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Tellurium(0) as a Ligand: Synthesis and Characterization of 2-Pyridyltellurolates of Platinum(II) and Structures of $[\mathrm{Pt}\{2\text{-Te-3-(R)}C_5H_3N\}_2\mathrm{Te}(PR'_3)]$ (R = H or Me)

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Treatment of toluene solutions of the ditellurides $[Te_2\{C_5H_3N(R)\text{-}3\}_2]$ (R = H or Me) with $[Pt(PPh_3)_4]$ yielded two types of complexes, $[\mathrm{Pt}\{2\text{-Te-3-(R)}C_5H_3N\}_2(PPh_3)_2]$ (**1a**−**d**) as the major products and $[\mathrm{Pt}\{2\text{-Te-3-(R)}C_5H_3N\}_2\mathrm{Te}(PPh_3)]$ (**2a**−**d**) as minor products. The above complexes can also be obtained by the reaction of $[PtCl_2(PR'_3)_2]$ (PR'_3 = PPh_3 or $PPh_2(2\text{-}C_5H_4N)$) with 2 equiv of $Na(2\text{-Te-}C_5H_3R)$. The complexes were characterized by elemental analyses and UV−vis, NMR (^{1}H and ^{31}P), and (in part) XPS spectroscopy. The molecular structures of $[Pt(2\text{-Te-}C_5H_4N)_2Te(PPh_3)]$ (**2a**) and $[\mathrm{Pt}\{2\text{-Te-}C_5H_3(Me)N\}_2\mathrm{Te}(PPh_3)]$ (**2b**) were established by single crystal X-ray diffraction. Both complexes exhibit a distorted square-planar configuration at the platinum(II) centers. The two mutually trans positioned 2-pyridinetellurolate ligands $[2\text{-Te-}C_5H_3(R)N]$ coordinate to the central platinum atom in a monodentate fashion through the tellurium atoms. The tellurium(0) atom adopts a “bent T” configuration as it is bridging the 2-Te- $C_5H_3(R)N$ molecules via N−Te−N bonds (166° angle) and coordinates to Pt^{II} in the trans position to PPh_3. The novel bis(pyridine)tellurium(0) arrangement resembles the bis(pyridine)iodonium structure. The calculated NICS indices and ELF functions clearly show that the compounds **2a** and **2b** are aromatic in the region defined by the Te−C−N−Te−Pt five-membered rings.

Introduction

Oxidative addition reactions of diorganodichalcogenides (REER) to palladium(0) and platinum(0) complexes have been of considerable interest for quite some time.[1] This reaction finds applications in regio- and stereoselective E−E addition to C≡C bonds in organic synthesis[2−9] and also provides a convenient route to metal chalcogenolate complexes which have relevance in materials science.[10]

Oxidative addition of diorgano-disulfides and -diselenides to platinum(0) complexes such as $[Pt(PPh_3)_4]$ or $[Pt(PPh_3)_2\text{-(olefin)}]$ yields mononuclear $[Pt(ER)_2(PPh_3)_2]$ as isolable products,[5,11−15] while similar reactions with palladium(0) derivatives (e.g., $[Pd(PPh_3)_4]$, $Pd_2(dba)_3/PR'_3$) result in the formation of dinuclear complexes $[Pd_2(\mu\text{-ER})_2(ER)_2(PR'_3)_2]$ (E = S or Se).[2,5,13,15,16] However, reactions of diorganoditellurides with Pd(0) and Pt(0) complexes were shown to be much more complex, affording several products.[17] For instance, the reaction of $[Pd(PPh_3)_4]$ with Th_2Te_2 (Th = 2-thienyl) in dichloromethane yields a hexanuclear complex,

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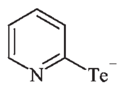
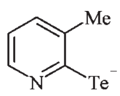
$[Pd_6Cl_2(Te_4)(TeTh)_2(PPh_3)_6]$, together with several other unidentified products.[14,17] When carried out in toluene, this reaction affords yet another hexanuclear complex, $[Pd_6(Te_4)(TeTh)_4(PPh_3)_6]$, while Chia and McWhinnie[18] have reported the formation of the expected dinuclear compound $[Pd_2(\mu\text{-}TeTh)_2(TeTh)_2(PPh_3)_2]$. A similar reaction with $[Pt(PPh_3)_4]$, however, yielded $[Pt_3Te_2(Th)(PPh_3)_5]Cl$ and $[PtCl(Th)(PPh_3)_2]$.[17,19] The complexes $[Pd_6Cl_2(Te_4)(TeTh)_2(PPh_3)_6]$, $[Pd_6(Te_4)(TeTh)_4(PPh_3)_6]$, and $[Pt_3Te_2(Th)(PPh_3)_5]Cl$ have tellurido bridges which are formed via cleavage of Te−C bonds. The cleavage of Te−C bonds has also been reported in reactions of telluro-ethers with platinum(0) compounds.[20,21]

Recently, we have examined the chemistry of palladium(II) and platinum(II) complexes with hemilabile 2-pyridyltellurolate ligands (2-Te-C_5H_4N).[22] The complexes observed exhibited distinct structural and reactivity features which were different from those containing more simple organotellurolate ligands. It was of interest, therefore, to study oxidative addition reactions of bis(2-pyridyl)ditellurides with $[Pt(PPh_3)_4]$ in the expectation of isolating new structural motifs. The reaction gave yellow $[Pt(2\text{-}Te\text{-}C_5H_4N)_2(PPh_3)_2]$ as described earlier,[22] together with a small amount of a crystalline serendipituous product, $[Pt(2\text{-}Te\text{-}C_5H_4N)_2Te(PPh_3)]$, containing bare tellurium (Te^0) coordinated to platinum(II). The results of this work are described herein.



