

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

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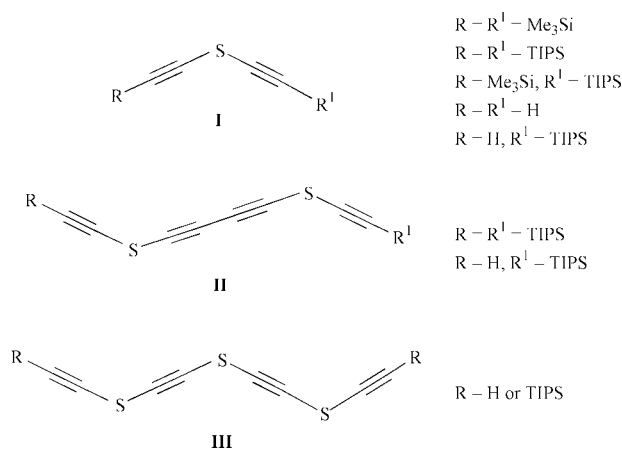
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A series of novel platinum(II) acetylide complexes incorporating sulfur-linked oligoalkynes have been prepared. The CuI-catalysed dehydrohalogenation reactions of the mono-protected dialkyne ligand $\text{HC}\equiv\text{CSC}\equiv\text{C}(\text{TIPS})$ ($\text{TIPS} = \text{Pr}^t_3\text{Si}$) with *trans*-[Pt(PBu₃)₂Cl₂], *cis*-[Pt(dppe)Cl₂] or *cis*-[Pt(Me₂bipy)Cl₂] (Me₂bipy = 4,4'-dimethyl-2,2'-bipyridine), in the presence of a base, readily produced *trans*-[Pt(PBu₃)₂{C≡CSC≡C(TIPS)}₂] **1**, *cis*-[Pt(dppe){C≡CSC≡C(TIPS)}₂] **3** and *cis*-[Pt(Me₂bipy){C≡CSC≡C(TIPS)}₂] **7**, respectively, in good yields. Similar synthetic procedures using a diacetylenic sulfide species $\text{HC}\equiv\text{CSC}\equiv\text{CC}\equiv\text{CSC}\equiv\text{C}(\text{TIPS})$ afforded *trans*-[Pt(PBu₃)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(Et₃P)₂Pt-C≡CSC≡C-Pt(PEt₃)₂Ph] **5** and *trans*-[Ph(Et₃P)₂Pt-C≡CSC≡CC≡CSC≡C-Pt(PEt₃)₂Ph] **6** were also synthesized in moderate yields by reactions of two equivalents of *trans*-[PtPh(Cl)(PEt₃)₂] and the diterminal acetylenic sulfides $\text{HC}\equiv\text{CSC}\equiv\text{CH}$ and $\text{HC}\equiv\text{CSC}\equiv\text{CC}\equiv\text{CSC}\equiv\text{CH}$ in a CuI/(Me₃Si)₂NH system. All of the compounds **1–7** have been characterized by IR, NMR (¹H, ¹³C and ³¹P) 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 optical⁵ 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 SCl₂.¹¹ 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

