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ORGANOTELLURIUM COMPOUNDS AS LIGANDS. SOME COMPLEXES OF PALLADIUM(II) AND PLATINUM(II)

LIN-YING CHIA and WILLIAM R. McWHINNIE
Department of Chemistry, University of Aston in Birmingham, Birmingham B4 7ET (Great Britain)

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Summary

The syntheses and characterisations of six new diaryl telluride complexes of palladium(II) and platinum(II) are reported. It is suggested that the stereochemistry of platinum(II) telluride complexes is determined as much by kinetic factors as by any tendency of tellurium to accept $d\pi$ electrons from platinum. The far infrared spectra of $Pd(Ph_2Te)_2X_2$ (X = Cl, Br) are discussed.

The oxidative addition of two diorganoditellurides to $Pd(PPh_3)_4$ is demonstrated. Dimeric compounds are isolated containing both bridging and terminal RTe groups.

Introduction

Investigations of organotellurium(II) compounds as ligands are relatively sparce. The bulk of information available suggests that they have pronounced class (b) character [1] in the Ahrland, Chatt, Davies sense [2]. There appears to us no particularly good reason to suppose that bonding from metal into empty tellurium *d* orbitals will be a significant feature of the metal to ligand bond, but the contrary view has been expressed [3].

Previous reports have described some diorganotelluride complexes with palladium(II) and platinum(II). Thus for example, $\{[(PhCH_2)_2Te]_2PtCl_2\}$ was reported by Fritzman [4] (solubility in chloroform probably implies *trans* stereochemistry) which, although stable as a solid, is reported to undergo decomposition to platinum, tellurium and dibenzyl in solution. More relevant to the present investigation is Jensen's claim [5] that the reaction of K_2PtCl_4 with diphenyl telluride in aqueous ethanol affords *cis*-$\{Pt(Ph_2Te)_2Cl_2\}$. Chatt and co-workers [6] included some dialkyl telluride complexes of palladium(II) and platinum(II) in their classic series of papers investigating mesomeric and inductive effects in complexes of these metals. The *trans*-bis(dialkyl telluride) complexes $\{(R_2Te)_2PdX_2\}$ will react with Grignard reagents to afford $(R_2Te)_2Pd(R')X$ (R' = Ph, o-tol, o-ClC_6H_4, p-ClC_6H_4; X = halogen). Combining these results with other work with dialkyl sulphide and selenide complexes [8] afforded a trend in the stability of $\{Pd(Et_2M)(R)X\}$ of $M = S < M = Se < M = Te$. The view was again expressed that π-bonding was more important in the selenium and tellurium cases.

Normally, when a diorganoditelluride, R_2Te_2, reacts with a transition metal in a low oxidation state, rupture of the Te—Te bond occurs, e.g. the reaction of $(p\text{-}EtOC_6H_4)_2Te_2$ with $Fe_3(CO)_{12}$ [9,10]. However, some instances are known where the bond remains intact [10].

Our interest in organotellurium derivatives of palladium and platinum arose specifically in the context of an investigation of the reactivity of some thiophen derivatives with ML_2X_2 (M = Pd, Pt; L = Lewis base; X = Cl, Br) and this has determined the choice of compounds studied, also more generally, as part of an effort to map out the ligand properties of organotellurium(II) compounds [1,10].

Experimental and results

Synthesis of organotellurium compounds. Diphenyl telluride was obtained by hydrazine reduction of diphenyltellurium dichloride prepared by the method of Günther [11]. Bis(p-ethoxyphenyl) telluride was prepared by hydrazine reduction of bis(p-ethoxyphenyl)tellurium dichloride obtained by the method of Morgan and Kellett [12]. Bis(p-ethoxyphenyl) ditelluride was prepared by the method of Morgan and Drew [13].

