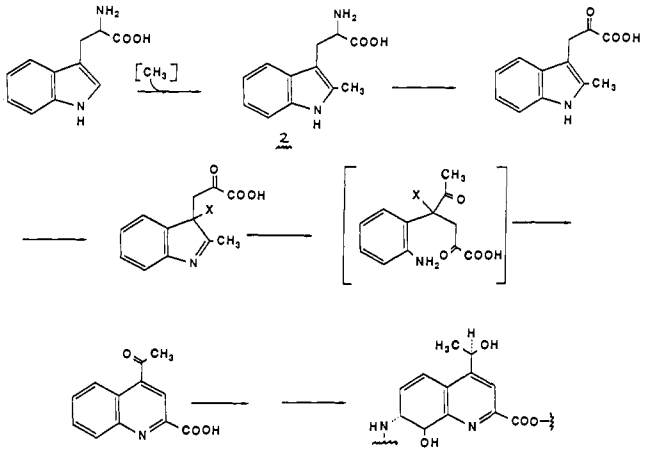
Scheme II



quinaldic acid moiety of **1**

volving an intermediate methylene group, as in sterol side-chain methylation,[21] because L-[*methyl*-^{13}C,^{2}H$_3$]methionine is incorporated with complete retention of all three deuterium atoms (data not shown). No change in methyl group configuration takes place after the initial transfer to C2 of the indole ring since in another series of experiments (*methyl-R*)-[*methyl*-^{2}H$_1$,^{3}H]methionine[24] gave **2** carrying an *R* methyl group (acetic acid from Kuhn–Roth oxidation: $F = 69$; 65% ee *R*) and the *S* isomer gave **2** carrying an *S* methyl group ($F = 31$; 66% ee *S*). Whether the unusual retention stereochemistry reflects the transient methylation of a site on the enzyme, e.g., a cobalamin cofactor,[25] in the process or results from initial transfer of the methyl group to a different site on the substrate followed by intramolecular migration remains to be established.

The further conversion of **2** into the quinaldic acid moiety of **1** may involve either (a) cleavage of the N1/C7a bond and connection of the side-chain nitrogen to C7a or (b) cleavage of the N1/C2 bond and connection of C2′ to N1. This issue was decided in favor of option (b) by feeding L-[*indole*-^{15}N,1′,2′-^{13}C$_2$]tryptophan.[26] The resulting **1** showed ^{13}C enrichment in the carboxyl group and C2 of the quinaldic acid moiety and one-bond coupling of these two signals to each other. In addition, the QC2 signal at 143.56 ppm displayed 3.02 Hz one-bond coupling to ^{15}N, and the QCO showed a two-bond coupling of 8.08 Hz to the ^{15}N,[28] indicating that C2′ of tryptophan has been intramolecularly connected to the ^{15}N-labeled indole nitrogen. A mechanistically reasonable pathway for the transformation of the indole to the quinoline system, which is consistent with the experimental data, is portrayed in Scheme II. This process has chemical precedent in the hypochlorite-catalyzed conversion of **2** into 4-acetylquinoline.[29]

Acknowledgment. We are indebted to Dr. Edith W. Miles, Bethesda, for a generous gift of tryptophan synthase, to E. R. Squibb and Co. for supplying thiostrepton, to Drs. Koji Kobayashi and Motomasa Kobayashi for the chiral methionine samples, and to Kyungok Lee and Lynda Callicotte for chirality analyses of acetate samples. This work was supported by NIH research Grants AI 20264 and GM 32333 and by NIH (RR02231)-US-DOE/OHER grants to the Stable Isotope Program at Los Alamos.

Supplementary Material Available: Table I, ^{13}C enrichments in **1** derived from ^{13}C-labeled amino acids, and Table II, ^{13}C–^{13}C coupling patterns in **1** derived from L-[1,2-^{13}C$_2$]- and L-[2,3-^{13}C$_2$]serine (3 pages). Ordering information is given on any current masthead page.

