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Platinum(II) Alkynyl Complexes Containing *N*- and *S*-Propargylated Ligands: Synthesis, Structures and Formation of Pt^{II}/Ag^{I} Coordination Compounds

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Alkylation of 2-hydroxypyridine, 2-pyridinethiol, 2-hydroxy-4-methylquinoline, phthalimide and pyrazole with propargyl bromide gave a series of alkynes in high yield. These alkynes were reacted with the chloroplatinum(II) compounds *trans*-$[PtCl_2(PPh_3)_2]$ and *cis*-$[PtCl_2(dppe)]$ to afford the respective *trans*- and *cis*-bis(alkynyl)platinum(II) complexes, which were characterised by spectroscopic analysis and by X-ray diffraction. The platinum(II) complexes containing the thiopyridyl- and pyrazolyl-substituted alkynes react with 1 or 2 equiv. of $[Ag(NO_3)(PPh_3)]$ to give dimetallic Pt^{II}/Ag^{I} complexes.

Introduction

Platinum(II) alkynyl complexes have been known for many years, but since the discovery of their luminescence and nonlinear optical (NLO) properties the field has experienced rapid growth.[1–5] Numerous platinum(II) alkynyl complexes have been synthesised by a variety of different routes and some complexes have been structurally characterised.[6,7] O-Propargylated compounds, in particular those derived from bisphenols, have been extensively used as C-donor ligands in the supramolecular assembly of gold(I) polymers, macrocycles and catenanes;[8–13] however, no examples of their use as ligands in other transition-metal complexes have been reported. Whereas the preparation, some organic transformations and applications of selected *N*-propargylated compounds have been published,[14–17] the organometallic chemistry of these species acting as C-donor ligands is a relatively unexplored field. Silver alkynyl complexes of various propargylamines have been used as alkyne transfer reagents in the synthesis of analogues of the opium derivative cotarnine.[18] Similarly, gold(I) phosphane complexes containing *N*-propargylphthalimide have been used to transfer the Au-phosphane moiety to tetra- and penta-iron clusters.[19] A series of alkynyl tin and silicon complexes containing C-coordinated *N*-propargylpyrazole have been prepared from the lithium salt.[20] Alkynyl complexes of mercury containing *N*-propargylated acridone are strongly fluorescent and have been used as sensitive sensors for the detection of organomercury compounds in water or biological systems.[21,22] *S*-Propargylated compounds are even less well-studied; their preparation and some organic chemistry of only a small number of compounds has been reported.[23,24] The only known example of a metal-containing derivative of an *S*-propargylated compound is the tin complex of propargylthiotriazole, which was patented as a fungicide.[25] In light of this lack of organometallic chemistry of *N*- and *S*-propargylated compounds, we wished to pursue our interest in metal alkynyl complexes[26–28] and the chemistry of platinum complexes with N,S-donor ligands[29] by preparing and structurally characterising some platinum(II) alkynyl complexes of various *N*- and *S*-propargylated compounds.

Results and Discussion

The tautomerism of 2-hydroxypyridine has been studied both experimentally and computationally in great detail by various groups. Spectroscopic data indicates that the hydroxy form is the major tautomer in the gas phase.[30–32] In the solid state, however, the formation of hydrogen bonded dimers seems to favour the 2-pyridone tautomers.[33] Similarly, we found, by ^1H and ^{13}C NMR spectroscopy in acetone, that 2-hydroxypyridine and 2-pyridinethiol exist exclusively as the 2-pyridone and 2-pyridinethione tautomers, respectively. Upon reaction of these compounds with propargyl bromide in the presence of base in acetone, these two starting materials gave two different propargylated products. In the case of 2-hydroxypyridine, the *N*-propargylated product ($R^1CH_2C{\equiv}CH$) was obtained, whereas from 2-pyridinethiol the *S*-propargylated compound ($R^2CH_2C{\equiv}CH$)

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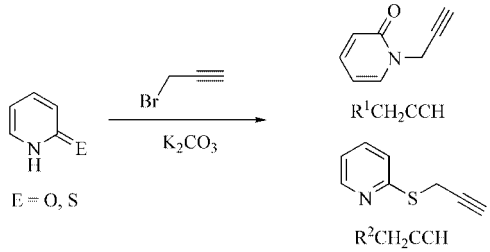
was isolated (Scheme 1). We calculated the relative energies of each of the four possible propargylated isomers using density functional theory (DFT) methods. In the case of 2-hydroxypyridine, the *N*-propargylated compound is 8.8 kcal/mol more stable than the O-propargylated tautomer. In contrast, for 2-pyridinethione the *S*-propargylated species is 2.5 kcal/mol more stable than the *N*-propargylated tautomer (Figure 1). These computational results are in agreement with our, and previously reported, experimental observations.[16,23] In addition to the two alkynes discussed above, the previously reported *N*-propargylated compounds derived from 2-hydroxy-4-methylquinoline,[14] phthalimide[17] and pyrazole[15] (designated as $R^nCH_2C{\equiv}CH$; n = 3–5) were prepared similarly (Scheme 2). In our hands, the procedure using K_2CO_3 in acetone was much simpler in terms of work up (filtration and evaporation of acetone) than the previously described methods. *N*-Alkylation in R^1CH_2CCH and R^3CH_2CCH is evident from their NMR- (particularly ^{13}C) and IR spectra. The methylene carbon signal in the ^{13}C NMR spectra of these two compounds is shifted by ca. 17 ppm downfield relative to that of the *S*-propargyl derivative R^2CH_2CCH. Similarly, although less pronounced, the NCH_2 proton signals of R^1CH_2CCH and R^3CH_2CCH are shifted ca. 2 ppm downfield relative to the SCH_2 resonance of R^2CH_2CCH, which is consistent with the difference in electronegativity of sulfur and nitrogen. Further evidence for *N*-propargylation is seen in the IR spectra of R^1CH_2CCH and R^3CH_2CCH, which show strong C=O absorption bands.



Scheme 1.

These alkynes react with the dichloroplatinum(II) complexes *trans*-$[PtCl_2(PPh_3)_2]$ and *cis*-$[PtCl_2(dppe)]$ [dppe = $Ph_2P(CH_2)_2PPh_2$] in the presence of Et_2NH and a catalytic amount of [CuI][34–36] to afford the air- and water-stable alkynyl platinum(II) complexes *trans*-$[Pt(C{\equiv}CCH_2R)_2(PPh_3)_2]$ (R^1 = **1**, R^2 = **3**, R^3 = **5**, R^4 = **7**, R^5 = **9**) and *cis*-$[Pt(C{\equiv}CCH_2R)_2(dppe)]$ (R^1 = **2**, R^2 = **4**, R^3 = **6**, R^4 = **8**, R^5 = **10**), respectively, in high yields (Scheme 3). Complexes **1**–**10** were characterised spectroscopically including ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, mass spectrometry, IR spectroscopy and elemental analysis. The $^{31}P\{^1H\}$ NMR spectra of complexes **1**–**10** show sharp singlet resonances with Pt satellites having J_{Pt-P} values of ca. 2600 and 2300 Hz for the *trans* and *cis* isomers, respectively, which indicates the presence of a single species in solution. In principle, there are two possible configurations of the R groups for all but complexes **7** and **8**, namely the *exo–exo* and *endo–exo* configurations as illustrated for complex **2** in Figure 2. The ^1H

