

# Transition Metal Complexes of NHC Ligands Functionalized with the Cationic ( $\eta^5$ -Cyclopentadienyl)( $\eta^6$ -phenyl)iron(II) Motif

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Starting from [( $\eta^5$ -cyclopentadienyl)( $\eta^6$ -phenyl)iron(II)]imidazole, dicationic imidazolium salts were prepared by *N*-alkylation. Reaction of these compounds with basic metal precursors such as mesityl copper(I) or palladium(II) acetate led to mono respectively dicationic transition metal NHC complexes (NHC = *N*-heterocyclic carbene). Transmetalation using the copper(I) complexes opened up the access to NHC gold(I) compounds. PEPPSI-type NHC complexes of palladium(II) and platinum(II) were prepared by offering a neutral pyridine ligand to the transition metal center. A rhodium(I) NHC complex was accessible by deprotonation of the dicationic imidazolium precursor and subsequent treatment with [(COD)Rh( $\mu^2$ -Cl)]<sub>2</sub>

(COD = 1,5-cyclooctadiene). The new NHC complexes were investigated by means of NMR spectroscopy, mass spectrometry as well as single crystal X-ray structure analysis. Both, the palladium(II) containing PEPPSI-type and the gold(I) complex, were investigated for their catalytic properties in typical model reactions such as cyclization reactions, Suzuki coupling and cyanation. In addition, a selenium adduct was synthesized in order to study the electronic properties of the underlying ligand backbone. Based on the chemical shift in the <sup>77</sup>Se NMR spectrum, it is evident that these NHC ligands possess rather poor  $\pi$ -acidity.

## Introduction

The origins of research on NHC ligands date back to the work of Öfele and Wanzlick in the late 1960s.<sup>[1]</sup> After their pioneering results, Arduengo set another landmark for the understanding of NHCs with the isolation of the first free carbene in 1991.<sup>[2]</sup> A great variety of catalytically relevant NHC metal complexes were developed in the following years.<sup>[3]</sup> To date, numerous applications in catalysis have been reported for miscellaneous metal NHC complexes. Out of them, in particular cross-coupling reactions,<sup>[4]</sup> aminations,<sup>[5]</sup> C–H activation,<sup>[6]</sup> cyclization<sup>[7]</sup> and cyanation reactions<sup>[8]</sup> are worth mentioning. The complexes employed herein are preferentially based on the imidazole structure. However, a series of triazole and pyrazole derived ligands have also been reported.<sup>[1b,9]</sup> The apparent similarity of NHC to certain phosphine complexes in terms of electronic properties can be taken as a

roadmap in this context.<sup>[1b]</sup> In the course of the research on NHCs, one major aim was to find a convenient alternative to the handling of the generally sensitive free carbenes, obtained by deprotonation of the underlying imidazolium or triazolium salts. To date, the use of silver(I) NHC complexes for the exploitation of miscellaneous transition metal complexes by transmetalation is a common strategy, as reported for example for the reaction with chloro(dimethylsulfide)gold(I) or chloro(tetrahydrothiophene)gold(I).<sup>[10]</sup> This technique has been proven to provide access to ruthenium, rhodium, iridium, and palladium complexes as well.<sup>[11]</sup> Its major benefit is drawn from the superior stability of the silver(I) NHC complexes against air and moisture in comparison to the free carbene.<sup>[12]</sup> However, copper(I) NHC complexes are also suitable intermediates, which can be converted to the desired complexes by transmetalation reactions.<sup>[13]</sup>

In the broad community of *N*-heterocyclic carbenes, there are also some cationic representatives. Most commonly the positive charge is localized on a functional group, while there are only few examples that feature an organometallic backbone causing the positive charge.<sup>[14]</sup> By expectation, these ought to be electron-poor NHCs. In order to properly evaluate the electronic properties of NHCs in general, several methods have been established. Of particular significance are the well-known Tolman electronic parameter (TEP) and the studies of the <sup>31</sup>P NMR shift of phosphinidene adducts carried out by Bertrand and coworkers.<sup>[15]</sup> Also worth mentioning is a more recent approach by Ganter et al. who investigated the <sup>77</sup>Se NMR resonances of the selenium adducts of NHCs.<sup>[16]</sup> Following the example of Bertrand, they found a correlation between the shifts in the <sup>77</sup>Se NMR spectra and the  $\pi$ -back donation ability of the NHCs.<sup>[16]</sup> The simple one-pot synthesis of the selenium

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adducts and the lack of influences caused by other substituents are advantageous.

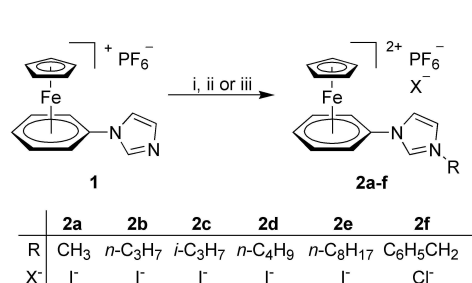
After reporting the first heterobimetallic complex based on the  $[(\eta^5\text{-cyclopentadienyl})(\eta^6\text{-diphenylphosphino-benzene})\text{iron(II)}]^+$  ligand in 2016, we were able to expand the scope of this ligand to various multinuclear transition metal complexes during the following years.<sup>[17]</sup> Beside the investigation of cationic phosphine complexes, our interest turned to imidazole-based NHC complexes possessing a  $[(\eta^6\text{-arene})(\eta^5\text{-cyclopentadienyl})\text{iron(II)}]^+$  backbone. The first reported example featured iridium(III) as second, cyclometalated nucleus and provided superior activity in the transfer hydrogenation of ketones compared to its neutral monometallic analogue.<sup>[14c,18]</sup> For this reason, it seemed to be promising to prepare further multinuclear complexes based on these novel cationic imidazolylidene ligands.

## Results and Discussion

### Syntheses

Similar to the synthetic procedure of the previously reported ligand  $(\eta^5\text{-cyclopentadienyl})(\eta^6\text{-1-phenyl-1H-imidazol})\text{iron(II)hexafluorophosphate}$  (**2a**), the nucleophilic substitution of precursor **1** with different alkyl halides led to eligible dicationic imidazolium salts that can serve as NHC precursors (Scheme 1).<sup>[19]</sup>

Alkyl iodides were used for the derivatization due to their high reactivity in substitution reactions. Only for the synthesis of the benzyl derivative, benzyl chloride was used instead. All dicationic salts **2a–f** were characterized by means of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. The NMR spectra show the expected resonances of the  $(\eta^5\text{-cyclopentadienyl})(\eta^6\text{-phenylimidazolylidene})\text{iron(II)}$  backbone and of the imidazolium ring. The aliphatic region of the  $^1\text{H}$  NMR spectra of compounds **2a–f** is dominated by the resonances of the various alkyl moieties (for further details see the Experimental Section and the Supporting Information). A major challenge in handling compounds **2a–f** is their commonly poor solubility in organic media. Spectroscopic data could only be obtained in highly polar solvents such as acetonitrile, nitromethane or dimethylsulfoxide. Likewise, the subsequent reactions can only be carried out in such solvents,



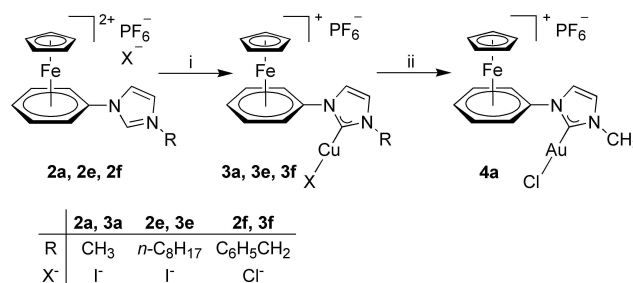
**Scheme 1.** Synthesis of the dicationic NHC precursors **2a–f**. i) RX = CH<sub>3</sub>I, CH<sub>3</sub>CN, r.t., 16 h; ii) RX = *n*-C<sub>3</sub>H<sub>7</sub>I, *i*-C<sub>3</sub>H<sub>7</sub>I, *n*-C<sub>4</sub>H<sub>9</sub>I, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>-Cl, CH<sub>3</sub>CN, 70 °C, 16 h; iii) *n*-C<sub>8</sub>H<sub>17</sub>-I, DMF, 110 °C, 16 h.

which is a limitation for certain transformations with sensitive transition metal precursors. We tried to overcome this problem by varying the alkyl moiety and thus strengthening the non-polar functionalities of the compounds ascending from the methyl (**2a**) to the octyl substituent (**2e**).

Miscellaneous representatives (**2a**, **2e** and **2f**) were allowed to react with an excess of mesityl copper(I), henceforth also abbreviated as CuMes, to afford heterobimetallic iron(II)/copper(II) complexes in good to excellent yields (Scheme 2).

First evidence for the successful synthesis of the bimetallic iron(II)/copper(II) complexes **3a**, **3e** and **3f** can be obtained directly from their  $^1\text{H}$  NMR spectra: The absence of the resonance assigned to the N–CH=N proton, observed in the spectra of the precursors **2a–f**, indicates that a deprotonation at this site has occurred. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR resonances of all other fragments of the copper complexes are observed in the expected regions. The  $^{13}\text{C}$  NMR resonances of the carbene carbon atoms are observed at 181.0 (**3a**), 182.6 (**3e**) and 179.0 ppm (**3f**) as singlets of low intensity. By  $^{31}\text{P}$  NMR spectroscopy the hexafluorophosphate counter anion is unambiguously pointed due to the presence of the typical septet. To explicitly provide evidence for the complexation of the copper(I) center, ESI mass spectrometry was carried out. The cations of **3a**, **3e** and **3f** can be identified at  $m/z = 468.84$  (calcd.  $m/z = 468.90$ )  $[\text{C}_{15}\text{H}_{15}\text{CuFeIN}_2]^+$ ,  $m/z = 566.94$  (calcd.  $m/z = 567.00$ )  $[\text{C}_{22}\text{H}_{29}\text{CuFeIN}_2]^+$  and  $m/z = 453.00$  (calcd.  $m/z = 452.99$ )  $[\text{C}_{21}\text{H}_{19}\text{ClCuFeN}_2]^+$ . All three compounds provided consistent elemental analyses.

