High-Yield Synthesis of a C∧N∧C Tridentate Platinum Complex

Gareth W. V. Cave, Nathaniel W. Alcock, and Jonathan P. Rourke*

Department of Chemistry, Warwick University, Coventry, U.K. CV4 7AL

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Summary: 2,6-Diphenylpyridine is metalated twice by potassium tetrachloroplatinate in acetic acid to give in high yield a complex with a tridentate ligand bound to the metal via a C∧N∧C donor set. This complex and three derivatives have been characterized, including the single-crystal X-ray analysis of one derivative.

Introduction

Cyclometalation is a reaction that has been both widely used[1,2] and widely studied.[3,4] Typically, a ligating species coordinates to a metal center and a proximal C−H bond is activated, generating a five- or six-membered chelate ring.[3] Our own use of the reaction has been to generate novel cyclopalladated metallomesogens[5−7] and some unusual platinum complexes.[8] Tridentate cyclometalated species where two coordinating groups hold a C−H bond close to the metal and this bond becomes activated are relatively common; thus, N∧C∧N[9] donor sets,[10] P∧C∧P donor sets,[11−14] or S∧C∧S donor sets[15] are well-known. Indeed, some groups have used two ligating groups to induce C−C activation[16] or C−Si activation.[17] In addition, the use of a chelating N∧N donor set to yield N∧N∧C tridentate cyclometalated species has been reported.[18] The double cyclometalation of two ligands by one metal center is also known.[19−22] What is not common are tridentate C∧N∧C or C∧P∧C donor sets where two cyclometalated rings have been formed via two C−H activations. One paper reports the isolation, in low yield, of the dicyclometalated platinum complex of 2,6-diphenylpyridine.[23] The subject of this paper is the high-yield synthesis of such tridentate C∧N∧C compounds of platinum.

Results and Discussion

The reaction of potassium tetrachloroplatinate with diphenylpyridine in acetic acid to give a complex we tentatively formulate as **2** is essentially quantitative (Scheme 1). While we could get no solution data on **2**, as it either is insoluble or reacts with solvent, solid-state characterization is consistent with this formulation. Thus, elemental analysis and mass spectrometry (both positive and negative ion) confirm our hypothesis. On dissolution in dimethyl sulfoxide (dmso) **2** gives complex **3**, which has been fully characterized (NMR, elemental analysis, single-crystal X-ray diffraction). Characterization of **3** provides additional support for our formulation of **2**.

The synthesis of **2** is simplicity itself and has been used for monocycloplatination before.[24] Complex **2** is a robust yellow powder stable to air and water, which decomposes without melting at 320−370 °C (TGA analysis shows this decomposition process to be complete, leaving only platinum). Our major use of **2** is in the synthesis of complexes **3** and **4**. Complex **3** was isolated in essentially quantitative yield by the simple act of dissolution in dmso. Thus, the isolated yield of **3**, starting from our platinum source, is 98%. The NMR spectrum of **3** is unexceptional, and crystals suitable for X-ray analysis were grown. The X-ray structure itself is as expected (Figure 1): three molecules are found within the asymmetric unit, with little to distinguish among them. The diphenylpyridine and the Pt are essentially flat, though the dmso is bent out of plane with the N−Pt−S angles being 170.9(2), 173.3(2), and 173.8(2)° in the three molecules in the asymmetric unit. The C1−Pt−S−O torsion angles also differ, being −14.1, 13.2, and 6.6° in the three molecules. Quite why the

* To whom correspondence should be addressed. E-mail: j.rourke@warwick.ac.uk.

