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Synthesis, Structural Characterization, and Luminescence Properties of Branched Palladium(II) and Platinum(II) Acetylide Complexes

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Three luminescent palladium(II) and platinum(II) acetylide complexes, $1,3\text{-}[\mathrm{Cl(PEt_3)_2PdC{\equiv}CC_6H_4C{\equiv}C}]_2\text{-}5\text{-}[(^i\mathrm{Pr})_3\mathrm{SiC{\equiv}C}]\mathrm{C_6H_3}$ and $1,3,5\text{-}[\mathrm{Cl(PEt_3)_2MC{\equiv}CC_6H_4C{\equiv}C}]_3\mathrm{C_6H_3}$ (M = Pd or Pt), have been synthesized by the reaction of the corresponding starting complexes, *trans*-$\mathrm{M(PEt_3)_2Cl_2}$ (M = Pd or Pt), with branched alkynyl ligands. Their crystal structures, together with their luminescence behavior, have been reported.

Introduction

There has been an increasing interest in the studies of hyperbranched and dendritic molecules due to their interesting physical,[1a] electrochemical,[1b] catalytic,[1c] nonlinear optical (NLO),[1d] and energy transfer properties[1e,f] as well as their potential application as the active layer of light-emitting diodes (LEDs).[2] Organometallic dendrimers have also aroused much attention in recent years owing to the presence of some of their unique and interesting properties which are inaccessible by their organic counterparts.[1a,3] The attractive advantage of organometallic dendrimers over their polymeric counterparts, particularly the one-dimensional rigid-rod polymers, lies in their precise molecular architecture, better solubility and processability, and their predetermined chemical composition. Recently, a growing number of branched alkynyl complexes of titanium,[4a] zirconium,[4b] chromium,[4c] iron,[4d] and ruthenium[4e] have been reported involving the use of various rigid multitopic alkynyl ligands as the organic backbone. Most organometallic dendrimers, however, are modified with metal atoms at the surface,[5] while those with metal moieties in every generation have so far been less explored due to a lack of appropriately designed building blocks.[1a,6] Recent works by Takahashi[7a−c] and Stang[7d] have shown that 1,3,5-triethynylbenzene could serve as versatile building blocks for platinum-containing organometallic dendrimers. Although the luminescence behavior of platinum(II) alkynyl complexes[8] and linear platinum alkynyl polymers[9] are known, corresponding studies on the hyperbranched and dendritic molecules have not been much explored.[10] With our recent interest in the search for luminescent metal alkynyl complexes as well as carbon-rich rigid-rod materials,[8b−e,11] we

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become interested in extending the work to investigate luminescence properties of hyperbranched molecules. Herein are reported the synthesis, structural characterization, and luminescence behavior of three branched palladium(II) and platinum(II) complexes containing the rigid conjugated arylalkynyl ligand 1,3,5-$(HC\equiv CC_6H_4C\equiv C)_3C_6H_3$ (**L1**),[4e] which is the extended version of 1,3,5-triethynylbenzene. Attempts have also been made to employ the tri(isopropyl)silyl-protected derivative 1,3-$(HC\equiv CC_6H_4C\equiv C)_2$-5-$[(^iPr)_3SiC\equiv C]C_6H_3$ (**L2**),[12] for the construction of dinuclear palladium(II) dendrimeric precursors.

Experimental Section

Materials and Reagents. *trans*-Dichlorobis(triethylphosphine)platinum(II) was obtained from Aldrich Chemical Co. *trans*-Dichlorobis(triethylphosphine)palladium(II) was prepared according to a literature method.[13] All solvents were purified and distilled using standard procedures before use.[14] All other reagents were of analytical grade and were used as received.

Synthesis of Palladium and Platinum Complexes. All reactions were performed under anaerobic and anhydrous conditions using standard Schlenk techniques under an inert atmosphere of nitrogen.

