Unprecedented Behavior of 2,2':6',2"-Terpyridine: Dinuclear Platinum(II) Derivatives with a New N,C^C,N Bridging Ligand

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We report the synthesis and characterization of some dinuclear organoplatinum(II) species where 2,2':6',2"-terpyridine (terpy) behaves as a 2-fold-deprotonated N,C^C,N ligand bridging two [Pt(CH₃)(L)] units (L = neutral ligand). Each platinum atom is further bonded to a nitrogen of a terminal pyridine and to a 3' or 5' carbon atom of the inner pyridine ring. As far as we know, these are the first examples of cyclometalated terpy as well as of a 3,5dimetalated pyridine ring. The X-ray structure of one of these species (L = CO) shows it to be an organoplatinum polymer.

Introduction

2,2':6',2"-Terpyridine (terpy) has been studied for many years as a strong chelating agent to metal ions.¹ Its most common bonding mode is as an N,N',N" neutral ligand, either in octahedral or square-planar geometry.² Examples of N,N' endobidentate behavior are much less common;³ at least one example where it acts as a monodentate ligand is known.⁴ Metalated derivatives have been reported only when a nitrogen of a terminal pyridine ring has been protected by quaternization. In the latter case, terpy coordinates either as a bidentate N,N' donor or as an anionic tridentate N,N',C ligand.⁵

Platinum(II) derivatives of terpy and its analogues have been widely studied, because of their interaction with biomolecules $^{6a-d}$ and their outstanding photophysical properties, $^{6e-m}$ which make them play a key role in several fields of current interest.

Here we report the synthesis and characterization of dinuclear cyclometalated platinum(II) derivatives where terpy displays an unprecedented behavior acting as a 2-fold deprotonated N,C^C,N ligand. This demonstrates that, despite the great number of studies devoted to this old ligand, its coordination behavior still has surprises in store for us.

Results and Discussion

The reaction between terpy and *cis*-[Pt(CH₃)₂(DMSO)₂] (DMSO = dimethyl sulfoxide), in toluene at 90 °C (molar ratio Pt:terpy 2:1), affords, almost quantitatively, the dinuclear species **1** (see Scheme 1), having C_{2v} symmetry. Each platinum atom is bonded to a nitrogen of an outer pyridine and to a *meta*-carbon of the inner pyridine; the coordination spheres of the platinum atoms are completed by DMSO and a methyl group.

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Metalation, which affords two C,N five-membered rings, entails $C(sp^2)$ -H activation and elimination of methane. Although examples of C(3)-metalated pyridine rings are known,⁷ albeit not common, to the best of our knowledge no C(3),C(5)-dimetalated species have been reported.

When the reaction is carried out in a 1:1 Pt:terpy molar ratio, only the dimetalated species 1 is formed, and the unreacted ligand can be recovered from the reaction mixture.

It seems therefore that one platinum on the pyridine ring activates it toward further substitution. It is worth noting that the same behavior was reported several years ago by Trofimenko in the cyclopalladation of some di(aminomethyl)benzenes and taken as evidence for an electrophilic reaction.⁸

Compound **1** is soluble in DMSO but sparingly soluble in solvents such as dichloromethane and acetone. The ¹H NMR spectrum of **1** ([D₆]acetone) shows interesting features: in the aromatic region only five signals in a 2:2:1:2:2 ratio are observed, two doublets, a singlet, and two triplets. The singlet (H(4'), δ 8.38 ppm) unambiguously shows coupling to two equivalent ¹⁹⁵Pt nuclei (main signal/inner satellites ratio ca. 1:2:1).⁹ On the whole, signals in the aromatic region integrate to nine protons, showing that two protons of the neutral terpy are missing. In the aliphatic region, the signals of DMSO and of the methyl group are coupled to one ¹⁹⁵Pt nucleus. The *J*(Pt,H) value of the protons of DMSO (18.1 Hz) suggests it is *S*-bonded and *trans* to a carbon atom.¹⁰ spectrum pattern, are a first indication of the nature of compound **1**. The ¹³C{¹H} NMR spectrum in [D₆]DMSO and an APT (attached proton test) experiment confirm the structure proposed on the basis of ¹H NMR. Further support is provided by the microanalyses and the FAB (positive ions) mass spectrum, which shows the molecular ion at m/z 807⁺.

