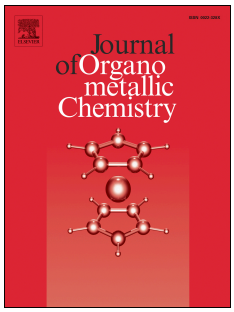


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Graphical Abstract

# Rollover cyclometalation of 6-methoxy-2,2′-bipyridine

Luca Maidich, Maria Agostina Cinellu, Fabio Cocco, Sergio Stoccoro, Mondina Sedda, Simona Galli and Antonio Zucca

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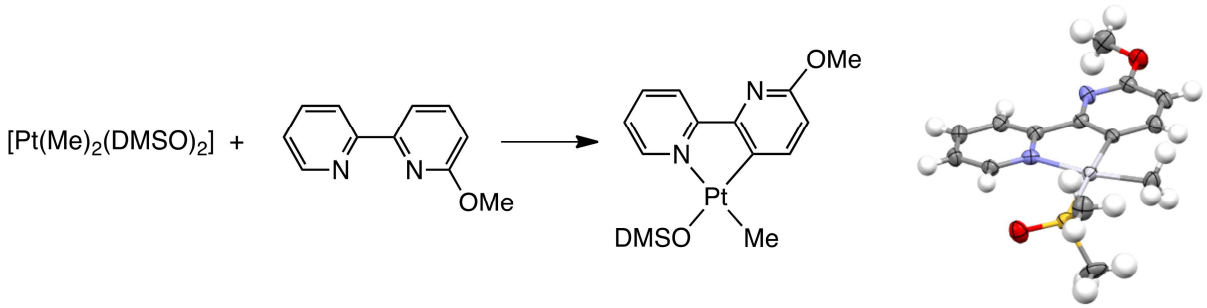

# Platinum(II), palladium(II) and gold(III) adducts and cyclometalated derivatives of 6-methoxy-2,2'-bipyridine: a comparative study

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**Abstract**

Reaction of 6-methoxy-2,2'-bipyridine ($bpy^{6OMe}$) with the electron-rich platinum(II) complex $[Pt(Me)_2(DMSO)_2]$ gave the rollover cyclometalated complex $[Pt(\kappa^2\text{-N,C-}bpy^{6OMe}\text{-H})(Me)(DMSO)]$ under mild conditions. The occurrence of rollover cyclometalation was demonstrated by single crystal X-ray diffraction structure determination. In contrast, reaction of $bpy^{6OMe}$ with $[Pt(Ph)_2(DMSO)_2]$ and $[Pt(Cl)_2(DMSO)_2]$ under mild conditions gave only adduct species of the type $[Pt(X)_2(bpy^{6OMe})]$ (X = Ph, Cl). Under harsher conditions, activation of a C-H bond in the methoxy substituent yielded the terdentate cyclometalated complex $[Pt(\kappa^3\text{-N,N,C-}bpy^{6OMe}\text{-H})Cl]$. Finally, reaction of Pd(II) and Au(III) derivatives invariably gave adduct species, with the exception of the dimeric complex $[Pd(\kappa^2\text{-N,C-}bpy^{6OMe}\text{-H})(OAc)]_2$, which, however, was not isolated in pure form. The reactivity of $bpy^{6OMe}$, as emerged from this study, was compared with that of the corresponding disubstituted ligand 6,6'-dimethoxy-2,2'-bipyridine, previously studied by us.

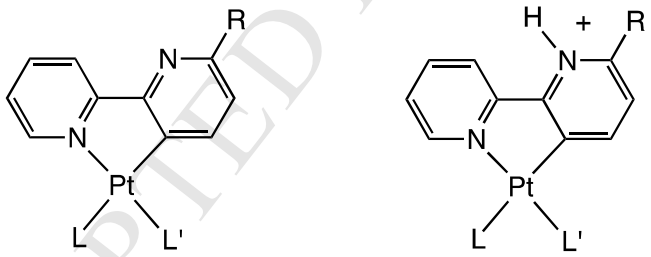
## Introduction

Cyclometalated compounds constitute one of the most important classes of organometallic complexes.[1] Their intrinsic stability, due to the chelated organometallic ligand, is at the basis of their rich range of applications in traditional domains, such as catalysis, organic synthesis, and C-H bond activation, as well as in advanced materials (e.g. anticancer agents, sensors, photophysiscal devices, switches, etc.)[1,2]

Unconventional cyclometalation reactions constitute interesting special cases,[3] among which the so-called "rollover cyclometalation" is attracting a growing interest;[4] this behaviour is shown by, but not limited to, bidentate heteroaromatic ligands able to undergo internal rotation and activation of C-H bonds in remote positions. This reactivity, initially considered rare, is receiving a remarkable attention due to applications in catalysis (with different processes promoted by Pd(II),[5] Rh(III),[6] and Ru(II)[7]), organic synthesis,[8] and as advanced materials (e.g. chemosensors[9] and chiroptical switches[10]) and anticancer agents.[11] In addition, a series of studies in the gas phase has envisaged further potential applications.[12]

In recent years, we have directed our attention to rollover cyclometalation, investigating and rationalizing the behaviour of a series of ligands and of the resulting complexes.[13]

The peculiarity of rollover cyclometalated complexes is given by the presence of an uncoordinated donor atom, usually a nitrogen atom, able to provide additional properties to the complex. For example, protonation of the uncoordinated nitrogen atom affords mesoionic species, also classified as abnormal-remote pyridylenes,[14] allowing rollover cyclometalated complexes to belong to the so-called "compounds with multiple personalities" class.[4b,13c-d,15]




L, L' = neutral or anionic ligands

Most of the studies in rollover cyclometalation have been devoted to 2,2'-bipyridines, the reactivity of which has shown to be strongly dependent on the nature of their substituents. In the case of platinum(II), it has been postulated a nucleophilic behaviour of the metal centre in the cyclometalation process,[4c, 16] which is highly accelerated by electron-withdrawing substituents on the ligand (e.g. $CF_3$).[17] Steric hindrance also plays a non negligible role in the regioselectivity of the process: bulky substituents (e.g. *t*-butyl groups) in position 6, i.e. α to a nitrogen atom, accelerate the process.[4c] The steric factor dominates over the electronic one for electron releasing substituents such as $CH_3$.[4c]

The complex interplay of electronic and steric factors in the reactivity of platinum rollover complexes is well exemplified by two processes involving the oxidative addition of Pt(II) phosphane complexes of the kind [Pt(N,C)(Me)($PR_3$)] (N,C = cyclometalated bipyridine, $PR_3$ = $PPh_3$, $PMe_3$, $PCy_3$, etc.). The reaction with MeI showed to be dominated by steric factors,[8b, 18] whereas the "retrorollover process" (protonation of the uncoordinated nitrogen atom followed by H transfer to Pt and Pt-C bond rupture) is governed by electronic factors.[13c]

We have recently reported on the behaviour of 6,6'-dimethoxy-2,2'-bipyridine,[19] the reactivity of which is particularly rich, due to the presence of two methoxy substituents. In particular, we were able to synthesize and isolate in the solid state the first rollover complex of gold,[20] and rollover cyclometalation was achieved for the first time with an electron poor Pt(II) complex, [$PtCl_2(DMSO)_2$]. In addition, regioselectivity could be controlled in order to give terdentate N,N,C complexes through C($sp^3$)-H bond activation of the methoxy substituent.[19]

With the aim of getting further insights into the influence of electronic and steric factors, both in the rollover process and in the behaviour of the resulting rollover complexes, we have decided to extend the study to 6-methoxy-2,2'-bipyridine, taking advantage of the ambivalent nature of the methoxy group, being electron withdrawing by inductive effect (-I), but electron releasing by mesomeric effect (+M).[21]

**Results and discussion**

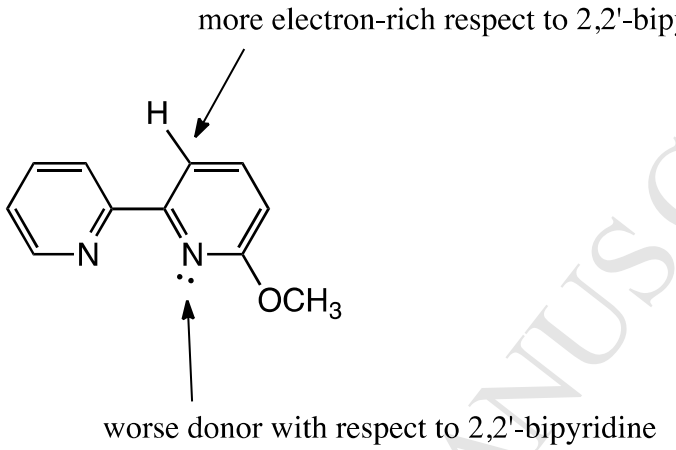
The ligand 6-methoxy-2,2'-bipyridine, $bpy^{6OMe}$, was synthesized through a Suzuki-Miyaura reaction by coupling of 2-bromo-6-methoxypyridine with 2-pyridineboronic acid *N*-phenyldiethanolamine ester in the presence of [$Pd(PPh_3)_4$] as catalyst.[22]

As anticipated above, the OMe substituent has opposite inductive and mesomeric effects.[21] As a consequence, its influence on the coordinating behaviour of the closest nitrogen atom and C-H bond activation in the pyridine ring might not be trivial.

In order to evaluate the electronic influence of the substituent on a 2,2'-bipyridine-type ligand, we searched for literature data regarding monosubstituted pyridines. Proton affinity and basicity data in the gas phase, as well as pKa values of the pyridinium ions are reported in Table S1 of the supporting information. These data show that $CH_3$ and $CF_3$ have, as expected, clear electron-donating and -withdrawing effects, respectively. The pKa values for 2-, 3- and 4-methoxypyridinium are 3.28, 4.88 and 6.62, indicating that 2-methoxypyridine is

significantly less basic than pyridine (pKa around 5.2), due to inductive effect, whereas 4-methoxypyridine is more basic, likely due to mesomeric effect.

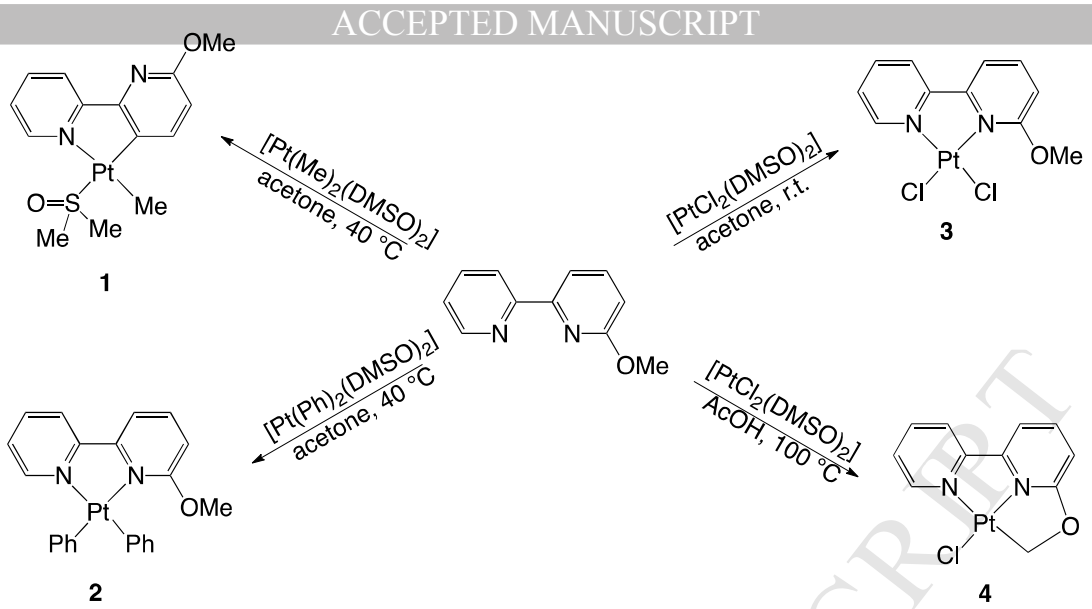
These data suggest that, in 6-methoxy-2,2'-bipyridine, the nitrogen atom of the substituted ring should be a weak donor compared to 2,2'-bipyridine. In contrast, the position *para* to the substituent, *i.e.* the $C^3$-H position, should have a higher electron density than in unsubstituted bipyridine, a factor which should contrast rollover C-H bond activation in the case of nucleophilic attack of the metal centre to the C-H bond.




