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Novel mixed-metal–alkynyl complexes stabilised by di-imine ligands: synthesis, characterisation and electrochemistry of $[(^t\mathrm{Bu}_2\mathrm{bipy})\mathrm{Pt}(\mathrm{C{\equiv}CR})_2\mathrm{M}(\mathrm{SCN})]$ ($\mathrm{R} = \mathrm{C}_6\mathrm{H}_4\mathrm{Me}$, SiMe_3; M = Cu, Ag)

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Abstract

Reaction of (4,4′-bis-*tert*-butyl-2,2′-dipyridyl) platinum bis-alkynyl $[(^t\mathrm{Bu}_2\mathrm{bipy})\mathrm{Pt}(\mathrm{C{\equiv}CR})_2]$ ($\mathrm{R} = \mathrm{C}_6\mathrm{H}_4\mathrm{Me}$ **1a**, SiMe_3 **1b**) with Group 11 metal thiocyanate salts (M = Cu, Ag) affords 1:1 mixed-metal complexes $[(^t\mathrm{Bu}_2\mathrm{bipy})\mathrm{Pt}(\mathrm{C{\equiv}CR})_2\mathrm{M}(\mathrm{SCN})]$ (M = Cu, $\mathrm{R} = \mathrm{C}_6\mathrm{H}_4\mathrm{Me}$ **2a**, SiMe_3 **2b**; M = Ag, $\mathrm{R} = \mathrm{C}_6\mathrm{H}_4\mathrm{Me}$ **3a**, SiMe_3 **3b**). X-ray analyses of the complexes **2a** and **3b** show that the group 11 metal is bonded in an η^2 fashion to two carbon–carbon triple bonds so that the co-ordination geometry is trigonal planar. The Pt atom geometry in both complexes is square planar. An electrochemical study of the copper complexes **2a** and **2b** reveals one fully reversible one electron reduction that is consistent with the first reduction of the co-ordinated bipyridyl ligand. There is also an irreversible one electron oxidation that corresponds to the Cu^{I} to $\mathrm{Cu}^{\mathrm{II}}$ transition. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Platinum; Copper; Silver; Bipyridyl; Alkynes; Crystal structures

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1. Introduction

The area of carbon-rich organometallic polymers is rapidly expanding because of the interesting electronic properties that they exhibit, and because of their potential use in the electronics industry [1]. Within this field *rigid-rod* polymers based on metals linked by alkynyl groups have proved particularly fruitful [2], and a number of new materials with novel electronic properties have been produced [3]. In all the polymers and polymer precursors synthesised the metals have been stabilised by the presence of ancillary ligands, and these ligands are almost invariably phosphines because of the ready availability of phosphine-containing metal halide starting materials and because of the ability of the phosphine to stabilise late transition metals in relatively low oxidation states [4]. Recently, we have undertaken a series of studies in order to synthesise organometallic polymers and their precursors which are stabilised by ancillary ligands other than phosphines in order to investigate whether the nature of the ancillary ligand has a significant influence on the chemistry and electronic properties of these materials. Imine donor ligands are expected to impart strikingly different properties to both monomeric and polymeric systems from the phosphine-stabilised ligands, particularly with respect to their optical and redox behaviour [5] as well as to their reactivity [6]. We have recently reported the synthesis of a series of novel bipyridyl-stabilised platinum bis-alkynyl complexes in which the alkynyl groups adopt the *cis*-configuration [7], and also a series for *trans*-bis-alkynyl platinum complexes that are stabilised by monodentate pyridine ligands [8].

The formation of the *cis*-platinum–bis-alkynyl complexes facilitates the synthesis of a series of bimetallic complexes in which the second metal is linked to the bis-alkynyl complex *via* co-ordination to the two

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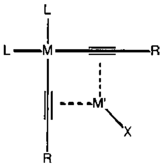
alkynyl C≡C triple bonds **I** [9]. This type of chemistry has been exploited extensively by several groups, and is exemplified by the reactions of $[(\eta^5\text{-}C_5H_5)_2Ti(C{\equiv}CSiMe_3)_2]$ with CuX and AgX systems (X = OTf, Cl, CN, alkyl, vinyl, aryl, alkynyl) [10,11], by the reaction of *cis*-$[(Me_2PhP)_2Pt(C{\equiv}CR)_2]$ (R = Ph or ^{t}Bu) with CuCl [12], and by the reaction of the anionic species $[Pt(C{\equiv}CR)_4]^{2-}$ and $[(C_6H_5)_2Pt(C{\equiv}CR)_2]^{2-}$ with a range of mercury, copper and silver salts [13,14]. These bimetallic complexes have been shown to exhibit a range of novel chemical and physical properties [14]. The authors now report the synthesis and characterisation of a new class of bimetallic complex obtained from the reaction of the bipyridyl-stabilised platinum *cis*-bis-alkynyl complexes with copper and silver thiocyanates.



