Aminocarbene Complexes as Intermediates in the Ruthenium-Assisted Aminolysis of Phenylacetylene to Isonitriles and Toluene

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Various primary amines and NH_3 have been found to react in THF with the Ru(II) vinylidene complex *fac,cis*-[(PNP)$RuCl_2${C═C(H)Ph}], affording aminocarbene derivatives of the general formula *fac,cis*-[(PNP)$RuCl_2${C(NHR)(CH_2Ph)}] (PNP = $CH_3CH_2CH_2N(CH_2CH_2PPh_2)_2$; R = $CH_3CH_2CH_2$, Ph, cyclo-C_6H_{11}, (*R*)-(+)-CH(Me)(Ph), (*R*)-(−)-CH(Me)(Et), (*S*)-(−)-CH(Me)(1-naphthyl), H). With piperidine as the starting material, the tertiary aminocarbene *fac,cis*-[(PNP)$RuCl_2${C(NC_5H_{10})(CH_2Ph)}] has been obtained. The aminocarbene complexes are formed through an unforeseen mechanism in which 2 equiv of amine is involved: one serves to deprotonate the vinylidene C_β carbon atom, while the other coordinates the metal center and then brings about an intramolecular nucleophilic attack onto the C_α carbon atom of a σ-phenylethynyl ligand. The (phenylethynyl)amine intermediates have been isolated and characterized. The aminocarbene derivative *fac,cis*-[(PNP)$RuCl_2$-{C(NH(*S*)-(−)-CH(Me)(1-naphthyl))(CH_2Ph)}] has been authenticated by a single-crystal X-ray diffraction analysis. Upon thermolysis in wet solvents, generally THF, the secondary aminocarbene complexes generate toluene and transform quantitatively into the corresponding isonitrile derivatives *fac,cis*-[(PNP)$RuCl_2$(C≡NR)] (R = $CH_3CH_2CH_2$, Ph, cyclo-C_6H_{11}, (*R*)-(+)-CH(Me)Ph, (*R*)-(−)-CH(Me)Et). In contrast, the primary aminocarbene *fac,cis*-[(PNP)-$RuCl_2${C(NH_2)(CH_2Ph)}] and the tertiary aminocarbene [(PNP)$RuCl_2${C(NC_5H_{10})(CH_2Ph)}] are thermally stable up to 150 °C. The mechanism for the aminocarbene to isonitrile conversion has been found to involve the intermediacy of iminoacyl and (benzyl)isonitrile Ru(II) compounds, which have been intercepted and identified from independent reactions.

Introduction

The reactivity of the metal−vinylidene moiety is dominated by the electrophilicity of the α-carbon atom. Several examples of addition of nucleophiles, including water[1−4] alcohols,[1,3,5] thiols,[3,6] phosphines,[7] and fluoride[8] and cyanide ions[9] have been reported. Primary amines conform to this general protocol, as they have been found to attack the C_α carbon atom of disubstituted vinylidene ligands to give aminocarbene derivatives.[3,10] It is generally agreed that the formation of the aminocarbene group proceeds via an intermolecular-concerted process in which the primary amine adds across the highly polarized C−C double bond (Scheme 1).[3,10] In this concerted process, the metal center does not seem to play a direct role in assisting the hydroamination reaction of the C−C double bond, although the metal does control the electronic nature and consequently the reactivity of the vinylidene ligand.[11]

In this paper we describe the synthesis of a new family of ruthenium aminocarbene complexes and report experimental evidence of a different mechanism for the hydroamination reaction of the vinylidene functional group. In addition, we show that aminocarbene complexes are effective precursors, by simple thermolysis, to products containing isonitrile ligands with various organic substituents. Despite their environmentally

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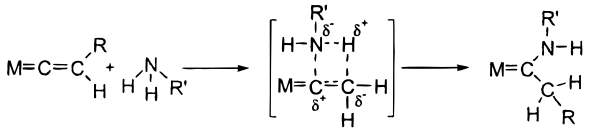
Scheme 1



intermolecular/concerted

hostile nature,[12] isonitriles are indeed useful ligands in coordination, organometallic chemistry, and catalysis.[13] Very few isonitriles, however, are commercially available due to their tendency for polymerization as well as the complicated synthetic procedures.[12] For this reason, several metal-mediated syntheses have been developed with the ultimate goal of assembling the isonitrile moiety from less toxic and readily available reagents. Common procedures involve (i) the attack of primary amines on dihalo-, thio-, and dithiocarbene complexes,[14,15] (ii) the oxidative addition of Cl_2CNPh to low-valent metal complexes,[16] and (iii) the alkylation of transition-metal cyanides.[17] An effective protocol for the synthesis of isonitriles would be the isomerization of nitriles which can catalytically be produced by Ru(II)-assisted dehydrogenation of amines.[18,19] Unfortunately, no example of nitrile to isonitrile isomerization via amine oxidation has been reported so far. Although restricted to a precise metal fragment, the novel synthetic procedure described in this work has the great advantages of being quite simple and selective and of providing access to a large variety of isonitrile ligands, including optically pure derivatives.

A preliminary communication of part of this work has already appeared.[20]

Experimental Section

General Procedures. Tetrahydrofuran (THF) and dichloromethane were purified by distillation under nitrogen over $LiAlH_4$ and P_2O_5, respectively. Amines were purchased from Aldrich, their purity was checked by ^1H NMR spectroscopy, and, when necessary, they were dried over KOH and distilled from BaO under an Ar or N_2 atmosphere prior to use. All the other reagents and chemicals were reagent grade and, unless otherwise stated, were used as received by commercial suppliers. All reactions and manipulations were routinely performed under a dry nitrogen atmosphere by using standard Schlenk-tube techniques. The solid complexes were collected on sintered-glass frits and washed with light petroleum ether (bp 40−60 °C) before being dried in a stream of nitrogen. The ligand $CH_3CH_2CH_2N(CH_2CH_2PPh_2)_2$ (PNP)[21] and the complexes *mer,trans*-[(PNP)$RuCl_2(PPh_3)$] (**1**),[22,23] and *fac,cis*-[(PNP)-$RuCl_2${C═C(H)Ph}] (**2**)[24] were prepared as described in the literature. Deuterated solvents for NMR measurements (Merck and Aldrich) were dried over molecular sieves (0.4 nm). ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Varian VXR 300, Bruker AC200, or Bruker AVANCE DRX 500 spectrometers operating at 299.94, 200.13, or 500.13 MHz (^1H) and 75.42, 50.32, or 125.80 MHz (^{13}C), respectively. Peak positions are relative to tetramethylsilane and were calibrated against the residual solvent resonance (^1H) or the deuterated solvent multiplet (^{13}C). ^{13}C-DEPT experiments were run on the Bruker AC200 spectrometer. $^1H,^{13}C$-2D HETCOR NMR experiments were recorded on either the Bruker AC200 spectrometer using the XHCORR pulse program or the Bruker AVANCE DRX 500 spectrometer equipped with a 5 mm triple-resonance probe head for ^1H detection and inverse detection of the heteronucleus (inverse correlation mode, HMQC experiment, with no sample spinning). The $^1H,^1H$-2D COSY NMR experiments were routinely conducted on the Bruker AC200 instrument in the absolute magnitude mode using a 45 or 90° pulse after the incremental delay or were acquired on the AVANCE DRX 500 Bruker spectrometer using the phase-sensitive TPPI mode with double quantum filter. $^{31}P\{^1H\}$ NMR spectra were recorded on either the Varian VXR 300 or Bruker AC200 instrument operating at 121.42 or 81.01 MHz, respectively. Chemical shifts were measured relative to external 85% H_3PO_4 with downfield values taken as positive. The proton NMR spectra with broad-band phosphorus decoupling were recorded on the Bruker AC200 instrument equipped with a 5 mm inverse probe and a BFX-5 amplifier device using the wide-band phosphorus decoupling sequence GARP. Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 1600 series FT-IR spectrometer between KBr plates. A Shimadzu GC-14A/GCMS-QP2000 instrument was employed for all GC-MS investigations. Elemental analyses (C, H, N) were performed using a Carlo Erba Model 1106 elemental analyzer.

Synthesis of the Secondary Aminocarbene Complexes *fac,cis*-[(PNP)$RuCl_2${C(NHR)(CH_2Ph)}] (R = $CH_3CH_2CH_2$ (3), Ph (4), cyclo-C_6H_{11} (5), (*R*)-(+)-CH(Me)(Ph) (6), (*R*)-(−)-CH(Me)(Et) (7), (*S*)-(−)-CH(Me)(1-naphthyl) (8)). A 3-fold excess of the appropriate primary amine, NH_2R (R = $CH_3CH_2CH_2$, Ph, cyclo-C_6H_{11}, (*R*)-(+)-CH(Me)(Ph), (*R*)-(−)-CH(Me)(Et), (*S*)-(−)-CH(Me)(1-naphthyl), was syringed at room temperature into a stirred suspension of the vinylidene complex **2** (0.40 g, 0.53 mmol) in 30 mL of THF. The reaction mixture was stirred in the dark for 1 h to give a canary yellow solution which was evaporated to ca. 5 mL. Addition of light petroleum ether gave canary yellow microcrystals of the aminocarbene complex, which were recrystallized from CH_2Cl_2 and light petroleum ether. Yield: ca. 90%.

***fac,cis*-[(PNP)$RuCl_2${C(N(H)$CH_3CH_2CH_2$)(CH_2Ph)}] (3).** Anal. Calcd for $C_{42}H_{50}N_2Cl_2P_2Ru$: C, 61.76; H, 6.17; N, 3.43.

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Found: C, 61.55; H, 6.26; N, 3.32. IR: ν(NH) 3450 cm^{-1} (br, w). ^{31}P{^{1}H} NMR (22 °C, $CDCl_3$, 121.42 MHz): δ 51.31 (s). ^{1}H NMR (22 °C, CD_2Cl_2, 299.94 MHz): δ_{NH} 10.62 (br s, 1H), δ_{CH_2Ph} 4.58 (s, 2H), $\delta_{NCH_2CH_2CH_3}$ 3.30 (t, ^3J(HH) = 7.1 Hz, 2H), $\delta_{NCH_2CH_2CH_3}$ 1.67 (sextet, ^3J(HH) = 7.1 Hz, 2H), $\delta_{NCH_2CH_2CH_3}$ 0.96 (t, ^3J(HH) = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (22 °C, CD_2Cl_2, 75.42 MHz): $\delta_{Ru=C}$ 254.4 (t, ^2J(CP) = 11.6 Hz), δ_{CH_2Ph} 59.0 (s), $\delta_{NCH_2CH_2CH_3}$ 52.8 (s), $\delta_{NCH_2CH_2CH_3}$ 23.2 (s), $\delta_{NCH_2CH_2CH_3}$ 12.1 (s).