Another factor to be considered is the value of ζ-angle, a useful parameter recently developed by us, which accounts for the bulkiness of the substituted bipyridine ligand.[17] In fact, the value of 152.3 for the angle ζ for 6-methoxy-2,2'-bipyridine is somewhat remarkable being only a few degrees below that for *t*-Bu (157.1) and almost 15 degrees above that for $CF_3$, which showed to undergo rollover cyclometalation very easily. However, it has to be noted that the reported value corresponds to the maximum hindrance of the methoxy group; when the latter points away from the nitrogen atom, the ζ-angle is 109.3°, *i.e.* still greater than the values for H (98.8°) and F (107.3°).

In order to investigate the organometallic reactivity of 6-methoxy-2,2'-bipyridine, $bpy^{6OMe}$, we have chosen the $d^8$ metal ions Pt(II), Pd(II) and Au(III), *i.e.* the only metal ions known to be able to give rollover cyclometalation with 6,6'-dimethoxy-2.2'-bipyridine.[19,20]

Reaction of $bpy^{6OMe}$ with Pt(II) complexes gave different results depending on the electronic properties of the starting complex (see Scheme 1).




**Scheme 1**. Syntheses of the platinum(II) complexes reported in the present work

Methyl platinum(II) complexes experience facile cyclometallation reactions and their behaviour has been extensively studied.[23]

Reaction of the electron-rich complex $[Pt(Me)_2(DMSO)_2]$ with $bpy^{6OMe}$ easily gives rollover C-H bond activation even at room temperature, to yield the cyclometalated complex $[Pt(bpy^{6OMe}\text{-}H)(Me)(DMSO)]$, **1**. The reaction was followed in $(CD_3)_2CO$ at room temperature by $^1H$ NMR spectroscopy showing, in parallel to the formation of **1**, the appearance of a signal at 0.20 ppm due to free methane, confirming metalation. Only starting compounds ($[Pt(Me)_2(DMSO)_2]$ and $bpy^{6OMe}$) and reaction products (**1** and methane) were detected in solution: no intermediate species, such as the $\kappa^1$-N or $\kappa^2$-N,N adducts ($[Pt(Me)_2(bpy^{6OMe})(DMSO)]$ or $[Pt(Me)_2(bpy^{6OMe})]$, respectively) were observed by $^1H$ NMR, indicating that, after coordination of $bpy^{6OMe}$, the cyclometalation process is extremely fast even at room temperature. It follows that, in these conditions, the kinetic limiting step of the reaction is the substitution of DMSO by $bpy^{6OMe}$, to give an adduct that was not detected in solution due to its rapid conversion into the cyclometalated complex **1**.

The influence of the methoxy substituent on the reaction rate is noteworthy, as 6-alkyl or aryl-substituted 2,2'-bipyridines usually give the $[Pt(N,N)(Me)_2]$ adduct as intermediate, easily detectable species.[4c]

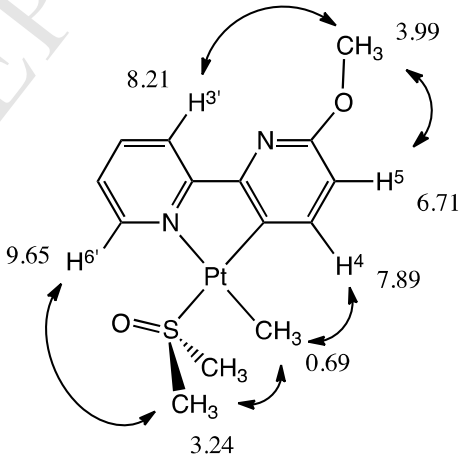
Operating in acetone at 40 °C helps in completing the cyclometalation in 2 h. In this respect, it is worth to remind that the analogous reaction with the unsubstituted 2,2'-bipyridine occurs only in refluxing toluene with prolonged reaction times.[4d]

Complex **1** was isolated in the solid state in high yields (ca. 80%) and thoroughly characterised in solution by means of NMR spectroscopy ($^{1}$H, $^{13}$C, $^{1}$H-$^{1}$H COSY, $^{1}$H-$^{13}$C HSQC and $^{1}$H-$^{1}$H NOESY).[24] All $^{1}$H and $^{13}$C signals were assigned.

In particular, in the aromatic region, the $^{1}$H NMR spectrum shows only 6 resonances, due to the absence of the $H^{3}$ proton and the presence of an AX system given by $H^{4}$ and $H^{5}$, both coupled to $^{195}$Pt. In addition, the $H^{6'}$ proton is strongly deshielded and coupled to platinum, indicating coordination of the external nitrogen atom (δ = 9.65 ppm, $^{3}J_{Pt\text{-}H}$ = 15 Hz). Coordination of Me and DMSO is also confirmed: $\delta_{CH_3}$= 0.69 ppm, $^{2}J_{Pt\text{-}H}$ = 82.0 Hz; $\delta_{DMSO}$ = 3.24 ppm, $^{3}J_{Pt\text{-}H}$ = 18.2 Hz.

In the $^{13}$C NMR spectrum, a singlet at 136.76 ppm, strongly coupled to $^{195}$Pt ($^{1}J_{Pt\text{-}C}$ = 1092 Hz) and attributable to the $C^{3}$ carbon atom, proved metalation. In addition, two singlets with satellites at δ = -14.08 ($^{1}J_{Pt\text{-}C}$ = 761 Hz) and 43.47 ppm ($^{2}J_{Pt\text{-}C}$ = 43 Hz) were assigned to the coordinated methyl and DMSO, respectively.

The $^{1}$H-$^{1}$H NOESY spectrum highlighted the following through-space interactions: 0.69 ppm (Pt-$CH_3$) with 7.89 ($H^{4}$) and 3.24 ppm (DMSO); 3.24 ppm (DMSO) with 9.65 ($H^{6'}$, very weak, likely suggesting an $H^{6'}$-O interaction, which stabilizes a conformation with the DMSO methyl groups close in space to the coordinated $CH_3$) and 0.69 ppm (Pt-$CH_3$); 3.99 ppm ($OCH_3$) with 6.71 ($H^{5}$) and 8.21 ppm ($H^{3'}$) (sections of the $^{1}$H-$^{1}$H NOESY spectrum are reported in the Supplementary Information, Figure S1).




**1**

In the solid state, the molecular structure of complex **1** was confirmed by single crystal X-ray diffraction. **1** crystallizes in the triclinic space group *P*-1. The asymmetric unit is composed by two [Pt($\kappa^2$-N,C-bpy$^{6OMe}$-H)(Me)(DMSO)] complexes lying in general positions. Selected bond distances and angles for both complexes are gathered in Table S2 of the Supplementary Information. The determination of the crystal structure confirmed the molecular features suggested by solution NMR spectroscopy. As a matter of fact, both independent Pt(II) ions possess a square planar stereochemistry of the kind *cis*-$PtC_2NS$, defined by the carbon atom of one methyl group, the sulphur atom of one DMSO molecule and a *C*,*N*-chelating bpy$^{6OMe}$-H ligand, which underwent cyclometalation. As expected on the basis of the so called *trans*-influence rules, the nitrogen atom of bpy$^{6OMe}$-H and the sulphur atom of DMSO are *trans* to the methyl group and to the coordinating carbon atom ($C^3$) of the ligand, respectively. Focusing the attention on the metallacycles, it is worth noting that, in both complexes, the bond distances not involving the metal ion can be assimilated to those typical of a double bond ($N^{1'}$-$C^{2'}$ and $C^2$-$C^3$) separated by that typical of a single bond ($C^{2'}$-$C^2$), this suggesting a weak metalloaromaticity. Both complexes show only a slight deviation from planarity: the angles between the root mean square (r.m.s.) plane describing the metallacycle and that containing the Pt($CH_3$)S fragment are lower than 9°; the angles between the r.m.s. plane describing the ligand and that describing the coordination sphere of the metal centre are less than 7°. The complexes pack, staggered, as dimers, along two different directions (approximately [011] and [0-12]): no Pt-Pt interactions can be invoked.

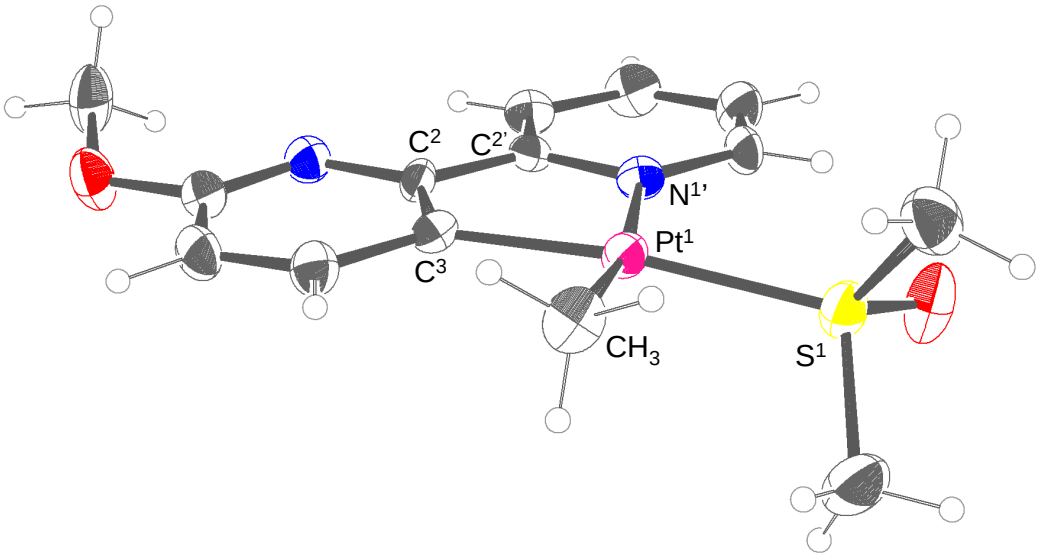
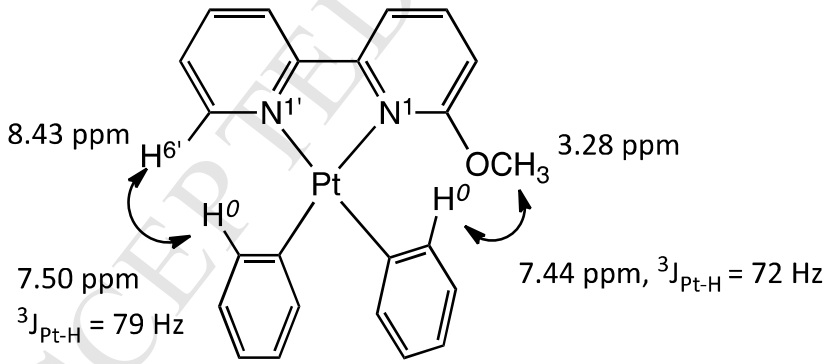



