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Synthesis and redistribution reactions of asymmetric σ-arylplatinum(II) complexes containing 4,7-phenanthroline

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Abstract

The mononuclear σ-aryl complexes of the type *trans*-[Pt(σ-C_6H_4R)(4,7-phen)(PPh_3)$_2$]OTf (R = 4-$CO_2Si^tBuPh_2$, 4-CONHMe, 3-$CO_2Si^tBuPh_2$, 3-CONHMe; OTf = trifluoromethanesulfonate) containing a monodentate 4,7-phenanthroline (4,7-phen) ligand were prepared by an oxidative addition reaction of an aryl iodide with $Pt(PPh_3)_4$ to yield the key iodoplatinum(II) precursors *trans*-[PtI(σ-C_6H_4R)(PPh_3)$_2$], followed by halogen metathesis with one equivalent of 4,7-phen. The reaction of *trans*-[Pt(σ-C_6H_4R)(4,7-phen)(PPh_3)$_2$]OTf with labile complexes of the type *trans*-[Pt(OTf)L_2(σ-C_6H_4R')] (L = PEt_3, R′ = H; L = PPh_3, R′ = 4-$CO_2Si^tBuPh_2$, 3-$CO_2Si^tBuPh_2$, 3-CONHMe) afforded the asymmetric dinuclear complexes of the type *trans*-[Pt(σ-C_6H_4R)L_2(μ-4,7-phen)Pt(σ-C_6H_4R')L'_2](OTf)$_2$ (L = PPh_3, R = 4-$CO_2Si^tBuPh_2$, L′ = PEt_3, R′ = H; L = L′ = PPh_3, R = 4-CONHMe, R′ = 4-$CO_2Si^tBuPh_2$; R = 4-$CO_2Si^tBuPh_2$, R′ = 3-CONHMe; R = 3-CONHMe, R′ = 3-$CO_2Si^tBuPh_2$) in which the 4,7-phen acts as a bridging bidentate ligand. The novel dinuclear species undergo an unusual redistribution reaction that is essentially thermoneutral at 298 K. The exchange process involves facile cleavage of a Pt–N bond and the rapid exchange of *trans*-[PtL_2(σ-aryl)] units in the equilibrium mixture.

Keywords: 4,7-Phenanthroline; Platinum(II) complex; σ-Aryl ligand; Redistribution reaction; NMR Spectroscopy

1. Introduction

Diimine ligands are versatile subunits in the construction of supramolecular polygons and polyhedra using the metal–ligand paradigm (for recent reviews, see [1–9]). 4,7-Phenanthroline (4,7-phen) is a rigid N-donor ligand with a 60° directing angle that favours coordination to transition metals in a bridging bidentate manner rather than chelation. Recently, it has been used in the synthesis of a variety of coordination polymers [10–17], the majority of which contain copper(I), and in the supramolecular assembly of discrete polygons, e.g., a cyclic nanostructure comprising of six palladium(II) ions [18]. 4,7-Phen has also proved useful in the formation of supramolecular H-bonded networks containing hydrated first-row transition metal ions [19,20]. These systems represent remarkably unusual examples of a diimine undergoing second-sphere N...H–O–M interactions in preference to metal complexation.

In an exploration of new classes of platinum complexes that possess various H-bonding functionalities for potential use as building blocks in supramolecular assembly [21,22], we have recently reported the synthesis of dinuclear organoplatinum(II) complexes that are bridged by various N-donor ligands including 4,7-phen, 4,4′-bipyridine, and bis(4-pyridyl)ketone [23]. Their preparation involved a novel protection–deprotection strategy that was successfully used to incorporate two carboxylic acid groups into the complexes that had the potential to direct the assembly of such entities into discrete nanostructures by intermolecular H-bonding. However, in all cases the complexes possessed C2 symmetry and both of the N-donor ligands bearing the carboxylic acid group, e.g., nicotinic acid, were identical. Indeed, all attempted preparations of analogous asymmetric complexes in which the two H-bonding

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functionalities were different proved to be unsuccessful by this route.

Herein, we report the synthesis and characterisation of novel mono- and di-nuclear σ-arylplatinum(II) complexes containing the 4,7-phen ligand. Notably, the diimine ligand is capable of coordinating to the metal centre in a monodentate manner, and the synthesis of asymmetric, dinuclear organoplatinum(II) complexes bearing H-bonding functionalities such as carboxylic acids and *N*-methyl amides can be realised by the addition of a second metal fragment to the mononuclear species. Furthermore, we report an unusual redistribution reaction involving the dinuclear complexes which proceeds by a facile exchange of the 4,7-phen ligand between metal centres.

2. Results and discussion

2.1. Synthesis of complexes containing a monodentate 4,7-phen ligand

The σ-aryl(iodo)platinum(II) precursor complexes **5**–**8** containing either a silyl-protected carboxylic acid or a *N*-methyl amide functionality were readily prepared by an oxidative addition reaction involving a suitably-functionalised aryl iodide **1**–**4** with $Pt(PPh_3)_4$ (Scheme 1). As reported previously [23], protection of the carboxylic acid functionality in the aryl iodides **1** and **2** as a *tert*-butyl(diphenylsilyl) ester was found to be necessary in order to obtain the desired σ-arylplatinum(II) product in a reproducible, high yield whereas protection of the amide functionality in **3** and **4** proved unnecessary.

