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A platinum(II) phosphine complex containing the $OTeF_5^-$ ligand

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Abstract

Although the pentafluorooxotellurate(VI) and phosphine(III) ligands were believed to be mutually incompatible, the reaction of $HOTeF_5$ with *cis*- or *trans*-$[PtCl_2(PEt_3)_2]$ readily affords the air-sensitive yellow *cis*-$[Pt(OTeF_5)_2(PEt_3)_2]$ (**1**) which has been characterised by IR spectroscopy and multinuclear NMR techniques.

Keywords: Teflate ligand; Platinum(II) phosphine complex; NMR spectroscopy; IR spectroscopy

1. Introduction

The pentafluorooxotellurate(VI) or teflate ($OTeF_5$) ligand, which has an electronegativity comparable to that of fluoride [1], is well established as a ligand in Main Group and high oxidation state transition-metal chemistries [2]. Investigations of its chemistry with low-valent transition metals have been limited; characterised complexes include $[Mn(CO)_5(OTeF_5)]$ [3], $[Pt(nbd)(OTeF_5)_2]$ (nbd = norbornadienyl) [4], $[Pd(C_6H_5CN)_2(OTeF_5)_2]$ [4] and $[Zn(PhNO_2)_n(OTeF_5)_2]$ ($n = 2, 3$) [5]. We are currently investigating low-valent and organometallic transition metal fluoride complexes [6,7] and are investigating the fluoride/teflate analogy in these lower valent metal complexes. Stable $[Pt(PR_3)_2FX]$ (X = Cl, Br, Me) complexes [8,9] have been reported, but the only report [4] of an attempt to prepare analogous platinum(II) phosphine/teflate complexes describe decomposition and the generation of metallic deposits, suggesting that the teflate ligand is unsuitable for phosphine-containing metal complexes. Here, we report that, with a suitable choice of ligand, phosphine-containing metal–teflate complexes are stable.

2. Experimental details

cis- and *trans*-Platinum dichlorobis(triethylphosphine) and *cis*-platinum dichlorobis(triphenylphosphine) (Aldrich Chemical Co. Ltd.) were used as supplied. CD_2Cl_2 was purified, dried, transferred under vacuum to a glass ampoule fitted with a Young's greaseless tap and degassed immediately prior to use. $HOTeF_5$ [10] and *cis*-platinum dimethyl bis(triethylphosphine) [11] were prepared using literature methods.

Analysis of the reactions was carried out by IR spectroscopy on a Digilab FTS40 spectrometer and by ^{19}F, ^{31}P, ^{125}Te and ^{195}Pt NMR spectroscopies on a Bruker AM-300 NMR spectrometer at 282.41, 121.50, 94.69 and 64.52 MHz, respectively, with 5 mm and 10 mm bore selective and broadband probes. NMR chemical shifts are reported as positive to high frequency of 85% H_3PO_4 (for ^{31}P), CCl_3F (for ^{19}F), neat Me_2Te (for ^{125}Te) and Na_2PtCl_6 in D_2O (for ^{195}Pt). In typical experiments, the platinum reagents (ca. 2 mmol) were loaded in a dry box into pre-fluorinated 4 mm o.d. (0.5 mm wall thickness) FEP tubes (Production Techniques Ltd., Fleet, Hampshire, UK) and evacuated on a metal vacuum line. A four-fold molar excess of $HOTeF_5$ (ca. 2 g, 8 mmol) and CD_2Cl_2 (ca. 10 cm^3) were distilled into the tube under static vacuum and the tube allowed to warm slowly to room temperature with occasional venting to remove HCl or CH_4, affording either clearly yellow solutions or rapid decomposition and the production of platinum mirrors (see below). Solvent and excess teflic acid were removed in vacuo to leave yellow air-sensitive crystalline solids from the clear yellow solutions which were manipulated in the dry box or redissolved in CD_2Cl_2, sealed as described previously [12] and used for NMR studies.