By transmetalation, a series of other bimetallic complexes are accessible through the copper(I) NHC complexes, which behave in this context similar to silver(I) NHC complexes, which were probably employed for this purpose first by Albrecht et al.<sup>[20]</sup> As a proof of concept we chose (tht)AuCl (tht = tetrahydrothiophene) as the precursor in order to generate the heterobimetallic iron(II)/gold(I) complex **4a** (Scheme 2). Therefore, **3a** was stirred with the gold precursor in nitromethane under the exclusion of light, yielding 98% of **4a**. As expected, the pattern of the  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra of complexes **3a** and **4a** are almost identical at a first sight. However, **4a** provided better solubility in acetonitrile, which was used to measure the NMR spectra in this case. In order to prove the outcome of the transmetalation reaction, ESI mass spectrometry and elemental analysis were carried out. In addition to a fitting elemental analysis, the cation of **4a** was identified by



**Scheme 2.** Reaction of **2a**, **2e** and **2f** with mesityl copper(I) followed by transmetalation with (tht)AuCl. i) Cu(C<sub>6</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>), THF, 50 °C, 16 h; ii) (tht)AuCl, CH<sub>3</sub>CN. R.t., 16 h.

mass spectrometry at  $m/z=510.94$  (calcd.  $m/z=510.99$ ) additionally exhibiting a matching isotope pattern. Single crystal structure data could neither be obtained for the copper(I) nor for the gold(I) complexes. However, we propose heteroleptic molecular structures as shown in Scheme 2 based on the ESI mass spectrometry data. A homoleptic complex featuring two NHC units bound to the metal center and an additional dichloridoaurate(I) respectively diiodidocuprate(I) anion might also be considered in both cases. Such compounds are described considerably less frequently in the literature.<sup>[21]</sup> Nevertheless, traces of impurities in the  $^1\text{H}$  NMR spectra of the gold(I) complex **4a** can be interpreted as an indication that this form might be present, too. For the copper(I) complexes **3a**, **3e** and **3f**, dicationic dimeric structures with bridging iodides are also conceivable.<sup>[22]</sup> However, neither spectroscopic nor mass spectrometric data gave any hint for such a structure.

By treatment of the dicationic NHC precursors **2c** and **2e** with palladium(II) acetate, the square-planar, trinuclear iron(II) palladium(II) compounds **5c** and **5e** were obtained in good yields (Scheme 3).

Just as in the case of the copper complexes discussed above, the absence of the  $^1\text{H}$  NMR resonance of the imidazolium proton in the 2-position is indicative for a successful complex formation. The carbene carbon atoms can be assigned to signals at 166.1 (**5c**) and 167.1 ppm (**5e**) in the  $^{13}\text{C}$  NMR spectra. The presence of the hexafluorophosphate

counterion is evident by the typical septet at  $-144.2$  ppm in the  $^{31}\text{P}$  NMR spectrum. Matching elemental analyses and peaks at  $m/z=486.91$  (calcd.  $m/z=486.95$ ) respectively  $m/z=556.94$  (calcd.  $m/z=557.03$ ) in mass spectrometric analyses provide a further hint for the successful synthesis of the dicationic complexes. This dicationic character prevents obtaining single crystals that are suitable for X-ray diffraction. However, a single crystal X-ray structure analysis was possible, when the dicationic imidazolium salt **2a** was reacted with palladium(II) acetate in the presence of KI and pyridine as the solvent. Pyridine in this case serves as a second neutral ligand in addition to one NHC ligand.

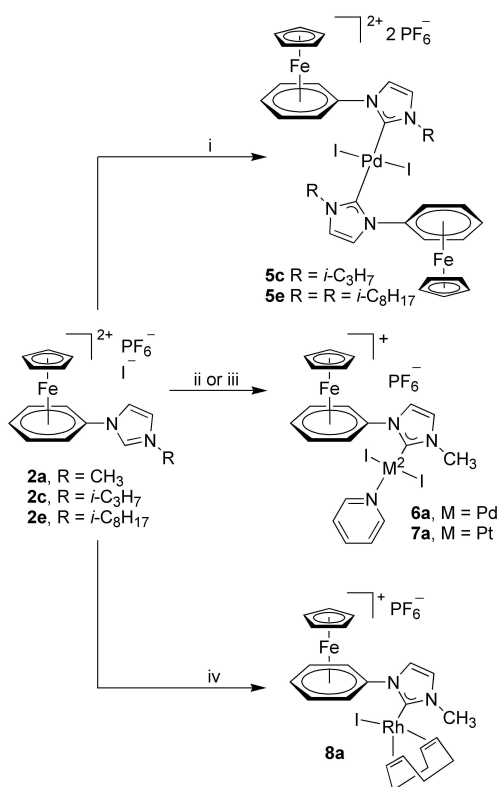
Scheme 3 also depicts the synthesis of the dinuclear iron(II)/palladium(II) complex **6a** and the structurally analogue iron(II)/platinum(II) complex **7a**, which is accessible from  $\text{PtCl}_2/\text{NaI}$  in pyridine. The reaction conditions were chosen based on complexation reactions recently published by Choudhury et al.<sup>[6b]</sup> and Bellemin-Laponnaz et al.<sup>[23]</sup> The molecular structures of **6a** and **7a** are that of so-called PEPPSI-type complexes, which gained application as catalysts in C–C coupling reactions.

Complexes **6a** and **7a** were obtained in moderate to good yields. In addition to the typical pattern of the  $(\eta^5\text{-cyclopentadienyl})(\eta^6\text{-phenylimidazolylidene})\text{iron(II)}$  backbone, the aromatic region of the  $^1\text{H}$  NMR spectra is completed by the set of signals of the pyridine ligand. The expected signals of the carbene carbon atoms in the  $^{13}\text{C}$  NMR spectra appear to be too weak in intensity to be observed. In both cases the  $^{31}\text{P}$  NMR spectra reveal the hexafluorophosphate anion. Elemental analyses and ESI mass spectrometry allow a clear distinction between the palladium(II) and the platinum(II) system. The signal at  $m/z=717.78$  (calcd.  $m/z=717.82$ ) for the cation of **6a** and the signal at  $m/z=806.81$  (calcd.  $m/z=806.87$ ) for the cation of **7a** were observed in the ESI mass spectra. Furthermore, single crystals suitable for X-Ray analysis could be obtained by slow diffusion of diethyl ether into saturated solutions of **6a** in acetonitrile and **7a** in the even more polar solvent nitromethane. The molecular structure of **7a** is included in the Supporting Information. Figure 1 exemplarily depicts the molecular structure of the bimetallic complex **6a** and summarizes typical bond parameters.

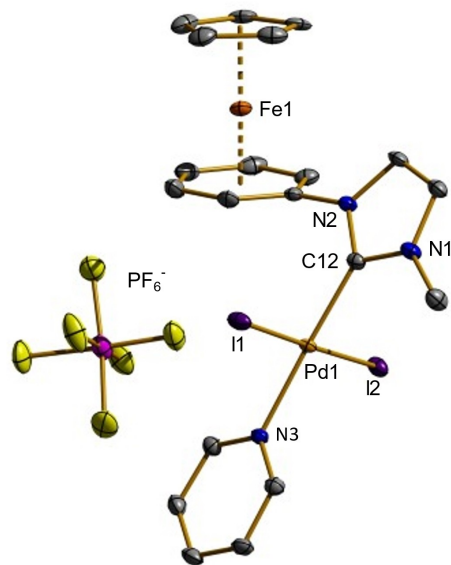
The distances between the iron(II) center and the centroids of cyclopentadienyl and arene ring are 1.6620(4) and 1.5400(3) Å, respectively. Thus, they are within the expected range in comparison to similar structures that we have preliminary obtained.<sup>[14c,17]</sup> From the bond parameters of the palladium(II) center, its square-planar coordination is evident. Slight deviations of the angles from  $90^\circ$  are a result of the spacial requirement of the nitrogen-bound methyl group at the imidazolylidene ring.

In addition, ligand **2a** could also be reacted with the dimeric rhodium(I) precursor  $[(\eta^4\text{-COD})\text{Rh}(\mu^2\text{-Cl})_2]$  (COD = 1,5-cyclooctadiene) in the presence of sodium ethanolate (see Scheme 3) according to a protocol published by Messerle et al.<sup>[24]</sup>

Again, the successful synthesis of **8a** is indicated by NMR spectroscopy. However, the  $^1\text{H}$  NMR spectrum of **8a** differs significantly from all other complexes discussed so far. Since the



**Scheme 3.** Direct formation cationic NHC complexes from ligands **2a**, **2c** or **2e**. i) **2c** or **2e**, 0.5 equiv. of  $\text{Pd}(\text{O}_2\text{CCH}_3)_2$ ,  $\text{MeNO}_2$  or THF,  $65^\circ\text{C}$ , 16 h; ii)  $\text{Pd}(\text{O}_2\text{CCH}_3)_2$ , KI, pyridine, r.t., 48 h; iii)  $\text{PtCl}_2$ ,  $\text{K}_2\text{CO}_3$ , NaI, pyridine,  $100^\circ\text{C}$ , 16 h; iv) 0.5 equiv. of  $[(\eta^4\text{-COD})\text{Rh}(\mu^2\text{-Cl})_2]$ , 2.0 equiv. of  $\text{NaOC}_2\text{H}_5$ ,  $\text{CH}_3\text{OH}$ ,  $65^\circ\text{C}$ , 1 h.