***fac,cis*-[(PNP)RuCl$_2${C(N(H)Ph)(CH$_2$Ph)}] (4)**. Anal. Calcd for $C_{45}H_{48}N_2Cl_2P_2Ru$: C, 63.53; H, 5.69; N, 3.29. Found: C, 63.44; H, 5.56; N, 3.21. IR: ν(NH) 3466 cm^{-1} (br, w). ^{31}P{^{1}H} NMR (22 °C, $CDCl_3$, 121.42 MHz): δ 50.17 (s); ^{1}H NMR (22 °C, $CDCl_3$, 299.94 MHz): δ_{NH} 12.35 (s, 1H), δ_{CH_2Ph} 4.88 (s, 2H). ^{13}C{^{1}H} NMR (20 °C, $CDCl_3$, 75.42 MHz): $\delta_{Ru=C}$ 264.9 (t, ^2J(CP) = 11.7 Hz), δ_{CH_2Ph} 59.8 (s).

***fac,cis*-[(PNP)RuCl$_2${C(N(H)-cyclo-C$_6$H$_{11}$)(CH$_2$Ph)}] (5)**. Anal. Calcd for $C_{45}H_{54}N_2Cl_2P_2Ru$: C, 63.08; H, 6.35; N, 3.27. Found: C, 62.96; H, 6.31; N, 3.26. IR: ν(NH) 3440 cm^{-1} (br, w). ^{31}P{^{1}H} NMR (22 °C, $CDCl_3$, 81.01 MHz): δ 49.73 (s). ^{1}H NMR (22 °C, CD_2Cl_2, 200.13 MHz): δ_{NH} 10.69 (br d, J(HH) = 9.3 Hz, 1H), δ_{CH_2Ph} 4.69 (s, 2H), δ_{NCH}(cyclohexyl) 3.65 (m, 1H), δ_{CH_2}(cyclohexyl) 1.2−2.5 (m, superimposed to the PNP aliphatic protons). ^{13}C{^{1}H} NMR (23 °C, CD_2Cl_2, 50.32 MHz): $\delta_{Ru=C}$ 251.9 (t, ^2J(CP) = 11.6 Hz), δ_{CH_2Ph} 58.4 (s), δ_{NCH}(cyclohexyl) 58.5 (s), δ_{CH_2}(cyclohexyl) 33.3, 25.9, 25.2 (all s).

(*R*)-(+)-*fac,cis*-[(PNP)RuCl$_2${C(N(H)CHMePh)(CH$_2$-Ph)}] (6). Anal. Calcd for $C_{47}H_{52}N_2Cl_2P_2Ru$: C, 64.23; H, 5.96; N, 3.19. Found: C, 64.08; H, 5.89; N, 3.11. IR: ν(NH) 3460 cm^{-1} (br, w). ^{31}P{^{1}H} NMR (22 °C, $CDCl_3$, 81.01 MHz): AB system, δ_A 50.32, δ_B 48.04, $^2J(P_AP_B)$ = 29.7 Hz. ^{1}H NMR (22 °C, CD_2Cl_2, 200.13 MHz): δ_{NH} 11.13 (br d, ^3J(HH) = 9.6 Hz, 1H), δ_{CHMe} 4.94 (dq, ^3J(HH) = 9.6, 6.6 Hz, 1H), δ_{CH_2Ph} 4.80, 4.48 (AB system, ^3J(HH) =,16.8 Hz, 2H), δ_{CHMe} 1.58 (d, ^3J(HH) = 6.6 Hz, 3H). ^{13}C{^{1}H} NMR (22 °C, CD_2Cl_2, 75.42 MHz): $\delta_{Ru=C}$ 255.3 (t, ^2J(CP) = 11.3 Hz), δ_{CHMe} 59.3 (s), δ_{CH_2Ph} 58.6 (t, ^3J(CP) = 4.6 Hz), δ_{CHMe} 24.6 (s).

(*R*)-(−)-*fac,cis*-[(PNP)RuCl$_2${C(N(H)CHMeEt)(CH$_2$-Ph)}] (7). Anal. Calcd for $C_{43}H_{52}N_2Cl_2P_2Ru$: C, 62.16; H, 6.31; N, 3.37. Found: C, 62.05; H, 6.44; N, 3.20. IR: ν(NH) 3440 cm^{-1} (br, w). ^{31}P{^{1}H} NMR (22 °C, $CDCl_3$, 81.01 MHz): AB system, δ_A 51.21, δ_B 50.59, $^2J(P_AP_B)$ = 28.2 Hz. ^{1}H NMR (25 °C, CD_2Cl_2, 500.13 MHz): δ_{NH} 10.82 (br d, ^3J(HH) = 9.6 Hz, 1H), δ_{CH_2Ph} 4.70, 4.54 (AB system, ^2J(HH) = 17.1 Hz, 2H), $\delta_{CH(Me)Et}$ 3.70 (m, 1H), $\delta_{CH(Me)CH_2CH_3}$ 1.81, 1.64 (m, diastereotopic protons, 2H), $\delta_{CH(Me)Et}$ 1.36 (d, ^3J(HH) = 6.4 Hz, 3H), $\delta_{CH(Me)CH_2CH_3}$ 1.06 (t, ^3J(HH) = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (25 °C, CD_2Cl_2, 125.80 MHz): $\delta_{Ru=C}$ 251.3 (t, ^2J(CP) = 11.4 Hz), $\delta_{CH(Me)Et}$ 57.0 (s), δ_{CH_2Ph} 56.5 (s), $\delta_{CH(Me)CH_2CH_3}$ 30.4 (s), $\delta_{CH(Me)Et}$ 20.6 (s), $\delta_{CH(Me)CH_2CH_3}$ 12.6 (s).

(*S*)-(−)-*fac,cis*-[(PNP)RuCl$_2${C[N(H)CHMe(1-naphthyl)]-(CH$_2$Ph)}] (8). Anal. Calcd for $C_{51}H_{54}N_2Cl_2P_2Ru$: C, 65.94; H, 5.86; N, 3.02. Found: C, 65.86; H, 5.89; N, 2.92. IR: ν(NH) 3460 cm^{-1} (br, w). ^{31}P{^{1}H} NMR (22 °C, $CDCl_3$, 81.01 MHz): AB system, δ_A 51.25, δ_B 48.03, $^2J(P_AP_B)$ = 29.9 Hz. ^{1}H NMR (22 °C, CD_2Cl_2, 200.13 MHz): δ_{NH} 11.46 (br d, ^3J(HH) = 9.3 Hz, 1H), $\delta_{CH(Me)Np}$ 5.85 (dq, ^3J(HH) = 9.3, 6.6 Hz, 1H), δ_{CH_2Ph} 4.80, 4.47 (AB system, ^2J(HH) = 17.1 Hz, 2H), δ_{CHMeNp} 1.75 (d, ^3J(HH) = 6.6 Hz, 3H). ^{13}C{^{1}H} NMR (22 °C, CD_2Cl_2, 50.32 MHz): $\delta_{Ru=C}$ 255.8 (t, ^2J(CP) = 11.6 Hz), δ_{CH_2Ph} 59.5 (s), δ_{CHMeNp} 58.4 (s), δ_{CHMeNp} 24.4 (s).

Synthesis of the Primary Aminocarbene Complexes *fac,cis*-[(PNP)RuCl$_2${C(NH$_2$)(CH$_2$Ph)}] (9). A regular stream of NH_3 was slowly bubbled through an orange solution of **2** (0.40 g, 0.53 mmol) in $CHCl_3$ (30 mL) for 30 min. During this period the solution become yellow, while a colorless solid separated. The ammonia was then replaced by nitrogen, and the solution was slowly heated to the boiling point and then refluxed with stirring for 2 h. During this time the solid dissolved to give a bright yellow solution, which was evaporated under a brisk current of nitrogen to ca. 8 mL. After the residue was cooled to room temperature, the addition of 15 mL of *n*-hexane led to the precipitation of yellow microcrystals of *fac,cis*-[(PNP)RuCl$_2${C(NH$_2$)(CH$_2$Ph)}] (**9**), which were filtered off and washed several times with light petroleum ether before being dried in vacuo. Recrystallization from CH_2Cl_2 and light petroleum ether (2:1 v/v) gave **9** as light yellow crystals. Yield: 86%. Anal. Calcd for $C_{39}H_{44}N_2Cl_2P_2Ru$: C, 60.46; H, 5.72; N, 3.62. Found: C, 60.19; H, 5.94; N, 3.56. IR: ν(NH) 3383 (m), 3276 cm^{-1} (w). ^{31}P{^{1}H} NMR (22 °C, $CDCl_3$, 81.01 MHz): δ 53.36 (s). ^{1}H NMR (22 °C, CD_2Cl_2, 200.13 MHz): δ_{NH} 10.14, 8.34 (br singlets, 1H each), δ_{CH_2Ph} 4.65 (s, 2H). ^{13}C{^{1}H} NMR (22 °C, CD_2Cl_2, 50.32 MHz): $\delta_{Ru=C}$ 261.6 (t, ^2J(CP) = 11.4 Hz), δ_{CH_2Ph} 58.7 (s).

Synthesis of the Tertiary Aminocarbene Complex *fac,cis*-[(PNP)RuCl$_2${C(NC$_5$H$_{10}$)(CH$_2$Ph)}] (10). Complex **10** was prepared as described above for the secondary aminocarbene complexes by using piperidine in place of primary amines. Anal. Calcd for $C_{44}H_{52}N_2Cl_2P_2Ru$: C, 62.70; H, 6.22; N, 3.32. Found: C, 62.48; H, 6.17; N, 3.12. ^{31}P{^{1}H} NMR (22 °C, C_6D_6, 81.01 MHz): δ 50.07. ^{1}H NMR (22 °C, C_6D_6, 200.13 MHz): δ_{CH_2Ph} 4.62 (s). ^{13}C{^{1}H} NMR (22 °C, C_6D_6, 50.32 MHz): $\delta_{Ru=C}$ 252.4 (t, ^2J(CP) = 14.2 Hz), δ_{CH_2Ph} 57.9 (s), δ_{CH_2}(piperidine) 51.8, 27,7, 25.4 (all s).

Synthesis of the Phenylethynyl−Amine Complexes *fac*-[(PNP)RuCl(C≡CPh)(NH$_2$R)] (R = CH$_3$CH$_2$CH$_2$ (11), cyclo-C$_6$H$_{11}$ (12), (*R*)-(−)-CH(Me)Et (13)). **Method A**. To a solution of **2** (0.40 g, 0.53 mmol) in 25 mL of THF was added 2 equiv of the appropriate primary amine with vigorous stirring. After the yellow solution was stirred for 3 h, it was concentrated to ca. half its volume. The addition of 20 mL of *n*-hexane, followed by slow concentration under nitrogen, gave the alkynyl complexes *fac*-[(PNP)RuCl(C≡CPh)(NH$_2$R)] (R = $CH_3CH_2CH_2$ (**11**), cyclo-C_6H_{11} (**12**), (*R*)-(−)-CH(Me)Et (**13**)) in yields higher than 90%. While **11** was obtained as a pure product, **12** (and **13**) were always contaminated by variable amounts (<10%) of **5** (and **7**).

