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Mono- and di-nuclear complexes of *ortho*-palladated and -platinated 4,4′-dimethylazobenzene with bis(diphenylphosphino)methane. More data on *transphobia*

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Dedicated to Professor Pascual Royo on the occasion of his 65th birthday

Abstract

Complexes $[Pd(\kappa^2\text{-R})(\mu\text{-Cl})]_2$ [κ^2-R = κ^2-*C,N′*-C_6H_3(N=NC_6H_4–Me-4′)-2-Me-5 (**1**)] and $[Pd(\kappa^1\text{-R})Cl(\kappa^1\text{-dppm})(\kappa^2\text{-dppm})]$TfO [dppm = bis(diphenylphosphino)methane (**2**)] have been used to prepare new palladium derivatives containing dppm. Thus, complex **1** reacts with one equivalent of dppm to afford $[\{Pd(\kappa^2\text{-R})Cl\}_2(\mu\text{-dppm})]$ (**3**) and with $AgClO_4$ and dppm (1:2:2 molar ratios) to give $[Pd(\kappa^2\text{-R})(\kappa^2\text{-dppm})]ClO_4$ (**4**·**ClO$_4$**). The triflate salt of this complex (**4**·**TfO**) reacts with PPh_3 to yield $[Pd(\kappa^1\text{-R})(PPh_3)(\kappa^2\text{-dppm})]$TfO (**5**). Dinuclear complexes were obtained by reacting **2**, (i) with $[AuCl(PPh_3)]$ or [AuCl(tht)] (tht = tetrahydrothiophene) (1:1, −60 °C) and (ii) with **1** (2:1) to give, respectively, $[Pd(\kappa^1\text{-R})Cl(\mu\text{-dppm})_2Au]$TfO (**6**) and the A-frame complex $[\{Pd(\kappa^1\text{-R})(\mu\text{-dppm})\}_2(\mu\text{-Cl})]$TfO (**7**). The latter decomposes in solution to give, among other products, $[Pd(\kappa^2\text{-R})(\kappa^2\text{-}P,O\text{-dppmO})]$TfO (**8**), containing the monoxide of dppm (dppmO). Complex **8** can be obtained by refluxing a toluene solution of **4**·**TfO** under aerial conditions. The platinum complex *trans*-$[Pt(\kappa^1\text{-R})Cl(PPh_3)_2]$ reacts with an excess of dppm to give $[Pt(\kappa^1\text{-R})(\kappa^1\text{-dppm})(\kappa^2\text{-dppm})]Cl$ (**10**·**Cl**) which reacts with TlOTf to give **10**·**TfO**. The crystal structures of complexes **3**, **8** and **10**·**TfO** have been determined by X-ray diffraction studies. The structure of complex **3** consists of a dimer formed by a dppm ligand bridging two $Pd(\kappa^2\text{-R})Cl$ units. The structure of the cation of complex **8** shows both the aryl and dppmO acting as chelating ligands with the O atom *trans* to the C atom. The structure of complex **10**·**TfO** shows the κ^1-R ligand, one chelating and one monocoordinate dppm ligand.

Keywords: Palladium complexes; Platinum complexes; Transphobia

1. Introduction

The chemistry of the bis(diphenylphosphino)methane ligand (dppm) has developed tremendously over the last 25 years due its ability to act as a mono- or di-coordinating ligand as well as to adopt a chelating or bridging mode leading to the synthesis of di-, tri- or poly-, homo- or hetero-nuclear complexes [1–5]. The interest in the synthesis of palladium(II) and platinum(II) dppm complexes persists in the recent literature [6–18]. This ligand has a bite size suitable to hold two metals atoms in close proximity and hence promote reactions involving two metal centers [8,10,13,19]. Such reactions are often invoked in catalysis. The role of the phosphine is to prevent dissociation of dimer to monomer, to promote bridging by other groups and reactions involving formation and cleavage of metal–metal bonds [1]. In this paper, we describe the preparation of new organo-palladium and -platinum complexes with dppm.

We have reported the use of the *ortho* palladation products of azotoluene and azobenzene, $[Pd(\kappa^2\text{-R})(\mu\text{-Cl})]_2$ (R = κ^2-*C,N′*-C_6H_3(N=NC_6H_4–R′-4′)-2-R′-5, R′ = H, Me), in the synthesis of a family of palladium phosphino, perchlorato, triflato and aquo-2-(aryla-

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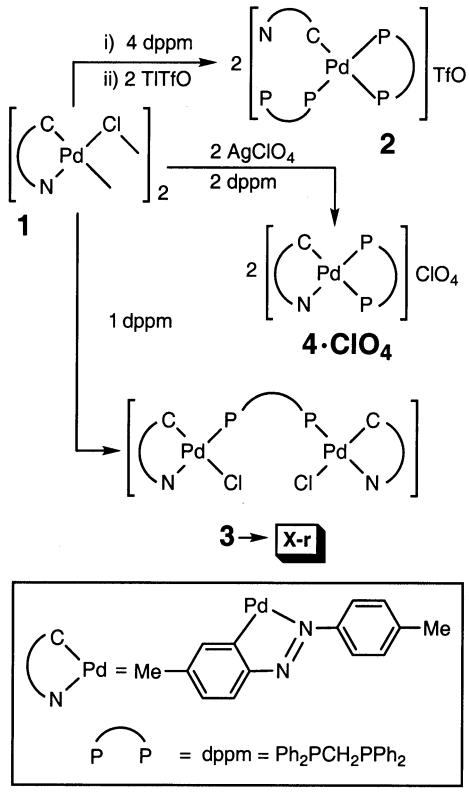
zo)aryl palladium complexes [20] and a new method of synthesis of iminophosphorane complexes which result from the attack of organic azides at the noncoordinated phosphorus atom in the complex [Pd(κ^1-R)(κ^1-*P*-dppm)(κ^2-*P,P*-dppm)]TfO (κ^1-R = κ^1-*C*-C_6H_3(N=NC_6H_4–Me-4′)-2-Me-5) [21]. In this paper, we describe an extension of the use of these complexes to the preparation of new azotoluene palladium complexes with dppm. In particular, we describe the synthesis of mononuclear and dinuclear complexes, including homobimetallic complexes (one of them is an A-frame species that contain a Cl bridging ligand) and a heterobimetallic complex with palladium and gold. The only reported heterobimetallic compounds containing dppm and gold are platinum complexes [15,22–27]. We also report the synthesis of some azotolyl platinum–dppm complexes.