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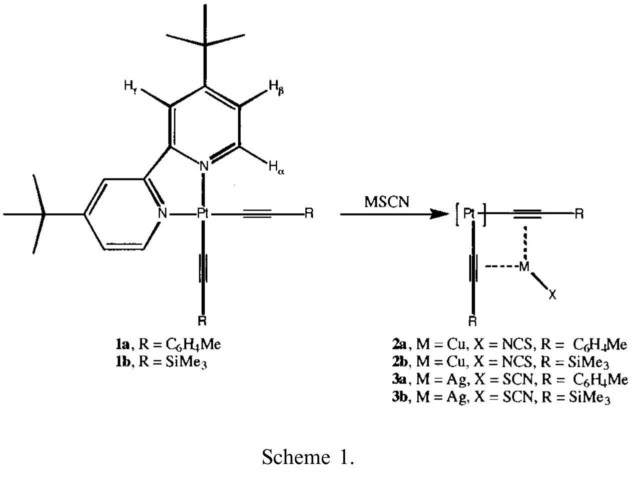
2. Results and discussion

2.1. Syntheses and spectroscopic characterisation

The 1:1 bimetallic complexes $[(^t\mathrm{Bu}_2\mathrm{bipy})Pt(C{\equiv}CR)_2M(SCN)]$ (M = Cu, R = C_6H_4Me **2a**, $SiMe_3$ **2b**; M = Ag, R = C_6H_4Me **3a**, $SiMe_3$ **3b**) were prepared by the room temperature reaction of the (4,4′-bis-*tert*-butyl-2,2′-dipyridyl) platinum bis-alkynyls $[(^t\mathrm{Bu}_2\mathrm{bipy})Pt(C{\equiv}CR)_2]$ (R = C_6H_4Me **1a**, $SiMe_3$ **1b**) [7] with [M(SCN)] (M = Cu, Ag), in acetonitrile (Scheme 1). The compounds are sparingly soluble in acetonitrile but soluble in dichloromethane and chloroform. They are all air stable, and range in colour from yellow (**2a**) to pale green (**3b**). The reaction time needed for the trimethylsilyl salts was generally considerably in excess of that needed for the tolyl salts, with the maximum time for the reaction being 24 h. The products were initially characterised by spectroscopic techniques (Table 1). All the compounds exhibit the IR $\nu_{(C\equiv N)}$ stretches, in dichloromethane solution, at around 2090 cm^{-1} for the copper complexes **2**, and at 2100 cm^{-1} for the silver complexes **3**. The NCS^- ligand is potentially ambidentate; it can bond through the S atom, as a thiocyanate, or through the N atom, as an isothiocyanate. It would be predicted from the simple *hard* and *soft* metal and ligand analogy that the *softer* Ag(I) atom would be S-bonded and the *harder* Cu(I) atom would be N-bonded. The slightly higher $\nu_{(C\equiv N)}$ stretching frequency observed for the Ag complexes **3** is consistent with the presence of the S-bonded thiocyanate, while in the copper complexes **2** this ligand appears to be N-bonded. The IR $\nu_{(C\equiv C)}$ stretch is not observed for the tolyl complexes, but is seen for the trimethylsilyl analogues where it occurs some 40–60 cm^{-1} lower than in the starting bis-alkynyl complexes (**1b**, $\nu_{(C\equiv C)}$ = 2056, 2040 cm^{-1}) [7]. ^{1}H-NMR spectroscopic data for the complexes **2** and **3** is similar to that in the parent complex **1** although there are small differences in chemical shift; the bipyridyl H_6 signal moves to higher field and the H_5 signal moves to lower field. Attempts to record the ^{13}C-NMR spectra for the complexes were hampered by their relatively low solubility, and no signals for the acetylenic carbon atoms were observed, however, for the trimethylsilyl derivatives a peak at 131.67 ppm, corresponding to the thiocyanate carbon atom, was observed. Mass spectral data for the complexes **2** and **3** showed peaks corresponding to the molecular ion minus the NCS^- group.



Scheme 1.

2.2. Crystal structure analyses

In order to establish the crystal structures of compounds **2** and **3**, and to establish the co-ordination geometries of the metal atoms, X-ray diffraction studies were undertaken on a single crystals of compounds **2a** and **3b**.

The crystal structure of $[(^t\mathrm{Bu}_2\mathrm{bipy})Pt(C{\equiv}CC_6H_4Me)_2Cu(SCN)]$ **2a** consists of neutral molecules of the 1:1 Pt:Cu complex together with uncoordinated molecules of MeCN solvent. The molecular structure of **2a** is illustrated in Fig. 1 while selected bond parameters are presented in Table 2. The X-ray analysis confirms that the thiocyanate ligand is bonded to the Cu atom through nitrogen with the Cu(1)–N(100)–C(100) angle of 176.5(9)°. The Cu(1) atom adopts a trigonal planar geometry (maximum deviation from Cu(1), N(100), C(31), C(32), C(41), C(42) plane is 0.102 Å for C(32)), and lies approximately in the plane of the two alkynyl groups so that the acetylenic C≡C triple bonds each form a η^2 interaction with the copper. The Pt(1) atom

Table 1
Spectroscopic data for the new complexes **2a**, **2b**, **3a** and **3b**