Method B. To a solution of **2** (0.40 g, 0.53 mmol) in 25 mL of CH_2Cl_2 was added 2 equiv of the appropriate primary amine in water (25 mL) with vigorous stirring. The resulting biphasic system was vigorously stirred for 2 h at room temperature in the dark. The organic layer was separated, dried over $MgSO_4$ or Na_2SO_4, and then concentrated to ca. 5 mL under vacuum. Addition of light petroleum ether (10 mL) gave pale yellow microcrystals of the alkynyl−amine complexes *fac*-[(PNP)-RuCl(C≡CPh)(NH$_2$R)] (R = $CH_3CH_2CH_2$ (**11**), cyclo-C_6H_{11} (**12**), (*R*)-(−)-CH(Me)Et (**13**)) in yields ranging from 76 to 89%. The crude products were recrystallized from CH_2Cl_2/*n*-hexane solution.

After concentration of the water phase under reduced pressure, the corresponding ammonium salt [NH$_3$R]Cl was isolated in quantitative yield.

***fac*-[(PNP)RuCl(C≡CPh)(NH$_2$CH$_3$CH$_2$CH$_2$)] (11)**. Yield: 92% (method A), 85% (method B). Anal. Calcd for $C_{42}H_{49}N_2ClP_2Ru$: C, 64.65; H, 6.33; N, 3.59. Found: C, 64.54; H, 6.39; N, 3.28. IR: ν(NH) 3320 (w), ν(C≡C) 2054 (vs), 1999 cm^{-1} (sh, m). ^{31}P{^{1}H} NMR (20 °C, CD_2Cl_2, 81.01 MHz): AB system, δ_A 58.89, δ_B 57.13, $^2J(P_AP_B)$ = 34.9 Hz. ^{1}H NMR (20 °C, CD_2Cl_2, 500.13 MHz): δ_{NH_2} 2.10 (br s, 2H), $\delta_{NH_2CH_2CH_2CH_3}$ 3.4−2.1 (m, superinposed with PNP aliphatic protons), $\delta_{NH_2CH_2CH_2CH_3}$ 0.63 (t, ^3J(HH) = 7.2 Hz). ^{13}C{^{1}H} NMR (22 °C, CD_2Cl_2, 50.32 MHz): δ_{RuC} 138.0 (dd, ^2J(CP) = 20.0, 6.1 Hz), $\delta_{C\equiv C}$ 112.8 (s), $\delta_{NCH_2CH_2CH_3}$ 56.9 (s), $\delta_{NCH_2CH_2CH_3}$ 27.7 (s), $\delta_{NCH_2CH_2CH_3}$ 12.4 (s).

***fac*-[(PNP)RuCl(C≡CPh){NH$_2$-cyclo-C$_6$H$_{11}$}] (12)**. Yield: 89% (method B). Anal. Calcd for $C_{45}H_{53}N_2ClP_2Ru$: C, 65.88; H, 6.51; N, 3.41. Found: C, 65.43; H, 6.26; N, 3.16. IR: ν(NH) 3318 (w), ν(C≡C) 2058 (vs), 1997 cm^{-1} (sh, m). ^{31}P{^{1}H} NMR (CD_2Cl_2, 81.01 MHz): fluxional AB system at 22 °C, δ_A 58.0 (br), δ_B 56.8 (br), $^2J(P_AP_B) \approx$ 33 Hz; AB system at −50 °C, δ_A 58.08, δ_B 56.25, $^2J(P_AP_B)$ = 35.2 Hz. ^{1}H NMR (22 °C, CD_2Cl_2, 200.13 MHz): δ_{NH_2} not assigned, likely buried in the crowded aliphatic region of the spectrum. ^{13}C{^{1}H} NMR (22

°C, CD_2Cl_2, 50.32 MHz): δ_{RuC} 138.4 (t, ^2J(CP) = 10.4, 6.1 Hz), $\delta_{C\equiv C}$ 112.4 (s), δ_{NCH} 53.2 (s).

***fac*-[(PNP)RuCl(C≡CPh)(NH$_2$(*R*)-(−)-CH(Me)Et)] (13)**. Yield: 76% (method B). Anal. Calcd for $C_{43}H_{51}N_2ClP_2Ru$: C, 65.02; H, 6.47; N, 3.53. Found: C, 65.28; H, 6.60; N, 3.38. IR: ν(NH) 3320 (w), ν(C≡C) 2057 cm^{-1} (vs). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 81.01 MHz): fluxional AB system at 22 °C, δ_A 57.6 (v br), δ_B 56.7 (v br); AB system at 0 °C, δ_A 57.82, δ_B 56.44, $^2J(P_AP_B)$ = 34.1 Hz. ^1H NMR (22 °C, $CDCl_3$, 200.13 MHz): δ_{NH_2} 2.3 (br s, 2H). $^{13}C\{^1H\}$ NMR (22 °C, CD_2Cl_2, 50.32 MHz): δ_{RuC} 137.2 (dd, ^2J(CP) = 10.0, 6.8 Hz), $\delta_{C\equiv C}$ 112.7 (t, ^3J(CP) = 3.5 Hz).

Synthesis of the Phenylethynyl−Ammonia Complex *fac*-[(PNP)RuCl(C≡CPh)(NH$_3$)] (14). A solution of **2** (0.40 g, 0.53 mmol) in 30 mL of $CHCl_3/H_2O$ (1:1 v/v) was saturated with gaseous ammonia at 0 °C (ice bath) with vigorous stirring. The resulting biphasic system was stirred overnight in the dark at room temperature. The organic layer was separated, dried over Na_2SO_4, and concentrated to ca. 5 mL under vacuum. Addition of light petroleum ether (10 mL) gave the complex *fac*-[(PNP)RuCl(C≡CPh)(NH$_3$)] (**14**), which was recrystallized from CH_2Cl_2/*n*-hexane solution. Yield: 71%.

After evaporation of the water phase under reduced pressure, off-white microcrystals of NH_4Cl were obtained in quantitative yield.

Alternatively, **14** was prepared by reacting a solution of **2** (0.40 g, 0.53 mmol) in 20 mL of $CHCl_3$ with a small excess of diluted ammonium hydroxide (20 μL, NH_3 30% in water). Workup as described above gave **14** in 85% yield.

Anal. Calcd for $C_{39}H_{43}N_2ClP_2Ru$: C, 63.46; H, 5.87; N, 3.79. Found: C, 63.16; H, 5.79; N, 3.24. IR: ν(NH) 3394 (w), ν(C≡C) 2054 cm^{-1} (vs). $^{31}P\{^1H\}$ NMR (22 °C, $CDCl_3$, 121.42 MHz): AB system, δ_A 59.48, δ_B 57.53, $^2J(P_AP_B)$ = 35.4 Hz. ^1H NMR (22 °C, $CDCl_3$, 299.94 MHz): δ_{NH_3} 1.89 (br s, 3H).

Reaction of the Amino−Alkynyl Complexes 11−14 with HCl. A stoichiometric amount of gaseous HCl (1.3 mL, 0.06 mmol) was syringed into a 5 mm NMR tube containing a CD_2Cl_2 (1.0 mL) solution of the amino−alkynyl complexes **11**−**14**. $^{31}P\{^1H\}$ and ^1H NMR analysis at room temperature showed the transformation of the alkynyl complexes **11**−**14** into the corresponding amminocarbenes **3**, **5**, **7**, and **9** in quantitative yield (based on $^{31}P\{^1H\}$ NMR integration).

Reaction of the Amino−Alkynyl Complex 11 with [NH$_3$(CH$_2$CH$_2$CH$_3$)]Cl. A THF solution (15 mL) of **11** (0.20 g, 0.26 mmol) was reacted with a small excess (30 mg, 0.31 mmol) of *n*-propylammonium chloride with stirring. Stirring was continued for 30 min. Addition of *n*-heptane (10 mL) and slow concentration under nitrogen gave yellow crystals of **3**. Yield: 85%.

In situ NMR experiments showed that the amino−alkynyls **12**−**14** react with 1 equiv of the appropriate alkylammonium salt to give the corresponding aminocarbene in excellent yield (≥95%, based on $^{31}P\{^1H\}$ NMR integration).

Crossing Experiments. **(A) Reaction of *fac*-[(PNP)RuCl(C≡CPh)(NH$_2$CH$_3$CH$_2$CH$_2$)] (11) with [NH$_3$(cyclo-C$_6$H$_{11}$)]Cl**. **NMR Experiment**. A 5 mm NMR tube was charged under nitrogen with **11** (20 mg, 0.026 mmol), [NH_3-(*cyclo*-C_6H_{11})]Cl (4.0 mg, 0.029 mmol), and THF-d_8 (0.8 mL). The tube was shaken for 30 s and then placed into an NMR probe. $^{31}P\{^1H\}$ NMR monitoring of the reaction showed the fast conversion of **11** into a 9:1 mixture of the aminocarbenes **3** and **5**. The composition of the reaction mixture did not change over a period of 2 days at room temperature.

Preparative Experiment. A THF (15 mL) solution of **11** (0.20 g, 0.26 mmol) was stirred in the presence of 1.1 equiv of [NH_3(cyclo-C_6H_{11})]Cl (40 mg, 0.29 mmol) for 2 h. The addition of *n*-heptane (10 mL), followed by concentration under a stream of nitrogen, gave yellow crystals of **3** (yield 80%) occasionally contaminated by trace amounts of **5**. GC-MS analysis of the solution showed the presence of about 1 equiv of cyclohexylamine.

(B) Reaction of *fac*-[(PNP)RuCl(C≡CPh){NH$_2$(cyclo-C$_6$H$_{11}$)}] (12) with [NH$_3$(CH$_3$CH$_2$CH$_2$)]Cl. A 5 mm NMR tube was charged under nitrogen with **12** (20 mg, 0.024 mmol), [NH_3($CH_3CH_2CH_2$)]Cl (2.5 mg, 0.026 mmol), and THF-d_8 (0.8 mL). The tube was shaken for 30 s and then placed into a NMR probe. $^{31}P\{^1H\}$ NMR analysis of the reaction revealed the conversion of **12** to **5**. Occasionally, **3** was also formed (≤5%). The composition of the reaction mixture did not change over a period of 2 days at room temperature.

