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Synthesis of new bis(acetylide)-substituted fluorene derivatives and their bimetallic and polymeric complexes

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Abstract

A new series of bis(acetylide) organic ligands having fluorene or fluorenone moieties in the backbone, 2,7-di(trimethylsilylethynyl)fluorene (**1a**), 2,7-di(ethynyl)fluorene (**1b**), 2,7-di(trimethylsilylethynyl)fluoren-9-one (**2a**) and 2,7-di(ethynyl)fluoren-9-one (**2b**), has been prepared. Reaction of the diterminal alkynyl fluorene derivatives **1b** and **2b** with two equivalents of the complex *trans*-[(Ph)(PEt$_3$)$_2$Pt(Cl)] in CH$_2$Cl$_2$/^{i}Pr$_2$NH with catalyic CuI readily affords the diplatinum(II) bis(acetylide) complexes *trans*-[(Ph)(PEt$_3$)$_2$Pt-C≡C-R^1-C≡C-Pt(PEt$_3$)$_2$(Ph)] (R^1 = 2,7-fluorenyl **3**) and *trans*-[(Ph)(PEt$_3$)$_2$Pt-C≡C-R^2-C≡C-Pt(PEt$_3$) $_2$(Ph)] (R^2 = 2,7-fluoren-9-onyl **4**) in good yields. Two new rigid-rod organometallic polymers *trans*-[−Pt(PBu$^n_3$)$_2$-C≡C-R^1-C≡C−]∞ (**5**) and *trans*-[−Pt(PBu$^n_3$)$_2$-C≡C-R^2-C≡C−]∞ (**6**) have also been prepared in good yields, in a similar manner to their dinuclear complexes **3** and **4**, by the CuI-catalysed dehydrohalogenation reaction of *trans*-[Pt(PBu$^n_3$)$_2$Cl$_2$] with one equivalent of **1b** or **2b**, in an amine solvent, at ambient temperature. Both poly-yne polymers (colourless **5**, deep red **6**) exhibit good solubility in common organic solvents and readily cast into thin films. The organometallic terminal alkyne complexes *trans*-[Cl(dppm)$_2$M-C≡C-R^2-C≡CH] (M = Ru **7**, Os **8**), obtained by treatment of **2b** with one equivalent of *cis*-[M(dppm)$_2$Cl$_2$] (M = Ru, Os), based on a NaPF$_6$/DBU method have been utilised as starting products for access to the homobimetallic *trans*-[Cl(dppm)$_2$M-C≡C-R^2-C≡C-M(dppm)$_2$Cl] (M = Ru **9**, Os **10**) and heterobimetallic *trans*-[Cl(dppm)$_2$Ru-C≡C-R^2-C≡C-Os(dppm)$_2$Cl] (**11**) systems by reaction with a suitable choice of *cis*-M(dppm)$_2$Cl$_2$ (M = Ru or Os). All the new compounds have been characterised by analytical and spectroscopic methods, and the single-crystal X-ray structure of **1b** has been determined. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Fluorenyl ligand; Platinum; Ruthenium; Osmium; Acetylide

1. Introduction

Conjugated organometallic systems represent an interesting and active area of research in the materials industry [1]. Rigid-rod poly-yne complexes of the type *trans*-[−Pt(PBu$^n_3$)$_2$-C≡C-R-C≡C−]∞ (R = phenyl [2], pyridyl [3], oligothienyl [4], alkynyl [5], etc.) have been prepared and extensively studied by our group. However, to our knowledge, there is no report on such systems bearing fluorenyl derivatives in the backbone. It has been shown that fluorene electron acceptors and their derivatives are widely used in the preparation and investigation of charge transfer complexes [6], in activation of photoconductivity of organic semiconductors ([6]h), and as electron transport materials [7]. Among them, 9-oxo-substituted fluorenes (i.e. fluoren-9-ones) have been most extensively studied [8]. Studies of some 2,7-substituted-9-fluorenyl-ferrocenes as well as the formation of their copolymers with 2,5-diethynyl-1,4-bis(decyloxy)benzene have appeared recently [9].

Bearing this in mind, a program was initiated to investigate the possibility of using fluorenyl moieties in the design of new organometallic dimers, oligomers and polymers. In view of the fact that acetylides are ideal moieties for the synthesis of rigid-rod organometallic species, we believe that the introduction of acetylene-functionalised fluorene derivatives would impart new

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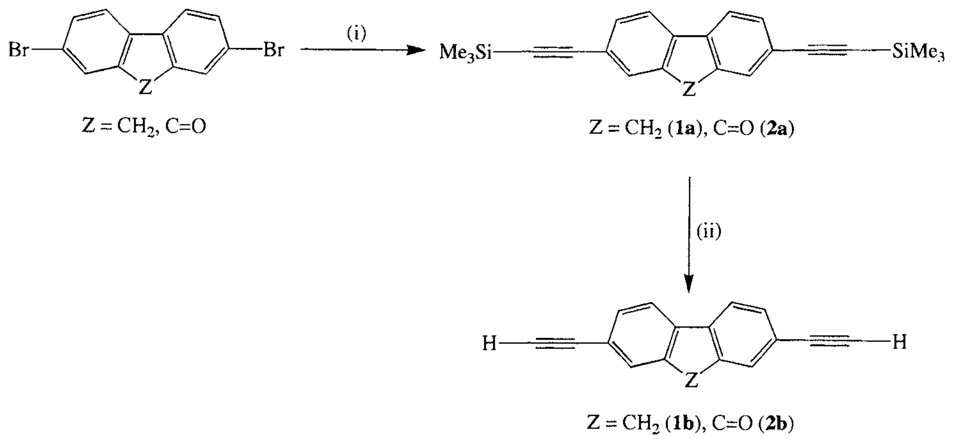
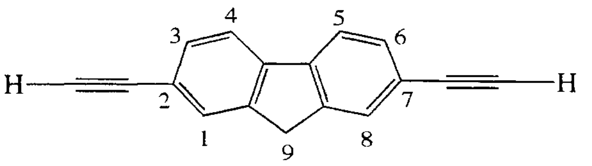


(i) $\mathrm{Me_3SiC{\equiv}CH}$, $\mathrm{Pd(OAc)_2}$, $\mathrm{PPh_3}$, CuI, $\mathrm{{}^iPr_2NH}$

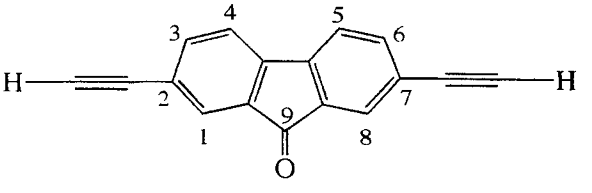
(ii) $\mathrm{K_2CO_3}$, MeOH

Scheme 1. Cross-coupling reactions producing compounds **1a**, **2a** and **1b**, **2b**.

properties to these systems. Here, we report the synthesis and characterisation of some 2,7-disubstituted bis(acetylide) fluorene (**I**) and fluoren-9-one (**II**) compounds and their use in the formation of new bimetallic (both homo- and hetero-bimetallic) di-yne complexes and polymers. The molecular structure of $\mathrm{Me_3Si\text{-}C{\equiv}C\text{-}R^1\text{-}C{\equiv}C\text{-}SiMe_3}$ ($\mathrm{R^1}$ = 2,7-fluorenyl) has been determined by X-ray crystallography.



