ORGANOMETALLICS

Heterobimetallic Rollover Derivatives

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S Supporting Information

ABSTRACT: Heterobimetallic complexes with metal centers connected by a small delocalized ligand constitute an interesting class of compounds. Here we report that starting from the mononuclear platinum(II) rollover complexes [Pt(bipy-H)(L)Cl] (bipy-H = 2,2'-bipyridine C(3')-N cyclometalated, L= DMSO, PPh₃) a second rollover cyclometalation may produce a series of Pt(II)/Pd(II) heterobimetallic complexes where the two metals are linked by the planar, highly delocalized, doubly deprotonated 2,2'-bipyridine.



INTRODUCTION

The synthesis of bimetallic complexes has had a long and venerable history. The interest in these systems arises from the idea that two metal centers in close proximity may influence each other and affect both the chemical and physical properties of the molecule, often with surprising results.¹ The mutual influence may produce significant modifications of the individual properties of the metal centers or even develop novel characteristics which do not occur in the analogous mononuclear compounds.

One of the most fascinating aspects of bimetallic systems is the electronic contact created when a π -conjugated ligand is used to connect the metal centers. Interesting developments may arise when the system contains metal atoms with different properties: examples are mixed-valence compounds, i.e. compounds with two metals in different oxidation states, which are particularly suitable for electron transfer processes,² and heterobimetallic complexes which are expected to display unique properties due to the cooperation of metal centers with different physical and chemical characteristics.

Heterobimetallic complexes where the metal centers are connected by a delocalized carbon chain are of great interest in the fields of materials science, biology, and homogeneous catalysis.³

This family of compounds includes polypyridyl complexes, such as those derived from 2,2'-bipyrimidine, which have been studied as models for energy and electron transfer processes.⁴ Applications in photocalysis are particularly promising: a recent paper reports a dinuclear Ru/Pd complex with bridging substituted bipyrimidines containing a photosensitizing Ru(II) fragment that operates as an antenna device able to collect solar light and transfer energy to a Pd(II) center. Under irradiating

conditions this system catalyzes the selective dimerization of α -methylstyrene.⁵



We sought to investigate the properties of complexes where two different metals are held in close proximity via an unsaturated organic linker, building on our early work with "rollover" Pt(II) complexes;⁶ the so-called "rollover" compounds originate from a particular coordinating behavior of 2,2'-bipyridine, which, under well-defined conditions, is able to activate the C(3')–H bond and act as a cyclometalated ligand.⁷



M = Pt, Pd, Rh, Ir, Au

Only a few metals, such as Pt(II),⁸ Pd(II),⁹ Au(III),¹⁰ Rh(III),¹¹ Ir(III),¹² and Cu(II)¹³ are, to the best of our knowledge, able to display this behavior, which has interesting potentialities due, inter alia, to the presence of an

Received:
 July 21, 2011

 Published:
 March 22, 2012

uncoordinated nitrogen atom. Platinum(II) rollover compounds have recently received attention due to their activity in the gas phase, with promising applications in catalysis and C–C and C–H bond formation.¹⁴

In the case of platinum(II), reaction of 1 equiv of the electron-rich $[Pt(Me)_2(DMSO)_2]$ with 2,2'-bipyridine (bipy) results in the high yield of complex **1a** (Scheme 1), which can



be converted to the corresponding chloride [Pt(bipy-H)-(DMSO)Cl] (2a) by reaction with HCl. The coordinated DMSO in 1a and 2a can be easily displaced by neutral ligands to give complexes with an array of electronic and steric properties: e.g., [Pt(bipy-H)(L)Me] (L = PPh₃, 1b; L = CO, 1c) and [Pt(bipy-H)(L)Cl] (L = PPh₃, 2b; L = CO, 2c).

The "rollover" geometry allows for further reaction with either the same or a different metal source. Thus, biorganometallic complexes can potentially be prepared with the two metals in very close proximity. Such complexes might potentially have many uses, with the adjacent metals being in effective electronic communication with each other.

RESULTS AND DISCUSSION

The rollover cyclometalated compounds closely resemble the analogous derivatives of 2-phenylpyridine.¹⁵ A striking difference between the two families of complexes is the presence (or absence) of the uncoordinated nitrogen atom. For this reason compounds **1** and **2** are able to further react to give dinuclear species **3** of general formula $[L(X)Pt(\mu-bipy-2H)Pt(X')L']$ (*X*, *X'* = Me, Cl; L, L' = PPh₃, DMSO, CO, etc.), where the doubly deprotonated 2,2'-bipyridine acts as a planar, delocalized dianionic bridging ligand (reaction 1).



This synthetic approach has made possible the synthesis of both symmetric (L = L', X = X'; e.g. $[(PPh_3)(Me)Pt(\mu\text{-bipy-}2H)Pt(Me)(PPh_3)]$ (3a)) and unsymmetric (L \neq L', X \neq X'; e.g. $[(PPh_3)(Me)Pt(\mu\text{-bipy-}2H)Pt(Cl)(CO)]$ (3b)) species.⁶ A logical consequence of this approach is that the second cyclometalation may involve a different metal from the first one and hence may produce heterodinuclear species where the metal centers are strictly connected by the delocalized bridging ligand.

