Chapter One

MAIN GROUP COMPOUNDS

1. DIBORANE(4) COMPOUNDS

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Diborane(4) compounds are key reagents in transition-metal-catalyzed diboration[1] and Suzuki–Miyaura coupling reactions.[2] Two of the most widely used compounds are the pinacolate derivative $B_2(pin)_2$ (pin = $OCMe_2CMe_2O$)[3] and the catecholate species $B_2(cat)_2$ (cat = 1,2-$O_2C_6H_4$),[4] both of which are prepared from tetrakis(dimethylamino) diborane(4), $B_2(NMe_2)_4$, described initially by Brotherton.[5] Detailed preparations for $B_2(pin)_2$ and $B_2(NMe_2)_4$ have been described in Ref. 3b. Here we present a slightly different preparation for $B_2(NMe_2)_4$ together with details of the synthesis of 1,2-$B_2Cl_2(NMe_2)_2$[6] and $B_2(cat)_2$. Simple modifications of the $B_2(cat)_2$ synthesis given here allow for the preparation of a host of diol-derived diborane(4) compounds.

A. TETRAKIS(DIMETHYLAMINO)DIBORANE(4), $B_2(NMe_2)_4$

$$BCl_3 + 2\,B(NMe_2)_3 \longrightarrow 3\,BCl(NMe_2)_2$$

$$2\,BCl(NMe_2)_2 + 2\,Na \longrightarrow B_2(NMe_2)_4$$

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General Comments

All solvents were freshly distilled under dinitrogen from an appropriate drying agent immediately prior to use. Glassware was either kept in an oven at 150°C overnight or flame-dried under vacuum. All manipulations were carried out under dinitrogen using standard Schlenk techniques.

Procedure

■ **Caution.** *Sodium can spontaneously ignite on exposure to water or air. BCl_3 fumes vigorously in air, producing HCl. These reagents should only be handled in a fume hood.*

To a two-necked 250-mL round-bottomed flask equipped with a sidearm and a magnetic stirring bar and mounted on a magnetic stirrer, $B(NMe_2)_3$ (Aldrich, 33 mL, 0.2 mol) is added under a constant stream of nitrogen and stirring is started. The flask is then cooled to about −78°C by means of an external dry-ice ethanol bath, and a solution of BCl_3 in heptane (Aldrich, 100 mL of a 1.0 M solution) is added. (*Note*: It is important that heptane rather than hexane be used, since yields are much lower when hexane is employed.) The reaction mixture is then stirred at low temperature for 1 h, after which time the cooling bath is removed, and the reaction flask and contents are allowed to warm to room temperature. Stirring is continued for a further 3 h. After this time the reaction mixture forms a pale yellow solution with small quantities of a white solid. [*Note*: Checkers state that at this stage the reaction can be assayed by ^{11}B NMR, although this is rarely necessary if freshly distilled or purchased BCl_3 and $B(NMe_2)_3$ are used. The solid can be removed by filtration, although its presence in subsequent steps seems not to affect the yield.] Clean metallic sodium (6.9 g, 0.3 mol) is then slowly added in small pieces, and afterward a Liebig condenser is attached to the reaction flask. The magnetic stirrer is replaced with a stirrer–heating mantle, and the reaction mixture is then refluxed for 16 h, resulting in a brown solution and a purple precipitate. After cooling to room temperature, the condenser is removed, and the reaction mixture is then filtered through a glass frit into a separate flask. The filter cake is washed with hexanes (2 × 10 mL). All solvent is removed from the filtered reaction solution by vacuum pumping (standard vacuum pump) at room temperature, affording a brown oil. Fractional vacuum distillation (0.2 mmHg) of the brown oil affords small quantities of unreacted $B(NMe_2)_3$ (1.5 g, 10%) as the first fraction (20–25°C) followed by a second fraction (38–42°C) forming $B_2(NMe_2)_4$ (16.8 g, 85%) (checkers' yields 79 and 87%) as a colorless liquid.

Properties

$B_2(NMe_2)_4$ is a thermally stable but moisture-sensitive colorless liquid (bp 70–73°C at 3 mmHg) that is soluble in most common solvents. Samples can be stored in a sealed tube at 4°C for indefinite periods. ^1H and ^{11}B NMR spectra ($CDCl_3$) at room temperature show singlets at δ 2.60 and 34.9 (broad) ppm, respectively (the latter referenced to $BF_3 \cdot Et_2O$). Traces of $B(NMe_2)_3$, if present, can be identified by its ^{11}B NMR signal at 25.4 ppm.

B. 1,2-DICHLORO-1,2-BIS(DIMETHYLAMINO)DIBORANE(4), $B_2Cl_2(NMe_2)_2$

$$B_2(NMe_2)_4 + 4\,HCl \longrightarrow 1,2\text{-}B_2Cl_2(NMe_2)_2 + 2\,[NH_2Me_2]Cl$$

Procedure

■ **Caution.** *HCl in Et_2O is corrosive and lachrymatory. All manipulations should be carried out in a fume hood and gloves worn.*

This procedure is similar to that described in Ref. 6. To a rapidly stirred solution of $B_2(NMe_2)_4$ (3.31 g, 16.7 mmol) in Et_2O (25 mL) in a 100-mL Schlenk flask, a solution of HCl in Et_2O (66.8 mL of a 1.0 M solution) is added over a period of 10 min, during which time a large amount of a white precipitate forms. The reaction mixture is allowed to stir for 1 h, after which time it is filtered. The solid filtercake is washed with Et_2O (2×10 mL), and all solvent is then carefully removed from the colorless filtrate by vacuum pumping (standard vacuum pump) at room temperature affording a colorless oil. Vacuum distillation of this oil (48°C, 0.2 mmHg) affords pure $1,2\text{-}B_2Cl_2(NMe_2)_2$ as a colorless liquid (2.08 g, 69%).*

Properties

$1,2\text{-}B_2Cl_2(NMe_2)_2$ is a thermally stable but moisture-sensitive colorless liquid (bp 48°C at 0.2 mmHg) that is soluble in most common solvents. Samples can be stored in a sealed tube at 4°C for indefinite periods. The ^1H NMR spectrum ($CDCl_3$) at room temperature shows two singlets at δ 2.90 (s, 6H) and 2.87

*Checkers indicate that product can be easily lost if care is not exercised in removing the solvent. Best results (75 and 80% yields for two preparations) were obtained by removing Et_2O at 0°C.

(s, 6H). The ^{11}B NMR spectrum shows a broad singlet at 35.7 ppm. Additional data on the reactions of $B_2(NMe_2)_4$ with HCl can be found in Refs. 6 and 7, including the preparation of the synthetically useful compound $[B_2Cl_4(NHMe_2)_2]$.[4]

C. 2,2′-BIS(1,3,2-BENZODIOXABOROLE), $B_2(1,2\text{-}O_2C_6H_4)_2$

$$B_2(NMe_2)_4 + 2\,1,2\text{-}(HO)_2C_6H_4 \longrightarrow [B_2(1,2\text{-}O_2C_6H_4)_2(NHMe_2)_2] + 2\,NHMe_2$$

$$[B_2(1,2\text{-}O_2C_6H_4)_2(NHMe_2)_2] + 2\,NHMe_2 + 4\,HCl \longrightarrow B_2(1,2\text{-}O_2C_6H_4)_2 + 4\,[NH_2Me_2]Cl$$

Procedure

A magnetically stirred solution of catechol (1.22 g, 11.1 mmol) in Et_2O (20 mL) is prepared in a 100-mL Schlenk flask and cooled to 0°C. A solution of $B_2(NMe_2)_4$ (1.0 g, 5.0 mmol) in Et_2O (5 mL) is then added, and stirring is continued for 20 min. After this time the solution is allowed to warm to room temperature, and stirring is continued overnight. At this stage the reaction mixture contains a large amount of a white precipitate of the amine adduct $[B_2(1,2\text{-}O_2C_6H_4)_2(NHMe_2)_2]$. The reaction mixture is then recooled to 0°C, and a solution of HCl in Et_2O (20 mL of a 1.0 M solution) is added, with stirring continued for 20 min. This amount of HCl is a slight excess over the amount required to remove all the amine present (free or coordinated), specifically, 4 equiv relative to the $B_2(NMe_2)_4$; the use of a larger excess can lead to reductions in the yield of $B_2(cat)_2$. The reaction mixture is then allowed to warm to room temperature and stir overnight, after which time a white precipitate of $[NH_2Me_2]Cl$ is present. All volatiles are then removed by vacuum pumping, affording a white solid. Addition of hot toluene, filtration, and subsequent concentration of the filtrate then affords white crystals of crude $B_2(cat)_2$. Crystallization is completed by cooling the mixture to −30°C. The mother liquor is then removed by syringe, and the white solid is dried by vacuum pumping (alternatively, if a drybox is being used, the solid may be isolated by filtration). Washing with MeCN (2 × 1 mL) and then with hexanes (2 × 1 mL), and finally drying by vacuum affords analytically pure $B_2(cat)_2$ (1.01 g, 85%) (checkers' yields 88 and 93%.) as a white solid.

Properties

$B_2(cat)_2$ is a white solid that is stable in air for brief periods but can be stored indefinitely in sealed flasks under a nitrogen atmosphere. It is soluble in hot toluene, $CHCl_3$, CH_2Cl_2, and tetrahydrofuran (THF), although solutions are susceptible to hydrolysis. The ^1H NMR spectrum ($CDCl_3$) at room temperature

shows multiplets at δ 7.42 (m, 4H) and 7.21 (m, 4H) and the ^{11}B NMR spectrum ($CDCl_3$) exhibits a broad singlet at 28.8 ppm. Commonly encountered minor decomposition products in the crude solid (which are removed by washing with MeCN) are $B_2(cat)_3$ (δ ^{11}B 16.6),[8] (cat)BOB(cat) (δ ^{11}B 18.1)[9] and $[NH_2Me_2][B(cat)_2]$ [δ ^{11}B (sharp) 14.0]. Traces of $[B_2Cl_4(NHMe_2)_2]$ [δ ^{11}B (sharp) 9.5][4] may also be present.

References

1. T. B. Marder and N. C. Norman, *Top. Catal.* **5**, 63 (1998).
2. N. Miyaura and A. Suzuki, *Chem. Rev.* **95**, 2457 (1995).
3. (a) H. Nöth, *Z. Naturforsch., Teil B* **39**, 1463 (1984); (b) T. Ishiyama, M. Murata, T. Akiko, and N. Miyaura, *Org. Synth.* **77**, 176 (2000).
4. F. J. Lawlor, N. C. Norman, N. L. Pickett, E. G. Robins, P. Nguyen, G. Lesley, T. B. Marder, J. A. Ashmore, and J. C. Green, *Inorg. Chem.* **37**, 5282 (1998); W. Clegg, M. R. J. Elsegood, F. J. Lawlor, N. C. Norman, N. L. Pickett, E. G. Robins, A. J. Scott, P. Nguyen, N. J. Taylor, and T. B. Marder, *Inorg. Chem.* **37**, 5289 (1998).
5. A. L. McCloskey, R. J. Brotherton, J. L. Boone, and H. M. Manasevit, *J. Am. Chem. Soc.* **82**, 6245 (1960). See also R. J. Brotherton, in *Progress in Boron Chemistry*, H. Steinberg and A. L. McCloskey, eds., Macmillan, New York, 1964, Chapter 1.
6. H. Nöth and W. Meister, *Z. Naturforsch.*, *Teil B* **17**, 714 (1962).
7. S. C. Malhotra, *Inorg. Chem.* **3**, 862 (1964).
8. S. A. Westcott, H. P. Blom, T. B. Marder, R. T. Baker, and J. C. Calabrese, *Inorg. Chem.* **32**, 2175 (1993).
9. W. Gerrard, M. F. Lappert, and B. A. Mountfield, *J. Chem. Soc.* 1529 (1959).

2. SODIUM TETRAKIS(3,5-BIS(TRIFLUOROMETHYL) PHENYL)BORATE, $Na[B(3,5\text{-}(CF_3)_2C_6H_3)_4]$

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The anion $[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]^-$ is a highly soluble, noncoordinating counterion that has gained considerable attention.[1] The anion is typically prepared as the sodium[1a] or potassium[2] salt, which are extremely versatile reagents that can be converted to the acid form, $[H(OEt_2)_2]$ $[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$,[1a] the silver salt $Ag[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$,[2,3] or the thallium salt $Tl[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$[4] for

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further reactions. A significant disadvantage in previous preparations of the sodium and potassium salts is that the Grignard reagent prepared in situ is potentially explosive.[5] We have dramatically improved the synthesis of Na[B{3,5-$(CF_3)_2C_6H_3$}$_4$].[6] The critical modification is to add $NaBF_4$ to the reaction mixture before forming the Grignard reagent from magnesium and 1-Br-3,5-$(CF_3)_2C_6H_3$. Presumably, most of the potentially explosive Grignard reagent formed first in the reaction is consumed immediately by the $NaBF_4$ present and does not build up in solution, thereby reducing the danger of explosion. Also, 1,2-dibromoethane is added at the beginning of the reaction to ensure that the Grignard reaction initiates immediately on the dropwise addition of 1-Br-3,5-$(CF_3)_2C_6H_3$. This preparation of Na[B{3,5-$(CF_3)_2C_6H_3$}$_4$] is safer and leads to pure product in very high yield.

■ **Caution.** *The $(CF_3)_2C_6H_3MgBr$ generated in situ in this preparation is potentially explosive.[5] The reaction solution should not be allowed to go to dryness before addition of the solution of Na_2CO_3 in water. Care should be taken to ensure that the reaction vessels are tightly sealed before initiating the Grignard reaction by using a heat gun because of the flammability of the ether solvent. Benzene is a human carcinogen.*

General Considerations

The Grignard reaction is carried out under a nitrogen atmosphere by using standard Schlenk techniques. All solvents are dried and distilled prior to use. Magnesium metal turnings from EM Science and Na_2SO_4 (anhydrous) from Fisher Scientific are used as received. The compounds $NaBF_4$, 1,2-dibromoethane, and 3,5-bis(trifluoromethyl)bromobenzene are purchased from Aldrich and used as received. The unopened bottle of $NaBF_4$ is opened and subsequently stored in a Vacuum Atmospheres HE-493 drybox. Decolorizing carbon, NORIT 211, is purchased from Acros and used as received.

Procedure

A 500-mL three-necked flask containing a stirring bar is fitted with a reflux condenser, a pressure-equalizing addition funnel, and a glass stopper. This apparatus is flame-dried under vacuum, cooled under nitrogen, and then charged with Mg turnings (1.01 g, 41.7 mmol) against a stream of nitrogen. The Mg turnings are stirred under nitrogen in the empty flask for 2 h.* $NaBF_4$ (0.70 g, 6.4 mmol) is

*One of the checkers activated the Mg turnings by submerging them in 1.0 M HNO_3 until a metallic shine was visible. The solution was decanted, and the turnings were washed 3 times with distilled water, with acetone, and then 2 times with diethyl ether.

weighed in the glovebox and then is transferred quickly to the reaction flask against a stream of nitrogen. Also, 150 mL Et_2O is added via syringe. Then 1,2-dibromoethane (0.49 mL, 5.7 mmol) is added through the addition funnel, and the flask is heated for several minutes with a heat gun to initiate reaction.* The heating is stopped and the solution stirred until the refluxing stops. Tiny bubbles coming off the Mg turnings indicates that the reaction has initiated, and the solution slowly becomes cloudy. Then 3,5-bis(trifluoromethyl)bromobenzene (6.2 mL, 36 mmol), diluted with 50 mL Et_2O, is added dropwise over $\sim$30 min. The addition causes the solution to gently reflux, and the solution slowly darkens to light brown by the end of the addition. The reaction mixture is heated with a heating mantle to continue the reflux for an additional 30 min. The heat is then removed, and the reaction mixture is stirred overnight at room temperature under nitrogen.