2-Te-C_5H_4N



2-Te-3-(Me)C_5H_3N

Experimental Section

The complexes $[Pt(PPh_3)_4]$, $[PtCl_2(PPh_3)_2]$, $[PtCl_2(PPh_2(2\text{-}C_5H_4N))_2]$,[23] $(C_5H_4N)_2Te_2$ and $(3\text{-}MeC_5H_3N)_2Te_2$,[24] and diphenyl(2-pyridyl)phosphine[23] were prepared according to literature methods. All reactions were carried out under an argon atmosphere in dry and distilled analytical grade solvents at room temperature. The ^1H, $^{31}P\{^1H\}$, and $^{195}Pt\{^1H\}$ NMR spectra were recorded on a Bruker Avance-II spectrometer operating at 300, 121.49, and 64.52 MHz, respectively. Chemical shifts are relative to internal chloroform (δ 7.26) for ^1H, external 85% H_3PO_4 for ^{31}P, and Na_2PtCl_6 in D_2O for ^{195}Pt. Elemental analyses were carried out on a Thermo Finnigan Flash EA1112 CHNS analyzer. UV−vis absorption spectra were recorded on a Chemito Spectroscan UV 2600 double beam UV−vis spectrophotometer. XPS studies were conducted in a UHV chamber (base pressure $< 2 \times 10^{-8}$ mbar) using an AVG make CLAM-2 model analyzer with a nonmonochromatic twin Al/Mg X-ray source.

Intensity data for $[Pt(2\text{-}Te\text{-}C_5H_4N)_2Te(PPh_3)]$ (**2a**) and $[Pt\{2\text{-}Te\text{-}C_5H_3(Me)N\}_2Te(PPh_3)]$ (**2b**) were measured on a Rigaku AFC7S diffractometer with Mo Kα radiation at 298 K so that $\theta_{max} = 27.5°$. The structures were solved by direct methods,[25] and refinement[25] was on F^2 using data that had been corrected for absorption effects with an empirical procedure.[26] Non-hydrogen atoms were modeled with anisotropic displacement parameters, hydrogen atoms in their calculated positions. Molecular structures were drawn using ORTEP.[27] Crystallographic and structural determination data are listed in Table 1.

Table 1. Crystallographic and Structural Determination Data for $[Pt(2\text{-}Te\text{-}C_5H_4N)_2Te(PPh_3)]$ (**2a**) and $[Pt\{2\text{-}Te\text{-}C_5H_3(Me)N\}_2Te(PPh_3)]\cdot C_6H_6$ (**2b.**C_6H_6)

complex	**2a**	**2b**·C_6H_6
chemical formula	$C_{28}H_{23}N_2PPtTe_3$	$C_{30}H_{27}N_2PPtTe_3.C_6H_6$
formula wt.	996.34	1102.53
crystal system	monoclinic	triclinic
space group	$C2/c$	$P\overline{1}$
unit cell dimensions		
a (Å)	39.040(7)	12.300(12)
b (Å)	13.261(4)	15.251(8)
c (Å)	11.9426(11)	10.029(7)
α (deg)	90.00	107.38(3)
β (deg)	93.850(11)	99.51(6)
γ (deg)	90.00	83.25(4)
volume (Å^3)	6169(2)	1766(2)
ρ_{calcd}, g cm^{-3}	2.146	2.073
Z	8	2
μ (mm^{-1})/F(000)	7.400/3632	6.473/1024
θ for data collection (deg)	2.72−27.49	2.52−27.50
data/restraints/params	7078/0/317	8092/0/390
final R_1, ωR_2 indices	0.0419/0.0980	0.0562/0.1249
R_1, ωR_2 (all data)	0.0874/0.1082	0.1775/0.1628
goodness of fit on F^2	0.933	0.951