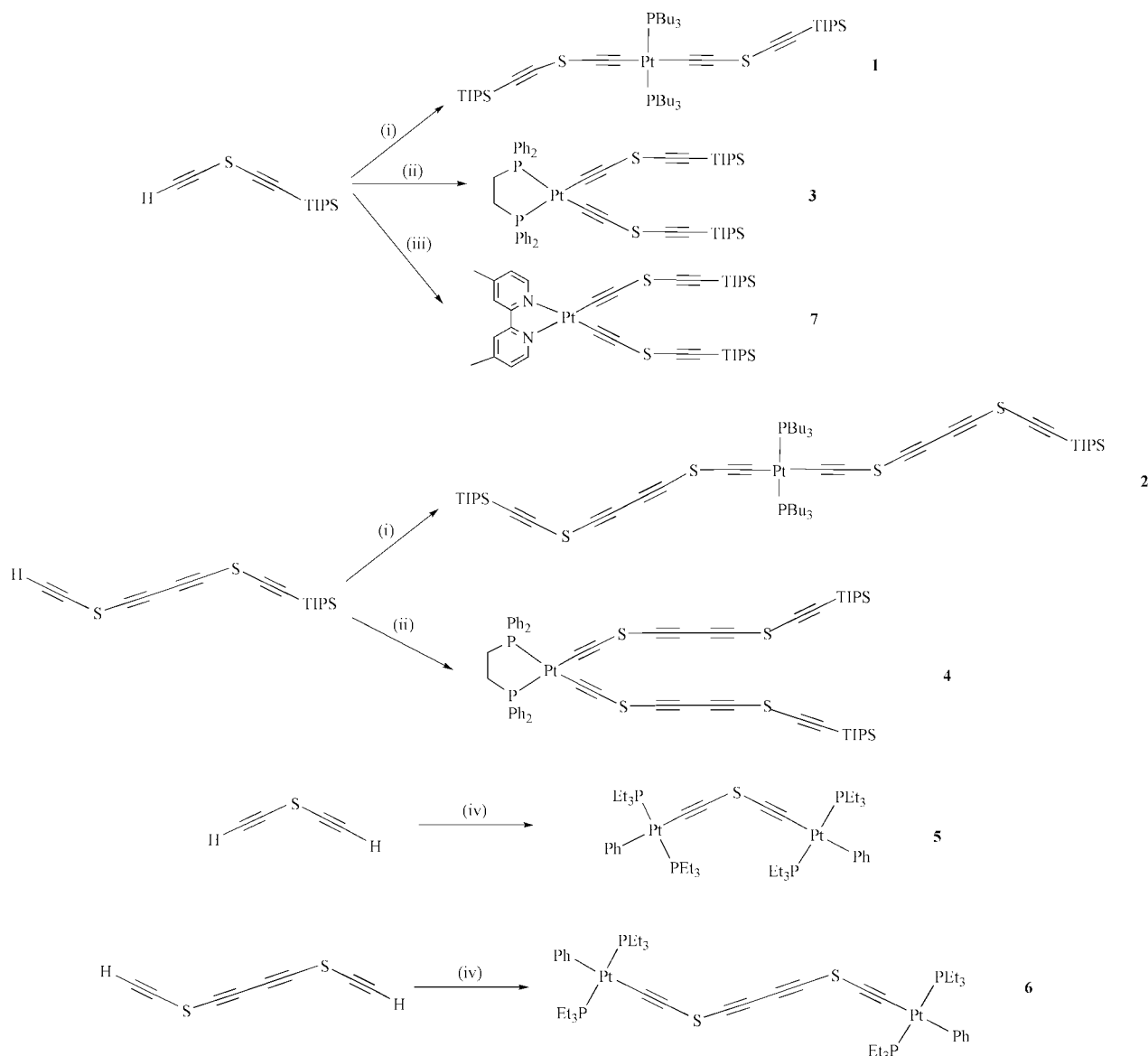
oligoacetylenic sulfides. As an extension of our interest in this important field, it seemed an attractive goal to us to synthesize new organometallic acetylenic sulfide complexes of different chain lengths. Here we report the first synthesis and physical characterization of a series of monomeric and 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.



