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Synthesis and Characterization of Ag(I) and Pd(II) Complexes with a Pyridine Substituted *N*-Heterocyclic Carbene Ligand

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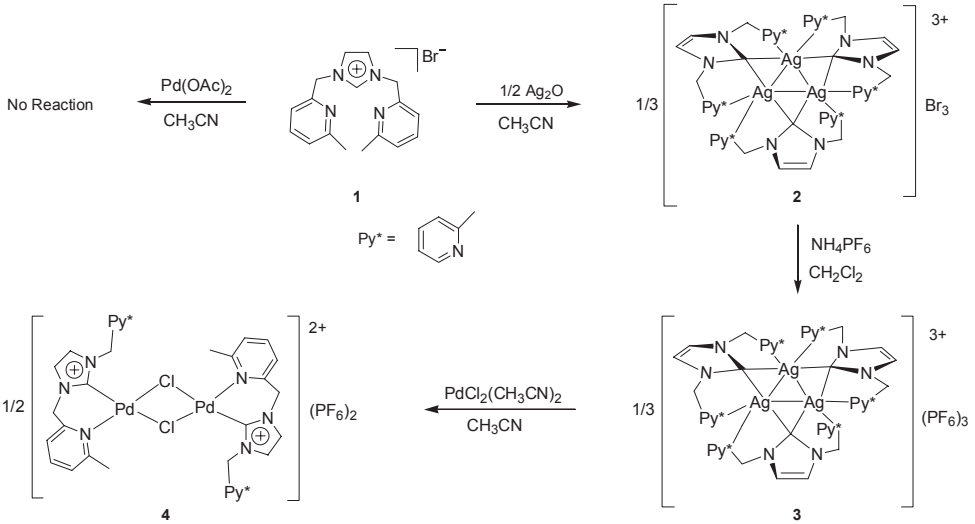
Since Arduengo's discovery of the first isolable free carbene in 1991, *N*-heterocyclic carbenes (NHC) have been extensively utilized as ligands for transition metals.[1,2] NHC are generally more stable than two extreme types of carbenes, the Fischer and the Schrock carbenes. They are good σ donors like most tertiary phosphins, PR_3, but the π-bonding with the metal is rather weak. The thriving studies of NHC-coordinated metal complexes produced a wide range of applications from homogeneous catalysts to materials science.[3]

Silver NHC complexes have recently been highlighted as promising reagents for initiators for ring-opening polymerization (ROP),[4] potential anticancer and antimicrobial agents,[5] and catalytic reagents.[6] Silver NHC complexes are also very useful precursors for NHC complexes of other metals because silver can be easily replaced by another metal ions when reacted with chloride salts of the metal of concern. The formation of insoluble AgCl(s) drives the transmetallation to completion. Employing this transmetallation strategy, a variety of late transition metal-NHC complexes such as Pd, Au, Rh and Ir have been successfully synthesized.[7] In this paper we report the synthesis of a new pyridine substituted NHC ligand and its complexes with silver and palladium.

The new silver and palladium complexes of a NHC were prepared through multistep syntheses which are summarized in Scheme 1. A pyridine substituted *N*-heterocyclic chelate, 1,3-bis[(6-methyl-2-pyridyl)methyl] imidazolium bromide [H(MepyCH$_2$)$_2$-Im]Br, **1**, was previously synthesized and X-ray crystallographically characterized by us.[8] Attempts to produce a Pd(II)-NHC complex by directly reacting the ligand **1** with palladium(II) acetate, or bis(acetonitrile)dichloropalladium failed. We therefore turned our attention to the synthesis of the more readily accessible Ag-carbene complex. Treatment of **1** with Ag_2O in CH_3CN while protecting from light readily yielded a trinuclear Ag_3 complex, [((MepyCH$_2$)$_2$-Im)$_3$Ag$_3$]Br$_3$, **2**. The chemical formula was deduced from the counter anion exchange reaction with PF_6^- (*vide infra*). However, ^{1}H and ^{13}C NMR analysis of **2** in $CDCl_3$ clearly revealed the formation of Ag-carbene bond, which was indicated by the absence of the imidazolium C2-^{1}H resonance and the presence of a typical Ag-^{13}C carbene resonance at 181.3 ppm. Unfortunately, it was impossible to get single crystals of **2** suitable for X-ray diffraction analysis.

