1928 *Organometallics* **2004,** *23,* 1928−1931

Synthesis and Structural Characterization of *N*-Heterocyclic Carbene Complexes of Silver(I) and Rhodium(I) from Caffeine

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Received December 15, 2003

The imidazolium cation 1,3,7,9-tetramethylxanthinium methyl sulfate (**1a**) is obtained by the reaction of caffeine with dimethyl sulfate. The anion exchange of **1a** gives 1,3,7,9-tetramethylxanthinium hexafluorophosphate (**1b**). Ligand **1a** reacts with Ag_2O in water to yield an *N*-heterocyclic carbene (NHC) silver(I) complex (**2a**). Similarly, ligand **1b** reacts with Ag_2O in DMSO to yield NHC silver(I) complex **2b** in high yield. A carbene transfer reaction of **2b** with $[Rh(COD)Cl]_2$ gives NHC Rh(I) complex **3**. All compounds were characterized by ^1H NMR, ^{13}C NMR, and mass spectrometry. The solid-state structures of **1b**, **2b**, and **3** were determined by X-ray crystallography.

Introduction

Imidazol-2-ylidene carbenes, also known as *N*-heterocyclic carbenes (NHCs), can be obtained through deprotonation of *N,N′*-disubstituted imidazolium salts. These nucleophilic carbenes have become a very attractive class of ligands due to their strong σ-donor ability to complex very strongly to main group and transition metals.[1] The synthesis of transition metal complexes of NHCs was first described by Öfele[2]and Wanzlick[3] in 1968. Arduengo isolated the first free NHC in 1991[4] and synthesized the first homoleptic silver(I) carbene complex two years later.[5] It has been shown that transition metal complexes of NHCs are very good catalysts in many chemical transformations.[6] Recently, the use of silver carbene complexes as carbene transfer reagents has proven to be an effective method for the synthesis of other transition metal carbene complexes.[7−9] The gold(I) and palladium(II) NHC complexes synthesized by Wang and Lin in 1998 are the first examples of this method.[10] Tungsten carbene complexes have also been used as effective carbene transfer reagents for the formation of Pt, Pd, Au, and Rh complexes.[11]

Caffeine, 1,3,7-trimethylxanthine, is one of the xanthine derivatives that are generally used in medicines as diuretics, central nervous system stimulants, and inhibitors of cyclic adenosine monophosphate (c-AMP) phosphodiesterase.[12] The presence of the methylimidazole moiety in the structure of caffeine makes it a valuable candidate for the synthesis of an *N*-heterocyclic carbene. The first step is to obtain an imidazolium cation, such as 1,3,7,9-tetramethylxanthinium or methylated caffeine, from caffeine. 1,3,7,9-Tetramethylxanthinium was synthesized by methylation of caffeine with dimethyl sulfate,[12,13] methyl tosylate,[13] or methyl iodide.[14] The physiological action of 1,3,7,9-tetramethylxanthinium hydroxide in frogs has been reported.[15] Silver(I) complexes with xanthine and some methylated xanthine derivatives including caffeine in which xanthine derivatives are linked to silver(I) through the N-9 atom have been reported.[16] Ru(II) and Ru(III) complexes in which the ligand is the protonated imidazolylidene from caffeine also have been described.[17,18] We report herein the synthesis and characterization of the NHC silver(I) complexes **2a** and **2b** from methylated caffeine, **1a** and **1b**, and the Rh(I) complex, **3**, via transfer of the NHC from **2b** (Figure 1).

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10.1021/om030689r CCC: $27.50
Publication on Web 03/19/2004

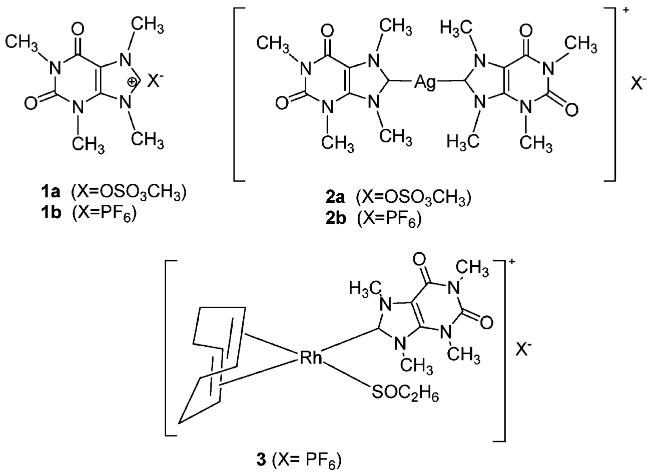

Figure 1.

