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Synthesis, Structures, and Electronic Spectroscopy of Luminescent Acetyleneand (Buta-1,3-diyne)platinum Complexes

Ke Zhang,^[a] Jian Hu,^[a] Kwok Chu Chan,^[b] Kwok Yin Wong,^[b] and John H. K. Yip*^[a]

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The electronic absorption and emission spectroscopy of a series of diphenylaceylene- and (buta-1,3-diyne)-Pt⁰ complexes (L)Pt[(1,2- η^2)-R-(C=C)_n-R] and [(dppp)Pt]₂[μ -(1,2- η^{2} :(3,4- η^{2})-R-(C=C)₂-R] {R = Ph or CH₃, L = dppp or $(PPh_3)_{2}$, n = 1 or 2} was investigated. The structures of $(dppp)Pt[(1,2-\eta^2)-Ph-C\equiv C-Ph],$ $(dppp)Pt[(1,2-\eta^2)-PhC_4Ph]$ and $[(dppp)Pt]_{2}[\mu - (1, 2 - \eta^{2}): (3, 4 - \eta^{2}) - Ph - (C \equiv C)_{2} - Ph]$ characterized by X-ray diffraction. The complexes all display intense absorptions that were attributed to $Pt \rightarrow P(d\pi^*)$ and $Pt \rightarrow acetylene(\pi_x^*)$ transitions. Except for the $CH_3C_4CH_3$ complexes, the complexes all exhibit two emissions at 380-550 nm and 500-800 nm. The higher energy emission could arise from the ${}^{3}[P(d\pi^{*})\rightarrow Pt]$ transition, and the lower energy emission, which has a longer lifetime than the higher energy one, was attributed to the ³[acetylene(π_x^*) \rightarrow Pt] transition. The energy of the MLCT absorption and emission was affected by the electronic properties of the acetylenes and the ancillary phosphanes.

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Introduction

Recent interest in linear organometallics that have a lowlying metal-to-ligand charge-transfer (MLCT) excited state arose from their potential as molecular devices.^[1] For example, it had been demonstrated that the intense MLCT absorption of Ru^{II} acetylides is associated with their large second-order nonlinear optical effect.^[1c] In addition, MLCT excitation is accompanied with charge separation, which is pertinent for the operation of photonic wires.^[2]

Currently, organometallic complexes containing π -conjugated ligands are receiving a lot of attention mainly because of their wire-like geometry and the ability of π -conjugated carbon chains to mediate electron transfer.^[3] Most of the studies have focused on metal acetylides and metal polyyne σ complexes. One way to lower the MLCT energy is to increase π -conjugation of the polyyne ligand. For instance, the complex $[Re(L)(CO)_3(C \equiv CC \equiv C)Re(L)(CO)_3]$ (L = 4,4'-di-tert-butyl-2,2'-bipyridine) displayed a low-energy MLCT transition $[d\pi(Re) \rightarrow \pi^*(C \equiv CC \equiv C - Re)]$ and ³MLCT emission.^[4] However, a potential drawback of this approach is that the gap between the metal $d\pi$ - and the ligand π -orbitals is reduced, resulting in substantial mixing of the orbitals, and hence introduction of significant intraligand $\pi\pi^*$ character to the MLCT excited state. In principle, the mixing could be subdued if the metal orbitals are much higher in energy than the ligand orbitals. This requires an electron-rich metal center. In search of organometallics showing low-energy MLCT transition, our attention was therefore drawn to acetyleneplatinum(0) π complexes, which possess an electron-rich metal center and low-lying π^* -orbitals.

Although the π complexes have a fairly long history,^[5] most studies to date focus on the structures and reactivity aspects of the compounds.^[6] On the other hand, electronic spectroscopy and photophysics of the complexes remain sparsely studied^[7] The luminescent properties of a series of acetylene-Pt⁰ complexes have been reported by Forniés and co-workers.^[7a] They assigned the vibronic phosphorescence exhibited by $[(PPh_3)_2Pt_2]_2(HC \equiv C-1, 4-C_6H_4-C \equiv CH)$ to ³MLCT emission. The assignment was supported by extended Hückel calculations that showed that the HOMO contains a substantial metal character and the LUMO is mainly localized in the π^* -orbital of the acetylene.

A better understanding of the electronic structures and photophysics of the complexes could be achieved by expanding the scope of spectroscopic study to cover molecules that contain different acetylenes and ancillary ligands. To this end, we have carried out a comparative study of a series of acetylene- and (buta-1,3-diyne)platinum(0) (LPt)[(1,2- η^2)-R-(C=C)_n-R] {L = (PPh_3)_2 or dppp [1,3-bis(diphenylphosphanyl)propane]; R = Ph or CH_3 ; n = 1 or 2} and binuclear $[(dppp)Pt]_2[\mu - (1,2-\eta^2):(3,4-\eta^2)-R - (C \equiv C)_2 - R]$ complexes (Scheme 1). The complexes are different by the substituents attached to the $C \equiv C$ bond, extent of conjugation, number of metal atoms or ancillary phosphane atoms.

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[[]a] Department of Chemistry, National University of Singapore, 10 Kent Ridge Crescent, 119260 Singapore, Singapore Fax: +65-7791691

E-mail: chmyiphk@nus.edu.sg [b] Department of Applied Biology and Chemical Technology, Hong Kong Polytechnic University, Hunghom, Kowloon, Hong Kong SAR, People's Republic of China

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Scheme 1.

