# Multiple C−H Bond Activation. Threefold-Deprotonated 6-Phenyl-2,2′-bipyridine as a Bridging Ligand in Dinuclear Platinum(II) Derivatives

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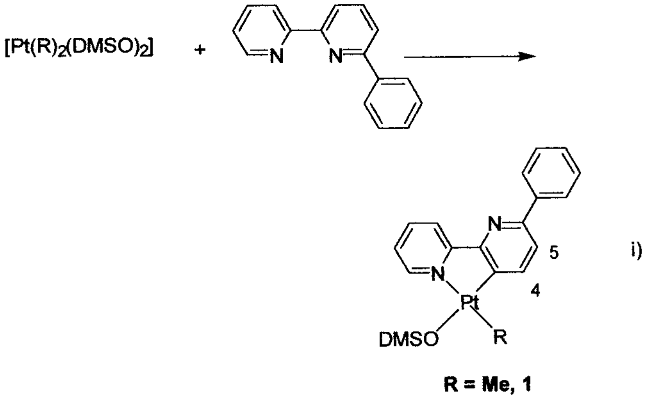
*Summary: Unusual platinum(II) trimetalated derivatives have been synthesized and characterized by reaction of cis-[Pt(R)$_2$(DMSO)$_2$] (R = Me, Ph) and 6-phenyl-2,2′-bipyridine. The behavior of the substituted 2,2′-bipyridine as a threefold-deprotonated ligand is unprecedented.*

The so-called "rollover" metalation of 2,2′-bipyridine, which entails cleavage of a C−H bond of a pyridine ring, was first observed several years ago in an iridium(III) complex.[1] Since then, examples of cyclometalated N′,C(3) species have been described by Wimmer and co-workers in the case of N-substituted 2,2′-bipyridines.[2] Activation of C−H bonds has been invoked to explain the formation of Ar−H in a process of thermal rearrangement of (Ar)$_2$Pt(bipy) complexes:[3] no simple mononuclear species was isolated, but the metalation was confirmed by the X-ray structure of a more complex dinuclear species. Quite recently, we have reported palladium(II) and platinum(II) derivatives where 6-alkyl-substituted-2,2′-bipyridines, LH, are N′- and C(3)-coordinated to give five-membered cycles.[4] The complexes [Pd(L)Cl]$_2$ (HL = 6-CHMe$_2$-2,2′-bipy) and [Pt(L)Cl(SMe$_2$)] (HL = 6-CMe$_3$-2,2′-bipy) have been characterized also in the solid state by X-ray diffraction.

Here we report the unusual behavior of one of the 6-substituted 2,2′-bipyridines currently investigated by us.

Reaction of *cis*-[(Me)$_2$Pt(DMSO)$_2$] and *cis*-[(Ph)$_2$Pt(DMSO)$_2$] with 6-Ph-2,2′-bipy in a 1/1 HL/Pt molar ratio (reaction i) gives compounds **1** and **2**,[5] respectively, which are new examples of rollover cyclometalation.



**R = Me, 1**
**R = Ph, 2**

The $^1$H NMR spectra provide evidence for the formation of one isomer only. The reactions imply elimination of methane or benzene, respectively. An AB system due to H(4) and H(5) accompanied by satellites (e.g., for compound **1**: $\delta$ 7.65, H(5), $^4J_{Pt-H} = 25$ Hz; $\delta$ 8.07, H(4), $^3J_{Pt-H} = 52$ Hz) confirms coordination of platinum with the C(3) atom. The Pt−H coupling constants of the methyls in the coordinated DMSO, equal to 18.3 Hz (**1**) and 17.6 Hz (**2**), are consistent with DMSO trans to a carbon atom.[6]

