Nickel N-heterocyclic carbene complexes in homogeneous catalysis

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Chapter 2

Another silver complex of 1,3-dibenzylimidazol-2-ylidene: structure and reactivity[†]

Abstract. *The reaction of 1,3-dibenzylimidazolium bromide ($Bn_2Im{\cdot}HBr$) with silver(I) oxide yields the dinuclear compound $\{(Bn_2Im)AgBr\}_2$, as determined with X-ray crystallography. The structure turned out to differ significantly from the mononuclear complex $(Bn_2Im)_2AgBr$ that was reported during the current study. It appears that the kind of structure is the result of different crystallization conditions. A new classification of solid-state structures of these and other silver(I) complexes containing monodentate N-heterocyclic carbenes is presented. The silver complex was used to synthesize the novel compound trans-$[(Bn_2Im)_2NiBr_2]$.*

[†] Based on: J. Berding, H. Kooijman, A. L. Spek, E. Bouwman, *J. Organomet. Chem.*, **2009**, *694*, 2217.

2.1 Introduction

In recent years the study and application of N-heterocyclic carbenes (NHCs) has increased rapidly, most notably as spectator ligands in various homogeneous catalysts.[1] As these ligands are strong σ-donors, they form stable transition-metal NHC complexes with strong metal-carbon bonds. Many synthetic methods leading to these useful carbene complexes have been investigated. One of these methods is the generation of a silver(I) NHC complex, followed by transfer of the carbene to another transition metal.[2] Such a reaction has successfully been applied to a variety of metals, including rhodium, iridium, gold, palladium, and nickel,[2] and may lead to NHC complexes that cannot be obtained via other synthetic routes, such as the addition of the free carbene to a metal salt. Furthermore, Ag NHC complexes have been used as catalysts,[3, 4] and as antimicrobial agent.[5]

Three common approaches toward the synthesis of Ag NHC complexes are: (1) the reaction of a free NHC with silver salts, (2) the reaction of azolium salts with silver salts under basic phase-transfer conditions and (3) the reaction of azolium salts with silver bases. The latter method, in which Ag_2O is used as a base (Equation 1) is now by far the most commonly employed.[2] Soon after the first report in 1998,[6] the Ag_2O route was recognized for its attractive features, such as its stability towards air and the tolerance towards other reactive hydrogen atoms.

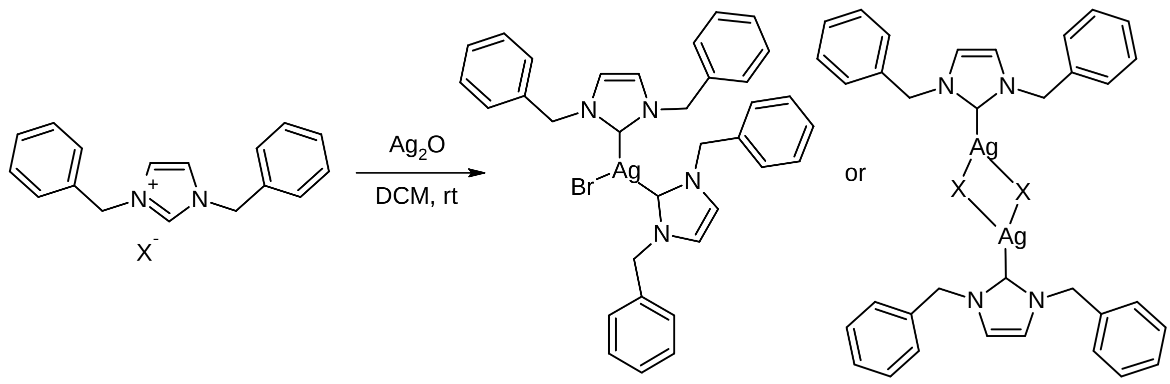
$$2\ \mathrm{NHC{\cdot}HX} + \mathrm{Ag_2O} \rightarrow 2\ \mathrm{(NHC)AgX} + \mathrm{H_2O} \qquad (1)$$

During the research described in this thesis attempts have been made to prepare nickel(II)-NHC complexes with the aid of silver(I) NHC intermediates. During these studies the unusual structure of $[(NHC)_2AgBr]$, in which NHC is 1,3-dibenzylimidazol-2-ylidene, was reported,[7] whereas with the same NHC and the same synthetic procedure the current study resulted in the isolation of the compound $\{(NHC)AgBr\}_2$. In this chapter, the synthesis and crystal structure of this compound is reported, including an attempt to rationalize the formation of the different complexes. Moreover, the subsequent transmetalation of the carbene from silver(I) to nickel(II) is described.