1,3-$[Cl(PEt_3)_2PdC\equiv CC_6H_4C\equiv C]_2$-5-$[(^iPr)_3SiC\equiv C]C_6H_3$ (1). *trans*-$Pd(PEt_3)_2Cl_2$ (248 mg, 0.60 mmol) was dissolved in THF (20 mL) containing copper(I) chloride (0.3 mg, 0.003 mmol) and NEt_3 (20 mL). **L2** (96.5 mg, 0.20 mmol) in 15 mL of THF was added dropwise at 0 °C, and the reaction mixture was stirred overnight at room temperature. The mixture was then filtered, and the solvent was removed under reduced pressure. The yellow solid residue was dissolved in CH_2Cl_2, and the solution was successively washed with aqueous ammonium chloride solution and deionized water. The organic fraction was then dried over anhydrous $MgSO_4$ and filtered. The dried organic fraction was then concentrated under reduced pressure and passed through a short column of basic aluminum oxide (50−200 μm) using CH_2Cl_2−petroleum ether (1:1, v/v) as the eluent. A yellow solution containing *trans*-$Pd(PEt_3)_2Cl_2$ was eluted out. **1** was eluted out with CH_2Cl_2 and was very pale yellow in color. Subsequent recrystallization from benzene−*n*-pentane afforded **1** as pale yellow crystals. Yield: 79%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ 1.14 (s, 21H, ^{i}Pr), 1.20 (vq, $J = 5$ Hz, 36H, $-CH_3$), 1.90−2.02 (m, 24H, $-CH_2-P$), 7.22 (d, 4H, $J_{HH} = 11$ Hz, aromatic H's on the peripheral phenyl rings), 7.38 (d, 4H, $J_{HH} = 11$ Hz, aromatic H's on the peripheral phenyl rings), 7.56 (s, 2H, aromatic H's on the central phenyl ring), 7.60 (s, 1H, aromatic H's on the central phenyl ring). ^{13}C NMR (75.5 MHz, CD_2Cl_2, 298 K, relative to Me_4Si): δ 8.36 (s, $-CH_3$), 11.28 (s, ^{i}Pr), 15.41 (t, $J_{C-P} = 19$ Hz, $-CH_2-P$), 18.67 (s, ^{i}Pr), 88.58, 90.79, 92.15 (s, acetylenic C's), 99.42 (t, $J_{C-P} = 16$ Hz, acetylenic C's), 105.32 (s, acetylenic C's), 106.63 (t, $J_{C-P} = 5$ Hz, acetylenic C's), 119.63, 124.00, 124.19, 124.62, 128.17, 130.65, 131.45, 133.94, 134.25 (s, aromatic C's). ^{31}P NMR (121.5 MHz, CD_2Cl_2, 298 K, relative to 85% H_3PO_4): δ 19.38 (s). IR (KBr disk, ν/cm^{-1}): 2112(s), 2209(w) $\nu(C\equiv C)$. UV−vis [λ/nm (ϵ/dm^3 mol^{-1} cm^{-1})]: CH_2Cl_2, 273 (62 530), 329 (101 010), 351 (104 540). Anal. Found: C, 58.16; H, 7.47. Calcd for **1**: C, 58.10; H, 7.35.

1,3,5-$[Cl(PEt_3)_2PdC\equiv CC_6H_4C\equiv C]_3C_6H_3$ (2). *trans*-$Pd(PEt_3)_2Cl_2$ (92 mg, 0.22 mmol) was dissolved in $HNEt_2$ (25 mL) [copper(I) chloride (0.35 mg, 0.0035 mmol)]. **L1** (26 mg, 0.057 mmol) was added, and the reaction mixture was stirred overnight at room temperature. The mixture was then filtered, and the solvent was removed under reduced pressure. CH_2Cl_2 was added to dissolve the yellow solid residue, and the solution was successively washed with aqueous ammonium chloride solution and deionized water. The organic fraction was then dried over anhydrous $MgSO_4$ and filtered. The dried organic fraction was then concentrated under reduced pressure and passed through a short column of basic aluminum oxide (50−200 μm) using CH_2Cl_2 as the eluent. The yellow fraction containing *trans*-$Pd(PEt_3)_2Cl_2$ was eluted out first. **2** was eluted out later and was very pale yellow in color. Subsequent recrystallization from benzene−*n*-pentane afforded **2** as pale yellow crystals. Yield: 49%. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K, relative to Me_4Si): δ 1.20 (vq, $J = 5$ Hz, 54H, $-CH_3$), 1.90−2.02 (m, 36H, $-CH_2-P$), 7.22 (d, 6H, $J_{HH} = 11$ Hz, aromatic H's on the peripheral phenyl rings), 7.40 (d, 6H, $J_{HH} = 11$ Hz, aromatic H's on the peripheral phenyl rings), 7.62 (s, 3H, aromatic H's on the central phenyl ring). ^{13}C NMR (125 MHz, CD_2Cl_2, 298 K, relative to Me_4Si): δ 9.02 (s, $-CH_3$), 16.13 (t, $J_{C-P} = 19$ Hz, $-CH_2-P$), 88.21, 92.13, 100.98, 106.84 (s, acetylenic C's), 120.08, 124.94, 129.11, 131.17, 132.12, 134.05 (s, aromatic C's). ^{31}P NMR (202 MHz, CD_2Cl_2, 298 K, relative to 85% H_3PO_4): δ 19.63 (s). IR (KBr disk, ν/cm^{-1}): 2111(s), 2209(w) $\nu(C\equiv C)$. UV−vis [λ/nm (ϵ/dm^3 mol^{-1} cm^{-1})]: CH_2Cl_2, 274 (78 640), 332 (160 100), 352 (174 500). Anal. Found: C, 55.00; H, 6.61. Calcd for **2**: C, 54.66; H, 6.69.