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(5) Synthesis of [Pt(L)(R)(DMSO)] (R = Me, **1**; R = Ph, **2**). A suspension of 6-Ph-2,2′-bipy (HL; 0.100 mmol) and *cis*-[Pt(R)$_2$(DMSO)$_2$] (i, R = Me; ii, R = Ph; 0.100 mmol) in toluene (5.0 mL) was stirred under argon at 90 °C for 2 h (i) or 8 h (ii). The mixture was cooled to room temperature and evaporated to dryness. The solid obtained was dissolved in CH$_2$Cl$_2$ (10 mL): the resulting solution was filtered over Celite and then concentrated to a small volume and treated with diethyl ether. The yellow precipitate formed was filtered and washed with diethyl ether to give the analytical sample. Compound **1**: yield 93%; mp 174−176 °C dec; $^1$H NMR (299.9 MHz, CDCl$_3$) $\delta$ 9.71 (d, 1H, H(6′), $^3J_{H-H} = 5.6$ Hz, $J_{Pt-H} = 19.5$ Hz), 8.50 (d, 1H, H(3′), $^3J_{H-H} = 7.3$ Hz), 8.14 (d, 2H, H$_o$ Ph, $^3J_{H-H} = 7.8$ Hz), 8.07 (d, 1H, H(4), $^3J_{H-H} = 8.1$ Hz, $^3J_{Pt-H} = 52$ Hz), 7.97 (dt, 1H, H(4′), $^4J_{H-H} = 1$ Hz, $^3J_{H-H} = 7.8$ Hz), 7.65 (d, 1H, H(5), $^3J_{H-H} = 8.1$ Hz, $^4J_{Pt-H} = 25$ Hz), 7.54−7.32 (m, 4H), 3.26 (s, 6H, CH$_3$ (DMSO), $^3J_{Pt-H} = 18.3$ Hz), 0.75 (s, 3H, CH$_3$−Pt, $^2J_{Pt-H} = 81.8$ Hz); $^{13}$C NMR (75.4 MHz, [D$_6$]DMSO) $\delta$ 164.0 (s, $J_{Pt-C} \approx 25$ Hz), 161.6 (s, $J_{Pt-C} = 56.4$ Hz), 151.4 (s, $J_{Pt-C} = 214.7$ Hz), 149.9 (s), 145.5 (s), 140.8(s, $J_{Pt-C} = 90.2$ Hz), 139.3 (s), 138.9 (s, $J_{Pt-C} = 90.6$ Hz), 128.7 (s), 128.5 (s), 125.9 (s), 125.1 (s), 121.1 (s, $J_{Pt-C} \approx 20$ Hz), 120.1 (s, $J_{Pt-C} = 60.0$ Hz), −13.8 (s, *C*H$_3$−Pt, $J_{Pt-C} = 772.5$ Hz). Compound **2**: yield 51%; mp 240 °C; $^1$H NMR (299.9 MHz, CDCl$_3$) $\delta$ 2.98 (s, 6H, CH$_3$(DMSO), $^3J_{Pt-H} = 17.6$ Hz); 6.94 (d, 1H, H(4), $^3J_{H-H} = 7.8$ Hz), 7.03−7.47 (m, 8H, aromatics), 7.51 (d, 2H, H$_o$ (Ph−Pt), $^3J_{H-H} = 6.8$ Hz, $^3J_{Pt-H}$ 65.0 Hz), 7.98 (t, 1H, H(4′), $^3J_{H-H} = 7.7$ Hz), 8.02 (d, 2H, H$_o$ Ph bipy, $^3J_{H-H} = 7.8$ Hz), 9.63 (d, 1H, H(6′), $^3J_{H-H} = 5.4$ Hz).

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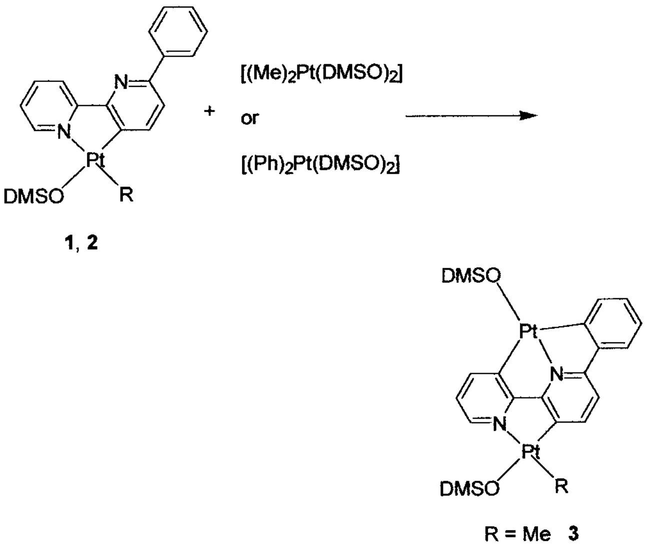
Compounds **1** and **2** react further, in a separate step, with [(Me)$_2$Pt(DMSO)$_2$] or [(Ph)$_2$Pt(DMSO)$_2$] in excess, to give **3** and **4**.[7]



**1**, **2**

R = Me **3**
R = Ph **4**

Compounds **3** and **4** can be obtained also in an one-pot reaction with a 1/2.5 HL/Pt molar ratio. Compounds **3** and **4** show a remarkable thermal stability: mp >250 °C for **3** and >240 °C for **4**). They have been fully characterized by elemental analyses, by $^1$H and $^{13}$C{$^1$H} NMR and FAB-MS spectroscopy, and, in the case of **4**, by X-ray diffraction.[8-10]

An ORTEP view of the complex molecule is shown in Figure 1, with selected interatomic distances and angles given in the figure caption.