(1) Ryabov, A. D. *Synthesis* **1985**, 233.
(2) Pfeffer, M. *Pure Appl. Chem.* **1992**, *64*, 335.
(3) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403.
(4) Steenwinkel, P.; Gossage, R. A.; van Koten, G. *Chem. Eur. J.* **1998**, *4*, 759.
(5) Lydon, D. P.; Cave, G. W. V.; Rourke, J. P. *J. Mater. Chem.* **1997**, *7*, 403.
(6) Lydon, D. P.; Rourke, J. P. *Chem. Commun.* **1997**, 1741.
(7) Cave, G. W. V.; Lydon, D. P.; Rourke, J. P. *J. Organomet. Chem.* **1998**, *555*, 81.
(8) Cave, G. W. V.; Hallett, A. J.; Errington, W.; Rourke, J. P. *Angew. Chem.* **1998**, *37*, 3466; *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3270.
(9) The abbreviation N∧C∧N refers to a tridentate ligand bonding through two N donors and one C donor, with the ligand conectivity being N linked to C linked to N. Thus, N∧N∧C also represents a tridentate ligand bonding through two N donors and one C donor, but this time the ligand conectivity is N linked to N linked to C.
(10) Terheijden, J.; van Koten, G.; Muller, F.; Grove, D. M.; Vrieze, K.; Nielsen, E.; Stam, C. H. *J. Organomet. Chem.* **1986**, *315*, 401.
(11) Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1020.
(12) Rimml, H.; Venanzi, L. M. *J. Organomet. Chem.* **1983**, *259*, C6.
(13) Bennett, M. A.; Jin, H.; Willis, A. C. *J. Organomet. Chem.* **1993**, *451*, 249.
(14) Weisman, A.; Gozin, M.; Kraatz, H.-B.; Milstein, D. *Inorg. Chem.* **1996**, *35*, 1792.
(15) Dupont, J.; Beydon, N.; Pfeffer, M. *J. Chem. Soc., Dalton Trans.* **1989**, 1715.
(16) Rybtchinski, R.; Vigalok, A.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **1996**, *118*, 12406.
(17) Steenwinkel, P.; Gossage, R. A.; Maunula, T.; Grove, D. M.; van Koten, G. *Chem. Eur. J.* **1998**, *4*, 763.
(18) Constable, E. C.; Henney, R. P. G.; Leese, R. A.; Tocher, D. A. *J. Chem. Soc., Chem. Commun.* **1990**, 513.
(19) Cheney, A. J.; McDonald, W. S.; O'Flynn, K.; Shaw, B. L.; Turtle, B. L. *J. Chem. Soc., Chem. Commun.* **1973**, 128.
(20) Chassot, L.; Muller, E.; von Zelewsky, A. *Inorg. Chem.* **1984**, *23*, 4249.
(21) van der Boom, M. E.; Liou, S.-Y.; Shimon, L. J.; Ben-David, Y.; Milstein, D. *Organometallics* **1996**, *15*, 2562.
(22) Thorn, D. L. *Organometallics* **1998**, *17*, 348.
(23) Cornioley-Deuschel, C.; Ward, T.; von Zelewsky, A. *Helv. Chim. Acta* **1988**, *71*, 130.
(24) Ceder, R. M.; Sales, J. *J. Organomet. Chem.* **1985**, *294*, 389.

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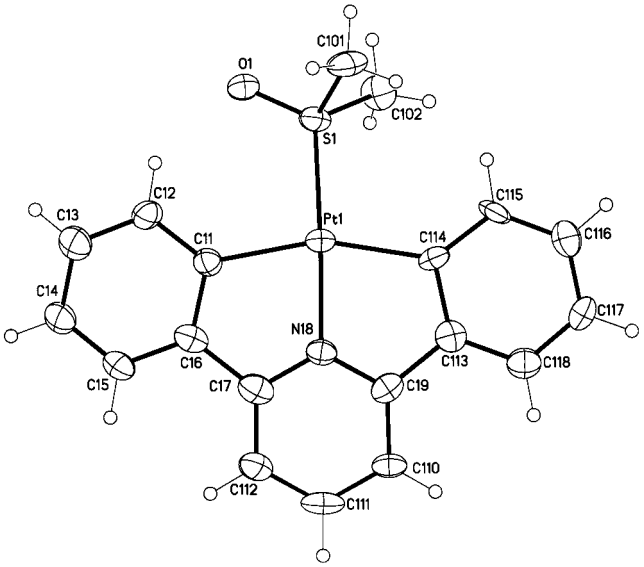
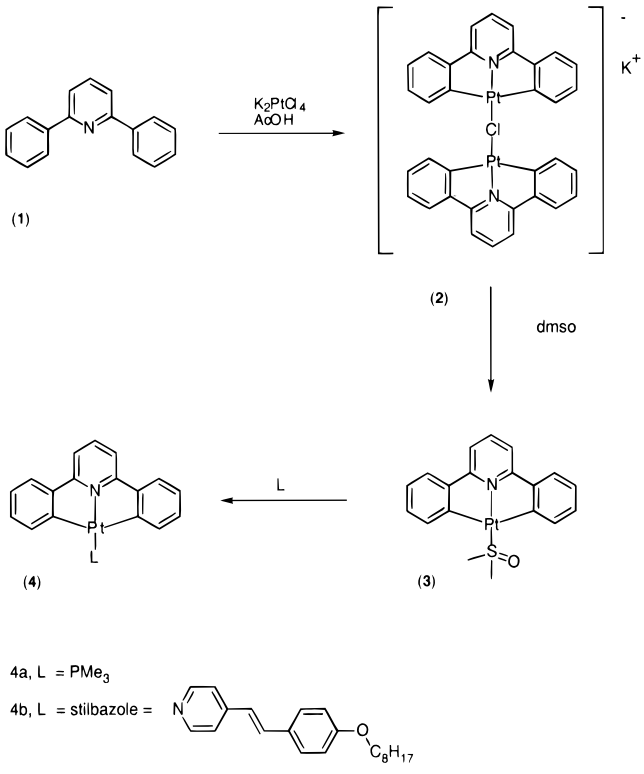