1,3,5-$[Cl(PEt_3)_2PtC\equiv CC_6H_4C\equiv C]_3C_6H_3$ (3). *trans*-$Pt(PEt_3)_2Cl_2$ (335 mg, 0.67 mmol) was dissolved in benzene (40 mL) containing copper(I) iodide (1 mg, 0.005 mmol) and diethylamine (20 mL) and cooled to 0 °C. To this mixture was added **L1** (50 mg, 0.11 mmol) in benzene (20 mL) in a dropwise manner. The reaction mixture was then stirred under nitrogen for 24 h at room temperature, after which it was filtered and the solvent was removed under reduced pressure. The yellow solid residue was dissolved in CH_2Cl_2 and washed successively with aqueous ammonium chloride solution and deionized water. The organic fraction was then dried over anhydrous $MgSO_4$ and filtered. With purification using column chromatography (basic aluminum oxide, 50−200 μm), the excess *trans*-$Pt(PEt_3)_2Cl_2$ was first eluted out with CH_2Cl_2−petroleum ether (1:1, v/v), followed by the elution of **3** with CH_2Cl_2. Subsequent recrystallization with CH_2Cl_2−*n*-hexane afforded **3** as colorless crystals. Yield: 33%. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K, relative to Me_4Si): δ 1.20 (vq, $J = 5$ Hz, 54H, $-CH_3$), 1.93−2.20 (m, 36H, $-CH_2-P$), 7.17 (d, 6H, $J_{HH} = 10$ Hz, aromatic H's on the peripheral phenyl rings), 7.35 (d, 6H, $J_{HH} = 10$ Hz, aromatic H's on the peripheral phenyl rings), 7.62 (s, 3H, aromatic H's on the central phenyl ring). ^{13}C NMR (125 MHz, CD_2Cl_2, 298 K, relative to Me_4Si): δ 7.55 (s, $-CH_3$), 14.28 (t, $J_{C-P} = 17$ Hz, $-CH_2-P$), 87.11, 88.10, 90.68, 101.41 (s, acetylenic C's), 118.76, 124.04, 129.24, 130.57, 131.12, 133.25 (s, aromatic C's). ^{31}P NMR (202 MHz, CD_2Cl_2, 298 K, relative to 85% H_3PO_4): δ 16.33 (s, $J_{Pt-P} = 2383$ Hz). ^{195}Pt NMR (107 MHz, CD_2Cl_2, 298 K, relative to H_2PtCl_6): δ −4412 (t, $J_{Pt-P} = 2383$ Hz). IR (KBr disk, ν/cm^{-1}): 2114(s), 2205(w) $\nu(C\equiv C)$. Positive ion FAB-MS: m/z 1848 ($[M]^+$). UV−vis [λ/nm (ϵ/dm^3 mol^{-1}cm^{-1})]: CH_2Cl_2, 290 sh (45 190), 342 sh (168 300), 362 (194 170). Anal. Found: C, 47.39; H, 5.93. Calcd for **3**: C, 47.67; H, 6.06.

Physical Measurements and Instrumentation. UV−visible spectra were obtained on a Hewlett-Packard 8452A diode array spectrophotometer, IR spectra as KBr disks on a Bio-Rad FTS-7 Fourier transform infrared spectrophotometer (4000−400 cm^{-1}), and steady-state excitation and emission spectra on a Spex Fluorolog-2 Model F 111 fluorescence spectrophotometer equipped with a Hamamatsu R-928 photomultiplier tube. Low-temperature (77 K) spectra were

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recorded by using an optical Dewar sample holder. ^{1}H NMR spectra were recorded on a Bruker DPX-300 (300 MHz) Fourier transform NMR spectrometer, while ^{13}C{^{1}H}, ^{31}P{^{1}H}, and ^{195}Pt{^{1}H} NMR spectra were recorded on either a Bruker DPX-300 (300 MHz) or a Bruker DPX-500 (500 MHz) Fourier transform NMR spectrometer. Chemical shifts (δ ppm) of ^{1}H and ^{13}C NMR spectra were recorded relative to tetramethylsilane (Me_4Si), while that of ^{31}P and ^{195}Pt NMR spectra were recorded relative to 85% H_3PO_4 and H_2PtCl_6, respectively. Positive ion FAB mass spectra were recorded on a Finnigan MAT95 mass spectrometer. Elemental analyses of the new complexes were performed on a Carlo Erba 1106 elemental analyzer at the Institute of Chemistry, Chinese Academy of Sciences.

All solutions for photophysical studies were degassed on a high-vacuum line in a two-compartment cell consisting of a 10 mL Pyrex bulb and a 1 cm path length quartz cuvette and sealed from the atmosphere by a Bibby Rotaflo HP6 Teflon stopper. The solutions were subjected to at least four freeze−pump−thaw cycles.

Crystal Structure Determination. Crystals of **1** were obtained by recrystallization from benzene−*n*-pentane. *Crystal data*: [$C_{61}H_{92}SiP_4Cl_2Pd_2$], $M = 1261.08$, triclinic, space group $P\bar{1}$ (No. 2), $a = 13.393(2)$ Å, $b = 14.946(2)$ Å, $c = 19.253(3)$ Å, $\alpha = 80.43(2)°$, $\beta = 83.98(2)°$, $\gamma = 68.35(2)°$, $V = 3528(1)$ Å^3, $Z = 2$, $D_c = 1.187$ g cm^{-3}, μ(Mo Kα) = 7.25 cm^{-1}, $F(000) = 1316$, $T = 301$ K. A colorless crystal of dimensions 0.35 × 0.15 × 0.07 mm inside a glass capillary was used for data collection at 28 °C on a MAR diffractometer with a 300 mm image plate detector using graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). Data collections were made with 3° oscillation (105 images) at 120 mm distance and 600 s exposure. The images were interpreted and intensities integrated using the program DENZO.[15] A total of 7366 unique reflections were obtained from a total of 44 951 measured reflections ($R_{int} = 0.055$). A total of 3827 reflections with $I > 3\sigma(I)$ were considered observed and used in the structural analysis. These reflections were in the range of h: 0 to 15; k: −15 to 16; l: −20 to 22 with $2\theta_{max} = 49.8°$. The space group was determined on the basis of a statistical analysis of intensity distribution, the successful refinement of the structure was solved by Patterson methods and expanded by Fourier methods (PATTY[16]), and refinement was by full-matrix least-squares using the software package TeXsan[17] on a Silicon Graphics Indy computer. A crystallographic asymmetric unit consists of one molecule. In the least-squares refinement, nine non-H atoms were refined anisotropically, all 61 C atoms were refined isotropically, and 92 H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. Convergence for 326 variable parameters by least-squares refinement on F with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.045F_o^2)^2]$ for 3827 reflections with $I > 3\sigma(I)$ was reached at $R = 0.103$ and $wR = 0.135$ with a goodness of fit of 3.32. $(\Delta/\sigma)_{max} = 0.05$ for atoms refined anisotropically. The final difference Fourier map was featureless, with maximum positive and negative peaks of 1.20 and 0.74 e Å^{-3}, respectively. Selected bond distances and angles are summarized in Table 1. Tables of crystal data, atomic coordinates, and thermal parameters are given as Supporting Information.