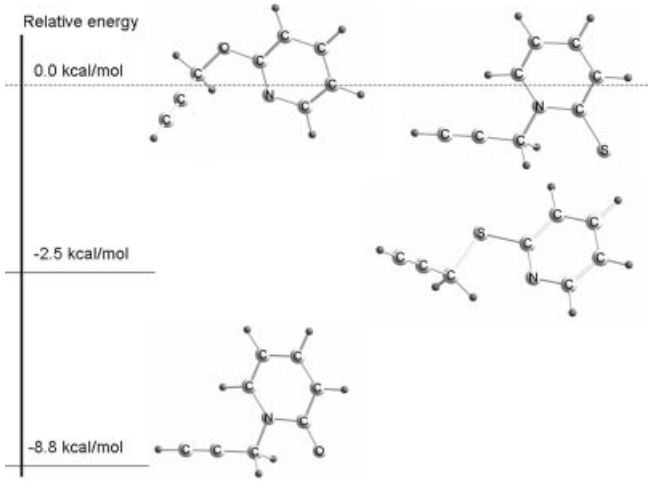
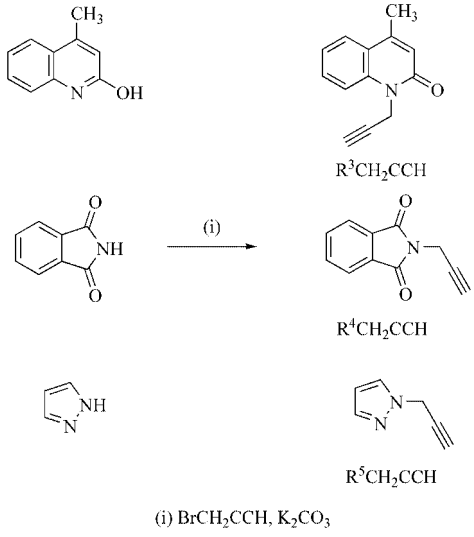


Figure 1. DFT optimised structures of the propargylated tautomers of 2-propargyloxypyridine and 2-propargylthiopyridine showing the energy differences between the two forms.



Scheme 2.

NMR spectrum of complex **2** in $CDCl_3$ at room temperature shows only one set of signals (doublets and triplets) for the R substituents, which indicates that rotation about the C–N bond is rapid in solution on the NMR timescale. Lowering the temperature to –80 °C has no effect on the appearance of the ^1H NMR spectrum, which suggests that any of the possible conformations rapidly interconvert in solution. In the solid-state structures, however, the *endo–exo* configuration is found. It is worth mentioning here that some of

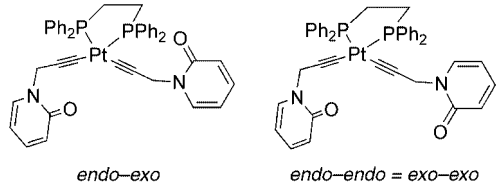
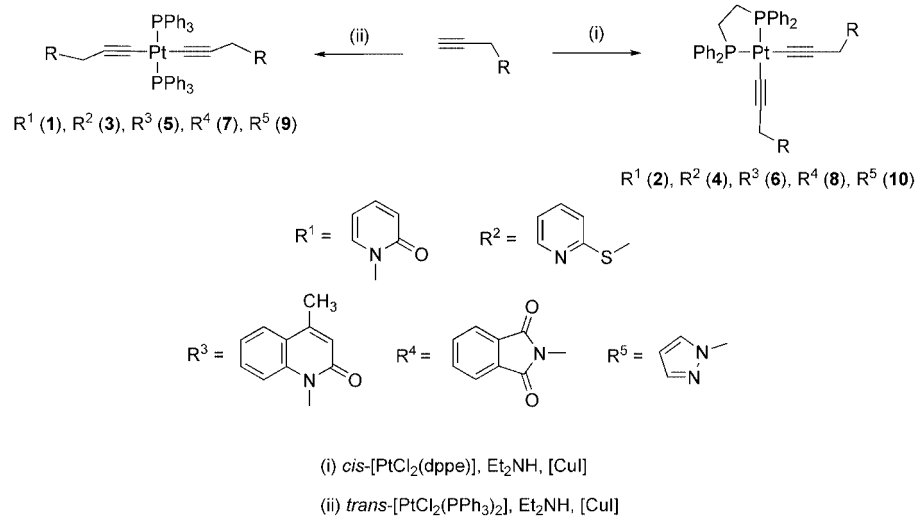


Figure 2. Illustration of the isomeric configurations of the pyridone substituents in complex **2**.



Scheme 3.

these complexes hold water tenaciously, as is evident from H_2O signals in the ^1H NMR spectra and confirmed by elemental analysis. Even prolonged drying under high vacuum does not seem to remove this solvated water. The LSIMS mass spectra of all ten complexes show molecular ion peaks whose isotopic distributions match the expected patterns. The solid-state structures of the complexes *trans*-[Pt(C≡CCH_2R^1)$_2$(PPh_3)$_2$] (**1**), *cis*-[Pt(C≡CCH_2R^1)$_2$(dppe)] (**2**), *trans*-[Pt(C≡CCH_2R^3)$_2$(PPh_3)$_2$] (**5**), *trans*-[Pt(C≡CCH_2R^5)$_2$(PPh_3)$_2$] (**9**) and *cis*-[Pt(C≡CCH_2R^5)$_2$(dppe)] (**10**) were determined by single-crystal X-ray diffraction. The molecular structure of **1** (Figure 3) consists of a platinum atom coordinated by two triphenylphosphane ligands and two acetylide molecules in a *trans* geometry. The coordination about the platinum atom is square planar, and the angle subtended at the Pt centre is 92.90(14)°. The Pt–C, Pt–P and C≡C bond lengths [1.998(5), 2.3163(12) and 1.201(7) Å, respectively] are very similar to those observed in other *trans*-bis(triphenylphosphane)platinum(II) acetylide complexes such as *trans*-[Pt(C≡CC_6H_4-4-NH_2)$_2$(PPh_3)$_2$] [Pt–P = 2.310(1), Pt–C = 2.005(4) and C≡C = 1.206(6) Å][37] or *trans*-[Pt{C≡CC_6H_4-4-SC(O)Me}$_2$(PPh_3)$_2$] [Pt–P = 2.3177(15), Pt–C = 2.027(6) and C≡C = 1.179(9) Å].[38] A unique feature of the solid-state structure of complex **1** is the presence of a hydrogen-bonding interaction between the alkyne ligand carbonyl group oxygen atom and a *meta* hydrogen of one of the Ph_3P phenyl rings with a H···O=C distance of ca. 2.7 Å, a distance typically found in weak hydrogen-bonding interactions.[39] The molecular structure of *cis* complexes **2** (Figure 4) and **10** (Figure 5) consist of a distorted [P–Pt–C angle ca. 173°] square planar platinum centre to which one dppe unit and two C-bonded alkyne molecules are coordinated in a mutually *cis* arrangement. The Pt–C and Pt–P bond lengths (see Table 1) are similar to those of the *trans* derivative (see above) and also similar to other *cis* platinum alkynyl complexes including *cis*-[Pt(C≡CH)$_2$(dppe)] [Pt–C = 2.025(5), Pt–P = 2.2851(12) and C≡C = 1.164(8) Å][40] and *cis*-[Pt(C≡CC≡CH)$_2$(dppe)] [Pt–C = 2.20(1), Pt–P = 2.269(3) and C≡C = 1.218(6) Å].[41]

