

1 Article

2 Transmetalation from Magnesium NHCs – 3 Convenient Synthesis of Chelating π -Acidic NHC 4 Complexes

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14 **Abstract:** The synthesis of chelating NHC complexes with considerable π -acceptor properties can
15 be a challenging task. This is due to the dimerization of free carbene ligands, the moisture sensitivity
16 of reaction intermediates or reagents, and challenges associated with the workup procedure. Herein,
17 we report a general route using transmetalation from magnesium NHCs. Notably, this route gives
18 transition metal complexes in quantitative conversion without the formation of byproducts.
19 Accordingly, it allows for the facile access to transition metal complexes where the conventional
20 routes via the free or lithium coordinate carbene, the silver complexes, or in situ metalation in
21 dimethyl sulfoxide (DMSO) fail. We therefore propose transmetalation from magnesium NHCs as
22 a convenient and general route to NHC complexes.

23 **Keywords:** NHC; transmetalation; magnesium; palladium; carbene

24

25 1. Introduction

26 *N*-heterocyclic carbene (NHC) ligands have become the powerhouse of modern transition metal
27 chemistry [1]. This is largely due to the ease of tuning their electronic and steric properties targeting
28 a specific application. After Arduengo's report on the first crystalline carbene [2], it became common
29 believe that NHCs should be considered strong σ -donor ligands with negligible π -acceptor
30 properties. It was later however realized that the π -acceptor properties of ancillary carbene ligands
31 are equally important [3]. This led to the design of π -electron withdrawing carbenes such as
32 Bertrand's cyclic (alkyl)(amino) carbenes (CAACs) [4], diamido carbenes (DACs) [5-8], or
33 ferrocenium [9-12] decorated NHCs. Also the NHCs with saturated backbones (saNHCs,
34 imidazolidin-2-ylidenes) as well as benzannulated congeners (benzNHCs, benzimidazolin-2-
35 ylidenes) show considerable backbonding capabilities. This is either due to the pyramidalization of
36 the amino groups, which reduces the overlap with the π -system within the *N*-heterocycle, or due to
37 the π -acidic character of the benzannulated π -system. An excellent example for the importance of
38 these π -effects are conjugated organic singlet biradicaloids derived from carbene scaffolds, where the
39 stability and electronic properties are largely dependent on the nature of the carbene [13-17]. Another
40 outstanding example from transition metal chemistry is the capability of CAACs and saNHCs to
41 stabilize low-valent metal complexes [18].

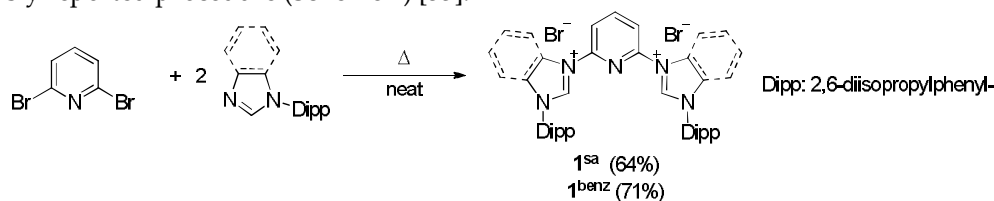
42 We showed recently, that a strong ligand field as exerted by carbene ligands with strong σ -donor
43 and strong π -acceptor properties stabilizes multiple bonded late transition metal complexes [19-21].
44 We therefore became interested in the synthesis of complexes with π -acidic CNC pincer type ligands
45 derived from the saNHC or benzNHC scaffold bridged by a pyridine moiety [22-24]. In contrast to

46 the ubiquitous conventional imidazoline derived NHCs, examples for the saturated imidazolidine
 47 derivatives are still comparably scarce in the literature [25-27]. This applies even more to CNC pincer
 48 type ligands with saNHC or benzNHC congeners [28-33]. In fact, only one example has been reported
 49 for the saNHC derivative, which is Chirik's iron complex [34, 35]. This iron complex was synthesized
 50 via in-situ deprotonation/metalation using iron hexamethyldisilazane ($\text{Fe}[\text{N}(\text{SiMe}_3)_2]_2$) as precursor.
 51 Note that this precursor is inconvenient to handle. Besides its high air sensitivity, it has to be distilled
 52 prior to use [36, 37]. Accordingly, we decided to investigate more expedient and general routes to
 53 access metal complexes.

54 NHC complexes of the s-block metals are still rarely explored [38]. This is also true for
 55 magnesium, although the first example of an NHC magnesium complex dates back to 1993 [39].
 56 Subsequent investigations with s-block metals focused largely on anionic ligands due to the weak
 57 magnesium–NHC bond [40]. For magnesium NHC complexes, examples for saturated and
 58 benzannulated NHCs remain extraordinarily scarce [41]. We hypothesized that transmetalation from
 59 magnesium NHCs should be an exceptional mild method to synthesize NHC complexes. In
 60 particular, we were hoping for a suppression of carbene-dimerization processes as well as a beneficial
 61 template effect by the magnesium metal. Accordingly, we were intrigued by the low cost as well as
 62 ease of handling of the related magnesium compounds. Inspiration came especially from two reports
 63 in the literature, in which the transmetalation of an anionic NHC ligand to iron [40e] and of an acyclic
 64 diaminocarbene ligand to copper [42] was reported. In sight of the recent report of heavy alkaline
 65 earth NHC complexes embedded in a tridentate coordination environment [43], we decided to
 66 explore the transmetalation from magnesium NHCs in more detail. Herein, we report a convenient
 67 method for the synthesis of late transition metal complexes with tridentate ligands with π -acidic
 68 NHCs based on transmetalation from the magnesium complexes. Notably, other routes commonly
 69 applied [44] failed entirely in our hands or gave low yields and/or impure products. Our results hence
 70 suggest transmetalation from magnesium NHCs as a general and convenient method to access π -
 71 acidic and chelating NHC complexes with high yields.
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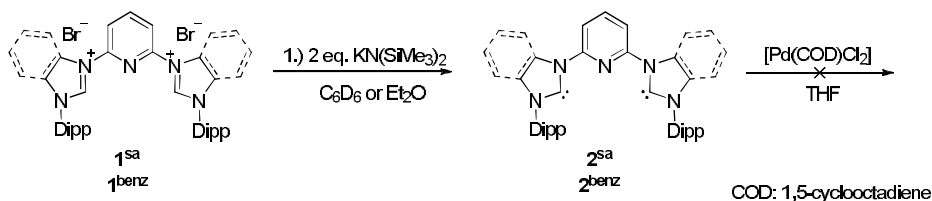
73 2. Results and Discussion

