Ruthenium Trispyrazolylborate Complexes. 18.[1] Aminocarbene Ruthenium Complexes Derived from Terminal Alkynes and 2-Aminopyridines

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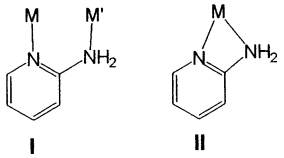
Received June 3, 2002

The reactions of RuTp(COD)Cl with the bidentate ligands 2-aminopyridine (apy), 2-amino-4-picoline (apic), and 2-(methylamino)pyridine (mapy) in the presence of terminal alkynes HC≡CR (R = Ph, *n*-Bu, C_6H_9) afford the cyclic aminocarbene complexes RuTp(=CCH_2R-apy)Cl, RuTp(=CCH_2R-apic)Cl, and RuTp(=CCH_2R-mapy)Cl. This reaction proceeds most likely via the intermediacy of both a reactive RuTp complex containing a strained, and thus labile, κ^2-N,N-coordinated aminopyridine ligand and a vinylidene intermediate. As side products, except for mapy, the dimeric complexes [RuTp(μ-apy)Cl]$_2$ and [RuTp(μ-apic)Cl]$_2$, featuring bridging aminopyridine ligands, were isolated. Representative complexes were characterized by X-ray crystallography.

Introduction

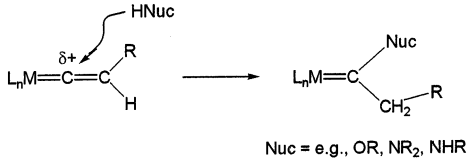
Transition metal vinylidene complexes are known to be capable of adding nucleophiles such as amines or alcohols at the electrophilic α-carbon atom of the vinylidene moiety. In this way, according to Scheme 1, heteroatom-stabilized carbene complexes become available.[2] Such reactions have been shown to be particularly facile in the intramolecular mode through utilizing hemilabile and/or bifunctional ligands, for instance 2-acetamido pyridines.[3] In this context, also 2-aminopyridines may prove to be interesting ligand systems. Bifunctional ligands can act as effective bridging ligands (**I**)[4] and, less common, also as bidendate ligands affording strained four-membered chelate complexes (**II**).[5] In



I II

the latter case, subsequent ring opening may provide a vacant coordination site to bind substrates such as alkynes, ultimately yielding vinylidenes and cyclic aminocarbenes.

Scheme 1



In the present work we extend the scope by reacting RuTp(COD)Cl with the bifunctional ligands 2-aminopyridine (apy), 2-(methylamino)pyridine (mapy), and 2-amino-4-picoline (apic), both in the presence and in the absence of terminal alkynes.

Experimental Section

General Information. Manipulations were performed under an inert atmosphere of purified argon by using Schlenk techniques and/or a glovebox. All chemicals were standard reagent grade and used without further purification. The solvents were purified according to standard procedures.[6] The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. RuTp(COD)Cl (**1**) was prepared according to the literature.[7] ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AVANCE−250 spectrometer operating at 250.13 and 62.86 MHz, respectively, and were referenced to $SiMe_4$.

Synthesis. RuTp(=CCH_2Ph-apy)Cl (2). A suspension of **1** (100 mg, 0.218 mmol) and 2-aminopyridine (41 mg, 0.436 mmol) was stirred in dmf (3 mL) at 150 °C for 2 h. After the solution was cooled to about 100 °C HC≡CPh (44.5 mg, 0.436 mmol) was added, and the mixture was stirred for an additional 3 h at 80 °C. The solvent was then removed under vacuum, and the crude product was dissolved in CH_2Cl_2. Solid materials were removed by filtration. Upon addition of Et_2O,

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(1) Part 17: Kremel, S.; Mereiter, K.; Slugovc, C.; Gemel, C.; Pfeiffer, J.; Schmid, R.; Kirchner, K. *Monatsh. Chem.* **2001**, *132*, 551.

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10.1021/om020441m CCC: $22.00
Publication on Web 10/11/2002

a precipitate was formed, which was collected on a glass frit, washed with Et_2O (5 × 2 mL), and dried under vacuum. Yield: 73.2 mg (62%). Anal. Calcd for $C_{22}H_{22}BClN_8Ru$: C, 48.41; H, 4.06; N, 20.53. Found: C 48.44; H, 4.09; N, 20.76. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 12.34 (s, N*H*), 8.47 (d, J_{HH} = 5.7 Hz, 1H, apy^6), 8.40 (bs, 1H, Tp), 8.16 (bs, 1H, Tp), 7.86 (bs, 2H, Tp), 7.46 (bs, 1H, Tp), 7.26 (bs, 1H, Tp), 7.10 (d, J_{HH} = 8.1 Hz, 1H, apy^3), 6.99−6.75 (m, 5H, Ph), 6.56 (m, 2H, apy^{4,5}), 6.47 (bs, 1H, Tp), 6.37 (bs, 1H, Tp), 5.50−5.32 (m, 2H, CH_2, Tp), 4.94 (bs, 1H, Tp), 4.54 (d, J_{HH} = 12.3 Hz, 1H, CH_2).

