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Studies of Ligand Exchange in N-Heterocyclic Carbene Silver(I) Complexes

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Supporting Information

ABSTRACT: A series of N-heterocyclic carbene (NHC) Ag(I) complexes have been prepared and used to study the dynamics of NHC ligand exchange in these Ag(I) complexes. These studies used solution-state variable-temperature (VT) ^{13}C NMR spectroscopy and the temperature-dependent changes in $^{13}\text{C}-^{107/109}\text{Ag}$ coupling to determine activation energies for the ligand exchange



process. The effects of concentration, bridging anions, and additives on the exchange process have been studied. The experimental activation energies for the NHC ligand exchange processes of these silver complexes are also compared with DFT calculations. The results are consistent with an associative mechanism for the Ag(I)-NHC exchange process.

■ INTRODUCTION

N-heterocyclic carbenes (NHCs) have been become increasingly important as organocatalysts^{1,2} and as ligands for transition metals.³⁻⁵ The importance of these species in organic and biological chemistry was originally recognized in seminal studies by Breslow in the 1950s,^{6,7} and their importance as strong σ -donor and weak π -acceptor ligands in organometallic chemistry was recognized after key reports by Arduengo in 1991⁸ and Herrmann in 1995.⁹ The tunability of electron density and sterics make NHC ligands useful as alternatives to phosphines, and many examples of NHCcomplexed transition-metal catalysts have now been decomplexed transition-metal catalysts have now been de-scribed.^{3,5,10,11} This has been especially true for Ru-based olefin metathesis catalysts^{12,13} and for Pd cross-coupling catalysts.^{3,5,10,11,14} NHC-ligated Ag(I) complexes have been used both as catalysts^{15,16} and as intermediates in the synthesis of other NHC transition metal complexes by transmetalation.^{17–22} However, while Lin has proposed an associative mechanism for NHC exchange in Ag(I) halide complexes (Figure 1),¹⁷ relatively little attention has been paid to the dynamic behavior of NHC ligands on metals.

Evidence that ligand exchange in NHC-Ag(I) complexes can occur at varying rates comes from literature reports that



Figure 1. Proposed mechanism of NHC ligand exchange of NHC–Ag complexes described in ref 17.

have described NHC–Ag complexes which have carbene carbons that appear as doublets of doublets, as broad doublets, as broad singlets, or as sharp singlets in ¹³C NMR spectroscopy.^{23–27} Since Ag has two almost equally abundant spin ¹/₂ nuclei (52% of ¹⁰⁷Ag and 48% of ¹⁰⁹Ag), the carbene carbon of a NHC–Ag(I) complex should be a doublet of doublets if the NHC ligand does not exchange rapidly on the NMR time scale. If NHC ligand exchange were fast on the NMR time scale, this carbene carbon peak would be a singlet. This exchange process could also be temperature dependent, in which case dynamic behavior could be observed. Indeed, one report noted that the carbene carbon peak of a bithiophene-substituted silver NHC complex was a broad singlet at room temperature and a doublet of doublets at -50 °C.²⁸

VT NMR spectroscopy has been used previously to study such exchange processes of other ligands on Ag(I).^{29–37} For example, the VT ³¹P NMR spectrum of a P-containing Ag ligand is a doublet of doublets at low temperature that coalesces to a broad doublet, then to a broad singlet, and finally to a singlet when the temperature is increased. Such temperaturedependent spectra have proven to be useful in studying mechanistic details of such ligand exchange processes.^{33–37}

Recently, we observed that the carbene carbon signal of (*N*-mesityl-*N'*-methylimidazolylidene)silver iodide is a singlet at room temperature and a doublet of doublets at -80 °C in 13 C NMR spectroscopy. This suggested that these complexes could be used to study the dynamics of NHC exchange in (NHC)Ag^I exchange processes using line-shape studies of these complexes'

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VT NMR spectra. As shown below, NHC ligands with 13 C labels at the carbene carbon allow these processes to be studied in detail. The results show that the exchange process is an associative process and that both counterions and added ligands significantly affect exchange rates for NHC ligands on Ag(I).

RESULTS AND DISCUSSION

Synthesis of NHC–Silver Halide Complexes. The very low intensity of the ¹³C signal for the carbene carbon makes studying NHC–Ag(I) exchange processes problematic. To address this issue, we used the strategy first reported by Clyburne to prepare ¹³C-labeled NHC ligands to facilitate solution and solid-state NMR spectroscopic studies of (N,N'-dimesitylimidazolylidene)silver chloride ((IMes)AgCl).³⁸ In this work, we prepared *N*-mesityl-*N'*-methylimidazolium salts with a ¹³C-labeled carbon at the 2-position of the imidazolium ring and used these species to prepare Ag(I) halide complexes with ¹³C labels at the carbene carbon. This provided spectra with sufficient signal to noise to study line broadening in the VT ¹³C NMR spectra of these Ag complexes, even when the NHC–Ag(I) complexes were present at mN concentrations.

Our synthesis of ¹³C-labeled imidazole 1 and NHC–Ag halide complexes from ¹³C-labeled formaldehyde used Arduengo's method (Scheme 1).³⁹ Integration of the doublet

Scheme 1. (N-Mesityl-N'-methylimidazolylidene)silver Halide Complex Syntheses



due to ${}^{13}\text{C}-{}^{1}\text{H}$ coupling in the ${}^{1}\text{H}$ NMR spectrum of the labeled imidazole versus the singlet for the ${}^{12}\text{C}$ -containing impurity showed that 1 was 92% enriched with a ${}^{13}\text{C}$ label. N-methylation of 1 with methyl halides formed the imidazolium salts (2–4). While methyl iodide reacted readily, methylations with methyl bromide or methyl chloride required forcing conditions and sealed-tube reactions. The most difficult of these reactions was methylation with methyl chloride, which had to be carried out at 120 °C in CH₃CN in a sealed tube with an excess of methyl chloride. ${}^{13}\text{C}$ -enriched NHC–silver halide complexes were then prepared from these ${}^{13}\text{C}$ -labeled imidazolium halide salts using Ag₂O (Scheme 1).

