CHEMISTRY
A EUROPEAN JOURNAL

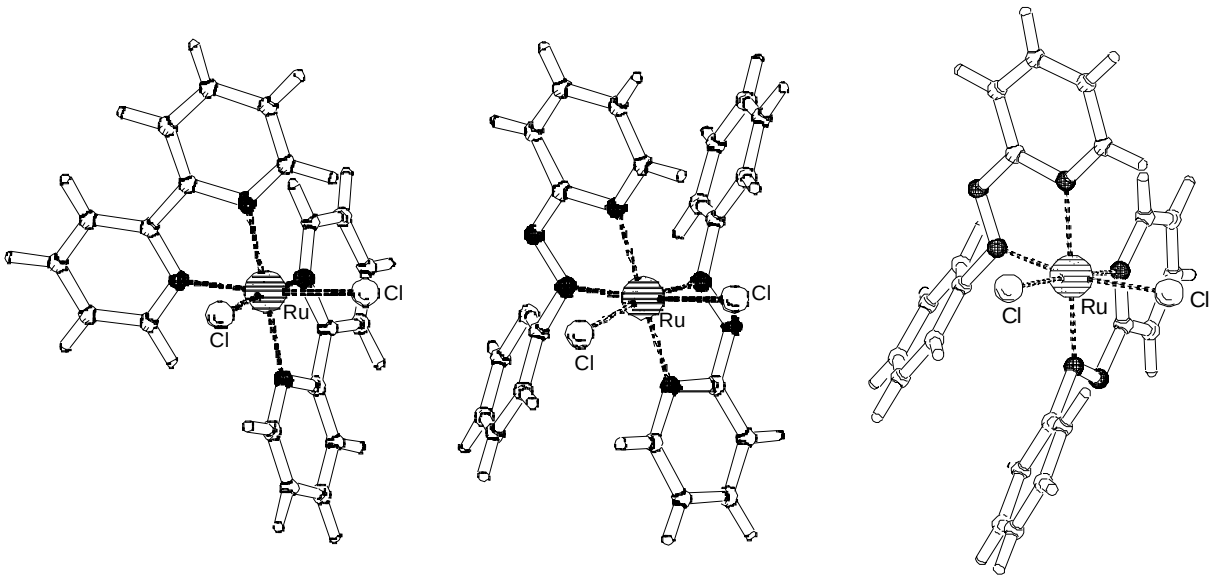
# Supporting Information

# Ligands Rock & Roll; Stepwise Twisting of Two *cis*-Coordinated Lopsided N-Heterocycles in an Octahedral Bis(2-phenylazopyridine)ruthenium(II) Complex with Seven Atropisomers.

Aldrik H. Velders,* Anna C. G. Hotze, Jan Reedjik

*[a] Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University*
*P.O. Box 9502, 2300 RA Leiden (The Netherlands)*
*a.velders@chem.leidenuniv.nl*

**Figure S1.** Molecular structures of the structurally similar complexes , ***cis***-$[Ru(bpy)_2Cl_2]$ (left),[&] α-$[Ru(azpy)_2Cl_2]$ (middle),[$] and β-$[Ru(azpy)_2Cl_2]$ (right).[$]




&: Eggleston, D.S., Goldsby, K.A., Hodgson, D.J., Meyer, T.J. ***Inorg. Chem.*****1985** 24 pg 4573
$: Seal, A. and Ray, S. ***Acta Cryst.*****1984** C40 pg.932

**Figure S2.** Schematic drawing of 16 theoretical orientation modes of two lopsided ligands (represented by the arrows) in a six-coordinated octahedral complex (the arches represent a didentate ligand like bpy or azpy). For ***cis***-$[Ru(bpy)_2(MeBim)_2](PF_6)_2$ and **2** the number of different conformers reduces due to the intrinsic $C_2$ axis (of the $[Ru(didentate)_2]$ moieties) in these complexes; however, for example, for β-$[Ru(azpy)_2(MeBim)_2](PF_6)_2$ the orientation of the two didentate ligands is such that no $C_2$ symmetry is present and all 16 orientations depicted below are different.

