Assembly of symmetrical and unsymmetrical platinum(II) rollover complexes with bidentate phosphine ligands

ARTICLE *in* DALTON TRANSACTIONS · AUGUST 2014

Impact Factor: 4.2 · DOI: 10.1039/c4dt02080d · Source: PubMed

5 AUTHORS, INCLUDING:

Giuseppina Zuri
Glycom A/S
4 PUBLICATIONS **24** CITATIONS
SEE PROFILE

Sergio Stoccoro
Università degli Studi di Sassari
84 PUBLICATIONS **1,643** CITATIONS
SEE PROFILE

Maria Agostina Cinellu
Università degli Studi di Sassari
137 PUBLICATIONS **2,985** CITATIONS
SEE PROFILE

Antonio Zucca
Università degli Studi di Sassari
92 PUBLICATIONS **1,630** CITATIONS
SEE PROFILE

Dalton Transactions

PAPER

View Article Online
View Journal | View Issue

Cite this: *Dalton Trans.*, 2014, **43**, 14806

Assembly of symmetrical and unsymmetrical platinum(II) rollover complexes with bidentate phosphine ligands†

Luca Maidich,‡§ Giuseppina Zuri, Sergio Stoccoro,§ Maria Agostina Cinellu§ and Antonio Zucca*§

Received 9th July 2014,
Accepted 5th August 2014

DOI: 10.1039/c4dt02080d

www.rsc.org/dalton

The reaction of the cyclometalated rollover complex [Pt(bpy-H)(Me)(DMSO)] (bpy-H = cyclometalated 2,2′-bipyridine) with two diphosphines, dppm (1,1-bis(diphenylphosphino)methane) and dppe (1,2-bis-(diphenylphosphino)ethane), was investigated. According to the reaction conditions, dppm behaves as a monodentate, bridging or chelated ligand, whereas dppe gave only chelated species. Some aspects of the reactivity of the isolated species were studied, including protonation with [H_3O·18-crown-6][BF_4] and coordination reactions of mononuclear complexes, obtaining, *inter alia*, rare examples of unsymmetrical organometallic species with bridging dppm.

Introduction

The chemistry of cyclometalated complexes of platinum group metals is of great current interest,[1] both for the wide range of applications and for the role of the cyclometalation reaction in the activation and functionalization of C–H bonds.[2] In this context, many efforts have been made to elucidate the factors which govern cyclometalation, *i.e.* metal-mediated intramolecular C–H bond activation, in order to gain insight into the corresponding intermolecular process. At the same time, extensive studies have been devoted to the properties and the reactivity of cyclometalated complexes.

In recent years there has been interest shown in the synthesis of cyclometalated platinum complexes with bi- or polydentate phosphorus ligands for potential applications which span from catalysis to supramolecular chemistry.[3] In general, diphosphines may coordinate to a metal fragment as chelated, monodentate or bridging ligands.[4] The chelating tendency is maximum for five-membered cycles, as in the case of dppe, $Ph_2P(CH_2)_2PPh_2$, whereas small bite diphosphines, such as dppm, $Ph_2PCH_2PPh_2$, usually act as bridging ligands.[5]

The di- and oligo-nuclear complexes with bridging dppm and related ligands have attracted great interest because the metal centres held in close proximity may interact with each other leading to dramatic changes in their properties and chemical behaviour.[6]

As a part of long-standing interest in the chemistry of cyclometalated complexes, in recent years we have investigated a particular area of such compounds, that of the so-called "rollover" complexes, which derive from internal rearrangement of chelated ligands, such as 2,2′-bipyridine, followed by intramolecular C–H bond activation.[7]

Rollover complexes display a different behaviour from that of classical cyclometalated complexes, due to the presence of the uncoordinated nitrogen. This peculiar reactivity includes polymerization,[8] multiple cyclometalations,[9] protonation[7b] and "retro-rollover".[10] Protonated rollover species, which may be regarded as abnormal pyridylenes or simply as mesoionic compounds, also belong to the peculiar class of "complexes with multiple personalities",[11] *i.e.* compounds able to mutate their chemical behaviour after protonation or deprotonation. Recent applications of rollover complexes in catalytic[12] and stoichiometric[13] C–C bond formation are revealing part of the potentiality of this class of compounds. In a previous paper we were interested in investigating the properties of some dinuclear rollover complexes connected by the doubly metalated 2,2′-bipyridine, in that case the interaction between the two metals was mediated by the extended delocalized system of the heteroaromatic ligand.[14]

Herein we report some aspects of the reactivity of platinum(II) rollover complexes with two bidentate phosphine ligands, 1,1-bis-(diphenylphosphino)methane (dppm), and 1,2-bis-(diphenylphosphino)ethane (dppe), in order to check the influence of different lengths of the backbone on the properties of the dinuclear complexes, and also look for peculiarities due to the rollover scaffold.

Dipartimento di Chimica e Farmacia, Università degli Studi di Sassari, via Vienna 2, 07100 Sassari, Italy. E-mail: zucca@uniss.it

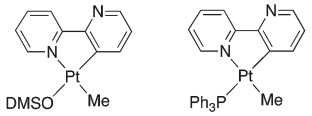
†Electronic supplementary information (ESI) available. See DOI: 10.1039/c4dt02080d

‡Present address: Dipartimento di Fisica, Università degli Studi di Pavia, via Bassi 6, 27100 Pavia, Italy.

§CIRCC (Consorzio Interuniversitario Reattività Chimica e Catalisi), http://www.circc.uniba.it/index_ita.htm

Results and discussion

The rollover complex [Pt(bpy-H)(Me)(DMSO)], **1**, (bpy = 2,2′-bipyridine) is the parent compound of a family of cyclometalated complexes [Pt(bpy-H)(Me)(L)] (L = neutral ligand),[15] obtained by displacement of the labile DMSO by neutral donors under mild conditions: as an example, reaction of **1** with PPh_3 occurs at room temperature, to give [Pt(bpy-H)(Me)-(PPh_3)], **2**, in high yields.



1 **2**

The diphosphines bis(diphenylphosphino)methane (dppm) and bis-(diphenylphosphino)ethane (dppe) may behave both as mono- or bidentate ligands, so their reaction with **1** was studied with a 1 : 1 and 2 : 1 molar ratio.

(1) dppm complexes

Reaction of **1** with dppm in a 1 : 1 molar ratio gives with high yields the monodentate complex [Pt(bpy-H)(Me)(dppm-κ*P*)], **3**, where dppm acts as a monodentate pendant ligand (Scheme 1). This formulation is demonstrated by analytical and spectroscopic data; in particular, the ^{31}P NMR spectrum shows two sets of signals: one, centred at 19.7 ppm, attributable to a coordinated phosphorus ($^1J_{Pt-P}$ = 2209 Hz, typical of P–Pt–C *trans* arrangement[16]), and one at −24.8 ppm, due to an unbonded phosphorus. The latter assumption is demonstrated by the chemical shift value, not so far from that of free dppm (δ = −23.6 ppm) and, mostly, by the ^{195}Pt–^{31}P coupling constant value, $^3J_{Pt-P}$ = 57.2 Hz.

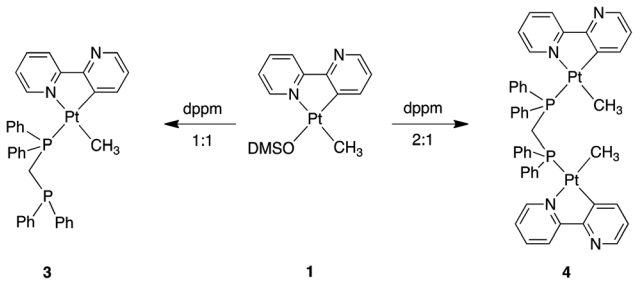
The ^1H NMR spectrum of **3** is in agreement with the proposed formulation. The presence of one dppm unit in the complex is indicated by integration of dppm *vs.* bipyridine protons. The spectrum shows a doublet with satellites for the Pt–CH_3 protons (δ = 0.79 ppm, $^2J_{Pt-H}$ = 83.4 Hz, $^3J_{P-H}$ = 7.9 Hz), with Pt–H and P–H coupling constants comparable to those of the analogous PPh_3 complex **2**.[15] Complex **3** was also obtained with a "one pot" reaction, starting from *cis*-[$Pt(Me)_2(DMSO)_2$] and bpy, followed by dppm addition directly to the reaction mixture, in order to avoid isolation of **1** which may be sometimes troublesome due to its predisposition to decompose in solution.

When the reaction was carried out with a Pt–dppm 2 : 1 molar ratio the dinuclear symmetric complex [(bpy-H)(Me)-Pt(μ-dppm)Pt(Me)(bpy-H)], **4**, was isolated in high yields. Accordingly, the ^1H and ^{31}P NMR spectra show only one set of signals for methyl (δ = 0.74 ppm, multiplet with satellites) and phosphorus (δ = 21.9 ppm). In the interpretation of NMR spectra several isotopomers should be considered, due to 33.83% natural abundance of the only NMR active ^{195}Pt isotope (I = 1/2). Collecting together all Pt isotopes with I = 0, four isotopomers should be considered, as depicted in Chart 1. In this case, due to the symmetry of complex **4**, isotopomers B and C coincide, giving a single isotopic isomer with an overall 44.78 percentage.