(24) The methionine samples used in these experiments were synthesized independently from the ones used to label **1**; as a control, one of them was also shown to be incorporated into **1** with retention of methyl group configuration.

(25) Zydowsky, T. M.; Courtney, L. F.; Frasca, V.; Kobayashi, K.; Shimizu, H.; Yuen, L.-D.; Matthews, R. G.; Benkovic, S. J.; Floss, H. G. *J. Am. Chem. Soc.* **1986**, *108*, 3152.

(26) Synthesized from [^{15}N]indole[27] (90.4% ^{15}N) and L-[1,2-^{13}C$_2$]serine with tryptophan synthase.[9]

(27) Murray, A. W.; Williams, D. L. *Organic Synthesis with Isotopes*; Interscience: New York, 1958; pp 931–932.

(28) Levy, G. C.; Lichter, R. L. *Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy*; John Wiley and Sons: New York, 1979; p 119.

(29) van Tamelen, E. E.; Haarstad, V. B. *Tetrahedron Lett.* **1961**, 390.

{Tris(pyrazolyl)hydroborato}magnesium and -aluminum Alkyl Derivatives: Alkyl Exchange with Methyl Iodide and Enolate Formation with Acetone

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Organometallic derivatives of the *s*- and *p*-block elements, e.g., Li, Mg, and Al, are extremely important reagents in both organic and organometallic chemistry,[1] and significant efforts have been directed to determine the mechanisms of their reactions.[2] For example, studies have shown that, in addition to the conventional view of Grignard reactions with ketones as simple nucleophilic additions, an additional pathway involves single electron-transfer processes and the formation of radicals.[3] However, mechanistic studies of Grignard reagents are complicated by the complexity of the species present in solution.[3,4] Mechanistic investigations of the reactions of *s*- and *p*-block organometallic complexes would be aided by the synthesis of well-defined monomeric derivatives, L$_n$M-R. This paper describes the use of {η^3-tris(pyrazolyl)hydroborato} ligands[5,6] to prepare alkyl derivatives of Mg and Al, in which chelation of the three nitrogen atom donors would be expected to provide a sterically demanding ligand environment[7]

(1) (a) Negishi, E. *Organometallics in Organic Synthesis*; Wiley: New York, 1980; Vol. 1. (b) Wakefield, B. J. *Comprehensive Organometallic Chemistry*, Pergamon Press: Oxford, 1982; Vol. 7, p 1.

(2) Matteson, D. S. *Organometallic Reaction Mechanisms of the Nontransition Elements*; Academic Press: New York, 1974.

(3) (a) Blomberg, C.; Mosher, H. S. *J. Organomet. Chem.* **1968**, *13*, 519–522. (b) Ashby, E. C.; Laemmle, J.; Neumann, H. M. *Acc. Chem. Res.* **1974**, *7*, 272–280. (c) Ashby, E. C. *Acc. Chem. Res.* **1988**, *21*, 414–421. (d) Ashby, E. C. *Pure Appl. Chem.* **1980**, *52*, 545–569. (e) Holm, T. *Acta Chem. Scand., Ser. B* **1983**, *B37*, 567–584. (f) Walling, C. *J. Am. Chem. Soc.* **1988**, *110*, 6846–6850. (g) Maruyama, K.; Katagiri, T. *J. Am. Chem. Soc.* **1986**, *108*, 6263–6270.

(4) Although "RMgX" adequately represents the overall composition of Grignard reagents, it does not satisfactorily represent the nature of the species present in solution (or the solid state). Grignard reagents are complex mixtures, and the simple model of the Schlenk equilibrium ($2RMgX \rightleftharpoons R_2Mg + MgX_2$) for describing the composition is complicated by a variety of factors including (i) the formation of complexes of each component with either solvent, reactant, or product, (ii) the formation of dimeric (or higher order) species, and (iii) the presence of ionic species. (a) Wakefield, B. J. *Pure Appl. Chem.* **1966**, *1*, 131–156. (b) Kharasch, M. S.; Reinmuth, O. *Grignard Reactions of Nonmetallic Substances*; Prentice-Hall: New York, 1954. (c) Toney, J.; Stucky, G. D. *J. Organomet. Chem.* **1971**, *28*, 5–20. (d) Ashby, E. C.; Smith, M. B. *J. Am. Chem. Soc.* **1964**, *86*, 4363–4370. (e) Ashby, E. C.; Becker, W. E. *J. Am. Chem. Soc.* **1963**, *85*, 118–119.