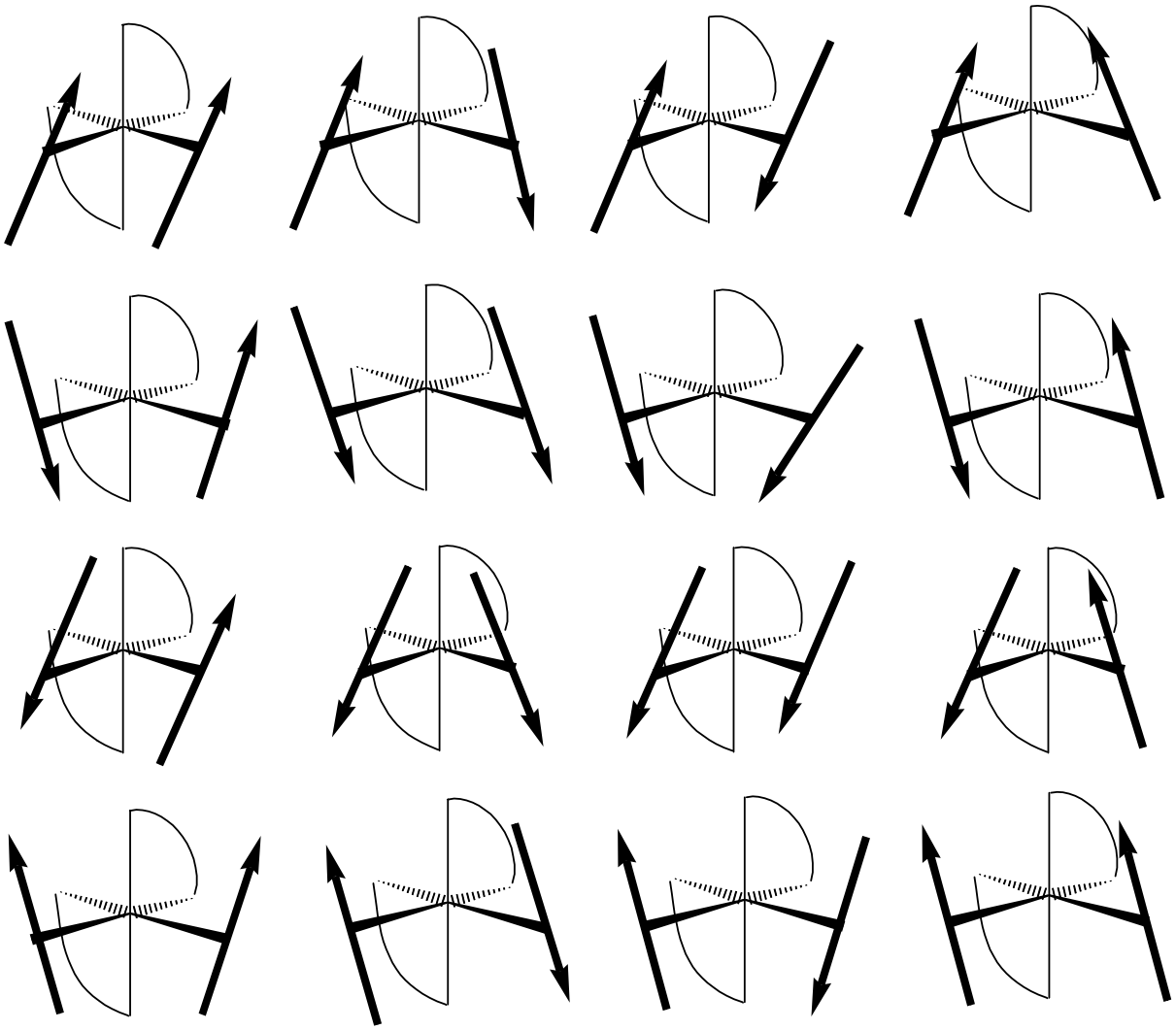


**Figure S3** Possible pathway for the interconversion of B<=>B

