Six- and seven-membered ring carbenes: Rational synthesis of amidinium salts, generation of carbenes, synthesis of Ag(I) and Cu(I) complexes

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ABSTRACT

Reactions of neat 1,3- and 1,4-dibromides with N,N'-diarylformamidines in the presence of diisopropylethylamine (DIPEA) afford corresponding amidinium salts in high yields (>80%). Six- and seven-membered ring amidinium salts bearing bulky Mes (2,4,6-$Me_3C_6H_2$) and Dipp (2,6-$^iPr_2C_6H_3$) aryl groups were prepared using this method. Free six-membered ring carbene **6-Dipp** was generated from amidinium salt using LiHMDS as a base. NHC–Ag(I) complexes were obtained by the reactions of amidinium salts with Ag_2O. NHC complexes of Pd and Rh are not accessible by deprotonation of amidinium salts, nor by transmetallation of Ag(I) complexes. However NHC–Cu(I) complexes were obtained by transmetallation of NHC–Ag(I). Thus, transmetallation of six- and seven-membered NHC–Ag(I) complexes was documented for the first time.

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1. Introduction

N-heterocyclic carbenes (NHC) [1] were first proposed by Breslow as intermediates in B1 catalytic cycle as early as in 1957 [2]. A decade later Wanzlick and Schonherr [3] and Öfele [4] prepared complexes of imidazole-2-ylidene with transition metals. Later, Lappert and coworkers obtained a series of carbene–metal complexes starting from electron rich olefins (EROs) [5].

Nevertheless, intensive development of NHC chemistry started in 1991 with Arduengo's isolation of free imidazole-2-ylidene **1** [6]. In 1995 Arduengo obtained imidazoline-2-ylidene **2**, thus showing that the presence of imidazole aromatic system is not obligatory for stabilization of a free carbene [7].

Initially it was supposed that NHCs as ligands are phosphane mimics [8]. Although a wealth of experimental data show that NHCs surpass their phosphane counterparts in donor properties, bonding energies and steric properties [9], many metal NHC complexes have been show to be tolerant to air and moisture. Their synthetic accessibility [10] and ease of functionalization [11] opened wide possibilities in utilization of such complexes in catalysis [12].
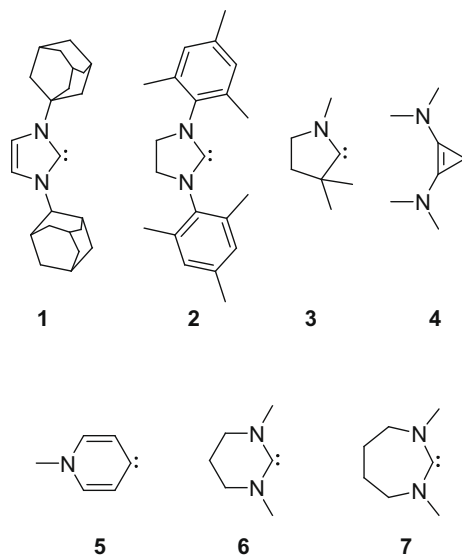
Most of NHC–metal complexes known to date are derived from imidazolylidene **1** and imidazolinyliden **2** type carbenes. There are two main strategies of enhancing NHC's donor properties: (i) decrease of number of nitrogen atoms attached to ylidene center,

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3 [13,14], **4** [15], **5** [16] and (ii) expansion of heterocycle to six- and seven-membered rings, **6** [17–23] and **7** [14,24,25].

In this contribution we report on the rational approach to the synthesis of six- and seven-membered ring amidinium salts, generation of free carbenes, synthesis of carbene complexes with silver(I), and synthesis of (NHC)CuX complexes via transmetallation of silver(I) complexes. During the preparation of this manuscript a paper by Cavell et al. has appeared which has many intersections (synthesis and X-ray of amidinium salts, free NHCs and Ag(I) complexes) with this contribution [23].

2. Results and discussion
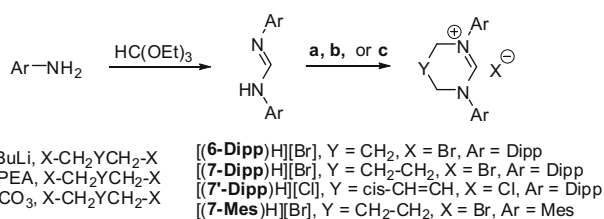
2.1. Amidinium salts

There are two main approaches for synthesis of cyclic amidinium salts bearing aryl substituents at nitrogen atoms known to date. First approach is cyclization of arylated diamines (Scheme 1, **a** [19], **b** [26], **c** [20,27]). Such diamines are not readily available. Moreover, cyclization reactions require harsh conditions and have low reproducibility.

An alternative approach, proposed recently by Bertrand, is deprotonation of amidine with BuLi and further cyclization with 1,3- or 1,4-dihalide (Scheme 2, **a**) [14]. Formamidines bearing bulky aryl substituents are easily prepared from triethyl orthoformate and anilines. This method has been modified by Grubbs [28]. Five-membered imidazolinium salts were obtained by alkylation of formamidines with dichloroethane in the presence of sterically hindered diisopropylethylamine (DIPEA; Scheme 2, **b**). Cavell obtained a row of five, six and seven-membered ring amidinium salts by alkylation of formamidines by dibromides and diiodides in the presence of K_2CO_3 in refluxing acetonitrile (Scheme 2, **c**) [23].

We obtained four amidinium salts in moderate yields (Scheme 2a, Table 1) using Bertrand's method. The same salts but [(**7'-Dipp**)H][Cl] were prepared using modified Grubbs' method (Scheme 2, **b**). DIPEA (1.1 equiv.) was added to a stirred mixture of formamidine (1 equiv.) and dibromide (3 equiv.) with no solvent. The products are white crystalline substances stable in air and moisture. All salts were characterized by ^1H, ^{13}C NMR, and elemental analysis. This method provides the highest yields of six- and seven-membered ring N,N'-diarylated amidinium salts (Table 1). Moreover, excess of dibromide and expensive DIPEA may be
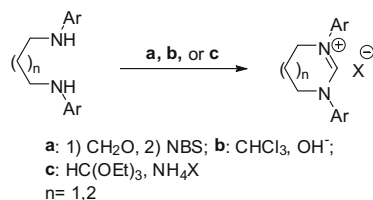
Table 1
The yields (%) of cyclic amidinium salts obtained by different methods (Scheme 2).

