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Alina A Grineva, Oleg Filippov, Sergei Nefedov, Noël Lugan, Vincent César, et al.. Direct Access to IMes F and IMes F 2 by Electrophilic Fluorination of Abnormal N-Heterocyclic Carbenes. *Organometallics*, 2019, 38 (11), pp.2330-2337. 10.1021/acs.organomet.9b00151 . hal-02333068

HAL Id: hal-02333068

<https://hal.science/hal-02333068v1>

Submitted on 5 Nov 2020

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Direct Access to IMes^{F} and IMes^{F_2} by Electrophilic Fluorination of Abnormal N-Heterocyclic Carbenes

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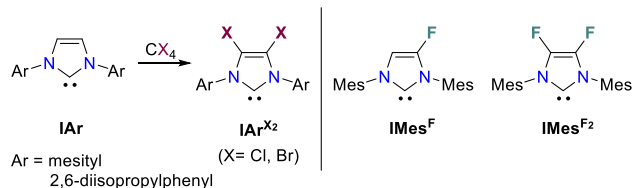
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ABSTRACT: The incorporation of fluorine atoms into NHC ligand backbone in Mn(I) complex $[\text{CpMn}(\text{CO})_2(\text{IMes})]$ was achieved *via* a sequence of the C–H bond deprotonation and electrophilic fluorination of the anionic abnormal carbene moiety with NFSI. The demetallation of resulting complexes $[\text{CpMn}(\text{CO})_2(\text{IMes}^{\text{F}_{1-2}})]$ with triflic acid afforded the imidazolium salts $\text{IMes}^{\text{F}_{1-2}}\text{HOTf}$, the precursors of the corresponding fluorinated NHCs. Interestingly, IMes^{F_2} ligand was found to be more electron donating than its well known analogue $\text{IMes}^{\text{Cl}_2}$ notwithstanding the higher electronegativity of fluorine atoms. A systematic experimental and DFT study for this NHC series allowed to fully rationalize this unexpected behavior revealing that the weaker σ -donation of IMes^{F_2} is compensated by its lower π -accepting properties due to the strong mesomeric $+M$ effect of the fluorine substituents.

INTRODUCTION

Thanks to their beneficial stereoelectronic properties, N-Heterocyclic Carbenes (NHCs) have emerged as game changer ligands in organometallic chemistry and homogeneous catalysis providing in some cases outstanding catalytic systems.^{1,2} NHCs indeed combine a strong σ -donation, resulting in highly stable metal ligation, with a good steric protection of the catalytic center, due to their shell-like shape.³ As the 1,3-dimesitylimidazol-2-ylidene (IMes) and 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) became the most emblematic NHC ligands, a great deal of research efforts were directed toward their fine tuning in view of expanding their application scope and the substitution of the 4 and 5 imidazolyl-positions by heteroatoms appeared an astounding lever to that purpose.⁴ Focusing on the halogen series, the 4,5-dichloro IAR^{Cl_2} and dibromo IAR^{Br_2} derivatives were readily obtained by a simple treatment of the free IAR NHCs with CCl_4 or CBr_4 respectively (Scheme 1).⁵



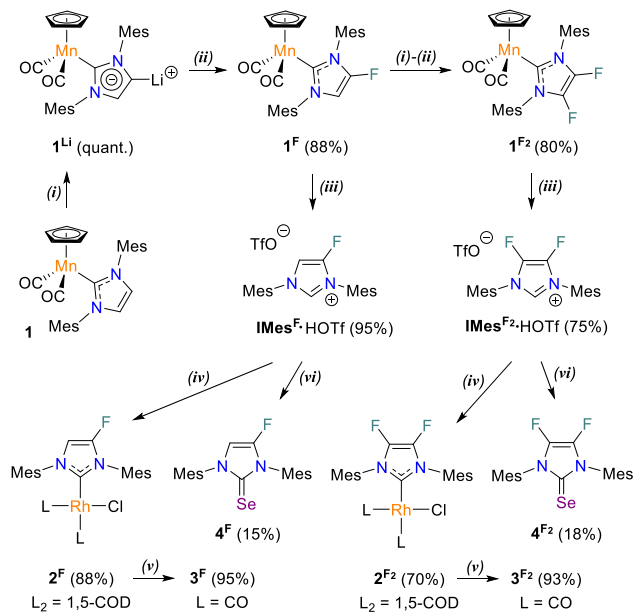
Scheme 1. Bis-chlorination and bis-bromination of imidazol-2-ylidenes (left) and target fluorine-substituted NHCs under study (right).

In view of the well-known inertness of the C–F bond and high solubility of organofluorine compounds in non-polar media, the 4,5-difluoro analogue IAR^{F_2} would be also of great interest. Unfortunately, it cannot be obtained through the previous protocol, due to the lack of reactivity of perfluoroalkanes,⁶ and its synthesis was reported only very recently through a protocol using somehow toxic and difficult to handle gaseous tetrafluoroethylene.⁷ This prompted us to disclose our own results on an alternative access to the 4-fluoro IMes^{F} and 4,5-difluoro IMes^{F_2} derivatives (Scheme 1), relying on the unprecedented electrophilic fluorination of an abnormal imidazol-4-ylidene moiety as a key step.^{8,9}

RESULTS AND DISCUSSION

Our strategy was based on the use of Mn(I) complex $[\text{CpMn}(\text{CO})_2(\text{IMes})]$ (**1**) easily available on multi-gram scale, from which we had previously shown that the anionic “abnormal” imidazol-4-ylidene compound **1^{Li}** could be quantitatively generated by treatment with $n\text{BuLi}$ at room temperature, the C2-position being protected by the metallic fragment (Scheme 2).¹⁰ Such ditopic imidazol-2,4-diylidene species were first disclosed by Robinson in 2010,¹¹ and their chemistry was then extended by several groups.¹² The abnormal carbene moiety in these compounds usually reacts with various electrophiles leading, in some cases, to new backbone-functionalized NHCs.^{11,13} In our case, **1^{Li}** smoothly reacted at low temperature with N-fluorobenzenesulfonimide (NFSI), a classical reagent for electrophilic fluorination,¹⁴ to give the mono-fluoro derivative **1^F** in 88% isolated yield.¹⁵ Gratifyingly, a second fluorine atom could be installed through the same

sequence of lithiation/electrophilic fluorination by which complex $\mathbf{1}^{\text{F}_2}$ was obtained in 80% yield. As previously reported,^{10a} treatment of the Mn(I) NHC complexes with triflic acid in CH_2Cl_2 at -40°C led to a clean demetallation of the complexes to afford the corresponding imidazolium triflates $\mathbf{IMes}^{\text{F}}\text{-HOTf}$ and $\mathbf{IMes}^{\text{F}_2}\text{-HOTf}$ in 95% and 75% yields, respectively, as white, analytically pure powders.



Scheme 2. Synthesis of imidazolium salts $\mathbf{IMes}^{\text{F}_1-2}\text{-HOTf}$, and the corresponding selenoureas and Rh(I) complexes derived from $\mathbf{IMes}^{\text{F}_1-2}$ carbenes. Reaction conditions: (i) 1.1 equiv. of $n\text{BuLi}$, THF, RT; (ii) 1.5 equiv. of NFSI, toluene, -80°C ; (iii) 1.5 equiv. of TfOH, CH_2Cl_2 , -40°C to RT; (iv) 1.1 equiv. of KHMDS, THF, -40°C then 0.5 equiv. of $[\text{RhCl}(\text{COD})]_2$, -40°C to RT; (v) CO, CH_2Cl_2 , RT; (vi) 1.1 equiv. of KHMDS, THF, -40°C then 1.15 equiv. of elemental Se, -40°C to RT.