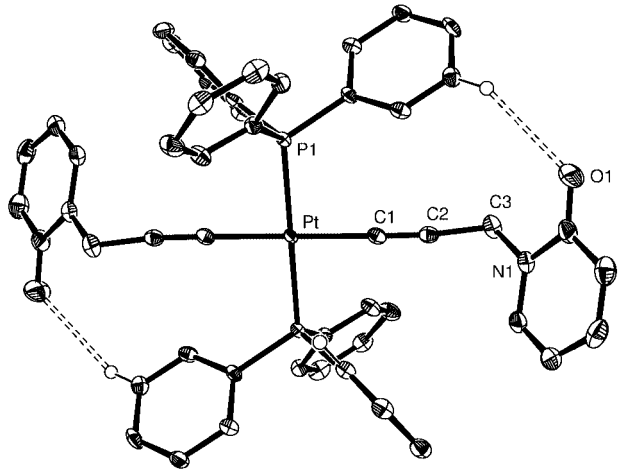


Figure 3. Molecular structure of *trans*-[Pt(C≡CCH_2R^1)$_2$(PPh_3)$_2$] (**1**). Thermal ellipsoids show 50% probability levels. Hydrogen atoms (except those involved in H-bonding interactions) omitted for clarity.

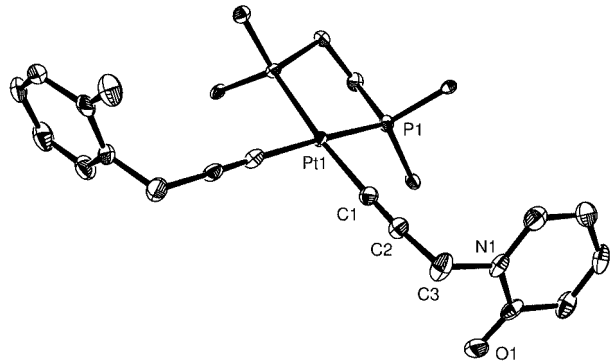


Figure 4. Molecular structure of *cis*-[Pt(C≡CCH_2R^1)$_2$(dppe)] (**2**). Thermal ellipsoids show 50% probability levels. Hydrogen atoms have been omitted for clarity and only the *ipso* carbon atoms of the phenyl groups are shown.

Table 1. Selected structural parameters for complexes **1**, **2**, **5**, **9** and **10**.

	1	**2**	**5**	**9**	**10**
P–Pt–C angle [°]	92.90(14)	173.96(14)	88.39(12)	93.12(17)	173.64(18), 174.7(2)
Pt–C [Å]	1.998(5)	2.018(5)	2.013(4)	2.006(6)	2.046(8), 2.060(7)
Pt–P [Å]	2.3163(14)	2.2823(13)	2.2872(13)	2.2896(15)	2.2802(18), 2.2807(17)
C≡C [Å]	1.201(7)	1.168(7)	1.190(6)	1.191(9)	1.135(10), 1.114(9)

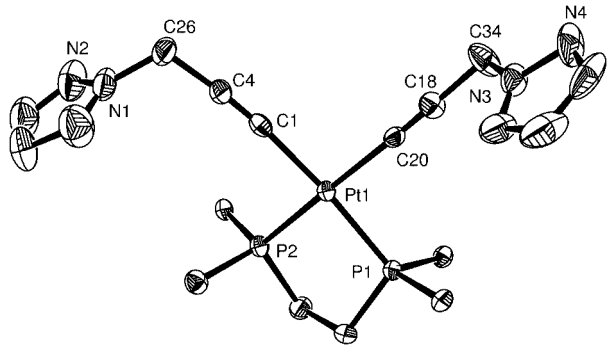


Figure 5. Molecular structure of *cis*-[Pt(C≡CCH$_2$R^5)$_2$(dppe)] (**10**). Thermal ellipsoids show 50% probability levels. Hydrogen atoms have been omitted for clarity and only the *ipso* carbon atoms of the phenyl groups are shown.

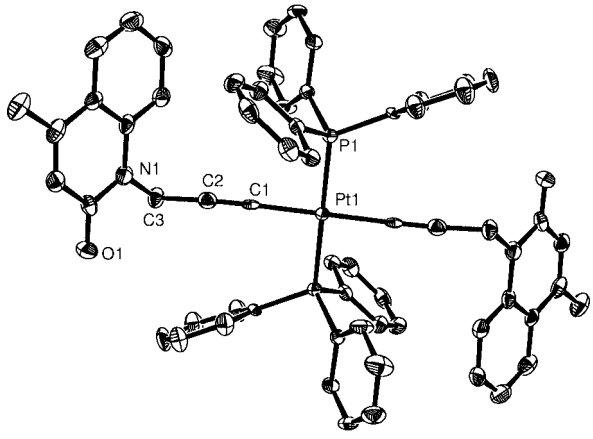


Figure 6. Molecular structure of *trans*-[Pt(C≡CCH$_2$R^3)$_2$(PPh$_3$)$_2$] (**5**). Thermal ellipsoids show 50% probability levels. Hydrogen atoms have been omitted for clarity.

As a consequence of the *trans* effect, the C≡C bond lengths in *cis* complexes **2** [1.1687(7) Å] and **10** [1.135(10) and 1.114(9) Å] are slightly shorter than those of the *trans* complexes. The other two *trans* complexes **5** (Figure 6) and **9** (Figure 7) are structurally very similar to complex **1**, although with slightly longer Pt–P distances. For comparison, important structural data for the *trans* and *cis* complexes is summarised in Table 1.

The platinum(II) complexes containing the alkynes R^{2}CH$_2$C≡CH and R^{5}CH$_2$C≡CH (**3**, **4**, **9** and **10**) possess an uncoordinated nitrogen atom which could allow theses compounds to act as organometallic ligands to give heterodimetallic species upon coordination to other metals. Indeed, *trans* complexes **3** and **9** react with 2 equiv. of [Ag-