Treatment of the iodo complexes **5**–**8** with one equivalent of AgOTf followed by the addition of one equivalent of 4,7-phen in CH_2Cl_2 solution afforded a kinetic mixture containing both the mononuclear and corresponding dinuclear species in which the N-donor ligand coordinates to the platinum(II) centre in a monodentate and bridging bidentate manner, respectively. When the solution was left to stand for ca. 48 h at room temperature, the mononuclear platinum(II) derivatives **9**–**12** were formed exclusively under thermodynamic control.

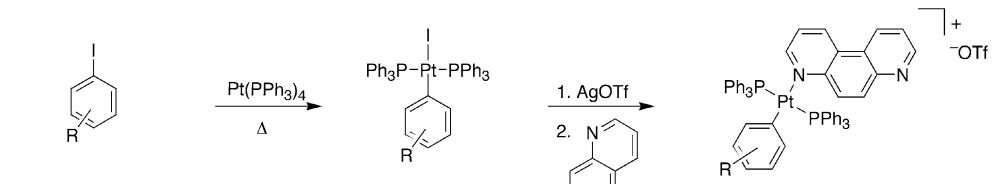
The assignment of the aromatic proton resonances in **9**–**12** was facilitated by 2D-COSY and 2D-ROESY NMR experiments. The latter experiments were performed in order to unambiguously assign some of the protons in the 4,7-phen ligand, where the PPh_3 protons showed distinct cross-peaks to the H^3 and H^5 protons of 4,7-phen. 2D-COSY NMR spectroscopy experiments allowed the assignment of the remaining 4,7-phen protons. The $^{31}P\{^1H\}$ NMR spectra of **9**–**12** display a singlet resonance that is flanked by ^{195}Pt satellite signals at ca. δ 19 ($^1J_{PPt}$ = ca. 3000 Hz), values that are consistent with the presence of mutually *trans*-PPh_3 ligands about a σ-arylplatinum(II) centre [21–24].

2.2. Synthesis of asymmetric dinuclear complexes containing the 4,7-phen ligand

Treatment of complexes of the type *trans*-[$PtIL_2$(σ-C_6H_4R')] (L = PEt_3, R′ = H; L = PPh_3, R′ = 4-$CO_2Si^tBuPh_2$, 3-$CO_2Si^tBuPh_2$, 3-CONHMe) with one equivalent of AgOTf in CH_2Cl_2 solution afforded the corresponding, labile triflato species *trans*-[Pt(OTf)L_2(σ-C_6H_4R')]. Its reaction with one equivalent of the 4,7-phen complexes **9**–**12** resulted in a rapid formation of the asymmetric, dinuclear species **13**–**16** (Scheme 2). As described above for the mononuclear complexes **9**–**12,** 2D-COSY and ROESY NMR experiments were performed with **13**–**16** in order to confirm the assignment of the 4,7-phen ring protons. In addition, the PEt_3 protons in **13** showed distinct cross-peaks with the H^6 and H^8 protons in the 2D-ROESY NMR spectrum.

The $^{31}P\{^1H\}$ NMR spectra of **13**–**16** display two singlet resonances that are each flanked by ^{195}Pt satellite signals. For example, in **13** the PPh_3 and PEt_3 resonances appear at distinct chemical shifts (δ 19.4 and δ 11.5, respectively). The chemical shift of the PEt_3 resonance and the magnitude of the Pt–P coupling constant (ca. 2733 Hz) are comparable to those reported for other σ-arylplatinum(II) complexes with mutually *trans*-PEt_3 ligands [21,25].

The addition of HOTf to **13**–**16** resulted in the facile cleavage of the silyl-protecting group to afford the corresponding carboxylic acid derivatives as described

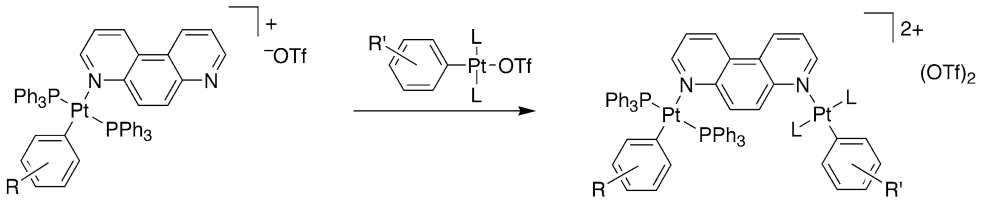


(**1**) R = 3-$CO_2Si^tBuPh_2$
(**2**) R = 4-$CO_2Si^tBuPh_2$
(**3**) R = 3-CONHMe
(**4**) R = 4-CONHMe

(**5**) R = 3-$CO_2Si^tBuPh_2$
(**6**) R = 4-$CO_2Si^tBuPh_2$
(**7**) R = 3-CONHMe
(**8**) R = 4-CONHMe

(**9**) R = 3-$CO_2Si^tBuPh_2$
(**10**) R = 4-$CO_2Si^tBuPh_2$
(**11**) R = 3-CONHMe
(**12**) R = 4-CONHMe

Scheme 1.



