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Bridging and Chelating Roles of Bis(2-(diphenylphosphino)ethyl)phenylphosphine in Stabilizing Binuclear Platinum(II) Complexes

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ABSTRACT: The diorganoplatinum(II) complexes $[PtR_2(triphos-P,P')]$ (1; R = Me, *p*-MeC₆H₄ and triphos = bis(2-(diphenylphosphino)ethyl)phenylphosphine), containing one free phosphine atom, react with cyclometalated platinum complexes $[PtR'(C^N)(SMe_2)]$ (2; R' = Me, *p*-MeC₆H₄ and C[^]N is deprotonated 2-phenylpyridine (ppy) or deprotonated benzo[*h*]quinoline (bhq)) to give the cyclometalated diplatinum(II) complexes $[Pt_2R_2R'(C^N)(triphos)]$ (3). In these binuclear platinum(II) compounds, triphos acts as both a chelating and bridging ligand to stabilize the produced diplatinum complexes. The complexes 3 were readily characterized by multinuclear NMR spectroscopy and elemental microanalysis. The crystal structure of complex 3f (R = Me, R' = *p*-MeC₆H₄, and C[^]N = bhq) was



further determined by X-ray crystallography, giving the first example of an X-ray structural determination of a diplatinum complex with a triphos ligand acting simultaneously as both a chelating and bridging ligand.

■ INTRODUCTION

In the past few years, the chemistry of cyclometalated platinum complexes has attracted much attention. The most well-studied examples of these compounds are five-membered-ring complexes containing nitrogen—Pt and C(phenyl)—Pt bonds.¹ They exhibit a wide range of applications which range from the synthesis of new organic and organometallic compounds to mesogenic species and catalytic materials as well as supra-molecular entities.² On the other hand, there has been a growing interest in the synthesis of platinum complexes containing polydentate phosphine ligands, due to their applications as homogeneous and heterogeneous catalysts.³

In the past, we have been interested in platinum(II) cyclometalated complexes derived from 2-phenylpyridine ligands; for example, 2-phenylpyridine, benzo[h]quinoline, and 2-(p-tolyl)pyridine ligands readily react with platinum(II) precursor complexes, such as those with the formula $[PtR_2(SMe_2)_2]$ or $[Pt_2R_4(\mu$ -SMe_2)_2] through cyclometalation reactions to give cyclometalated platinum complexes. Treatment of the resulting cycloplatinated complexes with diphosphine ligands such as 1,1'-bis(diphenylphosphino)-ferrocene, bis(diphenylphosphino)methane, and bis-(diphenylphosphino)ethane, in different molar ratios, produces mono- or dinuclear complexes with biphosphines as mono-dentate, bidentate, or bridging ligands.⁴

The ligand triphos (=bis(2-(diphenylphosphino)ethyl)phenylphosphine) is an interesting and useful ligand in the synthesis of many chelating, binuclear, and cluster complexes of transition metals.⁵ In the present work, we have synthesized a series of mixed diorgano and cyclometalated diplatinum(II) complexes, $[Pt_2R_2R'(C^N)(triphos)]$ (3), in which R, R' = Me, p-MeC₆H₄ and C^N is deprotonated 2-phenylpyridine (ppy) or deprotonated benzo[h]quinoline (bhq), using a general synthetic approach involving ligand replacement from the corresponding precursor having the labile ligand SMe₂.

EXPERIMENTAL SECTION

The ¹H NMR spectra were recorded by using either a Bruker Avance DPX 250 spectrometer or a Varian Mercury 400 spectrometer in CDCl₃ with TMS as reference. The ³¹P and ¹⁹⁵Pt NMR spectra were recorded on a Bruker Avance DRX 500 spectrometer in CDCl₃ with 85% H₃PO₄ and aqueous Na₂PtCl₄ as references, respectively. The microanalyses were performed using a Thermo Finnigan Flash EA-1112 CHNSO rapid elemental analyzer. [Pt₂Me₄(μ -SMe₂)₂]⁶ and the monomeric precursors *cis*-[Pt(p-MeC₆H₄)₂(SMe₂)₂],⁷ [PtMe(C^N)-(SMe₂)] (C[^]N = ppy, bhq),^{4b} and [Pt(p-MeC₆H₄)(C[^]N)(SMe₂)] (C[^]N = ppy, bhq),^{4c} were prepared by the literature methods. Bis(2-(diphenylphosphino)ethyl)phenylphosphine (triphos) was purchased from commercial sources. The NMR labeling of complexes **3** is depicted in Figure 1.

[PtMe₂(triphos-P,P')] (1a). A solution of [PtMe₂(triphos-P,P')] (1a) was prepared⁸ by addition of triphos (186.7 mg, 0.33 mmol) to a solution of $[Pt_2Me_4(\mu-SMe_2)_2]$ (100 mg, 0.17 mmol) in acetone at room temperature. This solution was stirred for 30 min and used freshly for preparation of complexes **3**.

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Figure 1. NMR labeling of complexes 3.

[Pt(*p*-MeC₆H₄)₂(triphos-P,P')] (1b). To a solution of *cis*-[Pt(*p*-MeC₆H₄)₂(SMe₂)₂] (100 mg, 0.2 mmol) in dichloromethane was added triphos (110 mg, 0.21 mmol), and the reaction mixture was stirred at room temperature for 3 h. The solvent was removed, and the residue was dissolved in a minimum amount of CH₂Cl₂. The white solid product was formed after dropwise addition of *n*-hexane at 0 °C. Yield: 60 mg, 66%. Mp: 165 °C dec. Anal. Calcd for C₄₈H₄₇P₃Pt: C, 63.2; H, 5.2. Found: C, 63.1; H, 5.2. NMR data in CDCl₃: δ ⁽¹H) 2.07 (s, 3H, CH₃ of *p*-MeC₆H₄ ligand), 2.11 (s, 3H, CH₃ of *p*-MeC₆H₄ ligand), 1.70–2.71 (m, 8H, CH₂ of triphos), 6.61 (d, ³J_h^o m^m = 6.8 Hz, 2H^m of *p*-MeC₆H₄ ligand), 6.73 (d, ³J_H^o H^m, = 7.0 Hz, 2H^m' of *p*-MeC₆H₄ ligand); δ ⁽³¹P) 45.7 (t, 1P, ¹J_{PtP} = 1695 Hz, ³J_{PP} = 20 Hz).

