Chiral spiro Cu(I) complexes. Supramolecular stereocontrol and isomerisation dynamics by the use of TRISPHAT anions†

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Association of enantiopure TRISPHAT anion (**1**) with chiral spiro [Cu(LL′)$_2$] complexes (LL′ = 2-R-phen, **2**, 6-R-bpy, **3**, and 2-iminopyridine, **4**) leads to an efficient NMR enantiodifferentiation. Variable temperature ^{1}H NMR spectroscopy has been used to determine the isomerisation kinetics of these pseudo-tetrahedral complexes and to evaluate their configurational stability; the latter depending on the structure of the diimine ligands. In the case of the 2-anthracenyl-phen derivative, a decent level of supramolecular stereocontrol was noted (d.e. up to 45%); the configuration of the complex being determined by electronic circular dichroism (ECD).

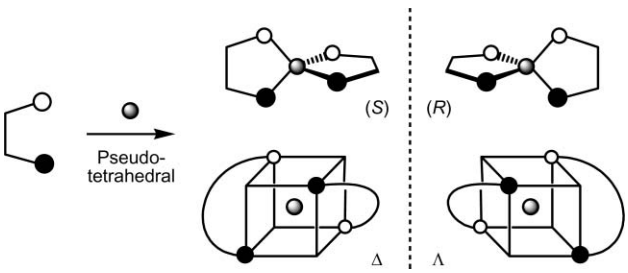
Introduction

Copper(I) complexes of heteroaromatic chelating bidentate ligands of general 1,4-diimine type form an important class of coordination compounds. They possess interesting physicochemical properties,[1] and also play a large role in the field of asymmetric catalysis.[2] From a topological perspective, these complexes can intervene in the construction of sophisticated molecular architectures such as catenates, knots, rotaxanes, *etc.*[3]

Copper(I) complexes prefer adopting a pseudo-tetrahedral geometry. They are often sensitive to oxidation and their stability is closely related to the nature of the ligands attached to the metal centre. In the absence of restricting steric effects from the ligands, these complexes are often oxidized to the more stable square-planar Cu(II) species. For example, CuL_2 complexes of 2,2′-bipyridines (bpy) and 1,10-phenanthrolines (phen) tend to be oxidized by O_2.[4]

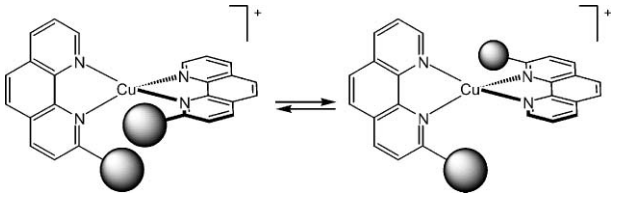
To avoid the geometric reorganization that occurs upon oxidation and ensure air stability, bulky substituents are usually introduced in ligand positions adjacent to the N-coordinating atoms. These substituents sterically impede the complex's ability to become planar and thus increase the Cu(I) to Cu(II) interconversion barrier sufficiently to allow the air stability of Cu(I) species. In 1961, the stabilisation of Cu(I) complexes by this approach was demonstrated by James and Williams who determined stability constants and redox potentials for a series of Cu(I)/Cu(II) complexes bearing different alkyl-substituted phenanthroline and bipyridine ligands.[5] Even though alkyl groups tend to be electron donating, their presence increases the Cu^{2+}/Cu^{+} reduction potential.[6]

In pseudo-tetrahedral geometry, the formation of a coordination complex with two identical symmetrical bidentate ligands leads invariably to an achiral D_{2d} symmetric structure. However the complexation of a central Cu(I) atom with two identical unsymmetrical bidentate ligands results in the formation of chiral cationic adducts of type $[Cu(LL')_2]^+$.[7] The pseudo-tetrahedral mononuclear complex formed in this way has a chirality centred around the metal which occupies the centre of the tetrahedron. Chiral spiro entities are formed, whose configuration can be assigned using either *S*/*R* or Δ/Λ descriptors (Scheme 1).[8,9] Many such bis(diimine)copper(I) complexes with unsymmetrical 2-R-phen, 6-R-bpy and 2-iminopyridines have been synthesised and studied as racemates.[10,11,12]



Scheme 1 Chiral spiro Cu(LL′)$_2$ complexes of (Δ,*S*) or (Λ,*R*) configuration.

These pseudo-tetrahedral Cu(I) complexes are chemically and configurationally labile, with an equilibrium between the enantiomers occurring rapidly in solution (Scheme 2). It can be slowed down to some extent by incorporating bulky substituents *ortho* to



Scheme 2 Configurational lability of chiral Cu(I) complexes exemplified with a 2-R-phen derivative.

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the ligand's imine nitrogen.[12b,13] While the flexibility of the diimine scaffold[14] has been shown to favor isomerization,[15] interligand π-stacking interactions may stabilize the $[Cu(LL)_2]^+$ structure.[10a,c]

The configurational lability of such Cu(I) complexes can be precisely evaluated by NMR using ligands which present magnetically non-equivalent signals after complexation. Van Koten *et al*. reported a dynamic study on complexes made of 2-iminopyridine moieties.[12a] Free energies of activation ($\Delta G^{\neq}$) around 58 kJ mol^{-1} were measured in $CDCl_3$ using, for instance, the diastereotopic methyl groups of isopropyl substituents as NMR probes. Recently, faster kinetics of racemization were measured in MeOH-d_4 on complexes of anionic taurine-derived 2-iminopyridine ligands ($\Delta G^{\neq}$ 46 kJ mol^{-1}).[16] Thummel *et al*. used VT-NMR to study the racemisation's kinetics and the rates of ligand exchange using phenanthroline ligands bearing enantiotopic geminal methyl groups and 2,2′-bipyrimidines with substituents at the 4,4′ and 6,6′ positions that become inequivalent when two ligands are bound to a single metal in a tetrahedral fashion.[13] Dynamics were found to be fast at ambient temperature and low temperature measurements were necessary for the determination of the energy barriers by ^{1}H NMR. Free energy of activation values around 61.4–63.5 kJ mol^{-1} were measured in $CDCl_3$ for 1,10-phenanthroline and 2,2′-bipyrimidine derivatives. The lower values measured in CD_3CN solutions (around 56.5–58.5 kJ mol^{-1}) were attributed to solvent participation in the exchange process.

Chiral ligands can also be used to induce an NMR differentiation.[17] However, as a high diastereoselectivity is often observed upon complex formation, only the signals of the major diastereomer appear prohibiting the determination of epimerization kinetics. Indeed, this occurred when enantiopure ligands derived from (1*S*)-(−)-β-pinene and (1*R*)-(+)-β-pinene were used from which the corresponding bis(diimine) complexes were obtained with high selectivity (d.e. > 96%).[18] Circular dichroism (CD) spectra of these complexes exhibited equal and opposite Cotton effects in the region of MLCT absorption which were assigned to Λ and Δ configurations respectively. Recently, Pianet and Vincent used chiral racemic atropisomer diimine ligands to study the exchange processes in pseudo-tetrahedral $[CuL_2]^+$ complexes by using two-dimensional exchange NMR spectroscopy.[19]

Although highly efficient, these methods for the evaluation of the isomerisation kinetics cannot be applied—by definition—to complexes made of achiral ligands deprived of enantiotopic substituents. For these substrates we hypothesized that a chiral counterion could be a source of NMR differentiation.[20] The association of chiral cationic $[Cu(LL')_2]^+$ complexes with enantiopure anions form diastereoisomeric salts and distinct NMR signals could thus result from the asymmetric ion pairing. Furthermore, as the complexes are configurationally labile, the possibility of a supramolecular stereocontrol was considered. We envisioned that stereoselective discriminating interactions might occur between the chiral ions and favor one diastereomeric salt over the other (Pfeiffer effect).[20,21]

Previously, the synthesis of tris(tetrachlorobenzenediolato)-phosphate(V) anions **1** has been reported.[22] This chiral anion, named TRISPHAT (Δ and Λ enantiomers, Fig. 1), can be resolved by association with an enantiopure ammonium ion. The overall efficiency of TRISPHAT to behave as an NMR chiral solvating and asymmetry-inducing agent for chiral cationic derivatives[20,23] led us to its use for the proposed study.[24] Recently, another chiral

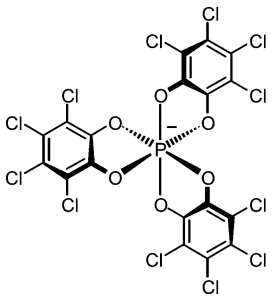

Fig. 1 The Δ enantiomer of TRISPHAT anion **1**.

anion, namely the bis[(*R*)-1,1′-bis-2-naphtholato]borate, was used by Arndtsen to distinguish effectively individual enantiomers of chiral Cu(I) complexes.[25]

Herein, we present a full report on the use of chiral TRISPHAT counterion as the source of NMR differentiation for isomerization dynamics and stereoselective induction studies on chiral Cu(I) complexes. Simple bpy, phen and iminopyridine ligands were used and the configurational stability of the resulting chiral complexes compared.

