Formation, Characterization, and Bonding of *cis*- and *trans*-[$PtCl_2\{Te(CH_2)_6\}_2$], *cis-trans*-[$Pt_3Cl_6\{Te(CH_2)_6\}_4$], and *cis-trans*-[$Pt_4Cl_8\{Te(CH_2)_6\}_4$]: Experimental and DFT Study †

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Supporting Information

1. NMR spectroscopy

1.1 *^{1}H NMR Spectra of the mixture of cis- and trans-[$PtCl_2\{Te(CH_2)_6\}_2$]*

Figure 1S. ^{1}H NMR spectra of the mixture of *cis*- and *trans*-[$PtCl_2\{Te(CH_2)_6\}_2$] (a) 30 s and (b) 1.2 h after the dissolution of *cis*-[$PtCl_2\{Te(CH_2)_6\}_2$].
Figure 2S. Fluxionality of the $Te(CH_2)_6$ ligand in *cis*- and *trans*-[$PtCl_2\{Te(CH_2)_6\}_2$].

1.2 *^{125}Te{^{1}H} and ^{195}Pt{^{1}H} NMR Spectra of the reaction mixture of cis-[$PtCl_2(NCPh)_2$] and $Te(CH_2)_6$*

Figure 3S. (a) The ^{125}Te{^{1}H} NMR and (b) the ^{195}Pt{^{1}H} NMR spectra from the reaction solution of *cis*-[$PtCl_2(NCPh)_2$] and $Te(CH_2)_6$.

2. X-ray crystallography

Table 1S. Crystal data and refinement details for the X-ray structure determinations of *cis*-[$PtCl_2\{Te(CH_2)_6\}_2$] (**1**$_{cis}$), *cis-trans*-[$Pt_3Cl_6\{Te(CH_2)_6\}_4$] ·1¼CH_2Cl_2 (**2**·1¼CH_2Cl_2), *cis-trans*-[$Pt_4Cl_8\{Te(CH_2)_6\}_4$] ·4$CDCl_3$ (**3**·4$CDCl_3$), and [$PtCl_2\{S(O)(CD_3)_2\}\{Te(CH_2)_6\}$] (**4**).
Table 2S. Selected bond lengths (Å) and angles (°) in *cis-trans*-[$Pt_3Cl_6\{Te(CH_2)_6\}_4$]·1¼CH_2Cl_2 (**2**·1¼CH_2Cl_2) and *cis-trans*-[$Pt_4Cl_8\{Te(CH_2)_6\}_4$]·4$CDCl_3$ (**3**·4$CDCl_3$).

3. DFT Computations

3.1 Optimum geometries

Table 3S. Atomic coordinates (Å) of the PBE0-D3/def2-TZVP optimized species discussed in this contribution.
Table 4S. PBE0-D3/def2-TZVP optimized geometries of the [$Pt_nCl_{2n}\{Te(CH_2)_6\}_m$] ($n$ = 1-4; m = 2-4).
Table 5S. Total energies of optimized species at PBE0-D3/def2-TZVP level of theory in vacuum (Hartree).
Table 6S. Total energies of optimized species at PBE0-D3/def2-TZVP level of theory in dichloromethane (Hartree).

3.2 Secondary bonding interactions

Figure 4S. The Pt···Pt interactions result in the square-planar coordination plane to become slightly concave in (a) **1**$_{cis}$, (b) **2**, and (c) **3**.

3.3 Formation energetics

Table 7S. Gibbs formation energies calculated at PBE0-D3/def2-TZVP level of theory (kJ mol^{-1}) in dichloromethane.

1. NMR spectroscopy

1.1 ^{1}H NMR spectra of the mixture of cis- and trans-[PtCl$_2${Te(CH$_2$)$_6$}$_2$]

The ^{1}H spectra of the mixture of *cis*- and *trans*-[PtCl$_2${Te(CH$_2$)$_6$}$_2$] has been shown in Figure 1S both after 30 s and 1.2 h after the dissolution of *cis*-[PtCl$_2${Te(CH$_2$)$_6$}$_2$]. The multiplets were assigned to the *cis*- and *trans*-form based on relative intensities.

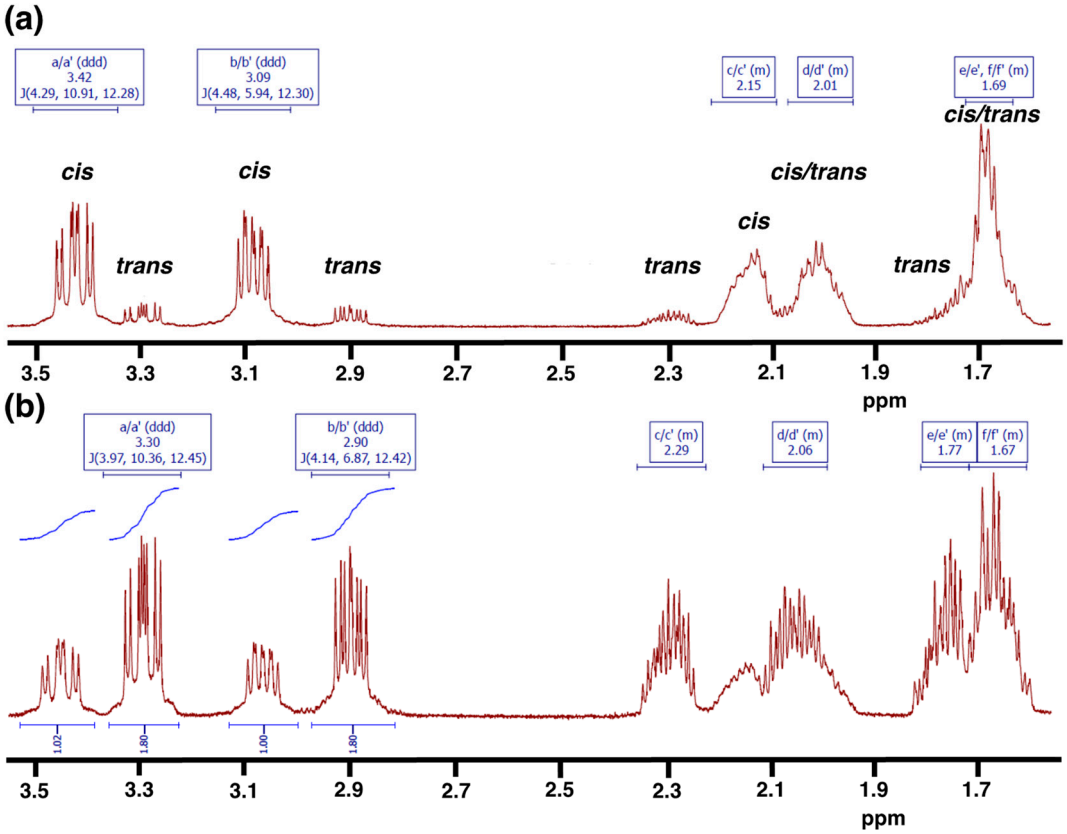


Figure S1. ^{1}H NMR spectra of the mixture of *cis*- and *trans*-[PtCl$_2${Te(CH$_2$)$_6$}$_2$] (a) 30 s and (b) 1.2 h after the dissolution of *cis*-[PtCl$_2${Te(CH$_2$)$_6$}$_2$].

