

**Table I.** Results of Lasalocid-Mediated Transport of Co(III) Amine Complexes through a CHCl<sub>3</sub> Bulk Liquid Membrane after 6 h at 25 °C

complex	initial source phase concn/10 <sup>-3</sup> mol dm <sup>-3</sup>	av flux rate/10 <sup>-4</sup> mmol h <sup>-1</sup> cm <sup>-2</sup>	% enantiomeric purity (receiving phase)	% transport
2	10.0 <sup>a</sup>	4.3 ± 0.1 <sup>b</sup>		6.3
3 <sup>c</sup>	20.0 <sup>d</sup>	5.9 ± 0.8	10 ± 1 <sup>e</sup>	4.3
4 <sup>c</sup>	20.0 <sup>f</sup>	7.1 ± 0.3	27 ± 4 <sup>g</sup>	5.2

<sup>a</sup>The initial pH was 6.0, rising to 6.8 at the completion of the run. <sup>b</sup>Mean and average deviation from three separate runs. <sup>c</sup>Racemic mixture. <sup>d</sup>Initial pH 5.9. <sup>e</sup>Corresponds to 55% Δ isomer, 45% Λ isomer. <sup>f</sup>Initial pH 5.5. <sup>g</sup>Corresponds to 36.5% Δ isomer, 63.5% Λ isomer.

host-guest adduct formation between ammine complexes and crown polyethers.

Lasalocid A has also been employed previously for the optical resolution of chiral amines by fractional crystallization of their lasalocid salts.<sup>8</sup> Similarly, synthetic chiral macrocycles have been used as ionophores for the selective enantiomeric recognition and transport of a number of optically active guests such as asymmetric ammonium ions.<sup>9,10</sup> The aim of the present project was to investigate the potential of lasalocid A as an ionophore for the transport of inert metal complexes such as [Co(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub> (2), [Co(1,2-diaminoethane)<sub>3</sub>]Cl<sub>3</sub> (3), and *u-cis*-[Co(diethylenetriamine)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> (4). In addition, the prospect of achieving chiroselective transport of the latter two complexes was of especial interest.

Successful transport of the Co(III) complexes 2-4 was achieved by using a system involving aqueous source and receiving phases separated by a chloroform phase containing a 1 mM concentration of the ionophore as its sodium salt.<sup>11</sup> The arrangement used for the transport of [Co(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub> (2) is illustrated in Figure 1, and details of the experiment are summarized in Table I; it should be noted that, given sufficient time, transport proceeds to completion.

For 3 and 4, a racemic mixture of the respective complex (total concentration 20 mM) was present in the source phase at the beginning of each transport run. Details of the experiments, which were terminated after 6 h, are also summarized in Table I. At the end of these experiments, partial resolution of the complex in the receiving phase was observed in each case. For 3, the observed optical rotation of the receiving phase corresponded to 55% of the Δ isomer and 45% of the Λ isomer being present.<sup>12</sup> For 4, the resolution was greater, with 36.5% of the Δ isomer and 63.5% of the Λ isomer occurring in the source phase. In each case,

(7) Very recently, crown ether ionophores incorporating proton-ionizable groups have been shown to facilitate the hydrophobic membrane transport of Co(II) and Ni(II) from a source phase consisting of ammonium hydroxide (pH 12). The evidence indicated that transport to the acid receiving phase involved adduct formation between the crown ionophore and the respective metal(II) ammine species. See: Strzelbicki, J.; Charewicz, W. A.; Liu, Y.; Bartsch, R. A. *J. Inclusion Phenom.* **1989**, *7*, 349.

(8) Westley, J. W.; Evans, R. H.; Blount, J. F. *J. Am. Chem. Soc.* **1977**, *99*, 6057.

(9) Lindoy, L. F. In *The Chemistry of Macrocyclic Ligand Complexes*; Cambridge University Press: Cambridge, U.K., 1989.

(10) See, for example: Lehn, J.-M.; Simon, J.; Moradpour, A. *Helv. Chim. Acta* **1978**, *61*, 2407. Newcomb, M.; Toner, J. L.; Helgeson, R. C.; Cram, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 4941.