(**I**)



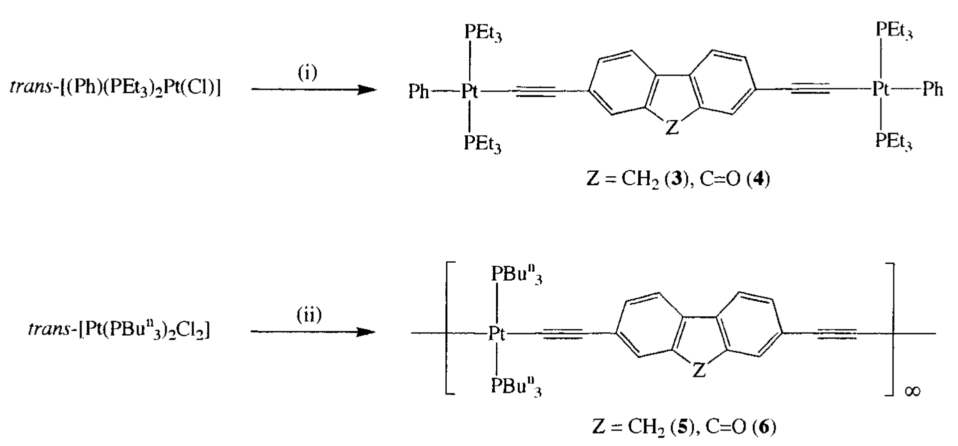
(**II**)

2. Results and discussion

2.1. Syntheses

2,7-Di(trimethylsilylethynyl)fluorene (**1a**) and 2,7-di(trimethylsilylethynyl)fluoren-9-one (**2a**) were prepared via a $\mathrm{Pd^{II}}$/CuI-catalysed cross-coupling reaction of the respective dibromo fluorenes with trimethylsilylacetylene [10] (Scheme 1). Transformation of these trimethylsilyl (TMS)-substituted acetylides to the diterminal ligands $\mathrm{H\text{-}C{\equiv}C\text{-}R^1\text{-}C{\equiv}C\text{-}H}$ ($\mathrm{R^1}$ = 2,7-fluorenyl **1b**) and $\mathrm{H\text{-}C{\equiv}C\text{-}R^2\text{-}C{\equiv}C\text{-}H}$ ($\mathrm{R^2}$ = 2,7-fluoren-9-onyl **2b**) proceed smoothly at room temperature (r.t.) by desilylation of **1a** and **2a** with $\mathrm{K_2CO_3}$ in MeOH [11] (Scheme 1). All the products were purified by column chromatography on silica gel and isolated as white (**1a** and **1b**) and bright yellow (**2a** and **2b**) solids in yields of 69–75%. They were fully characterised by IR, NMR (^{1}H and ^{13}C), UV/VIS spectroscopy, EI-mass spectrometry as well as satisfactory elemental analyses. These diterminal acetylenes are found to be air- and light-stable.

The synthesis of the platinum(II) dimers and polymers is outlined in Scheme 2. The complex *trans*-$\mathrm{[(Ph)(PEt_3)_2Pt(Cl)]}$ was reacted with half an equivalent of **1b** and **2b** in $\mathrm{CH_2Cl_2/{}^iPr_2NH}$, in the presence of CuI, at r.t., to afford the dimeric platinum(II) complexes *trans*-$\mathrm{[(Ph)(PEt_3)_2Pt\text{-}C{\equiv}C\text{-}R^1\text{-}C{\equiv}C\text{-}Pt(PEt_3)_2(Ph)]}$ (**3**) and *trans*-$\mathrm{[(Ph)(PEt_3)_2Pt\text{-}C{\equiv}C\text{-}R^2\text{-}C{\equiv}C\text{-}Pt(PEt_3)_2(Ph)]}$ (**4**), respectively, after TLC purification. Subsequent recrystallisation from a dichloromethane/hexane mixture gave crystals of **3** (colourless) and **4** (red) in good yields. Moreover, the dehydrohalogenation reaction between *trans*-$\mathrm{[Pt(Bu^n_3)_2Cl_2]}$ and the bis(acetylide) reagents **1b** or **2b** (1:1 equivalent) in diisopropylamine, with a catalytic amount of CuI, readily provided a colourless polymer *trans*-$\mathrm{[-Pt(PBu^n_3)_2\text{-}C{\equiv}C\text{-}R^1\text{-}C{\equiv}C-]_\infty}$ (**5**) and a bright red polymer *trans*-$\mathrm{[-Pt(PBu^n_3)_2\text{-}C{\equiv}C\text{-}R^2\text{-}C{\equiv}C-]_\infty}$ (**6**), respectively. Purification of these polymers was accomplished by alumina column chromatography using dichloromethane as eluent, and they were isolated in high purity and good yields (57% **5**, 65% **6**). Both polymers **5** and **6** are soluble in common organic solvents and cast tough, free-standing films. Gel permeation chromatography (GPC) measurements show that



(i) **1b** or **2b** (1/2 equiv.), CuI, $^{i}Pr_2NH/CH_2Cl_2$

(ii) **1b** or **2b** (1 equiv.), CuI, $^{i}Pr_2NH/CH_2Cl_2$

Scheme 2. Synthesis of platinum(II) dimers and polymers.

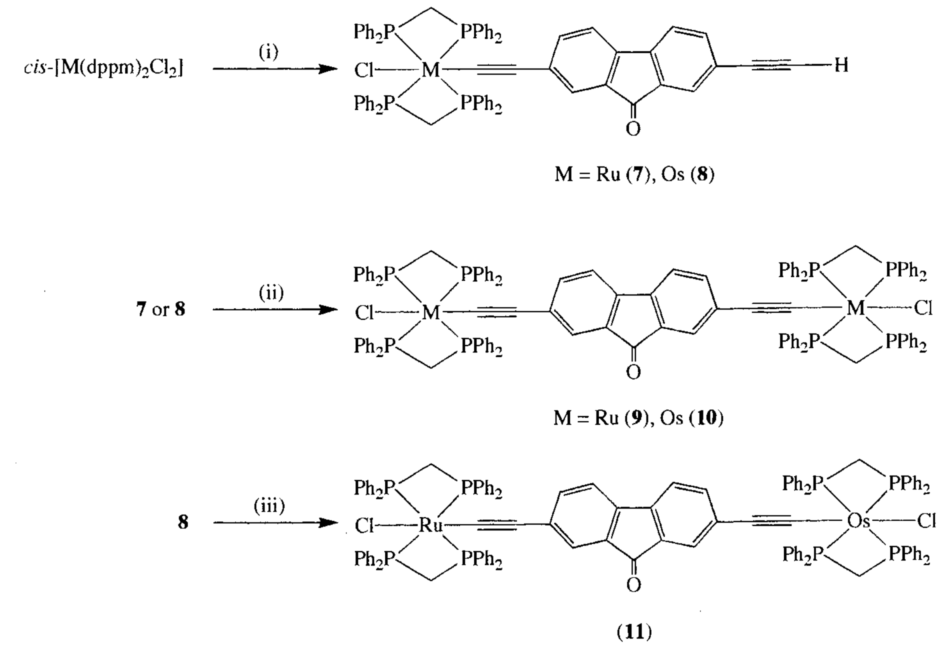
the weight-average molecular-weight (M_w) values for **5** and **6** are 38960 ($n = 1.820$) and 76460 ($n = 1.970$), respectively. This indicates a high degree of polymerisation. The number-average molecular weight (M_n) values of **5** and **6** correspond to 26 and 47 repeating units per chain, respectively. All the spectroscopic and analytical data of **3**–**6** are in accord with the proposed structures and all these metal complexes are air-stable and soluble in common organic solvents.