[Pt₂Me₃(ppy)(triphos)] (3a). To a solution of [Pt₂Me₄(μ-SMe₂)₂] (30 mg, 0.052 mmol) in acetone was added triphos (56 mg, 0.1 mmol). The reaction mixture was stirred at room temperature for 30 min. After this time, [PtMe(ppy)(SMe₂)] (45 mg, 0.11 mmol) was added to the solution, and the reaction mixture was stirred for 2 h. The solvent was evaporated, and the residue was washed with ether and dried under vacuum to give a light yellow powder of **3a**. Yield: 42 mg, 36%. Mp 179 °C dec. Anal. Calcd for C₄₈H₅₀NP₃Pt₂; C, 51.2; H, 4.4; N, 1.2. Found: C, 50.7; H,4.2; N, 1.2. NMR in CDCl₃: δ(¹H) 0.42 (t, ³J_{HP}^b = ³J_{HP}^c = 7.3 Hz, ²J_{Pt}^bH = 70.0 Hz, 3H, Me trans to P), 0.44 (t, ³J_{HP}^b = ³J_{HP}^c = 7.3 Hz, ²J_{Pt}^bH = 70.4 Hz, 3H, Me trans to P), 0.71 (d, ³J_{HP}^a = 7.5 Hz, ²J_{Pt}^bH = 85.0 Hz, 3H, Me trans to N), 1.81–2.50 (m, 8H, CH₂ of triphos), 6.30–7.72 (br, 34H, hydrogens of aromatic region); δ (³¹P) 23.9 (d, ³J_{PT}^b^b = 45 Hz, ¹J_{Pt}^b^b = 1798 Hz, 1P, P^a), 47.3 (dd, ³J_{PT}^b^c = 1806 Hz, 1P, P^c); δ (¹⁹⁵Pt) –2559 (d, ¹J_{Pt}^bP^a = 2078 Hz, 1Pt, Pt^a), -3005 (t, ¹J_{Pt}^bP^b = ¹J_{Pt}^bP^b = 1802 Hz, 1Pt, Pt^b).

[Pt₂Me₂(*p*-MeC₆H₄)(ppy)(triphos)] (3b). To a freshly prepared solution of [PtMe₂(triphos-P,P')] (132 mg, 0.17 mmol in 20 mL of acetone) was added [Pt(*p*-MeC₆H₄)(ppy)(SMe₂)] (87.5 mg, 0.17 mmol), and the solution was stirred for 3 h. A pale yellow precipitate was formed, which was isolated by filtration and dried under vacuum. Yield: 148 mg, 71%. Mp: 222 °C dec. Anal. Calcd for C₅₄H₅₄NP₃Pt₂; C, 54.1; H, 4.5; N, 1.2. Found: C, 54.0; H,4.3; N, 1.1. NMR in CDCl₃: $\delta(^{1}\text{H})$ 0.10 (t, $^{3}J_{\text{HP}^{b}} = ^{3}J_{\text{HP}^{c}} = 7.4 \text{ Hz}, ^{2}J_{\text{Pt}^{b}} = 70.0 \text{ Hz}, 3\text{H}, \text{Me trans to P}$, 0.32 (t, $^{3}J_{\text{HP}^{b}} = ^{3}J_{\text{HP}^{c}} = 7.2 \text{ Hz}, ^{2}J_{\text{Pt}^{b}} = 69.1 \text{ Hz}, 3\text{H}, \text{Me trans to P}$), 1.90 (s, 3H, Me of *p*-MeC₆H₄ ligand), 1.38–2.31 (m, 8H, CH₂ of triphos), 6.30–7.72 (br, 37H, hydrogens of aromatic region); $\delta(^{31}\text{P})$ 22.1 (d, $^{3}J_{\text{Pt}^{b}} = 46 \text{ Hz}, ^{1}J_{\text{Pt}^{b}} = 2008 \text{ Hz}, 1P, P^{a}), 48.7$ (d, $^{3}J_{\text{Pt}^{b}} = 46 \text{ Hz}, ^{1}J_{\text{Pt}^{b}} = 1812 \text{ Hz}, 1P, P^{b}), 48.8$ (s, $^{1}J_{\text{Pt}^{b}} = 1817 \text{ Hz}, 1P, P^{c})$; $\delta(^{195}\text{Pt}) -2406$ (d, 1Pt, $^{1}J_{\text{Pt}^{b}} = 2010 \text{ Hz} \text{ Pt}^{a}), -3001$ (t, $^{1}J_{\text{Pt}^{b}} = ^{1}J_{\text{Pt}^{b}}$ = 1820 Hz, 1P, P^b).