The silver complexes 5–7 so formed were characterized by ¹H and ¹³C NMR spectroscopy and by elemental analysis. The (*N*-mesityl-*N'*-methylimidazolylidene)silver chloride (5) and bromide (6) products were also crystallized from CH₃CN/ ether and characterized crystallographically. Their crystal structures are shown in Figure 2, and selected bond distances and bond angles are given in Table 1.

Attempts to crystallographically characterize (*N*-mesityl-*N*'-methylimidazolylidene)silver iodide 7 were less successful.



Figure 2. ORTEP views of X-ray crystal structures of (a) (*N*-mesityl-N'-methylimidazolylidene)silver chloride (5) and (b) (*N*-mesityl-N'-methylimidazolylidene)silver bromide (6) with thermal ellipsoids at the 50% probability level. Further details regarding the crystal structures are available in the Supporting Information.

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) of Compounds 5 $(C_{26}H_{32}Ag_2N_4Cl_2)$ and 6 $(C_{26}H_{32}Ag_2N_4Br_2)$

	5 (X = Cl)	$6 \ (\mathrm{X} = \mathrm{Br})$				
Bond Lengths						
Ag(1) - C(1)	2.074(6)	2.082(10)				
Ag(1)-X(1)	2.3844(14)	2.495(3)				
Ag(1)-X(1A)	2.9017(13)	2.928(3)				
C(1)-N(1)	1.346(6)	1.350(12)				
C(1) - N(2)	1.374(7)	1.363(14)				
	Bond Angles					
C(1) - Ag(1) - X(1)	163.18(14)	158.42(30)				
C(1)-Ag(1)-X(1A)	108.38(14)	110.82(31)				
X(1)-Ag (1) -X $(1A)$	88.43(4)	90.76(7)				
Ag(1)-X(1A)-Ag(1A)	91.57(4)	89.27(7)				
N(1)-C(1)-N(2)	103.2(5)	102.3(9)				
N(1)-C(1)-Ag(1)	129.4(4)	128.9(7)				
N(2)-C(1)-Ag(1)	127.4(4)	128.4(7)				

After repeated attempts, two different crystals were obtained, but neither had a structure for a neutral (NHC)AgI complex like that seen for **5** and **6**. Elemental analysis of the first type of crystals had a C, H, and N ratio consistent with an (NHC)AgI complex containing a 1:1 NHC:AgI ratio. X-ray structural analysis of these crystals was inconclusive, as attempts to model the anion failed to produce a sensible model. When the program PLATON/SQUEEZE was employed to subtract the electron density from the final refinement of the cation, results consistent with the structure for the (NHC)₂Ag⁺ cation in Figure 3 were obtained. Others have noted that complex anions form during recrystallization of (NHC)AgI complexes. For



Figure 3. Ball and stick representation of the bis(N-mesityl-N'-methylimidazolylidene)silver cation that is thought to be present in 7. Hydrogen atoms are omitted for clarity. Results from an attempted X-ray structural determination for 7 suggesting this structure is present are given in the Supporting Information.

example, Nolan reported a crystal structure for an NHC–Ag ion pair complex with a complex $[Ag_4I_6]^{2-}$ anion.²⁶ EDX (energy dispersive X-ray) analysis of these crystals showed that the crystals had a 1:1 Ag:I ratio. On the basis of the elemental analysis and EDX results, the disordered anion in crystals of 7 with the formula (NHC)AgI is presumed to be a silver iodide cluster with a formula equivalent to that of AgI_2^- , though we cannot exclude the presence of other more complex anions. A second crystalline product was also isolated from these recrystallizations. This product 8 was formed by loss of AgI and had the formula (NHC)₂AgI. This product appeared to form as a result of loss of AgI due to exposure of 7 to ambient laboratory light during a recrystallization (eq 1). When 7 was



prepared with exposure to ambient lighting, **8** was the major product. The crystals of **8** so formed were characterized by ¹H and ¹³C NMR spectroscopy and elemental analysis. The X-ray structure of this product is shown in Figure 4, and the selected bond distances and bond angles are given in Table 2.



Figure 4. ORTEP view of the X-ray crystal structure of bis(N-mesityl-N'-methylimidazolylidene)silver iodide (8) with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Further details regarding the crystal structure are available in the Supporting Information.

Table 2. Se	lected Bond	Distances (Á) and	Bond	Angles
(deg) of Co	ompound 8	$(C_{26}H_{32}AgN$	4I)		

Bond Lengths								
Ag(1)-C(1)	2.075(11)	C(1) - N(1)	1.328(14)					
Ag(1)-I(1)	3.256(4)	C(1) - N(2)	1.3464(15)					
Bond Angles								
C(1)-Ag(1)-C(1A)	175.0(6)	N(1)-C(1)-Ag(1)	125.3(8)					
C(1) - Ag(1) - I(1)	92.5(3)	N2)-C(1) $-Ag(1)$	130.1(9)					
N(1)-C(1)-N(2)	103.7(9)							

NMR Studies of NHC–Silver Halide Complexes. A 0.06 N solution of ¹³C-labeled (NHC)AgI (7) in CD_2Cl_2 had a carbene carbon signal that appeared as a broad singlet at 21 °C in ¹³C NMR spectroscopy. When the temperature was lowered to -85 °C, this singlet changed into a doublet of doublets (Figure 5). VT NMR spectra of solutions of 7 at higher



Figure 5. (a–c) Variable-temperature ¹³C NMR spectra over a –85 to +21 °C temperature range for (a) 0.06 N, (b) 0.12 N, and (c) 0.24 N CD₂Cl₂ solutions of ¹³C-enriched (NHC)AgI (7). Coalescence is seen in all the cases, with the coalescence temperature increasing as the concentration of 7 decreases. (d) Minor component (7b) clearly visible in a 0.24 N solution at –85 °C. The concentrations and ratios of the two components are given on the side.

concentrations of 7 exhibited similar changes, with the difference that the coalescence temperature was observed to decrease as the concentration of 7 was increased from 0.06 to 0.12 to 0.24 N.