2.2 Results and Discussion

2.2.1 Synthesis of the silver complex

The ligand precursor 1,3-dibenzylimidazolium bromide ($Bn_2Im{\cdot}HBr$, **1**) was obtained by the alkylation of *N*-benzylimidazole with benzyl bromide in hot 1,4-dioxane. In accordance with the general reaction for the generation of silver-NHC complexes (Equation 1) and the literature procedure,[7] **1** was reacted with 0.5 equivalents of silver(I) oxide in dichloromethane. This reaction yielded an off-white solid product, which was assumed to be compound **2** (Scheme 2.1).[7] The ^1H NMR



1 **2** **3** X = Br
4 X = Cl

Scheme 2.1. Reaction of imidazolium halide with Ag_2O, yielding **2** or **3**(**4**).

spectrum of this solid product in CD_2Cl_2 lacked the downfield NCHN signal, indicating successful carbene formation, while the ^{13}C NMR spectrum showed the Ag-C resonance at 182 ppm. No ^{13}C–$^{107/109}Ag$ coupling was observed, consistent with the fluxional behavior known for other Ag(I) NHC complexes.[6] The elemental analysis, however, revealed a clear 1:1:1 ligand to silver to bromide ratio, in disagreement with the reported structure **2**. To elucidate the identity of this new compound **3**, its solid-state structure was determined.

2.2.2 X-ray crystal structure determination of the silver complex 3

Single crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into a chloroform solution of the silver compound at room temperature. The complex has a dinuclear solid-state structure (**3**), as depicted in Figure 2.1. In the structure of **3**, two (Bn_2Im)AgBr moieties are present around an inversion center to give a dinuclear species with, in addition to the end-on Ag–Br bond, side-on Ag…Br interaction. The Ag_2Br_2 4-membered ring is planar with an Ag–Ag distance of 4.0296(6) Å. The two bridging bromide ions are asymmetrically bound with Ag–Br distances of 2.4913(5) and 3.0415(5) Å. The Ag1–C2 distance is comparable to those in other silver-carbene complexes.[8] The silver center is shifted slightly out of the trigonal [CBr_2] coordination plane, while the plane through the imidazole ring is rotated with respect to the Ag_2Br_2-plane by 36.82(12)°. A weak stacking interaction of the aromatic phenyl side groups is observed in the crystal structure with a center-to-center distance of 3.90 Å, with the center of one ring directly above the quaternary carbon of the other ring (Figure 2.2). Several similar $\{(NHC)AgX\}_2$ structures have been reported in literature (see below).

Apart from the mononuclear compound **2,** in which two NHC ligands are bound to one silver ion (Scheme 2.1), Newman *et al.*[7] obtained the dinuclear $\{(Bn_2Im)AgCl\}_2$ (**4**) with a structure similar to **3**, with only minor differences in bond

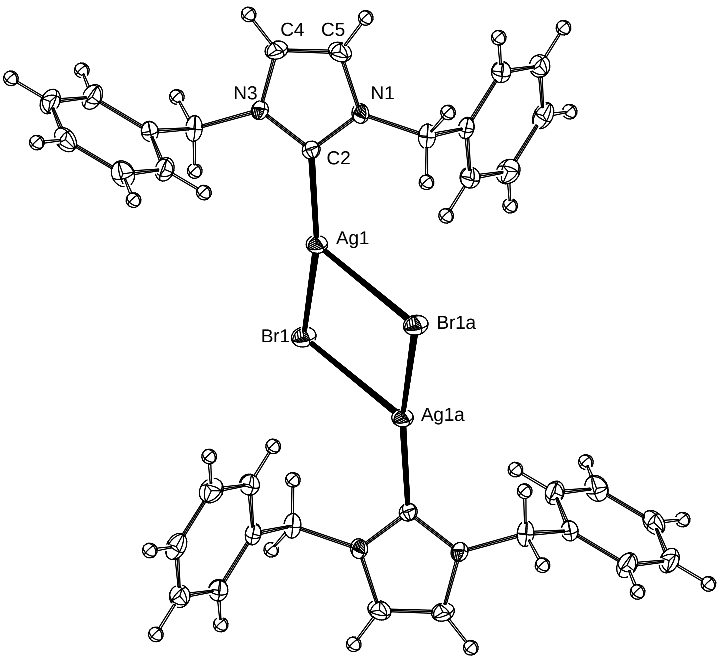


Figure 2.1. ORTEP projection of **3** with displacement ellipsoids drawn at the 50% probability level. The molecule is located at a crystallographic inversion centre. Symmetry transformation used to generate equivalent atoms: –x, 1–y, 1–z. Selected bond distances (Å) and angles (°): Ag1–C2 2.102(2); Ag1–Br1 2.4913(5); Ag1–Br1a 3.0415(5); N1–C2 1.355(3); N3–C2 1.471(4); C4–C5 1.349(4); Ag1–Ag1a 4.0296(6); Br1–Ag1–C2 159.30(6); Br1a–Ag1–C2 112.77(6); Br1–Ag1–Br1a 87.05(2); Ag1–Br1–Ag1a 92.95(2); N1–C2–N3 104.21(18).

