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# A Monomeric Imidazol-2-ylidene–Silver(I) Chloride Complex: Synthesis, Structure, and Solid State $^{109}$Ag and $^{13}$C CP/MAS NMR Characterization

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The structure of 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene–silver(I) chloride, **1**, has been determined to be a monomer with weak head-to-tail H···Cl interactions in the solid state. A multinuclear NMR study using a $^{13}C_{carbene}$ labeled derivative, **1($^{13}$C)**, exhibits $^{13}$C–$^{107,109}$Ag coupling in solution. Further, the solid state CP/MAS NMR parameters, including the principal components of the chemical shift tensors for both the $^{13}$C and $^{109}$Ag centers, have been determined. With the aid of DFT calculations, the orientation of the chemical shift tensors have been assigned.

The study of transition metal complexes containing *N*-heterocyclic carbene ligands is becoming increasingly important since many of these compounds are now used extensively as catalysts for C−C bond-forming reactions.[1] There is current interest in silver(I) complexes of *N*-heterocyclic carbenes due to their ease of preparation and their function as carbene transfer reagents.[2,3] The use of $Ag_2O$ to afford these silver carbene complexes by in situ deprotonation of precursor imidazolium halides is now widespread.[4] As both the reactants and the silver carbene complexes are air-stable, this reaction is a convenient entry point into metal carbene chemistry without the need for the rigorously anaerobic conditions required for syntheses of free *N*-heterocyclic carbenes.

Silver(I) monocarbene complexes display a wide variety of structural motifs depending on the size of the coordinated carbene.[4] These species tend to oligomerize via silver−silver interactions, bridging halide ligands, or even Ag−($\mu_2$-$C_{carbene}$)−Ag interactions.[5] Monomeric examples of such complexes are rare. In fact, only one monomeric carbene complex of AgCl has been characterized to date.[6] Furthermore, $^{109}$Ag is a challenging NMR nucleus to study,[7−9] and only a few CP/MAS NMR studies have been performed till now.[10−12]

Due to the great variety of structures adopted by silver(I) carbene complexes and to the presence of NMR active nuclei $^{13}$C and $^{109}$Ag, the study of these complexes offers many insights into the nuances of *N*-heterocyclic carbene−transition metal bonding. In this context, it is surprising that a CP/MAS NMR study on these species has not yet been performed as this technique has recently yielded valuable insights into phosphine silver halide complexes.[5,13]

Herein we report the synthesis, structure, and a CP/MAS solid-state NMR study of 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene−silver(I) chloride, **1**. We also report the use of the $^{13}C_{carbene}$ labeled complex,[14] **1($^{13}$C)**, to determine both the $^{13}C_{carbene}$ and $^{109}$Ag chemical shift tensors while the orientations of these tensors are assigned using DFT calculations.

Complex **1** was prepared by reaction of 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride, with $Ag_2O$.[15] Its molecular structure, determined by X-ray diffraction, is that of a monomer with $C_2$ symmetry (Figure 1).[15] The spectroscopic data obtained are in accord with the crystallographically determined structure; the $^{13}$C resonance for the $C_{carbene}$ is, however, not observed at natural abundance.

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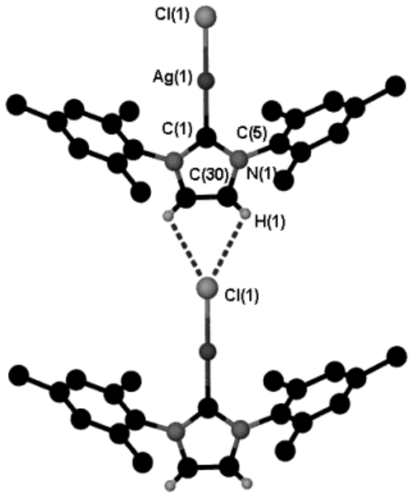

**Figure 1.** Selected bond lengths (Å) and angles (deg) for **1**, thermal ellipsoids are shown at 50% probability level: Cl(1)−Ag(1) 2.314(2), Ag(1)−C(1) 2.056(7), C(1)−N(1) 1.357(5), N(1)−C(5) 1.438(4), N(1)−C(30) 1.386(4), H(1)···Cl 2.954, C(1)···Cl 3.378; Ag(1)−C(1)−N(5) 127.8-(2), C(1)−N(1)−C(5) 121.8(3), C(1)−N(1)−C(30) 111.5(3).