The synthesis of these dinuclear complexes, however, is not trivial. As shown by the X-ray crystal structure of $[Pt(bipy-H)(PPh_3)Cl]$ (1b),⁶ the distance between the hydrogen atom bonded to C(3') and the uncoordinated nitrogen is 2.579 Å (average distance in two independent molecules), slightly less

than the sum of van der Waals radii (1.09 + 1.55 Å). According to these data the uncoordinated nitrogen may not be easily available for coordination, at least on the basis of steric considerations.

As a starting point we reacted [Pt(bipy-H)(DMSO)Cl] (2a) with palladium acetate in refluxing benzene to obtain the tetranuclear species $[(DMSO)ClPt(\mu-bipy-2H)Pd(\mu-OAc)]_2$ (4) (reaction 2).



The ¹H NMR spectrum of the isolated product shows two sets of resonances, indicating the presence of two species in a 4:1 molar ratio. The subspectra of these species are very similar: in both cases the aromatic region contains six protons, suggesting a second C-H bond activation. In the aliphatic region the main species has two signals ascribable to coordinated DMSO ligands (δ 3.83 ppm, 6H, J_{Pt-H} = 17 Hz; δ 3.49 ppm, 6H, J_{Pt-H} = 19 Hz) and only one for the acetato groups (δ 2.22 ppm, 6H). In contrast, the minor species possesses two signals for the DMSO methyls (3.79 and 3.49 ppm, 6H + 6H partially overlapping) and two singlets for the acetato ligands (2.64 and 2.17 ppm, 3H + 3H). This is in line with tetranuclear species of general formula [(DMSO)(Cl)Pt- $(\mu$ -bipy-2H)Pd $(\mu$ -OAc $)_{2}$, present as the trans and cis isomers 4trans and 4cis. The main species, 4trans, should have two equivalent acetato bridging ligands; the DMSO ligands should be chemically equivalent as well.



Acetato dimeric species usually have a folded structure,¹⁶ which in our case should render diastereotopic the methyls of the same DMSO (planar chirality). The minor species **4cis** possesses chemically inequivalent acetato ligands but equivalent coordinated DMSO. Due to the folded conformation of the complex, in this case, again the methyl groups in the same DMSO should be diastereotopic.

In the absence of a structural characterization we investigated the nature of complexes 4 through mono- and multidimensional ¹H NMR spectroscopy (COSY and GOESY¹⁷ experiments). For complex **4trans** the ¹H GOESY experiments show, inter alia, enhancement of the signals at 7.04 (H₄) and 7.55 ppm (H_{6'}) after irradiation of the acetato signal, confirming that they are adjacent to the Pd atom. Irradiation of aromatic signals confirms that peaks that in a planar conformation would not be expected to be in close proximity to each other actually are: e.g., irradiation at 7.04 ppm (H₄) enhances the signal at 7.55 ppm (H_{6'}) and vice versa. In addition an extremely small, but significant, enhancement is present between the H_{5} and $H_{5^{\prime}}$ protons.

The DMSO signal at 3.85 ppm enhances the peaks at 8.26 (H_4) and 8.55 (H_6) , whereas the other signal, at 3.49 ppm, enhances only the $H_{4'}$ peak. All these data fit with a bent molecule having, on the NMR time scale, a nonrotating DMSO, with the S=O bond in the plane, one methyl (at 3.85 ppm) inside the folded molecule, and the other one (at 3.49 ppm) pointing out.

In addition, the spectra seem to indicate that there may be some exchange between the two Me groups on the same DMSO, as both are diminished in intensity upon irradiation of the other one, rather than each enhancing the other. This is consistent with a dynamic behavior of the molecule which inverts the structure, so that the methyl pointing out becomes in and vice versa.



Furthermore, irradiation of some of the peaks of the major compound causes a small amount of negative enhancement of the peaks of the minor component. This would imply that they are in slow chemical exchange.

In agreement with the proposed formulation the IR spectrum shows bands in the region 1390-1570 cm⁻¹ (see the Experimental Section) consistent with bridging acetato ligands.¹⁸

The reaction of **2a** with palladium acetate may be followed by treatment with LiCl, to give the corresponding chloride $[(DMSO)CIPt(\mu-bipy-2H)Pd(\mu-Cl)]_2$ (**5a**). Analogously, starting from **2b**, $[(PPh_3)CIPt(\mu-bipy-2H)Pd(\mu-Cl)]_2$ (**5b**) may be isolated in the solid state in good yields and characterized. In contrast to the acetato species **4**, the chloride-bridged complexes **5a**,**b** are flat, with evidence coming from the ¹H NMR spectra which show only one resonance for the DMSO protons (reaction 3).