Having established the synthetic access to the imidazolium $\mathbf{IMes}^{\text{F}}\text{-HOTf}$ and $\mathbf{IMes}^{\text{F}_2}\text{-HOTf}$, we next turned our attention to the possible use of the respective \mathbf{IMes}^{F} and $\mathbf{IMes}^{\text{F}_2}$ derivatives as supporting ligands in transition metal complexes, and to the complete quantification of their electronic properties. The Rh(I) complexes $\mathbf{2}^{\text{F}}$ and $\mathbf{2}^{\text{F}_2}$ were obtained in good yields by generating the free NHCs from $\mathbf{IMes}^{\text{F}}\text{-HOTf}$ and $\mathbf{IMes}^{\text{F}_2}\text{-HOTf}$, respectively, with potassium bis(trimethylsilyl)amide (KHMDS) at -40°C and trapping with $[\text{RhCl}(\text{COD})]_2$ (Scheme 2). Both complexes were fully characterized by spectroscopic and analytical techniques, including by XRD for complex $\mathbf{2}^{\text{F}}$ (Figure 1). Complex $\mathbf{2}^{\text{F}}$ displaying a typical square-planar geometry around the Rh(I) center is isostructural to the parent $[\text{RhCl}(\text{COD})(\text{IMes})]$ derivative and exhibits the same main metrical parameters within experimental error.¹⁶ The COD complexes $\mathbf{2}^{\text{F}}$ and $\mathbf{2}^{\text{F}_2}$ were then further converted to their dicarbonyl analogues $\mathbf{3}^{\text{F}}$ and $\mathbf{3}^{\text{F}_2}$ by bubbling gaseous CO into a solution of $\mathbf{2}^{\text{F}}$ or $\mathbf{2}^{\text{F}_2}$ in CH_2Cl_2 , respectively. Measuring the average IR-stretching frequency of the carbonyl ligands allowed the quantification of the overall electronic donation of the NHCs by calculating the Tolman Electronic parameter (TEP) values through linear regression (Table 1).³ Comparing their TEP values (\mathbf{IMes}^{F} : TEP = 2052 cm^{-1} , $\mathbf{IMes}^{\text{F}_2}$: TEP = 2054

cm^{-1}) with the non-substituted \mathbf{IMes} (TEP = 2051 cm^{-1}) revealed that the introduction of each fluorine atom onto the imidazolyl heterocycle is accompanied by a stepwise decrease of the overall electronic donation of the carbene ligand. More surprisingly, although the electronegativity of fluorine is the highest across the periodic table, the overall donation of $\mathbf{IMes}^{\text{F}_2}$ was found to be slightly higher than the one of its chlorine-analogue $\mathbf{IMes}^{\text{Cl}_2}$ (TEP = 2055 cm^{-1}) being in a slight discrepancy with computed TEP values reported by Gusev for similar $\text{Ni}(\text{CO})_3(\text{IME}^{\text{X}_2})$ complexes (TEP of 2059.1 and 2059.0 for X = F and Cl, respectively).¹⁷ In order to rationalize this unexpected experimental observation, we carried out a deeper analysis by the deconvolution of the σ -donation and π -acidity over this NHC series.

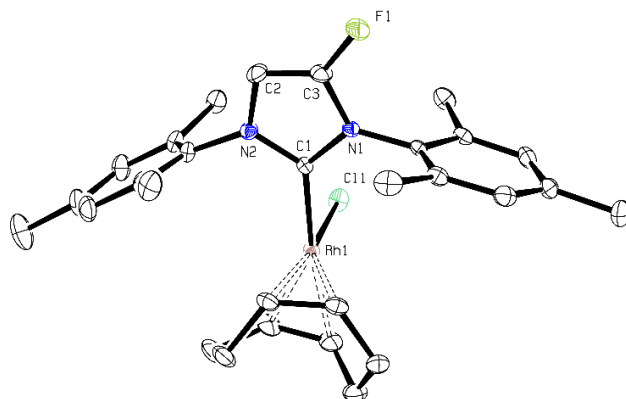


Figure 1. Molecular structure of $\mathbf{2}^{\text{F}}$ (ellipsoids drawn at 30% probability level, hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Rh1–Cl1 2.060(3), Rh1–Cl1 2.3991(7), C3–F1 1.339(3), N2–C1–N1 103.3(2), N1–C1–Rh1–Cl1 88.5(2).

According to Ganter's work, the σ -donation of the imidazol-2-ylidenes correlates well with the coupling constant $^1J_{\text{CH}}$ between the carbon and hydrogen atoms of the pre-carbenic position.¹⁸ Starting from $^1J_{\text{CH}} = 225$ Hz for \mathbf{IMes} , the strong electron withdrawing effect of the fluorine was evidenced by the 5 Hz increase of the $^1J_{\text{CH}}$ coupling constant, when adding one ($\mathbf{IMes}^{\text{F}}\text{-HOTf}$: $^1J_{\text{CH}} = 230$ Hz) and two ($\mathbf{IMes}^{\text{F}_2}\text{-HOTf}$: $^1J_{\text{CH}} = 235$ Hz) fluorine atoms onto the backbone (Table 1). Moreover, the σ -donation of $\mathbf{IMes}^{\text{F}_2}$ appeared to be lower than of $\mathbf{IMes}^{\text{Cl}_2}$ ($^1J_{\text{CH}} = 232$ Hz), which was quite expected in regard to the respective electronegativity trend. As the ^{77}Se chemical shift in NHC=Se adducts was shown to provide a good and precise scale for the π -acidity of the NHCs,¹⁹ the selenoureas $\mathbf{4}^{\text{F}}$ and $\mathbf{4}^{\text{F}_2}$ were synthesized by trapping the corresponding free \mathbf{IMes}^{F} and $\mathbf{IMes}^{\text{F}_2}$ with metallic selenium. Low isolated yields for these compounds arose probably from the decomposition during the chromatographic purification. While the π -accepting properties of \mathbf{IMes}^{F} ($\delta_{\text{Se}} = 55.3$ ppm) and $\mathbf{IMes}^{\text{F}_2}$ ($\delta_{\text{Se}} = 60.9$ ppm) are higher than the one of \mathbf{IMes} ($\delta_{\text{Se}} = 35.0$ ppm), they remain much lower compared to $\mathbf{IMes}^{\text{Cl}_2}$ ($\delta_{\text{Se}} = 114.0$ ppm) or to the cationic $\mathbf{IMes}^{\text{NMe}_3^+}$ ($\delta_{\text{Se}} = 102.0$ ppm) bearing a σ -withdrawing ammonium group on the backbone.²⁰ This can be explained considering that fluorine substituents are much better electron donors by mesomeric effect (+M) than chlorine ones and especially than ammonium group having no accessible lone electron pair.

Table 1. Experimental and theoretical electronic parameters of IMes-derived NHCs.

IMes ^{XY}	IMes	IMes ^F	IMes ^{F₂}	IMes ^{Cl₂}
$\nu_{\text{CO}}^{\text{av}}$ for 3^{XY} (cm ⁻¹) ^[a]	2038	2040	2042.5	2043
TEP value (cm ⁻¹) ^[b]	2051	2052	2054	2055
$^1J_{\text{CH}}$ (Hz) for IMes^{XY}HOTf	225	230	235	232
$\delta(^{77}\text{Se})$ for 4^{XY} (ppm) ^[c]	35.0	55.3	60.9	114.0
$\epsilon(\text{n}^{\text{C}}(\sigma))$ (eV) ^[d]	-5.87	-6.05	-6.25	-6.24
$\epsilon(2\text{p}^{\text{C}}(\pi^*))$ (eV) ^[d]	0.19	0.09	0.06	0.08

[a] Recorded in CH₂Cl₂ with the resolution of 0.5 cm⁻¹; [b] TEP (Tolman Electronic Parameter) values calculated by using the equation TEP = (0.8001ν_{CO^{av}} + 420.0 cm⁻¹); [c] Recorded in acetone-*d*₆; [d] Calculated at B3LYP/6-31+G** level of theory.

To consolidate the experimental quantification of the electronic properties of halogen-substituted IMes ligands, the energies of the occupied n^C(σ) and empty 2p^C(π*) orbitals (Figure S1) for this series of free NHCs were calculated at the B3LYP/6-31+G** level of theory (Table 1). In agreement with chemical intuition, the nucleophilicity of singlet NHCs decreased in **IMes** > **IMes^F** > **IMes^{Cl₂}** > **IMes^{F₂}** row as reflected by the energy level of the corresponding HOMO n^C(σ) orbitals. The calculated relative energies of empty 2p^C(π*) orbitals within this **IMes^{XY}** series (Table 1) reflecting their electrophilic character are also in agreement with experimental estimation by ⁷⁷Se NMR spectroscopy for the corresponding selenoureas **4^{XY}**.

