

Synthesis and Structures of Platinum(0) Alkyne Complexes with Extended π -Conjugated Systems

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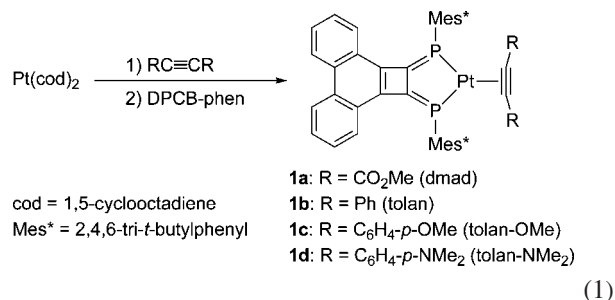
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Summary: 1,2-Bis[(2,4,6-tri-*tert*-butylphenyl)phosphinidene]cyclobuta[l]phenanthrene (DPCB-phen) as a low-coordinated phosphorus ligand forms the platinum(0) alkyne complexes [Pt(alkyne)(DPCB-phen)] with extended π -conjugated systems. The colors of the complexes are highly dependent on alkyne ligands, showing a marked variation from reddish orange to teal.

Organotransition-metal complexes with extended π -conjugated systems have attracted continuous research interest.¹ Considering the great utility of organic molecules with extensive $p\pi$ – $p\pi$ interactions in materials science,² organometallic complexes with effective $d\pi$ – $p\pi$ interactions between transition metals and unsaturated hydrocarbon ligands are of particular interest.³ Although platinum alkyne and alkynyl species are frequently employed as the key components of such complexes, $d\pi$ – $p\pi$ interaction between the $d\pi$ orbital of platinum and the out-of-plane π orbitals (i.e., the π orbitals perpendicular to the coordination plane; denoted as π_{\perp}) of alkyne and alkynyl ligands is insignificant in most cases because the $d\pi$ orbital is commonly occupied and undergoes repulsive interaction with the π_{\perp} orbital.⁴

We herein describe that platinum(0) alkyne complexes with extended π -conjugated systems are successfully prepared using 1,2-bis[(2,4,6-tri-*tert*-butylphenyl)phosphinidene]cy-

clobuta[l]phenanthrene (DPCB-phen)⁵ as an auxiliary ligand (eq 1), which is a 1,2-fused compound of 1,2-diphenyl-3,4-bis[(2,4,6-tri-*tert*-butylphenyl)phosphinidene]cyclobutene (DPCB).⁶ As has been already demonstrated for group 9 and 10 metal complexes, DPCB as a low-coordinated phosphorus compound possesses extremely low-lying π^* orbitals and acts as a strong π -acceptor toward transition metals.^{7,8} It has been found that this unique electronic property effectively induces π -conjugation over the molecules.



Complexes **1a–d** were synthesized from [Pt(cod)₂] (cod = 1,5-cyclooctadiene) by stepwise displacement of the cod ligands.⁹ Thus, the alkyne ligands were initially introduced, and then the DPCB-phen ligand was introduced to the resulting [Pt(alkyne)(cod)] complexes.¹⁰ Although the ligand exchange

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(9) A typical procedure is reported for **1c**. To a Schlenk tube containing [Pt(cod)₂] (78 mg, 0.19 mmol) was added hexane (4 mL). The heterogeneous mixture was cooled to –20 °C, and a solution of 1,2-bis(4-methoxyphenyl)ethyne (tolan-OMe; 45 mg, 0.19 mmol) in Et₂O (2 mL) was added dropwise with stirring. After 1 h, the pale yellow precipitate of [Pt(tolan-OMe)(cod)] that formed in the system was collected by filtration, washed with hexane (2 mL × 3), and dried under vacuum (77 mg, 75%). This product was used in the next step without purification. The complex [Pt(tolan-OMe)(cod)] (22 mg, 0.040 mmol) was placed in a Schlenk tube and dissolved in CH₂Cl₂ (1.5 mL). A solution of DPCB-phen (30 mg, 0.040 mmol) in CH₂Cl₂ (1 mL) was added, and the resulting mixture was stirred at room temperature for 3 h, giving a deep purple solution. Completion of the ligand displacement was confirmed by ³¹P{¹H} NMR spectroscopy. The solution was concentrated to dryness under reduced pressure, and the resulting solid was washed with hexane (1 mL × 3) to afford a purple powder of [Pt(tolan-OMe)(DPCB-phen)] (**1c**; 28 mg, 59%). Complexes **1a,b,d** were similarly prepared in 60, 58, and 63% yields, respectively.

