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Metal Complexes of Very Bulky *N*,*N*′-Diarylimidazolylidene N-Heterocyclic Carbene (NHC) Ligands with 2,4,6-Cycloalkyl Substituents

Roman Savka[a] and Herbert Plenio*[a]

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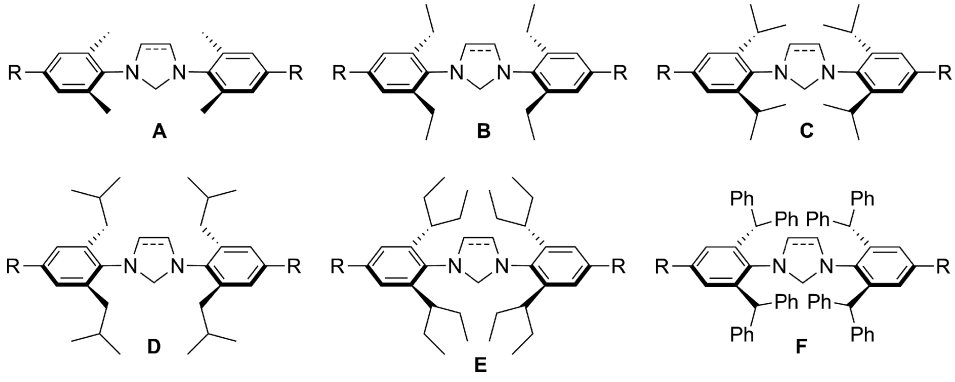
1,3,5-Tricycloalkylbenzene (cycloalkyl = C_5H_9, C_6H_{11}) was converted into the respective anilines (by means of nitration and reduction) and then into the corresponding diimines (with glyoxal), the cyclization of which with $(HCHO)_n/ZnCl_2$ provided the respective 1,3-bis(2,4,6-tricyclopentylphenyl)-imidazolium salt in modest yields. An analogous reaction sequence that employed acenaphthene-1,2-dione instead of glyoxal yielded the two azolium salts in good yields, which were converted into the respective N-heterocyclic carbene (NHC) complexes [(NHC)AgCl], [(NHC)AuCl], [(NHC)-RhCl(cod)] (cod = cyclooctadiene), and [(NHC)RhCl$(CO)_2$].

Introduction

N-Heterocyclic carbenes are an established class of ligands, and a large number of these complexes with metals from all over the periodic table have been synthesized.[1] Consequently, the electronic and steric properties of NHC ligands have been modified in many ways to modulate the properties of the respective NHC metal complexes.[2] Different σ-donor or π-acceptor behavior of NHC ligands change the electronic properties and can lead to unexpected reactivity patterns[3] or unusual complexes.[4] Sterically demanding NHC ligands lend kinetic stability to fleeting intermediates in catalytic transformations, thus enabling more efficient catalysis.[5]

One of the prevalent structural motifs in NHC ligands is the 1,3-bis(2,6-dialkylphenyl)imidazol-2-ylidene-type carbenes.[6] Four alkyl substituents in the 2,6-position enhance the stability of the metal complexes relative to the respective complexes with sp^2-CH bonds, which are much more prone to CH activation than sp^3-CH bonds. Another important factor is added stability owing to steric shielding of the metal center by utilizing the bulk of the 2,6-substituents. Modification of the four *ortho*-alkyl groups thus has a pronounced influence on the stability of the respective metal complexes.[7] The two most commonly applied substituents are methyl and isopropyl groups (Scheme 1, A and C) since the respective anilines (2,6-dimethylaniline and 2,6-diisopropylaniline) needed for the synthesis of the respective carbenes are commercially available at low cost. The ethyl group (Scheme 1, B) is used less often,[8] since the respective aniline is expensive; furthermore, the stability of the respective NHC metal complexes appears to be slightly inferior



Scheme 1. *N*,*N*′-Diaryl-NHC ligands with sterically demanding *ortho* substituents.

[a] Organometallic Chemistry, TU Darmstadt,
Alarich-Weiss-Strasse 12, 64287 Darmstadt, Germany
E-mail: plenio@tu-darmstadt.de
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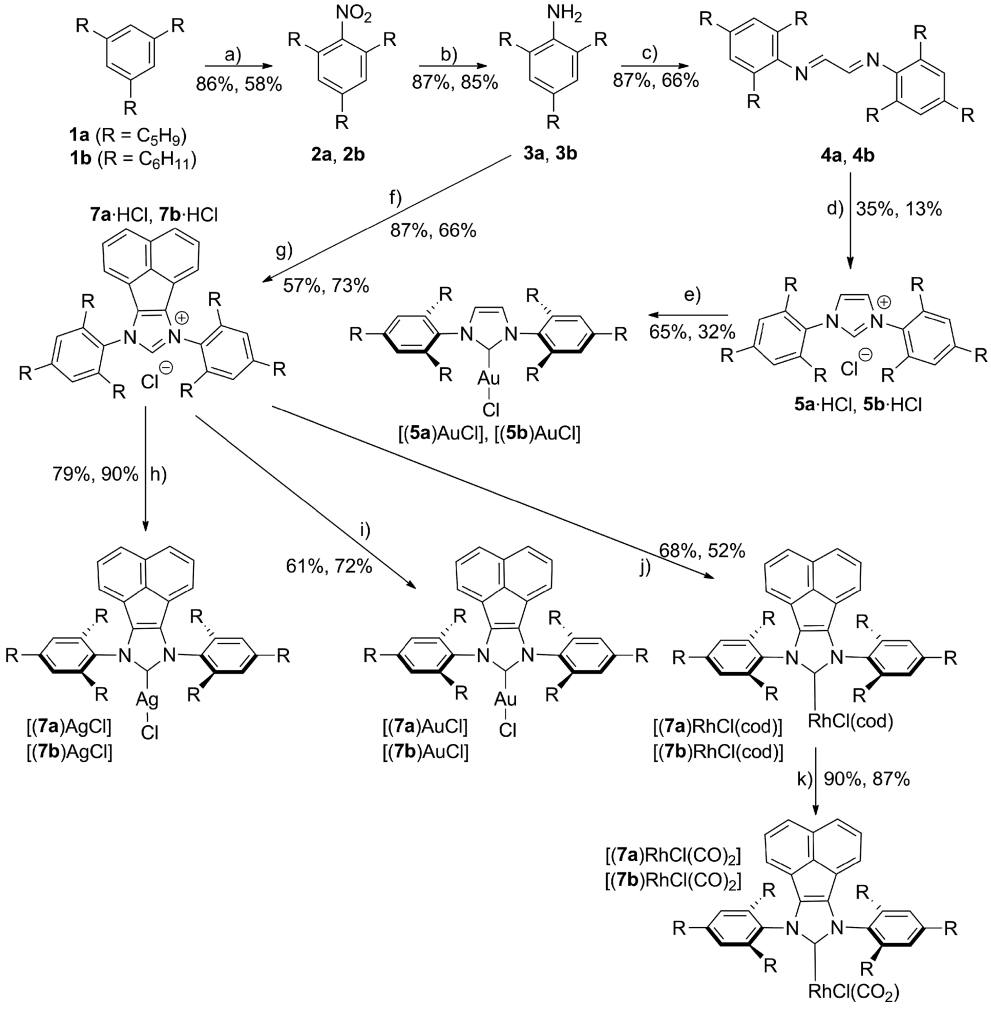
to those with A- and C-type ligands (Scheme 1).[8a] NHC ligands with larger alkyl groups are desirable since this can lead to more powerful NHC–metal catalysts, as was demonstrated convincingly by Organ et al. for various Pd-catalyzed cross-coupling reactions.[4b] Several different D-[9] and E-type[10] NHC ligands (Scheme 1) were synthesized to provide even more bulk next to the metal center. However, in some cases the synthesis of the respective anilines requires significant synthetic effort[11] and consequently the availability of such NHC ligands is limited; cyclization of the linear precursors to the cyclic azolium can also be fraught with problems. Originating from work of Marko et al., several sterically even more demanding F-type ligands (Scheme 1) have been synthesized.[12]