Fig 1. Ortep representation of the molecular structure in [Pt($\kappa^2$-N,C-bpy$^{6OMe}$-H)(Me)(DMSO)], **1**, at the 30% probability level (one of the two independent complexes has been arbitrarily chosen). Colour code: carbon, grey; hydrogen, light grey; nitrogen, blue; oxygen, red; platinum, fuchsia; sulphur, yellow. Selected bond distances (Å) and angles (°): $Pt^1$-$C^3$, 2.01(1); $Pt^1$-$CH_3$, 2.06(1); $Pt^1$-$N^{1'}$, 2.125(8); $Pt^1$-$S^1$, 2.270(3); $C^2$-$C^{2'}$, 1.46(2); $C^2$-$C^3$, 1.39(1); $C^{2'}$-$N^{1'}$, 1.35(1); $Pt^{1A}$-$C^{3A}$, 2.00(1); $Pt^{1A}$-$CH_3$, 2.047(12); $Pt^{1A}$-$N^{1A'}$, 2.13(1); $Pt^{1A}$-$S^{1A}$, 2.268(3); $C^{2A}$-$C^{2A'}$, 1.46(2); $C^{2A}$-$C^{3A}$, 1.39(1); $C^{2A'}$-$N^{1A'}$, 1.35(1); $C^3$-$Pt^1$-$CH_3$, 91.4(5); $C^3$-$Pt^1$-$N^{1'}$, 79.5(4); $H_3C$-$Pt^1$-$N^{1'}$, 169.8(4); $C^3$-$Pt^1$-$S^1$, 172.3(3); $H_3C$-$Pt^1$-$S^1$, 89.8(4); $N^{1'}$-$Pt^1$-$S^1$, 99.8(2); $C^{3A}$-$Pt^{1A}$-$CH_3$, 90.6(5); $C^{3A}$-$Pt^{1A}$-$N^{1A'}$, 79.6(4); $H_3C$-$Pt^{1A}$-$N^{1A'}$, 170.1(4); $C^{3A}$-$Pt^{1A}$-$S^{1A}$, 174.5(3); $H_3C$-$Pt^{1A}$-$S^{1A}$, 89.4(4); $N^{1A'}$-$Pt^{1A}$-$S^{1A}$, 100.5(3).

In contrast to the "Pt($Me_2$)" analogue, reaction of [Pt($Ph)_2$($DMSO)_2$] with bpy$^{6OMe}$ does not give cyclometalation, at least under the reaction conditions adopted. In acetone, only the adduct [Pt($Ph)_2$(bpy$^{6OMe}$)], **2**, was obtained, which was characterized in solution by mono- and bi-dimensional NMR experiments ($^1$H NMR, $^1$H-$^1$H COSY, $^1$H-$^1$H NOESY). Cyclometalation does not take place even in refluxing acetone.

In particular, the $H^{6'}$ proton of **2** is downfield shifted (δ = 8.43 ppm, $^{3}J_{Pt\text{-}H}$ = 21 Hz), likely due to the shielding effect of the adjacent phenyl ring. The $^{195}Pt$-$^{1}H$ coupling constant is in line with a N-Pt-C($sp^2$) *trans* arrangement. The methoxy protons appear strongly shielded with respect to the free ligand and complex **1** (3.28 *vs* 4.40 and 3.99 ppm, respectively), likely due to the presence of one coordinated phenyl ligand in *cis* position.

The $^{1}H$-$^{1}H$ NOESY spectrum shows correlations between the methyl group at 3.28 ppm and the *ortho* hydrogens on the phenyl ring in *cis* position, which are coupled to $^{195}Pt$ (δ = 7.44 ppm, $^{3}J_{Pt\text{-}H}$ = 72 Hz). The $H^{6'}$ proton (δ = 8.43 ppm) shows contacts with the *ortho* hydrogens of the other phenyl ring (δ = 7.50 ppm, $^{3}J_{Pt\text{-}H}$ = 79 Hz). These data confirm the chelating coordination mode of bipyridine and the presence of two phenyl ligands. It is also interesting to note that the *ortho* hydrogens ($H^{0}$) of the two phenyl rings show different Pt-H coupling constant values. The largest value ($^{3}J_{Pt\text{-}H}$ = 79 Hz vs. 72 Hz) corresponds to $N^1$ of the substituted pyridine ring, suggesting a minor *trans* influence of this nitrogen atom, as a consequence of its poorer donor ability due to the electron-withdrawing effect of the OMe substituent. In addition to electronic factors, it should be noted that also the steric hindrance of the methoxy group can play a non negligible role, elongating the Pt-$N^1$ bond.




**2**

(only one *ortho* hydrogen per phenyl ring is indicated for clarity)

The reaction of the electron poorer complex [$PtCl_2(DMSO)_2$] with $bpy^{6OMe}$ (acetone, rt, 3 h) is very slow and affords the adduct [$PtCl_2(bpy^{6OMe})$], **3**, the $^{1}H$ NMR spectrum of which shows, inter alia, the $H^{6'}$ proton strongly deshielded, at 9.81 ppm, as expected due to the proximity of the Cl ligand, with a $^{195}Pt$-$^{1}H$ coupling constant ($^{3}J_{Pt\text{-}H}$ =39 Hz) in line with a nitrogen atom coordinated in *trans* to Cl.

At higher temperature and for longer reaction times (acetone 50 °C, 24 h), complex **3** remains the principal reaction product, even if, under prolonged reaction times (several days), a second unidentified species appears in solution.

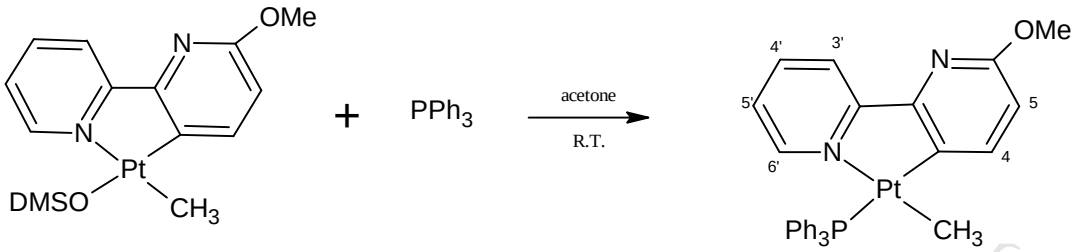
Under different experimental conditions (acetic acid, 100 °C, 7 d), reaction of $[PtCl_2(DMSO)_2]$ with $bpy^{6OMe}$ gives a different product, which was identified as the cyclometalated complex $[Pt(\kappa^3\text{-}N,N,C\text{-}bpy^{6OMe}\text{-}H)Cl]$, **4**, resulting from activation of a C-H bond in the methoxy substituent. $^1H$ NMR data indicate a terdentate coordination of the bipyridine ligand, with an *N,N,C* sequence of donor atoms: the absence of the methyl signals and the presence of a singlet with satellites at 7.00 ppm, integrating 2 H and coupled with $^{195}Pt$ ($^2J_{Pt\text{-}H}$ = 77 Hz), are in agreement with this formulation, and are in line with those reported for the analogous terdentate complex isolated with the 6,6'-dimethoxybipyridine ligand.[19]

The signals at 9.11 ppm (d with sat, $^3J_{Pt\text{-}H}$ ca. 12 Hz, $H^{6'}$) and 7.44 ppm (d with sat, $^4J_{Pt\text{-}H}$ = 11 Hz, $H^5$) also support this formulation.

These results show that the cyclometalation reaction follows different paths depending on the electronic properties of the platinum(II) precursor and also on the reaction conditions. Rollover cyclometallation usually demands an electron-rich Pt(II) complex such as $[Pt(Me)_2(DMSO)_2]$. The electron poorer complex $[PtCl_2(DMSO)_2]$ follows a different reaction pathway, involving the activation of the methyl group. It is likely that different reaction mechanisms are operating in the two cases.

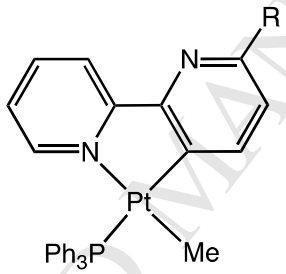
For example, in the intermediate species, *i.e.* the adducts $[Pt(bpy^{6OMe})(Me)_2]$ and $[Pt(bpy^{6OMe})Cl_2]$, the lability of the Pt-N bonds may be very different, due to the different *trans* effect of the $CH_3$ and Cl ligands. In the first one the nitrogen atom of the substituted pyridine may easily detach from the metal ion (both for electronc and steric factors) facilitating the rollover process. However, this does not explain why the $[Pt(bpy^{6OMe})(Ph)_2]$ adduct does not give rollover metalation, showing to be very stable in solution (on the contrary $[Pt(bpy^{6OMe})(Me)_2]$ was not even detected in solution). In the case of $[Pt(N,N)(Ph)_2]$ the last part of the reaction, which is likely an oxidative-addition/reductive-elimination process, probably plays a fundamental role. It must be reminded, in addition, that the analogous di-substituted ligand 6,6'-dimethoxy-2,2'-bipyridine gave rollover metalation (for the first and only time) with $[PtCl_2(DMSO)_2]$,[19] showing, once again,[25] that the course of intramolecular C-H bond activation is in large part unpredictable.

The DMSO ligand in complex **1** can be easily displaced at room temperature by good donors such as triphenylphosphine to give the corresponding complex $[Pt(bpy^{6OMe}\text{-}H)(Me)(PPh_3)]$, **5**.




