Dalton Transactions

PAPER

View Article Online
View Journal | View Issue

Open Access Article. Published on 17 June 2016. Downloaded on 12/26/2025 12:30:17 AM.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

Cite this: *Dalton Trans.*, 2016, **45**, 11015

Received 2nd May 2016,
Accepted 4th June 2016

DOI: 10.1039/c6dt01724j

www.rsc.org/dalton

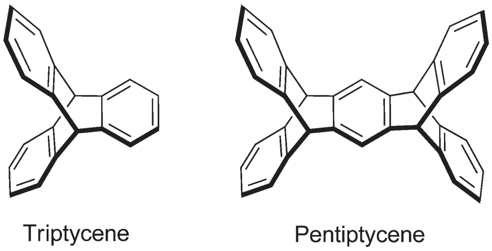
Pentiptycene-based concave NHC–metal complexes†

Roman Savka, Sabine Foro and Herbert Plenio*

The reaction of 1-amino,4-hydroxy-pentiptycene with diacetyl or acenaphthene-1,2-dione gave the respective diimines, followed by alkylation of the hydroxyl groups, and cyclization of the alkylated diimines to the respective bispentiptycene-imidazolium salts NHC·HCl. The azolium salts, being precursors to N-heterocyclic carbenes, were converted into metal complexes [(NHC)MX] (MX = CuI, AgCl, AuCl) and [(NHC)IrCl(cod)] and [(NHC)IrCl(CO)$_2$] in good yields. In the solid state [(NHC)AgCl] displays a bowl-shaped structure of the ligand with the metal center buried within the concave unit.

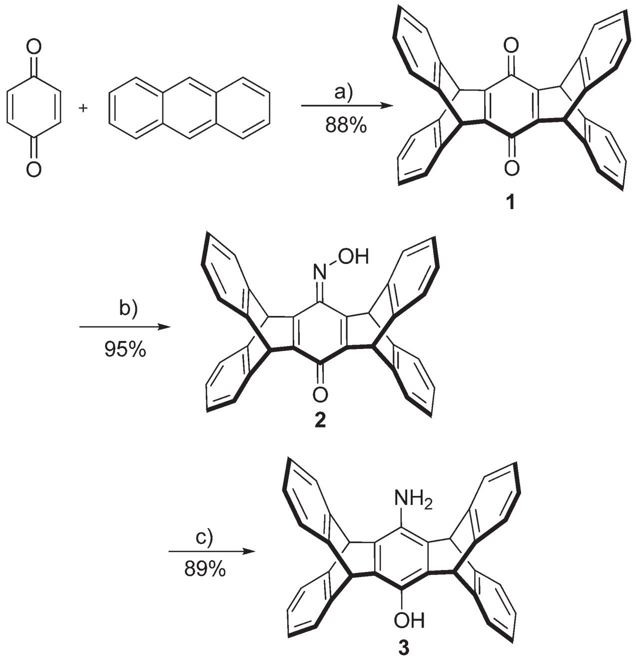
Introduction

Iptycenes are a class of aromatic molecules with arenes fused to a bicyclo[2.2.2]octane framework,[1] which have found numerous applications in polymer chemistry,[2] molecular machines,[3,4] materials science and in host–guest chemistry.[5–7] Triptycene, the first representative of this family of compounds was published by Bartlett *et al.* in 1942 (Scheme 1).[8] The synthesis of pentiptycene was reported in 1974 by Skvarche and Shalaev,[9] but despite significant improvements,[10] its synthesis remains cumbersome.[1] Pentiptycene quinone, on the other hand, is easily available from the reaction of anthracene and benzoquinone followed by the oxidation of the initial Diels–Alder product.[11,12] This quinone can be converted into the respective amino-pentiptycene (Scheme 2), which (like most anilines)[13] should serve as an excellent precursor for N-heterocyclic carbenes and the respective transition metal complexes.



Scheme 1 Structures of triptycene and pentiptycene.

Triptycene phosphines have been used in organometallic chemistry,[14–19] as well as the recently reported bistriptycene-based NHC ligands,[20] but to the best of our knowledge, pentiptycene-based NHC ligands have not been reported. The use of pentiptycenes for NHC ligands offers interesting prospects, since the pentiptycene unit confers a bowl type shape to the respective NHC. In this contribution, we want to report on the synthesis of bispentiptycene-based NHC ligands and metal



Scheme 2 Three-step synthesis of pentiptycene aminophenol. Reagents and conditions: (a) *p*-chloranil, AcOH, reflux 16 h; (b) NH$_2$OH·HCl, 4% aq. HCl, THF, reflux 3 d; (c) N$_2$H$_4$·H$_2$O, Pd/C (5%), THF reflux 3 h.

Organometallic Chemistry, Alarich-Weiss-Str. 12, TU Darmstadt, 64287 Darmstadt, Germany. E-mail: plenio@tu-darmstadt.de

† Electronic supplementary information (ESI) available. CCDC 1424889. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6dt01724j

Open Access Article. Published on 17 June 2016. Downloaded on 12/26/2025 12:30:17 AM.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

complexes with this new ligand as well as preliminary catalytic studies.

Results and discussion

Synthesis of pentiptycene NHC ligands

The reaction of two equivalents of anthracene with 1,4-benzoquinone in the presence of chloranil leads to pentiptycene quinone **1** according to a procedure from Chen *et al.* (Scheme 2).[12]

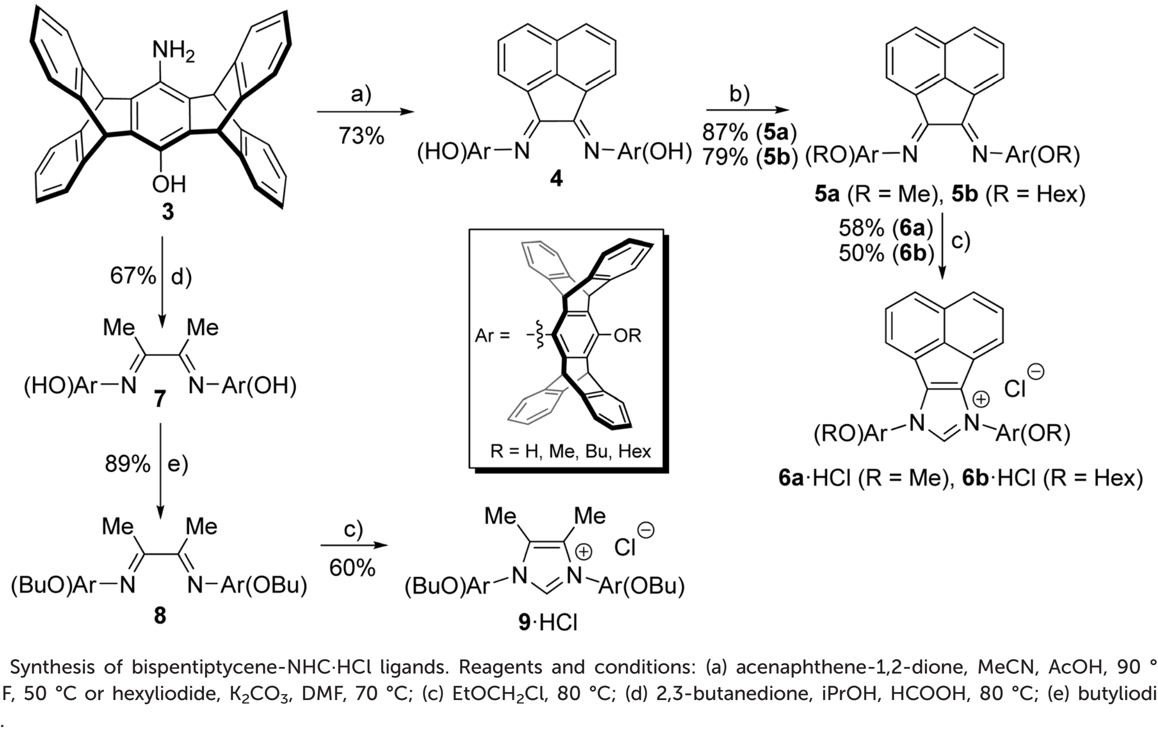
In order to obtain a sufficient amount of pentiptycene for the synthesis of the NHC ligands, the scale of the reaction was considerably increased (almost 20-fold) with respect to the literature procedure. This scaling up turned out to be unproblematic and it is now possible to synthesize 75 g of pentiptycene quinone **1** in a single run, using cheap commercially available starting materials. Quinone **1** was converted into monooxime **2** employing a literature procedure. In contrast to literature reports claiming low stability of this compound,[21] in our hands **2** turned out to be stable. Monooxime **2** was reduced to the amino-hydroxy-pentiptycene **3** using hydrazine hydrate and Pd/C. This procedure appears to be more convenient than the literature procedure using $SnCl_2$/HCl, which in our hands provided impure materials, whose purification required significant effort. In contrast to literature reports,[21] the pentiptycene aminophenol **3** displays reasonable solubility in several organic solvents and recording ^1H and ^{13}C NMR spectra poses no problem. In general, we notice that the pentiptycene derivatives display significantly better solubility than the related triptycene compounds also reported by us.[20]

Our attempts to obtain the respective diimines with glyoxal and aminophenol **3** appeared promising. However, an impure product was always obtained, which could neither be purified to a satisfactory level nor cleanly converted into the desired azolium salts. Based on the idea, that this might be due to the incomplete conversion of reactants and the formation of diimine isomers with extremely bulky pentiptycene units, we tried the analogous reactions of aminophenol **3** with acenaphthene-1,2-dione. The clean formation of such diimines with conventional anilines[22] as well as their cyclization to azolium salts has been shown before.[23,24] Furthermore, the acenaphthene backbone enforced *Z*-geometry of the diimines facilitates the formation of the respective azolium salts with sterically highly demanding *N*-aryl substituents,[25] whose formation can be very difficult otherwise.[26] The respective azolium salts were obtained in good yields as shown in Scheme 3.

