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Pd(II) and Ni(II) complexes featuring a "phosphasalen" ligand: synthesis and DFT study[†]

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A phosphorus analog of salen ligands featuring iminophosphorane functionalities in place of the imine groups was synthesised in 2 steps from *o*-diphenylphosphinophenol *via* the preparation of the corresponding bis-aminophosphonium salt. This novel tetradentate ligand (1), which we named phosphasalen, was coordinated to Pd(II) and Ni(II) metal centres affording complexes **6** and **7** respectively, which were characterised by multinuclear NMR, elemental and X-ray diffraction analyses. Both neutral complexes adopt a nearly square-planar geometry around the metal with coordination of all iminophosphorane and phenolate moieties. The electronic properties of these new complexes were investigated by cyclic voltammetry and comparison with known salens was made when possible. Moreover, the particular behaviour of the phosphasalen nickel complex **7** was further investigated through magnetic moment measurements and a DFT study.

Introduction

N,N'-Bis(salicylidine)ethylenediamines generally named "salen" are among the most renowned ligands in catalysis (Scheme 1). Their tremendous popularity can be ascribed to their easy access (a simple condensation of a diamine with a salicylaldehyde) allowing large skeleton variation, their ability to stabilise numerous metals in various oxidation states,¹ and the facile introduction of chirality which has led to the development of a myriad of very successful asymmetric catalysts,² including recoverable ones.³ Salen complexes were demonstrated to be active either for C–C⁴



Scheme 1 Carbon and phosphorus based salen type ligands.

‡ Deceased on March 17th, 2010

or heteroatom– X^5 (X = C or heteroatom) bond formations. For those processes, the electronic properties of the metal centre is of most importance. Therefore, replacing the imine of a salen ligand by an iminophosphorane will open the way to a new class of complexes whose potential in catalysis would contrast with that of salen complexes. With this in mind, we targeted the synthesis of the phosphorus counterparts of salen ligands featuring two phenolates and two iminophosphoranes (P=N) which we propose to name "phosphasalen" (Scheme 1). We expected them to exhibit markedly different steric and electronic properties compared to salen derivatives. Whereas the pyramidal phosphorus of an iminophosphorane bears two R substituents (Scheme 1), the carbon of an imine is trigonal planar with only one R group. In terms of electronics, iminophosphoranes do not possess any π accepting ability because of the absence of any π system and behave as strong σ and π donors thanks to the presence of two lone pairs at the nitrogen atom. All these features explain why iminophosphorane ligands, though much less investigated compared to imine derivatives have attracted the attention of numerous research groups, who have demonstrated their potential in coordination chemistry⁶ and developed catalytic applications.⁷

Synthetically, iminophosphoranes are commonly prepared by a Staudinger reaction⁸ involving the condensation of an azide and a phosphine. This methodology though very clean requires the handling of azides which are generally difficult to prepare or hazardous, so that most research groups employ commercially available derivatives. In order to introduce more functional diversity at the nitrogen atom, we and others preferred a synthetic methodology relying on the Kirsanov reaction⁹ consisting in the initial formation of an aminophosphonium bromide salt followed by its deprotonation. In particular, this has allowed us to develop

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[†] Electronic supplementary information (ESI) available: Crystallographic data for **6**, and **7** as cif files, complete Gaussian reference, computed Cartesian coordinates, energies, three lower frequencies of all optimised structures. CCDC reference numbers 804616 and 804617. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10906e



Scheme 2 Synthesis of phosphasalen ligand 1.

iminophosphorane based tetradentate ligands.¹⁰ In this paper we show how this synthetic methodology can be applied to the preparation of a phosphorus containing salen derivative. Its coordination in a tetradentate manner to Pd(II) and Ni(II) centres is also presented. Cyclovoltammetric studies were conducted to get a quantitative assessment of the electronic properties of phosphasalen complexes compared to salen ones. In the case of the [Ni(phosphasalen)] complex further insight into the electronic and magnetic properties was gained through a comparative DFT study.

Results and discussion

Synthesis of ligand 1 and its coordination to group 10 metal centres

The synthesis of the phosphasalen ligand 1 featuring an ethylene diamine link was first attempted from the protected odiphenylphosphinophenol 2 (Scheme 2), which was prepared following a literature procedure.¹¹ The corresponding phosphonium bromide salt was reacted with ethylenediamine (0.5 equiv.) in the presence of triethylamine (1 equiv.) to give the bisaminophosphonium salt 3 in 70% yield after aqueous work-up. Nevertheless, as the following step involving deprotection of the phenol with anhydrous HCl gas gave irreproducible results, we decided to modify our strategy and performed first the deprotection of the phenol functionality and then the Kirsanov reaction. Odiphenylphosphinophenol 4 was obtained from 2 as decribed,¹¹ its bromination followed by reaction with ethylenediamine in the presence of tributylamine (1 equiv.) gave the expected bisaminophosphonium salt 5 in 63% yield (Scheme 2). Tributylamine was used in place of triethylamine because of the solubility of its ammonium hydrobromine salt in THF which enabled its easy removal. 5 is only poorly soluble in chloroform but was characterised by multinuclear NMR (³¹P, ¹H, ¹³C) in CDCl₃. In ³¹P{¹H} spectroscopy the equivalent phosphorus atoms of 5 appear as a singlet at $\delta(CDCl_3) = 39.3$ ppm. In the ¹H NMR spectrum, the resonances of the bridging methylene protons appear as a doublet $({}^{3}J_{PH} = 10.5)$ Hz) with a chemical shift (δ (CDCl₃) = 3.43 ppm) similar to the one observed for bis(phosphine-aminophosphonium) salts featuring such an ethylenediamine linker.^{10a} On the contrary the resonance of the NH proton appears as a multiplet around 6.80 ppm which is quite shielded compared to the same reference. Then, the phosphasalen ligand 1 was generated from 5 by deprotonation using potassium hexamethyldisilazane (KHMDS, 4 equiv.) in THF at room temperature (Scheme 2). The formation of 1 was monitored by *in situ* ³¹P{¹H} NMR, the completeness of the reaction was indicated by the presence of one singlet at δ (THF) = 18.6 ppm. Potassium bromide salts formed were filtered off, the solvent was evaporated and the obtained residue was washed with petroleum ether to deliver 1 as a white powder in 99% yield. The structure of 1 was unambiguously established by NMR spectroscopy, and elemental analysis.

