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FULL PAPER

Synthesis, structures and properties of platinum(II) complexes of oligoacetylenic sulfides

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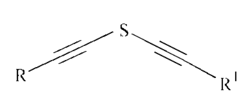
A series of novel platinum(II) acetylide complexes incorporating sulfur-linked oligoalkynes have been prepared. The CuI-catalysed dehydrohalogenation reactions of the mono-protected dialkyne ligand HC≡CSC≡C(TIPS) (TIPS = Pr^i_3Si) with *trans*-[Pt(PBu_3)$_2$$Cl_2$], *cis*-[Pt(dppe)$Cl_2$] or *cis*-[Pt($Me_2$bipy)$Cl_2$] ($Me_2$bipy = 4,4′-dimethyl-2,2′-bipyridine), in the presence of a base, readily produced *trans*-[Pt(PBu_3)$_2${C≡CSC≡C(TIPS)}$_2$] **1**, *cis*-[Pt(dppe){C≡CSC≡C(TIPS)}$_2$] **3** and *cis*-[Pt(Me_2bipy){C≡CSC≡C(TIPS)}$_2$] **7**, respectively, in good yields. Similar synthetic procedures using a diacetylenic sulfide species HC≡CSC≡CC≡CSC≡C(TIPS) afforded *trans*-[Pt(PBu_3)$_2$-{C≡CSC≡CC≡CSC≡C(TIPS)}$_2$] **2** and *cis*-[Pt(dppe){C≡CSC≡CC≡CSC≡C(TIPS)}$_2$] **4**, both of which contain eight triple-bond units within the molecular entity. Two new metallo-end-capped derivatives *trans*-[Ph(Et_3P)$_2$Pt–C≡CSC≡C–Pt(PEt_3)$_2$Ph] **5** and *trans*-[Ph(Et_3P)$_2$Pt–C≡CSC≡CC≡CSC≡C–Pt(PEt_3)$_2$Ph] **6** were also synthesized in moderate yields by reactions of two equivalents of *trans*-[PtPh(Cl)(PEt_3)$_2$] and the diterminal acetylenic sulfides HC≡CSC≡CH and HC≡CSC≡CC≡CSC≡CH in a CuI/(Me_3Si)$_2$NH system. All of the compounds **1**–**7** have been characterized by IR, NMR (^{1}H, ^{13}C and ^{31}P) and UV/VIS spectroscopies, luminescence measurements and mass spectrometry. The solid-state molecular structures of **5** and **7** have been established by X-ray crystallography.

Conjugated cyclic or linear oligoacetylene systems are a rapidly developing area and it is anticipated that these acetylene-based molecules have opened new avenues of fundamental and technological research at the interface between chemistry and materials science.[1] In fact, these carbon-rich networks have been shown to exhibit a variety of unusual structural, electronic, electrical and optical properties.[1b,d,2] Linear rigid acetylenic frameworks could also function as molecular wires and are widely used for the fabrication of molecular nanostructures.[3] Recently, the synthesis of extended rigid-rod structures containing transition-metal σ-bound acetylides and diacetylides has attracted considerable attention,[4] in view of their potential non-linear optical[5] and liquid-crystalline properties.[6] Insertion of a transition metal within the skeleton is especially intriguing since the d electrons of transition metals are polarizable and induce polarization in these systems.[4c] Transition-metal bis(acetylides) are numerous and both *cis*- and *trans*-substituted systems have been reported for platinum complexes.[7] A few cyclic structures involving platinum centres have been prepared.[4b–d] Molecular wires end-capped with redox-active metal centres containing conjugated acetylene units are also known.[8]

We are interested in the synthesis and uses of acetylenic sulfoxides and related compounds as two-carbon synthons in organic synthesis.[9] A systematic approach to the preparation of new oligoacetylenic sulfides **I**–**III** has recently been communicated in preliminary form.[10] The synthesis relies on simple but efficient procedures such as Hay and Glaser-type coupling of terminal acetylenic units and formation of alkynyl sulfides with electrophilic sulfur transfer reagents such as SCl_2.[11] In this way, linear acetylenic and diacetylenic sulfides consisting of up to eight triple-bond units with alternating sulfur atoms and acetylenic units were successfully prepared.[10] These oligomeric acetylenic sulfides are attractive building blocks for molecular architectures. However, to the best of our knowledge, there is no report on transition metal-containing oligoacetylenic sulfides. As an extension of our interest in this important field, it seemed an attractive goal to us to synthesize new organometallic acetylenic sulfide complexes of different chain lengths. Here we report the first synthesis and physical characterization of a series of monomeric and dimeric platinum(II) complexes of oligoacetylenic sulfides. These complexes adopt either a *cis* or *trans* configuration about the metal centre. The crystal structures of two of them are among the first platinum acetylenic sulfide complexes to have been characterized crystallographically.