We next tested the reaction of aminophenol **3** with diacetyl according to standard procedures,[27,28] which also leads to the respective diimine in good yields (Scheme 3). Following alkylation of the phenolic –OH group with MeI or BuI, the diimines were cyclized to the respective azolium salts **6a**/**6b**·HCl or **9**·HCl using $ClCH_2OEt$.[25,29] The use of this alkylating agent provides much better yields than with paraformaldehyde employed previously for the cyclization of related diimines.[30]

Synthesis of metal complexes

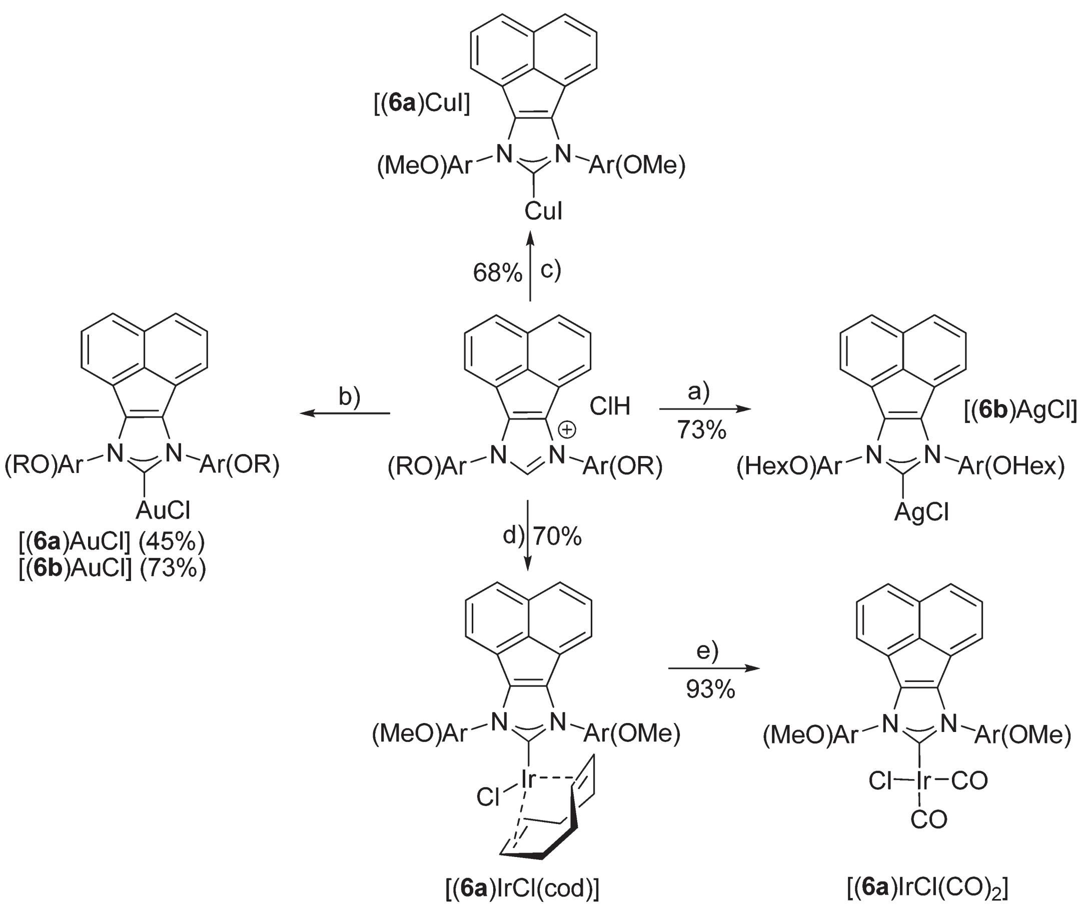
In order to evaluate the coordinating properties of the new NHC ligands, several new metal complexes were synthesized. The synthesis of metal complexes with the new carbenes **6a**,



Scheme 3 Synthesis of bispentiptycene-NHC·HCl ligands. Reagents and conditions: (a) acenaphthene-1,2-dione, MeCN, AcOH, 90 °C; (b) MeI, K_2CO_3, DMF, 50 °C or hexyliodide, K_2CO_3, DMF, 70 °C; (c) $EtOCH_2Cl$, 80 °C; (d) 2,3-butanedione, iPrOH, HCOOH, 80 °C; (e) butyliodide, K_2CO_3, DMF, 70 °C.

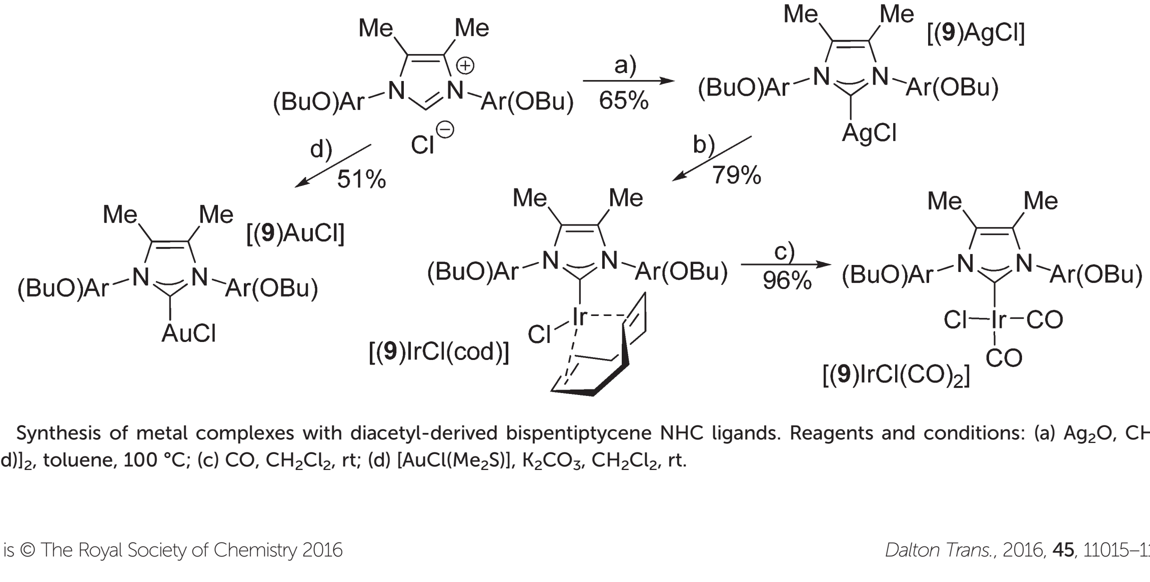
This journal is © The Royal Society of Chemistry 2016

Open Access Article. Published on 17 June 2016. Downloaded on 12/26/2025 12:30:17 AM. This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.



Scheme 4 Synthesis of metal complexes with acenaphthene-based bispentiptycene NHC ligands. Reagents and conditions: (a) Ag_2O, CH_2Cl_2, 40 °C; (b) $[AuCl(Me_2S)]$, K_2CO_3, acetone, 60 °C; (c) CuI, K_2CO_3, acetone, 60 °C; (d) $[IrCl(cod)]_2$, sodium *tert*-pentoxide, THF, rt; (e) CO, CH_2Cl_2, rt.

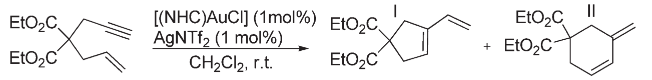
6b and **9** turned out to be unproblematic (Schemes 4 and 5). Several metal complexes with Cu, Ag and Au with coordination number 2 were prepared in good yields according to standard procedures for Cu,[31] Ag[32] and Au.[33,34] The crystal structure of [(**9**)AgCl] indicated that due to the pronounced steric bulk of NHC **9** (see below), metal complexes with higher coordination numbers might be difficult to obtain. Despite testing several different approaches the respective Pd(II) complex with carbene **9** could not be synthesized. On the other hand, the synthesis of the four coordinate Ir complexes turned out to be straightforward, even though the higher coordination number of Ir in the expected complexes might have caused problems



Scheme 5 Synthesis of metal complexes with diacetyl-derived bispentiptycene NHC ligands. Reagents and conditions: (a) Ag_2O, CH_2Cl_2, 40 °C; (b) $[IrCl(cod)]_2$, toluene, 100 °C; (c) CO, CH_2Cl_2, rt; (d) $[AuCl(Me_2S)]$, K_2CO_3, CH_2Cl_2, rt.

