

The First Example of Facile Oxidative Addition of Carbon–Tellurium Bonds to Zero-Valent Pt, Pd, and Ni Complexes

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Oxidative addition of a carbon–heteroatom bond to a transition metal complex constitutes the key catalytic step involved in a number of transition metal-catalyzed transformations.¹ Particularly successful examples in view of organic synthesis are those that involve carbon–halogen bonds. Organotelluriums, easily accessible *via* reactions of tellurium tetrachloride, metallic tellurium, or alkali tellurides, are playing increasingly important roles in organic synthesis² and materials chemistry.³ Some of the synthetic reactions starting with organotelluriums are efficiently promoted by transition metal compounds added as reagent or catalyst.⁴ In addition, similar to diorganyl sulfides and selenides, diorganyl tellurides are known to coordinate to a variety of transition metals.⁵ However, to our knowledge, oxidative addition of a carbon–tellurium bond to a transition metal has never been documented. Herein we disclose the first example of facile oxidative addition of a C–Te bond of diorganyl tellurides (R₂Te) with group 10 transition metal complexes M(PEt₃)_n (M = Pt, Pd, Ni; n = 3, 4) affording MR(RTe)(PEt₃)₂ in high yields.

When Ph₂Te (61.9 mg, 0.220 mmol) was slowly added to Pt(PEt₃)₃ (0.135 mmol) in benzene (0.5 mL) at 25 °C, the color of the solution immediately changed from brown to pale yellow. As evidenced by ³¹P NMR, the starting Pt(PEt₃)₃ (δ 41.5 ppm) was consumed within 0.5 h while two new singlets ascribable to free PEt₃ (δ –19.8 ppm) and *trans*-PtPh(PhTe)(PEt₃)₂ (**1a**, δ 5.1 ppm, J_{Pt} = 2688 Hz) were emerging. Evaporation of the solvent *in vacuo* followed by recrystallization from hexane at –30 °C afforded pure **1a** as a deep yellow solid in 92% yield (88.6 mg, 0.124 mmol) (eq 1). Both ¹H and ¹³C NMR spectra were in good agreement with the proposed structure; in the ¹H NMR spectra, the *ortho*-protons of the phenyl group bonded to platinum showed a satellite due to platinum (³J_{HPt} = 56.2 Hz)

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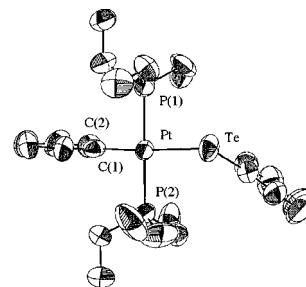
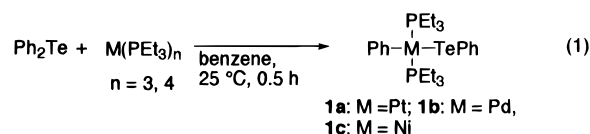


Figure 1. Molecular structure of *trans*-PtPh(PhTe)(PEt₃)₂ (**1a**). Selected bond lengths (Å) and angles (deg): C(1)–Pt = 2.032(1), Te–Pt = 2.693(2), P(1)–Pt = 2.304(4), P(2)–Pt = 2.299(4); C(1)–Pt–P(2) = 91.5(4), C(1)–Pt–P(1) = 89.0(4), P(1)–Pt–Te = 87.6, P(2)–Pt–Te = 91.9(1), C(1)–Pt–Te = 174.9(4), P(1)–Pt–P(2) = 178.9(2), C(2)–C(1)–Pt–P(1) = 92.0(1).

while those of the other phenyl (PhTe) did not. ¹³C NMR displayed, at 152 ppm as a triplet due to the coupling with the



two *cis*-PEt₃ ligands, the platinum-bound *ipso*-carbon, which was also accompanied by a satellite arising from coupling with platinum (¹J_{Cpt} = 819.7 Hz).⁶ The structure of the complex was confirmed by X-ray crystallography (Figure 1). Complex **1a** has a slightly distorted square planar geometry with the two PEt₃ ligands (Ph and PhTe groups) *trans* to each other. The phenyl group bonded to Pt lies almost perpendicular to the CTePtP₂ mean plane. The C–Pt bond length of **1a** is 2.032(12) Å, longer than the 1.98 Å expected for a typical sp² C–Pt bond,^{7a} reflecting a moderate *trans*-influence of PhTe.⁷