(11) The cell design was based on that of Di Casa et al.: Di Casa, M.; Fabbri, L.; Perotti, A.; Poggi, A.; Tundo, P. *Inorg. Chem.* **1985**, *24*, 1610. The interfacial area (for each half of the cell) was 4.9 ± 0.5 cm<sup>2</sup>. The volume of each phase was 20 mL, each phase was stirred independently, and the temperature was maintained at 25 ± 0.1 °C. For all experiments, the receiving phase was 0.1 mol dm<sup>-3</sup> in ammonium chloride.

(12) Measured rotations were converted to enantiomeric purity by using the specific rotation measured for the levo isomer of [Co(1,2-diaminoethane)<sub>3</sub>]I<sub>3</sub> in 0.1 M NH<sub>4</sub>Cl [ $[\alpha]_{436}^{25} = +1512 \pm 4^\circ$ ]. By way of example, a typical observed rotation at 436 nm for the receiving phase in a 10-cm cell was +0.029 ± 0.002°; the enantiomeric purities derived from measurements at four other wavelengths, although of lower accuracy since smaller rotations were involved, were still within experimental error of the value quoted in Table I. The specific rotation for *u-cis*-[Co(diethylenetriamine)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> at (546 nm) was taken from the following: Keene, F. R.; Searle, G. H. *Inorg. Chem.* **1972**, *11*, 148. Once again, enantiomeric purity derived from measurements at other wavelengths agreed within experimental error with the value quoted in Table I.

the measured optical rotation of the source phase at the end of the experiment was of equivalent magnitude but opposite in sign to that measured for the corresponding receiving phase, thus confirming the internal consistency of the individual experiments.

Apart from its considerable intrinsic interest, the differential transport of intact metal complexes across bulk hydrophobic membranes provides a new technique for the separation of such species. In particular, the present study demonstrates that the procedure has special promise for the (partial) resolution of suitable optically active metal complexes. The latter remains a classical requirement in coordination chemistry that is not always readily met by conventional methods.

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### Synthesis and Structural Characterization of the Cyclic Species [GeN(2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>]: The First "Germanazene"

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Inorganic cyclic systems that involve potentially delocalized, multiply bonded rings have been known for many years.<sup>1</sup> Perhaps the best known examples are borazine,<sup>2</sup> the cyclic phosphazenes,<sup>3</sup> certain cyclic sulfur nitrogen compounds,<sup>4</sup> and homocyclic cations of S, Se, or Te.<sup>5</sup> Recent additions have included the cyclic six-membered rings based upon B<sub>3</sub>P<sub>3</sub><sup>6</sup> and Al<sub>3</sub>N<sub>3</sub><sup>7</sup> skeletons and the cyclopentadiene-like P<sub>5</sub><sup>-</sup> ion.<sup>8</sup> Oddly, there do not appear to be any stable counterparts of these compounds that involve the heavier main group 4 elements Si-Pb as an integral part of an unsaturated system for which a classical quasi-aromatic bonding model is possible.<sup>9</sup> In this paper, the first synthesis and characterization of such a compound, the trimeric species (GeNAr)<sub>3</sub> (where Ar = 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (1), is described.

The title compound 1 was synthesized by the treatment of Ge[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub><sup>10</sup> with H<sub>2</sub>NAr<sup>11</sup> as follows: Ge[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>

(1) (a) Haiduc, I.; Sowerby, D. B. *The Chemistry of Inorganic Homo- and Heterocycles*; Academic: London, 1987. (b) Woolins, J. D. *Non-Metal Rings, Cages and Clusters*; Wiley: Chichester, 1988. There are also numerous related compounds that feature inorganic atoms as part of a delocalized organic ring system that are not strictly regarded as inorganic rings. Examples are the phosphabenzenes: (c) Märkl, G. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 846. (d) Ashe, A. J. *J. Am. Chem. Soc.* **1971**, *93*, 3293.

(2) Stock, A.; Pohland, E. *Chem. Ber.* **1926**, *59*, 2215. See also in ref 1a: Maringgele, W. Vol. 1, p 17.

(3) Allcock, H. R. *Phosphorus Nitrogen Compounds*; Academic: London, 1972. Allen, C. W. Ref 1a, Vol. 2, p 501.

(4) Chivers, T. Vol. 2, p 793 of ref 1a. Chivers, T. *Chem. Rev.* **1985**, *85*, 341. Roesky, H. W. *Adv. Inorg. Chem. Radiochem.* **1979**, *22*, 239.

