C−C Bond Formation between Vinylidene and Alkynyl Ligands at Ruthenium(II) Leading to either Enynyl or Dienynyl Complexes†

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The Ru(II) complex *mer,trans*-(PNP)$RuCl_2(PPh_3)$ (**1**) reacts with either phenylacetylene or *p*-tolylacetylene to give *fac,cis*-(PNP)$RuCl_2${C═CH(R)} (R = Ph (**2**), *p*-tolyl (**3**)) in refluxing tetrahydrofuran (THF) and *mer,trans*-(PNP)$RuCl_2${C═CH(R)} (R = Ph (**4**), *p*-tolyl (**5**)) in a refluxing THF/EtOH mixture (1:2 v:v) [PNP = $CH_3CH_2CH_2N(CH_2CH_2PPh_2)_2$]. The *fac,cis* vinylidene complexes **2** and **3** react with an excess of LiC≡CPh converting to the σ-alkynyl−η^3-enynyl complexes *anti,mer*-(PNP)Ru(C≡CPh){η^3-PhC_3═CH(Ph)} (**8**) and *anti,mer*-(PNP)-Ru(C≡CPh){η^3-PhC_3═CH(*p*-tolyl)} (**9**), respectively. Conversely, treatment of the *mer,trans* vinylidene isomers with an excess of LiC≡CPh, followed by addition of a primary alcohol, exclusively gives the σ-alkynyl−η-dienynyl complexes *mer*-(PNP)Ru(C≡CPh){η-PhC═C-(C≡CPh)CH═CH(R)} (R = Ph, **12**; R = *p*-tolyl, **13**). Single-crystal X-ray analyses have been carried out on **8** and **13**. In both compounds the coordination geometry around the Ru atom approximates an octahedron with three positions taken by a *mer* PNP ligand and one position taken by a phenylethynyl group. The coordination sphere around the metal center is completed by an η^3-1,4-diphenylbut-3-en-1-ynyl ligand in **8** and by a 1-*p*-tolyl-3-(phenylethynyl)-4-phenylbuta-1(*E*),3(*Z*)-dien-4-yl ligand in **13**. The latter ligand essentially uses the C_1 carbon atom to bind the metal, although a weak bonding interaction may be envisaged also with the alkynyl substituent in the 3-position. A single-crystal X-ray analysis has also been carried out on the octahedral *fac,cis*-(PNP)$RuCl_2$(CO) complex obtained by treatment of the vinylidenes **2** and **3** with molecular oxygen. The influence of the bonding mode of the PNP ligand on the different reactivity shown by the *fac* and *mer* vinylidene complexes toward LiC≡CPh is discussed in light of a multiform experimental study (X-ray structure determinations, multinuclear NMR spectroscopy, deuterium- and *p*-tolyl-labeling experiments, independent reactions with isolated compounds).

There have been several breakthroughs recently regarding the mechanism by which iron group metal complexes promote the coupling of 1-alkynes.[1] The dimerization to butenynyl complexes or, more rarely, to butatrienyl isomers apparently occurs at iron, ruthenium, and osmium by C−C bond formation between alkynyl and vinylidene ligands.[1] The C_4 unsaturated products are eventually liberated from intermediate (σ-organyl)metal species by σ-bond metathesis with an additional 1-alkyne molecule.

In contrast to the mechanistic progress made in the elucidation of the C−C bond-forming step, little is known about the factors governing the formation of either butenynyl or butatrienyl ligands.[1b,j,2] Similarly, the propensity of iron group metals to favor the dimerization of 1-alkynes over higher oligomerization has still eluded a detailed explanation.

The results reported in this paper confirm that alkynyl(vinylidene) ruthenium(II) complexes are key intermediates to C−C coupling reactions involving 1-alkynes and show that subtle factors, such as the bonding mode of an ancillary ligand, can tip the balance in favor of the formation of either enynyl or dienynyl complexes (dimerization and trimerization of 1-alkynes, respectively).

In this work, it is also shown that a common synthetic route to butenynyl ruthenium(II) complexes, *i.e.* the metathesis reaction of chloride−vinylidene complexes

† Dedicated to Professor Max Herberhold on the occasion of his 60th birthday.

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with acetylide salts, may not mechanistically be as simple as it appears.

Experimental Section

General Procedures. Tetrahydrofuran (THF) and dichloromethane were purified by distillation under nitrogen over $LiAlH_4$ and P_2O_5, respectively. Phenylacetylene and *p*-tolylacetylene were purchased from Aldrich; their purity was checked by ^1H NMR spectroscopy, and when necessary, they were distilled under nitrogen 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) or *n*-pentane before being dried in a stream of nitrogen. The ligand $CH_3CH_2CH_2N(CH_2CH_2PPh_2)_2$ (PNP)[3] and the complex *mer,trans*-(PNP)$RuCl_2(PPh_3)$[4] (**1**) were prepared as described in the literature. Lithium phenylacetylide (1.0 M solution in THF) was purchased from Aldrich. Lithium *p*-tolylacetylide was prepared just prior to use by reacting 1 equiv of *n*-BuLi with *p*-tolylacetylene in THF at 0 °C under nitrogen.[5] Deuterated solvents for NMR measurements (Merck) were dried over molecular sieves. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian VXR 300, Bruker AC 200P, or Bruker AVANCE DRX 500 spectrometer 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 ACP 200 spectrometer. $^1H,^{13}C$-2D HETCOR NMR experiments were recorded on either the Bruker ACP 200 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). The $^1H,^1H$-2D COSY NMR experiments were routinely conducted on the Bruker 200 ACP instrument in the absolute magnitude mode using a 45 or 90° pulse after the incremental delay. The $^1H,^1H$-2D COSY NMR experiments on the butenynyl and dienynyl complexes were acquired on the AVANCE DRX 500 Bruker spectrometer using the phase-sensitive TPPI mode with double quantum filter. $^1H,^1H$-2D NOESY NMR experiments were conducted on the same instrument in the phase-sensitive TPPI mode in order to discriminate between positive and negative cross peaks. $^{31}P\{^1H\}$ NMR spectra were recorded on either the Varian VXR 300 or Bruker AC 200P 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 ACP 200 instrument equipped with a 5-mm inverse probe and a BFX-5 amplifier device using the wideband 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 *fac,cis*-(PNP)$RuCl_2${C=CH(Ph)} (2). Neat phenylacetylene (0.50 mL, 4.50 mmol) was pipetted into a well-stirred THF (50 mL) slurry of *mer,trans*-(PNP)$RuCl_2(PPh_3)$ (**1**) (0.46 g, 0.50 mmol), and the mixture was refluxed with stirring for 1 h. During this time, all **1** dissolved to produce an orange solution which, after cooling to room temperature, separated pale orange needle crystals of **2**. Yield: 92%. Anal. Calcd for $C_{39}H_{41}NCl_2P_2Ru$: C, 61.83; H, 5.45; N, 1.85; Cl, 9.36. Found: C, 61.72; H, 5.51; N, 1.69; Cl, 9.17. IR (cm^{-1}): ν(C=C) 1644 (m), 1615 (s); phenyl reinforced vibration 1593. $^{31}P\{^1H\}$ NMR (22 °C, $CDCl_3$, 81.01 MHz): δ 47.92 (s). ^1H NMR (22 °C, $CDCl_3$, 200.13 MHz): δ(C=C*H*) 5.32 [t, ^4J(HP) 3.1 Hz]. $^{13}C\{^1H\}$ NMR (40 °C, DMF-d_7, 50.32 MHz): δ(Ru=*C*=CH) 356.31 [t, ^2J(CP) 17.2 Hz], δ(Ru=C=*C*H) 113.37 [t, ^3J(CP) 2.2 Hz], $\delta(CH_3CH_2CH_2N)$ 57.02 (s), $\delta(NCH_2CH_2P)$ 49.79 [vt, $N = J$(CP) + J(CP′) = 1.5 Hz], $\delta(NCH_2CH_2P)$ 31.86 [vt, $N = J$(CP) + J(CP′) = 12.3 Hz], $\delta(CH_3CH_2CH_2N)$ 14.52 (s), $\delta(CH_3CH_2CH_2N)$ 11.04 (s). Compound **2** is poorly soluble in common organic solvents, whereas it slightly dissolves in halogenated solvents.