**Figure 1.** Molecular structure of the cationic PEPPSI-type complex **6a** in the solid state. The hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at 50%. Characteristic bond lengths (Å) and angles (deg): Fe1–Cp 1.6620(4), Fe1–Ar 1.5400(3), C12–Pd1 1.9657(2), Pd1–I1 2.6105(2), Pd1–I2 2.5919(2), Pd1–N3 2.0785(2), I1–Pd1–I2 178.44(9), C12–Pd1–N3 177.96(7), C12–Pd1–I1 87.74(5), C12–Pd1–I2 90.74(5), N3–Pd1–I1 91.86(4), N3–Pd1–I2 89.67(4). Cp denotes the centre of the  $\eta^5$ -coordinated cyclopentadienyl ring. Ar denotes the centre of the  $\eta^6$ -coordinated phenyl ring.

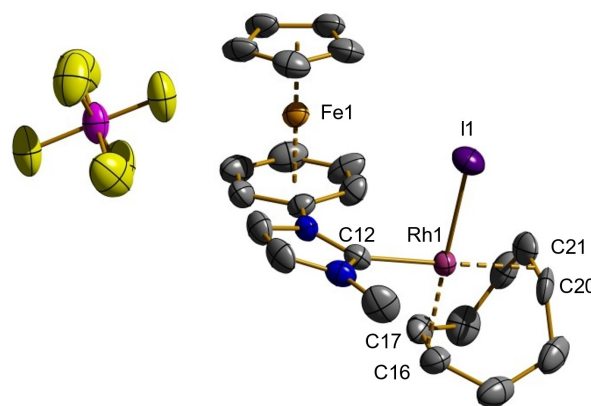
free rotation around the phenyl-nitrogen bond is restricted by the bulky chelating 1,5-cyclooctadiene ligand, all protons of the  $\eta^6$ -coordinated phenyl ring exhibit individual signals. Thereby, the signal at 9.28 ppm that is particularly shifted to lower field can be assigned to the proton, which is in the *ortho*-position of the phenyl ring facing the rhodium(I) metal center. This pronounced low-field shift might indicate a preagostic interaction with the rhodium(I) center (see discussion below). The  $^{13}\text{C}$  NMR spectrum of **8a** reveals a doublet at 183.7 ppm ( $^1J_{\text{RhC}} = 49.3$  Hz) for the carbene carbon atom, which demonstrates the coupling with the  $^{103}\text{Rh}$  nucleus. Notably, this resonance is almost in accordance with the resonance of the carbene carbon atom (183.1 ppm) of the comparable complex without the  $[(\eta^5\text{-Cp})(\eta^6\text{-phenyl})\text{Fe}]^+$  unit.<sup>[24]</sup> Furthermore, the coupling constant of both complexes are almost identically (49.3 Hz), implying that the rhodium's electronic situation is very little affected by the differences in the ligand's backbone. Some other cyclooctadiene(iodido)rhodium(I) NHC complexes that are structurally related to compound **8a** have been reported in the literature. In these cases also  $^1J_{\text{RhC}}$  coupling constants around 49.5 Hz have been measured.<sup>[25]</sup> For a more detailed discussion on the electronic situation of the cationically functionalized NHC ligands, see below. The 1,5-cyclooctadiene ligand exhibits a known set of signals in the olefinic and aliphatic region of the  $^{13}\text{C}$  NMR spectrum. The typical septet of the hexafluorophosphate anion in the  $^{31}\text{P}$  NMR spectrum indicates the existence of the non-coordinating anion. In addition, **8a** was characterized by ESI mass spectrometry. The signal at  $m/z = 616.94$  with the expected isotopic pattern is dominant and consistent with the presence of the cation of **8a** (calcd.  $m/z = 616.97$ ). Crystals suitable for a single

crystal X-ray structure analysis could be obtained by slow diffusion of diethyl ether into a saturated solution of **8a** in acetonitrile at 4 °C. The solid state structure of **8a** is depicted in Figure 2.

Distances of 1.6999(2) and 1.5512(2) Å for Fe1–Cp and Fe1–Ar respectively are comparable to the distances observed in the solid-state structures of **6a** and **7a**. The newly forged C12–Rh1 bond covers a distance of 2.043(11) Å, which is in good agreement with the findings of Messerle et al. for the carbene-rhodium(I) bond.<sup>[24]</sup> The same is true for the Rh1–C12–I1 angle that slightly deviates from the expected 90° angle of the square-planar coordination geometry. Distances from the rhodium(I) center to the cyclooctadiene carbon atoms indicate an evasion of the COD-ligand with respect to the presence of the phenyl ring in order to reduce sterical repulsion in the molecule. However, all values are within the typical range for transition metal olefin complexes.<sup>[26]</sup> One of the two *ortho*-protons of the  $\eta^6$ -coordinated arene ring is in a special situation: It is located with a distance of 2.41 Å in the axial position of the square-planar coordinated rhodium(I) center. In combination with the unusual low-field shift of its  $^1\text{H}$  NMR resonance and according to the literature, this brings us to the conclusion to describe this situation as a preagostic interaction.<sup>[27]</sup>

## Catalysis

In order to gain more information about the influence of the cationic  $[(\eta^5\text{-Cp})(\eta^6\text{-phenyl})\text{Fe}]^+$  motif on the reactivity of the transition metal centers bound to the NHC-site, we investigated a series of catalytic transformations. The heterobimetallic iron(II)/gold(I) complex **4a** was investigated in the cyclization of *N*-propargylcarboxamid to 4,5-dihydrooxazol, which is typically catalyzed by gold centers according to the literature.<sup>[28]</sup> Compound **4a** showed no catalytic activity at all. The activation of gold(I) complexes with different additives is also described in



**Figure 2.** Molecular structure of **8a** in the solid state. Hydrogen atoms and the disorder of the cyclopentadienyl ring and the hexafluorophosphate anion are omitted for clarity. Thermal ellipsoids are set at 50%. Characteristic bond lengths (Å) and angles (deg): Fe1–Cp 1.6999(2), Fe1–Ar 1.5512(2), C12–Rh1 2.043(11), Rh1–C16 2.154(13), Rh1–C17 2.137(13), Rh1–C20 2.269(10), Rh1–C21 2.252(10), Rh1–I1 2.6919(10), Rh1–C12–I1 86.0(3). Cp denotes the centre of the  $\eta^5$ -coordinated cyclopentadienyl ring. Ar denotes the centre of the  $\eta^6$ -coordinated phenyl ring.

the literature.<sup>[29]</sup> But even in the presence of 1 equiv. of silver hexafluorophosphate, catalytic activity was not observed, as it was the case for the cyclization of pent-4-en-1-ol to 2-methyl-tetrahydrofuran. The monocationic iron(II)/copper(I) complexes **3a**, **3e** and **3f** and the dicationic iron(II)/palladium(II) complexes **5c** and **5e** were not further investigated in catalysis as they are not sufficiently soluble in organic solvents. The monocationic PEPPSI-type iron(II)/palladium(II) complex **6a** was thus investigated as catalyst in the Suzuki coupling and the cyanation of aromatic compounds. In contrast to other PEPPSI-type palladium(II) complexes,<sup>[30]</sup> the rather electron-deficient palladium center in compound **6a** fails to satisfactorily perform the Suzuki coupling of phenylboronic acid with chloroaromatic compounds. We dispensed with the investigation of bromo and iodoaromatics, which are already sufficiently studied in Suzuki coupling reactions.<sup>[31]</sup> However, there are still significant issues in cyanation reactions, in particular when potassium ferrocyanide(II) is supposed to be used as the cyanide source. Originally, this strategy was established by Beller et al. to provide an alternative to the highly toxic potassium cyanide.<sup>[32]</sup> The cationic palladium(II) complex **6a** appeared to be a promising candidate, since this structural motif of a palladium-NHC complex has already been shown for this type of reaction.<sup>[33]</sup> However, no coupling of bromo- or chloroaromatics to the corresponding nitrile derivatives could be observed by applying complex **6a** as the catalyst. Preliminary tests with iodobenzenes led to a mixture of the desired cyanated product and biphenyls. Thus, this was not further investigated.