5

PCy₃,

In compound **1**, the DMSO can be easily replaced by other ligands, like acetonitrile and carbon monoxide: unfortunately, the obtained species, **2** and **3**, respectively, are too insoluble to allow their characterization by NMR spectroscopy. However, the microanalyses are in agreement and the IR spectra show a very weak absorption peak at 2282 cm⁻¹ (C–N stretching of the coordinate acetonitrile) for **2** and two strong absorption peaks at 2043 and 2030 cm⁻¹ (C–O stretching for terminal carbon monoxide) for **3**, as expected for a molecule with C_{2v} symmetry.¹¹ **1** and **3** show an extraordinary thermal stability: they decompose without melting at a temperature higher than 250 °C.

Orange-red crystals of 3, suitable for an X-ray analysis, were obtained by carbonylation of a very dilute unstirred dichloromethane solution of 1. An ORTEP view of the complex molecule is shown in Figure 1. Principal bond parameters are listed in the Figure 1 caption. The molecule possesses an idealized C_{2v} symmetry, with the 2-fold axis passing through atoms N2 and C8. Each of the two Pt atoms displays a squareplanar coordination with a slight square-pyramidal distortion. The Pt1-C7 and Pt2-C9 distances, 2.050-(6) and 2.051(5) Å, respectively, are slightly longer than the Pt-C bond length, 1.990(5) Å, found in [PtCl(L)- $(S(CH_3)_2)$ (HL = 6-*tert*-butyl-2,2'-bipyridine),^{7a} thus suggesting that the *trans*-influence of CO is slightly larger than that of Cl. The Pt1-C16 and Pt2-C18 distances, 2.061(6) and 2.066(8) Å, respectively, are in

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⁽⁹⁾ In a symmetric dinuclear species the ratio among the three isotopomers, Pt–Pt (43.8%), ¹⁹⁵Pt–Pt (44.8%), ¹⁹⁵Pt–¹⁹⁵Pt (11.4%) (where ¹⁹⁵Pt is the isotope with I = 1/2 in 33.8% abundance and Pt represents all the other isotopes with I = 0), is ca. 4:4:1. A hydrogen coupled to both platinum nuclei should display a five-line pattern with a 1:8:18:8:1 ratio.

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Figure 1. ORTEP view of a molecule of 3. Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (deg): Pt1-N1 2.137(5), Pt1-C7 2.050(6), Pt1-C16 2.061(6), Pt1-C17 1.914(7), C17-O1 1.103(10), Pt2-N3 2.124(5), Pt2-C9 2.051(5), Pt2-C18 2.066(8), Pt2-C19 1.866(6), C19-O2 1.148(7), N1-Pt1-C7 79.4(2), N1-Pt1-C16 170.7(3), N1-Pt1-C17 101.4(2), C7-Pt1-C16 91.4(3), C7-Pt1-C17 178.5(3), C16-Pt1-C17 87.8(3), N3-Pt2-C9 79.7(2), N3-Pt2-C18 170.2(3), N3-Pt2-C19 100.2(3), C9-Pt2-C18 91.4(3), C9-Pt2-C19 179.4(3), C18-Pt2-C19 88.7(3).



Figure 2. View of the crystal packing of compound 3, showing the short Pt···Pt intermolecular contacts (see text).

agreement with the Pt-CH₃ bond lengths observed in other trans CH₃-Pt-N systems.¹² The Pt1-N1 and Pt2-N3 bond lengths, 2.137(5) and 2.124(5) Å, respectively, are typical of Pt-N interactions *trans* to alkyl groups.¹³ The two Pt-CO bond lengths, 1.914(7) and 1.866(6) Å, average 1.890 Å, are in good agreement with the Pt(II)–CO distance, 1.897(7) Å, found in [Pt(COPh)-(CH₃)(CO)(PPh₃)].¹⁴

The strain imposed on the terpyridine molecule by its bridging behavior is apparent in the deviation from the ideal value of 120° in the intra-ring angles of the N2-C6-C7-C8-C9-C10 ring, which range from 115.3(5)° to 126.6(6)°. However, no loss of aromaticity is present, and the three pyridinic rings are all strictly planar.

