Paul, S., Schweizer, W.B., Rugg, G., Senn, H.M., and Gilmour, R. (2013)
The fluorine-NHC gauche effect: a structural and computational study.
Tetrahedron . ISSN 0040-4020

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Graphical Abstract

The fluorine-NHC *gauche* effect: a structural and computational study.

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The fluorine-NHC *gauche* effect: a structural and computational study.

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ARTICLE INFO

Article history:

Received

Received in revised form

Accepted

Available online

Keywords:

computational chemistry

conformational analysis

fluorine

gauche effect

molecular design

ABSTRACT

Herein, we report the synthesis and X-ray structural analysis of a collection of fluorinated metal *N*-heterocyclic carbenes (Ag, Au, Pd, Rh, Ir) and their precursor salts. The common structural feature of these species is a flanking fluoroethyl group which is either freely rotating or embedded within a bicyclic framework. Solid state analysis confirmed a *gauche* conformational preference in all cases with the fluorine adopting a *syn* clinal arrangement ($\phi_{\text{[NCCF]}} \sim 60^\circ$) with respect to the triazolium nitrogen at the vicinal position of the NHC. A density functional theory analysis was employed to quantify these effects and evaluate the influence of electronic modulation of the carbenic carbon [(C=N⁺); neutral carbene (C:); metal-bound carbene (C=M)], on the relative *gauche*–*anti* preference, thus highlighting the potential of this conformational phenomenon as a useful molecular design strategy for controlling the topology of organometallic complexes.

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Fluorinated *N*-heterocyclic carbenes are emerging as valuable organocatalysts and powerful ancillary ligands for transition-metal catalysed processes.^[1] Pertinent examples include the triazolium Stetter catalyst reported by Rovis and co-workers (**1**) where the introduction of fluorine improves efficiency,^[2] and the ruthenium metathesis catalyst disclosed by Grubbs *et al.* (**2**)^[3] in which a fluorine-metal interaction leads to a rate acceleration. In both cases, the fluorine atom that is inextricably linked to catalyst performance is vicinal to one of the flanking nitrogens of the NHC (Figure 1). In these examples, the fluorine atom influences the overall conformation of the catalysts by virtue of stereoelectronic refinement^[4] or remote metal-fluorine interactions,^[5] whilst the inductive effect is likely diminished relative to an aliphatic β -fluoroamine motif (+I _{π} versus -I _{σ}).

Figure 1. Examples of fluorinated *N*-heterocyclic carbenes.

Our interest in *N*-heterocyclic carbene (NHC) complexes containing a single, aliphatic fluorine substituent positioned vicinal to one of the

flanking nitrogens stems from our efforts to exploit the fluorine *gauche* effect^[6] as an approach to acyclic conformational control in catalysis.^[7]

Scheme 1. Pre-organisation of metal *N*-heterocyclic carbene complexes by a fluorine-NHC *gauche* effect. X = C or N; M = coinage or transition metal; L = ligand.

This phenomenon, which is principally associated with fluorinated organic molecules, is a manifestation of hyperconjugative interactions between the low lying σ^* antibonding orbital of the C-F bond and adjacent σ -orbitals or non-bonding electron pairs.^[8] Consequently, it is possible to access conformer populations, whilst keeping the steric footprint of the steering group to a minimum, in a manner that is complementary to steric conformational control. As a

general rule, fluoro substituents prefer to be *gauche* to vicinal electron-withdrawing groups ($F^{\delta-}-CH_2-CH_2-EWG$; $\phi_{[F-C-C-EWG]} \approx 60^\circ$) rendering this phenomenon potentially useful for molecular design (Scheme 1; top). However, in the case of freely rotatable scaffolds such as 1,2-difluoroethane, it is important to note that two possible *gauche* conformers can be populated with equal probability ($\phi_{[F-C-C-EWG]} \approx \pm 60^\circ$).

Herein, we disclose the synthesis, structural analysis and DFT study of various fluorinated NHCs and explore this conformational effect within the framework of organometallic complexes. The possibility of discriminating between two *gauche* scenarios (*gauche*¹ and *gauche*²) by relying on remote metal-fluorine interactions is also considered (Scheme 1; bottom). Moreover, a computational study to evaluate the influence of electronic modulation of the carbenic carbon [$C=N^+$; neutral carbene ($C:$); metal-bound carbene ($C=M$)], on the relative *gauche* / *anti* preference of these ligands is disclosed.

• *N*-heterocyclic carbene precursors

• metal *N*-heterocyclic carbene complexes

Figure 2. Synthetic targets for this study.

Previously, this laboratory has reported the synthesis and conformational analysis of a representative Au(I) NHC. It was noted that by inserting a C-F bond in a vicinal relationship to the triazolium nitrogen atom at the ring junction of the ligand, the relative molecular topology of a flanking diphenylfluoromethyl group could be controlled ($\phi_{[NCCF]} = -61.9^\circ$ and -48.6°) by the aforementioned effect.^[9] To establish the generality of this *gauche* conformational preference in NHC scaffolds bearing a pendant fluoroethyl motif, three ligand substructures were conceived (Figure 2). Scaffolds **3** and **7** would partially embed the fluoroethyl motif in a bicyclic triazolium framework thus restricting rotation around one of the two bonds of the fluoroethyl group (τ_1 and τ_2). Similarly, structures **4** and **8** would also reduce torsional freedom but offer the possibility of *syn* clinal-*endo* versus *syn* clinal-*exo* arrangements due to the removal of the bulky phenyl substituents from the fluorine-bearing carbon atom.

• synthesis of the *N*-heterocyclic carbene precursors

Scheme 2. Synthesis of the bicyclic *N*-heterocyclic carbene precursor salts **15** and **19**.

Finally, the non-constrained species **5/9** and **6/10** may allow for the detection of remote metal-fluorine interactions by relaxing the C-C-N bond angle (θ). In all of these ligand classes, Plenio's criteria of having the metal and fluorine atom separated by a minimum of 4 bonds is satisfied.^[5] A solid state analysis of complexes **7-10**, containing a group 11 coinage metal (Ag, Au) or a group 9 or 10 transition metal (Pd, Rh, Ir) allows for comparison of the metal on the conformational behaviour. The synthesis of bicyclic triazolium salts of type **3** and **4** proved facile from commercially available (*S*)-pyroglutamic acid **11** (Scheme 2). Preparation of the diphenylfluoromethyl derivative **15** began by esterification of **11** to form the methyl ester **12** (81%). Addition of phenylmagnesium bromide furnished the expected carbinol **13** in a respectable 70% yield. Deoxyfluorination using diethylaminosulfur trifluoride (DAST) successfully installed the tertiary fluorine centre in 64% yield. Subsequent treatment with the Meerwein's reagent, phenylhydrazine and trimethylorthoformate furnished the desired triazolium tetrafluoroborate in a three step, one pot sequence (61% overall). NHC precursor **19** was also prepared from the methyl ester **12** by reduction and subsequent protection as the TBS ether.

Figure 3. X-ray crystal structure of the triazolium tetrafluoroborate salt **19** ($\phi_{[NCCF]} = 67.9^\circ$; *syn* clinal-*exo*). Thermal ellipsoids set at the 50% probability level.^[10]

Construction of the triazolium ring followed the same three step, one pot procedure as previously described to deliver the TBS precursor **18** in 17% yield (3 steps). Finally, treatment of this species with an excess of DAST effected an *in situ* deprotection / deoxyfluorination sequence to deliver the desired product in up to 98% yield. Unfortunately, this last step proved capricious and yields were variable.

An alternate route to access compound **19** was explored involving the conversion of alcohol **16** to the corresponding bromide by treatment with CBr_4 and PPh_3 .^[11] Halogen exchange proved facile by simple treatment of **20** with AgF in a Finkelstein reaction to furnish the primary fluoride **21** in a respectable 54% yield. The three step alkylation / phenylhydrazine addition / cyclisation sequence furnished the target structure **19** in 78% yield over three steps.

