DOI: 10.1002/ejic.200701049

Synthesis and Complexation Properties of Allenic Bipyridines, a New Class of Axially Chiral Ligands for Transition Metal Catalysis

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Dedicated to Prof. Gerard van Koten on the occasion of his 65th birthday

Keywords: Allenes / Axial chirality / Bipyridines / Catalysis / Transition metal complexes

The allenic bipyridines **3**, which represent a new class of axially chiral ligands for transition metal catalysis, were synthesized and their complexation properties were studied. The synthesis was achieved by copper-mediated or palladium-catalyzed S_N2'-substitution of the tertiary propargyl acetates **2**. The allenic bipyridines form 1:1 complexes with Cu^+ and Ag^+ ions that were characterized by electrospray mass spectrometry and temperature-dependent NMR spectroscopy. In the case of the C_2-symmetrical allene **3b**, a crystalline silver complex was isolated that exists as a 2:2-(L_2M_2) complex in the solid state.

Introduction

Transition metal catalysis is of pivotal importance for synthetic chemistry. The fine-tuning of the catalytic activity of transition metal complexes relies strongly on the properties of the ligands; this is particularly evident in enantioselective catalysis since the chirality of the ligand controls the preferred formation of one enantiomeric product over the other.[1] Privileged ligands that afford high enantioselectivities in different transformations are often bidentate and C_2-symmetrical, e.g., chiral bisoxazolines,[2] salens,[3] TADDOLs,[4] bipyridines,[5] or binaphthyls.[6] In spite of recent progress in the field, it is still necessary to develop novel ligand systems since many established catalysts have serious limitations in terms of substrate scope, catalyst loading, etc.

With regard to the chirality elements, ligands with stereogenic centers (diols, diamines) and axial chirality (BINOL, BINAP) are predominant. However, it seems that the prototype of an axially chiral molecule, an allene, has never been introduced into a ligand for stereoselective transition metal catalysis. This is all the more surprising in view of the multitude of (frequently stereoselective) methods for the synthesis of allenes which are known today.[7] Possible reasons for the absence of allenic structures in axially chiral ligands might be the high reactivity of the allenic π-system, as well as the tendency of allenes to racemize in the presence of transition metals.[8] Based on our experience with the synthesis and application of functionalized allenes,[7e,9] we now report on the preparation and the complexation properties of allenic bipyridines **A** (Figure 1). Depending on the presence or absence of bulky substituents and the coordination geometry of the metal, we expect the formation of 1:1- (**B**) or 2:1-chelate complexes (**C**), as well as 2:2

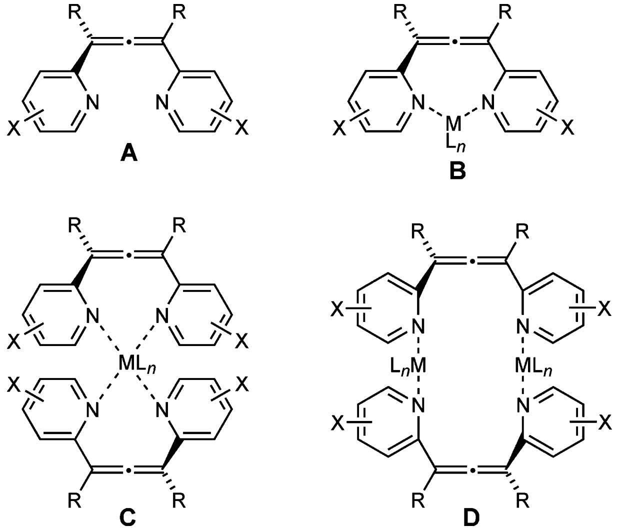

Figure 1. Structure of allenic bipyridines **A** and possible metal complexes.

