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N-Alkylfluorenyl-substituted N-heterocyclic carbenes as bimodal pincers†

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Two N-heterocyclic carbene precursors having their nitrogen atoms substituted by the expanded 9-ethyl-9-fluorenyl group, namely imidazolinium chloride **6** and imidazolium chloride **7**, have been synthesized in high yields from fluorenone (**1**). The key intermediate of their syntheses is the new primary amine 9-ethyl-9-fluorenylamine (**3**), which was prepared in 75% yield. Both salts were readily converted into the corresponding PEPPSI-type palladium complexes, **8** and **9** (PEPPSI: pyridine-enhanced precatalyst preparation stabilisation and initiation). Despite rotational freedom of the ethylfluorenyl moieties about the N-C(fluorenyl) bond in their cationic precursors, the carbene ligands of the Pd(II)-complexes **8** and **9** both behave as bimodal pincers in solution and in the solid state, the resulting confinement being essentially due to (weak) attractive anagostic interactions between the CH_2(fluorenyl) groups and the metal centre. Unlike in **8** and **9**, there was no indication for similar anagostic interactions in the imidazolylidene chlorosilver complex **11**, which could be obtained from **7**. In the solid state, however, **11** adopts a remarkable "open sandwich" structure, with the two alkylfluorenilidene planes η^2-bonded to the silver, this constituting a further bimodal pincer-type bonding mode of this ligand class. Complexes **8** and **9** were assessed in Suzuki-Miyaura cross-coupling reactions. The imidazolylidene complex **9** displayed high activity towards unencumbered aryl chlorides. Its activity is comparable to that of the previously reported, highly efficient benzimidazolylidene analogue **10**.

Introduction

The current increasing interest in N-heterocyclic carbenes (NHCs) as metallocatalyst components is primarily due to the strong donor ability of these ligands which, in most cases, exceeds that of tertiary phosphines.[1] Their particular electronic properties alone do not, however, necessarily confer optimised reactivity on their metal complexes. Improved ligand efficiency is often achieved, exactly as in phosphine chemistry, through subtle control of the NHC sterics. For example, in palladium-catalysed Suzuki-Miyaura cross-coupling reactions, N-heterocyclic carbenes with N atoms substituted by side-expanded aryl rings (with N-substituents such as, e.g., mesityl,[2] 2,6-diisopropylphenyl,[3] adamantyl,[4] 2,6-diisopentylphenyl,[3i, 5] 2,6-diisopropyl-4-tritylphenyl,[6] mesitylmethyl,[7] phenanthrenyl,[8] calixarenyl,[9] resorcinarenyl,[10] 2,6-di(diphenylmethyl)-4-methoxyphenyl[11]) have been shown to result in much higher activities than those obtained with analogs bearing smaller N-substituents. In fact, the high degree of crowding created with the former ligands not only facilitates the final reductive elimination step of the coupling reaction, but also favours monoligation and increases the lifetime of key intermediates. Further, Glorius et al. have exposed the beneficial role in these reactions of bulky *N*-substituents that display structural flexibility, thereby enabling their adaptation to the steric requirements of each individual step of the catalytic cycle.[12]

In some recent publications, we have described a series of benzimidazole-based NHCs bearing nitrogen-grafted alkylfluorenyl (AF) substituents (Fig. 1).[13] In their complexes, the metal centre was shown to be firmly protected in a permanent manner by the alkyl groups as a consequence of the orientating properties of the large, planar fluorenylidene unit combined with a high rotational barrier of the AF group about the N–C(fluorenyl) bond. In the case of Pd(II) complexes obtained with these ligands, anagostic CH···M interactions between the metal and the two alkyl chains were shown to contribute to the high steric protection. In the present study we describe the coordinative properties of related ligands, which instead of the benzimidazolylidene moiety contain the smaller imidazolylidene and imidazolinylidene ring moieties. These were expected to confer rotational freedom to the AF groups

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and accordingly to modify the confining properties of the ligand. In the following, the term *bimodal pincer* designates any tridentate ligand containing a strongly coordinating atom (in our case a carbenic C atom) and two other donor atoms (or functions) able to interact in a non covalent manner with the complexed metal ion.

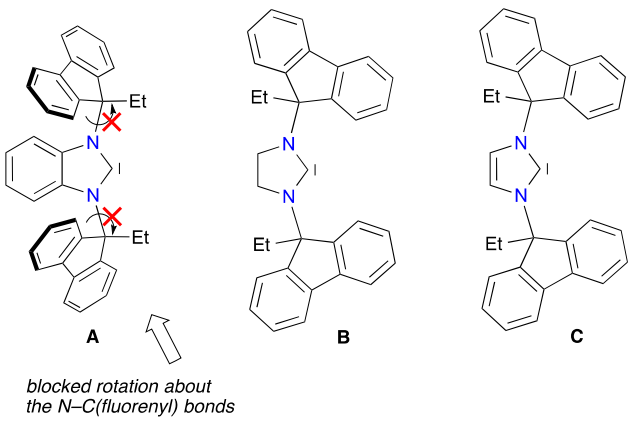


Fig. 1 Carbene ligands used in this study: benzimidazol-2-ylidene (**A**), imidazolin-2-ylidene (**B**) and imidazol-2-ylidene (**C**)