Crystals of **2** were obtained by recrystallization from benzene−*n*-pentane. *Crystal data*: [$C_{72}H_{105}P_6Cl_3Pd_3$], $M = 1582.02$, trigonal, space group $P\bar{3}$ (No. 147), $a = 19.947(3)$ Å, $c = 14.09(1)$ Å, $V = 4855(3)$ Å^3, $Z = 2$, $D_c = 1.082$ g cm^{-3}, μ(Mo Kα) = 9.09 cm^{-1}, $F(000) = 1632$, $T = 301$ K. A yellow crystal of dimensions 0.30 × 0.10 × 0.07 mm in a glass capillary was used for data collection at 28 °C on a Rigaku AFC7R diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) using $\omega-2\theta$ scans with ω-scan angle $(0.63 + 0.35 \tan\theta)°$ at a scan speed of 8.0 deg min^{-1} (up to 6 scans for reflection with $I < 15\sigma(I)$). Unit-cell dimensions were determined on the basis of the setting angles of 25 reflections in the 2θ range of 30.5−34.4°. Intensity data (in the range of $2\theta_{max} = 50°$; h: −20 to 20; k: 0 to 23; l: 0 to 16 and three standard reflections measured after every 300 reflections showed no decay) were corrected for Lorentz and polarization effects, and empirical absorption corrections were based on the ψ-scan of five strong reflections (minimum and maximum transmission factors 0.952 and 1.000). A total of 6222 reflections were measured, of which 5699 were unique and $R_{int} = 0.021$. A total of 3385 reflections with $I > 3\sigma(I)$ were considered observed and used in the structural analysis. The space group was determined on the basis of a statistical analysis of intensity distribution, and the successful refinement of the structure was solved by direct methods (SIR92[18]), expanded by the Fourier method, and refined by full-matrix least-squares using the software package TeXsan[17] on a Silicon Graphics Indy computer. One crystallographic asymmetric unit consists of one-third of a molecule. In the least-squares refinement, all 28 non-H atoms were refined anisotropically, and 35 H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. Convergence for 253 variable parameters by least-squares refinement on F with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.030F_o^2)^2]$, for 3385 reflections with $I > 3\sigma(I)$ was reached at $R = 0.069$ and $wR = 0.120$ with a goodness-of-fit of 4.41. $(\Delta/\sigma)_{max} = 0.05$ except for the H atoms. The final difference Fourier map was featureless, with maximum positive and negative peaks of 1.17 and 0.79 e Å^{-3}, respectively. Selected bond distances and angles are summarized in Table 1. Tables of crystal data, atomic coordinates, and thermal parameters are given as Supporting Information.

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for 1−3

1	Pd(1)−C(1)	1.90(2)	Pd(1)−Cl(1)	2.345(5)
	Pd(1)−P(1)	2.296(8)	Pd(1)−P(2)	2.298(8)
	Pd(2)−P(3)	2.304(9)	Pd(2)−P(4)	2.301(9)
	Pd(2)−Cl(2)	2.342(6)	Pd(2)−C(26)	1.92(2)
	C(1)−C(2)	1.23(2)	C(9)−C(10)	1.23(2)
	C(17)−C(18)	1.20(2)	C(28)−Si(1)	1.84(2)
	C(25)−C(26)	1.24(3)	C(27)−C(28)	1.21(2)
	P(1)−Pd(1)−Cl(1)	91.9(3)	P(2)−Pd(1)−Cl(1)	89.2(3)
	C(1)−Pd(1)−Cl(1)	179.5(6)	P(1)−Pd(1)−P(2)	176.0(3)
	Pd(1)−C(1)−C(2)	177(1)	Pd(2)−C(26)−C(25)	174(2)
	C(1)−C(2)−C(3)	175(2)	C(15)−C(27)−C(28)	178(2)
	C(22)−C(25)−C(26)	171(3)		
2	Pd(1)−C(1)	1.97(1)	Pd(1)−Cl(1)	2.338(3)
	Pd(1)−P(1)	2.312(4)	Pd(1)−P(2)	2.232(4)
	C(1)−C(2)	1.18(1)	C(9)−C(10)	1.17(1)
	P(1)−Pd(1)−Cl(1)	90.0(1)	P(2)−Pd(1)−Cl(1)	92.3(1)
	C(1)−Pd(1)−Cl(1)	178.0(4)	P(1)−Pd(1)−P(2)	176.7(2)
	C(1)−C(2)−C(3)	176(1)		
3	Pt(1)−C(1)	1.95(2)	Pt(1)−Cl(1)	2.358(6)
	Pt(1)−P(1)	2.297(8)	Pt(1)−P(2)	2.276(9)
	C(1)−C(2)	1.14(3)	C(9)−C(10)	1.16(3)
	P(1)−Pt(1)−Cl(1)	89.0(3)	P(2)−Pt(1)−Cl(1)	91.6(3)
	C(1)−Pt(1)−Cl(1)	177.5(8)	P(1)−Pt(1)−P(2)	175.9(4)
	C(1)−C(2)−C(3)	173(3)		