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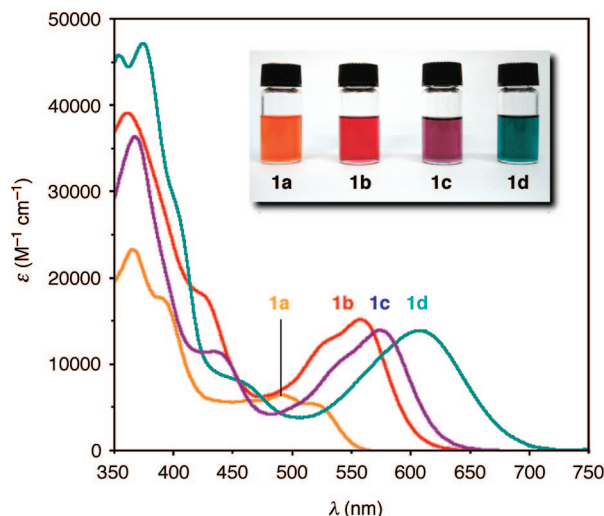


Figure 1. Absorption spectra of **1a–d** in CHCl_3 .

reactions may be operative in the opposite order, the intermediate $[\text{Pt}(\text{cod})(\text{DPCB-phen})]$ is poorly reactive and the use of excess alkyne was required in the subsequent reaction. All complexes were isolated as crystalline (**1a–c**) or powdery (**1d**) solids and characterized by NMR spectroscopy and elemental analysis. The $^{31}\text{P}\{^1\text{H}\}$ NMR signals appeared at δ 150.7 (**1a**, $^1J_{\text{PtP}} = 3913$ Hz), 155.7 (**1b**, $^1J_{\text{PtP}} = 3455$ Hz), 156.6 (**1c**, $^1J_{\text{PtP}} = 3436$ Hz), and 157.4 (**1d**, $^1J_{\text{PtP}} = 3406$ Hz), respectively; the chemical shifts are higher than that of DPCB-phen (δ 173.8). The $^{13}\text{C}\{^1\text{H}\}$ NMR signals of acetylenic carbons were observed at δ 121.4–122.3; the chemical shifts are somewhat higher than those of the dppe^{11} and PPh_3^{10} analogues of **1b** (δ 135.6 and 127.9, respectively) but are still in the normal range for alkyne complexes with a d^{10} metal center.¹²

Platinum(0) alkyne complexes are usually almost colorless, showing no significant absorption in the visible region. On the other hand, the present alkyne complexes **1a–d** bearing DPCB-phen ligands exhibited vivid colors that vary remarkably with alkyne ligands. Thus, the dimethyl acetylenedicarboxylate (dmad) complex **1a** is reddish orange, whereas the complexes coordinated with nonsubstituted (tolan) and para-substituted diphenylacetylenes (tolan-Y; Y = OMe, NMe_2) are dark red (**1b**), mulberry (**1c**), and teal (**1d**), respectively.

Figure 1 shows the UV–vis spectra of **1a–d**, where the characteristic absorption bands of medium or strong intensity are observed at 450–700 nm. In accordance with the marked color variation of the complexes, the absorption maximum is shifted significantly depending on the alkyne ligands: λ_{max} (nm) 492 (**1a**, $\log \epsilon = 3.82$), 558 (**1b**, 4.18), 573 (**1c**, 4.14), 607 (**1d**, 4.15). Since no solvatochromic shift was observed in cyclohexane, CHCl_3 , acetone, and DMF, these absorptions are assignable to π – π^* transitions, not to MLCT. Hence, the occurrence of strong $\text{d}\pi$ – $\text{p}\pi$ interaction between the $[\text{Pt}(\text{DPCB-phen})]$ moiety and the alkyne ligands causing notable extension of π -conjugated systems is evidenced. The strong dependence of the absorption maxima upon para substituents of diphenylacetylene ligands in **1b–d** is consistent with this consideration.

