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# A fluorene-based diphosphinite ligand, its Ni, Pd, Pt, Fe, Co and Zn complexes and the first structurally characterized diphosphinate metal chelates

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Dedicated to Professor Achim Müller, in recognition for his outstanding and diverse contributions to chemistry.

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# ABSTRACT

The diphosphinite ligand 9,9-(Ph<sub>2</sub>POCH<sub>2</sub>)<sub>2</sub>-fluorene (**1**) was reacted with group 10 metal dichlorides to form chelate complexes of formula [MCl<sub>2</sub>(**1**)] (M=Ni, **2**; M=Pd, **3**; M=Pt, **4**) showing 8-membered metal-locycles. Chloride abstraction from **3** with AgOTf afforded the dinuclear complex [M( $\mu$ -Cl)Pd(**1**)]<sub>2</sub>(OTf)<sub>2</sub> (**5**), in which the ligand adopts a different conformation with respect of **3**. In **5**, the fluorene moiety and the phenyl groups display stabilizing interactions with the anion which is located close to the metal centre. With Fe(II), Co(II) and Zn(II) chlorides, the non-isolated intermediates [MCl<sub>2</sub>(**1**)] readily undergo oxidation to [MCl<sub>2</sub>(**1**<sub>ox</sub>)] (M=Fe, **6**; M=Co, **7**; M=Zn, **8**; **1**<sub>ox</sub> = 9,9-(Ph<sub>2</sub>P(O)OCH<sub>2</sub>)<sub>2</sub>-fluorene) in which the diphosphinate ligand and the metal centre form 10-membered metallocycles. Complexes **6–8** are the first examples of structurally characterized diphosphinate metal chelates. The Zn(II) diphosphinite complex [ZnCl<sub>2</sub>(**1**)] (**9**) could be observed by NMR spectroscopy, along with the mixed phosphinite-phosphinate, mono-oxidized complex which is an intermediate in the formation of **8**. Complex [ZnCl<sub>2</sub>(9.9-fluorene-dimethanol)(Ph<sub>2</sub>P(O)H)] (**10**) was also observed as hydrolysis product of **9**. The X-ray molecular structures of **2**, **3**, **5**.2OTf, **6**, **7**, **8** and **10** are reported.

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# 1. Introduction

Diphosphinite ligands are generally readily available and their metal complexes find numerous applications, mostly in homogeneous catalysis [1]. For example, the POCOP class of metallated ligands (POCOP =  $\kappa_3$ -1,3-(PR<sub>2</sub>O)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) has been much studied recently [2], and has often been proven to be superior to the related PCP tertiary diphosphines, in terms of stability of the complexes and catalytic activity [3]. The axial chiral diphosphinites BINOP, similar to the famous BINAP diphosphines, represent another important class of ligands [4].

We recently reported the almost quantitative synthesis of the new ligand  $9,9-(Ph_2POCH_2)_2$ -fluorene, by reaction of  $Ph_2PCl$  with 9H-fluorene-9,9-dimethanol (Scheme 1), in the presence of NEt<sub>3</sub> as HCl scavenger [5]. This stable compound, which shows only moderate sensitivity towards hydrolysis, air and moisture, can be included in the family of large bite angle phosphorus donors. Because of the resulting steric and/or electronic influence of the P-M-P angle, this often results in specific reactivities of the metal complexes [6].

Ligand **1** has been previously used for the formation of cationic dinuclear Pd(II) complexes of formula  $[Pd(\mu-Cl)(1)]_2(X)_2$  (X = BF<sub>4</sub>, PF<sub>6</sub>) [5]. In the solid state, the anions were found close to the metal centres, positioned in cavities delimitated by the aryl groups (Ph, fluorene) of the chelating ligands. The stabilization of these cation–anions couples was improved by close H…F contacts between the aryl protons and the fluorinated anions. The flat fluorene moiety was found to be orthogonal to the metal coordination planes, giving rise, with the phenyl groups, to the aforementioned cavities. These host–guest systems were identified in solution by means of <sup>1</sup>H–<sup>19</sup>F HOESY NMR experiments whose results were fully consistent with the intermolecular connectivities observed in the solid state.

The dinuclear complex  $[Ag(PF_6)(1)]_2$  was formed by reaction of **1** with AgPF<sub>6</sub> and it displays a 16-membered metallocyclic structure resulting from the bridging bonding mode of **1**. In its solid state structure, the phenyl groups and the fluorene rings are disposed in such a way that two large, mutually centrosymmetric cavities are formed. Because of their size and favorable H...F contacts similar to those described above, the PF<sub>6</sub><sup>-</sup> anions were inserted in these cavities and interacted with the metal centres in a remarkable F<sub>5</sub>P-( $\mu$ -F) coordination mode, which is unprecedented for the hexafluorophosphate anion (Scheme 2) [5].

In order to study the reactivity of this diphosphinite ligand **1** with other transition metals, we have reacted it with halide com-





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Scheme 1. Synthesis of the diphosphinite ligand 1.



**Scheme 2.** Ag–PF<sub>6</sub> interactions through a remarkable  $F_5P$ -(µ-F) coordination mode in  $[Ag(PF_6)(1)]_2$  [5].

plexes of Fe(II), Co(II), Ni(II), Zn(II), Pd(II) and Pt(II) and report here the results of these studies.