74 Following our computational predictions [19, 20], we decided to synthesize 2,6-pyridine diNHC
 75 (CNC) complexes with bulky 2,6-diisopropylphenyl substituents. As NHCs with moderate to fairly
 76 strong π -accepting properties, we chose the saNHC ($\mathbf{1}^{\text{sa}}$) and the benzNHC ($\mathbf{1}^{\text{benz}}$) scaffolds. Both
 77 ligand precursors were conveniently synthesized by reaction of 2,6-bromopyridine with 1-(2,6-
 78 diisopropylphenyl)-2-imidazoline (benzimidazole, respectively) following a modification of the
 79 previously reported procedure (Scheme 1) [35].



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Scheme 1. Synthesis of ligand precursor.

83 Deprotonation of the carbene precursors with $\text{KN}(\text{SiMe}_3)_2$ led to the clean formation of the free
 84 carbenes as evidenced by ^1H NMR spectroscopic analysis (SI). The carbenes were stable over the
 85 course of days in tetrahydrofuran (THF) or benzene solutions. Unfortunately, we repeatedly obtained
 86 a mixture of compounds when treating solutions of the free carbene $\mathbf{1}^{\text{sa}}$ with metal precursors such
 87 as dichloro(1,5-cyclooctadiene)palladium(II) [$\text{Pd}(\text{COD})\text{Cl}_2$] (Scheme 2; cf. vide infra, Table 1). In fact,
 88 reaction control by ^1H NMR suggested a crude yield of only 18% of the desired, chelated palladium
 89 complex for the reaction in THF. When running the reaction in benzene, we observed the formation
 90 of the palladium complex in 40% yield.



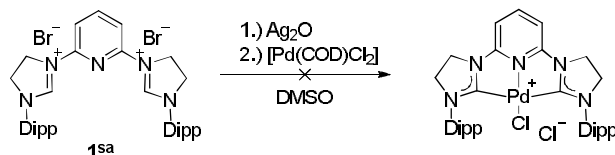
Scheme 2. The free carbenes do not give a clean reaction with a common palladium precursor such as [Pd(COD)Cl₂].

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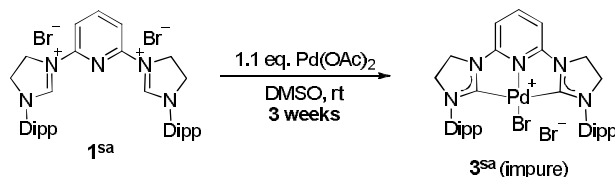
Upon treatment of **1^{sa}** with LiN(SiMe₃)₂, we observed the quantitative formation of HN(SiMe₃)₂ with concomitant precipitation of an orange compound, which we believe to be the lithium complex. However, treatment of this compound with [Pd(COD)Cl₂] did not result in the clean conversion to the chelated palladium complex (selectivity for desired palladium complex in THF or benzene: ≈ 60%). Treating the free carbene **2^{benz}** in THF with [Pd(COD)Cl₂] afforded equally a mixture of compounds (≈ 40% crude selectivity according to ¹H NMR) with the concomitant strong formation of palladium black.

We subsequently evaluated two other commonly applied synthetic routes to generate NHC complexes. These rely either on the transmetalation from coinage metal complexes generated upon addition of a coinage metal(I) oxide to the conjugated acid of the carbene, or in situ metalation by Pd(OAc)₂ in DMSO. Whereas the latter method worked well with **2^{benz}** (SI), we did not obtain satisfactory results for **2^{sa}**. Notably, the attempted metalation of **1^{sa}** using Ag₂O followed by addition of [Pd(COD)Cl₂] consistently gave an impure product mixture due to supposedly hydrolysis of the saNHC scaffold (Scheme 3, I.). Whereas the isolation of the (moderately light-sensitive) silver complex might have remedied this issue, we nevertheless conclude that this route is neither convenient, nor time- or cost efficient.

I. Transmetalation from Silver Carbene Complex



II. In-situ metalation by Pd(OAc)₂

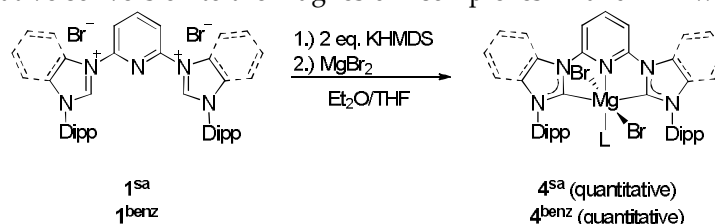


Scheme 3. Both the “silver oxide” transmetalation route as well as metalation in DMSO by palladium acetate are not suitable for the synthesis of complexes with an imidazolidine based ligand.