Synthesis of *mer,trans*-(PNP)$RuCl_2${C=CH(Ph)} (4). Neat phenylacetylene (0.50 mL, 4.50 mmol) was pipetted into a well-stirred THF/EtOH (1:2 v:v, 50 mL) slurry of **1** (0.46 g, 0.50 mmol). The mixture was slowly brought to the boiling point and then refluxed with stirring for 14 h. During this time the orange color of **1** disappeared to give a pale solution which, after cooling to room temperature, separated ivory colored microcrystals of **4**. Addition of ethanol (50 mL) and concentration of the solution to half-volume under a stream of nitrogen completed the precipitation of **4**. Yield: 83%. Anal. Calcd for $C_{39}H_{41}NCl_2P_2Ru$: C, 61.83; H, 5.45; N, 1.85. Found: C, 61.66; H, 5.39; N, 1.58. IR (cm^{-1}): ν(C=C) 1650 (m), 1613 (s); phenyl reinforced vibration 1591. $^{31}P\{^1H\}$ NMR (23 °C, CD_2Cl_2, 81.01 MHz): 26.72 (s). ^1H NMR (23 °C, CD_2Cl_2, 200.13 MHz): δ(C=C*H*) 3.69 [t, ^4J(HP) 3.9 Hz]. $^{13}C\{^1H\}$ NMR (40 °C, DMF-d_7, 50.32 MHz): δ(Ru=*C*=CH) 356.69 [t, ^2J(CP) 15.4 Hz], δ(Ru=C=*C*H) 107.21 [t, ^3J(CP) 4.1 Hz], $\delta(CH_3CH_2CH_2N)$ 63.04 (s), $\delta(NCH_2CH_2P)$ 54.36 [vt, $N = J$(CP) + J(CP′) = 3.3 Hz], $\delta(NCH_2CH_2P)$ 26.23 [vt, $N = J$(CP) + J(CP′) = 11.8 Hz], $\delta(CH_3CH_2CH_2N)$ 14.04 (s), $\delta(CH_3CH_2CH_2N)$ 9.93 (s). Compound **4** is practically unsoluble in common organic solvents with the exception of halogenated solvents (CH_2Cl_2 or $CHCl_3$) in which it readily dissolves.

Synthesis of *fac,cis*-(PNP)$RuCl_2${C=CH(*p*-tolyl)} (3) and of *mer,trans*-(PNP)$RuCl_2${C=CH(*p*-tolyl)} (5). The two *p*-tolylvinylidene complexes **3** and **5** were prepared as described above for the corresponding phenylvinylidene complexes by using *p*-tolylacetylene (0.50 g, 4.30 mmol) in place of phenylacetylene.

***fac,cis*-(PNP)$RuCl_2${C=CH(*p*-tolyl)} (3).** Yield: 90%. Anal. Calcd for $C_{40}H_{43}NCl_2P_2Ru$: C, 62.34; H, 5.62; N, 1.82. Found: C, 62.07; H, 5.60; N, 1.74. IR (cm^{-1}): ν(C=C) 1632 (s), 1610 (m). $^{31}P\{^1H\}$ NMR (22 °C, $CDCl_3$, 121.42 MHz): 48.53 (s). ^1H NMR (22 °C, $CDCl_3$, 299.94 MHz): δ(C=C*H*) 5.30 [t, ^4J(HP) 4.0 Hz], $\delta[CH_3$(*p*-tolyl)] 2.40 (s). $^{13}C\{^1H\}$ NMR (22 °C, CD_2Cl_2, 50.32 MHz): δ(Ru=*C*=CH) 356.90 [t, ^2J(CP) 22.6 Hz], δ(Ru=C=*C*H) 114.80 [t, ^3J(CP) 2.1 Hz], $\delta(CH_3CH_2CH_2N)$ 58.01 (s), $\delta(NCH_2CH_2P)$ 50.95 [vt, $N = J$(CP) + J(CP′) = 1.8 Hz], $\delta(NCH_2CH_2P)$ 27.10 [vt, $N = J$(CP) + J(CP′) = 14.0 Hz, this multiplet has been computed using the parameters J_{CP} 28.9 Hz, $J_{CP'}$ −0.6 Hz, and $J_{PP'}$ 22.6 Hz], $\delta[CH_3$(*p*-tolyl)] 21.64 (s), $\delta(CH_3CH_2CH_2N)$ 15.92 (s), $\delta(CH_3CH_2CH_2N)$ 12.33 (s).

***mer,trans*-(PNP)$RuCl_2${C=CH(*p*-tolyl)} (5).** Yield: 78%. Anal. Calcd for $C_{40}H_{43}NCl_2P_2Ru$: C, 62.34; H, 5.62; N, 1.82. Found: C, 62.20; H, 5.55; N, 1.60. IR (cm^{-1}): ν(C=C) 1621 (s), 1603 (m). $^{31}P\{^1H\}$ NMR (22 °C, $CDCl_3$, 121.42 MHz): 26.68 (s). ^1H NMR (22 °C, CD_2Cl_2, 299.94 MHz): δ(C=C*H*) 3.66 [t, ^4J(HP) 3.8 Hz], $\delta[CH_3$(*p*-tolyl)] 2.29 (s). $^{13}C\{^1H\}$ NMR (22 °C, CD_2Cl_2, 50.32 MHz): δ(Ru=*C*=CH) 359.30 [t, ^2J(CP) 15.3 Hz], δ(Ru=C=*C*H) 108.13 [t, ^3J(CP) 4.0 Hz], $\delta(CH_3CH_2CH_2N)$ 63.91 (s), $\delta(NCH_2CH_2P)$ 55.39 [vt, $N = J$(CP) + J(CP′) = 3.3 Hz], $\delta(NCH_2CH_2P)$ 27.56 [vt, $N = J$(CP) + J(CP′) = 11.4 Hz], $\delta[CH_3$(*p*-tolyl)] 21.48 (s), $\delta(CH_3CH_2CH_2N)$ 15.27 (s), $\delta(CH_3CH_2CH_2N)$ 11.44 (s).

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***In Situ* NMR Studies.** A 5-mm NMR tube was charged under nitrogen with a solution of **1** (23 mg, 0.025 mmol) and a 5-fold excess of phenylacetylene in THF-d_8 (0.7 mL), flame sealed, and then placed into a NMR probe at 20 °C. The reaction was monitored by variable-temperature $^{31}P\{^1H\}$ NMR spectroscopy. The conversion of **1** to **3** started already at *ca.* 40 °C with no detection of intermediate species.

Attempted Isomerization of 2 (4) into 3 (5). A stirred solution of **2** (0.10 g, 0.13 mmol) in a THF/EtOH mixture (1:2 v:v, 10 mL) was heated at reflux temperature for 12 h and then cooled to room temperature. Concentration of the resulting solution under nitrogen gave quantitatively the starting compound. In a similar way, the *mer*-isomer **4** did not convert to the *fac*-isomer **3** upon prolonged reflux (12 h) in THF. No isomerization of either **2** or **4** was observed in refluxing toluene.

Thermolysis of 1. A 5-mm NMR tube was charged under nitrogen with a solution of **1** (20 mg, 0.022 mmol) in THF-d_8 (0.7 mL), flame sealed, and then placed into a NMR probe at 20 °C. The reaction was monitored by variable-temperature $^{31}P\{^1H\}$ NMR spectroscopy. The conversion of **1** to the known face-sharing bioctahedral complex $[Ru(\mu\text{-}Cl)_3(PNP)_2]Cl$[4] and free PPh_3 started already at *ca.* 60 °C.