Open Access Article. Published on 17 June 2016. Downloaded on 12/26/2025 12:30:17 AM.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

Table 1 (NHC)AuCl/AgNTf$_2$-catalyzed cyclization of diethyl 2-allyl-2-(prop-2-ynyl)malonate



Catalyst	Reaction time, h	Isolated yield (%) (I : II)
[(**6b**)AuCl]	16	91 (2.6 : 1)
[(**9**)AuCl]	16	93 (2.4 : 1)
[(IMes)AuCl]	18	35 (1 : 2.1)

when binding to the very bulky NHC ligand. Two different established approaches (Schemes 4 and 5) were tried, both of them afforded the desired complexes. The transmetalation *via in situ* formed [(**9**)AgCl] complexes to give [(**9**)IrCl(cod)] requires harsh reaction conditions. The formation of [(**6**)IrCl(cod)] *via* the free carbene works under mild reaction conditions. Despite the very different reaction conditions employed, both methods produce the respective Ir complexes in good yields of 70% and 79%. Both complexes were converted into the respective [(NHC)IrCl(CO)$_2$] complexes in excellent yields.[35] In order to evaluate the donor properties of NHC ligands **6** and **9**, the redox potentials of [(**6a**)IrCl(cod)] ($E_{1/2}$ = 0.862 V) and [(**9**)IrCl(cod)] ($E_{1/2}$ = 0.804 V) were determined and found to be comparable to those of the analogous complexes with SIMes ligands.[27,36]

Preliminary catalytic studies[37] of the gold complexes [(**6b**)AuCl] and [(**9**)AuCl] show better catalytic activity in the cyclization of diethyl 2-allyl-2-(prop-2-ynyl)malonate[38,39] (Table 1) than the closely related [(IMes)AuCl] (Table 1), furthermore the pentiptycene-based catalysts give a much higher selectivity for the formation of the five-membered ring than the IMes type catalysts. More detailed studies of the catalytic properties of such complexes are underway. This appears promising, since gold complexes with sterically highly demanding ligands have been shown to exhibit excellent catalytic activity.[40,41]

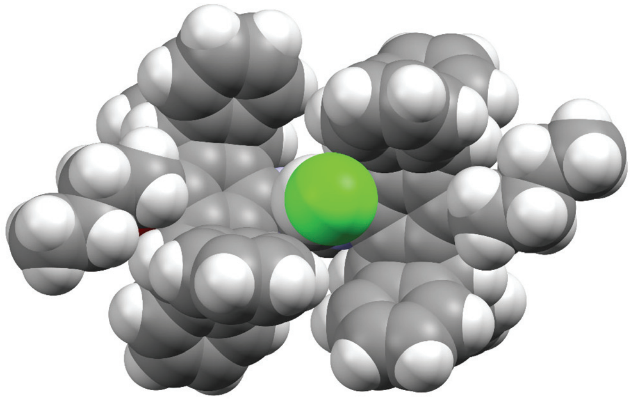


Fig. 1 X-ray crystal structure of [(**9**)AgCl] (space-filling plot). CCDC 1424889 contains the supplementary crystallographic data for this structure.

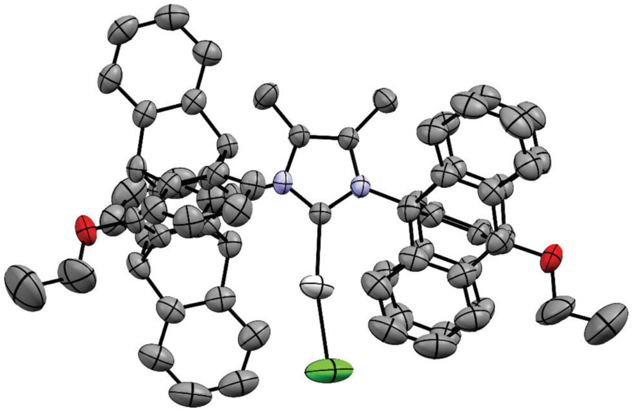


Fig. 2 X-ray crystal structure[49] of [(**9**)AgCl] (ORTEP-plot) (hydrogen atoms omitted, only α and β-carbon atoms of the disordered butyl chain are shown). Important bond lengths (pm): Ag–C(NHC) 209.0(5), Ag–Cl 234.8(3).

Crystal structure of [(9)AgCl]

Single crystals of [(**9**)AgCl] were obtained by slow evaporation of an isopropanol/CH$_2$Cl$_2$ solution. The NHC ligand has an approximately rectangular bowl type shape, which is defined by six phenyl rings of the two pentiptycene units and the two butoxy groups on the metal-facing side (Fig. 1 and 2). However, the angles of the planes of the six-membered *N*-aryl rings and of the five-membered heterocyclic ring are tilted by 17°. Since the two *N*-aryl units are tilted in opposite directions, the two pentiptycene units are inclined at an angle of *ca.* 35°. This leads to an interdigitized structure of the four phenyl rings forming the walls of the bowl. Consequently, two phenyl rings are close to the silver ion (shortest Ag–C distances *ca.* 350 pm), while the two closest carbon atoms of the other pair of phenyl rings are at an Ag–C distance of *ca.* 510 pm. Two pairs of Ag–C distances are sufficient for the description of the structure, since the silver atom and the carbene carbon of the NHC ligand both lie on a two-fold crystallographic axis. The bond distances and angles within the coordination sphere of silver are unspectacular, since the steric bulk of the NHC ligand cannot act on the two-coordinate metal center. The silver ion is deeply buried in the roughly hemispherical NHC ligand and even the chloro ligand[42] hardly extends beyond the upper rim of the pentiptycene unit. The buried volume[43] of the NHC ligand in complex [(**9**)AgCl] was calculated as V_{bur} = 48.8% (r = 350 pm, d = 200 pm), which is considerably larger than in the related [(iPr)AgCl] complexes (V_{bur} = 46.5%).[44] The rigidity of the pentiptycene units in the crystal results in a porous solid structure with large empty voids into which the chloro ligands and the methyl groups of the heterocyclic unit are pointing. The formation of porous solids has been observed in other iptycene structures.[45] The presence of solvent accessible pores also explains, why it is very difficult to remove solvent from such compounds – even after prolonged heating under vacuum, elemental analysis provides unsatisfactory values.

Open Access Article. Published on 17 June 2016. Downloaded on 12/26/2025 12:30:17 AM. This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

Such bowl shaped NHC ligands are rare[46,47] and hold potential for selective catalysis or the stabilization of otherwise unstable species.[48]

Summary and conclusions

Based on a large scale synthesis of 1-amino,4-hydroxy-pentiptycene this aniline was converted into various azolium salts, which are convenient precursors for the synthesis of N-heterocyclic carbenes. The steric shielding of the pentiptycene wings provides bowl-shaped NHC ligands, in which the metal center is buried in a pocket – as shown in the crystal structure of the respective (NHC)AgCl complex. Such ligands offer the possibility for the kinetic stabilization of unusual coordination geometries and could thus lead to highly active catalysts, which will be the topic of future studies. Preliminary catalytic tests employing (NHC)AuCl/$AgNTf_2$ reveal good catalytic activities in the cyclization of diethyl 2-allyl-2-(prop-2-ynyl)malonate.

Experimental

General experiments

All chemicals were purchased as reagent grade from commercial suppliers and used without further purification, unless otherwise noted. All reactions involving metal complexes were performed under an atmosphere of nitrogen (except gold and copper complexes). Tetrahydrofuran was dried over sodium, distilled under an argon atmosphere and stored over molecular sieves (4 Å). Dichloromethane and toluene were refluxed over calcium hydride, distilled under a nitrogen atmosphere and stored over molecular sieves (4 Å). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC300 or a DRX500 spectrometer. The chemical shifts are given in parts per million (ppm) on the delta scale (δ) and are referenced to the residual peak of chloroform (^{1}H NMR = 7.26, ^{13}C NMR = 77.16 ppm), dimethyl sulfoxide (^{1}H NMR = 2.50, ^{13}C NMR = 39.52 ppm) or methylene chloride (^{1}H NMR = 5.32, ^{13}C NMR = 53.84 ppm). Abbreviations for NMR: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sep = septet, sex = sextet, m = multiplet, br = broad signal. Thin layer chromatography (TLC) was performed by using silica 60 F 254 (0.2 mm) on aluminum plates. Preparative chromatography was done on Merck silica 60 (0.063–0.2 mm). 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 pseudo-reference electrode was an Ag wire. Potentials were calibrated internally against the formal potential of octamethylferrocene ($E_{1/2}$ = −0.01 V (CH_2Cl_2)) and NBu_4PF_6 (0.1 mol L^{-1}) was used as a supporting electrolyte. Compounds **1**, **2** and **3** have been reported previously in the literature, however no ^{13}C data were given.[12,21]

Synthesis of pentiptycene quinone 1. Anthracene (66.0 g, 0.370 mol), 1,4-benzoquinone (20.0 g, 0.185 mol) and *para*-chloranil (90.0 g, 0.370 mol) were dissolved in 100% AcOH (2.4 L) and heated under reflux for 16 h. The reaction mixture was cooled to room temperature and a yellow precipitate filtered off, washed extensively with diethyl ether, and then dried *in vacuo* to provide 77.0 g (88% yield) of a yellow product. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41–7.38 (m, aromatic, 8H), 7.02–6.99 (m, aromatic, 8H), 5.80 (s, 4H).^{13}C NMR (75 MHz, $CDCl_3$): δ 180.11 (C═O), 151.09 (C═C), 143.83 (Ar–C), 125.61 (Ar–CH), 124.39 (Ar–CH), 47.56 ($CHAr_3$).