Reaction of *fac*-[(PNP)RuCl(C≡CPh){NH$_2$R}] with CO. Carbon monoxide was bubbled throughout a stirred CH_2Cl_2 solution (10 mL) of **11**−**14** (ca. 100 mg) at room temperature for 20 min. Addition of ethanol (10 mL), followed by slow concentration under nitrogen, gave pale yellow microcrystals of the known alkynyl−carbonyl complex *fac*-[(PNP)RuCl(C≡CPh)(CO)] (**15**): yield 95%.[24]

Synthesis of the Isonitrile Complexes *fac,cis*-[(PNP)-RuCl$_2$(C≡NR)] (R = CH$_3$CH$_2$CH$_2$ (16), Ph (17), cyclo-C$_6$H$_{11}$ (18), (*R*)-(+)-CH(Me)Ph (19), (*R*)-(−)-CH(Me)Et (20)). A solution of 0.5 mmol (0.41−0.44 g) of the aminocarbene complexes **3**−**7** in 50 mL of THF/H_2O (20:1 v/v) was introduced into a 100 mL Schlenk flask equipped with a stirring bar, a reflux condenser, and a nitrogen inlet. The canary yellow solution was gently refluxed for ca. 16 h. During this time, the yellow color faded to give a pale yellow solution, which was evaporated to dryness under vacuum. The solid residue was washed with *n*-pentane (2 × 5 mL), dissolved in ca. 15 mL of CH_2Cl_2, and dried over $MgSO_4$ for ca. 30 min. The CH_2Cl_2 solution was then filtered, and its volume was reduced to ca. 5 mL under reduced pressure. Addition of light petroleum ether (bp 40−60 °C, 10 mL) gave cream-colored microcrystals of the isonitrile complexes *fac,cis*-[(PNP)RuCl$_2$(C≡NR)] (R = $CH_3CH_2CH_2$ (**16**), Ph (**17**), cyclo-C_6H_{11} (**18**), (*R*)-(+)-CH(Me)-Ph (**19**), (*R*)-(−)-CH(Me)Et (**20**)). The yields were generally higher than 90%.

***fac,cis*-[(PNP)RuCl$_2$(C≡NCH$_2$CH$_2$CH$_3$)] (16)**. Anal. Calcd for $C_{35}H_{42}N_2Cl_2P_2Ru$: C, 58.01; H, 5.84; N, 3.87. Found: C, 57.88; H, 5.76; N, 3.62. IR: ν(C≡N) 2117 cm^{-1} (vs). $^{31}P\{^1H\}$ NMR (20 °C, $CDCl_3$, 121.42 MHz): 59.23 (s). ^1H NMR (20 °C, $CDCl_3$, 200.13 MHz): $\delta_{NCH_2CH_2CH_3}$ 4.07 (t, ^3J(HH) = 6.6 Hz, 2H), $\delta_{NCH_2CH_2CH_3}$ 2.01 (sex, ^3J(HH) = 7.1 Hz, 2H), $\delta_{NCH_2CH_2CH_3}$ 1.24 (t, ^3J(HH) = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (20 °C, CD_2Cl_2, 75.42 MHz): $\delta_{C\equiv N}$ 159.2 (t, ^2J(CP) = 15.6 Hz), $\delta_{NCH_2CH_2CH_3}$ 52.1 (s), $\delta_{NCH_2CH_2CH_3}$ 24.5 (s), $\delta_{NCH_2CH_2CH_3}$ 12.1 (s).

***fac,cis*-[(PNP)RuCl$_2$(C≡NPh)] (17)**. Anal. Calcd for $C_{38}H_{40}N_2Cl_2P_2Ru$: C, 60.16; H, 5.31; N, 3.69. Found: C, 59.98; H, 5.25; N, 3.48. IR: ν(C≡N) 2062 cm^{-1} (vs). $^{31}P\{^1H\}$ NMR (20 °C, CD_2Cl_2, 121.42 MHz): δ 57.74 (s). $^{13}C\{^1H\}$ NMR (20 °C, CD_2Cl_2, 75.42 MHz): $\delta_{C\equiv N}$ 171.4 (t, ^2J(CP) = 16.9 Hz).

***fac,cis*-[(PNP)RuCl$_2${C≡N(cyclo-C$_6$H$_{11}$)}] (18)**. Anal. Calcd for $C_{38}H_{46}N_2Cl_2P_2Ru$: C, 59.68; H, 6.06; N, 3.66. Found: C, 59.59; H, 6.10; N, 3.49. IR: ν(C≡N) 2108 cm^{-1} (vs). $^{31}P\{^1H\}$ NMR (22 °C, CD_2Cl_2, 81.01 MHz): δ 58.45 (s). $^{13}C\{^1H\}$ NMR (20 °C, CD_2Cl_2, 75.42 MHz): $\delta_{C\equiv N}$ 158.9 (t, ^2J(CP) = 15.9 Hz).

(*R*)-(+)-*fac,cis*-[(PNP)RuCl$_2${C≡NCH(Me)Ph}] (19). Anal. Calcd for $C_{40}H_{44}N_2Cl_2P_2Ru$: C, 61.07; H, 5.64; N, 3.56. Found: C, 60.94; H, 5.70; N, 3.48. IR: ν(C≡N) 2100 cm^{-1} (vs). $^{31}P\{^1H\}$ NMR (22 °C, $CDCl_3$, 81.01 MHz): AB system, δ_A 58.02, δ_B 57.76, $^2J(P_AP_B)$ = 26.1 Hz. ^1H NMR (20 °C, THF-d_8, 200.13 MHz): δ_{CHMe} 5.6 (q, ^3J(HH) = 6.5 Hz, 1H), δ_{CHMe} 2.08 (d, ^3J(HH) = 6.8 Hz, 3H). $^{13}C\{^1H\}$ NMR (20 °C, CD_2Cl_2, 75.42 MHz): $\delta_{C\equiv N}$ 160.9 (t, ^2J(CP) = 15.2 Hz), δ_{CHMe} 57.9 (s), δ_{CHMe} 25.9 (s). $[\alpha]_D^{25}$ = +11.50 (c = 1.4, $CHCl_3$).

(*R*)-(−)-*fac,cis*-[(PNP)RuCl$_2${C≡NCH(Me)Et}] (20). Anal. Calcd for $C_{36}H_{44}N_2Cl_2P_2Ru$: C, 58.54; H, 6.00; N, 3.79. Found: C, 58.36; H, 5.99; N, 3.71. IR: ν(C≡N) 2085 cm^{-1} (vs). $^{31}P\{^1H\}$ NMR (22 °C, CD_2Cl_2, 81.01 MHz): AB system, δ_A 59.31, δ_B 59.20, $^2J(P_AP_B)$ = 26.3 Hz. ^1H NMR (20 °C, THF-d_8, 200.13 MHz): $\delta_{CH(Me)Et}$ 4.30 (sextet, ^3J(HH) = 6.4 Hz, 1H), $\delta_{CH(Me)CH_2CH_3}$ 1.98, 1.89 (ABXY$_3$ spin system, ^2J(HH) = 14.2 Hz, $^3J(H_AH_X)$ = 7.3, $^3J(H_BH_X)$= 5.5, $^3J(H_AH_Y)$ = 7.5, $^3J(H_BH_Y)$ =

7.3 Hz, 2H), $\delta_{CH(Me)Et}$ 1.64 (d, $^3J(HH) = 6.2$ Hz, 3H). $\delta_{CH(Me)CH_2CH_3}$ 1.24 (t, $^3J(HH) = 7.1$ Hz, 3H). $^{13}C\{^1H\}$ NMR (22 °C, CD_2Cl_2, 50.32 MHz): $\delta_{C\equiv N}$ 159.2 (t, $^2J(CP) = 15.5$ Hz), $\delta_{CH(Me)Et}$ 56.2 (s), $\delta_{CH(Me)CH_2CH_3}$ 31.7 (s), $\delta_{CH(Me)Et}$ 22.6 (s), $\delta_{CH(Me)CH_2CH_3}$ 12.4 (s). $[\alpha]_D^{25} = -5.93$ ($c = 1.2$, $CHCl_3$).

Synthesis of (*S*)-(−)-*fac,cis*-[(PNP)RuCl$_2${C≡NCH(Me)-(1-naphthyl)}] (21). When the (1-naphthyl)aminocarbene complex **8** was refluxed as described above, only partial conversion (≤15%) to the corresponding isonitrile derivative (*S*)-(−)-*fac,cis*-[(PNP)RuCl$_2${C≡NCH(Me)(1-naphthyl)}] (**21**) was obtained. Complete conversion of **8** to the isonitrile complex **21** was obtained when the thermal reaction was carried out in refluxing monoglyme/H_2O (20:1,v/v; bp = 124 °C) for 14 h. Yield: 88%. Anal. Calcd for $C_{44}H_{46}N_2Cl_2P_2Ru$: C, 63.16; H, 5.54; N, 3.35. Found: C, 63.01; H, 5.38; N, 3.28. IR: ν(C≡N) 2088 cm^{-1} (vs). $^{31}P\{^1H\}$ NMR (22 °C, CD_2Cl_2, 81.01 MHz): AB system, δ_A 58.19, δ_B 58.04, $^2J(P_AP_B) = 26.2$ Hz. ^1H NMR (22 °C, CD_2Cl_2, 200.13 MHz): $\delta_{CH(Me)Nap}$ 6.26 (q, $^3J(HH) = 6.8$ Hz, 1H), $\delta_{CH(Me)Nap}$ 2.16 (d, $^3J(HH) = 6.8$ Hz, 3H). $^{13}C\{^1H\}$ NMR (20 °C, CD_2Cl_2, 50.32 MHz): $\delta_{C\equiv N}$ 162.1 (t, $^2J(CP) = 15.9$ Hz), $\delta_{CH(Me)Nap}$ 54.5 (s), $\delta_{CH(Me)Np}$ 24.7 (s). $[\alpha]_D^{25} = +12.6$ ($c = 0.9$, $CHCl_3$).

One-Pot Synthesis of the Isonitrile Complexes 16−20. A 3-fold excess of phenylacetylene was pipetted into a stirred slurry of **1** (0.23 g, 0.25 mmol) in THF (40 mL). The mixture was slowly brought to reflux temperature, and heating was continued for 30−45 min. Three equivalents of the appropriate primary amine NH_2R (R = $CH_3CH_2CH_2$, cyclo-C_6H_{11}, (*R*)-(+)-CH(Me)Ph, (*R*)-(−)-CH(Me)Et) was then syringed into the hot red solution, which immediately became light yellow. The clear yellow solution was refluxed overnight to afford, after the usual workup, pure samples of the isonitrile complexes **16**−**20**. Yield: ≥85%.

When **1** was replaced by the vinylidene complex **2** in the above reaction, the corresponding isonitrile complexes were obtained in similar yields.

Reaction of *fac,cis*-[(PNP)RuCl$_2${C(N(H)Ph)(CH$_2$Ph)}] with ^{n}BuLi: Synthesis of *mer,trans*-[(PNP)RuCl(CH$_2$Ph)-(C≡NPh)] (22). To a THF (25 mL) solution of **4** (0.250 mg, 0.29 mmol) cooled to 0 °C was added a stoichiometric amount of ^{n}BuLi (0.19 mL, 0.30 mmol, 1.6 M solution in THF) dropwise with stirring. Stirring was continued for 30 min while the solution was warmed to room temperature. Addition of ethanol (20 mL) and slow concentration under nitrogen gave pale yellow crystals of *mer,trans*-[(PNP)RuCl(CH$_2$Ph)(C≡NPh)] (**22**) in 86% yield. Following this procedure, **22** was similarly prepared from **4** by using NaOH instead of ^{n}BuLi.