New terminal acetylide complexes of ruthenium and osmium *trans*-[Cl(dppm)$_2$M-C≡C-R^2-C≡C-H] (M = Ru **7**, Os **8**) were made by a modification of the published procedure through the formation of vinylidene intermediates followed by deprotonation ([1]d) [12]. The reaction of *cis*-[M(dppm)$_2$Cl$_2$] (M = Ru, Os) with one equivalent of **2b** and two equivalents of $NaPF_6$ generated vinylidene complexes which were not isolated but, instead, were deprotonated in situ by one equivalent of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (Scheme 3). In a similar manner, homometallic di-yne complexes *trans*-[Cl(dppm)$_2$M-C≡C-R^2-C≡C-M(dppm)$_2$Cl] (M = Ru **9**, Os **10**) and a mixed metal di-yne complex of ruthenium and osmium *trans*-[Cl(dppm)$_2$Ru-C≡C-R^2-C≡C-Os(dppm)$_2$Cl] (**11**) have been prepared via the $NaPF_6$/DBU method involving *cis*-[Ru(dppm)$_2$Cl$_2$] and **8** in a 1:1 molar ratio (Scheme 3). All these newly synthesised compounds were isolated as bright to dark green solids with yields ranging from 49 to 72% and display good solubility in dichloromethane. The identities of these complexes were based on their IR, ^1H- and $^{31}P\{^1H\}$-NMR spectra and positive FAB-mass spectra.

2.2. Solution spectroscopy

Table 1 summarises basic spectroscopic data for all the new compounds in this study. The all-*trans* configuration of the Pt σ-acetylide dimers and polymers was clearly shown by the simple singlet pattern of their $\nu_{C\equiv C}$ IR and $^{31}P\{^1H\}$-NMR spectra. The $\nu_{C\equiv C}$ values for the diterminal acetylide precursors **1b** and **2b** (2104–2110 cm^{-1}) are much lower than those for the TMS-substituted ligands **1a** and **2a** (2148–2155 cm^{-1}). The fact that terminal acetylenes (HC≡CR) have lower $\nu_{C\equiv C}$ frequencies than their RC≡CR′ counterparts (by about 43 cm^{-1} in this case) is well established [13]. Furthermore, the platinum complexes **3**–**6** display smaller $\nu_{C\equiv C}$ values than those in the corresponding organic ligands, which is attributed to the metal-to-alkyne ligand charge transfer process [14]. For those ligands and platinum(II) complexes containing fluoren-9-one moieties, strong absorption bands due to $\nu_{C\equiv C}$ stretching were detected in the IR spectra. In all cases, signals arising from the aromatic protons of the fluorene fragments were also observed. From the $^{31}P\{^1H\}$-NMR spectral data of all the di-ynes and poly-ynes of platinum, it is clearly seen that the $^1J_{Pt-P}$ coupling constants for the dimers (**3** and **4**) are larger than those for the polymers (**5** and **6**) by almost 300 Hz. Also, we note that the J values associated with the electron deficient fluorenone spacer are slightly lower than those observed in the corresponding polymers.

For **7** and **8**, characteristic $\nu_{C\equiv C}$ and ν_{C-H} IR vibrations were observed at 2063–2068 and 1717 cm^{-1}, respectively. The acetylenic moieties in all these homo- and hetero-bimetallic ruthenium and osmium complexes (**9**–**11**) were characterised by IR spectroscopy in the range 2064–2069 cm^{-1}, with the $\nu_{C\equiv C}$ value of **11** lying in the middle of **9** and **10**. The fluorenone unit in all these metal complexes were also evident from the $\nu_{C=O}$ stretching modes. The terminal protons of both



(i) **2b** (1 equiv.), $NaPF_6$, CH_2Cl_2, DBU

(ii) For (**9**): *cis*-[Ru(dppm)$_2$Cl$_2$], $NaPF_6$, CH_2Cl_2, DBU; for (**10**): *cis*-[Os(dppm)$_2$Cl$_2$], $NaPF_6$, CH_2Cl_2, DBU

(iii) *cis*-[Ru(dppm)$_2$Cl$_2$], $NaPF_6$, CH_2Cl_2, DBU

Scheme 3. Generation of the vinylidene complexes **7**–**11**, demonstrating deprotonation in situ by 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).

complexes **7** and **8** show a singlet resonance at about 3.13 ppm whereas the dppm ligands give a strong signal at − 147.81 and − 190.25 ppm, respectively. In the $^{31}P\{^1H\}$-NMR spectra of **9** and **10**, each shows only a singlet for the eight equivalent ^{31}P nuclei, in accord with a *trans*-chloroalkynylruthenium or osmium compound. A singlet in the $^{31}P\{^1H\}$-NMR spectra of **9** and **10** was observed, characteristic of a $-M(dppm)_2-$ unit in a *trans* geometry. The mixed metal bis(acetylide) complex **11** displays two signals at − 147.69 and − 190.20 ppm due to the ruthenium and osmium-bound P atoms, respectively.

2.3. Electronic absorption spectra

The data for the electronic absorption spectra in the range 300–700 nm for compounds **3**–**11**, at r.t., in CH_2Cl_2, are presented in Table 1, together with data for the corresponding bis(acetylide) fluorene ligands. The UV/VIS absorption spectra of **1a** and **1b** display similar structured intense bands in the UV range (ca. 304–335 nm) which arise from fluorene-localised $\pi \rightarrow \pi^*$ transitions of these ligands. Similarly, the spectra of **2a** and **2b** essentially consist of $\pi \rightarrow \pi^*$ ligand transitions in the near UV (ca. 308–340 nm) and in the visible region at 431 and 421 nm, respectively. For the fluorene-containing complexes **3** and **5**, only intense intraligand $\pi \rightarrow \pi^*$ bands were observed in the near UV region. Apart from the ligand-based $\pi \rightarrow \pi^*$ band at 374 (**4**) and 382 nm (**6**), complexes **4** and **6** also exhibit a broader, intense low-energy absorption feature in the visible region (494 nm **4**, 506 nm **6**), which is tentatively assigned to a metal-to-ligand charge transfer (MLCT) transition. The MLCT nature of this transition was partly supported by solvatochromatic studies. The red shift of 18 nm from hexane (λ 487 nm) to acetone (λ 505 nm) for **4** indicates a change in the dipole moment of the excited state with respect to that of the ground state and is consistent with a dipolar excited state ([9]a)[15]. Due to these MLCT absorptions, the solutions of **4** and **6** have an intense red colour in CH_2Cl_2. It is noteworthy that this lowest MLCT energy band is red-shifted from dimer to polymer and this suggests a higher degree of π-conjugation through the platinum centre in the latter.