RuTp(=CCH$_2$Ph-apic)Cl (3a). This compound was prepared analogously to **2** using **1** (100 mg, 0.218 mmol), 2-amino-4-picoline (25.9 mg, 0.240 mmol), and HC≡CPh (44.53 mg, 0.436 mmol) as starting materials. Yield: 78.1 mg (64%). Anal. Calcd for $C_{23}H_{24}BClN_8Ru$: C, 49.35; H, 4.32; N, 20.02. Found: C 49.31; H, 4.39; N, 19.97. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 12.51 (s, 1H, N*H*), 8.44 (d, J_{HH} = 1.6 Hz, 1H, Tp), 8.30 (d, J_{HH} = 5.8 Hz, 1H, py^6), 8.17 (d, J_{HH} = 1.6 Hz, 1H, Tp), 7.87 (d, J_{HH} = 2.3 Hz, 2H, Tp), 7.44 (d, J_{HH} = 2.3 Hz, 1H, Tp), 6.94 (s, 1H, py^3), 6.89−6.44 (m, 7H, py,^{5} Ph, Tp), 6.38 (vt, J_{HH} = 2.3 Hz, 1H, Tp), 5.50 (d, $^2J_{HH}$ = 11.4 Hz, 1H, CH_2), 5.33 (vt, J_{HH} = 2.3 Hz, 1H, Tp), 4.85 (d, J_{HH} = 1.6 Hz, 1H, Tp), 4.53 (d, $^2J_{HH}$ = 11.4 Hz, 1H, CH_2), 2.32 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 283.7 (1C, Ru=C), 159.7 (1C, py^2), 150.6 (1C, py^6), 147.7 (1C, py^4), 145.2 (1C, Tp), 142.4 (1C, Tp), 140.8 (1C, Tp), 135.6 (1C, Tp), 135.2 (1C, Tp), 135.0 (1C, Tp), 134.3 (1C, Ph^1), 129.5 (2C, Ph^{3,5}), 128.5 (2C, Ph^{2,6}), 126.0 (1C, Ph^4), 119.9 (1C, py^5), 112.2 (1C, py^3), 106.7 (1C, Tp), 106.2 (1C, Tp), 105.5 (1C, Tp), 52.9 (1C, CH_2), 21.3 (1C, CH_3).

RuTp(=CCH$_2$-*n*-Bu-apic)Cl (3b). This compound was prepared analogously to **2** using **1** (100 mg, 0.218 mmol), 2-amino-4-picoline (25.9 mg, 0.240 mmol), and HC≡CBu^n (35.8 mg, 0.436 mmol) as starting materials. Yield: 78.8 mg (67%). Anal. Calcd for $C_{21}H_{28}BN_8RuCl$: C 46.72; H, 5.23; N, 20.76. Found: C 46.60; H, 5.19; N, 20.67. ^{1}H NMR (δ, DMSO-d_6, 20 °C): 13.07 (s, 1H, N*H*), 8.15 (d, J_{HH} = 5.8 Hz, 1H, apic^6), 8.05 (d, J_{HH} = 1.7 Hz, 1H, Tp), 7.97 (d, J_{HH} = 1.7 Hz, 1H, Tp), 7.87 (d, J_{HH} = 2.4 Hz, 1H, Tp), 7.75 (dd, J_1 = 2.4 Hz, J_2= 0.6 Hz, 1H, Tp), 7.73 (d, J_{HH}= 1.3 Hz, 1H, Tp), 7.43 (s, 1H, apic^3), 6.98 (d, J_{HH} = 5.8 Hz, 1H, apic^5), 6.44 (vt, J_{HH} = 2.1 Hz, 1H, Tp), 6.28 (vt, J_{HH} = 2.1 Hz, 1H, Tp), 5.88 (d, J_{HH} = 2.2 Hz, 1H, Tp), 5.76 (d, J_{HH} = 1.3 Hz, Tp), 3.49−3.28 (m, 2H, CH_2), 3.25−3.07 (m, 2H, CH_2), 2.51 (s, 3H, CH_3^{apic}), 1.12−0.89 (m, 2H, CH_2), 0.63 (t, J_{HH} = 7.0 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (δ, DMSO-d_6, 20 °C): 289.7 (1C, Ru=C), 160.0 (1C, apic^2), 150.7 (1C, apic^6), 148.5 (1C, apic^4), 145.0 (1C, Tp), 142.6 (1C, Tp), 141.5 (1C, Tp), 136.5 (1C, Tp), 135.7 (1C, Tp), 135.6 (1C, Tp), 120.7 (1C, apic^5), 111.9 (1C, apic^3), 106.5 (1C, Tp), 106.4 (1C, Tp), 106.3 (1C, Tp), 47.0 (1C, CH_2), 32.2 (1C, CH_2), 25.7 (1C, CH_2), 22.5 (1C, CH_2), 21.5 (1C, CH_3^{apic}), 16.0 (1C, CH_3).

