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Metal-assisted conversion of an *N*-ylide mesomeric betaine into its carbenic tautomer: generation of *N*-(fluoren-9-yl)imidazol-2-ylidene complexes†

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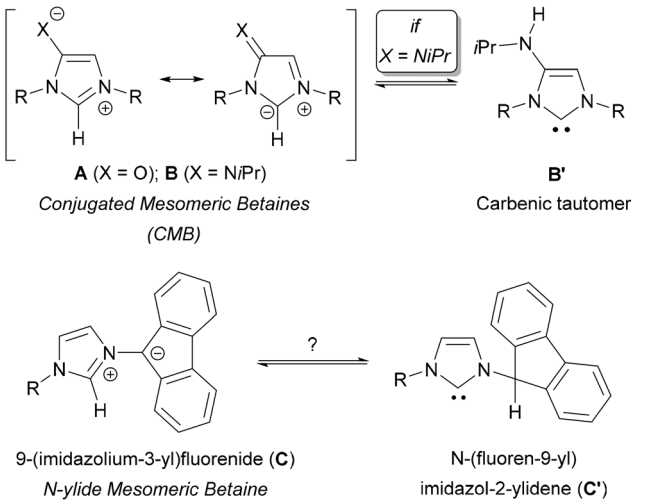
Whereas the *N*-ylide mesomeric betaine **2**, consisting of a fluorenyl anion directly attached to an imidazolium ring, is not in equilibrium with its putative free *N*-(fluoren-9-yl)imidazol-2-ylidene tautomer, its reaction with a metallic centre induces its interconversion to yield the corresponding monoligated N-heterocyclic carbene complex (Au(I) and Rh(I)). Deprotonation of **2** and coordination to the Rh^{I}(COD) fragment allows the isolation of complex **7** displaying a rarely observed four-membered NHC-containing metallacycle and an enforced η^1-fluorenyl ligand. Upon reaction with $CpFe(CO)_2I$ precursor, insertion of a carbonyl ligand into the Fe–fluorenyl bond occurs and yields the acyl–Fe complex **8**.

Introduction

The growing success story of N-heterocyclic carbenes (NHCs)[1,2] during the past two decades is certainly due to the breadth of their applicability to various domains of chemistry. Indeed, while being extensively developed as highly donating and sterically protecting ligands in organometallic chemistry and catalysis,[3] they are also of high interest in their own right as organocatalysts[4] and as stabilizing agents for elusive polyatomic main group allotropes.[5] The advent of well established synthetic methods for these NHCs, allowing a facile functionalization of their heterocyclic framework,[6] has been beneficial to all these developments, giving access to, *inter alia*, chiral,[7] electronically tunable,[8] or polydentate/polytopic[9] carbenic architectures.

In this respect, we are interested in the conceptual design of backbone-functionalized NHCs combining a diaminocarbene unit with a functional organic backbone such as malonate,[10] imidate,[11] enolate[12] or enamine.[13] A recurrent characteristic of these carbenic structures, potentially useful in a retrosynthetic approach, is their relationship with mesomeric betaines, defined long ago as neutral compounds which can exclusively be represented by dipolar canonical formulas, in which the positive and negative charges are delocalized within a common π-electron system.[14,15] In particular, our previously reported mesoionic compounds **A** and **B** both belong to the subclass of conjugated mesomeric betaines (CMB), and we have shown that the imidazolium-4-aminide **B** is in tautomeric equilibrium with the free 4-(isopropylamino)imidazol-2-ylidene **B′** (Scheme 1).[16] Schmidt reported very recently an



Scheme 1 Conjugated mesomeric betaines **A** and **B**, in equilibrium with the free NHC tautomer **B′** and relevant system **C**/**C′** considered here.

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(imidazolium)indolate, existing in equilibrium with its free NHC tautomer and belonging to the subclass of *N*-ylides related to the CMB.[14a] With the aim of expanding this growing family of compounds, we thus became interested in studying the chemistry of the *N*-ylide **C**, constituted by a fluorenide anion directly linked (through the C_9 position) to a nitrogen of the imidazolium ring, and its possible interconversion with its free NHC tautomeric form **C′**. A closely related system, albeit with an ethylene linker, has been previously reported by Danopoulos and colleagues and shown to involve an equilibrium between the zwitterionic imidazolium–fluorenide form and the free neutral (fluorenylethyl)imidazol-2-ylidene.[17]

Herein, we describe the synthesis and reactivity of an archetype of 9-(imidazolium-3-yl)fluorenide, belonging to the *N*-ylide subclass of mesomeric betaines. We also show that, even though it does not interconvert into its free NHC tautomer, it constitutes a suitable precursor to a complexed form of the latter with various transition metals. In addition, the coordination behaviour of the fully-deprotonated anionic *N*-(fluorenide)imidazol-2-ylidene is reported and leads to the observation of a chelating mode for this new anionic bidentate ligand.

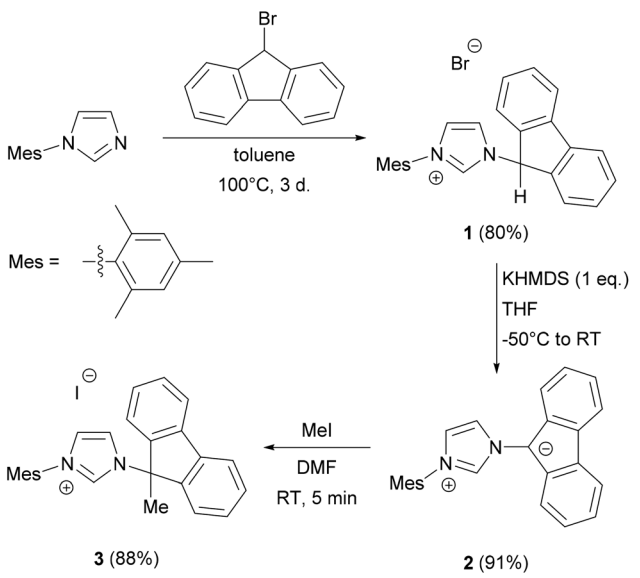
Results and discussion

The *N*-(fluoren-9-yl)imidazolium bromide **1** was prepared in 80% yield by quaternization of 1-mesitylimidazole with 9 bromofluorene upon heating the two reagents in toluene (Scheme 2). The ionic compound **1** was seen to precipitate along the reaction course and was subsequently purified by simple washings with a THF–Et_2O mixture. Mono-deprotonation of **1** cleanly took place with 1 equiv. of potassium bis(trimethylsilyl)amide (KHMDS) in THF at low temperature. Noticeably, alternate attempts to use other bases such as DBU or KO*t*Bu and/or operating at higher temperature were less efficient, leading to the desired compound, albeit with considerable amounts of impurities. Under our optimized conditions, the mesomeric betaine **2** was isolated as an intensively orange-coloured powder in excellent yield (91%), and was found to be extremely air-sensitive and well-soluble only in CH_2Cl_2. Its formulation as an imidazolium–fluorenide betaine was inferred from the disappearance of the signal corresponding to the proton on position 9 of the fluorenyl group in the ^{1}H NMR spectrum and from the occurrence of a set of three signals at δ = 8.12, 7.94 and 7.22 ppm, being characteristic of the three protons of the imidazolium ring. In the ^{13}C NMR spectrum, the quaternary sp^2-type C_9 carbon atom of the fluorenide unit appeared to be relatively deshielded at δ = 92.5 ppm with respect to the sp^3-hybridized *C*H carbon atom in **1** (δ = 63.3 ppm). Most importantly, we performed a VT NMR experiment to determine if the betaine **2** might be in equilibrium with its free NHC tautomer. Clearly, the ^{1}H NMR spectra recorded in the −70 °C–25 °C range, revealed no signal broadening, thereby indicating that no equilibrium with the free NHC form was taking place.