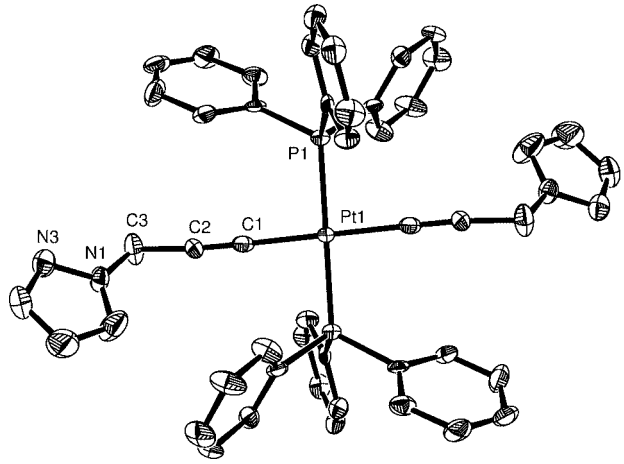
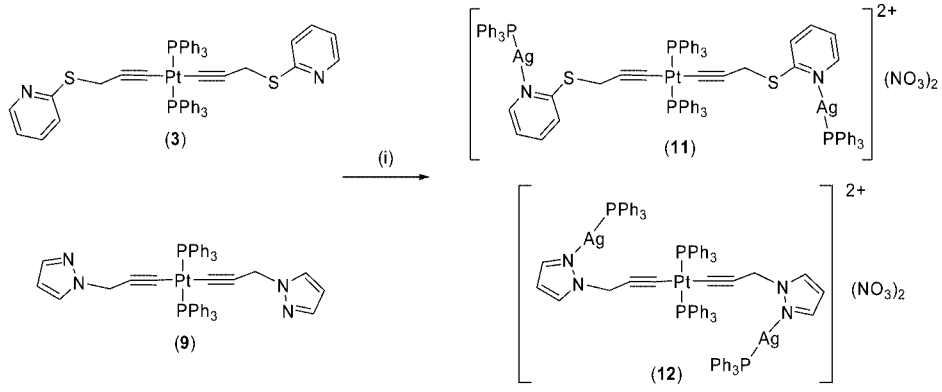
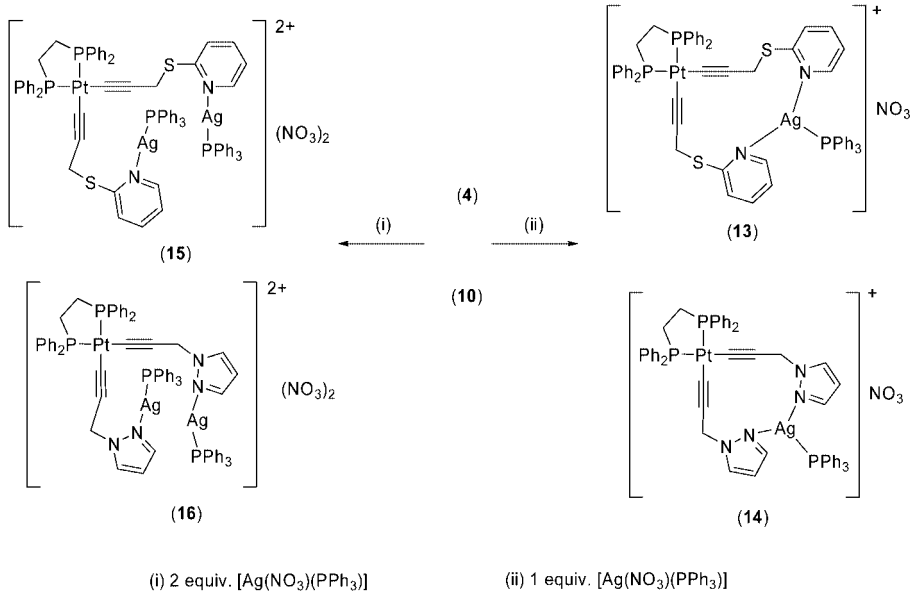


Figure 7. Molecular structure of *trans*-[Pt(C≡CCH$_2$R^5)$_2$(PPh$_3$)$_2$]·2CHCl$_3$ (**9**). Thermal ellipsoids show 50% probability levels. Hydrogen atoms and CHCl$_3$ of solvation have been omitted for clarity.



Scheme 4.

$(NO_3)(PPh_3)$] to give the cationic platinum(II)/silver(I) complexes *trans*-[Pt(C≡CCH$_2$R^n)$_2$(PPh_3)$_2$($AgPPh_3$)$_2$](NO_3)$_2$ (*n* = 2, **11**; *n* = 5, **12**) (Scheme 4). The reaction of complexes **3** and **9** with only 1 equiv. of [Ag(NO_3)PPh_3] gave mixtures of products which were not analysed further. NMR spectroscopic data of these mixtures seems to indicate the presence of both starting material (i.e. complex **3** or **9**) as well as dimetallic complexes **11** or **13**. Clearly, the *trans* geometry does not allow the system to bend in such a manner that a macrocyclic complex incorporating only one silver ion can be formed. Similarly, *cis* complexes **4** and **10** react with either 1 or 2 equiv. of the silver compound to give the heterodimetallic compounds *cis*-[Pt(C≡CCH$_2$R^n)$_2$(dppe)($AgPPh_3$)]NO_3 (*n* = 2, **13**; *n* = 5, **14**) or *cis*-[Pt(C≡CCH$_2$R^n)$_2$(dppe)($AgPPh_3$)$_2$](NO_3)$_2$ (*n* = 2, **15**; *n* = 5, **16**), respectively (Scheme 5). Complexes **11**–**16** were characterised spectroscopically; attempts to grow X-ray quality crystals so far have failed as the stability of these compounds in solution is limited. The $^{31}P\{^1H\}$ NMR spectra of complexes **11**–**16** consist of a singlet resonance with ^{195}Pt satellites due to the Pt–phosphane unit and, at room temperature, a very broad (almost invisible) signal for the Ag–PPh_3 moiety. At –80 °C, this broad signal is resolved into a pair of doublets arising from coupling of the phosphorus nucleus to both the ^{109}Ag and ^{107}Ag isotopomers (Figure 8). The ^{195}Pt–^{31}P coupling constants of dimetallic Pt/Ag macrocycles **13**–**14** are ca. 100 Hz larger than those of the "free-ligand" Pt complexes, consistent with a change of angle about the platinum centre



Scheme 5.

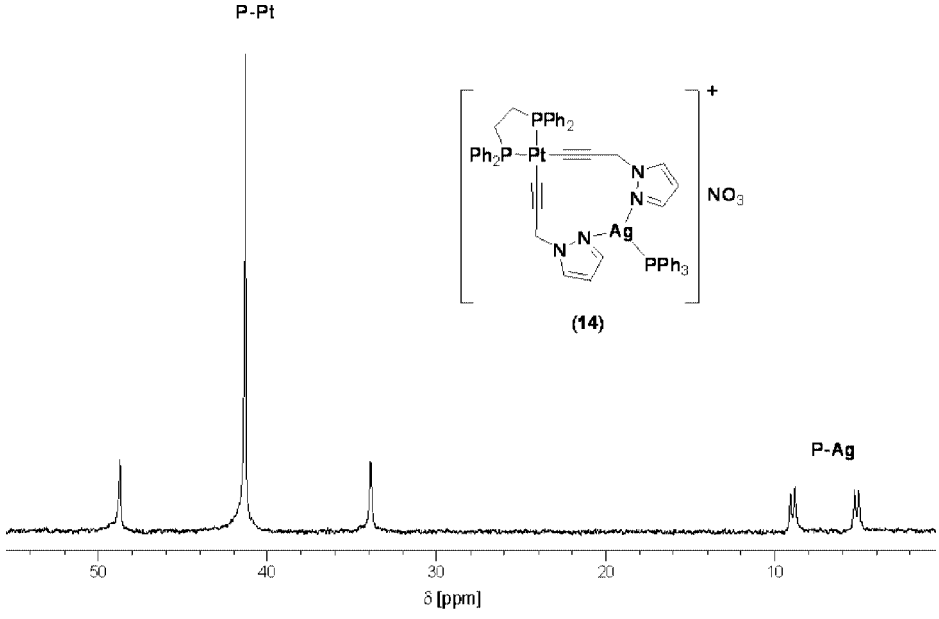


Figure 8. $^{31}P\{^1H\}$ NMR (162 MHz) spectrum of *cis*-[Pt(C≡CCH$_2$R^5)$_2$(dppe)($AgPPh_3$)]NO_3 (**14**) in CD_2Cl_2 at –80 °C.

