Supplementary Material

Cyclopalladation of telluro ether ligands: synthesis, reactivity and structural characterization

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Preparation of dimesityldiditelluride (Mes_2Te_2)

To a THF solution of mesityl magnesium bromide (prepared from mesityl bromide (20.82 g, 104 mmol) and magnesium turnings (2.52 g, 104 mmol) in 50 cm^3 THF), a freshly grind tellurium powder (13.34 g, 104 mmol) was added under a nitrogen atmosphere with stirring which continued overnight. The contents were exposed to air for two hrs with stirring and the solvent was evaporated under reduced pressure. The residue was extracted with diethylether (3 × 50 cm^3) and filtered. The filtrate was concentrated to 50 cm^3 which on slow evaporation afforded red crystals (15.00 g, 58%); m.p. 120°C (literature[1] 125-127°C). ^{125}Te $\{^1H\}$ NMR ($CDCl_3$) δ = 200.3 ppm.

Similarly diphenylditelluride [Ph_2Te_2, (62%); m.p. 62°C; ^{125}Te $\{^1H\}$ NMR ($CDCl_3$) δ = 421.5 ppm] and di-*o*-tolylditelluride [$Te_2(o\text{-tol})_2$], (54%); ^{125}Te $\{^1H\}$ NMR ($CDCl_3$) δ = 282.1 ppm] were prepared.

Preparation of dimesityl telluride (Mes_2Te)

To an ice cold solution (50 cm^3) of dimesityldiditelluride (2.5 g, 5.06 mmol) bromine (0.261 ml) in 5 cm^3 toluene was added dropwise. To this MesTeBr solution, a THF solution of MesMgBr (0.5M, 25ml) was added dropwise with stirring whereupon a colorless solution was formed. After one hour of stirring at room temperature, water (50 cm^3) was introduced to the reaction flask. The organic layer was evaporated under reduced pressure and the aqueous phase was extracted with diethyl ether (20 cm^3 × 4) and the combined ether extracts were washed with aqueous NH_4Cl followed by saturated aqueous NaCl. The organic phase was dried over anhydrous $MgSO_4$ for 2 hr. The contents were filtered and concentrated under vacuum to give colourless crystals of the title compound (3.12g, 84% yield), m.p 110°C (literature[1] 123-125 °C). Anal.Calcd for $C_{18}H_{22}Te$: C, 59.07; H, 6.06%. Found, C, 58.21; H, 5.89%.^1H NMR ($CDCl_3$) δ: 2.28 (s, Me-4); 2.39 (s, 2,6-Me); 6.91(s, 3,5-CH).$^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 20.8 (s, 4-Me); 28.2 (s, 2,6-Me); 119.1 (Te-C), 127.8 (3,5-CH); 137.9,144.2 ppm. ^{125}Te $\{^1H\}$ NMR ($CDCl_3$) δ = 260.8 ppm (NMR data were consistent with literature[2]).

Diphenyl telluride (Ph_2Te)

Prepared similar to dimesityl telluride employing PhTeBr and PhMgBr. The product was purified by converting into Ph_2TeBr_2, by oxidation of crude Ph_2Te with bromine, which was recrystallized from toluene as yellow crystals. The latter was reduced with $Na_2S.15H_2O$ in refluxing methanol for 15 min. The contents were diluted with water and methanol was evaporated under reduced pressure. The aqueous phase was extracted with diethyl ether (4 × 20 cm^3) and after processing gave cream colored oily liquid in 66% yield. Anal.Calcd.for

$C_{12}H_{10}Te$: C, 51.14; H, 3.58%. Found,C, 50.55; H, 3.46%. ^{1}H NMR ($CDCl_3$) δ: 7.23-7.36(m), 7.74-7.77 (m)(Ph).$^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ: 114.8 (C-Te), 127.9, 129.6, 138.0 ppm. ^{125}Te $\{^{1}H\}$ NMR ($CDCl_3$) δ = 693.4 ppm.

Di-*o*-tolyltellurie (*o*-tol_2Te)

Prepared and purified similar to diphenyl telluride and isolated as a cream colored liquid in 60% yield. Anal.Calcd.for $C_{14}H_{14}Te$: C, 54.27; H, 4.55%. Found,C, 53.56; H, 4.53%. ^{1}H NMR ($CDCl_3$) δ: 2.72(s, Me); 7.22 (t, 6.8 Hz), 7.48 (br, m), 7.82 (d, 7.5 Hz). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ: 26.7 (Me), 119.0 (C-Te), 127.3, 128.8, 129.8, 138.5, 142.8 (C-2) ppm. ^{125}Te $\{^{1}H\}$ NMR ($CDCl_3$) δ = 499.3 ppm.