3. Results and discussion

As reported previously [4], the reaction of *cis*-$[PtCl_2(PPh_3)_2]$ with teflic acid ($HOTeF_5$) in dichlorome-

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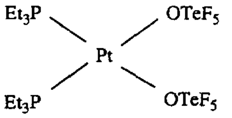
thane at room temperature yielded a platinum mirror and triphenylphosphine oxide within 5 min. However, the reaction between $HOTeF_5$ and either *cis*- or *trans*-$[PtCl_2(PEt_3)_2]$ occurred rapidly in dichloromethane with the evolution of HCl, but without decomposition. After removal of the solvent and excess teflic acid, the same air-sensitive yellow solid **1** was obtained for both reactions, *cis*-/*trans*-isomerisation for $[PtL_2X_2]$ complexes in solution being well documented [13]. The IR spectrum of this solid exhibited bands typical of coordinated teflate and phosphine ligands, but no Pt–Cl stretches. Of particular interest is the magnitude of the value of ν(Te–O), which in related complexes is known to vary consistently with the degree of covalency of the metal–teflate bond [14]. The value of ν(Te–O) for **1** at 835 cm^{-1} is higher than those for the only two previously reported Group 10 teflate complexes, $[Pt(nbd)(OTeF_5)_2]$ and $[Pd(C_6H_5CN)_2(OTeF_5)_2]$ (804 and 800 cm^{-1}, respectively) [4], but is lower than those for highly ionic metal teflate complexes such as $[Mn(CO)_5(OTeF_5)]$, $[Re(CO)_5(OTeF_5)]$ and $[CpFe(CO)_2(OTeF_5)]$ (848, 838 and 852 cm^{-1}, respectively) [3]. Elemental analyses, although notoriously unreliable for metal–teflate complexes as a consequence of hydrolysis, confirmed the expected P/C/H/F ratio of 2:12:30:10. The product has limited solution stability (see below) which precluded all attempts to grow crystals suitable for X-ray analysis and, therefore, complete characterisation was achieved in solution by NMR spectroscopies.

The $^{31}P\{^1H\}$ NMR spectrum showed only a singlet (δ 17.75 ppm) with ^{195}Pt satellites (3586 Hz), while the ^{195}Pt NMR spectrum showed only a triplet (δ -4277 ppm) with the same platinum–phosphorus coupling, which indicates a *cis*-PtP_2 formulation [15]. The ^{125}Te NMR spectrum displayed the expected overlapping doublet of quintets centred at δ 600 ppm. No coupling between ^{125}Te and ^{195}Pt was observed, as noted previously for $[Pt(nbd)(OTeF_5)_2]$ [4], which has been accounted for by rapid intermolecular exchange of the weakly coordinated teflate ligands. The ^{19}F NMR spectrum showed a well-separated, almost first-order, AB_4 spectrum, with ^{125}Te satellites typical [2–5] of coordinated $OTeF_5$ ligands. This could be simulated by $\delta F_A = -36.5$ ppm, $\delta F_B = -46.1$ ppm, $^2J(F_AF_B) = 182$ Hz, $^1J(TeF_A) = 3228$ Hz and $^1J(TeF_B) = 3562$ Hz ($R = 0.067$) [1]. Like the magnitude of the value of ν(Te–O), the value of R affords an insight into the covalency of the metal–teflate bond [14]. The ^{19}F NMR spectrum, particularly R, suggests that the oxygen–platinum bond is highly ionic, and supports the absence of ^{125}Te–^{195}Pt coupling and the IR data; i.e. the O–Pt bond is more ionic than that in $[Pt(nbd)(OTeF_5)_2]$ ($R = 0.090$) and $[Pd(C_6H_5CN)_2(OTeF_5)_2]$ ($R = 0.092$) [4], and less ionic than that in $[Mn(CO)_5(OTeF_5)]$ ($R = 0.046$), $[Re(CO)_5(OTeF_5)]$ ($R = 0.040$) and $[CpFe(CO)_2(OTeF_5)]$ ($R = 0.040$) [3]. These data indicate a single product from both reactions, with two equivalent phosphorus atoms bound to platinum, with NMR chemical shifts and coupling constants consistent with the *cis*-$[Pt(PEt_3)_2(OTeF_5)_2]$ formulation.

