Novel Expanded Ring N-Heterocyclic Carbenes: Free Carbenes, Silver Complexes, And Structures

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The addition of aromatic formamidines to dihaloalkanes proceeds in air under mildly basic conditions and in polar solvents to afford the corresponding amidinium salts in high yields. To demonstrate the wide scope of this methodology, several five-, six-, and seven-membered saturated N-heterocyclic amidinium salts have been prepared. The free carbenes **7-Mes**, **7-Xyl**, **7-Pr^{i}**, **6-Mes**, and **6-Xyl** have also been isolated as stable white solids, and for the first time the solid state structures of free seven-membered N-heterocyclic carbenes have been determined (**7-Mes** and **7-Xyl**). The syntheses and characterization of their Ag(I) halide complexes are also described and the X-ray structures for Ag(**6-Pr^{i}**)Br, Ag(**7-Mes**)Br, Ag(**7-Xyl**)I, and Ag(**Xyl7-Mes**)Br determined. On the basis of NMR data the silver halide species form either neutral, Ag(NHC)X, or ionic, $[Ag(NHC)_2][AgX_2]$ complexes in solution. A feature of the expanded ring carbenes is the extremely large NCN angle ($\geq 120°$) and the consequential steric impact of the N-substituents on the metal center. For the free seven-membered ring carbenes the ^{13}C NMR shifts are 258−260 ppm, well down field from those observed for the six- and five-membered ring carbenes.

Introduction

The strong σ-donating properties of N-heterocyclic carbenes make them effective stabilizing ligands in organometallic chemistry as well as important ligands in some forms of catalysis.[1,2] To date, research has largely focused on five-membered ring carbenes. Examples of "expanded ring", six-membered,[3] and seven-membered carbenes[3e,g,4,5] have also been reported (although free carbenes of seven-membered ring systems had not previously been isolated). Recently, we reported the first examples of novel, saturated, seven-membered diazepanylidene carbenes (including one with a dioxolane backbone) and their Rh, Ir, and Pt complexes.[5]

In virtually all cases the protonated carbene ring (whether, five-, six-, or seven-membered) is formed by the reaction of diamines (or diimines) with a formyl unit to close the ring (Scheme 1a). This synthetic methodology is often poorly reproducible or low yielding, which has limited the availability of the very basic and relatively unexplored six- and seven-membered ring carbenes, and until very recently functionalized examples of these carbenes had not been reported.[3h] Recently, Bertrand published a process for the synthesis of the heterocyclic ring that is the reverse of the normal synthetic approach, in which a formamidine fragment is first prepared and the ring is closed with a dibromohydrocarbyl unit (Scheme 1b) using BuLi as base and THF as the solvent.[3e,f] This is a potentially very useful synthetic methodology; however, it requires inert moisture-free conditions and is limited to substrates that tolerate strong organolithium bases.

Six- and in particular seven-membered ring carbenes are intriguing from several points of view. They are very basic, somewhat more basic than the saturated five-membered-ring carbenes, which are in turn more basic than their unsaturated counterparts.[5–7] Structurally they also offer some unique features; the saturated seven-membered ring is highly twisted,

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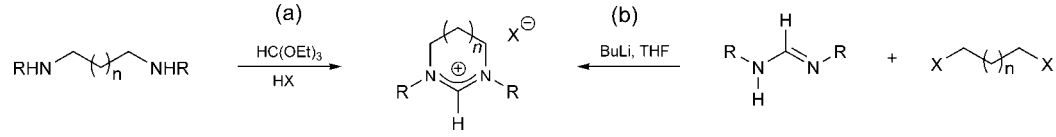
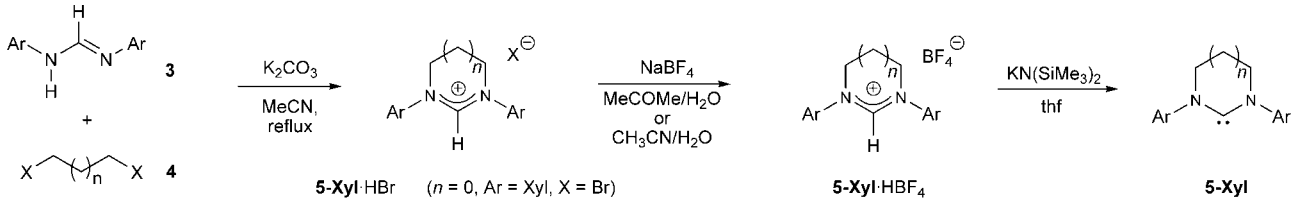
Scheme 1. Synthetic Routes to NH-Precursors: (a) via Diamines, (b) via Formamidines

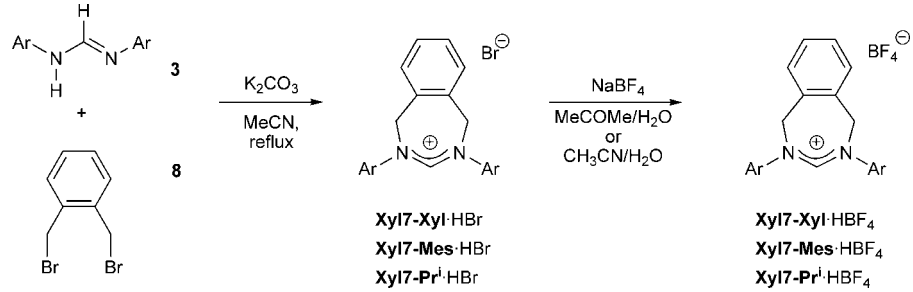


Scheme 2. Synthesis of Five-, Six-, and Seven-Membered Saturated NHC Ligands (n = 0−2, X = Br, I)



5-Xyl·HBr	(n = 0, Ar = Xyl, X = Br)	**5-Xyl**·HBF_4	**5-Xyl**
5-Mes·HBr	(n = 0, Ar = Mes, X = Br)	**5-Mes**·HBF_4	**5-Mes**
5-Pr^i·HBr	(n = 0, Ar = 2,6-Pr^i, X = Br)	**5-Pr^i**·HBF_4	**5-Pr^i**
6-Xyl·HBr	(n = 1, Ar = Xyl, X = Br)	**6-Xyl**·HBF_4	**6-Xyl**
6-Mes·HBr	(n = 1, Ar = Mes, X = Br)	**6-Mes**·HBF_4	**6-Mes**
6-Pr^i·HBr	(n = 1, Ar = 2,6-Pr^i, X = Br)	**6-Pr^i**·HBF_4	**6-Pr^i**
7-Xyl·HI	(n = 2, Ar = Xyl, X = I)	**7-Xyl**·HBF_4	**7-Xyl**
7-Mes·HI	(n = 2, Ar = Mes, X = I)	**7-Mes**·HBF_4	**7-Mes**
7-Pr^i·HI	(n = 2, Ar = 2,6-Pr^i, X = I)	**7-Pr^i**·HBF_4	**7-Pr^i**

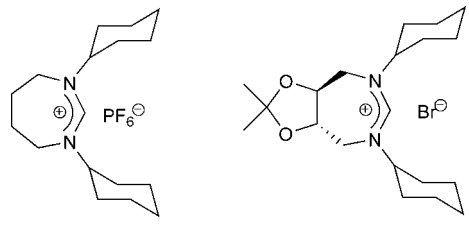
Scheme 3. Synthesis and Structures of Benzo-diazepanyl NHC Salts



Xyl7-Xyl·HBr
Xyl7-Mes·HBr
Xyl7-Pr^i·HBr

Xyl7-Xyl·HBF_4
Xyl7-Mes·HBF_4
Xyl7-Pr^i·HBF_4

providing an opportunity to design new chiral ligands, and of considerable interest, the large heterocyclic rings lead to extremely large N−C_{NHC}−N angles. For the diazepanylidene systems angles of 127.35(15)° and 135.9(10)° are reported for the salts **1**·HPF_6 and **2**·HPF_6, respectively. The corresponding angles for the Rh/Ir(cod)(**1**)Cl and Ir(cod)(**2**)Br complexes are 120.4(2)° and 122.2(11)°.[5] This compares to a typical N−C_{NHC}−N angle of around 107° for related Rh complexes of the five-membered imidazol-2-ylidines.[8] The effect of this opening of the N−C_{NHC}−N angle is to twist the N-substituents (Cy in the present case) toward the metal center, effectively blocking two faces of the metal coordination sphere.



1·HPF$_6$ **2·HBr**

Here we report a simple, versatile, and high-yielding route to several six- and seven-membered carbenes (and saturated five-membered NHCs) and describe their spectroscopic and solid state properties. This methodology allows the isolation of a range of carbenes, and hence metal complexes, which are not available via other routes. Our approach is based on the methodology reported by Bertrand. This modified synthetic method can be performed in air on a large scale and generally proceeds with high yields for a cross-section of ring sizes and N-substituents.

The electronic and structural features of these expanded ring carbenes have been investigated. To demonstrate the coordination behavior of the new carbenes and to investigate the effect of coordination on features such as NCN angle, a number of silver complexes were synthesised and their crystal structures determined.

Results and Discussion

The amidinium salts are prepared under aerobic conditions by reaction of the appropriate *N*,*N*′-diaryl amidine with a dihaloalkane in refluxing acetonitrile and in the presence of a mild base (half an equivalent of potassium carbonate) to catalyze the reaction (Schemes 2 and 3). By "clipping" the appropriate dihalo-alkyl species to the selected formamidine, the corresponding five-, six-, and seven-membered rings, containing a variety of substitution patterns, can be prepared in high yields

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Table 1. ^{1}H and ^{13}C NMR Data for the C_{NHC}-*H* and C_{NHC} in the Amidinium Salts[a]

	R		
	Mes	Xyl	Pr^i
7-R·HI	7.22 (157.8)	7.28 (157.6)	7.27 (157.0)
6-R·HBr	7.57 (153.5)	7.68 (153.3)	7.55 (152.8)
5-R·HBr	8.92 (159.0)	9.20 (159.0)	8.10 (158.0)
7-R·HBF_4	7.21 (158.2)	7.28 (158.0)	7.29 (157.3)
6-R·HBF_4	7.52 (154.0)	7.83 (154.3)	7.57 (153.1)
5-R·HBF_4	7.96 (158.9)	8.16 (160.1)[b]	7.66 (160.0)[b]

[a] Values given in ppm; ^{13}C NMR data are in parentheses, measured in $CDCl_3$. [b] In d_6-DMSO.

Table 2. ^{13}C NMR Data for C_{NHC} in the Free Carbene[a]

	R		
	Mes	Xy	Pr^i
7-R	257.3	258.8	260.2
6-R	244.9	244.5	245.1
5-R	241.2	242.0	244.0

[a] Values given in ppm, measured in C_6D_6.