Consequently, we were interested in developing new protocols for the synthesis of NHC ligands with very bulky alkyl substituents. In the present manuscript we wish to report on the synthesis of new NHC ligands with cycloalkyl groups in the 2,4,6-positions. The respective anilines are easily available on a large scale from benzene by employing a classic Friedel–Crafts/nitration/reduction sequence.

Results and Discussion

Synthesis of New NHC Ligands

The synthesis of the respective azolium salts and NHC metal complexes is summarized in Scheme 2. Starting from the known 1,3,5-tricycloalkylbenzenes[13] **1a** and **1b** [R = cyclopentyl (**a**), cyclohexyl (**b**)], the nitration with HNO_3 leads to the 1-nitro-2,4,6-tricycloalkylbenzenes **2a** and **2b**. A minor impurity (<2%) in such compounds is the 1,2,4-substituted benzene formed as a byproduct in the 1,3,5-alkylation. For most metal complexes, this impurity is not visible in the NMR spectra. Reduction of the nitro group gave the anilines **3a** and **3b**, which were treated with glyoxal according to standard procedures[2b] to provide the respective diimines in good yields. However, the cyclization of the sterically demanding diimines to the respective azolium salts turned out to be difficult as the standard procedure[2b] did not lead to the formation of the desired products. Next, the Hintermann synthesis[14] was tested for the cyclization reaction of diimine **4a**. The desired azolium salt was ob-



Scheme 2. Synthesis of new NHC ligands and metal complexes. Reagents and reaction conditions: (a) HNO_3, HOAc/Ac_2O in CH_2Cl_2, 0 °C; (b) Zn/HCl in AcOH under reflux conditions; (c) glyoxal, HCHO in CH_3OH; (d) $ZnCl_2$, $(HCHO)_x$, HCl in $CHCl_3$, 60 °C; (e and h) [AuCl(Me_2S)], K_2CO_3, acetone; (f) acenaphthene-1,2-dione, HOAc, in CH_3CN, 14 h, 95 °C; (g) $CH_2Cl(OEt)$, neat, 100 °C, 24 h; (h) Ag_2O in CH_2Cl_2; (j) [{RhCl(cod)}$_2$], Na amylate in thf; and (k) CO in CH_2Cl_2 (yields given on reaction arrows for **a**-and **b**-type products).

tained in approximately 25% yield, but turned out to be highly impure and could not be purified. The reaction of **4a** with $ClCH_2OEt$ gave a black oil of unknown composition.[15] However, a procedure developed by Marko et al.[12a] using $ZnCl_2$ and $(HCHO)_x$ produced the desired azolium salt **5a** in moderate yield (Scheme 2). The same procedure was then applied to the cyclization of diimine **4b**. The hexakis-cyclohexyl azolium salt **5b** was obtained in low yield and with modest purity. It was not possible to purify this salt to a satisfactory level of purity.

The attempted cyclization of the respective diamines derived from the reduction of **4a** and **4b** using $HC(OEt)_3$ led to a mixture of the respective mono- and bis-formamides instead of the desired azolium salts. The same problems were reported by Organ et al. during the attempted synthesis of related azolium salts with 3-pentyl instead of the cyclohexyl or cyclopentyl groups employed by us.[9] A reasonable explanation for the poor yields of the cyclization reaction is the low population of the favorable *syn* orientation of the two nitrogen groups owing to the bulky alkyl substituents. For diimines with sterically highly demanding N substituents, the diimine should preferentially exist as the *anti* isomer, which is not amenable to cyclization. With a view to the modest overall yields of the azolium salts, we decided to study the synthesis of more easily available NHC ligands.

To enable the synthesis of NHC ligands with highly demanding *N*-aryl groups, it was decided to employ diimines with an enforced *syn* orientation. The diimines derived from acenaphthene-1,2-dione appear to be ideal in this respect. The respective diimines obtained with 2,4,6-trimethylaniline or 2,6-diisopropyl aniline were first reported by Cowley at al.[15] and shown to form stable metal complexes.[16] The respective Pd complexes were successfully employed in various cross-coupling reactions.[17] The reaction of anilines **3a** and **3b** with glyoxal provided the respective dimines **6a** and **6b**, which were cyclized to yield the azolium salts **7a**·HCl and **7b**·HCl.

Synthesis of the Metal Complexes

Owing to the limited availability of NHC ligands **5a** and **5b**, only the respective NHC–Au complexes were prepared. The synthesis of the respective gold complexes [(**5a**)AuCl] and [(**5b**)AuCl] was possible, which in turn could be purified easily by chromatography to provide the first NHC metal complexes with six cyclohexyl or six cyclopentyl groups (Scheme 2). An NHC ligand with four cyclopentyl groups in the 2,6-positions, which is closely related to imidazolium salt **5a** (which has six cyclopentyl groups in the 2,4,6-positions), was first mentioned by Organ et al.,[18] but neither a synthetic protocol nor any characterization data were reported.