A view of the crystal packing of the molecules of **3** is shown in Figure 2. The packing is dictated by a short Pt…Pt contact of 3.283(1) Å between the Pt1 and Pt2 atoms of two neighboring, parallel molecules, translated with respect to each other by one unit cell length along the *a* axis, 6.869(1) Å. Pt(II)…Pt(II) contacts below 3.50 Å are not unusual and are generally considered as

weakly bonding,^{6f,15} so that the packing in the present compound can be described as based on infinite monodimensional organoplatinum chains. Neighboring chains are kept together partly by graphitic interactions (interplanar distance 3.52(2) Å) and partly by normal van der Waals contacts.

Displacement of DMSO in complex 1 by triphenylphosphine (PPh₃) and tricyclohexylphosphine (PCy₃) affords almost quantitatively compounds 4 and 5, respectively (see Scheme 1). These compounds are much more soluble than 1-3 in organic solvents and allow a better characterization in solution by ${}^{1}H$, ${}^{13}C{}^{1}H$, and ${}^{31}P{}^{1}H$ NMR spectroscopy. In particular, for compound 5, the lack of aromatic rings besides those of terpy, makes assignment of ¹³C resonances much easier.

The unusual coordination of terpy as a tetradentate bridging ligand yields species still having a noncoordinated nitrogen. This suggests their potential either to act as N ligands or to give cyclometalated C,N,C species, similar to those arising from 2,6-diphenylpyridine.¹⁶ These features open up possibilities for new interesting homo- or heteropolynuclear assemblies.

Experimental Section

The platinum complex *cis*-[Pt(CH₃)₂(DMSO)₂] was prepared according to literature methods.¹⁷ All the solvents were purified and dried before use according to standard procedures. Elemental analyses were performed with a Perkin-Elmer elemental analyzer 240B by Mr. A. Canu (Dipartimento di Chimica, Università di Sassari). Infrared spectra were recorded with a Perkin-Elmer 983 using Nujol mulls. ¹H, ¹³C-{¹H}, and ³¹P{¹H} NMR spectra were recorded with a Varian VXR 300 spectrometer operating at 299.9, 75.4, and 121.4 MHz, respectively. Chemical shifts are given in ppm relative to internal TMS (¹H, ¹³C) and external 85% H_3PO_4 (³¹P). The mass spectrometric measurements were performed on a VG 7070EQ instrument, equipped with a PDP 11-250J data system and operating under positive ion fast atom bombardment (FAB) conditions with 3-nitrobenzyl alcohol as supporting matrix.

Compound 1. To a solution of 2,2':6',2"-terpyridine (0.312) g, 1.31 mmol) in anhydrous toluene (10 mL) was added cis-[Pt(CH₃)₂(DMSO)₂] (1.000 g, 2.62 mmol), and a red color rapidly appeared. The stirred suspension, kept under an atmosphere of argon, was heated to 90 °C. During the heating, the solution became yellow and a yellow precipitate began to form. After 3 h, the mixture was cooled to room temperature and diethyl ether (20 mL) was added. The product was filtered and washed with diethyl ether $(3 \times 5 \text{ mL})$. Yield: 1.03 g (97%, 1.28 mmol) Mp > 270 °C. ¹H NMR (299.9 MHz, $[D_6]$ acetone, 25 °C): δ 9.78 (dd, 2H, ³J(H,H) = 5.6 Hz, ⁴J(H,H) \approx 1 Hz, ${}^{3}J(\text{Pt,H}) \approx 21 \text{ Hz}$, 8.47 (d, 2H, ${}^{3}J(\text{H,H}) = 8.1 \text{ Hz}$), 8.38 (s, 1H, ${}^{3}J(Pt,H) = 53.7$ Hz), 8.10 (td, 2H, ${}^{3}J(H,H) = 7.8$ Hz, ${}^{4}J(H,H)$ \approx 2 Hz), 7.45 (td, 2H, ³J(H,H) = 5.6 Hz, ⁴J(H,H) \approx 2 Hz), 3.24 (s, 12H, ${}^{3}J(Pt,H) = 18.1$ Hz), 0.76 (s, 6H, ${}^{2}J(Pt,H) = 84.0$ Hz). ¹³C{¹H} NMR (75.4 MHz, [D₆]DMSO): δ 162.27 (s, *J*(Pt,C) = 55.0 Hz; C), 159.83 (s; C), 149.70 (s; CH), 147.85 (s, J(Pt,C) = 52.0 Hz; C), 143.71 (s, J(Pt,C) = 89.0 Hz; CH), 139.01 (s; CH), 124.19 (s; CH), 120.38 (s; CH), -13.40 (s, J(Pt,C) = 782.1 Hz;

