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Some platinum(II) complexes derived from aromatic alkynes

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Several *trans*-platinum(II) complexes, of the type $R'-\{Pt(PBu_3)_2\}-R''-\{Pt(PR_3)_2\}-R'$, where R′ and R″ are groups derived from a series of aromatic alkynes and diynes, have been prepared and characterized. Extensive spectroscopic data for these and other known related complexes are presented. A more precise structural study of *trans*-$Pt(C{\equiv}CC_6H_4C{\equiv}CPh)_2(PBu_3)_2$ (cf. *Z. Kristallogr.* 1998; 213: 483) is reported. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: platinum; alkynes; X-ray structure

INTRODUCTION

Platinum(II) complexes containing extended alkynyl ligands have been known since Hagihara's group reported the synthesis of *cis* and *trans* isomers of $Pt(C{\equiv}CR)_2(PBu_3)_2$ ($R = C{\equiv}CH$, $C_6H_4C{\equiv}CH$-4)[1] and later polymers containing groups such as $-C{\equiv}CXC{\equiv}C-$ ($X = 1,4$-C_6H_4, 4-$C_6H_4C_6H_4$-4) linking two platinum centres.[2] More recently, Lewis and coworkers[3,4] described a general synthetic route to compounds of this type which used organotin derivatives of the alkynes. Interest in these materials, which have rigid-rod structures, arises from the presence of partially delocalized π systems resulting from interaction of the platinum d orbitals with π^* orbitals of the alkyne.[5–8] More recently, attention has been drawn to the linear and non-linear optical properties of platinum(II) complexes, such as *trans*-$Pt(C{\equiv}CC_6H_4C{\equiv}CPh-4)_2(PBu_3)_2$ (**11**; see Scheme 1 for compound numbers).[11–15]

A search of the earlier literature revealed that although the majority of studies had been carried out using either *trans*-$Pt(C{\equiv}CC_6H_4C{\equiv}CH-4)_2(PBu_3)_2$ (**10**)[4] or **11**, several related compounds had been reported previously. These included the intermediate chloro-platinum(II) complexes 1,4-$\{$*trans*-$PtCl(PBu_3)_2C{\equiv}C\}_2C_6H_4$ (**1**),[16] 1,3,5-$\{$*trans*-$PtCl(PBu_3)_2C{\equiv}C\}_3C_6H_3$ (**8**)[17] and the bis(alkynyl)platinum(II) complex *trans*-$Pt\{C{\equiv}CC_6H_4C{\equiv}C[PtCl(PBu_3)_2]\}_2(PBu_3)_2$ (**6**).[4,16] In addition, several polymeric species have been described, although such materials were not obtained during this study, which was undertaken to prepare and characterize further examples of these complexes, containing between one and three platinum centres, most of which have not been reported previously. Conventional methods of synthesis have been employed, often in sequence, to give polynuclear compounds. The non-linear optical properties of these materials are currently under investigation and will be reported elsewhere, as will spectroscopic and computational studies of their electronic structures.

RESULTS

Scheme 2 illustrates the general types of reaction we have used, with individual compounds being numbered below the scheme. Conventional methods of synthesis of alkynyl-platinum(II) complexes generally involve condensation of the appropriate alkyne with the chloro-platinum(II) complex, a reaction that is usually carried out in a polar solvent in the presence of a base, often a secondary amine, together with a copper(I) catalyst.[1,3,4] In the present work, we have used piperidine–toluene mixtures and copper(I) iodide. The following chloro-platinum(II) intermediates were prepared