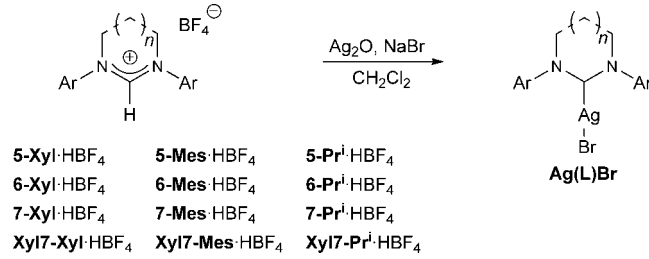
(typically 70−90%). The reaction proceeds rapidly for the larger ring sizes and lesser sterically congested amidines [for example 1,4-diiodobutane and *N*,*N*′-bis(2,4,6-trimethylphenyl)amidine], while increasing steric congestion and/or decreasing the ring size results in longer reaction times [1,2-dibromopropane and *N*,*N*′-bis(2, 6-diisopropylphenyl)amidine require extended periods of reflux]. It is worth noting that under Bertrand's conditions (Scheme 1b) the five-membered heterocycles were not accessible from the corresponding 1,2-dibromides due to HBr elimination, whereas with the present protocol (Scheme 2) the five-membered NHC salts were obtained in moderate to high yields.

Initial attempts to deprotonate several of the halide salts to give the free carbenes resulted in partial decomposition; consequently the halide was exchanged for a tetrafluoroborate anion. After recrystallization from dichloromethane/ether the BF_4^- salts were obtained in high yields and could be readily converted to the free carbene, with the exception of the benzodiazepanyl derivatives, **Xyl7-R**, where decomposition took place. The tetrafluoroborate salts, shown in Scheme 2, could also be obtained in a one-pot synthesis from the corresponding formamidines, without prior isolation of the intermediate amidinium halide salts.

In the ^{1}H NMR spectra of the **5-**, **6-**, and **7-R**·HBF_4 salts (in $CDCl_3$) the C_{NHC}-*H* proton shifts upfield with increasing ring size, indicating reduced acidity for this hydrogen, and as a corollary, increased basicity of the conjugate base: the free carbene (Table 1). A similar trend is not evident in the ^{13}C NMR for the amidinium carbon shift (C_{NHC}), where the five- and seven-membered rings display downfield shifts when compared to the six-membered rings.

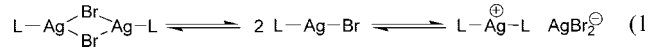
The free NHCs were prepared from deprotonation of the corresponding $^-BF_4$ salt in THF using $KN(SiMe_3)_2$ as the base. Many of the free carbenes generated are surprisingly stable and could, in general, be isolated in good yields as crystalline solids. The free carbenes of the seven-membered ring species show intriguing structural and electronic properties, and it is constructive to review the relationship between singlet and triplet contributions for these carbenes. For the seven-membered rings the carbene carbon ^{13}C NMR shift is observed at around 258−260 ppm (Table 2). This shift is at considerably lower field than that for five- and six-membered ring carbenes, which commonly occur in the region 235−245 ppm. It is only for acyclic NE-aminocarbenes (E = N, O, S) that such significant

Scheme 4. Synthesis of Five-, Six-, and Seven-Membered Saturated NHC Silver Complexes



5-Xyl·HBF_4 **5-Mes**·HBF_4 **5-Pr^i**·HBF_4
6-Xyl·HBF_4 **6-Mes**·HBF_4 **6-Pr^i**·HBF_4
7-Xyl·HBF_4 **7-Mes**·HBF_4 **7-Pr^i**·HBF_4
Xyl7-Xyl·HBF_4 **Xyl7-Mes**·HBF_4 **Xyl7-Pr^i**·HBF_4

low-field shifts for the carbene carbon are noted; in particular for NO carbenes the chemical shift is in the range 262−278 ppm and for NS = 297 ppm.[6,9] There are several examples of NN acyclic carbenes with large downfield shifts (255−259 ppm), although commonly they are smaller. In a comprehensive computational study looking at specific features of diaminocarbenes, Alder ascribes the large down-field shift in acyclic NS carbenes to the paramagnetic contribution to the isotropic shielding constant.[6] In turn, he attributes the origin of this large paramagnetic contribution as stemming from the singlet−triplet gap brought about by the relatively poor interaction between the S(π) orbital and the C_{NHC}(π^*) orbital and the consequential reduced donation of electron density from the S into the carbene π^* orbital. Extending this argument to the present seven-membered ring carbenes would suggest that there is less effective electron donation, from the N atoms to the carbene C, and hence a higher triplet contribution to the electronic structure of these carbenes when compared to the five- and six-membered carbenes. In a recent theoretical paper by Alder et al., looking at the carbene dimerization mechanism, calculated structural data are provided for five-, six-, seven-membered ring carbenes and for acyclic carbenes; figures for the singlet−triplet gap are also provided (five-membered 301.2 kJ mol^{-1}; six-membered 258.9 kJ mol^{-1}; seven-membered 210.7 kJ mol^{-1}; acyclic 173.0 kJ mol^{-1}).[1b]



(1)

Synthesis and Structure of the Silver Complexes. Reaction of the amidinium bromide salts with a slight excess of Ag_2O generally gave the corresponding silver 1:1 complexes in good yields, while results with the iodide salts were variable. Best yields, however, were obtained from the reaction of amidinium-BF_4^- salts with Ag_2O in the presence of NaBr, forming the corresponding silver bromide complexes shown in Scheme 4. Ag^I halide complexes of NHCs with 1:1 stoichiometry have been reported in the literature to afford a variety of bonding motifs, forming either neutral or ionic species (eq 1).[10,3d] Assignment of the linear L−Ag−Br structure to the Ag^I−NHC complexes reported here (Scheme 4) was made according to their solid state structures. However, it was evident from their ^{1}H and ^{13}C NMR data (Table 3) that the neutral Ag(NHC)Br complex was not always present in solution or that it existed in equilibrium with the ionic $[Ag(NHC)_2][AgBr_2]$ species. Two observations assisted us in the assignment of the silver complexes formed in solution; first it was noted that the

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Table 3. ^{1}H and ^{13}C NMR Data for the Ag^I(NHC) Complexes[a]

	C_{NHC} (ppm)	$^1J_{AgC}$ (Hz)	^{1}H notable shifts (ppm)	ref
Ag(**7-Mes**)Br	218.4	226/261	2.25 (12H, Me), 2.18 (6H, Me)	
[Ag(**7-Mes**)$_2$]BF_4	215.4	178/205	2.29 (6H, Me), 1.75 (6H, Me)	
Ag(**Xyl7-Mes**)Br	214.3	225/261	2.27 (6H, Me), 2.23 (12H,Me)	
Ag(**6-Mes**)Br	-[d]		2.33 (18H, Me)	
Ag(**6-Mes**)Cl[b]	205.9	228/260	2.30 (12H, Me),2.27 (6H, Me)	3c
[Ag(**6-Mes**)$_2$][$AgBr_2$]	204.5	174/201	2.27 (6H, Me), 1.69 (12H, Me)	
[Ag(**6-Mes**)$_2$][Pd_2Cl_6]$_{1/2}$[b]	205.8	174/201	2.33 (12H, Me), 1.76 (6H, Me)	3d
[Ag(**6-Mes**)$_2$][Rh_2(cod)$(CF_3CO_2)_3$][c]	206.3	173/199	2.32 (6H, Me), 1.81 (12H, Me)	23
Ag(**5-Mes**)Br	-[d]		2.23 (18 H, Me)	
Ag(**5-Mes**)Cl[b]	207.5	222/256	2.30 (12H, Me),2.28 (6H, Me)	13b
[Ag(**5-Mes**)$_2$][$AgBr_2$]	207.0	167/193	2.30 (6H, Me), 1.78 (12H, Me)	
[Ag(**Im-Mes**)$_2$][CF_3SO_3][c]	183.6	209/188	2.43 (6H, Me), 1.75 (12H, Me)	24
Ag(**7-Xyl**)Br	218.2	228/259	2.32 (12H, Me)	
[Ag(**7-Xyl**)$_2$][$AgBr_2$]	-[d]		1.64 (12H, Me)	
Ag(**Xyl7-Xyl**)Br	214.5	226/259	2.22 (12H, Me)	
[Ag(**Xyl7-Xyl**)$_2$][$AgBr_2$]	210.07	179/206	1.68 (12H, Me)	
Ag(**6-Xyl**)Br	206.4	259/224	2.32 (12H, Me)	
Ag(**5-Xyl**)Br	-[d]		2.29 (12H, Me)	
[Ag(**5-Xyl**)$_2$][$AgBr_2$]	-[d]		1.84 (12H, Me)	
Ag(**Xyl7-Pr^i**)Br	214.1	260/225		
Ag(**6-Pr^i**)Br	207.5	224/257		

[a] In $CDCl_3$. [b] In CD_2Cl_2. [c] In d_8-thf. [d] Not observed.

$J(^{109/107}Ag-^{13}C)$ of the neutral complexes was ca. 55−60 Hz greater than the corresponding ionic complexes and secondly that higher field ^{1}H NMR shifts were observed for the $[Ag(NHC)_2]^+$ species. The later observation was particularly useful in the case of NHCs with mesityl and xylyl aromatic substituents, where a significant high-field shift was observed for the ortho-methyl aromatic substituents from ∼2.3 ppm in the neutral complex to ∼1.8 ppm in the ionic complex (Table 3). Accordingly, five- and six-membered carbenes with mesityl substituents afforded the cationic [Ag(**5/6-Mes**)$_2$][$AgBr_2$] complexes as the major product, whereas the seven-membered carbenes, **7-Mes** and **Xyl7-Mes**, formed the neutral Ag(NHC)Br complexes. For comparison, the ionic complex [Ag(**7-Mes**)$_2$]BF_4 was prepared independently, and spectroscopic data observed are in agreement with the assignments made in Table 3.

The carbene ligands bearing xylyl substituents gave mixtures of Ag(NHC)Br complexes and the corresponding disproportionation products $[Ag(NHC)_2][AgBr_2]$ in various ratios depending on the reaction conditions. The only exception here was the **6-Xyl** ligand, which formed only the neutral silver complex. For the five-, six-, and seven-membered carbenes bearing isopropyl aromatic substituents only the linear Ag(NHC)Br complexes were observed.

Mass spectrometry data are in line with the NMR observations made in solution, and for most of the complexes the $[Ag(NHC)(CH_3CN)]^+$ fragment was observed (CH_3CN is used as the carrier solvent). However, for the Ag(**Xyl7-Mes**)Br, Ag(**6-Mes**)Br, Ag(**5-Mes**)Br, and Ag(**5-Xyl**)Br complexes the $[Ag(NHC)_2]^+$ fragment was observed as well, matched by the $[AgBr_2]^-$ fragment in the negative MS mode.

Coordination of the free carbenes to Ag does lead to changes in the main structural parameters associated with the heterocyclic ring; however, the essential trends remain the same. The ^{13}C NMR spectra of the seven-membered Ag−NHC complexes reveal a significant downfield shift of the C_{NHC} (214−218 ppm, Table 3) when compared to that of the corresponding five- and six-membered Ag−NHC complexes (δ C_{NHC} = 204−207 ppm), consistent with the observed trend for the free carbenes (Table 2).[11]

Silver(I)−carbene complexes have been extensively used as carbene transfer agents to other transition metals, most commonly palladium and to a lesser extent rhodium and iridium.[10a] Several attempts were made employing different synthetic routes to use the six- and seven-membered Ag(I)−carbene complexes as transfer agents on Pd(II), Rh(I), and Ir(I), all of which failed, with the free carbene route being the preferred method for the formation of complexes with these metals.