### Electronic properties

In 2013 Ganter et al. reported the correlation of the <sup>77</sup>Se NMR shift of selenium adducts with the  $\pi$ -acceptor properties of carbene ligands. We used this tool to evaluate our cationically functionalized NHC ligands.<sup>[16]</sup> Therefore, the selenium adduct **9f** derived from **2f** was synthesized as an example and investigated using <sup>77</sup>Se NMR spectroscopy (Scheme 4). The reaction conditions were chosen according to a procedure published by Nolan, Cavallo et al. and allowed access to the selenone **9f** in quantitative yield.<sup>[34]</sup>

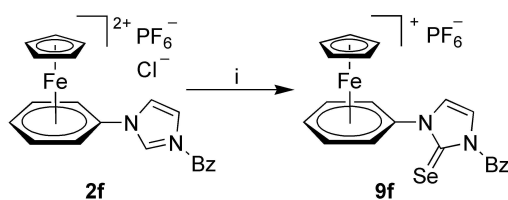
As for the <sup>1</sup>H NMR spectra of the NHC complexes discussed above, the resonance of the imidazolium proton in the 2-position that is visible in the NMR spectra of the precursor **2f** has disappeared. Furthermore, the reduced charge of compound **9f** is reflected in a general high-field shift of all resonances. While <sup>13</sup>C and <sup>31</sup>P NMR spectra exhibit the expected

set of signals, elemental analysis and mass spectrometry provide further evidence of a successful selenation reaction. The <sup>77</sup>Se NMR spectrum of **9f** recorded in acetonitrile-d<sup>3</sup> displays a singlet resonance at 77.9 ppm with respect to the KSeCN in D<sub>2</sub>O as the external standard. Taking into account that Ganter's original scale covers a chemical shift range from 87 to 856 ppm, the NHC- $\pi$ -acidity of imidazolylidene ligands with a cationic ( $\eta^5$ -cyclopentadienyl)( $\eta^6$ -phenyl)iron(II) substituent appears to be relatively low. However, it has to be mentioned at this point that Nolan, Cavallo et al. were able to cover a range of 197 to -22 ppm indicating NHC ligands with even weaker  $\pi$ -acceptor abilities than our system.<sup>[34]</sup> Roy and Mugesh reported <sup>1</sup>J<sub>SeC</sub> coupling constants of about 200–230 Hz for a series of selenones.<sup>[35]</sup> In the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of compound **9f** there are two tiny resonances at 160.1 and 158.5 ppm (mean value: 159.3 ppm, see the Supporting Information), which are close to the resonance of the carbon atom of the C–Se unit (160.9 ppm). The difference in chemical shift calculates to 233 Hz, which corresponds to the reports in the literature. However, the difference of the chemical shift (1.6 ppm) seems to be rather pronounced for isotopologues in <sup>13</sup>C NMR spectroscopy.

In combination with the <sup>1</sup>J<sub>RhC</sub> coupling constants we measured for compound **8a** (see above) the <sup>77</sup>Se NMR data reveals a rather normal electronic situation of the cationically functionalized NHC ligands, which is contrary to the results of our study with a phosphine carrying a cationic CpFe(arene) fragment bound directly to the phosphorus site.<sup>[17]</sup> We explain this by a pure electrostatic interaction between the cation and the imidazolylidene fragment. Nevertheless, there is a negative influence on the catalytic activity at least for the gold and palladium complexes studied here.

### Conclusion

Novel cationic and multinuclear complexes based on various ( $\eta^5$ -cyclopentadienyl)iron(II)( $\eta^6$ -phenylimidazolylidene) ligands could be obtained from the according imidazolium precursors with transition metal precursors of Groups IX, X and XI. Hereby, we were able to demonstrate that copper(I) carbene complexes are highly useful intermediates for transmetalation reactions paving the way for further multimetallic complexes. Investigation of the novel compounds for their catalytic activity resulted in somewhat mixed results: While no suitable application could be found for the iron(II)/gold(I) complex **4a** yet, the PEPPSI-type iron(II)/palladium(II) complex **6a** at least showed its principal ability to perform C,C-coupling reactions for iodobenzenes. Based on the information about the electronic properties of the ligand system derived from <sup>77</sup>Se NMR data, precisely targeted applications in catalysis will be examined in the future. The aim is to investigate the mutual interaction of the metal centers and whether synergistic effects can be achieved by their combination in a multinuclear complex.



Scheme 4. Synthesis of the selenium adduct **9f**. i) Se, KO<sup>t</sup>Bu, THF, r.t., 16 h.

## Experimental Section

All reactions were carried out under an argon atmosphere using standard Schlenk techniques. The solvents were either freshly distilled or dried and degassed before use according to standard techniques. Commercially available chemicals were purchased from ABCR, Alfa Aesar, Sigma Aldrich, Strem or TCI.  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  and  $^{77}\text{Se}$  NMR spectra were recorded on BRUKER Spectrospin Avance 400 and 600 spectrometers. The chemical shifts of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra are referenced to internal solvent resonances. The multiplicities are reported as s=singlet, d=doublet, t=triplet, q=quartet, sept=septet and m=multiplet. The NMR resonances are assigned according to the numbering schemes given in the Supporting Information. ESI-mass spectrometric measurements were performed on an AmaZon ETD device by introducing solutions of the compound in acetonitrile. Elemental analyses were carried out with a Vario MICRO Cube elemental analyzer at the Analytical Laboratory of the Technische Universität Kaiserslautern. We have already published compounds **1** and **2a** elsewhere.<sup>[14c]</sup> For the purpose of providing completeness, their synthesis is nevertheless described here as well.

**( $\eta^5$ -Cyclopentadienyl)(1- $\eta^6$ -phenyl)iron(II)-1*H*-imidazole hexafluorophosphate (**1**):** 4.96 g (13.1 mmol) of ( $\eta^5$ -chlorobenzene)( $\eta^5$ -cyclopentadienyl)iron(II) hexafluorophosphate and 2.03 g (22.5 mmol) of freshly prepared sodium imidazolidate were stirred at room temperature for 2 h in 50 mL of acetonitrile. The reaction mixture was filtered over neutral aluminum oxide and the solvent was removed under vacuum. The product precipitated as a yellow powder after the addition of 25 mL of diethyl ether. Yield: 3.92 g (73%) of a yellow solid. Anal. calcd. for  $\text{C}_{14}\text{H}_{13}\text{F}_6\text{FeN}_2\text{P}$  (410.08): C 41.01, H 3.20, N 6.83; found: C 40.50, H 2.91, N 6.82%.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  8.15 (s, H-8, 1H), 7.67 (s, H-7, 1H), 7.22 (s, H-6, 1H), 6.71 (d,  $^3J_{\text{HH}}=6.7$  Hz, H-4, 2H), 6.43 (t,  $^3J_{\text{HH}}=6.5$  Hz, H-3, 2H), 6.28 (t,  $^3J_{\text{HH}}=6.2$  Hz, H-2, 1H), 5.04 (s, H-1, 5H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CD}_3\text{CO}$ ):  $\delta$  137.4 (C-8), 132.6 (C-7), 119.0 (C-6), 108.0 (C-5), 88.6 (C-3), 88.2 (C-2), 81.0 (C-4), 79.2 (C-1).  $^{31}\text{P}$  NMR (243 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  -144.3 (sept,  $J=711.3$  Hz). ESI-MS ( $\text{CD}_3\text{CN}$ ):  $m/z$  265.03 (calcd. 265.05) [ $\text{C}_{14}\text{H}_{13}\text{FeN}_2$ ] $^+$ .

**General procedure for the synthesis of the imidazolium salts **2a–2f**:** An excess (for details see below) of the appropriate organohalide and compound **1** were stirred in 20 mL of acetonitrile (**2a–d** and **2f**) or *N,N*-dimethylformamide (**2e**) for 12 h at room temperature (**2a**) respectively 70 °C (**2b–2f**). After the addition of 50 mL of diethyl ether a precipitate formed. Decanting the solvent revealed the desired products as saffron yellow powders that were further dried under vacuum.

**( $\eta^5$ -Cyclopentadienyl)(1- $\eta^6$ -phenyl)iron(II)-3-methylimidazolium hexafluorophosphate iodide (**2a**):** From 6.00 g (14.6 mmol) of **1** and 22.8 g (159 mmol, 10 mL) of iodomethane in acetonitrile; yield: 5.70 g (71%). Anal. calcd. for  $\text{C}_{15}\text{H}_{16}\text{F}_6\text{FeI}_2\text{N}_2\text{P}$  (552.02): C 32.64, H 2.92, N 5.07; found: C 32.91, H 2.97, N 5.16%.  $^1\text{H}$  NMR (600 MHz,  $\text{CD}_3\text{NO}_2$ ):  $\delta$  10.12 (s, H-8, 1H), 8.30 (s, H-7, 1H), 7.73 (s, H-6, 1H), 7.29 (d,  $^3J_{\text{HH}}=6.5$  Hz, H-4, 2H), 6.75 (t,  $^3J_{\text{HH}}=6.4$  Hz, H-3, 2H), 6.62 (d,  $^3J_{\text{HH}}=6.2$  Hz, H-2, 1H), 5.41 (s, H-1, 5H), 4.17 (s, H-9, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CD}_3\text{NO}_2$ ):  $\delta$  138.5 (C-8), 127.0 (C-7), 123.0 (C-6), 105.7 (C-5), 90.2 (C-4), 89.2 (C-3), 83.8 (C-2), 80.9 (C-1), 38.2 (C-9).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CD}_3\text{NO}_2$ ):  $\delta$  -142.4 (sept,  $J_{\text{PF}}=711.3$  Hz). ESI-MS ( $\text{CH}_3\text{CN}$ ):  $m/z$  424.94 (calcd. 425.04) [ $\text{C}_{15}\text{H}_{16}\text{FeN}_2\text{PF}_6$ ] $^+$ , 406.91 (calcd. 406.98) [ $\text{C}_{15}\text{H}_{16}\text{FeN}_2$ ] $^+$ , 279.00 (calcd. 279.07) [ $\text{C}_{15}\text{H}_{15}\text{FeN}_2$ ] $^+$ .