**1** **5**

Among the spectroscopic data supporting this formulation, the $^{31}P$ NMR signal at 32.59 ppm, with $^{1}J_{Pt\text{-}P}$ = 2257 Hz, is fully consistent with a C-Pt-P *trans* arrangement. In the comparison with the corresponding complexes derived from 2,2'-bipyridine,[4d] 6-Me-2,2'-bipyridine,[8b] and 6-$CF_3$-2,2'-bipyridine[17] (complexes **6**, **7** and **8**, Scheme 2), although the differences are not dramatic some trends can still be seen:




| | R = H | R = $CH_3$ | R = $CF_3$ | R = $OCH_3$ |
|---|---|---|---|---|
| δ (ppm) | 33.59 | 33.68 | 32.12 | 32.59 |
| $^{1}J_{Pt\text{-}P}$ (Hz) | 2229 | 2226 | 2279 | 2259 |
| | **6** | **7** | **8** | **5** |

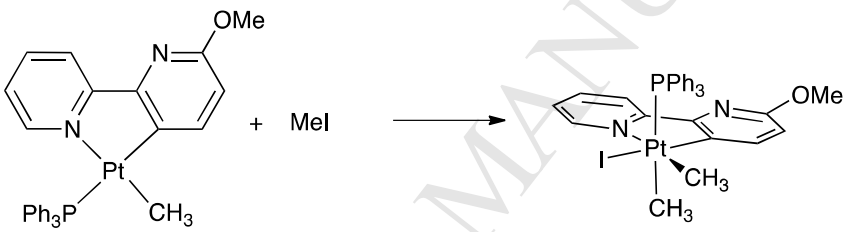
Scheme 2

$^{31}P$ NMR data for **6**, **7** and **8** show only a slight chemical shift trend in line with the inductive properties of the substituent on the bipyridine ligand: with respect to **6** and **7**, R = H and $CH_3$, the P atom is slightly shielded with the electron attracting group $CF_3$. A second trend is given by the $^{31}P$-$^{195}Pt$ coupling constants: $^{1}J_{Pt\text{-}P}$ = 2226 (**7**, R = $CH_3$), 2229 (**6**, R = H), 2279 Hz (**8**, R =$CF_3$). A similar trend was reported for Pt(II)-phosphane complexes with 4-substituted pyridines.[26] It was observed that substituents with high electronegativity on the pyridine ring decrease the electron donation of the nitrogen atom coordinated to the metal ion and, consequently, the platinum 6s orbital is more available for the platinum-phosphorus bond. Stronger Pt-P bonds result in greater Pt-P coupling constants. In agreement with this, $^{1}J_{Pt\text{-}P}$

values are greater for $CF_3$-substituted bipyridines (complex **8**) and smaller for $CH_3$-substituted ones (complex **7**). The $^{31}P$ NMR data for complexes **5** and **8** are comparable (Scheme 2); this seems to indicate that, overall, the electron-attracting effect is the predominant one for the methoxy substituent, as it is in the case of $CF_3$.

In addition, the $^{1}H$ NMR spectrum of **5** shows a doublet with satellites for the coordinated methyl group; the values, $\delta$ = 0.73 ppm, $^{2}J_{Pt\text{-}H}$ = 82.8 Hz and $^{3}J_{P\text{-}H}$ = 7.8 Hz, are in agreement with the proposed formulation.[4d,17] In the case of the $^{1}H$ NMR spectra, no meaningful correlations were found for the Pt-$CH_3$ protons in complexes **5**-**8**, as the differences are very small.

The electron rich complex **5** easily gives oxidative addition with $CH_3I$ at room temperature, affording the Pt(IV) complex [Pt(bpy$^{6OMe}$-H)$(Me)_2I(PPh_3)$], **9**.




**9**

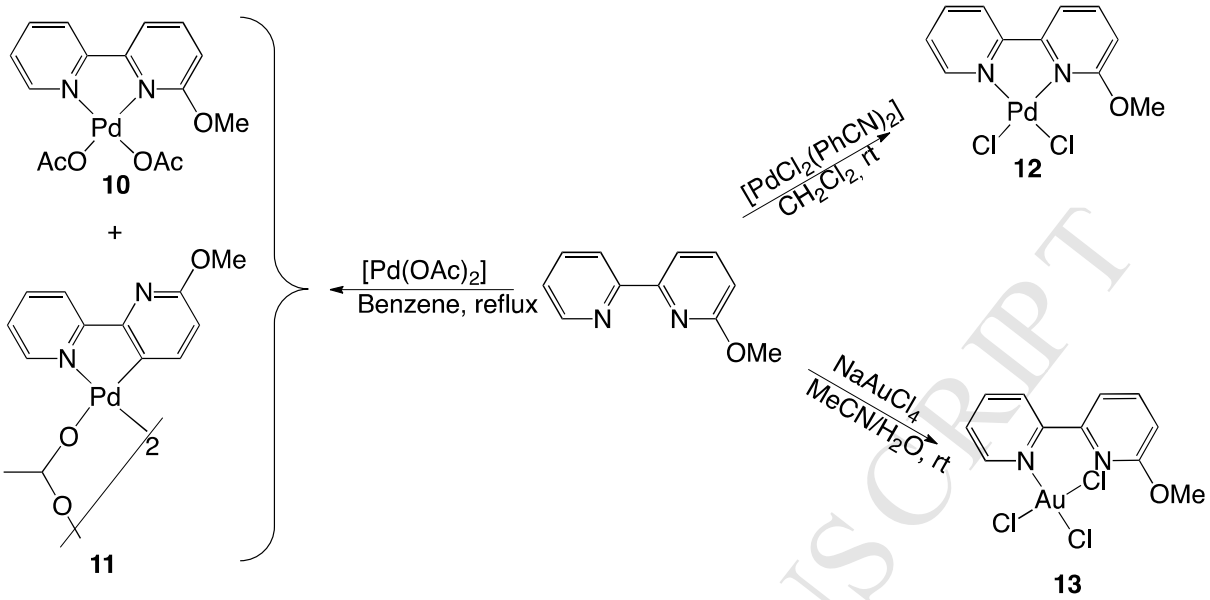
Reaction of cyclometalated Pt(II) complexes with MeI may result in the formation of different isomers, depending on electronic and steric factors.[18]

In this case, only one Pt(IV) species was observed in solution and isolated in the solid state: all the spectroscopic data indicate the isomer with the $PPh_3$ and one $CH_3$ ligand in "axial" position with respect to the cyclometalated plane. The $^{31}P$ NMR spectrum shows a singlet with satellites at $\delta$ = -10.84 ppm with $^{1}J_{Pt\text{-}P}$ = 959 Hz.

The $^{1}H$ NMR spectrum shows two doublets with satellites ascribable to the two methyl groups: the resonance at 1.23 ppm ($^{3}J_{P\text{-}H}$ = 7.6 Hz, $^{2}J_{Pt\text{-}H}$ = 60 Hz) is assigned to the one in axial position, whereas the resonance at 1.67 ppm ($^{3}J_{P\text{-}H}$ = 8.0 Hz, $^{2}J_{Pt\text{-}H}$ = 71 Hz) is assigned to the one *trans* to nitrogen in the plane of the cyclometalated bipyridine.[8b] The $H^{6'}$ proton is strongly deshielded ($\delta$ = 9.59 ppm), as it is affected by the presence of an iodide ligand in adjacent position.

With the intention to extend the study to other $d^8$ metals, the reactions of bpy$^{6OMe}$ with a series of Au(III) and Pd(II) metal salts were tested as a part of a preliminary study (Scheme

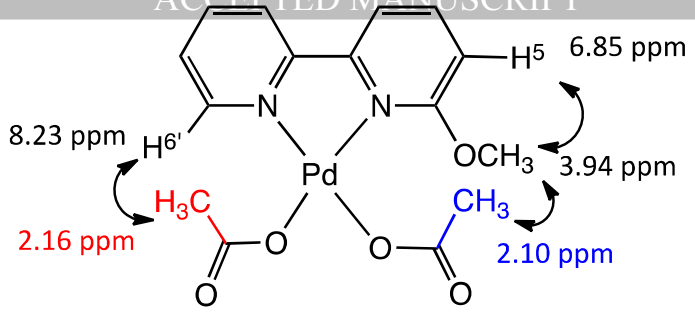
3).




**Scheme 3**. Syntheses of the palladium(II) and gold(III) complexes reported in the present work

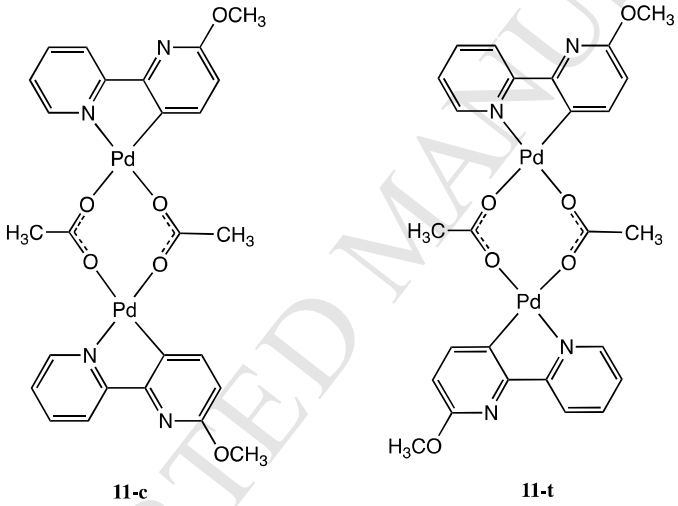
Reaction of $bpy^{6OMe}$ with $[Pd(OAc)_2]$ in refluxing benzene gave a main species characterized as the adduct $[Pd(bpy^{6OMe})(OAc)_2]$, **10**; the presence, in its $^1H$ NMR spectrum, of 7 resonances in the aromatic region and of resonances ascribable to two acetate ligands supports this formulation.

In addition, a $^1H$-$^1H$ COSY spectrum allowed a complete $^1H$ NMR attribution and a $^1H$-$^1H$ NOESY spectrum (see Supplementary Information) showed cross peaks between the methyl groups of the acetato moieties and the adjacent protons, *i.e.* 2.10 ppm (OAc *cis* to OMe) with 3.94 ppm (OMe); 2.16 ppm (OAc *trans* to OMe) with 8.23 ppm ($H^{6'}$). In addition a clear cross peak is observed between the methyoxy methyl (3.94 ppm) and the adjacent $H^5$ proton (6.85 ppm).




**10**

Extraction with dichloromethane gave a second sample containing two species, in a 4:1 molar ratio, together with other impurities (NMR evidence). We were not able to obtain these species in pure form; however, the $^{1}$H NMR spectrum supports their identification as two geometric isomers of the dimeric rollover complex [Pd(bpy$^{6OMe}$-H)(OAc)]$_2$, **11-c** and **11-t**.




**11-c** **11-t**

Proposed formulations for **11-c** and **11-t**

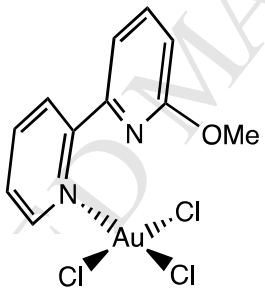
Our interpretation is supported, for both species, by the lack of the signal of the H$^3$ hydrogen and by the presence of an AX system compatible with a cyclometalated bpy$^{6OMe}$ (i.e. as in complex **1**, vide supra) given by the H$^4$ and H$^5$ hydrogens. The coordination around Pd is completed by two bridging acetate ligands in each species. Rollover cyclometalation with Pd(II) acetate has been observed for other 6-substituted 2,2'-bipyridines.[25] In all cases, a mixture of species was formed, witnessing that the isolation in pure form of these complexes is not always easy.

At variance, reaction of *trans*-[Pd(PhCN)$_2$Cl$_2$] in $CH_2Cl_2$ gave the adduct [PdCl$_2$(bpy$^{6OMe}$)], **12,** isolated in the solid state and characterised.

In particular, the $^{1}$H NMR spectrum shows seven aromatic protons, one of which is, as expected, strongly deshielded ($H^{6'}$, 9.20 ppm) due to proximity with one chloride ligand. Complex **12** was obtained also by reaction of **10** with LiCl in acetone.

In the case of Au(III), two salts, $NaAuCl_4$ and $Au(OAc)_3$, were used as starting material. Reaction at room temperature of $bpy^{6OMe}$ with $NaAuCl_4$ in a $MeCN/H_2O$ mixture gives the adduct $[Au(bpy^{6OMe})Cl_3]$, **13**, where $bpy^{6OMe}$ likely acts as a monodentate ligand, as previously observed with gold(III) adducts of 6-substituted 2,2'-bipyridines.[27] The characterization of **13** is based on analytical and NMR data (Fig. 2). In particular, the $^{1}$H NMR spectrum shows that almost all the signals are downfield shifted with respect to the free ligand (*e.g.* $H^{6'}$ from 8.65 to 9.03 ppm, OMe from 4.04 to 4.32 ppm). In contrast, the signals of the $H^{3}$ and $H^{3'}$ protons are strongly shielded (ca -0.35 and -0.60 ppm).