# 2. Results and discussion

The reaction of **1** with divalent metal complexes from the group 10, namely [NiCl<sub>2</sub>(DME)] (DME = 1,2-dimethoxyethane), [PdCl<sub>2</sub>(NCPh)<sub>2</sub>] and [PtCl<sub>2</sub>(NCPh)<sub>2</sub>] afforded in good yields complexes [NiCl<sub>2</sub>(**1**)] (**2**), [PdCl<sub>2</sub>(**1**)] (**3**) and [PtCl<sub>2</sub>(**1**)] (**4**), respectively (Scheme 3). The crystal structures of **2** and **3** were determined by single crystal X-ray diffraction. Complex **4** was found to be isostructural with **3**, and their unit cell parameters share analogous values. ORTEP views of the molecular structure of **2** and **3** are depicted in Figs. 1 and 2. Selected bond distances and angles are reported and compared in Table 1.







Fig. 1. ORTEP of the molecular structure of complex 2 in  $2 \cdot CH_2Cl_2$ . Displacement parameters include 40% of the electron density.



**Fig. 2.** ORTEP of the molecular structure of compound **3** in **3**·2CHCl<sub>3</sub>, which is isostructural with **4**·2CHCl<sub>3</sub>. Displacement parameters include 40% of the electron density.

In the molecular structure of complex **2**, the metal centre is chelated by diphosphinite **1** and coordinated by two mutually *cis* terminal chlorides, in a slightly distorted square planar geometry. As expected, the structural features of **3** are analogous to those of **2**, although the M–P and M–Cl bond distances are longer, as expected, considering the difference in ionic radii between these metals ( $r_{Pd}-r_{Ni} = 0.11$  Å) [7]. A slight distortion from planarity is observed in **3**, and the P1–P2–Cl2–Cl1 torsion angle of 9.35(3)° is larger than in **2** [2.62(3)°]. The P–M–P bite angle is 104.27(4)° for **2** and 102.67(4)° for **3**.

The  ${}^{31}P{}^{1}H$  NMR spectra of **3** and **4** show typical values for Pd and Pt phosphinite complexes, with singlets at 125.4 and

 Table 1

 Comparison between selected bond distances (Å) and angles (°) in compounds

 2·CH<sub>2</sub>Cl<sub>2</sub> (M=Ni), 3·2CHCl<sub>3</sub> (M=Pd) and 5·2OTf·2CHCl<sub>3</sub> (M=Pd).

$2 \cdot \mathrm{CH}_2 \mathrm{Cl}_2 \qquad 3 \cdot \mathrm{2CHCl}_3 \qquad 5 \cdot \mathrm{2}$	OTf-2CHCl₃
M-P1 2.1727(9) 2.237(1) 2.2	45(1)
Pd2-P3 2.2	39(1)
M-P2 2.1458(9) 2.238(1) 2.2	51(1)
Pd2-P4 2.2	52(1)
M-Cl1 2.1923(9) 2.361(1) 2.3	98(1)
Pd2-Cl1 2.4	00(1)
M-Cl2 2.1948(9) 2.357(1) 2.4	055(1)
Pd2-Cl2 2.4	335(1)
P1-01 1.626(2) 1.607(3) 1.5	93(4)
P3-03 1.6	01(3)
P2-02 1.624(2) 1.616(3) 1.6	04(3)
P4-04 1.6	00(3)
P1-M-P2 104.27(4) 102.67(4) 90.	31(4)
P3-Pd2-P4 91.	18(4)
Cl1-M-Cl2 91.87(4) 91.74(4) 84.	23(4)
Cl1-Pd2-Cl2 83.	58(4)
P1-P2-Cl1-Cl2 2.62(3) 9.35(3) 1.9	2(5)
P3-P4-Cl1-Cl2 0.4	8(5)

96.1 ppm, respectively, flanked in the case of **4** with <sup>195</sup>Pt satellites and the  ${}^{1}J({}^{31}P,{}^{195}Pt)$  coupling constant of 4149 Hz is consistent with the presence of chloride ligands in *trans* position to the P donors [8].

In CD<sub>2</sub>Cl<sub>2</sub> solution, complex **2** was found to be paramagnetic. The <sup>31</sup>P{<sup>1</sup>H} NMR signal was not detected in saturated solutions, while the <sup>1</sup>H spectra display temperature-dependent isotropic shifts typical of a square planar – tetrahedral equilibrium [9] (see ESI). Consistently, the nuclei less affected by the paramagnetic metal centre of the tetrahedral isomer are those of the fluorene ring, which (*vide infra*), are relatively far from it.

Reaction of **3** with one equivalent AgOTf resulted in abstraction of one of the chloride ligands and precipitation of AgCl and afforded the dinuclear complex  $[Pd(\mu-Cl)(1)]_2(OTf)_2$  (**5**·2OTf, OTf = trifluoromethanesulfonate). Its crystal structure was determined by single crystal X-ray diffraction and an ORTEP of the structure of **5**·OTf in **5**·2OTf·2CHCl<sub>3</sub> is depicted in Fig. 3. The cation shares strong similarities with that of  $[Pd(\mu-Cl)(1)]_2(BF_4)_2$  (**5**·2BF<sub>4</sub>) [5].

Each metal centre in cationic **5** is chelated by ligand **1**. Two chloride ligands symmetrically bridge the Pd atoms (see Table 1) which are separated by 3.5081(6) Å. The geometry around the metal centres is slightly distorted from planarity, the distance of the metal centre to the mean plane defined by the surrounding donor atoms being 0.1617(4) Å for Pd1 and 0.1952(4) Å for Pd2. This pyramidal distortion, directed towards the anion, suggests the occurrence of  $0 \cdots$ Pd interactions with one of the two triflate anions [Pd1 $\cdots$ O5 and Pd2 $\cdots$ O7 separations: 2.966(4) Å and



Fig. 3. ORTEP of the molecular structure of 5-OTf in 5-2OTf-2CHCl<sub>3</sub>. Displacement parameters include 40% of the electron density.