In the ^1H NMR spectrum the methyl resonance appears as a doublet with a broad central peak (see Fig. 1), as already reported for analogous complexes.[17] The unusual appearance of this resonance arises because ^1H, ^{195}Pt and ^{31}P atoms form a series of spin systems, according to the isotopomer distribution: $A_3A'_3XX'$ (isotopomer A), $A_3A'_3MXX'$ (isotopomers B and C), $A_3A'_3MM'XX'$ (isotopomer D), where A = ^1H, M = ^{195}Pt, X = ^{31}P. This kind of spectra has already been described,[18] the central doublet splitting (due to isotopomer A), 7.1 Hz, is given by the sum of the coupling constants $^3J_{P-H}$ and $^5J_{P-H}$. The latter, however, is likely to be almost zero, so the splitting is equal to $^3J_{P-H}$, and the spin system of species A may be considered an A_3X one.

The ^1H spectrum was simulated by means of the iNMR software,[19] and is reported in Fig. 1 along with the experimental one. The simulation gave the following coupling constant values: $^2J_{Pt-H}$ = 82.0 Hz, $^3J_{P-H}$ = 7.1 Hz, $^2J_{P-P}$ = 38.9 Hz; $^5J_{P-H} \cong 0$ Hz.

Also the ^{31}P NMR spectrum shows a complex pattern (see Fig. 2). In addition to the central resonance, at 21.9 ppm, a series of small satellites is present. Apart from the central



3 **1** **4**

Scheme 1

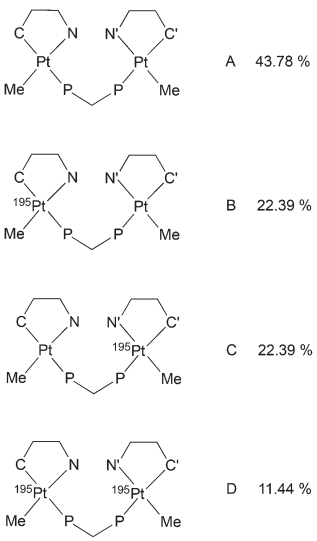


Chart 1 Isotopomers of dinuclear cyclometalated complexes considering ^{195}Pt isotopic abundance, 33.83%.

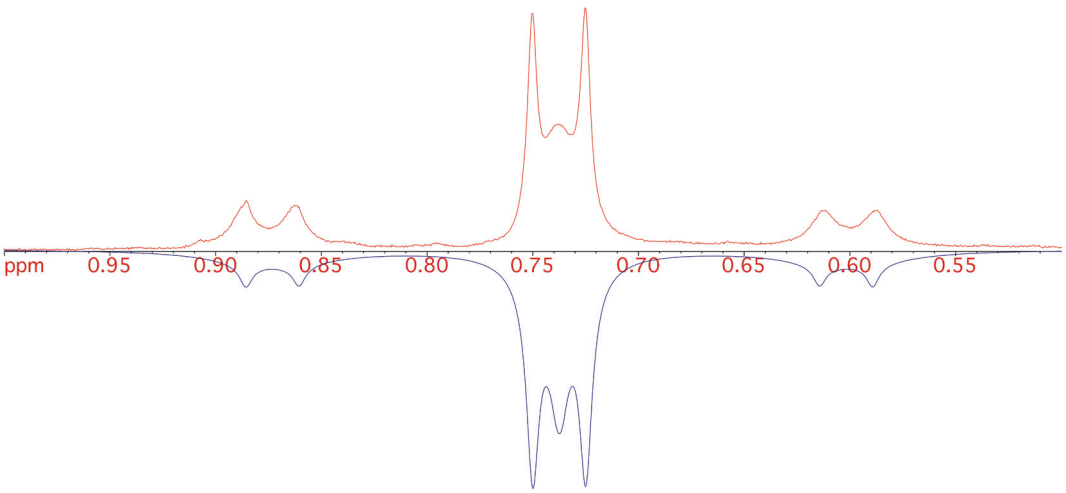


Fig. 1 ^{1}H NMR spectrum (Pt–Me region) of complex **4** in $CDCl_3$ at room temperature. Above spectrum (red), experimental; below (blue), simulated.

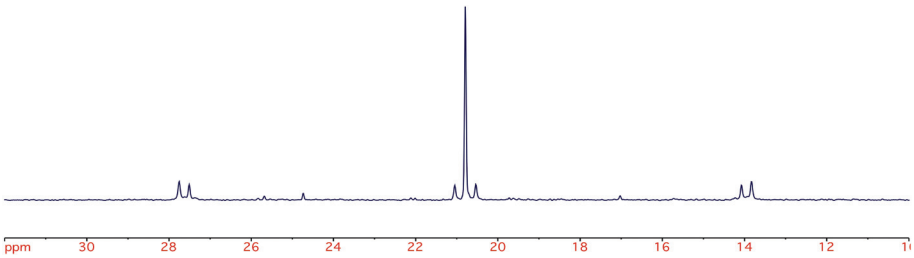


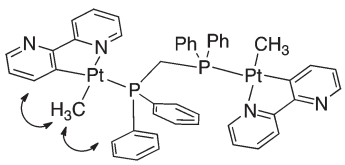
Fig. 2 ^{31}P NMR spectrum of complex **4** in $CDCl_3$ at room temperature.

singlet, due to the predominant isotopomer (A, 43.78%, Chart 1), the satellite system is due to the isotopomers which contain NMR active Pt nuclei. In the isotopomer having one ^{195}Pt atom (isomers B and C, 44.78%) the ^{31}P and ^{195}Pt give rise to a second order AA′X spin system, whereas the isotopomer containing two ^{195}Pt atoms gives a second-order AA′XX′ spin system (A,A′ = ^{31}P; X,X′ = ^{195}Pt).

The NMR simulation gave the following data: $^{1}J_{Pt-P}$ = 2215 Hz, $^{2}J_{P-P}$ = 38.9 Hz, $^{3}J_{Pt-P}$ = 44.2 Hz. The positions of the small satellite signals of the isotopomer having two ^{195}Pt atoms indicate that $^{1}J_{Pt-P}$ and $^{3}J_{Pt-P}$ have the same sign (both positive[17]).

The ^{13}C NMR spectra of **3** and **4** show, *inter alia*, the methyl signals at δ −14.1 and −11.8 ppm, respectively, with ^{195}Pt–^{13}C and ^{31}P–^{13}C coupling constants in line with the proposed formulations and comparable to those found for the corresponding triphenylphosphine complex **2**[10] (**2**: δ −12.4 ppm, $^{1}J_{Pt-C}$ = 725 Hz, $^{2}J_{P-C}$ = 5 Hz; **3**: $^{1}J_{Pt-C}$ = 730 Hz, $^{2}J_{P-C}$ = 6 Hz; **4**: $^{1}J_{Pt-C}$ = 735 Hz, $^{2}J_{P-C}$ = 6 Hz).

Furthermore, an NOE-1d experiment showed that irradiation of the methyl protons resulted in enhancement of the bpy-H_4 and of the *ortho* protons of the phenyl groups of dppm (Fig. 3).



4

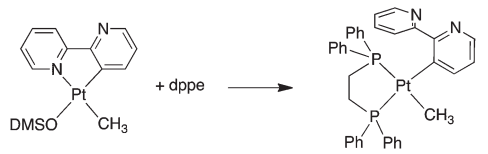
Fig. 3 NOE contacts between Pt–CH_3 protons, bpy-H_4 and H_{ortho} of dppm.

(2) dppe complexes

In contrast to dppm, reaction of dppe with **1** gave the chelated complex [Pt(bpy-H-κC)(Me)(dppe-κ^{2}P,P)], **5**, both in Pt–L 1 : 1 and 2 : 1 molar ratios. Analytical and spectroscopic methods confirm the presence of one dppe, one deprotonated bpy and one coordinated methyl. The ^{31}P NMR spectrum indicates a chelated coordination of dppe, shown by the presence of two different phosphorus atoms, both coupled to ^{195}Pt (δ = 44.7 ppm, J_{Pt-P} = 1953 Hz; δ = 43.3 ppm, J_{Pt-P} = 1814 Hz). It is well known that chemical shift is a good indicator of chelation in dppe and dppm,[20] resulting in a marked downfield shift for dppe and a marked upfield shift for dppm. Chemical shift values account for dppe chelation, whereas Pt–P coupling constant values, less than 2000 Hz, support a P–Pt–C *trans* arrangement for both phosphorus; these data are in good agreement with those found for the corresponding phenylpyridine complex.[21b] In addition, the absence of appreciable coupling between the two phosphorus atoms is another indicator

of chelation. A P–P coupling constant close to zero is due to the fact that the J_{P-P} coupling is the sum of two contributions, $^2J_{P-P}$ (P–Pt–P) and $^3J_{P-P}$ (P–C–C–P), having similar absolute value but opposite sign.

All NMR data may be explained by assuming displacement of the pyridine nitrogen by means of dppe, as observed for the related species,[21] and is ascribable to the high chelating ability of the dppe ligand. In very rare cases, however, dppe can act as a bridging ligand between two cyclometalated complexes.[21b] The methyl resonance in the ^{1}H NMR spectrum appears, at 0.49 ppm, as a triplet with satellites ($^3J_{P-H}$ = 7.5 Hz), confirming the presence of two phosphorus atoms in the complex. The ^{195}Pt–H coupling constant value, $^2J_{Pt-H}$ = 71 Hz, is in agreement with a *trans* P–Pt–C arrangement.