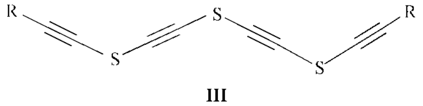


I

R – R^1 – Me_3Si
R – R^1 – TIPS
R – Me_3Si, R^1 – TIPS
R – R^1 – H
R – H, R^1 – TIPS

II

R – R^1 – TIPS
R – H, R^1 – TIPS



III

R – H or TIPS

Results and discussion

Syntheses

Our strategy to prepare the desired platinum(II) complexes of oligoacetylenic sulfides rests on a reaction sequence developed for the synthesis of some platinum mono(acetylide) and bis(acetylide) species.[7] Chelating diphosphines and bipyridines

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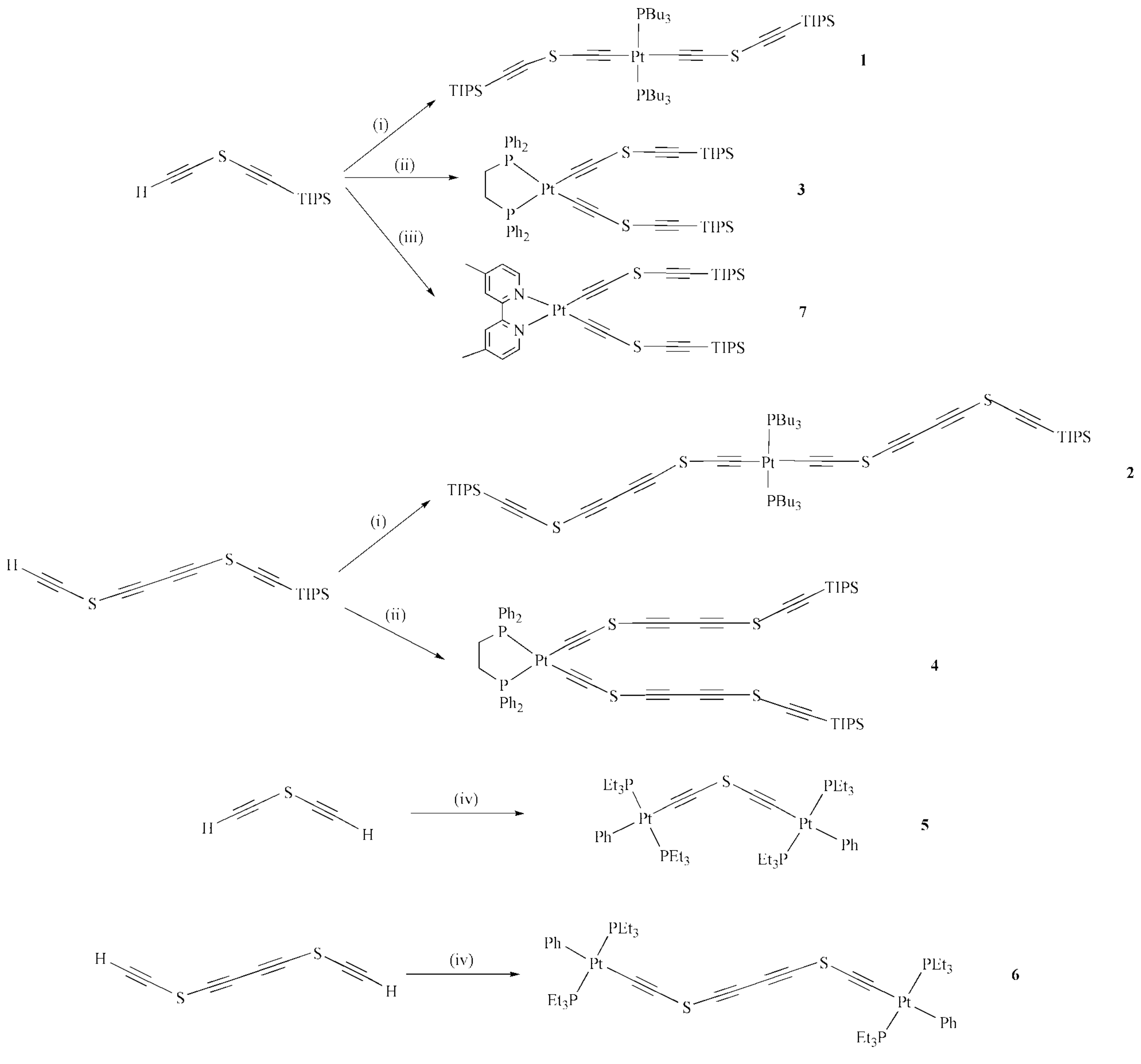

Scheme 1 (i) *trans*-[$\mathrm{Pt(PBu_3)_2Cl_2}$] (0.5 equivalent), CuI, $\mathrm{CH_2Cl_2/(Me_3Si)_2NH}$; (ii) *cis*-[Pt(dppe)$\mathrm{Cl_2}$] (0.5 equivalent), CuI, $\mathrm{CH_2Cl_2/(Me_3Si)_2NH}$; (iii) *cis*-[$\mathrm{Pt(Me_2bipy)Cl_2}$] (0.5 equivalent), CuI, $\mathrm{CH_2Cl_2/NHPr^i_2}$; (iv) *trans*-[$\mathrm{PtPh(Cl)(PEt_3)_2}$] (2 equivalents), CuI, $\mathrm{CH_2Cl_2/(Me_3Si)_2NH}$.

