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The reaction of 2-(2-pyridyl)phenyl(*p*-ethoxyphenyl)-tellurium(II) with mercury(II) chloride; a case of reverse *trans*-metallation

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Abstract

2-(2-Pyridyl)phenyl(*p*-ethoxyphenyl)tellurium(II) (RR′Te) reacts with $HgCl_2$ at room temperature to give white $HgCl_2 \cdot (RR')Te$. On setting aside, or on warming the reaction mixture a yellow material, $[R'HgCl \cdot (RTeCl)_2]$ is formed. Multinuclear NMR (^{125}Te, ^{199}Hg, ^{1}H) and mass spectroscopy confirm the formulation, and confirm the ease of transfer of the *p*-ethoxyphenyl group between the metal centres.

Introduction

There is a growing interest in the ligand chemistry of organotellurium(II) compounds [1–8]. Recently the synthesis and crystal structure of 2-(2-pyridyl)phenyl(*p*-ethoxyphenyl)tellurium(II) were reported [9]; this is a potential ligand having two centres of Lewis basicity (Te and N). Since a related ligand is known to react with mercury(II) chloride to give a complex in which only tellurium was coordinated to mercury [10], we decided to examine the reaction of the new ligand with $HgCl_2$. Different behaviour was observed, involving the transfer of organic groups from tellurium and the details are presented below.

Experimental

2-(2-Pyridyl)phenyl(*p*-ethoxyphenyl)tellurium(II) was prepared by a published procedure [9].

Preparation of the complexes. A solution of 2-(2-pyridyl)phenyl(*p*-ethoxyphenyl)tellurium(II) (RR′Te) (0.404 g, 1 mmol) in acetonitrile or ethanol (10 cm^3)

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Table 1

Analytical data for mercury complexes

Compound	Analysis (Found (calcd.) (%))			M.p. (°C)	Colour
	C	H	N		
$HgCl_2(RR'Te)$ [a]	33.7	2.42	1.99	145–147	white
	(33.8)	(2.52)	(2.08)		
$R'HgCl(RTeCl)_2$	36.5	2.40	2.78	150–152	yellow
	(36.3)	(2.52)	(2.82)		

[a] R = 2-(2-pyridyl)phenyl; R′ = *p*-ethoxyphenyl.

Table 2

^{125}Te and ^{199}Hg NMR data [a]

Compound	Solvent	δ(Te)	δ(Hg)
$[HgCl_2 \cdot RR'Te]$	dmso	641.5	–
$[R'HgCl(RTeCl)]$	$CDCl_3$	1323.9	469.7
RR′Te	$CDCl_3$	649.1	–

[a] Te chemical shifts relative to Me_2Te; Hg relative to aqueous $HgCl_2$.

was added to a solution of mercury(II) chloride (0.272 g, 1 mmol) in acetonitrile or ethanol (10 cm^3). The solution was very slightly warmed, and the white precipitate was filtered off, washed with fresh solvent, dried in vacuo and shown to be $[HgCl_2 \cdot (RR'Te)]$.

When the above solution was allowed to evaporate slowly, or refluxed for 45 min, a yellow product, $[R'HgCl \cdot (RTeCl)_2]$, was obtained. The yield in both cases was 60%.

Table 3

^1H NMR Data (ppm vs. TMS)

Compound (solvent)	δ (ppm vs. TMS) [a,b]
RR′Te ($CDCl_3$)	1.45(t,C17), 4.08(q,C16), 6.85(d,C14), 7.05(t,C3), 7.25(m,C4,C5,C8), 7.78(d,C2), 7.85(d,C13), 7.95(2 t,C9,C10), 8.74(d,C11).
HgCl RR′Te (dmso-d_6)	set 1 1.40(t,C17), 4.10(q,C16), 6.95(d,C14), 7.10(d,C5), 7.25(t,C3), 7.45(m,C4,C8), 7.85(d,C13), 8.30(m,C9,C10), 8.70(d,C2). set 2 1.30(t,C17), 3.95(q,C16), 6.85(d,C14), 7.35(d,C13), 7.65(m,C3,C4,C10), 8.05(t,C9), 8.35(d,C5), 8.55(d,C8), 8.75(d,C2), 9.25(d,C11).
$R'HgCl \cdot (RTeCl)_2$ (dmso-d_6)	1.30(t,C17), 3.95(q,C16), 6.85(d,C14), 7.35(d,C13), 7.65(m,C3,C4,C10), 8.25(t,C9), 8.40(d,C5), 8.55(d,C8), 8.70(d,C2), 9.25(d,C11).
($CDCl_3$)	1.40(t,C17), 4.04(q,C16), 6.95(d,C14), 7.18(d,C13), 7.35(t,C3) 7.50(t,C4), 7.60(t,C10), 8.00(t,C9), 8.20(d,C5), 8.25(d,C8), 8.60(d,C2), 8.8(d,C11).

[a] d = doublet; t = triplet; q = quartet; m = multiplet. [b] carbon numbers in parentheses refer to the protons attached to the numbered carbon atoms in ref. 9.

Analytical and physical data. Elemental analyses were by Elemental Microanalysis Ltd., Exeter Road, Oakhampton, Devon EX20 1QA (Table 1). Melting points (uncorrected) were determined with a Gallenkamp electrically heated apparatus. Infrared spectra, for KBr discs and mulls within CsI plates, were recorded on a Perkin Elmer FTIR model 1710 instrument, NMR data (Tables 2 and 3) (^{125}Te, ^{199}Hg, ^{1}H, and ^{13}C) were recorded with a Bruker AC300 spectrometer at 94.7, 53.7, 300, and 75.4 MHz respectively. References were external bis(*p*-ethoxyphenyl) ditelluride in $CDCl_3$ for ^{125}Te (chemical shifts are relative to Me_2Te), external $HgCl_2$ in water for ^{199}Hg and internal Me_4Si for ^{1}H and ^{13}C.