Except for complexes 1 and 3, all of the complexes are new. While binuclear metal complexes of buta-1,3-diyne in μ -(1,2- η^2):(3,4- η^2) coordination mode are known, the complex 5 is the first Pt₂-butadiyne π complex ever characterized by X-ray crystallography.^[8] The first diplatinum complex of PhC₄Ph, [(PPh₃)₂Pt]₂[μ -(1,2- η^2):(3,4- η^2)-PhC₄Ph], was synthesized by Stone but its crystal structure was not available.^[9]

Results and Discussion

(A) Synthesis and Characterization

There are two literature methods for the preparation of acetylene-Pt⁰ complexes. The first method^[10] involves reduction of the Pt(PPh₃)₂Cl₂ ion by N₂H₄ in the presence of the acetylene ligand in alcohol. In this work, (PPh₃)₂Pt[(1,2- η^{2})-PhC₂Ph] (1) and (PPh₃)₂Pt[(1,2-\eta^{2})-PhC₄Ph] (3) were prepared by this method. However, synthesis of (dppp)- $Pt[(1,2-\eta^2)-PhC_2Ph]$ (2) and (dppp) $Pt[(1,2-\eta^2)-PhC_4Ph]$ (4) by the same methods was not successful. Instead the stronger reductant NaBH₄ is needed to reduce Pt(dppp)Cl₂ to Pt⁰(dppp). This could be due to the fact that dppp is more electron-donating than PPh₃, making Pt(dppp)Cl₂ more difficult to reduce than Pt(PPh₃)₂Cl₂. Another literature method^[9] involves substitution of ethylene in (R₃P)₂- $Pt(C_2H_4)$ by acetylenes. This method was used to prepare $(dppp)Pt[(1,2-\eta^2)-CH_3C_4CH_3]$ (6) and the dinuclear $[(dppp)Pt]_{2}[\mu-(1,2-\eta^{2}):(3,4-\eta^{2})-PhC_{4}Ph]$ (5) and $[(dppp)Pt]_{2}$ - $[\mu - (1, 2 - \eta^2): (3, 4 - \eta^2) - CH_3C_4CH_3]$ (7).

The ESI-MS spectra of the complexes all show peaks attributable to the corresponding molecular ion M⁺. The IR spectra of 1 and 2 display weak bands at 1741 and 1748 cm⁻¹, respectively, which are assigned to stretching of the coordinated C=C bonds. Absorption bands of similar

frequency and intensity have been observed for other reported acetylene-Pt⁰ complexes.^[5,6] The low stretching frequency is due to the metal-to-ligand π -back donation.^[11] The IR spectra of **3**, **4** and **6** show two resonance signals at 1719–1749 and 2160–2196 cm⁻¹ arising from stretching of the coordinated and the uncoordinated C=C bonds. The dinuclear complexes **5** and **7** show only a single peak at 1758 and 1705 cm⁻¹ for v(C=C), respectively. This indicates that both C=C bonds in the complexes are equivalent.

(B) Structures

The complexes 2, 4, and 5 were characterized by singlecrystal X-ray diffraction analysis, while crystal structures of $1^{[12]}$ and $3^{[6b]}$ have been previously reported by other research groups (Table 3). The selected bond lengths and angles are listed in Table 1.

$(dppp)Pt[(1,2-\eta^2)-PhC_2Ph] (2)$

There are two independent molecules 2a and 2b of very similar structure in a unit cell of crystal 2. THF (Figure 1 for structure of 2a).

Like the reported structure of 1, complex 2 displays an approximate $C_{2\nu}$ symmetry. The acetylene bond length (C1–C1A) [1.301(7) Å] is significant longer than the average C=C bond length (ca. 1.2 Å). This indicates a weakening of the bond due to σ -donation from the acetylene to the metal and π -back donation from the metal to the acetylene. The Pt center adopts a distorted square-planar coordination geometry with a small dihedral angle of 2.98° between the two C1-Pt1-C1A and P1-Pt1-P1A triangles. The Pt-C and the Pt-P bond lengths are normal. Similar to 1, the linear C2-C1=C1A-C2A backbone is distorted with the C2-C1-C1A angle being 144.5(2)°. It is slightly smaller

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2a		4		5	
Distances [Å]					
Pt1–C1	2.041(3)	Pt1–C2	2.043(4)	Pt1–C1	2.034(3)
Pt1–P1	2.2705(9)	Pt1–C1	2.044(4)	Pt1–C2	2.051(3)
C1–C1A	1.301(7)	Pt1–P1	2.2629(10)	Pt1–P1	2.2478(9)
C1–C2	1.464(5)	Pt1–P2	2.2686(10)	Pt1–P2	2.2581(9)
		C1-C2	1.299(6)	Pt2–C4	2.017(3)
		C1-C5	1.463(6)	Pt2–C3	2.063(3)
		C2–C3	1.393(6)	Pt2–P3	2.2423(8)
		C3–C4	1.201(6)	Pt2–P4	2.2755(9)
		C4-C6	1.433(6)	C1–C2	1.303(5)
				C1–C5	1.451(5)
				C2–C3	1.411(4)
				C3–C4	1.296(5)
				C4–C6	1.454(5)
Angles [°]	25.2(2)		25.05(1.0)		25.20(12)
CIA-PtI-CI	37.2(2)	C2-PtI-CI	37.05(16)	CI-PtI-C2	37.20(13)
CI-PtI-PIA	150.4/(10)	C2-Pt1-P1	155.79(13)	CI-PtI-PI	118.33(10)
CI-PtI-PI	113.35(10)	CI-PtI-PI	118.81(11)	C2-Pt1-P1	155.45(10)
PI-PtI-PIA	96.02(5)	C2-Pt1-P2	111.48(12)	CI-PtI-P2	150.64(10)
CIA-CI-C2	144.5(2)	CI-PtI-P2	148.40(11)	C2-Pt1-P2	113.44(10)
C2-CI-Pt1	144.0(3)	PI-PtI-P2	92.44(4)	PI-PtI-P2	91.00(3)
CI-CIA-PtI	/1.42(10)	C2-C1-C5	13/./(4)	C4-Pt2-C3	37.02(13)
		C2-CI-PtI	/1.5(2)	C4–Pt2–P3	109.14(10)
		C5-CI-Pti	150.1(3)	C3-Pt2-P3	145.49(10)
		C1-C2-C3	146./(4)	C4-Pt2-P4	154.86(10)
		C1-C2-Pt1	/1.5(2)	C3-Pt2-P4	118.57(10)
		C3-C2-Pt1	141.3(3)	P3-Pt2-P4	95.76(3)
		C4-C3-C2	1/4./(5)	C2-C1-C5	138.6(3)
		C3-C4-C6	1/6.5(5)	C2–C1–Pt1	/2.1(2)
				C5–C1–Pt1	149.3(3)
				CI-C2-C3	146.8(3)
				CI-C2-Pt1	70.7(2)
				C3–C2–Pt1	142.0(3)
				C4–C3–C2	146.4(3)
				C4–C3–Pt2	69.6(2)
				C2–C3–Pt2	144.0(3)
				C3–C4–C6	138.6(3)
				C3–C4–Pt2	73.4(2)
				C6–C4–Pt2	147.6(2)



