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Notes

Synthesis, Structures, and Catalytic Properties of Late-Transition-Metal 2,6-Bis(2-phosphaethenyl)pyridine Complexes

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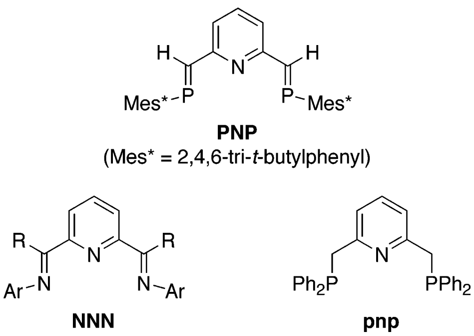
Summary: 2,6-Bis(2-phosphaethenyl)pyridine (PNP) complexes of Rh(I), Cu(I), and Ag(I) have been prepared and examined by NMR and X-ray diffraction analyses. The PNP ligand adopts κ^3(P,N,P) coordination for Rh(I) and Cu(I) and κ^2(P,P) coordination for Ag(I). The rhodium complex [RhCl(PNP)] in combination with AgOTf catalyzes conjugate addition of benzyl carbamate to enones.

Electronic and steric properties of ancillary ligands are crucial factors for designing functional transition-metal complexes. Our recent effort in this area has focused on development of transition-metal complexes coordinated with phosphaalkenes as low-coordinated phosphorus compounds.[1,2] Phosphaalkenes with $P{=}C$ double bond(s) possess extremely low lying π^* orbitals mainly located around phosphorus and exhibit a marked tendency to engage in strong π-back-bonding with transition metals.[2] We have demonstrated with diphosphinidenecyclobutene ligands (DPCB-Y) that this property is useful for catalysis, leading to highly efficient organic transformations with hitherto unknown reactivity and selectivity.[3]

Chart 1



PNP
(Mes* = 2,4,6-tri-*t*-butylphenyl)

NNN

pnp

In this study, we turn our research interest to 2,6-bis(2-phosphaethenyl)pyridine as a tridentate ligand (PNP; Chart 1), which consists of a σ-donative pyridine core and two π-accepting phosphaethenyl arms. This compound is a phosphaalkene analogue of bis(imino)pyridines (NNN) and was first synthesized by Geoffroy et al. in 1992.[4] In contrast to thorough studies on NNN complexes,[5,6] however, its utility in transition-metal chemistry has been scarcely explored. We herein describe the synthesis and structures of PNP complexes of group 9 and 11 metals.[7] The complex [RhCl-

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10.1021/om700488y CCC: $37.00

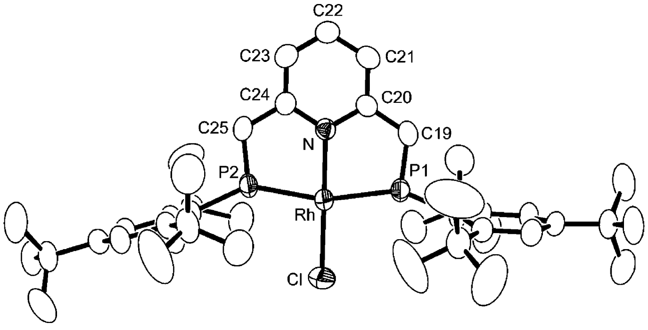
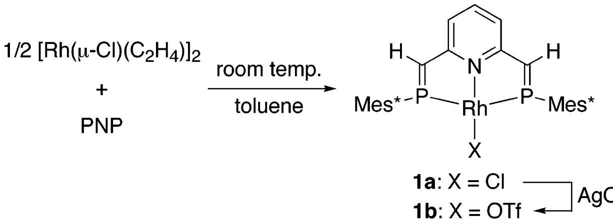


Figure 1. Molecular structure of [RhCl(PNP)](2Et$_2$O) (**1a**·2Et$_2$O) with thermal ellipsoids at the 50% probability level. Hydrogen atoms and two molecules of Et$_2$O are omitted for clarity. Selected bond distances (Å) and angles (deg): Rh−P1 = 2.233(1), Rh−P2 = 2.231(1), Rh−N = 2.053(3), Rh−Cl = 2.311(1), P1−C19 = 1.662(4), P2−C25 = 1.664(4); N−Rh−P1 = 81.23(8), N−Rh−P2 = 80.78(8), P1−Rh−Cl = 99.29(4), P2−Rh−Cl = 98.93(4), P1−Rh−P2 = 161.58(4), N1−Rh−Cl = 175.82(9).