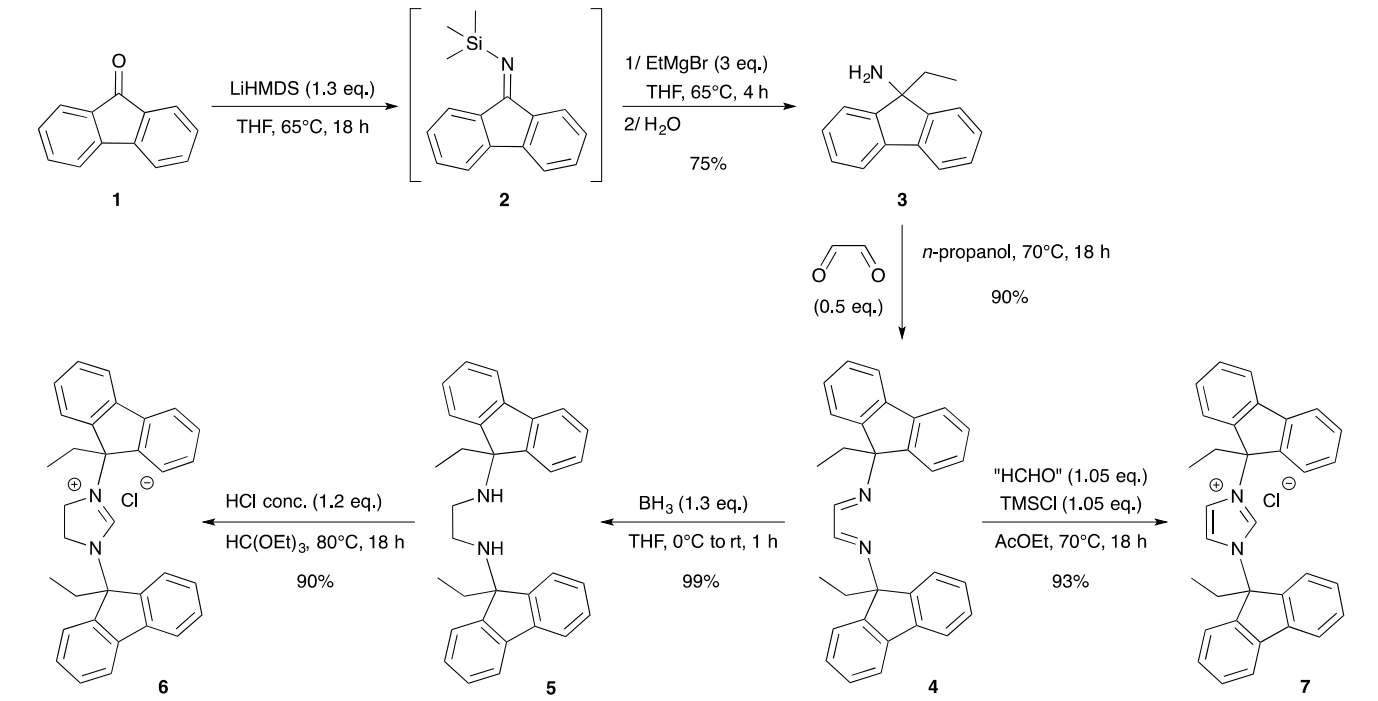
Results and discussion

Syntheses of the N-heterocyclic carbene precursors 6 and 7

The syntheses of imidazolinium chloride **6** and imidazolium chloride **7** required the preparation of the (new) primary amine **3**, which was obtained by applying a one-flask procedure inspired from the literature (Scheme 1).[14] Thus, reaction of fluorenone with lithium bis(trimethylsilyl)amide (1.3 equiv.) in refluxing THF afforded a pale orange solution, which was subsequently treated with EtMgBr in excess. Silyl imine **2**, formed in the first step of this sequence, was not isolated. After workup, amine **3** was obtained in 75% yield. Reaction of **3** with glyoxal in propanol at 70°C then gave diimine **4** in high yield. Reduction of 4 with BH_3 in THF, followed by reaction of the resulting diamine with $HC(OEt)_3$-HCl gave **6** in 90% overall yield. Applying Hintermann's nonclassical protocol for the synthesis of imidazolium salts,[15] **4** was further reacted with paraformaldehyde and Me_3SiCl (**4**:HCHO:Me_3SiCl ratio 1:1:1) in AcOEt, giving **7** in 93% yield. In the ^1H NMR spectra of both salts, **6** and **7**, the signal of the NCHN proton appears, as expected, at relatively low field (10.25 (**6**) and 11.85 (**7**) ppm). Furthermore, the 2D ROESY spectra of both salts revealed correlations between the methylene protons of the Et groups and the protons connected to all three C atoms of the NHC ring, this being a clear indication of freely rotating akylfluorenyl goups. Both salts are strongly hygroscopic and therefore need to be kept in a dry atmosphere.

Syntheses of Metal Complexes

The PEPPSI-type complex **8** was obtained in 75% yield by the following two-step, one-flask synthesis: a) reaction of imidazolinium salt **6** with LiHDMS in THF at room temperature; b) after 1h, addition of $[PdCl_2(pyridine)_2]$ to the reaction mixture with subsequent heating for 18 h at 65°C (Scheme 2). The related imidazolylidene complex **9** was obtained in 85% yield by refluxing a suspension of precursor **7**, K_2CO_3 and $PdCl_2$ in pyridine for 18 h. The ^{13}C NMR spectrum of both complexes shows a signal corresponding to a carbenic C atom, respectively at 174.9 (**8**) and 144.2 (**9**) ppm.



