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Silver, Palladium and Rhodium Complexes of Acenaphthylene-Anullated N-Heterocyclic Carbene Ligands: A Comparative Study

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The newly prepared carbene precursor 1,3-dimesitylacenaphtho[1,2-*d*]imidazolinium chloride, (NHC–H)Cl, **3**, could be readily converted into the NHC-silver(I) complex, **4**, which is an efficient carbene transfer agent and has been used to synthesise thione **5**, *trans*-[$PdCl_2(NHC)_2$], **6** and [RhCl(NHC)(COD)], **7**. All compounds synthesised were characterised by elemental analysis, NMR spectroscopy and the molecular structures of the thione **5** and complex **7** were determined by X-ray crystallography. Complex **7** was converted into *cis*-[$RhCl(NHC)(CO)_2$] and the electron donating properties and *trans* influence of the NHC ligand were compared with nonanullated counterparts. The catalytic activity in the Heck reaction of **6** and the in situ formed palladium complex was evaluated. The activity of the in situ formed complexes for the Heck coupling of alkenes was high.

Introduction

Owing to their bonding versatility and the relative ease with which their electronic and steric properties can be modified, increasing attention has been focused on using imidazole-based N-heterocyclic carbene (NHC) compounds as ancillary ligands for a number of transition metal mediated catalytic reactions.[1–4] Their donating properties are superior to those of the most basic phosphanes. The ability of NHCs to coordinate to metal centres makes them excellent candidates for the design of well-defined catalysts. In a recent study, we observed that the variation of *p*-substituents on the phenyl ring of 1,3-diarylimidazolin-2-ylidenepalladium(II) complexes has a significant influence on the catalytic behaviour of the Suzuki coupling of NHC-Pd complexes.[5] Increasing knowledge of the chemical properties of ligands and complexes derived from them has led to a growing demand for systems with more and more complex structures. Anullated NHCs have attracted increasing attention in recent years since the introduction of carbo- and heterocyclic groups may give an opportunity for better control of the stability of the active species and improve catalytic activity. In this context, benzo-, pyrido-, naphtha- and quinoxalino-anullated imidazol-2-ylidenes have been reported.[6] These studies have demonstrated that the electron density at C^2 varies with the π donor/acceptor properties of the anullated rings. The 4,5-positions of the imidazolidine ring seem to be ideally suited for substitution since they are quite far from the catalytically active metal site. Therefore, we focused on the design of an acenaphthylene-anullated NHC ligand to modify the environment of the metal centre. Model studies showed that the tetracyclic ring system is highly strained. Our main aim was to determine how these properties are reflected in the electron donating properties of its complexes.

Results and Discussion

Preparation of Ligand Precursor 3, Thione 5 and NHC Complexes 6–8

The general route to the targeted NHC ligand precursor and metal complexes is shown in Scheme 1. The amine **2** was readily synthesised in good yield as a red, crystalline solid by means of the reduction of the corresponding imine **1** which served as a chelating ligand for several transition metal complexes.[7] Cyclisation of **2** with $CH(OEt)_3$ in the presence of one equiv. of NH_4Cl gave the diazolinium salt **3**. For the sake of comparison, the 4,5-dimethyl-1,3-dimesityl imidazolinium salt and related compounds (**4′**–**8′**) were also prepared (Scheme 2).

Treatment of **3** with NaO*t*Bu or NaH/NaO*t*Bu resulted in the deprotonation of the imidazolinium salt. However, attempted isolation of the free carbene failed. These precursor salts were subsequently deprotonated using basic silver oxide. Silver(I) NHC complexes are easy to make and can be used as air- and moisture-stable carbene transfer agents.[8] Such silver(I) NHC complexes with coordinating halides are well known to oligomerise by means of silver-silver interactions, bridging halides or carbenes[9] and they

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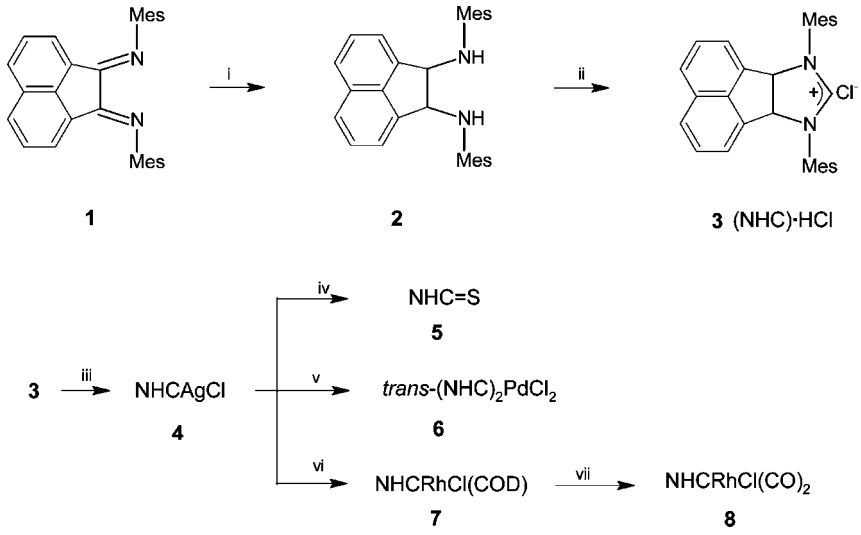
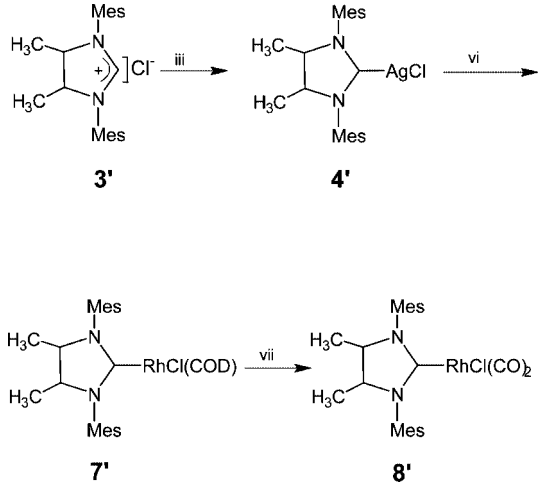


