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It's all about Me: Methyl-Induced Control of Coordination Stereochemistry by a Flexible Tridentate *N,C,N'* Ligand

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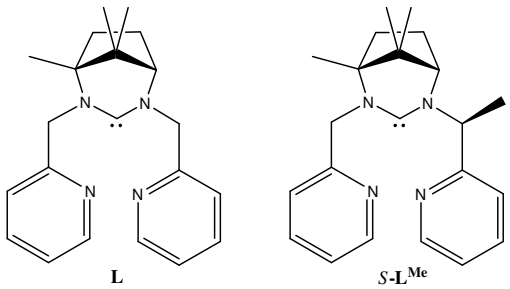
A chiral, tridentate, pyridyl-functionalised NHC pro-ligand, *S*-$\mathbf{L^{Me}}$-**H[PF$_6$]**, has been prepared diastereoselectively via a five step synthesis starting from 1*R*,3*S*-diamino-1,2,2-trimethylcyclopentane. The *S* prefix refers to the stereochemistry of a methyl substituted stereogenic carbon in one of the pyridyl arms which is generated by a stereoselective BH_4^- reduction of an imine precursor. The ligand has been coordinated to Rh(I) and Ir(I) to give trigonal bipyramidal complexes of the type [M(κ^3-*N,C,N'*-*S*-$\mathbf{L^{Me}}$)(1,5-COD)]PF$_6$ (M = Rh, Ir) as single diastereomers. A combination of spectroscopic and X-ray techniques confirm the stereoselective formation of the thermodynamically preferred *endo,endo* isomer. Similar reactions with *R*,*S*-$\mathbf{L^{Me}}$-**H[PF$_6$]** gave a mixture of *endo,endo*-[M(κ^3-*N,C,N'*-*S*-$\mathbf{L^{Me}}$)(1,5-COD)]$^+$ and *exo,exo*-[M(κ^3-*N,C,N'*-*R*-$\mathbf{L^{Me}}$)(1,5-COD)]$^+$. The absolute configuration at the metal is, therefore, solely dictated by the stereochemistry of the single methylpyridyl carbon. The observation of stereoselection extends to the square planar Ni(II) complex [Ni(δ-κ^3-*N,C,N'*-*S*-$\mathbf{L^{Me}}$)Cl]$^+$ which is isolated as one (δ) of the two possible conformational isomers. DFT studies have been employed to explain the observed stereoselectivity with the configurations observed in the solid state being confirmed as those of lowest energy.

Introduction

The design of asymmetric ligands for stereoselective coordination to metal centres is a mature area of academic and industrial research. Certain structural frameworks can be highly effective and have led to the development of so-called privileged ligands.[1] Although the characteristics that promote stereoselection are well understood for bidentate and many multidentate systems, a few ligand types remain underexplored. Conformationally constrained ligands possessing only sp^2-hybridised donors are one such class. Tridentates where each chelate consists solely of sp^2 hybridised atoms, e.g. terpy, are so restricted that they can only bind in a planar fashion. Greater flexibility can be achieved if one or more sp^3 carbon centres are introduced into a sp^2-rich backbone.[2] This modification allows increased conformational freedom and provides a point(s) for chiral elaboration.

Our interest in coordination stereoselectivity has lead us to explore the factors that govern stereo-control in metal systems of diverse geometry.[3] Within this remit we have been examining the coordination of dipyridylcarbene (*N,C,N'*) ligands to Rh(I) and Ir(I) to generate five-coordinate, trigonal-bipyramidal complexes of the type [M(κ^3-*N,C,N'*-**L**)(1,5-COD)]$^+$.[3c] The facial coordination of tridentate **L** (figure 1) in these complexes gives rise to two isomers, *exo,exo* and *endo,endo*, that differ in the relative orientation of the pyridyl rings with respect to the dimethylmethylene bridge of the central NHC unit. A negligible energy difference between these two configurations results in a lack of stereo-control upon coordination of **L** and a mixture of the two isomers is obtained. In order to promote stereospecific coordination this energy difference needs to be increased. One method to achieve this is through the introduction of substituents at one or both of the methylene groups linking the pyridyl rings to the bicyclic NHC. The rationale being that this would introduce unfavourable steric contacts in one of the two possible isomers. However, this is only possible if the chirality at the developing stereogenic centre can be controlled. The current work details a stereoselective synthetic route to the methylated derivative of **L**, namely *S*-$\mathbf{L^{Me}}$, and describes the stereospecific coordination of the ligand to trigonal bipyramidal Rh(I)/Ir(I) and square planar Ni(II).



L *S*-$\mathbf{L^{Me}}$

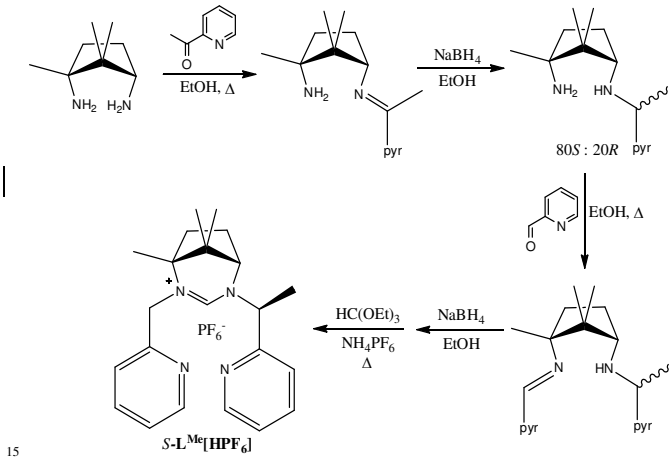
Fig. 1 The two *N,C,N'* ligands **L** and *S*-$\mathbf{L^{Me}}$.

