DALTON
FULL PAPER

Synthesis and structural characterisation of luminescent di- and tri-nuclear palladium(II) acetylide complexes as building blocks for metallodendrimers †

Vivian Wing-Wah Yam,* Lingjun Zhang, Chi-Hang Tao, Keith Man-Chung Wong and Kung-Kai Cheung

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, P. R. China. Fax (852) 2857-1586; E-mail: wwyam@hku.hk

Received 11th December 2000, Accepted 8th February 2001
First published as an Advance Article on the web 5th March 2001

The reaction of the starting complex *trans*-$Pd(PEt_3)_2Cl_2$ with branched alkynyl ligands, 1,3,5-triethynylbenzene (**L1**) and 1,3-diethynyl-5-triisopropylsilylethynylbenzene (**L2**), in the presence of $HNEt_2$ and copper(I) catalyst led to formation of the respective luminescent branched acetylide complexes, 1,3,5-$[Cl(Et_3P)_2PdC{\equiv}C]_3C_6H_3$ **1** and 1,3-$[Cl(Et_3P)_2PdC{\equiv}C]_2$-5-$[(^iPr)_3SiC{\equiv}C]C_6H_3$ **2**, which can serve as building blocks for the construction of metallodendrimers either by a divergent or a convergent approach. Photophysical studies of these complexes showed the di- and tri-nuclear palladium complexes **1** and **2** are emissive in EtOH–MeOH (4 : 1, v/v) glass at low temperature. Synthesis of the first generation metallodendrimers using **1** as a building block has also been attempted and shows promising results.

Introduction

Dendrimers are currently attracting widespread interest in many areas of science and technology[1] due to their relatively high solubilities and better processabilities compared to the rod-like counterparts. Despite numerous studies on organic dendrimers,[1,2] some of which may show potential application as the active layers of LEDs,[3] corresponding work on metallodendrimers is still rather limited. Organometallic complexes may possess unique physical, optical, electrochemical, photochemical, biological, and catalytic properties,[4] which are inaccessible with pure organic systems. Transition metal alkynyl systems, with their ability to perturb electronic properties through metal alkynyl d_π–p_π interactions[5] and their rigid framework, appear to serve as ideal candidates for the construction of metallodendrimers. In the past decade, branched titanium,[6a] zirconium,[6b] chromium,[6c] iron,[6d] ruthenium,[6e–g] osmium,[6d,e,g] cobalt,[6h] nickel,[6g] and gold[6g] alkynyl complexes have extensively been studied. Recent works by Stang[7a] and Takahashi[7b,c] and co-workers have shown that 1,3,5-triethynylbenzene could be used as a building block for organoplatinum dendrimers, which represent one of the very few organometallic dendrimers known with metal centres in the interior due to a lack of appropriately designed building blocks,[8] while corresponding studies on the palladium counterpart are not known despite the presence of a wide interest in the catalytic activities of palladium compounds. Also, in contrast with the organic dendrimers, the luminescence properties of organometallic dendrimeric materials are relatively less explored.[9] Although there were reports on the luminescence properties of organoplatinum(II) alkynyl systems,[9,10] corresponding studies on the palladium analogue are almost unknown. These, together with the recent efforts by us[11] and others[6f,12] on the use of rigid alkynyl bridges in the design and construction of bimetallic and polymetallic complexes, have prompted us to extend our work to the dendritic system. Herein we report the synthesis and structural characterisation of luminescent di- and tri-nuclear organopalladium complexes with rigid conjugated alkynyl–aryl bridges (Scheme 1) and preliminary experiments on the formation of the first generation metallodendrimer using **1** as the backbone (Scheme 2).

Experimental

Materials and reagents

trans-Dichlorobis(triethylphosphine)palladium(II) was prepared according to a literature method[13] as were 1,3,5-triethynylbenzene (**L1**)[14] and 1,3-diethynyl-5-triisopropylsilylethynylbenzene (**L2**).[7b] All solvents were purified and distilled using standard procedures before use.[15] All other reagents were of analytical grade used as received.

