Cluster Compounds

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Synthesis of Tellurido-Bridged $IrPt_2$, $IrPd_2$, and IrPtPd Clusters by Inserting Zero-Valent Pt and Pd Centers into Te–C Bonds[**]

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Soluble transition-metal sulfido clusters have been investigated extensively because of their relevance to biological and industrial catalysts. In contrast, the chemistry of the analogues of tellurium, the heavier congener of sulfur, has been less-well developed.[1] This difference is presumably because, at least in

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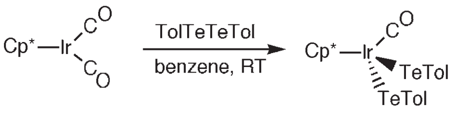
part, good tellurido sources that can be used in organic media are scarce.[2]

In the last decade, studies in our group have focused on the pursuit of rational methods to construct metal sulfido and selenido cluster cores with desired structures and atom compositions.[3] In the course of these studies, we have demonstrated that newly prepared dinuclear μ-hydrosulfido and μ-hydroselenido complexes of the type [Cp*MCl(μ-EH)$_2$MCp*Cl] (M = Ru, Ir, Rh; E = S, Se; Cp* = η^5-C_5Me_5) can serve as versatile building blocks to synthesize a variety of homo- and heterometallic sulfido, selenido, and sulfido–selenido clusters.[3,4] However, preparation of the corresponding tellurido clusters is not yet feasible, as the hydrotellurido analogues of these μ-EH complexes are not accessible.

Formations of tellurido ligands from coordinated tellurolates have been observed for isolated or in situ-generated complexes of Cr,[5] Mo,[6] Re,[7] Pd,[8] Ag,[9] and Cu.[10] Furthermore, cleavage of the E–C bonds of organochalcogen compounds has also been demonstrated in a well-defined manner for the reactions with low-valent late transition metals,[11] which include the oxidative addition reactions of Ph_2Te with zero-valent Group 10 metal complexes.[12] On the basis of these findings, we have attempted the synthesis of mixed-metal tellurido clusters by a new route, which involves the initial preparation of an Ir tellurolato complex by using readily available RTeTeR compounds (in which R = aryl) as the Te source and subsequent transformation of this complex into the tellurido clusters through Te–C bond cleavage of the tellurolato ligands by using Group 10 noble metals.

Treatment of [Cp*Ir(CO)$_2$] with one equivalent of TolTeTeTol (Tol = p-$CH_3C_6H_4$) in benzene at room temperature afforded a bis(tellurolato) complex [Cp*Ir(CO)(TeTol)$_2$] (**1**) in high yield [Eq. (1)], which has been characterized by single-crystal X-ray analysis (Figure 1).[13] Complex **1** has an expected three-legged structure, for which the interatomic distances and angles are not unusual. Related thiolato and selenolato complexes [Cp*Ir(CO)(EPh)$_2$] (E = S, Se) are known, which were prepared from [Cp*Ir(CO)$_2$] and PhEEPh in THF by photo-irradiation. However, X-ray structures were not determined.[14]



$$\mathrm{Cp^*Ir(CO)_2} \xrightarrow[\text{benzene, RT}]{\text{TolTeTeTol}} \mathrm{Cp^*Ir(CO)(TeTol)_2} \quad (1)$$

