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N-Alkoxyimidazolylidene Transition-Metal Complexes: Application to [5+2] and [4+2] Cycloaddition Reactions

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Silver(I) bis[(benzyloxy)imidazol-2-ylidene] complex **6** is prepared by reaction of an alkoxyimidazolium bromide (**4**) with Ag_2O. In situ deprotonation of the alkoxyimidazolium bromide **4** afforded the rhodium(I) and palladium(II) complexes **7** and **8**, whose structures were verified by X-ray crystallography. Rhodium(I) (benzyloxy)imidazolylidene complex **7** efficiently catalyzes the [5+2] cycloaddition reaction of an yne−vinylcyclopropane (93%) and the [4+2] cycloaddition reaction of a diene−yne (99%) at room temperature in minutes.

N-heterocyclic carbenes (NHCs) have recently emerged as a versatile class of ligands for organo-transition-metal complexes.[1−5] NHCs are potent σ-donors, offering steric and electronic properties different from those of the well-established phosphine ligands in organometallic catalysts.[5−16] Significantly, variation of the substituents of the NHCs allows for tuning of their steric and electronic properties and consequently control of their reactivity and performance as ligands in metal complexes and catalysts.

Despite the growing attention devoted to transition-metal complexes incorporating diverse carbene ligands, examples of imidazolylidene complexes (and those of other heterocyclic and acyclic carbenes)[4] in which the carbene α-substituent bears heteroatoms are rare.[17−22] Relative to their carbon-substituted counterparts, heteroatom-substituted NHCs offer a more direct means to perturb the electronic characteristics of the complex and also a proximate coordination site for directed reactivity. An early report by Balch described a templated synthesis of an *N*-amino-substituted N-heterocyclic carbene from the reaction of biacetyldihydrazone with $M(CNCH_3)_4^{2+}$ (M = Pt, Pd).[17] Subsequently, Weiss reported novel dinitroxylcarbenes bound to palladium bearing an oxygen atom as a direct substituent of an imidazol-2-ylidene nitrogen.[21,22] Lassaletta described the synthesis, reactivity, and transition-metal complexes of a new class of N-heterocyclic carbenes based on bis(*N*,*N*-dialkylamino)imidazolin-2-ylidines.[18,19] The ν(CO) stretching frequencies of the rhodium carbonyl complexes of these carbenes indicate[23] that they are more potent σ-donors than the analogous (*N*,*N*-aryl)imidazolin-2-ylidenes, but the catalytic behavior of this new class of rhodium carbene complexes was not explored. Herein, we describe the synthesis of *N*-alkoxyimidazol-2-ylidines, their coordination chemistry to palladium and rhodium, and the catalytic behavior of the rhodium carbene complexes in [5+2] and [4+2] cycloaddition reactions.[23−39]

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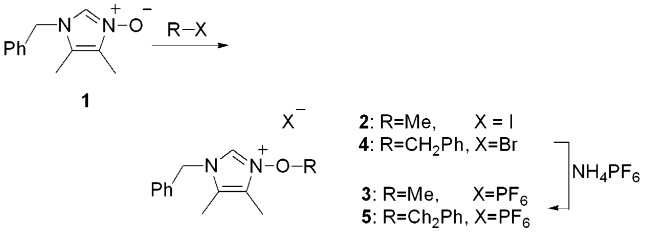
Scheme 1. Synthesis of Various *N*-Alkoxyimidazol-2-ylidinium Salts



Synthesis and Coordination Chemistry

Syntheses of the *N*-alkoxyimidazolium salts were carried out by alkylation of imidazole *N*-oxides as shown in Scheme 1. 1-Benzyl-4,5-dimethylimidazole 3-oxide (**1**) was synthesized by refluxing 1,3,5-tribenzylhexahydro-1,3,5-triazine with 2,3-butanedione monoxime in ethanol[24] and isolated as a slightly off-white crystalline solid after recrystallization. Alkylation of imidazole *N*-oxide **1** yields crude *N*-alkoxyimidazol-2-ylidinium halides **2** and **4** as viscous oils. (Benzyloxy)imidazolium bromide **4** was isolated as a solid in 73% yield from an ether/pentane mixture, whereas the corresponding iodide remained as an oil. For ease of handling and subsequent synthesis studies, anion exchange with hexafluorophosphate afforded salts **3** and **5** as crystalline solids.

