

Heteroleptic silver(I) and zinc(II) bis(phenanthroline) complexes

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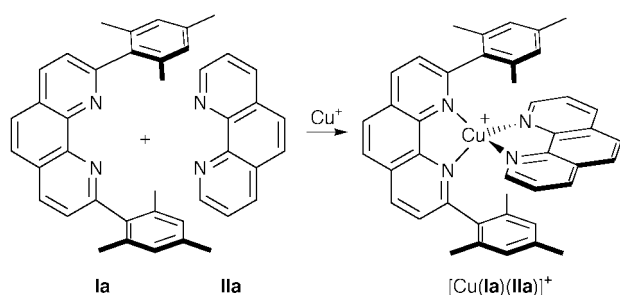
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Using sterically hindered 2,9-diarylphenanthrolines (**I**) as well as unsubstituted or 4,7-disubstituted phenanthrolines (**II**) the first preparation of open chain heteroleptic bis(phenanthroline) complexes $[M(I)(II)]^{n+}$ with $M = Ag^+$ or Zn^{2+} has been realised. Their structure was confirmed by electrospray MS, NMR and in one case X-ray data. With two sets of phenanthroline ligands, three stereoisomers of $[M(I)(II)]^+$ were detected in the silver(I) and for comparative reasons in the corresponding copper(I) complexes. On the basis of NMR experiments these were assigned as *in-in*, *in-out* and *out-out* isomers.

Introduction

Over the last years, transition metal ion complexes have found widespread use in supramolecular chemistry to fabricate structurally well defined assemblies.¹ In this context metal ions fostering either octahedral or tetrahedral co-ordination of ligands² have received conspicuous attention. With regard to tetrahedral frameworks the most prominent examples from the literature rely on copper(I) ions as templating species, but silver(I) complexes can also be found frequently.³ Much less attention has been attributed to zinc(II),⁴ which, however, plays a key role as the metal centre in porphyrin assemblies.⁵

We recently developed a procedure to prepare defined heteroleptic (mixed) copper(I) bis(phenanthroline) complexes based on the fine interplay of steric and electronic factors of the ligands involved.⁶ Our strategy makes use of sterically hindered 2,9-diarylphenanthrolines, such as **Ia**, which despite a strong thermochemical driving force cannot form a 2:1 complex with copper(I) ions because of steric reasons. Hence, only a 1:1 complex is obtained that can readily be treated with a less hindered ligand, such as phenanthroline **IIa**, to afford solely the bisheteroleptic compound $[Cu(Ia)(IIa)]^+$ in a basically quantitative yield (Scheme 1).^{6a} Rewardingly, this methodology has



Scheme 1

been utilised by others⁷ for the fabrication of luminescent copper(I) bis(phenanthroline) complexes.⁸

Moreover, the clean formation of heteroleptic copper(I) complexes is paving the way to the controlled self-assembly of

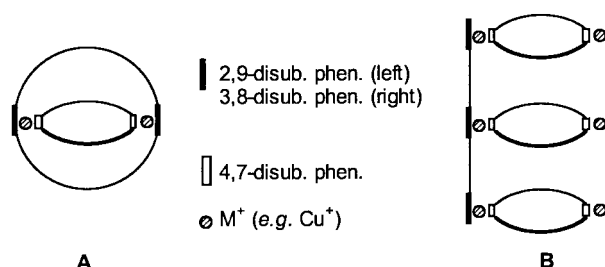


Chart 1 Heteroleptic bis(phenanthroline) complexes as key building blocks for the construction of ring-in-ring structures (**A**) and double or triple deckers (**B**).

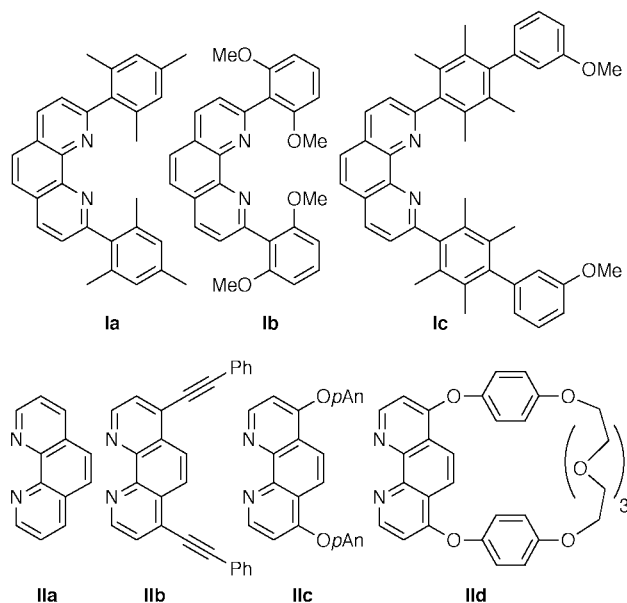
supramolecular structures as depicted in Chart 1, some of which have been realised in the meantime.^{6b,9} As our main interest is directed towards the construction of redoxactive supramolecular boxes^{6b} with a defined interior the question arose as to whether other metal ions, for example with a higher redox potential, larger radius or a higher charge, would equally comply with our method. Therefore, we now describe our investigations on using other d¹⁰ metal ions resulting in the first preparation of open chain heteroleptic (mixed) silver(I) and zinc(II) bis(phenanthroline) complexes. So far, only heteroleptic complexes had been prepared, whose synthesis relied on geometrical constraints brought about by the macrocyclic endotopic phenanthroline co-ordination sites.¹⁰ To support the viability of our concept we present the first crystal structure of a heteroleptic silver(I) bis(phenanthroline) complex.

Results and discussion

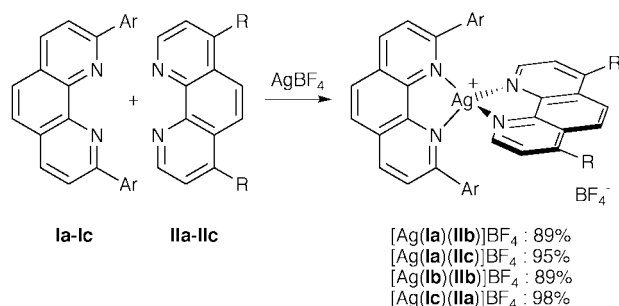
As described earlier,^{6a} one set of the phenanthroline ligands has to carry sterically bulky aryl groups at positions 2 and 9 (Chart 2, see compounds **Ia–Ic**) that impede the formation of the bishomoleptic complex. The other set of phenanthrolines can be varied in a wide range, but so far we have mostly concentrated on 4,7-disubstituted systems, such as **IIb–IIId**. Their preparation has been described elsewhere.¹¹

Table 1 Characteristic ^1H NMR chemical shifts of free **Ia** and **Ib** and in $[\text{Ag}(\text{Ia})(\text{Ib})]^+$