Scheme 1. i) $NaCNBH_3$, MeOH; ii) NH_4Cl, $HC(OEt)_3$; iii) Ag_2O, CH_2Cl_2; iv) S_8, CH_2Cl_2; v) $PdCl_2(CNCH_3)_2$, CH_2Cl_2; vi) $[RhCl(COD)]_2$, $PhCH_3$; vii) CO, CH_2Cl_2.



Scheme 2. iii) Ag_2O, CH_2Cl_2; vi) $[RhCl(COD)]_2$, $PhCH_3$; vii) CO, CH_2Cl_2.

have been characterised by ^1H and ^{13}C NMR spectroscopy.

The clearest spectroscopic evidence identifying **4** as a silver NHC complex is the appearance of a highly deshielded ^{13}C NMR signal for C_{carb} at δ = 205.5 ppm [dd, $^1J_{^{109}Ag,C}$ = 221.9, $^1J_{^{107}Ag,C}$ = 255.4 Hz]. The chemical shift and splitting pattern is consistent with the monomeric structure of **4**.[10] By comparison, the dimers consisting of $(NHC)_2Ag^+$ cations and AgX_2^- anions or $(NHC–Ag–\mu–X)_2$ structures display C_{carb} singlets due to partial dissociation and monomer/dimer equilibrium in solution. Ionic $(NHC)_2Ag^+$ complexes exhibit smaller $J_{^{107,109}Ag,C}$ coupling constants (180–190 and 200–215 Hz).[9] The chemical shift is also indicative of the donating nature of the carbene in the carbene–Ag interaction (Scheme 1).

Despite its large coupling constant, complex **4** is a good carbene transfer agent. Interaction of **4** with elemental sulfur readily afforded the thione **5**. This thione is a stable crystalline substance, the structure of which was elucidated by NMR spectroscopy and X-ray analysis. The most important peak in the ^{13}C NMR spectrum is the peak corresponding to C=S at δ = 179.6 ppm. X-ray diffraction analysis of **5** allowed us to draw some conclusions about the structure of **5**. The structure and the atom numbering scheme are shown in Figure 1. Very few cyclic thiones with bulky substituents at the N atoms of the NHC ligand have been reported[8] and this appears to be the first such compound with an anullated group.

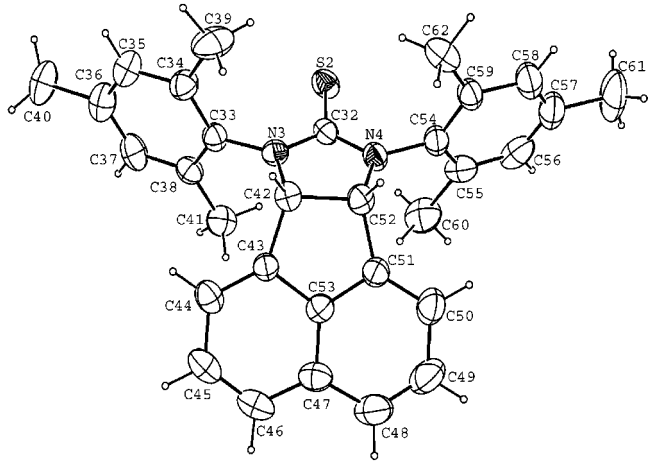


Figure 1. Molecular structure of **5**. Selected bond lengths [Å] and bond angles [°]: C32–S2 1.661(6), C32–N3 1.357(7), C32–N4 1.344(6), C33–N3 1.357(7), C54–N4 1.442(5), C42–C52 1.553(5); N3–C32–N4 108.6(5), N3–C32–S2 124.9(4), N4–C32–S2 126.5(4).

Crystallographic data for the structural analysis of **5** are given in Table 3. An ORTEP representation of the structure is shown in Figure 1 and selected bond lengths and angles are listed in the caption. The C(1)–S(1) bond length of 1.661 Å in **5** compares well with known C(32)–S(2) bond lengths in derivatives of imidazolidin-2-thiones.[8,11]

The reaction of the Ag complex **4** with palladium species bearing weakly coordinated CH_3CN ligands yielded the disubstituted carbene complexes **6**. The *trans* configuration of

the carbene ligands was confirmed by ^{13}C NMR spectroscopy in which the C_2 signal occurs at δ = 198.9 ppm, a value typical for *trans* carbene complexes.[12] At room temperature, the ^1H NMR spectrum of **6** shows that the NHC ligands are nonequivalent. Four signals can be observed at 1.22, 1.27, 2.25 and 2.33 ppm for each CH_3 group in the 2,6-positions of the aryl ring. This indicates that there is hindered rotation around the Pd–C_{carb} bond arising from the bulky phenyl substituent on the NHC ligand. The Pd^{II} carbene complex **6** and the in situ formed complexes between **3** and $Pd(OAc)_2$ were tested as catalysts in C–C coupling reactions.

