

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 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  $\text{BF}_3\text{-OEt}_2$ .

**Acknowledgment.** This work was supported by NATO International Collaborative Research Grant No. 0196/85 and by National Science Foundation Grant No. CHE 8721657 (to R.N.G.). We thank Dr. James Davis for the mass spectra.

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

Tim Kemmitt and William Levason\*

Department of Chemistry, The University, Southampton SO9 5NH, United Kingdom

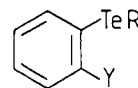
Received November 1, 1988

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  $o\text{-C}_6\text{H}_4(\text{TeMe})\text{Y}$  ( $\text{Y} = \text{NMe}_2, \text{PMe}_2, \text{AsMe}_2, \text{SbMe}_2, \text{OMe}, \text{SMe}, \text{SeMe}, \text{and Cl}$ ) 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,  $\text{RTe}(\text{CH}_2)_n\text{TeR}$  ( $\text{R} = \text{Me}$  or  $\text{Ph}$ ,  $n = 1, 3, 6, 10$ ), 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  $o\text{-C}_6\text{H}_4(\text{TeR})_2$  ( $\text{R} = \text{Me}$  or  $\text{Ph}$ ) 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



$\text{R} \square \text{Me}$	$\text{Y} \square \text{TeMe}$	(1)	$\text{R} = \text{Me}$	$\text{Y} = \text{PMe}_2$	(6)
$\text{Me}$	$\text{OMe}$	(2)	$\text{Me}$	$\text{AsMe}_2$	(7)
$\text{Me}$	$\text{SMe}$	(3)	$\text{Me}$	$\text{SbMe}_2$	(8)
$\text{Me}$	$\text{SeMe}$	(4)	$\text{Me}$	$\text{Cl}$	(9)
$\text{Me}$	$\text{NMe}_2$	(5)	$\text{Ph}$	$\text{TePh}$	(10)

hence the  $\text{TeR}$  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-

(1) Hope, E. G.; Kemmitt, T.; Levason, W. *Organometallics* 1988, 7, 78.

(2) Pluscec, J.; Westland, A. D. *J. Chem. Soc.* 1965, 5371.

(3) DeSilva, K. G. K.; Monsef-Mirzai, Z.; McWhinnie, W. R. *J. Chem. Soc., Dalton Trans.* 1983, 2143.

(4) Hope, E. G.; Kemmitt, T.; Levason, W. *J. Chem. Soc., Perkin Trans. 2* 1987, 487.

(5) Jewiss, H. C.; Levason, W.; Spicer, M. D.; Webster, M. *Inorg. Chem.* 1987, 26, 2102.

amples of SeMe groups bonded to these hard metal centers. One hybrid telluroether of this type, *o*-C<sub>6</sub>H<sub>4</sub>-(TePh)(PPh<sub>2</sub>), has been reported by Gysling.<sup>7</sup>

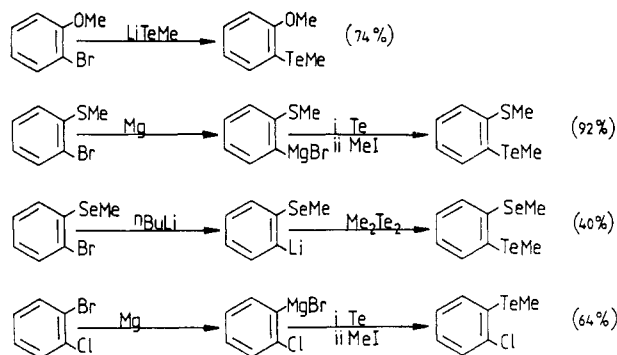
## Results and Discussion

**Syntheses.** Our initial attempts to prepare *o*-phenylene backboned ditelluroethers involved routes successfully applied to the selenium analogues *o*-C<sub>6</sub>H<sub>4</sub>(SeR)<sub>2</sub>.<sup>4,8</sup> For *o*-C<sub>6</sub>H<sub>4</sub>(SeMe)<sub>2</sub> addition of Me<sub>2</sub>Se<sub>2</sub> to benzyne or preparation of a polymeric diselenide (*o*-SeC<sub>6</sub>H<sub>4</sub>Se)<sub>n</sub> followed by cleavage with Rongalite (NaO<sub>2</sub>SCH<sub>2</sub>OH) and alkylation were both successful, while *o*-C<sub>6</sub>H<sub>4</sub>(SePh)<sub>2</sub> was prepared in very poor yield from Ph<sub>2</sub>Se<sub>2</sub> and benzyne. However neither Me<sub>2</sub>Te<sub>2</sub> nor Ph<sub>2</sub>Te<sub>2</sub> added to benzyne under the same conditions, and our attempts to prepare a ditelluride polymer from *o*-C<sub>6</sub>H<sub>4</sub>Br<sub>2</sub> and Na<sub>2</sub>Te<sub>2</sub><sup>9</sup> gave unreplicable results. The successful addition of Ph<sub>2</sub>Te<sub>2</sub> to benzyne was reported some time ago,<sup>10</sup> but the claim was subsequently withdrawn<sup>11</sup> although ditellurides with more electron-donating groups such as *p*-tolyl or *p*-methoxyphenyl do add successfully.<sup>11</sup> Recalling that LiTeMe and C<sub>6</sub>H<sub>5</sub>I in tetrahydrofuran gave PhTeMe,<sup>1</sup> we examined the reactions of LiTeMe with various *o*-dihalobenzenes, initially in a 1:1 mole ratio in an attempt to obtain the potentially useful *o*-C<sub>6</sub>H<sub>4</sub>X(TeMe) (X = Cl or Br). Since neither MeS<sup>-</sup> nor MeSe<sup>-</sup> react under these conditions, we were surprised to find that LiTeMe and *o*-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> gave a fair yield of *o*-C<sub>6</sub>H<sub>4</sub>(TeMe)<sub>2</sub>. With use of a 1:2 ratio of *o*-C<sub>6</sub>H<sub>4</sub>X<sub>2</sub>:LiTeMe, the yield of the ditelluroether was ca. 60%. In fact we subsequently established that even with a large excess of *o*-dihalobenzene at low temperatures, it was not possible to limit the reaction to monosubstitution. The *o*-C<sub>6</sub>H<sub>4</sub>-(TePh)<sub>2</sub> was obtained similarly from *o*-C<sub>6</sub>H<sub>4</sub>BrI and LiTePh, although the yield is poorer, and the preparation needs careful control.