Synthesis of *fac,cis*-(PNP)RuCl$_2$(CO) (6). A solid sample of **2** (0.20 g, 0.26 mmol) was dissolved in dichloromethane (30 mL) saturated with dioxygen. Addition of ethanol (20 mL) after 12 h, followed by partial removal of the solvent in vacuo, gave pale yellow crystals of the carbonyl complex **6**. Yield: 98%. GC-MS analysis of the reaction mixture showed the formation of *ca.* 1 equiv of benzaldehyde. Complex **6** can be prepared in similar yield from **5**. In this case, however, *p*-tolylaldehyde is formed. Anal. Calcd for $C_{32}H_{35}NCl_2OP_2Ru$: C, 56.23; H, 5.16; N, 2.05. Found: C, 56.14; H, 5.05; N, 1.90. IR (cm^{-1}): ν(C≡O) 1942 (s). $^{31}P\{^1H\}$ NMR (22 °C, CD_2Cl_2, 81.01 MHz): 58.27 (s). $^{13}C\{^1H\}$ NMR (22 °C, CD_2Cl_2, 50.32 MHz): δ(*C*≡O) 203.61 [t, ^2J(CP) 15.9 Hz], δ($CH_3CH_2CH_2N$) 58.60 (s), δ(NCH_2CH_2P) 52.69 (s), δ(NCH_2CH_2P) 27.08 [vt, $N = J(CP) + J(CP') = 12.8$ Hz], δ($CH_3CH_2CH_2N$) 16.12 (s), δ($CH_3CH_2CH_2N$) 12.17 (s).

Synthesis of *mer,trans*-(PNP)RuCl$_2$(CO) (7). Method A. A solution of **4** (0.20 g, 0.26 mmol) [or **5**, (0.20 g, 0.26 mmol)] in dichloromethane (30 mL) was saturated with dioxygen and slowly heated at reflux temperature for 4 h. After cooling of the solution to room temperature, addition of ethanol (20 mL) and concentration of the solution under a brisk current of nitrogen gave pale cream microcrystals of **7**. Yield: 90%. GC-MS analysis of the solution showed the formation of *ca.* 1 equiv of benzaldehyde (or *p*-tolylaldehyde).

Method B. A sample of **1** (0.46 g, 0.50 mmol) was dissolved in dichloromethane (60 mL) under a stream of carbon monoxide at room temperature. The solution was then brought to reflux temperature and refluxed under a carbon monoxide atmosphere for 1 h during which time the starting orange color faded to produce a pale yellow solution. After cooling of the solution to room temperature, addition of ethanol (30 mL) and concentration of the resulting solution under nitrogen gave pale cream colored microcrystals of **7**. Yield: 94%. Anal. Calcd for $C_{32}H_{35}NCl_2OP_2Ru$: C, 56.23; H, 5.16; N, 2.05. Found: C, 56.09; H, 5.12; N, 1.88. IR (cm^{-1}): ν(C≡O) 1955 (s). $^{31}P\{^1H\}$ NMR (22 °C, CD_2Cl_2, 81.01 MHz): 27.76 (s). $^{13}C\{^1H\}$ NMR (22 °C, CD_2Cl_2, 50.32 MHz): δ(C≡O) 201.19 [t, ^2J(CP) 13.5 Hz], δ($CH_3CH_2CH_2N$) 63.77 (s), δ(NCH_2CH_2P) 55.20 [vt, $N = J(CP) + J(CP') = 3.2$ Hz], δ(NCH_2CH_2P) 27.76 [vt, $N = J(CP) + J(CP') = 12.0$ Hz], δ($CH_3CH_2CH_2N$) 15.56 (s), δ($CH_3CH_2CH_2N$) 11.56 (s).

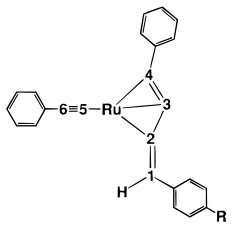
Reaction of 2 with O$_2$ in a Sealed NMR Tube. Solid **2** (25 mg, 0.033 mmol) was dissolved in chloroform-d_1 saturated with dioxygen (1.0 mL) and then transferred into a 5-mm NMR tube which was flame-sealed in a liquid nitrogen bath. The reaction was followed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy in the temperature range from 20 to 55 °C. At the latter temperature, **2** completely disappeared within 2 h to give **6** with no formation of other phosphorus-containing species. GC-MS analysis of the solution showed the formation of an equivalent amount of benzaldehyde.

Synthesis of *anti,mer*-(PNP)Ru(C≡CPh){η^3-PhC$_3$═CH(Ph)} (8). A 2-fold amount of LiC≡CPh (1.0 M THF solution, 1.35 mL, 1.35 mmol) was added dropwise over a period of 5 min to a stirred suspension of **2** (0.50 g, 0.66 mmol) in THF (50 mL) mantained at *ca.* 5 °C with an ice bath. Stirring was continued for 30 min, during which time the color of the solution changed from pale orange to red orange. By addition of ethanol (30 mL) and slow evaporation of the solvent in a stream of nitrogen at room temperature, orange microcrystals of **8** precipitated. The crude product was recrystallized from CH_2Cl_2/EtOH (1:1 v:v) to afford crystals of **8** as orange cubes. Yield: 66%. Anal. Calcd for $C_{55}H_{51}NP_2Ru$: C, 74.31; H, 5.78; N, 1.58. Found: C, 74.08; H, 5.64; N, 1.45. IR (cm^{-1}): ν(C≡C) 2069 (s), ν(C═C) 1569 (w); phenyl reinforced vibration 1591. $^{31}P\{^1H\}$ NMR (22 °C, CD_2Cl_2, 81.01 MHz): 36.01 (s). ^1H NMR (22 °C, CD_2Cl_2, 200.13 MHz) (the numbering scheme of the hydrogen and carbon resonances is given in footnote 6): δ(C═C*H*) 8.28 [t, ^4J(HP) 1.4 Hz]. $^{13}C\{^1H\}$ NMR (22 °C, CD_2Cl_2, 50.32 MHz): δ(C_4) 154.97 [t, ^2J(CP) 7.8 Hz], δ(C_5) 135.86 [t, ^2J(CP) 15.9 Hz], δ(C_1) 130.50 [t, ^2J(CP) 1.3 Hz], δ(C_2) or δ(C_6) 115.14 [t, ^2J(CP) 2.0 Hz] and 110.98 [t, ^2J(CP) 1.4 Hz], δ($CH_3CH_2CH_2N$) 62.98 (s), δ(C_3) 56.88 [t, ^2J(CP) 1.7 Hz], δ(NCH_2CH_2P) 53.28 [vt, $N = J(CP) + J(CP') = 3.7$ Hz], δ(NCH_2CH_2P) 27.19 [vt, $N = J(CP) + J(CP') = 11.2$ Hz], δ($CH_3CH_2CH_2N$) 14.75 (s), δ($CH_3CH_2CH_2N$) 10.65 (s).

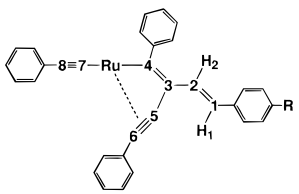
Synthesis of *anti,mer*-(PNP)Ru(C≡CPh){η^3-PhC$_3$═CH(*p*-tolyl)} (9). This compound was prepared like **8** using the *p*-tolylvinylidene complex **3** in the place of **2**. Yield: 72%. Anal. Calcd for $C_{56}H_{53}NP_2Ru$: C, 74.48; H, 5.92; N, 1.55. Found: C, 74.21; H, 5.83; N, 1.50. IR (cm^{-1}): ν(C≡C) 2073 (s), ν(C═C) 1520 (w); phenyl reinforced vibration 1592. $^{31}P\{^1H\}$ NMR (22 °C, CD_2Cl_2, 81.01 MHz): 36.18 (s). ^1H NMR (24 °C, CD_2Cl_2, 500.13 MHz): δ(C═C*H*) 8.28 (br s), δ[CH_3(*p*-tolyl)] 2.34 (s). $^{13}C\{^1H\}$ NMR (22 °C, CD_2Cl_2, 50.32 MHz): δ(C_4) 153.27 [t, ^2J(CP) 7.8 Hz], δ(C_5) 136.18 [t, ^2J(CP) 14.6 Hz], δ(C_1) 130.69 [t, ^2J(CP) 1.5 Hz], δ(C_2) or δ(C_6) 115.33 [t, ^2J(CP) 1.8 Hz] and 110.68 [t, ^2J(CP) 1.3 Hz], δ($CH_3CH_2CH_2N$) 62.27 (s), δ(C_3) 57.25 [t, ^2J(CP) 1.6 Hz], δ(NCH_2CH_2P) 53.56 [vt, $N = J(CP) + J(CP') = 3.9$ Hz], δ(NCH_2CH_2P) 27.46 [vt, $N = J(CP) + J(CP') = 11.4$ Hz], δ[CH_3(*p*-tolyl)] 21.89 (s), δ($CH_3CH_2CH_2N$) 15.01 (s), δ($CH_3CH_2CH_2N$) 10.92 (s).