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



Scheme 1 (i) *trans*-[Pt(PBu₃)₂Cl₂] (0.5 equivalent), CuI, CH₂Cl₂/(Me₃Si)₂NH; (ii) *cis*-[Pt(dppe)Cl₂] (0.5 equivalent), CuI, CH₂Cl₂/(Me₃Si)₂NH; (iii) *cis*-[Pt(Me₂bipy)Cl₂] (0.5 equivalent), CuI, CH₂Cl₂/NHPrⁱ₂; (iv) *trans*-[PtPh(Cl)(PEt₃)₂] (2 equivalents), CuI, CH₂Cl₂/(Me₃Si)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 (Prⁱ₃Si), reactions of two molar equivalents of HC≡CSC≡C(TIPS) with *trans*-[Pt(PBu₃)₂Cl₂], *cis*-[Pt(dppe)Cl₂] or *cis*-[Pt(Me₂bipy)Cl₂] (Me₂-bipy = 4,4'-dimethyl-2,2'-bipyridine) via a CuI-catalysed dehydrohalogenation process using (Me₃Si)₂NH or NHPrⁱ₂ as a base afforded three bis(acetylide) complexes *trans*-[Pt(PBu₃)₂{C≡CSC≡C(TIPS)}₂] **1**, *cis*-[Pt(dppe){C≡CSC≡C(TIPS)}₂] **3** and *cis*-[Pt(Me₂bipy){C≡CSC≡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*-[Pt(PBu₃)₂{C≡CSC≡CC≡CSC≡C(TIPS)}₂] **2** and *cis*-[Pt(dppe){C≡CSC≡CC≡CSC≡C(TIPS)}₂] **4** having a longer chain length can be prepared in good yields by treatment of the mono-TIPS-protected diacetylenic sulfide HC≡CSC≡CC≡CSC≡C(TIPS) separately with *trans*-[Pt(PBu₃)₂Cl₂] and *cis*-[Pt(dppe)Cl₂]. 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 Bu₄NF, Me₃SiC≡CSC≡CSiMe₃ and Me₃SiC≡CSC≡CC≡CSC≡CSiMe₃ were converted into HC≡CSC≡CH and HC≡CSC≡CC≡CSC≡CH, respectively, which can be used in the formation of dimeric complexes *trans*-[Ph(Et₃P)₂Pt–C≡CSC≡C–Pt(PEt₃)₂Ph] **5** (70%) and *trans*-[Ph(Et₃P)₂Pt–C≡CSC≡CC≡CSC≡C–Pt(PEt₃)₂Ph] **6** (52%) under basic conditions by treating with *trans*-[PtPh(Cl)(PEt₃)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, ¹H, ¹³C and ³¹P 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 ν_{C≡C} absorptions in the

region 2033–2105 cm^{−1}. The presence of a singlet accompanied by a Pt–P satellite signal in the ³¹P-{¹H} 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, ¹H NMR signals stemming from the protons of the organic fragments were observed, and all the alkyne carbon atoms were identified in the ¹³C-{¹H} 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 CH₂Cl₂ are found to be reminiscent of those for [Pt(bipy)Cl₂] and [Pt(Me₂bipy)(C≡CPh)₂] and its spectrum is dominated by two bands at λ_{max} = 413 and 283 nm.¹³ We assign the former peak as a metal-to-ligand charge transfer (MLCT) band due to the Me₂bipy ligand and the latter band possibly to a second MLCT transition of the Me₂bipy ligand, as suggested for [Pt(bipy)Cl₂]. 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(PR₃)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) **7**] is typical of metal–acetylide σ bonding. For **5**, two PtPh(PET₃)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–PR₃ acetylide complexes. The structure of **7** consists of a platinum(II) centre with a bidentate Me₂bipy-*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)

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) |

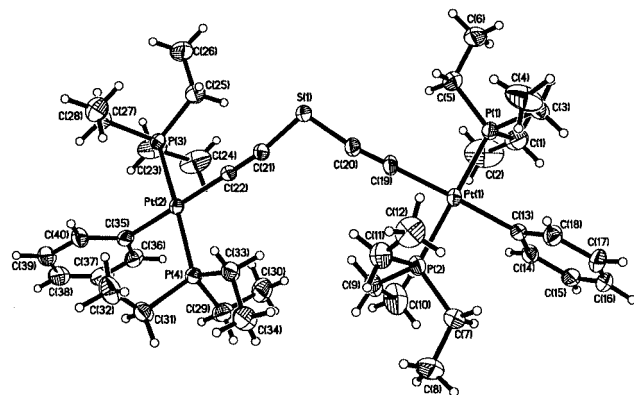


Fig. 1 The molecular structure of compound **5**.