consistent with the expected "tweezer-motion" of the alkyne substituents to coordinate to the silver atom. The possibility that the silver ions are coordinated to the triple bond rather than the N atom can be disproved from the IR data; the C≡C stretching frequency of both the "free" and "coordinated" Pt complexes are almost identical. Complexes **11**–**16** represent examples of complexes in which an organometallic compound acts as metalloligand. Some examples of such metalloligands include the alkynyl gold(I) macrocycles and [2]catenanes containing pyridyl and bipyridyl backbones that are coordinated to a Pt^{IV} centre,[42] the pyrazolyl- and pyridyl-substituted ferrocenes that are N-coordinated to various Au and Ag species,[43,44] the alkynyl-functionalised bis(pyrazolyl)methane derivatives containing Au/Pd and Pt/Pd[45] and various supramolecular assemblies based on the M–C≡C (4-C_6H_4N) (M = Pt, Ru) unit.[40,46–48]

Conclusion

We have shown that various *N*- and *S*-propargylated compounds form platinum(II) alkynyl complexes in high yields and that these compounds can act as N-donor ligands to Ag^{I} ions. In the case of *cis*-Pt complexes, dimetallic macrocycles are formed. Further work on the use of these organometallic ligands is currently in progress.

Experimental Section

General: NMR spectra were recorded with a 400 MHz Varian Inova spectrometer. Chemical shifts are quoted relative to external TMS (^{1}H, ^{13}C) or 85% H_3PO_4 (^{31}P). LSIMS mass spectra were measured with a Micromass Autospec spectrometer in positive ion mode by using NBA as matrix. IR spectra were recorded with a Nicolet Impact 410 instrument. Elemental analyses were obtained in-house by using a LECO CHNS-932 microanalyser. *N*-Propargyl-2-pyridone, 2-propargylthiopyridine, *N*-propargyl-4-methyl-2-quinolidone, *N*-propargylphthalimide and 2-propargylpyrazole were prepared by modified literature procedures.[14–17,23] Spectroscopic data of these alkynes is given here since only very few details have been previously reported. The Pt^{II} phosphane complexes *trans*-[$PtCl_2(PPh_3)_2$] and *cis*-[$PtCl_2$(dppe)] were prepared by the reaction of [$PtCl_2(NCMe)_2$] with appropriate amounts of the phosphanes. The silver(I) complex [$Ag(NO_3)(PPh_3)$] was prepared by a literature procedure.[49] All other reagents and solvents were obtained commercially and used as received. DFT calculations were carried out with the PRIRODA software package incorporating relativistic Stevens, Basch, Krauss basis sets.[50,51] Geometries were fully optimised and the located minima were confirmed by the absence of imaginary frequencies.

Preparation of the Alkynes: A mixture of the appropriate NH or SH derivatives (2-pyridone, 2-hydroxy-4-methylquinoline, phthalimide and 2-pyridinethiol), K_2CO_3 (excess) and propargyl bromide (1.6 equiv.) was heated at reflux in acetone for ca. 8 h. The cooled mixture was filtered, and the filtrate was evaporated to dryness. The resulting crude products were purified by chromatography on silica gel using CH_2Cl_2 as eluent.

Preparation of the [Pt(C≡CR)$_2$(P)] Complexes: A mixture of the alkyne (0.228 mmol), [$PtCl_2$(P)] (0.098 mmol), [CuI] (5 mg) in Et_2NH (5 mL) and EtOH (5 mL) was heated at reflux for ca. 1 h. The solid products were isolated by filtration, washed with H_2O, EtOH and Et_2O and dried in vacuo.

***N*-Propargyl-2-pyridone (R^{1}CH$_2$C≡CH):** Yield: 2.10 g (75%), dark orange oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.27 (t, J = 2.5 Hz, 1 H, ≡CH), 4.74 (d, J = 2.5 Hz, 2 H, NCH_2), 6.22 (dt, J = 6.6, 1.3 Hz, 1 H, H^5), 6.55 (dd, J = 9.1, 0.8 Hz, 2 H, H^3), 7.33 (m, 1 H, H^4), 6.61 (ddd, J = 6.8, 2.0, 0.5 Hz, 1 H, H^6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 37.45 (NCH_2), 75.21 (C≡CH), 76.73 (C≡CH), 106.24 (C5), 120.32 (C3), 135.74 (C4), 139.68 (C6), 161.80 (C2) ppm.

***trans*-[Pt(C≡CR^1)$_2$(PPh$_3$)$_2$] (1):** Yield: 0.258 g (83%), pale brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.01 (t, J = 1.8 Hz, 4 H, NCH_2), 5.61 (dt, J = 6.8, 1.5 Hz, 2 H, H^5), 6.33 (ddd, J = 8.8, 2.0, 0.5 Hz, 2 H, H^3), 6.88 (dd, J = 6.8, 2.0 Hz, 2 H, H^6), 7.12 (dt, J = 6.6, 2.0 Hz, 2 H, H^4), 7.31–7.44 (m, 18 H, *p*-, *m*-Ph_3P), 7.70–7.77 (m, 12 H, *o*-Ph_3P) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 18.89 ($J_{Pt,P}$ = 2619 Hz) ppm. IR (KBr disk): $\tilde{\nu}$ = 2135 (C≡C), 1657 (C=O) cm^{-1}. FAB MS: m/z = 984 [M + H]$^+$. $C_{52}H_{42}N_2O_2P_2Pt$ (983.9): calcd. C 63.48, H 4.30, N 2.85; found C 63.03, H 4.32, N 3.02. X-ray quality crystals were grown by slow diffusion of Et_2O into a CH_2Cl_2 solution of the complex.

***cis*-[Pt(C≡CR^1)$_2$(dppe)] (2):** Yield: 0.242 g (75%), colourless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.30–2.48 (m, 4 H, PCH_2CH_2P), 4.76 (t, J = 6.6 Hz, 4 H, NCH_2), 5.81 (dt, J = 6.6, 1.2 Hz, 2 H, H^5), 6.42 (d, J = 8.6 Hz, 2 H, H^3), 7.19 (m, 2 H, H^4), 7.38–7.51 (m, 12 H, *p*-, *m*-Ph_2P), 7.80–7.88 (m, 8 H, *o*-Ph_2P), 7.89 (dd, J = 7.0, 1.9 Hz, 2 H, H^6) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 43.23 ($J_{Pt,P}$ = 2316 Hz) ppm. IR (KBr disk): $\tilde{\nu}$ = 2137 (C≡C), 1652 (C=O) cm^{-1}. FAB MS: m/z = 858 [M + H]$^+$. $C_{42}H_{36}N_2O_2P_2Pt$ (857.8): calcd. C 58.81, H 4.23, N 3.27; found C 58.88, H 4.24, N 3.35. X-ray quality crystals were grown by slow diffusion of Et_2O into a CH_2Cl_2 solution of the complex.

2-Propargylthiopyridine (R^{2}CH$_2$C≡CH): Yield: 2.01 g (75%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.18 (t, J = 2.7 Hz, 1 H, ≡CH), 3.94 (d, J = 2.7 Hz, 2 H, SCH_2), 7.00 (ddd, J = 7.4, 4.7, 0.8 Hz, 1 H, H^5), 7.20 (d, J = 8.2 Hz, 1 H, H^3), 7.49 (ddd, J = 9.4, 7.4, 1.9 Hz, 1 H, H^4), 8.44 (ddd, J = 5.1, 1.9, 1.1 Hz, 1 H, H^6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.11 (SCH_2), 70.40 (C≡CH), 80.01 (C≡CH), 119.80 (C5), 121.93 (C3), 136.05 (C4), 149.44 (C6), 156.96 (C26) ppm. *Caution*: On several occasions this alkyne decomposed spontaneously producing large amounts of extremely malodorous fumes and black soot.