Figure 1. ORTEP diagram (thermal ellipsoid = 50%) of **2a**. H atoms and solvent molecules are omitted; C3 and C3X represent two positions of the disordered carbon atom, with 80% and 20% occupancy, respectively.

than the corresponding angles of 140 and 139° in **1**. The phenyl rings and the coordination triangle C1–Pt1–C1A are not coplanar, showing a dihedral angle of 26.89°.

$(dppp)Pt[(1,2-\eta^2)-PhC_4Ph] (4)$

The molecular structure of complex **4** (Figure 2) is similar to that of $\{[(PPh_3)_2Pt](PhC_4Ph)\}$ (3) reported by Deeming.^[6b] The lengths of the coordinated C=C bond (C1–C2) and the uncoordinated one (C3–C4) are 1.299(6) and 1.201(6) Å.

The coordination geometry at the Pt center in **4** is also nearly planar with the dihedral angle between triangles of C1–Pt1–C2 and P1–Pt1–P2 being 4.31°. The two Pt–C and Pt–P bond lengths are almost identical [Pt1–C1, 2.044(4) Å; Pt1–C2, 2.043(4) Å; Pt1–P1, 2.2629(10) Å; Pt1–P2, 2.2686(10) Å]. While the C5–C1–C2–C3 linkage is bent [\angle C5–C1–C2 137.7(4)°; \angle C1–C2–C3 146.7(4)°] like that in **2a**, the uncoordinated triple bond remains linear [\angle C2–C3– C4 = 174.7(5)°; \angle C3–C4–C6 176.5(5)°]. The dihedral angle between the coordination triangle of C1–Pt1–C2 and the adjacent phenyl ring of the acetylene is 18.36°.

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Figure 2. ORTEP diagram (thermal ellipsoid = 50%) of **4**. H atoms and solvent molecules are omitted.



Figure 3. (a) ORTEP diagram (thermal ellipsoid = 50%) of 5. H atoms and solvent molecules are omitted; (b) a side view showing the staggered conformation of 5.

$[(dppp)Pt]_{2}[\{\mu-(1,2-\eta^{2}):(3,4-\eta^{2})-PhC_{4}Ph\}]$ (5)

The molecular structure of complex 5 is shown in Figure 3. The butadiyne is coordinated to the two Pt atoms in μ -(1.2- η^2):(3,4- η^2) mode. Both Pt atoms show nearly square-planar coordination geometry. The C1-C2-C3-C4 backbone of the butadiyne shows a gauche conformation with a torsion angle of 94.79°. Similar conformation has been observed in the μ -(1,2- η^2):(3,4- η^2)-butadiyne complexes (PvCl₄W)₂(Me₃SiC=CC=CPh),^[8d] (Cp₂V)₂(Me₃Si- $C \equiv CC \equiv C - SiMe_3$,^[8e] and $[(R_2PCH_2CH_2PR_2)Ni]_2$ - $(R'C \equiv CC \equiv CR')^{[8f]} (R = iPr, R' = H \text{ or } R = tBu, R' = Ph)$ which display a torsion angle of 74-98°. The two Pt atoms are related by a C2-rotation. The C1-Pt1-C2 and C3-Pt2-C4 metallacycles show a gauche conformation with a dihedral angle of 86.01°. The lengths of the two acetylene bonds are 1.303(5) Å (C1-C2) and 1.296(5) Å (C3-C4), similar to the acetylene bond lengths observed in 2a and 4.

Notably, the "inner" Pt–C bonds, Pt1–C2 [2.051(3) Å] and Pt2–C3 [2.063(3) Å] and the "inner" Pt–P bonds, Pt1– P2 [2.2581(9) Å] and Pt2–P4 [2.2755(9) Å], are slightly but consistently longer than the "outer" Pt1–C1 [2.034(3) Å], Pt2–C4 [2.017(3) Å], and Pt1–P1 [2.2478(9) Å] and Pt2–P3 [2.2423(8) Å], respectively. Such differences could be caused by the steric repulsions between two neighboring dppp ligands. Similar to compounds **1**–**4**, the carbon atoms at the two ends of the acetylene bond are bent away from the metal atom. The phenyl rings of the butadiyne are almost coplanar with the PtC₂ unit, showing dihedral angles of 15.14 and 16.95°.

³¹P-NMR Spectroscopy

The ³¹P NMR spectra of all the complexes are consistent with the X-ray crystal structures of the complexes. The spectra of 1 and 2 show only two singlets at $\delta = 27.07$ and 4.11 with Pt satellites (${}^{1}J_{\text{Pt-P}} = 3448$ and 3155 Hz, respectively), and the spectrum of 3 shows two doublets of triplets at $\delta = 26.53$ and 26.19 ppm (${}^{1}J_{\text{Pt-P}} = 3521$ and 3456 Hz, ${}^{2}J_{\text{P-P}}$ = 22.9 Hz). The spectra of **4** and **6** show similar [AB]₂ splitting patterns. On the other hand, the spectrum of 5 is poorly resolved, because of the similar chemical shifts of different P atoms in the complexes (4.18 and 3.94 ppm, ${}^{2}J_{P-P} = 26.7$ Hz). In the spectrum of 7 the signals of the two phosphorus atoms are isochronous at δ = 8.54 ppm with very close ${}^{1}J_{\text{Pt-P}}$ (3227 and 3258 Hz). Although the X-ray crystal structures of 6 and 7 are not available, the similar NMR spectra suggest the molecular structures of 6 and 7 should resemble their PhC₄Ph counterparts, 4 and 5, respectively.