X-ray Structures. The solid state structures of **7-Mes**, **7-Xyl**,[12] **6-Mes**, and representative Ag(NHC)X complexes of the six- and seven-membered carbenes were determined. Selected crystal data are shown in Tables 4 and 5, and ORTEP[13] representations in Figures 1–6. The amidinium salt **Xyl7-Ph**·HPF_6 and the hydrolysis product **7-Xyl**·H_2O have also been characterized, and data are presented in the Supporting Information.

Contrary to the solution data above, only linear Ag(NHC)X silver complexes were characterized by X-ray, presumably due to the lower solubility of the neutral species in solution. No Ag−Ag interactions were observed in the crystal lattice. As shown in Tables 4 and 5, small differences are observed in the Ag−C(1) distances [r_{av} = 2.108(6) Å] for the AgBr complexes. These values are somewhat longer than the observed average for five-membered carbene complexes, r_{av} = 2.077(8) Å.[10a,11] The C(1)−Ag−X bond angles show small deviations from linearity, within the range 174.26(18)° to 178.65(11)°. Previously, somewhat shorter C_{NHC}−N bonds have been observed in Ag−carbene complexes when compared to the free ligand. This has been attributed to an increased π-donation of the nitrogen atoms to the carbene π^* orbital upon complexation, caused by donation of electron density from the carbene to the metal.[10a] However, no significant differences are observed in the C_{NHC}−N bond distances of free and coordinated **6-Mes**, with values 1.3464(12) and 1.334(4) Å, respectively,[3d,14] and in the case of **7-Mes** the bond lengths remain virtually unchanged, at

(11) de Fremont, P.; Scott, N. M.; Stevens, E. D.; Ramnial, T.; Lightbody, O. C.; Macdonald, C. L. B.; Clyburne, J. A. C.; Abernethy, C. D.; Nolan, S. P. *Organometallics* **2005**, *24*, 6301.

(12) Crystal data are not given for **7-Xyl** in the main article, due to the poor structure model (R_1 = 0.2097), which however confirms the overall composition and geometry of **7-Xyl**. The CIF file has been included in the Supporting Information.

(13) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

(14) Alder, R. W.; Blake, M. E.; Bortolotti, C.; Bufali, S.; Butts, C. P.; Linehan, E.; Oliva, J. M.; Orpen, A. G.; Quayle, M. J. *Chem. Commun.* **1999**, 241.

Table 4. Selected Bond Lengths (Å) and Angles (deg) of the Free Carbenes and Corresponding Silver Complexes

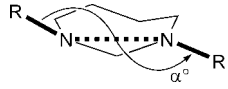
	7-Mes	Ag(**7-Mes**)Br	**6-Mes**[a]	Ag(**6-Mes**)Cl[b]
Ag−C(1)		2.097(6)		2.095(3)
Ag−X		2.3792(11)		2.3213(10)
N(1)−C(1)	1.349(5)	1.346(8)	1.3464(12)	1.338(4)
N(2)−C(1)	1.346(5)	1.347(8)		1.329(4)
N(1)−C(2)	1.483(5)		1.4809(14)	
C(2)−C(3)	1.507(7)		1.5125(16)	
C(3)−C(4)	1.525(7)			
C(4)−C(5)	1.525(7)			
C(5)−N(2)	1.502(6)			
N(1)-C_{Ar}	1.444(5)		1.4381(15)	
N(2)-C_{Ar}	1.438(5)			
N(1)−C(1)−N(2)	116.6(4)	118.8(6)	114.65(13)	118.3(3)
C(1)−Ag−X		174.56(16)		
C(1)−N(1)−C(2)	126.9(4)	129.4(5)	126.28(10)	
C(1)−N(1)−C_{Ar}	115.5(3)	117.0(5)	117.08(9)	119.4(2)
C_{Ar}-N(1)−C(2)	115.5(3)	113.5(5)	116.52(9)	
C(1)−N(2)−C(5)	130.6(4)	124.2(5)		
C(1)−N(2)−C_{Ar}	115.0(4)	117.3(5)		118.5(2)
C(5)−N(2)−C_{Ar}	114.0(3)	116.8(5)		
N(1)−C(2)−C(3)	113.5(4)		108.88(10)	
C(2)−C(3)−C(4)	111.4(4)		108.37(14)	
C(3)−C(4)−C(5)	112.7(4)			
C(4)−C(5)−N(2)	112.6(4)			
C_{Ar}-NN-C_{Ar}(α)	13.6	30.3	0	5.1

[a] **6-Mes** is C_2 symmetric. [b] Selected data included for comparison only, previously reported by Herrmann et al.[3d]

Table 5. Selected Bond Lengths (Å) and Angles (deg) of the Silver Carbene Complexes

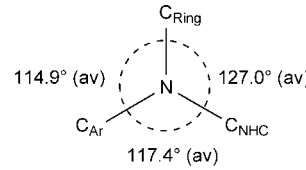
	Ag(**6-Pr^i**)Br	Ag(**7-Xyl**)I	Ag(**Xyl7-Mes**)Br
Ag−C(1)	2.104(6)	2.114(6)	2.122(3)
Ag−X	2.4254(9)	2.5659(7)	2.4475(7)
N(1)−C(1)	1.318(8)	1.329(9)	1.342(4)
N(2)−C(1)	1.340(7)	1.334(8)	1.328(4)
N−C(1)−N	118.8(5)	121.2(5)	121.6(3)
C(1)−Ag−X	174.26(18)	175.92(17)	177.42(9)
C(1)−N(1)−C(2)	125.0(5)	128.8(5)	128.6(3)
C(1)−N(1)−C_{Ar}	118.7(5)	116.8(5)	117.9(3)
C_{Ar}−N(1)−C(2)	116.3(5)	114.0(6)	113.5(3)
C(1)−N(2)−C(5)	123.8(5)	123.7(5)	127.5(3)
C(1)−N(2)−C_{Ar}	120.6(5)	117.8(5)	117.5(3)
C(5)−N(2)−C_{Ar}	115.6(5)	117.5(5)	115.0(3)
C_{Ar}−NN−C_{Ar}(α)	3.4	23.1	3.8

r_{av} = 1.347(8) Å. Another notable feature is the increase in the N−C−N angle upon coordination of the free carbene. The **7-Mes** angle changes from 116.6(4)° to 118.8(6)° in the silver complex, and for **6-Mes** the angle increases from 114.65(13)° to 118.3(3)°.



The coordination geometry of the two nitrogen atoms in the seven-membered carbenes remains nearly planar (in both the free and coordinated form), as evidenced by the observation that the sum of the C−N−C angles is close to 360° (Tables 4 and 5). However, unlike the five- and six-membered carbenes the two nitrogen coordination planes twist to accommodate the ring strain. The torsional angle α between the planes, defined by the C_{Ar}−NN−C_{Ar} atoms, is a measure of this spatial twist and the relative position of the aromatic substituents, which point directly into the metal's coordination sphere. The torsional angle α in **7-Mes** is 13.6°, whereas in Ag(**7-Mes**)Br it is 30.3° (compared with α = 0° for **6-Mes** and α = 5.1° for Ag(**6-Mes**)Cl).

Of interest also is a comparison between the C−N−C angles in seven-membered carbenes with those in five- and six-membered carbenes. Typically, the C_{NHC}−N−C_{Ring} angle in free and coordinated seven-membered carbenes is the largest of the C−N−C angles, with an average value of 127.0° in the silver complexes. Average values for the C_{NHC}−N−C_{Ar} and C_{Ar}−N−C_{Ring} angles are 117.4° and 114.9°, respectively (Tables 4 and 5). Smaller C_{NHC}−N−C_{Ar} values lead to greater steric congestion at the carbene center and influence metal reactivity. The average 117.4° value for C_{NHC}−N−C_{Ar} in the silver complexes is smaller but close to the one for the Ag(**6-Mes**)Cl complex (av 119.0°), although significantly smaller than the typical value of 124° for five-membered carbenes.[10,13]



Conclusions

In summary, a convenient route to a wide range of protonated NHCs from readily available formamidines and dihaloalkanes has been reported. We have also isolated and characterised several examples of free N-heterocyclic carbenes with ring sizes of six and, for the first time, seven atoms. The stability of many of the free carbenes provides several synthetic options for the preparation of transition metal complexes of these new ligands. The upfield shift of the C_{NHC}-*H* signal in the ^{1}H NMR spectrum, for the amidinium salts, as well as the large downfield ^{13}C shift of the carbene (the conjugate base) suggests that these carbenes are extremely strong σ donors. The NCN angle in the large ring carbenes is substantial and represents one of the least bent singlet carbenes so far reported, matched only by sterically hindered acyclic carbenes. Such large (open) NCN angles are likely to lead to substantial steric congestion, which will impact on coordination behavior, complex reactivity, and catalytic performance. Further efforts are currently directed toward the synthesis of carbenes with functionalized backbones and N-substituents. The unique features of the expanded ring carbenes lead to unique properties, and in following publications we report on the synthesis of Pd, Pt, Rh, and Ir complexes and their applications in catalysis.

Experimental Section

General Remarks. All manipulations were performed in air, except where otherwise noted. The solvents thf and hexane (analytical grade) were freshly distilled from sodium/potassium alloy, dichloromethane was distilled from calcium hydride, and the other solvents (acetonitrile, diethyl ether, acetone) were used as purchased. Deuterated solvents for NMR measurements were distilled from the appropriate drying agents under N_2 immediately prior to use following standard literature methods.[15] Air-sensitive compounds were stored and weighed in a glovebox. The amidines bis(2,6-diisopropylphenyl)formamidine, bis(2,6-dimethylphenyl)formamidine, and bis(2,4,6-trimethylphenyl) formamidine were synthesized according to literature methods.[16] The following amidinium salts have been previously prepared via a different route: **6-Mes**·HBr,[3c] **5-Mes**·HBr,[17] **5-Xyl**·HBr,[17] **5-Pr^i**·HBr,[17] **6-Mes**·HBF_4,[3c] **5-Mes**·HBF_4,[18] **5-Xyl**·HBF_4,[19] **5-Pr^i**·HBF_4.[18] All

(15) Perrin, D. D.; Armarego, W. F. A. *Purification of Laboratory Chemicals*; Pergamon: Oxford, 1988.
(16) Edward, T. C.; Wendell, A. E. *J. Org. Chem.* **1963**, *28*, 1108.

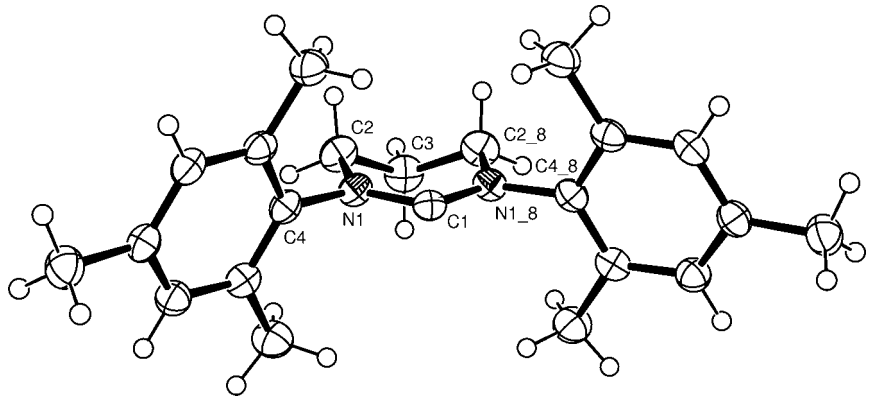


Figure 1. ORTEP ellipsoid plots at 30% probability of the molecular structure of **6-Mes**.