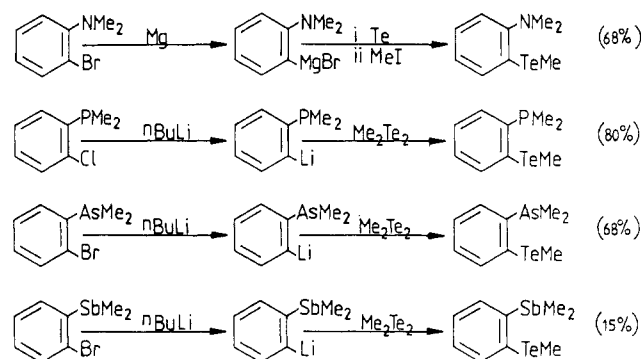
In view of this unexpected result, we reexamined the reactions between *o*-dihalobenzenes and NaSMe and LiSeMe by using the higher boiling *N,N*-dimethylformamide (dmf) as solvent. Testaferri et al.<sup>12</sup> reported that *p*-C<sub>6</sub>H<sub>4</sub>(SR)<sub>2</sub> could be made from *p*-C<sub>6</sub>H<sub>4</sub>X<sub>2</sub> and a large excess (ca. 5-fold) of NaSR in dmf, in the case of R = Me with subsequent addition of MeI to reverse the accompanying dealkylation. With use of NaSMe and *o*-C<sub>6</sub>H<sub>4</sub>Br<sub>2</sub> in a 4:1 mole ratio refluxed in dmf for 48 h and with subsequent addition of MeI, we found a small yield of *o*-C<sub>6</sub>H<sub>4</sub>(SMe)<sub>2</sub> (ca. 5%) but the major product was *o*-C<sub>6</sub>H<sub>4</sub>Br(SMe). From *o*-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> and NaSMe (1:3 ratio) 16 h, after alkylation with MeI, a very good yield of *o*-C<sub>6</sub>H<sub>4</sub>Cl(SMe) (ca. 90%) was obtained without significant amounts of dithioether. The dithioether was readily obtainable from *o*-C<sub>6</sub>H<sub>4</sub>X(SMe), <sup>n</sup>BuLi, and Me<sub>2</sub>S<sub>2</sub>. Even more usefully the reaction of LiSeMe with *o*-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> in dmf gives 52% yield of *o*-C<sub>6</sub>H<sub>4</sub>Cl(SeMe), which is much more convenient than the usual route to *o*-haloselenoanisoles from *o*-haloaniline and KSeCN.<sup>13</sup>

On the basis of these results it seemed that reaction of LiTeMe and *o*-C<sub>6</sub>H<sub>4</sub>BrY (Y = NMe<sub>2</sub>, OMe, SMe, etc.)

## Scheme I. Synthetic Routes to Hybrid Group 16 Telluroethers



## Scheme II. Synthetic Routes to Hybrid Group 15 Telluroethers



would be an easy route to hybrid telluroethers. Disappointingly this was only true for the orthomethoxy compound *o*-C<sub>6</sub>H<sub>4</sub>(OMe)(TeMe) (74%), but the reaction failed in the other cases. The alternative routes which were successful for combinations of TeMe and group 16 donors are shown in Scheme I, and the Grignard route was also used to prepare *o*-C<sub>6</sub>H<sub>4</sub>(NMe<sub>2</sub>)(TeMe) (Scheme II). As described above, the direct reaction of LiTeMe and *o*-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> could not be stopped at monosubstitution nor could we isolate the material from the reaction of diazotized *o*-haloaniline and Me<sub>2</sub>Te<sub>2</sub>, but a good yield of this potentially useful intermediate was finally obtained from the mono-Grignard *o*-C<sub>6</sub>H<sub>4</sub>Cl(MgBr),<sup>14</sup> Te, and MeI.

The syntheses of group 15 substituted telluroethers also proved rather more difficult than those of the selenoether analogues.<sup>4</sup> (Methyltelluro)lithium did not appear to react with *o*-C<sub>6</sub>H<sub>4</sub>Br(AsMe<sub>2</sub>)<sup>15</sup> in thf, while the room temperature reaction of NaAsMe<sub>2</sub> and *o*-C<sub>6</sub>H<sub>4</sub>Cl(TeMe) in thf resulted in Ph-Te bond cleavage as well as C-Cl cleavage, and a complex mixture of products was obtained including *o*-C<sub>6</sub>H<sub>4</sub>(AsMe<sub>2</sub>)<sub>2</sub>, unreacted *o*-C<sub>6</sub>H<sub>4</sub>Cl(TeMe), and a small amount of material with  $\delta(^{125}\text{Te}) = 276$  ppm. Conducting the reaction at -78 °C decreased the amount of diarsine produced but did not yield the desired product in useful amounts. The required *o*-C<sub>6</sub>H<sub>4</sub>(TeMe)(AsMe<sub>2</sub>) was finally obtained from *o*-C<sub>6</sub>H<sub>4</sub>Br(AsMe<sub>2</sub>), <sup>n</sup>BuLi, and Me<sub>2</sub>Te<sub>2</sub> (Scheme III), along with <sup>n</sup>BuTeMe and some Me<sub>2</sub>Te<sub>2</sub> which were easily separated by distillation. The ligand had  $\delta(^{125}\text{Te}) = 276$  ppm, showing that the minor product of the reaction of NaAsMe<sub>2</sub> and *o*-C<sub>6</sub>H<sub>4</sub>Cl(TeMe) was indeed the product required. The corresponding *o*-C<sub>6</sub>H<sub>4</sub>(TeMe)-(PMe<sub>2</sub>) was prepared from *o*-C<sub>6</sub>H<sub>4</sub>Br(PMe<sub>2</sub>),<sup>16</sup> <sup>n</sup>BuLi, and

(6) Harbron, S. K.; Higgins, S. J.; Hope, E. G.; Kemmitt, T.; Levason, W. *Inorg. Chim. Acta* **1987**, *130*, 43.

(7) Gysling, H. J.; Luss, H. R. *Organometallics* **1984**, *3*, 596.

(8) Gulliver, D. J.; Hope, E. G.; Levason, W.; Murray, S. G.; Potter, D. M.; Marshall, G. L. *J. Chem. Soc., Perkin Trans. 2* **1984**, 429.

(9) Sandman, D. S.; Stark, J. C.; Acampora, L. A.; Gagne, P. *Organometallics* **1983**, *2*, 549.

(10) Petragani, N.; Toscano, V. G. *Chem. Ber.* **1970**, *103*, 1652.

(11) Bonilha, J. B. S.; Petragani, N.; Toscano, V. G. *Chem. Ber.* **1978**, *111*, 2510.

(12) Testaferri, L.; Tiecco, M.; Tingoli, M.; Chionelli, D.; Montanuccio, M. *Synthesis* **1983**, 751.

(13) Dyer, G.; Meek, D. W. *Inorg. Chem.* **1967**, *6*, 149.

(14) Hart, F. A. *J. Chem. Soc.* **1960**, 3324.

(15) Levason, W.; Smith, K. G.; McAuliffe, C. A.; McCullough, F. P.; Sedgwick, R. D.; Murray, S. G. *J. Chem. Soc., Dalton Trans.* **1979**, 1718.

(16) Werner, D.; Dahlenburg, L. *Z. Naturforsch.* **1987**, *42B*, 1110.