**( $\eta^5$ -Cyclopentadienyl)(1- $\eta^6$ -phenyl)iron(II)-3-propylimidazolium hexafluorophosphate iodide (**2b**):** From 500 mg (1.22 mmol) of **1** and 3.48 g (20.3 mmol, 2 mL) of 1-iodopropane in acetonitrile; yield: 253 mg (36%). Anal. calcd. for  $\text{C}_{17}\text{H}_{20}\text{F}_6\text{FeI}_2\text{N}_2\text{P}$  (580.07): C 35.20, H 3.48, N 4.83; found: C 35.46, H 3.45, N 4.89%.  $^1\text{H}$  NMR (400 MHz,

$\text{CD}_3$ ) $_2\text{SO}$ ):  $\delta$  10.09 (s, H-8, 1H), 8.57 (s, H-7, 1H), 8.17 (s, H-6, 1H), 7.09 (d,  $^3J_{\text{HH}}=6.6$  Hz, H-4, 2H), 6.77 (t,  $^3J_{\text{HH}}=6.5$  Hz, H-3, 2H), 6.59 (t,  $^3J_{\text{HH}}=6.2$  Hz, H-2, 1H), 5.32 (s, H-1, 5H), 4.26 (t,  $^3J_{\text{HH}}=7.2$  Hz, H-9, 2H), 1.94 (dt,  $^3J_{\text{HH}}=7.3$  Hz, H-10, 2H), 0.96 (t,  $^3J_{\text{HH}}=7.4$  Hz, H-11, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CD}_3$ ) $_2\text{SO}$ ):  $\delta$  137.5 (C-8), 123.9 (C-7), 121.8 (C-6), 103.7 (C-5), 88.5 (C-2), 87.5 (C-3), 82.2 (C-4), 78.9 (C-1), 51.3 (C-9), 22.4 (C-10), 10.5 (C-11). ( $\text{CD}_3$ ) $_2\text{SO}$ ):  $\delta$  -142.2 (sept,  $J_{\text{PF}}=711.3$  Hz). ESI-MS ( $\text{CD}_3\text{CN}$ ):  $m/z$  434.91 (calcd. 435.00) [ $\text{C}_{17}\text{H}_{20}\text{FeN}_2$ ] $^+$ , 307.06 (calcd. 307.08) [ $\text{C}_{17}\text{H}_{19}\text{FeN}_2$ ] $^+$ , 187.09 (calcd. 187.12) [ $\text{C}_{12}\text{H}_{15}\text{N}_2$ ] $^+$ .

**( $\eta^5$ -Cyclopentadienyl)(1- $\eta^6$ -phenyl)iron(II)-3-isopropylimidazolium hexafluorophosphate iodide (**2c**):** From 3.68 g (8.97 mmol) of **1** and 8.40 g (48.4 mmol, 5 mL) of 2-iodopropane in acetonitrile; yield: 1.41 g (27%). Anal. calcd. for  $\text{C}_{17}\text{H}_{20}\text{F}_6\text{FeI}_2\text{N}_2\text{P}$  (580.07): C 35.20, H 3.48, N 4.83; found: C 35.92, H 3.59, N 4.80%.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3$ ) $_2\text{SO}$ ):  $\delta$  10.07 (s, H-8, 1H), 8.61 (s, H-7, 1H), 8.30 (s, H-6, 1H), 7.14 (d,  $^3J_{\text{HH}}=6.3$  Hz, H-4, 2H), 6.77 (t,  $^3J_{\text{HH}}=5.9$  Hz, H-3, 2H), 6.59 (t,  $^3J_{\text{HH}}=5.9$  Hz, H-2, 1H), 5.34 (s, H-1, 5H), 4.75 (sept,  $^3J_{\text{HH}}=6.5$  Hz, H-9, 1H), 1.60 (d,  $^3J_{\text{HH}}=6.5$  Hz, H-10, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CD}_3$ ) $_2\text{SO}$ ):  $\delta$  136.3 (C-8), 122.2 (C-7), 121.8 (C-6), 103.8 (C-5), 88.4 (C-2), 87.4 (C-3), 82.2 (C-4), 78.9 (C-1), 53.4 (C-9), 22.0 (C-10).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CD}_3$ ) $_2\text{SO}$ ):  $\delta$  -142.2 (sept,  $J_{\text{PF}}=711.3$  Hz). ESI-MS ( $\text{CD}_3\text{CN}$ ):  $m/z$  434.91 (calcd. 435.00) [ $\text{C}_{17}\text{H}_{20}\text{FeN}_2$ ] $^+$ , 325.06 (calcd. 324.91) [ $\text{C}_{11}\text{H}_{10}\text{FeI}$ ] $^+$ , 307.03 (calcd. 307.08) [ $\text{C}_{17}\text{H}_{19}\text{FeN}_2$ ] $^+$ , 187.06 (calcd. 187.12) [ $\text{C}_{12}\text{H}_{15}\text{N}_2$ ] $^+$ .

**( $\eta^5$ -Cyclopentadienyl)(1- $\eta^6$ -phenyl)iron(II)-3-butyylimidazolium hexafluorophosphate iodide (**2d**):** From 6.95 g (16.9 mmol) of **1**, 8.05 g (43.7 mmol, 5 mL) of 1-iodobutane in acetonitrile; yield: 5.92 g (59%). Anal. calcd. for  $\text{C}_{18}\text{H}_{22}\text{F}_6\text{FeI}_2\text{N}_2\text{P}$  (594.10): C 36.39, H 3.73, N 4.72; found: C 35.93, H 3.52, N 4.66%.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3$ ) $_2\text{SO}$ ):  $\delta$  10.04 (s, H-8, 1H), 8.54 (s, H-7, 1H), 8.15 (s, H-6, 1H), 7.07 (d,  $^3J_{\text{HH}}=6.6$  Hz, H-4, 2H), 6.74 (t,  $J=6.4$  Hz, H-3, 2H), 6.57 (t,  $^3J_{\text{HH}}=6.2$  Hz, H-2, 1H), 5.30 (s, H-1, 5H), 4.28 (t,  $^3J_{\text{HH}}=7.2$  Hz, H-9, 2H), 1.98–1.79 (m, H-10, 2H), 1.37 (dd,  $^3J_{\text{HH}}=15.0$ , H-11, 7.5 Hz, 2H), 0.95 (t,  $^3J_{\text{HH}}=7.4$  Hz, H-12, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CD}_3$ ) $_2\text{SO}$ ):  $\delta$  137.3 (C-8), 123.8 (C-7), 121.6 (C-6), 103.7 (C-5), 88.4 (C-2), 87.4 (C-3), 82.0 (C-4), 78.8 (C-1), 49.4 (C-9), 30.7 (C-10), 18.7 (C-11), 13.2 (C-12).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CD}_3$ ) $_2\text{SO}$ ):  $\delta$  -144.2 (sept,  $J_{\text{PF}}=711.4$  Hz). ESI-MS ( $\text{CD}_3\text{CN}$ ):  $m/z$  467.03 (calcd. 467.03) [ $\text{C}_{18}\text{H}_{22}\text{FeI}_2\text{N}_2\text{H}_2\text{O}$ ] $^+$ , 448.91 (calcd. 449.02) [ $\text{C}_{18}\text{H}_{22}\text{FeI}_2\text{N}_2$ ] $^+$ , 321.09 (calcd. 321.10) [ $\text{C}_{18}\text{H}_{21}\text{FeN}_2$ ] $^+$ , 201.09 (calcd. 201.14) [ $\text{C}_{13}\text{H}_{17}\text{N}_2$ ] $^+$ .

**( $\eta^5$ -Cyclopentadienyl)(1- $\eta^6$ -phenyl)iron(II)-3-octylimidazolium hexafluorophosphate iodide (**2e**):** From 2.27 g (5.54 mmol) of **1** and 3.99 g (16.6 mmol, 3 mL) of 1-iodooctane in DMF; yield: 2.43 g (68%). Anal. calcd. for  $\text{C}_{22}\text{H}_{30}\text{F}_6\text{FeI}_2\text{N}_2\text{P}$  (650.21): C 40.64, H 4.65, N 4.31; found: C 40.70, H 4.51, N 4.37%.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3$ ) $_2\text{SO}$ ):  $\delta$  10.07 (s, H-8, 1H), 8.55 (s, H-7, 1H), 8.15 (s, H-6, 1H), 7.09 (d,  $^3J_{\text{HH}}=6.2$  Hz, H-4, 2H), 6.75 (t,  $^3J_{\text{HH}}=6.0$  Hz, H-3, 2H), 6.58 (t,  $^3J_{\text{HH}}=5.9$  Hz, H-2, 1H), 5.31 (s, H-1, 5H), 4.27 (t,  $^3J_{\text{HH}}=7.1$  Hz, H-9, 2H), 1.92 (m, H-10, 2H), 1.42–1.16 (m, H-octyl, 10H), 0.84 (t,  $^3J_{\text{HH}}=6.2$  Hz, H-16, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CD}_3$ ) $_2\text{SO}$ ):  $\delta$  137.4 (C-8), 123.9 (C-7), 121.7 (C-6), 103.7 (C-5), 88.5 (C-2), 87.5 (C-3), 82.2 (C-4), 78.9 (C-1), 49.8 (C-9), 31.1 (C-10), 28.8 (C-octyl), 28.4 (C-octyl), 28.4 (C-octyl), 25.5 (C-octyl), 22.0 (C-octyl), 13.9 (C-16).  $^{31}\text{P}$  NMR (243 MHz,  $\text{CD}_3$ ) $_2\text{SO}$ ):  $\delta$  -144.2 (sept,  $J_{\text{PF}}=711.5$  Hz). ESI-MS ( $\text{CH}_3\text{CN}$ ):  $m/z$  504.97 (calcd. 505.08) [ $\text{C}_{22}\text{H}_{30}\text{FeI}_2\text{N}_2$ ] $^+$ , 377.13 (calcd. 377.17) [ $\text{C}_{22}\text{H}_{29}\text{FeN}_2$ ] $^+$ , 257.16 (calcd. 257.20) [ $\text{C}_{17}\text{H}_{25}\text{N}_2$ ] $^+$ .