The coordination behaviour of **1** towards Pd(II) and Ni(II) metal centres was then evaluated (Scheme 3). As we noted that it was unnecessary to isolate the free ligand **1**, all coordination experiments were conducted from the bis-aminophosphonium salt **5**. Thus, for the synthesis of the palladium complex **6**, deprotonation of **5** was carried out in THF, the potassium bromide salts were removed and $[PdCl_2(PhCN)_2]$ was added to the *in situ* generated ligand **1**. The solution turned immediately yellow and after one night stirring at room temperature a brown solid precipitated from the reaction mixture. This solid was dissolved in dichloromethane to eliminate the insoluble potassium salt. After evaporation of dichloromethane and washing of the residue with petroleum ether,



Scheme 3 Coordination of 1 to Pd(II) and Ni(II).

the palladium complex **6** was obtained in 73% yield as a yellow solid. It was characterised by multinuclear NMR spectrocopy and elemental analysis. In ³¹P{¹H} NMR, coordination is indicated by a significant deshielding of the phosphorus nuclei appearing as a singlet at $\delta(CD_2Cl_2) = 33.7$ ppm. In contrast, in the ¹H NMR spectrum little change was seen from ligand **1** except the resonance of the methylene protons which are shifted upfield (2.54 ppm *vs.* 3.42 ppm in **1**).

Note that reactions performed with other palladium precursors failed; with $[Pd(PPh_3)_2Cl_2]$ no coordination was observed whereas with $[Pd(COD)Cl_2]$ the reaction was very slow. Importantly whereas the free ligand is sensitive to moisture, the obtained complex proved to be stable on the bench for weeks as already shown for other iminophosphorane complexes.^{10a}

Definitive evidence concerning the structure of 6 was provided by X-ray crystal analysis of the complex. Suitable crystals were obtained by diffusing petroleum ether into a saturated dichloromethane solution of 6 at room temperature. A view of one molecule of 6 is presented in Fig. 1. The complex crystallised with four molecules of dichloromethane. As expected for a diamagnetic d^8 complex **6** adopts a square planar geometry around the metal with almost no deviation from planarity (O2-N2-N1-O1 dihedral angle $0.05(13)^{\circ}$). The four coordination sites are occupied by the two iminophosphorane and phenolate groups. The bond lengths of the Pd-N and Pd-O were measured at 2.014(3), 2,017(3) and 2.029(2), 2.039(2) Å respectively. Thus these bonds are longer than the Pd-N and Pd-O distances (1.952(2), 1.957(2) and 1.9981(16), 2.0087(16) Å respectively) measured in the corresponding salen complex.¹² Due to the presence of two phenyl substituents on each phosphorus atom, the molecule is also much less planar than related [Pd(salen)]12, as an example the dihedral angle N1-C4-C3-P1 was measured at $25.64(38)^{\circ}$ vs. -3.02° in the imine derivative. In the same manner the flexible ethylene diamine chain is also much more largely deviated from the median plan in 6 than in [Pd(salen)] (N1–C1–C2–N2: 55.76(29)° vs. 34.5°). Concerning the crystal packing no peculiarity was observed for **6** whereas the molecules of the salen complex were axially packed because of π -stacking interactions between the phenyl rings.

A similar procedure was adopted to prepare the phosphasalen nickel complex 7 (Scheme 3). [NiBr₂(DME)₂] (DME: dimethoxyethane) was added to an in situ generated potassium bromide salt free THF solution of 1, inducing a rapid colour change of the solution from pale yellow to deep purple. After 30 min a purple solid precipitated out of the reaction mixture, the colour of which faded. This solid was filtered off and a work-up similar to that described for 6 was carried out. This allowed the isolation of 7 as a purple solid in 82% yield. As for 6, no decomposition in air was noticed. This complex was characterised by multinuclear spectroscopy and elemental analysis. Interestingly, the ³¹P{¹H} NMR spectrum realised in CD₂Cl₂ at room temperature exhibited a broad signal around 33 ppm whereas at -80 °C the signal sharpened to give a nice singlet at $\delta(CD_2Cl_2) = 32.8$ ppm, confirming the coordination of the iminophosphorane moieties. ¹H and ¹³C $\{^{1}H\}$ NMR spectra were recorded at room temperature on a concentrated CD₂Cl₂ solution. The spectra were very similar to those of complex 6, except that the resolution of peaks was lower. Definitive evidence concerning the structure of 7 was brought by X-ray diffraction analysis (see Fig. 2) realised on single crystals obtained by diffusing petroleum ether into a saturated dichloromethane solution of 7. The complex crystallised with one molecule of dichloromethane. In the solid state, complex 7 adopts a nearly square planar geometry with a small deviation from planarity (N2-N1-O1-O2 dihedral angle at 3.64(35)°). The Ni-O bonds are measured at 1.863(4) and 1.881(3) Å while the Ni–N distances are at 1.888(4) and 1.905(4) Å. These bond lengths are on average longer than those recorded for the [Ni(salen)] complex¹³ (1.853 and 1.851 Å for the Ni–O bonds and 1.851 and 1.849 Å for the Ni-N bonds). As observed for



Fig. 1 ORTEP view of complex **6**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected distances (Å) and angles (°): Pd1–N1 2.014(3), Pd1–N2 2.017(3), N1–P1 1.620(3), N2–P2 1.623(3), Pd1–O1 2.029(2), Pd1–O2 2.039(2), N1–Pd1–O1 96.6(1), N1–Pd1–N2 82.6(1), N2–Pd1–O2 96.1(1), O1–Pd1–O2 84.7(2), N1–P1–C3 107.4(2), N2–P2–C21 106.6(2), N1–C1–C2–N2 55.76(29), N1–C4–C3–P1 25.64(38), O2–N2–N1–O1 0.05(13).