The ^{1}H NMR spectra of both species exhibit very complex multiplets. Since tellurium donates its *n*p lone pair to the Pt-Te bond, the C-Te-C plane will be approximately perpendicular to this bond. The Te(CH$_2$)$_6$ ring is fluxional interconverting between two conformations, appearing planar in the NMR time scale (see Figure 2S). Therefore, the protons on the side of the ring pointing towards the platinum center in Te(CH$_2$)$_6$ aren't chemically equivalent to the ones pointing away from the metal center giving rise to a complicated [AA'BB'CC'DD'EE'FF'] spin system. In case of the free ligand, significantly simpler [ABC]$_4$ spin system is observed [1].

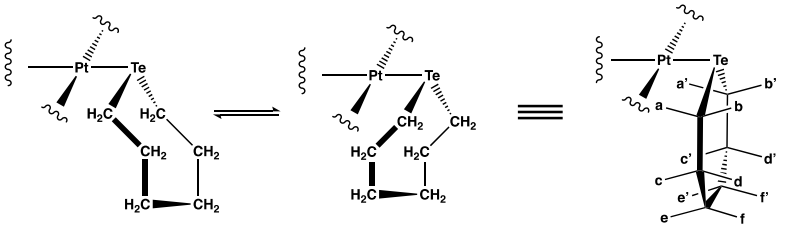


Figure 2S. Fluxionality of the Te(CH$_2$)$_6$ ligand in *cis*- and *trans*-[PtCl$_2${Te(CH$_2$)$_6$}$_2$].

The chemical shifts of the geminal methylene protons closest to tellurium lie at lowest field and are sufficiently different for the second order effects to play only a minor role, which can therefore be ignored in the estimation of coupling constants between the protons a and b (closest to tellurium), and between the protons of position a/b and c/d (see Figure 1S). The geminal coupling constants of $|^2J_{aa'}|$=12.3 Hz (*cis* isomer) and $|^2J_{aa'}|$=12.4 Hz (*trans* isomer) are rather typical for cycloalkane derivatives. The signal assignment to hydrogens **a** and **a'** is not unambiguous but that does not preclude the assignment of these two multiplets to the pair ***α*/a'.** This model is consistent with the slight lowfield shift all *α*-methylene signals experience compared to the free ligand [1].

It can clearly be seen in Figure 1S(a) that immediately after the dissolution, *cis*-$[PtCl_2\{Te(CH_2)_6\}_2]$ is the major species, but the relative concentration of *trans*-$[PtCl_2\{Te(CH_2)_6\}_2]$ rapidly increases as a function of time [Figure 1S(b)].

1.2 $^{125}Te\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectra of the reaction mixture of cis-$[PtCl_2(NCPh)_2]$ and $Te(CH_2)_6$

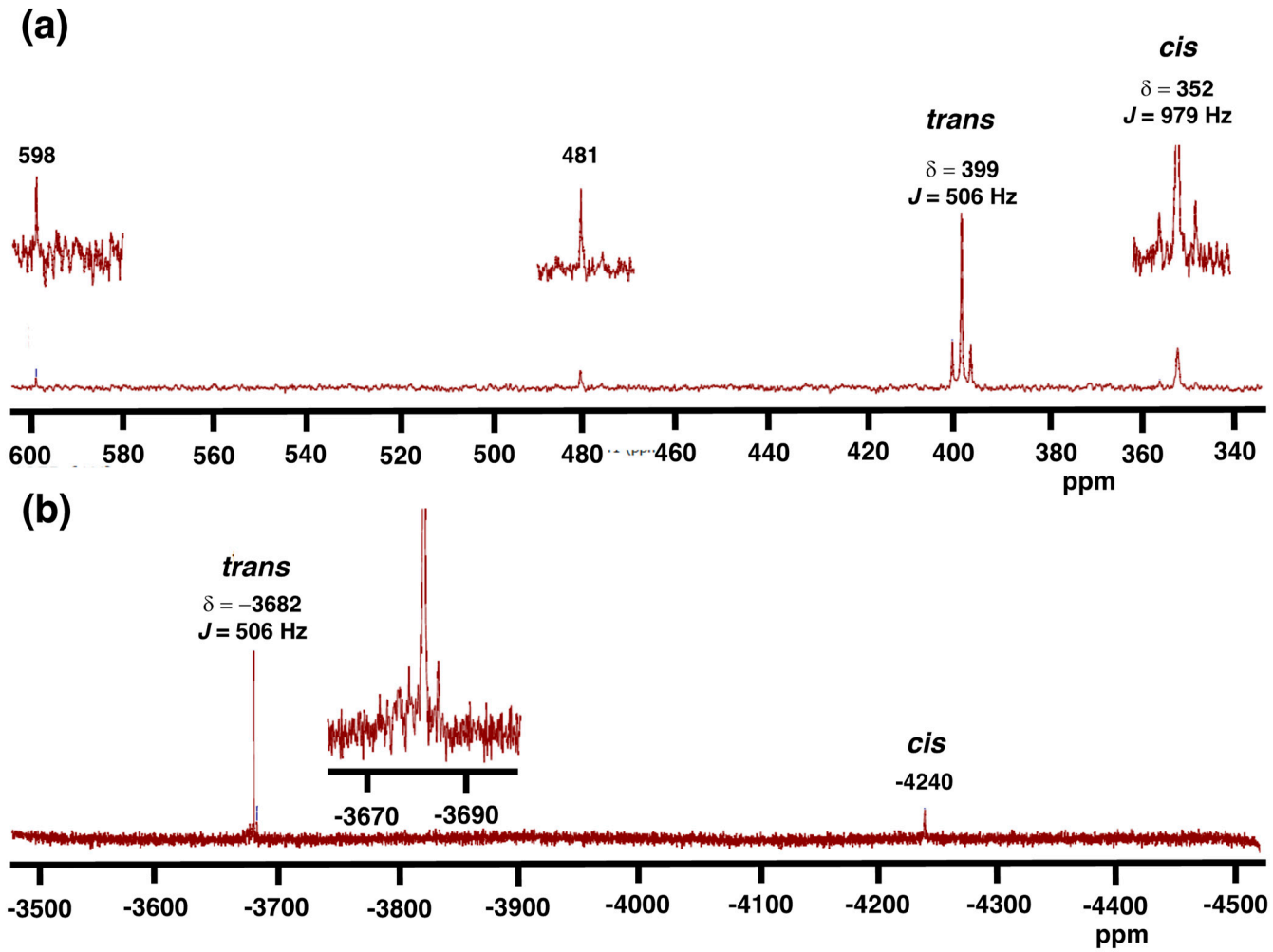


Figure S3. (a) The $^{125}Te\{^1H\}$ NMR and (b) the $^{195}Pt\{^1H\}$ NMR spectra from the reaction solution of *cis*-$[PtCl_2(NCPh)_2]$ and $Te(CH_2)_6$.

2. X-ray crystallography

Table S1. Crystal data and refinement details for the X-ray structure determinations of *cis*-$[PtCl_2\{Te(CH_2)_6\}_2]$ (**1**$_{cis}$), *cis-trans*-$[Pt_3Cl_6\{Te(CH_2)_6\}_4]\cdot 1¼CH_2Cl_2$ (**2**$\cdot 1¼CH_2Cl_2$), *cis-trans*-$[Pt_4Cl_8\{Te(CH_2)_6\}_4]\cdot 4CDCl_3$ (**3**$\cdot 4CDCl_3$), and $[PtCl_2\{S(O)(CD_3)_2\}\{Te(CH_2)_6\}]$ (**4**).