	IR (cm^{-1}) $\nu_{(\mathrm{C{\equiv}C})}$ [a]	^{1}H-NMR δ ppm [b]	Mass spec [c] m/z
$[(^t\mathrm{Bu_2bipy})\mathrm{Pt}(\mathrm{C{\equiv}CC_6H_4Me})_2\mathrm{Cu(SCN)}]$ **2a**	2090 (C≡N)	1.35 (s, 18H, ^tBu) 2.37 (s, 6H, CH_3) 6.86 (d, $^3J_{\mathrm{HH}} = 5.69$, Hz, 2H, H_β) 7.05 (d, $^3J_{\mathrm{HH}} = 8.06$ Hz, 4H, –C$_6H_4$–) 7.26 (d, $^3J_{\mathrm{HH}} = 8.02$ Hz, 4H, –C$_6H_4$–) 8.14 (s, 2H, $H\gamma$) 8.79 (d, $^3J_{\mathrm{HH}} = 5.83$ Hz, 2H, $H\alpha$)	758 (757) M$^+$–NCS
$[(^t\mathrm{Bu_2bipy})\mathrm{Pt}(\mathrm{C{\equiv}CsiMe_3})_2\mathrm{Cu(SCN)}]$ **2b**	1989, 1975, 2093 (C≡N)	0.33 (s, 18H, SiMe_3) 1.45 (s, 18H, ^tBu) 7.58 (d, $^3J_{\mathrm{HH}} = 5.97$ Hz, 2H, $H\beta$) 7.96 (s, 2H, $H\gamma$) 8.96 (d, $^3J_{\mathrm{HH}} = 5.85$ Hz, 2H, $H\alpha$)	721 (721) M$^+$–NCS
$[(^t\mathrm{Bu_2bipy})\mathrm{Pt}(\mathrm{C{\equiv}CC_6H_4Me})_2\mathrm{Ag(SCN)}]$ **3a**	2103 (C≡N)	1.43 (s, 18H, ^tBu) 2.31 (s, 6H, CH_3) 6.86 (d, $^3J_{\mathrm{HH}} = 5.69$, Hz, 2H, $H\beta$) 7.02 (d, $^3J_{\mathrm{HH}} = 7.93$ Hz, 4H, –C$_6H_4$–) 7.40 (d, $^3J_{\mathrm{HH}} = 7.97$ Hz, 4H, –C$_6H_4$–) 7.51 (d, $^3J_{\mathrm{HH}} = 5.94$ Hz, 2H, $H\beta$) 7.96 (s, 2H, $H\gamma$) 9.48 (d, $^3J_{\mathrm{HH}} = 6.00$ Hz, 2H, $H\alpha$)	801 (801) M$^+$–SCN
$[(^t\mathrm{Bu_2bipy})\mathrm{Pt}(\mathrm{C{\equiv}CsiMe_3})_2\mathrm{Ag(SCN)}]$ **3b**	2016, 1999, 2100 (C≡N)	0.32 (s, 18H, SiMe_3) 1.46 (s, 18H, ^tBu) 7.58 (d, $^3J_{\mathrm{HH}} = 5.95$ Hz, 2H, $H\beta$) 8.02 (s, 2H, $H\gamma$) 9.15 (d, $^3J_{\mathrm{HH}} = 5.95$ Hz, 2H, $H\alpha$)	766 (765) M$^+$–SCN

[a] A CH$_2$Cl$_2$ solution.
[b] 200 MHz, CDCl$_3$ solvent.
[c] +FAB.

adopts a square planar geometry (maximum deviation from Pt(1), N(1), N(2), C(31), C(41) plane is 0.016 Å for N(2)) with the two alkynyl ligands in the *cis* configuration, as required by the presence of the chelating bipyridyl ligand. The Cu(1) atom lies 0.23 Å out of this square plane, a distance that is significantly less than the deviation for the Cu atom out of the P$_2$PtC$_2$ square plane in [(Me$_2$PhP)$_2$Pt(C$_2^t$Bu)$_2$CuCl] [12]. The bipyridyl group in **2a** is also essentially planar with an angle of 8.6° between the planes of the two six-membered rings. This is the arrangement adopted in the parent precursor [(^{t}Bu$_2$bipy)Pt(C≡CC$_6$H$_4$Me)$_2$] **1** [15], but the angle between the two alkynyl ligands has narrowed significantly (C(31)–Pt(1)–C(41) 83.9(4)°), compared to the value of 92.1(7)°. Thus the two alkynyl bend towards the Cu(1) atom, presumably to maximise the orbital overlap between the copper orbitals and the ligand π orbitals. This bonding interaction renders the two alkynyl ligands non-linear with C(31)–C(32)–C(33) 162.8(11)° and C(41)–C(42)–C(43) 163.4(11)°. Similar trends have been observed by Lang in mixed titanium–copper complexes [10,11] and by Deeming in [(Me$_2$PhP)$_2$Pt(C$_2^t$Bu)$_2$CuCl] [12].

An analysis of the crystal packing (Fig. 2) shows a hydrogen bonding interaction between a bipyridyl H atom, H(22A), and the nitrogen atom of the acetonitrile solvent, N(3), related by the symmetry operation $1-x, -y, -z$ at a distance of 2.578 Å, and an interaction between the thiocyanate sulfur atom, S(100), and a hydrogen atom, H(2A), of the methyl group of the acetonitrile ligand, at 2.804 Å, related by the symmetry operation $x, 1+y, 1+z$. An intermolecular contact of 3.309(2) Å occurs between Cu(1) and Pt(1) related by $-x, -y, -z$, and similarly related contacts of 3.490 and 3.544 Å occur between Cu(1) and the bipyridyl nitrogen atoms N(1) and N(2). This metal–metal intermolecular contact is only marginally longer than the intramolecular Pt(1)...Cu(1) distance of 3.148(2) Å, which is not considered to be a bonding interaction.