Results and discussion

The reaction of 2-(2-pyridyl)phenyl(*p*-ethoxyphenyl)tellurium(II), RR′Te, with mercury(II) chloride under mild conditions gives a white complex $[HgCl_2 \cdot (RR'Te)]$. The presence of RR′Te is confirmed by the IR spectrum. The complex is sparingly soluble in solvents of low polarity, and so NMR data were obtained with dmso-d_6 solutions. The ^{125}Te NMR spectrum shows a single resonance at 641.5 ppm (vs. Me_2Te), close to that of the free ligand at 649.1 in $CDCl_3$. The small difference in chemical shift almost certainly arises from a solvent effect and not a coordination shift, since coordination shifts are generally much larger (around 50 ppm) and in the opposite direction [5,6], and so the strongly coordinating dmso must have displaced RR′Te from the coordination sphere of mercury. The ^{1}H NMR spectrum of a fresh solution of the complex in dmso-d_6 was similar to that of the free ligand in $CDCl_3$ solution (Table 3), but on standing a second set of resonances developed.

When the reaction between RR′Te and $HgCl_2$ was carried out under more forcing conditions (see Experimental section), a yellow material, more soluble in less polar solvents, was obtained. Its ^{1}H NMR spectrum in dmso-d_6 is identical to the second set of resonances which develop in an aged solution of the white complex in the same solvent. The C/N ratio for the yellow compound is 15/1 (cf. 19/1 for RR′Te), but it is clear from the IR and ^{1}H and ^{13}C NMR spectra that both the 2-(2-pyridyl)phenyl and *p*-ethoxyphenyl groups are present in the molecule. The ^{125}Te NMR spectrum of the yellow complex shows a single resonance at 1323.9 ppm (vs. Me_2Te), a figure well outside the range normally associated with tellurides [11], but well within the range associated with the related phenylazophenyl-*C*,*N*′ tellurium(II) halides e.g. $(C_{12}H_9N_2)TeCl$, δ 1486.5 ppm (vs. Me_2Te in $CDCl_3$) [12]. The formulation $R'HgCl \cdot (RTeCl)_2$ provides an excellent fit to the elemental analysis, and the ratio of the integrals of the R and R′ protons is 1.87, in good agreement with the value of 1.77 calculated for the above formula. Multinuclear NMR and mass spectroscopy provided further confirmation of the correctness of the formulation, $[R'HgCl(RTeCl)_2]$; thus the ^{199}Hg NMR spectrum of the material ($CDCl_3$ solution), accumulated over three days, consisted of a 1/2/1 triplet of 1/2/1 triplets with a central line at δ 469.96 ppm. The relative intensities of the spectral components are inconsistent with coupling to ^{125}Te (7% abundance), but consistent with a major coupling to the equivalent *ortho*-protons of the *p*-ethoxyphenyl group (J(HgH) 370 Hz) and a minor coupling to the equivalent *meta*-protons (J(HgH) 50 Hz); thus there is clear evidence for the transfer of the *p*-ethoxphenyl group from tellurium to mercury. A solution of R′HgCl (prepared by reaction of mercury(II) acetate and phenetole, followed by treatment with lithium chloride) and RTeBr [9] in $CDCl_3$ gave a ^{125}Te resonance at 1306 ppm; as with $[R'HgCl \cdot (RTeCl)_2]$ no Hg–Te coupling was observed, implying that if there is any interaction between the components in solution it must be very weak.

The electron impact mass spectrum of $[R'HgCl(RTeCl)_2]$ was particularly interesting. It is well known that organotellurium compounds and their complexes often undergo thermolysis in the mass spectrometer and true parent ions are rarely seen [13], but useful information may be obtained since in the case of complexes the ligand ions are often dominant. The most abundant ions were RTe^+ (*m/e* 100%, 282) and $RTeCl^+$ (*m/e* 100%, 319), but weak features were noted for R'_2Te^+ (*m/e* 100%, 372), $RR'Te^+$ (*m/e* 100%, 405), $[R_2Te_2Cl]^+$ (*m/e* 100%, 601) and $[R_2Te_2Cl_2]^+$ (*m/e* 100%, 636). The identities of all fragments were confirmed by analysis of the isotopic patterns. There is thus strong evidence for the presence of RTeCl, and it is of interest that the dimer of the species is detectable in the gas phase, and we note that phenylazophenyl-*C,N'* tellurium(II) chloride forms a weak dimer in the solid state [14]. Thermolysis of the yellow complex evidently results in further migrations of the organic groups as evidenced by the observation of ions derived from R'_2Te and RR'Te. The analytical data, multinuclear NMR, and mass spectroscopic data together provide compelling support for the formulation $[R'HgCl(RTeCl)_2]$.

Many years ago organomercury reagents were shown to be effective *trans*-metallation reagents in the presence of inorganic tellurium compounds [15]. We have observed the opposite process which we term "reverse *trans*-metallation". We have encountered many examples of this process, and believe that the phenomenon may have significance in the context of the mechanistic aspects of the organometallic vapour phase epitaxy (MOVPE) of telluride semi-conductors [16]. It is known that triorganotelluronium salts are often labile with respect to reductive elimination of an organic halide [17]. Interestingly, the ^{125}Te Mossbauer quadrupole splittings of telluronium salts and of mercury(II) complexes of simple diorganotellurides are very similar [18], implying some similarity in electronic environment of tellurium in the two cases. Whilst this does not account for the lability of the organic groups, it does suggest that if the salts are labile, the complexes may also be so.

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