2.890(4) Å], which bridges the Pd atoms through two sulfonate oxygens. Indeed, the  $\alpha_B$  parameter (93.9(1)° for Pd1 and 94.7(1)° for Pd2), defined as the mean value of the L–Pd…O angles (L = P or Cl) is fully consistent with an oxygen atom donating electron density into the empty  $P_z$  orbital of the metal from the aforementioned distances [10]. These represent the shortest interactions reported between a non-coordinating, bridging triflate and Pd(II) centres. Indeed, the closest separations between two triflate oxygen atoms and two tetracoordinated Pd(II) centres found in the CCDC database [11] is 3.073 and 3.234 Å for a trinuclear species [12]. The shortest Pd(II)…O separation between a non-coordinating triflate and a Pd(II) centre is 2.796 Å [13].

The conformation of the diphosphinite ligand in **5**·2OTf differs from that in its mononuclear precursor **3**. Simplified structural diagrams of **3** and **5** are compared in Fig. 4.

Ligand 1 changes conformation on going from 3 to 5.20Tf. In 3, the C–O bonds are oriented in almost orthogonal directions, pointing below and above the P, P, Cl, Cl plane. In 5, probably constrained by the dramatically decreased bite angle  $[102.67(4)^{\circ}$  in 3,  $90.31(4)^{\circ}$  and  $91.18(4)^{\circ}$  in 5], the two C–O bonds are almost parallel to each other [angle between the lines defined by C1–O1 and C2–O2 in 5:  $9.9(3)^{\circ}$  vs.  $79.4(2)^{\circ}$  in 3]. Consequently, the fluorene group is almost perfectly orthogonal to the metal coordination plane [angles between the mean planes defined by P1, P2, Pd1, Cl1, Cl2 and the atoms forming the fluorene groups:  $62.80(5)^{\circ}$  for 3 and  $89.37(5)^{\circ}$  for 5.20Tf]. In turn, this allows the triflate in the 5.0Tf moiety to interact with the fluorene ring and the metal centre in a host–guest arrangement, through H…O contacts between the sulfonate oxygen atoms and some of the fluorene protons, as shown in Fig. 5.

Of the contacts displayed in Fig. 5, the shortest  $H \cdots O$  and  $H \cdots F$  separations are 2.633(4) Å ( $O5 \cdots H2B$ ) and 2.487(5) Å ( $H14 \cdots F3$ ), respectively. Other contacts, not shown for clarity, involve the phenyl groups and the triflate oxygens [shortest  $H \cdots O$  separation: 2.418(4) Å for  $H39 \cdots O5$ ]. This is clearly in favor of a combined



**Fig. 4.** Structural diagram of: (a) complex **3** and (b) the analogous fragment in dinuclear **5** (phenyls omitted for clarity).



**Fig. 5.** Structural diagram of the cationic **5**·OTf moiety, emphasizing the network of H···O and H···F contacts between the fluorene group and one of the two triflate anions. The H···O and H···F contacts are depicted with red dashed lines, and the Pd···O contacts with blue dashed lines. Phenyls omitted for clarity.



Fig. 6. van der Waals plots of 5-2BF<sub>4</sub> (a and b) and 5-2OTf (c and d). The two anions closest to the metal centres are shown. In figures a and d, the orientation is similar to that in Fig. 5, while in figures b and c, the opposite side with respect to the palladium coordination planes is shown.

influence of the fluorene and phenyl protons on the host-guest anion stabilization.

The smaller size of the  $BF_4^-$  anion compared to  $OTf^-$  allows for a second tetrafluoroborate to approach the metal centres in  $5\cdot 2BF_4$  [5] and to occupy a second cavity located on the opposite side to that depicted in Fig. 5 (see Fig. 6b). In  $5\cdot 2OTf$ , this cavity is partially occupied by two chloroform molecules. van der Waals diagrams of  $5\cdot OTf$  in  $5\cdot 2OTf$  and of  $5\cdot 2BF_4$  are shown in Fig. 6.

When the reaction was carried out with AgPF<sub>6</sub> instead of AgOTf, compound **5**·2PF<sub>6</sub> was obtained which, in the solid state, has two  $PF_6^-$  anions encapsulated in centrosymmetric cavities, at variance with the situation in **5**·2OTf where only one triflate is involved in a host–guest system. Furthermore, the cation in **5**·2PF<sub>6</sub> displays  $C_{2h}$  symmetry rather than  $C_{2v}$ , as found in **5**·2OTf and **5**·2BF<sub>4</sub> (a and b in Scheme 3, respectively) [5].

These two conformations are probably both present in solution and in rapid exchange, as suggested by multinuclear VT NMR spec-



Fig. 7. Variable-temperature <sup>1</sup>H NMR spectra of 5 2BF<sub>4</sub> in CD<sub>2</sub>Cl<sub>2</sub> (from Ref. [5]).

troscopy. The methylene protons of **5**·20Tf give rise to a broad singlet at 298 K in the <sup>1</sup>H NMR spectrum, similarly to what has been observed for **5**·2BF<sub>4</sub> [5]. In the latter case, the <sup>1</sup>H NMR spectrum contained four broad signals at 220 K (Fig. 7).

This, together with the observation of two different conformations in the solid-state for the cation in  $5 \cdot 2PF_6$  (a in Scheme 4) and in  $5 \cdot 2OTf$  (b), suggests the equilibrium shown in Scheme 4.



