

NEW ORGANYTELLURIUM LIGANDS. 1,2-BIS(*p*-ETHOXYPHENYLTELLUROMETHYL)BENZENE AND TETRAKIS(*p*-ETHOXYPHENYLTELLUROMETHYL)METHANE

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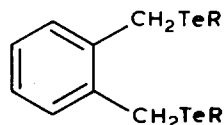
Summary

The synthesis and characterisation, particularly by ^{13}C NMR spectroscopy, of 1,2-bis(*p*-ethoxyphenyltelluromethyl)benzene and tetrakis(*p*-ethoxyphenyltelluromethyl)methane are reported.

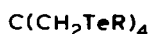
A preliminary investigation of the coordination chemistry of 1,2-bis(*p*-ethoxyphenyltelluromethyl)benzene (I) has given complexes of stoichiometry $[\text{PdCl} \cdot (\text{I})]$, $[\text{PtCl} \cdot (\text{I})]$ and $[\text{HgCl} \cdot (\text{I})]$, which are insoluble and generally intractable. Some physical data, particularly low frequency infrared spectra and ^{125}Te Mössbauer spectra, are briefly discussed.

Introduction

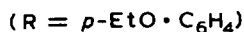
There has been a recent growth of interest in the ligand chemistry of tellurium [1,2] but despite this growth of activity the literature contains few reports of bi- or multi-dentate ligands containing tellurium. We have recently initiated a programme of synthesis to extend the range of bi- and multi-dentate ligands available, thus both the series $\text{RTe}(\text{CH}_2)_n\text{TeR}$ ($n = 1, 5, 6, 7, 9, 10$; $\text{R} = p\text{-EtO} \cdot \text{C}_6\text{H}_4$) [3] together with $(\text{Bu}^n\text{Te})\text{C}_6\text{H}_4\text{CHN}(\text{CH}_2)_2\text{NCHC}_6\text{H}_4(\text{TeBu}^n)$ [4] are available. In this short paper we wish to report two additions to the range (I and II) together with a brief preliminary consideration of some coordination compounds of I.



(I)



(II)



Experimental

(a) Synthesis

1,2Bis(p-ethoxyphenyltelluromethyl)benzene (I). This preparation was carried out in the dark and under an atmosphere of dinitrogen. Bis(*p*-ethoxyphenyl)ditelluride (4.97 g, 10 mmol) in benzene (10 cm³) and ethanol (20 cm³) was heated to reflux. Sodium tetrahydroborate (0.6 g) in sodium hydroxide (1 mol dm⁻³) solution was added dropwise. The mixture became colourless on completion of the addition, at which stage a solution of 1,2-bis(bromomethyl)benzene (2.64 g, 10 mmol) in benzene was added. The reaction mixture was stirred at room temperature for 2 h, after which the now yellow solution was added to distilled water and stirred. The organic layer was separated, washed with distilled water, and treated with petroleum ether (40–60°C) to precipitate the yellow product which was dried over P₄O₁₀. Recrystallisation from petroleum ether (40–60°C) gave a bright yellow compound (I) in 50% yield.

Tetrakis(p-ethoxyphenyltelluromethyl)methane (II). The reaction was carried out under an atmosphere of dinitrogen. A solution of NaTe(C₆H₄·OEt-*p*) was prepared as in the above synthesis and treated with C(CH₂Br)₄ (1.94 g, 5 mmol) in THF (25 cm³); a further 145 cm³ was added and the mixture was refluxed for 5 h. The mixture was added to distilled water, stirred and filtered to remove a small quantity of tellurium. The organic layer was then separated, washed with distilled water and treated with acetonitrile to give a white precipitate. Recrystallisation from acetonitrile gave a poor (5%) yield of II.

Metal complexes of I. All reactions were carried out under dinitrogen.

(a) Palladium. K₂[PdCl₄] (0.163 g, 0.5 mmol) in distilled water was added to a solution of I (0.301 g, 0.5 mmol) in acetone and stirred for 12 h. The orange-yellow precipitate was filtered and dried in vacuo over P₄O₁₀ (yield 49%).

(b) Platinum. An identical procedure starting with K₂[PtCl₄] (0.208 g, 0.5 mmol) gave a yellow precipitate (48% yield).

TABLE 1
PHYSICAL DATA FOR NEW COMPOUNDS

Compound	M.p. (°C)	Colour	Analysis (Found calcd.) (%)		Λ_M (DMF)	$\nu(\text{MCl})$ (cm ⁻¹)	δ^a	Δ^b
			C	H				
I	69–70	Bright- yellow	47.9 (47.9)	4.00 (4.30)	8.0	–	0.03	10.72
II	146–147	White	42.1 (41.8)	3.70 (4.10)		–	–	–
[PdCl·(I)] _n	145–146(d)	Orange- yellow	38.6 (38.8)	3.20 (3.50)	17	265	–	–
[PtCl·(I)] _n	160–161(d)	Yellow	34.6 (34.6)	2.65 (3.10)	22	290	0.53	6.45
[HgCl ₂ ·(I)] _n	120–121	Yellow	33.0 (33.0)	2.90 (3.00)	39	–	–	–

^a Chemical isomer shift, δ , ± 0.08 mm s⁻¹ relative to Sb/Cu. ^b Quadrupole splitting, Δ , ± 0.1 mm s⁻¹.

(c) Mercury. HgCl_2 (0.136 g, 0.5 mmol) in acetone was treated as above to give a yellow complex (68% yield).

(b) *Physical measurements*

^1H NMR data were obtained with a Perkin-Elmer R12B instrument at 60 MHz, correct aliphatic/aromatic ratios were observed for I; the data were unremarkable and are not tabulated. Proton decoupled ^{13}C NMR spectra were obtained with a Jeol FX 90Q instrument at 22.5 MHz. ^{125}Te Mössbauer measurements were obtained as described previously using a $^{125}\text{Sb}/\text{Cu}$ source [5]; both source and absorber were at 4 K.