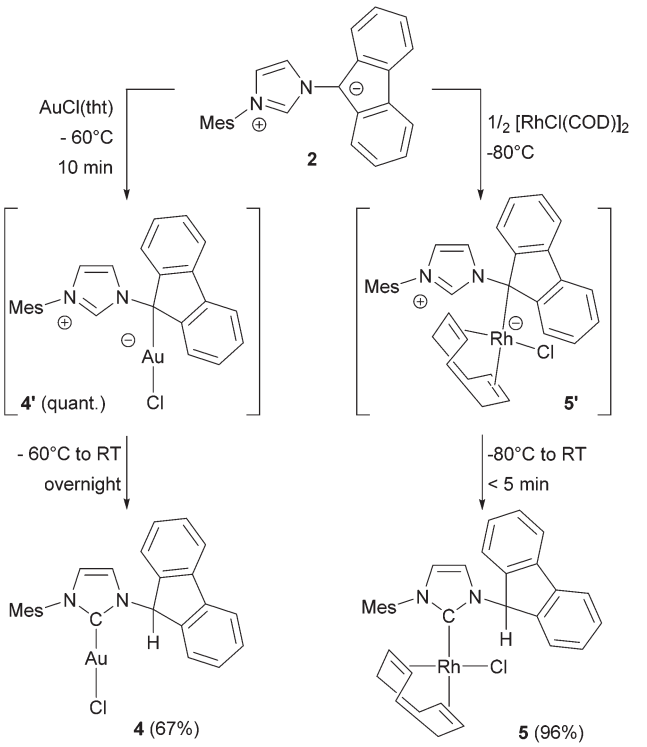
Further evidence for the total absence of a free NHC was provided by reacting compound **2** with sulphur or carbon disulfide – two classical trapping reagents of a free NHC – both reactions yielding only intractable mixtures and decomposition products. Moreover, the pronounced ylidic character of the betaine **2** could be illustrated by its reaction with methyl iodide, leading to rapid and selective methylation at the fluorenyl position to yield cleanly the imidazolium iodide **3**.

We next turned our attention toward a possible use of the betaine **2** as a precursor for the synthesis of N-heterocyclic carbene complexes, and started our investigations with a gold(I) precursor (Scheme 3). To our delight, addition of 1 equivalent of AuCl(tht) to a solution of **2** in CH_2Cl_2 at −60 °C followed by warming to room temperature yielded the desired NHC–gold(I) complex **4** in good yield (67%). Its identity was established by the ^{1}H and ^{13}C NMR spectra, revealing the presence, respectively, of a singlet at δ = 7.02 ppm corresponding to the fluorenyl-proton, and of a signal at δ = 173.2 ppm typical of an AuCl-ligated imidazol-2-ylidene.[18] The connectivity in **4** was also firmly confirmed by the analysis of its solid-state molecular structure (Fig. 1), in which the Au–C distance [1.987(4) Å] falls into the normal range of Au–imidazolylidene bond lengths.

In order to gain more insight into the mechanism of formation of complex **4**, a low temperature NMR experiment was carried out aiming at detecting any intermediate. Thus, AuCl(tht) was added at low temperature to a solution of **2** in CD_2Cl_2 and the ^{1}H and ^{13}C NMR spectra of the reaction mixture were directly recorded at −60 °C (see the ESI†). They were both found to be fully consistent with the clean and almost quantitative formation of the zwitterionic complex **4′**, where the AuCl unit is linked to the fluorenyl carbon atom forming an anionic alkyl–gold(I) complex, placed in close proximity of the cationic imidazolium ring. Diagnostic signals for such a formulation consist of a singlet at δ = 9.36 ppm and



Scheme 2 Synthesis and reactivity of the mesomeric betaine **2**.



Scheme 3 Complexation of the betaine **2** with Au(I) and Rh(I) centres leading to NHC-complexes **4** and **5** respectively (tht = tetrahydrothiophene).

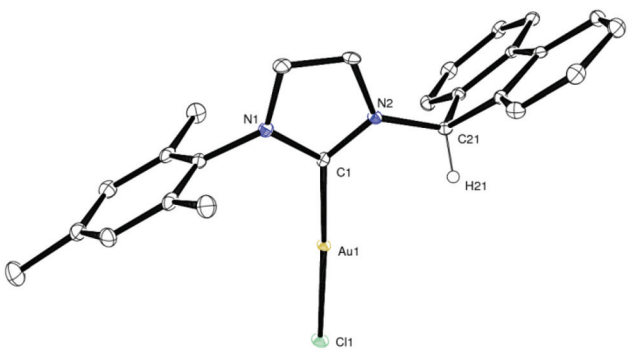


Fig. 1 Molecular structure of **4** (ellipsoids drawn at 30% probability level). All hydrogen atoms except on C21 have been omitted for clarity. Selected bond lengths [Å]: Au1–C1 1.987(4), Au1–Cl1 2.2794(10). Selected bond angle [°]: C1–Au1–Cl1 177.17(12).

a signal at δ = 138.3 ppm in the ^{1}H and ^{13}C NMR spectra respectively, corresponding to the pre-carbenic position of the imidazolium ring. In addition, we were able to detect in the solution the presence of free tetrahydrothiophene, resulting from its displacement by the fluorenide ligand. Complex **4′** was found to isomerise cleanly into the NHC-complex **4** upon warming the NMR tube up to room temperature.

The reaction between the betaine **2** and half an equivalent of [RhCl(COD)]$_2$ was found to be very rapid at room temperature and gave the expected imidazolylidene–rhodium(I) complex **5** in excellent yield (96%) (Scheme 3). The latter was

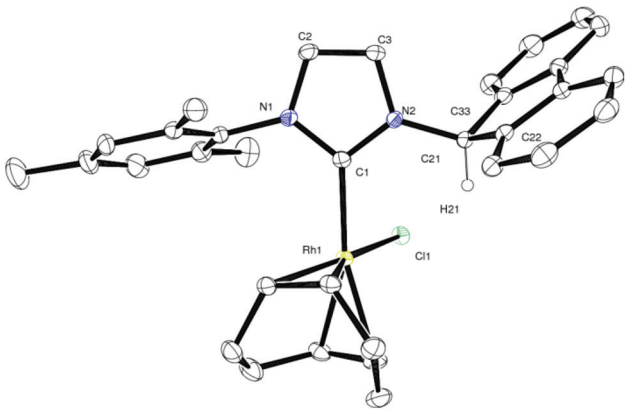
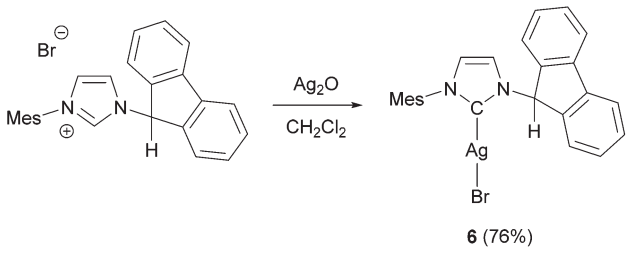


Fig. 2 Molecular structure of complex **5** (ellipsoids drawn at 30% probability level). Solvent molecule and hydrogen atoms except on C21 have been omitted for clarity. Selected bond length [Å]: Rh1–C1 2.043(3). Selected bond angles [°]: N2–C21–C22 114.3(2), N2–C21–C33 111.6(2), C22–C21–C33 102.4(2). Selected torsion angle [°]: N1–C1–Rh1–Cl1 115.07.

fully characterized spectroscopically and analytically, including by an X-ray diffraction analysis (Fig. 2). In order to establish the transition through the intermediate alkyl–rhodium(I) complex **5′**, the same low-temperature NMR experiment as for **4′** was carried out. Despite being stable for several hours at −80 °C, complex **5′** was seen to interconvert rapidly into its NHC–rhodium(I) tautomer **5** at slightly higher temperatures, since one half of complex **5′** was transformed into **5** during the time of introduction of the NMR tube in the spectrometer (see the ESI†). Nevertheless, its nature was firmly confirmed by a complete NMR analysis and especially by the presence of broad signals at δ = 9.18 ppm and δ = 137.4 ppm in the ^{1}H and ^{13}C NMR spectra respectively corresponding to the N_2CH proton and N_2CH carbon of the imidazolium ring and by the appearance of a doublet at δ = 73.8 ppm ($^{1}J_{Rh-C}$ = 20.1 Hz) characteristic of the coordination of the fluorenyl C_9 onto the Rh(I) center. Although not proven, two plausible alternative mechanistic pathways can be reasonably proposed for this interconversion. The first one may proceed *via* a two-step sequence consisting of (i) a protonolysis of the alkyl–metal bond by the acidic proton of the imidazolium,[19] *in situ* generating the carbene, and (ii) the immediate trapping of the latter by the neighbouring metal centre. The alternate possibility would involve an intramolecular proton-transfer between the imidazolyl and the fluorenyl carbon atoms, in a manner similar to that operating in the exchange between sp^2- and sp^3-hybridized carbon atoms on Pd(II) and Pt(II) centers.[20] This process may occur through the σ-CAM mechanism proposed by Perutz and Sabo-Etienne, although the intermediacy of a Rh(III) intermediate through an oxidative addition–reductive elimination sequence cannot be totally excluded in the rhodium case.[21]

More classically, the imidazolylidene–silver(I) complex **6** could be obtained directly from the imidazolium salt **1** using the well-known procedure first described by Lin,[22] employing silver oxide (Scheme 4). Its molecular structure is depicted in



Scheme 4 Synthesis of the silver(I) complex **6**.