**Scheme 4.** Possible conformations of the dication **5** in solution (phenyl groups omitted for clarity).

Each conformation is characterized by four equivalent pairs of diastereotopic protons and gives rise to two broad signals at low temperature. The  ${}^{31}P{}^{1}H{}$  spectrum remains unchanged in the temperature range examined.

#### 2.1. Coordination properties of 1 towards FeCl<sub>2</sub>, CoCl<sub>2</sub> and ZnCl<sub>2</sub>

Ligand **1** readily reacted with anhydrous FeCl<sub>2</sub>, CoCl<sub>2</sub> and ZnCl<sub>2</sub> under inert atmosphere. However, only complexes featuring the diphosphinate ligand  $\mathbf{1}_{ox}$  could be isolated after purification by crystallization, most likely because of the sensitivity of the hypothetical intermediates [MCl<sub>2</sub>(1)] towards oxidation. When this reaction was performed under air, yellow [FeCl<sub>2</sub>( $\mathbf{1}_{ox}$ )] (**6**), blue [Co-Cl<sub>2</sub>( $\mathbf{1}_{ox}$ )] (**7**) and colourless [ZnCl<sub>2</sub>( $\mathbf{1}_{ox}$ )] (**8**) were obtained in good yields (Scheme 5).

Although pure **1** does not rapidly oxidize when exposed to air or moisture, it is known that Co(II) promotes insertion of aerobic oxygen into the P–M bond, possibly *via* dioxygen coordination [14]. The oxidation is quantitative and can be detected in the FT-IR spectra of **6–8** by the strong P=O stretching absorption around 1190 cm<sup>-1</sup>. In the case of Zn(II), we were able to characterize spectroscopically the diphosphinite complex [ZnCl<sub>2</sub>(1)] (**9**), although its sensitivity prevented the obtention of a pure sample. In addition, the mono-oxidized phosphinite–phosphinate complex depicted in Scheme 6 was observed as intermediate in the formation of **8**.

Thus, as expected, the oxidation proceeds stepwise, with, qualitatively, similar kinetics for the first and second oxidation steps.

The superimposability of the FT-IR spectra of **6–8** suggests the isostructural character of these complexes in the solid state. This was confirmed by single crystal X-ray diffraction, the three complexes share the same molecular structure and crystal packing. An ORTEP view of the molecular structure of **7** is shown in Fig. 8.

In the molecular structure of **6–8**, the diphosphinate ligand  $1_{ox}$  chelates the metal centre through the two P=O oxygen atoms [Co1–O3 and Co1–O4 distances in **7**: 1.991(4) Å and 2.000(4) Å, respectively]. The two chlorides are terminally bound to the metal centres, which have a distorted tetrahedral coordination geometry. Selected bond distances and angles are compared in Table 2. Ligand chelation results in the formation of a 10-membered metallocycle (see Fig. 8).

Interestingly, complexes **6-8** crystallize in the chiral space group  $P2_12_12_1$ . One crystallographically independent molecule is present in the unit cell of the three compounds and the refinement resulted in parameters consistent with a spontaneous resolution of one of the possible conformational enantiomers.

Only few 10-membered rings formed by chelation to Fe and Co have been reported in the literature, and they mostly involve multidentate ligands [15]. In the case of bidentate ligands, and to the



Scheme 5.



Scheme 6. Stepwise oxidation of 9 to form 8. <sup>31</sup>P{<sup>1</sup>H} NMR chemical shifts (in ppm) are reported.



**Fig. 8.** ORTEP of the molecular structure of **7**. ORTEP diagrams of the isostructural complexes **6** and **8** are provided in the supplementary information. Displacement parameters include 40% of the electron density.

Table 2
Comparison between selected distances (Å) and angles (°) in 6 (M=Fe), 7 (M=Co) and
<b>8</b> (M=Zn).

	6	7	8
M-03	2.031(3)	1.991(4)	1.988(2)
M-04	1.941(5)	2.000(4)	2.004(2)
M-Cl1	2.252(2)	2.243(2)	2.219(1)
M-Cl2	2.247(2)	2.237(2)	2.2107(9)
P1-01	1.582(3)	1.575(4)	1.575(2)
P2-02	1.579(3)	1.585(4)	1.580(2)
P1-03	1.470(4)	1.482(3)	1.491(2)
P2-04	1.437(5)	1.492(4)	1.495(2)
03-M-04	105.2(2)	103.5(2)	101.36(9)
Cl1-M-Cl2	125.37(7)	121.03(7)	123.38(4)
V1-V2 <sup>a</sup>	89.96(8)	89.92(6)	89.84(4)

<sup>a</sup> Angle between the Cl1 $\cdots$ Cl2 and O3 $\cdots$ O4 vectors.



Scheme 7. Different types of chelating diphosphinate complexes.



**Fig. 9.** ORTEP of the molecular structure of **10**. Displacement parameters include 40% of the electron density. Only the H atoms bound to heteroatoms are depicted. Selected distances (Å) and angles (°): Zn1–O1 2.032(2), Zn1–O3 1.970(2), Zn1–Cl1 2.236(1), Zn1–Cl2 2.177(1), O1–Cl 1.441(3), O2–C3 1.431(3), O3–P1 1.510(2); O3–Zn1–O1 101.39(9), Cl2–Zn1–Cl1 120.10(5).

best of our knowledge, only one example was reported for Zn [16], while no example is available for Fe and Co. In addition, complexes **6–8** appear to be the first examples of structurally characterized chelating diphosphinate metal complexes. In the few diphosphinate metal complexes reported in the literature [17], the alkoxy group, differently from the cases reported herein, is not comprised in the chelating ring but instead is terminally bound to phosphorus [See (a) in Scheme 7].