1

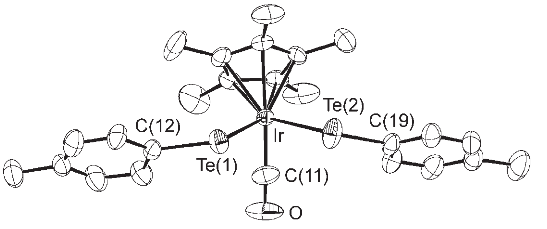
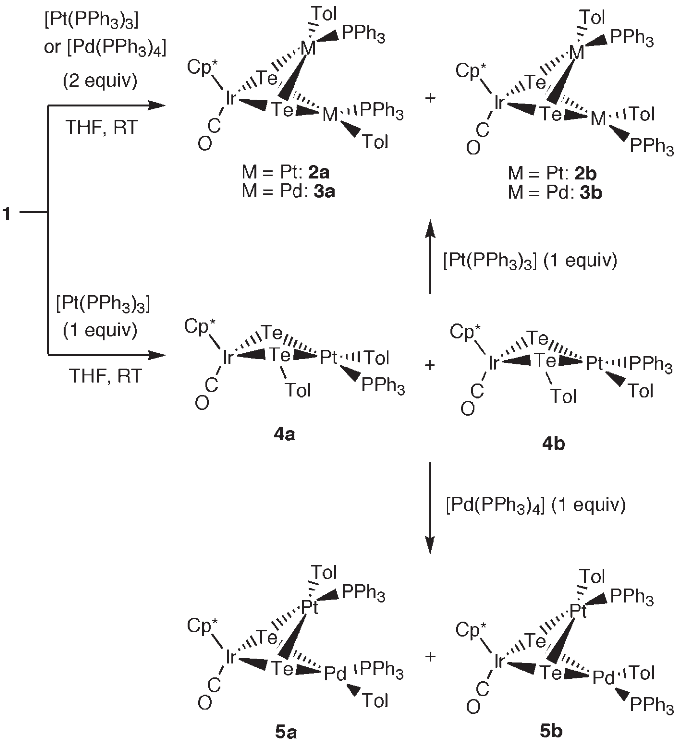


Figure 1. An ORTEP drawing of **1**. Hydrogen atoms are omitted for clarity (thermal ellipsoids shown at 30% probability). Selected bond lengths [Å] and angles [°]: Ir–Te(1) 2.6654(6), Ir–Te(2) 2.6579(8); Te(1)-Ir-Te(2) 79.46(2).

When **1** was treated with two equivalents of [Pt(PPh$_3$)$_3$] in THF at room temperature, the mixed-metal tellurido cluster [{Cp*Ir(CO)}(μ_3-Te)$_2${PtTol(PPh$_3$)}$_2$] (**2**) was obtained. The NMR spectra of the residue obtained from the reaction mixture after removal of solvent by evaporation showed the presence of the two isomers, **2a** and **2b** (Scheme 1). After crystallization of the residue from a mixture of benzene and hexane, only the major isomer, **2a**, was isolated as single crystals and fully characterized by X-ray diffraction.[13] As shown in Figure 2, **2a** has a triangular IrPt$_2$ core with two capped tellurido ligands, for which, separations of Ir(1) from Pt(1) and Pt(2) by 3.8049(5)–3.8588(6) Å as well as Pt···Pt interatomic distances of 3.1539(6) and 3.2523(7) Å indicate the absence of any metal–metal bonding interactions. The Ir center has a three-legged geometry, while the geometry around two Pt atoms is square-planar. Two phosphine ligands are mutually *trans* with respect to the Pt–Pt vector, as are the two Tol ligands. The X-ray structure was not available for **2b**, but its NMR data are analogous to those of **2a** and suggest a structure with two mutually *cis*-phosphine ligands (shown in Scheme 1 for **2b**). Because of steric repulsion between the two phosphine ligands, **2b** is the less-favored isomer. Note that **2a** redissolved in C_6D_6 and converted readily into an equilibrium mixture of **2a** and **2b** at room temperature, the ratio of which was 4:1, thus indicating that the isomerization of **2a** into **2b** is fast for this IrPt$_2$ cluster.



Scheme 1. Synthetic routes for mixed-metal tellurido clusters.