Fig. 2 ORTEP view of complex **7**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected distances (Å) and angles (°): Ni1–N1 1.905(4), Ni1–N2 1.888(4), P1–N1 1.613(4), P2–N2 1.617(4), Ni1–O1 1.881(3), Ni1–O2 1.863(4), O1–Ni1–N1 95.4(2), N2–N11–N1 85.4(2), O2–Ni1–N2 95.4(2), O2–Ni1–O1 83.9(2), N1–P1–C3 108.2(2), N2–P2–C21 108.1(2), N2–C2–C1–N1 –45.00(56), N1–C4–C3–P1 22.57(68), N2–N1–O1–O2 3.64(35).

Table 1 Crystal data and structure refinement details for 6 and 7

Complex	6	7
Mol. formula	$C_{38}H_{32}N_2O_2P_2Pd.4(CH_2Cl_2)$	C ₃₈ H ₃₂ N ₂ NiO ₂ P ₂ ,CH ₂ Cl ₂
Mol. weight	1056.70	754.23
Crystal habit	Orange block	Purple needle
Crystal dimens./mm	$0.28 \times 0.18 \times 0.16$	$0.32 \times 0.10 \times 0.04$
Crystal system	Orthorhombic	Monoclinic
Space group	$Pna2_1$	Pc
a/Å	23.441(1)	14.095(1)
b/Å	10.218(1)	9.040(1)
c/Å	19.401(1)	16.233(1)
α (°)	90.00	90.00
$\beta(\circ)$	90.00	122.384(4)
γ (°)	90.00	90.00
V/Å ³	4646.9(6)	1746.7(3)
Z	4	2
$d/g \text{ cm}^{-3}$	1.510	1.434
F(000)	2136	780
μ/cm^{-1}	0.965	0.838
$\theta_{\mu\alpha^{\sharp}}$ ($\delta\epsilon\gamma$.)	30.02	26.00
HKL ranges	-33 31: -10 14: -27 20	-13 17: -10 11: -19 20
No of measd/indep. rflns	44198/12183	9847/5021
No. reflections used	10068	4499
$R_{\rm int}$	0.0323	0.0244
Abs. corr.	multi-scan; 0.7738 min, 0.8608 max	multi-scan; 0.7753 min, 0.9672 max
N° params refined	515	433
Rflns/param.	19	10
$R_1, W R_2$ (I > 2 σ I)	0.0432/0.1104	0.0449/0.1219
Flack's parameter	0.38(2)	0.22(16)
GoF	1.092	1.044
difference peak/hole/e Å ⁻³	1.382(0.082)/-0.874(0.082)	0.909(0.069)/-0.722(0.069)
CCDC number	804616	804617

palladium complex **6**, the overall geometry of the phosphasalen complex is much less planar than the salen counterpart, thus the dihedral angle N1–C4–C3–P2 was measured at 22.57(68)° *vs.* 3.30° on average in the imine derivative. Moreover, while molecules of [Ni(salen)] complexes were axially packed either thanks to π -stacking interactions between the phenyl rings when the carbon of the imine function is unsubstituted¹⁴ or through weak H-bond when this carbon bears a phenyl group,¹⁵ no particular packing was seen for **7**.

In order to compare the electronic properties of phosphasalen and salen complexes the electrochemical properties of **6** and 7 were examined by cyclic voltammetry in a mixture of dicholoromethane/dimethylformamide (volume ratio 60/40) at room temperature using a gold disk as a working electrode and a Pt gauze as a counter electrode. The potentials measured relative to SCE are reported in Table 2. For the sake of comparison with literature data, the potential of ferrocene is also indicated.

For nickel complex 7, no reduction was observed within the potential window (0 V, -2.0 V) considered, and a reversible one electron oxidation took place at 0.58 V ($\Delta E p = 152$ mV). Interestingly for the salen complex oxidation takes place at $E_{1/2}$ (DMF) = 0.81 V, in conditions where oxidation of ferrocene occurs at 0.48 V.¹⁶ Thus, the oxidation potential of the phosphasalen nickel complex 7 is only 0.1 V higher than that of ferrocene, whereas that of the [Ni(salen)] derivative is 0.33 V higher compared to the same reference. This clearly illustrated the better donating ability of the phosphasalen ligand which renders the nickel centre more electron rich and allows an easier oxidation. For the palladium complex 6, electrochemical studies were more difficult due to the more limited solubility of this complex in presence of DMF, thus lower

Table 2Electrochemical data for phosphasalen complexes 6 and 7^a

Complexes	7 ^b	6 ^{<i>d</i>}	Fc
$\overline{E^{\mathrm{a}}_{\mathrm{P1}},\mathrm{V}}$	0.65	0.76	0.55
E^{c}_{P1}, V	0.51		0.43
$E^{1}_{1/2}$	0.58		0.49
$i_{\rm pa}/i_{\rm pc}$	1.00^{c}		1.01
E^{a}_{P2} , V		1.10	
E^{c}_{P2}, V		1.03	
$E^{1}_{1/2}$		1.06	
$i_{\rm pa}/i_{\rm pc}$		1.12"	