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*C*H₃). IR (Nujol, cm⁻¹): ν_{max} 1607(s), 1564(s), 1106(m), 1093-(s), 1013(s). FAB⁺-MS (3-nitrobenzyl alcohol matrix): *m/z* (%) 807(20) [M⁺], 792(15) [M⁺ - CH₃], 729(30) [M⁺ - DMSO], 714-(70) [M⁺ - CH₃ - DMSO], 699(15) [M⁺ - 2CH₃ - DMSO], 651-(40) [M⁺ - 2DMSO], 636(100) [M⁺ - CH₃ - 2DMSO], 621(65) [M⁺ - 2CH₃ - 2DMSO]. Anal. Calcd for C₂₁H₂₇N₃O₂S₂Pt₂ (*M_r* = 807.81): C 31.22, H 3.38, N 5.20. Found: C 31.39, H 3.40, N 5.31.

Compounds 2 and 3 were obtained in almost quantitative yields by reaction, at room temperature, of a suspension of 1 (ca. 0.1 g) in CH_2Cl_2 (10 mL) with excess acetonitrile (5 mL), 2, and with CO (1 bar), 3, respectively. Compounds 4 and 5 were obtained in almost quantitative yields by reaction of 1 (ca. 0.1 g) in CH_2Cl_2 (5 mL) under argon, with the stoichiometric amount of phosphine.

Compound 2. Mp: 198 °C (decomposition without melting). IR (Nujol, cm⁻¹) ν_{max} : 2281(vw), 1602(s), 1562(s). FAB⁺-MS m/z (%): 733(10) [M⁺], 692(10) [M⁺ - CH₃CN], 677(15) [M⁺ - CH₃ - CH₃CN], 662(10) [M⁺ - 2CH₃ - CH₃CN], 651(15) [M⁺ - 2CH₃CN], 636(20) [M⁺ - CH₃ - 2CH₃CN], 621(20) [M⁺ - 2CH₃ - 2CH₃CN], 636(20) [M⁺ - CH₃ - 2CH₃CN], 621(20) [M⁺ - 2CH₃ - 2CH₃CN]. Anal. Calcd for C₂₁H₂₁N₅Pt₂ (M_r = 733.71): C 34.38, H 2.89, N 9.55. Found: C 34.20, H 2.75, N 9.45.

Compound 3. Mp: 250 °C (decomposition without melting). IR (Nujol, cm⁻¹) ν_{max} : 2043(vs), 2030(vs), 1608(m), 1563(m). Anal. Calcd for C₁₉H₁₅N₃O₂Pt₂ (M_r = 707.53): C 32.25, H 2.14, N 5.94. Found: C 32.02, H 2.15, N 5.77.