The IR spectrum shows a band at 363 $cm^{-1}$, due to Au-Cl stretching, in line with what previously found for analogous Au(III) bipyridine adducts.[27]




**13**

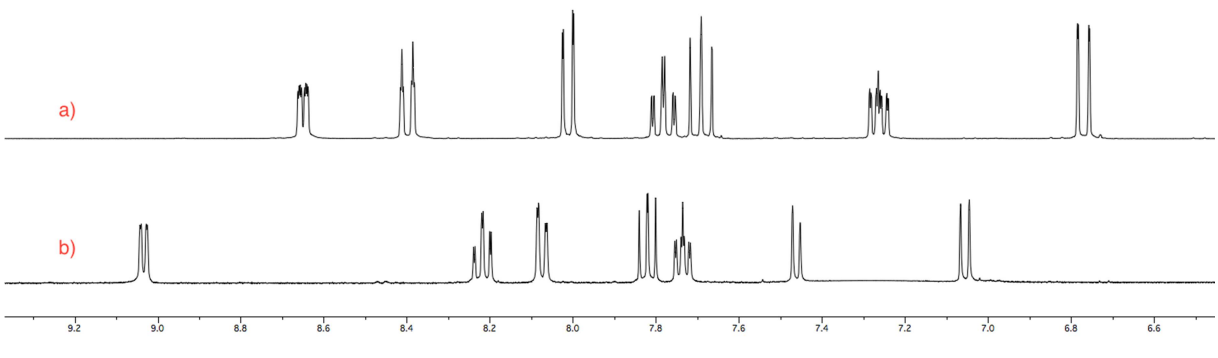
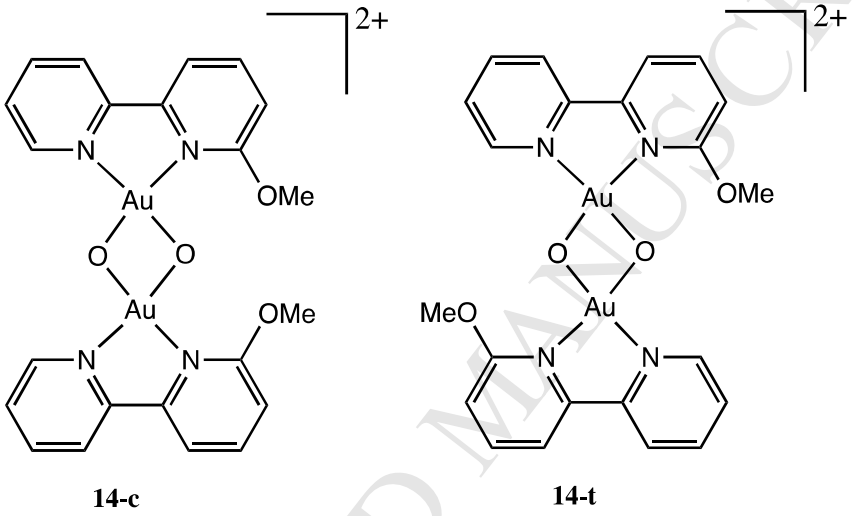



Fig 2: Comparison of the $^{1}$H NMR spectra (aromatic region) of $bpy^{6OMe}$ (a) and complex **13** (b).

Treatment of the chlorido complex **13** with $CH_3COONa$ and $KPF_6$ in aqueous solution resulted in hydrolysis reaction affording the dinuclear oxo complex $[Au(bpy^{6Me})(\mu\text{-}O)]_2[PF_6]_2$, **14**, in line with what previously observed, under analogous reaction conditions, with similar gold(III) complexes of 6-substituted 2,2'-bipyridines;[28] no C-H bond activation was observed. The $^1H$ NMR spectrum of **14** shows two set of signals in an approximate 4:1 molar ratio corresponding, respectively, to the *trans*, **14-t**, and *cis*, **14-c**, isomer. We were not able to separate the two isomers in the solid state.




Proposed formulations for **14-c** and **14-t**

Complexes **14 c-t** concur to enrich the small but interesting family of gold(III)-oxo complexes.[29] Indeed, these complexes have shown interesting reactivities both in solution,[30] in stoichiometric reactions[31] and in catalysis,[32] and in the gas phase.[33] Also noteworthy is their biological activity.[34]

Unexpectedly, under the same reaction conditions recently used with 6,6'-dimethoxy-2,2'-bipyridine to give rollover cyclometalation, *i.e.* reaction of $bpy^{6OMe}$ with $Au(OAc)_3$ (AcOH, 80 °C), no cyclometalation was achieved. The $^1H$ NMR spectra indicate that, at room temperature, the adduct $[Au(bpy^{6OMe})(OAc)_2]$ is likely formed. In contrast to the corresponding dimethoxy ligand, heating the solution resulted in heavy decomposition.

**Conclusions**

Activation of C-H bonds by means of transition metal complexes is a topic still far to be completely understood. In the case of substituted 2,2'-bipyridines, a delicate balance of electronic and steric factors may drive the reaction towards unpredictable results. As a part of our investigation on this class of ligands, we have reported here that the 6-methoxy substituent promote a very easy bipyridine "rollover" activation and metallation by reaction with the electron-rich Pt(II) precursor $[Pt(Me)_2(DMSO)_2]$. In this case, the process is very fast even at room temperature. Under different experimental conditions the methoxy substituent is activated to give a terdentate N,N,C cyclometalated complex. In all the other cases studied, starting from Au(III) and Pd(II) salts and other $[PtX_2(DMSO)_2]$ precursors (X = Ph, Cl), the rollover process did not occur or (in the case of Pd(II) acetate) proceeds only in limited amount. This is likely ascribable to the peculiar properties of the methoxy substituent, which has both electron withdrawing and releasing properties (-I and +M, respectively).

The overall behaviour of 6-methoxy-2,2'-bipyridine, $bpy^{6OMe}$, can be compared to that of other 6-substituted-2,2'-bipyridines, as well as to the corresponding di-substituted ligand, 6,6'-dimethoxy-2,2'-bipyridine.

Comparison with 6-substituted 2,2'-bipyridines (*e.g.* 6-$CH_3$, -$CF_3$, -*t*-but, -Ph, -$CR_2Ph$, etc) showed that, in the case of platinum(II), electron-withdrawing groups such as $CF_3$ greatly accelerate the rollover process. Also bulky substituents, such as *t*-butyl, facilitate the process. In the case of $bpy^{6OMe}$ the fast rollover activation is likely to be associated with the inductive effect of the substituent on the nitrogen atom, as for $CF_3$.

The comparison of $bpy^{6OMe}$ with the corresponding disubstituted bipyridine is more complex. In the case of platinum(II) an opposite behaviour was found for the two ligands: in contrast to $bpy^{6OMe}$, the di-substituted ligand gives rollover metalation with the electron-poor complex $[Pt(DMSO)_2Cl_2]$ and no reaction (or decomposition) with $[Pt(DMSO)_2(Me)_2]$. At variance, both ligands activate the methoxy group in refluxing acetic acid, to yield the corresponding terdentate N,N,C complex. As for palladium(II) and gold(III), the disubstituted ligand showed an overall tendency to give an easier metalation: with $bpy^{6OMe}$ the palladium rollover complex was found only as a secondary product and no gold(III) rollover complex was observed. In contrast, 6,6'-dimethoxy-2,2'-bipyridine gave rollover metalation with both metals. As an example, under the same reaction conditions ($Au(OAc)_3$, acetic acid, 80 °C), 6,6'-dimethoxy-2,2'-bipyridine gave

rollover cyclometalation whereas 6-methoxy-2,2'-bipyridine gave an adduct at room temperature and heavy decomposition under heating. The comparison is probably complicated by the subtle balance between electronic and steric factors on both the nitrogen donors and pyridine rings.

On the whole, a rationale of the reactivity of substituted 2,2'-bipyridines with noble metals is still far to be reached and further investigations are needed to shed light into the chemistry of this class of ligands.

**Aknowledgements**

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**Experimental Section**

All the solvents were purified and dried according to standard procedures.[35] Elemental analyses were performed with a Perkin-Elmer 240B elemental analyzer by Mr. Antonello Canu (Dipartimento di Chimica e Farmacia, Università degli Studi di Sassari, Italy). 6-methoxy-2,2'-bipyridine ($bpy^{6OMe}$) was prepared by a Suzuki-Miyaura coupling.[22]

Infrared spectra were recorded with a FT-IR Jasco 480P using Nujol mulls. Melting points were measured in capillary tubes on a Büchi 530 melting points apparatus.

$^{1}H$, $^{13}C$, and $^{31}P$ NMR spectra were obtained on a Bruker Avance III 400 spectrometer operating at 400.0, 100.5 and 161.8 MHz, respectively. Chemical shifts are given in ppm relative to internal TMS for $^{1}H$ and $^{13}C\{^{1}H\}$ and external 85% $H_3PO_4$ for $^{31}P\{^{1}H\}$. $^{1}H$-$^{1}H$ COSY, $^{1}H$-$^{1}H$ NOESY and $^{1}H$-$^{13}C$ HSQC experiments were performed by means of standard pulse sequences.[36]

**X-ray Crystal Structure Determination**

The single crystal X-ray diffraction data for species **1** were acquired at room temperature from a yellow, prismatic single crystal of approximate dimensions 0.2×0.2×0.3 $mm^3$, on an

Enraf Nonius CAD4 automated diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The unit cell was determined on the basis of the setting angles of 25 randomly distributed reflections in the range 9.2 < θ < 11.8°. The data collection was performed in the range 3.0 < θ < 25.3° by applying the ω-scan mode [Δω = 1.7 + (0.35tanθ)°]. A total of 5578 reflections, of which 3900 observed [I>2σ(I); R(int) = 0.029, R(sigma) = 0.059], were collected and used for structure solution and structure refinement against 361 parameters. Prior to structure solution, the data were corrected for absorption.[37] The structure was solved by direct methods[38] and it was refined by full-matrix least-squares on $F^2$.[39] All non-hydrogen atoms were assigned anisotropic temperature factors, while hydrogen atoms were made riding their parent atoms with isotropic temperature factors 1.2 times higher than those of their parent atoms.

Relevant crystallochemical data for **1**, $C_{28}H_{36}N_4O_4Pt_2S_2$, *FW* = 946.86 g/mol: triclinic, space group *P*-1, *a* = 10.569(5) Å, *b* = 11.537(5) Å, *c* = 13.680(7) Å, $\alpha$ = 82.52(4)°, $\beta$ = 83.75(4)°, $\gamma$ = 68.22(3)°, *V* = 1540(1) $Å^3$, *Z* = 2, *F*(000) = 904, $\rho$ = 2.04 g/$cm^3$, $\mu$(Mo-Kα) = 9.25 1/mm. The *R*, w*R* figures of merit reached final values of 0.045, 0.090 for the 3900 observed reflections, and 0.079, 0.103 for all the 5578 reflections. The goodness of fit, highest peak and deepest hole reached final values of 1.03, 1.60 e/$Å^3$ and -1.05 e/$Å^3$, respectively.