Mesityl(phenyl)telluride (MesTePh)

This was prepared by treatment of MesTeBr (from Mes_2Te_2 (5.0g, 10.0 mmol) and bromine (1.62g, 10.3 mmol) in THF) with PhMgBr (0.6 M, 40 cm^3) and processed in a way similar to Ph_2Te, and was isolated as a cream colored liquid (49% yield). ^{1}H NMR ($CDCl_3$) δ: 2.36 (s, 4-Me); 2.60 (s, 2,6-Me); 7.06(s, 3,5-CH);7.14-7.19(m); 7.36-7.39(m) (Ph).$^{125}Te\{^{1}H\}$ NMR ($CDCl_3$) δ = 427.2 ppm.

Mesityl(o-tolyl)telluride (MesTe(o-tol))

This was prepared from *o*-tolTeBr (from *o*-tol_2Te_2 (5.0 g, 11.31mmol) and bromine (1.826 g, 11.57 mmol) in THF) and MesMgBr (0.5 M, 50 cm^3) and processed in a way similar to dimesityl telluride, and isolated as a cream crystalline solid (5.2 g, 68% yield); m.p. 50°C. Anal.Calcd.for $C_{16}H_{18}Te$: C, 56.87; H, 5.37%. Found,C, 56.00; H, 5.56%. ^{1}H NMR ($CDCl_3$) δ: 2.47, 2.52, 2.70 (each s for Me); 6.97-7.29 (m, 3,5-CH of Mes, o-tol). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ: 21.0 (s), 24.8(s), 29.3(s),(Me); 117.8, 120.1, 126.4, 126.6, 127.6, 129.3, 132.9, 139.3, 140.2, 145.6 ppm. ^{125}Te $\{^{1}H\}$ NMR ($CDCl_3$) δ = 336.8 ppm.

Table S1. Crystallographic and structural determination data for *trans*-[$PdCl_2(TeMes_2)_2$].2 MeCN, *trans*-[$PdCl_2(TeMes_2)_2$].toluene, [$Pd_2(\mu\text{-}Cl)_2Cl_2(TeMes_2)_2$]. 2 acetone and *cis*-[$PdCl_2\{MesTeCH_2C_6H_2(4,6\text{-}Me_2)TeMes\}$]

	trans-[$PdCl_2(TeMes_2)_2$].2 MeCN	*trans*-[$PdCl_2(TeMes_2)_2$].toluene	[$Pd_2(\mu\text{-}Cl)_2Cl_2(TeMes_2)_2$]. 2acetone	*cis*-[$PdCl_2\{MesTeCH_2C_6H_2(4,6\text{-}Me_2)TeMes\}$]
	1a. $2CH_3CN$	**1a**.C_6H_5Me	**2a.**2 acetone	4
chemical formula	$C_{36}H_{44}Cl_2PdTe_2.$ $2CH_3CN$	$C_{36}H_{44}$ $Cl_2PdTe_2.C_7H_8$	$C_{36}H_{44}Cl_4Pd_2Te_2.$ $C_6H_{12}O_2$	$C_{27}H_{32}Cl_2PdTe_2$
formula weight	991.32	1001.35	1202.67	789.03
cryst size (mm^3)	0.15 0.05 x 0.02	0.1 x 0.1 x 0.05	0.15 x 0.13 x 0.10	0.14 x 0.05 x 0.01
crysta system	monoclinic	Triclinic	monoclinic	Monoclinic
space group	$P2_1/n$	*P*-1	$P2_1/c$	$P2_1/c$
Radiation (wavelength Å)	Cu K/α (1.5418)	Cu K/α (1.5418)	Cu K/α (1.5418)	Mo K/α (0.71073)
temperature (K)	298 (2)	298 (2)	298 (2)	298 (2)
unit cell dimensions				
a (Å)	8.8514(16)	11.3836(8)	9.9444(3)	12.8111(3)
b (Å)	10.3908(17)	12.8965(7)	22.0756(8)	19.8187(4)
c (Å)	23.3718(5)	16.0242(9)	10.5502(4)	12.0377(2)
α (°)	90.00	87.937(5)	90.00	90.00
β (°)	100.804(18)	78.771(5)	95.709(3)	114.103(10)
γ (°)	90.00	67.794(6)	90.00	90.00
volume ($Å^3$)	2111.47(7)	2134.5(2)	2304.58(13)	2789.89(10)
Z	2	2	2	4
ρ_{calcd} (g cm^{-3})	1.559	1.558	1.733	1.879
μ (mm^{-1})/F(000)	15.596/ 976	15.421/ 988	18.466/ 1176	2.920/ 1512
limiting indices	$-9 \le h \le 10$	$-13 \le h \le 12$	$-11 \le h \le 11$	$-16 \le h \le 15$
	$-12 \le k \le 12$	$-14 \le k \le 15$	$-26 \le k \le 26$	$-24 \le k \le 24$
	$-28 \le l \le 28$	$-19 \le l \le 18$	$-6 \le l \le 12$	$-15 \le l \le 15$
θ for data collection (°)	3.85 – 69.91	2.81 – 70.04	4.01 – 69.90	1.74 – 26.39
no. of reflns collected	3981	7925	4259	5696
no. of independent reflns	3585	5758	3132	5053
data/restraints/parameters	3981/0/221	7925/0/447	4259 /0 /235	5696/ 0/ 298
final R_1, wR_2 indices	0.0459/0.1302	0.0507/0.1151	0.0674/ 0.1643	0.0238/ 0.0645
R_1, wR_2 (all data)	0.0504/0.1344	0.0773/0.1281	0.0958/ 0.1747	0.0297/ 0.0755
goodness of fit on F^2	1.130	1.057	1.189	1.176