RuTp(=CCH$_2$C$_6$H$_9$-apic)Cl (3c). This compound was prepared analogously to **2** using **1** (100 mg, 0.218 mmol), 2-amino-4-picoline (25.9 mg, 0.240 mmol), and 1-ethynylcyclohexene (46.3 mg, 0.436 mmol) as starting materials. Yield: 88.5 mg (72%). Anal. Calcd for $C_{23}H_{28}BClN_8Ru$: C, 48.99; H, 5.01; N, 19.87. Found: C 48.94; H, 5.10; N, 19.74. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 12.05 (s, 1H, N*H*), 8.36 (d, J_{HH} = 1.6 Hz, 1H, Tp), 8.30 (d, J_{HH} = 5.8 Hz, 1H, apic^6), 7.99 (d, J_{HH} = 1.6 Hz, 1H, Tp), 7.84 (d, J_{HH} = 2.2 Hz, 1H, Tp), 7.75 (d, J_{HH} = 2.2 Hz, 1H, Tp), 7.55 (d, J_{HH} = 2.2 Hz, 1H, Tp), 7.10 (s, 1H, apic^3), 6.79 (d, J_{HH} = 6.3 Hz, 1H, apic^5), 6.44 (vt, J_{HH} = 2.1 Hz, 1H, Tp), 6.30 (vt, J_{HH} = 2.1 Hz, 1H, Tp), 5.76 (vt, J_{HH} = 2.1 Hz, 1H, Tp), 5.59 (d, J_{HH} = 1.6 Hz, 1H, Tp), 5.07 (bs, 1H, Cy^2), 4.57 (d, J_{HH} = 12.5 Hz, 1H, CH_2), 3.74 (d, J_{HH} = 12.5 Hz, 1H, CH_2), 2.37 (s, 3H, CH_3), 1.88−1.10 (m, 8H, CH_2^{Cy}). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 285.4 (1C, Ru=*C*), 159.5 (1C, apic^2), 150.7 (1C, apic^6), 147.6 (1C, apic^4), 145.2 (1C, Tp), 142.4 (1C, Tp), 141.2 (1C, Tp), 135.5 (1C, Tp), 135.2 (1C, Tp), 135.1 (1C, Tp), 131.8 (1C, Cy^1), 126.6 (1C, apic^3), 120.0 (1C, apic^5), 112.1 (1C, Cy^2), 106.2 (1C, Tp), 106.1 (1C, Tp), 105.4 (1C, Tp), 55.5 (1C, CH_2), 29.1 (1C, CH_2^{Cy}), 25.8 (1C, CH_2^{Cy}), 23.1 (1C, CH_2^{Cy}), 22.1 (1C, CH_2^{Cy}), 21.4 (1C, CH_3).