Results and discussion

Ligand and complex synthesis

Our goal was thus to associate TRISPHAT anions (**1**) with a large variety of complexes made from structurally different ligands (**2** to **4**, Fig. 2). Care was taken to choose diimine moieties derived from phen and bpy backbones as the differences in the skeletons (rigidity/flexibility, planar/nonplanar) could influence the selectivity and the configurational stability of the resulting Cu(I) complexes. Several monosubstituted 1,10-phenanthroline and 2,2′-bipyridine ligands were prepared following conditions previously reported by Sauvage *et al*.,[26] *i.e.* a nucleophilic addition of alkyl- or aryl-lithium reagents to the parent phen and bpy followed by the rearomatisation in the presence of an excess of manganese dioxide. The aromatic lithium compounds were obtained by reaction of the corresponding bromo-arene with metallic lithium. This synthesis afforded the ligands 2-R-phen (**2a–c** and **2e–h**) and 6-R-bpy (**3a–c** and **3e–f**) in low to good yields (16–95%; R = Me (**a**); *n*-Bu (**b**); *t*-Bu (**c**); *i*-Pr (**d**); Ph (**e**); 4-CH_3–Ph (**f**); 4-OMe–Ph (**g**); anthracenyl (**h**); Fig. 2).

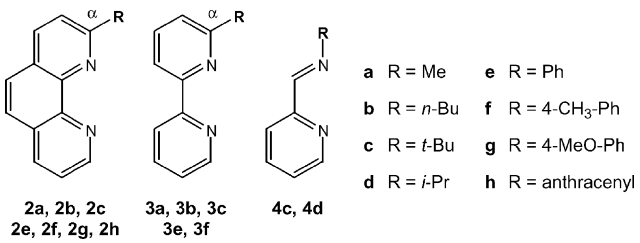

Fig. 2 2-R-phen (**2**), 6-R-bpy (**3**) and 2-iminopyridine (**4**).

The synthesis of the 2-imino-pyridine ligands **4c** and **4d** was also realised following a literature procedure,[12c] *via* an easy condensation between pyridine-2-carbaldehyde and the corresponding amines.

Table 1 Relevant data for the stereodynamics among diastereomeric [Cu(LL′)$_2$][Δ-**1**] salts

Entry	Ligand	R	Yield	d.e. (Temp./K)	Δδ/ppm[a]	T_c/K	Δν/Hz	$\Delta G^{\neq}$/ kJ mol^{-1}[b]	$\Delta H^{\neq}$/ kJ mol^{-1}[c]	$\Delta S^{\neq}$/ J K^{-1} mol^{-1}[d]	$\Delta G^{\neq}$/ kJ mol^{-1}[e]
1	**2a**	Me	85	0 (295 K)	0.10[f]	>328	45.2	>68.0	—	—	—
2	**2b**	*n*-Bu	78	10 (295 K)	0.16[f]	>323	62.4	>66.0	—	—	—
3	**2c**	*t*-Bu	82	8 (273 K)	0.03[f]	>328	11.4	>71.8	—	—	—
4	**2e**	Ph	79	4 (295 K)	0.07	>328	28.4	>69.3	—	—	—
5	**2f**	*p*-Tol	97	6 (295 K)	0.06	>328	25.2	>69.7	—	—	—
6	**2g**	*p*-anisyl	90	4 (295 K)	0.08	>328	34.0	>68.8	—	—	—
7	**2h**	anthracenyl	80	45 (253 K)	0.06	>328	26.0	>69.6	—	—	—
8	**3a**	Me	84	8 (233 K)	0.04[f]	303	16.8	65.2	92.2	87.1	66.2
9	**3b**	*n*-Bu	90	4 (243 K)	0.04[f]	313	17.2	67.3	—[h]	—	—
10	**3c**	*t*-Bu	88	7 (253 K)	0.05[g]	263	19.6	55.9	64.8	44.3	51.6
11	**3e**	Ph	86	0 (253 K)	0.08	—	—	—	—	—	—
12	**3f**	*p*-Tol	79	0 (263 K)	0.07	—	—	—	—	—	—
13[i]	**4c**	*t*-Bu	80	9 (243 K)	0.03	285	9.35	62.5	76.5	51.1	61.3
14[i]	**4d**	*i*-Pr	79	9 (253 K)	0.02[j]	267	10.35	58.1	75.1	65.6	55.6

[a] The precision of the measurement is about 0.01 ppm. [b] $\Delta G^{\neq} = RT_c(22.96 + \mathrm{Ln}(T_c/\Delta\nu))$. [c] $\Delta H^{\neq} = E_a - RT$. [d] $\Delta S^{\neq} = R\,[\ln(hA/k_BT) - 1]$. [e] $\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$; calculated at $T = 298$ K. [f] Hα. [g] H(*t*-Bu). [h] Not applicable. [i] In CD_2Cl_2. [j] H(imine).

Formation of the corresponding [Cu(LL′)$_2$][PF$_6$] salts was performed by reacting the different ligands with [Cu(CH$_3$CN)$_4$][PF$_6$] in acetonitrile. Association of these complexes with anion Δ-**1** was performed by ion pairing metathesis; salts [Cu(**2a–c**)$_2$][Δ-**1**], [Cu(**2e–h**)$_2$][Δ-**1**], [Cu(**3a–c**)$_2$][Δ-**1**], [Cu(**3e–f**)$_2$][Δ-**1**] and [Cu(**4c–d**)$_2$][Δ-**1**] being isolated by chromatography as the first eluted fractions (SiO$_2$, CH$_2$Cl$_2$, $R_f = \sim 0.6$–0.9, 78–97%, Table 1).[20,27]

Phen complexes

The effect of anion **1** as an NMR chiral solvating reagent was investigated. Solutions of [Cu(**2a–c**)$_2$][Δ-**1**] and [Cu(**2e–h**)$_2$][Δ-**1**] salts were prepared in CDCl$_3$ and analysed by ^{1}H NMR spectroscopy at room temperature.[28] Due to the presence of TRISPHAT anion, an enantio-differentiation was observed in the spectra of the diastereomeric [(*R*)–Cu(**2**)$_2$][Δ-**1**] and [(*S*)–Cu(**2**)$_2$][Δ-**1**] complexes showing partial or complete separation of the signals (Fig. 3). Of all the split signals, those of the higher frequency H9 protons were particularly easy to monitor. In [Cu(**2c**)$_2$][Δ-**1**], the H8 proton was better split than H9; this most probably indicates that the steric bulk of the *tert*-butyl groups hinders the approach of the TRISPHAT anion along the C_2 axis of the complex.

