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Telluronium Ions as σ-Acceptor Ligands**

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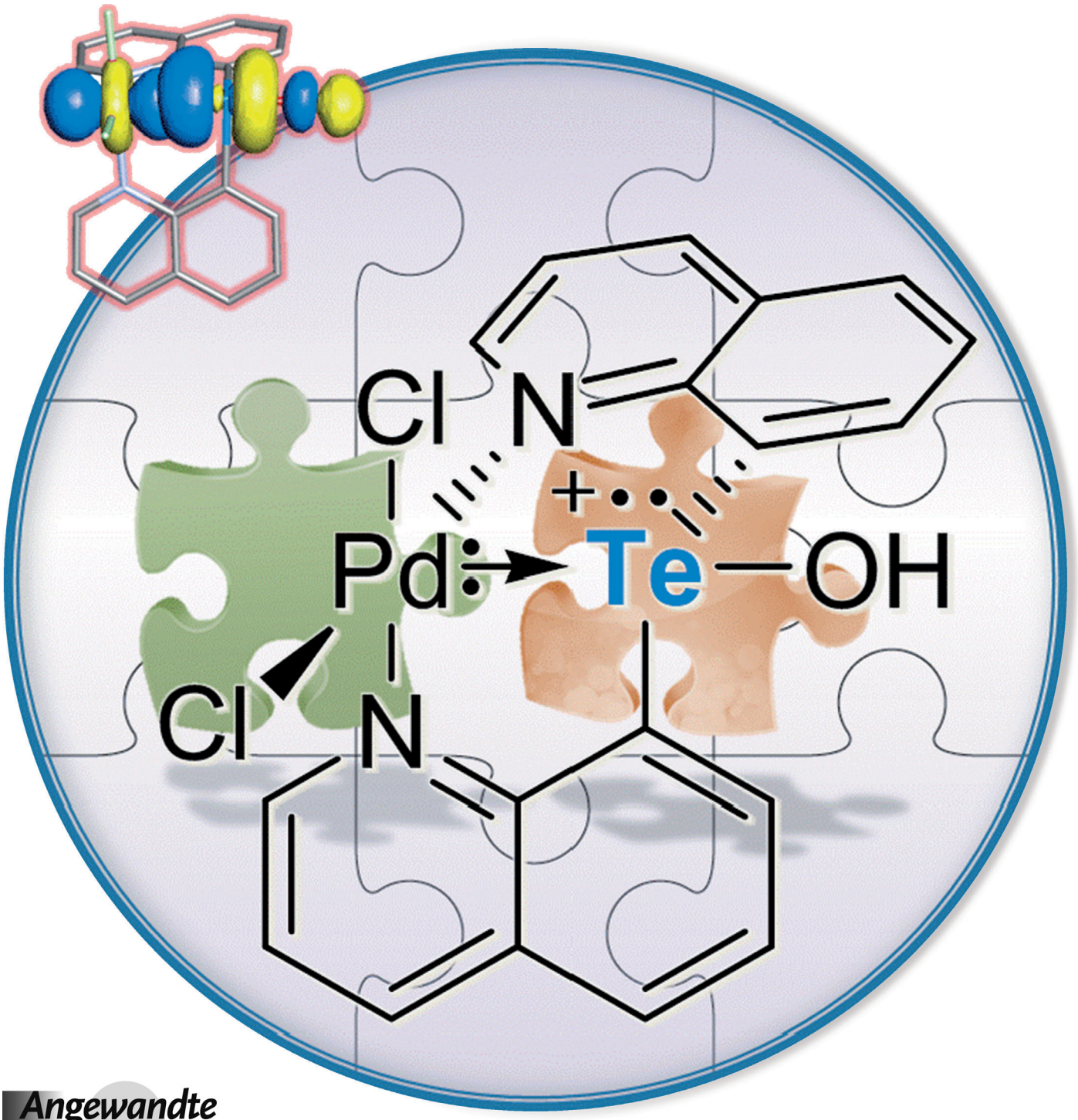
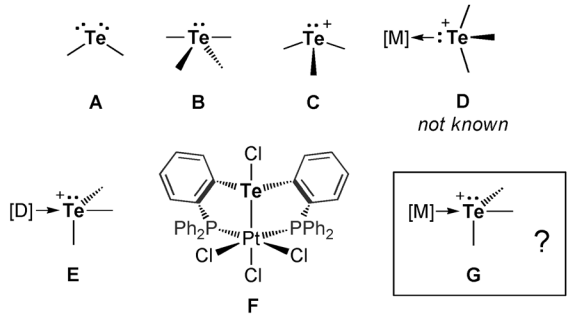