Figure 1. Crystal structure of **3** (50% thermal ellipsoids).

Scheme 1



dmso is not in plane is unclear: presumably it arises through packing constraints, constraints which cannot be equal for all three molecules, given the 3° variation in the N−Pt−S angle. All other bond lengths and angles are normal. Selected bond lengths and angles are listed in Table 1.

Complex **3** may be reacted with other ligating species to give complexes **4** (Scheme 1). A sample of **3** in an NMR tube was treated with 1 equiv of trimethylphosphine, whereupon an instantaneous reaction took place to give **4a** in quantitative yield. The complex may be isolated by the simple expedient of solvent removal. Likewise, the pyridine-based stilbazole ligand reacts to give **4b**. Hence, **3** is a very convenient source of the C∧N∧C−Pt moiety.

Table 1. Selected Bond Lengths (Å) and Angles (deg) in the Crystal Structure of 3

	$n = 1$	$n = 2$	$n = 3$
Pt(n)−N(n8)	2.004(7)	2.014(7)	2.016(7)
Pt(n)−C(n1)	2.068(9)	2.069(9)	2.074(9)
Pt(n)−C(n14)	2.082(9)	2.106(9)	2.085(9)
Pt(n)−S(n)	2.201(2)	2.190(2)	2.197(2)
S(n)−O(n)	1.469(6)	1.474(6)	1.485(6)
S(n)−C(n01)	1.772(9)	1.766(9)	1.772(9)
S(n)−C(n02)	1.773(9)	1.777(9)	1.775(10)
N(n8)−Pt(n)−C(n1)	79.8(3)	80.3(3)	80.0(3)
N(n8)−Pt(n)−C(n14)	80.6(3)	80.6(3)	79.8(3)
C(n1)−Pt(n)−C(n14)	159.8(3)	160.4(3)	159.2(3)
N(n8)−Pt(n)−S(n)	170.9(2)	173.8(2)	173.3(2)
C(n1)−Pt(n)−S(n)	98.4(2)	98.6(3)	100.3(2)
C(n14)−Pt(n)−S(n)	101.7(2)	100.9(2)	100.3(3)
O(n)−S(n)−Pt(n)	117.7(3)	119.3(3)	119.3(3)
C(n01)−S(n)−Pt(n)	114.6(3)	112.2(3)	112.7(3)
C(n02)−S(n)−Pt(n)	110.1(3)	109.9(3)	109.8(3)
C(n6)−C(n1)−Pt(n)	112.8(6)	111.5(6)	111.9(6)
C(n9)−N(n8)−Pt(n)	118.7(6)	118.1(6)	118.5(6)
C(n7)−N(n8)−Pt(n)	118.6(6)	118.5(6)	117.7(6)
C(n13)−C(n14)−Pt(n)	110.8(6)	110.5(6)	111.6(7)

The dicyclometalated platinum complex of 2,6-diphenylpyridine has been reported previously: a synthetic procedure involving the double lithiation of diphenylpyridine followed by reaction with $PtCl_2(SEt_2)_2$ gave **4** (L = SEt_2) in 10% yield;[23] the same paper reports the analogous palladium complex in 1.4% yield. Other than this report there are only three structurally characterized species containing a C∧N∧C or a C∧P∧C donor set. The first reported example was a platinum phosphine complex, though this C∧P∧C,P complex is unstable with respect to the $(P\wedge C)_2$ isomer;[19] the other examples are palladium species metalated to a pyridine with pendant β-dicarbonyls, where the reaction is with a fairly acidic hydrogen.[25,26]

We are at present investigating the reactivity of both **2** and **3** and seeking to broaden the scope of this reaction to other metals (for instance, preliminary studies indicate that the palladium analogue of **2** may be isolated in a yield of around 20%).

