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Remote control: stereoselective coordination of electron-deficient 2,2′-bipyridine ligands to Re(I) and Ir(III) cores†

Kimberley Jerwood,[a] Phoebe Lowy,[a] Laura Deeming,[a] Benson M. Kariuki [a] and Paul D. Newman *[b]

Highly diastereoselective coordination of unsymmetrical cationic 2,2′-bipyridine ligands bearing a chiral amidinium substituent to [Re(CO)$_3$Cl] and [Ir(PhPy)$_2$]$^+$ cores is reported. Binding strength and stereoselectivity have been correlated with the position of the amidinium group on the bipy. The 4-, 5- and 6-substituted ligands all produce *C*-[Re(CO)$_3$(LH)Cl]X selectively, while only the 4-derivative gives preferred formation of Δ-[Ir(Phpy)$_2$(4-LH)](BF$_4$)$_2$.

Stereogenic-at-metal complexes are proving increasing useful in the fields of photo-, outer-sphere (hydrogen-bonding) and Lewis acid catalysis.[1] Adopted coordination motifs are dictated by the choice of metal/ligand combination and are dominated by tetrahedral (including piano-stool complexes) and octahedral geometries. Bis- or tris-chelate complexes of the latter can have Δ or Λ configuration about the metal and are either true enantiomers (solely stereogenic-at-metal)[1h,2] or exist as diastereomers through the presence of one or more chiral element in a ligand(s).[2,3] The advantage of the latter is that the asymmetric ligand can control the resultant stereochemistry at the metal centre precluding often laborious separation of the Λ and Δ forms; the judicious choice of a chiral-pool derived ligand is, of course, essential.

Metallaphotoredox catalysis combines photo- and organometallic catalysts to enable transformations that are otherwise infeasible.[4] The two catalysts are usually separate species that are required to come into close contact for electron-transfer or to capture reactive radicals during critical reaction stages.[4] The combination of both functions within a single entity should enable more efficient performance by ensuring close proximity of all reactive species throughout the catalytic cycle.[5] We are investigating the possibility of constructing single-molecule catalysts containing both a photo-active centre and an organometallic unit for light-induced metallaphotoredox catalysis and/or application as theranostic agents. To meet these future aspirations, controlled formation of a carefully designed hetero-bimetallic complex is critical. Our approach involves synthesising ligands with two distinct features: a polyaromatic core capable of binding a d^6 transition metal; and a tethered masked donor for coordinating a second metal ion. A protected function is chosen to enable discreet inclusion of the first metal before release of the latent donor to sequester the second metal ion. Our initial ligand design combines a bipy unit with an amidinium group which acts as the latent form of an NHC ligand (Fig. 1). The intended route to heterobimetallics is through initial binding of the bipy prior to utilisation of the NHC for capture of a second metal ion.

The cationic amidinium substituent will deplete the electron-density in one, or both, of the pyridine rings, potentially reducing the donor capability of the bipy to transition metals. As downstream application of these compounds demands robust coordination of the bipy it was critical to establish any inherent limitations in its binding. The remit of the current study was hence threefold: to establish the coordination chemistry of the 4-, 5- and 6-bipy substituted ligands; to assess the

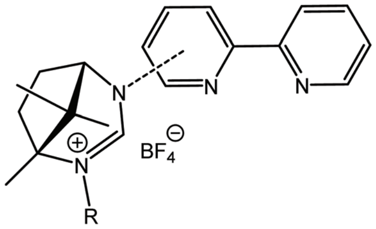

Fig. 1 General structure of the ligands. The abbreviations [n-L^{R}H]BF$_4$ are used throughout the manuscript where n indicates the position of substitution on the bipy and R is methyl (Me) or mesityl (Mes). Abbreviations of the type [n-L^R] represent the deprotonated NHC derivative.

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[a] *School of Chemistry, Cardiff University, Cardiff, Wales, CF10 3AT, UK*
[b] *Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff, Wales, CF10 3AT, UK. E-mail: newmanp1@cardiff.ac.uk*

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impact of the position of the amidinium group on coordination; and to explore any stereochemical diversity in the resultant complexes.

