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Formation and Characterization of Platinum and Palladium Complexes of Bis(trimethylsilylmethyl)tellane

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The mononuclear (telluroether)platinum and -palladium complexes *cis*-[$PtCl_2\{Te(CH_2SiMe_3)_2\}_2$] (**2c**), *trans*-[$PtCl_2\{Te(CH_2SiMe_3)_2\}_2$] (**2t**), and *trans*-[$PdCl_2\{Te(CH_2SiMe_3)_2\}_2$] (**3t**) have been prepared from bis(trimethylsilylmethyl)tellane and bis(benzonitrile)dichloridoplatinum and -palladium and structurally characterized by single-crystal X-ray diffraction and NMR spectroscopy. The isomer distribution of the platinum complex depends on the initial molar ratio of the reactants. When [$PtCl_2(NCPh)_2$] was used in excess, **2c** was the main product. Upon increasing the initial ligand/metal molar ratio, the relative amount of **2t** increased. The stoichiometric reaction afforded approximately equal amounts of the *cis* and *trans* isomers. Further increase of the initial amount of the ligand yielded **2t**. The mononuclear palladium complex was the *trans* isomer **3t**, regardless of the initial molar ratio of the reactants. Small amounts of the dinuclear complex [$Pt_2Cl_4\{\mu\text{-}Te(CH_2SiMe_3)_2\}\{Te(CH_2SiMe_3)_2\}_2$] (**4**) were also formed, when the initial ligand/metal molar ratio was low. Compound **4** shows a rare bridging telluroether ligand and two different platinum coordination environments, one exhibiting a *cis*-Cl/*cis*-TeR_2 arrangement and the other a *trans*-Cl/*trans*-TeR_2 arrangement. In case of palladium, the equimolar reaction afforded [$Pd_2(\mu\text{-}Cl)_2Cl_2\{Te(CH_2SiMe_3)_2\}_2$] (**5**) in good yields. As the relative amount of the ligand was increased, also **3t** was formed. When the ligand/metal ratio was >2:1, **3t** was the only product.

Introduction

In the absence of steric and chelating effects, many [$MX_2(ERR')_2$] (M = Pd, Pt; X = Cl, Br, I; E = S, Se, Te; R, R′ = alkyl, aryl) complexes show the presence of both *trans* and *cis* isomers in solution with the *trans*/*cis* ratio increasing in the order Pt < Pd and Cl < Br < I (for some selected reviews, see refs.[1–7]). Facile pyramidal inversion has been deduced to take place about the chalcogen center and has also been extensively investigated.[8] In the solid state, the monodentate [$PtX_2(SRR')_2$] complexes show approximately an even distribution of the occurrence of *trans* and *cis* isomers.[9] While information on the corresponding seleno- and telluroether complexes is much sparser, the existence of both *trans* and *cis* isomers has also been established.[10–16] By contrast, most [$PdX_2(SRR')_2$] complexes[9] as well as their seleno- and telluroether analogues[17–25] exist as *trans* isomers both in solution and in the solid state, the sole exceptions being [$PdCl_2(TeMeR)_2$] [R = 2-thienyl (C_4H_3S) or 2-furyl (C_4H_3O)].[13] Even these latter two complexes show the presence of both isomers in solution.

Our recent DFT calculations using [$MCl_2(EMe_2)_2$] (M = Pt, Pd; E = S, Se, Te) as model complexes have consistently indicated that, while the *trans* isomers of the Pd complexes lie at significantly lower energy than the *cis* isomers, in the case of Pt complexes the energy difference is smaller and decreases, as the chalcogen atom of the chalcogenoether ligand becomes heavier.[9]

Gysling et al.[26] have reported the preparation of related [$PdCl_2\{Te[(CH_2)_nSiMe_3]_2\}_2$] ($n$ = 1,3) complexes involving bis(trimethylsilylalkyl)tellane ligands. Both complexes were inferred to be *trans* isomers on the basis of far-IR and Raman spectra. In solution of the corresponding thiocyanate complex [$Pd(SCN)_2\{Te[(CH_2)_3SiMe_3]_2\}_2$], a small amount of the *cis* isomer was also inferred to be present. The crystal structure revealed the *trans* isomer of the complex.[26]

In this work we explore further the factors affecting the formation and isomerism of mono- and dinuclear bis(trimethylsilylmethyl)tellane ($(Me_3SiCH_2)_2Te$) (**1**) complexes of platinum and palladium. The formation and structural characterization of mononuclear *cis*-[$PtCl_2\{Te(CH_2SiMe_3)_2\}_2$] (**2c**), *trans*-[$PtCl_2\{Te(CH_2SiMe_3)_2\}_2$] (**2t**), and *trans*-[$PdCl_2\{Te(CH_2SiMe_3)_2\}_2$] (**3t**) are described. The reaction involving platinum also affords a small amount of dinuclear [$Pt_2Cl_4\{\mu\text{-}Te(CH_2SiMe_3)_2\}\{Te(CH_2SiMe_3)_2\}_2$] (**4**) that shows unprecedented structural features. By contrast, a dinuclear palladium complex [$Pd_2(\mu\text{-}Cl)_2Cl_2\{Te(CH_2SiMe_3)_2\}_2$] (**5**) is produced in good yields.

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Results and Discussion

Complex Formation

The reaction of **1** with [$PtCl_2(NCPh)_2$] (molar ratio 2:1) produces mononuclear [$PtCl_2\{Te(CH_2SiMe_3)_2\}_2$] in good yield. The ^{195}Pt and ^{125}Te NMR spectra were recorded for the reaction mixture. Two resonances are observed in the ^{125}Te NMR spectrum at δ = 266 ($^1J_{Pt–Te}$ = 804 Hz) and 292 ($^1J_{Pt–Te}$ = 469 Hz) ppm and assigned to *cis* and *trans* isomers (**2c** and **2t**), respectively. The assignment of the ^{125}Te chemical shifts is based on the $^1J_{Pt–Te}$ coupling information reported previously for *cis*- and *trans*-[$PtCl_2(TeMe_2)_2$] (824 Hz and 489 Hz, respectively).[27] The larger coupling constant of the *cis* isomer than that of the *trans* isomer is consistent with the stronger *trans* influence of tellurium compared to that of chlorine.[4,27] The ^{195}Pt NMR spectrum also exhibits two resonances observed at δ = –4236 and –3707 ppm. They are assigned to **2c** and **2t**, respectively, based on their relative intensities compared to those of the ^{125}Te resonances. Both ^{195}Pt resonances exhibit ^{125}Te satellites that yield $J_{Pt–Te}$ coupling constants, which are consistent with this assignment.