(9) R = 3-$CO_2Si^tBuPh_2$
(10) R = 4-$CO_2Si^tBuPh_2$
(11) R = 3-CONHMe
(12) R = 4-CONHMe

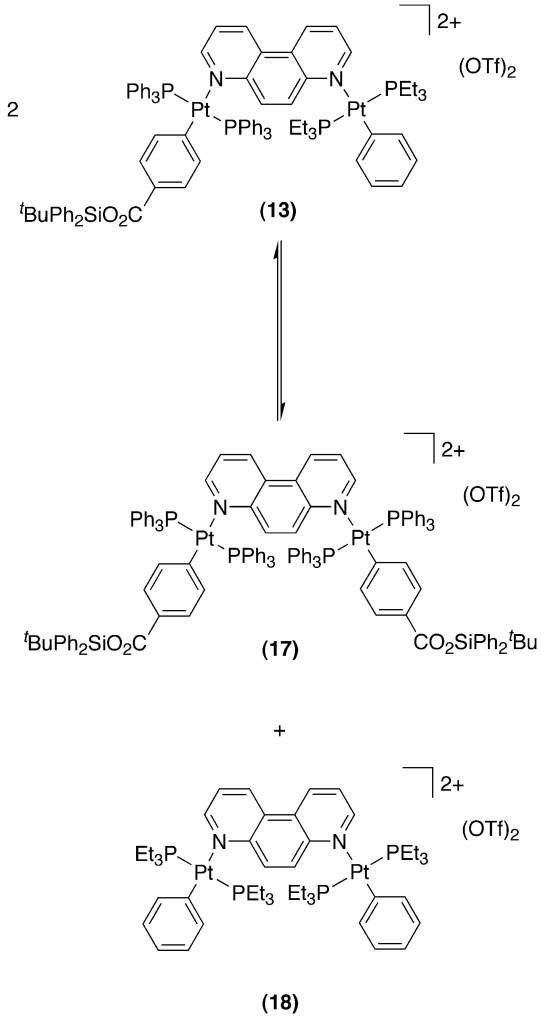
(13) L = PEt_3; R = 4-$CO_2Si^tBuPh_2$; R' = H
(14) L = PPh_3; R = 4-CONHMe; R' = 4-$CO_2Si^tBuPh_2$
(15) L = PPh_3; R = 4-$CO_2Si^tBuPh_2$; R' = 3-CONHMe
(16) L = PPh_3; R = 3-CONHMe; R' = 3-$CO_2Si^tBuPh_2$

Scheme 2.

previously [23], but their isolation proved difficult owing to a redistribution reaction that is described as follows.

2.3. Redistribution reactions involving *13–16*

Redistribution reactions in platinum(II) chemistry are well known, and all involve the transfer of a halogen, alkyl or aryl group between metal centres [26–29]. The dinuclear complexes **13–16** were found to undergo an unusual redistribution in CH_2Cl_2 solution to afford an equilibrium mixture of the asymmetric and two symmetrical dinuclear components. For example, when **13** was left to stand in CH_2Cl_2 solution for several hours at 298 K, it equilibrated with the symmetrical species **17** and **18** (Scheme 3). The identities of each component in the equilibrium mixture were confirmed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. For example, four distinct resonances at δ 21.7 ($^1J_{PPt} = 3002$ Hz), δ 21.1 ($^1J_{PPt} = 2962$ Hz), δ 15.3 ($^1J_{PPt} = 2674$ Hz), and δ 14.7 ($^1J_{PPt} = 2696$ Hz) were observed in the $^{31}P\{^1H\}$ NMR spectrum. The resonances at δ 21.1 and δ 14.7 were assigned to **13,** while those at δ 21.7 and δ 15.3 were attributed to **17** and **18,** respectively. To further confirm the identity of the components in the equilibrium mixture, **17** and **18** were independently prepared and characterised [23]. Indeed, the addition of one equivalent of **17** to **18** in CH_2Cl_2 solution resulted in an identical redistribution reaction. In all cases, the proportion of asymmetric species was approximately twice that of each of the other complexes at equilibrium indicating that the redistribution reaction is essentially thermoneutral at 298 K. As a statistical distribution of components was found in these systems, there is no evidence for any significant steric and electronic effects associated with the σ-aryl or phosphine ligands.



Scheme 3.

One can envisage the redistribution reaction involves a facile cleavage of either one of the Pt–N bonds in **13–16** as a consequence of the strong *trans* effect associated with the σ-aryl group, followed by complexation of the free N-atom with another Pt unit. It is clear from the redistribution reaction involving the mixed-phosphine complex **13** that Pt–C bond cleavage does not occur as products resulting from a loss of the σ-aryl ligand, such as the PPh_3 analogue of **18,** are not observed. The cleavage of only Pt–N bonds during the redistribution reaction is further supported by ESI-MS experiments that demonstrate a facile loss of the 4,7-phen ligand from the complexes, an effect that has been observed

previously in related systems containing other types of N-donor ligands, e.g., nicotinic acid [22,23]. Intermediate species could not be detected by NMR spectroscopy, even at low temperatures, indicating that once formed the labile triflato complex *trans*-[Pt(OTf)L_2(σ-C_6H_4R)] (L = PEt_3, R = H; L = PPh_3, R = 4-$CO_2Si^tBuPh_2$) must rapidly react with the free N-atom of the mononuclear species *trans*-[Pt(4,7-phen)L_2(σ-C_6H_4R)]. These results clearly demonstrate that the isolation of the dinuclear species **13**–**16** must be completed within a short period (ca. 1 h) at room temperature or significant amounts of the symmetrical exchange products are also formed in the reaction mixture.