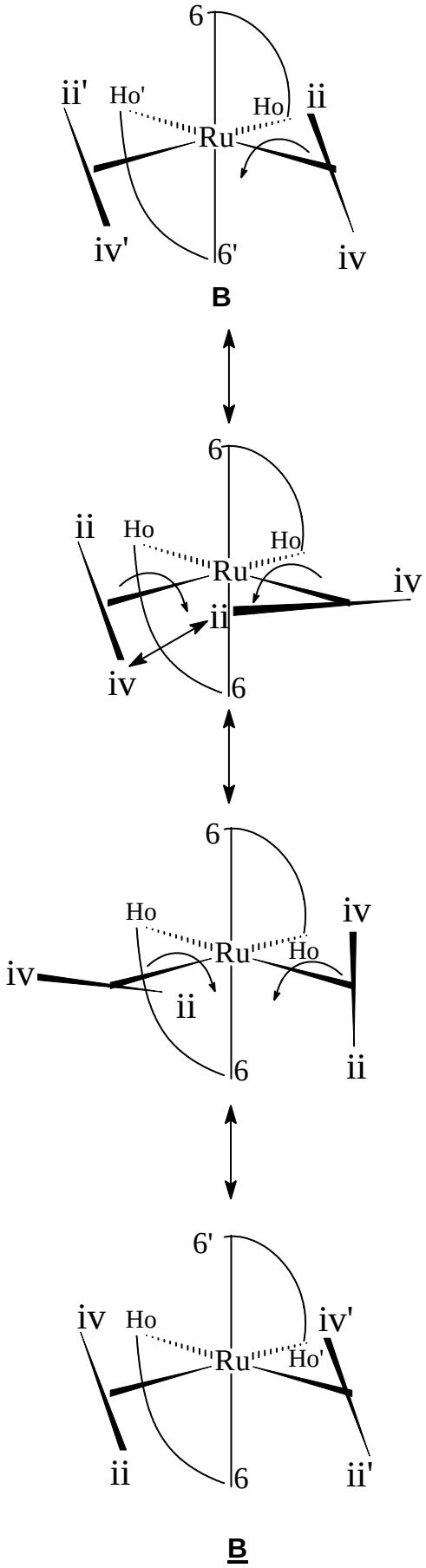


**Figure S4** Interconversion of C and E by synchronous rotation of both MeBim ligands by 90°