The crude product was recrystallized from CH_2Cl_2/ethanol (1:1). Anal. Calcd for $C_{45}H_{47}N_2ClP_2Ru$: C, 66.37; H, 5.82; N, 3.44. Found: C, 66.17; H, 5.91; N, 3.40. IR: ν(C≡N) 2050 cm^{-1} (vs). $^{31}P\{^1H\}$ NMR (20 °C, CD_2Cl_2, 81.01 MHz): δ 31.69 (s). ^1H NMR (20 °C, CD_2Cl_2, 200.13 MHz): δ_{CH_2Ph} 3.11 (t, $^2J(CP) = 4.4$ Hz, 2H). $^{13}C\{^1H\}$ NMR (20 °C, CD_2Cl_2, 50.32 MHz): $\delta_{C\equiv N}$ 160.8 (t, $^2J(CP) = 2.9$ Hz), δ_{CH_2Ph} 10.31 (t, $^2J(CP) = 6.5$ Hz).

Reaction of *mer,trans*-[(PNP)RuCl(CH$_2$Ph)(C≡NPh)] with HCl. A slight excess of HCl (1 M solution in H_2O) was added via syringe into a 5 mm screw cap NMR tube containing a THF-d_8 (0.8 mL) solution of **22** (30 mg, 0.037 mmol) cooled to −40 °C. $^{31}P\{^1H\}$ NMR spectroscopy showed the quantitative transformation of **22** into **17**. GC-MS analysis of the solution confirmed the formation of 1 equiv of toluene.

Reaction of *fac,cis*-[(PNP)RuCl$_2${C(N(H)Ph)(CH$_2$Ph)}] (4) with ^{n}BuLi in the Presence of CO: Synthesis of *fac*-[(PNP)RuCl{C═NPh(CH$_2$Ph}(CO)] (23). A double proportion of ^{n}BuLi (0.37 mL, 0.59 mmol, 1.6 M solution in THF) was added dropwise to a stirred THF solution (20 mL) of **4** (0.250 g, 0.29 mmol) saturated with carbon monoxide and cooled to −78 °C. The temperature was slowly raised to −18 °C, during which time the yellow color of the starting solution faded. After 2 h, cold *n*-hexane purged with CO (25 mL) was added and the off-white precipitate of the iminoacyl−carbonyl complex *fac*-[(PNP)RuCl{C═NPh(CH$_2$Ph}(CO)] (**23**) was filtered off. Yield: 73%. Anal. Calcd for $C_{46}H_{47}N_2ClOP_2Ru$: C, 65.59; H, 5.62; N, 3.33. Found: C, 65.43; H, 5.61; N, 3.12. IR: ν(C≡O) 1920 (vs), ν(C═N) 1643 cm^{-1} (m). $^{31}P\{^1H\}$ NMR (−25 °C, CD_2Cl_2 saturated with CO, 121.42 MHz): AB spin system, δ_A 66.98, δ_B 30.01, $^2J(P_AP_B) = 8.7$ Hz. ^1H NMR (−25 °C, CD_2Cl_2 saturated with CO, 299.94 MHz): δ_{CH_2Ph} ABX spin system (X = ^{31}P), δ_A 4.71, δ_B 4.12, $^2J(H_AH_B) = 13.0$ Hz, $^4J(H_BX) = 4.4$ Hz, 2H). $^{13}C\{^1H\}$ NMR (−25 °C, CD_2Cl_2 saturated with CO, 50.32 MHz): $\delta_{C=N}$ 208.0 [dd, $^2J(CP_{cis}) = 15.8$, 10.7 Hz], $\delta_{C\equiv O}$ 215.0 (dd, $^2J(CP_{trans}) = 101.0$ Hz, $^2J(CP_{cis}) = 8.9$ Hz), δ_{CH_2Ph} 52.7 (s).

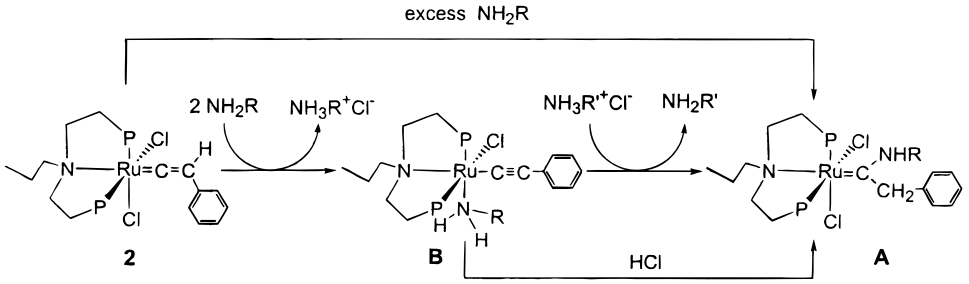
Reaction of *fac,cis*-[(PNP)RuCl$_2${C(NH$_2$)(CH$_2$Ph)}] (9) with ^{n}BuLi in the Presence of CO: Synthesis of *fac*-[(PNP)RuCl{C═NH(CH$_2$Ph)}(CO)] (24). A double proportion of ^{n}BuLi (0.49 mL, 0.78 mmol, 1.6 M solution in THF) was added dropwise to a stirred THF solution (20 mL) of **9** (0.300 g, 0.39 mmol) saturated with carbon monoxide and cooled to −78 °C. The temperature was slowly raised to −10 °C, during which time the yellow color of the starting solution faded. After 1 h, cold *n*-hexane purged with CO (25 mL) was added until cream-colored crystals of the iminoacyl−carbonyl complex *fac*-[(PNP)RuCl{C═NH(CH$_2$Ph)}(CO)] (**24**) precipitated. Yield: 80%. Anal. Calcd for $C_{40}H_{43}N_2ClOP_2Ru$: C, 62.70; H, 5.66; N, 3.66. Found: C, 62.42; H, 5.66; N, 3.39. IR: ν(C≡O) 1916 (vs), ν(C═N) 1638 cm^{-1} (m). $^{31}P\{^1H\}$ NMR (20 °C, THF-d_8 saturated with CO, 81.01 MHz): AB spin system, δ_A 62.43, δ_B 31.06, $^2J(P_AP_B) = 9.0$ Hz. ^1H NMR (20 °C, THF-d_8 saturated with CO, 200.13 MHz): δ_{NH} 9.09 (d, $^4J(HP) = 27.3$ Hz, 1H); δ_{CH_2Ph} AB spin system, δ_A 5.00, δ_B 3.53, $^2J(H_AH_B) = 16.4$ Hz, 2H.

X-ray Diffraction Study of *fac,cis*-[(PNP)RuCl$_2${C{NH$_2$-(1-naphthyl)}(CH$_2$Ph)}] (8). Canary yellow crystals (0.25 × 0.20 × 0.12 mm) suitable for an X-ray diffraction analysis were grown in the air by slow evaporation from a diluted dichloromethane/*n*-hexane solution of **8**. A summary of crystal and intensity data for the compound is presented in Table 1. Experimental data were recorded at room temperature on a ENRAF-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation. A set of 25 carefully centered reflections in the range $5.5° \le \theta \le 7°$ was used for determining the lattice constants. As a general procedure, the intensities of three standard reflections were measured periodically every 2 h for orientation and intensity control. This procedure revealed a minimum decay (5%) of intensities. The data were corrected for Lorentz and polarization effects. Atomic scattering factors were those tabulated by Cromer and Waber,[25] with anomalous dispersion corrections taken from ref 26. An

Table 1. Summary of Crystallographic Data for 8

formula	$C_{51}H_{54}Cl_2N_2P_2Ru$
mol wt	928.94
cryst size, mm	0.37 × 0.37 × 0.30
cryst syst	orthorhombic
space group	$P2_1P2_1P2_1$ (No. 19)
a, Å	13.551(4)
b, Å	14.115(3)
c, Å	27.662(6)
V, Å^3	5290.98
Z	4
d_{calcd}, g cm^{-3}	1.17
μ(Mo Kα), cm^{-1}	4.82
radiation	graphite-monochromated Mo Kα, $\lambda = 0.710\ 69$ Å
scan type	$\omega-2\theta$
2θ range, deg	5−46
scan width, deg	$0.9 + 0.34 \tan\theta$
scan speed, deg min^{-1}	5.49
total no. of data	4131
no. of unique data, $I > 3\sigma(I)$	2573
no. of params	212
R	0.078
R_w	0.081

Scheme 2



A: R = $CH_3CH_2CH_2$, **3**; Ph, **4**; *cyclo*-C_6H_{11}, **5**; *(R)-(+)*-CH(Me)Ph, **6**; *(R)-(+)*-CH(Me)Et, **7**; *(R)-(+)*-CH(Me)(1-naphthyl), **8**; H, **9**
B: R = $CH_3CH_2CH_2$, **11**; *cyclo*-C_6H_{11}, **12**; *(R)-(+)*-CH(Me)Et, **13**; H, **14**

empirical absorption correction was applied using the program DIFABS[27] with transmission factors in the range 0.77−1.41. The computational work was performed with a Pentium-II personal computer using the program SHELX76.[28] The programs PARST[29] and ORTEP[30] were also used. Final atomic coordinates with equivalent isotropic thermal parameters of all atoms and structure factors are available as Supporting Information.

The structure was solved via direct methods using the SIR92 program,[31] and all the non hydrogen atoms were found through a series of F_o Fourier maps. Refinement was done by full-matrix least-squares calculations, initially with isotropic thermal parameters and then, in the last least-squares cycle, with anisotropic thermal parameters for the ruthenium, chlorine, and phosphorus atoms. All of the phenyl rings were treated as rigid bodies with D_{6h} symmetry and C−C distances fixed at 1.39 Å. Hydrogen atoms were introduced in calculated positions but not refined. Constraint distances were used for the naphthyl substituent. No significant peaks were detected in the final least-squares cycles.

Results and Discussion

Synthesis and Characterization of the Aminocarbene Complexes. Treatment of the vinylidene complex *fac,cis*-[(PNP)$RuCl_2${C=C(H)Ph}] in THF with a 3-fold excess of a primary amine yields neutral aminocarbene complexes of the general formula *fac,cis*-[(PNP)$RuCl_2${C(NHR)(CH_2Ph)}] (R = $CH_3CH_2CH_2$ (**3**), Ph (**4**), cyclo-C_6H_{11} (**5**), (*R*)-(+)-CH(Me)(Ph) (**6**), (*R*)-(−)-CH(Me)(Et) (**7**), (*S*)-(−)-CH(Me)(1-naphthyl) (**8**)) (Scheme 2). All the reactions are generally fast even at room temperature, as shown by an immediate color change from orange to light yellow. Only with the least basic amine, aniline (pK_a = 4.63),[32] does the reaction require 3 h to be complete.