Synthesis of pentiptycene monooxime 2. Pentiptycene quinone **1** (36.0 g, 0.078 mol) was dissolved in THF (1.2 L) and a solution of $NH_2OH\cdot HCl$ (27.15 g, 0.39 mol) in water (90 mL) was added, followed by HCl (11.9 mL, aq. 37%). The mixture was heated under reflux for 7 days. Next THF was removed under reduced pressure. The remaining orange solid was dissolved in CH_2Cl_2 and washed with brine. The organic layer was separated and dried over anhydrous $MgSO_4$, filtered and the volatiles evaporated under reduced pressure. The residue was triturated with pentane, filtered and the product was dried *in vacuo* (35.4 g, 95% yield). This material thus obtained is sufficiently pure for the next steps; the product may be purified further by recrystallization from ethanol/DMF. However, this leads to the formation of a stable solvate complex **2**·DMF, from which it is very difficult to completely remove DMF. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.12 (s, OH, 1H), 7.40–7.30 (m, aromatic, 8 H), 6.98–6.95 (m, aromatic, 8 H), 6.77 (s, 1 H), 5.95 (s, 1 H), 5.90 (s, 1 H), 5.84 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.35 (C═O), 154.55, 148.50, 146.05, 145.14, 144.57, 144.43, 144.37, 144.25, 143.82, 125.56 (Ar–CH), 125.53 (Ar–CH), 125.28 (Ar–CH), 125.14 (Ar–CH), 124.32 (Ar–CH), 124.21 (Ar–CH), 124.01 (Ar–CH), 123.92 (Ar–CH), 52.99 ($CHAr_3$), 49.16 ($CHAr_3$), 47.36 ($CHAr_3$), 47.13 ($CHAr_3$).

Synthesis of pentiptycene aminophenol 3. Monooxime **2** (26.9 g, 0.056 mol) was dissolved in THF (800 mL). To the solution was added Pd/C (5% Pd, 3.38 g), followed by the slow addition of hydrazine hydrate (14.5 mL, 0.3 mol) and leading to the evolution of gas. The reaction mixture was refluxed for 3 hours. The cold suspension was filtered over a glass filter, to separate Pd/C. Since the product is poorly soluble in THF, the residue remaining on the filter should be extensively washed with CH_2Cl_2. The volatiles were removed under reduced pressure and the residue was triturated with pentane. The white precipitate was collected by filtration and dried *in vacuo* to yield the product (23.0 g, 89% yield). ^{1}H NMR (300 MHz, DMSO-d$_6$) δ 8.38 (s, OH, 1H), 7.34–7.30 (m, aromatic, 8 H), 6.92–6.88 (m, aromatic, 8 H), 5.84 (s, 2 H), 5.80 (s, 2 H). ^{13}C NMR (75 MHz, DMSO-d$_6$) δ 146.16, 145.96, 138.25, 131.78, 130.49, 128.34 (Ar–CH), 124.36 (Ar–CH), 123.26 (Ar–CH), 123.21 (Ar–CH), 46.88 ($CHAr_3$), 46.82 ($CHAr_3$).

Synthesis of diimine 4. Acenaphthene-1,2-dione (395 mg, 2.17 mmol) was suspended in acetonitrile (30 mL) and the mixture was heated to 90 °C. After 10 min acetic acid (10 mL) was added and heated until the dione had dissolved completely. To the hot solution was added aniline **3** (2.0 g,

Open Access Article. Published on 17 June 2016. Downloaded on 12/26/2025 12:30:17 AM. This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

4.33 mmol) in several portions. Within a few minutes the formation of an orange precipitate was observed. The suspension was stirred at 90 °C overnight and then cooled to −30 °C and an orange precipitate was collected by filtration. After washing the solid with acetonitrile and drying *in vacuo* at 70 °C, diimine **4** was obtained as an orange powder (1.69 g, 73% yield). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.73 (d, J = 8.1 Hz, 2H), 7.46 (dd, J = 6.6, 1.7 Hz, 4H), 7.42 (dd, J = 6.6, 1.7 Hz, 4H), 7.38 (d, J = 7.2 Hz, 4H), 6.98 (quint d, J = 7.5, 1.3 Hz, 8H), 6.87 (td, J = 7.3, 1.2 Hz, 4H), 6.61–6.51 (m, 10H), 5.85 (s, 4H, $CHAr_3$), 5.74 (d, J = 7.2 Hz, 2H), 5.61 (s, 4H, $CHAr_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.90 (C=N), 145.56, 145.45, 145.23, 144.85, 142.52, 141.33, 137.57, 132.58, 131.16, 130.60, 128.81, 128.48, 127.72, 125.38, 125.31, 124.75, 124.56, 124.44, 123.67, 123.44, 123.42, 49.96 ($CHAr_3$), 47.88 ($CHAr_3$). HRMS (EI): *m*/*z* calcd for $C_{80}H_{48}N_2O_2$: 1068.3710 $[M]^+$; found: 1068.3723.

Synthesis of alkylated diimines 5a and 5b. To the solution of diimine **4** (1.5 g, 1.4 mmol) in DMF (75 mL) at 50 °C was added K_2CO_3 (2.3 g, 16.8 mmol). The mixture was stirred for 1 min and MeI (348.8 μL, 5.6 mmol) was added. The reaction mixture was stirred overnight at 50 °C. The orange suspension was cooled to room temperature and poured into 300 mL of water. The orange precipitate was collected by filtration, washed with water, methanol and diethyl ether. After drying *in vacuo* at 70 °C, the product was obtained as an orange powder (1.34 g, 87% yield). Diimine **5b** was prepared following the same procedure using 2.5 equiv. of 1-iodohexane. The mixture was stirred overnight at 70 °C. The orange precipitate obtained after addition of water was collected by filtration, washed with water and methanol (1.37 g, 79% yield).

5a: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, J = 8.1 Hz, 2H), 7.51–7.47 (m, 4H), 7.46–7.42 (m, 4H), 7.38 (d, J = 7.4 Hz, 4H), 7.04–6.96 (m, 8H), 6.86–6.80 (m, 4H), 6.51–6.44 (m, 10H), 5.86 (s, 4H, $CHAr_3$), 5.62 (s, 4H, $CHAr_3$), 5.40 (d, J = 7.2 Hz, 2H), 4.11 (s, 6H, OMe). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.71 (C=N), 147.60, 145.59, 145.39, 145.06, 143.82, 141.30, 139.81, 136.52, 132.70, 130.53, 128.81, 128.37, 127.69, 125.62, 125.44, 125.38, 124.81, 124.72, 124.45, 124.41, 123.56, 123.54, 123.33, 63.53 (OCH_3), 49.96 ($CHAr_3$), 48.55 ($CHAr_3$). MS (ESI) calcd for $C_{82}H_{53}N_2O_2$ (M + H) 1097.4, found 1097.6.

5b: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, J = 8.1 Hz, 2H), 7.52–7.47 (m, 4H), 7.44–7.40 (m, 4H), 7.37 (d, J = 7.2 Hz, 4H), 7.03–6.98 (m, 8H), 6.85–6.79 (m, 4H), 6.48–6.44 (m, 8H), 6.42 (t, J = 7.7 Hz, 2H), 5.83 (s, 4H, $CHAr_3$), 5.62 (s, 4H, $CHAr_3$), 5.33 (d, J = 7.2 Hz, 2H), 4.17 (t, J = 6.6 Hz, 4H, OHex), 2.17 (quint, J = 6.7 Hz, 4H, OHex), 1.84 (quint, J = 7.3 Hz, 4H, OHex), 1.66–1.52 (m, 8H, OHex), 1.09 (t, J = 7.1 Hz, 6H, OHex). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.85 (C=N), 146.73, 145.56, 145.47, 145.43, 145.12, 141.26, 139.75, 136.63, 130.48, 128.74, 128.36, 127.57, 125.39, 125.34, 124.73, 124.68, 124.44, 123.60, 123.52, 123.24, 76.63 (OCH_2), 49.95 ($CHAr_3$), 48.76 ($CHAr_3$), 32.09 (CH_2), 30.83 (CH_2), 26.41 (CH_2), 22.98 (CH_2), 14.37 (CH_3). HRMS (EI): *m*/*z* calcd for $C_{86}H_{59}N_2O_2$: 1151.4571 $[M - C_6H_{13}]^+$; found: 1151.4561.

Synthesis of diimine 7. To the solution of pentiptycene **3** (3.21 g, 6.95 mmol) in iPrOH (250 mL) at 80 °C were added diacetyl (303 μL, 3.48 mmol) and three drops of formic acid. The reaction mixture was stirred for 4 days at 80 °C. The formed yellow suspension was cooled to room temperature and concentrated to a half of its original volume. The yellow precipitate was collected by filtration, washed with iPrOH and dried *in vacuo* (2.27 g, 67% yield). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.47–7.33 (m, 16H), 7.07–6.92 (m, 16H), 5.80 (s, 4H, $CHAr_3$), 5.33 (s, 4H, $CHAr_3$), 5.14 (s, 2H, OH), 2.17 (s, 6H, Me). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.29 (C=N), 145.66, 145.36, 145.17, 142.14, 136.06, 131.94, 130.47, 125.41, 125.39, 123.90, 123.79, 123.68, 50.00 ($CHAr_3$), 47.85 ($CHAr_3$), 17.74 (CH_3). HRMS (EI): *m*/*z* calcd for $C_{72}H_{48}N_2O_2$: 972.3710 $[M]^+$; found: 972.3720.