Crystals of **3** were obtained by recrystallization from dichloromethane−*n*-hexane. *Crystal data*: [$C_{72}H_{105}P_6Cl_3Pt_3$], $M = 1848.09$, trigonal, space group $R\bar{3}$ (No. 148), $a = 19.944(3)$ Å, $c = 41.509(3)$ Å, $V = 14298(2)$ Å^3, $Z = 6$, $D_c = 1.288$ g cm^{-3},

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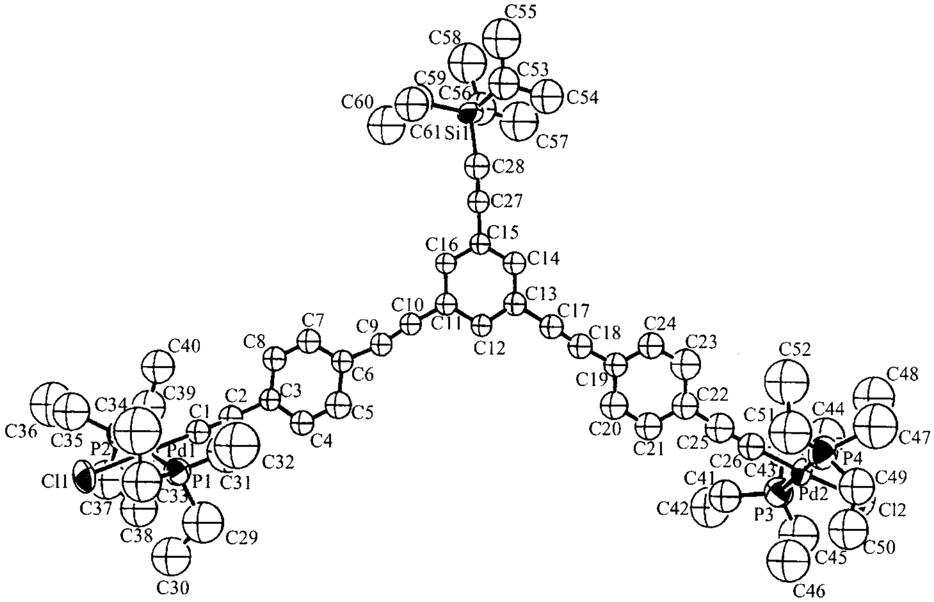

Figure 1. Perspective drawing of **1** with atomic numbering. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 40% probability level.

μ(Mo Kα) = 45.89 cm^{-1}, F(000) = 5472, T = 301 K. A colorless crystal of dimensions 0.15 × 0.15 × 0.05 mm mounted on a glass fiber was used for data collection at 28 °C on a MAR diffractometer with a 300 mm image plate detector using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). Data collections were made with 1.5° oscillation (94 images) at 120 mm distance and 720 s exposure. The images were interpreted and intensities integrated using the program DENZO.[15] A total of 4742 unique reflections were obtained from a total of 36 914 measured reflections (R_{int} = 0.059). A total of 2969 reflections with $I > 3\sigma(I)$ were considered observed and used in the structural analysis. These reflections were in the range of h: 0 to 23; k: −20 to 0; l: −48 to 48 with $2\theta_{\max}$ = 51°. The space group was determined on the basis of a systematic absence and a statistical analysis of intensity distribution, the successful refinement of the structure was solved by Patterson methods and expanded by Fourier methods (PATTY[16]), and refinement was by full-matrix least-squares using the software package TeXsan[17] on a Silicon Graphics Indy computer. A crystallographic asymmetric unit consists of one-third of one molecule. In the least-squares refinement, 16 non-H atoms were refined anisotropically, C(13) to C(24) having large thermal motions were refined isotropically, and 35 H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. Convergence for 274 variable parameters by least-squares refinement on F with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.022F_o^2)^2]$ for 4108 reflections with $I > 3\sigma(I)$ was reached at R = 0.072 and wR = 0.136 with a goodness-of-fit of 4.29. $(\Delta/\sigma)_{\max}$ = 0.05 for atoms refined anisotropically. The final difference Fourier map was featureless, with maximum positive and negative peaks of 1.59 and 0.81 e Å^{-3}, respectively. Selected bond distances and angles are summarized in Table 1. Tables of crystal data, atomic coordinates, and thermal parameters are given as Supporting Information.

Results and Discussion

The branched complexes were obtained by modifications of literature procedures reported for the synthesis of the related platinum(II) complexes.[7] To minimize the formation of undesirable insoluble oligomeric materials, the alkynyl ligands were added dropwise to a 6-fold excess of *trans*-M(PEt$_3$)$_2$Cl$_2$ (M = Pd, Pt) in the presence of copper(I) catalyst and afforded the respective air and moisture stable complexes 1,3-[Cl(PEt$_3$)$_2$PdC≡CC$_6$H$_4$C≡C]$_2$-5-[(^{i}Pr)$_3$SiC≡C]C$_6$H$_3$ (**1**), 1,3,5-[Cl(PEt$_3$)$_2$PdC≡CC$_6$H$_4$C≡C]$_3$C$_6$H$_3$ (**2**), and 1,3,5-[Cl(PEt$_3$)$_2$PtC≡CC$_6$H$_4$C≡C]$_3$C$_6$H$_3$ (**3**) as yellow to colorless crystals in reasonable yields.

