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Oxidative Addition of Ph_2TeCl_2 to a Dimethylplatinum(II) Complex: Effects of Secondary Bonding in the Platinum–Tellurium Products

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In the first example of oxidative addition of tellurium–halide bonds to a transition-metal complex, Ph_2TeCl_2 reacts with [$PtMe_2$(bu_2bpy)], **1**, bu_2bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine, to give an organoplatinum(IV) complex that can be formulated as an ionic diphenyl telluride complex [$PtClMe_2(TePh_2)(bu_2bpy)$]Cl or as a neutral chlorodiphenyltelluryl complex [$PtClMe_2(TePh_2Cl)(bu_2bpy)$]; the complex contains an unusually long Te···Cl bond length of 3.43 Å. The weakly bound chloride ligand is easily removed by reaction with AgO_3SCF_3 to give the cationic complex [$PtClMe_2(TePh_2)(bu_2bpy)$]($CF_3SO_3$) in which the triflate anion is not coordinated to tellurium. This complex reacts with a second 1 equiv of AgO_3SCF_3 to give the aqua complex [$PtMe_2(OH_2)(TePh_2..O_3SCF_3)(bu_2bpy)$]($CF_3SO_3$), in which a triflate anion forms secondary bonds with both the aqua and $TePh_2$ ligands. In these platinum(IV) complexes, the magnitude of the coupling constant ^1J(PtTe) is strongly influenced by the presence of the weakly bonded Te···X groups.

Introduction

There is increasing use of organotellurium reagents in organic synthesis[1] and in materials chemistry,[2] and some of the reactions involved are efficiently promoted by transition-metal complex catalysts or reagents.[3] Dialkyl and diaryl tellurides (R_2Te) are known to coordinate to many transition metals.[4] Since many transition-metal-promoted reactions involve bond activation by oxidative addition, it is surprising that the oxidative addition of Te−X (X = H, Me, halogen, etc.) bonds to transition-metal centers is relatively unexplored. The first example of an oxidative addition of a Te−C bond of diorganyl tellurides to group 10 transition-metal complexes [$M(PEt_3)_n$] (M = Pt, Pd, Ni; n = 3, 4) to give [$MR(TeR)(PEt_3)_2$] was reported in 1997[5] and was followed by reports on the oxidative addition of Te−M bonds (M = Si, Ge, Sn) of RTe−MR_3 to [$Pt(PEt_3)_n$] to give *trans*-[Pt(TeR)(MMe_3)($PEt_3)_2$][6] and of ($Me_2SnTe)_3$ with [$PtMe_2$(bu_2bpy)], **1** (bu_2bpy = 4,4′di-*tert*-butyl-2,2′-bipyridine), to give [$PtMe_2(TeSnMe_2TeSnMe_2)(bu_2bpy)$].[7] No studies on the oxidative addition of tellurium−halogen bonds to transition-metal complexes appear to have been reported, and there are very few compounds of platinum(IV) with Pt−Te bonds.[4−7] This paper describes the oxidative addition reaction of Ph_2TeCl_2 with [$PtMe_2$(bu_2bpy)], **1** (bu_2bpy = 4,4′−di-

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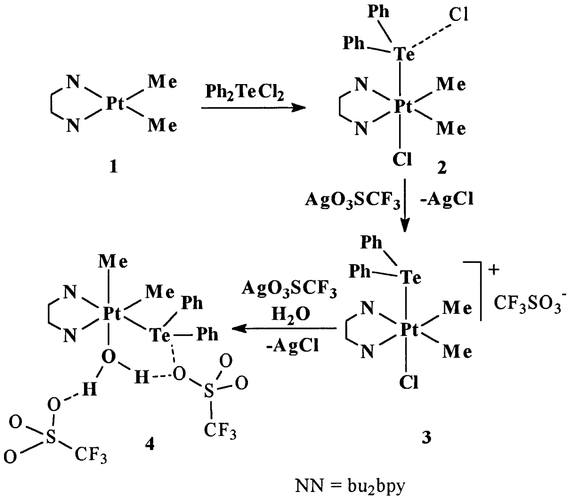
Scheme 1



tert-butyl-2,2′-bipyridine), and the structure and chemistry of the platinum(IV) complex product.