Gratifyingly, it was possible to grow crystals of the triazolium tetrafluoroborate salt **19** that were suitable for X-ray crystallographic analysis (Figure 3). The compound crystallised in the orthorhombic spacegroup $\text{P2}_1\text{2}_1\text{2}_1$ with four molecules in the unit cell.^[10] A completely different packing arrangement shows the fluorodiphenylmethyl tetrafluoroborate salt **15** which crystallised in the monoclinic space group C2 .^[9] Importantly, measurement of the NCCF torsion angle (ϕ) confirmed the expected *gauche* conformation ($\phi_{[\text{NCCF}]} = 67.9^\circ$). Intriguingly, whereas in the fluorodiphenylmethyl species a *syn* clinal-*endo* conformation was found, possibly due to the steric hindrance of the two phenyl groups, a *syn* clinal-*exo* arrangement is present in **19**. It is also noteworthy that the plane of the *N*-phenyl substituent and the plane of the triazolium ring system of an adjacent molecule are pointing away from each other in contrast to **15** where the planes are almost parallel with an angle of 5.3° .

Inspired by a recent study by Kysilka and co-workers describing the alkylation of imidazoles with fluoroalkyltriflates,^[12] the imidazolium and triazolium triflates **23** and **25** were prepared by alkylation of **22** and **24** with fluoroethyltriflate in toluene at reflux (95% and 94%, respectively, Scheme 3). Phenylimidazole **22** was synthesised via the copper-catalysed amination of phenylbromide with imidazole.^[13] Similarly, the 1,2,4-triazole **24** was obtained by copper-catalysed coupling of triazole with phenyl iodide.

Scheme 3. Synthesis of the imidazolium and triazolium triflates **23** and **25**.

It was possible to grow crystals of the imidazolium and triazolium salts **23** and **25** that were suitable for single crystal X-ray analysis.^[14,15] The solid state structure of **23** revealed a clear *gauche* relationship of the fluorine relative to the nitrogen centre ($\phi_{\text{NCCF}} \pm 71.1^\circ$, Figure 4). The molecule crystallised in the monoclinic space group $\text{P2}_1/\text{c}$ with four molecules in the unit cell. Short fluorine-fluorine contacts between the fluorine of the pendant arm of the imidazole and the triflate anion were observed with a distance of $d_{\text{C-F} \cdots \text{F-C}} = 2.72 \text{ \AA}$ which is less than the sum of the van der Waals-radii of $2.94 \text{ \AA}$ (Figure 5).^[16] This is certainly the effect of the disorder and not the correct distance in the crystal. The nature of these interactions is the subject of much conjecture.^[17]

Figure 4. X-ray crystal structure of the imidazolium triflate **23** showing the fluorine *gauche* effect ($\phi_{[\text{NCCF}]} = \pm 71.1^\circ$). Reliability of the $\text{F} \cdots \text{F}$ contacts indicated in red ($d = 2.72 \text{ \AA}$) suffer from the disordered CF_3 group. Thermal ellipsoids set at the 50% probability level.^[14]

Figure 5. $\text{F} \cdots \text{F}$ contacts of type II in **23**. Thermal ellipsoids set at the 50% probability level.^[14]

Figure 6. X-ray crystal structure of the triazolium triflate **25**. The fluorine *gauche* effect ($\phi_{\text{NCCF}} = 71^\circ$) is indicated. Thermal ellipsoids set at the 50% probability level.^[15]

Murray-Rust and co-workers have classified such halogen-halogen interactions into two classes (Figure 5): type I in which the C-X-X angles are equal ($\theta_1 = \theta_2$) and the less common type II in which one angle (θ_1) is approximately 180° and the other (θ_2) around 90° . The fluorine-fluorine interaction found in the crystal structure of **23** is reminiscent of type II with $\theta_1 = 157.1^\circ$ and $\theta_2 = 103.2^\circ$.^[17a]

Pd *N*-Heterocyclic Carbene Complexes (Type 7).

In order to investigate the potential application of the fluorine-NHC *gauche* effect for controlling the molecular topology of transition metal complexes and thus complement our recent study of Ag(I) and Au(I) systems,^[9] a synthesis and structural analysis of palladium complexes was initiated. In contrast to Ag(I) and Au(I) species in which the coordination geometry is predominantly linear, Pd(II) complexes would allow this conformational analysis to be extended to square-planar arrangements. Moreover, a study of transition metal complexes would allow the notion of further conformational refinement by remote metal-fluorine interactions to be investigated (Scheme 4). Given the importance of Pd(II) species in catalysis, we envisaged that new approaches to control the ligand topology may find further applications.

Scheme 4. Possible *gauche* effect / remote metal-fluorine interactions in transition metal complexes.

Regarding the synthesis of these Pd, and other transition metal complexes described herein, modified literature procedures were followed.^[18,19] Generally, transmetalation from the corresponding silver-NHC complexes proved to be the method of choice. This process has attracted broad attention due to the capability of such species to act as carbene transfer agents.^[18,20-22] Initially, the palladium *bis*-NHC complex **26** was prepared from the tetrafluoroborate salt **15** by a two step procedure involving transmetalation from the silver complex with PdCl₂, to furnish the desired species in a moderate 33% yield (Scheme 5).

Scheme 5. Synthesis of the PdCl₂(NHC)₂ complex **26**.

Single crystal X-ray analysis of the PdCl₂(NHC)₂ complex **26** (Figure 7)^[23] confirmed the expected *gauche* orientation of the fluorine with respect to the nitrogen of the triazolium ring system ($\phi_{[\text{NCCF}]}$ = 60.4°). Interestingly, the *syn* clinal-*endo* conformation is observed, in contrast to the Ag(I) and Au(I) complexes with the identical NHC ligand where the *syn* clinal-*endo* conformer is present.^[9] This is possible due to the *bis* structure of compound **26**. It is interesting to note that the NHC ligands are tilted at an angle of 81.1° relative to each other. Furthermore, the *N*-phenyl group is rotated by 42.7° with respect to the triazolium ring plane (Figure 7). The interatomic distance of 2.30 Å is considerably smaller than the

sum of the Van der Waals radii of fluorine and hydrogen (2.67 Å). O'Hagan *et al.* have disclosed the results of a Cambridge Structural Database (CSD) search for short F...H contacts in fluorine-containing organic compounds which revealed that C-F...H-C interactions are the most common contacts.^[24] The authors also mention that the C-F...H-C interactions have practically no influence on packing arrangements.

Figure 7. X-ray structure of the PdCl₂(NHC)₂ complex **26**; $\phi_{[\text{NCCF}]}$ = 60.4°, $d_{\text{H-F}}$ = 2.296 Å, $d_{\text{Pd-F}}$ = 3.24 Å. Thermal ellipsoids set at the 50% probability level.^[23]

In this example, the distance between fluorine and palladium was measured to be 3.24 Å which is greater than the threshold value of 3.0 Å.^[5] The characteristic square-planar coordination geometry of palladium(II) complexes is satisfied in this particular case, and thus the fluorine atom is not necessary to complete the coordination sphere. Therefore, the preparation of a palladium complex bearing a single NHC-ligand was attempted. To that end, the Pd(II)(allyl)(NHC) complex **28** was prepared by transmetalation of the silver NHC complex **27** with the allyl palladium(II)chloride dimer (52%, Scheme 6).

Scheme 6. Synthesis of the Pd(allyl)(NHC)₂ complex **28**.

X-ray analysis revealed that the molecule crystallised in the same tetragonal space group P4₁2₁2 as the PdCl₂(NHC)₂ complex **26** with eight molecules in the unit cell (Figure 8).^[25] However, in contrast to **26**, the fluorine atom adopts a *syn* clinal-*endo* conformation with respect to the nitrogen of the triazolium ring system ($\phi_{[\text{NCCF}]}$ = -51.7°) comparable to the conformations observed in the corresponding Au and Ag species. In addition, the plane of the *N*-phenyl substituent is rotated by 29.5° with respect to the triazolium ring plane which is very similar to the precursor salt **15**. Furthermore, the X-ray analysis also revealed a distorted square-planar coordination around the Pd(II) and the expected η^3 coordination mode of the allyl-palladium fragment. The distances between the palladium and the allylic carbon atoms

were found to be similar (2.097, 2.137 and 2.183 Å), with the longest bond being to the carbon *trans* to the NHC ligand. Solid state analysis of the complex revealed that the fluorine atom is pointing away from the metal centre ($d = 4.95$ Å), thus no remote fluorine-palladium interaction was detected. Unfortunately, attempts to generate the corresponding cationic palladium complex by abstraction of the chloride ligand by treatment with AgPF₆ yielded a complex mixture of decomposition products.