1 5

The ^{13}C NMR spectrum of **5** shows the methyl as a double doublet with satellites, at δ −1.9 ppm, ($^1J_{Pt-C}$ = 605 Hz) with markedly different *trans* and *cis* ^{31}P–^{13}C coupling constants, as expected (*trans*-$^2J_{P-C}$ = 90 Hz, *cis*-$^2J_{P-C}$ = 7 Hz). Two CH_2 carbons are also present in the spectrum, at δ 20.1 ppm (dd, $^2J_{P-C}$ = 39 Hz, $^3J_{P-C}$ = 17 Hz) and 29.0 ppm (dd, $^2J_{P-C}$ = 32 Hz, $^3J_{P-C}$ = 15 Hz).

In the absence of X-ray structural data, complex **5** was characterised in solution by means of bidimensional NMR spectroscopy, namely H–H COSY and H–H NOESY experiments. The COSY spectrum allowed assignment of all ^{1}H bpy resonances and the NOESY spectrum gave structural information. In particular the NOESY spectrum showed NOE cross-peaks between the methyl, at 0.49 ppm, and the $H_{3'}$ proton (δ 7.99 ppm) as well as with the H_4 proton, at 7.80 ppm (see Fig. 4).

This is in line with a C-bonded bipyridine, disposed perpendicular to the coordination plane; if both the uncoordinated nitrogens are opposite to the platinum centre, the $H_{3'}$ and H_4 hydrogens should be located above and below the coordination plane, in proximity to the metal and the CH_3 group. Accordingly, the H_6 and $H_{6'}$ protons do not show appreciable NOE contacts with the H_{ortho} protons of the dppe phenyls, as should be expected if the nitrogen were positioned far from the metal centre. In contrast, the CH_3, $H_{3'}$ and H_4 protons have clear cross-peaks with dppe aromatic hydrogens.

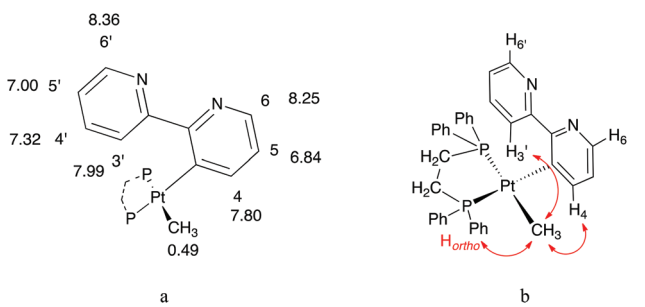
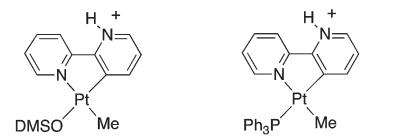


Fig. 4 Complex **5**: (a) numbering scheme with ^{1}H NMR assignments; (b) NOE contacts revealed by NOESY cross-peaks.

The relative stabilities of the two isomers κ^1-C-cyclometalated ligand [Pt(κ^1-C,N)(κ^2-P,P)(Me)] (as in **5**) and κ^1-P-diphosphine [Pt(κ^2-C,N)(κ^1-P,P)(Me)] (as in **3**) have been studied by means of Density Functional Theory calculations for metalated 2-phenylpyridine and benzo[*h*]quinoline,[21b] showing that the κ^1-P isomer is favoured for dppm complexes, whereas the κ^1-C isomer is favoured for dppe.

(3) Protonation on mononuclear complexes 3 and 5

As previously reported, mononuclear rollover complexes, such as **1** and **2**, have a rich chemical behaviour due to the presence of a free nitrogen, which can be protonated to give a rare example of cationic mesoionic complexes [Pt(bpy*)(Me)(DMSO)]$^+$, **1***, and [Pt(bpy*)(Me)(PPh$_3$)]$^+$, **2***, where bpy* is a cyclometalated isomer of 2,2′-bipyridine. These ligands also belong to a restricted family of ligands, called "ligands with multiple personality",[11] due their ability to change chemical properties after protonation or deprotonation.



[Pt(bpy*)(Me)(DMSO)]$^+$ [Pt(bpy*)(Me)(PPh$_3$)]$^+$

1* **2***

Depending on the electronic properties of the neutral ligand, the protonated complexes may be stable in solution or may isomerize, following an interesting "retro-rollover" reaction, to give the corresponding cationic adduct [Pt(bpy-κ^{2}N,N)(Me)(L)]$^+$.[10] The pair of rollover/retro-rollover processes may have the potentiality for catalytic applications. Under certain reaction conditions protonation of complex **1** may also result in the Pt–CH_3 bond breaking, with release of methane.[10]

Protonation of the mononuclear complexes **3** and **5** may promote, in principle, Pt–C(sp^2) or Pt–C(sp^3) bond breaking.

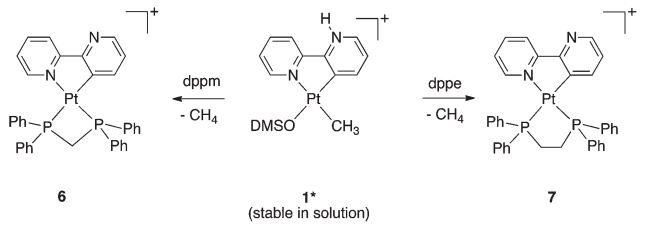
In neither case Pt–C(sp^2) protonolysis is observed after treatment of complexes **3** and **5** with [H_3O·18-crown-6][BF_4]. The reactions were followed by ^{1}H and ^{31}P NMR spectroscopy: in both cases the reaction is very fast, as we did not observe any intermediate species (*i.e.* protonated complexes **3*** and **5*** or Pt(IV) hydrides) as soon as the first spectra after the addition could be recorded (*ca.* 1 minute). Only the final products, [Pt(bpy-H)(dppm-κ^{2}P,P)]$^+$ (**6**) or [Pt(bpy-H)(dppe-κ^{2}P,P)]$^+$ (**7**) and methane (δ = 0.23 ppm), were detected in solution. The bis-chelated cationic species **6** and **7** were also isolated in the solid state as BF_4 salts, [Pt(bpy-H)(dppm-κ^{2}P,P)][BF_4], **6**-BF_4, and [Pt(bpy-H)(dppe- κ^{2}P,P)][BF_4], **7**-BF_4 (Scheme 2).

Chelation of dppm and dppe is supported by ^{31}P NMR spectra, which show in both cases two sets of signals, highly

shielded (−30.4 and −36.9 ppm) in **6**, and highly deshielded (+42.6 and +51.8 ppm) in **7**, as should be expected for chelation of dppm and dppe, respectively. In both cases, one of the phosphorus atoms is bonded *trans* to a nitrogen and the other one *trans* to a carbon, as indicated by ^{195}Pt–^{31}P coupling constant values. The corresponding bis-chelated complexes of 2-phenylpyridine and benzo[*h*]quinoline have comparable ^{31}P NMR data.[22]

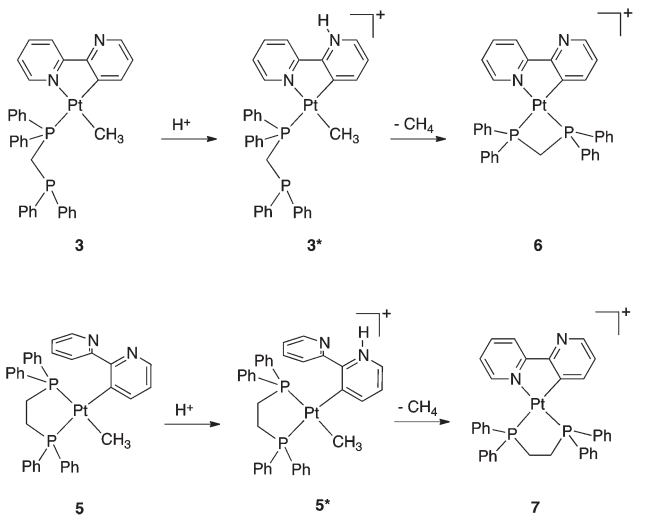
The protonolysis reaction of complex **5** to give the bis-chelated complex **7** is reminiscent of the reaction of the corresponding κ^1-C phenylpyridine and benzo[*h*]quinoline complexes with CF_3COOH.[22b]

Interestingly, the same result was obtained by reaction of **1***, [Pt(bpy*)(Me)(DMSO)]$^+$, with the diphosphine (dppm or dppe) in a 1 : 1 molar ratio. The reaction of **1*** with dppe has been recently reported by us.[10] It is worth recalling that, in contrast to the PPh_3 complex **2***, complex **1*** is stable in solution and does not isomerise through a retro-rollover reaction.



Starting from complex **1**, reversing the reagents' order ([H_3O·18-crown-6][BF_4] and diphosphine) gave the same products, **6** and **7**. These reactions may support the hypothesis that the intermediate species in the synthesis of **6** and **7** is, in both cases, the N-protonated species (**3*** and **5***); however, other possibilities should not be ruled out.

All these reactions are likely to proceed through oxidative addition of H^+ at the metal centre followed by reductive elimination of methane.[10]



Scheme 2

(4) Protonation of the dinuclear complex 4

The reaction of the dinuclear complex **4** with [H_3O·18-crown-6][BF_4] was followed by means of NMR spectroscopy in CD_2Cl_2 solution.