Experimental Section

Technical Details of the X-ray Structure Determinations. Crystal of **1b**, **2b**, and **3** were coated in paraffin oil, mounted on a kryo loop, and placed on a goniometer under a stream of nitrogen. X-ray data sets were collected on a Bruker Apex CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Unit cell determination was achieved by using reflections from three different orientations. An empirical absorption correction and other corrections were done by using multiscan SADABS. Structure solution, refinement, and modeling were accomplished by using the Bruker SHELXTL package.[19] The structure was obtained by full-matrix least-squares refinement of F^2 and the selection of appropriate atoms from the generated difference map.

General Considerations. All manipulations were carried out in air. The compounds dimethyl sulfate and Ag_2O were purchased from Aldrich and used without further purification. Caffeine was purchased from Acros and used without further purification. $[Rh(COD)Cl]_2$ (COD = cyclooctadiene) was purchased from Strem and used without further purification. ^{1}H and ^{13}C NMR data were recorded on a Gemini 300-MHz instrument and referenced to residual protons and ^{13}C signals of deuterated solvents. Mass spectrometry data were collected on a Bruker Daltons (Billerica, MA) Esquire-LC mass spectrometer equipped with a ESI and VG Autospec tandem mass spectrometer equipped with FAB.

Synthesis of 1,3,7,9-Tetramethylxanthinium Methyl Sulfate[12] (1a). Caffeine (10.0 g, 51.5 mmol) was dissolved in nitrobenzene (150 mL) at 100 °C for 1 h. Dimethyl sulfate (10.5 mL) was added to the solution and the mixture was refluxed at 100 °C for 24 h. The reaction mixture was cooled to room temperature, excess diethyl ether was added, and the solvent was decanted. The residue was washed with diethyl ether several times and a white solid **1a** (2.38 g, 7.43 mmol, 72%) was obtained. Mp: 175 °C. ^{1}H NMR (300 MHz, D_2O): δ 8.93 (s, 1H, NCHN), 4.17 (s, 3H, CH_3), 4.05 (s, 3H, CH_3), 3.73 (s, 3H, CH_3), 3.35 (s, 3H, O_3SOCH_3), 3.27 (s, 3H, CH_3). ^{13}C {^{1}H} NMR (75 MHz, D_2O): δ 154.9 (C=O), 151.8 (C=O), 140.1 (C=C), 139.8 (NCHN), 109.0 (C=C), 55.3 (O_3SOCH_3), 37.2, 36.0, 31.9, 28.8 (NCH_3). ESI-MS (*m*/*z*): [M$^+$] calcd for $C_{10}H_{16}N_4O_6S$ 209.2, found 209.1.

Synthesis of 1,3,7,9-Tetramethylxanthinium Hexafluorophosphate (1b). **1a** (1.44 g, 4.50 mmol) was dissolved in water and NH_4PF_6 (0.75 g, 4.6 mmol) was added. The white crystalline product **1b** (1.20 g, 3.39 mmol, 76%) was obtained by filtration. Mp: 240 °C. Anal. Calcd for $C_9H_{13}F_6N_4O_2P$: C, 30.52; H, 3.70; N, 15.82. Found: C, 30.40; H, 3.71; N, 15.71. ^{1}H NMR (300 MHz, d_6-DMSO): δ 9.25 (s, 1H, NCHN), 4.13 (s, 3H, CH_3), 4.05 (s, 3H, CH_3), 3.73 (s, 3H, CH_3), 3.27 (s, 3H, CH_3). ^{13}C {^{1}H} NMR (75 MHz, d_6-DMSO): δ 153.4 (C=O), 150.3 (C=O), 139.7 (C=C), 139.4 (NCHN), 107.9 (C=C), 36.8, 35.7, 31.4, 28.5 (NCH_3). FAB-MS (*m*/*z*): [M$^+$] calcd for $C_9H_{13}F_6N_4O_2P$, 209.2; found 209.0.