Table I. Selected  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR Data

compd	$\delta(^1\text{H})$ ( $^2J(^{125}\text{Te}-^1\text{H})$ , Hz) <sup>a,b</sup>		$\delta(^{13}\text{C}\{^1\text{H}\})$ ( $^1J(^{125}\text{Te}-^{13}\text{C})$ , Hz) <sup>a,b</sup>			
	TeMe	EMe	TeMe	EMe	ipso Te	ipso E
PhMeTe	2.09 (22)		-16.7 (164)		112.5 (...)	
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (NMe <sub>2</sub> )(TeMe)	1.92 (25)	2.64	-20.0 (169)	45.3	110.6 (...)	154.9
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (PMe <sub>2</sub> )(TeMe)	200 (27, $^5J(^{31}\text{P}-^1\text{H})$ = 1.6 Hz)	1.27 ( $^2J(^{31}\text{P}-^1\text{H})$ = 2.4 Hz)	-15.9 (180, $^4J(^{31}\text{P}-^{13}\text{C})$ = 29 Hz)	14.3 ( $^1J(^{31}\text{P}-^{13}\text{C})$ = 13 Hz, $^4J(^{125}\text{Te}-^{13}\text{C})$ = 14 Hz)	124.9 (...)	144.1 ( $^1J(^{31}\text{P}-^{13}\text{C})$ = 10 Hz, $^2J(^{125}\text{Te}-^{13}\text{C})$ = 26 Hz)
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (AsMe <sub>2</sub> )(TeMe)	2.08 (25)	1.17	-15.3 (174)	11.4	123.0 (272)	148.8 ( $^2J(^{125}\text{Te}-^{13}\text{C})$ = 30 Hz)
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (SbMe <sub>2</sub> )(TeMe)	2.15 (23)	0.94	-13.5 (180)	1.0	124.5 (...)	148.7
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (OMe)(TeMe)	1.95 (24)	3.66	-19.6 (166)	55.8	104.4 (293)	158.9
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (SMe)(TeMe)	1.98 (25)	2.35	-16.5 (171)	18.6	120.1 (...)	141.5
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (SeMe)(TeMe)	2.00 (26)	2.25 ( $^2J(^{77}\text{Se}-^1\text{H})$ = 12 Hz)	-15.9 (172)	10.0 ( $^1J(^{77}\text{Se}-^{13}\text{C})$ = 64 Hz)	122.8 (...)	127.1
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (TeMe) <sub>2</sub>	2.03 (24)		-12.6 (171, $^4J(^{125}\text{Te}-^{13}\text{C})$ = 16 Hz)		125.5 (262)	
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (Cl)(TeMe)	2.06 (25)		-16.3 (169)		117.1 (305)	137.0 ( $^2J(^{125}\text{Te}-^{13}\text{C})$ = 44 Hz)
PhMe <sub>2</sub> TeI	2.23 (24)					
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (NMe <sub>2</sub> )(TeMe <sub>2</sub> I)	2.60 (25)	2.78				
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (PMe <sub>2</sub> )(TeMe)	2.28 (24)	2.36 ( $^2J(^{31}\text{P}-^1\text{H})$ = 15 Hz)				
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (AsMe <sub>2</sub> I)(TeMe)	2.33 (23)	2.41				
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (SbMe <sub>2</sub> I)(TeMe)	2.1 (24)	1.88				
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (OMe)(TeMe <sub>2</sub> I)	2.32 (24)	3.81				
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (SMe)(TeMe <sub>2</sub> I)	2.27 (25)	2.59				
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (SeMe)(TeMe <sub>2</sub> I)	2.46 (26)	2.46 ( $^2J(^{77}\text{Se}-^1\text{H})$ = 11 Hz)				
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (TeMe <sub>2</sub> I) <sub>2</sub>	2.50 (26)					
<i>o</i> -C <sub>6</sub> H <sub>4</sub> Cl(TeMe <sub>2</sub> I)	2.54 (25)					
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (OMe)(TeMeCl <sub>2</sub> )	3.21 (24)	3.98				

<sup>a</sup>  $\delta$  relative to internal Me<sub>4</sub>Si in CDCl<sub>3</sub> solution. <sup>b</sup> Aromatic protons at 6.8–7.4 ppm, and other aryl C resonances at 123–130 ppm not listed.

Me<sub>2</sub>Te<sub>2</sub>. Since LiPMe<sub>2</sub> is an even more powerful nucleophile than the arsenide, its reaction with *o*-C<sub>6</sub>H<sub>4</sub>Cl(TeMe) was not thought likely to proceed successfully and was not investigated. Cleavage of the C–Sb bond in *o*-C<sub>6</sub>H<sub>4</sub>Br(SbMe<sub>2</sub>) by strong nucleophiles is a problem encountered in the synthesis of hybrid stibines,<sup>17</sup> although it can be overcome by control of the reaction conditions. It would seem that Ph–Te cleavage is an even greater problem with the present compounds. The reaction of *o*-C<sub>6</sub>H<sub>4</sub>Br(SbMe<sub>2</sub>)<sup>15</sup> with <sup>2</sup>BuLi in thf at low temperatures followed by addition of Me<sub>2</sub>Te<sub>2</sub> gave a complex mixture of products, which included starting materials, PhMe<sub>2</sub>Sb, *o*-C<sub>6</sub>H<sub>4</sub>(TeMe)<sub>2</sub>, and *o*-C<sub>6</sub>H<sub>4</sub>(SbMe<sub>2</sub>)(TeMe), identified by a combination of multinuclear NMR spectroscopy, and similar studies on the iodomethane-quaternized products. The complexity arises at least in part from the ready cleavage of Ph–Sb bonds by alkyllithiums.<sup>18</sup> Distillation of the mixture gave a fraction boiling over the range 144–146 °C (0.3 Torr), which contained the stibine telluroether, *o*-C<sub>6</sub>H<sub>4</sub>(TeMe)<sub>2</sub>, and *o*-C<sub>6</sub>H<sub>4</sub>Br(SbMe<sub>2</sub>), which were separated by flash column chromatography on silica, using 40–60 °C petroleum ether. The chromatography was conducted with rigorous exclusion of air due to the ease of oxidation of the antimony centers. The yield of pure *o*-C<sub>6</sub>H<sub>4</sub>(SbMe<sub>2</sub>)(TeMe) was ca. 15%, although no attempt to optimize the reaction conditions was made.

**Properties.** These hybrid telluroethers appear to be much less air sensitive at the tellurium than the ditelluroalkanes,<sup>1</sup> although **6**, **7**, and **8** oxidize readily at the group 15 center. In addition to the spectroscopic characterization (below), the compounds were also characterized by the preparation of derivatives. For *o*-C<sub>6</sub>H<sub>4</sub>(TePh)<sub>2</sub>

(**10**) and *o*-C<sub>6</sub>H<sub>4</sub>(OMe)(TeMe) (**2**), treatment with Cl<sub>2</sub>/CH<sub>2</sub>Cl<sub>2</sub> gave the crystalline chlorides *o*-C<sub>6</sub>H<sub>4</sub>(TePhCl<sub>2</sub>)<sub>2</sub> and *o*-C<sub>6</sub>H<sub>4</sub>(OMe)(TeMeCl<sub>2</sub>), respectively, but since chlorine attacks most of the other hybrids at the heteroatom, quaternization with MeI in acetone solution was generally used.

Unlike aryl alkyl selenides which do not react with MeI under these conditions,<sup>4</sup> PhMeTe readily forms the telluronium salt PhMe<sub>2</sub>TeI, and hence for the hybrid telluroethers quaternization at TeMe, Y, or both are possibilities. The site(s) of quaternization was (were) determined by NMR studies, and the nature and purity of the products confirmed analytically (Tables I and II). The *o*-C<sub>6</sub>H<sub>4</sub>(TeMe)<sub>2</sub> readily quaternized at both tellurium centers to give *o*-C<sub>6</sub>H<sub>4</sub>(TeMe<sub>2</sub>I)<sub>2</sub>, its behavior contrasting with group 15 analogues such as *o*-C<sub>6</sub>H<sub>4</sub>(PMe<sub>2</sub>)<sub>2</sub> or *o*-C<sub>6</sub>H<sub>4</sub>(AsMe<sub>2</sub>)<sub>2</sub> which only quaternize at *one* group 15 atom under these conditions.<sup>15</sup> The reactions with ligands **2**, **3**, **4**, **5**, and **9** were straightforward, with reaction at the –TeMe group only, the Y centre being unreactive. For **6**, **7**, and **8** the opposite was observed, in that the phosphorus, arsenic, and antimony groups were quaternized and the –TeMe was not. Although this might appear unusual in comparison with the behavior of *o*-C<sub>6</sub>H<sub>4</sub>(TeMe)<sub>2</sub>, it does parallel that of group 15 bidentates and is most likely due to the fact that the inductive effects of the –EMe<sub>3</sub><sup>+</sup> (E = P, As, or Sb) deactivate the tellurium. This explanation is supported by the large high-frequency shifts in  $\delta(^{125}\text{Te})$  observed between the ligands and [*o*-C<sub>6</sub>H<sub>4</sub>(EMe<sub>3</sub>)TeMe]I (Table II), although it should be noted that the shifts are substantially less than would be observed if the tellurium center itself had been the site of reaction. Prolonged reflux of *o*-C<sub>6</sub>H<sub>4</sub>(AsMe<sub>2</sub>)(TeMe) with excess MeI gave in addition to [*o*-C<sub>6</sub>H<sub>4</sub>(AsMe<sub>3</sub>)(TeMe)]I, a second product with  $\delta(^{125}\text{Te})$  at 567.5, characteristic of a –TeMe<sub>2</sub>I unit, which suggests that diquaternization of **6**, **7**, and **8** will be possible under more forcing conditions, although this was not studied in the present work.