Figure 8. X-ray structure of the Pd(allyl)(NHC)₂ complex **28**; $\phi_{[\text{NCCF}]}$ = -51.7° , $d_{\text{H-F}}$ = 2.46 Å. Thermal ellipsoids set at the 50% probability level (top). C-F...H-C contacts highlighted with dotted lines (bottom).^[25]

Rh and Ir *N*-Heterocyclic Carbene Complexes (Type 7).

Like palladium(II) complexes, the coordination behaviour of rhodium(I) and iridium(I) complexes is dominated by the formation of square-planar complexes due to their d^8 configuration. To extend this study of metal NHC systems of type 7 (Figure 2), the synthesis of complexes **29** (M = Rh) and **30** (M = Ir) was attempted. This proved facile by treating the common Ag(I) transfer agent **27** with either the chloro(1,5-cyclooctadiene)-rhodium(I) or -iridium(I) dimer at 40 °C in CH₂Cl₂ (Scheme 7). The desired complexes **29** and **30** were isolated in 70% and 83% yield, respectively. It is important to note that a one pot procedure can also be employed to deliver the desired target molecule directly from the starting NHC precursor **15**. This process involves suspending the chloro(1,5-cyclooctadiene)-

rhodium(I) or -iridium(I) dimer complexes in ethanol followed by the addition of a solution of sodium ethoxide in ethanol. The triazolium precursor **15** can then be added in one portion to generate the Rh(COD)(NHC)Cl complex **29** and Ir(COD)(NHC)Cl complex **30**. Despite the reduction in yield (Rh, 41%; Ir, 61%) the advantage of this route is that the preparation of the Ag(I) NHC precursor **27** is avoided.^[26]

Scheme 7. Synthesis of the Rh and Ir complex **29** and **30**.

However, repeated attempts to crystallise these complexes proved fruitless, with the complexes rapidly decomposing. Fortunately, some structural insights could be gleaned from spectroscopic studies. In the ¹⁹F-NMR spectra of both complexes **29** and **30**, two signals were observed in a ratio of 1 : 0.07 and 1 : 0.16, respectively, indicating the presence of two discrete species. The signals of the minor isomer could also be detected in the ¹H-NMR spectra of both complexes but could not be assigned to the individual protons. This observation can be rationalised by considering two isomers that differ in the orientation of the M-Cl bond with respect to the NHC ligand. This is consistent with a report from Ganter *et al.* describing two sets of signals in the ¹H-NMR spectrum of a Rh(COD)(NHC)Cl complex.^[27] In the absence of crystallographic data, it was envisaged that determination of the ¹J_{CF} coupling constants might give insights as to the presence or absence of remote metal-fluorine interactions, since the coupling constant would likely decrease upon coordination with the metal centre.^[28,29] However, by comparing the coupling constants of the NHC precursor salt **15** ($J = 185.0$ Hz) with those of the Rh complex **29** ($J = 185.0$ Hz) and the Ir complex **30** ($J = 186.4$ Hz), no significant deviation was observed.

Ag and Au *N*-Heterocyclic Carbene Complexes (Type 8).

To complement the aforementioned structural studies of the fluorodiphenylmethyl NHCs, selected NHC metal complexes of the analogous fluoromethyl species were synthesised. Deletion of the phenyl groups leads to a sterically less congested scaffold and may conceivably give a clearer picture of the interactions of interest. The investigation began with the synthesis of the silver and gold complexes **32** and **33** (Scheme 8).

Scheme 8. Synthesis of type 8 Ag and Au complexes **32** and **33**.

The desired Ag(NHC)Cl complex **33** was prepared from the tetrafluoroborate salt **19** and Ag₂O in presence of NMe₄Cl in 86% yield (Scheme 8, right).^[30] This complex was subsequently processed to the analogous Au(I) NHC **32** by treatment with AuCl(SMe₂) (76% from **19**). Intriguingly, treatment of **19** with Ag₂O under basic phase transfer conditions (Scheme 8, left)^[18] furnished the *bis*-NHC **31** in a modest 51% yield.

It was possible to grow crystals of the silver *mono*- and *bis*-NHC complexes **33** and **31** that were suitable for X-ray analysis (Figures 9 and 10). The complex **33** crystallised in the same orthorhombic space group P2₁2₁2₁ as the NHC precursor salt **19** (Figure 3) with four molecules in the unit cell.^[31]

Figure 9. X-ray structure (top) and intermolecular connections (bottom) of the Ag(*mono*-NHC)Cl complex **33**; $\phi_{\text{[NCCF]}} = -61.0^\circ$; $d_{\text{Ag-Cl}} = 2.07$ and 2.76 Å. Thermal ellipsoids set at the 50% probability level.^[31]

The measurement of the NCCF torsion angle revealed a *syn* clinal-*endo* conformation ($\phi_{\text{[NCCF]}} = -61^\circ$), whereas the corresponding tetrafluoroborate salt **19** showed a *syn* clinal-*exo* orientation of the fluorine with respect to the nitrogen of the triazolium ring system. Furthermore, it is noteworthy that the silver atom is not in the expected linear coordination environment as in the case of the fluorodiphenyl-NHC complex **27**, but instead has a C-Ag-Cl bond angle of 132.5° ($d_{\text{Ag-Cl}} = 2.60$ Å). The silver atom is tetrahedrally coordinated by one carbenic carbon atom and three chloride atoms. This arrangement results in two parallel zigzag chains in which the Ag(NHC)Cl units are connected in a head-to-tail manner via the bridging chlorine atoms with Ag-Cl distances of 2.07 Å and 2.76 Å (Figure 9). This alignment is consistent with previous reports from Lin, Zhang, Chen and Lee who have also observed this staircase type arrangement of silver imidazolyliene and triazolyliene halides.^[32-35] The distance between the fluorine atom and the silver atom in **33** is 4.29 Å, which is considerably longer than the threshold of about 3 Å that is indicative of a remote metal-fluorine interaction.^[5] The silver carbene bond length is marginally longer than in the fluorodiphenyl complex **27** (2.09 Å) which might be a consequence of the differences in the coordination environments of the silver atom. The distance between two adjacent silver atoms that are connected via two bridging chlorine atoms is about 3.62 Å which is longer than the sum of the Van der Waals radii of 3.44 Å,^[16]

indicating that there are no argentophilic interactions in this structure. A distinct feature is the almost planar alignment of the triazole ring and the *N*-phenyl substituent which are rotated by only 4.3° to each other. The NHC ligands of one zigzag chain are stacked with long ring to ring distances of 4.48 Å and the triazole planes of both zigzag chains are tilted by 80.7° relative to each other. This rotation might be a result of a weak C-F $\cdots$ H-C contact between the fluorine atom and an *ortho* hydrogen atom of the *N*-phenyl group of a molecule of the neighbouring zigzag chain with a distance of 2.33 Å.^[24]

Single crystal X-ray analysis of the Ag(I) *bis*-NHC complex **31** (Figure 10) revealed two symmetry independent molecules Ag1 and Ag2 in the asymmetric unit in which the silver atoms are in an almost linear environment with C-Ag-C bond angles of 171.5° and 175.2° (Figure 10, upper).^[36] The C-Ag bond lengths are similar with 2.09 Å and 2.08 Å for molecule Ag1 and 2.11 Å and 2.12 Å in molecule Ag2. In molecule Ag1, both fluorine atoms adopt a *syn* clinal-*exo* conformation with respect to the triazolium nitrogens with $\phi_{\text{[NCCF]}} = 57.4^\circ$ and 63.0° . In molecule Ag2 a NCCF torsion angle of $\phi_{\text{[NCCF]}} = 68.5^\circ$ (*syn* clinal-*exo*) was measured for one NHC ligand, whereas in the other ligand a *syn* clinal-*endo* orientation of the fluorine atom to the triazolium nitrogen was found ($\phi_{\text{[NCCF]}} = -65.5^\circ$). Curiously, one fluorine atom orients towards the silver atom with a short F-Ag contact of 2.93 Å, whilst the other points away ($d = 4.91$ Å).