Results and Discussion

c

Synthesis of S-L^{Me}[HPF_6] and R,S-L^{Me}[HPF_6]

The current N,C,N' ligand *S*-$\mathbf{L^{Me}}$ is based on the parent framework **L** shown in figure 1 but has a methyl substituent on the 3-amino pyridyl arm. As alluded above the introduction of this methyl is desirable as it is anticipated that it will demand an equatorial disposition off the six-membered chelate ring and/or show unfavourable contacts with the bicyclic skeleton in one or other of the possible isomers. These latter interactions might be exacerbated if the methyl is positioned on the other pyridyl arm, *i.e.* α to the 1-amino group. However this is synthetically more challenging and is a longer term goal. Any attempt at improving coordination stereochemistry will only be effective if the chirality at the new carbon centre is fixed. This proved to be possible through the synthetic pathway shown in scheme 1.



Scheme. 1 Synthetic pathway to *S*-$\mathbf{L^{Me}}$**-H[PF$_6$]**.

Two aspects of the synthesis are critical for the successful formation of the amidinium precursor *S*-$\mathbf{L^{Me}}$**-H[PF$_6$]**. The first involves the regioselective reaction of 2-acetylpyridine at the 3-amino group of 1,2,2-trimethyl-1,3-diaminocyclopentane. This is achieved in essentially quantitative yield with no evidence of formation of the 1-amino regio-isomer. Indeed the 1-amino group is completely unreactive towards the ketone as shown by reactions performed with >1 mol equivalent of 2-acetylpyridine. The second crucial step of the synthesis is the subsequent reduction of the imine to generate, at the ideal, a single isomer. When the reduction was performed with $NaBH_4$ in MeOH an approximately 4:1 diastereomeric mixture of the diamines was produced. Although not stereospecific, this was a very pleasing result and, given the simple nature of the hydridic reagent, it is clear that the discrimination during reduction derives purely from the effect of the bicyclic framework. No attempt was made to separate the diastereomeric mixture of diamines which was used for the subsequent ring closure with triethylorthoformate to give, after work-up, a single isomer of $\mathbf{L^{Me}}$**-H[PF$_6$]** in 52% overall yield. The pure major isomer was isolated in two ways. Firstly from the initial precipitate of the ring-closure reaction by a single crystallisation from n-BuOH and, secondly, from the mother liquor upon standing at RT. Interestingly, in both cases, the second crop of crystals obtained were a 1:1 mixture of the two diastereomers *R*-$\mathbf{L^{Me}}$**-H[PF$_6$]** and *S*-$\mathbf{L^{Me}}$**-H[PF$_6$]**.

Although the absolute stereochemistry of the newly formed chiral carbon in the predominant isomer of $\mathbf{L^{Me}}$**-H[PF$_6$]** could not be ascertained directly, the crystal structures of two related compounds derived by the same synthetic route but substituting the 2-pyridinecarboxaldehyde with salicylaldehyde or 2-methoxybenzaldehyde at the penultimate stage show the stereochemistry at this centre to be *S* (one example is shown in figure 2). Thus it is reasonable to assign the same stereochemistry to $\mathbf{L^{Me}}$**-H[PF$_6$]** (this is confirmed by the single crystal X-ray structure of the iridium complex below).

As for the related **L-H[PF$_6$]** the NC*H*N hydrogen is seen as a singlet at δ = 8.27 ppm in the ^{1}H NMR spectrum of *S*-$\mathbf{L^{Me}}$**-H[PF$_6$]**. Other features of note are the two doublets for the two unique pyridine ortho-hydrogens, the quartet for the methine hydrogen at the chiral pyridyl carbon and the AB pattern of two doublets for the diastereotopic CH_2 hydrogens of the other pyridyl arm. Although some of the resonances for each isomer in the ^{1}H NMR spectrum of the diastereomeric mixture were inevitably overlapping, both NC*H*N signals, the two doublets for the methine hydrogen at the 3-position of the bicyclic ring and some of the methyl signals were clearly distinct. These resonances were employed to confirm the 1:1 composition of the mixture.

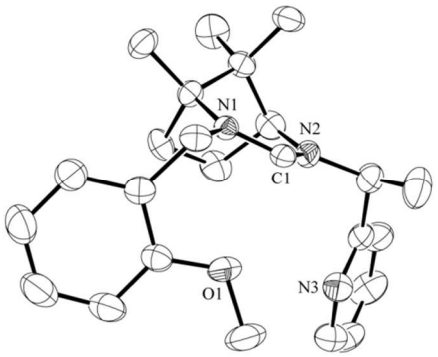


Fig. 2 Ortep view of the molecular structure of the major isomer of 4-(2-methoxybenzyl)-2*S*-[1-(pyridin-2-yl)ethyl]-5,8,8-trimethyl-4-aza-2-azoniabicyclo[3.2.1]oct-2-ene. Thermal ellipsoids are drawn at 50% probability, hydrogens are omitted for clarity. Selected bond lengths (Å) and angles(º): C1-N1 1.327(4), C1-N2 1.312(4), N1-C1-N2 123.2(3).