Compound	**1**$_{cis}$	**2**$\cdot 1¼CH_2Cl_2$	**3**$\cdot 4CDCl_3$ [a]	**4** [a]
formula	$C_{12}H_{24}Cl_2PtTe_2$	$C_{25.5}H_{51}Cl_9Pt_3Te_4$	$C_{28}H_{52}Cl_{20}Pt_4Te_4$	$C_8H_{18}Cl_2OPtS\ Te$
fw ($g\cdot mol^{-1}$)	689.50	1772.38	2388.45	555.87
T/°C	-140(2)	-140(2)	-140(2)	-140(2)
crystal system	orthorhombic	triclinic	monoclinic	monoclinic
space group	*Pbca*	*P*ī	*C*2/*c*	$P2_1/c$
a/ Å	12.4443(3)	12.5826(4)	12.7358(3)	9.9274(2)
b/ Å	12.8290(3)	12.6959(4)	18.6821(5)	16.3202(4)
c/ Å	21.2611(4)	26.7884(8)	24.5098(6)	9.0309(2)
α/°	90	93.341(1)	90	90
β/°	90	98.757(1)	97.857(1)	108.8660(10)
γ/°	90	90.571(1)	90	90
V/Å^3	3394.29(13)	4221.5(2)	5776.9(3)	1384.56(5)
Z	8	4	4	4
ρ ($g\cdot cm^{-3}$)	2.699	2.789	2.746	2.667
μ (cm^{-1})	119.33	132.15	125.85	127.07
measured data	19066	35285	32246	15959
data with I > 2σ(I)	3337	14448	6312	3092
unique data (R_{int})	3887/0.0784	18271/0.0417	6614/0.0381	3167/0.0263
wR_2 (all data, on F^2) [b]	0.0825	0.2461	0.0939	0.0339
R_1 ($I > 2\sigma(I)$) [b]	0.0433	0.0787	0.0411	0.0150
S [c]	1.093	1.067	1.114	1.119
Res. Dens./e·Å^{-3}	1.993/-1.591	6.215/-1.735	5.661/-2.911	0.612/-0.903
absorpt method	multi-scan	multi-scan	multi-scan	multi-scan
absorpt corr $T_{min}/_{max}$	0.3791/0.7456	0.2703/0.7456	0.4244/0.7456	0.5337/0.7456
CCDC No.	2298160	2298161	2298162	2301073

[a] D atoms have been designated as H. [b] Definition of the *R* indices: $R_1 = (\Sigma ||F_o| - |F_c||)/\Sigma |F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = {}^2(F_o^2) + (aP)^2 + bP$; $P = [2F_c^2 + \mathrm{Max}(F_O^2]/3$; [c] $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(N_o - p..)\}^{1/2}$.

Table S2. Selected bond lengths (Å) and angles (°) in *cis-trans*-$[Pt_3Cl_6\{Te(CH_2)_6\}_4]\cdot 1¼CH_2Cl_2$ (**2**·$1¼CH_2Cl_2$), and *cis-trans*-$[Pt_4Cl_8\{Te(CH_2)_6\}_4]\cdot 4CDCl_3$ (**3**·$4CDCl_3$).

2·$1¼CH_2Cl_2$						**3**·$4CDCl_3$			
	A [a]	B [a]		A [a]	B [a]				
Pt1-Te1	2.5178(15)	2.5140(15)	Te1-Pt1-Te4	92.26(5)	92.13(5)	Pt1-Te1	2.5045(7)	Te1-Pt1-Te2	94.86(2)
Pt1-Te4	2.5170(16)	2.5219(16)	Te1-Pt1-Cl1	178.57(13)	178.57(14)	Pt1-Te2	2.5226(6)	Te1-Pt1-Cl1	88.16(6)
Pt2-Te1	2.5774(15)	2.5768(17)	Te1-Pt1-Cl2	88.88(13)	88.249(2)	Pt2-Te1	2.5577(6)	Te1-Pt1-Cl2	175.20(7)
Pt2-Te2	2.5560(15)	2.568(2)	Te4-Pt1-Cl1	89.16(14)	89.35(14)	Pt2-Te2	2.5546(6)	Te2-Pt1-Cl1	173.72(7)
Pt3-Te3	2.5608(17)	2.5626(15)	Te4-Pt1-Cl2	177.75(14)	178.45(15)	Pt1-Cl1	2.321(2)	Te2-Pt1-Cl2	87.06(7)
Pt3-Te4	2.5640(15)	2.5635(14)	Cl1-Pt1-Cl2	88.88(14)	88.28(15)	Pt1-Cl2	2.309(3)	Cl1-Pt1-Cl2	90.35(9)
Pt1-Cl1	2.331(5)	2.330(5)	Te1-Pt2-Te2	176.56(5)	173.87(6)	Pt2-Cl3	2.305(2)	Te1-Pt2-Te2	178.92(2)
Pt1-Cl2	2.311(6)	2.328(6)	Te1-Pt2-Cl3	84.33(13)	83.57(13)	Pt2-Cl4	2.302(2)	Te1-Pt2-Cl3	93.43(6)
Pt2-Cl3	2.307(5)	2.313(5)	Te1-Pt2-Cl4	95.79(14)	94.97(13)	Pt2···Pt2	3.0765(6)	Te1-Pt2-Cl4	86.29(6)
Pt2-Cl4	2.305(6)	2.316(5)	Te2-Pt2-Cl3	94.74(13)	94.32(13)	Te1···Cl3	3.527(2)	Te2-Pt2-Cl3	85.52(6)
Pt3-Cl5	2.309(5)	2.325(6)	Te2-Pt2-Cl4	85.16(13)	87.29(13)	Te2···Cl4	3.556(2)	Te2-Pt2-Cl4	94.77(6)
Pt3-Cl6	2.313(6)	2.320(6)	Cl3-Pt2-Cl4	179.8(2)	178.3(2)			Cl3-Pt2-Cl4	175.77(7)
Pt2···Pt3	3.1499(13)	3.1170(11)	Te3-Pt3-Te4	178.14(6)	179.28(5)				
Te1···Cl6	3.481(7)	3.512(5)	Te3-Pt3-Cl5	85.47(14)	86.53(15)				
Te2···Cl5	3.922(6)	3.964(6)	Te3-Pt3-Cl6	95.62(16)	95.26(13)				
Te3···Cl4	3.594(6)	3.435(6)	Te4-Pt3-Cl5	92.72(14)	92.78(15)				
Te4···Cl3	3.590(5)	3.590(5)	Te4-Pt3-Cl6	86.16(16)	85.44(13)				
			Cl5-Pt3-Cl6	174.70(14)	175.3(2)				

[a] The asymmetric unit contains two independent molecules that have been denoted by A and B.

3. DFT Computations*1*

3.1 Optimum geometries

Table S3. Atomic coordinates (Å) of the PBE0-D3/def2-TZVP optimized species discussed in this contribution.

PhCN C_{2v} E=-324.228470092 a.u.