After the addition of one equivalent of acid the colour of the solution turned from amber to red, and the ^{31}P NMR spectrum shows the presence of a first product which rapidly converts into a second one. The first product, complex **8**, has a single set of ^{31}P resonances, centred at 22.2 ppm (singlet with satellites). Coupling constant values ($^1J_{Pt-P}$ = 2324 Hz, $^3J_{Pt-P}$ = 52.5 Hz, $^2J_{P-P}$ = 55 Hz) are in agreement with protonation of an uncoordinated nitrogen, but the equivalence of the two phosphorus atoms indicates a fluxional exchange between the two nitrogens on the NMR time scale, giving the appearance of a symmetric species. $^1J_{Pt-P}$ = 2324 Hz has an intermediate value between those observed for the protonation of the analogous PPh_3 complex **2**, $^1J_{P-P}$ = 2229 Hz for neutral **2**, and $^1J_{P-P}$ = 2500 Hz for protonated **2***; the averaged *J* value supports "half protonation" of the nitrogens (Scheme 3).

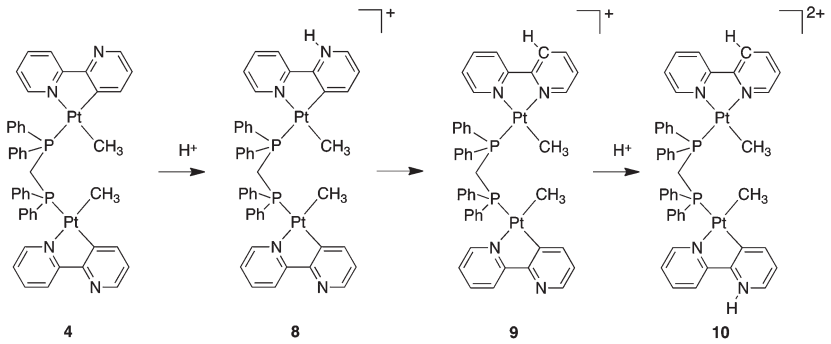
Complex **8** rapidly converts into a new species, **9**, which shows two sets of ^{31}P NMR signals: one at 19.7 ppm (doublet with satellites, $^1J_{Pt-P}$ = 2267 Hz, $^3J_{Pt-P}$ = 79 Hz, $^2J_{P-P}$ = 45 Hz) and the other one at 11.4 ppm (doublet with satellites, $^1J_{Pt-P}$ = 4458 Hz, $^3J_{Pt-P}$ = 70 Hz, $^2J_{P-P}$ = 45 Hz). These data fit well with a retro-rollover reaction of one bipyridine to give the chelated *N*,*N* adduct **9**, [Pt(bpy-H)(Me)(μ-dppm)Pt(bpy)(Me)][BF_4].

This behaviour is in contrast to that showed by the mononuclear dppm species **3**, for which Pt–C(sp^3) bond breaking occurred, followed by dppm chelation. This is further evidence of the fact that in the presence of an external donor protonated rollover derivatives release methane with Pt–C(sp^3) rupture, whereas in the absence of a free donor Pt–C(sp^2) bond breaking occurs, followed by a retro-rollover reaction.

Addition of a second equivalent of [H_3O·18-crown-6][BF_4] to a solution of **9** gave an orange solution, whose ^{31}P NMR data (17.4 ppm, $^1J_{Pt-P}$ = 2516 Hz, $^3J_{Pt-P}$ = 79.5 Hz, $^2J_{P-P}$ = 42 Hz, P *trans* C; 10.1 ppm, $^1J_{Pt-P}$ = 4421 Hz, $^3J_{Pt-P}$ = 71 Hz, $^2J_{P-P}$ = 42 Hz, P *trans* N) are in agreement with protonation of the free nitrogen, to give the dicationic species [Pt(bpy*)(Me)(μ-dppm)-Pt(bpy)(Me)][BF_4]$_2$. **10** is the only reaction product. Complex **10** is stable in solution for several days (NMR criterion) and does not isomerise through a retro-rollover process (at least under the conditions followed in the experiment).

Complex **10** was isolated in the solid state and characterised. Analytical data fit well with the proposed formulation, as well as conductivity measurements (5×10^{-4} M, acetone, 25 °C), Λ_M = 190 Ω cm^2 mol^{-1}, which is in agreement with a 2 : 1 electrolytic species.

Dinuclear dppm complexes of cyclometalated ligands bearing uncoordinated nitrogens may have interesting applications: in two recent papers protonation/deprotonation of a pyrazole-substituted cyclometalated ligand promoted the reversible "opening" and "closing" of a "molecular pivot hinge", with dramatic changes in the luminescent properties.[23]



4 8 9 10

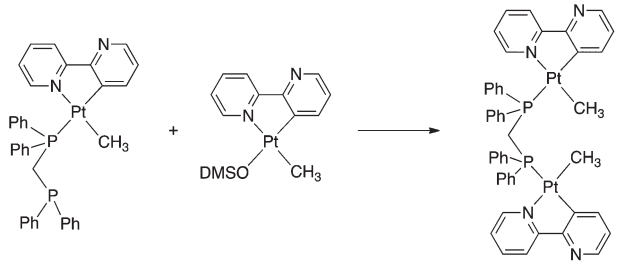
Scheme 3

Attempts to reproduce a similar behaviour in dinuclear complex **4** failed due to the retro-rollover process. However, it is likely that the protonated complex **8** has a "closed" conformation, due to its "symmetric" NMR and due to its orange-red colour, usually associated with stacking interactions in Pt(II) square planar complexes.

(5) Coordination of 3

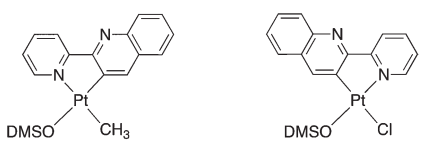
Complexes **3** and **5** have free P and N donor atoms and can be considered as organometallic ligands, namely P and *N*,*N* donors, respectively.

When complex **3** is reacted with **1** it behaves as a monodentate ligand, to give almost quantitatively the dinuclear complex **4**.



3 1 4

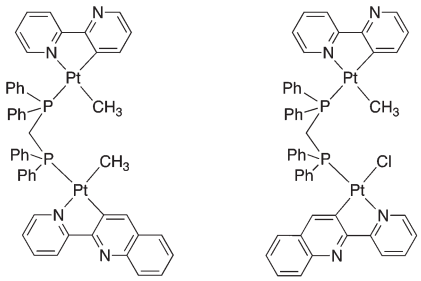
Taking advantage of this behaviour, unsymmetric dinuclear complexes can be synthesized.[24] In order to verify this possibility we reacted complex **3** with two rollover complexes derived from 2-pyridylquinoline[25] (pyq): a methyl complex, [Pt(pyq-H)(Me)(DMSO)], **11**, and a chloride one, [Pt(pyq-H)(Cl)-(DMSO)], **12**, respectively.



11 12

Cyclometalated complexes of the general formula [Pt(NC)(X)-(DMSO)] (X = anionic ligand) such as **1**, **11** or **12**, can exist in two isomeric forms, *i.e.* DMSO-*trans*-C(sp^2) or DMSO-*trans*-N. The same is true for phosphine complexes, such as **2** or **3**. However, due to the great *trans*-influence difference of CH_3 and Cl, only one isomer is usually formed, *i.e.* having the higher *trans*-influence ligand coordinated in *trans* to the lower *trans*-influence ligand, DMSO-*trans*-C(sp^2) for the methyl complex **11** and DMSO-*trans*-N for the chloride complex **12**.

In both cases the reactions produced with high yields complexes **13**, [(bpy-H)(Me)Pt(μ-dppm)Pt(Me)(pyq-H)], and **14**, [(bpy-H)(Me)Pt(μ-dppm)Pt(Cl)(pyq-H)], in which the methyl groups are always *trans* to nitrogen atoms.



13 14

Complex **14** is unsymmetrical for several reasons: the two platinum centers have different cyclometalated ligands, different anionic ligands and different isomeric forms.

The characterization of **13** and **14** relies on analytical and spectroscopic data, in particular, ^{1}H and ^{31}P NMR.

Complex **13** shows ^{1}H and ^{31}P NMR spectra similar to those of complex **4**, with the difference that it is not symmetric. As a consequence, the two phosphorus atoms and methyls are not equivalent, and in the isotopomer distribution (Chart 1) isomers B and C are different species. The methyls give the same unusual signal as in **4**, two doublets each with an inner broad peak (δ 0.73 and 0.83 ppm).

In the ^{31}P spectrum the two phosphorus atoms resonate at 20.4 and 20.9 ppm with similar ^{195}Pt–^{31}P coupling constants (2234 and 2249 Hz, respectively) (Fig. 5).