(17) Cook, B. R.; McAuliffe, C. A.; Meek, D. W. *Inorg. Chem.* **1971**, *10*, 2628.

(18) Doak, G. O.; Freedman, L. D. *Organometallic Compounds of Arsenic, Antimony, and Bismuth*; Wiley: New York, 1970; Chapter 8 and references therein.

Table II.  $^{125}\text{Te}$  and  $^{77}\text{Se}$  NMR Data on Hybrid Telluroethers and Selenium Analogues

compd	$\delta(^{125}\text{Te}\{^1\text{H}\})^a$	$\delta(\text{other})^b$	$\delta(^{77}\text{Se}\{^1\text{H}\})^c$
PhMeTe	329		202
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (NMe <sub>2</sub> )(TeMe)	236		173
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (PMe <sub>2</sub> )(TeMe)	258 ( $^3J(^{125}\text{Te}-^{31}\text{P}) = 695 \text{ Hz}$ )	-43.7 ( $\delta(^{31}\text{P})$ )	201
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (AsMe <sub>2</sub> )(TeMe)	275		187
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (SbMe <sub>2</sub> )(TeMe)	332		221.5
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (OMe)(TeMe)	206 (lit. <sup>d</sup> 205)		148.5
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (SMe)(TeMe)	268		185
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (SeMe)(TeMe)	303 ( $^3J(^{125}\text{Te}-^{77}\text{Se}) = 330 \text{ Hz}$ )	242 ( $\delta(^{77}\text{Se})$ )	200
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (TeMe) <sub>2</sub>	372		(242)
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (TePh) <sub>2</sub>	692		
<i>o</i> -C <sub>6</sub> H <sub>4</sub> Cl(TeMe)	304		201
PhMe <sub>2</sub> TeI	550		
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (NMe <sub>2</sub> )(TeMe <sub>2</sub> I)	476		
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (PMe <sub>2</sub> I)(TeMe)	367 ( $^3J(^{125}\text{Te}-^{31}\text{P}) = 61 \text{ Hz}$ )	+27.8 ( $\delta(^{31}\text{P})$ )	205
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (AsMe <sub>2</sub> I)(TeMe)	366		207
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (SbMe <sub>2</sub> I)(TeMe)	423		240
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (OMe)TeMe <sub>2</sub> I	510		
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (SMe)(TeMe <sub>2</sub> I)	524		
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (SeMe)(TeMe <sub>2</sub> I)	553 ( $^3J(^{125}\text{Te}-^{77}\text{Se}) = 110 \text{ Hz}$ )	235 ( $\delta(^{77}\text{Se})$ )	
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (TeMe <sub>2</sub> I) <sub>2</sub>	588		
<i>o</i> -C <sub>6</sub> H <sub>4</sub> Cl(TeMe <sub>2</sub> I)	554		
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (TePhCl <sub>2</sub> ) <sub>2</sub>	940		

<sup>a</sup> Ca. 40% solution (w/v) in CHCl<sub>3</sub> relative to external neat Me<sub>2</sub>Te. <sup>b</sup>  $^{31}\text{P}$  data relative to 85% H<sub>3</sub>PO<sub>4</sub> and  $^{77}\text{Se}$  relative to external neat Me<sub>2</sub>Se. <sup>c</sup>  $^{77}\text{Se}$  chemical shift for selenium analogue—data from ref. 4. <sup>d</sup> O'Brien, D. H.; Irgolic, K. J.; Huang, C.-K. *Proc. Int. Conf. Org. Chem. Selenium, Tellurium, 4th* 1983, 468-491.

**NMR Spectra.  $^1\text{H}$ .** The proton NMR spectra (Table I) are unexceptional with  $\delta(\text{TeMe})$  at ca. 2.0 ppm and  $^2J(^{125}\text{Te}-^1\text{H})$  at ca. 25 Hz, while  $\delta(\text{EMe})$ s are similar to those in related *o*-phenylene bidentates.<sup>4,15</sup> On quaternization of the -TeMe group to -TeMe<sub>2</sub>I  $\delta(\text{TeMe})$  shifts to ca. 2.5 ppm, but the coupling constant is little changed. Small high-frequency shifts are evident in the resonances due to the unquaternized -TeMe or -Y groups, as a result of inductive effects from the ortho quaternized group (Table I).

**$^{13}\text{C}\{^1\text{H}\}$ .** The  $\delta(\text{TeMe})$  resonances are found to low frequency of Me<sub>4</sub>Si in the range -12 to -20 ppm with  $^1J(^{125}\text{Te}-^{13}\text{C})$  of 160-180 Hz (Table I). For *o*-C<sub>6</sub>H<sub>4</sub>(TeMe)<sub>2</sub>  $^4J(^{125}\text{Te}-^{13}\text{C})$  of 16 Hz and for *o*-C<sub>6</sub>H<sub>4</sub>(PMe<sub>2</sub>)(TeMe)  $^4J(^{31}\text{P}-^{13}\text{C})$  of 29 Hz were observed. The  $\delta(\text{EMe})$  resonances were consistent with the literature ranges of Me groups upon the various non-metals.<sup>19</sup> The ipso<sub>Te</sub> and ipso<sub>E</sub> carbon resonances that lack any NOE enhancement were weak and  $^1J(^{125}\text{Te}-^{13}\text{C})$  was often not clearly resolved. The ipso<sub>Te</sub> resonances showed significant variation in chemical shift with variation in the ortho E group and lay in the range 104-126 ppm, and where they could be identified,  $^1J(^{125}\text{Te}-^{13}\text{C})$  was 260-300 Hz. Smaller  $^2J(^{125}\text{Te}-^{13}\text{C})$  couplings were sometimes resolved upon the ipso<sub>E</sub> carbon resonance.