Complexes of S-$\mathbf{L^{Me}}$ with Rh(I) and Ir(I)

Although there are a number of examples of bis(pyridin-2-ylmethyl)NHC ligands in the literature,[4] there has only been one rhodium or iridium complex reported outside of our own studies.[5] Furthermore, not one of the known bis(pyridin-2-ylmethyl)NHC ligands has substituents on the pyridyl arm and hence there are no extant examples bearing a chiral centre in these chelates. This serves to emphasise the unique features of the current ligand system. It is noteworthy however that similar inverse pincers (CNC) with a central pyridine are known.[6]

Synthesis of the rhodium and iridium complexes was achieved upon reflux of *S*-$\mathbf{L^{Me}}$**-H[PF$_6$]** with 0.5 mol equivalents of $[Rh(1,5\text{-COD})(\mu\text{-OMe})]_2$ or $[Ir(1,5\text{-COD})(\mu\text{-OMe})]_2$ in MeOH. $[Ir(\kappa^3\text{-}N,C,N'\text{-}S\text{-}\mathbf{L^{Me}})(1,5\text{-COD})]PF_6$ was obtained as a

colourless solid that could be recrystallised from MeOH as blocky crystals. The ^{1}H NMR spectrum of the isolated solid is consistent with the formation of a single isomer as evidenced by the presence of three singlets and a doublet for the methyls, three separate resonances for the benzylic type hydrogens and a total of eight signals for the pyridine hydrogens. Thus, of the four possible isomers of [Ir(κ^3-*N,C,N'*-*S*-**L^{Me}**)(1,5-COD)]$^+$, namely *exo-exo*, *endo-endo*, *exo-endo* and *endo-exo*, only one is formed. There was no evidence of the latter two isomers in [Ir(κ^3-*N,C,N'*-**L**)(1,5-COD)]PF_6 and the isolated complex proved to be an *exo-exo*/*endo-endo* mixture.[3c] Thus although there was a degree of diastereoselectivity in this system, complete stereospecificity was lacking. The NMR data highlighted above prove that this is not the case with *S*-**L^{Me}** where selective formation of one isomer is observed. Closer inspection of the ^{1}H NMR spectrum shows one of the methyl resonances to high field of TMS (figure 3). This is highly characteristic of the *endo,endo* isomer and results from a methyl group of the dimethylmethylene bridge residing over the aromatic ring of both pyridines.[3] This is confirmed on determination of the molecular structure by single-crystal X-ray techniques (figure 4).

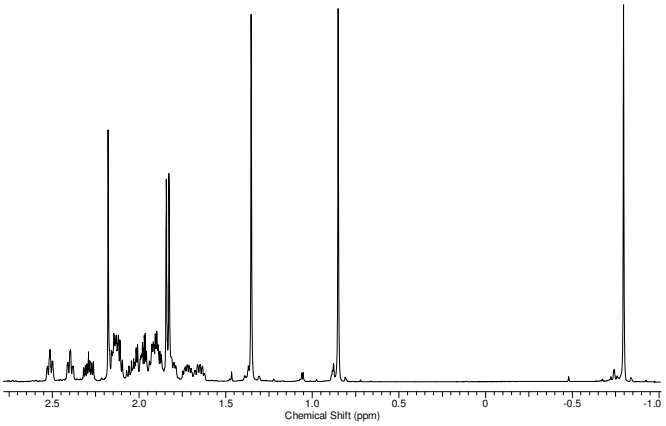


Fig. 3 The high-field region of the 1H NMR spectrum of *endo,endo*-[Ir(κ^3-*N,C,N'*-*S*-**L^{Me}**)(1,5-COD)]$^+$.

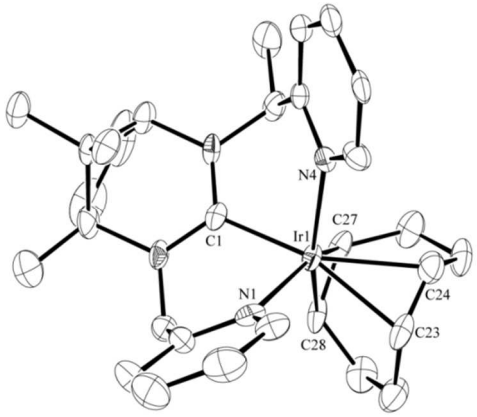


Fig. 4 Ortep view of the molecular structure of *endo,endo*-[Ir(κ^3-*N,C,N'*-*S*-**L^{Me}**)(1,5-COD)]$^+$. Thermal ellipsoids are drawn at 50% probability, hydrogens are omitted for clarity. Selected bond lengths (Å) and angles(°): Ir1-C1 2.058(11), Ir1-N1 2.282(8), Ir1-N4 2.221(8), Ir1-C23 2.228(11), Ir1-C24 2.244(12) Ir1-C27 2.116(8), Ir1-C28 2.093(8), C1-Ir1-N1 84.5(4), C1-Ir1-N4 84.4(4), N1-Ir1-N4 88.9(3), C1-Ir1-C27 90.3(4), C1-Ir1-C28 93.7(4).

The structure, which is both trigonal bipyramidal and *endo,endo*, mimics that already reported for [Ir(κ^3-*N,C,N'*-**L**)(1,5-COD)]PF_6.[3c] The Ir-C_{NHC} bond length of 2.058(11) Å is essentially the same as that for the related complex with **L** where a value of 2.008(13) Å was observed.[3c] It is noteworthy that the shorter Ir-N bond length is to the pyridyl arm containing the methyl substituent: 2.221(8) Å vs. 2.282(8) Å. Other metrics of note are the relatively acute N-Ir-C bite angles of around 84 ° and the increased Ir-C_{COD} bond lengths for the bonds opposite the NHC donor compared to those trans to the pyridines. The two six-membered chelates have a boat conformation with the metal and the chiral carbon out of the square plane and an equatorially disposed methyl group. The boat conformation is common for six-membered chelates where the ligand atoms have the hybridisation sequence $(sp^2)_2(sp^3)(sp^2)_2$.[7] The *endo,endo* conformation is presumably enforced by the requirement for the methyl to be equatorial (see below).

