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Synthesis, Reactions and Ligand Properties of Some New Unsymmetrical Telluride Containing Pyrazole.

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ABSTRACT

Reaction of benzyl tellurocyanate with 1-(2-hydroxyethyl) pyrazole and 1-(2-hydroxyethyl)-3,5-dimethylpyrazole in presence of tri-n-butyl phosphine gave [2-(1-pyrazolyl)ethyl] benzyl telluride(**1**) and [2-(3,5-dimethyl-1-pyrazolyl)ethyl] benzyl telluride(**2**), respectively in moderate yields. Reaction of **1** or **2** with bromine and iodine gave dibromo (*i.e.* **3** and **5**) and diiodo (**4** and **6**) derivatives, respectively. Complex of type [PdCl₂. (**1**)] (**7**) and [PdCl₂. (**2**)] (**8**) were formed in reaction of **1** and **2** with [PdCl₂(PhCN)₂]. Both ligands behave as bidentate ligands. Conductivity measurements in DMSO and DMF indicate that compounds **3**, **4**, **5** and **6** behave as weak electrolytes. IR and NMR data are reported and discussed for all new compounds.

Keywords: Unsymmetrical tellurides, pyrazoles, palladium(II) complexes, Te, N ligands.

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INTRODUCTION

A variety of pyrazole-based ligands have recently been considerable interested in the study for chelating nature and properties of their compounds in design of new pyrazole-based chelating ligands in coordination chemistry [1-5]. Thus, pyrazole ligands such as bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl] ether [3], 1-hydroxymethyl-pyrazole[4] and 1-(2-hydroxyethyl)pyrazole[4,5] have been reacted with transition metal ions to form new type of complexes[3-6].

Our current interest in organotellurocyanates as tellurating agents[7] together with the fact that there is no organotellurium compounds containing pyrazole moieties were reported in the literature, as far as we aware, prompted us to prepare some new unsymmetrical tellurides containing pyrazole. Furthermore, these new tellurides will be used as ligands to prepare new Pd(II) complexes.

EXPERIMENTAL

Physical measurements:

^1H and ^{13}C NMR spectra were recorded on Bruker MW-250 spectrometers with TMS as an internal reference. Infrared spectra were recorded with KBr discs in the range of 4000-200 cm^{-1} on a Pye-Unicam SP-300s infrared spectrophotometer. Microanalysis for carbon, hydrogen and nitrogen was obtained on a Carlo-Ebra EA1-108 Elemental Analyzer. Conductivity measurements were carried out by WTW conductivity meter LBR, using a standard cell with cell constant of 1.0850. The conductivities of DMSO and DMF were $1-2 \times 10^{-8}$ $\text{ohm}^{-1} \text{cm}^{-1}$ and $7-8 \times 10^{-8}$ $\text{ohm}^{-1} \text{cm}^{-1}$, respectively. All melting points were determined by a Gallenkamp melting point apparatus and are uncorrected.

Synthesis:

The experiments were carried out under pure, dry nitrogen. Solvents were dried and saturated with nitrogen and glassware was oven-dried and filled with nitrogen. Benzyl tellurocyanate [8], 1-(2-hydroxyethyl)pyrazole[9], 1-(2-hydroxyethyl)-3,5-dimethylpyrazole [10] and bis (benzonitrile) dichloro palladium(II) [11] were prepared according to literature methods.

[2-(1-Pyrazolyl)ethyl] benzyl telluride (1)

To a stirred solution of 1-(2-hydroxyethyl) pyrazole (1.12g; 10 mmol) and benzyl tellurocyanate (2.45g; 10 mmol) in 50mL of dry THF at room temperature was added tri-n-butyl phosphine (3.03g; 15 mmol) via a syringe. The resulting mixture was stirred at room temperature for 6 h under nitrogen atmosphere. Evaporation of solvent left a yellow liquid, which was subjected to column chromatography on silica gel with hexane as eluent to afford yellow viscous oil (1.32g; 42% yield).