Treatment of **1** with two equivalents of [Pd(PPh$_3$)$_4$] gave the Pd analogue of **2**, [{Cp*Ir(CO)}(μ_3-Te)$_2${PdTol(PPh$_3$)}$_2$]

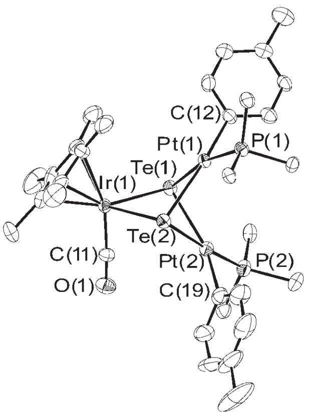


Figure 2. An ORTEP drawing of **2a**. Only one of the two independent molecules is shown (thermal ellipsoids shown at 30% probability). For clarity all the hydrogen atoms are omitted and only the carbon atom bound to P is shown for the phenyl groups of the PPh_3 units. Selected bond lengths [Å] and angles [°]: Ir–Te 2.6769(7)–2.6985(7), Pt–Te, 2.6347(8)–2.7052(7); Ir-Te-Pt, 89.82(2)–92.69(2), Pt-Te-Pt, 72.39(2)–75.23(2), Te-Ir-Te 75.26(2), 75.60(2), Te-Pt-Te, 75.86(2)–76.44(2). In isostructural **3a**: Ir···Pd 3.784(1)–3.837(1), Pd···Pd 3.185(2), 3.089(1), Ir-Te, 2.666(1)–2.689(1), Pd-Te, 2.605(1)–2.702(2), Ir-Te-Pd 89.49(4)–92.91(3), Pd-Te-Pd, 71.31(4)–74.12(4), Te-Ir-Te 75.68(3), 75.91(3), Te-Pd-Te, 76.60(4)–76.98(4).

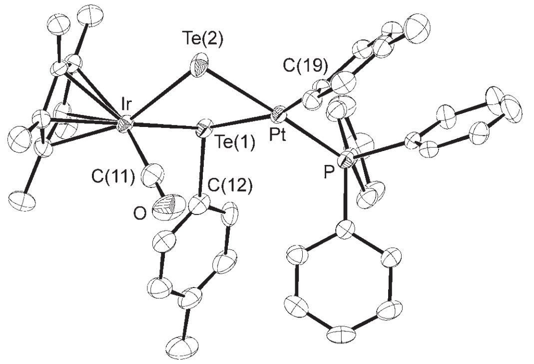


Figure 3. An ORTEP drawing of **4a**. Hydrogen atoms are omitted for clarity (thermal ellipsoids shown at 30% probability). Selected bond lengths [Å] and angles [°]: Ir···Pt 3.9198(5); Ir-Te(1)-Pt 95.98(2), Ir-Te(2)-Pt 95.50(2), Te-Ir-Te 76.38(2), Te-Pt-Te 77.42(2).

(**3**), which is present as a mixture of **3a** and **3b** under the reaction conditions (Scheme 1). Workup of the product solution afforded only **3a** as single crystals and the X-ray analysis disclosed its structure to be analogous to that of **2a**.[13] When redissolved in C_6D_6, **3a** slowly converted into an equilibrium mixture of **3a** and **3b** to reach a molar ratio of 3:1. This isomerization of the $IrPd_2$ cluster is considerably slower than that of the $IrPt_2$ cluster, **2a**. As addition of 0.1 equivalents of PPh_3 to the solution of **3a** significantly decreases the rate of the formation of **3b**, this isomerization presumably proceeds through dissociation of PPh_3. The much-faster isomerization of **2a** than that of **3a** may be ascribable to the higher ability of PPh_3 to dissociate from a Pt center than from a Pd center.

