Inorganic Chemistry

Unexpected Reactivity of PdCl$_2$ and PtCl$_2$ Complexes of the Unsaturated Diphosphine *o*-Me$_2$TTF(PPh$_2$)$_2$ toward Chloride Abstraction with Thallium Triflate

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Attempted thallium triflate abstraction of chloride anions from the MCl$_2$ complexes of the unsaturated chelating diphosphines *o*-dimethyl-bis(diphenylphosphino)tetrathiafulvalene (**P2**) (M = Pd, Pt) and *cis*-1,2-bis(diphenylphosphino)ethylene (dppen) (M = Pd) affords, surprisingly, a Tl(OTf) adduct in the case of (**P2**)PdCl$_2$ and (**P2**)PtCl$_2$, with no chloride abstraction, and a dicationic bis(palladium) bis(triflate) salt in the case of (*cis*-dppen)PdCl$_2$, in which only one Cl anion was removed. The crystal structures of these complexes were determined by X-ray analysis, which established the formulations (**P2**)MCl$_2$·Tl(OTf) (M = Pd, Pt) and [(dppen)PdCl]$_2$(OTf)$_2$, respectively. These compounds can be seen as possible intermediates in the general chloride abstraction process between (P–P)MCl$_2$ (M = Pd, Pt) and thallium triflate.

Introduction

Numerous palladium or platinum complexes such as (P–P)M(OTf)$_2$, where OTf is the triflate anion and P–P is a chelating diphosphine, have been widely used within the past decade as building blocks for the formation of supramolecular assemblies,[1] upon triflate displacement and subsequent complexation with bis(pyridines). A variety of chelating diphosphines were accordingly investigated, with different bridges such as an alkyl chain, chiral (BINAP,[2] DIOP[3]) moiety, ferrocenyl group,[4] or crown ether.[5] In that respect, redox-active chelating diphosphines such as dimethyl-bis-(diphenylphosphino)tetrathiafulvalene[6] (**P2**) or tetrakis(diphenylphosphino) tetrathiafulvalene[7] (**P4**) are of particular interest since the TTF redox moiety in **P2** or **P4** can be reversibly oxidized to the radical cation species, not only in the free ligands but also in its metal complexes.[8]

P2   **P4**
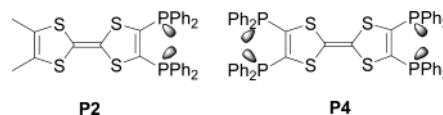
Their coordinating ability has been demonstrated with various d^8 metal cations, as in the mono chelate complex (**P2**)NiBr$_2$,[6] or in bis chelate complexes such as [(**P2**)$_2$M]$^{n+}$ with M = Rh, $n = 1$[7] or M = Pd, Pt, $n = 2$.[9] In both cases, however, these complexes do not offer any free coordination site which would allow the formation of extended networks or supramolecular assemblies upon coordination with various bis(pyridines). Therefore, the availability of the corresponding (**P2**)M(OTf)$_2$ triflate complexes, M = Pd, Pt, could be a key step for the elaboration of extended networks with collective electronic properties, upon bis(pyridine) complexation and TTF oxidation. In this paper, we describe first the synthesis of the redox active square planar complexes (**P2**)-MCl$_2$ (M = Pd, Pt), and subsequently our unexpected results toward the synthesis of (P–P)M(OTf)$_2$ (M = Pd, Pt) complexes, by analogy with that described for (dppp)M-

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(OTf)$_2$,[1,10] (dppp = 1,3-bis(diphenylphosphino)propane; M = Pd, Pt). Chloride abstraction from the corresponding (**P2**)-PdCl$_2$ and (**P2**)PtCl$_2$ complexes with thallium triflate proved to be difficult, and unprecedented tetrametallic Tl(OTf) adducts of (**P2**)MCl$_2$ (M = Pd, Pt) were obtained instead, whose structure can be deduced from that of Tl$_2$(PdCl$_4$). Similar difficulties were encountered with another conjugated diphosphine such as dppen (dppen = *cis*-1,2-bis(diphe-nylphosphino)ethylene) since Cl abstraction from (dppen)-PdCl$_2$ led to the substitution of only one Cl atom, as described hereafter.