The ruthenium and osmium complexes **7**–**11** are intensely coloured compounds and their absorption spectra are characterised by a strong featureless absorption band around 400 nm and a low-energy band beyond 400 nm. These bands are ascribed to the ligand-based $\pi \rightarrow \pi^*$ and the MLCT transitions, respectively. We observe that both transitions appear at longer

Table 1
Some spectroscopic data for the ligand precursors and their metal complexes

Compounds	IR in CH2Cl2 (cm^{-1})			^{31}P{^{1}H}-NMR (ppm)[a]	λ_{max} in CH_2Cl_2 (nm)[b]
	$\nu_{C\equiv C}$	$\nu_{C=O}$	ν_{C-H}		
1a	2148				304 (1.9), 314 (1.8), 327 (1.6), 335 (1.8)
1b	2104		3299		314 (1.2), 319 (1.1), 324 (1.1), 327 (1.2)
2a	2155	1720			313 (0.9), 326 (1.5), 340 (1.7), 431 (0.1)
2b	2110	1738, 1720	3298		308 (1.7), 321 (2.3), 334 (1.6), 421 (0.2)
3	2090			−131.18 (2645)[c]	374 (5.2)
4	2088	1715		−131.07 (2637)[c]	374 (3.4), 494 (0.3)
5	2094			−138.03 (2363)[c]	394 (5.9)[d]
6	2093	1715		−137.87 (2340)[c]	382 (5.1), 506 (0.4)[d]
7	2068	1716	3297	−147.81	400 (3.1), 563 (0.5)
8	2063	1718	3299	−190.25	415 (2.2), 601 (0.3)
9	2069	1711		−147.70	404 (6.1), 579 (0.6)
10	2064	1712		−190.23	412 (4.3), 603 (0.6)
11	2065	1713		−147.69, −190.20	409 (2.6), 590 (0.4)

[a] Referenced to $P(OMe)_3$. [b] Extinction coefficient (in 10^4 cm^{-1} M^{-1}) is given in parentheses. [c] $^{1}J_{Pt-P}$ value (in Hz) is given in parentheses. [d] Molarity is based on the repeating unit of the polymer.

wavelengths for the osmium complexes than those in the ruthenium counterparts.

2.4. Crystal structure of Me_3Si-C≡C-R^1-C≡C-$SiMe_3$ (R^1 = 2,7-fluorenyl)

Single crystals of **1a** suitable for X-ray diffraction studies were grown by slow evaporation of its solution in hexane/CH_2Cl_2 at r.t. Fig. 1 shows a perspective view of the molecule together with the atom-numbering scheme and some selected bond parameters are presented in Table 2. Due to the poorly diffracting nature of the crystal sample of **1a**, the bond parameters should be considered approximate only. There are two independent molecules per asymmetric unit in **1a** and no intermolecular stacking interactions between individual fluorene units in the lattice is observed. In the solid state, each molecule of **1a** consists of two trimethylsilylacetylenic groups appended to a fluorene unit at the 2,7-disubstituted positions. Basically, the molecule has a coplanar conformation and no deviation of the fluorene ring from planarity is apparent (mean deviation 0.05 Å). The two fragments C(4)–C(14)–C(15)–Si(1) and C(11)–C(16)–C(17)–Si(2) are essentially linear, as evident from the mean angles of 175(2) and 177(2)° for the Si–C≡C units in the two independent molecules. The C≡C bond distance [av. 1.18(2) Å] in the trimethylsilylacetylide moiety is typical of terminal acetylides [16].

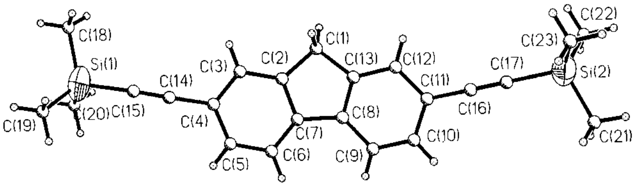


Fig. 1. Molecular structure of Me_3Si-C≡C-R^1-C≡C-$SiMe_3$ (R^1 = 2,7-fluorenyl **1a**).

For **3**, a preliminary X-ray diffraction analysis shows that it consists of discrete diplatinum(II) molecules, with no apparent intermolecular stacking interaction between individual molecules [17]. There are one and a half molecules in the asymmetric unit. Because of poor refinement caused by the disorder of the solvent molecules and the ethyl groups, the detailed molecular dimensions for **3** will not be reported in this article. Structurally, the molecule itself is similar to the dimeric complexes reported recently with oligothienyl spacer groups [4].

3. Conclusion

Our present work has demonstrated the versatility of preparing bis(acetylide)-functionalised fluorene derivatives at the 2,7-positions and that complexation of these organic acetylides with transition metals can occur with good yields at r.t. to afford fluorenyl-bridged conjugated bimetallic and polymeric species. The results have shown that electronic absorption spectral features of these complexes extend over a wide range and can be easily tuned by switching from a fluorene to a fluoren-9-one moiety. Work is currently in progress to further investigate the extent of electron delocalisation and other photophysical properties in these systems. Preliminary work also indicates that the polymers are photoresponsive and their photovoltaic behaviour will be the subject of a future article.

Table 2
Selected bond lengths (Å) and angles (°) for 1a

Molecule 1					
Si(1)–C(15)	1.83(2)	C(14)–C(15)	1.18(2)	C(4)–C(14)	1.46(2)
Si(2)–C(17)	1.83(2)	C(16)–C(17)	1.17(2)	C(11)–C(16)	1.44(2)
C(4)–C(14)–C(15)	178(2)			C(14)–C(15)–Si(1)	175(1)
C(11)–C(16)–C(17)	179(2)			C(16)–C(17)–Si(2)	180(2)
C(2)–C(1)–C(13)	101(1)				
Molecule 2					
Si(3)–C(38)	1.81(2)	C(37)–C(38)	1.19(2)	C(27)–C(37)	1.50(2)
Si(4)–C(40)	1.82(2)	C(39)–C(40)	1.20(2)	C(34)–C(39)	1.44(2)
C(27)–C(37)–C(38)	175(2)			C(37)–C(38)–Si(3)	175(2)
C(34)–C(39)–C(40)	175(2)			C(39)–C(40)–Si(4)	174(1)
C(25)–C(24)–C(36)	104(1)				

4. Experimental

4.1. General procedures

Solvents were predried and distilled from appropriate drying agents [18]. All chemicals, except where stated, were from commercial sources and used as received. The compounds *trans*-[(Ph)$(PEt_3)_2$Pt(Cl)] [19] and *trans*-[Pt$(PBu^n_3)_2Cl_2$] [20] were prepared via literature procedures. NMR spectra were recorded on a Bruker WM-250 or AM-400 spectrometer in appropriate solvents. $^{31}P\{^1H\}$-NMR spectra were referenced to external trimethylphosphite, and the ^1H- and $^{13}C\{^1H\}$-NMR spectra were referenced to solvent resonances. Infrared spectra were recorded as CH_2Cl_2 solutions, in a NaCl cell, on a Perkin-Elmer 1710 Fourier Transform IR spectrometer and mass spectra on a Kratos MS890 spectrometer by either the electron impact or fast atom bombardment technique. Microanalyses were performed in the Department of Chemistry, University of Cambridge. Electronic absorption spectra were obtained with a Perkin-Elmer Lambda UV/NIR spectrometer. Preparative TLC was carried out on commercial Merck plates with a 0.25 mm layer of silica, or on 1 mm silica plates prepared at the University Chemical Laboratory, Cambridge. Column chromatography was performed either on Kieselgel 60 (230–400 mesh) silica gel or alumina (Brockman Grade II–III).