The reaction of **1** with one equivalent of $[Pt(PPh_3)_3]$ in THF at room temperature resulted in the isolation of the intermediate in the conversion of **1** into **2**. Workup of the reaction mixture afforded the tellurido- and tellurolato-bridged dinuclear complex $[Cp^*Ir(CO)(\mu\text{-}Te)(\mu\text{-}TeTol)PtTol(PPh_3)]$ (**4**), which was isolated as a mixture of isomers, **4a** and **4b** (Scheme 1). For the major isomer, **4a**, the structure has been determined unambiguously by X-ray analysis of single crystals obtained after repeated crystallization of this mixture (Figure 3).[13] Two metal centers are connected by one μ-telluride and one μ-tellurolate, in which the tellurido and Tol ligands around Pt are mutually *cis*. Oxidative addition of a Pt^0 center across one Te–Tol bond in **1** and coordination of a Te atom of the other intact TeTol ligand to Pt affords **4a**. There are no bonding interactions between metal centers in **4a**. The Pt–Te(1) bond at 2.6563(7) Å is considerably longer than the Pt–Te(2) bond at 2.6013(7) Å presumably because of the strong *trans* influence exerted by the Tol ligand. Around the Ir center, the Ir-μ-tellurolato bond (Ir–Te(1) 2.6243(6) Å) is shorter than the Ir-μ-tellurido bond (Ir–Te(2) 2.6934(8) Å; Figure 3). Unfortunately, an X-ray crystal structure was not obtainable for **4b**. However, spectroscopic data of **4b** are consistent with the structure shown in Scheme 1, in which only the geometry around Pt differs from that of **4a**. Complex **4a** dissolved in C_6D_6 and converted into a 2.2:1 mixture of **4a** and **4b** in equilibrium after 30 h at room temperature. A similar isomerization was reported for the reaction of $[Pt(PEt_3)_3]$ with *i*PrTePh, in which the initial product *cis*-$[PtPh(Te\textit{i}Pr)(PEt_3)_2]$ transformed smoothly into *trans*-$[PtPh(Te\textit{i}Pr)(PEt_3)_2]$.[11] Treatment of an equilibrium mixture of **4a** and **4b** with one equivalent of $[Pt(PPh_3)_3]$ afforded a mixture of **2a** and **2b**, which indicates that the complexes **4** are the intermediates in the reaction course of **1** to **2**.

It is noteworthy that from the reaction of **1** with $[Pd(PPh_3)_4]$, the telluride–tellurolato complex corresponding to **4** was not obtained. The reaction of equimolar **1** and $[Pd(PPh_3)_4]$ resulted in the formation of a mixture of the trinuclear tellurido cluster, **3**, and residual **1**, as indicated by the NMR spectra of the reaction mixture recorded soon after mixing.

It was also found that from the reaction of the Ir–Pt complex, **4**, with $[Pd(PPh_3)_4]$, another trinuclear cluster $[\{Cp^*Ir(CO)\}(\mu_3\text{-}Te)_2\{PtTol(PPh_3)\}\{PdTol(PPh_3)\}]$ (**5**) was available through the facile insertion of a Pd^0 center into the remaining Te–Tol bond in complex **4** (Scheme 1). The NMR spectra of the reaction mixture showed the presence of **5a**. After removal of the solvent by evaporation, crystallization of the residue from a mixture of THF and hexane afforded **5a** as single crystals. The NMR spectra of **5a** in C_6D_6 indicated its rapid transformation into an equilibrium mixture of **5a** and **5b** in a 3:1 molar ratio. The X-ray crystal structure of **5a** is depicted in Figure 4.[13] Cluster **5a** has the expected triangular core capped by two μ_3-tellurido ligands, in which the Pd atom occupies the vertex close to the CO ligand, presumably because the insertion of the Pd center into the Te–Tol bond occurs selectively at the sterically less-crowding side with respect to the $IrPtTe_2$ core in **4**, namely, from the direction opposite the Cp* ligand. Two PPh_3 ligands are mutually *trans* as observed for **2a** and **3a**, and similarly the structure of **5b** may be assigned as that with two PPh_3 ligands mutually *cis* around the Pt···Pd vector.