were employed to enforce the *cis* geometry at the metal atom. The synthetic methodologies leading to the target molecules are shown in Scheme 1. With one end protected as the relatively more stable TIPS group ($\mathrm{Pr^i_3Si}$), reactions of two molar equivalents of $\mathrm{HC{\equiv}CSC{\equiv}C(TIPS)}$ with *trans*-[$\mathrm{Pt(PBu_3)_2Cl_2}$], *cis*-[Pt(dppe)$\mathrm{Cl_2}$] or *cis*-[$\mathrm{Pt(Me_2bipy)Cl_2}$] ($\mathrm{Me_2bipy}$ = 4,4′-dimethyl-2,2′-bipyridine) *via* a CuI-catalysed dehydrohalogenation process using $\mathrm{(Me_3Si)_2NH}$ or $\mathrm{NHPr^i_2}$ as a base afforded three bis(acetylide) complexes *trans*-[$\mathrm{Pt(PBu_3)_2\{C{\equiv}CSC{\equiv}C(TIPS)\}_2}$] **1**, *cis*-[$\mathrm{Pt(dppe)\{C{\equiv}CSC{\equiv}C(TIPS)\}_2}$] **3** and *cis*-[$\mathrm{Pt(Me_2bipy)\{C{\equiv}CSC{\equiv}C(TIPS)\}_2}$] **7**, respectively. Purification was effected by silica column chromatography, leading to the isolation of the products as white (**1** and **3**) and bright yellow (**7**) solids. The yields were 70–76%. Following similar synthetic procedures, platinum(II) complexes *trans*-[$\mathrm{Pt(PBu_3)_2\{C{\equiv}CSC{\equiv}CC{\equiv}CSC{\equiv}C(TIPS)\}_2}$] **2** and *cis*-[$\mathrm{Pt(dppe)\{C{\equiv}CSC{\equiv}CC{\equiv}CSC{\equiv}C(TIPS)\}_2}$] **4** having a longer chain length can be prepared in good yields by treatment of the mono-TIPS-protected diacetylenic sulfide $\mathrm{HC{\equiv}CSC{\equiv}CC{\equiv}CSC{\equiv}C(TIPS)}$ separately with *trans*-[$\mathrm{Pt(PBu_3)_2Cl_2}$] and *cis*-[Pt(dppe)$\mathrm{Cl_2}$]. They were obtained as viscous oils after purification by column chromatography and found to be spectroscopically pure. Attempts have also been made to provide oligomeric acetylenic sulfides end-capped with platinum centres. Upon desilylation with $\mathrm{Bu_4NF}$, $\mathrm{Me_3SiC{\equiv}CSC{\equiv}CSiMe_3}$ and $\mathrm{Me_3SiC{\equiv}CSC{\equiv}CC{\equiv}CSC{\equiv}CSiMe_3}$ were converted into $\mathrm{HC{\equiv}CSC{\equiv}CH}$ and $\mathrm{HC{\equiv}CSC{\equiv}CC{\equiv}CSC{\equiv}CH}$, respectively, which can be used in the formation of dimeric complexes *trans*-[$\mathrm{Ph(Et_3P)_2Pt{-}C{\equiv}CSC{\equiv}C{-}Pt(PEt_3)_2Ph}$] **5** (70%) and *trans*-[$\mathrm{Ph(Et_3P)_2Pt{-}C{\equiv}CSC{\equiv}CC{\equiv}CSC{\equiv}C{-}Pt(PEt_3)_2Ph}$] **6** (52%) under basic conditions by treating with *trans*-[$\mathrm{PtPh(Cl)(PEt_3)_2}$]. Both compounds were chromatographically isolated and compound **5** appears as a white solid whereas **6** is an oily substance.

Compounds **1**, **3**, **5** and **7** with monoacetylenic sulfide units were found to be air-stable in the solid state. However, the corresponding oily diacetylenic sulfide species **2**, **4** and **6** turned dark within several days when kept at room temperature under air and exposed to light. The instability of these three products precludes satisfactory elemental analyses but they were fully characterized by common spectroscopic methods (IR, FAB-MS, ^{1}H, ^{13}C and ^{31}P NMR).

Spectroscopic properties

All the spectroscopic data of complexes **1**–**7** are in accord with their structures (Scheme 1). The IR spectra of these platinum σ-acetylide complexes display strong $\nu_{\mathrm{C{\equiv}C}}$ absorptions in the region 2033–2105 cm^{-1}. The presence of a singlet accompanied by a Pt–P satellite signal in the ^{31}P-{^{1}H} NMR spectra for **1**–**6** indicates that the phosphorus atoms are magnetically equivalent which conforms to the symmetrical arrangement of the phosphine groups in these complexes. In all cases, ^{1}H NMR signals stemming from the protons of the organic fragments were observed, and all the alkyne carbon atoms were identified in the ^{13}C-{^{1}H} NMR spectra. The formulae of the platinum(II) oligoacetylenic sulfides were successfully established by positive FAB mass spectrometry and the respective molecular ion peaks were detected in each case.

The photophysical properties of complexes **1**–**7** have also been studied. The absorption and emission data are collected in the Experimental section. Complexes **1**–**6** exhibit intense ligand-localized absorption bands in the near-UV region but we observe a bathochromic shift of these peaks upon incorporation of the platinum(II) centre(s) as compared to the "free" ligand.[10] Like other platinum–alkynyl compounds, the electronic spectra of **1**–**6** also display a band just beyond 300 nm, which is attributable to alkynyl–platinum ligand-to-metal charge transfer transitions.[7d,12] The absorption spectral features of **7** in CH_2Cl_2 are found to be reminiscent of those for [Pt(bipy)Cl_2] and [Pt(Me_2bipy)(C≡CPh)$_2$] and its spectrum is dominated by two bands at $\lambda_{max} = 413$ and 283 nm.[13] We assign the former peak as a metal-to-ligand charge transfer (MLCT) band due to the Me_2bipy ligand and the latter band possibly to a second MLCT transition of the Me_2bipy ligand, as suggested for [Pt(bipy)Cl_2]. Overlapping of the 283 nm absorption with other bands arising from π to π* transitions of the bipyridyl and acetylide groups is also possible. Any charge-transfer type absorption due to the acetylide moiety, as predicted for [Pt(PR_3)$_2$(C≡CR′)$_2$], could be obscured by the aforementioned ligand-based absorptions. In the solution state, all these new platinum(II) sulfur-linked materials are luminescent at room temperature and the emission peaks range from 340 to 589 nm. Compounds **2** and **4** having a diacetylenic unit in each case show a significant red shift in the emission wavelength relative to the monoacetylenic counterparts **1** and **3**, respectively.