Several strategies were explored for the preparation of transition-metal complexes from the salts **2**−**5**. Initial attempts to generate the free carbene via direct deprotonation of the salts following literature procedures were unsuccessful. However, silver, palladium, and rhodium complexes were readily prepared by the in situ deprotonation of the *N*-alkoxyimidazol-2-ylidinium bromide **4** in the presence of the appropriate metal compound (Scheme 2).

Silver(I) carbenes are versatile precursors to a wide range of transition-metal carbene complexes.[25,26] The silver complex **6** was formed by reaction of **4** with the mildly basic silver oxide in CH_2Cl_2. The product was isolated as a microcrystalline solid after recrystallization in THF. The imidazolylidene carbon signal in the ^{13}C NMR appears as a singlet, suggesting the absence of a tight coordination to the silver center. No ^{13}C−^{109}Ag coupling is observed, consistent with the previously proposed solution equilibrium between Ag(carbene)Br and Ag(carbene)$_2^+$ species.[25,27]

Complex **7** was prepared from a rhodium−COD dimer which reacts with the alkoxyimidazol-2-ylidinium salt in situ.[28] Complex **7** can be easily isolated by flash chromatography on silica gel. Analysis of the ^{1}H NMR spectrum reveals two diastereotopic AX methylenes (NCH$_2$ and OCH$_2$) with $\Delta\delta \approx$ 190 Hz (J = 16 Hz) and 170 Hz (J = 10 Hz), respectively. Pale yellow rhombic crystals of X-ray quality were grown by ether vapor diffusion into a CH_2Cl_2 solution of complex **7**. Analysis of the X-ray structure of **7** reveals a square planar coordination geometry [C(2)−Rh−Br angle of 93.1°] and bonding parameters analogous to those of other Rh(I)−NHC complexes.[18,29−34] The C2−Rh, C2−N1, and C2−N3 bond distances of 2.020(5), 1.352(6), and 1.362(5) Å, respectively, are in close agreement with alkyl-, amino-, and aryl-substituted imidazolylidene−Rh complexes. A negligible contribution of the oxygen atom in the NCN π system can be implied from both the angle about O1 (109.8°) and the O1−N1 distance of 1.390(5) Å. Figure 1 lists selected bond angles and distances.

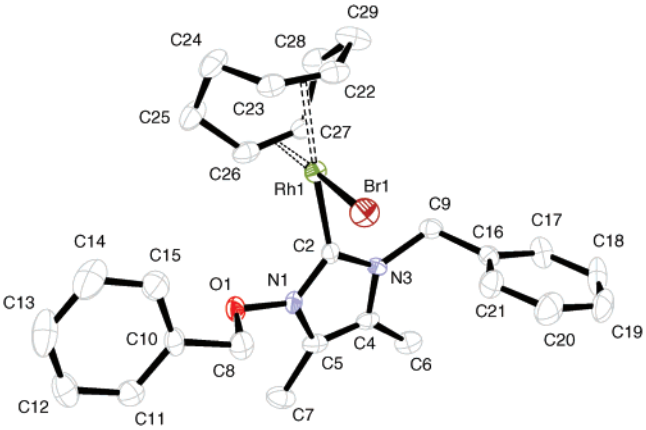


Figure 1. ORTEP diagram of **7**. Selected bond distances (Å) and angles (deg): Rh1−C2, 2.020(5); Rh1−C22, 2.185(5); Rh1−C27, 2.121(5); Rh1−C23, 2.225(4); Rh1−C26, 2.103(5); Rh1−Br, 2.5030(6); C2−N1, 1.352(6); N1−O1, 1.390(5); O1−C8, 1.468; C2−N3, 1.362(5); C2−Rh1−C26, 88.86(18), C2−Rh1−Br1, 93.19(13); N1−C2−N3, 101.1(4); C2−N1−O1, 122.6(4); N1−O1−C8, 109.8(3).