Dithienyl ditelluride. 2-Thienylmercuric chloride [14] (3.5 g, 10 mmol) and tellurium tetrachloride (2.7 g, 10 mmol) were refluxed in 1,4-dioxane (30 ml), for 4 h. The white crystalline mercury(II) chloride—dioxane complex was filtered and, on addition of n-hexane to the filtrate, a white precipitate (2.5 g) was obtained. This material was added to hot ethanol and treated dropwise with an ethanolic solution of hydrazine hydrate until evolution of nitrogen ceased. The mixture was then diluted with water and extracted with ether, The ethereal layer was dried over anhydrous magnesium sulphate and evaporated to dryness to give an orange compound, which recrystallised from ethanol.

Palladium(II) complexes. Dichlorobis(benzonitrile)palladium(II) was prepared by Doyles method [15]. $Pd(PhCN)_2Cl_2$ (0.38 g, 1 mmol) was dissolved in ahydrous benzene (100 ml). The solution was filtered and the appropriate telluride (2 mmol) was added. The solution was shaken for 24 h after which n-hexane was added to afford the chloro complex. The bromo complex was obtained by metathesis with an excess of sodium bromide. No reaction was observed between $Pd(PhCN)_2Cl_2$ and $(p\text{-}EtOC_6H_4)_2Te_2$ or diethienylditelluride under similar conditions.

Platinum(II) complexes. Dichlorobis(benzonitrile)platinum(II) was prepared following Ramberg [16] and reacted with bis(p-ethoxyphenyl) telluride following the procedure outlined for palladium above.

Reactions of tetrakis(triphenylphosphine)palladium with ditellurides. Tetrakis-(triphenylphosphine)palladium was prepared following Coulson [17] and dissolved (1.15 g, 1 mmol) in anhydrous benzene (50 ml) under nitrogen. The appropriate ditelluride $(p\text{-}EtOC_6H_4)_2Te_2$ (or dithienyl ditelluride (1 mmol) was added to afford, immediately, a brown material. The suspension was stirred overnight under nitrogen, then filtered washed with ether and dried over P_4O_{10} in vacuo.

TABLE 1

ANALYTICAL AND CONDUCTIVITY DATA FOR SOME COMPLEXES OF ORGANOTELLURIUM(II) COMPOUNDS

Compound	Colour	M.p. (°C)	Analysis found (calcd.) (%))			Λ_M (10^{-3} *M*, DMF)	λ_{max} (cm^{-1}) (ϵ_{max}) [a]
			C	H	M		
(2-thienyl)$_2$Te$_2$	Orange	88	22.9 (22.9)	1.43 (1.43)	459 (421)		23.8 (63); C_6H_6
[Pd(Ph$_2$Te)$_2$Cl$_2$]	Orange	164	39.8 (38.9)	2.73 (2.70)	742 (740.6)	3.5	24.81 (0.58 × 10^5); C_6H_6
[Pd(Ph$_2$Te)$_2$Br$_2$]	Brown	180	34.1 (34.7)	2.39 (2.41)	— (829.6)	81	—
[Pd{(*p*-EtOC$_6$H$_4$)$_2$Te}$_2$Cl$_2$]	Orange	125	42.3 (41.9)	3.80 (3.93)	919 (916.6)	3.2	23.53 (0.32 × 10^5); C_6H_6
[Pd{(*p*-EtOC$_6$H$_4$)$_2$Te}$_2$Br$_2$]	Brown	105	37.6 (38.2)	3.46 (3.58)	— (1005.6)	89	—
[Pt{(*p*-EtOC$_6$H$_4$)$_2$Te}$_2$Cl$_2$]	Yellow	134	38.1 (38.2)	3.53 (3.58)	— (1005.3)	5.5	26.28 (60); CH_3CN
[Pt{(*p*-EtOC$_6$H$_4$)$_2$Te}$_2$Br$_2$]	Orange-brown	150	34.2 (35.1)	3.31 (3.29)	— (1094.3)	Insoluble	—
[Pd(Ph$_3$P)(2-thienylTe)$_2$]$_2$	Dark brown	145	7.90 [b] (8.09)	—	1625 (1581.2)	2.3	26.25 (0.13 × 10^5); C_6H_6
[Pd(Ph$_3$P)(*p*-EtOC$_6$H$_4$Te)$_2$]$_2$	Dark brown	117	44.5 (47.1)	3.06 (3.81)	— (1733)	3.3	26.25 (0.24 × 10^5); C_6H_6

[a] Longest wavelength electronic transition, measured in solution in the solvent indicated. ϵ_{max} determined from slope of optical density *vs.* concentration graph.