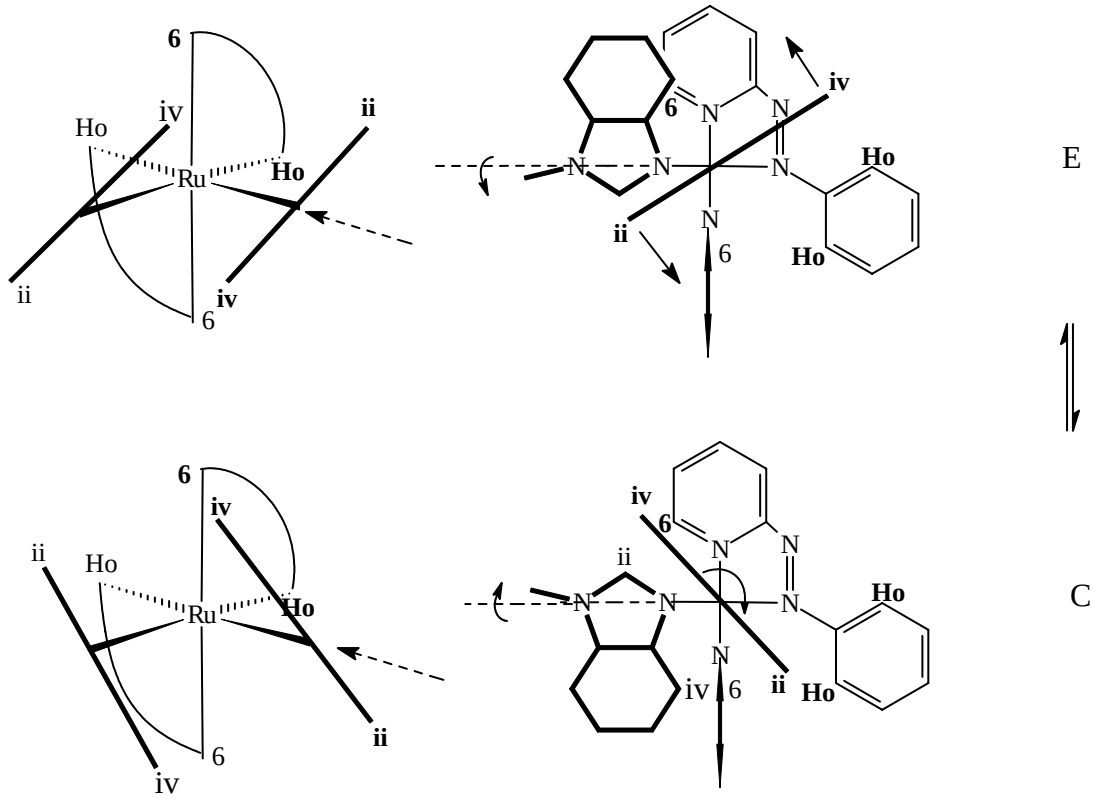
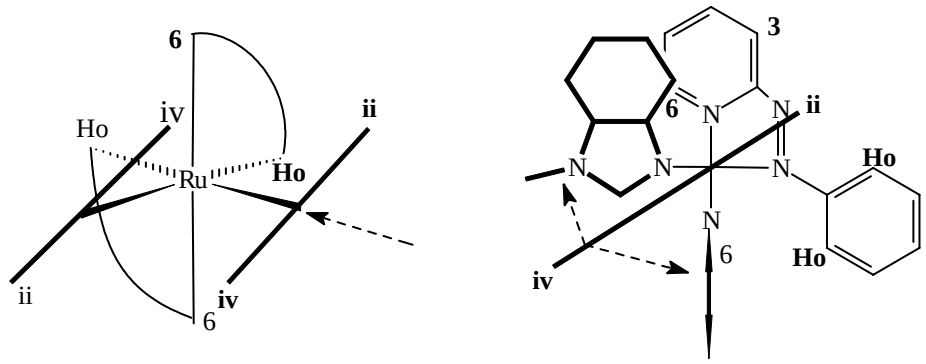
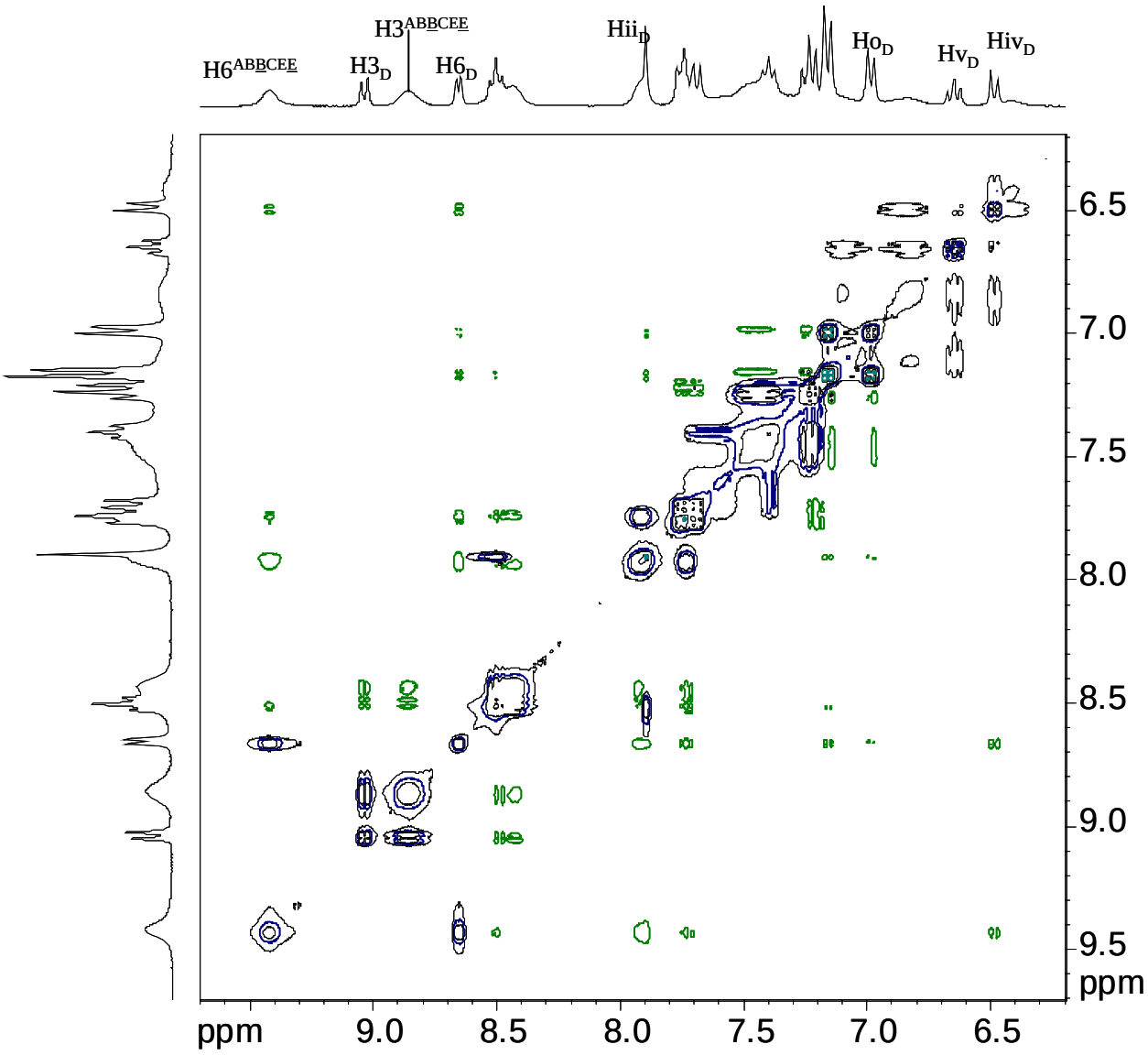


