

# Dihydrodiborolyl-Transition Metal-Carboranyl Triple-Decker Sandwich Complexes

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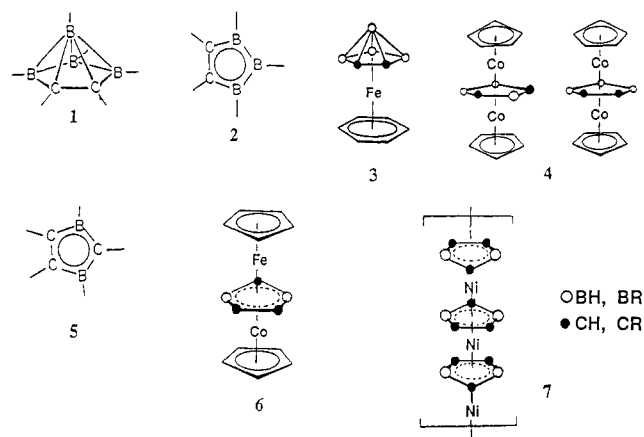
The first designed complexes incorporating boron heterocycles and carborane ligands face-bound to common metal centers have been prepared and characterized, effectively joining two large but heretofore separately developed areas of boron cluster chemistry. Controlled preparative routes to the heterobimetallic species  $(\eta^5\text{-R}_2\text{C}_2\text{B}_4\text{H}_4)\text{Fe}(\mu,\eta^5\text{-Et}_2\text{MeC}_3\text{B}_2\text{Et}_2)\text{Co}(\eta^5\text{-C}_5\text{H}_5)$  ( $\text{R} = \text{PhCH}_2, \text{Et}$ ) via displacement of  $\text{C}_8\text{H}_{10}$  (cyclooctatriene) from  $(\eta^6\text{-C}_8\text{H}_{10})\text{Fe}(\text{R}_2\text{C}_2\text{B}_4\text{H}_4)$  substrates, and their apparent "decapitation" to produce  $(\eta^5\text{-R}_2\text{C}_2\text{B}_3\text{H}_5)\text{Fe}(\mu,\eta^5\text{-Et}_2\text{MeC}_3\text{B}_2\text{Et}_2)\text{Co}(\eta^5\text{-C}_5\text{H}_5)$  triple-decker complexes, are reported. Probes of the electronic structure of the paramagnetic parent complexes and their redox chemistry via ESR, NMR, and electrochemical measurements are described.

## Introduction

Metallacarborane chemistry in its two and a half decades of existence has evolved into an exceedingly rich and varied field affording many novel modes of structure and reactivity.<sup>2</sup> Paralleling this work, the synthesis and study of metal sandwich  $\pi$ -complexes of boron heterocycles has given rise to a different, yet clearly related, area that has experienced similar growth and attracted wide interest.<sup>3,4</sup> For example, extensive chemistry based on metal sandwich complexes of the carborane ligands  $\text{R}_2\text{C}_2\text{B}_4\text{H}_4^{2-}$  (1) and  $\text{R}_2\text{C}_2\text{B}_3\text{H}_3^{4-}$  (2) (both isoelectronic with cyclopentadienide ( $\text{C}_5\text{H}_5^-$ )) has been reported,<sup>2</sup> typical compounds including a family of arene-iron-carboranyl sandwiches<sup>5</sup> such as 3 and the first neutral triple deckers<sup>6</sup> (4), as illustrated in Chart I. Similarly, numerous complexes have been prepared<sup>4</sup> having alkylated 2,3-dihydro-1,3-diborolyl ligands ( $\text{R}_3\text{C}_3\text{B}_2\text{R}'_2$ , 5), which are three  $\pi$ -electron donor units; examples are complexes 6 and 7 (the first polydecker sandwich<sup>7</sup>).

Thus far, these fields have developed entirely separately, largely because of the very different synthetic starting points and required expertise. We anticipated that carboranyl-metal-dihydrodiborolyl "hybrid" molecules would exhibit chemical behavior typical of both parent classes and conceivably lead to novel types of multidecker complexes; moreover, we considered that it might be possible to generate unprecedented carbon-rich metallaborane cluster systems (e.g.,  $\text{C}_5\text{B}_n$ ) via oxidative fusion of  $\text{C}_2\text{B}_4$  and

Chart I



$\text{C}_3\text{B}_2$  ligands. In a collaborative effort of our groups, we are investigating the preparation and chemistry of mixed carboranyl-metal-dihydrodiborolyl sandwich complexes and here report on our initial findings.