A similar yield of **1a** (89%) could be obtained when Pt(PEt₃)₄ was used instead of Pt(PEt₃)₃. Pd(PEt₃)₄ also reacted efficiently to afford **1b** as an orange solid in 94% isolated yield. The reaction of Ph₂Te with Ni(PEt₃)₄, which proceeded as fast as its Pd and Pt analogues, produced **1c** as a deep red oil. Although pure **1c** has not been isolated, its formation is strongly supported by NMR spectroscopy; first, monitoring the reaction at 25 °C by ³¹P NMR revealed that the starting Ni(PEt₃)₄ completely disappeared within 10 min; singlets for **1c** at δ 10.3 ppm and free PEt₃ were the only recognizable signals. Secondly, the ¹H NMR exhibited a coupling pattern similar to **1a** and **1b**. Furthermore, in ¹³C NMR, the *ipso*-carbon bound to Ni was clearly observed at 162.3 ppm as a triplet due to the coupling with two PEt₃ ligands (J_{PC} = 30.9 Hz). Unlike its Pd and Pt analogues, however, **1c** slowly decomposed at room temperature to deposit black solids.⁸

Dibutyl telluride (*n*-Bu₂Te) was as reactive as Ph₂Te toward Pt(PEt₃)₃ to quantitatively give *trans*-Pt(*n*-Bu)(*n*-BuTe)(PEt₃)₂

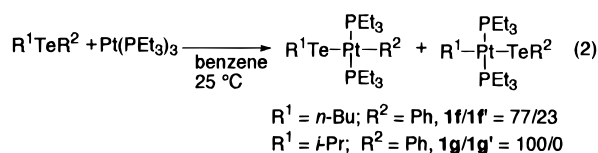
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(8) Heating the solution accelerated the decomposition. After a toluene solution of the complex was refluxed overnight, **1c** disappeared completely to afford biphenyl in a quantitative yield.

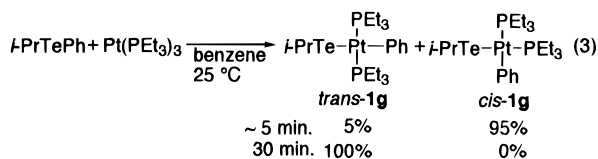
(**1d**) as a yellow oil.⁹ Other dialkyl tellurides also reacted smoothly. Although the complexes obtained from *n*-Bu₂Te, Me₂Te, and (PhCH₂CH₂)₂Te failed to crystallize, orange crystals of Pt(*t*-BuCH₂)(*t*-BuCH₂Te)(PEt₃)₂ (**1e**) were successfully isolated from the reaction of (*t*-BuCH₂)₂Te with Pt(PEt₃)₃ (83% yield). As expected, two nonequivalent neopentyl groups of **1e** were observed in ¹H NMR; the methylene group bonded directly to platinum was observed at δ 1.78 ppm as a triplet due to the coupling with PEt₃ (*J*_{HP} = 8.0 Hz), accompanied by a satellite due to platinum (²*J*_{HPt} = 65.6 Hz).

Interesting regioselectivity of the oxidative addition of C–Te bonds with the platinum complex was encountered when an unsymmetrical telluride was employed as the substrate (eq 2).



The reaction of *n*-BuTePh with Pt(PEt₃)₃ quantitatively produced **1f** and **1f'**, as a result of the oxidative addition of Ph–Te and *n*-Bu–Te bonds, respectively, in 77:23 ratio. *i*-PrTePh more selectively reacted to afford only *trans*-**1g**, the product arising from the exclusive Ph–Te bond oxidative addition.

The mechanism of the oxidative addition remains to be further clarified. However, the following comments merit consideration. When the two C–Te bond strengths of the tellurides are compared, the foregoing regioselectivity appears opposite to what would be expected if the reaction of the telluride with Pt(PEt₃)₃ took place *via* a radical mechanism, which was proposed for most cases of sp³ carbon–halogen bond oxidative additions.^{7a} Alternatively, the C–Te bond oxidative addition to the platinum complex can be envisioned to occur by the insertion of the nucleophilic platinum(0) to the more positively charged C–Te bond of the telluride, resulting in the preferential cleavage of the C–Te bonds (i.e., Ph–Te rather than *n*-Bu–Te or *i*-Pr–Te). An NMR study strongly indicated that the oxidative addition of the C–Te bonds took place in a *cis* fashion to afford a *cis*-complex, which isomerized rapidly to the *trans*-form on standing. Thus, monitoring of the reaction of *i*-PrTePh with Pt(PEt₃)₃ at 25 °C by ³¹P NMR revealed that Pt(PEt₃)₃ disappeared within 5 min to form *cis*-**1g** (*J*_{Pt} (*trans* to Ph) = 1771.2 Hz, *J*_{Pt} (*trans* to *i*-PrTe) = 2944.1 Hz) and *trans*-**1g** (*J*_{Pt} = 2722.7 Hz) in 95:5 ratio (eq 3). Upon standing the solution at room temperature, *cis*-**1g** isomerized completely to *trans*-**1g** within 0.5 h, leaving *trans*-**1g** as the sole complex in the solution.