Experimental Section

Synthesis. The reactions were carried out under an N$_2$ inert atmosphere by using standard Schlenk techniques. Elemental analyses were performed at the Service de Microanalyse, Institut de Chimie des Substances Naturelles, CNRS, Gif/Yvette (France), while SEM (scanning electron microscopy) analyses were per-formed on a JEOL JSM-5800 LV microscope operating at 15 kV and equipped with an energy dispersion spectrometer PGT IMIX-PTS at the Institut Jean Rouxel, CNRS, Nantes (France). ^{1}H and ^{31}P NMR spectra were taken on a Bruker Avance DRX 500 spectrometer operating at 500.04 MHz for ^{1}H and 202.39 MHz for [31]P. Chemical shifts are expressed in parts per million (ppm) downfield from external TMS (^{1}H) and H$_3$PO$_4$ (^{31}P). The following abbreviations are used: m, multiplet; b, broad. Mass spectra (electrospray) were obtained from a JEOL JMS 700 B/ES spec-trometer. Thallium triflate is known for its toxicity and should be handled with due precautions. *o*-Me$_2$TTF(PPh$_2$)$_2$ (**P2**) was prepared according to the published procedure.[6]

Dichloro{dimethylbis(diphenylphosphino)tetrathiafulvalene}-palladium (II), (P2)PdCl$_2$. PdCl$_2$ (176 mg, 9.9 × 10^{-4} mol) and **P2** (300 mg, 5 × 10^{-4} mol) were suspended in CHCl$_3$ (25 mL), and the mixture was warmed to reflux overnight. The cooled red suspension was filtered and the solution concentrated to 10 mL. Et$_2$O was added to precipitate a red solid, which was washed with Et$_2$O and dried under vacuum to afford (**P2**)PdCl$_2$ (353 mg, 91%). Crystals of good quality for X-ray diffraction were obtained by slow diffusion of EtOH into a CHCl$_3$ solution of (**P2**)PdCl$_2$.

^{1}H NMR (δ, CDCl$_3$): 7.88 (m, 8H, Ph), 7.59 (m, 4H, Ph), 7.52 (m, 8H, Ph), 1.90 (s, 6H, Me). ^{31}P NMR (δ, CDCl$_3$): 47.5. MS (electrospray) *m/z* (ion, rel intensity): 776 (M$^+$, 100). Anal. Calcd for C$_{32}$H$_{26}$Cl$_2$P$_2$PdS$_4$: C, 49.40; H, 3.37. Found: C, 49.09; H, 3.36. Anal. (SEM) Calcd (normalized weight %): Cl, 19.3; P, 16.9; Pd, 29.0; S, 34.9. Found: Cl, 19.4; P, 15.3; Pd, 30.2; S, 35.1.

Dichloro{dimethylbis(diphenylphosphino)tetrathiafulvalene}-platinum (II), (P2)PtCl$_2$. PtCl$_2$ (176 mg, 6.6 × 10^{-4} mol) and **P2** (200 mg, 3.3 × 10^{-4} mol) were suspended in CHCl$_3$ (25 mL), and the mixture was warmed to reflux overnight. The cooled red suspension was filtered and the solution concentrated to 10 mL. Et$_2$O was added to precipitate a red solid, which was washed with Et$_2$O and dried under vacuum to afford (**P2**)PtCl$_2$ (203 mg, 70%). ^{1}H NMR (δ, CDCl$_3$): 7.86 (m, 8H, Ph), 7.59 (m, 4H, Ph), 7.51 (m, 8H, Ph), 1.90 (s, 6H, Me). ^{31}P NMR (δ, CDCl$_3$): 27.5 ([1]J_{P-Pt} = 3640 Hz). MS (electrospray) *m/z* (ion, rel intensity): 866 (M$^+$, 100). Anal. Calcd for C$_{32}$H$_{26}$Cl$_2$P$_2$PtS$_4$: C, 44.34; H, 3.02. Found: C, 44.10; H, 3.14. Anal. (SEM) Calcd (normalized weight %): Cl, 15.5; P, 13.6; Pt, 42.8; S, 28.1. Found: Cl, 16.9; P, 12.9; Pt, 39.3; S, 30.9.