¹³C NMR spectra of higher concentrations of 7 at -85 °C showed that solutions of 7 contained more than one component. This is most apparent in the -85 °C spectrum of the 0.24 N solution, where two sets of doublets of doublets are seen, indicating that two kinds of NHC silver species are present (Figure 5d). The major component had ¹*J*(¹³C-¹⁰⁷Ag) and ¹*J*(¹³C-¹⁰⁹Ag) coupling constants of 241 and 274 Hz, while the minor component had smaller coupling constants of 179 and 207 Hz. The minor component was also present in more dilute solutions at a lower relative concentration. The ratio of the two components was ~5:1 in a 0.24 N solution of 7 and was ~20:1 in a 0.06 N solution of 7. This minor component had not been noted in our initial studies that did not use a ¹³C-enriched version of 7 because of the low intensity of the unlabeled carbene carbon.

The qualitative change in the ratio of the two components with changes in the concentration of 7 and the coalescence of all the peaks seen in the VT NMR spectra suggested that the two components are in equilibrium with one another. As discussed below, we believe that the two species in this equilibrium mixture are the neutral NHC-silver iodide complex 7a (the major component) and the bis(*N*-mesityl-*N'*-methylimidazolylidene)silver(I) diiodoargentate ionic species ((NHC)₂Ag⁺AgI₂⁻) (7b) (the minor component) (eq 2).



VT ¹³C NMR spectroscopic studies of CD_2Cl_2 solutions of silver chloride complex **5** at various concentrations are shown in Figure 6. The dynamic behavior of **5** is qualitatively similar to



Figure 6. VT ^{13}C NMR spectra of ^{13}C -enriched (NHC)AgCl (5) at concentrations of (a) 0.01 N, (b) 0.02 N, (c) 0.06 N, and (d) 0.12 N in CD₂Cl₂.

the behavior of 7 seen in Figure 4. For 5, coalescence of the doublet of doublets at low temperature to form a broad singlet was only seen for the 0.12 N solution of 5. In more dilute solutions, and in particular in the 0.02 and 0.01 N solutions of 5, the 22 °C spectra only show broadened doublets. The spectra of 5, like those of 7, show small amounts of a second species whose relative ratio increases with concentration. These two species are presumed to be the neutral (*N*-mesityl-*N*'-methylimidazolylidene)silver chloride complex (NHC)AgCl (5a) as the major component and the bis(*N*-mesityl-*N*'-methylimidazolylidene)silver(I) dichloroargentate ionic species ((NHC)₂Ag⁺AgCl₂⁻) (5b) as the minor component (eq 2).

Our assignment of ionic structures for **5b** and **7b** as the minor peak in the low-temperature spectra above is based on the assumption that the Ag–C coupling constant is lower for the ion pair than for the neutral species. This premise is based on prior reports that have described NHC-ligated Ag(I) with various anions.^{17,23,24,40,41} These reports consistently note that (NHC)₂Ag⁺ complexes have ¹⁰⁷Ag–¹³C coupling constants for ionic species that are in the range of 168–186 Hz. These ¹⁰⁷Ag–¹³C coupling constants are consistently lower than those of neutral complexes, whose ¹ $J(^{107}Ag-^{13}C)$ values are in the range of 219–253 Hz. Our measured ¹⁰⁷Ag–¹³C and ¹⁰⁹Ag–¹³C coupling constants for the assigned neutral (NHC)-AgX species and ionic (NHC)₂Ag⁺AgX₂⁻ species are in the same range of coupling constant values for these other neutral and ion pair NHC–Ag complexes in the literature.

These prior reports also suggest that mixtures of neutral and ionic NHC-ligated silver halide complexes exist in equilibrium with one another.^{23,24,40} While the concentration dependence of the neutral and ion pair structures we noted here has not been reported, Nolan did observe that the ratio of the two carbene complexes formed in the synthesis of (IMes)AgCl varied with solvent polarity.²⁶ Higher solvent polarity favored

formation of the ion pair. In this work, Nolan assigned the structure (IMes)AgCl to the major component and the structure $(IMes)_2Ag^+AgCl_2^-$ to the minor component. We prepared solutions of (IMes)AgCl that contained both the neutral (IMes)AgCl and ionic (IMes)2Ag+AgCl2- species and also observed that the ratio of the neutral and ion pair forms of this complex changed with changes in solvent polarity. In a ca. 0.4 N CD₂Cl₂ solution, the ratio of (IMes)AgCl to $(IMes)_2Ag^+AgCl_2^-$ was 3:1 at 23 °C and 4:1 at -80 °C, on the basis of ¹H NMR spectroscopic analysis of the signals for two sets of the four different protons of the neutral and ion pair. The ¹³C NMR spectrum at -80 °C showed two doublets of doublets with ¹⁰⁷Ag⁻¹³C and ¹⁰⁹Ag⁻¹³C coupling constants of 238 and 273 Hz for the major component (the neutral complex) and ¹⁰⁷Ag-¹³C and ¹⁰⁹Ág-¹³C coupling constants of 180 and 209 Hz for the minor component (the ionic species). In a 0.1 N DMSO- d_6 solution, the ratio of (IMes)AgCl/ $(IMes)_2Ag^+AgCl_2^-$ was ca. 1:1 on the basis of ¹H NMR spectroscopic analysis at 23 °C. Nolan reported that the ratio (IMes)AgCl:(IMes)₂Ag⁺AgCl₂⁻ was 4:1 in acetonitrile- d_3 and 2:1 in DMSO-*d*₆.