3. Conclusion

Novel asymmetric, dinuclear organoplatinum(II) complexes containing 4,7-phen have been prepared by the use of a robust intermediate in which the diimine ligand is coordinated to the metal centre in a monodentate manner. Although the use of the dinuclear species in the construction of H-bonded supramolecular assemblies is compromised by an unusual redistribution reaction, the isolation of the mononuclear complexes of 4,7-phen allows one to explore the possibility of preparing hybrid species in which the free N-atom undergoes second-sphere H-bonding interactions. We are currently exploring the chemistry of such systems.

4. Experimental

4.1. General

All procedures were performed under an inert atmosphere of high purity N_2 using standard Schlenk techniques. CH_2Cl_2 and diethyl ether were distilled from CaH_2 and sodium, respectively. Toluene was pre-dried over $CaSO_4$, followed by distillation from sodium. All 1-D NMR spectra were recorded by means of a Varian Gemini 2000 NMR spectrometer (^{1}H at 300.10 MHz and ^{31}P at 121.50 MHz). 2-D NMR spectroscopy experiments were performed by means of a Varian Unity INOVA 600 MHz NMR instrument. Chemical shifts are reported in ppm with respect to a TMS reference (^{1}H) or a sealed external standard of 85% H_3PO_4 (^{31}P). Melting points were determined using a Kofler hot-stage apparatus under a Reichert microscope, and are uncorrected. IR spectra were recorded on a Perkin–Elmer FT-IR 1920× spectrophotometer. Elemental analyses were determined by Chemical and Micro Analytical Services Pty. Ltd., Vic. (Australia).

4,7-Phen and AgOTf were obtained commercially (Aldrich). Tetrakis(triphenylphosphine)platinum(0) [30], tetrakis(triethylphosphine)platinum(0) [31], *tert*-butyldiphenylsilyl-3-iodobenzoate (**1**) [23], *tert*-butyldiphenylsilyl-4-iodobenzoate (**2**) [23], *trans*-iodo(*tert*-butyldiphenylsilylbenzoate-C^3)bis(triphenylphosphine) platinum(II) (**5**) [23] and *trans*-iodo(*tert*-butyldiphenylsilylbenzoate-C^4)bis(triphenylphosphine)platinum (II) (**6**) [23] were prepared according to the literature procedures.

4.2. N-methyl-3-iodobenzamide (3)

3-Iodobenzoic acid (5.00 g, 0.02 mol) was added to $SOCl_2$ (25 mL, 0.35 mol) and the mixture was stirred at room temperature for 18 h to afford a clear solution. $SOCl_2$ was removed in vacuo, the residual clear orange oil dried for 30 min, and NH_2Me (40% in H_2O, 5 mL) was added dropwise at 10 °C. The reaction mixture was stirred for 16 h to afford a homogeneous white mixture which was extracted with $CHCl_3$ (2 × 20 mL). The organic extracts were combined, and all volatiles were removed in vacuo to afford **3** as a cream-coloured solid (5.0 g, 96%); m.p. 95–97 °C (lit. 105 °C [32]). ^{1}H NMR ($CDCl_3$): δ 8.23 (s, 1H, H^2), 7.93 (d, 1H, $^3J_{HH}$ = 7.5 Hz, H^6), 7.85 (d, 1H, $^3J_{HH}$ = 7.5 Hz, H^4), 7.23 (t, 1H, $^3J_{HH}$ = 7.9 Hz, H^5), 6.41 (br s, 1H, NH), 3.12 (d, 3H, $^3J_{HH}$ = 4.4 Hz, NMe). Anal. Calc. for C_8H_8INO: C, 36.81; H, 3.09; N, 5.37. Found: C, 36.81; H, 3.10; N, 5.40%.

4.3. N-methyl-4-iodobenzamide (4)

A solution of 4-iodobenzoic acid (1.02 g, 4.12 mmol) in $SOCl_2$ (25 mL, 0.34 mol) was stirred for 30 min at room temperature. CH_2Cl_2 (30 mL) was added to increase solubility of the acid and the mixture was heated to reflux for 1 h until all of the solid had dissolved. CH_2Cl_2 and unreacted $SOCl_2$ were removed by distillation, and the residue was dried in vacuo. The residue was re-dissolved in CH_2Cl_2 (30 mL) and NH_2Me (40% in H_2O, 1 mL) was added. The mixture was stirred at room temperature for 2 h. The solvent was removed in vacuo, and the crude solid was extracted with CH_2Cl_2 (2 × 50 mL). The combined extracts were washed with H_2O (2 × 50 mL), dried over anhydrous $MgSO_4$, and reduced in vacuo to afford **4** (0.99 g, 92%); m.p. 161–162 °C (lit. 165 °C [32]). ^{1}H NMR ($CDCl_3$): δ 7.77 (d, 2H, $^3J_{HH}$ = 8.1 Hz, $H^{2,6}$), 7.48 (d, 2H, $^3J_{HH}$ = 8.7 Hz, $H^{3,5}$), 6.30 (s, 1H, NH), 2.99 (d, 3H, $^3J_{HH}$ = 4.8 Hz, NMe). Anal. Calc. for C_8H_8INO: C, 36.81; H, 3.09; N, 5.37. Found: C, 36.78; H, 2.98; N, 5.33%.