Simple anion metathesis of **2** with NH_4PF_6 in CH_3CN led to the isolation of a silver solid, [((MepyCH$_2$)$_2$-Im)$_3$Ag$_3$](PF$_6$)$_3$, **3**, in 85% yield. Along with the fact that the ^{1}H and ^{13}C NMR results of the latter were very similar to those of **2**, elemental analysis supported the successful anion exchange. Colorless single crystals of **3** suitable for X-ray crystallography were



Scheme 1

Table 1. X-ray data collection and structure refinement for $[((MepyCH_2)_2\text{-}Im)_3Ag_3](PF_6)_3\cdot 2DMSO$

Empirical formula	$C_{55}H_{66}Ag_3F_{18}N_{12}O_2P_3S_2$	
Formula weight	1749.84	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 21.137(2) Å	α = 90°
	b = 21.718(2) Å	β = 91.023(2)°
	c = 14.9689(16) Å	γ = 90°
Volume	6870.4(13) Å^3	
Z	4	
Density (calculated)	1.692 Mg/m^3	
Absorption coefficient	1.076 mm^{-1}	
F(000)	3504	
Crystal size	0.50 × 0.38 × 0.20 mm^3	
Theta range for data collection	0.96 to 28.34°	
Reflections collected	41231	
Independent reflections	16116 [R(int) = 0.0283]	
Completeness to theta = 28.34°	94.0%	
Max. and min. transmission	0.8136 and 0.6153	
Data / restraints / parameters	16116 / 6 / 933	
Goodness-of-fit on F^2	1.090	
Final R indices [I > 2 sigma(I)]	R_1 = 0.0521, wR_2 = 0.1189	
R indices (all data)	R_1 = 0.0722, wR_2 = 0.1291	

Table 2. Selected bond lengths [Å] and angles [°] for $[((MepyCH_2)_2\text{-}Im)_3Ag_3](PF_6)_3\cdot 2DMSO$

Ag(1)-C(1)	2.234(4)	Ag(3)-Ag(1)-Ag(2)	59.810(13)
Ag(1)-C(35)	2.240(5)	Ag(3)-Ag(2)-Ag(1)	59.956(12)
Ag(1)-N(12)	2.510(4)	Ag(2)-Ag(3)-Ag(1)	60.234(12)
Ag(1)-N(1)	2.520(4)	C(1)-Ag(1)-C(35)	161.46(16)
Ag(1)-Ag(3)	2.8233(5)	C(1)-Ag(2)-C(18)	161.28(16)
Ag(1)-Ag(2)	2.8312(5)	C(18)-Ag(3)-C(35)	162.41(16)
Ag(2)-C(1)	2.232(4)	Ag(2)-C(1)-Ag(1)	78.68(14)
Ag(2)-C(18)	2.250(5)	Ag(1)-C(35)-Ag(3)	78.01(16)
Ag(2)-N(5)	2.511(4)	Ag(3)-C(18)-Ag(2)	77.95(15)
Ag(2)-N(4)	2.535(4)	N(12)-Ag(1)-N(1)	98.85(13)
Ag(2)-Ag(3)	2.8192(5)	N(5)-Ag(2)-N(4)	99.88(14)
Ag(3)-C(18)	2.232(5)	N(9)-Ag(3)-N(8)	101.57(13)
Ag(3)-C(35)	2.246(5)		
Ag(3)-N(9)	2.539(4)		
Ag(3)-N(8)	2.553(4)		

grown by Et_2O diffusion into the DMSO solution of the metal complex. A summary of crystal parameters and refinement results is given in Table 1 and selected bond lengths and angles are listed in Table 2. The structure of **3** consists of a discrete trinuclear silver NHC moiety containing a six-coordinate Ag(I) center and three PF_6 counter anions along with two free solvent molecules, DMSO (Fig. 1). The Ag atoms are symmetrically bridged by the NHC carbon and coordinated by two nitrogen atoms on two different pyridyl rings, and two adjacent Ag atoms, resulting in overall distorted octahedral geometry. The cyclic Ag(I) center in the cation forms a nearly equilateral triangle with the following bond distances and angles: Ag(1)-Ag(2), 2.8132(5); Ag(1)-Ag(3), 2.8233(5); Ag(2)-Ag(3), 2.8192(10) Å; Ag(3)-Ag(1)-Ag(2), 59.810(13); Ag(3)-Ag(2)-Ag(1), 59.956