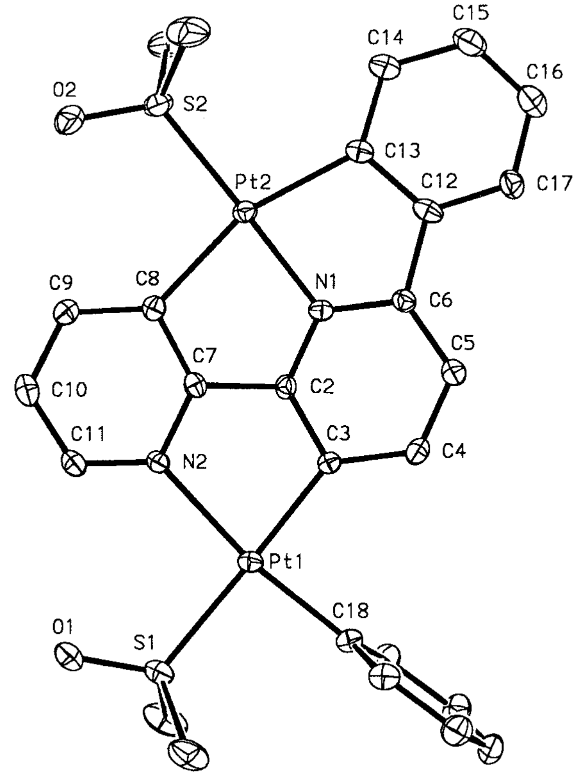


**Figure 1.** ORTEP view of **4**. Ellipsoids are drawn at the 30% probability level. Selected interatomic distances (Å) and angles (deg): Pt(1)–S(1) = 2.281(1), Pt(1)–N(2) = 2.166(4), Pt(1)–C(3) = 2.018(5), Pt(1)–C(18) = 2.031(6), Pt(2)–S(2) = 2.187(2), Pt(2)–N(1) = 1.996(4), Pt(2)–C(8) = 2.105(5), Pt(2)–C(13) = 2.079(6); S(1)–Pt(1)–N(2) = 97.7(1), S(1)–Pt(1)–C(3) = 178.4(1), S(1)–Pt(1)–C(18) = 91.1(2), N(2)–Pt(1)–C(3) = 81.4(2), N(2)–Pt(1)–C(18) = 171.1(2), C(3)–Pt(1)–C(18) = 89.8(2), S(2)–Pt(2)–N(1) = 178.0(1), S(2)–Pt(2)–C(8) = 97.8(2), S(2)–Pt(2)–C(13) = 101.9(2), N(1)–Pt(2)–C(8) = 80.8(2), N(1)–Pt(2)–C(13) = 79.5(2), C(8)–Pt(2)–C(13) = 160.2(2).

The two platinum atoms are in a slightly distorted square planar coordination, the main distortion being that due to the bites of the chelating ligands, whereas no loss of planarity is observed. The dihedral angle between the best planes of the two PtSNC$_2$ moieties is 1.7(6)°, so that the whole molecule can be described as approximately planar, with the obvious exceptions of the methyl and oxygen moieties and ortho and meta phenyl C–H groups. All the metric parameters are as expected if the trans influence of the three coordinated carbon atoms is taken into account.[4,11,12] The phenyl ligand is nearly perpendicular to the Pt(1) coordination plane, with a dihedral angle of 94.3(1)°.

In the case of **3**, 2D H–H COSY and NOESY NMR spectra allowed the assignment of all the signals in the spectra.

In complexes **3** and **4**, 6-Ph-2,2′-bipy displays an unprecedented behavior, acting as a threefold-deprotonated ligand. All three Pt–C bonds originate from activation of C(sp$^2$)–H bonds. The resulting compounds **3** and **4** are unique in several aspects. (i) The two platinum(II) ions are bridged through a ten-electron donor. (ii) Three five-membered rings are assembled in the same molecule. (iii) The tridentate dianionic system has a C,N,C sequence which is not unprecedented but