Starting from the azolium salts **7a**·HCl and **7b**·HCl, the direct reaction with Ag_2O in CH_2Cl_2 led to the respective complexes [(**7a**)AgCl] and [(**7b**)AgCl] in excellent yields. Single crystals of the latter complex were grown by slow evaporation of a CH_2Cl_2/2-propanol solution (see the crystal structure). The related gold complexes [(**7a**)AuCl] and [(**7b**)AuCl] were also synthesized directly from the respective azolium salts by using and $[AuCl(Me_2S)]$ and K_2CO_3 in acetone, analogous to recent procedures from Gimeno et al.[19] and Nolan et al.[20] The synthesis of the rhodium complexes followed established procedures.[21] To characterize the electron-donating ability of the new carbenes, the redox potentials of [(**7a**)RhCl(cod)] (cod = cyclooctadiene) and [(**7b**)RhCl(cod)] in CH_2Cl_2 were both determined to be $E_{1/2}$ = 0.78 V. This redox potential is close to that of the related rhodium complexes [(SIMes)RhCl(cod)] ($E_{1/2}$ = 0.83 V) [SIMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene].[21] The infrared spectroscopic determination of ν(CO) in [(**7a**)RhCl$(CO)_2$] confirms similar donating properties of NHC ligands **7a** and IMes. It is evident from these data that the influence of the strained acenaphthene backbone on the donor properties of the respective NHC ligands is not large. Compounds **7a** and **7b** are normal carbenes with respect to their donating properties.[15] Owing to the six cycloalkyl groups, the complexes reported here display excellent solubility in all solvents other than highly polar ones.

Crystal Structure of the Complex

For [(**7b**)AgCl],[22] in the solid state the six cyclohexyl groups form an extended array, such that the lower part of ligand **7b** can be considered to be a large, diamond-shaped plate with dimensions of 2.1 nm × 1.3 nm (Figures 1 and 2). This shape renders this ligand much larger than the conventional SIMes-type ligand in two dimensions.

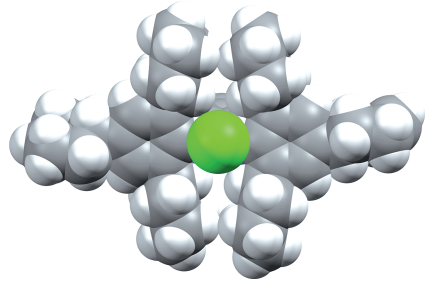


Figure 1. Space-filling plot of [(**7b**)AgCl] viewed along the Cl–Ag–NHC axis.

To evaluate the steric properties of the new NHC **7b** more precisely, the buried volume according to Cavallo et al. was calculated[23] and compared with that of the analogous Ag complex with four 2,6-*i*Pr groups reported by Cowley et al.[15,24] To our surprise, the buried volume of carbene [(**7b**)AgCl], V_{bur} = 35%, was calculated to be smaller than that of the related *i*Pr-substituted Ag complex reported by Cowley with V_{bur} = 39 and 43% (two V_{bur} for two crystallographically independent molecules).[25] This result is unexpected since (concerning the carbon atoms) an isopropyl group is a subset of a cyclohexyl group and the latter unit can be only slightly sterically less demanding.[26]

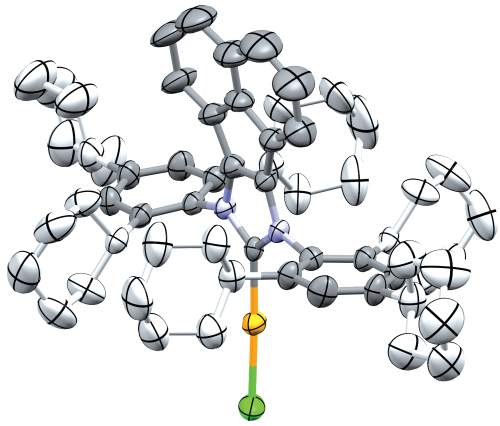


Figure 2. X-ray crystal structure of complex [(**7b**)AgCl] (ORTEP plot; cyclohexyl groups: light gray, other carbon atoms: dark gray, N: blue, Ag: orange, Cl: green). Important bond lengths [pm] and angles [°]: Ag–C 206.8(4), Ag–Cl 231.63(14); C–Ag–Cl 177.29(12).

We therefore believe that for the present ligands the static picture of the buried volume approach is not useful.

The coordination sphere around silver behaves according to expectations with a two-coordinate, almost linear silver ion (Figure 2). The Ag–C(NHC) distance and the Ag–Cl distances are also in the expected range for such complexes.[27]

Conclusion

We have reported the preparation of several very bulky NHC ligands. Based on a classic sequence of Friedel–Crafts alkylation/nitration/Zn reduction, the new 2,4,6-cycloalkylanilines (cycloalkyl = C_5H_9 and C_6H_{11}) were synthesized and converted into the respective azolium salts by utilizing the respective diimines. This cyclization reaction tends to be very difficult for diimines with sterically demanding N substituents. However, when employing the enforced *syn* orientation in the acenaphthene-1,2-diimines, such bulky azolium salts can be prepared easily by facilitating the critical cyclization step. Several metal complexes with Ag, Au, and Rh were synthesized and shown to display normal electronic properties relative to the analogous complexes with the established SIMes NHC ligand. Future studies will be directed towards testing the properties of such ligands in catalysis.

Experimental Section

General Experimental: See the Supporting Information.

Synthesis of 1,3,5-Tricycloalkylbenzenes 1a and 1b: According to a modified literature procedure,[13] $AlCl_3$ (38.0 g, 284.8 mmol) was added under an argon atmosphere to a 1 L three-necked round-bottomed flask cooled to 0 °C that contained benzene (8.0 mL, 89.7 mmol) in CH_2Cl_2 (60 mL). Cyclopentyl bromide (30.7 mL, 287 mmol) or cyclohexyl bromide (35.3 mL, 287 mmol) was added dropwise, and the temperature in the flask was kept close to 0 °C. Stirring was continued for 2 h and the reaction mixture was then allowed to cool to room temp. for approximately 30 min (if the reaction was allowed to stir for longer periods of time at room temp., the yield of product dropped dramatically). The reaction mixture was then placed in an ice bath, carefully quenched with ice, and diluted with diethyl ether (200 mL). The layers were separated, and the ethereal solution was washed twice with water and brine. The organic layer was dried with $MgSO_4$, filtered, and the solvent was removed under vacuum. The resulting oily mixture was filtered through a silica plug and washed with *n*-pentane. After removing the volatiles under vacuum, 1,3,5-tricyclopentylbenzene (22.9 g, 90% yield) or 1,3,5-tricyclohexylbenzene (26.0 g, 89.6% yield) were obtained as colorless oils, which crystallized upon standing in the refrigerator. NMR spectra are in accord with the literature data.