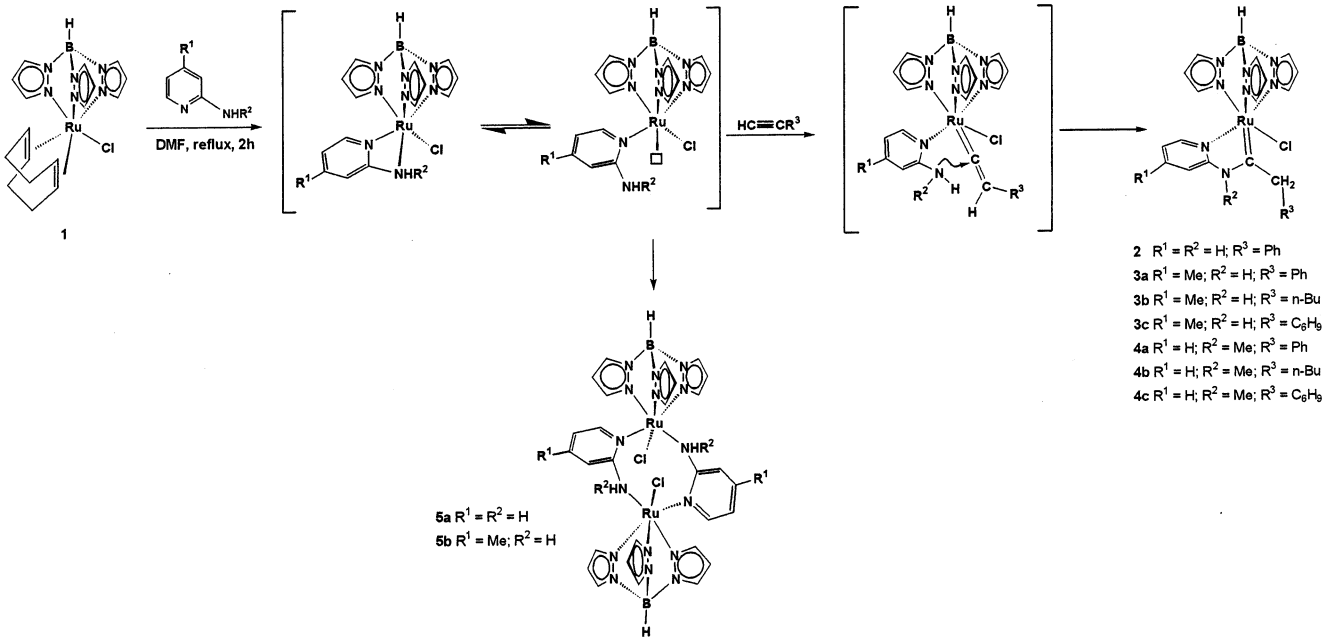
RuTp(=CCH$_2$Ph-mapy)(Cl) (4a). This compound was prepared analogously to **2** using **1** (100 mg, 0.218 mmol), 2-(methylamino)pyridine (25.9 mg, 0.240 mmol), and HC≡CPh (44.5 mg, 0.436 mmol) as starting materials. Yield: 85.4 mg (70%). Anal. Calcd for $C_{23}H_{24}BClN_8Ru$: C, 49.35; H, 4.32; N, 20.02. Found: C 49.34; H, 4.35; N, 19.96. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 8.58 (d, J_{HH} = 5.8 Hz, 1H, mapy^6), 8.33 (bs, 1H, Tp), 7.82 (d, J_{HH} = 2.0 Hz, 1H, Tp), 7.77 (bs, 1H, Tp), 7.72 (d, J_{HH} = 2.4 Hz, 1H, Tp), 7.69 (dd, J_{HH} = 7.0 Hz, J_{HH} = 8.5 Hz, 1H, mapy), 7.60 (d, J_{HH} = 2.4 Hz, 1H, Tp), 7.40 (d, J_{HH} = 8.5 Hz, 1H, mapy), 7.29−7.11 (m, 5H, Ph), 7.08 (dd, J_{HH} = 7.0.4 Hz, J_{HH} = 5.8 Hz, 1H, mapy), 6.41 (vt, J_{HH} = 2.0 Hz, 1H, Tp), 6.13 (vt, J_{HH} = 2.0 Hz, 1H, Tp), 5.78 (vt, J_{HH} = 2.0 Hz, 1H, Tp), 5.62 (d, J_{HH} = 1.6 Hz, 1H, Tp), 5.32 (d, $^2J_{HH}$ = 16.0 Hz, 1H, CH_2), 4.74 (d, $^2J_{HH}$ = 16.0 Hz, 1H, CH_2), 3.81 (s, 3H, N−CH_3). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 289.6 (1C, Ru=C), 161.2 (1C, mapy^2), 152.3 (1C, mapy^6), 144.9 (1C, Tp), 142.6 (1C, Tp), 141.0 (1C, Tp), 137.7 (1C, mapy^4), 136.6 (1C, Tp), 135.9 (1C, Tp), 135.3 (1C, Tp), 135.1 (1C, Ph^1), 129.3 (2C, Ph^{3,5}), 129.2 (2C, Ph^{2,6}), 126.5 (1C, Ph^4), 119.5 (1C, mapy^5), 110.1 (1C, mapy^3), 106.4 (1C, Tp), 106.2 (1C, Tp), 105.7 (1C, Tp), 49.7 (1C, CH_2), 36.9 (1C, NCH_3).

TpRu(=CCH$_2$-*n*-Bu-mapy)Cl (4b). This compound was prepared analogously to **2** using **1** (100 mg, 0.218 mmol), 2-(methylamino)pyridine (25.9 mg, 0.240 mmol), and HC≡CBu^n (35.8 mg, 0.436 mmol) as starting materials. Yield: 85.9 mg (73%). Anal. Calcd for $C_{21}H_{28}BClN_8Ru$: C, 46.72; H, 5.23, N; 20.76. Found: C 46.74; H, 5.24; N, 20.67. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 8.53 (d, 1H, J_{HH} = 5.5 Hz, mapy^6), 8.24 (bs, 1H, Tp), 7.94 (bs, 1H, Tp), 7.80 (d, 1H, J_{HH} = 1.3 Hz, Tp), 7.73 (d, 1H, J_{HH} = 1.7 Hz, Tp), 7.68−7.52, (m, 2H, Tp, mapy), 7.42 (bs, 1H, mapy^3), 7.00 (t, 1H, J_{HH} = 6.2 Hz, mapy^5), 6.35 (t, 1H, J_{HH} = 2.1 Hz, Tp), 6.22 (t, 1H, J_{HH} = 2.2 Hz, Tp), 5.80 (t, 1H, J_{HH} = 2.2 Hz, Tp), 5.65 (d, 1H, J_{HH} = 1.3 Hz, Tp), 3.95−3.71 (m, 2H, N−CH_3, CH_2), 3.60−3.40 (m, 1H, CH_2), 1.31−0.96 (m, 4H, CH_2), 0.71 (t, 3H, J_{HH} = 6.7 Hz, CH_3). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 292.6 (1C, Ru=*C*), 163.0 (1C, mapy^2), 152.3 (1C, mapy^6), 144.8 (1C, Tp), 142.3 (1C, Tp), 141.2 (1C, Tp), 136.5, 136.0, 135.3, 135.1 (4C, Tp, mapy^4), 119.6 (1C, mapy^5), 110.5 (1C, mapy^3), 106.2 (2C, Tp), 105.6 (1C, Tp), 44.2 (1C, CH_2), 35.5 (1C, *N*−CH_3), 32.2 (1C, CH_2^{Cy}), 24.0 (1C, CH_2^{Cy}), 22.4 (1C, CH_2^{Cy}), 14.2 (1C, CH_3).

