 (*p*-Ph), 145.30 (C═N). Anal. Calcd for $C_{14}H_{19}NOSe$: C, 56.74; H, 6.46; N, 4.73; Found: C, 57.08; H, 6.23; N, 4.67.

2,2,4,4-Tetramethyl-5-(toluene-4-sulfonyl)-3,4-dihydro-2*H*-pyrrole 1-oxide, 9i. The product was isolated by chromatography on Al_2O_3 (hexane/EtOAc, 3:1), and the residue obtained after solvent evaporation was triturated with hexane to give **9i** as colorless crystals (0.22 g, 40%): mp 201−203 °C (from hexane/EtOAc, 1:1). IR (KBr, cm^{-1}): 1531 (C═N), 1325 (S═O asym.), 1152 (S═O sym.). UV (EtOH, λ_{max}): 231 nm (ϵ = 12331), 272 nm (ϵ = 8296). ^{1}H NMR ((CD_3)$_2$CO) δ (ppm): 1.27, 1.56 (each s, 6H, CH_3), 2.15 (s, 2H, CH_2), 2.43 (s, 3H, *p*-CH_3), 7.41 (d, arom 2H, J_{HH} = 8 Hz), 7.96 (d, arom 2H, J_{HH} = 8 Hz). ^{13}C NMR ((CD_3)$_2$CO) δ (ppm): 21.72 (CH_3−Ar) 27.52, 29.19 (CH_3), 42.49 (C4), 49.74 (CH_2), 76.70 (C2), 129.58, 129.85, 130.25 (arom), 136.95 (*i*-1-arom), 145.87 (*i*-

4-arom), 145.74 (C═N). Anal. Calcd for $C_{15}H_{21}NO_3S$: C, 60.99; H, 7.17; N, 4.74; S, 10.85. Found: 61.18; H, 7.30; N, 4.69; S, 10.77.

5-Chloro-2,2,4,4-tetramethyl-3,4-dihydro-2*H*-pyrrole 1-oxide, 9j. The crude product obtained after removal of solvents was dissolved in hexane, and the precipitate was filtered off. Hexane was removed under reduced pressure (the temperature of the water bath did not exceed 20 °C), affording the solid crystalline product, which was dissolved at room temperature in a minimal amount of dry hexane and allowed to stay at −20 °C overnight to give **9j** as colorless crystals (0.28 g, 85%): mp 89−90 °C (hexane). IR (KBr, cm^{-1}): 1567 (C═N). UV (EtOH, λ_{max}): 238 ($\epsilon = 7397$). ^{1}H NMR (CCl_4, δ, ppm): 1.27, 1.40 (both s, 6H, $2CH_3$), 2.03 (c, 2H, CH_2). ^{13}C NMR (CCl_4, δ, ppm): 29.47, 29.76 (CH_3), 42.21 (C4), 49.17 (CH_2), 74.18 (C2), 137.32 (C═N). Anal. Calcd for $C_8H_{14}ClNO$: C, 54.70; H, 8.03; N, 7.97; Cl, 20.18. Found: C, 54.67; H, 8.24; N, 7.85; Cl, 19.29. MS (M^+): calcd for $C_8H_{14}ClNO$ 175.07639, found 175.07663.

Bis(2,2,4,4-tetramethyl-3,4-dihydro-2*H*-pyrrole-1-oxide-4-yl)-mercury, 9k. The residue, obtained after the solvent evaporation, was triturated with hexane, and the solid product formed was washed with ether to give **9k** as colorless crystals (0.22 g, 48%): mp 202−204 °C (from hexane/EtOAc, 10:1). IR (KBr, cm^{-1}): 1533, 1544 (C═N). UV (EtOH, λ_{max}): 266 nm ($\epsilon = 5603$). ^{1}H NMR ($CDCl_3$) δ (ppm): 1.21, 1.44 (each s, 6H, CH_3), 1.97 (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$) δ (ppm): 28.08, 29.48 (CH_3), 42.85 (C4), 50.93 (CH_2), 75.87 (C2), 183.72 (C═N). Anal. Calcd for $C_{16}H_{28}HgN_2O_2$: C, 39.95; H, 5.87; N, 5.82. Found: C, 40.13; H, 6.03; N, 5.77. MS (M^+): calcd for $C_{16}H_{28}HgN_2O_2$ 482.18570, found 482.20115.