[Pt₂(p-MeC₆H₄)₃(ppy)(triphos)] (3c). To a freshly prepared solution of $[Pt(p-MeC_6H_4)_2(triphos-P,P')]$ (1b, by addition of triphos (53.4 mg, 0.1 mmol) to a solution of $[Pt(p-MeC_6H_4)_2(SMe_2)_2]$ (50 mg, 0.1 mmol) in acetone at room temperature for 3 h) was added a solution of [Pt(p-MeC₆H₄)(ppy)(SMe₂)] (50.1 mg, 0.1 mmol). The mixture was stirred for 3 h. The solvent was evaporated, and the residue was washed with n-hexane and dried under vacuum. Yield: 63 mg, 47%. Mp: 165 °C dec. Anal. Calcd for C₆₆H₆₂NP₃Pt₂; C, 58.6; H, 4.6; N, 1.0. Found: C, 59.0; H, 4.5; N, 1.0. NMR in CDCl₃: δ(¹H) 2.05 (s, 3H, Me of p-MeC₆H₄ ligand), 2.10 (s, 3H, Me of p-MeC₆H₄ ligand), 2.12 (s, 3H, Me of p-MeC₆H₄ ligand), 1.49–2.11 (m. 8H, CH₂ of triphos), 6.47–8.04 (br, 45H, hydrogens of aromatic region); δ ⁽³¹P) 21.5 (d, ${}^{3}J_{P^{a}P^{b}} = 46$ Hz, ${}^{1}J_{Pt^{a}P^{a}} = 2027$ Hz, 1P, P^a), 42.9 (d, ${}^{3}J_{P^{a}P^{b}} = 46$ Hz, ${}^{1}J_{Pt}{}^{b}P^{b} = 1724$ Hz, 1P, P^b), 41.9 (s, ${}^{1}J_{Pt}{}^{b}P^{c} = 1725$ Hz, 1P, P^c); $\delta({}^{195}\text{Pt}) - 2405 \text{ (d, } {}^{1}J_{\text{Pt}^{a}\text{P}^{a}} = 2030 \text{ Hz}, 1\text{Pt}, \text{Pt}^{a}), -2952 \text{ (t, } {}^{1}J_{\text{Pt}^{b}\text{P}^{b}} = {}^{1}J_{\text{Pt}^{b}\text{P}^{c}}$ = 1724 Hz, 1Pt, Pt^b).

[Pt₂Me(*p***-MeC₆H₄)₂(ppy)(triphos)] (3d).** To a solution of [PtMe(ppy)(SMe₂)] (2a; 19 mg, 0.04 mmol) in acetone was added [Pt(*p*-MeC₆H₄)₂(triphos)] (1b; 41 mg, 0.05 mmol). The mixture was stirred at room temperature for 20 h. The solvent was removed, and the residue was purified to a pale yellow powder by treatment with diethyl ether and drying under vacuum. Yield: 32 mg, 26%. Mp: 160 °C dec. Anal. Calcd for C₆₀H₅₈NP₃Pt₂; C, 56.5; H, 4.5; N, 1.1. Found: C, 57.5; H, 4.3; N, 1.2. NMR in CDCl₃: δ (¹H) 0.68 (d, ³*J*_{HP}^{*} = 7.6 Hz, ²*J*_{Pt}^{*}H = 83.1 Hz, 3H, MePt), 1.86 (s, 3H, Me of *p*-MeC₆H₄ ligand), 1.93 (s, 3H, Me of *p*-MeC₆H₄ ligand), 1.71–2.53 (m, 8H, CH₂ of triphos), 6.02–7.67 (br, 41H, hydrogens of aromatic region); δ (³¹P) 24.9 (d, ³*J*_P^{*}p^{*} = 45 Hz, ¹*J*_{Pt}^{*}p^{*} = 2094 Hz, 1P, P^a), 42.1 (d, ³*J*_P^{*}p^{*} = 45 Hz, ¹*J*_{Pt}^{*}p^{*} = 1702 Hz, 1P, P^b), 40.8 (s, ¹*J*_{Pt}^{*}p^{*} = 1708 Hz, 1P, P^c).

[Pt₂Me₃(bhq)(triphos)] (3e). This was prepared by the method described above for preparation of complex **3a** using the starting material [PtMe(bhq)(SMe₂)]. Yield: 83%. Mp 210 °C dec. Anal. Calcd for C₅₀H₅₀NP₃Pt₂; C, 52.3; H, 4.5; N, 1.2. Found: C, 52.4; H,4.3; N, 1.4. NMR in CDCl₃: $\delta(^{1}\text{H}) 0.67$ (t, $^{3}J_{\text{HP}^{b}} = ^{3}J_{\text{HP}^{c}} = 7.6$ Hz, $^{2}J_{\text{Pt}^{b}\text{H}} = 69.0$ Hz, 3H, Me trans to P), 0.69 (t, $^{3}J_{\text{HP}^{b}} = ^{3}J_{\text{HP}^{c}} = 7.0$ Hz, $^{2}J_{\text{Pt}^{b}\text{H}} = 70.0$ Hz, 3H, Me trans to P), 1.15 (d, $^{3}J_{\text{HP}^{b}} = 7.5$ Hz, $^{2}J_{\text{Pt}^{b}\text{H}} = 83.9$ Hz, 3H, Me trans to N), 1.80–2.75 (m, 8H, CH₂ of triphos), 6.92–8.12 (br, 33H, hydrogens of aromatic region), 9.31 (d, 1H, $^{3}J_{\text{HH}} = 7.2$ Hz, CH group adjacent to coordinated N atom); $\delta(^{31}\text{P}) 23.5$ (d, $^{3}J_{\text{Pt}^{b}^{b}} = 45$ Hz, $^{1}J_{\text{Pt}^{b}^{a}} = 2132$ Hz, 1P, P^a), 47.2 (d, $^{3}J_{\text{Pt}^{b}} = 45$ Hz, $^{1}J_{\text{Pt}^{b}^{b}} = 1797$ Hz, 1P, P^b), 48.0 (s, $^{1}J_{\text{Pt}^{b}^{c}} = 1807$ Hz, 1P, P^c); $\delta(^{195}\text{Pt}) - 2590$ (d, $^{1}J_{\text{Pt}^{c}^{a}} = 2131$ Hz, 1Pt, Pt^a), -3006 (t, $^{1}J_{\text{Pt}^{b}^{b}} = ^{1}J_{\text{Pt}^{b}^{c}} = 1800$ Hz, 1Pt, Pt^b).