The line-shape changes seen in spectra in Figures 5 and 6 are like those seen for phosphine or alkyl group exchange in other Ag complexes.^{29–37} The spectra in Figures 5 and 6 show that the ¹³C NMR peaks for 7 at different concentrations coalesce at different temperatures. For example, the coalescence temperature for 7 was ca. -42 °C for a 0.24 N solution, ca. -25 °C for a 0.12 N solution, and ca. -5 °C for a 0.06 M solution. This same trend was also seen in the VT NMR spectroscopic studies of solutions of (NHC)AgCl (5) and (NHC)AgBr (6). The coalescence temperature of 5 was ca. 20 °C for a 0.12 N solution and was greater than room temperature for a 0.06 N solution (Figure 6). This concentration-dependent increase of the coalescence temperatures with a decrease of concentration is consistent with Lin's proposed mechanism for NHC ligand exchange via an associative process.

Anion Effects on NHC Ligand Exchange Rates in NHC–Silver Halide Complexes. Lin's study of NHC–Ag complexes¹⁷ postulated that halides were bridging anions connecting two silvers, facilitating NHC exchange (Figure 1). This postulate is supported by the VT NMR spectra of 5-7, which show that halide identity has a significant effect on the coalescence temperature, with the exchange rate variance being lowest with Cl. Figure 7a shows that when the concentration was 0.01 or 0.02 N, the coalescence temperatures for complexes 5 and 6 were above and about 20 °C, respectively, suggesting



Figure 7. ¹³C NMR CD_2Cl_2 spectra (20 °C) of (a) 0.01 and 0.02 N of 5 and 6 and (b) 0.12 and 0.06 N of 5 and 7, showing the different coalescence temperatures with different anions.

that the ligand exchange in **6** is more rapid than in **5**. Likewise, **5** and 7 at 0.06 or 0.12 N have coalescence temperatures about and below 20 $^{\circ}$ C, respectively, suggesting that NHC ligand exchange in 7 is more rapid than in **5**.

Addition of tetrabutylammonium halides to 0.06 N solutions of **5** provides further evidence of the effects of halide on the exchange process. Figure 8 shows that adding $(n-Bu)_4N^+Cl^-$ or



Figure 8. VT NMR spectra of a 0.06 N solution of 5 (center) and a 0.06 N solution of 5 with addition of 1 equiv of $(n-Bu)_4N^+Cl^-$ (left) or 0.9 equiv of $(n-Bu)_4N^+Br^-$ (right).

 $(n-Bu)_4N^+Br^-$ to a 0.06 N solution of **5** leads to decreased coalescence temperatures, consistent with a faster NHC exchange rate. This effect follows the trend noted above, with bromide anion having a larger effect than chloride anion. Figure 9 shows that increasing the amount of added $(n-Bu)_4N^+Br^-$



Figure 9. VT 13 C NMR spectra of (a) a 0.06 N solution of 5 with addition of (b) 0.3, (c) 0.6, (d) 0.9, and (e) 1.69 equiv of $(n-Bu)_4N^+Br^-$.

both decreases the coalescence temperature and affects the ratio of the neutral (NHC)AgX form and ion pair (NHC)₂Ag⁺AgX₂⁻. This result is consistent with Nolan's work,²⁶ as an increase in the amount of $(n-Bu)_4N^+Br^-$ would increase solution polarity and the relative amount of the ion pair.

As noted above, we were unable to obtain crystals of (*N*-mesityl-*N'*-methylimidazolylidene)silver(I) iodide (7) but did obtain a derivative, bis(*N*-mesityl-*N'*-methylimidazolylidene)-silver(I) iodide (8). We briefly examined the dynamic behavior of the NHC groups in 8. Exchange of the NHC ligands of 8 did not occur on the NMR time scale. A doublet of doublets was observed at all temperatures from -80 to +20 °C. The

 107 Ag $^{-13}$ C and 109 Ag $^{-13}$ C coupling constants of 178 and 206 Hz seen for 8 were the same as the 107 Ag $^{-13}$ C and 109 Ag $^{-13}$ C coupling constants seen for the minor component present in a 0.24 N solution of 7 (i.e., the presumed ionic species). This may indicate that the same (NHC)₂Ag⁺ cation is present in both 7b and 8.

VT ¹³C NMR studies 8 showed that adding very small amounts of 7 to solutions of 8 promotes NHC ligand exchange. When 0.01 equiv of 7 was added to a 0.04 N solution of 8, the carbene signal in the ¹³C NMR spectrum became a broad doublet at room temperature. When 0.03 equiv of 7 was added, the carbene signal became a broad singlet at room temperature. This shows that NHC ligand exchange between ionic species and neutral species is fast on the NMR time scale.

Effects of Added Phosphine Ligands on (NHC)AgI Solutions. When 0.2, 0.4, 0.9, 1.2, 1.6, and 3.0 equiv of triphenylphosphine (Ph₃P) were added to a 0.12 M solution of 7, ¹³C NMR spectroscopy showed that the solution of 7 containing primarily the neutral complex 7a was gradually converted into a complex that had a ¹³C NMR spectrum identical with that of 8. As shown in Figure 10, the -85 °C ¹³C



Figure 10. ^{13}C NMR spectra (-85 °C) showing the effect of Ph_3P on the ratio of 7 and 8 when (a) 0.0, (b) 0.2, (c) 0.4, and (d) 1.2 equiv of Ph_3P were added to 0.12 N of 7 in CD_2Cl_2 .