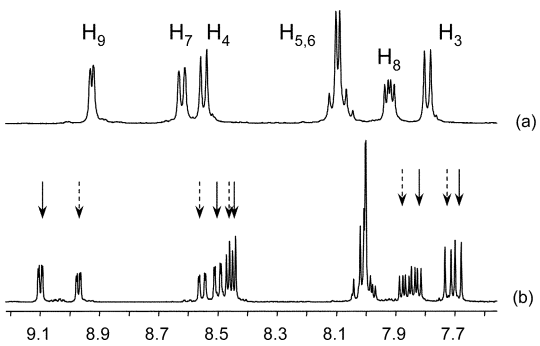

Fig. 3 ^{1}H NMR analyses (CDCl$_3$, 400 MHz, 298 K) of salts (a) [Cu(**2b**)$_2$][PF$_6$] and (b) [Cu(**2b**)$_2$][Δ-**1**], with a diastereomeric excess of 10%.

Such large differences in chemical shifts ($\Delta\Delta\delta_{max} = \sim 0.16$ ppm, 253 K) observed for analogous protons allowed a ready determination of the asymmetry induction by integration of the respective signals (diastereomeric excess d.e., Table 1, entries 1–7).

In view of the results gathered in Table 1, it is apparent that the nature of the α-substituent has a direct influence on the observed asymmetry inductions. Two types of α-substituent, aliphatic and aromatic groups, were used. For the former the best asymmetric excess was obtained with the complex bearing a monosubstituted *n*-butyl ligand (d.e. = 10%, Table 1, entry 2). Amongst aromatic groups of various sizes, the results were generally low (d.e. 4–6% at 295 K, entries 4–6, Table 1). Only in the case of the complex made with a phen ligand bearing an α-anthracenyl group (**2h**) was a decent diastereomeric excess measured at room temperature (d.e. 30% at 298 K, Fig. 4). An increase of this excess from 30 to 45% (233 K) was obtained by lowering the temperature (see Fig. 4).

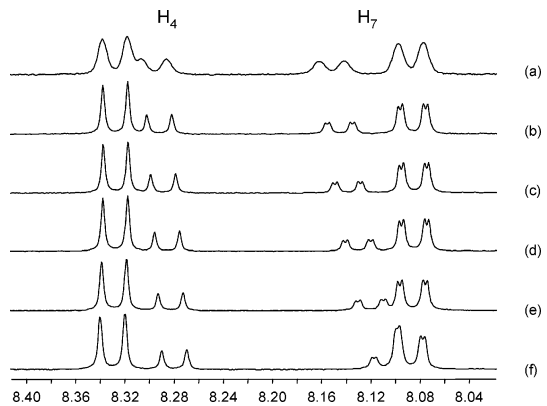

Fig. 4 VT-NMR analysis (^{1}H, 400 MHz, CDCl$_3$) of salt [Cu(**2h**)$_2$][Δ-**1**] and resulting diastereoselectivity: (a) 298 K, 30%, (b) 283 K, 40%, (c) 273 K, 42%, (d) 263 K, 44%, (e) 253 K, 45%, (f) 243 K, 45%.

The assignment of the configuration of the metal complex was realized by a CD analysis (Fig. 5). The salt [Cu(**2h**)$_2$][Λ-**1**] was prepared in addition to [Cu(**2h**)$_2$][Δ-**1**] and opposite Cotton effects were observed in the region of π–π* and MLCT bands (for MLCT, $\Delta\varepsilon_{396} = +6.3$ and -6.4 M^{-1} cm^{-1}, $\Delta\varepsilon_{377} = +4.8$ and -4.8 M^{-1} cm^{-1}, in CHCl$_3$ with $c = 7.44$ and 6.86×10^{-5} M respectively). By comparison with the work of Thummel *et al.*,[18]

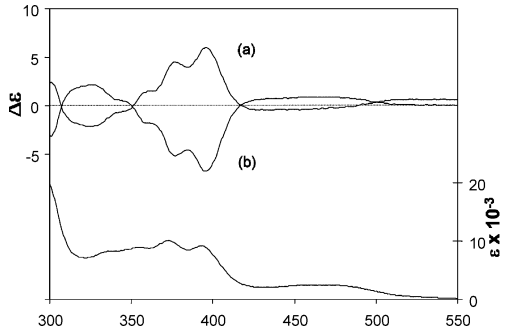

Fig. 5 CD (top) and absorption (bottom) spectra of (a) [Λ-Cu(**2h**)$_2$][Λ-**1**] and (b) [Δ-Cu(**2h**)$_2$][Δ-**1**] in $CHCl_3$ (298 K, $c = 7.44$ and 6.86×10^{-5} M respectively).

these two CD spectra can be assigned to Δ and Λ configurations for the Cu(I) cationic complexes associated with Δ-**1** and Λ-**1** anions respectively. It indicates that a homochiral association between the ions is favored over a heterochiral association.

Moreover, ^{1}H NMR analyses at higher temperatures were performed (up to 328 K) to determine the racemization barrier of these complexes. However, only small differences in chemical shifts ($\Delta\Delta\delta$) were observed for the split signals of H9 or H8 protons demonstrating the high configurational stability of these derivatives as compared to the NMR time scale. Should stereodynamic phenomena occur, they will appear at temperatures higher than 328 K.

The activation energy value ($\Delta G^{\neq}$), which quantifies the *R*/*S* or Λ/Δ inversion barrier, is thus unknown and can only be estimated by the "coalescence" method considering $\Delta\nu$ values at lower temperature and $T_c \geq 328$ K (Table 1, entries 1–7). For [(Cu(**2c**)$_2$][Δ–**1**], a $\Delta G^{\neq}$ value higher than 71.8 kJ mol^{-1} was determined ($\Delta\nu = 11.4$ Hz).

Bpy complexes

A similar study of Cu(I) complexes bearing 6-R-bipyridine ligands **3a–c** was undertaken. However, room temperature ^{1}H NMR analyses of these bpy-derived [Cu(**3a–c**)$_2$][Δ-**1**] salts revealed broad resonances or lack of signal separation (see Fig. 6 and ESI†). Rather than consider a lack of NMR enantio-differentiation from the TRISPHAT anion, we reasoned, in view of the results

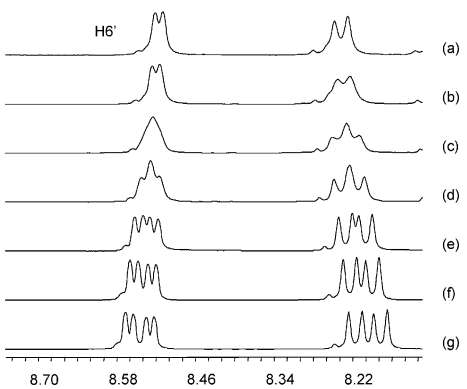

Fig. 6 Variable temperature ^{1}H NMR ($CDCl_3$, 400 MHz, δ 8.75–8.10 ppm) of [Cu(**3a**)$_2$][Δ-**1**]: (a) 323 K, (b) 313 K, (c) 303 K, (d) 293 K, (e) 283 K, (f) 273 K, (g) 263 K.

obtained previously,[10] that dynamic processes were occurring and that the spectra were recorded around or above the coalescence temperatures.

^{1}H VT-NMR experiments on [Cu(**3a–c**)$_2$][Δ-**1**] were therefore performed (253–328 K) in $CDCl_3$. For bpy-derived [Cu(**3a–b**)$_2$][Δ-**1**] salts, dynamic configurational isomerism was detected, with a separation of the NMR signals occurring at lower temperature (coalescence temperature for H6′ protons, $T_c = \sim 303$–313 K, Fig. 6, Table 1, entries 8–9). Racemization barriers were determined from T_c and $\Delta\nu$ values ($\Delta G^{\neq} = \sim 65.2$–67.3 kJ mol^{-1} in $CDCl_3$) and were similar to those obtained by Thummel *et al*.[13] For the [Cu(**3c**)$_2$][Δ-**1**] salt, faster stereodynamics ($\Delta G^{\neq} = \sim 55.9$ kJ mol^{-1}) were monitored as lower coalescence temperatures were measured for the H6′ and *t*-butyl protons ($T_c = \sim 263$ K, Table 1, entry 10).