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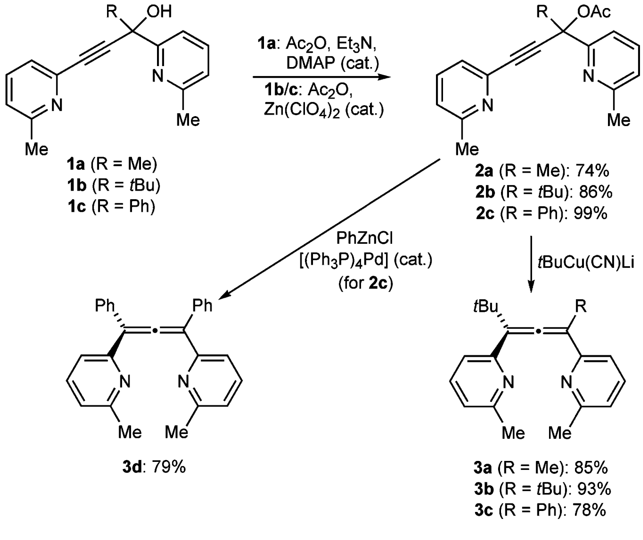
complexes **D** or larger aggregates of this type. Evidently, the complexation properties will strongly influence possible applications in transition metal catalysis.

Results and Discussion

The hitherto unknown allenic bipyridines were synthesized using the copper-mediated or palladium-catalyzed S_N2'-substitution of propargyl acetates (Scheme 1).[7] The propargyl alcohols **1**[10] (which are readily accessible by addition of lithium acetylides to the appropriate ketones) were converted in good yield into the corresponding tertiary acetates **2** by Steglich esterification[11] or (in case of the sterically hindered substrates **1b/c**) by treatment with acetic anhydride and catalytic amounts of zinc perchlorate.[12] In accordance with previous observations[13] the attempted introduction of a methyl group by reaction of propargyl acetates **2** with methylmagnesium cuprates was not successful; in contrast to this, the *tert*-butyl-substituted allenes **3a–c** were obtained in good yields using the highly reactive lower-order cyanocuprate *t*BuCu(CN)Li.[14] The doubly phenyl-substituted allene **3d**, on the other hand, was synthesized by palladium-catalyzed S_N2'-substitution of propargyl acetate **2c** with phenylzinc chloride. Allene **3a** was also synthesized in enantiomerically pure form by HPLC separation of the enantiomers of precursor **2a** (DIACEL Chiracel OD) and reaction of the enantiomerically pure propargyl acetates with *t*BuCu(CN)Li.[15] The allenes (+)-**3a** (99% *ee*) and (–)-**3a** (>99% *ee*) thus obtained have unstructured CD spectra with a single band at 310 nm (see Supporting Information);[16] the absolute configuration could not be determined so far.



Scheme 1. Synthesis of allenic bipyridines **3**.

The allenic bipyridines were characterized by the usual spectroscopic methods. In case of the racemic bis-*tert*-butyl-substituted allene **3b** the solid-state structure could also be determined (Figure 2).[17] The allene crystallizes in a triclinic unit cell which contains two molecules. Interestingly, the pyridine nitrogen atoms are facing away from each other.

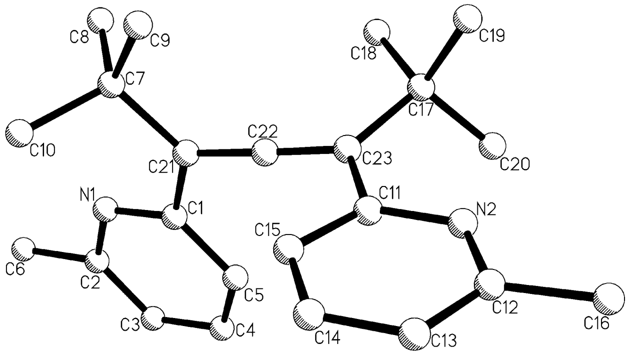


Figure 2. Solid state structure of allenic bipyridine **3b** (hydrogen atoms were omitted for clarity).[17]

The complexation properties of the allenic bipyridines **3** in the presence of Cu^+ or Ag^+ ions was examined by means of electrospray (ESI) mass spectrometry and temperature-dependent NMR spectroscopy. We treated a solution of the ligand in CD_2Cl_2 with 0.5 or 1.0 equiv. of a copper (CuI or $[Cu(MeCN)_4PF_6]$) or silver salt (AgOTf or $AgBF_4$). In all cases, the ESI spectra show the presence of the 1:1 complexes of type **B** (Table 1), regardless of the ratio of ligand to metal. The isotopic pattern of the molecular ions clearly excludes the presence of 2:2-(L_2M_2) complexes **D** (see Supporting Information) and 2:1-(L_2M) complexes **C** were not observed as well.