Syntheses of Complexes. $[Pt(2\text{-}Te\text{-}C_5H_4N)_2(PPh_3)_2]$ (1a) and $[Pt(2\text{-}Te\text{-}C_5H_4N)_2Te(PPh_3)]$ (2a). Method i: To a toluene solution (10 cm^3) of $(C_5H_4N)_2Te_2$ (67 mg, 0.16 mmol) was added a solution (30 cm^3) of $[Pt(PPh_3)_4]$ (201 mg, 0.16 mmol) in the same solvent, with stirring being continued for 4 h at room temperature. The solvent was evaporated in vacuo, and the residue was washed thoroughly with hexane followed by diethyl ether to remove liberated triphenylphosphine. The residue was recrystallized from benzene-acetone to afford two different products, viz., a yellow powder (**1a**; yield 113 mg (0.10 mmol), 62%; mp 145 °C (dec.)) and orange crystals of $[Pt(2\text{-}Te\text{-}C_5H_4N)_2Te(PPh_3)]$ (**2a**) which were separated manually (yield 24 mg (0.02 mmol), 15%; mp 138 °C (dec.)). Compound **1a**, Anal. Calcd. for $C_{46}H_{38}N_2P_2PtTe_2$: C, 48.8; H, 3.4; N, 2.5%. Found: C, 48.3; H, 3.3; N 2.3%. Since there is always dissociation of PPh_3, the analytical values varied from sample to sample. UV−vis ($C_6H_5CH_3$), λ_{max}: 415 nm (sh). ^1H NMR (C_6D_6): δ 7.08 (m, Ph + C_5H_4N), 7.49 (br), 7.88 (m); 7.99 (br, C_5H_4N). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 23.5 (^1J(Pt−P) = 3241 Hz] (−5.39 (PPh_3) ~5%). $^{195}Pt\{^1H\}$ NMR (C_6D_6): δ −4228 (t, ^{1}J(Pt−P) = 3251 Hz). Compound **2a**, Anal. Calcd. for $C_{28}H_{23}N_2PPtTe_3$: C, 33.8; H, 2.3; N, 2.8%. Found: C, 34.0; H, 2.4; N 2.6%. UV−vis ($C_6H_5CH_3$), λ_{max}: 404 nm. ^1H NMR (C_6D_6): δ 6.15 (t, 6.6 Hz, C_5H_4N 2-H), 6.33 (td, 1.2 Hz (d), 6.6 Hz (t), C_5H_4N 2-H), 7.13 (m, C_6H_5), 7.48 (d, C_5H_4N), 8.11 (m, Ph), 8.59 (d, 6 Hz, 2-H, C_5H_4N). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 21.1 (^{1}J(Pt−P) = 3028 Hz). XPS (eV): 72.6 (Pt $4f_{7/2}$), 76.06 (Pt $4f_{5/2}$), 575.0 (Te $3d_{5/2}$), 585.4 (Te $3d_{3/2}$).

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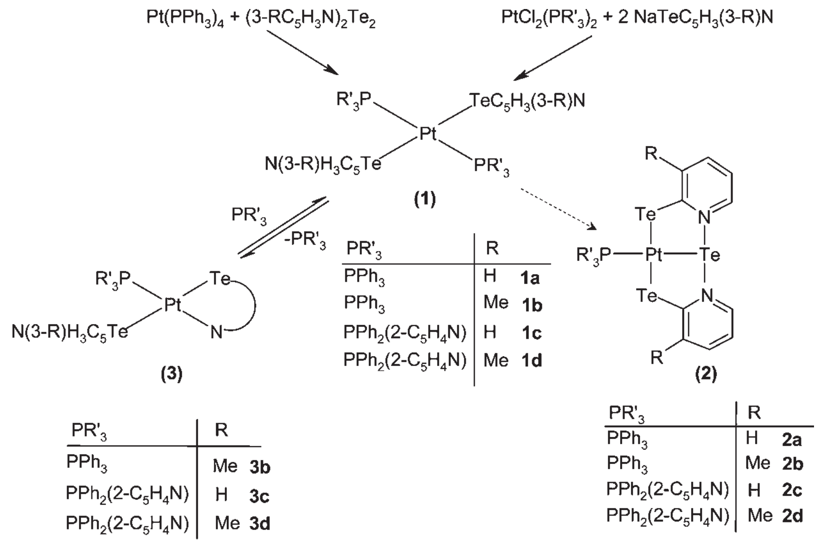
Scheme 1



Method ii: To a dichloromethane solution (15 cm^3) of [$PtCl_2(PPh_3)_2$] (150 mg, 0.19 mmol) was added a methanolic solution (12 cm^3) of Na(2-Te-C_5H_4N) [freshly prepared from $(C_5H_4N)_2Te_2$ (80 mg, 0.19 mmol) and $NaBH_4$ (16.4 mg, 0.22 mmol)]. The mixture was stirred for 5 h, whereupon a clear orange solution was obtained. The solvents were evaporated under a vacuum. The residue was washed thoroughly with hexane followed by diethylether. The product was extracted with benzene, was filtered, and was passed through a Florisil column. To the resulting solution was added acetone to produce orange crystals of **2a** (yield 57 mg (0.06 mmol), 30%; Anal. Calcd. for $C_{28}H_{23}N_2PPtTe_3$: C, 33.8; H, 2.3; N, 2.8%. Found: C, 34.1; H, 2.2; N 2.7%) and yellow **1a** (yield 112 mg (0.10 mmol), 52%; mp 145 °C (dec.); Anal. Calcd. for $C_{46}H_{38}N_2P_2PtTe_2$: C, 48.8; H, 3.4; N, 2.5%. Found: C, 48.2; H, 3.5; N 2.4%). The NMR data are consistent with complexes **1a** and **2a**.

[Pt{2-Te-C_5H_3(Me)N}$_2$(PPh_3)$_2$] (1b) and [Pt{2-Te-C_5H_3-(Me)N}$_2$Te(PPh_3)] (2b). Method i: Preparation was done in a similar fashion as **1a**, adopting method i (above), and a 69% yield was achieved as an orange powder (mp 171 °C dec.). Anal. Calcd. for $C_{48}H_{42}N_2P_2PtTe_2$: C, 49.7; H, 3.7; N, 2.4%. Found: C, 50.3; H, 3.7; N 1.9%. UV−vis ($C_6H_5CH_3$), λ_{max}: 302, 425 nm. ^1H NMR ($CDCl_3$): δ 2.25 (s, Me); 6.97 (m, 6-H), 7.37 (m, C_6H_5), 7.81 (br), 8.65 (br, C_5H_3(Me)N). $^{31}P\{^1H\}$ NMR (toluene-d_8): δ 7.2 [^1J(Pt−P) = 3768 Hz], −5.3 (PPh $_3$). $^{195}Pt\{^1H\}$ NMR (toluene-d_8): δ −4810 [d, ^1J(Pt−P) 3713 Hz].