In a similar fashion to that described for **6**, the reaction between **4** and the dimer $[RhCl(COD)]_2$ in boiling toluene generates the monocarbene complex **7**. The ^1H NMR spectrum shows singlets at δ = 1.46, 1.86, 2.53 and 2.82 ppm for the *o*-Me groups and 6.90, 6.99, 7.01 and 7.11 ppm for the *m*-protons of the mesityl groups, respectively, presumably because of the restricted rotation around the Rh–C_{carb} bond.[13] The detection of a doublet at δ = 213.7 ppm in the ^{13}C NMR spectrum together with a characteristic $J_{103Rh,13C}$ coupling of 48.8 Hz indicated the formation of the proposed complex. Further information was obtained from the crystal structure of [RhCl(NHC)(COD)], **7**, presented in Figure 2.

The single-crystal X-ray diffraction study of complex **7** confirmed the square-planar coordination geometry of the rhodium atom. The structure is represented in Figure 2 and selected bond lengths and angles are listed in the caption. The structural parameters of **7** are similar to those in other rhodium carbene complexes. The rhodium-carbene distance Rh(1)–C(1) [2.047(3) Å] is slightly longer than that observed in saturated analogues (2.003 Å), which may reflect the steric hindrance. However, the distance Rh(1)–Cl(1) [2.3768(9) Å] lies within the expected range.[14] The N(1)–C(1)–N(2) angle of 107.6° is close to that of thione **5** but slightly larger than that reported for [RhCl(SIMes)(COD)].[15] The difference in the *trans* influences of the carbene and the chloride ligands leads to different C=C bond lengths in the coordinated COD ligand: C32–C33 1.355(6) Å and C36–C37 1.385(6) Å.

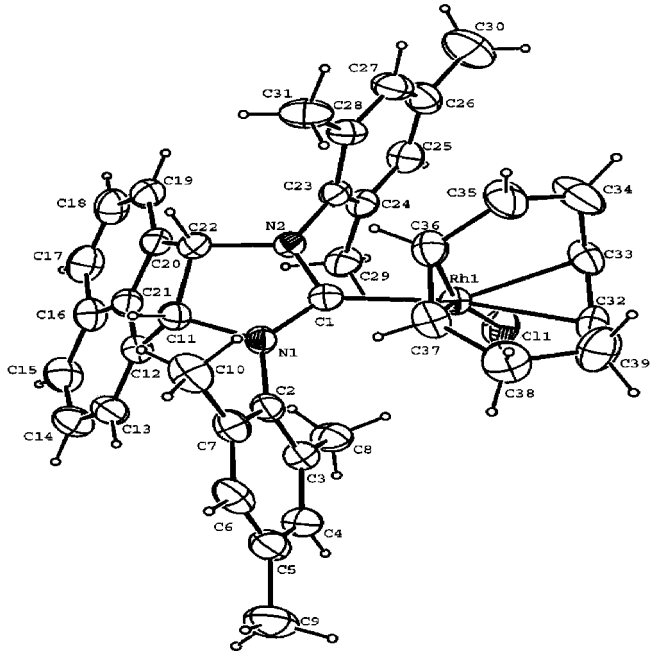


Figure 2. Structure of one molecule of **7** in the crystal. Selected bond lengths [Å] and bond angles [°]: C1–Rh1 2.047(3), C1–N1 1.357(4), C1–N2 1.341(4), C2–N1 1.427(4), C11–N1 1.476(4), C11–C22 1.538(5), C22–N2 1.488(4), C23–N2 1.435(4), C32–Rh1 2.219 (3), C32–C33 1.355(6), C33–Rh1 2.181(4), C36–Rh1 2.114(3), C36–C37 1.385(6), C37–Rh1 2.106(3), Cl1–Rh1 2.376(9); N1–C1–N2 107.6(3), N1–C1–Rh1 128.9(2), N2–C1–Rh1 122.7(2), N1–C11–C12 116.4(3), N1–C11–C22 102.3(2), N2–C22–C11 102.1(2), N2–C22–C20 114.9(3), C1–Rh1–Cl1 96.63(8).

The C–O stretching frequencies of *cis*-$[RhCl(CO)_2(NHC)]$ are considered as an excellent measure for the σ donor/π acceptor properties of the NHC ligands.[15] Therefore, we synthesised complexes of the type **8/8′** by replacing the COD ligand with excess CO. The IR spectra of **8/8′** revealed two bands corresponding to symmetric and asym-

Table 1. Selected NMR and IR spectroscopic data for **4/4′**–**8/8′**.

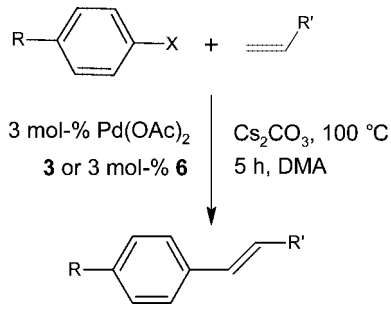
Complex	δ [ppm]	Appearance of signal	$J_{M,C}$	$\tilde{\nu}$(CO) sym	$\tilde{\nu}$ (CO) asym	Ref.
(IMes)AgCl	185.0	dd	270/234	–	–	[7b]
(SIMes)AgCl	207.5	dd	256/222	–	–	[7b]
4	205.5	dd	256/222	–	–	this work
4′	206.0	dd	255/223	–	–	this work
$(IMes)_2PdCl_2$	171.2	s	–	–	–	[17]
$(SIMes)_2PdCl_2$	199.2	s	–	–	–	[5]
6	198.9	s	–	–	–	this work
6′	196.7	s	–	–	–	[5]
(IMes)RhCl(COD)	183.7	d	52	–	–	[19]
(SIMes)RhCl(COD)	211.9	d	47	–	–	[15]
7	213.7	d	49	–	–	this work
7′	212.5	d	48	–	–	this work
$(IMes)RhCl(CO)_2$	–	–	–	2076	2006	[15]
$(SIMes)RhCl(CO)_2$	205.7	d	41	2081	1996	[15]
8	206.5	d	42	2074	1988	this work
8′	206.8	d	42	2078	1994	this work

metric vibrations. A comparison of IR data compiled for *cis*-[RhCl(CO)$_2$(NHC)] complexes of NHCs in Table 1 shows that acenaphthylene-anullated NHCs are stronger donors than corresponding nonanullated analogues bearing the imidazole skeleton.