Synthesis of *fac*-(PNP)RuCl(C≡CPh)(CO) (10). Method A. Carbon monoxide was bubbled throughout a stirred THF solution (50 mL) of **2** (0.20 g, 0.26 mmol) maintained at *ca.* −5 °C to which 1 equiv of LiC≡CPh (1.0 M THF solution, 0.26 mL, 0.26 mmol) was added dropwise over a period of 2 min. Stirring was continued for 20 min. Addition of ethanol (20 mL) to the resulting pale yellow solution and concentration under a brisk current of nitrogen gave yellow microcrystals of **10**. Yield: 95%. Anal. Calcd for $C_{48}H_{46}NClOP_2Ru$: C, 67.72; H, 5.45; N, 1.65. Found: C, 67.63; H, 5.40; N, 1.53. IR (cm^{-1}): ν(C≡C) 2089 (s); ν(C≡O) 1968 (vs). $^{31}P\{^1H\}$ NMR (24 °C, CD_2Cl_2, 81.01 MHz); (AM spin system): δ_A 49.43 [d, J(PP) 27.9 Hz], δ_M 23.33 (d). $^{13}C\{^1H\}$ NMR (24 °C, CD_2Cl_2, 50.32 MHz): δ(*C*≡O) 200.20 [dd, $^2J(CP_{trans})$ 100.6 Hz, $^2J(CP_{cis})$ 14.9 Hz], δ(*C*≡C) 107.65 [t, ^2J(CP) 17.1 Hz], δ(C≡*C*) 113.70 (br s), δ(CH_3-

(6) Numbering schemes for the hydrogen and carbon atoms in complexes **8**, **9** and **12**, **13** are as follows:



R = H, **8**; Me, **9**



R = H, **12**; Me, **13**

CH_2CH_2N) 65.15 (s), $\delta(NCH_2CH_2P)$ 55.45 [d, J(CP) 4.0 Hz], $\delta(NCH_2CH_2P)$ 52.58 (br s), $\delta(NCH_2CH_2P)$ 28.33 [d, J(CP) 29.7 Hz], $\delta(NCH_2CH_2P)$ 26.06 [d, J(CP) 22.1 Hz], $\delta(CH_3CH_2CH_2N)$ 17.23 (s), $\delta(CH_3CH_2CH_2N)$ 12.02 (s).

Method B. Compound **10** was analogously obtained by reaction of **2** with a freshly prepared solution of lithium *p*-tolylacetylide in THF.

Method C. NEt_3 (56 μL, 0.4 mmol) was added to a stirred solution of **2** (0.20 g, 0.26 mmol) in THF (50 mL) under a CO atmosphere at −5 °C. Stirring was continued at room temperature until a pale yellow solution was obtained. Addition of ethanol (30 mL) and concentration of the resulting solution under a brisk current of nitrogen gave **10** in almost quantitative yield.

In a separate experiment, the solvent was removed in vacuo before adding EtOH to give a mixture of **10** and $[Et_3NH]Cl$ (^{1}H NMR).

Isomerization of *fac*-(PNP)RuCl(C≡CPh)(CO) to *mer*-(PNP)RuCl(C≡CPh)(CO) (11). NMR Reaction. A 20 mg-sample of **10** was dissolved in CD_2Cl_2 (0.7 mL) under nitrogen in a 5-mm NMR tube which was flame sealed and introduced into a NMR probe preheated at 50 °C. $^{31}P\{^1H\}$ NMR spectra were acquired every 30 min. After 3 h, the AM pattern of **10** had completely disappeared, while a new singlet at 34.18 ppm was the only signal detected. The tube was cooled to room temperature, and $^{13}C\{^1H\}$ and ^{1}H NMR were acquired (see below).

Preparative Reaction. A sample of 200 mg of **10** (0.23 mmol) was dissolved in CH_2Cl_2 (40 mL) and then refluxed with stirring for 4 h. After cooling of the sample to room temperature, EtOH was added (20 mL) and the solution was concentrated under a stream of nitrogen until pale yellow crystals of *mer*-(PNP)RuCl(C≡CPh)(CO) (**11**) precipitated (yield >90%). Anal. Calcd for $C_{48}H_{46}NClOP_2Ru$: C, 67.72; H, 5.45; N, 1.65. Found: C, 67.78; H, 5.35; N, 1.63. IR (cm^{-1}): ν(C≡C) 2099 (s); ν(C≡O) 1954 (vs). $^{31}P\{^1H\}$ NMR (23 °C, CD_2Cl_2, 81.01 MHz): 34.18 (s). $^{13}C\{^1H\}$ NMR (23 °C, CD_2Cl_2, 50.32 MHz): $\delta(C{\equiv}O)$ 200.64 [t, ^2J(CP) 12.8 Hz], $\delta(C{\equiv}C)$ 107.92 [t, ^2J(CP) 13.9 Hz], $\delta(C{\equiv}C)$ 112.44 [t, ^2J(CP) 1.6 Hz], $\delta(CH_3CH_2CH_2N)$ 60.62 (s), $\delta(NCH_2CH_2P)$ 52.57 [vt, $N = J(CP) + J(CP') = 3.2$ Hz], $\delta(NCH_2CH_2P)$ 28.55 [vt, $N = J(CP) + J(CP') = 12.0$ Hz], $\delta(CH_3CH_2CH_2N)$ 14.62 (s), $\delta(CH_3CH_2CH_2N)$ 11.82 (s).

Synthesis of *mer*-(PNP)Ru(C≡CPh){η-PhC=C(C≡CPh)-CH=CH(Ph)} (12). A 3-fold amount of LiC≡CPh (1.0 M THF solution, 2.0 mL, 2.0 mmol) was added over a period of 5 min to a well-stirred suspension of **4** (0.50 g, 0.66 mmol) in THF (50 mL) at room temperature. During a period of 20 min the color of the solution changed from cream to orange and finally to red. On addition of ethanol (30 mL) the solution turned deep orange and, after concentration at room temperature under nitrogen, separated red orange crystals of **12**. Yield: 58%. Anal. Calcd for $C_{63}H_{57}NP_2Ru$: C, 76.34; H, 5.80; N, 1.41. Found: C, 76.20; H, 5.69; N, 1.36. IR (cm^{-1}): ν(C≡C) 2062 (s), ν(C=C) 1514 (m); phenyl reinforced vibration 1590. $^{31}P\{^1H\}$ NMR (22 °C, THF-d_8, 81.01 MHz): 31.06 (s). ^{1}H NMR (24 °C, CD_2Cl_2, 500.13 MHz) (the numbering scheme of the hydrogen and carbon resonances is given in footnote 6): $\delta(H_2)$ 6.11 [d, $^3J(H_1H_2)$ 15.6 Hz], $\delta(H_1)$ *ca.* 7.1 (obscured by aromatic proton resonances, assigned by a ^{1}H,^{1}H-2D COSY NMR experiment). $^{13}C\{^1H\}$ NMR (20 °C, CD_2Cl_2, 75.42 MHz): $\delta(C_4)$ or $\delta(C_7)$ 139.91 [t, ^2J(CP) 18.9 Hz] and 139.21 [t, ^2J(CP) 16.2 Hz], $\delta(C_2)$ 130.56 (s, assigned by a ^{1}H,^{13}C-2D HETCOR NMR experiment; the remaining resonance due to the butadienyl carbon C_1 could not unambiguously be assigned), $\delta(C_6)$ or $\delta(C_8)$ 118.27 [t, ^2J(CP) 1.2 Hz] and 116.07 (br s), $\delta(C_3)$ or $\delta(C_5)$ 84.16 (s) and 73.73 (s), $\delta(CH_3CH_2CH_2N)$ 60.73 (s), $\delta(NCH_2CH_2P)$ 54.80 [vt, $N = J(CP) + J(CP') = 3.2$ Hz], $\delta(NCH_2CH_2P)$ 32.72 [vt, $N = J(CP) + J(CP') = 11.2$ Hz], $\delta(CH_3CH_2CH_2N)$ 14.92 (s), $\delta(CH_3CH_2CH_2N)$ 12.18 (s).