(5) (a) Trofimenko, S. *Acc. Chem. Res.* **1971**, *4*, 17–22. (b) Trofimenko, S. *Chem. Rev.* **1972**, *72*, 497–509. (c) Trofimenko, S. *Prog. Inorg. Chem.* **1986**, *34*, 115–210. (d) Shaver, A. *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, 1987; Vol. 2, pp 245–259. (e) Shaver, A. *J. Organomet. Chem. Library* **1977**, *3*, 157–188.

(6) Studies have shown that tris(pyrazolyl)hydroborato ligands may bind to *s*- and *p*-block elements. (a) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3170–3177. (b) Nicholson, B. K. *J. Organomet. Chem.* **1984**, *265*, 153–157. (c) Lee, S. K.; Nicholson, B. K. *J. Organomet. Chem.* **1986**, *309*, 257–265. (d) Cowley, A. H.; Carrano, C. J.; Geerts, R. L.; Jones, R. A.; Nunn, C. M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 277–278. (e) Cowley, A. H.; Geerts, R. L.; Nunn, C. M.; Carrano, C. J. *J. Organomet. Chem.* **1988**, *341*, C27–C31.

(7) The cone angles of the ligands {η^3-HB(pyz)$_3$}, {η^3-HB(3,5-Me$_2$pyz)$_3$}, and {η^3-HB(3-Bu^{t}pyz)$_3$} have been estimated as 184°, 224°, and 244°, respectively. (a) Trofimenko, S.; Calabrese, J. C.; Thompson, J. S. *Inorg. Chem.* **1987**, *26*, 1507–1514. (b) Frauendorfer, E.; Brunner, H. *J. Organomet. Chem.* **1982**, *240*, 371–379.

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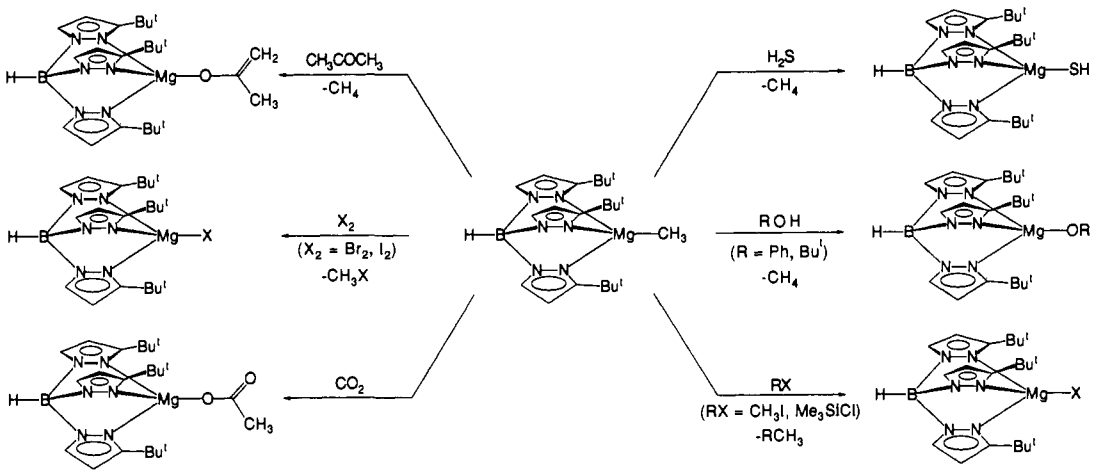
Scheme I



