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Notes

Formation of N-Heterocyclic Complexes of Rhodium and Palladium from a Pincer Silver(I) Carbene Complex

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*Summary: The pincer ligands 2,6-bis(n-butylimidazoliummethyl)pyridine dihalide (halide = Cl (**3a**), Br (**3b**) are easily obtained by the reaction of n-butylimidazole with 2,6-bis(chloromethyl)pyridine and 2,6-bis(bromomethyl)pyridine in a 2:1 molar ratio, respectively. Ligand **3a** readily reacts with Ag_2O in CH_2Cl_2 to yield the bis(silver carbene) complex [2,6-bis(n-butylcarbenemethyl)pyridine][AgCl]$_2$ (**4**) in 70% yield. The reaction of **4** with $(PhCn)_2PDCl_2$ in CH_2Cl_2 yields the palladium carbene complex Pd[2,6-bis(N-n-butylcarbenemethyl)pyridine]Cl_2 (**5**). The reaction of equimolar amounts of **4** and [Rh(COD)Cl]$_2$ (COD = cyclooctadiene) in CH_2Cl_2 gave the dirhodium(I) complex [2,6-bis(N-n-butylcarbenemethyl)pyridine][Rh(COD)Cl]$_2$ (**6**). All compounds were characterized by ^1H and ^{13}C NMR spectroscopy. The solid-state structures of **4** and **6** were determined by X-ray crystallography.*

Introduction

The use of Arduengo carbenes as ligands has attracted considerable attention, due to their ability to complex very strongly to transition metals and main-group elements from virtually the entire periodic table.[1] Currently, the chemistry of bis-N-heterocyclic carbene cyclophane complexes and pincer N-heterocyclic carbene ligand complexes that incorporate pyridine subunits is being explored.[2,3] The pincer ligand 2,6-bis(*N*-methylimidazoliummethyl)pyridine (**1**; R = Me) was first reported by Herrmann.[4] This ligand has caught our interest due to the structural similarities it has with the pyridine-functionalized cyclophane **2** (Figure 1). Cyclophane **2** has been used to provide novel silver[2a] and nickel[2b] complexes with unique bonding and coordination chemistry. The attraction of **1** is partly due to the ease with which the bonding and electronic properties might be altered simply by changes in the N functionality (R). It was predicted that increasing the steric bulk of R would produce monomeric silver complexes rather than dimeric structures and that these complexes would be excellent carbene transfer reagents.

The use of silver−carbene complexes as carbene transfer reagents was first discovered by Lin and co-workers to provide carbene complexes of gold(I) and palladium(II).[5] Since this discovery, they have been employed by other researchers to provide complexes with M−carbene (M = Pd,[3c] Cu[6]) bonds. Tungsten−carbene complexes have also proved to be useful carbene transfer reagents, providing complexes with M−carbene (M = Pt, Pd, Au, Rh) bonds.[7] The formation of transition-metal−carbene bonds, using carbene transfer reagents, is favored in many situations because the reactions proceed under mild conditions and without the use of strong bases. In light of these developments, it is suprising that carbene transfer techniques have only been explored in the chemistry of a few transition metals.

During our investigations, two reports of metal complexes of **1** (R = Me) have appeared in the literature. Cavell and co-workers report that **1** forms silver complexes with the expected dimeric structure.[3c] The silver complex of **1** can be used as a carbene transfer reagent to yield a palladium complex of **1**. In another report, Crabtree and co-workers report that **1** forms palladium complexes by the reaction of **1** and $Pd(OAc)_2$.[8] Repoted herein is the synthesis of **3** (R = *n*-Bu) and the monomeric silver complex **4**. The N-heterocyclic carbene transfer chemistry of **4** is remarkable. We report the formation of N-heterocyclic carbene complexes of rhodium and palladium from **4** under mild nonbasic conditions.