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The reaction with Pd(OAc)₂ in DMSO evolved to be very unpractical for **3^{sa}**. At room temperature, the reaction proceeded extremely slowly (three weeks) and still gave few palladium black byproduct, which necessitated the addition of an excess of palladium acetate precursor (Scheme 3, II.). Furthermore, the purification of the product proved challenging due to the charged character of the product and supposedly as well the unidentified byproducts. Upon elevating the temperature to 40 °C, we however observed not only a faster reaction, but also strongly reduced product selectivity and instead the strong formation of palladium black. The quantitative removal of DMSO evolved to be challenging as well and could neither be quantitatively accomplished through washing with diethyl ether or heating overnight to 190 °C.

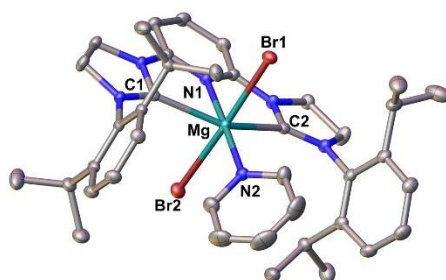
125 We consequently evaluated the generation of the magnesium NHC complexes for subsequent
 126 transmetalation. Indeed, upon addition of magnesium bromide to the in situ generated **1^{sa}** and **1^{benz}**,
 127 the clean and quantitative conversion to the magnesium complexes **4^{sa}** and **4^{benz}** was evidenced.



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 129 **Scheme 4.** Convenient synthesis of magnesium complexes through complexation of MgBr_2 .
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131 These complexes could be isolated in quantitative yields and coordinated either THF or pyridine
 132 upon dissolution in the latter. The magnesium complexes **2^{sa}** and **2^{benz}** could be also obtained
 133 straightforwardly by treatment of the salt precursors with $\text{Mg}[\text{N}(\text{SiMe}_3)_2]$ in benzene. In this case, no
 134 further coordinated solvent molecules seemed to be present as judged from the ^1H NMR
 135 spectroscopic analysis in pyridine- D_5 .

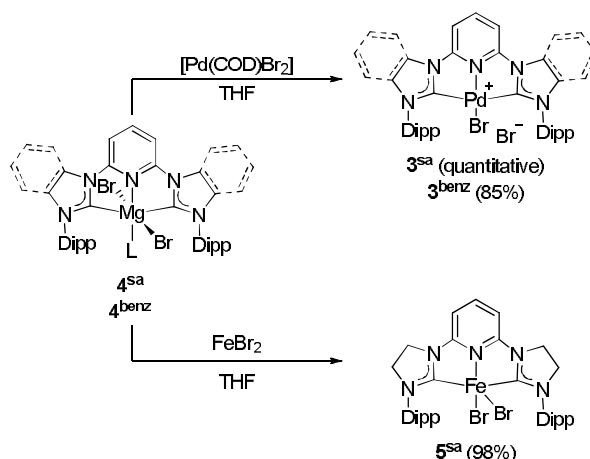
136 Single crystals suitable for the determination of the solid state structure could be obtained for **4^{sa}**
 137 through vapor diffusion of pentane into a saturated solution in pyridine (Fig. 1).



138 **Figure 1.** Solid-state structures of **4^{sa}**. Ellipsoids are shown at the 50% probability level; solvent molecules and
 139 hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: N1–Mg 2.162(2), C1–Mg
 140 2.311(2), C2–Mg 2.301(2), Br1–Mg 2.6502(6), Br2–Mg 2.7074(6), N2–Mg 2.171(2); C1–Mg–N 89.27(1), N1–Mg–Br1
 141 73.14(7).
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143 Complex **4^{sa}** crystallized with a distorted pseudo-octahedral coordination geometry with the two
 144 bromido ligands in the apical positions and a coordinate pyridine molecule in the equatorial position.
 145 The magnesium–carbene bonds are unusually long (C1–Mg 2.311(2) Å, C2–Mg 2.301(2) Å) and exceed
 146 all previously reported magnesium carbene complexes in length [40b,k,q]. Contrarily, the bond
 147 length between the central pyridine moiety and the metal (N1–Mg 2.162(2) Å) is in the common range
 148 for pyridine coordinate magnesium complexes as was also found for the coordinate pyridine
 149 molecule (N2–Mg 2.171(2) Å).

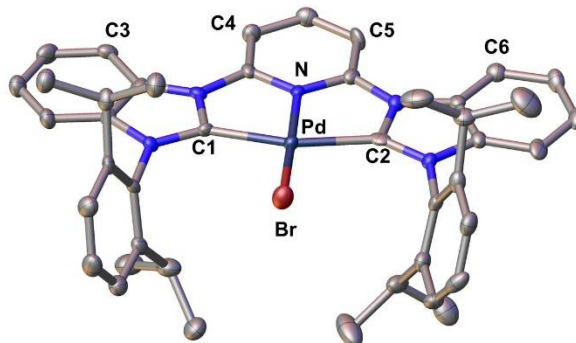
150 To our delight, **4^{sa}** and **4^{benz}** evolved to be excellent transmetalating reagents. Treatment of a
 151 solution of **4^{sa}** and **4^{benz}** in THF with either $[\text{Pd}(\text{COD})\text{Br}_2]$ or FeBr_2 led to the rapid formation of
 152 suspensions due to the formation of the desired transition metal complexes. Preliminary
 153 investigations with nickel(II) bromide, cobalt(II) bromide, bismuth(III) chloride, and lead(II) bromide
 154 indicate that the transmetalation is also feasible with these metal precursors.



Scheme 5. High-yielding and expedient formation of palladium and iron complexes through transmetalation from magnesium complex.