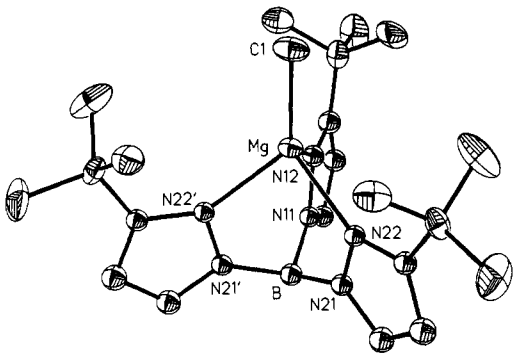


Figure 1. ORTEP diagram of $\{\eta^3\text{-HB(3-Bu}^t\text{pyz)}_3\}\text{MgCH}_3$. For clarity, thermal ellipsoids are shown at 20% probability. Selected bond distances (Å) and angles (deg) are as follows: Mg–C1 = 2.118 (11), Mg–N12 = 2.130 (10), Mg–N22 = 2.137 (7), N11–N12 = 1.375 (13), N21–N22 = 1.390 (8), B–N11 = 1.524 (16), B–N21 = 1.532 (11); N12–Mg–N22 = 91.3 (3), N22–Mg–N22′ = 90.6 (4), N11–B–N21 = 109.7 (7), N21–B–N21′ = 108.8 (10).

that would inhibit both ligand exchange processes[8] and oligomerization,[3,4] and thus provide a well-defined system that may (a) prove to be more amenable to mechanistic investigations and (b) exhibit unique reactivity,

Tris(pyrazolyl)hydroborato alkyl derivatives of Mg and Al are readily prepared by metathesis of R_2Mg or R_3Al with either $K\{HB(3,5\text{-Me}_2\text{pyz})_3\}$ ($3,5\text{-Me}_2\text{pyz} = 3,5\text{-C}_3N_2(CH_3)_2H$)[9] or $Tl\{HB(3\text{-Bu}^t\text{pyz})_3\}$ ($3\text{-Bu}^t\text{pyz} = 3\text{-C}_3N_2Bu^tH_2$).[7a] Thus, the complexes $\{\eta^3\text{-HB(3,5-Me}_2\text{pyz)}_3\}\text{MgCH}_3$, $\{\eta^3\text{-HB(3-Bu}^t\text{pyz)}_3\}\text{MgR}$ (R = CH_3, CH_2CH_3), and $\{HB(3,5\text{-Me}_2\text{pyz})_3\}Al(CH_3)_2$ have been isolated, for example, as illustrated by eq 1 and 2.

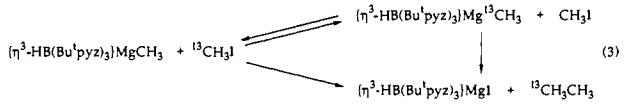
$$(CH_3)_2Mg \xrightarrow[\text{THF}]{Tl\{HB(3\text{-Bu}^t\text{pyz})_3\}} \{\eta^3\text{-HB(3-Bu}^t\text{pyz)}_3\}\text{MgCH}_3 \quad (1)$$

$$(CH_3)_3Al \xrightarrow[CH_2Cl_2]{K\{HB(3,5\text{-Me}_2\text{pyz})_3\}} \{HB(3,5\text{-Me}_2\text{pyz})_3\}Al(CH_3)_2 \quad (2)$$

The molecular structure of $\{\eta^3\text{-HB(3-Bu}^t\text{pyz)}_3\}\text{MgCH}_3$ has been determined by single-crystal X-ray diffraction (Figure 1) and confirms both the monomeric nature of the complex and the η^3-coordination mode of the tris(pyrazolyl)hydroborato ligand.[10,11]