The reaction mixture is added to Na_2CO_3 (16 g) in water (200 mL), stirred for 30 min, and then filtered. (*Note*: Typical benchtop procedures can be used for the workup at this point, but an inert atmosphere must be used for the Dean–Stark trap azeotropic distillation step and manipulations of the solid after that point.) The ether layer is separated, and the aqueous layer is extracted with ether (3$\times$ 50 mL). The combined organic solution is dried over sodium sulfate (10 g) and then treated with decolorizing charcoal (2 g). The mixture is filtered and the ether is removed with a rotary evaporator. The remaining oily solid is suspended in 200 mL of benzene, and the water is removed with a Dean–Stark trap by azeotropic distillation (under nitrogen) for 2 h. The solvent volume is reduced to $\sim$50 mL via distillation of the benzene and removal through the stopcock on the Dean–Stark trap. The remaining solution is then cooled to room temperature, and the solvent is removed via cannula filtration.† The residual light tan solid‡ is dried under vacuum overnight (5.04 g, 5.6 mmol, 89%). ^{1}H NMR (acetone d_6), δ 7.79 (8H, br, O–H), 7.67 (4H s, p-H).

Anal. (for a sample protected from air). Calcd. for $C_{32}H_{12}F_{24}BNa$: C, 43.37; H, 1.36. Found: C, 43.48; H, 1.61.

Properties

The compound $Na[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$ is a light brown solid, mp 300–306°C. Elemental analysis shows that pure $Na\{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}$ obtained in this procedure picks up two equivalents of water when handled in air.

*One of the checkers added both the dibromoethane and subsequently the ether solution of bis(trifluoromethyl)bromobenzene via syringe through a rubber septum stopper in place of the addition funnel.
†Filtration of the benzene solution removes unreacted starting material and other soluble impurities.
‡The tan solid obtained after drying by the benzene azeotrope procedure is much less soluble in CH_2Cl_2 than the oily solid present before.

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References

1. (a) M. Brookhart, B. Grant, and J. A. F. Vople, *Organometallics* **11**, 3920 (1992); (b) J. Ledford, C. S. Shultz, D. P. Gates, P. S. White, J. M. DeSimone, and M. Brookhart, *Organometallics* **20**, 5266 (2001); (c) A. Llamazares, H. W. Schmalle, and H. Berke, *Organometallics* **20**, 5277 (2001); (d) A. E. Enriquez, P. S. White, and J. L. Templeton, *J. Am. Chem. Soc.* **123**, 4992 (2001); (e) S. Reinartz, P. S. White, M. Brookhart, and J. L. Templeton,. *J. Am. Chem. Soc.* **123**, 12724 (2001); (f) D. M. Tellers and R. G. Bergman, *Organometallics* **20**, 4819 (2001); (g) X. Fang, J. G. Watkin, B. L. Scott, and G. L. Kubas, *Organometallics* **20**, 3351 (2001); (h) W. B. Sharp, P. Legzdins, and B. O. Patrick, *J. Am. Chem. Soc.* **123**, 8143 (2001).
2. W. E. Buschmann and J. S. Miller, *Inorg. Chem.* **33**, 83 (2002).
3. Y. Hayashi, J. J. Rohde, and E. J. Corey, *J. Am. Chem. Soc.* **118**, 5502 (1996).
4. R. P. Hughes, D. C. Lindner, A. L. Rheingold, and G. A. P. Yap, *Inorg. Chem.* **36**, 1726 (1997).
5. E. J. Moore and R. Waymouth, *Chem. Eng. News* 6 (March 17, 1997).
6. D. L. Reger, T. D. Wright, C. A. Little, J. J. S. Lamba, and M. D. Smith, *Inorg. Chem.* **40**, 3810 (2001).

3. ANIONIC TRIS- AND BIS(DIPHENYLPHOSPHINOMETHYL)BORATES

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Chelating phosphines are perhaps more widely used than any other ligand class in synthetic inorganic and organic chemistry.[1] A wealth of literature exists describing the utility of neutral chelating phosphines for applications in catalytic and stoichiometric reaction chemistry. By comparison, the chemistry of anionic phosphine ligands remains relatively unexplored. Anionic (phosphino)borate ligands enable access to a wide range of charge neutral metal complexes whose reaction chemistry may be studied with respect to that of related discrete salt complexes supported by neutral phosphine chelates.[2] Herein we describe convenient procedures for the preparation of the tris(phosphino)borate ligand, $[PhB(CH_2PPh_2)_3]^-$,[3,4] and the bis(phosphino)borate ligand, $[Ph_2B(CH_2PPh_2)]^-$,[2b] as their tetra-*n*-butylammonium salts. The ammonium salts are

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versatile reagents for the preparation of metal complexes of these (phosphino)-borate ligands, offering certain synthetic advantages by comparison to the lithium salt precursors. Additionally, the thallium complex $[PhB(CH_2PPh_2)_3]Tl$ provides a very useful transmetallation reagent for the tris(phosphino)borate ligand.[5] Its synthesis is also described.

A. TETRABUTYLAMMONIUM PHENYLTRIS (DIPHENYLPHOSPHINOMETHYL)BORATE, $[^nBu_4N][PhB(CH_2PPh_2)_3]$

$$3\,Li(TMEDA)CH_2PPh_2 + PhBCl_2 \longrightarrow [Li(TMEDA)][PhB(CH_2PPh_2)_3] + 2\,LiCl + 2\,TMEDA$$

$$[Li(TMEDA][PhB(CH_2PPh_2)_3] + [^nBu_4N][Cl] \longrightarrow [^nBu_4N][PhB(CH_2PPh_2)_3] + LiCl + TMEDA$$

■ **Caution.** *$PhBCl_2$ reacts vigorously with water and fumes in air. It should be handled under a nitrogen atmosphere, and care should be taken to minimize skin contact and respiratory exposure.*

Procedure

A 1-L round-bottomed Schlenk flask is equipped with a magnetic stirring bar and rubber septum and is charged with 33.3 g (103 mmol) of $Li(TMEDA)CH_2PPh_2$ (TMEDA = tetramethylethylenediamine),[6] suspended in 500 mL of dry and deoxygenated Et_2O, under a dinitrogen atmosphere. The stirring, yellow suspension is chilled to $-78°C$ and, under a dinitrogen counterflow, the septum is replaced by a 150-mL dropping funnel charged with a solution of $PhBCl_2$* (5.475 g, 34.5 mmol) dissolved in toluene (70 mL). The phenyldichloroborane solution is added dropwise to the stirring suspension over a period of 20 min. The resulting yellow mixture is allowed to gradually warm to room temperature and stirring is continued for 20 h. A representative aliquot is analyzed by ^{31}P NMR spectroscopy to ensure complete consumption of $Li(TMEDA)CH_2PPh_2$ (addition of several drops of dry tetrahydrofuran to the sample aliquot affords a homogeneous solution that provides an accurate spectroscopic assay).

The remainder of the procedure is carried out under air and is executed relatively quickly to minimize ligand degradation. To precipitate the [Li(TMEDA)][$PhB(CH_2PPh_2)_3$] product, the reaction mixture is cooled to $-78°C$ and

*Available from Aldrich Chemical Company.

hexanes (400 mL) are added while stirring. The suspension is allowed to settle for at least 30 min at −78°C. The resulting white solid is collected by filtration on a coarse frit, and the filtrate is discarded. The off-white filtercake is washed with hexanes (2 × 300 mL) and extracted with methanol (75 mL), resulting in a somewhat cloudy suspension. This suspension is filtered through Celite on a medium-porosity sintered-glass frit. The methanol solution is added slowly to a solution of [^{n}Bu$_4$N]Cl (19.2 g, 69 mmol), prepared by dissolving the [^{n}Bu$_4$N]Cl in a mixture of 300 mL of deionized H_2O and 20 mL of diethyl ether. After the addition is complete, a sticky white solid results, which is collected on a medium-porosity frit and is repeatedly washed with copious amounts of water and diethyl ether (2 × 100 mL each). The resulting white powder is then dissolved in acetonitrile (100 mL), yielding a somewhat cloudy solution. The solution is then stirred over anhydrous sodium sulfate and subsequently filtered through Celite on a sintered-glass frit. The filtrate is thoroughly dried on a rotovap (rotary evaporator) and on a vacuum line, and then it is triturated several times with diethyl ether to ensure complete removal of acetonitrile. Finally, the resulting powder is suspended in diethyl ether (250 mL) and collected on a medium-porosity frit, affording 15.5 g (48.4%) of white [^{n}Bu$_4$N][PhB(CH$_2$PPh$_2$)$_3$]. This material is typically pure enough for further work (showing only trace acetonitrile impurities), but recrystallization from cold tetrahydrofuran/diethyl ether yields analytically pure material.

Properties

[^{n}Bu$_4$N][PhB(CH$_2$PPh$_2$)$_3$] is a white, crystalline solid that is moderately air-stable and can be handled in nonacidic aqueous solutions for short periods without appreciable degradation. The ammonium salt is not soluble in hydrocarbons such as pentane and diethyl ether, nor aromatic solvents such as benzene and toluene, when in pure form. It is, however, appreciably soluble in toluene and diethyl ether prior to purification, partly accounting for the reduced yield. The salt is very soluble in tetrahydrofuran, acetone, acetonitrile, and methanol. The ^{1}H NMR spectrum (CD_3CN, 300 MHz) displays signals at δ 6.7–7.5 (m, 35H), 3.05 (m, 8H), 1.56 (m, 8H), 1.14 (br, 6H), 0.95 (t, 12H). The ^{31}P{^{1}H} NMR spectrum shows a single resonance at −10.9 ppm. Resonances in the ^{1}H and ^{31}P NMR are broadened when spectra are obtained in nonpolar solvents such as C_6D_6. Doping such solvents with small amounts of d_8-THF or d_6-acetone helps solubilize the ligand and affords sharper spectra. It is worth noting that the initial metathesis reaction of Ph_2PCH_2Li(TMEDA) with $PhBCl_2$ proceeds in high yield according to ^{31}P NMR, and that the cation exchange also appears to be quantitative. The synthetic procedure described here ensures the isolation of a clean product free of LiCl, borane, and phosphine byproducts. Halogenated solvents such as chloroform and dichloromethane, even when dried and freshly distilled

under dinitrogen, rapidly decompose both [Li(TMEDA)][$PhB(CH_2PPh_2)_3$] and [$^nBu_4N$][$PhB(CH_2PPh_2)_3$]. The inability to use chlorinated solvents in the purification procedure partly accounts for the relatively tedious workup we recommend to obtain pure material. This problem is circumvented by preparation of the thallium complex of the ligand.

B. TETRABUTYLAMMONIUM DIPHENYLBIS (DIPHENYLPHOSPHINOMETHYL)BORATE, [$^nBu_4N$][$Ph_2B(CH_2PPh_2)_2$]

$$2\,Li(TMEDA)CH_2PPh_2 + Ph_2BCl \longrightarrow [Li(TMEDA)_2][Ph_2BCH_2PPh_2)_2] + LiCl$$

$$[Li(TMEDA)_2][Ph_2B(CH_2PPh_2)_2] + [^nBu_4N][Cl] \longrightarrow [^nBu_4N][Ph_2B(CH_2PPh_2)_2] + LiCl + 2\,TMEDA$$

■ **Caution.** *Ph_2BCl reacts vigorously with water and fumes in air. It should be handled under a nitrogen atmosphere, and care should be taken to minimize skin contact and respiratory exposure.*

Procedure

Under a dinitrogen atmosphere, a 500-mL round-bottomed Schlenk flask is charged with solid yellow $Ph_2PCH_2Li(TMEDA)$ (4.82 g, 15.0 mmol), and then diethyl ether (180 mL) to form a suspension. The reaction vessel is cooled to $-78°C$ in a dry-ice/acetone bath. A toluene solution (10 mL) of Ph_2BCl* (1.514 g, 7.553 mmol) is added to the reaction vessel, dropwise, via syringe through a rubber septum under a constant dinitrogen purge. The reaction temperature is maintained at $-78°C$ throughout the addition. The reaction mixture is stirred thoroughly and gradually allowed to warm to ambient temperature. Stirring is continued for an additional 14 h and affords a pale yellow precipitate. (*Note*: Analysis by ^{31}P NMR spectroscopy shows quantitative conversion to the desired product. The reaction volatiles are removed in vacuo, and the resulting solids are isolated by filtration onto a medium-porosity sintered-glass frit under a dinitrogen atmosphere. The white powder is then thoroughly washed with diethyl ether (5×10 mL). Drying this solid in vacuo provides light yellow, solid [$Li(TMEDA)_2$] [$Ph_2B(CH_2PPh_2)_2$] (5.67 g) and remaining LiCl salt. This product is completely freed from LiCl by extraction into warm toluene, filtering through Celite, and evaporation of the solvent. However, it is straightforward to

*Ph_2BCl is available from Organometallics, Inc., East Hampstead, NH.

perform the ammonium for lithium exchange without this final step. An ethanol solution (20 mL) of $[Li(TMEDA)_2][Ph_2B(CH_2PPh_2)_2]$ (3.51 g, 4.42 mmol) is first prepared. A solution of tetrabutylammonium chloride (1.424 g, 4.42 mmol) in dry ethanol (15 mL) is prepared separately. The ammonium chloride solution is then added dropwise to the ethanol solution of $[Li(TMEDA)_2][Ph_2B(CH_2PPh_2)_2]$ with stirring. The reaction mixture turns cloudy quickly, and after addition is complete, the mixture is allowed to settle for 30 min. The white solid precipitate is collected by filtration and is thoroughly washed with ethanol (30 mL) and then with diethyl ether (50 mL). Drying the powder in vacuo produces 3.13 g (88%) of the ammonium salt $[^nBu_4N][Ph_2B(CH_2PPh_2)_2]$.

Properties

$[^nBu_4N][Ph_2B(CH_2PPh_2)_2]$ is modestly air-stable, although less so than its tridentate derivative $[^nBu_4N][PhB(CH_2PPh_2)_3]$. Accordingly, it should be stored under nitrogen and handled with dry and deoxygenated solvents. Its ^1H NMR spectrum (d_6-acetone, 300 MHz) displays resonances at δ 7.29 (br s, 4H), 7.17 (m, 8H), 7.00 (m, 12H), 6.73 (m, 4H), 6.61 (t, 2H), 3.42 (m, 8H), 1.81 (m, 8H), 1.65 (br, 4H), 1.41 (sextet, 8H), 0.97 (t, 12H). The ^{31}P NMR spectrum (d_6-acetone, 121 MHz) shows a resonance at -8.8 ($^2J_{P-B} = 10$ Hz) ppm. The ^{11}B NMR spectrum (d_6-acetone, 128.3 MHz) features one resonance at -12.6 ppm. In contrast to $[^nBu_4N][PhB(CH_2PPh_2)_3]$, $[^nBu_4N][Ph_2B(CH_2PPh_2)_2]$ decomposes rapidly in aqueous solution and water and therefore is not used in the workup procedure. The ammonium salt is very soluble in acetone, acetonitrile, and tetrahydrofuran and modestly soluble in warm toluene. Like the tris(phosphino)borate ligand, $[^nBu_4N][Ph_2B(CH_2PPh_2)_2]$ is unstable in chloroform and dichloromethane. A paper that generalizes this protocol to a family of $[R_2BPR'_2]^-$ ligands, and describes reliable procedures for the preparation of Ar_2BCl precursors, has been published.[7]

C. THALLIUM PHENYLTRIS(DIPHENYLPHOSPHINOMETHYL) BORATE, $[PhB(CH_2PPh_2)_3]Tl$

$$[Li(TMEDA)][PhB(CH_2PPh_2)_3] + TlPF_6 \longrightarrow [PhB(CH_2PPh_2)_3]Tl + LiPF_6 + TMEDA$$

■ **Caution.** *Thallium is a toxic heavy metal, and care should be taken to minimize skin and respiratory exposure to $TlPF_6$, and with respect to disposing of thallium waste products.*

Procedure

The following preparation is carried out on the benchtop under air. Solid [Li(TMEDA)][$PhB(CH_2PPh_2)_3$] (7.1 g, 8.6 mmol), generated as described above (LiCl impurities are not problematic as they are removed by the following procedure), is added to a 250-mL Erlenmeyer flask charged with a stirring bar and suspended in methanol (60 mL). To this stirring suspension is added an aqueous solution (30 mL) of $TlPF_6$ (3.00 g, 8.6 mmol) over a period of 5 min. A cloudy white suspension results, which is stirred for an additional 5 min, followed by extraction with dichloromethane (2×150 mL). The solution is filtered through Celite and thoroughly dried in vacuo to afford a light yellow powder. This powder is then washed with hexanes and diethyl ether (40 mL each), extracted into benzene (150 mL), stirred over $MgSO_4$, filtered, and then dried thoroughly in vacuo, affording the thallium complex as a fine yellow powder (5.00 g, 65%).