Replacing EtOH with EtOD in the above reaction gave the isotopomer *mer*-(PNP)Ru(C≡CPh){η^1-PhC=C(C≡CPh)CD=CH-(Ph)} (**12**-d_1) in which the selective incorporation of deuterium into the 2-position of the butadienyl ligand was determined by ^{1}H NMR spectroscopy (disappearance of the signal at 6.11 ppm).

Synthesis of *mer*-(PNP)Ru(C≡CPh){η-PhC=C(C≡CPh)-CH=CH(*p*-tolyl)} (13). This compound was prepared as described above for complex **12**, by replacing **2** with **3**. Yield: 50%. Anal. Calcd for $C_{64}H_{59}NP_2Ru$: C, 76.47; H, 5.92; N, 1.39. Found: C, 76.31; H, 5.80; N, 1.38. IR (cm^{-1}): ν(C≡C) 2063 (s), ν(C=C) 1556 (w); phenyl reinforced vibration 1590. $^{31}P\{^1H\}$ NMR (22 °C, $CDCl_3$, 81.01 MHz): 30.72 (s). ^{1}H NMR (24 °C, CD_2Cl_2, 500.13 MHz): $\delta(H_2)$ 6.14 [d, $^3J(H_1H_2)$ 15.7 Hz], $\delta(H_1)$ *ca.* 7.1 (superimposed to aromatic proton resonances, the assignment was confirmed by a ^{1}H,^{1}H-2D COSY NMR experiment), $\delta[CH_3(p\text{-tolyl})]$ 2.31 (s). $^{13}C\{^1H\}$ NMR (22 °C, CD_2Cl_2, 50.32 MHz): $\delta(C_4)$ or $\delta(C_7)$ 137.14 [t, ^2J(CP) 16.1 Hz] and 122.75 [t, ^2J(CP) 19.1 Hz], $\delta(C_2)$ 128.61 (s, assigned by a ^{1}H,^{13}C-2D HETCOR NMR experiment), $\delta(C_1)$ 120.60 (s, assigned by a ^{1}H,^{13}C-2D HETCOR NMR experiment), $\delta(C_6)$ or $\delta(C_8)$ 116.93 (s) and 114.18 (s), $\delta(C_3)$ or $\delta(C_5)$ 82.77 (s) and 68.45 (s), $\delta(CH_3CH_2CH_2N)$ 59.22 (s), $\delta(NCH_2CH_2P)$ 53.39 (s), $\delta(NCH_2CH_2P)$ 30.21 [vt, $N = J(CP) + J(CP') = 11.4$ Hz], $\delta[CH_3(p\text{-tolyl})]$ 21.51 (s), $\delta(CH_3CH_2CH_2N)$ 13.71 (s), $\delta(CH_3CH_2CH_2N)$ 10.91 (s).

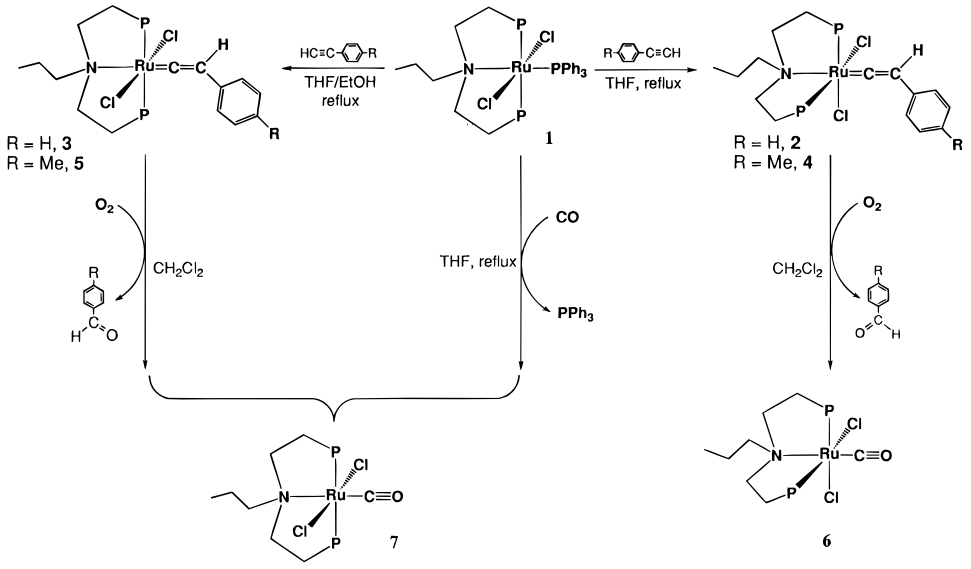
Reaction of 4 with CO/NEt_3. A slight excess of NEt_3 was added to stirred solution of **4** (0.25 g, 0.33 mmol) in CH_2Cl_2 (20 mL) saturated with CO at −5 °C. During a period of 20 min at room temperature the color of the solution changed from cream to pale yellow. Removal of the solvent in vacuo gave the *mer* carbonyl complex **11** and $[HNEt_3]Cl$ in quantitative yield.

X-ray Diffraction Studies. A summary of crystal and intensity data for the compounds **6**, **8**, and **13**·CH_2Cl_2, is presented in Table 4 (**6** and **8**) and Table 5 (**13**·CH_2Cl_2). Experimental data were recorded at room temperature on either an Enraf-Nonius CAD4 diffractometer (**6** and **8**) or a Philips-PW1100 diffractometer (**13**·CH_2Cl_2) with an upgraded computer control (FEBO system) using graphite-monochromated Mo Kα radiation (**6** and **8**) and graphite-monochromated Cu Kα radiation (**13**·CH_2Cl_2). A set of 25 carefully centered reflections in the range $7° \le \theta \le 10°$ (**6**), $8° \le \theta \le 12°$ (**8**), and $10° \le \theta \le 15°$ (**13**·CH_2Cl_2), respectively, was used for determining the lattice constants. As a general procedure, the intensity of three standard reflections were measured periodically every 2 h for orientation and intensity control. This procedure did not reveal an appreciable decay of intensities. The data were corrected for Lorentz and polarization effects. Atomic scattering factors were those tabulated by Cromer and Waber[7] with anomalous dispersion corrections taken from ref 8. An empirical absorption correction was applied for compound **13**·CH_2Cl_2 using the program DIFABS[9] with transmission factors in the range 0.57−1.00. The computational work was performed with a Digital Dec 5000/200 workstation using the programs SIR92,[10] SHELX-76,[11] and SHELX-93.[12] The programs PARST[13] and ORTEP[14] were also used. Final atomic coordinates of all atoms and structure factors are available as Supporting Information.

***fac,cis*-(PNP)RuCl$_2$(CO) (6).** Pale yellow crystals (0.18 × 0.22 × 0.16 mm) suitable for an X-ray diffraction analysis were grown in the air by slow evaporation from a diluted dichloromethane/ethanol solution of **6**. The structure was solved *via*

(7) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.
(8) *International Tables of Crystallography*; Kynoch Press: Birmingham, U.K., 1974.
(9) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.
(10) Altomare, A.; Burla, M.; Camalli, G.; Cascarano, G.; Giacovazzo, C.; Guagliandi, A.; Polidori, G. *J. Appl. Crystallogr.* **1994**, *27*, 435.
(11) Sheldrick, G. M. SHELX-76. A program for crystal structure determination. University of Cambridge, 1976.
(12) Sheldrick, G. M. SHELXL93, Program for structure refinement. University of Göttingen, Germany, 1993.
(13) Nardelli, M. *Comput. Chem.* **1983**, *7*, 95.
(14) Johnson, C. K. *Report ORNL-5138*; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

Scheme 1



Patterson methods. Refinement was done by full-matrix least-squares calculations, initially with isotropic thermal parameters and then with anisotropic thermal parameters for all the 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.