(C) Absorption Spectroscopy

The UV/Vis absorption spectra of complexes 1, 2, and the parent ligand diphenylacetyleme are shown in Figure 4. The ligand displays intense ($\varepsilon > 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) vibronic absorptions at 250–310 nm. Similar vibronic bands are ob-



Figure 4. UV/Vis absorption spectra of complexes 1, 2, and ligand PhC_2Ph in CH_2Cl_2 at room temperature.

served in the spectrum of **1**. In addition, the spectrum displays a broad and moderately intense absorption ($\varepsilon = 1-3.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) ranging from 310–400 nm. No vibronic structure is observed in the spectrum of **2**. Instead the spectrum shows a broad and intense band peaked at 270 nm ($\varepsilon_{\text{max}} = 2.34 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and a broad intense absorption at 300–420 nm. The latter absorption consists of more than one band, showing a peak at 327 nm ($\varepsilon_{\text{max}} = 1.38 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and a shoulder at ca. 355 nm ($\varepsilon = 9.1 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$).

The absorption spectrum of the ligand PhC₄Ph shows a clear vibronic structured band at 270–340 nm with a progression of 2000 cm⁻¹ which should be associated with the vibration of the C=C bond in the $\pi\pi^*$ excited state (Figure 5). The three complexes exhibit very intense absorption around 250 nm with no distinct vibronic peak. While the parent ligand does not absorb beyond 350 nm, the complexes display broad intense absorption bands extending to 450 (**3** and **4**) or 500 nm (**5**). The low energy absorption



Figure 5. UV/Vis absorption spectra of complexes 3, 4, 5, and ligand PhC_4Ph in CH_2Cl_2 at room temperature.

bands of **3** and **4** maximize at 370 nm ($\varepsilon_{max} = 9 \times 10^3 \text{ m}^{-1} \text{ cm}^{-1}$) and 374 nm ($\varepsilon_{max} = 1.09 \times 10^4 \text{ m}^{-1} \text{ cm}^{-1}$), respectively. The low energy absorption ($\lambda_{max} \approx 360 \text{ nm}$, $\varepsilon_{max} = 2.31 \times 10^4 \text{ m}^{-1} \text{ cm}^{-1}$) of **5** is more intense than that of **3** and **4**.

The absorption spectra of **6**, **7**, and CH₃C₄CH₃ are shown in Figure 6. Unlike PhC₂Ph and PhC₄Ph, the spectrum of CH₃C₄CH₃ shows little absorption at wavelengths longer than 250 nm ($\varepsilon < 200 \text{ M}^{-1} \text{ cm}^{-1}$). However, the spectra **6** and **7** show intense absorption bands around 250 nm and a less intense band at ca. 320 nm ($\varepsilon_{\text{max}} = 4.3 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) and 315 nm ($\varepsilon_{\text{max}} = 1.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), respectively.



Figure 6. UV/Vis absorption spectra of complexes 6, 7, and $CH_3C_4CH_3$ in CH_2Cl_2 at room temperature.

(D) Emission Spectroscopy

Table 2 summarizes the photophysical data of the complexes. The complexes are all not luminescent in degassed solution at room temperature. On the other hand, the solids of 1–5 are emissive at room temperature, showing two emission bands at 380–550 nm and 520–800 nm (Figure 7). The lifetimes (τ) of the higher energy emissions are shorter than the detection limit of our nanosecond laser flash photolysis set-up (<0.1 µs), but the 520–800 nm emissions show long lifetimes ($\tau = 1.57$ –3.86 µs).

Table 2. Photophysical data of the acetylene-Pt complexes.

	Emission (in EtOH, frozen at 77 K) λ_{max} [nm] (τ [µs])	Emission (solid state at 298 K) λ_{max} [nm] (τ [µs])
1	447 (<0.1), 547 (58.32)	446 (<0.1), 562 (3.86)
2	429 (<0.1), 570 (39.97)	443 (<0.1), 588 (2.19)
3	404 (<0.1), 589 (21.76)	457 (<0.1), 597 (2.72)
4	475 (<0.1), 622 (10.07)	459 (<0.1), 617 (1.57)
5	468 (<0.1), 605 (5.65)	458 (<0.1), 630 (too weak to be measured)
6	490 (19.00)	No emission
7	518 (29.20)	No emission



Figure 7. Solid-state emission spectra of complexes 1-5 at room temperature [a: intensities of the emission maximum in the low energy region (550–700 nm) are normalized; asterisks at ca. 485 and 529 nm denote instrumental artifacts]. The excitation wavelength is 320 nm.

The energy of the long-lived emissions of PhC₄Ph complexes **3**, **4**, and **5** ($\lambda_{max} = 594-630$ nm) is lower than PhC₂Ph complexes **1** ($\lambda_{max} = 562$ nm) and **2** ($\lambda_{max} = 588$ nm). Apart from the acetylene, the emission energy is also affected by the ancillary phosphane atoms: the PPh₃containing complexes **1** and **3** emit at slightly higher energy than their dppp counterparts **2** and **4**.

The emission spectra of 77 K frozen EtOH solutions of **1** and **2** are shown in Figure 8. Excitation at 320 nm leads to relatively weak emissions of short lifetimes ($\tau < 0.1 \,\mu$ s) located at 350–500 nm. In addition, the spectra of **1** and **2** display more intense lower energy emissions of long lifetimes at 547 nm ($\tau = 58.32 \,\mu$ s) and 570 nm ($\tau = 39.97 \,\mu$ s), respectively.



Figure 8. 77 K frozen ethanol solution emission spectra of complexes 1 and 2. The excitation wavelength is 320 nm.

The lower energy emissions show vibronic shoulders. The spacing is estimated at 1750 cm^{-1} in the spectrum of **1**.