Both fluorine atoms in Ag2 form short C-F $\cdots$ H-C contacts with the *para* hydrogen atom of the *N*-phenyl group of the adjacent Ag2 molecule ($d = 2.40$ Å and 2.54 Å). Similar intermolecular contacts are present in molecule Ag1 in which a short C-F $\cdots$ H-C contact is formed between the fluorine atom and the *meta* hydrogen atom of the adjacent Ag1 molecule with a distance of 2.13 Å. The shortest F-Ag distance was measured to be 3.15 Å which creates a T-shaped coordination at the silver atom. However, ¹³C NMR analysis revealed similar ¹*J*_{CF} coupling constants of 175.4 Hz and 173.9 Hz for the silver *mono*- and *bis*-NHC complexes **33** and **31**. These values are close to the ¹*J*_{CF} coupling constant of the precursor salt **19** (173.2 Hz). In this case, no remote metal-fluorine interactions could be identified. The tetrafluoroborate anions form several F $\cdots$ H contacts in the range of 2.30 - 2.64 Å with the hydrogen atoms of the phenyl groups and of the NHC backbones. Thus, the tetrafluoroborate is bridging the strands of Ag1 and Ag2 molecules (Figure 10, bottom).

Unfortunately, it was not possible to grow single crystals of the corresponding gold complex **32** that were suitable for X-ray analysis. ¹³C NMR analysis revealed a ¹*J*_{CF} coupling constant of 177.2 Hz which is similar to those of the silver complexes **31** and **33**, and the precursor salt **19**, thus indicating that no interaction between the fluorine atom and the gold centre occurs.

Figure 10. X-ray structure of the Ag(I) bis-NHC complex **31**; $\phi_{[\text{NCCF}]}$ (Ag1) = 57.4° and 63.0°; $\phi_{[\text{NCCF}]}$ (Ag2) = 68.5 and -65.5°; two symmetry independent molecules in the asymmetric unit (upper); enlarged view of the crystal lattice with intermolecular contacts (dotted lines, bottom). Thermal ellipsoids set at the 50% probability level.^[36]

Rh and Ir *N*-Heterocyclic Carbene Complexes (Type 8).

In order to investigate possible remote metal-fluorine interactions involving aliphatic fluorine centres, rhodium and iridium complexes were synthesised. Recently, Togni *et al.* disclosed an elegant study describing the synthesis and structural analysis of various iridium complexes displaying the aforementioned interaction.^[37] Consequently, Rh and Ir complexes **34** and **35** were synthesised to complement the previously described structural study of fluorodiphenyl NHC structures **31** and **33**. Both complexes were obtained from the chloro(1,5-cyclooctadiene)-rhodium(I) or

iridium(I) dimer complexes that were initially suspended in ethanol and treated with a solution of sodium ethoxide in ethanol (Scheme 9). Addition of the NHC precursor salt **19** furnished the desired Rh(COD)(NHC)Cl complex **34** and Ir(COD)(NHC)Cl complex **35** in 47% and 36% yield, respectively (over 2 steps).

Scheme 9. Synthesis of the Rh and Ir complex **34** and **35**.

Figure 11. X-ray structure of the Rh complex **34**; $\phi_{[\text{NCCF}]} = -59.9^\circ$; $d_{\text{Rh-F}} = 4.67 \text{ \AA}$ (top) and visualisation of the square planar coordination geometry (bottom). Thermal ellipsoids set at the 50% probability level.^[38]

Pleasingly, single crystals of the rhodium complex **34** were obtained that were suitable for X-ray crystal analysis (Figure 11).^[38] The compound crystallised in the orthorhombic space group $P2_12_12_1$ with four molecules in the unit cell. The fluorine atom adopts a clear *syn* clinal-*endo* orientation with respect to the triazolium nitrogen with $\phi_{\text{NCCF}} = -59.9^\circ$. Importantly, no interaction between the fluorine and rhodium centres was evident ($d_{\text{Rh-F}} = 4.67 \text{ \AA}$). The short contacts between the fluorine atom and an olefinic proton of the cyclooctadiene ligand of an adjacent molecule ($d = 2.56 \text{ \AA}$), and the weak $\text{Rh-Cl}\cdots\text{H-C(phenyl)}$ interactions might be due to crystal packing forces. A slightly distorted square-planar coordination geometry around the rhodium atom was found with bond angles of carbene-rhodium-centroid(c2) = 176.3° and chloride-rhodium-centroid(c1) = 177.7° (see Figure 11, bottom). Measurement of the distances between the rhodium atom and the centroids c1 and c2 of the cyclooctadiene double bonds revealed a $0.1 \text{ \AA}$ longer distance to the double bond located trans to the NHC ligand with $d_{\text{Rh-C2}} = 2.096 \text{ \AA}$. As was observed for the corresponding Rh and Ir fluorodiphenyl complexes **29** and **30**, two discrete species were found by ^{19}F -NMR spectroscopy occurring in a ratio of approximately 1 : 0.15. The chemical shifts of the NHC ligand are very similar for both complexes. For example, the protons at carbon atom 6 appear at $\delta = 6.53 \text{ ppm}$ and 4.87 ppm for the rhodium species and at $\delta = 6.19 \text{ ppm}$ and 4.83 ppm for the iridium compound. The ^{13}C chemical shift was found to be almost identical ($\delta = 82.7 \text{ ppm}$ and 82.6 ppm). The largest shifts were observed for the carbon and hydrogen atoms of the cyclooctadiene ligand. These are shifted upfield by 12 to 17 ppm in the ^{13}C -NMR spectrum and about 0.3 ppm in the ^1H -NMR from the rhodium to the iridium complex. These slight shift differences are consistent with literature reports of isostructural Rh and Ir(NHC) complexes reported by Messerle and Hazari who compared the molecular structures of such compounds by X-ray crystallographic analysis.^[39,40]

Ag and Au *N*-Heterocyclic Carbene Complexes (Type 9 and 10).

In order to investigate the possibility of molecular preorganisation by a fluorine *gauche* effect, as well as by a remote metal-fluorine interaction, structurally simplified metal triazolium and imidazolium complexes were synthesised bearing a pendant fluoroethyl moiety to allow greater degrees of rotational freedom (Scheme 10). Naturally, two *gauche* conformations can be populated with equal probability in these structures, either with the fluorine oriented towards the metal centre, thus allowing a possible remote metal-fluorine interaction, or the fluorine atom is oriented away from the metal centre.

To that end, the silver triazolyl complex **37** was obtained in 58% yield upon treatment of the triazolium salt **25** with Ag_2O in presence of NMe_4Cl . Analogously, reaction of imidazolium salt **23** with Ag_2O furnished the silver *bis*-imidazolyl complex **36** in 82% yield (*vide infra*).

Scheme 10. Synthesis of the Ag complexes **36** and **37**.

Figure 12. X-ray structure of the Ag triazolyl complex **37**; $\phi_{\text{NCCF}} = \pm 61.8^\circ$ and $\pm 67.9^\circ$; $d_{\text{Ag-O}} = 2.93 \text{ \AA}$; $d_{\text{Ag-F}} = 3.68$ and $3.64 \text{ \AA}$ (top) and visualisation of the T-shape structure (bottom). Thermal ellipsoids set at the 50% probability level.^[41]

It was possible to grow single crystals of the silver triazolyl complex **37** that were suitable for X-ray crystal analysis (Figure 12).^[41] Measurement of the NCCF torsion angles revealed the expected *gauche* arrangement with $\phi_{\text{NCCF}} = \pm 61.8^\circ$ and $\pm 67.9^\circ$. The compound crystallised in the orthorhombic space group $Pbca$ with eight molecules in the unit cell. A marginal distortion of the linear environment of the silver centre was found with a C-Ag-C bond angle of 170° . This is possibly the consequence of a weak coordination between the silver atom and an oxygen atom of the triflate anion ($d = 2.93 \text{ \AA}$) resulting in an overall T-shape geometry at the metal centre (Figure 12, bottom). Both fluorine atoms orient towards the metal with F-Ag distances of $3.64 \text{ \AA}$ and $3.69 \text{ \AA}$.

Cationic Pd type 9 and 10 NHC complexes.

With the silver complexes **36** and **37** in hand, attention was focussed on preparing a representative palladium(II) complex of this monocyclic type for comparison. Upon treatment of the silver NHC complexes **36** and **37** with dimeric palladium allyl chloride $[\text{Pd(allyl)Cl}]_2$, the structurally novel palladium *bis*-NHC complexes

38 and **39** were obtained in moderate yields (58% and 78%, respectively, Scheme 11).

Scheme 11. Synthesis of the Pd complexes **38** and **39**.

Figure 13. X-ray structures of **38** and **39** (upper, lower).^[42,43] Thermal ellipsoids shown at the 50% probability level. Hydrogen atoms and the counter ions have been omitted for clarity.

