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Contribution from the Department of Chemistry,
University of New Mexico, Albuquerque, New Mexico 87131

Tridentate Coordination by a Tripodal Ligand System: Synthesis and Crystal and Molecular Structure of [Diisopropyl [1,2-bis(diethylcarbamoyl)ethyl]phosphonate]erbium(III) Nitrate

D. J. McCabe, E. N. Duesler, and R. T. Paine*

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Combination of $Er(NO_3)_3 \cdot 5H_2O$ with mixtures of $(C_2H_5O)_3P(O)$ and the trifunctional ligand $(i\text{-}C_3H_7O)_2P(O)CH[C(O)N(C_2H_5)_2][CH_2C(O)N(C_2H_5)_2]$ leads to the formation of a crystalline complex, $Er(NO_3)_3\{(i\text{-}C_3H_7O)_2P(O)CH[C(O)N(C_2H_5)_2][CH_2C(O)N(C_2H_5)_2]\}$. The complex was characterized by elemental analysis, infrared and NMR spectroscopy, and single-crystal X-ray diffraction analysis. The complex was found to crystallize in the monoclinic space group $P2_1/n$ with $a = 13.994$ (3) Å, $b = 14.914$ (4) Å, $c = 15.104$ (3) Å, $\beta = 103.74$ (2)°, $Z = 4$, and $V = 3062$ (1) Å^3. The structure was solved by heavy-atom techniques, and blocked least-squares refinement converged with $R_F = 6.5\%$ and $R_{wF} = 5.7\%$ on 352 parameters and 3563 reflections with $F > 4\sigma(F)$. The Er ion is nine-coordinate by bonding with six oxygen atoms contributed by three bidentate nitrate ions and three oxygen atoms provided by one tripodal ligand. The important internal coordination sphere bond distances are Er–O(1) = 2.298 (6) Å, Er–O(4) = 2.326 (7) Å, and Er–O(5) = 2.267 (8) Å, which involve the ligand coordination sites, and Er–O(nitrate)$_{av}$ = 2.407 (9) Å.

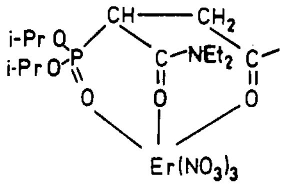
Introduction

Multifunctional ligands possess potential selective coordination and separation properties for metal ions, and there continues to be great interest in designing new ligands that have applications for selective chemistry with a single or small group of metal ions. We have previously reported[1] that the trifunctional ligand $(i\text{-}PrO)_2P(O)CH[C(O)NEt_2][CH_2C(O)NEt_2]$ (**1**) forms bis bidentate coordination complexes with early lanthanides La–Eu and bis monodentate coordination complexes with late lanthanides. In the latter case, the crystal structure of the Er complex, $Er(NO_3)_3\{(i\text{-}PrO)_2P(O)CH[C(O)NEt_2][CH_2C(O)NEt_2]\}_2 \cdot H_2O$, was determined.[1] It was found that the phosphoryl oxygen atom of the ligand was directly bonded to the lanthanide, while the short-leg, $CH[C(O)NEt_2]$, carbamide oxygen atom was hydrogen bonded to a metal-coordinated water molecule. Surprisingly, no evidence was found in any of the complexes for a tridentate coordination condition for **1**, and it was assumed that the three functional groups could not adopt a conformation that was favorable for tripodal coordination.

Horwitz and Kalina[2] have reported that addition of tributyl phosphate (TBP) to bifunctional ligands such as $(HxO)_2P(O)CH_2C(O)NEt_2$[3] and $Ph(OctO)P(O)CH_2C(O)N(i\text{-}Bu)_2$, at certain acid concentrations, produced enhanced or synergistic[4] extractions of Nd(III) and Am(III). It was proposed that this behavior is a result of TBP acting as a phase modifier without the formation of a stable mixed-ligand complex. Attempts to clarify the role of TBP and to isolate mixed-ligand complexes of this type, in fact, have been unsuccessful, and the molecular mechanism describing neutral-ligand synergistic effects is not clear. Nonetheless, the known influence of TBP on the bifunctional carbamoylmethylphosphonate ligand extractions suggested to us that a simple organophosphate might alter the coordination chemistry of trifunctional ligand **1** with lanthanide ions. We report here on the coordination chemistry of a mixture of **1** and triethyl phosphate (TEP) with $Er(NO_3)_3 \cdot 5H_2O$ and on the crystal structure determination for the novel tripodal ligand complex $Er(NO_3)_3\{(i\text{-}PrO)_2P(O)CH[C(O)NEt_2][CH_2C(O)NEt_2]\}$ (**2**).