Catalytic Arylation of Alkenes

We were interested in exploring the influence of substituents located at the 4,5-positions of the imidazolidine ring. Consequently, we tested in situ formed complexes [by use of 3 mol-% Pd(OAc)$_2$ and 3 mol-% **3**] and preformed **6** for activity in the Heck reaction[16] using a set of standard substrates, under standard reaction conditions in terms of solvent, temperature and base (Table 2).

Table 2. The Heck reaction catalysed by in situ formed [**3** + Pd(OAc)$_2$] or preformed complex **6**.[a]



Entry	Cat	R	R′	X	Yield (%)
1	**3**	Me	COO*n*Bu	Br	80
2	**6**	Me	COO*n*Bu	Br	30
3	**3**	Me	Ph	Br	86
4	**6**	Me	Ph	Br	33
5	**3**	Me(O)C	Ph	Br	89
6	**6**	Me(O)C	Ph	Br	35
7	**3**	Me(O)C	Ph	Cl	38
8	**6**	Me(O)C	Ph	Cl	10
9	**3′**	Me(O)C	COO*n*Bu	Br	67
10	**3**	Me(O)C	COO*n*Bu	Br	80
11	SIMesHCl	Me(O)C	COO*n*Bu	Br	62

[a] Reactions conditions: 1.0 mmol of the aryl halide, 1.5 mmol of olefin, 1.5 mmol Cs_2CO_3, 3 mL DMA, 100 °C, 5 h. GC yields (diethylene glycol dibutyl ether used as internal standard, average of two runs).

The coupling of 4-bromoacetophenone or 4-bromotoluene with alkenes was found to proceed in good yield in the presence of 3% of in situ formed catalyst (entries 1, 3 and 5). In the presence of preformed catalyst **6**, deactivated aryl bromides and activated 4-chloroacetophenone were less reactive under the same reaction conditions (entries 2, 4 and 6). The electron-donating capability of the substituents located at the 4,5-positions of the imidazolidine ring appear to play a role in the complex's catalytic activity. Thus, yields of 80%, 67% and 62% were achieved with complexes formed in situ between Pd(OAc)$_2$ and the salts **3**, **3′** and SIMesHCl, respectively, under identical conditions (entries 9–11). Clearly, acenapthene anullation has an unexpected effect of increasing the complex reactivity. This is somewhat surprising, since there is no conjugation between the imidazoline and naphthalene rings.

Conclusions

In order to further extend the possibilities of ligand tuning and the scope of NHC based catalysts, anullation of the imidazole ring by acenaphthylene was studied. Thione **5** and the transition metal complexes **6**–**8** of the anullated NHC ligand were easily obtainable from the silver-NHC complex **4** which was prepared from the salt **3** and Ag_2O. Silver is readily replaced by other metals to give, for example, Pd^{II} and Rh^{I} complexes in high yield. A comparison of NMR and IR spectroscopic data indicates that the new carbene seems to range between saturated and unsaturated imidazol-2-ylidene in terms of its electronic properties. A preliminary study has indicated that the in situ formed palladium complex is an active catalyst for arylation of alkenes.

The greater rigidity of the NHC complexes afforded by the tetracyclic imidazole framework exemplified by **6**–**8** can be anticipated to provide selective transformations. Investigations along these lines are in progress.

Experimental Section

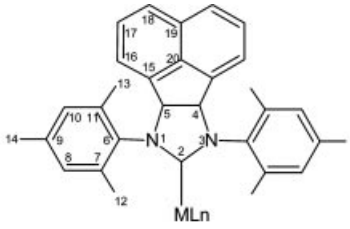
General: All manipulations were carried out in vacuo using Schlenk techniques. Anhydrous solvents were either distilled from appropriate drying agents or purchased from Merck and were degassed prior to use by purging with dry argon. The solvents were then kept over molecular sieves. All other reagents were commercially available and were used as received.

NMR spectra were recorded at 297 K on a Varian Mercury AS 400 instrument at 400 MHz (^{1}H) or 100.56 MHz (^{13}C). Elemental analyses were carried out by the analytical service of TUBITAK with a Carlo–Erba Strumentazione Model 1106 instrument. FTIR Spectra were recorded on a Perkin–Elmer Spectrum 100 series instrument. Compound **1** was prepared according to the literature.[18] The structural characterisations of **1′**, **2′**, **3′** and **6′** are given elsewhere.[5]