Single crystal X-ray analysis of the palladium complexes **38**^[42] and **39**^[43] revealed the expected η^3 -coordination of the allyl fragment and the distorted square planar coordination sphere of the palladium centres (Figure 13). The two NHC ligands attached to the palladium atom are almost perpendicular to each other with C-Pd-C bond angles of 97.5° in complex **39** and 96.0° in the Pd imidazolyl complex **38**.

The triazolyl complex **39** crystallised in the monoclinic space group P2₁/n. The fluorine atoms adopt a clear *gauche* conformation with respect to the triazolium ring nitrogen with NCCF torsion angles of $\phi_{[\text{NCCF}]} = \pm 65.3^\circ$ and $\pm 66.1^\circ$. Although one of the pendant fluorine substituents adopts a *gauche* conformation that might allow for a remote metal-fluorine interaction, the Pd-F distance was measured to be 4.05 Å. Furthermore, the second fluorine atom is oriented away from the Pd centre ($d_{\text{Pd-F}} = 5.43$ Å). A similar observation was found for the imidazolyl complex **38** which crystallised in the triclinic space group P $\bar{1}$ with two molecules in the unit cell. One fluorine atom adopts a *gauche* conformation with respect to the imidazolium nitrogen orienting towards the metal centre with a NCCF torsion angle $\phi_{[\text{NCCF}]} = \pm 67.7^\circ$ ($d_{\text{Pd-F}} = 4.13$ Å). In contrast, the second *gauche* conformation orients the fluorine away from the metal with an NCCF torsion angle of $\phi_{[\text{NCCF}]} = \pm 72.9^\circ$ and a Pd-F distance of $d = 5.65$ Å.

In this synthesis and structural survey of a small collection of bicyclic fluorinated NHC complexes, we have observed that in the solid state, a *syn* clinal-*endo* arrangement dominates the conformational behaviour of the bicyclic species **27**, **28**, **33**, and **34**, irrespective of the steric demand of the fluorine-bearing carbon (Figure 14). However, in the case of the *bis*-NHC palladium complex **26**, both a *syn* clinal-*exo* arrangement predominates with the fluorine atoms pointing towards the metal centre. Intriguingly, both *gauche* arrangements can be observed in one of the two solid state species of complex **31(I)**. Notably, in the monocyclic NHCs evaluated in this study, both *gauche* arrangements (*gauche*¹ and *gauche*²) are present in the palladium complexes **38** and **39**, yet the silver species **37** displays the *gauche*² arrangement (Scheme 14, right).

Figure 14. An overview of X-ray structural studies.

Computational conformational studies

Although, strictly speaking, we have been unable to detect remote-fluorine interactions in the complexes studied, a number of intriguing candidates have been identified which clearly adopt conformations in which the fluorine atoms point towards the metal centre (**26**, **31**, **37–39**). Common to all of these studies is the postulated *gauche* preference. Therefore to quantify this phenomenon, a theoretical study at the DFT level was instigated. We selected the imidazolium cation **23**, the neutral NHC derived by deprotonation, and the cationic *bis*(NHC) allyl palladium complex **39** (where NHC is the triazolyl carbene derived from **25**).

For each system, we calculated the NCCF rotational profile and optimised the three rotamers; results are summarized in Table 1 and Figure 15. The optimised structures of **23** and **39** agree very well with the experiment (*vide supra*, Figures 4 and 11). In **23**, the largest deviation is for ϕ_{NCCF} (expt. 71° , calc. 62°), which is caused by the F...F interactions in the solid state (see Figure 4). In the palladium complex **39**, the NCCF torsions are in good agreement (expt. 65° and 66° , calc. both 63°).

However, the torsion angles between the phenyl and triazolyl rings deviate somewhat (expt. -39° and -53° , calc. -44° and -42°), which is again due to intermolecular interactions in the solid state.

In all three systems, the relative energies of the two *gauche* rotamers are within 2 kJ mol^{-1} , i.e., practically degenerate. Because the 2-fluoroethyl group is oriented almost perpendicularly to the NHC ring system (the $\text{C}_{\text{carb}}\text{NCC}$ torsion angle is between 90° and 105°), there are no differential interactions between the fluorine and the nitrogen lone pair. This is unlike the situation in (2-fluoroethyl)imines,^[44] where one *gauche* rotamer is destabilised by the repulsion between the fluorine and imine lone pairs, to the extent that it becomes even less stable than the *anti* rotamer.

Table 1. Calculated^[a] energies and torsion angles of rotamers of the imidazolium ion **23**, the neutral NHC derived from **23**, and the Pd(NHC) complex **39**. Energies are relative to the lowest-energy rotamer for each compound.

Compound	Rotamer	$\Delta E [\text{kJ mol}^{-1}]$	$\phi_{\text{(NCCF)}} [^\circ]$
NHC-H ⁺ (23)	– <i>gauche</i>	1	–63
	+ <i>gauche</i>	0	62
	<i>anti</i>	11	–178
NHC	– <i>gauche</i>	0	–65
	+ <i>gauche</i>	2	64
	<i>anti</i>	6	–179
[Pd(C ₃ H ₅)(NHC) ₂] ⁺ (39)	– <i>gauche</i>	0	–63
	+ <i>gauche</i>	0	63
	<i>anti</i>	7	–173

[a] Results obtained with M06-L/def2-TZVP in continuum CH₂Cl₂.

For the imidazolium cation **23**, the preferred +*gauche* rotamer is more stable than the *anti* by 11 kJ mol^{-1} . The magnitude of this stabilisation is characteristic of an electrostatic *gauche* effect, which orients the partially negatively charged fluorine preferentially towards the cationic moiety, similarly to the situation seen in *N*-(2-fluoroethyl)iminium,^[7a] -pyridinium,^[45] or -ammonium^[6,46,47] systems. The Hirshfeld partial charges for **23** (which are practically independent of the torsion angle) are $-0.13e$ (F), 0.00 (both N), and $+0.24e$ (C_{carb} H). Considering only the charge–charge interactions

between fluorine and the atoms of the $[\text{N}=\text{CH}-\text{N}]^+$ unit, the +*gauche* rotamer is stabilised by 5 kJ mol^{-1} relative to the *anti* rotamer. In the neutral NHC, however, there is no such electrostatic stabilisation. While the charge on fluorine does not change much ($-0.15e$), the formally neutral $[\text{N}-\text{C}:-\text{N}]$ unit now has a charge of $-0.27e$ (of which $-0.18e$ on C_{carb}). The preferred –*gauche* rotamer is therefore electrostatically destabilised relative to the *anti* by 3 kJ mol^{-1} . Consequently, the net preference for the –*gauche* rotamer reduces to 6 kJ mol^{-1} . This value is typical of the stabilisation imparted by antiperiplanar hyperconjugative $\sigma_{\text{C-H}} \rightarrow \sigma^*_{\text{C-F}}$ and $\sigma_{\text{C-H}} \rightarrow \sigma^*_{\text{C-N}}$ interactions, in preference to $\sigma_{\text{C-N}} \rightarrow \sigma^*_{\text{C-F}}$ and $\sigma_{\text{C-F}} \rightarrow \sigma^*_{\text{C-N}}$. Similar stereoelectronic *gauche* effects in NCCF systems have previously been described for imines,^[44] amines,^[6,45–47] and amides.^[6,48] Free NHCs and their precursor cations therefore follow the pattern found in other NCCF systems as far as the *gauche* preference is concerned.

Figure 15. Rotational profiles, calculated at M06-L/def2-TZVP/PCM(CH₂Cl₂) level, for **23**, its neutral NHC, and the bis(NHC) Pd complex **39**. In **39**, the NCCF torsion was scanned only in one NHC, while the other was freely optimized.

In the complex **39**, the +*gauche* rotamer is preferred to the *anti* by 7 kJ mol^{-1} , only slightly more than in the free NHC. The analysis of Hirshfeld partial charges reveals that the main difference between the free and the Pd-bound NHC is the decreased amount of charge on C_{carb} ($+0.01e$) and also the adjacent nitrogens. This is consistent with the NHC donating electron density towards the metal centre. Overall, the $[\text{N}-\text{C}:-\text{N}]$ unit is almost neutral ($-0.01e$). The charge–charge electrostatic interaction between fluorine and $[\text{N}-\text{C}:-\text{N}]$ is therefore small in magnitude and differs insignificantly ($<1 \text{ kJ mol}^{-1}$) between the rotamers. The absence of the destabilising electrostatic component in the complexed NHC compared to the free NHC thus accounts for the slightly stronger *gauche* preference in the latter. However, the electron-withdrawing effect of the metal on the $[\text{N}-\text{C}:-\text{N}]$ unit is not nearly as strong as the effect of protonation in the cation. A Natural Bond Orbital analysis confirmed that the torsion-dependent hyperconjugative interactions in the NCCF unit are practically the same for free and complexed NHC. The metal-bound NHC thus essentially behaves as a free NHC with respect to *gauche* preference.