Diphosphine monoxides (R^1R^2P–Y–$P(O)R^3R^4$, Y = divalent spacer) constitute one of the most important classes of hemilabile ligands [28,29]. Grushin has recently reported a highly selective Pd-catalyzed mono-oxidation of diphosphines, including dppm [30]. We reported the first aerial mono-oxidation of dppm from a complex containing a chelating dppm [20] and explained the selective oxidation of the phosphorus atom *trans* to the aryl ligand as a consequence of the aryl–phosphine *transphobia*, a term that we proposed and that have been used for many authors since then [20,31,32]. Afterwards, we have described the insertion of oxygen into a C–Pd bond *trans* to a P-donor ligand [32]. In this paper we report a new example of a selective aerial mono-oxidation of chelating dppm and new data on *transphobia*.

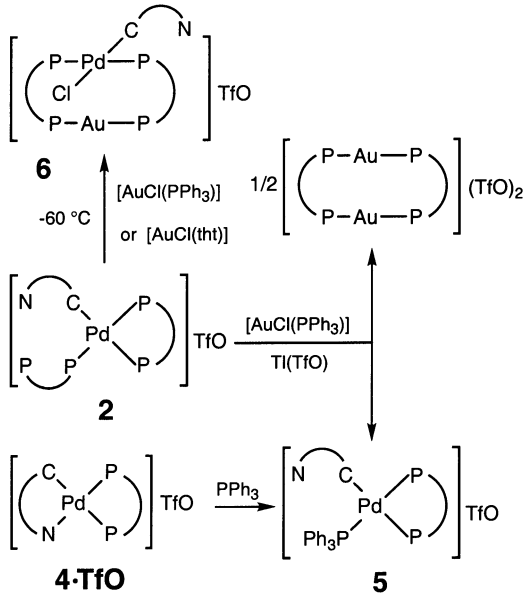
2. Results

We have reported that complex [Pd(κ^2-R)(μ-Cl)]$_2$ [κ^2-R = κ^2-*C,N*′-C_6H_3(N=NC_6H_4–Me-4′)-2-Me-5] (**1**) (Scheme 1)] reacts with bis(diphenylphosphino)methane (dppm) to give *trans*-[Pd(κ^1-R)Cl(κ^1-dppm)$_2$] [κ^1-R = κ^1-*C*-C_6H_3(N=NC_6H_4–Me-4′)-2-Me-5] that in turn reacts with TlOTf (TfO = CF_3SO_3) in an 1:1 molar ratio to give [Pd(κ^1-R)(κ^1-dppm)(κ^2-dppm)]TfO (**2**) [20]. Now, we describe that treatment of a CH_2Cl_2 suspension of **1** with one equivalent of dppm affords complex [{Pd(κ^2-R)Cl}$_2$(μ-dppm)] (**3**). This complex does not react with TlOTf but it does with $AgClO_4$ to give a mixture that, according to its ^{1}H- and ^{31}P-NMR spectra, contains mainly [Pd(κ^2-R)(κ^2-dppm)]ClO_4 (**4**·**ClO$_4$**) and another product that could not be separated. However, **4**·**ClO$_4$** could be obtained by treating **1** with $AgClO_4$ and dppm (1:2:2 molar ratios). We have previously reported the preparation of complexes **4**·**X** (X = SbF_6, TfO), and the crystal structure of **4**·**TfO** [20]. The analogous complex derived from azobenzene has been reported [33].



Scheme 1.

When a CH_2Cl_2 solution of complex **2** was treated at room temperature with [AuCl(PPh_3)] in a 1:1 molar ratio, a mixture of compounds that could not be separated was obtained. When this reaction was carried out in the presence of TlOTf in acetone as solvent (1:1 molar ratio), and the resulting mixture was separated by crystallization, the products [Au(dppm)]$_2$(TfO)$_2$ and



Scheme 2.

[Pd(κ^1-R)(PPh$_3$)(κ^2-dppm)]TfO (**5**) (see Scheme 2) were obtained. Complex **5** can also be obtained by reacting **4**·**TfO** with PPh$_3$. Because complex **2** shows at −60 °C a first-order ^{31}P-NMR spectrum corresponding to the static structure shown in Scheme 2, we reasoned that at −60 °C an 1:1 reaction of **2** with a gold complex like [AuCl(PPh$_3$)] or [AuCl(tht)] (tht = tetrahydrothiophene) could give an heterodinuclear complex avoiding the interchange process observed in the previous reaction. In accord with our expectation, such reaction led to [Pd(κ^1-R)Cl(μ-dppm)$_2$Au]TfO (**6**), which was characterized by elemental analysis, NMR spectroscopy and FAB$^+$. We are not aware of related 'Pd(μ-dppm)$_2$Au' complexes but heterobimetallic platinum–gold, –silver and –mercury complexes have been reported [15,22–27,34].

The reaction of **2** with **1** (2:1 molar ratio) afforded the A-frame complex [{Pd(κ^1-R)(μ-dppm)}$_2$(μ-Cl)]TfO (**7**) (see Scheme 3) which contains a Cl bridge, in agreement with its elemental analyses, ^{1}H- and ^{31}P-NMR spectra. A family of chloro-bridged A-frame complexes [{RPd(μ-dppm)$_2$PdR′}(μ-Cl)]$^+$ have been reported. The symmetric ones with R = R′ = Et, Bu, CH$_2$Ph and C$_6$H$_2$Me$_3$ (the latest was characterized by X-diffraction studies) were obtained by reacting [PdX$_2$(κ^2-*P,P*-dppm)] with RMgX (X = Cl, Br) [12] and the complex with R = R′ = Me by reacting [PdMe(κ^1-*P*-dppm)(κ^2-*P,P*-dppm)]$^+$ with [PdCl(Me)(cod)] (cod = 1,5-cyclooctadiene) [35]. Using the last method a series of unsymmetrical complexes were also reported [35].