Synthesis of Nitrobenzenes 2a and 2b: 1,3,5-Tricyclopentylbenzene (14.0 g, 49.6 mmol) or 1,3,5-tricyclohexylbenzene (26.0 g, 80.2 mmol) was dissolved in CH_2Cl_2, Ac_2O, and AcOH [for the 1,3,5-tricyclopentylbenzene reaction: CH_2Cl_2 (210 mL), Ac_2O (140 mL), AcOH (105 mL); for the 1,3,5-tricyclohexylbenzene reaction: CH_2Cl_2 (340 mL), Ac_2O (217 mL), AcOH (170 mL)]. The solution was cooled to 0 °C and fuming nitric acid (20.8 mL for 1,3,5-tricyclopentylbenzene; 34 mL for 1,3,5-tricyclohexylbenzene) was added dropwise for 1 h while keeping temperature between 0 and 5 °C. The resulting solution was stirred for an additional 5 h at 0 °C and then warmed to room temp. Next, water (300 mL) and CH_2Cl_2 (200 mL) were added. The organic layer was separated and washed with cold aqueous NaOH (0.1 M) to remove acids as well as unreacted Ac_2O. The organic solution was then washed with brine, dried with $MgSO_4$, and filtered. The volatiles were removed under reduced pressure and the residue recrystallized from hot ethanol to provide 1-nitro-2,4,6-tricyclopentylbenzene (14.0 g, 86% yield) or 1-nitro-2,4,6-tricyclohexylbenzene (17.3 g, 58% yield) as white crystals. Compound **2a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.06 (s, 2 H, H_{Ar}), 3.05–2.91 (m, 1 H, *p*-CH, cyclopentyl), 2.91–2.77 (m, 2 H, *o*-CH, cyclopentyl), 2.15–1.48 (m, 24 H, CH_2, cyclopentyl) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.12, 148.74, 137.10, 123.23, 46.24, 40.67, 35.05, 34.81, 25.78, 25.63 ppm. HRMS (EI): *m*/*z* calcd. for $C_{21}H_{29}NO_2$: 327.2198 $[M]^+$; found 327.2211. Compound **2b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.01 (s, 2 H, H_{Ar}), 2.58–2.44 (m, 1 H, *p*-CH, cyclohexyl), 2.44–2.31 (m, 2 H, *o*-CH, cyclohexyl), 1.96–1.16 (m, 30 H, CH_2, cyclohexyl) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.99, 148.91, 138.00, 123.30, 44.92, 39.81, 34.49, 34.37, 26.93, 26.79, 26.18, 26.14 ppm. HRMS (EI): *m*/*z* calcd. for $C_{24}H_{35}NO_2$: 369.2668 $[M]^+$; found 369.2655.

Synthesis of Anilines 3a and 3b: 1-Nitro-2,4,6-tricyclopentylbenzene (**2a**; 14.0 g, 42.8 mmol) or 1-nitro-2,4,6-tricyclohexylbenzene (**2b**; 17.3 g, 46.9 mmol) was dissolved in AcOH (205 mL for **2a**; 235 mL for **2b**) under reflux conditions and concentrated HCl (31 mL for **2a**; 39 mL for **2b**) was added in one portion. Next, Zn powder (22.4 g, 344.6 mmol for **2a**; 28.0 g, 430.7 mmol for **2b**) was carefully added in several portions. The mixture was heated to reflux for 1 h and then cooled to room temperature. Next, a cold (0 °C) 1 M solution of NaOH was added in several portions to adjust the reaction mixture to approximately pH 9–10. The product was extracted with diethyl ether, then the extract was washed with brine, dried with $MgSO_4$, and filtered. The solvent was removed under reduced pressure to give 1-amino-2,4,6-tricyclopentylbenzene (**3a**) (11.0 g, 87% yield) as a yellow-orange oil or 1-amino-2,4,6-tricyclohexylbenzene (**3b**) (13.5 g, 85% yield) as an off-white powder. These compounds could be purified by recrystallization from hot ethanol. In the case of **3a**, its concentrated solution in hot ethanol was slowly cooled to room temp. and then to 0 °C in the refrigerator. The ethanol was decanted and the oily residue dried under vacuum. Compound **3a**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.95 (s, 2 H, H_{Ar}), 3.66 (br.,

2 H, NH_2), 3.07–2.98 (m, 1 H, *p*-CH, cyclopentyl), 2.97–2.87 (m, 2 H, *o*-CH, cyclopentyl), 2.14–1.52 (m, 24 H, CH_2, cyclopentyl) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 139.92, 135.84, 130.14, 122.22, 46.05, 40.56, 35.01, 32.54, 25.58, 25.38 ppm. HRMS (EI): *m/z* calcd. for $C_{21}H_{31}N$: 297.2457 $[M]^+$; found 297.2420. Compound **3b**: ^1H NMR (300 MHz, $CDCl_3$): δ = 6.86 (s, 2 H, H_{Ar}), 3.56 (br., 2 H, NH_2), 2.59–2.33 (m, 3 H, CH, cyclohexyl), 2.05–1.16 (m, 30 H, CH_2, cyclohexyl) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.31, 138.16, 131.82, 121.82, 44.50, 39.24, 35.01, 33.23, 27.44, 27.25, 26.60, 26.43 ppm. HRMS (EI): *m/z* calcd. for $C_{24}H_{37}N$: 339.2926 $[M]^+$; found 339.2905.

Synthesis of Imines 4a and 4b: Aniline **3a** (2.7 g, 9.09 mmol) or aniline **3b** (3.09 g, 9.09 mmol) was dissolved in hot methanol (ca. 50 mL for **3a**; 150 mL for **3b**). Next, a glyoxal solution (40 wt.-%, 521.3 µL, 4.54 mmol) and two drops of formic acid were added to the hot solution, thereby resulting in the formation of yellow precipitate within a few minutes. The reaction mixture was stirred at room temperature overnight and then cooled in an ice bath. After filtration, the solid yellow product was washed with cold methanol and dried under vacuum. The respective imine **4a** (2.26 g, 81% yield) or **4b** (2.23 g, 70% yield) was obtained as a bright-yellow solid. The diimines could be purified by recrystallization from hot ethanol. Compound **4a**: ^1H NMR (500 MHz, C_6D_6): δ = 8.24 (s, 2 H, NCH), 7.21 (s, 4 H, H_{Ar}), 3.25–3.16 (m, 4 H, *o*-CH, cyclopentyl), 2.99–2.91 (m, 2 H, *p*-CH, cyclopentyl), 2.11–1.50 (m, 48 H, CH_2, cyclopentyl) ppm. ^{13}C NMR (126 MHz, C_6D_6): δ = 163.86, 148.96, 142.95, 134.46, 122.85, 46.67, 41.44, 35.32, 34.66, 26.09, 25.90 ppm. HRMS (EI): *m/z* calcd. for $C_{44}H_{60}N_2$: 616.4757 $[M]^+$; found 616.4739. Compound **4b**: ^1H NMR (500 MHz, C_6D_6): δ = 8.21 (s, 2 H, NCH), 7.17 (s, 4 H, H_{Ar}), 2.84 (tt, *J* = 11.8, 3.3 Hz, 4 H, *o*-CH, cyclohexyl), 2.56 (tt, *J* = 12.1, 3.4 Hz, 2 H, *p*-CH, cyclohexyl), 2.06–1.16 (m, 60 H, CH_2, cyclohexyl) ppm. ^{13}C NMR (126 MHz, C_6D_6): δ = 163.61, 147.40, 144.71, 136.12, 122.62, 45.24, 39.61, 35.28, 34.41, 27.70, 27.48, 26.77, 26.66 ppm. HRMS (EI): *m/z* calcd. for $C_{50}H_{72}N_2$: 700.5696 $[M]^+$; found 700.5691.