Table 1. Molecular ions detected by ESI mass spectrometry for complexes formed from allenic bipyridines **3** and copper or silver salts.[a]

Allene	Cation	*m*/*z* (exp.)[b]	*m*/*z* (1:1)[c]	*m*/*z* (2:1)[d]
3a	Cu^+	355.2	355.1	647.3
3a	Ag^+	399.1	399.2	691.3
3b	Cu^+	397.2	397.2	731.4
3b	Ag^+	441.2	441.2	775.4
3c	Cu^+	417.2	417.1	771.4
3c	Ag^+	461.2	461.1	815.3
3d	Cu^+	437.3	437.1	811.3
3d	Ag^+	481.3	481.1	855.3

[a] Solvent: CD_2Cl_2. [b] Determined experimentally for 1:1 and 2:1 mixtures of ligand and metal salt; see text. [c] Calculated for the 1:1 complex. [d] Calculated for the 2:1 complex.

Insight into the dynamics of complexation of the allenic ligands **3** by copper and silver ions was obtained by temperature-dependent NMR spectroscopy. In many cases, observation of the line broadening caused by slow ligand exchange during cooling was hampered by the limited symmetry of the ligand (**3a/c**) and/or insufficient solubility of the metal complex at low temperature. An exception is the complex formed from the C_2-symmetrical allene **3b** and $[Cu(MeCN)_4PF_6]$. In this case, addition of 1.0 equiv. of the copper salt to a solution of the ligand in CD_2Cl_2 caused a distinct shift of the resonances for the *tert*-butyl and methylpyridine protons from δ = 1.35/2.50 (free ligand) to δ =