Method	[(**6-Dipp**)H][Br]	[(**7-Dipp**)H][Br]	[(**7'-Dipp**)H][Cl]	[(**7-Mes**)H][Br]
a	64	52	46	49
b	88	82	–	92
c[a]	71	64	–	89

[a] Ref. [23].

readily recovered. This procedure has been further reproduced on the tens of gram scale.

Single crystals of six- and seven-membered Dipp derivatives were obtained from CH_2Cl_2 or $CHCl_3$. The structures were determined by X-ray (Fig. 1). [(**7'-Dipp**)H][Cl] is the first amidinium salt bearing isolated CH=CH moiety in the back-bone. This feature opens wide possibilities for modification.

2.2. Generation of free carbenes

Free carbene **6-Dipp** was generated on NMR scale by deprotonation of [(**6-Dipp**)H][Br] with LiHMDS in absolute THF-d_8 under argon (Scheme 3). In ^{13}C NMR spectrum characteristic 245.9 ppm signal corresponding to ylidene carbon and no signals at ~160 ppm characteristic to amidinium carbon of the salt were found.

Deprotonation of the salt [(**7-Dipp**)H][Br] does not proceed under the same conditions. According to NMR the solution contains only reactants. Interaction of [(**7-Dipp**)H][Br] with KO^{t}Bu leads to unidentified mixture of products which does not contain free carbene according to ^{13}C NMR (see Scheme 4).

We tried to obtain free carbene **7-Dipp** by vacuum pyrolysis of carbene adduct with methanol [29]. Adduct (**7-Dipp**)(H)(OMe) was obtained by the reaction of equimolar amounts of the salt [(**7-Dipp**)H][Br] and NaOMe in absolute THF. Heating under 0.04 Torr
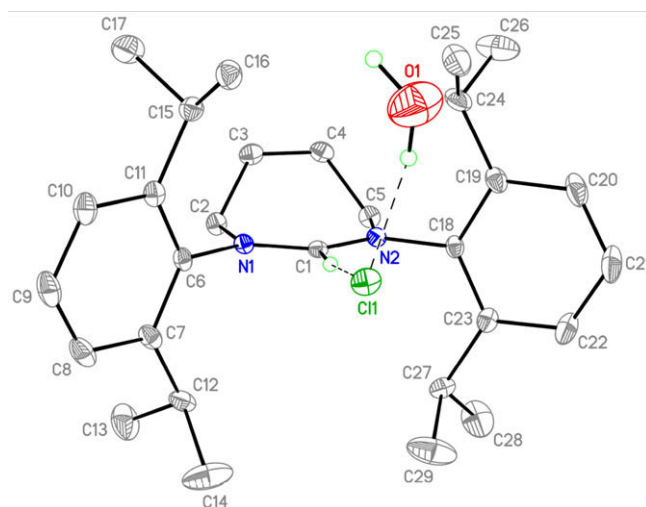
Fig. 1. X-ray crystal structure of [(**7'-Dipp**)H][Cl] · 0.5H$_2$O (thermal ellipsoids are drawn at the 50% level).

a: 1) CH$_2$O, 2) NBS; **b**: CHCl$_3$, OH$^-$;
c: HC(OEt)$_3$, NH$_4$X
n= 1,2

Scheme 1.

a: n-BuLi, X-CH$_2$YCH$_2$-X
b: DIPEA, X-CH$_2$YCH$_2$-X
c: K$_2$CO$_3$, X-CH$_2$YCH$_2$-X

[(**6-Dipp**)H][Br], Y = CH$_2$, X = Br, Ar = Dipp
[(**7-Dipp**)H][Br], Y = CH$_2$-CH$_2$, X = Br, Ar = Dipp
[(**7'-Dipp**)H][Cl], Y = cis-CH=CH, X = Cl, Ar = Dipp
[(**7-Mes**)H][Br], Y = CH$_2$-CH$_2$, X = Br, Ar = Mes

Scheme 2.

[(**6-Dipp**)H][Br]   **6-Dipp**
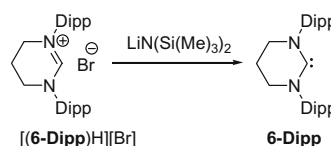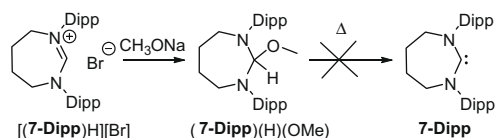
Scheme 3.

Scheme 4.

vacuum has lead only to sublimation of (**7-Dipp**)(H)(OMe) with no decomposition (according to ^{1}H and ^{13}C NMR). The structure of (**7-Dipp**)(H)(OMe) was unambiguously established by single-crystal X-ray (Fig. 2).

2.3. NHC–metal complexes via deprotonation

The ultimate goal of our studies is the synthesis of NHC–metal complexes and testing of their catalytic properties. Unfortunately, we were unable to obtain free carbenes in quantities sufficient for further synthesis. Although, the alternative method – transfer of NHC ligand from Ag(I) complex could be relied upon to produce sufficient quantities [30].

Three NHC–Ag(I) complexes were obtained by the reactions of amidinium salts with silver oxide in dichloromethane at room temperature for 2 days (Scheme 5). These complexes are white crystalline solids stable in air and in the presence of moisture, not sensitive to sun light, melt with decomposition at 280–300 °C, characterized by ^{1}H, ^{13}C NMR, elemental analysis and X-ray (Fig. 3).

Both **6-Dipp** and **7-Dipp** form 1:1 complex with AgBr while **7-Mes** forms ionic 2:1 complex [Ag(**7-Mes**)$_2$][Cl]. It can be supposed that bulkier Dipp groups prevent formation of 2:1 complexes. Interestingly, the counter ion in [Ag(**7-Mes**)$_2$][Cl] is chloride in-

Fig. 3. X-ray crystal structure of [Ag(**7-Mes**)$_2$][Cl] · 2H$_2$O (thermal ellipsoids are drawn at the 50% level).
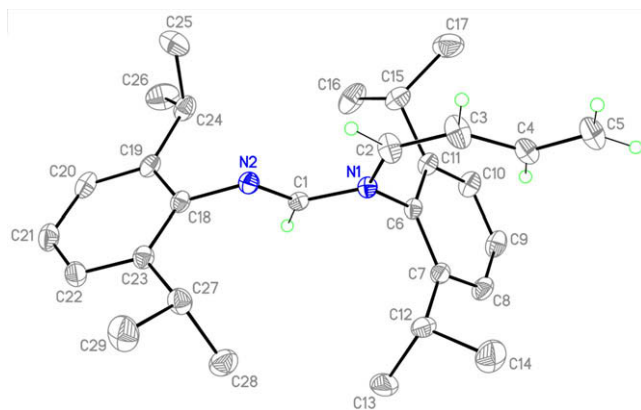
Fig. 4. X-ray crystal structure of **8** (thermal ellipsoids are drawn at the 50% level).

stead of AgBr$_2^-$ [23,30]. We suppose that chloride is abstracted from methylene chloride under exposure to light.