The ¹H NMR spectra of **5a**,**b** show only one set of signals and support the given formulation. In particular, the coupling constants of the DMSO signal in the ¹H spectrum of **5a** $({}^{3}J(Pt-H) = 25.2 \text{ Hz})$ and of the coordinated phosphorus in **5b** $({}^{1}J(Pt-P) = 4154 \text{ Hz})$ agree with neutral ligands coordinated trans to a nitrogen atom.¹⁹

Starting from the tetranuclear species 5a,b subsequent reactions lead to cleavage of the anionic bridge between the two palladium centers and the generation of relatively simple bimetallic species. Starting from 5a, apart from opening the chloride bridge, the neutral ligand may also displace the coordinated DMSO: the reactions with PPh₃ or 3,5-lutidine, driven with at least a 4:1 ligand:complex molar ratio, gave the heterodinuclear "symmetric" species **6a** ($L = L' = PPh_3$) and **6b** (L = L' =lutidine) (reaction 4).



The ¹H and ³¹P NMR spectra of complex **6a** clearly show the different influences of palladium and platinum on the chemical shifts. In the ³¹P NMR spectrum the phosphorus coordinated to platinum is unambiguously assigned by the presence of satellites. The coupling constant value (¹ $J_{Pt-P} = 4155$ Hz) is in agreement with a trans P–Pt–N arrangement. The chemical shifts of the two phosphorus atoms are very different (41.89 ppm, P–Pd; 19.80 ppm, P–Pt), as previously observed in corresponding cyclometalated palladium and platinum complexes.²⁰

The protons adjacent to the nitrogen, H_6 and $H_{6'}$, are slightly deshielded by coordination; as is often observed, the deshielding effect of the platinum is greater than that of palladium (δ_{Pt} 9.05 ppm, δ_{Pd} 8.85 ppm). A comparison between analogous mono- and dinuclear rollover species (Scheme 2,



compounds **6a**, **3c**, and **2b**) evidences the shielding of the $H_{6'}$ proton upon the second metalation (9.85, 9.06, and 9.05 ppm in **2b**, **3c**, and **6a**, respectively), apparently independent from the nature of the second metal. The second metalation has consequences also in the ³¹P NMR spectra, in both chemical shift and coupling constant values.

Operating under mild conditions, starting from **5b** (L = PPh₃), the "unsymmetric" complex **6c** (L = PPh₃, L' = 3,5-lutidine) can be isolated in the solid state by reaction with 3,5-lutidine. As expected, 3,5-lutidine opens the chloride bridge but does not displace PPh₃.

The NMR spectra of **6c** confirm in solution the coordination of the neutral ligands trans to the bipy nitrogen, as indicated by ${}^{1}J(\text{Pt}-\text{P})$ and ${}^{3}J(\text{Pt}-\text{H})$ (ortho lutidine protons) coupling constants (4155 and 55.8 Hz, respectively). Furthermore, the position of H₄ and H_{4'} in the spectrum (multiplet at ca. 6.6–6.8 ppm) is due to the shielding effect of the adjacent PPh₃ and lutidine, respectively. The structure of complex **6c** was definitely confirmed by the resolution of the crystal structure in the solid state by X-ray diffraction (Figure 1).

Distances and angles are in line with those previously reported for the analogous homodinuclear rollover complex $[Pt_2(bipy-2H)(PPh_3)_2Cl_2]$ (3c; e.g., Pt-Cl = 2.352 Å, Pt-C = 2.113 Å, Pd-C = 2.004 Å, Pd-Cl = 2.394 Å).⁶ The bipy-2H bridging ligand is almost completely planar.



Figure 1. Solid-state structure of one of the crystallographically independent but chemically identical molecules in the asymmetric unit of **6c**. Hydrogens and disordered solvent have been removed for clarity. Thermal parameters are drawn at the 50% probability level.

Electronic delocalization through the two planar deprotonated bipyridine rings and the cyclometalated rings (metalloaromaticity) may be deduced by the short C2–C2' bond, whose length decreases from 1.490 Å in free 2,2'-bipyridine²¹ to 1.463/1.468 Å in **2b**, 1.438 Å in **3c**, and 1.445 Å in **6c** (see Scheme 3). Similar trends were used to identify metal-

Scheme 3. Variation of Selected C–C and C–N Bond Lengths (Å) in the Free bipy and in Mono- and Dinuclear Rollover Complexes^a



^{*a*}For complex 3c, $M = Pt(PPh_3)Cl$; for complex 6c, $M = Pd(3,5-Me_2-py)Cl$.

loaromaticity in palladium(II) five-membered cyclometalated species.²² It should be noted, however, that in species **2b**, **3c**, and **6c** no clear corresponding elongation is observed in C2–N and C2'–C3 bond lengths and the shortening of the C2–C2' bond may be due to double chelation effects of the bipy-2H ligand (see Scheme 2).

The crystal structure of 6a was partially solved by X-ray diffraction,²³ but extensive disorder, in particular that arising from the interchange of Pd and Pt, meant that a satisfactory solution could not be found.

The acetato species $[{(PPh_3)(Cl)Pt(\mu-bipy-2H)Pd}\mu-OAc]_2$ was not isolated in the solid state but was directly treated with LiCl to give the corresponding chloride $[{(PPh_3)(Cl)Pt(\mu-bipy-2H)Pd}\mu-Cl]_2$ (**5b**). If Na(acac) is added instead of LiCl, the dinuclear species $[{(PPh_3)(Cl)Pt(\mu-bipy-2H)Pd(acac)}]$ (7) may be isolated in good yields and characterized (reaction 5).