It is interesting to note that the isomeric composition of the reaction solution containing [$PtCl_2\{Te(CH_2SiMe_3)_2\}_2$] is dependent on the initial molar ratios of **1** and [$PtCl_2(NCPh)_2$] (see Figure S1 in the Supporting Information). Upon using an excess of [$PtCl_2(NCPh)_2$], *cis*-[$PtCl_2\{Te(CH_2SiMe_3)_2\}_2$] (**2c**) is the predominant isomer. As the ligand/metal molar ratio increases, the relative concentration of the *trans* isomer increases and that of the *cis* isomer decreases. The nominally stoichiometric reaction (reactant ligand/metal molar ratio is 2:1) affords approximately equimolar amounts of *cis* and *trans* isomers, as has previously been observed for many chalcogenoether complexes.[4] As the initial amount of the ligand **1** is further increased, the relative concentration of *trans*-[$PtCl_2\{Te(CH_2SiMe_3)_2\}_2$] (**2t**) quickly increases and the species becomes the main isomer in solution.

By contrast, *trans*-[$PdCl_2\{Te(CH_2SiMe_3)_2\}_2$] (**3t**) is the sole mononuclear product in the reaction of **1** with [$PdCl_2(NCPh)_2$], regardless of the initial ligand/metal molar ratio. The ^{125}Te chemical shift of the complex is observed at δ = 306 ppm.

At low initial ligand/metal ratio, the reaction of **1** and [$PtCl_2(NCPh)_2$] afforded small amounts of dinuclear [$Pt_2Cl_4\{Te(CH_2SiMe_3)_2\}_3$] (**4**) in addition to the mononuclear complexes **2c** and **2t**. A crop of crystals, the habits of which were sufficiently different to allow for their manual separation from the main mononuclear products, was obtained upon crystallization of the reaction solution. The yield of **4** was too small to facilitate bulk characterization. X-ray quality crystals, however, could be obtained upon recrystallization from dichloromethane.

The equimolar reaction of **1** and [$PdCl_2(NCPh)_2$] afforded the dinuclear palladium complex [$Pd_2(\mu\text{-}Cl)_2Cl_2\{Te(CH_2SiMe_3)_2\}_2$] (**5**) in good yields. Only one resonance is observed in the ^{125}Te NMR spectrum at δ = 501 ppm. As the relative amount of **1** was increased, the formation of the mononuclear complex **3t** was also observed in the reaction mixture. The stoichiometric reaction and that with an excess of **1** afforded only *trans*-[$PdCl_2\{Te(CH_2SiMe_3)_2\}_2$] (**3t**).

Crystal Structures

The lattices of **2c**, **2t**, **3t**, **4**, and **5** each consists of discrete complexes and show slightly distorted square-planar coordination environments around the platinum and palladium centers [Σa_M(M = Pt or Pd) span a very narrow range of 360.00–360.02°]. In addition, the lattice of complex **4** contains ½ mol of benzene for each mol of **4**. This molecule is a carry-over from the initial synthesis that was performed in benzene.

Mononuclear Complexes

The molecular structures of the mononuclear complexes **2c**, **2t**, and **3t** are shown in Figures 1 and 2 and their selected bond parameters in Table 1. The Pt–Te bond lengths in **2c** and **2t** are 2.537(1)–2.525(1) Å and 2.5807(6) Å, respectively. The longer bond length in the *trans* complex is consistent with the stronger *trans* influence of tellurium compared to that of chlorine. It also supports the assignments of the ^{125}Te and ^{195}Pt resonances. The same trend can also be deduced by comparing the Pt–Te distances in, for instance, *cis*-[$PtCl_2\{Te(nBu)CH_2\}_2SiMe_2$] [2.497(1) and 2.506(2) Å][28] and *trans*-[$PtCl_2\{Te(CH_2)_2O(CH_2)_2\}_2$] [2.5945(3) Å].[15] The relative magnitudes of the *trans* influence of tellurium and chlorine can also be inferred by the Pt–Cl distances of 2.321(3)–2.351(3) Å and 2.309(2) Å in **2c** and **2t**, respectively. They can again be compared to the corresponding distances in *cis*-[$PtCl_2\{Te(nBu)CH_2\}_2SiMe_2$] [2.335(6)–2.353(5) Å][28] and in *trans*-[$PtCl_2\{Te(CH_2)_2O(CH_2)_2\}_2$] [2.317(3) Å].[15]

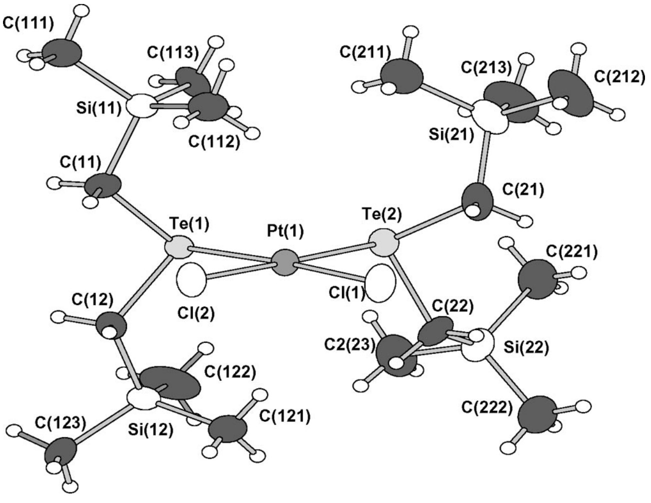


Figure 1. Molecular structure of *cis*-[$PtCl_2\{Te(CH_2SiMe_3)_2\}_2$] (**2c**) indicating the numbering of atoms. The thermal ellipsoids have been drawn at 50% probability level.