Properties

The thallium complex [$PhB(CH_2PPh_2)_3$]Tl is a yellow solid. ^{1}H NMR (C_6D_6, 300 MHz, 25°C): δ 8.13 (d, $J = 6.6$ Hz, 2H), 7.67 (m, $J = 7.5$ Hz, 2H), 7.42 (tt, $J = 6.6$, 1.2 Hz, 1H), 7.18–7.11 (m, 12H), 6.80–6.77 (m, 18H), 1.96 (br m, 6H). ^{31}P NMR (C_6D_6, 121.4 MHz, 25°C): 21.6 ppm (d, $^1J_{Tl-P} = 5214$ Hz for ^{205}Tl (70.5% abundance), $^1J_{Tl-P} = 5168$ Hz for ^{203}Tl (29.5% abundance). ^{13}C NMR (C_6D_6, 125.7 MHz, 25°C): δ 139.8, 132.5, 128.8–129.1 (overlapping resonances), 124.6, 17.0 (br). ^{11}B NMR (C_6D_6, 128.3 MHz, 25°C): -10.96 ppm. The compound is a versatile precursor to a wide range of transition metal complexes supported by the tris(phosphino)borate ligand. It is air- and water-stable for extended periods, and, unlike the lithium and ammonium salts of $[PhB(CH_2PPh_2)_3]^-$, it is both soluble and stable in chloroform and dichloromethane for days, making these useful solvents available for subsequent transmetallation chemistry.

Acknowledgments

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References

1. F. A Cotton and B. Hong, *Prog. Inorg. Chem.* **40**, 179 (1992).
2. (a) T. A. Betley and J. C Peters, *Angew. Chem., Int. Ed. Engl.* **42**, 2385 (2003); (b) J. C. Thomas and J. C. Peters, *J. Am. Chem. Soc.* **125**, 8870 (2003); (c) C. C. Lu and J. C. Peters, *J. Am. Chem. Soc.* **124**, 5272 (2002).
3. J. C. Peters, J. D. Feldman, and T. D. Tilley, *J. Am. Chem. Soc.* **121**, 9871 (1999).
4. A. A. Barney, A. F. Heyduk, and D. G. Nocera, *Chem. Commun.* 2379 (1999).
5. I. R. Shapiro, D. M. Jenkins, J. C. Thomas, M. W. Day, and J. C. Peters, *Chem. Commun.* 2152 (2001).
6. N. E. Schore, L. S. Benner, and B. E. Labelle, *Inorg. Chem.* **20**, 3200 (1981).
7. J. C. Thomas and J. C. Peters, *Inorg. Chem.* **42**, 5055 (2003).

4. SIX-COORDINATE ALUMINUM CATIONS BASED ON SALEN LIGANDS

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Checked by MICHAEL J. SCOTT[†]

Aluminum compounds with organic ligands are widely used as reagents in organic synthesis.[1] Transformations that can be achieved with these Lewis acid reagents include the reduction of ketones and aldehydes,[1] enantioselective Diels–Alder reactions,[2] and the ''living'' polymerization of oxiranes.[3,4] We have introduced a class of air-stable, cationic, six-coordinate aluminum complexes of general formula [(Schiff base)Al(solv)$_2$]X,[5–9] and have shown their utility as catalysts for the polymerization of propylene oxide.[8,9] Here we present detailed preparations for representative members of this class based on Salen (*N*,*N*′-bis(2-hydroxybenzylidene)ethylenediamine) and related ligands (see Fig. 1). These preparations may be applied with equal facility to related Schiff base ligands that have different connections between the two nitrogen atoms.

General Comments

All manipulations are conducted by using appropriate inert-atmosphere techniques. Toluene and THF are refluxed over sodium benzophenone and MeOH over Mg and then distilled prior to use. The ligands SalenH$_2$ and Salen^{t}BuH$_2$ were synthesized as described previously.[7] Dimethylaluminum chloride is available from Aldrich Chemical Co.

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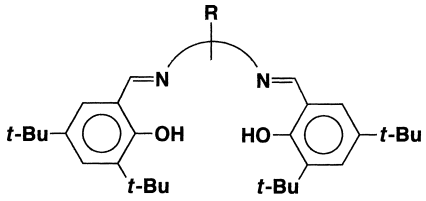

R	Ligand name
$(CH_2)_2$	Salen(^{t}Bu)
$(CH_2)_3$	Salpen(^{t}Bu)
$(CH_2)_4$	Salben(^{t}Bu)
C_6H_4	Salophen(^{t}Bu)
$C_6H_2Me_2$	Salomphen(^{t}Bu)

Figure 1. Naming scheme for Salen(^{t}Bu) class of ligands.

A. CHLORO-1,2-BIS(2-HYDROXYBENZYLIDENEIMINO) ETHANEALUMINUM, Al(Salen)Cl

$$\text{SalenH}_2 + \text{Me}_2\text{AlCl} \xrightarrow[25^\circ\text{C}]{\text{toluene}} \text{Al(Salen)Cl} + 2\,\text{CH}_4$$

■ **Caution.** *Dimethylaluminumchloride (Me_2AlCl) is a pyrophoric liquid. It must be handled under an inert atmosphere.*

Procedure

In a drybox, 5.0 g (18.6 mmol) of $SalenH_2$ is placed into a 250-mL side arm flask containing a 1-in. magnetic stirring bar. The ligand is dissolved in 125 mL of toluene, and then 1.72 g (18.6 mmol) of dimethylaluminumchloride is added slowly over the course of 2 min with stirring. A yellow solution and pale yellow solid results. The mixture is stirred for 2 h at 25°C, and then the solvent is removed by filtration. The stopcock of the sidearm flask is closed, a rubber septum placed in the neck, and the flask containing the precipitate is brought out of the drybox and placed onto a vacuum line equipped with a dry N_2 source. The side arm is evacuated, and then the flask is pressurized with nitrogen. The septum is replaced with a glass stopper, and the residue is dried under vacuum to yield 5.81 g (97%) of the desired product.

Anal. Calcd. for C, 58.46; H, 4.29. Found: C, 58.26; H, 4.54.

Properties

The product shows no appreciable solubility in Et_2O or THF; it will dissolve in protic solvents but in so doing forms the solvated salts. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.83 (m, 2H), 4.23 (m, 2H), 6.76–7.44 (m, 8H), 8.38 (s, 2H, CH=N).

IR (KBr) 3040 w, 2974 w, 1647 s, 1550 s, 1477 s, 1340 s, 756 s. The synthesis for AlLCl L = SalenCl, Acen, Salophen,[10] Salen^{t}Bu,[8] Salpen^{t}Bu, Salben^{t}Bu, Salophen^{t}Bu, Salomphen^{t}Bu is similar and leads to organic soluble compounds. The preparations for L = Salen, SalenCl, Acen, and Salophen are facilitated by the insolubility of the compounds, which precipitate essentially quantitatively from toluene.

B. DIAQUA-1,2-BIS(2-HYDROXYBENZYLIDENEIMINO) ETHANEALUMINUM CHLORIDE, [Al(Salen)$(H_2O)_2$]Cl

$$\text{Al(Salen)} \xrightarrow[25^\circ\text{C}]{H_2O} [\text{Al(Salen)}(H_2O)_2]\text{Cl}$$

Procedure

In a drybox, a 100-mL flask containing a 1-in. magnetic stir bar is loaded with 1.0 g (3.04 mmol) of SalenAlCl. The stopcock is closed, a rubber septum is placed in the neck, and the flask is brought out of the drybox and placed onto a vacuum line equipped with a dry N_2 source. While stirring, 20 mL of distilled water is added by syringe over the course of a few seconds. The mixture is stirred for 2 h at 25°C, resulting in a pale yellow solution and a solid. Evaporation of the water over a period of 3 days results in quantitative yields of the product as a crystalline solid.

Anal. Calcd.: C, 52.69; H, 4.97. Found: C, 52.65; H, 5.02.

Properties

The compound [Al(Salen)$(H_2O)_2$]Cl is not air-sensitive. It has mp 162–165°C dec. The cation is soluble only in water. IR (KBr): 3057 s (br) 1639 s, 1560 m, 1473 s, 1296 s, 814 m, 760 s cm^{-1}. The synthesis and properties of the SalenCl and Acen derivatives are described in Ref. 7. Salophen, Salen(^{t}Bu), Salpen(^{t}Bu), Salben(^{t}Bu), Salophen^{t}Bu, and Salomphen^{t}Bu derivatives can also be prepared in a similar manner. In the solid state these compounds have been shown by X-ray crystallography to contain six-coordinate octahedral aluminum. The solvent molecules are trans to one another and the ligand coplanar with the aluminum atom. The chloride anions are connected by hydrogen bonds to the solvents on the aluminum as well as additional solvent in the crystal lattice.

C. DIMETHANOL-1,2 BIS-(2-HYDROXY-3,5-BIS(*tert*-BUTYL)BENZYLIDENEIMINO)ETHANEALUMINUM CHLORIDE, [Al (Salen^{t}Bu)(MeOH)$_2$]Cl

$$\mathrm{Al(Salen^tBu)Cl} \xrightarrow[25^\circ\mathrm{C}]{\mathrm{MeOH}} [\mathrm{Al(Salen^tBu)(MeOH)_2}]\mathrm{Cl}$$

Procedure

In a drybox a 100-mL sidearm flask containing a 1-in. magnetic stirring bar is loaded with 0.350 g (0.633 mmol) of (Salen^{t}Bu)AlCl. The stopcock is closed, a rubber septum placed on the neck, and the flask brought out of the drybox and placed onto a vacuum line equipped with a dry N_2 source. The flask is pressurized with N_2, and with stirring, 7 mL of MeOH is added by syringe over the course of a few seconds. The product turns white and dissolves over 5 min. Slow evaporation of the solvent in air leads to a nearly quantitative yield of pale yellow crystals. The solid can also be prepared by stirring Salen(^{t}Bu)AlCl in MeOH for 3 h and then removing the solvent under vacuum.

Anal. Calcd.: C, 66.16; H, 8.82. Found: C, 65.78; H, 8.68.

Properties

The compound (mp $>$ 260 dec.) dissolves in organic solvents such as CH_2Cl_2 and $CHCl_3$. In the solid state the compound has been shown by X-ray crystallography to contain six-coordinate, octahedral aluminum.[7] As with the water cation, the solvent molecules are trans to one another and the ligand is coplanar with the aluminum atom. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.29 (s, 18H, ^{t}Bu), 1.53 (s, 18H, ^{t}Bu), 3.46 (s, 6H, CH_3OH), 3.79 (s, 2H, CH_2CH_2), 4.12 (s, 2H, CH_2CH_2), 7.04 (d, 2H, PhH), 7.55 (d, 2H, PhH), 8.38 (s, 2H, HC=N). IR (KBr): 3406 w, 2955 s, 1639 s, 1554 m, 1442 m, 1276 m, 875 m, 756 m cm^{-1}. The Salen, Acen, Salophen, Salen^{t}Bu, Salen^{t}Bu, Salophen^{t}Bu, and Salomphen^{t}Bu derivatives can be prepared in a similar manner.

D. DIMETHANOL-1,2-BIS(2-HYDROXY-3,5-BIS(*tert*-BUTYL)BENZYLIDENEIMINO)ETHANEALUMINUM TETRAPHENYLBORATE, [Al(Salen^{t}Bu)(MeOH)$_2$][BPh$_4$]

$$\mathrm{Al(^tBuSalen)Cl} + \mathrm{Na[BPh_4]} \xrightarrow[25^\circ\mathrm{C}]{\mathrm{MeOH}} [\mathrm{Al(Salen^tBu)(MeOH)_2}][\mathrm{BPh_4}] + \mathrm{NaCl}$$

Procedure

In a drybox a 250-mL sidearm flask containing a 1-in. magnetic stirring bar is loaded with a mixture of 1.50 g (2.71 mmol) of (Salen^{t}Bu)AlCl and 0.928 g (2.71 mmol) of sodium tetraphenylborate ($NaBPh_4$). As solids, they do not react. The stopcock of the sidearm flask is closed, a rubber septum placed on the neck, and the flask brought out of the drybox and placed onto a vacuum line equipped with a dry N_2 source. Then 20 mL of MeOH is added to the reactants. A yellow solid appears and then goes back into solution. The yellow solution is stirred for 18 h and then allowed to stand for 24 h. During this time a small amount of white precipitate settles out of solution. The solution is filtered, and the filtrate concentrated to 15 mL and then cooled to $-30°C$. After several days, pale yellow plates are formed. These are isolated by filtration under nitrogen and dried under vacuum to give the product in essentially quantitative yield.

Anal. Calcd. for C, 77.32; H, 8.28. Found: C, 77.32; H, 8.42.

Properties

The compound (mp 118–121°C) is soluble in solvents such as $CHCl_3$, $CHCl_2$, and THF. It is moderately sensitive to ambient conditions and forms an uncharacterized hydrate on exposure to air. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (s, 18H, ^{t}Bu), 1.46 (s, 18H, ^{t}Bu), 2.93 (s, 6H, CH_3OH), 3.14 (s, 4H, CH_2CH_2), 6.71–7.66 (m, 26H, PhH, and CH=N)). IR (KBr) 3437 m, 3057 m, 1626 s, 1543 m, 1473 s, 1255 s, 850 m, 705 s cm^{-1}. The Salen, Acen, SalenCl,[6] Salophen, Salpen^{t}Bu, Salben^{t}Bu, Salophen^{t}Bu, and Salomphen^{t}Bu derivatives can be prepared in a similar manner.

E. DIMETHANOL-1,2-BIS(2-HYDROXY-3,5-BIS(*tert*-BUTYL) BENZYLIDENEIMINO)ETHANEALUMINUM *para*-TOLUENESULFONATE, [Al(^{t}BuSalen)(MeOH)$_2$][OTs]

$$[\mathrm{Al(Salen}^t\mathrm{Bu]Cl} \xrightarrow[\mathrm{HOTs}]{\mathrm{MeOH}} [\mathrm{Al(Salen}^t\mathrm{Bu)(MeOH)_2}][\mathrm{OTs}] + \mathrm{HCl}$$

In a drybox, a 250-mL sidearm flask containing a 1-in. magnetic stirring bar is loaded with a mixture of 1.00 g (1.81 mmol) of (Salen^{t}Bu)AlCl and 0.351 g (1.81 mmol) of sodium *para*-toluenesulfonate (NaOTs). As solids, they do not react. The stopcock of the sidearm flask is closed, a rubber septum placed on the neck, and the flask brought out of the drybox and placed onto a vacuum

line equipped with a dry N_2 source. Then 20 mL of MeOH is added to the reactants. The mixture is stirred, and after a few minutes the solids dissolve to form a yellow solution. The mixture is further stirred for 24 h, and then the small amount of white solid formed is removed by filtration. The resulting solution is cooled to $-30°C$, and after several days, opaque yellow crystals form that are isolated by filtration and dried under vacuum (0.624 g, 41%).

Anal. Calcd. for C, 65.40; H, 8.17. Found: C, 65.37; H, 7.95

Properties

The compound (mp 135–138°C) is soluble in toluene, chloroform, and THF. It is moderately air-stable. X-ray analysis shows it to contain a six-coordinate, distorted octahedral aluminum with the Salen^{t}Bu ligand occupying the four equatorial positions and the two methanol molecules in the axial positions. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20 (s, 18H, ^{t}Bu), 1.36 (s, 18H, ^{t}Bu), 3.03 (m, 3H, CH_3OH), 3.70 [s (br), 4H, CH_2CH_2], 6.77 (d, 2H, OTs PhH), 6.82 (d, 2H ligand PhH), 7.15 (d, 2H, OTs PhH), 7.37 (d, 2H ligand PhH), 7.96 (s, 2H, CH=N). IR (KBr): 3142 m, 2955 s, 1637 s, 1550 m, 1444 m, 1257 s, 1172 s, 860 m, 682 m cm^{-1}.