The bulky fluorene group probably hinders the formation of conceivable coordination polymers or, more generally, of a bridging coordination mode for ligand **1**.

A hydrolysis product of the Zn(II) complex has been obtained as colourless crystals and its structure, determined by X-ray diffraction (**10**, Fig. 9), established its nature as  $[ZnCl_2(9,9-fluorene-dimethanol){Ph_2P(O)H}]$  (**10**).

In the structure of **10**, the Zn(II) centre is coordinated by 9,9-fluorene-dimethanol through the oxygen of one of the alcohol functions, by a O-bound diphenylphosphine oxide ligand and by two terminal chlorides. The coordination geometry is distorted tetrahedral. The non-coordinated alcohol function is involved in an intramolecular hydrogen bond with one of the terminal chlorides, in such a way that a 8-membered pseudo-chelate ring is formed. The coordinated alcohol group interacts, intermolecularly, with a neighbouring molecule of **10** through hydrogen bonding with O2.

In solution, the  $CH_2$  groups of compound **10** give rise to two, well separated sets of  ${}^{13}C{}^{1}H$  NMR signals and to two AB spin systems in the  ${}^{1}H$  NMR spectrum. This suggests that if an exchange occurs between O1 and O2, it is slow on the NMR time scale.

Compound **10** likely stems from the hydrolysis of the diphosphinite intermediate  $[ZnCl_2(1)]$  (Scheme 5), by cleavage of the two O– P bonds and formation of two molecules of Ph<sub>2</sub>P(O)H (one is found coordinated in **10**) and the corresponding alcohol. Hydrolysis of the phosphinate ligand  $\mathbf{1}_{ox}$  in **8** would give phosphinic acids instead of the observed secondary phosphine oxide Ph<sub>2</sub>P(O)H [18]. Consistently, **10** was obtained during an attempt to crystallize [ZnCl<sub>2</sub>(1)] in THF, in which water has a higher solubility than in CH<sub>2</sub>Cl<sub>2</sub>, the solvent used for the formation of **10**.

# 3. Conclusion

Ligand **1** is a versatile diphosphinite that features a variable bite angle (see complexes **3** vs. **5**.20Tf) when it chelates a metal centre. This angle largely determines the position of the fluorene group, which can be brought orthogonal to the metal coordination plane (bite angle ca. 90°, complex 5.20Tf). The latter conformation facilitates the host-guest capabilities of its complexes [Ag(I) [5], Pd(II)], since the fluorene group, along with the phenyls, participates in the stabilization of cation-anion pairs through multiple H...F and/or H···O interactions. With Fe(II), Co(II) and Zn(II), oxidation of the diphosphinite ligand 1 to diphosphinate 1<sub>ox</sub> occurs. Complexes [MCl<sub>2</sub>(1<sub>ox</sub>)] (M = Fe(II) 6, Co(II) 7, Zn(II) 8) represent the first structurally characterized diphosphinate metal chelates. The diamagnetic Zn(II) diphosphinite complex 9 could be observed and we have shown that its oxidation to 8 proceeds stepwise, through the intermediacy of a mono-oxidized phosphinite-phosphinate complex.

# 4. Experimental

# 4.1. General information

All solvents were dried and freshly distilled under nitrogen prior to use using common techniques. All manipulations were carried out using Schlenk techniques. <sup>1</sup>H (300 MHz), <sup>13</sup>C{<sup>1</sup>H} (75 MHz), <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz) spectra were recorded on a Bruker AC300 instrument. FT-IR spectra were recorded on a Thermo-Electron 6700 spectrometer with ATR techniques (key to infrared absorption intensities: vs, very strong; s, strong; m, medium; w, weak). Elemental analyses were performed by the "Service de Microanalyses", Université de Strasbourg. Ligand **1**, complex [PdCl<sub>2</sub>(**1**)] (**3**) [5], [NiCl<sub>2</sub>(DME)] [19] and [PtCl<sub>2</sub>(NCPh)]<sub>2</sub> [20] were prepared according to published procedures. Anhydrous FeCl<sub>2</sub> and ZnCl<sub>2</sub> were obtained by treating the hydrated salts in refluxing thionyl chloride and anhydrous blue CoCl<sub>2</sub> by heating the hydrated salt under vaccum.

# 4.2. Synthesis of complex $[NiCl_2(1)]$ (2)

Solid  $[NiCl_2(DME)]$  (DME = dimethoxyethane) (0.110 g, 0.50 mmol) was added to a solution of ligand 1 (0.298 g, 0.50 mmol) in  $CH_2Cl_2$  (50 mL). The colour of the reaction mixture became orange immediately. The solution was stirred at room temperature under N2 for 3 h. The volatiles were removed under vacuum, affording a red solid which was washed with diethyl ether  $(2 \times 20 \text{ mL})$ . The red powder obtained was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (30 mL). Petroleum ether (60 mL) was slowly layered onto the solution, yielding red crystals of **2** CH<sub>2</sub>Cl<sub>2</sub> (0.312 g, yield: 77%). The NMR data of **2** revealed a tetrahedral-square planar equilibrium, which resulted in broad resonances due to the paramagnetism of the solution. The <sup>1</sup>H NMR spectrum is reported in the supplementary information, while no <sup>31</sup>P NMR signals were observed, even from saturated solutions (see main text). Selected IR absorption: 1183(w), 1108(m), 1068(s), 1011(vs), 996(vs), 828(s), 742(s), 731(s), 697(vs). Anal. Calc. for C<sub>39</sub>H<sub>32</sub>O<sub>2</sub>P<sub>2</sub>Cl<sub>2</sub>Ni·CH<sub>2</sub>Cl<sub>2</sub> (M<sub>w</sub> = 809.15): C, 59.37; H, 4.24. Found: C, 58.59; H, 4.40%.