**$^{125}\text{Te}\{^1\text{H}\}$ .** The tellurium chemical shifts of *o*-C<sub>6</sub>H<sub>4</sub>-(TeMe)Y are very sensitive to the nature of the Y group (Table II) ranging from 206 ppm in *o*-C<sub>6</sub>H<sub>4</sub>(OMe)(TeMe) to 372 ppm for *o*-C<sub>6</sub>H<sub>4</sub>(TeMe)<sub>2</sub>. Inspection of the values shows that  $\delta(^{125}\text{Te})$  increases as the Y group descends groups 15 or 16. Various studies on meta- or para-substituted phenyl selenides and phenyl tellurides<sup>19-21</sup> have shown systematic variations in the selenium or tellurium chemical shifts with the electronic properties of the substituents (e.g. with the Hammett  $\sigma$  constant), but for ortho-substituted compounds the variations are irregular. For ortho-substituted selenoethers<sup>4,20,21</sup> it was suggested

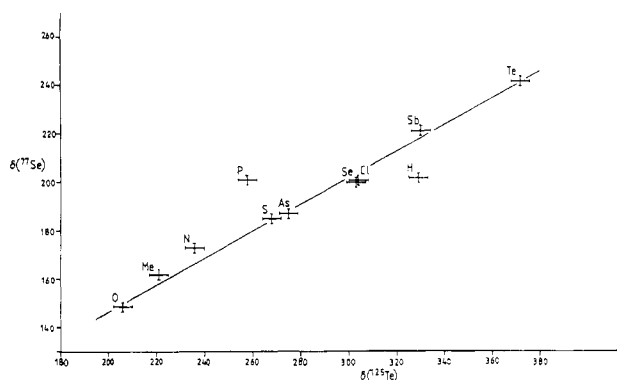


Figure 1.  $\delta(^{77}\text{Se})$  of the hybrid selenoethers versus  $\delta(^{125}\text{Te})$  of the corresponding telluroethers. The error bars are arbitrarily set at 8 ppm for Te and 4 ppm for Se chemical shifts. The slope is 1.8.

that the irregularities were due to several different effects operating: a, an electronic effect transmitted through the benzene ring (the only effect common to meta and para analogues); b, a steric effect whereby the substituent effects the orientation of the -SeMe group with respect to the benzene ring and hence effects the lone pair- $\pi$ -ring interaction; and c, "through-space" direct interaction between the ortho groups. We previously<sup>4</sup> pointed out the much greater variation in  $\delta(^{77}\text{Se})$  in *o*-C<sub>6</sub>H<sub>4</sub>(SeMe)Y, compared with that of  $\delta(^{31}\text{P})$  in *o*-C<sub>6</sub>H<sub>4</sub>(PMe<sub>2</sub>)Y,<sup>15</sup> even allowing for the greater chemical shift range of selenium. In Figure 1 a plot of  $\delta(^{77}\text{Se})$  in *o*-C<sub>6</sub>H<sub>4</sub>(SeMe)Y versus  $\delta(^{125}\text{Te})$  in the corresponding *o*-C<sub>6</sub>H<sub>4</sub>(TeMe)Y is shown, and as can be seen the relationship is linear, which is taken as evidence that the same effects are operating in both series. [Note that the tellurium shift of *o*-C<sub>6</sub>H<sub>4</sub>(TeMe)(SeMe) should be compared to the selenium shift of *o*-C<sub>6</sub>H<sub>4</sub>(SeMe)<sub>2</sub>, i.e. both ortho to SeMe, and similarly the tellurium shift of *o*-C<sub>6</sub>H<sub>4</sub>(TeMe)<sub>2</sub> to the selenium shift of *o*-C<sub>6</sub>H<sub>4</sub>(SeMe)-(TeMe).] Since both selenium and especially tellurium chemical shifts are concentration, solvent, and temperature dependent, error bars have been placed upon the plot

(19) Mason, J., Ed. *Multinuclear NMR*; Plenum: New York, 1987.

(20) Luthra, N. P.; Odum, J. D. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1986; Vol. 1, pp 189-241.

(21) McFarlane, W.; Wood, R. J. *J. Chem. Soc., Dalton Trans.* 1972, 1397.

(22) Meek, D. W.; Dyer, G.; Workman, M. O.; Chia, P. S. K.; Livingstone, S. E. *Inorg. Synth.* 1976, 16, 168.

reflecting the relative sensitivities. However since attempts were made to record the data under comparable conditions, it is believed that these error bars *overestimate* the errors.

Quaternization of the  $-\text{TeMe}$  groups to  $-\text{TeMe}_2\text{I}$  produces large high-frequency shifts  $\geq 250$  ppm, whereas in  $[\text{o}-\text{C}_6\text{H}_4(\text{EMe}_3)(\text{TeMe})]\text{I}$  inductive effects produce smaller shifts in the same direction  $\leq 110$  ppm.

The large couplings between the heteroatoms in  $\text{o}-\text{C}_6\text{H}_4(\text{SeMe})(\text{TeMe})$  and  $\text{o}-\text{C}_6\text{H}_4(\text{PMe}_2)(\text{TeMe})$  are notable. The  $^3J(^{125}\text{Te}-^{31}\text{P})$  coupling in the phosphine telluroether of 695 Hz decreases on quaternization at phosphorus to 61 Hz and, taken together with the absence of a similar large coupling in  $\text{o}-\text{C}_6\text{H}_4(\text{PMe}_2)(\text{SeMe})$ , suggests that in the telluroether the coupling may be due to a through space interaction between the phosphorus lone pair and the large tellurium.

**Mass Spectra.** The mass spectral fragmentations (Experimental Section) are much as expected in comparison with the selenium analogues<sup>4</sup> and serve to confirm the constitution of the new telluroethers. All show prominent parent ions and fragments due to successive loss of Me groups. When the other Te isotopes were taken into consideration, the base peaks were often either the parent or  $\text{P}-\text{Me}^+$  ions.

### Experimental Section

Physical measurements were made as described in ref 1.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  chemical shifts are reported relative to internal  $\text{Me}_4\text{Si}$ , and  $^{125}\text{Te}\{^1\text{H}\}$  shifts are relative to neat external  $\text{Me}_2\text{Te}$  and were obtained for approximately 40% w/v solutions for liquid samples and for solids from saturated solutions in the solvents specified. The  $m/z$  data in the mass spectra refer to  $^{130}\text{Te}$ ,  $^{35}\text{Cl}$ , and  $^{80}\text{Se}$  isotopomers and are uncorrected for other ions.

Reagents were obtained as described.<sup>1</sup> Halobenzenes were dried over calcium hydride and distilled before use. All synthetic work was conducted under a dry dinitrogen atmosphere, except for the preparation of derivatives. The telluroether ligands were usually stored in sealed containers under dinitrogen.

**1. *o*-Bis(methyltelluro)benzene,  $\text{o}-\text{C}_6\text{H}_4(\text{TeMe})_2$ .** To a frozen solution ( $-196^\circ\text{C}$ ) of  $\text{LiTeMe}$  in tetrahydrofuran<sup>1</sup> (0.1 mol) was added *o*-dibromobenzene (11.5 g, 0.05 mol). The mixture was allowed to warm to room temperature, stirred for 0.5 h, and then hydrolyzed with deoxygenated water (100  $\text{cm}^3$ ), and the organic products were extracted with diethyl ether ( $3 \times 50 \text{ cm}^3$ ). The organic extract was dried over  $\text{MgSO}_4$  for 16 h, the solvent removed in vacuo, and the residue fractionated yielding an orange oil (bp  $126^\circ\text{C}$  0.1 Torr) which crystallized upon standing: yield 11.0 g, 60%; mass spectrum,  $m/z$  (relative intensity) 366 ( $\text{C}_9\text{H}_{10}\text{Te}_2^+$ , 36), 351 (50), 336 (45), 260 (14), 206 (12), 91 (32). Observed base peak is  $m/z$  347 due to other isotopomers.

The ditelluronium salt  $\text{o}-\text{C}_6\text{H}_4(\text{TeMe}_2\text{I})_2$  was prepared by heating an acetone solution of the ligand (0.1 g) with excess  $\text{MeI}$  for 1 h; the white crystalline precipitate was filtered off, washed with ether, and dried; mp  $174\text{--}175^\circ\text{C}$  dec. Anal. Calcd for  $\text{C}_{10}\text{H}_{16}\text{I}_2\text{Te}_2$ : C, 18.5; H, 2.5. Found: C, 18.5, H, 2.4.