Experimental Section

General Considerations. All chemicals were used as supplied; unless noted otherwise, the stilbazole was synthesized via the published route.[27] All elemental analyses were performed by Warwick Analytical Service.

Synthesis of $K^+[(2,6\text{-diphpyPt})_2Cl]^-$ (2). Potassium tetrachloroplatinate (374 mg, 0.900 mmol) was added to a solution of 2,6-diphenylpyridine (233 mg, 1.00 mmol) in glacial acetic acid (250 mL). The reaction mixture was stirred at 80 °C until the red platinum salt was no longer visible (3 days). The reaction mixture was filtered, yielding the product as an insoluble yellow powder which was washed with water, acetone, and ether. Yield: 407 mg (98%, 0.441 mmol). Anal. Found (calcd): C, 43.7 (44.2); H, 2.6 (2.4); N, 3.0 (3.0). MALDI MS (2,5-dihydroxybenzoic acid matrix): negative ion peaks at m/z 35 and 37 indicating Cl^-; positive ion peaks at m/z 39 and 425 corresponding to K^+ and (diphpy)Pt.

(25) Newkome, G. R.; Kawato, T.; Kohli, D. K.; Puckett, W. E.; Oliver, B. D.; Chiari, G.; Fronczek, F. R.; Deutsch, W. A. *J. Am. Chem. Soc.* **1981**, *103*, 3423.
(26) Newkome, G. R.; Kohli, D. K.; Fronczek, F. R. *J. Am. Chem. Soc.* **1982**, *104*, 994.
(27) Bruce, D. W.; Dunmur, D. A.; Lalinde, E.; Matilis, P. M.; Styring, P. *Liq. Cryst.* **1988**, *3*, 385.

Synthesis of [(2,6-diphpy)Pt(dmso)] (3). The yellow $K^+[(2,6\text{-diphpyPt})_2Cl]^-$ produced above was dissolved in hot dmso (1 mL), the solution was cooled, and precipitation was induced with water (1 mL) to give a yellow crystalline product. Yield: 443 mg (98%, 0.882 mmol). Anal. Found (calc): C, 45.0 (45.4); H, 3.4 (3.4); N, 2.8 (2.8). NMR data: δ_H (250 MHz, $CDCl_3$) 7.80 (2H, dd, ^3J = 7.6, ^4J = 1.2, ^3J(Pt−H) = 24 Hz, phenyl ortho to Pt), 7.62 (1H, t, ^3J = 7.3 Hz, central pyridine), 7.47 (2H, dd, ^3J = 7.6, ^4J = 1.2 Hz, phenyl ortho to pyridine, meta to Pt), 7.30 (2H, d, ^3J = 7.3 Hz, pyridine), 7.28 (2H, td, ^3J = 7.6, ^4J = 1.2 Hz, phenyl), 7.21 (2H, td, ^3J = 7.6, ^4J = 1.2 Hz, phenyl), 3.68 (6H, s, ^3J(Pt−H) = 26.8 Hz, dmso).