Starting Materials

1,2-Bis(mesitylamino)acenaphthylene (2): A suspension of **1** (2250 mg, 5.4 mmol) in MeOH (50 mL) was treated at room temperature under argon with $NaCNBH_3$ (2050 mg, 32.6 mmol) in portions of 1 g over a period of 20 min. To the resultant mixture was added bromocresol green and then 0.1 N HCl was added until the colour changed from green to yellow. The solution was stirred for 20 h and heated subsequently for 4 h under reflux. The mixture was then cooled to room temperature and 0.1 N KOH (10 mL), H_2O (100 mL) and CH_2Cl_2 (50 mL) were added. The aqueous phase was washed with CH_2Cl_2 several times. After this step, the CH_2Cl_2 washings were combined and dried with $MgSO_4$. The solvent was concentrated and then methanol was added. The precipitate was separated and washed with methanol. Drying under vacuum provided NMR spectroscopically pure off-white crystals of **2**. Yield: 1.82 g, 81%. M.p. 156–157 °C. $C_{30}H_{32}N_2$ (420.59): calcd. C 85.67, H 7.67, N 6.66; found C 86.10, H 7.82, N 6.93. ^{1}H NMR (400 MHz, $CDCl_3$, 297 K): δ = 2.18 (s, 12 H, $H^{12,13}$), 2.31 (s, 6 H, H^{14}), 3.84 (s, 2 H, NH), 5.31 (s, 2 H, $H^{4,5}$), 6.86 (s, 2 H, $H^{8,10}$),

6.96 (d, J = 1.6 Hz, 2 H, H^{16}), 7.39 (t, J = 1.9 Hz, 2 H, H^{17}), 7.68 (d, J = 2 Hz, 2 H, H^{18}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 297 K): δ = 19.1 ($C^{12,13}$), 20.9 (C^{14}), 62.4 ($C^{4,5}$), 120.5 (C^{16}), 124.3 (C^{18}), 128.2 (C^{17}), 129.3 ($C^{8,10}$), 129.9 (C^{7-11}), 130.9 (C^{19}), 131.6 (C^{9}), 135.8 (C^{20}), 142.4 (C^{6}), 144.4 (C^{15}) ppm.



M = Ag, Pd, Rh

Ln = others

1,3-Dimesitylacenaphtho[1,2-*d*]imidazolinium Chloride (3): A mixture of **2** (1170 mg, 2.78 mmol), triethyl orthoformate (10 mL) and ammonium chloride (150 mg, 2.84 mmol) was heated in a distillation apparatus until the ethanol distillation ceased. The temperature of the reaction mixture reached 130 °C. After cooling to room temp., ether (30 mL) was added. A colourless solid precipitated which was collected by filtration. Purification was achieved by repeated recrystallisations from ethanol/ether. Yield: 1.20 g, 93%. M.p. 393–395 °C. $C_{31}H_{31}N_2Cl$ (467.05): calcd. C 79.72, H 6.69, N 6.00; found C 79.10, H 7.02, N 6.13. ^1H NMR (400 MHz, $CDCl_3$, 297 K): δ = 1.56, 2.34 (s, 12 H, $H^{12,13}$), 2.68 (s, 6 H, H^{14}), 6.61 (s, 2 H, $H^{4,5}$), 6.86 (d, J = 1.8 Hz, 2 H, H^{16}), 6.88 (s, 2 H, $H^{8,10}$), 7.08 (s, 2 H, $H^{8,10}$), 7.48 (t, J = 1.9 Hz, 2 H, H^{17}), 7.89 (d, J = 2.2 Hz, 2 H, H^{18}), 10.21 (s, 1 H, H^2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 297 K): δ = 18.5, 19.1 ($C^{12,13}$), 21.4 (C^{14}), 70.6 ($C^{4,5}$), 122.3 (C^{16}), 126.9 (C^{18}), 128.7 (C^{17}), 129.1 (C^{8}), 130.4 (C^{10}), 130.7 (C^{19}), 131.9 (C^{9}), 135.4 (C^{20}), 136.3 (C^{7}), 136.4 (C^{11}), 137.5 (C^{6}), 140.8 (C^{15}), 159.3 (C^{2}) ppm.

Chloro(1,3-dimesitylacenaphtho[1,2-*d*]imidazolin-2-ylidene)silver(I) (4): A suspension of **3** (470 mg, 1 mmol) and an equivalent amount of Ag_2O in dichloromethane (50 mL) was stirred at room temperature for 24 h with exclusion of light. The colour of the suspension gradually changed from black to colorless. The suspension was then filtered, washed with dichloromethane and dried under vacuum to give a white solid. 0.52 g, 90%. M.p. 363–365 °C. $C_{31}H_{30}AgClN_2$ (573.90): calcd. C 64.88, H 5.27, N 4.88; found C 65.02, H 5.33, N 4.99. ^1H NMR (400 MHz, $CDCl_3$, 297 K): δ = 1.50, 2.35 (s, 12 H, $H^{12,13}$), 2.49 (s, 6 H, H^{14}), 6.09 (s, 2 H, $H^{4,5}$), 6.83 (d, J = 1.8 Hz, 2 H, H^{16}), 6.88, 7.08 (s, 4 H, $H^{8,10}$), 7.44 (q, 2 H, H^{17}), 7.82 (d, J = 2.0 Hz, 2 H, H^{18}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 297 K): δ = 18.4, 18.7 ($C^{12,13}$), 21.3 (C^{14}), 71.1, 71.3 ($C^{4,5}$), 121.8 (C^{16}), 126.0 (C^{18}), 128.5 (C^{17}), 130.3 (C^{8}), 130.4 (C^{10}), 131.8 (C^{19}), 134.0 (C^{9}), 135.2 (C^{20}), 136.9 (C^{7}), 137.2 (C^{11}), 138.7 (C^{6}), 139.1 (C^{15}), 205.5 (2d, $^1J_{^{13}C,^{107,109}Ag}$ = 221.9, 255.4 Hz, C^2) ppm.