4.4. trans-Iodo(N-methylbenzamide-C^3)bis(triphenylphosphine)platinum(II) (7)

A solution of **3** (186 mg, 0.71 mmol) in toluene (50 mL) was added to $Pt(PPh_3)_4$ (743 mg, 0.60 mmol). The mixture was stirred at 75 °C for 17 h to afford a white

precipitate that was collected by filtration, washed with *n*-hexane, and air dried (455 mg, 77%). IR (nujol): 1632 cm^{-1} ν(C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.51–7.57 (m, 12H, PPh_3), 7.23–7.35 (m, 18H, PPh_3), 6.97 (d, 1H, $^3J_{HH} = 7.5$, $^3J_{PtH} = 56.4$ Hz, H^6), 6.72 (d, 1H, $^3J_{HH} = 7.5$ Hz, H^4), 6.67 (s, 1H, $^3J_{PtH} = 57$ Hz, H^2), 6.24 (t, 1H, $^3J_{HH} = 7.5$ Hz, H^5), 4.97 (d, 1H. $^3J_{HH} = 4.5$ Hz, NH), 2.76 (d, 3H, $^3J_{HH} = 4.5$ Hz, NMe). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 22.0 (s, $^1J_{PtP} = 3026$ Hz). Anal. Calc. for $C_{44}H_{38}INOP_2Pt$: C, 53.89; H, 3.91; N, 1.43. Found: C, 53.57; H, 3.85; N, 1.45%.

4.5. *trans*-Iodo(*N*-methylbenzamide-C^4)bis(triphenylphosphine)platinum(II) (**8**)

Following a similar procedure to that described in Section 4.4, a suspension of **4** (0.50 g, 1.92 mmol) in toluene (50 mL) was added to $Pt(PPh_3)_4$ (1.98 g, 1.59 mmol) to afford a white microcrystalline solid (1.06 g, 68%). IR (nujol): 1640 cm^{-1} ν(C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.51–7.57 (m, 12H, PPh_3), 7.22–7.35 (m, 18H, PPh_3), 6.73 (d, 2H, $^3J_{HH} = 8.1$, $^3J_{PtH} = 56.4$ Hz, $H^{2,6}$), 6.50 (d, 2H, $^3J_{HH} = 8.1$ Hz, $H^{3,5}$); 5.62 (d, 1H, $^3J_{HH} = 4.5$ Hz, NH), 2.89 (d, 3H, $^3J_{HH} = 4.5$ Hz, NMe). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 21.2 (s, $^1J_{PtP} = 3025$ Hz). Anal. Calc. for $C_{44}H_{38}INOP_2Pt$: C, 53.89; H, 3.91; N, 1.43. Found: C, 53.90; H, 3.91; N, 1.38%.

4.6. *trans*-4,7-Phenanthroline(*tert*-butyldiphenylsilylbenzoate-C^3)bis(triphenylphosphine)platinum(II) triflate (**9**)

To a stirred solution of **5** (360 mg, 0.298 mmol) in CH_2Cl_2 (40 mL) was added a solution of AgOTf (73 mg, 0.284 mmol) in distilled acetone (2 mL). The mixture was stirred for 16 h in the absence of light at room temperature. AgI was removed by filtration through a pad of Celite filter aid, and the filtrate was reduced in vacuo to yield the corresponding triflato complex as a white solid (348 mg). A solution of the triflato complex (61 mg, 4.97×10^{-5} mol) and 4,7-phen (10.4 mg, 5.77×10^{-5} mol) in CH_2Cl_2 (30 mL) was stirred for 48 h. The solvent was removed in vacuo and the residue was recrystallised twice from CH_2Cl_2/*n*-hexane to afford **9** as a white solid (53 mg, 75%); m.p. >250 °C (dec.). IR (nujol): 1701 ν(C=O), 1277, 1263, 1225, 1179, 1152, 1031 (OTf) cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.37 (d, 1H, $^3J_{HH} = 9.3$ Hz, H^5), 9.08 (dd, 1H, $^3J_{HH} = 1.5$ Hz, $^3J_{HH} = 4.5$ Hz, H^3), 9.07 (br s, 1H, H^8), 8.90 (t, 2H, $^3J_{HH} = 8.4$ Hz, $H^{1,10}$), 8.30 (d, 1H, $^3J_{HH} = 9.3$ Hz, H^6), 7.70–7.80 (m, 6H, $H^{2,9}$, SiPh), 7.00–7.60 (m, 38H, SiPh, PPh_3, $H^{4',2',6'}$), 6.41 (t, 1H, $^3J_{HH} = 7.5$ Hz, $H^{5'}$), 1.20 (s, 9H, ^{t}Bu). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 19.1 (s, $^1J_{PtP} = 2962$ Hz). Anal. Calc. for $C_{72}H_{61}F_3N_2O_5P_2PtSSi$: C, 61.40; H, 4.37; N, 1.99. Found: C, 61.34; H, 4.36; N, 1.83%.