In an attempt to obtain single crystals of **7** a few crystals of [Pd(κ^2-R)(κ^2-*P,O*-dppmO)]TfO (**8**), containing the monoxide of dppm (dppmO), were obtained. This complex could be obtained by refluxing a toluene solution of [Pd(κ^2-R)(κ^2-dppm)]TfO (**4**·**TfO**) under aerial conditions. We have reported that the SbF_6^- salt of the complex similar to **8** derived from azobenzene was obtained when attempting to obtain single crystals of [Pd(κ^2-R′)(κ^2-dppm)]SbF$_6$ (R′ = C$_6$H$_4$N=NPh-2) [20]. In both cases, the oxidation takes place at the phosphorus atom *trans* to the aryl ligand. This unusual reactivity and the selectivity observed can be explained as a consequence of the high *transphobia* of aryl and P-donor ligands [20,31,32].

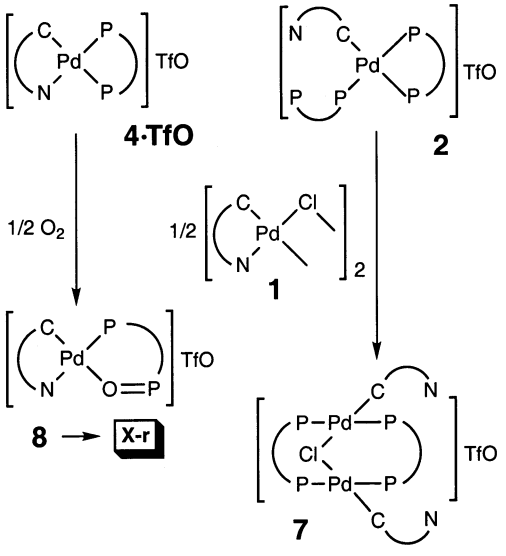
We attempted to prepare a heterobimetallic complex of palladium and platinum by reacting complex **2** with [PtCl$_2$(NCMe)$_2$] in acetone at low temperature (−60 °C). However, this reaction gave a mixture of compounds, which we could not separate. In this mixture was detected (by ^{1}H- and ^{31}P-NMR spectroscopy) [PdRCl(μ-dppm)]$_2$ [20], [PtCl$_2$(dppm)] and a little amount of [PdCl$_2$(dppm)].

When an excess of dppm was added to *trans*-[Pt(κ^1-R)Cl(PPh$_3$)$_2$] (**9**), which we prepared from [Hg(κ^1-R)Cl] and [Pt(PPh$_3$)$_3$] [20], (Scheme 4), the PPh$_3$ ligand was displaced to give [Pt(κ^1-R)(κ^1-dppm)(κ^2-dppm)]Cl (**10**·**Cl**) which reacts with TlOTf to give **10**·**TfO**, homologous to the palladium complex **2**. However, all attempts to prepare homo- and heterobimetallic platinum(II) complexes from **10**·**Cl** or **10**·**TfO** gave mixtures that could be resolved. The following reactions were attempted: **10**·**Cl** with [AuCl$_3$(tht)]; **10**·**TfO** with [AuCl$_3$(tht)] or **1** or [PdCl$_2$(NCPh)$_2$] or [AuCl(tht)]. The synthesis of iminophosphorane platinum(II) complexes was also unsuccessfully attempted by reacting **10**·**TfO** with N$_3$C$_6$H$_4$Me-4.

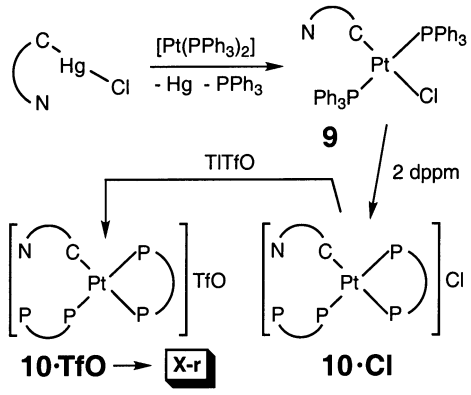
3. Discussion

3.1. X-ray structure determinations

The crystal structures of complexes **3**, **8** and **10**·**TfO** have been determined by X-ray diffraction (Figs. 1–3; Tables 1–4). The molecular structure of **3** consists of a dimer formed by a dppm ligand bridging two Pd(κ^2-R)Cl units. The dimer has a two fold symmetry with



Scheme 3.



Scheme 4.

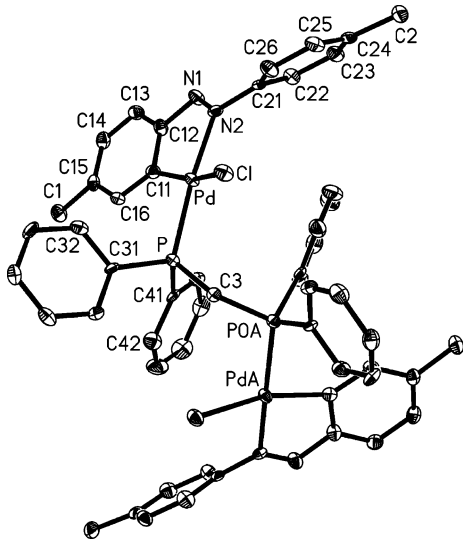


Fig. 1. Thermal ellipsoid plot (50% probability level) of **3**. Hydrogen atoms have been omitted for clarity.

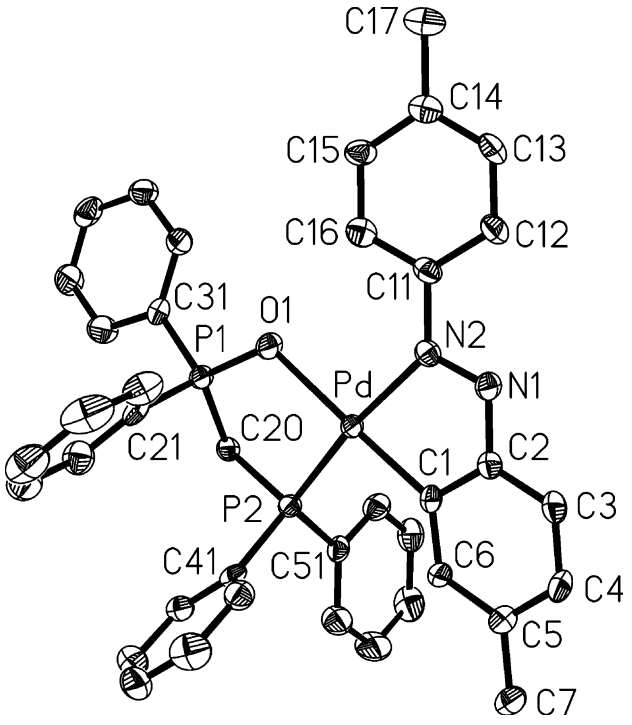


Fig. 2. Thermal ellipsoid plot (50% probability level) of the cation of **8**. Hydrogen atoms have been omitted for clarity.