NMR spectra of these experiments show that the ratio of $(NHC)_2Ag^+$ and (NHC)AgI increased when more Ph_3P was added. We suggest that formation of 8 from 7 occurs according to the process shown in Scheme 2. In this scheme, additional

Scheme 2. Proposed Equilibria Forming Ph₃P-AgI Complexes on Addition of Ph₃P to a Solution of 7

$\begin{array}{ccc} NHC & NHC \\ & Ag \xrightarrow{I} & Ag^{I} & Agl_2^{I} \\ & I & NHC \end{array}$	PPh ₃ NHC Åg⁺ + I⁻ + (Ph ₃ P)A NHC	.gl
NHC Åg⁺ + I⁻ + (Ph ₃ P) ₂ A NHC	excess NHC Agl <u>PPh3</u> Åg⁺ + I⁻ + (P NHC	h₃P)₃Agl

phosphine can coordinate to silver iodide to form complexes of AgI and Ph₃P. Increasing amounts of Ph₃P shifted the equilibrium according to Le Châtelier's principle. When more than 0.5 equiv of Ph₃P was added, only a trace amount of (NHC)AgI (7) remained. The Ag species were present as a combination of phosphine–silver complexes and **8**. ³¹P NMR spectroscopy confirmed the formation of (triphenylphosphine) silver iodide complexes in accordance with the equilibria shown in Scheme 2.

VT ^{13}C spectroscopy showed that Ph_3P addition also affected the NHC exchange rate. As the amount of added Ph_3P increased, NHC exchange was slowed to the point that coalescence was not observed below 25 °C. These experiments



Figure 11. MPW1PW91 results for the ligand exchange process of (N-mesityl-N'-methylimidazolylidene)silver halides.

showed that less than 0.5 equiv of added Ph₃P had only a small effect on the coalescence temperature but that addition of 0.9 equiv or more of Ph₃P resulted in higher coalescence temperatures. The slower NHC exchange rate in the presence of ca. 1 equiv of Ph₃P is understandable in the context of our other results and Scheme 2 if larger amounts of added Ph₃P shift the equilibria such that the NHC–silver complex left in solution is 8 ((NHC)₂Ag⁺I⁻). While we have not characterized the AgI–triphenylphosphine complexes that form, we noted several new signals (as doublets of doublets consistent with Ag–P coupling) in ³¹P NMR spectra of -85 °C CD₂Cl₂ solutions—results that would be consistent with the formation of a series of different AgI–triphenylphosphine complexes.

DNMR Studies of Exchange Kinetics. The use of NMR line-shape phenomena to study dynamic processes in spin systems has a long history both in organometallic chemistry and in studies of ligand exchange for Ag complexes.^{33,36,42–48} By matching simulated spectra to observed spectra, it is possible to determine kinetic parameters for these exchange processes. In this work, we matched the observed VT NMR spectra with the simulated spectra calculated using MEXICO, a computer program for NMR chemical exchange line-shape calculation.^{45,49,50} The calculated rate constants obtained in this way were then used with the Eyring equation to determine the activation parameters for the exchange process. Activation free energies at 20 °C for 5–7 are ca. 12.6, 11.2, and 11.5 kcal/mol, respectively (details of these calculations are given in the Supporting Information).

Computational Studies of the NHC Exchange Process. To further understand the mechanism for the NHC ligand exchange for (NHC)AgX (X = Cl, Br, I) complexes, we carried out a series of computational studies using density functional theory⁵¹ (MPW1PW91)⁵² as implemented in Gaussian 09.⁵³ Two mechanisms for NHC exchange were evaluated. First, a mechanism involving (NHC)AgCl bond dissociation was considered. It was found that the dissociation energy is ca. 55 kcal/mol in the gas phase and 43 kcal/mol in solution (CH₂Cl₂). While these results suggest that the (NHC)AgCl bond is not a strong bond, the bond dissociation energy is too large to explain the results of the DNMR spectroscopy studies described above. Calculations for an associative reaction pathway shown in Figure 1 for a process in CH₂Cl₂ solution⁵⁴ yielded the results shown in Figure 11.

The ΔG^{\ddagger} values calculated for this associative reaction path are 19.5, 17.5, and 12.5 kcal/mol for X = Cl, Br, I, respectively. While the calculated ΔG^{\ddagger} values are somewhat larger than the experimentally determined values (12.6, 11.2, and 11.5 kcal/mol), they are consistent with our results.

In our calculation results, a structure with a halide bridging two silvers is the energy maximum in the reaction pathway, indicating that the bridging halide plays an important role in stabilizing the transition state. This transition-state structure helps explain the experimental results in this report and in the literature. First, more polarizable halides may serve as better bridging groups and stabilize this proposed transition state. Thus, complexes with a bromide or iodide exchange NHC ligands faster than a complex with a less polarizable chloride anion. Second, this transition-state structure could also explain how different N substituents on the NHC ligands affect NHC exchange rates. In this transition-state structure, one of the N- substituent groups (the methyl group in this case) of the transferring NHC has steric interactions with the *N*-mesityl group of the other NHC groups. These steric interactions are minimized with *N*-methyl substitutuents. However, when there are two bulky substitution groups on the nitrogens (e.g., two mesityl groups in (*N*,*N'*-dimesitylimidazolylidene)silver chloride ((IMes)AgCl)), these same steric interactions would be less favorable, leading to the observed slower NHC ligand exchange rate. This explains the lower NHC exchange rate for more bulky (NHC)Ag^I halide complexes, where the carbene carbon signal at 23 °C is a doublet of doublets.^{26,38}

CONCLUSIONS

¹³C-labeled (N-mesityl-N'-methylimidazolylidene)silver halides have been prepared, and VT ¹³C NMR spectroscopy has been used to study the NHC ligand exchange processes for these complexes. Using ¹³C-labeled derivatives in this study improved the signal to noise ratio of the low-intensity carbene carbon signals and made it possible to obtain spectra at a broader range of concentrations. The use of these labeled NHC complexes also facilitated the detection of low concentrations of ion species that are in equilibrium with neutral NHC silver halide complexes. The concentration-dependent coalescence temperature suggested that an associative process was involved in the exchange, and this mechanism is in agreement with DFT calculations for such an exchange process. Bridging anions are shown to affect the rate of NHC ligand exchange. Added phosphine ligands also affect the nature of these spectra and decrease the NHC ligand exchange rate. These studies provide a more detailed understanding of the solution behavior of NHC-silver complexes that underlies the use of these materials in reactions such as transmetalation and organocatalysis.