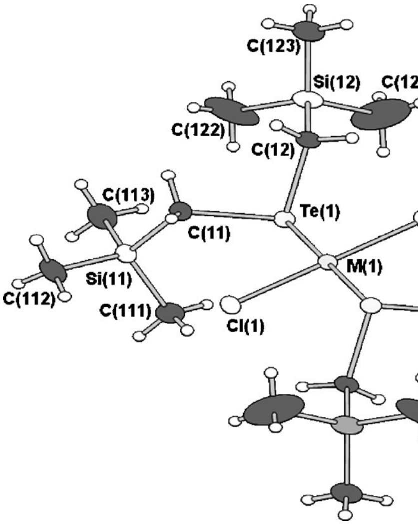


Figure 2. Molecular structure of *trans*-[$MCl_2\{Te(CH_2SiMe_3)_2\}_2$] [M = Pt (**2t**), Pd (**3t**)] indicating the numbering of atoms. The thermal ellipsoids have been drawn at 50% probability level.

trans-[$PdCl_2\{Te(CH_2SiMe_3)_2\}_2$] (**3t**) is isomorphic with the platinum complex **2t**. The Pd–Te and Pd–Cl bond lengths in **3t** are 2.5910(5) and 2.302(1) Å, respectively, in agreement with those reported for other telluroether complexes of palladium {see, for instance *trans*-[$PdCl_2\{Te(C_6H_2Me_3)_2\}_2$] [Pd–Te 2.569(3)–2.596(4) Å, Pd–Cl 2.270(4)–2.318(4) Å][29] and *trans*-[$PdCl_2\{Te(CH_2)_4\}_2$] [Pd–Te 2.593(2)–2.593(2) Å, Pd–Cl 2.319(3)–2.326(3) Å][23]}. The higher *trans* influence of tellurium to chlorine can again be deduced for all *trans* complexes by comparing these bond lengths to those in *cis*-[$PdCl_2(TeMeR)_2$] [R = 2-thienyl (C_4H_3S) or 2-furyl (C_4H_3O)] [Pd–Te 2.538(1)–2.546(1) and 2.530(1) Å, and Pd–Cl 2.351(1)–2.352(1) and 2.356(1)–2.359(1) Å, for the (methyl)(2-thienyl)tellane and (2-furyl)(methyl)tellane complexes, respectively].[13]

Table 1. Selected bond lengths [Å] and angles [°] of *cis*-[$PtCl_2\{Te(CH_2SiMe_3)_2\}_2$] (**2c**), *trans*-[$PtCl_2\{Te(CH_2SiMe_3)_2\}_2$] (**2t**), and *trans*-[$PdCl_2\{Te(CH_2SiMe_3)_2\}_2$] (**3t**).

Parameter	**2c**	**2t** (M = Pt)	**3t** (M = Pd)
M(1)–Te(1)	2.537(1)	2.5807(6)	2.5910(5)
M(1)–Te(2)	2.525(1)		
M(1)–Cl(1)	2.351(3)	2.309(2)	2.302(1)
M(1)–Cl(2)	2.321(3)		
Te(1)–M(1)–Te(1)[a]		180.0	180.0
Te(1)–M(1)–Te(2)	89.92(4)		
Te(1)–M(1)–Cl(1)	176.5(1)	92.34(6)	92.50(4)
Te(1)–M(1)–Cl(1)[a]		87.66(6)	87.50(4)
Te(1)–M(1)–Cl(2)	88.61(8)		
Te(2)–M(1)–Cl(1)	91.57(9)		
Te(2)–M(1)–Cl(2)	178.46(8)		
Cl(1)–M(1)–Cl(1)[a]		180.0	180.0
Cl(1)–M(1)–Cl(2)	89.9(1)		

[a] Symmetry operation: $-x + 1/2$, $-y + 1/2$, $-z + 1$.

The molecular packing of **2c** and **2t** and **3t** is shown in the Supporting Information (see Figure S2). Weak H···Cl hydrogen bonds [2.665(1)–2.994(1) Å] link *cis*-[$PtCl_2\{Te(CH_2SiMe_3)_2\}_2$] (**2c**) complexes into a two-dimensional quasi-planar network. Only van der Waals interactions are found between the layers. In the case of *trans*-[$MCl_2\{Te(CH_2SiMe_3)_2\}_2$] [M = Pt (**2t**), Pd (**3t**)] the respective H···Cl hydrogen bonds of 2.765(2)–2.882(2) Å and 2.761(1)–2.827(1) Å result in the formation of skewed stacks like in *trans*-[$MCl_2\{Se(Me)CH_2QMe_3)_2\}$],[12] [$MCl_2(SeMeTh)_2$] (M = Pd, Pt; Q = Si, Ge; Th = 2-thienyl C_4H_3S),[13] and [$PdCl_2(SeEt_2)_2$].[17] By contrast to *cis*-[$PdCl_2(TeMeR)_2$] (R = thienyl, furyl C_4H_3O),[13] *trans*-[$PtI_2(TeMePh)_2$]),[14] *cis*-[$PdCl_2\{$*meso*-$(TeC_6H_4OMe\text{-}4)_2CH_2\}$],[30] and *cis*-[$PdBr_2\{$*meso*-$(PhTe)_2(CH_2)_3\}$],[31] no Te···Cl interactions were found in **2c** or in **2t** and **3t**.