respect to the methylene carbon atom of the dppm ligand. Each Pd atom is in a highly distorted square-planar coordination with 19.7° dihedral angle between the ClPdP and N(2)PdC(11) planes. The *cis* position of C and P around the palladium atom can be explained as a consequence of the *transphobia* of ligands with such donor atoms [20,31,36]. The Pd–Cl bond length [2.3941(9) Å] is significantly shorter than the corresponding bond length in *trans*-[Pd(κ^1-R)Cl(κ^1-dppm)$_2$] [2.4119(8) Å][20] in spite of being both *trans* to the same aryl ligand.

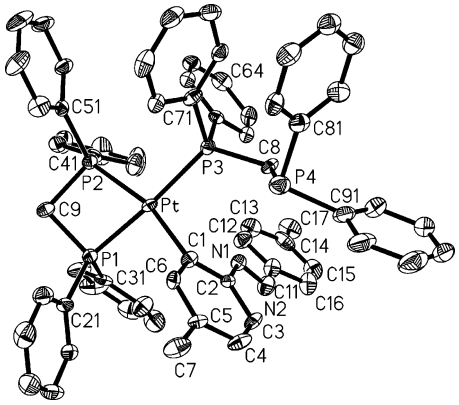


Fig. 3. Thermal ellipsoid plot (50% probability level) of **10**·**TfO**. Hydrogen atoms have been omitted for clarity.

The structure of the cation of complex **8** shows both the aryl and dppmO acting as chelating ligands. As far as we aware, the only other X-ray crystal structures of palladium complexes with the dppmO ligand is that of [Pd(Me)Cl(κ^2-*P,O*-dppmO)] [37] and that of the homologous of **8**, [Pd(κ^2-R)(κ^2-*P,O*-dppmO)]SbF_6 (where R is derived from azobenzene) [20]. The three structures show the O atom *trans* to the C atom. This geometry can also be explained having in mind the *transphobia* of the ligands with P- and C-donor atoms [20,31,32].

The molecular structure of **10**·**TfO** shows a platinum center with a κ^1-R ligand, one chelating and one monocoordinate dppm ligand. The square-planar coordination at platinum is slightly distorted with the planes determined for P(1)P(2)Pt and P(3)PtC(1) forming an angle of 6.1°. The Pt–P bond *trans* to the aryl group [2.337(2) Å] is longer than those *trans* to a P atom [2.299(2) and 2.310(2) Å] as a consequence of the stronger *trans* influence of the aryl group than the phosphine ligands. We have reported the crystal structure of the homologous palladium complex [20]. The two M–C bond distances are not significantly different [Pd–C = 2.040(5), Pt–C = 2.058(5) Å] but the M–P bonds lengths are. Thus, the Pd–P distances are 2.3592(15) (*trans* to C), 2.3181(15) and 2.3243(15) Å whereas the corresponding Pt–P bond lengths in **10**·**TfO** are shorter: 2.337(2), 2.299(2) and 2.310(2) Å, respectively. These data suggest that, although the scale of *trans* influence of ligands does not change with the metal (that of the aryl ligand is greater than that of PPh_3) its weakening influence depends on the metal. The above data clearly point that the *trans* influence of the aryl ligand, as well as the mutual *trans* influence of the phosphorus ligands, are greater in Pd than in Pt. The M–C bond distances do not appear affected by the nature of the metal. We have recently concluded,

Table 1
Crystal data for complexes **3**, **8**·CH_2Cl_2 and **10**·**TfO**

Compound	**3**	**8**·CH_2Cl_2	**10**·**TfO**
Crystal color	Orange	Yellow	Orange
Crystal habit	Prism	Tablet	Tablet
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$C2/c$	$P2_1/c$	$P\bar{1}$
Crystal size (mm)	0.48 × 0.24 × 0.18	0.47 × 0.32 × 0.14	0.26 × 0.24 × 0.08
Chemical formula	$C_{53}H_{48}Cl_2N_4P_2Pd_2$	$C_{41}H_{37}Cl_2F_3N_2O_4P_2PdS$	$C_{65}H_{57}F_3N_2O_3P_4PtS$
Unit cell parameters			
a (Å)	17.860(2)	10.769(1)	11.610(1)
b (Å)	14.985(1)	21.186(2)	13.368(2)
c (Å)	18.943(2)	18.147(3)	19.641(2)
α (°)	90	90	100.145(5)
β (°)	112.958(7)	91.38(1)	91.882(7)
γ (°)	90	90	105.177(5)
V (Å^3)	4668.2(8)	4139.3(8)	2886.0(6)
Radiation	Mo–K_α	Mo–K_α	Mo–K_α
λ (Å)	0.71073	0.71073	0.71073
T (K)°	173(2)	173(2)	173(2)
Z	4	4	2
Diffractometer	Siemens P4	Siemens P4	Siemens P4
Scan method	ω	ω	ω
Number of data collected	6191	7906	13 443
Number of unique data	3089	7268	10 108
R_{int}	0.0456	0.0439	0.0429
2θ max (°)	50	50	50
Absorption correction	Ψ-scans	Ψ-scans	Ψ-scans
R_1 [a]	0.0370	0.0572	0.0416
wR_2 [b]	0.0676	0.1430	0.0836
Number of parameters	284	476	712
Form of refinement	F^2	F^2	F^2
Treatment of hydrogen atoms	Riding	Riding	Riding

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ for reflections with $I > 2\sigma I$.
[b] $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)2]]0.5$ for all reflections; $w^{-1} = \sigma^2(F^2)+(aP)^2+bP$, where $P = (2F_c^2+F_o^2)/3$ and a and b are constants set by the program.