Compound 4. Mp: 250 °C (decomposition without melting). ¹H NMR (CDCl₃): δ 8.84 (t, 1H, ⁴*J*(H,P) = 5.4 Hz, ³*J*(Pt,H) = 48.1 Hz), 8.43 (d, 2H, ³*J*(H,H) = 7.3 Hz), 7.85–7.62 (m, 16H), 7.45–7.30 (m, 18H), 6.58 (m, 2H), 0.86 (d, 6H, ³*J*(H,P) = 7.8 Hz, ²*J*(Pt,H) = 84.0 Hz). ³¹P{¹H} NMR (121.4 MHz, CDCl₃): δ 33.67 (s, ¹*J*(Pt,P) = 2133 Hz). ¹³C{¹H} NMR (CDCl₃): δ 165.94 (s), 161.10 (d, *J*(C,P) \approx 120 Hz), 161.04 (s), 150.27 (s), 144.08 (t, *J*(H,P) \approx 40 Hz), 136.88 (s), 135.12 (d, *J*(C,P) = 12.1 Hz), 132.82 (d, *J*(C,P) = 42.3 Hz), 129.97 (s), 128.14 (d, *J*(C,P) = 9.7 Hz), 122.41 (s), 120.73 (s), -12.18 (d, *J*(C,P) = 5.0 Hz). IR (Nujol, cm⁻¹) ν_{max} : 1603(s), 1560(m), 694(s). FAB⁺-MS *m/z*(%): 898(10) [M⁺ - CH₃ - PPh₃], 636(10) [M⁺ - CH₃ -2PPh₃], 621(10) [M⁺ - 2CH₃-2PPh₃]. Anal. Calcd for C₅₃H₄₅N₃P₂-Pt₂ (*M*_r = 1176.17): C 54.12, H 3.86, N 3.57. Found: C 53.97, H 3.70, N 3.40.

Compound 5: Mp: 220 °C (decomposition). ¹H NMR (CD₂-Cl₂): δ 8.74 (d, 2H, ³J(H,H) = 5.6 Hz), 8.61 (t, 1H, ⁴J(H,P) = 5.1 Hz, ${}^{3}J(Pt,H) = 42.0$ Hz), 8.47 (dd, 2H, ${}^{3}J(H,H) = 7.8$ Hz, ${}^{4}J(\text{H},\text{H}) \approx 1$ Hz), 7.92 (td, 2H, ${}^{3}J(\text{H},\text{H}) = 7.3$ Hz, ${}^{4}J(\text{H},\text{H}) \approx 1$ Hz), 7.21 (td, 2H, ${}^{3}J(H,H) =$ 5.6 Hz, ${}^{4}J(H,H) \approx$ 1 Hz), 2.42– 0.82 (m, 72H). ³¹P{¹H} NMR (CD₂Cl₂) δ : 24.52 (s, ¹J(Pt,P) = 1993 Hz). ¹³C{¹H} NMR (CD₂Cl₂): δ 166.33 (m, J(Pt,C) = 45.2 Hz; C), 162.05 (dd, J(C,P) = 113.5 Hz, J(C,P) = 3.7 Hz; C), 160.43 (s, $J(Pt,C) \approx 19$ Hz; C), 152.06 (s; CH), 142.57 (t, J(C,P)= 39.1 Hz; CH), 137.25 (s; CH), 122.86 (s; CH), 121.10 (s, J(Pt,C) = 18.9 Hz; CH), 32.77 (d, J(C,P) = 20.1 Hz; CH), 30.23 (s; CH_2), 28.32 (d, J(C,P) = 9.8 Hz; CH_2), 27.01 (s; CH_2), -16.11 (d, J(C,P) = 7.3 Hz, J(Pt,C) = 762.4 Hz; CH_3). IR (Nujol, cm⁻¹) v_{max} : 1602(s), 1560(m). Anal. Calcd for C₅₃H₈₁N₃P₂Pt₂ ($M_{\text{r}} =$ 1212.47): C 52.50, H 6.75, N 3.47. Found: C 52.70, H 6.61, N 3.31.