As for complex **14**, only one methyl is present at 0.72 ppm. In this case the phosphorus atoms are clearly different: one of the P atoms resonates at 18.5 ppm, with $^1J_{Pt-P}$ = 4305 Hz which indicates a P–Pt–N *trans* arrangement, whereas the second

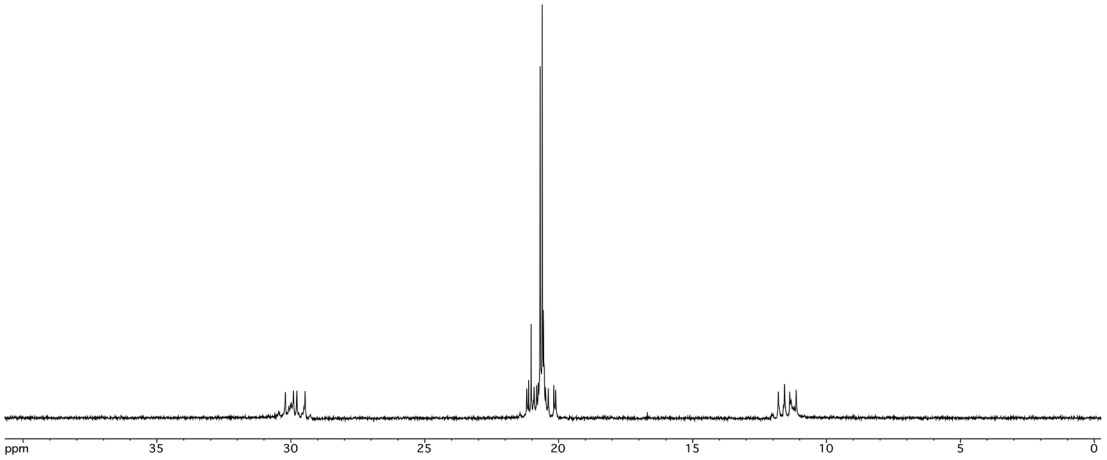


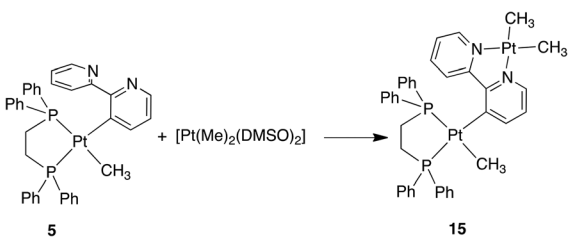
Fig. 5 ^{31}P NMR spectrum of **13** in $CDCl_3$.

one, at 12.77 ppm, with a *J* value of 2232 Hz, is in agreement with a P–Pt–C *trans* coordination.

Dinuclear complexes such as **4**, **13** and **14** may be of certain interest. It has been recently demonstrated that dinuclear cyclometalated complexes with bridging dppm display a different reactivity from that of the corresponding mononuclear triphenylphosphine complexes.[26]

(6) Coordination of 5

Complex **5** may be considered as a 3-functionalised, organometallic 2,2′-bipyridine. In order to verify its proneness to coordinate it was reacted with *cis*-$[Pt(Me)_2(DMSO)_2]$ under mild conditions. The reaction was followed in an NMR tube by means of ^1H and ^{31}P NMR spectroscopy. NMR data indicate a rapid reaction, interpretable as substitution of DMSO ligands by the nitrogens to give the adduct [(dppe)(Me)Pt(μ-bpy-H)-$Pt(Me)_2$], **15**.



5 **15**

In particular, the ^1H NMR spectrum shows three coordinated methyls, two almost overlapping with $^2J_{Pt-H}$ values in line with *trans* N–Pt–C arrangement (δ 0.96 ppm, $^2J_{Pt-H} \cong 84$ Hz) and one at 0.50 ppm, coupled to two phosphorus atoms (0.50 ppm, triplet with satellites, $^3J_{P-H} = 7.1$ Hz, $^2J_{Pt-H} = 69$ Hz). The H_6 and $H_{6'}$ signals experience after reaction a marked downfield shift (δ 8.94, $^3J_{Pt-H} = 26$ Hz; δ 8.74, $^3J_{Pt-H} = 28$ Hz), the presence of satellites for both signals confirms coordination of the nitrogens. One aromatic signal, a doublet at 9.73 ppm, experiences a significant coordination shift to higher frequencies. This signal may be attributed to the H_3 hydrogen and the notable shift may be due to interaction with the metal centre, probably an anagostic interaction.[27] Displacement of coordinated DMSO is demonstrated by the appearance in the spectrum of a singlet due to free DMSO (integration 6H).

The ^{31}P NMR spectrum of **15** shows two singlets with satellites, at 45.7 and 44.5 ppm, slightly shifted with respect to complex **5**. The coupling constant values with the ^{195}Pt nucleus ($^1J_{Pt-P} = 2034$ and 1744 Hz, respectively), are in agreement with P–Pt–C *trans* arrangements. Chelation of dppe is indicated by chemical shift values, diagnostic for chelated dppe, and by the absence of appreciable coupling between the two phosphorus atoms.

Conclusions

The reaction of the rollover cyclometalated complex [Pt(bpy-H)-(Me)(DMSO)] with the diphosphanes dppm (1,1-bis(diphenylphosphino)methane) and dppe (1,2-bis(diphenylphosphino)-ethane) gave different products due to the different coordinating abilities of these ligands. In particular, dppe easily displaces the bpy nitrogen to give the mononuclear chelated complex [Pt(bpy-H-κ^1C)(Me)(dppe-κ^2PP)]. In contrast, the small bite dppm gave mononuclear or dinuclear complexes ([Pt(bpy-H-κ^2CN)(Me)(dppm-κ^1P)] and $[Pt_2(bpy\text{-}H)_2(Me)_2(\mu\text{-}dppm)]$), according to the reaction conditions. Reaction of the mononuclear species with $[H_3O{\cdot}18\text{-crown-}6][BF_4]$ resulted in both cases (dppm and dppe complexes) in methane elimination to give the bischelated cationic complexes $[Pt(N,C)(P,P)]^+$, whereas the dinuclear complex $[Pt_2(bpy\text{-}H)_2(Me)_2(\mu\text{-}dppm)]$ follows a retro-rollover process.

The mononuclear rollover complexes containing one diphosphine can be used as metalloligands to bind a second platinum unit: the dppm complex [Pt(bpy-H)(Me)(dppm-κ^1)] acts as a P-metalloligand to give unsymmetrical bridged complexes [(Me)(N,C)Pt(μ-dppm)Pt(N′,C′)(X)]; the dppe complex [Pt(bpy-H-κ^1)(Me)(dppe-κ^2)] acts as a chelating substituted bipyridine.

Experimental section

All the solvents were purified and dried according to standard procedures.[28] *cis*-[Pt(Me)$_2$(DMSO)$_2$] was synthesized according to ref. 29. Complexes **1**, **11** and **12** were obtained as described in ref. 15 and 25. Elemental analyses were performed with a Perkin-Elmer elemental analyser 240B. ^{1}H, ^{13}C^{1}H and ^{31}P^{1}H NMR spectra were recorded with Varian VXR 300 and Bruker Avance III 400 spectrometers. Chemical shifts are given in ppm relative to internal TMS for ^{1}H and ^{13}C, and external 85% H_3PO_4 for ^{31}P; *J* values are given in Hz. ^{1}H–^{1}H COSY, ^{1}H–^{1}H NOESY and NOE-1d experiments were performed by means of standard pulse sequences. Conductivities were measured with a Philips PW 9505 conductometer.

[Pt(bpy-H)(CH$_3$)(dppm-κ^{1}P)], 3

Method A. To a solution of **1** (61.2 mg, 0.138 mmol) in CH_2Cl_2 (10 mL) dppm (65.8 mg, 0.171 mmol) was added under a nitrogen atmosphere. The solution was stirred for 2 h, then it was concentrated to a small volume, treated with Et_2O, filtered off and dried to give the analytical sample as a yellow solid. Yield 75%.

Method B. To a solution of *cis*-[Pt(CH$_3$)$_2$(DMSO)$_2$] (212.3 mg, 0.557 mmol) in anhydrous toluene an excess of 2,2′-bipyridine (171.6 mg, 1.099 mmol) was added under a nitrogen atmosphere. The solution became suddenly red and was heated to reflux for 3 h. At the end of the reaction the solution was cooled down to room temperature and dppm (237.8 mg, 0.619 mmol) was added. After 1 h the solution was concentrated to a small volume and treated with Et_2O to form a precipitate. The solid was filtered off, washed with Et_2O, and dried to give the analytical sample as a yellow solid. Yield 60%. M.p. 176–180 °C. Anal. calcd for $C_{36}H_{32}N_2P_2Pt{\cdot}2H_2O$: C 56.99, H 4.38, N 3.69%; found C 57.16, H 4.24, N 3.77%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, ppm): 8.39 (d br, 1H, H_6); 8.24 (d, 1H, J_{H-H} = 7.8 Hz, $H_{3'}$); 8.16 (m sat, 1H, $^3J_{Pt-H}$ = 48 Hz, H_4); 7.84 (m, 4H, H_o(Ph–P–Pt)); 7.74 (td, 1H, $H_{4'}$); 7.62 (d sat, 1H, $^3J_{Pt-H}$ = n.r., J_{H-H} = 5.5 Hz, $H_{6'}$); 7.42–7.10 (m, 17H, PPh_2 + H_5); 6.65 (ddd, 1H, J_{H-H} = 7.1, 5.6, 1.5 Hz, $H_{5'}$); 3.42 (m, 2H, CH_2); 0.79 (d sat, 3H, $^2J_{Pt-H}$ = 83.4 Hz, $^3J_{P-H}$ = 7.9 Hz, Pt–CH_3). ^{31}P NMR (121.4 MHz, $CDCl_3$, 298 K, ppm): 19.7 (d sat, $^1J_{Pt-P}$ = 2210 Hz, $^2J_{P-P}$ = 78.5 Hz, coordinated P); −24.8 (d sat, $^3J_{Pt-P}$ = 57 Hz, $^2J_{P-P}$ = 78.5 Hz, not coordinated P).