[b] % Sulphur.

TABLE 2

FAR INFRARED SPECTRA (400—40 cm^{-1}) OF $[Pd(Ph_2Te)_2X_2]$ (X = Cl, Br)

$[Pd(Ph_2Te)_2Cl_2]$	$[Pd(Ph_2Te)_2Br_2]$	Assignment [a]
382 w		phenyl w
250 s		ν(PdCl)
295 w(br)		combination (94 + 199)
270 m-s	268(sh)	phenyl t [ν(TePh)]
259 m-s	264 m-s(br)	phenyl t' + ν(PdBr) + phenyl u
229 m	239 m	phenyl u'
199 m	200 w	ν_{as}(PdTe)
184 m	189 w	phenyl x
171 (sh)	178 w	phenyl x'
133 w		δ(PdCl) ?
94 m-s	92 w	
	86 w	

[a] Assignments fllow refs. [20,21].

Addition of n-hexane to the filtrate gave a further batch of product.

Analytical and other data are given in Table 1. Physical data, including low frequency infrared data are given in Table 2.

Infrared spectra were recorded as Nujol mulls using Perkin—Elmer 457 (400—250 cm^{-1}) and 225 (400—200 cm^{-1}) instruments. Spectra in the region 400—40 cm^{-1} were obtained with a Fourier spectrometer (R.I.I.C. FS720/ FS200). The output from the interferometer was computed with an ICL 1605 computer. ^1H NMR spectra were taken with a Varian EA 100D spectrometer using TMS as internal standard. Conductivity measurements were made with a Mullard bridge and molecular weight determinations in benzene were obtained by vapour phase osmometry. Electronic spectral measurements were made with a Unicam SP800 instrument and X-ray powder data were obtained with a Jeol Diffractometer, Model DX-GO-5.

The results of the X-ray investigations indicated possible isomorphism of the chloro/bromo pairs viz: $Pd(Ph_2Te)_2X_2$, $Pd\{(p\text{-}EtOC_6H_4)_2Te\}_2X_2$ and $Pt\{(p\text{-}EtOC_6H_4)_2Fe\}_2X_2$ (X = Cl, Br) [18]. It is also significant that, with the exception of those regions associated with metal—halogen vibrations, the solid state infrared spectra of the chloro/bromo pairs were extremely similar. Thus it is likely that the corresponding chloro and bromo complexes have the same solid state structure. Beer's law was obeyed, in dilute (10^{-3}—10^{-5} *M*) solution in benzene or acetonitrile, by those complexes sufficiently soluble for the determinations to be made. The bromo complexes were insufficiently soluble for the measurements to be carried out (Table 1).

Discussion

The solubility of the diaryl telluride complexes $M(R_2Te)_2X_2$ (M = Pd, Pt; X = Cl, Br, Table 1) in benzene, coupled with the observation of one metal halogen stretching frequency (Tables 2 and 3), provides good evidence for *trans* stereochemistry. It has previously been suggested [3] that the tendency to synthesise *cis* complexes of dialkyl tellurides and platinum(II) could be attributed to sig-