By contrast, the crystal packing of [(^{t}Bu$_2$bipy)Pt(C≡CSiMe$_3$)$_2$Ag(SCN)] **3b** is different to that of the platinum–copper complex **2a**. In this case there is no solvent molecule present, and the shortest contact involving the silver atom is 2.695 Å between Ag(1) and H(7A) related by the symmetry operation $1+x, 1+y, 1+z$. The shortest Ag(1)...Pt(1) contact is 4.779 Å which is well outside the range for any direct interaction.

The molecular structure of **3b** is illustrated in Fig. 3 while selected bond parameters are presented in Table 3.

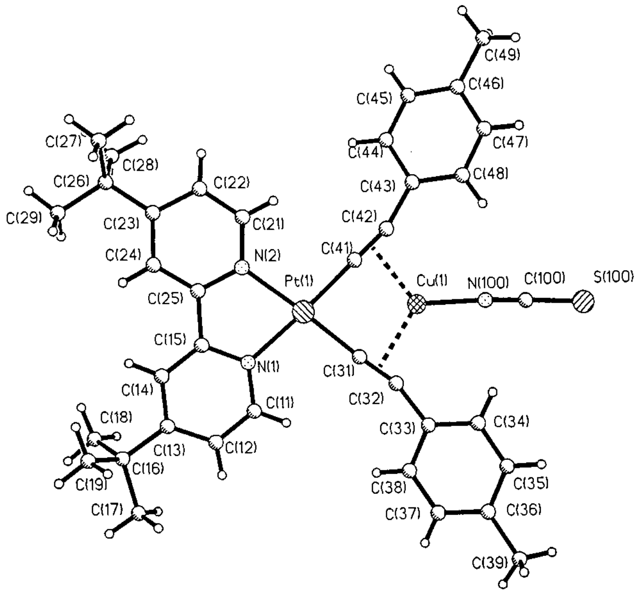


Fig. 1. The molecular structure of [(^{t}Bu$_2$bipy)Pt(C≡CC$_6$H$_4$Me)Cu-(SCN)] **2a** showing the atom numbering scheme.

The structure of this bimetallic complex is generally similar to that of the platinum–copper complex **2a** apart from the co-ordination mode of the thiocyanate ligand. The platinum atom adopts the expected square planar geometry with the two alkynyl groups adopting the *cis* configuration as required by the presence of the chelating bipyridyl ligand. The silver atom is in an uncommon trigonal planar environment, co-ordinated by the two η^2 carbon–carbon triple bonds (C(19)–C(20) and C(24)–C(25)) and in a σ-fashion by the sulfur atom (S(1)) of the thiocyanate ion. The Ag(1)–S(1)–C(100) angle of 105.3(3)° confirms the presence of the stereochemically active lone pair on the sulfur atom.

Table 2
Selected bond lengths (Å) and angles (°) for [(^{t}Bu$_2$bipy)Pt-(C≡CC$_6$H$_4$Me)Cu(NCS)] **2a**

Bond length (Å)			
Pt(1)–N(1)	2.052(8)	Pt(1)–N(2)	2.060(8)
Pt(1)–C(31)	1.971(12)	Pt(1)–C(41)	1.985(11)
Cu(1)–N(100)	1.908(9)	Cu(1)–C(31)	2.156(11)
Cu(1)–C(32)	2.254(11)	Cu(1)–C(41)	2.128(11)
Cu(1)–C(42)	2.225(10)	C(31)–C(32)	1.24(2)
C(41)–C(42)	1.203(14)	N(100)–C(100)	1.147(13)
C(100)–Si(100)	1.654(12)		
Bond angles (°)			
N(1)–Pt(1)–N(2)	78.4(3)	C(31)–Pt(1)–C(41)	83.9(4)
C(31)–Pt(1)–N(1)	98.7(4)	C(41)–Pt(1)–N(1)	177.4(4)
C(31)–Pt(1)–N(2)	176.6(4)	C(41)–Pt(1)–N(2)	99.0(4)
N(100)–Cu(1)–C(31)	141.2(4)	N(100)–Cu(1)–C(41)	142.1(4)
N(100)–Cu(1)–C(32)	108.7(4)	N(100)–Cu(1)–C(42)	110.1(4)
N(100)–C(100)–S(100)	178.5(11)	Cu(1)–N(100)–C(100)	176.5(9)
Pt(1)–C(31)–C(32)	175.5(9)	Pt(1)–C(41)–C(42)	177.0(10)
C(31)–C(32)–C(33)	162.8(11)	C(41)–C(42)–C(43)	163.4(11)

The alkyne carbon atoms, the platinum atom and the silicon atoms all lie in a plane (maximum deviation 0.09 Å), below which the silver atom protrudes by 0.44 Å. The sulfur atom is still further below the plane (deviation of 1.13 Å from the plane), so that the plane Ag(1)S(1)C(100)N(3) makes an angle of 128.7° to that of the Pt(1)C(19)C(20)C(24)C(25)Si(1)Si(2) unit. Furthermore, the silver atom is not equidistant from the two triple bonds but is significantly closer to one than the other {average Ag(1)–C(19)/C(20) = 2.44 Å compared to average Ag(1)–C(24)/C(25) = 2.50 Å}. Much of the previous structural work in this area has focused on the chemistry of anionic complexes, and there have been few reports of neutral platinum compounds co-ordinated to copper or silver centres [12,14]. The only previously reported example of a dinuclear bimetallic alkynyl complex in which the silver atom is truly trigonal planar is in the anions [(C$_6$F$_5$)$_2$Pt(C≡CPh)$_2$Ag-(PPh$_3$)]$^-$ and [{(C$_6$F$_5$)$_2$Pt(C≡CPh)$_2$Ag}$_2$(μ-dppe)]$^{2-}$ where the silver is co-ordinated to two alkynyl groups and a phosphine [16]. Both these complexes also show a similar asymmetry in the co-ordination of the Ag(I) atom to the two alkynyl groups.