(5) Gillespie, R. J. *Chem. Soc. Rev.* **1979**, *8*, 315. Steudel, R.; Strauss, E.-M. Vol. 2, p 769 of ref 1a.

(6) Dias, H. V. R.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1270; *J. Am. Chem. Soc.* **1989**, *111*, 144.

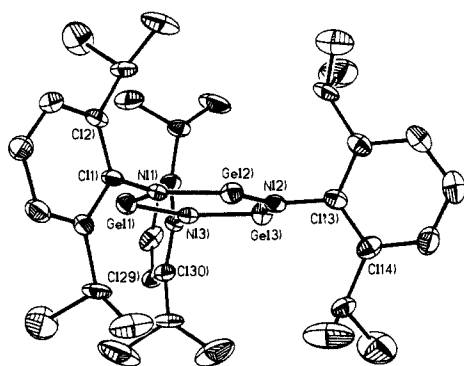
(7) Waggoner, K. M.; Hope, H.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1699.

(8) Baudler, M.; Duster, D.; Ouzounis, D. *Z. Anorg. Allg. Chem.* **1987**, *544*, 87. Baudler, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 419. Janoshek, R. *Chem. Ber.* **1989**, *122*, 2121. Six-membered P<sub>6</sub> rings stabilized by complexation to transition metals have also been obtained; Scherer, O. J.; Sitzmann, H.; Wolmerhäuser, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 351.

(9) (a) Species such as SiC<sub>5</sub>H<sub>6</sub> have been studied at low (10 K) temperatures in an argon matrix,<sup>9b</sup> and its aromatic character was proved by PE spectroscopy and UV-vis data. Greater stability has been introduced by using bulky substituents, but no structures have been reported to date. (b) Soulu, B.; Rosmus, P.; Bock, H.; Maier, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 51. (c) Märkl, G.; Schlosser, W. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 963. Jutz, P.; Meyer, M.; Reisenauer, H. D.; Maier, G. *Chem. Ber.* **1989**, *122*, 1227.

(10) Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1974**, 895.

(11) H<sub>2</sub>N(2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) was obtained commercially and purified by distillation from CaH<sub>2</sub> under reduced pressure.



**Figure 1.** Perspective drawing of the molecule **1**. Average Ge–N distance = 1.859 (2) Å; average N–C = 1.452 (5) Å; average values for NGeN and GeNGe = 101.84 (1)° and 138.0 (2)°, respectively. The average dihedral angle between the Ge<sub>3</sub>N<sub>3</sub> plane and the Ar planes = 86.2°. Average Ge···Ge distance = 3.471 Å.

(0.84 g, 2.14 mmol) and H<sub>2</sub>NAr (0.38 g, 2.14 mmol), under anaerobic and anhydrous conditions, were heated together to ca. 60 °C for 5 min. The volatile byproduct HN(SiMe<sub>3</sub>)<sub>2</sub> was removed under reduced pressure, to leave the crude product as a yellow solid. Purification was effected by dissolving the solid in pentane (25 mL) with slight warming. Subsequent filtration and evaporation to incipient crystallization (~20 mL total volume) under reduced pressure afforded **1** upon slow cooling to –20 °C for 24 h. The large yellow crystals gradually became orange upon heating to a temperature >250 °C and finally melted at 273–275 °C. Yield = 0.45 g, 85%.

The structure of **1** (Figure 1) was determined by X-ray crystallography.<sup>12</sup> The compound crystallizes as well-separated trimeric units with no crystallographically imposed symmetry. The main feature of the structure is the essentially planar Ge<sub>3</sub>N<sub>3</sub> array,<sup>13</sup> which also includes the three ipso carbons of the aromatic substituent rings. The Ge–N bonds are essentially equal, and they average 1.859 (2) Å in length. The internal ring angles average 101.8 (1)° at germanium and 138.0 (2)° at nitrogen.