Crystal structure analyses

In order to ascertain the solid-state structure of this new class of oligoacetylenic sulfide complexes, the molecular structures of **5** and **7** have been established by X-ray crystallography. Perspective drawings of their crystal structures are shown in Figs. 1 and 2, which include the atom numbering scheme. Pertinent bond distances and angles are listed in Tables 1 and 2. In each case, the co-ordination geometry at the platinum atom is square planar and the C≡C bond length [av. 1.195(7) **5**, 1.17(2) Å **7**] is typical of metal–acetylide σ bonding. For **5**, two PtPh(PEt$_3$)$_2$ groups are bridged by a C≡CSC≡C unit and both essentially linear Pt–C≡C–S fragments intersect at S(1) with the angle C(20)–S(1)–C(21) being 105.0(3)°. The fragment Pt–C≡CSC≡C–Pt is nearly planar and the mean S–C distance is 1.703(6) Å. The Pt–P bond lengths [2.282(2)–2.292(1) Å] are similar to those observed in other Pt–PR$_3$ acetylide complexes. The structure of **7** consists of a platinum(II) centre with a bidentate Me_2bipy-*N*,*N*′ ligand and two *cis* C≡CSC≡C(TIPS) ligands. To the best of our knowledge, there are only five structurally characterized platinum acetylide complexes with nitrogen donors.[7b,13b,15] The two alkynyl units make an angle of C(13)–Pt(1)–C(26) 88.3(7)° at Pt(1). The average Pt–N and S–C distances are 2.05(2) and 1.72(2) Å, respectively, and the mean C–S–C bond angle is 106(1)°. The average length of the Pt–C bond is 1.95(2) Å, a little shorter than those generally found in platinum acetylide complexes with phosphine ligands (*cf.* 2.021(5) Å in **5**)[16] but agrees well with those in other previously published bis(acetylide) structures containing a diimine ligand.[17] In both cases the average bond angles of 176.1(5) (**5**) and 176(1)° (**7**) for the fragment Pt–C≡C conform to the linear geometry of the bis(acetylide) complexes and greater deviation from linearity is observed for the adjacent C–C–S angle (av. 170.5(6)° for **5**; 170(1)° for **7**) than for the Pt–C–C angle.

Table 1 Selected bond lengths (Å) and angles (°) for complex **5**

Pt(1)–P(1)	2.290(2)	Pt(2)–P(4)	2.287(2)
Pt(1)–P(2)	2.282(2)	Pt(2)–C(22)	2.018(5)
Pt(1)–C(13)	2.071(5)	Pt(2)–C(35)	2.076(6)
Pt(1)–C(19)	2.023(5)	C(21)–C(22)	1.201(7)
C(19)–C(20)	1.189(7)	S(1)–C(20)	1.709(6)
Pt(2)–P(3)	2.292(1)	S(1)–C(21)	1.696(5)
P(1)–Pt(1)–P(2)	179.31(6)	P(4)–Pt(2)–C(22)	92.3(2)
P(1)–Pt(1)–C(19)	92.5(2)	C(22)–Pt(2)–C(35)	177.6(2)
P(2)–Pt(1)–C(19)	87.0(2)	Pt(2)–C(22)–C(21)	175.9(5)
C(13)–Pt(1)–C(19)	178.3(2)	S(1)–C(20)–C(19)	170.8(6)
Pt(1)–C(19)–C(20)	176.3(5)	S(1)–C(21)–C(22)	170.1(5)
P(3)–Pt(2)–P(4)	177.69(5)	C(20)–S(1)–C(21)	105.0(3)
P(3)–Pt(2)–C(22)	90.0(2)		

Table 2 Selected bond lengths (Å) and angles (°) for complex **7**

Pt(1)–N(1)	2.05(1)	C(15)–C(16)	1.16(3)
Pt(1)–N(2)	2.05(2)	Si(1)–C(16)	1.84(3)
Pt(1)–C(13)	1.96(2)	C(26)–C(27)	1.18(2)
Pt(1)–C(26)	1.94(2)	S(2)–C(27)	1.71(2)
C(13)–C(14)	1.14(2)	S(2)–C(28)	1.71(2)
S(1)–C(14)	1.74(2)	C(28)–C(29)	1.20(2)
S(1)–C(15)	1.70(3)	Si(2)–C(29)	1.82(2)
N(1)–Pt(1)–N(2)	79.1(8)	S(1)–C(15)–C(16)	175(2)
N(1)–Pt(1)–C(26)	95.4(8)	Si(1)–C(16)–C(15)	175(2)
N(2)–Pt(1)–C(13)	97.1(8)	Pt(1)–C(26)–C(27)	175(1)
C(13)–Pt(1)–C(26)	88.3(7)	S(2)–C(27)–C(26)	169(1)
Pt(1)–C(13)–C(14)	176(1)	C(27)–S(2)–C(28)	105.4(9)
S(1)–C(14)–C(13)	170(1)	S(2)–C(28)–C(29)	174(1)
C(14)–S(1)–C(15)	106(1)	Si(2)–C(29)–C(28)	175(2)