4.2. Ligand syntheses

4.2.1. 2,7-Di(trimethylsilylethynyl)fluorene (**1a**)

To an ice-cooled mixture of 2,7-dibromofluorene (3.89 g, 12 mmol) in 70 cm^3 of freshly distilled diisopropylamine under nitrogen were added CuI (30 mg, 0.16 mmol), $Pd(OAc)_2$ (30 mg, 0.13 mmol) and PPh_3 (90 mg, 0.34 mmol). The solution was stirred for 20 min. $Me_3SiC{\equiv}CH$ (2.95 g, 30.0 mmol) was then added and the suspension was stirred for another 30 min in an ice bath before being warmed to r.t. After reacting for 30 min at r.t., the reaction mixture was heated to 75°C for 20 h. The completion of the reaction was determined by IR and silica TLC. The solution was allowed to cool down to r.t., Et_2O (100 cm^3) was added and the precipitate was filtered off. The pale yellow filtrate was evaporated to dryness. The residue was redissolved in Et_2O (100 cm^3) and washed sequentially with 10% HCl (3×100 cm^3), H_2O (3×100 cm^3), $NaHCO_3$ (3×100 cm^3) and H_2O (3×100 cm^3). The resulting organic solution was then dried ($MgSO_4$), the solvent removed, and the yellow residue chromatographed over a silica gel column by eluting with a 90:10 v/v mixture of hexane and CH_2Cl_2. The product eluted as an off-white band and the pure fraction was evaporated to dryness and recrystallised from hexane/CH_2Cl_2 to give **1a** as an off-white solid in 75% yield (3.23 g). IR (CH_2Cl_2): ν (cm^{-1}) 2148 (C≡C). ^1H-NMR (250 MHz, $CDCl_3$): δ 0.26 (s, 18H, $SiMe_3$), 3.84 (s, 2H, CH_2) and 7.47–7.69 (m, 6H, aromatic H). $^{13}C\{^1H\}$-NMR (100.6 MHz, $CDCl_3$): δ 0.03 ($SiMe_3$), 36.44 (CH_2), 94.45 (C≡C), 105.67 (C≡C), 119.97 (fluorenyl CH), 121.59 (fluorenyl quat. C), 128.55 (fluorenyl CH), 131.00 (fluorenyl CH), 141.32 (fluorenyl quat. C) and 143.38 (fluorenyl quat. C). EI-mass spectrum: m/z 358 (M^+). Calc. for $C_{23}H_{26}Si_2$: C, 77.06; H, 7.32. Found: C, 76.79; H, 7.29%.

4.2.2. 2,7-Di(ethynyl)fluorene (**1b**)

A mixture of **1a** (0.50 g, 1.4 mmol) and K_2CO_3 (0.19 g, 1.4 mmol) in MeOH (50 cm^3) was stirred at r.t. for 20 h. IR spectroscopy showed that all the starting material had been consumed. Solvent was removed under reduced pressure to leave a pale yellow residue. This residue was dissolved in the minimum amount of CH_2Cl_2 and subjected to column chromatography on silica using hexane/CH_2Cl_2 (60:40 v/v) as eluent to afford a major off-white product identified as **1b** (0.22 g, 73%). IR (CH_2Cl_2): ν (cm^{-1}) 2104 (C≡C), 3299 (C≡CH). ^1H-NMR (250 MHz, $CDCl_3$): δ 3.12 (s, 2H, C≡CH), 3.88 (s, 2H, CH_2) and 7.51–7.72 (m, 6H, aromatic H). $^{13}C\{^1H\}$-NMR (100.6 MHz, $CDCl_3$): δ 36.52 (CH_2), 77.43 (C≡C), 84.18 (C≡C), 120.14

(fluorenyl CH), 120.69 (fluorenyl quat. C), 128.78 (fluorenyl CH), 131.20 (fluorenyl CH), 141.55 (fluorenyl CH) and 143.48 (fluorenyl quat. C). EI-mass spectrum: m/z 214 (M^+). Calc. for $C_{17}H_{10}$: C, 95.29; H, 4.71. Found: C, 95.23; H, 4.96%.

4.2.3. *2,7-Di(trimethylsilylethynyl)fluoren-9-one (**2a**)*

2,7-Dibromofluoren-9-one (4.06 g, 12.0 mmol), $Me_3SiC{\equiv}CH$ (2.95 g, 30.0 mmol) and $^iPr_2NH$ (100 cm^3) were mixed as in **1a** with catalytic amounts of CuI (30 mg), $Pd(OAc)_2$ (30 mg) and PPh_3 (90 mg). The crude product was worked-up, as before, to yield a yellow residue which was then applied to a silica column, eluting with hexane/CH_2Cl_2 (1:1, v/v). The desired compound **2a** was isolated as a bright yellow solid (3.10 g, 69%). IR (CH_2Cl_2): ν (cm^{-1}) 2155 (C≡C), 1720 (C=O). ^{1}H-NMR (250 MHz, $CDCl_3$): δ 0.24 (s, 18H, $SiMe_3$) and 7.43–7.72 (m, 6H, aromatic H). ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ −0.40 ($SiMe_3$), 96.73 (C≡C), 103.91 (C≡C), 120.49 (fluoren-9-onyl CH), 124.39 (fluoren-9-onyl quat. C), 128.46 (fluoren-9-onyl CH), 134.31 (fluoren-9-onyl quat. C), 138.19 (fluoren-9-onyl CH), 143.36 (fluoren-9-onyl quat. C), 143.36 (fluoren-9-onyl quat. C) and 192.11 (C=O). EI-mass spectrum: m/z 372 (M^+). Calc. for $C_{23}H_{24}OSi_2$: C, 74.17; H, 6.50. Found: C, 74.24; H, 6.49%.