RuTp(=CCH$_2$C$_6$H$_9$-mapy)Cl (4c). This compound was prepared analogously to **2** using **1** (100 mg, 0.218 mmol), 2-(methylamino)pyridine (25.9 mg, 0.240 mmol), and 1-ethynylcyclohexene (46.3 mg, 0.436 mmol) as starting materials. Yield: 94.6 mg (77%). Anal. Calcd for $C_{23}H_{28}BClN_8Ru$: C, 48.99; H, 5.01; N, 19.87. Found: C 49.04; H, 5.11; N, 19.94. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 8.49 (d, J_{HH} = 4.7 Hz, 1H, mapy^6), 8.24 (d, J_{HH} = 1.4 Hz, 1H, Tp), 7.90 (d, J_{HH} = 1.4 Hz, 1H, Tp), 7.75 (d, J_{HH} = 1.9 Hz, 1H, Tp), 7.72−7.63 (m, 2H, Tp, mapy), 7.53 (d, J_{HH} = 1.9 Hz, 1H, Tp), 7.39 (d, J_1 = 8.4 Hz, 1H, mapy^3), 7.01 (t, J_{HH} = 6.1 Hz, 1H, mapy^5), 6.33 (vt, J_{HH} = 2.1 Hz, 1H, Tp), 6.14 (vt, J_{HH} = 2.1 Hz, 1H, Tp), 5.75 (vt, J_{HH} = 2.1 Hz, 1H, Tp), 5.63 (d, J_{HH} = 1.4 Hz, 1H, Tp), 5.53 (bs, 1H, Cy), 4.28 (d, 1H, J_{HH} = 15.8 Hz, CH_2), 3.87 (s, 3H, N−CH_3) 3.51 (d, 1H, J_{HH} = 15.8 Hz, CH_2), 2.15−0.98 (m, 8H, CH_2^{Cy}). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 291.3 (1C, Ru=C), 161.1 (1C, mapy^2), 152.3 (1C, mapy^6), 144.8 (1C, Tp), 142.6 (1C, Tp), 141.0 (1C, Tp), 136.4 (1C, Tp), 135.8 (1C, Tp), 135.0 (1C, Tp), 132.6 (1C, Cy^1), 125.5 (1C, apy^4), 119.2 (1C, apy^5), 112.8 (1C, Cy^2), 109.9 (1C, apy^3), 106.1 (1C, Tp), 106.0 (1C, Tp), 105.5 (1C, Tp), 52.0 (1C, CH_2), 36.3 (1C, N-CH_3), 29.8 (1C, CH_2^{Cy}), 25.8 (1C, CH_2^{Cy}), 23.4 (1C, CH_2^{Cy}), 22.6 (1C, CH_2^{Cy}).

[RuTp(μ-apy)Cl]$_2$ (5a). A suspension of **1** (100 mg, 0.218 mmol) and 2-aminopyridine (41 mg, 0.436 mmol) was stirred in dmf (3 mL) at 150 °C for 2 h. After removal of the solvent under vacuum the crude product was redissolved in acetone and purified by column chromatography (acetone/neutral

Scheme 2



Al_2O_3). The first yellow band was collected, the solvent was evaporated, and the residue was dried under vacuum. Yield: 36.8 mg (38%). Anal. Calcd for $C_{28}H_{32}B_2Cl_2N_{16}Ru_2$: C, 37.90; H, 3.64; N, 25.26. Found: C 37.88; H, 3.69; N, 25.17. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 10.64 (d, J_{HH} = 9.9 Hz, 2H, NH_2), 8.00 (d, J_{HH} = 2.4 Hz, 2H, Tp), 7.89 (m, 4H, Tp), 7.82 (d, J_{HH} = 1.5 Hz, 2H, Tp), 7.73 (d, J_{HH} = 2.4 Hz, 2H, Tp), 7.52 (dd, J_{HH} = 8.0 Hz, J_{HH} = 6.9 Hz, 2H, apy), 7.01 (d, J_{HH} = 1.5 Hz, 2H, Tp), 6.82 (d, J_{HH} = 8.0 Hz, 2H, apy), 6.69 (d, J_{HH} = 6.0 Hz, 2H, apy), 6.61 (dd, J_{HH} = 6.9 Hz, J_{HH} = 6.0 Hz, 2H, apy), 6.41 (vt, J_{HH} = 2.2 Hz, 2H, Tp), 6.32 (vt, J_{HH} = 2.2 Hz, 2H, Tp), 6.08 (vt, J_{HH} = 2.2 Hz, 2H, Tp), 4.84 (d, J_{HH} = 9.9 Hz, 2H, NH_2).