[Pt₂Me₂(*p*-MeC₆H₄)(bhq)(triphos)] (3f). This was prepared by the method used for preparation of complex 3b using [Pt(*p*-MeC₆H₄)(bhq)(SMe₂)]. Yield: 82%. Mp 232 °C dec. Anal. Calcd for C₅₆H₅₄NP₃Pt₂; C, 54.9; H, 4.4; N, 1.2. Found: C, 54.8; H,4.5; N, 1.1. NMR in CDCl₃: δ (¹H) 0.12 (t, ³*J*_{HP^b} = ³*J*_{HP^c} = 7.2 Hz, ²*J*_{Pt^bH} = 68.9 Hz, 3H, Me trans to P), 0.33 (t, ³*J*_{HP^b} = ³*J*_{HP^c} = 7.0 Hz, ²*J*_{Pt^bH} = 68.9 Hz, 3H, Me trans to P), 2.0 (s, 3H, Me of *p*-MeC₆H₄ ligand), 1.91–2.41 (m, 8H, CH₂ of triphos), 6.37–7.89 (br, 37H, hydrogens of aromatic region); δ (³¹P) 21.7 (d, ³*J*_{Pt^bP^s} = 46 Hz, ¹*J*_{Pt^bP^s} = 2070 Hz, 1P, P^a), 48.8 (d, ³*J*_{Pt^{Pb}} = 46 Hz, ¹*J*_{Pt^bP^s} = 1823 Hz, 1P, P^b), 48.7 (s, ¹*J*_{Pt^bP^s} = 1819 Hz, 1P, P^c); δ (¹⁹⁵Pt) –2431 (d, ¹*J*_{Pt^bP^s} = 2067 Hz, 1Pt, Pt^a), -3002 (t, ¹*J*_{Pt^bP^s}).

[Pt₂(*p*-MeC₆H₄)₃(bhq)(triphos)] (3g). This was prepared by the method used for preparation of complex 3c using [Pt(*p*-MeC₆H₄)-(bhq)(SMe₂)]. Yield: 73%. Mp: 175 °C dec. Anal. Calcd for C₆₈H₆₂NP₃Pt₂; C, 59.3; H, 4.5; N, 1.0. Found: C, 59.7; H,4.7; N, 1.1. NMR in CDCl₃: δ (¹H) 2.02 (s, 3H, Me of *p*-MeC₆H₄ ligand), 2.06 (s, 3H, Me of *p*-MeC₆H₄ ligand), 2.12 (s, 3H, Me of *p*-MeC₆H₄ ligand), 1.58–2.82 (m, 8H, CH₂ of triphos), 6.50–8.00 (br, 45H, hydrogens of aromatic region); δ (³¹P) 21.1 (d, ³*J*_{PⁱP^b} = 46 Hz, *J*_{PtⁱP^s} = 2089 Hz, 1P, P^a), 43.1 (d, ³*J*_{PⁱP^b} = 46 Hz, ¹*J*_{PtⁱP^b} = 1724 Hz, 1P, P^b), 42.1 (s, ¹*J*_{PtⁱP^b} = 1723 Hz, 1P, P^c); δ (¹⁹⁵Pt) –2430 (d, ¹*J*_{PtⁱP^s} = 2086 Hz, 1Pt, Pt^a), -2952 (t, ¹*J*_{PtⁱP^b} = ¹*J*_{PtⁱP^c} = 1723 Hz, 1Pt, Pt^b).

[Pt₂Me(*p***-MeC₆H₄)₂(bhq)(triphos)] (3h).** This complex was prepared by the method used for synthesis of complex **3d** using the starting material [PtMe(bhq)(SMe₂)]. Yield: 36%. Mp: 165 °C dec. Anal. Calcd for C₆₂H₅₈NP₃Pt₂; C, 57.3; H, 4.5; N, 1.1. Found: C, 56.9; H,4.2; N, 1.1. NMR in CDCl₃: δ (¹H) 0.89 (d, ³J_{HP³} = 7.4 Hz, ²J_{Pt³H} = 83.8 Hz, 3H, Me trans to N), 1.86 (s, 3H, Me of *p*-MeC₆H₄ ligand), 1.91 (s, 3H, Me of *p*-MeC₆H₄ ligand), 1.51–2.49 (m, 8H, CH₂ of triphos), 6.05–8.01 (br, 41H, hydrogens of aromatic region); δ (³¹P) 24.4 (d, ³J_{P³P³} = 45 Hz, J_{Pt³P³} = 2148 Hz, 1P, P^a), 42.0 (d, ³J_{P³P³} = 45 Hz, ¹J_{Pt³P³} = 1702 Hz, 1P, P^b), 40.7 (s, ¹J_{Pt³P⁵} = 1709 Hz, 1P, P^c).

X-ray Structure Determination. X-ray diffraction data for complex 3f were collected at 100(1) K by the ω -scan technique on an Agilent Technologies four-circle Xcalibur (Eos detector) diffractometer with graphite-monochromatized Mo K α radiation (λ = 0.71073 Å). The data were corrected for Lorentz–polarization and absorption effects.⁹ Accurate unit-cell parameters were determined by a least-squares fit of 29756 reflections of highest intensity, chosen from the whole experiment. The structure was solved with SIR92¹⁰ and refined with the full-matrix least-squares procedure on F^2 by SHELXL97.¹¹ Scattering factors incorporated in SHELXL97 were used. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were placed in the calculated positions and refined as a "riding model" with the isotropic displacement parameters set at 1.2 (1.5 for methyl groups) times the $U_{\rm eq}$ value for the appropriate non-hydrogen atom. Relevant crystal data are given in Table 1, together

 Table 1. Crystal Data and Structure Refinement for Complex 3f

formula	C56H54NP3Pt2
formula wt	1224.09
cryst syst	monoclinic
space group	$P2_{1}/c$
a (Å)	15.0322(4)
b (Å)	10.3813(3)
c (Å)	32.3098(10)
α (deg)	90
β (deg)	103.450(5)
γ (deg)	90
$V(Å^3)$	4903.7(2)
Ζ	4
$D_{\rm calcd} ({\rm g/cm^3})$	1.66
$\mu \ (\mathrm{mm}^{-1})$	5.84
F(000)	2392
no. of rflns	9644
R1 $(I > 2\sigma(I))$	0.039
R1 (all data)	0.050
wR2 $(I > 2\sigma(I))$	0.082
wR2 (all data)	0.086
S	1.08
max/min Δho (e Å ⁻³)	1.97/-1.35

with refinement details. In the crystal structure of **3f** there are relatively large voids (of ca. 240 Å³); however, no significant and interpretable electron density has been found in these voids.