	δ_{H} (phenanthroline)				δ_{H} (aryl)	
	2,9-H	4,7-H	5,6-H	3,8-H	Aryl H	Me
Free Ia	—	8.28	7.86	7.57	6.93	2.31, 2.13
Ia in $[\text{Ag}(\text{Ia})(\text{Ib})]^+$	—	8.65	8.17	7.78	6.31	1.92, 1.72
Free Ib	9.16	—	8.46	7.80	7.70, 7.45	—
Ib in $[\text{Ag}(\text{Ia})(\text{Ib})]^+$	8.56	—	8.53	7.89	7.74, 7.49	—

**Chart 2** $p\text{An} = p\text{-anisyl}$.**Silver(I) complexes**

Rewardingly, the transfer of our concept to silver(I) bis(phenanthroline) complexes proved to be straightforward. When we mixed equivalent amounts of silver(I) tetrafluoroborate with the sterically shielded ligands **Ia–Ic** in a mixture of methanol–dichloromethane and added the less hindered ligands **IIa–IIc** the quantitative formation of the heteroleptic complexes was observed (Scheme 2). The products could readily be isolated

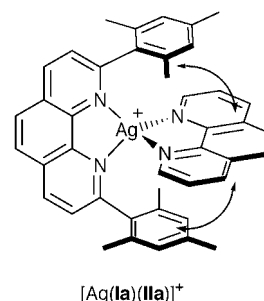
**Scheme 2**

by removing the solvent to furnish the analytically pure compounds after recrystallisation. The complexes were stable in the solid as well as in the solution state for several days or even longer if stored under an inert atmosphere.

The structure of the complexes could be demonstrated convincingly by electrospray (ES)-MS analysis. Notably, only the molecular ions corresponding to the heteroleptic compounds were detected, but none of the homoleptic complexes. In tandem MS experiments daughter ions were observed that resulted exclusively from loss of one phenanthroline **II** ligand. Thus, for example, the collision activated dissociation of $[\text{Ag}(\text{Ia})(\text{IIc})]^+$ at m/z 947.1 resulted in the formation of an ion peak at m/z 523.9

corresponding to the fragment $[\text{Ag}(\text{Ia})]^+$. Such fragmentation patterns are consistent with other investigations on the stability of phenanthroline adducts $[\text{M}(\text{L})]^+$, as those with **L** representing a phenanthroline with aryl groups in 2,9 positions showed a higher stability than adducts with 4,7-disubstituted ligands.¹² In addition, the isotopic pattern of the molecular ions is in accordance with the calculated one for the heteroleptic species.

Moreover, the ^1H NMR spectra of the new complexes display characteristic chemical shifts. To illustrate some distinctive shifts, data for complex $[\text{Ag}(\text{Ia})(\text{Ib})]^+$ are depicted in Table 1. Owing to the pseudo-tetrahedral co-ordination of the two phenanthroline ligands, the arene substituents of ligands **I** are situated below and above the aromatic plane of the second phenanthroline ligand **II**. As a consequence the arene-H and arene- CH_3 ^1H NMR signals experience a strong high field shift due to the shielding of **II**. *Vice versa*, while the binding of **Ia** to the silver(I) ion results in sizeable lowfield shifts for all protons at the phenanthroline core, this is not the case for the phenanthroline **Ib** protons in the heteroleptic complex since they experience the shielding of the mesityl groups of **Ia** (Chart 3).

**Chart 3** π - π Interactions between 2,9-mesityl groups and phenanthroline **IIa**.

After several days of exposure to daylight the compounds changed from a light yellow to brown, indicating a photochemical reaction that is characteristic of silver(I) phenanthroline complexes.¹³

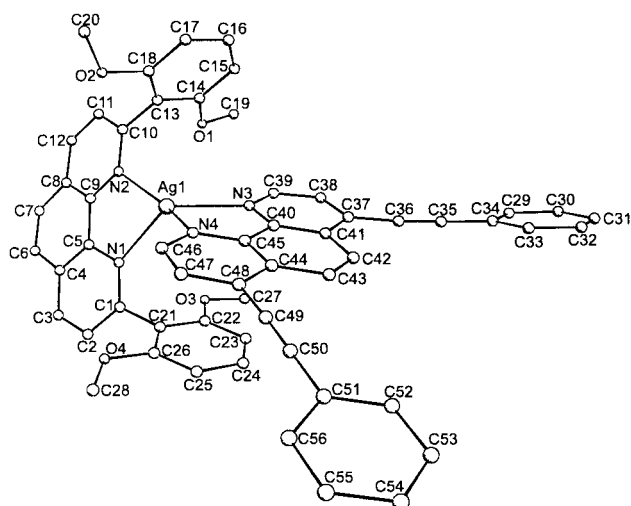
In order to investigate the potential of the silver complexes as redox relays, their oxidation potentials were investigated by cyclic voltammetry. Of the new complexes, $[\text{Ag}(\text{Ia})(\text{IIb})]\text{BF}_4$ and $[\text{Ag}(\text{Ib})(\text{IIb})]\text{BF}_4$ both display a reversible oxidation wave in dichloromethane at $E_{1/2}^{\text{ox}} = +1.28$ and $+1.04$ V,[†] respectively. These potentials are about 1.0 V higher than the oxidation potentials of the corresponding copper(I) complexes ($+0.30$ and $+0.04$ V respectively).^{11a} When compared to the homoleptic complex $[\text{Ag}(\text{IIa})_2]^+$ ¹⁴ the shielding of the silver ion by the 2,9-aryl groups in phenanthroline **Ia, Ib** leads to a higher oxidation potential for $[\text{Ag}(\text{Ia})(\text{IIb})]^+$ and $[\text{Ag}(\text{Ib})(\text{IIb})]^+$.

In contrast, the silver(I) complexes with ligands containing remote methoxy groups display an irreversible oxidation wave, *i.e.* $E_{\text{pa}} = +1.50$ V for $[\text{Ag}(\text{Ia})(\text{IIc})]\text{BF}_4$ and $+0.94$ V for $[\text{Ag}(\text{Ic})(\text{IIa})]\text{BF}_4$. Additionally, strong deposition on the electrode was observed upon oxidation of these complexes. There are two

[†] All potentials are referenced to the ferrocene–ferrocenium redox couple unless otherwise noted. To obtain values *vs.* SCE, simply add $+0.39$ V.

Table 2 Selected bond lengths (Å) and angles (°) of [Ag(Ib)(IIb)]BF₄

Ag–N(1)	2.374(2)	N(1)–Ag–N(2)	72.6(1)
Ag–N(2)	2.266(2)	N(1)–Ag–N(3)	126.7(1)
Ag–N(3)	2.316(3)	N(1)–Ag–N(4)	109.7(1)
Ag–N(4)	2.312(3)	N(2)–Ag–N(3)	129.1(1)
		N(2)–Ag–N(4)	152.9(1)
		N(3)–Ag–N(4)	72.4(1)

**Fig. 1** Crystal structure of [Ag(Ib)(IIb)]⁺.

mechanistic scenarios for such a behaviour. Either the phenanthroline ligand is oxidised at a lower potential than that of Ag⁺, or after oxidation of Ag⁺ to Ag²⁺ the silver(II) acts as an oxidant for the donor substituted arene groups which undergo irreversible follow-up reactions after intramolecular electron transfer.