(PNP)] in combination with AgOTf exhibits catalytic performance in the conjugate addition of benzyl carbamate to enones.

Results and Discussion

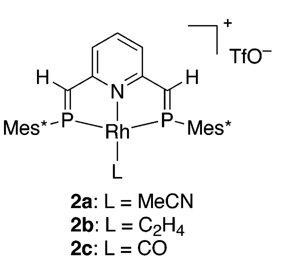
Synthesis of Rhodium(I) Complexes. The PNP ligand readily reacted with [Rh(μ-Cl)(C$_2$H$_4$)$_2$]$_2$ in toluene at room temperature to give [RhCl(PNP)] (**1a**), which was isolated as a green crystalline solid in 68% yield (eq 1). Complex **1a** was converted to the rhodium triflate **1b** in 90% yield by treatment with AgOTf (1 equiv) in toluene.



(1)

Figure 1 depicts the X-ray structure of **1a**, which adopts a slightly distorted square planar geometry; the sum of the four bond angles around rhodium is 360.23°. The Rh−P lengths (2.233(1), 2.231(1) Å) are shorter than those of [RhCl(pnp)] (2.260(13), 2.263(2) Å) bearing a phosphine-based 2,6-bis(diphenylphosphinomethyl)pyridine ligand (pnp; Chart 1).[8] The Rh−P, Rh−N, and Rh−Cl distances are unexceptional.[9]

Complex **1b** reacted with MeCN (10 equiv), ethylene (1 atm), or CO (1 atm) in CH$_2$Cl$_2$ to afford cationic complexes of the formula [Rh(L)(PNP)](OTf) (L = MeCN (**2a**), C$_2$H$_4$ (**2b**), CO (**2c**)), respectively. The same complexes were prepared by the reaction of **1a** with AgOTf (1 equiv) in CH$_2$Cl$_2$ in the presence of MeCN, ethylene, or CO. Complex **2c** was formed from **2a** and CO as well.



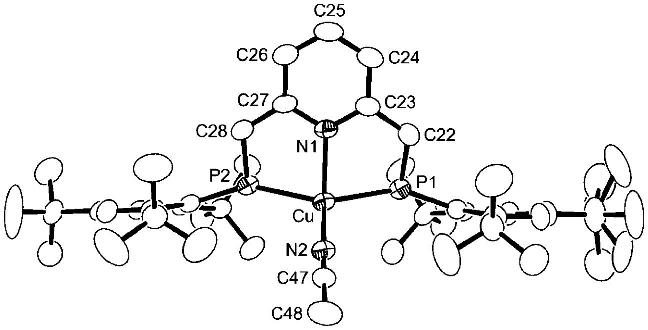
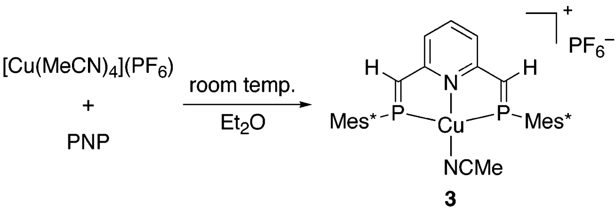


Figure 2. Molecular structure of [Cu(MeCN)(PNP)](PF$_6$) (**3**) with thermal ellipsoids at the 50% probability level. Hydrogen atoms and the counteranion are omitted for clarity. Selected bond distances (Å) and angles (deg): Cu−P1 = 2.313(1), Cu−P2 = 2.303(1), Cu−N1 = 2.071(4), Cu−N2 = 1.939(4), P1−C22 = 1.672(6), P2−C28 = 1.674(6), N2−C47 = 1.130(6); N1−Cu−P1 = 81.8(1), N1−Cu−P2 = 81.9(1), P1−Cu−N2 = 109.3(1), P2−Cu−N2 = 108.5(1), P1−Cu−P2 = 141.43(5), N1−Cu−N2 = 126.5(2), Cu−N2−C47 = 175.6(4).