Inversion barriers were also determined by line-shape analysis (WinDNMR) of the broadened exchange signals from which rate constants (*k*) were obtained. Representative experimental and calculated line shapes are depicted in Fig. 7. The inversion barriers were determined at different temperatures and the activation parameters ($\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta G^{\neq}$) of the Δ(*S*)/Λ(*R*) interconversion were calculated by using an Arrhenius plot (ln *k vs* 1/*T*) and Eyring equation (see Table 1 and ESI†). Precise results were thus obtained which are in good agreement with those obtained by the coalescence method.

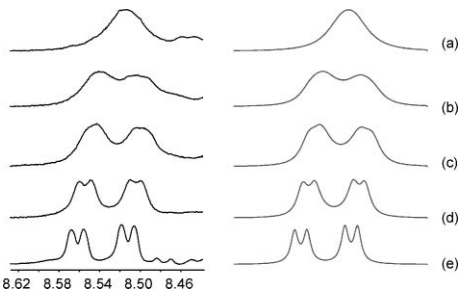

Fig. 7 Experimental (left, ^{1}H NMR, 400 MHz, $CDCl_3$, 233–263 K) and best fit calculated (right, WinDNMR, *k* kinetic constant (s^{-1})) spectra of [Cu(**3c**)$_2$Cu][Δ-**1**] (imine proton, δ 8.63–8.44 ppm): (a) 263 K, 160 s^{-1}; (b) 253 K, 50 s^{-1}; (c) 243 K, 30 s^{-1}; (d) 233 K, 12 s^{-1}; (e) 223 K, 0.2 s^{-1}.

Low asymmetry induction was also observed with monosubstituted 2,2′-bipyridine ligands (maximum diastereomeric excess 8% with R = Me, Table 1, entry 8) showing a poor efficiency of TRISPHAT anion to behave as a supramolecular chiral auxiliary for such ligands. Moreover, as an NMR chiral solvating agent, anion **1** is less efficient with bpy than phen derivatives, at least for Hα′ protons: $\Delta\Delta\delta_{max} = \sim 0.04$ ppm in bpy series (R = *n*-Bu) *vs* $\Delta\Delta\delta_{max} = \sim 0.16$ ppm in phen series (R = *n*-Bu).

Iminopyridine complexes

Copper(I) complexes of unsymmetrical pyridine imine ligands (**4**) were similarly analyzed. Compound [Cu(**4d**)$_2$][PF_6] had been previously studied,[12] and a racemization barrier measured ($\Delta G^{\neq} = \sim 58.2$ kJ mol^{-1} in CD_2Cl_2) using diastereotopic methyl groups of the *i*-propyl substituents as an NMR probe. For the analogous TRISPHAT salt, [Cu(**4d**)$_2$][Δ-**1**], broadened signals were observed at room temperature, similar to bpy-derived complexes.

However, a decrease of temperature revealed well separated signals for most of the protons. The racemization barrier was

determined using the signals of the imine hydrogen atoms, and the obtained value ($\Delta G^{\neq} = \sim 58.1$ kJ mol^{-1} in CD_2Cl_2, Table 1, entry 14) was in complete agreement with the results previously reported for [Cu(**4d**)$_2$][PF$_6$].[12] This result demonstrates without ambiguity that TRISPHAT anion does not influence the kinetics of racemization of the Cu(I) complex. A slightly higher barrier was measured for complex [Cu(**4c**)$_2$][Δ-**1**] using the split *t*-butyl signals ($\Delta G^{\neq} = \sim 62.5$ kJ mol^{-1}, Table 1, entry 13). As for the bpy derivatives, a careful line shape analysis was performed for the VT-NMR behaviour of the TRISPHAT salts of complexes **4c** and **4d** ($\Delta H^{\neq} \sim 75$–76 kJ mol^{-1} and $\Delta S^{\neq} = 51$ and 66 J K^{-1} mol^{-1}, respectively). Although a decent NMR enantio-differentiation was observed at low temperature, the measured diastereomeric excess remained low (d.e. = ~ 9%).

Conclusion

The TRISPHAT anion **1** is an efficient NMR chiral solvating agent for chiral pseudo-tetrahedral Cu(I) complexes. Diastereomeric ion pairs [(Δ/*S*)–Cu(LL′)$_2$][Δ-**1**] and [(Λ/*R*)–Cu(LL′)$_2$][Δ-**1**] can indeed be distinguished by ^{1}H NMR. Low asymmetry inductions were measured, although these were not negligible in the case of a 2R-phenanthroline ligand bearing an anthracenyl α-substituent (d.e. up to 45%), with the absolute configuration of the metal complex being determined by ECD.

The observed NMR enantio-differentiation can be used to measure the kinetics of racemization of these chiral configurationally labile Cu(I) complexes. This method, based on the use of a chiral anion, does not require the use of ligands bearing enantiotopic groups. Moreover it is simple to implement and very efficient. VT-NMR experiments on these salts were performed and revealed rather different results depending upon the nature of the α-substituent and the diimine backbone. Amongst the studied Cu(I) complexes the following stability order was determined: [Cu(2-R-phen)$_2$] > [Cu(2-R-bpy)$_2$] ≥ [Cu(2-R-iminopyridine)$_2$].

VT-NMR experiments also allowed us to determine the activation parameters for the Δ/Λ interconversion of a pseudo-tetrahedral Cu(I) complexes made of bpy and 2-iminopyridine ligands. The dynamic process requires positive activation enthalpy ($\Delta H^{\neq}$ from 65–92 kJ mol^{-1}) and shows rather strong and positive entropy values ($\Delta S^{\neq}$ from 52–66 J K^{-1} mol^{-1}). It is unfortunate that no data exists—to our knowledge—on the dissociation energy of Cu–N bonds as a comparison of these and $\Delta H^{\neq}$ values would have shed light on the nature of the exchange mechanism.

Experimental

General

All reactions were conducted under dry N_2 or Ar by means of an inert gas/vacuum double manifold line with magnetic stirring. $CHCl_3$, CH_2Cl_2, $CDCl_3$ and CD_2Cl_2 (SDS) were filtered on basic alumina. Analytical thin layer chromatography (TLC) was performed with Merck SIL G/UV$_{254}$ plates or Fluka 0.25 mm basic alumina (pH = 9.9) plates. Visualization of the developed chromatogram was performed by UV/Vis detection. Organic solutions were concentrated under reduced pressure on a Buchi rotary evaporator. Unless otherwise noted, column chromatography (silica gel 60, 40 μm or Fluka basic alumina type 5016A) was performed in air.

NMR data were obtained on Bruker 400 MHz spectrometer, IR and mass spectra were recorded. NMR spectra were recorded on a Bruker AMX-400 spectrometer at room temperature unless otherwise stated. ^{1}H NMR chemical shifts are given in ppm relative to Me_4Si with the solvent resonance used as the internal standard. ^{31}P NMR (162 MHz) chemical shifts were reported in ppm relative to H_3PO_4. ^{13}C NMR (100 MHz) chemical shifts were given in ppm relative to Me_4Si, with the solvent resonance used as the internal standard ($CDCl_3$ δ 77.0 ppm, CD_2Cl_2 δ 53.8 ppm). Assignments may have been achieved using COSY, HETCOR and/or NOESY experiments. IR spectra were recorded with a Perkin–Elmer 1650 FTIR spectrometer using a diamond ATR Golden Gate sampling. Melting points (mp) were measured in open capillary tubes on a Stuart Scientific SMP3 melting point apparatus and were uncorrected. Electrospray mass spectra (ES-MS) were obtained on a Finnigan SSQ 7000 spectrometer and EI-MS spectra were obtained on a Varian CH4 or SM1 spectrometer (ionizing voltage 70 eV; *m*/*z* (intensity in %)) by the Department of Mass Spectroscopy of the University of Geneva. UV spectra were recorded on a CARY-1E spectrometer in a 1.0 cm quartz cell; λ_{max} are given in nm and molar adsorption coefficient ε in cm^{-1} dm^3 mol^{-1}. CD spectra were recorded on a JASCO J-715 polarimeter in a 1.0 cm quartz cell; λ are given in nm and molar circular dichroic absorptions ($\Delta\varepsilon$) in cm^2 mmol^{-1}. Optical rotations were measured on a Perkin-Elmer 241 polarimeter in a thermostated (20 °C) 10.0 cm long microcell with high pressure lamps of sodium or mercury and are reported as follows: $[\alpha]_{\lambda}^{20}$ (*c* (g per 100 mL), solvent).