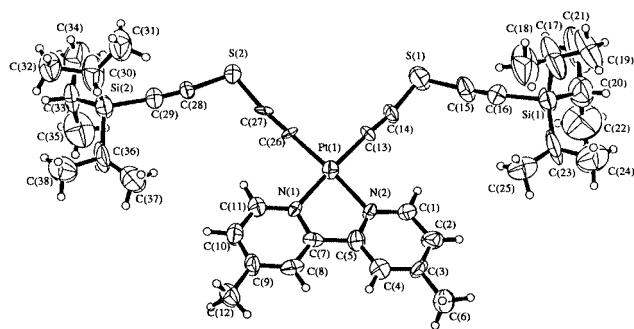


Fig. 2 The molecular structure of compound **7**.

(**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.

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 ^1H , 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 ^1H 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*- $[\text{Pt}(\text{PBU}_3)_2\text{Cl}_2]$,¹⁸ *cis*- $[\text{Pt}(\text{dppe})\text{Cl}_2]$ ¹⁹ and *trans*- $[\text{PtPh}(\text{Cl})(\text{PEt}_3)_2]$ 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*- $[\text{Pt}(\text{PBU}_3)_2\{\text{C}\equiv\text{CSC}\equiv\text{C}(\text{TIPS})\}_2]$ 1.** To a solution of the terminal acetylenic sulfide $\text{HC}\equiv\text{CSC}\equiv\text{C}(\text{TIPS})$ (24.0 mg, 0.10 mmol) in dried CH_2Cl_2 (25 cm^3) containing $(\text{Me}_3\text{Si})_2\text{NH}$ (3 cm^3), *trans*- $[\text{Pt}(\text{PBU}_3)_2\text{Cl}_2]$ (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 \times 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} ($\nu_{\text{C}\equiv\text{C}}$). ^1H NMR (CDCl_3): δ 0.93 (t, 18 H, $\text{P}(\text{CH}_2)_3\text{CH}_3$), 1.03 (m, 42 H, Pr^t), 1.43 (m, 24 H, $\text{PCH}_2(\text{CH}_2)_2\text{CH}_3$) and 1.91 (m, 12 H, $\text{PCH}_2(\text{CH}_2)_2\text{CH}_3$). ^{13}C - $\{^1\text{H}\}$ NMR (CDCl_3): δ 11.45, 18.70 (Pr^t), 13.91, 24.06, 24.49, 26.42 (Bu), 78.76, 92.81, 96.92 and 116.25 ($\text{C}\equiv\text{C}$). ^{31}P - $\{^1\text{H}\}$ NMR (CDCl_3): δ 5.20 ($^1J_{\text{Pt-P}}$ = 2305 Hz). FAB mass spectrum: m/z 1075 (M^+). UV/VIS (CH_2Cl_2): λ_{max} ($\epsilon \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)/nm 258 (1.3) and 327 (1.2). Emission (CH_2Cl_2 , $\lambda_{\text{excitation}}$ = 291 nm): 361 nm. Calc. for $\text{C}_{50}\text{H}_{96}\text{P}_2\text{PtS}_2\text{Si}_2$: C, 55.88; H, 9.00. Found: C, 56.09; H, 9.12%.