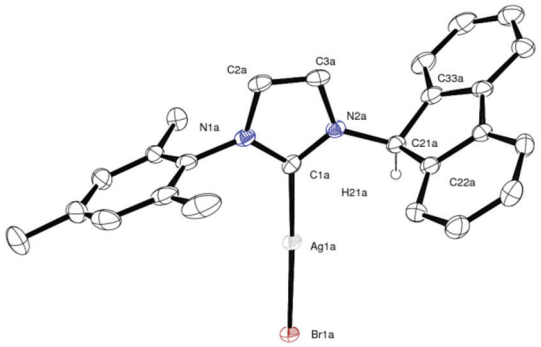
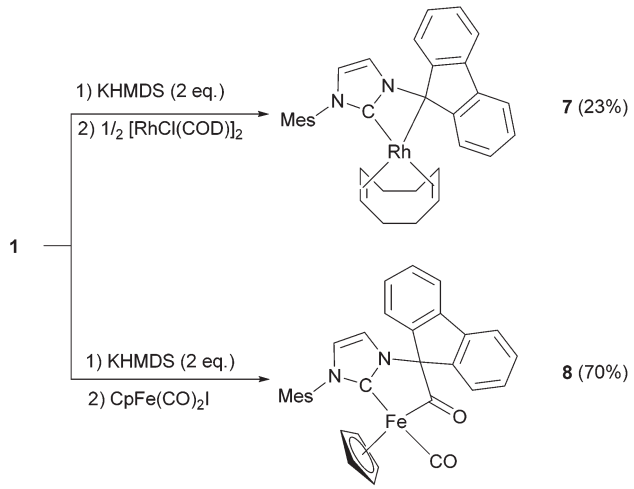


Fig. 3 Molecular structure of complex **6** (molecule **A**,[23] ellipsoids drawn at 30% probability level). All hydrogen atoms except on C21a have been omitted for clarity. Selected bond length [Å]: Ag1a–C1a 2.103(4). Selected bond angles [°]: C1a–Ag1a–Br1a 172.76(9), N2a–C21a–C22a 111.5(3), N2a–C21a–C33a 114.9(3), C22a–C21a–C33a 102.7(3).

Fig. 3. As expected, we observed that complex **6** functions as a carbene-transfer agent with $[RhCl(COD)]_2$ to form complex **5** albeit with *ca.* 5% contamination by its bromide-analogue.

The coordination properties of the anionic *N*-(fluorenide)-imidazol-2-ylidene was then investigated, as the strongly binding NHC ligand might influence the coordination mode (η^1, η^3 or η^5) of the fluorenyl anion,[24] as previously observed by Bourissou and colleagues with a phosphazene side arm on the fluorenyl.[25] Hence, after a double deprotonation, the imidazolium bromide **1** was reacted with 0.5 equivalent of $[RhCl(COD)]_2$ at low temperature (Scheme 5). The resulting complex **7** was isolated in 23% yield after separation of the inorganic salts and crystallisation. The low isolated yield can be ascribed to the high solubility of complex **7** in organic solvents such as toluene or Et_2O, making less efficient the purification process. The ^1H NMR spectrum of **7** featuring a symmetry-plane in the molecule was in agreement with the occurrence of a bidentate coordination mode for the anionic NHC ligand, and the latter was definitely established from the ^{13}C NMR spectrum, in which the N_2C carbene and the fluorenyl C_9 carbon atoms resonate as doublets at δ = 160.8 ppm ($^1J_{Rh-C}$ = 44.3 Hz) and δ = 63.5 ppm ($^1J_{Rh-C}$ = 10.7 Hz) respectively. This spectrum provided also a first evidence for the η^1-coordination mode of the fluorenyl ligand as the other quaternary carbon atoms appear as singlets. This was unambiguously confirmed by the solid-state molecular structure of **7** (Fig. 4). Complex **7** represents a rare example of an NHC-containing four-membered



Scheme 5 Coordination behaviour of the anionic *N*-(fluorenide)imidazol-2-ylidene ligand toward Rh(I) and Fe(II) centres.

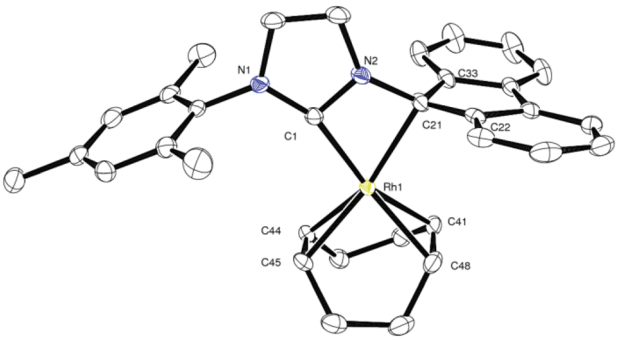


Fig. 4 Molecular structure of the rhodium(I) complex **7** (ellipsoids drawn at 30% probability level). Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å]: Rh1–C1 2.037(2), Rh1–C21 2.2148(18). Selected bond angles [°]: C1–Rh1–C21 65.26(7), N1–C1–Rh1 156.70(14), N2–C1–Rh1 97.60(13), N2–C21–C22 123.74(16), N2–C21–C33 118.14(17), C22–C21–C33 105.65(16).

metallacycle.[26] The rhodium(I) centre adopts a distorted square-planar geometry, with a (κ-C,κ-C) metal coordination and an extraordinarily small bite angle [C1–Rh1–C21 65.26(7)°]. The fluorenyl moiety effectively coordinates the Rh(I) centre in an η^1-fashion, substantiated by the Rh1–C21 bond length [2.2148(18) Å] comparable to the one previously reported by Bourissou (Rh–C 2.188(3) Å), by the significant pyramidalization of the C21 atom ($\sum C_{21\alpha}$ = 347.53°) and by the remoteness of the other carbons (C22 and C33 in particular) from the Rh centre (>3 Å).

An interesting reactivity was observed when this anionic *N*-(fluorenide)imidazol-2-ylidene was reacted with the carbonyl complex $CpFe(CO)_2I$ (Scheme 5). Indeed, the presence of only one $\nu_{C\equiv O}$ stretching band at 1923 cm^{-1} in the IR spectrum of the crude product (recorded in THF) clearly suggested that only one carbonyl ligand remains coordinated to the iron centre. The appearance of a band at 1669 cm^{-1} typical of a $\nu_{C=O}$ stretching band provided conclusive evidence that the

second carbonyl had been inserted into the transient Fe–fluorenyl bond. This was firmly confirmed in particular by the ^{13}C NMR spectrum revealing a highly-deshielded signal at δ = 257.8 ppm corresponding to the carbon atom of an iron-bound acyl group.