Consistent with the view of bonding between the triple bonds and the silver atom as an η^2 interaction is the significant non linearity in the alkynyl fragments (C(19)–C(20)–Si(1) = 166.2(7)°, C(24)–C(25)–Si(2) = 170.0(2)°), and the C(19)–Pt(1)–C(24) bite angle of 87.0(3)°. This compares with an equivalent angle of 92.1(7)° in the starting material **1a** [15]. There is also the reduction in the carbon–carbon triple bond IR stretching frequency from 2056, 2040 cm^{-1} in **1b** to 1989, 1975 cm^{-1} in **2b** and 2016, 1999 cm^{-1} in **3b**; this is the first report of the C≡C stretching frequency of a neutral bimetallic platinum bis-alkynyl fragment. This would imply that the triple bond to metal bonding interaction is somewhat stronger in the copper complexes **2** than in the silver complex **3b**, probably because the smaller size of the heteroatom allows a better fit of the copper atom between the two perpendicular alkynyl arms.

2.3. Electrochemistry

Electrochemical studies on the complexes **2a** and **2b** in CH$_2$Cl$_2$, using 0.5 M [^{n}Bu$_4$N]BF$_4$ as the supporting electrolyte, reveal one fully reversible one electron reduction at approximately −1.3 V vs. Ag/AgCl (Table 4) which is consistent with the first reduction of the co-ordinated bipyridyl ligand, but shows a shift to a slightly lower potential than in the parent platinum bis-acetylene complexes [5]. There is also an irreversible one electron oxidation process, which can be assigned to the Cu^{I} → Cu^{II} couple (Table 4); the latter species does not favour co-ordination by the acetylide ligands

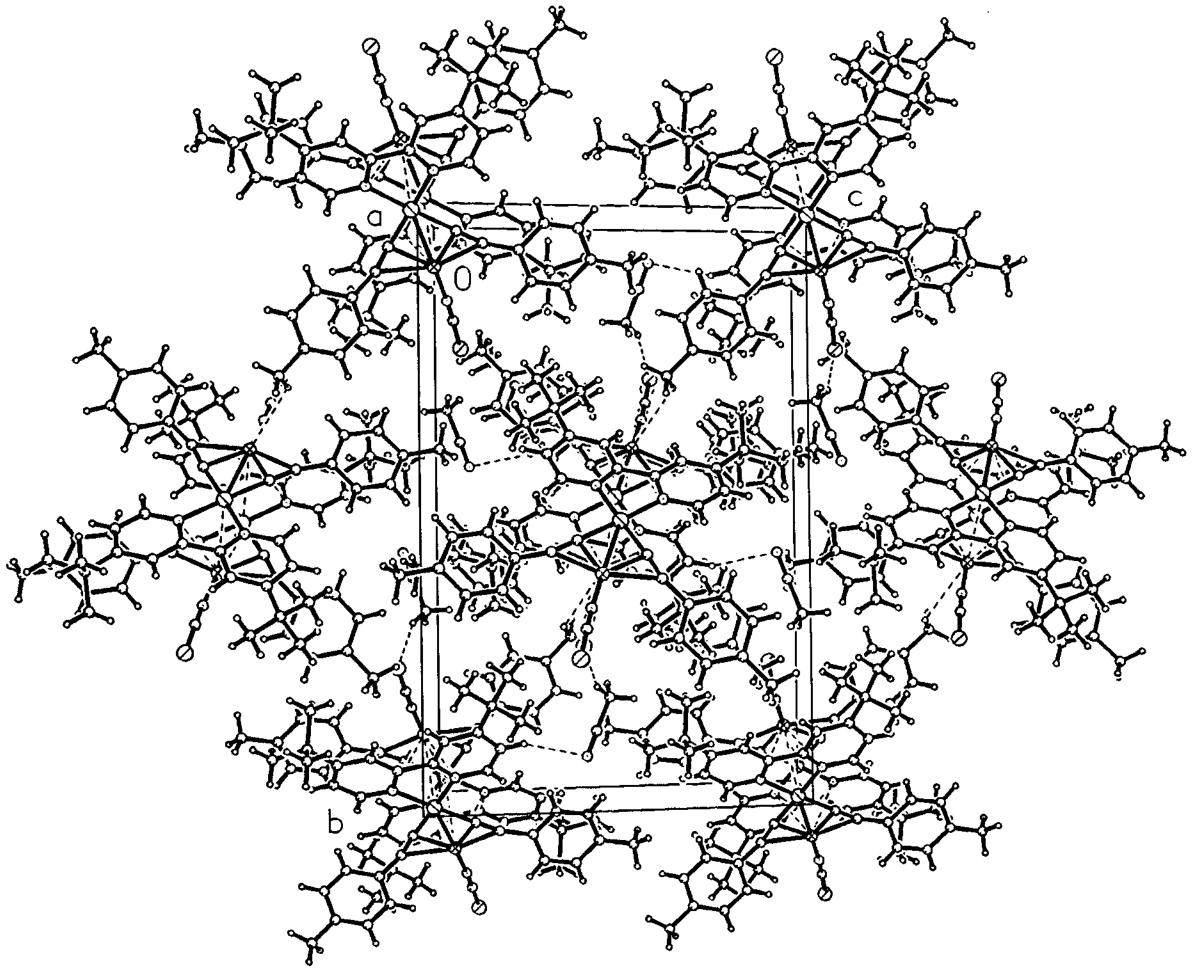


Fig. 2. The crystal packing in **2a**.MeCN, viewed down the *a* axis, showing the intermolecular interactions.