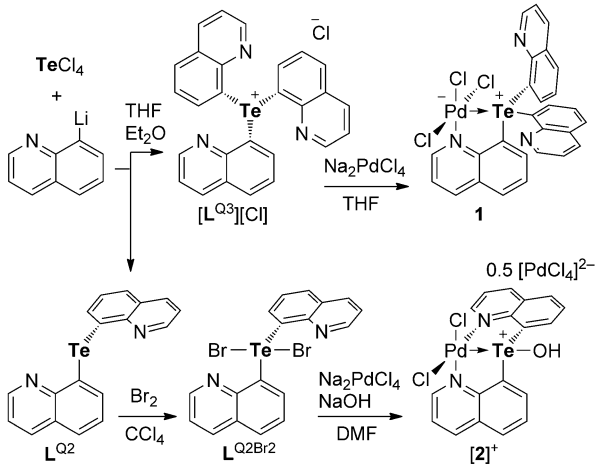
Unlike telluroethers (**A**), which are well-known L-type ligands,[1] telluranes (**B**) have never been incorporated as donor ligands in transition metal complexes. The contrasting ligative behavior of these divalent and tetravalent tellurium species is explained by the decreased capacity for donation of the remaining tellurium lone pair in the tetravalent state. These largely electrostatic effects are magnified in telluronium cations (**C**) which, despite their isoelectronic relationship to stibines, have not been found to form transition metal complexes of type **D**. Although the Lewis basic character of telluronium cations may be negligible,[2] such species behave as Lewis acids and readily form hypervalent adducts of type **E**.[3]



[D] = Lewis base; [M] = transition metal

As part of our ongoing effort to develop the chemistry of metallated hypervalent main group compounds,[4] we recently isolated a Te–Pt complex (**F**) possessing a covalent Te–Pt bond polarized toward the platinum atom.[5] This result has led us to speculate that telluronium ions may behave as σ-acceptors or Z-ligands[6] for transition metals to form complexes of type **G**. In this paper, we describe a series of results which support this notion.

To promote the formation of a metal→telluronium bond, we decided to target a telluronium ligand whose interaction with the metal fragment is supported by auxiliary donor groups. Toward this end, 8-lithio-quinoline was allowed to react with $TeCl_4$ to afford tris(8-quinolinyl) telluronium ($[\mathbf{L}^{Q3}]^+$) as a chloride salt (Scheme 1). This reaction also produced bis(8-quinolinyl) telluroether ($\mathbf{L}^{Q2}$), which could be easily separated from $[\mathbf{L}^{Q3}][Cl]$. The chemical shift of the ^{125}Te NMR resonance of $[\mathbf{L}^{Q3}][Cl]$ at 669 ppm is comparable to that



Scheme 1. Synthesis of **1** and $[\mathbf{2}]^+$.