Synthesis of alkylated diimine 8. To a suspension of diimine **7** (1.09 g, 1.12 mmol) in 50 mL of DMF was added K_2CO_3 (1.85 g, 13.4 mmol). The mixture was stirred for 1 min and then BuI (510 μL, 4.48 mmol) was added in one portion. The reaction mixture was stirred overnight at 70 °C. The yellow suspension was cooled to room temperature and poured into water (300 mL). The yellow precipitate was collected by filtration and washed few times with water and methanol. After drying *in vacuo*, the product was obtained as a yellow powder (1.08 g, 89% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48–7.38 (m, 12H, H_{Ar}), 7.36 (d, J = 7.2 Hz, 4H, H_{Ar}), 7.08–6.90 (m, 16H, H_{Ar}), 5.81 (s, 4H, $CHAr_3$), 5.34 (s, 4H, $CHAr_3$), 4.05 (t, J = 6.7 Hz, 4H, OCH_2), 2.19 (s, 6H, Me), 2.10 (dt, J = 14.5, 6.8 Hz, 4H, $OCH_2\mathit{CH_2}CH_2CH_3$), 1.82 (sep, J = 7.3 Hz, 4H, $OCH_2CH_2\mathit{CH_2}CH_3$), 1.22 (t, J = 7.3 Hz, 6H, $OCH_2CH_2CH_2\mathit{CH_3}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.96 (C=N), 146.54, 145.87, 145.45, 145.29, 137.92, 135.99, 131.83, 125.43, 125.33, 123.85, 123.59, 76.31 (OCH_2), 50.00 ($CHAr_3$), 48.69 ($CHAr_3$), 32.90 (CH_2), 19.98 (CH_2), 17.84 (CH_3), 14.39 (CH_3, hexyl). HRMS (EI): *m*/*z* calcd for $C_{80}H_{64}N_2O_2$: 1084.4962 $[M]^+$; found: 1084.4965.

Synthesis of imidazolium salts 6a·HCl and 6b·HCl. A flame dried Schlenk flask containing diimine **5a** (600 mg, 0.546 mmol) was evacuated and back-filled with nitrogen three times. Next, chloromethyl ethyl ether (2.5 mL, 26.9 mmol stored overnight over K_2CO_3 under nitrogen) was added. The reaction mixture was stirred for 5 h at 80 °C. After cooling to room temperature, diethyl ether was added, the insoluble material was collected by filtration and washed with diethyl ether. Purification by column chromatography (first CH_2Cl_2 to remove impurities, followed by CH_2Cl_2/MeOH, 1 : 1, v/v to elute pure product) provides the azolium salt **6a**·HCl (363 mg, 58% yield) as a pale yellow powder. The azolium salt **6b**·HCl (272 mg, 50% yield) was obtained as a pale yellow powder from diimine **5b** (530 mg, 0.428 mmol) and chloromethyl ethyl ether (2.5 mL, 26.9 mmol stored overnight over K_2CO_3 under nitrogen) using a similar procedure. After stirring the mixture for 20 h at 80 °C, diethyl ether was added and the obtained solution was sonicated for a few minutes. The obtained precipitate was collected by filtration and washed with diethyl ether affording the pure product.

6a·HCl: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, J = 8.2 Hz, 2H, acenaph.), 8.07 (s, 1H, NCHN), 7.49–7.42 (m, 12H, H_{Ar}), 7.32 (t, J = 7.3 Hz, 2H, acenaph.), 7.26 (d, J = 7.1 Hz, 4H, H_{Ar}),

Open Access Article. Published on 17 June 2016. Downloaded on 12/26/2025 12:30:17 AM. This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

7.05–6.96 (m, 8H, H_{Ar}), 6.87–6.80 (m, 8H, H_{Ar}), 6.73 (d, J = 7.0 Hz, 2H, acenaph.), 6.34 (s, 4H, $CHAr_3$), 5.95 (s, 4H, $CHAr_3$), 4.18 (s, 6H, OMe). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.70 (NCHN), 144.64, 144.32, 144.16, 143.96, 142.04, 139.81, 139.22, 135.57, 131.66, 131.33, 130.19, 127.96, 126.14, 126.04, 125.75, 125.58, 124.53, 124.16, 123.79, 122.23, 120.80, 63.23 (OCH_3), 49.34 ($CHAr_3$), 48.41 ($CHAr_3$). MS (ESI) calcd for $C_{83}H_{53}N_2O_2$ $(M - Cl)^+$ 1109.4, found 1109.8.

6b·HCl: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, J = 8.0 Hz, 2H), 8.08 (s, 1H, NCHN), 7.48–7.40 (m, 12H), 7.31 (t, J = 7.4 Hz, 2H), 7.27–7.20 (br, 4H), 7.02 (t, J = 7.4 Hz, 4H), 6.99 (t, J = 7.4 Hz, 4H), 6.88–6.80 (m, 8H), 6.71 (d, J = 6.9 Hz, 2H), 6.24 (s, 4H, $CHAr_3$), 5.92 (s, 4H, $CHAr_3$), 4.23 (t, J = 6.7 Hz, 4H, OHex), 2.19 (quint, J = 6.8 Hz, 4H, OHex), 1.81 (quint, J = 7.4 Hz, 4H, OHex), 1.65–1.51 (m, 8H, OHex), 1.07 (t, J = 7.1 Hz, 6H, OHex). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.17 (NCHN), 144.66, 144.34, 144.13, 143.92, 141.77, 139.74, 139.24, 135.65, 131.62, 131.45, 130.19, 127.97, 126.11, 126.02, 126.00, 125.74, 125.57, 125.49, 124.46, 124.15, 123.79, 122.12, 120.48, 76.65 (OCH_2), 49.44 ($CHAr_3$), 48.62 ($CHAr_3$), 31.98 (CH_2), 30.81 (CH_2), 26.23 (CH_2), 22.93 (CH_2), 14.32 (CH_3). HRMS (EI): m/z calcd for $C_{87}H_{60}N_2O_2$: 1164.4649 $[M - Cl - C_6H_{13}]^+$; found: 1164.4620.

Synthesis of imidazolium salt 9·HCl. A flame dried Schlenk flask containing diimine **8** (1.09 g, 1.0 mmol) was evacuated and back-filled with nitrogen three times. Next, chloromethyl ethyl ether (stored overnight over K_2CO_3 under nitrogen, 2.50 mL, 26.9 mmol) was added under a stream of nitrogen. The reaction mixture was stirred overnight at 80 °C. After cooling to room temperature, diethyl ether was added, the insoluble material was collected by filtration and recrystallized from CH_2Cl_2/Et_2O. The corresponding salt **9**·HCl (680 mg, 60% yield) was obtained as an off-white powder. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (br, 4H, H_{Ar}), 7.80 (s, 1H, NCHN), 7.44–7.38 (m, 8H, H_{Ar}), 7.34 (d, J = 7.2 Hz, 4H, H_{Ar}), 7.09 (br, 4H, H_{Ar}), 7.05 (t, J = 6.9 Hz, 4H, H_{Ar}), 6.95 (t, J = 7.2 Hz, 4H, H_{Ar}), 6.79 (t, J = 7.0 Hz, 4H, H_{Ar}), 6.09 (s, 4H, $CHAr_3$), 5.84 (s, 4H, $CHAr_3$), 4.14 (t, J = 6.7 Hz, 4H, OCH_2), 2.45 (s, 6H, Me), 2.16–2.09 (m, 4H, $OCH_2\mathit{CH_2}CH_2CH_3$), 1.86–1.77 (m, 4H, $OCH_2CH_2\mathit{CH_2}CH_3$), 1.22 (t, J = 7.4 Hz, 6H, $OCH_2CH_2CH_2\mathit{CH_3}$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.88 (NCHN), 144.85, 144.34, 144.28, 141.96, 138.70, 133.41, 131.63, 126.20, 125.98, 125.82, 125.63, 124.34, 124.16, 123.72, 119.97, 76.31 (OCH_2), 49.24 ($CHAr_3$), 48.53 ($CHAr_3$), 32.90 (CH_2), 19.86 (CH_3), 14.32 (CH_3, hexyl). HRMS (EI): m/z calcd for $C_{81}H_{65}N_2O_2$: 1097.5041 $[M - Cl]^+$; found: 1097.5024.

Synthesis of [(6a)CuI]. A vial was charged, under air, with **6a**·HCl (60 mg, 0.052 mmol), CuI (10.8 mg, 0.056 mmol) and finely powdered K_2CO_3 (50 mg, 0.362 mmol). To the mixture was added acetone (1.5 mL) and stirred overnight at 60 °C. After this time the solvent was removed *in vacuo* and dichloromethane was added. The mixture was filtered through a pad of celite. The pad of celite was washed with dichloromethane. The solvent was concentrated and pentane (5 mL) was added, affording a yellow solid which was washed with more pentane and dried under vacuum (46 mg, 68% yield). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.91 (d, J = 8.2 Hz, 2H, acenapht.), 7.50 (d, J = 7.5 Hz, 4H, H_{Ar}), 7.48 (d, J = 7.1 Hz, 4H, H_{Ar}), 7.41 (d, J = 7.3 Hz, 4H, H_{Ar}), 7.18 (t, J = 7.3 Hz, 2H, acenapht.), 7.04–6.99 (m, 8H, H_{Ar}), 6.91–6.86 (m, 8H, H_{Ar}), 6.81 (td, J = 7.3, 1.2 Hz, 4H, H_{Ar}), 6.45 (d, J = 7.0 Hz, 2H, acenapht.), 5.96 (s, 4H, $CHAr_3$), 5.46 (s, 4H, $CHAr_3$), 4.16 (s, 6H, OMe). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 189.58 ($C_{carbene}$), 152.18, 145.88, 145.04, 145.02, 144.27, 141.91, 139.62, 138.26, 131.44, 130.32, 129.35, 128.07, 126.50, 126.40, 126.21, 125.62, 125.59, 125.43, 124.63, 124.31, 123.67, 63.87 (OCH_3), 50.92 ($CHAr_3$), 48.86 ($CHAr_3$). MS (ESI) calcd for $C_{83}H_{52}CuN_2O_2$ $(M - I)^+$ 1171.3, found 1171.7.