EXPERIMENTAL SECTION

General Procedures. All reactions were carried out under an inert atmosphere unless otherwise noted. All reagents and solvents were purchased from commercial sources and used without further purification. ¹H NMR spectra were obtained using 300, 400, and 500 MHz spectrometers. ¹³C NMR spectra were measured on these spectrometers operating at 75, 100, and 125 MHz. Chemical shifts of ¹H and ¹³C NMR spectra are reported in parts per million (δ) relative to residual proton resonances in the deuterated solvents (CDCl₃ and CD₂Cl₂). Coupling constants (*J* values) are reported in hertz (Hz), and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet), br (broad), and m (multiplet). Temperatures recorded for VT NMR experiments were calibrated with 100% MeOH. Simulated spectra were calculated using MEXICO version 3.0.

¹³C-Labeled N-Mesitylimidazole (1). In a 25 mL roundbottomed flask equipped with a magnetic stir bar and rubber septum was added glacial acetic acid (1.83 g, 30.5 mmol), 20% aqueous ¹³Clabeled formaldehyde (1.1 g, 7.11 mmol), and 40% aqueous glyoxal (1.04 g, 7.17 mmol). The reaction vessel was flushed with dry nitrogen, and then the flask was placed in an oil bath regulated at 70 °C. A mixture of glacial acetic acid (1.82 g, 30.3 mmol), ammonium acetate (0.546 g, 7.1 mmol), water (0.16 g), and mesitylamine (0.89 g, 6.6 mmol) was added dropwise over a period of about 20 min with a glass syringe. The reaction mixture was stirred for 19 h at 70 °C. At this point, the reaction mixture was cooled to room temperature and added dropwise into a saturated NaHCO₃ aqueous solution (60 mL). The mixture was stirred for 1 h at room temperature. The precipitate that formed was isolated by filtration and washed with 20 mL of water to yield a brown solid, which was purified by column chromatography with silica gel (hexane then ethyl acetate) to give 0.83 g (67%) of 1 as a yellow solid. ¹H NMR (400 MHz, CDCl₃, room temperature): δ 7.46 (d, ${}^{1}J({}^{13}C-{}^{1}H) = 200$ Hz, 1H), 7.23 (d, J = 7 Hz, 1H), 6.95 (s,

2H), 6.89 (d, J = 7 Hz, 1H), 2.32 (s, 3H) and 1.97 (s, 6H). ¹³C NMR (100 MHz, CDCl₃, room temperature): large peak at δ 137.3, multiple small peaks between 140 and 132, 129.0, 120.1, 21.0, and 17.3. The 92% ¹³C labeling in 1 was determined by integrating the signal for the doublet due to ¹³C–¹H coupling for the proton signal on C2 of the *N*-mesitylimidazole versus the singlet for the ¹²C-containing *N*-mesitylimidazole.

N-Mesityl-N'-methylimidazolium Chloride (2). In a pressure tube equipped with a magnetic stir bar was added N-mesitylimidazole (0.192 g, 1.03 mmol), a 1.0 M solution of chloromethane in tert-butyl methyl ether (5 mL, 5 mmol), and acetonitrile (5 mL). The reaction mixture was stirred in a sand bath regulated at 120 °C for 4 days. After the mixture was cooled to room temperature, the solvent was removed under reduced pressure to yield a white solid. Analysis of this solid with ¹H NMR spectroscopy showed a 75% conversion of the starting material. The desired imidazolium chloride product was separated from this mixture by first dissolving this solid in 0.2 mL of acetonitrile and adding this solution to 10 mL of hexanes. Isolation of the white precipitate afforded 2 as a white solid (0.122 g, 50%). ¹H NMR (500 MHz, CDCl₃, room temperature): δ 10.63 (s, 1H), 7.57–7.54 (m, 1H), 7.11-7.09 (m, 1H), 6.98 (s, 2H), 4.37 (s, 3H), 2.32 (s, 3H), and 2.05 (s, 6H). ¹³C NMR (125 MHz, CDCl₃, room temperature): δ 141.1, 138.5, 134.2, 130.7, 129.7, 124.4, 122.9, 37.3, 21.1, and 17.6. Anal. Calcd for C₁₃H₁₇ClN₂ (236.74): C, 65.95; H, 7.24; N, 11.83. Found: C, 65.78; H, 7.26; N, 11.80. In addition to a much more intense C2 carbon in its ¹³C NMR spectrum, ¹³C-labeled **2** had a doublet at δ 10.56 (¹I(¹³C-¹H) = 224 Hz) in its ¹H NMR spectrum.

N-Mesityl-N'-methylimidazolium Bromide (3). In a pressure tube equipped with a magnetic stir bar was added N-mesitylimidazole (0.183 g, 0.98 mmol), a 2.0 M solution of bromomethane in tert-butyl methyl ether (2 mL, 4 mmol), and acetonitrile (2.5 mL). The reaction mixture was stirred in a sand bath regulated at 60 °C for 20 h. After the mixture was cooled to room temperature, the solvent was removed under reduced pressure until there was 0.5 mL of the solution. When the solution was slowly added to 10 mL of hexanes, a white precipitate formed. Filtration of the mixture afforded a yellowish solid (0.188 g, 68%). ¹H NMR (300 MHz, CDCl₃, room temperature): δ 10.17– 10.11 (m, 1H), 8.02-7.99 (m, 1H), 7.12-7.09 (m, 1H), 6.92 (s, 2H), 4.29 (s, 3H), 2.27 (s, 3H), and 2.00 (s, 6H). ¹³C NMR (75 MHz, CDCl₃, room temperature): δ 141.1, 137.9, 134.1, 130.5, 129.7, 124.7, 122.9, 37.2, 21.0, and 17.6. Anal. Calcd for C₁₃H₁₇BrN₂ (281.19): C, 55.53; H, 6.09; N, 9.96. Found: C, 55.39; H, 6.11; N, 9.93. In addition to a much more intense C2 carbon in its ^{13}C NMR spectrum, $^{13}\text{C}\text{-}$ labeled 3 had a doublet at δ 10.43 (¹J(¹³C-¹H) = 214 Hz) in its ¹H NMR spectrum.