X-ray crystal structure analysis of **1b**: formula $C_9H_{13}F_6N_4O_2P$, $M_w = 354.20$, colorless crystal 0.20 × 0.10 × 0.02 mm^3, $a = 12.776(1)$ Å, $b = 6.4242(7)$ Å, $c = 17.118(2)$ Å, $\alpha = 90°$, $\beta = 111.836(2)°$, $\gamma = 90°$, $V = 1304.1(3)$ Å^3, $D_{calc} = 1.804$ Mg cm^{-3}, $\mu = 0.299$ mm^{-1}, $Z = 4$, monoclinic, space group $P2_1/c$ (no. 14), $\lambda = 0.71073$ Å, $T = 100$ K, ω and φ scans, 8899 reflections collected, 2290 independent ($R_{int} = 0.0236$), 252 refined parameters, R1/wR2 ($I \geq 2\sigma(I)$) = 0.0528/0.1249 and R1/wR2 (all data) = 0.0584/0.1285, maximum (minimum) residual electron density 0.779 (−0.366) e Å^{-3}, hydrogen atoms were found from the difference map and their positions refined.

Synthesis of NHC Silver(I) complex (2a). **1a** (0.64 g, 2.0 mmol) was dissolved in water (72 mL) and Ag_2O (0.46 g, 2.0 mmol) was added. The mixture was stirred at room temperature for 2.5 h. The brown suspension was filtered to give a colorless solution. The volatiles were removed in vacuo. Compound **2a** (0.52 g, 0.82 mmol, 92%) was obtained as an off-white solid. Mp: 125 °C. ^{1}H NMR (300 MHz, D_2O): δ 4.21 (s, 6H, CH_3), 4.13 (s, 6H, CH_3), 3.82 (s, 6H, CH_3), 3.36 (s, 3H, O_3SOCH_3), 3.27 (s, 6H, CH_3). ^{13}C {^{1}H} NMR (75 MHz, D_2O): δ 187.1 (C−Ag), 155.0 (C=O), 152.1 (C=O), 141.1 (C=C), 110.1 (C=C), 55.6 (O_3SOCH_3), 39.5, 38.2, 37.0, 35.9, 32.2, 31.9, 28.8 (d, CH_3). ESI-MS (*m*/*z*): [M$^+$] calcd for $C_{19}H_{27}AgN_8O_8S$ 523.1, found 523.1.

Synthesis of NHC Silver(I) Complex (2b). **1b** (1.4 g, 4.0 mmol) was dissolved in DMSO (144 mL) and Ag_2O (0.93 g, 4.0 mmol) added. The mixture was stirred at 60 °C for 2.5 h to form a brown suspension. After filtration a clear, pale brown solution was obtained. The solvent was removed in vacuo to yield the brick red solid **2b** (2.59 g, 3.87 mmol, 97%). Mp: 205 °C. ^{1}H NMR (300 MHz, d_6-DMSO): δ 4.15 (s, 6H, CH_3), 4.01 (s, 6H, CH_3), 3.72 (s, 6H, CH_3), 3.38 (s, 2H, H_2O), 3.21 (s, 6H, CH_3). ^{13}C {^{1}H} NMR (75 MHz, d_6-DMSO): δ 186.6 (C−Ag), 153.0 (C=O), 150.3 (C=O), 140.2 (C=C), 108.6 (C=C), 40.1, 37.5, 31.2, 27.9 (N−CH_3). FAB-MS (*m*/*z*): [M$^+$] calcd for $C_{18}H_{24}AgF_6N_8O_4P$ 523, found 523.

X-ray crystal structure analysis of **2b**: formula $C_{32}H_{40}AgF_6N_8O_4P$, $M_w = 853.56$, colorless crystal 0.33 × 0.18 × 0.10 mm^3, $a = 32.090(12)$ Å, $b = 6.590(2)$ Å, $c = 8.354(3)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $V = 1766.6(11)$ Å^3, $D_{calc} = 1.605$ Mg cm^{-3}, $\mu = 0.697$ mm^{-1}, $Z = 2$, orthorhombic, space group $Imm2$ (no. 44), $\lambda = 0.71073$ Å, $T = 100$ K, ω and φ scans, 7814 reflections collected, 2332 independent ($R_{int} = 0.0273$), 174 refined parameters, R1/wR2 ($I \geq 2\sigma(I)$) = 0.0294/0.0762 and R1/wR2 (all data) = 0.0307/0.0857, maximum (minimum) residual electron density 0.559 (−0.494) e Å^{-3}, all hydrogen atoms were calculated and refined as riding atoms.