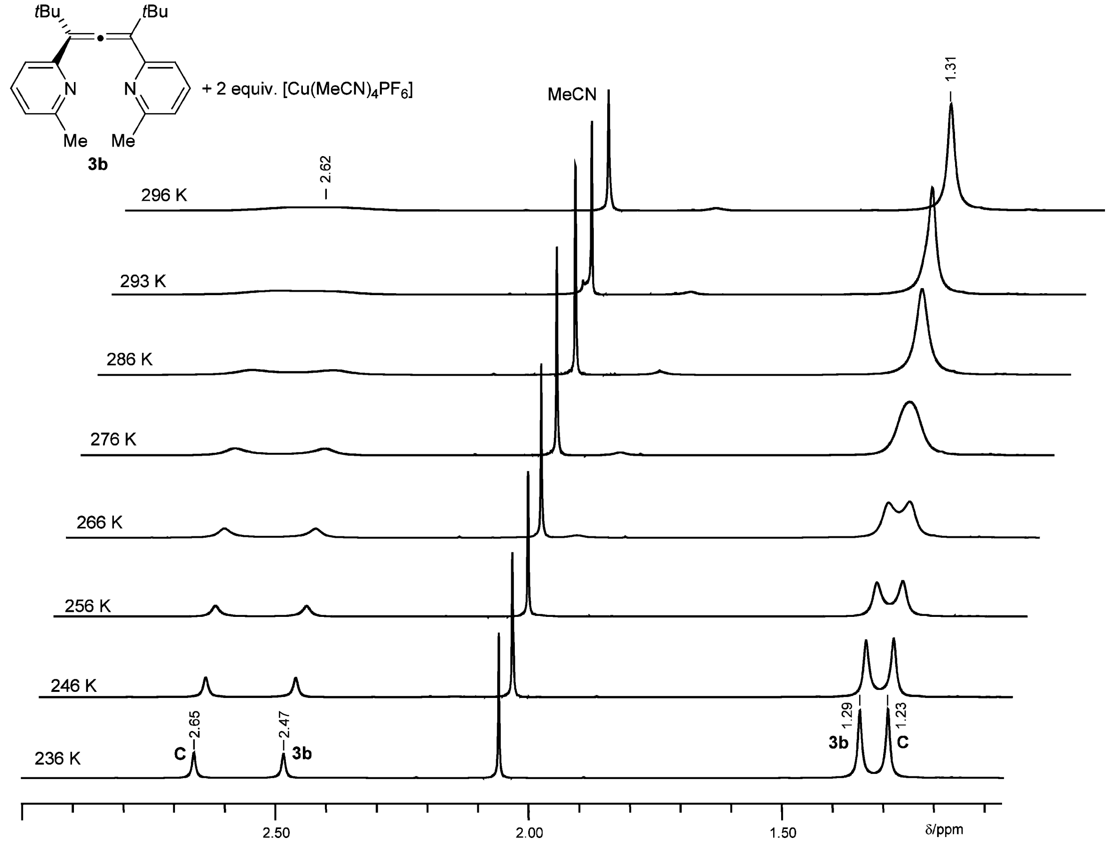


Figure 3. ^{1}H NMR spectra (400 MHz, CD_2Cl_2) of a 2:1 mixture of bipyridine **3b** and [Cu(MeCN)$_4$PF$_6$] at different temperatures between 236 and 296 K (**3b**: free ligand, C: 1:1 complex).

1.29/2.74 (296 K). At 236 K, the resonances were observed at δ = 1.29/2.47 (free ligand **3b**) and δ = 1.23/2.65 (1:1 complex; see Supporting Information). The observation of only one resonance for the *tert*-butyl and methylpyridine protons, respectively, proves the formation of a symmetric complex and excludes a monodentate complexation.

In contrast to this, a 2:1-mixture of **3b** and [Cu(MeCN)$_4$PF$_6$] in CD_2Cl_2 at 296 K shows a broadened *tert*-butyl resonance at δ = 1.31 and a very broad signal for the pyridine methyl protons at $\delta \approx 2.62$ (Figure 3). By variation of temperature, it was shown that this is not a 2:1 complex but rather a slowly exchanging mixture of a complex with 1:1-stoichiometry and the free ligand. Hence, cooling induces a splitting of the signals (Figure 3), and the resonances observed at 236 K correspond to the 1:1 complex (δ = 1.23/2.65) and the free ligand **3b** (δ = 1.29/2.47). Using the coalescence temperature and the chemical shift difference between the resonances of the *tert*-butyl and pyridine methyl protons at slow exchange, the free activation enthalpy of the ligand exchange was estimated to be $\Delta G^{\neq}$ = 55–57 kJ/mol (see Supporting Information).[18]

Since the NMR experiments were carried out under similar conditions (solvent, concentration) as the measurement of the ESI mass spectra, we assume that the observed complex with 1:1 stoichiometry is actually a 1:1-(LM) chelate complex of type **C** rather than a 2:2-(L_2M_2) complex **D** or