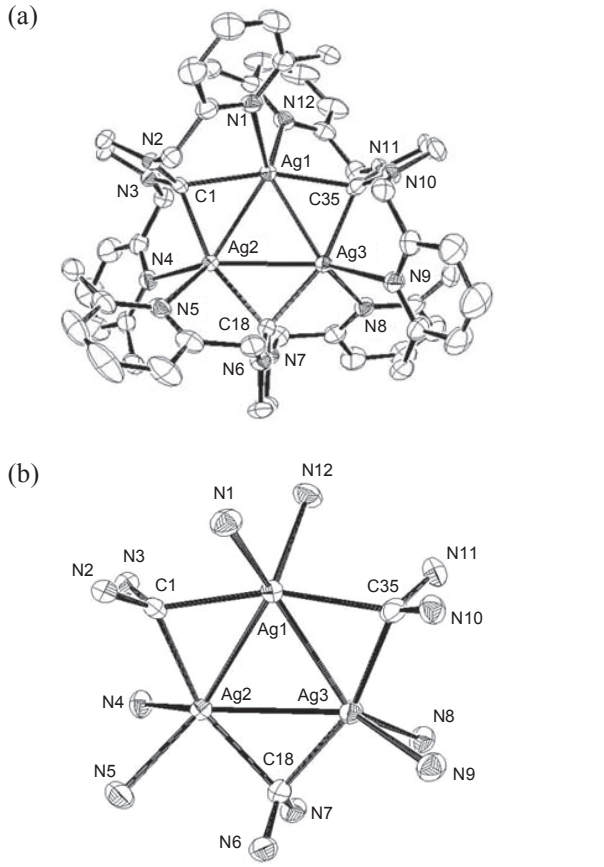


Figure 1. (a) X-ray structure of the cationic portion of trimetallic $[((MepyCH_2)_2\text{-}Im)_3Ag_3](PF_6)_3\cdot 2DMSO$ with 50% displacement of ellipsoids and (b) the core of trimetallic $[((MepyCH_2)_2\text{-}Im)_3Ag_3](PF_6)_3\cdot 2DMSO$ showing Ag_3 core. The counter anions and DMSO are omitted for clarity.

(12); Ag(2)-Ag(3)-Ag(1), 60.234(12) Å. Because the bridging carbene ligands of **3** are oriented perpendicularly to the triangle face of the Ag_3 core, the pyridine rings must alternate their coordination above and below the Ag_3 plane affording the complex D_{3d} symmetry. There were only very few reported structures having Ag-NHC complexes similar to **3**.[9] The Ag-Ag separations observed in **3** are slightly longer than those in previously reported values, which range from 2.7249(9) to 2.8070(5) Å.[9] The incidence of metallophilic interaction between closed-shell species of Group 11 elements is a well-documented phenomenon which is possibly due to the dispersion forces magnified by relativistic effects.[10] It is well known that the strength of an aurophilic interaction (7 - 11 kcal mol^{-1}) is comparable to that of a typical hydrogen bond.[11] On the other hand, argentophilicity, Ag(I)-Ag(I) interactions, have been less investigated and shown weaker interactions compared to aurophilicity.[12]

In an endeavor to synthesize a palladium(II) complex of **1** that was not formed previously in the direct reaction between the free carbene **1** and Pd(II) precursors, we reacted **3** with $PdCl_2(CH_3CN)_2$ in CH_2Cl_2 to obtain a pale yellow compound. It was formulated as a dimeric Pd complex with bridging chlorine atoms as shown in Scheme **1**, $[(MepyCH_2)_2\text{-}ImPdCl]_2(PF_6)_2$, **4**, which has the similar structure to those that have been reported previously.[13] The conductivity measurement of **4** in CH_2Cl_2 and CH_3CN showed that it is a 1:2 electrolyte. The ^{13}C NMR analysis of **4** in $CDCl_3$ revealed a presence of a typical Pd-carbene resonance at 163.9 ppm. The ^1H NMR spectra of **4** display two singlets with the 3H intensity at 3.06 and 2.37 ppm attributed to the two methyl (CH_3) protons resonances on the two pyridine rings. Also two multiplets with the 2H intensity are observed at 5.35 and 5.96 ppm and are attributed to the two methylene (CH_2) proton resonances. The methyl and methylene moieties each have two sets of proton peaks, pointing to the fact that the two pyridines are linked by the imidazolium ring do not occupy symmetrical positions in the metal coordination environment.