Chloro(1,3-dimesityl-4,5-dimethylimidazolidin-2-ylidene)silver(I) (4′): Yield: 0.39 mg, 82%. M.p. 368–370 °C (dec.). $C_{23}H_{30}AgClN_2$ (477.82): calcd. C 57.81, H 6.33, N 5.86; found C 64.86, H 5.38, N 5.00. ^1H NMR (400 MHz, $CDCl_3$, 297 K): δ = 1.17–1.13 [s, 6 H, $NCH(CH_3)CH(CH_3)N$], 1.96 (s, 6 H, p-CH_3), 2.03, 2.01 (s, 12 H, o-CH_3), 4.01–3.98 [m, 2 H, $NCH(CH_3)CH(CH_3)N$], 7.13, 7.10 (s, 4 H, Mes) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 297 K): δ = 18.0, 17.8, [$NCH(CH_3)CH(CH_3)N$], 20.1, 19.9 (o-CH_3), 19.7 (p-CH_3), 52.3, 52.1 [$NCH(CH_3)CH(CH_3)N$], 127.8, 131.0, 131.3, 137.4, 138.1, 138.2, (Mes), 206.0 (2d, $^1J_{^{13}C,^{107,109}Ag}$ = 223.0, 255.0 Hz, C^2) ppm.

1,3-Dimesitylacenaphtho[1,2-*d*]imidazole-2-thione (5): A mixture of the silver complex **4** (570 mg, 1 mmol) and sulfur (32 mg, 1 mmol) was suspended in dichloromethane (50 mL) and stirred for 24 h at room temperature. After removal of silver chloride by filtration, the solution was concentrated in vacuo and hexane was added to afford white crystals of **5**. Yield: 0.40 g, 87%. M.p. 323–325 °C. $C_{31}H_{30}N_2S$ (462.64): calcd. C 80.48, H 6.54, N 6.06; found C 79.12, H 6.83, N 5.98. ^1H NMR (400 MHz, $CDCl_3$, 297 K): δ = 1.40, 2.26 (s, 12 H, $H^{12,13}$), 2.42 (s, 6 H, H^{14}), 6.23 (s, 2 H, $H^{4,5}$), 6.71 (d, J = 1.8 Hz, 2 H, H^{16}), 6.91 (s, 2 H, $H^{8,10}$), 7.11 (s, 2 H, $H^{8,10}$), 7.42 (t, J = 1.9 Hz 2 H, H^{17}), 7.85 (d, J = 2.1 Hz, 2 H, H^{18}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 297 K): δ = 18.4, 18.5 ($C^{12,13}$), 21.5 (C^{14}), 67.2 ($C^{4,5}$), 122.0 (C^{16}), 125.7 (C^{18}), 128.3 (C^{17}), 129.9 130.0 (C^{10}), 132.1 (C^{19}), 133.5 (C^{9}), 135.9 (C^{11}), 137.6 (C^{7}), 138.5 (C^{6}), 138.8 (C^{15}), 179.6 (C^{2}) ppm.

Dichloro(1,3-dimesitylacenaphtho[1,2-*d*]imidazolin-2-ylidene)-palladium(II) (6): $PdCl_2(MeCN)_2$ (260 mg, 1 mmol) and **4** (1140 mg, 2 mmol) were stirred in dichloromethane (50 mL) at 60 °C for 24 h in a sealed ampoule. The resultant mixture was filtered and the solvent was removed to yield a cream-colored solid. The solid was purified by crystallisation from CH_2Cl_2 layered with ethanol. 0.87 g, 84%. M.p. 390–392 °C. $C_{62}H_{60}Cl_2N_4Pd$ (1038.49): calcd. C 71.71, H 5.82, N 5.40; found C 71.79, H 5.88, N 4.96. ^1H NMR (400 MHz, $CDCl_3$, 297 K): δ = 1.22, 1.27, 2.25, 2.33 (s, 24 H, $H^{12,13}$), 2.49 (s, 12 H, H^{14}), 5.68 (d, J = 1.3 Hz 4 H, $H^{4,5}$), 6.67 (t, J = 1.7 Hz, 4 H, H^{16}), 6.73, 6.79, 6.86, 6.94 (s, 8 H, $H^{8,10}$), 7.28 (q, 4 H, H^{17}), 7.65 (q, 4 H, H^{18}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 297 K): δ = 19.7, 19.8, 20.3, 20.4 ($C^{12,13}$), 21.5 (C^{14}), 71.0 ($C^{4,5}$), 122.0 (C^{16}), 125.3 (C^{18}), 128.0 (C^{17}), 129.9, 129.6 ($C^{8,10}$), 131.5 (C^{19}), 134.6,134.8 (C^{9}), 136.5, 136.6, 136.7 ($C^{7,11}$), 137.4, 137.5 (C^{20}), 138.9, 139.0 (C^{6}), 139.4, 139.5 (C^{15}), 198.9 (C^{2}) ppm.