Crystallographic data (excluding structure factors) for species **1** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number 1436235. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

**[Pt(bpy$^{6OMe}$-H)(Me)(DMSO)], 1**

To a solution of bpy$^{6OMe}$ (61.0 mg, 0.327 mmol) in acetone (15 mL) solid $[Pt(Me)_2(DMSO)_2]$ (119.0 mg, 0.312 mmol) was added. The resulting solution, kept under inert atmosphere, was heated at 40 °C for 2 h under stirring; then it was concentrated under vacuum and *n*-hexane was added. The precipitate formed was filtered off, washed with *n*-hexane and dried to give the analytical sample as a yellow solid. Yield 80%. M.p. (dec) = 130 °C. Anal. Calcd. for $C_{14}H_{18}N_2OPtS$ (%): C, 35.50; H, 3.83; N, 5.92. Found: C, 35.38; H, 3.89; N, 5.63. $^1$H NMR ($CDCl_3$, ppm): 9.65 (d with sat, 1H, $J_{H-H}$ = 5.2 Hz, $^3J_{Pt-H}$ = 14.9 Hz, $H^{6'}$), 8.21 (d, 1H, $J_{H-H}$ = 7.6 Hz, $H^{3'}$), 7.90 (t, 1H, $J_{H-H}$ = 7.6 Hz, $H^{4'}$), 7.88 (d with sat, 1H, $J_{H-H}$ = 8.2 Hz, $^3J_{Pt-H}$ = 50 Hz, $H^4$), 7.30 (m, 1H, $J_{H-H}$ = 7.6 Hz, $J_{H-H}$ = 5.2 Hz, $H^{5'}$), 6.71 (d with sat, 1H, $J_{H-H}$ = 8.2 Hz, $^4J_{Pt-H}$ = 15.8 Hz, $H^5$), 4.00 (s, 3H, $OCH_3$), 3.24 (s with sat, 6H, $^3J_{Pt-H}$ = 18.2 Hz, DMSO), 0.69 (s with sat, 3H, $^2J_{Pt-H}$ = 82

Hz, Pt-$CH_3$). $^{13}$C NMR ($CDCl_3$, ppm): 162.70 (s with sat, $J_{Pt-C}$ = 58 Hz, $C^2$), 162.13 (s with sat, $J_{Pt-C}$ = 6 Hz, $C^{2'}$), 161.42 (s, $C^6$), 150.22 (s with sat, $J_{Pt-C}$ = 7.6 Hz, $C^{6'}$), 142.96 (s with sat, $J_{Pt-C}$ = 95 Hz, $C^4$), 138.35 (s, $C^{4'}$), 136.76 (s with sat, $J_{Pt-C}$ = 1092 Hz, $C^3$), 123.33 (s with sat, $J_{Pt-C}$ = 9 Hz, $C^{5'}$), 120.98 (s with sat, $J_{Pt-C}$ = 24 Hz, $C^{3'}$), 111.15 (s with sat, $J_{Pt-C}$ = 63 Hz, $C^5$), 52.90 (s, OMe), 43.74 (s with sat, $J_{Pt-C}$ = 42.5 Hz, DMSO), -14.08 (s with sat, $J_{Pt-C}$ = 761 Hz, Pt-$CH_3$). Assignments based on $^1$H-$^1$H COSY, $^1$H-$^1$H NOESY, and $^1$H-$^{13}$C HSQC experiments.

**[Pt(Ph)$_2$(bpy$^{6OMe}$)], 2**

To a solution of bpy$^{6OMe}$ (18.3 mg, 0.098 mmol) in acetone (10 mL) solid [Pt(Ph)$_2$(DMSO)$_2$] (47.2 mg, 0.093 mmol) was added. The resulting solution was stirred under inert atmosphere for 30 min. The precipitate formed was filtered off and dried under vacuum to give the analytical sample as a yellow solid. From the filtered solution, a second crop (containing the same product) was obtained after concentration and treatment with diethyl ether. Yield 60%. M.p. (dec) = 200 °C. Anal. Calcd. for $C_{23}H_{20}N_2OPt$ (%): C, 51.59; H, 3.76; N, 5.23. Found: C, 51.21; H, 4.02; N, 5.33. $^1$H NMR ($CDCl_3$), δ (ppm): 8.43 (d, 1H, $J_{H-H}$ = 5.7 Hz, $J_{Pt-H}$ = 21 Hz, $H^{6'}$), 7.99 (m, 2H, $H^3$+$H^4$), 7.97 (t, 1H, part. overlapd., $H^{4'}$), 7.67 (d, 1H, $J_{H-H}$ = 7.7 Hz, $H^{3'}$), 7.50 (d with sat, 2H, $J_{H-H}$ = 8.2 Hz, $J_{Pt-H}$ = 79 Hz, $H^o$ Ph in *trans* to $N^1$), 7.44 (d with sat, 2H, $J_{H-H}$ = 8.2 Hz, $J_{Pt-H}$ = 72 Hz, $H^o$ Ph in *trans* to $N^{1'}$), 7.29 (m, 1H, $H^{5'}$), 6.97 (m, 2H, $H^m$ Ph in *trans* to $N^1$), 6.91 (m, 2H, $H^m$ Ph in *trans* to $N^{1'}$), 6.85 (m, 1H, part. overlapd., $H^p$ Ph in *trans* to $N^1$), 6.82 (m, 1H, part. overlapd., $H^5$), 6.67 (t, 1H, $H^p$ Ph in *trans* to $N^{1'}$), 3.28 (s, 3H, $OCH_3$). Assignments based on $^1$H-$^1$H COSY and $^1$H-$^1$H NOESY experiments. $^{13}$C NMR ($CDCl_3$, ppm): 166.84 (s, Cq), 156.68 (s, Cq), 155.37 (s, Cq), 149.97 (s, CH), 144.06 (s, Cq), 143.57 (s, Cq), 140.68 (s, CH), 137.86 (s, CH), 137.55 (s, CH), 136.91 (s, CH), 127.10 (s, CH), 126.51 (s, CH), 126.01 (s, CH), 122.43 (s, CH), 121.56 (s, CH), 120.15 (s, CH), 114.49 (s, CH), 108.54(s, CH), 55.69 (s, $CH_3$). Cq = quaternary carbon atom.

**[PtCl$_2$(bpy$^{6OMe}$)], 3**

Solid [$PtCl_2$(DMSO)$_2$] (73.5 mg, 0.1740 mmol) was added to 15 mL of an acetone solution of bpy$^{6OMe}$ (34.2 mg, 0.1836 mmol) under vigorous stirring. The resulting mixture was stirred for 2 days at room temperature. The precipitate formed was filtered off and dried under vacuum to give the analytical sample as a yellow solid. Yield 55 %. M.p.> 250 °C. Anal. Calcd. for $C_{11}H_{10}Cl_2N_2OPt$ (%): C, 29.22; H, 2.23; N, 6.19. Found: C, 29.69; H, 1.73; N 6.03. $^1$H NMR

($CD_2Cl_2$, ppm): 9.81 (d with sat, 1H, $J_{H-H}$ = 5.4 Hz, $J_{Pt-H}$ =39 Hz, $H^{6'}$), 8.17 (t, 1H, $J_{H-H}$ = 7.6 Hz, $H_4$ or $H_{4'}$), 8.13 (t, 1H, $J_{H-H}$ = 7.6 Hz, $H^4$ or $H^{4'}$), 7.98 (d, 1H, $J_{H-H}$ = 7.6 Hz, $H^{3'}$ or $H^3$), 7.69 (d, 1H, $J_{H-H}$ = 7.6 Hz, $H^3$ or $H^{3'}$), 7.57 (m, 1H, $J_{H-H}$ = 7.8 Hz, $H^{5'}$), 7.06 (d, 1H, $J_{H-H}$ = 7.8 Hz, $J_{Pt-H}$ = 17 Hz, $H^5$), 4.13 (s, 3H, $OCH_3$).

**[Pt(bpy$^{6OMe}$-H)Cl], 4**

To a solution of bpy$^{6OMe}$ (41.2 mg, 0.221 mmol) in acetic acid (15 mL) solid [$PtCl_2(DMSO)_2$] (88.8 mg, 0.210 mmol) was added. The resulting mixture was heated at 100 °C for 1 week. The precipitate formed was filtered off and dried to give the analytical sample as an orange solid. Yield 20%. Anal. Calcd. for $C_{11}H_9ClN_2OPt$ (%): C, 31.78; H, 2.18; N, 6.74. Found: C, 31.92; H, 2.34; N, 6.57. $^1$H NMR ($CDCl_3$, ppm) = 9.11 (d with sat, 1H, $J_{H-H}$ = 5.4 Hz, $^3J_{Pt-H}$ *ca.* 12 Hz, $H^{6'}$), 8.17 ppm (t, 1H, $J_{H-H}$ = 7.8 Hz, $H^4$ or $H^{4'}$), 8.03 (d, 1H, $J_{H-H}$ = 7.8 Hz, $H^{3'}$), 7.96 (t, 1H, $J_{H-H}$ = 7.8 Hz, $H^4$ or $H^{4'}$), 7.76 (m, 1H, $J_{H-H}$ = 7.8 Hz, $H^{5'}$), 7.44 (d with sat, 1H, $^3J_{H-H}$ = 7.6 Hz, $^4J_{Pt-H}$ = 11 Hz, $H^3$), 7.03 (d, 1H, $J_{H-H}$ = 8.0 Hz, $H^5$), 7.00 (s with sat, 2H, $^2J_{Pt-H}$ = 77 Hz, Pt-$CH_2$). $^{13}$C NMR ($CD_2Cl_2$, ppm): 147.87 (s, CH), 138.61 (s, CH), 138.35 (s, CH), 127.11 (s, CH), 122.17 (s, CH), 112.99 (s, CH), 110.47 (s, CH), 70.88 (s, $CH_2$).

**[Pt(bpy$^{6OMe}$-H)(Me)($PPh_3$)], 5**

a) One pot synthesis: to a solution of bpy$^{6OMe}$ (25.5 mg, 0.134 mmol) in acetone (7 mL) [$Pt(Me)_2(DMSO)_2$] (48.1 mg, 0.126 mmol) was added. The resulting solution was heated at 40 °C for 3 h under an inert atmosphere, then $PPh_3$ (34.2 mg, 0.130 mmol) was added and left to react for 1 h. The solution was concentrated to a small volume and treated with diethyl ether. The precipitate formed was filtered off, washed with diethyl ether and dried to give the analytical sample as a yellow solid. Yield 65%.

b) Complex **5** may also be obtained by reaction of complex **1** with $PPh_3$ in a 1:1 molar ratio in acetone at room temperature for 1 h. Yield 80%.

M.p. 230 °C. Anal. Calcd. for $C_{30}H_{27}N_2OPPt$ (%): C, 54.79; H, 4.14; N, 4.26. Found: C, 54.69; H, 3.56; N, 4.15. $^1$H NMR ($CDCl_3$, ppm): 8.27 (d, 1H, $J_{H-H}$ = 7.9 Hz, $H^3$), 8.15 (dd, 1H, $J_{H-H}$ = 8.2 Hz, $J_{P-H}$ 4.8 Hz, $J_{Pt-H}$ = 44 Hz, $H^4$), 7.84 – 7.68 (m, 8H), 7.45 – 7.34 (m, 9H), 6.79 (d with sat, 1H, $J_{H-H}$ = 8.2 Hz, $J_{Pt-H}$ = 14 Hz, $H^5$), 6.64 (m, 1H, $J_{H-H}$ = 5.8, 6.2 Hz, $H^{5'}$), 3.99 (s, 3H, OMe), 0.73 (d with sat, 3H, $J_{P-H}$ = 7.8 Hz, $J_{Pt-H}$ = 82.8 Hz, Pt-Me). $^{31}$P NMR ($CDCl_3$, ppm): 32.59 (s, $J_{Pt-P}$ = 2257 Hz, $PPh_3$).