The synthesis of the title compound was prompted by recent work in this laboratory that resulted in the synthesis of the first "alumazene" compound (MeAlNAr)<sub>3</sub><sup>7</sup> via a two-step alkane elimination reaction. The use of the 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> group on nitrogen affords the planar six-membered Al<sub>3</sub>N<sub>3</sub> ring adequate stability and prevents the further aggregation normally found in iminoalanes.<sup>14</sup> The similar sizes of Al and Ge<sup>15</sup> suggested that the same configuration might be obtainable for a Ge<sub>3</sub>N<sub>3</sub> system. The readily available starting material Ge[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub><sup>10</sup> was selected as the source of Ge. Treatment with H<sub>2</sub>NAr under mild conditions afforded **1** in good yield.<sup>16</sup> Reactions analogous to this synthesis have been used to obtain more highly aggregated metal imides. For example, treatment of the metallacycle :MNRSiMe<sub>2</sub>NR (R = *t*-Bu) with H<sub>2</sub>NR' (R' = *i*-Pr, *t*-Bu, CH<sub>2</sub>Ph, NMe<sub>2</sub>) gives the tetrameric cubane species (MNR')<sub>4</sub><sup>17</sup> or the alkoxides (TIOR)<sub>4</sub>.<sup>18</sup> The structures of a number of the

tin compounds have been published.<sup>19</sup> However, it is notable that no aggregates involving numbers less than 4 have appeared. The lower aggregates (MNR)<sub>n</sub> (*n* = 1–3) are of interest because their structures allow the possibility of some multiple bonding whereas the higher (*n* = 4 or greater) aggregates can generally be accounted for in terms of purely σ bonding.

The planar skeleton of **1** indicates that the p orbitals on the N and Ge atoms have the correct orientation to give some degree of delocalization over the ring. The average Ge–N distance, 1.859 (2) Å, is marginally shorter than the distances found in the acyclic Ge(II) amides, Ge[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub><sup>20</sup> and Ge[NCMe<sub>2</sub>–(CH<sub>2</sub>)<sub>3</sub>CMe<sub>2</sub>]<sub>2</sub>,<sup>21</sup> where both Ge–N bonds are ~1.89 Å (but see also ref 22), which suggests that there is some increased interaction between the empty Ge p orbitals and the nitrogen orbitals containing the lone pairs.<sup>23–25</sup> With regard to the question of delocalization, a more significant structural feature of this molecule is, perhaps, its planarity. This is because considerable strain is imposed on the ring by a planar conformation. This is manifested in the large (~20°) internal angular distortions from the idealized 120° values. The deviations are, in fact, much greater than those (~5°) observed in the Al<sub>3</sub>N<sub>3</sub><sup>7</sup> or B<sub>3</sub>P<sub>3</sub><sup>6</sup> systems. The increased reluctance of the heavier main-group elements to engage in hybridization accounts for the low angle at Ge. In order to maintain ring planarity, an unusually wide angle, ~138.0°, is therefore imposed at N. Molecular models suggest that, for this ring system, much of the strain could be avoided if the ring were to assume an approximately "twist" conformation. Apparently, the molecule assumes the more strained planar conformation because this maximizes overlap of the six p orbitals. This enhanced overlap presumably compensates for the resultant strain in terms of an increased stabilization. An alternative explanation for the internal ring strain could involve the existence of transannular non-bonded repulsions as observed in [Fe<sub>3</sub>(SR)<sub>3</sub>X<sub>6</sub>]<sup>–</sup> ring systems.<sup>26</sup>

Finally, it is notable that the relatively small size of the Ge atom played a key role in enabling the isolation of the unique configuration observed in **1**. Similar experiments in the case of Sn or Pb afforded the tetrameric cubane products (SnNAr)<sub>4</sub> and (PbNAr)<sub>4</sub>.<sup>27</sup> The structures of these as well as investigations of the chemical properties of **1** will be reported in a fuller account of this work.

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(18) Dahl, L. F.; Davies, G. L.; Wamfler, D. L.; West, K. J. *Inorg. Nucl. Chem.* **1962**, *24*, 357.

(19) Veith, M.; Schlemmer, G. *Chem. Ber.* **1982**, *115*, 2141. More recent results in this area feature data on the reactions of these compounds: Veith, M.; Hobein, P.; Rösler, R. *Z. Naturforsch.* **1989**, *44b*, 1067. Veith, M.; Becker, S.; Huch, V. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1237. The latter paper features a very interesting Ge–S double bond.

(20) Fjeldberg, T.; Hope, H.; Lappert, M. F.; Power, P. P.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1983**, 639.

(21) Lappert, M. F.; Slade, M. J.; Atwood, J. L.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1980**, 621.