Experimental Section

General Information. The trifunctional ligand $(i\text{-}C_3H_7O)_2P(O)CH[C(O)N(C_2H_5)_2][CH_2C(O)N(C_2H_5)_2]$ (**1**) was prepared as described previously.[5] $Er(NO_3)_3 \cdot 5H_2O$ was obtained from Alfa Products (Ventron). Infrared spectra were recorded on a Nicolet Model 6000 Fourier transform spectrometer, and samples were prepared as KBr pellets. NMR spectra were recorded on a Varian FT-80 or GE-NT360 spectrometer. Spectral standards were 85% H_3PO_4 and Me_4Si.



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Preparation of the Complex. The complex was prepared by addition of 2.5 mmol (0.98 g) of $Er(NO_3)_3 \cdot 5H_2O$ in 10 mL of 95% ethanol to a solution containing $(C_2H_5O)_3P(O)$, 2.5 mmol (0.40 g), and **1**, 2.5 mmol (0.89 g), in 10 mL of ethanol. The mixture was stirred, the volume was reduced to 4 mL, and 10 mL of diethyl ether was added. The resulting oil was washed with diethyl ether (2 × 15 mL), and the solution was decanted and discarded. The oil was then redissolved in ethanol, and the solvent was allowed to evaporate slowly. The resulting crystals were collected and characterized. The complex is soluble in $CHCl_3$, CH_2Cl_2, and alcohols. Anal. Calcd for $ErPO_{14}N_5C_{18}H_{37}$: C, 28.99; H, 5.00. Found: C, 30.73; H, 6.41. Infrared spectrum (cm^{-1}): 2978 (w), 1635 (ν_{CO}, s), 1602 (ν_{CO}, s), 1506 (ν_{NO_3}, s), 1497 (ν_{NO_3}, s), 1292 (ν_{NO_3}, s), 1185 (ν_{PO}, m), 1030 (m), 1018 (m). NMR spectra (27 °C): $^{31}P\{^1H\}$ (EtOH solvent) δ 19.0; $^{13}C\{^1H\}$ δ 75.0 (*C*HO), 44.3 (N*C*H$_2$), 43.8 (N*C*H$_2$), 42.8 (N*C*H$_2$), 42.6 (N*C*H$_2$), 39.5 (J_{PC} = 123.7 Hz, *C*HC(O)), 31.0 (CH*C*H$_2$C(O)), 24.6 (P(O)CH*C*H$_3$), 14.3 (NCH$_2$*C*H$_3$), 14.0 (NCH$_2$*C*H$_3$), 13.4 (NCH$_2$*C*H$_3$).

Crystallographic Measurements and Structure Solution. A clear pink crystal (0.23 × 0.30 × 0.32 mm) was placed in a glass capillary, which was centered on a Syntex P3/F automated diffractometer. Determinations of the crystal class, orientation matrix, and unit cell dimensions were performed in a standard manner.[6] Data were collected at 20 °C in the θ–2θ scan mode with use of Mo Kα radiation, a scintillation counter, and a pulse height analyzer. The data collection parameters are summarized in Table I. Preliminary examination of a short data set indicated the space group to be $P2_1/n$ (No. 14, alternate setting).[7] The data were corrected for Lorentz and polarization effects, and a small correction for absorption was applied. The agreement factors for averaging azimuthal-scan data before and after the absorption correction were 5.99% and 2.60%.[8] The minimum and maximum transmission factors were empirically estimated as 0.05 and 0.09. The data were scaled on the average standard intensity, which decreased 12% during data collection.