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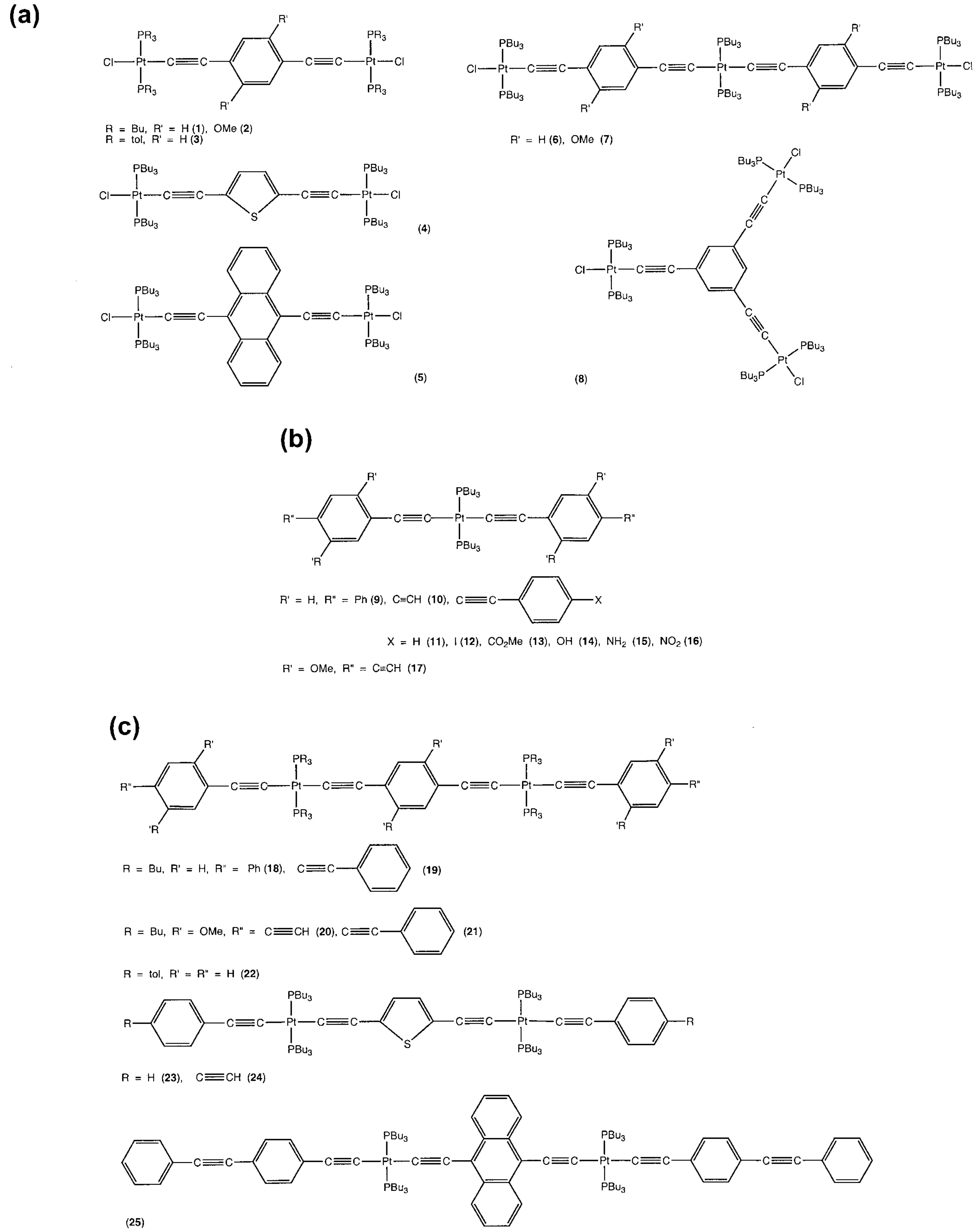
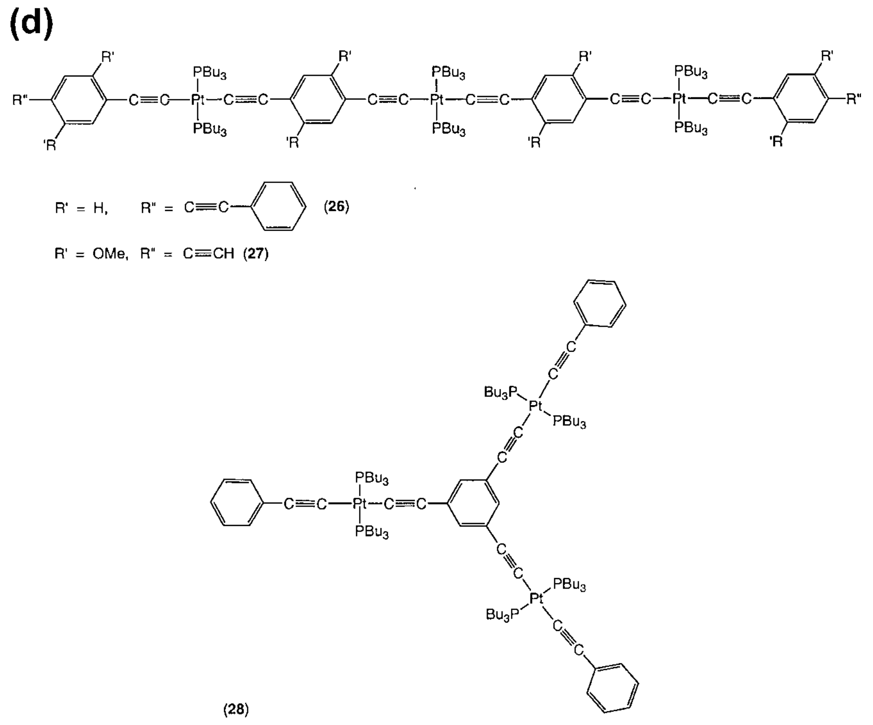
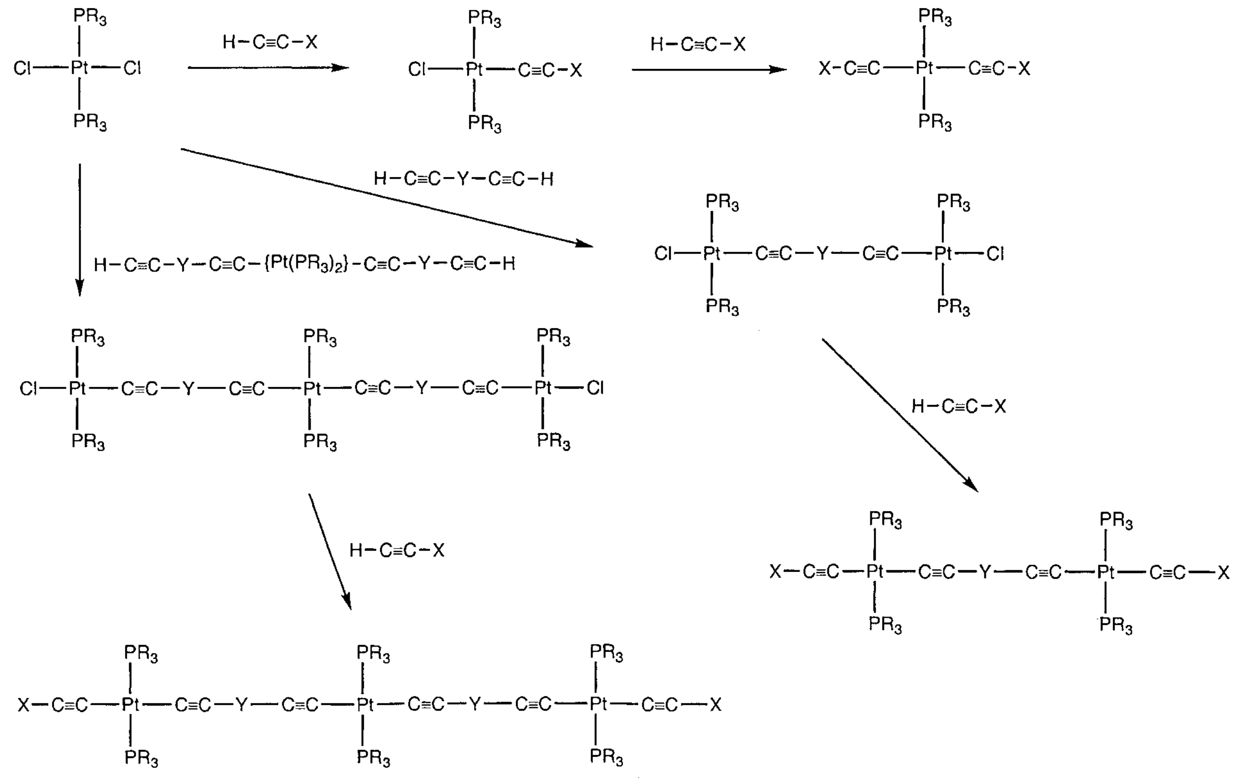


Scheme 1. (a) Chloro-platinum(II) complexes; (b) mononuclear complexes; (c) binuclear complexes; (d) trinuclear complexes.



Scheme 1. (Continued).