Results

Oxidative Addition Reaction. The tellurium(IV) derivative Ph_2TeCl_2 reacted rapidly with [$PtMe_2(bu_2bpy)$], **1**, to give the air-stable platinum(IV) complex [$PtClMe_2(TePh_2\cdots Cl)(bu_2bpy)$], **2**, by trans oxidative addition of the Te−Cl bond of Ph_2TeCl_2 to the platinum(II) center of complex **1** (Scheme 1). There was an associated change in color from the intense orange-red of **1** to the light yellow of **2**. Unsuccessful attempts were made to synthesize some related complexes. Thus, the reaction of complex **1** with $TeCl_4$ gave a complex mixture of products, while complex **1** failed to react with Ph_3TeCl. Reaction of **1** with Ph_2SeCl_2 yielded the platinum(IV) product [$PtCl_2Me_2(bu_2bpy)$] as a result of trans chlorination, identical to the product formed by direct reaction of complex **1** with chlorine.

The ^1H NMR spectrum of complex **2** contained a single methylplatinum resonance, with coupling constant $^2J(PtMe) = 65$ Hz in the expected range for a methylplatinum(IV) complex with methyl group trans to nitrogen.[8] The symmetry of complex **2**, arising from trans oxidative addition, was evident by the presence of only three aromatic resonances and one one *tert*-butyl resonance for the bu_2bpy ligand. The presence of a Pt−Te bond was demonstrated by the observation of the long-range coupling constant $^3J(TeMe) = 14$ Hz to the methylplatinum protons and by the ^{125}Te NMR spectrum, which contained a single resonance at $\delta(Te) = 693$, with $^1J(PtTe) = 350$ Hz.

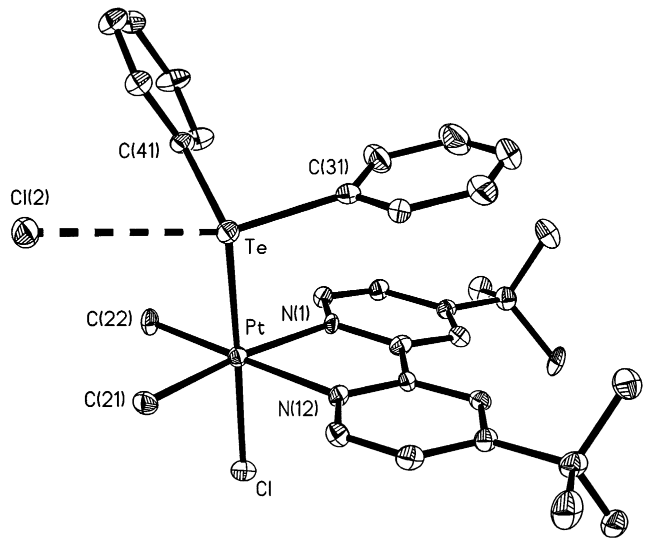


Figure 1. View of the molecular structure of **2**. The secondary bond Te···Cl is indicated by a dashed line.

Table 1. Comparison of Selected Bond Distances (Å) and Angles (deg) for Complexes **2**−**4**

param	**2** (X = Cl)	**3** (X = Cl)	**4** [X = O(23)]
Pt−X	2.365(1)	2.358(3)	2.188(4)
Pt−Te	2.5730(5)	2.5734(7)	2.5871(3)
Pt−N(1)	2.169(5)	2.130(8)	2.084(3)
Pt−N(12)	2.163(4)	2.116(8)	2.149(3)
Pt−C(21)	2.077(6)	2.08(1)	2.046(5)
Pt−C(22)	2.077(5)	2.09(1)	2.069(4)
Pt−Te−C(31)	99.4(1)	104.9(3)	108.43(8)
Pt−Te−C(41)	109.6(1)	102.8(3)	106.3(1)
C(31)−Te−C(41)	118.8(5)	102.8(4)	95.6(1)
Te−Pt−X	174.76(4)	172.74(7)	91.4(1)

The structure of complex **2** is shown in Figure 1 with relevant bond parameters listed in Table 1. It confirms the trans oxidative addition to give an octahedral platinum(IV) complex, with chloride and tellurium atoms mutually trans. The bond length Pt−Te = 2.5730(5) Å, with Te trans to Cl, is shorter than that in the only other platinum(IV)−tellurium-bonded complex [$PtMe_2(Ph_2SnTe)_2(bu_2bpy)$)], in which Te is trans to methyl and has Pt−Te = 2.719(1) Å.[7] Most known complexes with platinum−tellurium bonds contain square planar platinum(II) in combination with R_2Te or RTe^- ligands, and the Pt−Te distances range from 2.51 to 2.76 Å, determined mostly by the nature of the trans ligand.[5,6,9−12] The shortest is found in [$PtCl_2(MeSCH_2CH_2TeAr)$)][12] [Pt−Te trans to chloride = 2.514(1) Å], and the longest, in *trans*-[$Pt(4-PhC_6H_4Te)(SiMe_3)(PEt_3)_2$][6] [Pt−Te trans to silyl = 2.764(2) Å].