CONCLUSION

In summary, we have disclosed a viable and practical synthetic access towards the mono and bis backbone-fluorinated 1,3-dimesitylimidazol-2-ylidenes **IMes^F** and **IMes^{F₂}**, respectively. The key step of the synthesis is an unprecedented electrophilic fluorination of imidazol-2,4-diylidene carbene scaffold, whose C2 position is protected by a [CpMn(CO)₂] fragment. The fluorine substituents were shown to exert a strong decrease on the σ-donation of the NHCs due to their electron withdrawing character, but this effect is counterbalanced with only marginally changed π-acidity due to a non-negligible mesomeric donor effect of the fluorine lone pairs. Extension of this methodology to other original backbone-functionalized NHCs as well as the application of the newly formed fluorinated NHCs in organometallic chemistry and catalysis are underway in our laboratories.

EXPERIMENTAL SECTION

General information. All manipulations besides handling of air stable imidazolium salts and selenoureas were carried out using Schlenk techniques under an atmosphere of dry nitrogen. Dry and oxygen-free organic solvents (THF, toluene, CH₂Cl₂) were obtained using Lab-Solv (Innovative Technology) solvent purification system. Solvents used for the purification of organometallic complexes by column chromatography (hexane, toluene,

CH₂Cl₂, THF) were deoxygenated by nitrogen bubbling during 10-15 min. Deuterated benzene for NMR experiments was deoxygenated by three freeze-pump-thaw cycles and kept over 4Å molecular sieves. CDCl₃ was passed through a short column of basic alumina, deoxygenated by three freeze-pump-thaw cycles and kept over 4Å molecular sieves. Chromatographic purification of the compounds was performed on silica (0.060-0.200 mm, 60 Å) and activated alumina (neutral, Brockmann type 3, 0.050-0.200 mm) obtained from Acros Organics. The compounds Cp(CO)₂Mn(IMes) (**1**),^{10a} [Rh(cod)Cl]₂²¹, and IMes·HCl²² were prepared according to previously described methods. Commercial NFSI was purified by crystallization from dry THF at -20 °C. All other reagent grade chemicals purchased from commercial sources were used as received.

Solution IR spectra were recorded in 0.1 mm CaF₂ cells using a Perkin Elmer Frontier FT-IR spectrometer and given in cm⁻¹ with relative intensity in parentheses. ¹H, ¹³C and ¹⁹F and ⁷⁷Se NMR spectra were obtained on Bruker Avance 400, Avance III HD 400 and Avance NEO 600 spectrometers and referenced against the residual signals of deuterated solvents (¹H and ¹³C),²³ BF₃·OEt₂ (¹⁹F, external standard) and Me₂Se (⁷⁷Se, external standard). Elemental analyses were carried out at the LCC-CNRS (Toulouse) using Perkin Elmer 2400 series II analyzer. High-resolution mass spectra (ESI, positive mode) were obtained using a Xevo G2 QToF (Waters) spectrometer.

Synthesis of [Cp(CO)₂Mn(IMes^F)] (1^F**).** To a yellow solution of complex **1** (960 mg, 2.0 mmol) in THF (10 mL), a 2.5 M solution of *n*BuLi in hexane (0.9 mL, 2.2 mmol, 1.1 equiv) was added dropwise at RT. The resulting deep red solution was stirred for an additional 30 min until the full conversion of starting **1** into the complex **1^{Li}** (ν_{CO} 1900.5 (s), 1831.0 cm⁻¹ (s)) was evidenced by IR spectroscopy. The solvent was then removed under vacuum and the resulting red residue was dissolved in toluene (10 mL). This solution was then added dropwise to a solution of NFSI (946 mg, 3 mmol, 1.5 equiv) in toluene (60 mL) at -80 °C to give a dark green suspension. The reaction mixture was slowly warmed to the room temperature, stirred for an additional 1 h and then filtered through a short column of silica (2×4 cm) using dry toluene as eluent. The solvent was removed under vacuum and the brown residue was purified by column chromatography on silica (2×20 cm). Elution with 2:1 CH₂Cl₂/hexane mixture afforded a yellow band containing desired complex **1^F**, followed by a yellow band containing starting complex **1** (eventually recovered, 200 mg) eluted with 4:1 CH₂Cl₂/hexane mixture. The first fraction was evaporated under vacuum and the crude product was crystallized from toluene/hexane mixture to afford complex **1^F** (690 mg, 70% yield, 88% yield based on the starting material consumed) as yellow crystals. ¹H NMR (400.2 MHz, C₆D₆, 25°C): δ 6.84 (s, 2H, CH_{Mes}), 6.82 (s, 2H, CH_{Mes}), 5.73 (d, ³J_{FH} = 6.5 Hz, 1H, CH_{Im-5}), 3.97 (s, 5H, Cp), 2.16 (s, 3H, CH_{3 p-Mes}), 2.12 (s, 6H, CH_{3 o-Mes}), 2.11 (s, 3H, CH_{3 p-Mes}), 2.08 (s, 6H, CH_{3 o-Mes}); ¹⁹F{¹H} NMR (376.5 MHz, C₆D₆, 25°C): δ -145.7 (s, C_{Im-4-F}); ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 25°C): δ 234.0 (s, Mn-CO), 203.8 (d, ³J_{CF} = 12.5 Hz, Mn-CN₂), 149.6 (d, ¹J_{CF} = 261.8 Hz, C_{Im-4-F}), 139.6, 138.9 (s, C_{p-Mes}), 138.4 (s, C_{i-Mes}), 137.1, 136.2 (s, C_{o-Mes}), 132.8 (s, C_{i-Mes}), 129.7, 129.5 (s, CH_{Mes}), 102.3 (d, ²J_{CF} = 21.8 Hz,

CH_{Im-5}), 81.5 (s, Cp), 21.2 (s, CH_{3 p-Mes}), 18.4 (s, CH_{3 o-Mes}). IR (toluene): ν_{CO} 1918.0 (s), 1851.0 cm⁻¹ (s). Anal. Found: C, 67.12; H, 5.52; N, 5.55. Calcd. for C₂₈H₂₈FN₂O₂Mn: C, 67.47; H, 5.66; N, 5.62.

Synthesis of [Cp(CO)₂Mn(IMes^{F2})] (1^{F2}). To a yellow solution of complex **1^F** (250 mg, 0.5 mmol) in THF (5 mL), a 2.5 M solution of *n*BuLi in hexane (0.22 mL, 0.55 mmol) was added dropwise at room temperature. The resulting deep red solution was stirred for an additional 20 min until the full conversion of starting **1^F** into the complex **1^{FLi}** (ν_{CO} 1902.5 (s), 1833.0 cm⁻¹ (s)) was evidenced by IR spectroscopy. After removal of volatiles under vacuum, the red residue was dissolved in toluene (10 mL) and then added dropwise to a solution of NFSI (237 mg, 0.75 mmol, 1.5 equiv) in toluene (35 mL) at -80 °C to give a dark green suspension. The reaction mixture was stirred for 1 h at -80 °C, slowly warmed to -40 °C over 1 h then cooled again to -80 °C and filtered in cold through a short alumina column (2×4 cm) using dry toluene as eluent. The solvent was removed under vacuum and the brown residue was purified on alumina column (2×20 cm). Elution with 2:1 CH₂Cl₂/hexane mixture afforded a yellow band containing the desired product. The solvent was evaporated under vacuum and residue was crystallized from ether/hexane mixture to afford complex **1^{F2}** (205 mg, 80% yield) as yellow crystals. ¹H NMR (400.2 MHz, C₆D₆, 25 °C): δ 6.81 (s, 4H, CH_{Mes}), 3.94 (s, 5H, Cp), 2.11 (s, 6H, CH_{3 p-Mes}), 2.10 (s, 12H, CH_{3 o-Mes}); ¹⁹F{¹H} NMR (376.5 MHz, C₆D₆, 25 °C): δ -156.5 (s) (C_{Im-4,5-F}); ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 25 °C): δ 233.7 (s, Mn-CO), 198.1 (t, ³J_{CF} = 13.6 Hz, Mn-CN₂), 140.0 (s, C_{p-Mes}), 137.2 (s, C_{o-Mes}), 132.6 (s, C_{i-Mes}), 129.8 (s, CH_{Mes}), 129.3 (dd overlapped with C₆D₆ signal, ¹J_{CF} = 258.4 Hz, ²J_{CF} = 17.7 Hz, C_{Im-4,5-F}), 81.6 (s, Cp), 21.2 (s, CH_{3 p-Mes}), 18.3 (s, CH_{3 o-Mes}). IR (toluene): ν_{CO} 1920.5 (s), 1854.0 cm⁻¹ (s). Anal. Found: C, 65.05; H, 5.30; N, 5.37. Calcd. for C₂₈H₂₇F₂N₂O₂Mn: C, 65.12; H, 5.27; N, 5.47.