#### 4.3. Synthesis of complex $[PtCl_2(1)]$ (4)

Solid [PtCl<sub>2</sub>(NCPh)<sub>2</sub>] (0.236 g, 0.50 mmol) was added to a solution of ligand 1 (0.298 g, 0.50 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL). The pale yellow reaction mixture was stirred at room temperature under N<sub>2</sub> for 3 h. The volatiles were removed under vacuum, affording a pale yellow powder which was washed with diethyl ether (2  $\times$  20 mL). The pale yellow solid obtained was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and pentane (40 mL) was slowly layered onto the solution, yielding colourless crystals of 4 2CH<sub>2</sub>Cl<sub>2</sub> (0.324 g, yield: 63%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 3.90 \text{ (d, 4H }^{3}\text{/}(^{31}\text{P},^{1}\text{H}) = 9.2 \text{ Hz}; \text{ CH}_{2}\text{)}, 7.23-8.12 \text{ ppm (m, 28H; 28H)}$ aryls);  ${}^{31}P{}^{1}H$  NMR (CDCl<sub>3</sub>):  $\delta$  = 96.1 ppm (s, with  ${}^{195}Pt$  satellites,  ${}^{1}J({}^{31}P,{}^{195}Pt) = 4150 \text{ Hz}); {}^{13}C{}^{1}H} \text{ NMR} (CD_2Cl_2): \delta = 53.5 (s;)$ CH<sub>2</sub>CCH<sub>2</sub>), 70.4 (s; CH<sub>2</sub>), 120.4 (s; fluorene), 125.7 (s; fluorene), 127.7 (s; fluorene), 128.5 (virtual triplet,  ${}^{3+5}J({}^{31}P, {}^{13}C) = 12.0$  Hz, <sup>2</sup>*I*(<sup>31</sup>P, <sup>31</sup>P) = 6.8 Hz; *m*-phenyls), 129.1 (s; fluorene), 132.2 (s; *p*phenyls), 132.2 (d, <sup>1</sup>/(<sup>31</sup>P,<sup>13</sup>C) = 32.2 Hz; *i*-phenyls), 133.7 (virtual triplet,  ${}^{2+4}I({}^{31}P,{}^{13}C) = 11.6$  Hz,  ${}^{2}I({}^{31}P,{}^{31}P) = 6.8$  Hz; o-phenyls), 140.8, (s; fluorene) 143.2 (s; fluorene). Anal. Calc. for C<sub>39</sub>H<sub>32</sub>O<sub>2</sub>P<sub>2</sub> Cl<sub>2</sub>Pt·2CH<sub>2</sub>Cl<sub>2</sub> (M<sub>w</sub> = 1030.47): C, 47.79; H, 3.52. Found: C, 48.41; H, 3.51%.

# 4.4. Synthesis of complex $[Pd(\mu-Cl)(1)]_2(OTf)_2$ (5.20Tf)

A solution of AgOTf (0.051 g, 0.20 mmol) in MeCN (5 mL) was added dropwise to a solution of complex 3 (0.154 g, 0.20 mmol) in THF (30 mL). The colourless suspension was stirred for 1 h at room temperature. The reaction mixture was filtered and the volatiles removed under vacuum affording a yellow solid, which was washed with diethyl ether ( $2 \times 20$  mL). The yellow powder obtained was dissolved in CHCl<sub>3</sub> (10 mL). Pentane (20 mL) was layered onto the solution, affording yellow crystals of 5.20Tf 2CHCl<sub>3</sub> (0.113 g, yield (based on Pd) = 56%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 4.5 \text{ (br,}$ 8H; CH<sub>2</sub>), 7.30–8.10 ppm (m, 56H; aryls); <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta = 114.3 \text{ ppm}$  (s);  ${}^{13}C{}^{1}H{}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 55.0$  (t,  ${}^{3}J({}^{31}P,{}^{13}C) = 5.7 \text{ Hz}; CH_{2}CCH_{2}), 74.4 (s; CH_{2}), 120.7 (s; fluorene),$ 126.2 (s; fluorene), 127.9 (s; fluorene), 129.1 (br; *m*-phenyls), 129.4 (s; fluorene), 132.5 (br; o-phenyls), 133.4 (s; p-phenyls), 133.8 (br; fluorene), 140.8 (s; fluorene). Anal. Calc. for  $C_{80}H_{64}O_{10}P_4F_6S_2Cl_2Pd_2 \cdot 2CHCl_3$  (M<sub>W</sub> = 2009.87): C, 49.00; H, 3.31. Found: C, 49.40; H, 3.77%.

#### Table 3

ollection and structure refinement data for <b>2</b> CH <sub>2</sub> Cl <sub>2</sub> , <b>3</b> 2CHCl <sub>3</sub> , <b>5</b> 2OTf 2CHCl <sub>3</sub> .
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#### 4.5. Synthesis of complex $[FeCl_2(1_{ox})]$ (6)

Anhydrous FeCl<sub>2</sub> (0.063 g, 0.50 mmol) was added to a solution of ligand **1** (0.297 g, 0.50 mmol) in THF (40 mL). The yellow reaction mixture was stirred for 24 h at room temperature. The volatiles were removed under vacuum affording a viscous yellow oil, which was washed with ethyl ether ( $2 \times 30$  mL). The yellow powder obtained was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL). Pentane (20 mL) was layered onto it, yielding yellow crystals of **6** after 3 days (0.203 g, yield: 54%). The FT-IR spectrum of **6** is reported in the supporting information. Selected IR absorptions: v(P=0) 1191(vs), 1170(s, sh). Anal. Calc. for C<sub>39</sub>H<sub>32</sub>O<sub>4</sub>Cl<sub>2</sub>P<sub>2</sub>Fe (M<sub>W</sub> = 753.37): C, 62.18; H, 4.28. Found: C, 62.16; H, 4.38%.