***trans*- $[\text{Pt}(\text{PBU}_3)_2\{\text{C}\equiv\text{CSC}\equiv\text{CC}\equiv\text{CSC}\equiv\text{C}(\text{TIPS})\}_2]$ 2.** This complex was synthesized as described above for **1** from $\text{HC}\equiv\text{CSC}\equiv\text{CC}\equiv\text{CSC}\equiv\text{C}(\text{TIPS})$ (44.0 mg, 0.14 mmol) and *trans*- $[\text{Pt}(\text{PBU}_3)_2\text{Cl}_2]$ (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} ($\nu_{\text{C}\equiv\text{C}}$). ^1H NMR (CDCl_3): δ 0.93 (t, 18 H, $\text{P}(\text{CH}_2)_3\text{CH}_3$), 1.07 (m, 42 H, Pr^t), 1.45 (m, 24 H, $\text{PCH}_2(\text{CH}_2)_2\text{CH}_3$) and 2.07 (m, 12 H, $\text{PCH}_2(\text{CH}_2)_2\text{CH}_3$). ^{13}C - $\{^1\text{H}\}$ NMR (CDCl_3): δ 11.17, 18.49 (Pr^t), 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 ($\text{C}\equiv\text{C}$). ^{31}P - $\{^1\text{H}\}$ NMR (CDCl_3): δ 5.03 ($^1J_{\text{Pt-P}}$ = 2280 Hz). FAB mass spectrum: m/z 1234 (M^+). UV/VIS (CH_2Cl_2): λ_{max} ($\epsilon \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)/nm 270 (3.6), 333 (2.1) and 379 (2.5). Emission (CH_2Cl_2 ,

$\lambda_{\text{excitation}}$ = 382 nm): 517 nm. Microanalytical data are not available due to the instability.

***cis*- $[\text{Pt}(\text{dppe})\{\text{C}\equiv\text{CSC}\equiv\text{C}(\text{TIPS})\}_2]$ 3.** A mixture of *cis*- $[\text{Pt}(\text{dppe})\text{Cl}_2]$ (133.0 mg, 0.20 mmol), $\text{HC}\equiv\text{CSC}\equiv\text{C}(\text{TIPS})$ (119.0 mg, 0.50 mmol), CuI (3 mg) and $(\text{Me}_3\text{Si})_2\text{NH}$ (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} ($\nu_{\text{C}\equiv\text{C}}$). ^1H NMR (CDCl_3): δ 0.91 (m, 42 H, Pr^t), 2.37 (m, 4 H, CH_2) and 7.39–7.86 (m, 20 H, Ph). ^{13}C - $\{^1\text{H}\}$ NMR (CDCl_3): δ 11.20, 18.51 (Pr^t), 27.93 (CH_2), 85.58, 92.62, 96.70 and 113.97 ($\text{C}\equiv\text{C}$). ^{31}P - $\{^1\text{H}\}$ NMR (CDCl_3): δ 42.22 ($^1J_{\text{Pt-P}}$ = 2311 Hz). FAB mass spectrum: m/z 1067 (M^+). UV/VIS (CH_2Cl_2): λ_{max} ($\epsilon \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)/nm 320 br (1.4). Emission (CH_2Cl_2 , $\lambda_{\text{excitation}}$ = 286 nm): 361 nm. Calc. for $\text{C}_{52}\text{H}_{46}\text{P}_2\text{PtS}_2\text{Si}_2 \cdot 0.5\text{C}_6\text{H}_{14}$: C, 60.53; H, 4.90. Found: C, 60.32; H, 5.14%.