All calculations were performed with the R3/SHELXTL structure determination package.[9] Least-squares refinements in this package use a

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(1) McCabe, D. J.; Duesler, E. N.; Paine, R. T. *Inorg. Chem.* **1985**, *24*, 4626.

(2) Horwitz, E. P.; Kalina, D. G. *Solvent Extr. Ion Exch.* **1984**, *2*, 179.

(3) Abbreviations used in the text include: Et = ethyl, *i*-Pr = isopropyl, Hx = *n*-hexyl, Oct = *n*-octyl, *i*-Bu = isobutyl, Ph = phenyl.

(4) Sekine, T.; Hasegawa, Y. *Solvent Extraction Chemistry, Fundamentals and Applications*; Dekker: New York, 1977.

(5) McCabe, D. J.; Bowen, S. M.; Paine, R. T. *Synthesis* **1986**, 319.

(6) Bowen, S. A.; Duesler, E. N.; Paine, R. T. *Inorg. Chem.* **1982**, *21*, 261.

(7) Space group symmetry notation as given in: *International Tables for X-Ray Crystallography*; Reidel: Dordrecht, Holland, 1983; Vol. I, pp 73-346.

(8) The empirical absorption correction uses an ellipsoidal model fitted to azimuthal scans and then applied to the intensity data. Transmission factors were determined empirically. Corrections for extinction were found to be unnecessary.

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Table I. Experimental Data for the X-ray Diffraction Study of $Er(NO_3)_3\{(i\text{-}PrO)_2P(O)CH[C(O)NEt_2][CH_2C(O)NEt_2]\}$

(A) Crystal Parameters at 20 (2) °C

cryst syst: monoclinic
space group: $P2_1/n$
$a = 13.994$ (3) Å
$b = 14.914$ (4) Å
$c = 15.104$ (3) Å
$\beta = 103.74$ (2)°
$Z = 4$

formula: $ErPO_{14}N_5C_{18}H_{37}$
mol wt = 745.8
$V = 3062$ (1) Å^3
$\rho_{calcd} = 1.62$ g cm^{-3}
$\rho_{measd} = 1.5$ g cm^{-3}
$\mu = 29.5$ cm^{-1}
$F(000) = 1500$

(B) Data Collection

diffractometer: Syntex P3/F
radiation: Mo K_α (I = 0.71069 Å)
monochromator: highly oriented graphite cryst
reflcns measud: $\pm h,+k,+l$
2θ range: 1–55°
scan type: θ–2θ
scan speed: 4–30° min^{-1}
scan range: $[2\theta(K\alpha_1) - 1.3]$–$[2\theta(K\alpha_2) + 1.3]$°
bkd measurement: stationary cryst and counter; at beginning and end of 2θ scan, each for half of the total scan time
std reflcns: 3 measud every 141 reflcns [402; 060; 117]; 12% decay
no. of total reflcns collcd: 7820
no. of unique reflcns: 7082
no. of obsd reflcns used in refinement: 3563
weighting scheme: $1/[\sigma^2(F) + |g|F^2]$, $g = 0.00038$
GOF = 1.528

blocked-cascade algorithm with full-matrix blocks of 103 parameters.[10] The Er atom was located by Patterson methods, and phasing on this atom was sufficient to obtain positions of 23 of the 39 non-hydrogen atoms. After phasing on a subsequent Fourier map, the remaining non-hydrogen atom positions were obtained. Isotropic refinement on the non-hydrogen atoms gave an agreement factor $R = 13.9\%$. Treating the thermal parameters anisotropically reduced the R to 7.0%. Neutral-atom scattering factors were used throughout. The hydrogen atoms were included in idealized positions (C–H = 0.96 Å), riding on the position of the parent atom, and their U_{iso}'s were fixed at 1.2 times the last U_{equiv} of the parent carbon atom. Final refinements converged at $R_F = 6.5\%$ and $R_{wF} = 5.7\%$ on 352 parameters and 3563 reflections. The final difference map showed the highest peak to be 2.8 e Å^{-3}, situated 0.96 Å from Er. The next two peaks were 1.84 and 1.16 e Å^{-3} at 1.00 and 1.03 Å from the Er atom. The observed and calculated structure factor amplitudes, hydrogen atom positions (Table S-I), anisotropic thermal parameters (Table S-II), and full listings of bond angles and distances (Tables S-III and S-IV) are given in the supplementary material. The non-hydrogen atom positional parameters are listed in Table II.