**( $\eta^5$ -Cyclopentadienyl)(1- $\eta^6$ -phenyl)iron(II)-3-benzylimidazolium chloride hexafluorophosphate (**2f**):** From 6.00 g (14.6 mmol) of **1** and 11.0 g (86.9 mmol, 10 mL) of benzylic chloride in acetonitrile; yield: 5.50 g (70%). Anal. calcd. for  $\text{C}_{21}\text{H}_{20}\text{ClF}_6\text{FeN}_2\text{P}$  (536.67): C 47.00, H 3.76, N 5.22; found: C 46.42, H 3.67, N 5.53%.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3$ ) $_2\text{SO}$ ):  $\delta$  10.73 (s, H-8, 1H), 8.69 (s, H-7, 1H), 8.17 (s, H-6, 1H), 7.60 (d,  $^3J_{\text{HH}}=6.9$  Hz, H-11, 2H), 7.51–7.33 (m, H-12, H-13, 3H), 7.19 (d,  $^3J_{\text{HH}}=6.3$  Hz, H-4, 2H), 6.75 (t,  $^3J_{\text{HH}}=6.1$  Hz, H-3, 2H), 6.57 (t,



$^3J_{\text{HH}} = 5.9$  Hz, H-2, 1H), 5.59 (s, H-9, 2H), 5.34 (s, H-1, 5H).  $^{13}\text{C}$  NMR (101 MHz,  $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  138.2 (C-8), 134.1 (C-10), 128.9 (C-11), 128.9 (C-13), 128.8 (C-12), 123.7 (C-7), 122.5 (C-6), 103.9 (C-5), 88.6 (C-2), 87.6 (C-3), 82.4 (C-4), 79.1 (C-1), 52.6 (C-9).  $^{31}\text{P}$  NMR (243 MHz,  $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  -144.2 (sept,  $^1J_{\text{PF}} = 711.4$  Hz) ppm. ESI-MS ( $\text{CH}_3\text{CN}$ ):  $m/z$  501.00 (calcd. 501.07)  $[\text{C}_{21}\text{H}_{20}\text{F}_6\text{FeN}_2\text{P}]^+$ , 355.13 (calcd. 355.09)  $[\text{C}_{21}\text{H}_{19}\text{FeN}_2]^+$ , 235.00 (calcd. 235.12)  $[\text{C}_{16}\text{H}_{15}\text{N}_2]^+$ .

**General procedure for the synthesis of the NHC copper complexes 3a, 3e and 3f:** The corresponding dicationic imidazolium salt (2a, 2e or 2f) was stirred in 10 mL of THF for 16 h at 50 °C in the presence of an excess of mesitylcopper(I). After removal of the solvent under vacuum, the residues were washed three times with 10 mL of diethyl ether yielding the copper complexes as pale yellow powders.

**((( $\eta^5$ -Cyclopentadienyl)(1- $\eta^6$ -phenyl)iron(II))-3-methylimidazol-2-ylidene)iodidocopper(I) hexafluorophosphate (3a):** From 3.31 g (6.00 mmol) of 2a and 1.56 g (8.54 mmol) mesitylcopper(I); yield: 3.60 g (98%). Anal. calcd. for  $\text{C}_{15}\text{H}_{15}\text{CuF}_6\text{FeN}_2\text{P}$  (614.56): C 29.32, H 2.46, N 4.56; found: C 29.13, H 2.51, N 4.34%.  $^1\text{H}$  NMR (400 MHz,  $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  8.15 (s, H-7, 1H), 7.71 (s, H-6, 1H), 7.17 (d,  $^3J_{\text{HH}} = 6.0$  Hz, H-4, 2H), 6.59 (t,  $^3J_{\text{HH}} = 6.0$  Hz, H-3, 2H), 6.44 (t,  $^3J_{\text{HH}} = 5.8$  Hz, H-2, 1H), 5.23 (s, H-1, 5H), 3.89 (s, H-9, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  181.0 (C-8), 124.8 (C-7), 120.7 (C-6), 108.9 (C-5), 87.6 (C-2), 87.1 (C-3), 82.4 (C-4), 78.1 (C-1), 38.2 (C-9).  $^{31}\text{P}$  NMR (243 MHz,  $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  -141.3 (sept,  $^1J_{\text{PF}} = 711.4$  Hz). ESI-MS ( $\text{CH}_3\text{CN}$ ):  $m/z$  468.84 (calcd. 468.90)  $[\text{C}_{15}\text{H}_{15}\text{CuFeN}_2]^+$ .

**((( $\eta^5$ -Cyclopentadienyl)(1- $\eta^6$ -phenyl)iron(II))-3-octylimidazol-2-ylidene)iodidocopper(I) hexafluorophosphate (3e):** From 780 mg (1.20 mmol) of 2e and 338 mg (1.85 mmol) of mesitylcopper(I); yield: 646 mg (75%). Anal. calcd. for  $\text{C}_{22}\text{H}_{29}\text{CuF}_6\text{FeN}_2\text{P}$  (712.75): C 37.07, H 4.10, N 3.93; found: C 36.43, H 4.00, N 3.96%.  $^1\text{H}$  NMR (400 MHz,  $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  8.12 (s, H-7, 1H), 7.74 (s, H-6, 1H), 7.28 (d,  $^3J_{\text{HH}} = 5.5$  Hz, H-4, 2H), 6.58 (t,  $^3J_{\text{HH}} = 5.7$  Hz, H-3, 2H), 6.43 (m, H-2, 1H), 5.23 (s, H-1, 5H), 4.30–4.20 (t,  $^3J_{\text{HH}} = 6.7$  Hz, H-9, 2H), 1.85 (m, H-10, 2H), 1.37–1.12 (m, H-octyl, 10H), 0.85 (m, H-16, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  182.6 (C-8), 123.4 (C-7), 120.3 (C-6), 109.0 (C-5), 87.4 (C-2), 87.1 (C-3), 82.0 (C-4), 78.1 (C-1), 50.9 (C-9), 31.2 (C-octyl), 30.5 (C-octyl), 28.6 (C-octyl), 28.6 (C-octyl), 25.9 (C-octyl), 22.1 (C-octyl), 14.0 (C-16).  $^{31}\text{P}$  NMR (243 MHz,  $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  -144.2 (sept,  $^1J_{\text{PF}} = 711.4$  Hz). ESI-MS ( $\text{CH}_3\text{CN}$ ):  $m/z$  566.94 (calcd. 567.00)  $[\text{C}_{22}\text{H}_{29}\text{CuFeN}_2]^+$ .

**((( $\eta^5$ -Cyclopentadienyl)(1- $\eta^6$ -phenyl)iron(II))-3-benzylimidazol-2-ylidene)chloridocopper(I) hexafluorophosphate (3f):** From 537 mg (1.00 mmol) of 2f and 415 mg (2.27 mmol) of mesitylcopper(I); yield: 484 mg (81%). Anal. calcd. for  $\text{C}_{21}\text{H}_{19}\text{ClCuF}_6\text{FeN}_2\text{P}$  (599.21): C 42.09, H 3.20, N 4.68; found: C 41.28, H 3.00, N 4.59%.  $^1\text{H}$  NMR (400 MHz,  $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  8.17 (s, H-7, 1H), 7.82 (s, H-6, 1H), 7.48 (d,  $^3J_{\text{HH}} = 6.8$  Hz, H-11, 2H), 7.46–7.30 (m, H-12, H-13, 3H), 7.20 (d,  $^3J_{\text{HH}} = 6.0$  Hz, H-4, 2H), 6.60 (t,  $^3J_{\text{HH}} = 5.5$  Hz, H-3, 2H), 6.46 (t,  $^3J_{\text{HH}} = 5.6$  Hz, H-2, 1H), 5.47 (s, H-9, 2H), 5.25 (s, H-1, 5H).  $^{13}\text{C}$  NMR (151 MHz,  $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  179.0 (C-8), 136.6 (C-10), 128.8 (C-11), 128.3 (C-13), 128.1 (C-12), 123.6 (C-7), 121.5 (C-6), 108.8 (C-5), 87.7 (C-2), 87.1 (C-3), 82.5 (C-4), 78.3 (C-1), 54.4 (C-9) ppm.  $^{31}\text{P}$  NMR (243 MHz,  $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  -144.2 (sept,  $^1J_{\text{PF}} = 711.6$  Hz). ESI-MS ( $\text{CH}_3\text{CN}$ ):  $m/z$  453.00 (calcd. 452.99)  $[\text{C}_{21}\text{H}_{19}\text{ClCuFeN}_2]^+$ .