Synthesis of Imidazolium Salts 5a·HCl and 5b·HCl: An $HCl/ZnCl_2/(CH_2O)_n$ mixture [36% HCl, 460 µL, 5.47 mmol, 2.4 equiv; anhydrous $ZnCl_2$, 372 mg, 2.73 mmol, 1.2 equiv; $(CH_2O)_n$, 82.1 mg, 2.73 mmol, 1.2 equiv.] was added dropwise to a solution of diimine **4a** (1.41 g, 2.28 mmol) in $CHCl_3$ (20 mL) at 60 °C. The reaction was stirred at 60 °C for 1 h. The solution was cooled, diluted with CH_2Cl_2 (30 mL), and washed with HCl (2 M) and brine, then dried with anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure, and the brownish residue was washed with Et_2O. The off-white precipitate was collected by filtration, washed a few times with Et_2O, and dried under vacuum (530 mg, 35% yield). Imidazolium chloride **5b**·HCl (96 mg, 13% yield) was synthesized similarly from diimine **4b** (731 mg). Compound **5a·HCl**: ^1H NMR (300 MHz, $CDCl_3$): δ = 8.88 (t, *J* = 1.6 Hz, 1 H, NCHN), 8.33 (d, *J* = 1.6 Hz, 2 H, NCH=CHN), 7.16 (s, 4 H, H_{Ar}), 3.10–2.95 (m, 2 H, *p*-CH, cyclopentyl), 2.54–2.37 (m, 4 H, *o*-CH, cyclopentyl), 2.19–1.39 (m, 48 H, CH_2, cyclopentyl) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.77, 142.79, 136.72, 129.32, 127.96, 123.86, 46.31, 40.71, 35.73, 35.42, 34.82, 26.08, 25.97, 25.63 ppm. HRMS (EI): *m/z* calcd. for $C_{45}H_{60}N_2$: 628.4757 $[M – HCl]^+$; found 628.4725. Compound **5b·HCl**: This compound contained impurities that could not be removed. Chemical shifts for only aromatic/imidazolium protons are given: ^1H NMR (500 MHz, $[D_6]$DMSO): δ = 9.89 (s, 1 H, NCHN), 8.45 (s, 2 H, NCH=CHN), 7.36 (s, 4 H, H_{Ar}) ppm.

Synthesis of Imines 6a and 6b: Acenaphthene-1,2-dione (1.0 g, 5.49 mmol) was suspended in acetonitrile (30 mL) and the mixture was heated to 95 °C for 1 h, then acetic acid (7 mL) was added. Heating was continued until the dione had dissolved completely. Aniline **3a** (3.42 g, 11.53 mmol) or **3b** (3.91 g, 11.53 mmol) was added to this hot solution in one portion. The resulting solution was heated under reflux conditions overnight and cooled to room temperature. The mixture was cooled to –30 °C and an orange precipitate was collected by filtration. After washing with methanol and drying under vacuum, the imine **6a** (3.52 g, 87% yield) or **6b** (2.92 g, 66% yield) was obtained as an orange powder. Compound **6a**: ^1H NMR (500 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 8.3 Hz, 2 H, acenapht.), 7.33 (t, *J* = 7.7 Hz, 2 H, acenapht.), 7.12 (s, 4 H, H_{Ar}), 6.45 (d, *J* = 7.2 Hz, 2 H, acenapht.), 3.12–2.98 (m, 6 H, CH, cyclopentyl), 2.22–1.24 (m, 48 H, CH_2, cyclopentyl) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 161.49, 147.29, 141.96, 140.81, 132.68, 131.09, 129.97, 128.63, 127.98, 123.48, 122.58, 46.19, 41.21, 35.02, 34.39, 33.49, 25.75 ppm. HRMS (EI): *m/z* calcd. for $C_{54}H_{64}N_2$: 740.5070 $[M]^+$; found 740.5032. Compound **6b**: ^1H NMR (500 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 8.2 Hz, 2 H, acenapht.), 7.30 (t, *J* = 7.7 Hz, 2 H, acenapht.), 7.06 (s, 4 H, H_{Ar}), 6.38 (d, *J* = 7.2 Hz, 2 H, acenapht.), 2.68–2.60 (m, 4 H, *o*-CH, cyclohexyl), 2.60–2.54 (m, 2 H, *p*-CH, cyclohexyl), 2.14–0.99 (m, 60 H, CH_2, cyclohexyl) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 161.93, 145.56, 143.84, 141.06, 134.44, 131.20, 129.55, 128.73, 127.77, 123.83, 122.68, 44.69, 39.34, 35.11, 34.42, 34.27, 27.27, 27.20, 26.51, 26.38 ppm. HRMS (EI): *m/z* calcd. for $C_{54}H_{65}N_2$: 741.5148 $[M – C_6H_{11}]^+$; found 741.5111.

Synthesis of Imidazolium Chlorides 7a·HCl and 7b·HCl: Imine **4a** (2.0 g, 2.7 mmol) or imine **4b** (2.0 g, 2.4 mmol) and $CH_2(OEt)Cl$ (5.0 mL, 53.3 mmol) were added to a Schlenk flask under a nitrogen atmosphere. The reaction mixture was stirred at 100 °C for 24 h and then cooled to room temperature. Diethyl ether (20 mL) was added, and the resulting pale yellow solid was filtered, washed with diethyl ether, hot toluene, and dried under vacuum to afford **7a**·HCl (1.21 g, 57% yield) or **7b**·HCl (1.54 g, 73% yield). Compound **7a**·HCl: ^1H NMR (500 MHz, $CDCl_3$): δ = 10.91 (s, 1 H, NCHN), 8.03 (d, *J* = 8.3 Hz, 2 H, acenapht.), 7.61 (t, *J* = 7.7 Hz, 2 H, acenapht.), 7.28 (s, 4 H, H_{Ar}), 7.25 (d, *J* = 7.0 Hz, 2 H, acenapht.), 3.12 (p, *J* = 8.5 Hz, 2 H, *p*-CH, cyclopentyl), 2.80 (p, *J* = 8.0 Hz, 4 H, *o*-CH, cyclopentyl), 2.27–2.09 (m, 8 H, CH_2, cyclopentyl), 1.96–1.46 (m, 36 H, CH_2, cyclopentyl), 1.46–1.34 (m, 4 H, CH_2, cyclopentyl) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 150.59, 142.79, 142.69, 137.95, 130.81, 130.47, 130.19, 128.70, 128.38, 124.10, 123.48, 123.26, 46.34, 40.95, 35.37, 35.05, 34.74, 26.03, 26.00, 25.6 ppm. HRMS (EI): *m/z* calcd. for $C_{55}H_{65}N_2$: 753.5148 $[M – Cl]^+$; found 753.5119. Compound **7b·HCl**: ^1H NMR (500 MHz, $CDCl_3$): δ = 10.19 (s, 1 H, NCHN), 8.03 (d, *J* = 8.3 Hz, 2 H, acenapht.), 7.58 (t, *J* = 7.7 Hz, 2 H, acenapht.), 7.28 (s, 4 H, H_{Ar}), 7.19 (d, *J* = 7.0 Hz, 2 H, acenapht.), 2.68–2.60 (m, 2 H, *p*-CH, cyclohexyl), 2.24 (t, *J* = 11.7 Hz, 4 H, *o*-CH, cyclohexyl), 2.15 (d, *J* = 13.2 Hz, 4 H, CH_2, cyclohexyl), 2.01 (d, *J* = 11.8 Hz, 4 H, CH_2, cyclohexyl), 1.91 (d, *J* = 12.1 Hz, 4 H, CH_2, cyclohexyl), 1.80 (d, *J* = 12.8 Hz, 6 H, CH_2, cyclohexyl), 1.66–1.15 (m, 37 H, CH_2, cyclohexyl), 0.99–0.86 (m, 5 H, CH_2, cyclohexyl) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 151.78, 143.99, 141.45, 138.12, 130.77, 130.22, 128.29, 126.79, 124.75, 123.58, 123.14, 44.90, 39.89, 35.45, 34.45, 34.24, 26.93, 26.68, 26.45, 26.19, 25.68 ppm. MS (ESI): *m/z* calcd. for $C_{61}H_{77}N_2$: 837.6 $[M – Cl]^+$; found 837.8.