Scheme 1 Synthesis of imidazolinium salt **6** and imidazolium salt **7**

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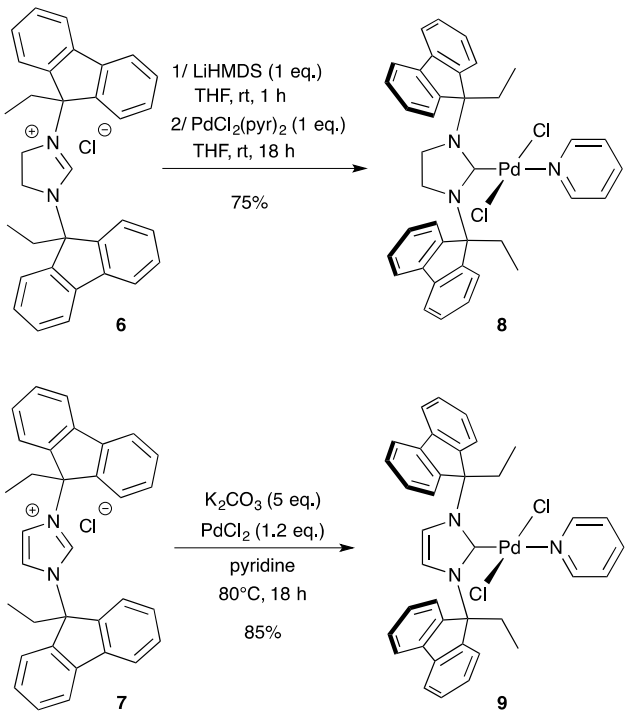
The NCCH_2 signals of **8** and **9** are considerably downfield shifted with respect to those of the corresponding precursor salts ($\Delta\delta$ = 1.59 (**8** vs. **6**), and 1.42 (**9** vs. **7**) ppm). The observed



Scheme 2 Synthesis of palladium complexes **8** and **9**

downfield shifted signals, together with relatively "standard" ^1J(CH) values (all close to 130 Hz) are indicative of anagostic C–H···Pd interactions,[16] that is of interactions being essentially electrostatic in nature (with the d_{z^2} orbital being not significantly involved). 2D NMR experiments further revealed that while for the precursors **6** and **7** the ethyl-fluorenylidene groups freely rotate about the corresponding N–C(fluorenylidene) bonds, the same groups are blocked in **8** and **9**, with the ethyl groups being permanently turned towards the "Pd(pyridine)" unit. The particular orientation of the ethyl groups was confirmed by single crystal X-ray analyses carried out for each complex (Fig. 2 and Fig. 3). It is noteworthy that this orientation is the same as the one seen in the solid state for the Et groups of the previously reported benzimidazolylidene analogue **10** (Fig. 4). The Pd-C(carbene) and Pd-N bond lengths in **8** and **9** are comparable to those found in related Pd-PEPPSI complexes.[1j, 5]

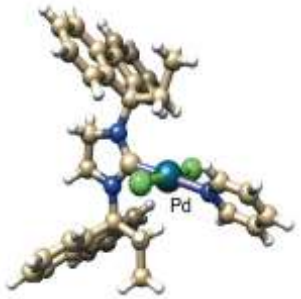
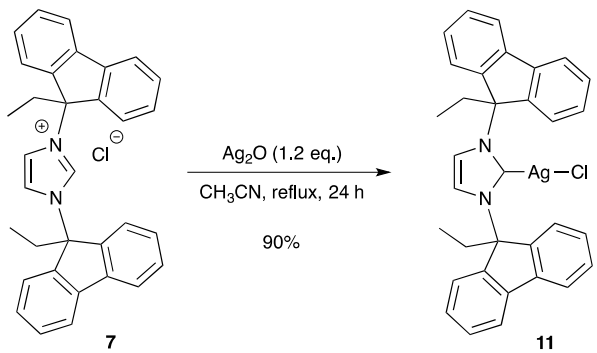


Fig. 2 Molecular structure of complex **8**. Pd···H(Et) anagostic bond separations: 2.61, 2.78, 2.60, 2.72 Å. Important bond distances (Å): C(carbene)-Pd 1.951(4), Pd-N 2.100(3). Pd-Cl 2.311(1) and 2.329(1).

Fig. 3 Molecular structure of complex **9**. Pd···H(Et) anagostic bond separations: 2.74, 2.62, 2.60, 2.80 Å. Other important bond lengths (Å): C(carbene)-Pd 1.961(2), Pd-N 2.093(2). Pd-Cl 2.301(6) and 2.322(6).

How does an ethylfluorenyl-substituted imidazolylidene ligand behave towards a metal ion, such as Ag(I), less prone[16a] to form anagostic interactions ? To answer this question, imidazolium salt **7** was reacted with Ag_2O in refluxing acetonitrile. This reaction led to silver complex **11** in high yield (Scheme 3).



Scheme 3 Synthesis of silver complex **11**

Complex **11** is highly stable under light. The 2D ROESY spectrum of **11** displayed cross peaks between the CH_2CH$_3$ and

the two protons of the NHC ring, thus suggesting that the alkyl groups are remote from the silver centre and that therefore the fluorenylidene plane is turned towards the silver ion. Probably this orientation is permanent, as in contrast to those of **8**-**10** (Fig. 4), the chemical shift of the CH_2CH_3 protons of **11** (2.75 ppm) is normal, this ruling out significant Ag···H(Et) interactions.

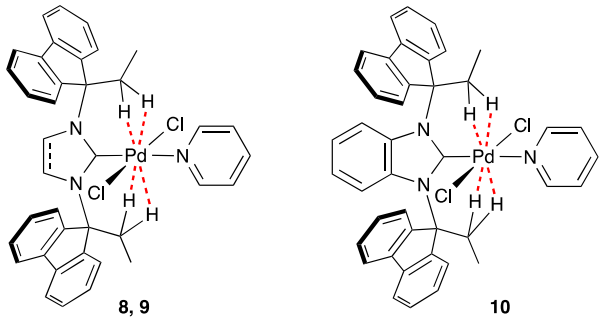


Fig. 4 Anagostic interactions (red) observed in the palladium complexes **8**-**10**