The MeCN complex **2a** was isolated as a dark blue powder in 74% yield. On the other hand, since the ethylene ligand in **2b** is labile, this complex was obtained as a mixture with [Rh(OTf)(PNP)] (**1b**; **2b**:**1b** = 82:18) even by precipitation from an ethylene-saturated solution using Et$_2$O as a poor solvent. The CO complex **2c** was obtained in pure form, as confirmed by NMR spectroscopy, but this product did not give satisfactory elemental analysis data. This is probably due to the occurrence of partial dissociation of the CO ligand upon isolation.

Complex **2c** exhibited a strong ν_{CO} band at 2022 cm^{-1}, the value of which is much higher than that of [Rh(CO)(pnp)]Cl (1980 cm^{-1}).[10] Thus, it is likely that the strong π-accepting ability of PNP ligand forms an electron-deficient metal center in **2c**, making the CO coordination unstable.

Synthesis of Copper(I) and Silver(I) Complexes. The complex [Cu(MeCN)$_4$]PF$_6$ smoothly reacted with PNP in Et$_2$O at room temperature to give [Cu(MeCN)(PNP)]PF$_6$ (**3**) as a reddish brown solid in 61% yield, which showed a singlet at δ 269.0 in the ^{31}P{^{1}H} NMR spectrum (eq 2).



3

(2)

Figure 2 shows the X-ray structure of **3**, which adopts a distorted-tetrahedral geometry surrounded by a PNP ligand in κ^3(P,N,P) fashion, together with a MeCN ligand. The Cu−N1 (2.071(4) Å), Cu−N2 (1.939(4) Å), and Cu−P (2.313(1), 2.303(1) Å) lengths are typical for single bonds.[9]

Treatment of AgOTf with PNP in CH$_2$Cl$_2$ afforded the aqua complex **4**, having PNP and OTf ligands (eq 3). Complex **4** was isolated as an orange solid in 74% yield when the reaction was carried out in the presence of water, while the same complex

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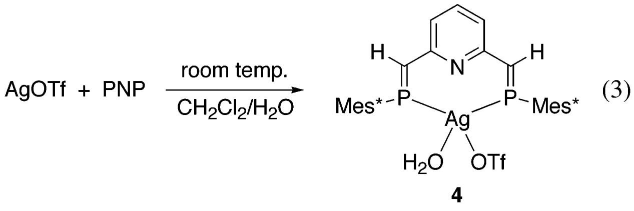


(3)

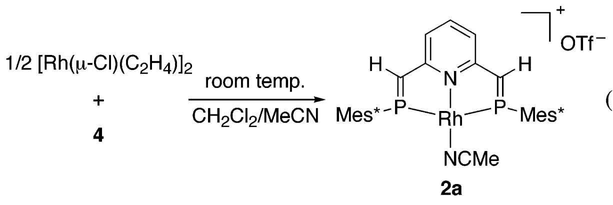
was generated without added water, as confirmed by NMR spectroscopy. Thus, the residual water in CH_2Cl_2 after drying over CaH_2 was sufficient for formation of **4**, showing high oxophilicity of the PNP-coordinated silver atom.

Two phosphorus atoms of PNP were observed to be chemically equivalent in the $^{31}P\{^1H\}$ NMR spectrum, showing a signal at δ 250.1 with ^{109}Ag (J = 507 Hz) and ^{107}Ag (J = 433 Hz) couplings. The IR spectrum (KBr) exhibited a strong $\nu(SO_3)$ band at 1395 cm^{-1}, which is assignable to a coordinated, rather than ionic, triflate.[11]

Figure 3 illustrates the crystal structure of **4**. The silver atom is connected with two phosphorus atoms of the PNP ligand and two oxygen atoms of the OH_2 and OTf ligands. The Ag−P (2.5006(9), 2.5229(9) Å) and Ag−O lengths (2.495(2), 2.389(3) Å) are in a typical range.[9] On the other hand, the nitrogen atom of the PNP ligand is notably distant from the silver atom (2.680(2) Å); a covalent bond is normally within 2.2−2.4 Å. Since the complex has an 18e configuration without coordination of nitrogen, no specific bonding interaction should be expected between the nitrogen and silver atoms. Consequently, it is concluded that **4** has a distorted-tetrahedral structure.