Synthesis of IMes^F·HOTf. Triflic acid (53 μ L, 0.6 mmol, 1.5 equiv) was added dropwise to a yellow solution of complex **1^F** (200 mg, 0.4 mmol) in CH₂Cl₂ (10 mL) at -40 °C. The resulting brown solution was warmed to room temperature, filtered through a short pad of Celite and the filter was washed with additional CH₂Cl₂ (15 mL). The volatiles were removed under vacuum and the crude product was purified by chromatography on silica gel (2×15 cm). Elution with CH₂Cl₂ afforded several yellow-brown bands containing some cymantrene and unidentified impurities, followed by the product **IMes^F·HOTf** which was finally eluted with 10:1 CH₂Cl₂/acetone mixture. The eluate was evaporated under vacuum and the product was washed with Et₂O (3×5 mL) and dried under vacuum to give **IMes^F·HOTf** (180 mg, 95%) as a white powder. ¹H NMR (400.2 MHz, CDCl₃, 25 °C): δ 9.42 (t, ⁴J_{HH} = ⁴J_{FH} = 1.8 Hz, 1H, N₂CH), 7.28 (dd, ³J_{FH} = 6.2 Hz, ⁴J_{HH} = 1.8 Hz, CH_{Im-5}), 7.06 (s, 2H, CH_{Mes}), 7.01 (s, 2H, CH_{Mes}), 2.36 (s, 3H, CH_{3 p-Mes}), 2.34 (s, 3H, CH_{3 p-Mes}), 2.16 (s, 6H, CH_{3 o-Mes}), 2.14 (s, 6H, CH_{3 o-Mes}); ¹⁹F{¹H} NMR (376.5 MHz, CDCl₃, 25 °C): δ -79.0 (s, CF₃SO₃⁻), -141.8 (C_{Im-4-F}); ¹³C{¹H} NMR (100.6 MHz, CDCl₃, 25 °C): δ 146.7 (d, ¹J_{CF} = 271.7 Hz, C_{Im-4-F}), 142.5, 142.0 (s, C_{p-Mes}), 134.9 (s, C_{o-Mes}), 134.2 (d, ³J_{CF} = 4.2 Hz, N₂CH), 134.1 (s, C_{o-Mes}), 130.7 (s, C_{i-Mes}), 130.2, 130.1 (s, CH_{Mes}), 125.5 (s, C_{i-Mes}), 120.5 (q, ¹J_{CF} = 320.5 Hz, CF₃SO₃⁻), 104.3 (d, ²J_{CF} = 19.6 Hz, CH_{Im-5}), 21.3, 21.25 (s,

CH_{3 p-Mes}), 17.5, 17.3 (s, CH_{3 o-Mes}). Anal. Found: C, 55.85; H, 4.77; N, 5.52; Calcd. for C₂₂H₂₄F₄N₂O₃S: C, 55.92; H, 5.12; N, 5.93.

Synthesis of IMes^{F2}·HOTf. Triflic acid (15 μ L, 0.225 mmol, 1.5 equiv) was added dropwise to a yellow solution of complex **1^{F2}** (80 mg, 0.15 mmol) in CH₂Cl₂ (8 mL) at -40 °C. The resulting brown solution was warmed to room temperature, filtered through a short pad of Celite and the filter was washed with CH₂Cl₂ (15 mL). The solvent was removed under vacuum and the solid residue was purified by chromatography on silica column (2×15 cm). Elution with CH₂Cl₂ afforded several yellow-brown bands containing some cymantrene and unidentified impurities, followed by the target product **IMes^{F2}·HOTf**, which was finally eluted with 10:1 CH₂Cl₂/acetone mixture. Solvents were removed from the eluate under vacuum and the residue was washed with Et₂O (3×5 mL). The solvent was removed under vacuum to give **IMes^{F2}·HOTf** (55 mg, 75%) as a white powder. ¹H NMR (400.2 MHz, CDCl₃, 25 °C): δ 9.73 (t, ⁴J_{FH} = 2.2 Hz, 1H, N₂CH), 7.10 (s, 4H, CH_{Mes}), 2.38 (s, 6H, CH_{3 p-Mes}), 2.22 (s, 12H, CH_{3 o-Mes}); ¹⁹F{¹H} NMR (376.5 MHz, CDCl₃, 25 °C): δ -79.0 (s, CF₃SO₃⁻), -154.4 (C_{Im-4,5-F}); ¹³C{¹H} NMR (100.6 MHz, CDCl₃, 25 °C): δ 143.1 (s, C_{p-Mes}), 134.9 (s, C_{o-Mes}), 130.4 (s, CH_{Mes}), 128.3 (t, ³J_{CF} = 4.9 Hz, N₂CH), 128.3 (dd, ¹J_{CF} = 269.4 Hz, ²J_{CF} = 15.3 Hz, C_{Im-4,5-F}), 125.6 (s, C_{i-Mes}), 120.5 (q, ¹J_{CF} = 320.5 Hz, CF₃SO₃⁻), 21.4 (s, CH_{3 p-Mes}), 17.6 (s, CH_{3 o-Mes}). Anal. Found: C, 54.04; H, 4.73; N, 5.58. Calcd. for C₂₂H₂₃F₅N₂O₃S: C, 53.87; H, 4.73; N, 5.71.

Synthesis of [Rh(cod)Cl(IMes^F)] (2^F). A 0.5 M solution of KHMDS (0.44 mL, 0.22 mmol, 1.1 equiv) in toluene was added dropwise to a suspension of **IMes^F·HOTf** (95 mg, 0.2 mmol) in THF (3 mL) at -40 °C. The resulting brown solution of the carbene **IMes^F** was stirred for 15 min at this temperature then solid [RhCl(cod)]₂ (49.3 mg, 0.1 mmol, 0.5 equiv) was added in one portion. The reaction mixture was slowly warmed to room temperature over a 2 h period of time. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (1×10 cm). Elution with toluene afforded a yellow band containing traces of unreacted complex [RhCl(cod)]₂, followed by a yellow-orange band of the product that was eluted with 10:1 toluene/THF mixture. The eluate was evaporated under vacuum to afford complex **2^F** (100 mg, 88% yield) as yellow powder. Single crystals of **2^F** suitable for an X-ray diffraction study were obtained by crystallization from Et₂O/hexane mixture at room temperature. ¹H NMR (400.2 MHz, CDCl₃, 25 °C): δ 7.07 (s, 1H, CH_{Mes}), 7.06 (s, 1H, CH_{Mes}), 7.03 (s, 1H, CH_{Mes}), 6.99 (s, 1H, CH_{Mes}), 6.59 (d, ³J_{FH} = 6.7 Hz, 1H, CH_{Im-5}), 4.53 (br s, 2H, CH_{cod}), 3.29 (br s, 2H, CH_{cod}), 2.16 (s, 3H, CH_{3 p-Mes}), 2.44 (s, 3H, CH_{3 o-Mes}), 2.43 (s, 3H, CH_{3 o-Mes}), 2.385 (s, 3H, CH_{3 p-Mes}), 2.375 (s, 3H, CH_{3 p-Mes}), 2.17 (s, 3H, CH_{3 o-Mes}), 2.13 (s, 3H, CH_{3 o-Mes}), 1.93–1.75 (m, 4H, CH_{2 cod}), 1.62–1.48 (m, 4H, CH_{2 cod}); ¹⁹F{¹H} NMR (376.5 MHz, CDCl₃, 25 °C): δ -147.3 (s) (C_{Im-4-F}); ¹³C{¹H} NMR (100.6 MHz, CDCl₃, 25 °C): δ 180.5 (dd, ¹J_{CRh} = 53.3 Hz, ³J_{CF} = 12.8 Hz, Rh-CN₂), 149.0 (d, ¹J_{CF} = 265.9 Hz, C_{Im-4-F}), 139.6, 139.1 (s, C_{p-Mes}), 138.4, 137.6 (s, C_{o-Mes}), 136.4 (s, C_{ipso-Mes}), 135.2, 134.4 (s, C_{o-Mes}), 130.9 (s, C_{i-Mes}), 129.9, 128.3 (s, CH_{Mes}), 102.2 (d, ²J_{CF} = 22.6 Hz, CH_{Im-5}), 96.8 (d, ¹J_{CRh} = 7.0 Hz, CH_{cod}), 96.5 (d, ¹J_{CRh} = 6.9 Hz, CH_{cod}), 68.4 (d, ¹J_{CRh} = 14.2 Hz, CH_{cod}), 68.0 (d, ¹J_{CRh} = 14.2 Hz, CH_{cod}),

32.9, 32.6, 28.6, 28.3 (s, CH_{2cod}), 21.3, 21.2 (CH_3 *p*-Mes), 19.8, 18.2 (br s, CH_3 *o*-Mes). Anal. Found: C, 61.19; H, 6.28; N, 4.88. Calcd. for $C_{29}H_{35}FCIN_2Rh$: C 61.22; H 6.20; N 4.92.