$\{\eta^3\text{-HB(3-Bu}^t\text{pyz)}_3\}\text{MgCH}_3$ is a precursor to a variety of other derivatives, e.g., $\{\eta^3\text{-HB(3-Bu}^t\text{pyz)}_3\}\text{MgX}$ (X = Cl, Br, I), $\{\eta^3\text{-HB(3-Bu}^t\text{pyz)}_3\}\text{MgSH}$, $\{\eta^3\text{-HB(3-Bu}^t\text{pyz)}_3\}\text{MgOR}$ (R = Bu^t, Ph), $\{\eta^3\text{-HB(3-Bu}^t\text{pyz)}_3\}\text{MgOC(CH}_3)\text{=CH}_2$, and $\{\eta^3\text{-HB(3-Bu}^t\text{pyz)}_3\}\text{Mg}(\eta^1\text{-O}_2\text{CCH}_3)$ via metathesis and insertion reactions (Scheme I).

The metathesis reaction that occurs between $\{\eta^3\text{-HB(3-Bu}^t\text{pyz)}_3\}\text{MgCH}_3$ and CH_3I to give $\{\eta^3\text{-HB(3-Bu}^t\text{pyz)}_3\}\text{MgI}$ and CH_3CH_3 is of particular interest. Remarkably, the reaction with $^{13}CH_3I$ demonstrates that in addition to alkylation (to give $\{\eta^3\text{-HB(3-Bu}^t\text{pyz)}_3\}\text{MgI}$ and $^{13}CH_3CH_3$) there is also a competitive metathesis process involving alkyl exchange (to give $\{\eta^3\text{-HB(3-Bu}^t\text{pyz)}_3\}\text{Mg}^{13}\text{CH}_3$ and CH_3I), as shown in eq 3.[12] Furthermore,



alkyl exchange between $\{\eta^3\text{-HB(3-Bu}^t\text{pyz)}_3\}\text{MgCH}_2\text{CH}_3$ and CH_3I, giving $\{\eta^3\text{-HB(3-Bu}^t\text{pyz)}_3\}\text{MgCH}_3$, is also observed and is competitive with the irreversible formation of $\{\eta^3\text{-HB(3-Bu}^t\text{pyz)}_3\}\text{MgI}$.

The reaction of $\{\eta^3\text{-HB(3-Bu}^t\text{pyz)}_3\}\text{MgCH}_3$ with acetone gives the enolate complex, $\{\eta^3\text{-HB(3-Bu}^t\text{pyz)}_3\}\text{MgOC(CH}_3)\text{=CH}_2$, rather than the product that would be expected on the basis of conventional Grignard reactions, i.e., the alkoxide derivative $\{\eta^3\text{-HB(3-Bu}^t\text{pyz)}_3\}\text{MgOBu}^t$. Although magnesium enolate complexes have previously been isolated for ketones with sterically demanding substituents, e.g., $Bu^tC(O)Et$[13] and $(1,3,5\text{-Me}_3C_6H_2)C(O)CH_3$,[14] the isolation of this magnesium enolate derivative of acetone, $\{\eta^3\text{-HB(3-Bu}^t\text{pyz)}_3\}\text{MgOC(CH}_3)\text{=CH}_2$, is particularly significant in view of the susceptibility of acetone toward aldol condensation.

(8) Alkyl exchange and inversion of configuration at carbon bound to magnesium have been shown to be rapid on the NMR time scale for a variety of organomagnesium complexes. (a) House, H. O.; Latham, R. A.; Whitesides, G. M. *J. Org. Chem.* **1967**, *32*, 2481–2496. (b) Fraenkel, G.; Cottrell, C. E.; Dix, D. T. *J. Am. Chem. Soc.* **1971**, *93*, 1704–1708. (c) Fraenkel, G.; Dix, D. T. *J. Am. Chem. Soc.* **1966**, *88*, 979–985. (d) Parris, G. E.; Ashby, E. C. *J. Am. Chem. Soc.* **1971**, *93*, 1206–1213. (e) Witanowski, M.; Roberts, J. D. *J. Am. Chem. Soc.* **1966**, *88*, 737–741. (f) Whitesides, G. M.; Witanowski, M.; Roberts, J. D. *J. Am. Chem. Soc.* **1965**, *87*, 2854–2862. (g) Whitesides, G. M.; Roberts, J. D. *J. Am. Chem. Soc.* **1965**, *87*, 4878–4888. (h) Allen, P. E. M.; Hagias, S.; Lincoln, S. F.; Mair, C.; Williams, E. H. *Ber. Bunsenges. Phys. Chem.* **1982**, *86*, 515–519. (i) Allen, P. E. M.; Hagias, S.; Lincoln, S. F.; Mair, C.; Williams, E. H. *Ber. Bunsenges. Phys. Chem.* **1984**, *88*, 623–626. (j) Ford, W. T.; Grutzner, J. B. *J. Org. Chem.* **1972**, *37*, 2561–2564.