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The products 3^{sa} , 3^{benz} and 5^{sa} could be obtained analytically pure after extraction with dichloromethane and subsequent precipitation using diethyl ether (3^{sa} , 3^{benz}) or washing with diethyl ether (5^{sa}) in quantitative (3^{sa}), 85% (3^{benz}) and 98% (5^{sa}) yield. Surprisingly, 3^{benz} hydrolyzed slowly in wet solvents, whereas 3^{sa} was perfectly stable also in the presence of a large excess of water. The identity of the palladium complex 3^{benz} was therefore confirmed by a solid state structure. The structural parameters of the complex are well in line with previous reports on related conventional NHC complexes [24]. All three aromatic rings of the pyridine and benzannulated are positioned in one plane with a distance between C3 and C4 (C5, C6, respectively) of 3.352 Å (3.329 Å, respectively). Thus, steric stress of the hydrogen atoms bound to C3, C4, C5, and C6 might be responsible for the sensitivity of 3^{benz} to water, which was not found for 3^{sa} .



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Figure 2. Solid-state structures of 3^{benz} . Ellipsoids are shown at the 50% probability level; the non-coordinated bromide anion and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–Pd 2.012(7), C2–Pd 2.027(7), N(pyridine)–Pd 1.977(6), Br–Pd 2.393(1), C3–C4 3.352, C5–C6 3.329; C1–Pd–N(pyridine) 79.5(3).

175 3. Materials and Methods

176 3.1. General Information

177 All air sensitive compounds were synthesized using Schlenk techniques or a dinitrogen filled
178 glovebox. ^1H and ^{13}C NMR spectra were recorded on a JEOL ECX 270, JEOL ECX 400, Bruker Avance
179 III HD 600 MHz or a Bruker AVANCE DRX400 WB instrument operating at 269.71, 399.79 and 600.13
180 MHz for ^1H and at 67.82 MHz, 100.62 MHz and 150.90 MHz for ^{13}C , respectively and at a probe
181 temperature of 23 °C. The solvent residual signals were used as internal reference for the ^1H NMR
182 and ^{13}C NMR spectra. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t =
183 triplet, q = quartet, spt = septet, m = multiplet. All coupling constants J are given in Hertz. Solvents
184 were purified using a two-column solid-state purification system (Glass Contour System, Irvine, CA).
185 Pentane, hexanes, benzene, and toluene were stored over a mirror of potassium, all other solvents
186 were stored over activated molecular sieves. NMR solvents were obtained dry and packaged under
187 argon and stored over activated molecular sieves or a mirror of potassium (C_6D_6). Electrospray-
188 ionization MS (ESI-MS) measurements were performed on a UHR-TOF Bruker Daltonik (Bremen,
189 Germany) maXis plus, equipped with an ESI-quadrupole time-of-flight (qToF) mass spectrometer
190 capable of resolution of at least 60.000 FWHM. Detection was in positive ion mode, the source voltage
191 was 3.2 kV. The flow rates were 180 $\mu\text{L}/\text{hour}$. The drying gas (N_2), to aid solvent removal, was held
192 at 180 °C and the spray gas was held at 20 °C. The machine was calibrated prior to every experiment
193 via direct infusion of the Agilent ESI-TOF low concentration tuning mixture, which provided an m/z
194 range of singly charged peaks up to 2700 Da in both ion modes. Melting points were determined
195 using a Bibby Scientific SMP10 melting point apparatus. 1-(2,6-diisopropylphenyl)benzimidazole, 1-
196 (2,6-diisopropylphenyl)imidazoline, dibromo(1,5-cyclooctadiene)palladium(II), dichloro(1,5-
197 cyclooctadiene)palladium(II), MgBr_2 , and magnesium bis(trimethylsilyl)amide were synthesized
198 according to literature procedures [35, 45-50]. All other reagents were obtained from commercial
199 sources and used as is without further purification.

200 3.2. Synthesis and Characterization of Imidazolinium Salt 1^{sa}

201 This compound was synthesized according to a modified literature procedure [35]. An ACE pressure
202 tube was loaded with 2,6-dibromopyridine (581 mg, 2.45 mmol, 1.0 eq.) and 1-(2,6-
203 diisopropylphenyl)imidazoline (1.30 g, 5.64 mmol, 2.3 eq.). The mixture was heated to 150 °C for 2
204 days. The dark crude product was finely dispersed in ethyl acetate. The suspension was refluxed for
205 1 h. It was cooled to room temperature and filtered. The tan product was further purified by
206 dissolving it in dichloromethane followed by precipitation with ethyl acetate. Colorless needles were
207 washed with ethyl acetate, diethyl ether and dried in vacuo to give 1^{sa} in 64% yield (1.10 g). The
208 analytical data correspond to the literature [35].

209 3.3. Synthesis and Characterization of Benzimidazolium Salt 1^{benz}

210 An ACE pressure tube was loaded with 2,6-dibromopyridine (969 mg, 4.09 mmol, 1.0 eq.) and 1-(2,6-
211 diisopropylphenyl)benzimidazole (2.30 g, 8.25 mmol, 2.0 eq.). The mixture was heated to 220 °C for
212 3 days. The product was purified by fractionate precipitation: It was dissolved in CH_2Cl_2 and Et_2O
213 was added dropwise, until a brown precipitate formed. The mother liquor was decanted. Further

214 addition of more Et₂O induced then the precipitation of the product. Drying in vacuo afforded **1^{benz}**
215 as a colorless solid in 71% yield (2.30 g).