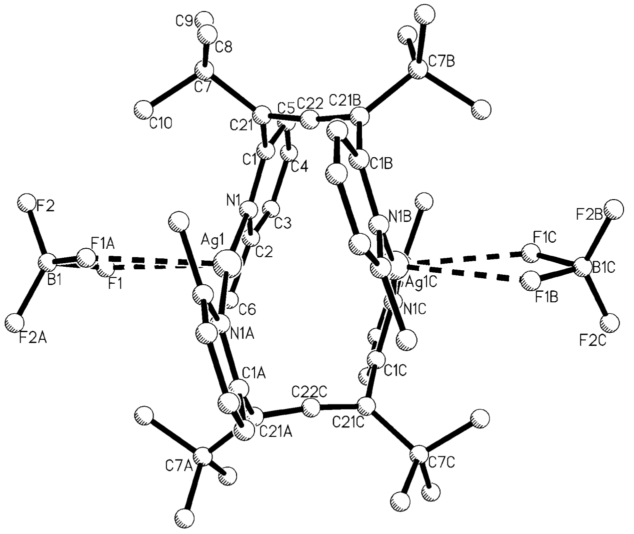


Figure 4. Solid state structure of the complex [**3b**·$AgBF_4$]$_2$ (symmetry transformations used to generate equivalent atoms: a = 0.25 – x, y, 0.25 – z; b = x, 0.25 – y, 0.25 – z; c = 0.25 – x, 0.25 – y, z; d = 0.75 – y, 0.25 – y, z; hydrogen atoms and 2 CH_2Cl_2 molcules were omitted).[19] Selected bond lengths [Å] and bond angles [°]: Ag1–N1 2.150(2), Ag1–N1A 2.150(2), Ag1–F1 2.942(4), Ag1–F1A 2.942(4), Ag1–Ag1C 3.5098(5), N1–N1B 4.953(3), N1–N1C 3.753(3), C22–C21b 1.314(2), C21–C22–C21B 173.3(3), C1–C21–C7 118.7(2), C7–C21–C21B–C7B 89.9.

a larger aggregate. Interestingly, we were able to obtain the X-ray structure of a complex formed from ligand **3b** and silver tetrafluoroborate; this crystallizes in an orthorhombic unit cell that contains eight molecules of a 2:2 complex of the type **D** (Figure 4; see Supporting Information).[19] The silver ions are coordinated by pyridine nitrogen atoms of two ligand molecules in a linear fashion. Each pyridine ring of one ligand is parallel to the distal pyridine ring of the other ligand. The dihedral angle at the allenic bridges is 89.9°, the length of the allene double bonds is 1.314 Å. The allene moieties of the two ligand molecules are in parallel planes that are twisted to each other by 65.7°. The discrepancy between this solid-state structure and the results obtained in solution may be due to a preferential crystallization of the 2:2 complex.

Conclusions

In this paper, we report on the first synthesis of the allenic bipyridines **3** and their complexation properties. The axially chiral allenes were efficiently obtained by copper-mediated or palladium-catalyzed S_N2'-substitution of the tertiary propargyl acetates **2**. The allenic bipyridines form 1:1 complexes with Cu^+ and Ag^+ ions that were characterized by electrospray mass spectrometry and temperature-dependent NMR spectroscopy. In the case of the C_2-symmetrical allene **3b**, a crystalline silver complex was isolated that exists as a 2:2-(L_2M_2) complex in the solid state. We are now engaged in the development of efficient procedures for the synthesis of enantiomerically pure allenic bipyridines, as well as in their application in transition metal catalysis.[20]

Experimental Section

General Information: All reactions were performed in oven-dried glassware under argon. Diethyl ether and THF were distilled from sodium/benzophenone. *t*BuLi was titrated according to the procedure of Kofron and Baclawski.[21] Column chromatography was carried out with Merck silica gel F_{60} (70–230 mesh). ^{1}H and ^{13}C NMR spectra were recorded with Bruker DRX 400 and DRX 500 spectrometers at room temperature in $CDCl_3$ as solvent and internal standard (^{1}H NMR: δ = 7.27 ppm. ^{13}C NMR: δ = 77.0 ppm). Signals of carbon atoms were assigned with APT experiments; abbreviations: (+) for CH_3, CH; (–) for CH_2; (×) for $C_{quat.}$ IR spectra were measured with a Nicolet Avatar 320 FT-IR as a liquid film between NaCl plates or in the case of solids as KBr pellet. FAB mass spectra (HRMS) were measured with a Jeol SX102A spectrometer, ESI spectra with a LTQ ORBITRAP spectrometer.