4.2.4. *2,7-Di(ethynyl)fluoren-9-one (**2b**)*

The TMS-derivative **2a** (1.00 g, 2.7 mmol) was desilylated using K_2CO_3 (0.37 g, 2.7 mmol) in 50 cm^3 MeOH and the mixture was stirred overnight. The solvent was then removed under reduced pressure to afford a bright yellow residue which was dissolved in CH_2Cl_2 rather than Et_2O, due to its limited solubility in Et_2O. Subsequent washing with H_2O (3 × 100 cm^3) on a separatory funnel left the crude product **2b** in CH_2Cl_2 layer as a yellow solution. The organic layer was dried over $MgSO_4$ and filtered. The filtrate was concentrated and applied to a silica column. The desired yellow band was collected with the aid of pure CH_2Cl_2 to afford **2b** (0.45 g, 73%) as a leathery yellow solid. IR (CH_2Cl_2): ν (cm^{-1}) 2110 (C≡C), 3298 (C≡CH), 1738, 1720 (C=O). ^{1}H-NMR (250 MHz, $CDCl_3$): δ 3.18 (s, 2H, C≡CH) and 7.48–7.77 (m, 6H, aromatic H). $^{13}C\{^1H\}$-NMR (100.6 MHz, $CDCl_3$): δ 79.24 (C≡C), 82.57 (C≡C), 120.65 (fluoren-9-onyl CH), 123.48 (fluoren-9-onyl quat. C), 128.02 (fluoren-9-onyl CH), 134.34 (fluoren-9-onyl quat. C), 138.50 (fluoren-9-onyl CH), 143.64 (fluoren-9-onyl quat. C) and 191.91 (C=O). EI-mass spectrum: m/z 228 (M^+). Calc. for $C_{17}H_8O$: C, 89.46; H, 3.53. Found: C, 89.51; H, 3.65%.

4.3. *Complex and polymer preparations*

4.3.1. *Trans-[(Ph)(PEt$_3$)$_2$Pt-C≡C-R^1-C≡C-Pt(PEt$_3$)$_2$(Ph)] (R^1 = 2,7-fluorenyl, **3**)*

Treatment of the diterminal alkyne **1b** (43 mg, 0.2 mmol) with two equivalents of *trans*-$[(Ph)(PEt_3)_2Pt(Cl)]$ (0.22 g, 0.4 mmol) for 15 h at r.t., in the presence of CuI (3 mg), in $CH_2Cl_2/^iPr_2NH$ (50 cm^3, 1:1 v/v) gave the title complex as a colourless solid in 65% yield (0.16 g) after purification on silica TLC plates using hexane/CH_2Cl_2 (40:60, v/v) eluent. IR (CH_2Cl_2): ν (cm^{-1}) 2090 (C≡C). ^{1}H-NMR (250 MHz, $CDCl_3$): δ 1.10 (m, 36H, CH_3), 1.77 (m, 24H, CH_2), 3.77 (s, 2H, fluorenyl CH_2), 6.79 (t, 2H, H_{para} of Ph), 6.96 (t, 4H, H_{meta} of Ph), 7.26 (m, 2H, fluorenyl CH), 7.32 (br, 4H, H_{ortho} of Ph), 7.41 (s, 2H, fluorenyl CH) and 7.53 (d, 2H, $^3J_{HH}$ = 7.9 Hz, fluorenyl CH). $^{31}P\{^1H\}$-NMR (101.3 MHz, $CDCl_3$): δ −131.18, $^1J_{Pt-P}$ = 2645 Hz. FAB-mass spectrum: m/z 1229 (M^+). Calc. for $C_{53}H_{78}P_4Pt_2$: C, 51.79; H, 6.40. Found: C, 52.32; H, 6.58%.

4.3.2. *Trans-[(Ph)(PEt$_3$)$_2$Pt-C≡C-R^2-C≡C-Pt(PEt$_3$)$_2$(Ph)] (R^2 = 2,7-fluoren-9-onyl, **4**)*

To a mixture of **2b** (46 mg, 0.2 mmol) and two equivalents of *trans*-$[(Ph)(PEt_3)_2Pt(Cl)]$ (0.22 g, 0.4 mmol) in $CH_2Cl_2/^iPr_2NH$ (60 cm^3, 1:1 v/v) was added CuI (3 mg). The solution was stirred at r.t. over a period of 15 h, after which all volatile components were removed under reduced pressure. The product was purified on preparative TLC plates with hexane/CH_2Cl_2 (30:70, v/v) as eluent, giving compound **4** as a red solid in an isolated yield of 68% (0.17 g). IR (CH_2Cl_2): 2088 (C≡C), 1715 (C=O). ^{1}H-NMR (250 MHz, $CDCl_3$): δ 1.09 (m, 36H, CH_3), 1.75 (m, 24H, CH_2), 6.80 (t, 2H, H_{para} of Ph), 6.93 (t, 4H, H_{meta} of Ph), 7.26 (m, 4H, fluoren-9-onyl CH), 7.32 (br, 4H, H_{ortho} of Ph) and 7.49 (m, 2H, fluoren-9-onyl CH). $^{31}P\{^1H\}$-NMR (101.3 MHz, $CDCl_3$): δ −131.07, $^1J_{Pt-P}$ = 2637 Hz. FAB-mass spectrum: m/z 1243 (M^+). Calc. for $C_{53}H_{76}OP_4Pt_2$: C, 51.20; H, 6.16. Found: C, 51.27; H, 6.13%.

4.3.3. *Trans-[–Pt(PBu$^n_3$)$_2$-C≡C-R^1-C≡C–]∞ (**5**)*

To a mixture of *trans*-$[Pt(PBu^n_3)_2Cl_2]$ (0.10 g, 0.15 mmol) and one equivalent of H-C≡C-R^1-C≡C-H (**1b**, 32 mg, 0.15 mmol) in $CH_2Cl_2/^iPr_2NH$ (50 cm^3, 1:1 v/v) was added CuI (3 mg). The solution mixture was stirred at r.t. over a period of 15 h, after which all volatile components were removed under reduced pressure. The residue was redissolved in dichloromethane and filtered through a short alumina column. After removal of solvent by rotary evaporator, an almost colourless film was obtained readily, and it was then washed with methanol to give the polymer **5** in 57% yield (0.07 g). Further purification can be accomplished by precipitating the polymer solution in toluene from methanol. IR

(CH_2Cl_2): ν (cm^{-1}) 2094 (C≡C). ^{1}H-NMR (250 MHz, CD_2Cl_2): δ 0.96 (t, 18H, CH_3), 1.42–1.67 [m, 24H, $(CH_2)_2$], 2.05–2.21 (m, 12H, PCH_2), 3.79 (s, 2H, fluorenyl CH_2), 7.25 (d, 2H, $^3J_{HH} = 7.7$, fluorenyl CH), 7.41 (s, 2H, fluorenyl CH) and 7.57 (d, 2H, $^3J_{HH} = 7.9$ Hz, fluorenyl CH]. $^{31}P\{^1H\}$-NMR (101.3 MHz, $CDCl_3$): δ -138.03, $^1J_{Pt-P} = 2363$ Hz. Calc. for $[C_{41}H_{62}P_2Pt]_n$: C, 60.65; H, 7.70. Found: C, 60.20; H, 7.73%. $M_w = 38960$, $M_n = 21410$ ($n = 1.820$).