Crystals of **11** suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into a solution of the complex. In the solid state two distinct molecules, A and B, are present (Fig. 5). Their most striking feature concerns the orientation of the fluorenylidene planes, which, in keeping with the NMR data (vide supra), are both bent towards the metal atom, thus resulting in an "open sandwich" structure. The X-ray data indicate that molecule A has both fluorenylidene moieties η^2-coordinated to the metal (see Figure 5; shortest Ag···C distances: 2.93 and 3.02 Å for fluorenylidene A1; 3.10 and 3.12 Å for fluorenylidene A2). A similar π–arene-metal interaction can also be seen in molecule B, but only for one of its two ethylfluorenyl groups (shortest Ag···C distances: 3.00 and 3.18 Å). DFT calculations (see computational details) revealed that conformers having the fluorenylidene planes bent towards the silver atom (exactly as observed for **11** in the solid state) are favoured over those in which these planes are turned away from the metal. However, the interaction energy of each fluorenylidene group with the silver atom is of only *ca.* 2 kcal.mol^{-1}. Molecules of type A and B are further supramolecularly linked (in the solide state) through H···Cl bonds involving H atoms of the fluorenylidene moieties and the imidazolyl rings. The two Ag-C(carbene) bond lengths (2.102(5) and 2.110 (6) Å) lie in the range expected for [Ag(NHC)X] complexes.[17]

It is noteworthy that in the palladium complexes **8** and **9**, the AF planes are turned away from the metal as a result of anagostic interactions between the CH_2CH_3 protons and the palladium atom. These interactions are seemingly dominant over other possible weak interactions in the palladium complexes. Overall, the present study shows that alkylfluorenylidene substituted NHCs may behave as carbene-centered bimodal pincers functioning in two possible bonding modes, one involving two weak (mainly electrostatic) CH···M interactions, the other involving two weak η^2-arene···M interactions. It is further interesting to note that determination of the percent buried volume[18] (pbv) of the carbene ligand resulted in markedly different values (35.8% and 58.3%, respectively) according to which structure, **9** or **11**, was used account time dependent conformational changes. Note that for the calculation. This makes the relevance of the pbv concept questionable, as in fact it does not take into

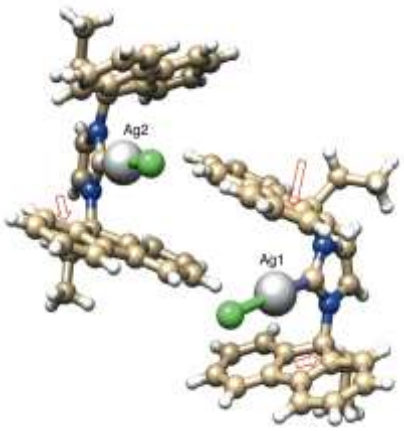
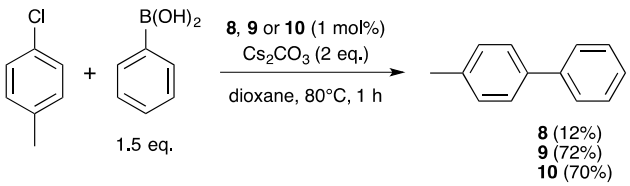


Fig. 5 Silver complex **11** existing in the solid state as two distinct molecules with "sandwiched" metal atoms. The red arrows indicate CC bonds π-interacting with the metal centres (Ag···C(arom.) separations 2.93-3.18 Å). Important distances (Å): Ag-C(carb) 2.102(5) (A) and 2.110 (6) (B); Ag-Cl 2.342(1) (A) and 2.379(2) (B)

the two NHC's of the literature with the highest reported pbv are a NHC which caps a cyclodextrin unit (pbv = 58.5%),[19] and IPr*$^{(2\text{-Np})}$ (pbv = 57.4%).[20]

Suzuki-Miyaura cross coupling

Complexes **8** and **9** were assessed in Suzuki-Miyaura cross coupling between phenyl boronic acid and various aryl chlorides. The catalytic runs were performed in dioxane at 80°C using 1 mol% of complex and 2 equiv. of Cs_2CO_3 per aryl chloride. Preliminary tests carried out with *p*-tolyl chloride revealed that the activity of the imidazolylidene complex **9** was 6 times higher than that of the electronically richer complex **8** (Scheme 4), but we have no rationalisation for the observed activity difference. In fact the performance of **9** for this particular reaction compares with that of the previously reported benzimidazolidene complex **10**,[13a] which is one of the fastest Suzuki-Miyaura cross coupling catalyst reported so far for this reaction. The latter complex turned out to be two times more active than its analogue with IPr.



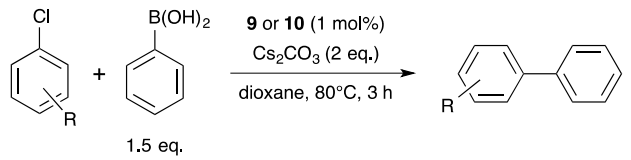
Scheme 4 Suzuki-Miyaura cross-coupling of $PhB(OH)_2$ with *p*-tolylchloride using palladium complexes **8**-**10**

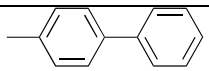
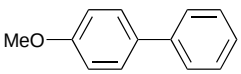
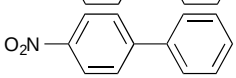
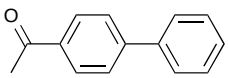
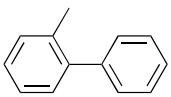
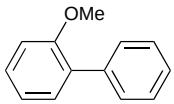
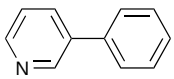
In view of the lower activity of **8**, tests with other aryl chlorides (see below) were achieved with **9** only. To allow comparaison, the same tests were also carried out with **10**. The relative activity of these complexes turned out to be dependant on the substrate.

Thus, aryl chlorides bearing electron-withdrawing groups in para position resulted in activities similar to those obtained for *p*-tolyl chloride (Table 1, entries 3 and 4), whether **9** or **10** was used. In contrast, for *p*-chloroanisole, the coupling reaction occurred ca. 3 times faster with **9** than with **10** (Table 1, entry 2). This possibly reflects the better donor properties of the

carbene ligand of **9**, which consequently facilitates the oxidative addition step. With *o*-substituted arylchlorides, the activity of both catalysts dropped significantly (Table 1, entries 5 and 6), suggesting that the encumbrance of the carbene ligands hinders the approach of the reagent. A similar decrease in activity was observed with 3-chloropyridine. Probably competition occurs in that case between the expected oxidative addition step and (reversible) coordination of the arylchloride through its nitrogen atom, this slowing down the coupling reaction. Overall, complex **9** may be regarded as a highly Suzuki-Miyaura cross coupling catalyst, but only for unencumbered aryl chlorides.