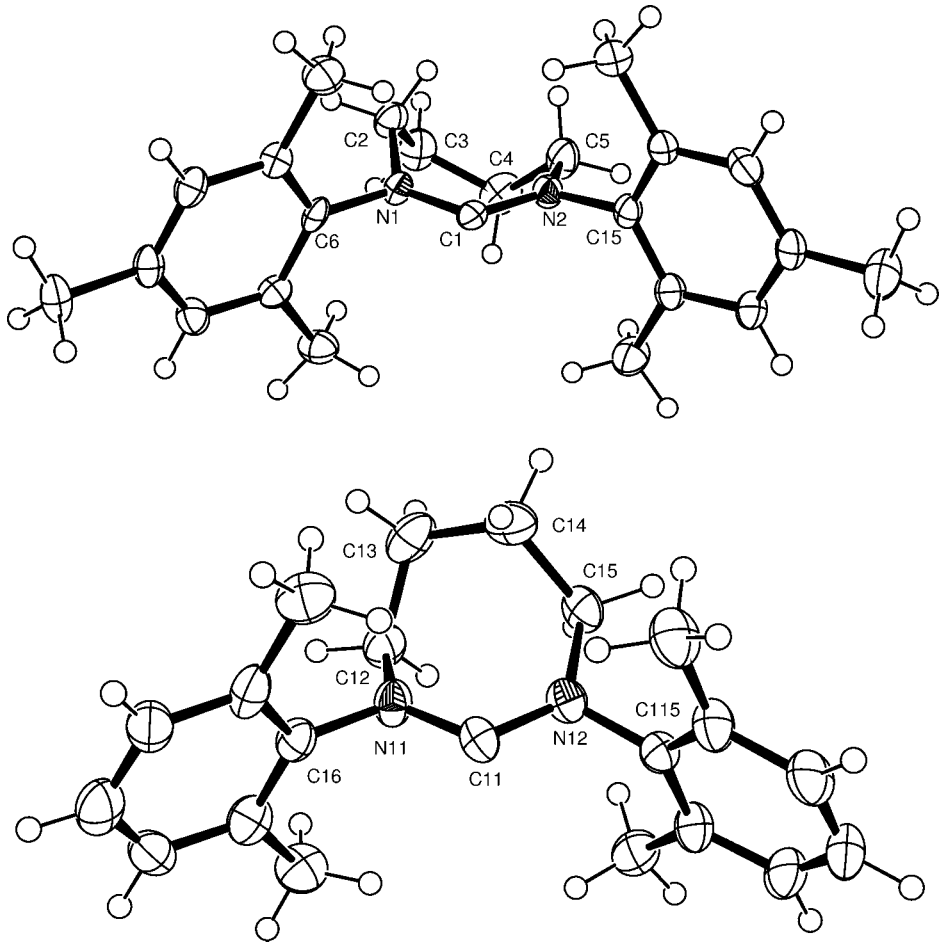


Figure 2. ORTEP ellipsoid plots at 30% probability of the molecular structures of **7-Mes** and **7-Xyl**.

other reagents (1,2-dibromoethane, 1,3-dibromopropane, 1,4-diiodobutane, 2,6-dimethylaniline, 2,4,6-trimethylaniline, 2,6-diisopropylaniline, triethylorthoformate, sodium tetrafluoroborate, and potassium bis(trimethylsilyl)amide) were used as received. ^{1}H and ^{13}C NMR spectra were obtained on Bruker Avance AMX 400 and 500 or Jeol Eclipse 300 spectrometers. The chemical shifts are given as dimensionless δ values and are frequency referenced relative to TMS. Coupling constants J are given in hertz (Hz) as positive values regardless of their real individual signs. Abbreviations used: st = septet, br = broad. Mass spectra (MS) and high-resolution mass spectra (HRMS) were obtained in positive electrospray (ES) mode unless otherwise reported, on a Waters Q-TOF micromass spectrometer.

General Protocol for the Synthesis of the Halide Salts (5-RHX, 6-RHX, and 7-RHX). A mixture of the amidine (11.0 mmol), K_2CO_3 (5.6 mmol), and 1.1 molar equiv of the dihalide in 0.4 L of acetonitrile was heated under reflux overnight. At the end of the reaction, the volatiles were removed *in vacuo*. The residue was dissolved in 50 mL of dichloromethane and filtered through a

(17) Delaude, L.; Szypa, M.; Demonceau, A.; Noels, A. F. *Adv. Synth. Catal.* **2002**, *344* (6+7), 749.

(18) (a) Scholl, M.; Ding, S.; Woo Lee, C.; Grubbs, R. H. *Org. Lett.* **1999**, *1* (6), 953. (b) Viciu, M. S.; Navarro, O.; Germaneau, R. F.; Kelly, R. A., III; Sommer, W.; Marion, N.; Stevens, E. D.; Cavallo, L.; Nolan, S. P. *Organometallics* **2004**, *23*, 1629.

(19) Kingsbury, J. S.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2005**, *127* (12), 4510.

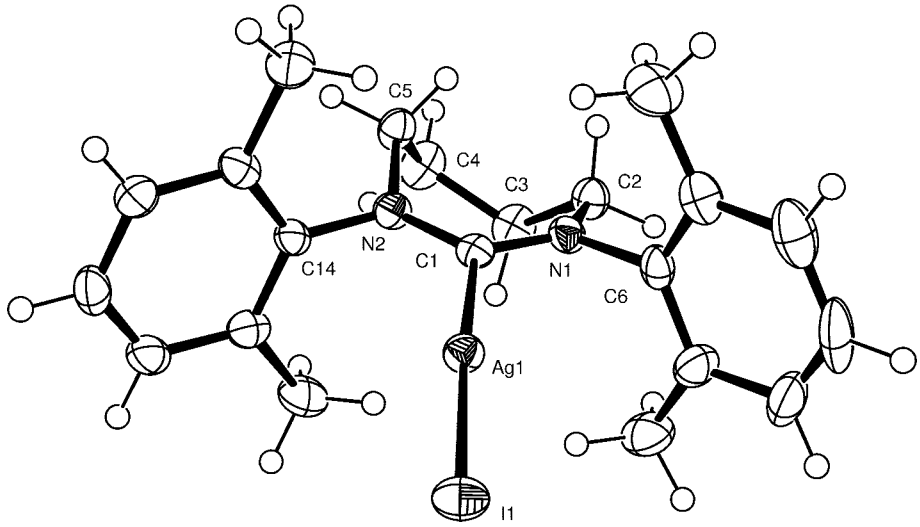


Figure 3. ORTEP ellipsoid plots at 30% probability of the molecular structure of Ag(**7-Xyl**)I.

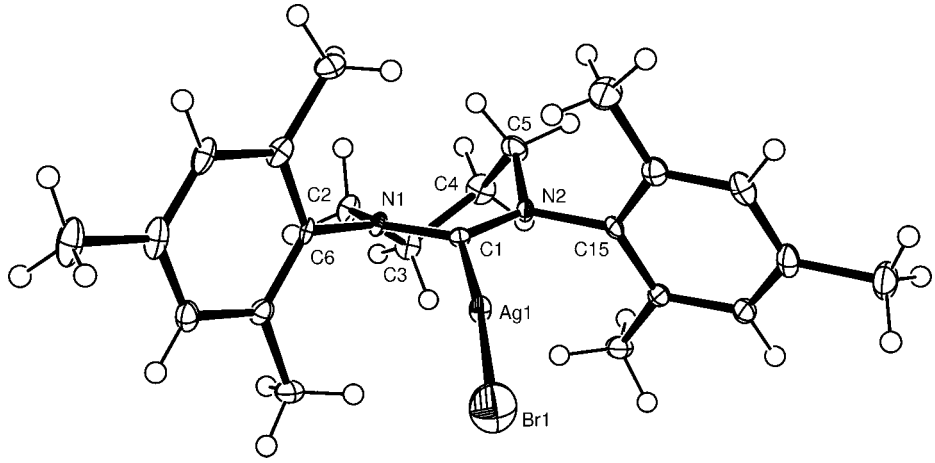


Figure 4. ORTEP ellipsoid plots at 30% probability of the molecular structure of Ag(**7-Mes**)Br.

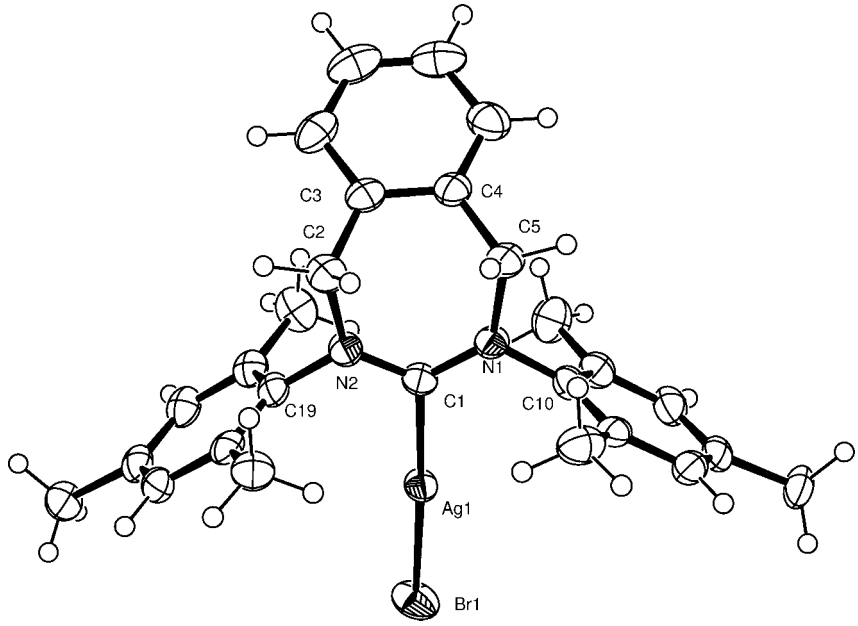


Figure 5. ORTEP ellipsoid plots at 30% probability of the molecular structure of Ag(Xyl**7-Mes**)Br.

short column (0.5 cm) of silica to remove the potassium salts. Addition of diethyl ether to the dichloromethane solution resulted in precipitation of the product as a crystalline white solid.