Table 2
Selected bond lengths (Å) and bond angles (°) for compound **3**

Bond lengths			
Pd–C(11)	1.997(3)	Pd–P	2.2729(10)
Pd–Cl	2.3941(9)	Pd–N(2)	2.116(3)
N(2)–N(1)	1.299(4)	P–C(31)	1.828(3)
P–C(41)	1.828(3)	P–C(3)	1.842(2)
Bond angles			
C(11)–Pd–P	95.48(10)	C(11)–Pd–N(2)	78.67(12)
N(2)–Pd–Cl	97.31(8)	P–Pd–Cl	91.26(3)

Table 3
Selected bond lengths (Å) and bond angles (°) for compound **8**

Bond lengths			
Pd–C(1)	1.971(6)	Pd–P(2)	2.262(2)
Pd–O(1)	2.163(4)	Pd–N(2)	2.146(5)
N(2)–N(1)	1.270(7)	P(1)–C(21)	1.798(6)
P(1)–C(31)	1.787(6)	P(2)–C(41)	1.811(6)
P(2)–C(51)	1.821(6)	P(1)–C(20)	1.794(6)
P(2)–C(20)	1.839(6)		
Bond angles			
C(1)–Pd–P(2)	94.9(2)	C(1)–Pd–N(2)	79.0(2)
N(2)–Pd–O(1)	98.7(2)	O(1)–Pd–P(2)	87.48(1)

comparing ^{31}P-NMR and X-ray structural data of isostructural Pd and Pt complexes with the same ligands (1,1-ethylenedithiolato and PPh_3), that the Pt–P bonds are stronger than their corresponding Pd–P bonds [38]. All the above facts are in agreement with the observation that *transphobia* of any couple of ligands is greater in Pd than in Pt complexes and that ligands with great *trans* influence show strong *transphobia* when placed in *trans* [20].

3.2. Spectroscopic properties of complexes

In agreement with the proposed symmetric structure of complex **3**, the $^{31}P\{^1H\}$-NMR spectrum exhibits a singlet at 30.68 ppm and the ^{1}H-NMR spectrum a triplet (5.02, $^2J_{HP} = 14$ Hz) for the methylene protons of the dppm ligand. A related complex shows these resonances at 30.1 and 4.70 ppm, respectively [17].

Table 4
Selected bond lengths (Å) and bond angles (°) for compound **10·TfO**

Bond lengths			
Pt–C(1)	2.058(5)	Pt–P(1)	2.299(2)
Pt–P(2)	2.337(2)	Pt–P(3)	2.310(2)
N(1)–N(2)	1.251(6)	P(1)–C(21)	1.813(6)
P(1)–C(31)	1.800(6)	P(2)–C(41)	1.812(5)
P(2)–C(51)	1.802(6)	P(3)–C(61)	1.819(5)
P(3)–C(71)	1.817(6)	P(4)–C(81)	1.835(6)
P(4)–C(91)	1.858(7)	P(1)–C(9)	1.827(5)
P(2)–C(9)	1.853(6)	P(3)–C(8)	1.832(5)
P(4)–C(8)	1.870(5)		
Bond angles			
C(1)–Pt–P(1)	93.2(2)	C(1)–Pt–P(3)	93.5(2)
P(1)–Pt–P(2)	71.60(6)	P(3)–Pt–P(2)	101.98(6)

In the $^{31}P\{^1H\}$-NMR spectrum of **4·ClO$_4$**, the doublet appearing at higher-field (−31.17 ppm, $^2J_{PP} = 68$ Hz) is assigned to the phosphorus *trans* to the aryl ligand [based on the data obtained for complex **2** (−34 ppm [20]), **4·TfO** (−30.60 ppm [20]), **5** (−35.77 ppm, see below) and related complexes (−33 to -36 ppm [35])] and the other one to the phosphorus *trans* to N (−5.70 ppm) [based on the data for **4·TfO** (−5.35 ppm [20]) and **4·SbF$_6$** (−4.76 ppm [20]). The ^{1}H-NMR spectrum shows the expected doublets of doublets (4.52 ppm, $^2J_{PH} = 12$ and 8 Hz) due to the methylene protons.

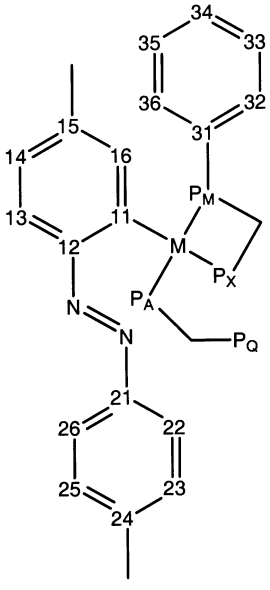
The $^{31}P\{^1H\}$-NMR spectrum of **5** shows at room temperature broad resonances around 19, −16 and −32 ppm. However, at -60 °C a first-order spectrum is obtained. The doublets of doublets corresponding to the phosphorus *trans* to the aryl ligand is again, as for **2** [20] and **4·ClO$_4$**, that appearing at the highest-field (−35.77 ppm) and is recognized by its smaller $^2J_{PP}$ values (67 and 25 Hz). The doublets of doublets appearing at the lowest field (23.15 ppm, $^2J_{PP} = 332$ and 25 Hz) is assigned to PPh_3 by comparison with the spectra of the complex [Pd(κ^1-R)Cl(PPh_3)$_2$] [20.6 ppm (br) at room temperature and 21.66 ppm (s) at −60 °C] [36]. Therefore, the intermediate doublet of doublets, appearing at −23.49 ppm, must correspond to the phosphorus of dppm *trans* to PPh_3. It is reasonable to assume that the broadening of signals at room temperature is due to the equilibrium **5**↔**4·TfO** + PPh_3.

The $^{31}P\{^1H\}$-NMR spectrum of **6** shows at room temperature broad signals around at 32 and 11 ppm. At −60 °C the first signal transforms into an apparent triplet at 31.56 ppm (assigned to the P nuclei bonded to Au) but the second one remains broad and moves to 13.39 ppm. The assignments are based on data reported for complexes containing the unit '*trans*-Pd$_2$(μ-(dppm)$_2$' [δ(P)$_{Pd}$ are in the range 21–5 ppm [6,9,12,16,20]] and on complexes [Pt(R)Cl(μ-dppm)$_2$Au]$^+$ (R = Me, Et, Ph, PhC≡C) [δ(P)$_{Au}$ are around 30 ppm [15,25]].