Experimental Section

General Considerations. All manipulations were carried out in air except for the synthesis of **6**, which was carried out

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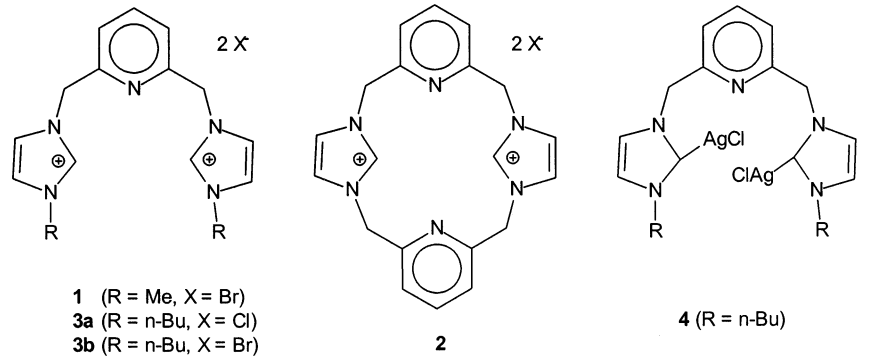

1 (R = Me, X = Br)
3a (R = n-Bu, X = Cl)
3b (R = n-Bu, X = Br)

2

4 (R = n-Bu)

Figure 1.

under an atmosphere of nitrogen. The compounds *n*-butylimidazole and 2,6-bis(bromomethyl)pyridine were purchased from Aldrich and used without further purification. $[Rh(COD)Cl]_2$ (COD = cyclooctadiene) was purchased from Strem and used without further purification. The compound 2,6-bis(chloromethyl)pyridine was prepared according to a literature procedure.[9] ^1H and ^{13}C NMR data were recorded on a Gemini 300 MHz instrument and referenced to deuterated solvent. IR data were recorded on a Bomem FTIR instrument. Due to the hygroscopic properties of **3a**,**b** and **5**, reliable elemental analyses were not obtained.

Synthesis of 2,6-Bis(*n*-butylimidazoliummethyl)pyridine Dichloride (3a). A neat solution of 2,6-bis(chloromethyl)pyridine (3.5 g, 20.0 mmol) and *n*-butylimidazole (10.0 mL g, 80.0 mmol) was stirred at 60 °C for 16 h. After the mixture was cooled to ambient temperature, acetone (500 mL) was added and stirring was continued for 2 days. Filtration yielded **3a** as a white precipitate. Yield: 7.2 g, 17 mmol, 85%. Mp: 220 °C dec. ^1H NMR (300 MHz, d_6-DMSO): δ 0.87 (t, 6 H, CH_3), 1.24 (m, 4 H, CH_2), 1.78 (m, 4 H, CH_2), 4.31 (t, 4 H, NCH_2), 5.65 (s, 4 H, CH_2), 7.54 (d, 2 H, $J = 7.8$ Hz, *m*-pyr), 7.91 (s, 2 H, NC(H)CH), 7.97 (s, 2 H, NC(H)CH), 7.94 (t, 1 H, $J = 7.8$ Hz, *p*-pyr), 9.84 (s, 2 H, NC(H)N). $^{13}C\{^1H\}$ NMR (75 MHz, d_6-DMSO): δ 13.3 (CH_3), 18.8 (CH_2), 31.4 (CH_2), 48.5 (CH_2), 52.5 (CH_2), 122.2, 122.3, 123.2, 136.9, 138.8, 153.7.