(22) Veith, M.; Lisowsky, R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1087. This paper features a short Ge–N bond of 1.856 (6) Å in a highly strained four-membered-ring system. A short Ge–N (1.844 Å) bond has also been observed in the ring compound [GeN(2,4,6-*t*-Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>]<sub>2</sub>; Lappert, M. F., and co-workers., unpublished results.

(23) In the acyclic Ge(NR<sub>2</sub>)<sub>2</sub> compounds,<sup>20,21</sup> some degree of multiple Ge–N bonding is possible so that the observed shortening in **1** is not as dramatic as it is in other systems.<sup>6,7</sup> The acyclic M–N multiple bonding can arise from the overlap of the empty p orbital on Ge with the lone-pair orbitals on the nitrogen ligands. This partial occupation of the metal p orbital may also explain, at least in part, why Ge, Sn, and Pb bivalent amides do not form double metal–metal bonds whereas their isoelectronic dialkyl counterparts do.<sup>24</sup> A further point of importance is that after this work was completed we learned of a compound containing a Ge–N double bond in the system (>N–)–(>N+–)Ge=NSiMe<sub>3</sub>.<sup>25</sup> It has a length of 1.688 (9) Å.

(24) Hitchcock, P. B.; Lappert, M. F.; Miles, S. J.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1984**, 480.

(25) Veith, M.; Becker, S.; Huch, V. *Angew. Chem., Int. Ed. Engl.*, in press.

(26) Whitener, M. A.; Bashkin, J. K.; Hagen, K. S.; Girerd, J.-J.; Gamp, E.; Edelstein, N.; Holm, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 5607.

(27) Bartlett, R. A.; Olmstead, M. M.; Power, P. P., unpublished work.

(12) Crystal data for **1** at 130 K with Cu Kα (λ = 1.54178 Å) radiation at 130 K: **1**, C<sub>36</sub>H<sub>51</sub>N<sub>3</sub>Ge<sub>3</sub>, *a* = 10.551 (3) Å, *b* = 13.158 (3) Å, *c* = 16.187 (4) Å, α = 66.93 (2)°, β = 73.22 (2)°, γ = 70.03 (2)°, *Z* = 2, triclinic, space group *P*1, *d*<sub>calc</sub> = 1.294 g cm<sup>–3</sup>, *V* = 1908.0 (8) Å<sup>3</sup>, 4887 unique observed data with *I* > 2σ(*I*), *R* = 0.061.

(13) The mean deviation from the calculated Ge<sub>3</sub>N<sub>3</sub> plane is 0.03 Å. The following are the deviations (in parentheses) for each atom: N(1) (–0.044), Ge(1) (–0.005), N(2) (–0.004), Ge(2) (0.04), N(3) (0.05), Ge(3) (–0.038).

(14) Cesari, M.; Cucinella, S. Ref 1, Vol. 1, p 167.

(15) Covalent radii, Al (1.3 Å) and Ge (1.22 Å), estimated from homonuclear bond lengths: Sutton, L., Ed.; Tables of Interatomic Distances and Configuration in Molecules and Ions. *Spec. Publ.—Chem. Soc.* **1958**, No. 11; *Spec. Publ.—Chem. Soc.* **1965**, No. 18. Slater, J. C. *J. Chem. Phys.* **1964**, *41*, 3199.

(16) Compound **1** was further characterized by a satisfactory C, H, and N elemental analysis and NMR studies: <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>) δ = 1.12 (d, CHMe<sub>2</sub>, *J* = 7 Hz), 3.4 (septet, CHMe<sub>2</sub>, *J* = 7 Hz), 7.1 (t, *p*-H, *J* = 6 Hz), 7.16 (d, *m*-H, *J* = 6 Hz).

(17) Veith, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1.

assistance and useful discussions. We are also grateful to Professor M. F. Lappert and Professor M. Veith for supplying details of their work prior to publication.

**Supplementary Material Available:** A full table of crystallographic data and refinement, positional parameters for non-hydrogen atoms, bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates for **1** (7 pages); table of observed and calculated structure factors for **1** (19 pages). Ordering information is given on any current masthead page.