**Figure S5** In atropisomer D a MeBim ligand is "trapped" in between a pyridine ring and the other MeBim ligand



**S6** Aromatic region of the NOESY spectrum of 2 recorded ar –10 °C. The proton resonance signals of the atropisomers A, B/B, C and E/E coalesced and broad, whilst the resonances of D are well-resolved. EXSY (black/blue signals) signals between resonances of D and ABBCEE and NOE cross peaks of D show 3J coupling information; NOE cross peaks of the ABBCEE signals are broad, whilst NOE-EXSY peaks show fine-structure (*e.g.* $H6^{ABBCEE}$ – $Hiv_D$).



**S7** Orientation of the two MeBim ligands in the different atropisomers:

***Atropisomer A (4 %).*** The signals of A are relatively weak and many of them overlap with the more intense peaks of the other atropisomers. Nevertheless, the characteristic resonances of the H6 and H(iv) resonances can readily be found. The $H6_A$ resonance (9.09 ppm) is visible in the high-resolution 600 MHz $^1$H NMR spectrum just in between the intense $H(ii)_C$ singlet and the $H3_D$ doublet, and shows strong NOE interactions with the $H(ii)_A$ and the $H(iv)_A$ resonances. The H(ii) signal is overlapping with several intense signals of other atropisomers and furthermore lying close to the $H4_A$ triplet, but careful examination of the two dimensions of the 2D spectra unambiguously prove the H(ii)-H6 connection. The proposed orientation of the MeBim ligands in atropisomer A is identical with that of the most abundant rotamer in the analogous bpy complex ***cis***-$[Ru(bpy)_2(MeBim)_2](PF_6)_2$, ***i.e.*** the HT atropisomer with the six-membered ring of a MeBim wedged in between the pyridine of one azpy and the phenyl ring of the other azpy ligand.[31, 32] This is further confirmed by the relatively up-field position of the $H6_A$ resonance which is nicely explained with the absence of (de)shielding effects of the MeBim ligands, vide infra.