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre as No. CCDC-933960. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road,



Cambridge CB2 1EZ, UK (fax +44(1223)336-033, e-mail deposit@ ccdc.cam.ac.uk, or web www.ccdc.cam.ac.uk.

Computational Details. Density functional calculations were performed with the program suite Gaussian03¹² using the B3LYP level of theory.¹³ The LANL2DZ basis set¹⁴ was chosen to describe Pt. The 6-31G(d) basis set was used for other atoms. The geometries of complexes were fully optimized by employing the density functional theory without imposing any symmetry constraints. To evaluate and ensure the optimized structures of the molecules, frequency calculations were carried out using analytical second derivatives. The NBO analyses were carried out on the stationary points using the NBO 3.1 program¹⁵ as implemented in the Gaussian 03 suite of programs.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Complexes. As shown in Scheme 1, the reaction of the diorganoplatinum(II) complexes $[Pt_2Me_4(\mu$ -SMe_2)_2] and $[Pt(p-MeC_6H_4)_2(SMe_2)_2]$ with triphos gave the platinum(II) complexes $[PtR_2(triphos-P,P')]$ (1a, R = Me; 1b, R = p-MeC₆H₄).

Although the dimethylplatinum complex **1a** has previously been reported⁸ through the slow addition of triphos to a solution of $[PtMe_2(COD)]$ (COD = 1,5-cyclooctadiene) in CH₂Cl₂, it was easily prepared by the reaction of $[Pt_2Me_4(\mu-SMe_2)_2]$ with 2 equiv of triphos at room temperature in acetone. The new complex **1b** was similarly prepared by the reaction of $[Pt(p-MeC_6H_4)_2(SMe_2)_2]$ with 1 equiv of triphos at room temperature in acetone and isolated as a pure and stable product. As previously reported, the reaction of complexes $[Pt_2Me_4(\mu-SMe_2)_2]$ and $[Pt(p-MeC_6H_4)_2(SMe_2)_2]$ with 2-phenylpyridine or benzo[h]quinoline gave the cyclometalated platinum(II) complexes $[PtR'(C^N)(SMe_2)]$ (**2a**, R' = Me, C^N = ppy; **2b**, R' = p-MeC₆H₄, C^N = ppy; **2c**, R' = Me, C^N = bhq; **2d**, R' = p-MeC₆H₄, C^N = bhq).

The general synthetic route to diplatinum complexes 3 is described in Scheme 1. The reaction of diorganoplatinum(II) complexes $[PtR_2(triphos-P,P')]$ (1) with cyclometalated platinum(II) complexes $[PtR'(C^N)(SMe_2)]$ (2) gave diplatinum(II) complexes 3a-h. For example, the reaction of $[PtMe(ppy)(SMe_2)]$ (2a), containing a labile SMe₂ ligand, with



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Figure 2. ¹H (A, in Me region), ³¹P (B), and ¹⁹⁵Pt (C) NMR spectra of the complex [Pt₂Me₃(ppy)(triphos)] (3a).

 $[Pt(p-MeC_6H_4)_2(triphos-P,P')]$ (1b), having a dangling P atom of the triphos ligand, at room temperature yielded the diplatinum(II) complex $[Pt_2Me(p-MeC_6H_4)_2(ppy)(triphos)]$ (3d). The complexes were fully characterized using multinuclear (¹H, ³¹P, and ¹⁹⁵Pt) NMR spectroscopy, and the structure of complex $[Pt_2Me_2(p-MeC_6H_4)(bhq)(triphos)]$ (3f) was further identified by X-ray crystallography.

In the ¹H NMR spectrum of complex **3a** (see Figure 2A), the Me groups *trans* to P were observed at δ 0.42 and 0.44 as triplets (${}^{3}J_{\rm HP^{b}} \approx {}^{3}J_{\rm HP^{c}} = 7.3$ Hz), with ${}^{2}J_{\rm Pt^{b}H}$ values being close to 70 Hz, while the Me group located *trans* to N ligating atom appeared as a doublet (${}^{3}J_{\rm HP^{a}} = 7.5$ Hz) at δ 0.71, with a

considerably higher ${}^{2}J_{\text{Pt}^{*}\text{H}} = 85.0$ Hz, due to the lower *trans* influence of the N atom in comparison with that of the P atom.^{4a,16} In the ³¹P NMR spectrum of the Pt(II)–Pt(II) complex **3a**, three different P signals were observed (see Figure 2B). The P^a atom, located *trans* to the coordinating C atom of the phenyl ring of the ppy ligand, appeared as a doublet signal at δ 23.9 (with ${}^{3}J_{\text{P}^{*}\text{P}^{b}} = 45$ Hz) which is coupled to the Pt^a atom to give satellites with ${}^{1}J_{\text{Pt}^{*}\text{P}^{a}} = 2076$ Hz. Two other P atoms, P^b and P^c, each of which is *trans* to the Me group, were observed at δ 47.3 and 47.9, respectively. The P^b atom was coupled with P^a and P^c atoms with ${}^{3}J_{\text{P}^{*}\text{P}^{b}} = 45$ and ${}^{3}J_{\text{P}^{*}\text{P}^{c}} = 5$ Hz,¹⁷ respectively, which is further coupled to the Pt^b atom, giving a satellite with