The primary aminocarbene complex *fac,cis*-[(PNP)-$RuCl_2${C(NH_2)(CH_2Ph)}] (**9**) is prepared by stirring a $CHCl_3$ solution of **2** for 30 min under a NH_3 atmosphere, followed by overnight reflux under nitrogen.

Compounds **3**−**9** are canary yellow crystalline solids with good solubility in polar organic solvents and excellent stability to moisture and oxygen. Their unequivocal characterization was achieved by means of standard spectroscopic techniques as well as elemental analyses, which were all consistent with the incorporation of one molecule of amine into the complex framework. Selected NMR and IR data are given in the Experimental Section. Briefly, all the IR spectra contain a broad and weak absorption in the N−H stretching region (3466−3440 cm^{-1}), while the primary aminocarbene **9** shows two bands at slightly lower wavenumbers (3383, 3276 cm^{-1}).

Indicative of a facial arrangement of the PNP ligand, the $^{31}P\{^1H\}$ NMR spectra in $CDCl_3$ show singlet resonances from 53.36 to 48.03 ppm.[2,24,33,34] The ^{31}P NMR signals do not vary with the temperature from +20 to −110 °C (in a $CDCl_3/CD_2Cl_2$ mixture), which indicates a rapid rotation of the carbene ligand around the Ru−C axis irrespective of the bulkiness of the N-substituent. The existence of a low-energy rotational barrier about the Ru−C bond in carbene and vinylidene derivatives has several precedents and is consistent with a substantial degree of Ru−C single bond.[35] As a consequence, structures containing a C−N double bond should significantly contribute to the description of the aminocarbenes **3**−**9**. Indeed, the different chemical shifts exhibited by the hydrogens of the NH_2 group in **9** support this hypothesis. Due to the presence of a chiral substituent on the aminocarbene ligand, the $^{31}P\{^1H\}$ NMR spectra of **6**−**8** show slightly perturbed second-order AB splitting patterns with homonuclear geminal coupling constants $^2J_{PP}$ equal to ca. ∼29 Hz. In the chiral aminocarbenes **6**−**8**, the hydrogen atoms of the benzyl substituent are diastereotopic and thus give rise to an AB multiplet in the ^1H NMR spectra. In contrast, the achiral derivatives **3**−**5** and **9** show only a singlet resonance for the benzylic protons. Irrespective of the presence of a chiral N-substituent, the NH proton appears as either a broad hump or a broad doublet ($^3J_{HH}$ ≈ 9 Hz) (δ_{NH} 12.35−10.62) due to coupling to the quadrupolar nitrogen nucleus ($I(^{14}N) = 1$).[36] The NH_2−

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(32) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley-Interscience: New York, 1972; p 59.
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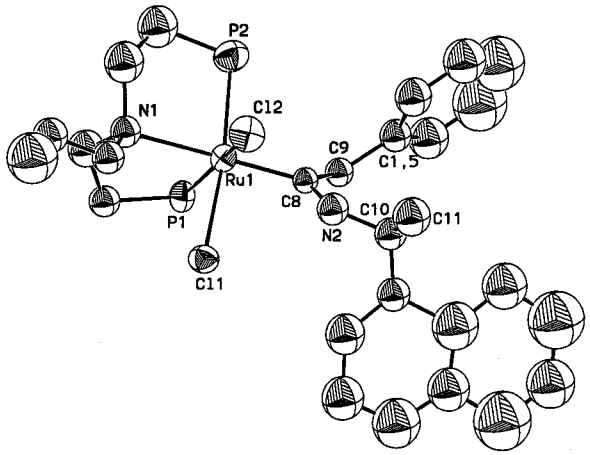

Figure 1. ORTEP drawing of complex **8**. For the sake of clarity the phenyl rings in the PNP ligand have been omitted.

carbene **9** exhibits two slightly downfield shifted resonances (δ_{NH_2} 10.14 and 8.34).[37]

The $^{13}C\{^1H\}$ NMR spectra of **3**−**9** confirm the presence of a carbene ligand trans to the nitrogen donor atom. The carbene carbons appear as triplets with chemical shifts ($\delta_{Ru=C}$ 265−251) and coupling constants in the expected range for ruthenium(II) Fischer-type carbenes ($^2J_{CP} \approx 11$ Hz).[2,37,38] All the proton and carbon resonances of the aminocarbene complexes were unambiguously assigned by means of HMQC (^1H,^{13}C-heterocorrelated 2D-NMR spectra), ^1H,^1H-2D COSY NMR, and $^{13}C\{^1H\}$ DEPT-135 NMR experiments.

With the exception of piperidine, which gives *fac,cis*-[(PNP)$RuCl_2${$C(NC_5H_{10})(CH_2Ph)$}] (**10**), secondary and tertiary amines do not form aminocarbene products by reaction with **2**. Since piperidine is indeed the least sterically demanding secondary amine,[39] it is reasonable to conclude that the formation of the aminocarbene group is also controlled by steric effects (vide infra). The chemical and physical properties of the tertiary aminocarbene complex **10** do not differ from those of the germane compounds bearing NHR or NH_2 substituents on the carbene carbon and thus do not deserve any additional comment.

Crystal Structure of *fac,cis*-[(PNP)$RuCl_2${C(NH-(*S*)-(−)-CH(Me)(1-naphthyl))(CH_2Ph)}] (8). To confirm the stereochemistry of the present aminocarbene complexes and to collect further geometrical information on this class of compounds, an X-ray analysis was carried out on a single crystal of the chiral complex **8**. An ORTEP drawing of the complex is shown in Figure 1 with the atomic numbering scheme. A list of selected bond distances and angles is given in Table 2.

The coordination geometry of the ruthenium atom may be described as a slightly distorted octahedron with the aminodiphosphine ligand occupying three facial coordination sites. Two chloride ligands and one aminocarbene group complete the coordination polyhedron.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 8

Ru−P1	2.285(5)	Ru−C8	1.99(2)
Ru−P2	2.292(6)	N2−C8	1.32(2)
Ru−Cl1	2.472(5)	N2−C10	1.46(2)
Ru−Cl2	2.478(5)	C8−C9	1.51(2)
Ru−N1	2.37(2)		
Cl1−Ru−Cl2	83.4(2)	P2−Ru−N1	83.3(4)
P1−Ru−P2	99.6(2)	Cl1−Ru−N1	89.2(4)
P1−Ru−Cl1	83.5(2)	Cl2−Ru−N1	87.1(4)
P1−Ru−C12	163.7(2)	Cl1−Ru−C8	89.9(5)
P2−Ru−C11	171.4(2)	Cl2−Ru−C8	90.4(5)
P2−Ru−C12	92.1(2)	Ru−C8−N2	117(1)
P1−Ru−C8	99.2(5)	Ru−C8−C9	127(1)
P2−Ru−C8	97.6(5)	N2−C8−C9	116(1)
P1−Ru−N1	83.1(4)		

The two chloride ligands are cis to each other and trans to the two phosphorus atoms of the PNP ligand. The carbene ligand is located trans to the nitrogen atom.

The principal geometrical features of **8** are in line with those found for other ruthenium(II)−PNP complexes.[22−24,41] The most evident distortion from the idealized geometry is the bending of the PPh_2 wings toward the N(1) atom (P(1)−Ru−N(1) = 83.1(4)°; P(2)−Ru−N(1) = 83.3(4)°) and toward the two chlorine atoms (P(1)−Ru−P(2) = 99.6(2)°). A similar distortion was observed in *fac,cis*-[(PNP)$RuCl_2$(CO)].[24] In keeping with the smaller trans influence of the aminocarbene vs CO, the Ru−N(1) separation (2.37(2) Å) is larger than that found in the CO complex (2.310(8) Å).[24]

The bond lengths and angles pertaining to the aminocarbene ligand are typical for Fischer-type carbene complexes[38] and quite similar to those found in CpRuI(CO){C(NHMe)P}, which was the only Ru(II) aminocarbene complex to have been authenticated by X-ray methods.[40] The angles around the carbene carbon C(8) are 117(1)° (Ru−C(8)−N(2)), 127(1)° (Ru−C(8)−C9)), and 116(1)° (N(2)−C(8)−C(9)), which sum up to 360°, reflecting the sp^2 hybridization at the carbon C(8). The naphthyl substituent on the carbon stereocenter lies in the plane that bisects the two chlorine atoms. The coordination plane of the carbene ligand (Ru−C(8)−C(9)−N(2), rms deviation 0.0095) is twisted by ca. 41° from the plane N(1)−Cl(2)−C(8)−P(1)−Ru (rms deviation 0.0292). This deformation, which reflects the presence of a bulky group, has already been observed in Fischer-type carbenes bearing sterically demanding substituents.[38]

Mechanistic Studies of the Hydroamination of the Vinylidene Ligand. Monitoring the reaction between **2** and primary amines by $^{31}P\{^1H\}$ NMR spectroscopy provides evidence of a new mechanism for the hydroamination of metal vinylidenes by primary amines. The formation of the PNP aminocarbene complexes indeed requires 2 equiv of amine to occur and involves a mechanism in which one molecule of amine deprotonates the vinylidene C_β carbon atom, while a second molecule coordinates the metal center prior to be transferred onto the C_α carbon atom of a σ-alkynyl intermediate (Scheme 3).

Experimental evidence of this mechanism was provided by an in situ NMR study carried out as follows.

(37) Gamasa, M. P.; Gimeno, J.; Martín-Vaca, B.; Borge, J.; García-Granda, S.; Perez-Carreño, E. *Organometallics* **1994**, *13*, 4045.

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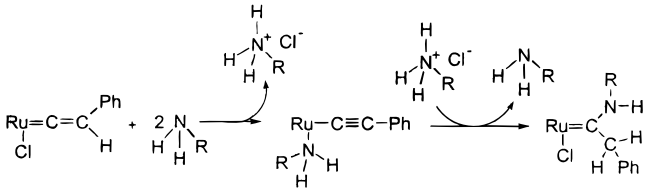
(41) Bianchini, C.; Masi, D.; Peruzzini, M.; Romerosa, A.; Zanobini, F. *Acta Crystallogr.* **1996**, *C52*, 1973.

Scheme 3



One equivalent of propylamine was syringed into an NMR tube containing a CD_2Cl_2 solution of **2** at 20 °C. A ^{31}P NMR spectrum was immediately acquired, showing the vinylidene resonance at 47.9 ppm to have almost disappeared with formation of a new AB spin system centered at 58.0 ppm (δ_A 58.89, δ_B 57.13, $^2J(P_AP_B)$ = 34.9 Hz). The addition of a second equivalent of amine completed the transformation of **2** into this new product and also led to the formation of a very small amount of the aminocarbene **3** (singlet at 51.31 ppm). With time this latter complex became the only PNP complex in solution.