Synthesis of [(6b)AgCl] and [(9)AgCl]. A flame dried Schlenk flask containing azolium salt **6b**·HCl (155.6, 0.121 mmol) or **9**·HCl (138 mg, 0.121 mmol) and Ag_2O (84.8 mg, 0.365 mmol) was evacuated and backfilled with nitrogen three times. CH_2Cl_2 (5 mL) was added *via* syringe. The reaction mixture was stirred overnight at 40 °C, cooled to room temperature and filtered through celite. The filtrate was concentrated under reduced pressure, the residue was washed with pentane and the precipitate was collected by filtration, to afford the desired silver complex [(**6b**)AgCl] as a yellow powder (123 mg, 73% yield) or [(**9**)AgCl] as a white powder (97.5 mg, 65% yield). The limited solubility and the weak signal of the carbene C (two doublets) prevent the detection of the ^{13}C signal.

[(**6b**)AgCl]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, J = 8.2 Hz, 2H), 7.47 (d, J = 7.4 Hz, 4H), 7.43 (d, J = 7.2 Hz, 4H), 7.33 (d, J = 7.3 Hz, 4H), 7.10 (t, J = 7.6 Hz, 2H), 6.99 (q, J = 6.1 Hz, 8H), 6.93 (t, J = 7.4 Hz, 4H), 6.79–6.72 (m, 8H), 6.29 (d, J = 7.0 Hz, 2H), 5.91 (s, 4H, $CHAr_3$), 5.41 (s, 4H, $CHAr_3$), 4.27 (t, J = 6.7 Hz, 4H, OHex), 2.21 (quint, J = 6.8 Hz, 4H, OHex), 1.85 (quint, J = 7.4 Hz, 4H, OHex), 1.69–1.54 (m, 8H, OHex), 1.10 (t, J = 7.1 Hz, 6H, OHex). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.09, 145.40, 144.49, 144.24, 143.67, 141.33, 139.76, 139.71, 137.90, 130.68, 129.70, 128.81, 127.61, 126.47, 126.16, 125.68, 125.05, 124.79, 124.34, 124.24, 124.13, 123.94, 123.77, 123.69, 76.62 (OCH_2), 50.59 ($CHAr_3$), 48.74 ($CHAr_3$), 32.07 (CH_2), 30.90 (CH_2), 26.28 (CH_2), 23.01 (CH_2), 14.38 (CH_3). HRMS (EI): m/z calcd for $C_{87}H_{60}N_2O_2$: 1164.4649 $[M - AgCl - C_6H_{12}]^+$; found: 1164.4630.

[(**9**)AgCl]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, J = 6.7 Hz, 4H, H_{Ar}), 7.41 (d, J = 7.0 Hz, 4H, H_{Ar}), 7.37 (d, J = 7.1 Hz, 4H, H_{Ar}), 7.32 (d, J = 6.6 Hz, 4H, H_{Ar}), 7.07–6.97 (m, 12H, H_{Ar}), 6.94 (t, J = 7.3 Hz, 4H, H_{Ar}), 5.85 (s, 4H, $CHAr_3$), 5.19 (s, 4H, H_{Ar}), 4.20 (t, J = 6.7 Hz, 4H, OCH_2), 2.18–2.12 (m, 4H, $OCH_2\mathit{CH_2}CH_2CH_3$), 1.88 (s, 6H, Me), 1.87–1.80 (m, 4H, $OCH_2CH_2\mathit{CH_2}CH_3$), 1.24 (t, J = 7.4 Hz, 6H, $OCH_2CH_2CH_2\mathit{CH_3}$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.66, 144.74, 144.22, 143.59, 141.53, 137.46, 128.23, 128.18, 126.31, 126.19, 125.89, 125.41, 124.77, 124.34, 124.26, 124.18, 123.44, 76.35 (OCH_2), 50.59 ($CHAr_3$), 48.65 ($CHAr_3$), 32.97 (CH_2), 19.86 (CH_2), 14.38 (CH_3), 10.20 (CH_3, butyl). HRMS (EI): m/z calcd for $C_{81}H_{64}N_2O_2$: 1096.4962 $[M - AgCl]^+$; found: 1096.4950.

Synthesis of [(6a)AuCl] and [(6b)AuCl]. A vial was charged with **6a**·HCl (60 mg, 0.052 mmol), $[AuCl(Me_2S)]$ (16.7 mg, 0.056 mmol) and finely powdered K_2CO_3 (50 mg, 0.362 mmol). To the mixture was added acetone (1.5 mL) and stirred over-

Open Access Article. Published on 17 June 2016. Downloaded on 12/26/2025 12:30:17 AM.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

night at 60 °C. After this time the solvent was removed *in vacuo* and dichloromethane was added. The mixture was filtered through a pad of silica. The pad of silica was washed with dichloromethane. The solvent was concentrated and pentane (5 mL) was added, affording a yellowish solid which was washed with further portions of pentane and dried under vacuum (31 mg, 45% yield). The gold complex [(**6b**)AuCl] (84 mg, 73% yield) was prepared using a similar procedure from **6b**·HCl (100 mg, 0.077 mmol), [AuCl(Me_2S)] (23 mg, 0.077 mmol), K_2CO_3 (32 mg, 0.233 mmol) in acetone (2 mL) at 60 °C for 3 h.

[(**6a**)AuCl]: ^1H NMR (500 MHz, CD_2Cl_2) δ 7.84 (d, J = 8.1 Hz, 2H, acenapht.), 7.52–7.47 (m, 12H, H_{Ar}), 7.06–6.95 (m, 14H, H_{Ar}), 6.76 (dd, J = 7.3, 1.4 Hz, 4H, H_{Ar}), 6.73 (td, J = 7.2, 1.1 Hz, 4H, H_{Ar}), 6.08 (d, J = 6.9 Hz, 2H, acenapht.), 5.98 (s, 4H, $CHAr_3$), 5.47 (s, 4H, $CHAr_3$), 4.21 (s, 6H, OMe). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 180.39 ($C_{carbene}$), 145.81, 145.02, 144.75, 144.29, 141.96, 139.08, 138.42, 130.76, 130.15, 129.45, 127.96, 126.43, 126.40, 126.20, 125.60, 125.48, 125.07, 124.59, 124.32, 123.78, 63.79 (OCH_2), 51.08 ($CHAr_3$), 48.89 ($CHAr_3$). MS (ESI) calcd for $C_{83}H_{52}AuClNaN_2O_2$ ($M + Na^+$) 1363.3, found 1363.5; calcd for $C_{83}H_{52}AuClKN_2O_2$ ($M + K^+$) 1379.3, found 1379.5.

[(**6b**)AuCl]: ^1H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, J = 8.1 Hz, 2H), 7.46 (d, J = 7.3 Hz, 8H), 7.42 (d, J = 7.1 Hz, 4H), 7.05–6.91 (m, 14H), 6.73–6.67 (m, 8H), 6.11 (d, J = 7.0 Hz, 2H), 5.90 (s, 4H, $CHAr_3$), 5.44 (s, 4H, $CHAr_3$), 4.27 (t, J = 6.7 Hz, 4H, OHex), 2.21 (quint, J = 6.8 Hz, 4H, OHex), 1.85 (quint, J = 7.4 Hz, 4H, OHex), 1.69–1.50 (m, 8H, OHex), 1.10 (t, J = 7.1 Hz, 6H, OHex). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.53 ($C_{carbene}$), 151.03, 145.50, 144.51, 144.22, 143.68, 141.37, 138.47, 137.84, 130.20, 129.54, 128.79, 127.58, 126.11, 126.01, 125.58, 125.08, 125.04, 124.45, 124.13, 123.89, 123.57, 76.61 (OCH_2), 50.71 ($CHAr_3$), 48.75 ($CHAr_3$), 32.07 (CH_2), 30.89 (CH_2), 26.28 (CH_2), 23.01 (CH_2), 14.38 (CH_3). HRMS (EI): m/z calcd for $C_{87}H_{60}N_2O_2$: 1164.4649 $[M - AuCl - C_6H_{12}]^+$; found: 1164.4640.