Table S2. Crystallographic and structural determination data for $[Pd_2(\mu\text{-}OAc)_2\{CH_2C_6H_2(4,6\text{-}Me_2)TeMes\}_2]$.toluene, $[Pd_2(\mu\text{-}OAc)_2\{CH_2C_6H_2(4,6\text{-}Me_2)Tetol\text{-}o\}_2]$ and $[Pd(\mu\text{-}OAc)(\mu\text{-}TeMes)]_4$

	$[Pd_2(\mu\text{-}OAc)_2\{CH_2C_6H_2(4,6\text{-}Me_2)TeMes\}_2]$.toluene	$[Pd_2(\mu\text{-}OAc)_2\{CH_2C_6H_2(4,6\text{-}Me_2)Tetol\text{-}o\}_2]$	$[Pd(\mu\text{-}OAc)(\mu\text{-}TeMes)]_4$
	5a.toluene	5b	6
chemical formula	$C_{40}H_{48}O_4Pd_2Te_2.C_7H_8$	$C_{36}H_{40}O_4Pd_2Te_2$	$C_{44}H_{56}O_8Pd_4Te_4$
Fw	1152.92	1004.68	1648.89
cryst size (mm^3)	0.20 x 0.15 x 0.10	0.12 x 0.10 x 0.05	0.18 x 0.05 x 0.05
crysta system	Monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/n$	*P*-1
Radiation	Cu K/α (1.5418)	Cu K/α (1.5418)	Cu K/α (1.5418)
temperature (K)	130.00(10)	298(2)	298(2)
unit cell dimensions			
a (Å)	11.1936(3)	12.2913(3)	8.2911(4)
b (Å)	33.0163(13)	17.9732(5)	12.0292(5)
c (Å)	11.9487(3)	16.5408(5)	13.7289(6)
α (°)	90.00	90.00	72.307(4)
β (°)	92.641(2)	101.904(3)	72.599(4)
γ (°)	90.00	90.00	89.423(4)
volume ($Å^3$)	4411.2(2)	3575.50(18)	1239.86(10)
Z	4	4	1
ρ_{calcd} (g cm^{-3})	1.736	1.866	2.208
μ (mm^{-1})/F(000)	17.127/ 2264	21.018/ 1936	30.102/ 776
limiting indices	$-13 \le h \le 7$	$-14 \le h \le 14$	$-9 \le h \le 10$
	$-33 \le k \le 39$	$-21 \le k \le 20$	$-14 \le k \le 14$
	$-14 \le l \le 13$	$-13 \le l \le 20$	$-16 \le l \le 16$
θ for data collection (°)	3.94 – 70.24	3.675 – 69.879	3.56-70.07
no. of reflns collected	8254	6614	4648
no. of independent reflns	6016	4494	3616
data/restraints/parameters	8254/37/490	6614/ 0 /405	4648/ 0/ 279
final R_1, wR_2 indices	0.0739/0.1838	0.0704/ 0.1732	0.0376/ 0.0846
R_1, wR_2 (all data)	0.1009/0.2024	0.1110/ 0.1972	0.0600/ 0.0948
goodness of fit on F^2	1.047	1.066	1.042