Results and Discussion

An equimolar mixture of TEP and **1** in ethanol was combined with $Er(NO_3)_3{\cdot}5H_2O$ in ethanol, and workup led to the isolation of an oily complex. Extractions with diethyl ether and slow recrystallization from ethanol resulted in isolation of a pink crystalline product **2**, subsequently identified as $Er(NO_3)_3\{(i\text{-}PrO)_2P(O)CH[C(O)NEt_2][CH_2C(O)NEt_2]\}$. The complex was characterized by partial elemental analysis and by infrared and NMR spectroscopy. The elemental analyses are consistent with the proposed formulation of **2**, and they provide no evidence for the formation of a mixed-ligand complex. The infrared spectrum of **2** (KBr) shows bands at 1635, 1602, and 1185 cm^{-1}. The first two bands are assigned to carbonyl stretching frequencies that are downshifted by 10 and 43 cm^{-1}, respectively, from the single carbonyl band in **1**,[2] 1645 cm^{-1}. This observation contrasts with that for the spectrum of $Er(NO_3)_3\{(i\text{-}PrO)_2P(O)CH[C(O)NEt_2][CH_2C(O)NEt_2]\}_2{\cdot}H_2O$ (**3**), which shows one unshifted band at 1645 cm^{-1} and one shifted band at 1615 cm^{-1}. The third band is assigned to ν_{PO}, and it is downshifted 74 cm^{-1} from the phosphoryl band in **1**[5] and 30 cm^{-1} from ν_{PO} in **3**. The $^{31}P\{^1H\}$ NMR spectrum of **2** shows a single resonance centered at δ 19.0, which can be compared with the resonance positions for **1**, δ 22.7, and **3**, δ 17.8. There is no evidence for a resonance attributable to coordinated or uncoordinated TEP.[11] Unfortunately, these

Table II. Fractional Coordinates and Their Esd's for $Er(NO_3)_3\{(i\text{-}PrO)_2P(O)CH[C(O)NEt_2][CH_2C(O)NEt_2]\}$

atom	*x/a*	*y/b*	*z/c*
Er	0.08334 (4)	0.23706 (3)	0.80056 (3)
P(1)	0.25030 (23)	0.13327 (21)	0.97088 (19)
O(1)	0.1835 (5)	0.1264 (4)	0.8781 (4)
O(2)	0.2314 (6)	0.0582 (5)	1.0369 (5)
O(3)	0.3608 (6)	0.1302 (5)	0.9697 (5)
O(4)	0.0716 (5)	0.2571 (5)	0.9503 (4)
O(5)	0.2254 (6)	0.3089 (5)	0.8655 (5)
O(6)	−0.0014 (6)	0.1280 (5)	0.6929 (5)
O(7)	−0.0322 (6)	0.1263 (6)	0.8248 (5)
O(8)	−0.1141 (7)	0.0397 (7)	0.7185 (7)
O(9)	0.1958 (6)	0.1991 (5)	0.7072 (5)
O(10)	0.0997 (7)	0.3090 (6)	0.6621 (5)
O(11)	0.2099 (9)	0.2758 (7)	0.5890 (7)
O(12)	−0.0791 (7)	0.2967 (7)	0.7429 (7)
O(13)	0.0326 (6)	0.3906 (5)	0.8101 (6)
O(14)	−0.1166 (9)	0.4362 (8)	0.7585 (9)
N(1)	0.0956 (7)	0.2759 (7)	1.0999 (6)
N(2)	0.3050 (7)	0.4350 (6)	0.9176 (6)
N(3)	−0.0513 (8)	0.0965 (7)	0.7453 (8)
N(4)	0.1699 (9)	0.2612 (8)	0.6514 (7)
N(5)	−0.0564 (8)	0.3768 (8)	0.7713 (8)
C(1)	0.2343 (7)	0.2311 (7)	1.0378 (6)
C(2)	0.1279 (7)	0.2535 (7)	1.0275 (6)
C(3)	0.2954 (8)	0.3153 (7)	1.0263 (7)
C(4)	0.2721 (8)	0.3546 (7)	0.9314 (7)
C(5)	0.1560 (10)	0.2745 (10)	1.1951 (8)
C(6)	0.1478 (12)	0.1869 (12)	1.2400 (10)
C(7)	−0.0072 (10)	0.3004 (10)	1.0880 (10)
C(8)	−0.0198 (14)	0.3984 (13)	1.0772 (16)
C(9)	0.2857 (10)	0.4688 (8)	0.8223 (8)
C(10)	0.3574 (10)	0.4355 (10)	0.7732 (9)
C(11)	0.3653 (11)	0.4928 (10)	0.9908 (9)
C(12)	0.3054 (14)	0.5618 (11)	1.0217 (12)
C(13)	0.2183 (10)	−0.0345 (9)	1.0120 (9)
C(14)	0.1115 (11)	−0.0556 (10)	0.9778 (10)
C(15)	0.2638 (11)	−0.0884 (8)	1.0950 (9)
C(16)	0.4013 (10)	0.1338 (11)	0.8894 (9)
C(17)	0.4337 (12)	0.0441 (11)	0.8711 (11)
C(18)	0.4820 (12)	0.2005 (11)	0.9087 (13)