2,2,5,5-Tetramethyl-4-triethylgermanyl-2,5-dihydro-1*H*-imidazole 3-oxide, 11b. The length of the lithiation step was extended to 30 min, and 2 equiv of *s*-BuLi was used in the reaction. The reaction was quenched with water, and the oily product obtained after solvent evaporation was separated by chromatography (silica gel, $CHCl_3$ + 10% CH_3OH) to give **11b** as a colorless oil (0.17 g, 30%). IR (neat, cm^{-1}): 1527 (C═N), 3273 (N−H). UV (EtOH, λ_{max}): 249 ($\epsilon = 7943$). ^{1}H NMR ($CDCl_3$, δ, ppm): 0.95−1.15 (m, 15H, Ge−Et_3), 1.30, 1.53 (both s, 6H, CH_3), 1.94 (br s, 1H, N−H). ^{13}C NMR ($CDCl_3$, δ, ppm): 3.61 (Ge−CH_2CH_3), 9.0 (Ge−CH_2CH_3), 29.07, 29.23 (CH_3), 63.93 (C5), 99.74 (C2), 150.47 (C═N→O). Anal. Calcd for $C_{13}H_{28}GeN_2O$: C, 51.87; H, 9.38; N, 9.31. Found: C, 51.94; H, 9.44; N, 9.29.

5-(Diphenylphosphinoyl)-2,2-dimethyl-3,4-dihydro-2*H*-pyrrole 1-oxide, 15e. The length of the lithiation step was extended to 40 min, and 2 equiv of *s*-BuLi was used in the reaction. The reaction was quenched with water, and the oily product obtained after solvent evaporation was separated by chromatography (Al_2O_3, EtOAc) to give **15e** as colorless crystals (0.35 g, 60%): mp 111−113 °C (from hexane). IR (KBr, cm^{-1}): 1533 (C═N). UV (EtOH, λ_{max}): 225 nm ($\epsilon = 28183$), 265 nm ($\epsilon = 14454$). ^{1}H NMR ($CDCl_3$, δ, ppm): 1.32 (s, 6H, $2CH_3$), 2.11 (t, 2H 3-CH_2), 2.96 (dt, 2H, 4-CH_2, $^3J_{P-H} = 2.5$ Hz), 7.3−7.6 (m, 6H, arom.), 7.7−7.9 (m, 4H, arom.). ^{13}C NMR ($CDCl_3$, δ, ppm): 25.01 (s, $2CH_3$), 26.72 (d, CH^2, $^3J_{C-P} = 9$ Hz, C4), 33.61 (d, CH_2, $^4J_{C-P} = 7$ Hz, C3), 77.79 (d, $^3J_{C-P} = 6.5$ Hz, C2), 128.24 (d, $^2J_{C-P} = 13$ Hz, *o*-arom.), 129.23 (s, *i*-arom.), 131.27 (d, $^3J_{C-P} = 11$ Hz, *m*-arom.), 132.20 (d, $^4J_{C-P} = 3$ Hz, *p*-arom.), 135.87 (d, $^1J_{C-P} = 105$ Hz, C═N). Anal. Calcd for $C_{18}H_{20}NO_2P$: C, 69.00; H, 6.43; N, 4.47; P, 9.89. Found: C, 69.11; H, 6.53; N, 4.61; P, 9.74. MS (M^+): calcd for $C_{18}H_{20}NO_2P$ 313.12316, found 313.12281.

2,2-Dimethyl-4-phenyl-5-phenylsulfanyl-2*H*-imidazole 1-oxide, 18g. The reaction mixture was quenched with 5% aqueous NaOH solution (20 mL), 15 mL of ether was added, and the organic layer was separated from the aqueous phase, washed once with 5% aqueous NaOH solution (10 mL), and dried over $MgSO_4$. The residue obtained after the solvent evaporation was chromatographed on Al_2O_3 (hexane/CH_2Cl_2/EtOAc, 5:1:1) to give **18g** as colorless crystals (0.36 g, 65%): mp 76−78 °C (from hexane/EtOAc, 5:1). IR (KBr, cm^{-1}): 1579, 1539, 1499, 1475, 1447 (C═C, C═N). UV (EtOH, λ_{max}): 241 nm ($\epsilon = 14310$). ^{1}H NMR ($(CD_3)_2CO$) δ (ppm): 1.57 (s, 6H, CH_3), 7.10−7.33 (m, 5H, Ph), 7.42−7.60 (m, 3H, Ph), 8.00−8.15 (m, 2H, Ph). ^{13}C NMR ($(CD_3)_2CO$) δ (ppm): 24.98 (CH_3), 101.08 (C2), 128.06 (*p*-Ph−S), 131.80 (*p*-Ph), 129.11, 129.18 (both *o*-Ph), 129.59, 130.17 (both *m*-Ph), 132.20, 133.18 (both *i*-Ph), 137.95 (C═N→O), 166.50 (C═N). Anal. Calcd for $C_{17}H_{16}N_2OS$: C, 68.89; H, 5.44; N, 9.45; S, 10.82. Found: 68.88; H, 5.52; N, 9.29; S, 10.95. MS (M^+): calcd for $C_{17}H_{16}N_2OS$ 296.09833, found 296.09829.