## Results and Discussion

**Synthesis of Mixed-Ligand Complexes via Cyclooctatriene Displacement.** The preparation of mixed-ligand complexes via direct reaction of a metal reagent with the ligands, as in the process  $\text{M} + \text{L} + \text{L}' \rightarrow \text{L-M-L}'$ , is usually inefficient owing to competitive formation of the corresponding  $\text{L-M-L}$  and  $\text{L'-M-L}'$  homoligand complexes.<sup>8</sup> (If the rates of complexation of M toward L and L' are very different, the mixed-ligand product may not be obtained at all.) Although in some cases this approach has been employed with limited success, e.g., in the preparation of borane-metal-carborane species<sup>8a</sup> and mixed-carborane sandwich complexes<sup>8b</sup> for the present study we adopted a different strategy utilizing controlled ligand displacement. This method exploits the fact, discovered several years ago,<sup>5,9,10</sup> that the  $\eta^6\text{-C}_8\text{H}_{10}$  (cyclooctatriene) ligand is readily subrogated from  $(\text{R}_2\text{C}_2\text{B}_4\text{H}_4)\text{Fe}(\text{C}_8\text{H}_{10})$  complexes (e.g., 8, 11) by arenes. Recent work has shown that  $\text{C}_8\text{H}_{10}$  can also be displaced,

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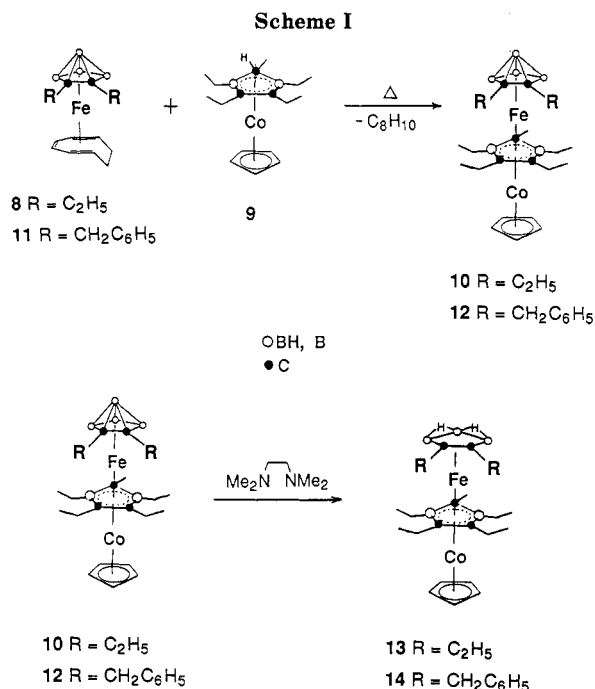
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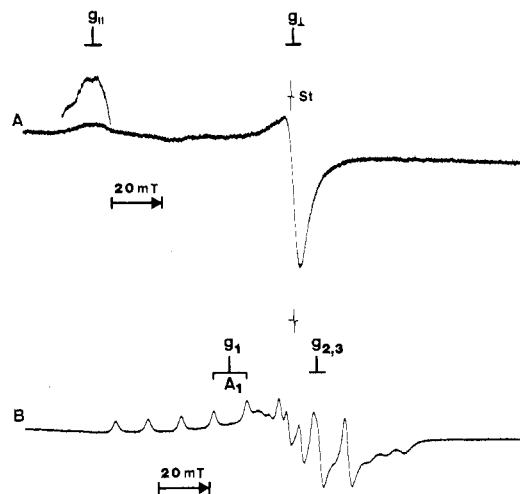


at elevated temperature, by *nido*-R'<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>5</sub><sup>-</sup> carborane anions,<sup>11</sup> suggesting that similar thermal displacement might be effected with the neutral (dihydrodiborole)cobalt complex<sup>12</sup> CpCo(Et<sub>2</sub>MeHC<sub>3</sub>B<sub>2</sub>Et<sub>2</sub>) (9). This is indeed the case, and the mixed-ligand species 10 and 12 were obtained as shown in Scheme I.