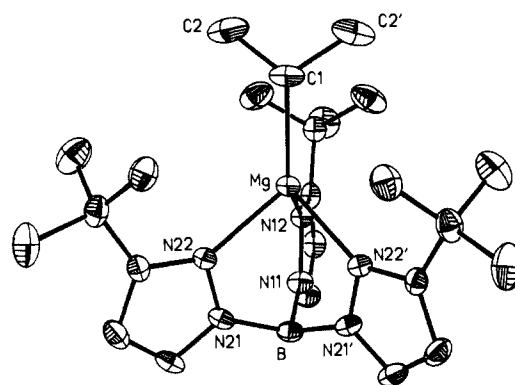
### Insertion of O<sub>2</sub> into the Mg-C Bonds of the Alkyl Derivatives { $\eta^3$ -HB(3-Bu<sup>t</sup>p<sub>z</sub>)<sub>3</sub>}MgR (R = CH<sub>3</sub>, CH<sub>2</sub>CH<sub>3</sub>, CH(CH<sub>3</sub>)<sub>2</sub>, C(CH<sub>3</sub>)<sub>3</sub>): Formation of Alkylperoxy Derivatives and Oxygen Atom Transfer

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The selective oxidation of organic substrates by molecular oxygen plays a crucial role in a variety of industrial and biological processes.<sup>1</sup> Control of these oxidations is achieved by catalysts in which the active sites are metal centers, and as a consequence, the reactivity of metal complexes toward molecular oxygen is of fundamental importance. Furthermore, stoichiometric reactions of molecular oxygen with organometallic derivatives have also provided useful synthetic methods for the formation of alkyl hydroperoxides and alcohols.<sup>2</sup> In order to control such metal-based oxidation processes using molecular oxygen, it is essential to understand the factors that influence the reactivity of dioxygen with metal-alkyl derivatives. However, the reactions of organometallic derivatives with oxygen often produce complex mixtures, in part as a result of the indiscriminate reactivity of radical intermediates, and relatively few reactions result in the formation of single products. In this regard, the isolation of discrete products by the reaction of dioxygen with metal-alkyl derivatives, along with their subsequent reactivity, has provided a major challenge. Here we describe (i) the quantitative insertion of dioxygen into the Mg-C bond of the alkyl complexes { $\eta^3$ -HB(3-Bu<sup>t</sup>p<sub>z</sub>)<sub>3</sub>}MgR (3-Bu<sup>t</sup>p<sub>z</sub> = 3-C<sub>3</sub>N<sub>2</sub>Bu<sup>t</sup>H<sub>2</sub>; R = CH<sub>3</sub>, CH<sub>2</sub>CH<sub>3</sub>, CH(CH<sub>3</sub>)<sub>2</sub>, C(CH<sub>3</sub>)<sub>3</sub>), to give alkylperoxy derivatives { $\eta^3$ -HB(3-Bu<sup>t</sup>p<sub>z</sub>)<sub>3</sub>}MgOOR, and (ii) the conversion of the alkylperoxy complexes to alkoxy derivatives, { $\eta^3$ -HB(3-Bu<sup>t</sup>p<sub>z</sub>)<sub>3</sub>}MgOR, by



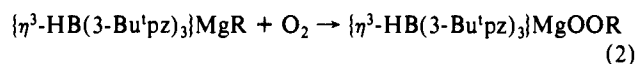
**Figure 1.** ORTEP diagram of { $\eta^3$ -HB(3-Bu<sup>t</sup>p<sub>z</sub>)<sub>3</sub>}MgCH(CH<sub>3</sub>)<sub>2</sub>. For clarity, thermal ellipsoids are shown at 20% probability. Selected bond distances (Å) and angles (deg): Mg-C1, 2.182 (8); Mg-N12, 2.157 (6); Mg-N22, 2.170 (4); C1-C2, 1.515 (9); N11-N12, 1.377 (8); N21-N22, 1.375 (5); B-N11, 1.541 (11); B-N21, 1.537 (6); C1-Mg-N12, 124.8 (3); C1-Mg-N22, 124.0 (2); Mg-C1-C2, 119.1 (4); C2-C1-C2', 106.6 (7); N12-Mg-N22, 93.1 (2); N22-Mg-N22', 87.8 (2); N11-B-N21, 109.8 (4); N21-B-N21', 110.8 (6).

oxygen atom transfer to either { $\eta^3$ -HB(3-Bu<sup>t</sup>p<sub>z</sub>)<sub>3</sub>}MgR or PPh<sub>3</sub>.