measured for other telluronium salts, such as $[Ph_3Te][Cl]$ (773 ppm),[7] and notably downfield from that of the telluroether $\mathbf{L}^{Q2}$ at 488 ppm. The reaction of $[\mathbf{L}^{Q3}][Cl]$ with Na_2PdCl_4 afforded $[\mathbf{L}^{Q3}][PdCl_3]$ (**1**) in high yield (Scheme 1). Complex **1** has been fully characterized and its crystal structure determined (Figure 1).[8] The most important feature in the structure of **1** is the Pd–Te bond distance of 2.9201(8) Å, which exceeds the sum of the covalent radii (2.56–2.77 Å)[9] by only 5.4–14.1%. The orientation of the telluronium moiety with respect to the palladium center also offers some important insights. In particular, the large Pd-Te-C_{ax} angle of 157.40(12)° and the narrow C_{eq1}-Te-C_{eq2} angle of 94.88(18)° suggest that the tellurium atom is in a distorted seesaw geometry, with the palladium atom and one quinolinyl group acting as axial ligands. In favor of this view, we also note that the sum of the C-Te-C bond angles (285.8°) in **1** is essentially identical to that in $[\mathbf{L}^{Q3}][Cl]$ (285.7°, see the Supporting Information for structural details).[8] As indicated by the absence of variation in these angles, the degree of s–p hybridization of the tellurium center remains constant, thus

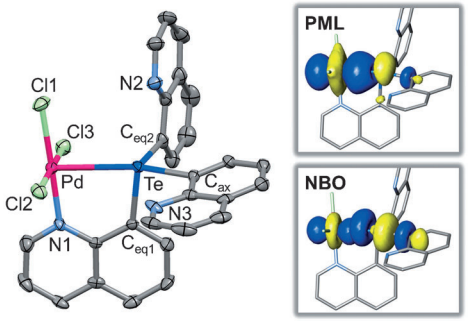


Figure 1. Left: Solid state structure of **1**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Pertinent metrical parameters can be found in the text. Right: Pd–Te Pipek–Mezey localized (PML) orbital (top, isovalue = 0.02), and natural bond orbital (NBO) plot showing the d(Pd)→σ*(Te-C_{ax}) donor–acceptor interactions (bottom, isovalue = 0.05). Hydrogen atoms are omitted for clarity.

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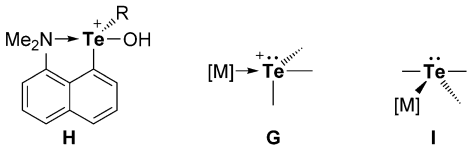
supporting the lack of involvement of the remaining tellurium lone pair in a donor interaction with the palladium atom. The formation of a Te→Pd dative bond should also have resulted in a trigonal bipyramidal geometry at palladium, but this phenomenon is not observed. Instead, the palladium center is square pyramidal with a τ value of 0.029.[10] Altogether, these structural features are best reconciled by invoking a Pd→Te bonding motif with the telluronium ion behaving as a σ-acceptor ligand.