(9) Trofimenko, S. *J. Am. Chem. Soc.* **1966**, *88*, 1842–1844.

(10) Molecular weight measurements demonstrate that $\{\eta^3\text{-HB(3-Bu}^t\text{pyz)}_3\}\text{MgCH}_3$ is also monomeric in benzene solution.

(11) Solvent-free, neutral monoalkyl complexes derived from trimethylenediamine are monomeric when the magnesium alkyl substituent is sterically demanding, e.g., $Bu^tMg\{\eta^2\text{-MeNCH}_2\text{CH}_2\text{NMe}_2\}$, but dimeric for the methyl derivative, $[CH_3Mg\{\eta^2\text{-MeNCH}_2\text{CH}_2\text{NMe}_2\}]_2$. (a) Coates, G. E.; Heslop, J. A. *J. Chem. Soc. (A)* **1966**, 26. (b) Coates, G. E.; Heslop, J. A. *J. Chem. Soc. (A)* **1968**, 514.

(12) Alkyl exchange has not previously been observed to occur between Grignard reagents and simple alkyl halides. However, there is indirect evidence for alkyl exchange (as determined by the *organic* products after quenching with CO_2) with more complex derivatives, e.g., (a) Kharasch, M. S.; Fuchs, C. F. *J. Org. Chem.* **1945**, *10*, 292–297. (b) Kharasch, M. S.; Lambert, F. L.; Urry, W. H. *J. Org. Chem.* **1945**, *10*, 298–306.

(13) Willard, P. G.; Salvino, J. M. *J. Chem. Soc., Chem. Commun.* **1986**, 153–154.

(14) Pinkus, A. G.; Lindberg, J. G.; Wu, A.-B. *Chem. Commun.* **1969**, 1350–1351.

Acknowledgment. We thank Dr. S. Trofimenko (E. I. du Pont de Nemours & Co., Inc.) for a generous gift of $Tl\{HB(3\text{-}Bu^tpyz)_3\}$, Dr. Michael Chiang (Washington University) and Professor Leslie Lessinger (Barnard College) for crystallographic advice, and Drs. Rita Upmacis and Katie Hunt (Rohm and Haas Company) for measuring NMR spectra.

Supplementary Material Available: Tables of spectroscopic data for all new compounds, crystal and intensity collection data, atomic coordinates, bond distances and angles, and anisotropic displacement parameters and an ORTEP drawing for $\{\eta^3\text{-}HB(3\text{-}Bu^tpyz)_3\}MgCH_3$ (20 pages); listing of observed and calculated structure factors (4 pages). Ordering information is given on any current masthead page.

Oxygen-17 Labeling of Oxides and Zeolites†

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Over the past few years there has been a growth in interest in obtaining ^{17}O-labeled materials for solid-state ^{17}O NMR spectroscopy,[1-10] For many oxides, or complex oxides, we have used wet chemical methods or O-17 labeled precursors (e.g., $Si^{17}O_2$) to make group II oxides, silicates, aluminosilicates (zeolites), and aluminum phosphates (e.g., $AlPO_4$-5), whereas we and other groups have used $^{17}O_2$ gas to label metallic high-T_c superconductors, including $La_{1.85}Sr_{0.15}CuO_4$, $YBa_2Cu_3O_{7-x}$, $Bi_2Sr_2CaCu_2O_{8+x}$, and $Tl_2Ba_2CaCu_2O_{8+x}$,[11] Unfortunately, however, all of the hydrothermal routes are quite lengthy and involve use of significant quantities of $H_2{}^{17}O$, and, in our hands, wet chemical approaches to the preparation of some high-T_c superconductor precursors, such as Y_2O_3, have been somewhat unsuccessful.