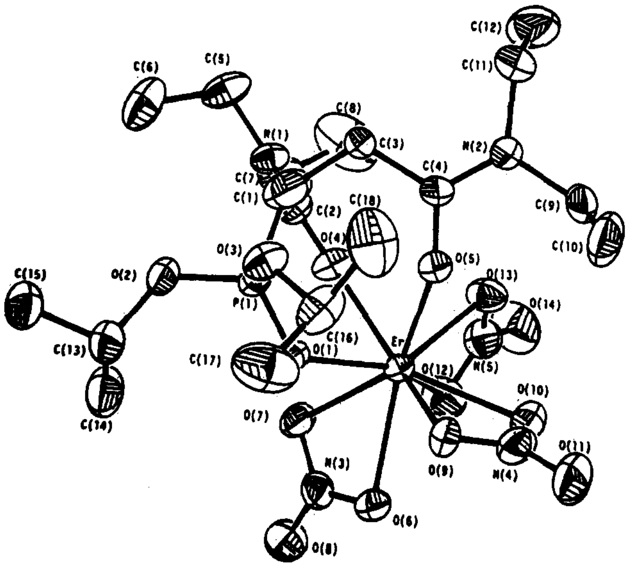

Figure 1. Molecular geometry and atom-labeling scheme for $Er(NO_3)_3\{(i\text{-}PrO)_2P(O)CH[C(O)NEt_2][CH_2C(O)NEt_2]\}$ (25% probability ellipsoids).

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(9) Sheldrick, G. M. *Nicolet SHELXTL Operations Manual*; Nicolet XRD Corp.: Cupertino, CA, 1981. SHELXTL uses absorption, anomalous dispersion, and scattering factor data compiled in: *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1970; Vol. 4, pp 55–60, 99–101, 149–150. Anomalous-dispersion terms were included for all atoms with atomic numbers greater than 2.

(10) A general description of the least-squares algebra is found in: *Crystallographic Computing*; Ahmed, F. R., Hall, S. R., Huber, C. P., Eds.; Munksgaard: Copenhagen, 1970; p 187. The least-squares refinement minimizes $\sum w(|F_o| - |F_c|^2)$, where $w = 1/[\sigma(F)^2 + gF^2]$, $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_{wF} = [\sum(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, and GOF = $[\sum w(|F_o| - |F_c|))^2/(NO - NV)]^{1/2}$ where NO = number of observations and NV = number of variables.