The characterization of 7 mainly rests on NMR spectroscopy. In particular, in the ³¹P NMR spectrum a singlet at 17.5 ppm flanked by satellites (${}^{1}J_{Pt-P} = 4136 \text{ Hz}$) is in line with a P trans to N.

An HMQC ¹⁹⁵Pt-¹H spectrum shows a ¹⁹⁵Pt signal at -4029 ppm, coupled to ³¹P. The marked difference of ¹⁹⁵Pt chemical shifts between 7 and 4 (δ -3562 ppm) is an indication of the significant electronic effect of a different palladium center to the platinum. A mass spectrum confirms the proposed formulation, showing a peak at m/z 817, corresponding to protonation and loss of Cl.

As mentioned above, the second nitrogen atom is not completely available for coordination, and up to now only Pt–Pt double-rollover cyclometalated species have been reported for 2,2'-bipyridine. Furthermore, the second cyclometalation reaction requires the use of a mononuclear rollover species as a ligand, with the drawback that reaction conditions often are not compatible with a reactive metal–carbon bond or a metal center. With the intention to extend the study to other metals, the reactions of the mononuclear derivative [Pt(bipy-H)-(PPh_3)Cl] (2b) with a series of Au(III), Hg(II), and Rh(I) metal salts were tested as a part of a preliminary study.

In no cases were heterodinuclear doubly cyclometalated species formed: the reaction of [Pt(bipy-H)(DMSO)Cl] (2a) with NaAuCl₄ was previously reported⁶ and resulted in the oxidation of the Pt(II) center to give a Pt(IV) complex, $[Pt(bipy-H)(DMSO)Cl_3]$.²⁴

The reaction of **2b** with mercury(II) acetate was performed in order to obtain an organomercurial, useful for transmetalation reactions. Under standard experimental conditions no reaction was observed and only the starting complex **2b** was recovered from the reaction mixture.

NMR and MS Spectra. The ¹⁹⁵Pt NMR spectra of **2b**, **4**, **6a–c**, and 7 were obtained by means of ${}^{1}\text{H}-{}^{195}\text{Pt}$ correlation spectra using a variant of the HMBC pulse sequence. A first comparison of the spectra shows, as expected, that the major influence on the chemical shift is provided by the nature of the ligands on the platinum center, so that the species having the same Pt(N^C)(PPh_3)Cl environment (**2b**, **6a**,**c**, and 7) have similar chemical shifts (see Table 1), whereas complex **6b**, having a 3,5-lutidine instead of a PPh₃, shows a deshielding of more that 1000 ppm. This is in line with literature data, which indicate the same trend when a nitrogen donor is replaced by a

Table 1. Selected NMR Data

| | $\delta(^{195}	ext{Pt})$, ppm | $\delta(^{31}\text{P})$, ppm | $J_{\rm Pt-P}$, Hz | $\delta(\mathbf{H}_{6'})$, ^a ppm |
|---------------------|---|-------------------------------|---------------------|--|
| 2b | -4195 | 23.60 | 4285 | 9.85 (31) |
| 4trans | -3562 | | | |
| 4cis | -3568 | | | |
| 6a | -4050 | 19.80 | 4155 | 9.05 (30) |
| 6b | -2953 | | | 8.81 (29) |
| 6c | -4034 | 18.87 | 4155 | 9.07 (30) |
| 7 | -4136 | 17.51 | 4136 | 8.95 (30) |
| ¹³ 1 (in | $\mathbf{U}_{\mathbf{z}}$) in normathe | | | |

³J_{Pt–H} (in Hz) in parentheses.

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phosphine.²⁵ The same behavior is observed for complexes 4 (trans and cis), which have a Pt-S instead of a Pt-P bond.

The differences in chemical shift values between the dinuclear complexes **6a**,**c** and 7 is only attributable to the different environments around the palladium (ca. 100 ppm between **6a** and 7), reflecting the influence of the palladium center on the platinum atom, connected via the delocalized planar doubly cyclometalated 2,2'-bipyridine. The substitution of a PPh₃ on the palladium with a 3,5-lutidine results in a 16 ppm shift to lower field of the ¹⁹⁵Pt, following the trend expected for a P/N substitution, but with a smaller effect due to the Pt–Pd distance.

A comparison between the ¹H and ³¹P spectra of **2b**, **6a**,**c**, and 7, all having a $Pt(N^C)(PPh_3)Cl$ coordination, shows a clear difference between the H₆ chemical shifts in mono- and dinuclear species (9.85, 9.05, 9.07, and 8.95 ppm in **2b**, **6a**,**c**, and 7, respectively), a sharp effect due to the second cyclometalation. Conversely, the second metalation has minor consequences on the chemical shift of the H_{6'} proton but greater effects on its ¹⁹⁵Pt-H coupling constants (see Scheme 1), showing also a clear dependence on the nature of the palladium center. Furthermore, the ³¹P NMR spectra also show consequences, both in chemical shift and coupling constant values (Scheme 4), due to the second cyclometalation.