Conclusions

The existence of known cases where a conjugated mesomeric betaine can be visualized as a masked carbene through a simple tautomeric H-shift is an interesting source of inspiration for the conceptual design of new carbenic architectures. In our initial attempts to apply this to 9-(imidazolium-3-yl)-fluorenide, readily available in high yield by simply grafting a fluorenyl arm to 1-mesitylimidazole, we were first slightly frustrated by the fact that such a compound exists only in the form of the *N*-ylide mesomeric betaine. Gratifyingly, however, we were led to observe that it reacts spontaneously at low temperature with Au(I) and Rh(I) precursors to afford primarily new alkyl complexes in which the *N*-ylide is first bound through the fluorenide C_9, and subsequently undergoes a "metal-assisted" isomerisation leading to an *N*-(fluoren-9-yl)imidazol-2-ylidene complex. Further de-protonation of the fluorenyl side arm can be made to occur in specific cases, as illustrated by the generation of a rhodium complex in which the anionic *N*-(fluoren-9-ide)imidazol-2-ylidene is forming an uncommon four-membered chelate through its coordination *via* the carbenic center and the alkyl center. Not surprisingly, CO insertion in the metal–alkyl bond was also observed when the ligand was reacted with carbonyl derivatives such as $CpFe(CO)_2I$. On account of these observations, it may be anticipated that the *N*-(fluoren-9-ide)imidazol-2-ylidene ligand will have a promising future for the design of a variety of new transition-metal pre-catalysts.

Experimental section

General considerations

All manipulations were performed under an inert atmosphere of dry nitrogen using a standard vacuum line and Schlenk tube techniques. Glassware was dried at 120 °C in an oven for at least three hours. THF and diethyl ether were distilled from sodium/benzophenone, toluene from sodium. Pentane, dichloromethane and chloroform were dried over CaH_2 and subsequently distilled. NMR spectra were recorded on Bruker ARX250, AV300 or AV400 spectrometers. Chemical shifts are reported in ppm (δ) compared to TMS (^1H and ^{13}C) using the residual peak of a deuterated solvent as the internal standard.[27] Infrared spectra were obtained on a Perkin-Elmer Spectrum 100 FT-IR spectrometer. MS spectra were performed by the mass spectrometry service of the "Institut de Chimie de Toulouse". $CpFe(CO)_2I$[28] and *N*-mesitylimidazole[29] were synthesized following literature procedures.

1-Mesityl-3-(fluoren-9-yl)imidazolium bromide (1). A solution of 1-mesitylimidazole (2.16 g, 11.6 mmol) and 9-bromofluorene (3.13 g, 12.8 mmol, 1.1 eq.) in toluene (50 mL) was stirred at 100 °C for 3 days. A white solid precipitated along the reaction course. After cooling to room temperature, the reaction mixture was poured into Et_2O (70 mL), filtered through a fritted funnel and the solid was washed several times with a THF–Et_2O mixture (1/5 v/v, 30–40 mL) until the solution became clear (usually 3 times). After drying, the pure product was isolated as an off-white powder (4.0 g, 80%). mp = 267–268 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 11.43 (s, 1H, N_2CH), 7.83 (s, 1H, $CH_{Flu\text{-}9}$), 7.77 (d, J = 7.7 Hz, 2H, CH_{Flu}), 7.64 (d, J = 7.6 Hz, 2H, CH_{Flu}), 7.51–7.47 (m, 2H, CH_{Flu}), 7.37–7.33 (m, 2H, CH_{Flu}), 7.03 (br, 3H, CH_{Mes} + CH_{Im}), 6.84 (t, J = 1.8 Hz, 1H, CH_{Im}), 2.36 (s, 3H, $CH_{3\ para}$), 2.14 (s, 6H, $CH_{3\ ortho}$); $^{13}C\{^1H\}$ NMR (105.5 MHz, $CDCl_3$): δ = 141.5, 140.9, 140.0 (C_{Ar}), 139.5 (N_2CH), 134.1 (C_{Ar}), 130.5, 130.0, 128.9 (2 CH_{Flu} + CH_{Mes}), 125.7 (CH_{Flu}), 123.3 (CH_{Im}), 120.7 (CH_{Flu}), 120.0 (CH_{Im}), 63.2 ($CH_{Flu\text{-}9}$), 21.1 ($CH_{3\ para}$), 17.7 ($CH_{3\ ortho}$); IR (ATR): ν = 3024, 2947, 2897, 1606, 1559, 1537, 1482, 1448, 1378, 1275, 1199, 1149, 1058, 1030, 850, 747 cm^{-1}; MS (ESI): m/z (%): 351 (100) $[M - Br]^+$, 165 (30) $[fluorenyl]^+$; elemental analysis calcd (%) for $C_{25}H_{23}BrN_2$ (M_W = 431.37): C 69.61, H 5.37, N 6.49; found: C 69.17, H 5.23, N 6.35.

1-Mesityl-3-(fluorenide-9-yl)imidazolium (2). A solution of KHMDS (0.5 M in toluene, 4.86 mL, 2.44 mmol, 1.05 eq.) was added dropwise to a suspension of **1** (1.0 g, 2.32 mmol) in THF (20 mL) at −50 °C. After 1 hour, the cooling bath was removed and the mixture was allowed to warm up to room temperature. Volatiles were removed under vacuum and the orange crude product was taken up in CH_2Cl_2 (15 mL) and filtered through Celite. After evaporation, the orange solid was washed with pentane (2 × 5 mL) and Et_2O (5 mL) to yield an orange powder after drying (740 mg, 91%). ^1H NMR (400 MHz, CD_2Cl_2): δ = 8.28 (s, 1H, N_2CH), 8.12 (d, J = 7.8 Hz, 2H, CH_{Flu}), 7.94 (s, 1H, CH_{Im}), 7.50 (d, J = 8.2 Hz, 2H, CH_{Flu}), 7.25–7.20 (m, 2H, CH_{Flu}), 7.22 (s, 1H, CH_{Im}), 7.13 (s, 2H, CH_{Mes}), 6.87–6.83 (m, 2H, CH_{Flu}), 2.42 (s, 3H, $CH_{3\ para}$), 2.19 (s, 6H, $CH_{3\ ortho}$); $^{13}C\{^1H\}$ NMR (105.5 MHz, CD_2Cl_2): δ = 141.4, 135.5, 132.3, 131.8 (C_{Ar}), 130.2 (CH_{Mes}), 129.4 (N_2CH), 124.4 (CH_{Flu}), 122.8 (CH_{Im}), 122.6 (CH_{Flu}), 122.0 (C_{Ar}), 120.1 (CH_{Im}), 112.9 (CH_{Flu}), 111.0 (CH_{Flu}), 92.5 ($C^-_{Flu\text{-}9}$), 21.5 ($CH_{3\ para}$), 17.8 ($CH_{3\ ortho}$); IR (ATR): ν = 3155, 3111, 3034, 2972, 2916, 1608, 1574, 1528, 1474, 1441, 1322, 1222, 1140, 1113, 1093, 1059, 1028, 986, 850, 742, 721, 666 cm^{-1}.

1-Mesityl-3-(9-methylfluoren-9-yl)imidazolium iodide (3). At room temperature, methyl iodide (33 μL, 0.52 mmol, 1.5 eq.) was added to a solution of the zwitterion **2** (123 mg, 0.350 mmol) in DMF (2 mL). The reaction was monitored by ^1H NMR and quantitative conversion was observed after 5 min of reaction. All volatiles were then evaporated and the residue was washed with Et_2O (3 × 5 mL) in air and using an ultrasonic bath. Further purification by flash chromatography (SiO_2, CH_2Cl_2–MeOH: 95/5) furnished the product in pure analytical form as a very pale beige powder (151 mg, 88%). ^1H NMR (300 MHz, $CDCl_3$): δ = 10.47 (s, 1H, N_2CH), 7.79–7.75 (m, 4H,

3 CH_{Flu} + CH_{Im}), 7.54–7.49 (m, 2H, CH_{Flu}), 7.44–7.39 (m, 2H, CH_{Flu}), 7.10 (br, 1H, CH_{Im}), 7.09–7.08 (m, 1H, CH_{Flu}), 7.00 (br, 2H, CH_{Mes}), 2.61 (s, 3H, C$H_{3\ Flu\text{-}9}$), 2.32 (s, 3H, C$H_{3\ para}$), 2.12 (s, 6H, C$H_{3\ ortho}$); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 145.0, 141.6, 139.3 (C_{Ar}), 137.3 (N_2CH), 134.2 (C_{Ar}), 130.8, 130.1, 129.6 (2 CH_{Flu} + CH_{Mes}), 124.3 (CH_{Flu}), 124.0, 121.5 (CH_{Im}), 121.1 (CH_{Flu}), 71.8 ($C(CH_3)_{Flu\text{-}9}$), 25.6 ($CH_{3\ Flu\text{-}9}$), 21.3 ($CH_{3\ para}$), 18.2 ($CH_{3\ ortho}$); IR (ATR): ν = 3168, 3118, 3073, 2971, 1606, 1534, 1478, 1444, 1216, 1186, 1154, 1087, 1031, 994, 878, 845, 770, 744, 735 cm^{-1}; MS (ESI): *m*/*z* (%): 365 (100) $[M - I]^+$, 187 (56) $[Mes - ImH]^+$; elemental analysis calcd (%) for $C_{26}H_{25}IN_2$ (M_W = 492.40): C 63.42, H 5.12, N 5.69; found: C 63.20, H 5.08, N 5.55.