1,3-Bis(2,4,6-trimethylphenyl)-4,5,6,7-tetrahydro-3*H*-[1,3]diazepin-1-ium Iodide, 7-Mes·HI. Yield: 63.0 mmol (89 %). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.22 (1H, s, NC*H*N), 6.92 (4H,

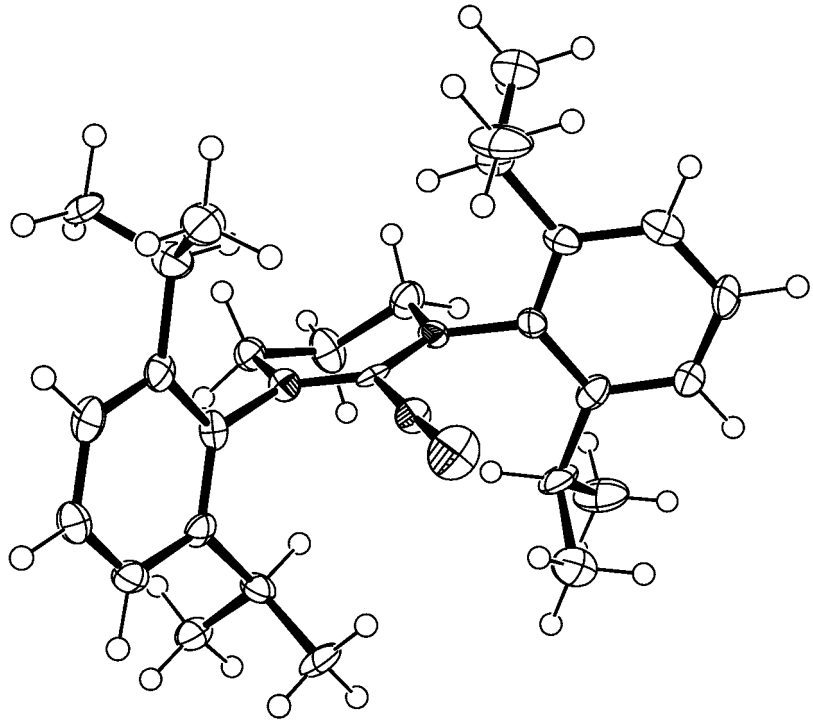


Figure 6. ORTEP ellipsoid plots at 30% probability of the Ag(**6-Pr^i**)Br complex. Solvent molecules have been omitted for clarity.

s, Ar-C*H*), 4.49 (4H, m,$^3J_{HH}$ = 5.4, NCH_2), 2.53 (4H, m, $^3J_{HH}$ = 5.4, NCH$_2$CH_2), 2.37 (s, 12H, *o*-CH_3), 2.24 (s, 6H, *p*-CH_3). ^{13}C NMR (CDCl$_3$, 100 MHz, 298 K): δ 157.8 (s, NC*H*N), 140.3 (s, Ar-*C*), 139.2 (s, Ar-*C*), 133.5 (s, Ar-*C*), 130.2 (s, Ar-*C*H), 55.1 (s, NCH_2), 25.0 (s, NCH$_2$CH_2), 20.8 (s, *p*-CH_3), 18.4 (s, *o*-CH_3). HRMS (ES): *m/z* 335.2477 (M $-$ I$^+$; $C_{23}H_{31}N_2$ requires 335.2487).

1,3-Bis(2,6-dimethylphenyl)-4,5,6,7-tetrahydro-3*H*-[1,3]diazepin-1-ium Iodide, 7-Xyl·HI. Yield: 34.2 mmol (79 %). ^{1}H NMR (CDCl$_3$, 400 MHz, 298 K): δ 7.28 (1H, s, NC*H*N), 7.23 (2H, dd, $^3J_{HH}$ = 6.8, $^3J_{HH}$ = 8.5, *p*-CH), 7.15 (4H, d, $^3J_{HH}$ = 7.6, *m*-CH), 4.61 (4H, m, $^3J_{HH}$ = 5.6, N-CH$_2$), 2.58 (4H, m, $^3J_{HH}$ = 5.6, NCH$_2$CH_2), 2.46 (12H, s, *o*-CH_3). ^{13}C NMR (CDCl$_3$, 100 MHz, 298 K): δ 157.6 (s, NCHN), 141.6 (s, Ar-*C*), 134.0 (s, Ar-*C*), 130.2 (s, Ar-*C*H), 129.7 (s, Ar-*C*H), 55.2 (s, NCH$_2$), 25.1 (s, NCH$_2$CH$_2$), 18.7 (s, *C*H$_3$). HRMS (ES): *m/z* 307.2168 (M $-$ I$^+$; $C_{21}H_{27}N_2$ requires 307.2174).

1,3-Bis(2,6-diisopropylphenyl)-4,5,6,7-tetrahydro-3*H*-[1,3]diazepin-1-ium Iodide, 7-Pr^i·HI. Yield: 7.1 mmol (64 %). ^{1}H NMR (CDCl$_3$, 400 MHz, 298 K): δ 7.40 (2H, m, $^3J_{HH}$ = 7.8, *p*-CH), 7.27 (1H, s, NC*H*N), 7.23 (4H, d, $^3J_{HH}$ = 7.8, *m*-C*H*), 4.63 (4H, br s, NCH_2), 3.20 (4H, st, $^3J_{HH}$ = 6.8, C*H*(CH$_3$)$_2$), 2.60 (4H, br s, NCH$_2$CH_2), 1.39 (12H, d, $^3J_{HH}$ = 6.8, CH(CH_3)$_2$), 1.24 (12H, d, $^3J_{HH}$ = 6.8, CH(CH_3)$_2$). ^{13}C NMR (CDCl$_3$, 100 MHz, 298 K): δ 157.0 (s, NCHN), 144.7 (s, Ar-*C*), 138.7 (s, Ar-*C*), 130.9 (s, Ar-*C*H), 125.3 (s, Ar-*C*H), 56.4 (s, NCH$_2$), 28.9 (s, *C*H(CH$_3$)$_2$), 25.1 (s, CH(CH$_3$)$_2$), 24.7 (s, NCH$_2$CH$_2$), 24.6 (s, CH(CH$_3$)$_2$). HRMS (ES): *m/z* 419.3426 (M $-$ I$^+$; $C_{29}H_{43}N_2$ requires 419.3426).

2,4-Bis(2,4,6-trimethylphenyl)-4,5-dihydro-1*H*-benzo[*e*][1,3]diazepin-2-ium Bromide, Xyl7-Mes·HBr. An alternative synthesis has been reported previously for this compound.[3e] Yield: 26.2 mmol (73%). ^{1}H NMR (CDCl$_3$, 400 MHz, 298 K): δ 7.41$-$7.39 (2H, m, Xy-C*H*), 7.28$-$7.24 (2H, m, Xy-C*H*), 7.13 (1H, s, NC*H*N), 6.94 (4H, s, *m*-C*H*), 2.36 (12H, br s, *o*-CH_3), 2.27 (6H, s, *p*-CH_3). The NCH$_2-$ groups are not observed at 298 K in CDCl$_3$. ^{13}C NMR (CDCl$_3$, 100 MHz, 298 K): δ 155.7 (s, NCHN), 140.4 (s, Ar-*C*), 140.2 (s, Ar-*C*), 135.1 (s, Ar-*C*), 130.0 (s, Ar-*C*H), 129.8 (s, Ar-*C*H), 129.3 (s, Ar-*C*H), 57.9 (s, NCH$_2$), 20.9 (s, *p*-CH_3), 18.9 (s, *o*- CH_3). CH$_2-$C not observed in the ^{13}C DEPT experiment.

2,4-Bis(2,6-dimethylphenyl)-4,5-dihydro-1*H*-benzo[*e*][1,3]diazepin-2-ium Bromide, Xyl7-Xyl·HBr. Yield: 6.9 mmol (87 %). ^{1}H NMR (CDCl$_3$, 400 MHz, 298 K): δ 7.42 (2H, dd, $^3J_{HH}$ = 3.3, $^3J_{HH}$ = 5.5, Xy-C*H*), 7.27 (2H, dd, $^3J_{HH}$ = 3.3, $^3J_{HH}$ = 5.5, Xy-C*H*), 7.22 (2H, m, $^3J_{HH}$ = 7.5, *p*-C*H*), 7.19 (1H, s, NC*H*N), 7.13 (4H, br d, $^3J_{HH}$ = 7.6, *m*-C*H*), 2.35 (12H, br s, CH_3). The NCH$_2-$ groups are not observed at 298 K. ^{13}C NMR (CDCl$_3$, 100 MHz, 298 K): δ 155.6 (s, NCHN), 142.5 (s, Ar-*C*), 134.9 (s, Ar-*C*), 130.1 (s, Ar-*C*H), 130.0 (s, Ar-*C*H), 129.5 (s, Ar-*C*H), 129.3 (s, Ar-*C*H), 57.7 (s, NCH$_2$), 18.9 (s, *C*H$_3$). One Ar-C not observed, NCH$_2$ is not visible in the ^{13}C DEPT experiment. HRMS (ES): *m/z* 355.2158 (M $-$ Br$^+$; $C_{25}H_{27}N_2$ requires 355.2174).

2,4-Bis(2,6-diisopropylphenyl)-4,5-dihydro-1*H*-benzo[*e*][1,3]diazepin-2-ium Bromide, Xyl7-Pr^i·HBr. Yield: 4.9 mmol (45%). ^{1}H NMR (CDCl$_3$, 400 MHz, 298 K): δ 7.90 (1H, s, NCHN), 7.59$-$7.55 (2H, m, Xy-C*H*), 7.56$-$7.45 (4H, m, Xy-C*H* and *p*-C*H*), 7.37 (4H, d, $^3J_{HH}$ = 7.7, *m*-C*H*), 1.97 (4H, st, $^3J_{HH}$ = 2.5, CH(CH_3)$_2$), 1.33 (12H, t, $^3J_{HH}$ = 6.7, CH(CH_3)$_2$), 1.18 (12H, t, $^3J_{HH}$ = 6.7, CH(CH_3)$_2$). The NCH$_2-$ groups are not observed at 298 K. ^{13}C NMR (CDCl$_3$, 100 MHz, 298 K): δ 155.0 (1C, s, NCHN), 139.5 (s, Ar-*C*), 134.4 (s, Ar-*C*), 130.8 (s, Ar-*C*H), 129.8 (s, Ar-CH), 129.2 (s, Ar-CH), 125.2 (2s, Ar-CH), 58.8 (s, NCH$_2$), 28.6 (s, *C*H(CH$_3$)$_2$), 25.3 (s, CH(*C*H$_3$)$_2$), 24.6 (s, CH(*C*H$_3$)$_2$). HRMS (ES): *m/z* 467.3420 (M $-$ Br$^+$; $C_{33}H_{43}N_2$ requires 467.3426).

1,3-Bis(2,6-dimethylphenyl)-3,4,5,6-tetrahydropyrimidin-1-ium Bromide, 6-Xyl·HBr. Yield: 6.2 mmol (69 %). ^{1}H NMR (CDCl$_3$, 400 MHz, 298 K): δ 7.68 (1H, s, NC*H*N), 7.23 (2H, dd, $^3J_{HH}$ = 7.1, $^3J_{HH}$ = 8.1, *p*-C*H*), 7.12 (4H, br d, $^3J_{HH}$ = 7.6, *m*-C*H*), 4.21 (4H, m, $^3J_{HH}$ = 5.6, NCH_2), 2.61 (2H, m, $^3J_{HH}$ = 5.6, NCH$_2$CH_2), 2.38 (12H, s, CH_3). ^{13}C NMR (CDCl$_3$, 100 MHz, 298 K): δ 153.3 (s, NCHN), 138.6 (s, Ar-*C*), 134.7 (s, Ar-*C*), 130.3 (s, Ar-*C*H), 129.4 (s, Ar-*C*H), 46.7 (s, NCH$_2$), 19.4 (s, NCH$_2$CH$_2$), 18.0 (*C*H$_3$). HRMS (ES): *m/z* 293.2014 (M $-$ Br$^+$; $C_{20}H_{25}N_2$ requires 293.2018).