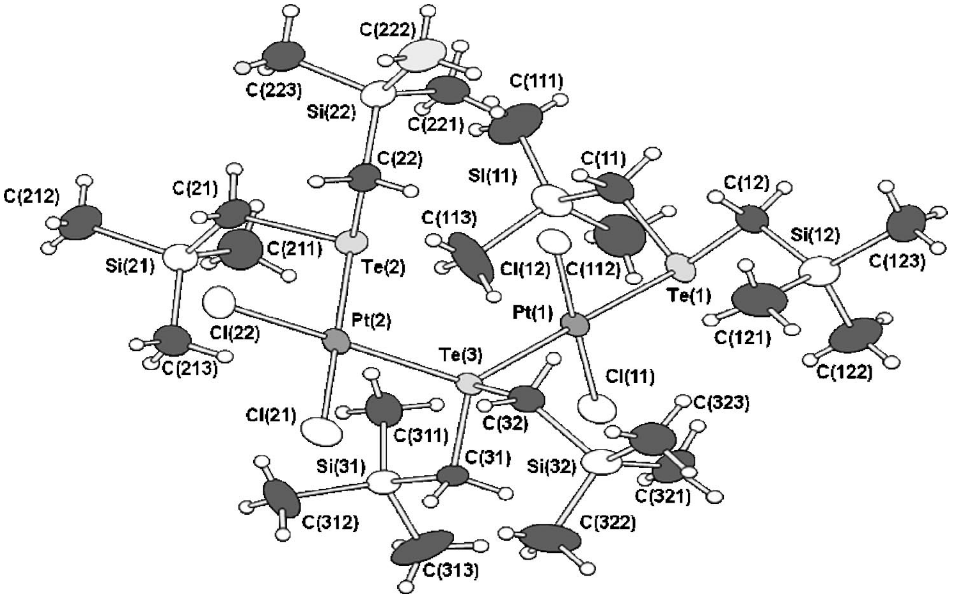


Figure 3. Molecular structure of [$Pt_2Cl_4\{\mu\text{-}Te(CH_2SiMe_3)_2\}\{Te(CH_2SiMe_3)_2\}_2$] (**4**) indicating the numbering of atoms. The thermal ellipsoids have been drawn at 50% probability level.

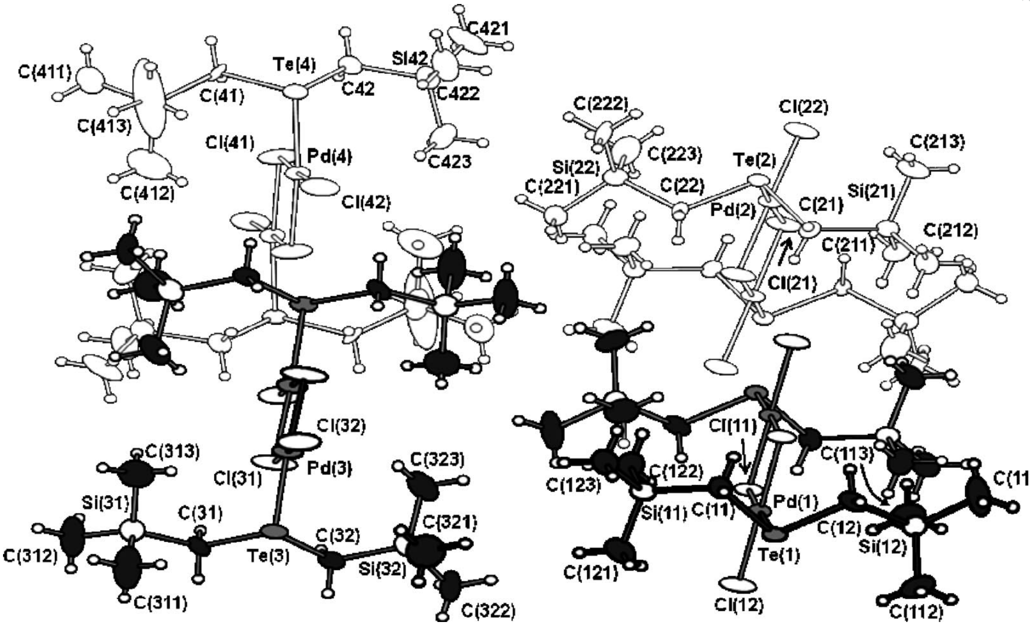


Figure 4. Molecular structure of $[Pd_2(\mu\text{-}Cl)_2Cl_2\{Te(CH_2SiMe_3)_2\}_2]$ (**5**) indicating the numbering of atoms. The thermal ellipsoids have been drawn at 50% probability level.

Dinuclear Complexes

The molecular structures indicating the numbering of the atoms are shown in Figures 3 and 4 for $[Pt_2Cl_4\{\mu\text{-}Te(CH_2SiMe_3)_2\}\{Te(CH_2SiMe_3)_2\}_2]$ (**4**) and $[Pd_2(\mu\text{-}Cl)_2Cl_2\{Te(CH_2SiMe_3)_2\}_2]$ (**5**), respectively. Their selected bond parameters are presented in Table 2.

The two slightly distorted square-planar coordination environments of the Pt(1) and Pt(2) centers in **4** are linked by a bridging $Te(CH_2SiMe_3)_2$ ligand and further coordinated by two chlorido ligands and one terminal $Te(CH_2SiMe_3)_2$ ligand. Interestingly, one platinum center exhibits a *cis*-Cl,*cis*-$Te(CH_2SiMe_3)_2$ coordination environment, while the other shows *trans*-Cl,*trans*-$Te(CH_2SiMe_3)_2$ coordination (see Figure 3). Both the co-existence of *cis* and *trans* environments in the same dinuclear complex and the presence of a bridging telluroether ligand are very rare. The only previous examples of the latter are provided by polymeric *trans*-$[PtClTh\{Te(Me)(Th)\}_2]_n$ (Th = 2-thienyl)[32] and $[CuCl(TeEt_2)]_n$.[33]