lengths and angles; e.g., the carbene–silver distances are 2.090(2) and 2.102(2) Å, respectively. Only the distance between the silver center and the closest halide is significantly different due to the different van der Waals radii of Br^- and Cl^-. The two silver-carbene bond lengths in **2** of 2.116(4) and 2.117(4) Å are slightly longer than those in **3**. The silver-bromide distance of 2.89 Å in **2** is intermediate between the two

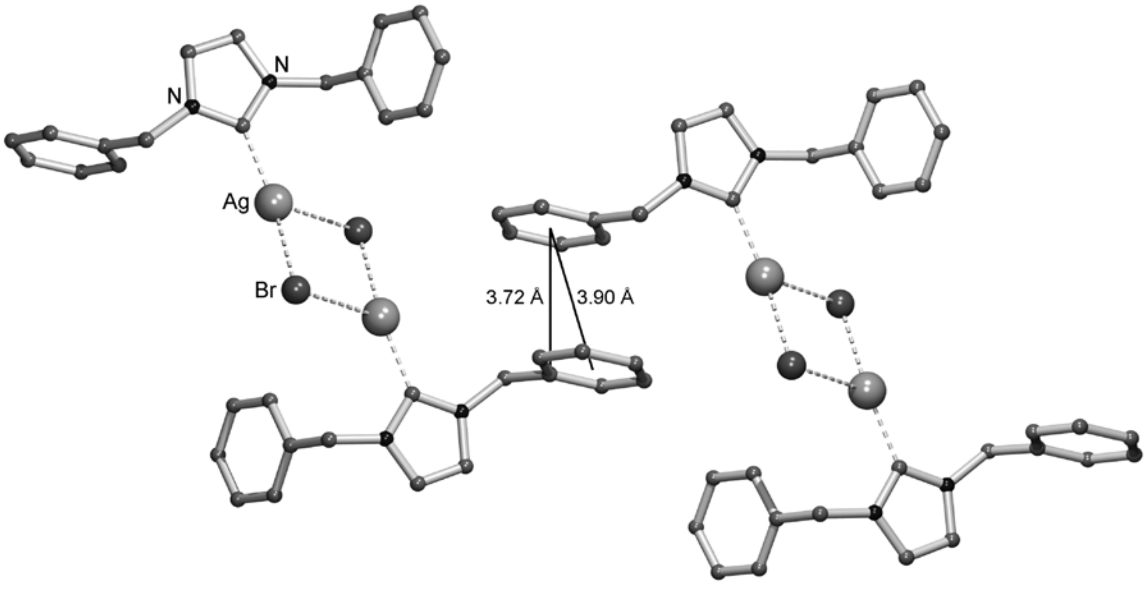


Figure 2.2. Stacking interaction in the solid-state structure of **3**.

Ag-Br distances in **3** and it was suggested that **2** is better described as ionic complex [(NHC)$_2$Ag]$^+$Br$^-$.[7] A silver chloride complex containing the ligand 1,3-bis(2-pyridylmethyl)imidazol-2-ylidene does indeed yield the ionic complex [L$_2$Ag]$^+$Cl$^-$ in which two silver ions are in close contact (Ag–Ag = 3.65 Å).[9]

2.2.3 NMR studies

Two distinct solid-state structures of silver halide complexes with the ligand Bn$_2$Im were described in the previous section. It was decided to investigate the structures of these compounds in solution. An attempt was undertaken to monitor the formation of the silver complex in solution. Thus, a 2:1 mixture of **1** and Ag$_2$O was taken into deuterated dichloromethane and the NMR spectrum of the mixture was recorded within 5 minutes. This spectrum already showed full conversion of the ligand precursor to the silver complex. Repeating this procedure with spectra measured at 243 K allowed for the reaction to be monitored. However, no peaks other than those of the precursor and a single silver complex could be observed in the ^{1}H and ^{13}C NMR spectra (the latter shown in Figure 2.3). After full conversion was reached, the ^{1}H and ^{13}C NMR spectra were found to be identical to spectra of