[Cu(diimine)$_2$][PF$_6$] complexes, general procedure

In a 10 mL flask under an inert argon atmosphere, 10 mg (Acros, 2.6 10^{-5} mol, 1 equiv.) of [Cu(CH$_3$CN)$_4$PF$_6$] salt and 2.0 equiv. (5.2 10^{-5} mol) of the desired ligand were dissolved in acetonitrile (SDS) and stirred at room temperature for 10–30 min. Concentration *in vacuo* then afforded the desired products as orange and brown solids. No further purification was required.

[Cu(diimine)$_2$][TRISPHAT] complexes, general procedure

In a 10 mL conical flask under an argon atmosphere, the [Cu(I)bis(diimine)][PF$_6$] salt (2.5 10^{-5} mol, 1 equiv.) and the source of the desired anion [cinchonidinium][Δ-**1**] (1 equiv.) were dissolved in CH_2Cl_2–acetone (SDS, 50 : 50, 5 mL). After 30 min of stirring, the solution was evaporated to dryness and the product was purified by chromatography (silica gel) using CH_2Cl_2 as the eluent. A and A′ represent the major and minor diastereomers, respectively.

[Cu(2a)$_2$][Δ-1]. This compound was prepared following the general procedure and isolated after column chromatography (R_f 0.89 (SiO_2, CH_2Cl_2)) in 62% yield. ^{1}H NMR ($CDCl_3$, 400 MHz, 293 K): δ 8.90 (dd, ^3J = 1.5 Hz, ^3J = 4.5 Hz, 1H, A), 8.84 (dd, ^3J = 1.5 Hz, ^3J = 4.5 Hz, 1H, A′), 8.50 (m, 2H, A and A′), 8.42 (d, ^3J = 8.3 Hz, 2H, A and A′), 7.98 (m, 4H, A and A′), 7.79 (m, 2H, A and A′), 7.70 (m, 2H, A and A′), 2.43 (s, 3H, A′), 2.38 (s, 3H, A). ^{31}P NMR ($CDCl_3$, 162 MHz): δ −77.9. IR (cm^{-1}): *v* 2921w, 2846w, 1618w, 1587w, 1564w, 1509w, 1491w, 1449s, 1389m,

1302m, 1236m, 1146w, 992s, 848m, 818s, 719s, 670s, 619s, 582m. $[\alpha]^{20}_{D} = -313$, $[\alpha]^{20}_{578} = -339$, $[\alpha]^{20}_{546} = -366$, $[\alpha]^{22}_{436} = -562$, $[\alpha]^{22}_{365} = -1255$ ($c = 0.00765$, $CHCl_3$). UV/Vis ($CHCl_3$, 3.03×10^{-5} M) λ_{max} (ε) 452 (6.0×10^3), 273 (4.6×10^4), 241 (5.0×10^4), 227 (2.8×10^4), 214 (2.3×10^4), 202 (1.9×10^4). MS (ES): (+) 451.3 ($[Cu(L)_2]^+$), 257.2 ($[Cu(L)]^+$); (−) 768.5 ($[\mathbf{1}]^-$).

[Cu(2b)$_2$][Δ-1]. This compound was prepared following the general procedure and isolated after column chromatography (R_f 0.86 (SiO_2, CH_2Cl_2)) in 50% yield. ^{1}H NMR ($CDCl_3$, 400 MHz, d.e. = 10%): δ 9.08 (dd, $^3J = 1.5$ Hz, $^3J = 4.8$ Hz, 1H, A), 8.95 (dd, $^3J = 1.5$ Hz, $^3J = 4.8$ Hz, 1H, A′), 8.54 (dd, $^3J = 1.5$ Hz, $^3J = 8.1$ Hz, 1H, A′), 8.48 (dd, $^3J = 1.5$ Hz, $^3J = 8.1$ Hz, 1H, A), 8.44 (d, $^3J = 8.3$, 1H, A′), 8.43 (d, $^3J = 8.3$, 1H, A), 7.98 (m, 4H, A and A′), 7.86 (dd, $^3J = 4.5$ Hz, $^3J = 8.1$ Hz, 1H, A′), 7.82 (dd, $^3J = 4.5$ Hz, $^3J = 8.1$ Hz, 1H, A), 7.71 (d, $^3J = 8.3$ Hz, 1H, A′), 7.67 (d, $^3J = 8.3$ Hz, 1H, A), 2.64 (m, 2H, A′), 2.52 (m, 2H, A), 1.29 (m, 4H, A and A′), 0.55 (m, 2H, A′), 0.50 (m, 2H, A), 0.22 (t, $^3J = 7.6$ Hz, 3H, A′), 0.22 (t, $^3J = 7.6$ Hz, 3H, A). ^{31}P NMR ($CDCl_3$, 162 MHz): δ − 79.6. IR (cm^{-1}): ν 2960w, 2924w, 2854w, 1618w, 1587w, 1566w, 1494w, 1445s, 1389m, 1301m, 1235m, 1223m, 1147w, 1098w, 990s, 850m, 818s, 718s, 668s, 619s, 564m. $[\alpha]^{20}_{D} = -313$, $[\alpha]^{20}_{578} = -339$, $[\alpha]^{20}_{546} = -366$, $[\alpha]^{20}_{436} = -562$, $[\alpha]^{20}_{365} = -1255$ ($c = 0.00765$, $CHCl_3$). UV/Vis ($CHCl_3$, 5.86×10^{-5} M): λ_{max} (ε) 458 (6.3×10^3), 274 (5.0×10^4), 243 (5.2×10^4), 233 (2.5×10^4), 231 (2.4×10^4), 229 (2.4×10^4), 226 (2.3×10^4), 224 (2.2×10^4), 221 (2.2×10^4); MS (ES): (+) 535.3 ($[Cu(L)_2]^+$), 300.1 ($[Cu(L)]^+$); (−) 768.6 ($[\mathbf{1}]^-$).

[Cu(2c)$_2$][Δ-1]. This compound was prepared following the general procedure and isolated after column chromatography (R_f 0.76 (SiO_2, CH_2Cl_2)) in 66% yield. ^{1}H NMR ($CDCl_3$, 400 MHz, d.e. = 0%). δ 8.88 (td, 2H, $^3J = 4.5$ Hz, A and A′), 8.55 (dd, $^4J = 1.3$ Hz, $^3J = 8.1$ Hz, 1H, A), 8.48 (dd, $^4J = 1.3$ Hz, $^3J = 8.1$ Hz, 1H, A′), 8.47 (d, $^3J = 8.5$ Hz, 1H, A), 8.45 (d, $^3J = 8.5$ Hz, 1H, A′), 8.02 (d, $^3J = 3$ Hz, 1H, A′), 7.99 (d, $^3J = 2.8$ Hz, 1H, A), 7.97–7.94 (m, 4H, A and A′), 7.83 (dd, $^3J = 4.8$ Hz, $^3J = 8.1$ Hz, 1H, A′), 7.77 (dd, $^3J = 4.8$ Hz, $^3J = 8.1$ Hz, 1H, A), 1.25 (s, 9H, A), 1.22 (s, 9H, A′). ^{31}P NMR ($CDCl_3$, 162MHz): δ − 79.6. IR (neat) (cm^{-1}): ν 2964w, 2924w, 2857w, 1626w, 1589w, 1564w, 1510w, 1491m, 1446s, 1384m, 1301m, 1235m, 1136w, 1088w, 990s, 851m, 817s, 717s, 669s, 619s, 583m. UV/Vis ($CHCl_3$, 9.6×10^{-6} M): λ_{max} (ε) 202.0 (2.7×10^4), 212.0 (2.9×10^4), 222.0 (3.1×10^4), 227.0 (3.3×10^4), 231.0 (3.4×10^4), 240.0 (6.0×10^4), 274.0 (5.9×10^4). $[\alpha]^{20}_{D} = -133$, $[\alpha]^{20}_{578} = -244$, $[\alpha]^{20}_{546} = -281$, $[\alpha]^{20}_{365} = -1111$ ($c = 0.0135$, $CHCl_3$). MS (ES): (+) 535.2 ($[Cu(L)_2]^+$), 299.2 ($[Cu(L)]^+$); (−) 768.7 ($[\mathbf{1}]^-$).