Complex **1** readily dissociates when dissolved in [D_6]DMSO, thus pointing to the lability of this complex and the weakness of the Pd→Te interaction. To determine if an increase in the Lewis acidity of the tellurium center could be used to stabilize this interaction, we decided to target a telluronium ligand featuring an electronegative element directly bound to tellurium. With this in mind, $\mathbf{L}^{Q2}$ was converted into $\mathbf{L}^{Q2Br2}$ by reaction with bromine (Scheme 1). This new ligand was then allowed to react with Na_2PdCl_4 in DMF (used as provided with ca. 1% of H_2O based on NMR) in the presence of NaOH to afford the salt $[\mathbf{2}]_2[PdCl_4]$ in moderate yield (Scheme 1). The ^{125}Te NMR resonance measured for $[\mathbf{2}]^+$ (753 ppm) is slightly more downfield than that of $\mathbf{L}^{Q2Br2}$ (688 ppm). The ^{1}H NMR spectrum of $[\mathbf{2}]^+$ features one set of quinoline proton resonances, which indicates that the two quinolinyl arms are magnetically equivalent. Additional information on the structure of this cation were derived from a ESI mass spectrum (*m*/*z* 578.8510) and a crystallographic measurement, which indicates that $[\mathbf{2}]^+$ is the $PdCl_2$ complex of the cationic telluronium hydroxide ligand ($[\mathbf{L}^{Q2(OH)}]^+$).[8] Inspection of the structure of $[\mathbf{2}]^+$ indicates that both quinolinyl arms are ligated to the palladium center through the nitrogen atoms. This arrangement places the tellurium atom at 2.7823(8) Å from the palladium center. This Pd–Te distance exceeds the sum of the covalent radii (2.56–2.77 Å)[9] by only 0.4–8.7% and is notably shorter than that in **1** (2.9201(8) Å). The tellurium atom is also bound to a hydroxide ligand (Te–O 1.941(4) Å), which originates from the basic conditions used to synthesize this complex. As indicated by the Pd-Te-O (169.3(2)°) and C_{eq1}-Te-C_{eq2} (91.8(3)°) angles, the tellurium atom is in a seesaw geometry with the palladium atom oriented *trans* to the hydroxide ligand. In addition to the tellurium atom, the coordination sphere of the palladium atom involves the two quinolinyl nitrogen atoms (N1 and N2) and two chloride ligands (Cl1 and Cl2), which define an approximate square plane as well as a bridging chloride (Pd–Cl2′ 3.221 Å, Cl2′-Pd-Te 174.50°) provided by a neighboring molecule of the complex. Despite the length of the Pd–Cl2′ bond, which exceeds that of Pd–Cl1 (2.3228(14) Å) and Pd–Cl2 (2.3100(15) Å), the presence of this additional ligand indicates that the coordination sphere of the palladium center is intermediate between square pyramidal ($\tau = 0.003$) and octahedral, a situation that is reminiscent of the tetravalent state. Taken collectively, these structural results indicate that $[\mathbf{2}]^+$ possesses a Pd→Te interaction, the magnitude of which exceeds that in **1**. It is also interesting to note the parallel that exists between the structure of $[\mathbf{2}]^+$ and that of $[(8\text{-}Me_2NC_{10}H_6)_2Te(OH)]^+$ (**H**),[11] a complex with an intramolecular N→Te interaction and a Te–O distance of 1.957(4) Å, which is close to that of $[\mathbf{2}]^+$ (1.941(4) Å).



H **G** **I**

The above structural analyses suggest that the telluronium cations $[\mathbf{L}^{Q3}]^+$ and $[\mathbf{L}^{Q2(OH)}]^+$ can coordinate to late transition metals as Z-ligands. A unique characteristic of the resulting structures comes from the positioning of the palladium atom with respect to the tellurium center. Indeed, in both structures the palladium atom adopts an axial position of the disphenoid telluronium center (**G**). This places the palladium atom on the axis of the formally three-center four-electron "hypervalent" interaction. This situation contrasts with that found in known transition metal telluranyl complexes,[12] where the tellurium–metal bond lies in the equatorial plane of the disphenoid telluronium center (**I**).[13] In such complexes, the telluranyl ligand has been described as acting as a classic X-ligand.[13a] Although the observation that telluronium cations can behave as Z-ligands is unprecedented, a Mn→Te dative bond has been reported in [PPN][$(CO)_5$Mn-$TeCl_4$].[14] In this case, a tellurane ligand ($TeCl_4$) acts as a σ-acceptor for a manganate center, leading to a square pyramidal tellurium geometry. It is also important to note the parallel that exists between these new results and the known ability of SO_2 to act as a Z-ligand in transition metal complexes.[6f,15]