***Atropisomer B(B) (25 %).*** The set of peaks of B constitutes of 12 signals at −65 °C, but 24 signals are observed in the slow-exchange range at −95 °C. The two sets of signals for the two azpy and the two MeBim ligands indicate that they belong to a non-$C_2$ symmetric (***i.e.*** HH) rotamer. Even at −95 °C, rotamer B exchanges with the identical rotamer B, vide infra, causing NOE data to become difficult to interpret because of NOE-EXSY peaks, due to exchange of protons during NOE build up (see the highlighted boxes in figure 8). Therefore, a series of spectra has been recorded with decreasing mixing time, in order to diminish the NOE-EXSY cross peaks. The aromatic region of the NOESY spectrum of **2** recorded with a mixing time of 500 ms is shown in figure 9. It is observed nicely that one H6 proton ($H6'_B$), is showing NOE cross peaks with both the H(iv) and H(iv') proton resonances, whilst the other H6 doublet ($H6_B$), shows cross peaks with both the H(ii) and H(ii')signals. These NOE interactions point to the rotamer B (B) in which the two MeBim ligands are both oriented with their imidazole rings (Hii/Hii') towards the pyridine ring of one azpy ligand, whilst the six-membered rings of both MeBim ligands (Hiv/Hiv') point towards the pyridine ring of the other azpy ligand. The atropisomer B is also found in the related complex ***cis***-$[Ru(bpy)_2(MeBim)_2](PF_6)_2$, and with a similar abundance.

***Atropisomer C (31 %).*** The second most abundant set of signals, C, belongs also to a $C_2$-symmetric (and therefore HT) rotamer, as can be concluded from the total of only 12 signals present in the aromatic region. The NOE cross peaks between the H(ii) and the H6 and H(o) peaks suggest an HT orientation in which the H(ii) of the MeBim is oriented wedged between the pyridine of one azpy and the phenyl ring of the other azpy ligand; this hypothesis is confirmed by the

cross peak of the H6 with H(iv) resonance. The orientation of the MeBim ligands in this atropisomer is the same as the orientation of the MeBim ligands in the least abundant HT rotamer of the analogous bpy complex ***cis***-$[Ru(bpy)_2(MeBim)_2](PF_6)_2$. A recent crystallographic study of **2** has revealed the molecular structure of this atropisomer C,[59] strongly confirming details of the above-mentioned NMR discussion, as well as the (de)shielding discussion.

***Atropisomer D (37 %).*** The most important NOE cross peaks observed for the most abundant set of signals D (12 signals, $C_2$-symmetric, HT rotamer) are the H(ii)-H(o), and H(iv)-H6. In addition, weak cross peaks are observed between the H(ii)-H(iv), and the H(ii)-H3 resonance. All these cross peaks, and in particular the H(ii)-H3 NOE, point to a conformer in which the H(ii) of the benzimidazole is oriented above the aza binding of the ***fac***-coordinated azpy ligand, and with the phenyl ring (H(iv)) along, face-to-face, the pyridine of the ***mer***-coordinated azpy ligand (see Scheme 4). This HT atropisomer is different from the ones found in the bpy complex ***cis***-$[Ru(bpy)_2(MeBim)_2](PF_6)_2$ [31, 32] (figure 4, A-C) in which none of the rotamers has the lopsided parts of the MeBim ligands being oriented above the didentate ligand. Interestingly, this rotamer D is the most abundant one in complex **2**, and furthermore thermodynamically more stable than the other atropisomers, as concluded from the VT and the EXSY data.