[2-(3, 5-Dimethyl-1-pyrazolyl)ethyl] benzyl telluride (2):

This compound was prepared by reaction of 1-(2-hydroxyethyl)-3, 5-dimethyl pyrazole (1.40g; 10 mmol) with benzyl tellurocyanate (2.45g; 10 mmol) in presence of tri-n-tributyl phosphine (3.03g; 15 mmol) by the same above method. Purification by column chromatography on silica gel gave a semi-solid yellow product in 35% yield, 1.21 g.

[2-(1-Pyrazolyl) ethyl] benzyl tellurium dibromide (3):

To a solution of compound **1** (0.628g ; 2 mmol) in 25 mL of dry diethyl ether was added drop wise with stirring , a solution of bromine (0.76g ; 4.8 mmol) in 25 mL of dry diethyl ether under nitrogen atmosphere. A fine yellow precipitate was formed immediately. Bromine was added in this way until a permanent colour of bromine resulted when an additional drop of bromine was added. When a solvent was allowed to evaporate, a dark yellow precipitate of **3** was obtained. Recrystallization from ethanol gave a yellow solid of pure **3**, 0.87g (92%); m.p. 103°C.

[2-(1-Pyrazolyl) ethyl] benzyl tellurium diiodide (4):

Iodine (0.254g; 1 mmol) in dry ether (30 mL) was added to a well stirred solution of **1** (0.314g; 1 mmol) in 20 mL dry diethyl ether at room temperature. The orange-red crystals which formed in high yield, were collected by filtration, washed with dry diethyl ether and recrystallized from 2-ethoxyethanol to give an orange-red product in 94% yield, 0.533g, m.p. 182°C.

[2-(3, 5-Dimethyl-1-pyrazolyl) ethyl] benzyl tellurium dibromide (5):

This compound was prepared by oxidative addition of bromine to compound **2** using the same conditions for the preparation of **3**. Yellow precipitate was obtained in 88% yield, m.p. 126-128°C.

[2-(3,5-Dimethyl-1-pyrazolyl)ethyl] benzyl tellurium diiodide (6):

This compound was prepared by the reaction of iodine with compound **2** by the same method described for **4**. An orange-red solid was obtained in 75% yield, m.p. 210-212°C.

Dichloro [{2-(1-Pyrazolyl) ethyl] benzyl telluride}] palladium (II) (7):

To a solution of 0.128g (0.33 mmol) of bis(benzonitrile) dichloropalladium(II) in 15 mL of dry toluene was added 0.105g (0.33 mmol) of [2-(Pyrazolyl)ethyl] benzyl telluride(**1**) in 10 mL of dry toluene. The mixture was stirred for 24 h at room temperature under nitrogen atmosphere. Evaporation of toluene yielded an orange solid which was washed with hexane until no yellow colour appeared in washing, and dried *in vacuo* to give orange precipitate of **7** in 78% yield (0.128g), m.p. 165-166°C.

Dichloro [{2-(3,5-dimethyl-1-pyrazolyl)ethyl]benzyl telluride}]palladium(II) (8):

Reaction of compound **2** (0.114g; 0.33 mmol) with [(C₆H₅CN)₂PdCl₂] (0.128g; 0.33 mmol) in dry toluene was carried out by the same method for compound **7** and gave a dark yellow precipitate in 68% yield (0.117g), m.p. 172-173°C.

RESULTS AND DISCUSSION

The reaction of benzyl tellurocyanate with 1-(2-hydroxyethyl)pyrazole and 1-(2-hydroxyethyl)-3,5-dimethylpyrazole in presence of tri-n-butyl phosphine in stirred THF for 6 h gave [2-(1-Pyrazolyl)ethyl] benzyl telluride (**1**) and [2-(3,5-Dimethyl-1-pyrazolyl)ethyl] benzyl telluride (**2**), respectively in moderate yield, Scheme 1. Compounds **1** and **2** are soluble in common organic solvents and deposited tellurium on storage for few days.