Complex **2** contains a very long Te−Cl distance of 3.43 Å, but this distance is shorter than the sum of the van der Waals radii of about 3.9 Å. For comparison, the terminal and bridging TeCl distances in [Te_2Cl_{10}]$^{2-}$ average 2.45 and 2.82 Å, respectively.[12] The stereochemistry at tellurium in **2** is unusual. One phenyl group of the $TePh_2\cdots Cl$ group stacks between the N(12) and N(1) pyridyl rings with intercentroid distances of 4.08 and 4.20 Å, respectively, and the associated angle Pt−Te−C(31) = 99.4(1)°, presumably distorted from tetrahedral to allow the aryl−aryl attraction. The other angle Pt−Te−C(41) = 109.6(1)° is close to

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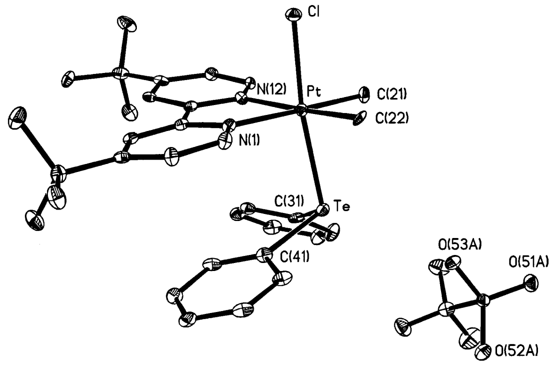


Figure 2. View of the molecular structure of **3**. The triflate anion with the shortest TeO distance is shown: Te···O(53A) = 4.03 Å is longer than the sum of the van der Waals distances (3.6 Å) and is too long to indicate any bonding interaction.

tetrahedral. If the Te···Cl unit is considered to be bonded, the stereochemistry at tellurium appears to be based on a distorted square pyramid, with the two phenyl groups, the chloride, and a lone pair of electrons in the equatorial sites and platinum in the axial position (Figure 1). The other relevant angles are Pt−Te−Cl(2) = 104.4(1)°, C(31)−Te−C(41) = 96.7(2)°, Cl(2)−Te−C(41) = 81°, and Cl(2)−Te−C(31) = 155°. The lone pair of electrons on Te is therefore considered to be trans to C(41). If the chloride is considered to be ionic, the stereochemistry at tellurium is distorted trigonal pyramidal.

Chloride Abstraction Reactions. To test if the chloride group in **2** was ionic in solution, anion exchange was carried out. No exchange was observed with NH_4PF_6. However, the reaction of complex **2** with AgO_3SCF_3 led to the removal of the chloride anion, with formation of $[PtClMe_2(TePh_2)(bu_2bpy)][CF_3SO_3]$, **3**, Scheme 1, which was isolated as an air-stable yellow solid. The ^1H NMR spectrum of complex **3** was similar to that of complex **2**, indicating the same stereochemistry at platinum though with some significant variations in chemical shifts. However, the ^{125}Te NMR spectrum of complex **3** contained a resonance at $\delta(Te) = 667$, with $^1J(PtTe) = 144$ Hz, much different from the values for complex **2** [$\delta(Te) = 693$, $^1J(PtTe) = 350$ Hz]. This clearly indicates that the structures of **2** and **3** in solution are different and, hence, that the secondary Te···Cl bond in **2** is maintained in solution.

The structure of complex **3** is shown in Figure 2, with relevant bond parameters listed in Table 1. The stereochemistry at platinum and the associated bond distances are very similar to those in complex **2** (Figures 1 and 2). For example, the distances Pt−Cl = 2.358(3) Å in **3** and 2.365(1) Å in **2** and Pt−Te = 2.5734(7) Å in **3** and 2.5730(5) Å in complex **2** are very similar. However, the triflate anion, $CF_3SO_3^-$, is not coordinated to tellurium in complex **3**, since the shortest distance Te···O(53A) = 4.03(1) Å, and so complex **3** is clearly a diphenyl telluride complex of platinum(IV). The geometry of the $PtTePh_2$ unit is significantly different in **3** compared to **2**. One phenyl group of the Ph_2Te ligand stacks above the N(1) pyridyl ligand with an intercentroid distance of 3.66 Å, and the second phenyl group stacks above the N(12) pyridyl ligand with a longer intercentroid distance of 4.47 Å. The corresponding angles Pt−Te−C = 102.8(3) and 104.9(3)° allow effective π-stacking, and the angle C−Te−C = 102.8(4)°. The stereochemistry at tellurium is thus distorted trigonal pyramidal, with a stereochemically active lone pair of electrons.