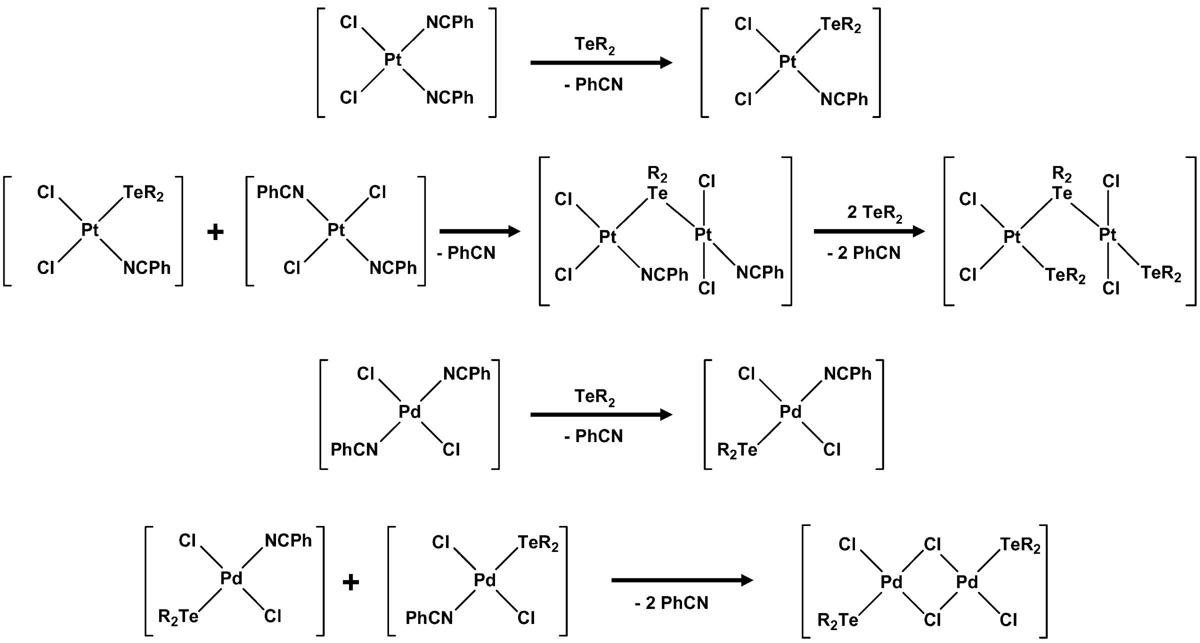
The geometries and bond parameters involving the *cis*- and *trans*-Pt centers are very similar to those observed for **2c** and **2t** and are consistent with the relative magnitudes of the *trans* influence. The Pt(1)–Te(1) [2.5581(7) Å] and Pt(1)–Te(3) [2.5728(7) Å] bonds are longer than the Pt(2)–Te(2) [2.5436(8) Å] and Pt(2)–Te(3) [2.518(1) Å] bonds, while Pt(1)–Cl(11) of 2.293(2) Å and Pt(1)–Cl(12) of 2.303(2) Å are shorter than Pt(2)–Cl(21) of 2.344(2) Å and Pt(2)–Cl(22) of 2.313(2) Å.

$[Pd_2(\mu\text{-}Cl)_2Cl_2\{Te(CH_2SiMe_3)_2\}_2]$ (**5**) shows a coplanar arrangement of the $Cl(Te)PdCl_2Pd(Te)Cl$ framework (see Figure 4) with Pd–Te bond lengths of 2.503(1)–2.511(1) Å, terminal Pd–Cl bond lengths of 2.280(4)–2.291(4) Å, and pairs of asymmetrical bridging Pd–Cl bond lengths of 2.312(4)–2.320(4) Å and 2.419(4)–2.433(4) Å. This asym-

Table 2. Selected bond lengths [Å] and angles [°] of $[Pt_2Cl_4\{Te(CH_2SiMe_3)_2\}_3]$ (**4**) and $[Pd_2(\mu\text{-}Cl)_2Cl_2\{Te(CH_2SiMe_3)_2\}_2]$ (**5**).

$[Pt_2Cl_4\{Te(CH_2SiMe_3)_2\}_3]$ (**4**)			
Pt(1)–Te(1)	2.5581(7)	Pt(2)–Te(2)	2.5436(8)
Pt(1)–Te(3)	2.5728(7)	Pt(2)–Te(3)	2.518(1)
Pt(1)–Cl(11)	2.293(2)	Pt(2)–Cl(21)	2.344(2)
Pt(1)–Cl(12)	2.303(2)	Pt(2)–Cl(22)	2.313(2)
Te(1)–Pt(1)–Te(3)	179.2(2)	Te(2)–Pt(2)–Te(3)	93.79(3)
Te(1)–Pt(1)–Cl(11)	87.07(6)	Te(2)–Pt(2)–Cl(21)	179.69(6)
Te(1)–Pt(1)–Cl(12)	93.20(5)	Te(2)–Pt(2)–Cl(22)	89.65(7)
Te(3)–Pt(1)–Cl(11)	92.13(6)	Te(3)–Pt(2)–Cl(21)	86.52(6)
Te(3)–Pt(1)–Cl(12)	87.61(5)	Te(3)–Pt(2)–Cl(22)	173.57(7)
Cl(11)–Pt(1)–Cl(12)	178.91(8)	Cl(21)–Pt(2)–Cl(22)	90.06(9)
Pt(1)–Te(3)–Pt(2)	125.29(3)		
$[Pd_2(\mu\text{-}Cl)_2Cl_2\{Te(CH_2SiMe_3)_2\}_2]$ (**5**)			
Pd(1)–Te(1)	2.506(1)	Pd(3)–Te(3)	2.503(2)
Pd(1)–Cl(11)	2.314(3)	Pd(3)–Cl(31)	2.312(4)
Pd(1)–Cl(11)[a]	2.431(3)	Pd(3)–Cl(31)[c]	2.419(4)
Pd(1)–Cl(12)	2.291(4)	Pd(3)–Cl(32)	2.288(4)
Pd(2)–Te(2)	2.511(1)	Pd(4)–Te(4)	2.506(1)
Pd(2)–Cl(21)	2.315(4)	Pd(4)–Cl(41)	2.320(4)
Pd(2)–Cl(21)[b]	2.433(3)	Pd(4)–Cl(41)[d]	2.431(4)
Pd(2)–Cl(22)	2.286(4)	Pd(4)–Cl(42)	2.280(4)
Te(1)–Pd(1)–Cl(11)	93.23(9)	Te(3)–Pd(13)–Cl(31)	92.9(1)
Te(1)–Pd(1)–Cl(11)[a]	178.6(1)	Te(31)–Pd(13)–Cl(31)[c]	177.2(1)
Te(1)–Pd(1)–Cl(12)	85.8(1)	Te(3)–Pd(3)–Cl(32)	86.2(1)
Cl(11)–Pd(1)–Cl(11)[a]	86.6(1)	Cl(31)–Pd(3)–Cl(31)[c]	86.6(1)
Cl(11)–Pd(1)–Cl(12)	178.9(1)	Cl(31)–Pd(3)–Cl(32)	178.8(1)
Cl(11)[a]–Pd(1)–Cl(12)	94.5(1)	Cl(31)[c]–Pd(3)–Cl(32)	94.4(1)
Te(2)–Pd(2)–Cl(21)	93.4(1)	Te(4)–Pd(4)–Cl(41)	91.9(1)
Te(2)–Pd(2)–Cl(21)[b]	177.8(2)	Te(4)–Pd(4)–Cl(41)[d]	175.6(1)
Te(2)–Pd(2)–Cl(22)	85.8(1)	Te(4)–Pd(4)–Cl(42)	86.7(1)
Cl(21)–Pd(2)–Cl(21)[b]	86.7(1)	Cl(41)–Pd(4)–Cl(41)[d]	87.5(1)
Cl(21)–Pd(2)–Cl(22)	178.9(1)	Cl(41)–Pd(4)–Cl(42)	177.3(2)
Cl(21)[b]–Pd(2)–Cl(22)	94.1(1)	Cl(41)[d]–Pd(4)–Cl(42)	94.1(1)