The analogous rhodium complex *endo,endo*-[Rh(κ^3-*N,C,N'*-*S*-**L^{Me}**)(1,5-COD)]PF_6 was prepared in a similar manner to the iridium except that the methoxy dimer was generated in situ from $[Rh(1,5\text{-COD})Cl]_2$ and NaOMe. All the spectroscopic features highlighted for the iridium complex were present in the ^{1}H NMR spectrum of *endo,endo*-[Rh(κ^3-*N,C,N'*-*S*-**L^{Me}**)(1,5-COD)]PF_6 establishing the configuration at Rh. The spin ½ ^{103}Rh nucleus results in an observable $^1J_{C\text{-}Rh}$ coupling constant of 40.8 Hz to the N*C*N carbon which is seen at δ_C 205 ppm in the $^{13}C\{^1H\}$ NMR spectrum. Both these values are similar to those for [Rh(κ^3-*N,C,N'*-**L**)(1,5-COD)]PF_6[3c] and other expanded ring NHC complexes.[8]

When the iridium complexation was performed with a 1:1 diastereomeric mixture of *R,S*-**L^{Me}-H[PF$_6$]**, a 1:1 mixture of two diastereomeric complexes was obtained. One of these was identified from the spectrum of the pure isomer detailed above as *endo-endo*-[Ir(κ^3-*N,C,N'*-*S*-**L^{Me}**)(1,5-COD)]PF_6. The second isomer did not show the high-field methyl resonance characteristic of the *endo,endo* form and hence appeared to be an *exo,exo* species. This was confirmed by a single-crystal X-ray structure determination of the complex as shown in figure 5. The stereogenic pyridyl carbon has the *R* configuration as anticipated and the conformation about the metal is indeed *exo-exo*. The change in configuration appears to be driven by the desire to avoid an axial projecting methyl substituent which would necessarily result if the coordination mode was *endo,endo*. Thus the stereochemistry about the metal appears to be controlled by this single carbon centre such that inversion at this carbon results in a change in configuration at the metal. The bond lengths and angles differ very little from those observed for *endo-endo*-[Ir(κ^3-*N,C,N'*-*S*-**L^{Me}**)(1,5-COD)]PF_6 with the Ir-N bond to the pyridyl arm with the methyl substituent again being observably shorter than the other Ir-N bond.

The deductions drawn from the empirical data have been supported by DFT calculations as shown by the relative energies in Table 1. For the ligand without the methyl

substituent (**L**), the energy difference between the *endo,endo* and *exo,exo* isomers of [Ir(κ^3-*N,C,N*'-**L**)(1,5-COD)]$^+$ is less than 1 kJ mol^{-1} which explains the lack of stereoselection observed upon coordination. However, as predicted, the introduction of the methyl group has a profound effect on the relative stability of the two isomers and, significantly, when the methyl-bearing carbon has the *S* stereochemistry the *endo,endo* conformation is preferred whilst the *exo,exo* is favoured when the stereogenic carbon is *R*.

Table 1 DFT derived relative energies for the *endo,endo* and *exo,exo* diastereomers of [Ir(κ^3-*N,C,N*')(1,5-COD)]$^+$ where *N,C,N*' is L, *S*-L^{Me} and *R*-L^{Me}.

Ligand	Stereochemistry	E / kJ mol^{-1}
L	*endo,endo*	0.91
L	*exo,exo*	0.00
S-**L^{Me}**	*endo,endo*	0.00
S-**L^{Me}**	*exo,exo*	8.44
R-**L^{Me}**	*endo,endo*	15.02
R-**L^{Me}**	*exo,exo*	0.00

*Complexes of S-**L^{Me}** with Ni(II)*

To examine whether this stereoselectivity extends to metals in other geometries we investigated the reaction of *S*-**L^{Me}-H[PF$_6$]** with Ni(COD)$_2$. We have shown previously that **L-H[PF$_6$]** undergoes oxidative addition at Ni(0) to give, ultimately, the square planar complex [Ni(κ^3-*N,C,N*'-**L**)Cl]PF$_6$ as a mixture of two conformational isomers (λ and δ).[3d] When the reaction was performed with *S*-**L^{Me}-H[PF$_6$]** the resultant [Ni(κ^3-*N,C,N*'-*S*-**L^{Me}**)Cl]PF$_6$ complex was obtained as a single diastereomer. The ^{1}H NMR spectrum of the isolated complex shows an AB pattern of doublets for the pyridyl CH$_2$ hydrogens at 5.91 and 4.95 ppm and a quartet for the methine hydrogen on the chiral carbon of the other pyridyl arm. The resonance for the methyl group on the chiral chelate carbon is observed as a doublet at 3.05 ppm, a shift of 1.21 ppm downfield from its position in the amidinium salt. A further distinguishing feature is the presence of one methyl resonance at relatively high field (0.27 ppm) which reflects its location in a shielding region of one of the pyridine rings. Such an orientation is seen in the crystal structure of [Ni(κ^3-*N,C,N*'-**L**)Cl]PF$_6$ which also reveals a boat conformation for both 6-membered chelates. It might be anticipated that the selective adoption of the δ or λ conformation in [Ni(κ^3-*N,C,N*'-*S*-**L^{Me}**)Cl]PF$_6$ results from a preference for an equatorially disposed methyl group. However, this is apparently not the case.