Figure 3. Perspective view of the complex $[Pt_2Me_2(p-MeC_6H_4)(bhq)(triphos)]$ (**3f**) together with the numbering scheme. Ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Pt1-N2 = 2.148(5), Pt1-C13 = 2.043(6), Pt1-P16 = 2.3010(15), Pt1-C29 = 2.005(6), Pt2-P37 = 2.2681(15), Pt2-P46 = 2.2799(18), Pt2-C59 = 2.138(5), Pt2-C60 = 2.095(6); N2-Pt1-C29 = 170.4(2), C13-Pt1-P16 = 178.1(2), P37-Pt2-C59 = 178.86(15), P46-Pt2-C60 = 177.57(17).

Table 2. Selected Calculated Bond Distances (Å) and Angles (deg) for Complexes 3a–h Compared to the Experimental Data of
Complex 3f	

bond distance or angle	3a	3b	3c	3d	3e	3f	3f (exptl)	3g	3h
Pt01-C100	2.069	2.028	2.027	2.069	2.067	2.025	2.003(6)	2.024	2.067
Pt01-C400	2.046	2.045	2.046	2.046	2.049	2.047	2.043(6)	2.049	2.049
Pt01-N006	2.215	2.208	2.211	2.215	2.230	2.223	2.147(5)	2.228	2.229
Pt01-P03	2.405	2.421	2.423	2.408	2.399	2.416	2.3010(14)	2.418	2.403
Pt02-C300	2.103	2.103	2.069	2.069	2.103	2.103	2.095(6)	2.070	2.070
Pt02-C200	2.105	2.105	2.067	2.068	2.105	2.105	2.139(5)	2.067	2.068
Pt02-P04	2.368	2.373	2.393	2.383	2.367	2.373	2.2684(15)	2.393	2.382
Pt02-P05	2.368	2.369	2.400	2.405	2.370	2.369	2.2799(16)	2.400	2.406
P03-C050	1.872	1.872	1.875	1.873	1.872	1.871	1.849(5)	1.876	1.873
P04-C015	1.865	1.865	1.863	1.860	1.865	1.865	1.833(5)	1.863	1.860
P04-C009	1.842	1.842	1.841	1.841	1.842	1.842	1.840(5)	1.841	1.841
P04-C022	1.877	1.877	1.871	1.871	1.877	1.877	1.844(6)	1.871	1.871
P05-C1	1.878	1.878	1.873	1.878	1.878	1.877	1.828(5)	1.873	1.878
C015-C050	1.535	1.534	1.533	1.535	1.535	1.534	1.526(7)	1.534	1.535
C1-C022	1.537	1.536	1.535	1.535	1.537	1.536	1.518(7)	1.535	1.535
C100-Pt01-C400	91.2	91.8	91.6	91.1	90.6	91.2	90.3(2)	90.9	90.5
C100-Pt01-N006	168.9	170.7	170.3	169.0	169.2	170.7	170.4(2)	170.1	169.3
C400-Pt01-N006	78.9	79.0	78.9	78.9	79.4	79.5	80.8(2)	79.4	79.5
C100-Pt01-P03	92.3	91.3	91.4	92.5	93.0	92.0	91.48(16)	92.3	93.2
C400-Pt01-P03	175.4	176.4	176.5	175.3	175.9	176.3	178.1(2)	176.4	175.5
N006-Pt01-P03	97.9	98.0	98.1	97.7	97.1	97.2	97.35(14)	97.4	97.0
C300-Pt02-C200	85.9	85.9	86.3	86.4	85.9	85.9	85.6(2)	86.3	86.4
C300-Pt02-P04	95.4	95.3	95.2	94.1	95.4	95.3	94.23(16)	95.1	94.1
C200-Pt02-P04	178.5	178.8	178.4	179.3	178.6	178.8	178.82(14)	178.5	179.2
C300-Pt02-P05	179.4	179.3	177.3	176.8	179.2	179.2	177.55(16)	177.4	176.6
C200-Pt02-P05	93.7	93.8	94.1	95.0	93.7	93.8	94.64(14)	94.1	95.0
P04-Pt02-P05	85.0	85.0	84.5	84.5	84.9	85.0	85.61(5)	84.5	84.5
C011-P03-C050	102.0	103.6	104.7	102.8	102.2	103.6	102.8(3)	104.7	102.9
C050-P03-Pt01	119.9	120.1	120.6	119.7	119.7	119.8	121.06(18)	120.5	119.5
C050-C015-P04	111.3	111.0	110.9	111.4	111.3	111.0	113.0(4)	110.8	111.4
C015-C050-P03	114.3	116.0	117.0	114.3	114.5	116.0	114.5(4)	117.0	114.3

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Figure 4. DFT optimized structures of the diplatinum(II) complexes 3.



Figure 5. Atom numbering of complexes 3.

 ${}^{1}J_{Pt^{b}P^{b}} = 1798$ Hz. The P^c atom is also coupled to Pt^b with a value of ${}^{1}J_{Pt^{b}P^{c}} = 1806$ Hz.

The above assignment for phosphorus atoms, shown in Figure 1 and Scheme 1, is based on the following observations. First, from the chemical shift values, it can be realized that the P^c and P^b atoms (47.9 and 47.3 ppm, respectively) are in a fivemembered ring while the P^a atom (23.9 ppm) is in agreement



Figure 6. Qualitative frontier molecular orbitals for complex 3a.