X-ray Data Collections and Structure Determinations. Crystal data and other experimental details are summarized in Table 1. The diffraction experiment was carried out on a Bruker SMART CCD area-detector diffractometer at room temperature using Mo K α radiation ($\lambda = 0.71073$ Å) with a graphite crystal monochromator in the incident beam. Cell parameters and orientation matrix were obtained from the least-squares refinement of 55 reflections measured in three different sets of 15 frames each, in the range 3° < θ < 23°. At the end of data collections the first 50 frames, containing 89 reflections, were recollected to have a monitoring of crystal decay, which was not observed, so that no time-decay correction was needed. The 2450 collected frames were processed

Table 1. Crystallographic Data

	3
formula	C19H15N3O2Pt2
Μ	707.53
color	orange-red
cryst syst	triclinic
space group	<i>P</i> 1 (no. 2)
â/Ă	6.869(1)
b/Å	10.007(1)
c/Å	14.821(2)
α/deg	98.36(1)
β/deg	103.31(1)
γ/deg	108.39(1)
U/\dot{A}^3	914.2(2)
Z_{\perp}	2
<i>F</i> (000)	644
$D_{\rm c}/{ m g~cm^{-3}}$	2.57
T/K	293
cryst dimens (mm)	0.04 imes 0.10 imes 0.45
μ (Mo K α)/cm ⁻¹	154.6
min. and max. transmn	
factors	0.51 - 1.00
scan mode	ω
frame width/deg	0.30
time per frame/s	25
no. of frames	2450
detector-sample	5.00
distance/cm	0.00
θ -range/deg	3-26
reciprocal space explored	$\pm h, \pm k, \pm I$
no. of refins (total; ind)	11 723; 4575
	0.048
final R_2 and R_{2w} indices ^a	0.058, 0.069
$(F^{2}, \text{ all refins})$	
conventional R_1 index	0.032
$(I > 2\sigma(I))$	
refins with $I > 2\sigma(I)$	2915
no. of variables	235
goodness of fit ^p	0.98

^a $R_2 = [\sum (|F_0^2 - kF_c^2|)/\sum F_0^2], R_{2w} = [\sum w(F_0^2 - kF_c^2)^2/\sum w(F_0^2)^2]^{1/2}.$ ^b $[\sum w(F_0^2 - kF_c^2)^2/(N_0 - N_v)]^{1/2}$, where $w = 4F_0^2/\sigma(F_0^2)^2, \sigma(F_0^2) = [\sigma^2(F_0^2) + (0.04F_0^2)^2]^{1/2}, N_0$ is the number of observations and N_v the number of variables.

with the software SAINT,18 and an empirical absorption correction was applied (SADABS¹⁹) to the 11 723 collected reflections, 4575 of which are unique with $R_{\rm int} = 0.048$ ($R_{\rm int} =$ $\sum |F_0^2 - F_{\text{mean}}^2| / \sum F_0^2$). Scattering factors and anomalous dispersion corrections were taken from ref 20. The calculations were performed on an AST Power Premium 486/33 computer using the Personal Structure Determination Package²¹ and the physical constants tabulated therein. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares, using all reflections and minimizing the function $\sum w(F_o^2 - k|F_c|^2)^2$ (refinement on F^2). Anisotropic thermal factors were refined for all the non-hydrogen atoms. The hydrogen atoms of the methyl groups were detected in the final Fourier maps and not refined. All the other hydrogen atoms were placed in their ideal positions (C-H = 0.97 Å, B 1.10 times that of the carbon atom to which they are attached) and not refined. The final Fourier map shows a maximum residual of 2.1(5) e/Å³ at 0.96 Å from Pt(1). The atomic coordinates of the structure model have been deposited with the Cambridge Crystallographic Data Centre.

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⁽¹⁸⁾ SAINT, Reference manual; Siemens Energy and Automation: Madison, WI, 1994–1996.

⁽¹⁹⁾ Sheldrick, G. M. SADABS, Empirical Absorption Correction Program, University of Gottingen, 1997.

⁽²⁰⁾ International Tables for X-ray Crystallography, Vol. 4; Kynoch Press: Birmingham, 1974.
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⁽²¹⁾ Frenz, B. A. *Comput. Phys.* **1988**, *2*, 42. *Crystallographic Computing 5*; Oxford University Press: Oxford, 1991; Chapter 11, p 126.

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Supporting Information Available: Positional and thermal parameters (*Us*) for the refined atoms of **3**, atomic

coordinates for non-hydrogen atoms of **3**, and a full list of bond lengths and angles for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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