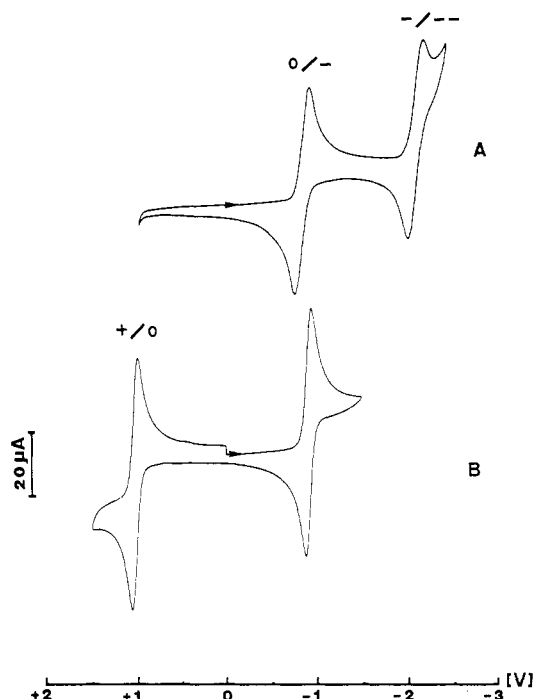
Compounds 10 and 12 were isolated via preparative-scale high-performance liquid chromatography as dark green-brown crystalline solids. Both complexes are slightly air-sensitive and are paramagnetic with one unpaired electron. In each case the composition was established by high- and unit-resolution mass spectra, supported by NMR spectra of 12 and 12<sup>-</sup> (vide infra), but unfortunately crystals suitable for X-ray diffraction have not been obtained. In comparison to 12 and 12<sup>-</sup>, the proton NMR spectra of paramagnetic 10 and its diamagnetic counterpart 10<sup>-</sup> contained more lines (arising from the alkyl substituents) and were too complex to be useful in structural assignment. However, the nearly identical ESR and electrochemical properties of 10 and 12, described below, strongly support the structural analogy between 10 and 12 that is implied by their compositions and syntheses.

**Electronic Structure and Redox Chemistry.** The electron spin resonance spectra of 10 and 12 between 25 and -160 °C are closely similar (Figure 1A) with  $g_{\parallel} = 2.583$  and  $g_{\perp} = 2.000$  for 10 and  $g_{\parallel} = 2.615$  and  $g_{\perp} = 1.998$  for 12, consistent with the presence of one unpaired electron. The absence of any indication of cobalt hyperfine structure in either spectrum implies that the unpaired electron is localized in the vicinity of the Fe atom and supports the designation of a formal iron oxidation state of +3; hence cobalt is also formally +3 if the C<sub>5</sub>H<sub>5</sub><sup>-</sup>, R<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub><sup>2-</sup>, and Et<sub>2</sub>MeC<sub>3</sub>B<sub>2</sub>Et<sub>2</sub><sup>3-</sup> ligands are assigned their conventional charges.

Both 10 and 12 were rapidly reduced by potassium metal to give the diamagnetic monoanions 10<sup>-</sup> and 12<sup>-</sup> and the paramagnetic dianions 10<sup>2-</sup> and 12<sup>2-</sup>. As will be described, these reductions have been observed electrochemically and



**Figure 1.** X-band ESR spectra in THF glass at -160 °C of 12 (A) and 12<sup>2-</sup> (B, obtained via reduction on a potassium mirror) (St = Li(TCNQ);  $g = 2.0025$ ).



**Figure 2.** Cyclic voltammograms of 12 at Pt electrodes vs SCE at 20 °C ( $v = 100$  mV/s): A, in 1,2-dimethoxyethane/tetra-*n*-butylammonium hexafluorophosphate; B, in dichloromethane/tetra-*n*-butylammonium hexafluorophosphate.

followed via proton NMR spectroscopy. The ESR spectra of both dianions reveal clear cobalt hyperfine structure (for 10<sup>2-</sup>,  $g_1 = 2.168$ ,  $g_{2,3} \approx 1.95$ ,  $A_1 = 13.12$ ,  $A_{2,3} \approx 3.3$  mT; for 12<sup>2-</sup> (Figure 1B),  $g_1 = 2.168$ ,  $g_{2,3} \approx 1.95$ ,  $A_1 = 13.12$ ,  $A_{2,3} \approx 3.3$  mT). These spectra are very similar to the ESR patterns of anionic 19-valence electron cobalt sandwich complexes,<sup>13</sup> supporting an isoelectronic relationship between these groups of compounds.