Synthesis of NHC Rh(I) Complex (3). Compound **2b** (0.67 g, 1.0 mmol) was dissolved in DMSO (40 mL) and $[Rh(COD)Cl]_2$ (0.50 g, 1.0 mmol) added. The mixture was stirred at 60 °C for 1 h to form a suspension. After filtration a clear, brick red solution was obtained. The solvent was removed in vacuo to yield **3** (0.63 g, 0.98 mmol, 99%). Mp: 157 °C. ^{1}H NMR (300 MHz, d_6-DMSO): δ 4.23 (s, CH_3), 3.72 (s, CH_3), 3.50 (s, CH_3), 3.22 (s, CH_3), 2.50 (m, 6H, C_2H_6OS), 4.93 (m, 2H, $CH_{(COD)}$), 4.44 (m, 2H, $CH_{(COD)}$), 2.28 (m, 4H, $CH_{2(COD)}$), 1.96 (m, 4H, $CH_{2(COD)}$). ^{13}C {^{1}H} NMR (75 MHz, d_6-DMSO): δ 188.4 (d, C−Rh, $^1J_{Rh-C} = 43.8$ Hz), 152.3 (C=O), 150.0 (C=O), 141.0 (C=C), 110.0 (C=C), 98.3 ($CH_{(COD)}$, $^1J_{CH-Rh} = 7.35$ Hz), 97.8 ($CH_{(COD)}$, $^1J_{CH-Rh} = 7.35$ Hz), 40.4, 37.1, 30.0, 27.9 (N−CH_3), 30.6 ($CH_{2(COD)}$), 29.0 ($CH_{2(COD)}$). ESI-MS (*m*/*z*): [M$^+$] calcd for $C_{19}H_{30}RhF_6N_4O_3PS$ 419.0, found 419.1.

X-ray crystal structure analysis of **3**: formula $C_{19}H_{30}F_6N_4O_3PRhS$, $M_w = 642.41$, colorless crystal 0.16 × 0.11 × 0.07 mm^3, $a = 12.4032(17)$ Å, $b = 14.879(2)$ Å, $c = 15.685(2)$ Å, $\alpha = 81.515(2)°$, $\beta = 68.783(2)°$, $\gamma = 74.762(2)°$, $V = 2599.2(6)$ Å^3,

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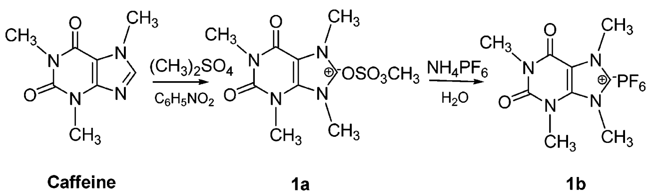
Scheme 1



D_{calc} = 1.642 Mg cm^{-3}, μ = 0.870 mm^{-1}, Z = 4, triclinic, space group $P\bar{1}$ (no. 2), λ = 0.71073Å, T = 100 K, ω and φ scans, 18806 reflections collected, 9123 independent (R_{int} = 0.0327), 872 refined parameters, R1/wR2 ($I \geq 2\sigma(I)$) = 0.0364/0.0909 and R1/wR2 (all data) = 0.0452/0.0940, maximum (minimum) residual electron density 0.955 (−0.902) e Å^{-3}, hydrogen atoms were found from the difference map and their positions refined.

Results and Discussions

Methylated caffeine, 1,3,7,9-tetramethylxanthinium **1a**, is synthesized by the reaction of caffeine with dimethyl sulfate in a 1:2 molar ratio and converted to **1b** by ion exchange with NH_4PF_6 (Scheme 1). The ^{1}H and ^{13}C NMR spectra of **1a** and **1b** are similar and consistent with their molecular structures. In the ^{1}H NMR spectra of **1a** and **1b**, the imidazolium protons appear at 8.93 and 9.25 ppm, respectively. This is consistent with the general C−H acidic proton shift of imidazolium salts (δ 8−10).[1b] The ^{13}C NMR shift of the N−C−N sp^2 carbons, which later become the carbene centers, appear at 139.8 and 139.4 ppm for **1a** and **1b**, respectively.