C	0.000000000	0.000000000	0.604835000	H	0.000000000	2.141688000	-2.014339000
C	0.000000000	1.209525000	-0.089890000	H	0.000000000	0.000000000	-3.248749000
C	0.000000000	1.203159000	-1.473355000	H	0.000000000	-2.141688000	-2.014339000
C	0.000000000	0.000000000	-2.165113000	H	0.000000000	-2.141617000	0.461061000
C	0.000000000	-1.203159000	-1.473355000	C	0.000000000	0.000000000	2.031910000
C	0.000000000	-1.209525000	-0.089890000	N	0.000000000	0.000000000	3.183492000
H	0.000000000	2.141617000	0.461061000				

$Te(CH_2)_6$ C_1 E=-503.704254999 a.u.

Te	-1.210147000	-0.092563000	-0.101255000	C	2.574441000	-0.570581000	-0.086381000
C	-0.142466000	1.767622000	0.146456000	H	3.411818000	-0.895108000	-0.712723000
H	-0.249894000	2.288014000	-0.807522000	H	2.966064000	-0.528994000	0.937879000
H	-0.672345000	2.335706000	0.910062000	C	1.501412000	-1.646643000	-0.166658000
C	1.320721000	1.610532000	0.506850000	H	1.189195000	-1.776675000	-1.207944000
H	1.411655000	1.145454000	1.493685000	H	1.962004000	-2.595596000	0.137101000
H	1.726403000	2.622252000	0.625499000	C	0.273519000	-1.425347000	0.698719000
C	2.172907000	0.840225000	-0.509266000	H	0.529626000	-1.090026000	1.704770000
H	1.652078000	0.801754000	-1.472985000	H	-0.295924000	-2.351006000	0.806406000
H	3.093740000	1.402635000	-0.687287000				

cis-[$PtCl_2(NCPh)_2$] C_s E=-1688.06794514 a.u.

C	*-1.448801000*	*-3.655410000*	*0.000000000*	*Cl*	*2.748639000*	*1.625916000*	*0.000000000*
C	*-2.843133000*	*-3.708134000*	*0.000000000*	*N*	*-0.148166000*	*1.446649000*	*0.000000000*
C	*-3.472666000*	*-4.938992000*	*0.000000000*	*C*	*-0.765694000*	*2.413804000*	*0.000000000*
C	*-2.721177000*	*-6.106566000*	*0.000000000*	*C*	*-1.448598000*	*3.655540000*	*0.000000000*
C	*-1.333906000*	*-6.049577000*	*0.000000000*	*C*	*-2.842946000*	*3.708161000*	*0.000000000*
C	*-0.687992000*	*-4.827309000*	*0.000000000*	*C*	*-0.687892000*	*4.827497000*	*0.000000000*
H	*-3.417083000*	*-2.790020000*	*0.000000000*	*C*	*-3.472576000*	*4.938963000*	*0.000000000*
H	*-4.554686000*	*-4.988661000*	*0.000000000*	*H*	*-3.416816000*	*2.789996000*	*0.000000000*
H	*-3.220818000*	*-7.068098000*	*0.000000000*	*C*	*-1.333906000*	*6.049717000*	*0.000000000*
H	*-0.751248000*	*-6.962619000*	*0.000000000*	*H*	*0.393210000*	*4.759767000*	*0.000000000*
H	*0.393104000*	*-4.759480000*	*0.000000000*	*C*	*-2.721176000*	*6.106599000*	*0.000000000*
C	*-0.765938000*	*-2.413644000*	*0.000000000*	*H*	*-4.554600000*	*4.988549000*	*0.000000000*
N	*-0.148356000*	*-1.446524000*	*0.000000000*	*H*	*-0.751316000*	*6.962802000*	*0.000000000*
Pt	*1.166735000*	*-0.000007000*	*0.000000000*	*H*	*-3.220893000*	*7.068092000*	*0.000000000*
Cl	*2.748412000*	*-1.626185000*	*0.000000000*				

trans-[$PtCl_2(NCPh)_2$] D_{2h} E=-1688.07709399 a.u.

C	0.000000000	0.000000000	4.484879000	C	0.000000000	0.000000000	3.068206000
C	0.000000000	1.214614000	5.173137000	N	0.000000000	0.000000000	1.922951000
C	0.000000000	1.205326000	6.555534000	Pt	0.000000000	0.000000000	0.000000000
C	0.000000000	0.000000000	7.244835000	Cl	0.000000000	-2.307595000	0.000000000
C	0.000000000	-1.205326000	6.555534000	Cl	0.000000000	2.307595000	0.000000000
C	0.000000000	-1.214614000	5.173137000	N	0.000000000	0.000000000	-1.922951000
H	0.000000000	2.144470000	4.618226000	C	0.000000000	0.000000000	-3.068206000
H	0.000000000	2.142823000	7.097943000	C	0.000000000	0.000000000	-4.484879000
H	0.000000000	0.000000000	8.328483000	C	0.000000000	-1.214614000	-5.173137000
H	0.000000000	-2.142823000	7.097943000	C	0.000000000	1.214614000	-5.173137000
H	0.000000000	-2.144470000	4.618226000	C	0.000000000	-1.205326000	-6.555534000

H	0.000000000	-2.144470000	-4.618226000	H	0.000000000	-2.142823000	-7.097943000
C	0.000000000	1.205326000	-6.555534000	H	0.000000000	2.142823000	-7.097943000
H	0.000000000	2.144470000	-4.618226000	H	0.000000000	0.000000000	-8.328483000
C	0.000000000	0.000000000	-7.244835000				

cis-[PtCl$_2${Te(CH$_2$)$_6$}$_2$] C$_1$ E=-2047.06703240 a.u.

Pt	-0.146560000	-1.095428000	0.099196000	H	2.839265000	-1.458772000	-1.370607000
Te	1.532599000	0.680053000	-0.550223000	H	3.569919000	-0.015892000	-2.124201000
Te	-2.219050000	-0.074417000	-0.933730000	C	-1.805695000	2.019445000	-1.171011000
Cl	-1.724300000	-2.744233000	0.613361000	H	-1.004865000	2.017458000	-1.914054000
Cl	1.557618000	-2.281023000	1.147292000	H	-2.684170000	2.458469000	-1.648274000
C	2.318033000	1.174401000	1.378314000	C	-1.401339000	2.790625000	0.074782000
H	1.462031000	1.550590000	1.939703000	H	-0.815591000	2.151988000	0.746843000
H	2.576882000	0.203201000	1.797820000	H	-0.729820000	3.597640000	-0.239314000
C	3.464858000	2.172227000	1.332542000	C	-2.557514000	3.414072000	0.845472000
H	4.025965000	2.079756000	2.270148000	H	-3.207767000	3.942179000	0.136931000
H	3.054136000	3.186251000	1.322355000	H	-2.144831000	4.186098000	1.502725000
C	4.421598000	2.047322000	0.153133000	C	-3.402168000	2.486623000	1.707071000
H	3.863665000	2.241474000	-0.772732000	H	-2.764176000	2.008478000	2.459752000
H	5.148153000	2.862974000	0.219700000	H	-4.099736000	3.117589000	2.266281000
C	5.192048000	0.740076000	0.012122000	C	-4.212003000	1.404125000	0.995034000
H	5.845451000	0.609768000	0.881429000	H	-4.620035000	1.788384000	0.052997000
H	5.859166000	0.849909000	-0.850067000	H	-5.086396000	1.177388000	1.615270000
C	4.372891000	-0.536219000	-0.164548000	C	-3.492531000	0.084668000	0.792957000
H	5.052469000	-1.331090000	-0.493132000	H	-4.188977000	-0.738043000	0.635485000
H	3.967926000	-0.891236000	0.783303000	H	-2.862215000	-0.181446000	1.639656000
C	3.252532000	-0.469616000	-1.182676000				

trans-[PtCl$_2${Te(CH$_2$)$_6$}$_2$] C$_1$ E=-2047.08131913 a.u.