Although empirical confirmation of this was not possible (crystals suitable for structural analysis proved elusive), DFT calculations show the species with an axial methyl and a δ conformation to be preferred by ~15 kJ mol^{-1} (Figure 6). This conclusion is fully endorsed by spectroscopy with the 2D ^{1}H-NOESY spectrum of the complex showing clear proximity contacts between the pyr-C*H*(CH$_3$) hydrogen and the methine hydrogen of the bicyclic frame and between the pyr-CH(C*H*$_3$) hydrogens and the high-field methyl group. Both are only possible in the predicted structure. Further support comes from DFT prediction of ^{1}H chemical shifts where a good correlation between the calculated and empirical chemical shift is seen for the δ conformer. For the alternative λ conformer the agreement between experiment and prediction is acceptable for most nuclei but poor for the chemical shifts of the chiral methine and methyl protons (see supplementary material).

There is little of distinction in the ^{13}C{^{1}H} NMR spectrum of [Ni(δ- κ^3-*N,C,N*'-*S*-**L^{Me}**)Cl]PF$_6$ other than the resonance of the NHC carbon which is seen at δ$_C$ 177.5 ppm, a position ~30 ppm upfield of the analogous carbon in [Ni(κ^3-*N,C,N*'-**L**)Cl]PF$_6$. The chemical shift seen here is more like those reported for Ni(II) complexes with saturated 5-NHCs.[9]

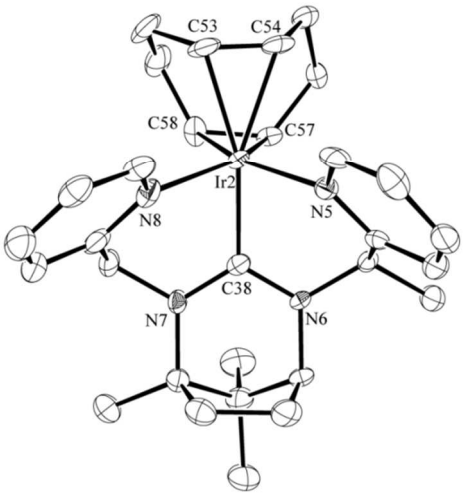


Fig 5 Molecular structure of *exo,-exo*-[Ir(κ^3-*N,C,N*'-*R*-**L^{Me}**)(1,5-COD)]$^+$. The asymmetric unit of the crystal also contains a molecule of *endo,endo*-[Ir(κ^3-*N,C,N*'-*S*-**L^{Me}**)(1,5-COD)]PF$_6$ (not shown). Thermal ellipsoids are drawn at 50% probability, hydrogens are omitted for clarity. Selected bond lengths (Å) and angles(°): Ir2-C38 2.039(7), Ir2-N5 2.214(6), Ir2-N8 2.303(6), Ir2-C53 2.203(7), Ir2-C54 2.243(7) Ir2-C57 2.124(7), Ir2-C58 2.115(7), C38-Ir2-N5 84.9(3), C38-Ir2-N8 83.7(2), N5-Ir2-N8 88.2(2), C38-Ir2-C57 92.0(3), C38-Ir2-C58 96.1(3).

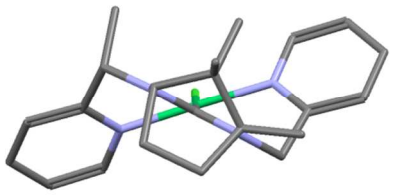


Fig 6 Geometry optimised molecular structure of [Ni(δ-κ^3-*N,C,N*'-*S*-**L^{Me}**)(Cl)]$^+$. Hydrogens are omitted for clarity.

Conclusions

The introduction of a methyl group at one of the pyridyl arms of a dipyridyl-NHC ligand converts a non-selective tridentate *N,C,N*' donor to a highly stereoselective ligand for trigonal pyramidal Rh(I) and Ir(I). The failure of the non-methylated ligand to enforce coordination stereoselectivity is ascribed to a very small energy difference between the two possible isomers designated *endo,endo* and *exo,exo*. The mono-methyl derivative is able to discriminate between the two by virtue of a larger energy difference resulting from a preferred

equatorial disposition of the methyl that is only available in one of the diastereomers. The absolute configuration at the metal in the five-coordinate Rh(I) and Ir(I) complexes is controlled solely by the chirality of the pyridyl carbon with the *S* isomer producing the *endo,endo* complex and the *R* isomer the *exo,exo*. In the square planar Ni(II) complex *S*-$\mathbf{L^{Me}}$ exhibits conformational control with only the δ isomer being observed. The extension of these ligand systems to metal ions that prefer other coordination geometries, most notably tetrahedral, is currently being investigated.

Experimental

Methods and materials

All synthetic procedures and manipulations were performed under dry argon or nitrogen using standard Schlenk line techniques. All solvents were freshly distilled from sodium (toluene), sodium/benzophenone (THF) or calcium hydride (acetonitrile, methanol and dichloromethane) under nitrogen before use. All other chemicals were obtained commercially and used as received. The ^{1}H and ^{13}C NMR spectra were recorded on a Jeol Eclipse 300 MHz or Bruker 400, 500 or 600 MHz spectrometers and referenced to tetramethylsilane (δ = 0 ppm). Mass spectra were obtained using a Waters LCT Premier XE mass spectrometer. Elemental analyses were performed by Medac Ltd, UK.[10]