The palladium biscarbene complex **8** was prepared by refluxing a mixture of Pd(OAc)$_2$ and *N*-(benzyloxy)imidazolium bromide **4** in THF. The presence of two singlets assigned to the NC*H*$_2$ groups (at 5.63 and 5.67 ppm) and that of four distinct resonances attributable to the 4- and 5-methyl substituents reveal that the product was isolated as a mixture of the two *trans* diastereomers (*trans-syn* and *trans-anti*). The OC*H*$_2$ signals for both diastereomeric complexes appear as overlapped singlets at 5.78 ppm. Upon standing in a $CDCl_3$ solution for several days, the product isomerizes to a mixture of both *cis* diastereomers (*cis-syn* and *cis-anti*), as judged by the appearance of four AX systems (eight doublets) in the methylene region. In addition to the expected square planer geometry, structural analysis of **8** shows that two carbene ligands are in a *cis* arrangement and twisted relative to the PdBr$_2$ plane. The C1−Pd, C1−N1, and C1−N2 bond distances of 1.980(3), 1.360(4), and 1.341(4) Å are comparable to those of other square planar, *cis*-substituted biscarbene dihalide palladium complexes.[35,36] Similar to the rhodium(I) carbene complex, the contribution of the oxygen atom in the NCN π system is negligible as implied from the angle about O1 (112.2(2) Å) and the O1−N2 distance of 1.386(3) Å. Figure 2 lists selected bond angles and distances.

Catalytic Behavior in [5+2] and [4+2] Cycloaddition Reactions

Rhodium(I) complexes have proven to be effective catalysts in both inter- and intramolecular cycloadditions for the construction of six-, seven-, and eight-membered rings.[23−39] The Wilkinson catalyst RhCl(PPh$_3$)$_3$, [Rh(CO)$_2$Cl]$_2$, rhodium(I) phosphine complexes, and [(arene)Rh(COD)]SbF$_6$ complexes are among the Rh(I) complexes that have been shown to catalyze both the [4+2] cycloaddition of dienes and other π systems[37−44] and [5+2] cycloaddition of vinylcyclopropanes and π systems.[40,43,45−53]

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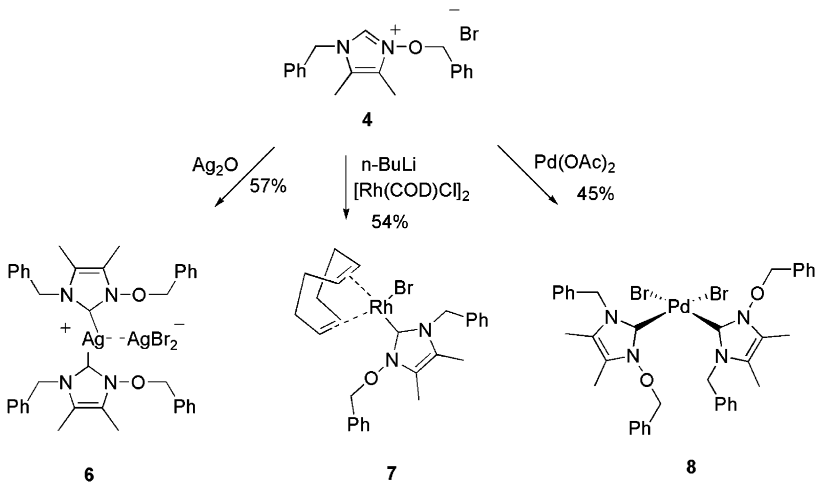
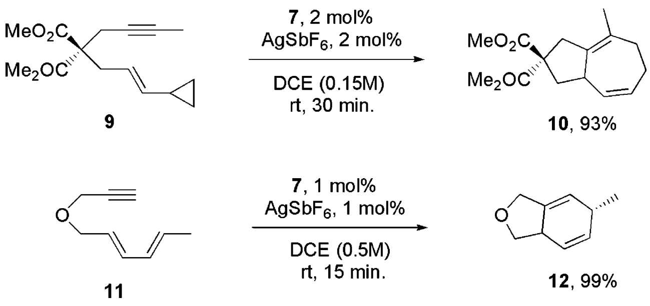
Scheme 2. Synthesis of Transition-Metal Complexes 6−8 from 4



Scheme 3. Catalytic Activity of Rhodium(I) Carbene Complex 7 in the [5+2] and [4+2] Reactions



Cationic arene rhodium(I) complexes successfully catalyze intramolecular [4+2][42] and [5+2][51] cycloaddition reactions quantitatively in minutes at room temperature. For the [5+2] cycloadditions, the cationic arene rhodium(I) complexes offer advantages over other Rh(I) systems: they catalyze transformations where Wilkinson's catalyst is ineffective and, in contrast to $[Rh(CO)_2Cl]_2$, do not isomerize olefins. The success of these air-stable, arene-based Rh(I) systems has led to the development of other robust, air-stable Rh(I) complexes where ancillary ligands such as phosphines or N-heterocyclic carbenes could potentially be fine-tuned to achieve the appropriate steric and electronic conditions for successful cycloaddition transformations.