Crystals, suitable for X-ray analysis, could be obtained from a dichloromethane–diethyl ether solution of [Ag(Ib)(IIb)]⁺. The crystal structure (Fig. 1) shows a distorted pseudo-tetrahedral geometry of the two phenanthroline ligands with respect to the silver(I) ion. Bond lengths (Table 2) for Ag^I–N range from 2.27 to 2.37 Å; hence, they are comparable with those of other silver(I) bis(imine) complexes, for example, the bishomoleptic complex of 2,9-dimethyl-1,10-phenanthroline [Ag(III)₂]⁺ (*i.e.* 2.25–2.41 Å)⁴ or a recently reported silver(I) complex containing the 6,6'-diphenyl-2,2'-bipyridine ligand [Ag(IV)₂]⁺ (*i.e.* 2.30–2.40 Å).^{3b}

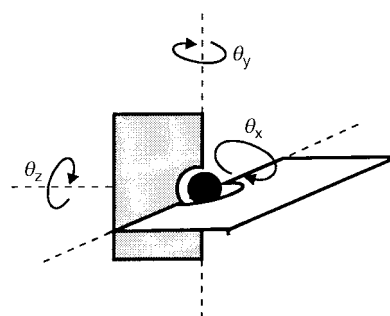
It is characteristic for all complexes that one Ag–N bond length is considerably shorter and another equally longer, indicating a certain degree of distortion. The “bite” angle between the two nitrogen atoms at the same ligand and silver(I) of 72.6° is not out of the ordinary, in contrast to the angles between two nitrogen atoms at two ligands and silver(I). Here, a stronger distortion than in comparable complexes can be observed.

The deviation from the ideal tetrahedral D_{2d} geometry can be stated more clearly in terms of the angles θ_x , θ_y and θ_z , as defined by Dobson *et al.*¹⁵ (Table 3, Fig. 2). A distortion from the ideal tetrahedral geometry (θ_x , θ_y and $\theta_z = 90^\circ$) is observed in all three directions. Whereas the deviation of θ_x can be neglected in [Ag(III)₂]⁺, it is more pronounced in [Ag(Ib)(IIb)]⁺ and [Ag(IV)₂]⁺, both complexes containing aryl groups flanking the chelating sites. This effect may originate from aromatic π – π interactions,^{6a,7,16} for example between the phenanthroline moiety of IIb and one arene substituent of Ib (Fig. 1). Indeed, a closer inspection of [Ag(Ib)(IIb)]⁺ indicates that there is an almost perfect coplanar arrangement of the phenanthroline core of IIb with one dimethoxyphenyl group of Ib (bite angle of 2°) at a phenanthroline–phenyl distance of 345 pm.

All three complexes show conspicuous distortions along the angles θ_y and θ_z to varying degrees. In spite of different sub-

Table 3 Distortion angles (°) of [Ag(Ib)(IIb)]BF₄ in comparison to other silver(I) complexes (Chart 4)^{3b,4}

Angle	[Ag(Ib)(IIb)] ⁺	[Ag(III) ₂] ⁺ ⁴	[Ag(IV) ₂] ⁺ ^{3b}
θ_x	97.1	91.2	96.1
θ_y	107.9	111.4	105.3
θ_z	110.6	103.6	109.8

**Fig. 2** Distortion of tetrahedral bis(phenanthroline) complexes.¹⁵

stituents at the ligands (four Me in [Ag(III)₂]⁺, four Ph in [Ag(IV)₂]⁺, two aryl in [Ag(Ib)(IIb)]⁺), the distortions are comparable.

Zinc(II) complexes

Zinc(II) has the ability to expand its co-ordination sphere and hence is known to react with phenanthrolines to form the corresponding bis-⁴ and/or tris-¹⁷phenanthroline complexes. It was hoped that the shielding exerted by the large 2,9-aryl groups in phenanthroline I would prevent formation of the tris-(phenanthroline) complexes and lead exclusively to tetrahedral bisheteroleptic complexes when using the weakly co-ordinating tetrafluoroborate counter ion.

As a consequence, we studied the synthesis of the corresponding Zn²⁺ complexes using the ligands depicted in Chart 2. The co-ordination processes were easily followed by ¹H NMR spectroscopy. Treating zinc(II) tetrafluoroborate in methanol with equimolar amounts of Ia and IIa in dichloromethane furnished the heteroleptic complex [Zn(Ia)(IIa)][BF₄]₂ in a yield of 73%. Likewise, the reaction of Zn²⁺ with equimolar amounts of Ic and IIa afforded the heteroleptic complex [Zn(Ic)(IIa)][BF₄]₂ in a yield of 93%. Again, the heteroleptic products were identified unambiguously by characteristic chemical shifts in the ¹H NMR spectrum and by elemental analysis.

However, in contrast to the situation with the copper(I) and silver(I) complexes, the bisheteroleptic zinc(II) complexes are apparently formed under kinetic control as evidenced by ES-MS and NMR investigations on aged solutions. Owing to follow-up equilibria the solution of [Zn(Ia)(IIa)][BF₄]₂ exhibited besides the expected signal at *m/z* 330.5 a further signal at *m/z* 301.9 (about 10%) that could be ascribed to the tris-homoleptic product [Zn(IIa)₃]²⁺. With [Zn(Ic)(IIa)]²⁺ rapid follow-up equilibrations were even more pronounced. ES-MS analysis displayed the heteroleptic complex [Zn(Ic)(IIa)]²⁺ only in traces, whereas the fragment [Zn(Ic)(H₂O)_{*n*}]²⁺ as well as [Zn(IIa)₃]²⁺ appeared as the main products. Hence, for the clean preparation of the heteroleptic complex it was advisable to remove the solvent as soon as the second ligand II was added. Otherwise, the homoleptic complexes were increasingly afforded.

Using ligand Ib as a control element the heteroleptic complex [Zn(Ib)(IIb)]²⁺ was only found in traces according to the ¹H NMR spectrum. As the main product the bishomoleptic complex [Zn(Ib)₂]²⁺ was detected by NMR as well as ES-MS analysis at *m/z* 485.2, beside a large amount of free IIb. After a few hours in solution the heteroleptic compound disappeared completely.

