

Electronic Supplementary Information

How Innocent Is Thallium(I)? Correct Formulations of $[\text{Tl}_2\text{Pd}_{14}(\text{CO})_9(\text{PMe}_3)_{11}][\text{PF}_6]_2$ and $[\text{TlPd}_9(\text{CO})_9(\text{PPh}_3)_6][\text{PF}_6]$ Clusters Previously Reported as Corresponding $\text{Au}_2\text{Pd}_{14}$ and AuPd_9 Clusters

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Experimental part.

General Remarks. $\text{Pd}_{10}(\text{CO})_{12}(\text{PMe}_3)_6$ was obtained in accordance with the approach developed for $\text{Pd}_{10}(\text{CO})_{12}(\text{PAlk}_3)_6$ clusters^{1a} and recrystallized from CH_2Cl_2 /heptane. $\text{Pd}_{10}(\text{CO})_{12}(\text{PPh}_3)_6$ was obtained from the literature method^{1b} and recrystallized from CHCl_3 /hexane. $[(\text{Ph}_3\text{P})_2\text{N}]\text{Cl}$ was recrystallized from acetone/*i*-Pr₂O. All other reagents were used without additional purification, but before use solvents were purged with nitrogen for at least 20 min. All operations except crystallization of $[\text{TlPd}_9(\text{CO})_9(\text{PPh}_3)_6][\text{PF}_6]$ were performed under N₂. ³¹P{¹H} NMR spectra were obtained on Bruker AC-300 spectrometer and referenced to 85% H₃PO₄ in D₂O as an external standard. IR spectra were recorded on Bruker Tensor 27 FT-IR spectrometer. X-Ray diffraction data collections were performed on Bruker APEX2 area-detector diffractometer (Mo K α radiation, $\lambda = 0.71073 \text{ \AA}$).

X-Ray Crystallographic Determinations of $[\text{Tl}_2\text{Pd}_{14}(\mu_2\text{-CO})_2(\mu_3\text{-CO})_7(\text{PMe}_3)_{11}][\text{PF}_6]_2 \cdot \text{Me}_2\text{CO}$ [(1a-Me)·Me₂CO] and $[\text{TlPd}_9(\text{CO})_9(\text{PPh}_3)_6][\text{PF}_6] \cdot 1.65\text{THF} \cdot 0.66\text{CH}_2\text{Cl}_2$ (2a-Ph).

X-Ray data for crystals (1a-Me)·Me₂CO and 2a-Ph were collected at 100(2) K; reflections from both crystals were empirically corrected for absorption (SADABS).^{2a} The crystal structures were obtained by use of direct methods followed by difference Fourier maps. Least-squares refinements (based on F²) were carried out with SHELXTL.^{2a, b}

In the crystal structure of **(1a-Me)·Me₂CO** one of two [PF₆]⁻ anions and the methyl groups attached to P3, P6, and P8 atoms are disordered over two sites with refined occupancy factors of 0.60/0.40, 0.51/0.49, 0.71/0.29 and 0.61/0.39, respectively. All non-hydrogen atoms with the exception of most of those that are disordered were refined anisotropically.

In the crystal structure of **2a-Ph** the crystallographically independent part of the unit cell contains: (a) one-third of the [Pd₉Tl(CO)₉(PPh₃)₆][PF₆]; and (b) THF and CH₂Cl₂ solvent molecules that are disordered over the same site with the refined partial occupancies of 0.55 and 0.22, respectively. The [PF₆]⁻ anion is disordered around crystallographic threefold axis at two independent positions (the refined s.o.f. 0.56/0.44) giving rise to six different orientations of [PF₆]⁻. All non-hydrogen atoms with the exception of the Cl (of CH₂Cl₂), F (of [PF₆]⁻), and C and O atoms of solvent molecules were refined anisotropically. A rigid-group constraint (AFIX 66) was applied to all phenyl groups. EADP constraints were used for the F atoms of the disordered [PF₆]⁻ anion and the Cl, C and O atoms of the solvent molecules. Distance restraints were applied to the P-F bonds, to disordered Ph groups, and to the Cl, C, and O atoms of the solvent molecules.

In both structures the hydrogen atoms were generated geometrically and refined as riding atoms with corresponding default C-H distances. Structural CIF/PLATON tests performed by the <http://journals.iucr.org/services/cif/checking/checkform.html> are in accordance with the crystal structure determinations. CCDC reference numbers are 906532 [**(1a-Me)·Me₂CO**] and 906531 (**2a-Ph**).

References

1. (a) E. G. Mednikov and N. K. Eremenko, *Koordin. Khim. (Sov. J. Coord. Chem.)* 1983, **9**, 243;
(b) E. G. Mednikov, N. K. Eremenko and S. P. Gubin, *Koordin. Khim. (Sov. J. Coord. Chem.)* 1984, **10**, 711.