We have recently reported the synthesis and reactivity of the primary alkyl derivatives { $\eta^3$ -HB(3-Bu<sup>t</sup>p<sub>z</sub>)<sub>3</sub>}MgR (R = CH<sub>3</sub>, CH<sub>2</sub>CH<sub>3</sub>).<sup>3</sup> The secondary and tertiary alkyl derivatives { $\eta^3$ -HB(3-Bu<sup>t</sup>p<sub>z</sub>)<sub>3</sub>}MgR (R = CH(CH<sub>3</sub>)<sub>2</sub>, C(CH<sub>3</sub>)<sub>3</sub>)<sup>4</sup> may also be prepared by a similar procedure (eq 1), and the molecular structure of { $\eta^3$ -HB(3-Bu<sup>t</sup>p<sub>z</sub>)<sub>3</sub>}MgCH(CH<sub>3</sub>)<sub>2</sub> has been determined by single-crystal X-ray diffraction (Figure 1).<sup>5</sup>



Treatment of the alkyl complexes { $\eta^3$ -HB(3-Bu<sup>t</sup>p<sub>z</sub>)<sub>3</sub>}MgR (R = CH<sub>3</sub>, CH<sub>2</sub>CH<sub>3</sub>, CH(CH<sub>3</sub>)<sub>2</sub>, C(CH<sub>3</sub>)<sub>3</sub>) with excess O<sub>2</sub> at room temperature results in the formation of the alkylperoxy derivatives { $\eta^3$ -HB(3-Bu<sup>t</sup>p<sub>z</sub>)<sub>3</sub>}MgOOR (eq 2). The reactions of the deriv-



atives { $\eta^3$ -HB(3-Bu<sup>t</sup>p<sub>z</sub>)<sub>3</sub>}MgR (R = CH<sub>2</sub>CH<sub>3</sub>, CH(CH<sub>3</sub>)<sub>2</sub>, C(CH<sub>3</sub>)<sub>3</sub>) with O<sub>2</sub> are both instantaneous (<5 min) and quantitative, as judged by <sup>1</sup>H NMR spectroscopy. In contrast, the reaction of O<sub>2</sub> with { $\eta^3$ -HB(3-Bu<sup>t</sup>p<sub>z</sub>)<sub>3</sub>}MgCH<sub>3</sub> is significantly slower (*t*<sub>1/2</sub> ~ 9h at room temperature) than for the other alkyl derivatives.<sup>6</sup>

The products obtained from the reactions of { $\eta^3$ -HB(3-Bu<sup>t</sup>p<sub>z</sub>)<sub>3</sub>}MgR with <sup>17</sup>O<sub>2</sub> (41%) have been investigated by <sup>17</sup>O NMR spectroscopy. Specifically, each complex shows two <sup>17</sup>O NMR resonances in the ranges  $\delta$  102-183 and 323-427 for the peroxy (MgOOR) unit, which thus suggests that <sup>17</sup>O NMR spectroscopy may be a powerful method for the characterization of alkylperoxy complexes. The MgOOR group is further characterized by IR absorption bands in the ranges 889-935 cm<sup>-1</sup> ( $\nu_{\text{O-O}}$ ) and 608-660 cm<sup>-1</sup> ( $\nu_{\text{Mg-O}}$ ) that are assigned on the basis of the shifts observed for the isotopomers { $\eta^3$ -HB(3-Bu<sup>t</sup>p<sub>z</sub>)<sub>3</sub>}Mg<sup>18</sup>O<sup>18</sup>OR.<sup>7</sup> Other supporting evidence that the products are

(3) Han, R.; Looney, A.; Parkin, G. *J. Am. Chem. Soc.* **1989**, *111*, 7276-7278.

(4) In view of the sterically demanding nature of the tris(3-*tert*-butylpyrazolyl)hydroborato ligand, it is possible that the ground state of the *tert*-butyl derivative is  $\eta^2$ -coordinated, { $\eta^2$ -HB(3-Bu<sup>t</sup>p<sub>z</sub>)<sub>3</sub>}MgC(CH<sub>3</sub>)<sub>3</sub>, although this structure cannot be observed down to -90 °C in the <sup>1</sup>H NMR spectrum.