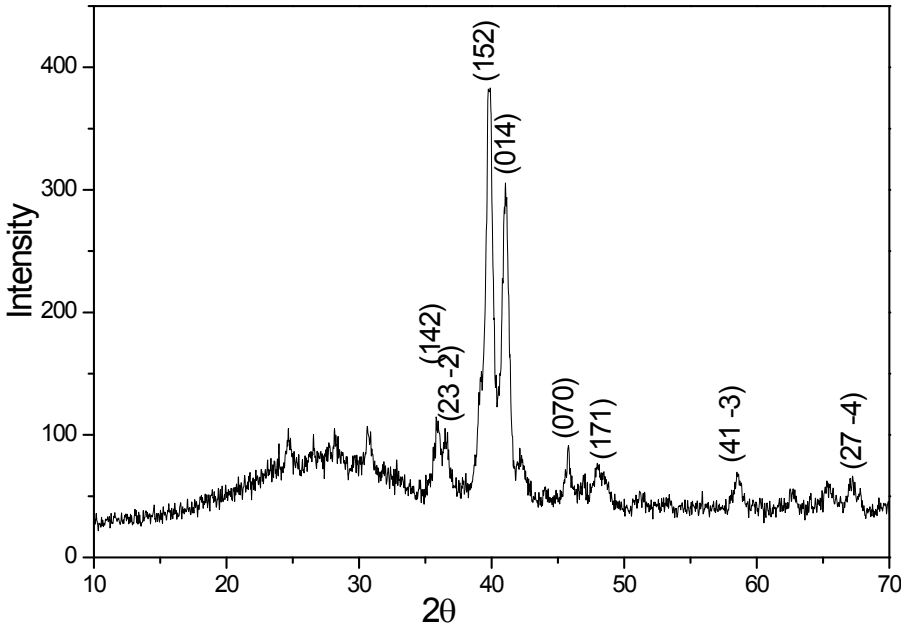

Fig S1 XRD pattern of Pd_7Te_3 obtained from *trans*-$[PdCl_2(TeMes_2)_2]$ in refluxing xylene.

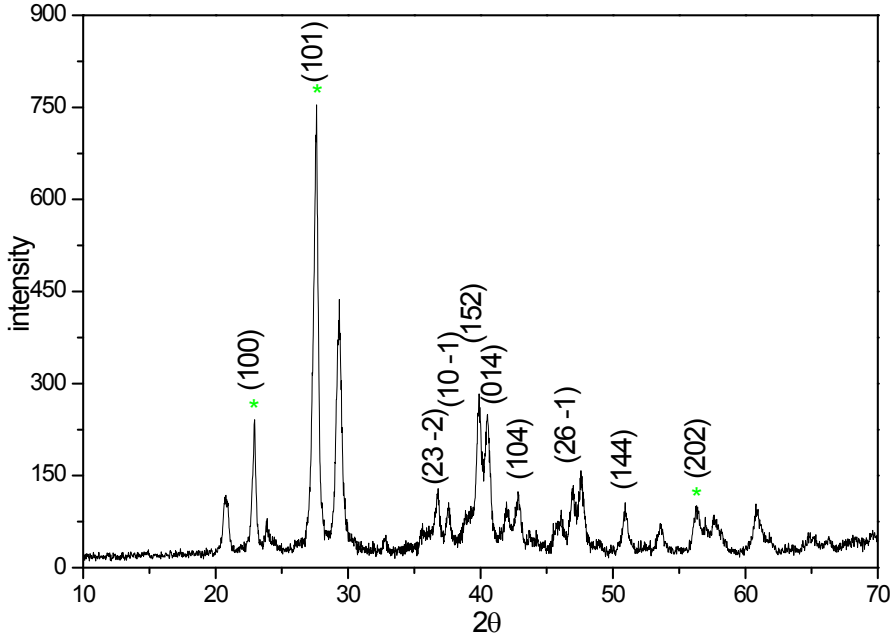

Fig S2 XRD pattern of Pd_7Te_3 obtained from *trans*-$[PdCl_2(TeMes_2)_2]$ in refluxing 2-ethoxy ethanol. Peaks due to elemental tellurium are marked with *.