Reaction of **1** and **2** with bromine gave the dibromo derivatives **3** and **5**, respectively while their reaction with iodine gave compound **4** and **6** in quantitative yield, Table 1, Scheme 1. Compounds **3** – **6** are solids and soluble in common organic solvents. They are stable in room temperature and deposited tellurium on standing in solution. All compounds **1** – **6** gave a satisfactory CHN analysis, Table 1.

The conductivity data of compounds **3**, **4**, **5** and **6** indicates that they behave as weak electrolytes. An appreciable ion-pairing was noted in all cases, but in DMSO at least their behavior approaches the expected values for 1:1 electrolytes. Other workers [1, 12] have also observed low conductivities in DMF. Thus, it appears more likely that these compounds are extensively associated in DMF solution, Table 2.

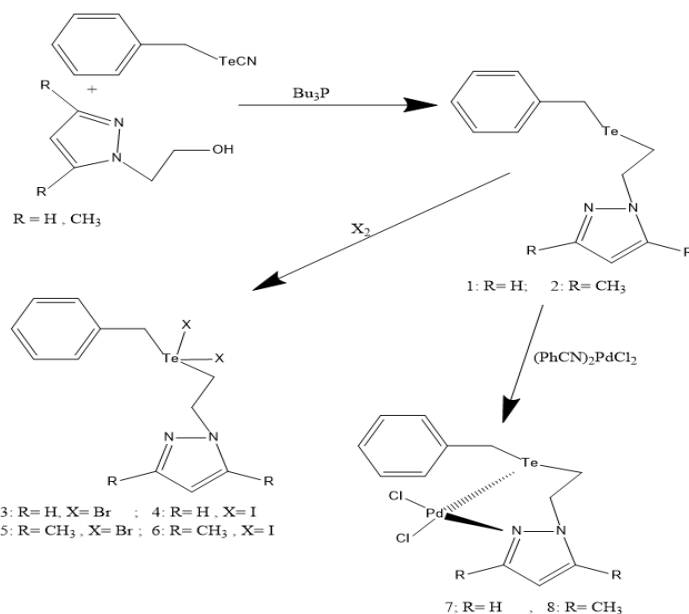
¹H NMR spectra for compounds **1** and **2** are a similar pattern except dimethyl of pyrazolyl groups. Compound **1** shows signals corresponding to methylene, pyrazole and aromatic protons in exact ratio. As can be seen from ¹H NMR data, Table 1, the chemical shifts of methylene protons (*i.e.* Ph-CH₂-Te and Te-CH₂-CH₂), for compounds **3-6**, depend on the size and electro negativity of the halogen attached covalently to tellurium atom. These observations agree well with previous works [12-14].

Reaction of compounds **1** and **2** with $[(C_6H_5CN)_2PdCl_2]$ afforded complexes $PdCl_2(C_{12}H_{14}N_2Te)$ (**7**) and $[PdCl_2(C_{14}H_{18}N_2Te)]$ (**8**), respectively, in the benzonitrile molecules. Furthermore, the spectra of **7** and **8** reveal the presence of $\nu(Te-CH_2)$ bands in the range of $470 - 485\text{ cm}^{-1}$.

In conclusion we prepared a new series of unsymmetrical tellurides good yields, Scheme1. The IR spectra of **7** and **8** show no ν_{CN} band due to containing pyrazole moieties for the first time in literature, as far as we are aware. These unsymmetrical tellurides can act as bidentate ligands with Pd(II) salts.

Table 1: Physical and analytical data for compounds 1 – 8.