The difference in the PNP coordination modes between **3** and **4** is probably due to the sizes of Cu(I) (0.74 Å) and Ag(I) (1.16 Å). Thus, the long M−P bonds in **4** (2.5006(9), 2.5229(9) Å) compared with those in **3** (2.313(1), 2.303(1) Å) put the nitrogen atom in a remote position where direct coordination to silver is not possible.

Complex **4** served as a good precursor for rhodium complexes with PNP and OTf. For example, treatment of $[Rh(\mu\text{-}Cl)(C_2H_4)_2]_2$ with a stoichiometric amount of **4** in the presence of MeCN in CH_2Cl_2 at room temperature resulted in quantitative formation of **2a** (eq 4). This observation indicates the coordination ability of PNP is higher toward Rh(I) than toward Ag(I).



(4)

Catalytic Hydroamidation of Enones. Finally, the catalytic activity of the PNP rhodium complexes **1a** and **1b** was evaluated in the conjugate addition of benzyl carbamate ($CbzNH_2$) to 2-cyclohexenone (eq 5). Highly Lewis acidic metal complexes have been shown to catalyze this reaction.[12]

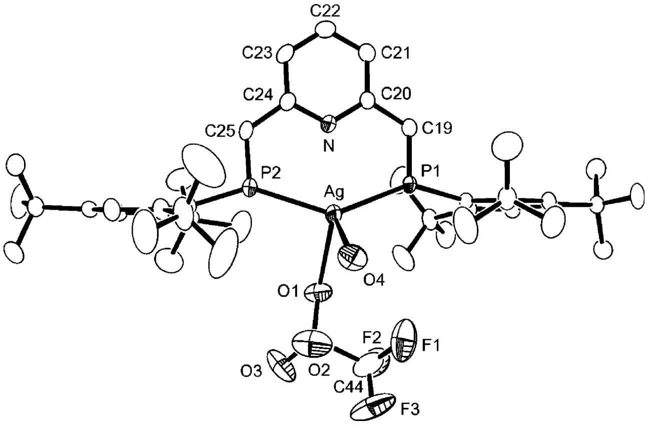
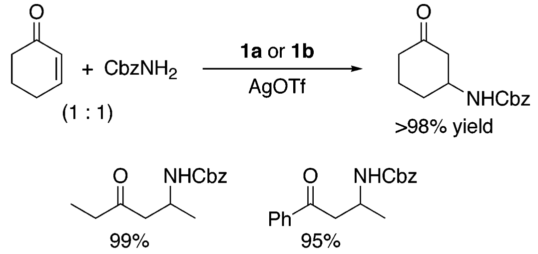


Figure 3. The molecular structure of $[Ag(OTf)(OH_2)(PNP)](OTf)$ (**4**) with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ag−P1 = 2.5006(9), Ag−P2 = 2.5229(9), Ag−O1 = 2.495(2), Ag−O4 = 2.389(3), Ag···N = 2.680(2), P1−C19 = 1.658(3), P2−C25 = 1.659(3); P1−Ag−P2 = 136.27(3), P1−Ag−O1 = 110.64(7), P1−Ag−O4 = 104.73(8), P2−Ag−O1 = 95.82(7), P2−Ag−O4 = 112.34(8), O1−Ag−O4 = 84.03(8).

Table 1. Conjugate Addition of Benzyl Carbamate to 2-Cyclohexanone[a]

run no.	Rh complex (amt (mol %))	amt of AgOTf (mol %)	time (h)	yield (%)[b]
1	**1a** (2)	4	3	94
2	**1a** (2)	10	2	>99
3[c]	**1a** (0.5)	1	5.5	98
4		4	9	39
5	**1b** (2)	0	12	49
6	**1b** (2)	4	4.5	99

[a] Reactions were run at room temperature using 2-cyclohexanone (1 mmol) and $CbzNH_2$ (1 mmol) without solvent unless otherwise noted. [b] Determined by ^1H NMR using anisole as an internal standard. [c] The reaction was run at 50 °C.



(5)

Table 1 gives the results. All reactions were carried out using a 1:1 ratio of substrates without solvent. Rhodium chloride **1a** itself was inactive but successfully catalyzed the reaction in the presence of AgOTf (run 1). The catalytic activity increased with an increasing amount of AgOTf (run 2), while the reaction also proceeded smoothly with a smaller amount of catalyst upon heating (run 3). Since AgOTf alone was not as effective (run 4), the highly active species must be generated from **1a** and AgOTf. Although the rhodium triflate **1b** is a very probable species, the isolated one was modestly reactive (run 5) and high catalytic activity developed when excess AgOTf was added (run 6).