Cyclic voltammetry on both 10 and 12 (Figure 2) exhibited solvent-dependent redox behavior, with corresponding redox potentials within 0.1 V in each case. In dichloromethane, oxidation (10, +0.96 V; 12, +1.01 V) and reduction (10, -1.01 V; 12, -0.91 V) are reversible, whereas in 1,2-dimethoxyethane the oxidation is irreversible for

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both compounds. However, in the latter solvent one also observes the reversible formation of dianions (**10**,  $-2.11$  V; **12**,  $-2.12$  V). A similar solvent effect has been observed in the oxidation of 33-valence electron triple-decker complexes, which are cleaved by dimethoxyethane.<sup>14</sup>

The monoanions **10**<sup>-</sup> and **12**<sup>-</sup> were directly observed via 360-MHz proton NMR spectroscopy during in situ reduction in deuterated THF solutions, conducted in sealed tubes which contained a potassium mirror above the solution meniscus.<sup>15</sup> The initial spectra, recorded prior to any contact of the solution with the mirror, exhibited signals of the paramagnetic neutral species **10** and **12**. Spectra obtained following repeated short exposures to the potassium revealed shifts of the signals until the diamagnetic monoanion (**10**<sup>-</sup> or **12**<sup>-</sup>) was reached.

**Reactions of Carboranyl-Metal-Dihydrodiboroly Complexes.** Both **10** and **12** undergo apparent "decapitation" (apex BH removal), a general reaction of seven-vertex  $MC_2B_4$  metallocarboranes on treatment with Lewis bases such as TMEDA<sup>5</sup> (Scheme I). The products **13** and **14**, both light green neutral complexes, were formulated as  $(\eta^5-R_2C_2B_3H_5)Fe(\mu, \eta^5-Et_2MeC_3B_2Et_2)Co(\eta^5-C_5H_5)$  (**13**, R = Et; **14**, R = PhCH<sub>2</sub>) from their mass spectra and by analogy with earlier well-defined examples of base-induced apex BH removal.<sup>5</sup> However, full characterization of these complexes has not been achieved, and the structure proposed for **13** and **14** in Figure 1 is tentative. These compounds offer possibilities for the synthesis of larger multidecker sandwiches via addition of metal-ligand units to the open  $C_2B_3$  faces, a prospect which is currently under investigation.

### Conclusions

The preparation of the dihydrodiboroly-carboranyl-metal sandwich complexes **10** and **12** effectively joins the two previously separate areas of metallocarborane and metal-dihydrodiborole complex chemistry and also illustrates the developing role of designed synthesis in organometallic boron chemistry. Since the products were obtained in a rational manner via the controlled displacement of cyclooctatriene, this approach appears promising as a potential entry to many other varieties of multidecker mixed-ligand heteroborane-carborane-metal complexes.

Recently, a different class of "hybrid" complex containing the  $\eta^5$ -2,3,5-tricarbahexaboranyl and  $\eta^5$ -dihydro-1,3-diboroly ligands,  $[\eta^5-R_2HC_3(MeB)_3]Ni[\eta^5-(RC)_2(MeB)_2CH]$ ,  $[\eta^5-R_2HC_3(MeB)_3]Ni[\mu, \eta^5-(RC)_2(MeB)_2CH]Ni(\eta^5-C_5H_5)$ , and  $[\eta^5-R_2HC_3(MeB)_3]Ni[\mu, \eta^5-(RC)_2(MeB)_2CH]Ni[\mu, \eta^5-R_2HC_3(MeB)_3CH]$ , has been obtained and fully characterized.<sup>14,16</sup> However, the 2,3,5-tricarbahexaboranyl ligand is formed from bis(2,3-dihydro-1,3-diborole)nickel sandwiches, via capping of the already complexed ligand **5** with an MeB group, in contrast to the present work in which the complex products were assembled from preexisting ligands.