(1-Mesityl-3-(fluoren-9-yl)imidazol-2-ylidene)gold(I) chloride (4). Solid AuCl(tht) (63 mg, 0.196 mmol) was added all at once into a solution of **2** (75 mg, 0.214 mmol, 1.1 eq.) in CH_2Cl_2 (5 mL) at −60 °C. The solution was allowed to warm up to room temperature overnight. Volatiles were removed under vacuum and the yellow residue was purified by flash chromatography (SiO_2, hexane–CH_2Cl_2: 1/1) to yield the product as a white powder (76 mg, 67%). X-Ray-quality crystals were grown by slow diffusion of pentane into a CH_2Cl_2 solution of **4**. ^1H NMR (400 MHz, CD_2Cl_2): δ = 7.84 (d, *J* = 7.6 Hz, 2H, CH_{Flu}), 7.59–7.56 (m, 2H, CH_{Flu}), 7.55–7.51 (m, 2H, CH_{Flu}), 7.38 (td, *J* = 7.5 Hz, *J* = 1.1 Hz, 2H, CH_{Flu}), 7.08 (s, 2H, CH_{Mes}), 7.02 (s, 1H, C$H_{Flu\text{-}9}$), 6.86 (d, *J* = 2.0 Hz, 1H, CH_{Im}), 6.54 (d, *J* = 2.0 Hz, 1H, CH_{Im}), 2.39 (s, 3H, C$H_{3\ para}$), 2.13 (s, 6H, C$H_{3\ ortho}$); $^{13}C\{^1H\}$ NMR (105.5 MHz, CD_2Cl_2): δ = 173.2 (N_2C), 141.9, 141.1, 140.4, 135.4, 135.2 (C_{Ar}), 130.3, 129.7, 128.7 (2 CH_{Flu} + CH_{Mes}), 125.3 (CH_{Flu}), 123.5 (CH_{Im}), 121.0 (CH_{Flu}), 118.6 (CH_{Im}), 65.4 ($CH_{Flu\text{-}9}$), 21.3 ($CH_{3\ para}$), 18.0 ($CH_{3\ ortho}$); IR (ATR): ν = 3159, 3133, 3039, 2916, 1722, 1606, 1553, 1486, 1446, 1418, 1407, 1377, 1304, 1224, 1211, 1031, 950, 856, 824, 739, 734, 696 cm^{-1}; MS (ESI): *m*/*z* (%): 588 (100) $[M - Cl + MeCN]^+$; elemental analysis calcd (%) for $C_{25}H_{22}AuCl$ (M_W = 582.87) + 0.75 CH_2Cl_2: C 47.83, H 3.66, N 4.33; found: C 47.80, H 3.65, N 4.18.

(9-(1-Mesitylimidazolium-3-yl)fluoren-9-yl)gold(I) chloride (4′). Solid AuCl(tht) (25 mg, 0.078 mmol) was added all at once into a solution of **2** (29 mg, 0.083 mmol, 1.05 eq.) in CD_2Cl_2 (0.8 mL) at −80 °C. The reaction mixture was then transferred to a NMR tube placed in a cold bath at −80 °C. The NMR tube was kept at this temperature until its introduction into the NMR spectrometer with the probe temperature set up and stabilized at 214 K. The following NMR data were recorded at this temperature. ^1H NMR (400 MHz, CD_2Cl_2, 214 K): δ = 9.36 (s, 1H, N_2CH), 7.82–7.76 (m, 2H, CH_{Flu}), 7.41–7.37 (m, 2H, CH_{Flu}), 7.35–7.28 (m, 4H, CH_{Flu}), 7.06 (s, 1H, CH_{Im}), 7.05 (s, 2H, CH_{Mes}), 6.60 (s, 1H, CH_{Im}), 2.34 (s, 3H, C$H_{3\ para}$), 2.05 (s, 6H, C$H_{3\ ortho}$); $^{13}C\{^1H\}$ NMR (105.5 MHz, CD_2Cl_2, 214 K): δ = 148.7, 140.9 (C_{Ar}), 138.3 (N_2CH), 136.0, 134.3, 130.3 (C_{Ar}), 129.2 (CH_{Mes}), 126.6 (CH_{Flu}), 126.1 (CH_{Flu}), 123.7 (CH_{Im}), 123.2 (CH_{Flu}), 121.9 (CH_{Im}), 120.1(CH_{Flu}), 71.1 (Au-$C_{Flu\text{-}9}$), 20.9 ($CH_{3\ para}$), 17.3 ($CH_{3\ ortho}$).

Chloro-(η⁴-cycloocta-1,5-diene)-(1-mesityl-3-(fluoren-9-yl)-imidazol-2-ylidene) rhodium(I) (5). Solid $[RhCl(1,5\text{-}COD)]_2$ (102 mg, 0.206 mmol) was added all at once into a solution of mesoionic **2** (159 mg, 0.453 mmol, 2.2 eq.) in CH_2Cl_2 (12 mL) at room temperature. The reaction was complete after less than 30 min as judged by TLC and all volatiles were removed under vacuum. The residue was purified by flash chromatography (neutral Al_2O_3, Brockmann's type 3, hexane–CH_2Cl_2: 2/1 then 1/1) to yield a yellow powder (235 mg, 96%). X-Ray-quality crystals were grown by slow diffusion of pentane into a $CHCl_3$ solution of **5**. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.27 (d, *J* = 8.2 Hz, 1H, CH_{Flu}), 8.12 (s, 1H, C$H_{Flu\text{-}9}$), 7.82 (d, *J* = 7.5 Hz, 1H, CH_{Flu}), 7.76 (d, *J* = 7.5 Hz, 1H, CH_{Flu}), 7.50–7.42 (m, 3H, CH_{Flu}), 7.36–7.33 (m, 2H, CH_{Flu}), 7.14 (s, 1H, CH_{Mes}), 6.96 (s, 1H, CH_{Mes}), 6.64 (d, *J* = 1.9 Hz, 1H, CH_{Im}), 6.30 (d, *J* = 1.9 Hz, 1H, CH_{Im}), 5.00–4.96 (m, 1H, CH_{COD}), 4.91–4.87 (m, 1H, CH_{COD}), 3.86–3.82 (m, 1H, CH_{COD}), 3.27–3.24 (m, 1H, CH_{COD}), 2.54 (s, 3H, C$H_{3\ Mes}$), 2.45–2.36 (m, 1H, CH_{2COD}), 2.41 (s, 3H, C$H_{3\ Mes}$), 2.18–1.95 (m, 3H, CH_{2COD}), 1.90 (s, 3H, C$H_{3\ Mes}$), 1.85–1.58 (m, 3H, CH_{2COD}), 1.33–1.24 (m, 3H, CH_{2COD}); $^{13}C\{^1H\}$ NMR (105.5 MHz, $CDCl_3$): δ = 184.0 (d, $J_{Rh\text{–}C}$ = 51.2 Hz, N_2C), 144.1, 143.4, 141.3, 140.3, 138.9, 138.8, 137.4, 136.2, 134.5 (C_{Ar}), 129.8 (CH_{Mes}), 129.3, 129.2, 128.6, 128.3 (CH_{Flu}), 127.9 (CH_{Mes}), 127.8 (CH_{Flu}), 124.2 (CH_{Im}), 124.1, 120.5, 119.7 (CH_{Flu}), 118.8 (CH_{Im}), 98.1 (d, $J_{Rh\text{–}C}$ = 7.5 Hz, CH_{COD}), 97.6 (d, $J_{Rh\text{–}C}$ = 6.9 Hz, CH_{COD}), 68.6 (d, $J_{Rh\text{–}C}$ = 14.3 Hz, CH_{COD}), 68.3 (d, $J_{Rh\text{–}C}$ = 14.3 Hz, CH_{COD}), 66.0 ($CH_{Flu\text{-}9}$), 33.9, 32.0, 29.0, 28.3 (CH_{2COD}), 21.5, 19.9, 17.9 ($CH_{3\ Mes}$); IR (ATR): ν = 2953, 2916, 2869, 2828, 1607, 1489, 1450, 1381, 1301, 1233, 1220, 955, 860, 824, 732, 697 cm^{-1}; MS (ESI): *m*/*z* (%): 561 (100) $[M - Cl]^+$; elemental analysis calcd (%) for $C_{33}H_{34}ClN_2Rh$ (M_W = 597.00) + 0.25 CH_2Cl_2: C 64.60, H 5.62, N 4.53; found: C 64.40, H 5.92, N 4.33.