Synthesis of [(9)AuCl]. A vial was charged with **9**·HCl (100 mg, 0.088 mmol), [AuCl(Me_2S)] (29 mg, 0.098 mmol) and finely powdered K_2CO_3 (100 mg, 0.724 mmol). To the mixture was added CH_2Cl_2 (10 mL) and vigorously stirred for 3 h at room temperature in the absence of light. After this time the mixture was filtered through celite which was finally washed with dichloromethane. The solvent was concentrated and pentane (10 mL) was added, affording an off-white solid which was purified by column chromatography on silica (cyclohexane/ethyl acetate, 2 : 1, v/v) (60 mg, 51% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 7.50–7.45 (m, 8H), 7.41 (d, J = 6.7 Hz, 4H), 7.30 (d, J = 6.6 Hz, 4H), 7.07–6.93 (m, 16H), 5.85 (s, 4H, $CHAr_3$), 5.23 (s, 4H, $CHAr_3$), 4.20 (t, J = 6.7 Hz, 4H, OCH_2), 2.19–2.12 (m, 4H, $OCH_2\mathit{CH_2}CH_2CH_3$), 1.85 (sext, J = 7.4 Hz, 4H, $OCH_2CH_2\mathit{CH_2}CH_3$), 1.77 (s, 6H, Me), 1.25 (t, J = 7.4 Hz, 6H, $OCH_2CH_2CH_2\mathit{CH_3}$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.17 ($C_{carbene}$), 150.85, 145.78, 144.78, 144.18, 143.60, 141.54, 137.38, 127.59, 126.05, 125.99, 125.84, 125.39, 124.99, 124.28, 124.23, 123.96, 123.37, 76.35 (OCH_2), 50.65 ($CHAr_3$), 48.67 ($CHAr_3$), 32.98 (CH_2), 19.87 (CH_2), 14.38 (CH_3), 10.20 (CH_3, butyl). MS (ESI) calcd for $C_{81}H_{64}N_2O_2AuClNa$ ($M + Na^+$) 1351.4, found 1351.6.

Synthesis of [(6a)IrCl(cod)]. A flame dried Schlenk flask containing azolium salt **6a**·HCl (169.38 mg, 0.148 mmol) and $[IrCl(cod)]_2$ (50 mg, 0.074 mmol) was evacuated and back-filled with nitrogen three times. Next, THF (15 mL) and a solution of sodium *tert*-pentoxide in THF (2.5 M, 71 μL, 0.177 mmol) were added at room temperature. The mixture was stirred at room temperature for 2 h and the solvent was removed *in vacuo*. The residue was purified by column chromatography (ethyl acetate/cyclohexane, 2 : 1, v/v) to afford the desired product as an orange microcrystalline powder (150 mg, 70% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 8.37 (br, 2H, H_{Ar}), 7.60 (br, 2H, H_{Ar}), 7.50–7.45 (m, 4H, H_{Ar}), 7.39–7.34 (m, 6H, H_{Ar}), 7.14–7.00 (m, 8H, H_{Ar}), 6.77 (t, J = 6.8 Hz, 4H, H_{Ar}), 6.61 (br, 2H, H_{Ar}), 6.38 (dd, J = 8.2, 7.1 Hz, 2H, acenapht.), 6.31 (br, 6H), 6.15 (br, 2H, H_{Ar}), 5.93 (s, 4H, $CHAr_3$), 5.37 (br, 2H, H_{Ar}), 4.63 (d, J = 7.0 Hz, 2H, acenapht.), 4.33–4.27 (m, 2H, cod), 4.21 (s, 6H, OMe), 3.32–3.27 (m, 2H, cod), 1.16–1.07 (m, 4H, cod), 1.06–0.96 (m, 2H, cod), 0.92–0.84 (m, 2H, cod). ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.09 ($C_{carbene}$), 151.06, 146.71–143.08 (br multiplet), 140.27, 128.80, 128.73, 128.61, 126.86, 125.85 (br), 125.24 (br), 124.78 (br), 123.80, 123.43 (br), 121.01, 86.12 (H^{cod}), 63.40 (OCH_3), 52.73 (H^{cod}), 50.72 (br, $CHAr_3$), 48.59 (br, $CHAr_3$), 32.93 (H^{cod}), 28.31 (H^{cod}). HRMS (EI): m/z calcd for $C_{83}H_{53}N_2O_2$: 1109.4102 $[M + H - IrCl(cod)]^+$; found: 1109.4103.

Synthesis of [(9)IrCl(cod)]. A flame dried Schlenk flask containing azolium silver complex [(**9**)AgCl] (150 mg, 0.121 mmol) and $[IrCl(cod)]_2$ (40.6 mg, 0.06 mmol) was evacuated and back-filled with nitrogen three times. Next, toluene (5 mL) was added and the mixture was stirred overnight at 100 °C. After this time the solvent was removed *in vacuo* and dichloromethane was added. The mixture was filtered through a pad of silica. The pad of silica was washed with dichloromethane. The solvent was concentrated and pentane (5 mL) was added, affording a yellow solid, which was washed with pentane and dried under vacuum (137 mg, 79% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 8.41 (br, 2H, H^{Ar}), 7.68 (br, 2H, H^{Ar}), 7.47–7.37 (m, 8H, H^{Ar}), 7.30–7.24 (m, 4H, H^{Ar}), 7.10–7.02 (m, 8H, H^{Ar}), 6.99–6.92 (m, 8H, H^{Ar}), 6.37 (br, 2H, $CHAr_3$), 5.88 (s, 4H, $CHAr_3$), 5.27 (br, 2H, $CHAr_3$), 4.22 (t, J = 6.7 Hz, 4H, OCH_2), 4.11–4.06 (m, 2H, H^{cod}), 3.23–3.18 (m, 2H, H^{cod}), 2.18–2.12 (m, 4H, CH_2, butyl), 1.90–1.81 (m, 4H, CH_2, butyl), 1.23 (t, J = 7.4 Hz, 6H, CH_3, butyl), 0.99–0.93 (m, 4H, H^{cod}), 0.90 (s, 6H, CH_3, imidazol), 0.88–0.81 (m, 2H, H^{cod}), 0.81–0.73 (m, 2H, H^{cod}). ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.38 ($C_{carbene}$), 149.90, 146.82 (br), 144.47 (br), 137.25 (br), 128.67, 128.31, 125.13, 123.93, 123.47 (br), 83.60 (H^{cod}), 76.21 (OCH_2), 52.18 (H^{cod}), 50.30 ($CHAr_3$), 48.75 ($CHAr_3$), 32.80 (CH_2), 28.21 (H^{cod}), 19.95 (CH_2), 14.36 (CH_3), 9.89 (CH_3, butyl). HRMS (EI): m/z calcd for $C_{81}H_{65}N_2O_2$: 1097.5041 $[M + H - IrCl(cod)]^+$; found: 1097.5028.

Synthesis of [(6a)IrCl(CO)$_2$] and [(9)IrCl(CO)$_2$]. [(**6a**)IrCl(cod)] (100 mg, 0.069 mmol) or [(**9**)IrCl(cod)] (100 mg, 0.069 mmol) was dissolved in CH_2Cl_2 (7 mL) and CO was bubbled through this solution for 20 min. The solvent was evaporated *in vacuo* and the residue was washed with pentane to obtain the yellow complex [(**6**)IrCl$(CO)_2$] (90 mg, 93% yield) or [(**9**)IrCl$(CO)_2$] (93 mg, 96% yield).

This journal is © The Royal Society of Chemistry 2016

Open Access Article. Published on 17 June 2016. Downloaded on 12/26/2025 12:30:17 AM.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

[(**6a**)IrCl(CO)$_2$]: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.79 (d, J = 7.0 Hz, 4H, H$_{Ar}$), 7.65 (d, J = 8.2 Hz, 2H, acenapht.), 7.44 (d, J = 7.0 Hz, 8H, H$_{Ar}$), 7.01 (td, J = 7.3, 1.4 Hz, 4H, H$_{Ar}$), 6.97 (td, J = 7.4, 1.3 Hz, 4H, H$_{Ar}$), 6.90 (td, J = 7.1, 1.7 Hz, 4H, H$_{Ar}$), 6.76 (dd, J = 8.2, 7.0 Hz, 2H, acenapht.), 6.60–6.53 (m, 8H, H$_{Ar}$), 5.94 (s, 4H, CHAr$_3$), 5.72 (s, 4H, CHAr$_3$), 5.52 (d, J = 7.0 Hz, 2H, acenapht.), 4.19 (s, 6H, Me). ^{13}C NMR (126 MHz, CDCl$_3$) δ 184.63 (C$_{carbene}$), 179.87 (CO), 167.79 (CO), 151.28, 145.99, 144.81, 144.26, 144.21, 141.95, 140.01, 137.65, 129.92, 129.26, 128.13, 127.47, 126.72, 126.58, 125.58, 125.28, 125.19, 125.03, 124.17, 123.75, 123.67, 123.33, 123.11, 63.41 (OCH$_3$), 50.82 (CHAr$_3$), 48.52 (CHAr$_3$). Recording of mass spectra with complex [(**6a**)Ir(CO)$_2$Cl] was unsuccessful, due to instability of this complex.