N-Mesityl-*N'*-methylimidazolium lodide (4). In a 25 mL round-bottomed flask equipped with a magnetic stir bar and rubber septum was added 0.107 g of *N*-mesitylimidazole (0.57 mmol), methyl iodide (0.12 g, 0.85 mmol), and dichloromethane (2 mL). The reaction mixture was stirred at room temperature for 18 h. At this point, the solvent was removed under reduced pressure to yield 0.16 g (86%) as a yellow oil. ¹H NMR (500 MHz, CDCl₃, room temperature): δ 9.85–9.83 (m, 1H), 7.88–7.86 (m, 1H), 7.18–7.16 (m, 1H), 6.96 (s, 2H), 4.32 (s, 3H), 2.30 (s, 3H), and 2.06 (s, 6H). ¹³C NMR (125 MHz, CDCl₃, room temperature): δ 141.3, 137.5, 134.2, 130.4, 129.8, 124.7, 123.1, 37.9, 21.0, and 17.9. Anal. Calcd for C₁₃H₁₇IN₂ (328.19): C, 47.58; H, 5.22; N, 8.54. Found: C, 47.48; H, 5.24; N, 8.56. In addition to a much more intense C2 carbon in its ¹³C NMR spectrum, ¹³C-labeled 4 had a doublet at δ 9.90 (¹*J*(¹³C-¹H) = 224 Hz) in its ¹H NMR spectrum.

(*N*-Mesityl-*N*'-methylimidazolylidene)silver(I) Chloride (5). In a 10 mL round-bottomed flask equipped with a magnetic stir bar and rubber septum was added a solution of *N*-mesityl-*N*'methylimidazolium chloride (56 mg, 0.24 mmol) in acetonitrile (2 mL) and silver oxide (28 mg, 0.12 mmol). The flask was covered with aluminum foil, and the reaction mixture was stirred under nitrogen for 18 h. At this point, the stirring was stopped and the reaction mixture was filtered through Celite. The resulting solid was washed twice with 1 mL of acetonitrile. The acetonitrile solutions were combined, and the solvent was removed under reduced pressure to yield a white solid (65 mg, 79%). The product was crystallized from acetonitrile/ether. ¹H NMR (400 MHz, CD₂Cl₂, room temperature): δ 7.22–7.18 (m, 1H), 7.00 (s, 2H), 6.98–6.96 (m, 1H), 3.91 (br, 3H), 2.35 (s, 3H), and 1.97 (br, 6H). ¹³C NMR (100 MHz, CD₂Cl₂, room temperature): δ 182.1, 140.1, 136.1, 135.5, 129.8, 123.3, 122.8, 39.3, 21.4, and 18.0. Anal. Calcd for C₁₃H₁₆AgClN₂ (343.60): C, 45.44; H, 4.69; N, 8.15. Found: C, 45.33; H, 4.67; N, 8.12. In addition to a much more intense C2 carbon in its ¹³C NMR spectrum, ¹³C-labeled **5** had a doublet at δ 39.3 ($J(^{13}C-^{13}C_{methyl}) = 11.2$ Hz) in its ¹³C NMR spectrum.

(*N*-Mesityl-*N*'-methylimidazolylidene)silver(I) Bromide (6). This complex was prepared by following the procedure used for 5 and was isolated as a yellowish solid (111 mg, 95%). The product was crystallized from acetonitrile/ether. ¹H NMR (300 MHz, CD₂Cl₂, room temperature): δ 7.33 (d, *J* = 1.8, 1H), 6.97–6.93 (m, 3H), 3.85 (s, 3H), 2.36 (s, 3H), and 1.85 (s, 6H). ¹³C NMR (100 MHz, CD₂Cl₂, room temperature): δ 182.5, 139.8, 136.0, 135.4, 129.6, 123.3, 123.2, 39.1, 21.4, and 17.9. Anal. Calcd for C₁₃H₁₆AgBrN₂ (388.05): C, 40.24; H, 4.16; N, 7.22. Found: C, 40.26; H, 4.15; N, 7.20. In addition to a much more intense C2 carbon in its ¹³C NMR spectrum, ¹³C-labeled 6 had a doublet at δ 39.2 (*J*(¹³C–¹³C_{methyl}) = 11.1 Hz) in its ¹³C NMR spectrum.

(*N*-Mesityl-*N*′-methylimidazolylidene)silver(I) lodide (7). This complex was prepared by following the procedure used for **5** and isolated as a yellowish solid (0.12 g, 90%). ¹H NMR (400 MHz, CD_2Cl_2 , room temperature): δ 7.35–7.33 (m, 1H), 6.93–6.96 (m, 3H), 3.85 (3H), 2.36 (s, 3H), and 1.84 (s, 6H). ¹³C NMR (100 MHz, CD_2Cl_2 , room temperature): δ 182.7, 139.7, 135.9, 135.4, 129.6, 123.3, 122.2, 39.1, 21.3, and 17.8. Anal. Calcd for $C_{13}H_{16}AgIN_2$ (435.05): C, 38.89; H, 3.71; N, 6.44. Found: C, 35.93; H, 3.69; N, 6.48. In addition to a much more intense C2 carbon in its ¹³C NMR spectrum, ¹³C-labeled 7 had a doublet at δ 38.8 ($J(^{13}C-^{13}C_{methyl}) = 11.2$ Hz) in its ¹³C NMR spectrum. Repeated recrystallizations of 7 yielded a mixture of crystals of 7b and 8, as described in the text.