Method ii: Preparation was done in a similar fashion to that for **1a** using method ii (above), and recrystallization from benzene-acetone afforded [Pt{2-Te-C_5H_3(Me)N}$_2$(PPh_3)$_2$] (**1b**; yield 126 mg (0.11 mmol), 58%) and [Pt{2-Te-C_5H_3(Me)N}$_2$Te-(PPh_3)] (**2b**; yield: 22 mg (0.02 mmol), 12%; mp 158 °C (dec.)). The latter was separated manually as needle-shaped orange crystals. Anal. Calcd. for $C_{30}H_{27}N_2PPtTe_3\cdot C_6H_6$ (**2b**·C_6H_6): C, 39.2; H, 3.0; N, 2.5%. Found: C, 38.7; H, 2.9; N, 2.6%. UV−vis ($C_6H_5CH_3$), λ_{max}: 398 nm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 21.3 [^1J(Pt−P) = 2982 Hz]. When **1b** was left in $CDCl_3$ solution for several hours, a new species [PtCl{2-Te-C_5H_3(Me)N}(PPh_3)] ($^{31}P\{^1H\}$ NMR: δ −0.8 ppm, ^1J (Pt−P) = 3692 Hz)[22] together with a small amount of Ph_3PO (29.3 ppm) was identified.

[Pt(2-Te-C_5H_4N)$_2$(PPh_2(2-C_5H_4N))$_2$] (1c) and [Pt(2-Te-C_5H_4N)$_2$Te(PPh_2(2-C_5H_4N))] (2c). To a dichloromethane solution (20 cm^3) of [$PtCl_2$(PPh_2(2-C_5H_4N))$_2$] (110 mg, 0.14 mmol) was added a methanolic solution (8 cm^3) of Na(2-Te-C_5H_4N) [freshly prepared from $(C_5H_4N)_2Te_2$ (57 mg, 0.14 mmol) and $NaBH_4$ (11 mg, 0.29 mmol)], and the mixture was stirred for 6 h. The solvents were evaporated under reduced pressure. The residue was washed thoroughly with hexane followed by diethylether. The residue was extracted with dichloromethane, filtered, and passed through a Florisil column. Addition of a few drops of hexane and slow evaporation gave a yellow powder of [Pt(2-Te-C_5H_4N)$_2$(PPh_2(2-C_5H_4N))$_2$] (**1c**) (yield 103 mg (0.09 mmol), 65%; mp 118−120 °C (dec.)) and red crystals of [Pt(2-Te-C_5H_4N)$_2$Te(PPh_2(2-C_5H_4N))] (**2c**), which were separated manually (yield 21 mg (0.02 mmol), 15%; mp 131 °C (dec.)). Compound **1c**, Anal. Calcd. for $C_{44}H_{36}N_4P_2PtTe_2\cdot 2CH_2Cl_2$: C, 42.4; H, 3.1; N, 4.2%. Found: C, 42.1; H, 3.1; N 4.1%. Compound **2c**, Anal. Calcd. for $C_{27}H_{22}N_3PPtTe_3\cdot 2CH_2Cl_2$: C, 29.8; H, 2.2; N, 3.6%. Found: C, 30.1; H, 2.1; N 3.6%. ^1H NMR ($CDCl_3$): δ 5.32 (CH_2Cl_2), 6.20−8.12 (m, C_5H_4N + Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (**1c**) 23.3 (^1J(Pt−P) = 3222 Hz); (**3b**) 10.5 (^1J(Pt−P) = 3840 Hz). Compound **2c**, ^1H NMR ($CDCl_3$): δ 5.31 (CH_2Cl_2); 6.90 (t, 6 Hz, Te−C_5H_4N), 7.14 (t, 6 Hz, Te−C_5H_4N) 7.43 (br, C_6H_5); 7.67 (d, 8 Hz, Te−C_5H_4N), 7.74 (br), 7.90 (br, C_6H_5); 8.39 (t), 8.72 (d, 6 Hz, Te−C_5H_4N), 8.81 (d, 6 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 17.8 (^1J(Pt−P) = 2992 Hz).

