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Preliminary communication

SYNTHESIS AND LIGAND PROPERTIES OF $Te(CH_2CH_2C_6H_5)_2$: ^{125}Te NMR AS A PROBE OF *cis—trans* ISOMERISM IN $PtCl_2[Te(CH_2CH_2C_6H_5)_2]_2$

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Summary

The new dialkyl telluride $Te(CH_2CH_2C_6H_5)_2$ has been prepared by alkylation of Na_2Te with the corresponding alkyl bromide. The resulting slightly air-sensitive liquid telluride can be converted to a stable diiodide by oxidation and forms stable coordination complexes with palladium and platinum dichlorides. The geometries of these complexes ($MCl_2[Te(CH_2CH_2C_6H_5)_2]_2$; M = Pd, Pt) have been studied by far-infrared and Raman spectroscopy. The Pt complex was also studied by ^{125}Te NMR spectroscopy, a useful probe for observing *cis—trans* isomerization in such complexes, and we report here the first Te-metal coupling constants for such complexes ($J(^{125}Te—^{195}Pt)$ *cis*, 900 Hz; *trans*, 544 Hz).

The ligand properties of diorganotellurides have been of considerable recent interest [1,2]. We recently reported the synthesis of several new dialkyl tellurides and the first crystal-structure determination of a transition metal coordination complex with such a ligand, *trans*-$Pd(SCN)_2(Te[CH_2CH_2CH_2Si(CH_3)_3]_2)_2$ [1]. The new dialkyl telluride $Te(CH_2CH_2C_6H_5)_2$, prepared by alkylation of Na_2Te [1], has been isolated as a moderately air-sensitive liquid (75% yield, b.p. 102°C/0.1 mmHg, n^D 1.6288) [3]. Iodine oxidation of this product in ether gave the diiodide ($TeI_2(CH_2CH_2C_6H_5)_2$, m.p. 103°C), a reaction typical of diorganotellurides [4]. Reaction of the telluride with methanolic solutions of K_2MCl_4 (M = Pd, Pt) gave the corresponding $MCl_2[Te(CH_2CH_2C_6H_5)_2]_2$ complexes (M = Pd, m.p. 101°C (recryst. from toluene); M = Pt, m.p. 126°C (recryst. from toluene)).

The palladium complex was assigned a *cis* configuration in the solid state on the basis of two ν(Pd—Cl) bands, characteristic of C_{2v} symmetry [5], observed in its far-infrared spectrum (285, 305 cm^{-1}). Although the *trans* geometry is the most common for PdX_2L_2 complexes [1,5], a number of *cis* com-

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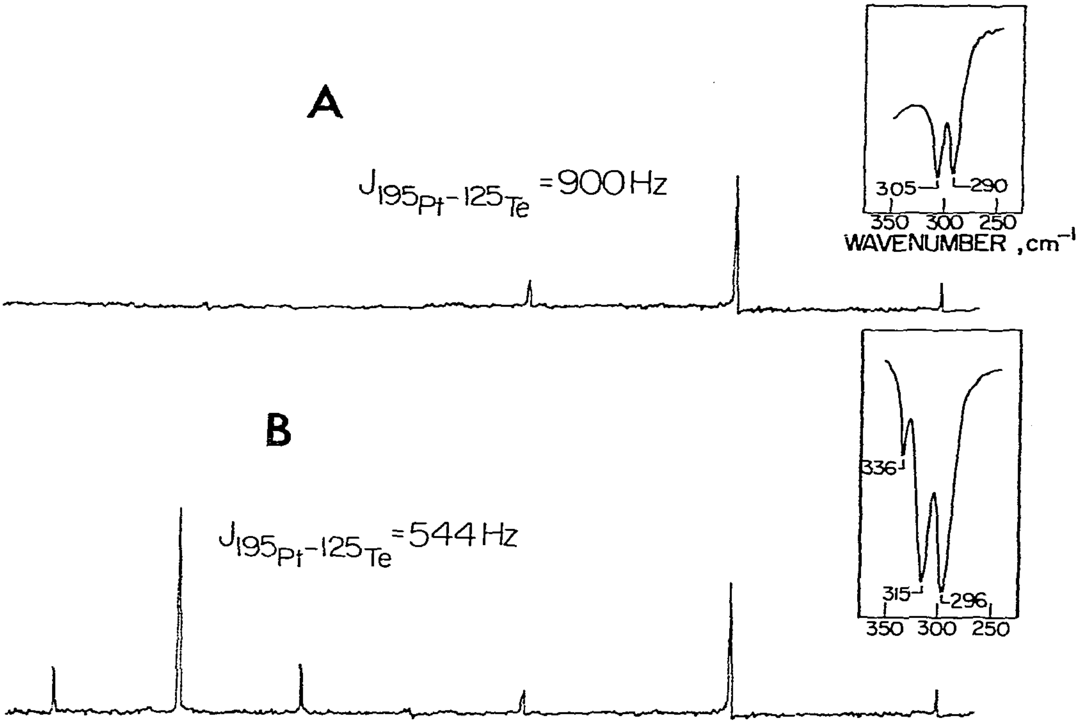

Fig. 1. ^{125}Te NMR and far-infrared spectra of $PtCl_2[Te(CH_2CH_2C_6H_5)_2]_2$; (a) fresh CH_2Cl_2 solution, (b) aged (1 h) CH_2Cl_2 solution.

plexes have been reported [6]. As expected for C_{2v} symmetry, coincident ν(Pd—Cl) bands are observed in the Raman spectrum [7].