Table 1 Efficiency of complexes **9** and **10** in Suzuki-Miyaura cross-coupling of aryl chlorides[a]



Entry	Product	Yield (%)[b]	
		9	**10**
1		99	99
2		96	29
3		96	90
4		98	96
5		9 (24 h)	15
6		20	23
7		20	20

[a]Reaction conditions: aryl chloride (1 mmol), phenyboronic acid (1.5 mmol), Cs_2CO_3 (2 mmol), [Pd] (1 mol%), dioxane (3 mL), 3 h. [b]Isolated yields; average of two runs.

Conclusion

In summary, a useful synthetic route for the preparation of imidazolinium salt **6** and imidazolium salt **7** has been described. The key intermediate for these syntheses is the primary amine **3**, which was obtained according to a one-flask procedure starting from fluorenone. Both salts were converted into the PEPPSI-type palladium complexes **8** and **9** by applying the classical procedure developped by Organ.[2c, 21] While complex **8** showed low efficiency, complex **9** based on a NHC with weaker donor properties behaved as a fast catalyst for the cross coupling of phenyl boronic acid with *p*-substituted aryl chlorides, its activity being comparable to the best catalysts reported to date. In solution as well as in the solid state, anagostic (mainly electrostatic) interactions were seen in both complexes between the C*H*$_2$(fluorenyl) groups and the palladium centre, thus confirming that these carbene ligands may behave as bimodal pincers. As suggested by the solid state structure of the "open sandwich" silver complex **11**, another type of bimodal pincer may be envisaged with such carbenes. Overall, our findings unambiguously demonstrate that alkylfluorenyl-substituted NHCs constitute a new class of ligands displaying variable encumbrance.

Experimental section

General procedures

All commercial reagents were used as supplied. The syntheses were performed in Schlenk-type flasks under dry nitrogen. Solvents were dried by conventional methods and distilled immediately prior to use. Routine ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a FT Bruker AVANCE 300 (^{1}H: 300.1 MHz, ^{13}C: 75.5 MHz) instrument at 25°C. ^{1}H NMR spectral data were referenced to residual protonated solvent ($CHCl_3$, δ 7.26), ^{13}C chemical shifts are reported relative to deuterated solvent ($CDCl_3$, δ 77.16). In the NMR data given hereafter, Cq denotes a quaternary carbon atom. Flash chromatography was performed as described by Still et al.,[22] employing Geduran SI (E. Merck, 0.040-0.063 mm) silica. Routine thin-layer chromatography analyses were carried out by using plates coated with Merck Kieselgel 60 GF254. Elemental analyses were performed by the Service de Microanalyse, Institut de Chimie (UDS-CNRS), Strasbourg. Melting points were determined with a Büchi 535 capillary melting-point apparatus and are uncorrected. Palladium complex **10** was prepared following a procedure described in the literature.[13a]

(9-Ethyl-9*H*-fluoren-9-yl)amine (3). LiHMDS (1 M in THF, 21.7 mL, 21.7 mmol) was added to a stirred solution of fluorenone (**1**) (3.0 g, 16.7 mmol) in THF (10 mL) at room temperature. The reaction mixture was then heated at 65°C for 18 h. The resulting dark solution was then cooled to 0°C and ethylmagnesium bromide (1.5 M in THF, 33.5 mL, 50.3 mmol) was added dropwise. The mixture was heated at 65°C during 4 h and then cooled to 0°C. Water (100 mL) was slowly added and the mixture was extracted with AcOEt (3 × 100 mL). The combined organic layers were dried over Na_2SO_4 and the solvent removed under vacuum. The crude product was purified by flash chromatography (SiO_2; AcOEt) to afford **3** as a pale yellow oil (2.62 g, 75%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.63-7.56 (m, 2 H, ArH), 7.50-7.45 (m, 2 H, ArH), 7.39-7.30 (m, 4 H, ArH), 2.10 (q, ^3J = 7.5 Hz, 2 H, CH_2), 2.02 (br s, 2 H, NH_2), 0.47 (t, ^3J = 7.5 Hz, 3 H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 150.8 (arom. Cq), 139.9 (arom. Cq), 128.1 (arom. CH), 127.8 (arom. CH), 123.0 (arom. CH), 120.0 (arom. CH), 66.0 (Cq), 34.1 (CH_2), 8.8 (CH_3). Anal. Calcd for $C_{15}H_{15}N$ (209.29): C, 86.08; H, 7.22; N, 6.69. Found: C, 86.15; H, 6.92; N, 6.49.

***N*,*N*'-(Ethane-1,2-diylidene)bis(9-ethyl-9*H*-fluoren-9-amine) (4).** To a solution of amine **3** (2.47 g, 11.8 mmol) in *n*-propanol (23 mL) was added glyoxal (40%, 0.675 mL, 5.89 mmol). The solution was then heated at 70°C for 18 h under vigorous stirring. A white precipitate was observed. The suspension was allowed to reach room temperature and was then concentrated

under vacuum. The residue was recrystallized from *n*-propanol to afford pure diimine **4** as a white crystalline solid (2.33 g, 90%); mp > 220°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.74 (s, 2 H, NCH), 7.68-7.61 (m, 4 H, ArH), 7.37-7.23 (m, 12 H, ArH), 2.28 (q, ^3J = 7.5 Hz, 4 H, CH_2), 0.47 (t, ^3J = 7.5 Hz, 6 H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 159,3 (NCH), 146.6 (arom. Cq), 140.6 (arom. Cq), 128.4 (arom. CH), 127.8 (arom. CH), 124.7 (arom. CH), 120.3 (arom. CH), 78.4 (Cq), 32.8 (CH_2), 8.4 (CH_3). Anal. Calcd for $C_{32}H_{28}N_2$ (440.59): C, 87.24; H, 6.41; N, 6.36. Found C: 87.15; H, 6.35; N, 6.39.