216 ¹H NMR (270 MHz, DMSO-D₆) δ = 11.21 (s, 2 H, Benzimidazolium-H), 8.84 (t, J = 8.0 Hz, 1H, ArCH),
217 8.74 (d, J = 8.0 Hz, 2H, ArCH), 8.59 (d, J = 8.0 Hz, 2H, ArCH), 7.95 - 7.75 (m, 6H, ArCH), 7.68 - 7.59
218 (m, 6H, ArCH), 2.41 (spt, J = 6.8 Hz, 4H, CH(CH₃)₂), 1.21 (d, J = 6.8 Hz, 12H, CH₃), 1.06 (d, J = 6.5 Hz,
219 12H, CH₃) ppm. ¹³C NMR (68 MHz, DMSO-D₆) δ = 146.1 (ArC), 145.9 (ArC), 144.6 (ArC), 143.4 (ArCH/
220 Benzimidazolium CH), 133.1 (ArCH/ Benzimidazolium CH), 132.4 (ArCH), 129.3 (ArC), 128.8
221 (ArCH), 128.7 (ArCH), 127.1 (ArC), 125.2 (ArCH), 119.0 (ArCH), 116.3 (ArCH), 113.7 (ArCH), 28.0
222 (CH(CH₃)₂/CH(CH₃)₂), 24.2 (CH(CH₃)₂/CH(CH₃)₂), 23.8 (CH(CH₃)₂/CH(CH₃)₂) ppm. UHR ESI-MS:
223 m/z calculated for ([C₄₃H₄₆N₅⁺]) 632.3748, found 632.3743. Melting point: 211-213 °C.

224 3.4. Synthesis and Characterization of Free Carbene **2^{sa}**

225 A solution of KN(SiMe₃)₂ (117 mg, 0.585 mmol, 2.0 eq.) in toluene was added dropwise to a
226 suspension of **1^{sa}** (204 mg, 0.292 mmol, 1.0 eq.) in toluene at -40 °C. The suspension was allowed to
227 warm to room temperature, filtered and the volatiles were removed in vacuo. The colorless product
228 was obtained in quantitative yield (154 mg). In case of the presence of adventitious water, the product
229 can be purified by washing with hexanes.

230 ¹H NMR (400 MHz, C₆D₆) δ = 8.10 (d, J = 8.0 Hz, 2H, ArCH), 7.27 - 7.13 (m, 7H, ArCH, superimposed
231 by solvent), 3.97 - 3.91 (m, 4H, CH₂), 3.51 - 3.44 (m, 4H, CH₂), 3.17 (spt, J = 6.9 Hz, 4H, CH(CH₃)₂), 1.28
232 (d, J = 6.9 Hz, 12H, CH₃), 1.21 (d, J = 7.1 Hz, 12H, CH₃) ppm. ¹³C NMR (101 MHz, C₆D₆) δ = 243.8
233 (C carbene), 156.2 (ArC), 147.2 (ArC), 139.5 (ArC), 139.2 (ArCH), 129.0 (ArCH), 124.5 (ArCH), 106.2
234 (ArCH), 54.5 (CH₂), 46.5 (CH₂), 29.2 (CH(CH₃)₂/CH(CH₃)₂), 25.5 (CH(CH₃)₂/CH(CH₃)₂), 24.2
235 (CH(CH₃)₂/CH(CH₃)₂) ppm.

236 3.5. Synthesis and Characterization of Free Carbene **2^{benz}**

237 A solution of KN(SiMe₃)₂ (56 mg, 0.28 mmol, 2.0 eq.) in benzene was added dropwise to a suspension
238 of **1^{benz}** (112 mg, 0.14 mmol, 1.0 eq.) in benzene. The suspension was stirred for 10 min, filtered and
239 the volatiles were removed in vacuo to afford **2^{benz}** as a colorless solid in quantitative yield (89 mg).

240 In case of the presence of adventitious water, the product can be purified by washing with hexanes.
241 ¹H NMR (270 MHz, C₆D₆) δ = 8.78 - 8.66 (m, 2 H, ArCH), 8.45 (d, J = 7.9 Hz, 2H, ArCH), 7.31 - 7.21
242 (m, 3H, ArCH), 7.13 (s, 2H, ArCH), 7.05 (s, 2H, ArCH), 6.89 - 6.79 (m, 4H, ArCH), 6.64 (m, 2H, ArCH),
243 2.63 (spt, J = 6.9 Hz, 4H, CH(CH₃)₂), 1.11 (d, J = 6.9 Hz, 12H, CH₃), 0.84 (d, J = 6.9 Hz, 12 H CH₃) ppm.
244 ¹³C NMR (68 MHz, C₆D₆) δ = 231.8 (C carbene), 154.8 (ArC), 147.5 (ArC), 140.7 (ArCH), 139.0 (ArC),
245 135.9 (ArC), 133.6 (ArC), 130.1 (ArCH), 124.6 (ArCH), 124.1 (ArCH), 123.8 (ArCH), 123.8 (ArCH),
246 116.8 (ArCH), 111.4 (ArCH), 29.2 (CH(CH₃)₂/CH(CH₃)₂), 25.2 (CH(CH₃)₂/CH(CH₃)₂), 23.9
247 (CH(CH₃)₂/CH(CH₃)₂) ppm.

248 3.6. Synthesis and Characterization of Palladium Complex **3^{sa}**

249 **Method A:** The bisimidazolium salt **1^{sa}** (551 mg, 0.79 mmol, 1.0 eq.) and Pd(OAc)₂ (195 mg,
250 0.87 mmol, 1.1 eq.) were dissolved in DMSO. The dark red solution was stirred for three weeks at
251 room temperature. The solvent was removed under reduced pressure at elevated temperatures
252 (100 °C). The solid was dissolved in CH₂Cl₂ and filtered over diatomaceous earth. The complex was