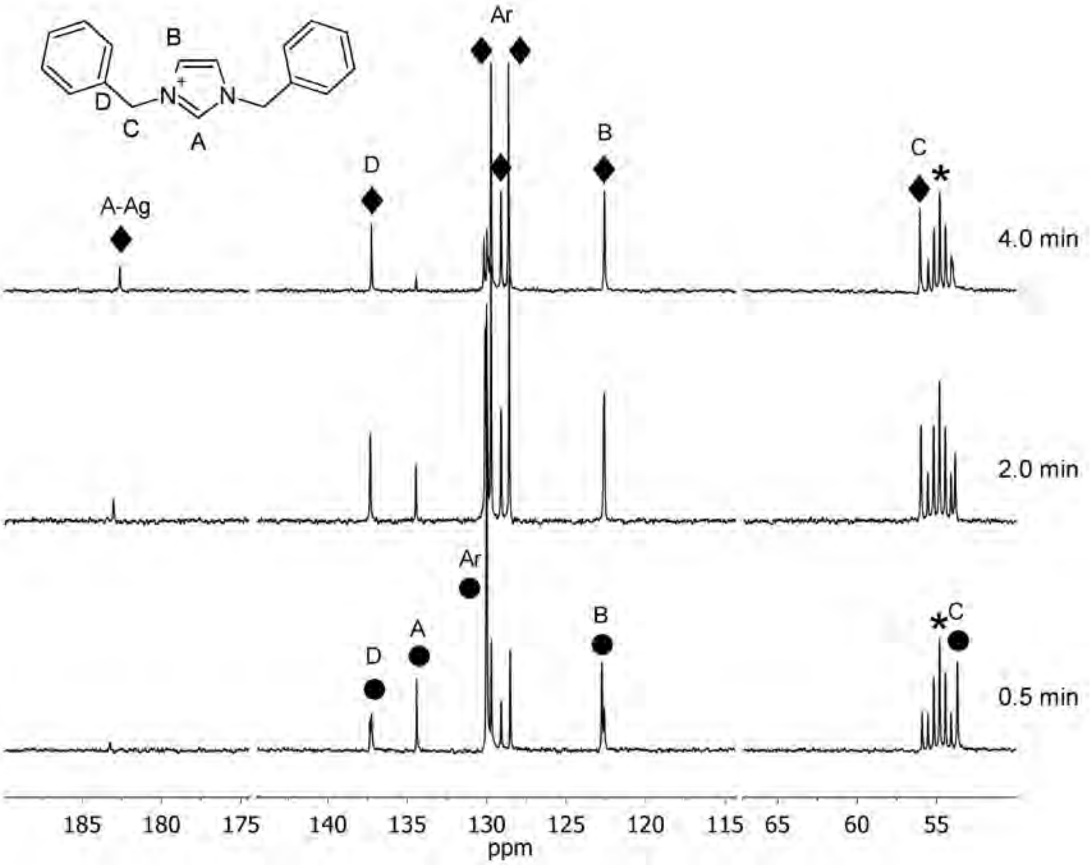


Figure 2.3. Synthesis of **3** in CD$_2$Cl$_2$, followed by ^{13}C NMR spectroscopy at 243 K. The time indicated is the reaction time at room temperature. Peaks have been assigned as the starting material (●), the product (♦) and the residual solvent (*).

complex **3**. After standing in the dark for several hours, colorless crystals formed in the NMR tube. Elemental analysis of these crystals revealed a 1:1 ligand to silver ratio, consistent with **3**. Some of the crystals were redissolved in CD_2Cl_2, and the NMR spectra confirmed that the crystals are identical to the bulk compound in solution. Repetition of the NMR experiment in deuterated DMSO yielded comparable ^1H and ^{13}C NMR spectra.

A silver complex with the non-coordinating anion tetraphenylborate (BPh_4^-) was also prepared. The required ligand precursor $Bn_2Im{\cdot}HBPh_4$ (**5**) was obtained by anion exchange of $Bn_2Im{\cdot}HCl$ and $NaBPh_4$ in dichloromethane. It is presumed that the ionic complex $[(Bn_2Im)_2Ag]BPh_4$ (**6**) is formed by subsequent reaction of **5** with Ag_2O. This complex was prepared in hot DMSO, as the reaction did not proceed well in dichloromethane. The ^{13}C NMR spectrum shows an unresolved doublet at 180 ppm, with a separation of about 190 Hz, consistent with coupling constants reported for other ionic Ag(I) NHC complexes.[10] The fact that this ionic species exhibits Ag–C coupling, while compound **3** does not, is in agreement with compound **3** being a non-ionic species in solution.

The ^{13}C NMR spectrum of the chloride complex **4** is reported to show an Ag–C resonance at 151 ppm.[7] However, repeating the kinetic NMR study described above for the reaction between $Bn_2Im{\cdot}HCl$ and Ag_2O, the Ag–C signal was observed as a singlet at 181 ppm. Therefore it is concluded that, in our experiments, the solution structures of silver complexes obtained from $Bn_2Im{\cdot}HCl$ and $Bn_2Im{\cdot}HBr$ are very similar, in contrast to what has been reported earlier.

The mass spectra of **3** and the crystals obtained from the NMR experiment described above both show one peak at *m/z* 605, indicating a $[(Bn_2Im)_2Ag]^+$ moiety. It has been shown, however, that mass spectrometry cannot be used to unambiguously distinguish (ligand)AgX from $[Ag(ligand)_2]^+$,[11] as is confirmed by the present studies.

2.2.4 Structural considerations

In a recent review seven types of solid-state structures obtained from the reaction between Ag_2O and monodentate azolium salts have been described.[2] For the current discussion, another classification is proposed, shown in Figure 2.4.[12]

Structure types **A** and $\mathbf{A_n}$ (n = 2, 3, …) are characterized by a 1:1 ligand to silver ratio and coordination of both the ligand and the halide to the same metal center. Structure types **B** and $\mathbf{B_2}$ show the same ratio; however, in this case two ligands and two halides are bound separately over two metal centers. Structure types **C**, **C′** and $\mathbf{C'_2}$ have a ligand to silver ratio of 2:1.