$^{13}$C NMR ($CDCl_3$, ppm): 164.96 (d with sat, $J_{Pt-C}$ = 49 Hz, $J_{P-C}$ = 5 Hz, Cq), 161.65 (s, Cq), 150.47 (d with sat, $J_{Pt-C}$ = 976 Hz, $J_{P-C}$ = 22 Hz $C^{3'}$), 150.46 (s, CH), 150.38 (s, CH), 143.09 (d with sat, $J_{Pt-C}$ = 90 Hz, $J_{P-C}$ = 1 Hz), 137.33 (s, CH), 135.04 (d with sat, $J_{Pt-C}$ = 17 Hz, $J_{P-C}$ = 12 Hz), 132.36 (d with sat, $J_{Pt-C}$ = 44 Hz, $J_{P-C}$ = 18 Hz, C-$PPh_{3\ ipso}$), 130.19 (d with sat, $J_{P-C}$ = 2 Hz, C-$PPh_{3para}$), 128.25 (d with sat, $J_{P-C}$ = 10 Hz, C-$PPh_{3meta}$), 123.27 (s with sat, $J_{Pt-C}$ = 9.5 Hz), 121.21 (s with sat, $J_{Pt-C}$ = 19 Hz), 111.62 (d with sat, $J_{Pt-C}$ = 56 Hz, $J_{P-C}$ = 6 Hz), 52.95 (s, OMe), -13.14 (d with sat, $J_{Pt-C}$ = 723 Hz, $J_{P-C}$ = 5 Hz, Pt-$CH_3$).

**[Pt(bpy$^{6OMe}$-H)(Me)$_2$(I)($PPh_3$)], 9**

To a solution of complex **5** (70 mg, 0.1064 mmol) in acetone (15 mL) MeI (32 µL) was added in excess. The resulting solution was stirred for 3 h at room temperature under an inert atmosphere, then it was concentrated to a small volume and treated with *n*-hexane. The precipitate formed was filtered off, washed with *n*-hexane and dried to give the analytical sample. Yield 65%. Anal. Calcd for $C_{31}H_{30}IN_2OPPt$ (%): C, 46.57; H, 3.78; N, 3.50. Found: C, 47.71; H, 4.05; N, 3.67. $^1$H NMR ($CDCl_3$, ppm): 9.50 (d with sat, 1H, $J_{H-H}$ = 5.4 Hz, $J_{Pt-H}$ = 12 Hz, $H^{6'}$), 8.14 (d, 1H, $J_{H-H}$ = 8.1 Hz, $H^{3'}$), 7.74 (m, 1H, $H^{4'}$), 7.29 (m, 9H, $PPh_3$), 7.18 (m, 6H, $PPh_3$), 7.09 (m, 1H, $H^{5'}$), 6.92 (d with sat, 1H, $J_{H-H}$ = 8.2 Hz, $J_{Pt-H}$ = 42 Hz, $H^4$), 6.40 (d with sat, 1H, $J_{H-H}$ = 8.2 Hz, $J_{Pt-H}$ = 11 Hz, $H^5$), 4.02 (s, 3H, $OCH_3$), 1.67 (d with sat, 3H, $J_{H-H}$ = 7.9 Hz, $J_{Pt-H}$ = 71 Hz, Pt-Me), 1.23 (d with sat, 3H, $J_{H-H}$ = 7.6 Hz, $J_{Pt-H}$ = 60 Hz, Pt-Me). $^{31}$P NMR ($CDCl_3$, ppm): -10.84 ppm (s with sat, $J_{Pt-P}$ = 959 Hz, $PPh_3$).

**[Pd(bpy$^{6OMe}$)(OAc)$_2$], 10, and Pd(bpy$^{6OMe}$-H)(OAc)]$_2$, , 11-t + 11-c**

To a solution of bpy$^{6OMe}$ (93.0 mg, 0.50 mmol) in benzene (50 mL), solid $Pd(OAc)_2$ (112 mg, 0.50 mmol) was added. The resulting solution was heated at 80 °C for 1 h under stirring. The precipitate formed was filtered off, washed with benzene and vacuum dried to give complex **10** as a creamy solid (Yield 80%). The filtered solution was concentrated to a small volume and treated with diethyl ether to give a mixture of products. The main species were identified as the *trans* and *cis* isomers of [Pd(bpy$^{6OMe}$-H)(OAc)]$_2$, **11-t** and **11-c**, present in 1:4 molar ratio.

**[Pd(bpy$^{6OMe}$)(OAc)$_2$], 10**

Anal. Calcd for $C_{15}H_{16}N_2O_5Pd$ (%): C, 43.86; H, 3.93; N, 6.82. Found: C, 43.72; H, 4.09; N, 6.57.

$^1$H NMR ($CDCl_3$, ppm): 8.30 (d, 1H, $J_{H-H}$ = 8.2 Hz, $H^{3'}$), 8.23 (d, 2H, $J_{H-H}$ = 5.4 Hz, $H^{6'}$), 8.08 (m, part. overlappd, $J_{H-H}$ = 7.7, 8.2 Hz, $H^{4'}$), 8.04 (m, part. overlappd, $J_{H-H}$ = 7.7, 8.2 Hz, $H^4$), 7.96 (d, 1H, $J_{H-H}$ = 7.7 Hz; $H^3$), 7.34 (m, 1H, $J_{H-H}$ = 7.8, 5.4 Hz, $H^{5'}$), 6.85 (d, 1H, $J_{H-H}$ = 8.2 Hz; $H^5$), 3.94 (s, 3H; OMe), 2.16 (s, 3H; OAc *cis* to $H^{6'}$), 2.10 (s, 3H; OAc *cis* to $OCH_3$). Assignments based on $^1$H-$^1$H COSY and $^1$H-$^1$H NOESY experiments.

*trans*-[Pd(bpy$^{6OMe}$-H)(OAc)]$_2$, **11-t**. $^1$H NMR ($CDCl_3$, ppm), selected $^1$H NMR signals: 8.03 (d, 2H, $J_{H-H}$ = 5.5 Hz, $H^{6'}$), 7.07 (d, 2H, $J_{H-H}$ = 8.4 Hz, $H^4$), 6.32 (d, 2H, $J_{H-H}$ = 8.4 Hz, $H^5$), 3.84 (s, 6H, $OCH_3$), 2.27 (s, 6H, $CH_3COO$).

*Cis*-[Pd(bpy$^{6OMe}$-H)(OAc)]$_2$, **11-c.** $^1$H NMR ($CDCl_3$, ppm), selected $^1$H NMR signals: 7.86 (d, 2H, $J_{H-H}$ = 5.5 Hz, $H^{6'}$), 6.87 (d, 2H, $J_{H-H}$ = 8.4 Hz, $H^4$), 6.20 (d, 2H, $J_{H-H}$ = 8.4 Hz, $H^5$), 3.84 (s, 6H, $OCH_3$).

**[Pd(bpy$^{6OMe}$)Cl$_2$], 12**

a) To a solution of bpy$^{6OMe}$ (93 mg, 0.50 mmol) in $CH_2Cl_2$ (50 mL) *trans*-(PhCN)$PdCl_2$ (192 mg, 0.50 mmol) was added. The mixture was stirred for 6 days at room temperature and then filtered off and dried under vacuum. Recrystallization from MeCN–diethyl ether gave **12** as a dark yellow crystalline product. Yield 90%.

b) To a solution of **10** (40 mg, 0.06 mmol) in acetone (30 mL) an excess of LiCl was added. The mixture was stirred for 12 h at room temperature, then filtered off. The filtered solution was concentrated to a small volume and treated with diethyl ether to give **12**. Yield 90%. Anal. Calcd. for $C_{11}H_{10}Cl_2N_2OPd$ (%): C, 36.34; H, 2.77; N, 7.71. Found: C, 37.01; H, 2.38; N, 7.51. $^1$H NMR ($CD_3CN$, ppm): 9.20 (d, 1H, $J_{H-H}$ = 5.5 Hz, $H^{6'}$), 8.16-8.10 (m, 3H, $H^{4'}$ $H^4$, $H^{3'}$), 7.82 (d, 1H, $J_{H-H}$ = 7.7 Hz, $H^3$), 7.57 (dd, 1H, $J_{H-H}$ = 5.0, 8.6 Hz, $H^{5'}$), 7.13 (d, 1H, $J_{H-H}$ = 8.6 Hz, $H^5$), 3.98 (s, 3H, Me).

**[Au(bpy$^{6OMe}$)Cl$_3$], 13**

To a solution of bpy$^{6OMe}$ (93 mg, 0.50 mmol) in MeCN (5 mL) an aqueous solution (30 mL) of $Na[AuCl_4]\cdot 2H_2O$ (199 mg, 0.50 mmol) was added. The resulting yellow suspension was stirred for 72 h at room temperature. During this period the colour of the suspension turned to dark orange. The solid product was filtered off and air-dried under vacuum to give **13** (200 mg, yield 81%). Recrystallization from chloroform–diethyl ether gave a dark orange crystalline product, m.p. 170–171°C. Anal. Calcd for $C_{11}H_{10}AuCl_3N_2O$ (%): C, 26.99; H, 2.06; N, 5.72. Found: C 27.19; H 1.84; N 5.63. $^1$H NMR ($CDCl_3$, ppm): 9.01 (dd, 1H, $J_{H-H}$ = 5.6, 1.3 Hz; $H^{6'}$),

8.20 (td, 1H, $J_{H-H}$ = 7.7, 1.4 Hz, $H^{3'}$), 8.05 (dd, 1H, $J_{H-H}$ = 7.9, 1.6 Hz, $H^{3}$), 7.80 (td, 1H, $J_{H-H}$ = 7.9, 0.6 Hz, $H^{4'}$), 7.71 (td, 1H, $J_{H-H}$ = 6.7, 1.6 Hz, $H^{4}$), 7.44 (d, 1H, $J_{H-H}$ = 7.2 Hz, $H^{5'}$), 7.03 (d, 1H, $J_{H-H}$ = 8.5 Hz, $H^{5}$), 4.32 (s, 3H, Me). IR (Nujol): 363 $cm^{-1}$, ν Au-Cl.