Formation of a Cationic Platinum(IV) Aqua Complex. The reaction of complex **3** with a second 1 equiv of silver triflate led to abstraction of the chloride ligand and to formation of the cationic aqua complex $[PtMe_2(OH_2)(TePh_2 \cdots O_3SCF_3)(bu_2bpy)][CF_3SO_3]$, **4**, Scheme 1, which was isolated as an air-stable pale yellow solid. Complex **4** was also prepared by the direct reaction of complex **2** with 2 equiv of AgO_3SCF_3, and the aqua ligand is derived from adventitious water in both syntheses.

The ^1H NMR spectrum of complex **4** indicated the absence of mirror symmetry. Thus, there were two *tert*-butyl peaks and two methylplatinum peaks, whereas the spectra of **2** and **3** contained only one resonance for each of these. Methylplatinum resonances at $\delta = 1.63$, $^2J(PtMe) = 60$ Hz, and $\delta = 1.29$, $^2J(PtMe) = 76$ Hz, can be assigned to the methyl groups trans to N and O respectively, on the basis of the coupling constants, since nitrogen has the higher trans-influence. There was a large difference in coupling constants $^3J(PtH^6)$ for the aromatic protons H^6 (*ortho* to nitrogen) of the bu_2bpy ligand trans to methyl [$^3J(PtH^6) = 17$ Hz] or trans to $TePh_2$ [$^3J(PtH^{6'}) = 34$ Hz], indicating the lower trans influence of the $TePh_2$ group. The ^{125}Te NMR spectrum of complex **4** contained a singlet, with coupling constant $^1J(PtTe) = 376$ Hz, much larger than the coupling constant $^1J(PtTe) = 144$ Hz for **3**, but similar to the coupling constant $^1J(PtTe) = 350$ Hz for **2**. Two triflate resonances were observed in the ^{19}F NMR spectrum, indicating that the two triflate groups are nonequivalent in solution.

The structure of complex **4** is shown in Figure 3, with relevant bond parameters listed in Table 1. There is an octahedral platinum(IV) center, with one methyl group trans to the aqua ligand and the other trans to N and with the tellurium-bonded ligand trans to N. The distance Pt−Te = 2.5871(3) Å is similar to the values in complexes **2** and **3** (Table 1). The Pt−N bond distance trans to methyl [2.149(3) Å] is longer than the one trans to $TePh_2$ [2.084(3) Å] as a result of the higher trans influence of methyl compared to $TePh_2$. The Pt−Te−C angles are 108.4(1) and 106.3(1)°, and the C−Te−C angle is 95.6(1)°. In this complex the stereochemistry with tellurium trans to nitrogen does not allow π-stacking of the phenyl and pyridyl groups and the PtTeC angles are closer to tetrahedral than in **2** and **3**.

There is particularly complex secondary bonding in complex **4**. The aqua ligand is hydrogen bonded to both triflate anions with distances O(23)···O(53) = 2.62(1) Å and O(23)···O(63A) = 2.59(1) Å and angle O(53)O(23)O(63) = 132(1)°. One of these triflate anions also forms a secondary bond to tellurium, with Te···O(53) = 3.185(2) Å, as shown in Figure 3a. Finally, the individual units associate loosely into dimer units in the crystal by forming longer secondary tellurium−oxygen bonds to one of the triflate groups of a neighboring molecule, with Te···O(51A) = Te(A)···O(51) = 3.514(2) Å as shown in Figure 3b. The