2. (a) G. M. Sheldrick, SHELXTL (version 6.10 (2000)) program library, Bruker Analytical X-Ray Systems, Madison, WI; (b) Bruker-AXS. 2009. Apex2 v2010.7-0, Bruker-AXS Inc., Madison, Wisconsin, USA.

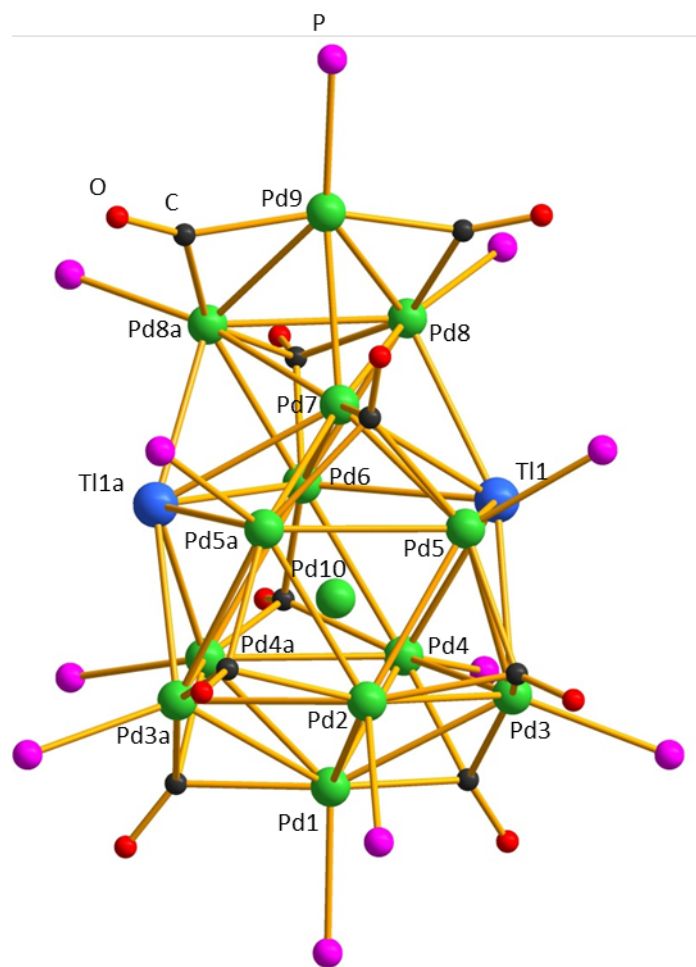


Fig. S1 Entire $[\text{Tl}_2\text{Pd}_{14}(\text{CO})_9(\text{PMe}_3)_{11}]^{2+}$ dication **1a-Me** of *pseudo*- C_s symmetry without Me-substituents.

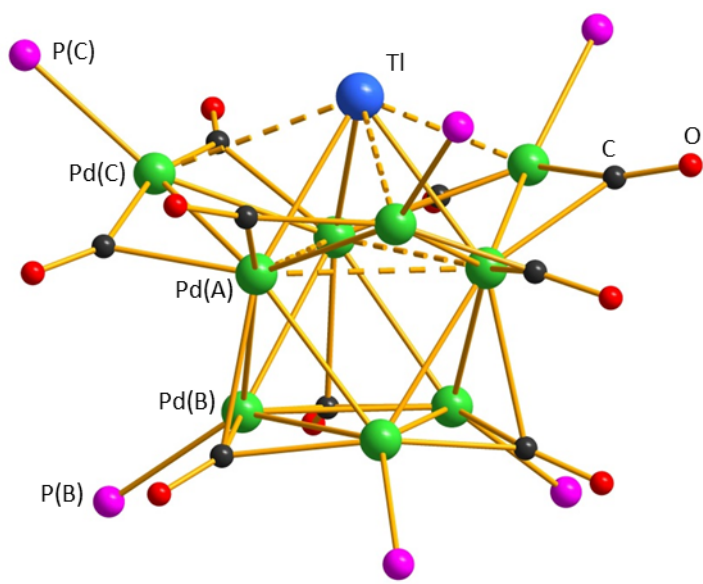


Fig. S2 Entire view of the $[\text{TlPd}_9(\text{CO})_9(\text{PPh}_3)_6]^+$ cluster cation **2a-Ph** of C_{3v} symmetry without Ph-substituents .

Table S1. Comparative Means (Å) and Individual Ranges (Å) under *Pseudo-C_s* Symmetry between the $\text{Tl}_2\text{Pd}_{14}(\text{CO})_9\text{P}_{11}$ Fragment of $[\text{Tl}_2\text{Pd}_{14}(\mu_2\text{-CO})_2(\mu_3\text{-CO})_7(\text{PMe}_3)_{11}][\text{PF}_6]_2 \cdot \text{Me}_2\text{CO}$ [(**1a-Me**)·**Me₂CO**] and Corresponding Crystallographic-*C_s* Fragment of the non-Solvated $[\text{Au}_2\text{Pd}_{14}(\text{CO})_9(\text{PMe}_3)_{11}][\text{PF}_6]_2$ (**1-Me**)^a Relabeled as $[\text{Tl}_2\text{Pd}_{14}(\text{CO})_9(\text{PMe}_3)_{11}][\text{PF}_6]_2$.