To further evaluate the nature of the Pd–Te bonds in **1** and $[\mathbf{2}]^+$, DFT structural optimizations were performed using the Gaussian program (functional: BP86;[16] mixed basis set: Pd/Te: cc-pVDZ; N/O/Cl: 6-31g(d′); C/H: 6-31g). The level of theory chosen for these calculations was first validated by the optimization of **1** and $[\mathbf{2}]^+$, which produced structures very close to those determined experimentally (see the Supporting Information). The optimized structures were then subjected to a Pipek–Mezey localization (PML) analysis.[17] The resulting localized orbitals (see the Supporting Information), which span the Pd–Te bond, show a major contribution from palladium atomic orbitals (84% in **1** and 83% in $[\mathbf{2}]^+$) and only a minor contribution from tellurium (6% in **1** and 11% in $[\mathbf{2}]^+$). These results indicate that these complexes possess an extremely polar Pd–Te bond, the nature of which was further investigated by NBO analysis. For both complexes, this analysis identifies a donor–acceptor interaction involving a palladium lone pair with a d character and a vacant σ*(Te–X) orbital (X = C_{ax} for **1**, X = O for $[\mathbf{2}]^+$).[18] Deletion calculations obtained by the concurrent zeroing of the Kohn–Sham matrix elements corresponding to the d(Pd)→σ*(Te–X) interactions afforded stabilization energies of 22.5 and 69.8 kcal mol^{-1} for **1** and $[\mathbf{2}]^+$, respectively.[19] The resulting deletion energies can be correlated to the experimentally measured Pd–Te bond distances (2.9201(8) Å for **1** vs. 2.7823(8) Å for $[\mathbf{2}]^+$), which also point to a stronger Pd→Te interaction in $[\mathbf{2}]^+$ (Figure 2).

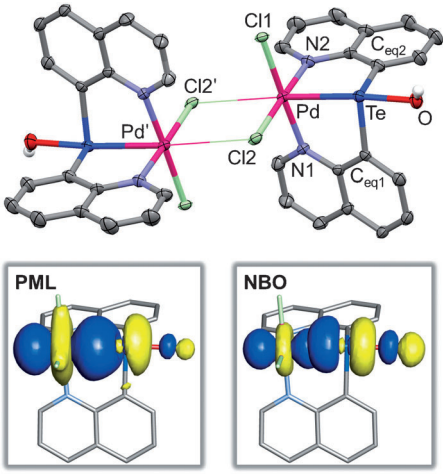


Figure 2. Top: Molecular view showing the dimeric structure of $[\mathbf{2}]_2[PdCl_4]$ in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, solvent molecules, and counteranions ($[PdCl_4]^{2-}$) are omitted for clarity. Pertinent metrical parameters can be found in the text. Bottom: Pd–Te Pipek–Mezey localized (PML) orbital (left, isovalue = 0.02), and natural bond orbital (NBO) plot showing the d(Pd)→σ*(Te-O) donor–acceptor interaction (right, isovalue = 0.05). Hydrogen atoms are omitted for clarity.

In summary, we have shown that telluronium cations may behave as Z-ligands toward transition metals. These results allow us to generalize the propensity of high-valent fifth period species to act as Lewis acidic ligands for transition metals.[4,20] As for related Sn^{IV} [20a–d] and Sb^{V} ligands,[4] the Z-ligative behavior of the telluronium ions originates from the ability of tellurium to achieve a hypervalent configuration. Efforts are underway to exploit the properties of hypervalent tellurium–metal complexes in applications ranging from energy storage to small molecule activation.

Experimental Section

General considerations: 8-lithio-quinoline[21] was prepared according to the reported procedure. Solvents were dried by passing through an alumina column (*n*-hexane, *n*-pentane, and CH_2Cl_2) or by reflux under N_2 over Na/K (Et_2O and THF). DMF and CCl_4 were used as received. $TeCl_4$, Na_2PdCl_4, Br_2, and NaOH were purchased from Aldrich and used as received. Ambient temperature NMR spectra were recorded on a Varian Unity Inova 400 FT NMR (399.59 MHz for ^1H, 100.45 MHz for ^{13}C, 126.14 MHz for ^{125}Te) spectrometer. Chemical shifts (δ) are given in ppm and are referenced against residual solvent signals (^1H, ^{13}C) or external Ph_2Te_2 (^{125}Te). Elemental analyses were performed by Atlantic Microlab (Norcross, GA). Compounds with non-coordinated quinolyl groups ($\mathbf{L}^{Q2}$, $[\mathbf{L}^{Q3}][Cl]$, $\mathbf{L}^{Q2Br2}$, and **1**) proved to be hygroscopic upon exposure to air and became sticky. Elemental analysis confirmed the presence of water. Electrospray mass spectra were obtained with a SciexQstarr Pulsar and a Protana Nanospray ion source.