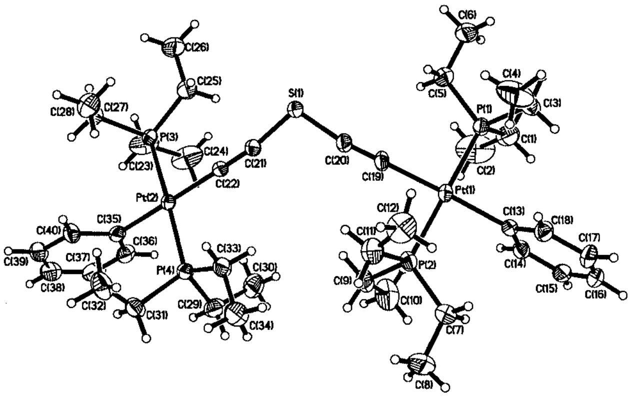

Fig. 1 The molecular structure of compound **5**.

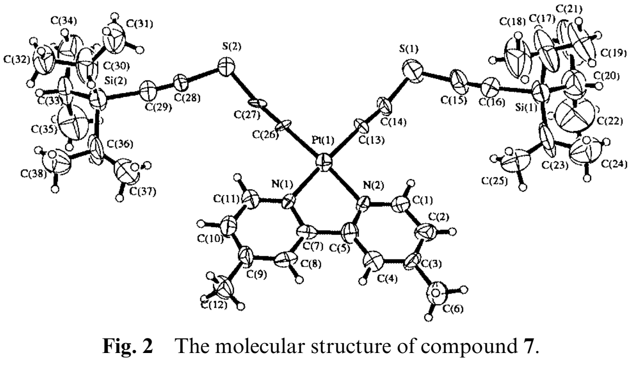

Fig. 2 The molecular structure of compound **7**.

Experimental

General

All reactions were conducted under an atmosphere of dry nitrogen with the use of standard Schlenk techniques. Solvents for preparative work were dried and distilled before use. IR spectra were recorded on a Nicolet FTIR-550 spectrometer, NMR spectra on a JEOL JNM-EX 270 spectrometer (270 MHz for ^{1}H, 67.8 MHz for ^{13}C, 109.3 MHz for ^{31}P). The chemical shifts were referenced to residual solvent resonance (δ 7.24 for ^{1}H and 77.0 for ^{13}C) and to external 85% H_3PO_4 for ^{31}P spectra. Fast atom bombardment (FAB) mass spectra were recorded in *m*-nitrobenzyl alcohol matrices on a Finnigan-SSQ 710 spectrometer, electronic absorption and luminescence spectra in CH_2Cl_2 solutions with a Varian Cary 100 UV-visible spectrophotometer and a Perkin-Elmer LS50B luminescence spectrometer, respectively. Microanalyses were performed by the Shanghai Institute of Organic Chemistry. The starting platinum halides *trans*-[Pt(PBu$_3$)$_2$Cl$_2$],[18] *cis*-[Pt(dppe)Cl$_2$][19] and *trans*-[PtPh(Cl)(PEt$_3$)$_2$][20] were prepared by literature procedures. The syntheses of the acetylenic sulfides were carried out as reported previously.[10] Separation of products was accomplished by column chromatography on silica or preparative silica TLC plates (Merck, Kieselgel 60).

Synthetic procedures

***trans*-[Pt(PBu$_3$)$_2${C≡CSC≡C(TIPS)}$_2$] 1.** To a solution of the terminal acetylenic sulfide HC≡CSC≡C(TIPS) (24.0 mg, 0.10 mmol) in dried CH_2Cl_2 (25 cm^3) containing $(Me_3Si)_2NH$ (3 cm^3), *trans*-[Pt(PBu$_3$)$_2$Cl$_2$] (27.0 mg, 0.04 mmol) and CuI (3 mg) were added. The reaction mixture was stirred vigorously under nitrogen for 20 h at room temperature. During the course of the reaction a white precipitate was formed. After complete consumption of the starting platinum halide, as revealed by TLC, the suspension was passed through a short column of neutral alumina, eluting with CH_2Cl_2. The eluate was then washed with 1 mol dm^{-3} HCl (10 cm^3) and water (2 × 10 cm^3). The organic phase was dried over anhydrous Na_2SO_4 and the crude product obtained after evaporation of the solvent under reduced pressure. Purification of the product was accomplished by flash column chromatography on silica ($R_f = 0.58$) using hexane–CH_2Cl_2 (3:1, v/v) as eluent to afford a white solid in 76% yield (33.0 mg). IR (KBr): 2094 and 2045 cm^{-1} ($\nu_{C\equiv C}$). ^{1}H NMR (CDCl$_3$): δ 0.93 (t, 18 H, P(CH$_2$)$_3$C*H*$_3$), 1.03 (m, 42 H, Pr^i), 1.43 (m, 24 H, PCH$_2$(C*H*$_2$)$_2$CH$_3$) and 1.91 (m, 12 H, PC*H*$_2$(CH$_2$)$_2$CH$_3$). ^{13}C-{^{1}H} NMR (CDCl$_3$): δ 11.45, 18.70 (Pr^i), 13.91, 24.06, 24.49, 26.42 (Bu), 78.76, 92.81, 96.92 and 116.25 (C≡C). ^{31}P-{^{1}H} NMR (CDCl$_3$): δ 5.20 ($^1J_{Pt\text{-}P} = 2305$ Hz). FAB mass spectrum: *m*/*z* 1075 (M$^+$). UV/VIS (CH$_2$Cl$_2$): λ_{max} ($\varepsilon \times 10^{-4}$ dm^3 mol^{-1} cm^{-1})/nm 258 (1.3) and 327 (1.2). Emission (CH$_2$Cl$_2$, $\lambda_{excitation} = 291$ nm): 361 nm. Calc. for $C_{50}H_{96}P_2PtS_2Si_2$: C, 55.88; H, 9.00. Found: C, 56.09; H, 9.12%.