Connectivity	N ^b	Mean [Range] in (1a-Me)· Me₂CO ^c	Mean [Range] in 1-Me ^{a,d,e}
Radial in $\text{Tl}_2\text{Pd}_{11}$ icosahedron			
Pd(cent)-Tl	2	2.839 [2.8370(5)-2.8405(5)]	2.853(2) [2.853(2)]
Pd(cent)-Pd(1)	1	2.6883(4)	2.678(5)
Pd(cent)-Pd(2)	1	2.6415(4)	2.649(5)
Pd(cent)-Pd(3)	2	2.824 [2.8144(6)-2.8342(6)]	2.826(4) [2.826(3)]
Pd(cent)-Pd(4)	2	2.740 [2.7357(5)-2.7448(5)]	2.757(4) [2.757(4)]
Pd(cent)-Pd(5)	2	2.755 [2.7521(5)-2.7580(5)]	2.759(4) [2.759(4)]
Pd(cent)-Pd(6)	1	2.7571(4)	2.777(5)
Pd(cent)-Pd(7)	1	2.7416(4)	2.747(5)
Mean [Range] for Pd-Pd		2.747 [2.6415(4)-2.8342(6)]	2.754 [2.649(5)-2.826(3)]
Tangential in $\text{Tl}_2\text{Pd}_{11}$ icosahedron			
Tl-Pd(3)	2	2.960 [2.9487(5)-2.9712(5)]	2.967(3) [2.967(3)]
Tl-Pd(4)	2	2.884 [2.8707(5)-2.8975(4)]	2.911(3) [2.911(3)]
Tl-Pd(5)	2	2.918 [2.8988(5)-2.9370(5)]	2.914(3) [2.914(3)]
Tl-Pd(6)	2	2.963 [2.9625(5)-2.9635(5)]	2.985(2) [2.985(2)]
Tl-Pd(7)	2	2.970 [2.9695(5)-2.9706(5)]	2.966(2) [2.966(2)]
Mean [Range] for Tl-Pd		2.939 [2.8707(5)-2.9712(5)]	2.949 [2.911(3)-2.985(2)]
Pd(1)-Pd(2)	1	3.0187(4)	3.008(4)

Pd(1)-Pd(3)	2	2.928 [2.9185(6)-2.9370(6)]	2.914(3) [2.914(3)]
Pd(1)-Pd(4)	2	2.831 [2.8267(6)-2.8347(6)]	2.850(4) [2.850(4)]
Pd(2)-Pd(3)	2	2.900 [2.8798(6)-2.9199(6)]	2.919(4) [2.919(4)]
Pd(2)-Pd(5)	2	2.805 [2.7985(6)-2.8112(6)]	2.820(4) [2.820(4)]
Pd(3)-Pd(4)	2	2.999 [2.9979(6)-2.9992(6)]	3.000(4) [3.000(4)]
Pd(3)-Pd(5)	2	2.986 [2.9803(6)-2.9909(6)]	3.012(4) [3.012(4)]
Pd(4)-Pd(4A)	1	2.8386(4)	2.845(5)
Pd(4)-Pd(6)	2	2.804 [2.8004(6)-2.8081(6)]	2.810(4) [2.810(4)]
Pd(5)-Pd(5A)	1	2.8674(4)	2.864(5)
Pd(5)-Pd(7)	2	2.818 [2.8024(5)-2.8332(5)]	2.825(4) [2.825(4)]
Pd(6)-Pd(7)	1	2.9028(4)	2.901(4)
Mean [Range] for Pd-Pd		2.888 [2.7985(6)-3.0187(4)]	2.896 [2.810(4)-3.012(4)]
Between Tl_2Pd_{11} icosahedron and Pd_5 trigonal bipyramid			
Tl-Pd(8)	2	2.903 [2.8762(5)-2.9303(5)]	2.919(2) [2.919(2)]
Pd(6)-Pd(8)	2	2.755 [2.7477(6)-2.7625(5)]	2.765(4) [2.765(4)]
Pd(7)-Pd(8)	2	2.735 [2.7171(5)-2.7538(5)]	2.746(4) [2.746(4)]
Pd(7)-Pd(9)	1	2.7061(4)	2.728(5)
Mean [Range] for Pd-Pd		2.737 [2.7061(4)-7625(5)]	2.750 [2.728(5)-2.765(4)]
In Pd_5 trigonal bipyramid			
Pd(8)-Pd(8A)	1	2.8451(4)	2.858(2)
Pd(8)-Pd(9)	2	2.717 [2.7066(5)-2.7281(5)]	2.727(3) [2.727(3)]