Synthesis of $[Rh(cod)Cl(IMes^{F2})]$ (2^{F2}). A 0.5 M solution of KHMDS (0.24 mL, 0.12 mmol) in toluene was added dropwise to the suspension of $IMes^{F2}$ -HOTf (50 mg, 0.1 mmol) in THF (3 mL) at $-40^\circ C$. The resulting brown solution of the carbene $IMes^{F2}$ was stirred for 15 min at this temperature then solid $[RhCl(cod)]_2$ (25 mg, 0.05 mmol, 0.5 equiv) was added in one portion. The reaction mixture was slowly warmed to room temperature over a 2 h period of time. The solvent was removed under vacuum and the residue was purified by column chromatography on silica (1×10 cm). Elution with toluene afforded a yellow band containing traces of unreacted complex $[RhCl(cod)]_2$, followed by a yellow-orange band of the product that was eluted with 10:1 toluene/THF mixture. The eluate was evaporated under vacuum to afford complex 2^{F2} (40 mg, 70% yield) as yellow powder. 1H NMR (400.2 MHz, $CDCl_3$, $25^\circ C$): δ 7.09 (s, 2H, CH_{Mes}), 7.03 (s, 2H, CH_{Mes}), 4.59–4.52 (m, 2H, CH_{cod}), 3.32–3.24 (m, 2H, CH_{cod}), 2.45 (br s, 6H, CH_3 *o*-Mes), 2.39 (s, 3H, CH_3 *p*-Mes), 2.16 (br s, 6H, CH_3 *o*-Mes), 1.92–1.75 (m, 4H, CH_{2cod}), 1.62–1.50 (m, 4H, CH_{2cod}); $^{19}F\{^1H\}$ NMR (376.5 MHz, $CDCl_3$, $25^\circ C$): δ –158.0 (s) ($C_{Im-4,5-F}$); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, $25^\circ C$): δ 173.3 (dt, $^1J_{CRh} = 54.2$ Hz, $^3J_{CF} = 14.6$ Hz, Rh– CN_2), 140.1 (s, C *p*-Mes), 138.5, 135.3 (s, C *o*-Mes), 131.0 (s, C *i*-Mes), 130.1 (s, CH_{Mes}), 129.1 (dd, $^1J_{CF} = 261.4$ Hz, $^2J_{CF} = 18.8$ Hz, $C_{Im-4,5-F}$), 128.4 (s, CH_{Mes}), 97.1 (d, $^1J_{CRh} = 7.5$ Hz, CH_{cod}), 96.5 (d, $^1J_{CRh} = 6.9$ Hz, CH_{cod}), 68.6 (d, $^1J_{CRh} = 14.2$ Hz, CH_{cod}), 32.8, 28.5, 21.4 (CH_3 Mes), 19.9, 32.6, 28.6, 28.3 (s, CH_{2cod}), 19.8, 18.2 (br s, CH_{2cod}). HRMS (ESI, positive mode): m/z 551.1750. Calculated for $C_{29}H_{34}F_2N_2O^{103}Rh^+$ ($M^+ - Cl$): 551.1740. The complex 4^{F2} was assessed to be >95% pure by 1H , ^{19}F and ^{13}C NMR spectroscopy with main impurity being residual *n*-hexane.

Synthesis of $[Rh(CO)_2Cl(IMes^F)]$ (3^F). Gaseous CO was bubbled slowly through a solution of complex 2^F (60 mg, 0.1 mmol) in CH_2Cl_2 (2 mL) under stirring for ca. 15 min. The solution was further stirred for 30 min, filtered through Celite, and evaporated to dryness. The residue was washed with hexane at $-80^\circ C$ and dried under vacuum to afford complex 3^F (48 mg, 95% yield) as a white powder. 1H NMR (400.2 MHz, $CDCl_3$, $25^\circ C$): δ 7.04 (s, 2H, CH_{Mes}), 7.01 (s, 2H, CH_{Mes}), 6.76 (d, $^3J_{FH} = 6.7$ Hz, 1H, CH_{Im-5}), 2.38 (s, 3H, CH_3 *p*-Mes), 2.37 (s, 3H, CH_3 *p*-Mes), 2.26 (s, 6H, CH_3 *o*-Mes), 2.25 (s, 6H, CH_3 *o*-Mes); $^{19}F\{^1H\}$ NMR (376.5 MHz, $CDCl_3$, $25^\circ C$): δ –145.9 (s) (C_{Im-4-F}); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, $25^\circ C$): δ 184.8 (d, $^1J_{CRh} = 54.6$ Hz, Rh–CO), 182.7 (d, $^1J_{CRh} = 73.9$ Hz, Rh–CO), 174.0 (dd, $^1J_{CRh} = 45.8$ Hz, $^3J_{CF} = 11.5$ Hz, Rh– CN_2), 148.9 (d, $^1J_{CF} = 267.1$ Hz, C_{Im-4-F}), 140.4, 139.9 (s, C *p*-Mes), 138.4, 137.6 (s, C *o*-Mes), 136.1 (s, C *o*-Mes), 135.5 (s, C *i*-Mes), 135.3 (s, C *o*-Mes), 129.9 (s, C *i*-Mes), 129.6, 129.55 (s, CH_{Mes}), 102.7 (d, $^2J_{CF} = 22.1$ Hz, CH_{Im-5}), 21.4, 21.35 (CH_3 *p*-Mes), 19.0, 18.55 (s, CH_3 *o*-Mes). IR (CH_2Cl_2): ν_{CO} 2081.5 (s), 1998.5 cm^{-1} (s). HRMS (ESI, positive mode): m/z 494.1124. Calculated for $C_{24}H_{26}FN_3O^{103}Rh^+$ ($M^+ - Cl - CO + MeCN$): 494.1109. The complex 5^F was assessed to be pure by 1H , ^{19}F and ^{13}C NMR spectroscopy with main impurity being silicon grease.

Synthesis of $[Rh(CO)_2Cl(IMes^{F2})]$ (3^{F2}). Gaseous CO was bubbled slowly through a solution of complex 2^{F2} (20 mg, 0.03 mmol) in CH_2Cl_2 (2 mL) under stirring for ca. 15 min. The solution was further stirred for 30 min, filtered through Celite, and evaporated to dryness to afford complex 3^{F2} (14 mg, 93%) as a white powder. 1H NMR (400.2 MHz, $CDCl_3$, $25^\circ C$): δ 7.04 (s, 4H, CH_{Mes}), 2.38 (s, 6H, CH_3 *p*-Mes), 2.27 (s, 12H, CH_3 *p*-Mes); $^{19}F\{^1H\}$ NMR (376.5 MHz, $CDCl_3$, $25^\circ C$): δ –156.8 (s) (C_{Im-4-F}); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, $25^\circ C$): δ 184.5 (d, $^1J_{CRh} = 55.1$ Hz, Rh–CO), 182.5 (d, $^1J_{CRh} = 74.1$ Hz, Rh–CO), 140.8 (s, C *p*-Mes), 136.1 (s, C *o*-Mes), 130.2 (s, C *ipso*-Mes), 129.7 (s, CH_{Mes}), 129.3 (dd, $^1J_{CF} = 263.6$ Hz, $^2J_{CF} = 18.0$ Hz, $C_{Im-4,5-F}$), 29.9, 21.4, 18.5 (CH_3 Mes). Carbene signal was not detected due to its expected multiplicity (td) and insufficient sample concentration. IR (CH_2Cl_2): ν_{CO} 2084.0 (s), 2001.0 cm^{-1} (s). HRMS (ESI, positive mode): m/z 512.1054. Calculated for $C_{24}H_{25}F_2N_3O^{103}Rh^+$ ($M^+ - Cl - CO + MeCN$): 512.1015. The complex 5^{F2} was assessed to be >95% pure by 1H and ^{19}F NMR spectroscopy and gradually decomposed at room temperature during the acquisition of its ^{13}C NMR spectrum.