The emission spectra of frozen solutions of **3**, **4**, and **5** at 77 K (supporting materials) also show two bands at 380–550 and 520–750 nm. Similar to the solid-state emission, the energy of the lower energy luminescence ($\lambda_{max} = 590-620$ nm) is slightly lower than the corresponding emissions of **1** and **2**. The lifetime of the low energy emissions ($\tau = 5.65-21.76 \,\mu$ s) is much longer than that of the higher energy ones ($\tau < 0.1 \,\mu$ s).

Unlike the PhC₄Ph and PhC₂Ph complexes, **6** and **7** are not emissive in the solid state at room temperature. At 77 K, the solids show weak emission at ca. 500 nm with τ of 5.10 µs (**6**) and 3.25 µs (**7**). The frozen solution spectra display similar emissions at 490 nm (**6**, $\tau = 19.00$ µs) and 518 nm (7, $\tau = 29.20$ µs) (Figure 9). The emissions of **6** and 7 are far less intense than those of **1–5**.



Figure 9. 77 K frozen ethanol solution emission spectra of complexes 6 and 7. The excitation wavelength is 320 nm.

Spectroscopic Assignments

In previous spectroscopic studies on acetylene-Pt⁰ complexes, the low energy absorptions, which were absent in the spectra of the free acetylenes, were assigned to the Pt(5d)→acetylene(π^*) charge transfer transition.^[7a,7c] This assignment was further supported by semi-empirical calculations showing that the HOMO and LUMO are mainly composed of the d_{z²}-orbital and acetylene π^* -orbital.^[7a] Likewise, the complexes 1–7 all exhibit intense absorption bands that are lower in energy than the ligand absorptions.

Scheme 2 shows a qualitative molecular orbital of acetylene-Pt complexes constructed from orbital interactions between a two-coordinate phosphane-Pt⁰ and a bent acetylene.

Three metal orbitals d_{z^2} , d_{xz} , and $d_{x^2-y^2}$ are destabilized by interacting with either the π_{x^-} or the π_z -orbital of the acetylenes. The d_{z^2} -orbital is expected to be the HOMO of the complexes as its energy is raised by the strong antibonding interactions with the π_z -orbital. Similarly, the $d_{x^2-y^2}$ or-





bital is involved in σ -interaction with the π_z -orbital but the interactions should be weak because of the poor overlap. The d_{xz} is in the correct symmetry to overlap with the π_x -orbital. On the other hand, the d_{yz} -orbital should be strongly stabilized via π -back bonding with the π_z^* -orbital. The d_{yx} -orbital is involved in δ -interactions with the π_x^* -orbital and should be slightly lowered in energy.

The π_z^* -orbital of the acetylene, strongly destabilized by the back bonding, should be higher energy than the π_x^* orbital which is slightly destabilized by the weak δ -interactions. In this molecular orbital picture, the lowest energy allowed Pt→acetylene transition is the ${}^{1}(d_{z^{2}}\rightarrow\pi_{x}^{*})$ transition. The ${}^{1}(d_{xz} \rightarrow \pi_{x}^{*})$ and ${}^{1}(d_{x^{2}-\nu^{2}} \rightarrow \pi_{x}^{*})$ transitions should be close in energy to the ${}^{1}(d_{z^{2}} \rightarrow \pi_{x}^{*})$. Because of the mixing between the metal and ligand orbitals, these transitions have some intraligand character. Especially the ${}^{1}(d_{xz} \rightarrow \pi_{x}^{*})$ transition, which could mix with the ${}^{1}(\pi_{x} \rightarrow \pi_{x}^{*})$ transition, should be more intense than the other two transitions. Apart from the Pt \rightarrow acetylene transition, a Pt \rightarrow P(d π^*) charge transfer from Pt to the $d\pi^*$ -orbitals of the phosphane atoms is also possible. Gray showed that the complex Pt⁰(dppp)₂ exhibited an intense Pt($d_{x^2-v^2}, d_{z^2}$) \rightarrow (d $\sigma^*, d\pi^*$) charge transfer absorption ($\varepsilon_{max} = 24,000 \text{ M}^{-1} \text{ cm}^{-1}$) at 360 nm.^[13] As PhC₂Ph and PhC₄Ph are better π -acceptors and weaker σ -donors than dppp, it is likely that the $Pt \rightarrow P(d\pi^*)$ transitions in the present complexes locate at wavelengths shorter than 360 nm in view of the position and energy of the very intense bands peaked at ca. 320 nm in the spectra of 2, 6, and 7. Both position and intensity of the absorption bands are consistent with the $Pt \rightarrow P(d\pi^*)$ transition.

The low energy absorption of the complexes at wavelengths longer than 320 nm should belong to the $Pt \rightarrow P(d\pi^*)$ and $Pt \rightarrow acetylene(\pi_x^*)$ transitions. The order of these MLCT transitions primarily depends on the energy gap between the d-orbitals and π_x^* -orbitals. Results of semi-empirical calculations show that the HOMO and the LUMO of the acetylene are mainly composed of π_x and π_x^* of the acetylene, respectively. The HOMO-LUMO gap is 8.25, 8.38, and 10.48 eV for PhC_4Ph , PhC_2Ph , and $CH_3C_4CH_3$, respectively (supporting information), and is consistent with the order of the $\pi \rightarrow \pi^*$ absorption energy of the acetylenes. Because of the π -conjugation, the order of the LUMO energy is PhC_4Ph (-0.65) $< PhC_2Ph$ (-0.51 eV) $< CH_3C_4CH_3$ (0.73 eV). On the other hand, the HOMOs of PhC₄Ph and PhC₂Ph have almost the same energy (-8.89 eV) and are higher energy than the HOMO of $CH_3C_4CH_3$ (-9.75 eV). Although the acetylenes in the complexes are distorted from linearity, the energy order of the HOMOs and LUMOs should be the same as that of the free ligands. Accordingly, the Pt \rightarrow acetylene(π_x^*) MLCT transition energy of the complexes should follow the order 3, 4, 5 < 1, 2 < 6, 7. The same trend is observed in the absorption of the complexes. Given their low-lying π_x^* -orbitals, the Pt \rightarrow acetylene(π_x^*) transitions in 1, 2, 3, 4, and 5 should be lower in energy than the $Pt \rightarrow P(d\pi^*)$. In addition, it is reasonable to expect the MLCT transitions of 3 and 4 to be lower in energy than those of 1 and 2. Indeed, the MLCT absorption of the PhC₄Ph complexes extends to 500 nm while the PhC₂Ph complexes do not absorb beyond 400 nm. On the other hand, the energy of the Pt->acetylene(π_x^*) transition could be close to or even higher than that of the $Pt \rightarrow P(d\pi^*)$ for the complexes 6 and 7 as the π_{x}^{*} -orbitals of CH₃C₄CH₃ are high in energy.