**Table 1.** Solution and Solid State NMR Data for **1** ($^{13}$C and $^{109}$Ag) and **3**, 1,3,4,5- Tetramethyl-imidazol-2-ylidene[25]

| param | $^{109}$Ag | $^{13}$C | **3** | [**3**H$^+$] |
|---|---|---|---|---|
| $\delta_{iso}$ | 532.2(0.3) | 184.1(0.1)[a] | 209 | 136.6 |
| $\delta_{11}$ | 1228(39) | 299(4), 295(3)[b] | 370 ± 20 | 179 |
| $\delta_{22}$ | 1036(58) | 163(4), 164(3) | 177 ± 18 | 141 |
| $\delta_{33}$ | −667(49) | 88(3), 85(5) | 82 ± 15 | 92 |
| Ω (span) | 1895(40) | 211(3), 210(3) | | |
| K (skew) | 0.80(0.07) | −0.28(0.05), −0.22(0.04) | | |
| $\delta_{solution}$[c] | 597 | 185[d] | | |

[a] $^1J_{C-Ag} = 250(1)$ Hz, ($^{109}$Ag−$^{107}$Ag); $^{13}$C splitting not resolved. [b] The two components of *J*-split doublet. [c] $CD_2Cl_2$ solution. [d] $^1J_{^{13}C-^{109}Ag} = 270$ Hz, $^1J_{^{13}C-^{107}Ag} = 234$ Hz.

Solution and solid state NMR data for $^{13}$C and $^{109}$Ag nuclei of **1($^{13}$C)** are presented in Table 1.[16,17] These results allow direct comparison with the multinuclear NMR study of the first silver(I) carbene complex, 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene−silver(I) triflate, **2**, by Arduengo et al.[19] The $^{13}$C signal obtained in $CD_2Cl_2$ solution for the $C_{carbene}$ appears as two doublets, consistent with splitting by the two spin $^1/_2$ nuclei, $^{107}$Ag and $^{109}$Ag. These $^{13}$C resonances for the $C_{carbene}$ are centered at 185 ppm in $CDCl_3$ solution, very close to the value given for **2** (183 ppm)[19] and well within the characteristic range for coordinated *N*-heterocyclic carbenes (170−190 ppm). For silver(I) carbene complexes in solution, [$^{13}$C−$^{107,109}$Ag] coupling cannot always be identified, and this absence has been attributed to silver−carbon bond lability.[3] The $^{13}$C−$^{107,109}$Ag coupling constants are large (270 Hz $^{109}$Ag−$^{13}$C and 234 Hz $^{107}$Ag−$^{13}$C), some 60 Hz greater than those observed for **2**.[19]