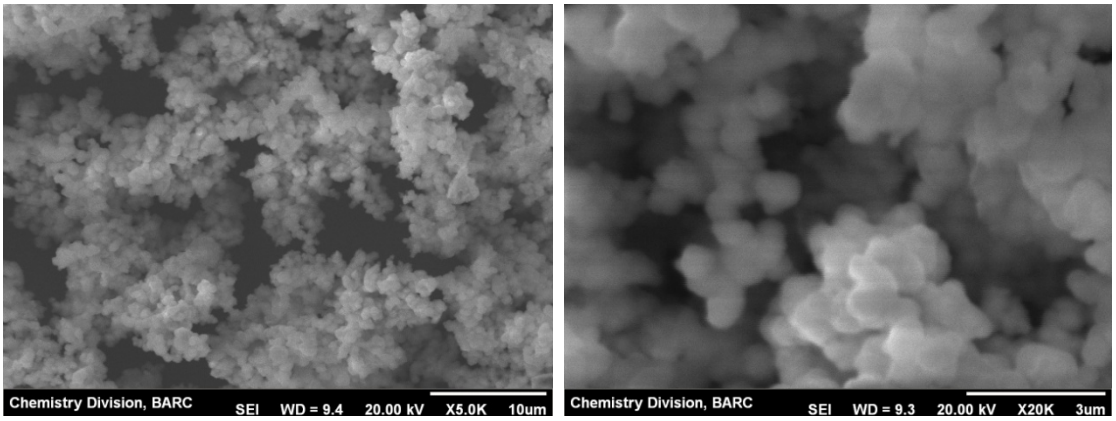

Fig S3 SEM image of Pd_7Te_3 obtained from *trans*-$[PdCl_2(TeMes_2)_2]$ in refluxing xylene.

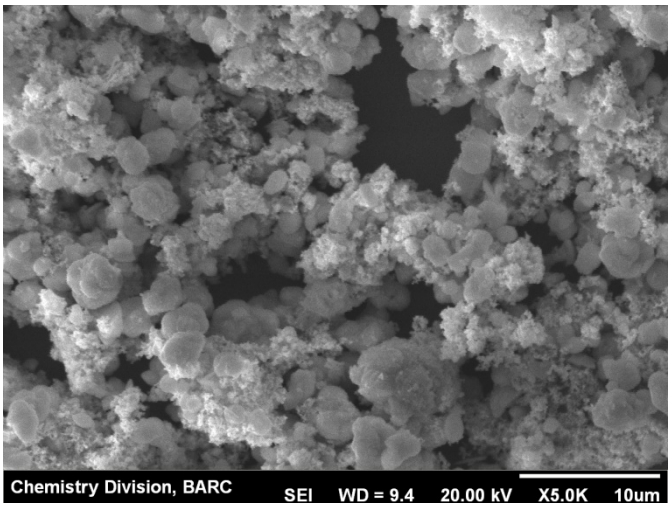

Fig S4 SEM image of Pd_7Te_3 obtained from *trans*-$[PdCl_2(TeMes_2)_2]$ in refluxing 2-ethoxy ethanol.

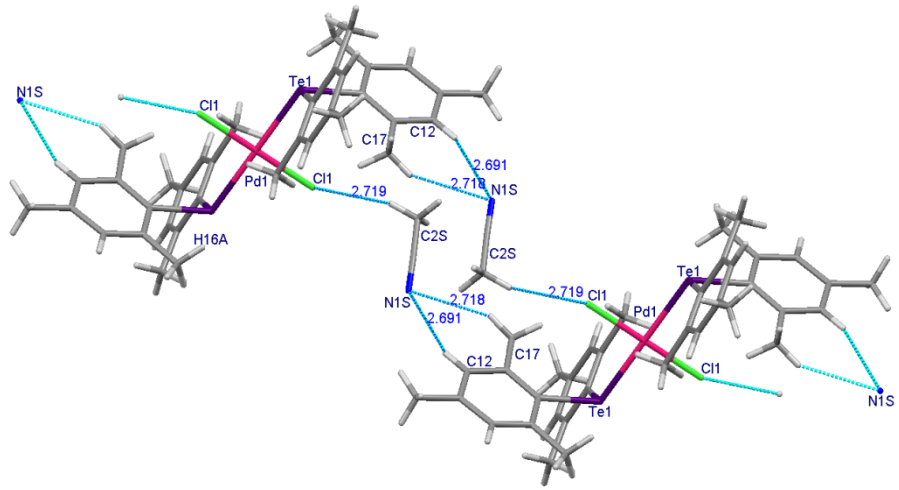

Fig S5 Short interactions between solvent acetonitrile and *trans*-$[PdCl_2(TeMes_2)_2]$ in *trans*-$[PdCl_2(TeMes_2)_2].2CH_3CN$ (**1a**.2 acetonitrile)

References

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2. T. M. Klapotke, B. Krumm, P. Mayer, K. Polborn and I. Schwab, *Z. Ang. Allg. Chem.* 2005, **631**, 2677.