2-Methyl-6-[2,2-dimethyl-5-(6-methylpyridin-2-yl)hexa-3,4-dien-3-yl]pyridine (3a): To a suspension of CuCN (40 mg, 0.45 mmol) in THF (2 mL) was added dropwise at –40 °C *t*BuLi (0.3 mL, 0.44 mmol, 1.5 M solution in pentane). The mixture was cooled to –80 °C and a solution of propargyl acetate **2a** (26 mg, 0.088 mmol) in THF (1 mL) was added. The mixture was stirred at –80 °C for 2 h, treated with satd. aq. NH_4Cl (5 mL) and washed with diethyl ether. The combined organic layers were washed with aq. NH_3/NH_4Cl and dried with Na_2SO_4. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography (SiO_2, cyclohexane/ethyl acetate/triethylamine 66:33:1). Yield 22 mg (85%) of **3a** as a colorless solid, m.p. 39 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.45 (t, J = 7.6 Hz, 1 H), 7.40 (t, J = 7.6 Hz, 2 H), 7.12 (d, J = 7.6 Hz, 1 H), 6.92 (dd, J = 2.1/7.6 Hz, 2 H), 2.55 (s, 6 H), 2.25 (s, 3 H), 1.37 (s, 9 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 207.7 (×), 157.6 (×), 156.9 (×), 156.2 (×), 155.6 (×), 135.9 (+), 135.9 (+), 121.1 (+), 120.3 (+), 120.2 (+), 118.3 (+), 35.7 (×) 30.1 (+), 24.6 (+), 15.8 (+) ppm. IR: $\tilde{\nu}$ = 3045 (m), 1930 (w), 1570 (s), 1448 (s) cm^{-1}. MS (FAB): m/z (%) = 293 (100) [M + H]$^+$, 237 (30). HRMS (FAB): $C_{20}H_{24}N_2$: calcd. 292.1939 (M$^+$), found 292.1916.

2-Methyl-6-[2,2,6,6-tetramethyl-5-(6-methylpyridin-2-yl)hepta-3,4-dien-3-yl]pyridine (3b): According to the synthesis of **3a**, reaction of CuCN (297 mg, 3.3 mmol) in THF (5 mL) with *t*BuLi (2.2 mL, 3.3 mmol, 1.5 M solution in pentane) and propargyl acetate **2b** (280 mg, 0.65 mmol) in THF (5 mL) afforded 202 mg (93%) of **3b** as a colorless solid, m.p. 59 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (t, J = 7.7 Hz, 2 H), 7.26 (d, J = 7.8 Hz, 2 H), 6.93 (d, J = 7.6 Hz, 2 H), 2.55 (s, 6 H), 1.38 (s, 18 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.1 (×), 156.8 (×), 156.2 (×), 135.9 (+), 120.4 (+), 120.1 (+), 118.4 (×), 35.2 (×), 30.1 (+), 24.6 (+) ppm. IR: $\tilde{\nu}$ = 3054 (m), 2961 (s), 1920 (w), 1571 (s) cm^{-1}. MS (FAB): m/z (%) = 335 (100) [M + H]$^+$, 223 (10). HRMS (FAB): $C_{23}H_{30}N_2$: calcd. 335.2482 ([M + H]$^+$), found 335.2482.

2-Methyl-6-[4,4-dimethyl-1-(6-methylpyridin-2-yl)-1-phenylpenta-1,2-dien-3-yl]pyridine (3c): According to the synthesis of **3a**, reaction of CuCN (376 mg, 4.2 mmol) in THF (10 mL) with *t*BuLi (2.7 mL, 4.1 mmol, 1.5 M solution in pentane) and propargyl acetate **2c** (250 mg, 0.70 mmol) in THF (5 mL) afforded 193 mg (78%) of **3c** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.56 (m, 3 H), 7.43 (t, J = 7.7 Hz, 1 H), 7.35 (m, 4 H), 7.28 (m, 1 H), 7.05 (d, J = 7.6 Hz, 1 H), 6.96 (d, J = 7.5 Hz, 1 H), 2.59 (s, 3 H), 2.58 (s, 3 H), 1.48 (s, 9 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 208.9 (×), 157.9 (×), 157.0 (×), 155.5 (×), 155.4 (×), 136.5 (+), 136.0 (+), 135.6 (×), 128.1 (+), 128.0 (+), 126.8 (+), 121.2 (+), 121.1 (+), 120.6 (+), 120.5 (+), 120.0 (×), 111.9 (×), 36.0 (×), 30.1 (+), 24.6 (+), 24.5 (+) ppm. IR: $\tilde{\nu}$ = 3057 (s), 2959 (s), 1920 (m), 1584 (s) cm^{-1}. MS (FAB): m/z (%) = 355 (100) [M + H]$^+$, 299 (30). HRMS (FAB): $C_{25}H_{26}N_2$: calcd. 354.2096 (M$^+$), found 354.2098.