Dichloro{dimethylbis(diphenylphosphino)tetrathiafulvalene}-palladium(II) Thallium(I) Triflate Adduct, (P2)PdCl$_2$,Tl(OTf). (**P2**)PdCl$_2$ (120 mg, 1.54 × 10^{-4} mol) and Tl(OTf) (170 mg, 4.8 × 10^{-4} mol) were suspended in CH$_2$Cl$_2$ (25 mL) and stirred for 18 h. The suspension was filtered and the red solution concentrated to 15 mL, and slow Et$_2$O diffusion afforded (**P2**)PdCl$_2$,Tl(OTf) as red needles (80 mg, 46%).

^{31}P NMR (δ, CDCl$_3$): 48.0 (b). Anal. Calcd for C$_{37}$H$_{36}$Cl$_2$F$_3$O$_4$P$_2$-PdS$_5$Tl: C, 36.86; H, 3.01. Found: C, 36.32; H, 2.90. Anal. (SEM) Calcd (normalized weight %): Cl, 11.7; P, 10.3; Pd, 17.6; S, 26.5; Tl, 33.8. Found: Cl, 17.8; P, 9.1; Pd, 17.0; S, 26.5; Tl, 29.6 (no standard was available for this element).

Dichloro{dimethylbis(diphenylphosphino)tetrathiafulvalene}-platinum(II) Thallium(I) Triflate Adduct, (P2)PtCl$_2$,Tl(OTf). (**P2**)PtCl$_2$ (133 mg, 1.54 × 10^{-4} mol) and Tl(OTf) (170 mg, 4.8 × 10^{-4} mol) were suspended in CH$_2$Cl$_2$ (25 mL) and stirred for 18 h. The suspension was filtered, and the red solution concentrated to 15 mL, and slow Et$_2$O diffusion afforded (**P2**)PtCl$_2$,Tl(OTf) as red needles (90 mg, 49%).

^{31}P NMR (δ, CDCl$_3$): 27.5 (b, [1]J_{P-Pt} = 3640 Hz). Anal. Calcd for C$_{37}$H$_{36}$Cl$_2$F$_3$O$_4$P$_2$PtS$_5$Tl: C, 34.33; H, 2.80. Found: C, 33.90; H, 2.71.

Di-μ-chloro-bis{1,2-bis(diphenylphosphino)ethylene}dipal-ladium(II)bis(triflate), [(dppen)PdCl(OTf)]$_2$. A suspension of (dppen)PdCl$_2$ (107 mg, 1.87 × 10^{-4} mol) and thallium triflate (198 mg, 5.61 × 10^{-4} mol) was stirred in CH$_2$Cl$_2$ (20 mL) for 3 days. After filtration and concentration to 5 mL, the solution was layered with Et$_2$O to afford pale yellow crystals of [(dppen)PdCl(OTf)]$_2$ (100 mg, 78%).

^{31}P NMR (δ, CH$_2$Cl$_2$): 80.6 (b), 75.7 (b). Anal. Calcd for C$_{54}$H$_{44}$-Cl$_2$F$_6$O$_6$P$_4$Pd$_2$S$_2$: C, 47.18; H, 3.23. Found: C, 46.90; H, 3.13.

X-ray Crystallography. Details about data collection and solution refinement are given in Table 1. Data were collected on a Stoe imaging plate system for the structures (**P2**)PdCl$_2$·(CHCl$_3$)$_2$, (**P2**)PdCl$_2$·Tl(OTf)·(OEt$_2$), and [(dppen)PdCl(OTf)]$_2$ and on a Bruker-CCD system for the structure (**P2**)PtCl$_2$·Tl(OTf)·(OEt$_2$), both operating with a Mo Kα X-ray tube with a graphite monochromator. The structures were solved (SHELXS-97) by direct methods and refined (SHELXL-97) by full-matrix least-squares procedures on F^2.[11] Hydrogen atoms were introduced at calculated positions (riding model), and included in structure factor calcula-tions, but not refined. The solvent (Et$_2$O) atoms in the structure (**P2**)PdCl$_2$·Tl(OTf)·(OEt$_2$) and the C37 carbon atom of Et$_2$O in the structure (**P2**)PtCl$_2$·Tl(OTf)·(OEt$_2$) have been refined isotropically. All the other heavy atoms have been refined anisotropically. The moderate $R(F_o)$ value for the structure of (**P2**)PdCl$_2$ is very likely due to a partial loss of solvent molecules during the X-ray diffraction analysis, since the data collection has been performed at room temperature.