Synthesis of Silver Complexes [(7a)AgCl] and [(7b)AgCl]: The Schlenk flask that contained imidazolium chloride **7a**·HCl (300 mg, 0.38 mmol) or **7b**·HCl (300 mg, 0.34 mmol) and Ag_2O (45.2 mg, 0.19 mmol for **7a**·HCl; 39.5 mg, 0.17 mmol for **7b**·HCl) was evacuated and back-filled with nitrogen. CH_2Cl_2 (8 mL) was added with a syringe. The reaction mixture was stirred overnight at 40 °C,

cooled to room temperature, and filtered through Celite. The filtrate was concentrated to half the volume and then pentane (25 mL) was added. The yellowish precipitate was removed by filtration and washed with pentane to afford complex [(**7a**)AgCl] (270 mg, 79% yield) or [(**7b**)AgCl] (303 mg, 90% yield) as a yellowish microcrystalline solid. Compound [(**7a**)AgCl]: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.79 (d, J = 8.3 Hz, 2 H, acenapht.), 7.42 (t, J = 7.7 Hz, 2 H, acenapht.), 7.22 (s, 4 H, H_{Ar}), 6.98 (d, J = 7.0 Hz, 2 H, acenapht.), 3.11 (p, J = 8.8 Hz, 2 H, *p*-CH, cyclopentyl), 2.82 (p, J = 8.9 Hz, 4 H, *o*-CH, cyclopentyl), 2.26–2.16 (m, 4 H, CH_2, cyclopentyl), 2.16–2.05 (m, 4 H, CH_2, cyclopentyl), 1.94–1.31 (m, 40 H, CH_2, cyclopentyl) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 190.14 (d, $J_{C,Ag}$ = 259.0 Hz), 189.99 (d, $J_{C,Ag}$ = 259.8 Hz), 148.85, 143.01, 139.60, 139.54, 132.87, 130.90, 129.92, 128.27, 127.84, 125.57, 123.71, 121.31, 46.36, 40.73, 35.89, 35.19, 34.71, 26.11, 26.03, 25.71 ppm. HRMS (EI): *m*/*z* calcd. for $C_{55}H_{64}N_2$: 752.5070 [M – AgCl]$^+$; found 752.5028. Compound [(**7b**)AgCl]: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.77 (d, J = 8.3 Hz, 2 H, acenapht.), 7.39 (dd, J = 8.3, 7.0 Hz, 2 H, acenapht.), 7.22 (s, 4 H, H_{Ar}), 6.88 (d, J = 6.9 Hz, 2 H, acenapht.), 2.63 (tt, J = 11.7, 3.1 Hz, 2 H, *p*-CH, cyclohexyl), 2.42 (tt, J = 11.9, 3.2 Hz, 4 H, *o*-CH, cyclohexyl), 2.11–2.01 (m, 8 H, CH_2, cyclohexyl), 1.97–1.89 (m, 4 H, CH_2, cyclohexyl), 1.86–1.73 (m, 6 H, CH_2, cyclohexyl), 1.64–1.15 (m, 38 H, CH_2, cyclohexyl), 1.03–0.90 (m, 4 H, CH_2, cyclohexyl) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 189.78 (d, $J_{C,Ag}$ = 257.6 Hz), 189.63 (d, $J_{C,Ag}$ = 257.5 Hz), 149.89, 144.49, 139.85, 139.78, 131.02, 129.91, 128.32, 127.69, 125.51, 124.31, 121.50, 44.91, 39.19, 35.34, 34.73, 34.56, 27.08, 26.75, 26.59, 26.34, 25.89 ppm. MS (ESI): *m*/*z* calcd. for $C_{61}H_{76}N_2$: 836.6 [M – AgCl]$^+$; found 837.8.

General Procedure for the Synthesis of [(NHC)AuCl] Complexes: A vial was charged with the corresponding NHC·HCl (1 equiv.), [AuCl(Me_2S)] (1 equiv.), and K_2CO_3 (3 equiv.). The resulting mixture was suspended in acetone (1.0 mL) and stirred for the specified time at 60 °C. Next the solvent was removed under vacuum and CH_2Cl_2 (5 mL) was added. The mixture was filtered through silica, which was washed with CH_2Cl_2. Most of the CH_2Cl_2 was evaporated, and methanol (10 mL) was added to the concentrated solution. A precipitate was formed, collected by filtration, washed with methanol, and dried under vacuum.

Preparation of [(7a)AuCl]: Compound **7a**·HCl (61 mg, 0.077 mmol), [AuCl(Me_2S)] (24.2 mg, 0.077 mmol), K_2CO_3 (32 mg, 0.231 mmol); reaction time: 2 h; yellow complex 46 mg (61% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.79 (d, J = 8.3 Hz, 2 H, acenapht.), 7.42 (t, J = 7.4 Hz, 2 H, acenapht.), 7.22 (s, 4 H, H_{Ar}), 6.94 (d, J = 7.0 Hz, 2 H, acenapht.), 3.11 (p, J = 8.6 Hz, 2 H, *p*-CH, cyclopentyl), 2.85 (p, J = 8.8 Hz, 4 H, *o*-CH, cyclopentyl), 2.29–2.15 (m, 8 H, CH_2, cyclopentyl), 1.94–1.84 (m, 4 H, CH_2, cyclopentyl), 1.84–1.44 (m, 32 H, CH_2, cyclopentyl), 1.43–1.31 (m, 4 H, CH_2, cyclopentyl) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 179.74 ($C_{carbene}$), 148.82, 143.05, 138.35, 132.42, 130.57, 129.83, 128.40, 127.88, 125.78, 123.67, 121.41, 46.39, 40.88, 35.75, 35.15, 34.73, 26.14, 26.02, 25.73 ppm. HRMS (EI): *m*/*z* calcd. for $C_{55}H_{64}N_2$: 752.5070 [M – AuCl]$^+$; found 752.5035.