[Pt{2-Te-C_5H_3(Me)N}$_2$(PPh_2(2-C_5H_4N))$_2$] (1d) and [Pt{2-Te-C_5H_3(Me)N}$_2$Te{PPh_2(2-C_5H_4N)}] (2d). Method i: Preparation was done in a similar fashion to that for **1c** with recrystallization from benzene-acetone to obtain a yellow powder (**1d**; yield 98 mg (0.08 mmol), 61%; mp 158 °C (dec.). Anal. Calcd. for $C_{46}H_{40}N_4P_2PtTe_2$: C, 47.6; H, 3.5; N, 4.8%. Found: C, 47.7; H, 3.3; N 4.7%) and orange crystals of [Pt{2-Te-C_5H_3-(Me)N}$_2$Te(PPh_2(2-C_5H_4N))] (**2d**), which were separated manually (yield 20 mg (0.02 mmol), 14%. Anal. Calcd. for $C_{29}H_{26}N_3PPtTe_3$: C, 34.0; H, 2.6; N, 4.1%. Found: C, 33.7; H, 2.7; N 4.0%). Compound **1d**, $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 22.2 (^1J(Pt−P) = 3231 Hz). Compound **3c**, $^{31}P\{^1H\}$ NMR: 5.4 (^1J(Pt−P) = 3829 Hz). Compound **2d**, ^1H NMR ($CDCl_3$): δ 2.26 (s, Me); 6.91 (t, 6 Hz, H-5, 2-Te-C_5H_3(Me)N), 7.11 (d, 7.2 Hz, H-4, 2-Te-C_5H_3(Me)N); 8.67 (d, 6 Hz, H-6, 2-Te-C_5H_3(Me)N); 7.43 (br), 7.95 (br) [Ph-P]; 7.77 (br m), 8.56 (t, 6 Hz) [NC_5H_4−P]. ^{31}P {^1H} NMR ($CDCl_3$): δ 20.5 (^1J(Pt−P) = 2945 Hz).

Results and Discussion

Synthesis and Spectroscopy. Reaction of [$Pt(PPh_3)_4$] with $(3\text{-}RC_5H_3N)_2Te_2$ (R = H or Me) at room temperature afforded yellow to orange products of oxidative addition, [Pt{2-Te-3-(R)C_5H_3N}$_2$(PPh_3)$_2$] (**1**), together with small amounts of crystalline material, [Pt{2-Te-3-(R)C_5H_3N}$_2$Te(PPh_3)] (**2**) (Scheme 1). Compounds **1** can also be obtained by treatment of [$PtCl_2(PR_3)_2$]

with Na$\{$2-Te-3-(R)$C_5H_3N\}$, readily prepared by the reductive cleavage of the Te−Te bond of corresponding bis(pyridyl)ditellurides with $NaBH_4$ in methanol (Scheme 1), as described earlier by us for **1b**.[22] On attempted recrystallization of the products obtained from these reactions, compounds **1** were obtained as yellow-orange powders, accompanied by crystalline **2**. Except **1a**, all other complexes (**1**) dissociate in solution to give PR_3 and [Pt$\{$Te−C_5H_3(R)N$\}\{\eta^2$-Te-C_5H_3(R)N$\}$(PR_3)] (**3**) as revealed by NMR spectroscopy.

The ^{31}P NMR spectra of **1** displayed single resonance signals with ^{195}Pt−^{31}P coupling. Compounds **1** undergo dissociation of the phosphine ligand in solution to give **3** and thus establish a dynamic equilibrium with **1**. The complexes **1a**, **1c**, and **1d** exhibited a ^{31}P NMR resonance at δ ~22 ppm with ^1J ~ 3230 Hz. The ^{195}Pt NMR spectrum of **1a** displayed a triplet at δ = −4228 ppm (^1J(Pt−P) = 3251 Hz), indicating coordination of two mutually trans positioned triphenylphosphine ligands.[28,29] The ^{31}P$\{^1$H$\}$ NMR spectrum of [Pt$\{$2-Te-C_5H_3(Me)N$\}_2$(PPh_3)$_2$] consists of a single resonance at 7.2 ppm with ^1J(Pt−P) = 3711 Hz. The former resonance has been assigned to [Pt$\{$Te-C_5H_3(Me)N$\}\{\eta^2$-Te-C_5H_3(Me)N$\}$(PPh_3)] (**3b**). Coordination of one PPh_3 ligand in **3a** is further corroborated by the ^{195}Pt NMR spectrum, which showed a doublet centered at −4810 ppm due to coupling with one ^{31}P nucleus. Several attempts to remove PPh_3 from the complex either by repeated recrystallization or by treatment with air to convert into $OPPh_3$ were unsuccessful. In solution, complex **1b** exists as **3b**, in which the PPh_3 ligand is trans to the nitrogen atom of the chelated 2-Te-C_5H_3(Me)N ligand. The complexes **1c** and **1d**, when left in solution for a few hours, showed signals due to **3c** and **3d** in their ^{31}P NMR spectra with ^1J(Pt−P) of ~3830 Hz. Attempts to record ^{125}Te$\{^1$H$\}$ NMR spectra of these complexes were thwarted due to their reactivity in chlorinated solvents (CD_2Cl_2 or $CDCl_3$) during long NMR acquisition times.

The complexes **2**, isolated in low yields as orange crystalline solids during the synthesis of **1**, exhibit one single ^{31}P$\{^1$H$\}$ NMR resonance at ~20 ppm with ^{195}Pt satellites. The magnitude of ^1J(Pt−P) (2945−3028 Hz) is indicative of a strong trans influence of the new, formally Te^0 ligand (see below). It is also within the range expected for platinum(II) telluride and tellurolate complexes.[30] In an attempt to differentiate between tellurolate and the coordinated tellurium atom, XPS measurements were carried out as ^{125}Te$\{^1$H$\}$ NMR spectra could not be obtained (*vide supra*). However, the XPS chemical shifts for tellurium ($3d_{5/2}$ and $3d_{3/2}$) in different oxidation states appear in a narrow region. For instance, the shifts for Te metal [573.1 ($3d_{5/2}$) and 583.5 ($3d_{3/2}$) eV],[31] diphenylditelluride [573.9 ($3d_{5/2}$) and 584.3 ($3d_{3/2}$) eV],[31] and CdTe [576 ($3d_{5/2}$) and 586 ($3d_{3/2}$) eV][32] differ only slightly and are only of limited diagnostic value[33] (cf. below). The XPS study of **2a** exhibited signals for tellurium at 575.0 ($3d_{5/2}$) and 585.4 ($3d_{3/2}$) eV.