Mean [Range] for Pd-Pd		2.760 [2.7066(5)-2.8451(4)]	2.771 [2.727(3)-2.858(2)]
Mean [Range] for Pd-P		2.33 [2.2863(11)-2.3550(15)]	2.34 [2.28(2)-2.39(1)]
Mean [Range] for Pd-C for μ_2 -CO		2.06 [1.978(6)-2.142(6)]	2.02 [1.98(3)-2.06(3)]
Mean [Range] for C-O in μ_2 -CO	2	1.16 [1.148(7)-1.170(7)]	1.26 [1.26(4)]
Mean [Range] for Pd-C for μ_3 -CO		2.13 [2.014(5)-2.314(7)]	2.13 [1.98(5)-2.22(4)]
Mean [Range] for C-O in μ_3 -CO		1.18 [1.159(5)-1.186(7)]	1.18 [1.13(5)-1.23(5)]

^a Data are taken from the crystal structure deposited in CCDC, refcode YUXFEC (R. C. B. Copley, C. M. Hill and D. M. P. Mingos, *J. Cluster Sci.*, 1995, **6**, 71); ^b denotes the total number of individual connectivities under *pseudo*- C_s symmetry; ^c crystallographic analysis of the acetone-solvated crystal structure of $[Ti_2Pd_{14}(CO)_9(PMe_3)_{11}][PF_6]_2$ (**1a-Me**) under centrosymmetric monoclinic symmetry ($P2_1/n$) with $Z=4$ required the determination of atomic parameters for one independent dication, two independent $[PF_6]^-$ anions, and one independent solvated Me_2CO molecule. The entire $[Ti_2Pd_{14}(CO)_9(PMe_3)_{11}]^{2+}$ dication (without Me substituents) possesses *pseudo* mirror-plane symmetry; ^d in the reported unsolvated crystal structure of **1-Me**, which has a centrosymmetric orthorhombic unit cell ($Pmcn$) with $Z=4$, four dications and eight $[PF_6]^-$ anions each lie on a crystallographic mirror plane that corresponds to the crystallographically independent unit being composed of one-half dication and two one-half $[PF_6]^-$ anions; ^e in **1a-Me** one of the two $[PF_6]^-$ anions and the nine methyl substituents of three PMe_3 ligands are crystallographically disordered, whereas in **1-Me** both the cluster dication and two $[PF_6]^-$ anions are ordered.

Table S2. Interatomic Angles ($^{\circ}$) about Tl Atoms in $[\text{Tl}_2\text{Pd}_{14}(\mu_2\text{-CO})_2(\mu_3\text{-CO})_7(\text{PMe}_3)_{11}][\text{PF}_6]_2 \cdot \text{Me}_2\text{CO}$ [(**1a-Me**)·**Me₂CO**] and the non-Solvated $[\text{Au}_2\text{Pd}_{14}(\text{CO})_9(\text{PMe}_3)_{11}][\text{PF}_6]_2$ (**1-Me**)^a Relabeled as $[\text{Tl}_2\text{Pd}_{14}(\text{CO})_9(\text{PMe}_3)_{11}][\text{PF}_6]_2$.