***N,N'*-Bis(9-ethyl-9*H*-fluoren-9-yl)ethane-1,2-diamine (5).** BH_3 (1 M in THF, 3 mL, 3.00 mmol) was added dropwise to a stirred solution of diimine **4** (1.0 g, 2.27 mmol) in THF (10 mL) at 0°C. The reaction mixture was allowed to reach room temperature and stirred for 1 h. Water was slowly added (40 mL) and the reaction mixture was extracted with AcOEt (3 x 40 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The light yellow crude diamine was taken in CH_2Cl_2 and charcoal was added. The black mixture was heated to reflux and then allowed to reach room temperature. After filtration through Celite the filtrate was concentrated under reduced pressure to afford pure diamine **5** as a white solid (997 mg, 99%); mp 174°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62 (d, ^3J = 7.3 Hz, 4 H, ArH), 7.35-7.24 (m, 12 H, ArH), 2.04-1.96 (m, 6 H, overlapping signals, 4 H CH_2CH_3 and 2 H NH), 1.85 (s, 4 H, NCH_2), 0.41 (t, ^3J = 7.5 Hz, 6 H, CH_2CH_3).^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 148.1 (arom. Cq), 141.0 (arom. Cq), 128.0 (arom. CH),127.5 (arom. CH), 123.4 (arom. CH), 119.8 (arom. CH), 71.0 (Cq), 43.5 (NCH_2), 33.9 (CH_2CH_3), 8.3 (CH_2CH_3). Anal. Calcd for $C_{32}H_{32}N_2$ (444.62): C, 86.44; H, 7.25; N, 6.30. Found: C, 86.20; H, 7.32; N, 6.55.

1,3-Bis(9-ethyl-9*H*-fluoren-9-yl)imidazolinium chloride (6). Diamine **5** (512 mg, 1.15 mmol) was dissolved under magnetic stirring in $HC(OEt)_3$ (3 mL). HCl (12 M, 116 µL, 1.39 mmol) was added and he mixture was heated at 80°C for 18 h. A white precipitate was observed. The suspension was then cooled to room temperature, and petroleum ether was added (ca. 20 mL). The precipitate was collected by filtration and washed with petroleum ether (3 × 15 mL) to afford **6** (507 mg, 90%) as a hygroscopic white solid; mp > 230°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 10.25 (s, 1 H, NCHN), 7.99-7.92 (m, 4 H, ArH), 7.68-7.61 (m, 4 H, ArH), 7.46-7.38 (m, 8 H, ArH), 3.27 (q, ^3J = 7.4 Hz, 4 H, CH_2CH_3), 3.01 (s, 4 H, NCH_2), 0.41 (t, ^3J = 7.4 Hz, 6 H, CH_2CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 156.1 (NCHN), 142.2 (arom. Cq), 140.7 (arom. Cq), 130.0 (arom. CH), 129.1 (arom. CH), 124.5 (arom. CH), 120.3 (arom. CH), 73.6 (Cq), 45.2 (NCH_2), 29.4 (CH_2CH_3), 7.9 (CH_2CH_3). Anal. Calcd for $C_{33}H_{31}ClN_2$ (491.08): C, 80.71; H, 6.36; N, 5.70. Found: C, 80.91; H, 6.36; N, 5.40.

1,3-Bis(9-ethyl-9*H*-fluoren-9-yl)imidazolium chloride (7). TMSCl (189 µL, 1.50 mmol) was slowly added to a mixture of diimine **4** (635 mg, 1.44 mmol) and paraformaldehyde (45 mg, 1.50 mmol) in AcOEt (5 mL). The mixture was then heated at 70°C for 18 h. A white precipitate was observed. The suspension was then cooled to room temperature and petroleum ether was added (ca. 20 mL). The precipitate was collected by filtration and washed with petroleum ether (3 × 15 mL) to afford compound **7** (654 mg, 93%) was obtained as a hygroscopic white solid; mp 212°C. ^{1}H NMR ($CDCl_3$, 500 MHz), δ 11.85 (s, 1 H, NCHN), 7.87 (d, ^3J = 7.5 Hz, 4 H, ArH), 7.71 (d, ^3J = 7.5 Hz, 4 H, ArH), 7.46 (dd, ^3J = $^3J'$ = 7.5 Hz, 4 H, ArH), 7.40 (dd, 4 H, ^3J = $^3J'$ = 7.5 Hz, ArH), 6.37 (s, 2 H, NCH), 3.47 (q, 4 H, ^3J = 6.3 Hz, CH_2), 0.50 (t, 6 H, ^3J = 6.3 Hz, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz), δ 143.0 (arom. Cq), 140.3 (arom. Cq), 137.7 (NCHN), 130.4 (arom. CH), 129.2 (arom. CH), 124.7 (arom. CH), 120.6 (arom. CH), 119.8 (NCH), 75.7 (Cq), 30.5 (CH_2), 8.0 (CH_3). Anal. Calcd for $C_{33}H_{29}ClN_2$ (489.06): C, 81.05; H, 5.98; N, 5.73. Found: C, 81.38; H, 5.97; N, 5.55.