We were unable to obtain Ag(I) complex from [(**7′-Dipp**)H][Cl] using the same method. The only product obtained in 80% yield was **8** (Scheme 7). The structure of **8** was established by ^{1}H, ^{13}C NMR, X-ray and elemental analysis (Fig. 4). We suppose that **8** is formed via Hoffman 1,4-elimination under Ag$_2$O action as a base. It can be also supposed that all attempts by Cavell et al. [23] to obtain free seven-membered ring carbenes bearing xylyl backbone were unsuccessful due to the analogous elimination (see Scheme 6).

Fig. 2. X-ray crystal structure of (**7-Dipp**)(H)(OMe) (thermal ellipsoids are drawn at the 50% level).

Scheme 5.

Scheme 6.

Scheme 7.

We have also tackled the possibility of preparation of Pd and Rh complexes via deprotonation of amidinium salts. [(**6-Dipp**)H][Br] and [(**7-Dipp**)H][Br] were treated with different palladium reagents: (1) Pd(OAc)$_2$ in DMSO at 120 °C [31], (2) Pd(OAc)$_2$ in the presence of NaI and t-BuOK in THF [25,32], and (3) PdCl$_2$ in 3-bromopyridine in the presence of K$_2$CO$_3$ [33]. Dark-red materials which contain amidinium cations (^{1}H NMR) and, probably, complex palladium anions were obtained. Furthermore, starting materials only were recovered after refluxing for 15 h of the mixture of [(**6-Dipp**)H][Br], [RhCl(COD)]$_2$ and t-BuOK in THF [22].

2.4. Transmetallation of NHC–Ag(I) complexes

The possibility of ligand transfer from silver(I) complexes to other metals is still arguable for six- and seven-membered NHCs. Thus, Buchmeiser reported on **6-Mes** transfer from silver(I) to palladium [19]. However, Herrmann et al. [20] has later shown that the formation of [Ag(**6-Mes**)$_2$]$_2$[Pd$_2$Cl$_6$] complex salt takes place. It was also supposed that transmetallation does not take place due to higher energy of NHC–Ag bond for six-membered ring carbenes in respect to five-membered ring counterparts. Moreover, the formation of Ag(I) from Rh(I) and Pd(II) complexes was documented [18,25]. Our attempts to obtain Pd and Rh complexes via transmetallation of (**6-Dipp**)AgBr and (**7-Dipp**)AgBr were also unsuccessful. Prolonged stirring of silver(I) complexes with PdCl$_2$(PPh$_3$)$_2$, PdCl$_2$(COD), Pd(OAc)$_2$ or [RhCl(COD)]$_2$ at elevated temperatures in different solvents lead to isolation of starting materials only.

There are three main routes to NHC–Cu(I) complexes: (1) interaction of a free NHC with copper salt [21], (2) deprotonation of amidinium salt by Cu$_2$O [34], and (3) transmetallation of NHC–Ag(I) complex with copper salt [30].

We attempted to prepare NHC–Cu(I) complexes via deprotonation by Cu$_2$O (route 2). Heating of amidinium salt [(**7-Dipp**)H][Br] with Cu$_2$O in the presence of sodium acetate in DMSO at 100 °C for 12 h [34] has lead to formation of a Cu(I) complex in trace amounts (according to TLC). The attempts to obtain Cu(I) complexes via transmetallation were more successful. Thus, interaction of equimolar amounts of (**6-Dipp**)AgBr or (**7-Dipp**)AgBr with copper(I) bromide in CH$_2$Cl$_2$ have lead to formation of (**6-Dipp**)CuBr and (**7-Dipp**)CuBr, respectively, in high yields (Scheme 7). The products were isolated in pure form by filtration through Celite and further concentration of the filtrate to dryness in vacuo. The complexes obtained, were characterized by ^{1}H, ^{13}C NMR, m.p. and elemental analysis.

^{13}C NMR spectra of (**6-Dipp**)CuBr and (**7-Dipp**)CuBr contain characteristic ylidene carbon signals at 201.1 and 210.5 ppm, respectively. As for NHC–silver(I) complexes [23], a downfield shift of ylidene carbon was observed upon enlargement of carbene heterocycle from six- to seven-membered ring.

Single crystals of copper(I) complexes were obtained from CHCl$_3$, the structures were determined by X-ray (Fig. 5). (**6-Dipp**)-CuBr is the first 1:1 complex of N,N'-diarylated six-membered ring NHC [21] and (**7-Dipp**)CuBr is the first seven-membered ring NHC complex of copper(I). Moreover we have shown the possibility of transmetallation of six- and seven-membered ring NHC–Ag(I) complexes for the first time.

2.5. X-ray

One six- and three seven-membered amidinium salts were characterized by X-ray crystallography. The crystal structures of [(**6-Dipp**)H][Br] · 1.5CHCl$_3$, [(**7-Dipp**)H][Br] · 3CHCl$_3$, [(**7-Dipp**)H]-[Br] · CH$_2$Cl$_2$ and [(**7'-Dipp**)H][Cl] · 0.5H$_2$O are shown in Fig. 1, and S1–S3, and selected geometrical parameters are listed in Table S1. It should be noted that the structures of [(**7-Dipp**)H][Br] · 3CHCl$_3$ and [(**7-Dipp**)H][Br] · CH$_2$Cl$_2$ have an important difference: in the latter, contrary to the former, the proton at the amidinium carbon atom participates in the hydrogen bonding with the bromide anion. Because of that, in the structures [(**6-Dipp**)H][Br] · 1.5CHCl$_3$ and [(**7'-Dipp**)H][Cl] · 0.5H$_2$O, the amidinium proton also

(**6-Dipp**)CuBr•CHCl$_3$ (**7-Dipp**)CuBr•CHCl$_3$

Fig. 5. X-ray crystal structures of (**6-Dipp**)CuBr · CHCl$_3$ and (**7-Dipp**)CuBr · CHCl$_3$ (thermal ellipsoids are drawn at the 50% level). (**6-Dipp**)CuBr · CHCl$_3$ (**7-Dipp**)CuBr · CHCl$_3$

takes part in the hydrogen bonding with the halogen atom, the geometrical parameters of [(**7-Dipp**)H][Br] · CH_2Cl_2 are considered in discussion below.