Simple access to the ligands was imperative and this proved to be the case through the synthetic procedure shown for the 4-substituted ligand, $[4\text{-L}^{\text{Me}}\text{H}]\text{BF}_4$, $\mathbf{4^{Me}}$, in Scheme 1. All synthetic steps occurred in high yield and the ligands could be prepared on multigram scale with easy final purification through recrystallisation as necessary. The 6-mesityl derivative, $[6\text{-L}^{\text{Mes}}\text{H}]\text{BF}_4$ ($\mathbf{6^{Mes}}$) was prepared by a modified method with the Mes group introduced before the final ring closure (see ESI†).

Introduction of the $[\text{Ir(Phpy)}_2]^+$ core was readily achieved using standard protocols (see ESI†). $[\text{Ir(Phpy)}_2(4\text{-L}^{\text{Me}}\text{H})](\text{BF}_4)_2\cdot(\text{EtOEtOH})$, **Ir-4**$^{\mathbf{Me}}$, precipitated from the reaction mixture as a bright orange solid in good yield with a further crop of crystalline material being obtained from the mother liquor on standing. The isomeric $[\text{Ir(Phpy)}_2(5\text{-L}^{\text{Me}}\text{H})](\text{BF}_4)_2$, **Ir-5**$^{\mathbf{Me}}$, also precipitated from solution as a dark rust-orange solid in low yield. The bulk of this complex was then obtained upon leaving the mother liquor to stand for several days and/or precipitation with water. The crystalline nature of the **Ir-4**$^{\mathbf{Me}}$ complex enabled characterisation by single-crystal X-ray diffraction techniques and the molecular structure of the cation is shown in Fig. 2. As is typical, the introduction of the bipy to the $[\text{Ir(Phpy)}_2]^+$ core induces a rearrangement of the cyclometallated Phpy ligands so that the nitrogens become mutually *trans* and the carbon donors lie *trans* to the bipy. Surprisingly, upon inspection of the molecular structure, there is no difference in the Ir–N$_{\text{bipy}}$ bond lengths with both being 2.144(4) Å. These compare with those for related complexes where values of 2.156(6) and 2.144(6) Å for a diphenylbipy derivative,[6] 2.137(5) Å for a CF_3 substituted derivative[7] and 2.123(7) Å for an unsymmetrical, 4-substituted bipy with an electron-rich antimony group[8] are reported. The other metrics about the metal are as expected for a structure of this type. The amidinium group, which can give rise to atropisomers if C–N bond rotation is restricted (see later), is canted with respect to its supporting pyridine ring with the two planes at an angle of 32.8°. The combination of the asymmetric $\mathbf{4^{Me}}$ with the Ir(III) core can generate two configurational isomers of $[\text{Ir(Phpy)}_2(4\text{-L}^{\text{Me}}\text{H})](\text{BF}_4)_2$, namely $\Delta_{R,S}$ and $\Lambda_{R,S}$ where the *R,S* notation refers to the pre-defined stereochemistry in $\mathbf{4^{Me}}$. Whilst both isomers might be expected to form, inspection of the solid-state structure shows the presence of only the $\Delta_{R,S}$ isomer and, given that the yield of the initially isolated solid was 71%, the complex is clearly formed diastereoselectively (see later). Similar discrimination has been observed in related systems[9] but remains rare[10] and, in this case given the remote position of the asymmetric unit, somewhat unexpected.