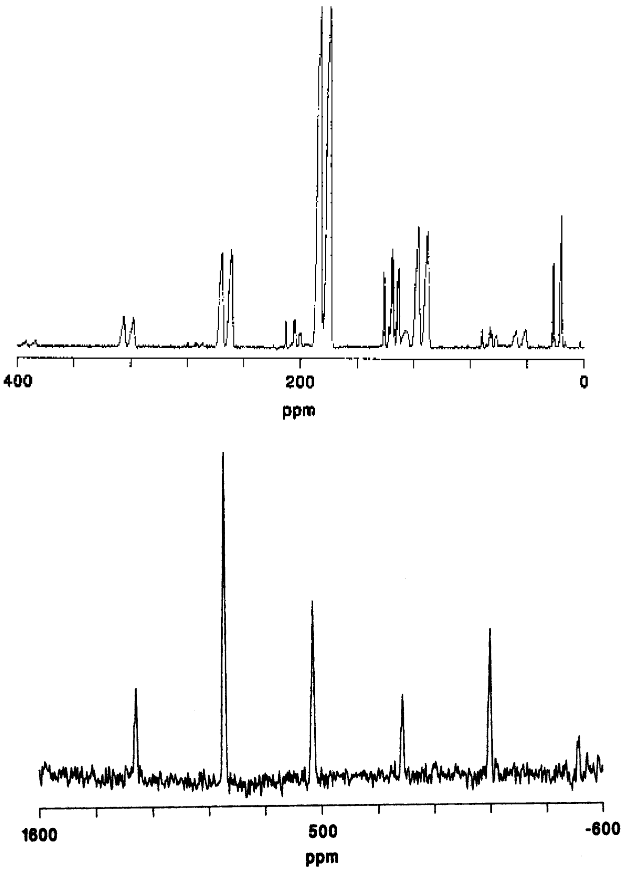

**Figure 2.** Solid state NMR spectra. Top: $^{13}$C spectrum of **1($^{13}$C)**, MAS 2600 Hz, frequency 37.5 MHz, contact time 2 ms, relaxation delay 3 s, 11146 scans. Bottom:$^{109}$Ag spectrum of **1**, MAS 2400 Hz, frequency, 6.95 MHz contact time 50 ms, relaxation delay 5 s, 54134 scans.

The $^{109}$Ag resonance for **1($^{13}$C)** occurs at 597 ppm, which is very close to that observed for **2** (642.4 ppm). In contrast to **2**, no $^{109}$Ag−$^1$H coupling is observed.[19] This is most probably due to line broadening of the $^{109}$Ag resonance of **1($^{13}$C)** caused by the adjacent quadrupolar chloride nucleus.

The monomeric nature and high molecular symmetry of **1** make it ideal for a solid state CP/MAS NMR study. The $^{13}$C CP/MAS spectra of the enriched compound, **1($^{13}$C)** (Figure 2), recorded at different spinning speeds establish that the isotropic peaks are the doublet centered at 184 ppm.[17] The peaks are broad and asymmetric, due to interaction with the neighboring $^{14}$N. Further splitting arises from coupling to the $^{107,109}$Ag nuclei; the lines are too broad to resolve the

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(16) Spectroscopic and analytical data. **1**: $^1$H NMR (400 MHz, $CD_2Cl_2$) δ 2.05 (s, 12 *H*, *o*-C*H*$_3$), 2.37 (s, 6 *H*, *p*-C*H*$_3$), 6.97 (s, 4*H*, Ar*H*), 7.12 (s, 2*H*, C=C*H*); $^{13}$C{$^1$H} NMR (100.61 MHz, $CD_2Cl_2$) 19.6 (s, *o*-*C*H$_3$), 23.0 (s, *p*-*C*H$_3$), 125.0 (s, N*CC*), 131.5 (s, Ar-*C*-3,5), 136.9 (s, Ar-*C*-2,6), 137.6 (s, Ar-*C*1), 141.9 (s, Ar-*C*-4), Ag−C signal is not observed (vide infra). $^{109}$Ag{$^1$H} (18.61 MHz, $CD_2Cl_2$) 630. IR (Nujol): 3158, 2915, 1607, 1486, 1236, 1075, 930, 865, 744. Anal. Calcd for $C_{21}H_{24}AgClN_2$: C, 56.33; H, 5.40; N, 6.26. Found: C, 56.14; H, 5.41; N, 6.31. For **1($^{13}$C)**, the $^{13}$C NMR spectrum also contained new signals at δ 183.59, d, $^1$*J*($^{13}$C−$^{107}$Ag) 234 Hz, 186.09, d, $^1$*J*($^{13}$C−$^{109}$Ag) 270 Hz, and these were assigned to the carbenic carbon.

(17) Solid state spectra were recorded on a home-built instrument operating at 3.5 T, which produces a resonance frequency of 37.55 MHz for $^{13}$C and 6.95 MHz for $^{109}$Ag. All spectra were obtained by cross-polarization (CP), with a proton back flip. For $^{13}$C, matched radio frequency fields of 55 kHz were used for cross-polarization, and the same field was used for proton decoupling; a contact time of 2 ms was used. For $^{109}$Ag, cross-polarization used matched fields of 25 kHz, with contact times of 30−50 ms, and a decoupling field of 45 kHz was used during data acquisition. Spinning speeds of 2−3 kHz were used, electronically controlled to ±1 Hz. $^{13}$C spectra were referenced to TMS, taking the high frequency peak of adamantane to be at 38.56 ppm. $^{109}$Ag spectra were referenced to dilute aqueous Ag$^+$ via the proton resonance of TMS, assuming a Ξ value of 4.653623 (*Multinuclear NMR*; Mason, J., Ed.; Plenum: New York, 1987; p 627).