The X-ray structure analysis reveals the usual *chair* conformation for the saturated six-membered and the unsaturated seven-membered carbene rings, and the highly twisted conformation for the saturated seven-membered carbene ring. It is well known that the larger heterocyclic rings lead to the increased N–C_{carb}–N angles which, in turn, result in the ring strain. The same geometrical peculiarities are also observed when going from six- to seven-membered carbene rings of the amidinium salts. The N–C_{carb}–N angle in the [(**6-Dipp**)H] cation is 123.7(4)°, whilst in the [(**7-Dipp**)H] and [(**7′-Dipp**)H] cations have angles of 125.1(2) and 127.5(1)°, respectively. The increase of the N–C_{carb}–N angle in the seven-membered amidinium cations gives rise to the substantial distortion of the tetrahedral geometry of the ring carbon atoms in comparison with the related six-membered cations. So, in the [(**7-Dipp**)H] and [(**7′-Dipp**)H] cations, the *endo*-angles at the quaternary carbon atoms range from 111.8(2) to 114.6(2)° and from 111.1(1) to 111.2(1)°, respectively, whereas the corresponding angle range in the [(**6-Dipp**)H] cation is 109.5(3)–110.6(4)°. The C–N–C angle distribution is similar in the six- and seven-membered amidinium cations. They change in the order of C_{ring}–N–C_{carb} > C_{Ar}–N–C_{carb} > C_{ring}–N–C_{Ar} (Table S1).

The two nitrogen atoms have a trigonal planar configuration. Of interest is the angle between the nitrogen coordination planes (α) which is a useful gauge for the spatial orientation of the aryl substituents. For the saturated six-membered as well as the unsaturated seven-membered rings having the *chair* conformation the angle α is very close to 0° (2.0(1) and 0.37(5)°, respectively), while for the twisted saturated seven-membered ring one is 23.38(5)°. The twisting effect of the *N*-substituents in the saturated seven-membered carbene ring provides an opportunity to design new chiral ligands.

The silver and copper complexes of six- and seven-membered carbenes were investigated by single-crystal X-ray diffraction studies. The molecular structures of the (**6-Dipp**)AgBr · CH_2Cl_2, (**6-Dipp**)CuBr · $CHCl_3$, (**7-Dipp**)AgBr · CH_2Cl_2, (**7-Dipp**)CuBr · $CHCl_3$, and [Ag(**7-Mes**)$_2$][Cl] · H_2O are shown in Figs. 3 and 5, S4 and S5, selected geometrical parameters are presented in Table S1.

As it can be seen from Table S1, the Ag–C_{carb} distances for the Ag-complexes of six- and seven-membered carbenes are close to each other and lie in the range of values reported for the related complexes very recently (2.097(6)–2.122(3) Å). The C_{carb}–Ag–X bond angles are practically linear (177.6(2) and 177.59(5)°). Somewhat larger difference is observed in the Cu–C_{carb} distances for the Cu-complexes of six- and seven-membered carbenes. Interestingly, in contrast to the Ag-complexes, the C_{carb}–Cu–X bond angles (173.97(6) and 173.5(2)°) in the Cu-complexes indicate more significant deviations from linearity.

As compared to the amidinium salts, the increase in the N–C_{carb} bond lengths is observed upon complexation with transition metals, while the N–C_{ring} and N–C_{Ar} bond lengths are kept virtually unchanged. The coordination geometry of the two nitrogen atoms in the six- and seven-membered carbenes remains nearly planar upon the complexation, however, the dihedral angle (α) between the nitrogen coordination planes is slightly decreased (Table S1). Moreover, the C_{ring}–N–C_{carb} bond angles are increased, but the N–C_{carb}–N, C_{Ar}–N–C_{carb} and C_{ring}–N–C_{Ar} bond angles are decreased upon the complexation. Thus, contrary to the amidinium salts, the values of the C_{ring}–N–C_{carb} bond angles in the transition metal complexes of six- and seven-membered carbenes exceed the values of the N–C_{carb}–N bond angles, apparently, due to the repulsive steric interactions between the transition metal and the bulky substituents at the nitrogen atoms. Furthermore, the complexation offers little relief to the ring strain; for example, the *endo*-angles at

the sp^3-hybridized carbon atoms in the (**7-Dipp**)AgBr and (**7-Dipp**)CuBr range from 111.9(2) to 113.5(2)° and from 111.6(6) to 113.8(6)°, respectively.

A feature of the [Ag(**7-Mes**)$_2$]$^{(+)}$ cation is practically perpendicular arrangement of two seven-membered carbene ligands to accommodate the bulky mesityl substituents at the nitrogen atoms. The dihedral angle between the two N–C_{carb}–N planes is 84.49(5)°.

No Ag–Ag and Cu–Cu interactions are observed in the crystals.

3. Conclusion

A new effective method of preparation of *N,N′*-diarylated six- and seven-membered ring amidinium salts was developed. Seven-membered amidinium salt [(**7′-Dipp**)H][Cl] bearing isolated C=C double bond in back-bone was prepared for the first time.

Free carbene **6-Dipp** was generated upon treatment of amidinium salt with LiHMDS. It was also found that vacuum thermolysis of seven-membered carbene adduct with alcohol (**7-Dipp**)(H)(OMe) is not applicable for carbene generation.

A series of NHC–Ag(I) complexes were prepared via interaction of amidinium salts with Ag_2O. It was found that the presence of isolated C=C double bond in the back-bone prevent the formation of silver(I) complexes leading to ring opening via 1,4-elimination.

Two new six- and seven-membered ring NHC–Cu(I) complexes were prepared from corresponding NHC–Ag(I). Thus, transmetallation of *N,N′*-diarylated six- and seven-membered NHC–Ag(I) complexes was documented for the first time.