***mer*-(PNP)Ru(C≡CPh){η^3-PhC$_3$=CH(Ph)} (8).** Crystals suitable for an X-ray diffraction analysis were grown by slow evaporation from a diluted THF/ethanol solution of **8**. A red parallelepiped crystal with dimensions 0.12 × 0.32 × 0.21 mm was used for data collection. The structure was solved *via* Patterson methods. Refinement was done by full-matrix least-squares calculations, initially with isotropic thermal parameters and then with anisotropic thermal parameters for the Ru, P, N, and C carbon atoms. The phenyl rings were treated as rigid bodies with D_{6h} symmetry (C−C = 1.39 Å). Hydrogen atoms were introduced in calculated positions but not refined.

***mer*-(PNP)Ru(C≡CPh){η-PhC=C(C≡CPh)CH=CH(*p*-tolyl)}·CH$_2$Cl$_2$ (13·CH$_2$Cl$_2$).** Crystals suitable for an X-ray diffraction analysis were grown by slow evaporation from a diluted dichloromethane/ethanol solution of **13**. A red-orange parallelepiped crystal with dimensions of 0.28 × 0.30 × 0.27 mm was used for the data collection. The structure was solved by the heavy atom technique, and all of the non-hydrogen atoms were found through a series of F_o Fourier maps. The refinement was done by full-matrix least-squares calculations, initially with isotropic thermal parameters and then with anisotropic thermal parameters for the Ru, P, and N atoms. All of the phenyl rings, but the *p*-tolyl one, were treated as rigid bodies with D_{6h} symmetry and C−C distances fixed at 1.39 Å. Hydrogen atoms bonded to the carbon atoms were introduced in calculated positions using C−H bond values of 0.96 and 0.93 Å for the sp^3-hybridized carbons and the phenyl rings, respectively. A molecule of dichloromethane solvent was found and successfully refined. The final difference map was featureless.

Results

The preparations and principal reactions described in this paper are reported in Schemes 1−3. Selected spectroscopic data for the new complexes are given in the Experimental Section

Synthesis and Characterization of the Vinylidene Complexes *fac,cis*- and *mer,trans*-(PNP)RuCl$_2$-{C=CH(R)}. Treatment of the complex *mer,trans*-(PNP)RuCl$_2$(PPh$_3$)[4] (**1**) in THF with an excess of either phenylacetylene or *p*-tolylacetylene at reflux temperature results in the decoordination of triphenylphosphine and formation of the vinylidene complexes *fac,cis*-(PNP)-RuCl$_2${C=CH(R)} (R = Ph (**2**), *p*-tolyl (**3**)).[15]

Monitoring the reaction with phenylacetylene (3 equiv) in THF-d_8 by ^{31}P{^{1}H} NMR spectroscopy over the temperature range from 20 to 50 °C does not show the formation of any ruthenium intermediate species in the course of the conversion of **1** to the vinylidene **2**. Evidently, both the 1-alkyne to vinylidene tautomerization[16,17] and the *mer* to *fac* isomerization[18] of the [(PNP)RuCl$_2$] fragment are faster than the NMR time scale. The *mer* to *fac* isomerization does not take place when the reaction of **1** with 1-alkynes is carried out in a 1:2 (v:v) mixture of THF and ethanol. In this case, in fact, the *mer,trans*-(PNP)RuCl$_2${C=CH(R)} vinylidene isomers (R = Ph (**4**), *p*-tolyl (**5**)) are selectively obtained. No isomerization of **2**, **3** (**4**, **5**) to **4**, **5** (**2**, **3**) occurs when the compounds are refluxed in THF/ethanol (THF or toluene).

Since the starting complex **1** readily loses PPh$_3$ as a thermal step in THF above 60 °C to give the *fac* dimer [Ru(μ-Cl)$_3$(PNP)$_2$]Cl,[4] the *fac* complexes **2** and **3** are probably produced by interaction of the 1-alkyne with the five-coordinate transient species *fac*-(PNP)RuCl$_2$. Accordingly, the role of EtOH in the formation of the *mer,trans* isomers **4** and **5** might simply be that of preventing the *mer*-(PNP)RuCl$_2$ fragment from isomerizing to the *fac* arrangement prior to its interaction with

(15) The synthesis and partial characterization of **2** have already been communicated: Bianchini, C.; Glendenning, L.; Peruzzini, M.; Romerosa, A.; Zanobini, F. *J. Chem. Soc., Chem. Commun.* **1994**, 2219.

(16) For leading references on the alkyne to vinylidene tautomerization, see: (a) Fryzuk, M. D.; Huang, L.; McManus, N. T.; Paglia, P.; Rettig, S. J.; White, G. S. *Organometallics* **1992**, *11*, 2979. (b) Lumprey, J. R.; Selegue, J. P. *J. Am. chem. Soc.* **1992**, *114*, 5518. (c) Werner, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1077. (d) Bianchini, C.; Peruzzini, M.; Vacca, A; Zanobini, F. *Organometallics* **1991**, *10*, 3697. (e) Xiao, J.; Cowie, M. *Organometallics* **1993**, *12*, 463.

(17) For a theoretical study, see: Silvestre, J.; Hoffmann, R. *Helv. Chim. Acta* **1985**, *68*, 1461.

(18) See, for example: (a) Jia, G.; Rheingold, A. L.; Hoggerthy, B. S.; Meek, D. W. *Inorg. Chem.* **1992**, *31*, 900. (b) Whinnery, L. L.; Yue, H. J.; Marsellar, J. A. *Inorg. Chem.* **1986**, *25*, 4236. (c) Jia, G.; Lee, I.; Meek, D. W.; Gallucci, J. A. *Inorg. Chim. Acta* **1990**, *177*, 81.

the 1-alkyne (probably *via* EtOH coordination to the unsaturated Ru(II) center).

Once formed, the *fac* vinylidene complexes do not convert to the *mer* isomers probably because of a higher energy barrier to isomerization than that experienced. Indeed, *meridional* complexes of linear tridentate ligands are generally favored over facial complexes due to steric interaction.[18c] However, the *fac* geometry may be preferred for triphosphine ligands (as well as PNP) when there is a possibility that the phosphine atoms are *trans* to weak *trans*-influence ligands to eliminate the *trans*-phosphine interaction.[18a] In the PNP complexes described in this work, steric effects generally prevail over electronic effects in determining the geometry of the PNP ligand. On the other hand, the selective formation of the *fac* isomers **2** and **3** occurring in THF suggests that a subtle balance of electronic and steric effects can effectively determine the geometry of the PNP ligand.

The IR spectra of **2**−**5** contain medium- to strong-intensity bands ranging between 1650 and 1603 cm^{-1} which are typical of ν(C═C) of vinylidene ligands.[19] Both the *fac,cis* and the *mer,trans* complexes exhibit a singlet resonance in the $^{31}P\{^1H\}$ NMR spectra for the two chemically equivalent phosphorus atoms of the PNP ligand (*ca.* 48 and 27 ppm, respectively). As previously observed,[20] the chemical shifts of the phosphorus atoms are diagnostic for the coordination mode of PNP. In particular, the phosphorus nuclei of the *mer* complexes, due to the remarkable *trans* influence of the phosphine ligands, resonate invariably at higher field (20−35 ppm) than those of the *fac* isomers (40−60 ppm).

The magnetic equivalence of the two phosphine donors of PNP in the *facial* complexes **2** and **3** is consistent with a *cis* structure in which the vinylidene ligand is located *trans* to the nitrogen and excludes a structure in which the vinylidene ligand and one of the phosphorus atoms are mutually *trans*. The ^{31}P NMR spectra of all compounds are temperature invariant down to −90 °C, consistent with a low-energy barrier to rotation of the vinylidene group around the Ru−C−C axis.[21,22]

The ^1H NMR spectra of **2**−**5** show the vinylidene hydrogens to appear as triplets that transform into sharp singlets in the $^1H\{^{31}P\}$ spectra. The vinylidene hydrogens in the *mer, trans* compounds **4** and **5** are shifted upfield by *ca.* 1.6 ppm as compared to those in the *fac,cis* isomers **2**, **3**, probably because of the larger shielding effect provided by the phenyl rings of the mutually *trans* PPh_2 groups.