Synthesis of 2,6-Bis(*n*-butylimidazoliummethyl)pyridine Dibromide (3b). A neat solution of 2,6-bis(bromomethyl)pyridine (5.3 g, 20.0 mmol) and *n*-butylimidazole (5.3 mL, 40.0 mmol) was stirred at 60 °C for 16 h. After the mixture was cooled to ambient temperature, acetone (500 mL) was added and stirring was continued for 2 days. Filtration yielded **3b** as a white precipitate. Yield: 8.3 g, 16.2 mmol, 81%. Mp: 194 °C dec. ^1H NMR (300 MHz, d_6-DMSO): δ 0.81 (t, 6 H, CH_3), 1.32 (m, 4 H, CH_2), 1.81 (m, 4 H, CH_2), 4.50 (t, 4 H, NCH_2), 5.61 (s, 4 H, CH_2), 7.62 (d, 2 H, $J = 7.8$ Hz, *m*-pyr), 7.90 (s, 2 H, NC(H)CH), 7.93 (s, 2 H, NC(H)CH), 7.82 (t, 1 H, $J = 7.8$ Hz, *p*-pyr), 9.80 (s, 2 H, NC(H)N). $^{13}C\{^1H\}$ NMR (75 MHz, d_6-DMSO): δ 13.1 (CH_3), 18.0 (CH_2), 31.9, (CH_2), 48.4 (CH_2), 53.5 (CH_2), 121.0, 121.9, 123.9, 137.4, 138.1, 154.7.

Synthesis of [2,6-Bis(*n*-butylcarbenemethyl)pyridine][AgCl]$_2$ (4). A CH_2Cl_2 (50 mL) solution of **3a** (0.85 g, 2.0 mmol) and Ag_2O (0.46 g, 2.0 mmol) was stirred at ambient temperature for 2 h. The solution was filtered through Celite, and 300 mL of Et_2O was added to precipitate a white solid. Isolation by filtration yielded **4**. Yield: 0.9 g, 1.4 mmol, 70%. Mp: 220 °C dec. Anal. Calcd for $C_{21}H_{29}Ag_2Cl_2N_5$: C, 39.53; H, 5.48; N, 10.97. Found: C, 39.30; H, 5.11; N, 10.77. ^1H NMR (300 MHz, $CDCl_3$): δ 0.95 (m, 6 H, CH_3), 1.34 (m, 4 H, CH_2), 1.77 (m, 4 H, CH_2), 4.10 (m, 4 H, NCH_2), 5.38 (s, 4 H, CH_2), 7.04 (s, 2 H, NC(H)CH), 7.25 (d, 2 H, $J = 7.8$ Hz, *m*-pyr), 7.33 (s, 2 H, NC(H)CH), 7.70 (broad triplet, 1 H, *p*-pyr) (aromatic). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 13.6 (CH_3), 19.7, 33.8, 52.0 (CH_2), 56.7 (CH_2), 121.0, 121.9, 122.3, 139.0, 155.6, 179.8.

Synthesis of Pd[2,6-bis(*n*-butylcarbenemethyl)pyridine]Cl$_2$ (5). A CH_2Cl_2 (15 mL) solution of **4** (0.16 g, 0.25 mmol) and $(PhCN)_2PdCl_2$ (0.13 g, 0.25 mmol) was stirred at ambient temperature for 1 h. The solution was filtered through Celite, and 100 mL of hexane was added to precipitate **5** as an off-white solid. Yield: 0.1 g, 0.2 mmol, 80%. Mp: 220 °C dec. ^1H NMR (300 MHz, $CDCl_3$): δ 0.85 (m, 6 H, CH_3), 1.41 (m, 4 H, CH_2), 1.70 (m, 4 H, CH_2), 4.41 (m, 4 H, $N-CH_2$), 5.62 (s, 4 H, CH_2), 7.41, 7.60, 7.84, 8.20 (aromatic). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 13.7 (CH_3), 19.3, 33.1, 48.8 (CH_2), 54.7 (CH_2), 121.9, 122.3, 125.8, 142.0, 155.6, 164.2.