1,3-Bis(2,6-diisopropylphenyl)-3,4,5,6-tetrahydropyrimidin-1-ium Bromide, 6-Pr^i·HBr. Yield: 4.9 mmol (71%). ^{1}H NMR (CDCl$_3$, 400 MHz, 298 K): δ 7.55 (1H, s, NC*H*N), 7.41 (2H, m, $^3J_{HH}$ = 7.7, *p*-C*H*), 7.23 (4H, d, $^3J_{HH}$ = 7.7, *m*-C*H*), 4.21 (4H, m, $^3J_{HH}$ = 5.5, NCH_2), 3.00 (4H, st, $^3J_{HH}$ = 6.75, C*H*(CH$_3$)$_2$), 2.74

(2H, m, $^3J_{HH}$ = 5.5, NCH_2CH_2), 1.35 (d, $^3J_{HH}$ = 6.75, 12H, $CH(CH_3)_2$), 1.20 (d, $^3J_{HH}$ = 6.75, 12H, $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 152.8 (s, NCHN), 145.5 (s, Ar-*C*), 135.6 (s, Ar-*C*), 131.2 (s, Ar-*C*H), 125.1 (s, Ar-*C*H), 48.8 (s, NCH_2), 28.8 (s, $CH(CH_3)_2$), 24.8 (s, $CH(CH_3)_2$), 24.7 (s, $CH(CH_3)_2$), 19.3 (1C, s, NCH_2CH_2). HRMS (ES): *m/z* 405.3265 ($M - Br^+$; $C_{28}H_{41}N_2$ requires 405.3270).

1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydro-3*H*-imidazol-1-ium Bromide, 5-Mes·HBr. Yield: 27.1 mmol (76 %). Spectroscopic data for **5-Mes**·HBr are in agreement with those reported in the literature.[17]

1,3-Bis(2,6-dimethylphenyl)-4,5-dihydro-3*H*-imidazol-1-ium Bromide, 5-Xyl·HBr. Yield: 7.1 mmol (69%) of a light yellow, crystalline material. Spectroscopic data for **5-Xyl**·HBr are in agreement with those reported in the literature.[17]

1,3-Bis(2,6-diisopropylphenyl)-4,5-dihydro-3*H*-imidazol-1-ium Bromide, 5-Pr^i·HBr. Yield: 7.3 mmol (94 %). Spectroscopic data for **5-Pr^i**·HBr are in agreement with those reported in the literature.[17]

General Protocol for the Anion Exchanges. The halide salt was dissolved in acetone or acetonitrile, and a water solution of an excess of $NaBF_4$ added. After stirring the solution for 5−10 min the organic solvent was removed *in vacuo*. The residue was dissolved in dichloromethane and washed several times with water. The organic solution was subsequently collected and dried over $MgSO_4$. After filtration of the $MgSO_4$, ether was added to precipitate the product as a white crystalline powder. Individual synthetic procedures and spectroscopic data for all $^-BF_4$ salts can be found in the Supporting Information.

General Protocol for the Isolation of Free Carbenes. All manipulations for the preparation of the free carbenes were performed using standard Schlenk techniques under an argon atmosphere. To a suspension of 1.0 mmol of the amidinium tetrafluoroborate salt in 15−20 mL of THF was added 1.0 mmol of $KN(SiMe_3)_2$. The resulting suspension was stirred for 30 min, after which the volatiles were evaporated. Et_2O (15−20 mL) was added to the residue to dissolve the free carbene, and any undissolved material was filtered off. The filtrate was partially evaporated under reduced pressure until the solution became cloudy, then left at −30 °C to form colorless crystals of the product. The crystals were then isolated by filtration and dried *in vacuo*. Due to the unstable nature of the free carbenes, elemental analyses data could not be obtained.

7-Mes. Yield: 0.9 mmol (56%). ^1H NMR (C_6D_6, 400 MHz, 298 K): δ 6.96 (4H, s, Ar-C*H*), 3.40 (4H, m, NCH_2), 2.43 (12H, s, *o*-CH_3), 2.30 (6H, s, *p*-CH_3), 1.81 (4H, br s, NCH_2CH_2). ^{13}C NMR (C_6D_6, 100 MHz, 298 K): δ 257.3 (s, NCHN), 148.1 (s, Ar-*C*), 135.3 (s, Ar-*C*), 134.5 (s, Ar-*C*), 129.6 (s, Ar-C*H*), 51.6 (s, NCH_2), 26.9 (s, NCH_2CH_2), 21.0 (s, *p*-Me), 18.9 (s, *o*-Me).

7-Xyl. Yield: 0.67 mmol (67%). ^1H NMR (C_6D_6, 400 MHz, 298 K): δ 7.03 (6H, m, *m*-Ar-C*H* and *p*-Ar-C*H*), 3.26 (4H, m, $^3J_{HH}$ = 5.7, NCH_2), 2.31 (12H, s, CH_3), 1.68 (4H, p, $^3J_{HH}$ = 5.7, NCH_2CH_2). ^{13}C NMR (C_6D_6, 100 MHz, 298 K): δ 258.8 (s, NCHN), 150.5 (s, Ar-*C*), 135.0 (s, Ar-*C*), 128.8 (s, Ar-*C*H), 126.2 (s, Ar-*C*H), 51.3 (s, NCH_2), 27.0 (s, NCH_2CH_2), 18.9 (s, CH_3).

7-Pr^i. Yield: 0.61 mmol (61%). ^1H NMR (C_6D_6, 400 MHz, 298 K): δ 7.22 (2H, dd, $^3J_{HH}$ = 6.6, $^3J_{HH}$ = 8.5, *p*-Ar-CH), 7.13 (4H, m, $^3J_{HH}$ = 1.24, *m*-Ar-C*H*), 3.56 (4H, st, $^3J_{HH}$ = 6.9, $CH(CH_3)_2$), 3.48 (4H, br m, $^3J_{HH}$ = 5.4, NCH_2), 1.80 (4H, m, $^3J_{HH}$ = 5.4, NCH_2CH_2), 1.29 (12H, d, $^3J_{HH}$ = 6.9, $CH(CH_3)_2$), 1.24 (12H, d, $^3J_{HH}$ = 6.9, $CH(CH_3)_2$). ^{13}C NMR (C_6D_6, 100 MHz, 298 K): δ 260.2 (s, NCHN), 148.1 (s, Ar-*C*), 145.4 (s, Ar-C), 127.0 (s, *m*-Ar-*C*H), 124.1 (s, *p*-Ar-*C*H), 53.2 (s, NCH_2), 28.7 (s, $CH(CH_3)_2$), 26.5 (s, NCH_2CH_2), 24.8 (s, $CH(CH_3)_2$), 24.6 (s, $CH(CH_3)_2$).

6-Mes. Yield: 1.51 mmol (73%). ^1H NMR (C_6D_6, 400 MHz, 298 K): δ 6.84 (4H, s, Ar-C*H*), 2.73 (4H, m, $^3J_{HH}$ = 6.0, NCH_2), 2.30 (12H, s, *o*-CH_3), 2.17 (6H, s, *p*-CH_3), 1.66 (2H, m, $^3J_{HH}$ = 6.0, NCH_2CH_2). ^{13}C NMR (C_6D_6, 100 MHz, 298 K): δ 244.9 (1s, NCHN), 145.7 (s, Ar-*C*), 135.5 (s, Ar-*C*), 135.2 (s, Ar-*C*), 129.3 (s, Ar-C*H*), 42.1 (s, NCH_2), 21.8 (s, NCH_2CH_2), 20.7 (s, *p*-CH_3), 17.9 (s, *o*-CH_3).

6-Xyl. Yield: 1.28 mmol (27 %). ^1H NMR (C_6D_6, 400 MHz, 298 K): δ 6.04 (6H, m, *m*-Ar-C*H* and *p*-Ar-C*H*), 2.67 (4H, m, $^3J_{HH}$ = 6.0, NCH_2), 2.28 (12H, s, CH_3), 1.60 (2H, m, $^3J_{HH}$ = 6, NCH_2CH_2). ^{13}C NMR (C_6D_6, 100 MHz, 298 K): δ 244.5 (s, NCHN), 147.9 (s, Ar-*C*), 135.6 (s, Ar-*C*), 128.7 (s, *m*-Ar-C*H*), 126.6 (s, *p*-Ar-C*H*), 41.8 (s, NCH_2), 22.1 (s, NCH_2CH_2), 18.3 (s, CH_3).

5-Xyl. Yield: 0.42 mmol (45%). ^1H NMR (C_6D_6, 400 MHz, 298 K): δ 7.02 (6H, br s, *m*-Ar-C*H* and *p*-Ar-*C*H), 3.17 (4H, s, NCH_2), 2.26 (12H, s, *o*-CH_3). ^{13}C NMR (C_6D_6, 100 MHz, 298 K): δ 242.0 (s, NCHN), 141.7 (s, Ar-*C*), 136.6 (s, Ar-*C*), 128.8 (s, Ar-*C*H), 127.4 (2s, Ar-*C*H), 50.5 (s, NCH_2), 18.3 (CH_3).

General Protocol for the Synthesis of the Silver Complexes. The mixture obtained from the addition of the amidinium tetrafluouroborate salt (1.0 mmol), Ag_2O (0.5−1.0 mmol), and NaBr (5.0 mmol) in 25 mL of dichloromethane was stirred in the dark for 3 days. The resulting off-white precipitate was filtered and washed with three 25 mL portions of dichloromethane. The combined filtrates were collected, and the solvent was reduced until the solution became cloudy. Subsequently hexane was added to afford after crystallization colorless crystals of the product.

Ag(7-Mes)Br. Yield: 2.3 mmol (78%). ^1H NMR ($CDCl_3$, 400 MHz, 298 K): δ 6.84 (4H, s, Ar-C*H*), 3.85 (4H, m, $^3J_{HH}$ = 5.4, NCH_2), 2.25 (12H, s, *o*-CH_3), 2.23 (4H, m, $^3J_{HH}$ = 5.4, NCH_2), 2.18 (6H, s, *p*-CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 218.6 (dd, $^1J_{C^{107}Ag}$ = 226, $^1J_{C^{109}Ag}$ = 262, NCHN), 145.6 (s, Ar-*C*), 138.3 (s, Ar-*C*), 134.3 (s, Ar-*C*), 130.4 (s, Ar-*C*H), 52.8 (s, NCH_2), 25.9 (s, NCH_2CH_2), 21.4 (s, *p*-CH_3), 18.9 (s, *o*-CH_3). HRMS (ES): *m/z* 482.1715 [M − Br + CH_3CN]$^+$ (5%) ($C_{25}H_{33}N_3Ag$ requires 482.1725); 335.2397 [(**7-Mes**)H]$^+$ (100%).