Synthesis of $IMes^F=Se$ (4^F). A 0.5 M solution of KHMDS (0.4 mL, 0.2 mmol, 1.15 equiv) in toluene was added dropwise to the suspension of $IMes^F$ -HOTf (80 mg, 0.17 mmol) in THF (4 mL) at $-40^\circ C$. The resulting solution was stirred for 15 min and then solid selenium (16 mg, 0.2 mmol, 1.15 equiv) was added in one portion. The reaction mixture was warmed to room temperature and stirred overnight. The solvent was removed under vacuum and the solid residue was dissolved in CH_2Cl_2 (2 mL) and filtered through a short pad of Celite. The solvent was removed under vacuum and the crude product was purified by chromatography on silica column (1×10 cm). Elution with 4:1 CH_2Cl_2 /EtOAc mixture afforded a desired product 4^F (10 mg, 15% yield) as a white powder. 1H NMR (400.2 MHz, $CDCl_3$, $25^\circ C$): δ 7.05 (s, 2H, CH_{Mes}), 7.01 (s, 2H, CH_{Mes}), 6.58 (d, $^3J_{FH} = 5.7$ Hz, CH_{Im-5}), 2.36 (s, 3H, CH_3 *p*-Mes), 2.34 (s, 3H, CH_3 *p*-Mes), 2.18 (s, 6H, CH_3 *o*-Mes), 2.16 (s, 6H, CH_3 *o*-Mes); $^{19}F\{^1H\}$ NMR (376.5 MHz, $CDCl_3$, $25^\circ C$): δ –144.4 (C_{Im-4-F}); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, $25^\circ C$): δ 154.1 (d, $^3J_{CF} = 6.6$ Hz, $N_2C=Se$), 146.4 (d, $^1J_{CF} = 264.1$ Hz, C_{Im-4-F}), 140.5, 139.9 (s, C *p*-Mes), 136.2, 135.5 (s, C *o*-Mes), 133.9 (s, C *i*-Mes), 130.2, 130.1 (s, CH_{Mes}), 125.5 (s, C *i*-Mes), 129.7, 129.5 (s, CH_{Mes}), 98.5 (d, $^2J_{CF} = 19.8$ Hz, CH_{Im-5}), 21.45, 21.35 (s, CH_3 *p*-Mes), 18.15, 18.1 (s, CH_3 *o*-Mes); ^{77}Se NMR (114.5 MHz, acetone-*d*₆, $25^\circ C$): δ 55.3 (d, $^4J_{SeF} = 14.2$ Hz). HRMS (DCI- CH_4 , positive mode): m/z 403.1079, correct isotope pattern was observed. Calculated for $C_{21}H_{24}N_2F^{80}Se^+$ (M^{++H}): 403.1083. The compound 6^F was assessed to be >95% pure by 1H , ^{19}F and ^{13}C NMR spectroscopy.

Synthesis of $IMes^{F2}=Se$ (4^{F2}). A 0.5 M solution of KHMDS (0.31 mL, 0.156 mmol, 1.2 equiv) in toluene was added dropwise to the suspension of $IMes^{F2}$ -HOTf (60 mg, 0.13 mmol) in THF (3 mL) at $-40^\circ C$. The resulting solution was stirred for 15 min and then solid selenium (12 mg, 0.15 mmol, 1.15 equiv) was added in one portion. The reaction mixture was warmed to room temperature and stirred overnight. The solvent was removed under vacuum and the residue was dissolved in CH_2Cl_2 (2 mL) and filtered through a short pad of Celite. The solvent was removed under vacuum and crude product was purified

by chromatography on silica column (1×10 cm) using 4:1 CH₂Cl₂/EtOAc mixture to afford after solvent evaporation a desired product **4^{F2}** (10 mg, 18% yield) as a white powder. ¹H NMR (400.2 MHz, CDCl₃, 25°C): δ 7.05 (s, 4H, CH_{Mes}), 2.36 (s, 6H, CH_{3 p-Mes}), 2.20 (s, 12H, CH_{3 o-Mes}); ¹⁹F{¹H} NMR (376.5 MHz, CDCl₃, 25°C): δ -158.8 (C_{Im-4,5}-F); ¹³C{¹H} NMR (100.6 MHz, CDCl₃, 25°C): δ 148.6 (br. t, ³J_{CF} = 7.2 Hz, N₂C=Se), 140.8 (s, C_{p-Mes}), 136.3 (s, C_{o-Mes}), 129.8 (s, CH_{Mes}), 128.8 (s, C_{i-Mes}), 126.5 (dd, ¹J_{CF} = 261.6 Hz, ²J_{CF} = 15.2 Hz, C_{Im-4,5}-F), 21.5 (s, CH_{3 p-Mes}), 18.1 (s, CH_{3 o-Mes}); ⁷⁷Se NMR (114.5 MHz, acetone-*d*₆, 25°C): δ 60.9 (br. t, ⁴J_{SeF} = 16.5 Hz). HRMS (DCI-CH₄, positive mode): *m/z* 421.0995, correct isotope pattern was observed. Calculated for C₂₁H₂₃N₂F₂⁸⁰Se⁺ (M⁺+H): 421.0989. The compound **6^{F2}** was assessed to be >95% pure by ¹H, ¹⁹F and ¹³C NMR spectroscopy.

Synthesis of IMes^{Cl2}=Se (4^{Cl2}**).** A 0.5 M solution of KHMDS (0.64 mL, 0.32 mmol, 1.1 equiv) in toluene was added dropwise to a suspension of **IMes**-HCl (100 mg, 0.29 mmol) in THF (10 mL) at RT. The resulting brown solution was sonicated for 15 min and then stirred for 15 min at RT. Then CCl₄ (56 μL, 0.58 mmol) was added and the resulting dark-brown solution was stirred for 40 min at RT. The solid selenium (28 mg, 0.35 mmol) was added in one portion and the reaction mixture was stirred at room temperature overnight. The solvent was removed under vacuum and the residue was dissolved in CH₂Cl₂ (2 mL) and filtered through a short pad of Celite. The solvent was removed under vacuum and the crude product was purified by chromatography on silica column (1×10 cm) using 4:1 CH₂Cl₂/EtOAc mixture to afford after solvent evaporation the desired product **4^{Cl2}** (90 mg, 81% yield) as a white powder. ¹H NMR (400.2 MHz, CDCl₃, 25°C): δ 7.05 (s, 4H, CH_{Mes}), 2.36 (s, 6H, CH_{3 p-Mes}), 2.16 (s, 12H, CH_{3 o-Mes}); ¹³C{¹H} NMR (100.6 MHz, CDCl₃, 25°C): δ 157.8 (s, N₂C=Se), 140.5 (s, C_{p-Mes}), 136.1 (s, C_{o-Mes}), 131.4 (s, C_{i-Mes}), 129.7 (s, CH_{Mes}), 114.7 (s, C_{Im-4,5}-Cl), 21.5 (s, CH_{3 p-Mes}), 18.0 (s, CH_{3 o-Mes}); ⁷⁷Se NMR (114.5 MHz, acetone-*d*₆, 25°C): δ 114.0 (s). Anal. Found: C, 55.73; H, 4.61; N, 6.15. Calcd. for C₂₁H₂₂Cl₂N₂Se: C, 55.77; H, 4.90; N, 6.19.

Synthesis of IMes^{Cl2} HOTf. A 0.5 M solution of KHMDS (0.64 mL, 0.32 mmol) in toluene was added dropwise to the suspension of **IMes** HCl (100 mg, 0.29 mmol) in THF (10 mL) at RT. The resulting brown solution was sonicated for 15 min, stirred for 15 min at RT and then CCl₄ (56 μL, 0.58 mmol) was added. The resulting dark-brown solution was stirred for 30 min at RT and neat triflic (30 μL, 0.34 mmol) acid was added dropwise. The reaction mixture was stirred for 1 hour at RT, the solvent was removed under vacuum and the solid residue was purified by chromatography on silica gel column (1×10 cm). Elution with CH₂Cl₂ afforded several bands containing unidentified impurities followed by the target product **IMes^{Cl2} HOTf**, which was finally eluted with 10:1 CH₂Cl₂/acetone mixture. The eluate was evaporated under vacuum, the solid residue was washed with Et₂O (3×5 mL) and dried under vacuum to give **IMes^{Cl2} HOTf** (105 mg, 69%) as a white powder. ¹H NMR (400.2 MHz, CDCl₃, 25°C): δ 10.10 (s, 1H, N₂CH), 7.10 (s, 4H, CH_{Mes}), 2.39 (s, 6H, CH_{3 p-Mes}), 2.15 (s, 12H, CH_{3 o-Mes}); ¹³C{¹H} NMR (100.6 MHz, CDCl₃, 25°C): δ 142.8 (s, C_{p-Mes}), 139.4 (s, N₂CH), 134.9 (s, C_{o-Mes}), 130.3 (s, CH_{Mes}), 127.6 (s, C_{i-Mes}), 121.0

(s, C-Cl_{Im-4,5}), 21.4 (s, CH_{3 p-Mes}), 17.5 (s, CH_{3 o-Mes}). Anal. Found: C, 50.22; H, 4.25; N, 5.21. Calcd. for C₂₂H₂₃Cl₂F₃N₂O₃S: C, 50.49; H, 4.43; N, 5.35.