Synthesis of [2,6-bis(*n*-butylcarbenemethyl)pyridine][Rh(COD)Cl]$_2$ (6). Under an atmosphere of nitrogen, a CH_2Cl_2 (15 mL) solution of **4** (0.32 g, 0.5 mmol) and $[Rh(COD)Cl]_2$ (0.25 g, 0.5 mmol) was stirred at ambient temperature for 1 h. The solution was filtered, and 30 mL of Et_2O was added to precipitate **6** as a light yellow solid. Yield: 0.28 g, 0.3 mmol, 65%. Mp: 201−204 °C dec. Anal. Calcd for $C_{38}H_{53}N_5Rh_2Cl_2$: C, 53.28; H, 6.24; N, 18.18. Found: C, 39.10; H, 4.33; N, 10.77. ^1H NMR (300 MHz, $CDCl_3$): δ 1.1 (m, 6 H, CH_3), 1.5 (m, 4 H, CH_2), 1.8 (m, 4 H, CH_2), 2.3 (m, 8 H, CH_2), 3.2 (m, 4 H, CH_2), 4.5 (m, 4 H, NCH_2), 5.0 (s, 4 H, CH_2), 5.9 (m, 8 H, CH), 6.9, 7.4, 7.70 (aromatic). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 14.0, 20.3, 28.9, 28.9, 29.1, 29.1, 33.0, 33.1, 33.2, 33.2, 50.7, 56.1, 56.3, 68.0, 68.1, 68.4, 68.5, 68.6, 68.7, 98.7, 98.8, 120.6, 120.8, 121.2, 121.4, 122.1, 122.2, 138.3, 138.5, 156.4, 183.1 ($J_{Rh-C} = 47.2$ Hz).

X-ray Structure Determinations. Crystal data and structure refinement parameters are presented in Table 1. Crystals of **4** and **6** were coated in paraffin oil, mounted on glass fibers, and placed under a stream of nitrogen.[10] X-ray data were collected under a stream of nitrogen at 100 K on a Bruker Apex CCD diffractometer using Mo Kα radiation ($\lambda = 0.710\,73$ Å). Intensity data were integrated using Saint, and an empirical absorption correction was applied using SADABS. Structures **4** and **6** were solved by direct methods and refined using full-matrix least-squares procedures. In the structure of **4**, the terminal butyl carbon atom was disordered between two positions at approximately 50% occupancy for each. A DFIX restraint was applied to the disordered carbon atoms (C11 and C12). For **4**, all non-hydrogen atoms were refined with anisotropic displacement parameters. For **6**, all non-hydrogen atoms were refined with anisotropic displacement parameters, except for C7, C15, and C30, which were refined using the ISOR restraint. All hydrogen atoms for **4** and **6** were refined using a riding model.

Results and Discussion

The pincer ligands 2,6-bis(*n*-butylimidazoliummethyl)pyridine dihalide (halide = Cl (**3a**), Br (**3b**)) are easily obtained by the reaction of *n*-butylimidazole with 2,6-

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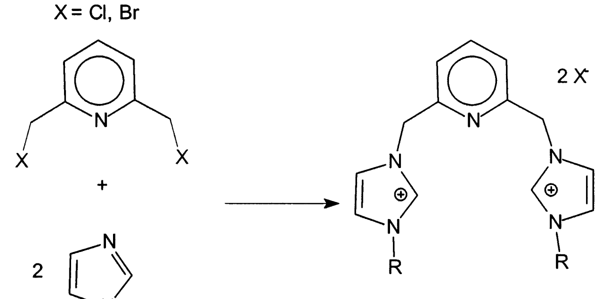
Table 1. Crystal Data and Structure Refinement for 4 and 6