[Cu(2e)$_2$][Δ-1]. This compound was prepared following the general procedure and isolated after column chromatography (R_f 0.91 (SiO_2, CH_2Cl_2)). Mp = 200 °C (decomposes). ^{1}H NMR ($CDCl_3$, 400 MHz, d.e. 4%): δ 9.11 (d, $^3J = 3.8$ Hz, 1H, A′), 9.04 (d, $^3J = 3.8$ Hz, 1H, A), 8.52 (d, $^3J = 8.1$ Hz, 1H, A′), 8.45 (d, $^3J = 7.8$ Hz, 1H, A), 8.36 (d, $^3J = 8.1$ Hz, 1H, A′), 8.32 (d, $^3J = 8.3$ Hz, 1H, A′), 7.98–7.90 (m, 5H), 7.80–7.74 (m, 3H), 7.16 (d, $^3J = 7.3$ Hz, 2H, A′), 7.11 (d, $^3J = 7.3$ Hz, 2H, A), 6.58 (m, 2H, A and A′), 6.30 (m, 4H, A and A′). ^{31}P NMR ($CDCl_3$, 162 MHz): δ − 80.8. IR (cm^{-1}): ν 3051w, 1620w, 1586w, 1559w, 1489w, 1444s, 1386m, 1301m, 1235m, 1142w, 1110w, 989s, 853m, 817s, 717s, 667s, 619s, 580m. UV/Vis ($CHCl_3$, 1.9×10^{-5} M): λ_{max} (ε) 202.0 (2.7×10^4), 212.0 (3.5×10^4), 228.0 (3.9×10^4), 230.0 (4.0×10^4), 241.0 (8.4×10^4), 289.0 (5.8×10^4). MS (ES): (+) 575.2 ($[Cu(L)_2]^+$), 320.2 ($[Cu(L)]^+$); (−) 768.6 ($[\mathbf{1}]^-$).

[Cu(2f)$_2$][Δ-1]. This compound was prepared following the general procedure and isolated after column chromatography (R_f 0.7 (SiO_2, CH_2Cl_2)) in 97% yield. Mp = 175 °C (decomposes). ^{1}H NMR ($CDCl_3$, 400 MHz, d.e. = 9%): δ 9.19 (d, $^3J = 4.8$ Hz, 2H, A′), 9.10 (d, $^3J = 4.8$ Hz, 2H, A), 8.54 (d, $^3J = 7.8$ Hz, 2H, A′), 8.47 (d, $^3J = 7.8$ Hz, 2H, A), 8.35 (d, $^3J = 8.3$ Hz, 2H, A), 8.31 (d, $^3J = 8.3$ Hz, 2H, A′), 8.0–7.9 (m, 6H), 7.79 (dd, $^3J = 8.1$ Hz, $^3J = 4.8$ Hz, 2H, A), 7.73 (d, $^3J = 8.1$ Hz, 2H, A), 7.72 (d, $^3J = 8.1$ Hz, 2H, A′), 7.03 (d, $^3J = 8.1$ Hz, 4H, A′), 6.95 (d, $^3J = 8.1$ Hz, 4H, A), 6.08 (d, $^3J = 7.6$ Hz, 4H, A′), 6.05 (d, $^3J = 8.1$ Hz, 4H, A), 1.83 (s, 6H, A and A′). ^{31}P NMR ($CDCl_3$, 162 MHz): δ − 79.7. IR (cm^{-1}): ν 3456m, 2964w, 1586w, 1450s, 1387m, 1301m, 1262m, 1236m, 992s, 824s, 719m, 673s, 620w. UV/Vis ($CHCl_3$, 2.39×10^{-5} M): λ_{max} (ε) 246.0 (8.3×10^4), 291.0 (6.9×10^4), 439.0 (5.6×10^3). CD ($CHCl_3$, $2.39\ 10^{-5}$ M, 20 °C): λ ($\Delta\varepsilon$) 250.0 (−35), 290.0 (−19). $[\alpha]^{20}_{D} = -415$, $[\alpha]^{20}_{578} = -430$, $[\alpha]^{20}_{546} = -459$, ($c = 0.014$, $CHCl_3$). MS (ES): (+) 603.4 ($[Cu(L)_2]^+$); 332.5 ($[Cu(L)]^+$); (−) 768.9 ($[\mathbf{1}]^-$).

[Cu(2g)$_2$][Δ-1]. This compound was prepared following the general procedure and isolated after column chromatography (R_f 0.67 (SiO_2, CH_2Cl_2)) in 88% yield. ^{1}H NMR ($CDCl_3$, 400 MHz, d.e. = 7%): δ 9.19 (d, $^3J = 4.4$ Hz, 2H, A), 9.10 (d, $^3J = 4.4$ Hz, 2H, A′), 8.52 (d, $^3J = 8.4$ Hz, 2H, A′), 8.46 (d, $^3J = 7.9$ Hz, 2H, A), 8.33 (d, $^3J = 7.9$ Hz, 2H, A), 8.28(d, $^3J = 8.4$ Hz, 2H, A′), 8.0–7.85 (m, 6H), 7.79 (dd, $^3J = 7.9$ Hz, $^3J = 4.9$ Hz, 2H, A), 7.73 (m, 2H, A and A′), 7.13 (d, $^3J = 8.4$ Hz, 4H, A′), 7.08 (d, $^3J = 8.4$ Hz, 4H, A), 5.81 (4H, A and A′), 3.38 (s, 6H, A and A′). ^{31}P NMR ($CDCl_3$, 162 MHz): δ − 80.6. IR (cm^{-1}): ν 3422m, 2934w, 1653w, 1559w, 1498w, 1450s, 1388w, 1252m, 992s, 825s, 719w, 673m. UV/Vis ($CHCl_3$, $c = 5.05 \times 10^{-5}$ M): λ_{max} (ε) 205.0 (1.9×10^4), 216.0 (2.2×10^4), 228.0 (2.5×10^4), 242.0 (4.7×10^4), 300.0 (2.8×10^4), 437.0 (2.2×10^3). MS (ES): (+) 635.1 ($[Cu(L)_2]^+$), 349.2 ($[Cu(L)]^+$); (−) 768.7 ($[\mathbf{1}]^-$).