***cis*- $[\text{Pt}(\text{dppe})\{\text{C}\equiv\text{CSC}\equiv\text{CC}\equiv\text{CSC}\equiv\text{C}(\text{TIPS})\}_2]$ 4.** Treatment of *cis*- $[\text{Pt}(\text{dppe})\text{Cl}_2]$ (66.0 mg, 0.10 mmol) with $\text{HC}\equiv\text{CSC}\equiv\text{CC}\equiv\text{CSC}\equiv\text{C}(\text{TIPS})$ (80.0 mg, 0.25 mmol) for 20 h at room temperature, in the presence of CuI (3 mg), in CH_2Cl_2 – $(\text{Me}_3\text{Si})_2\text{NH}$ (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} ($\nu_{\text{C}\equiv\text{C}}$). ^1H NMR (CDCl_3): δ 1.07 (m, 42 H, Pr^t), 2.41 (m, 4 H, CH_2) and 7.45–7.79 (m, 20 H, Ph). ^{13}C - $\{^1\text{H}\}$ NMR (CDCl_3): δ 11.16, 18.51 (Pr^t), 28.02 (CH_2), 66.62, 73.98, 77.20, 80.48, 82.91, 85.50, 101.96, 117.34 ($\text{C}\equiv\text{C}$), 128.42, 128.96, 131.56 and 133.30 (Ph). ^{31}P - $\{^1\text{H}\}$ NMR (CDCl_3): δ 42.80 ($^1J_{\text{Pt-P}}$ = 2309 Hz). FAB mass spectrum: m/z 1227 (M^+). UV/VIS (CH_2Cl_2): λ_{max} ($\epsilon \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)/nm 270 (5.5) and 324 br (1.9). Emission (CH_2Cl_2 , $\lambda_{\text{excitation}}$ = 355 nm): 412 nm. Microanalytical data are not available due to the instability.

$\text{HC}\equiv\text{CSC}\equiv\text{CH}$ and $\text{HC}\equiv\text{CSC}\equiv\text{CC}\equiv\text{CSC}\equiv\text{CH}$. Two equivalents of a solution of Bu_4NF in CH_2Cl_2 were added dropwise to a solution of the corresponding $\text{Me}_3\text{SiC}\equiv\text{CSC}\equiv\text{CSiMe}_3$ or $\text{Me}_3\text{SiC}\equiv\text{CSC}\equiv\text{CC}\equiv\text{CSC}\equiv\text{CSiMe}_3$ 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*- $[\text{Ph}(\text{Et}_3\text{P})_2\text{Pt}-\text{C}\equiv\text{CSC}\equiv\text{C}-\text{Pt}(\text{PEt}_3)_2\text{Ph}]$ 5.** Reaction of the diterminal alkyne $\text{HC}\equiv\text{CSC}\equiv\text{CH}$ (8.2 mg, 0.10 mmol) with 2 equivalents of *trans*- $[\text{PtPh}(\text{Cl})(\text{PEt}_3)_2]$ (109.0 mg, 0.20 mmol) for 20 h at room temperature, in the presence of CuI (3 mg), in CH_2Cl_2 – $(\text{Me}_3\text{Si})_2\text{NH}$ (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} ($\nu_{\text{C}\equiv\text{C}}$). ^1H 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 - $\{^1\text{H}\}$ NMR (CDCl_3): δ 8.00, 15.17 (C_2H_5), 77.29, 81.81 ($\text{C}\equiv\text{C}$), 121.42, 127.34, 138.97 and 153.97 (Ph). ^{31}P - $\{^1\text{H}\}$ NMR (CDCl_3): δ 11.09 ($^1J_{\text{Pt-P}}$ = 2621 Hz). FAB mass spectrum: m/z 1097 (M^+). UV/VIS (CH_2Cl_2): λ_{max} ($\epsilon \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)/nm 264 (1.7) and 325 (0.9). Emission (CH_2Cl_2 , $\lambda_{\text{excitation}}$ = 297 nm): 352 nm. Calc. for $\text{C}_{40}\text{H}_{70}\text{P}_4\text{Pt}_2\text{S}\cdot\text{C}_6\text{H}_{14}$: C, 46.69; H, 7.16. Found: C, 47.08; H, 7.10%.