F. BIS(TETRAHYDROFURAN)-1,2-BIS(2-HYDROXY-3,5-BIS (*tert*-BUTYL)BENZYLIDENEIMINO)ETHANEALUMINUM TETRAPHENYLBORATE, [Al(^{t}BuSalen)(THF)$_2$][BPh$_4$]

$$\mathrm{Al(Salen^tBu)Cl + NA[BPh_4]} \xrightarrow{\mathrm{THF}} \mathrm{[Al(^t(BuSalen)(THF)_2][BPh_4] + NaCl}$$

Procedure

In a drybox, a 250-mL sidearm flask containing a 1-in. magnetic stirring bar is loaded with a mixture of 4.00 g (7.23 mmol) of (Salen^{t}Bu)AlCl and 2.51 g (7.35 mmol) of sodium tetraphenylborate ($NaBPh_4$). As solids, they do not react. The stopcock of the sidearm flask is closed, a rubber septum placed on the neck, and the flask brought out of the drybox and placed onto a vacuum line equipped with a dry N_2 source. Then 50 mL of degassed THF is added to the reactants. The pale yellow suspension is refluxed for 12 h. The solution is filtered under N_2. The THF is removed under vacuum, yielding 5.93 g (84%) of the compound as a pale yellow solid.

Anal. Calcd. for C, 78.35; H, 8.42. Found: C, 78.44; H, 8.29.

Properties

The compound is soluble in toluene, chloroform, and THF. It is moderately air-stable. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.28 (s, 18H, ^{t}Bu), 1.33 (s, 18H, ^{t}Bu), 1.83 (m, 4H, THF), 2.74 (s, 2H, CH_2CH_2), 3.18 (s, 2H, CH_2CH_2), 3.71 (m, 8H, THF), 6.90–7.61 [m, 26H, PhH, and CH=N)]. IR (KBr) 3055 m, 2957 s, 1629 s, 1556 m, 1446 m, 1276 m, 1047 s, 862 m, 734 m cm^{-1}. The Salpen-^{t}Bu, Salben^{t}Bu, Salophen^{t}Bu, and Salomphen^{t}Bu derivatives can be prepared in a similar manner. The Salpen^{t}Bu derivative was shown by x-ray studies to contain a six-coordinate, octahedral aluminum with the Salpen^{t}Bu ligand occupying the four equatorial positions and the two THF molecules in the axial positions.

References

1. (a) D. Schinzer, ed., *Selectivities in Lewis Acid Promoted Reactions*, Kluwer Academic Publishers, Dordrecht, 1989; (b) H. Yamamoto, in *Organometallics in Synthesis*, M. Schlosser, ed., Wiley, Chichester, UK, 1994, Chapter 7.
2. Y. Hayashi, J. J. Rohde, and E. J. Corey, *J. Am. Chem. Soc.* **118**, 5502 (1996).
3. (a) K. Maruoka, S. Nagahara, and H. Yamamoto, *J. Am. Chem. Soc.* **112**, 6115 5475 (1990); (b) K. Maruoka, S. Nagahara, and H. Yamamoto, *Tetrahedron Lett.* **31**, 5475 (1990); (c) K. Maruoka, A. B. Concepcion, N. Murase, M. Oishi, N. Hirayama, and H. Yamamoto, *J. Am. Chem. Soc.* **115**, 3943 (1993).
4. (a) E. J. Vandenberg, *J. Polym. Sci., A-1*, **7**, 525 (1969); (b) C. L. Jun, A. Le Borgne, and N. Spassky, *J. Polym. Sci., Polym. Symp.* **74**, 31 (1986); (c) V. Vincens, A. Le Borgne, and N. Spassky, *Makromol. Chem. Rapid Commun.* **10**, 623 (1989); (d) A. Le Borgne, V. Vincens, M. Jouglard, and N. Spassky, *Makromol. Chem. Macromol. Symp.* **73**, 37 (1993); (e) H. Sugimoto, C. Kawamura, M. Kuroki, T. Aida, and S. Inoue, *Macromolecules* **27**, 2013 (1994); (f) T. Aida, R. Mizutta, Y. Yoshida, and S. Inoue, *Makromol. Chem.* **182**, 1073 (1981); (g) K. Shimasaki, T. Aida, and S. Inoue, *Macromolecules* **20**, 3076 (1987); (h) S. Asano, T. Aida, and S. Inoue, *J. Chem. Soc. Chem.Comm.* 1148 (1985).
5. D. A. Atwood, J. A. Jegier, and D. Rutherford, *Inorg. Chem.* **35**, 63 (1996).
6. D. Rutherford and D. A. Atwood, *Organometallics* **15**, 4417 (1995).
7. D. A. Atwood, J. A. Jegier, and D. Rutherford, *J. Am. Chem. Soc.* **117**, 6779 (1995); D. A. Atwood and M. J. Harvey, *Chem. Rev.*, **101**, 37 (2001).
8. J. A. Jegier, M. A. Munoz-Hernandez, and D. A. Atwood, *J. Chem. Soc., Dalton Trans.* 2583 (1999).
9. M. A. Munoz-Hernandez, M. L. McKee, T. S. Keizer, B. C. Yearwood, and D. A. Atwood, *J. Chem Soc., Dalton Trans.* 410 (2002).
10. R. H. Holm, G. W. Everett, and A. Chakravorty, *Prog. Inorg. Chem.* **7**, 83 (1966).
11. P. L. Gurian, L. K. Cheatham, J. W. Ziller, and A. R. Barron, *J. Chem. Soc., Dalton Trans.* 1449 (1991).

5. TABULAR α-ALUMINA

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Checked by TIMOTHY BOYLE[¶]

The chemical and physical properties of alumina make it one of the most industrially significant bulk electronic and structural ceramic materials produced worldwide.[1] The material has a wide structural diversity, adopting at least 15 crystallographic phases. The most prominent, α-Al_2O_3 and δ-Al_2O_3, are made commercially in tonnage quantities by using well-developed chemical processes. Ceramic-grade, calcined α-Al_2O_3 powders are usually obtained as agglomerates that are dry ground, sorted, and classified into specific product lines. The resulting irregularly shaped particles are suitable for many uses; however, there are increasing fundamental scientific and practical needs for higher-quality materials with well-defined morphologies. In particular, spherical and tabular morphologies are in demand. Tabular aluminas are typically obtained by grinding and sintering powders calcined in the temperature region 1600–1850°C, and the resulting high-density, recrystallized particles have an elongated (50–400-μm), flat, platelike morphology. Unfortunately, these powders have a wide size distribution and contain large amounts of fines that reduce their utility for adsorbent, catalyst support and ceramic filler applications. For fundamental laboratory studies in these application fields it would be useful to have available more well-characterized tabular α-Al_2O_3 powders. Patent literature suggests that fluoride may be used to promote alumina crystal growth,[2,3] and we have reported the use of boehmite/hydrofluoric acid (HF_{aq}) gel slurries as a starting material for tabular α-Al_2O_3 synthesis.[4] Here we provide a simplified procedure for obtaining α-Al_2O_3 platelets with a narrow diameter and size distribution (average size 8 μm distribution 5–12 μm).

Equipment

All manipulations, including sample heatings, are performed in a well-ventilated fume hood. A small, handheld stirrer is used initially to mix the reaction components.

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Materials

Boehmite alumina powder is obtained from Condea-Vista as plural-grade 200 (Inorganic Specialties Division, Condea Vista, 900 Threadneedle, #100, Houston, TX 70079) and aqueous HF (50 wt%) is purchased from J. T. Baker.

Procedure

■ **Caution.** *Hydrofluoric acid causes severe burns and all appropriate safety literature describing precautions should be consulted before use. Lab coat, faceshield, and heavy vinyl gloves should be worn when preparing, stirring, and transferring aqueous HF solutions. The fume hood should be approved for use with hydrofluoric acid. The high-temperature oven should also be placed in the hood since aluminum fluoride and HF are evolved in the heat treatment.*

A solution of aqueous hydrofluoric acid (1.7 wt%) is prepared by diluting commercial, 50 wt%, HF with deionized water in a polypropylene bottle. A 100 g portion of the diluted HF was transferred to a Nalgene plastic beaker and boehmite alumina powder (20 g) is added over 5 min with manual stirring using a stainless-steel spatula. After approximately 5 min, the mixture has the appearance of a moderately thick, white paste. An additional quantity (100 g) of water is added, and the mixture is stirred for 3 min. Additional boehmite powder (100 g) is added with continuous stirring. The resulting slurry forms a thick gel. This gel is stirred for 5 min at high speed using a standard laboratory paddle mixer[*] until the slurry takes the consistency of plumber's putty. (*Note*: This is an important variable, since the paste should not separate into solid and liquid components during subsequent processing. If a powerful stirrer is not available, the final mixing can be accomplished by hand mixing using a spatula. The checker found hand mixing to be adequate.) The resulting paste is dried at 140°C overnight in a standard laboratory oven.[†] This produces an agglomerated solid mass that is easily ground with a large mortar and pestle to give a powder (maximum agglomerate size 5 mm). A portion of this solid (25.6 g) is transferred to a tapered 50-mL [5 × 4.8 × 3.0-cm (height × top × bottom)] alumina crucible fitted with a flat, smooth-fitting alumina lid. The covered crucible is placed in a furnace[‡]

[*]Cole-Parmer Instrument Co. Chicago, IL. Alternatively, a variable-speed shop drill may be used with a standard stirrer shaft.

[†]Since the inside of the oven will be exposed to corrosive HF and AlF_3 vapors, an old drying oven is preferred that is vented through the top to a fume hood. Alternatively, a small vacuum oven may be used, but the vacuum applied should be minimal.

[‡]This may be any high-temperature tube or muffle furnace. The furnace should be placed in a fume hood.

with an air atmosphere and is heated from 20 to 1075°C at a rate of 10°C/min. This temperature is maintained for 180 min, then the temperature is increased to 1200°C at 5°C/min. This temperature is maintained for 180 min. At the end of this time, the covered crucible is briefly withdrawn from the furnace with appropriate tongs, the lid is removed, and the uncovered crucible is returned to the furnace. Heating at 1200°C is continued for another 300 min. During the heating of the covered crucible at 1200°C, AlF_3 sublimes to the top of the crucible, forming a seal that prevents most of the AlF_3 vapors from escaping. This results in intimate Al_2O_3/AlF_3 contact that enhances the platelet growth. When the crucible lid is removed and the crucible reheated, AlF_3 sublimes from the sample, as indicated by formation of white vapor. At the end of the heating cycle, the crucible and contents are cooled to room temperature, and the resulting powder (20.3 g) is removed from the crucible. The powder can be deagglomerated with a mortar and pestle, using very light pressure, and then is screened through a 325-mesh sieve.

Anal. Calcd. for Al, 52.92; O, 47.08. Found: Al, 52.88; O, 47.05. C, H, $N < 0.5\%$, $F < 380$ ppm.

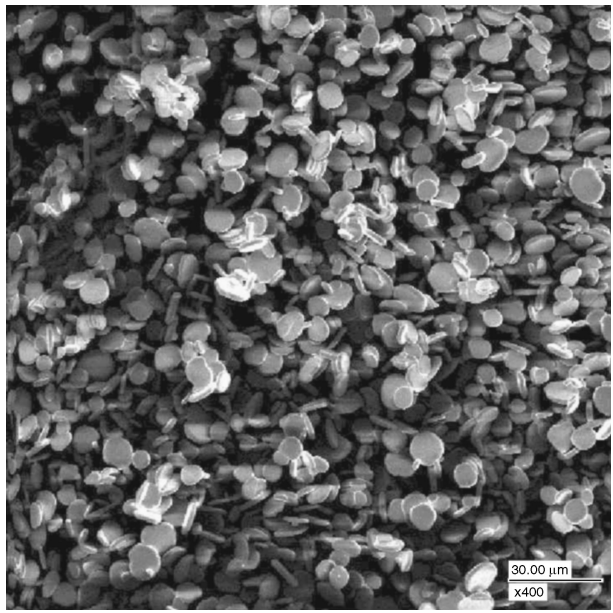

Figure 1. Scanning electron micrograph of tabular α-Al_2O_3.

Properties

The compound is a free-flowing white solid. The powder X-ray diffraction (XRD) is in complete agreement with that for α-Al_2O_3 (corundum JCPDS) card file 46-1212: *XRD:* (d, Å; I,%): 3.487 (33), 2.555 (73); 2.382 (25), 2.088 (100); 1.741 (35); 1.603 (86); 1.512 (6); 1.405 (22); 1.374 (40); 1.240 (12). A scanning electron micrograph (SEM) (Fig. 1) shows the particles have the desired platelike morphology with average particle diameter of 8 μm. If fines appear in the SEM, this indicates that the last heating stage was not of sufficient length. The surface area for typical samples is 0.1 m^2/g. There is some variability found in average particle size. The variables include size of the crucible and the amount of powder calcined in the crucible. Larger platelets are obtained when the crucible is nearly filled to the top with the ground agglomerate.

References

1. M. Howe-Grant, ed., *Encyclopedia of Chemical Technology*, 4th ed., Wiley, New York,
2. J. Black and J. W. K. Lau, U.S. Patent 5,137,959 (1992).
3. W. W. Weber and J. A. Herbst, U.S. Patent 4,379,134 (1983).
4. R. F. Hill, R. Danzer, and R. T. Paine, *J. Am. Ceram. Soc.* **84**, 514 (2001).

6. PARA-SUBSTITUTED ARYL ISOCYANIDES

Submitted by NICOLE L. WAGNER,[*] KRISTEN L. MURPHY,[*] DANIEL T. HAWORTH,[*] and DENNIS W. BENNETT[*]
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Isocyanides behave as unique ligands in transition metal complexes, capable of strong coordination to both low- and high-valence metal centers. Subtle changes in the substituent para to the isocyanide moiety of these ligands result in modification of their π acidity, which can subsequently alter the geometry of the transition metal complexes dramatically.[1,2] In the course of studying these complexes, the general synthetic routes to representative isocyanides have been modified, and these procedures are detailed in this contribution.

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Starting Materials

All starting materials are commercial samples used without further purification. The following reagents are available from Acros-Fisher: *p*-phenylenediamine (99%), *p*-anisidine (99%), trisphosgene (99%), and tungsten(VI) chloride (99%). 2,5-Dimethyl,1,4-phenyldiamine is obtained from Aldrich Chemical Co. Phosgene (99%) is obtained from Matheson. Reagent-grade solvents (99.5%) are obtained from VWR, with the exception of THF(Fisher). Solvents for the synthesis of the isocyanides are used without further purification. Solvents used for the organometallic synthesis are purified as described in procedure D.