Stimulated by the ease of labeling the high-T_c superconductor materials with $^{17}O_2$ gas, together with the previous observations of oxygen diffusion at high temperature in Al_2O_3,[12] three Mg–Al spinels,[13] and in Li_2O,[14] we decided to investigate the possibilities of ^{17}O-labeling a series of metal oxides and zeolites, by using $^{17}O_2$ gas at relatively low temperatures. To our surprise, we found that all materials investigated readily exchange ^{16}O for ^{17}O, producing a variety of ^{17}O-labeled materials, many of which are, we believe, otherwise rather difficult to obtain.

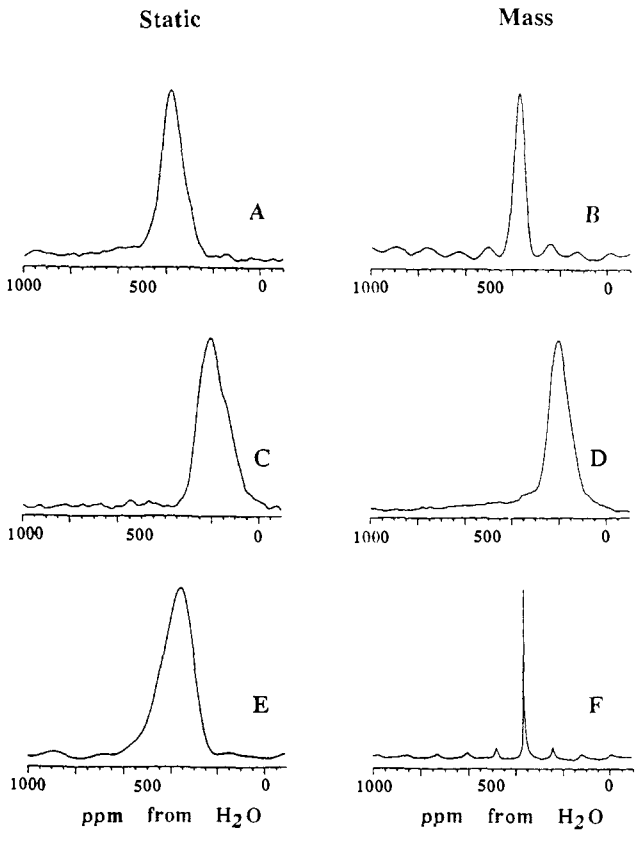

Figure 1. Static and MASS ^{17}O NMR spectra at 11.7 T of ^{17}O-labeled Tl_2O_3, Bi_2O_3, and Y_2O_3: (A) $Tl_2{}^{17}O_3$, static, 1400 scans, 100 ms recycle; (B) $Tl_2{}^{17}O_3$, 7.9 kHz spin rate, 11 330 scans, 1 s recycle; (C) $Bi_2{}^{17}O_3$, static, 380 scans, 10 s recycle; (D) $Bi_2{}^{17}O_3$, 7.9 kHz spin rate, 708 scans, 1 s recycle; (E) $Y_2{}^{17}O_3$, static, 2352 scans, 5 s recycle; (F) $Y_2{}^{17}O_3$, 7.9 kHz spin rate, 31 750 scans, 1 s recycle. Static spectra were recorded with use of a spin-echo pulse sequence with pulse widths of 2.33 μs (solution 90° pulse width = 7 μs) and a 40 μs interpulse delay. MASS spectra used a 3.2 μs pulse width. Line broadenings due to exponential multiplication were in the range of 100–1000 Hz.