Scheme 2.

by using a ratio of *trans*-$PtCl_2(PR_3)_2$ (R = Bu, tol) to 1-alkyne of between two and three:

1,4-{*trans*-$\{PtCl(PBu_3)_2C{\equiv}C\}_2\{C_6H_2(OMe)_2$-3,5} (**2**)
1,4-{*trans*-$PtCl[P(tol)_3]_2C{\equiv}C\}_2C_6H_4$ (**3**)
{*trans*-$PtCl(PBu_3)_2C{\equiv}C\}_2X$ (X = C_4H_2S-2,5 (**4**), $C_{14}H_8$-9,10 (**5**))
trans-Pt{$[C{\equiv}CC_6H_2(OMe)_2$-3,5][$PtCl(C{\equiv}CC_6H_4C{\equiv}C$-4) $(PBu_3)_2\}_2(PBu_3)_2$ (**7**).

Alkynyl complexes of several types have been obtained, all of which contain *trans*-disubstituted platinum(II) centres also carrying two PBu_3 ligands:

(i) *trans*-$Pt(C{\equiv}CC_6H_4Ph\text{-}4)_2(PBu_3)_2$ (**9**)
(ii) *trans*-$Pt\{C{\equiv}C(C_6H_2R'_2\text{-}3,5)C{\equiv}CH\text{-}4\}_2(PBu_3)_2$ (R′ = H (**10**), OMe (**17**))
(iii) *trans*-$Pt\{C{\equiv}CC_6H_4C{\equiv}CC_6H_4R''\text{-}4\}_2(PBu_3)_2$ (R″ = H (**11**), I (**12**), CO_2Me (**13**), OH (**14**), NH_2 (**15**), NO_2 (**16**))
(iv) 1,4-{*trans*-$Pt(C{\equiv}CC_6H_4Ph\text{-}4)_2(PBu_3)_2C{\equiv}C\}_2C_6H_4$ (**18**)
(v) *trans*-$Pt\{C{\equiv}C(C_6H_2R'_2\text{-}3,5)C{\equiv}CR\}_2$ $(PBu_3)_2$ (R = H, R′ = OMe (**27**); R = Ph, R′ = OMe (**26**))
(vi) 1,4-{*trans*-$Pt(C{\equiv}CC_6H_4C{\equiv}CR\text{-}4)(PBu_3)_2C{\equiv}C\}_2$ $C_6H_2R'_2$-3,5 (R′ = H R = Ph (**19**); R′ = OMe, R = H (**20**), Ph (**21**))
(vii) {*trans*-$Pt(C{\equiv}CR)(PBu_3)_2\}_2X$ (X = C_4H_2S-2,5, R = Ph (**23**), $C_6H_4C{\equiv}CH$-4 (**24**); X = $C_{14}H_8$-9,10, R = $C{\equiv}CC_6H_4C{\equiv}CPh$ (**25**))
(viii) 1,3,5-{$PhC{\equiv}CC_6H_4C{\equiv}C[Pt(PBu_3)_2]C{\equiv}C\}_3C_6H_3$ (**28**).

It is necessary to adjust the stoichiometry of the reagents in order that the desired products are obtained. Generally, one equivalent of *trans*-$PtCl_2(PBu_3)_2$ was treated with between two and five equivalents of alkyne in toluene containing piperidine as base together with a catalytic amount of CuI. After stirring for several hours at room temperature work-up by chromatography on an alumina column afforded the desired compounds, which could be purified by recrystallization or reprecipitation from dichloromethane–methanol mixtures.

Exceptions to this general method are the reactions of **2** with the appropriate iodoarenes, which afforded compounds **12**–**16**, and the preparation of **4** from 2,5-bis(trimethylsilyl)thiophene in the presence of $[NBu_4]F$, which acted as a proto-desilylating agent to generate 2,5-bis(ethynyl)thiophene *in situ* for the subsequent reaction with the chloro-platinum(II) complex.

The compounds are yellow to orange in colour and have been characterized by elemental analyses and spectroscopic methods. The IR spectra contained $\nu(C{\equiv}C)$ bands around between 2090 and 2115 cm^{-1}, together with characteristic bands of other functional groups (≡CH at 3270–3320 cm^{-1}, NH at 3400 cm^{-1}) if present. If more than one C≡C triple bond was present, multiple $\nu(C{\equiv}C)$ bands may be observed (as in **13** or **15**, which showed a higher energy band at *ca* 2205 cm^{-1}). The ^1H NMR spectra contained multiplet resonances for the Bu groups (one Me at δ 0.89–0.95, three CH_2 signals between δ 1.42 and 2.24) and for the aromatic protons. In the ^{13}C NMR spectra, these signals were at δ *ca* 13.70 (Me), between δ 23.60 and 30.90 (CH_2) and between δ 123.3 and 145.9 (aromatic). If present, characteristic resonances for OMe (δ_H *ca* 3.80, δ_C *ca* 56.0) and ≡CH (δ_H 3.09–3.34) were found; the C≡C resonances occurred between δ 82.7 and 117.3, but these have low relative