The solid-state structure of a silver NHC complex will depend heavily on the nature of the ligand (type of NHC, bulk of ligand and functional groups), the halide, the solvent and the temperature. For instance, imidazole- and benzimidazole-based

$(\mathrm{NHC})\mathrm{AgX}$ $\{(\mathrm{NHC})\mathrm{AgX}\}_n$

A $\mathbf{A}_n$ (n = 2, 3, ...)

$(\mathrm{NHC})_2\mathrm{Ag}\text{-}\mathrm{AgX}_2$ $(\mathrm{NHC})_2\mathrm{Ag}\text{-}\mathrm{Ag}_2\mathrm{X}_4\text{-}\mathrm{Ag}(\mathrm{NHC})_2$

B $\mathbf{B}_2$

$(\mathrm{NHC})_2\mathrm{AgX}$ $[(\mathrm{NHC})_2\mathrm{Ag}]^+\,\mathrm{X}^-$ $\{(\mathrm{NHC})_2\mathrm{Ag}\}_2^{2+}\,2\mathrm{X}^-$

C **C'** $\mathbf{C'}_2$

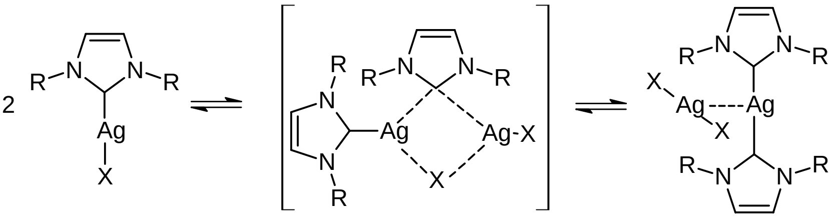
Figure 2.4. Classification of various silver NHC species discussed in this chapter.

carbenes with short alkyl-chain substituents yield complexes of type **B** in the solid state,[6, 13] while those bearing long alkyl chains often result in complexes of type $\mathbf{A}_2$.[14] The exact geometry of this dimer $\mathbf{A}_2$ can vary and a number of different structures has been reported, including the Ag_2X_2 4-membered ring of **3** and **4** and a dimer formed by Ag-Ag interaction.[8, 15] A study to determine the influence of the solvent showed that an increase in solvent polarity shifts the solution equilibrium from **A** to **B** for (IMes)AgCl (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene).[8] Coordination polymers derived from **A** ($\mathbf{A}_n$, n > 3) and dimers derived from **B** ($\mathbf{B}_2$) have been reported in the solid state, but in solution they are most likely in equilibrium with **A** and **B**.[3, 13, 16, 17] The 1,3-bis(2-pyridylmethyl)imidazol-2-ylidene silver complex mentioned above, is an example of a type $\mathbf{C'}_2$ structure.[9]

The current classification does not include complexes with non-coordinating anions that will adopt a type **C′** structure,[18-20] or silver clusters.[9, 16, 21] One example is known with a $[\{(NHC)_2Ag\}_3I]^{2+}2I^-$ structure, in which the NHC has pendant pyridine groups, that may be considered intermediate between structure **C** and **C′**.[22] Chelating NHC ligands are not included explicitly, but are expected to form similar species.

Type **C′** is not likely to be a major product in the solid state with potentially coordinating halides and only few solid-state structures of this type have been reported with bulky ligands.[4] It is argued that in the structure reported by Wang *et al.* (CCDC code: PENJIC) the iodide counter ion may be considered weakly bound to the silver center at 3.36 Å, as this is shorter than the sum of the van der Waals radii of silver and iodine of 3.70 Å.[23]

Even though kinetic evidence was not found, it is assumed that structure **A** is the direct outcome of the reaction between the azolium salt and Ag_2O in solution. This notion is corroborated by recent quantum chemical calculations.[24] The other structures are most likely generated subsequently, due to the fluxional behavior between the ionic and neutral complexes observed in solution for most of the Ag-NHC compounds (Scheme 2.2), and the known equilibrium between AgX_2^- and AgX + X^-.[2] The fact that with the ligand Bn_2Im both type $\mathbf{A}_2$ (**3** and **4**) and type **C** (**2**) structures have been characterized in the solid state, demonstrates that the ligand and the halide are not the only factors determining the solid state structure. The only