The solid state and frozen solution emission spectra of 1-5 show emissions of short lifetimes at ca. 380-550 nm and of longer lifetimes at ca. 500-800 nm. The long lifetimes of the lower energy emission suggests that luminescence arises from a triplet excited state. It is further supported by the large Stoke shift between the absorption and the emission. The frozen solution spectrum of 1 shows a vibronic spacing of ca. 1750 cm⁻¹, that is close to the ground state stretching frequency of the coordinated acetylene. This suggests the excited state could be ³MLCT(π_x^*) arising from the Pt \rightarrow acetylene(π_x^*) excitation. The order of the emission energy is 3, 4, 5 < 2 < 1 and is in agreement with the energy of the π_x^* -orbitals of the complexes and hence the MLCT assignment. That the MLCT emission of 1 is slightly higher in energy than that of 2 could be due to the fact that the PPh₃ in 1 is a strong electron-acceptor and weaker electron-donor than the dppp in 2.

The short-lived 350–550 nm emission displayed by 1–5 could arise from an intraligand (acetylene) $\pi\pi^*$ excited state and/or a ³MLCT(d π^*). PhC₂Ph and PhC₄Ph fluoresce at 330 and 365 nm in solution, respectively (supporting information), while CH₃C₄CH₃ is not emissive. To a different extent, the metal–ligand interactions in the acetylene complexes stabilize the π_{x^-} and π_z -orbitals and destabilize the π_x^* - and π_z^* -orbitals. Accordingly, the lowest energy intrali-

gand $\pi_x \rightarrow \pi_x^*$ transition, and hence the corresponding $\pi\pi^*$ emission should be blue shifted from that of the free acetylene. Possibly, the higher energy emissions of the complexes come from a ³MLCT($d\pi^*$) that arises from the Pt \rightarrow P($d\pi^*$) transition. It should be noted that the complex Pt⁰(dppp)₂ exhibits ³MLCT($d\pi^*$) phosphorescence at 622 nm. As the Pt center in the acetylene complexes is less electron rich than the one in Pt⁰(dppp)₂, it is reasonable for the ³MLCT($d\pi^*$) emission to occur at a higher energy.

Unlike the other complexes, **6** and **7** are not luminescent at room temperature and show a single emission at low temperature. The emission energy is slightly higher than that of **1–5** by 1800–3800 cm⁻¹. Given the fact that the π_x^* -orbital of CH₃C₄CH₃ is about ca. 1.3 eV or 10000 cm⁻¹ higher than those of PhC₄Ph and PhC₂Ph, it is unlikely the emissive state in **6** and **7** is ³MLCT(π_x^*). The emissive excited state is therefore tentatively assigned to the ³MLCT($d\pi^*$).

Concluding Remarks

In this work, MLCT emission of a series of phosphanesupported acetylene-Pt⁰ complexes in both the solid state and frozen solution was observed. All of the complexes display intense charge transfer absorptions. Dual emissions are observed in the spectra of 1-5. The higher energy emission could arise from intraligand $\pi\pi^*$ and/or ³MLCT($d\pi^*$) excited states. It is demonstrated that the MLCT emission energy is subject to the electron-donating ability of the phosphane atom and the electronic structures of the acetylene. The lowest energy emissive excited state of 1-5 is assigned to ³MLCT(π_x^*) as the π_x^* -orbitals of PhC₄Ph and PhC₂Ph are substantially stabilized via conjugation with the phenyl rings. On the other hand, we assign the phosphorescence of 6 and 7 to $^{3}(d\pi^{*}\rightarrow Pt)$ transitions. It is believed that for the two complexes, the $d\pi^*$ -orbitals of dppp are lower in energy than the π_x^* -orbitals.

Experimental Section

General Methods: All reactions were carried out using standard Schlenk techniques. 1,4-diphenylbuta-1,3-diyne, PPh₃, dppp, NaBH₄, and N₂H₄·H₂O purchased from Aldrich, 2,4-hexa-1,3-diyne purchased from TCI, and PtCl₂ purchased from Oxkem were used without further purification. Diphenylacetylene and ethylene were obtained from Aldrich. All solvents used for syntheses and spectroscopic measurements were purified according to literature methods. Pt(CH₃CN)₂Cl₂ was prepared by refluxing PtCl₂ in a large excess of CH₃CN. *cis*-Pt(PPh₃)₂Cl₂ and Pt(dppp)Cl₂ were prepared by reacting 2 equiv. of PPh₃ and 1 equiv. of dppp, respectively, with Pt(CH₃CN)₂Cl₂ in CH₂Cl₂. (dppp)Pt[(1,2- η^2)-CH₂=CH₂] was prepared by reduction of Pt(dppp)Cl₂ in the presence of ethylene in ethanol. 1^[5a] and 3^[6b] were synthesized according to the reported methods. Their NMR spectra are identical to the reported ones.