	4	6
empirical formula	$C_{21}H_{29}Cl_2Ag_2N_5$	$C_{37}H_{53}Cl_2N_5Rh_2$
fw	638.13	844.56
temp (K)	100	100
wavelength (Å)	0.71073	0.71073
cryst syst, space group, *Z*	orthorhombic, *Pbcn*, 4	triclinic, $P\bar{1}$, 2
unit cell dimens		
a (Å)	11.7633(11)	10.725(2)
b (Å)	11.8800(11)	11.673(2)
c (Å)	17.6299(17)	15.883(3)
α (deg)	90	105.983(4)
β (deg)	90	99.157(4)
γ (deg)	90	97.918(4)
V ($Å^3$)	2463.7(4)	1852.3(6)
D_{calcd} (Mg m^{-3})	1.720	1.514
abs coeff (mm^{-1})	1.824	1.068
θ range for data collecn (deg)	2.31−24.99	1.36−22.05
no. of rflns collected/unique	16 666/2165 (*R*(int) = 0.0729)	10814/4841 (*R*(int) = 0.0745)
goodness of fit on F^2	1.224	1.015
final *R* indices ($I > 2\sigma(I)$)	0.0997	0.0749
R indices (all data)	0.2209	0.1851
largest diff peak and hole (e $Å^{-3}$)	2.483 and−1.850	1.465 and−0.939

bis(chloromethyl)pyridine or 2,6-bis(bromomethyl)pyridine in a 2:1 molar ratio respectively (eq 1). Ligands

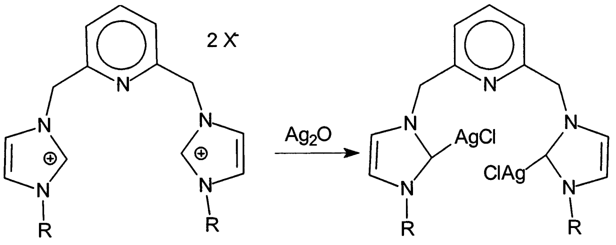


3a (R = n-Bu, X = Cl)
3b (R = n-Bu, X = Br)

(1)

3a,**b** are thermally stable up to their melting points and stable in air; however, they are hygroscopic, giving unreliable elemental analyses. Ligand **3a** is less hygroscopic than **3b**, and for this reason, it is used for further reactions. The ^1H and ^{13}C NMR spectra for **3a**,**b** are essentially identical and are consistent with their molecular structures. The imidazolium protons appear at ca. 9.8 ppm and are consistent with similar ligand systems. For example, the imidazolium proton for 2,6-bis(methylimidazoliummethyl)pyridine dibromide appears in the ^1H NMR spectrum at 9.22 ppm.

Ligand **3a** readily reacts with Ag_2O in CH_2Cl_2 to yield the silver carbene complex **4** in 70% yield (eq 2).



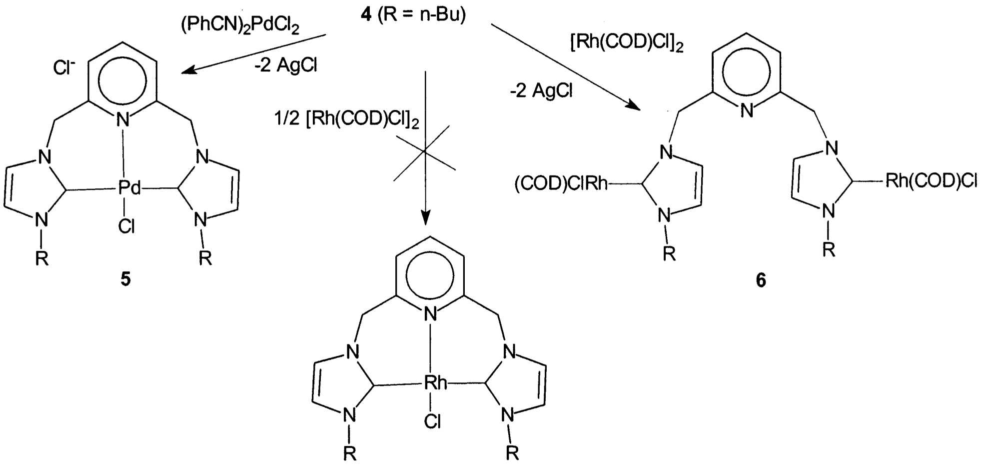
3a (R = n-Bu, X = Cl) **4** (R = n-Bu)