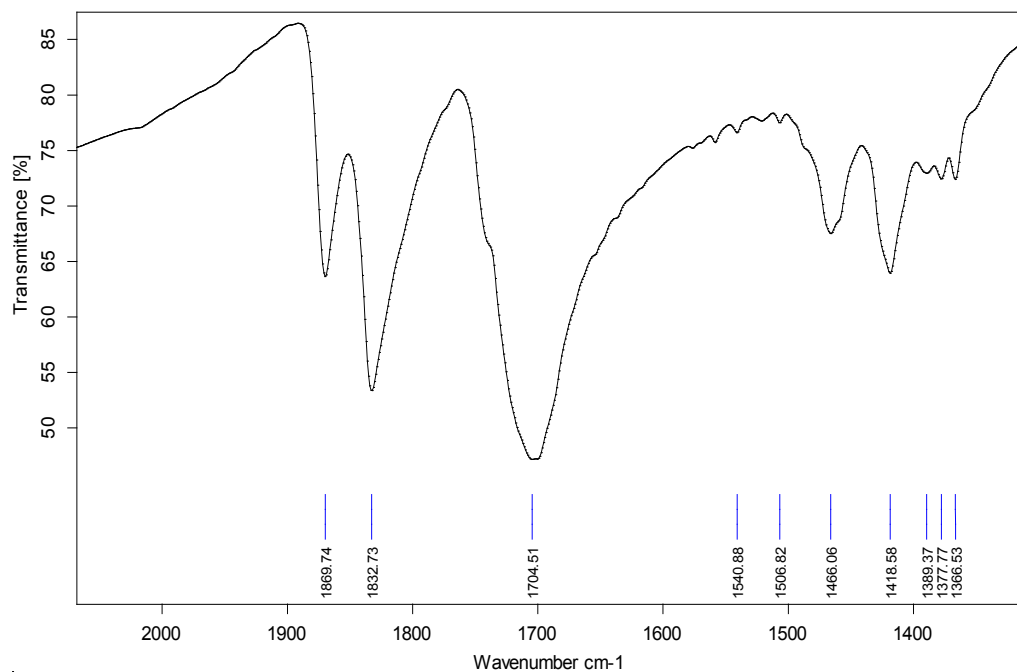
Angle	N ^b	Mean [Range] in (1a-Me)· Me₂CO	Mean [Range] in 1-Me ^a
Pd(3)-Tl-Pd(4)	2	61.72(2) [61.722(14)-61.724(13)]	61.38(7)
Pd(3)-Tl-Pd(5)	2	61.05(2) [60.844(13)-61.250(13)]	61.61(7)
Pd(3)-Tl-Pd(6)	2	106.82(2) [106.651(12)-106.997(13)]	106.34(7)
Pd(3)-Tl-Pd(7)	2	106.12(2) [106.061(13)-106.169(13)]	106.47(7)
Pd(3)-Tl-Pd(8)	2	158.76(2) [158.122(15)-159.392(15)]	158.73(8)
Pd(3)-Tl-Pd(10)	2	58.25(2) [58.138(12)-58.359(12)]	58.05(5)
Pd(4)-Tl-Pd(5)	2	107.99(2) [107.771(14)-108.215(15)]	108.11(8)
Pd(4)-Tl-Pd(6)	2	57.30(2) [57.082(11)-57.517(11)]	56.91(6)
Pd(4)-Tl-Pd(7)	2	104.33(2) [104.154(12)-104.505(12)]	103.93(7)
Pd(4)-Tl-Pd(8)	2	109.41(2) [109.366(14)-109.456(14)]	108.74(7)
Pd(4)-Tl-Pd(10)	2	57.21(1) [57.147(10)-57.275(10)]	57.15(6)
Pd(5)-Tl-Pd(6)	2	104.68(2) [104.651(12)-104.700(12)]	104.69(7)
Pd(5)-Tl-Pd(7)	2	57.18(2) [57.037(11)-57.314(10)]	57.43(6)
Pd(5)-Tl-Pd(8)	2	108.29(2) [107.839(13)-108.733(13)]	108.69(7)
Pd(5)-Tl-Pd(10)	2	57.17(1) [56.998(10)-57.334(10)]	57.14(6)
Pd(6)-Tl-Pd(7)	2	58.58(1) [58.583(10)-58.585(10)]	58.35(3)
Pd(6)-Tl-Pd(8)	2	56.01(2) [55.910(10)-56.112(11)]	55.85(4)
Pd(6)-Tl-Pd(10)	2	56.70(1) [56.688(10)-56.712(10)]	56.75(3)
Pd(7)-Tl-Pd(8)	2	55.50(1) [54.828(10)-56.181(10)]	55.64(5)
Pd(7)-Tl-Pd(10)	2	56.27(1) [56.247(10)-56.295(10)]	56.31(3)
Pd(8)-Tl-Pd(10)	2	100.53(2) [100.024(12)-101.044(12)]	100.68(6)

^a Data are taken from the crystal structure deposited in CCDC, refcode YUXFEC (R. C. B. Copley, C. M. Hill and D. M. P. Mingos, *J. Cluster Sci.*, 1995, **6**, 71); ^b denotes the total number of individual angles under *pseudo-C_s* symmetry in (**1a-Me**)·**Me₂CO** and crystallographic-*C_s* symmetry in unsolvated **1-Me** relabeled as unsolvated (**1a-Me**).