Bis(N-mesityl-N'-methylimidazolylidene)silver(I) lodide (8). This complex was prepared using the procedure used to form 7, with the difference that no effort was made to avoid exposure of the solution to ambient laboratory lighting. After filtration and concentration, a yellowish solid containing of a mixture of 8 and a trace amount of 7 was afforded. Recrystallization of this mixture afforded 8. ¹H NMR (400 MHz, CD₂Cl₂, room temperature): δ 7.36– 7.34 (m, 1H), 6.93–6.92 (m, 3H), 3.82 (3H), 2.37 (s, 3H), and 1.79 (s, 6H). ¹³C NMR (100 MHz, CD₂Cl₂, room temperature): δ 139.7, 135.9, 135.4, 129.6, 123.3, 123.2, 39.0, 21.4, and 17.8. Anal. Calcd for C₂₆H₃₂AgIN₄ (635.33): C, 49.15; H, 5.08; N, 8.82. Found: C, 49.01; H, 5.10; N, 8.79. At room temperature, the ¹³C-labeled form of 8 had a dominant carbene carbon peak at δ 182.1 (¹J(¹³C–¹⁰⁷Ag) = 179 Hz and ¹J(¹³C–¹⁰⁹Ag) = 207 Hz) in its ¹³C NMR spectrum.

Crystal Structure Determination. A Leica MZ 75 microscope was used to identify a suitable multifaceted crystal with very welldefined faces from a representative sample of crystals of the same habit. The crystal mounted on a nylon loop was then placed in a cold nitrogen stream maintained at 150 K. An Bruker APEXII X-ray (threecircle) diffractometer was employed for crystal screening, unit cell determination, and data collection. The goniometer was controlled using the APEX2 software suite. The sample was optically centered with the aid of a video camera such that no translations were observed as the crystal was rotated through all positions. The detector was set at 6.0 cm from the crystal sample. The X-ray radiation employed was generated from a Mo sealed X-ray tube (λ (Mo K α) = 0.701 73 Å with a potential of 40 kV and a current of 40 mA) fitted with a graphite monochromator in the parallel mode (175 mm collimator with 0.5 mm pinholes). The reflections were used in the autoindexing procedure to determine the unit cell. A suitable cell was found and refined by nonlinear least squares and Bravais lattice procedures. The unit cell was verified by examination of the hkl overlays on several frames of data. No supercell or erroneous reflections were observed. After careful examination of the unit cell, a standard data collection procedure was initiated using ω scans. Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX2. The integration method employed a threedimensional profiling algorithm, and all data were corrected for Lorentz and polarization factors, as well as for crystal decay effects. Finally the data were merged and scaled to produce a suitable data set. The absorption correction program SADABS was employed to correct the data for absorption effects. Systematic reflection conditions and statistical tests for the data suggested the space group. A solution was obtained readily using SHELXTL (SHELXS). All non-hydrogen atoms were refined with anisotropic thermal parameters. The Hydrogen atoms bound to carbon were placed in idealized positions (C–H = 0.96 Å, $U_{\rm iso}({\rm H}) = 1.2[U_{\rm iso}({\rm C})]$). The structure was refined (weighted least-squares refinement on F) to convergence.

Energy Dispersive X-ray Analysis (EDX). Elemental analysis of Ag, I, and Cl was analyzed using a Cameca SX50 electron microprobe equipped with four wavelength-dispersive spectrometers (WDS). A WDS spectrometer is a monochromator which consists of a rotatable, oriented diffraction crystal coupled with a proportional gas-filled ionization detector in a geometric relationship following Bragg's law. WDS was used rather than EDS because of the former's better resolution, detection limits, accuracy, and reproducibility. Analyses were carried out at an accelerating voltage of 15 kV at a beam current of 10 nA and a beam diameter of 20 μ m using PET diffracting crystals. The sample was prepared by pressing several milligrams of the powdered material between two highly polished (0.25 μ m) stainless steel cylinders to yield a thin millimeter diameter smooth-surfaced pellet that was then transferred onto a conductive carbon tape. The pellet was coated with approximately 150 Å of spec pure carbon to prevent charge buildup under the electron beam. During analysis, the sample stage was moved repetitively between 10 adjacent points at 2 s intervals to obtain more representative sampling of the pellet surface and to minimize any possible thermal damage to the sample. The following standards were used: Ag₂S for Ag, RbI for I, and NaCl for Cl. All analyses were processed through the Cameca PAP (Pouchot and Pichoir) full-quantitative ZAF type matrix correction program. In order to more properly correct for interelement matrix effects, carbon was calculated by difference to sum the analyses to 100% by weight. BSE (backscattered electron) imaging was used to examine the surface for homogeneity. BSE examination yields an image where the brightness is directly proportional to the mean atomic number.

Computational Methodology. All calculations were performed with the Gaussian 09 (G09) suite of programs.⁵³ Full geometry optimizations were performed using density functional theory $(DFT)^{51}$ with the MPW1PW91 (Barone's modified Perdew–Wang 1991 exchange functional and Perdew and Wang's 1991 correlation functional)⁵² using the SDD (Stuttgart–Dresden) basis set and effective core potential (ECP)⁵⁵ for the silver atoms and the 6-311G(d,p) basis set⁵⁶ for all other elements. To estimate solvation effects, the geometry optimizations were performed with the SMD parametrized⁵⁴ PCM (polarized continuum model) for CH₂Cl₂. Geometry optimizations were performed on **5a**–**7a** and the transition states to their respective ionic species [NHC₂Ag][AgX₂] (X = Cl, Br, I: **5b**–**7b**, respectively), and the theoretical models of free NHC and free AgCl.

ASSOCIATED CONTENT

S Supporting Information

Text, figures, tables, and CIF files giving spectroscopic data, NMR line shape analysis, computational details, and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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