Syntheses

***S*-$\mathbf{L^{Me}}$-H[$\mathbf{PF_6}$].** A solution of *R*,*S*-tmcp[11] (2.00 g, 0.014 mol) and 2-acetylpyridine (1.70 g, 1 mol equiv) in EtOH (50 ml) was heated close to boiling for 4 hrs. After cooling, the solvent was removed on the rotavap and the residue redissolved in EtOH (50 ml). To this solution was added solid $NaBH_4$ (0.80 g, 0.021 mol) portionwise over 20 mins. The resulting mixture was stirred overnight before adding conc. HCl (1 ml) carefully with stirring. After stirring for a further 30 mins the volatiles were removed in vacuo, the residue dissolved in water (50 ml) and the mixture made strongly basic by addition of solid NaOH. The diamine that oiled out of solution was extracted into CH_2Cl_2 (3 x 50 ml), which was subsequently dried over $MgSO_4$, filtered and all volatiles removed *in vacuo* to give the monopyridyl diamine as a pale yellow oil. ^{1}H NMR analysis of this intermediate showed it to be a mixture of two isomers in a 3.5:1 ratio. The oil was dissolved in EtOH (50 ml) to which 2-pyridinecarboxaldehyde (1.50 g, 0.014 mol) was added. The solution was heated close to boiling for 2 hrs and then stirred overnight at RT. The solvent was removed in vacuo and the residue redissolved in EtOH (50 ml). To this solution was added solid $NaBH_4$ (0.80 g, 0.021 mol) portionwise over 20 mins. The resulting mixture was stirred overnight then conc. HCl (1 ml) added carefully with stirring. After stirring for a further 30 mins the volatiles were removed *in vacuo*, the residue dissolved in water (50 ml) and the mixture made strongly basic by addition of solid NaOH. The product that oiled out of solution was extracted into CH_2Cl_2 (3 x 50 ml), which was subsequently dried over $MgSO_4$, filtered and all volatiles removed in vacuo to give the dipyridyl diamine as a pale yellow oil. The oil was taken into triethylorthoformate (40 ml) and NH_4PF_6 (2.51 g, 1.1 equivs) added thereto. The mixture was heated at 120 °C for 2 hrs, cooled and the solubles decanted off from the sticky orange precipitate. Upon leaving to stand overnight colourless crystals formed in the mother liquor. These were filtered, washed sparingly with cold EtOH then diethyl ether and air-dried. Yield of *S*-$\mathbf{L^{Me}}$-H[$\mathbf{PF_6}$] = 0.95 g (14%). The orange gum was triturated in Et_2O to give a free-flowing solid which was crystallised from hot *n*-BuOH. The first crop of crystals proved to be a single isomer (*S*-$\mathbf{L^{Me}}$-H[$\mathbf{PF_6}$], yield = 2.40 g, 35%) whereas a second crop was a 1:1 diastereomeric mixture. The following spectroscopic details are for *S*-$\mathbf{L^{Me}}$-H[$\mathbf{PF_6}$]. ^{1}H NMR (CD_3CN, 250 MHz) δ 8.75 (1H, d, *J* 5.0 Hz), 8.69 (1H, d, *J* 4.8 Hz), 8.27 (1H, s), 7.93 (2H, m), 7.52 (3H, m), 5.01 (1H, q, *J* 7.0 Hz), 4.85 (1H, d, *J* 16.3 Hz), 4.77 (1H, d, *J* 16.3 Hz), 3.73 (1H, d, *J* 5.1 Hz), 2.15 (2H, m), 2.00 (2H, m), 1.84 (3H, d, *J* 7.0 Hz), 1.30 (3H, s), 1.09 (3H, s), 0.74 (3H, s) ppm. ^{13}C{^{1}H} DEPT NMR ($CDCl_3$, 125.8 MHz) δ 156.2 (C), 154.3 (CH), 154.2 (CH), 149.5 (CH), 149.2 (CH), 138.1 (CH), 137.7 (CH), 124.1 (CH), 123.6 (CH), 123.3 (CH), 122.7 (CH), 71.8 (C), 64.1 (CH), 63.9 (CH), 54.4 (CH_2), 40.7 (C), 39.9 (CH_2), 32.4 (CH_2, s), 21.4 (CH_2, s), 17.5 (CH_3, s), 16.4 (CH_3, s), 14.5 (CH_3, s) ppm.

***endo,endo*-[Rh(κ^3-*N,C,N'*-*S*-$\mathbf{L^{Me}}$)(1,5-COD)]$\mathbf{PF_6}$.** To a solution of [Rh(1,5-COD)(μ-OMe)]$_2$ generated in situ from [Rh(1,5-COD)(μ-Cl)]$_2$ (100 mg, 2.03 x 10^{-4} mol) and 2 equivalents of NaOMe in MeOH (10 ml) was added *S*-$\mathbf{L^{Me}}$-H[$\mathbf{PF_6}$] (200 mg, 4.06 x 10^{-4} mol) and the solution refluxed for 48 hrs under N_2. On return, the cooled solution was filtered and the orange filtrate concentrated to give a pale yellow ppt which was filtered off and recrystallised from MeOH. Yield = 175 mg (62%). ^{1}H NMR (CD_3CN, 250 MHz) δ 8.80 (2H, d, *J* 5.2 Hz), 7.89 (2H, m), 7.53 (2H, m), 7.40 (2H, m), 6.38 (1H, q, *J* 7.5 Hz), 5.36 (1H, d, *J* 15.0 Hz), 5.11 (1H, m), 4.95 (1H, d, *J* 15.0 Hz), 4.92 (1H, m), 3.36 (1H, d, *J* 4.7 Hz), 2.88 (1H, t br), 2.72 (1H, t br, *J* 7.4 Hz), 2.35 (2H, m), 2.20-1.80 (10H, m obscured), 1.81 (3H, d, *J* 7.5 Hz), 1.42 (3H, s), 0.79 (3H, s), - 0.91 (3H, s) ppm. ^{13}C{^{1}H} DEPT NMR (CD_3CN, 75.6 MHz) δ 205.0 (C, d, *J*C-Rh 40.8 Hz), 159.8 (C), 158.2 (CH), 151.5 (CH), 150.9 (CH), 138.3 (CH), 138.2 (CH), 124.3 (C), 124.0 (CH), 123.6 (CH), 120.6 (CH), 106.0 (CH), 104.9 (CH), 71.6 (C), 63.6 (CH), 63.3 (CH), 55.9 (CH_2), 54.7 (CH, d, *J* 17.3 Hz), 53.8 (CH, d, *J* 17.2 Hz), 42.0 (C), 38.6 (CH_2), 34.7 (CH_2), 33.4 (CH_2), 32.6 (CH_2), 29.2 (CH_2), 27.6 (CH_2), 21.0 (CH_3), 16.1 (CH_3), 15.8 (CH_3), 13.4 (CH_3) ppm. MS: 560 ([M^+], 100%). *Anal.*: Calc. for $C_{30}H_{41}N_4RhPF_6$: C, 51.06; H, 5.87; N, 7.94%. Found: C, 51.2; H, 6.0; N, 7.7%.