Results and Discussion

PdCl$_2$ and PtCl$_2$ complexes of the chelating, redox active *o*-MeTTF(PPh$_2$)$_2$ (**P2**) diphosphine were obtained directly from **P2** and the metal chloride in refluxing chloroform, as already described for (**P2**)NiCl$_2$ or (**P2**)NiBr$_2$.[6] Chemical shifts in ^{31}P NMR spectra (see Experimental Section) are in the expected range for both complexes, downfield shifts being observed when compared to the free **P2** (δ = −18 ppm). Interestingly, the [1]J_{P-Pt} coupling constant for the (**P2**)-
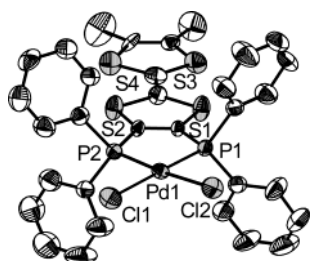
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Table 1. Crystallographic Data

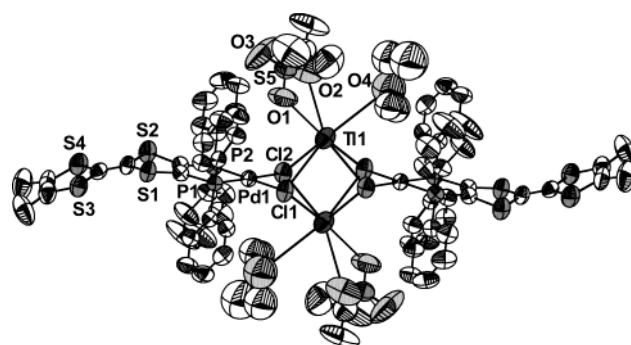|	(P2)PdCl$_2$·(CHCl$_3$)$_2$	(P2)PdCl$_2$·Tl(OTf)·(OEt$_2$)	(P2)PtCl$_2$·Tl(OTf)·(OEt$_2$)	[(dppen)PdCl(OTf)]$_2$
formula	C$_{34}$H$_{28}$Cl$_8$P$_2$PdS$_4$	C$_{37}$H$_{36}$Cl$_2$F$_3$O$_4$P$_2$PdS$_5$Tl	C$_{37}$H$_{36}$Cl$_2$F$_3$O$_4$P$_2$PtS$_5$Tl	C$_{54}$H$_{44}$Cl$_2$F$_6$O$_6$P$_4$Pd$_2$S$_2$
mw	1016.74	1205.57	1294.26	1374.59
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a (Å)	17.0352(13)	9.9545(5)	10.0411(4)	9.1915(9)
b (Å)	15.7744(11)	18.5549(13)	18.958(2)	13.5486(15)
c (Å)	17.8266(14)	23.9138(13)	23.730(4)	23.500(3)
α (deg)				97.939(13)
β (deg)	118.152(8)	96.044(6)	97.363(5)	99.110(13)
γ (deg)				95.102(13)
V (Å^3)	4223.7(5)	4392.4(4)	4479.9(9)	2843.5(5)
Z	4	4	4	2
d_{calcd}, g cm^{-3}	1.599	1.823	1.919	1.605
μ (mm^{-1})	1.244	4.556	7.185	0.98
T (K)	293(2)	293(2)	293(2)	293(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
$R(F_o)^a$	0.0892	0.0394	0.0493	0.0439
$R_w(F_o^2)^a$	0.2806	0.0945	0.1156	0.0840

^{a} $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Figure 1. ORTEP view of (**P2**)PdCl$_2$·(CHCl$_3$)$_2$.