Table III. Selected Bond Distances (Å) for $Er(NO)_3)_3\{(i\text{-}PrO)_2P(O)CH[C(O)NEt_2][CH_2C(O)NEt_2]\}$

Er–O(1)	2.298 (6)	P(1)–O(3)	1.551 (9)
Er–O(4)	2.326 (7)	P(1)–C(1)	1.819 (11)
Er–O(5)	2.267 (8)	C(1)–C(2)	1.498 (15)
Er–O(6)	2.404 (8)	C(1)–C(2)	1.498 (15)
Er–O(7)	2.399 (9)	C(1)–C(3)	1.552 (16)
Er–O(9)	2.416 (9)	C(2)–O(4)	1.243 (10)
Er–O(10)	2.409 (9)	C(2)–N(1)	1.322 (14)
Er–O(12)	2.404 (9)	C(3)–C(4)	1.511 (15)
Er–O(13)	2.411 (8)	C(4)–O(5)	1.254 (12)
P(1)–O(1)	1.492 (6)	C(4)–N(2)	1.319 (15)
P(1)–O(2)	1.563 (9)		

spectroscopic data do not provide for an unambiguous assignment of the solution-state structure of **2**.

The availability of single crystals of **2** allowed for the determination of the solid-state molecular structure by X-ray diffraction techniques. A view of the molecule is shown in Figure 1, and selected bond distances are listed in Table III. The structure determination confirms the proposed molecular composition, but more importantly, it reveals the interesting ligand coordination transformation from complex **3** to **2**. Addition of TEP results in the loss of a water molecule from the inner Er(III) coordination sphere and tridentate coordination of **1** with $Er(NO_3)_3$. The Er ion is nine-coordinate with the three oxygen atoms, O(1), O(4), and O(5), donated by **1** and six oxygen atoms, O(6), O(7), O(9), O(10), O(12) and O(13), provided by bidentate nitrate groups. The Er–O(nitrate) distances are nearly identical: $Er\text{–}O(nitrate)_{av} = 2.407$ (9) Å; range 2.399 Å–2.416 Å. The Er–O(phosphoryl) distance, Er–O(1) = 2.298 (6) Å, can be compared with the distances in **3**[1], 2.279 (4) and 2.289 (5) Å, and the distances in the CMP complex $Er(NO_3)_3\{(i\text{-}PrO)_2P(O)CH_2C(O)NEt_2\}_2 \cdot H_2O$ (**4**),[12] which contains two bifunctional CMP ligands bonded in a monodentate manner: Er–O(phosphoryl) = 2.259 (6) and 2.290 (6) Å. Variations in P═O bond distances between the ligand **1** and the complexes **2** and **3** are dramatic: **1**, 1.459 (3) Å; **2**, 1.492 (6) Å; **3**, 1.469 (4) and 1.476 (5) Å. The bond lengthening going from **1** to **2** is consistent with the large infrared coordination shift in ν_{PO}.

The Er–O carbonyl distances in **2**, Er–O(4) = 2.326 (7) Å and Er–O(5) = 2.267 (8) Å, are significantly different, and it is interesting to note that the Er–O(5) distance associated with the larger seven-membered chelate ring and the long-leg carbonyl group, $CH[CH_2C(O)NEt_2]$, provides the shorter Er–O coordination distance. The carbonyl distances, C(2)–O(4)(short-leg) = 1.243 (10) Å and C(4)–O(5)(long-leg) = 1.254 (12) Å, are longer than the respective distances in **1**, 1.228 (3) and 1.223 (3) Å. As expected, the carbonyl distances in **2** are longer than the carbonyl distances in **3** and **4**. $CH[C(O)NEt_2]$: **3**, 1.231 (9) and 1.232 (8) Å; **4**, 1.239 (11) and 1.240 (11) Å. $CH[CH_2C(O)NEt_2]$: **3**, 1.228 (8) and 1.234 (13) Å.