^{13}C NMR selected data (100.6 MHz, $CDCl_3$, 298 K, ppm): −14.1 (dd sat, J_{Pt-C} = 730 Hz, J_{P-C} = 6 Hz, J_{P-C} = 2.5 Hz, CH_3), 26.4 (dd sat, J_{Pt-C} = 30 Hz J_{P-C} = 30.5 Hz, J_{P-C} = 24.5 Hz, CH_2), 121.3 (s sat, J_{Pt-C} = 20 Hz), 123.5 (s sat, J_{Pt-C} = 11 Hz), 124.3 (d sat, J_{Pt-C} = 50 Hz, J_{P-C} = 5 Hz, $C_{5'}$), 139.8 (s sat, J_{Pt-C} = 80 Hz, C_4), 144.7, 150.4, 155.6 (J_{P-C} = 118 Hz, C_3), 164.6, 165.5.

[{Pt(bpy-H)(CH$_3$)}$_2$(μ-dppm)], 4

To a solution of *cis*-[Pt(CH$_3$)$_2$(DMSO)$_2$] (54.1 mg, 0.142 mmol) in anhydrous toluene an excess of 2,2′-bipyridine (72.4 mg, 0.464 mmol) was added under a nitrogen atmosphere. The solution became suddenly red and was heated to reflux for 3 h. At the end of the reaction dppm (28.1 mg, 0.073 mmol) was added and left to react for 1 h; then the mixture was concentrated to a small volume and treated with *n*-pentane to form a precipitate. The solid was filtered off, washed with *n*-pentane, and dried to give the analytical sample as a yellow solid. Yield 75%. M.p.: >265 °C. Anal. calcd for $C_{47}H_{42}N_4P_2Pt_2{\cdot}2H_2O$: C 49.04, H 4.03, N 4.87%; found C 48.85, H 3.86, N 4.51%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, ppm): 8.24 (dd, 2H, J_{H-H} = 4.3 Hz, H_6); 7.94–7.84 (m, 10H, $H_{3'}$ + H_o(Ph)); 7.77 (m sat, 2H, $^3J_{Pt-H}$ = 46.2 Hz, H_4); 7.54 (d sat, 2H, $^3J_{Pt-H}$ = 21 Hz, $H_{6'}$); 7.42 (td, 2H, J_{H-H} = 15.3, 1.5 Hz, $H_{4'}$); 7.32–7.18 (m, 12H, H_m(Ph) + Hp(Ph)); 7.00 (ddd, 2H, H_5); 6.28 (ddd, 2H, J_{H-H} = 7.1, 5.6, 1.6 Hz, $H_{5'}$); 4.09 (m, 2H, CH_2); 0.74 (m sat, $^2J_{Pt-H}$ = 82.0 Hz, $^3J_{P-H}$ = 7.1 Hz, Pt–CH_3). ^{31}P NMR (121.4 MHz, $CDCl_3$, 298 K, ppm): 21.9 (s sat, $^1J_{Pt-P}$ = 2215 Hz, $^2J_{P-P}$ = 39 Hz, $^3J_{Pt-P}$ = 44 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$, 298 K, ppm): −11.8 (m sat, J_{Pt-C} = 735 Hz, J_{P-C} = 6 Hz, CH_3), 21.5 (m, J_{P-C} = 16 Hz, CH_2), 120.9, 123.1, 123.4 (J_{P-C} = 5 Hz), 128.3 (d, J_{P-C} = 10 Hz, C_o dppm or C_m dppm), 129.9, 133.4 (d, J_{P-C} = 12 Hz, C_o dppm or C_m dppm), 134.5 (d, J_{P-C} = 44 Hz, C_i dppm), 136.7, 138.6, 144.4, 151.0, 157.6 (C_2 or $C_{2'}$ bpy), 163.7, 165.0.

[Pt((bpy-H)κ^1-C)(CH$_3$)(dppe-κ^{2}P,P)], 5

Dppe (51.0 mg, 0.128 mmol) was added to a solution of [Pt-(bpy-H)(CH$_3$)(DMSO)] (46.1 mg, 0.104 mmol) in CH_2Cl_2 (15 mL). The solution was stirred for 2 h, then it was concentrated to a small volume and treated with Et_2O. The precipitate formed was filtered off and dried to give the analytical sample as a yellow solid. Yield 65%. M.p.: 198 °C. Anal. calcd for $C_{37}H_{34}N_2P_2Pt$: C 58.19, H 4.49, N 3.67%; found C 58.34, H 4.43, N 3.46%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, ppm): 8.35 (m, 1H, J_{H-H} = 4.5 Hz, $H_{6'}$); 8.22 (m, 1H, J_{H-H} = 4.5 Hz, H_6); 7.99 (d, 1H, J_{H-H} = 8.2 Hz, $H_{3'}$); 7.86 (m, 2H); 7.80 (m, 1H, H_4); 7.75–7.34 (m, 13H); 7.32 (m, 1H, partially overlapping, 1H, $H_{4'}$); 7.20 (m, 1H); 7.05 (m, 2H); 7.00 (m, 1H, $H_{5'}$); 6.93 (m, 2H); 6.84 (m, 1H, H_5); 2.50–2.22 (m, 2H, CH_2); 2.15–1.95 (m, 2H, CH_2); 0.49 (t sat, 3H, $^2J_{Pt-H}$ = 71 Hz, $^3J_{P-H}$ = 7.5 Hz, Pt–CH_3). ^{31}P NMR (121.4 MHz, $CDCl_3$, 298 K, ppm): 44.7 (s sat, J_{Pt-P} = 1953 Hz); 43.3 (s sat, J_{Pt-P} = 1814 Hz). ^{13}C NMR selected data (100.6 MHz, $CDCl_3$, 298 K, ppm): −1.9 (dd sat, J_{Pt-C} = 605 Hz, J_{P-C} = 90 Hz, J_{P-C} = 7 Hz, CH_3), 20.1 (dd, J_{P-C} = 39 Hz, J_{P-C} = 17 Hz), 29.0 (dd, J_{P-C} = 32 Hz, J_{P-C} = 15 Hz), 120.6, 122.0 (d sat, J_{Pt-C} = 57 Hz, J_{P-C} = 4 Hz), 123.7, 143.2, 145.7, 147.9, 160.7, 162.3.

[Pt(bpy-H)(dppm-κ^{2}P,P)][BF$_4$], 6

Method A. To a solution of [Pt(bpy-H)(CH$_3$)(dppm-κ^{1}P)], **3**, (104.9 mg, 0.140 mmol) in acetone (15 mL) was added [H_3O·18-crown-6][BF_4] (53.3 mg, 0.144 mmol). The solution was stirred for 1 h, then it was concentrated to a small volume and treated with Et_2O to give a white solid. Yield: 95%.

Method B. To a solution of [Pt(bpy*)(CH$_3$)(DMSO)][BF_4] (219.8 mg, 0.414 mmol) in acetone (15 mL) was added dppm (159.3 mg, 0.414 mmol). The solution was stirred for 1 h, then was concentrated to a small volume and treated with Et_2O to give a white solid. Yield: 90%. Anal. calcd for $C_{35}H_{29}N_2P_2Pt$: C 57.22, H 3.98, N 3.81%; found C 57.03, H 3.66, N, 3.58%.

^{1}H NMR (300 MHz, $CDCl_3$, 298 K, ppm): 8.59 (m, 2H); 8.44 (t, 1H); 8.27 (t, 1H); 7.88–7.72 (m, 9H); 7.62–7.48 (m, 13H);

7.36 (t, 1H); 4.91 (t, 2H, $^2J_{P-H}$ = 10.8 Hz, $^3J_{Pt-H}$ = n.r., CH_2). ^{31}P NMR (121.4 MHz, $CDCl_3$, 298 K, ppm): −30.4 (d sat, $^1J_{Pt-P}$ = 1582 Hz, $^2J_{P-P}$ = 51 Hz, P *trans* C); −36.9 (d sat, $^1J_{Pt-P}$ = 3186 Hz, $^2J_{P-P}$ = 51 Hz, P *trans* N).

[Pt(bpy-H)(dppe-κ^{2}P,P)][BF_4], 7

Method A. see ref. 10.

Method B. To a solution of [Pt(bpy-H)(CH_3)(dppe-κ^{2}P,P)], **5**, (32.0 mg, 0.042 mmol) in acetone (15 mL) was added [H_3O·18-crown-6][BF_4] (20.6 mg, 0.052 mmol). The solution was stirred for 80 minutes, then it was concentrated to a small volume and treated with Et_2O to give a white solid. Yield: 85%. M.p.: 162 °C.

^{1}H NMR (300 MHz, CD_2Cl_2, 298 K, ppm): 8.39 (br, 1H); 8.34 (br, 1H); 8.17 (br, 1H); 7.98 (br, 1H); 7.82 (br, 6H); 7.58 (br, 10H); 7.30 (br, 1H); 7.08 (br, 1H); 6.73 (br, 1H); 2.57 (br, 4H). ^{31}P NMR (121.4 MHz, $CDCl_3$, 298 K, ppm): 51.8 (s sat, J_{Pt-P} = 1949 Hz, P *trans* C); 42.6 (s sat, J_{Pt-P} = 3691 Hz, P *trans* N).