and so decomplexes upon formation, making the process irreversible. A similar pattern is seen for the bimetallic platinum–silver complex $[(^t\text{Bu}_2\text{bipy})\text{Pt}(\text{C}{\equiv}\text{CSiMe}_3)_2\text{Ag(SCN)}]$ **3b**, where the $\text{Ag}^{\text{I}} \rightarrow \text{Ag}^{\text{II}}$ appears at the lower potential of 0.85 V (Table 4). This couple has a lower redox potential than the analogous platinum–copper complexes **2**, and this would suggest that there is perhaps less stabilisation of the silver in the complex than in the copper complexes. The other silver complex **3a** was too insoluble to allow an electrochemical technique.

3. Conclusion

This study reveals the suitability of the bis-alkynyl platinum complexes **1** as co-ordinating agents for low oxidation state group 11 metal salts. The use of the *soft* co-ordinating thiocyanate anion affords the formation of di-nuclear bimetallic species and seems to preclude aggregation into the larger 2:1 or 2:2 species that have previously been isolated [17]. However, the complexes **2** and **3** can act as precursors for further controlled aggregation reactions, and the reactivity and removal of the thiocyanate group is under investigation.

4. Experimental

4.1. General procedures

Solvents were pre-dried and distilled from appropriate drying agents [18]. All chemicals, except where stated, were from commercial sources and used as received. The complexes (4,4′-bis-*tert*-butyl-2,2′-dipyridyl) platinum bis-alkynyls $[(^t\text{Bu}_2\text{bipy})\text{Pt}(\text{C}{\equiv}\text{CR})]$ ($\text{R} = \text{C}_6\text{H}_4\text{Me}$ **1a**, SiMe_3 **1b**) [7] were prepared via modified literature procedures. NMR spectra were recorded on a Bruker WM-250 or AM-400 spectrometer in appropriate solvents. The ^{1}H- and $^{13}\text{C}\{^1\text{H}\}$-NMR spectra were referenced to internal solvent resonances. Infrared spectra were recorded in CH_2Cl_2 solutions, in a NaCl cell, on a Perkin–Elmer 1710 Fourier Transform IR spectrometer, and mass spectra on a Kratos

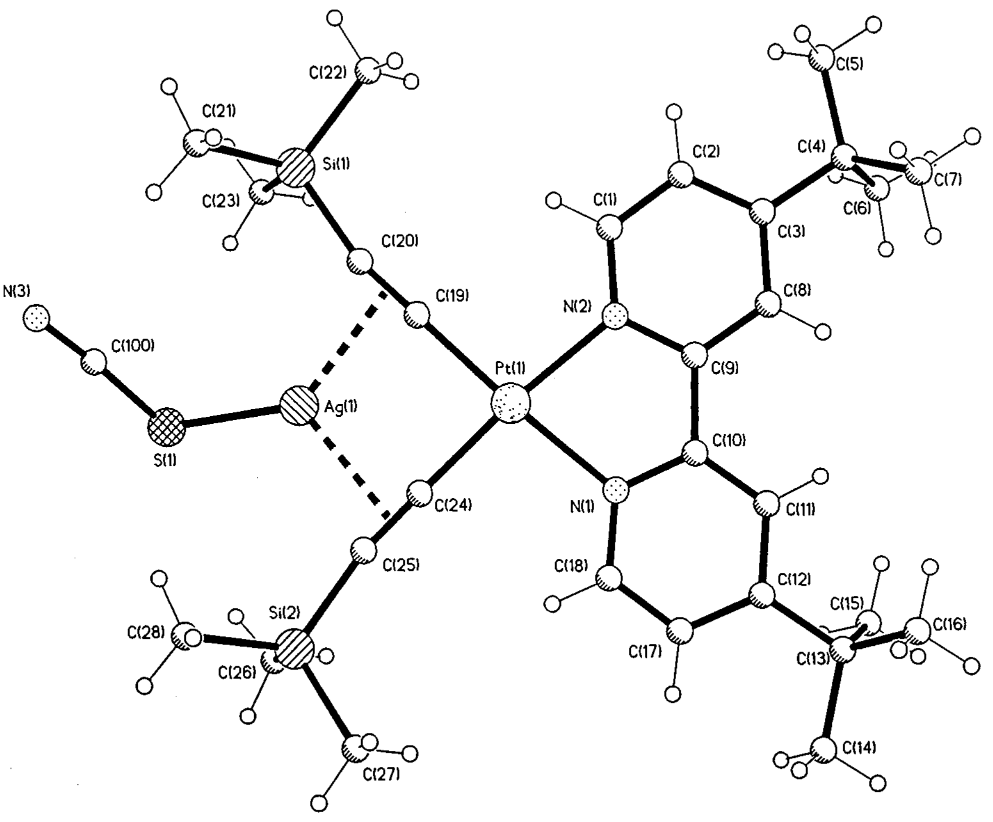


Fig. 3. The molecular structure of [(^{t}Bu$_2$bipy)Pt(C≡CSiMe$_3$)Ag(SCN)] **3b** showing the atom numbering scheme.