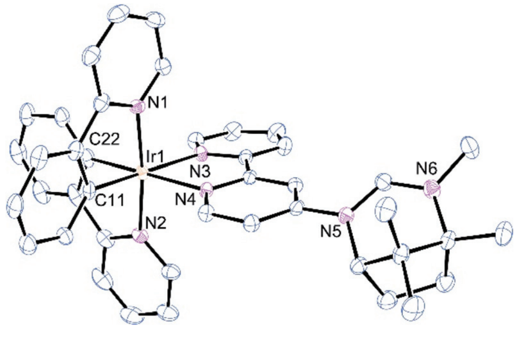
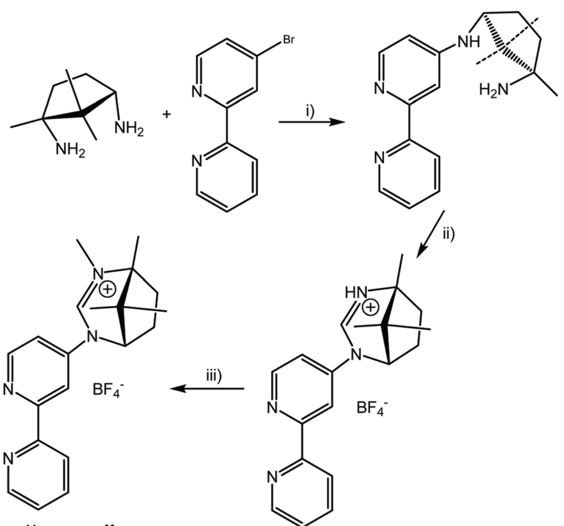


Fig. 2 Molecular structure of Δ-$[\text{Ir(Phpy)}_2(4\text{-L}^{\text{Me}}\text{H})]^{2+}$, **Ir-4$^{\mathbf{Me}}$**. The BF_4^- anions, hydrogen atoms and residual solvent have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ir1–N1 2.049(5); Ir1–N2 2.041(5); Ir1–C11 2.030(5); Ir1–C22 2.040(6); Ir1–N3 2.144(4); Ir1–N4 2.144(4); N1–Ir1–N2 174.13(19); C11–Ir1–C22 86.9(2); N3–Ir1–N4 76.41 (18).



$[4\text{-L}^{\text{Me}}\text{H}]\text{BF}_4$, $\mathbf{4^{Me}}$

Scheme 1 Synthesis of $[4\text{-L}^{\text{Me}}\text{H}]\text{BF}_4$, $\mathbf{4^{Me}}$. $[5\text{-L}^{\text{Me}}\text{H}]\text{BF}_4$, $\mathbf{5^{Me}}$ and $[6\text{-L}^{\text{Me}}\text{H}]\text{BF}_4$, $\mathbf{6^{Me}}$ were prepared in the same manner using 5- and 6-bromo-1,10-bipyridine respectively. $[6\text{-L}^{\text{Mes}}\text{H}]\text{BF}_4$, $\mathbf{6^{Mes}}$ was prepared by a different route (see ESI†). (i) Pd_2dba_3, $^t\text{BuONa}$, BINAP, PhMe, Δ; (ii) HC(OEt)_3, NH_4BF_4; (iii) MeI, K_2CO_3, MeCN.

As alluded above, the initial crop of Δ-**Ir-4$^{\mathbf{Me}}$** was obtained in 71% yield and confirmed as a single isomer by ^{1}H and ^{13}C NMR spectroscopy (see ESI†). A later crop isolated in 17% yield did show the presence of a second isomer at ∼20% abundance which translates to <4% of the total isolated yield (88%). This second species is likely to be Λ-**Ir-4$^{\mathbf{Me}}$**. Restricted rotation about the C$_{\text{bipy}}$–N$_{\text{amidinium}}$ bond can give rise to the observation of rotamers but this is considered unlikely here as there is no evidence of this for uncoordinated $\mathbf{4^{Me}}$ and no obvious obstruction in the complex to prevent facile interconversion of rotamers.

The stereoselectivity does not translate to $\mathbf{5^{Me}}$ as two diastereomers in ∼1 : 1 ratio are evident in the ^{1}H and ^{13}C{^{1}H} NMR spectra (see ESI†) of **Ir-5$^{\mathbf{Me}}$**. The clearest evidence is provided by the two doublets for the bridgehead hydrogen and two singlets for the N-C*H*$_3$ hydrogens in the ^{1}H NMR spectrum. This may indicate the presence of Δ and Λ forms or represent non-exchanging rotamers (atropisomers); there is no indication of four species from both configurational and rotational isomers. Heating a solution of **Ir-5$^{\mathbf{Me}}$** in d$_6$-dmso did not lead to the observation of a single species with only some broadening of the peaks being seen. Furthermore, there are no cross-peaks observed between the two isomers in the 2D NOESY ^{1}H/^{1}H NMR spectrum with selective radiation of notable signals in 1D ^{1}H NOESY NMR experiments corroborating this. These experiments confirm the presence of non-exchanging isomers but provide no evidence regarding the nature of the diastereomers. This is best addressed by reference to the CD spectra of the complexes.