From the preliminary indications obtained in this study, it appears that the hybrid complexes **10** and **12** exhibit chemical and physical properties typical of their parent species, as illustrated by their decapitation to generate **13** and **14**. The electrochemical and ESR observations on

these species further indicate their general robustness and ability to undergo changes in metal oxidation states without decomposition. These findings augur well for the synthetic development of this new area of hybrid complex chemistry and suggest that the designed synthesis of molecules possessing prescribed sets of desired properties is within reach.<sup>17</sup>

### Experimental Section

**Materials.** The ferracarboranes  $(\eta^5-C_5H_5)Fe(R_2C_2B_4H_4)$  (**8**, R = Et; **11**, R = PhCH<sub>2</sub>) and the dihydrodiborole complex  $CpCo(Et_2MeHC_3B_2Et_2)$  (**9**) were obtained as described in earlier publications.<sup>10,12</sup> Tetrahydrofuran (THF) was degassed and distilled from Na/benzophenone, and *n*-butyl ether (Aldrich) was used as received.

**Instrumentation.** <sup>1</sup>H (300 MHz) NMR spectra were acquired on a GE QE-300 spectrometer, and visible-ultraviolet spectra were recorded on a Hewlett-Packard 8452A diode-array spectrophotometer with HP Vectra computer interface. High-resolution mass measurements were obtained on a Finnegan MAT 8230 instrument using an SSX 300 data system with perfluorokerosene as a reference standard. Infrared spectra were recorded on a Nicolet 5DXB FTIR spectrometer. Preliminary chromatographic separations were conducted on silica gel 60 columns and precoated silica gel plates (Merck), and final purification of products was achieved on a Waters Delta Prep 3000 chromatograph using silica columns. ESR spectra were recorded on a Varian E3 spectrometer fitted with an electrolytic cell. Electrochemical measurements were conducted on a Princeton Applied Research Model 173 potentiostat and 179 digital coulometer, with a Methrom electrochemical cell having platinum electrodes and a saturated calomel reference electrode.

**Synthesis of  $(\eta^5-Et_2C_2B_4H_4)Fe(\mu, \eta^5-Et_2MeC_3B_2Et_2)Co(\eta^5-C_5H_5)$  (**10**).** A 200-mL 3-neck Pyrex flask, equipped with a water-cooled condenser, side arm with connecting stopcock, and rubber septum, was charged with 63 mg (0.21 mmol) of **8** and a stirbar, connected to a vacuum line, and evacuated. Dry *n*-butyl ether (1–2 mL) was added through the septum via syringe, and the flask was pressurized with ~400 Torr of dry dinitrogen. The cobalt complex **9** (65 mg) was added from the side arm, and the mixture was heated with stirring at ~130 °C for 2 h, during which the apparatus was open to a manometer on the vacuum line in order to monitor pressure changes. The reaction mixture was observed to darken considerably during heating. The ether was removed by vacuum evaporation, and the residue was taken up in dichloromethane and filtered through 2 cm of silica gel and washed with dichloromethane until the washings were colorless. The solution was rotary-evaporated to dryness, placed on a 2-mm TLC plate, and eluted with 50/50 *n*-hexane/dichloromethane to give a brown band, **10** ( $R_f$  0.63), which was contaminated with starting material. This material was purified via HPLC on a silica column using 15% dichloromethane in *n*-hexane as eluent. The first band eluted was unreacted orange **8**, followed by **10**, obtained as dark green-brown crystals (27 mg, 26% yield). No other products were detected. Unit-resolution mass spectrum: parent peak at  $m/z$  499, profile closely matching the pattern calculated from natural isotopic abundances. Exact mass calcd for  $^{59}Co^{56}Fe^{12}C_{23}^{11}B_6^1H_{42}^+$ : 499.2526. Found: 499.2547. Visible-UV absorptions (nm) in CH<sub>2</sub>Cl<sub>2</sub>: 210 (23%), 240 (48%), 306 (95%), 352 (82%), 424 (19%). IR absorptions (cm<sup>-1</sup>, NaCl plate) 2956 s, 2923 vvs, 2871 sh, 2852 vvs, 2546 m, 1743 m, 1464 s, 1378 m, 828 m, 721 m.