Experimental section

General

All reactions using air or moisture sensitive compounds were carried out in flame-dried and evacuated glassware under an atmosphere of argon. Solvents were dried according to standard procedures or were taken from the solvent drying system. All chemicals were reagent grade and used as supplied. Solvents for extractions and chromatography were technical grade and distilled prior to use. Reactions were monitored by thin layer chromatography, using pre-coated Merck silica gel 60 F254 glass plates (0.25 mm). Visualisation was accomplished using ultraviolet light ($\lambda = 254$ nm) or by dipping in cerium ammonium molybdate (CAM) stain $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (50 g), $\text{Ce}(\text{SO}_4)_2$ (10 g) and H_2SO_4 (100 ml) in water (900 ml)] or in ninhydrin stain (prepared by dissolving 0.3 g of ninhydrin in 100 ml of *n*-BuOH containing 1 ml of acetic acid), followed by heating. Flash column chromatography was carried out using Fluka silica gel 60 (230-400 mesh). Concentration in vacuo was performed at ~ 8 mbar and 30-40 °C, drying at the high vacuum at $\sim 10^{-2}$ mbar and r.t. ^1H -NMR, ^{19}F -NMR and ^{13}C -NMR spectra were recorded on Varian Mercury-vx 300 MHz, Bruker AVANCE 300 MHz, Bruker DRX 400 MHz or Bruker AV 400 MHz spectrometers. Chemical shifts δ are reported in ppm relative to the residual solvent. Melting points were measured on a Büchi B540 melting point apparatus and are uncorrected. IR spectra were measured on a Perkin-Elmer Spectrum 100 FTIR spectrometer and reported in cm^{-1} . Optical rotations were obtained using a JASCO DIP-370 polarimeter. High-resolution mass spectra were performed by the MS service at the Laboratory for Organic Chemistry (ETH Zürich). Elemental analysis was performed by the micro-laboratory at the Laboratory for Organic Chemistry (ETH Zürich).

bis[(S)-5-(fluorodiphenylmethyl)-2-phenyl-6,7-dihydro-2H-pyrrolo[2,1-c][1,2,4]triazol-3(5H)ylidene]palladium(II) chloride (26).

A mixture of (S)-5-(fluorodiphenylmethyl)-2-phenyl-6,7-dihydro-5H-pyrrolo[2,1-c][1,2,4]triazol-2-ium tetrafluoroborate **15** (93 mg, 0.2 mmol), Ag_2O (25 mg, 0.12 mmol) and NMe_4Cl (22 mg, 0.2 mmol) in anhydrous CH_2Cl_2 (6.8 mL) was stirred for 24 h at r.t. The mixture was filtered through an Acrodisc (Chromafil PET 20/25), which was washed with CH_2Cl_2 (1 mL). The filtrate was concentrated and the residue re-dissolved in CH_2Cl_2 (5 mL). PdCl_2 (18 mg, 0.1 mmol) was added and the mixture stirred for an additional 24 h. The solvent was removed *in vacuo* and the crude product was purified by column chromatography (cyclohexane/ethyl acetate 1/0 $\rightarrow$ 1/1) to the title compound as a pale brown solid (30 mg, 33%); mp: 150 °C (decomposition); R_f 0.28 (cyclohexane/ethyl acetate 1/1); $[\alpha]_D^{20} = -197.7$ (c 0.09, CH_2Cl_2); ^1H NMR (400 MHz, CD_2Cl_2) δ 8.22-8.21 (m, 4H, Ph), 7.54-7.02 (m, 26H, Ph), 6.10-6.07 (m, 2H, H5), 3.10-2.99 (m, 2H, H4), 2.63-2.50 (m, 2H, H4), 2.46-2.39 (m, 2H, H3), 1.52-1.40 (m, 2H, H3); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 170.7, 161.5, 140.8, 139.9 & 138.8, 130.5-128.5, 125.5, 98.8, 63.3, 31.3, 20.5; ^{19}F NMR (376 MHz, CD_2Cl_2) δ -114.7, -119.2; IR (neat) 3060, 2925, 1733, 1683, 1602, 1499, 1449, 1407, 1353, 1252, 1037, 973, 910, 860, 761, 724, 692, 635; mass spectrum HRMS (MALDI+) found 879.2016 (M^+-Cl). $\text{C}_{48}\text{H}_{40}\text{ClF}_2\text{N}_6\text{Pd}$ requires 879.2014.

(S)-5-(fluorodiphenylmethyl)-2-phenyl-6,7-dihydro-5H pyrrolo[2,1-c][1,2,4]triazol-3(5H)ylidene(allyl)palladium(II) chloride (28)

A flask was charged with (S)-5-(fluorodiphenylmethyl)-2-phenyl-6,7-dihydro-5H-pyrrolo[2,1-c][1,2,4]triazol-3(5H)ylidene silver(I) chloride **27** (76.9 mg, 0.15 mmol) and $[\text{Pd}(\text{allyl})\text{Cl}]_2$ (27.5 mg, 0.075 mmol) under an atmosphere of argon. CH_2Cl_2 (5.5 mL) was added and the reaction was stirred at r.t. for 20 h. The mixture was then filtered through a pad of Celite. Evaporation of the solvent and recrystallisation of the resulting solid from CH_2Cl_2 /pentane yielded the product as a pale brown solid (43 mg, 52%). mp: decomposition > 136 °C; $[\alpha]_D^{20} = -96.3$ (c 0.11, CHCl_3); two rotamers were identified with a ratio of 1:0.2 (* denotes the minor rotamer): ^1H NMR (400 MHz, CDCl_3) δ 7.84-7.82 (m, 2H, Ph*), 7.77-7.75 (m, 2H, Ph), 7.67-7.57 (m, 2H, Ph; m, 2H, Ph*), 7.49-7.17 (m, 9H, Ph;

m, 10H, Ph*), 7.10-7.07 (m, 1H, Ph_a), 6.77 (dd, $J=30.7$ Hz, 8.5 Hz, 1H, H5_a), 6.47 (dd, $J=28.2$ Hz, 8.2 Hz, 1H, H5*), 4.90-4.80 (m, 1H, CH-allyl), 4.42-4.32 (m, 1H, CH-allyl*), 4.06 (dd, $J=7.4$ Hz, 1.5 Hz, 1H, CH₂-allyl), 3.98 (dd, $J=7.4$ Hz, 1.7 Hz, 1H, CH₂-allyl*), 3.23-3.14 (m, 1H, H3), 3.08-2.95 (m, 1H, H4; m, 2 $\times$ H4*, 3H, CH₂-allyl*), 2.91-2.82 (m, 1H, H3_a; m, 1H, H3*), 2.66-2.57 (m, 2H, H4, CH₂-allyl; m, 2H, H3*, CH₂-allyl*), 2.16 (d, $J=6.5$ Hz, 1H, CH₂-allyl), 1.34-1.26 (m, 1H, CH₂-allyl*); 1.01 (d, $J=12.0$ Hz, 1H, CH₂-allyl); not all quaternary carbons of the minor rotamer could be assigned: ^{13}C NMR (100 MHz, CDCl_3) δ 179.9, 163.0, 162.7*, 141.9, 140.9*, 140.7, 140.4*, 129.1, 129.0, 128.8, 128.78, 128.7, 128.5, 128.4, 128.3, 127.9, 127.5, 126.6, 126.55, 126.4, 126.0, 125.5, 125.4, 125.1, 125.0, 124.9, 116.0*, 115.1, 101.8, 71.4, 70.9*, 62.6, 52.5, 50.8*, 34.2*, 32.2, 22.5*, 21.6; ^{19}F NMR (376 MHz, CDCl_3) δ -161.6*, -167.8; IR (neat) 3060, 1671, 1598, 1543, 1493, 1449, 1391, 1343, 1247, 1203, 762, 752, 694; mass spectrum HRMS (ESI+) m/z : (M^+-Cl), found: 516.1082. $\text{C}_{27}\text{H}_{25}\text{PdF}_3\text{N}_3$ requires 516.1072.