***trans*-[1,3-Bis(9-ethyl-9*H*-fluoren-9-yl)imidazolin-2-ylidene](pyridine)palladium(II) dichloride (8).** To a suspension of imidazolinium salt **6** (491 mg, 1,00 mmol) in THF (5 mL) cooled at 0°C, was added LiHMDS (1 M in THF, 1 mL, 1,00 mmol). The suspension was allowed to reach room temperature and was stirred for 1 h. To the resulting orange solution was added $PdCl_2(pyridine)_2$ (335 mg, 1 mmol) and the mixture was stirred at room temperature for 18 h. The mixture was filtered through Celite and the collected solid washed with CH_2Cl_2 (ca. 20 mL). The filtrate was concentrated under reduced pressure and the residue purified by flash chromatography (SiO_2; CH_2Cl_2/petroleum ether, 50:50) to afford **8** as a yellow solid (534 mg, 75%); mp > 230°C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ 9.11-9.06 (m, 2 H, *o*-NC_5H_5), 7.95-7.89 (m, 4 H, ArH), 7.84-7.77 (m, 1 H, *p*-NC_5H_5), 7.64-7.57 (m, 4 H, ArH), 7.44-7.31 (m, 10 H, overlapping signals, 8 H ArH and 2 H *m*-NC_5H_5), 4.86 (q, ^3J = 7.2 Hz, 4 H, CH_2CH_3), 2.57 (s, 4 H, NCH_2), 0.36 (t, ^3J = 7.2 Hz, 6 H, CH_2CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 174.9 (NCN), 151.7 (arom. CH), 146.0 (arom. Cq), 140.6 (arom. Cq), 138.1 (arom. CH), 128.9 (arom. CH), 128.8 (arom. CH), 124.9 (arom. CH), 124.7 (arom. CH), 119.8 (arom. CH), 75.2 (Cq), 45.7 (NCH_2), 33.8 (CH_2CH_3), 9.06 (CH_2CH_3). Anal. Calcd for $C_{38}H_{35}Cl_2N_3Pd$ (711.04): C, 64.19; H, 4.96; N, 5.91. Found: C, 64.42; H, 5.08; N, 5.66.

***trans*-[1,3-Bis(9-ethyl-9*H*-fluoren-9-yl)imidazol-2-ylidene](pyridine)palladium(II) dichloride (9).** A suspension of imidazolium salt (**7**) (1.23 g, 2.51 mmol), finely crushed K_2CO_3 (1.72 g, 12.4 mmol), and $PdCl_2$ (534 mg, 3.01 mmol) in pyridine (5 mL) was heated at 80°C for 18 h under vigorous stirring. The mixture was cooled to room temperature, filtered through Celite and the collected solid washed with CH_2Cl_2 (ca. 20 mL). The filtrate was evaporated to dryness and the residue purified by flash chromatography (SiO_2; CH_2Cl_2/petroleum ether, 50:50) to afford **9** as a yellow solid (1.51 g, 85%); mp > 220°C. ^{1}H NMR ($CDCl_3$, 500 MHz), δ 9.14-9.12 (m, 2 H, *o*-NC_5H_5), 7.82 (tt, ^3J = 7.6 Hz, ^4J = 1.7 Hz, 1 H, *p*-NC_5H_5), 7.75 (d, ^3J = 7.5 Hz, 4 H, ArH), 7.66 (d, ^3J = 7.5 Hz, 4 H, ArH), 7.44-7.40 (m, 2 H, *m*-NC_5H_5), 7.37 (ddd, ^3J = $^3J'$ = 7.5 Hz, ^4J = 1.2 Hz, 4 H, ArH), 7.31 (ddd, ^3J = $^3J'$ = 7.5 Hz, ^4J = 1.2 Hz, 4 H, ArH), 5.85 (s, 2 H, NCH), 4.99 (q, ^3J = 7.3 Hz, 4 H, CH_2), 0.47 (t, ^3J = 7.3 Hz, 6 H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 151.8 (arom. CH), 147.6 (arom. Cq), 144.2 (NCN), 140.1 (arom. Cq), 138.1 (arom. CH), 129.2 (arom. CH), 129.0 (arom. CH), 125.0 (arom. CH), 124.8 (arom. CH), 122.8 (arom. CH), 120.0 (arom. CH), 75.8 (Cq), 33.1 (CH_2), 8.9 (CH_3). Anal. Calcd for $C_{38}H_{33}Cl_2N_3Pd$ (709.02): C, 64.37; H, 4.69; N, 5.93. Found: C, 64.52; H, 4.62; N, 5.65.

***trans*-[1,3-Bis(9-ethyl-9*H*-fluoren-9-yl)imidazol-2-ylidene]silver(I) chloride (11).** A mixture of imidazolium salt **7** (210 mg, 0.43 mmol) and Ag_2O (119 mg, 0.516 mmol) in CH_3CN (8 mL) was stirred at reflux for 24 h, protected from light. The mixture was cooled to room temperature, filtered

through Celite and the collected solid washed with CH_2Cl_2 (ca. 20 mL). The filtrate was evaporated to dryness to afford **11** as a white solid (230 mg, 90%); mp 215°C decomposition. ^{1}H NMR ($CDCl_3$, 300 MHz), δ 7.77 (d, ^3J = 7.6 Hz, 4 H, ArH), 7.46 (dd, ^3J = $^3J'$ = 7.6 Hz, 4 H, ArH), 7.29 (dd, ^3J = $^3J'$ = 7.6 Hz, 4 H, ArH), 7.22 (d, ^3J = 7.6 Hz, 4 H, ArH), 7.02 (s, 2 H, NCH), 2.75 (q, 4 H, ^3J = 7.2 Hz, CH_2), 0.39 (t, 6 H, ^3J = 7.2 Hz, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 145.8 (arom. Cq), 140.3 (arom. Cq), 129.7 (arom. CH), 128.5 (arom. CH), 123.4 (arom. CH), 121.0 (arom. CH), 119.0 (NCH), 73.9 (Cq), 32.2 (CH_2), 8.2 (CH_3). The signal of the carbenic C atom was not detected. Anal. Calcd for $C_{33}H_{28}AgClN_2$ (595.92): C, 66.51; H, 4.74; N, 4.70. Found: C, 66.32; H, 4.81; N, 4.65.