The combination of **1a** and AgOTf was sufficiently effective for conjugate addition of $CbzNH_2$ to 4-hexen-3-one and 1-phenyl-2-butenone, giving the corresponding 1,4-addition products in 99 and 95% yields, respectively, under the conditions of run 3 in Table 1 (eq 5). On the other hand, the reaction of 4-methyl-3-penten-2-one was very slow (10% yield for 24 h at 50 °C), and methyl cyclohexenyl ketone as a trisubstituted olefin was unreactive.

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Conclusion

We have confirmed that 2,6-bis(2-phosphaethenyl)pyridine (PNP) successfully forms neutral and cationic complexes with Rh(I), Cu(I), and Ag(I) centers. The Rh(I) center forms square-planar complexes having κ^3(P,N,P) coordination of PNP, whereas Cu(I) and Ag(I) centers adopt a distorted-tetrahedral geometry with the PNP ligand in κ^3(P,N,P) and κ^2(P,P) fashion, respectively. It is noteworthy that the ν(CO) band of [Rh(CO)(PNP)]$^+$ (**2c**) appears at a significantly high wavenumber (2022 cm^{-1}) as compared with the case for the phosphine analogue [Rh(CO)(pnp)]$^+$ (1980 cm^{-1}). This observation indicates a strong π-accepting ability of PNP ligand to afford a highly electron-deficient metal center, consistent with the catalytic activity of **1a** in combination with AgOTf toward conjugate addition of benzyl carbamate to enones.

Experimental Section

Synthesis of [RhCl(PNP)] (1a). To a light yellow solution of PNP (207.2 mg, 0.316 mmol) in toluene (5.0 mL) was added [Rh(μ-Cl)(C_2H_4)$_2$]$_2$[13] (61.9 mg, 0.159 mmol) at room temperature, and the solution was stirred for 1 h. The solution gradually turned dark brown. Insoluble materials were removed by filtration through a Celite pad, and the filtrate was concentrated to dryness. The residue was washed with Et_2O at −78 °C and dried under reduced pressure to give **1a** as a green powder. Yield: 169.4 mg (68%). Recrystallization from Et_2O at −70 °C formed single crystals suitable for X-ray diffraction study. Mp: 195 °C dec. Anal. Calcd for $C_{43}H_{63}ClNP_2Rh$: C, 65.02; H, 7.99; N, 1.76. Found: C, 64.65; H, 7.89; N, 1.59.

Synthesis of [Rh(OTf)(PNP)] (1b). To a dark green solution of **1a** (39.8 mg, 0.0501 mmol) in toluene (2.0 mL) was added AgOTf (13.1 mg, 0.0510 mmol) at 0 °C. The solution immediately turned deep green. After the mixture was stirred for 1 h, a precipitate of AgCl was removed by filtration through a Celite pad, and volatiles were removed under reduced pressure. The residue was washed with Et_2O at 0 °C and dried under vacuum to give a green powder of **1b**. Yield: 41.1 mg (90%). Mp: 170 °C dec. IR (KBr, cm^{-1}): 1397 (SO_3). Anal. Calcd for $C_{44}H_{63}F_3NO_3P_2RhS$: C, 58.21; H, 6.99; N, 1.54. Found: C, 58.60; H, 7.10; N, 1.61.

Synthesis of [Rh(MeCN)(PNP)](OTf) (2a). To a dark green solution of **1a** (76.8 mg, 0.0967 mmol) in CH_2Cl_2 were added MeCN (51 μL, 0.977 mmol) and AgOTf (25.5 mg, 0.0992 mmol) in this order at room temperature, and the solution was stirred for 2 h. A precipitate of AgCl was removed by filtration through a Celite pad. Volatiles were removed under reduced pressure, and the residue was washed with Et_2O at 0 °C and dried under reduced pressure to give **2a** as a dark blue powder. Yield: 68.4 mg (74%). Mp: 188 °C dec. IR (KBr, cm^{-1}): 1269 (SO_3). Anal. Calcd for $C_{46}H_{66}F_3N_2O_3P_2RhS$: C, 58.22; H, 7.01; N, 2.95. Found: C, 58.31; H, 7.20; N, 2.84.