1,5-cyclooctadienyl-(S)-5-(fluorodiphenylmethyl)-2-phenyl-6,7-dihydro-5H-pyrrolo[2,1-c][1,2,4]triazol-3(5H)ylidene)rhodium(I) chloride (29)

A freshly prepared solution of NaH (9.6 mg, 0.24 mmol, 60% dispersion in mineral oil) in EtOH (1.2 mL) was added slowly to a suspension of $[\text{Rh}(\text{COD})\text{Cl}]_2$ (29.6 mg, 0.06 mmol) in EtOH (0.8 mL). After stirring at r.t. for 45 min, **15** (55 mg, 0.12 mmol) was then added and the mixture was stirred for a further 24 h at r.t. The solvent was evaporated and the crude product was purified by column chromatography (hexane/ethyl acetate 1/0 $\rightarrow$ 3/5) to yield the title compound as a pale brown solid (30 mg, 41%). mp: 133 °C (decomposition); R_f 0.15 (hexane/ethyl acetate 3/1); $[\alpha]_D^{20} = -155.0$ (c 0.10, CH_2Cl_2); ^1H NMR (400 MHz, CDCl_3) δ 8.45 (d, $J=7.5$ Hz, 2H, Ph), 7.59-7.49 (m, 8H, Ph), 7.46-7.29 (m, 3H, Ph), 7.01 (d, $J=7.5$ Hz, 2H, Ph), 6.28 (dd, $J=8.3$ Hz, 5.6 Hz, 1H, H5), 5.10 [s, br, 1H, CH(COD)], 4.86 [s, br, 1H, CH(COD)], 3.76 [s, br, 1H, CH(COD)], 3.04-2.99 (m, 1H, H4), 2.92 [s, br, 1H, CH(COD)], 2.51-2.38 (m, 2H, H3, H4), 2.28-2.20 [m, 3H, CH₂(COD)], 1.81-1.69 [m, 3H, CH₂(COD)], 1.63-1.54 [m, 1H, CH₂(COD)], 1.47-1.38 (m, 1H, H3); ^{13}C NMR (100 MHz, CDCl_3) δ 185.6, 162.1, 141.1, 139.9, 139.0, 129.5, 129.1, 128.8, 128.7, 128.5, 128.3, 128.2, 128.1, 127.5, 125.6, 98.6, 97.3, 96.8, 71.2, 70.6, 62.5, 32.6, 32.0, 31.7, 29.2, 28.3, 20.2; ^{19}F NMR (376.6 MHz, CDCl_3) δ -120.2* (minor), -127.7; IR (neat) 2924, 2872, 1598, 1497, 1447, 1393, 1330, 1251, 1076, 1032, 966, 910, 861, 808, 761, 723, 692, 635, 618; mass spectrum HRMS (MALDI+) m/z : (M^+-Cl), found 580.1634. $\text{C}_{32}\text{H}_{32}\text{FN}_3\text{Rh}$ requires 580.1630.

1,5-cyclooctadienyl-(S)-5-(fluorodiphenylmethyl)-2-phenyl-6,7-dihydro-5H-pyrrolo[2,1-c][1,2,4]triazol-3(5H)ylidene)iridium(I) chloride (30)

A freshly prepared solution of NaH (4.8 mg, 0.12 mmol, 60% dispersion in mineral oil) in EtOH (0.6 mL) was added slowly to a suspension of $[\text{Ir}(\text{COD})\text{Cl}]_2$ (20.0 mg, 0.03 mmol) in EtOH (0.4 mL). After stirring at r.t. for 45 min, **15** (48 mg, 0.105 mmol) was added and the mixture was stirred for further 24 h at r.t. The solvent was removed and the crude product was purified by column chromatography (cyclohexane/ethyl acetate 3/1 $\rightarrow$ 1/1) to yield the product as a pale brown solid (26 mg, 61%). mp: 115 °C (decomposition); R_f 0.29 (cyclohexane/ethyl acetate 2/1); $[\alpha]_D^{20} = -112.5$ (c 0.12, CH_2Cl_2); ^1H NMR (400 MHz, CDCl_3) δ 8.31-8.29 (m, 2H, Ph), 7.50-7.28 (m, 11H, Ph), 7.04-7.02 (m, 2H, Ph), 6.19 (dd, $J=7.9$ Hz, 5.5 Hz, 1H, H5), 4.82 [s, br, 1H, CH(COD)], 4.43 [s, br, 1H, CH(COD)], 3.37 [s, br, 1H, CH(COD)], 3.05-3.00 (m, 1H, H4), 2.53-2.42 (m, 3H, H3, H4), 2.11-1.95 [m, 3H, CH₂(COD)], 1.62-1.50 [m, 3H, CH₂(COD)], 1.46-1.38 [m, 1H, CH₂(COD)], 1.30-1.24 [m, 1H, CH₂(COD)]; ^{13}C NMR (100 MHz, CDCl_3) δ 182.3,

161.8, 141.0, 139.8, 139.1, 129.4, 129.1, 128.8, 128.5, 128.4, 128.1, 128.0, 127.6, 127.5, 125.7, 98.3, 84.2, 84.16, 62.3, 54.5, 54.4, 33.4, 32.7, 31.8, 29.5, 28.9, 20.4; ^{19}F NMR (376.6 MHz, CDCl_3) δ -121.4* (minor), -128.2; IR (neat) 2929, 2879, 1596, 1493, 1447, 1329, 1251, 1075, 1032, 971, 907, 808, 760, 724, 693, 635; mass spectrum HRMS (MALDI+) m/z : (M^+ -Cl), found 670.2202. $\text{C}_{32}\text{H}_{32}\text{FIrN}_3$ requires 670.2205.

1,5-cyclooctadienyl-(S)-(5-(fluoromethyl)-2-phenyl-6,7-dihydro-2H-pyrrolo[2,1-c][1,2,4]-triazol-3(5H)-ylidene)rhodium(I) chloride (34)

A freshly prepared solution of NaH (9.6 mg, 0.24 mmol, 60% dispersion in mineral oil) in EtOH (1.2 ml) was added slowly to a suspension of $[\text{Rh}(\text{COD})\text{Cl}]_2$ (29.6 mg, 0.06 mmol) in EtOH (0.8 ml). After stirring at r.t. for 45 min, **19** (36.6 mg, 0.12 mmol) was added and the mixture was stirred for a further 24 h at r.t. The solvent was removed *in vacuo* and the crude product was purified by column chromatography (cyclohexane/ethyl acetate 1/0 $\rightarrow$ 1/2) to yield the product as a pale brown solid (26 mg, 47%) [Found: C, 51.91; H, 5.30; N, 8.92; F, 3.96; Cl, 7.81. $\text{C}_{20}\text{H}_{24}\text{N}_3\text{FCIrRh}$ requires C, 51.80; H, 5.22; N, 9.06; F, 4.10; Cl, 7.64]. mp: 198 °C (decomposition); R_f 0.49 (cyclohexane/ethyl acetate 1/1); $[\alpha]_D^{20} = -84.0$ (c 0.1, CH_2Cl_2); ^1H NMR (400 MHz, CDCl_3) δ 8.43 (d, $J=7.6$ Hz, 2H, H9, H13), 7.56-7.52 (m, 2H, H10, H12), 7.47-7.43 (m, 1H, H11), 6.53 (dd, $J=48.4$ Hz, 10.1 Hz, 1H, H6), 5.21-5.17 [m, 1H, CH(COD)], 5.10-4.97 [m, 2.5H, H6, H5, CH(COD)], 4.87 (d, $J=10.2$ Hz, 0.5H, H6), 3.35 [s, br, 1H, CH(COD)], 3.07-2.94 (m, 2H, H3), 2.87-2.73 [m, 3H, H4, CH(COD)], 2.37-2.26 [m, 3H, $\text{CH}_2(\text{COD})$], 1.94-1.77 [m, 4H, $\text{CH}_2(\text{COD})$], 1.67-1.59 [m, 1H, $\text{CH}_2(\text{COD})$]; ^{13}C NMR (100 MHz, CDCl_3) δ 181.4, 160.8, 140.6, 128.8, 128.5, 124.0, 99.15, 99.06, 82.7, 71.1, 69.6, 58.0, 33.1, 32.0, 29.2, 28.7, 28.3, 21.2; ^{19}F (376.6 MHz, CDCl_3) δ -236.8; IR (neat) 2939, 2229, 1967, 1596, 1493, 1449, 1331, 1069, 973, 910, 865, 812, 760, 725, 693, 639; mass spectrum HRMS (ESI+) m/z : (M^+ -Cl), found 428.0999. $\text{C}_{20}\text{H}_{24}\text{FN}_3\text{Rh}$ requires 428.1004.