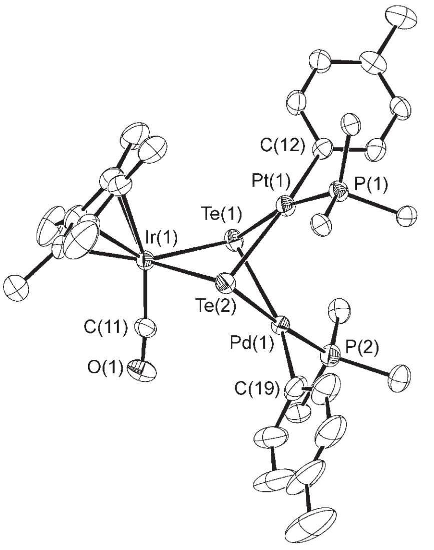


Figure 4. An ORTEP drawing of **5a**. Only one of the two independent molecules is shown (thermal ellipsoids shown at 30% probability). For clarity all the hydrogen atoms are omitted and only the carbon atom bound to P is shown for the phenyl groups of the PPh_3 units. Selected bond lengths [Å] and angles [°]: Ir···Pt, 3.8534(6), 3.8505(6), Ir···Pd 3.7821(8), 3.7879(7), Pt···Pd 3.2002(9), 3.1053(7), Ir-Te 2.6712(8)–2.6870(8), Pt-Te 2.6162(8)–2.6827(8), Pd-Te 2.6179(9)–2.718(1), Ir-Te-Pt 91.72(2)–93.52(2), Ir-Te-Pd 89.22(3)–91.47(3); Pt-Te-Pd, 71.39(2)–74.34(2), Te-Ir-Te 75.43(2), 75.85(2), Te-Pt-Te 76.44(2), 76.72(2), Te-Pd-Te 75.88(3), 76.55(2).

In conclusion, a versatile route for synthesizing mixed-metal tellurido clusters in solution has been developed, which involves the use of a readily available tellurolato complex as a metal–tellurido building block through Te–C bond scission with M^0 centers (M = Pt, Pd). Note that the reactions of **1** with Pt^{II} and Pd^{II} complexes $[MCl_2(cod)]$ (cod = cyclooctadiene) result in the formation of only the tellurolato-bridged dinuclear and trinuclear complexes $[Cp^*Ir(CO)(\mu\text{-}TeTol)_2MCl_2]$ (M = Pt, Pd) and $[\{Cp^*Ir(CO)(\mu\text{-}TeTol)_2\}_2Pt]$, which will be described elsewhere. Application of the method reported herein to the synthesis of a wide range of mixed-metal tellurido clusters is now in progress.

Experimental Section

All manipulations were carried out under an atmosphere of N_2 by using Schlenk techniques. Complexes $[Cp^*Ir(CO)_2]$,[15] $[Pt(PPh_3)_3]$,[16] $[Pd(PPh_3)_4]$,[17] and TolTeTeTol[18] were prepared by reported methods.

1: TolTeTeTol (230 mg, 0.526 mmol) was added to a solution of $[Cp^*Ir(CO)_2]$ (191 mg, 0.498 mmol) in benzene (10 mL) at room temperature. The reaction mixture was stirred for 3 h at room temperature and the resultant deep red solution was concentrated in vacuo. Addition of hexane afforded **1** as deep red crystals (315 mg, 79% yield). IR (KBr): $\tilde{\nu} = 1982\ cm^{-1}$, ν(CO); ^1H NMR (C_6D_6): δ = 1.55 (s, 15H, Cp*), 2.06 (s, 6H, Me in Tol), 6.75, 7.96 ppm (d, J = 7.9 Hz, 4H each, C_6H_4); elemental analysis (%) calcd for $C_{25}H_{29}OIrTe_2$: C 37.87, H 3.69; found: C 37.51, H 3.53.