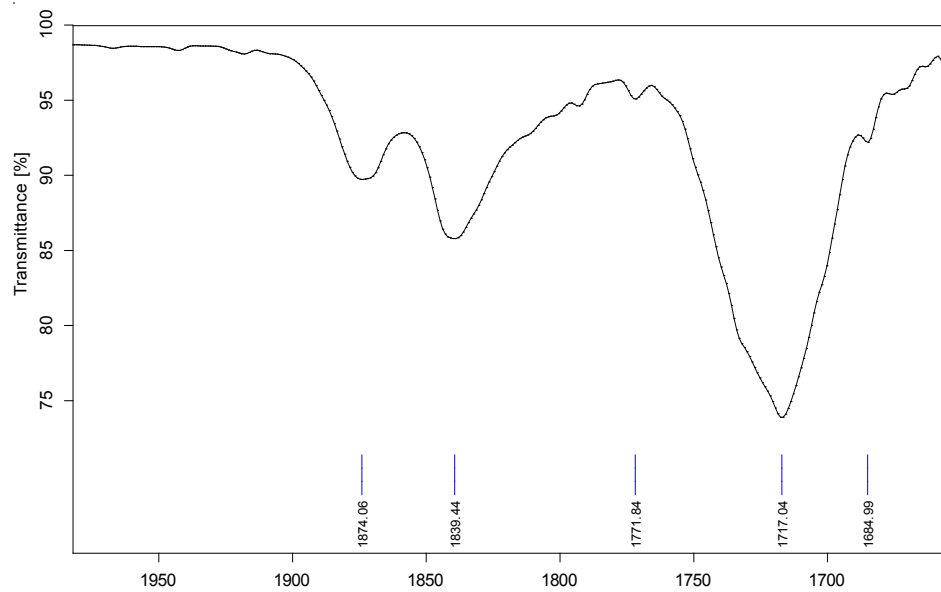
Table S3. Comparative Means (Å) and Individual Ranges (Å) for Connectivities and Angles (°) under *Pseudo-C_{3v}* Symmetry between the $\text{TiPd}_9(\text{CO})_9\text{P}_6$ Fragment of $[\text{TiPd}_9(\mu_2\text{-CO})_6(\mu_3\text{-CO})_3(\text{PPh}_3)_6][\text{PF}_6] \cdot 1.65\text{THF} \cdot 0.66\text{CH}_2\text{Cl}_2$ (**2a-Ph**) and the Corresponding Fragment of Crystallographically Isomorphous $[\text{TiPd}_9(\mu_2\text{-CO})_6(\mu_3\text{-CO})_3(\text{PPh}_3)_6][\text{PF}_6] \cdot 3\text{THF}$ Formulated Originally as $[\text{AuPd}_9(\mu_2\text{-CO})_6(\mu_3\text{-CO})_3(\text{PPh}_3)_6][\text{PF}_6] \cdot 3\text{THF}$ (**2-Ph**)^a.

Connectivity, Angle	N ^b	Mean [Range] in 2a-Ph		Mean [Range] in 2-Ph ^a	
Tl – Pd(A)	3	2.83	2.831(1)	2.84	2.837(1)
Tl ... Pd(C)	3	3.15	3.147(1)	3.16	3.157(1)
Pd(A) – Pd(C)	6	2.71	2.684(1)-2.742(1)	2.72	2.687(1)-2.747(1)
Pd(A) – Pd(A)	3	3.10	3.097(1)	3.09	3.092(1)
Pd(A) – Pd(B)	6	2.75	2.746(1)-2.747(1)	2.75	2.748(1)-2.752(1)
Pd(B) – Pd(B)	3	2.82	2.822(1)	2.83	2.826(1)
Pd(B) – P(B)	3	2.33	2.334(2)	2.34	2.337(2)
Pd(C) – P(C)	3	2.34	2.336(2)	2.34	2.340(2)
Pd(A) – (μ ₂ -CO)	6	2.13	2.090(8)-2.172(8)	2.11	2.064(7)-2.154(8)
Pd(C) – (μ ₂ -CO)	6	1.99	1.991(7)-1.996(9)	2.02	2.018(8)-2.021(9)
Pd(A) – (μ ₃ -CO)	3	2.45	2.450(7)	2.45	2.454(7)
Pd(B) – (μ ₃ -CO)	6	2.10	2.091(7)-2.118(7)	2.10	2.079(8)-2.114(8)
μ ₂ -C – O	6	1.15	1.151(10)-1.152(9)	1.15	1.139(10)-1.153(10)
μ ₃ -C – O	3	1.15	1.150(9)	1.16	1.155(10)
Tl-Pd(A)-Pd(C)	6	69.2	68.75(2)-69.55(2)	69.2	68.83(2)-69.65(2)
Pd(A)-Tl-Pd(A)	3	66.3	66.31(2)	66.0	66.03(2)