PtCl$_2$ complex is 3640 Hz (vide infra). Slow diffusion of Et$_2$O into CHCl$_3$ solutions led to crystallization of (**P2**)PdCl$_2$ and (**P2**)PtCl$_2$. Both complexes are isostructural with (**P2**)-NiBr$_2$·(CHCl$_3$)$_2$ and crystallize in the monoclinic system, space group $P2_1/n$, with two CHCl$_3$ molecules included. Only the structure of (**P2**)PdCl$_2$ has been solved completely and is reported here. The Pd atom adopts a square-planar configuration (Figure 1) while the two Cl atoms are engaged in a C−H···Cl hydrogen bond interaction with the chloroform molecules. Such hydrogen bonds with the activated CH moiety of chloroform are now well established,[12] and their geometrical characteristics (d(C···Cl) = 3.51(1), 3.59(1) Å, d(H···Cl) = 2.60, 2.74 Å, and ∠(C−H···Cl) = 154.0, 146.4°) are in the expected range.

Chloride abstraction of (**P2**)PdCl$_2$ to form (**P2**)Pd(OTf)$_2$ was not attempted with silver triflate, because of the oxidation sensitive nature of the TTF core, but rather with thallium triflate. The latter is also known to react more rapidly as checked on (dppp)PdCl$_2$ by ^{31}P NMR. Even with prolonged heating in refluxing CH$_2$Cl$_2$, the reaction of (**P2**)-PdCl$_2$ with Tl(OTf) (Scheme 1) did not afford the expected triflate salt. The red crystals recovered from the CH$_2$Cl$_2$ solution upon slow diffusion of Et$_2$O proved to be, somewhat surprisingly, a thallium triflate adduct of the starting material, i.e., (**P2**)PdCl$_2$·Tl(OTf), crystallizing as Et$_2$O solvate.
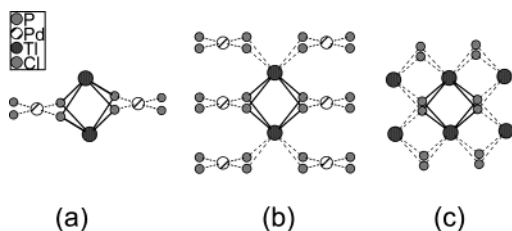
This complex adduct crystallizes in the monoclinic system, space group $P2_1/n$, with one (**P2**)PdCl$_2$·Tl(OTf)·Et$_2$O frag-

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Figure 2. The tetrametallic motif associating two (**P2**)PdCl$_2$ and two Tl$^+$ cations in (**P2**)PdCl$_2$·Tl(OTf)·Et$_2$O.

Scheme 1
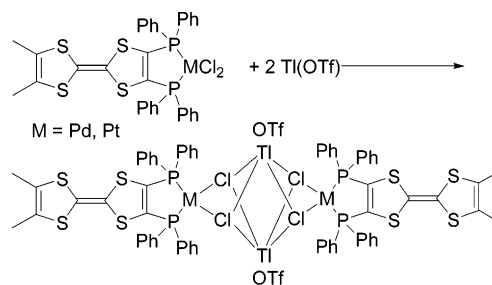
ment in general position in the unit cell, associated two by two through inversion center (Figure 2). Each Tl cation is coordinated by four Cl atoms, with Tl···Cl distances of 3.157(2), 3.195(2), 3.207(2), and 3.356(2) Å. Further coordination involves two oxygen atoms of the triflate anion (Tl···O distances at 2.916(8) and 3.37(1) Å) and the oxygen atom of the diethyl ether molecule at a Tl···O distance of 3.84(1) Å.

A similar reactivity was observed for the platinum complex (**P2**)PtCl$_2$ upon reaction with Tl(OTf). The red crystalline needles of the adduct (**P2**)PtCl$_2$·Tl(OTf), recovered by layering Et$_2$O onto a CH$_2$Cl$_2$ solution of the complex, proved to be isostructural with the palladium counterpart. The Pt-(II) center lies, as expected, in a square planar environment formed by the two chlorine atoms (Pt−Cl(1) 2.368(2) Å and Pt−Cl(2) 2.3671(18) Å) and the two phosphorus atoms (Pt−P(1) 2.2236(17) Å and Pt−P(2) 2.225(2) Å). The P(1)−Pt−
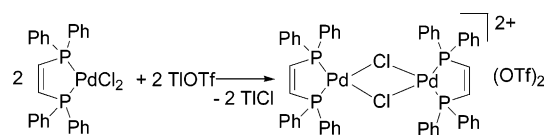
Figure 3. Comparison of the Tl⁺ environment in (**P2**)PdCl₂·Tl(OTf)·Et₂O (a), Tl₂PdCl₄ (b), and TlCl (c).