***trans*-[Pt(C≡CR^2)$_2$(PPh$_3$)$_2$] (3):** Yield: 0.260 g (81%), pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.19 (s, 4 H, SCH_2), 6.74 (d, J = 8.6 Hz, 2 H, H^3), 6.80 (t, J = 5.8 Hz, 2 H, H^5), 7.11 (dt, J = 7.8, 1.6 Hz, 2 H, H^4), 7.28–7.40 (m, 18 H, *p*-, *m*-Ph_3P), 7.66–7.77 (m, 12 H, *o*-Ph_3P), 8.25 (d, J = 4.7 Hz, 2 H, H^6) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 19.47 ($J_{Pt,P}$ = 2662 Hz) ppm. IR (KBr disk): $\tilde{\nu}$ = 2125 (C≡C) cm^{-1}. FAB MS: m/z = 1016 [M + H]$^+$. $C_{52}H_{42}N_2O_2P_2PtS_2{\cdot}H_2O$ (1033.2): calcd. C 60.39, H 4.29, N 2.71; found C 59.94, H 4.28, N 3.02.

***cis*-[Pt(C≡CR^2)$_2$(dppe)] (4):** Yield: 0.134 g (40%), pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.31 (m, 4 H, PCH_2CH_2P), 3.99 (t, J = 7.0 Hz, 4 H, SCH_2), 6.75 (dt, J = 5.1, 1.6 Hz, 2 H, H^5), 7.06–7.15 (m, 4 H, H^3, H^4), 7.28–7.41 (m, 12 H, *p*-, *m*-Ph_2P), 7.79–7.89 (m, 8 H, *o*-Ph_2P), 8.24 (ddd, J = 5.1, 2.7, 12 Hz, 2 H, H^6) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 41.43 ($J_{Pt,P}$ = 2305 Hz) ppm. IR (KBr disk): $\tilde{\nu}$ = 2128 (C≡C) cm^{-1}. FAB MS: m/z = 890 [M + H]$^+$. $C_{42}H_{36}N_2O_2P_2PtS_2{\cdot}1/2H_2O$ (898.1): calcd. C 56.12, H 4.15 N 3.12; found C 55.83, H 4.11, N 3.34.

***N*-Propargyl-4-methyl-2-quinolidone ($R^3CH_2C{\equiv}CH$):** Yield: 1.36 g (55%), brown solid. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.33 (t, J = 2.6 Hz, 1 H, ≡CH), 2.47 (s, 3 H, Me), 5.11 (d, J = 2.6 Hz, 2 H, NCH_2), 6.60 (s, 1 H, H^3), 7.29 (t, J = 7.7 Hz, 1 H, H^6), 7.53 (d, J = 8.1 Hz, 1 H, H^5), 7.61 (dt, J = 7.3, 1.3 Hz, 1 H, H^7), 7.72 (dd, J = 8.1, 1.3 Hz, 1 H, H^8) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.01 (Me), 31.28 (NCH_2), 72.22 (C≡CH), 78.16 (C≡CH), 114.86 (C3), 120.68 (C8), 121.63 (C10), 122.29 (C6), 125.33 (C5), 130.53 (C7), 138.35 (C9), 147.23 (C4), 161.02 (C2) ppm.

***trans*-[Pt(C≡CR^3)$_2$(PPh$_3$)$_2$] (5):** Yield: 0.225 g (64%), tan solid. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.40 (s, 6 H, Me), 4.36 (s, 4 H, NCH_2), 6.40 (s, 2 H, H^3), 6.82 (d, J = 8.2 Hz, 2 H, H^5), 6.94 (t, J = 8.2 Hz, 2 H, H^6), 7.02 (t, J = 7.4 Hz, 2 H, H^7), 7.13–7.24 (m, 18 H, *p*-, *m*-Ph_3P), 7.51 (dd, J = 7.8, 0.8 Hz, 2 H, H^8), 7.54–7.62 (m, 12 H, *o*-Ph_3P) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 19.79 ($J_{Pt,P}$ = 2663 Hz) ppm. IR (KBr disk): $\tilde{\nu}$ = 2128 (C≡C), 1652 (C=O) cm^{-1}. FAB MS: m/z = 1112 [M + H]$^+$. $C_{62}H_{50}N_2O_2P_2Pt{\cdot}2H_2O$ (1147.3): calcd. C 64.84, H 4.74, N 2.44; found C 64.56, H 4.70, N 2.84.

***cis*-[Pt(C≡CR^3)$_2$(dppe)] (6):** Yield: 0.245 g (66%), tan solid. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.23 (m, 4 H, PCH_2CH_2P), 2.38 (s, 6 H, Me), 5.15 (s, 4 H, NCH_2), 5), 6.43 (s, 2 H, H^3), 7.05 (t, J = 7.4 Hz, 2 H, H^7), 7.10–7.22 (m, 10 H, *m*-Ph_2P, H^6), 7.23–7.32 (m, 4 H, *p*-Ph_2P), 7.52 (d, J = 7.8 Hz, 2 H, H^8), 7.57–7.72 (m, 10 H, *o*-Ph_2P, H^5) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 41.62 ($J_{Pt,P}$ = 2295 Hz) ppm. IR (KBr disk): $\tilde{\nu}$ = 2138 (C≡C), 1650 (C=O) cm^{-1}. FAB MS: m/z = 986 [M + H]$^+$. $C_{52}H_{44}N_2O_2P_2Pt{\cdot}H_2O$ (1003.3): calcd. C 62.20, H 4.62, N 2.79; found C 61.98, H 4.45, N 3.04.

***N*-Propargylphthalimide ($R^4CH_2C{\equiv}CH$):** Yield: 1.29 g (65%), pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.22 (t, J = 2.3 Hz, 1 H, ≡CH), 4.44 (d, J = 2.3 Hz, 2 H, NCH_2), 7.73 (m, 2 H, arom), 7.87 (m, 2 H, arom) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.93 (NCH_2), 71.46 (C≡CH), 77.12 (C≡CH), 123.52, 131.90, 134.17 (arom) ppm.

***trans*-[Pt(C≡CR^4)$_2$(PPh$_3$)$_2$] (7):** Yield: 0.286 g (82%), ivory solid. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.75 (s, 4 H, NCH_2), 7.11–7.31 (m, 18 H, *p*-, *m*-Ph_3P), 7.60–7.76 (m, 20 H, *o*-Ph_3P, arom) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 19.56 ($J_{Pt,P}$ = 2646 Hz) ppm. IR (KBr disk): $\tilde{\nu}$ = 1231 (C≡C), 1713 (C=O) cm^{-1}. FAB MS: m/z = 1088 [M + H]$^+$. $C_{58}H_{42}N_2O_4P_2Pt{\cdot}H_2O$ (1105.2): calcd. C 62.97, H 4.01, N 2.53; found C 62.98, H 4.17, N 2.85.