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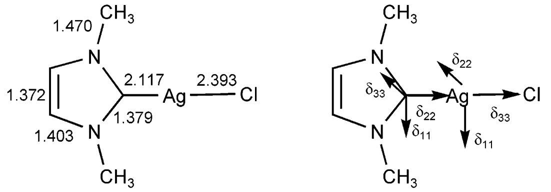

**Figure 3.** Calculated structure of **4**. Left: Structural parameters, bond lengths are in angstroms; bond angles in degrees (N−C−N 104.2). Right: Calculated orientation of the chemical shift tensors.

two isotopic splittings. By fitting sideband intensities for the spectra obtained at 1400, 1700, and 2000 Hz spinning speeds,[20] we find the principal components presented in Table 1. It is interesting to observe that two of the three components are similar for **1** and for the free carbene (1,3,4,5-tetramethylimidazol-2-ylidene, **3**) and [carbene−H$^+$] (1,3,4,5-tetramethylimidazolium, [**3**H$^+$]) tensors (Table 1). The differences lie almost entirely in $\delta_{11}$ (Figure 3).

To date, determination of the $^{109}$Ag NMR parameters of Ag−carbene complexes by a CP/MAS study has not been reported, and this is probably due to the fact that the gyromagnetic ratios of the silver isotopes are extremely low. We have, however, successfully obtained the $^{109}$Ag spectral data for **1** in both the solid and solution phase.

Figure 2 shows the $^{109}$Ag spectrum of a sample with natural-abundance carbon, recorded at a spinning speed of 2400 Hz. Spectra at other speeds show the line at 532 ppm to be the center band. There is a ca. 65 ppm difference between the isotropic chemical shift obtained in $CD_2Cl_2$ solution and in the solid state. A spectrum of **1($^{13}$C)** shows the same splitting due to C−Ag coupling as was observed in the $^{13}$C spectrum. Fitting sidebands obtained at 2200, 2400, and 2700 Hz leads to the principal values shown in Table 1. The $^{109}$Ag shielding is nearly axially symmetric, which is to be expected from the linear C−Ag−Cl geometry. This axis coincides with the crystallographic 2-fold axis, so one of the tensor components must lie along this axis. From the near axial symmetry, this must be $\delta_{33}$ (Figure 3). An expanded view of the $^{109}$Ag lines shows them to be asymmetric, and they appear to contain unresolved structure. This probably arises from scalar or dipolar coupling to the quadrupolar Cl, which can give rise to complicated patterns.[21]

In order to assign the orientation of the chemical shift tensor, a theoretical study was performed on a simplified model, 1,3-dimethylimidazol-2-ylidene−silver(I) chloride, **4**.[22] The geometry of the molecule was optimized using the B3LYP functional[23] with the LanL2DZ basis set.[24] The calculated bond lengths for the molecule are shown in Figure 3 and are in excellent agreement with the experimental values for **1** determined by X-ray crystallography (Figure 1). The chemical shifts were calculated at the same level of theory using the gauge-invariant atomic orbital (GIAO) method.[18] On the basis of these calculations, the principal directions of the chemical shift tensors for the $^{13}$C and Ag centers are shown in Figure 3. The orientation of the $^{13}$C chemical shift tensor is the same in **1** and the free carbene with the only significant change occurring for value $\delta_{11}$.[25]

In conclusion, 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene−silver(I) chloride, **1**, has been synthesized and its structure confirmed using X-ray crystallography. Solution and solid state multinuclear NMR studies have been conducted using a $^{13}$C-enriched analogue allowing observation of both the $^{13}C_{carbene}$ and $^{109}$Ag nuclei and the orientations of their chemical shift tensors to be assigned. Realization of the full potential of silver(I) carbene complexes as carbene transfer reagents requires a complete understanding of the thermodynamic and kinetic properties of these species. Solution and solid state $^{13}$C and $^{109}$Ag NMR provides much needed data for this system.

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**Supporting Information Available:** Crystallographic information in CIF format. Input coordinates and details on theoretical calculations and synthesis of 1,3-dimethylimidazol-2-ylidene silver(I) chloride. This material is available free of charge via the Internet at http://pubs.acs.org.

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