Chloro-(η⁴-cycloocta-1,5-diene)-(9-(1-mesitylimidazolium-3-yl)-fluoren-9-yl)rhodium(I) (5′). A solution of compound **2** (30.5 mg, 87 μmol) in CD_2Cl_2 (0.8 mL) pre-cooled at −80 °C was slowly transferred *via* a cannula into an NMR tube containing solid $[RhCl(COD)]_2$ (21.5 mg, 43 μmol, 1.0 eq.) placed in a cold bath at −80 °C. The NMR tube was rapidly shaken and kept at this temperature until its introduction into the NMR spectrometer with the probe temperature set up and stabilized at 193 K. The complete NMR data were recorded at this temperature and indicated a mixture consisting of complexes **5′** and **5** in a ~1/1 ratio along with excess $[RhCl(COD)]_2$ (due to the incomplete transfer of the solution of **2**). Warming up the solution to room temperature gave a quantitative and clean conversion into complex **5**. NMR data for complex **5′** are as follows: ^1H NMR (500 MHz, CD_2Cl_2, 193 K): δ = 9.18 (br s, 1H, N_2CH), 7.85–7.79 (m, 3H, CH_{Flu}), 7.38–7.31 (m, 1H, CH_{Flu}), 7.31–7.22 (m, 4H, CH_{Flu}), 7.05 (s, 2H, CH_{Mes}), 6.93 (s, 1H, CH_{Im}), 4.16 (br s, 3H, CH_{COD}), 3.88 (br s, 1H, CH_{COD}), 2.33 (s, 3H, C$H_{3\ para}$), 2.16 (br s, 6H, C$H_{3\ ortho}$), 2.41–1.23 (m, 8H, C$H_{2\ COD}$); $^{13}C\{^1H\}$ NMR (125.8 MHz, CD_2Cl_2, 193 K): δ = 142.9, 141.0, 140.0, 138.7, 136.3, (C_{Ar}), 137.4 (br, N_2CH), 135.2, 134.7 (C_{Ar}), 129.0 (CH_{Mes}), 127.8, 127.7, 125.2, 123.6 (CH_{Flu}), 120.4 (CH_{Im}), 119.6 (CH_{Flu}), 86.1 (br, CH_{COD}), 77.1 (d, $J_{Rh\text{–}C}$ = 10.1 Hz, CH_{COD}), 73.8 (d, $J_{Rh\text{–}C}$ = 21.1 Hz, Rh-$C_{Flu\text{-}9}$), 31.4, 30.5, 29.3 ($CH_{2\ COD}$), 21.0 ($CH_{3\ para}$), 15.2 ($CH_{3\ ortho}$).

(1-Mesityl-3-(fluoren-9-yl)imidazol-2-ylidene)silver(I) bromide (6). CH_2Cl_2 (10 mL) was syringed into solid imidazolium bromide **1** (249 mg, 0.577 mmol), silver(I) oxide (80 mg,

0.346 mmol, 0.6 eq.) and 4 Å molecular sieves and the mixture was stirred under exclusion of light for 19 h. After filtration over Celite, the orange solution was evaporated to dryness and the crude product was washed with Et_2O (3 × 5 mL) to yield after drying a beige powder (235 mg, 76%). Single crystals suitable for an X-ray diffraction experiment were grown by slow diffusion of pentane into a solution of **6** in CH_2Cl_2. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, J = 7.6 Hz, 2H, CH_{Flu}), 7.51 (t, J = 7.6 Hz, 2H, CH_{Flu}), 7.43 (d, J = 7.6 Hz, 2H, CH_{Flu}), 7.37–7.33 (m, 2H, CH_{Flu}), 7.00 (s, 2H, CH_{Mes}), 6.86 (t, J = 1.8 Hz, 1H, CH_{Im}), 6.65 (s, 1H, C$H_{Flu\text{-}9}$), 6.57 (s, 1H, CH_{Im}), 2.35 (s, 3H, C$H_{3\ para}$), 2.06 (s, 6H, C$H_{3\ ortho}$); ^{13}C{^{1}H} NMR (105.5 MHz, $CDCl_3$): δ = 141.8, 140.8, 139.9, 135.4, 134.2 (C_{Ar}), 130.2, 129.7, 128.5 (2 CH_{Flu} + CH_{Mes}), 124.9 (CH_{Flu}), 123.6 (CH_{Im}), 120.8 (CH_{Flu}), 118.9 (CH_{Im}), 66.0 (C$H_{Flu\text{-}9}$), 21.2 (C$H_{3\ para}$), 17.9 (C$H_{3\ ortho}$); IR (ATR): ν = 3013, 2971, 2916, 1609, 1489, 1448, 1411, 1389, 1300, 1232, 1222, 1163, 1104, 1082, 1026, 938, 849, 824, 742 cm^{-1}; MS (ESI): m/z (%): 459 (100) [M − Br]$^+$; elemental analysis calcd (%) for $C_{25}H_{22}AgBrN_2$ (M_W = 538.23): C 55.79, H 4.12, N 5.20; found: C 55.83, H 4.17, N 5.05.

(η^4-Cycloocta-1,5-diene)(1-mesityl-3-(fluoren-9-yl-κ*C*^{9})imidazol-2-ylidene-κ*C*^{2})rhodium(I) (7). KHMDS (0.5 M in toluene, 2.1 mL, 1.06 mmol, 2.1 eq.) was added dropwise to a suspension of imidazolium bromide **1** (218 mg, 0.505 mmol, 2.0 eq.) in THF (20 mL) at −50 °C. After the addition, the cooling bath was removed. After 40 min, the solution was again cooled down to −70 °C and solid [RhCl(COD)]$_2$ (124 mg, 0.252 mmol) was added. The reaction mixture was stirred overnight in the cooling bath (final temperature = 10 °C) and all volatiles were removed *in vacuo*. Toluene (10 mL) was syringed into the Schlenk tube and the mixture was filtered through Celite. After evaporation of toluene, the red residue was washed with pentane (2 × 5 mL) and dried. Addition of a small volume of Et_2O (1 mL) induced the formation of small red-orange crystals of the complex (65 mg, 23%), suitable for an X-ray diffraction experiment. ^{1}H NMR (400 MHz, C_6D_6): δ = 8.11 (d, J = 7.6 Hz, 2H, CH_{Flu}), 7.79 (d, J = 7.6 Hz, 2H, CH_{Flu}), 7.51 (d, J = 7.8 Hz, 2H, CH_{Flu}), 7.33 (d, J = 7.4 Hz, 2H, CH_{Flu}), 6.67 (s, 2H, CH_{Mes}), 6.07 (d, J = 1.8 Hz, 1H, CH_{Im}), 5.76 (d, J = 1.8 Hz, 1H, CH_{Im}), 4.05–4.03 (m, 2H, CH_{COD}), 2.82–2.80 (m, 2H, CH_{COD}), 2.09 (s, 6H, C$H_{3\ ortho}$), 2.04 (s, 3H, C$H_{3\ para}$), 2.00–1.92 (m, 2H, CH_{2COD}), 1.76–1.68 (m, 2H, CH_{2COD}), 1.49–1.42 (m, 2H, CH_{2COD}), 1.30–1.23 (m, 2H, CH_{2COD}); ^{13}C{^{1}H} NMR (105.5 MHz, $CDCl_3$): δ = 160.8 (d, J_{Rh-C} = 44.3 Hz, N_2C), 148.8, 138.7, 135.2, 132.2 (C_{Ar}), 129.2 (CH_{Mes}), 125.0 (CH_{Flu}), 121.9 (CH_{Im}), 121.5, 120.3 (CH_{Flu}), 119.4 (CH_{Im}), 119.3 (CH_{Flu}), 88.9 (d, J_{Rh-C} = 8.2 Hz, CH_{COD}), 74.3 (d, J_{Rh-C} = 10.8 Hz, CH_{COD}), 63.5 (d, J_{Rh-C} = 10.7 Hz, Rh-$C_{Flu\text{-}9}$), 32.1, 29.7 (CH_{2COD}), 21.0 (C$H_{3\ para}$), 17.5 (C$H_{3\ ortho}$); IR (ATR): ν = 3002, 2913, 2869, 2826, 1609, 1486, 1474, 1436, 1413, 1326, 1304, 1212, 1179, 1142, 1091, 1033, 1014, 970, 935, 849, 758, 725, 678 cm^{-1}; MS (ESI): m/z (%): 561 (100) [M + H]$^+$; HR-MS (ESI): m/z: calcd for $C_{33}H_{34}N_2Rh$: 561.1777, found: 561.1781.