Chloro(η^4-1,5-cylooctadiene)(1,3-dimesitylacenaphtho[1,2-*d*]-imidazolin-2-ylidene)rhodium(I) (7): A suspension of $[RhCl(COD)]_2$ (250 mg, 0.5 mmol) and silver complex **4** (570 mg, 1 mmol) in toluene (10 mL) was stirred for 4 h at 100 °C. The resultant yellowish suspension was cooled to room temperature, filtered through celite and the yellow filtrate was concentrated. Addition of hexane (10 mL) precipitated a yellow powder, which was collected and dried in vacuo. Crystals of **7** suitable for X-ray analysis were obtained by crystallisation from CH_2Cl_2/C_2H_5OH. 0.59 g, 87%. M.p. 363–365 °C. $C_{39}H_{42}ClN_2Rh$ (677.12): calcd. C 69.18, H 6.25, N 4.14; found C 69.12, H 6.33, N 4.08. ^1H NMR (400 MHz, $CDCl_3$, 297 K): δ = 1.35–1.73 (m, 8 H, COD-CH_2), 1.46, 1.86, 2.53, 2.82 (s, 12 H, $H^{12,13}$), 2.23 (s, 6 H, H^{14}), 3.40 (d, J = 0.7 Hz, 2 H, COD-CH), 4.40 (t, J = 1 Hz, 2 H, COD-CH), 5.92, 6.00 (s, 2 H, $H^{4,5}$), 6.78 (d, J = 1.8 Hz, 1 H, H^{16}), 6.84 (d, J = 1.8 Hz, 1 H, H^{16}), 6.90, 6.99, 7.01, 7.11 (s, 4 H, $H^{8,10}$), 7.38 (m, 2 H, H^{17}), 7.74 (t, J = 2.2 Hz, 2 H, H^{18}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 297 K): δ = 19.3, 19.5, 20.6, 21.3 ($C^{12,13}$), 21.4, 21.5 (C^{14}), 28.3, 28.4, 32.7, 32.8 (COD-CH_2), 67.3 (d, J = 14.5 Hz, COD-CH), 68.0 (d, J = 13.7 Hz, COD-CH), 71.1, 71.4 ($C^{4,5}$), 96.2 (d, J = 6.9 Hz, COD-CH), 97.5 96.2 (d, J = 6.9 Hz, COD-CH), 121.9, 122.2 (C^{16}), 125.6, 125.7 (C^{18}), 128.1, 128.2 (C^{17}), 128.7, 128.9, 130.4 130.6 (C^{8-10}), 131.6, 131.8 (C^{19}), 134.5, 135.0 (C^{9}), 135.3, 137.3 (C^{11}), 137.6, 138.0 (C^{7}), 138.1, 138.3 (C^{6}), 139.7, 139.8 (C^{15}), 213.7 (d, ^1J = 48.8 Hz, Rh-C^2) ppm.

(Chloro)(η^4-1.5-cylooctadiene)(1,3-dimesityl-4,5-dimethylimidazolidin-2-ylidene)rhodium(I) (7′): Yield: 0.20 g, 70%. M.p. 210–212 °C (dec.). $C_{31}H_{42}ClN_2Rh$ (581.07): calcd. C 64.08, H 7.29, N 4.82; found C 63.89, H 7.08, N 4.96. ^1H NMR (400 MHz, $CDCl_3$, 297 K): δ = 1.17, 1.18, 1.19, 1.20 [s, 6 H, $NCH(CH_3)CH(CH_3)N$], 1.31–1.35 (m, 1 H, COD-CH_2), 1.58–1.56 (m, 3 H, COD-CH_2),

1.64–1.66 (m, 3 H, COD-CH_2), 1.93–2.71, (m, 19 H, COD-CH_2, *p*-CH_3, *o*-CH_3), 3.13–3.17 (m, 1 H, COD-CH), 3.36–3.37 (m, 1 H, COD-CH), 3.76–3.81, 3.86–3.91 [m, 2 H, NCH(CH_3)CH(CH_3)N], 4.36–4.38 (m, 1 H, COD-CH), 4.51–4.42 (m, 1 H, COD-CH), 7.06, 7.01, 6.95, 6.89 (s, 4 H, Mes) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 297 K): δ = 18.8, 18.9, [NCH(CH_3)CH(CH_3)N], 19.0, 20.3 (*p*-CH_3), 21.0, 21.2, 21.3, 21.4, (*o*-CH_3), 27.0, 29.6, 32.4 (COD-CH_2), 65.4 (d, *J* = 14.5 Hz, COD-CH=CH), 66.0, 66.7 [NCH(CH_3)CH(CH_3)-N], 70.2 (d, *J* = 14.5 Hz, COD-CH=CH), 96.6, 98.1, (d, *J* = 6.9 Hz, COD-CH=CH), 128.6, 128.9, 130.3, 130.4, 135.0, 135.2, 135.7, 136.8, 137.7, 137.8, 138.9, 139.5 (Mes), 212.5 (d, *J* = 48.0 Hz, Rh-C^2) ppm.

(Chloro)(dicarbonyl)(1,3-dimesitylacenaphtho[1,2-*d*]imidazolin-2-ylidene)rhodium(I) (8): Compound **7** (50 mg, 73 μmol) was dissolved in CH_2Cl_2 in a Schlenk flask and carbon monoxide was bubbled through the solution for 50 min. The reaction mixture was stirred at room temperature for 1.5 h and then concentrated to dryness giving a cream powder. Yield 40 mg, 86%. $C_{33}H_{32}ClN_2O_2Rh$ (624.96): calcd. C 63.42, H 4.84, N 4.48; found C 63.54, H 5.00, N 4.52. ^{1}H NMR (400 MHz, $CDCl_3$, 297 K): δ = 1.50, 2.30 (s, 12 H, $H^{12,13}$), 2.62 (s, 6 H, H^{14}), 6.03 (s, 2 H, $H^{4,5}$), 6.78 (d, *J* = 1.8 Hz, 2 H, H^{16}), 6.84, 7.00 (s, 4 H, $H^{8,10}$), 7.36 (t, *J* = 1.8 Hz 2 H, H^{17}), 7.74 (d, *J* = 2.1 Hz, 2 H, H^{18}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 297 K): δ = 19.3, 19.6 ($C^{12,13}$), 21.4 (C^{14}), 71.4 ($C^{4,5}$), 122.1 (C^{16}), 125.9 (C^{18}), 128.4 (C^{17}), 129.7 (C^{10}), 130.4 (C^{19}), 131.8 (C^9), 133.8 (C^{11}), 136.6 (C^7), 138.7 (C^6), 138.9 (C^{15}), 183.6 [d, CO, $^1J_{^{103}Rh,^{13}C}$ = 76 Hz], 185.3 [d, CO, $^1J_{^{103}Rh,^{13}C}$ = 52.4 Hz], 206.5 [d, $^1J_{^{103}Rh,^{13}C}$ = 42 Hz, Rh-C^2] ppm. IR (KBr): $\tilde{\nu}$ = 2074, 1988 (CO) cm^{-1}.