# 4.6. Synthesis of complex [CoCl<sub>2</sub>(**1**<sub>ox</sub>)] (**7**)

Anhydrous CoCl<sub>2</sub> (0.065 g, 0.50 mmol) was added to a solution of ligand **1** (0.297 g, 0.50 mmol) in THF (40 mL). The blue reaction mixture was stirred for 24 h at room temperature. The volatiles were removed under vacuum affording a blue solid, which was washed with ethyl ether (2 × 30 mL). The blue powder obtained was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 mL). Pentane (40 mL) was layered onto it, yielding blue crystals of **7** (0.280 g, yield: 74%). The FT-IR spectrum of **7** is reported in the supporting information. Selected IR absorptions: v(P=O) 1189(vs), 1167(s, sh). Anal. Calc. for C<sub>39</sub>H<sub>32</sub>O<sub>4</sub>P<sub>2</sub>Cl<sub>2</sub>Co (M<sub>W</sub> = 756.46): C, 61.92; H, 4.26. Found: C, 61.59; H, 4.25%.

#### 4.7. Synthesis of complex $[ZnCl_2(1_{ox})]$ (8), observation of $[ZnCl_2(1)]$ (9)

Solid ZnCl<sub>2</sub> (0.068 g, 0.50 mmol) was added to a solution of ligand **1** (0.297 g, 0.50 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL). The colourless mixture was stirred for 24 h at room temperature. The volatiles were removed under vacuum affording a white solid, which was washed with diethyl ether (2 × 30 mL) (0.362 g, yield: 95%). The powder was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and diethyl ether was layered onto it, yielding colourless crystals of **8**. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 4.44 (d, 4H, <sup>3</sup>J(H,<sup>31</sup>P) = 6.5 Hz; CH<sub>2</sub>); 7.3–8.0 ppm (m, 28H; aryls); <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = 39.1 ppm; the poor solubility of **8** in chlorinated solvents prevented the recording of <sup>13</sup>C{<sup>1</sup>H} spectra. *Anal.* Calc. for

	$2 \cdot CH_2 Cl_2$	3·2CHCl <sub>3</sub>	5.OTf.2(CHCl <sub>3</sub> )
Chemical formula	$C_{39}H_{32}Cl_2NiO_2P_2\cdot CH_2Cl_2$	$C_{39}H_{32}Cl_2O_2P_2Pd\cdot 2(CHCl_3)$	$C_{78}H_{64}Cl_2O_4P_4Pd_2 \cdot 2(CF_3O_3S) \cdot 2(CHCl_3)$
Formula mass	809.12	1010.62	2009.75
Crystal system	Monoclinic	Monoclinic	Triclinic
a (Å)	14.9275(10)	14.9987(7)	15.9078(7)
b (Å)	15.1626(10)	14.8495(3)	16.0971(7)
<i>c</i> (Å)	19.404(2)	19.8687(8)	19.9586(9)
α (°)	90.00	90.00	86.327(2)
β (°)	121.036(10)	96.073(1)	69.724(2)
γ (°)	90.00	90.00	61.915(2)
Unit cell volume (Å <sup>3</sup> )	3763.2(5)	4400.4(3)	4199.2(3)
Temperature (K)	173(2)	173(2)	173(2)
Space group	$P2_1/c$	$P2_1/c$	ΡĪ
Number of formula units per unit cell (Z)	4	4	2
Absorption coefficient ( $\mu/mm^{-1}$ )	0.919	1.015	0.880
Number of reflections measured	22 487	30 999	33 646
Number of independent reflections	9755	9605	16 333
R <sub>int</sub>	0.0535	0.0743	0.0599
Final $R_1$ values $(I > 2\sigma(I))$	0.0594	0.0517	0.0572
Final $wR(F^2)$ values $(I > 2\sigma(I))$	0.1532	0.1156	0.1227
Final $R_1$ values (all data)	0.1075	0.1072	0.1138
Final $wR(F^2)$ values (all data)	0.1772	0.1309	0.1418
Goodness of fit on $F^2$	1.047	0.980	1.032

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Collection and structure refinement data for **6**, **7**, **8** and **10**.

Compound reference	6	7	8	10
Chemical formula	C39H32Cl2FeO4P2	C <sub>39</sub> H <sub>32</sub> Cl <sub>2</sub> CoO <sub>4</sub> P <sub>2</sub>	C <sub>39</sub> H <sub>32</sub> Cl <sub>2</sub> O <sub>4</sub> P <sub>2</sub> Zn	C27H25Cl2O3PZn
Formula mass	753.34	756.42	762.86	564.71
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic
a (Å)	9.9473(3)	10.0142(10)	10.007(4)	12.4850(4)
b (Å)	18.6615(8)	18.4845(11)	18.579(4)	19.7120(8)
<i>c</i> (Å)	19.2969(8)	19.3294(10)	19.247(7)	11.7270(4)
β (°)	90.00	90.00	90.00	116.369(2)
Unit cell volume (Å <sup>3</sup> )	3582.1(2)	3578.0(5)	3578.4(2)	2585.78(16)
Temperature (K)	173(2)	173(2)	173(2)	173(2)
Space group	$P2_{1}2_{1}2_{1}$	$P2_{1}2_{1}2_{1}$	$P2_{1}2_{1}2_{1}$	$P2_1/c$
Number of formula units per unit cell $(Z)$	4	4	4	4
Absorption coefficient ( $\mu/mm^{-1}$ )	0.700	0.758	0.965	1.245
Number of reflections measured	22 234	15 796	7799	13 453
Number of independent reflections	7032	6302	7799	5093
R <sub>int</sub>	0.0593	0.1010	0.0611	0.0836
Final $R_1$ values $(I > 2\sigma(I))$	0.0591	0.0830	0.0456	0.0479
Final $wR(F^2)$ values $(I > 2\sigma(I))$	0.1415	0.0926	0.0801	0.1138
Final R <sub>1</sub> values (all data)	0.0932	0.1279	0.0875	0.0832
Final $wR(F^2)$ values (all data)	0.1529	0.1012	0.0899	0.1264
Goodness of fit on $F^2$	1.038	1.098	0.955	1.010
Flack parameter	0.05(3)	-0.02(2)	0.013(10)	