4. Experimental

4.1. General comments

Unless otherwise stated, all manipulations were carried out using standard Schlenk technique under an argon atmosphere. All solvents for use in an inert atmosphere were purified by standard procedures and distilled under argon immediately prior to use.[35] Other chemicals were obtained from commercial sources and used without further purification. NMR spectra were obtained on a Bruker "Avance 400" spectrometer (400.13 MHz ^{1}H, 100.62 MHz ^{13}C). The chemical shifts are frequency referenced relative to solvent peaks. Coupling constants *J* are given in Hertz as positive values regardless of their real individual signs. The multiplicity of the signals is indicated as "s", "d", or "m" for singlet, doublet, or multiplet, respectively. The abbreviation "br" is given for broadened signals. Elemental analyses were performed on a Carlo Erba EA1108 CHNS-O elemental analyzer at the Institute of Petrochemical Synthesis, Russian Academy of Sciences. Melting points were measured in an unsealed capillary using a SANYO Gallenkamp PLC melting point apparatus without any additional corrections.

4.2. X-ray structure determination

Data were collected on a Bruker SMART APEX II CCD and a Bruker SMART 1000 CCD diffractometers (λ(Mo Kα)-radiation, graphite monochromator, ω and φ scan mode) and corrected for absorption using the SADABS program (versions 2.03 [36] and 2.01 [37]). For details, see Table S2. The structures were solved by direct methods and refined by full-matrix least-squares technique on F^2 with anisotropic displacement parameters for non-hydrogen atoms. One of the three dichloromethane solvate molecules in [(**6-Dipp**)H][Br] · 1.5CHCl$_3$ is disordered over two sites with the occupancies of 0.5:0.5. The dichloromethane solvate molecule in [(**7-Dipp**)H][Br] · CH_2Cl_2 is disordered over two sites with the

occupancies of 0.7:0.3. The water solvate molecule in [(**7′-Dipp**)H][Cl] · 0.5H$_2$O has the position occupancy of 0.5. The methyl group and hydrogen atom at the carbenoid carbon atom in (**7-Dipp**)(H)(OMe) are disordered over two sites with the occupancies of 0.8:0.2. Two of the four isopropyl groups of one of the two independent molecules in the formamidine are disordered over two sites with the occupancies of 0.5:0.5 and 0.6:0.4. The dichloromethane solvate molecule in (**6-Dipp**)AgBr · CH$_2$Cl$_2$ is disordered over two sites with the occupancies of 0.5:0.5. The absolute structures of (**6-Dipp**)CuBr · CHCl$_3$ and (**7-Dipp**)CuBr · CHCl$_3$ were objectively determined by the refinement of Flack parameters which have become equal to 0.002(5) and 0.01(2), respectively. The hydrogen atoms of the solvate water molecules in [(**7′-Dipp**)H][Cl] · 0.5H$_2$O and [Ag(**7-Mes**)$_2$][Cl] · H$_2$O were localized in the difference-Fourier map and included in the refinement with fixed positional and isotropic displacement parameters. The other hydrogen atoms in all compounds were placed in calculated positions and refined within the riding model with fixed isotropic displacement parameters (U_{iso}(H) = 1.5U_{eq}(C) for the CH$_3$-groups and U_{iso}(H) = 1.2U_{eq}(C) for the other groups). All calculations were carried out using the SHELXTL PLUS program (versions 6.12 [38] and 5.10 [39]).

4.3. General procedure for the preparation of formamidines

In a distillation apparatus, a mixture of aniline (50 g, 1 equiv.), triethyl orthoformate (0.5 equiv.) and glacial acetic acid (0.05 equiv.) was heated under an air atmosphere while temperature of reaction mixture rise up to 180 °C (approximately 2–3 h), during which time ethanol distilled off. The crystalline mass obtained upon cooling was recrystallized from toluene or acetone [40].

4.4. N,N′-bis(2,6-diisopropylphenyl)formamidine

Yield: 44.59 g, 86%, white fluffy crystalline powder. ^{1}H NMR (CDCl$_3$): δ 7.16 (m, 6H, Dipp*H*), 5.54 (br s, 1H, NC*H*N), 3.28 (m, 4H, DippC*H*), 1.20 (m, 24H, DippC*H*$_3$). ^{13}C NMR (CDCl$_3$): δ 147.6 (N*C*HN), 145.8 (*o*-Dipp), 139.0 (Dipp), 127.8 (*p*-Dipp), 123.3 (*m*-Dipp), 28.1 (DippC*H*), 24.4 (DippC*H*$_3$), 23.8 (DippC*H*$_3$), 23.6 (DippC*H*$_3$), 22.7 (DippC*H*$_3$). Anal. Calc. for C$_{25}$H$_{36}$N$_2$: C, 82.36; H, 9.95; N, 7.68. Found: C, 82.45; H, 10.04; N, 7.66%.

4.5. N,N′-bis(2,4,6-trimethylphenyl)formamidine

Yield: 41.63 g, 82%, colorless crystals. ^{1}H NMR (CDCl$_3$): δ 7.30 (s, 0.4H, Mes*H*), 7.19 (s, 0.6H, Mes*H*), 6.92 (s, 1.2H, Mes*H*), 6.87 (s, 2.8H, Mes*H*), 5.52 (br s, 1H, NC*H*N), 2.24 (m, 12H, MesC*H*$_3$). ^{13}C NMR (CDCl$_3$): δ 147.1 (N*C*HN), 142.6 (Mes), 133.9 (Mes), 129.2 (Mes), 128.9 (Mes), 128.8 (Mes), 20.7 (*o*-MesC*H*$_3$), 18.6 (*p*-MesC*H*$_3$). Anal. Calc. for C$_{19}$H$_{24}$N$_2$: C, 81.38; H, 8.63; N, 9.99. Found: C, 81.24; H, 8.53; N, 9.91%.

4.6. General procedure for the preparation of amidinium salts

(A) *n*-BuLi (2.5 M in hexane, 1.05 equiv.) was added at room temperature to a THF solution (100 mL) of formamidine (30 g, 1 equiv.). The resulting yellow solution was stirred at room temperature for 20 min before dihalogenide (1.5 equiv.) was added dropwise. The solution was stirred at room temperature overnight. After evaporation of the solvent under vacuum, the resulting solid was washed with hexane (100 mL) and Et$_2$O (100 mL). The residue was dissolved in CH$_2$Cl$_2$ (100 mL), and filtered through short pad of Celite. After evaporation of the solvent the crude product was recrystallized from ethyl acetate/CH$_2$Cl$_2$ or ethyl acetate (compound **1**) and dried in vacuo at 100 °C.