■ **Caution.** *Isocyanides are toxic and have a distinctive odor that is very offensive. Care should be taken to avoid inhalation, particularly when handling liquid isocyanides. All reactions should be carried out in a well-ventilated hood. Phosgene gas is a relatively common synthetic reagent and can be safely used with care, but it is extremely toxic and should be handled only by the most experienced personnel in the laboratory. The use of a self-contained breathing apparatus is strongly recommended when phosgene is used in these reactions. Although phosgene is less costly, liquid diphosgene (trichloromethylchloroformate) or solid triphosgene [bis(trichloromethyl)carbonate] can be used as safer alternatives to phosgene in the synthetic approaches described here. It is, nevertheless, important to note that all three phosgenation reagents are extremely irritating to the eyes and skin, and if inhaled, either directly or via their decomposition products, can cause severe respiratory damage.*

A. 1,4-DIISOCYANOBENZENE, *p*-CNC_6H_4NC

$$p\text{-}H_2N(C_6H_4)NH_2 + 2\,HCOOH \longrightarrow p\text{-}OHCHN(C_6H_4)NHCHO + 2\,H_2O$$

$$p\text{-}OHCHN(C_6H_4)NHCHO + 2\,COCl_2 + 4\,Et_3N \longrightarrow p\text{-}CN(C_6H_4)NC + 4\,[Et_3NH]Cl + 2\,CO_2$$

Procedure

This is a modification of a synthetic method initially reported by Ugi.[3]

■ **Caution.** *Phosgene is a highly toxic gas that reacts with water to form HCl and has a characteristic odor of freshly mown hay. It is necessary to carry out this portion of the reaction using standard Schlenk techniques and in a well-ventilated fume hood. Unreacted phosgene can be neutralized with aqueous base.*

A 250-mL round-bottomed flask equipped with a water collector (Dean–Stark trap), condenser, and magnetic stirrer is charged with *p*-$H_2N(C_6H_4)NH_2$ (36 g, 0.33 mol), formic acid (69 mL, 1.8 mol, 3 : 1 excess), and toluene (80 mL, reagent grade). The mixture is heated to reflux until the water is collected ($\sim$3 h). The flask is cooled, and formamide is collected by filtration, and rinsed with copious amounts of ethanol and diethylether until formic acid is washed away. Color and percent yield of formamide ($\sim$70%) is dependent on the purity of the amine. The reaction can be scaled up, depending on collector size.

A 1-L three-necked round-bottomed flask equipped with a mechanical stirrer and dry-ice/propanol-cooled cold fingers is charged with *p*-$OHCHN(C_6H_4)NHCHO$ (48.2 g, 0.294 mol) dissolved in CH_2Cl_2 (500 mL, reagent grade), and triethylamine (125 mL, 1.7 mol). The mixture is cooled in an ice/salt bath and flushed with nitrogen. Phosgene* (32 mL, 0.587 mol), collected into a liquid nitrogen cooled collector under reduced pressure, is allowed to warm slowly and drip into the reaction mixture ($\sim$3 h) under a slow stream of nitrogen. Excess phosgene is vented through a series of flasks filled with air, oil, and saturated NaOH, respectively. The mixture is stirred for an additional 2 h and allowed to warm to room temperature. $NaHCO_3$ (10%, 200 mL) is added to neutralize any remaining phosgene. The mixture is washed with water (200 mL), HCl (0.1 M, 200 mL) and saturated NaCl (150 mL), and the separated CH_2Cl_2 layer is dried over Na_2SO_4. The solvent is removed under vacuum, and the solid isocyanide is sublimed under vacuum at 30–60°C. Yield 50–80%.

Anal. Calcd. for $C_8H_4N_2$: C, 74.99; H, 3.15; N, 21.85. Found: C, 74.75; H, 3.08; N, 21.78.

The analogous compounds *p*-$CN(C_6H_4)CN$, *p*-$CN(C_6H_{10})NC$, *p*-$CN(C_6(CH_3)_4)NC$, and *p*-$CN(C_6H_4)R$ where R = NO_2, SH, COOH, and Cl can be prepared in a similar manner.

B. 1,4-DIISOCYANO-2,5-DIMETHYLBENZENE, *p*-$CN(C_6H_2(CH_3)_2)NC$

$$p\text{-}H_2N(C_6H_2(CH_3)_2)N_2H + HCOOH \longrightarrow p\text{-}OHCHN(C_6H_2(CH_3)_2)NHCHO + H_2O$$

$$3\,p\text{-}OHCHN(C_6H_2(CH_3)_2)NHCHO + 2\,CO(COCl_3)_2 + 12\,Et_3N \longrightarrow 3\,p\text{-}CN(C_6H_2(CH_3)_2)NC + 12\,[Et_3NH]Cl + 6\,CO_2$$

*Checkers used liquid Diphosgene (Aldrich) with no loss in yield.

Procedure

This is a modification of a synthetic method reported by Sahu.[4] This method can be adapted for the synthesis of the isocyanides prepared in Section 6.A. Substitution of triphosgene for phosgene provides a safer alternative for the synthesis of isocyanides, in general. On the other hand, phosgene is less expensive and the phosgene reaction is easier to scale up. *p*-$H_2N(C_6H_2(CH_3)_2)NH_2$ is converted to the corresponding formamide by the procedure outlined in Section 6.A.

A 250-mL two- or three-necked round-bottomed flask equipped with magnetic stirrer, condenser, and dropping funnel is charged with *p*-$OHCHN(C_6H_2(CH_3)_2)NHCHO$ (0.75 g, 3.9 mmol), triphosgene (0.77 g, 2.6 mmol), and $CHCl_3$ (40 mL, reagent grade) to dissolve the solids. Triethylamine (2.2 mL, 15.6 mmol) in $CHCl_3$ (10 mL) is added dropwise to the stirring mixture. The mixture is gradually warmed to 50°C and stirred for 3 h. The solution is washed with water (10 mL), HCl (0.1 M, 20 mL), $NaHCO_3$ (10%, 20 mL), and saturated NaCl (15 mL), then the separated organic layer is dried over Na_2SO_4. After filtration the solvent is removed under vacuum. The product is purified by sublimation at 30–60°C.

Anal. Calcd. for $C_{10}H_8N_2$: C, 76.90; H, 5.17; N, 17.93. Found: C, 76.96; H, 5.17; N, 17.95.

C. 1-ISOCYANO-4-METHOXYBENZENE, *p*-$CN(C_6H_4)OCH_3$

$$p\text{-}H_2N(C_6H_4)OCH_3 + CHCl_3 \longrightarrow p\text{-}CN(C_6H_4)OCH_3 + 3\,HCl$$

Procedure

This is a modification of a synthetic method reported by Weber.[5] This single-step phase transfer synthesis provides obvious advantages over the methods described in Sections 6.A and 6.B. It is especially useful for the preparation of liquid isocyanides, since they are stabilized in the presence of the unreacted amine that remains in the reaction system until final purification. Unfortunately, the method does not appear to be general. In addition to *p*-$H_2N(C_6H_4)OCH_3$, *p*-$CN(C_6H_4)CF_3$, *p*-$CN(C_6H_4)F$ and *p*-$CN(C_6H_4)CH_3$ can be synthesized by this method.

A 125-mL round-bottomed flask equipped with a condenser and magnetic stirrer is charged with *p*-$H_3CO(C_6H_4)NH_2$ (12.3 g, 0.10 mol), $CHCl_3$ (10.5 mL,

reagent grade), benzyltriethylammoniumchloride (BTEAC, 0.32 g, 1.4 mmol), and CH_2Cl_2 (33 mL, reagent grade). NaOH (50%, 35 mL) is added to the mixture after cooling to room temperature. The mixture is warmed to refluxing temperature and allowed to reflux for 3–5 h. Then the reaction mixture is diluted with cold water (100 mL) and extracted with portions of CH_2Cl_2 (100 mL). The CH_2Cl_2 washings are combined and washed with water (25 mL) and saturated NaCl (25 mL) and then dried over $MgSO_4$. The solvent is removed under vacuum. Any unreacted amine is separated from the isocyanide using a silicagel column with CH_2Cl_2 as the eluant. The isocyanide elutes first, and remaining amine is washed from the column using THF.

Anal. Calcd. for C_8H_7NO: C, 72.15; H, 5.31; N, 10.52. Found: C, 72.34; H, 5.20; N, 10.33.

D. BIS(1,4-DIISOCYANOBENZENE)BIS(1,2-BIS (DIPHENYLPHOSPHINO)ETHANE)TUNGSTEN(0), $W(dppe)_2(CNC_6H_4NC)_2$

$$W(dppe)_2(N_2)_2 + 2\,p\text{-}CN(C_6H_4)NC \longrightarrow cis\text{-}W(dppe)_2(CNC_6H_4NC)_2 + 2\,N_2$$

This synthesis has been reported by Bennett and co-workers.[1,2] A 100-mL round-bottomed flask equipped with sidearm and magnetic stirrer is charged with *trans*-$(N_2)_2W(dppe)_2$ (0.31 g, 0.3 mmol, synthesized according to literature[7]), *p*-$CN(C_6H_4)NC$ (1.9 g, 1.5 mmol, 2.5 : 1 excess), and THF (80 mL, distilled with $Na[Ph_2CO]$) and refluxed for 6 h. (*Note*: alternatively the reaction may be stirred under irradiation from a 75-W incandescent tungsten filament source for 48 h.) Hexanes (50 mL, distilled from P_2O_5) are added, and the flask is allowed to sit for 3–5 days to grow crystals, or the reaction solvent volume is reduced to 20–30 mL and hexanes (40 mL) are added to precipitate the product. The red product is filtered, rinsed with 4 : 1 hexanes/toluene (distilled with $Na[Ph_2CO]$), and dried under vacuum.

Properties of Intermediates and Products

Both formamides and solid isocyanides are moderately stable in air but tend to oxidize over time. Consequently, they should be stored under nitrogen at or below 4°C. Accurate percent yields for the isocyanide compounds are not given, since, as previously observed,[6] they are stabilized in the presence of excess starting materials and are generally purified only as needed for further synthesis.

Characterization of product is confirmed via ^{1}H NMR, IR, and mass spectra. Mass spectra of all these isocyanides exhibit a parent ion of maximum intensity and characteristic fragmentation peaks. Mass spectroscopy is also a useful tool for detecting unreacted amine or formamide. Isocyanides decompose in acid and are soluble in hexane, THF, toluene, CH_2Cl_2, CH_3CN, and alcohols.

1,4-Diisocyanobenzene is a colorless crystalline solid. The IR spectrum exhibits the strong characteristic ν_{CN} stretching frequency at 2127 cm^{-1} (KBr). ^{1}H NMR: aromatic singlet at 7.45 ppm. The sublimed solid exhibits a melting point of 152°C.

1,4-Diisocyano-2,5-dimethylbenzene is a colorless crystalline solid. IR: $\nu_{CN} = 2120$ cm^{-1} (KBr). ^{1}H NMR: aromatic singlet at δ 7.3; methyl proton peak at δ 2.4. The sublimed solid exhibits a melting point of 160°C.

1-Isocyano-4-methoxybenzene is a colorless liquid. IR: $\nu_{CN} = 2122$ cm^{-1}; ^{1}H NMR: pair of doublets for the nonequivalent aromatic protons at δ 7.3 and 6.9; methoxy singlet at δ 3.8. The purified solid exhibits a melting point of 32°C.

Bis(1,4-diisocyanobenzene)bis(1,2–bis(diphenylphosphino)ethane)tungsten(0) is a deep red crystalline solid. It is remarkably air-stable in the solid state. IR: ν_{CN} (sym) = 1761 cm^{-1} and ν_{CN} (asym) = 1662 cm^{-1} for the coordinated isocyanide stretching frequencies, and ν(CN) = 2115 cm^{-1} for the uncoordinated end of the ligand. ^{31}P NMR: 32.1 ppm ($J_{WP} = 196$ Hz); 47.5 ppm ($J_{WP} = 280$ Hz).

Acknowledgments

The submitters wish to provide a special note of thanks to the checkers, Professor Hunter and his students. Their useful and constructive comments were of great assistance in the final preparation of this manuscript. The checkers would also like to acknowledge the contributions of Cynthia Perrine, James Updegraff, Robert Wilcox, Les McSparrin, Lisa Walther, Floyd Snuder, and Monique Peace for checking one or more variants of these reactions.

References

1. C. Hu, W. C. Hodgeman, and D. W. Bennett, *Inorg. Chem.* **35**, 1621 (1996).
2. N. L. Wagner, F. E. Laib, and D. W. Bennett, *J. Am. Chem. Soc.* **122**, 10856 (2000).
3. I. Ugi, U. Fetzer, U. Eholzer, H. Knupfer, and K. Offermann, *Angew. Chem., Int. Ed. Eng.* **4**, 472 (1965).
4. D. P. Sahu, *Indian J. Chem.* **32B**, 385 (1993).
5. W. P. Weber and G. W. Gokel, *Tetrahedron Lett.* **17**, 1637 (1972).
6. L. Malatesta, F. Bonati, *Isocyanide Complexes of Metals*, Wiley, Chichester, UK, 1969.
7. J. R. Dilworth and R. L. Richards, *Inorg. Synth.* 119 (1980).

7. UNSYMMETRIC TRIPOD LIGANDS RELATED TO TRIS(PYRAZOL-1-YL)METHANE

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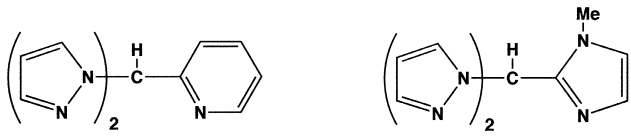
Checked by JAMES R. GARDINIER[‡] and DANIEL L. REGER[‡]

Tripodal ligands with a bridgehead carbon atom have assumed an important role in coordination and organometallic chemistry. Of particular interest are tris(pyrazol-1-yl)methanes,[1] isoelectronic with widely used tris(pyrazol-1-yl)borates. Unsymmetric ligands closely related to tris(pyrazol-1-yl)methane have been reported,[2,3] and their lower symmetry is useful in a range of applications,[2–6] including spectroscopic studies,[3,4] and studies of isomerism[2,5] and cycloplatination reactions.[2b,5d] Symmetric tris(pyridin-2-yl)methane as a ligand has also been widely studied,[7] and we describe here the facile syntheses of an unsymmetric mixed pyrazole/pyridine tripod ligand bis(pyrazol-1-yl)(pyridin-2-yl)methane, $(pz)_2(py)CH$, and closely related bis(pyrazol-1-yl)(*N*-methylimidazol-2-yl)methane, $(pz)_2(mim)CH$ (see Fig. 1). These ligands contain heterocycles with closely related but different donor properties,[4a,6,8] and subtle differences in donor group geometries presented to the metal center in complexes.[4a] The synthetic strategy developed by Peterson is employed, relying on the condensation of bis(pyrazol-1-yl)methanone, $(pz)_2C{=}O$, with aldehydes, $R(H)C{=}O$, to give $(pz)_2(R)CH$ and carbon dioxide.[9] The syntheses of the precursor reagents $(pz)_2C{=}O$[9c] and *N*-methylimidazole-2-carbaldehyde {(mim)(H)C=O},[10] developed from reported syntheses, are given as procedures 6.A and 6.B, respectively.



$(pz)_2(py)CH$ **$(pz)_2(mim)CH$**

Figure 1. Tripod ligands.

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General Comment

Anaerobic techniques and dry solvents and reagents are used for all preparations.

A. BIS(PYRAZOL-1-YL)METHANONE, $(pz)_2C{=}O$

$$2\,pzH + 2\,Et_3N + Cl_2C{=}O \longrightarrow (pz)_2C{=}O + 2\,[Et_3NH]Cl$$

■ **Caution.** *Because phosgene is volatile (bp 8°C) and highly toxic by inhalation or skin contact, is a severe lachrymator and is moisture-sensitive, this reaction should be performed in a well-ventilated hood. See general comments for choosing phosgene or related reagents elsewhere in this volume.*

Procedure

Pyrazole (5.0 g, 73.5 mmol, Aldrich) and triethylamine (10.25 mL, 73.5 mmol) are added to diethyl ether (200 mL) in a three-necked 500-mL round-bottomed flask fitted with an overhead stirrer and nitrogen inlet. The mixture is stirred for 5 min using an overhead stirrer.* Phosgene (19 mL, 1.93 M in toluene, as received from Fluka) is added in two portions using a pressure equalized dropping funnel. Stirring is continued for 15 min, the precipitate removed by filtration under vacuum, and the volume of the filtrate reduced by rotary evaporation† to give a pale yellow oil. Hexane (10 mL) is added and colorless crystals of the product form over 3 h at room temperature or 1 h when cooled in ice. The product is collected by filtration and dried under high vacuum. The yield is 5.65 g (95%).‡

Properties

The solid product is unstable at ambient temperature and should be stored at −20°C; mp lit.[10a] 61.5–62.5°C. ^{1}H NMR in $CDCl_3$: δ 8.72 (1H, dd, $J = 3.1$ Hz, H_5), 7.89 (1H, d, $J = 1$ Hz, H_3), 6.54 (1H, dd, $J = 3.1$ Hz, H_4).