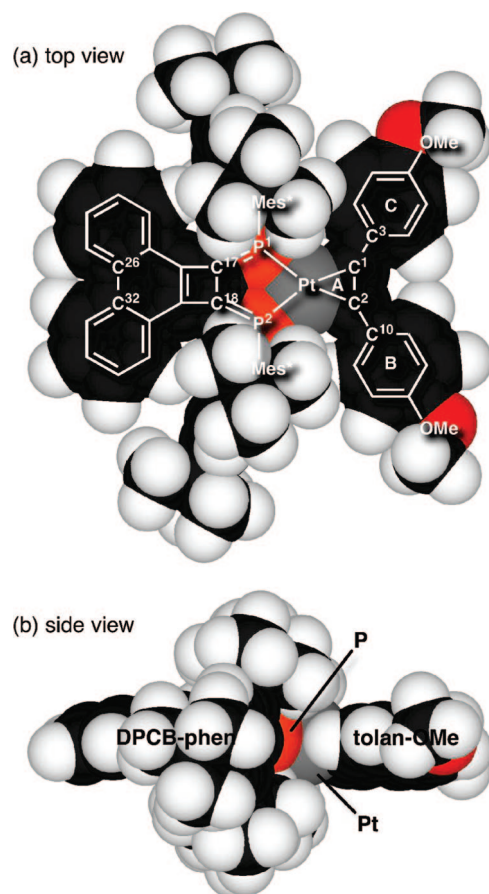


Figure 2. Chem3D view of the X-ray structure of **1c**. Selected bond distances (Å) and angles (deg): C1–C2 = 1.299(3), Pt–C1 = 2.038(2), Pt–C2 = 2.053(2), Pt–P1 = 2.2884(6), Pt–P2 = 2.3117(6), P1–Pt–P2 = 83.29(2), C1–Pt–C2 = 37.02(9), C2–C1–C3 = 151.7(2), C1–C2–C10 = 147.0(2).

Figure 2 depicts the top and side views of the X-ray crystal structure of **1c**,¹³ which adopts a square-planar configuration around platinum, taking the two phosphorus atoms of DPCB-phen and the two acetylenic carbons of tolan-OMe as coordination atoms. The bond length between the acetylenic carbons (C1–C2 = 1.299(3) Å) is similar to those of $[\text{Pt}(\text{tolan})(\text{dppbn})]$ (1.301(4) Å)¹⁴ and $[\text{Pt}(\text{tolan})(\text{PPh}_3)_2]$ (1.280(5) Å).¹⁵ The Pt–C bond distances (2.038(2), 2.053(2) Å) are also comparable to those of dppbn (2.038(3), 2.041(3) Å) and PPh_3 (2.047(3), 2.048(3) Å) complexes. On the other hand, the bent angles of the phenyl groups against the C1–C2 axis (28.3(2), 33.1(2)°) are somewhat smaller than those of dppbn (34.6(3), 33.6(3)°) and PPh_3 (37.7(3), 37.4(3)°) complexes.

The most striking feature of the structure of **1c** is the extremely planar arrangements of the diphenylacetylene, platinum, and 1,2-diphosphinidenecyclobuta[*l*]phenanthrene units, while the 2,4,6-tri-*tert*-butylphenyl groups (Mes*) on the phosphorus atoms are almost perpendicular to the coordination

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(13) Crystallographic data for **1c**: $\text{C}_{68}\text{H}_{80}\text{O}_2\text{Pt}$, fw 1186.35, monoclinic, space group $P2_1/c$ (No. 14), $a = 14.684(3)$ Å, $b = 22.008(4)$ Å, $c = 18.693(3)$ Å, $\beta = 107.720(2)^\circ$, $V = 5754.3(18)$ Å³, $Z = 4$, $d_{\text{calcd}} = 1.369$ g cm^{−3}, $\mu(\text{Mo K}\alpha) = 2.538$ mm^{−1}, $2\theta < 55.0^\circ$. Of the 45340 reflections collected, 13140 were independent ($R_{\text{int}} = 0.0347$) and used for the refinement of 898 parameters: $R1 = 0.0319$, $wR2 = 0.0610$, $\text{GOF} = 1.085$ for all data ($R1 = 0.0266$ for $I > 2\sigma(I)$).

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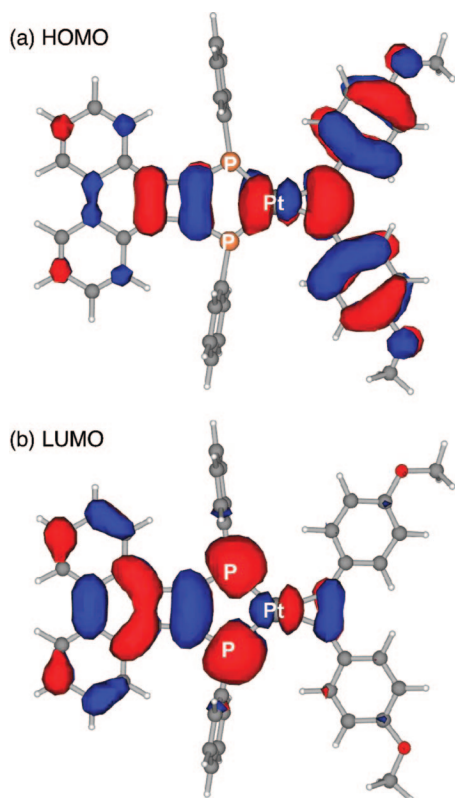