***trans*-[Pt(PBu$_3$)$_2${C≡CSC≡CC≡CSC≡C(TIPS)}$_2$] 2.** This complex was synthesized as described above for **1** from HC≡CSC≡CC≡CSC≡C(TIPS) (44.0 mg, 0.14 mmol) and *trans*-[Pt(PBu$_3$)$_2$Cl$_2$] (42.0 mg, 0.06 mmol). After the usual work-up, the residue was purified by column chromatography on silica ($R_f = 0.68$) using hexane–CH_2Cl_2 (4:1, v/v) to give a brown thick oil (55.0 mg, 71%). IR (KBr): 2096, 2088 and 2050 cm^{-1} ($\nu_{C\equiv C}$). ^{1}H NMR (CDCl$_3$): δ 0.93 (t, 18 H, P(CH$_2$)$_3$C*H*$_3$), 1.07 (m, 42 H, Pr^i), 1.45 (m, 24 H, PCH$_2$(C*H*$_2$)$_2$CH$_3$) and 2.07 (m, 12 H, PC*H*$_2$(CH$_2$)$_2$CH$_3$). ^{13}C-{^{1}H} NMR (CDCl$_3$): δ 11.17, 18.49 (Pr^i), 13.80, 23.75, 24.28, 26.23 (Bu), 67.37, 73.92, 75.93, 81.11, 82.56, 85.32, 102.03 and 119.56 (C≡C). ^{31}P-{^{1}H} NMR (CDCl$_3$): δ 5.03 ($^1J_{Pt\text{-}P} = 2280$ Hz). FAB mass spectrum: *m*/*z* 1234 (M$^+$). UV/VIS (CH$_2$Cl$_2$): λ_{max} ($\varepsilon \times 10^{-4}$ dm^3 mol^{-1} cm^{-1})/nm 270 (3.6), 333 (2.1) and 379 (2.5). Emission (CH$_2$Cl$_2$, $\lambda_{excitation} = 382$ nm): 517 nm. Microanalytical data are not available due to the instability.

***cis*-[Pt(dppe){C≡CSC≡C(TIPS)}$_2$] 3.** A mixture of *cis*-[Pt(dppe)Cl$_2$] (133.0 mg, 0.20 mmol), HC≡CSC≡C(TIPS) (119.0 mg, 0.50 mmol), CuI (3 mg) and $(Me_3Si)_2NH$ (3 cm^3) in CH_2Cl_2 (25 cm^3) was stirred at room temperature for 20 h. TLC showed that all the starting material had been consumed. After work-up and purification by column chromatography ($R_f = 0.50$) on silica eluting with hexane–CH_2Cl_2 (1:1, v/v), a white solid of complex **3** was obtained in 70% yield (150.0 mg). IR (KBr): 2088 cm^{-1} ($\nu_{C\equiv C}$). ^{1}H NMR (CDCl$_3$): δ 0.91 (m, 42 H, Pr^i), 2.37 (m, 4 H, CH$_2$) and 7.39–7.86 (m, 20 H, Ph). ^{13}C-{^{1}H} NMR (CDCl$_3$): δ 11.20, 18.51 (Pr^i), 27.93 (CH$_2$), 85.58, 92.62, 96.70 and 113.97 (C≡C). ^{31}P-{^{1}H} NMR (CDCl$_3$): δ 42.22 ($^1J_{Pt\text{-}P} = 2311$ Hz). FAB mass spectrum: *m*/*z* 1067 (M$^+$). UV/VIS (CH$_2$Cl$_2$): λ_{max} ($\varepsilon \times 10^{-4}$ dm^3 mol^{-1} cm^{-1})/nm 320 br (1.4). Emission (CH$_2$Cl$_2$, $\lambda_{excitation} = 286$ nm): 361 nm. Calc. for $C_{52}H_{46}P_2PtS_2Si_2\cdot 0.5C_6H_{14}$: C, 60.53; H, 4.90. Found: C, 60.32; H, 5.14%.

