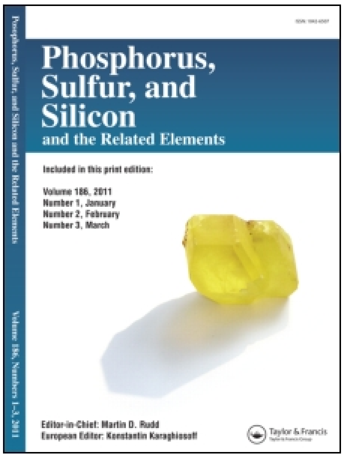

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Selective Light Induced Cyclometalation in *trans*-$(MesPh_2P)_2PtCl_2$

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Selective Light Induced Cyclometalation in *trans*-$(MesPh_2P)_2PtCl_2$

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Reaction of mesityl diphenylphosphine (1) with $PtCl_2$(cod) at room temperature afforded trans-$PtCl_2[(1)]_2$ (2). Using K_2PtCl_4 as starting material in refluxing mesitylene, the cyclometalated complex trans-PtCl[(1)(1 – H)] (3) was isolated. Irradiation of complex 2 in dichloromethane with sunlight for 5 h provided a mixture of complexes 2 and 3 in a 1:4 ratio. The structures of 2 and 3 were established by X-ray crystallography.

Keywords Cyclometalation; P ligands; platinum

INTRODUCTION

Bisphosphine platinum complexes of the type $(R_3P)_2PtX_2$ (X = Cl, Br, I) are widely used as starting compounds in the coordination chemistry. The reactivity of the complex fragment $(R_3P)_2Pt(II)$ depends on the bite angle of the phosphine ligand. In this work, we investigated the reactions of mesityl diphenylphosphine with $PtCl_2$(cod) and K_2PtCl_4, respectively. This ligand was chosen considering the reactivity similar to that of triphenyl phosphine, hopefully to find a linear representative of our series of zerovalent platinum complexes.[1] It is also known that *ortho*-tolyphosphines $tol_xPh_{3-x}Pt$ (x = 1–3) form cyclometalated pallaldium(II) and platinum(II) compounds[2] but usually at higher temperatures.

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Dedicated to Professor Marian Mikołajczyk, CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

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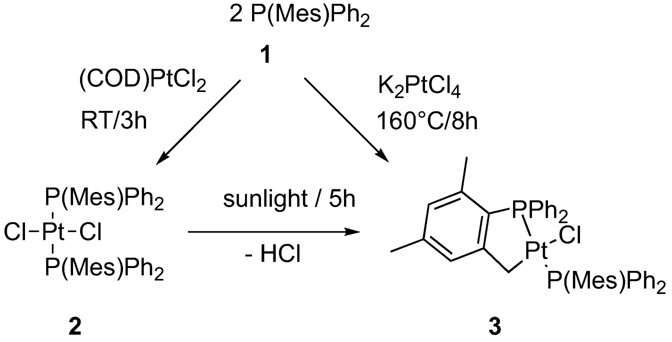
RESULTS AND DISCUSSION

Mesityl diphenylphosphine ($MesPPh_2$) (**1**) was obtained by the reaction of mesityl Grignard with diphenylphosphine chloride.[3] The reaction of phosphine **1** with $PtCl_2$(cod) in a 2:1 ratio at room temperature in a solution of dichloromethane afforded the yellow complex **2** in high yields (Scheme 1). The ^{31}P NMR spectrum of **2** showed one singlet at 14.0 ppm, which was assigned to *trans*-$PtCl_2$[(**1**)]$_2$ according the $^1J_{P-Pt} = 2584$ Hz. These data are comparable with those found for other complexes of the type *trans*-$PtCl_2L_2$ (L = phosphine).[2a] The ^1H NMR spectrum showed two singlets in a ratio 2:1 according to the different types of methyl groups. In contrast to the usual syntheses of $(Ph_3P)_2PtCl_2$ starting from Ph_3P and K_2PtCl_4, with phosphine **1** as starting material, we did not obtain the expected *cis* dichloro complex in refluxing mesitylene, but a colorless solid **3** was yielded after removing the solvent (Scheme 1). ^{31}P NMR spectroscopic investigation displayed the pattern of a typical AB spin system at 22.5 and 44.9 ppm with $^1J_{P-Pt} = 2857$ and 3215 Hz, respectively and $^2J_{P-P} = 430$ Hz. The ^1H NMR spectrum showed four singlets in a ratio 1:1:1:2 and one doublet at 2.87 ppm with $^3J_{H-P} = 5.0$ Hz and $^2J_{Pt-H} = 92$ Hz.



SCHEME 1 Synthesis of complexes **2** and **3**.