B. *N*-METHYLIMIDAZOLE-2-CARBALDEHYDE, (mim)CHO

$$Li(mim) + (Me_2N)(H)C{=}O + 2\,HCl \longrightarrow (mim)(H)C{=}O + [Me_2NH_2]Cl + LiCl$$

*The checkers used magnetic stirring with intermittent shaking as needed.
†Checkers used cannula filtration and vacuum distillation of solvent.
‡The checkers report a yield of 76%, m.p. 59–60°C.

Procedure

Butyllithium (140 mL of 1.2 M solution in diethyl ether, 168 mmol, prepared as reported[11]) is added dropwise to a stirred solution of *N*-methylimidazole (13.4 mL, 168 mmol, Aldrich) in diethyl ether (50 mL) at $-80°C$ in a three-necked 500-mL round-bottomed flask fitted with a nitrogen inlet. The solution is allowed to warm slowly to 0°C, then cooled to $-80°C$, and added dropwise at this temperature via a jacketed dropping funnel to a mixture of *N*,*N*-dimethylformamide (25 mL, Aldrich) and diethyl ether (30 mL) stirred with an overhead stirrer at $-80°C$ in a three-necked 500-mL round-bottomed flask fitted with a nitrogen inlet.* The white suspension is allowed to warm to room temperature, and stirred for 6 h, and aqueous HCl (100 mL, 5 M) added dropwise over a few minutes. The organic layer is removed using a separating funnel and washed with 5 M aqueous HCl (2×20 mL). The combined acid extracts are made slightly alkaline with Na_2CO_3, extracted with dichloromethane (2×40 mL), and the combined extracts are dried over $MgSO_4$. After filtration, removal of solvent, and vacuum distillation (60–65°C, 1 torr), the product is obtained as a clear oil that crystallizes on standing (12.8 g, 69%).†

Properties

The product should be stored at $-20°C$. ^1H NMR in $CDCl_3$: δ 9.82 (s, 1H, CHO), 7.28 [s, 1H, H(4 or 5)], 7.12 [s, 1H, H(5 or 4)], 4.03 (s, 3H, NMe).

C. BIS(PYRAZOL-1-YL)(PYRIDIN-2-YL)METHANE, $(pz)_2(py)CH$

$$(pz)_2C{=}O + (py)(H)C{=}O \longrightarrow (pz)_2(py)CH + CO_2$$

Procedure

Bis(pyrazol-1-yl)methanone (0.98 g, 6.3 mmol) and pyridine-2-aldehyde (0.60 mL, 6.3 mmol, Merck) are added to a 50-mL Schlenk tube under nitrogen. A catalytic amount of anhydrous cobalt(II) chloride (0.01 g) is added, although the reaction does proceed satisfactorily without the catalyst. The mixture is gently warmed to $\sim 40°C$ via an external water bath until evolution of carbon dioxide is observed, and the mixture is then cooled and set aside until the reaction has subsided. Water (5 mL) is added and the mixture extracted with dichloromethane

*The checkers used a 1.6 M solution of butyllithium in hexanes (Aldrich) and cannula transfer of DMF/Et_2O solution to the Li(mim) suspension.

†The checkers report a yield of 50% at half-scale, crystals at 0°C melting at $\sim 23°C$.

(2×20 mL). The combined extracts are dried over $MgSO_4$ and filtered, and the solvent is removed in a vacuum.* The product is recrystallized from hot hexane (0.64 g, 45%).

Properties

^{1}H NMR in $CDCl_3$: δ 8.61 [ddd, 1H, H(6)], 7.88 (s, 1H, CH), $\sim$7.85 [m, 3H, $H(4)_{py}$ and $H(5)_{pz}$], 7.42 [ddd, 1H, $H(5)_{py}$], 7.15 [d, 1H, $H(3)_{py}$], 6.36 [dd, 2H, H(4)].

D. BIS(PYRAZOL-1-YL)(*N*-METHYLIMIDAZOL-2-YL)METHANE, $(pz)_2(mim)CH$

$$(pz)_2C{=}O + (mim)(H)C{=}O \longrightarrow (pz)_2(mim)CH + CO_2$$

Procedure

Bis(pyrazol-1-yl)methanone (0.98 g, 6.3 mmol) and *N*-methylimidazole-2-aldehyde (0.60 mL, 6.3 mmol) are added to a 50-mL Schlenk tube under nitrogen in an open system. A vigorous reaction commences immediately to produce a red-brown tar and carbon dioxide. The material thus obtained is dissolved in dichloromethane and chromatographed on a column ($\sim 2 \times 15$ cm; Merck 60, 230/240-mesh silicagel; 1 atm or medium pressure of nitrogen applied) with dichloromethane used as the eluent. A colorless solution of the product is obtained, as other product(s) are either not eluted or have low R_f values.† Addition of hexane (20 mL) to the dichloromethane eluent, followed by slow removal of dichloromethane under a vacuum at room temperature gives $(pz)_2(mim)CH$ as white crystals (1.7 g, 49%).‡

Properties

^{1}H NMR in $CDCl_3$: δ 8.00 (s, 1H, CH), 7.93 [d, 2H, H(5)], 7.52 [s. 2H. H(3)]. 7.16 [d, 1H, $H(4 \text{ or } 5)_{mim}$], 6.87 [d, 1H, $H(5 \text{ or } 4)_{mim}$], 3.56 [s, 3H, NMe].

*The checkers monitored purity by thin-layer chromatography (TLC) (silica/Et_2O, product $R_f \sim 0.4$). Hot hexane extract was evaporated, residue extracted with Et_2O, and solution passed over a silica column. Evaporation gave a pale yellow oil that crystallized on standing. Recrystallization from hot hexane cooled to -20°C overnight gave colorless needles in a yield of 30%, mp 78.5–79.0°C.

†The checkers found pyrazole in the first fraction eluting.

‡The checkers obtained 0.84 g (58% yield, mp 119–120°C) using 13 mg $CoCl_2$ as catalyst with $(pz)_2CO$ in 2 mL of THF, and adding the solution of (mim)(H)C=O in 2 mL THF by cannula.

References

1. (a) S. Trofimenko, *Progr. Inorg. Chem.* **34**, 115 (1986); (b) D. L. Reger, J. E. Collins, D. L. Jameson, and R. K. Castellano, *Inorg. Synth.* **32**, 63 (1998).
2. (a) P. K. Byers, A. J. Canty, and R. T. Honeyman, *J. Organomet. Chem.* **385**, 417 (1990); (b) A. J. Canty and R. T. Honeyman, *J. Organomet. Chem.* **387**, 247 1990).
3. (a) T. C. Higgs and C. J. Carrano, *Inorg. Chem.* **36**, 291 (1997); (b) T. C. Higgs and C. J. Carrano, *Inorg. Chem.* **36**, 298 (1997).
4. T. Astley, A. J. Canty, M. A. Hitchman, G. L. Rowbottom, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.* 1981 (1991); (b) A. J. Canty, P. R. Traill, R. Colton, and I. M. Thomas, *Inorg. Chim. Acta* **210**, 91 (1993).
5. (a) P. K. Byers and A. J. Canty, *Organometallics* **9**, 210 (1990); (b) P. K. Byers, A. J. Canty, B. W. Skelton, and A. H. White, *Organometallics* **9**, 826 (1990); (c) A. J. Canty, R. T. Honeyman, B. W. Skelton, and A. H. White, *J. Organomet. Chem.* **396**, 105 (1990); (d) P. K. Byers, A. J. Canty, and R. T. Honeyman, *Adv. Organomet. Chem.* **34**, 1 (1991); (e) A. J. Canty, R. T. Honeyman, B. W. Skelton, and A. H. White, *J. Organomet. Chem.* **424**, 381 (1992).
6. T. Astley, M. A. Hitchman, B. W. Skelton, and A. H. White, *Aust. J. Chem.* **50**, 145 (1997); (b) P. A. Anderson, T. Astley, M. A. Hitchman, F. R. Keene, B. Moubaraki, K. S. Murray, B. W. Skelton, E. R. Tiekink, H. Toftlund, and A. H. White, *J. Chem. Soc., Dalton Trans.* 3512 (2000).
7. For convenient preparations of tris(pyridin-2-yl)methane from bis(pyridin-2-yl)methanone, see (a) G. R. Newkome, V. K. Gupta, H. C. R. Taylor, and F. R. Fronczek, *Organometallics* **3**, 1549 (1984); (b) A. J. Canty and N. J. Minchin, *Aust. J. Chem.* **39**, 1063 (1986); (c) A. J. Canty, N. Chaichit, B. M. Gatehouse, E. E. George, and G. Hayhurst, *Inorg. Chem.* **20**, 2414 (1981); (d) F. R. Keene, M. R. Snow, P. J. Stephenson, and E. R. T. Tiekink, *Inorg. Chem.* **27**, 2040 (1988).
8. A. J. Canty and C. V. Lee, *Organometallics* **1**, 1063 (1982).
9. (a) K. I. Thé and L. K. Peterson, *Can. J. Chem.* **51**, 422 (1973); (b) K. I. Thé, L. K. Peterson, and E. Kiehlmann, *Can. J. Chem.* **51**, 2448 (1973); (c) L. K. Peterson, E. Kiehlmann, A. R. Sanger, and K. I. Thé, *Can J. Chem.* **52**, 2367 (1974).
10. P. E. Iversen and H. Lund, *Acta Chem, Scand.* **20**, 2649 (1966).
11. R. G. Jones and H. Gilman, *Org. React.* **6**, 339 (1951).

8. DIFLUOROTRIPHENYLARSENIC(V), AsF_2Ph_3

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Checked by JOHN R. SHAPLEY†

$$AsPh_3 + H_2O_2 + 2\,HF \longrightarrow AsPh_3F_2 + 2\,H_2O$$

The pentavalent triphenylarsenic dihalides are of interest because they present structures that are dependent on the halogen[1–3] and are convenient sources for the preparation of arsenic ylides.[4,5] The chemistry of triphenylarsenic difluoride,

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by far the most air-stable of the halide derivatives, has not been much explored. This is probably because of the synthetic procedures currently available: (1) prolonged heating of triphenylarsine with sulfur tetrafluoride[6] or (2) halogen exchange between triphenylarsenic dichloride and silver fluoride.[7] However, we have found that triphenylarsenic difluoride precipitates in good yield when a saturated solution of triphenylarsine oxide in methanol is treated with concentrated hydrofluoric acid. Here we describe a simple one-pot synthesis based on triphenylarsine, that is especially useful when the oxide is not available. It is based in the facile oxidation of triphenylarsine with hydrogen peroxide and the immediate conversion of the oxide into the fluoride.

Procedure

■ **Caution.** *Arsenic compounds are poisonous. Concentrated hydrogen peroxide can cause severe burns. Hydrofluoric acid is neurotoxic and corrosive, and causes severe burns. All manipulations should be conducted in an efficient fume hood, and gloves and goggles should be worn.*

In a 100-mL Teflon* beaker immersed in a bath at 80–100°C are placed 10 g (32.7 mmol) of $AsPh_3$,† 10 g of glacial acetic acid and a magnetic stirring bar. Then 10 g (88.2 mol) of 30% H_2O_2 is added dropwise to the abovementioned mixture with stirring. Some boiling or frothing of the solution may occur, since the reaction is exothermic and oxygen is released. Then 10 g (240 mmol) of 48% HF is added with stirring to the warm solution. During the addition, a white precipitate forms. The beaker is immersed in an ice-cold water bath, and the mixture is stirred for 10 min. Then, 20 g of cold distilled water is added to the mixture and the stirring is continued for further 10 min. The solid product is collected by vacuum filtration, washed with three 5-mL portions of methanol, and dried in air for 10 min. The solid is transferred to a Teflon vial, which is introduced into a round-bottomed flask and maintained under vacuum at room temperature for 2 h. Yield: 10 g (90%).

Anal. Calcd. for $AsPh_3F_2$: C, 62.81; H, 4.39; F, 11.04. Found: C, 62.6; H, 4.3; F, 11.3.

Properties

White AsF_2Ph_3 melts at 137–139°C. The IR spectrum, taken as a Nujol mull, has the characteristic band $\nu_{as}(AsF_2)$ at 517 cm^{-1}. The ^{19}F NMR spectrum in $CDCl_3$

*Similar results are obtained by using a variety of plastic vessels.
†The procedure was checked at half-scale (yield 93%).

shows only a singlet at -87.78 ppm respect to $CFCl_3$ (-86.01 in acetone-d_6). It is insoluble in water, slightly soluble in diethyl ether and cold methanol, and soluble in acetone, ethanol, dichloromethane, chloroform, acetonitrile, dimethyl formamide, and dimethyl sulfoxide, solvents from which it can be recrystallized. It reacts with KOH in aqueous solution to yield Ph_3AsO, but it resists the action of cold water for hours. It is very stable at room temperature and can be manipulated in air without special precautions. A very pure product (mp 139–140°C) is obtained by recrystallization from ethanol.

References

1. A. Augustine, G. Ferguson, and F. C. March, *Can. J. Chem.* **53**, 1647 (1975).
2. N. Bricklebank, S. M. Godfrey, H. P. Lane, C. A. McAuliffe, R. G. Pritchard, and J. M. Moreno, *J. Chem. Soc., Dalton Trans.* 3873 (1995) and refs. therein.
3. B. Neumüller, S. Chitsatz, and K. Dehnicke, *Z. Naturforsch.* **54b**, 1611 (1999).
4. G. O. Doak and L. D. Freedman, *Organometallic Compounds of Arsenic, Antimony and Bismuth*, Wiley-Interscience, New York, 1970.
5. S. Chitsatz, B. Neumüller, and K. Dehnicke, *Z. Anorg. Allg. Chem.* **626**, 634 (2000) and refs. therein.
6. W. C. Smith, *J. Am. Chem. Soc.* **82**, 6176 (1960).
7. M. H. O'Brien, G. O. Doak, and G. G. Long, *Inorg. Chim. Acta.* **1**, 34 (1967).

9. TETRAMETHYLAMMONIUM SALTS OF SUPEROXIDE AND PEROXYNITRITE

Submitted by D. SCOTT BOHLE[*†] and ELISABETH S. SAGAN[*]
Checked by WILLEM H. KOPPENOL[‡] and REINHARD KISSNER[‡]

Peroxynitrite is an important cytotoxin that results in vivo from the direct reaction of superoxide and nitric oxide. There are several methods to synthesize peroxynitrite, including the solid-state photolysis of KNO_3,[1] the ozonation of sodium azide,[2] or the alkaline reaction of nitrite esters with hydrogen peroxide.[3] Perhaps the most common peroxynitrite synthesis involves treating an acidified solution of hydrogen peroxide with nitrite, followed by an immediate quench with base.[4] Although this synthesis is facile, quick, and affordable, it results in

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contamination with nitrite, nitrate, and/or hydrogen peroxide. Hydrogen peroxide may be removed from these solutions by treatment with manganese dioxide, but the peroxynitrite from this method has not yet been isolated free from the nitrite or nitrate contaminants. The presence of nitrite or nitrate may be inconsequential for many applications of peroxynitrite, in which case this synthesis is quite adequate. However, for mechanistic studies, either for accurate determination of product stoichiometry or for isotopic exchange experiments, such as with ^{18}O, the abovementioned methods cannot be used. The method described here involves two stages: a 3-day solid-state synthesis/mixing reaction that is followed by a pair of liquid ammonia extraction/lyophilization steps to produce pure tetramethylammonium superoxide; the second stage requires less than 2 h to dissolve the tetramethylammonium superoxide, nitrosylate it, and then lyophilize the product to give pure tetramethylammonium peroxynitrite. Several synthetic routes to tetramethylammonium superoxide have been reported over the years.[5,6] However, some of these methods involve cumbersome separations. The synthesis of tetramethylammonium superoxide from a solid-state metathesis reaction between potassium superoxide and tetramethylammonium hydroxide pentahydrate has proved to be the most reliable with the highest purity. The synthesis of the tetramethylammonium peroxynitrite salt mimics the biosynthesis of peroxynitrite, in which nitric oxide reacts directly with superoxide. The improved synthesis has ensured 100% purity of the peroxynitrite salt with no contamination of starting material, nitrate, or nitrite. Nitric oxide is generated by the reduction of nitrite with iron sulfate under acidic conditions, which guarantees that the gas is readily dried and free of nitrous oxide or nitrogen dioxide, as is found in commercially available nitric oxide gas cylinders. In addition, the exact control of stoichiometry means over nitrosylation is avoided, and ^{15}N can be efficiently incorporated into the product by the use of commonly available ^{15}N nitrite salts.