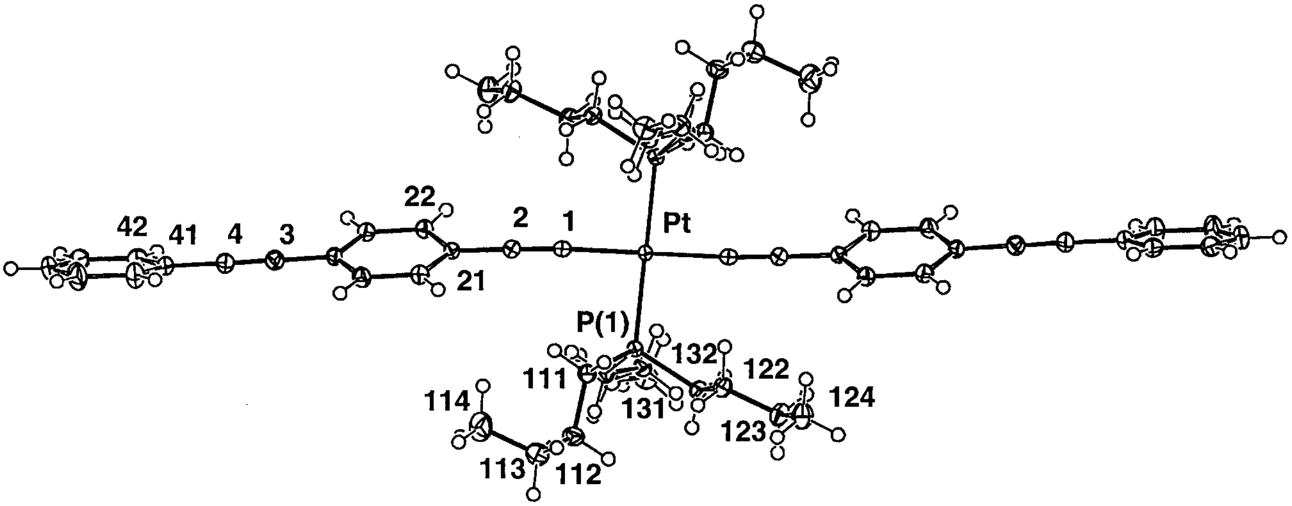
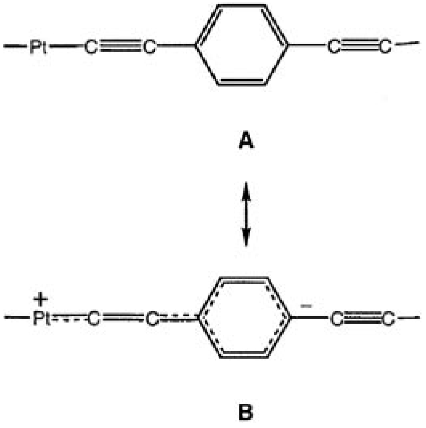


Figure 1. Plot of a molecule of *trans*-$Pt(C{\equiv}CC_6H_4C{\equiv}CPh\text{-}4)_2(PBu_3)_2$ (**11**), showing atom numbering system. Non-hydrogen atoms are shown with 50% thermal envelopes, hydrogen atoms having arbitrary radii of 0.1 Å. Selected bond parameters: Pt—P(1) 2.3079(3), Pt—C(1) 1.996(2), C(1)—C(2) 1.214(2), C(2)—C(21) 1.437(2), C(21)—C(22, 26) 1.400, 1.406(2), C(22)—C(23) 1.386(2), C(24)—C(23, 25) 1.401, 1.401(2), C(24)—C(3) 1.435(2), C(3)—C(4) 1.199(2), C(4)—C(41) 1.438(2) Å. P(1)—Pt—C(1) 86.59(4), Pt—C(1)—C(2) 176.9(1), C(1)—C(2)—C(3) 177.4(1), C(24)—C(3)—C(4) 179.8(1), C(3)—C(4)—C(41) 177.4(1)°.

intensities (slow relaxation times) and were not always observed. The ^{31}P NMR spectra contained resonances between δ_P 1.37 and 8.0, showing the usual pseudo-triplet structure: the outer pair of lines result from splitting by ^{195}Pt and the J_{PPt} values (*ca* 2350 Hz) confirm the *trans* geometry for these complexes. We attempted to confirm the compositions of these complexes using electrospray (ES) mass spectrometry, but were thwarted by failure to observe M^+ ions in most cases, even when chemical aids to ionization were employed.[18]

The advent of an area detector instrument enabled a low-temperature X-ray structure determination of **11** to be carried out, which is of superior precision to the previously reported study.[19] Details are given in the Experimental section and in Fig. 1. Of interest is the significant difference between the two C≡C triple bond lengths [C(1)−C(2) 1.214(2), C(3)−C(4) 1.199(2) Å], the constancy of the C(sp)−C(sp^2) separations [1.435–1.438(2) Å] and the shortening of the 'middle' C−C separations in the central C_6H_4 ring [C(22)−C(23), C(25)−C(26) 1.386, 1.395(2) versus C(21)−C(22, 26) and C(24)−C(23, 25) 1.400–1.406(2) Å]. As a result of the latter, internal angles at C(21, 24) are smaller [118.2, 118.5(1)°] than those at C(22, 23, 25, 26) [120.7–120.9(1)°]. These data are consistent with a contribution from the vinylidene tautomer **B** to the overall structure:



CONCLUSIONS

Conventional methodologies have been used to synthesize a range of *trans*-bis(phosphine)platinum(II) complexes derived from aromatic alkynes, several of which have 'molecular rod' structures.

EXPERIMENTAL

General

All reactions were carried out under dry high purity nitrogen unless stated otherwise, using standard Schlenk techniques. Common solvents were dried, distilled under nitrogen, and degassed before use. Elemental analyses were performed by Chemical and Micro-analytical Services (CMAS), Melbourne.

Instrumentation

IR spectra were obtained with a Perkin–Elmer 1720X FT spectrometer. Solution spectra were obtained with a 0.5 mm path-length solution cell with NaCl windows. Nujol mull spectra were obtained from samples mounted between NaCl plates. NMR spectra were recorded on Bruker ACP 300 (^1H at 300.13 MHz, ^{13}C at 75.47 MHz, ^{31}P at 121.50 MHz) or Varian Gemini 200 (^1H at 199.80 MHz, ^{13}C at 50.29 MHz) spectrometers. Samples were dissolved in $CDCl_3$ (Sigma) and measured using 5 mm tubes. ES mass spectra were obtained from samples dissolved in MeOH unless indicated otherwise. VG Platform II: solutions were injected into the spectrometer via a 10 μl injection loop. Nitrogen was used as the drying and nebulizing gas, and samples were examined at cone voltages in the range 20–80 V to find the best conditions. Finnegan LCQ: by direct infusion. Where used, chemical aids to ionization are indicated.[15] All spectroscopic data are summarized in Table 1.

Reagents

CuI, PBu_3, $P(tol)_3$ (Aldrich) and $K_2[PtCl_4]$ (Johnson Matthey) were used as received. $K[PtCl_3(\eta\text{-}C_2H_4)]$,[20] *trans*-$PtCl_2(PR_3)_2$ (R = Bu, tol)[21] and the alkynes 1,4-$(HC{\equiv}C)_2C_6H_4$,[22] 4-$HC{\equiv}CC_6H_4C{\equiv}CC_6H_4R$ (R = H, I, OH, NH_2, CO_2Me, NO_2),[23] 4-$HC{\equiv}CC_6H_4Ph$,[24] 1,3,5-$(HC{\equiv}C)_3C_6H_3$,[21] 2,5-$(Me_3SiC{\equiv}C)_2C_4H_2S$[25] and 9,10-$(Me_3SiC{\equiv}C)_2C_{14}H_8$[26,27] were prepared according to the cited procedures.