**Synthesis of  $(\eta^5-(PhCH_2)_2C_2B_4H_4)Fe(\mu, \eta^5-Et_2MeC_3B_2Et_2)Co(\eta^5-C_5H_5)$  (**12**).** The procedure described for the synthesis of **10** was followed, using 118 mg (0.28 mmol) of **11** and 89 mg (0.28 mmol) of **9**, to give 34 mg of pure **12** as greenish brown crystals (24% yield based on the starting amount of **11**);  $R_f$  0.61 in 50/50 dichloromethane/*n*-hexane. Visible-UV absorptions (nm) in CH<sub>2</sub>Cl<sub>2</sub>: 238 (79%), 268 (55%), 304 (95%), 354 (86%). IR absorptions (cm<sup>-1</sup>, NaCl plate) 2956 s, 2922 vvs, 2871 sh, 2853 vvs,

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(17) In very recent work, we have prepared diamagnetic dicobalt analogues of **10** and **12**,  $(R_2C_2B_4H_4)Co(Et_2MeC_3B_2Et_2)Co(C_5H_5)$  (R = Et, PhCH<sub>2</sub>), whose synthesis and chemistry will be described in full in a later publication.

2562 m, 2358 m, 1464 s, 1457 s, 1437 m, 1378 m, 1420 m. Unit-resolution mass spectrum: parent peak at  $m/z$  623, profile closely matching the pattern calculated from natural isotopic abundances. Exact mass calcd for  $^{59}\text{Co}^{56}\text{Fe}^{12}\text{C}_{33}^{11}\text{B}_6^{1}\text{H}_{46}^+$ : 623.2839. Found: 623.2841.

**Synthesis of  $(\eta^5\text{-Et}_2\text{C}_2\text{B}_3\text{H}_5)\text{Fe}(\mu, \eta^5\text{-Et}_2\text{MeC}_3\text{B}_2\text{Et}_2)\text{Co}(\eta^5\text{-C}_5\text{H}_5)$  (13) via Decapitation of 10.** A 40-mg sample of 10 was refluxed in excess tetramethylethylenediamine (TMEDA) in an open flask for 1 h, following which the TMEDA was removed by rotary evaporation and vacuum-line evacuation. The residue was taken up in dichloromethane, filtered through 2 cm of silica, and washed with dichloromethane until the washings were colorless. The solution was rotary-evaporated to dryness, placed on 0.25-mm silica TLC plates, and eluted with 50/50 dichloromethane/*n*-hexane to give one band, light green 13:  $R_f$  0.7; 31 mg (79% yield).

**Synthesis of  $[(\eta^5\text{-PhCH}_2)_2\text{C}_2\text{B}_3\text{H}_5]\text{Fe}(\mu, \eta^5\text{-Et}_2\text{MeC}_3\text{B}_2\text{Et}_2)\text{Co}(\eta^5\text{-C}_5\text{H}_5)$  (14).** The same procedure as employed in the synthesis of 13 was used to generate 14 as a light green, slightly air-sensitive solid in 23% yield ( $R_f$  0.67).

**Reduction of 12 Monitored by Proton NMR Spectroscopy.** A 4-mg sample of 12 was dissolved in  $\text{THF-}d_8$  and carefully transferred to a 5-mm NMR tube containing a potassium mirror

deposited on its upper surface. The spectrum of paramagnetic 12 exhibited 16 signals (as expected) in the range +31 to -21 ppm: 30.7 (br), 24.1 (br), 13.8 (br), 12.9 (br), 11.1 (br), 9.8 (br), 9.40, 8.50, 8.08, 7.17, 3.55 (THF), 2.72, 1.70 (THF), -4.3, -4.7, -9.3 (br), -10.8 (br), -21 (v br). On repeated contact (11 times) of the solution with the potassium, the signals moved gradually into the diamagnetic region. The spectrum of diamagnetic 12<sup>-</sup> exhibited peaks at 6.97, 6.90, 6.87, 4.64 (d), 4.21 (d), 4.15 (s), 3.58 (s), 3.58 (m, THF), 2.90 (m), 2.40 (m), 1.93 (s), 1.80 (t), 1.73 (m, THF), 1.50 (t), 1.28 (s), 0.86 (d), 0.08 (s), and -0.2 ppm. Assignments of individual lines in these spectra are nontrivial and will require detailed study including two-dimensional NMR experiments, to be reported at a later date. The  $^{11}\text{B}$  NMR spectrum of 12<sup>-</sup> was uninformative, exhibiting broad peaks at  $\delta$  +29 and +3 relative to  $\text{BF}_3\text{-OEt}_2$ .