***Atropisomer E (3 %).*** Interestingly, in some NOESY spectra of **2** the diagonal peaks for resonances of E are absent (see figure 8, the H6 and H(iv) region), whereas pronounced EXSY and NOE-EXSY cross peaks with resonances of atropisomer C (H6, H(ii) and H(iv)) are visible. The low intensity of the resonances belonging to rotamer E, in combination with the interconversion to rotamer C, even at the lowest recording temperatures, vide infra, prevents the build-up of NOE intensity in the resonances of E, and makes interpretation of the orientation of the MeBim ligands in E harsh (see figure 8 and 9). However, assuming that the six different atropisomers depicted in scheme 3 are the most likely structures to be present in this system, the fact that rotamer E has a double set of signals, indicates it to be a non-$C_2$-symmetric (***i.e.***, HH) atropisomer. The most abundant HH atropisomer already being assigned to B, the signals of E can be attributed to the other HH atropisomer, E (E). In rotamer E, one MeBim ligand is oriented like in rotamer D, with the imidazole proton close to the aza bond of an azpy ligand, whilst the second MeBim is oriented with the six-membered ring above the aza bond.

**S8** Characteristic (de)shielding effects in the atropiosmers of **2**:

The H6 resonances are significantly influenced by the (presence or absence of the) shielding effect of the phenyl ring of one of the benzimidazoles and deshielding effect of the other benzimidazole. The (de)shielding effects of the ***cis*** bis MeBim ligands on the H6 and H6' protons have been discussed in detail for atropisomers A-C in the related complex ***cis***-$[Ru(bpy)_2(MeBim)_2](PF_6)_2$,[31, 32] and this discussion appears to be valid for the atropisomers of **2**, too. The pattern of the H6 resonances of A-C is in fact very similar to that observed for the analogous bpy complex. The $H6_C$ (9.72 ppm) is shifted downfield most of all the H6 resonances, which is due to the fact that the six-membered rings of the ***fac***-coordinated MeBim ligands deshield the azpy H6 protons, confirming the proposed orientation. The $H6_A$ resonance is observed at relatively high field (9.09 ppm), perfectly in correspondence with the fact that both MeBim ligands are rotated by 180' with respect to conformer C, and the H6 resonances are shielded by the aromatic six-membered rings of the ***mer***-positioned benzimidazole. Conformer B has one of the MeBim ligands oriented like in A, whilst the other one is oriented like in C. The $H6'_B$ resonance (9.62 ppm) is upfield shifted with respect to the $H6_C$ resonance as the former proton is deshielded by the six-membered ring of the ***fac***-coordinated MeBim ligand (like in C), but is shielded by the six-membered ring of the ***mer***-oriented MeBim ligand. The $H6_B$ resonance (9.36 ppm) on the other hand is upfield shifted with respect to the $H6'_B$ resonance, but still downfield with respect to the $H6_A$ resonance, which is due to the fact that it is not deshielded by the six-membered ring of the ***fac***-coordinated MeBim, but neither strongly shielded by the ***mer***-positioned five-membered ring of the benzimidazole. For conformer D the H6 resonance (8.51 ppm) is observed most upfield with respect to the H6 (and H6') resonances of the other four different atropisomers. The proposed orientation of the two MeBim ligands in D is in fact such that the H6 protons are very close to the shielding cone of the six-membered ring of the ***mer***-positioned benzimidazole ligands (see Scheme 4). In atropisomer E, finally, one MeBim ligand is oriented like in D, and therefore is expected to exhibit a strong shielding effect on the $H6_E$ proton. This is not as much as observed for atropisomer D, most likely because the proximity of the bulky six-membered ring of the second MeBim ligand prevents a more shielding orientation of the MeBim ligand. The $H6'_E$ on the other hand, is not shielded and is found more downfield than the $H6_E$.