Reaction of [{Pt(bpy-H)(CH_3)}$_2$(μ-dppm)], **4**, with [H_3O·18-crown-6][BF_4]

To a solution of **4** (18.0 mg, 0.016 mmol) in $CDCl_3$ (1 mL) was added [H_3O·18-crown-6][BF_4] (6.0 mg, 0.016 mmol): the reaction was followed by means of ^{1}H and ^{31}P NMR spectroscopy. NMR spectra showed initial formation of [(Me)(bpy*)-Pt(μ-dppm)Pt(bpy-H)(Me)]$^+$, **8**, which converted into [(Me)(bpy)-Pt(μ-dppm)Pt(bpy-H)(Me)]$^+$, **9**. After 6 h additional 6.0 mg of [H_3O·18-crown-6][BF_4] were added and complete conversion of **9** to **10**, [(Me)(bpy)Pt(μ-dppm)Pt(bpy*)(Me)]$^+$, was observed.

Selected ^{31}P NMR data:

Complex **8**. δ 22.2 (d sat, $^1J_{Pt-P}$ = 2324 Hz, $^3J_{Pt-P}$ = 52.5 Hz, $^2J_{P-P}$ = 55 Hz).

Complex **9**. 19.7 ppm (d sat, $^1J_{Pt-P}$ = 2267 Hz, $^3J_{Pt-P}$ = 79 Hz, $^2J_{P-P}$ = 45 Hz, P *trans* C); 11.4 ppm (d sat, $^1J_{Pt-P}$ = 4458 Hz, $^3J_{Pt-P}$ = 70 Hz, $^2J_{P-P}$ = 45 Hz, P *trans* N).

Complex **10**, see below.

[(Me)(bpy)Pt(μ-dppm)Pt(bpy*)(Me)][BF_4]$_2$, 10

To a solution of **4** (37.9 mg (0.034 mmol) in CH_2Cl_2 was added [H_3O·18-crown-6][BF_4] (26.0 mg, 0.070 mmol). The solution was stirred at room temperature for 1 h, then it was concentrated to a small volume and treated with Et_2O. The precipitate formed was filtered off, washed with Et_2O and dried to give the analytical sample as an orange-red solid. Yield 95%. M.p. 185 °C. Anal. calcd for $C_{47}H_{44}B_2F_8N_4P_2Pt_2$: C 43.74, H 3.44, N 4.34%; found C 43.65, H 3.88, N 4.16%.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): 8.55–8.40 (m, 3H, aromatics) 8.20–7.31 (m, 29H, aromatics); 7.06–6.96 (m, 2H, aromatics); 4.33 (m, 2H, CH_2 dppm); 0.99 (d sat, 3H, $^3J_{P-H}$ = 6.6 Hz, $^2J_{Pt-H}$ = 80 Hz, CH_3); 0.93 (d sat, 3H, $^3J_{P-H}$ = 2.4 Hz, $^2J_{Pt-H}$ *ca*. 60 Hz, CH_3). ^{31}P NMR (161.9 MHz, $CDCl_3$, 298 K, ppm): δ 17.4 ppm ($^1J_{Pt-P}$ = 2516 Hz, $^3J_{Pt-P}$ = 79.5 Hz, $^2J_{P-P}$ = 42 Hz, P *trans* C); 10.1 ppm ($^1J_{Pt-P}$ = 4421 Hz, $^3J_{Pt-P}$ = 71 Hz, $^2J_{P-P}$ = 42 Hz, P *trans* N). Λ_M (5×10^{-4} M, acetone, 25 °C): 190 Ω cm^2 mol^{-1}.

[(Me)(bpy-H)Pt(μ-dppm)Pt(pyq-H)(Me)], 13

To a solution of [Pt(bpy-H)(Me)(κ^1-dppm)], **3**, (67.0 mg, 0.089 mmol) in CH_2Cl_2 was added 43.9 mg 0.089 mmol) of [Pt(pyq-H)(Me)(DMSO)], **11**. The solution was stirred for 2 h, then it was concentrated to a small volume and treated with Et_2O, to give a precipitate which was filtered off, washed with Et_2O and dried to give the analytical sample as an orange solid. Yield 85%. Anal. calcd for $C_{51}H_{44}N_4P_2Pt_2$·H_2O: C 51.78, H 3.92, N 4.74%; found: C 51.68, H 3.99, N 4.54%. M.p.: 230 °C.

^{1}H NMR (300 MHz, $CDCl_3$, 298 K, ppm): 0.73 (d sat, 3H, CH_3, J_{P-H} = 7.2 Hz, J_{Pt-H} = 82.4 Hz); 0.83 (d sat, 3H, CH_3, J_{P-H} = 7.2 Hz, J_{Pt-H} = 81.8 Hz); 4.18 (m, 2H, CH_2 (dppm)); 6.21 (m, 1H); 6.31 (m, 1H); 6.95 (m, 1H); 7.16–7.30 (m, 8H); 7.38–7.64 (m, 6H); 7.81–7.96 (m, 8H); 8.12–8.20 (m, 2H). ^{31}P NMR (121.4 MHz, $CDCl_3$, 298 K, ppm): 20.4 ppm ($^1J_{Pt-P}$ = 2234 Hz, $^2J_{P-P}$ = 52 Hz, $^3J_{Pt-P}$ n.r.); 20.9 ppm, $^1J_{Pt-P}$ = 2249 Hz, $^2J_{P-P}$ = 52 Hz, $^3J_{Pt-P}$ n.r.).

[(Me)(bpy-H)Pt(μ-dppm)Pt(pyq-H)(Cl)], 14

Complex **14** was obtained following the same procedure as used for **13**, reacting the chloride complex [Pt(pyq-H)(Cl)-(DMSO)], **12**, in place of the methyl complex [Pt(pyq-H)(Me)-(DMSO)], **11**. Yield 80%. Anal. calcd for $C_{50}H_{41}ClN_4P_2Pt_2$: C 50.66, H 3.49, N 4.73%; found: C 50.42, H 3.19, N 4.41%.

^{1}H NMR (300 MHz, $CDCl_3$, 298 K, ppm): 0.72 (d sat, 3H, CH_3, J_{P-H} = 7.4 Hz, J_{Pt-H} = 82.6 Hz); 4.55 (m, 2H, CH_2 (dppm)); 6.51 (m, 1H); 6.69 (m, 2H); 6.95 (m, 1H); 7.15–7.32 (m, 14H); 7.43 (m, 1H); 7.60 (m, 2H); 7.43–7.80 (m, 6H); 8.05–8.24 (m, 8H); 9.38 (ddd, 1H, H_6). ^{31}P NMR (121.4 MHz, $CDCl_3$, 298 K, ppm): 12.8 ppm ($^1J_{Pt-P}$ = 2232 Hz, $^3J_{Pt-P}$ = 80 Hz, $^2J_{P-P}$ = 20 Hz, P *trans* C); 18.5 ppm ($^1J_{Pt-P}$ = 4305 Hz, $^3J_{Pt-P}$ = 44 Hz, $^2J_{P-P}$ = 20 Hz, P *trans* N).

[(CH_3)(dppe-κ^{2}P,P)Pt(μ-bpy-H)Pt(CH_3)$_2$], 15

To a solution of complex **5** in $CDCl_3$ (15.2 mg, 0.02 mmol) were added 7.8 mg of [Pt(Me)$_2$(DMSO)$_2$] (0.02 mmol) in an NMR tube. The solution immediately changed from whitish to bright yellow. ^{1}H and ^{31}P NMR spectra were registered within 10 min.

^{1}H NMR (300 MHz, $CDCl_3$, 298 K, ppm): 9.73 (d, 1H, J_{H-H} = 7.4 Hz, H_3); 8.94 (d sat, 1H, J_{H-H} = 4.8 Hz, J_{Pt-H} = *ca*. 26 Hz, H_6 or $H_{6'}$); 8.74 (d sat, 1H, J_{H-H} = 4.6 Hz, J_{Pt-H} = *ca*. 28 Hz, H_6 or $H_{6'}$); 8.07 (m, 1H); 7.86–6.79 (m, 23H); 3.15 (m, 4H, CH_2 dppe); 0.96 (two overlapping d with sat, 6H, $^2J_{Pt-H}$ = *ca*. 84 Hz, Pt–CH_3); 0.50 (t with sat, 3H, $^3J_{P-H}$ = 7.1 Hz, $^2J_{Pt-H}$ = 69 Hz, Pt–CH_3). ^{31}P NMR (121.4 MHz, $CDCl_3$, 298 K, ppm): 45.7 ppm (s sat, $^1J_{Pt-P}$ = 2034 Hz), 44.5 ppm (s sat, $^1J_{Pt-P}$ = 1744 Hz).

Acknowledgements

Financial support from Università di Sassari (FAR) is gratefully acknowledged. L. M. gratefully acknowledges a PhD fund, financed on POR/FSE 2007–2013, from Regione Autonoma della Sardegna. M. A. C. and S. S. gratefully acknowledge the Regione Autonoma della Sardegna (RAS) for the Grants "Premialità Regionale 2011" and "Premialità Regionale 2012", respectively.

References

1 (*a*) *e.g* M. Albrecht, *Chem. Rev.*, 2010, **110**(2), 576–623; (*b*) I. Omae, *Cyclometalation Reactions. Five-Membered Ring*

Products as Universal Reagents, Springer, Japan, 2014; (*c*) M. Crespo, *Inorganics*, 2014, 115–131.

2 *e.g.* (*a*) T. W. Lyons and M. S. Sanford, *Chem. Rev.*, 2010, **110**, 1147–1169; (*b*) C. P. Newman, K. Casey-Green, G. J. Clarkson, G. W. Cave, V. Errington and J. P. Rourke, *Dalton Trans.*, 2007, 3170–3182.