Complexes **1**−**3** have been characterized by IR, ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy and gave satisfactory elemental analyses. Complex **3** has also been characterized by positive FAB-MS and ^{195}Pt{^{1}H} NMR spectroscopy. The X-ray crystal structures of complexes **1**−**3** have been determined.

The ^{31}P NMR spectra of **1**−**3** all show a singlet which is indicative of the highly symmetrical structure of the molecules. Platinum satellites were observed in the ^{31}P NMR spectrum of **3**, with $^1J_{\text{Pt-P}}$ = 2383 Hz, in line with that found in the ^{195}Pt NMR spectrum, in which a triplet signal was observed with identical coupling constants. Such a $^1J_{\text{Pt-P}}$ value is characteristic of a *trans*-P−Pt−P configuration.[19]

The IR spectra of the three complexes show two stretches at ca. 2111−2114 cm^{-1} and 2205−2209 cm^{-1} in the alkynyl region. The band at higher frequency was assigned as the ν(C≡C) stretch due to the inner alkynyl groups or the tri(isopropyl)silyl-protected alkynyl group, while the other one at lower frequency was assigned as the ν(C≡C) stretch due to the alkynyl group attached to the metal center.[4e] The lower stretching frequency of the C≡C bond adjacent to the transition metal compared with the others is probably due to back π-bonding from the Pd(II) or Pt(II) metal centers, which subsequently weakens the corresponding C≡C bonds.

Figures 1−3 depict the perspective drawings of the respective complexes **1**, **2**, and **3**. The palladium and platinum atoms in complexes **1**−**3** adopt a slightly distorted *trans*-square-planar geometry with the P−M−Cl bond angles in the range 91.6(3)−92.3(1)°. It is understandable that a slight distortion from an ideal

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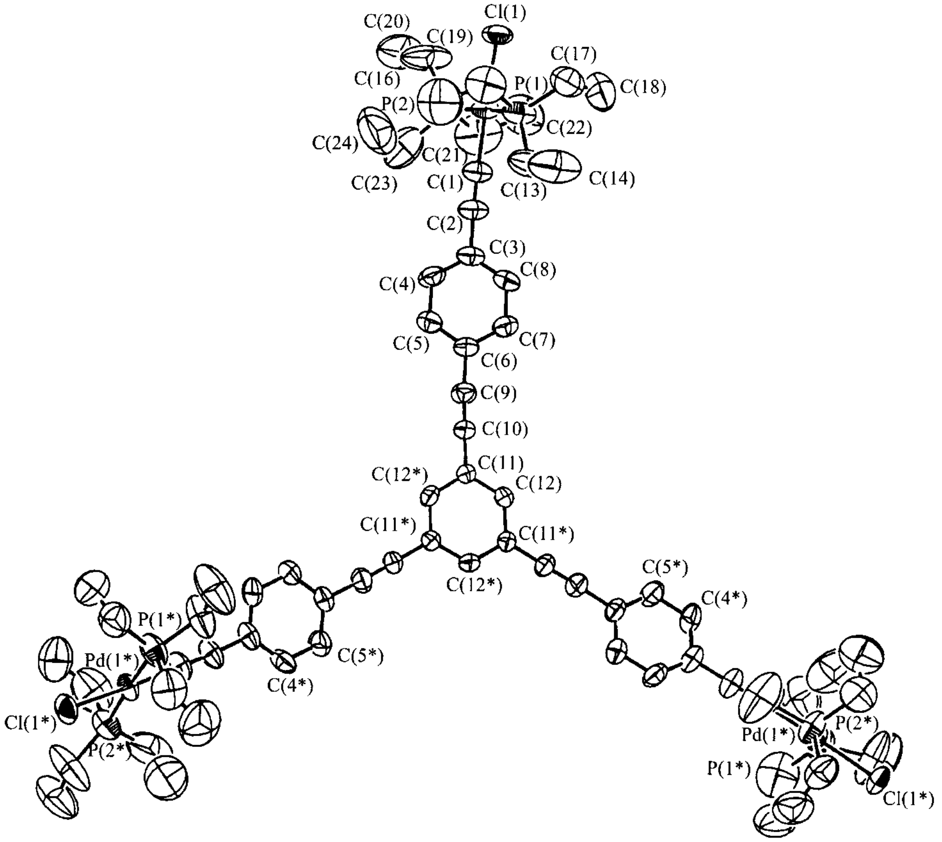

Figure 2. Perspective drawing of **2** with atomic numbering. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 40% probability level.