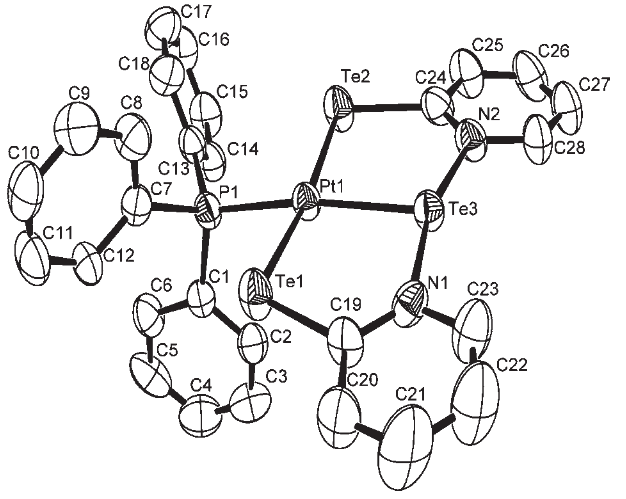


Figure 1. Crystal structure of [Pt(2-Te-C_5H_4N)$_2$Te(PPh_3)] (**2a**) with atomic number scheme. The ellipsoids were drawn at the 50% probability.

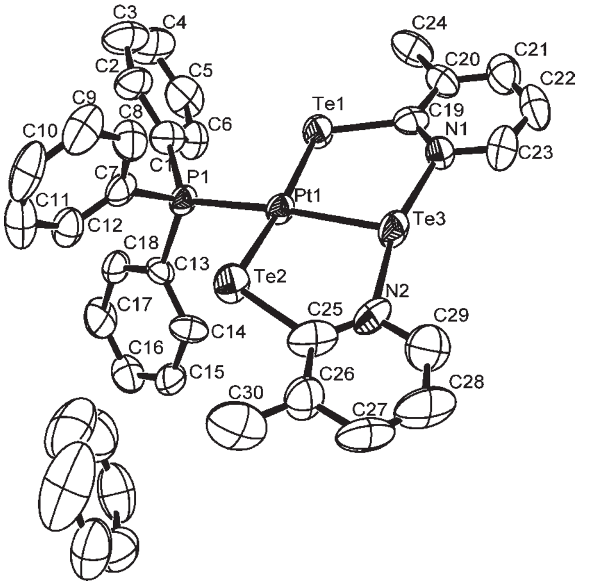


Figure 2. Crystal structure of [Pt$\{$2-Te-C_5H_3(Me)N$\}_2$Te(PPh_3)]·C_6H_6 (**2b**·C_6H_6) with atomic number scheme. The ellipsoids were drawn at the 50% probability.

All complexes are colored and show absorption in their UV−vis spectra in toluene solutions (see the Experimental Section). The bands are red-shifted with respect to the ditelluride ligands. The highest occupied molecular orbital (HOMO) is considered to be centered on the tellurolate ligands, whereas the lowest unoccupied molecular orbital (LUMO) is probably delocalized with significant contributions from the phosphine coligand.[34]

X-Ray Crystallography. The molecular structures of **2a** and **2b**·C_6H_6 were established by single crystal X-ray diffraction analyses. ORTEP drawings with the atomic numbering scheme are shown in Figures 1 and 2, and selected inter atomic parameters are summarized in

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Table 2. Selected Bond Lengths (Å) and Angles (deg) of **2a** and **2b**·C_6H_6

	[Pt(2-Te-$C_5H_4N)_2$Te(PPh_3)] (**2a**)		[Pt{2-Te-C_5H_3(Me)N}$_2$Te(PPh_3)].C_6H_6 (**2b.**C_6H_6)	
	exp.	calc.[a]	exp.	calc.[a]
Pt1−Te1	2.5940(7)	2.659	2.588(3)	2.662
Pt1−Te3	2.5752(6)	2.631	2.569(2)	2.643
Pt1−Te2	2.5720(7)	2.638	2.612(3)	2.686
Te3−N1	2.357(7)	2.386	2.35(1)	2.388
Te3−N2	2.297(7)	2.373	2.32(1)	2.410
Pt1−P1	2.282(2)	2.298	2.283(3)	2.297
Te2−C24	2.103(9)	2.119	2.11(2) (Te2−C25)	2.162
Te1−C19	2.088(8)	2.119	2.10(1)	2.162
N2−Te3−N1	166.1(2)	166.3	165.4(4)	166.8
N2−Te3−Pt1	96.6(2)	96.4	97.1(3)	96.1
N1−Te3−Pt1	96.6(2)	96.6	97.5(3)	96.9
C24−Te2−Pt1	104.6(2)	104.2	104.8(5) (C25−Te2−Pt1)	104.3
C19−Te1−Pt1	104.6(2)	104.4	106.4(4)	104.9
Te3−Pt1−Te1	92.83(2)	92.4	91.59(6)	91.9
Te2−Pt1−Te3	92.56(2)	92.5	91.40(7)	91.5
Te2−Pt1−Te1	172.74(2)	173.4	173.99(4)	171.6
P1−Pt1−Te2	89.29(6)	89.4	86.99(10)	86.8
P1−Pt1−Te3	171.40(6)	171.8	175.56(9)	173.6
P1−Pt1−Te1	86.10(6)	86.3	90.40(10)	90.4

[a] PBE/ZORA+SO calculations.