4.7. *trans*-4,7-Phenanthroline(*tert*-butyldiphenylsilylbenzoateC^4)bis(triphenylphosphine)platinum(II) triflate (**10**)

Following a similar procedure to that described in Section 4.6, **6** (360 mg, 0.298 mmol) was treated with AgOTf (73 mg, 0.284 mmol) to afford the corresponding triflato complex as a white solid (348 mg). The triflato complex (100 mg, 8.14×10^{-5} mol) was then treated with 4,7-phen (15.1 mg, 8.38×10^{-5} mmol) to afford **10** as a white solid (79 mg, 69%); m.p. >250 °C (dec.). IR (nujol): 1696 ν(C=O), 1279, 1224, 1180, 1154, 1031 (OTf) cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.35 (d, 1H, $^3J_{HH} = 9.6$ Hz, H^5), 9.12 (d, 1H, $^3J_{HH} = 5.1$ Hz, H^3), 9.08 (d, 1H, $^3J_{HH} = 4.2$ Hz, H^8), 8.91 (d, 1H, $^3J_{HH} = 8.4$ Hz, H^{10}), 8.83 (d, 1H, $^3J_{HH} = 8.4$ Hz, H^1), 8.29 (d, 1H, $^3J_{HH} = 9.3$ Hz, H^6), 7.77 (dd, 1H, $^3J_{HH} = 4.2$, $^3J_{HH} = 8.4$ Hz, H^9), 7.71 (dd, 4H, $^3J_{HH} = 1.5$ Hz, $^3J_{HH} = 7.8$ Hz, SiPh), 7.59 (dd, 1H, $^3J_{HH} = 5.4$ Hz, $^3J_{HH} = 8.4$ Hz, H^2), 7.00–7.50 (m, 40H, PPh_3, SiPh, $H^{2',3',5',6'}$), 1.13 (s, 9H, ^{t}Bu). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 19.1 (s, $^1J_{PtP} = 2961$ Hz). Anal. Calc. for $C_{72}H_{61}F_3N_2O_5P_2PtSSi$: C, 61.40; H, 4.37; N, 1.99. Found: C, 61.45; H, 4.24; N, 2.00%.

4.8. *trans*-4,7-Phenanthroline(*N*-methylbenzamide-C^3)bis(triphenylphosphine)platinum(II) triflate (**11**)

Following a similar procedure to that described in Section 4.6, **7** (229 mg, 0.233 mmol) was treated with AgOTf (58.6 mg, 0.228 mmol) to afford the corresponding triflato complex as a pale-yellow solid (228 mg). The triflato complex (148 mg, 1.47×10^{-4} mol) was then treated with 4,7-phen (27 mg, 1.50×10^{-4} mol) to afford **11** as a white solid (133 mg, 76%); m.p. >250 °C (dec.). IR (nujol): 1655 ν(C=O), 1277, 1262, 1225, 1178, 1150, 1030 (OTf) cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.34 (br s, 1H, H^5), 9.33 (br d, 1H, $^3J_{HH} = 7.5$ Hz, $H^{3\text{ or }8}$), 9.07 (d, 1H, $^3J_{HH} = 3.6$ Hz, $H^{1\text{ or }10}$), 8.77 (d, 1H, $^3J_{HH} = 8.7$ Hz, $H^{1\text{ or }10}$), 8.61 (br d, 1H, $^3J_{HH} = 7.5$ Hz, $H^{3\text{ or }8}$), 8.31 (br s, 1H, H^6), 7.70 (dd, 1H, $^3J_{HH} = 4.5$ Hz, $^3J_{HH} = 8.7$ Hz, $H^{2\text{ or }9}$), 7.10–7.50 (m, 33H, PPh_3, $H^{4',6',2\text{ or }9}$), 7.01 (d, 1H, $^3J_{HH} = 7.2$ Hz, $H^{2'}$), 6.42 (t, 1H, $^3J_{HH} = 7.5$ Hz, $H^{5'}$), 6.11 (d, 1H, $^3J_{HH} = 4.8$ Hz, NH), 2.90 (d, 3H, $^3J_{HH} = 4.8$ Hz, NMe). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 19.5 (s, $^1J_{PtP} = 3000$ Hz). Anal. Calc. for $C_{57}H_{46}F_3N_2O_4P_2PtS$: C, 57.87; H, 3.92; N, 3.55. Found: C, 57.74; H, 4.01; N, 3.61%.bb

4.9. *trans*-4,7-Phenanthroline(*N*-methylbenzamide-C^4)bis(triphenylphosphine)platinum(II) triflate (**12**)

Following a similar procedure to that described in Section 4.6, **8** (301 mg, 0.307 mmol) was treated with AgOTf (75 mg, 0.292 mmol) to afford the corresponding triflato complex as a pale-yellow solid (293 mg). The triflato complex (92 mg, 9.17×10^{-5} mol) was then treated with 4,7-phen (18 mg, 10.15×10^{-5} mol) to

afford **12** as a white solid (90 mg, 83%); m.p. >250 °C (dec.). IR (nujol): 1660 *ν*(C=O), 1276, 1260, 1228, 1176, 1150, 1030 (OTf) cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.38 (d, 1H, $^3J_{HH} = 9.3$ Hz, H^5), 9.15 (d, 1H, $^3J_{HH} = 4.5$ Hz, $H^{3\text{ or }8}$) 9.08 (d, 1H, $^3J_{HH} = 4.5$ Hz, $H^{3\text{ or }8}$), 8.87 (d, 1H, $^3J_{HH} = 8.4$ Hz, $H^{1\text{ or }10}$), 8.76 (d, 1H, $^3J_{HH} = 8.4$ Hz, $H^{1\text{ or }10}$), 8.33 (d, 1H, $^3J_{HH} = 9.3$ Hz, H^6), 7.74 (dd, 1H, $^3J_{HH} = 4.5$ Hz, $^3J_{HH} = 8.4$ Hz, H^9), 7.50 (dd, 1H, $^3J_{HH} = 4.5$ Hz, $^3J_{HH} = 8.4$ Hz, H^2), 7.10–7.40 (m, 30H, PPh_3), 6.86 (br s, 2H, $H^{2',6'}$), 6.71 (br d, 2H, $^3J_{HH} = 8.1$ Hz, $H^{3',5'}$), 5.87 (d, 1H, $^3J_{HH} = 4.5$ Hz, NH), 2.88 (d, 3H, $^3J_{HH} = 4.5$ Hz, NMe). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 19.1 (s, $^1J_{PtP} = 2962$ Hz). Anal. Calc. for $C_{57}H_{46}F_3N_2O_4P_2PtS$: C, 57.87; H, 3.92; N, 3.55. Found: C, 57.72; H, 3.93; N, 3.50%.