[a] Symmetry operation: –*x* + 2, –*y*, –*z* + 1. [b] Symmetry operation: –*x* + 1, –*y* + 1, –*z* + 1. [c] Symmetry operation: –*x* + 1, –*y*, –*z* + 2. [d] Symmetry operation: –*x*, –*y* + 1, –*z* + 2.



Scheme 1.

metric bridging arrangement agrees well with many dinuclear thioether complexes of palladium, as exemplified by those in [Pd(Me)(SMe$_2$)(μ-Cl)$_2$Pd(SMe$_2$)(Me)][34] and [Pd{CH(COOMe)(CH$_2$C$_6$F$_5$)}(tht)(μ-Cl)$_2$Pd{CH(COOMe)-(CH$_2$C$_6$F$_5$)}(tht)] (tht = tetrahydrothiophene)[35] that show the respective pairs of bridging Pd–Cl distances of 2.358(1) and 2.498(1) Å, and 2.365(2) and 2.437(2) Å.

The packing of the dinuclear complexes **4** and **5** is shown in the Supporting Information (see Figure S3). Respective weak H···Cl hydrogen bonds of 2.689(1)–2.963(1) Å and 2.797(3)–2.989(4) Å again link the complexes into skewed stacks or layers (**4** and **5**, respectively). Like in the case of mononuclear complexes **2c**, **2t**, and **3t**, there are no Te···Cl close contacts.

Conclusions

A series of [bis(trimethylsilylmethyl)tellane]platinum and -palladium complexes have been prepared from bis(trimethylsilylmethyl)tellane and bis(benzonitrile)dichloridoplatinum and -palladium. When the ligand/metal ratio was >2:1, the main products in both reactions were mononuclear [MCl$_2${Te(CH$_2$SiMe$_3$)$_2$}$_2$] (M = Pt, Pd) complexes. The NMR spectroscopic information indicates that the isomer distribution of the platinum complex depends on the initial molar ratio of the reactants. When [PtCl$_2$(NCPh)$_2$] was used in excess, *cis*-[PtCl$_2${Te(CH$_2$SiMe$_3$)$_2$}$_2$] (**2c**) was the main isomer. Upon increasing the initial ligand/metal molar ratio, the relative amount of the *trans* isomer increased. The stoichiometric reaction afforded approximately equal amounts of the *cis* and *trans* isomers. Increase of the initial amount of the ligand even further mainly yielded *trans*-[PtCl$_2${Te(CH$_2$SiMe$_3$)$_2$}$_2$] (**2t**). Both isomers could be structurally characterized in the solid state by single-crystal X-ray crystallography.

The corresponding reaction involving [PdCl$_2$(NCPh)$_2$] and Te(CH$_2$SiMe$_3$)$_2$ (**1**) afforded only the *trans* isomer of [PdCl$_2${Te(CH$_2$SiMe$_3$)$_2$}$_2$] (**3t**).

In addition to the mononuclear complexes, the reactions of [MCl$_2$(NCPh)$_2$] (M = Pt, Pd) and Te(CH$_2$SiMe$_3$)$_2$ resulted in the formation of dinuclear complexes [Pt$_2$Cl$_4${μ-Te(CH$_2$SiMe$_3$)$_2$}{Te(CH$_2$SiMe$_3$)$_2$}$_2$] (**4**) and [Pd$_2$(μ-Cl)$_2$Cl$_2$-{Te(CH$_2$SiMe$_3$)$_2$}$_2$] (**5**). Their formation probably involves first the substitution of PhCN by Te(CH$_2$SiMe$_3$)$_2$ followed by the condensation of the resulting mononuclear complexes (see Scheme 1).

The dinuclear complexes were observed with an initial ligand/metal molar ratio between 1:1 and 2:1. It is therefore possible that the monosubstituted [MCl$_2$(TeR$_2$)(NCPh)] (M = Pt, Pd) complexes are involved in their formation. We note that the bridging telluroether ligand and the presence of both *cis*-Cl and *trans*-Cl centers in **4** is virtually unprecedented. In case of palladium, the formation of **5** is easily understood in similar terms. With an excess of the tellane ligand, only mononuclear [MCl$_2$(TeR$_2$)$_2$] complexes are formed.