The $^{31}P\{^1H\}$-NMR spectrum of **7** exhibits a singlet at 7.35 ppm characteristic of an A-frame complex [12]. The ^{1}H-NMR spectrum shows two singlets corresponding to the methyl groups and a doublet of multiplets for the methylene hydrogens of the dppm ligand.

The ^{1}H-NMR spectrum of **8** shows a doublet of doublets (4.18, $^2J_{HP} = 12$ and 10 Hz) for the methylene hydrogens of the dppmO ligand. The ^{1}H- and $^{31}P\{^1H\}$-NMR spectra of **8** are similar to those in the analogous [Pd(η^2-R)(η^2-*P,O*-dppmO)]SbF6 (R = azobenzene) derivative [20]. The $^{31}P\{^1H\}$-NMR spectrum of **8** exhibits two doublets at 55.61 and 33.12 with $^2J_{PP} = 16$ Hz. The first one is attributed to $Ph_2P{=}O$ in agreement with the assignments reported for *cis*-[Pd(dppmO)$_2$]$^+$ [59.2 ($Ph_2P{=}O$) and 36.0 (Ph_2P) ppm] [39], [Pd(η^3-allyl)(dppmO)]$^+$ [62 ($Ph_2P{=}O$) and 22 (Ph_2P) ppm] and [Pd(Me)Cl(dppmO)] [45 ($Ph_2P{=}O$) and 26.8 (Ph_2P) ppm] [37].

The ^{31}P-NMR spectra of the platinum complexes **10·Cl** and **10·TfO**, like its homologous palladium complex **2**, show broad signals at room temperature presumably due to the intra- or intermolecular exchange of the dppm ligands. Probably, in such exchange the anions do not intervene because the ^{31}P-NMR spectra of **10·Cl** and **10·TfO** are similar at room temperature. At −60 °C the spectra are first order. The resonance due to P_A (see Chart) is recognized by its high frequency (5.77, 6.13 ppm, respectively), corresponding to a coordinated nonchelated dppm ligand, and its large coupling to P_M (373, 375 Hz, respectively). Similarly, the resonance due to P_M is assigned by its negative chemical shift (−35.49, −34.47 ppm, respectively) and its large coupling to P_A. The doublet of doublets corresponding to P_X was distinguished from that due to P_Q by its larger coupling constants and the platinum satellites. The ^{31}P resonances of these platinum complexes appear at lower frequency than those in the homologous Pd complex **2**. The same has been observed previously [38,40]. The



difference is in the range 5–11 ppm. The chemical shifts and coupling constants are similar to those in the analogous [PtR(κ^1-dppm)(κ^2-dppm)]PF_6 (R = Me, Et, Ph, mesityl) derivatives [35]. The small value of $^1J_{PtPX}$ (around 1500 Hz) compared with the other two J_{PtP} (around 2800 and 2400 Hz) is due to the high *trans* influence of the aryl ligand.

4. Experimental

4.1. General

All reactions were carried out under normal laboratory conditions. All solvents were distilled before use. The conductivity of complexes sufficiently soluble in acetone was measured in solutions of ca. 5×10^{-4} mol l^{-1} concentration. ^{1}H-, ^{31}P{^{1}H}- and ^{13}C-NMR spectra were measured in $CDCl_3$ solutions on a Varian Unity 300 spectrometer at room temperature unless otherwise stated. Chemical shifts are referred to TMS (^{1}H, ^{13}C) and H_3PO_3 (^{31}P). The complex [Pd(κ^2-R)(μ-Cl)]$_2$ (**1**) was prepared following a reported procedure [41]. [Pd(κ^1-R)Cl(κ^1-dppm)(κ^2-dppm)]TfO (**2**), [Pd(κ^2-R)(κ^2-dppm)]TfO (**4**·**TfO**), and *trans*-[PtRCl(PPh_3)$_2$] (**9**), were prepared as we previously reported [20]. The atom labeling for NMR assignments is shown in the Chart.

4.2. [{Pd(κ^2-R)Cl}$_2$(μ-dppm)] (3)

To a suspension of **1** (105 mg, 0.15 mmol) in CH_2Cl_2 (10 ml) was added dppm (57 mg, 0.15 mmol) and the resulting solution was stirred for 30 min. The solution was concentrated (1 ml) under vacuum and Et_2O (10 ml) was added to give yellow complex **3**. Yield: 145 mg, 89%. M.p. 195 °C. ν_{max} (cm^{-1}) (Pd–Cl), 278 cm^{-1}. ^{1}H-NMR (δ ppm): 8.11–8.05 (m, 8H, aromatic protons) 7.77–7.73 (m, 6H, aromatic protons), 7.38–7.20 (m, 16H), 6.84 (d, 2H, H_{14}, $^3J_{HH}$ = 8 Hz), 5.73 (d, 2H, H_{16}, $^4J_{HP}$ = 8 Hz), 5.02 [t, 2H, CH_2, $^2J_{HP}$ = 14 Hz], 2.42 (s, 6H, Me), 1.71 (s, 6H, Me). ^{31}P{^{1}H}-NMR (δ ppm): 30.68 (s). ^{13}C-NMR (δ ppm): 162.95 (s, C_{12}), 156.79 (s, C_{11}), 149.83 (d, C_{21}, $^3J_{CP}$ = 5 Hz), 142.54 (d, C_{15}, $^4J_{CP}$ = 6 Hz), 140.67 (s, C_{24}), 137.99 (d, C_{16}, $^3J_{PC}$ = 8 Hz), 135.74 (d, C_{32}≡C_{36}, $^2J_{PC}$ = 13 Hz), 131.19 (d, C_{34}, $^4J_{PC}$ = 3 Hz), 130 27 (s, C_{13}) 129.15 (d of the apparent dd corresponding to C_{31}, 'J' = 4 Hz), 128.48, 128.44, 128.33 (one signal of the apparent dd corresponding to C_{31} plus C_{23}≡C_{25} and C_{33}≡C_{35}), 125.99 (s, C_{14}), 124.40 (s, C_{22}≡C_{26}), 28.67 (t, CH_2, $^1J_{PC}$ = 25 Hz), 22.17, 21.46 (4Me). Anal. Calc. for $C_{53}H_{48}Cl_2N_4P_2Pd_2$: C, 58.57; H, 4.46; N, 5.16. Found: C, 58.72; H, 4.51; N, 5.09%. Single crystals of **3** were obtained by slow diffusion of *n*-pentane into a solution of **3** in CH_2Cl_2.