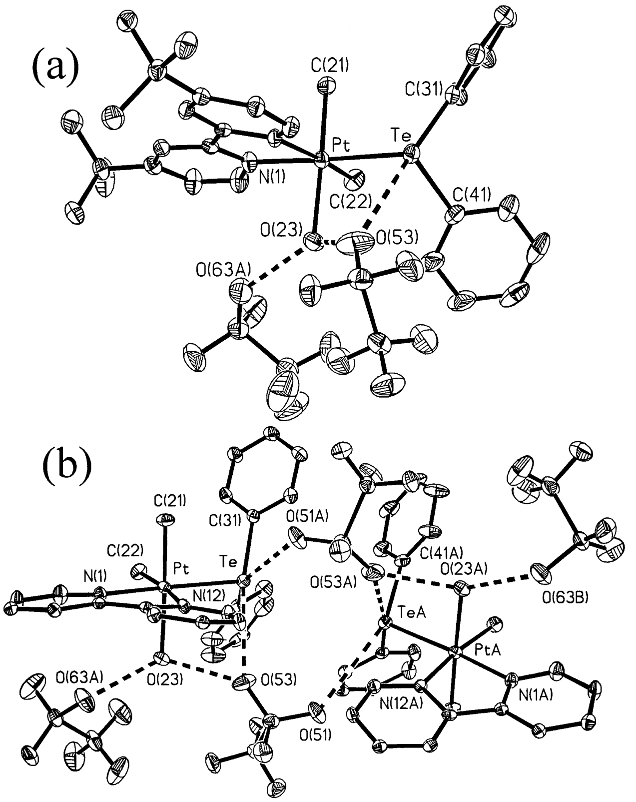


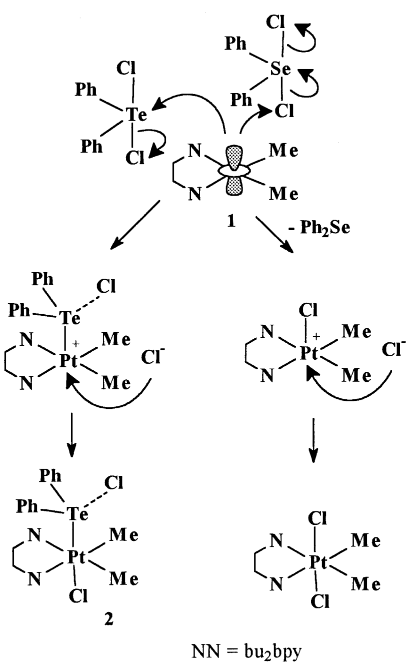
Figure 3. Views of the molecular structure of **4**: (a) the dication showing hydrogen bonding between triflate anions and the aqua ligand; (b) the additional, longer secondary Te···O interaction, which leads to formation dimers.

two Te···O bonds are roughly trans to the phenyl groups, with C(31)TeO(53) = 171.0(1) and C(41)TeO(51) = 158.2(1)°. If the extreme bonding form with full Te−O bonds is considered, the geometry at tellurium can be considered to be based on an octahedron with a stereochemically active lone pair of electrons trans to platinum, while, if both are ignored, the stereochemistry at tellurium is trigonal pyramidal.

Discussion

Complex **1** reacts with Ph_2TeCl_2 by trans oxidative addition of the Te−Cl bond to yield complex **2** and is the first example of an oxidative addition reaction of a tellurium−halide bond to a transition-metal complex. The stereochemistry of the oxidative addition suggests a two step, rather than concerted, mechanism, and the polar S_N2 mechanism is likely.[8] Since the reaction of complex **1** with Ph_2SeCl_2 gives only $[PtCl_2Me_2(bu_2bpy)]$ and Ph_2Se, it seems that the nucleophilic platinum(II) center of complex **1** can attack Ph_2ECl_2 at either E (E = Te) or at Cl (E = Se) as shown in Scheme 2. The oxidative addition of Ph_2TeCl_2 occurs with considerable weakening of the remaining TeCl bond.

Scheme 2



The platinum(IV)−tellurium bonded products **2**−**4** display unusual structure and bonding properties. The simplest complex is the cation $[PtClMe_2(TePh_2)(bu_2bpy)]^+$ present in complex **3** and illustrated in Figure 2. This is clearly a diphenyl telluride complex of platinum(IV), and the most notable feature is the π-stacking of the phenyl substituents with the pyridyl rings. Complexes **2** and **4** show unusual secondary bonding effects. Complex **2** contains a long Te···Cl bond (3.43 Å) in the solid state, which is still shorter than the sum of the van der Waals radii of 3.81 Å. The NMR evidence clearly indicates that this bond is maintained in solution. To understand this effect, it is useful to consider an analogy with organotellurium compounds of the type R_3TeCl which exist in the solid state in associated forms with weak Te···Cl bonds.[1,13] For example, Et_3TeCl exists as a tetrameric cubane with Te···Cl = 3.45 Å and Ph_3TeCl exists as a dimer with Te···Cl = 3.14 and 3.23 Å,[13] and these distances are similar to the long Te···Cl bond in **2**. The organotellurium compounds are often considered as primarily ionic $R_3Te(IV)^+Cl^-$, with secondary bonding between the organotellurium cation and chloride anion.[1,13,14] The bonding in **2** can be considered to be similar, the main difference being that the bulky organoplatinum substituent does not allow further aggregation like that found for the organotellurium chlorides.[1,13−15] The parent organotellurium compound Ph_2TeCl_2 exists as a coordination polymer in which molecular units associate through intermolecular, secondary Te···Cl bonding with Te···Cl = 3.68 Å.[15] These examples illustrate the prevalence of secondary bonding to tellurium in organotellurium compounds,[13] and so it is surprising that there appear to be no clear examples of Te···X secondary bonding in transition-metal complexes of dialkyl or diaryl tellurides.[1,9−16] An early report of a close contact C···Te = 3.31 Å in *trans*-$[Pd(SCN)_2\{Te(CH_2CH_2CH_2SiMe_3)_2\}_2]$ is noted, in which it was unclear if the contact