P(2) bite angle within the metallacycle amounts to 88.49(7)°. As in the case of the palladium adduct, the thallium center is coordinated by four Cl atoms, with Tl···Cl distances of 3.192(2), 3.241(2), 3.253(2), and 3.411(2) Å, two oxygen atoms of the triflate anion (Tl···O distances at 2.847(10) and 3.291(12) Å), and the oxygen atom of the Et₂O molecule at a Tl···O distance of 3.717(7) Å. Full details about structural parameters are given in the Supporting Information.

The coordination chemistry of the Tl⁺ cation has been the subject of recent investigations,[13,14] mainly concerned with the exceedingly low coordination numbers in geometries which leave a large part of the coordination sphere seemingly unoccupied, a phenomenon tentatively ascribed to the stereochemically active $6s^2$ lone pair. Besides, the recurrent observation of Tl–Tl contacts (up to 4 Å) in such complexes has been tentatively described as a "thallophilic" interaction,[15] by analogy with well-established aurophilic bonding between Au⁺ complexes.[16] In the complexes described here, the coordination sphere appears largely covered despite the steric hindrance of the phenyl groups while the Tl–Tl distance amounts to 4.0130(8) Å in the case of the palladium adduct, at the limit value where "thallophilic" contacts could be invoked. Note also that the coordination sphere of Tl⁺ within the (**P2**)PdCl₂·Tl(OTf) adduct (Figure 3a), or the platinum one, is reminiscent of that observed for example in Tl₂PdCl₄ (Figure 3b) where each Tl⁺ cation is surrounded by eight Cl atoms,[17] at Tl–Cl distances [3.324(1) Å] close to those observed in (**P2**)PdCl₂·Tl(OTf). Remarkably, the same environment is even found in the TlCl structure (Figure 3c) with an interionic distance of 3.32 Å.[18]

Clearly, these tetrametallic complexes which we crystallized can be seen as intermediate adducts between the starting (**P2**)MCl₂ and the targeted (**P2**)M(OTf)₂ (M = Pd, Pt). Very likely, the M–Cl···Tl interaction occurs also in solution and not only in the solid state, since a significant broadening of the peaks at δ = 48 ppm (Pd adduct) and δ = 27.5 ppm (Pt adduct) in the ³¹P NMR spectra of the reaction mixtures or of the redissolved (**P2**)MCl₂·Tl(OTf) crystals is observed. At a first glance, this lack of reactivity toward the chloride abstraction from the starting complex appears to be somewhat

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Scheme 2

surprising, when considering the proved efficiency of the thallium triflate for this purpose. Indeed, in the case of saturated links between the phosphino groups, i.e., dppe (1,2-bis(diphenylphosphino)ethane) or dppp, the corresponding adducts cannot be isolated, but one obtains directly the triflate salts. However, the formation of a Tl(OTf) adduct with a halogenated transition metal complex was also observed recently in the case of a iodinated Ni₃ cluster.[19] Indeed, in this case, instead of the expected iodide abstraction, an insertion of the Tl⁺ ion into the Ni−I bonds occurred.

In order to evaluate whether the reluctance of (**P2**)MCl₂ (M = Pd, Pt) to undergo chloride abstraction was due to some specificity of the **P2** ligand, we investigated this reaction in the case of palladium with another chelating diphosphine such as dppen[20,21] with a similar double bond between the two diphenylphosphino groups. Reaction of (dppen)PdCl₂, prepared according to the published procedure,[20,21] with an excess of thallium triflate in CH₂Cl₂ (Scheme 2) afforded a complex salt, formulated as [(dppen)-PdCl]₂(OTf)₂, i.e., indicating a partial dechlorination, despite prolonged treatment with an excess of thallium triflate.