Scheme 4



Further evidence for the characterization of the complexes were provided by high-resolution mass spectra of species **2b**, **6a**-**c**, and 7, showing in all cases the $[M - Cl]^+$ peak, with an excellent match between calculated and experimental values (e.g., **6b**: m/z found 704.0373, calculated for $C_{24}H_{24}ClN_4^{-106}Pd^{195}Pt$, (M – Cl)⁺, 704.0373).

CONCLUSIONS

Rollover compounds constitute a new emerging class of cyclometalated complexes having the additional key feature of an uncoordinated donor atom, which can be exploited in a way not feasible for classic cyclometalated species. One of the possibilities is the double-cyclometalation reaction, which may be used to obtain heterobimetallic species where the metals are linked by the highly delocalized, doubly deprotonated bipyridine. The coordination of the second metal center is not a trivial task: the uncoordinated nitrogen doublet in mononuclear rollover species is engaged in an N---H interaction, and hence it is not easily feasible for coordination. Furthermore, the cyclometalation reaction conditions are often not compatible with the presence of a metal-carbon bond. The new heterobimetallic Pt-Pd species reported here have been thoroughly characterized, revealing electronic influence between the metal centers, mediated by the bipyridine spacer, as indicated by NMR and IR data.

EXPERIMENTAL SECTION

 $[Pt(Me)_2(DMSO)_2],^{26}$ [Pt(bipy-H)(DMSO)Cl] (2a),⁶ and $[Pt(bipy-H)(PPh_3)Cl]$ (2b)⁶ were synthesized according to the literature. All reactions were carried out under an inert atmosphere. The solvents were purified and dried before use according to standard procedures.²⁷ Elemental analyses were performed with a Perkin-Elmer 240B elemental analyzer by Mr. Antonello Canu (Dipartimento di Chimica, Università degli studi di Sassari, Sassari, Italy) or by the Warwick Analytical Service (University of Warwick, Coventry, U.K.). Infrared spectra were recorded with a FT-IR Jasco 480P using Nujol mulls. ¹H, $^{13}C{^{1}H}$, and $^{31}P{^{1}H}$ NMR spectra were recorded with Bruker AV 400, 500, or 600 MHz and Varian VXR 300 MHz spectrometers. Chemical shifts are given in ppm relative to internal TMS for ¹H and ${}^{13}C{}^{1}H$ and external 85% H_3PO_4 for ${}^{31}P{}^{1}H$. Coupling constant values are given in Hz. NOE difference (GOESY) and 2D-COSY experiments were performed by means of standard pulse sequences. Pt NMR spectra were recorded on a Bruker Avance 500 using ¹H-¹⁹⁵Pt correlation spectra; these were recorded using a variant of the HMBC pulse sequence with the ¹⁹⁵Pt chemical shifts quoted taken from the 2D HETCOR spectra and referenced to external Na₂PtCl₆. All accurate mass spectra were run on a Bruker MaXis mass spectrometer.



Complex 2b. ¹⁹⁵Pt NMR (CDCl₃): –4195 ppm. Accurate mass: m/z 612.1173, calculated for C₂₈H₂₂N₂P¹⁹⁵Pt (M – Cl)⁺ 612.1165.

Synthesis of [(DMSO)(Cl)Pt(μ -bipy-2H)Pd(μ -OAc)]₂ (4). To a solution of [Pt(bipy-H)(DMSO)(Cl)] (2a; 131 mg, 0.39 mmol) in 30 mL of benzene was added 91.8 mg of [Pd(OAc)₂] (0.41 mmol). The solution was heated to 80 °C for 12 h and then filtered and concentrated to dryness under reduced pressure. The solid residue was dissolved in CH₂Cl₂, filtered over Celite, concentrated to a small volume, and treated with diethyl ether. The precipitate that formed was filtered, washed with diethyl ether, and vacuum-pumped to give the analytical sample as an orange-yellow solid. Yield: 60%. Anal. Calcd for C₂₈H₃₀Cl₂N₄O₆Pd₂Pt₂S₂: C, 26.76; H, 2.41; N, 4.46. Found: C, 26.48; H, 2.45; N, 4.49.

The ¹H NMR spectrum shows the presence of two species in a 4:1 molar ratio. ¹H NMR (CDCl₃; main species, **4trans**): 8.53 (dd, 2H, $J_{H-H} = 5.6$, 1.2 Hz, $J_{Pt-H} = 30$ Hz, H_6), 8.26 (dd, 2H, $J_{H-H} = 7.9$, 1.2 Hz, $J_{Pt-H} = ca. 26$ Hz, H_4), 7.55 (dd, 2H, $J_{H-H} = 5.5$, 1.1 Hz, H_6), 7.04 (dd, 2H, $J_{H-H} = 7.6$, 1.2 Hz, H_4), 6.67 (dd, 2H, $J_{H-H} = 7.9$, 5.5 Hz, H_5), 6.38 (dd, 2H, $J_{H-H} = 7.6$, 5.6 Hz, H_5), 3.83 (s, 6H, $J_{Pt-H} = ca. 17$ Hz, CH₃ DMSO), 3.49 (s, 6H, $J_{Pt-H} = ca. 19$ Hz, CH₃ DMSO), 2.22 (s, 6H, CH₃ OAc). ¹⁹⁵Pt NMR (CDCl₃): -3562.