**((( $\eta^5$ -Cyclopentadienyl)(1- $\eta^6$ -phenyl)iron(II))-3-methylimidazol-2-ylidene)chloridogold(I) hexafluorophosphate (4a):** 108 mg (0.18 mmol) of 3a and 56.0 mg (0.18 mmol) of chlorido(tetrahydrothiophene)gold(I) were stirred in 10 mL of nitromethane for 16 h at room temperature and in the absence of light. After filtration, the solvent was removed under vacuum and the crude product was purified by slow diffusion of diethyl ether into a saturated solution in nitromethane. Yield: 113 mg (98%, 172 mmol)

of a yellow solid. Anal. calcd. for  $\text{C}_{15}\text{H}_{15}\text{AuClFeN}_2\text{P}$  (656.53): C 27.44, H 2.30, N 4.27; found: C 27.75, H 2.24, N 4.60%.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  7.67 (s, H-7, 1H), 7.43 (s, H-6, 1H), 7.05 (d,  $^3J_{\text{HH}} = 6.3$  Hz, H-4, 2H), 6.51 (t,  $^3J_{\text{HH}} = 6.3$  Hz, H-3, 2H), 6.38 (t,  $^3J_{\text{HH}} = 6.1$  Hz, H-2, 1H), 5.19 (s, H-1, 5H), 3.94 (s, H-9, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  172.8 (C-8), 125.5 (C-7), 122.9 (C-6), 109.8 (C-5), 89.3 (C-2), 88.3 (C-3), 84.7 (C-4), 79.7 (C-1), 40.1 (C-9).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  -144.6 (sept,  $^1J_{\text{PF}} = 706.3$  Hz). ESI-MS ( $\text{CH}_3\text{CN}$ ):  $m/z$  510.94 (calcd. 510.99)  $[\text{C}_{15}\text{H}_{15}\text{AuClFeN}_2]^+$ .

**Bis((( $\eta^5$ -cyclopentadienyl)(1- $\eta^6$ -phenyl)iron(II))-3-isopropylimidazol-2-ylidene)diiodidopalladium(II) bis(hexafluorophosphate) (5c):** 181 mg (0.40 mmol) of 2c were stirred with 44.9 mg (0.20 mmol) of palladium(II) acetate in 10 mL of nitromethane at 65 °C for 16 h. After removal of the solvent, the crude product was washed with 10 mL of diethyl ether. Yield: 186 mg (74%) of an ocher yellow solid. Anal. calcd. for  $\text{C}_{34}\text{H}_{38}\text{F}_{12}\text{Fe}_2\text{I}_2\text{N}_4\text{P}_2\text{Pd}$  (1264.53): C 32.29, H 3.03, N 4.43; found: C 32.21, H 3.03, N 4.92%.  $^1\text{H}$  NMR (400 MHz,  $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  8.20 (s, H-7, 2H), 7.99 (s, H-6, 2H), 7.16 (d,  $^3J_{\text{HH}} = 6.4$  Hz, H-4, 4H), 6.73 (t,  $^3J_{\text{HH}} = 6.2$  Hz, H-3, 4H), 6.58 (t,  $^3J_{\text{HH}} = 6.1$  Hz, H-2, 2H), 5.31 (s, H-1, 10H), 5.01 (sept,  $^3J_{\text{HH}} = 6.6$  Hz, H-9, 2H), 1.39 (d,  $^3J_{\text{HH}} = 6.7$  Hz, H-10, 12H).  $^{13}\text{C}$  NMR (101 MHz,  $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  166.1 (C-8), 123.6 (C-7), 120.7 (C-6), 109.9 (C-5), 88.1 (C-2), 86.8 (C-3), 83.9 (C-4), 78.1 (C-1), 53.2 (C-9), 21.3 (C-10).  $^{31}\text{P}$  NMR (162 MHz,  $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  -144.2 (sept,  $^1J_{\text{PF}} = 711.4$  Hz). ESI-MS ( $\text{CH}_3\text{CN}$ ):  $m/z$  486.91 (calcd. 486.95)  $[\text{C}_{34}\text{H}_{38}\text{Fe}_2\text{I}_2\text{N}_4\text{Pd}]^{2+}$ .

**(((Bis( $\eta^5$ -cyclopentadienyl)(1- $\eta^6$ -phenyl)iron(II))-3-octylimidazol-2-ylidene)diiodidopalladium(II) bis(hexafluorophosphate) (5e):** Complex 5e was synthesized as described above for 5c by using 260 mg (0.40 mmol) of 2e and 44.9 mg (0.20 mmol) of palladium(II) acetate in 10 mL of tetrahydrofuran. Yield: 218 mg (78%) of an ocher yellow solid. Anal. calcd. for  $\text{C}_{44}\text{H}_{58}\text{F}_{12}\text{Fe}_2\text{I}_2\text{N}_4\text{P}_2\text{Pd}$  (1404.80): C 37.62, H 4.16, N 3.99; found: C 37.62, H 4.43, N 3.93%.  $^1\text{H}$  NMR (400 MHz,  $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  8.16 (s, H-7, 2H), 7.84 (s, H-6, 2H), 7.20 (d,  $^3J_{\text{HH}} = 6.3$  Hz, H-4, 4H), 6.74 (t,  $^3J_{\text{HH}} = 6.3$  Hz, H-3, 4H), 6.58 (t,  $^3J_{\text{HH}} = 6.0$  Hz, H-2, 2H), 5.30 (s, H-1, 10H), 4.14 (sept,  $^3J_{\text{HH}} = 6.9$  Hz, H-9, 4H), 1.75 (s, H-10, 4H), 1.45–1.07 (m, H-octyl, 20H), 0.86 (t,  $^3J_{\text{HH}} = 6.9$  Hz, H-16, 6H).  $^{13}\text{C}$  NMR (151 MHz,  $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  167.1 (C-8), 124.4 (C-7), 123.3 (C-6), 109.8 (C-5), 88.0 (C-2), 87.0 (C-3), 84.4 (C-4), 78.2 (C-1), 50.9 (C-9), 31.2 (C-10), 28.9 (C-octyl), 28.7 (C-octyl), 28.5 (C-octyl), 26.1 (C-octyl), 22.1 (C-octyl), 14.0 (C-16).  $^{31}\text{P}$  NMR (243 MHz,  $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  -144.2 (sept,  $^1J_{\text{PF}} = 711.4$  Hz) ppm. ESI-MS ( $\text{CH}_3\text{CN}$ ):  $m/z$  556.94 (calcd. 557.03)  $[\text{C}_{44}\text{H}_{58}\text{Fe}_2\text{I}_2\text{N}_4\text{Pd}]^{2+}$ .

**((( $\eta^5$ -Cyclopentadienyl)(1- $\eta^6$ -phenyl)iron(II))-3-methylimidazol-2-ylidene)diiodido(pyridine)palladium(II) hexafluorophosphate (6a):** 166 mg (0.30 mmol) of 2a were stirred with 67.4 mg (0.30 mmol) palladium(II) acetate and 75.5 mg (0.45 mmol) potassium iodide in 3.5 mL of pyridine for 48 h at room temperature. After the addition of 15 mL of dichloromethane the mixture was filtered over Celite®. The volume of the solvent was reduced to 5 mL and the product was precipitated by the addition of 20 mL of diethyl ether. Slow diffusion of diethyl ether into a saturated solution of 6 in acetonitrile gave the analytically pure compound. Yield: 165 mg (64%) of an orange solid. Anal. calcd. for  $\text{C}_{20}\text{H}_{20}\text{F}_6\text{FeI}_2\text{N}_3\text{P}\text{Pd}$  (863.42): C 27.82, H 2.33, N 4.87; found: C 28.00, H 2.47, N 4.87%.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  8.82 (d,  $^3J_{\text{HH}} = 4.9$  Hz, H-10, 2H), 7.89 (t,  $^3J_{\text{HH}} = 7.7$  Hz, H-12, 1H), 7.85 (d,  $^3J_{\text{HH}} = 2.2$  Hz, H-7, 1H), 7.58 (d,  $^3J_{\text{HH}} = 6.7$  Hz, H-4, 2H), 7.54 (d,  $^3J_{\text{HH}} = 2.2$  Hz, H-6, 1H), 7.49–7.38 (m, H-11, 2H), 6.61 (t,  $^3J_{\text{HH}} = 6.5$  Hz, H-3, 2H), 6.45 (t,  $^3J_{\text{HH}} = 6.3$  Hz, H-2, 1H), 5.16 (s, H-1, 5H), 4.10 (s, H-9, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  154.3 (C-10), 139.7 (C-12), 127.3 (C-7), 126.0 (C-6), 123.5 (C-11), 110.4 (C-5), 89.1 (C-2), 88.2 (C-3), 84.5 (C-4), 79.2 (C-1), 40.9 (C-9). The resonance of the carbene carbon atom (C-8) is too weak in intensity and thus not detectable.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  -144.6 (sept,  $^1J_{\text{PF}} = 706.4$  Hz). ESI-MS ( $\text{CH}_3\text{CN}$ ):  $m/z$  717.78 (calcd. 717.82)  $[\text{C}_{20}\text{H}_{20}\text{FeI}_2\text{N}_3\text{P}\text{Pd}]^+$ .