X-ray Crystallographic Study of 3. Crystals suitable for structural analysis were grown from dmso. A golden yellow prism (dimensions 0.2 × 0.06 × 0.06 mm) was mounted with oil on a thin glass fiber. Data were collected at 180(2) K using a Siemens SMART CCD area-detector diffractometer. Crystal data for **3**: $C_{19}H_{17}NOSPt$, M_r = 502.49, monoclinic, space group $P2_1/c$, a = 17.9050(10) Å, b = 9.9528(5) Å, c = 27.658(2) Å, β = 97.885(5)°, V = 4882.2(5) Å^3, Z = 12, D(calcd) = 2.051 Mg/m^3. Refinement was by full-matrix least squares on F^2 for 7378 reflection positions using SHELXL-96[28] with additional light atoms 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. The weighting scheme was calculated using $w = 1/[\sigma^2(F_o^2) + (0.0520P)^2]$, where $P = (F_o^2+2F_c^2)/3$. The goodness of fit on F^2 was 0.914, R1 (for 7378 reflections with $I > 2\sigma(I)$) = 0.0481, wR2 = 0.1076. The data/parameter ratio was 11 487/628. The largest difference Fourier peak and hole were 1.912 and −1.431 e Å^{-3}; the only large peaks are near the Pt atoms. The asymmetric unit contains three essentially identical molecules. Selected bond lengths and angles are listed in Table 1.

(28) Sheldrick, G. M. SHELXL-96, Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1996.

Synthesis of [(2,6-diphpy)Pt(PMe_3)] (4a). Trimethylphosphine (9 mg, 0.12 mmol) was added to a solution of [(2,6-diphpy)Pt(dmso)] (56 mg, 0.108 mmol) in chloroform (1 mL). All solvents were removed in vacuo to give a yellow product. Yield: 54 mg (99%, 0.107 mmol). Anal. Found (calcd): C, 48.2 (48.0); H, 4.0 (4.0); N, 3.0 (2.8). NMR data: δ_P (161.9 MHz, $CDCl_3$) −20.98 (s, ^1J(Pt−P) = 1606 Hz); δ_H (250 MHz, $CDCl_3$) 8.38 (1H, t, ^3J = 8.5 Hz, central pyridine), 8.11 (2H, d, ^3J = 8.5 Hz, pyridine), 7.93 (2H, dd, ^3J = 7.6, ^4J = 1.2 Hz, phenyl ortho to pyridine, meta to Pt), 7.80 (2H, dd, ^3J = 7.6, ^4J = 1.2, ^3J(Pt−H) = 16 Hz, phenyl ortho to Pt), 7.41 (2H, td, ^3J = 7.6, ^4J = 1.2 Hz, phenyl), 7.34 (2H, td, ^3J = 7.6, ^4J = 1.2 Hz, phenyl), 3.68 (6H, d, ^2J(P−H) = 1.8, ^3J(Pt−H) = 64.5 Hz, PMe_3).

Synthesis of [(2,6-diphpy)Pt(stilbazole)] (4b). Octyloxystilbazole (33 mg, 0.119 mmol) was added to a solution of [(2,6-diphpy)Pt(dmso)] (56 mg, 0.108 mmol) in chloroform (1 mL). The mixture was stirred (30 min), solvents were removed in vacuo, and the residue was washed with ether to give a yellow product. Yield: 76 mg (99%, 0.108 mmol). Anal. Found (calcd): C, 61.0 (61.3); H, 4.8 (4.9); N, 4.0 (4.0). NMR data: δ_H (400 MHz, $CDCl_3$) 8.92 (2H, AA′XX′, ^3J(Pt−H) = 43.5 Hz, stilbazole pryidine, ortho to N), 7.53 (2H, AA′XX′, stibazole phenyl ring), 7.51 (1H, t, ^3J = 8 Hz, central pyridine), 7.46 (2H, m, phenyl ortho to Pt), 7.44 (2H, AA′XX′, stilbazole pyridine), 7.41 (1H, d, ^3J = 16.6 Hz, stilbazole double bond), 7.23 (2H, d, ^3J = 8 Hz, pyridine), 7.20 (2H, dt, ^3J = 7.5, ^4J = 1.3 Hz, phenyl), 7.05 (2H, dt, ^3J = 7.5, ^4J = 1.3 Hz, phenyl), 7.00 (2H, dd, ^3J = 7.5, ^4J = 1.3 Hz, phenyl ortho to pyridine), 6.93 (2H, AA′XX′, stilbazole), 6.91 (1H, d, ^3J = 16.6 Hz, stilbazole double bond), 3.99 (2H, t, ^3J = 6.5 Hz, OCH_2), 1.80 (2H, m), 1.46 (2H, m), 1.31 (8H, m), 0.89 (3H, t, ^3J = 6.5 Hz).

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Supporting Information Available: Tables of positional parameters, bond distances, bond angles, and anisotropic parameters for the structural analysis of **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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