General Procedure for Suzuki-Miyaura Cross-couplings

Procedure applied for the runs shown in Scheme 4. A mixture of palladium complex (0.01 mmol), phenylboronic acid (183 mg, 1.50 mmol) and Cs_2CO_3 (652 mg, 2 mmol) was suspended in dioxane (3 mL). After addition of p-tolylchloride (126 mg, 1 mmol), the mixture was vigorously stirred at 80°C for 1 h. The hot mixture was filtered through Celite. 1,4-Dimethoxybenzene (69 mg, 0.5 mmol; internal standard) was then added to the filtrate. The solvent was removed under reduced pressure, and the crude mixture was analysed by ^{1}H NMR spectroscopy. The yields were determined by comparing the intensity of the methyl signal of the product [δ(Me) = 2.41 ppm] with that of the internal reference [δ(Me) = 3.78 ppm]. In some experiments the product was isolated chromatographically. The isolated yield turned out to be very close (deviation less than %) to that determined by NMR.

Procedure applied for the runs shown in Table 1. A mixture of palladium complex (0.01 mmol), phenylboronic acid (183 mg, 1.50 mmol) and Cs_2CO_3 (652 mg, 2 mmol) was suspended in dioxane (3 mL). After addition of the arylchloride (1 mmol), the mixture was vigorously stirred at 80°C for 3 h. The hot mixture was filtered through Celite and the collected solid washed with CH_2Cl_2 (ca. 20 mL). The filtrate was evaporated to dryness and the residue purified by flash chromatography (SiO_2; AcOEt/petroleum ether, 0.5:99.5) to afford the desired product. All products were unambiguously identified by NMR after their isolation. The NMR spectra were compared to those reported in the literature.[10b]

X-ray chrystallography

Crystal Data for Complex 8. Crystals suitable for X-ray diffraction were obtained by slow diffusion of ether into a dichloromethane solution of the complex: $C_{38}H_{35}Cl_2N_3Pd$, M = 710.99, orthorhombic, space group $P2_12_12_1$, a = 11.6715(2), b = 13.6877(2), c = 20.5488(4) Å, β = 90.00, V = 3282.79(10) Å^3, Z = 4, μ = 0.760 mm^{-1}, F(000) = 1456. Crystals of the compound were mounted on a Oxford Diffraction CCD Saphire 3 Xcalibur diffractometer. Data collection with Mo-Kα radiation (λ = 0.71073 Å) was carried out at 120 K. 23091 reflections were collected (2.64 < θ < 27.00°), 7149 were found to be unique and 5389 were observed (merging R = 0.0620). The structure was solved with SHELXS-97.[23] Final results: R_2, R_1, wR_2, wR_1, Goof; 0.0592, 0.0378, 0.0631, 0.0598, 0.869. Residual electron density minimum/maximum = –0.460/0.899 e Å^{-3}.

Crystal Data for Complex 9. Crystals suitable for X-ray diffraction were obtained by slow diffusion of ether into a dichloromethane solution of the complex: $C_{38}H_{33}Cl_2N_3Pd$, M = 708.97, orthorhombic, space group $P2_12_12_1$, a = 11.6469(2), b = 13.7077(2), c = 20.4229(3) Å, β = 90.00, V = 3260.56(9) Å^3, Z = 4, μ = 0.765 mm^{-1}, F(000) = 1448. Crystals of the compound were mounted on a Oxford Diffraction CCD Saphire 3 Xcalibur diffractometer. Data collection with Mo-Kα radiation (λ = 0.71073 Å) was carried out at 120 K. 27148 reflections were collected (2.65 < θ < 27.00°), 7099 were found to be unique and 6467 were observed (merging R = 0.0335). The structure was solved with SHELXS-97.[23] Final results: R_2, R_1, wR_2, wR_1, Goof; 0.0289, 0.0244, 0.0526, 0.0517, 0.969. Residual electron density minimum/maximum = –0.251/0.476 e Å^{-3}.

Crystal Data for Complex 11. Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a dichloromethane solution of the complex: $C_{33}H_{28}AgClN_2$, M = 1191.79, triclinic, space group P–1, a = 10.2170(7), b = 13.5390(10), c = 20.073(2) Å, β = 78.226(8), V = 2660.9(4) Å^3, Z = 4, μ = 0.883 mm^{-1}, F(000) = 1216. Crystals of the compound were mounted on a Oxford Diffraction CCD Saphire 3 Xcalibur diffractometer. Data collection with Mo-Kα radiation (λ = 0.71073 Å) was carried out at 140 K. 21631 reflections were collected (3.05 < θ < 27.00°), 11591 were found to be unique and 6846 were observed (merging R = 0.0708). The structure was solved with SHELXS-97.[23] Final results: R_2, R_1, wR_2, wR_1, Goof; 0.1315, 0.0645, 0.1176, 0.0941, 1.019. Residual electron density minimum/maximum = –0.621/0.759 e Å^{-3}.

CCDC-875396 (for **8**), -901467 (for **9**) and -1004245 (for **11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational details

Calculations were performed using the ADF 2013 package.[24] All electrons Slater type orbitals were used with all-electron triple-ζ quality basis sets at DFT level with PBE functional.[25] Dispersive interactions were taken into account applying Grimme corrections.[26] Scalar relativistic effects were included through ZORA Hamiltonian.[27] Full geometry optimization was performed on the complexes. Interaction energy between the silver atom of 11 and the fluorenyl moiety was calculated by two methods. First, the ethylfluorenyl groups were rotated around the corresponding N–C bond moving the fluorenylidene plane from a position in which it is bent towards the metal centre to the opposite one (calculation 1). Secondly, we computed the substitution energy of a NHC-complex having two propyl chains instead of ethylfluorenyl groups by the NHC bearing two ethylfluorenyl groups (calculation 2). Both calculations showed that the complex where interaction between the silver atom and the fluorenyl groups occurs is more stable (ΔE = 3.2 kcal.mol^{-1} for calculation 1; ΔE = 3.8 kcal.mol^{-1} for calculation 2).

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