^{*a*} Tetrabutylammonium tetrafluoroborate salt as electrolyte (c = 0.12 mol L⁻¹); scan rate = 100 mV s⁻¹; ^{*b*} c = 3.8 mmol L⁻¹; ^{*c*} ratio was observed to change with scan rate with a value of 1.46 at 50 mV s⁻¹; ^{*d*} c = 2.0 mmol L⁻¹; ^{*e*} ratio was observed to change with scan rate with a value of 1.27 at 50 mV s⁻¹.

concentrations were employed. Nevertheless, no reduction was observed within the potential range explored and two oxidation waves were seen. The first one is irreversible at 0.76 V and the second one at 1.06 V which is pseudo-reversible ($I_{\rm pc}/I_{\rm pa} \sim 1.12$) in the presence of a coordinating solvent. Thus, the first oxidation of the palladium complex **6** occurred at a higher potential compared to the nickel counterpart **7** which implies a less electron rich metal centre. Nevertheless a second oxidation can only be seen in the case of the palladium derivative which may be related to the increase of the thermodynamic stability of the highest oxidation states of elements within the row Ni–Pd–Pt.¹⁷ Indeed, for the [Pd(salen)] complex two irreversible oxidation waves were observed¹⁸ at 0.96 and 1.07 V in acetonitrile namely 0.44 and 0.55 V higher than the oxidation potential of ferrocene in the

 Table 3
 Comparison of selected geometric parameters coming from X-ray diffraction analysis and DFT calculations

[Ni(salen)] complex $\begin{array}{c} & & \\ & $		Complex 7 $C_2^{-C_1}$ $P_2Ph_2=N_2$ $N_1=P_1Ph_2$ C_{21} Ni C_3 $C_{22}O_2$ O_1-C_4					
	X-ray	Optimised singlet structure	Optimised triplet structure		X-ray	Optimised singlet structure	Optimised triplet structure
N2–Ni1	1.851(3)	1.857	1.986	N2–Ni1	1.888(4)	1.897	1.966
N1–Ni1	1.849(3)	1.856	1.989	N1-Ni1	1.905(4)	1.894	2.011
Ni–O2	1.853(3)	1.847	1.900	Ni–O2	1.863(4)	1.865	1.914
Ni–O1	1.851(5)	1.848	1.899	Ni-O1	1,881(3)	1.883	1.953
O2–Ni–N2	94.1(4)	94.31	91.6	O2-Ni-N2	95.4(2)	94.7	97.5
O1–Ni–N1	94.2(4)	93.99	91.5	O1-Ni-N1	95.4(2)	95.1	96.3
01–Ni–O2	85.5(4)	85.4	105.2	O1-Ni-O2	83.9(2)	84.4	101.1
N1–Ni–N2	86.3(5)	86.4	82.9	N1-Ni-N2	85.4(2)	85.8	85.8
N1-Ni-N2-O2	178.5	177.5	153.4	N2-Ni-N1-O1	176.40(35)	179.4	127.2
N2-Ni-N1-O1	178.6	177.8	151.4	N1-Ni-N2-O2	178.68(39)	178.8	155.1
02-Ni-01-N1	178.7	177.5	158.5	01-Ni-02-N2	176.38(42)	179.4	130.6
01-Ni-02-N2	178.5	177.8	156.1	02-Ni-O1-N1	178.64(39)	178.8	162.0

same conditions (0.518 V). The first oxidation is thus easier for the phosphasalen derivative (only 0.27 V higher than the ferrocene oxidation potential) in agreement with the presence of a better electron-donating ligand. The second oxidation occurs on the contrary at a comparable potential for the salen derivative and the phosphasalen one (namely 0.55 and 0.58 V higher than $E^{1}_{1/2}$ (Fc⁺/Fc)), but as already established this oxidation in the [Pd(salen)] complex corresponds to the electron transfer from a molecular orbital localised predominantly on the ligand and not on the metal centre.^{186,19}

Contrary to the palladium phosphalen complex which is undoubtedly diamagnetic giving finely resolved NMR spectra, the difficulty to obtain nicely resolved spectra for the nickel derivative at room temperature prompted us to further investigate this complex. Indeed, we wondered if at room temperature the phosphasalen nickel complex 7 would exist under two different spin states (a singlet and a triplet one, the latter perturbing the NMR measurements). Therefore, we also measured the magnetic moment of phosphasalen complex 7 by the Evans method.²⁰ At room temperature a magnetic moment of 1.40 μ_B was measured. This value is very low compared to literature values of $3.0-4.0 \ \mu_B$ expected for fully tetrahedral Ni(II) complexes.²¹ but values around 1.3 μ_B were reported by Braunstein and coworkers for Ni(II) complexes²² adopting a distorted tetrahedral geometry in solution. Therefore the magnetic moment measured in solution for 7 may suggest a distorted geometry (the rigidity of the phosphasalen ligand should exclude a tetrahedral geometry) and/or that the triplet state is partially populated (the NMR is not silent at room temperature).23

As such an observation was not made for salen Ni(II) complexes either we undertook a theoretical study to compare the electronic properties of the [Ni(salen)] and [Ni(phosphasalen)] complexes.

Theoretical study of Ni(II) phosphasalen and salen complexes

Density functional theory (DFT) calculations were performed on (N,N'-ethylene-bis(salicylideneiminato))nickel and phosphasalen

nickel complex 7 with the Gaussian 03 set of programs²⁴ in combination with the B3PW91 functional²⁵ (see experimental section for further details). Optimizations of both complexes 7 and [Ni(salen)] were performed in the singlet and triplet states. Table 3 gathers some selected geometric parameters for each optimised structure together with the available experimental data from X-ray diffraction analysis.¹³ On the whole there is an excellent agreement between the experimental structure and the theoretical parameters optimised for the singlet state.