Preparation of binuclear chloro-platinum(II) complexes

Typical preparation

CuI (*ca* 2 mg) was added to a solution of *trans*-$PtCl_2(PBu_3)_2$ (500 mg, 0.75 mmol) and 1,4-diethynyl-2,5-dimethoxybenzene (46 mg, 0.25 mmol) in a toluene (8 ml)–piperidine (2 ml) mixture at 0 °C. After stirring for 7 h, the solution had turned green. Removal of solvent and chromatography of a dichloromethane solution of the residue on alumina (15 cm × 2 cm column) afforded a yellow fraction, which was eluted with hexane. Evaporation and recrystallization (CH_2Cl_2–MeOH) gave 1,4-$\{PtCl(PBu_3)_2C{\equiv}C\}_2C_6H_2(OMe)_2$-2,5 (**2**) as a yellow powder (291 mg, 80%).

Compounds **3** (62%), **5** (80%), and **7** (98%) were also prepared in this manner. Analytical and spectroscopic data for all complexes are given in Tables 1 and 2.

Preparation of 2,5-{trans-$PtCl(PBu_3)_2C{\equiv}C\}_2C_4H_2S$ (**4**)

To a solution of *trans*-$PtCl_2(PBu_3)_2$ (500 mg, 0.75 mmol) and 2,5-bis(trimethylsilylethynyl)thiophene (69 mg, 0.25 mmol) dissolved in a mixture of toluene (10 ml) and piperidine (3 ml) was added CuI (*ca* 3 mg) and $[NBu_4]F$ (130 mg, 0.5 mmol). After stirring for 2 days at room temperature, solvent was removed and a dichloromethane extract of

Table 1. Spectroscopic data

Compound no.	IR/cm^{-1} ν(C≡C)	NMR ^{1}H	NMR ^{13}C	NMR ^{31}P	M (calc.) ES MS/m/z
1	2101	0.98 (Me), 1.58, 1.89, 2.18 (CH_2), 6.73–7.14 (Ar)	13.73 (Me), 23.60, 26.07, 29.66 (CH_2), 115.55, 117.25 (C≡C), 126.45–130.28 (Ar)	7.93 (2371)	(1394) 1400, [M + MeCN − Cl]$^+$; 1359, [M − Cl]$^+$
2	2109	0.94 (Me), 1.45, 1.60, 2.09 (CH_2), 3.74 (OMe), 6.68 (Ar)	13.78 (Me), 21.63, 24.36, 26.09 (CH_2), 55.86 (OMe)	7.60 (2375)	(1453) 1460, [M + MeCN − Cl]$^+$
3	2107	2.32 (Me), 7.04–7.63 (Ar)	–	17.71 (2634)	(1800)
4	2102	0.93 (Me), 1.46, 1.79, 2.02 (CH_2), 6.59 (Ar)	13.77 (Me), 23.37, 24.15, 26.33 (CH_2), 99.99 (C≡C), 126.77 (Ar)	5.58 (2376)	(1398)
5	2096	0.97 (Me), 1.58, 1.89 (CH_2), 7.41, 8.80 (Ar)	13.75 (Me), 22.35, 24.24, 26.07 (CH_2), 127.47–132.87 (Ar)	5.58 (2379)	(1492)
6	2101	0.91 (Me), 1.44, 1.57, 2.10 (CH_2), 7.08–7.26 (Ar)	13.78 (Me), 21.98, 24.28, 26.34 (CH_2), 125.28–137.84 (Ar)	4.10 (2367), 7.97 (2378)	(2118)
7	2095	0.91 (Me), 1.41, 1.56, 2.18 (CH_2), 3.71 (OMe), 6.69–6.75 (Ar)	13.81 (Me), 24.43, 26.83, 29.65 (CH_2), 56.92 (OMe), 117.28 (C≡C), 123.38–125.45 (Ar)	4.13 (2364), 7.97 (2378)	(2246)
8	2112	0.93 (Me), 1.49–1.55, 1.99 (CH_2), 7.15–7.27 (Ar)	13.75 (Me), 21.70, 24.26, 26.07 (CH_2), 128.19–131.11 (Ar)	8.21 (2366)	(2049)
9	2098	0.96 (Me), 1.50, 1.64, 2.20 (CH_2), 7.26–7.62 (Ar)	13.83 (Me), 24.19, 26.32 (CH_2), 108.84, 109.47 (C≡C), 126.54–141.97 (Ar)	4.32 (2356)	(953)
10	2096; ν(≡CH) 3318	0.95 (Me), 1.48, 1.62, 2.14 (CH_2), 3.13 (≡CH), 7.13–7.52 (Ar)	13.77 (Me), 23.99, 26.37 (CH_2), 130.56–132.37 (Ar)	4.45 (2339)	(850) 851, [M + H]$^+$
11	2096	0.93 (Me), 1.43, 1.62, 2.14 (CH_2), 7.19–7.57 (Ar)	13.78 (Me), 24.08, 26.37, 29.69 (CH_2), 89.77, 90.06, 109.34, 111.77 (C≡C), 127.99–132.42 (Ar)	4.31 (2344)	(1002) 1003, [M + H]$^+$; 800, [M − PBu_3]$^+$ or [M − $C_2C_6H_4C_2Ph$]$^+$
12	2096	0.94 (Me), 1.47, 1.64, 2.14 (CH_2), 7.26–7.73 (Ar)	13.69 (Me), 24.27, 27.15, 30.60 (CH_2), 88.87, 93.29, 118.81 (C≡C), 128.40–139.32 (Ar)	4.41 (2344)	(1253)
13	2211, 2097	0.66 (Me), 1.14, 1.34, 1.86 (CH_2), 3.66 (CO_2Me), 6.85–7.76 (Ar)	13.76 (Me), 23.96, 26.63, 29.60 (CH_2), 52.14 (CO_2Me), 89.15, 93.19, 118.59 (C≡C), 127.74–135.04 (Ar)	4.28 (2345)	(1118) 1141, [M + Na]$^+$
14	2096	0.95 (Me), 1.45, 1.74, 2.14 (CH_2), 4.79 (OH), 7.13–7.75 (Ar)	13.76 (Me), 23.96, 26.35, 29.68 (CH_2), 127.75–132.08 (Ar)	4.46 (2327)	(1034)
15	2206, 2093	0.89 (Me), 1.30, 1.61, 2.14 (CH_2), 3.71 (NH_2), 6.49–7.46 (Ar)	13.78 (Me), 23.76, 26.36, 29.68 (CH_2), 128.30–132.99 (Ar)	4.30 (2335)	(1032)
16	2214	0.89 (Me), 1.49, 2.02, 2.24 (CH_2), 7.27–8.21 (Ar)	–	–	(1089) 1346, [M + 2Ag + MeCN]$^+$
17	2091; ν(≡CH) 3221	0.90 (Me), 1.42, 1.59, 2.18 (CH_2), 3.34 (≡CH), 3.75–3.86 (OMe), 6.79–6.85 (Ar)	13.80 (Me), 24.24, 26.50, 30.87 (CH_2), 56.18 (OMe), 80.89 (≡CH), 82.71, 104.87, 107.47 (C≡C), 115.27–120.48 (Ar)	4.44 (2345)	(970) 971, [M + H]$^+$; 825, [M + MeCN − $C_2C_6H_2(OMe)_2C_2H$]$^+$