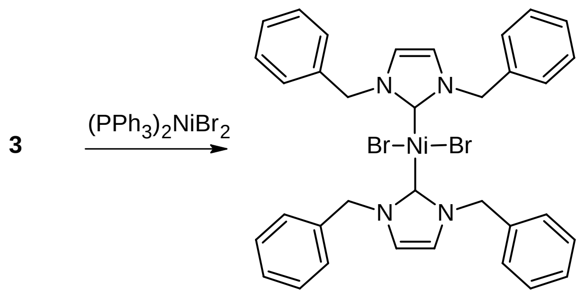
Scheme 2.2. Fluxional behavior of Ag-NHC complexes in solution.[6]

distinction in the reaction conditions of the syntheses of **2** and **3** is the reaction time. Whereas **3** was obtained after 2 hours, compound **2** was isolated after 15 hours of stirring. This seems to suggest that the dimeric **3** is the kinetic product, while three-coordinate **2** is thermodynamically favored under the conditions used. However, repeating the synthesis with 18 hours stirring yielded a solid which again analyzed as complex **3**. Therefore, the fact that it was possible to isolate **3** in crystalline form is ascribed to a subtle difference in crystallization conditions. The observation that different crystallization conditions may lead to different crystal structures of Ag(I) NHC complexes has been noted before.[14] In addition, very recently another example of a type **C** solid-state structure was reported, obtained from a tetra-ether substituted imidazolium bromide.[25] In that case, however, the parent silver complex analyzed as a 1:1 complex and AgBr is reported to be formed at the bottom of the crystallization tube upon crystallization by slow evaporation of a dichloromethane solution. Unfortunately, no NMR data are given for the crystalline compound.

Several attempts to obtain the 2:1 complex by using different crystallization conditions were undertaken, including the use of different solvents, the absence and presence of light and a low temperature. In all cases, however, crystals that formed analyzed (by elemental analysis) as the 1:1 complex. Moreover, stirring a sample of **3** in THF at 70 °C for 14 hours, followed by precipitation with diethyl ether, did not change the composition of the compound. In conclusion, it appears that the isolation of **2** with the type **C** structure should be regarded as serendipitous.

2.2.5 Transmetalation

The Ag NHC complexes are widely used as carbene transfer reagent. Indeed, both **3** and its chloride-analogue **4** have been used in the synthesis of $(Bn_2Im)Rh(COD)Cl$.[26-28] In this study it was chosen to attempt the transfer of the ligand to a nickel center. Several nickel(II) complexes bearing monodentate NHC ligands have been reported. To date, the two routes employed to obtain these complexes, *i.e.* heating a mixture of imidazolium salt with nickel acetate,[29, 30] and the reaction of the free carbene with a suitable nickel source,[31] have limitations in stability and application. Transmetalation from the silver salt may be an attractive alternative.



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Scheme 2.3. Transmetalation of (Bn_2Im) from silver to nickel.

When a freshly prepared solution of **3** in dichloromethane was added to a solution of $(PPh_3)_2NiBr_2$ in the same solvent, a rapid color change from green to red was observed (Scheme 2.3). Additional stirring led to an off-white precipitate in a red solution. Filtration and concentration *in vacuo* gave a red, diamagnetic precipitate which was isolated by filtration. The color of compound **7** is consistent with square-planar *trans*-$[(Bn_2Im)_2NiBr_2]$.[29, 30] The ^1H and ^{13}C NMR spectra of **7** are similar to those of silver complex **3**, with small shifts due to the difference in electronegativity between the two metal fragments. The carbene C resonance is shifted to 169 ppm in the ^{13}C NMR spectrum, comparable to the values found for other nickel NHC complexes.[30] The catalytic properties of this nickel compound are discussed in Chapter 3.

2.3 Conclusion

In summary, an Ag(I) NHC complex was synthesized starting from 1,3-dibenzylimidazolium bromide, following a common procedure. This complex displays a solid-state structure that is significantly different from a structure that was reported by others. It appears that the difference originates from the crystallization procedure and it is believed that the 1:1 ligand to silver complex is the major product after the first isolation. With this in mind, it is recommended to use elemental analysis, rather than mass spectrometry, for the determination of the composition of the crude product. In addition, NMR experiments indicate that the formation of the silver complex is fast and evidence was found that in solution the complex is present as a neutral species. Furthermore, a novel classification of the solid-state structures of monodentate NHC silver complexes is introduced.

The silver compound was successfully used in a transmetalation reaction to obtain the novel compound *trans*-dibromidobis(1,3-dibenzylimidazol-2-ylidene)nickel(II).

2.4 Experimental Section

General procedures. All chemicals were obtained from commercial sources and used as received. Solvents were reagent grade and used without further purification, except for 1,4-dioxane which was distilled from CaH_2 and stored on molecular sieves under argon. NMR spectra were obtained on a Bruker DPX300 spectrometer and are referenced against TMS. IR spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer. C,H,N determinations were performed on a Perkin–Elmer 2400 Series II analyzer. Electrospray mass spectra were recorded on a Finnigan TSQ-quantum instrument using an electrospray ionization technique (ESI-MS), using water/acetonitrile solutions. $(PPh_3)_2NiBr_2$,[32] and 1,3-dibenzylimidazolium chloride,[33] were synthesized according to literature procedures. Imidazolium bromide **1** has been prepared before;[7, 34, 35] however, a full characterization was never reported.