TABLE 3

METAL—HALOGEN STRETCHING FREQUENCIES OF $(p\text{-EtOC}_6H_4)_2Te$ COMPLEXES

Compound	ν(MCl) (cm^{-1})	ν(MBr) (cm^{-1})
$[Pd\{(p\text{-EtOC}_6H_4)_2Te\}_2Cl_2]$	351	
$[Pd\{(p\text{-EtOC}_6H_4)_2Te\}_2Br_2]$		275
$[Pt\{(p\text{-EtOC}_6H_4)_2Te\}_2Cl_2]$	296	

nificant back bonding from platinum to tellurium which would be more favoured in the *cis* isomer [3]. However, a comparison of our results where complexes were formed according to:

$$trans\text{-}PtX_2(NCPh)_2 + 2R_2Te \rightarrow trans\text{-}[PtX_2(R_2Te)_2] + 2PhCN$$

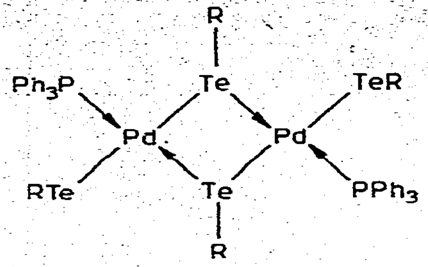
with, say, the method of Jensen [5]:

$$K_2[PtCl_4] + 2Ph_2Te \rightarrow cis\text{-}[PtCl_2(Ph_2Te)_2] + 2KCl$$

implies that kinetic factors determine the initial product in the case of platinum and that it would be unwise to read too much relating to bonding into these observations.

The six new telluride complexes reported in Table 1 are in most respects unremarkable. They have been adequately characterised and the only aspect requiring further discussion is their low frequency infrared data. It is of interest to compare the assignments of the diphenyl telluride complexes with those for dimethyl telluride complexes given by Allkins and Hendra [3]. The assignments of ν_{as}(MX) seems quite comparable to those given for the stretching of non-bridging palladium/platinum halide system generally [3,19]. The rather more full assignments given in Table 2 for $Pd(Ph_2Te)_2X_2$ (X = Cl, Br) follow from earlier work on phenyltellurium compounds [20,21]. For complexes of dimethyl telluride assignments of ν_{as}(PtTe) have been made in the region around 230 cm^{-1} [3]. Comparing the spectrum of free Ph_2Te [20] with those of the complexes, new bands are seen at 229 and 199 cm^{-1} (chloride) and 239 and 200 cm^{-1} (bromide). The bands at 229 and 239 cm^{-1} may arise from the u' vibration of the phenyl group [21]. It is often weak and may, in these cases, have been enhanced by coordination. Previous work does not suggest an obvious assignment for the feature close to 200 cm^{-1} which must therefore be a candidate for assignment as ν_{as}(PdTe). The spectra are consistent with formulation as monomeric *trans* complexes, thus the significant conductivity exhibited by the bromides in DMF probably arises from a solvolysis reaction.

The cleavage of the S—S bond promoted by triphenylphosphine complexes of palladium(0) and platinum(0) is known [22]. We are not aware of accounts of similar reaction involving ditellurides. Hence we report two examples of the reaction, one involving the previously unknown di-2-thienylditelluride, $(C_4H_3S)_2$-Te_2 (Table 1), the other with bis(p-ethoxyphenyl)ditelluride. In both cases brown materials are produced which molecular weight studies indicate to be dimers. The compounds are non-electrolytes in DMF and are reasonably formulated involving both bridging and terminal RTe groups (I).



(I)

We have no information as to whether the oxidative addition goes via a radical or concerted pathway, but both must be regarded as possible.

The reaction of the new compounds with carbon monoxide was investigated. Ditelluride and triphenylphosphine were released, together with metallic palladium: It seems likely that the decomposition follows the following route:

$$[(Ph_3P)(RTe)Pd(RTe)_2Pd(RTe)(PPh_3)] + 2CO \rightarrow 2[(RTe)_2Pd(Ph_3P)CO] \xrightarrow{\text{fast}}$$

$$2\,R_2Te_2 + 2Pd + 2Ph_3P + 2CO$$

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