Based on the ^1H and ^{31}P NMR spectroscopic data as well as the elemental analysis of complex **3**, it was suggested that this compound could be seen as the result of elimination of one equivalent of HCl from **2**. The X-ray structure analyses of **2** and **3** (Figures 1 and 2), respectively, unambiguously confirmed the conversion of the *trans*-$(MesPh_2P)_2PtCl_2$ **(2)** to the cyclometalated complex **3**. In this compound, only one of the four *ortho*-methyl groups in **2** was converted to a methylene group coordinating to the platinum(II).

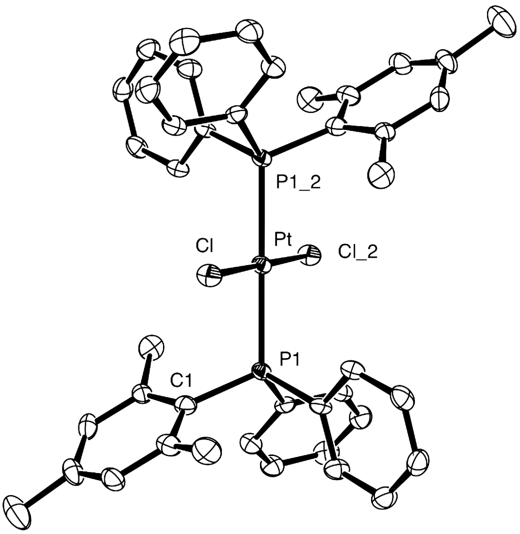


FIGURE 1 ORTEP drawing of the molecular structure of the dithiolato complex **2** (for clarity, hydrogen atoms are omitted). Selected bond lengths [Å] and angles [°]: Pt-P(1) 2,3312(13); Pt-Cl 2,3053(11); P(1)-Pt-Cl 85,86(4); P(1)-Pt-Cl′ 94,14(4).

Crystals were obtained from diffusion of pentane into a solution of **2** in dichloromethane. The molecular structure of **2** (Figure 1) can be compared with that of *trans*-$(Ph_3P)_2PtCl_2$, which crystallizes in the same space group P-1.[4] Whereas the Pt-Cl bond length with 2.3053(11) Å is comparable with that found for *trans*-$(Ph_3P)_2PtCl_2$, the Pt-P bond length with 2.3312(13) Å is slightly longer than that observed in *trans*-$(Ph_3P)_2PtCl_2$.[4] As *trans*-$(Ph_3P)_2PtCl_2$, complex **2** exhibits a distorted square-planar geometry with a P-Pt-Cl angle of 85.86(4) degrees and with P-Pt-Cl^i angle of 94.14(4) degrees.

Crystals of **3** suitable for X-ray crystallography were obtained from THF and pentane. The molecular structure (Figure 2) reveals the *trans* configuration of the phosphine ligands, which fits well to the observed coupling constant $^2J_{P-P} = 430$ Hz. The most important features are the remarkably different Pt-P distances: The Pt-P distances in the five membered chelate ring were determined as 2.2592(9) Å versus 2.3307(9) Å. These different distances align with the observed $^1J_{P-Pt}$ coupling constants (2857 and 3215 Hz); this huge difference obviously indicates a different electronic structure of the Pt-P bond. Moreover, the strong *trans* influence of the platinum(II) coordinated methylene group

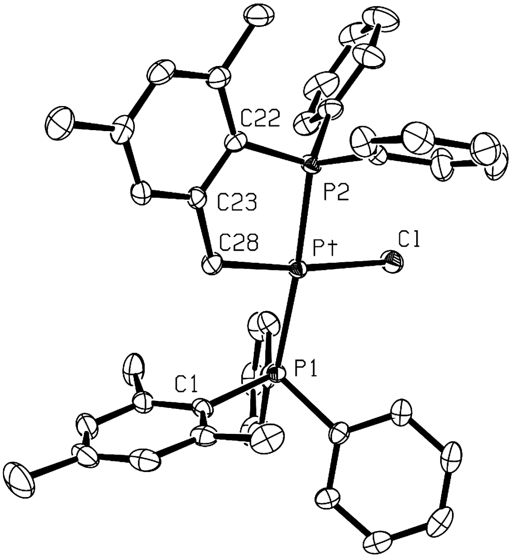


FIGURE 2 ORTEP drawing of the molecular structure of the dithiolato complex **3** (for clarity, hydrogen atoms are omitted). Selected bond lengths [Å] and angles [°]:Pt-P(1) 2,3307(9); Pt-P(2) 2,2592(9); Pt-Cl 2,4193(8); Pt-C(28) 2,062(3); C(28)-C(23) 1,513(5); C(23)-C(22) 1,394(5); P(2)-C(22) 1,809(3); P(1)-Pt-Cl 94,04(3); P(1)-Pt-C(28) 91,82(11); P(1)-Pt-P(2) 175,50(3); P(2)-Pt-Cl 90,46(3); P(2)-Pt-C(28) 83,68(11); Cl-Pt-C(28) 173,68(11).