***cis*-[Pt(dppe){C≡CSC≡CC≡CSC≡C(TIPS)}$_2$] 4.** Treatment of *cis*-[Pt(dppe)Cl$_2$] (66.0 mg, 0.10 mmol) with HC≡CSC≡CC≡CSC≡C(TIPS) (80.0 mg, 0.25 mmol) for 20 h at room temperature, in the presence of CuI (3 mg), in CH_2Cl_2–$(Me_3Si)_2NH$ (30 cm^3, 9:1 v/v) gave the desired compound as a brown thick oil after chromatographic purification on silica ($R_f = 0.68$) using hexane–CH_2Cl_2 (1:1, v/v) as eluent. The yield was 74.0 mg (60%). IR (KBr): 2105, 2088 and 2055 cm^{-1} ($\nu_{C\equiv C}$). ^{1}H NMR (CDCl$_3$): δ 1.07 (m, 42 H, Pr^i), 2.41 (m, 4 H, CH$_2$) and 7.45–7.79 (m, 20 H, Ph). ^{13}C-{^{1}H} NMR (CDCl$_3$): δ 11.16, 18.51 (Pr^i), 28.02 (CH$_2$), 66.62, 73.98, 77.20, 80.48, 82.91, 85.50, 101.96, 117.34 (C≡C), 128.42, 128.96, 131.56 and 133.30 (Ph). ^{31}P-{^{1}H} NMR (CDCl$_3$): δ 42.80 ($^1J_{Pt\text{-}P} = 2309$ Hz). FAB mass spectrum: *m*/*z* 1227 (M$^+$). UV/VIS (CH$_2$Cl$_2$): λ_{max} ($\varepsilon \times 10^{-4}$ dm^3 mol^{-1} cm^{-1})/nm 270 (5.5) and 324 br (1.9). Emission (CH$_2$Cl$_2$, $\lambda_{excitation} = 355$ nm): 412 nm. Microanalytical data are not available due to the instability.

HC≡CSC≡CH and HC≡CSC≡CC≡CSC≡CH. Two equivalents of a solution of Bu_4NF in CH_2Cl_2 were added dropwise to a solution of the corresponding Me$_3$SiC≡CSC≡CSiMe$_3$ or Me$_3$SiC≡CSC≡CC≡CSC≡CSiMe$_3$ in the same solvent. The reaction mixture was stirred vigorously at room temperature for 2 h. The course of the reaction was monitored closely by TLC using hexane as eluent. When the respective bis(trimethylsilyl) derivative was exhausted, water was added and the mixture extracted with CH_2Cl_2. The combined organic phase was dried over anhydrous $MgSO_4$ and evaporated to afford the desired diacetylene products for the following preparations.

***trans*-[Ph(Et$_3$P)$_2$Pt–C≡CSC≡C–Pt(PEt$_3$)$_2$Ph] 5.** Reaction of the diterminal alkyne HC≡CSC≡CH (8.2 mg, 0.10 mmol) with 2 equivalents of *trans*-[PtPh(Cl)(PEt$_3$)$_2$] (109.0 mg, 0.20 mmol) for 20 h at room temperature, in the presence of CuI (3 mg), in CH_2Cl_2–$(Me_3Si)_2NH$ (18 cm^3, 5:1 v/v) gave the required complex as a white solid (77.0 mg, 70%) after purification on silica TLC plates ($R_f = 0.50$) using hexane–CH_2Cl_2 (1:1, v/v) as eluent. IR (KBr): 2043 cm^{-1} ($\nu_{C\equiv C}$). ^{1}H NMR (CDCl$_3$): δ 1.04 (m, 36 H, CH$_3$), 1.66 (m, 24 H, CH$_2$), 6.75 (m, 2 H, H$_{para}$ of Ph), 6.92 (m, 4 H, H$_{meta}$ of Ph) and 7.25 (m, 4 H, H$_{ortho}$ of Ph). ^{13}C-{^{1}H} NMR (CDCl$_3$): δ 8.00, 15.17 (C$_2$H$_5$), 77.29, 81.81 (C≡C), 121.42, 127.34, 138.97 and 153.97 (Ph). ^{31}P-{^{1}H} NMR (CDCl$_3$): δ 11.09 ($^1J_{Pt\text{-}P} = 2621$ Hz). FAB mass spectrum: *m*/*z* 1097 (M$^+$). UV/VIS (CH$_2$Cl$_2$): λ_{max} ($\varepsilon \times 10^{-4}$ dm^3 mol^{-1} cm^{-1})/nm 264 (1.7) and 325 (0.9). Emission (CH$_2$Cl$_2$, $\lambda_{excitation} = 297$ nm): 352 nm. Calc. for $C_{40}H_{70}P_4Pt_2S\cdot C_6H_{14}$: C, 46.69; H, 7.16. Found: C, 47.08; H, 7.10%.

***trans*-[Ph(Et$_3$P)$_2$Pt–C≡CSC≡CC≡CSC≡C–Pt(PEt$_3$)$_2$Ph] 6.** To a mixture of HC≡CSC≡CC≡CSC≡CH (13.0 mg, 0.08 mmol) and 2 equivalents of *trans*-[PtPh(Cl)(PEt$_3$)$_2$] (87.0 mg, 0.16 mmol) in CH$_2$Cl$_2$–(Me$_3$Si)$_2$NH (18 cm^3, 1 : 1 v/v) was added CuI (3 mg). The solution was stirred at room temperature over 20 h, after which all volatile components were removed under reduced pressure. The product was purified on preparative TLC plates with hexane–CH$_2$Cl$_2$ (1 : 1, v/v) as eluent, affording compound **6** as a viscous oil (49.0 mg, 52%). IR (KBr): 2067 and 2033 cm^{-1} ($\nu_{C\equiv C}$). ^{1}H NMR (CDCl$_3$): δ 1.04 (m, 36 H, CH$_3$), 1.64 (m, 24 H, CH$_2$), 6.77 (m, 2 H, H$_{para}$ of Ph), 6.92 (m, 4 H, H$_{meta}$ of Ph) and 7.24 (m, 4 H, H$_{ortho}$ of Ph). ^{13}C-{^{1}H} NMR (CDCl$_3$): δ 7.96, 14.93 (C$_2$H$_5$), 73.22, 73.25, 77.20, 81.28 (C≡C), 121.47, 127.36, 138.91 and 154.45 (Ph). ^{31}P-{^{1}H} NMR (CDCl$_3$): δ 11.11 ($^1J_{\text{Pt-P}}$ = 2616 Hz). FAB mass spectrum: *m*/*z* 1177 (M$^+$). UV/VIS (CH$_2$Cl$_2$): $\lambda_{\max}$ ($\varepsilon \times 10^{-4}$ dm^3 mol^{-1} cm^{-1})/nm 263 br (2.1) and 318 (0.7). Emission (CH$_2$Cl$_2$, $\lambda_{\text{excitation}}$ = 288 nm): 340 nm. Microanalytical data are not available due to the instability.