A nearly square planar geometry was found for both complexes with dihedral angles around the metal centre lying between 176 and 179°. Mean deviations of 0.01 Å were found for the bond lengths and 1° for the bond angles.

In both complexes, the HOMO involves a d orbital on the metal centre in π antibonding interaction with the oxygen and nitrogen ligands (Fig. 3). However the HOMO of the phosphasalen complex is significantly higher in energy than that of the salen complex (-4.56 instead of -5.12 eV). As a consequence the vertical ionisation energy calculated for the phosphasalen complex (5.73 eV) is lower than that for the salen complex (6.49 eV), a result in agreement with the easier oxidation found experimentally for the former.

Two major geometrical changes were found going from the singlet to the triplet state. First there is a distortion from the square planar geometry toward a distorted tetrahedral geometry. This change is illustrated by the dihedral angles given in Table 3 which vary from nearly 180° (the value for an ideal square planar arrangement) in the singlet state to values between 162 and 127° (instead of 120° for an ideal tetrahedral structure) in the triplet state. Such a rearrangement was expected for the low spin-high spin change in complexes of d⁸-ML₄ type. Note however that the geometrical evolution is larger for the more flexible phosphasalen than for the salen complex (mean value of 143.7° for the dihedral angles instead of 154.9° for the latter). On the other hand, the metal–ligand bond distances were found to be significantly longer in the triplet than in the singlet state, by 0.094 and 0.076 Å in the salen and the phosphasalen complexes, respectively (mean values).



Fig. 3 HOMO of [Ni(salen)] (a) and [Ni(phosphasalen)] (b) complexes given by DFT calculations.

Formation of the triplet state in the square planar singlet state involves first removing one electron of the HOMO. According to the metal–ligand π antibonding character of this orbital (see Fig. 3), it should shorten the metal–ligand bond distances. However the electron left from the HOMO now occupies an orbital which was vacant in the singlet state, the fifth d orbital of these d⁸ complexes. Since it is strongly σ antibonding between the metal and the ligands (Fig. 4), its occupation entails a lengthening of the metal–ligand bonds. So two factors work in opposite directions but the latter dominates (the σ antibonding interactions are stronger than the π ones). A lengthening of the metal–ligand distances thus occurs on going to the high spin state, a trend which is preserved upon distortion toward a pseudo-tetrahedral arrangement (see Table 3).

From an energetic point of view the singlet state was found to be 9.0 kcal mol⁻¹ more stable than the triplet state for the salen complex in agreement with the experimental evidence for a low spin complex in solution.²⁶ A strikingly different situation was found for the phosphasalen complex with a triplet state slightly more stable than the singlet state ($\Delta E = -1.4$ kcal mol⁻¹). A triplet ground state in solution as well as a small singlet-triplet energy difference (which suggests that both spin configurations could coexist in solution), are in agreement with the experimental measurement of the magnetic moment of complex 7. In order to rationalise the evolution of the singlet-triplet energy difference $(\Delta E_{\rm ST})$, we made use of the following thermodynamical cycle (Scheme 4): i) starting from the optimised square planar singlet state (¹[SP]), one electron is removed from the HOMO keeping the geometry of the complex unchanged (\rightarrow [SP]⁺); the energy associated with this first step (ΔE_1) is the vertical ionisation



Fig. 4 Antibonding d orbital involved in the singlet triplet excitation for the salen (a) and phosphasalen (b) complex.



Scheme 4 Thermodynamical cycle to determine the singlet–triplet energy difference (ΔE_{ST}).

energy of the complex; ii) the removed electron is placed in the antibonding d orbital depicted in Fig. 4 leading to the triplet state in the square planar geometry (\rightarrow ³[SP] with an energy change of ΔE_2); iii) finally, the geometry is relaxed to reach the equilibrium geometry for the triplet state (\rightarrow distorted tetrahedral structure, ³["Td"] with an energy change of ΔE_3).

The computed energy changes associated with each step as well as the total energy change ($\Delta E_{\rm ST}$) are reported in Table 4 for both salen and phosphasalen complexes. It clearly appears that the electronic factor responsible for the lowering of the $\Delta E_{\rm ST}$ energy difference between the singlet and the triplet states (by 10.4 kcal mol⁻¹) is the major lowering (by 17.5 kcal mol⁻¹) of the ionisation energy in going from the salen to the phosphasalen complex (see third line in Table 4).

Table 4	Energy decomposition (kcal mol ⁻¹), according to Scheme 4, of
the single	et-triplet energy difference for salen and phosphasalen complexes

	ΔE	ΔE_2	ΔE_3	$\Delta E_{ m ST}$
[Ni(salen)] [Ni(phosphasalen)] ΔE([Ni(salen)]-[Ni(phosphasalen)])	149.6 132.1 -17.5	-129.6 -122.0 +7.0	-11.0 -11.5 -0.5	+9.0 -1.4 -10.4

Conclusions

In conclusion we have presented the synthesis of a novel tetradentate ligand combining iminophosphoranes and phenolates designated as phosphasalen since it can be viewed as a phosphorous analog of a salen derivative. The coordination of this ligand to Pd(II) and Ni(II) metal centres gave stable neutral nearly square planar complexes, which were characterised by NMR spectrocopy, elemental analyses and X-ray diffraction analysis. In order to shed light on the electronic differences between the salen and phosphasalen complexes, cyclic voltammetry experiments were realised. As anticipated considering the better donating ability of the iminophosphorane based ligands, oxidation was easier for the phosphorus contained complexes compared to the salen ones. Moreover as the [Ni(phosphasalen)] complex 7 displayed a magnetic moment measured at 1.40 μ_B suggesting a low lying triplet state, we carried out a comparative DFT study of [Ni(salen)] and [Ni(phosphasalen)] to shed light on the differences observed for these two complexes. Calculations confirm a small singlettriplet energy difference (1.4 kcal mol⁻¹) in favour of the triplet state. This divergent behaviour for carbon and phosphorus based complexes was mainly traced to an easier ionisation of the phosphasalen complex. We are now pursuing a coordination study of phosphasalen ligands. They are currently applied in homogeneous catalysis and results on this topic will be reported in due course. The synthesis of chiral derivatives is also currently explored.