Table 2. The two structures are rather similar, involving discrete molecules with distorted square planar environments around the platinum(II) center and a "Te_3P" coordination core. The two mutually trans 2-pyridinetellurolate ligands are bound by the central platinum(II) atom in a monodentate fashion through the tellurolate atoms. A conceivable tellurone resonance structure is not supported by the structural data. For both **2a** and **2b**, the nitrogen atoms of the pyridyl rings are connected to the "bare" tellurium atom (Te3) with a N1−Te3−N2 angle of about 166°. The deviation of the N−Te−N angle from linearity is rather small and may be assigned to repulsion from two nonbonding pairs of electrons. The tellurium(0) atoms (Te3) thus adopt a "bent T" configuration. Its geometry can be defined as distorted trigonal-bipyramidal with the platinum and two lone pairs at the equatorial positions and two pyridyl nitrogen atoms occupying the axial sites. On the basis of the isoelectronic relationship between Te^0 and I^{+I}, the observed novel bis(pyridine)-tellurium(0) structural motif in **2a** and **2b** can be compared with the well-known,[35,36] theoretically studied[37] and synthetically applied[38] bis(pyridine)iodonium cations.

$$[C_5H_5N{-}I{-}C_5H_5N]^+ \quad [C_5H_5N{-}Te{-}C_5H_5N]^0$$

In both cases, the empty 5p orbital interacts with the pyridine lone pairs, leading to the straightened N−E−N angle and, for **2a**, to the observed XPS shift in the direction of Te^{-II}. The chelate-promoted coplanarity of the bis(pyridine)element entity in **2a** and **2b** was noted[36] and analyzed[37] similarly for $[C_5H_5N{-}I{-}C_5H_5N]^+$. The steric requirements by the 2-pyridyltellurolate groups are probably responsible for the slightly increased deviation of $(C_5H_4)N{-}E{-}N(C_5H_4)$ from 180°[36] in the present situation. This arrangement receives additional stabilization through coordination of all three Te atoms to the metal in a tridentate fashion. Remarkably, all Pt−Te distances (2.5690(19)−2.612(3) Å) are similar, which could mean that Te is gaining a significant amount of negative charge from the lone pairs of nitrogen that leave them positively charged. The Pt−Te bonds are slightly longer than those reported for [PtCl($TeCH_2CH_2NMe_2$)-(PR_3)] (2.5261(5) Å)[34] but are comparable to those in complexes containing tellurolate ligands trans to phosphine (e.g., *cis*-[Pt(TeTh)$_2$(dppe)] (2.607, 2.6594(9) Å),[39] *cis*-[Pt(1,2-$Te_2C_6H_4$)(PPh_3)$_2$] (2.586(1) Å),[40] or *trans*-[Pt-($TeCOC_6H_4Me$-4)$_2$(PEt_3)$_2$] (2.592(1), 2.632(2) Å).[41] The Pt−P distances are as expected.[39,40] The slight lengthening of the Pt−Te distances may be attributed to the strong trans influence of tellurolate. The Te−N distances (2.297(7)−2.357(7) Å) are well within the range reported in organotellurium compounds, e.g., $R_2Te(N_3)_2$ (2.180−2.253 Å),[42] [{Ph_2TeN_3}$_2$O] (2.397(8) Å),[43] or [{Ph_2Te-(NCS)}$_2$O] (2.40(1) Å).[44]

Density Functional Calculations. In order to gain more insight over the charge distribution in **2a** and **2b**, all-electron density functional calculations were done, employing the Hirshfeld and Voronoi deformation densities (VDD), which are partitioning schemes for selected

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Table 3. Hirshfeld and VDD Charge Analyses for Selected Atoms and Fragments of **2a** and **2b**

	2a		**2b**	
	Hirshfeld	VDD	Hirshfeld	VDD
		atoms		
Te3	−0.001	−0.081	−0.004	−0.072
Pt1	−0.059	−0.115	−0.078	−0.142
Te1	−0.001	−0.061	−0.003	−0.049
Te2	−0.005	−0.060	−0.007	−0.047
		fragments		
$[2\text{-Te-py}]^-$ 1[a]	−0.034	−0.008	−0.041	−0.017
$[2\text{-Te-py}]^-$ 2[b]	−0.038	−0.006	−0.045	−0.017
PPh_3	+0.132	+0.208	+0.150	+0.251