The structure of **2** is unique, and its formation may provide one clue to the mechanism for phase modification chemistry observed in extractions of Nd(III) and Am(III) by carbamoylmethylphosphonate and phosphine oxide ligands with TBP.[2] It is known that organophosphates, such as TBP and presumably TEP, act to dehydrate otherwise highly aquated lanthanide and actinide ions.[2] Whether formation of **2** occurs by dehydration of **3** or by dehydration of $Er(NO_3)_3 \cdot 5H_2O$ followed by ligand coordination is not clear; however, it appears that **3** is a likely intermediate. In the present synthesis, the competing water may be removed in the ether washes, and the coordinatively unsaturated Er(III) ion is able to coordinate with two carbonyl groups. This coordination mode is apparently quite stable, once formed, since water/ethanol mixtures dissolve the complex, but dissolution does not result in water coordination. Clearly, additional studies are required in order to understand the molecular mechanisms of neutral-ligand phase modification and synergism. The observations made here provide a useful guide to those studies.

Acknowledgment. R.T.P. wishes to recognize financial support for this work from the Department of Energy, Office of Basic Energy Sciences, Contract No. 85ER 10465. He also wishes to recognize NSF Grants CHE-7802921 and CHE-8201374, which facilitated the purchases of the X-ray diffractometer and the NMR spectrometer.

Registry No. 2, 113086-34-3.

Supplementary Material Available: Tables S-I–S-IV, listing hydrogen atom positions, anisotropic thermal parameters, bond angles, and bond distances (7 pages); a table of calculated and observed structure factors (17 pages). Ordering information is given on any current masthead page.

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(11) More detailed NMR studies of the paramagnetic shifts experienced by **1** in the presence of various lanthanide ions will be undertaken in the future.

(12) Bowen, S. M.; Duesler, E. N.; Paine, R. T. *Inorg. Chim. Acta* **1982**, *61*, 155.

Contribution from the Department of Chemistry,
University of New Mexico, Albuquerque, New Mexico 87131

Reaction Chemistry of Tris(trimethylsilyl)amine with Monohaloboranes

Jerzy Fr. Janik, Chaitanya K. Narula, Eric G. Gulliver, E. N. Duesler, and Robert T. Paine*

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Reactions of tris(trimethylsilyl)amine, $N(SiMe_3)_3$, with several monochloroboranes, $CH_3\overline{NCH_2CH_2N(CH_3)B}Cl$, $o\text{-}\overline{OC_6H_4OB}Cl$, and $\overline{SCH_2CH_2SB}Cl$, have been examined, and the ((trimethylsilyl)amino)boranes $o\text{-}\overline{OC_6H_4OB}N(SiMe_3)_2$, $[o\text{-}\overline{OC_6H_4OB}]_2NSiMe_3$, $\overline{SCH_2CH_2SB}N(SiMe_3)_2$, and $[\overline{SCH_2CH_2SB}]_2NSiMe_3$ have been prepared and characterized by spectroscopic methods. The molecular structure of $[o\text{-}\overline{OC_6H_4OB}]_2NSiMe_3$ has been determined by single-crystal X-ray diffraction analysis and found to crystallize in the orthorhombic space group $P2_12_12_1$ (No. 19) with $a = 7.189$ (1) Å, $b = 19.387$ (4) Å, $c = 24.508$ (4) Å, $Z = 8$, $V = 3416$ (1) Å^3, and $\rho_{calcd} = 1.26$ g cm^{-3}. The structure was solved by direct methods, and blocked least-squares refinement converged with $R_F = 10.1\%$ and $R_{wF} = 9.2\%$ on 3012 unique data with $F > 2\sigma(F)$. The structure contains two independent molecules in the unit cell, and the central nitrogen atoms have a trigonal-planar geometry. Important bond distances include $B\text{–}N_{av} = 1.421$ (13) Å, $Si\text{–}N_{av} = 1.783$ (7) Å, and $B\text{–}O_{av} = 1.390$ (13) Å. Attempts to prepare the 1,3,2-diazaborolidine $CH_3\overline{NCH_2CH_2N(CH_3)B}N(SiMe_3)_2$ and triborylamine compounds by this synthetic method were unsuccessful.

Introduction

Reactions of haloboranes with hexamethyldisilazane (HMDS) have been thoroughly studied,[1-10] and these reactions provide a generally useful route to the formation of a variety of (silylamino)boranes. In turn, several monomeric (silylamino)boranes,

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