(5) Crystal data for { $\eta^3$ -HB(3-Bu<sup>t</sup>p<sub>z</sub>)<sub>3</sub>}MgCH(CH<sub>3</sub>)<sub>2</sub>; orthorhombic, *Pnma*, *a* = 17.171 (2) Å, *b* = 15.893 (7) Å, *c* = 10.034 (3) Å, *V* = 2738 Å<sup>3</sup>, *Z* = 4,  $\rho$ (calcd) = 1.09 g cm<sup>-3</sup>,  $\mu$ (calcd) = 0.9 cm<sup>-1</sup>,  $\lambda$ (Mo K $\alpha$ ) = 0.71073 Å (graphite monochromator); 4115 unique reflections with 3° < 2 $\theta$  < 60° were collected, of which 1024 reflections with *F* > 5 $\sigma$ (*F*) were used in refinement; *R* = 6.44%, *R*<sub>w</sub> = 6.06%, goodness of fit = 1.4.

(6) The reaction of O<sub>2</sub> with { $\eta^3$ -HB(3-Bu<sup>t</sup>p<sub>z</sub>)<sub>3</sub>}MgCH<sub>3</sub> is also accompanied by ca. 30% decomposition, so that the product { $\eta^3$ -HB(3-Bu<sup>t</sup>p<sub>z</sub>)<sub>3</sub>}MgOCH<sub>3</sub> has only been characterized spectroscopically.

(1) (a) Mimoun, H. *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, 1987; Vol. 6, pp 317-410. (b) Sheldon, R. A.; Kochi, J. K. *Metal Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981. (c) Grasselli, R. K.; Burrington, J. D. *Adv. Catal.* **1981**, *30*, 133-163. (d) Grasselli, R. K.; Burrington, J. D.; Brazdil, J. F. *Faraday Discuss. Chem. Soc.* **1981**, *72*, 203-223. (e) Sheldon, R. A. *J. Mol. Catal.* **1983**, *20*, 1-26. (f) Martell, A. E. *Pure Appl. Chem.* **1983**, *55*, 125-135. (g) Malmstrom, B. G. *Annu. Rev. Biochem.* **1982**, *51*, 21-59. (h) Perutz, M. F. *Annu. Rev. Biochem.* **1979**, *48*, 327-386. (i) Jones, R. D.; Summerville, D. A.; Basolo, F. *Chem. Rev.* **1979**, *79*, 139-179. (j) White, R. E. *Annu. Rev. Biochem.* **1980**, *49*, 315-356. (k) Guengerich, F. P.; Macdonald, T. L. *Acc. Chem. Res.* **1984**, *17*, 9-16. (l) Collman, J. P. *Acc. Chem. Res.* **1977**, *10*, 265-272.

(2) (a) Brilkina, T. G.; Shushunov, V. A. *Reactions of Organometallic Compounds with Oxygen and Peroxides*; Illiffe Books Ltd.: London, 1969. (b) Kharasch, M. S.; Reinmuth, O. *Grignard Reactions of Nonmetallic Substances*; Prentice-Hall: New York, 1954. (c) Davies, A. G. *Organic peroxides*; Swern, D., Ed.; Wiley-Interscience: New York, 1972; Vol. 2, Chapter 4, pp 337-354. (d) Walling, C.; Buckler, S. A. *J. Am. Chem. Soc.* **1955**, *77*, 6032-6038. (e) Blackburn, T. F.; Labinger, J. A.; Schwartz, J. *Tetrahedron Lett.* **1975**, 3041-3044. (f) Panek, E. J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1972**, *94*, 8768-8775. (g) Hock, H.; Kropf, H.; Ernst, F. *Angew. Chem.* **1959**, *71*, 541-545. (h) Sosnovsky, G.; Brown, J. H. *Chem. Rev.* **1966**, *66*, 529-566. (i) Porter, C. W.; Steele, C. *J. Am. Chem. Soc.* **1920**, *42*, 2650-2654. (j) Hock, H.; Ernst, F. *Chem. Ber.* **1959**, *92*, 2716-2723. (k) Hock, H.; Ernst, F. *Chem. Ber.* **1959**, *92*, 2723-2732. (l) Hock, H.; Ernst, F. *Chem. Ber.* **1959**, *92*, 2732-2740.