Synthesis of $\mathbf{L}^{Q2}$ and $[\mathbf{L}^{Q3}][Cl]$: An *n*-hexane solution of *n*BuLi (2.5 M, 7.15 mL, 17.89 mmol) was added to a THF solution (10 mL) of 8-bromo-quinoline (3.54 g, 17.02 mmol) at −78 °C. The mixture was stirred for 20 min at −78 °C, affording a brown solution. The solution was transferred to an Et_2O solution (5 mL) of $TeCl_4$ (1.15 g, 4.25 mmol) dropwise at −78 °C. The resulting solution was allowed to slowly warm up to room temperature over 3 h. After stirring for another 12 h, the solvents were removed under reduced pressure. The resulting solid was dissolved in CH_2Cl_2 (30 mL) and filtered through celite. Removal of CH_2Cl_2 afforded a brown oil containing $\mathbf{L}^{Q2}$ and $[\mathbf{L}^{Q3}][Cl]$. This brown oil was washed with Et_2O (3 × 5 mL) to give a light brown powder that was further washed with water (3 × 10 mL) and methanol (5 mL) to afford a pure sample of $[\mathbf{L}^{Q3}][Cl]$ (1.10 g, 47% yield). The Et_2O filtrate was collected, and the solvent was removed under reduced pressure to afford a brown oil. The addition of *n*-pentane (15 mL) with intense stirring gave a light yellow solid that was then washed with hot water and dried under vacuum, to afford a pure sample of $\mathbf{L}^{Q2}$ (0.23 g, 14% yield). Further recrystallization from Et_2O (5 mL) and *n*-pentane (1 mL) at −30 °C produced yellow crystals of $\mathbf{L}^{Q2}$ suitable for single-crystal diffraction analysis.[8] Light brown crystals of $[\mathbf{L}^{Q3}][Cl]\cdot 2CH_2Cl_2$ that were suitable for single-crystal diffraction analysis were obtained by slowly diffusing Et_2O into a CH_2Cl_2 solution of $[\mathbf{L}^{Q3}][Cl]$.[8] ^1H NMR for $\mathbf{L}^{Q2}$ (399.59 MHz; $CDCl_3$): $\delta = 7.33$ (pseudo t, 2H, $^3J_{H-H} = 7.61$ Hz), 7.46 (dd, 2H, $^3J_{H-H} = 8.20$ Hz, $^3J_{H-H} = 4.32$ Hz), 7.76 (d, 2H, $^3J_{H-H} = 7.70$ Hz), 7.91 (d, 2H, $^3J_{H-H} = 7.90$ Hz), 8.16 (d, 2H, $^3J_{H-H} = 7.90$ Hz), 8.96 ppm (d, 2H, $^3J_{H-H} = 7.70$ Hz). ^1H NMR for $[\mathbf{L}^{Q3}][Cl]$ (399.59 MHz; [D$_6$]DMSO): $\delta = 7.23$ (d, 2H, $^3J_{H-H} = 7.40$ Hz), 7.69 (pseudo t, 2H, $^3J_{H-H} = 7.40$ Hz), 7.81 (dd, 2H, $^3J_{H-H} = 8.41$ Hz, $^3J_{H-H} = 4.40$ Hz), 8.42 (d, 2H, $^3J_{H-H} = 8.21$ Hz), 8.72 (d, 2H, $^3J_{H-H} = 8.21$ Hz), 9.00 ppm (d, 2H, $^3J_{H-H} = 4.36$ Hz). $^{13}C\{^1H\}$ NMR for $\mathbf{L}^{Q2}$ (100.45 MHz; $CDCl_3$): $\delta = 121.6$, 122.2, 127.6, 128.1, 130.5, 132.9, 136.5, 138.2, 150.0 ppm. $^{13}C\{^1H\}$ NMR for $[\mathbf{L}^{Q3}][Cl]$ (100.45 MHz; [D$_6$]DMSO): $\delta = 124.2$, 125.5, 129.1, 129.4, 133.1, 136.4, 138.2, 147.4, 152.2 ppm. $^{125}Te\{^1H\}$ NMR for $\mathbf{L}^{Q2}$ (126.14 MHz; $CDCl_3$): $\delta =$ 488 ppm (s). $^{125}Te\{^1H\}$ NMR for $[\mathbf{L}^{Q3}][Cl]$ (126.14 MHz; [D$_6$]DMSO): $\delta = 676$ ppm (s). HRMS (ESI$^+$) calcd for $[\mathbf{L}^{Q2}+H]^+$ ($C_{27}H_{18}N_3Te^+$): 387.0135, found: 387.0810. HRMS (ESI$^+$) calcd for $[\mathbf{L}^{Q3}]^+$ ($C_{27}H_{18}N_3Te^+$): 514.0557, found: 514.0505. Elemental analysis calculated (%) for $\mathbf{L}^{Q2}\cdot H_2O$: C, 53.79; H, 3.51; found C, 53.05; H, 3.27 (performed on the crude product after exposure to atmosphere). Elemental analysis calculated (%) for $[\mathbf{L}^{Q3}][Cl]\cdot 1.5\,CH_2Cl_2$: C, 50.72; H, 3.14; found C, 50.92; H, 3.86 (performed on the recrystallized compound; 0.5 equiv of CH_2Cl_2 was lost upon drying).