4.3. [Pd(κ^2-R)(κ^2-dppm)]ClO_4 (4·ClO_4)

To a suspension of **1** (222 mg, 0.316 mmol) in acetone (20 ml) was added $AgClO_4$ (131 mg, 0.632 mmol) and the resulting suspension was refluxed for 30 min and then filtered through Celite. The ligand dppm (243 mg, 0.632 mmol) was added to the filtrate and the mixture stirred for 1 h. The solution was concentrated and Et_2O (8 ml) was added to give **4**·ClO_4 as an orange solid. Yield: 410 mg, 81%. M.p.: 206 °C (dec). ^{1}H-NMR (δ ppm): 7.94 (dd, 1H, H_{13}, $^3J_{HH}$ = 8 Hz, $^4J_{PH}$ = 3 Hz), 7.84–7.36 (m, 22H), 7.09 (d, 1H, H_{14}, $^3J_{HH}$ = 8 Hz), 6.91 (d, 2H, H_{23}, H_{25}, $^3J_{HH}$ = 8 Hz), 6.48 (t, 1H, H_{16}, $^4J_{HP}$ = 9 Hz), 4.52 [dd, 2H, CH_2, $^2J_{PH}$ = 12 and 8 Hz], 2.30 [s, 3H, Me], 2.02 [s, 3H, Me]. ^{31}P{^{1}H}-NMR (δ ppm): −5.70 (d, $P_{trans\ to\ N}$, $^2J_{PP}$ = 68 Hz), −31.17 (d, $P_{trans\ to\ C}$). Anal. Calc. for $C_{39}H_{35}ClN_2O_4P_2Pd$: C, 58.59; H, 4.41; N, 3.51. Found: C, 58.29; H, 4.27; N, 3.30%.

4.4. [Pd(κ^1-R)(PPh_3)(κ^2-dppm)]TfO (5)

To a solution of **2** (150 mg, 0.12 mmol) in acetone (6 ml) were added [AuCl(PPh_3)] (60 mg, 0.12 mmol) and, after 1 h of stirring, TlOTf (50 mg, 0.14 mmol). The reaction mixture was concentrated to dryness and CH_2Cl_2 (16 ml) was added. The resulting suspension was filtered through Celite, the filtrate was concentrated to 4 ml and Et_2O (11 ml) was added to give [Au(μ-dppm)$_2$](TfO)$_2$ (70 mg, 79%) as a yellow solid. The filtrate was concentrated (1 ml) and addition of Et_2O (14 ml) and *n*-hexane (1 ml) gave **5** as an orange solid. Yield: 77 mg, 50%. M.p. 108 °C. ^{1}H-NMR (δ ppm): 7.8–6.4 (m, 42H, aromatic protons), 4.54 [t, 2H, CH_2, $^2J_{HP}$ = 9 Hz], 2.40 (s, 3H, Me), 1.90 (s, 3H, Me). ^{31}P{^{1}H}-NMR (δ ppm): 19 (br), −16 (br), −32 (br). ^{1}H-NMR (−60 °C): 7.9–5.9 (m, 42H, aromatic protons), 4.5 (m, 2H, CH_2), 2.42 (s, 3H, Me), 1.73 (s, 3H, Me). ^{31}P{^{1}H}-NMR (−60 °C): 23.15 (dd, P_APh_3, $^2J_{AM}$ = 332 Hz, $^2J_{AX}$ = 25 Hz), −23.49 (dd, P_M, $^2J_{MX}$ = 67 Hz), −35.77 (dd, 1P, P_X). Anal. Calc. for $C_{58}H_{50}F_3N_2O_3P_3PdS$: C, 62.67; H, 4.54; N, 2.52; S, 2.88. Found: C, 62.41; H, 4.80; N, 2.48; S, 2.88%.

4.5. [Pd(κ^1-R)Cl(μ-dppm)$_2$Au]TfO (6)

To a solution of **2** (202 mg, 0.164 mmol) at −60 °C in CH_2Cl_2 (7 ml) was added [AuCl(PPh_3)] (81 mg, 0.164 mmol) and stirred for 3 h while its temperature was allowed to rise slowly up to 25 °C. The resulting solution was evaporated to dryness, Et_2O (4 ml) was added and vigorous stirred for 5 min to give **6** as an orange solid. Yield: 211 mg, 88%. M.p. 210 °C (dec). ^{1}H-NMR (−60 °C, δ ppm): 8.06–6.53 (m, 47 H, aromatic protons), 4.45–3.51 (m, 4H, CH_2), 2.45 (s, 3H, Me), 1.18 (s, 3H, Me). ^{31}P{^{1}H}-NMR (−60 °C, δ

ppm): 31.56 ('t', P_2Au, $|^2J_{PP}+{}^4J_{PP}| = 33$ Hz), 13.39 (br, P_2Pd). FAB$^+$: $m/z = 1312$ [M^+], 965 [$Au(dppm)_2^+$], 699 [$PdR(dppm)^+$]. Anal. Calc. for $C_{65}H_{57}AuClF_3N_2O_3P_4PdS$: C, 53.25; H, 3.93; N, 1.91; S, 2.19. Found: C, 53.15; H, 3.94; N, 1.76; S, 2.12%.

4.6. [{PdR(μ-dppm)}$_2$(μ-Cl)]TfO (7)