Table 4 Chemical shifts (δ) of the protons of the arene group of **Ic** in $[\text{Cu}(\text{Ic})(\text{IIId})]^+$ in CD_2Cl_2 at 600 MHz, assigned by HH-COSY experiment

	2''-H ^a	4''-H	5''-H	6''-H ^b
A	6.38	6.77	7.28	5.26
B	6.38	6.77	7.28	5.29
C	5.37	6.77	7.23	6.38
D	5.42	6.77	7.23	6.38

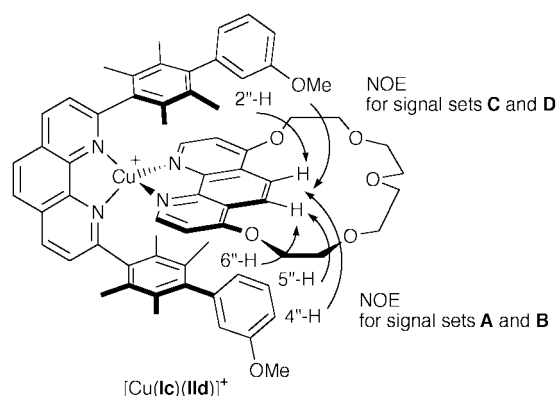
^a Singlet. ^b Doublet.

It is interesting that for zinc(II) ions the controlled formation of heteroleptic bis(phenanthroline) complexes cannot be achieved with ligand **Ib** although with copper(I) and silver(I) the heteroleptic complexes were readily isolable. Since the ion radii of zinc(II) and copper(I) ions are basically identical one can postulate that due to the higher Lewis acidity of zinc(II) co-ordination to the methoxy groups will become important. As the methoxy groups in **Ib** do not prevent the formation of homoleptic bis(phenanthroline) complexes, predominantly $[\text{Zn}(\text{Ib})_2]^{2+}$ is formed.

Stereoisomers of heteroleptic complexes

With complex $[\text{Ag}(\text{Ic})(\text{IIa})]\text{BF}_4$ an interesting phenomenon was observed. Each hydrogen of the methoxy substituted arene of **Ic** appeared as a set of four distinct signals **A**, **B**, **C** and **D** in the ^1H NMR, a phenomenon which was also observed, though to a minor degree, with signals stemming from the phenanthroline core. Nevertheless, the ES-MS as well as elemental analysis confirmed the high purity and the composition of the complex. In order to check whether this incident was related to the metal ion, we prepared the corresponding copper(I) complexes $[\text{Cu}(\text{Ic})(\text{IIa})]\text{PF}_6$ and $[\text{Cu}(\text{Ic})(\text{IIId})]\text{PF}_6$ according to a published method.^{11a} Analogously, four distinct sets of proton NMR signals were found for both copper complexes. As the splitting was most pronounced with $[\text{Cu}(\text{Ic})(\text{IIId})]\text{PF}_6$, a detailed NMR investigation was carried out with this complex, but the results are likewise valid for $[\text{Cu}(\text{Ic})(\text{IIa})]\text{PF}_6$ and $[\text{Ag}(\text{Ic})(\text{IIa})]\text{BF}_4$. The assignment of four different environments for the arene groups was carried out by HH-COSY experiments (Table 4). Notably, four singlets at δ 6.38, 6.38, 5.42 and 5.37 can be assigned to the protons in 2'' position, while four doublets at δ 6.38, 6.38, 5.29 and 5.26 correspond to the protons in 6'' position.

In a NOESY experiment on the complex $[\text{Cu}(\text{Ic})(\text{IIId})]^+$ two signal sets of the four that can be assigned to the proton in 2'' displayed an Overhauser effect with the 5,6-protons of phenanthroline **IIId** (**C** and **D** in Chart 4). Conversely, for the two

**Chart 4** Schematic representation of some selected Nuclear Overhauser Effects (NOEs) in $[\text{Cu}(\text{Ic})(\text{IIId})]^+$.

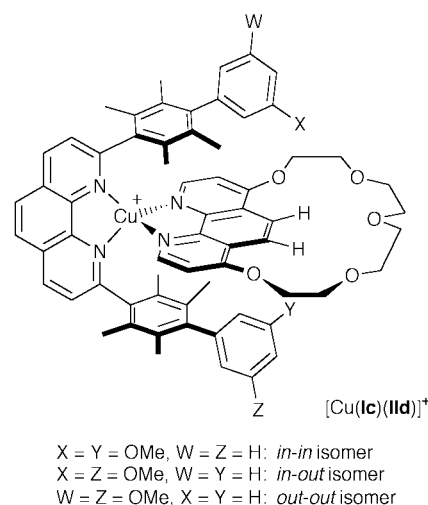
other sets (**A** and **B**) the protons in 5'' and 6'' position showed a weak interaction with the 5,6-protons of ligand **IIId**.

The possibility to have atropisomers at the duryl methoxy-

Table 5 Distribution (%) of isomers (determined by NMR spectroscopy) in complexes $[\text{M}(\text{Ic})(\text{II})]^+$

Heteroleptic complex	Isomer		
	out-out	in-out	in-in
$[\text{Cu}(\text{Ic})(\text{IIa})]\text{PF}_6$	29	51	20
$[\text{Cu}(\text{Ic})(\text{IIId})]\text{PF}_6$	31	40	29
$[\text{Ag}(\text{Ic})(\text{IIa})]\text{BF}_4$	11	46	43

phenyl linkage would mean that the observed set of four proton NMR signals at the methoxyphenyl unit may be attributed to different stereoisomers. According to the crystal structure data on a heteroleptic 2,9-dimesitylphenanthroline copper(I) complex⁷ an almost orthogonal orientation of the two phenanthroline units in complex $[\text{Cu}(\text{Ic})(\text{IIId})]^+$ is likely. Indeed, when we draw $[\text{Cu}(\text{Ic})(\text{IIId})]^+$ in a simplified tetrahedral D_{2d} symmetric representation two orientations appear likely for each methoxy group; it should either point towards or away from the second phenanthroline (*cf.* Chart 5). Altogether, this gives rise to three stereoisomers, *in-in*, *in-out* and *out-out*.

**Chart 5** Various conformations of complex $[\text{Cu}(\text{Ic})(\text{IIId})]^+$.

Detailed NMR investigations support the above picture as four signal sets are to be expected for the three stereoisomers. Owing to the proximity of phenanthroline **IIId** the methoxy groups in the *in* conformation experience a stronger high field shift than those in the *out* position. Likewise, the different orientations of the methoxy phenyl group should account for the splitting of the aromatic protons, leading to a high field shift for protons which come close to the aromatic moiety of ligand **IIId**. The assignment of the various signals to the different isomers was carried out with the following considerations. Since the *in-out* isomer contains two methoxy phenyl groups in different electronic environments, one signal corresponding to 2''-H (singlet) and one to 6''-H (doublet) must exhibit the same integration. Indeed, the well separated signals **B** and **D** at δ 5.29 (6''-H) and 5.42 (2''-H) display the same integration indicating that signal sets **B** and **D** belong to one diastereomer, *i.e.* the *in-out* isomer. Since from the NOE experiments the signals belonging to set **A** must be assigned to the *out-out* isomer, set **C** can be assigned to the *in-in* isomer. This leads to the results depicted in Table 5.

In all three cases the predominant product is the *in-out* isomer. It is known that silver(I) phenanthroline complexes are kinetically labile so that in a mixture always the thermodynamically most stable complex is formed preferentially.^{3b,18} The same is true for copper(I) complexes.¹⁹ After a statistical correction for the occurrence of the *in-out* isomer, the *out-out* complex is slightly favoured for copper and the *in-in* complex for

silver. However, since the observed thermochemical difference within the three stereoisomers is so small (<2 kJ mol⁻¹) no further interpretation is reasonable.