Synthesis of $\mathbf{L}^{Q2Br2}$: Br_2 (79 mg, 0.49 mmol) was added dropwise to a CCl_4 solution (3 mL) of $\mathbf{L}^{Q2}$ (188 mg, 0.49 mmol) at ambient temperature. After stirring for 10 min, the precipitate was collected by filtration and washed with Et_2O (3 mL), CH_2Cl_2 (3 mL), and hot water (10 mL). The resulting solid was dried under vacuum to afford $\mathbf{L}^{Q2Br2}$ (250 mg, 94% yield) as a light yellow solid. ^1H NMR (399.59 MHz; [D$_6$]DMSO): $\delta = 7.81$ (bs, 2H), 7.98 (pseudo t, 2H, $^3J_{H-H} = 6.78$ Hz), 8.37 (d, 2H, $^3J_{H-H} = 7.48$ Hz), 8.66 (pseudo d, 4H, $^3J_{H-H} = 8.01$ Hz), 9.16 ppm (bs, 2H). $^{13}C\{^1H\}$ NMR (100.45 MHz; [D$_6$]DMSO): $\delta = 124.0$, 128.7, 131.8, 135.2, 137.8, 146.0, 151.4 ppm (two quaternary carbon resonances were not observed). $^{125}Te\{^1H\}$ NMR (126.14 MHz; [D$_6$]DMSO): $\delta = 688$ ppm (s). Elemental analysis calculated (%) for $\mathbf{L}^{Q2Br2}\cdot 4H_2O$: C, 35.11; H, 3.27; found C, 35.29; H, 2.58 (performed on the product after exposure to atmosphere).