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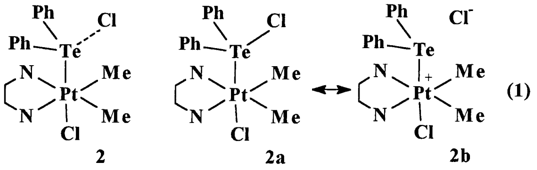
was attractive or repulsive in nature.[16] The secondary bonding effect is probably strong in **2** because the metal is in a high oxidation state and the complex (before secondary bonding) is cationic. The diphenyl telluride is likely to act as a strong σ-donor under these conditions and so become positively charged in the cation. It then forms a secondary bond to the chloride. In extreme bonding terms the complex **2** could be considered as a diphenyl telluride(II) complex, **2b**, as in complex **3**, or as a diphenylchlorotelluryl(IV) complex of platinum(IV), **2a**, as illustrated in eq 1.



Similarly, complex **4** can be considered as based on a dicationic aqua complex $[PtMe_2(OH_2)(TePh_2)(bu_2bpy)]^{2+}$, with two triflate anions strongly hydrogen bonded to the aqua group and with one of the triflate anions also forming an intramolecular secondary bond to tellurium, as shown in Figure 3a. The change in stereochemistry at platinum(IV) on formation of complex **4** is necessary to allow this bridging triflate. The secondary bond distance Te···O(53) = 3.185(2) Å is similar to those found in several organotellurium compounds, such as in $Ph_2Te(O_2CCCl_3)_2$, with secondary Te···O distances in the range 3.06−3.23 Å.[13] The significance of the contact that forms the dimer unit of Figure 3b, with Te···O(51A) = Te(A)···O(51) = 3.514(2) Å, is more debatable since it is close to the sum of the van der Waals radii of 3.6 Å. Nevertheless the O···Te contact is positioned roughly trans to a phenyl group, in a typical position for a secondary bonded atom. In either case, the structure of complex **4** clearly shows another case in which there is secondary bonding to a coordinated diphenyl telluride ligand.

The evidence that the secondary bonding to tellurium in complexes **2** and **4** is maintained in solution is derived from the tellurium NMR data. In particular, if the clearly ionic complex **3** is considered as a benchmark for a diphenyl telluride complex without secondary bonding [$\delta(^{125}Te) = 667$, $^1J(PtTe) = 144$ Hz], complex **2** has a higher chemical shift and a much higher coupling to platinum at $\delta(^{125}Te) = 693$, $^1J(PtTe) = 350$ Hz. Complex **4** has a stereochemistry different from both those of **2** and **3** so the comparison is less direct. Nevertheless, with a secondary bonding intereraction, the chemical shift and coupling constant, at $\delta(^{125}Te) = 705$, $^1J(PtTe) = 376$ Hz, are slightly higher than in **2** and much higher than in **3**. The reasons for the major differences in $^1J(PtTe)$ when secondary bonding is present or absent are not obvious. Most commonly, an increase in coordination number of an element leads to a decrease in coupling constants for that element, since the s-character used in each bond decreases. However, we note a recent calculation in which the magnitude of the coupling constant $^1J(PtTl)$ in a platinum−thallium-bonded complex $[Pt(CN)_5(TlCN)]^-$ more than doubled on solvation of thallium,[17] and we tentatively suggest that the secondary bond in **2** and **4** has an effect similar to this solvation effect. This NMR effect could be useful in identifying secondary bonding in other complexes, provided that there is a good benchmark for the coupling in the absence of the secondary bond. We are not aware of any other reports of $^1J(PtTe)$ coupling constants in platinum(IV) complexes, but there are several reports in platinum(II) complexes.[4,7,16] For example, the cation $[PtCl\{Te(CH_2CH_2TePh)_2\}_2]^+$ gives $^1J(PtTe)$ values of 1200 Hz (Te trans to Cl) and 485 Hz (Te trans to Te).[16]

Experimental Section

NMR spectra were recorded by using a Varian Mercury 400 MHz or Inova 600 MHz spectrometer. Chemical shifts are reported with respect to TMS (^1H) or external $TeMe_2$ (^{125}Te). Reactions involving Te(IV) or Se(IV) complexes were carried out under an atmosphere of dry nitrogen by using Schlenk techniques. The complex $[PtMe_2(bu_2bpy)]$, **1**, was prepared according to the literature procedure,[18] and tellurium derivatives were commercial samples. In the NMR labels for complex **4**, the protons $H^{3,5,6}$ and $H^{3',5',6'}$ are on the pyridine rings trans to Me and Te, respectively.