Pt	-0.000041000	-0.741429000	0.000040000	H	4.405765000	-0.660004000	-1.364909000
Te	2.532226000	-0.744071000	0.507497000	H	2.796224000	-0.441359000	-2.086707000
Te	-2.532314000	-0.744031000	-0.507416000	C	-3.476057000	-0.092042000	1.307286000
Cl	-0.231568000	-0.765587000	2.303753000	H	-4.405786000	-0.659616000	1.365060000
Cl	0.231469000	-0.765956000	-2.303673000	H	-2.796200000	-0.440928000	2.086753000
C	2.657679000	1.086279000	1.621284000	C	-3.725578000	1.397903000	1.417533000
H	2.349058000	0.748860000	2.611282000	H	-4.447712000	1.719968000	0.659700000
H	3.716294000	1.352034000	1.662675000	H	-4.228623000	1.550603000	2.379299000
C	1.774308000	2.223153000	1.144918000	C	-2.474393000	2.281446000	1.356699000
H	1.651074000	2.909937000	1.991249000	H	-1.590143000	1.679076000	1.589905000
H	0.778943000	1.822027000	0.933380000	H	-2.543101000	3.029761000	2.150895000
C	2.275387000	3.029405000	-0.042640000	C	-2.274995000	3.029457000	0.042342000
H	1.553719000	3.835630000	-0.211601000	H	-3.216730000	3.524885000	-0.226831000
H	3.217208000	3.524702000	0.226473000	H	-1.553196000	3.835576000	0.211247000
C	2.474635000	2.281258000	-1.356944000	C	-1.774030000	2.223015000	-1.145136000
H	2.543436000	3.029510000	-2.151192000	H	-0.778723000	1.821770000	-0.933544000
H	1.590285000	1.679013000	-1.590091000	H	-1.650693000	2.909690000	-1.991539000
C	3.725693000	1.397534000	-1.417757000	C	-2.657556000	1.086211000	-1.621384000
H	4.228643000	1.550030000	-2.379606000	H	-2.348972000	0.748639000	-2.611343000
H	4.447951000	1.719635000	-0.660058000	H	-3.716136000	1.352095000	-1.662807000
C	3.476059000	-0.092378000	-1.307263000				

[Pt$_2$Cl$_4${Te(CH$_2$)$_6$}$_3$] C$_1$ E=-3590.43986476 a.u.

Pt	2.623285000	1.047304000	0.075026000	Cl	2.845130000	3.353633000	0.420918000
Pt	-1.599956000	-0.241632000	-0.400069000	Cl	4.871370000	0.717947000	0.462798000
Te	2.249045000	-1.444715000	-0.326524000	Cl	-2.410751000	0.616068000	-2.383382000
Te	-3.473540000	-2.000594000	-0.639439000	Cl	-0.727353000	-1.107002000	1.567083000
Te	0.188951000	1.573352000	-0.140589000	C	4.055866000	-2.014874000	-1.322886000

H	4.024304000	-1.483250000	-2.275060000	H	-4.682453000	-0.380681000	3.493586000
H	4.853595000	-1.567493000	-0.734271000	H	-3.470772000	-0.356918000	2.238167000
C	4.182958000	-3.518191000	-1.506898000	C	-4.779341000	-2.078819000	2.187258000
H	5.231884000	-3.736226000	-1.741291000	H	-4.795021000	-2.606133000	3.147811000
H	3.604955000	-3.826567000	-2.383324000	H	-5.778977000	-2.221256000	1.763660000
C	3.739180000	-4.376090000	-0.328619000	C	-3.745224000	-2.788661000	1.338471000
H	2.654025000	-4.266941000	-0.200376000	H	-3.996630000	-3.840211000	1.193942000
H	3.885269000	-5.425825000	-0.601331000	H	-2.749400000	-2.718446000	1.779210000
C	4.428225000	-4.135458000	1.009867000	C	-0.078362000	3.171994000	-1.523538000
H	5.503976000	-4.311034000	0.903126000	H	0.939572000	3.422008000	-1.820214000
H	4.065478000	-4.905553000	1.699403000	H	-0.623595000	2.712868000	-2.349636000
C	4.220288000	-2.768649000	1.665093000	C	-0.813571000	4.354949000	-0.932956000
H	4.490819000	-2.856728000	2.723526000	H	-0.193537000	4.820693000	-0.161824000
H	4.902419000	-2.017500000	1.263098000	H	-0.883907000	5.093571000	-1.738910000
C	2.804186000	-2.236366000	1.606210000	C	-2.219027000	4.060494000	-0.390459000
H	2.663173000	-1.387634000	2.272366000	H	-2.594927000	3.123719000	-0.818727000
H	2.049551000	-2.991355000	1.833644000	H	-2.895947000	4.838519000	-0.752326000
C	-5.171637000	-0.689656000	-0.711354000	C	-2.337022000	4.030385000	1.131886000
H	-5.177585000	-0.411215000	-1.765567000	H	-1.832752000	4.913643000	1.541770000
H	-6.045506000	-1.315146000	-0.515905000	H	-3.393863000	4.138803000	1.396197000
C	-5.110505000	0.544654000	0.167806000	C	-1.822320000	2.787232000	1.842064000
H	-5.831592000	1.261782000	-0.242771000	H	-2.393521000	1.908877000	1.520923000
H	-4.126552000	1.007074000	0.049021000	H	-2.024014000	2.898232000	2.913681000
C	-5.426328000	0.356271000	1.642999000	C	-0.342535000	2.495255000	1.702261000
H	-5.383122000	1.346004000	2.109161000	H	-0.010816000	1.739332000	2.415100000
H	-6.465566000	0.021355000	1.752467000	H	0.311396000	3.364206000	1.784592000
C	-4.523906000	-0.587177000	2.431969000				

[Pt$_3$Cl$_6${Te(CH$_2$)$_6$}$_4$] C$_1$ E=-5133.82851344 a.u.