**2. Methyl *o*-Methoxyphenyl Telluride,  $\text{o}-\text{C}_6\text{H}_4(\text{OMe})\text{-TeMe}$ .** To a frozen solution of  $\text{LiTeMe}$  (0.05 mol) was added *o*-bromoanisole (9.3 g, 0.05 mol); the mixture was allowed to warm to room temperature and stirred for 1.5 h. Workup was as described in 1, and after fractionation of the oil obtained in vacuo, the product was obtained as a pale orange oil: bp  $96^\circ\text{C}$  (0.3 Torr); yield 9.3 g, 74%; mass spectrum,  $m/z$  (relative intensity) 252 ( $\text{C}_8\text{H}_{10}\text{OTe}^+$ , 53), 237 (10), 107 (100), 92 (10), 77 (48).

The telluronium salt was prepared as in 1: mp  $140\text{--}142^\circ\text{C}$ . Anal. Calcd for  $\text{C}_9\text{H}_{13}\text{IOTe}$ : C, 27.6; H, 3.3. Found: C, 27.5; H, 3.3.

The dichloride  $\text{o}-\text{C}_6\text{H}_4(\text{OMe})(\text{TeMeCl}_2)$  was made by stirring the ligand with excess  $\text{Cl}_2/\text{CH}_2\text{Cl}_2$ , filtering off the white product, and drying in vacuo: mp  $118\text{--}119^\circ\text{C}$ . Anal. Calcd for  $\text{C}_8\text{H}_9\text{Cl}_2\text{OTe}$ : C, 30.5; H, 3.2. Found: C, 30.1; H, 3.3.

**3. Methyl *o*-(Methylthio)phenyl Telluride,  $\text{o}-\text{C}_6\text{H}_4(\text{SMe})(\text{TeMe})$ .** The Grignard reagent prepared from *o*-bromothioanisole (5.4 g, 0.025 mol) in tetrahydrofuran was added via

a transfer needle to a frozen suspension of tellurium powder (3.19 g, 0.025 mol) in thf (100  $\text{cm}^3$ ) and the mixture allowed to warm and stirred at room temperature until all the tellurium dissolved. The resulting pale yellow solution was refrozen ( $-196^\circ\text{C}$ ) and  $\text{MeI}$  (3.55 g, 0.025 mol) added. The mixture was again thawed and stirred at room temperature, when much magnesium salt was deposited. The mixture was worked up as above, and after removal of the organic solvents in vacuo, the product was fractionated: bp  $102^\circ\text{C}$  (0.5 Torr); yield 5.9 g, 92%; mass spectrum,  $m/z$  (relative intensity) 268 ( $\text{C}_8\text{H}_{10}\text{STe}^+$ , 51.5), 253 (28.5), 238 (15), 123 (100), 108 (40.5), 91 (18.5).

The telluronium derivative  $\text{o}-\text{C}_6\text{H}_4(\text{SMe})(\text{TeMe}_2\text{I})$ , made as in 1 had a melting point of  $128^\circ\text{C}$ . Anal. Calcd for  $\text{C}_9\text{H}_{13}\text{ISTe}$ : C, 26.5; H, 3.2. Found: C, 26.7; H, 3.3.

**4. Methyl *o*-(Methylseleno)phenyl Telluride,  $\text{o}-\text{C}_6\text{H}_4(\text{SeMe})(\text{TeMe})$ .** *n*-Butyllithium (8  $\text{cm}^3$  of a 2.5 mol  $\text{dm}^{-3}$  solution) in hexane was added dropwise to a cooled ( $0^\circ\text{C}$ ) solution of *o*-bromoselenoanisole (5.0 g, 0.02 mol) in diethyl ether (100  $\text{cm}^3$ ). The resulting mixture was stirred at  $0^\circ\text{C}$  for 1 h, and then dimethyl ditelluride (5.1 g, 0.02 mol) was added dropwise. Immediate discharge of the deep red ditelluride color occurred. On completion of the addition, the mixture was allowed to warm to room temperature. Hydrolysis and workup as in 1, followed by fractionation, gave a pale orange oil: bp  $110^\circ\text{C}$  (0.4 Torr); yield 2.6 g, 40%; mass spectrum,  $m/z$  (relative intensity) 316 ( $\text{C}_8\text{H}_{10}\text{SeTe}^+$ , 45), 301 (72), 286 (79), 232 (81), 156 (66), 152 (45), 91 (88) (observed base  $m/z$  284 due to other isotopomers).

The telluronium derivative  $\text{o}-\text{C}_6\text{H}_4(\text{SeMe})(\text{TeMe}_2\text{I})$  made in the usual manner had a melting point of  $130\text{--}132^\circ\text{C}$ . Anal. Calcd for  $\text{C}_9\text{H}_{13}\text{ISeTe}$ : C, 23.8; H, 2.9. Found: C, 23.8; H, 2.9.

**5. Methyl *o*-(Dimethylamino)phenyl Telluride,  $\text{o}-\text{C}_6\text{H}_4(\text{NMe}_2)(\text{TeMe})$ .** This was prepared analogously to 2 by using the Grignard from (*o*-bromophenyl)dimethylamine.<sup>15</sup> Distillation of the product in vacuo gave an orange oil: bp  $76^\circ\text{C}$  (0.2 Torr); yield 68%; mass spectrum,  $m/z$  (relative intensity) 265 ( $\text{C}_9\text{H}_{13}\text{NTe}^+$ , 92), 250 (35), 235 (18), 120 (100), 105 (31), 104 (29), 91 (36), 77 (41).

The telluronium salt  $\text{o}-\text{C}_6\text{H}_4(\text{NMe}_2)(\text{TeMe}_2\text{I})$  had a melting point of  $167^\circ\text{C}$ . Anal. Calcd for  $\text{C}_{10}\text{H}_{16}\text{INTe}$ : C, 29.7; H, 4.0. Found: C, 30.0; H, 3.8.

**6. Methyl *o*-(Dimethylphosphino)phenyl Telluride,  $\text{o}-\text{C}_6\text{H}_4(\text{PMe}_2)(\text{TeMe})$ .** A solution of  $^t\text{BuLi}$  (8.8  $\text{cm}^3$  of a 2.5 mol  $\text{dm}^{-3}$  in hexane) was added dropwise to (*o*-bromophenyl)dimethylphosphine.<sup>16</sup> (4.1 g, 0.022 mol) in diethyl ether at  $0^\circ\text{C}$ , and the mixture was stirred at room temperature for 4 h. The solution was cooled back to  $0^\circ\text{C}$  and dimethyl ditelluride (6.25 g, 0.022 mol) added with vigorous stirring. After being warmed to room temperature and stirred for 1 h, the solution was worked up as in 1. Fractionation in vacuo gave a pale orange oil: bp  $98^\circ\text{C}$  (0.2 Torr); yield 4.4 g, 80%; mass spectrum,  $m/z$  (relative intensity) 372 ( $\text{C}_9\text{H}_{13}\text{PTe}^+$ , 18), 267 (100), 252 (9), 237 (8), 137 (29), 121 (21), 109 (44), 107 (51), 91 (53).

The phosphonium salt was made by stirring the ligand (0.1 g) with excess  $\text{MeI}$  in acetone at room temperature for 4 h. The white crystalline product was filtered off, rinsed with diethyl ether, and dried: mp  $192\text{--}194^\circ\text{C}$ . Anal. Calcd for  $\text{C}_{10}\text{H}_{16}\text{IPTe}$ : C, 28.5; H, 3.8. Found: C, 28.8; H, 3.9.