Transition-metal N-heterocyclic carbene complexes have recently proven effective as cycloaddition catalysts for the formation of six-, seven-, and eight-membered rings.[33,54−57] The Rh(I) complexes are especially effective in this regard,[33,56,57] catalyzing the [4+2] cycloaddition of diene−ynes and the [5+2] cycloaddition of alkyne−vinylcyclopropanes in minutes at room temperature.[57] To further expand the scope of Rh(I)−NHC complexes as catalysts for cycloaddition reactions, complex **7** was tested for catalytic activity in the [5+2] cycloaddition reaction of tethered alkyne−vinylcyclopropanes and the [4+2] cycloaddition reaction of a diene−yne.

A very efficient and high-yielding [5+2] cycloaddition reaction of yne−vinylcyclopropane **9** was observed at room temperature upon the addition of 2 mol % **7** pretreated with 2 mol % $AgSbF_6$ (Scheme 3). In the absence of $AgSbF_6$, compound **10** was not observed when yne−vinylcyclopropane **9** was treated with 5 mol % complex **7** in 1,2-dichloroethane (DCE) at 60 °C. The [4+2] reaction of the diene−yne **11** was accomplished using 1 mol % **7** and 1 mol % $AgSbF_6$ to give a nearly quantitative yield of **12**. In the presence of $AgSbF_6$, the catalytic activity of this novel Rh(I)−NHC complex **7** is comparable to the Rh(I)−NHC complex reported by Chung and co-workers.[57] The extraordinary activities of these NHC−Rh(I) catalysts are much higher than those of comparable Rh(I)

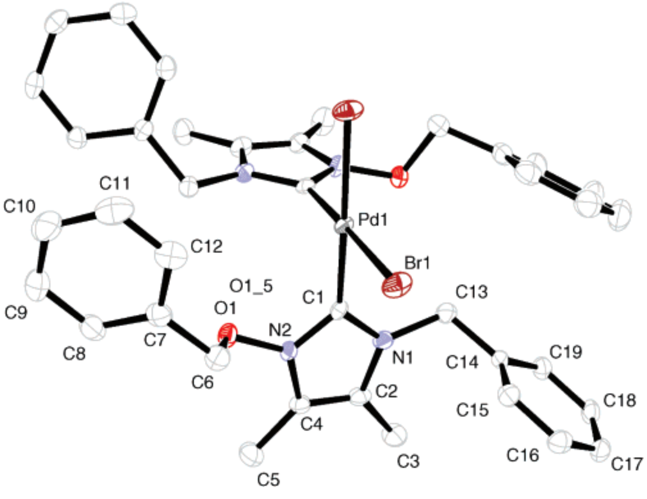


Figure 2. ORTEP diagram of **8**. Selected bond distances (Å) and angles (deg): Pd1−Br1, 2.490; Pd1−C1, 1.980(3), C1−N1, 1.360(4); C1−N2, 1.341(4); N2−O1, 1.396(3); O1−C6, 1.472(4); Br1−Pd1−C1, 88.56(8); N1−C1−N2, 111.7(2); C1−N2−O1, 121.8(2); N2−O1−C6, 112.2.

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systems for these cycloaddition reactions[42,44,58] and provide a promising avenue for the development of more active and selective catalysts for these cyclization reactions.

In summary, we have synthesized Ag(I), Rh(I), and Pd(II) complexes containing an *N*-alkoxyimidazolylidene ligand. Rhodium(I) (benzyloxy)imidazolylidene complex **7** was shown to be a highly effective catalyst for [5+2] cycloaddition reaction of an yne−vinylcyclopropane and the [4+2] cycloaddition reaction of a diene−yne under mild conditions.