[a] Refers to the fragment formed by Te1−C19−C20−C21−C22−C23−N1 for **2a**, and Te1−C19−C20−C24−C21−C22−C23−N1 for **2b**. [b] Refers to the fragment formed by Te2−C24−C25−C26−C27−C28−N2 for **2a**, and Te2−C25−C26−C30−C27−C28−C29−N2 for **2b.**

atoms and fragments.[45] The calculated data suggest that the three tellurium atoms (Te1, Te2, and Te3) exhibit similar charge densities. We performed a detailed analysis focusing on the charge distribution for the Te3 and Pt1 atoms, for the fragments denoted by the 2-pyridyltellurolate ($[2\text{-Te-}C_5H_4N]^-$ and $[2\text{-Te-}C_5H_3(Me)N]^-$ for **2a** and **2b**, respectively), and for the PPh_3 ligands (Table 3). Similar results were observed for Hirshfeld and VDD analyses; thus, herein we focus on the former. The Hirshfeld analysis for **2a** shows that the Pt^{II} (Pt1) atom gains about 0.132 ē from the triphenylphosphine and about 0.966 ē from each 2-pyridyltellurolate ligand to give a total charge of −0.059 in the region defined by the Hirshfeld scheme. Similar results were obtained for **2b**. Thus, the calculations are consistent with the suggestion that the tricoordinated tellurium(0) atoms (Te3) act as zero-valent ligands.

Additionally, the Nuclear Independent Chemical Shift index (NICS)[46] and the Electron Localization Function (ELF)[47] including spin−orbit interaction have been evaluated to determine the electronic structure of the five-membered ring constituted by the Te−C−N−Te−Pt atoms. The values of the NICS index in the center of the ring are −7.46 ppm and −7.55 ppm for **2a** and **2b**, respectively, which indicates a similar aromatic behavior to that of benzene (−7.89 ppm). Moreover, the values of the ELF (η) function are conveniently defined between 0 and 1 ($0 \leq \text{ELF} \leq 1$), where 0.5 is the parameter for a homogeneous electron gas at a density equal to the local density of the system. In this sense, ELF = 1 denotes perfect localization and 0.5 a perfect delocalization.[48] Values between ~0.0 and 0.5 indicate delocalization in low-density regions.[48] In Figure 3, the ELF values for **2b** are given for the Te−C−N−Te−Pt plane, denoting typical values for delocalization in the rings, ELF = 0.71 between Te−C− and C−N−, and values less than ELF = 0.5 between N−Te− (ELF = 0.43), Te−Pt− (ELF = 0.25), and Pt−Te− (ELF = 0.25), respectively. These ELF values are in accord with the electronic delocalization in the five-membered ring as suggested by the NICS index. Compound **2a** exhibits a similar aromatic behavior.

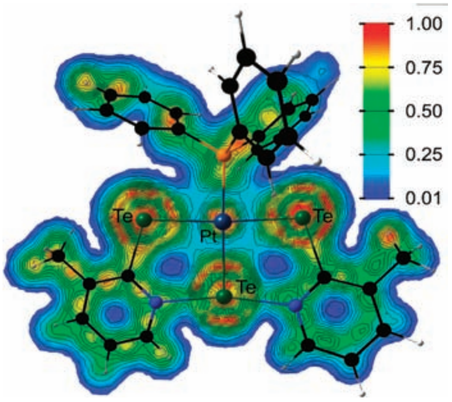

Figure 3. ELF values for the five-membered ring formed by Te−C−N−Te−Pt.

Conclusion

In an attempt to investigate the oxidative addition reaction alternatives between bis(2-pyridyl)ditellurides and platinum(0) compounds, we obtained not only the expected systems of the type $[Pt\{2\text{-Te-3-(R)-}C_5H_3N\}_2(PR'_3)_2]$ but also the crystalline products $[Pt\{2\text{-Te-3-(R)-}C_5H_3N\}_2Te(PR'_3)]$ in which formally zero-valent tellurium bridges two pyridine nitrogen rings of two trans-situated Te-coordinated 2-pyridyltellurolates. An all-tellurium-donor tridentate ligand is thus formed, and the otherwise conventional, slightly distorted square-planar coordination arrangement at platinum(II) consists of one triarylphosphine−P and three tellurium atoms. The little varied Pt−Te distances and the N−Te−N angles of about 166° signify an unstrained situation, the bis(pyridine)-tellurium(0) structural motif being isoelectronic with the well established[36,37] and synthetically useful[38] bis(pyridine)-iodonium cations. The calculated NICS indices and ELF functions clearly show that compounds **2a** and **2b** are aromatic in the region defined by the Te−C−N−Te−Pt five-membered rings.

CCDC numbers 754781 and 754782 for $[Pt(2\text{-Te-}C_5H_4N)_2\text{-}Te(PPh_3)]$ (**2a**) and $[Pt\{2\text{-Te-}C_5H_3(Me)N\}_2Te(PPh_3)]\cdot C_6H_6$ (**2b·C$_6$H$_6$**), respectively, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre,

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(45) Geometry optimizations and charge analyses calculations were done for **2a** and **2b**, employing the ADF2009 code (http://www.scm.com). We employed all-electron triple-ζ Slater basis sets plus polarization function (STO-TZP) within the generalized gradient approximation (GGA) of Perdew−Burke−Ernzerhof (PBE) for the exchange and correlation potentials, through the ZORA Hamiltonian for the inclusion of both scalar and spin−orbit effects. The NICS indexes were calculated by using the OPBE functional.

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Supporting Information Available: Crystallographic data for Pt(Tepy)$_2$Te(PPh$_3$) and Pt(TepyMe)$_2$Te(PPh$_3$) in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.