**7. Methyl *o*-(Dimethylarsino)phenyl Telluride,  $\text{o}-\text{C}_6\text{H}_4(\text{AsMe}_2)(\text{TeMe})$ .** A solution of  $^t\text{BuLi}$  (10.4  $\text{cm}^3$  of 2.5 mol  $\text{dm}^{-3}$  solution) was added dropwise to a solution of (*o*-bromophenyl)dimethylarsine<sup>23</sup> (6.8 g, 0.026 mol) in dry hexane (100  $\text{cm}^3$ ), and the mixture was refluxed for 4 h. After the mixture was cooled to room temperature,  $\text{Me}_2\text{Te}_2$  (7.4 g, 0.026 mol) was added dropwise and the mixture stirred for a further 1 h. Workup as in 1 gave an orange oil: bp  $105^\circ\text{C}$  (0.2 Torr); yield 7.5 g, 68%; mass spectrum,  $m/z$  (relative intensity) 326 ( $\text{C}_9\text{H}_{13}\text{AsTe}^+$ , 39), 311 (100), 296 (50), 281 (33), 205 (11), 151 (49.5), 91 (36).

The arsonium salt was made as for the derivative of 6: mp  $183^\circ\text{C}$  dec. Anal. Calcd for  $\text{C}_{10}\text{H}_{16}\text{AsITe}$ : C, 25.8; H, 3.4. Found: C, 25.8; H, 3.2.

**8. Methyl *o*-(Dimethylstibino)phenyl Telluride,  $\text{o}-\text{C}_6\text{H}_4(\text{SbMe}_2)(\text{TeMe})$ .** To a solution of (*o*-bromophenyl)dimethylstibine<sup>15</sup> (5.8 g, 0.019 mol) in dry diethyl ether (150  $\text{cm}^3$ )

(23) Levason, W.; McAuliffe, C. A.; Plaza, A. I.; Grim, S. O. *Inorg. Synth.* 1976, 16, 184.

at  $-63\text{ }^{\circ}\text{C}$  (chloroform slush) was added  ${}^n\text{BuLi}$  ( $7.6\text{ cm}^3$  of a  $2.5\text{ mol dm}^{-3}$  solution). After being stirred for 3 h, the solution was allowed to warm to room temperature and  $\text{Me}_2\text{Te}_2$  ( $5.4\text{ g}$ ,  $0.019\text{ mol}$ ) added dropwise. After a further 2 h the mixture was worked up as in 1. The fraction boiling at ca.  $144\text{ }^{\circ}\text{C}$  ( $0.3\text{ Torr}$ ) was further purified by flash column chromatography on silica (with rigorous exclusion of air), using  $40\text{--}60\text{ }^{\circ}\text{C}$  petroleum ether: yield  $1.15\text{ g}$ ,  $15\%$ ; mass spectrum,  $m/z$  (relative intensity)  $372$  ( $\text{C}_9\text{H}_9\text{SbTe}^+$ , 25),  $357$  (100),  $342$  ( $48.5$ ),  $327$  ( $51.5$ ),  $251$  ( $38.5$ ),  $91$  ( $36$ ).

The stibonium salt prepared similar to the derivative of 6 had a melting point of  $90\text{--}92\text{ }^{\circ}\text{C}$ . Anal. Calcd for  $\text{C}_{10}\text{H}_{16}\text{ISbTe}$ : C,  $23.4$ ; H,  $3.1$ . Found: C,  $23.7$ ; H,  $3.2$ .

**9. *o*-Chlorophenyl Methyl Telluride,  $\sigma\text{-C}_6\text{H}_4\text{Cl}(\text{TeMe})$ .** The mono-Grignard reagent prepared from *o*-bromochlorobenzene<sup>14</sup> ( $19.1\text{ g}$ ,  $0.1\text{ mol}$ ) was added via a cannula to a frozen suspension of tellurium powder ( $12.8\text{ g}$ ,  $0.1\text{ mol}$ ) in thf ( $200\text{ cm}^3$ ). The mixture was allowed to thaw and stirred at room temperature for 3 h giving an orange solution and leaving about  $10\%$  of the Te unreacted. The mixture was refrozen ( $-196\text{ }^{\circ}\text{C}$ ), iodomethane ( $12.9\text{ g}$ ,  $0.09\text{ mol}$ ) added, and the mixture again allowed to attain room temperature. Following workup as in 1, fractionation in vacuo gave a pale yellow oil: bp  $82\text{ }^{\circ}\text{C}$  ( $0.4\text{ Torr}$ ); yield  $16.0\text{ g}$ ,  $64\%$ ; mass spectrum,  $m/z$  (relative intensity)  $256$  ( $\text{C}_7\text{H}_7\text{ClTe}^+$ , 96),  $241$  (100),  $206$  (33),  $111$  (23),  $75$  (40).

The telluronium salt prepared as in 1 had a melting point of  $103\text{--}104\text{ }^{\circ}\text{C}$ . Anal. Calcd for  $\text{C}_8\text{H}_{10}\text{ClITe}$ : C,  $24.2$ ; H,  $2.5$ . Found: C,  $24.2$ ; H,  $2.5$ .

**10. 1,2-Bis(phenyltelluro)benzene,  $\sigma\text{-C}_6\text{H}_4(\text{TePh})_2$ .** *o*-Bromiodobenzene ( $7.08\text{ g}$ ,  $0.025\text{ mol}$ ) was added to a frozen solution of (phenyltelluro)lithium<sup>1</sup> ( $0.05\text{ mol}$ ). The mixture was allowed to thaw, stirred at room temperature for 3 h, and then worked up as in 1. Removal of the solvent gave a red oil, which was purified by flash column chromatography, leaving a pale yellow oil. Crystallization of this from petroleum ether ( $40\text{--}60\text{ }^{\circ}\text{C}$ ) gave yellow crystals:  $7.8\text{ g}$ ,  $32\%$ ; mass spectrum,  $m/z$  (relative intensity)  $490$  ( $\text{C}_{18}\text{H}_{14}\text{Te}_2^+$ , 26),  $408$  (15),  $282$  (100),  $207$  (27),  $152$  (39),  $77$  (51). Anal. Calcd for  $\text{C}_{18}\text{H}_{14}\text{Te}_2$ : C,  $44.5$ ; H,  $2.9$ . Found:

C,  $44.7$ ; H,  $3.0$ .

The tetrachloride was prepared by adding excess of a solution of chlorine in dichloromethane to a solution of 10 in the same solvent: mp  $115\text{--}116\text{ }^{\circ}\text{C}$  dec. Anal. Calcd for  $\text{C}_{18}\text{H}_{14}\text{Cl}_4\text{Te}_2$ : C,  $34.4$ ; H,  $2.2$ . Found: C,  $34.7$ ; H,  $2.3$ .