Experimental Section

General Considerations. All organometallic reactions were performed under an inert atmosphere of N_2 using standard Schlenk line techniques or in a drybox. Silver(I) oxide was purchased from Aldrich, and palladium(II) acetate and chloro(1,5-cyclooctadiene)rhodium(I) dimer were purchased from Strem Chemicals. All three reagents were stored in an inert atmosphere prior to use. Anhydrous reaction solvents were further purified by passing through a column of either Q5 and alumina or molecular sieves. Deuterated chloroform and methylene chloride were dried over CaH_2, degassed via multiple freeze−pump−thaw cycles, and vacuum transferred. Unless otherwise specified, all NMR spectra were recorded on a Varian GX-400 NMR spectrometer. Chemical shifts were referenced against peak for TMS or the residual protons of the deuterated solvents (^1H NMR ($CDCl_3$) 7.26 ppm, (CD_2Cl_2) 5.36 ppm; ^{13}C NMR ($CDCl_3$) 77.0 ppm, (CD_2Cl_2) 53.8 ppm). Elemental analyses were performed by Desert Analytics. 1-Benzyl-4,5-dimethylimidazole 3-oxide (**1**) was synthesized following a literature procedure.[24]

3-Benzyl-1-methoxy-4,5-dimethylimidazolium Iodide (2). Methyl iodide (0.5 mL, 7.8 mmol) was added via syringe to a solution of imidazole *N*-oxide **1** (1.0 g, 4.9 mmol) in ca. 20 mL of $CHCl_3$. The resulting mixture was stirred at room temperature overnight. Removal of the volatiles in vacuo afforded a thick yellow oil. ^1H NMR (δ, $CDCl_3$): 10.32 (s, 1H, NC*H*N); 7.39 (m, 5H, $\mathrm{C_6}H_5$); 5.56 (s, 2H, $\mathrm{NC}H_2$); 4.38 (s, 3H, $\mathrm{OC}H_3$); 2.27 (s, 3H, $\mathrm{C}H_3$); 2.20 (s, 3H, $\mathrm{C}H_3$).

3-Benzyl-1-methoxy-4,5-dimethylimidazolium Hexafluorophosphate (3). Crude iodide **2** was taken up in deionized (DI) water, which separated the product from small amounts of a dark, insoluble residue. The water solution was decanted to a second flask, and a solution of ammonium hexafluorophosphate (950 mg, ca. 5.8 mmol) in 10 mL of DI water was added in portions. An oil separated during the addition, and the supernatant solution was decanted out. The oil was crushed in cold pentane (0 °C) and subsequently recrystallized in methanol. Yield: 1.3 g (73% from **1**). ^1H NMR (δ, $CDCl_3$): 8.67 (s, 1H, NC*H*N); 7.39 (m, 3H, $\mathrm{C_6}H_5$); 7.29 (d, 2H, $\mathrm{C_6}H_5$); 5.24 (s, 2H, $\mathrm{NC}H_2$); 4.21 (s, 3H, $\mathrm{OC}H_3$); 2.27 (s, 3H, $\mathrm{C}H_3$); 2.17 (s, 3H, $\mathrm{C}H_3$).

1-(Benzyloxy)-3-benzyl-4,5-dimethylimidazolium Bromide (4). Benzyl bromide (1.2 mL, ca. 10 mmol) was added via syringe to a refluxing suspension of **1** (1.0 g, 5.0 mmol) in dry benzene. A dark orange oil separated after the suspension was refluxed for 6 h and cooled to room temperature. The supernatant was decanted, and the remaining oil was dried under vacuum overnight, which caused the product to solidify. The solid mass was crushed in pentane, filtered, and dried under vacuum. Yield: 1.34 g (63%). ^1H NMR (δ, $CDCl_3$): 11.04 (s, 1H, NC*H*N); 7.6−7.2 (ov m, 10H, 2 × $\mathrm{C_6}H_5$); 5.59, 5.58 (s + s, $\mathrm{NC}H_2$, $\mathrm{OC}H_2$); 2.09, 1.94 (s, 3H, $\mathrm{C}H_3$, $\mathrm{C}H_3$). ^{13}C NMR (δ, $CDCl_3$): 132.8 ($\mathrm{OCH_2}{}^{i}C_6\mathrm{H_5}$); 132.5 (N*C*N); 131.5 ($\mathrm{NCH_2}{}^{i}C_6\mathrm{H_5}$); 130.6, 130.3, 129.2, 129.0, 129.0, 128.9, 128.0 (${}^{omp}C_6\mathrm{H_5}$); 124.8; 124.1 (N*CC*N); 83.9 ($\mathrm{O}C\mathrm{H_2}$); 51.2 ($\mathrm{N}C\mathrm{H_2}$); 8.89 ($C\mathrm{H_3}$); 7.11 ($C\mathrm{H_3}$).