2: $[Pt(PPh_3)_3]$ (101 mg, 0.103 mmol) was added to a THF solution (5 mL) of **1** (41 mg, 0.051 mmol) and the mixture was stirred for 26 h at room temperature. The resultant red solution was evaporated to dryness in vacuo. The ^1H NMR spectrum of this residue indicated the presence of two products, **2a** and **2b**, in a molar ratio of 2:1. Crystallization of the residue from a mixture of benzene and hexane (1:10) afforded pure **2a**$\cdot 0.25\,C_6H_6$ as red crystals (43 mg, 48% yield). Complex **2a** dissolved in C_6D_6 and converted into an equilibrium mixture of **2a** and **2b** in the ratio of 4:1. **2a**: IR (KBr): $\tilde{\nu} = 1979\ cm^{-1}$, ν(CO); ^1H NMR (C_6D_6): δ = 1.70 (s, 15H, Cp*), 2.15, 2.21 (s, 3H each, Me in Tol), 6.73, 6.85, 7.53, 7.60 (d, J = 7.6 Hz, 2H each, C_6H_4), 7.0–7.1 (m, 18H, Ph), 7.8–8.0 ppm (m, 12H, Ph); $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 7.1 (d with ^{195}Pt satellites, J_{P-P} = 5 Hz, J_{Pt-P} = 3790 Hz), 7.4 ppm (d with ^{195}Pt satellites, J_{P-P} = 5 Hz, J_{Pt-P} = 3700 Hz); elemental analysis (%) calcd for $C_{62.5}H_{60.5}OIrP_2Pt_2Te_2$: C 43.46, H 3.53; found: C 43.65, H 3.52. Data assignable to **2b**: ^1H NMR (C_6D_6): δ = 1.71 (s, 15H, Cp*), 2.14, 2.16 ppm (s, 3H each, Me in Tol); $^{31}P\{^1H\}$ NMR (C_6D_6): 6.6 (d with ^{195}Pt satellites, J_{P-P} = 8 Hz, J_{Pt-P} = 3770 Hz), 6.9 ppm (d with ^{195}Pt satellites, J_{P-P} = 8 Hz, J_{Pt-P} = 3930 Hz).

3: $[Pd(PPh_3)_4]$ (116 mg, 0.100 mmol) was added to a THF solution (5 mL) of **1** (40 mg, 0.050 mmol) and the resultant black solution was stirred at room temperature for 23 h. The NMR spectrum of the reaction mixture showed the presence of two isomeric products, **3a** and **3b**, in a 3:1 ratio. Hexane was added to the concentrated product solution and kept at −20 °C to yield black crystals of **3a**$\cdot 0.25\,C_6H_{14}$ (32 mg, 41% yield). When redissolved in C_6D_6, **3a** was converted very slowly into an equilibrium mixture of **3a** and **3b**. The rate constants for the conversion of **3a** into **3b** and its reverse reaction at 293 K were calculated to be $4.5 \times 10^{-5}\ s^{-1}$ and $13 \times 10^{-5}\ s^{-1}$, respectively, based on the ^1H NMR spectral change. IR (KBr): $\tilde{\nu} = 1971\ cm^{-1}$, ν(CO); elemental analysis (%) calcd for $C_{62.5}H_{62.5}OIrP_2Pd_2Te_2$: C 48.37; H 4.06; found: C 47.64, H 3.83. Data assignable to **3a**: ^1H NMR (C_6D_6): δ = 1.71 (s, 15H, Cp*), 2.14, 2.23 (s, 3H each, Me in Tol), 6.73, 6.78, 7.40, 7.48 (d, J = 8.0 Hz, 2H each, C_6H_4), 7.0–7.1 (m, 18H, Ph), 7.8–8.0 ppm (m, 12H, Ph); $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 14.7 (d, J = 7 Hz), 14.9 ppm (d, J = 7 Hz). Data assignable to **3b**: ^1H NMR (C_6D_6): δ = 1.75 (s, 15H, Cp*), 2.13, 2.16 ppm (s, 3H each, Me in Tol); $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 14.7 (d, overlapping with the signal of **3a**), 15.5 ppm (d, J = 8 Hz).