[RuTp(μ-apic)Cl]$_2$ (5b). This compound was prepared analogously to **2** using **1** (100 mg, 0.218 mmol) and 2-amino-4-picoline (47.1 mg, 0.436 mmol) as starting materials. Yield: 33.9 mg (34%). Anal. Calcd for $C_{30}H_{36}B_2Cl_2N_{16}Ru_2$: C, 39.36; H, 3.96; N, 24.48. Found: C 39.29; H, 3.94; N, 24.45. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 10.49 (d, J_{HH} = 10.3 Hz, 2H, NH_2), 7.90 (d, J_{HH} = 6.8 Hz, 2H, apic), 7.90 (d, J_{HH} = 1.9 Hz, 2H, Tp), 7.78 (d, J_{HH} = 1.6 Hz, 2H, Tp), 7.70 (d, J_{HH} = 1.7 Hz, 2H, Tp), 7.62 (d, J_{HH} = 1.9 Hz, 2H, Tp), 7.42 (t, J_{HH} = 7.2 Hz, 2H, apic), 6.88 (d, J_{HH} = 1.4 Hz, 2H, Tp), 6.75 (d, J_{HH} = 8.4 Hz, 2H, apic), 6.55 (d, J_{HH} = 1.3 Hz, 2H, Tp), 6.29 (vt, J_{HH} = 2.2 Hz, 2H, Tp), 6.19 (vt, J_{HH} = 2.1 Hz, 2H, Tp), 5.95 (vt, J_{HH} = 2.1 Hz, 2H, Tp), 4.87 (d, J_{HH} = 10.1 Hz, 2H, NH_2), 2.47 (s, 6H, CH_3^{apic}).

X-ray Structure Determination for 3c·O(C_2H_5)$_2$ and 5b·2O(C_2H_5)$_2$. Well-crystallized solvates of **3c**·O(C_2H_5)$_2$ and **5b**·2O(C_2H_5)$_2$ were obtained by diffusion of diethyl ether into CH_2Cl_2 solutions. X-ray data were collected on a Bruker Smart CCD area detector diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.71073 Å, 0.3° ω-scan frames covering entire spheres of the reciprocal space) equipped with a Bruker Kryoflex cooling unit. Corrections for Lorentz and polarization effects, for crystal decay, and for absorption were applied. The structures of both complexes were solved with direct methods using the program SHELXS97.[8] Structure refinement on F^2 was carried out with the program SHELXL97.[9] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded.

3c·O(C_2H_5)$_2$: $C_{27}H_{38}BClN_8ORu$, M_r = 637.98, triclinic, space group $P\bar{1}$, T = 173(2) K, a = 11.183(1) Å, b = 11.248(1) Å, c = 13.081(1) Å, α = 112.45(2)°, β = 95.86(2)°, γ = 101.22(2)°, V = 1463(1) Å^3, Z = 2, μ = 0.633 mm^{-1}. Of 21 100 reflections collected, 8259 were independent; R_{int} = 0.027; final R values: R_1 = 0.029 (all data), wR_2 = 0.074 (all data).

5b·2O(C_2H_5)$_2$: $C_{38}H_{56}B_2Cl_2N_{16}O_2Ru_2$, M_r = 1063.64, orthorhombic, space group *Pbca*, T = 183(2) K, a = 15.674(4) Å, b = 16.711(4) Å, c = 17.955(4) Å, V = 4703(1) Å^3, Z = 4, μ = 0.808 mm^{-1}. Of 73 636 reflections collected, 6701 were independent; R_{int} = 0.073; final R values: R_1 = 0.070 (all data), wR_2 = 0.104 (all data).