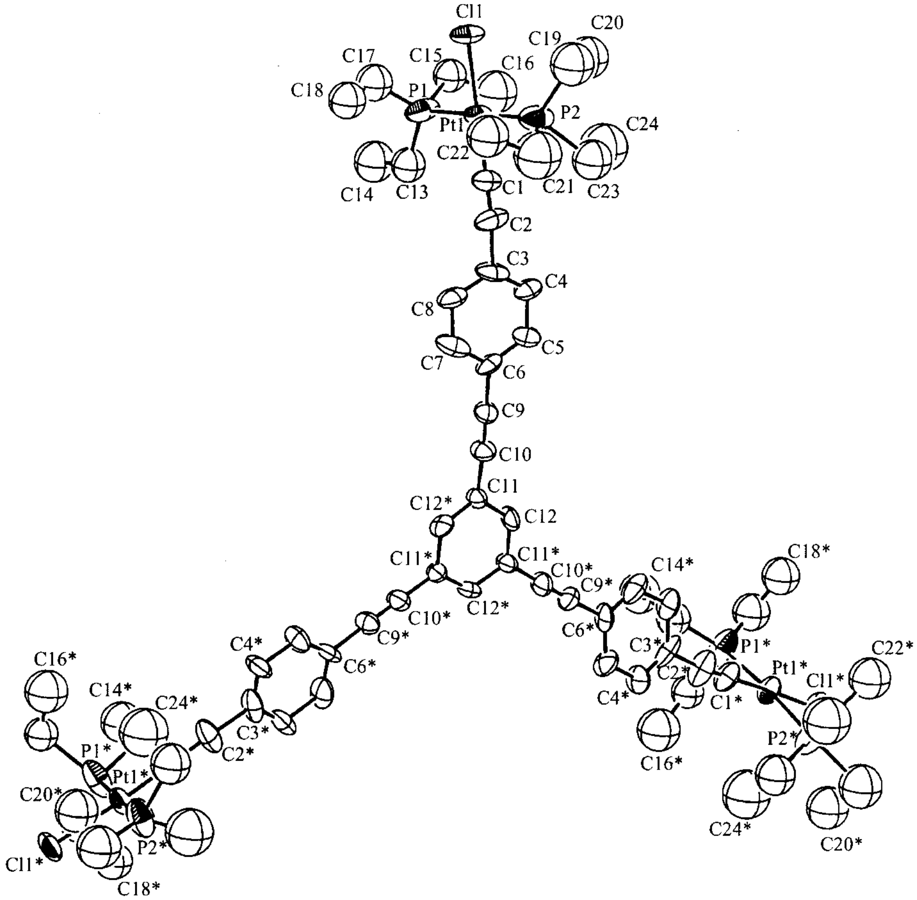

Figure 3. Perspective drawing of **3** with atomic numbering. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 40% probability level.

Table 2. Photophysical Data for L1, L2, and 1−3

compound	medium (T/K)	emission λ_{em}/nm	absorption[a] λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1})
L1	EtOH−MeOH glass (4:1, v/v) (77)	*b*	270 sh (42 940), 286 sh (75 210), 304 (130 500), 312 sh (113 800), 324 (14 4100)
L2	EtOH−MeOH glass (4:1, v/v) (77)	*b*	276 (81 150), 290 sh (91 300), 304 (129 620), 312 sh (108 460), 324 (128 700)
1	EtOH−MeOH glass (4:1, v/v) (77)	520	273 (62 530), 329 (101 010), 351 (104 540)
2	EtOH−MeOH glass (4:1, v/v) (77)	517	274 (78 640), 332 (160 100), 352 (174 500)
	solid (77)	527	
3	EtOH−MeOH glass (4:1, v/v) (77)	528	290 sh (45 190), 342 sh (168 300), 362 (194 170)
	solid (77)	537	

[a] In CH_2Cl_2 at 298 K. [b] Not measured.

square-planar arrangement could relieve steric interactions between the bulky ligands. This phenomenon has also been observed in the crystal structure of *trans*-[PtCl(C≡CPh)(PEt$_2$Ph)$_2$].[20] The Pt−P bond lengths in **3** differ by 0.021 Å, but their mean (2.287 Å) agrees well with Pt(II)−P bond distances for complexes containing mutually *trans* tertiary phosphine ligands[20] and also lies within the range found for related complexes.[7a,c,d] The Pt−Cl distances of 2.358(6) Å are slightly longer than that found in $K_2[PtCl_4]$ (2.308(2) Å).[20] The larger Pt−Cl distances in **3** are clearly due to the stronger *trans* influence of the alkynyl group than the chloro group in $K_2[PtCl_4]$. Similar findings on the Pd−Cl distances have also been observed in **1** and **2**. The C≡C bonds adjacent to the Pd atoms in **1** and **2** show bond distances in the range 1.14−1.18 Å, typical of that found in σ-bonded metal alkynyl systems.[20] The Pt−C(1)−C(2) and Pd−C(1)−C(2) bond angles in the range 177(1)−179.5(6)° are close to the ideal 180° of an sp-hybridized carbon, further establishing the σ-bonded nature of the alkynyl groups in these complexes. The coordination planes about each metal atom are twisted relative to the central phenyl ring, each at a different angle and in different direction, which has also been observed in other related palladium or platinum σ-alkynyl complexes.[7a,c,d] Complex **3** is essentially isostructural to that of **2**, with the Pt atoms replacing the Pd atoms, and the Pt−C bond distances are 1.95(2) Å.