4: A mixture of **1** (160 mg, 0.202 mmol) and $[Pt(PPh_3)_3]$ (200 mg, 0.204 mmol) in THF (5 mL) was stirred at room temperature for one day and the resultant dark green solution was evaporated to dryness in vacuo. The ^1H NMR spectra of the residue showed the presence of the products **4a** and **4b** in a molar ratio of 3:1. The residue was extracted with benzene and the addition of hexane to the concentrated extract afforded a 3:1 mixture of **4a** and **4b** as dark green crystals (177 mg, 70% combined yield). Single crystals of pure **4a** were obtained by repeated fractional crystallization from a mixture of benzene and hexane. **4a** was dissolved in C_6D_6 and allowed to stand for 30 h at room temperature; the resulting solution contained a mixture of **4a** and **4b** in equilibrium in a ratio of 2.2:1 as confirmed by ^1H NMR spectroscopy. IR (KBr): $\tilde{\nu} = 1991\ cm^{-1}$, ν(CO); elemental analysis (%) calcd for $C_{43}H_{44}OIrPPtTe_2$: C 41.31, H 3.55; found: C 41.06, H 3.69. Data assignable to **4a**: ^1H NMR (C_6D_6): δ = 1.63 (s, 15H, Cp*), 1.97, 2.10 (s, 3H each, Me in Tol), 6.59, 7.19, 7.39, 7.71 ppm (d, J = 8.0 Hz, 2H each, C_6H_4); $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 9.5 ppm (s with ^{195}Pt satellites, J_{Pt-P} = 3910 Hz). Data assignable to **4b**: ^1H NMR (C_6D_6): δ = 1.68 (s, 15H, Cp*), 1.97, 2.12 ppm (s, 3H each, Me in Tol); $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 20.4 ppm (s with ^{195}Pt satellites, J_{Pt-P} = 3900 Hz).

5: $[Pd(PPh_3)_4]$ (58 mg, 0.050 mmol) was added to a THF solution (5 mL) of **4a** and **4b** (65 mg, 0.052 mmol) and this mixture was stirred for 5 h at room temperature. The NMR spectra of the reaction mixture showed the presence of **5a**. Addition of hexane to the concentrated product solution afforded **5a**$\cdot 0.25\,C_6H_{14}$ as red crystals (40 mg, 46% yield). When dissolved in C_6D_6, **5a** converted into an equilibrium mixture of **5a** and **5b** at room temperature, the ratio of which was 3:1. IR (KBr): $\tilde{\nu} = 1968\ cm^{-1}$, ν(CO); elemental analysis (%) calcd for $C_{62.5}H_{62.5}OIrP_2PdPtTe_2$: C 45.76, H 3.84; found: C 45.55, H 3.76. Data assignable to **5a**: ^1H NMR (C_6D_6): δ = 1.72 (s, 15H, Cp*), 2.13, 2.21 (s, 3H each, Me in Tol), 6.72, 6.86, 7.38, 7.65 (d, J =

7.6 Hz, 2H each, C_6H_4), 7.0–7.1 (m, 18H, Ph), 7.8–8.0 ppm (m, 12H, Ph); $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 11.0$ (d with ^{195}Pt satellites, $J_{P\text{-}P} = 6$ Hz, $J_{Pt\text{-}P} = 3650$ Hz), 11.9 ppm (d, $J_{P\text{-}P} = 6$ Hz). Data assignable to **5b**: ^{1}H NMR (C_6D_6): $\delta = 1.69$ (s, 15H, Cp*), 2.15, 2.23 ppm (s, 3H each, Me in Tol); $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 10.8$ (d, $J_{P\text{-}P} = 6$ Hz; ^{195}Pt satellites could not be resolved), 11.4 ppm (d, $J_{P\text{-}P} = 6$ Hz).

X-ray crystallography: Single crystals of **1**, **2a**·$0.25\,C_6H_6$, **3a**·$0.25\,C_6H_{14}$, **4a**, and **5a**·$0.25\,C_6H_{14}$ were sealed in glass capillaries under argon and mounted on a Rigaku Mercury-CCD diffractometer equipped with a graphite-monochromatized $Mo_{K\alpha}$ source. All diffraction studies were carried out at room temperature.

Structure solution and refinements were carried out by using the CrystalStructure program.[19] The positions of the non-hydrogen atoms were determined by Patterson methods (PATTY[20]) and subsequent Fourier synthesis (DIRDIF 99[21]). Non-hydrogen atoms were refined anisotropically by minimizing $wR2$ based on all data, for which full-matrix least-squares techniques are employed. All hydrogen atoms were placed at the calculated positions and included at the final stages of the refinements with fixed parameters.

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[2] Precedent tellurido clusters were obtained by using either the organotellurium reagents such as $R_3P{=}Te$ and $(Me_3Si)_2Te$ or the inorganic tellurium sources, for example, Te powder, Te_n^{2-} ($n = 2, 4$), NaTeH.[1]

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