Synthesis

(dppp)Pt[(1,2- η^2)-PhC₂Ph] (2): Pt(dppp)Cl₂ (0.26 g, 0.39 mmol) was added to a 30-mL ethanolic solution of diphenylacetylene (0.085 g, 0.42 mmol). Slow addition of NaBH₄ (0.1 g, 2.6 mmol) to

the mixture gave a pale yellow suspension. The reaction mixture was stirred overnight at room temperature. The yellow solid collected by filtration was washed with excess ethanol. Analytically pure product was obtained by recrystallization in THF/*n*-hexane. Yield: 0.25 g (80%). C₄₁H₃₆P₂Pt (785.8): calcd. C 62.7, H 4.6; found C 62.5, H 4.5. ¹H NMR (300 MHz, CDCl₃): δ = 7.66–6.96 (m, 30 H, Ph), 2.61–2.58 (m, 4 H, -CH₂-P-Pt-), 2.05–1.91 (m, 2 H, -C-CH₂-C-) ppm. ³¹P{¹H} NMR (121.5 MHz, CDCl₃): δ = 4.11 [¹*J*(PtP) = 3155 Hz] ppm. IR (KBr): v(C=C) = 1748 (w) cm⁻¹. ESI-MS (*m*/*z*, assignment): 786 [M]⁺. Single crystals of **2**·THF for X-ray diffraction analysis were obtained by slow diffusion of *n*-hexane into a concentrated THF solution of **2**.

(dppp)Pt[(1,2- η^2)-PhC₄Ph] (4): The procedures were similar to those for preparing 2. Yield: 70%. C₄₃H₃₆P₂Pt (809.8): calcd. C 63.8, H 4.5; found C 63.9, H 4.3. ¹H NMR (300 MHz, CDCl₃): δ = 7.74–7.01 (m, 30 H, Ph), 2.64–2.55 (m, 4 H, -CH₂-P-Pt-), 2.09– 1.94 (m, 2 H, -C-CH₂-C-) ppm. ³¹P{¹H} NMR (121.5 MHz, CDCl₃): δ = 4.87 [²J(PP) = 15.3 Hz, ¹J(PtP) = 3349 Hz], 3.20 [²J(PP) = 15.3 Hz, ¹J(PtP) = 3086 Hz] ppm. IR (KBr): v(C=C) = 2160 (m, uncoordinated), 1719 (m, coordinated) cm⁻¹. ESI-MS (*m*/*z*, assignment): 810 [M]⁺. Single crystals of 4 for X-ray diffraction analysis were obtained by slow diffusion of *n*-hexane into a concentrated CH₂Cl₂ solution of 4.

[(dpp)Pt]₂|μ-(1,2-η²):(3,4-η²)-PhC₄Ph] (5): 4 (0.11 g, 0.14 mmol) and 1 mol equiv. of Pt(dppp)(CH₂=CH₂) (0.086 g, 0.14 mmol) were added to diethyl ether (15 mL) and stirred at room temperature for 24 h. The pale yellow suspension was then filtered and washed with diethyl ether. The pale yellow crude product was recrystallized from THF/diethyl ether to give the pure product. Yield: 0.11 g (55%). C₇₀H₆₂P₄Pt₂ (1417.3): calcd. C 59.3, H 4.4; found C 59.2, H 4.4. ¹H NMR (300 MHz, C₆D₆): δ = 6.81–7.91 (m, 50 H, Ph), 2.24 (m, 8 H, -CH₂-P-Pt-), 1.61–1.68 (m, 4 H, -C-CH₂-C-) ppm. ³¹P{¹H} NMR (121.5 MHz, C₆D₆): δ = 4.18 [²*J*(PP) = 26.7 Hz, ¹*J*(PtP) = 3258 Hz], 3.94 [²*J*(PP) = 26.7 Hz, ¹*J*(PtP) = 3267 Hz] ppm. IR (KBr): v(C=C) = 1758 (m) cm⁻¹. ESI-MS (*m*/*z*, assignment): 1417 [M]⁺. Single crystals of **5** for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into a concentrated THF solution of **5**.

(dppp)Pt[(1,2-η²)-CH₃C₄CH₃] (6): Pt(dppp)(CH₂=CH₂) (0.108 g, 0.17 mmol) was treated with twofold excess of 2,4-hexadiyne (0.027 g, 0.34 mmol) in diethyl ether at room temperature for 24 h. The pale yellow suspension was then filtered and washed with a small amount of diethyl ether. The product was purified by recrystallization in THF/diethyl ether. Yield: 0.08 g (70%). C₃₃H₃₂P₂Pt (685.6): calcd. C 57.8, H 4.7; found C 57.5, H 4.5. ¹H NMR (300 MHz, C_6D_6): $\delta = 7.98-7.92$, 7.71-7.65 and 7.10-6.98 (m, 20 H, Ph), 2.76 [doublet of triplets, ${}^{3}J(PtH) = 39.7$ Hz, ${}^{4}J(PH)$ = 7.6 Hz, 3 H, CH₃ on the coordinated C=C], 2.15 (m, 4 H, -CH₂-P-Pt-), 1.90 [doublet of triplets, ${}^{5}J(PtH) = 18.8$ Hz, ${}^{6}J(PH) =$ 3.5 Hz, 3 H, CH₃ on the uncoordinated C=C], 1.62 (m, 2 H, -C-CH₂-C-) ppm. ³¹P{¹H} NMR (121.5 MHz, C₆D₆): δ = 8.47 [²J(PP) = 31.1 Hz, ${}^{1}J(PtP)$ = 3353 Hz], 7.29 [${}^{2}J(PP)$ = 31.1 Hz, ${}^{1}J(PtP)$ = 3124 Hz] ppm. IR (KBr): v(C=C) = 2196 w (uncoordinated), 1749 s (coordinated) cm⁻¹. ESI-MS (m/z, assignment): 686 [M]⁺.

[(dpp)Pt]₂[μ-(1,2-η²):(3,4-η²)-CH₃C₄CH₃] (7): The preparative procedures for 7 were similar to those for preparing 5. Yield: 40%. C₆₀H₅₈P₄Pt₂ (1293.2): calcd. C 55.7, H 4.5; found C 55.5, H 4.5. ¹H NMR (300 MHz, C₆D₆): δ = 8.06–8.00, 7.86–7.80 and 7.10–6.93 (m, 40 H, Ph), 2.51 (m, 6 H, CH₃), 2.26 (br., 8 H, -CH₂-P-Pt-), 1.74 (br., 4 H, -C-CH₂-C-) ppm. ³¹P{¹H} NMR (121.5 MHz, C₆D₆): δ = 8.54 [¹J(PtP) = 3227 and 3258 Hz] ppm. IR (KBr): v(C≡C) = 1705 (w) cm⁻¹. ESI-MS (*m/z*, assignment): 1293 [M]⁺.