***cis*-[Pt(C≡CR^4)$_2$(dppe)] (8):** Yield: 0.148 g (41%), colourless solid. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.28 (m, 4 H, PCH_2CH_2P), 4.50 (t, J = 7.0 Hz, 4 H, NCH_2), 7.14–7.25 (m, 12 H, *p*-, *m*-Ph_2P), 7.54–7.80 (m, 16 H, *o*-Ph_3P, arom) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 42.01 ($J_{Pt,P}$ = 2289 Hz) ppm. IR (KBr disk): $\tilde{\nu}$ = 2140 (C≡C), 1709 (C=O) cm^{-1}. FAB MS: m/z = 962 [M + H]$^+$. $C_{49}H_{39}N_2O_4P_2Pt{\cdot}H_2O$ (994.2): calcd. C 59.14, H 4.16, N 2.82; found C 59.10, H 4.17, N 3.06.

2-Propargylpyrazole ($R^5CH_2C{\equiv}CH$): Yield: 1.31 g (42%), pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.49 (t, J = 2.7 Hz, 1 H, ≡CH), 4.94 (d, J = 2.3 Hz, 2 H, NCH_2), 6.29 (t, J = 2.3 Hz, 1 H, Pz-H^4), 7.53 (d, J = 1.6 Hz, 1 H, Pz-H^5), 7.59 (d, J = 2.3 Hz, 1 H, Pz-H^3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 41.65 (NCH_2), 74.83 (C≡CH), 76.98 (C≡CH), 106.39 (C4), 129.02 (C5), 140.23 (C3) ppm.

***trans*-[Pt(C≡CR^5)$_2$(PPh$_3$)$_2$] (9):** Yield: 0.312 g (83%), colourless solid. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.22 (s, 4 H, NCH_2), 5.48 (br. s, 2 H, Pz-H^4), 6.54 (br. s, 2 H, Pz-H^5), 7.27 (br. s, 2 H, Pz-H^3), 7.31–7.44 (m, 18 H, *p*-, *m*-Ph_3P), 7.70–7.80 (m, 12 H, *o*-Ph_3P) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 20.12 ($J_{Pt,P}$ = 2641 Hz) ppm. IR (KBr disk): $\tilde{\nu}$ = 2138 (C≡C) cm^{-1}. FAB MS: m/z = 853 [M + H]$^+$. $C_{48}H_{40}N_4P_2Pt$ (929.9): calcd. C 61.99, H 4.34, N 6.03; found C 61.56, H 4.35, N 5.82. X-ray quality crystals were grown by slow diffusion of Et_2O into a $CHCl_3$ solution of the complex.

***cis*-[Pt(C≡CR^5)$_2$(dppe)] (10):** Yield: 0.137 g (71%), tan solid. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.30–2.48 (m, 4 H, PCH_2CH_2P), 5.01 (t, J = 7.0 Hz, 4 H, NCH_2), 5.90 (br. s, J = 1.2 Hz, 2 H, Pz-H^4), 7.22 (br. s, 2 H, Pz-H^5), 7.34 (br. s, 2 H, Pz-H^3), 7.36–7.50 (m, 12 H, *p*-, *m*-Ph_2P), 7.79–7.90 (m, 8 H, *o*-Ph_2P) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 43.00 ($J_{Pt,P}$ = 2315 Hz) ppm. IR (KBr disk): $\tilde{\nu}$ = 2140 (C≡C) cm^{-1}. FAB MS: m/z = 804 [M + H]$^+$. $C_{38}H_{34}N_4P_2Pt$ (803.7): calcd. C 56.79, H 4.26, N 6.97; found C 56.63, H 4.27, N 7.04.

Preparation of Heterodimetallic Pt^{II}/Ag^{I} Complexes: To a solution of the Pt complex in CH_2Cl_2 (7 mL) was added either 1 or 2 equiv. of solid [Ag(NO_3)(PPh_3)]. After stirring for ca. 1 h, the solution was passed through Celite and concentrated in vacuo. Addition of Et_2O precipitated the complexes, which were isolated by filtration and dried in air.

***trans*-[Pt(C≡CR^2)$_2$(PPh$_3$)$_2$(AgPPh$_3$)$_2$](NO$_3$)$_2$ (11):** Yield: 0.038 g (81%), ivory solid. ^1H NMR (400 MHz, CD_2Cl_2): δ = 3.21 (s, 4 H, SCH_2), 6.81–6.99 (m, 4 H, H^3, H^5), 7.23–7.76 (m, 62 H, Ph_3P, H^4), 8.05 (m, 2 H, H^6) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, –80 °C): δ = 17.67 ($J_{Pt,P}$ = 2524 Hz), 11.07 (d, $J_{^{109}Ag,P}$ = 538, $J_{^{107}Ag,P}$ = 465 Hz) ppm. IR (KBr disk): $\tilde{\nu}$ = 2126, 2054 (C≡C), 1398 (N=O), 1294 (NO_2) cm^{-1}. FAB MS: m/z = 1385 [M – $AgPPh_3$]$^+$, 1123 [M – Ag – 2Ph_3P]$^+$. $C_{88}H_{72}Ag_2N_4O_6P_4PtS_2{\cdot}CH_2Cl_2$ (1965.3): calcd. C 54.39, H 3.80, N 2.85; found C 53.99, H 3.95, N 2.93.

***trans*-[Pt(C≡CR^5)$_2$(PPh$_3$)$_2$(AgPPh$_3$)$_2$](NO$_3$)$_2$ (12):** Yield: 0.040 g (78%), ivory solid. ^1H NMR (400 MHz, CD_2Cl_2): δ = 4.30 (s, 4 H, NCH_2), 6.10 (t, J = 2.2 Hz, 2 H, Pz-H^4), 6.97 (d, J = 1.5 Hz, 2 H, Pz), 7.14 (d, J = 1.5 Hz, 2 H, Pz), 7.22–7.72 (m, 60 H, Ph_3P) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, –80 °C): δ = 29.88 ($J_{Pt,P}$ = 2520 Hz), 11.18 (d, $J_{^{109}Ag,P}$ = 540, $J_{^{107}Ag,P}$ = 463 Hz) ppm. IR (KBr disk): $\tilde{\nu}$ = 2138, 2083 (C≡C), 1384 (N=O), 1297 (NO_2) cm^{-1}. $C_{84}H_{70}Ag_2N_6O_6P_4Pt{\cdot}1/2CH_2Cl_2$ (1836.7): calcd C 55.26, H 3.90, N 4.58; found C 55.39, H 4.12, N 4.62.

***cis*-[Pt(C≡CR^2)$_2$(dppe)(AgPPh$_3$)]NO$_3$ (13):** Yield: 0.035 g (83%), tan solid. ^1H NMR (400 MHz, CD_2Cl_2): δ = 2.39–2.57 (m, 4 H, PCH_2CH_2P), 3.77 (s, 4 H, SCH_2), 6.90 (t, J = 4.4 Hz, 2 H, Py), 6.97 (d, J = 7.7 Hz, 4 H, Py), 7.27–7.79 (m, 37 H, Ph_2P, Ph_3P, Py), 8.31 (d, J = 4.0 Hz, 2 H, H^6) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, –80 °C): δ = 40.13 ($J_{Pt,P}$ = 2433 Hz), 11.10 (d, $J_{^{109}Ag,P}$ = 541, $J_{^{107}Ag,P}$ = 469 Hz) ppm. IR (KBr disk): $\tilde{\nu}$ = 2098 (C≡C), 1384 (N=O) cm^{-1}. FAB MS: m/z = 997 [M – Ph_3P]$^+$. $C_{60}H_{51}AgN_3O_3P_3PtS_2{\cdot}CH_2Cl_2$ (1407.0) C 52.07, H 3.80 N 2.98; found C 52.06, H 4.00, N 3.09.