3 *e.g.* (*a*) M. Lopez-Torres, A. Fernandez, J. J. Fernandez, A. Suarez, S. Castro-Juiz, J. M. Vila and M. T. Pereira, *Organometallics*, 2001, **20**, 1350; (*b*) M. Frezza, Q. P. Dou, Y. Xiao, H. Samouei, M. Rashidi, F. Samari and B. Hemmateenejad, *J. Med. Chem.*, 2011, **54**, 6166–6176; (*c*) F. Samari, B. Hemmateenejad, M. Shamsipur, M. Rashidi and H. Samouei, *Inorg. Chem.*, 2012, **51**, 3454–3464; (*d*) S. C. F. Kui, S. S.-Y. Chui, C.-M. Che and N. Zhu, *J. Am. Chem. Soc.*, 2006, **128**, 8297–8309; (*e*) C. B. Lavery, M. J. Ferguson and M. Stradiotto, *Organometallics*, 2010, **29**, 6125; (*f*) G. Keglevich, P. Bagi, A. Szöllősy, T. Körtvélyesi, P. Pongrácz, L. Kollár and L. Drahos, *J. Organomet. Chem.*, 2011, **696**, 3557; (*g*) K. L. Toups and R. A. Widenhoefer, *Chem. Commun.*, 2010, **46**, 1712; (*h*) R. Martín, M. Crespo, M. Font-Bardia and T. Calvet, *Polyhedron*, 2009, **28**, 13698–11373; (*i*) T. C. Cheung, K. K. Cheung, S. M. Peng and C. M. Che, *J. Chem. Soc., Dalton Trans.*, 1996, 1645.

4 C. Diaz and E. Araya, *Polyhedron*, 1997, **16**(11), 1775–1781.

5 R. J. Puddephatt, *Chem. Soc. Rev.*, 1983, **12**, 99–127.

6 *e.g.* (*a*) W. Lu, M. C. W. Chan, K. Cheung and C. Che, *Organometallics*, 2001, 2477–2486; (*b*) M. Rashidi, S. Jamali and M. Hashemi, *J. Organomet. Chem.*, 2001, **633**, 105–113; (*c*) W. Lu, M. C. W. Chan, N. Zhu, C.-M. Che, C. Li and Z. Hui, *J. Am. Chem. Soc.*, 2004, **126**, 7639–7651; (*d*) S.-W. Lai, M. C.-W. Chan, T.-C. Cheung, S.-M. Peng and C.-M. Che, *Inorg. Chem.*, 1999, **38**, 4046–4055.

7 (*a*) B. Butschke and H. Schwarz, *Chem. Sci.*, 2012, **3**, 308–326; (*b*) A. Zucca, G. L. Petretto, S. Stoccoro, M. A. Cinellu, M. Manassero, C. Manassero and G. Minghetti, *Organometallics*, 2009, **28**(7), 2150–2159; (*c*) G. Minghetti, A. Doppiu, A. Zucca, S. Stoccoro, M. A. Cinellu, M. Manassero and M. Sansoni, *Chem. Heterocycl. Compd.*, 1999, **35**, 992–1000.

8 A. C. Skapski, V. F. Sutcliffe and G. B. Young, *J. Chem. Soc., Chem. Commun.*, 1985, 609–611.

9 (*a*) A. Zucca, G. L. Petretto, S. Stoccoro, M. A. Cinellu, G. Minghetti, M. Manassero, C. Manassero, L. Male and A. Albinati, *Organometallics*, 2006, **25**, 2253–2265; (*b*) A. Zucca, M. A. Cinellu, G. Minghetti, S. Stoccoro and M. Manassero, *Eur. J. Inorg. Chem.*, 2004, 4484–4490.

10 L. Maidich, G. Zuri, S. Stoccoro, M. A. Cinellu, M. Masia and A. Zucca, *Organometallics*, 2013, **32**, 438–448.

11 R. H. Crabtree, *Science*, 2010, **330**, 455–456.

12 (*a*) J. Kwak, Y. Ohk, Y. Jung and S. Chang, *J. Am. Chem. Soc.*, 2012, **134**(42), 17778–17788; (*b*) T. Shibata, S. Takayasu, S. Yuzawa and T. Otani, *Org. Lett.*, 2012, **14**(19), 5106–5109; (*c*) L. Taghizadeh Ghoochany, C. Kerner, S. Farsadpour, F. Menges, Y. Sun, G. Niedner-Schatteburg and W. R. Thiel, *Eur. J. Inorg. Chem.*, 2013, **24**, 4305–4317; (*d*) T. Shibata and S. Takayasu, *Heteroat. Chem.*, 2014, DOI: 10.1002/hc.21158.

13 (*a*) A. Zucca, A. L. Maidich, L. Canu, G. L. Petretto, S. Stoccoro, M. A. Cinellu, G. J. Clarkson and J. P. Rourke, *Chem. – Eur. J.*, 2014, **20**(18), 5501–5510; (*b*) G. L. Petretto, A. Zucca, S. Stoccoro, M. A. Cinellu and G. Minghetti, *J. Organomet. Chem.*, 2010, **695**, 256–259; (*c*) B. Butschke and H. Schwarz, *Int. J. Mass Spectrom.*, 2011, **306**, 108–113; (*d*) B. Butschke, M. Schlangen, D. Schröder and H. Schwarz, *Int. J. Mass Spectrom.*, 2009, **283**, 3–8; (*e*) B. Butschke, M. Schlangen, D. Schröder and H. Schwarz, *Chem. – Eur. J.*, 2010, **16**, 3962–3969; (*f*) B. Butschke and H. Schwarz, *Organometallics*, 2010, **29**, 6002–60141.

14 G. L. Petretto, J. P. Rourke, L. Maidich, S. Stoccoro, M. A. Cinellu, G. Minghetti, G. J. Clarkson and A. Zucca, *Organometallics*, 2012, **31**(8), 2971–2977.

15 A. Zucca, G. L. Petretto, S. Stoccoro, M. A. Cinellu, M. Manassero, C. Manassero and G. Minghetti, *Organometallics*, 2009, **28**, 2150.

16 *e.g.* (*a*) T. G. Appleton and M. A. Bennett, *Inorg. Chem.*, 1978, **17**, 738–747; (*b*) G. Minghetti, A. Zucca, S. Stoccoro, M. A. Cinellu, M. Manassero and M. Sansoni, *J. Organomet. Chem.*, 1994, **481**, 195–204.

17 M. Rashidi, S. M. Nabavizadeh, A. Zare, S. Jamali and R. J. Puddephatt, *Inorg. Chem.*, 2010, **49**, 8435–8443.

18 (*a*) H. Gunther, *Angew. Chem., Int. Ed. Engl.*, 1972, **11**, 861; (*b*) E. W. Garbisch, *J. Chem. Educ.*, 1968, **45**, 480.

19 *iNMR software, version 5.3.6*, MestreLab Research, http://www.inmr.net/.

20 P. E. Garrou, *Chem. Rev.*, 1981, **81**, 229–266.

21 (*a*) S. Jamali, S. M. Nabavizadeh and M. Rashidi, *Inorg. Chem.*, 2008, **47**, 5441–5452; (*b*) M. G. Haghighi, M. Rashidi, S. M. Nabavizadeh, S. Jamalib and R. J. Puddephatt, *Dalton Trans.*, 2010, **39**, 11396–11402.

22 (*a*) J. DePriest, G. Y. Zheng, N. Goswami, D. M. Eichhorn, C. Woods and D. P. Rillema, *Inorg. Chem.*, 2000, **39**, 1955–1963; (*b*) M. G. Haghighi, S. M. Nabavizadeh, M. Rashidi and M. Kubicki, *Dalton Trans.*, 2013, **42**, 13369–13380.

23 (*a*) C.-K. Koo, B. Lam, S.-K. Leung, M. H.-W. Lam and W.-Y. Wong, *J. Am. Chem. Soc.*, 2006, **128**, 16434–16435; (*b*) C.-K. Koo, K.-L. Wong, K.-C. Lau, W.-Y. Wong and M. H.-W. Lam, *Chem. – Eur. J.*, 2009, **15**, 7689–7697.

24 S. M. Nabavizadeh, M. G. Haghighi, A. R. Esmaeilbeig, F. Raoof, Z. Mandegani, S. Jamali, M. Rashidi and R. J. Puddephatt, *Organometallics*, 2010, **29**, 4893–4899.

25 A. Zucca, D. Cordeschi, L. Maidich, M. I. Pilo, E. Masolo, S. Stoccoro, M. A. Cinellu and S. Galli, *Inorg. Chem.*, 2013, **52**(13), 7717–7731.

26 S. J. Hoseini, S. M. Nabavizadeh, S. Jamali and M. Rashidi, *J. Organomet. Chem.*, 2007, **692**, 1990–1996.

27 M. Brookhart, M. L. H. Green and G. Parkin, *Proc. Natl. Acad. Sci. U. S. A.*, 2007, **104**, 6908–6914.

28 B. S. Furniss, A. J. Hannaford, P. W. G. Smith and A. R. Tatchell, *Vogel's Textbook of Practical Organic Chemistry*, Longman, Harlow, 5th edn, 1989.

29 (*a*) C. Eaborn, K. Kundu and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, 1981, 933; (*b*) R. Romeo and L. Monsù Scolaro, *Inorg. Synth.*, 1998, **32**, 153.