[Ag(7-Mes)$_2$]BF$_4$. Yield: 0.38 mmol (75%). ^1H NMR ($CDCl_3$, 500 MHz, 298 K): δ 6.84 (4H, s, Ar-C*H*), 3.57 (4H, m, NCH_2), 2.29 (6H, s, *p*-CH_3), 2.00 (4H, m, NCH_2), 1.75 (12H, s, *p*-CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K): δ 215.4 (dd, $^1J_{C^{107}Ag}$ = 178, $^1J_{C^{109}Ag}$ = 205, NCHN), 144.8 (s, Ar-*C*), 137.6 (s, Ar-*C*), 133.6 (s, Ar-*C*), 130.1 (s, Ar-*C*H), 52.4 (s, NCH_2), 25.2 (s, NCH_2CH_2), 20.9 (s, *p*-CH_3), 18.8 (s, *o*-CH_3).

Ag(7-Xyl)Br and [Ag(7-Xyl)$_2$][AgBr$_2$]. Yield: 4.4 mmol (70%). The ratio of the title compounds in solution was 78% and 22%, respectively. ^1H NMR ($CDCl_3$, 400 MHz, 298 K): δ Ag(**7-Xyl**)Br 7.16−6.93 (6H, m, Ar-C*H*), 3.90 (4H, m, $^3J_{HH}$ = 5.6, NCH_2), 2.32 (12H, s, CH_3), 2.28 (4H, m, $^3J_{HH}$ = 2.8, NCH_2CH_2); [Ag(**7-Xyl**)$_2$][$AgBr_2$] 7.16−6.93 (6H, m, Ar-C*H*), 3.61 (4H, m, $^3J_{HH}$ = 5.6, NCH_2), 2.02 (4H, m, $^3J_{HH}$ = 2.8, NCH_2CH_2), 1.64 (12H, s, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): Ag(**7-Xyl**)Br δ 147.9 (s, Ar-*C*), 134.9 (s, Ar-*C*), 129.9 (s, Ar-*C*H), 128.8 (s, Ar-*C*H) 52.8 (s, NCH_2), 26.0 (s, NCH_2CH_2), 19.1 (s, CH_3); [Ag(**7-Xyl**)$_2$][$AgBr_2$] 210.1 (dd, $^1J_{C^{107}Ag}$ = 179, $^1J_{C^{109}Ag}$ = 206, NCHN), 147.4 (s, Ar-*C*), 134.7 (s, Ar-*C*), 127.9 (s, Ar-*C*H), 128.6 (s, Ar-*C*H), 52.7 (s, NCH_2), 25.7 (s, NCH_2CH_2), 19.0 (s, CH_3). HRMS (ES): *m/z* 454.1434 ([M − Br + CH_3CN]$^+$; $C_{23}H_{29}N_3Ag$ requires 454.1412).

Ag(7-Pr^i)Br. 7-Pr^i. Yield: 1.35 mmol (62%) of the product as a white microcrystalline material. ^1H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.35 (2H, m, $^3J_{HH}$ = 7.9, *p*-Ar-C*H*), 7.12 (4H, d, $^3J_{HH}$ = 7.7, *m*-C*H*), 3.96 (4H, m, NCH_2), 3.18 (4H, st, $^3J_{HH}$ = 6.9, $CH(CH_3)_2$), 2.29 (4H, m, NCH_2CH_2), 1.28 (d, $^3J_{HH}$ = 6.9, 12H, $CH(CH_3)_2$), 1.25 (d, $^3J_{HH}$ = 6.9, 12H, $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 145.3 (s, Ar-*C*), 145.1 (s, Ar-*C*), 129.6 (s, Ar-*C*H), 125.4 (s, Ar-*C*H), 54.2(s, NCH_2), 29.1 (s, $CH(CH_3)_2$), 25.6 (s, $CH(CH_3)_2$), 25.3 (s, NCH_2CH_2), 25.1 (s, $CH(CH_3)_2$). HRMS (ES): *m/z* 566.2689 [M − Br + CH_3CN]$^+$ (100%) ($C_{31}H_{45}N_3Ag$ requires 566.2664).

Ag(Xyl7-Mes)Br. Yield: 1.36 mmol (42%). ^1H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.39 (2H, dd, $^3J_{HH}$ = 3.3, $^3J_{HH}$ = 5.4, Ar-C*H*), 7.21 (2H, dd, $^3J_{HH}$ = 5.4, $^3J_{HH}$ = 3.3, Ar-C*H*), 6.9 (4H, s,

Table 6. Crystal Data and Structure Refinement Details for 6-Mes, 7-Mes, Ag(6-Pr^i)Br, Ag(7-Xyl)I, Ag(7-Mes)Br, and Ag(Xyl7-Mes)Br

	6-Mes	**7-Mes**	Ag(**6-Pr^i**)Br	Ag(**7-Xyl**)I	Ag(**7-Mes**)Br	Ag(**Xyl7-Mes**)Br
empirical formula	$C_{22}H_{28}N_2$	$C_{23}H_{30}N_2$	$C_{28}H_{40}AgBrC_{l3}N_2$-$CHCl_3$	$C_{21}H_{26}AgIN_2$	$C_{23}H_{30}AgBrN_2$	$C_{27}H_{30}AgBrN_2$
fw/g mol^{-1}	320.46	334.49	711.76	541.21	522.27	570.31
cryst syst, space group	orthorhombic *Pnma*	orthorhombic $P2_12_12_1$	orthorhombic $P2_12_12_1$	orthorhombic $Pna2_1$	monoclinic $P2_1/n$	monoclinic $P2_1/n$
a/Å	9.870(2)	8.3994(6)	10.7457(3)	16.288	8.49590(10)	9.902(2)
b/Å	22.911(5)	10.5190(6)	16.7230(5)	15.495	19.0544(2)	17.068(3)
c/Å	8.2427(16)	22.0339(14)	17.9327(6)	8.3719	13.9272(2)	15.940(3)
α/deg	90	90	90	90	90	90
β/deg	90	90	90	90	104.7750(10)	107.68(3)
γ/deg	90	90	90	90	90	90
vol/Å^3	1863.9(6)	1946.8(2)	3222.51(17)	2112.9(7)	2180.05(5)	2566.8(9)
Z, calc density (Mg m^{-3})	4, 1.142	4, 1.141	4, 1.467	4, 1.701	4, 1.591	4, 1.476
abs coeff (mm^{-1})	0.066	0.066	2.134	2.421	2.767	2.358
F(000)	696	728	1448	1064	1056	1152
cryst	block, colorless	block, colorless	block, colorless	block, colorless	block, colorless	block, colorless
cryst dimens/mm^3	0.50 × 0.30 × 0.20	0.14 × 0.12 × 0.10	0.20 × 0.25 × 0.25	0.25 × 0.11 × 0.08	0.40 × 0.20 × 0.10	0.50 × 0.50 × 0.25
θ range (deg)	3.22−27.00	3.05−27.48	2.96−27.46	3.04−27.00	3.03−27.50	2.94−27.00
no. of reflns collected/unique	3811/2082	13 264/2541	15 340/7224	13 456/4175	29 583/4970	10 259/5524
R_{int}	0.0222	0.0677	0.085	0.1102	0.0353	0.0282
no. of data/restraints/params	2082/0/115	2541/0/232	7224/0/325	4175/1/231	4970/0/251	5524/0/286
final *R* indices [$F^2 < 2\sigma(F^2)$]: R_1, wR_2	0.0410, 0.1046	0.0819, 0.1367	0.0853, 0.1397	0.0452, 0.1049	0.0749, 0.2259	0.0414, 0.1028
R indices (all data) : R_1, wR_2	0.0521, 0.1115	0.1178, 0.1542	0.09486, 0.1397	0.0529, 0.1096	0.0807, 0.2322	0.0483, 0.1066

Ar-C*H*), 4.99 (4H, s, NCH_2), 2.27 (6H, s, *p*-CH_3), 2.23 (12H, s, *o*-CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): *δ* 146.5 (s, Ar-*C*), 138.1 (s, Ar-*C*), 135.8 (s, Ar-*C*), 133.6 (s, Ar-*C*), 130.0 (s, Ar-*C*H), 129.4 (s, Ar-*C*H), 128.1 (s, Ar-*C*H), 55.3 (s, N*C*H$_2$), 21.0 (*p*-CH_3), 18.5 (*o*-CH_3). HRMS (ES): *m/z* 530.1750 [M − Br + CH_3CN]$^+$ (5%) ($C_{29}H_{33}N_3Ag$ requires 530.1725); 383.2434 [(**Xyl7-Mes**) + H]$^+$ (100%).

Ag(7-Xyl)Br and [Ag(7-Xyl)$_2$][AgBr$_2$]. Yield: 4.4 mmol (70%). The ratio of the title compounds in solution was 78% and 22%, respectively. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): *δ* Ag(**7-Xyl**)Br 7.16−6.93 (6H, m, Ar-C*H*), 3.90 (4H, t, $^3J_{HH}$ = 5.6, NCH_2), 2.32 (12H, s, CH_3), 2.28 (4H, p, $^3J_{HH}$ = 2.8, NCH_2CH_2); [Ag(**7-Xyl)$_2$**][$AgBr_2$] 7.16−6.93 (6H, m, Ar-C*H*), 3.61 (4H, t, $^3J_{HH}$ = 5.6, NCH_2), 2.02 (4H, pent., $^3J_{HH}$ = 2.8, NCH_2CH_2), 1.64 (12H, s, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): *δ* Ag(**7-Xyl**)Br 147.9 (s, Ar-*C*), 134.9 (s, Ar-*C*), 129.9 (s, Ar-*C*H), 128.8 (s, Ar-*C*H) 52.8 (s, NCH_2), 26.0 (s, NCH_2CH_2), 19.1 (s, CH_3); [Ag(**7-Xyl**)$_2$][$AgBr_2$] 210.1 (dd, $^1J_{C^{107}Ag}$ = 206, $^1J_{C^{109}Ag}$ = 179, N*C*HN), 147.4 (s, Ar-*C*), 134.7 (s, Ar-*C*), 127.9 (s, Ar-*C*H), 128.6 (s, Ar-*C*H), 52.7 (s, N*C*H$_2$), 25.7 (s, NCH_2CH_2), 19.0 (s, CH_3). HRMS (ES): *m/z* 454.1434 ([M − Br + CH_3CN]$^+$; $C_{23}H_{29}N_3Ag$ requires 454.1412).

Ag(Xyl7-Pr^i)Br. Yield: 0.54 mmol (18%) of the product as a white microcrystalline material. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): *δ* 7.42 (2H, dd, $^3J_{HH}$ = 3.3, $^3J_{HH}$ = 5.5, Xy-C*H*), 7.35 (2H, m, $^3J_{HH}$ = 7.7, *p*-Ar-C*H*), 7.23 (2H, dd, $^3J_{HH}$ = 5.5, $^3J_{HH}$ = 3.3, Xy-C*H*) overlapping with 7.20 (4H, d, $^3J_{HH}$ = 7.7, *m*−Ar-C*H*), 5.07 (4H, br s, $\Delta\nu_{1/2}$ = 16.8 Hz, NCH_2), 3.12 (4H, st, $^3J_{HH}$ = 6.7, C*H*(CH_3)$_2$), 1.29 (12H, d, $^3J_{HH}$ = 6.7, CH(CH_3)$_2$), 1.28 (12H, d, $^3J_{HH}$ = 6.7, CH(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): *δ* 144.8 (s, Ar-*C*), 143.5 (s, Ar-*C*), 134.2 (s, Ar-*C*), 128.3 (s, Ar-*C*H), 127.2 (s, Ar-*C*H), 124.1 (s, Ar-*C*H), 55.8 (s, NCH_2), 27.6 (s, *C*H(CH_3)$_2$), 24.0 (s, CH(*C*H_3)$_2$), 23.9 (s, CH(*C*H_3)$_2$). HRMS (ES): *m/z* 614.2650 [M − Br + CH_3CN]$^+$ (100%) ($C_{35}H_{45}N_3Ag$ requires 614.2664).