becomes apparent in the elongated Pt-Cl distance [2.4194(8) Å] versus the Pt-Cl distance in **2** [2.3053(11) Å]. The Pt-CH_2 distance [2.062(3) Å] in **3** is in a similar range of those in other cyclometalated platinum(II) complexes.[2,5]

In contrast to *cis*-$(Ph_3P)_2PtCl_2$, reduction of **2** with $NaBH_4$ in the presence of norbornen (nb) does not lead to the expected nb adduct of the bisphosphine platinum(0) complex. Reduction of the similar *cis*-complex of **2** should be possible. In order to isomerize **2**, the complex was irradiated in a dichloromethane solution with sunlight for 5 h; interestingly, the ^{31}P NMR spectrum of the crude product resulting from this photochemical reaction exhibits only resonances that can be assigned to the unreacted complex **2** as well as **3** in a 1:4 ratio (Scheme 1). The reaction is surprisingly selective, and no evidence for side products was found. To the best of our knowledge, a light-induced cyclometalation of this type is not described in the readily available literature.

CONCLUSION

The reaction of mesityl diphenylphosphine (**1**) is different from that observed for Ph_3P. Although the reaction of $PtCl_2$(cod) with **1** easily leads to the *trans* complex **2**, our attempts to isolate the *cis* analogues of **2** were in vain; instead cyclometalation via HCl extrusion was observed. In contrast to the described reaction, a mononuclear complex **3** is yielded. The molecular structure in solid state revealed an about 0.07 Å shorter Pt-P bond to the cyclometalated phosphine ligand as well as an about 0.11 Å elongated Pt-Cl bond compared to those found in **2**. Irradiation with light is presumably a widely applicable reaction to yield such cyclometalated complexes. It is worth mentioning that the analogous palladium complexes are highly efficient catalysts for Suzuki and Heck cross-coupling reactions.

EXPERIMENTAL

Preparation of the Platinum Complexes 2 and 3

Preparation of trans-PtCl$_2$[(1)]2 (2)

Mesityl diphenylphosphine **1** (0.150 g, 0.5 mM)[3] was dissolved in 30 mL of dichloromethane, and $PtCl_2$(cod) (0.070 g, 0.18 mM) dissolved in 20 mL of dichloromethane was added dropwise. The resulting yellow solution was stirred at room temperature for 20 h. After removing the solvent, the crude product was washed two times with ether (5 mL) and dissolved in a small amount of dichloromethane. Ether was allowed to diffuse slowly into the solution. Yellow crystals showing a yellow fluorescence in solid state were yielded (130 mg, 83%). Anal. found C, 57.43; H, 5.03; Cl, 7.98. $PdCl_2P_2C_{42}H_{42}$. Anal. calculated C, 57.67; H, 4.84; Cl, 8.11. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 6 H, 2 p-CH_3), 2.29 (s, 12 H, 4 o-CH_3), 6.84 (s, 4 H, $Ar_{mesityl}$-H), 7.24–7.38 (m, 12 H), 7.76–7.86 (m, 8 H). ^{31}P-{^{1}H}NMR (81 MHz, $CDCl_3$) δ 14.0 (s, $^1J_{P-Pt} = 2584$ Hz).

Preparation of the Cyclometalated trans-PtCl[(1)(1 – H)] (3)

A. Mesityl diphenylphosphine **1** (0.300 g, 1.0 mM)[3] and K_2PtCl_4 (150 mg, 0.36 mmol) dissolved in mesitylene (10 mL) were heated at reflux for 10 h and then cooled to room temperature. The solvent was then removed in vacuo, the resulting mixture was separated by column chromatography (SiO_2, ether), and compound **3** ($R_f = 0.6$) was isolated. Complex **3** was dissolved in a small amount of dichloromethane, and pentane was allowed to diffuse slowly into the solution. Colorless crystals were yielded (120 mg, 37.5%). Anal. found C, 60.65; H, 5.38; Cl, 4.09.