2,2-Dimethyl-4-phenyl-5-phenylselenyl-2*H*-imidazole 1-oxide, 18h. The workup procedure was similar to that of **18g**. The crude material was purified by chromatography (Al_2O_3, THF/CCl_4, 1:12) to give **18h** as colorless crystals (0.32 g, 50%): mp 73−75 °C (from hexane). IR (KBr, cm^{-1}): 1576, 1556, 1541, 1496, 1470 (C═C, C═N). UV (EtOH, λ_{max}): 246 nm ($\epsilon = 12214$), 341 ($\epsilon = 3018$). ^{1}H NMR ($CDCl_3$) δ (ppm): 1.62 (s, 6H, CH_3), 7.05−7.50 (m, 8H, Ph), 7.80−7.95 (m, 2H, Ph). ^{13}C NMR ($CDCl_3$) δ (ppm): 24.66 (CH_3), 100.72 (C2), 127.98, 128.10, 128.16, 129.20, 130.74, 132.43 (arom.), 126.62, 131.93 (both *i*-Ph), 129.44 (C═N→O), 166.44 (C═N). Anal. Calcd for $C_{17}H_{16}N_2OSe$: C, 59.48; H, 4.70; N, 8.16. Found: 59.64; H, 4.62; N, 7.96.

3,3-Dimethyl-1-phenylsulfanyl-3,4-dihydroisoquinoline 2-oxide, 19g. The workup procedure was similar to that of **18g**. The crude material was purified by chromatography (Al_2O_3, THF/CCl_4, 1:8) to give **19g** as a colorless oil (0.28 g, 53%). IR (neat, cm^{-1}): 1581 (C═N). UV (EtOH, λ_{max}): 232 nm ($\epsilon = 1454$), 306 nm ($\epsilon = 1021$). ^{1}H NMR ($(CD_3)_2CO$) δ (ppm): 1.34 (s, 6H, CH_3), 3.21 (s, 2H, CH_2), 7.10−7.55 (m, 9H, arom.). ^{13}C NMR ($(CD_3)_2CO$) δ (ppm): 24.58 (CH_3), 41.74 (CH_2), 69.89 (C3), 126.48, 127.36, 127.80, 128.60, 128.86, 129.82, 129.86 (arom.), 131.68 (*i*-Ph−S), 130.92, 134.11 (both *i*-arom.), 135.71 (C═N). Anal. Calcd for $C_{17}H_{17}NOS$: C, 72.05; H, 6.05; N, 4.94; S, 11.31. Found: C, 72.13; H, 6.10; N, 4.90; S, 11.20. MS (M^+): calcd for $C_{17}H_{17}NOS$ 283.10308, found 283.10308.

3,3-Dimethyl-1-phenylselenyl-3,4-dihydroisoquinoline 2-oxide, 19h. The workup procedure was similar to that of **18g**. The crude material was purified by chromatography (Al_2O_3, THF/CCl_4, 1:8) to give **19h** as colorless crystals (0.4 g, 66%): mp 66−68 °C (hexane). IR (neat, cm^{-1}): 1577 (C═N). UV (EtOH, λ_{max}): 288 nm ($\epsilon = 4270$). ^{1}H NMR ($CDCl_3$) δ (ppm): 1.40 (s, 6H, CH_3), 3.07 (s, 2H, CH_2), 6.85−6.95 (m, 2H, arom); 7.05−7.28 (m, 5H, arom), 7.4−7.5 (m, 2H, arom). ^{13}C NMR ($CDCl_3$) δ (ppm): 24.18 (CH_3), 42.13 (CH_2), 68.17 (C3), 126.46, 127.28, 127.71, 128.05, 129.07, 133.78 (arom.), 129.12, 131.20 (*i*-Ph−Se). Anal. Calcd for $C_{17}H_{17}NOS$: C, 72.05; H, 6.05; N, 4.94; S, 11.31. Found: C, 72.15; H, 6.10; N, 4.94; S, 11.20.

Acknowledgment. The authors thank Dr. V. Bardin (Novosibirsk) for fruitful discussions and for the triethylgermanium chloride and tributyltin bromide, which were kindly donated. The comments of Drs. A. I. Smirnov and R. McArthur (Raleigh) are gratefully acknowledged.

Supporting Information Available: Crystallographic data in CIF format for complex [Cu(hfac)$_2$phln] and structures **2d, 2e**, **2h**, **9f**, **9i, 9k**, and **18h**; results of crystallographic analyses; discussions of the IR and ^{13}C NMR spectra, general comments (Experimental Section), synthesis of [Cu(hfac)$_2$phln] complex and details of its X-ray diffraction study, details of X-ray data collection and structure determination of **2d**, **2e**, **2h**, **9f**, **9i**, **9k**, and **18h**. These materials are available free of charge via the Internet at http://pubs.acs.org.

OM060883O