Ag(6-Mes)Br and [Ag(6-Mes)$_2$][AgBr$_2$]. The synthesis of Ag(**6-Mes**)Br has been previously reported.[3c] Yield: 2.1 mmol (49%). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): *δ* [Ag(**6-Mes**)$_2$][$AgBr_2$] 6.83 (4H, s, Ar-C*H*), 3.10 (4H, m, J_{HH} = 5.8, NCH_2), 2.27 (6H, s, *o*-CH_3), 2.09 (2H, m, J_{HH} = 5.4, NCH_2CH_2), 1.69 (s, 12H, *p*-CH_3), Ag(**6-Mes**)Br 7.20 (4H, m, Ar-C*H*), 3.45 (4H, m, NCH_2), 2.38 (2H, m, NCH_2CH_2), 2.33 (18H, s, *o*/*p*-CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): *δ* [Ag(**6-Mes**)$_2$][$AgBr_2$] 218.6 (dd, $^1J_{C^{107}Ag}$ = 174, $^1J_{C^{109}Ag}$ = 201, N*C*HN), 141.3 (s, Ar-*C*), 137.1(s, Ar-C), 133.6 (s, Ar-*C*), 128.6 (s, Ar-*C*H), 42.6 (s, N*C*H$_2$), 20.0 (s, *p*-CH_3), 19.5 (s, NCH_2CH_2), 16.6 (s, *o*-CH_3). HRMS (ES): *m/z* 747.3592 [M + (**6-Mes**) − Br]$^+$ (100%) ($C_{44}H_{56}N_4Ag$ requires 747.3556).

Ag(6-Xyl)Br. Yield: 2.16 mmol (72%). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): *δ* 7.22-7.13 (6H, m, Ar-C*H*), 3.45 (4H, m, $^3J_{HH}$ = 5.9, NCH_2), 2.38 (2H, m, $^3J_{HH}$ = 5.5, NCH_2CH_2), 2.32 (12H, s, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): *δ* 206.4 (dd, $^1J_{C^{107}Ag}$ = 224, $^1J_{C^{109}Ag}$ = 259, N*C*HN), 145.4 (s, Ar-*C*), 135.1 (s, Ar-*C*), 129.7 (s, Ar-*C*H), 129.1 (s, Ar-*C*H), 44.3 (s, N*C*H$_2$), 21.1 (s, NCH_2CH_2), 18.4 (s, CH_3). HRMS (ES): *m/z* 478.0163 [M]$^+$ (100%) ($C_{20}H_{24}N_2AgBr$ requires 478.0174).

Ag(6-Pr^i)Br. Yield: 2.34 mmol (74%). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): *δ* 7.37 (2H, m, $^3J_{HH}$ = 7.8, *p*-Ar-C*H*), 7.21 (4H, d, $^3J_{HH}$ = 7.8, *o*-Ar-C*H*), 3.47 (4H, m, $^3J_{HH}$ = 5.7, NCH_2), 3.05 (4H, st, $^3J_{HH}$ = 6.9, C*H*(CH_3)$_2$), 2.39 (2H, qt., $^3J_{HH}$ = 5.7, NCH_2CH_2), 1.34 (d, $^3J_{HH}$ = 6.9, 12H, CH(CH_3)$_2$), 1.31 (d, $^3J_{HH}$ = 6.9, 12H, CH(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): *δ* 145.3 (s, Ar-*C*), 129.5 (s, Ar-*C*H), 124.9 (s, Ar-*C*H), 46.0 (s, N*C*H$_2$), 28.6 (s, *C*H(CH_3)$_2$), 25.0 (s, *C*H(*C*H_3)$_2$), 24.7 (s, *C*H(*C*H_3)$_2$), 20.4 (s, NCH_2CH_2). HRMS (ES): *m/z* 554.2528 [M − Br + CH_3CN]$^+$ (100%) ($C_{30}H_{43}N_3Ag$ requires 554.2505).

Ag(5-Mes)Br and [Ag(5-Mes)$_2$][AgBr$_2$]. Yield: 1.68 mmol (84%). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): *δ* [Ag(**5-Mes**)$_2$][$AgBr_2$] 6.80 (4H, s, Ar-C*H*), 3.82 (4H, m, NCH_2), 2.30 (6H, s, *p*-CH_3), 1.78 (12H, s, *o*-CH_3); [Ag(**5-Mes**)Br] 6.88 (4H, s, Ar-C*H*), 3.93 (4H, m, NCH_2), 2.23 (18H, s, *o*/*p*-CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): *δ* [Ag(**5-Mes**)$_2$][$AgBr_2$] 207.0 (dd, $^1J_{C^{107}Ag}$ = 167, $^1J_{C^{109}Ag}$ = 193, N*C*HN), 138.7 (s, Ar-*C*), 135.4 (s, Ar-*C*), 135.8 (s, Ar-*C*), 129.7 (s, Ar-CH), 50.5 (s, N*C*H$_2$), 21.5 (s, *p*-*C*H_3), 17.7 (s, *o*-*C*H_3); Ag(**5-Mes**)Br 139.1 (s, Ar-*C*), 135.2 (s, Ar-*C*), 130.1 (s, Ar-CH), 50.6 (s, N*C*H$_2$), 21.4 (s, *p*-*C*H_3), 18.3 (s, *o*-*C*H_3). HRMS (ES): *m/z* 719.3234 [M + (**5-Mes**) − Br]$^+$ (100%) ($C_{42}H_{52}N_4Ag$ requires 719.3243).

Ag(5-Xyl)Br. Yield: 0.57 mmol (57%). The ratio of the title compounds in solution was 70% and 30%, respectively. ^{1}H NMR (CD_2Cl_2, 400 MHz, 298 K): *δ* [Ag(**5-Xyl**)$_2$][$AgBr_2$] 7.18 (4H, m, $^3J_{HH}$ = 7.0, Ar-C*H*), 6.81 (8H, d, $^3J_{HH}$ = 7.0, Ar-C*H*), 3.82 (8H, m, NCH_2), 1.84 (24H, s, CH_3); Ag(**5-Xyl**)Br 7.18 (2H, m, $^3J_{HH}$ = 7.6, Ar-C*H*), 6.81 (4H, d, $^3J_{HH}$ = 7.6, Ar-C*H*), 3.99 (4H, m, NCH_2), 2.29 (12H, s, CH_3). ^{13}C NMR (CD_2Cl_2, 100 MHz, 298 K): *δ* [Ag(**5-Xyl**)$_2$][$AgBr_2$] 138.0 (s, Ar-*C*), 136.6 (s, Ar-*C*H), 129.7 (s, Ar-*C*H), 51.8 (s, N*C*H$_2$), 19.2 (s, *C*H$_3$). Ag(**5-Xyl**)Br 138.6 (s, Ar-*C*), 137.0 (s, Ar-*C*H), 129.8 (s, Ar-*C*H), 51.9 (s, N*C*H$_2$), 19.7 (s, *C*H$_3$). HRMS (ES): *m/z* 663.2624 [M + (**5-Xyl**) − Br]$^+$ (70%) ($C_{38}H_{44}N_4Ag$ requires 663.2617), 426.12 [M + CH_3CN − Br]$^+$ (100%).

Ag(5-Pr^i)Br. Yield: 0.32 mmol (84%). ^{1}H NMR (DMSO-d_6, 400 MHz, 298 K): *δ* 7.41 (2H, m, $^3J_{HH}$ = 7.8, *p*-Ar-C*H*), 7.25 (4H, d, $^3J_{HH}$ = 7.7, *m*-Ar-C*H*), 4.07 (4H, s, NCH_2), 3.05 (4H, st,

$^3J_{HH}$ = 6.9, C*H*(CH_3)$_2$), 1.35 (12H, d, $^3J_{HH}$ = 1.6, CH(CH_3)$_2$), 1.33 (12H, d, $^3J_{HH}$ = 1.6, CH(CH_3)$_2$). ^{13}C NMR (DMSO-d_6, 100 MHz, 298 K): δ 146.5 (2C, s, Ar-*C*), 134.4 (4C, s, Ar-*C*H), 130.1 (4C, s, Ar-*C*), 124.7 (2C, s, Ar-*C*H), 53.9 (2C, s, N*C*H$_2$), 28.9 (4C, s, *C*H(CH_3)$_2$), 25.5 (4C, s, CH(*C*H$_3$)$_2$), 24.0 (4C, s, CH(*C*H$_3$)$_2$). HRMS (ES): *m/z* 538.2368 [M − Br + CH_3CN]$^+$ (100%) ($C_{29}H_{41}N_3Ag$ requires 538.2351).

X-ray Crystallography. Suitable crystals were selected, and a data set for **7-Mes** was measured on a Bruker-Nonius APEX II CCD camera on a κ-goniostat, while data sets for **6-Mes**, **7-Xyl**, **7-Xyl**·H_2O, Ag(**7-Mes**)Br, Ag(**Xyl7-Mes**)Br, Ag(**6-Pr^i**)Br, Ag(**7-Xyl**)I, and **Xyl7-PhPF$_6$** were measured on a Bruker-Nonius KappaCCD area detector, all at the window of a Bruker-Nonius FR591 rotating anode ($\lambda_{Mo-K\alpha}$ = 0.71073 Å) driven by COLLECT[20] and processed by DENZO[21] software at 120 K. For compounds **7-Mes** and Ag(**7-Mes**)Br an absorption correction was applied using SADABS 2007/2.[22a] The structure of **7-Mes** was determined with SIR2004[22b] and refined using SHELXL-97.[22c] All remaining structures were determined with SHELXS-97 and refined using SHELXL-97.[22c] Crystal data and refinement results for all samples are collated in Table 6. Crystallographic data for all compounds have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 671235 (**6-Mes**), 671236 (**7-Mes**), 671237 (**7-Xyl**), 671238 (**7-Xyl**·H_2O), 671239 (**7-Xyl**·H_2O), 671240 (Ag(**7-Mes**)Br), 671241 (Ag(**7-Xyl**)I), 671242 (Ag(**6-Pr^i**)Br), and 671243 (**Xyl7-PhPF$_6$**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44) 1223 336033; e-mail, deposit@ccdc.cam.ac.uk).

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Supporting Information Available: CIF files of the compounds **6-Mes**, **7-Mes**, **7-Xyl**, **7-Xyl**·H_2O, Ag(**Xyl7-Mes**)Br, Ag(**6-Pr^i**)Br, Ag(**7-Xyl**)I, Ag(**7-Mes**)Br, and **Xyl7-PhPF$_6$**. ORTEP drawings of **7-Xyl**·H_2O and **Xyl7-Ph**·PF_6 and additional experimental data. This material is available free of charge via the Internet at http://pubs.acs.org.

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