***endo,endo*-[Ir(κ^3-*N,C,N'*-*S*-$\mathbf{L^{Me}}$)(1,5-COD)]$\mathbf{PF_6}$.** A solution of [Ir(1,5-COD)(μ-OMe)]$_2$ (100 mg, 1.52 x 10^{-4} mol) and *S*-$\mathbf{L^{Me}}$-H[$\mathbf{PF_6}$] (150 mg, 3.03 x 10^{-4} mol) in methanol (10 ml) was refluxed for 72 hrs under N_2. On return, the cooled solution was filtered and the orange filtrate taken to dryness under reduced pressure. Recrystallisation was effected from MeOH to give colourless blocky crystals. Yield = 133 mg (56%). ^{1}H NMR (CD_3CN, 500 MHz) δ 8.85 (2H, d, *J* 5.7 Hz),

7.92 (2H, m), 7.54 (2H, m), 7.49 (1H, t, *J* 6.1 Hz), 7.43 (1H, t, *J* 6.0 Hz), 5.69 (1H, q, *J* 7.5 Hz), 5.08 (1H, d, *J* 15.1 Hz), 4.94 (1H, d, *J* 15.1 Hz), 4.71 (1H, m), 4.57 (1H, m), 3.44 (1H, d, *J* 5.0 Hz), 2.50 (1H, t, *J* 7.3 Hz), 2.40 (1H, t, *J* 7.7 Hz), 2.26 (1H, m), 2.11 (2H, m), 2.05-1.80 (5H, m obscured), 1.84 (3H, d, *J* 7.5 Hz), 1.72 (1H, m), 1.63 (1H, m), 1.33 (3H, s), 0.84 (3H, s), - 0.80 (3H, s) ppm. $^{13}C\{^{1}H\}$ DEPT NMR (CD_3CN, 125.8 MHz) δ 193.0 (C), 159.1 (C), 157.7 (CH), 151.3 (CH), 150.7 (CH), 138.0 (CH), 137.9 (CH), 124.6 (CH), 124.3 (CH), 123.0 (CH), 120.2 (CH), 91.7 (CH), 91.2 (CH), 71.3 (C), 63.5 (CH), 63.0 (CH), 56.2 (CH_2), 40.7 (C), 38.2 (CH_2), 35.0 (CH_2), 33.5 (CH_2), 33.0 (CH_2), 31.5 (CH), 30.0 (CH_2), 28.7 (CH_2), 20.5 (CH_3), 15.9 (CH_3), 15.4 (CH_3), 13.2 (CH_3) ppm. MS: 649 ([M^+], 100%). *Anal.*: Calc. for $C_{30}H_{41}N_4IrPF_6$: C, 45.33; H, 5.21; N, 7.05%. Found: C, 45.3; H, 5.2; N, 6.9%.

[Ir(κ³-*N,C,N'*-*R,S*-L^{Me})(1,5-COD)]PF_6. Prepared exactly as for the complex with *S*-L^{Me}**-H[PF_6]** but using *R,S*-L^{Me}**-H[PF_6]**. Yield = 114 mg (48%). Selected ^1H NMR data for *exo,-exo*-[Ir(κ³-*N,C,N'*-*R*-L^{Me})(1,5-COD)]PF_6 (CD_3CN, 500 MHz) δ 5.56 (1H, q, *J* 7.5 Hz), 5.00 (1H, d, *J* 15.2 Hz), 4.90 (1H, d, *J* 15.2 Hz), 4.71 (2H, m), 3.63 (1H, d, *J* 4.6 Hz), 1.81 (3H, d, *J* 7.5 Hz), 1.46 (3H, s), 1.07 (3H, s), 1.05 (3H, s) ppm. All other analytical data was the same as for the complex with *S*-L^{Me}.