Preparation of [(7b)AuCl]: Compound **7b**·HCl (89 mg, 0.102 mmol), [AuCl(Me_2S)] (30 mg, 0.102 mmol), and K_2CO_3 (42 mg, 0.306 mmol); reaction time: 20 h; yellow complex: 79 mg (72% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.77 (d, J = 8.3 Hz, 2 H, acenapht.), 7.39 (t, J = 7.7 Hz, 2 H, acenapht.), 7.21 (s, 4 H, H_{Ar}), 6.83 (d, J = 7.0 Hz, 2 H, acenapht.), 2.63 (tt, J = 11.8, 3.5 Hz, 2 H, *p*-CH, cyclohexyl), 2.43 (tt, J = 12.1, 3.4 Hz, 4 H, *o*-CH, cyclohexyl), 2.25–2.16 (m, 4 H, CH_2, cyclohexyl), 2.10–2.02 (m, 4 H, CH_2, cyclohexyl), 1.98–1.90 (m, 4 H, CH_2, cyclohexyl), 1.86–1.74 (m, 6 H, CH_2, cyclohexyl), 1.65–1.30 (m, 34 H, CH_2, cyclohexyl), 1.22 (qt, J = 13.0, 3.4 Hz, 4 H, CH_2, cyclohexyl), 1.05–0.93 (m, 4 H, CH_2, cyclohexyl) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 179.38 ($C_{carbene}$), 149.87, 144.52, 138.53, 130.65, 130.57, 129.80, 128.44, 127.72, 125.67, 124.26, 121.59, 44.91, 39.29, 35.29, 34.59, 34.49, 27.11, 26.78, 26.58, 26.37, 25.94 ppm. MS (ESI): *m*/*z* calcd. for $C_{61}H_{76}N_2AuClNa$: 1091.5 [M + Na]$^+$; found 1091.5.

Preparation of [(5a)AuCl]: Compound **5a**·HCl (112.5 mg, 0.169 mmol), [AuCl(Me_2S)] (50 mg, 0.169 mmol), and K_2CO_3 (70 mg, 0.507 mmol); reaction time: 12 h; off-white complex 95 mg (65% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.11 (s, 6 H, H_{Ar} + NCH=CHN), 3.07–2.98 (m, 2 H, *p*-CH, cyclopentyl), 2.63–2.51 (m, 4 H, *o*-CH, cyclopentyl), 2.24–2.06 (m, 8 H, CH_2, cyclopentyl), 1.92–1.45 (m, 40 H, CH_2, cyclopentyl) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 175.24 ($C_{carbene}$), 148.68, 143.19, 133.75, 123.43, 46.39, 40.79, 35.72, 35.61, 34.75, 26.25, 26.00, 25.68 ppm. MS (ESI): *m*/*z* calcd. for $C_{45}H_{60}N_2AuClNa$: 883.4 [M + Na]$^+$; found 883.7.

Preparation of [(5b)AuCl]: Compound **5b**·HCl (126.6 mg, 0.169 mmol), [AuCl(Me_2S)] (50 mg, 0.169 mmol), and K_2CO_3 (70 mg, 0.507 mmol); reaction time: 12 h; off-white complex 51 mg (32% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.09 (s, 4 H, H_{Ar}), 7.06 (s, 2 H, NCH=CHN), 2.55 (tt, J = 11.5, 3.3 Hz, 2 H, *p*-CH, cyclohexyl), 2.24–2.10 (m, 8 H, *o*-CH + CH_2, cyclohexyl), 2.00–1.21 (m, 56 H, CH_2, cyclohexyl) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 175.11 ($C_{carbene}$), 149.69, 144.42, 123.81, 123.39, 44.87, 39.28, 36.27, 34.49, 33.74, 27.07, 27.01, 26.52, 26.32, 26.00 ppm. MS (ESI): *m*/*z* calcd. for $C_{51}H_{72}N_2AuClNa$: 967.5 [M + Na]$^+$; found 967.7.

Synthesis of Rhodium Complexes [(7a)RhCl(cod)] and [(7b)RhCl(cod)]: A flame-dried Schlenk flask that contained imidazolium chloride **7a**·HCl (169.8 mg, 0.215 mmol) or **7b**·HCl (272.9 mg, 0.312 mmol) and [{RhCl(cod)}$_2$] (50.5 mg, 0.102 mmol for **7a**·HCl; 70 mg, 0.142 mmol for **7b**·HCl) was evacuated and back-filled with nitrogen three times. THF (20 mL) and a solution of sodium *tert*-pentoxide in THF (2.5 M, 103 µL, 0.215 mmol for **7a**·HCl; 150 µL, 0.312 mmol for **7b**·HCl) were added. The mixture was stirred for 2 h. Next the solvent was removed under vacuum and the residue was purified by column chromatography (silica, cyclohexane/ethyl acetate, 30:1, v/v), which afforded, after washing with methanol, the desired complex [(**7a**)RhCl(cod)] (139 mg, 68% yield) or [(**7b**)RhCl(cod)] (161 mg, 52% yield) as yellow microcrystalline solid. Compound [(**7a**)RhCl(cod)]: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.64 (d, J = 8.3 Hz, 2 H, acenapht.), 7.35–7.20 [m, J = 7.2 Hz, 2 H, 6 H (t, acenapht. + s, 4 H, H_{Ar})], 6.73 (d, J = 6.9 Hz, 2 H, acenapht.), 4.64–4.59 (m, 2 H, H_{cod}), 3.87 (br., 2 H, H_{cod}), 3.53–3.47 (m, 2 H, H_{cod}), 3.16 (p, J = 8.2 Hz, 2 H, *p*-CH, cyclopentyl), 2.77 (br., 2 H, H_{cod}), 2.38 (br., 2 H, H_{cod}), 2.28–0.96 (m, 54 H, *o*-CH, CH_2, cyclopentyl, H_{cod}) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 192.83 (d, $J_{C,Rh}$ = 53.0 Hz), 148.07, 144.53 (br.), 140.55, 134.42, 129.90, 129.60, 127.34, 127.22, 126.82, 123.17 (br.), 121.55, 96.31 (d, $J_{C,Rh}$ = 7.0 Hz, cod), 67.83 (d, $J_{C,Rh}$ = 14.1 Hz, cod), 46.44, 41.04 (br.), 37.22 (br.), 34.92, 34.13 (br.), 32.83, 28.48, 26.30 (br.), 25.77 ppm. MS (ESI): *m*/*z* calcd. for $C_{63}H_{76}N_2Rh$: 963.5 [M – Cl]$^+$; found 963.7. Compound [(**7b**)RhCl(cod)]: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.59 (d, J = 8.2 Hz, 2 H, acenapht.), 7.29–7.21 [m, J = 8.0 Hz, 2 H, 6 H (t, acenapht. + s, 4 H, H_{Ar})], 6.59 (d, J = 7.0 Hz, 2 H, acenapht.), 4.62–4.57 (m, 2 H, H_{cod}), 3.57–3.51 (m, 2 H, H_{cod}), 3.05 (br., 2 H, H_{cod}), 2.67 (tt, J = 11.9, 3.3 Hz, 2 H, *p*-CH, cyclohexyl), 2.58–0.75 (m, 68 H, *o*-CH, CH_2, cyclohexyl, H_{cod}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.78 (d, $J_{C,Rh}$ = 54.2 Hz), 150.14, 149.24, 140.27, 133.24, 129.95, 129.44,