To a suspension of **2** (137 mg, 0.11 mmol) in acetone (15 ml) was added **1** (39 mg, 0.05 mmol) and the resulting suspension was stirred for 6 h. The solvent was partially evaporated (1 ml) and Et_2O (10 ml) and *n*-hexane (10 ml) were added to give **7** as an orange solid. Yield: 154 mg, 88%. M.p. 198 °C. Δ_M (Ω^{-1} cm^2 mol^{-1}) = 133. ^{1}H-NMR (δ ppm): 7.59–6.47 (m, 54H, aromatic protons), 3.94 [dm, 4H, CH_2), 2.47 (s, 6H, Me), 1.96 (s, 6H, Me). ^{31}P{^{1}H}-NMR (δ ppm): 7.35 (s). ^{13}C{^{1}H}-NMR (δ ppm): 152.78, 151.71, 150.54 (C_{11}, C_{12}, C_{21}), 141.51, 140.37 (C_{15}, C_{24}), 138.99 (C_{16}), 133.43 ('t', one of the $C_{32}\equiv C_{36}$ pairs, $|^2J_{PC}+{}^4J_{PC}| = 7$ Hz, 132.51 (t″, the other $C_{32}\equiv C_{36}$ pair, $|^2J_{PC}+{}^4J_{PC}| = 3$ Hz), 130.58, 130.14, 129.39 (the pair of C_{34} carbons plus $C_{23}\equiv C_{25}$), 128.12 ('t', not resolved, one of the $C_{33}\equiv C_{35}$ pairs), 127.94 (t″, the other $C_{33}\equiv C_{35}$ pair, [$^3J_{PC}+{}^5J_{PC}$] = 3 Hz), 125.24 (C_{14}), 124.55 (C_{13}), 122.64 ($C_{22}\equiv C_{26}$), 30.12 ('t', not resolved, CH_2), 21.50 (2 Me), 21.22 (2 Me). Anal. Calc. for $C_{79}H_{70}ClF_3N_4O_3P_4Pd_2S$: C, 59.87; H, 4.46; N, 3.54; S, 2.02. Found: C, 59.78; H, 4.50; N, 3.38; S, 2.19%.

4.7. [Pd(κ^2-R)(κ^2-P,O-dppmO)]TfO (8)

A solution of **4**·**TfO** (72 mg, 0.08 mmol) in toluene (20 ml) was refluxed for 8 h. The resulting suspension was concentrated (5 ml) and Et_2O (20 ml) was added to give **8** as a yellow solid. Yield: 40 mg, 36%. M.p. 219 °C (dec). ^{1}H-NMR (δ ppm): 8.28 (d, 2H, H_{22}, H_{26}, $^3J_{HH}$ = 9 Hz), 7.90–7.36 (m, 23 H, aromatic protons), 6.98 (d, 1H, H_{14}, $^3J_{HH}$ = 8 Hz), 6.20 (d, 1H, H_{16}, $^4J_{HP}$ = 8 Hz), 4.18 [dd, CH_2, $^2J_{PH}$ = 12 and 10 Hz], 2.52 (s, 3H, Me), 1.85 (s, 3H, Me). ^{31}P{^{1}H}-NMR (δ ppm): 55.61 (d, Ph_2P=O, $^2J_{PP}$ = 16 Hz), 33.12 (d, Ph_2P). Anal. Calc. for $C_{40}H_{35}F_3N_2O_4P_2PdS$: C, 55.5; H, 4.08; N, 3.24; S, 3.70. Found: C, 55.3; H, 4.04; N, 2.89; S, 3.47%. Single crystals of **8** were obtained by slow diffusion of Et_2O into a solution of **7** in chloroform.

4.8. [Pt(κ^1-R)(κ^1-dppm)(κ^2-dppm)]Cl (10·Cl)

To a suspension of **9** (95 mg, 0.1 mmol) in acetone (25 ml) was added dppm (151 mg, 0.393 mmol) and the resulting solution was stirred for 30 min. Concentration of this solution (1 ml) and addition of Et_2O (16 ml) precipitated orange complex **10**·**Cl**. Yield: 60 mg, 67%. M.p. 178 °C. Δ_M (Ω^{-1} cm^2 mol^{-1}) = 110. ^{1}H-NMR (−60 °C, δ ppm): 7.9–6.5 (m, 47H, aromatic protons), 5.0–4.7 (m, 2H, CH_2), 2.59 (s, 3H, Me), 2.5–2.45 (m, 2H, CH_2), 1.98 (s, 3H, Me). ^{31}P{^{1}H}-NMR (−60 °C, δ ppm): 5.77 (ddd, P_A, $^2J_{AM}$ = 373 Hz, $^2J_{AQ}$ = 46 Hz, $^2J_{AX}$ = 18 Hz, $^1J_{PtPA}$ = 2800 Hz), −33.50 (dd, P_Q, $^4J_{MQ}$ = not resolved), −35.49 (ddd, P_M, $^2J_{MX}$ = 44 Hz, $^1J_{PtPM}$ = 2454 Hz), −39.74 (dd, P_X, $^1J_{PtPX}$ = 1510 Hz). Anal. Calc. for $C_{64}H_{57}ClN_2P_4Pt$: C, 63.59; H, 4.76; N, 2.32. Found: C, 63.76; H, 4.69; N, 2.28%.

4.9. [PtR(dppm-κ^1-P)(dppm-κ^2-P,P)]TfO (10·TfO)

To a solution of **10**·**Cl** (224 mg, 0.185 mmol) in CH_2Cl_2 (10 ml) was added TlOTf (66 mg, 0.187 mmol). The resulting suspension was stirred for 1 h and then filtered thorough Celite. The solution was concentrated to 2 ml and addition of Et_2O (20 ml) gave **10**·**TfO** as an orange solid. Yield: 196 mg, 80%. M.p. 198 °C. Δ_M (Ω^{-1} cm^2 mol^{-1}) = 131. ^{1}H-NMR (−60 °C, δ ppm): 7.9–6.3 (m, 47H, aromatic protons), 5.0–4.5 (m, 2H, CH_2), 2.60 (s, 3H, Me), 2.53–2.47 (m, 2H, CH_2), 1.97 (s, 3H, Me). ^{31}P{^{1}H}-NMR (−60 °C, δ ppm): 6.13 (ddd, P_A, $^2J_{AM}$ = 375 Hz, $^2J_{AQ}$ = 46 Hz, $^2J_{AX}$ = 19 Hz, $^1J_{PtPA}$ = 2780 Hz), −33.53 (dd, P_Q, $^2J_{MQ}$ = 6 Hz), −34.47 (ddd, P_M, $^2J_{MX}$ = 45 Hz, $^1J_{PtPM}$ = 2330 Hz), −39.08 (dd, P_X, $^1J_{PtPX}$ = 1520 Hz). Anal. Calc. for $C_{65}H_{57}F_3N_2O_3P_4PtS$: C, 59.04; H, 4.35; N, 2.12; S, 2.42. Found: C, 59.15; H, 4.47; N, 2.12; S, 2.49%. Single crystals of **10**·**TfO** were obtained by slow diffusion of *n*-hexane into a solution of **10**·**TfO** in chloroform.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 186694, 186695 and 186696 for compounds **3**, **8**·CH_2Cl_2 and **10**·**TfO**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336022; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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