(2)

Complex **4** is stable in air and light up to its melting point. The disappearance of the imidazolium proton in the ^1H NMR spectrum and the appearance of a resonance at 179.8 ppm in the ^{13}C NMR spectrum are indicative of a silver−carbene complex. In addition, the lack of C−^{107}Ag and C−^{109}Ag couplings indicates fluxional behavior on the ^{13}C NMR time scale. Typically, silver−carbene complexes that lack Ag−carbene couplings have dynamic behavior in solution and are useful as carbene transfer reagents.[11]

The reaction of **4** with $(PhCN)_2PdCl_2$ in CH_2Cl_2 yields the palladium carbene complex **5** and 2 equiv of AgCl in good yield (Scheme 1). The carbene resonance for **5** appears at 164.2 ppm, is shifted upfield when compared to the same value reported for **4**, and is in good agreement with the carbene resonance reported for the structurally analogous palladium complex of 2,6-bis(*N*-methylcarbenemethyl)pyridine dibromide (164.0 ppm).[3c] The ability of **4** to serve as a carbene transfer reagent was further demonstrated in two separate reactions. The reaction of equimolar amounts of **4** with $[Rh(COD)Cl]_2$ in CH_2Cl_2 gave the dirhodium(I) complex **6** in good yield (65%) as a yellow air-stable solid. It is notable that the reaction of **4** with $[Rh(COD)Cl]_2$ in a 2:1 molar ratio did not give the anticipated monorhod-

Scheme 1



5 **6**

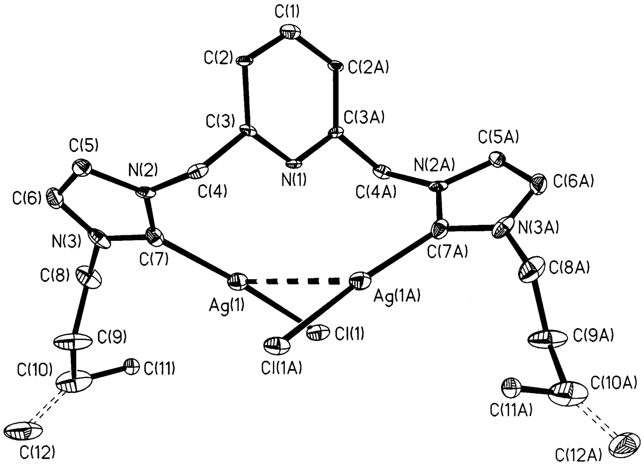


Figure 2. Molecular structure of **4** with thermal ellipsoids drawn at 30% probability. Hydrogen atoms attached to carbon atoms have been omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 4 and 6

Compound **4**			
Ag1−C7	2.064(13)	Ag1−Cl1	2.315(4)
C7−Ag1−Cl1		170.2(4)	
Compound **6**			
Rh1−C7	2.000(12)	Rh2−Cl2	2.375(3)
Rh1−Cl1	2.374(3)	Rh2−C17	2.009(13)
C7−Rh1−Cl1	87.4(4)	C17−Rh2−Cl2	90.1(4)

ium(I) complex. Instead, the only observable products were **6** and unreacted **4**. This result is consistent with previous work reported by Hermann. The reaction of the chelating ligand 1,1′-(1,2-ethylene)-3,3′-dimethyldiimidazoline-2,2′-diylidene with $[Rh(COD)Cl]_2$ in a 2:1 ratio yields a dinuclear complex instead of the expected mononuclear complex.[12] In the ^{13}C NMR spectrum for **6**, the carbon atom coordinated to the rhodium atom appears as a doublet centered at δ 183 ($J_{C-Rh} = 50$ Hz). The chemical shift and the value for the coupling constant are consistent with a rhodium−carbene complex.[12]