[Ni(δ-κ³-*N,C,N'*-*S*-L^{Me})(Cl)]PF_6, 4. To a solution of [Ni(1,5-$COD)_2$] (111 mg, 4.06 x 10^{-4} mol) in THF (10 ml) was added *S*-L^{Me}**-H[PF_6]** (70 mg, 4.06 x 10^{-4} mol) and the solution sirred for 72 hrs under N_2. On return, the solution was filtered and the volatiles removed *in vacuo*. The residue was dissolved in $CHCl_3$ (10 ml) and exposed to air for 24 hrs. After filtering the solvents were removed to give a yellow oil. Although the compound was pure by NMR efforts to obtain crystals by crystallisation proved fruitless and only an oil could be recovered. Yield = 50 mg (62%). ^1H NMR ($CDCl_3$, 250 MHz) δ 8.99 (1H, d, *J* 6.0 Hz), 8.97 (1H, d, *J* 5.9 Hz), 7.80 (2H, m), 7.56 (1H, d, *J* 7.4 Hz), 7.44 (1H, d, *J* 7.4 Hz), 7.24 (2H, m), 5.86 (1H, d, *J* 15.4 Hz), 5.00 (1H, m), 4.92 (1H, d, *J* 15.4 Hz), 3.48 (1H, d, *J* 4.3 Hz), 3.00 (3H, d, *J* 6.8 Hz), 2.10-1.30 (4H, m), 1.20 (3H, s), 0.90 (3H, s), 0.21 (3H, s) ppm. $^{13}C\{^{1}H\}$ DEPT NMR (CD_3CN, 75.6 MHz) δ 177.5 (C), 158.0 (C), 155.3 (CH), 155.2 (C), 155.1 (CH), 140.4 (CH), 140.2 (CH), 124.1 (CH), 124.0 (CH), 123.3 (CH), 123.1 (CH), 72.5 (C), 71.3 (CH), 66.0 (CH), 54.4 (CH_2), 40.9 (C), 40.7 (CH_2), 32.4 (CH_2), 25.9 (CH_3), 21.3 (CH_3), 17.0 (CH_3), 15.3 (CH_3) ppm. MS: 432 ([M^+ - Cl^- + CN^-], 100%). *Anal.*: Calc. for $C_{22}H_{28}N_4NiClPF_6$: C, 44.96; H, 4.81; N, 9.54%. Found: C, 44.4; H, 5.0; N, 9.5%.

Crystallography

Data collection was carried out on a Bruker-Nonius Kappa CCD diffractometer using graphite monochromoated Mo Kα radiation (λ(Mo-Kα) = 0.71073 Å). The instrument was equipped with an Oxford Cryosystems cooling apparatus. Data collection and cell refinement were carried out using COLLECT[12] and HKL SCALEPACK.[13] Data reduction was applied using HKL DENZO and SCALEPACK.[23] The structures were solved using direct methods (Sir92)[14] and refined with SHELX-97.[15] Absorption corrections were performed using SORTAV.[16] All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were inserted in idealised positions with Uiso set at 1.2 or 1.5 times the Ueq of the parent atom. In the final cycles of refinement, a weighting scheme that gave a relatively flat analysis of variance was introduced and refinement continued until convergence was reached. Both PF_6^- counterion sites in *endo,endo*-[Ir(κ³-*S*-L^{Me})(1,5-COD)]PF_6 are disordered with two components and were refined with restrained geometry and ADPs. For one PF_6^- ion in Ir(κ³-*R,S*-L^{Me})(1,5-COD)]PF_6, some ADPs were restrained lightly to prevent excessive anisotropy. The details of the data collection and structure solution are collected in Table 2.

DFT studies

Geometry optimisations were carried out using Turbomole 5.10[17] using B97-D functional[18] with SV(P) basis set.[19] Chemical shifts were predicted using B3LYP[20] using TZVP basis set,[21] using Gaussian09.[22]

Table 2 Details of X-ray crystallographic data collection

	endo,endo-[Ir(κ³-*S*-L^{Me})(1,5-COD)]PF_6	[Ir(κ³-*R,S*-L^{Me})(1,5-COD)]PF_6
Empirical formula	$C_{30}H_{40}F_6PN_4Ir$	$C_{30}H_{40}F_6PN_4Ir$
Formula weight	793.83	793.83
Crystal system	Triclinic	Triclinic
Space group	P1	P1
a/Å	10.3682(2)	10.4200(3)
b/Å	10.7035(2)	11.6201(3)
c/Å	14.4653(2)	14.6854(3)
α °	106.2400(10)	108.477(2)
β °	96.2640(10)	90.483(2)
γ °	90.7710(10)	116.2940(10)
U/Å^3	1530.42(5)	1488.64(7)
Z	2	2
D_c/Mg m^{-3}	1.723	1.771
F(000)	788	788
θ range/º	2.95 to 27.48	1.48 to 28.29
Index ranges	-13≤h≤13, -13≤k≤13,	-11≤h≤13, -14≤k≤15,
	-18≤l≤16	-18≤l≤19
Reflections collected	10368	10004
Independent reflections	10033	9453
R_{int}	0.0000	0.0000
Data / restraints / parameters	10368 / 74 / 893	10004 /213 / 765
Goodness of fit on F^2	1.046	1.024
Final *R*1, *wR*2 [*I*>2σ(*I*)]	0.0258, 0.0604	0.0308, 0.0722
(all data)	0.0273, 0.0614	0.0341, 0.0741
Largest difference peak		
And hole/e Å^{-3}	1.132, -1.190	1.391, -1.575
Flack parameter	0.034(7)	0.013(7)

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Notes and references

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Graphical Abstract

It's all about Me: Methyl-Induced Control of Coordination Stereochemistry by a Flexible Tridentate *N,C,N'* Ligand

Benson M. Kariuki, James A. Platts, Paul D. Newman.

The introduction of a single methyl group on one of the chelate arms of a dipyridyl-NHC ligand has been achieved stereoselectively and the resultant tridentate ligand (*S*-$\mathbf{L^{Me}}$) coordinated to Rh(I), Ir(I) and Ni(II). Unlike the non-methylated parent ligand which shows little to no coordination selectivity, *S*-$\mathbf{L^{Me}}$ binds with a high degree of stereoselectivity to the trigonal bipyramidal and square planar metal complexes.