Comd.	Colour	M.p.(°C)	Yield (%)	Analysis(%) ^a			¹ H NMR; CDCl ₃ TMS= Oppm
				C	H	N	
1	Yellow	Viscous oil	42	45.73 (45.92)	4.05 (4.50)	8.84 (8.93)	2.23(t, 2H, Te-CH ₂ -CH ₂); 2.78(t, 2H, CH ₂ -CH ₂ -N); 3.38(s, 2H, Ph-CH ₂ -Te); 6.12(t, 1H, Py); 7.10-7.32(m, 7H, Ph+Py).
2	Yellow	Semi-solid	35	49.32 (49.18)	5.11 (5.31)	7.98 (8.19)	2.25(t, 2H, Te-CH ₂ -CH ₂); 2.76(t, 2H, CH ₂ -CH ₂ -N); 2.86(s, 6H, CH ₃); 3.36(s, 2H, Ph-CH ₂ -Te); 5.56(s, 1H, Py); 7.08-7.12(m, 5H, Ph-H).
3	Yellow	103	92	30.31 (30.43)	3.03 (2.98)	5.76 (5.91)	2.78(t, 2H, Te-CH ₂ -CH ₂); 2.74(t, 2H, CH ₂ -CH ₂ -N); 4.18(s, 2H, Ph-CH ₂ -Te); 6.11(t, 1H, Py); 7.10-7.21(m, 5H, Ph-H); 7.31(d, 2H, Py-H).
4	Orange-red	182	94	24.89 (25.39)	2.35 (2.49)	4.76 (4.93)	2.83(t, 2H, Te-CH ₂ -CH ₂); 2.73(t, 2H, CH ₂ -CH ₂ -N); 4.30(s, 2H, Ph-CH ₂ -Te); 6.12(t, 1H, Py); 7.10-7.21(m, 5H, Ph-H); 7.30(d, 2H, Py-H).
5	Yellow	126-128	88	33.46 (33.52)	3.57 (3.62)	5.34 (5.58)	2.23(t, 2H, CH ₂ -CH ₂); 2.74(t, 2H, CH ₂ -CH ₂ -N); 2.87(s, 6H, CH ₃); 4.11(s, 2H, Ph-CH ₂ -Te); 5.58(s, 1H, Py); 7.08-7.12(m, 5H, Ph-H).
6	Orange-red	210-212	75	27.83 (28.23)	2.85 (3.05)	4.61 (4.70)	2.24(t, 2H, CH ₂ -CH ₂); 2.73(t, 2H, CH ₂ -CH ₂ -N); 2.88(s, 6H, CH ₃); 4.37(s, 2H, Ph-CH ₂ -Te); 5.56(s, 1H, Py); 7.09-7.14(m, 5H, Ph-H).
7	Orange	165-166	78	28.84 (29.34)	2.75 (2.87)	5.57 (5.70)	2.23(t, 2H, Te-CH ₂ -CH ₂); 2.78(t, 2H, CH ₂ -CH ₂ -N); 3.38(s, 2H, Ph-CH ₂ -Te); 6.12(t, 1H, Py); 7.10-7.32(m, 7H, Ph+Py). Not
8	Dark Yellow	172-173	68	32.13 (32.38)	3.31 (3.49)	5.36 (5.40)	2.25(t, 2H, CH ₂ -CH ₂); 2.76(t, 2H, CH ₂ -CH ₂ -N); 2.86(s, 6H, CH ₃); 3.36(s, 2H, Ph-CH ₂ -Te); 5.56(s, 1H, Py); 7.08-7.12(m, 5H, Ph-H).



Scheme 1: Synthesis of some new benzyl tellurides containing pyrazole moieties and their complexes with palladium salts

Table 2: Molar conductance for compounds 3 – 6 in DMSO and DMF solutions

Compounds	Δ_M (DMSO)	Δ_M (DMF)
3	26.52	58.85
4	29.45	60.23
5	25.63	57.19
6	30.03	60.21

 Λ_0 is in $S\text{ cm}^2\text{ mol}^{-1}$.

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