3-Benzyl-1-(benzyloxy)-4,5-dimethylimidazolium Hexafluorophosphate (5). A batch of crude bromide **4** (still as an oil before being dried under vacuum) was dissolved in DI water and extracted with hexanes. The aqueous layer was separated, and a solution of ammonium hexafluorophosphate (ca. 1.3 equiv) was added dropwise with constant stirring. The yellow oil deposited on the walls of the flask was dissolved in warm methanol, and a few drops of hexanes were added. Cooling to room temperature afforded off-white crystals of pure **5**, which were rinsed with pentane and dried under vacuum. Yield: 82% from **1**. ^1H NMR (δ, $CDCl_3$): 8.42 (s, 1H, NC*H*N); 7.45−7.35, 7.18 (ov m, $\mathrm{C_6}H_5$); 5.31, 5.20 (s + s, $\mathrm{NC}H_2$, $\mathrm{OC}H_2$); 2.13 (s, 3H, $\mathrm{C}H_3$); 2.05 (s, 3H, $\mathrm{C}H_3$).

Bis[1-(benzyloxy)-3-benzyl-4,5-dimethylimidazolylidene]silver(I) Dibromoargentate (6). A mixture of silver oxide (128 mg, 0.55 mmol) and imidazolium bromide **4** (396 mg, 1.06 mmol) was taken up in dry CH_2Cl_2 and stirred at room temperature for 90 min. The dark orange suspension was filtered through a pad of Celite and evaporated to dryness, yielding an orange powder. Crystallization from THF afforded a white powder (two crops). Yield: 291 mg (57%). ^1H NMR (δ, CD_2Cl_2): 7.47−7.32 (ov m, 10H, 2 × $\mathrm{C_6}H_5$); 5.23, 5.22 (s + s, $\mathrm{NC}H_2$, $\mathrm{OC}H_2$); 2.01, 1.95 (s, 3H + 3H, $\mathrm{C}H_3$, $\mathrm{C}H_3$). ^{13}C NMR (δ, CD_2Cl_2): 136.2 (N*C*N); 133.3 ($\mathrm{OCH_2}{}^{i}C_6\mathrm{H_5}$); 130.8 ($\mathrm{NCH_2}{}^{i}C_6\mathrm{H_5}$); 130.7, 130.0; 129.3, 129.3, 128.5, 127.1, 123.9 (${}^{omp}C_6\mathrm{H_5}$ + N*CC*N); 82.6 ($\mathrm{O}C\mathrm{H_2}$); 54.0 ($\mathrm{N}C\mathrm{H_2}$); 9.4 ($C\mathrm{H_3}$); 7.8 ($C\mathrm{H_3}$). Anal. Found: C, 47.56; H, 4.26; N, 5.79. Calcd for $C_{38}H_{40}Ag_2Br_2N_4O_2$: C, 47.53; H, 4.20; N, 5.83.