4.10. *trans-(tert-Butyldiphenylsilylbenzoate-C⁴)bis(triphenylphosphine)platinum(II)-μ-4,7-phenanthroline(σ-phenyl)bis(triethylphosphine)platinum(II) bis(triflate) (**13**)*

trans-[PtI(σ-C_6H_5)(PEt_3)$_2$] (0.075 g, 0.12 mmol) in CH_2Cl_2 (20 mL) was treated with AgOTf (0.030 g, 0.12 mmol) and the mixture was stirred for 16 h in the absence of light at room temperature. AgI was removed by filtration through a pad of Celite filter aid, and the filtrate was concentrated in vacuo (ca. 5 mL). **10** (0.134 g, 0.11 mmol) was added and the solution was stirred for 1 h at room temperature. The solvent was removed in vacuo to give **13** as a white solid (0.201 g, 82%); m.p. >250 °C (dec.). IR (nujol) 1695 *ν*(C=O), 1654, 1637, 1581 (C=C, C=N), 1277, 1263, 1225, 1179, 1152, 1031 (OTf) cm^{-1}; ^1H NMR (CD_2Cl_2): δ 9.77 (d, 1H, $^3J_{HH} = 9.6$ Hz, H^5), 9.53 (d, 1H, $^3J_{HH} = 8.4$ Hz, H^{10}), 9.51 (d, 1H, $^3J_{HH} = 9.6$ Hz, H^6), 9.29 (d, 1H, $^3J_{HH} = 5.4$ Hz, H^8), 9.22 (d, 1H, $^3J_{HH} = 5.4$ Hz, H^3), 9.17 (d, 1H, $^3J_{HH} = 8.4$ Hz, H^1), 8.19 (dd, 1H, $^3J_{HH} = 5.4$ Hz, $^3J_{HH} = 8.4$ Hz, H^9), 7.87 (m, 1H, PtPh), 7.66–7.64 (m, 4H, SiPh), 7.56 (dd, 1H, $^3J_{HH} = 5.4$ Hz, $^3J_{HH} = 8.4$ Hz, H^2), 7.47–6.99 (m, 44H, PPh_3, SiPh, PtPh, $H^{12,16}$, $H^{13,15}$), 1.28–1.02 (m, 30H, PCH_2CH_3), 1.11 (s, 9H, ^{t}Bu); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 19.4 (s, $^1J_{PPt} = 2996$ Hz, PPh_3), 11.5 (s,$^1J_{PPt} = 2733$ Hz, PEt_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 21.1 (s, $^1J_{PPt} = 2969$ Hz, PPh_3), 14.7 (s,$^1J_{PPt} = 2698$ Hz, PEt_3). Anal. Calc. for $C_{90}H_{96}F_6N_2O_8P_4Pt_2S_2Si$: C, 52.63; H, 4.71; N, 1.36. Found: C, 52.55; H, 4.42; N, 1.52%.

4.11. *trans-μ-4,7-Phenanthroline(tert-butyldiphenylsilylbenzoateC⁴)(N-methylbenzamide-C⁴)bis[bis(triphenylphosphine)platinum(II)] bis(triflate) (**14**)*

The triflato derivative of **6** was prepared as described in Section 4.7. To a solution of **12** (21.5 mg, 1.82×10^{-5} mol) in CH_2Cl_2 (25 mL) was added the triflato complex (22.3 mg, 1.82×10^{-5} mol). The mixture was stirred for 1 h at room temperature. The solvent was removed in vacuo and the residue was recrystallised from CH_2Cl_2/diethyl ether to give **14** as a white solid (36 mg, 82%); m.p. >250 °C (dec.). IR (nujol): 1698, 1620 *ν*(C=O), 1275, 1262, 1228, 1178, 1151, 1033 (OTf) cm^{-1}. ^1H NMR ($CDCl_3$): δ 10.00 (s, 2H, $H^{5,6}$), 9.18 (d, 1H, $^3J_{HH} = 8.7$ Hz, $H^{1\text{ or }10}$), 9.13 (d, 1H, $^3J_{HH} = 8.4$ Hz, $H^{1\text{ or }10}$), 8.62 (t, 2H, $^3J_{HH} = 6$ Hz, $H^{3,8}$), 7.71 (d, 4H, $^3J_{HH} = 6.9$ Hz, SiPh), 7.10–7.50 (m, 74H, SiPh, PPh_3,$H^{2,9}$, *p*-ester $H^{2',3',5',6'}$), 6.73 (br m, 2H, *p*-amide $H^{3',5'}$), 5.98 (d, 1H, $^3J_{HH} = 4.5$ Hz, NH), 2.88 (d, 3H, $^3J_{HH} = 4.2$ Hz, NMe), 1.17 (s, 9H, ^{t}Bu). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 19.9 (s, $^1J_{PtP} = 3029$ Hz), 19.7 (s, $^1J_{PtP} = 3029$ Hz). Anal. Calc. for $C_{117}H_{99}F_6N_3O_9P_4Pt_2S_2Si$: C, 58.28; H, 4.14; N, 1.74. Found: C, 58.15; H, 4.08; N, 1.82%.