On the basis of the in situ NMR evidence, the intermediate product with the AB pattern was isolated by simply scaling up the spectroscopic experiment and identified as the complex *fac*-[(PNP)RuCl(C≡CPh)(NH_2-$CH_3CH_2CH_2$)] (**11**), containing cis phenylethynyl and propylamine ligands. The analogous derivatives *fac*-[(PNP)RuCl(C≡CPh)(NH_2R)] (R = cyclo-C_6H_{11} (**12**), (*R*)-(−)-CH(Me)Et (**13**), H (**14**)) were similarly synthesized. A few examples of ruthenium amine−alkynyl complexes have been reported,[42] and the structure of [(NH_3)Ru(C≡CPh)(dppe)$_2$]PF_6 (dppe = $Ph_2PCH_2CH_2PPh_2$) has also been determined by an X-ray analysis.[43] Salient spectroscopic features of the PNP compounds **11**−**14** are (i) a strong and sharp ν(C≡CPh) absorption at ca. 2055 cm^{-1} in the IR spectrum,[44] (ii) the chemical inequivalence of the two PPh_2 groups (^{31}P NMR AB system) originated by the substitution of one chloride ligand by amine, and (iii) the appearance in the ^1H NMR spectrum of a broad resonance in the region of amine N−H groups.[18] The NH_2R ligands in **11**−**14** are quite labile and can readily be displaced by different σ- and π-donor ligands. As an example, treatment of a CH_2Cl_2 solution of any (phenylethynyl)amine complex with CO gives the known phenylethynyl−carbonyl complex *fac*-[(PNP)-RuCl(C≡CPh)(CO)] in almost quantitative yield.[24]

Consistent with the release of 1 equiv of alkylammonium chloride upon reaction of **2** with the first equivalent of primary amine, the use of aqueous biphasic media ($H_2O/CHCl_3$ or H_2O/CH_2Cl_2; 1:1 v/v) was found to greatly improve both the yield and purity of the amine−alkynyl complexes **11**−**14**. Once separated from the organic phases containing the ruthenium products, the aqueous phases were concentrated under vacuum until the alkylammonium chlorides separated. On the basis of this simple experiment, one may readily conclude that the formation of the aminocarbene complexes **3**−**9** involves a preliminary acid/base reaction between the first equivalent of amine and the vinylidene **2** (formal dehydroalogenation reaction)[45] to give five-coordinate phenylethynyl Ru(II) complexes and alkylammonium chlorides. At this point, the second equivalent of amine can occupy the vacant coordination site and ultimately generate the octahedral (phenylethynyl)-primary amine derivatives **11**−**14**. These complexes are stable in solution and *can be isolated in the solid state provided that alkylammonium chloride is removed from the reaction medium*. In fact, if not removed, the NH_3R^+ cations quickly reprotonate the alkynyl ligand. As a result, transient *cis*-amine−vinylidene complexes are formed which spontaneously degrade to the thermodynamically stable aminocarbene products via intramolecular attack by the amine onto the electrophilic C_α carbon atom of the vinylidene group. No amine−vinylidene intermediate was seen by NMR spectroscopy, however.

The occurrence of an intramolecular amine-migration step has been proved by means of several cross experiments. As an example, an isolated sample of the phenylethynyl−*n*-propylamine complex **11** was treated in an NMR tube with cyclohexylammonium chloride. After the tube was shaken for a few seconds, a ^{31}P NMR spectrum showed that the aminocarbene **3** was quickly and selectively formed. Vice versa, when *n*-propylammonium chloride was added to a solution of **12**, the aminocarbene **5** was selectively obtained. Analogous experiments with various combinations of phenylethynyl−amine complexes and alkylammonium chlorides confirmed that *the nucleophilic attack at the vinylidene C_α atom is selectively brought about by the coordinated amine*.[46]

In keeping with the overall mechanistic picture given in Scheme 3, the addition of gaseous HCl (ca. 1 equiv) to a CD_2Cl_2 solution of any phenylethynyl−amine complexes led to the quantitative formation of the corresponding aminocarbene. The protonation of the alkynyl ligand in **11**−**14** is thus a mandatory step to generate the vinylidene group susceptible to attack by the cis amine ligand. The occurrence of an intramolecular nucleophilic attack by the coordinated amine also accounts for the fact that only nonsterically demanding amines with good coordinating ability such as NH_3, primary amines, and piperidine react with **2,** yielding aminocarbene complexes. Secondary and tertiary amines do not coordinate the ruthenium center, although they are still able to deprotonate the vinylidene ligand in **2** to σ-alkynyl. From this reaction, however, no product was isolated unless CO was added. In this case, the known phenylethynyl−carbonyl complex *fac*-[(PNP)-RuCl(C≡CPh)(CO)] (**15**) was quantitatively formed.[24]

Transformation of the Aminocarbene Ligands into Isonitrile Ligands and Toluene. The aminocarbene complexes **3**−**7** transform into the corresponding isonitrile derivatives *fac,cis*-[(PNP)$RuCl_2$(C≡NR)] (R =

(42) (a) Touchard, D.; Haquette, P.; Guesmi, S.; Le Pichon, L.; Daridor, A.; Toupet, L.; Dixneuf, P. H. *Organometallics* **1997**, *16*, 3640. (b) Rappert, T.; Yamamoto, A. *Organometallics* **1994**, *13*, 4984. (c) Nürnberg, O.; Werner, H. *J. Organomet. Chem.* **1993**, *460*, 163. (d) Touchard, D.; Guasmi, S.; Le Pichon, L.; Daridor, A.; Dixneuf, P. H. *Inorg. Chim. Acta* **1998**, *280*, 118.

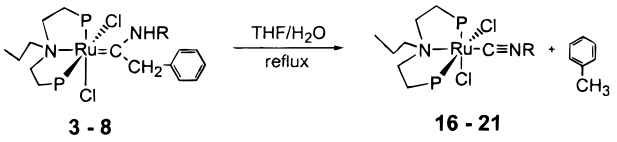
(43) Touchard, D.; Morice, C.; Cadierno, V.; Haquette, P.; Toupet, L.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1994**, 859.

(44) See for example: Bianchini, C.; Meli, A.; Peruzzini, M.; Vacca, A.; Laschi, F.; Zanello, P.; Ottaviani, F. M. *Organometallics* **1990**, *9*, 360.

(45) (a) Heyn, R. H.; Caulton, K. G. *J. Am. Chem. Soc.* **1993**, *115*, 3354. (b) Slugovc, C.; Mauthner, K.; Kacetl, M.; Mereiter, K.; Schmid, R.; Kirchner, K. *Chem. Eur. J.* **1998**, *4*, 2043.

(46) The conversion of vinylidene to hydroxycarbene by intramolecular attack of water through a similar mechanism has been proposed for the reaction of **2** with water.[2]

Scheme 4



R = $CH_3CH_2CH_2$, **16**; Ph, **17**; *cyclo*-C_6H_{11}, **18**; *(R)-(+)*-CH(Me)Ph, **19**; *(R)-(+)*-CH(Me)Et, **20**; *(R)-(+)*-CH(Me)(1-naphthyl) **21** (reflux in monoglyme/H_2O)

$CH_3CH_2CH_2$ (**16**), Ph (**17**), cyclo-C_6H_{11} (**18**), (*R*)-(+)-CH(Me)Ph (**19**), (*R*)-(−)-CH(Me)Et (**20**)) upon overnight reflux in THF/H_2O mixtures (20:1 v/v). A medium with a higher boiling point (monoglyme/H_2O) was employed to convert the aminocarbene complex **8** bearing the bulky (*S*)-(−)-1-(1-naphthyl)ethyl substituent. Each thermolysis was accompanied by the quantitative formation of free toluene and required the presence of some water in the reaction medium to occur (Scheme 4). Indeed, in truly anhydrous solvents, all the aminocarbene complexes were stable even under prolonged reflux. In contrast to this general behavior, both the primary aminocarbene **9** and the tertiary aminocarbene **10** did not convert to the isocyanide derivative even after prolonged heating in wet THF, monoglyme, or DMSO.

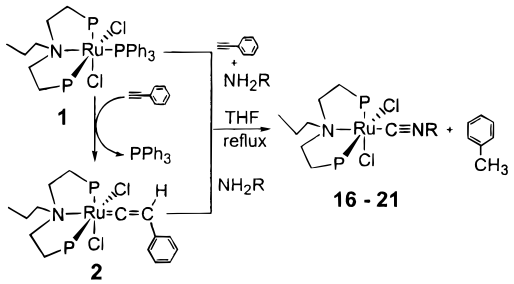
The isonitrile complexes **16**−**20** were straightforwardly authenticated by standard spectroscopic techniques. Diagnostic features are a strong C≡N band at ca. 2100 cm^{-1} in the IR spectra and a triplet resonance ($^2J_{CP} \approx 16$ Hz) at ca. 160 ppm in the $^{13}C\{^1H\}$ NMR spectra due to the C≡N carbon atom. No coupling of the latter nucleus to the ^{14}N nucleus was observed.[47] The phenylisonitrile complex **17** shows a slightly red-shifted CN absorption (ν(CN) 2062 cm^{-1}) and a slightly deshielded CN resonance (δ 171.4), indicating a significant π-electron delocalization over the N-bonded phenyl ring.

The $^{31}P\{^1H\}$ NMR spectra contain signals in the typical range for *fac,cis*-PNP metal complexes (ca. 59 ppm) and consist of either a singlet (**16**−**18**) or an AB spin system (**19**−**21**) depending on the achiral or chiral nature of the isonitrile substituent, respectively.

A one-pot synthesis of the isonitrile complexes **16**−**21** has also been developed, starting from reagent grade THF (or monoglyme for **21**) containing the precursor *mer,trans*-[(PNP)$RuCl_2(PPh_3)$] (**1**), phenylacetylene, and a primary amine among those employed in this work (Scheme 5). In light of the well-known reactivity of **1** with terminal alkynes,[24] there is little doubt that **2** is the first species to be formed via 1-alkyne to vinylidene tautomerization.[11,48] From the vinylidene intermediate, each isonitrile derivative is then obtained following the reaction sequence alkynyl−amine → aminocarbene → isonitrile.