253 precipitated by addition of Et₂O. The yellow solid was dried in vacuo overnight at 190 °C (585 mg,
254 92%, impure, considerable amount of undefined side products were identified in ¹H NMR spectrum).
255 **Method B:** The bisimidazolium salt **1^{sa}** (70 mg, 0.10 mmol, 1.0 eq.) was suspended in toluene. A
256 solution of KN(SiMe₃)₂ (40 mg, 0.20 mmol, 2.0 eq.) in toluene was added dropwise at -40 °C. The
257 suspension was allowed to warm to room temperature, filtered and the volatiles were removed in
258 vacuo. THF was added and the solution was added to a solution of MgBr₂ (18 mg, 0.10 mmol, 1.0 eq.)
259 in THF. The mixture was stirred for 10 minutes. [Pd(COD)Br₂] (37 mg, 0.10 mmol, 1.0 eq.) was added
260 and the suspension was stirred for another 16 h. The solvent was removed in vacuo and washed with
261 benzene. The product was extracted with CH₂Cl₂ and precipitated by addition of Et₂O. The yellow
262 solid was dried in vacuo to give **3^{sa}** in quantitative yield (80 mg).
263 ¹H NMR (600 MHz, DMSO-D₆) δ = 8.26 (t, *J* = 8.0 Hz, 1H, ArCH), 7.31 - 7.24 (m, 2H, ArCH), 7.12 (d,
264 *J* = 7.5 Hz, 4H, ArCH), 7.05 (d, *J* = 8.1 Hz, 2H, ArCH), 4.40 - 4.29 (m, 4H, CH₂), 4.23 - 4.23 (m, 4H, CH₂),
265 2.85 (spt, *J* = 6.4 Hz, 4H, CH(CH₃)₂), 1.15 (d, *J* = 6.1 Hz, 24H, CH₃) ppm. ¹³C NMR (151 MHz, DMSO-
266 D₆) δ = 190.8 (C carbene), 152.3 (ArC), 144.9 (ArCH), 144.3 (ArC), 133.8 (ArC), 129.4 (ArCH), 123.9
267 (ArCH), 102.6 (ArCH), 57.3 (CH₂), 43.4 (CH₂), 27.7 (CH(CH₃)₂/CH(CH₃)₂), 24.6 (CH(CH₃)₂/CH(CH₃)₂),
268 23.7 (CH(CH₃)₂/CH(CH₃)₂) ppm. UHR ESI-MS: *m/z* calculated for ([C₃₅H₄₅N₅PdBr⁺]) 722.1888, found
269 722.1859. Melting point: > 290 °C

270 3.7. Synthesis and Characterization of Palladium Complex **3^{benz}**

271 **Method A.** **1^{benz}** (544 mg, 0.69 mmol, 1.0 eq.) and Pd(OAc)₂ (154 mg, 0.69 mmol, 1.0 eq.) were dissolved
272 in DMSO and stirred for 24 h at room temperature, during which a yellow precipitate formed. The
273 suspension was heated to 40 °C for additional 24 h. The solvent was removed under reduced pressure
274 at elevated temperatures (100 °C). The residue was dissolved in CH₂Cl₂ and filtered over
275 diatomaceous earth. The yellow product was precipitated by addition of Et₂O and dried in vacuo to
276 give **3^{benz}** in 58% yield (362 mg).

277 **Method B.** **1^{benz}** (51 mg, 0.064 mmol, 1.0 eq.) was suspended in benzene. A solution of KN(SiMe₃)₂
278 (25 mg, 0.13 mmol, 2.0 eq.) in benzene was added dropwise. The suspension was stirred for 10
279 minutes, filtered and the volatiles were removed in vacuo. The residue was dissolved in THF and the
280 solution was added to a solution of MgBr₂ (12 mg, 0.065 mmol, 1.0 eq.) in THF. The mixture was
281 stirred for 10 minutes. [Pd(COD)Br₂] (24 mg, 0.064 mmol, 1.0 eq) was added. The suspension was
282 stirred for 16 h. It was evaporated to dryness and washed with benzene. The residue was extracted
283 with CH₂Cl₂ and the product was precipitated by Et₂O. The yellow solid was dried in vacuo to give
284 **3^{benz}** in 85% yield (49 mg).

285 ¹H NMR (270 MHz, DMSO-D₆) δ = 8.79 - 8.63 (m, 5H, ArCH), 7.78 (t, *J* = 7.6 Hz, 2H, ArCH), 7.65 - 7.48
286 (m, 4H, ArCH), 7.33 (d, *J* = 7.7 Hz, 4H, ArCH), 7.14 (d, *J* = 8.0 Hz, 2H, ArCH), 2.30 (spt, *J* = 6.8 Hz, 4H,
287 CH(CH₃)₂), 1.11 (d, *J* = 6.8 Hz, 12H, CH₃), 0.88 (d, *J* = 6.8 Hz, 12H, CH₃) ppm. ¹³C NMR (68 MHz,
288 DMSO-D₆) δ = 178.2 (C carbene), 151.0 (ArC), 146.4 (ArCH), 144.9 (ArC), 135.4 (ArC), 130.8 (ArCH),
289 130.4 (ArC), 129.5 (ArC), 127.2 (ArCH), 126.8 (ArCH), 124.2 (ArCH), 113.8 (ArCH), 113.2 (ArCH),
290 110.8 (ArCH), 28.0 (CH(CH₃)₂/CH(CH₃)₂), 24.2 (CH(CH₃)₂/CH(CH₃)₂), 23.1 (CH(CH₃)₂/CH(CH₃)₂)
291 ppm. UHR ESI-MS: *m/z* calculated for ([C₄₃H₄₅N₅PdBr⁺]) 818.1890, found 818.1858. Melting point:
292 >290 °C

293

294 3.8. Synthesis and Characterization of Magnesium Complex **4^{sa}**

295 **Method A:** The bisimidazolium salt **1^{sa}** (192 mg, 0.28 mmol, 1.0 eq.) was suspended in benzene. A
296 solution of magnesium bis(trimethylsilyl)amide (95 mg, 0.28 mmol, 1.0 eq.) in benzene was added
297 dropwise. The mixture was stirred for 16 hours. The precipitate was collected, washed with pentane
298 and dried in vacuo to give a colorless solid in 62% yield (122 mg). Further 38% (79 mg) were obtained
299 by precipitation from the mother liquor with pentane.