(η^5-Cyclopentadienyl)(carbonyl)(1-mesityl-3-(9-carboxylato-κ*C*-fluoren-9-yl)imidazol-2-ylidene-κ*C*^{2})iron(II) (8). KHMDS (0.5 M in toluene, 2.5 mL, 1.25 mmol, 2.1 eq.) was added dropwise into a suspension of imidazolium bromide **1** (254 mg, 0.589 mmol) in THF (15 mL) at −50 °C. After the addition, the cooling bath was removed and the reaction mixture was allowed to warm up to room temperature. After 40 min, the solution was again cooled down to −50 °C and solid CpFe(CO)$_2$I (179 mg, 0.589 mmol, 1.0 eq.) was added. After warming to room temperature, the stirring was continued for 1.5 h and all volatiles were removed under vacuum. The residue was dissolved in toluene (10 mL), filtered through Celite and again evaporated to dryness leaving a dark crude product. This was washed with Et_2O (2 × 5 mL) to leave a yellowish-brown powder (217 mg, 70%). ^{1}H NMR (250 MHz, C_6D_6): δ = 7.61–7.47 (m, 3H, CH_{Flu}), 7.28–7.03 (m, 5H, CH_{Flu}), 6.74 (s, 1H, CH_{Mes}), 6.65 (s, 1H, CH_{Mes}), 6.12 (d, J = 1.9 Hz, 1H, CH_{Im}), 5.88 (d, J = 1.9 Hz, 1H, CH_{Im}), 4.21 (s, 5H, CH_{Cp}), 2.32 (s, 3H, C$H_{3\ Mes}$), 2.08 (s, 3H, C$H_{3\ Mes}$), 1.84 (s, 3H, C$H_{3\ Mes}$); ^{13}C{^{1}H} NMR (105.5 MHz, C_6D_6): δ = 257.8 (Fe–*C*(=O)C$_{Flu}$), 221.8 (Fe–*C*O), 199.3 (N_2C), 146.2, 145.7, 141.8, 141.5, 138.9, 136.8, 136.6, 135.2 (C_{Ar}), 129.6, 129.0, 128.5, 128.4, 128.0, 127.5 (CH_{Flu} + CH_{Mes}), 124.4 (CH_{Im}), 123.3, 121.5, 120.7, 120.6 (CH_{Flu}), 118.3 (CH_{Im}), 92.2 ($C_{Flu\text{-}9}$), 83.3 (CH_{Cp}), 21.0, 18.5, 17.8 (C$H_{3\ Mes}$); IR (ATR): ν = 3017, 2915, 1911, 1648, 1482, 1446, 1410, 1340, 1278, 1181, 1103, 1003, 938, 917, 885, 847, 812, 778, 733, 699, 666 cm^{-1}; IR (THF): ν = 1923 (C≡O), 1669 (C=O) cm^{-1}; MS (ESI): m/z (%): 549 (27) [M + Na]$^+$, 527 (15) [M + H]$^+$, 493 (53) [M − 2CO + Na]$^+$, 471 (100) [M − 2CO + H]$^+$; elemental analysis calcd (%) for $C_{32}H_{26}FeN_2O_2$ (M_W = 526.42): C 73.01, H 4.98, N 5.32; found: C 72.21, H 5.49, N 5.10.

X-ray diffraction studies

Data were collected on a Bruker D8/APEX II/Incoatec IμS Microsource diffractometer (**4**, **7**), or a Bruker D8/APEX II diffractometer (**5**, **6**). All calculations were performed on a PC-compatible computer using the WinGX system.[30] Full crystallographic data are given in Table S1 (see the ESI†). The structures were solved using the SIR92 program,[31] 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 and difference electron density syntheses using the SHELX program.[32] Atomic scattering factors were taken from the usual tabulations. Anomalous dispersion terms for Ag, Au, Cl, and Rh atoms were included in Fc. All non-hydrogen atoms were allowed to vibrate anisotropically. All the hydrogen atoms were set in idealized positions (R_3CH, C–H = 0.96 Å; R_2CH_2, C–H = 0.97 Å; RCH_3, C–H = 0.98 Å; C(sp^2)–H = 0.93 Å; U_{iso} 1.2 or 1.5 times greater than the U_{eq} of the carbon atom to which the hydrogen atom is attached) and their positions were refined as "riding" atoms. The four structures have been deposited at the CCDC under reference numbers CCDC 969666 (**4**), CCDC 969667 (**5**), CCDC 969668 (**6**), and CCDC 969669 (**7**).

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Notes and references

1 For monographs, see: (*a*) *N-Heterocyclic Carbenes*, ed. S. Diez-Gonzales, RSC, Cambridge, 2011; (*b*) N-Heterocyclic Carbenes in Transition Metal Catalysis and Organocatalysis, ed. C. S. J. Cazin, *Catalysis by metal complexes*, Springer, Berlin, 2011, vol. 32, 2011; (*c*) N-Heterocyclic Carbenes in Transition Metal Catalysis, ed. F. Glorius, *Top. Organomet. Chem.*, Springer, Berlin, 2007, vol. 21, 2007; (*d*) *N-Heterocyclic Carbenes in Synthesis*, ed. S. P. Nolan, Wiley-VCH, Weinheim, 2007.

2 For general reviews, see: (*a*) D. J. Nelson and S. P. Nolan, *Chem. Soc. Rev.*, 2013, **42**, 6723; (*b*) T. Dröge and F. Glorius, *Angew. Chem., Int. Ed.*, 2010, **49**, 6940; (*c*) M. Melaimi, M. Soleilhavoup and G. Bertrand, *Angew. Chem., Int. Ed.*, 2010, **49**, 8810; (*d*) D. Bourissou, O. Guerret, F. P. Gabbai and G. Bertrand, *Chem. Rev.*, 1999, **100**, 39.

3 For selected reviews, see: (*a*) D. Bézier, J.-B. Sortais and C. Darcel, *Adv. Synth. Catal.*, 2013, **355**, 19; (*b*) C. Valente, S. Çalimsiz, K. H. Hoi, D. Mallik, M. Sayah and M. G. Organ, *Angew. Chem., Int. Ed.*, 2012, **51**, 3314; (*c*) F. Wang, L.-J. Liu, W. Wang, S. Li and M. Shi, *Coord. Chem. Rev.*, 2012, **256**, 804; (*d*) S. P. Nolan, *Acc. Chem. Res.*, 2010, **44**, 91; (*e*) G. C. Vougioukalakis and R. H. Grubbs, *Chem. Rev.*, 2009, **110**, 1746; (*f*) S. Díez-González, N. Marion and S. P. Nolan, *Chem. Rev.*, 2009, **109**, 3612.