In summary, we have used our new tridentate pyridine substituted *N*-heterocyclic carbene to generate an interesting trinuclear $[((MepyCH_2)_2\text{-}Im)_3Ag_3]^{3+}$ complex, displaying very short Ag-Ag separations. A Pd(II)-NHC complex was prepared from $[((MepyCH_2)_2\text{-}Im)_3Ag_3]^{3+}$ *via* a facile transmetallation, leading to a dimeric $[(MepyCH_2)_2\text{-}ImPdCl]_2^{2+}$ complex. Future plans are underway for the survey of the potential applications of these new NHC complexes as luminesent materials or homogeneous catalysts.

Experimental Section

Materials and methods. All the materials were of a research grade or a spectro-quality grade in the highest purity available and were generally used without further purification except for CH_2Cl_2, hexane, and Et_2O. CH_2Cl_2 and hexane were distilled from CaH_2, while Et_2O was distilled from Na/benzopheone and used immediately. All solvents were degassed with N_2 (g) in order to remove O_2 (g) as much as possible before the use. 2-Bromomethyl-6-methylpyridine, silver (I) oxide, bis(acetonitrile)dichloropalladium (II), 2,6-lutidine, *N*-bromosuccinimide, and imidazole were obtained from Aldrich.

^1H and ^{13}C NMR spectra were obtained using a JEOL-JNM EX (400 MHz). Chemical shifts are reported in ppm on the δ scale relative to TMS (DMSO-d_6, $CDCl_3$ or CD_3CN solutions). Proton chemical shifts are annotated as follows: ppm (multiplicity or spin system, coupling constant if measurable, integral, assignment). Electrical conductivity measurements were carried out in CH_2Cl_2 and CH_3CN with a Barnstead Model PM-70CB conductivity bridge and a YSI model 3403 conductivity cell.

Synthesis of $[((MepyCH_2)_2\text{-}Im)_3Ag_3](Br)_3$ (2): A mixture of $[H(MepyCH_2)_2\text{-}Im]Br$ (0.32 g, 9.0×10^{-4} mol) and Ag_2O (0.16 g, 7.0×10^{-4} mol) was introduced into the Schlenk flask connected with the additional funnel. The Schlenk flask was evacuated and filled up with argon. The mixture was protected from light and then 10 mL of degassed CH_3CN was added. The mixture was stirred at room temperature for 4.5 hours and Et_2O (20 mL) was slowly added to precipitate a pale silver powder. The supernatant was decanted and the residue was repeatedly washed with Et_2O (3 × 10 mL) and then dried under the reduced pressure to produce pale gray solid in 83.0% yield. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.56 (t, 2H, J = 7.8Hz, CH), 7.19 (s, 2H, CH), 7.09 (t, 4H, J = 8.3Hz, CH), 5.35 (s, 4H, CH_2), 2.54 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 181.3 (s, C=Ag), 158.6 (s, C), 154.2 (s, C), 137.4 (s, CH), 122.9 (s, CH), 121.8 (s, CH), 119.3 (s, CH), 57.3 (s, CH_2), 24.4 (s, CH_3).