Dicationic complexes of [(P−P)M(μ-Cl)]₂²⁺ type (M = Pd, Pt), although not synthesized via the procedure described herein, are well-known in the literature.[22] For example, the dppe based complex, formulated as [(dppe)Pd(μ-Cl)]₂[BF₄]₂, was crystallized upon evaporation of a CDCl₃ solution of [(dppe)Pd(MeCN)₂][BF₄]₂.[22a] A very similar complex, formulated as [(dppe)Pd(μ-Cl)]₂[ClO₄]₂, was synthesized by reacting (dppe)PdCl₂ with silver perchlorate.[22g]

[(dppen)PdCl]₂(OTf)₂ crystallizes in the triclinic system, space group P1̄, with a dimeric entity in general position in the unit cell (Figure 4).

Each Pd cation adopts a square-planar coordination, with two chloride anions in μ² position. The triflate anions act as hydrogen bond acceptors in weak C−H···O hydrogen bonds involving the H atoms of the ethylene bridge. While the dppe or dppp PdCl₂ complexes are known to afford the triflate salts upon treatment with Ag(OTf)[1] or Tl(OTf), it therefore

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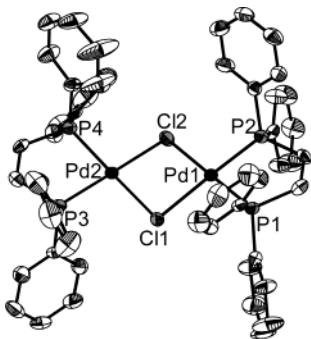
Figure 4. ORTEP view of the bimetallic motif [(dppen)PdCl]$_2^{2+}$ in [(dppen)PdCl]$_2$(OTf)$_2$.

Table 2. Pd−P and Pd−Cl Bond Distances in (P−P)PdCl$_2$ Complexes

	Pd−P (Å)	Pd−Cl (Å)	ref
(dppm)PdCl$_2$	2.234(1), 2.250(1)	2.362(1), 2.352(1)	29
(dppe)PdCl$_2$	2.284(3), 2.264(3)	2.415(3), 2.394(3)	30
(dppe)PdCl$_2$·(CH$_2$Cl$_2$)	2.226(2), 2.233(2)	2.361(2), 2.357(2)	29
(dppp)PdCl$_2$	2.244(1), 2.249(2)	2.351(1), 2.358(1)	29
(dppen)PdCl$_2$·(CHCl$_3$)$_2$	2.229(1)	2.367(1)	31
(**P2**)PdCl$_2$·(CHCl$_3$)$_2$	2.217(3), 2.220(3)	2.341(3), 2.349(3)	this work
[(**P2**)PdCl]·[Tl(OTf)]	2.227(2), 2.228(2)	2.353(2), 2.360(2)	this work

appears that the tetrathiafulvalenyl **P2** or the dppen unsaturated diphosphines are strongly reluctant to undergo such anion exchange under the experimental conditions we employed in the present study, indicating a possibly stronger Pd−Cl bond than in (dppe)PdCl$_2$ or (dppp)PdCl$_2$. The structural and reactivity differences between (dppen)MCl$_2$ and (dppe)MCl$_2$ (M = Pd, Pt) complexes have been widely addressed throughout a series of recent papers.[20,23] The authors assigned the special properties of the *cis*-dppen ligand when compared with the saturated dppe counterpart to an enhancement of the M-to-P π bonding interaction, due to the unsaturated nature of the aliphatic backbone in dppen. This assignment was based on earlier theoretical calculations dealing with the π-accepting abilities of phosphines in transition metal complexes,[24] although these studies refer to zerovalent metal complexes. Indeed, it seems more judicious to think that the M−P bonding in planar Pd(II) and Pt(II) complexes is dominated by the σ-bonding. The analysis of intramolecular bond lengths within (dppe)PdCl$_2$, (dppen)PdCl$_2$, and (**P2**)PdCl$_2$ (Table 2), all of these complexes including a five-membered ring chelate, shows only a very modest tendency to exhibit shorter Pd−P and Pd−Cl bonds with the unsaturated dppen and **P2** diphosphines when compared with dppe, and even with dppm (bis(diphenylphosphino)methane) or dppp. Note also that the Pd−P and Pd−Cl distances within (dppen)PdCl$_2$·(CHCl$_3$)$_2$ and (dppe)PdCl$_2$·(CH$_2$Cl$_2$) solvated complexes span the same range of values. The modest shortening of the Pd−P and Pd−Cl distances in the series (dppe)PdCl$_2$ (solvent free), (dppen)-PdCl$_2$, and (**P2**)PdCl$_2$ can be tentatively attributed to the π-back retrodonation from the metal to the unsaturated