(B) Diisopropylethylamine (33 mmol, 1.1 equiv.) was added to a stirred solution of formamidine (30 mmol, 1 equiv.) and dihalogenide (90 mmol, 3 equiv.) in a 50 mL round bottomed flack. The reaction mixture was heated to 125 °C for 2 h. The reaction mixture was then cooled to room temperature, and excess dihalogenide was removed in vacuo. The residue was dissolved in 100 mL dichloromethane and washed by saturated solution of potassium carbonate. Organic layer was mixed with 50 mL of toluene and the solution was evaporated in vacuo to 50 mL, precipitated white crystals filtered off and dried in vacuo providing pure product.

4.7. [(6-Dipp)H][Br]

Yield: *A* – 64%, *B* – 88%, white crystalline powder. M.p.: 269–270 °C. ^{1}H NMR (CDCl$_3$): δ 7.54 (s, 1H, NC*H*N), 7.42 (t, 2H, *J* = 7.8, *p*-Dipp*H*), 7.36 (d, 4H, *J* = 7.8, *m*-Dipp*H*), 4.24 (t, 4H, *J* = 5.4, NC*H*$_2$), 3.02 (dt, 4H, *J* = 13.6, 6.8, DippC*H*), 2.75 (m, 2H, C*H*$_2$), 1.36 (d, 12H, *J* = 6.8, DippC*H*$_3$), 1.21 (d, 12H, *J* = 6.8, DippC*H*$_3$). ^{1}H NMR (DMSO-*d*$_6$): δ 9.03 (s, NC*H*N), 7.48 (t, *J* = 7.3, *p*-Dipp*H*), 7.23 (d, 4H, *J* = 7.8, *m*-Dipp*H*), 3.84 (t, 4H, *J* = 5.5, NC*H*$_2$), 2.96 (dt, 4H, *J* = 13.6, 6.7, DippC*H*), 2.41 (t, 2H, *J* = 5.4, C*H*$_2$), 1.30 (d, 12H, *J* = 6.6, DippC*H*$_3$), 1.19 (d, 12H, *J* = 6.6, DippC*H*$_3$). ^{13}C NMR (CDCl$_3$): δ 152.7 (N*C*HN), 145.6 (*o*-Dipp), 135.7 (Dipp), 131.2 (*p*-Dipp), 125.1 (*m*-Dipp), 48.9 (N*C*H$_2$), 28.8 (DippC*H*), 24.8 (DippC*H*$_3$), 24.7 (DippC*H*$_3$), 19.4 (*C*H$_2$). Anal. Calc. for C$_{28}$H$_{41}$BrN$_2$: C, 69.26; H, 8.51; N, 5.77. Found: C, 69.24; H, 8.53; N, 5.81%.

4.8. [(7-Dipp)H][Br]

Yield: *A* – 52%, *B* – 82%, white crystalline powder, M.p.: 254–256 °C. ^{1}H NMR (CDCl$_3$): δ 7.38 (t, 2H, *J* = 7.8, *p*-Dipp*H*), 7.25 (s, 1H, NC*H*N), 7.22 (d, 4H, *J* = 7.8, *m*-Dipp*H*), 4.67 (br s, 4H, NC*H*$_2$), 3.20 (dt, 4H, *J* = 13.6, 6.8, DippC*H*), 2.61 (dt, 4H, *J* = 5.5, 2.7, C*H*$_2$C*H*$_2$), 1.37 (d, 12H, *J* = 6.8, DippC*H*$_3$), 1.23 (d, 12H, *J* = 6.8, DippC*H*$_3$). ^{1}H NMR (DMSO-*d*$_6$): δ 8.66 (s, 1H, NC*H*N), 7.45 (t, 2H, *J* = 7.8, *p*-Dipp*H*), 7.34 (d, 4H, *J* = 7.3, *m*-Dipp*H*), 4.27 (br s, 4H, NC*H*$_2$), 3.09 (dt, 4H, *J* = 13.6, 6.8, DippC*H*), 2.36 (m, 4H, C*H*$_2$C*H*$_2$), 1.31 (d, 12H, *J* = 6.6, DippC*H*$_3$), 1.21 (d, 12H, *J* = 6.8, DippC*H*$_3$). ^{13}C NMR (CDCl$_3$): δ 157.0 (N*C*HN), 144.8 (*o*-Dipp), 138.8 (Dipp), 130.9 (*p*-Dipp), 125.3 (*m*-Dipp), 56.2 (N*C*H$_2$), 28.9 (DippC*H*), 25.0 (DippC*H*$_3$), 24.8 (*C*H$_2$), 24.6 (DippC*H*$_3$). Anal. Calcd for C$_{29}$H$_{43}$BrN$_2$: C, 69.72; H, 8.68; N, 5.61. Found: C, 69.78; H, 8.65; N, 5.62%.

4.9. [(7′-Dipp)H][Cl]

Yield: *A* – 46%, white crystalline powder, M.p.: 253–255 °C (with decomp.). ^{1}H NMR (DMSO-*d*$_6$): δ 8.55 (s, 1H, NC*H*N), 7.44 (m, 2H, *p*-Dipp*H*), 7.32 (d, 4H, *J* = 7.8, *m*-Dipp*H*), 6.53 (t, 2H, *J* = 4.4, C*H* = C*H*), 4.93 (d, 4H, *J* = 5.6, NC*H*$_2$), 3.20 (dt, 4H, *J* = 13.5, 6.7, DippC*H*), 1.29 (d, 12H, *J* = 6.8, DippC*H*$_3$), 1.20 (d, 12H, *J* = 6.6, DippC*H*$_3$). ^{13}C NMR (DMSO-*d*$_6$): δ 158.8 (N*C*HN), 144.2 (*o*-Dipp), 139.7 (Dipp), 131.2 (*C*H=CH), 130.1 (*p*-Dipp), 124.6 (*m*-Dipp), 50.3 (N*C*H$_2$), 28.2 (DippC*H*), 24.4 (DippC*H*$_3$), 23.7 (DippC*H*$_3$). Anal. Calc. for C$_{29}$H$_{41}$ClN$_2$: C, 76.87; H, 9.12; N, 6.18. Found: C, 76.76; H, 9.02; N, 6.14%.