Experimental Section

General: (Chloromethyl)trimethylsilane (Aldrich), tellurium (powder; Johnson Matthey Chemicals), NaBH$_4$ (Riedel-de Haën), NaOH (Merck), CH$_3$OH (Lab-Scan), MgSO$_4$ (Fisher Scientific), diethyl ether (Lab-Scan), benzene (Appli-Chem), *n*-hexane (Lab-Scan) were commercially available and used without further purification. [PtCl$_2$(NCPh)$_2$] and [PdCl$_2$(NCPh)$_2$] were prepared according to the method of Kharasch et al.[36]

NMR Spectroscopy: ^{1}H, ^{13}C{^{1}H}, ^{125}Te, ^{195}Pt, and ^{29}Si NMR spectra were recorded with a Bruker DPX400 spectrometer operating at 400.13, 100.61, 126.28, 85.66 and 79.49 MHz, respectively. The typical spectral widths were 5.58, 20.16, 126.58, 100.00, and 14.37 kHz. The pulse widths were 4.50, 4.00, 10.00, 10.00, and 10.00 µs. ^{1}H pulse delay was 0.10 s, that for ^{13}C{^{1}H} was 3.00 s, for ^{125}Te 1.60 s for ^{195}Pt 0.4 s, and for ^{29}Si 8.00 s. ^{1}H accumulations contained ca. 30000 transients, those for ^{13}C{^{1}H} 50000 transients, those for ^{125}Te 30000 transients, those for ^{195}Pt 50000 transients, and those for ^{29}Si 23000 transients. Tetramethylsilane was used as an internal standard for ^{1}H and ^{13}C{^{1}H}, and as an external standard for ^{29}Si. A saturated solution of Ph_2Te_2 in $CDCl_3$ and a D_2O solution of $[PtCl_6]^{2-}$ were used as external standards for ^{125}Te and ^{195}Pt chemical shift, respectively. All the spectra were recorded in $CDCl_3$ which served as an internal ^{2}H lock. Chemical shifts (ppm) are reported relative to Me_4Si, and neat Me_2Te [$\delta(Me_2Te) = \delta(Ph_2Te_2) + 422$].[37]

Preparation of $Te(CH_2SiMe_3)_2$ (1): The preparation of **1** was carried out, as described previously.[26] The product was obtained as pale orange liquid. ^{1}H NMR ($CDCl_3$, 25 °C): $\delta = 1.71$ (m, CH_2), 0.07 (br. m, $SiMe_3$) ppm. ^{13}C NMR ($CDCl_3$, 25 °C): $\delta = -3.5$ (s, $SiMe_3$), –15.8 (s, CH_2) ppm. ^{125}Te NMR ($CDCl_3$, 25 °C): $\delta = 26$ (s) ppm. ^{29}Si NMR ($CDCl_3$, 25 °C): $\delta = 2.8$ (s) ppm.

Preparation of $[PtCl_2\{Te(CH_2SiMe_3)_2\}_2]$ (2c and 2t): $[PtCl_2(NCPh)_2]$ (0.236 g; 0.498 mmol) was dissolved in 5 mL of benzene, and an excess of **1** (0.375 g; 1.240 mmol) was added to the resulting solution. The reaction mixture was stirred at room temp. for 24 h and subsequently concentrated by evaporation of the solvent. The raw product was filtered, washed with a 1:1 mixture of methanol/*n*-hexane and recrystallized from CH_2Cl_2. Pale yellow solid (yield: 0.336 g; 78%). $C_{16}H_{44}Cl_2PtSi_4Te_2$ (870.05): calcd. C 22.09, H 5.10; found C 22.20, H 5.00. ^{125}Te NMR ($CDCl_3$, 25 °C): $\delta = 266$ ($^{1}J_{Pt-Te} = 804$ Hz; **2c**), 292 ($^{1}J_{Pt-Te} = 469$ Hz; **2t**) ppm. ^{195}Pt NMR ($CDCl_3$, 25 °C): $\delta = -4237$ ($^{1}J_{Pt-Te} = 804$ Hz, **2c**), –3707 ($^{1}J_{Pt-Te} = 463$ Hz, **2t**) ppm. The effect of the initial molar ratio of the reactants on the product distribution was explored by carrying out the reaction in a similar fashion as described above but keeping the molar amount of $[PtCl_2(NCPh)_2]$ virtually constant and varying that of **1**: Molar ratio 1:1: $[PtCl_2(NCPh)_2]$ (0.255 g; 0.540 mmol), $Te(CH_2SiMe_3)_2$ (0.163 g; 0.540 mmol). Molar ratio 1:1.5: $[PtCl_2(NCPh)_2]$ (0.238 g; 0.504 mmol), $Te(CH_2SiMe_3)_2$ (0.230 g; 0.755 mmol). Molar ratio 1:2: $[PtCl_2(NCPh)_2]$ (0.237 g; 0.502 mmol), $Te(CH_2SiMe_3)_2$ (0.304 g; 1.003 mmol). Molar ratio 1:3: $[PtCl_2(NCPh)_2]$ (0.253 g; 0.536 mmol), $Te(CH_2SiMe_3)_2$ (0.483 g; 1.602 mmol).

Preparation of $[PdCl_2\{Te(CH_2SiMe_3)_2\}_2]$ (3t): The preparation of $[PdCl_2\{Te(CH_2SiMe_3)_2\}_2]$ was carried out in a similar fashion by treating $[PdCl_2(NCPh)_2]$ (0.197 g; 0.514 mmol) with an excess of **1** (0.388 g; 1.285 mmol). Orange solid (yield: 0.301 g; 75%). $C_{16}H_{44}Cl_2PdSi_4Te_2$ (781.39): calcd. C 24.59, H 5.68; found C 24.13, H 5.61. ^{125}Te NMR ($CDCl_3$, 25 °C): $\delta = 306$ (**3t**) ppm. As with the platinum complexes, the effect of the initial molar ratio of the reactants on the isomerism was investigated by varying their relative amounts: Molar ratio 1:1: $[PdCl_2(NCPh)_2]$ (0.205 g; 0.534 mmol), $Te(CH_2SiMe_3)_2$ (0.161 g; 0.534 mmol). Molar ratio 1:1.5: $[PdCl_2(NCPh)_2]$ (0.193 g; 0.502 mmol), $Te(CH_2SiMe_3)_2$ (0.228 g; 0.754 mmol). Molar ratio 1:2: $[PdCl_2(NCPh)_2]$ (0.195 g; 0.509 mmol), $Te(CH_2SiMe_3)_2$ (0.308 g; 1.018 mmol).