¹H NMR (CDCl₃; minor species, **4cis**): 8.63 (dd, 2H, $J_{H-H} = 5.6$, 1.2 Hz, J_{Pt-H} n.r., H₆), 8.35 (dd, 2H, $J_{H-H} = 7.8$, 1.2 Hz, J_{Pt-H} n.r., H₄), 7.47 (dd, 2H, $J_{H-H} = 5.5$, 1.1 Hz, H₆), 6.94 (dd, 2H, $J_{H-H} = 7.6$, 1.2 Hz, H₄), 6.57 (dd, 2H, $J_{H-H} = 7.8$, 5.5 Hz, H₅ or H₅), 6.51 (dd, 2H, $J_{H-H} = 7.6$, 5.6 Hz, H₅ or H₅), 3.79 (s, 6H, $J_{Pt-H} =$ n.r., CH₃ DMSO), 3.49 (s, overlapping, 6H, J_{Pt-H} n.r., CH₃ DMSO), 2.64 (s, 3H, CH₃ OAc), 2.17 (s, 3H, CH₃ OAc). ¹⁹⁵Pt NMR (CDCl₃): -3568.

Synthesis of [(DMSO)(Cl)Pt(bipy-2H)Pd(\mu-Cl)] (5a). To a solution of [Pt(bipy-H)(DMSO)(Cl)] (2a; 131 mg, 0.39 mmol) in 30 mL of benzene was added 91.8 mg of [Pd(OAc)₂] (0.41 mmol). The solution was stirred for 8 h at 80 °C and then filtered through Celite and evaporated to dryness under reduced pressure. The solid residue was treated with a 3/1 water/acetone mixture and an excess of LiCl. The mixture was stirred for 12 h: the precipitate that formed was filtered, washed with diethyl ether, and vacuum-pumped to give the analytical sample as a yellow solid. Yield: 70%. Anal. Calcd for C₁₂H₁₂Cl₂N₂OPdPtS: C, 23.83; H, 2.00; N, 4.63. Found: C, 23.87; H, 1.65; N, 4.68. ¹H NMR (acetone- d_6): 8.83 (d, 1H, J_{H-H} = 5.4 Hz, H_6),

8.75 (d, 1H, J_{H-H} = 5.4 Hz, J_{Pt-H} = 36 Hz, H_6), 8.51 (dd, 1H, J_{H-H} = 7.6 Hz, J_{Pt-H} = 42 Hz, H_4), 8.24 (dd, 1H, J_{H-H} = 7.6 Hz, H_4), 7.04 (dd, 1H, J_{H-H} = 5.5, 7.6 Hz, H_5 or H_5), 7.00 (dd, 1H, J_{H-H} = 5.5, 7.6 Hz, H_5 or H_5) 3.61 (s, 6H, J_{Pt-H} = 25.2 Hz, DMSO).

Synthesis of [(PPh₃)(Cl)Pt(bipy-2H)Pd(\mu-Cl)] (5b). Complex 5b was synthesized as for complex 5a, starting from [Pt(bipy-H)(PPh₃)-(Cl)] (2b) instead of [Pt(bipy-H)(DMSO)(Cl)] (2a). Yield: 85% (yellow solid), Anal. Calcd for C₂₈H₂₁Cl₂N₂PPdPt-0.5H₂O: *C*, 42.15; H, 2.78; N, 3.51. Found: C, 42.04; H, 2.83; N, 3.44. ¹H NMR (CDCl₃): 9.03 (m, 1H, H₆), 7.99 (d, 1H, $J_{H-H} = 5.3$ Hz, H_6), 7.78–7.72 (m, 6H, H_{oPPh_3}) 7.47–7.37 (m, 10H, H_{m+PPh_3} , H_4), 6.97 (m, 1H, broad, H₅ or H₅), 6.69 (d, 1H, $J_{H-H} = 7.5$ Hz, J_{Pt-H} n.r. H_4), 6.33 (m, 1H, broad, H₅ or H₅). ³¹P NMR (CDCl₃): 18.15 (s, $J_{Pt-P} = 4154$ Hz).

Synthesis of [PtPd(bipy-2H)(PPh₃)₂(Cl)₂] (6a). To a solution of **5a** (50 mg, 0.083 mmol) in 20 mL of CH₂Cl₂ was added 43.3 mg of PPh₃ (0.165 mmol). The solution was stirred for 8 h and then filtered, concentrated to a small volume, and treated with diethyl ether. The precipitate that formed was filtered, washed with diethyl ether, and vacuum-pumped to give the analytical sample as a yellow solid. Yield: 85%. Mp: >260 °C. Anal. Calcd for C₄₆H₃₆Cl₂N₂P₂PdPt·0.5H₂O: *C*, 52.11; H, 3.52; N, 2.64. Found: *C*, 51.85; H, 3.67; N, 2.82. ¹H NMR (CDCl₃): 9.05 (m, 1H, *J*_{Pt-H} = ca. 30 Hz, H₆), 8.85 (dd, 1H, *J*_{H-H} = 5.7 Hz, H₆), 7.81–7.75 (m, 12H, H_{oPPh₃}), 7.47–7.38 (m, 18H, H_{m+pPPh₃}), 6.77 (dd, 1H, *J*_{Pt-H} = 42, *J*_{H-H} = 7.5 Hz, H₄), 6.72 (dd, 1H, *J*_{J-H} = 5.7, 7.8 Hz, H₅ or H₅), 6.43 (dd, 1H, *J*_{H-H} = 5.7, 7.8 Hz, H₅ or H₅), 1⁹⁵Pt NMR (CDCl₃): -4050 ppm (doublet). Accurate mass: *m*/z 1014.0761, calcd for C₄₆H₃₆ClN₂P₂¹⁰⁶Pd¹⁹⁵Pt (M – Cl)⁺ 1014.0732.