Table 4. Energies (eV) of the Relevant Frontier Orbitals of Complexes 3

complex	orbital	E (eV)	complex	orbital	E (eV)
3a	HOMO	-5.279	3e	НОМО	-5.265
	LUMO	-1.299		LUMO	-1.467
3b	HOMO	-5.237	3f	HOMO	-5.241
	LUMO	-1.412		LUMO	-1.567
3c	HOMO	-5.106	3g	HOMO	-5.107
	LUMO	-1.409		LUMO	-1.565
3d	HOMO	-5.136	3h	HOMO	-5.138
	LUMO	-1.295		LUMO	-1.463



Figure 7. Absorption spectra $(1 \times 10^{-4} \text{ M})$ of complexes 1a–3a. The spectrum for 3a was obtained immediately after addition of complex 1a to 2a under 1:1 stoichiometric conditions.

with a monodentate coordination mode.¹⁸ Second, the ${}^{1}J_{PtP}$ values for P^a, P^b, and P^c show that the P^a atom (with ${}^{1}J_{PtP}$ =

Table 3. NPA Charges on Pt Atoms of Complexes 3

Pt atom	3a	3b	3c	3d	3e	3f	3g	3h
Pt01	0.082	0.114	0.112	0.080	0.080	0.113	0.112	0.079
Pt02	-0.198	-0.196	-0.099	-0.101	-0.198	-0.196	-0.099	-0.101

Scheme 2. Suggested Mechanism for Formation of 3a





Figure 8. Calculated structures and energies (kcal mol⁻¹) of intermediate and compounds in the reaction of **1a** with **2a** in acetone solution. Energies are with respect to **1a** and **2a**; a molecule of free SMe_2 is included in the **IM** and **3a**.

2076 Hz) is *trans* to the C atom of the ppy ligand (the value being very close to that obtained for $[PtMe(ppy)(PPh_3)]^{19}$ with ${}^{1}J_{PtP} = 2105$ Hz), while the P^b and P^c atoms (with ${}^{1}J_{PtP}$ values of 1798 and 1806 Hz, respectively) are *trans* to Me ligands, as indicated by ${}^{1}J_{PtP}$ values comparable with the value of 1794 Hz in $[PtMe_2(dppe)]^{16a}$ (dppe = 1,2-bis-(diphenylphosphino)ethane). Note that the ${}^{1}J_{PtP}$ values observed for the P^c and P^b atoms are considerably smaller than the value for the P^a atom, indicating that the Me ligand exerts a higher *trans* influence than the C atom of ppy.^{4a,19,20} This assignment is in agreement with those reported for related complexes.^{18,21,22}

Consistent with the ³¹P NMR, in the ¹⁹⁵Pt NMR spectrum of **3a**, a triplet at -3005 with ${}^{1}J_{\text{Pt}}{}^{\text{pb}}{}^{\text{p}} = {}^{1}J_{\text{Pt}}{}^{\text{b}}{}^{\text{pc}} = 1802$ Hz and a doublet at $\delta -2559$ with ${}^{1}J_{\text{Pt}}{}^{\text{a}}{}^{\text{a}} = 2078$ Hz were observed for the Pt^b and Pt^a atoms, respectively (see Figure 2C).

The crystal structure of the complex $[Pt_2Me_2(p-MeC_6H_4)-$ (bhq)(triphos)] (3f) was also determined. The molecular structure of complex 3f is shown in Figure 3. Selected bond distances and angles for complex 3f are given in Table 2. The structure of 3f shows that triphos simultaneously acts as a chelating and bridging ligand. Triphos coordinates to Pt in a bidentate mode, the chelate ring being similar to that generated by dppe (dppe = 1,2-bis(diphenylphosphino)ethane). Another arm of the triphos ligand forms a bridge with the second Pt atom, giving diplatinum(II) complex 3f. The complex shows two different Pt-Me distances (2.095(6) and 2.138(5) Å), which is consistent with the two signals found in the ¹H NMR spectrum. The Pt1-P16 bond distance (2.3010(15) Å) is greater than the Pt2-P37 (2.2681(15) Å) and Pt2-P46 (2.2799(17) Å) bond lengths. This is due to the phosphorus atoms P37 and P46 being parts of a five-membered chelate ring. The Pt1-N2 and Pt1-C13 bond lengths are 2.148(5) and 2.043(6) Å, respectively, similar to the literature values of 2.149(6) and 2.046(7) Å.^{4b,c} Both Pt ions are four-coordinated and have square-planar environments, which can be shown by an analysis of the bond angles as well as by the calculations of the least-squares planes through the four coordinating atoms (maximum deviations are 0.032(3) Å for Pt1 and 0.035(2) Å for Pt2). To the best of our knowledge, this is the first X-ray structural determination of a diplatinum complex having a triphos ligand simultaneously acting as a chelating and bridging ligand, although crystal structures of some transition-metal complexes including triphos as either a bridging or chelating ligand have been reported.^{5c,f,22}

DFT Investigations of Complexes 3. To perform a reliable molecular modeling of the newly synthesized diplatinum complexes containing a triphos ligand and to analyze correctly their structures, an appropriate DFT method is needed. During the past decade DFT methods have proven to be suitable and useful alternatives for calculations of structures of transition-metal complexes. Thus, it is important to test the reliability of the computational method employed for complexes presented in this work. The dinuclear Pt(II) complex 3f has been structurally characterized by X-ray diffraction analysis and is used as a standard example to estimate the reliability of the DFT/B3LYP level of calculations as to the geometrical parameters. The structures of 3a-h are schematically presented in Figure 4. Selected calculated bond lengths of optimized geometries of 3a-h at the B3LYP/6-31G(d) level (LANL2DZ potential for Pt) and the corresponding experimental crystallographic data for complex 3f are given in Table 2 (see Figure 5 for atom labeling). The computed structural details are in good agreement with the experimental parameters. The mean error for the bond lengths is 0.036 Å for complex 3f. One reason for the bond length discrepancy in our calculations is due to a comparison of the geometrical parameters calculated in the gas phase with those obtained experimentally in the solid state. Considering the large molecules under consideration, the B3LYP/6-31G(d) method appears to be a reasonable compromise between accuracy and CPU time of calculations and therefore we used it together with LANL2DZ for Pt for structural characterization of the new diplatinum complexes 3a-h. The optimized structures are shown in Figure 4, and calculated results are presented in Table