Experimental section

Synthesis

General considerations. All experiments, unless otherwise stated, were performed under an atmosphere of dry nitrogen or argon using standard schlenk and glove box techniques. Solvents were freshly distilled under dry nitrogen from Na/benzophenone (THF, diethylether, petroleum ether), from P_2O_5 (dichloromethane). O-diphenylphosphinophenol 4,¹¹ [NiBr₂(DME)]²⁷ and [PdCl₂(PhCN)₂]²⁸ were prepared according to the literature. All other reagents and chemicals were obtained commercially and used without further purification. Nuclear magnetic resonance spectra were recorded on a Bruker Avance 300 spectrometer operating at 300 MHz for ¹H, 75.5 MHz for ¹³C and 121.5 MHz for ³¹P. Solvent peaks were used as internal references for ¹H and ¹³C chemical shifts (ppm). ³¹P are relative to a 85% H₃PO₄ external reference. Coupling constants are expressed in hertz. The following abbreviations are used: br, broad; s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiplet; v, virtual. The labeling schemes of the phosphasalen derivatives are given in Schemes 1 and 2. IR spectra were recorded on a Perkin Elmer spectrometer and are reported in terms of frequency of absorption

(cm⁻¹) using for the intensity the following abbreviations: w (weak), m (medium), s (strong). Electronic ionization mass spectra (EI-MS) were recorded with a JEOL GCmate instrument. Elemental analyses were performed by the elemental analysis service of the London Metropolitan University (United Kingdom).

Synthesis of 5. Br₂ (213 µL, 4.14 mmol) was added to a solution of *o*-diphenylphosphinophenol 4 (1.153 g, 4.14 mmol) in dichloromethane (30 mL) at -78 °C. The cold bath was then removed. After one hour stirring at room temperature, the resulting pale yellow solution was cooled down to -78 °C. Tributylamine (987 µL, 4.14 mmol) and then ethylenediamine (138.5 µL, 2.07 mmol) were added to this solution. Stirring was continued for 2 days at room temperature to yield a yellow solution and a white precipitate. Dichloromethane was evaporated under vacuum. THF (30 mL) was introduced resulting in the formation of a heavy white slurry. The white solid was separated by filtration under N₂, washed with THF (4 × 10 mL), and dried under vacuum (1.060 g, 63%).

³¹P{¹H} NMR (CDCl₃): δ 39.3 (s, P^{V}); ¹H NMR (CDCl₃): δ 7.67–7.59 (12H, m, *p*-C*H*(PPh₂), *o*-C*H*(PPh₂)), 7.52–7.46 (12H, m, *m*-C*H*(PPh₂), C_aH, C_bH), 6.86–6.75 (4H, m, C_cH, NH), 6.57 (2H, dd, ³J_{HH} = 8.0 Hz, ³J_{PH} = 14.5 Hz, C_dH), 3.43 (4H, d, ³J_{PH} = 10.5 Hz, CH₂); ¹³C{¹H} NMR (CDCl₃): δ 159.7 (d, ²J_{PC} = 0.5 Hz, OC^{IV}), 136.1 (d, ⁴J_{PC} = 1.0 Hz, C_bH), 133.3 (d, ²J_{PC} = 11.5 Hz, C_dH), 133.1 (d, ⁴J_{PC} = 3.0 Hz, *p*-CH(PPh₂)), 131.9 (d, ²J_{PC} = 11.5 Hz, *o*-CH(PPh₂)), 128.5 (d, ³J_{PC} = 13.5 Hz, *m*-CH(PPh₂)), 121.4 (d, ¹J_{PC} = 106.5 Hz, C^{IV}(PPh₂)), 119.6 (d, ³J_{PC} = 13.5 Hz, C_cH), 117.7 (d, ³J_{PC} = 7.0 Hz, C_aH), 106.8 (d, ²J_{PC} = 104.0 Hz, PPh₂C^{IV}), 43.3 (d, ²J_{PC} = 1.5 Hz, CH₂). HR-EI-MS: 307.1132 ([M–2Br]²⁺; C₃₈H₃₆N₂O₂P₂²⁺; calcd 307.1126.

Synthesis of 1. KHMDS (1.165 g, 5.84 mmol) was added to a suspension of **5** (1.130 g, 1.46 mmol) in THF (50 mL). After overnight stirring, potassium bromide was removed by filtration, giving a colorless solution. THF was evaporated *in vacuo* to yield a white solid, which was washed twice with petroleum ether (50 mL) giving **1** (0.992 g, 99%).