Physical measurements and instrumentation

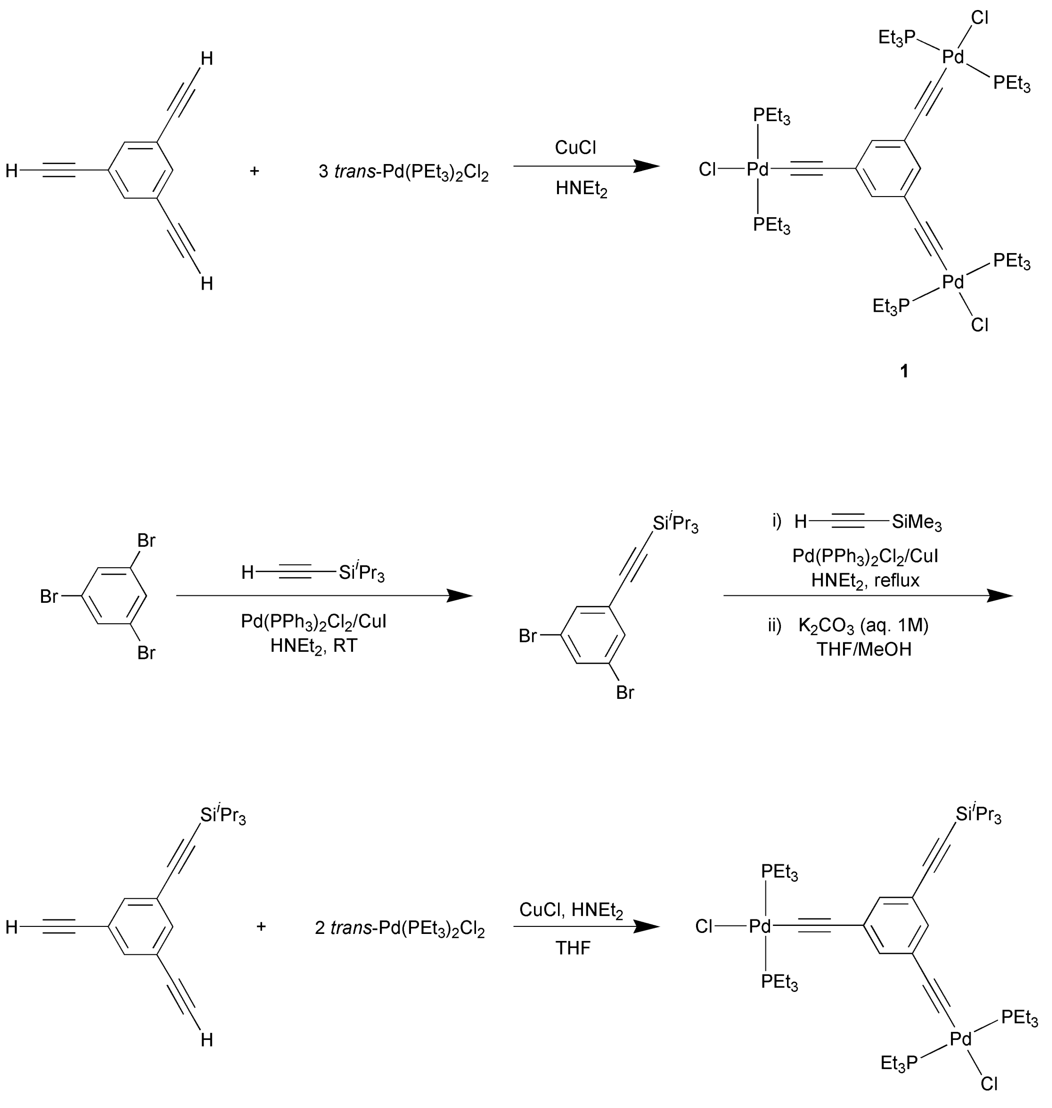
UV-visible spectra were obtained on a Hewlett-Packard 8452A diode array spectrophotometer, IR spectra as KBr discs on a Bio-Rad FTS-7 Fourier-transform infrared spectrophotometer (4000–400 cm^{-1}), and steady state excitation and emission spectra on a Spex Fluorolog-2 Model F 111 fluorescence spectrophotometer equipped with a Hamamatsu R-928 photomultiplier tube. Low-temperature (77 K) spectra were recorded by using an optical Dewar sample holder. ^1H NMR spectra were recorded on a Bruker DPX-300 (300 MHz) Fourier transform NMR spectrometer, ^{13}C-$\{^1H\}$ and ^{31}P-$\{^1H\}$ NMR spectra on either a Bruker DPX-300 (300 MHz) or a DPX-500 (500 MHz) Fourier-transform NMR spectrometer. ^1H and ^{13}C NMR chemical shifts (δ in ppm) were recorded relative to tetramethylsilane (Me_4Si), ^{31}P relative to 85% H_3PO_4. 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

---

† Electronic supplementary information (ESI) available: experimental crystallographic details. See http://www.rsc.org/suppdata/dt/b0/b009894i/

DOI: 10.1039/b009894i



1

2

Scheme 1 Synthesis of di- and tri-nuclear palladium complexes.

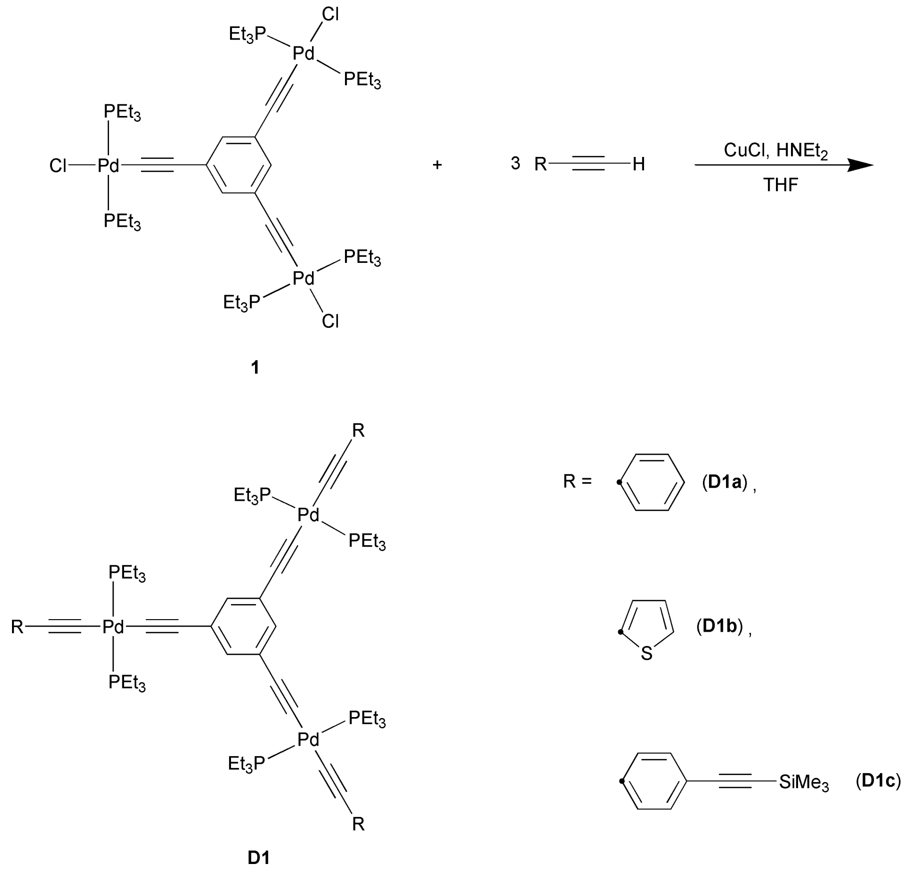
from the atmosphere by a Bibby Rotaflo HP6 Teflon stopper. The solutions were subject to at least four freeze–pump–thaw cycles.