Compound		NMR			M (calc.)
no.	IR/cm^{-1} ν(C≡C)	^{1}H	^{13}C	^{31}P	ES MS/m/z
18	2101	0.98 (Me), 1.52, 1.70, 2.21 (CH_2), 7.19–7.69 (Ar)	13.80 (Me), 24.30, 26.36 (CH_2), 108.71, 109.556 (C≡C), 125.44–145.94 (Ar)	4.21 (2361)	(1578)
19	2097	0.93 (Me), 1.43, 1.57, 2.15 (CH_2), 7.10–7.52 (Ar)	13.78 (Me), 24.39, 26.50, 30.69 (CH_2), 88.77, 90.06, 109.34, 111.77, 119.23, 123.62 (C≡C), 128.29–132.42 (Ar)	4.24 (2346)	(1726) 1726, M$^+$
20	2095; ν(≡CH) 3254	0.90 (Me), 1.44, 1.59, 2.19 (CH_2), 3.34 (≡CH), 3.72–3.86 (OMe), 6.70–6.98 (Ar)	13.79 (Me), 24.23, 26.33, 29.66 (CH_2), 57.02 (OMe), 117.20 (C≡C), 125.45–129.38 (Ar)	4.32 (2332)	(1759) 1755, [M + H]$^+$
21	2099	0.95 (Me), 1.43, 1.64, 2.22 (CH_2), 3.76 (OMe), 6.74–7.57 (Ar)	13.80 (Me), 24.20, 26.37, 29.69 (CH_2), 55.86 (OMe), 89.69, 115.07, 115.46 (C≡C), 127.97–132.42 (Ar)	1.37 (2314), 4.27 (2355)	(1786)
22	2103	2.38 (Me), 6.93–7.69 (Ar)	–	–	(1932)
23	2095	0.96 (Me), 1.50, 1.63, 2.15 (CH_2), 6.64 (C_4H_2S), 7.15–7.32 (Ar)	13.81 (Me), 24.28, 26.52 (CH_2), 101.71 (C≡C), 124.75–130.76 (Ar)	4.26 (2351)	(1526)
24	2097	0.91 (Me), 1.44, 1.59, 2.09 (CH_2), 3.10 (≡CH), 6.59 (C_4H_2S), 7.09–7.47 (Ar)	–	6.14 (2343)	(1722)
25	2098, 2078	0.92 (Me), 1.45, 1.68, 2.17 (CH_2), 7.11-7.43 (Ar), 7.51, 8.74 ($C_{14}H_8$)	13.77 (Me), 24.38, 26.64 (CH_2), 89.76, 90.02, 119.21 (C≡C), 123.57–131.78 (Ar)	5.60 (2358)	(1824)
26	2098	0.91 (Me), 1.42, 1.67, 2.07 (CH_2), 7.09–7.50 (Ar)	13.73 (Me), 23.64, 26.31, 29.89 (CH_2), 89.99, 109.51 (C≡C), 125.46–132.38 (Ar)	4.06 (2359)	(2450)
27	2099	0.92 (Me), 1.43, 1.55, 2.22 (CH_2), 3.73–3.86 (OMe), 6.72–7.27 (Ar)	13.83 (Me), 23.60, 24.32, 26.37 (CH_2), 55.91, 57.06 (OMe), 105.22, 110.57 (C≡C), 115.54–117.25 (Ar)	1.37 (2313), 4.21 (2365)	(2546)
28	2113, 2101	0.93 (Me), 1.32–1.58, 2.00 (CH_2), 7.11–7.57 (Ar)	13.77 (Me), 22.02, 24.19, 26.30 (CH_2), 127.97–131.61 (Ar)	8.21 (2366)	(2548)

the residue was chromatographed (alumina, 15 cm × 2 cm column). Elution with hexane gave 2,5-{*trans*-$PtCl(PBu_3)_2C\equiv C\}_2C_4H_2S$ (**4**) as a yellow oil (350 mg, 91%).

Preparation of mononuclear bis(alkynyl)platinum(II) complexes

Typical preparations

(a) Reactions of trans-$PtCl_2(PR_3)_2$ *with an excess of the alkyne*: addition of CuI (*ca* 3 mg) to a mixture of *trans*-$PtCl_2(PBu_3)_2$ (1.0 g, 1.5 mmol) and 1,4-diethynyl-2,5-dimethoxybenzene (1.5 g, 8.0 mmol) dissolved in a mixture of toluene (50 ml) and piperidine (15 ml) at 0 °C and stirring for 2 h gave a yellowish–green residue after removal of solvent. Chromatography (alumina, 15 cm × 2 cm column) gave a yellow–orange band with hexane, which was purified by recrystallization (CH_2Cl_2–MeOH) to give *trans*-$Pt\{C\equiv CC_6H_2(OMe)_2\text{-}2,5\text{-}C\equiv CH\text{-}4\}_2(PBu_3)_2$ (**17**) (920 mg, 63%).

Compound **9** (87%) and **16** (66%) were also prepared in this manner.