ligand, in the spirit of Dewar−Chatt−Duncanson model,[25,26] or as analyzed by Frenking through the CDA (charge decomposition analysis) model, to a more covalent character of the C$_2$P$_2$Pd metallacycle,[27] keeping in mind that within this class of complexes the M−P bonding is very likely dominated by the σ-interactions rather than by the π-bonding (vide supra). A more reliable experimental tool allowing us to compare the strengths of Pt−P bonds in a series of (P−P)PtCl$_2$ complexes, having the same metallacycle ring size, consists of the analysis of the $^1J_{P-Pt}$ coupling constants as measured by ^{31}P NMR. Thus, for the complex (**P2**)PtCl$_2$, a value of 3640 Hz for the $^1J_{P-Pt}$ coupling constant has been measured (see Experimental Section), which is larger than those described in the literature for the corresponding (dppen)PtCl$_2$ ($^1J_{P-Pt}$ = 3623 Hz) and (dppe)PtCl$_2$ ($^1J_{P-Pt}$ = 3600 Hz).[28] The variation of these coupling constants, although the range is very small, tends to confirm that the strength of the Pt−P bonds increases in the series (dppe)-PtCl$_2$, (dppen)PtCl$_2$, and (**P2**)PtCl$_2$, as a consequence of a stronger σ-bonding effect. Consequently, the strengths of the Pt−Cl bonds within this series should follow the same trend. Very likely, this is also the case within the palladium corresponding series, since we have shown that (**P2**)PdCl$_2$ and (**P2**)PtCl$_2$ have the same reactivity toward Tl(OTf).

The three examples shown here might resemble the intermediates or the transition states in the general process of (P−P)MCl$_2$ (M = Pd, Pt) chloride abstraction with Tl-(OTf): (i) coordination of Tl$^+$ of the chloride atoms in (P−P)MCl$_2$ complex as shown in the (**P2**)MCl$_2$·[Tl(OTf)] adduct as first step, (ii) in the case of palladium, removal of one Cl$^-$ anion to afford for example the lacunary [(dppen)-PdCl□]$^+$ which here dimerizes into [(dppen)PdCl]$_2^{2+}$, (iii) further coordination and chloride abstraction to give the dechlorinated (dppp)M(OTf)$_2$.[1]

Conclusions

PdCl$_2$ and PtCl$_2$ complexes of the redox active diphosphine **P2** have been synthesized, and the palladium one has been structurally characterized. Both complexes have been further reacted with thallium triflate, and instead of the expected dicationic bis(triflate) salt, a Tl(OTf) adduct of the starting complexes was isolated. The single crystal X-ray analyses proved the tetrametallic "M$_2$Tl$_2$" (M = Pd, Pt) nature of this adduct, formulated as [(**P2**)MCl$_2$·Tl(OTf)·Et$_2$O]$_2$, whose inner [TlCl] motif is that found in the extended solid TlCl. Another unexpected result was provided by the reaction of (dppen)PdCl$_2$ with Tl(OTf), which afforded a dicationic "Pd$_2$" complex, also analyzed by X-ray on single crystals. Thus, the compounds [(**P2**)MCl$_2$]·[Tl(OTf)] (M = Pd, Pt)

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and [(dppen)PdCl]₂(OTf)₂ can be seen as possible intermediates in the general chloride abstraction process from (P−P)MCl₂ (M = Pd, Pt) complexes with thallium triflate.

Supporting Information Available: Crystallographic data for the four X-ray crystal structures, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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