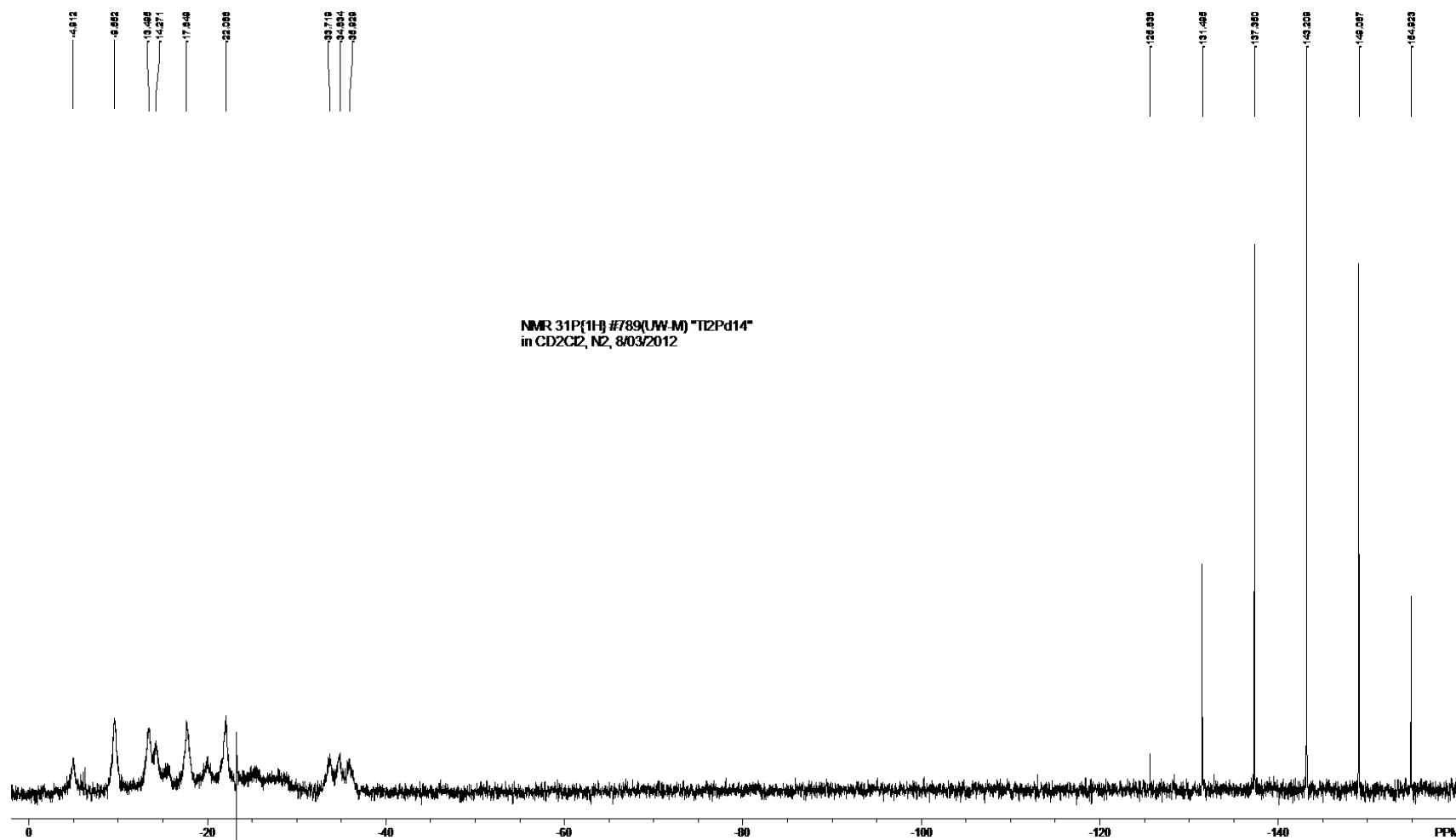
^a Data are taken from the crystal structure deposited in CCDC, refcode SOMGAD (C. Willocq, S. Hermans, M. Devillers, and B. Tinant, *Z. Kristallogr.*, 2008, **223**, 495); ^b denotes the total number of individual connectivities under *pseudo-C_{3v}* symmetry.



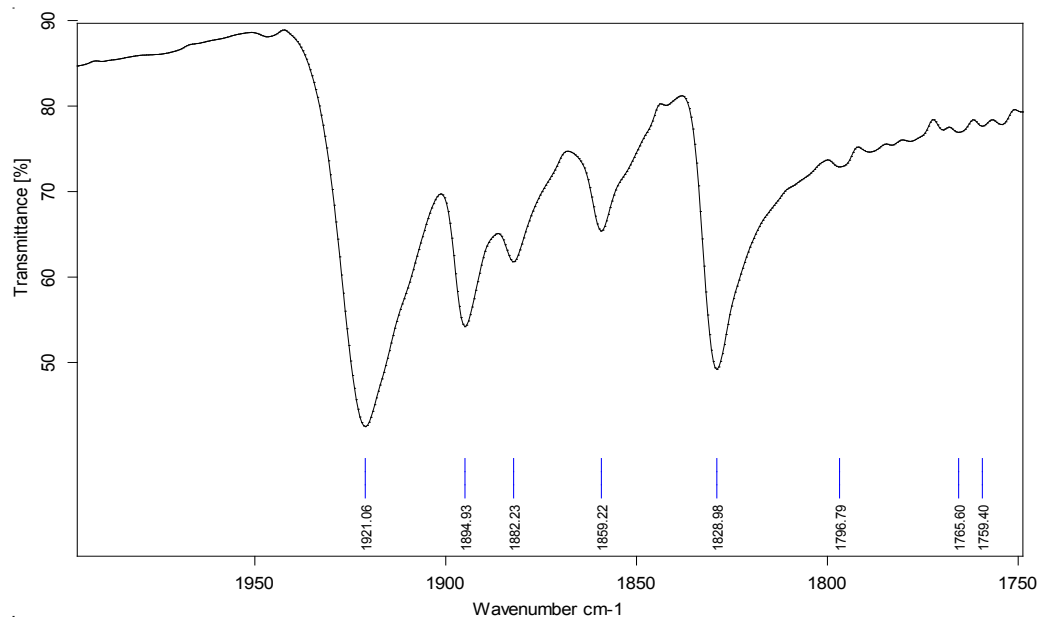
IR spectrum of $[\text{Tl}_2\text{Pd}_{14}(\text{CO})_9(\text{PMe}_3)_{11}](\text{PF}_6)_2 \cdot \text{Me}_2\text{CO}$ in paratone.