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## Synthesis and Properties of Two *o*-Phenylenebis(telluroether) Ligands, $o\text{-C}_6\text{H}_4(\text{TeR})_2$ (R = Me, Ph), and of Related Hybrids, $o\text{-C}_6\text{H}_4(\text{TeMe})\text{Y}$ (Y = NMe<sub>2</sub>, PMe<sub>2</sub>, AsMe<sub>2</sub>, SbMe<sub>2</sub>, OMe, SMe, SeMe, Cl)

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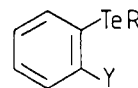
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The ditelluroether  $o\text{-C}_6\text{H}_4(\text{TeMe})_2$  was prepared from  $o\text{-C}_6\text{H}_4\text{Br}_2$  and  $\text{LiTeMe}$  in tetrahydrofuran, and  $o\text{-C}_6\text{H}_4(\text{TePh})_2$  was obtained similarly from  $o\text{-C}_6\text{H}_4\text{BrI}$  and  $\text{LiTePh}$ . Syntheses for the ortho-substituted telluroethers  $o\text{-C}_6\text{H}_4(\text{TeMe})\text{Y}$  (Y = NMe<sub>2</sub>, PMe<sub>2</sub>, AsMe<sub>2</sub>, SbMe<sub>2</sub>, OMe, SMe, SeMe, and Cl) are also reported. The compounds have been characterized by mass spectrometry, by multinuclear NMR spectroscopy ( $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ ,  $^{125}\text{Te}\{^1\text{H}\}$ ), and by the preparation of derivatives. The trends in the  $^{125}\text{Te}$  NMR chemical shifts are compared, and comparisons are also made with the  $^{77}\text{Se}$  NMR chemical shifts in corresponding selenoethers. Convenient syntheses for  $o\text{-C}_6\text{H}_4\text{Cl}(\text{SMe})$  and  $o\text{-C}_6\text{H}_4\text{Cl}(\text{SeMe})$  are reported.

### Introduction

We have recently reported<sup>1</sup> convenient syntheses for some ditelluroalkanes,  $\text{RTe}(\text{CH}_2)_n\text{TeR}$  (R = Me or Ph,  $n = 1, 3, 6, 10$ ), by reaction of  $\text{RTeLi}$  with the appropriate  $\text{Cl}(\text{CH}_2)_n\text{Cl}$  in tetrahydrofuran. When  $n = 4$  or 5, the major products were  $\text{R}_2\text{Te}$  and telluracycloalkane  $\text{TeCH}_2(\text{CH}_2)_{n-1}$ , while for  $n = 2$  only ethene and  $\text{R}_2\text{Te}_2$  were obtained. The failures to obtain  $\text{RTeCH}_2\text{CH}_2\text{TeR}^{1-3}$  (or *cis*  $\text{RTeCH}=\text{CHTeR}$ )<sup>1</sup> are unfortunate since two-carbon backbones form the most favorable ring size (5) upon chelation to a metal center. Here we report the synthesis of  $o\text{-C}_6\text{H}_4(\text{TeR})_2$  (R = Me or Ph) and of some related ligands  $o\text{-C}_6\text{H}_4(\text{TeMe})\text{Y}$  (Chart I). In addition to providing a series of functionally substituted telluroethers, the presence of other donor groups, especially  $\text{AsMe}_2$  or  $\text{PMe}_2$ , offers the prospect of coordination of the ligand (and

Chart I. The Telluroethers



R = Me	Y = TeMe	(1)	R = Me	Y = PMe <sub>2</sub>	(6)
Me	OMe	(2)	Me	AsMe <sub>2</sub>	(7)
Me	SMe	(3)	Me	SbMe <sub>2</sub>	(8)
Me	SeMe	(4)	Me	Cl	(9)
Me	NMe <sub>2</sub>	(5)	Ph	TePh	(10)

hence the TeR moiety) to hard metal ions, which would not normally bond to telluroethers. Similar hybrid selenoethers  $o\text{-C}_6\text{H}_4(\text{SeMe})\text{Y}^4$  have given complexes with  $\text{Co(III)}$ ,<sup>5</sup>  $\text{Ni(III)}$ ,<sup>6</sup> and  $\text{Pd(IV)}$ <sup>6</sup> which contained the first ex-

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