Pt	3.320924000	-0.226714000	0.008568000	C	1.569889000	-1.709282000	3.111812000
Pt	-0.869579000	-1.519234000	-0.060186000	H	2.158306000	-0.826126000	3.355465000
Pt	-0.643947000	1.638979000	0.021760000	H	0.538816000	-1.558335000	3.436483000
Te	1.482135000	-1.648664000	0.975738000	C	-2.907273000	-1.879476000	-3.225953000
Te	-3.203688000	-1.426418000	-1.152774000	H	-3.594027000	-1.211088000	-3.746995000
Te	-2.993066000	1.833247000	1.072322000	H	-1.885507000	-1.550825000	-3.418564000
Te	1.715626000	1.436328000	-0.981840000	C	-3.119186000	-3.325585000	-3.623769000
Cl	5.001649000	0.966308000	-1.047450000	H	-4.159014000	-3.621609000	-3.447720000
Cl	4.838720000	-1.632045000	1.049603000	H	-2.990674000	-3.358186000	-4.711829000
Cl	0.309214000	-1.633752000	-2.049264000	C	-2.168350000	-4.338940000	-2.976814000
Cl	-2.025225000	-1.450154000	1.953295000	H	-1.835774000	-5.035661000	-3.750997000
Cl	-1.753484000	1.786782000	-2.009437000	H	-1.266148000	-3.825366000	-2.629410000
Cl	0.498442000	1.547345000	2.035481000	C	-2.765533000	-5.170959000	-1.846638000
C	2.099841000	-3.643601000	0.579349000	H	-2.112554000	-6.033062000	-1.676234000
H	2.242952000	-3.648475000	-0.501642000	H	-3.725549000	-5.585908000	-2.179973000
H	3.081257000	-3.710661000	1.045638000	C	-2.958611000	-4.481135000	-0.505741000
C	1.101583000	-4.687963000	1.044216000	H	-3.320189000	-5.229008000	0.210314000
H	1.628435000	-5.648845000	1.083546000	H	-1.994931000	-4.130833000	-0.120534000
H	0.324763000	-4.792258000	0.281232000	C	-3.940258000	-3.325603000	-0.478946000
C	0.413158000	-4.421381000	2.376660000	H	-4.222405000	-3.081463000	0.546679000
H	-0.257105000	-3.560233000	2.265762000	H	-4.852913000	-3.527993000	-1.044275000
H	-0.255310000	-5.263797000	2.579692000	C	-3.415723000	3.868644000	0.545255000
C	1.295604000	-4.220560000	3.603814000	H	-3.658094000	3.755369000	-0.513219000
H	1.915973000	-5.108829000	3.764168000	H	-4.329632000	4.148737000	1.074270000
H	0.624960000	-4.161741000	4.467395000	C	-2.293717000	4.870448000	0.737301000
C	2.202929000	-2.988022000	3.624024000	H	-2.497830000	5.716487000	0.070000000
H	2.501171000	-2.803085000	4.662019000	H	-1.357583000	4.423314000	0.386879000
H	3.139199000	-3.166671000	3.090944000	C	-2.111908000	5.416797000	2.144188000

H	-1.356214000	6.206940000	2.089461000	H	3.256471000	2.943354000	-3.430613000
H	-3.039000000	5.911959000	2.461006000	H	2.279638000	2.518178000	-4.810177000
C	-1.684689000	4.427745000	3.223297000	C	1.298821000	3.892879000	-3.465923000
H	-1.332447000	5.013100000	4.077039000	H	0.305622000	3.527798000	-3.178051000
H	-0.821039000	3.849050000	2.879604000	H	1.154273000	4.430257000	-4.406771000
C	-2.776717000	3.473386000	3.718326000	C	1.797781000	4.906316000	-2.439177000
H	-2.704172000	3.383582000	4.808392000	H	2.838205000	5.164686000	-2.670785000
H	-3.766255000	3.904236000	3.530261000	H	1.223109000	5.829230000	-2.565508000
C	-2.702045000	2.058894000	3.182715000	C	1.696419000	4.509632000	-0.974147000
H	-3.467553000	1.417685000	3.621662000	H	0.650005000	4.311575000	-0.715254000
H	-1.725921000	1.607031000	3.360685000	H	1.998502000	5.369894000	-0.365951000
C	1.806736000	1.393621000	-3.109744000	C	2.555384000	3.340041000	-0.539043000
H	2.504913000	0.582044000	-3.312535000	H	2.635036000	3.274727000	0.547588000
H	0.799368000	1.093232000	-3.400628000	H	3.561347000	3.328251000	-0.958496000
C	2.232162000	2.704603000	-3.731434000				

[Pt$_4$Cl$_8${Te(CH$_2$)$_6$}$_4$ D$_2$ E=-6173.45185839 a.u.

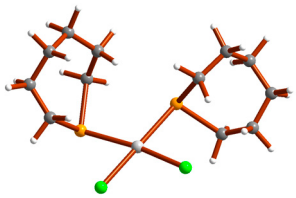
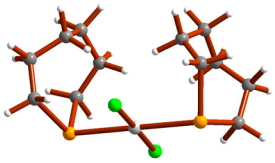
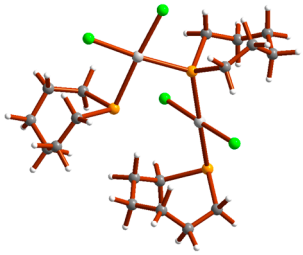
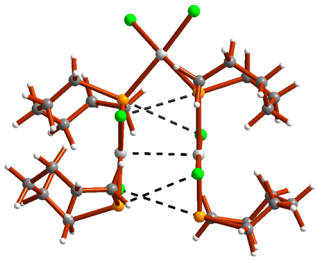
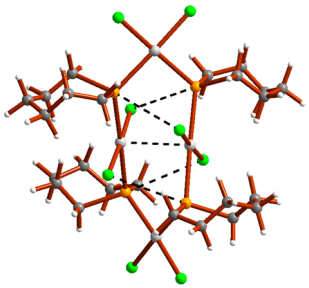
Pt	-4.082078000	0.000000000	0.000000000	H	-1.051492000	4.334381000	-0.649695000
Pt	0.000000000	1.537514000	0.000000000	C	-3.034708000	3.534092000	-0.456990000
Te	-2.376037000	-1.574905000	0.953694000	H	-4.043896000	3.618958000	-0.860323000
Te	-2.376037000	1.574905000	-0.953694000	H	-3.101099000	3.454079000	0.629550000
Cl	-5.673083000	-1.342847000	1.007258000	Pt	4.082078000	0.000000000	0.000000000
Cl	-5.673083000	1.342847000	-1.007258000	Pt	0.000000000	-1.537514000	0.000000000
Cl	-1.044504000	1.595352000	2.063720000	Te	2.376037000	1.574905000	0.953694000
Cl	1.044504000	1.595352000	-2.063720000	Te	2.376037000	-1.574905000	-0.953694000
C	-2.470431000	-1.573703000	3.081067000	Cl	5.673083000	1.342847000	1.007258000
H	-1.490885000	-1.197948000	3.378847000	Cl	5.673083000	-1.342847000	-1.007258000
H	-3.233489000	-0.824932000	3.291917000	Cl	1.044504000	-1.595352000	2.063720000
C	-2.792164000	-2.925414000	3.677689000	Cl	-1.044504000	-1.595352000	-2.063720000
H	-3.793588000	-3.239632000	3.369283000	C	2.470431000	1.573703000	3.081067000
H	-2.857911000	-2.758402000	4.758545000	H	1.490885000	1.197948000	3.378847000
C	-1.766944000	-4.032153000	3.400610000	H	3.233489000	0.824932000	3.291917000
H	-0.800364000	-3.585871000	3.138732000	C	2.792164000	2.925414000	3.677689000
H	-1.596200000	-4.577805000	4.331988000	H	3.793588000	3.239632000	3.369283000
C	-2.170020000	-5.059142000	2.345457000	H	2.857911000	2.758402000	4.758545000
H	-1.525597000	-5.935697000	2.463068000	C	1.766944000	4.032153000	3.400610000
H	-3.189339000	-5.404725000	2.555607000	H	0.800364000	3.585871000	3.138732000
C	-2.080245000	-4.628476000	0.889135000	H	1.596200000	4.577805000	4.331988000
H	-2.296454000	-5.500281000	0.261410000	C	2.170020000	5.059142000	2.345457000
H	-1.051492000	-4.334381000	0.649695000	H	1.525597000	5.935697000	2.463068000
C	-3.034708000	-3.534092000	0.456990000	H	3.189339000	5.404725000	2.555607000
H	-4.043896000	-3.618958000	0.860323000	C	2.080245000	4.628476000	0.889135000
H	-3.101099000	-3.454079000	-0.629550000	H	2.296454000	5.500281000	0.261410000
C	-2.470431000	1.573703000	-3.081067000	H	1.051492000	4.334381000	0.649695000
H	-1.490885000	1.197948000	-3.378847000	C	3.034708000	3.534092000	0.456990000
H	-3.233489000	0.824932000	-3.291917000	H	4.043896000	3.618958000	0.860323000
C	-2.792164000	2.925414000	-3.677689000	H	3.101099000	3.454079000	-0.629550000
H	-3.793588000	3.239632000	-3.369283000	C	2.470431000	-1.573703000	-3.081067000
H	-2.857911000	2.758402000	-4.758545000	H	1.490885000	-1.197948000	-3.378847000
C	-1.766944000	4.032153000	-3.400610000	H	3.233489000	-0.824932000	-3.291917000
H	-1.596200000	4.577805000	-4.331988000	C	2.792164000	-2.925414000	-3.677689000
H	-0.800364000	3.585871000	-3.138732000	H	3.793588000	-3.239632000	-3.369283000
C	-2.170020000	5.059142000	-2.345457000	H	2.857911000	-2.758402000	-4.758545000
H	-1.525597000	5.935697000	-2.463068000	C	1.766944000	-4.032153000	-3.400610000
H	-3.189339000	5.404725000	-2.555607000	H	1.596200000	-4.577805000	-4.331988000
C	-2.080245000	4.628476000	-0.889135000	H	0.800364000	-3.585871000	-3.138732000
H	-2.296454000	5.500281000	-0.261410000	C	2.170020000	-5.059142000	-2.345457000