Conclusion

Our concept to prepare heteroleptic bis(phenanthroline) complexes through steric and electronic control exerted by the ligands has successfully been extended from Cu⁺ to Ag⁺ and partly to Zn²⁺ complexes. With Zn^{II} the formation of heteroleptic bis(phenanthroline) complexes proved to be much more difficult; the tendency of Zn^{II} to assume different co-ordination numbers and geometries leads only initially to the desired complexes. Thereafter various species are formed by equilibration as evidenced by electrospray mass spectrometry.

Experimental

General

The ¹H and ¹³C NMR spectra were recorded on Bruker AC-200, AM-250 or DMX 600 instruments and calibrated with tetramethylsilane as an internal reference (TMS, δ 0.0), IR spectra on a Perkin-Elmer 1605 series FT-IR-spectrometer. Elemental analyses were measured on a Carlo Erba Elemental Analyzer 1106. Melting points were determined by using a Mettler FP5.0 apparatus. Electrospray (ES) MS spectra were recorded on a TSQ 7000 Triple-Quadrupol-Tandem-Mass spectrometer (Finnigan MAT) with Finnigan ESI-Interface. Data recording and evaluation was carried out using the ICIS 8.1 software package (Finnigan MAT). All reactions were carried out under an inert atmosphere. Solvents were dried using standard methods. Chemicals were purchased and used without further purification. Ligands were prepared as described earlier.^{11a,b}

Preparations

Silver(I) complexes. [Ag(Ia)(Iib)]BF₄. The salt AgBF₄ (23.4 mg, 120 μmol) was dissolved in methanol (3 cm³) and a solution of compound Ia (50.0 mg, 120 μmol) in dichloromethane (5 cm³) was added. After 10 min of stirring at room temperature a solution of Iib (45.6 mg, 120 μmol) in dichloromethane (5 cm³) was added. Instantaneously, the mixture assumed a yellow colour. After 1 h hexane was added to precipitate the product that was separated and dried. Yellow solid (105 mg, 89%), mp >250 °C (Found: C, 67.42; H, 5.27; N, 5.43. C₅₈H₄₄AgBF₄N₄·2H₂O requires C, 67.79; H, 4.71; N, 5.45%; $\tilde{\nu}_{\max}/\text{cm}^{-1}$ 3060w (aryl H), 2212s (≡CH), 1618m (C=C), 1588m (C=C), 1560s (C=C), 1509s (C=C), 1423s (CH₃), 1054 (B-F), 853s (aryl H), 752s (aryl H), 730m (aryl H) and 684s (aryl H); δ_{H} (200 MHz; CDCl₃) 1.72 (6 H, s, 4'-Me_{Ia}), 1.92 (12 H, s, 2'-Me_{Ia}, 6'-Me_{Ia}), 6.31 (4 H, s, 3'-H_{Ia}, 5'-H_{Ia}), 7.49 (6 H, m, 3'-H_{Iib}, 4'-H_{Iib}, 5'-H_{Iib}), 7.74 (4 H, m, 2'-H_{Iib}, 6'-H_{Iib}), 7.78 (2 H, d, *J* 8.4, 3-H_{Ia}, 8-H_{Ia}), 7.89 (2 H, d, *J* 4.8, 3-H_{Iib}, 8-H_{Iib}), 8.17 (2 H, s, 5-H_{Iib}, 6-H_{Iib}), 8.53 (2 H, s, 5-H_{Ia}, 6-H_{Ia}), 8.56 (2 H, d, *J* 4.8, 2-H_{Iib}, 9-H_{Iib}) and 8.65 (2 H, d, *J* 8.4 Hz, 4-H_{Ia}, 7-H_{Ia}); δ_{C} (63 MHz; CDCl₃) 19.3, 19.8, 84.2, 101.9, 121.5, 125.3, 125.8, 126.4, 127.1, 127.8, 127.9, 128.6, 128.8, 129.1, 130.2, 131.6, 132.2, 135.2, 138.1, 138.2, 138.7, 142.6, 149.5 and 160.4; *m/z* (ES-MS) 904.9 (M⁺).

[Ag(Ia)(Iic)]BF₄. According to the preparation of [Ag(Ia)(Iib)]⁺ the reaction of AgBF₄ (23.4 mg, 120 μmol), compound Ia (50.0 mg, 120 μmol) and Iic (50.9 mg, 120 μmol) afforded, after removal of the solvent, the product as a light yellow solid (117 mg, 95%), mp > 250 °C (Found: C, 61.24; H, 5.02; N, 5.10. C₅₆H₄₈AgBF₄N₄O₄·3.5H₂O requires C, 60.74; H, 4.55; N, 5.21%; $\tilde{\nu}_{\max}/\text{cm}^{-1}$ 2916m (CH), 1615m (C=C), 1587s (C=C), 1494s (C=C), 1444m (CH), 1426s (CH), 1403, 1281s (C-O), 1250s (C-O), 1203vs (C-O), 1056 (B-F), 989, 915s (aryl H), 846s (aryl H) and 729m (aryl H); δ_{H} (200 MHz; CDCl₃) 1.87 (12 H, s,

2'-Me_{Ia}, 6'-Me_{Ia}), 1.89 (6 H, s, 4'-Me_{Ia}), 3.86 (6 H, s, 4'-OMe_{Ic}), 6.38 (4 H, s, 3'-H_{Ia}, 5'-H_{Ia}), 6.81 (2 H, d, *J* = 5.5, 3-H_{Ic}, 8-H_{Ic}), 7.05 (4 H, d, *J* = 9.0, 3'-H_{Ic}, 5'-H_{Ic}), 7.18 (4 H, d, *J* = 9.0, 2'-H_{Ic}, 6'-H_{Ic}), 7.74 (2 H, d, *J* = 8.3, 3-H_{Ia}, 8-H_{Ia}), 8.16 (2 H, s, 5-H_{Ic}, 6-H_{Ic}), 8.25 (2 H, d, *J* = 5.5, 2-H_{Ic}, 9-H_{Ic}), 8.35 (2 H, s, 5-H_{Ia}, 6-H_{Ia}) and 8.66 (2 H, d, *J* = 8.3 Hz, 4-H_{Ia}, 7-H_{Ia}); δ_{C} (63 MHz; CDCl₃) 20.3, 21.1, 55.9, 107.0, 115.8, 119.7, 121.0, 122.1, 125.9, 127.1, 127.3, 128.1, 135.3, 138.1, 138.2, 139.0, 142.6, 143.3, 146.5, 151.3, 158.0, 160.2 and 163.3; *m/z* (ES-MS) 949.1 (M⁺); *m/z* (MS/MS of 947.1; -25 eV) 523.9 (Ag(Ia)⁺).