This *cis*-$[Pt(PEt_3)_2(OTeF_5)_2]$ is stable indefinitely as a solid or in solution at -196 °C, but decomposes slowly (days) in solution at room temperature. The decomposition was followed by NMR spectroscopies. A solution of **1** in CD_2Cl_2 left to stand at room temperature for a few hours showed a second triplet in the ^{195}Pt NMR spectrum at δ -4285 ppm and a related singlet at δ 17.6 ppm in the $^{31}P\{^1H\}$ NMR spectrum [$^1J(PtP) = 3621$ Hz], both still typical of the *cis*-PtP_2 formulation. These resonances gradually increased until they represented > 50% of the species in solution before further decomposition and the precipitation of an insoluble black solid. Similarly, after a few hours in solution at room temperature, the ^{19}F NMR spectrum had changed and now consisted of at least three overlapping AB_4 spectra, only one of which was due to **1**. These NMR data suggest that the high ligand lability of **1** ultimately results in isomerisation to **2**, which contains both the *cis*-PtP_2 and two $OTeF_5^-$ units, as a further example of the cationic bridged Pt d^8 species $[L_2Pt(\mu^2\text{-}X)_2PtL_2]^{2+}$ (teflate as a bridging ligand is well established for coordinatively unsaturated low-valent metal species) [17], with free $-OTeF_5^-$ as the counterion.



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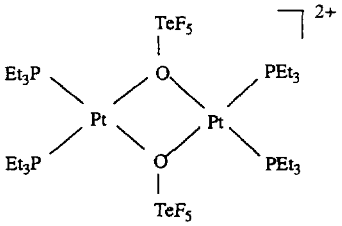

2

The substitution of the methyl groups by the teflate ligand is a convenient synthetic route to low-valent metal teflate complexes [4]. We were interested to see if this could also be applied in platinum–phosphine systems. The reaction of *cis*-$[Pt(CH_3)_2(PEt_3)_2]$ with $HOTeF_5$ occurs rapidly below 0 °C, producing a clear orange solution accompanied by the evolution of methane which was readily identified from its gas-phase IR spectrum. However, as the reaction mixture was warmed further, further methane was generated along with a platinum mirror. Since the final anticipated product, *cis*-$[Pt(OTeF_5)_2(PEt_3)_2]$, has stability in solution, we can only surmise that the intermediate, $\{Pt(OTeF_5)(CH_3)(PEt_3)_2\}$, has a very limited stability. This is in marked contrast to platinum–fluoride chemistry, where *cis*-$[PtF(CH_3)(PEt_3)_2]$ has not only been prepared and characterised, but also used in further synthetic chemistry at the metal centre [9]. We note that, in the reactions of $HOTeF_5$ with other multimethylated metal derivatives, such as $[Hg(CH_3)_2]$ [18],

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[1] Degenerate AB_4 spectra can be analysed by the method of Harris and Packer where the exact appearance of the spectra is dependent upon the parameter R where $R = J(AB)/\delta(AB)$, and where $J(AB)$ is the coupling constant between axial and equatorial fluorines and $\delta(AB)$ is their chemical shift difference (both parameters in Hz) [16].

[$SnCl(CH_3)_3$] [19] or [$Si(CH_3)_4$] [19], there is no evidence for the substitution of more than one methyl group.

4. Conclusions

Contrary to previous results, the pentafluorooxotellurate(VI) and phosphine ligands are not mutually incompatible in transition-metal complexes. A highly ionic, stable, *cis*-[$Pt(OTeF_5)_2(PEt_3)_2$] has been prepared and characterised in the solid state and in solution. Further work on other transition-metal/phosphine/teflate systems is in progress.

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