The quaternary α-carbons of the Ru═C═C moiety in **2**−**5** resonate at much lower field ($356.31 \le \delta \le 359.90$) than the β-carbon atoms (*ca.* 110 ppm).[19] The large deshielding of the vinylidene C_α carbon resonance, which is a consequence of its electron-deficient character, has recently been interpreted by Czech and coworkers as being due also to changes in the paramagnetic contribution, σ_p, to the nuclear shielding σ.[23] The observed triplet multiplicity, which arises from coupling of the C_α carbon to the two phosphorus atoms, shows ^2J(CP) values (15.2−22.6 Hz) in line with those reported for other Ru(II) vinylidenes containing tertiary phosphine ligands.[24]

Oxidative Cleavage of the Vinylidene C═C Bond. Synthesis of the Carbonyl Complexes *fac,mer*- and *mer,trans*-(PNP)$RuCl_2$(CO) (6 and 7). The vinylidene complexes **2** and **3** are air-stable in the solid state, whereas in aerobic solutions slowly decompose (4−5 days) to give the carbonyl complex *fac,cis*-(PNP)-$RuCl_2$(CO) (**6**) and aldehydes.[25] This chemical transformation is much faster by using pure oxygen. Under 1 atm of oxygen in CH_2Cl_2, **2** and **3** quantitatively transform into the carbonyl complex **6** in 12 h at room temperature and in *ca.* 30 min at reflux temperature. Monitoring the reactions in $CDCl_3$ by $^{31}P\{^1H\}$ and ^1H NMR spectroscopies in the temperature range from 0 to 55 °C shows only the resonances of the starting material and of the final carbonyl product (singlet at 58.27 ppm) with no detection of any intermediate adduct. One equivalent of either benzaldehyde or *p*-tolylaldehyde is produced during the oxidative degradation of the vinylidene ligands (^1H NMR, GC-MS).

The *mer,trans* vinylidene isomers **4** and **5** in CH_2Cl_2 undergo analogous transformations when exposed to air. At reflux temperature under oxygen, the complex *mer,trans*-(PNP)$RuCl_2$(CO) (**7**) (^{31}P NMR: singlet at 27.76 ppm) and aldehydes are formed in quantitative yield in *ca.* 4 h. Consistent with the *mer,trans* structure, **7** can also be prepared by refluxing **1** in THF under a carbon monoxide atmosphere.

Strong ν(C≡O) absorptions (1942 and 1955 cm^{-1}) in the IR spectra and low-field triplet resonances [δ 203.61, ^2J(CP) 15.9 Hz; δ 201.19, ^2J(CP) 13.5 Hz] in the $^{13}C\{^1H\}$ NMR spectra diagnose the presence of a terminal carbonyl ligand in **6** and **7**. The triplet multiplicity of the carbonyl carbon resonances points to the equivalence of the two phosphine groups in both compounds and thus supports a *trans* disposition between the PNP nitrogen and the CO ligand. In conclusion, the oxidative cleavage of the vinylidene ligands in **2**−**5** promoted by action of molecular oxygen does not change the stereochemical arrangement of the PNP precursors and thus is consistent with a regioselective attack by O_2 at the vinylidene ligand.

In order to confirm the stereochemistry of **6** and indirectly support the structures assigned to the parent vinylidenes **2** and **3**, an X-ray analysis has been carried out on a single crystal of **6**.

The molecular structure of the complex is shown in Figure 1 with the atomic labeling scheme. A list of selected bond distances and angles is presented in Table 1.

The crystal structure consists of discrete mononuclear *fac,cis*-(PNP)$RuCl_2$(CO) neutral molecules with no in-

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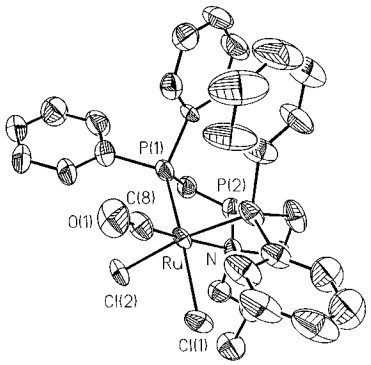


Figure 1. ORTEP drawing (30% thermal ellipsoids probability) of *fac,cis*-(PNP)$RuCl_2$(CO) (**6**). All the hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for *fac,cis*-(PNP)$RuCl_2$(C)) (6)

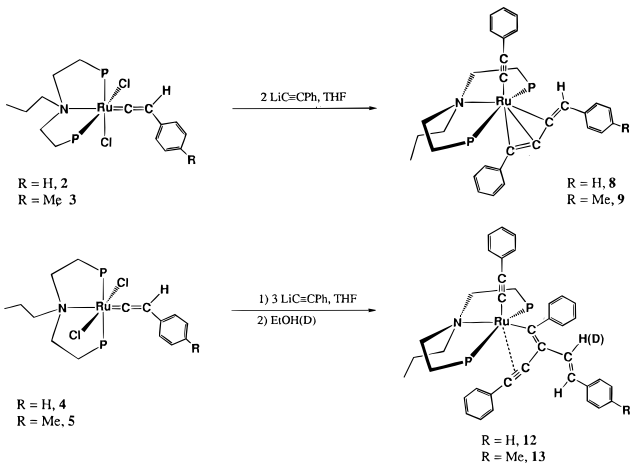
Ru−P_1	2.290(3)	Ru−N	2.310(8)
Ru−P_2	2.291(3)	Ru−C_8	1.814(11
Ru−C_1	2.433(3)	C_8−O	1.15(1)
Ru−Cl_2	2.446(3)		
P_1−Ru−P_2	99.9(1)	Cl_1−Ru−N	88.4(2)
P_1−Ru−C_1	167.7(1)	Cl_2−Ru−N	90.2(2)
P_2−Ru−Cl_1	88.2(1)	P_1−Ru−C_8	95.7(4)
P_1−Ru−Cl_2	85.0(1)	P_2−Ru−C_8	93.3(4)
P_2−Ru−Cl_2	171.8(1)	Cl_1−Ru−C_8	93.1(4)
Cl_1−Ru−Cl_2	86.0(1)	Cl_2−Ru−C_8	92.8(4)
P_1−Ru−N	83.3(3)	N−Ru−C_8	176.8(4)
P_2−Ru−N	83.9(2)	Ru−C_8−O	178(1)

terspersed solvent molecules in the crystal lattice. The coordination geometry around the ruthenium center is a distorted octahedron with the metal atom surrounded by the two phosphorus and the nitrogen atoms of PNP, by a carbonyl carbon atom *trans* to the nitrogen, and by two mutually *cis* Cl atoms.

The most evident distortion from the idealized geometry is the bending of the two PPh_2 groups toward the N atom [P1−Ru−N = 83.3(2)°; P2−Ru−N = 83.9(2)°] and toward the two Cl atoms [P1−Ru−P2 = 99.9(1)°]. A similar distortion, probably due to repulsion between the four phenyl rings, has been found in (PNP)Ir(σ,η^2-C_8H_{13}) which is the only other *fac*-PNP complex authenticated by an X-ray analysis.[26] The ruthenium atom is slightly displaced from the least-squares plane P1−P2−Cl1−Cl2 toward the N atom by 0.155(3) Å and from the least-squares plane P2−N−Cl2−C8 toward the P1 atom by 0.046(8) Å.

The Ru−P distances [2.290(3) and 2.291(3) Å] fall within the range reported in the literature for Ru(II) phosphine complexes.[27,28] These distances are shorter [0.085(3) and 0.084(3) Å, respectively] than those found in the starting *mer,trans* complex **1**,[29] consistent with the greater *trans* influence of phosphine vs chloride. The Ru−Cl separations [2.433(3) and 2.446(3) Å] match well with the values reported for several Ru−Cl distances in compounds containing the chlorine atom *trans* to a phosphine.[30] Finally, the Ru−N distance [2.310(8) Å] is in excellent agreement with those found in the *mer,trans*-(PNP)$RuCl_2(PPh_3)$[29] and *mer,trans*-(PNP)-$RuH(Cl)(PPh_3)$[4] complexes, but it is slightly longer than those found in Ru(tertiary amine) complexes.[28] These data are statistically significant and indicate that the phosphine and CO groups exhibit comparable *trans* influence in the present complexes.