$PtClP_2C_{42}H_{41}$∗ 0.5 thf. Anal. calculated C, 60.44; H, 5.19; Cl, 4.05. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.66 (s, 3 H, CH_3), 2.12 (s, 6 H, 2 CH_3), 2.25 (s, 3 H, CH_3), 2.31 (s, 3 H, CH_3), 2.87 (d, $^3J_{H-P} = 5.4$, $^2J_{H-Pt} = 92$ Hz, 2 H, CH_2), 6.68 (s, 1 H, $Ar_{mesityl}$-H), 6.80 (s, 1 H, $Ar_{mesityl}$-H), 6.84 (s, 2 H, $Ar_{mesityl}$-H), 7.24–7.29 (m, 4 H), 7.36–7.40 (m, 8 H), 7.90–7.76 (m, 8 H). ^{31}P-{^{1}H}NMR (81 MHz, $CDCl_3$) δ 22.5 (d, $^2J_{P-P} = 430$,$^1J_{P-Pt} = 2857$ Hz), 44.9 (d, $^2J_{P-P} = 430$,$^1J_{P-Pt} = 3215$ Hz). MS (FAB) *m/z* = 802 (M^+–Cl).

B. A yellow solution of 40 mg of **2** in dichloromethane (3 mL) was irradiated by sunlight for 5 h. The solvent of the resulting colorless solution was evaporated and the remaining colorless solid was dissolved in $CDCl_3$. The ^{31}P-{^{1}H}NMR spectrum displays resonance signals for **2** and **3**, respectively in a ratio 4:1. Pure **3** has been isolated by column chromatography (SiO_2, ether, $R_f = 0.6$).

Crystal Structure Determination

The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects and for absorption effects.[6–8]

The structures were solved by direct methods (SHELXS[9]) and refined by full-matrix least squares techniques against F_o^2 (SHELXL-97[10]). All hydrogen atoms of the structures were included at calculated positions with fixed thermal parameters. All non-disordered, non-hydrogen atoms were refined anisotropically.[10] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystal Data for 2[11]

$C_{42}H_{42}Cl_2P_2Pt$, Mr = 874.69 gmol^{-1}, colourless prism, size 0.03 × 0.03 × 0.03 mm^3, triclinic, space group $P\bar{1}$, a = 9.0444(5), b = 10.7649(7), c = 10.9280(7) Å, $\alpha = 108.021(3)$, $\beta = 102.374(3)$, $\gamma = 107.775(3)^\circ$, V = 905.75(10) Å^3, T = −90°C, Z = 1, $\rho_{calcd.} = 1.604$ gcm^{-3}, μ (Mo-K_α) = 41.39 cm^{-1}, multi-scan, transmin: 0.4800, transmax: 0.5744, F(000) = 436, 6222 reflections in h(-11/11), k(-13/13), l(-14/12), measured in the range $2.08^\circ \leq \Theta \leq 27.46^\circ$, completeness $\Theta_{max} = 98.5\%$, 4082 independent reflections, $R_{int} = 0.0444$, 3746 reflections with $F_o > 4\sigma(F_o)$, 217 parameters, 0 restraints, $R1_{obs} = 0.0440$, $wR^2_{obs} = 0.0793$, $R1_{all} = 0.0533$, $wR^2_{all} = 0.0844$, GOOF = 0.994, largest difference peak and hole: 0.751 / −1.132 e Å^{-3}.

Crystal Data for 3[11]

$C_{42}H_{41}ClP_2Pt^{*}$ ½ C_4H_8O, Mr = 874.28 gmol^{-1}, colourless prism, size 0.04 × 0.03 × 0.03 mm^3, triclinic, space group P$\bar{1}$, a = 10.2949(3), b = 12.6995(2), c = 14.8974(5) Å, $\alpha = 81.821(2)$, $\beta = 87.485(2)$, $\gamma = 80.704(2)^{\circ}$, V = 1902.12(9) Å^3, T = −90°C, Z = 2, $\rho_{\text{calcd.}} = 1.526$ gcm^{-3}, μ (Mo-K$_{\alpha}$) = 38.74 cm^{-1}, multi-scan, transmin: 0.4994, transmax: 0.6664, F(000) = 876, 13599 reflections in h(-13/11), k(-16/16), l(-19/17), measured in the range $2.62^{\circ} \leq \Theta \leq 27.47^{\circ}$, completeness $\Theta_{\max} = 99.1\%$, 8658 independent reflections, $R_{\text{int}} = 0.0281$, 7656 reflections with $F_o > 4\sigma(F_o)$, 435 parameters, 0 restraints, $R1_{\text{obs}} = 0.0321$, $wR^2_{\text{obs}} = 0.0755$, $R1_{\text{all}} = 0.0396$, $wR^2_{\text{all}} = 0.0795$, GOOF = 1.016, largest difference peak and hole: 1.580 / −1.477 e Å^{-3}.

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[11] CCDC-674036 for **2** and CCDC-674037 for **3** contains the supplementary crystallographic data for this article. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).