A. TETRAMETHYLAMMONIUM SUPEROXIDE, $[N(CH_3)_4]O_2$

$$11\,KO_2 + [N(CH_3)_4]OH \cdot 5\,H_2O \xrightarrow{NH_3(l)} [N(CH_3)_4]O_2 + 11\,KOH + 7.5\,O_2$$

■ **Caution.** *The use of predried tetramethylammonium hydroxide pentahydrate*[7] *has resulted in a serious explosion during the solid-phase metathesis of potassium superoxide with tetramethylammonium hydroxide pentahydrate. This can be avoided by using the pentahydrate as supplied without drying and by employing an increased amount of potassium superoxide. The latter can easily be separated during the liquid ammonia extraction.*

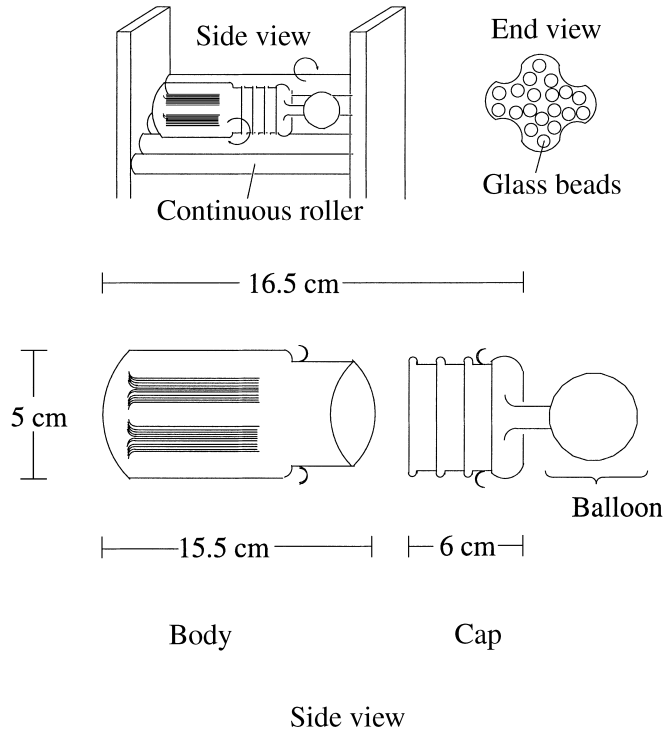

Figure 1. Solid-state reaction setup.

Procedure

Commercially available potassium superoxide and tetramethylammonium hydroxide pentahydrate from Aldrich were used as supplied without further purification. Industrial-grade nitrogen gas does not require any further purification, but the ammonia gas, 99.999%, should be at a minimum purged through Drierite before use. All work is done under a nitrogen flow unless otherwise stated.

The reaction apparatus is shown in Fig. 1 and consists of a beveled flask fit with male and female T45/50 ground-glass joints. The female top has a tapered joint such that a balloon, used to maintain positive pressures throughout the reaction, fastened with tape, fits easily. The female top is 6 cm in length, while the male bottom is 15.5 cm in length. The entire flask is 5 cm in height. The continuous roller is a Star Manufacturing, Inc. model 12 silvertone roller. The roller bed is 19.3 cm in length. Each roller has a circumference of 9.2 cm, with a spacing of 1.2 cm between each roller. The reaction vessel has a rotation rate of 2.5 revolutions per minute (rpm).

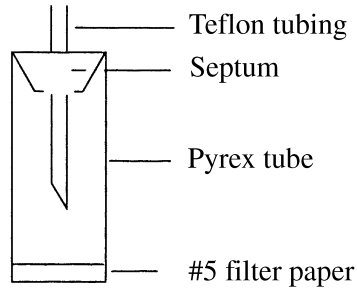

Figure 2. Canula filter. The Teflon tubing is inserted through the NMR tube septum. The filter paper is taped onto the pyrex tubing using Teflon tape.

In a drybox, 10.0 g (141 mmol) of potassium superoxide, 1.2 g (6.6 mmol) of tetramethylammonium hydroxide pentahydrate, and 15 mL of small glass beads are added to the reaction flask. The solid yellow mixture is continuously rotated slowly for 3 days. The reaction vessel is taken into the drybox daily to scrape any caked-up product from the sides of the flask and to ensure optimum mixing. For the first day, it is sufficient to tap the flask walls to obtain free-flowing contents. After 3 days, the mixture is taken into the drybox and transferred to a T14/20 100-mL round-bottomed flask fit with the canula filter (Fig. 2). The round-bottomed flask is connected to a receiving flask of the same type via Teflon tubing. Once taken out of the drybox, the reaction flask is immersed in a dry-ice/ethanol bath. A medium flow of nitrogen is purged through the flask. Liquid ammonia, 40 mL, is condensed into the reaction flask using a Teflon tube. The flow of nitrogen and ammonia is monitored by allowing it to escape into the hood through an oil bubbler filled with paraffin oil. After the ammonia has condensed, shaking the flask will produce a pale yellow slurry of dissolved tetramethylammonium superoxide to be filtered from the insoluble potassium hydroxide. The dry-ice/ethanol bath is switched to the receiving flask, and the ammonia/superoxide solution is filtered to the receiving flask with a forced nitrogen stream. After filtration the liquid ammonia is boiled off with a nitrogen flow to leave a pale yellow solid of tetramethylammonium superoxide. This extraction procedure is conducted 3 times to give 0.341 g, 49% yield of pure product.

Properties

The product is a very pale yellow to cream-colored solid. It is hygroscopic and is soluble in liquid ammonia, with limited solubility and stability in acetonitrile, dimethyl sulfoxide, and dimethylformamide.[6] Water or moisture from the air leads to disproportionation, and so the product must be stored under anhydrous

conditions. It is characterized in the solid state by Raman spectroscopy and has a single peak at 1118 cm^{-1}. The UV–vis, magnetic susceptibility, elemental analysis, and electrochemistry have been reported elsewhere.[5,6]

B. TETRAMETHYLAMMONIUM PEROXYNITRITE, $[N(CH_3)_4][ONOO]$

$$NaNO_2 + FeSO_4 \cdot 7\,H_2O \xrightarrow{H_2O} NO + Fe^{+3} + SO_4^{2-} + 6H_2O + Na^+ + 2OH^-$$

$$[N(CH_3)_4]O_2 + NO(g) \xrightarrow{NH_3(1)} [N(CH_3)_4][ONOO]$$

Procedure

Sodium nitrite, 99.99%, ferrous sulfate heptahydrate, sulfuric acid, sodium hydroxide, phosphorus pentoxide, and potassium hydroxide are reagent grade.

The experimental setup is shown in Fig. 3. The NO generator consists of a 100-mL T14/20 three-necked flask fitted with septa on the two outside necks. The central neck is connected to a dry-ice condenser that is filled with dry ice/ethanol during the synthesis. The condenser is connected to the NO line via clear tubing. The NO line consists of three drying tubes connected together in a line by

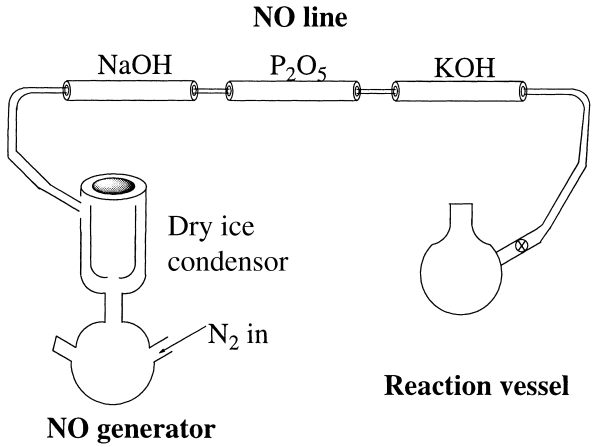

Figure 3. Experimental design for $ONOO^-$ synthesis. The dry-ice condensor of the "NO generator" is used to trap any water that may evolve after addition of iron sulfate. The three drying tubes of the "NO line" trap any remaining water before it reaches the reaction vessel.

clear tubing. The first tube contains sodium hydroxide pellets. The second and third tubes contain phosphorus pentoxide powder and potassium hydroxide pellets, respectively. The inside ends of each tube are packed with glass wool. The NO line is connected to a glass pipette fit with teflon tubing. The Teflon tube is inserted into the reaction vessel and under the liquid surface to introduce the NO.

For the nitric oxide gas generation, a degassed solution of sodium nitrite is prepared by charging a T14/20 100-mL three-necked flask with 0.200 g sodium nitrite (3 mmol) and adding 4 mL distilled water outside the hood. The solution is purged with nitrogen for 15 min. The purge rate is monitored through the exit oil bubbler. The nitrite solution flask is connected to a dry-ice condenser filled with a dry-ice/ethanol bath to capture any water that may escape. An acidified solution of iron sulfate is prepared in air by charging a 100-mL round-bottomed flask with 5 g ferrous sulfate heptahydrate (18 mmol), 20 mL distilled water, and 1 mL concentrated sulfuric acid. The light green solution is purged with nitrogen for 15 mins. Although the iron sulfate solution is stable for up to one week, fresh solutions are to be used when possible. In the drybox, a T14/20 100-mL Schlenk flask is charged with 120 mg (1.13 mmol) of tetramethylammonium superoxide and is fitted with a septum. The flask is removed from the drybox and is purged with nitrogen for 3 min. The flask is immersed in a dry-ice/ethanol bath. Liquid ammonia, 40 mL, is condensed into the flask by using a Teflon tube inlet. The nitric oxide scrubbing line is purged with nitrogen for 10 min. The Teflon tubing used to introduce the ammonia gas is replaced with the tubing from the nitric oxide line. Dry nitric oxide gas is generated by adding the iron sulfate solution dropwise to the nitrite solution. The clear, colorless nitrite solution turns from a green-brown sludge to a milky light brown to clear dark brown, indicating the completion of nitric oxide gas generation. The total volume of iron sulfate solution (0.856 M) used ranges from 1.25 to 2.0 mL. As the nitric oxide dissolves into the superoxide solution, the initially clear, colorless solution changes to light yellow to orange, indicating the formation of tetramethylammonium peroxynitrite. The dry-ice/ethanol bath and Teflon tubing are removed. Roughly 50% of the liquid ammonia is evaporated under a nitrogen flow. The remaining peroxynitrite/ammonia solution is lyopholized by freezing the solution with liquid nitrogen, placing it under a dynamic high vacuum, and removing the liquid nitrogen bath. After lyophilization, the fluffy orange solid, tetramethylammonium peroxynitrite, is brought into the drybox (0.162 g, 97% yield).

Properties

The product is a yellow-orange to orange, moisture-sensitive solid. It is stable for a minimum of 4 weeks if stored in a good inert-atmosphere box. It is stable in solution only in liquid ammonia and basic water. The product is soluble, but

slowly reacts with dimethylsulfoxide, acetonitrile, alcohols, and halocarbons. Characterization of this product is performed by Raman spectroscopy, which provides an accurate indication of purity. The solid-state peroxynitrite stretching frequencies are as follows: δ_{ONOO}, 591 cm^{-1}; δ_{ONOO^-}, 634 cm^{-1}; ν_{O-O}, 803 cm^{-1}; ν_{N-O}, 926 cm^{-1}; and $\nu_{N=O}$, 1459 cm^{-1}. Tetramethylammonium peroxynitrite begins to decompose even on dilution in 1 M NaOH, resulting in an inaccurate measurement of concentration and purity of the solid. Other methods of tetramethylammonium peroxynitrite characterization include UV–visible spectroscopy and ^{15}N NMR spectroscopy, which are reported in detail elsewhere.[8,9]

References

1. P. A. King, V. E. Anderson, J. O. Edwards, G. Gustafson, R. C. Plumb, and J. W. Suggs, *Am. Chem. Soc.* **114**, 5430–5432 (1992).
2. W. A. Pryor, R. Cueto, X. Jin, W. H. Koppenol, M. Ngu-Schwemlein, G. L. Squadrito, P. L. Uppu, and R. M. Uppu, *Free Rad. Biol. Med.* **18**, 75–83 (1995).
3. J. R. Luis, M. E. Peña, and A. Ríos, *J. Chem. Soc., Chem. Commun.* 1298–1299 (1993).
4. A. Saha, S. Goldstein, D. Cabelli, and G. Czapski, *Free Rad. Biol. Med.* **24**, 653–659 (1998).
5. A. D. McElroyand and J. S. Hashman, *Inorg. Chem.* **3**, 1798–1799 (1964).
6. D. T. Sawyer, T. S. Calderwood, K. Yamaguchi, and C. T. Angelis, *Inorg. Chem.*, **22**, 2577–2583 (1983).
7. K. Yamaguchi, T. S. Calderwood, and D. T. Sawyer, *Inorg. Chem.* **25**, 1289–1290 (1986).
8. D. S. Bohle, B. Hansert, S. C. Paulson, and B. D. Smith, *J. Am. Chem. Soc.* **116**, 7423–7424 (1994).
9. D. S. Bohle, P. A. Glassbrenner, and B. Hansert, *Meth. Enzymol.* **269**, 302–311 (1996).

10. TELLURIUM–NITROGEN COMPOUNDS

Submitted by TRISTRAM CHIVERS,[*] NICOLE SANDBLOM,[*] and GABRIELE SCHATTE[*]
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The first structural characterization of a tellurium diimide $RNTe(\mu\text{-}N^tBu)_2TeNR$ ($R = PPh_2NSiMe_3$) was reported in 1994.[1] Subsequently, the synthesis of the symmetric derivative, $R = {}^tBu$, was achieved by the reaction of $Li[HN^tBu]$ with $TeCl_4$ in a 4 : 1 molar ratio in toluene.[2] Several LiCl-containing byproducts are also obtained in this solvent.[3] In THF, however, the tellurium diimide, $^tBuN\text{-}Te(\mu\text{-}N^tBu)_2TeN^tBu$, is obtained in 90% yield and is readily purified.[4] Unlike sulfur or selenium diimides, the tellurium diimides are dimeric and form either cis or

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trans isomers in the solid state.[1,2] In *cis*-^{t}BuNTe(μ-N^{t}Bu)$_2$TeN^{t}Bu the terminal ^{t}Bu groups are in the endo positions with respect to the Te_2N_2 ring.[2]

This new reagent has proved useful for the development of TeN chemistry. For example, reactions of ^{t}BuNTe(μ-N^{t}Bu)$_2$TeN^{t}Bu with Li[HN^{t}Bu] or K[O^{t}Bu] generate the anions $[Te(N^tBu)_3]^{2-}$ and $[Te(N^tBu)_2(O^tBu)]^-$, respectively.[5,6] The dimer ^{t}BuNTe(μ-N^{t}Bu)$_2$TeN^{t}Bu may act as a bridging or chelating ligand toward Cu^+ and Ag.[7] The redistribution of ^{t}BuNTe(μ-N^{t}Bu)$_2$TeN^{t}Bu with tellurium tetrahalides yields the imidotellurium(IV) dihalides $(^tBuNTeX_2)_n$ (X = Cl, Br).[4] The cycloaddition reaction of ^{t}BuNTe(μ-N^{t}Bu)$_2$TeN^{t}Bu with ^{t}BuNCO generates the ureatotelluroxide $\{OC(\mu\text{-}N^tBu)_2TeO\}_2$.[8] The dimeric compound $\{Li_2[Te(N^tBu)_3]\}_2$ is a useful reagent for incorporating other elements, such as B,[5] P,[5] Sb,[9] Bi,[9] or In[10] into the TeN ring system. The stannatellurone $\{^tBuNSn(\mu\text{-}N^tBu)_2TeN^tBu\}(\mu_3\text{-SnTe})$ is obtained from the reaction of $\{Li_2[Te(N^tBu)_3]\}_2$ with Sn(II) salts.[11]

General Procedures

■ **Caution.** *$TeCl_4$ is highly toxic as well as hygroscopic. Consequently, reactions should be carried out in an efficient fume hood. Reaction vessels that come in contact with tellurium compounds are rinsed with water first (fume hood), the washings are combined in a beaker, and concentrated nitric acid is added the next day. The water-rinsed reaction vessels are placed into a concentrated nitric acid bath for 24 h before final cleaning.*

Because of the oxygen and moisture sensitivity of the starting materials and products, all operations are carried out under an atmosphere of dry argon using Schlenk or inert-atmosphere drybox techniques. Familiarity with solvent transfer using cannula techniques, filtration under inert-gas atmosphere, and vacuum techniques is required.[12] All glassware is dried in an oven at ≈120°C. The solvents *n*-hexane, tetrahydrofuran, and diethyl ether are twice dried over sodium/benzophenone and then distilled under argon. Solvents are stored over activated molecular sieves (3 Å) in 500-mL glass vessels equipped with PTFE piston valves (Chemglass) prior to use. Tellurium tetrachloride (ÆSAR, 99%) and *n*-BuLi (Aldrich, 2.5 M solution in hexanes) are used without further purification and are stored under argon.