300 **Method B:** The bisimidazolium salt **1^{sa}** (93 mg, 0.13 mmol, 1.0 eq.) was suspended in toluene. A
301 solution of KN(SiMe₃)₂ (53 mg, 0.26 mmol, 2.0 eq.) in toluene was added dropwise at -40 °C. The
302 mixture was stirred allowed to warm to room temperature and filtered. The volatiles were removed
303 in vacuo and THF was added. The solution was added to a solution of MgBr₂ (25 mg, 0.13 mmol, 1.0
304 eq.) in THF and stirred for 1 h. The solvent was evaporated. The colorless solid was dried in vacuo
305 and obtained in quantitative yield (95 mg).

306 ¹H NMR (400 MHz, Pyridine-D₅) δ = 7.71 (t, *J* = 8.1 Hz, 1H, ArCH), 7.37 - 7.26 (m, 2H, ArCH), 7.17 -
307 7.06 (m, 6H, superimposed by solvent, ArCH), 6.49 (d, *J* = 8.2 Hz, 2H, ArCH), 4.13 - 4.04 (m, 4H, CH₂),
308 3.96 - 3.91 (m, 4H, CH₂), 3.68 (spt, *J* = 6.3 Hz, 4H, CH(CH₃)₂), 1.24 (d, *J* = 6.3 Hz, 12H, CH₃), 1.05 (d, *J* =
309 6.9 Hz, 12H, CH₃) ppm. ¹³C NMR (101 MHz, Pyridine-D₅) δ = 221.3 (C carbene), 151.5 (ArC), 147.9
310 (ArCH), 142.8 (ArCH), 137.3 (ArC), 130.0 (ArC), 129.2 (ArCH), 125.1 (ArCH), 103.8 (ArCH), 57.1
311 (CH₂), 45.6 (CH₂), 28.4 (CH(CH₃)₂/CH(CH₃)₂), 26.9 (CH(CH₃)₂/CH(CH₃)₂), 25.0 (CH(CH₃)₂/CH(CH₃)₂)
312 ppm. Two signals are superimposed by the solvent signals. UHR ESI-MS: *m/z* calculated for
313 ([C₃₅H₄₆N₅⁺]) 536.3748, found 536.3731. Melting point: 220 °C, decomposition.

314 3.9. Synthesis and Characterization of Magnesium Complex **4^{benz}**

315 **Method A:** The bisbenzimidazolium salt **1^{benz}** (79 mg, 0.10 mmol, 1.0 eq.) was suspended in benzene.
316 A solution of Mg[N(SiMe₃)₂]₂ (35 mg, 0.10 mmol, 1.0 eq.) in benzene was added. The mixture was
317 stirred for 24 hours, the precipitate was collected, washed with pentane, and dried in vacuo to obtain
318 an off-white solid in 76% yield (62 mg). Further 24% (19 mg) were obtained by precipitation from the
319 mother liquor with pentane.

320 **Method B:** The bisbenzimidazolium salt **1^{benz}** (57 mg, 0.07 mmol, 1.0 eq.) was suspended in benzene.
321 A solution of KN(SiMe₃)₂ (36 mg, 0.14 mmol, 2.0 eq.) in benzene was added. The mixture was stirred
322 for 10 min and filtered. The volatiles were removed in vacuo and THF was added. The solution was
323 added to a solution of MgBr₂ (13 mg, 0.07 mmol, 1.0 eq) in THF and stirred for 1 h. The solvent was
324 removed in vacuo, the residue was washed with pentane and dried in vacuo to give the product as
325 an off-white solid in quantitative yield (45 mg).

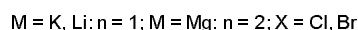
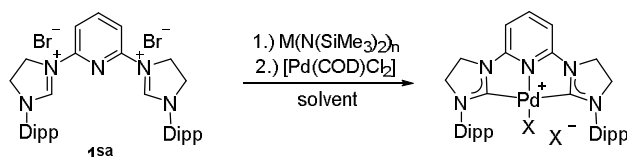
326 Note: The NMR spectra indicated that two species were formed in a ratio of 4:1. The formation of
327 these two species was observed in various solvents (pyridine-D₅, THF-D₈, THF or benzene).
328 Subsequent transmetalation with [Pd(COD)Br₂] however yields only one complex. We hence assign
329 these products to a mixture of two magnesium complexes. ¹H NMR (270 MHz, Pyridine-D₅) δ = 8.91
330 (d, *J* = 7.9 Hz, 2H, ArCH, Species a/b), 8.65 (d, *J* = 8.4 Hz, 2H ArCH, Species a/b), 8.11 - 8.27 (m, 2H,
331 ArCH, Species a/b), 8.01 (t, *J* = 7.9 Hz, 1H, ArCH, Species a/b), 7.61 - 7.73 (m, 2H, ArCH, Species a/b),
332 7.44 - 7.57 (m, 5H, ArCH, Species a/b), 7.25 - 7.42 (m, 6H, ArCH, Species a/b), 7.00 - 7.14 (m, 2H, ArCH,
333 Species a/b), 3.38 (spt, *J* = 6.7 Hz, 1H, CH(CH₃)₂, Species b), 2.75 (spt, *J* = 6.4 Hz, 4H, CH(CH₃)₂, Species
334 a), 1.32 (d, *J* = 6.4 Hz, 4H, CH₃, Species b), 1.23 (d, *J* = 6.9 Hz, 12H, CH₃, Species a), 1.03 (d, *J* = 6.9 Hz,