Results and Discussion

Treatment of RuTp(COD)Cl (**1**) with 1 equiv of apy, mapy, or apic, in boiling dmf for 2 h, affords yellow air-sensitive solutions, which on addition of the terminal alkynes HC≡CR (R = Ph, *n*-Bu, C_6H_9) transform into the respective cyclic aminocarbene complexes RuTp(=CCH_2R-apy)Cl, RuTp(=CCH_2R-apic)Cl, and RuTp(=CCH_2R-mapy)Cl (**2**, **3a**−**c**, **4a**−**c**) in high isolated yields (Scheme 2). All these compounds are thermally robust and air-stable both in solution and in the solid state. Characterization was accomplished by elemental analysis, ^{1}H NMR, and, with the exception of **2** due to its poor solubility, also with ^{13}C{^{1}H} NMR spectroscopy. The ^{1}H NMR spectrum of **3a** displays an AX pattern for the CH_2R moiety showing two doublets centered at 5.50 and 4.53 ppm with a coupling constant of 11.4 Hz. The NH proton gives rise to a characteristic low-field-shifted signal at 12.51 ppm. The ^{1}H NMR spectra of **3** and **4** exhibit similar resonance patterns. Characteristic ^{13}C{^{1}H} NMR spectroscopic features of **3** and **4** comprise a marked low-field resonance in the range 283.7−292.6 ppm assignable to the carbene carbon atom of the (=CCH_2R-) moiety.

The solid state structure of **3c** (as the diethyl ether solvate **3c**·O(C_2H_5)$_2$) could be resolved by single-crystal X-ray diffraction (Figure 1). Selected bond distances and

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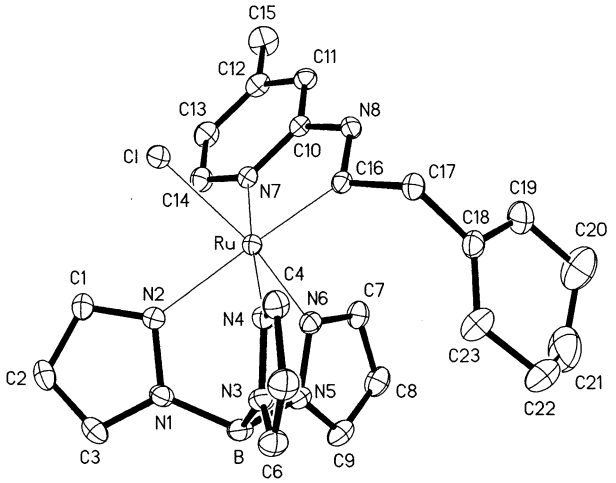

Figure 1. Structural view of RuTp(=$CCH_2C_6H_9$-apic)Cl·$O(C_2H_5)_2$ (**3c**·$O(C_2H_5)_2$); hydrogen atoms and solvent omitted for clarity, 50% ellipsoids). Selected bond lengths (Å) and angles (deg): Ru−C(16) 1.915(1), Ru−N(2) 2.198(1), Ru−N(4) 2.068(1), Ru−N(6) 2.046(1), Ru−N(7) 2.057(1), Ru−Cl 2.428(1), C(10)−N(8) 1.381(1), N(8)−C(16) 1.359(1), C(16)−C(17) 1.519(2), Ru−C(16)−N(8) 115.6(1), Ru−C(16)−C(17) 132.2(1), N(2)−Ru−N(4) 84.6(1), N(4)−Ru−N(6) 88.7(1), N(2)−Ru−N(6) 84.1(1), N(6)−Ru−Cl 171.2(1).

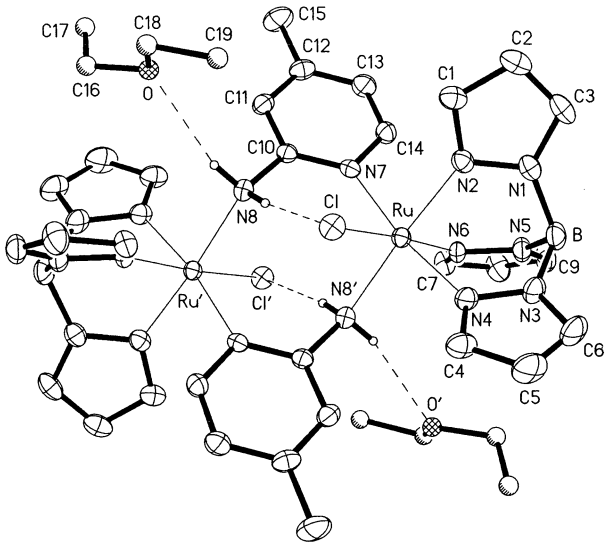

Figure 2. Structural view of [RuTp(μ-apic)Cl]$_2$·$2O(C_2H_5)_2$ (**5b**·$2O(C_2H_5)_2$); C- and B-bound H atoms omitted for clarity, 50% ellipsoids). Selected bond lengths (Å) and angles (deg): Ru−N(2) 2.043(3), Ru−N(4) 2.070(3), Ru−N(6) 2.054(3), Ru−N(7) 2.128(3), Ru−Cl 2.455(1), Ru−N(8)′ 2.192(3), N(2)−Ru−N(4) 84.8(1), N(2)−Ru−N(6) 89.7(1), N(4)−Ru−N(6) 88.4(1), N(6)−Ru−N(7) 88.3(1), N(6)−Ru−Cl 174.8(1).

angles are given in the caption. The coordination geometry around ruthenium is slightly distorted octahedral. Due to the strong *trans* influence of the carbene ligand, the Ru−N(Tp) bond distance (Ru−N(2) = 2.198(1) Å) *trans* to the carbene moiety is notably elongated compared to those in the *cis* position (Ru−N(4) = 2.068(1), Ru−N(6) = 2.046(1), Ru−N(7) = 2.057(1) Å). Further, the Ru−C(16) bond distance of 1.915(4) Å is typical of a ruthenium carbon double bond as found in other RuTp carbene complexes.[10] Noteworthily, the Ru complex of **3c**·$O(C_2H_5)_2$ is linked in the solid state with an inversion-related complex via a pair of clear-cut N−H- - -Cl hydrogen bonds, N- - -Cl = 3.163 Å.