 $C_{39}H_{32}O_4P_2Cl_2Zn$  (M<sub>W</sub> = 762.91): C, 61.40; H, 4.23. Found: C, 61.58; H, 4.47%. Selected IR absorptions: v(P=O) 1187(vs), 1167(s, sh).

When both reaction and crystallization procedures were performed under argon, complex [ZnCl<sub>2</sub>(1)] (9) was obtained with a spectroscopical 95% purity (impurities are 8 and the aforementioned monoxide, Scheme 5). Spectroscopic data for 9: <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 4.39 (triplet like m, 4H, simulated as ABX spin system (A = B = H; X = P): <sup>2</sup>J(A,B) = 5.8 Hz, <sup>3</sup>J(A,<sup>31</sup>P) = 3.6 Hz, <sup>3</sup>J(B,<sup>31</sup>P) = 1.0 Hz; CH<sub>2</sub>); 7.28–7.88 ppm (m, 28H; aryls); <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = 91.2 ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 55.2 (t, <sup>3</sup>J(<sup>13</sup>C,<sup>31</sup>P) = 4.9 Hz; CH<sub>2</sub>CCH<sub>2</sub>), 70.7 (s; CH<sub>2</sub>), 120.3 (s; fluorene), 126.3 (s; fluorene), 127.5 (s; fluorene), 128.9 (s; *p*-phenyl fluorene), 129.1 (virtual triplet, <sup>2+4</sup>J(<sup>13</sup>C,<sup>31</sup>P) = 17.0 Hz; *o*-phenyls), 131.5 (d, <sup>1</sup>J(<sup>13</sup>C,<sup>31</sup>P) = 25 Hz; *i*-phenyls), 132.4 (s; fluorene), 140.6 (s; fluorene), 143.5 (s; fluorene). The sensitivity of complex **9** prevented the obtention of satisfactory elemental analyses.

Spectroscopic data for **10**: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 2.89 (br, 2H; OH), 4.39 (s, 3H; A,B,B overlapped signals of two AB systems), 4.41 (m, 1H; A of one of the aforementioned AB systems, CH<sub>2</sub>), 7.10–7.95 (m, 18.5H; aryls and masked part of a PH doublet), 9.04 (part of the PH doublet) ppm; <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = 31.1 ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 57.3 (s; CH<sub>2</sub>CCH<sub>2</sub>), 66.4 (s; CH<sub>2</sub>), 71.0 (s; CH<sub>2</sub>) 120.0 (s; fluorene), 124.9 (s; fluorene), 127.2 (s; fluorene), 128.0 (s; fluorene), 129.2 (d, <sup>3</sup>J(<sup>13</sup>C,<sup>31</sup>P) = 13.6 Hz; *m*-phenyl), 131.3 (d, <sup>2</sup>J(<sup>13</sup>C,<sup>31</sup>P) = 12.3 Hz; *o*-phenyls), 131.4 (m; *i*-phenyls), 132.7 (s, *p*-phenyls), 131.5 (d, <sup>1</sup>J(<sup>13</sup>C,<sup>31</sup>P) = 25 Hz; *i*-phenyls), 132.4 (s; fluorene), 140.6 (s; fluorene), 146.1 (s; fluorene).

# 4.8. X-ray data collection, structure solution and refinement for compounds 2·CH<sub>2</sub>Cl<sub>2</sub>, 3·2CHCl<sub>3</sub>, 5·2OTf·2CHCl<sub>3</sub>, 6, 7, 8 and 10

Suitable crystals for the X-ray analysis of compounds  $2 \cdot CH_2 Cl_2$ , **3**·2CHCl<sub>3</sub>, **5**·2OTf·2CHCl<sub>3</sub>, **6**, **7**, **8** and **10** were obtained as described above. The intensity data was collected at 173(2) K on a Kappa CCD diffractometer [21] (graphite monochromated Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å). Crystallographic and experimental details for the structures are summarized in Tables 3 and 4. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (based on  $F^2$ , SHELXL-97) [22] with anisotropic thermal parameters for all the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions (0.97 Å aliphatic, 0.93 Å aromatic; SHELXS-97 procedures) and refined *riding* on the corresponding parent atoms, except those bound to the oxygen and phosphorus atoms in **10** which were found in the  $F_{o} - F_{c}$  maps and refined isotropically.

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# Appendix A. Supplementary material

CCDC 773099, 773100, 773101, 773102, 773103, 773104 and 773105 contain the supplementary crystallographic data for **2**·CH<sub>2</sub>Cl<sub>2</sub>, **3**·2CHCl<sub>2</sub>, **5**·2OTf·2CHCl<sub>3</sub>, **6**, **7**, **8** and **10**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.06.007.

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