Synthesis of palladium complexes

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

1,3,5-[Cl(Et$_3$P)$_2$PdC≡C]$_3$C$_6$H$_3$ 1. *trans*-Pd(PEt$_3$)$_2$Cl$_2$ (1.000 g, 2.418 mmol) was dissolved in HNEt$_2$ (60 ml) containing copper(I) chloride (3.8 mg, 0.038 mmol). **L1** (94.4 mg, 0.628 mmol) was added and the reaction mixture stirred for 3 hours at room temperature. The white amine salt formed during the course of the reaction was then filtered off and the solvent removed under reduced pressure. The yellow residue was dissolved in CH$_2$Cl$_2$ and the solution washed successively with aqueous ammonium chloride solution and deionised water to get rid of the copper(I) catalyst. The organic layer was then dried over anhydrous MgSO$_4$ and filtered. The dried organic fraction was concentrated under reduced pressure and passed through a column of aluminium oxide (basic, 50–200 μm) using CH$_2$Cl$_2$–light petroleum (bp 40–60 °C) (1 : 1, v/v) as the eluent to remove the excess of *trans*-Pd(PEt$_3$)$_2$Cl$_2$. The trinuclear complex **1** was eluted with CH$_2$Cl$_2$ and subsequent removal of the solvent gave **1** as a very pale yellow solid. Recrystallisation from benzene–*n*-pentane afforded **1** as colourless crystals. Yield 64%. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 1.20 (virtual quintet (vq), 54H, $J = 5.0$ Hz, CH$_3$), 1.93–2.03 (m, 36H, CH$_2$P) and 6.94 (s, 3H, aromatic H). ^{13}C-{^{1}H} NMR (CDCl$_3$, 75.5 MHz): δ 8.34 (CH$_3$), 15.39 ($J_{\text{C-P}} = 14.0$, CH$_2$P), 95.08 (t, $J_{\text{C-P}} = 15.9$, acetylenic C adjacent to Pd), 106.16 (t, $J_{\text{C-P}} = 5.6$ Hz, acetylenic C adjacent to aryl group), 128.86, 130.89 (aromatic C). ^{31}P-{^{1}H} NMR (CDCl$_3$, 109 MHz): δ 19.17 (s). IR (KBr, ν/cm^{-1}): 2108(s) ν(C≡C). Positive FAB-MS: *m*/*z* 1281, [M]$^+$; and 1245, [M − Cl]$^+$. Found: C, 44.98; H, 7.25%. C$_{16}$H$_{31}$ClP$_2$Pd requires C, 44.98; H, 7.31%.

1,3-[Cl(Et$_3$P)$_2$PdC≡C]$_2$-5-[(^{i}Pr)$_3$SiC≡C]C$_6$H$_3$ 2. *trans*-Pd(PEt$_3$)$_2$Cl$_2$ (1.215 g, 2.94 mmol) was dissolved in HNEt$_2$ (40 ml) containing copper(I) chloride (1.16 mg, 0.012 mmol). **L2** (300 mg, 0.98 mmol) in THF (40 ml) was added dropwise and stirred for 4 hours at room temperature. The white amine salt formed during the course of the reaction was then filtered off and the solvent removed under reduced pressure. The pale yellow residue was dissolved in CH$_2$Cl$_2$ and washed successively with aqueous ammonium chloride solution and deionised water. The organic layer was then dried over anhydrous MgSO$_4$, filtered and then concentrated under reduced pressure. Subsequent purification used column chromatography on aluminium oxide (basic, 50–200 μm) using CH$_2$Cl$_2$–light petroleum (bp 40–60 °C) (1 : 2, v/v) as the eluent to get rid of the excess of *trans*-Pd(PEt$_3$)$_2$Cl$_2$. The dinuclear complex **2** was eluted with CH$_2$Cl$_2$–light petroleum (bp 40–60 °C) (1 : 1, v/v) and subsequent



Scheme 2 Synthesis of first generation dendrimers using complex **1** as the building block.

removal of solvent gave **2** as a very pale yellow solid. Recrystallisation from benzene–*n*-pentane afforded **2** as colourless crystals. Yield 72%. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 1.12 (s, 21H, ^{i}Pr) 1.20 (vq, $J = 5.0$ Hz, 36H, CH$_3$), 1.93–2.00 (m, 24H, CH$_2$P), 7.07 (s, 1H, aryl H *para* to C$_2$Si^{i}Pr$_3$ group) and 7.12 (s, 2H, aryl H *ortho* to C$_2$Si^{i}Pr$_3$ group). ^{13}C-{^{1}H} NMR (CDCl$_3$, 125 MHz): δ 8.34 (CH$_3$), 11.34 (^{i}Pr), 15.42 (PCH$_2$, $J_{\text{C-P}} = 13.8$), 18.66 (^{i}Pr), 90.39, 96.52 (t, $J_{\text{C-P}} = 16.0$, acetylenic C adjacent to Pd), 105.71, 106.92 (t, $J_{\text{C-P}} = 5.7$ Hz, acetylenic C adjacent to aryl group), 123.26, 127.70, 131.33, 132.91 (s, aromatic C). ^{31}P-{^{1}H} NMR (CDCl$_3$, 202 MHz): δ 19.32 (s). IR (KBr, ν/cm^{-1}): 2091(s) and 2167(m) ν(C≡C). Positive FAB-MS: *m*/*z* 1061, [M]$^+$; and 1026, [M − Cl]$^+$. Found: C, 51.04; H, 8.19%. $C_{45}H_{84}Cl_2P_4Pd_2Si$ requires C, 50.95; H, 7.98%.