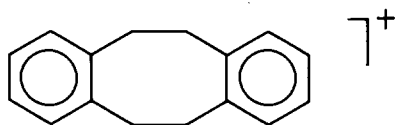
Infrared spectra in the range $400\text{--}200\text{ cm}^{-1}$ were obtained for Nujol mulls supported between polyethylene plates with a Perkin-Elmer 599B instrument. Mass spectra were recorded with an AEI MS9 instrument at 70 eV ($1\text{ eV} = 1.60 \times 10^{-19}\text{ J}$).

Molar conductivities (10^{-3} M solution in DMF) were measured with a Mullard conductivity bridge.

Analyses, conductivity data, IR, and ^{125}Te Mössbauer data are in Table 1 and ^{13}C NMR data constitute Table 2.

Discussion

Compound I is well characterised by the NMR data, particularly the ^{13}C data. The relatively high shielding of the methylene carbon atom parallels that seen for the series $\text{RTe}(\text{CH}_2)_n\text{TeR}$ ($n = 5, 6, 7, 9, 10$ [3]), where the methylene bonded to tellurium has a chemical shift of ~ 8 ppm. Interestingly the methylene carbons of compound II (with δ 21.2 ppm) are much less shielded (Table 2). Mass spectral studies of I and II showed $(\text{R}_2\text{Te}_2)^+$ as a major tellurium containing fragment (in neither case was the molecular ion seen in the 70 eV spectrum). For I a significant fragment was observed at $m/e = 208$, which corresponded to an ion $(\text{C}_{16}\text{H}_{16})^+$, doubtless III, suggesting that this is a thermolysis product arising from an elimination of tellurium. Three metal halide coordination complexes of I have been



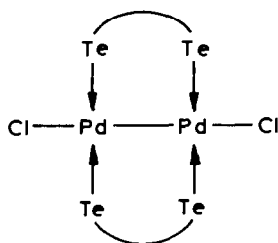
(III)

prepared to date. Unfortunately all are intractable in the sense that they are very insoluble in the majority of common solvents although 10^{-3} M solutions in DMF could be prepared. The materials are essentially non electrolytes in this solvent although there is evidence of significant solvolysis of the mercury(II) chloride complex. The stoichiometry of the palladium and platinum complexes is $[\text{MCl} \cdot (\text{I})]_n$, similar complexes are known for $\text{RTe}(\text{CH}_2)_n\text{TeR}$ [6]. The metal-halogen region of the infrared spectrum contains several significant ligand absorptions, and the assignments in Table 1 are tentative. The palladium figure is comparable to that observed (249 cm^{-1}) for $[\text{PdCl} \cdot \text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2]_2$ [7], thus a dimeric structure containing a Pd-Pd bond is possible (a) [7], but the data available do not eliminate possibilities (b) and (c).

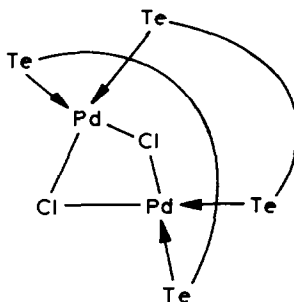
TABLE 2

 ^{13}C NMR DATA FOR COMPOUNDS I AND II ($\text{R} = p\text{-EtOC}_6\text{H}_4$)

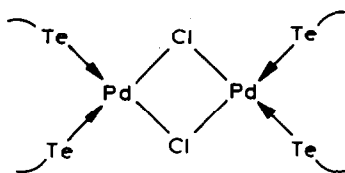
Ligand	Chemical shift (vs. TMS)										
	Aliphatic region				Aromatic region						
	CH_2	C	OCH_2	CH_3	C(2)	C(3)	C(4)	<i>ortho</i>	<i>meta</i>	<i>para</i>	<i>ipso</i>
I	10.1	—	68.4	14.7	137.8	129.8	126.5	115.6	142.0	159.3	102.4
II	21.2	25.4	63.3	14.8	—	—	—	115.4	136.8	159.9	109.6



(a)



(b)



(c)

The platinum complex shows $\nu(\text{PtCl})$ in a position more compatible with a terminal Pt-Cl bond. For this complex a good quality ^{125}Te Mössbauer spectrum was obtained. The data are consistent with coordination of the tellurium [8] and, further, testify to the equivalence of the tellurium atoms. The change in Δ on coordination is 4.27 mm s^{-1} which compares well with the change to Pt^{II} for coordination of $(p\text{-EtOC}_6\text{H}_4)_2\text{Te}(\text{L})$ in $\text{trans}[\text{PtCl}_2\text{L}_2]$ (4.50 mm s^{-1}) [8]. Thus the IR and Mössbauer data are compatible with those expected for a platinum(II) complex despite the stoichiometry which suggests platinum(I). No evidence for metallation of the ligand can be discerned from high frequency IR data.

The mercury(II) complex shows no band assignable to $\nu(\text{HgCl})$ above 200 cm^{-1} which, together with the insolubility, implies a polymeric structure with bridging chloride and a coordination number for mercury which is greater than four.

The insolubility of the complexes has severely limited the data available and further speculation as to their structure is not justified. Compound I is a bulky ligand and solvation energies of the complexes are likely to be low in polar solvents, despite the presence of OEt groups. Yet, frustratingly, the presence of those groups

may contribute to the lack of solubility in non polar solvents as, of course, may molecular complexity. Our present strategy is to modify the R groups of I in the hope that ligands producing more soluble complexes may be obtained. Even the limited data available here suggest that such compounds should lead to some interesting coordination chemistry.

Acknowledgement

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