The CD and electronic spectra of the complexes are given in Fig. 3 and in the ESI.† The CD manifold of **Δ-Ir-4$^{\mathbf{Me}}$** displays relatively large positive Cotton effects between 230 and 270 nm and 300 to 380 nm and a large negative band between 270–300 nm. This pattern is consistent with that observed for related systems having the Δ configuration about the metal.[11] By comparison, the CD spectrum of **Ir-5$^{\mathbf{Me}}$** is of low overall intensity with no evidence of the strong negative absorbance observed in the CD spectrum of the free ligand (see ESI†). The CD spectra of these complexes is expected to be dominated by a configurational component rather than a vicinal effect associated with the orientation of the amidinium group and the spectrum of [Ir(Phpy)$_2$(5-L^{Me}H)](BF$_4$)$_2$ is therefore indicative of a **Δ,Λ** diastereomeric mixture.

Coordination of the bipy ligands to the [Re(CO)$_3$Cl] core was achieved by heating 1 : 1 mixtures of [Re(CO)$_5$Cl] with [LH] BF$_4$ at 100 °C in chlorobenzene for 2–4 h. The resultant [Re(CO)$_3$(LH)Cl]BF$_4$ (**Re-4$^{\mathbf{Me}}$**, **Re-5$^{\mathbf{Me}}$**, **Re-6$^{\mathbf{Me}}$**, **Re-6$^{\mathbf{Mes}}$**) complexes were isolated as yellow to orange-yellow solids upon cooling and/or concentrating the reaction mixtures. Initial ^{1}H NMR analysis of the crude solid from the 1 : 1 reaction of **6$^{\mathbf{Me}}$** with [Re(CO)$_5$Cl] showed the presence of a major product with small amounts of up to three other products. A single recrystallisation from acetone/pentane gave a single product in 67% yield in a form suitable for structure determination by single-crystal X-ray means. The molecular structure of *C*-[Re(CO)$_3$(6-L^{Me}H)(Cl)$_{0.9}$(I)$_{0.1}$]I shown in Fig. 4 is typical with the bipy coordinated to the Re with slightly disparate Re–N bond lengths of 2.245(6) and 2.160(6) Å. The longer Re–N bond is to the pyridine ring bearing the amidinium group as expected based on both steric and electronic grounds. A related complex with a methylpyridinium group at the 6-position shows bond lengths of 2.198(4) and 2.155(5) Å.[12] The planar NCN unit of the amidinium group is canted with respect to the pyridine ring with a torsional angle of 63° and there appears to be an internal hydrogen bond between the NC*H*N hydrogen and the chloride. Approximately 10% of the cations contain iodide instead of chloride and the anions are I$^-$ not BF$_4$$^-$. Complications arising from mixed anions and competitive coordination were excluded in subsequent ligand preparations by implementation of a final treatment with saturated aqueous NH$_4$BF$_4$ to ensure complete removal of I$^-$.

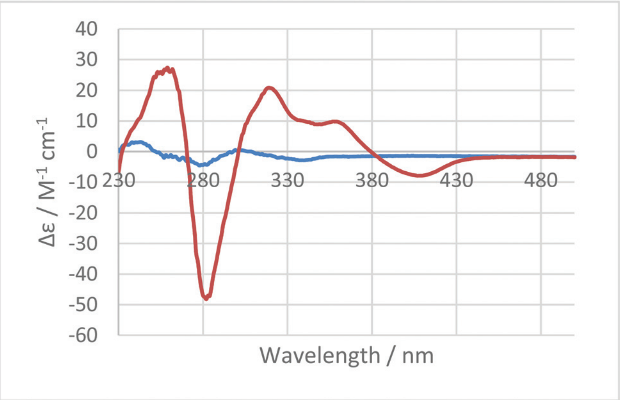


Fig. 3 CD spectra of Δ-[Ir(Phpy)$_2$(4-L^{Me}H)](BF$_4$)$_2$, **Δ-Ir-4$^{\mathbf{Me}}$** (red) and Δ,Λ-[Ir(Phpy)$_2$(5-L^{Me}H)](BF$_4$)$_2$, **Δ,Λ-Ir-5$^{\mathbf{Me}}$** (blue) recorded in CH$_2$Cl$_2$.