[Ag(Ib)(Iib)]BF₄. According to the preparation of [Ag(Ia)(Iib)]⁺ the reaction of AgBF₄ (23.4 mg, 120 μmol), compound Ib (54.2 mg, 120 μmol) and Iib (45.6 mg, 120 μmol) furnished after addition of hexane the product as a yellow solid (110 mg, 89%), mp >250 °C; $\tilde{\nu}_{\max}/\text{cm}^{-1}$ 2943w (CH), 2841w (OCH₃), 2209m (C≡C), 1599s (C=C), 1586s (C=C), 1560s (C=C), 1510s (C=C), 1474s (CH), 1436s (CH), 1251s (C-O), 1108vs (C-O), 1052vs (B-F), 855s (aryl H), 788m (aryl H), 758m (aryl H), 738m (aryl H) and 690m (aryl H); δ_{H} (200 MHz; CDCl₃) 3.45 (12 H, s, OMe_{Ib}), 5.83 (4 H, m, 3'-H_{Ib}, 5'-H_{Ib}), 6.62 (2 H, m, 4'-H_{Ib}), 7.49 (6 H, m, 3'-H_{Iib}, 4'-H_{Iib}, 5'-H_{Iib}), 7.75 (4 H, m, 2'-H_{Iib}, 6'-H_{Iib}), 7.78 (2 H, d, *J* = 8.4, 3-H_{Ib}, 8-H_{Ib}), 7.84 (2 H, d, *J* = 4.8, 3-H_{Iib}, 8-H_{Iib}), 8.04 (2 H, s, 5-H_{Iib}, 6-H_{Iib}), 8.40 (2 H, d, *J* = 4.8, 2-H_{Iib}, 9-H_{Iib}), 8.49 (2 H, d, *J* = 8.4 Hz, 4-H_{Ib}, 7-H_{Ib}) and 8.55 (2 H, s, 5-H_{Ib}, 6-H_{Ib}); δ_{C} (50 MHz; CDCl₃) 53.4, 80.2, 84.1, 101.9, 103.2, 121.4, 125.3, 126.3, 126.7, 127.5, 127.7, 128.5, 128.8, 128.9, 130.2, 131.5, 132.2, 137.3, 142.3, 149.6, 153.2, 155.3 and 157.8; *m/z* (ES-MS) 941.1 (M⁺); *m/z* (MS/MS of 939.2; -25 eV) 559.3 (Ag(Ib)⁺).

[Ag(Ic)(IIa)]BF₄. According to the preparation of [Ag(Ic)(Iib)]⁺ the reaction of AgBF₄ (23.4 mg, 120 μmol), compound Ic (78.7 mg, 120 μmol) and IIa (21.6 mg, 120 μmol) afforded after removal of the solvent a colourless solid (122 mg, 98%), mp >250 °C (Found: C, 66.19; H, 5.18; N, 5.38. C₅₈H₅₂AgBF₄N₄O₂·H₂O requires C, 66.36; H, 5.19; N, 5.34%; $\tilde{\nu}_{\max}/\text{cm}^{-1}$ 2918s (CH), 1586vs (C=C), 1551m (C=C), 1506s (C=C), 1493s (C=C), 1464s (CH), 1424s (CH), 1228s (C-O), 1142s (C-O), 1062 (B-F), 873s (aryl H), 847s (aryl H), 787s (aryl H) and 731s (aryl H); δ_{H} (200 MHz; CDCl₃) 1.16 (12 H, br, 3'-Me_{Ic}, 5'-Me_{Ic}), 1.86 (12 H, s, 2'-Me_{Ic}, 6'-Me_{Ic}), 3.46 + 3.66 + 3.81 (6 H, s, OMe_{Ic}), 4.29 + 4.88 (2 H, br, 2''-H_{Ic}, 6''-H_{Ic}), 6.31 + 6.36 (2 H, s, 2''-H_{Ic}, 6''-H_{Ic}), 6.68 (2 H, d, *J* = 8.1, 4''-H_{Ic}), 6.97 + 7.12 (2 H, t, *J* = 7.6 + 8.1, 5''-H_{Ic}), 7.78 (2 H, dd, ³*J* = 8.2, ³*J* = 4.60, 3-H_{IIa}, 8-H_{IIa}), 7.95 (2 H, dd, ³*J* = 8.2, ⁴*J* = 2.9, 4-H_{IIa}, 7-H_{IIa}), 8.11 (2 H, s, 5-H_{IIa}, 6-H_{IIa}), 8.25 (2 H, s, 5-H_{Ic}, 6-H_{Ic}), 8.51 (2 H, d, *J* = 8.1 Hz, 3-H_{Ic}, 8-H_{Ic}), 8.56 (2 H, dd, ³*J* = 4.6, ⁴*J* = 2.9, 2-H_{IIa}, 9-H_{IIa}) and 8.74 (2 H, d, *J* = 8.1 Hz, 4-H_{Ic}, 7-H_{Ic}); δ_{C} (63 MHz; CDCl₃) 17.0, 18.1, 55.1 + 55.4, 109.7, 111.8, 114.3, 115.7, 120.4, 121.1, 124.3, 125.8, 127.1, 127.6, 127.8, 128.8, 129.1, 129.2, 130.9, 131.8, 138.3, 138.7, 140.9, 142.0, 142.4, 142.6, 149.8, 159.3, 159.4 and 161.7; *m/z* (ES-MS) 945.1 (M⁺); *m/z* (MS/MS of 943.2; -25 eV) 763.4 (Ag(Ic)⁺).

Zinc(II) complexes. [Zn(Ia)(IIa)](BF₄)₂. The salt Zn(BF₄)₂·7H₂O²⁰ (87.6 mg, 240 μmol) was dissolved in methanol (5 cm³) and a solution of compound Ia (100 mg, 240 μmol) in dichloromethane (5 cm³) added. After 10 min of stirring at room temperature IIa (43.2 mg, 240 μmol) in dichloromethane (5 cm³) was added resulting in a yellow solution. After 1 h of stirring the solvent was removed *in vacuo* and the residual solid recrystallised from methanol. Yellow solid (145 mg, 73%), mp >250 °C (Found: C, 54.59; H, 4.44; N, 5.98. C₄₂H₃₆B₂F₈N₄Zn·5H₂O requires C, 54.49; H, 5.01; N, 6.05%; $\tilde{\nu}_{\max}/\text{cm}^{-1}$ 3078w (aryl H), 2919w (CH), 1611m (C=C), 1587m (C=C), 1561w (C=C), 1500w (C=C), 1434m (CH₃), 1384w (CH₃), 1062vs (B-F), 902w (aryl H), 873m (aryl H), 852m (aryl H) and 725m (aryl H); δ_{H} (200 MHz; CD₃CN) 1.43 (6 H, s, 4'-Me_{Ia}), 1.67 (12 H, s, 2'-Me_{Ia}, 6'-Me_{Ia}), 5.93 (4 H, s, 3'-H_{Ia}, 5'-H_{Ia}), 8.03 (2 H, dd, ³*J* = 8.3, ³*J* = 5.1, 3-H_{IIa}, 8-H_{IIa}), 8.16 (2 H, d, *J* = 8.3, 3-H_{Ia}, 8-H_{Ia}), 8.19 (2 H, s, 5-H_{IIa}, 6-H_{IIa}), 8.48 (2 H, s, 5-H_{Ia},