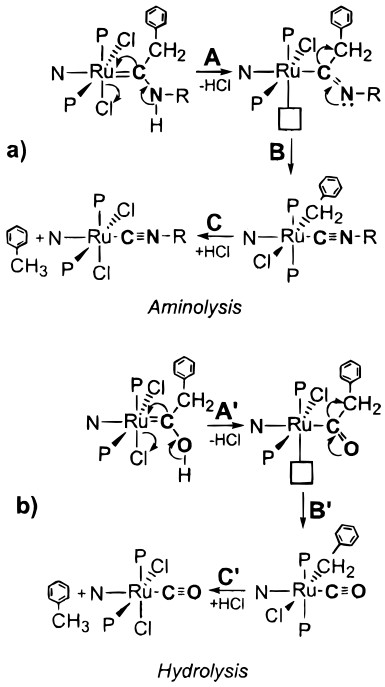
Mechanistic Studies of the Thermolysis of the Aminocarbene Ligands. A mechanism accounting for

Scheme 5



R = $CH_3CH_2CH_2$, **16**; Ph, **17**; *cyclo*-C_6H_{11}, **18**; *(R)-(+)*-CH(Me)Ph, **19**; *(R)-(+)*-CH(Me)Et, **20**; *(R)-(+)*-CH(Me)(1-naphthyl) **21** (reflux in monoglyme/H_2O)

Scheme 6



the formation of the isonitrile complexes *fac,cis*-[(PNP)-$RuCl_2$(C≡NR)] from the aminocarbene precursors *fac,-cis*-[(PNP)$RuCl_2${(NHR)(CH_2Ph)}] is proposed in Scheme 6a. The mechanism involves three steps: thermal elimination of HCl from the aminocarbene ligand to give a coordinatively unsaturated iminoacyl derivative (**A**), migration of the benzyl substituent from the iminoacyl group to the metal (this step may be seen as phenylisonitrile deinsertion) (**B**), and protonolysis of the Ru(II)−alkyl bond by the previously generated HCl (**C**). Through this final step, toluene is formed and the octahedral geometry around the metal is restored by chloride coordination. Traces of water in the reaction media are most likely necessary to favor both the deprotonation from the aminocarbene complexes and the subsequent protonation of the alkynyl ligand in the phenylethynyl−amine intermediates.

A quite similar mechanism has recently been reported for the hydrolysis of the vinylidene complex **2** to give *fac,cis*-[(PNP)$RuCl_2$(CO)] and toluene (Scheme 6b).[2] The identification of the principal intermediates along the hydrolysis pathway, in particular the acyl complex (**A′**) and the benzyl−carbonyl species (**B′**), was achieved by means of independent reactions with isolated compounds. This same strategy has been employed to gain

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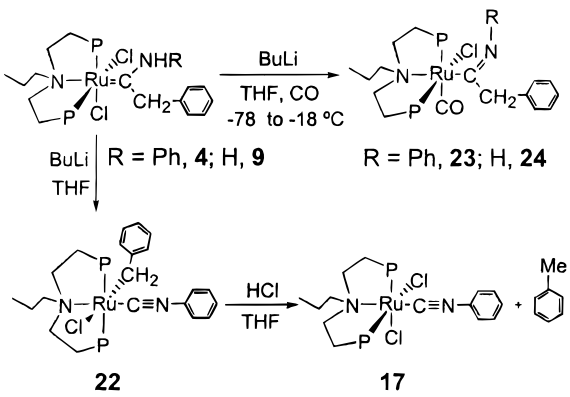
(48) Key references on metal-assisted alkyne to vinylidene tautomerization include: (a) Werner, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1077. (b) Bianchini, C.; Peruzzini, M.; Vacca, A.; Zanobini, F. *Organometallics* **1991**, *10*, 463. (c) Fryzuk, M. D.; Huang, L.; Mcmanus, N. T.; Paglia, P.; Rettig, S. J.; White, G. S. *Organometallics* **1992**, *11*, 2979. (d) Lumprey, J. R.; Selegue, J. P. *J. Am. Chem. Soc.* **1992**, *114*, 5518. (e) Bianchini, C. Marchi, A.; Marvelli, L.; Peruzzini, M.; Romerosa, A.; Rossi, R.; Vacca, A. *Organometallics* **1995**, *14*, 3203. (f) de los Ríos, I.; Jiménez Tenorio, M.; Puerta, M. C.; Valerga, P. *J. Am. Chem. Soc.* **1997**, *119*, 6529.

Scheme 7



mechanistic insight into the transformation of *fac,cis*-[(PNP)$RuCl_2${C(NHPh)(CH_2Ph)}] (**4**) into *fac,cis*-[(PNP)-$RuCl_2$(CNPh)] (**17**).

Monitoring the thermolysis of **4** by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy in either THF-d_8 or $CDCl_3$ did not show any intermediate along the transformation into **17**, even at the lowest temperature at which the degradation of the aminocarbene became visible (ca. 40 °C). The absence of detectable intermediates suggested that the degradation of the iminoacyl complex and the subsequent reaction of the benzyl−isonitrile derivative with HCl are much faster than the elimination of HCl from the aminocarbene (rate-determining step). In an attempt to intercept the iminoacyl and/or benzyl−isonitrile intermediates, the elimination of HCl from **4** was performed in the presence of reactants capable of stabilizing either intermediate. In a first attempt, **4** in THF was treated with ^{n}BuLi at 0 °C. As a result, the benzyl−phenylisonitrile complex *mer,trans*-[(PNP)RuCl-(CH_2Ph)(C≡NPh)] (**22**) was selectively obtained. This latter compound indeed gave toluene and **17** upon reaction with HCl even at very low temperature (−78 °C) (Scheme 7).

When the reaction between **4** and ^{n}BuLi was followed by variable-temperature NMR spectroscopy in THF-d_8, no intermediate species was seen prior to the selective formation of **22**, indicating that the conversion of the iminoacyl intermediate to the benzyl−isonitrile product is a downhill process, faster than the NMR time scale. In an attempt to intercept the iminoacyl complex, the reaction between **4** and ^{n}BuLi was carried out at low temperature (−78 °C) in the presence of a positive pressure of CO. As result, the iminoacyl complex was successfully intercepted and isolated as the CO adduct *fac*-[(PNP)RuCl{C═NPh(CH_2Ph}(CO)] (**23**).

Both **22** and **23** have been characterized by analytical and spectroscopic techniques. In particular, **22** was readily authenticated by comparison with the known complex *mer,trans*-[(PNP)RuCl(CH_2Ph)(CO)].[2] The presence of a phenylisonitrile ligand in **22** is shown by a ν(C≡N) band at 2050 cm^{-1} and by a triplet at 160.8 ppm in the ^{13}C NMR spectrum clearly due to the isonitrile carbon atom. A triplet at 10.31 ppm was assigned to the benzyl carbon on the basis of a DEPT-135 experiment. It is worth mentioning that the fragmentation of the aminocarbene group in **4** into benzyl and isonitrile ligands is associated with the isomerization of the PNP ligand from *fac* to *mer*.[2,49] Unlike **22**, the carbonyl complex **23** is stable in the solid state (ν(CO) 1920 cm^{-1}, ν(C═N) 1643 cm^{-1}) but decomposes in solution in the absence of a protective CO atmosphere. The solution structure of **23** was thus determined at −25 °C by multinuclear NMR spectroscopy in CD_2Cl_2 solution saturated with CO. The presence of a *fac*-PNP ligand in the complex is shown by a low-field AB ^{31}P pattern (δ_A 66.98, δ_B 30.01, $^2J(P_AP_B)$ = 8.7 Hz) with P_B being the phosphorus atom trans to CO.[50] The ^{13}C NMR spectrum contains two doublets of doublets for both the CO and C═N carbon nuclei (215.0 ppm, dd, $^2J(CP_{trans})$ = 101.0 Hz, $^2J(CP_{cis})$ = 8.9 Hz and 208.0 ppm, dd, $^2J(CP_{cis})$ = 15.8, 10.7 Hz, respectively). The chemical shift of the iminoacyl carbon atom is strongly indicative of an η^1-iminoacyl ligand.[51] The benzylic protons are diastereotopic because of the chiral nature of the metal center and give rise to a complex ABX pattern due to coupling to each other and to one phosphorus atom.

Quite similar spectroscopic characteristics are exhibited by the iminoacyl−carbonyl complex *fac*-[(PNP)-RuCl{C═NH(CH_2Ph}(CO)] (**24**), obtained by reaction of the primary aminocarbene **9** with ^{n}BuLi in the presence of CO. In the ^1H NMR spectrum, the C═N*H* hydrogen appears as a doublet at 9.09 ppm with $^4J(HP)$ = 27.3 Hz.

Besides incorporating all the experimental observables accumulated in the course of this study, the mechanism outlined in Scheme 6a also accounts for the thermal stability of the tertiary aminocarbene complex **10**. In this compound, the carbene nitrogen atom does not bear hydrogens and thus cannot be deprotonated to generate the iminoacyl group. Less straightforward is the explanation for the thermal stability of the primary aminocarbene **9**. Indeed, this complex contains a C═NH group and thus might undergo the thermal elimination of HCl to give the hydrogen isocyanide complex *fac,cis*-[(PNP)$RuCl_2$(C≡NH)] via iminoacyl and benzyl−hydrogen isocyanide intermediates. The fact that this does not happen might be due to both kinetic and thermodynamic factors. In particular, we suggest that the inverse reaction of the iminoacyl intermediate by HCl to regenerate **9** is faster than its degradation to the benzyl−hydrogen isocyanide complex. As a matter of fact, the iminoacyl−carbonyl complex **24** is quantitatively produced from **9** when HCl is neutralized by ^{n}BuLi in the presence of CO (Scheme 7). In the absence of CO, butane and LiCl were still formed but no stable ruthenium complex was obtained, most likely because of the inherent instability of the CNH molecule.

Finally, it is worth mentioning that the thermolytic degradation of aminocarbene ligands to isonitriles has no precedent in the literature.[52] To the best of our knowledge, the only related process may be identified in the transformation of the iron vinylidene complex

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(52) The addition of amine across alkyne triple bonds gives enamines that, similarly to enols, tautomerize to the more stable imines. No rearrangement of imine to nitrile or isonitriles has ever been reported, however.

$[Cp(CO)(PPh_3)Fe{=}C{=}CH_2]BF_4$ into the acetonitrile derivative $[Cp(CO)(PPh_3)FeN{\equiv}CCH_3]BF_4$ through the condensation of the vinylidene ligand with hydrazines, followed by an "organometallic" Beckmann-type rearrangement of a hydrazino−carbene intermediate.[53]

Conclusions

In conclusion, an unforeseen conversion of ruthenium vinylidene complexes to ruthenium isonitrile derivatives via aminocarbene intermediates has been carried out. From a formal viewpoint, the formation of the isonitrile complexes may be described as either a metal-assisted aminolysis of the alkyne triple bond[54] or a metal-assisted oxidation of amines.[19] The strong coordination of the isonitrile ligands to ruthenium, however, represents a drawback of the present procedure, as it precludes any chance of catalytic production. Nevertheless, the method is clean and selective and also provides access to very rare examples of chiral isonitrile ligands, starting from commercially available, optically pure amines.[55]

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Supporting Information Available: Tables containing crystal data and data collection parameters, positional parameters, anisotropic temperature factors, and bond distances and angles for **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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