(b) Reactions of iodoarenes with trans-$Pt(C\equiv CC_6H_4C\equiv CH\text{-}4)_2(PBu_3)_2$ (***10***): a mixture of CuI (*ca* 6 mg) and $PdCl_2(PPh_3)_2$ (20 mg, 0.024 mmol) was added to a solution containing **10** (200 mg, 0.24 mmol) and 4-$IC_6H_4CO_2Me$ (131 mg, 0.5 mmol) in $NHEt_2$ (20 ml). After stirring overnight at room temperature, examination of the solution by thin layer chromatography showed that an orange–brown compound was present. Solvent was removed and the residue was chromatographed on an alumina column (15 cm × 2 cm). Hexane eluted an orange–brown band, which, after recrystallization (CH_2Cl_2–

Table 2. Some alkynyl-platinum(II) complexes

	Synthetic precursors					
No.	Pt complex or reagent	Alkyne	Yield (%)	Formula	Analysis, found (calc. d)	Reference
1	$PtCl_2(PBu_3)_2$	1,4-$(HC\equiv C)_2C_6H_4$	91	$C_{58}H_{112}Cl_2P_4Pt_2$	C, 50.13 (49.96); H, 8.02 (8.10)	4, 7, 8, 16
2	$PtCl_2(PBu_3)_2$	1,4-$(HC\equiv C)_2$-2,5-$(OMe)_2C_6H_2$	80	$C_{60}H_{116}Cl_2O_2P_4Pt_2$	C, 49.66 (49.56): H, 8.09 (8.05)	
3	$PtCl_2\{P(tol)_3\}_2$	1,4-$(HC\equiv C)_2C_6H_4$	62	$C_{94}H_{88}Cl_2P_4Pt_2$	–[a]	
4	$PtCl_2(PBu_3)_2$	2,5-$(Me_3SiC\equiv C)_2C_4H_2S$	91	$C_{56}H_{110}Cl_2P_4Pt_2S$		17
5	$PtCl_2(PBu_3)_2$	9,10-$(HC\equiv C)_2C_{14}H_{10}$	80	$C_{66}H_{116}Cl_2P_4Pt_2$		7
6	$PtCl_2(PBu_3)_2$	**10**	93	$C_{92}H_{170}Cl_2P_6Pt_3$	C, 52.39 (52.16); H, 7.91 (8.09)	3, 4, 7
7	$PtCl_2(PBu_3)_2$	**17**	98	$C_{96}H_{178}Cl_2O_4P_6Pt_3$	–[a]	
8	$PtCl_2(PBu_3)_2$	1,3,5-$(HC\equiv C)_3C_6H_3$	92	$C_{84}H_{165}Cl_3P_6Pt_3$		17
9	$PtCl_2(PBu_3)_2$	$HC\equiv CC_6H_4Ph$-4	87	$C_{52}H_{72}P_2Pt$	C, 65.63 (65.45); H, 7.49 (7.61)	
10	$PtCl_2(PBu_3)_2$	1,4-$(HC\equiv C)_2C_6H_4$	86	$C_{44}H_{64}P_2Pt$	C, 61.99 (62.17); H, 7.50 (7.59)	
11	$PtCl_2(PBu_3)_2$	$HC\equiv CC_6H_4C\equiv CPh$-4	60	$C_{56}H_{72}P_2Pt$	C, 67.08 (67.11); H, 7.30 (7.24)	5, 10
12	1,4-$I_2C_6H_4$	**10**	73	$C_{56}H_{70}I_2P_2Pt$	C, 53.91 (53.62); H, 5.75 (5.63)	
13	$IC_6H_4CO_2Me$-4	**10**	43	$C_{60}H_{76}O_4P_2Pt$	C, 64.73 (64.44); H, 6.74 (6.85)	
14	IC_6H_4OH-4	**10**	51	$C_{56}H_{72}O_2P_2Pt$	–[a]	
15	$IC_6H_4NH_2$-4	**10**	60	$C_{56}H_{74}N_2P_2Pt$	C, 66.00 (65.16); H, 6.00 (7.22); N, 2.90 (2.71)	
16	$PtCl_2(PBu_3)_2$	$HC\equiv CC_6H_4(C\equiv CC_6H_4NO_2$-4)-4	66	$C_{56}H_{70}N_2O_4P_2Pt$	C, 62.05 (61.58); H, 4.46 (6.46); N, 3.59 (2.57)	
17	$PtCl_2(PBu_3)_2$	1,4-$(HC\equiv C)_2$-2,5-$(OMe)_2C_6H_2$	63	$C_{48}H_{72}O_4P_2Pt$	C, 59.31 (59.42); H, 7.67 (7.49)	
18	**1**	$HC\equiv CC_6H_4Ph$-4	95	$C_{86}H_{130}P_4Pt_2$	C, 62.14 (61.56); H, 8.36 (7.80)	
19	**1**	$HC\equiv CC_6H_4C\equiv CPh$	50	$C_{90}H_{130}P_4Pt_2$	C, 63.06 (62.63); H, 7.74 (7.59)	
20	**2**	1,4-$(HC\equiv C)_2$-2,5-$(OMe)_2C_6H_2$	85	$C_{84}H_{134}O_6P_4Pt_2$	C, 57.10 (57.52); H, 7.54 (7.70)	
21	**2**	$HC\equiv CC_6H_4C\equiv CPh$	42	$C_{92}H_{134}O_2P_4Pt_2$	C, 61.89 (61.87); H, 7.32 (7.56)	
22	**3**	$HC\equiv CPh$	21	$C_{110}H_{98}P_4Pt_2$	–[a]	
23	$PtCl(C\equiv CPh)(PBu_3)_2$	2,5-$(Me_3SiC\equiv C)_2C_4H_2S$	72	$C_{72}H_{120}P_4Pt_2S$	C, 56.51 (56.44); H, 8.01 (7.90)	
24	**4**	1,4-$(HC\equiv C)_2C_6H_4$	82	$C_{76}H_{120}P_4Pt_2S$	–[a]	
25	**5**	$HC\equiv CC_6H_4C\equiv CPh$	84	$C_{98}H_{134}P_4Pt_2$	–[a]	
26	**6**	$HC\equiv CC_6H_4C\equiv CPh$	87	$C_{124}H_{188}P_6Pt_3$	C, 59.74 (59.24); H, 7.47 (7.56)	
27	**7**	1,4-$(HC\equiv C)_2$-2,5-$(OMe)_2C_6H_2$	53	$C_{120}H_{196}O_8P_6Pt_3\cdot CHCl_3$	C, 54.27 (54.79); H, 7.07 (7.42)	
28	**8**	$HC\equiv CC_6H_4C\equiv CPh$	65	$C_{132}H_{192}P_6Pt_3$	C, 61.30 (62.16); H, 7.46 (7.59)	

[a] Consistent analyses not obtained.