6-H_{Ia}), 8.69 (2 H, dd, ³*J* = 5.1, ⁴*J* = 1.4, 2-H_{Ia}, 9-H_{Ia}), 8.87 (2 H, dd, ³*J* = 8.3, ⁴*J* = 1.4, 4-H_{Ia}, 7-H_{Ia}) and 9.12 (2 H, d, *J* = 8.3 Hz, 4-H_{Ia}, 7-H_{Ia}); δ_C (63 MHz; CD₃CN) 19.6, 19.8, 126.8, 127.8, 127.9, 128.1, 129.3, 129.5, 135.4, 135.8, 139.9, 141.1, 142.6, 143.3, 148.9, 150.2, 159.1 and 161.0; *m/z* (ES-MS) 330.5 (M²⁺), 301.9 (Zn(IIa)₃²⁺).

Failure to prepare [Zn(IIb)(IIb)]/[BF₄]₂. To a solution of Zn(BF₄)₂·7H₂O (44 mg, 120 μmol) in methanol (4 cm³) a solution of compound IIb (54.2 mg, 120 μmol) in dichloromethane (5 cm³) was added. After 20 min of stirring at room temperature, a solution of IIb (45.6 mg, 120 μmol) in dichloromethane (3 cm³) was added, and the solvent removed after 5 min to furnish a yellow solid (120 mg, 93%). In the ¹H NMR analysis the homoleptic complex [Zn(IIb)₂]²⁺ was found as main product beside the desired heteroleptic species [Zn(IIb)(IIb)]²⁺, both of which were identified by characteristic chemical shifts. [Zn(IIb)₂]²⁺: δ_H (250 MHz; [D₆]acetone) 3.47 (24 H, s, OMe), 6.18 (8 H, d, *J* = 8.3, 3'-H, 5'-H), 6.88 (4 H, t, *J* = 8.3, 4'-H), 8.24 (4 H, d, *J* = 8.5, 3-H, 8-H), 8.86 (4 H, s, 5-H, 6-H) and 9.12 (4 H, d, *J* = 8.5 Hz, 4-H, 7-H); *m/z* (ES-MS) 485.2 (M²⁺). [Zn(IIb)(IIb)]²⁺: δ_H (250 MHz; [D₆]acetone) 3.39 (12 H, s, OMe_{IIb}), 6.18 (4 H, d, *J* = 8.2, 3'-H_{IIb}, 5'-H_{IIb}), 7.05 (2 H, t, *J* = 8.2, 4'-H_{IIb}), 7.60 (6 H, m, 3'-H_{IIb}, 4'-H_{IIb}, 5'-H_{IIb}), 7.90 (4 H, m, 2'-H_{IIb}, 6'-H_{IIb}), 8.21 (2 H, d, *J* = 5.2, 3-H_{IIb}, 8-H_{IIb}), 8.23 (2 H, d, *J* = 8.3, 3-H_{IIb}, 8-H_{IIb}), 8.37 (2 H, s, 5-H_{IIb}, 6-H_{IIb}), 8.51 (2 H, s, 5-H_{IIb}, 6-H_{IIb}), 8.82 (2 H, d, *J* = 5.2, 2-H_{IIb}, 9-H_{IIb}) and 8.97 (2 H, d, *J* = 8.3 Hz, 4-H_{IIb}, 7-H_{IIb}).

[Zn(IIc)(IIa)]/[BF₄]₂. The salt Zn(BF₄)₂·7H₂O (44.0 mg, 120 μmol) in methanol (5 cm³) was mixed with a solution of compound IIc (78.7 mg, 120 μmol) in dichloromethane (5 cm³). After 20 min of stirring at room temperature IIa (21.6 mg, 120 μmol) in dichloromethane (5 cm³) was added; 3 min later the solvent was removed quickly. After evaporation of the solvent, the residue was dried to afford a yellow solid (120 mg, 93%), mp >250 °C (Found: C, 61.53; H, 5.21; N, 5.59. C₅₈H₅₂B₂F₈N₄O₂Zn·3H₂O requires C, 61.46; H, 5.52; N, 4.95%; ν_{max}/cm⁻¹ 3070s (=CH), 2940w (CH), 1626m (C=C), 1587s (C=C), 1498m (C=C), 1468m (CH₃), 1431s (CH₃), 1387, 1329, 1283, 1229s (C=O), 1055 (B-F), 874m (aryl H), 853m (aryl H), 787m (aryl H), and 725s (aryl H); δ_H (250 MHz; [D₆]acetone) 1.15 (12 H, s, 3'-Me_{IIc}, 5'-Me_{IIc}), 1.76 (12 H, s, 2'-Me_{IIc}, 6'-Me_{IIc}), 3.69 (6 H, m, OMe_{IIc}), 5.10 (2 H, m, 2''-H_{IIc}, 6''-H_{IIc}), 6.29 (2 H, m, 2''-H_{IIc}, 6''-H_{IIc}), 6.82 (2 H, m, 4''-H_{IIc}), 7.24 (2 H, m, 5''-H_{IIc}), 8.36 (4 H, m, 3-H_{IIa}, 5-H_{IIa}, 6-H_{IIa}, 8-H_{IIa}), 8.62 (2 H, s, 5-H_{IIc}, 6-H_{IIc}), 8.65 (2 H, d, *J* = 8.2, 3-H_{IIc}, 8-H_{IIc}), 9.23 (2 H, dd, ³*J* = 8.2, ⁴*J* = 1.5, 4-H_{IIa}, 7-H_{IIa}), 9.33 (2 H, d, *J* = 8.2, 4-H_{IIc}, 7-H_{IIc}) and 9.37 (2 H, dd, ³*J* = 4.9, ⁴*J* = 1.5 Hz, 2-H_{IIa}, 9-H_{IIa}); *m/z* (ES-MS) 424.5 (Zn(IIc)(H₂O)₇²⁺) and 302.4 (Zn(IIa)₃²⁺).