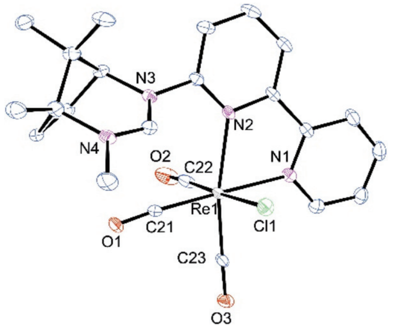


Fig. 4 Molecular structure of *C*-[Re(CO)$_3$(6-L^{Me}H)Cl]$^+$, **Re-6$^{\mathbf{Me}}$**. The I$^-$ anions, hydrogen atoms and residual solvent have been omitted for clarity. Selected bond lengths (Å) and angles (°): Re1–N1 2.160(6); Re1–N2 2.245(6); Re1–C21 1.904(8); Re1–C22 1.897(8); Re1–C23 1.907(7); N2–Re1–C23 169.6(3); N1–Re1–C21 177.8(3); N1–Re1–N2 75.0(2).

Mono-substituted bipy ligands coordinated to the [Re(CO)$_3$Cl] core can give rise to two enantiomeric forms, namely *A* and *C*, depending on the configuration of the ligands about the metal. When the *exo*-substituent itself is chiral, diastereomers will result. As the amidinium group in **6$^{\mathbf{Me}}$** has been derived from 1*R*,3*S*-camphoric acid, the carbon atoms at these positions retain their pre-defined stereochemistry and there are, therefore, two diastereomeric possibilities for **Re-6$^{\mathbf{Me}}$**; A_{Re} and C_{Re} (this assumes free rotation about the C–N bond to preclude the formation of atropisomers). As shown in Fig. 4, the complex adopts the *C*-configuration about the Re and there is no evidence of the *A* form in the unit cell. It would therefore appear that the coordination is stereoselective which was confirmed upon inspection of the ^{1}H and ^{13}C{^{1}H} NMR spectra where only a single set of signals were observed.

A second 6-substituted derivative, **6$^{\mathbf{Mes}}$**, showed the same configurational selectivity observed for *C*-**Re-6$^{\mathbf{Me}}$** (see the structure and data in the ESI†). An initial ^{1}H NMR examination of *C*-**Re-6$^{\mathbf{Mes}}$** showed the presence of two solution species, one of which proved to be **6$^{\mathbf{Mes}}$**. This was perplexing as the material used for the NMR analysis was the same as that for the structure determination. However, the NMR sample showed a loss of colour over time until the original bright yellow colour had dissipated completely to leave a colourless solution; at this stage only **6$^{\mathbf{Mes}}$** was detected in the ^{1}H NMR spectrum. It was clear that the ligand was being displaced in CD_3CN which was a surprise and reflects relatively weak binding of **6**$^{\mathbf{Mes}}$. No such ligand displacement was observed in CD_2Cl_2, $CDCl_3$ or d_6-acetone. Re-investigation of *C*-**Re-6**$^{\mathbf{Me}}$ showed similar ligand loss in CD_3CN although the timeframe here was appreciably longer with no substitution being observed upon leaving CD_3CN solutions overnight; slow progressive loss was seen upon monitoring the same solution for several weeks although complete ligand replacement was never achieved. The HRMS confirms the composition of both $[6\text{-LH}]^+$ complexes with parent ions at 627.1174 amu and 745.1955 amu respectively. The IR spectrum of the complexes in the solid state show the expected peaks at 2015, 1915 and 1880 cm^{-1} for *C*-**Re-6**$^{\mathbf{Me}}$ and 2019, 1913 and 1884 cm^{-1} for *C*-**Re-6**$^{\mathbf{Mes}}$.