1,3,5-[RC≡C(Et$_3$P)$_2$PdC≡C]$_3$C$_6$H$_3$ (R = Ph D1a, thienyl D1b or C$_6$H$_4$C≡CSiMe$_3$ D1c). A typical preparation of compound **D1** was carried out as follows. Phenylacetylene (81.6 mg, 0.800 mmol) in THF (8 ml) was added dropwise to a solution of **1** (100 mg, 0.242 mmol) in THF (8 ml) and NEt$_3$ (8 ml) containing copper(I) chloride (0.3 mg, 0.003 mmol) at 0 °C. The reaction mixture was stirred for 3 h at the same temperature. The amine salt formed was filtered off and the filtrate removed under reduced pressure. The residue was dissolved in CH$_2$Cl$_2$ and washed successively with aqueous ammonium chloride solution and water. The organic layer was separated and dried over anhydrous MgSO$_4$ which was then concentrated under reduced pressure. Subsequent purification with column chromatography on aluminium oxide (basic, 50–200 μm) using CH$_2$Cl$_2$–light petroleum (bp 40–60 °C) (1 : 2, v/v) and CH$_2$Cl$_2$ as eluent gave *trans*-Pd(PEt$_3$)$_2$Cl$_2$ and **D1a**, respectively. **D1a**: yield 8%; ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz) δ 1.20 (vq, 54H, $J = 5.0$ Hz, CH$_3$), 2.01–2.11 (m, 36H, CH$_2$P), 6.93 (s, 3H, central aryl H) and 7.11–7.27 (m, 15H, terminal phenyl H). **D1b**: yield 5%; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 1.17–1.28 (vq, 54H, $J = 5.0$ Hz, CH$_3$), 2.02–2.13 (m, 36H, CH$_2$P), 6.85–6.87 (m, 6H, thienyl H at 2 and 4 position) and 6.96–6.98 (m, 6H, thienyl H at 3 position and central aryl H). **D1c**: yield 9%; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 0.24 (s, 27H, SiMe$_3$), 1.20 (vq, 54H, $J = 5.0$, CH$_3$), 2.00–2.09 (m, 36H, CH$_2$P), 7.00 (s, 3H, central aromatic H), 7.16–7.19 (d, 6H, $J = 8.2$, peripheral aromatic H *ortho* to C$_2$Pd) and 7.28–7.31 (d, 6H, $J = 8.2$ Hz, peripheral aromatic H *ortho* to C$_2$SiMe$_3$).

Crystal structure determination

Crystals of compound **1** were obtained by recrystallisation from benzene–*n*-pentane. The space group was determined based on a statistical analysis of intensity distribution and the successful refinement of the structure solved by direct methods (SIR 92[16]) and 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 half of one formula unit with Pd(1), Cl(1), C(1), C(2), C(3) and C(6) at special positions. In the least-squares refinement the Pd, Cl and P atoms were refined anisotropically, all 26 C atoms isotropically and 47 H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. Final agreement factors for **1** and **2** are given in Table 1, selected bond distances and angles in Table 2.

Crystals of compound **2** were obtained by recrystallisation from benzene–*n*-pentane. The images were interpreted and intensities integrated using the program DENZO.[18] The space group was determined based on systematic absences and the structure was solved by Patterson methods and expanded by Fourier methods (PATTY[19]) and refinement as for **1**. A crystallographic asymmetric unit consists of one molecule. In the least-squares refinement 9 non-H atoms were refined anisotropically, all 45 C atoms isotropically, and 84 H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. Further

Table 1 Crystal and structure determination data for compounds **1** and **2**

	1	**2**
Molecular formula	$C_{48}H_{93}Cl_3P_6Pd_3$	$C_{45}H_{84}Cl_2P_4Pd_2Si$
M	1281.66	1060.85
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$ (no. 15)	$P2_1/n$ (No. 14)
a/Å	11.233(7)	12.786(2)
b/Å	31.389(6)	15.416(3)
c/Å	19.214(4)	29.024(3)
β/°	103.60(3)	94.63(2)
V/Å^3	6584(4)	5702(1)
Z	4	4
μ/cm^{-1}	11.05	8.84
T/K	301	301
Diffractometer	Rigaku AFC7R	MAR
λ/Å (graphite monochromated, Mo-Kα)	0.71073	0.71073
R	0.060	0.095
wR	0.088	0.137
No. of data collected	5574	45846
No. of unique data	5249	7882
R_{int}	0.036	0.062
No. of data used in refinement	2201	3158
No. of parameters refined	152	262

Table 2 Selected bond distances (Å) and bond angles (°) for compounds **1** and **2**