Figure 3. HOMO and LUMO of the model compound of **1c**.

plane. The torsion angle between C1–C2 (tolan-OMe) and C26–C32 (DPCB-phen) is 5.3(2)°, and the dihedral angles between the PtC1C2 plane **A** and benzene rings **B** and **C** of tolan-OMe are 7.6(1) and 5.3(1)°, respectively. Although there is a possibility that steric repulsion between the benzene rings (**B** and **C**) and the *t*-Bu groups of the Mes* substituents causes the highly planar orientation of the benzene rings, DFT calculations for the model compound without the *t*-Bu groups also suggested the stability of the planar geometry.¹⁶

Figure 3 illustrates the HOMO and LUMO of the model compound. While both the frontier orbitals, which correspond to π and π^* orbitals, respectively, are delocalized on the whole molecular plane, the HOMO is distributed over the [Pt(tolan-OMe)] moiety to a considerable extent, whereas the LUMO is located mainly on the [Pt(DPCB-phen)] moiety. In this situation,

(16) (a) The primary structure for geometry optimization was based on the X-ray structure of **1c**, where the *t*-Bu groups of the Mes* substituents were omitted and the dihedral angles of the phenyl groups with the P1–C17 and P2–C18 axes (see Figure 3) were fixed to the X-ray values. Selected bond distances (Å) and angles (deg) for the optimized structure: C1–C2 = 1.30, Pt–C1 = Pt–C2 = 2.05, Pt–P1 = Pt–P2 = 2.38; P1–Pt–P2 = 81.6, C1–Pt–C2 = 37.1, C2–C1–C3 = C1–C2–C10 = 147.8. (b) DFT calculations were carried out with the Gaussian 98 program (Revision A.9, Gaussian, Inc., 1998) using B3LYP in conjunction with the standard LanL2DZ basis set and effective core potentials for Pt and 6-31G(d) basis set for other atoms.

Table 1. Relationship between HOMO–LUMO Gaps (HLG) and $E_{\text{p,a}}$ Values

complex	UV–vis ^a			CV ^b $E_{\text{p,a}}$ (V)
	λ_{max} (nm)	λ_{edge} (nm)	HLG (eV)	
1a	492	553	2.24	0.755
1b	558	603	2.06	0.337
1c	573	623	1.99	0.289
1d	607	682	1.82	−0.023

^a In CHCl₃ at room temperature. ^b $E_{\text{p,a}}$ values vs Fc/Fc⁺, in CH₂Cl₂ (0.1 M Bu₄NBF₄, 100 mV s^{−1}) at room temperature.

the HOMO levels should be dependent predominantly on the electronic properties of the alkyne ligands. Therefore, we next examined oxidation potentials of **1a–d** by cyclic voltammetry.

The cyclic voltammograms measured in CH₂Cl₂ showed quasi-reversible (**1a,b**) or reversible (**1c,d**) one-electron oxidation waves. As given in Table 1, the oxidation potentials ([**1**]/[**1**]⁺) were shifted clearly to the negative side as the π -electron density of alkyne ligands increased. The $E_{\text{p,a}}$ values showed a good linear correlation ($r^2 = 0.982$) with the HOMO–LUMO gaps (HLG) estimated from the absorption edge wavelengths (λ_{edge}): $\text{HLG} = 0.54(5) \times E_{\text{p,a}} + 1.84(2)$.

As described in the introductory paragraph, the interaction of the $d\pi$ orbital of platinum with the out-of-plane π_{\perp} orbital of the alkyne ligand is generally negligible.⁴ Actually, [Pt(tolan)L₂] complexes bearing tertiary phosphine ligands as L show no notable absorption in the visible region. In this context, the strong π – π^* transition observed for **1a–d** is remarkable. As seen from Figure 3, the π_{\perp} orbital of tolan-OMe and the $d\pi$ orbital of platinum interact with each other in an antibonding manner. Furthermore, the ¹³C{¹H} NMR chemical shifts of the acetylenic carbons are in a typical range of alkyne ligands that serve as two-electron donors.¹² Nevertheless, the π orbitals are delocalized widely over the molecule, as typically seen in the HOMO and LUMO of **1c**, showing the establishment of efficient interaction between the two $p\pi$ orbital systems (i.e., DPCB-phen and alkynes) through the platinum $d\pi$ orbital. It is convincing that the combination of the electron-poor $p\pi$ system of DPCB-phen and the electron-rich $p\pi$ system of alkyne facilitates this orbital interaction, providing the extended π -conjugated systems with small HOMO–LUMO gaps.

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Supporting Information Available: Text giving experimental procedures and analytical data and a CIF file giving crystallographic data for **1c**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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