We first investigated the M(III) oxides, Tl_2O_3, Bi_2O_3, and Y_2O_3, since they are all precursors to high-T_c superconductors, and their ^{17}O NMR spectra provide a valuable data set with which to begin interpretation of the ^{17}O NMR spectra of the superconductors themselves. $Tl_2{}^{17}O_3$ was prepared by heating Tl_2O_3 (0.5 g) in a gold boat under 0.5 atm $^{17}O_2$ (40%, $^{17}O_2$) for 48 h at 500 °C. Since Tl_2O_3 is metallic, it is perhaps not surprising that ^{17}O exchange occurs readily, and we show in Figure 1A,B the static and magic angle sample spinning (MASS) NMR spectra of Tl_2O_3 taken at 67.8 MHz (corresponding to a magnetic field strength of 11.7 T). For MASS NMR, the sample was diluted 1:9 with Al_2O_3, since the undiluted material would not spin in the high magnetic field used. As can be seen from Figure 1, the isotropic chemical shift of $Tl_2{}^{17}O_3$ is 364 ppm from H_2O (where high frequency, low field, paramagnetic, or deshielded shifts are positive, IUPAC δ scale). Interestingly, the observed chemical shift of 364 ppm is close to the ≈315–345 ppm (two sites) observed in $Tl_2Ba_2CaCu_2O_{8+x}$,[11] one site of which can be attributed to the Tl–O planes in this material.[11]

We then prepared $Bi_2{}^{17}O_3$ by heating 2 g of Bi_2O_3 in a gold boat under 0.5 atm $^{17}O_2$ for 48 h at 600 °C. Bi_2O_3 is a semiconductor, so it was again not very surprising that ^{17}O exchange occurred readily, and we obtained the static and MASS ^{17}O NMR spectra shown in Figure 1C,D. There is little narrowing upon MASS, and the widths are field independent, suggesting exchange interactions or the presence of free Bi(0), as seen previously with

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(1) Schramm, S.; Kirkpatrick, R. J.; Oldfield, E. *J. Am. Chem. Soc.* **1983**, *105*, 2483.
(2) Schramm, S.; Oldfield, E. *J. Am. Chem. Soc.* **1984**, *106*, 2502.
(3) Timken, H. K. C.; Turner, G. L.; Gilson, J. P.; Welsh, L. B.; Oldfield, E. *J. Am. Chem. Soc.* **1986**, *108*, 7231.
(4) Timken, H. K. C.; Janes, N.; Turner, G. L.; Lambert, S. L.; Welsh, L. B.; Oldfield, E. *J. Am. Chem. Soc.* **1986**, *108*, 7236.
(5) Janes, N.; Oldfield, E. *J. Am. Chem. Soc.* **1986**, *108*, 5743.
(6) Turner, G. L.; Chung, S. E.; Oldfield, E. *J. Magn. Reson.* **1985**, *64*, 3116.
(7) Timken, H. K. C.; Schramm, S.; Kirkpatrick, R. J.; Oldfield, E. *J. Phys. Chem.* **1987**, *91*, 1054.
(8) Bleier, H.; Bernier, P.; Jérome, D.; Bassat, J. M.; Coutures, J. P.; Dubois, B.; Odier, Ph. *J. Phys. (Paris)* **1988**, *49*, 1825.
(9) Ishida, K.; Kitaoka, Y.; Asayama, K.; Katayama-Yoshida, H.; Okabe, Y.; Takahashi, T. *J. Phys. Soc. Jpn.* **1988**, *57*, 2987.
(10) Coretsopoulos, C.; Lee, H. C.; Ramli, E.; Reven, L.; Rauchfuss, T. B.; Oldfield, E. *Phys. Rev. B* **1989**, *39*, 781.
(11) Oldfield, E.; Coretsopoulos, C.; Yang, S.; Reven, L.; Shore, J.; Han, O. H.; Ramli, E.; Hinks, D. G. *Phys. Rev. B*, in press.

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