1			
Pd(1)–C(1)	1.91(2)	Pd(1)–Cl(1)	2.327(6)
Pd(1)–P(1)	2.307(4)	Pd(2)–P(2)	2.317(5)
Pd(2)–P(3)	2.290(5)	Pd(2)–Cl(2)	2.335(4)
Pd(2)–C(8)	1.94(1)	C(1)–C(2)	1.17(2)
C(7)–C(8)	1.21(2)		
P(1)–Pd(1)–Cl(1)	94.1(1)	P(1)–Pd(1)–C(1)	85.9(1)
C(1)–Pd(1)–Cl(1)	180.0	Pd(1)–C(1)–C(2)	180.0
P(2)–Pd(2)–Cl(2)	90.2(2)	P(3)–Pd(2)–Cl(2)	90.5(2)
P(2)–Pd(2)–C(8)	91.1(4)	P(3)–Pd(2)–C(8)	88.1(4)
C(8)–Pd(2)–Cl(2)	178.4(4)	Pd(2)–C(8)–C(7)	178(1)
P(2)–Pd(2)–P(3)	176.5(2)		
2			
Pd(1)–C(1)	1.94(2)	Pd(1)–Cl(1)	2.339(5)
Pd(1)–P(1)	2.317(6)	Pd(1)–P(2)	2.299(6)
Pd(2)–Cl(2)	2.352(7)	Pd(2)–P(3)	2.309(6)
Pd(2)–P(4)	2.293(6)	Pd(2)–C(22)	1.95(2)
C(1)–C(2)	1.17(2)	C(21)–C(22)	1.17(2)
C(36)–C(35)	1.25(3)	Si(1)–C(36)	1.74(2)
P(1)–Pd(1)–Cl(1)	87.9(2)	P(2)–Pd(1)–Cl(1)	92.2(2)
P(1)–Pd(1)–C(1)	89.4(6)	P(2)–Pd(1)–C(1)	88.6(6)
C(1)–Pd(1)–Cl(1)	177.7(6)	Pd(1)–C(1)–C(2)	177(1)
P(1)–Pd(1)–P(2)	176.2(2)	P(3)–Pd(2)–Cl(2)	92.9(2)
P(4)–Pd(2)–Cl(2)	90.0(2)	P(3)–Pd(2)–C(22)	86.7(5)
P(4)–Pd(2)–C(22)	90.5(5)	C(22)–Pd(2)–Cl(2)	175.8(5)
Pd(2)–C(22)–C(21)	172(1)	P(3)–Pd(2)–P(4)	176.7(2)
Si(1)–C(36)–C(35)	174(2)		

details of crystal and structural refinement are given as ESI supplementary information.

CCDC reference numbers 155061 and 155062.

See http://www.rsc.org/suppdata/dt/b0/b009894i/ for crystallographic data in CIF or other electronic format.

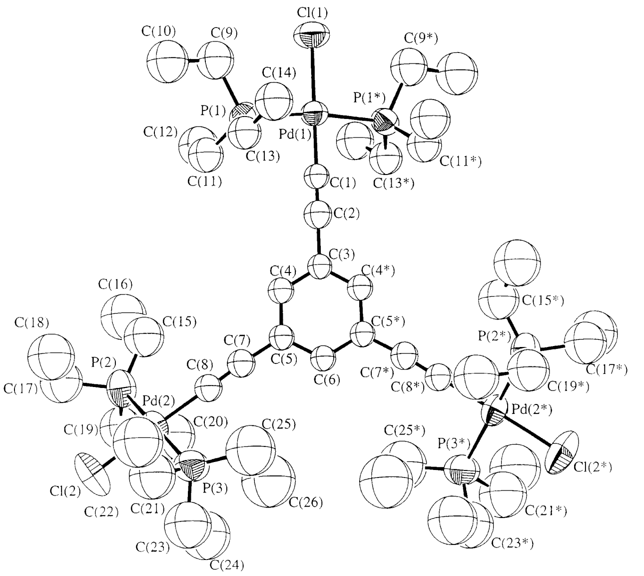


Fig. 1 Perspective drawing of compound **1** with atomic numbering. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are at the 40% probability level.

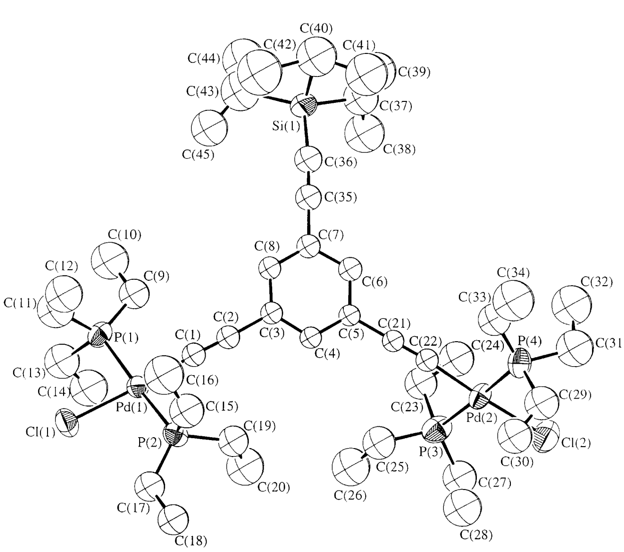


Fig. 2 Perspective drawing of compound **2**. Thermal ellipsoids are at the 30% probability level. Other details as in Fig. 1.

Results and discussion

The dendrimeric precursors were obtained by modifications of literature procedures reported for the synthesis of linear rigid-rod palladium polyynes.[20] The formation of undesirable polymeric materials can be minimised by slow addition of the alkynyl ligands to an excess of *trans*-Pd(PEt$_3$)$_2$Cl$_2$ in the presence of copper(I) catalyst at low temperature and the respective air- and moisture-stable complexes 1,3,5-[Cl(Et$_3$P)$_2$PdC≡C]$_3$C$_6$H$_3$ **1** and 1,3-[Cl(Et$_3$P)$_2$PdC≡C]$_2$-5-[(^{i}Pr)$_3$SiC≡C]C$_6$H$_3$ **2** were obtained in good yields. Both **1** and **2** have been characterized by ^{1}H, ^{13}C-{^{1}H}, and ^{31}P-{^{1}H} NMR, IR, positive FAB-MS, and gave satisfactory elemental analyses. Their crystal structures have also been determined.