4 (*a*) X. Bugaut and F. Glorius, *Chem. Soc. Rev.*, 2012, **41**, 3511; (*b*) V. Nair, S. Vellalath and B. P. Babu, *Chem. Soc. Rev.*, 2008, **37**, 2691; (*c*) D. Enders, O. Niemeier and A. Henseler, *Chem. Rev.*, 2007, **107**, 5606; (*d*) N. Marion, S. Díez-González and S. P. Nolan, *Angew. Chem., Int. Ed.*, 2007, **46**, 2988; (*e*) D. Enders and T. Balensiefer, *Acc. Chem. Res.*, 2004, **37**, 534.

5 (*a*) Y. Wang and G. H. Robinson, *Dalton Trans.*, 2012, **41**, 337; (*b*) D. Martin, M. Soleilhavoup and G. Bertrand, *Chem. Sci.*, 2011, **2**, 389.

6 Review on the synthesis of NHC-precursors: L. Benhamou, E. Chardon, G. Lavigne, S. Bellemin-Laponnaz and V. César, *Chem. Rev.*, 2011, **111**, 2705.

7 (*a*) F. Wang, L.-J. Liu, W. Wang, S. Li and M. Shi, *Coord. Chem. Rev.*, 2012, **256**, 804; (*b*) R. E. Douthwaite, *Coord. Chem. Rev.*, 2007, **251**, 702; (*c*) V. César, S. Bellemin-Laponnaz and L. H. Gade, *Chem. Soc. Rev.*, 2004, **33**, 619.

8 C. D. Varnado, Jr., E. L. Rosen, M. S. Collins, V. M. Lynch and C. W. Bielawski, *Dalton Trans.*, 2013, **42**, 13251 and references therein.

9 (*a*) M. Poyatos, J. A. Mata and E. Peris, *Chem. Rev.*, 2009, **109**, 3677; (*b*) A. J. Boydston and C. W. Bielawski, *Dalton Trans.*, 2006, 4073.

10 (*a*) V. César, S. Labat, K. Miqueu, J.-M. Sotiropoulos, R. Brousses, N. Lugan and G. Lavigne, *Chem.–Eur. J.*, 2013, **19**, 17113; (*b*) V. César, L. C. Misal Castro, T. Dombray, J.-B. Sortais, C. Darcel, S. Labat, K. Miqueu, J.-M. Sotiropoulos, R. Brousses, N. Lugan and G. Lavigne, *Organometallics*, 2013, **32**, 4643; (*c*) V. César, C. Barthes, Y. C. Farré, S. V. Cuisiat, B. Y. Vacher, R. Brousses, N. Lugan and G. Lavigne, *Dalton Trans.*, 2013, **42**, 7373; (*d*) V. César, N. Lugan and G. Lavigne, *Chem.–Eur. J.*, 2010, **16**, 11432; (*e*) V. César, N. Lugan and G. Lavigne, *J. Am. Chem. Soc.*, 2008, **130**, 11286.

11 N. Vujkovic, V. César, N. Lugan and G. Lavigne, *Chem.–Eur. J.*, 2011, **17**, 13151.

12 (*a*) L. Benhamou, V. César, H. Gornitzka, N. Lugan and G. Lavigne, *Chem. Commun.*, 2009, 4720; (*b*) L. Benhamou, N. Vujkovic, V. César, H. Gornitzka, N. Lugan and G. Lavigne, *Organometallics*, 2010, **29**, 2616.

13 V. César, J. C. Tourneux, N. Vujkovic, R. Brousses, N. Lugan and G. Lavigne, *Chem. Commun.*, 2012, **48**, 2349.

14 (*a*) N. Pidlypnyi, J. C. Namyslo, M. H. H. Drafz, M. Nieger and A. Schmidt, *J. Org. Chem.*, 2013, **78**, 1070; (*b*) A. Schmidt and Z. Guan, *Synthesis*, 2012, 3251.

15 For a comprehensive review on the classification of mesoionic compounds, see: W. D. Ollis, S. P. Stanforth and C. A. Ramsden, *Tetrahedron*, 1985, **41**, 2239.

16 For a similar equilibrium between nitrone and its free carbenic form, see: C. Farber, M. Leibold, C. Bruhn, M. Maurer and U. Siemeling, *Chem. Commun.*, 2012, **48**, 227.

17 (*a*) S. P. Downing, P. J. Pogorzelec, A. A. Danopoulos and D. J. Cole-Hamilton, *Eur. J. Inorg. Chem.*, 2009, 1816; (*b*) S. P. Downing, S. C. Guadaño, D. Pugh, A. A. Danopoulos, R. M. Bellabarba, M. Hanton, D. Smith and R. P. Tooze, *Organometallics*, 2007, **26**, 3762; (*c*) S. P. Downing and A. A. Danopoulos, *Organometallics*, 2006, **25**, 1337.

18 (*a*) P. de Frémont, N. M. Scott, E. D. Stevens and S. P. Nolan, *Organometallics*, 2005, **24**, 2411; (*b*) D. Tapu, D. A. Dixon and C. Roe, *Chem. Rev.*, 2009, **109**, 3385.

19 Protonolysis of alkyl-gold(I) bonds generally constitutes the final step of the catalytic cycles in Au(I)-catalyzed reactions, see for example: (*a*) E. S. Jiménez-Núñez and A. M. Echavarren, *Chem. Rev.*, 2008, **108**, 3326; (*b*) N. Marion and S. P. Nolan, *Chem. Soc. Rev.*, 2008, **37**, 1776; (*c*) A. Arcadi, *Chem. Rev.*, 2008, **108**, 3266; (*d*) A. S. Hashmi, *Chem. Rev.*, 2007, **107**, 3180.

20 (*a*) H. R. Thomas, R. J. Deeth, G. J. Clarkson and J. P. Rourke, *Organometallics*, 2011, **30**, 5641; (*b*) S. H. Crosby, G. J. Clarkson and J. P. Rourke, *J. Am. Chem. Soc.*, 2009, **131**, 14142.

21 R. N. Perutz and S. Sabo-Etienne, *Angew. Chem., Int. Ed.*, 2007, **46**, 2578.

22 H. M. J. Wang and I. J. B. Lin, *Organometallics*, 1998, **17**, 972.

23 Complex **6** crystallizes with two independent molecules per unit cell, molecule **A** and molecule **B**, displaying similar metrical features.

24 For reviews on the coordination mode of the fluorenyl ligand, see: (*a*) E. Kirillov, J.-Y. Saillard and J.-F. Carpentier, *Coord. Chem. Rev.*, 2005, **249**, 1221; (*b*) M. Stradiotto and M. J. McGlinchey, *Coord. Chem. Rev.*, 2001, **219–221**, 311; (*c*) H. G. Alt and E. Samuel, *Chem. Soc. Rev.*, 1998, **27**, 323.

25 (*a*) P. Oulié, C. Freund, N. Saffon, B. Martin-Vaca, L. Maron and D. Bourissou, *Organometallics*, 2007, **26**, 6793; (*b*) C. Freund, N. Barros, H. Gornitzka, B. Martin-Vaca, L. Maron and D. Bourissou, *Organometallics*, 2006, **25**, 4927.
26 For other examples of four-membered NHC-containing metallacycles, see: (*a*) P. Nägele, U. Herrlich, F. Rominger and P. Hofmann, *Organometallics*, 2012, **32**, 181; (*b*) Ref. 10*e*; (*c*) F. Wu, V. K. Dioumaev, D. J. Szalda, J. Hanson and R. M. Bullock, *Organometallics*, 2007, **26**, 5079; (*d*) N. Imlinger, K. Wurst and M. R. Buchmeiser, *J. Organomet. Chem.*, 2005, **690**, 4433; (*e*) Y. Zhang, D. Wang, K. Wurst and M. R. Buchmeiser, *J. Organomet. Chem.*, 2005, **690**, 5728.
27 Data taken from: G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176.
28 S. Yasuda, H. Yorimitsu and K. Ashima, *Organometallics*, 2008, **27**, 4025.
29 A. J. Arduengo III, F. P. Gentry, Jr., P. K. Taverkere and H. E. Howard III, *US Patent* 6177 575, 2001.
30 L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.
31 A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Crystallogr.*, 1993, **26**, 343.
32 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2008, **64**, 112.