2-Methyl-6-[3-(6-methylpyridin-2-yl)-1,3-diphenylpropa-1,2-dienyl]pyridine (3d): A mixture of PhMgCl (5.9 mL, 8.8 mmol, 1.5 M solution in THF) and $ZnCl_2$ (8.8 mL, 8.8 mmol, 1.0 M solution in Et_2O) in THF (5 mL) was stirred for 40 min at room temperature and then cooled to –40 °C. After addition of [$Pd(PPh_3)_4$] (104 mg, 0.09 mmol) and propargyl acetate **2c** (628 mg, 1.76 mmol) in THF (5 mL), the mixture was warmed up to –10 °C within 16 h. Satd. aq. NH_4Cl (50 mL) was added, the mixture was washed with diethyl ether, and the combined organic layers were dried with Na_2SO_4. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography (SiO_2, cyclohexane/ethyl acetate/triethylamine 79:20:1). Yield 519 mg (79%) of **3d** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.65 (d, J = 7.4 Hz, 4 H), 7.57 (*t*, J = 7.7 Hz, 2 H), 7.48 (d, J = 7.7 Hz, 2 H), 7.39 (t, J = 7.4 Hz, 4 H), 7.32 (t, J = 7.7 Hz, 2 H), 7.09 (d, J = 7.7 Hz, 2 H), 2.62 (s, 6 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 212.4 (×), 158.0 (×), 154.5 (×), 136.6 (+), 134.8 (×), 128.3 (+), 128.1 (+), 127.4 (+), 121.6 (+), 121.1 (+), 113.7 (×), 24.5 (+) ppm. IR: $\tilde{\nu}$ = 3057 (s), 2850 (s), 1921 (m), 1570 (s) cm^{-1}. MS (FAB): m/z (%) = 375 (100) [M + H]$^+$, 374 (40) [M$^+$]. HRMS (FAB): = $C_{27}H_{22}N_2$: calcd. 375.1856 ([M + H]$^+$), found 375.1852.

Supporting Information (see also the footnote on the first page of this article): Copies of CD, mass, and NMR spectra of representative compounds; estimation of free activation enthalpy for the ligand exchange in the 1:1 complex prepared from **3b** and [Cu(MeCN)$_4$PF$_6$]; color figure of the X-ray structure of complex [**3b**·AgBF$_4$·CH$_2$Cl$_2$]$_2$.

Acknowledgments

We thank the Deutsche Forschungsgemeinschaft (DFG) and the Fonds der Chemischen Industrie for financial support.

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[19] Crystal structure analysis of a colorless crystal of [**3b**·AgBF$_4$·CH$_2$Cl$_2$]$_2$ ($0.30\times0.15\times0.13$ mm^3) was performed on a Nonius-KappaCCD-Diffractometer at173(1) K. Crystal data for [**3b**·AgBF$_4$·CH$_2$Cl$_2$]$_2$: C$_{48}$H$_{64}$Ag$_2$B$_2$Cl$_4$F$_8$N$_4$, M = 1228.19 g mol^{-1}, orthorhombic, space group *Fddd*, a = 13.5824(8), b = 24.3346(8), c = 32.7072(16) Å, V = 10810.5(9) Å^3, Z = 8, μ(Mo-K_α) = 0.986 mm^{-1}, 23363 independent reflections ($\theta_{\min}$ = 2.99, $\theta_{\max}$ = 27.48), 1961 with $I \geq 2\sigma(I)$, R_1 = 0.0283, $wR2$ (all data) = 0.0574; residual electron density (max./min.): 0.497/–0.274 e Å^3. After merging symmetry-equivalent reflections and absorption correction with the program SCALEPACK ($T_{\min}$ = 0.751, $T_{\max}$ = 0.883) an internal R value of 0.044 was obtained. F (AgBF$_4$) and Cl atoms (CH$_2$Cl$_2$) are disordered over two positions with occupancies of 0.4 [F(1′), F(2′)], 0.5 [Cl(1), Cl(1′)] and 0.6 [F(1), F(2)]. CCDC-644737 (for **3b**·AgBF$_4$) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[20] Initial experiments on the aziridination of styrene with [*N*-(*p*-toluolsulfonyl)imino]phenyliodinane show the high catalytic activity of a copper complex formed from allenic bipyridine **3b**.

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Received: September 27, 2007