1,3-Dibenzylimidazolium bromide (1). Under argon, a mixture of *N*-benzylimidazole (3.96 g, 25 mmol) and benzyl bromide (5.13 g, 30 mmol) in 30 mL dry 1,4-dioxane was stirred at 100 °C for 4 hours. The resulting two-phase system was cooled and the layers were separated. The bottom layer was washed two times with 1,4-dioxane and once with diethyl ether. Drying *in vacuo* yielded a clear, colorless oil that crystallized very slowly. Yield: 7.6 g (92%). ^1H NMR (300 MHz, DMSO-d_6, 300K): $\delta = 9.51$ (s, 1H, NCHN), 7.85 (d, $J = 2$ Hz, 2H, NCH), 7.42 (m, 10H, Ar-H), 5.45 (s, 4H, CH_2). ^{13}C NMR (300 MHz, DMSO-d_6, 300K): $\delta = 136.2$ (NCHN), 134.7 (C_q), 129.0 (C_{Ar}), 128.7 (C_{Ar}), 128.3 (C_{Ar}), 122.8 (NCH), 52.0 (CH_2). IR (neat): $\nu =$ 3028 (w), 1557 (m), 1496 (w), 1458 (w), 1350 (w), 1210 (w), 1148 (m), 819 (w), 720 (s), 707 (s), 638 (s), 570 (w), 482 (m) cm^{-1}. MS (ESI): *m/z* 249 ($[M - Br]^+$, 100%). Anal. Calc. for $C_{17}H_{17}BrN_2$: C, 62.02; H, 5.20; N, 8.51. Found: C, 61.21; H, 5.23; N, 8.44%.

Bis(μ-bromido(1,3-dibenzylimidazol-2-ylidene)silver(I)) (3). 1,3-Dibenzylimidazolium bromide (0.32 g, 1.0 mmol) and silver(I) oxide (0.14 g, 0.5 mmol) were mixed in dichloromethane (10 mL) and stirred in the absence of light at room temperature for 2 h. The resulting solution was filtered with the aid of a membrane filter and concentrated *in vacuo*. Addition of diethyl ether gave an off-white precipitate which was isolated by filtration, washed with diethyl ether and dried *in vacuo*. Single crystals suitable for X-ray diffraction were grown by slow diffusion of diethyl ether into a chloroform solution at room temperature. Yield: 0.65 g (75%). ^1H NMR (300 MHz, $CDCl_3$, 300K): $\delta = 7.36$ (m, 6H, Ar-H), 7.23 (m, 4H, Ar-H), 6.92 (s, 2H, NCH), 5.30 (s, 4H, NCH_2). ^{13}C NMR (300 MHz, $CDCl_3$, 300K): $\delta = 181.9$ (Ag-C), 135.4 (C_q) 129.1 (C_{Ar}), 128.7 (C_{Ar}), 127.9 (C_{Ar}), 121.4 (NCH), 55.8 (NCH_2). IR (neat): $\nu = 3127$ (w), 1492 (w), 1452 (m), 1356 (w), 1226 (m), 1152 (w), 1027 (w), 752 (s), 700 (s), 662 (m), 582 (m) cm^{-1}. MS (ESI): *m/z* 605 ($[L_2Ag]^+$, 100%). Anal. Calc. for $C_{17}H_{16}AgBrN_2$: C, 46.82; H, 3.70; N, 6.42, Found: C, 46.85; H, 3.70; N, 6.48%.

Synthesis of 3, followed by NMR spectroscopy at 243 K. In an NMR tube, 1,3-dibenzylimidazolium bromide (0.2 mmol, 57 mg) and silver(I) oxide (0.1 mmol, 23 mg) were dissolved/suspended in 0.75 mL deuterated dichloromethane. The solution was immediately frozen in liquid nitrogen and transferred to an NMR apparatus, cooled to 243 K. After recording the ^1H and ^{13}C NMR spectra, the tube was removed from the NMR apparatus and shaken manually for 30 seconds. Then, the next ^1H and ^{13}C spectra were recorded and this procedure was repeated until no change in the spectra could be observed anymore.