The water-soluble ligand **1a** reacts with Ag_2O in water to form **2a**. Complex **2a** is stable in water and in the dark for 5 days. Similarly, ligand **1b** readily reacts with Ag_2O in DMSO at 60 °C to yield the silver NHC complex **2b** in high yield (Scheme 2). Complex **2b** is stable in air and light up to its melting point and only soluble in DMSO. It is stable in wet DMSO for months in the light. The formation of **2a** and **2b** can be monitored by changes in the ^{1}H NMR and ^{13}C NMR spectra. The disappearance of the resonance for the imidazolium protons of **1a** and **1b** and the appearance of the resonance for the carbene carbon atoms at 187.1 and 186.6 ppm, respectively, shows the formation of expected NHC silver carbene complexes. The lack of C−^{107}Ag and C−^{109}Ag couplings suggests fluxional behavior on the ^{13}C NMR time scale as observed with many silver(I) complexes.[7,8] It has been reported that silver−carbene complexes without Ag−carbene couplings are useful as carbene transfer reagents due to their dynamic behavior in solution.[20]

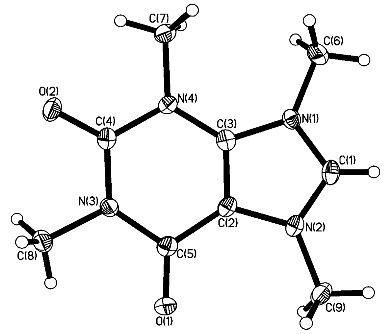


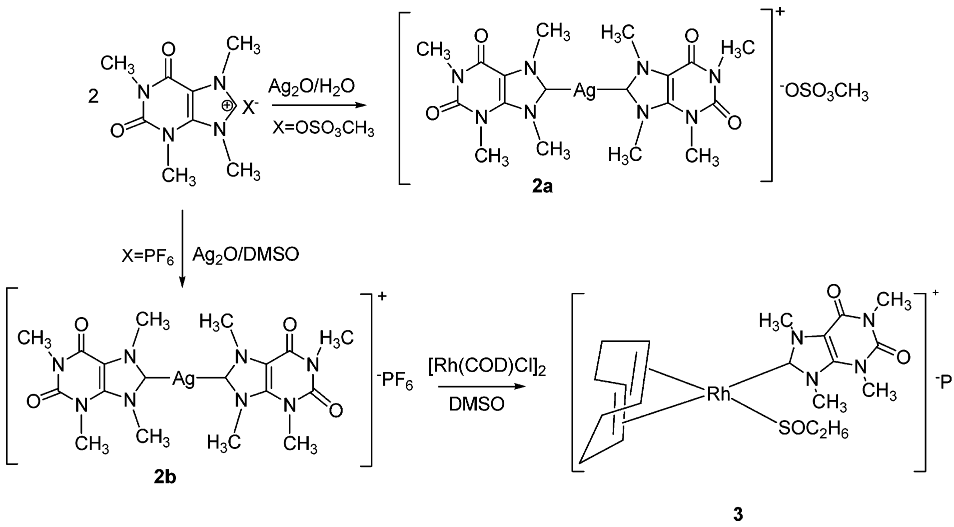
Figure 2. Molecular structure of the cationic part of **1b**.

The reaction of equimolar amounts of complex **2b** and $[Rh(COD)Cl]_2$ in DMSO to give the corresponding Rh(I) complex, **3**, shows the ability of **2b** to serve as a carbene transfer reagent (Scheme 2). Complex **3** is stable in air up to its melting point. In the ^{13}C NMR spectrum, the carbene carbon appears as a doublet at 188.46 ppm ($^1J_{C-Rh}$ = 43.8 Hz). The chemical shift of the carbene carbon and coupling constant are similar to those previously reported for other NHC rhodium complexes.[7,21]

Single crystals of **1b** were obtained by the anion exchange of **1a** in water. The asymmetric unit of this molecule consists of one methylated caffeine cation and one hexafluorophosphate counteranion. The ligand **1b** has an N1−C1−N2 angle of 110.9(3)°. The N1−C1 and N2−C1 bond lengths are 1.341(4) and 1.311(4) Å, respectively (Figure 2 and Table 1).