³¹P{¹H} NMR (THF-D₈): δ 18.6 (s, P^{V}); ¹H NMR (THF-d₈): δ 7.73–7.67 (8H, m, *o*-CH(PPh₂)), 7.62–7.57 (4H, m, ⁵J_{P,H} = 1.5 Hz, p-CH(PPh₂)), 7.55-7.49 (8H, m, m-CH(PPh₂), 7.09 (2H, ddd, ${}^{3}J_{H,H} = 8.5 \text{ Hz}, {}^{3}J_{H,H} = 7.0 \text{ Hz}, {}^{4}J_{H,H} = 1.5 \text{ Hz}, \text{ C}_{b}H$, 6.60 (2H, vt, ${}^{3}J_{\text{H,H}} = 8.5 \text{ Hz}, {}^{4}J_{\text{P,H}} = 8.5 \text{ Hz}, \text{C}_{a}H), 6.47 (2\text{H}, \text{ddd}, {}^{3}J_{\text{H,H}} = 7.0 \text{ Hz},$ ${}^{3}J_{P,H} = 16.0 \text{ Hz}, {}^{4}J_{H,H} = 1.5 \text{ Hz}, C_{d}H), 6.05 (2H, vtd, {}^{3}J_{H,H} = 7.0$ Hz, ${}^{4}J_{PH} = 3.0$ Hz, C_cH), 3.42 (4H, dd, ${}^{3}J_{PH} = 6.0$ Hz, ${}^{3}J_{P'H} = 6.5$ Hz, CH₂); ¹³C{¹H} NMR (THF-d₈): δ 174.3 (d, ²J_{PC} = 3.5 Hz, OC^{IV}), 132.9 (d, ${}^{2}J_{PC}$ = 13.0 Hz, C_{d} H), 132.8 (d, ${}^{1}J_{PC}$ = 77.0 Hz, $C^{IV}(PPh_2)$), 132.1 (d, ${}^{4}J_{P,C} = 1.5$ Hz, C_b H), 131.7 (d, ${}^{2}J_{P,C} = 8.0$ Hz, o-CH(PPh₂)), 129.0 (d, ${}^{4}J_{P,C} = 2.0$ Hz, p-CH(PPh₂)), 127.0 (d, ${}^{3}J_{PC} = 10.5 \text{ Hz}, m-CH(PPh_{2})), 121.8 (d, {}^{3}J_{PC} = 9.0 \text{ Hz}, C_{a}H), 112.5$ (d, ${}^{1}J_{P,C} = 128.5$ Hz, PPh₂C^{IV}), 107.0 (d, ${}^{3}J_{P,C} = 15.0$ Hz, C_cH), 50.4 $(dd, {}^{2}J_{P,C} = 27.0 \text{ Hz}, {}^{3}J_{P,C} = 8.0 \text{ Hz}, CH_{2}); \text{ IR } (cm^{-1}): 1588 \text{ (m)}, 1535$ (w), 1469 (s), 1455 (m), 1444 (m), 1349 (m), 1255 (m), 1136 (s), 1104 (m), 1060 (m), 1031 (w), 991 (w), 846 (m), 813 (w), 788 (w), 762 (s), 736 (m), 707 (s), 675 (w). Anal. Calcd for $C_{38}H_{32}K_2N_2O_2P_2$: C, 66.26; H, 4.68; N, 4.07. Found: C, 66.19; H, 4.73; N, 3.99.

Synthesis of 6. THF (5 mL) was added to a mixture of KHMDS (94.3 mg, 0.47 mmol) and 5 (91.4 mg, 0.12 mmol). After 2 h, potassium salt was removed by centrifugation and

 $[PdCl_2(PhCN)_2]$ (45.3 mg, 0.12 mmol) was added to the obtained colorless solution, which became immediately yellow. After 16 h, the precipitated brown solid was separated by centrifugation, dissolved in dichloromethane to remove the insoluble potassium salt. Then the solvent was evaporated and the obtained residue was washed with petroleum ether (5 mL) to give **6** as a yellow solid (63 mg, 73%)

³¹P{¹H} NMR (CD₂Cl₂): δ 33.7 (s, P^{V}); ¹H NMR (CD₂Cl₂): δ 7.55-7.46 (12H, m, o-CH(PPh₂), p-CH(PPh₂)), 7.44-7.38 (8H, m, m-CH(PPh₂)), 7.07 (2H, vtdd, ${}^{3}J_{H,H} = 7.0$ Hz, ${}^{3}J_{H,H} = 8.5$ Hz, ${}^{4}J_{H,H} =$ 1.5 Hz, ${}^{5}J_{P,H} = 0.5$ Hz, $C_{b}H$), 6.78 (2H, ddd, ${}^{3}J_{H,H} = 8.5$ Hz, ${}^{4}J_{H,H} =$ 1.0 Hz, ${}^{4}J_{PH} = 6.5$ Hz, $C_{a}H$), 6.32 (2H, ddd, ${}^{3}J_{H,H} = 8.0$ Hz, ${}^{4}J_{H,H} =$ 1.5 Hz, ${}^{3}J_{PH} = 16.0$ Hz, $C_{d}H$), 6.18 (2H, dddd, ${}^{3}J_{HH} = 8.0$ Hz, ${}^{3}J_{\rm H,H} = 7.0$ Hz, ${}^{4}J_{\rm H,H} = 1.0$ Hz, ${}^{4}J_{\rm P,H} = 3.0$ Hz, C_cH), 2.54 (4H, vt, $J_{P,H} = 4.5 \text{ Hz}, CH_2$; ¹³C{¹H} NMR (CD₂Cl₂): δ 172.5 (s, OC^{IV}-), 134.9 (br. s, C_b H); 134.2 (d, ${}^{2}J_{PC} = 10.0$ Hz, o-CH(PPh₂)), 133.3 (br. s, ${}^{4}J_{PC} = 1.0$ Hz, p-CH(PPh₂)), 133.1 (${}^{2}J_{PC} = 13.0$ Hz, C_{d} H), 129.7 (d, ${}^{3}J_{P,C} = 12.0$ Hz, m-CH(PPh₂)), 127.2 (d, ${}^{1}J_{P,C} = 89.0$ Hz, $C^{IV}(PPh_2)$), 122.8 (d, ${}^{3}J_{P,C} = 8.0$ Hz, C_a H), 114.0 (d, ${}^{3}J_{P,C} = 15.0$ Hz, C_{c} H), 110.4 (d, ${}^{1}J_{PC} = 122.0$ Hz, PPh₂ C^{IV}), 53.8 (dd, ${}^{2}J_{PC} =$ 17.5 Hz, ${}^{3}J_{P,C} = 5.0$ Hz, CH_{2}); IR (cm⁻¹): 1586 (m), 1534 (w), 1459 (m, v_{cc} aromatic), 1442 (s), 1327 (m), 1257 (m), 1124 (w), 1110(s), 1084(w), 1069(w), 1020 (w), 1000 (w), 867 (m, b), 800 (m), 769 (w), 747 (s), 722 (w), 710 (w), 693 (s). Anal. Calcd for $C_{38}H_{32}N_2O_2P_2Pd$: C, 63.65; H, 4.50; N, 3.91. Found: C, 63.74; H, 4.30; N, 3.94.