Synthesis of IMes HOTf. A solution of **IMes** HCl (100 mg, 0.29 mmol) in CH₂Cl₂ (10 mL) was vigorously shaken with a solution of NaOTf (78 mg, 0.44 mmol) in water (2 mL) at RT. The organic phase was separated, dried over MgSO₄ and evaporated under vacuum. The residue was washed with ether (2×10 mL) and dried under vacuum to afford **IMes** HOTf (118 mg, 90%) as a white powder showing similar ¹H and ¹³C NMR data to the previously reported in literature.²⁴ ¹H NMR (400.2 MHz, CDCl₃, 25°C): δ 9.14 (d, ⁴J_{HH} = 1.3 Hz, 1H, N₂CH), 7.57 (d, ⁴J_{HH} = 1.3 Hz, 2H, CH_{Im-4,5}), 6.98 (s, 4H, CH_{Mes}), 2.32 (s, 6H, CH_{3 p-Mes}), 2.06 (s, 12H, CH_{3 o-Mes}); ¹³C{¹H} NMR (100.6 MHz, CDCl₃, 25°C): δ 141.6 (s, C_{p-Mes}), 138.0 (s, N₂CH), 134.1 (s, C_{o-Mes}), 130.5 (s, C_{i-Mes}), 130.0 (s, CH_{Mes}), 125.1 (s, CH_{Im-4,5}), 21.2 (s, CH_{3 p-Mes}), 17.3 (s, CH_{3 o-Mes}).

X-ray diffraction study for complex **2^F.** The single-crystal X-ray diffraction data for **2^F** were collected on a Nonius Mach 3/APEX II/sealed Mo X-ray tube diffractometer at -173°C. All calculations were performed on a PC compatible computer using the WinGX system.²⁵ The structure was solved using the SIR92 program²⁶ which revealed in each instance the position of most of the non-hydrogen atoms. All the remaining non-hydrogen atoms were located by the usual combination of full matrix least-squares refinement on *F*² and difference electron density syntheses using the SHELXTL program.²⁷ Atomic scattering factors were taken from the usual tabulations. Anomalous dispersion terms for the Rh were included in Fc. All non-hydrogen atoms were allowed to vibrate anisotropically. The hydrogen atoms were set in idealized positions. The hydrogen atoms were set in idealized positions (RCH₃, C-H = 0.98 Å, U_{iso}(H) = 1.5U_{eq}(C); C(sp²)-H = 0.93 Å; U_{iso}(H) = 1.2U_{eq}(C)) and their positions refined as “riding” atoms, besides four hydrogen atoms of the coordinated diene moiety, whose positions were located from Fourier differences map and refined with the restrained C-H distance (C(sp²)-H = 0.93 Å) and isotropic thermal parameter (U_{iso}(H) = 1.2U_{eq}(C)). CCDC 1901419 contains the supplementary crystallographic data for the structure unveiled in this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational details. Optimizations of NHCs were performed in a gas phase with the Gaussian09²⁸ software utilizing B3LYP²⁹ functional and 6-31+G(d,p) basis set.³⁰ Molecular orbital analysis was performed using the Multiwfn program³¹ and the relevant n^c(σ) and 2p^c(π*) carbene orbitals for **IMes**, **IMes^F**, **IMes^{F2}** and **IMes^{Cl2}** are presented in Figure S1.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Copies of original NMR spectra for all compounds and plots of the occupied n^c(σ) and empty 2p^c(π*) orbitals for calculated **IMes^{XY}** carbenes (PDF)

Crystallographic information for complex **2^F** (CIF)

Cartesian coordinates for optimized **IMes^{XY}** carbenes (XYZ)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

We thank the Centre National de la Recherche Scientifique (CNRS, France) for a general support of this work. A.A.G. is grateful to French Embassy in Moscow for a joint PhD fellowship (Vernadski program).