Synthesis of [Rh(C_2H_4)(PNP)](OTf) (2b). To a dark green solution of **1a** (49.8 mg, 0.0627 mmol) in CH_2Cl_2 (2.0 mL) was added AgOTf (17.2 mg, 0.0669 mmol) at room temperature under an ethylene atmosphere. The solution immediately turned dark red. After the mixture was stirred for 30 min, a precipitate of AgCl was removed by filtration through a Celite pad. The filtrate was concentrated on bubbling with ethylene. Addition of Et_2O resulted in precipitation of a dark red powder, which was washed with Et_2O under an ethylene atmosphere at −78 °C and dried under reduced pressure to give a mixture (25 mg) of **2b** (82%) and [Rh(OTf)(PNP)] (**1b**; 18%), as confirmed by NMR spectroscopy.

Synthesis of [Rh(CO)(PNP)](OTf) (2c). A dark blue solution of **2a** (45.9 mg, 0.0484 mmol) in CH_2Cl_2 (1.5 mL) was degassed by freeze−pump−thaw cycles. Carbon monoxide was introduced into the degassed solution from a CO balloon, and the solution was stirred at room temperature for 1 h. The solution gradually turned dark green. Volatiles were removed under reduced pressure. The residue was washed with Et_2O at 0 °C and dried under vacuum to give a dark bluish green powder of **2c**. Yield: 39.8 mg (88%). Mp: 140 °C dec. IR (KBr, cm^{-1}): 2022 (CO), 1275 (SO_3).

Synthesis of [Cu(MeCN)(PNP)](PF_6) (3). To a yellow solution of PNP (97.5 mg, 0.149 mmol) in Et_2O (2.0 mL) was added [Cu(MeCN)$_4$](PF_6)[14] (54.8 mg, 0.147 mmol) at room temperature. Stirring the solution for 1 h produced a red precipitate, which was collected by filtration, washed with Et_2O, and dried under vacuum to give **3** as a reddish brown powder. Yield: 82.2 mg (61%). A single crystal for X-ray diffraction study was obtained by recrystallization from CH_2Cl_2 and Et_2O. Mp: 190 °C. IR (KBr, cm^{-1}): 2310, 2279 (CN). Anal. Calcd for $C_{45}H_{66}CuF_6N_2P_3$: C, 59.69; H, 7.35; N, 3.09. Found: C, 59.99; H, 7.69, N, 3.09.

Synthesis of [Ag(OTf)(OH_2)(PNP)] (4). To a yellow solution of PNP (98.7 mg, 0.150 mmol) in CH_2Cl_2 (3.0 mL) was added AgOTf (39.5 mg, 0.154 mmol) and H_2O (54 μL) at room temperature. The solution immediately turned reddish orange. The reaction vessel was wrapped with aluminum foil to protect it from light, and the solution was stirred for 1 h. Volatiles were removed under vacuum, and the residue was washed with Et_2O at 0 °C and dried under vacuum to give an orange powder of **4**. Yield: 104.1 mg (74%). A single crystal for X-ray diffraction analysis was obtained by slow diffusion of a CH_2Cl_2 solution into pentane. Mp: 219 °C. IR (KBr, cm^{-1}): 3452 (OH_2), 1395 (SO_3). Anal. Calcd for $C_{44}H_{65}AgF_3NO_4P_2S$: C, 56.77; H, 7.04; N, 1.50. Found: C, 56.57; H, 7.03; N, 1.46.

Conjugate Addition of Benzyl Carbamate to Enones. A 10 mL Schlenk tube was charged with benzyl carbamate ($CbzNH_2$, 151 mg, 1 mmol), 2-cyclohexenone (96 mg, 1 mmol), and anisole (30 μL). The mixture was stirred for 5 min, and then the catalyst (**1a** or **1b** and AgOTf) was added. The reaction progress was followed at intervals by GLC, and the product yield was determined by ^{1}H NMR spectroscopy using anisole as an internal standard. The addition products are known compounds.[12]

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Supporting Information Available: Text and a table giving NMR data for all new compounds and details of the X-ray structural analysis and CIF files giving crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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