127.37, 127.00, 126.82, 123.68 (br.), 121.87, 96.27 (d, $J_{C,Rh}$ = 7.5 Hz, cod), 67.80 (d, $J_{C,Rh}$ = 13.9 Hz, cod), 45.03, 39.78 (br.), 36.91, 34.77, 33.49, 32.81, 28.45, 27.17, 26.42, 26.25 ppm. MS (ESI): *m/z* calcd. for $C_{69}H_{88}N_2Rh$: 1047.6 $[M - Cl]^+$; found 1047.7.

Synthesis of Carbonyl Complexes [(7a)RhCl(CO)$_2$] and [(7b)RhCl(CO)$_2$]: Compound [(**7a**)RhCl(cod)] (100 mg, 0.096 mmol) or [(**7b**)RhCl(cod)] (108.5 mg, 0.096 mmol) was dissolved in CH_2Cl_2 (7 mL), and CO was bubbled through this solution for 20 min. The solvent was evaporated under vacuum, and the residue washed with methanol to obtain the yellow complex [(**7a**)RhCl(CO)$_2$] (86 mg, 90% yield) or [(**7a**)RhCl(CO)$_2$] (90 mg, 87% yield). Compound [(**7a**)RhCl(cod)]: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.71 (d, J = 8.3 Hz, 2 H, acenapht.), 7.34 (t, J = 7.6 Hz, 2 H, acenapht.), 7.25 (s, 4 H, H_{Ar}), 6.72 (d, J = 7.0 Hz, 2 H, acenapht.), 3.21–3.09 (m, 6 H, CH, cyclopentyl), 2.28–1.09 (m, 60 H, CH, cyclopentyl) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 185.18 (d, $J_{C,Rh}$ = 54.0 Hz, $C_{carbene}$), 184.25 (d, $J_{C,Rh}$ = 45.7 Hz, CO), 183.19 (d, $J_{C,Rh}$ = 74.0 Hz, CO), 148.65, 143.58, 140.84, 133.26, 130.06, 129.79, 127.97, 127.48, 126.28, 123.45, 121.89, 46.38, 41.15, 36.98, 34.77, 33.69, 25.99, 25.93, 25.77 ppm. The attempted determination of mass spectra with complex [(**7a**)RhCl(CO)$_2$] was unsuccessful owing to the instability of this complex. Compound [(**7b**)RhCl(CO)$_2$]: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.68 (d, J = 8.3 Hz, 2 H, acenapht.), 7.31 (dd, J = 8.3, 7.0 Hz, 2 H, acenapht.), 7.25 (s, 4 H, H_{Ar}), 6.66 (d, J = 7.0 Hz, 2 H, acenapht.), 2.69–2.59 (m, 6 H, CH, cyclohexyl), 2.24–2.18 (m, 4 H, CH_2, cyclohexyl), 2.10–2.03 (m, 4 H, CH_2, cyclohexyl), 1.97–1.91 (m, 4 H, CH_2, cyclohexyl), 1.86–1.80 (m, 2 H, CH_2, cyclohexyl), 1.79–1.72 (m, 4 H, CH_2, cyclohexyl), 1.68–1.44 (m, 24 H, CH_2, cyclohexyl), 1.41–1.31 (m, 6 H, CH_2, cyclohexyl), 1.24–1.07 (m, 8 H, CH_2, cyclohexyl), 0.95 (qt, J = 12.1, 3.2 Hz, 4 H, CH_2, cyclohexyl) ppm. ^{13}C NMR (126 MHz, CD_2Cl_2): δ = 185.74 (d, $J_{C,Rh}$ = 53.7 Hz, $C_{carbene}$), 184.96 (d, $J_{C,Rh}$ = 45.9 Hz, CO), 183.51 (d, $J_{C,Rh}$ = 73.6 Hz, CO), 150.61, 145.73, 141.11, 132.17, 130.52, 130.26, 128.54, 127.88, 126.52, 124.65, 122.71, 45.42, 39.93, 37.14, 35.09, 33.59, 27.62, 27.56, 26.86, 26.78, 26.50 ppm. The attempted determination of mass spectra with complex [(**7b**)RhCl(CO)$_2$] was unsuccessful owing to the instability of this complex.

Cyclic Voltammetry: Cyclic voltammograms were recorded in dry CH_2Cl_2 under an argon atmosphere at ambient temperature. A three-electrode configuration was employed. The working electrode was a Pt disk (diameter 1 mm) sealed in soft glass with a Pt wire as a counter electrode. The pseudoreference electrode was an Ag wire. Potentials were calibrated internally against the formal potential of octamethylferrocene [$E_{1/2}$ = –0.01 V (CH_2Cl_2)]. NBu_4PF_6 (0.1 mol L^{-1}) was used as a supporting electrolyte.

CCDC-1018406 contains 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.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra and mass spectra of all compounds, cyclic voltammograms, and tables (atomic coordinates, bond lengths, angles, etc.) concerning the X-ray crystal structure of [(**7b**)AgCl].

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N-Heterocyclic Carbene Complexes

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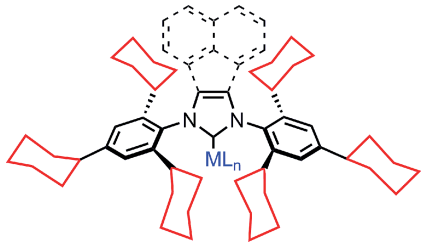

Sterically very demanding N-heterocyclic carbenes and metal complexes thereof were synthesized by means of a classic sequence of Friedel–Crafts alkylation, nitration, and nitro-to-amine reduction to lead to the respective anilines, which were then converted into the respective azolium salts through established synthetic routes.