***cis*-[Pt(C≡CR^5)$_2$(dppe)(AgPPh$_3$)]NO$_3$ (14):** Yield: 0.026 g (78%), ivory solid. ^1H NMR (400 MHz, CD_2Cl_2): δ = 2.41–2.60 (m, 4 H, PCH_2CH_2P), 4.76 (s, 4 H, NCH_2), 6.21 (t, J = 2.2 Hz, 2 H, Pz-H^4), 7.12–7.83 (m, 39 H, Ph_2P, Ph_3P, Pz) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, –80 °C): δ = 41.29 ($J_{Pt,P}$ = 2400 Hz), 6.97 (d, $J_{^{109}Ag,P}$ = 653, $J_{^{107}Ag,P}$ = 566 Hz) ppm. IR (KBr disk): $\tilde{\nu}$ = 2120 (C≡C), 1336 (N=O) cm^{-1}. $C_{56}H_{49}AgN_5O_3P_3Pt{\cdot}CH_2Cl_2$ (1320.8): calcd. C 51.83, H 3.89, N 5.30; found C 51.71, H 4.04, N 4.94.

***cis*-[Pt(C≡CR^2)$_2$(dppe)(AgPPh$_3$)$_2$](NO$_3$)$_2$ (15):** Yield: 0.041 g (76%), tan solid. ^1H NMR (400 MHz, CD_2Cl_2): δ = 2.40–2.59 (m, 4 H, PCH_2CH_2P), 3.74 (s, 4 H, SCH_2), 6.81 (m, 2 H, Py), 7.07 (m, 2 H, Py), 7.28–7.76 (m, 52 H, Ph_2P, Ph_3P, Py), 8.10 (m, 2 H, H^6)

Table 2. Crystal data and refinement details for complexes **1**, **2**, **5**, **9** and **10**.

	1	**2**	**5**	**9**	**10**
Empirical formula	$C_{52}H_{40}N_2O_2P_2Pt$	$C_{42}H_{36}N_2O_2P_2Pt$	$C_{62}H_{50}N_2O_2P_2Pt$	$C_{50}H_{42}N_4Cl_6P_2Pt$	$C_{38}H_{34}N_4P_2Pt$
Formula mass	981.89	857.76	1112.07	1168.61	803.72
Crystal system	triclinic	monoclinic	triclinic	triclinic	orthorhombic
Space group	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$Pbca$
a [Å]	9.0466(6)	14.973(6)	9.783(4)	8.277(2)	17.6036(17)
b [Å]	10.5428(6)	18.366(7)	10.836(5)	12.177(3)	13.4388(13)
c [Å]	11.3405(7)	12.819(5)	13.091(5)	12.714(3)	28.890(3)
α [°]	96.486(1)	90	104.27(4)	73.332(5)	90
β [°]	106.646(1)	104.474(8)	104.14(3)	79.273(6)	90
γ [°]	90.901(1)	90	108.94(3)	82.584(5)	90
V [Å^3]	1028.34(19)	3413(2)	1189.9(9)	1202.2(5)	6834.5(11)
Z	1	4	1	1	1
$\rho_{calcd.}$ [Mg/m^3]	1.586	1.669	1.552	1.614	1.562
μ [mm^{-1}]	3.535	4.245	3.065	3.358	4.232
$F(000)$	490	1704	560	580	3184
θ limits [°]	1.89–28.83	1.79–25.00	1.72–25.00	1.69–25.00	1.41–28.13
Measured reflections	6692	16271	11140	11602	63837
Unique reflections	3728	2997	4042	4209	7983
Parameters	268	222	314	286	406
GOF on F^2	0.755	1.182	1.160	1.084	1.004
R_1 [$I > 2\sigma(I)$]	0.0384	0.0254	0.0240	0.0354	0.0487
wR_2 (on F^2, all data)	0.0811	0.0792	0.0707	0.1116	0.1521
$\Delta\rho_{min/max}$ [e/Å^3]	2.142 and –1.392	0.728 and –1.204	0.750 and –0.582	0.710 and –0.979	0.964 and –3.012
CCDC deposition code	634848	634849	634850	634851	634052

ppm. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, –80 °C): δ = 41.70 ($J_{Pt,P}$ = 2389 Hz), 11.14 (d, $J_{^{109}Ag,P}$ = 593, $J_{^{107}Ag,P}$ = 468 Hz) ppm. IR (KBr disk): $\tilde{\nu}$ = 2097 (C≡C), 1384 (N=O) cm^{-1}. FAB MS: m/z = 997 [M – Ag – $2Ph_3P$]$^+$. $C_{78}H_{66}Ag_2N_4O_6P_4PtS_2 \cdot 1/2CH_2Cl_2$ (1796.7): calcd. C 52.48, H 3.76 N 3.12; found C 52.42, H 3.99, N 3.13.

***cis*-[Pt(C≡CR^5)$_2$(dppe)(AgPPh$_3$)]NO$_3$ (16):** Yield: 0.041 g (73%), ivory solid. ^1H NMR (400 MHz, CD_2Cl_2): δ = 2.40–2.57 (m, 4 H, PCH_2CH_2P), 4.79 (s, 4 H, NCH_2), 6.26 (t, J = 2.2 Hz, 2 H, Pz-H^4), 7.28–7.73 (m, 54 H, Ph_2P, Ph_3P, Pz) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, –80 °C): δ = 41.20 ($J_{Pt,P}$ = 2416 Hz), 11.07 (d, $J_{^{109}Ag,P}$ = 540, $J_{^{107}Ag,P}$ = 468 Hz) ppm. IR (KBr disk): $\tilde{\nu}$ = 2097 (C≡C), 1384 (N=O) cm^{-1}. FAB MS: m/z = 911 [M – Ph_3P]$^+$. $C_{74}H_{64}Ag_2N_6O_6P_4Pt \cdot 1/2CH_2Cl_2$ (1710.5): calcd. C 52.31, H 3.83, N 4.91; found C 52.21, H 4.18, N 4.92.

X-ray Crystallography: Crystals of complex **1** (colourless block, 0.09 × 0.12 × 0.21 mm), **2** (colourless block, 0.10 × 0.10 × 0.20 mm), **5** (yellow prism 0.10 × 0.20 × 0.20 mm), **9**·2CHCl$_3$ (colourless prism, 0.20 × 0.30 × 0.50 mm) and **10** (colourless prism, 0.60 × 0.10 × 0.10 mm) were mounted in oil on a glass fibre. Data was collected at 100 K (293 K for complex **10**) by using a Bruker Apex CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Data reduction and absorption corrections were applied by using SADABS.[52] The structures were solved by direct methods and refined to F_o^2 by using full-matrix least-squares.[53] All hydrogen atoms were placed in calculated positions and refined as riding on their respective carbon atoms. Crystallographic and refinement details are collected in Table 2.

CCDC-634848, -634849, -634850, -634851 and -634052 (for compounds **1**, **2**, **5**, **9** and **10**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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