Bromo(cyclooctadiene)[1-(benzyloxy)-3-benzyl-4,5-dimethylimidazolylidene]rhodium(I) (7). To a rapidly stirred solution of $[Rh(COD)Cl]_2$ (100 mg, 0.20 mmol) and bromide **4** (216 mg, 0.59 mmol) in 7.5 mL of 3:2 THF/EtOH was added ^{n}BuLi (0.5 mmol) at −78 °C. A color change from orange to yellow was observed upon warming of the resulting solution to room temperature. The solvents were removed in vacuo, and the yellow solid obtained was purified by flash column chromatography (silica gel, $MeOH/CH_2Cl_2$). Isolation of the second elution band afforded pure **7** as a yellow powder, which was recrystallized from $EtOH/CH_2Cl_2$ at −30 °C (yellow needles). Yield: 125 mg (54%). Evaporation of the filtrate and recrystallization in CH_2Cl_2/Et_2O (vapor diffusion) yielded single crystals suitable for X-ray analysis. ^1H NMR (δ, CD_2Cl_2): 7.77 (m, 2H), 7.47 (m, 2H), 7.40−7.20 (om, 6H) ($\mathrm{C_6}H_5$); 6.07 (d, $J_{AX} \approx 16$ Hz), 6.00 (d, $J_{AX} \approx 10$ Hz), 5.59 (d, $J_{AX} = 16.2$ Hz), 5.57 (d, $J_{AX} = 9.9$ Hz) ($\mathrm{NC}H_2$ + $\mathrm{OC}H_2$); 5.04 (bm, 2H, COD C*H*); 4.01 (bm, 1H, COD C*H*); 3.19 (bm, 1H, COD C*H*); 2.36, 2.22 (br m + br m, 3H, COD $\mathrm{C}H_2$); 1.87 (s), 1.82 (s), 1.8 (br m) (10H, 2 × CH_3, COD $\mathrm{C}H_2$); 1.62 (br m, 1H, COD $\mathrm{C}H_2$). ^{13}C NMR (δ, CD_2Cl_2): 137.9, 134.9 ($\mathrm{OCH_2}{}^{i}C_6\mathrm{H_5}$, $\mathrm{NCH_2}{}^{i}C_6\mathrm{H_5}$); 130.8, 129.4, 128.9, 128.8, 127.7, 127.1 ($C_6\mathrm{H_5}$); (N*CC*N), 97.2 (d, $J_{^{13}C-^{103}Rh} = 7$ Hz), 96.2 (d, $J_{^{13}C-^{103}Rh} = 7$ Hz) (COD *C*H); 81.7 ($\mathrm{O}C\mathrm{H_2}$); 71.2 (d, $J_{^{13}C-^{103}Rh} = 14$ Hz), 70.5 (d, $J_{^{13}C-^{103}Rh} = 14$ Hz) (COD *C*H); 53.4 ($\mathrm{N}C\mathrm{H_2}$); 33.2, 32.5, 29.6, 29.3 (COD $C\mathrm{H_2}$); 9.5 ($C\mathrm{H_3}$); 7.7 ($C\mathrm{H_3}$). Anal. Found: C, 55.54; H, 5.58; N, 4.82. Calcd for $RhON_2C_{27}H_{32}Br$: C, 55.59; H, 5.53; N, 4.80.

Dibromobis[1-(benzyloxy)-3-benzyl-4,5-dimethylimidazolylidene]palladium(II) (8). A solution of palladium acetate (100 mg, 0.45 mmol) and bromide **4** (395 mg, 0.9 mmol) in THF (12 mL) was refluxed for ca. 2.5 h, which caused a color change from dark orange to yellow and the precipitation of a powdery solid. Removal of the volatiles in vacuo yielded a yellow solid, which was washed with diethyl ether (3×) and methylene chloride (2×). The resulting pale yellow solid was dried under vacuum. A second batch of product was obtained by evaporating the collected rinses

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to dryness and washing with diethyl ether. Combined yield: 170 mg (45%) of a 2:1 mixture of the two *trans* isomers (*syn* and *anti*). ^{1}H NMR (δ, $CDCl_3$): 7.51 (d) 7.40−7.20 (ov m), 7.07 (t, 10H, 2 × C_6H_5); 5.78 (4H, s, OCH_2 major + minor); 5.63 (s, 2H, NCH_2 major); 5.57 (s, 2H, NCH_2 minor); 1.78 (s, 3H, CH_3 major); 1.77 (s, 3H, CH_3 minor); 1.75 (s, 3H, CH_3 major); 1.67 (s, 3H, CH_3 minor). Upon standing in $CDCl_3$, the compound isomerizes to a ca. 3:1 mixture of the two *cis* isomers (*syn* and *anti*). ^{1}H NMR (δ, $CDCl_3$): 7.62−7.66 (m, $^{o}C_6H_5$ minor); 7.58 (dd, $^{o}C_6H_5$ major); 7.36−7.16 (ov m, $^{mp}C_6H_5$ major + minor); 6.91−6.88 (br dd, $^{o}C_6H_5$ major); 6.86−6.82 (br m, $^{o}C_6H_5$ minor); 6.00 (d, J_{AX} = 9.5 Hz, OCH_2, major); 5.92 (d, J_{AX} = 10.6 Hz, OCH_2, minor); 5.75 (d, J_{AB} = 16.4 Hz, NCH_2, major); 5.70 (d, J_{AX} = 16.4 Hz, NCH_2, minor); 5.58 (d, J_{AX} = 10.6 Hz, OCH_2, minor); 5.52 (d, J_{AB} = 16.5 Hz, NCH_2, major); 5.38 (d, J_{AX} = 9.4 Hz, OCH_2, major); 4.89 (d, J_{AX} = 16.4 Hz, NCH_2, minor); 1.79 (s, 3H, CH_3 major); 1.67 (s, 3H, CH_3 minor); 1.63 (s, 3H, CH_3 major); 1.50 (s, 3H, CH_3 minor). ^{13}C NMR (δ, $CDCl_3$): 154.0 (NCN); 135.9, 134.1, 133.4, 131.1, 130.7, 129.2, 129.1, 128.6, 128.5, 128.1, 127.4, 127.2, 126.8, 126.4 (C_6H_5, major + minor); 125.1, 124.4, 123.9, 123.2 (NCCN, major + minor); 81.0 (OCH_2, minor); 80.9 (OCH_2, major); 54.1 (NCH_2, major); 52.6 (NCH_2, minor); 9.7 (CH_3, major); 9.5 (CH_3, major); 7.6 (CH_3, minor); 7.5 (CH_3, major). Anal. Found: C, 53.30; H, 4.73; N, 6.46. Calcd for $PdBr_2O_2N_4C_{38}H_{40}$: C, 53.63; H, 4.74; N, 6.58.