4.10. [(7-Mes)H][Br]

Yield: *A* – 47%, *B* – 92%, white crystalline powder, M.p.: 204–205 °C. ^{1}H NMR (DMSO-*d*$_6$): δ 8.27 (s, 1H, NC*H*N), 7.03 (s, 4H, *m*-Mes*H*), 4.19 (m, 4H, NC*H*$_2$), 2.33 (m, 16H, *o*-MesC*H*$_3$, C*H*$_2$C*H*$_2$), 2.25 (s, 6H, *p*-MesC*H*$_3$). ^{13}C NMR (DMSO-*d*$_6$): δ 160.2 (N*C*HN), 140.0 (Mes), 139.2 (Mes), 134.3 (Mes), 130.9 (Mes), 128.7 (Mes), 54.0 (N*C*H$_2$), 25.3 (*C*H$_2$C*H$_2$), 20.9 (*p*-MesC*H*$_3$); 18.1 (*o*-MesC*H*$_3$). Anal. Calc. for C$_{23}$H$_{31}$BrN$_2$: C, 66.50; H, 7.52; N, 6.74. Found: C, 66.53; H, 7.50; N, 6.72%.

4.11. General procedure for the preparation of silver(I) complexes

Mixture of amidinium salt (2 mmol, 1 equiv.) with silver(I) oxide (2 mmol, 1 equiv.) was dissolved in absolute dichloromethane (50 mL). The reaction mixture was stirred for 48 h at room temperature. The solution was filtered through short pad of silica gel, and then the filtrate was concentrated to dryness in vacuo.

4.12. (**6-Dipp**)AgBr

Yield: 83%, white crystalline powder, M.p.: 295–296 °C. ^{1}H NMR (CDCl$_3$): δ 7.34 (t, 2H, J = 7.8, p-DippH), 7.19 (d, 4H, J = 7.8, m-DippH), 3.44 (t, 4H, J = 5.9, NCH$_2$), 3.04 (dt, 4H, J = 13.7, 6.8, DippCH), 2.36 (dt, 2H, J = 11.7, 6.6, CH$_2$), 1.31 (d, 12H, J = 6.8, DippCH$_3$), 1.28 (d, 12H, J = 6.8, DippCH$_3$). ^{13}C NMR (CDCl$_3$): δ 207.4 (dd, $J(^{107}$Ag, ^{13}C) = 225.0, $J(^{109}$Ag, ^{13}C) = 260.4, NCHN), 145.3 (o-Dipp), 142.22 (Dipp), 129.4 (p-Dipp), 124.7 (m-Dipp), 46.0 (NCH$_2$), 28.5 (DippCH), 24.9 (DippCH$_3$), 24.7 (DippCH$_3$), 20.3 (CH$_2$). Anal. Calc. for C$_{28}$H$_{40}$AgBrN$_2$: C, 56.67; H, 6.96; N, 4.72. Found: C, 56.66; H, 6.93; N, 4.77%.

4.13. (**7-Dipp**)AgBr

Yield: 75%, white crystalline powder, M.p.: 288–291 °C. ^{1}H NMR (CDCl$_3$): δ 7.32 (m, 2H, p-DippH), 7.18 (d, 4H, J = 7.6, m-DippH), 4.01 (m, 4H, NCH$_2$), 3.24 (dt, 4H, J = 13.9, 6.9, DippCH), 2.34 (ddd, 4H, J = 5.8, 2.8, 2.7, CH$_2$CH$_2$), 1.33 (s d, 12H, J = 6.8, DippCH$_3$), 1.31 (d, 12H, J = 6.8, DippCH$_3$). ^{13}C NMR (CDCl$_3$): δ 217.3 (dd, $J(^{107}$Ag, ^{13}C) = 226.7, $J(^{109}$Ag, ^{13}C) = 262.9, NCHN), 144.7 (o-Dipp), 144.6 (Dipp), 129.0 (p-Dipp), 124.8 (m-Dipp), 53.8 (NCH$_2$), 53.7 (NCH$_2$), 28.6 (DippCH), 25.0 (CH$_2$), 24.7 (DippCH$_3$), 24.6 (DippCH$_3$), 20.34 (CH$_2$CH$_2$). Anal. Calc. for C$_{29}$H$_{42}$AgBrN$_2$: C, 57.34; H, 7.14; N, 4.61. Found: C, 57.32; H, 7.15; N, 4.61%.

4.14. [Ag(**7-Mes**)$_2$][Cl] · H$_2$O

Yield: 73%, white crystalline powder, M.p.: >300 °C. ^{1}H NMR (CDCl$_3$): δ 6.67 (s, 4H, m-MesH), 3.45 (br s, 4H, NCH$_2$), 2.14 (s, 6H, p-MesCH$_3$), 1.88 (br s, 4H, CH$_2$CH$_2$), 1.62 (s, 12H, o-MesCH$_3$). ^{13}C NMR (CDCl$_3$): δ 214.7 (dd, $J(^{107}$Ag, ^{13}C) = 175.9, $J(^{109}$Ag, ^{13}C) = 203.5, NCHN), 144.2 (Mes), 137.0 (Mes), 133.6 (Mes), 129.2 (Mes), 51.9 (NCH$_2$), 51.8 (NCH$_2$), 24.7 (CH$_2$CH$_2$), 20.5 (o-MesCH$_3$), 17.8 (p-MesCH$_3$). Anal. Calc. for C$_{46}$H$_{62}$AgClN$_4$O: C, 66.38; H, 7.75; N, 6.73. Found: C, 66.37; H, 7.72; N, 6.74%.

4.15. Formamidine **8**

Complex **8** was isolated using the same protocol as for Ag(I) complexes. Yield 80%, white crystalline powder. ^{1}H NMR (CDCl$_3$): δ 7.47 (t, 1H, J = 7.8, p-DippH), 7.31 (d, 2H, J = 7.8, m-DippH), 7.15 (m, 2H, m-DippH), 7.08 (dd, 1H, J = 8.6, 6.6, p-DippH), 5.33 (br s, 1H, =CH–CH=), 5.17 (m, 1H, =CH–CH=), 4.95 (dd, 1H, J = 16.4, 2.0, CH$_2$=), 4.63 (d, 1H, J = 9.8, CH$_2$=), 3.24 (dt, 4H, J = 13.5, 6.8, DippCH), 1.26 (m, 24H, DippCH$_3$). ^{13}C NMR (CDCl$_3$): δ 149.6 (NCHN), 147.3 (N–CH=), 139.4 (Dipp), 131.1 (Dipp), 129.7 (NCH), 124.5 (Dipp), 123.3 (Dipp), 122.8 (Dipp), 115.4 (CH$_2$=), 109.7 (CH$_2$=CH–CH), 28.4 (DippCH), 27.7 (DippCH), 24.6 (DippCH$_3$), 23.7 (DippCH$_3$). Anal. Calc. for C$_{29}$H$_{40}$N$_2$: C, 83.60; H, 9.68; N, 6.72. Found: C, 83.23; H, 9.73; N, 6.70%.