[Cu(2h)$_2$][Δ-1]. This compound was prepared following the general procedure and isolated after column chromatography (R_f 0.6 (SiO_2, CH_2Cl_2)) in 80% yield. ^{1}H NMR ($CDCl_3$, 400 MHz, d.e. = 30%): δ 8.29 (d, $^3J = 8.1$ Hz, 1H, H_4, A), 8.25 (d, $^3J = 8.1$ Hz, 1H, H_4, A′), 8.12 (d, $^3J = 8.3$ Hz, 1H, H_7, A′), 8.04 (d, $^3J = 8.3$ Hz, 1H, H_7, A), 7.83 (d, $^3J = 8.8$ Hz, 1H, A), 7.77 (d, $^3J = 8.8$ Hz, 1H, A′), 7.74–7.65 (m, 9H), 7.58 (d, $^3J = 4.0$ Hz, 1H, H_9, A), 7.50 (d, $^3J = 8.5$ Hz, 1H, A′), 7.45 (d, $^3J = 8.5$ Hz, 1H, A), 7.39–7.31 (m, 4H), 7.23 (m, 2H), 7.11–6.98 (m, 4H), 6.89–6.83 (m, 3H), 6.72 (dd, $^3J = 4.8$ Hz, $^3J = 8.3$ Hz, 1H, H_8, A). ^{31}P NMR ($CDCl_3$, 162 MHz): δ − 80.6. IR (cm^{-1}): ν 2923w, 2852w, 1730w, 1623w, 1586w, 1490w, 1446s, 1387m, 1302m, 1235m, 990s, 818s, 717w, 662m. UV/Vis ($CHCl_3$, $c = 7.44 \times 10^{-5}$ M): λ_{max} (ε) 228.0 (18.7×10^3), 247.0 (21.3×10^3), 300.0 (3.7×10^3), 373.0 (1.7×10^3), 396.0 (1.5×10^3), 473.0 (0.5×10^3). CD ($CHCl_3$, $c = 7.44 \times 10^{-5}$ M, 20 °C): λ ($\Delta\varepsilon$) 396.0 (−6.4), 377 (−4.9), 326.5 (+2.5), 301 (−2.9), 280.5 (+25.7). MS (ES): (+) 775.2 ($[Cu(L)_2]^+$); 419.3 ($[Cu(L)]^+$); (−) 768.7 ($[\mathbf{1}]^-$).

[Cu(2h)$_2$][Λ-1]. This compound was prepared following the general procedure using [Bu_3NH][Λ-**1**] as a source of TRISPHAT anion and isolated after column chromatography in 82% yield. ^{1}H NMR ($CDCl_3$, 400 MHz, d.e. = 30%). CD ($CHCl_3$,

$c = 6.86 \times 10^{-5}$ M, 20 °C): λ ($\Delta\varepsilon$) 395.5 (+6.3), 377 (+4.8), 326.0 (−1.8), 301 (+2.7), 278.0 (−27.3).

[Cu(3a)$_2$][Δ-1]. This compound was prepared following the general procedure and isolated after column chromatography (R_f 0.82 (SiO_2, CH_2Cl_2)) in 84% yield. ^{1}H NMR ($CDCl_3$, 400 MHz, 243 K, d.e. = 7%): δ 8.56 (d, ^3J = 4.5 Hz, 1H, $H_{6'}$, A), 8.53 (d, ^3J = 4.8 Hz, 1H, $H_{6'}$, A′), 8.20 (d, ^3J = 8.3 Hz, 1H, $H_{3'}$, A), 8.15 (d, ^3J = 8.3 Hz, 1H, $H_{3'}$, A′), 8.02 (d, ^3J = 2.8 Hz, 1H, H_3, A′), 8.00 (d, ^3J = 2.5 Hz, 1H, H_3, A), 7.94–7.77 (m, 4H, H_4 and $H_{4'}$, A and A′), 7.48–7.42 (m, 2H, $H_{5'}$, A and A′), 7.34 (d, 2H, ^3J = 7.6 Hz, H_5, A and A′), 2.17 (s, 3H, CH_3, A′), 2.14 (m, 3H, CH_3, A). ^{31}P NMR ($CDCl_3$, 162 MHz): δ − 80.8. IR (cm^{-1}): ν 2956w, 2928w, 2851w, 1595w, 1571w, 1445s, 1389m, 1301m, 1236m, 1159w, 1100w, 990s, 905m, 814s, 770s, 717s, 668s, 619m. MS (ES): (+) 403.3 ([Cu(2-methylbipy)$_2$]$^+$), 233.4 ([CuL]$^+$); (−) 768.8 ([**1**]$^-$).

[Cu(3b)$_2$][Δ-1]. This compound was prepared following the general procedure and isolated after column chromatography (R_f 0.87 (SiO_2, CH_2Cl_2)) in 65–95% yield. ^{1}H NMR ($CDCl_3$, 400 MHz, 243 K, e.d. = 4%): δ 8.66 (d, ^3J = 4.5 Hz, 1H, $H_{6'}$, A), 8.61 (d, ^3J = 4.8 Hz, 1H, $H_{6'}$, A), 8.25 (d, ^3J = 8.1 Hz, 1H, $H_{3'}$, A′), 8.19 (d, ^3J = 8.3 Hz, 1H, $H_{3'}$, A), 8.14–8.06 (m, 4H, H_3, A and A′), 7.99–7.82 (m, $H_{4'}$ and H_4, 4H, A and A′), 7.54 (t, ^3J = 5.8 Hz, 1H, $H_{5'}$, A′), 7.46 (t, ^3J = 5.8 Hz, 1H, $H_{5'}$, A), 7.38 (d, 2H, ^3J = 7.8 Hz, H_5, A and A′), 2.39 (m, 4H, CH_2, A and A′), 1.17 (m, 4H, CH_2, A and A′), 0.66 (m, 4H, CH_2, A and A′), 0.37 (m, 6H, CH_3, A and A′). ^{31}P NMR ($CDCl_3$, 162 MHz): δ − 80.8. IR (cm^{-1}): ν 2956w, 2928w, 2811w, 1595m, 1571w, 1445s, 1389m, 1301m, 1236m, 1159w, 1104w, 990s, 905m, 818s, 771m, 718m, 668s, 619m. UV/Vis ($CHCl_3$, 9.65 × 10^{-5} M): λ_{max} (ε) 202.0 (7.1 × 10^3), 205.0 (6.9 × 10^3), 209.0 (6.9 × 10^3), 211.0 (7.6 × 10^3), 216.0 (7.9 × 10^3), 218.0 (8.3 × 10^3), 222.0 (8.6 × 10^3), 225.0 (9.9 × 10^3), 244.0 (3.4 × 10^5), 263.0 (2.3 × 10^5), 300.0 (3.2 × 10^5), 452.0 (4.9 × 10^3). $[\alpha]^{20}_D$ = − 272, $[\alpha]^{20}_{578}$ = − 255, $[\alpha]^{20}_{546}$ = − 337, $[\alpha]^{20}_{365}$ = − 1267 (c = 0.012, $CHCl_3$). MS (ES): (+) 487.3 ([CuL_2]$^+$); 275.2 ([CuL]$^+$); (−) 768.6 ([**1**]$^-$).

[Cu(3c)$_2$][Δ-1]. This compound was prepared following the general procedure and isolated after column chromatography (R_f 0.79 (SiO_2, CH_2Cl_2)) in 74% yield. ^{1}H NMR ($CDCl_3$, 400 MHz, 233 K, d.e. = 8%): δ 8.56 (d, ^3J = 4.5 Hz, 1H, $H_{6'}$, A′), 8.51 (d, ^3J = 4.5 Hz, 1H, $H_{6'}$, A), 8.21–8.13 (m, 3H), 8.04–7.84 (m, 6H), 7.60–7.47 (m, 4H), 1.09 (s, 18H, A and A′). ^{31}P NMR ($CDCl_3$, 162 MHz): δ − 80.8. IR (cm^{-1}): ν 2956w, 2925w, 2845w, 1594w, 1573w, 1445s, 1389m, 1302m, 1236m, 1182w, 1164w, 1143w, 1106w, 990s, 818s, 775m, 718m, 668s, 619m, 551m. UV/Vis ($CHCl_3$, 3.10 × 10^{-5} M): λ_{max} (ε) 209.0 (1.9 × 10^4), 218.0 (2.2 × 10^4), 224.0 (2.3 × 10^4), 241.0 (4.9 × 10^4), 299.0 (3.4 × 10^4). MS (ES): (+) 487.3 ([CuL_2]$^+$); (+) 275.1 ([CuL]$^+$); (−) 768.8 ([**1**]$^-$).