MS890 spectrometer by fast atom bombardment techniques. Electronic absorption spectra were obtained with a Perkin–Elmer Lambda UV/NIR spectrometer. Microanalyses were performed in the Department of Chemistry, University of Cambridge. The electrochemical measurements were recorded on an Autolab PGSTAT 20 potentiostat with a standard three-electrode system (platinum working and auxiliary electrodes and Ag/AgCl reference electrode). The electrochemical experiments were measured at 298 K using 0.5 M [NBu$_4$][BF$_4$]/CH$_2$Cl$_2$ (solvent dried over CaH$_2$) solution as supporting electrolyte, and all solutions were N$_2$-purged. All electrochemical measurements were referenced against the ferrocene/ferrocenium redox couple ($E_{1/2} = 0.55$ V vs. Ag at 298 K in 0.5 M [NBu$_4$][BF$_4$]/CH$_2$Cl$_2$).

4.2. Complex preparations

4.2.1. [(^{t}Bu$_2$bipy)Pt(C≡CC$_6$H$_4$Me)$_2$Cu(NCS)] **2a**

[(^{t}Bu$_2$bipy)Pt(C$_2$C$_6$H$_4$Me)$_2$] **1a** (0.075g, 0.108 mmol) and [Cu(SCN)] (0.026 g, two equivalents) were stirred for 1 h in 20 cm^3 of acetonitrile. The solution was filtered, and the filtrate extracted with dichloromethane. This extract was filtered through celite. Addition of acetonitrile and slow evaporation of the solution gave **2a** as very pale green crystals (0.071 g, 76%). Anal. Calc. for C$_{37}$H$_{38}$N$_3$CuPtS: C, 54.5; H, 3.93; N, 5.15. Found: C, 53.97; H, 4.58; N, 4.48%.

Table 3
Selected bond lengths (Å) and angles (°) for [(^{t}Bu$_2$bipy)Pt(C≡CSiMe$_3$)Ag(SCN)] **3b**

Bond lengths (Å)			
Pt(1)–N(1)	2.070(6)	Pt(1)–N(2)	2.068(6)
Pt(1)–C(19)	1.970(8)	Pt(1)–C(24)	1.960(8)
Ag(1)–S(1)	2.422(2)	S(1)–C(100)	1.674(9)
C(100)–N(3)	1.157(10)	Ag(1)–C(19)	2.426(7)
Ag(1)–C(20)	2.459(8)	Ag(1)–C(24)	2.458(8)
Ag(1)–C(25)	2.536(7)	C(19)–C(20)	1.224(11)
C(24)–C(25)	1.232(10)	C(20)–Si(1)	1.837(9)
C(25)–Si(2)	1.840(8)		
Bond angles (°)			
N(1)–Pt(1)–N(2)	79.0(2)	C(19)–Pt(1)–C(24)	87.0(3)
N(1)–Pt(1)–C(19)	174.8(3)	N(1)–Pt(1)–C(24)	96.2(3)
N(2)–Pt(1)–C(19)	97.7(3)	N(2)–Pt(1)–C(24)	174.7(3)
S(1)–Ag(1)–C(19)	153.3(2)	S(1)–Ag(1)–C(24)	139.2(2)
S(1)–Ag(1)–C(20)	124.9(2)	S(1)–Ag(1)–C(25)	111.5(2)
Ag(1)–S(1)–C(100)	105.3(3)	S(1)–C(100)–N(3)	174.7(7)
Pt(1)–C(19)–C(20)	176.3(7)	Pt(1)–C(24)–C(25)	178.9(7)
C(19)–C(20)–Si(1)	166.2(7)	C(24)–C(25)–Si(2)	170.7(7)

Table 4
Redox potentials for the heterometallic compounds

	E_{red} (V) (reversible)	E_{ox} (V) (irreversible)
[(^{t}Bu$_2$bipy)Pt(C≡CC$_6$H$_4$Me)-Cu(NCS)] **2a**	−1.36	1.07
[(^{t}Bu$_2$bipy)Pt(C≡CSiMe$_3$)-Cu(NCS)] **2b**	−1.29	1.25
[(^{t}Bu$_2$bipy)Pt(C≡CSiMe$_3$)-Ag(SCN)] **3b**	–	0.85

4.2.2. [(^{t}Bu$_2$bipy)Pt(C≡CSiMe$_3$)$_2$Cu(NCS)] 2b

[(^{t}Bu$_2$bipy)Pt(C$_2$SiMe$_3$)$_2$] **1b** (0.088 g, 0.134 mmol) and [Cu(SCN)] (0.042 g, two equivalents) were stirred for 4 h in 10 cm^3 of acetonitrile. The solution was filtered, and the filtrate extracted with dichloromethane. This extract was filtered through celite. Addition of acetonitrile and slow evaporation of the solution gave **2b** as very pale green crystals (0.035 g, 33%). Anal. Calc. for $C_{29}H_{42}N_3CuPtSSi_2$: C, 44.6; H, 5.44; N, 5.40. Found: C, 44.72; H, 5.37; N, 5.46%.