4.16. General procedure for the preparation of copper(I) complexes

Mixture of silver(I) complex (1 mmol, 1 equiv.) with copper(I) bromide (1 mmol, 1 equiv.) was dissolved in absolute dichloromethane (30 mL). The reaction mixture was stirred for 48 h at room temperature in the dark. The solution was filtered through short pad of Celite, and then the filtrate was concentrated to dryness in vacuo.

4.17. (**6-Dipp**)CuBr

Yield: 83%, white crystalline powder, M.p.: >300 °C (with decomp.). ^{1}H NMR (CDCl$_3$): δ 7.35 (t, 2H, J = 7.7, p-DippH), 7.20 (d, 4H, J = 7.8, m-DippH), 3.42 (t, 4H, J = 5.9, NCH$_2$), 3.05 (quint, 4H, J = 6.9, DippCH), 2.36 (t, 4H, J = 5.8, CH$_2$), 1.34 (d, 12H, J = 6.9, DippCH$_3$), 1.30 (d, 12H, J = 7.1, DippCH$_3$). ^{13}C NMR (CDCl$_3$): δ 201.1 (NCHN), 145.5 (o-Dipp), 141.3 (Dipp), 129.4 (p-Dipp), 124.6 (m-Dipp), 46.2 (NCH$_2$), 28.6 (DippCH), 24.9 (DippCH$_3$), 24.6 (DippCH$_3$), 20.5 (CH$_2$). Anal. Calc. for C$_{28}$H$_{40}$CuBrN$_2$: C, 61.36; H, 7.36; N, 5.11. Found: C, 61.29; H, 7.38; N, 5.10%.

4.18. (**7-Dipp**)CuBr

Yield: 79%, white crystalline powder, M.p.: >300 °C (with decomp.). ^{1}H NMR (CDCl$_3$): δ 7.34 (t, 2H, J = 7.8, p-DippH), 7.20 (d, 4H, J = 7.8, m-DippH), 3.98 (br s, 4H, N–CH2), 3.26 (sept, 4H, J = 6.9, DippCH), 2.35 (br s, 4H, CH$_2$CH$_2$), 1.37 (d, 12H, J = 6.9, DippCH$_3$), 1.33 (d, 12H, J = 6.9, DippCH$_3$). ^{13}C NMR (CDCl$_3$): δ 210.5 (NCHN), 144.8 (o-Dipp), 143.7 (Dipp), 128.9 (p-Dipp), 124.7 (m-Dipp), 53.8 (NCH$_2$), 28.7 (DippCH), 25.1 (CH$_2$CH$_2$), 24.7 (DippCH$_3$), 24.6 (DippCH$_3$). Anal. Calc. for C$_{29}$H$_{42}$CuBrN$_2$: C, 61.96; H, 7.53; N, 4.98. Found: C, 62.02; H, 7.49; N, 4.95%.

4.19. 6-Dipp

Mixture of amidinium salt **1** (0.300 g, 0.62 mmol) and bis(trimethylsilyl)lithium (0.103 g, 0.62 mmol) was dissolved in 0.6 mL absolute THF in NMR tube. Amidinium salt dissolves in 10 min, during which an almost clear yellow solution formed. ^{1}H NMR (THF-d_8): δ 7.20 (m, 6H, DippH), 3.34 (dt, 4H, J = 13.5, 6.7, DippCH), 3.21 (t, 4H, J = 5.6, N–CH$_2$), 2.27 (br s, 2H, CH$_2$), 1.27 (d, J = 6.9, 12H, DippCH$_3$), 1.17 (d, 12H, J = 6.9, DippCH$_3$). ^{13}C NMR (THF-d_8): δ 245.9 (NCHN), 146.6 (o-Dipp), 131.1 (Dipp), 127.6 (p-Dipp), 124.2 (m-Dipp), 45.2 (N–CH$_2$), 29.0 (DippCH), 25.2 (DippCH$_3$), 24.6 (DippCH$_3$) 22.8 (CH$_2$).

4.20. (**7-Dipp**)(H)(OMe)

Mixture of amidinium salt **2** (1 g, 2 mmol) with sodium methoxide (0.1 g, 2 mmol) was dissolved in absolute THF (30 mL). The reaction mixture was stirred for 30 min at room temperature. The solution was concentrated to dryness in vacuo, dissolved in 10 mL of n-hexane and filtered through short pad of Celite. Evaporation of the solvent afforded a pure product. Yield: 0.792 g, 88%, colorless crystals. ^{1}H NMR (toluene-d_8): δ 7.15 (m, 4H, p-Dipp), 7.06 (m, 2H, m-Dipp), 5.03 (s, 1H, NCHN), 4.11 (dt, 2H, J = 13.7, 6.9, DippCH), 3.70 (m, 4H, DippCH, N–CH$_2$) 2.38 (s, 3H, OCH$_3$), 1.72 (m, 2H, CH$_2$), 1.60 (m, 2H, CH$_2$CH$_2$), 1.31 (m, 24H, DippCH$_3$). ^{13}C NMR (toluene-d_8): δ 150.3 (Dipp), 147.4 (Dipp), 144.7 (Dipp), 127.1 (Dipp), 124.8 (Dipp), 124.2 (Dipp), 107.58 (NCHN), 57.9 (OCH$_3$), 52.9 (N–CH$_2$), 31.1 (DippCH), 28.8 (CH$_2$), 28.5 (CH$_2$CH$_2$), 25.5 (DippCH$_3$), 25.4 (DippCH$_3$), 24.5 (DippCH$_3$), 24.4 (DippCH$_3$).

Appendix A. Supplementary material

CCDC 708130, 708131, 708132, 708133, 708134, 708135, 708136, 708137, 708138, 708139 and 708140 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.03.014.

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