**11. *o*-Chlorophenyl Methyl Sulfide,  $\sigma\text{-C}_6\text{H}_4\text{Cl}(\text{SMe})$ .** A solution of sodium methyl sulfide, NaSMe, was prepared from MeSH ( $14.4\text{ g}$ ,  $0.3\text{ mol}$ ) and sodium ( $6.9\text{ g}$ ,  $0.3\text{ mol}$ ) in ethanol. The ethanol was distilled off under nitrogen and dry dmf ( $200\text{ cm}^3$ ) added, followed by *o*-dichlorobenzene ( $14.7\text{ g}$ ,  $0.1\text{ mol}$ ). The mixture was refluxed for 16 h and cooled and iodomethane ( $42.6\text{ g}$ ,  $0.3\text{ mol}$ ) added slowly. The resulting solution was stirred for 0.5 h, hydrolyzed with water ( $200\text{ cm}^3$ ), and extracted with diethyl ether ( $3 \times 200\text{ cm}^3$ ). The ether extracts were dried, the solvent was distilled off, and the residue was fractionated in vacuo: bp  $60\text{ }^{\circ}\text{C}$  ( $0.4\text{ Torr}$ );  $14.3\text{ g}$ ,  $90\%$ ;  ${}^1\text{H NMR}$   $\delta$   $2.21$  (s, MeS),  $6.8\text{--}7.3$  ( $\text{C}_6\text{H}_4$ ).

**12. *o*-Chlorophenyl Methyl Selenide,  $\sigma\text{-C}_6\text{H}_4\text{Cl}(\text{SeMe})$ .** A solution of lithium methyl selenide, LiSeMe ( $0.05\text{ mol}$ ), was prepared,<sup>4</sup> the thf removed in vacuo, and dry dmf ( $150\text{ cm}^3$ ) and *o*-dichlorobenzene ( $7.35\text{ g}$ ,  $0.05\text{ mol}$ ) were added. The mixture was gently refluxed for 16 h and cooled and iodomethane ( $7.1\text{ g}$ ,  $0.05\text{ mol}$ ) added dropwise. The product was isolated as described for 11, fractionation in vacuo affording a pale yellow oil: bp  $67\text{ }^{\circ}\text{C}$  ( $0.5\text{ Torr}$ ); yield  $5.3\text{ g}$ ,  $52\%$ ; mass spectrum,  $m/z$  (relative intensity)  $206$  ( $\text{C}_7\text{H}_7\text{ClSe}^+$ , 100),  $191$  (74),  $156$  (29);  ${}^1\text{H NMR}$   $\delta$   $2.2$  (s, MeSe),  ${}^2J({}^{77}\text{Se}\text{--}{}^1\text{H}) = 12\text{ Hz}$ ,  $6.7\text{--}7.4$  ( $\text{C}_6\text{H}_4$ );  ${}^{77}\text{Se}\{^1\text{H}\}$   $\delta$   $201$  (lit.<sup>21</sup>  ${}^{77}\text{Se}\{^1\text{H}\}$   $\delta$   $201$ ).

**13. 1,2-Bis(methylthio)benzene,  $\sigma\text{-C}_6\text{H}_4(\text{SMe})_2$ .** Lithiation of *o*-chlorophenyl methyl sulfide ( $12.2\text{ g}$ ,  $0.08\text{ mol}$ ) with  ${}^n\text{BuLi}$  ( $0.08\text{ mol}$ ) in diethyl ether, followed by dropwise addition at  $0\text{ }^{\circ}\text{C}$  of  $\text{Me}_2\text{S}_2$  ( $0.08\text{ mol}$ ) and workup as in reaction 1, gave the product: bp  $82\text{ }^{\circ}\text{C}$  ( $0.4\text{ Torr}$ );  $90\%$ ;  ${}^1\text{H NMR}$   $\delta$   $2.20$  (s, MeS),  $7.0\text{--}7.4$  ( $\text{C}_6\text{H}_4$ ).

**Acknowledgment.** We thank the S.E.R.C. for support and J. M. Street for the  ${}^{13}\text{C}\{^1\text{H}\}$  NMR data.

## Chloro- and Hydrido(pentamethylcyclopentadienyl)ruthenium Complexes: Anomalous NMR Behavior of $\text{C}_5\text{Me}_5\text{RuH}_3\text{PR}_3$ ( $\text{R} = \text{CHMe}_2, \text{Cy}$ )

Thérèse Arliguie, Corinne Border, Bruno Chaudret,\* Jean Devillers, and René Poilblanc

Laboratoire de Chimie de Coordination du CNRS, Unité n° 8241 liée par convention à l'Université Paul Sabatier, 205 Route de Narbonne, 31077 Toulouse Cedex, France

Received November 6, 1987; Revised Manuscript Received December 7, 1988

The reaction of  $[\text{Cp}^*\text{RuCl}_2]_n$  ( $\text{Cp}^* = \text{C}_5\text{Me}_5$ ) with 1 equiv of various phosphines ( $\text{PR}_3$ ) leads to the ruthenium(III) derivatives  $\text{Cp}^*\text{RuCl}_2(\text{PR}_3)$  ( $\text{R} = \text{Me}, \text{Ph}, \text{Cy}, \text{or CHMe}_2$ ) (1–4). Reduction of these compounds by excess phosphine or zinc leads to the bis(phosphine) derivatives  $\text{Cp}^*\text{RuCl}(\text{PR}_3)_2$  ( $\text{R} = \text{Me}$ ) or the blue 16-electron complexes  $\text{Cp}^*\text{RuCl}(\text{PR}_3)$  ( $\text{R} = \text{Cy}$  (5) or  $\text{CHMe}_2$  (6)). A similar pink derivative,  $\text{Cp}^*\text{RuCl}[\text{P}(\text{CMe}_3)_3]$  (7), is obtained in a single step from  $[\text{Cp}^*\text{RuCl}_2]_n$ ,  $\text{P}(\text{CMe}_3)_3$ , and zinc. Carbonylation of 5 and 6 leads to the chloro carbonyl derivatives  $\text{Cp}^*\text{RuCl}(\text{CO})(\text{PR}_3)$  ( $\text{R} = \text{Cy}$  (8) or  $\text{CHMe}_2$  (9)) which react further with  $\text{NaBH}_4$  in ethanol to produce the hydrido carbonyl derivatives  $\text{Cp}^*\text{RuH}(\text{CO})(\text{PR}_3)$  ( $\text{R} = \text{Cy}$  (10) or  $\text{CHMe}_2$  (11)). Direct reaction of  $\text{Cp}^*\text{RuCl}_2(\text{PR}_3)$  with 2 equiv of  $\text{LiBHET}_3$  in THF or addition of 1 equiv of  $\text{LiBHET}_3$  to 5 or 6 leads to the formation of the trihydrido derivatives  $\text{Cp}^*\text{RuH}_3(\text{PR}_3)$  ( $\text{R} = \text{Me}$  (12),  $\text{Ph}$  (13),  $\text{Cy}$  (14),  $\text{CHMe}_2$  (15)); spectroscopic investigations at  $293\text{ K}$  are all in favor of a fluxional ruthenium trihydrido formulation. However, in the case of the bulky phosphine derivatives at low temperature, "anomalous"  ${}^1\text{H NMR}$  spectra are observed. An  $\text{AB}_2\text{X}$  spin system is observed for the hydrides, characterized by  $J_{\text{AX}} \sim 0\text{ Hz}$ ,  $J_{\text{BX}} \sim 30\text{ Hz}$ , and a temperature-dependent  $J_{\text{A-B}}$  with values as high as  $130\text{ Hz}$ . These observations are discussed, and an interpretation is proposed that involves an equilibrium between a classical trihydride (present at low temperature) and a species either showing a nonclassical interaction between a hydride and coordinated dihydrogen or containing a novel trihydrogen ligand.

### Introduction

The chemistry of polyhydrido transition-metal complexes has received considerable attention in the last few years, principally because of their great reactivity toward

hydrocarbons and as precursors for C–H activation reactions.<sup>1,2</sup>

(1) Hlatky, G. G.; Crabtree, R. H. *Coord. Chem. Rev.* 1985, 65, 1–48.