335 12H, CH₃, Species a), 0.87 (d, , J = 6.4 Hz, 4H, CH₃, Species b) ppm. ¹³C NMR (68 MHz, Pyridine-D₅) δ
 336 = 231.2 (C carbene), 154.7 (ArCH/ArC), 148.2 (ArCH/ArC), 147.5 (ArCH/ArC), 143.6 (ArCH/ArC),
 337 141.3 (ArCH/ArC), 139.1 (ArCH/ArC), 139.0 (ArCH/ArC), 135.7 (ArCH/ArC), 134.2 (ArCH/ArC),
 338 133.6 (ArCH/ArC), 131.6 (ArCH/ArC), 131.1 (ArCH/ArC), 130.5 (ArCH/ArC), 129.2 (ArCH/ArC),
 339 125.5 (ArCH/ArC), 125.2 (ArCH/ArC), 125.0 (ArCH/ArC), 124.5 (ArCH/ArC), 124.1 (ArCH/ArC),
 340 123.1 (ArCH/ArC), 116.6 (ArCH/ArC), 115.0 (ArCH/ArC), 114.9 (ArCH/ArC), 114.3 (ArCH/ArC),
 341 111.9 (ArCH/ArC), 111.6 (ArCH/ArC), 29.2 (CH(CH₃)₂/CH(CH₃)₂), 28.7 (CH(CH₃)₂/CH(CH₃)₂), 26.2
 342 (CH(CH₃)₂/CH(CH₃)₂), 25.1 (CH(CH₃)₂/CH(CH₃)₂), 24.8 (CH(CH₃)₂/CH(CH₃)₂), 24.0
 343 (CH(CH₃)₂/CH(CH₃)₂) ppm. The second carbene signal was not observed due to the low
 344 concentration of the second compound. UHR ESI-MS: m/z calculated for ([C₄₃H₄₆N₅⁺]) 632.3748, found
 345 632.3746. Melting point: >250 °C

346 3.10. Synthesis and Characterization of Iron Complex 5^{sa}

347 The free carbene (91 mg, 0.15 mmol, 1.0 eq., contained 1 eq. benzene) was dissolved in THF. MgBr₂
 348 (27.3 mg, 0.15 mmol, 1.0 eq.) was added. The mixture was stirred for 10 min and FeBr₂ (31.9 mg,
 349 0.15 mmol, 1.0 eq.) was added. The suspension was stirred for 16 h. The suspension was filtered and
 350 washed with copious amounts of Et₂O. The remaining red-purple/pink solid was dried in vacuo
 351 to give 5^{sa} in 98% yield (110 mg). The purity of the product was verified by reduction with Na/Hg as
 352 reported in literature [35].

353 3.11. Effects of Metal Cation on Transmetalation



354

355 **Scheme 6.** Different reaction conditions, which were evaluated in order to determine the impact of metal
 356 cations and solvents on the crude yield of palladium complex 3^{sa}.

357 **General procedure.** Each procedure was performed on a 30 mg scale. A solution of M[N(SiMe₃)₂]_x
 358 (Li, K: 2.0 eq., x = 2; Mg 1.0 eq., x = 1) in benzene/THF was added dropwise to a suspension of the
 359 bisimidazolium salt 1^{sa} (1.0 eq.) in benzene/THF. [Pd(COD)Cl₂] was added after 1 hour,. The
 360 reaction mixture was stirred for 16 hours and the solvent was evaporated. The product selectivity
 361 was determined by ¹H NMR spectroscopy in DMSO-D₆ using pyridine (8 μL) as internal standard.

362

Base	Solvent	Crude Product Selectivity
LiN(SiMe ₃) ₂	thf	≈60%
LiN(SiMe ₃) ₂	benzene	≈60%
KN(SiMe ₃) ₂	thf	≈40%
KN(SiMe ₃) ₂	benzene	≈40%
MgBr ₂ /KN(SiMe ₃) ₂	thf	≈80%
Mg[N(SiMe ₃) ₂] ₂	benzene	≈100%

363

Table 1. Product selectivity using different solvents and transmetalating reagents.

364

365 4. Conclusions

366 We report that transmetalation from magnesium complexes with pincer-type NHC ligands is a
367 convenient method to synthesize the related palladium and iron complexes. Of particular note, the
368 method is also suitable for complexes with imidazolidine (saturated) NHC ligands, which could not
369 be obtained by other routes. Transmetalation from the lithium carbene complex or reaction with the
370 free carbene led in this case only to mixtures which are difficult to purify and low yields.
371 Furthermore, the transmetalation from the magnesium carbene complex evolved to be also superior
372 to other commonly applied and well-established routes such as the transmetalation using silver(I)
373 oxide or the in situ metalation with palladium acetate in DMSO. We hence conclude that
374 transmetalation from magnesium NHCs shows promise as a general, convenient, selective and high-
375 yielding synthetic approach towards transition metal complexes with chelating NHC ligands.
376 Further work is directed at exploring magnesium complexes with other π -electron deficient carbenes
377 for transmetalation and exploiting magnesium NHCs as transmetalating reagents for f-block and p-
378 block elements. Preliminary experiments with Co, Ni and p-block metals such as Pb and Bi indicate
379 that this procedure should be indeed a versatile route to oligodentate carbene complexes.

380 **Supplementary Materials:** A Supplementary Information, which includes NMR spectra and crystallographic
381 details, is available at www.mdpi.com/xxx/s1,

382 **Author Contributions:** J.M. and A.G. performed the experiments. P.S. synthesized $\text{Mg}(\text{N}(\text{SiMe}_3)_2)_2$. L.S.
383 measured the UHR ESI-MS data. F.W.H. performed the determination of the solid state structures. D.M.
384 supervised the project and wrote the manuscript.

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