Copper(I) complexes. [Cu(IIc)(IIa)]/[BF₄]. The compound [Cu(MeCN)₄]BF₄ (24.0 mg, 76.0 μmol) was dissolved in dichloromethane (10 cm³) and a solution of IIc (50.0 mg, 76.0 μmol) and IIa (13.7 mg, 76.0 μmol) in dichloromethane (10 cm³) added. After 20 min at room temperature the solvent was removed and the red residue purified by column chromatography (silica gel, dichloromethane-methanol 10:1) to furnish [Cu(IIc)(IIa)]BF₄. Dark red solid (73 mg, 97%), mp >250 °C (Found: C, 65.76; H, 5.06; N, 5.34. C₅₈H₅₂BCuF₄N₄O₂·4H₂O requires C, 65.75; H, 5.71; N, 5.29%; ν_{max}/cm⁻¹ 2920m (CH), 1579s (C=C), 1506m (C=C), 1494m (C=C), 1454m (CH), 1423s (CH), 1383, 1358, 1328, 1283, 1238s (C=O), 1140m (C=O), 1044, 1006, 842, 728m (aryl H) and 709w (aryl H); δ_H (200 MHz; CDCl₃) 1.10 (12 H, s, 3'-Me_{IIc}, 5'-Me_{IIc}), 1.69 (12 H, m, 2'-Me_{IIc}, 6'-Me_{IIc}), 3.88 + 3.67 (6 H, s, OMe_{IIc}), 4.88 + 5.02 (2 H, m, 2''-H_{IIc}, 6''-H_{IIc}), 6.30 (2 H, m, 2''-H_{IIc}, 6''-H_{IIc}), 6.72 (2 H, m, 4''-H_{IIc}), 7.14 (2 H, m, 5''-H_{IIc}), 7.78 (2 H, dd, ³*J* = 7.7, ³*J* = 4.8, 3-H_{IIa}, 8-H_{IIa}), 7.91 (2 H, m, 3-H_{IIc}, 8-H_{IIc}), 8.07 (2 H, m, 5-H_{IIc}, 6-H_{IIc}), 8.29 (2 H, s, 5-H_{IIa}, 6-H_{IIa}), 8.46 (2 H, d, *J* = 7.7, 4-H_{IIa}, 7-H_{IIa}), 8.61 (2 H, d, *J* = 4.8 Hz, 2-H_{IIa}, 9-H_{IIa}) and 8.78 (2 H, m, 4-H_{IIc}, 7-H_{IIc}); δ_C (63 MHz; CDCl₃) 15.9, 16.8, 52.6, 54.1, 54.5,

Table 6 Crystal structure analysis data of [Ag(IIb)(IIb)]BF₄

Empirical formula	C ₅₆ H ₄₀ AgBF ₄ N ₄ O ₄
Formula weight	1027.60
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> /Å	11.448(2)
<i>b</i> /Å	11.891(2)
<i>c</i> /Å	18.190(4)
<i>α</i> /°	72.08(3)
<i>β</i> /°	89.71(3)
<i>γ</i> /°	78.22(3)
<i>V</i> /Å ³	2302.0(8)
<i>Z</i>	2
<i>μ</i> /mm ⁻¹	0.508
Reflections collected	12850
Independent reflections	9177 [<i>R</i> (int) = 0.0301]
Final <i>R</i> 1 [<i>I</i> > 2σ(<i>I</i>), <i>wR</i> 2	0.0426, 0.1214

108.9, 110.9, 113.2, 114.8, 119.2, 120.0, 123.6, 125.5, 125.9, 126.1, 126.9, 127.5, 128.0, 128.3, 129.4, 130.3, 135.4, 136.5, 138.5, 140.5, 141.5, 141.8, 142.7, 146.9, 158.5 and 159.2; *m/z* (ES-MS) 899.3 (M⁺).

[Cu(IIc)(IIId)]/[BF₄]. To a solution of [Cu(MeCN)₄]BF₄ (96.0 mg, 304 μmol) in dichloromethane (20 cm³) was added a solution of compound IIc (200 mg, 304 μmol) and IIId (172 mg, 304 μmol) in dichloromethane (10 cm³). After 20 min at room temperature the solvent was removed and the red residue purified by column chromatography (silica gel, dichloromethane-methanol 10:1) to furnish [Cu(IIc)(IIId)]BF₄. Dark red solid (267 mg, 65%), mp 160 °C (Found: C, 67.10; H, 5.71; N, 4.08. C₇₈H₇₄BCuF₄N₄O₉·2H₂O requires C, 67.02; H, 5.62; N, 4.01%; ν_{max}/cm⁻¹ 2918m (CH), 1618w (C=C), 1578s (C=C), 1492s (C=C), 1458w (CH), 1422m (CH₃), 1350w (CH₃), 1279m (=COC), 1228s (=COC), 1199s (COC), 1050 (B-F), 915m (aryl H), 845m (aryl H), 786w (aryl H) and 708w (aryl H); δ_H (200 MHz, CD₃CN) 1.20 (12 H, s, 3'-Me_{IIc}, 5'-Me_{IIc}), 1.64 (12 H, s, 2'-Me_{IIc}, 6'-Me_{IIc}), 3.53 (8 H, m, 3''-H_{IIId}, 4''-H_{IIId}), 3.70 (3 H, s, OMe_{IIc}), 3.83 (4 H, m, 2''-H_{IIId}), 3.86 (3 H, s, OMe_{IIc}), 4.11 (4 H, m, 1''-H_{IIId}), 5.21–5.37 (2 H, m, 2''-H_{IIc}, 6''-H_{IIc}), 6.35 (2 H, m, 2''-H_{IIc}, 6''-H_{IIc}), 6.72 (2 H, m, 4''-H_{IIc}), 6.83 (2 H, m, 3-H_{IIId}, 8-H_{IIId}), 7.02–7.06 (8 H, m, 2'-H_{IIId}, 3'-H_{IIId}, 5'-H_{IIId}, 6'-H_{IIId}), 7.28 (2 H, m, 5''-H_{IIc}), 7.92 (2 H, m, 3-H_{IIc}, 8-H_{IIc}), 8.26 (2 H, s, 5-H_{IIc}, 6-H_{IIc}), 8.33 (2 H, m, 5-H_{IIId}, 6-H_{IIId}), 8.54 (2 H, m, 2-H_{IIId}, 9-H_{IIId}) and 8.78 (2 H, d, *J* = 8.1 Hz, 4-H_{IIc}, 7-H_{IIc}); δ_C (50 MHz, CDCl₃) 16.9, 17.8, 55.1, 55.4, 67.2, 67.9, 69.5, 70.2, 70.5, 70.7, 72.3, 72.4, 106.6, 110.5, 112.1, 114.4, 115.7, 116.4, 120.0, 120.4, 120.6, 121.4, 121.8, 126.4, 126.7, 127.7, 127.8, 128.8, 129.4, 130.6, 131.0, 131.3, 137.2, 139.5, 141.5, 142.8, 143.6, 144.1, 145.9, 146.4, 148.9, 157.2, 159.6 and 162.3; *m/z* (ES-MS) 1273.6 (M⁺).

Crystal structure determination of [Ag(IIb)(IIb)]BF₄

A yellow crystal was used for data collection at 203(2) K on a STOE-IPDS diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods. Programs used were Siemens SHELXS 86²¹ and SHELXL 93.²² Full-matrix least-squares refinement on *F*² was carried out anisotropically for the non-hydrogen atoms. Hydrogen atoms were included at calculated positions using a riding model. Further structure analysis data are given in Table 6.

CCDC reference number 186/1745.

See <http://www.rsc.org/suppdata/doi/a907545c/> for crystallographic files in .cif format.

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