Chloro(dicarbonyl)(1,3-dimesityl-4,5-dimethylimidazolidin-2-ylidene)rhodium(I) (8′): Yield: 41.9 mg, 92%. M.p. 149–151 °C (dec.). $C_{25}H_{30}ClN_2O_2Rh$ (528.87): calcd. C 56.77, H 5.72, N 5.30; found: C 56.86, H 5.65, N 5.33. ^{1}H NMR (400 MHz, $CDCl_3$, 297 K): δ = 1.13 –1.27 [s, 6 H, NCH(CH_3)CH(CH_3)N], 1.99 (s, 6 H, *p*-CH_3), 2.05, 2.13 (s, 12 H, *o*-CH_3), 3.98–4.01 [m, 2 H, NCH(CH_3)-CH(CH_3)N], 7.11, 7.20 (s, 4 H, Mes) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 297 K): δ = 18.0, 18.2, [NCH(CH_3)CH(CH_3)N],19.9 (*p*-CH_3), 20.9, 21.4 (*o*-CH_3), 53.1, 53.3 [NCH(CH_3)CH(CH_3)N], 128.9, 130.3, 130.4, 137.8, 138.9, 139.5 (Mes), 182.8 [d, CO, $^1J_{^{103}Rh,^{13}C}$ = 73.3 Hz], 185.0 [d, CO, $^1J_{^{103}Rh,^{13}C}$ = 52.5 Hz], 206.7 [d, $^1J_{^{103}Rh,^{13}C}$ = 41.4 Hz, Rh-C^2] ppm. IR (KBr): $\tilde{\nu}$ = 2078, 1994 (CO) cm^{-1}.

General Procedure for Heck Coupling Reactions: A two-necked 25 mL flask fitted with a reflux condenser was charged with aryl halide (1.0 mmol), olefin (1.5 mmol), Cs_2CO_3 (1.5 mmol), diethylene glycol dibutyl ether (internal standard), DMA (3 mL) and 3 mol-% of in situ formed catalyst or preformed complex **6**. The mixture, under an atmosphere of argon, was placed in a preheated oil bath (100 °C) and stirred for 5 h. The conversion was monitored by gas chromatography.

X-ray Structural Analyses of 5 and 7: Crystals of thione **5** suitable for X-ray analysis were obtained from a dichloromethane solution layered with hexane. Similarly, we obtained crystals of **7**, suitable for X-ray analysis, from CH_2Cl_2 layered with EtOH.

A colourless single-crystal of **5** and a yellow crystal of **7** suitable for data collection were mounted on glass fibres and data collection was performed on a STOE IPDS II diffractometer with graphite monochromated Mo-K_α radiation at 296 K. The structures were solved by direct-methods using SHELXS-97[20] and refined by full-matrix least-squares methods on F^2 using SHELXL-97[21] from within the WINGX[22,23] suite of software. All non-hydrogen atoms were refined with anisotropic parameters. Hydrogen atoms bonded to carbon were placed in calculated positions (C–H = 0.93–0.98 Å) and treated using a riding model with *U* = 1.2 times the *U* value of the parent atom for CH, CH_2 and CH_3. Molecular diagrams were created using ORTEP-III.[24] Geometric calculations were performed with Platon.[25] Atomic coordinates and equivalent isotropic displacement parameters are listed in Table 3.

Table 3. Crystal data and structural refinements for **5** and **7**.

	$C_{31}H_{30}N_2S$	$C_{39}H_{40}ClN_2Rh$
Formula weight	462.63	675.09
Temperature [K]	296	296
Wavelength [Å]	0.71073	0.71073
Crystal system	orthorhombic	monoclinic
Space group	$Pna2_1$	$P2_1/c$
Unit cell dimensions		
a [Å]	19.5086(7)	9.0872(6)
b [Å]	7.1186(3)	17.0953(7)
c [Å]	37.5917(15)	21.0906(11)
α [°]	90	90
β [°]	90	93.293 (5)
γ [°]	90	90
Volume [Å^3]	5220.5(4)	3271.0(3)
Z	8	4
Calculated density [Mg m^{-3}]	1.177	1.371
Absorption coefficient [mm^{-1}]	0.145	0.634
F(000)	1968	1399.8
Crystal size [mm]	0.34 × 0.42 × 0.50	0.33 × 0.21 × 0.12
θ range for data collection [°]	1.50 to 24.07	1.53 to 27.19
Independent reflection	8204	6422
Collected reflection	35086	29998
Absorption correction	integration	integration
T_{min}	0.9389	0.8788
T_{max}	0.9685	0.9294
R_{int}	0.1013	0.047
θ_{max} [°]	24.11	26
h	–22 to 22	–11 to 11
k	–8 to 8	–21 to 24
l	–42 to 42	–25 to 26
Refinement method	full-matrix least-squares on F^2	
$wR(F^2)$	0.1161	0.0912
Goodness-of-fit on F^2	0.920	0.939
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.047	R_1 = 0.0359
R indices (all data)	R_1 = 0.076	R_1 = 0.0598
$(\Delta/\sigma)_{max}$	0.292	0.000
$\Delta\rho_{max}$ [e Å^{-3}]	0.132	0.404
$\Delta\rho_{min}$ [e Å^{-3}]	–0.196	–0.325

CCDC-610151 and -610150 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.

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