[(**9**)IrCl(CO)$_2$]: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.76 (d, J = 7.0 Hz, 4H, H$_{Ar}$), 7.43 (dd, J = 6.8, 1.6 Hz, 4H, H$_{Ar}$), 7.39 (dd, J = 6.8, 1.4 Hz, 4H, H$_{Ar}$), 7.33 (dd, J = 6.8, 1.7 Hz, 4H, H$_{Ar}$), 7.02–6.93 (m, 16H, H$_{Ar}$), 5.84 (s, 4H, CHAr$_3$), 5.52 (s, 4H, CHAr$_3$), 4.16 (t, J = 6.6 Hz, 4H, OCH$_2$), 2.16–2.09 (m, 4H, OCH$_2$*CH*$_2$CH$_2$CH$_3$), 1.83 (sex, J = 7.4 Hz, 4H, OCH$_2$CH$_2$*CH*$_2$CH$_3$), 1.54 (s, 6H, Me), 1.22 (t, J = 7.3 Hz, 6H, OCH$_2$CH$_2$CH$_2$*CH*$_3$). ^{13}C NMR (126 MHz, CDCl$_3$) δ 179.67 (C$_{carbene}$), 178.22 (CO), 167.89 (CO), 150.34, 146.58, 145.35, 144.26, 144.15, 141.90, 137.20, 128.95, 126.82, 126.22, 125.53, 125.51, 125.23, 125.21, 124.06, 123.57, 123.33, 76.27 (OCH$_2$), 50.73 (CHAr$_3$), 48.66 (CHAr$_3$), 32.89 (CH$_2$), 19.94 (CH$_2$), 14.37 (CH$_3$), 10.32 (CH$_3$, butyl). MS (ESI) calcd for C$_{83}$H$_{64}$ClIrNaN$_2$O$_4$ (M + Na) 1403.4, found 1403.1.

General procedure for cyclization of diethyl 2-allyl-2-(prop-2-ynyl)malonate

The respective (NHC)AuCl complex (0.01 equiv.) and AgNTf$_2$ (0.01 equiv.) were placed into a flame dried 10 mL Schlenk tube under a nitrogen atmosphere and CH$_2$Cl$_2$ (3 mL) was added. The mixture was stirred for 15 min at r.t. in the absence of light. Next, diethyl 2-allyl-2-(prop-2-ynyl)malonate (200 mg, 1 equiv.) was added and the mixture was stirred at r.t. in the absence of light for the indicated time. Finally, the solvent was removed on a rotary evaporator and the residue was purified by column chromatography on silica (pentane/diethyl ether, 10 : 1, v/v). The fraction containing the mixture of five- and six-membered products was collected and analyzed by NMR.

Acknowledgements

This work was supported by the DFG *via* grant Pl 178/13-2. We wish to thank Yuki Kanai and Andreas Hegelein for the synthesis of pentiptycene.

References

1 C. F. Chen and Y. X. Ma, *Iptycenes Chemistry: From Synthesis to Applications*, Springer Verlag, Berlin, 2012.
2 T. M. Swager, *Acc. Chem. Res.*, 2008, **41**, 1181–1190.
3 X. Jiang, B. Rodríguez-Molina, N. Nazarian and M. A. Garcia-Garibay, *J. Am. Chem. Soc.*, 2014, **136**, 8871–8874.
4 E. R. Kay, D. A. Leigh and F. Zerbetto, *Angew. Chem., Int. Ed.*, 2007, **46**, 72–191.
5 J. H. Chong and M. J. MacLachlan, *Chem. Soc. Rev.*, 2009, **38**, 3301–3315.
6 J. S. Yang and J. L. Yan, *Chem. Commun.*, 2008, 1501–1512.
7 Y. Jiang and C.-F. Chen, *Eur. J. Org. Chem.*, 2011, 6377–6403.
8 P. D. Bartlett, M. J. Ryan and S. G. Cohen, *J. Am. Chem. Soc.*, 1942, **64**, 2649–2653.
9 R. V. Skvarche and V. K. Shalaev, *Dokl. Akad. Nauk SSSR*, 1974, **216**, 110–112.
10 H. Hart, S. Shamouilian and Y. Takehira, *J. Org. Chem.*, 1981, **46**, 4427–4432.
11 J.-S. Yang and T. M. Swager, *J. Am. Chem. Soc.*, 1998, **120**, 11864–11873.
12 X.-Z. Zhu and C.-F. Chen, *J. Org. Chem.*, 2005, **70**, 917–924.
13 L. Benhamou, E. Chardon, G. Lavigne, S. Bellemin-Laponnaz and V. Cesar, *Chem. Rev.*, 2011, **111**, 2705–2733.
14 C. Azerraf and D. Gelman, *Organometallics*, 2009, **28**, 6578–6584.
15 O. Grossman, C. Azerraf and D. Gelman, *Organometallics*, 2005, **25**, 375–381.
16 C. Azerraf and D. Gelman, *Chem. – Eur. J.*, 2008, **14**, 10364–10368.
17 C. Azerraf, O. Grossman and D. Gelman, *J. Organomet. Chem.*, 2007, **692**, 761–767.
18 L. Bini, C. Müller, J. Wilting, L. von Chrzanowski, A. L. Spek and D. Vogt, *J. Am. Chem. Soc.*, 2007, **129**, 12622–12623.
19 S. Gonell, M. Poyatos and E. Peris, *Angew. Chem., Int. Ed.*, 2013, **52**, 7009–7013.
20 R. Savka, M. Bergmann, Y. Kanai, S. Foro and H. Plenio, *Chem. – Eur. J.*, 2016, **22**, DOI: 10.1002/chem.201601474.
21 J.-S. Yang and C.-W. Ko, *J. Org. Chem.*, 2006, **71**, 844–847.
22 C. S. Popeney, C. M. Levins and Z. Guan, *Organometallics*, 2011, **30**, 2432–2452.
23 S. Dastgir, K. S. Coleman, A. R. Cowley and M. L. H. Green, *Dalton Trans.*, 2009, 7203–7214.
24 K. V. Vasudevan, R. R. Butorac, C. D. Abernethy and A. H. Cowley, *Dalton Trans.*, 2010, **39**, 7401–7408.
25 R. Savka and H. Plenio, *Eur. J. Inorg. Chem.*, 2014, 6246–6253.
26 M. Tsimerman, D. Mallik, T. Matsuo, T. Otani, K. Tamao and M. G. Organ, *Chem. Commun.*, 2012, **48**, 10352–10354.
27 S. Leuthäußer, D. Schwarz and H. Plenio, *Chem. – Eur. J.*, 2007, **13**, 7195–7203.
28 H. Türkmen and B. Cetinkaya, *J. Organomet. Chem.*, 2006, **691**, 3749–3759.
29 T. Tu, Z. Sun, W. Fang, M. Xu and Y. Zhou, *Org. Lett.*, 2012, **14**, 4250–4253.
30 B. R. Van Ausdall, J. L. Glass, K. M. Wiggins, A. M. Aarif and J. Louie, *J. Org. Chem.*, 2009, **74**, 7935–7942.

Open Access Article. Published on 17 June 2016. Downloaded on 12/26/2025 12:30:17 AM.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

31 J. D. Egbert, C. S. J. Cazin and S. P. Nolan, *Catal. Sci. Technol.*, 2013, **3**, 912–926.

32 J. C. Garrison and W. J. Youngs, *Chem. Rev.*, 2005, **105**, 3978–4008.

33 R. Visbal, A. Laguna and M. C. Gimeno, *Chem. Commun.*, 2013, **49**, 5642–5644.

34 A. Collado, A. Gomez-Suarez, A. R. Martin, A. M. Slawin and S. P. Nolan, *Chem. Commun.*, 2013, **49**, 5541–5543.

35 R. Savka and H. Plenio, *Dalton Trans.*, 2015, **44**, 891–893.

36 S. Wolf and H. Plenio, *J. Organomet. Chem.*, 2009, **694**, 1487–1492.

37 D. Pflasterer and A. S. K. Hashmi, *Chem. Soc. Rev.*, 2016, **45**, 1331–1367.

38 M. Raducan, C. Rodriguez-Escrich, X. C. Cambeiro, E. C. Escudero-Adan, M. A. Pericas and A. M. Echavarren, *Chem. Commun.*, 2011, **47**, 4893–4895.

39 K. Fourmy, S. Mallet-Ladeira, O. Dechy-Cabaret and M. Gouygou, *Organometallics*, 2013, **32**, 1571–1574.

40 R. E. Ebule, D. Malhotra, G. B. Hammond and B. Xu, *Adv. Synth. Catal.*, 2016, **358**, 1478–1481.

41 M. C. Blanco Jaimes, C. R. Bohling, J. M. Serrano-Becerra and A. S. Hashmi, *Angew. Chem., Int. Ed.*, 2013, **52**, 7963–7966.

42 The chloro ligand displays a pronounced anisotropy of the displacement parameter along the axis defined by the two long Ag–C distances. It was therefore decided to refine the two chloro ligands with s.o.f = 0.5 in two separate positions, which are 105 pm apart.

43 A. Poater, B. Cosenza, A. Correa, S. Giudice, F. Ragone, V. Scarano and L. Cavallo, *Eur. J. Inorg. Chem.*, 2009, 1759–1766.

44 T. Dröge and F. Glorius, *Angew. Chem., Int. Ed.*, 2010, **49**, 6940–6952.

45 M. Mastalerz and I. M. Oppel, *Angew. Chem., Int. Ed.*, 2012, **51**, 5252–5255.

46 O. Winkelmann, C. Näther and U. Lüning, *Eur. J. Org. Chem.*, 2007, 981–987.

47 M. Guitet, P. Zhang, F. Marcelo, C. Tugny, J. Jiménez-Barbero, O. Buriez, C. Amatore, V. Mouriès-Mansuy, J.-P. Goddard, L. Fensterbank, Y. Zhang, S. Roland, M. Ménand and M. Sollogoub, *Angew. Chem., Int. Ed.*, 2013, **52**, 7213–7218.

48 M. W. Hussong, F. Rominger, P. Krämer and B. F. Straub, *Angew. Chem., Int. Ed.*, 2014, **53**, 9372–9375.

49 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2008, **64**, 112–122.