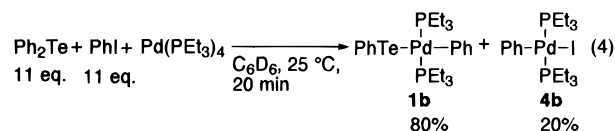


At room temperature, the reaction of Ph₂S with Pt(PEt₃)₃ did not proceed even after 1 day, and heating at 50 °C for an additional day gave only a trace of *trans*-PtPh(PhS)(PEt₃)₂ **2a** (<3%). The reaction proceeded slowly at a more elevated temperature (110 °C) to give complex **2a** as off-white crystals

(9) Upon mixing *n*-Bu₂Te (2 equiv) and Pt(PEt₃)₃ at 25 °C in C₆D₆, the starting Pt(PEt₃)₃ was consumed completely within 20 min. In ³¹P NMR, only two singlets which corresponded to **1d** (δ 7.8 ppm, *J*_{Pt} = 2878 Hz) and free PEt₃ were observed. Further evidence for the oxidative addition of the *n*-Bu–Te bond to platinum came from ¹³C NMR spectroscopy where the carbon directly bound to platinum displayed a triplet at δ 8.2 ppm (C–Pt, *J*_{PC} = 5.3 Hz, *J*_{CPt} = 604.4 Hz).

in 76% yield (in 6 h).^{10–12} Ph₂Se showed higher reactivity toward Pt(PEt₃)₃ than Ph₂S; the reaction of Ph₂Se with Pt(PEt₃)₃ readily took place at 50 °C over 5 h to produce *trans*-PtPh(PhSe)(PEt₃)₂ (**3a**) in 90% yield as orange crystals.¹² Therefore, the ease of oxidative addition of a carbon–chalcogen bond to Pt(PEt₃)₃ can be concluded to decrease in the order C–Te > C–Se > C–S, which is the reverse of the order of their bond strengths.^{2b}

Finally, it is interesting to note that the C–Te bond reacts with Pd(PEt₃)₄ even faster than the corresponding C–I bond, known as one of the most reactive bonds. As shown in eq 4, when Pd(PEt₃)₄ was treated at room temperature with an equimolar mixture of Ph₂Te (11 equiv) and PhI (11 equiv), **1b** was formed as the major product in 20 min and the ratio of **1b/4b** remained unchanged under these conditions over a period of 5 h.¹³ A separate experiment, in which pure **1b** was treated with pure **4b** in benzene at room temperature, also confirmed no reaction occurring between these complexes. Accordingly the ratio observed in eq 4 is likely to reflect kinetic control, indicating that Ph₂Te reacts about 4 times faster than PhI.



On the basis of the novel oxidative addition of the C–Te bond, numerous applications can be developed in organic synthesis and materials chemistry.

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Supporting Information Available: Experimental details, spectral and/or analytical data of the tellurium complexes; a perspective view and tables of crystallographic data, atomic coordinates and thermal parameters, and bond lengths and angles for **1a** (13 pages). See any current masthead page for ordering and Internet access instructions.

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(12) Comparison of the coupling constants (e.g., ¹*J*_{ppso-CPt} for **1a** (819.7 Hz), **2a** (797.7 Hz) and **3a** (818.8 Hz)) suggests the *trans*-influence is in the order PhS > PhSe ≥ PhTe.

(13) When the mixture shown in eq 4 was heated at 80 °C in benzene, however, **4b** gradually increased at the expense of **1b**; **1b** almost completely disappeared after 6 h heating at 80 °C (**1b/4b** < 2:98 by ³¹P NMR). Likewise, conversion of **1b** to **4b** was found when a mixture of pure **1b** and PhI in C₆D₆ was heated at 80 °C for 6 h. These results indicate that complex **4b** is thermodynamically more stable than **1b**.