As can be seen from Table 2, for complexes containing a bhq ligand (i.e., 3e-h), the Pt01–P03 (i.e., Pt^a-P^a ; see Figure 1) bond lengths are shorter than those of the corresponding platinum(II) products having a ppy ligand (i.e., 3a-d). For example, the Pt01–P03 bond in 3e (2.399 Å) is shorter than that in 3a (2.405 Å), complying with the larger ${}^{1}J_{Pt^{a}P^{a}}$ value for complex 3e as compared with that of complex 3a. These results suggest that the *trans* influence of the metalated C atom of the ppy derivative is greater than that of the bhq analogue.²⁰ Also, the Pt–P bond lengths for complexes with R' = p-MeC₆H₄ (i.e., **3b,c,f,g)** are longer than those with R' = Me (i.e., 3a,d,e,h), which is in agreement with the trends found for ${}^{1}J_{Pt}{}^{Pa}$ values in their ${}^{31}P$ NMR spectra. This may be attributed to the greater s character of Pt-C(sp²) and steric hindrance for an aryl ligand in comparison to Pt-C(sp³) and steric hindrance for Me.

Table 3 shows the atomic charges of the platinum centers for the complexes 3, obtained from a natural bond orbital (NBO) analysis.¹⁵ The calculated charge on the Pt02 atom is negative in comparison with the positive charge on the Pt01 atom, which is the result of the coordination of the nitrogen atom of C^N ligands to the Pt01 center. However, the Pt charge values for both centers in complexes 3 are lower than the formal charge of +2, as the ligands act as electron donors and therefore increase the electron density at the metal center. The charge on the Pt02 atom of complex 3d (-0.101), containing two *p*-tolyl ligands, is less negative in comparison with the Pt02 atom of complex 3a (-0.198), having two methyl ligands, which is related to the weaker electron donor ability of the *p*-MeC₆H₄ ligand compared to the Me ligand.

Qualitative representations of the highest occupied and lowest unoccupied molecular orbitals in complex 3a are presented in Figure 6. The energies of the relevant frontier orbitals of complexes 3 are also shown in Table 4. The HOMO-LUMO gap of 3a is equal to 3.980 eV. The highest occupied MO of 3a is mainly the Pt02 d_{r^2} orbital (Pt atom having two alkyl or aryl groups,; see Figure 4). The LUMO is predominately localized on the d orbitals of the Pt01 atom with significant contribution of the p_{π} orbitals of the C^N ligand. This means that complex 3a can act as a nucleophile or electrophile through the Pt02 or Pt01 atoms, respectively. The values of the energy separations between the HOMO and LUMO of 3b-h are smaller than that of 3a and are equal to 3.825, 3.697, 3.841, 3.798, 3.674, 3.542, and 3.675 eV, respectively. The highest occupied molecular orbital of 3b-h is essentially the d_{z^2} orbital of the Pt02 atom. The LUMO of these binuclear platinum(II) complexes can be ascribed to a combination of the Pt01 p_z orbital and p_{π} orbitals of the C^{Λ}N ligand.

Investigation of the Product Formation. As described above (related to the reactions in Scheme 1), when for example $[PtMe_2(triphos-P,P')]$ (1a) was reacted with 1 equiv of $[PtMe(ppy)(SMe_2)]$ (2a), the complex $[Pt_2Me_3(ppy)-(triphos)]$ (3a) was formed. The reactions of cyclometalated complexes 2 with complexes 1 were too fast to measure. As shown in Figure 7, immediately after addition of complex 1a to a solution of complex 2a under 1:1 stoichiometric conditions in acetone, complex 3a was formed.

In order to gain further insight into the mechanism, DFT calculations were carried out for the complexes and intermediate, using parameters for the solvent acetone. The complex 2a contains a labile SMe_2 ligand and two Pt-C bonds. The SMe₂ dissociation step is facilitated by the strong trans influence of the metalated C atom of ppy, which weakens the Pt-SMe2 bond. On the basis of DFT calculations, as shown in Scheme 2 and Figure 8, the mechanism of formation of 3a is proposed to occur by dissociation of a labile ligand, SMe₂, to form the intermediate complex IM with an energy barrier of 9.7 kcal mol⁻¹. In the second step, the P dangling atom in 1a attacks the vacant site of the Pt center of IM to form the binuclear platinum complex 3a. It has been shown that the substitution reactions in the complexes $[Pt(bph)(SMe_2)_2]$ (bph = 2,2'-biphenyl dianion) and $[PtPh_2(SMe_2)_2]$, each bearing two Pt-C bonds, with reagents potentially having bidentate chelate

donor abilities such as bipyridine and 1,2-(diphenylphosphino)ethane, occur through a dissociative path.²³ The ligand dissociation step is facilitated by the strong trans influence of the alkyl or aryl group, which weakens the metal–ligand bonds, while the alternative associative mechanism is less favored because the electron-rich platinum center is resistant to nucleophilic attack.²³

CONCLUSION

Several diplatinum(II) complexes were prepared, in which one Pt center contains a bidentate cyclometalated ppy or bhq ligand and the second Pt center has two methyl or aryl groups. For the first time, it has been possible to assemble pairs of these units in any combination by using triphos as the assembling agent. This triphosphine ligand acts at the same time as a chelating agent and bridging ligand, forming the complexes $[Pt_2R_2R'(C^N)-(triphos)]$ (3). The first X-ray structural determination of these diplatinum complexes confirms the square-planar environment around both platinum centers.

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Notes

The authors declare no competing financial interest.

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