4.12. *trans-μ-4,7-Phenanthroline(tert-butyldiphenylsilylbenzoateC⁴)(N-methylbenzamide-C³)bis[bis(triphenylphosphine)platinum(II)] bis(triflate) (**15**)*

Following a similar procedure to that described in Section 4.11, **10** (44 mg, 3.124×10^{-5} mol) was treated with the triflato derivative of **7** prepared in Section 4.8 (31 mg, 3.121×10^{-5} mol) to afford **15** as a white solid (45 mg, 60%); m.p. >250 °C (dec.). IR (nujol): 1696, 1632 *ν*(C=O), 1278, 1260, 1228, 1175, 1149, 1030 (OTf) cm^{-1}. ^1H NMR ($CDCl_3$): δ 10.20 (d, 1H, $^3J_{HH} = 9.3$ Hz, $H^{5\text{ or }6}$), 9.77 (d, 1H, $^3J_{HH} = 9.3$ Hz, $H^{5\text{ or }6}$), 9.22 (d, 1H, $^3J_{HH} = 8.1$ Hz, $H^{1\text{ or }10}$), 9.196 (d, 1H, $^3J_{HH} = 8.1$ Hz, $H^{1\text{ or }10}$), 8.71 (d, 1H, $^3J_{HH} = 5.1$ Hz, $H^{3\text{ or }8}$), 8.43 (d, 1H, $^3J_{HH} = 5.1$ Hz, $H^{3\text{ or }8}$), 8.36 (s, 1H, $H^{2\text{ or }9}$), 8.04 (s, 1H, $H^{2\text{ or }9}$), 7.71 (d, 4H, $^3J_{HH} = 7.5$ Hz, SiPh). 7.10–7.40 (m, 72H, SiPh, PPh_3, *p*-ester $H^{2',3',5',6'}$, *m*-amide $H^{2',4',6'}$), 6.67 (s, 1H, *m*-amide $H^{5'}$), 6.01 (m, 1H, NH), 3.18 (d, 3H, $^3J_{HH} = 3.6$ Hz, NMe), 1.19 (s, 9H, ^{t}Bu). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 20.4 (s, $^1J_{PtP} = 3005$ Hz) 19.9 (s, $^1J_{PtP} = 3026$ Hz). Anal. Calc. for $C_{117}H_{99}F_6N_3O_9P_4Pt_2S_2Si$: C, 58.28; H, 4.14; N, 1.74. Found: C, 58.14; H, 4.08; N, 1.91%.

4.13. *trans-μ-4,7-Phenanthroline(tert-butyldiphenylsilylbenzoate-C³)(N-methylbenzamide-C³)bis[bis(triphenylphosphine)platinum(II)] bis(triflate) (**16**)*

Following a similar procedure to that described in Section 4.11, **11** (60 mg, 5.06×10^{-5} mol) was treated with the triflato derivative of **5** prepared in Section 4.6 (62 mg, 5.05×10^{-5} mol) to afford **16** as a white solid (50 mg, 41%); m.p. >250 °C (dec.). IR (nujol): 1700, 1656 *ν*(C=O), 1275, 1227, 1174, 1150, 1031 (OTf) cm^{-1}. ^1H NMR ($CDCl_3$): δ 10.21 (d, 1H, $^3J_{HH} = 9.6$ Hz, $H^{5\text{ or }6}$), 9.72 (d, 1H, $^3J_{HH} = 9.6$ Hz, $H^{5\text{ or }6}$), 9.25 (d, 2H, $^3J_{HH} = 8.4$ Hz, $H^{1,10}$), 8.74 (br d, 1H, $^3J_{HH} = 5.4$ Hz, $H^{3\text{ or }8}$), 8.57 (br d, $^3J_{HH} = 5.4$ Hz, $H^{3\text{ or }8}$), 8.30 (br s, 1H, $H^{2\text{ or }9}$), 8.11 (br d, 1H, $^3J_{HH} = 5.4$ Hz, $H^{2\text{ or }9}$), 8.02 (br s, 1H, ArH), 7.64 (d, 4H, $^3J_{HH} = 6.3$ Hz, SiPh), 6.99–7.50

(m, 71H, PPh_3, SiPh, 5ArH), 6.87 (br s, 1H, *m*- amide $H^{5'}$), 6.77 (t, 1H, $^3J_{HH} = 7.2$ Hz, *m*-ester $H^{5'}$), 6.02 (t, 1H, $^3J_{HH} = 6.6$ Hz, NH), 3.19 (d, 3H, $^3J_{HH} = 3.6$ Hz, NMe), 1.09 (s, 9H, ^{t}Bu). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 20.3 (s, $^1J_{PtP} = 3033$ Hz), 20.2 (s, $^1J_{PtP} = 3033$ Hz). Anal. Calc. for $C_{117}H_{99}F_6N_3O_9P_4Pt_2S_2Si$: C, 58.28; H, 4.14; N, 1.74. Found: C, 58.22; H, 4.07; N, 1.68%.

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