The complex readily dissolves in CH_2Cl_2 to give a solution whose far-infrared spectrum indicates that complete isomerization to the *trans* isomer has occurred ($\nu(Pd—Cl)_{asym}$ 348 cm^{-1}). The complex is rather insoluble in benzene at room temperature but readily dissolves on warming to give a dark red solution whose far-infrared spectrum also indicates the presence of only the *trans* isomer ($\nu(Pd—Cl)_{asym}$ 350 cm^{-1}). The $\nu(Pd—Cl)_{sym}$ band occurs at 305 cm^{-1} in the Raman spectrum, noncoincidence of these absorptions being expected for D_{2h} symmetry [7].

The Pt complex was also formulated in the solid state as the *cis* isomer (far infrared and Raman: ν(Pt—Cl) 305, 290 cm^{-1}) (Fig. 1). The ^{125}Te NMR spectrum of a fresh CH_2Cl_2 solution (Fig. 1A) showed initially a set of 3 signals (δ –468.8 ppm upfield from $Te(S_2CNEt_2)_2$ [8], $J(^{125}Te—^{195}Pt)$ 900 Hz). The central signal is due to ^{125}Te nuclei bonded to Pt atoms without a nuclear spin, and the two satellites result from ^{125}Te bound to ^{195}Pt (natural abundance 33.7%, $S = 1/2$). After standing for about 1 h, however, the solution gave a spectrum (Fig. 1B) that showed a second set of 3 lines downfield from the first (δ –423.6 ppm) with a smaller $J(^{125}Te—^{195}Pt)$ (544 Hz). The free ligand exhibits a singlet at –556.6 ppm. The downfield shifts observed here upon coordination of the telluride ligand (i.e., 133 ppm (*trans* isomer), 89.8 ppm (*cis* isomer)) are comparable to the value recently reported [9] for *p*-tolylTeP(t-Bu)$_2$Ni(CO)$_3$ (i.e., a downfield shift of 146 ppm upon coordination of the tellurium ligand). The spectral changes observed for the Pt complex are consistent with a partial *cis* to *trans* isomerization of the complex, a phenomenon well established for Pt and Pd phosphine complexes (e.g., ^{31}P NMR [10] and dipole moment [11] studies). Indeed, the far-infrared spectrum of the aged CH$_2$Cl$_2$ solution (Fig. 1B) showed the presence of a new band at 336 cm^{-1} in addition to the lower-energy doublet assigned to the ν(Pt—Cl) of the initial *cis* complex. The singlet character and higher energy of this new band are both consistent with its assignment as the $\nu(\text{Pt—Cl})_{asym}$ of the *trans* isomer [5]. The *cis* isomer could not be thermally isomerized in the solid state and could be recovered isomerically pure by recrystallization from toluene (2 g dissolved in 75 ml of hot toluene, filtered, concentrated to 35 ml, and cooled in a freezer, gave 1.6 g of yellow crystals). A 0.05 *M* solution of this complex (*cis* in the solid state) could, however, be prepared by dissolving the solid in hot toluene and allowing the solution to cool to room temperature. The ^{125}Te NMR spectrum of this solution shows one triplet, characteristic of a *trans* configuration (Fig. 2). The far-infrared spectrum supports the presence of only the *trans* isomer in this solution, one ν(Pt—Cl) band at 337 cm^{-1} being observed (Fig. 2; the high-energy shoulder on this band is due to solvent, the spectrum of a benzene solution giving a sharp, symmetrical band at 335 cm^{-1}). The Raman spectrum of the toluene solution shows one ν(Pt—Cl) at 323 cm^{-1}.

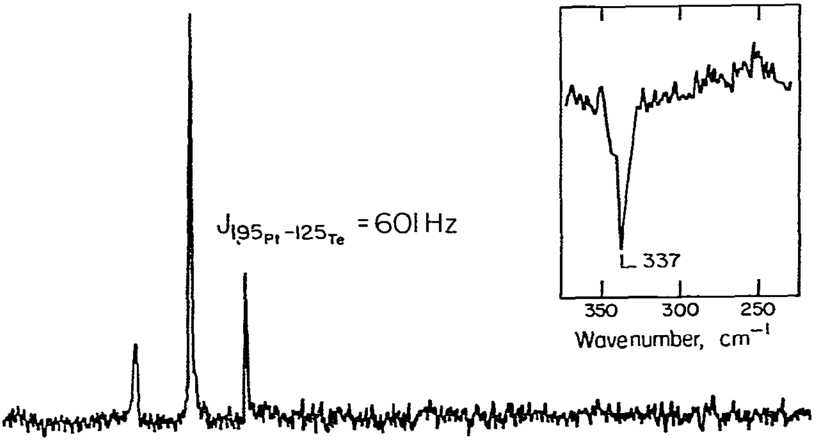

Fig. 2. ^{125}Te NMR and far-infrared spectra of 0.05 *M* solution of PtCl$_2$[Te(CH$_2$CH$_2$C$_6$H$_5$)$_2$]$_2$ in toluene.

We are continuing our investigation of such isomerization in metal complexes with organotellurium ligands by infrared, Raman, and multinuclear NMR studies as well as dipole moment measurements.

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