A. LITHIUM *tert*-BUTYLAMIDE, Li[HN^{t}Bu]

$$^tBuNH_2 + {}^nBuLi \rightarrow Li[HN^tBu] + C_4H_{10}$$

Procedure

The following procedure is suitable for the synthesis of Li[HN^{t}Bu] in large quantities. Neat ^{t}BuNH$_2$ (65 mL, 0.61 mol) and *n*-hexane (170 mL) are added to a 1-L round-bottomed flask equipped with a gas inlet sidearm and containing a magnetic stirring bar. (*Note*: ^{t}BuNH$_2$ is used in excess to ensure that all *n*-BuLi is used up during the reaction.) A calibrated 500-mL dropping funnel with pressure equalizer and Teflon key is connected to the flask. The reaction vessel is cooled to -10°C (ice/NaCl). The dropping funnel is charged with the yellow solution of *n*-BuLi in hexanes (2.5 M, 200 mL, 0.5 mol), and this solution is added dropwise (1 h) to the stirred solution of ^{t}BuNH$_2$ in *n*-hexane.

■ **Caution.** *The reaction is exothermic and n-butane gas is produced. Therefore, sufficient cooling and a slow addition of the n-BuLi/hexanes solution are required. n-BuLi can ignite on contact with water or air. During the addition of n-BuLi solutions the storage bottle should be kept in the metal container provided by the supplier, and leather gloves should be worn because disposable gloves react immediately with n-BuLi.*

The colorless solution becomes pale yellow, and a white precipitate of Li[HN^{t}Bu] is formed. The reaction mixture is stirred for an additional hour at -10°C and finally allowed to reach room temperature. After 0.5 h the volatile materials are removed under vacuum. The white solid (38.50 g, 0.487 mol, 97.4%) is pumped to dryness under vacuum by placing a warm water bath underneath the flask ($T = 30$°C) and stored in a 150-mL Nalgene container in the drybox. (*Note*: The solid readily adsorbs *n*-hexane and appears dry. If the solid forms big clumps during the process of removing the solvent, it is necessary to move the flask into a drybox and break up the clumps. Afterwards, the remaining solvent is removed under vacuum. This procedure ensures the complete removal of *n*-hexane.)

■ **Caution.** *Li[HN^{t}Bu] reacts violently with water. After recovering the product, the remaining Li[HN^{t}Bu] in the reaction vessel must be destroyed carefully. The closed flask (under an argon atmosphere) is taken out of the drybox, placed into an ice bath, and 200 mL of isopropanol is added carefully. After a few minutes 200 mL of ice water is added to the iso-propanol solution. The mixture is stirred until no solid remains, and then the contents treated as normal organic waste.*

Properties

Lithium *tert*-butyl amide is an air- and moisture-sensitive flammable solid that can be stored for up to 4 months in the drybox. In the solid state it has an

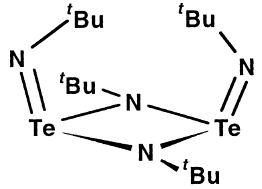
octameric, cyclic ladder structure.[13] ^{1}H NMR (23°C): in C_7D_8 or C_6D_6, δ 1.37 (9 H, ^{t}Bu); in d_8-THF, δ 1.07 (9 H, ^{t}Bu) and −1.55 (1 H, NH). ^{13}C NMR (23°C): in C_6D_6 (from Ref. 13), δ 51.84 ($C(CH_3)_3$) and 38.17 ($C(CH_3)_3$); in d_8-THF, δ 51.65 ($C(CH_3)_3$) and 38.82 ($C(CH_3)_3$). ^{7}Li NMR (23°C): in d_8-THF, 3.22 ppm ($\delta\nu_{1/2} = 13.4$ Hz).

B. BIS(*μ-tert*-BUTYLIMIDO)-BIS(*tert*-BUTYLIMIDO)DITELLURIUM, ^{t}BuNTe(μ-N^{t}Bu)$_2$TeN^{t}Bu (1)

$$2\,TeCl_4 + 8\,Li[HN^tBu] \longrightarrow {}^tBuNTe(\mu\text{-}N^tBu)_2TeN^tBu + 8\,LiCl + 4\,{}^tBuNH_2$$

Procedure

Li[HN^{t}Bu] (finely powdered; 11.90 g, 148.6 mmol) and $TeCl_4$ (finely powdered; 10.00 g, 37.1 mmol) are loaded in the drybox into two separate round-bottomed sidearm flasks (500 and 1000 mL, respectively). The two reaction vessels are removed from the drybox and connected to a standard argon gas/vacuum line. Dry THF (100 and 150 mL) is added to the flasks containing the $TeCl_4$ and Li[HN^{t}Bu], respectively. The yellow $TeCl_4$/THF solution is cooled immediately to −78°C (ethanol/dry ice), and then the white suspension of Li[HN^{t}Bu] in THF is transferred slowly via a double-tipped, stainless-steel cannula (16 gauge, length 2 ft). When 50 mL of the Li[HN^{t}Bu]/THF suspension have been added, an orange slurry is observed. After 100 mL, the slurry darkens to yellow-brown, and, on completion of the addition, the color of the reaction mixture is dark brown. The Li[HN^{t}Bu] vessel is rinsed with THF (20 mL), and the washings are added to the reaction mixture. The reaction mixture is stirred for 3 h at −78°C. (*Note*: For optimum yields, it is important to keep the cold bath at −78°C by addition of dry ice.) The cold bath is then allowed to reach 23°C slowly, whereupon the color of the reaction mixture changes to red-orange. The color intensifies to dark red after the solution is stirred for an additional 48 h at 23°C. Volatile materials are removed under vacuum, and the solid orange residue is extracted with diethyl ether (∼200 mL) during vigorous stirring. The precipitate is allowed to settle, and the dark red solution is then filtered by using a cannula through a fine-porosity sintered-glass frit (4–8 μm) into a second 500-mL Schlenk flask under slightly reduced pressure. The remaining solid is washed twice with Et_2O (∼30 mL), and the washings are filtered into the solution of the first extraction. Removal of solvent under vacuum affords ^{t}BuNTe(μ-N^{t}Bu)$_2$TeN^{t}Bu as an orange microcrystalline solid (9.03 g, 90% yield based on $TeCl_4$). This product contains small amounts of LiCl.



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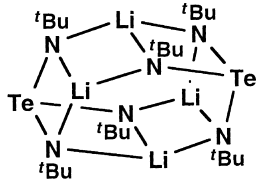

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Anal. Calcd. for $Te_2C_{16}H_{36}N_4$: C, 35.61; H, 6.72; N, 10.38. Found: C, 35.11; H, 6.58; N, 9.98; Cl, 0.16.

LiCl-free ^{t}BuNTe(μ-N^{t}Bu)$_2$TeN^{t}Bu is obtained via vacuum sublimation. In a typical experiment a sublimation apparatus is charged with 1.770 g of the crude product. Sublimation is conducted at 90–95°C/10^{-3} mbar with the cold finger at 18°C. Over 24 h pure ^{t}BuNTe(μ-N^{t}Bu)$_2$TeN^{t}Bu sublimes onto the cold finger as a yellow-orange solid (1.239 g).

Properties

^{t}BuNTe(μ-N^{t}Bu)$_2$TeN^{t}Bu is an air- and moisture-sensitive orange solid that can be stored in glass vials for up to 6 months in the drybox. It is extremely soluble in toluene, *n*-hexane, *n*-pentane, diethyl ether, and tetrahydrofuran, but it decomposes in chlorinated solvents (CH_2Cl_2, $CHCl_3$), acetonitrile or carbon disulfide. The dimer ^{t}BuNTe(μ-N^{t}Bu)$_2$TeN^{t}Bu melts without decomposition at 100–102°C. Solutions of ^{t}BuNTe(μ-N^{t}Bu)$_2$TeN^{t}Bu show the presence of two isomers, A and B (^{1}H and ^{13}C NMR; ratio A/B = 4 : 1; see Fig. 1). However, both isomers yield the same products in further reactions. ^{1}H NMR (23°C): in C_6D_6 (see Fig. 1), δ 1.66 (9H, ^{t}Bu), 1.25 (9H, ^{t}Bu), A; δ 1.58, 1.27, (9H, ^{t}Bu), B; in C_7D_8, δ 1 (9H, ^{t}Bu), 1.27 (9H, ^{t}Bu) A; 1.55, 1.29, (9H, ^{t}Bu), B; in d_8-THF, 1.43, A; 1.45, B. ^{13}C NMR (23°C): in C_7D_8, δ 63.68, 57.92 (CCH_3), and 37.00, 36.28 (CCH_3), A, δ 64.56, 58.21 (CCH_3) and 36.50, 35.34 (CCH_3), B. ^{125}Te NMR (23°C): in C_7D_8, δ 1476 ($\Delta\nu_{1/2} \approx 3000$ Hz).

C. BIS{DILITHIUM[TRIS(*tert*-BUTYLIMIDO)TELLURITE]}, {Li_2[Te(N^{t}Bu)$_3$]}$_2$ (2)

$$^t\text{BuNTe}(\mu\text{-N}^t\text{Bu})_2\text{TeN}^t\text{Bu} + 4\,\text{Li}[\text{HN}^t\text{Bu}] \longrightarrow \{\text{Li}_2[\text{Te}(\text{N}^t\text{Bu})_3]\}_2 + 2\,^t\text{BuNH}_2$$

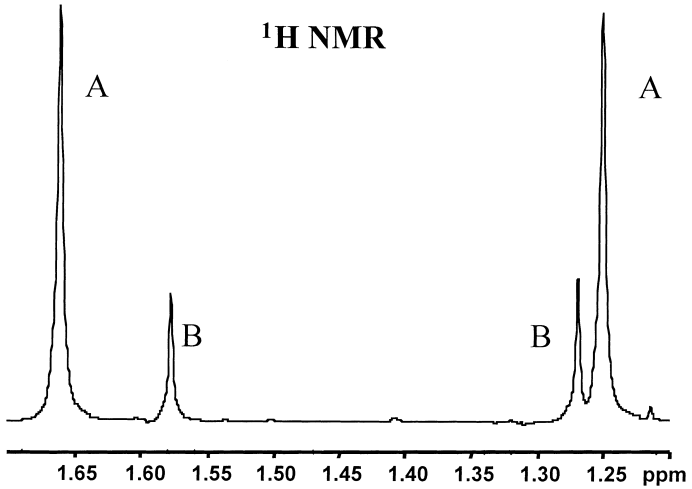

Figure 1. ^{1}H NMR spectrum of [^{t}BuNTe(μ-N^{t}Bu)$_2$TeN^{t}Bu] in C_6D_6.

Procedure

Li[HN^{t}Bu] (finely powdered; 0.720 g, 8.98 mmol) and [^{t}BuNTe(μ-N^{t}Bu)$_2$ TeN^{t}Bu] (1.200 g, 2.22 mmol) are loaded in the drybox into two separate pear-shaped Schlenk flasks (150 mL). The two reaction vessels are connected to a standard argon gas/vacuum line. Dried toluene (10 mL) is added to each flask. The colorless Li[HN^{t}Bu]/toluene solution is added dropwise by cannula, with stirring, to the red ^{t}BuNTe(μ-N^{t}Bu)$_2$TeN^{t}Bu/toluene solution cooled to $-78°$C. No immediate color changes are observed. The reaction mixture is warmed slowly to 23°C after 15 min at $-78°$C. The color of the reaction mixture changes slowly from red to golden brown-yellow, and the volatile materials are removed immediately under dynamic vacuum (after $\sim$1.5 h). Then $\sim$3 mL of toluene is added to the pale yellow-brown solid, resulting in a white precipitate and a brown-yellow solution. The solution is cooled to $-20°$C to produce more {Li$_2$[Te(N^{t}Bu)$_3$]}$_2$. The brown-yellow solution is transferred via a cannula into another Schlenk vessel. This purification process is repeated twice to give {Li$_2$[Te(N^{t}Bu)$_3$]}$_2$ (1.082 g, 3.05 mmol; 69%) as a pale yellow solid.

Anal. Calcd. for $Li_4Te_2C_{24}H_{54}N_6$: C, 40.62; H, 7.67; N, 11.84. Found: C, 40.22; H, 7.10; N, 12.19.

Properties

{Li$_2$[Te(N^{t}Bu)$_3$]}$_2$ is an air- and moisture-sensitive solid that can be stored for several months in the drybox. This dimeric cluster adopts a distorted hexagonal

prismatic (or cyclic ladder) structure.[5] ^{1}H NMR (23°C): in C_7D_8 or C_6D_6, δ 1.34 (^{t}Bu); in d_8-THF, δ 1.30 (^{t}Bu). ^{13}C NMR (23°C): in C_7D_8, δ 56.20 ($C(CH_3)_3$) and 37.85 ($C(CH_3)_3$); in d_8-THF, δ 56.09 ($C(CH_3)_3$) and 38.83 ($C(CH_3)_3$). ^{7}Li NMR (23°C): in C_7D_8, δ 0.77; in d_8-THF, δ 3.91.

References

1. (a) T. Chivers, X. Gao, and M. Parvez, *J. Chem. Soc., Chem. Commun.* 2149 (1994); (b) T. Chivers, X. Gao, and M. Parvez, *Inorg. Chem.* **35**, 9 (1996).
2. T. Chivers, X. Gao, and M. Parvez, *J. Am. Chem. Soc.* **117**, 2359 (1995).
3. T. Chivers, X. Gao, and M. Parvez, *Inorg. Chem.* **35**, 4336 (1996).
4. T. Chivers, G. D. Enright, N. Sandblom, G. Schatte, and M. Parvez, *Inorg. Chem.* **38**, 5431 (1999).
5. T. Chivers, X. Gao, and M. Parvez, *Angew. Chem., Int. Ed. Engl.* **34**, 2549 (1995).
6. T. Chivers, X. Gao, and M. Parvez, *Inorg. Chem.* **35**, 553 (1996).
7. T. Chivers, M. Parvez, and G. Schatte, *Angew. Chem., Int. Ed. Engl.* **38**, 2217 (1999).
8. T. Chivers, C. Jaska, N. Sandblom, and G. Schatte, *Chem. Commun*. 1657 (2000).
9. T. Chivers, M. Parvez, and G. Schatte, *Inorg. Chem.* **38**, 1380 (1999).
10. T. Chivers, and G. Schatte, *Eur. J. Inorg. Chem.* 2266 (2002).
11. T. Chivers and G. Schatte, *Chem. Commun.* 2264 (2001).
12. D. F. Shriver and M. A. Drezden, *The Manipulation of Air-Sensitive Compounds*, 2nd ed., Wiley-Interscience, New York, 1986.
13. N. D. R. Barnett, W. Clegg, L. Horsburgh, D. M. Lindsay, Qi-Y. Liu, F. M. Mackenzie, R. E. Mulvey, and P. G. Williard, *Chem. Commun.* 2321 (1996).