The ^{1}H NMR spectrum of compound **1** showed only one singlet at δ 6.94 in the aromatic region, whereas two singlets at δ 7.12 and 7.07 in an integral ratio of 2 : 1 were recorded for **2**, both of which showed an upfield shift in the aromatic resonances with respect to 1,3,5-triethynylbenzene which occurred at δ 7.57. The methyl protons of the triethylphosphine ligands show a virtual quintet pattern at δ 1.20 as a result of the coupling with their neighbouring methylene protons and phosphorus. Similar findings have been observed for related complexes.[7c] No signals for acetylenic proton were detected, eliminating the possibility of the existence of partially substituted products. The ^{31}P-{^{1}H} NMR spectra of **1** and **2** exhibited a singlet for the triethylphosphine ligands at δ 19.17 and 19.32 respectively, which shows the high symmetry of the complexes.

The IR spectra of compounds **1** and **2** show a band at *ca.* 2091–2108 cm^{-1} which is assigned as the ν(C≡C) stretch due to the alkynyl group attached to the metal centre. There is also a

Table 3 Photophysical data for compounds **1** and **2**

Compound	Medium (*T*/K)	Emission λ_{em}/nm	Absorption[a] λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})
1	EtOH–MeOH glass (4 : 1, v/v) (77)	446	232 (45240), 276 (107580), 292 sh (92780), 328 sh (7710), 340 sh (4060)
	Solid (77)	533	
2	EtOH–MeOH glass (4 : 1, v/v) (77)	440	238 (38290), 274 (85970), 290 sh (63420), 344 sh (3910)

[a] In CH_2Cl_2 at 298 K.

higher frequency band at *ca.* 2167 cm^{-1} in the spectrum of **2** which corresponds to the triisopropylsilyl protected alkynyl group.[21] The weakening of the C≡C bonds adjacent to the palladium metal compared with the triisopropylsilyl protected one is probably due to back π bonding from the metal centres.

Figs. 1 and 2 depict perspective drawings of compounds **1** and **2**, respectively. All the palladium atoms showed the expected square planar coordination geometry with slight distortion, with the P–Pd–Cl bond angles in the range of 89.7(2)–94.1(1). It is conceivable that a slight distortion from an ideal square-planar arrangement, which has also been observed in the crystal structure of *trans*-[PtCl(C≡CPh)$(PEt_2Ph)_2$],[22] could relieve steric interactions between bulky ligands. The coordination planes around Pd(1) and Pd(2) form interplanar angles of 22 and 42° with the central phenyl ring in **1**, and 31 and 64° in **2**, respectively. This out-of plane twisting of coordination planes around the palladium atoms of both **1** and **2** has also been observed in related palladium or platinum σ-alkynyl complexes.[7] In both complexes the bond distances of Pd–C (1.91(2)–1.94(2) Å) as well as the C≡C (1.17(2)–1.21(2) Å) adjacent to the palladium metal centre are almost identical, which is quite different from that observed for the platinum analogues.[7]

Table 3 summarises the photophysical data of the compounds. The electronic absorption spectra of **1** and **2** in dichloromethane solution showed intense bands at *ca.* 230–240 and 270–290 nm, with absorption coefficients in the order of 10^4–10^5 dm^3 mol^{-1} cm^{-1}. The large difference in absorption coefficients of the bands between the branched complexes and the precursor complex, *trans*-$Pd(PEt_3)_2Cl_2$, together with the close resemblance of their absorption patterns with that of the free alkynyl ligands,[23] are suggestive of the predominantly intra-ligand (IL) character of these transitions. However, with reference to previous spectroscopic studies on *trans*-[ML_2-$(C{\equiv}CR)_2$] (L = tertiary phosphine or stibine, M = Ni, Pd or Pt),[10e,24] in which absorption bands at *ca.* 300–360 nm were assigned as metal-to-alkynyl MLCT transitions, an involvement of such transitions is not unlikely. With our recent work on luminescent palladium(II) and platinum(II) branched alkynyl complexes,[21b] a red shift in absorption bands on going from 1,3,5-$[Cl(Et_3P)_2PdC{\equiv}CC_6H_4C{\equiv}C]_3C_6H_3$ to the platinum analogue 1,3,5-$[Cl(Et_3P)_2PtC{\equiv}CC_6H_4C{\equiv}C]_3C_6H_3$ can be observed which is best described as an admixture of $\pi \longrightarrow \pi^*(C{\equiv}CR)$ IL and $d_\pi(M) \longrightarrow \pi^*(C{\equiv}CR)$ MLCT transitions with predominant IL character. It is likely that the electronic absorption bands of **1** and **2** would also involve a certain degree of metal-to-alkynyl MLCT character.

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** and **2** show intense luminescence (Fig. 3). The glass state emission spectra at 77 K show rich vibronic structures with progressional spacings of *ca.* 1190–1270 and 2100 cm^{-1}, which correspond to the ring deformation mode and the ν(C≡C) stretching mode of the aromatic alkynyl system, respectively. This observation is supportive of the predominantly intra-ligand character of the emission origin.