$[PtClMe_2(TePh_2\cdots Cl)(bu_2bpy)]$, 2. To a stirred solution of **1** (100 mg, 0.203 mmol) in CH_2Cl_2 (2 mL) was added Ph_2TeCl_2 (72 mg, 0.203 mmol). The red solution immediately turned to a light yellow color. Pentane (40 mL) was added to precipitate the pale yellow product, which was isolated by filtration, washed with pentane, and dried in vacuo. Yield: 91%. Anal. Calcd for $C_{32}H_{40}Cl_2N_2Pt\cdot CH_2Cl_2$: C, 49.32; H, 5.27; N, 3.49. Found: C, 49.22; H, 5.15; N, 3.33. NMR in $CDCl_3$: $\delta(^1H) = 8.61$ [d, 2H, $^3J_{H^6H^5} = 6$ Hz, $^3J_{PtH^6} = 19$ Hz, H^6], 8.13 [d, 2H, $^4J_{H^3H^5} = 1$ Hz, H^3], 7.53 [dd, 2H, $^3J_{H^5H^6} = 6$ Hz, $^4J_{H^5H^3} = 1$ Hz, H^5], 7.25−7.19 [m, 10H, $TePh_2$], 1.92 [s, 6H, $^2J_{PtMe} = 65$ Hz, $^3J_{TeMe} = 14$ Hz, Pt−Me], 1.44 [s, 18H, bu]; $\delta(^{125}Te) = 693$ [s, $^1J_{PtTe} = 350$ Hz, Pt−Te]. Single crystals were grown by slow diffusion of pentane into a solution of **2** in CH_2Cl_2 at 5 °C.

$[PtClMe_2(TePh_2)(bu_2bpy)](CF_3SO_3)$, 3. To a solution of **2** (75 mg, 0.089 mmol) in CH_2Cl_2 (5 mL) was added AgO_3SCF_3 (23 mg, 0.089 mmol), and the mixture was stirred for 1 h in the dark. The solution was filtered through dry Celite to remove AgCl. Pentane (40 mL) was added to the filtrate to precipitate the pale yellow product, which was isolated by filtration, washed with pentane, and dried in vacuo. Yield: 88%. Anal. Calcd for $C_{33}H_{40}ClF_3N_2O_3PtSTe$: C, 41.29; H, 4.2; N, 2.92. Found: C, 41.41; H, 4.31; N, 2.82. NMR in $CDCl_3$: $\delta(^1H) = 8.38$ [s, 2H, H^3], 8.18 [d, 2H, $^3J_{H^6H^5} = 6$ Hz, $^3J_{PtH^6} = 14$ Hz, H^6], 7.40 [d, 2H, $^3J_{H^5H^6} = 6$ Hz, H^5], 7.38−7.15 [m, 10H, $TePh_2$], 1.66 [s, 6H, $^2J_{PtMe} = 63$ Hz, Pt−Me], 1.36 [s, 18H, bu]; $\delta(^{19}F) = -78.5$ [s, $CF_3SO_3^-$]; $\delta(^{125}Te) = 667$ [s, $^1J_{PtTe} = 144$ Hz, Pt−Te]. Crystals were grown as described for **2**.

$[PtMe_2(TePh_2\cdots O_3SCF_3)(H_2O)(bu_2bpy)](CF_3SO_3)$, 4. To a solution of **3** (100 mg, 0.104 mmol) in CH_2Cl_2 (5 mL) was added AgO_3SCF_3 (27 mg, 0.104 mmol), and the mixture was stirred for 1 h in the dark. The solution was filtered through dry Celite to

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Table 2. Crystal Data and Experimental Details