Synthesis of 7. THF (5 mL) was added to a mixture of KHMDS (94.3 mg, 0.47 mmol) and 5 (91.4 mg, 0.12 mmol). After 2 h, potassium salt was removed by centrifugation and [NiBr₂(DME)] (36.4 mg, 0.12 mmol) was added to the obtained colorless solution which became immediately deep purple. After 30 min, a purple solid precipitated out from the mixture and the color of the solution faded. The solid was separated by centrifugation, and then dissolved in dichloromethane to remove the insoluble potassium salt. Evaporation of the solvent residue and washing with petroleum ether (5 mL) gave 7 as a purple solid (65 mg, 82%).

³¹P{¹H} NMR (CD₂Cl₂): δ 32.8 (s, P^{V}); ¹H NMR (CD₂Cl₂): δ 7.76–7.66 (12H, m, o-CH(PPh₂), p-CH(PPh₂)), 7.62–7.56 (8H, m, m-CH(PPh₂), 7.10 (2H, vtd, ${}^{3}J_{H,H} = 7.5$ Hz, ${}^{4}J_{H,H} = 1.5$ Hz, C_bH), 6.69 (2H, dd, ${}^{3}J_{H,H} = 7.5$ Hz, ${}^{3}J_{P,H} = 6.5$ Hz, $C_{a}H$), 6.49 (2H, ddd, ${}^{3}J_{\rm H,H} = 7.5$ Hz, ${}^{4}J_{\rm H,H} = 1.5$ Hz, ${}^{3}J_{\rm P,H} = 15.0$ Hz, C_dH), 6.26 (2H, vtd, ${}^{3}J_{H,H} = 7.5 \text{ Hz}, {}^{4}J_{P,H} = 3.0 \text{ Hz}, C_{c}H), 2.16-2.13 (4H, m, CH_{2});$ ¹³C{¹H} NMR (CD₂Cl₂): δ 170.1 (s, OC^{IV}), 133.3 (d, ⁴J_{PC} = 1.0 Hz, C_b H), 133.1 (d, ${}^{2}J_{P,C} = 10.0$ Hz, o-CH(PPh₂)), 132.3 (d, ${}^{4}J_{P,C} =$ 2.0 Hz, p-CH(PPh₂)), 131.2 (${}^{2}J_{PC} = 12.0$ Hz, C_{d} H), 128.9 (d, ${}^{3}J_{PC} =$ 12.0 Hz, *m*-CH(PPh₂)), 127.4 (d, ${}^{1}J_{P,C} = 90.5$ Hz, $C^{IV}(PPh_{2})$), 122.7 (d, ${}^{3}J_{P,C} = 8.0$ Hz, C_{a} H), 113.1 (d, ${}^{3}J_{P,C} = 14.5$ Hz, C_{c} H), 108.0 (d, ${}^{1}J_{P,C} = 119.6$ Hz, PPh₂- C^{IV}), 50.0 (dd, ${}^{2}J_{P,C} = 16.0$ Hz, ${}^{3}J_{P,C} = 2.0$ Hz, CH₂); IR (cm⁻¹): 1586 (m), 1534 (w), 1459 (m), 1440 (s), (1300 m), 1275 (m), 1137 (w), 1116(s), 1098(m), 1081(m), 1027 (m), 1000 (w), 889 (w), 867 (w), 861(w), 811 (m), 778 (w), 752 (s), 727 (w), 710 (w), 697 (s). Anal. Calcd for C₃₈H₃₂N₂NiO₂P₂: C, 68.19; H, 4.82; N, 4.19. Found: C, 68.00; H, 4.74; N, 4.05.

X-ray crystallography

Data were collected at 150 K on a Kappa APEX II diffractometer using a Mo-K α ($\lambda = 0.71069$ Å) X-ray source and a graphite monochromator. Experimental details are described in Table 1 The crystal structure were solved using SIR 97²⁹ and Shelxl-97.³⁰ ORTEP drawings were made using ORTEP III for Windows.³¹

Electrochemical study

The electrochemical experiments were performed using a Vestastat potentiostat/galvanostat with a three-electrode cell using a Au disk as working electrode, a Pt gauze as the counter electrode, and a saturated calomel electrode as the reference electrode. Measurements were made in a CH_2Cl_2/DMF solvent mixture (60/40) with a concentration of 3.8 mmol L⁻¹ and 2.0 mmol L⁻¹ for the nickel and palladium complexes respectively. Tetrabutylammonium tetrafluoroborate salt served as electrolyte (concentration 0.12 mol L⁻¹). Potentials were recorded at 50 mV s⁻¹.

Computational details

DFT calculations were performed with the Gaussian 03 series of programs²⁴ with the B3PW91 functional.²⁵ Nickel was represented by the relativistic effective core potential of Hay and Wadt^{32a} and the associated triple zeta quality basis set,^{32b} augmented by a f polarization function as proposed by Frenking^{32c}. All non-metallic atoms were described with the 6-31G* Pople basis set. The optimised structures were characterised by vibration frequencies calculations.

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