4.3.4. *Trans-[–Pt(PBu$^n_3$)$_2$-C≡C-R^2-C≡C–]∞ (**6**)*

Similar procedures as in **5** were adopted using H-C≡C-R^2-C≡C-H (**2b**, 34 mg, 0.15 mmol) to produce a deep red polymer **6** in 65% yield (0.08 g). IR (CH_2Cl_2): ν (cm^{-1}) 2093 (C≡C), 1715 (C=O). ^{1}H-NMR (250 MHz, $CDCl_3$): δ 0.92 (t, 18H, CH_3), 1.37–1.70 [m, 24H, $(CH_2)_2$], 1.96–2.26 (m, 12H, PCH_2), 7.29 (m, 4H, fluoren-9-onyl CH) and 7.48 (m, 2H, fluoren-9-onyl CH). $^{31}P\{^1H\}$-NMR (101.3 MHz, $CDCl_3$): δ -137.87, $^1J_{Pt-P} = 2340$ Hz. Calc. for $[C_{41}H_{60}OP_2Pt]_n$: C, 59.62; H, 7.32. Found: C, 58.82; H, 7.40%. $M_w = 76460$, $M_n = 38820$ ($n = 1.970$).

4.3.5. *Trans-[Cl(dppm)$_2$M-C≡C-R^2-C≡C-H] (M = Ru **7**, Os **8**)*

A mixture of *cis*-[M(dppm)$_2$Cl$_2$] (M = Ru, 4.9 mg; Os, 54 mg; 0.05 mmol), H-C≡C-R^2-C≡C-H (**2b**, 12 mg, 0.05 mmol) and $NaPF_6$ (17 mg, 0.10 mmol) in CH_2Cl_2 (50 cm^3) were stirred for 10 h (20 h in the case of Os) at r.t. The resulting dark red solution was filtered through a pad of Celite to remove any excess $NaPF_6$ and NaCl by-product, and DBU (one equivalent) was added. The solution turned dark green immediately. After 3 h stirring, the solvent was filtered and then removed in vacuo. The green product was purified by washing with a small volume of dry methanol and hexane to afford a dark green (**7**) to deep green (**8**) powder (yield 40 mg, 71% **7**; 44 mg, 72% **8**). (**7**): IR (CH_2Cl_2): ν (cm^{-1}) 3297 (≡C–H), 2068 (C≡C), 1716 (C=O). ^{1}H-NMR (250 MHz, $CDCl_3$): δ 3.13 (s, 1H, ≡C–H), 4.91 (virtual t, 4H, PCH_2P), 6.05 (dd, 1H, $J_{HH} = 1.4$, 7.7, H_3), 6.26 (d, 1H, $J_{HH} = 1.4$, H_1), 7.00 (d, 1H, $J_{HH} = 7.7$ Hz, H_4) and 7.06–7.76 (m, 43H, Ph + $H_{5,6,8}$). $^{31}P\{^1H\}$-NMR (101.3 MHz, $CDCl_3$): δ -147.81. FAB-mass spectrum: *m/z* 1132 (M^+). Calc. for $C_{67}H_{51}ClOP_4Ru \cdot MeOH$: C, 70.13; H, 4.76. Found: C, 69.28; H, 4.61%. (**8**): IR (CH_2Cl_2): ν (cm^{-1}) 3299 (≡C–H), 2063 (C≡C), 1718 (C=O). ^{1}H-NMR (250 MHz, $CDCl_3$): δ 3.12 (s, 1H, ≡C–H), 5.45 (m, 4H, PCH_2P), 6.04 (dd, 1H, $J_{HH} = 1.4$, 7.8, H_3), 6.21 (d, 1H, $J_{HH} = 1.4$, H_1), 6.99 (d, 1H, $J_{HH} = 7.8$ Hz, H_4) and 7.06–7.77 (m, 43H, Ph + $H_{5,6,8}$). $^{31}P\{^1H\}$-NMR (101.3 MHz, $CDCl_3$): δ -190.25. FAB-mass spectrum: *m/z* 1222 (M^+). Calc. for $C_{67}H_{51}ClOP_4Os$: C, 65.87; H, 4.21. Found: C, 66.14; H, 4.12%.

4.3.6. *Trans-[Cl(dppm)$_2$M-C≡C-R^2-C≡C-M(dppm)$_2$Cl] (M = Ru **9**, Os **10**)*

To a solution of *cis*-[M(dppm)$_2$Cl$_2$] (M = Ru, Os; 0.03 mmol) in 40 cm^3 of CH_2Cl_2, *trans*-[Cl(dppm)$_2$M-C≡C-R^2-C≡C-H] (**7** for M = Ru, **8** for Os; 0.03 mmol) and $NaPF_6$ (10 mg, 0.06 mmol) were added. The reaction mixture was allowed to react for 8 h at ambient temperature. The dark solution was then filtered and subsequently treated with one equivalent of DBU for 3 h. Filtration and evaporation of all volatile components under reduced pressure permitted the isolation of the required product as a green solid in each case. Purification was achieved by washing the solid with methanol/hexane and both products were found to be pure (yield 51% **9**, 55% **10**). (**9**): IR (CH_2Cl_2): ν (cm^{-1}) 2069 (C≡C), 1711 (C=O). ^{1}H-NMR (250 MHz, $CDCl_3$): δ 4.92 (virtual t, 8H, PCH_2P), 5.93 (dd, 2H, $J_{HH} = 1.4$, 7.7, $H_{3,6}$), 6.33 (d, 2H, $J = 1.4$, $H_{1,8}$), 6.81 (d, 2H, $J = 7.7$ Hz, $H_{4,5}$) and 7.05–7.58 (m, 80H, Ph). $^{31}P\{^1H\}$-NMR (101.3 MHz, $CDCl_3$): δ -147.70. FAB-mass spectrum: *m/z* 2037 (M^+). Calc. for $C_{117}H_{94}Cl_2OP_8Ru_2$: C, 68.99; H, 4.65. Found: C, 68.67; H, 4.59%. (**10**): IR (CH_2Cl_2): ν (cm^{-1}) 2064 (C≡C), 1712 (C=O). ^{1}H-NMR (250 MHz, $CDCl_3$): δ 5.43 (m, 8H, PCH_2P), 5.91 (dd, 2H, $J_{HH} = 1.4$, 7.7, $H_{3,6}$), 6.27 (d, 2H, $J = 1.4$, $H_{1,8}$), 6.80 (d, 2H, $J = 7.7$ Hz, $H_{4,5}$) and 7.07–7.40 (m, 80H, Ph). $^{31}P\{^1H\}$-NMR (101.3 MHz, $CDCl_3$): δ -190.23. FAB-mass spectrum: *m/z* 2217 (M^+). Calc. for $C_{117}H_{94}Cl_2OP_8Os_2 \cdot CH_2Cl_2$: C, 61.62; H, 4.21. Found: C, 60.87; H, 4.30%.