In the case of apy and apic, as side products of the above reactions, the dimeric complexes [RuTp(μ-apy)Cl]$_2$ (**5a**) and [RuTp(μ-apic)Cl]$_2$ (**5b**) could be isolated albeit in low yields (Scheme 2). The same products could be obtained when apy and apic are reacted with **1** in the absence of alkynes. With mapy, on the other hand, obviously for steric reasons, no such complex could be detected. Complexes **5a** and **5b** are thermally robust and air-stable yellow solids and were characterized by elemental analysis and ^{1}H NMR spectroscopy. The recording of $^{13}C\{^1H\}$ NMR spectra was precluded for solubility reasons. Characteristic solution ^{1}H NMR spectroscopic data for **5a** and **5b** include two doublets at 10.64 (J_{HH} = 9.9 Hz) and 10.49 ppm (J_{HH} = 10.3 Hz) and 4.84 (J_{HH} = 9.9 Hz) and 4.87 (J_{HH} = 10.3 Hz) ppm, respectively, which are assigned to the NH_2 protons of the amine moiety of the apy and apic ligands.

Despite the fact that neither monomeric RuTp(κ^2-*N*,*N*-2-aminopyridine)Cl species nor vinylidene intermediates could be observed, such species are most likely key intermediates on the way to aminocarbene complexes, as suggested in Scheme 2. Strained four-membered chelates are known to undergo facile ring-opening reactions, thereby providing vacant coordination sites,[11] which facilitates the formation of vinylidene complexes. The dimeric complexes **5**, on the other hand, are not intermediates but rather side-products, which at least under similar conditions did not convert to aminocarbene complexes.

In the case of **5b** suitable crystals could be grown from a CH_2Cl_2 solution layered with diethyl ether. The molecular structure in the form of the diethyl ether solvate **5b**·$2O(C_2H_5)_2$ is depicted in Figure 2, confirming that apic is acting as a bridging ligand. In the solid state the dimeric complex is centrosymmetric and reinforced by a pair of intramolecular N−H- - -Cl hydrogen bonds with N- - -Cl = 3.116 Å, whereas the second N-bound hydrogen atom is exo-oriented, helping to anchor the diethyl ether solvent molecule via a weak N−H- - -O bond of N- - -O = 3.193 Å. This situation pertains obviously also in $CDCl_3$ solutions and explains the remarkable difference in the chemical shifts of the NH_2 protons in the ^{1}H NMR spectrum.[12] The overall geometry of the RuTp(apic)Cl unit of **5b** is nearly octahedral, with all angles at ruthenium between 85° and 95° and 172° and 175°. The three Ru−N(Tp) bond lengths deviate only slightly from the average of 2.056(3) Å, which is within the range of other RuTp complexes.[13] The Ru−N(py) and Ru−Cl distances are 2.128(3) and 2.455(1) Å, respectively.

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(12) We found the same dimeric Ru complex as in **5b**·$2O(C_2H_5)_2$ also in another solvated structure, **5b**·∼$2CH_2Cl_2$·∼$0.6O(C_2H_5)_2$, of distinctly different crystallography but identical Ru coordination chemistry. This structure has been deposited under CCDC-186560.

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In summary, we have shown that cyclic aminocarbene complexes are readily available in a one-pot procedure from RuTp(COD)Cl, 2-aminopyridines, and terminal alkynes. As side products, dimeric [RuTp(μ-2-aminopyridines)Cl]$_2$ complexes are formed. A key intermediate appears to be a monomeric species containing a labile κ^2-NN-coordinated aminopyridine ligand which is capable of facile ring opening. The formulation of a vinylidene intermediate is consistent with the known propensity of vinylidene complexes for being attacked by nitrogen donors to give Fischer type carbene complexes. In fact such a process is especially facile if nucleophilic attack occurs in the intramolecular, chelate-assisted fashion. In this way steric limitations are circumvented.[3]

Acknowledgment. Financial support by the "Fonds zur Förderung der wissenschaftlichen Forschung" is gratefully acknowledged (Project No. 14681).

Supporting Information Available: Listings of crystal data, atomic coordinates, anisotropic temperature factors, and complete bond lengths and angles for complexes **3c**·O(C_2H_5)$_2$ and **5b**·2O(C_2H_5)$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020441M