FULL PAPER

Compound	2	4	5
Empirical formula	C ₄₅ H ₄₄ OP ₂ Pt	$C_{43}H_{36}P_2Pt$	$C_{70}H_{62}P_4Pt_2$
Formula weight	857.83	809.75	1417.26
Temperature [K]	295(2)	223(2)	223(2) K
Wavelength [Å]	0.71073	0.71073	0.71073 Å
Crystal system	orthorhombic	triclinic	monoclinic
Space group	Pnma	$P\bar{1}$	P2(1)/n
Unit cell dimensions (Å and deg)	a = 30.0064(15)	a = 10.7412(5)	a = 10.8152(7)
	b = 23.4345(12)	b = 12.6475(6)	b = 20.0454(12)
	c = 10.7582(5)	c = 13.7503(6)	c = 26.8225(17)
	$a = \beta = \gamma = 90$	a = 83.3900(10)	$a = \gamma = 90$
		$\beta = 88.0370(10)$	$\beta = 92.4740(10)$
		$\gamma = 66.3590(10)$	
Volume [Å ³]	7565.0(6)	1699.68(14)	5809.6(6)
Ζ	8	2	4
Calculated density [mg/m ³]	1.506	1.582	1.620
Absorption coefficient [mm ⁻¹]	3.828	4.252	4.963
<i>F</i> (000)	3440	804	2792
Crystal size [mm ³]	$0.38 \times 0.26 \times 0.20$	$0.40 \times 0.10 \times 0.08$	$0.50 \times 0.20 \times 0.20$
θ range for data collection [°]	1.61 to 27.50	1.77 to 25.00	1.52 to 30.01
	$-38 \le h \le 36, -30 \le k \le$	$-12 \le h \le 12, -15 \le k \le$	$-14 \le h \le 15, -28 \le k \le$
Index ranges	$30, -12 \le l \le 13$	$15, -16 \le l \le 16$	$26, -20 \le l \le 37$
Reflections collected	51463	18338	46864
Independent reflections	8897 [R(int) = 0.0408]	5990 [R(int) = 0.0271]	16579 [R(int) = 0.0317]
Max. and min. transmission	0.5148 and 0.3241	0.7272 and 0.2811	0.4368 and 0.1904
Data/restraints/parameters	8897/17/459	5990/0/556	16579/0/685
Goodness-of-fit on F^2	1.021	1.080	1.025
Final <i>R</i> indices $[I > 2 \operatorname{sigma}(I)]$	R1 = 0.0318, wR2 = 0.0664	R1 = 0.0276, wR2 = 0.0695	R1 = 0.0325, wR2 = 0.0752
<i>R</i> indices (all data)	R1 = 0.0461, wR2 = 0.0707	R1 = 0.0287, wR2 = 0.0702	R1 = 0.0440, wR2 = 0.0792
Largest diff. peak and hole [e Å ⁻³]	1.222 and -1.152	3.840 and -0.667	2.971 and -0.682

Table 3. Crystal data and structure refinements for compounds 2, 4, and 5.

Physical Measurements: Elemental analyses of all the compounds prepared were carried out in the microanalysis laboratory in the Department of Chemistry, the National University of Singapore. ¹H- and ³¹P{¹H}-NMR spectra were recorded at room temperature with a Bruker ACF 300 spectrometer. Electrospray ionization mass spectra (ESI-MS) were measured with a Finnigan MAT 731 LCQ spectrometer. IR spectra (KBr) were recorded using a Bio-Rad Win-IR spectrophotometer. UV/Vis absorption spectra were recorded with a Shimadzu UV-1601PC UV/Vis spectrophotometer. Emission spectra were recorded with a SPEX-Fluorolog2 model F111A1 fluorescence spectrofluorometer. The lifetimes were measured using the Quanta Ray DCR3 Nd:YAG laser with a pulsewidth of 8 ns and excitation wavelength of 355 nm. Sample solutions for 77 K frozen glass emission spectra measurement were prepared as follows: (i) a small amount of solid samples were added to ethanol solution; (ii) the solutions were then dissolved using the ultra-sonic bath; (iii) the solutions were filtered; (iv) the filtrates were introduced into a quartz tube; (v) the quartz tubes were immersed in liquid nitrogen in a quartz optical Dewar flask for measuring.

Molecular Orbital Calculations: The calculations were performed using the SPARTAN semiempirical program SGI/R10K, release 5.1.3, with geometry optimization. The model RHF/PM3 was used in the calculations.

X-ray Crystallography: The diffraction experiments were carried out with a Bruker AXS SMART CCD 3-circle diffractometer at T= 223 K (except that: T = 295 K for crystal 2·THF), 20- ω scan with a sealed tube at 23 °C using graphite-monochromated Mo- K_a radiation (λ = 0.71073 Å). The software used were: SMART^[14] for collecting frames of data, indexing reflection, and determination of lattice parameters; SAINT^[14] for integration of intensity of reflections and scaling; SADABS^[15] for empirical absorption correction; and SHELXTL^[16] for space group determination, structure solution, and least-squares refinements on $|F|^2$. The crystals were mounted at the end of glass fibers and used for the diffraction experiments. Anisotropic thermal parameters were refined for the rest of the non-hydrogen atoms. The hydrogen atoms were placed in their ideal positions. The X-ray crystal data and parameters used in structural refinements are summarized in Table 3.

CCDC-623835 (for 2), -623836 (for 4), and -623837 (for 5) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Molecular orbitals of the acetylenes, emission spectra of diphenylacetylene and 1,4-diphenyl-buta-1,3-diyne, emission spectra of frozen glass solutions of **3–5** at 77 K, syntheses and characterizations of **1** and **3**.

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