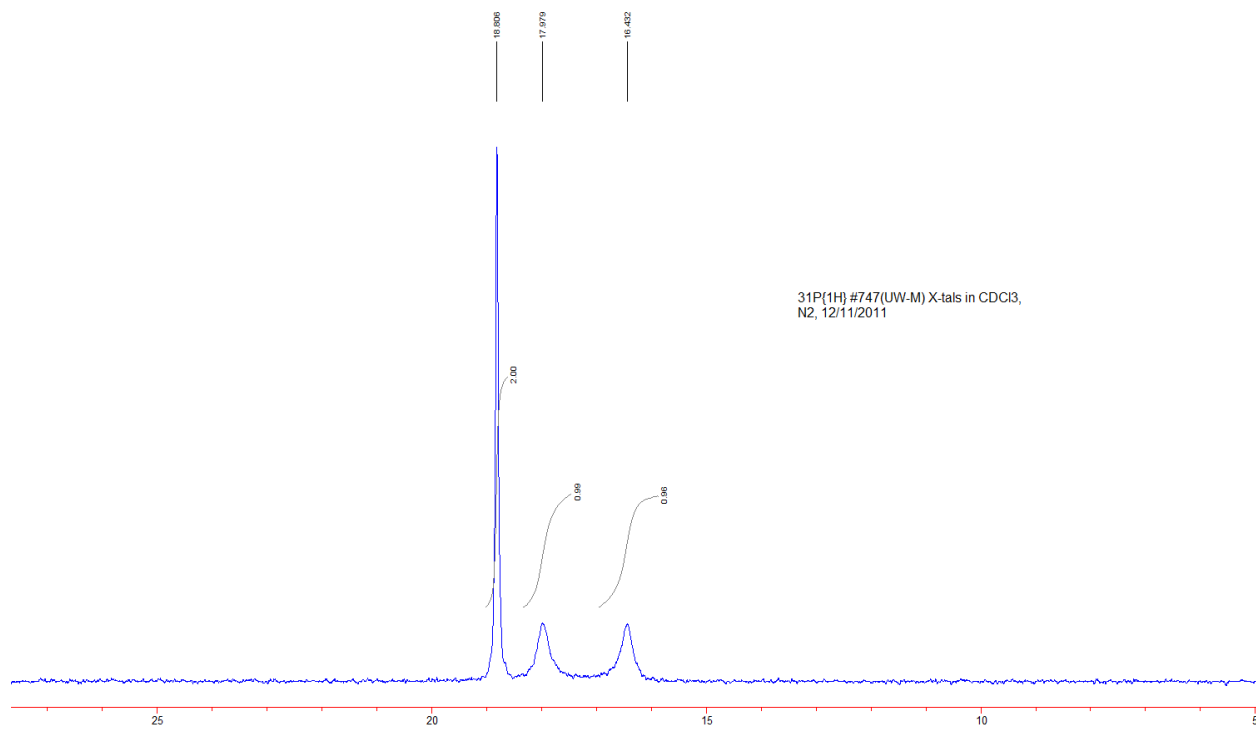
IR spectrum of $[\text{Tl}_2\text{Pd}_{14}(\text{CO})_9(\text{PMe}_3)_{11}](\text{PF}_6)_2 \cdot \text{Me}_2\text{CO}$ in CH_2Cl_2 .



$^{31}\text{P}\{^1\text{H}\}$ NMR (121.386 MHz) spectrum of $[\text{Ti}_2\text{Pd}_{14}(\text{CO})_9(\text{PMe}_3)_{11}](\text{PF}_6)_2 \cdot \text{Me}_2\text{CO}$ in CD_2Cl_2 .



IR spectrum of $[\text{TlPd}_9(\text{CO})_9(\text{PPh}_3)_6][\text{PF}_6]$ in paratone.



$^{31}\text{P}\{^1\text{H}\}$ NMR (121.386 MHz) spectrum of $[\text{TlPd}_9(\text{CO})_9(\text{PPh}_3)_6][\text{PF}_6]$ in CDCl_3 .