**[Au(bpy-$^{6OMe}$)(μ-O)]$_2$[$PF_6$]$_2$, 14**

To a suspension of **13** (303 mg, 0.62 mmol) in MeCN (3 mL) and water (30 mL) solid $KPF_6$ (344 mg, 1.87 mmol) and an aqueous solution (15 mL) of $MeCO_2Na$ (101 mg, 1.24 mmol) were added. The mixture was stirred for 6 days at room temperature and then filtered off and dried under vacuum to give **14** as a mixture of the *cis*, **14-c**, and *trans*, **14-t**, isomers (421 mg, yield 72%). Recrystallization from acetonitrile/diethyl ether gave the analytical sample as an orange solid, m.p. 198-200 °C. Anal. Calcd for $C_{22}H_{20}Au_2F_{12}N_4O_4P_2$ (%); C, 24.28; H, 1.85; N, 5.15. Found: C, 24.47; H, 1.38; N, 5.02. $^1$H NMR ($CD_3CN$, ppm) **14-t**: 8.61 (d, 2H, $J_{H-H}$ = 5.7 Hz, $H^{6'}$), 8.44 (m, 4H, overlappd signals, $H^{4'}$, $H^{3'}$), 8.37 (t, 2H, $J_{H-H}$ = 8.0 Hz, $H^{4}$), 8.06 (m, 4H, overlappd signals, $H^{5'}$, $H^{3}$), 7.46 (d, 2H, $J_{H-H}$ = 8.7 Hz, $H^{5}$), 4.24 (s, 6H, Me). **14-c**: 8.76 (d, 2H, $J_{H-H}$ = 5.6 Hz, $H^{6'}$), 8.44 (m, 4H, overlappd signals, $H^{4'}$, $H^{3'}$), 8.37 (t, 2H, $J_{H-H}$ = 8.2 Hz, $H^{4}$), 8.06 (m, 4H, $H^{5'}$, $H^{3}$), 7.46 (d, $J_{H-H}$ = 8.7 Hz, 2H, $H^{5}$), 4.19 (s, 6H, Me).

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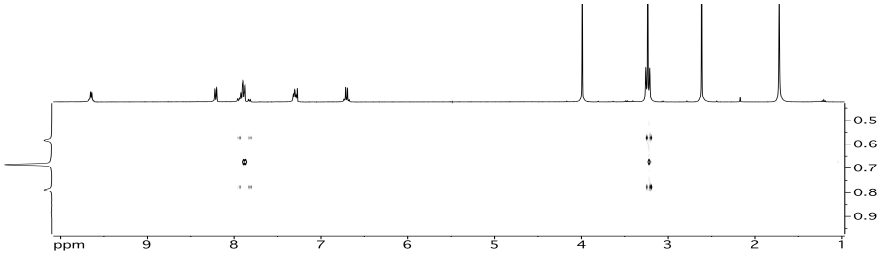
## Highlights

Highlights: rollover cyclometalation; C-H bond activation; bipyridine complexes; Pt(II), Pd(II) and Au(III) cyclometalated complexes.

**Supporting information**

a

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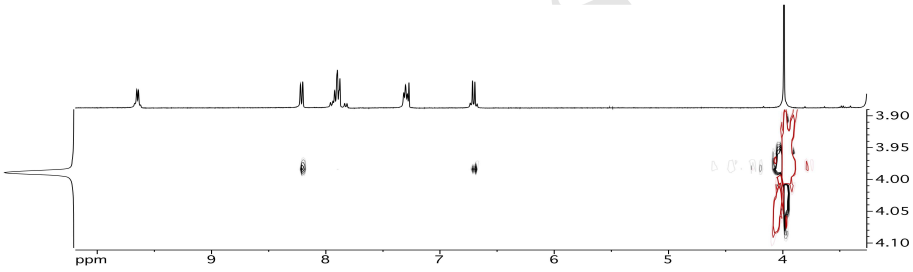


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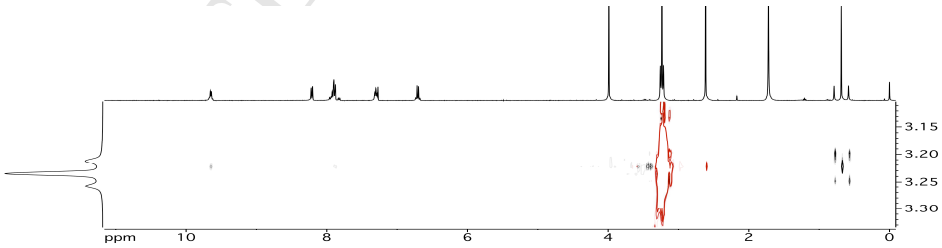


Fig S1. Sections of the $^{1}$H-$^{1}$H NOESY spectrum of **1**, showing through space interactions between: a) Pt-$CH_3$, $H^4$ and DMSO; b) $OCH_3$, $H^5$ and $H^3$; c) DMSO, Pt-$CH_3$ and $H^{6'}$.

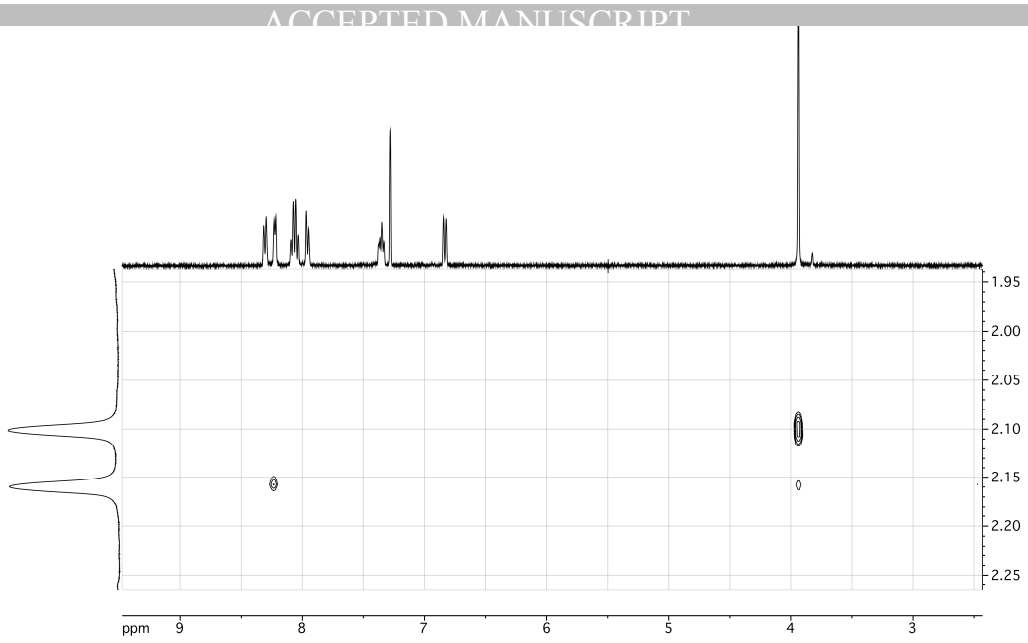


Fig S2: Section of the $^{1}H$-$^{1}H$ NOESY spectrum of complex **10**. The cross peaks between the $OCH_3$ group on $bpy^{6OMe}$ and the methyl of the acetato ligands are shown along with the interaction with $H^5$.

Table S1. Proton affinity and basicity data for substituted pyridines, $Py^R$

| $Py^R$ | Proton affinity[1] (a) | Proton affinity[1] (f) | Basicity[1] (a) | Basicity (gas phase)[1] (f) | pKa[2] | Ref[3] |
|---|---|---|---|---|---|---|
| pyridine | 930.0 | 922.2 | 898.1<br>898.3 (d) | 889.5 | 5.17<br>5.23<br>5.25<br>5.21<br>5.22 | (b)<br>(c)<br>(d)<br>(e)<br>(g) |
| 2-$CH_3$ | 949.1 | 936.0 | 917.3<br>917.1 (d) | 903.3 | 5.97<br>5.95<br>5.94<br>5.96 | (b)<br>(c)<br>(d)<br>(g) |
| 3-$CH_3$ | 943.4 | 932.2 | 911.6 | 899.6 | 5.68<br>5.71<br>5.63 | (b)<br>(c)<br>(g) |
| 4-$CH_3$ | 947.2 | 936.0 | 915.3 | 903.3 | 6.02<br>6.06<br>5.98 | (b), (e)<br>(c)<br>(g) |
| 2-$C_2H_5$ | 952.4 | 941.0 | 920.6 | 908.3 | 5.97 | (b) |
| 3-$C_2H_5$ | 947.4 | 936.8 | 915.5 | 904.2 | 5.70 | (b) |
| 4-$C_2H_5$ | 951.1 | 939.7 | 919.2 | 907.1 | 6.02 | (b) |
| 2-$CF_3$ | 877.1 | 885.3 | 855.2 | 852.7 | n.a. | |
| 3-$CF_3$ | 892.5 | 890.4 | 860.7 | 857.7 | 3.36 | |
| 4-$CF_3$ | 893.9 | 891.6 | 862.0 | 859.0 | 3.59 | |
| 2-$OCH_3$ | 934.7 | 925.9 | 902.8 | 893.3 | 3.28<br>3.1 | (b), (e)<br>(d) |
| 3-$OCH_3$ | 942.7 | 930.9 | 910.9 | 898.3 | 4.88 | (b) |
| 4-$OCH_3$ | 961.7 | 948.9 | 929.8<br>929.7 (d) | 916.3 | 6.62<br>6.50 | (b)<br>(d) |
| | | | | | | |

1) gas phase, kJ/mol.

2) referred to the pyridinium ion

3 a) E. P. L. Hunter, S. G. Lias, J. Phys. Chem. Ref. Data 27 (1988) 413-656; b) pKa Data Compiled by R. Williams, http://research.chem.psu.edu/brpgroup/pKa_compilation.pdf; c) S. Hanessian, J.-Y. Sancéau, Can. J. Chem. 74 (1996) 621-624; d) T. Rodima, I. Kaljurand, A. Pihl, V. Mäemets, I. Leito, I. A. Koppel, J. Org. Chem. 67 (2002) 1873-1881; e) F. M. Menger, T. D. Singh, F. L. Bayer, J. Am. Chem. Soc. 98, 16, (1976) 5011-5012; f) D. H. Aue, H. M. Webb, W. R. Davidson, P. Toure, H. P. Hopkins Jr, S. P. Moulik, D. V. Jahagirdar, J. Am. Chem. Soc. 113 (1991) 1770-1780; g) R. J. L. Andon, J. D. Cox, E. F. G. Herington, Trans. Faraday Soc. 50 (1954) 918-927.

Table S2. Selected bond distances (Å) and angles (°) for complex **1**

| | **Complex 1** | **Complex 2** |
|---|---|---|
| Pt-$N^{1'}$ | 2.13(1) | 2.13(1) |
| Pt-$C^{3}$ | 2.00(1) | 2.01(1) |
| Pt-$CH_3$ | 2.05(1) | 2.06(1) |
| Pt-S | 2.268(3) | 2.270(3) |
| $N^{1'}$-$C^{2'}$ | 1.35(1) | 1.35(1) |
| $C^{2'}$-$C^{2}$ | 1.47(2) | 1.46(2) |
| $C^{2}$-$C^{3}$ | 1.38(2) | 1.39(1) |
| $N^{1}\cdots H$ ($OCH_3$) | 2.455 | 2.495 |
| $H^{6'}\cdots O$ (DMSO) | 2.326 | 2.329 |
| | | |
| $N^{1'}$-Pt-$C^{3}$ | 79.6(4) | 79.5(4) |
| $C^{3}$-Pt-$CH_3$ | 90.6(5) | 91.4(5) |
| $CH_3$-Pt-S | 89.4(4) | 89.8(4) |
| S-Pt-$N^{1'}$ | 100.5(3) | 99.8(3) |
| $N^{1'}$-Pt-$CH_3$ | 170.1(4) | 169.8(4) |
| S-Pt-$C^{3}$ | 174.5(3) | 172.3(3) |