H	1.525597000	-5.935697000	-2.463068000	H	1.051492000	-4.334381000	-0.649695000
H	3.189339000	-5.404725000	-2.555607000	C	3.034708000	-3.534092000	-0.456990000
C	2.080245000	-4.628476000	-0.889135000	H	4.043896000	-3.618958000	-0.860323000
H	2.296454000	-5.500281000	-0.261410000	H	3.101099000	-3.454079000	0.629550000

[PtCl$_2${Te(CH$_2$)$_6$}$_2$]$_2$ dimer, cis conformation C$_i$ E=-4094.19210670 a.u.

Pt	1.137936000	-0.240996000	-1.241450000	H	3.583609000	4.392421000	0.574166000
Te	2.689410000	-1.742826000	0.089688000	H	5.130206000	1.843897000	0.237009000
Te	1.758327000	1.875665000	0.027578000	H	5.522670000	3.080346000	-0.925286000
Cl	-0.173537000	1.250464000	-2.517272000	H	3.737048000	1.536795000	-1.754688000
Cl	0.562846000	-2.015503000	-2.664614000	H	3.220190000	3.222257000	-1.719337000
C	1.667062000	-3.620496000	0.195201000	H	0.849006000	-3.420738000	0.886199000
C	2.510801000	-4.788858000	0.660670000	H	1.262070000	-3.753923000	-0.808790000
C	4.920755000	-4.205315000	-0.038368000	H	2.837993000	-4.626104000	1.693577000
C	3.724127000	-5.153198000	-0.191472000	H	1.837038000	-5.653700000	0.695245000
C	5.124989000	-3.192227000	-1.159949000	H	4.035901000	-6.159356000	0.100641000
C	3.897977000	-2.395242000	-1.561332000	H	3.428281000	-5.227446000	-1.243998000
C	3.537367000	2.382366000	-1.098090000	H	5.840772000	-4.789314000	0.051657000
C	4.733927000	2.743975000	-0.242773000	H	4.826187000	-3.669066000	0.913988000
C	4.487979000	3.822690000	0.822062000	H	5.925767000	-2.508096000	-0.862557000
C	4.399006000	3.306390000	2.257091000	H	5.488567000	-3.712829000	-2.054258000
C	3.116913000	2.590545000	2.658237000	H	3.193490000	-2.955781000	-2.176380000
C	2.762108000	1.358552000	1.844332000	H	4.154761000	-1.492450000	-2.115707000
Pt	-1.137936000	0.240996000	1.241450000	H	-3.630342000	-0.740735000	-1.613709000
Te	-1.758327000	-1.875665000	-0.027578000	H	-2.021037000	-0.740792000	-2.353670000
Cl	0.173537000	-1.250464000	2.517272000	H	-3.215965000	-2.275244000	-3.702787000
Cl	-0.562846000	2.015503000	2.664614000	H	-2.272859000	-3.287989000	-2.645941000
C	-2.762108000	-1.358552000	-1.844332000	H	-5.253088000	-2.641098000	-2.435035000
C	-3.116913000	-2.590545000	-2.658237000	H	-4.532043000	-4.152256000	-2.938918000
C	-4.399006000	-3.306390000	-2.257091000	H	-5.307630000	-4.544953000	-0.782170000
C	-4.487979000	-3.822690000	-0.822062000	H	-3.583609000	-4.392421000	-0.574166000
C	-4.733927000	-2.743975000	0.242773000	H	-5.130206000	-1.843897000	-0.237009000
C	-3.537367000	-2.382366000	1.098090000	H	-5.522670000	-3.080346000	0.925286000
Te	-2.689410000	1.742826000	-0.089688000	H	-3.737048000	-1.536795000	1.754688000
C	-3.897977000	2.395242000	1.561332000	H	-3.220190000	-3.222257000	1.719337000
C	-5.124989000	3.192227000	1.159949000	H	-4.154761000	1.492450000	2.115707000
C	-4.920755000	4.205315000	0.038368000	H	-3.193490000	2.955781000	2.176380000
C	-3.724127000	5.153198000	0.191472000	H	-5.925767000	2.508096000	0.862557000
C	-2.510801000	4.788858000	-0.660670000	H	-5.488567000	3.712829000	2.054258000
C	-1.667062000	3.620496000	-0.195201000	H	-2.837993000	4.626104000	-1.693577000
H	2.021037000	0.740792000	2.353670000	H	-1.837038000	5.653700000	-0.695245000
H	3.630342000	0.740735000	1.613709000	H	-1.262070000	3.753923000	0.808790000
H	3.215965000	2.275244000	3.702787000	H	-0.849006000	3.420738000	-0.886199000
H	2.272859000	3.287989000	2.645941000	H	-3.428281000	5.227446000	1.243998000
H	5.253088000	2.641098000	2.435035000	H	-4.035901000	6.159356000	-0.100641000
H	4.532043000	4.152256000	2.938918000	H	-4.826187000	3.669066000	-0.913988000
H	5.307630000	4.544953000	0.782170000	H	-5.840772000	4.789314000	-0.051657000

Table S4. PBE0-D3/def2-TZVP optimized geometries of the $[Pt_nCl_{2n}\{Te(CH_2)_6\}_m]$ (n = 1-4; m = 2-4).