Isolation of $[Pt_2Cl_4\{\mu\text{-}Te(CH_2SiMe_3)_2\}\{Te(CH_2SiMe_3)_2\}_2]$ (4): Upon crystallization of the 1:1.5 and 1:2 reaction mixtures from CH_2Cl_2, a small crop of crystals of the novel dimeric complex **4** was obtained in addition to **2c** and **2t**. The habit of the crystals

Table 3. Crystal data and details of the structure determinations of *cis*-$[PtCl_2\{Te(CH_2SiMe_3)_2\}_2]$ (**2c**), *trans*-$[PtCl_2\{Te(CH_2SiMe_3)_2\}_2]$ (**2t**), *trans*-$[PdCl_2\{Te(CH_2SiMe_3)_2\}_2]$ (**3t**), $[Pt_2Cl_4\{Te(CH_2SiMe_3)_2\}_3]$ (**4**) and $[Pd_2(\mu\text{-}Cl)_2Cl_2\{Te(CH_2SiMe_3)_2\}_2]$ (**5**).

	2c	**2t**	**3t**	**4**	**5**
Empirical formula	$C_{16}H_{44}Cl_2PtSi_4Te_2$	$C_8H_{22}ClPt_{0.5}Si_2Te$	$C_8H_{22}ClPd_{0.5}Si_2Te$	$C_{25.5}H_{67.5}Cl_4Pt_2Si_6Te_3$	$C_{16}H_{44}Cl_4Pd_2Si_4Te_2$
Formula mass	870.06	435.03	390.69	1457.61	958.67
Crystal system	orthorhombic	monoclinic	monoclinic	triclinic	triclinic
Space group	*Pbca*	*C*2/*c*	*C*2/*c*	$P\bar{1}$	$P\bar{1}$
a [Å]	12.452(5)	23.770(5)	23.809(5)	12.029(2)	12.330(3)
b [Å]	22.462(5)	6.529(1)	6.513(1)	13.509(3)	12.635(3)
c [Å]	22.991(5)	20.008(4)	20.003(4)	17.383(4)	22.457(5)
α [°]				75.68(3)	83.62(3)
β [°]		93.75(3)	93.74(3)	79.85(3)	87.81(3)
γ [°]				70.65(3)	89.81(3)
V [Å^3]	6431(3)	3098 (1)	3095(1)	2568.5(9)	3474(1)
Z	8	8	8	2	4
$F(000)$	3296	1648	1520	1369	1840
$D_{calcd.}$ [g cm^{-3}]	1.797	1.865	1.677	1.885	1.833
μ (Mo-K_α) [mm^{-1}]	6.460	6.704	2.777	7.474	3.132
Crystal size [mm]	0.30 × 0.10 × 0.05	0.20 × 0.10 × 0.07	0.30 × 0.12 × 0.05	0.20 × 0.15 × 0.12	0.15 × 0.15 × 0.10
θ range [°]	3.51–26.00	3.80–26.00	1.71–26.00	2.62–26.00	2.51–25.00
No. reflns. collected	20678	11185	6826	33361	10898
No. unique reflns.	5945	3011	2813	9878	10898
No. observed reflns.	4397	2704	2642	9094	9136
No. of parameters/restraints	239/0	121/0	118/0	383/2	509/0
R_{int}	0.1070	0.0586	0.0816	0.0576	0.0812
R_1 [$I \geq 2\sigma(I)$][a]	0.0651	0.0450	0.0473	0.0457	0.0851
wR_2 [$I \geq 2\sigma(I)$][a]	0.1675	0.1225	0.1301	0.1259	0.2165
R_1 (all data)[a]	0.0920	0.0517	0.0568	0.0496	0.0986
wR_2 (all data)[a]	0.1941	0.1250	0.1550	0.1294	0.2292
Goodness-of-fit on F_2	1.014	1.230	1.147	1.039	1.084
$\Delta\rho_{max/min}$ [e Å^{-3}]	2.692/–2.056	2.693/–2.383	1.598/–1.994	3.742/–2.113	2.780/–1.989

[a]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]1/2$.

was sufficiently different that they could be manually separated for the X-ray analysis. The amount obtained was, however, not sufficient for more detailed bulk analysis.

Preparation of $[Pd_2(\mu\text{-}Cl)_2Cl_2\{Te(CH_2SiMe_3)_2\}_2]$ (5): The equimolar reaction of $[PdCl_2(NCPh)_2]$ and **1** afforded dinuclear $[Pd_2(\mu\text{-}Cl)_2Cl_2\{Te[CH_2Si(CH_3)_3]_2\}_2]$ (**5**) (yield 0.179 g, 70%). $C_{16}H_{44}Cl_4Pd_2Si_4Te_2$ (958.72): calcd. C 20.05, H 4.63; found C 19.27, H 4.29. ^{125}Te NMR ($CDCl_3$, 25 °C): $\delta = 501$ (**5**) ppm.

X-ray Crystallography: Diffraction data of **2c**, **2t**, **3t**, **4**, and **5** were collected with a Nonius Kappa-CCD diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Crystallographic data and the details of crystal structure determinations are presented in Table 3. All structures were solved by direct methods using SIR-92[38] and refined using SHELXL-97.[39] After the full-matrix least-squares refinement of the non-hydrogen atoms with anisotropic thermal parameters, the hydrogen atoms were placed in calculated positions in methyl groups (C–H 0.98 Å) and in the CH_2 groups (C–H 0.99 Å). The scattering factors for the neutral atoms were those incorporated with the programs. CCDC-656720 to -656724 for **2c**, **2t**, **3t**, **4**, and **5** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Three figures displaying relative concentrations of *cis*- and *trans*-$[PtCl_2\{Te(CH_2SiMe_3)_2\}_2]$ as a function of the molar ratio of the reactants, and the packing of complexes in **2c**, **2t**, **3t**, **4**, and **5**.

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