***cis*-[Pt(Me$_2$bipy){C≡CSC≡C(TIPS)}$_2$] 7.** Compounds [Pt(Me$_2$bipy)Cl$_2$] (100.0 mg, 0.22 mmol), HC≡CSC≡C(TIPS) (158.5 mg, 0.67 mmol) and CuI (3 mg) were stirred together in a mixture of CH$_2$Cl$_2$ (25 cm^3) and NHPr$^i_2$ (3 cm^3) for 24 h. The volatile portion was evaporated under vacuum, the residue dissolved in the minimum amount of CH$_2$Cl$_2$ and passed through a short column (5 cm) of silica gel with hexane–CH$_2$Cl$_2$ as eluent. Evaporation of the solvent yielded complex **7** as a bright yellow solid in 74% yield (140.0 mg). IR (KBr): 2088 and 2057 cm^{-1} ($\nu_{C\equiv C}$). ^{1}H NMR (CDCl$_3$): δ 1.11 (m, 42 H, Pr^i), 2.64 (s, 6 H, CH$_3$), 6.94 (d, 2 H, *J* = 5.7, pyridyl H), 8.01 (s, 2 H, pyridyl H) and 8.48 (d, 2 H, *J* = 5.7 Hz, pyridyl H). ^{13}C-{^{1}H} NMR (CDCl$_3$): δ 11.43, 18.73 (Pr^i), 22.30 (CH$_3$), 71.56, 93.50, 94.43, 97.65 (C≡C), 125.27, 127.30, 148.97, 151.64 and 155.53 (pyridyl C). FAB mass spectrum: *m*/*z* 853 (M$^+$). UV/VIS (CH$_2$Cl$_2$): $\lambda_{\max}$ ($\varepsilon \times 10^{-4}$ dm^3 mol^{-1} cm^{-1})/nm 283 br (1.7) and 413 (0.5). Emission (CH$_2$Cl$_2$, $\lambda_{\text{excitation}}$ = 410 nm): 589 nm. Calc. for C$_{38}$H$_{54}$N$_2$PtS$_2$Si$_2$: C, 53.43; H, 6.37; N, 3.28. Found: C, 53.08; H, 6.15; N, 3.20%.

Crystallography

Colourless crystals of complex **5** and yellow crystals of complex **7** suitable for X-ray diffraction studies were grown by evaporation of their respective solutions in hexane–CH$_2$Cl$_2$. Geometric and intensity data were collected at 273 K using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) on a Bruker SMART CCD area-detector (**5**) and MAR research image plate scanner (**7**). Cell parameters and the orientation matrix for **5** were obtained from the least-squares refinement of reflections measured in three different sets of 15 frames each. The collected frames were processed with the software SAINT[21a] and an absorption correction was applied (SADABS[21b]) to the collected reflections. For **7** 65 × 3° frames with an exposure time of 5 min per frame were used for data acquisition and inter-frame scaling was employed for the absorption correction.

The space groups of each crystal were determined from the systematic absences and Laue symmetry check and confirmed by successful refinement of the structure. The structures of complexes **5** and **7** were solved by direct methods (SHELXTL[22] for **5**, SHELXS 86[23] for **7**) in conjunction with standard Fourier difference techniques and subsequently refined by full-matrix least-squares analyses. All non-hydrogen atoms were assigned anisotropic displacement parameters. In each case, hydrogen atoms were generated in their idealized positions (C–H, 0.95 Å) and allowed to ride on the respective carbon atoms. Crystallographic and other experimental details are collected in Table 3.

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See http://www.rsc.org/suppdata/dt/b0/b004253f/ for crystallographic files in .cif format.

Table 3 Summary of crystal structure data for complexes **5** and **7**

	5	**7**
Empirical formula	C$_{40}$H$_{70}$P$_4$Pt$_2$S	C$_{38}$H$_{54}$N$_2$PtS$_2$Si$_2$
M	1097.08	854.24
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
a/Å	21.205(4)	7.906(1)
b/Å	9.053(2)	14.018(1)
c/Å	24.430(5)	19.069(1)
α/°		98.66(1)
β/°	95.67(3)	92.38(1)
γ/°		97.83(1)
U/Å^3	4667(2)	2065.6(3)
Z	4	2
μ(Mo-Kα)/cm^{-1}	61.95	35.68
No. reflections collected	26410	22607
Unique reflections (R_{int})	10473 (0.033)	3228 (0.045)
Observed reflections [$I > n\sigma(I)$]	10473 (n = 2.0)	2139 (n = 1.5)
Residuals	R = 0.0291	R = 0.056
	$wR2$ = 0.0845	R_w = 0.060

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