(( $\eta^5$ -Cyclopentadienyl)(1- $\eta^6$ -phenyl)iron(II))-3-methylimidazol-2-ylidene)diodido(pyridine)platinum(II) hexafluorophosphate (**7a**): 243 mg (0.44 mmol) of **2a** were stirred with 106 mg (0.4 mmol) of platinum dichloride, 553 mg (4.00 mmol) of potassium carbonate and 600 mg (4.00 mmol) sodium iodide in 10 mL of pyridine at 100 °C for 18 h. After half of the pyridine was removed under vacuum, 10 mL of dichloromethane were added to the mixture. Filtration over Celite<sup>®</sup>, followed by removal of the solvent and washing with 20 mL of diethyl ether gave **7**. Yield: 171 mg (41 %) of a yellow solid. Anal. calcd. for C<sub>20</sub>H<sub>20</sub>F<sub>6</sub>FeI<sub>2</sub>N<sub>3</sub>Pt (952.11): C 25.23, H 2.12, N 4.41; found: C 25.35, H 2.19, N 4.37%. <sup>1</sup>H NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>SO):  $\delta$  8.81–8.77 (m, H-10, 2H), 8.20 (d, <sup>3</sup>J<sub>HH</sub> = 2.2 Hz, H-7, 1H), 7.93 (t, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, H-12, 1H), 7.84 (d, <sup>3</sup>J<sub>HH</sub> = 2.2 Hz, H-6, 1H), 7.62 (d, <sup>3</sup>J<sub>HH</sub> = 6.4 Hz, H-4, 2H), 7.56–7.49 (m, H-11, 2H), 6.76 (t, <sup>3</sup>J<sub>HH</sub> = 6.5 Hz, H-3, 2H), 6.58 (t, <sup>3</sup>J<sub>HH</sub> = 6.1 Hz, H-2, 1H), 5.28 (s, H-1, 5H), 4.01 (s, H-9, 3H). <sup>13</sup>C NMR (101 MHz, (CD<sub>3</sub>)<sub>2</sub>SO):  $\delta$  153.2 (C-10), 138.8 (C-12), 125.6 (C-11), 125.5 (C-7), 121.9 (C-6), 108.9 (C-5), 88.0 (C-2), 87.0 (C-3), 83.5 (C-4), 78.0 (C-1). The resonance of the carbene carbon atom (C-8) is too weak in intensity and thus not detectable. The resonance of the methyl group (C-9) expected at about 40 ppm is presumably superimposed by the solvent signal. <sup>31</sup>P NMR (162 MHz, (CD<sub>3</sub>)<sub>2</sub>SO):  $\delta$  144.2 (sept, <sup>1</sup>J<sub>PF</sub> = 711.3 Hz). ESI-MS (CH<sub>3</sub>CN): m/z 806.81 (calcd. 806.87) [C<sub>20</sub>H<sub>20</sub>FeI<sub>2</sub>N<sub>3</sub>Pt]<sup>+</sup>.

$\eta^4$ -Cycloocta-1,5-diene(( $\eta^5$ -cyclopentadienyl)(1- $\eta^6$ -phenyl)iron(II))-3-methylimidazol-2-ylidene)iodidorhodium(II) hexafluorophosphate (**8a**): 112 mg (0.20 mmol) of **2a**, 50.0 mg (0.10 mmol) of bis(( $\mu^2$ -chlorido)( $\eta^4$ -cycloocta-1,5-diene)rhodium(II)) and 28.6 (0.40 mmol) sodium ethoxide were heated to reflux for 1 h in 10 mL of methanol. After cooling to room temperature, a yellow microcrystalline solid precipitated, which was washed with methanol and dried under vacuum. Yield: 68.3 mg (44 %). Anal. calcd. for C<sub>23</sub>H<sub>27</sub>F<sub>6</sub>FeI<sub>2</sub>N<sub>3</sub>Prh (762.10): C 36.25, H 3.57, N 3.68; found: C 35.80, H 3.30, N 3.55%. <sup>1</sup>H NMR (600 MHz, (CD<sub>3</sub>)<sub>2</sub>SO)  $\delta$  9.28 (d, <sup>3</sup>J<sub>HH</sub> = 6.4 Hz, H-4, 1H), 8.26 (s, H-8, 1H), 7.77 (s, H-9, 1H), 6.91 (d, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, H-6, 1H), 6.84 (t, <sup>3</sup>J<sub>HH</sub> = 6.3 Hz, H-3, 1H), 6.65 (t, <sup>3</sup>J<sub>HH</sub> = 6.4 Hz, H-7, 1H), 6.51 (t, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, H-2, 1H), 5.25 (m, CH-COD, 1H), 5.18 (s, H-1, 5H), 5.13–5.04 (m, CH-COD, 1H), 4.06 (s, H-11, 3H), 3.51 (s, CH-COD, 1H), 2.69 (s, CH-COD, 1H), 2.37–2.13 (m, CH<sub>2</sub>-COD, 3H), 1.94–1.80 (m, CH<sub>2</sub>-COD, 2H), 1.73 (d, <sup>3</sup>J<sub>HH</sub> = 6.4 Hz, CH<sub>2</sub>-COD, 1H), 1.67–1.57 (m, CH<sub>2</sub>-COD, 1H), 1.50 (m, CH<sub>2</sub>-COD, 1H). <sup>13</sup>C NMR (151 MHz, (CD<sub>3</sub>)<sub>2</sub>SO):  $\delta$  183.7 (d, <sup>1</sup>J<sub>RhC</sub> = 49.3 Hz, C-10), 126.0 (C-8), 121.2 (C-9), 108.4 (C-5), 96.0 (d, <sup>1</sup>J<sub>RhC</sub> = 6.3 Hz, CH-COD), 95.5 (d, <sup>1</sup>J<sub>RhC</sub> = 5.8 Hz, CH-COD), 87.5 (C-4), 86.9 (C-3), 86.6 (C-6), 82.5 (C-7), 80.3 (C-2), 77.8 (C-1), 72.7 (d, <sup>1</sup>J<sub>RhC</sub> = 13.8 Hz, CH-COD), 72.4 (d, <sup>1</sup>J<sub>RhC</sub> = 13.7 Hz, CH-COD), 32.2 (CH<sub>2</sub>-COD), 30.8 (CH<sub>2</sub>-COD), 29.5 (CH<sub>2</sub>-COD), 28.5 (CH<sub>2</sub>-COD). The resonance of the methyl group (C-11) is expected at about 40 ppm is presumably superimposed by the solvent signal. <sup>31</sup>P NMR (243 MHz, (CD<sub>3</sub>)<sub>2</sub>SO):  $\delta$  -144.2 (sept, <sup>1</sup>J<sub>PF</sub> = 706.3 Hz). ESI-MS (CH<sub>3</sub>CN): m/z 616.94 (calcd. 616.97) [C<sub>23</sub>H<sub>27</sub>FeI<sub>2</sub>N<sub>3</sub>Rh]<sup>+</sup>.

1,3-Dihydro-(( $\eta^5$ -cyclopentadienyl)(1- $\eta^6$ -phenyl)iron(II))-3-methyl-2H-imidazole-2-selone hexafluorophosphate (**9f**): 50.0 mg (93.2  $\mu$ mol) of **2f**, 19.8 mg (168  $\mu$ mol) of potassium *tert*-butoxide and 30 mg (380  $\mu$ mol) of elemental selenium were stirred for 16 h at room temperature in 1 mL of tetrahydrofuran. After removal of the solvent under vacuum, 2 mL of dichloromethane were added and the resulting suspension was filtered through a pad of Celite<sup>®</sup>. Removal of the solvent under vacuum gave the desired selone as a dark red solid in quantitative yield (52.0 mg). Anal. calcd. for C<sub>21</sub>H<sub>19</sub>F<sub>6</sub>FeN<sub>2</sub>PSe (579.17): C 43.55, H 3.31, N 4.84; found: C 43.60, H 3.58, N 4.92%. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):  $\delta$  7.56 (d, <sup>3</sup>J<sub>HH</sub> = 2.5 Hz, H-7, 1H), 7.47–7.33 (m, H-benzyl, 5H), 7.32 (d, <sup>3</sup>J<sub>HH</sub> = 2.5 Hz, H-6, 1H), 7.06 (d, <sup>3</sup>J<sub>HH</sub> = 6.5 Hz, H-4, 2H), 6.46 (t, <sup>3</sup>J<sub>HH</sub> = 6.5 Hz, H-3, 2H), 6.33 (t, <sup>3</sup>J<sub>HH</sub> = 6.1 Hz, H-2, 1H), 5.44 (s, H-9, 2H), 5.15 (s, H-1, 5H). <sup>13</sup>C NMR (151 MHz, CD<sub>3</sub>CN):  $\delta$  160.9 (C-8), 136.8 (C-10), 129.7 (C-11), 129.2 (C-13), 129.1 (C-12), 122.4 (C-7), 121.2 (C-6), 109.5 (C-5), 88.6 (C-2), 87.7

(C-3), 86.4 (C-4), 79.1 (C-1), 53.4 (C-9). <sup>31</sup>P NMR (162 MHz, CD<sub>3</sub>CN):  $\delta$  -146.81 (sept, <sup>1</sup>J<sub>PF</sub> = 706.3 Hz). <sup>77</sup>Se NMR (114 MHz, CD<sub>3</sub>CN):  $\delta$  77.9 (s). ESI-MS (CH<sub>3</sub>CN): m/z 434.94 (calcd. 435.01) [C<sub>21</sub>H<sub>19</sub>FeN<sub>2</sub>Se]<sup>+</sup>. *Safety Note: selenium is highly toxic, especially when inhaled. The experiments were carried out in a well-ventilated fume hood and with adequate protective equipment. All materials contaminated with selenium were collected and disposed via a separate waste stream.*

**X-ray structure analyses:** Crystal data and refinement parameters are collected in Table S1. All structures were solved using direct method, SIR92 for **7a** and **8a**,<sup>[36]</sup> and SHELXT for **6a**,<sup>[37]</sup> completed by subsequent difference Fourier syntheses, and refined against *F*<sup>2</sup> by full-matrix least-squares procedures.<sup>[38]</sup> Numerical absorption correction based on gaussian integration was applied to **7a** and **8a**.<sup>[39]</sup> Semi-empirical absorption correction from equivalents was used for complex **6a**.<sup>[40]</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed on idealized positions and refined by using a riding model.

Deposition Numbers 2151845 (for **6a**), 2151846 (for **7a**), and 2151847 (for **8a**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures).

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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