1,3-Dibenzylimidazolium tetraphenylborate (5). 1,3-Dibenzylimidazolium chloride (0.28 g, 1.0 mmol) and $NaBPh_4$ (0.37 g, 1.1 mmol) were dissolved in 15 mL dichloromethane and vigorously stirred for 3 h. The solution was filtered with a membrane filter to separate the NaCl byproduct. The filtrate was evaporated to dryness. The remaining oil crystallized slowly and was dried *in vacuo* to yield a colorless solid. Yield: 0.48 g (84%). ^1H NMR (300 MHz, DMSO-*d6*, 300K): δ 9.35 (s, 1H, NCHN), 7.79 (d, *J* = 1.6 Hz, 2H, NCH), 7.40 (m, 10H, Ar-H), 7.18 (m, 8H, Ar-H), 6.92 (t, *J* = 7.2 Hz, 8H, Ar-H (BPh_4^-)), 6.78 (t, *J* = 7.2 Hz, 4H, Ar-H (BPh_4^-)), 5.40 (s, 4H, NCH_2). ^{13}C NMR (75 MHz, DMSO-*d6*, 300K): δ 163.3 (q, $J_{B\text{-}C}$ = 49 Hz, B-C_q), 136.3 (NCHN), 135.5 (C_{BPh4}), 134.7 (C_q), 129.1 (C_{Bn}), 128.8 (C_{Bn}), 128.3 (C_{Bn}), 125.3 (C_{BPh4}), 122.9 (NCH), 121.5 (C_{BPh4}), 52.1 (NCH_2). Anal. calcd for $C_{41}H_{37}BN_2$: C, 86.61; H, 6.56; N, 4.93. Found: C, 86.26; H, 6.55; N, 5.03%.

***In situ* synthesis of $[(Bn_2Im)_2Ag]BPh_4$ (6).** In a 10 mL round bottom flask, $Bn_2Im{\cdot}HBPh_4$ (57 mg, 0.2 mmol) and Ag_2O (12 mg, 0.1 mmol) were dissolved/suspended in 0.5 mL DMSO-d_6 and stirred for 14 h at 70 °C. After cooling, the mixture was transferred into a NMR tube and the ^1H and ^{13}C NMR spectra were recorded. No attempts were made to isolate the solid product.

Trans-dibromidobis(1,3-dibenzylimidazol-2-ylidene)nickel(II) (7). 1,3-Dibenzylimidazolium bromide (0.23 g, 1.0 mmol) and silver(I) oxide (0.14 g, 0.5 mmol) were mixed in dichloromethane (10 mL) and stirred in the absence of light at room temperature for 2 h. The resulting solution was filtered with the aid of a membrane filter and added to a solution of $(PPh_3)_2NiBr_2$ (0.34 g, 0.5 mmol) in dichloromethane. A rapid color change from green to red occurred and stirring was continued for 30 minutes. The off-white precipitate that had formed was removed by filtration to give an orange solution, which was concentrated *in vacuo* until a red solid started to precipitate. After filtration and washing with hexane the red product was recrystallized from DMF/diethyl ether. Yield: 0.15 g (42%). ^1H NMR (300 MHz, DMSO-d_6, 300K): δ = 7.55 (d, *J* = 4Hz, 4 H, Ar-H), 7.29 (m, 16H, Ar-H), 6.94 (s, 4H, NCH), 6.09 (s, 8H, NCH_2). ^{13}C NMR (75 MHz, DMSO-d_6, 300K): δ = 169.0 (Ni-C), 136.9 (C_q), 128.5 (C_{Ar}), 128.4 (C_{Ar}), 127.7 (C_{Ar}), 122.0 (NCH), 53.3 (NCH_2). IR (neat): ν = 3134 (w), 2930 (w), 1494 (w), 1452 (m), 1417 (m), 1342 (w), 1228 (m), 1150 (w), 1028 (w), 769 (w), 728 (m), 692 (s), 594 (m) cm^{-1}. MS (ESI): *m*/*z* 676 ($[M - Br + MeCN]^+$, 100%). Anal. Calc. for $C_{34}H_{32}Br_2N_4Ni{\cdot}0.25DMF$: C, 56.91; H, 4.64; N, 8.12. Found: C, 57.01; H, 5.06; N, 8.07%.

X-ray crystallographic structure determination of 3. $C_{34}H_{32}Ag_2Br_2N_4$, triclinic, space group *P-1*, a = 8.1258(10) Å, b = 10.0156(10) Å, c = 10.5681(10) Å, α = 89.427(12)°, β = 68.000(16)°, γ = 85.19(2)°, V = 794.43(17) Å^3, Z = 2, MW = 872.18, D(calc) = 1.8231(4) Mg m^{-3}. X-ray data were collected with a Nonius KappaCCD diffractometer on rotating anode (T = 150 K, MoKα radiation, λ = 0.71073 Å, θ(max) = 27.5°, 19982 reflections measured). The structure was solved by Patterson methods (DIRDIF)[36] and refined with SHELXL-97.[37] Hydrogen atoms were introduced at calculated positions and refined riding on their carrier atoms. Convergence was reached at R = 0.0236 for 3474 reflections with $I > 2\,\sigma(I)$, wR2 = 0.0628 for 3625 reflections, S = 1.045. Illustrations and structure validation were done with PLATON.[38]

2.5 References

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(12) Relation of our structures A-C' with the review in ref. 2: Type-1 = B, Type-2 = A, Type-3 = A_2, Type-4 = B_2, Type-7 = C'. Type-5 and Type 6 do not correspond to any of the types described here. Type A_n, C and C'_2 were not described as a common type in the review.

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