trans-[Ph(Et₃P)₂Pt–C≡CSC≡CC≡CSC≡C–Pt(PEt₃)₂Ph] 6. To a mixture of HC≡CSC≡CC≡CSC≡CH (13.0 mg, 0.08 mmol) and 2 equivalents of *trans*-[PtPh(Cl)(PEt₃)₂] (87.0 mg, 0.16 mmol) in CH₂Cl₂–(Me₃Si)₂NH (18 cm³, 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–CH₂Cl₂ (1 : 1, v/v) as eluent, affording compound **6** as a viscous oil (49.0 mg, 52%). IR (KBr): 2067 and 2033 cm^{−1} (ν_{C≡C}). ¹H NMR (CDCl₃): δ 1.04 (m, 36 H, CH₃), 1.64 (m, 24 H, CH₂), 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). ¹³C-{¹H} NMR (CDCl₃): δ 7.96, 14.93 (C₂H₅), 73.22, 73.25, 77.20, 81.28 (C≡C), 121.47, 127.36, 138.91 and 154.45 (Ph). ³¹P-{¹H} NMR (CDCl₃): δ 11.11 (¹J_{Pt–P} = 2616 Hz). FAB mass spectrum: *m/z* 1177 (M⁺). UV/VIS (CH₂Cl₂): λ_{max} (ε × 10^{−4} dm³ mol^{−1} cm^{−1})/nm 263 br (2.1) and 318 (0.7). Emission (CH₂Cl₂, λ_{excitation} = 288 nm): 340 nm. Microanalytical data are not available due to the instability.

cis-[Pt(Me₂bipy){C≡CSC≡C(TIPS)}₂] 7. Compounds [Pt(Me₂bipy)Cl₂] (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 CH₂Cl₂ (25 cm³) and NHPri₂ (3 cm³) for 24 h. The volatile portion was evaporated under vacuum, the residue dissolved in the minimum amount of CH₂Cl₂ and passed through a short column (5 cm) of silica gel with hexane–CH₂Cl₂ 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} (ν_{C≡C}). ¹H NMR (CDCl₃): δ 1.11 (m, 42 H, Prⁱ), 2.64 (s, 6 H, CH₃), 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). ¹³C-{¹H} NMR (CDCl₃): δ 11.43, 18.73 (Prⁱ), 22.30 (CH₃), 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 (CH₂Cl₂): λ_{max} (ε × 10^{−4} dm³ mol^{−1} cm^{−1})/nm 283 br (1.7) and 413 (0.5). Emission (CH₂Cl₂, λ_{excitation} = 410 nm): 589 nm. Calc. for C₃₈H₅₄N₂PtS₂Si₂: 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–CH₂Cl₂. 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 (SHELXTL²² for **5**, SHELXS 86²³ 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.

CCDC reference number 186/2152.

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 |
| <i>M</i> | 1097.08 | 854.24 |
| Crystal system | Monoclinic | Triclinic |
| Space group | <i>P</i> 2 ₁ / <i>n</i> (no. 14) | <i>P</i> 1̄ (no. 2) |
| <i>a</i> /Å | 21.205(4) | 7.906(1) |
| <i>b</i> /Å | 9.053(2) | 14.018(1) |
| <i>c</i> /Å | 24.430(5) | 19.069(1) |
| <i>α</i> /° | | 98.66(1) |
| <i>β</i> /° | 95.67(3) | 92.38(1) |
| <i>γ</i> /° | | 97.83(1) |
| <i>U</i> /Å ³ | 4667(2) | 2065.6(3) |
| <i>Z</i> | 4 | 2 |
| μ(Mo-Kα)/cm ^{−1} | 61.95 | 35.68 |
| No. reflections collected | 26410 | 22607 |
| Unique reflections (<i>R</i> _{int}) | 10473 (0.033) | 3228 (0.045) |
| Observed reflections [<i>I</i> > <i>nσ</i> (<i>I</i>)] | 10473 (<i>n</i> = 2.0) | 2139 (<i>n</i> = 1.5) |
| Residuals | <i>R</i> = 0.0291 <i>wR</i> = 0.0845 | <i>R</i> = 0.056 <i>wR</i> = 0.060 |

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