Synthesis of [PtPd(bipy-2H)(3,5-Me₂py)₂(Cl)₂] (6b). To a solution of **5a** (37.3 mg, 0.062 mmol) in acetone (20 mL) was added 0.62 mmol of 3,5-dimethylpyridine. The solution was heated to reflux for 8 h, filtered, concentrated to a small volume, and treated with diethyl ether. The precipitate that formed was filtered, washed with diethyl ether, and vacuum-pumped to give the analytical sample as a yellow solid. Yield: 80% Mp: >260 °C Anal. Calcd for C₂₄H₂₄Cl₂N₄PdPt·H₂O: C, 37.98; H, 3.45; N, 7.38. Found: C, 37.81; H, 3.08; N, 7.18. ¹H NMR (CD₂Cl₂): 8.81 (dd, 1H, $J_{Pt-H} = 29$ Hz, $J_{H-H} = 1.1$, 5.6 Hz, H_6), 8.64 (dd, 1H, $J_{H-H} = 1.4$, 5.4 Hz, H_6), 8.56 (s, 2H, $H_{opyN-Pt}$), 8.52 (s, 2H, $H_{opyN-Pd}$), 7.53 (s, 2H, H_{ppy}), 6.85–6.72 (m, 3H, H₅, H₅, H₄, or H₄), 6.65 (dd, 1H, $J_{H-H} = 6.6$, 7.6 Hz, H_4 or H_4), 2.37 (s, 12H, CH₃ py). ¹⁹⁵Pt NMR (CDCl₃): –2953 ppm. Accurate mass: m/z 704.0373, calcd for C₂₄H₂₄ClN₄¹⁰⁶Pd¹⁹⁵Pt (M - Cl)⁺ 704.0373.

Synthesis of [(PPh₃)(Cl)Pt(μ -bipy-2H)Pd(3,5-Me₂py)(Cl)] (6c). To a solution of 5b (51.7 mg, 0.066 mmol) in CHCl₃ (30 mL) was added 0.66 mmol of 3,5-dimethylpyridine. The solution was stirred at room temperature for 8 h, concentrated to a small volume, filtered, and treated with diethyl ether. The precipitate that formed was filtered, washed with diethyl ether, and vacuum-pumped to give the analytical sample as a yellow solid. Yield: 75%. Mp: >260 °C. Anal. Calcd for $C_{35}H_{30}Cl_2N_3PPdPt_2 \cdot H_2O$: C, 45.10; H, 3.68; N, 4.51. Found: C, 44.82; H, 3.62; N, 4.42. ¹H NMR (CDCl₃): 9.07 (m, 1H, $J_{Pt-H} = 30$ Hz, H₆), 8.66 (dd, 1H, $J_{H-H} = 5.4$ Hz, H₆), 8.54 (s, 2H, H_{opy}), 7.79– 7.73 (m, 6H, H_{oPPh₃}), 7.50–7.38 (m, 10H, H_{m+pPPh₃} + H_{ppy}), 6.89 (dd, 1H, $J_{H-H} = 7.5$ Hz, H₅ or H₅·), 6.68 (m, 2H, $J_{Pt-H} = ca. 45$ Hz, H₄ + H_{4'} partially overlapping), 6.34 (dd, 1H, $J_{H-H} = 5.4$, 7.5 Hz, H₅ or H₅·) 2.38 (s, 6H, CH₃ py). ³¹P NMR (CDCl₃): 18.87 (s, $J_{Pt-P} = 4155$ Hz). ¹⁹⁵Pt NMR (CDCl₃): -4034 ppm (doublet). Accurate mass: m/z859.0557, calcd for $C_{35}H_{30}ClN_3P^{106}Pd^{195}Pt$ (M – Cl)⁺ 859.0553.

Single crystals of **6c** suitable for X-ray crystallography were grown from CHCl₃, diisopropyl ether, and (wet) acetonitrile.

The asymmetric unit contained two mixed metal complexes which were crystallographically independent but chemically identical (4 complexes in the unit cell). Other electron density in the cell modeled as two chloroforms at 50% occupancy, two waters at 50% occupancy, and a molecule of acetonitrile at 50% occupancy. The two waters were modeled as disordered over the same position as chloroform C1–Cl3, with the occupancies fixed at 50% so that the region of the crystal is

occupied by either the chloroform or the two waters. Additionally, both of the partially occupied chloroforms were modeled as disordered over two positions related by rotation about the C–H bond. The two positions were fixed at 50:50 for C1–Cl3 but tied to a free variable for chlorofom C2–Cl6 and refined to an occupancy of 60:40. No hydrogens were found for the two partially occupied water molecules O100 and O200, but these were included in the formula so as to calculate the correct density. DFIX and SIMU restraints were used to give both disordered chloroform molecules chemically reasonable bond lengths and thermal parameters. SIMU restraints were used to give both 3,5-dimethylpyridine molecules and one of the phenyls (C119–C124) of the PPh₃ reasonable thermal parameters.