4.3.7. *Trans-[Cl(dppm)$_2$Ru-C≡C-R^2-C≡C-Os(dppm)$_2$Cl] (**11**)*

Cis-[Ru(dppm)$_2$Cl$_2$] (28 mg, 0.03 mmol) was reacted with *trans*-[Cl(dppm)$_2$Os-C≡C-R^2-C≡C-H] (**8**, 37 mg, 0.03 mmol) and $NaPF_6$ (10 mg, 0.06 mmol) in CH_2Cl_2 (40 cm^3) for 4 h. The dark brown vinylidene solution was filtered and DBU (one equivalent) was added to produce a deep green solution at once. Stirring was continued for 3 h and the solution was filtered and removed. Analytically pure fine powder of **11** (31 mg, 49%) was obtained after washing with methanol followed by hexane. IR (CH_2Cl_2): ν (cm^{-1}) 2065 (C≡C), 1713 (C=O). ^{1}H-NMR (250 MHz, $CDCl_3$): δ 4.91 [virtual t, 4H, Ru(PCH_2P)], 5.44 [m, 4H, Os(PCH_2P)], 5.92 (dd, 2H, $J_{HH} = 1.4$, 7.7, $H_{3,6}$), 6.27 (d, 1H, $J_{HH} = 1.4$, H_1 or H_8), 6.32 (d, 1H, $J_{HH} = 1.4$ Hz, H_1 or H_8), 6.82 (m, 2H, $H_{4,5}$) and 7.07–7.76 (m, 80H, Ph). $^{31}P\{^1H\}$-NMR (101.3 MHz, $CDCl_3$): δ -147.69, -190.20. FAB-mass spectrum: *m/z* 2127 (M^+). Calc. for $C_{117}H_{94}Cl_2OP_8RuOs \cdot CH_2Cl_2$: C, 64.10; H, 4.38. Found: C, 64.16; H, 4.58%.

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **1a**

Atom	x	y	z	U(eq)[a]
Si(1)	8718(2)	−1299(3)	9655(2)	101(2)
Si(2)	3294(2)	3216(2)	4665(2)	88(2)
Si(3)	8546(3)	−1235(3)	7268(2)	114(12
Si(4)	3418(2)	3389(2)	2058(2)	94(2)
C(1)	6085(6)	1348(6)	7454(5)	81(4)
C(2)	6252(7)	613(7)	7637(5)	65(4)
C(3)	6833(7)	339(7)	8086(6)	78(4)
C(4)	6900(7)	−371(8)	8177(6)	77(4)
C(5)	6372(7)	−790(7)	7803(5)	76(4)
C(6)	5799(7)	−519(7)	7348(6)	77(4)
C(7)	5740(6)	172(7)	7263(5)	51(4)
C(8)	5219(6)	604(7)	6820(5)	54(4)
C(9)	4614(6)	433(6)	6337(5)	67(4)
C(10)	4231(7)	935(7)	5944(6)	74(4)
C(11)	4431(6)	1624(7)	6017(5)	63(4)
C(12)	5039(7)	1787(7)	6524(6)	84(4)
C(13)	5425(7)	1270(7)	6919(6)	66(4)
C(14)	7503(8)	−673(8)	8652(7)	90(5)
C(15)	7998(8)	−901(7)	9038(7)	89(5)
C(16)	4052(7)	2137(8)	5580(6)	81(5)
C(17)	3757(7)	2558(8)	5224(6)	85(5)
C(18)	9238(8)	−616(8)	10175(8)	163(8)
C(19)	9214(8)	−1837(10)	9337(7)	185(9)
C(20)	8369(8)	−1854(8)	10105(6)	139(7)
C(21)	2626(6)	2783(7)	4020(5)	111(5)
C(22)	2914(8)	3826(7)	5031(6)	132(6)
C(23)	3888(7)	3657(8)	4389(7)	132(6)
C(24)	6443(7)	1179(7)	4450(6)	91(50
C(25)	6486(7)	764(6)	4992(5)	66(4)
C(26)	7036(7)	371(6)	5396(6)	84(5)
C(27)	6945(7)	50(7)	5871(6)	80(4)
C(28)	6335(8)	106(8)	5950(7)	114(6)
C(29)	5805(8)	491(8)	5552(7)	117(6)
C(30)	5889(7)	814(7)	5082(6)	75(4)
C(31)	5423(8)	1247(7)	4585(6)	91(5)
C(32)	4744(8)	1424(8)	4473(7)	119(6)
C(33)	4417(8)	1832(8)	3965(7)	113(6)
C(34)	4719(8)	2048(8)	3582(7)	94(5)
C(35)	5371(7)	1860(6)	3699(5)	75(4)
C(36)	5470(7)	1447(7)	4205(6)	75(4)
C(37)	7493(8)	−389(8)	6312(7)	91(5)
C(38)	7933(9)	−703(8)	6694(7)	110(6)
C(39)	4323(8)	2448(8)	3052(7)	97(5)
C(40)	3976(7)	2809(7)	2636(6)	88(5)
C(41)	9039(6)	−1708(8)	6905(6)	125(6)
C(42)	9110(8)	−662(7)	7882(7)	143(7)
C(43)	8074(8)	−1826(7)	7583(6)	132(6)
C(44)	3967(7)	3929(7)	1794(6)	129(6)
C(45)	2968(8)	3897(8)	2432(7)	150(7)
C(46)	2798(8)	2879(8)	1420(6)	137(7)

[a] Equivalent isotropic U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

4.4. Molecular weight measurements

Molar masses were determined by gel permeation chromatography (GPC) using two PL Gel 30 cm, 5 micron mixed C columns at 30°C running in THF at 1 cm^3 min-1 with a Roth Mocel 200 high precision pump. A DAWN DSP (Wyatt Technology) Multi-Angle Laser Light Scattering (MALLS) apparatus with 18 detectors and auxiliary Viscotek model 200 differential refractometer/viscometer detectors was used to calculate the absolute molecular weights (referred to GPC LS).

4.5. Crystallography

Geometric and intensity data for **1b** were collected using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71069$ Å) on the MAR Research image plate scanner and $65 \times 3°$ frames with an exposure time of 5 min per frame were used. The intensity data were corrected for Lorentz and polarisation effects and interframe scaling was applied. The structure was solved by direct methods (SHELXTL PLUS) [21] and subsequent Fourier-difference syntheses, and refined by full-matrix least squares on F^2 (SHELXL 93) [22]. *Crystal data*: $C_{23}H_{26}Si_2$, M 358.62, crystal size $0.22 \times 0.18 \times 0.17$ mm, monoclinic, space group $C2/c$, $a = 21.369(2)$, $b = 19.516(2)$, $c = 23.791(2)$ Å, $\beta = 113.09(2)°$, $U = 9127(2)$ Å^3, $Z = 16$, $F(000) = 3072$, $D_c = 1.044$ g cm^{-3}, $\mu = 0.158$ mm^{-1} $T = 293(2)$ K, $2\theta = 2.9–43.0°$, measured reflections 2870, independent reflections 2870 ($R_{int} = 0$), observed reflections [$I > 2\sigma(I)$] 2863, hydrogen atoms were included using a riding model, refined parameters 281, weight $w^{-1} = [\sigma^2(F_o^2) + (0.1513P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$, GOF on $F^2 = 0.962$, final $R_1 = 0.0863$, $wR_2 = 0.2172$ [$I > 2\sigma(I)$]. Because of the very weak diffracting capacity of **1a**, only the silicon and carbon atoms in the methyl groups were assigned with anisotropic displacement parameters to maintain a reasonable data-to-parameter ratio of ten. A final Fourier-difference electron density synthesis revealed maximum and minimum residual electron-density peaks of 0.31 and − 0.29 eÅ^{-3}. Atomic coordinates are given in Table 3.

Additional material is available from the Cambridge Crystallographic Data Centre (CCDC), comprising hydrogen atom coordinates, thermal parameters and full tables of bond lengths and angles.

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