1,5-cyclooctadienyl-(S)-(5-(fluoromethyl)-2-phenyl-6,7-dihydro-2H-pyrrolo[2,1-c][1,2,4]-triazol-3(5H)-ylidene)iridium(I) chloride (35)

A freshly prepared solution of NaH (2.4 mg, 0.06 mmol, 60% dispersion in mineral oil) in EtOH (0.3 ml) was added slowly to a suspension of $[\text{Ir}(\text{COD})\text{Cl}]_2$ (10.1 mg, 0.015 mmol) in EtOH (0.2 ml). After stirring at r.t. for 45 min, **19** (18.3 mg, 0.06 mmol) was added and the mixture was stirred for a further 24 h at r.t. The solvent was evaporated and the crude product was purified by column chromatography (cyclohexane/ethyl acetate 2/1) to yield the product as a pale brown solid (6 mg, 36%). mp: 175 °C (decomposition); R_f 0.74 ($\text{CH}_2\text{Cl}_2/\text{MeOH}$ 20/1); $[\alpha]_D^{20} = -6.6$ (c 0.06, CH_2Cl_2); ^1H NMR (400 MHz, CDCl_3) δ 8.30-8.29 (m, 2H, H9, H13), 7.50-7.43 (m, 3H, H10, H11, H12), 6.19 (dd, $J=47.8$ Hz, 9.7 Hz, 1H, H6), 5.01-4.65 [m, 4H, H5, H6, 2 $\times$ CH(COD)], 3.08-3.02 (m, 2H, H3), 2.89-2.76 [m, 3H, H4, CH(COD)], 2.45-2.40 [m, 1H, CH(COD)], 2.21-2.11 [m, 3H, $\text{CH}_2(\text{COD})$], 1.84-1.76 [m, 1H, $\text{CH}_2(\text{COD})$], 1.72-1.64 [m, 2H, $\text{CH}_2(\text{COD})$], 1.58-1.48 [m, 1H, $\text{CH}_2(\text{COD})$], 1.44-1.37 [m, 1H, $\text{CH}_2(\text{COD})$]; ^{13}C NMR (100 MHz, CDCl_3) δ 179.0, 160.5, 140.4, 128.7, 128.3, 124.1, 86.4, 86.35, 82.6, 57.8, 54.8, 53.3, 33.3, 33.2, 29.9, 29.2, 28.4, 21.3; ^{19}F NMR (376.6 MHz, CDCl_3) δ -236.9; IR (neat) 2921, 1969, 1729, 1595, 1498, 1448, 1384, 1353, 1287, 1155, 1066, 1018, 981, 934, 817, 765, 692; mass spectrum HRMS (MALDI+) m/z : (M^+ -Cl) found: 518.1578. $\text{C}_{20}\text{H}_{24}\text{FIrN}_3$ requires 518.1579.

allyl-bis(1-(2-fluoroethyl)-3-phenyl-1H-imidazol-2(3H)-ylidene)palladium(II) triflate (38)

bis(1-(2-fluoroethyl)-3-phenyl-1H-imidazol-2(3H)-ylidene) silver(I) triflate **36** (31 mg, 0.0486 mmol) and $[\text{Pd}(\text{allyl})\text{Cl}]_2$ (17 mg, 0.0486 mmol) were dissolved in CH_2Cl_2 (1 ml) and the mixture was stirred at r.t. for 19 h. The resulting suspension was filtered through a short

pad of Celite and the filtrate was concentrated to give a yellow oil which was purified by column chromatography ($\text{CH}_2\text{Cl}_2/\text{MeOH}$ 50/1) to yield the product as a white solid (19.1 mg, 58%). mp: 134.3-136.2 °C; R_f 0.47 ($\text{CH}_2\text{Cl}_2/\text{MeOH}$ 9/1); ^1H NMR (400 MHz, CDCl_3) δ 7.47-7.44 (m, 6H, H6, H7, H8), 7.25-7.24 (m, 2H, H3), 7.15-7.14 (m, 2H, H4), 7.09-7.07 (m, 4H, H6, H7, H8), 5.28 (tt, $J=13.2$ Hz, 7.3 Hz, 1H, H11), 4.52 (dm, $J=47.3$ Hz, 4H, H1), 3.88 (d, $J=7.3$ Hz, 2H, H10 or H12), 3.68 (dm, $J=27.7$ Hz, 2H, H2), 2.59 (d, $J=13.2$ Hz, 2H, H10 or H12); ^{13}C NMR (100 MHz, CDCl_3) δ 177.2, 140.2, 129.9, 129.3, 125.0, 123.7, 122.5, 119.1, 82.3, 61.3, 51.1; ^{19}F NMR (376.5 MHz, CDCl_3) δ -78.2 (s, 3F, OTf), -222.2 (tt, $J=47.3$ Hz, 27.9 Hz, 2F, CH_2F); IR (neat) 3097, 2920, 2851, 1598, 1497, 1415, 1363, 1261, 1221, 1141, 1101, 1030, 1013, 909, 863, 768, 741, 694, 635; mass spectrum HRMS (ESI+) m/z : (M^+) found, 527.1241. $\text{C}_{25}\text{H}_{27}\text{F}_2\text{N}_4\text{Pd}$ requires 527.1243.

allyl-bis(4-(2-fluoroethyl)-1-phenyl-1H-1,2,4-triazol-5(4H)-ylidene)palladium(II) triflate (39)

bis(4-(2-fluoroethyl)-1-phenyl-1H-1,2,4-triazol-5(4H)ylidene) silver (I) triflate **37** (23 mg, 0.036 mmol) and $[\text{Pd}(\text{allyl})\text{Cl}]_2$ (12.6 mg, 0.035 mmol) were dissolved in CH_2Cl_2 (0.7 ml) and the mixture was stirred at r.t. for 24 h. The resulting suspension was filtered through a short pad of Celite and the filtrate concentrated to give a crude product which was then purified by column chromatography ($\text{CH}_2\text{Cl}_2/\text{MeOH}$ 50/0 $\rightarrow$ 20/5) to furnish the product as a white solid (19.1 mg, 78%). mp: 115 °C (decomposition); R_f 0.31 ($\text{CH}_2\text{Cl}_2/\text{MeOH}$ 9/1); ^1H NMR (400 MHz, CD_2Cl_2) δ 8.28 (d, $J=1.1$ Hz, 2H, H3), 7.52-7.48 (m, 6H, H5, H6, H7), 7.39-7.36 (m, 2H, H5, H6), 5.56 (tt, $J=13.2$ Hz, 7.3 Hz, 1H, H10), 4.63-4.54 (m, 2H, H1), 4.52-4.42 (m, 2H, H1), 4.18 (d, $J=7.4$ Hz, 2H, H9 or H11), 3.94-3.91 (m, 2H, H2), 3.87-3.84 (m, 2H, H2), 2.97 (d, $J=13.2$ Hz, 2H, H9 or H11); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 180.9, 144.4, 139.9, 130.4, 130.3, 124.7, 120.9, 82.3, 121.5, 63.9, 49.7; ^{19}F NMR (376.5 MHz, CD_2Cl_2) δ -78.9 (s, 3F, OTf), -222.4 (tt, $J=47.2$ Hz, 28.0 Hz, 2F, CH_2F); IR (neat) 3119, 2924, 1597, 1539, 1499, 1463, 1409, 1374, 1357, 1263, 1220, 1151, 1076, 1029, 961, 911, 858, 766, 718, 696, 634; mass spectrum HRMS (ESI+) m/z : (M^+) found, 529.1133. $\text{C}_{23}\text{H}_{25}\text{F}_2\text{N}_6\text{Pd}$ requires 529.1147.

Full experimental details are provided in the supporting information.

Acknowledgments

We gratefully acknowledge generous financial support from the Alfred Werner Foundation, the ETH Zürich, the University of Glasgow and the Westfälische Wilhelms-Universität Münster. This article is dedicated, with respect and admiration, to Professor Melanie Sanford on her receipt of the Tetrahedron Young Investigator Award 2013.

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