Synthesis of **1**: A THF suspension (3 mL) of Na_2PdCl_4 (31.2 mg, 0.106 mmol) was added to a THF solution (1 mL) of $[\mathbf{L}^{Q3}][Cl]$ (58 mg, 0.106 mmol) at ambient temperature. The resulting mixture was allowed to stir for 12 h. The solvent was removed under reduced pressure to give an orange solid that was then washed with CH_2Cl_2 (3 × 5 mL) and hot water (3 × 20 mL) to afford **1** as an air stable orange solid (73 mg, 95% yield). Orange crystals of **1**·DMF suitable for single crystal diffraction analysis were obtained by slowly diffusing Et_2O into a DMF solution of **1** at ambient temperature.[8] ^1H NMR (399.59 MHz; [D$_6$]DMSO): $\delta = 7.23$ (d, 2H, $^3J_{H-H} = 7.34$ Hz), 7.68 (pseudo t, 2H, $^3J_{H-H} = 7.34$ Hz), 7.80 (dd, 2H, $^3J_{H-H} = 8.31$ Hz, $^3J_{H-H} = 4.45$ Hz), 8.41 (d, 2H, $^3J_{H-H} = 8.38$ Hz), 8.71 (d, 2H, $^3J_{H-H} = 8.31$ Hz), 8.99 ppm (d, 2H, $^3J_{H-H} = 4.45$ Hz). $^{13}C\{^1H\}$ NMR (100.45 MHz; [D$_6$]DMSO): $\delta = 124.2$, 125.5, 129.1, 129.4, 133.1, 136.4, 138.2, 147.4, 152.2 ppm. $^{125}Te\{^1H\}$ NMR (126.14 MHz; [D$_6$]DMSO): $\delta = 671$ ppm (s). Elemental analysis calculated (%) for **1**·2H$_2$O: C, 42.62; H, 2.91;

found C, 42.88; H, 2.83 (performed on the product after exposure to atmosphere and prior to recrystallization in DMF).

Synthesis of $[\mathbf{2}]_2[PdCl_4]$: Na_2PdCl_4 (64.9 mg, 0.22 mmol) and NaOH (4.4 mg, 0.11 mmol) were added to a DMF solution (3 mL) of $\mathbf{L}^{Q2Br2}$ (60 mg, 0.11 mmol) at ambient temperature. After stirring for 12 h, CH_2Cl_2 (1 mL) and Et_2O (10 mL) were added to the mixture. The resulting solution was further stirred for 30 min to give a red precipitate that was then collected by filtration and washed with CH_2Cl_2 (5 mL) and water (3 × 10 mL). The resulting solid was dried under vacuum to afford $[\mathbf{2}]_2[PdCl_4]$ as a red solid (29 mg, 37% yield). Red crystals of $[\mathbf{2}]_2[PdCl_4]\cdot 4\,DMF$ that were suitable for single-crystal diffraction analysis were obtained by slowly diffusing Et_2O into a DMF solution of $[\mathbf{2}]_2[PdCl_4]$ at ambient temperature.[8] ^1H NMR (399.59 MHz; $[D_6]$DMSO): $\delta = 7.82$ (dd, 2H, $^3J_{H-H} = 7.95$ Hz, $^3J_{H-H} = 4.62$ Hz), 8.00 (pseudo t, 2H, $^3J_{H-H} = 7.77$ Hz), 8.38 (d, 2H, $^3J_{H-H} = 7.77$ Hz), 8.63 (d, 2H, $^3J_{H-H} = 7.42$ Hz), 8.68 (d, 2H, $^3J_{H-H} = 7.77$ Hz), 9.16 ppm (d, 2H, $^3J_{H-H} = 3.96$ Hz). $^{13}C\{^1H\}$ NMR (100.45 MHz; $[D_6]$DMSO): $\delta = 123.9$, 128.7, 128.8, 131.8, 134.8, 137.8, 145.7, 151.6, 162.8 ppm. $^{125}Te\{^1H\}$ NMR (126.14 MHz; $[D_6]$DMSO): $\delta = 753$ ppm (s). HRMS (ESI^+) calcd for $[\mathbf{2}]^+$ ($C_{18}H_{13}Cl_2N_2OPdTe^+$): 578.8497, found: 578.8510. Elemental analysis calculated (%) for $[\mathbf{2}]_2[PdCl_4]$: C, 30.78; H, 1.87; found C, 31.27; H, 2.05 (performed on the product prior to recrystallization in DMF).

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