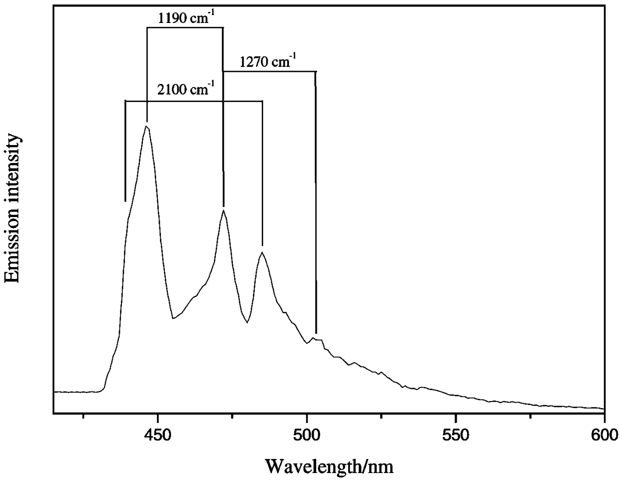


Fig. 3 Emission spectrum of 1,3,5-$[Cl(Et_3P)_2PdC{\equiv}C]_3C_6H_3$ **1** in EtOH–MeOH (4 : 1, v/v) glass at 77 K.

On the other hand, attempts have also been made to prepare the first generation dendrimers (**D1**) by reaction of compound **1** with monoacetylenes. The products **D1a**, **D1b** and **D1c** were isolated and confirmed by preliminary ^1H NMR characterisation. However, the yields were low. Instead $Pd(PEt_3)_2(C{\equiv}CR)_2$ was isolated as the major product in high yield with some other insoluble polymers. Attempts to purify **D1** by recrystallisation gave only insoluble polymers which precluded further characterisation. Further attempts to replace the chloro group with ligands other than the alkynyl group showed promising results. Work is in progress to apply the strategy to the construction of higher generation dendrimers involving the use of **1** in the divergent method. Synthesis of metallodendrimers using **2** as the dendron and **1** as the core by the convergent method is also under current investigation.

Acknowledgements

V. W.-W. Y. acknowledges support from The University of Hong Kong, and the receipt of a Croucher Senior Research Fellowship (2000–2001) from the Croucher Foundation. The work described in this paper has fully been supported by a grant from the Research Grants Council of the Hong Kong Special Administrative Region, China (Project No. HKU 7123/00P). C.-H. T. acknowledges the receipt of a Croucher Scholarship, administered by the Croucher Foundation, and K. M.-C. W. the receipt of a University Postdoctoral Fellowship, administered by The University of Hong Kong.

References and notes

1 *Dendritic Molecules: Concepts, Syntheses, Perspectives*, eds. G. R. Newkome, C. N. Moorefield and F. Vögtle, VCH, Weinheim, 1996; M. Fischer and F. Vögtle, *Angew. Chem., Int. Ed.*, 1999, **38**, 884; A. W. Bosman, H. M. Janssen and E. W. Meijer, *Chem. Rev.*, 1999, **99**, 1665.

2 C. Devadoss, P. Bharathi and J. S. Moore, *J. Am. Chem. Soc.*, 1996, **118**, 9635; Q. Hu, V. Pugh, M. Sabat and L. Pu, *J. Org. Chem.*, 1999, **64**, 7528.

3 X. T. Tao, Y. D. Zhang, T. Wada, H. Sasabe, H. Suzuki, T. Watanabe and S. Miyata, *Adv. Mater.*, 1998, **10**, 226.

4 *Advances in Dendritic Macromolecules*, ed. G. R. Newkome, JAI, Greenwich, CT, 1999; M. Venturi, S. Serroni, A. Juris, S. Campagna and V. Balzani, *Top. Curr. Chem.*, 1998, 193; G. R. Newkome, E. He and C. N. Moorefield, *Chem. Rev.*, 1999, **99**, 1689 and references therein.

5 D. L. Lichtenberger, S. K. Renshaw and R. M. Bullock, *J. Am. Chem. Soc.*, 1993, **115**, 3276; D. L. Lichtenberger, S. K. Renshaw and A. Wong, *Organometallics*, 1993, **125**, 3522.

6 (*a*) U. Rosenthal, P. M. Pellny, F. G. Kirchbauer and V. V. Burlakov, *Acc. Chem. Res.*, 2000, **33**, 119; (*b*) H. Fing, N. J. Long, A. J. Martin, G. Opromolla, A. J. P. White, D. J. Williams and P. Zanello, *Organometallics*, 1997, **16**, 2646; (*c*) T. J. J. Müller and H. Lindner, *Chem. Ber.*, 1996, **129**, 607; (*d*) U. H. F. Bunz and V. Enkelmann, *Organometallics*, 1994, **13**, 3823; (*e*) N. J. Long, A. J. Martin, F. F. de Biani and P. Zanello, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 2017; (*f*) M. Uno and P. H. Dixneuf, *Angew. Chem.*, *Int. Ed.*, 1998, **37**, 1714; (*g*) I. R. Whittall, M. G. Humphrey, S. Houbrechts, J. Maes, A. Persoons, S. Schmid and D. C. R. Hockless, *J. Organomet. Chem.*, 1997, **544**, 277; (*h*) E. C. Constable, O. Eich, D. Fenske, C. E. Housecroft and L. A. Johnston, *Chem. Eur. J.*, 2000, **6**, 4364.

7 (*a*) S. Leininger, P. J. Stang and S. Huang, *Organometallics*, 1998, **17**, 3981; (*b*) K. Onitsuka, M. Fujimoto, N. Ohshiro and S. Takahashi, *Angew. Chem.*, *Int. Ed.*, 1999, **38**, 689; (*c*) N. Ohshiro, F. Takei, K. Onitsuka and S. Takahashi, *J. Organomet. Chem.*, 1998, **569**, 195.

8 S. Achar and R. J. Puddephatt, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 1895; W. T. S. Huck, F. C. J. M. van Veggel, B. L. Kropman, D. H. A. Blank, E. G. Keim, M. M. A. Smithers and D. N. Reinhoudt, *J. Am. Chem. Soc.*, 1995, **117**, 8293.