MeOH), afforded *trans*- $\mathrm{Pt\{C{\equiv}CC_6H_4C{\equiv}CC_6H_4CO_2Me\}_2(PBu_3)_2}$ (**13**) as an orange–brown powder (115 mg, 43%).

Similar reactions were used to prepare **12** (73%), **14** (51%) and **15** (60%).

Preparation of binuclear complexes

Typical preparation

CuI (*ca* 4 mg) was added to a solution of 1,4-{*trans*-$\mathrm{PtCl(PBu_3)_2C{\equiv}C\}_2C_6H_4}$ (**1**; 200 mg, 0.14 mmol) and $\mathrm{HC{\equiv}CC_6H_4C{\equiv}CPh}$ (116 mg, 0.57 mmol) dissolved in a toluene (10 ml)–piperidine (4 ml) mixture. After stirring at 0 °C for 4 h, solvent was removed and the residue was chromatographed (alumina, 15 cm × 2 cm column). A yellow fraction was separated with hexane–ethyl acetate (9:1). Recrystallization ($\mathrm{CH_2Cl_2}$–MeOH) gave 1,4-{*trans*-$\mathrm{Pt(C{\equiv}CC_6H_4C{\equiv}CPh)(PBu_3)_2C{\equiv}C\}_2C_6H_4}$ (**19**) as a yellow microcrystalline powder (120 mg, 50%).

This method was used to prepare **18** (95%), **21** (42%), **24** (82%) and **25** (84%).

*Preparation of 2,5-{trans-Pt(C≡CPh)(PBu$_3$)$_2$C≡C}$_2$C$_4$H$_2$S (**23**)*

CuI (*ca* 3 mg) and $\mathrm{[NBu_4]F}$ (88 mg, 0.34 mmol) were added sequentially to a solution containing *trans*-$\mathrm{PtCl(C{\equiv}CPh)(PBu_3)_2}$ and 2,5-bis(trimethylsilylethynyl)thiophene (47 mg, 0.17 mmol) in a toluene (10 ml)–piperidine (3 ml) mixture. During stirring at room temperature for 18 h, the yellow solution turned orange, after which the solvent was removed and the residue was chromatographed on alumina (15 cm × 2 cm column). Hexane eluted 2,5-{*trans*-$\mathrm{Pt(C{\equiv}CPh)(PBu_3)_2C{\equiv}C\}_2C_4H_2S}$ (**23**) as an orange–yellow oil (187 mg, 72%).

Preparation of trinuclear complexes

Typical preparation

A solution containing *trans*-$\mathrm{Pt\{C{\equiv}CC_6H_4C{\equiv}C[}$*trans*-$\mathrm{PtCl(PBu_3)_2]\}_2(PBu_3)_2}$ (**6**; 0.07 mmol) and 4-$\mathrm{HC{\equiv}CC_6H_4C{\equiv}CPh}$ (57 mg, 0.28 mmol) in a toluene (10 ml)–piperidine (5 ml) mixture was treated with CuI (*ca* 2 mg) and stirred overnight at 0 °C. Solvent was removed and the residue chromatographed on an alumina column (15 cm × 2 cm) to give a yellow fraction, eluted with hexane. Addition of hexane to a dichloromethane solution afforded 4-$\mathrm{PhC{\equiv}CC_6H_4C{\equiv}C\{Pt(PBu_3)_2(C{\equiv}CC_6H_4C{\equiv}C)\}_2Pt(C{\equiv}CC_6H_4\text{-}C{\equiv}CPh\text{-}4)(PBu_3)_2}$ (**26**) as a yellow solid (200 mg, 87%). This method was also used to prepare **27** (53%).

*Preparation of 1,3,5-{trans-Pt(C≡CC$_6$H$_4$C≡CPh-4)(PBu$_3$)$_2$C≡C}$_3$C$_6$H$_3$ (**28**)*

CuI (2 mg) and $\mathrm{HC{\equiv}CC_6H_4C{\equiv}CPh}$ (150 mg, 0.73 mmol) were added to a solution of 1,3,5-{*trans*-$\mathrm{PtCl(PBu_3)_2C{\equiv}C\}_3C_6H_3}$ (**8**) (250 mg, 0.12 mg) in a mixture of toluene (10 ml) and piperidine (3 ml). After stirring at room temperature for 18 h, solvent was removed and the residue extracted with $\mathrm{CH_2Cl_2}$ and purified by chromatography on alumina to give a yellow fraction with hexane–ethyl acetate (9:1). This was recrystallized ($\mathrm{CH_2Cl_2}$–hexane) to give pure **28** (200 mg, 65%) as a yellow solid.

Structure determination

(**11**) $\mathrm{C_{56}H_{72}P_2Pt}$, $M = 1002.2$. Triclinic, space group $P\bar{1}$ (C_i^1, No. 2), $a = 10.0320(5)$, $b = 10.7229(5)$, $c = 12.9219(6)$ Å, $\alpha = 101.770(1)$, $\beta = 111.090(1)$, $\gamma = 94.935(1)$°, $V = 1250$ Å^3 ($T \approx 153$ K). D_c ($Z = 1$) = 1.331 g cm^{-3}. $\mu_{\mathrm{Mo}} = 29$ cm^{-1}; specimen: 0.35 × 0.25 × 0.1 mm; '$T_{\mathrm{min,max}}$' = 0.51, 0.72 ('empirical'/multiscan corrections). $2\theta_{\mathrm{max}} = 75$°; 25802 total reflections [Bruker AXS diffractometer, monochromatic Mo $K\alpha$ radiation ($\lambda = 0.7107_3$ Å), ω-scans] merging to 12840 unique ($R_{\mathrm{int}} = 0.026$), 12664 with $F > 4\sigma(F)$ considered 'observed' and used in the full matrix least-squares refinement [anisotropic thermal parameter forms (non-hydrogen atoms), $(x, y, z, U_{\mathrm{iso}})_{\mathrm{H}}$ refined]. Conventional R, R_w (weights: $[\sigma^2(F) + 0.0004F^2]^{-1}$) on $|F|$ 0.025, 0.021.

Crystallographic data for the structure determination have been deposited with the Cambridge Crystallographic Data Centre as CCDC No. 181000. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk; or www: http://www.ccdc.cam.ac.uk).

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