4.2.3. [(^{t}Bu$_2$bipy)Pt(C≡CC$_6$H$_4$Me)$_2$Ag(SCN)] 3a

[(^{t}Bu$_2$bipy)Pt(C$_2$C$_6$H$_4$Me)$_2$] **1a** (0.057 g, 0.082 mmol) and [Ag(SCN)] (0.013 g, one equivalent) were stirred for 4 h in 10 cm^3 of acetonitrile. The solution was filtered, and the product isolated as a bright yellow solid (0.050 g, 63%). Anal. Calc. for $C_{37}H_{38}N_3AgPtS$: C, 51.74; H, 4.46; N, 4.90. Found: C, 50.97; H, 4.66; N, 4.54%.

4.2.4. [(^{t}Bu$_2$bipy)Pt(C≡CSiMe$_3$)$_2$Ag(SCN)] 3b

[(^{t}Bu$_2$bipy)Pt(C$_2$SiMe$_3$)$_2$] **1b** (0.058 g, 0.088 mmol) and [Ag(SCN)] (0.014 g, one equivalent) were stirred for 24 h in 10 cm^3 of acetonitrile. The solution was filtered, and the filtrate extracted with dichloromethane. This extract was filtered through celite. Addition of acetonitrile and slow evaporation of the solution gave **3b** as very pale green crystals (0.064 g, 88%). Anal. Calc. for $C_{29}H_{42}N_3AgPtSSi_2$: C, 42.33; H, 5.15; N, 5.10. Found: C, 42.94; H, 5.19; N, 5.10%.

4.3. Crystallography

Suitable single crystals of **2a**.MeCN and **3b** were mounted on glass fibres, straight from solution, using perfluorocarbon oil (which protects the crystal from atmospheric oxygen and moisture) [19], and immediately cooled to 150 K on a Rigaku AFC5R diffractometer equipped with an Oxford Cryostream cooling apparatus. Data were recorded using graphite monochromated Mo–K$_\alpha$ radiation and an $\omega-2\theta$ scan procedure. Data were corrected for absorption using a semi-empirical method based on Ψ scans. Details of crystal data, data collection parameters and structure refinement are summarised in Table 5. The structures were solved by Patterson techniques [20] and by subsequent Fourier-difference syntheses, and refined by full-matrix least squares on F^2 [21], with all non-hydrogen atoms assigned anisotropic displacement parameters. Hydrogen atoms were placed in idealised positions and allowed to ride on the relevant carbon atom; aromatic H-atoms were assigned an isotropic displacement parameter that was 1.2 times that of the associated carbon atom, and methyl H-atoms were assigned a value that was 1.5 times that of the associated carbon atom. For each structure, in the final cycles of refine-

Table 5
Crystallographic data for **2a**.MeCN and **3b**[a]

Complex	**2a**.MeCN	**3b**
Molecular formula	$C_{39}H_{41}CuN_4PtS$	$C_{29}H_{42}AgN_3PtSSi_2$
M	856.45	823.86
Crystal system	Monoclinic	Triclinic
a (Å)	10.123(2)	11.694(4)
b(Å)	23.409(5)	14.569(5)
c (Å)	15.331(3)	11.456(5)
α (°)	90	111.50(3)
β (°)	103.00(3)	112.07(3)
γ (°)	90	81.86(3)
U (Å^3)	3539.9(12)	1682.9(11)
Space group	$P2_1/n$	$P\bar{1}$
Z	4	2
D_c (Mg m^{-3})	1.607	1.626
Crystal size (mm)	0.18 × 0.12 × 0.11	0.30 × 0.20 × 0.20
Crystal habit	Yellow block	Pale green block
F(000)	1704	812
μ (mm^{-1})	4.640	4.888
Maximum, minimum relative transmission	0.869, 1.000	0.748, 1.000
Data collection range (°)	$5<2\theta<50$	$6<2\theta<55$
Index ranges	$0\leq h\leq 12$ $0\leq k\leq 27$ $-18\leq l\leq 17$	$0\leq h\leq 15$ $-18\leq k\leq 18$ $-14\leq l\leq 13$
Reflections measured	6576	8101
Independent reflections	6204 ($R_{int}=0.108$)	7723 ($R_{int}=0.057$)
Parameters	424	345
wR_2 (all data)[b]	0.1630	0.1042
x, y[b]	0.0428, 0.00	0.018, 5.39
R_1 [$I>2\sigma(I)$][b]	0.0473	0.0439
Observed reflections	3654	5489
Goodness-of-fit on F^2 (all data)[b]	0.985	1.027
Maximum shift (σ)	0.001	0.001
Peak, hole in final difference map (e Å^{-3})	0.998, −1.250	0.998, −1.393

[a] Data in common: graphite-monochromated Mo–K$_\alpha$ radiation, $\lambda=0.71073$ Å, $T=150(2)$ K.

[b] $R_1=\Sigma\|F_o|-|F_c\|/\Sigma|F_o|$, $wR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^4]^{1/2}$, $w=1/[\sigma^2(F_o)^2+(xP)^2+yP)$, $P=(F_o^2+2F_c^2)/3$, where x and y are constants adjusted by the program; Goodness-of-fit $=[\Sigma[w(F_o^2-F_c^2)^2]/(n-p)]^{1/2}$ where n is the number of reflections and p the number of parameters.

ment, a weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$ where $P = (F_o^2 + 2F_c^2)/3$ was introduced which gave a relatively flat analysis of variance.

Additional material, comprising atomic co-ordinates, full listings of bond lengths and angles, and hydrogen atom co-ordinates, is available from the Cambridge Crystallographic Data Centre, Cambridge, UK.

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