9 V. Grosshenny, A. Harriman, M. Hissler and R. Ziessel, *J. Chem. Soc.*, *Faraday Trans.*, 1996, 2223; R. Ziessel, M. Hissler, A. El-ghayoury and A. Harriman, *Coord. Chem. Rev.*, 1998, **178**–**180**, 1251.

10 (*a*) L. Sacksteder, E. Baralt, B. A. DeGraff, C. M. Lukehart and J. N. Demas, *Inorg. Chem.*, 1991, **30**, 2468; (*b*) V. W. W. Yam, L. P. Chan and T. F. Lai, *Organometallics*, 1993, **12**, 2197; (*c*) V. W. W. Yam, P. K. Y. Yeung, L. P. Chan, W. M. Kwok, D. L. Phillips, K. L. Yu, R. W. K. Wong, H. Yan and Q. J. Meng, *Organometallics*, 1998, **17**, 2590; (*d*) V. W. W. Yam, K. L. Yu and K. K. Cheung, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 2913; (*e*) C. L. Choi, Y. F. Cheng, C. Yip, D. L. Phillips and V. W. W. Yam, *Organometallics*, 2000, **19**, 3192; (*f*) M. Hissler, W. B. Connick, D. K. Geiger, J. E. McGarrah, D. Lipa, R. J. Lachicotte and R. Eisenberg, *Inorg. Chem.*, 2000, **39**, 447; (*g*) M. S. Khan, A. K. Kakkar, N. J. Long, J. Lewis, P. R. Raithby, P. Nguyen, T. B. Marder, F. Wittmann and R. H. Friend, *J. Mater. Chem.*, 1994, **4**, 1227; (*h*) N. Chawdhury, A. Köhler, R. H. Friend, M. Younus, N. J. Long, P. R. Raithby and J. Lewis, *Macromolecules*, 1998, **32**, 722; (*i*) N. Chawdhury, A. Köhler, R. H. Friend, W. Y. Wong, J. Lewis, M. Younus, P. R. Raithby, T. C. Corcoran, M. R. A. Al-Mandhary and M. S. Khan, *J. Chem. Phys.*, 1999, **110**, 4963; (*j*) V. W. W. Yam, K. L. Yu, K. M. C. Wong and K. K. Cheung, *Organometallics*, 2001, **20**, 721.

11 V. W. W. Yam, V. C. Y. Lau and K. K. Cheung, *Organometallics*, 1996, **15**, 1740; V. W. W. Yam, W. K. M. Fung and K. K. Cheung, *Chem. Commun.*, 1997, 963; V. W. W. Yam, W. K. M. Fung, K. M. C. Wong, V. C. Y. Lau and K. K. Cheung, *Chem. Commun.*, 1998, 777; V. W. W. Yam, S. H. F. Chong, K. M. C. Wong and K. K. Cheung, *Chem. Commun.*, 1999, 1013; V. W. W. Yam, K. K. W. Lo and K. M. C. Wong, *J. Organomet. Chem.*, 1999, **578**, 3; A. Mayr, M. P. Y. Yu and V. W. W. Yam, *J. Am. Chem. Soc.*, 1999, **121**, 1760.

12 T. Weyland, K. Costuas, A. Mari, J. Halet and C. Lapinte, *Organometallics*, 1998, **17**, 5569; A. M. McDonagh, M. G. Humphrey, M. Samoc, B. Luther-Davies, S. Houbrechts, T. Wada, H. Sasabe and A. Persoons, *J. Am. Chem. Soc.*, 1999, **121**, 1405.

13 T. Okano, M. Iwahara, H. Konish and J. Kiji, *J. Organomet. Chem.*, 1988, **346**, 267.

14 E. Weber, M. Hedur, E. Koepp, W. Orlia and M. Czugler, *J. Chem. Soc., Perkin Trans. 2*, 1988, 1251.

15 D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*, 3rd edn., Pergamon, Oxford, 1988.

16 A. Altomare, M. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Crystaalogr.*, 1994, **27**, 435.

17 TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, The Woodlands, TX, 1985 and 1992.

18 *The HKL manual – A description of programs DENZO*, *XDISPLAYF* and *SCALEPACK*, written by D. Gewirth, with the co-operation of the program authors Z. Otwinowski and W. Minor, Yale University, New Haven, 1995.

19 P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, The DIRDIF program system, Technical Report of the Crystallography Laboratory, University of Nijimegen, 1992.

20 S. Takahashi, M. Kariya, T. Yatake, K. Sonogashira and N. Hagihara, *Macromolecules*, 1978, **11**, 1063.

21 (*a*) O. Lavastre, L. Ollivier and P. H. Dixneuf, *Tetrahedron*, 1996, **52**, 5495; (*b*) V. W. W. Yam, C. H. Tao, L. Zhang, K. M. C. Wong and K. K. Cheung, *Organometallics*, 2001, **20**, 453.

22 C. J. Cardin, D. J. Cardin, M. F. Lappert and K. W. Muir, *J. Chem. Soc.*, *Dalton Trans.*, 1978, 46.

23 UV-VIS of **L1** [λ/nm (ε/dm^3 mol^{-1} cm^{-1})]: CH_2Cl_2, 236 (67190) and 254 sh (31310).

24 H. Masai, K. Sonogashira and N. Hagihara, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 2226; W. M. Kwok, D. L. Phillips, P. K. Y. Yeung and V. W. W. Yam, *Chem. Phys. Lett.*, 1996, **262**, 699; W. M. Kwok, D. L. Phillips, P. K. Y. Yeung and V. W. W. Yam, *J. Phys. Chem. A*, 1997, **101**, 9286.