Although the H6 proton resonances are most informative for determination of the orientation of the MeBim ligands in the different atropisomers, also some of the H(ii) and H(iv) resonances show characteristic shifts, and in particular the HH atropisomers deserve a short discussion. From the MeBim proton resonances present in **2**, the H(ii) differs most between the conformers, found at 9.07 and 7.98 ppm for the C and D atropisomers, respectively, whilst the $H(ii/ii')_E$ are observed at even higher field, at 7.60 ppm. The H(ii) protons in D are oriented above the aza-bond of the azpy ligands and are strongly shielded. The H(ii') in E is pushed even closer to the

aza bond, because of sterical hindrance with the MeBim ligand at the H(iv') site. An additional confirmation of the assignment of E to the HH atropisomer stems from the observation that both H(iv)/H(iv') protons are found at relatively high field with respect to the H(iv) resonances of all the other rotamers; the H(iv) in E in fact is strongly shielded by the neighboring MeBim ligand, whilst the $H(iv')_E$ is close to the aza bond of the azpy. Also in atropisomer B the H(ii) and H(iv) resonances differ characteristically. From the (relatively downfield-shifted) H(ii) resonance of rotamer C it can be concluded that a proton oriented wedged in between the pyridine ring of one azpy and the phenyl ring of the other, experiences a deshielding effect. In atropisomer B this is indeed observed, with the H(iv) (7.41 ppm) and the H(ii') (8.82 ppm) at relatively low field with respect to the H(iv') (6.34 ppm) and the H(ii) (8.35 ppm) resonances.

**S9** Dynamic and NMR aspects of the least abundant isomers E/E.

The E/E isomers are the least abundant ones in this compound (3%) and therefore more difficult to investigate, also because of severe overlap with signals of the more abundant isomers. Whereas the exchange of the isomers in most cases has been validated by looking also at resonances in the more crowded parts of the spectra, this appears rather difficult for the E/E rotamers. These very low-abundant isomers are furthermore in exchange even at the lowest recording temperatures and slight changes in experimental conditions have influence on the line-shape and frequency of the resonances. Finally, the main factor complicating a quantitative interpretation of the data of the CEE exchange, is that we cannot consider it a simple two-site exchange between identical isomers, but actually have to consider exchange between non-identical sites. Exchange between non-identical sites in general means different forward and backward rate constants, ***i.e.*** $k_{C\text{-}E/\underline{E}}$ (C interconverting to E or E) is not equal to $k_{E/\underline{E}\text{-}C}$ (E or E interconverting to C).
Regarding the absence of the off-diagonal crosspeaks between E/E and possible exchange between E/E. The symmetrical two-site exchange between E and E ***can*** actually be ruled out on basis of absence of the off-diagonal cross-peaks. If there would be exchange between E and E faster than the used mixing times, still off-diagonal crosspeaks should be observed between the corresponding signals of E and E as their interconversion exchanges the two corresponding halves of an non-$C_2$-symmetric isomer with an intrinsic $C_2$ symmetry, exactly the same as is observed for BB. Also in experiments with shorter mixing times we did not observe exchange between E and E.
With regard to the presence/absence of diagonal crosspeaks, the situation is similar to what said above for the off-diagonal crosspeaks, ***i.e.*** EE exchange can be ruled out because of symmetry reasons. The line broadening of the E/E H6 at the lowest recording temperatures is modest, indicating eventual exchange processes of these isomers to be in the order of seconds. The fact that diagonal crosspeaks are absent indicates actually that the E/E rotamers interconvert to another, non-identical rotamer, ***e.g.*** rotamer C, with a rate constant $k_{E/\underline{E}\text{-}C}$ much higher than the backward rate constant $k_{C\text{-}E/\underline{E}}$. We do not want to focus too much on quantitative discussion of the exchange of the atropisomerisation processes, and particularly not on those of the least abundant isomer. However, a conclusion we might safely draw is that $k_{C\text{-}E/\underline{E}}$ is much smaller than $k_{E/\underline{E}\text{-}C}$; and if at all there is direct exchange between E and E , $k_{E\text{-}\underline{E}}$ is much smaller than $k_{C\text{-}E/\underline{E}}$.