param	**2**·CH_2Cl_2	**3**	**4**
formula	$C_{33}H_{42}Cl_4N_2PtTe$	$C_{33}H_{40}ClF_3N_2O_3PtSTe$	$C_{34}H_{42}F_6N_2O_7PtS_2Te$
fw	931.18	959.87	1091.51
T/K	150(2)	150(2)	200(2)
λ/Å	0.710 73	0.710 73	0.710 73
space group	Pbca	$P2_1$	Pbcn
a/Å	11.9630(3)	10.8085(3)	19.850(3)
b/Å	22.7735(8)	11.1557(3)	14.4878(2)
c/Å	25.9179(8)	14.8947(4)	27.9326(3)
β/deg	90	103.075(2)	90
V/Å^3	7061.1(4)	1749.39(8)	8033.1(2)
Z	8	2	8
d(calcd)/g cm^{-3}	1.752	1.822	1.805
μ/mm	5.112	5.015	4.384
F(000)	3616	932	4256
reflcns, ind reflcns	51 951, 8063	14 907, 6956	10 0873, 9202
abs corr	integration	integration	integration
data/restr/param	8063/0/346	6956/1/407	9202/2/460
R1 [$I > 2\sigma(I)$][a]	0.0429	0.0599	0.0350
wR2 [$I > 2\sigma(I)$][a]	0.0935	0.1513	0.0803

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $wR2 = [\sum(w(|F_o|^2 - |F_c|^2)^2)/\sum(w|F_o{}^2|^2)]^{1/2}$.

remove AgCl. Pentane (40 mL) was added to the filtrate to precipitate the pale yellow product which was isolated by filtration, washed with pentane, and dried in vacuo. Yield: 85%. Anal. Calcd for $C_{34}H_{42}F_6N_2O_7PtS_2Te$: C, 37.41; H, 3.88; N, 2.57. Found: C, 37.55; H, 3.96; N, 2.66. NMR in $CDCl_3$: $\delta(^1H) = 9.08$ [d, 1H, $^3J_{H^6H^5} = 5$ Hz, $^3J_{PtH^6} = 17$ Hz, H^6], 8.69 [d, 1H, $^3J_{H^{6'}H^{5'}} = 6$ Hz, $^3J_{PtH^{6'}} = 34$ Hz, $H^{6'}$], 8.26 [s, 1H, H^3], 8.24 [s, 1H, $H^{3'}$], 7.92−7.45 [2H, $H^{5,5'}$], 7.92−7.18 [m, 10H, Ph], 2.74 [H_2O], 1.63 [s, 3H, $^2J_{PtMe} = 60$ Hz, Pt−Me trans to N], 1.44 [s, 9H, bu], 1.40 [s, 9H, bu], 1.29 [s, 3H, $^2J_{PtMe} = 76$ Hz, Pt−Me *trans* to OH_2]; $\delta(^{19}F) = -78.4$ [s, 3F, $CF_3SO_3^-$], −78.5 [s, 3F, $CF_3SO_3^-$]; $\delta(^{125}Te) = 705$ [s, $^1J_{PtTe} = 376$ Hz, Pt−Te]. Complex **4** was also obtained by reaction of **2** (25 mg, 0.029 mmol) in CH_2Cl_2 (5 mL) with AgO_3SCF_3 (15 mg, 0.059 mmol). The mixture was stirred for 1 h in the dark, followed by isolation as described above. Crystals of **4** were grown by slow diffusion of pentane into a solution of **4** in dichloroethane at room temperature.

[$PtCl_2Me_2(bu_2bpy)$]. To a solution of **1** (50 mg, 0.10 mmol) in CH_2Cl_2 (10 mL) was bubbled Cl_2 briefly. The mixture was stirred for 10 min, and then pentane (40 mL) was added to precipitate the product, which was isolated by filtration, washed with pentane, and dried in vacuo. Yield: 67%. Anal. Calcd for $C_{20}H_{32}Cl_2N_2Pt$: C, 42.41; H, 5.69; N, 4.95. Found: C, 42.24; H, 5.92; N, 4.69. NMR in $CDCl_3$: $\delta(^1H) = 8.80$ [d, 2H, $^3J_{H^6}H^5 = 6$ Hz, $^3J_{PtH^6} = 24$ Hz, H^6], 8.16 [d, 2H, $^4J_{H^3H^5} = 1$ Hz, H^3], 7.65 [dd, 2H, $^3J_{H^5H^6} = 6$ Hz, $^4J_{H^5H^3} = 1$ Hz, H^5], 2.00 [s, 6H, $^2J_{PtMe} = 69$ Hz, Pt−Me], 1.42 [s, 18H, bu].

X-ray Structure Determinations. A crystal of **2**, **3**, or **4** was mounted on a glass fiber. Data were collected using a Nonius Kappa-CCD diffractometer using COLLECT (Nonius,1998) software. Crystal cell refinement and data reduction were carried out using the Nonius DENZO package, and the data were scaled using SCALEPACK (Nonius, 1998). The SHEXTL 5.1 (G. M. Sheldrick, Madison, WI) program was used to solve the structure by direct methods, followed by refinement by successive difference Fouriers. Crystal and refinement data are listed in Table 2.

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Supporting Information Available: Tables of X-ray data for the complexes in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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