Cycloaddition Reactions. Reactions were carried out in oven-dried borosilicate test tubes sealed with rubber septa and kept under a positive pressure of nitrogen. Teflon-coated magnetic stir bars were used. Organic solutions were concentrated using a Büchi rotary evaporator with a desktop vacuum pump. Thin layer chromatography plates were visualized by ultraviolet light and treatment with acidic *p*-anisaldehyde stain followed by gentle heating. Chromatographic purification of products was accomplished by flash chromatography, as described by Still and co-workers.[59] Silica gel 60, 230−400 mesh, was purchased from EM Science. $AgSbF_6$ and DCE (99+%, ACS reagent grade) were purchased from Aldrich Chemical Co. DCE was stored over 4 Å molecular sieves (activated in a vacuum oven). NMR spectra were measured on a Varian INOVA 500 (^{1}H at 500 MHz, ^{13}C at 125 MHz) or Varian MERCURY 400 (1H at 400 MHz, ^{13}C at 100 MHz) magnetic resonance spectrometer.

Catalyst Solution. Into an oven-dried 12 × 75 mm borosilicate glass test tube, equipped with a stir bar and capped with a rubber septum, were added $AgSbF_6$ (0.003 g, 0.0087 mmol), Rh(I) complex **7** (0.005 g, 0.0087 mmol), and DCE (2.9 mL, 0.003 M). The resulting yellow suspension was stirred for 30 min under a positive pressure of N_2 and was kept in the dark by wrapping the test tube with aluminum foil.

Cycloadduct 10. Yne−vinylcyclopropane substrate **9** (0.021 g, 0.079 mmol) was weighed into a separate oven-dried 12 × 75 mm borosilicate glass test tube equipped with a stir bar and capped with a rubber septum. The test tube was then wrapped in aluminum foil. The catalyst solution (0.53 mL, 0.0016 mmol of Rh(I)), prepared as given above, was added via syringe. The resulting yellow reaction mixture was stirred at ambient temperature for 1.5 h and was kept under a positive pressure of N_2. The mixture was purified by flash column chromatography on silica gel (5% diethyl ether in pentane). Product-containing fractions were concentrated to give **10** (0.0195 g) in 93% yield as a colorless oil. NMR spectroscopic data for **10** are consistent with previously reported values.[60]

Cycloadduct 12. Diene−yne substrate **11** (0.020 g, 0.076 mmol) was weighed into a separate oven-dried 12 × 75 mm borosilicate glass test tube equipped with a stir bar and capped with a rubber septum. The test tube was then wrapped in aluminum foil. The catalyst solution (0.50 mL, 0.0015 mmol of Rh(I)), prepared as described above, was added via syringe. The resulting yellow reaction mixture was stirred at ambient temperature for 2 min and was kept under a positive pressure of N_2. The mixture was purified by flash column chromatography on silica gel (5% diethyl ether in pentane). Product-containing fractions were concentrated to give **12 (**0.019 g) in 95% yield as a colorless oil. NMR spectroscopic data for **12** are consistent with previously reported values.[42]

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Supporting Information Available: X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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