[Cu(3e)$_2$][Δ-1]. This compound was prepared following the general procedure and isolated after column chromatography (R_f 0.97 (SiO_2, CH_2Cl_2)). ^{1}H NMR ($CDCl_3$, 400 MHz, 253 K, d.e. = 0%): δ 8.60 (d, ^3J = 4.8 Hz, 1H, $H_{6'}$), 8.52 (d, ^3J = 4.8 Hz, 1H, $H_{6'}$), 8.09–7.98 (m, 3H), 7.91–7.22 (m, 5H), 7.56 (t, ^3J = 6.0 Hz, 1H), 7.46–7.14 (m, 3H), 7.24 (d, ^3J = 5.8 Hz, 4H), 6.98 (t, ^3J = 7.3 Hz, 2H), 6.75 (t, ^3J = 7.5 Hz, 4H). ^{31}P NMR ($CDCl_3$, 162 MHz): δ − 80.83. IR (cm^{-1}): ν 3024w, 2927w, 2851w, 1593m, 1564w, 1444s, 1388m, 1301m, 1235m, 1177w, 1159w, 1075w, 989s, 817s, 780m, 757m, 717m, 696m, 619m. UV/Vis ($CHCl_3$, 5.94 × 10^{-5} M): λ_{max} (ε) 207.0 (1.5 × 10^4), 213.0 (1.6 × 10^4), 216.0 (1.6 × 10^4), 222.0 (1.8 × 10^5), 225.0 (1.8 × 10^5), 234.0 (2.2 × 10^5), 242.0 (4.0 × 10^5), 302.0 (2.2 × 10^5). $[\alpha]^{20}_D$ = − 221, $[\alpha]^{20}_{578}$ = − 182, $[\alpha]^{20}_{546}$ = − 221, $[\alpha]^{20}_{436}$ = − 441 and $[\alpha]^{20}_{365}$ = − 909 (c = 0.0077, $CHCl_3$). MS (ES): (+) 527.4 ([$Cu(L)_2$]$^+$), 295.1 ([Cu(L)]$^+$); (−) 769.0 ([**1**]$^-$).

[Cu(3f)$_2$][Δ-1]. This compound was prepared following the general procedure and isolated after column chromatography in 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 253 K, d.e. = 0%): δ 8.50 (d, ^3J = 4.8 Hz, 1H, $H_{6'}$), 8.44 (d, ^3J = 4.6 Hz, 1H, $H_{6'}$), 8.08 (d, ^3J = 8.1 Hz, 1H, $H_{3'}$), 8.01–7.95 (m, 3H), 7.85–7.81 (m, 4H), 7.72 (t, ^3J = 7.5 Hz, 1H), 7.45 (t, ^3J = 5.5 Hz, 1H, $H_{5'}$), 7.44 (t, ^3J = 5.5 Hz, 1H, $H_{5'}$), 7.40 (d, ^3J = 7.5 Hz, 2H, H_5), 7.16 (t, ^3J = 8.3 Hz, 4H), 6.53–6.50 (m, 4H), 2.07 (s, 6H, CH_3). IR (cm^{-1}): ν 2959w, 2922w, 2851w, 1594m, 1559w, 1445s, 1388m, 1301m, 1235m, 1180w, 1159w, 1091w, 989s, 817s, 770m, 717m, 668m, 619m, 551m. MS (ES): (+) 555.3 ([$Cu(L)_2$]$^+$), 309.3 ([Cu(L)]$^+$); (−) 768.8 ([**1**]$^-$).

[Cu(4c)$_2$][Δ-1]. This compound was prepared following the general procedure and isolated after column chromatography (R_f 0.64 (SiO_2, CH_2Cl_2)) in 79% yield. ^{1}H NMR (400 MHz, CD_2Cl_2, 295 K): δ 8.57 (s, 1H, H_7), 8.49 (d, ^3J = 3.8 Hz, 1H, H_6), 8.01 (t, ^3J = 7.6 Hz, 1H, H_4), 7.76 (d, ^3J = 7.6 Hz, 1H, H_3), 7.61 (t, ^3J = 5.6 Hz, 1H, H_5), 1.35 (s, 9H, H_9). ^{13}C NMR (100 MHz, CD_2Cl_2, 295K): δ 156.3 (C_7), 151.1 (C_2), 148.7 (C_6), 141.7 (d,$^3J(C,P)$ = 6.4 Hz, 6C, $C_{1'}$), 138.1 (C_4), 127.9 (C_5), 126.9 (C_3), 122.4 (6C, $C_{3'}$), 113.7 (d, $^3J(C,P)$ = 19.1 Hz, 6C, $C_{2'}$), 60.0 (C_8), 30.1 (C_9). ^{31}P NMR (162 MHz, CD_2Cl_2, 295K): δ − 79.9 (s). IR (cm^{-1}): ν 2970w, 2920w, 2870w, 1623w, 1446s, 1389m, 1301m, 1236m, 990s, 817s, 718s, 668s. UV/Vis ($CHCl_3$, 4.67 × 10^{-5} M): λ_{max} (ε) 231 (24 × 10^3), 242 (53 × 10^3), 281 (21 × 10^3), 289 (21 × 10^3), 300 (15.8 × 10^3), 479 (9.7 × 10^3). $[\alpha]^{20}_D$ = − 296; $[\alpha]^{20}_{578}$ = − 278; $[\alpha]^{20}_{546}$ = − 333; $[\alpha]^{20}_{436}$ = − 1000; $[\alpha]^{20}_{365}$ = − 1889 (c = 0.0054, $CHCl_3$). MS (ES): (−) 768.8 ([**1**]$^-$); (+) 387.3 [CuL_2]$^+$), 225.3 ([CuL]$^+$).

[Cu(4d)$_2$][Δ-1]. This compound was prepared following the general procedure and isolated after column chromatography (R_f 0.7 (SiO_2, CH_2Cl_2)) in 80% yield. ^{1}H NMR (400 MHz, CD_2Cl_2, 295 K): δ 8.61 (s, 1H, H_7), 8.48 (d, ^3J = 4.8 Hz, 1H, H_6), 8.02 (td,^3J = 7.6 Hz, ^3J = 1.5 Hz, 1H, H_4), 7.75 (d, ^3J = 7.8 Hz, 1H, H_3), 7.61 (ddd, ^3J = 5.1 Hz, ^3J = 4.8 Hz, ^3J = 1.3 Hz, 1H, $H_5$5), 4.03 (septet, ^3J = 6.3 Hz, 1H, H_8), 1.22 (br, 6H, H_9). ^{13}C NMR (100 MHz, CD_2Cl_2, 295K): δ 158.3 (C_7), 150.6 (C_2), 148.9 (C_6), 141.8 (d,$^3J(C,P)$ = 6.4 Hz, 6C, $C_{1'}$), 138.1 (C_4), 127.9 (C_5), 126.6 (C_3), 122.4 (6C, $C_{3'}$), 113.7 (d, $^3J(C,P)$ = 19.8 Hz, 6C, $C_{2'}$), 60.6 (C_8), 24.3 (C_9). ^{31}P NMR (162 MHz, CD_2Cl_2, 295K): δ − 79.7 (s). IR (cm^{-1}): ν 2969w, 2921w, 2862w, 1618w, 1592w, 1446s, 1387m, 1300m, 1235m, 1154w, 990s, 817s, 718m, 668s. UV/Vis ($CHCl_3$, 4.25 × 10^{-5} M): λ_{max} (ε) 228 (20 × 10^3), 241 (47 × 10^3), 280 (18 × 10^3), 289 (17.8 × 10^3), 301 (13.5 × 10^3), 476 (8.3 × 10^3). $[\alpha]^{20}_D$ = − 250; $[\alpha]^{20}_{578}$ = − 229; $[\alpha]^{20}_{546}$ = − 292; $[\alpha]^{20}_{436}$ = − 833; $[\alpha]^{20}_{365}$ = − 1500 (c = 0.0048, $CHCl_3$). MS (ES): (−) 768.8 ([**1**]$^-$); (+) 359.3 ([CuL_2]$^+$), 211.4 ([CuL]$^+$).

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