Table 2 summarized the photophysical data of the compounds. The electronic absorption spectra of complexes **1**−**3** in dichloromethane solution exhibited intense absorption bands at ca. 270−290 and 330−370 nm, with extinction coefficients on the order of 10^4−10^5 dm^3 mol^{-1} cm^{-1} (Figure 4). The much higher extinction coefficients of the absorption bands in **1**−**3** than their precursor complexes, *trans*-M(PEt$_3$)$_2$Cl$_2$ (M = Pd, Pt),[21] and the close resemblance of their absorption patterns and extinction coefficients with that of the free alkynyl ligands are suggestive of transitions of predominantly ligand character. However, a red shift in the absorption energies from **L1** (304−312 nm) to **2** (332−352 nm) to **3** (342−362 nm) is observed. With reference to previous spectroscopic studies on *trans*-[L$_2$M(C≡CR)$_2$] (L = tertiary phosphine or stibine, M = Ni, Pd or Pt),[8e,22] in which the absorption bands at ca. 300−360 nm were assigned as metal-to-alkynyl MLCT transitions, it is likely that the transitions in complexes **1**−**3** would also involve metal-to-alkynyl MLCT character. Thus the low-energy intense absorptions in the electronic absorption spectra of these complexes are best described as an admixture of $\pi\rightarrow\pi^*$(C≡CR) IL/d$_\pi$(M)$\rightarrow\pi^*$(C≡CR) MLCT transition with predominantly IL character or, alternatively, as a metal-perturbed IL transition.

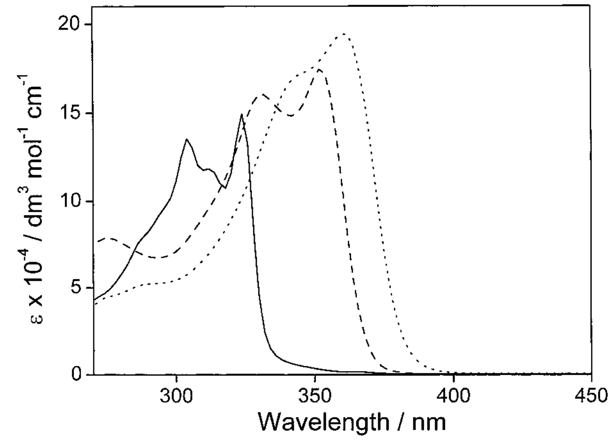

Figure 4. Electronic absorption spectra of **L1** (—), **2** (- - -), and **3** (···) in CH_2Cl_2 at room temperature.

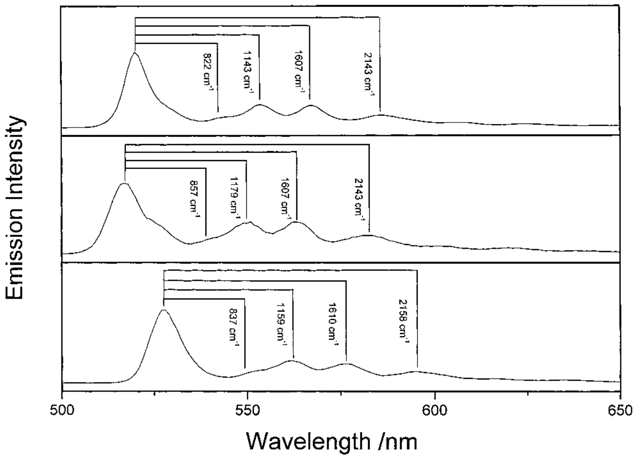

Figure 5. Emission spectra of **1** (top), **2** (middle), and **3** (bottom) in EtOH/MeOH (4:1, v/v) glass at 77 K. Excitation wavelength at 365 nm.

Upon excitation at $\lambda \geq 365$ nm, both the solid state and the EtOH/MeOH (4:1, v/v) glass at 77 K of complexes **1**−**3** show intense green to yellow luminescence (Figure 5). The large Stokes shift together with the lifetimes in the microsecond range is suggestive of their triplet parentage. Similar to the electronic absorption, the red shift in the emission energies on going from **2** to **3** is suggestive of an emission origin of a mixed $\pi\rightarrow\pi^*$(C≡CR) IL/d$_\pi$(M)$\rightarrow\pi^*$(C≡CR) MLCT triplet state with

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predominantly IL character. Similar assignments have also been reported for the related [{Pt(PBu$_3$)$_2$Cl}$_2${C≡CC$_6$H$_4$C≡C}],[23] in which the phosphorescence was assigned to originate from an excited state of IL character localized on the phenylene ring, and hybridization occurred between the metal d$_\pi$ orbitals and the p$_\pi$ orbitals of the alkynyl ligand. The glass state emission spectra of **1**−**3** at 77 K show rich vibronic structures with progressional spacings of ca. 840, 1150, 1610, and 2150 cm^{-1} from the highest energy emission band, corresponding to the δ(C−H), aromatic ring deformation, ν(C$\overset{...}{-}$C), and ν(C≡C) vibrational modes, respectively. Similar findings have also been observed in the related [{Pt(PBu$_3$)$_2$Cl}$_2${C≡CC$_6$H$_4$C≡C}].[23] Extension of the work to the construction of luminescent metallodendrimers using complexes **1**−**3** as the basic building block is in progress.

Conclusion

Three luminescent palladium(II) or platinum(II) branched alkynyl complexes were successfully synthesized and their crystal structures determined. The red shift in the emission energy upon substituting palladium(II) with platinum(II), together with the rich vibronic structures, suggests the emission origin as a mixed $\pi \rightarrow \pi^*$(C≡CR) IL/d$_\pi$(M)$\rightarrow \pi^*$(C≡CR) MLCT triplet state with predominantly IL character.

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Supporting Information Available: Tables of crystal data, atomic coordinates, thermal parameters, and a full list of bond distances and angles for **1**−**3** are deposited as Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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