Crystal data: $C_{36}H_{32.25}Cl_{3.50}N_{3.25}O_{0.50}PPdPt$, $M_r = 974.94$, triclinic, space group $P\overline{I}$, a = 9.8002(2) Å, b = 19.5809(5) Å, c = 20.0382(5) Å, $\alpha = 94.331(2)^{\circ}$, $\beta = 94.5328(19)^{\circ}$, $\gamma = 93.6782(19)^{\circ}$; V = 3812.77(16) Å³ (by least-squares refinement on 19 833 reflection positions); T = 150(2) K; $\lambda = 0.710$ 73 Å; Z = 4, D(calcd) = 1.698 Mg m⁻³, F(000) = 1894; $\mu(Mo K\alpha) = 4.454$ mm⁻¹; yellow block, dimensions 0.16 × 0.14 × 0.12 mm, no decay; $\theta_{max} = 27.50^{\circ}$; hkl ranges -12 to +12, -25 to +26; 64 011 reflections measured, 17 410 unique (R(int) = 0.0602); goodness of fit on F^2 1.166; R1 (for 14 509 reflections with $I > 2\sigma(I)$) = 0.0895, wR2 = 0.1980; 17 410/153/856 data/restraints/parameters; largest difference Fourier peak and hole 5.595 and -2.262 e Å⁻³.

The structure was solved by direct methods using SHELXS,²⁸ with additional light atoms being found by Fourier methods. Hydrogen atoms were added at calculated positions and refined using a riding model with freely rotating methyl groups. Anisotropic displacement parameters were used for all non-H atoms; H atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl hydrogen atoms) times the equivalent isotropic displacement parameter of the atom to which the H atom is attached.

Synthesis of [(PPh₃)(Cl)Pt(bipy-2H)Pd(acac)] (7). To a solution of [Pt(bipy-H)(PPh₃)(Cl)] (2b; 112 mg, 0.24 mmol) in benzene (15 mL) was added 65.1 mg of [Pd(OAc)₂] (0.28 mmol). The solution was heated to reflux under an argon atmosphere and then filtered and evaporated to dryness. The resulting solid was dissolved in acetone and treated with an excess of sodium acetylacetonate. The mixture was stirred for 24 h, and the precipitate that formed was filtered and washed with acetone and diethyl ether to give the analytical sample. Yield: 86%. Mp: >260 °C. Anal. Calcd for C₃₃H₂₈ClN₂O₂PPdPt: C, 46.49; H, 3.31; N, 3.29. Found: C, 46.39; H, 3.34; N, 3.32. ¹H NMR $(CDCl_3, 400 \text{ MHz})$: 8.95 (m, 1H, $J_{Pt-H} = 30 \text{ Hz}, H_6$), 8.02 (dd, 1H, $J_{\rm H-H}$ = 5.4 Hz, H₆'), 7.82 (d, 1H, $J_{\rm H-H}$ = 7.7 Hz, H₄), 7.72–7.68 (m, 6H, H_{oPPh_3}), 7.41–7.30 (m, 9H, H_{m+pPPh_3}), 7.00 (m, 1H, $J_{H-H} = 1.5$, 5.4, 7.7 Hz, H₅), 6.61 (dd, 1H, J_{Pt-H} = 36.5 Hz, J_{H-H} = 7.7 Hz, H₄), 6.27 (ddd, 1H, J_{H-H} = 6.2, 7.7 Hz, H₅), 5.33 (s, 1H, H_{acac}), 2.01 (s, 3H, CH₃), 1.95 (s, 3H, CH₃). ³¹P NMR (CDCl₃): 17.51 (s, PPh₃, J_{Pt-P} = 4136 Hz). ¹⁹⁵Pt NMR (CDCl₃): -4029 ppm, ESI-MS (CH₃CN/H₂O 80/20: m/z 817 [MH - Cl].

ASSOCIATED CONTENT

Supporting Information

CIF files and tables giving crystal data for **6c** and a figure giving the structure of **6a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support from the Università di Sassari (FAR) and the Ministero dell'Università e della Ricerca Scientifica (MIUR, PRIN 2007) is gratefully acknowledged. We thank Johnson

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Matthey for a generous loan of platinum salts. We are grateful for support from Advantage West Midlands (AWM) (partially funded by the European Regional Development Fund) for the purchase of a high-resolution mass spectrometer and the XRD system that was used to solve the crystal structures. L.M. gratefully acknowledges Regione Autonoma della Sardegna for a Ph.D. fund (POR/FSE 2007–2013).

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NOTE ADDED AFTER ASAP PUBLICATION

In the version of this paper published on March 22, 2012, one graphic appeared in duplicate and another had an incorrect structure. The version of this paper that appears as of March 22, 2012 has the correct structures.