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[7] Compounds **3** and **4** were obtained by following the same procedure described for **1** and **2**, with the exception that a 2.5/1 Pt/HL molar ratio was used. Compound **3**:. yield 62%; mp >250 °C; $^1$H NMR (CD$_2$Cl$_2$) $\delta$ 9.00 (dd, 1H, H(6′), $^4J_{\text{H-H}} = 1.2$ Hz, $^3J_{\text{H-H}} = 5.6$ Hz, $^3J_{\text{Pt-H}} = 15$ Hz), 8.17 (dd, 1H, H(4′), $^4J_{\text{H-H}} = 1.5$ Hz, $^3J_{\text{H-H}} = 7.6$ Hz, $^3J_{\text{Pt-H}} = 21$ Hz), 7.86 (d, 1H, H(4), $^3J_{\text{H-H}} = 8.1$ Hz, $^3J_{\text{Pt-H}} = 46.6$ Hz), 7.53 (dd, 1H, H(3″), $^3J_{\text{H-H}} = 7.3$ Hz, $^4J_{\text{H-H}} \approx 1$ Hz, $^3J_{\text{Pt-H}} = 25.6$ Hz), 7.45 (dd, 1H, H(6″), $^4J_{\text{H-H}} \approx 1$ Hz, $^3J_{\text{H-H}} = 7.3$ Hz), 7.21 (d, 1H, H(5), $^3J_{\text{H-H}} = 8.1$ Hz partially overlapping), 7.19 (dd, 1H, H(4″)), 7.12 (m, 1H, H(5′) partially overlapping), 7.09 (m, 1H, H(5″) partially overlapping), 3.61 (s, 6H, CH$_3$ (DMSO), $^3J_{\text{Pt-H}} = 26.1$ Hz), 3.19 (s, 6H, CH$_3$ (DMSO), $^3J_{\text{Pt-H}} = 20.0$ Hz), 0.72 (s, 3H, CH$_3$–Pt, $^2J_{\text{Pt-H}} = 83.0$ Hz). Compound **4**: yield 63%; mp >265 °C; $^1$H NMR (299.9 MHz, CDCl$_3$) 2.93 (s, 6H, CH$_3$ (DMSO) $^3J_{\text{Pt-H}} = 19.5$ Hz), 3.63 (s, 6H, CH$_3$ (DMSO), $^3J_{\text{Pt-H}} = 26.1$ Hz), 6.71 (d, 1H, H(4)), 6.90 (d, 1H, H(5)), 7.00–8.24 (m, 12H, aromatics), 8.94 (d, 1H, H(6′)).

[8] Crystal data for **4**: C$_{26}$H$_{26}$N$_2$O$_2$Pt$_2$S, $M_r = 852.8$, monoclinic, space group $P2_1/c$ (No. 14), $a = 11.973(1)$ Å, $b = 8.571(1)$ Å, $c = 25.141(3)$ Å, $\beta = 99.36(1)$°, $U = 2545.6(6)$ Å$^3$, $Z = 4$, $D_c = 2.225$ g cm$^{-3}$, $\mu = 112.8$ cm$^{-1}$, $F(000) = 1600$, $T = 223$ K, 39 758 reflections measured, 7576 independent reflections with $R_{\text{int}} = 0.048$, empirical absorption correction, SADABS[9] ($T_{\max} = 1.00$, $T_{\min} = 0.404$), final R1($F^2$, all reflections) = 0.055, wR2 = 0.097, conventional R1 = 0.036 for 307 parameters, SMART CCD area detector, Mo K$\alpha$ radiation ($\lambda = 0.710$ 73 Å), $\omega$ scan mode, $\theta_{\min} = 3$°, $\theta_{\max} = 26$°. The structure was solved by direct methods (SHELXS 86[10]) and refined by full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms; hydrogen atoms were placed in calculated positions. The program used was Personal SDP on a Pentium III computer. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Base.

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still very rare. Furthermore, most of the reported species do not arise from C−H activation: thus, platinum(II) species have been obtained from lithiated 2,6-diphenylpyridine,[13] palladium(II) derivatives from 2,6-(CH(COOR)$_2$)-functionalized pyridines able to generate, in the presence of alkali metal, a carbanion,[14] and gold(III) complexes by transmetalation with mercury intermediates.[15] Only quite recently has a C,N,C dicyclometalated platinum(II) complex been synthesized in good yields directly from $K_2PtCl_4$ and 2,6-diphenylpyridine.[12,16] The second metalation is induced by water. In addition, (iv) the neutral ligands (DMSO) are trans to atoms of very different trans effect and trans influence.

For comparison it is worth noting that reaction of 6-phenyl-2,2′-bipyridine with *trans*-[PtCl(Me)(SMe$_2$)$_2$] recently studied by us[17] only affords the adduct [PtCl(Me)(HL)] or the well-known N,N,C cyclometalated complex [Pt(L)Cl]. No transfer of hydrogen from the bipyridine rings was observed. It seems therefore that HL shows the behavior described here only toward the dialkyl and diaryl derivatives.

Quite recently in a paper of ours[18] we reported the unprecedented behavior of 2,2′:6′-2″-terpyridine as a twofold-deprotonated N,C∧C,N ligand bridging two [Pt(Me)(L)] units (L = neutral ligand). The present results confirm that, in the case of heterocyclic nitrogen ligands, metal-promoted intramolecular C−H activation is still a topic worthy of investigation.

Studies on the photophysical and photochemical properties of these new platinum species are ongoing.

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**Supporting Information Available:** Tables giving X-ray structural information on compound **4** and text and figures giving analytical and spectroscopic data of compounds **1**−**4** and NMR spectra of complex **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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