Synthesis of $[((MepyCH_2)_2\text{-}Im)_3Ag_3](PF_6)_3$ (3): A mixture of **2**, $[((MepyCH_2)_2\text{-}Im)_3Ag_3](Br)_3$, (1.3 g, 9.3×10^{-4} mol) and NH_4PF_6 (0.16 g, 9.8×10^{-4} mol) was introduced into the Schlenk flask connected with the additional funnel. The Schlenk was evacuated and purged with argon. Then, 10 mL of degassed CH_3CN was added. The mixture was stirred at room temperature for 3 hours and then the solid formed was filtered off. To the filtrate was slowly added Et_2O (20 mL) to precipitate a solid. The supernatant was decanted and the residue was repeatedly washed with Et_2O (3 × 10 mL) and then dried under the reduced pressure to produce a pale gray solid in 81.0% yield. Anal. Calcd. for $C_{51}H_{54}N_{12}Ag_3P_3F_{18}$: C, 38.44; H, 3.42; N, 10.55. Found: C, 37.97; H, 3.32; N, 10.35%. ^1H NMR (DMSO-d_6, 400 MHz) δ 7.90 (t, 2H, J = 7.8Hz, CH), 7.83 (s, 2H, CH), 7.50 (d, 2H, J = 7.8Hz, CH), 7.31 (d, 2H, J = 7.8Hz, CH), 5.49 (d, 2H, J = 14.6 Hz, CH_2), 5.30 (d, 2H, J = 14.2 Hz, CH_2), 1.31 (s, 6H, CH_3). ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.2 (s, C=Ag), 158.0 (s, C), 152.7 (s, C), 139 (s, CH), 126.2 (s, CH), 124.5 (s, CH), 121.8 (s, CH), 55.1 (s, CH_2), 22.8 (s, CH_3). Colorless single crystals of **3** suitable for X-ray crystallography were grown by Et_2O diffusion into the DMSO solution of the metal complex.

Synthesis of $[(MepyCH_2)_2\text{-}ImPdCl]_2(PF_6)_2$ (4): A mixture of $[((MepyCH_2)_2\text{-}Im)_3Ag_3](PF_6)_3$, **3**, (0.21 g, 1.31×10^{-4} mol) and $PdCl_2(CH_3CN)_2$ (0.10 g, 3.93×10^{-4} mol) was introduced into the Schlenk flask connected with the additional funnel. To the flask was added 10 mL of degassed CH_3CN dropwise. The solid formed was filtered off and the filtrate was concentrated by high-vacuum rotary evaporation. The product was repeatedly washed with Et_2O (3 × 10 mL) and then dried under the reduced pressure to produce a pale yellow solid in 75.0% yield. Anal. Calcd. for $C_{34}H_{36}Cl_2F_{12}N_8P_2Pd_2$: C, 36.13; H, 3.21; N, 9.91. Found: C, 35.77; H, 3.62; N, 9.79%. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.63 (t, H, J = 7.8 Hz, CH), 7.51 (m, 3H, CH), 7.26 (d, H, J = 1.5 Hz, CH), 7.15 (d, H, J = 7.8 Hz, CH), 7.02 (s, 2H, CH),

5.96 (m, 2H, CH_2), 5.36 (m, 2H, CH_2), 3.06 (s, 3H, CH_3), 2.37 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.9 (s, C), 158.2 (s, C), 154.4 (s, C), 153.2 (s, C), 151.5 (s, C), 139.1 (s, CH), 137.3 (s, CH), 126.0 (s, CH), 122.8 (s, CH), 122.4 (s, CH), 122.2 (s, CH), 121.5 (s, CH), 120.7 (s, CH), 56.8 (s, CH_2), 55.0 (s, CH_2), 28.7 (s, CH_3), 24.4 (s, CH_3).

X-ray crystallography. The structure of the title compound was determined by single crystal X-ray diffraction analyses. The intensity data were collected on a Siemens SMART CCD diffract meter with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation at 173(2) K. The crystal has a formula of $C_{55}H_{66}Ag_3F_{18}N_{12}O_2P_3S_2$, monoclinic, space group P2(1)/c with a = 21.137(2) Å, b = 21.718(2) Å, c = 14.969(2) Å, α = γ = 90°, β = 91.023(2)°, Z = 4, V = 6870.4(13) Å^3, F(000) = 3504, 41231 reflections were collected, 16116 of which were used in the refinement to give the final $R_1 = 0.0521$, $wR_2 = 0.1189$. All crystallographic data were corrected for Lorentz and polarization effects (SMART),[27] and semiempirical absorption corrections based on equivalent reflections were applied (SAINT). The structures were solved by direct methods and refined by full-matrix least-squares method on F^2 with appropriate software implemented in the SHELXTL[14] program package. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC-711043). These data can be obtained free of charge from www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information. CIF file for **3** is available on request from the correspondence author (dhl@chonbuk.ac.kr, +82-63-270-4262).

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