Crystals of **2b** suitable for single-crystal X-ray diffraction studies were grown from a concentrated solution of DMSO and toluene (Figure 3). The asymmetric unit contains one-quarter of both methylated caffeine silver complex and disordered hexafluorophosphate anion together with toluene as a noncoordinating solvent molecule located on the (x,0,z) mirror plane. The silver and phosphorus ions are on special positions

Scheme 2



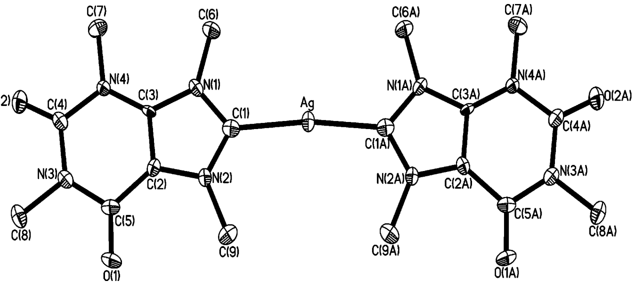


Figure 3. Molecular structure of the cationic part of **2b**. Hydrogen atoms have been omitted for clarity.

Table 1. Selective Bond Lengths (Å) and Angels (deg) for the Cationic Parts of 1b, 2b, and 3

bond lengths and angels	**1b**	**2b**	**3**
N1−C1	1.341(4)	1.372(6)	1.383(4)
N2−C1	1.311(4)	1.344(6)	1.335(4)
N1−C1−N2	110.9(3)	105.6(3)	106.2(3)
C1−M		2.068(4)	2.034(3)
C1−Ag−C1A		171.4(3)	

(0,0,*z*) and (0,$^1/_2$,*z*), respectively, with both having *mm*2 symmetry. Complex **2b** is a planar structure, crystallographically imposed, with a silver−carbene bond distance of 2.068(4) Å. The silver−carbene bond angle is 171.4(3)°, which deviates significantly from the linear geometry expected for the complex (Table 1). These values are comparable to those found in diethylbenzimidazol-2-ylidene silver complex ([Ag(Et$_2$-Bimy)$_2$]-[AgBr$_2$]) (silver carbene bond angle = 175.6°; silver carbene bond lengths = 2.073 and 2.052 Å) and other silver bis(carbene) complexes.[5,22]

Crystals of **3** suitable for single-crystal X-ray diffraction studies were grown from a concentrated solution of acetone and cyclohexane (Figure 4). The asymmetric unit contains two Rh(I) NHC complexes in different conformations and two hexafluorophosphate anions. Each Rh(I) center is bound to a methylated caffeine, DMSO, and cyclooctadiene in a square-planar fashion.

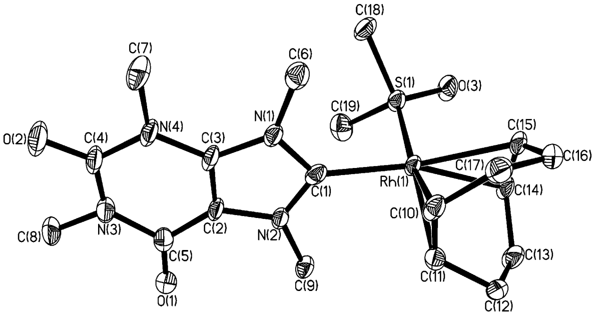


Figure 4. Molecular tructure of the cationic part of **3**. Hydrogen atoms have been omitted for clarity.

The two Rh(I) NHC bonds are 2.034(3) and 2.035(3) Å, respectively, and are comparable with those found in other NHC Rh(I) complexes.[7,23,24] The bond angles about the Rh centers deviate slightly from 90° ranging from 86.1° to 93.0° with an average of 90.1°. The greatest deviation is associated with the COD−Rh−COD bond angle most likely due to the bidentate nature of the COD. Deviations for other substituents are likely a result of the space created by the acute angle of the COD−Rh−COD bond angle (Table 1).

Conclusion

We have synthesized *N*-heterocyclic carbene silver(I) and rhodium(I) complexes **2a**, **2b**, and **3** from methylated caffeine. Both complex **2a** and **2b** show fluxional behavior in solution. The formation of an NHC rhodium(I) complex, **3**, from **2b** demonstrates the ability of **2b** to serve as a carbene transfer reagent in mild reaction conditions without the use of strong bases. We are currently exploring the carbene transfer chemistry of **2a** and **2b** with other transition metals.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. This research was supported in part by the National Institutes of Health. A.K.-N. would like to thank Abdulkareem Melaiye for useful conversations.

Supporting Information Available: Tables giving data and details for the crystal structure determinations of **1b**, **2b**, and **3**, including a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

OM030689R

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