Complex **4** exists in the solid state as a monomer with each N-heterocyclic carbene unit complexed to a AgCl metal fragment (Figure 2). The asymmetric unit consists of half of the molecule. The geometry at the silver atom is essentially linear, with bond distances Ag1−C7 = 2.064(13) Å and Ag1−Cl1 = 2.315(4) Å bond distances and the bond angle C7−Ag1−Cl1 = 170.2(4)° bond angle (Table 2). The molecular structure of **4** is very similar to the monomeric structure of $[m\text{-}C_6H_4(CH_2Im\text{-}MeAgCl)_2]$ (Im = imidazole) reported by Matsumoto and co-workers.[13] In contrast, the silver complex of **1**, $[m\text{-}C_5H_3N\text{-}(CH_2Im\text{-}Me)]_2[AgBr]_2$, is a dimer in the solid state.[3c] Complex **4** exists as discrete molecules with no intermolecular interactions between neighboring molecules. This is unusual. Monomeric silver carbene complexes typically form extended polymeric arrays that arise from Ag(I)−Ag(I) interactions or bridging Ag(I)−halide interactions. This type of macrocyclic aggregation is prevented during the crystal packing of **4**, presumably due to the difference in steric requirements for Me and *n*-Bu. However, **4** does have an intramolecular Ag(I)−Ag(I) interaction (2.374(3) Å) that is less than the sum of the van der Waals radii of silver (3.44 Å).

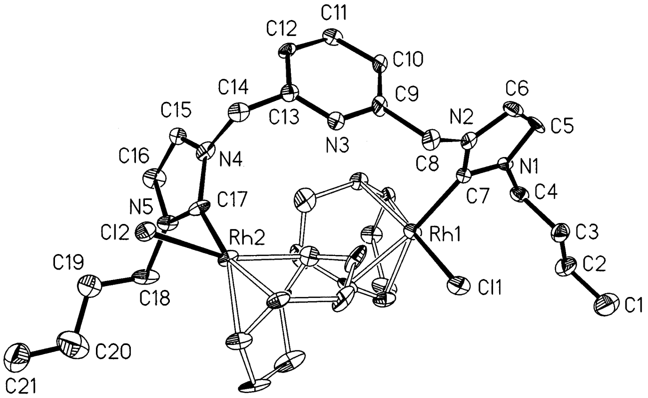


Figure 3. Molecular structure of **6** with thermal ellipsoids drawn at 30% probability. Hydrogen atoms attached to carbon atoms have been omitted for clarity.

Like **4**, the solid-state structure of **6** (Figure 3) is monomeric with each N-heterocyclic carbene unit complexed to a Rh(COD)Cl metal fragment. In contrast, **6** has no intermolecular or intramolecular interactions. The geometry at the rhodium atoms are nearly square planar, with the chloride atoms oriented trans to the carbene carbon atoms, resulting in the bond angles C7−Rh1−Cl1 = 87.4(4)° and C17−Rh2−Cl2 = 90.1(4)° and bond distances Rh1−C7 = 2.000(12) Å, Rh1−Cl1 = 2.374(3) Å, Rh2−C17 = 2.009(13) Å, and Rh2−Cl2 = 2.375(3) Å.

Conclusion

The bis(silver carbene) complex [2,6-bis(*n*-butylcarbenemethyl)pyridine]$[AgCl]_2$ (**4**) can be easily prepared in good yield. Complex **4** is an excellent carbene transfer reagent, providing N-heterocyclic carbene complexes of rhodium and palladium under mild nonbasic reaction conditions. We are currently exploring the chemistry of **4** as a carbene transfer reagent with a variety of transition metals and main-group metals.

Acknowledgment. We wish to thank the National Science Foundation, the University of Akron, and the Ohio Board of Reagents for financial support. This work was supported by an award from the American Heart Association.

Supporting Information Available: Tables giving data and details for the crystal structure determinations of **4** and **6** and figures giving NMR spectra for compounds **3a**,**b** and **4**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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