REFERENCES

- (1) Hopkinson, M. N.; Richter, C.; Schedler, M.; Glorius, F. An overview of N-heterocyclic carbenes. *Nature* **2014**, *510*, 485–496.
- (2) (a) Ogba, O. M.; Warner, N. C.; O'Leary, D. J.; Grubbs, R. H. Recent advances in ruthenium-based olefin metathesis. *Chem. Soc. Rev.* **2018**, *47*, 4510–4544; (b) Froese, R. D. J.; Lombardi, C.; Pompeo, M.; Rucker, R. P.; Organ, M. G. Designing Pd–N-Heterocyclic Carbene Complexes for High Reactivity and Selectivity for Cross-Coupling Applications. *Acc. Chem. Res.* **2017**, *50*, 2244–2253; (c) Janssen-Muller, D.; Schleppehorst, C.; Glorius, F. Privileged chiral N-heterocyclic carbene ligands for asymmetric transition-metal catalysis. *Chem. Soc. Rev.* **2017**, *46*, 4845–4854; (d) Melaimi, M.; Jazzar, R.; Soleilhavoup, M.; Bertrand, G. Cyclic (Alkyl)(amino)carbenes (CAACs): Recent Developments. *Angew. Chem. Int. Ed.* **2017**, *56*, 10046–10068.
- (3) (a) Huynh, H. V. Electronic Properties of N-Heterocyclic Carbenes and Their Experimental Determination. *Chem. Rev.* **2018**, *118*, 9457–9492; (b) Gomez-Suarez, A.; Nelson, D. J.; Nolan, S. P. Quantifying and understanding the steric properties of N-heterocyclic carbenes. *Chem. Commun.* **2017**, *53*, 2650–2660.
- (4) (a) Peris, E. Smart N-Heterocyclic Carbene Ligands in Catalysis. *Chem. Rev.* **2018**, *118*, 9988–10031; (b) Gaillard, S.; Renaud, J.-L. When phosphorus and NHC (N-heterocyclic carbene) meet each other. *Dalton Trans.* **2013**, *42*, 7255–7270; (c) Nasr, A.; Winkler, A.; Tamm, M. Anionic N-heterocyclic carbenes: Synthesis, coordination chemistry and applications in homogeneous catalysis. *Coord. Chem. Rev.* **2016**, *316*, 68–124.
- (5) (a) Arduengo, A. J.; Davidson, F.; Dias, H. V. R.; Goerlich, J. R.; Khasnis, D.; Marshall, W. J.; Prakasha, T. K. An Air Stable Carbene and Mixed Carbene “Dimers”. *J. Am. Chem. Soc.* **1997**, *119*, 12742–12749; (b) Arduengo, A. J.; Krafczyk, R.; Schmutzler, R.; Craig, H. A.; Goerlich, J. R.; Marshall, W. J.; Unverzagt, M. Imidazolylidenes, imidazolynilidene and imidazolidines. *Tetrahedron* **1999**, *55*, 14523–14534; (c) Cole, M. L.; Jones, C.; Junk, P. C. Studies of the reactivity of N-heterocyclic carbenes with halogen and halide sources. *New J. Chem.* **2002**, *26*, 1296–1303; (d) Furfari, S. K.; Gyton, M. R.; Twycross, D.; Cole, M. L. Air stable NHCs: a study of stereoelectronics and metallorganic catalytic activity. *Chem. Commun.* **2015**, *51*, 74–76.
- (6) Sandford, G. Perfluoroalkanes. *Tetrahedron* **2003**, *59*, 437–454.
- (7) Kenji, A.; Masato, O.; Sensuke, O. Fluorine-substituted nitrogen-containing heterocyclic compound, and the method for producing the same. *Patent JP 2018145183* 2018-09-20.
- (8) (a) Vivancos, A.; Segarra, C.; Albrecht, M. Mesoionic and Related Less Heteroatom-Stabilized N-Heterocyclic Carbene Complexes: Synthesis, Catalysis, and Other Applications. *Chem. Rev.* **2018**, *118*, 9493–9586; (b) Crabtree, R. H. Abnormal, mesoionic and remote N-heterocyclic carbene complexes. *Coord. Chem. Rev.* **2013**, *257*, 755–766.
- (9) Electrophilic fluorination of silver complexes bearing six-membered mesoionic isoquinolin-4-ylidene ligands has been reported: Liu, Q.; Yuan, Z.; Wang, H.; Li, Y.; Wu, Y.; Xu, T.; Leng, X.; Chen, P.; Guo, Y.; Lin, Z.; Liu, G. Abnormal Mesoionic Carbene Silver Complex: Synthesis, Reactivity, and Mechanistic Insight on Oxidative Fluorination. *ACS Catal.* **2015**, *5*, 6732–6737.
- (10) (a) Grineva, A. A.; Valyaev, D. A.; César, V.; Filippov, O. A.; Khrustalev, V. N.; Nefedov, S. E.; Lugan, N. Oxidative Coupling of Anionic Abnormal N-Heterocyclic Carbenes: Efficient Access to Janus-Type 4,4'-Bis(2H-imidazol-2-ylidene)s. *Angew. Chem. Int. Ed.* **2018**, *57*, 7986–7991; (b) Valyaev, D. A.; Uvarova, M. A.; Grineva, A. A.; César, V.; Nefedov, S. N.; Lugan, N. Post-coordination backbone functionalization of an imidazol-2-ylidene and its application to synthesize heteropolymetallic complexes incorporating the ambidentate IMesCO₂ ligand. *Dalton Trans.* **2016**, *45*, 11953–11957.
- (11) Wang, Y.; Xie, Y.; Abraham, M. Y.; Wei, P.; Schaefer, H. F.; Schleyer, P. v. R.; Robinson, G. H. A Viable Anionic N-Heterocyclic Dicarbene. *J. Am. Chem. Soc.* **2010**, *132*, 14370–14372.
- (12) (a) Waters, J. B.; Goicoechea, J. M. Coordination chemistry of ditopic carbanionic N-heterocyclic carbenes. *Coord. Chem. Rev.* **2015**, *293–294*, 80–94; (b) Uzelac, M.; Hevia, E. Polar organometallic strategies for regioselective C–H metallation of N-heterocyclic carbenes. *Chem. Commun.* **2018**, *54*, 2455–2462.
- (13) (a) Solovyev, A.; Lacôte, E.; Curran, D. P. Ring Lithiation and Functionalization of Imidazol-2-ylidene-boranes. *Org. Lett.* **2011**, *13*, 6042–6045; (b) Vogt, M.; Wu, C.; Oliver, A. G.; Meyer, C. J.; Schneider, W. F.; Ashfeld, B. L. Site specific carboxylation of abnormal anionic N-heterocyclic dicarbenes with CO₂. *Chem. Commun.* **2013**, *49*, 11527–11529; (c) Fukaya, N.; Mizusaki, T.; Hatakeyama, K.; Seo, Y.; Inaba, Y.; Matsumoto, K.; Lee, V. Y.; Takagi, Y.; Kuwabara, J.; Kanbara, T.; Choe, Y.-K.; Choi, J.-C. [Pd(4-R₃Si-IPr)(allyl)Cl], a Family of Silyl-Substituted Pd–NHC Complexes: Catalytic Systems for the Buchwald–Hartwig Amination. *Organometallics* **2018**, *38*, 375–384.
- (14) Baudoux, J.; Cahard, D. Electrophilic fluorination with N–F reagents. *Org. React.* **2007**, *69*, 347–672.
- (15) Noteworthy, the reaction between free IMes and NFSI only led to intractable mixture of products.
- (16) Evans, P. A.; Baum, E. W.; Fazal, A. N.; Pink, M. Diastereoselective metal-catalyzed [4+2+2] carbocyclization reactions utilizing a rhodium N-heterocyclic carbene (NHC) complex: the first example of a rhodium NHC-catalyzed [m+n+0] carbocyclization. *Chem. Commun.* **2005**, 63–65.
- (17) Gusev, D. G. Electronic and Steric Parameters of 76 N-Heterocyclic Carbenes in Ni(CO)₃(NHC). *Organometallics* **2009**, *28*, 6458–6461.
- (18) Verlinden, K.; Buhl, H.; Frank, W.; Ganter, C. Determining the Ligand Properties of N-Heterocyclic Carbenes from ⁷⁷Se NMR Parameters. *Eur. J. Inorg. Chem.* **2015**, 2416–2425.
- (19) (a) Liske, A.; Verlinden, K.; Buhl, H.; Schaper, K.; Ganter, C. Determining the π-Acceptor Properties of N-Heterocyclic Carbenes by Measuring the ⁷⁷Se NMR Chemical Shifts of Their Selenium Adducts. *Organometallics* **2013**, *32*, 5269–5272; (b) Vummaleti, S. V. C.; Nelson, D. J.; Poater, A.; Gomez-Suarez, A.; Cordes, D. B.; Slawin, A. M. Z.; Nolan, S. P.; Cavallo, L. What can NMR spectroscopy of selenoureas and phosphinidenes teach us about the π-accepting abilities of N-heterocyclic carbenes? *Chem. Sci.* **2015**, *6*, 1895–1904.
- (20) Ruamps, M.; Lugan, N.; César, V. A Cationic N-Heterocyclic Carbene Containing an Ammonium Moiety. *Organometallics* **2017**, *36*, 1049–1055.
- (21) Giordano, G.; Crabtree, R. H. Di-μ-chloro-bis(η⁴-1,5-cyclooctadiene)dirhodium(I). *Inorg. Synth.* **1990**, *28*, 88–90.
- (22) Hintermann, L. Expedient syntheses of the N-heterocyclic carbene precursor imidazolium salts IPr·HCl, IMes·HCl and IXy·HCl. *Beilstein J. Org. Chem.* **2007**, *3*, DOI:10.1186/1860-5397-3-22.

- (23) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010**, *29*, 2176–2179.
- (24) Kim, J. H.; Jo, K. A. Son, Y. H.; Park, S. R.; Ahn, K.-H.; Kang, E. J. Structural Elucidation and Characterization of N-Heterocyclic Salts with Various Anions. *Bull. Korean Chem. Soc.* **2009**, 2464–2466.
- (25) Farrugia, L. J. WinGX and ORTEP for Windows: an update. *J. Appl. Cryst.* **2012**, *45*, 849–854.
- (26) Altomare, A.; Casciarano, G.; Giacovazzo, C.; Guagliardi, A. SIR92 – a program for automatic solution of crystal structures by direct methods. *J. Appl. Crystallogr.* **1994**, *27*, 435–436.
- (27) Sheldrick, G. M. A short history of SHELX. *Acta Crystallogr.* **2008**, *A64*, 112.
- (28) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Rob, M. A.; Cheeseman, J. R.; Jr, J.A.M.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 09, Revision D.01*, Gaussian, Inc., Wallingford, CT, **2009**.
- (29) (a) Becke, A. D. Density-Functional Thermochemistry. The Role of Exact Exchange, *J. Chem. Phys.* **1993**, *98*, 5648–5652; (b) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. Ab-Initio Calculation of Vibrational Absorption and Circular-Dichroism Spectra Using Density-Functional Force-Fields. *J. Phys. Chem.* **1994**, *98*, 11623–11627.
- (30) (a) Hehre, W. J.; Ditchfield, R.; Pople, J. A. Self-Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian - Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules. *J. Chem. Phys.* **1972**, *56*, 2257–2261; (b) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. V. R. Efficient diffuse function-augmented basis sets for anion calculations. III. The 3-21+G basis set for first-row elements, Li–F. *J. Comput. Chem.* **1983**, *4*, 294–301; (c) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. Self-consistent molecular orbital methods. XXIII. A polarization-type basis set for second-row elements. *J. Chem. Phys.* **1982**, *77*, 3654–3665; (d) Frisch, M. J.; Pople, J. A.; Binkley, J. S. Self-consistent molecular orbital methods 25. Supplementary functions for Gaussian basis sets. *J. Chem. Phys.* **1984**, *80*, 3265–3269.
- (31) Lu, T.; Chen, F. Multiwfn: a multifunctional wavefunction analyzer. *J. Comput. Chem.* **2012**, *33*, 580–592.
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