The *C*-$[Re(CO)_3(4\text{-L}^{Me}H)Cl]BF_4$, *C*-**Re-4**$^{\mathbf{Me}}$, and $[Re(CO)_3(5\text{-L}^{Me}H)Cl]BF_4$, *C*-**Re-5**$^{\mathbf{Me}}$, complexes were prepared in a similar manner to that described for the **6**$^{\mathbf{Me}}$ derivative. Their synthesis was also stereoselective as there was no evidence of a second isomer in either case except when the ^1H NMR spectrum of *C*-**Re-5**$^{\mathbf{Me}}$ was recorded in d_6-dmso. Two species were apparent in this solvent as evidenced by duplicate peaks for certain resonances in the ^1H NMR spectrum. This may indicate the presence of atropisomers arising from restricted rotation about the C_{bipy}–$N_{amidinium}$ bond or the substitution of the chloride ligand by dmso. Two observations support the assignment of rotamers: the only peaks affected are those on or close to the amidinium unit (all methyls and the H4 and H6 hydrogens on the bipy) and the fact that an ∼1 : 1 mixture was always observed even after heating or prolonged standing of the solutions. The solid-state IR spectra of *C*-**Re-5**$^{\mathbf{Me}}$ showed ν(CO) stretches at 2025, 1929, and 1861 cm^{-1} and 2017, 1916 and 1877 cm^{-1} for *C*-**Re-4**$^{\mathbf{Me}}$.

The CD spectra for *C*-**Re-5**$^{\mathbf{Me}}$ and *C*-**Re-6**$^{\mathbf{Me}}$ are very similar but that of the 4-substituted ligand is somewhat different (ESI†). This does suggest a common configuration for both the 5- and 6- complexes which, given the established stereochemistry for the latter, must be *C*. The CD spectrum of *C*-**Re-4**$^{\mathbf{Me}}$ has less intense peaks and does not show the low energy negative maxima noted for the *C*-**Re-5**$^{\mathbf{Me}}$ and *C*-**Re-6**$^{\mathbf{Me}}$ derivatives. The +,- manifold is otherwise similar although both are shifted to low energy. The low values of $\Delta\varepsilon_{max}$ are commensurate with those reported by Autschbach for the separated *C* and *A* enantiomers of a $[Re(CO)_3(N\hat{}N')Br]$ complex where $N\hat{}N'$ is an unsymmetrical, achiral bipy.[13] These comparative values suggest little vicinal contribution from the stereogenic centres in the amidinium unit to the CD spectra which are dominated by the configuration effect. Although these authors were able to isolate the two enantiomers, they did not assign absolute configurations. It is noteworthy that the CD spectra recorded here show a strong correlation with one of the reported enantiomers with a –,+,– (complex) manifold between 330 and 230 nm.

The precise reasons for the selective formation of the *C*-$[Re(CO)_3(LH)Cl]BF_4$ and Δ-$[Ir(Phpy)_2(4\text{-L}^{Me}H)](BF_4)_2$ complexes and lack of selectivity with Δ,Λ-$[Ir(Phpy)_2(5\text{-L}^{Me}H)](BF_4)_2$ are not currently known but hydrogen-bonding between the coordinated chloride and the NC*H*N hydrogen of the amidinium group in the Re systems may be partly responsible as proposed previously in a related system.[12] Application of these systems to the formation of hetero-bimetallic complexes through the release and subsequent coordination-capture of the NHC donor is currently underway along with a theoretical exploration of the possible source(s) of the stereoselectivity reported herein.

In conclusion, a small library of $[Re(CO)_3(LH)Cl]BF_4$ and $[Ir(Phpy)_2(LH)](BF_4)_2$ complexes where LH is a cationic bipy derivative bearing a chiral amidinium group have been prepared and analysed. The Re(I) complexes were formed stereoselectively as the *C*-isomer irrespective of the position (4-, 5- or 6-) of the amidinium substituent on the bipy. Stereoselective formation of the Δ-configurational isomer was observed for the $[4\text{-LH}]^+$ ligand with the $[Ir(Phpy)_2]^+$ core whereas coordination of the 5-substituted analogue was non-stereoselective.

Conflicts of interest

There are no conflicts of interest to declare.

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