***cis*-$[PtCl_2\{Te(CH_2)_6\}_2]$**  Pt-Te 2.528-2.531 Pt-Cl 2.326-2.339	***trans*-$[PtCl_2\{Te(CH_2)_6\}_2]$**  Pt-Te 2.583 Pt-Cl 2.315
$[Pt_2Cl_4\{Te(CH_2)_6\}_3]$  Pt-Te(*cis*) 2.501-2.543 Pt-Te(*trans*) 2.565-2.580 Pt-Cl(*cis*) 2.307-2.339 Pt-Cl(*trans*) 2.301-2.325 Te···Cl 3.636	**$[Pt_3Cl_6\{Te(CH_2)_6\}_4]$**  Pt-Te(*cis*) 2.515-2.518 Pt-Te(*trans*) 2.572-2.581 Pt-Cl(*cis*) 2.316 Pt-Cl(*trans*) 2.315-2.323 Pt···Pt 3.167 Te···Cl 3.508-3.628
$[Pt_4Cl_8\{Te(CH_2)_6\}_4]$  Pt-Te(*cis*) 2.510 Pt-Te(*trans*) 2.561 Pt-Cl(*cis*) 2.313 Pt-Cl(*trans*) 2.314 Pt···Pt 3.075 Te···Cl 3.613	

3.2 Secondary bonding interactions

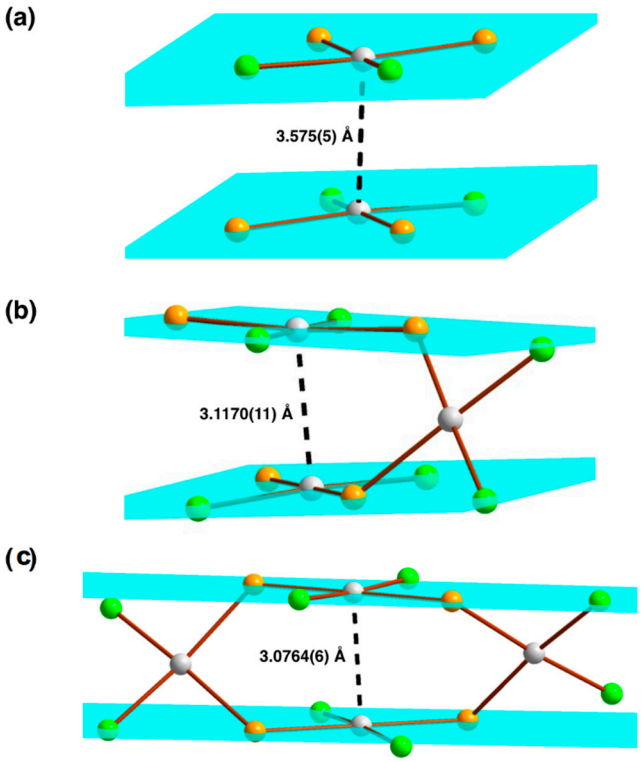


Figure S4. The Pt···Pt interactions lead to the square-planar coordination plane to become slightly concave in (a) **1**$_{cis}$, (b) **2**, and (c) **3**.

3.3 Formation energetics

Table S5. Total energies of optimized species at PBE0-D3/def2-TZVP level of theory in vacuum (Hartree).

Species	*E*	*H*	G_{298}
cis-[$PtCl_2(NCPh)_2$]	-1688.06795	-1687.84233	-1687.91708
trans-[$PtCl_2(NCPh)_2$]	-1688.07709	-1687.85113	-1687.92435
PhCN	-324.22847	-324.12182	-324.15846
$Te(CH_2)_6$	-503.70425	-503.52586	-503.56845
cis-[$PtCl_2\{Te(CH_2)_6\}_2$]	-2047.06703	-2046.69856	-2046.77953
trans-[$PtCl_2\{Te(CH_2)_6\}_2$]	-2047.08132	-2046.71280	-2046.79224
[$Pt_2Cl_4\{Te(CH_2)_6\}_3$]	-3590.44077	-3589.88192	-3589.99880
[$Pt_3Cl_6\{Te(CH_2)_6\}_4$]]	-5133.82851	-5133.07979	-5133.23107
[$Pt_4Cl_8\{Te(CH_2)_6\}_4$]]	-6173.45186	-6172.69360	-6172.85587
[$PtCl_2(NCPh)\{Te(CH_2)_6\}$]	-1867.57576	-1867.27869	-1867.35713

Table S6. Total energies of optimized species at PBE0-D3/def2-TZVP level of theory in dichloromethane (Hartree).

	E	*H*	G_{298}
cis-[$PtCl_2(NCPh)_2$]	-1688.09774	-1687.87197	-1687.94624
trans-[$PtCl_2(NCPh)_2$]	-1688.10200	-1687.87599	-1687.94883
PhCN	-324.23565	-324.12893	-324.16554
$Te(CH_2)_6$	-503.70723	-503.52904	-503.57170
cis-[$PtCl_2\{Te(CH_2)_6\}_2$]	-2047.09060	-2046.72240	-2046.80539
trans-[$PtCl_2\{Te(CH_2)_6\}_2$]	-2047.09323	-2046.72499	-2046.80445
[$Pt_2Cl_4\{Te(CH_2)_6\}_3$]	-3590.46723	-3589.90901	-3590.02745
[$Pt_3Cl_6\{Te(CH_2)_6\}_4$]]	-5133.85842	-5133.11156	-5133.26138
[$Pt_4Cl_8\{Te(CH_2)_6\}_4$]]	-6173.49395	-6172.73679	-6172.90005
[$PtCl_2(NCPh)\{Te(CH_2)_6\}$]	-1867.59427	-1867.29725	-1867.37482

Table S7. Gibbs PBE0-D3/def2-TZVP formation energies of $\mathbf{1}_{cis}$, $\mathbf{1}_{trans}$, **2**, and **3** from *cis*-[$PtCl_2(NCPh)_2$] and $Te(CH_2)_6$. In dichloromethane (kJ mol^{-1})-

Reaction	ΔE	ΔH	ΔG_{298}	ΔG/Pt	ΔG/Te
cis-[$PtCl_2(NCPh)_2$] + 2 $Te(CH_2)_6$ ⇌ cis-[$PtCl_2\{Te(CH_2)_6\}_2$] ($\mathbf{1}_{cis}$) + 2 PhCN	–130	–132	–123	-123	-61
cis-[$PtCl_2(NCPh)_2$] + 2 $Te(CH_2)_6$ ⇌ trans-[$PtCl_2\{Te(CH_2)_6\}_2$] ($\mathbf{1}_{trans}$) + 2 PhCN	–137	–139	–121	-121	-60
2 *cis*-[$PtCl_2(NCPh)_2$] + 3 $Te(CH_2)_6$ ⇌ [$Pt_2Cl_4\{Te(CH_2)_6\}_3$] + 4 PhCN	–243	–246	–215	-107	-71
3 *cis*-[$PtCl_2(NCPh)_2$] + 4 $Te(CH_2)_6$ ⇌ [$Pt_3Cl_6\{Te(CH_2)_6\}_4$] (**2**) + 6 PhCN	–394	–402	–339	-113	-85
4 *cis*-[$PtCl_2(NCPh)_2$] + 4 $Te(CH_2)_6$ ⇌ [$Pt_4Cl_8\{Te(CH_2)_6\}_4$] (**3**) + 8 PhCN	–418	–431	–401	-100	-100

4. References

[1] Rodewald, M.; Rautiainen, J. M.; Niksch, T.; Görls, H.; Oilunkaniemi, R.; Weigand, W.; Laitinen, R. S. Chalcogen-bonding interactions in telluroether heterocycles $[Te(CH_2)_m]_n$ (n = 1-4; m = 3-7). *Chem. Eur. J.* **2020**, *26*, 13806- 13818. doi.org/10.1002/chem.202002510