Scheme 2



Reactions of the *fac,cis*-Vinylidene Complexes with LiC≡CPh. Synthesis of the σ-Alkynyl−η^3-Butenynyl Complexes *anti,mer*-(PNP)Ru(C≡CPh)-{η^3-PhC_3═CH(R)} (R = Ph, 8; R = *p*-tolyl, 9). Addition of 2 equiv of lithium phenylacetylide to a THF solution of **2** at *ca.* 5 °C gives an orange solution from which crystals of the butenynyl complex *anti,mer*-(PNP)-Ru(C≡CPh){η^3-PhC_3═CH(Ph)} (**8**) separate by addition of ethanol and concentration of the resulting solution. When the *p*-tolyl derivative **3** is analogously reacted with LiC≡CPh, the complex *anti,mer*-(PNP)Ru(C≡CPh)-{η^3-PhC_3═CH(*p*-tolyl)} (**9**) is obtained. The ligand set surrounding the Ru center in **8** and **9** comprises a *meridional* PNP ligand, a terminal alkynyl group, and an η^3-bonded 1,4-disubstituted butenynyl ligand.

The IR spectra show the presence of a σ-alkynyl ligand in both complexes [ν(C≡C) at *ca.* 2070 cm^{-1} (s)]. The $^{31}P\{^1H\}$ NMR spectra consist of a singlet in the proper region of octahedral *mer*-PNP Ru complexes (*ca.* 36 ppm). The ^1H NMR spectrum of **8** contains a triplet at *ca.* 8.3 ppm [^4J(CP) 1.4 Hz] which is assigned to the vinylic hydrogen atom of the 1,4-disubstituted butenynyl ligand (the triplet collapses to a singlet in the broad-band ^{31}P-decoupled ^1H NMR spectrum and does not show any cross-peak in the ^1H,^1H-2D COSY spectrum). HMQC ^1H,^{13}C-2D HETCOR experiments correlate this signal with a triplet at *ca.* 130.5 ppm in the $^{13}C\{^1H\}$ NMR spectrum. The latter together with a series of DEPT spectra and an HMQC experiment allow one to almost completely assign the resonances of the six carbon atoms of the alkynyl and η^3-butenynyl ligands. In particular, three resonances at 154.97 [^2J(CP) 7.8 Hz], 130.50 [^3J(CP) 1.3 Hz], and 56.88 ppm [^2J(CP) 1.7 Hz] in the spectrum of **8** can unequivocally be assigned to the C_4, C_1, and C_3 carbon atoms of the butenynyl ligand,[1,6] while a triplet at 135.86 [^2J(CP) 15.9 Hz] is assigned to the C_α carbon atom of the σ-phenylethynyl ligand.[31,32] Uncertainty still affects the assignment of the quaternary C_2 and C_6 carbon atoms[6] for which quite

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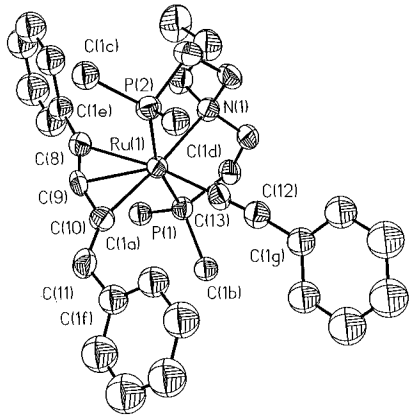

Figure 2. ORTEP drawing (30% thermal ellipsoids probability) of the complex *anti,mer*-(PNP)Ru(C≡CPh){η^3-PhC_3=CH(Ph)} (**8**). Only the *ipso* carbons of the phenyl rings of the PNP ligand are shown for the sake of clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for *anti,mer*-(PNP)Ru(C≡CPh){η^3-PhC_3=CH(Ph)} (8)

Ru−P_1	2.317(3)	C_8−C_9	1.23(2)
Ru−P_2	2.318(3)	C_8−C_{1E}	1.46(1)
Ru−N	2.271(9)	C_9−C_{10}	1.41(2)
Ru−C_8	2.39(1)	C_{10}−C_{11}	1.34(2)
Ru−C_9	2.19(1)	C_{11}−C_{1F}	1.48(2)
Ru−C_{10}	2.06(1)	C_{12}−C_{13}	1.21(2)
Ru−C_{13}	2.00(1)	C_{12}−C_{1G}	1.44(1)
P_1−Ru−P	165.0(1)	N−Ru−C_{13}	86.5(4)
P_1−Ru−N	81.4(2)	C_8−Ru−C_{13}	171.0(4)
P_2−Ru−N	84.1(2)	C_9−Ru−C_{13}	140.3(4)
P_1−Ru−C_8	93.5(3)	C_{10}−Ru−C_{13}	101.7(4)
P_2−Ru−C_8	93.4(3)	Ru−C_8−C_9	65.4(7)
N−Ru−C_8	102.5(4)	Ru−C_8−C_{1E}	140.8(8)
P_1−Ru−C_9	94.5(3)	C_9−C_8−C_{1E}	154(1)
P_2−Ru−C_9	98.2(3)	Ru−C_9−C_8	83.9(8)
N−Ru−C_9	133.0(4)	Ru−C_9−C_{10}	65.6(6)
C_8−Ru−C_9	30.7(4)	C_8−C_9−C_{10}	150(1)
P_1−Ru−C_{10}	95.9(3)	Ru−C_{10}−C_9	75.5(6)
P_2−Ru−C_{10}	99.0(3)	Ru−C_{10}−C_{11}	154(1)
N−Ru−C_{10}	171.3(4)	C_9−C_{10}−C_{11}	130(1)
C_8−Ru−C_{10}	69.3(4)	C_{10}−C_{11}−C_{1F}	125(1)
C_9−Ru−C_{10}	38.6(4)	C_{13}−C_{12}−C_{1G}	174(1)
P_1−Ru−C_{13}	87.5(3)	Ru−C_{13}−C_{12}	177(1)
P_2−Ru−C_{13}	87.7(3)		

similar magnetic parameters are found [115.14 ppm, ^2J(CP) 2.0 Hz; 110.98 ppm, 1.4 Hz].

An almost identical $^{13}C\{^1H\}$ NMR spectrum is displayed by the *p*-tolyl derivative **9**, the only significant difference being the presence of a singlet resonance at 21.89 ppm, which correlates with the proton singlet at 2.34 ppm in the ^1H,^{13}C-2D HETCOR spectrum, and thus is readily attributed to the *p*-tolyl CH_3 group.

A single-crystal X-ray analysis of **8** has confirmed the structure assigned in solution. An ORTEP drawing of the complex is shown in Figure 2, and selected bond lengths and angles are reported in Table 2. The coordination geometry around the ruthenium atom approximates an octahedron with three positions taken by a *mer* PNP ligand. A phenylethynyl ligand and an η^3-PhC_3=CH(Ph) group complete the coordination sphere about the metal center.

The largest deviation from the idealized geometry is represented by the P1−Ru−P2 angle which closes up to 165.0(1)° as a consequence of the bending of the two PPh_2 groups toward the N atom. The phenylethynyl ligand, *cis* to the three donor atoms of PNP, is nearly linear [Ru−C13−C12 = 177(1)°]. The Ru−C13 bond distance [2.00(1) Å] is appreciably shorter than those observed for other ruthenium σ-alkynyl complexes;[5,32] in particular it is shorter than a Ru−C(sp) single bond (2.127 Å).[33] The observed difference [$\Delta = |d_{\text{Ru−C found}} - d_{\text{Ru−C calcd}}| = 0.127(1)$ Å] is statistically significant and is consistent with the high-energy ν(C≡C) absorption in the IR spectra (**8**, 2069 cm^{-1}; **9**, 2073 cm^{-1}). This experimental observable suggests a scarce dπ(metal) → π^*(ligand) back-bonding,[34] and in fact, the C13−C12 separation [1.21(2) Å] does not practically differ from the C−C distance found in disubstituted alkynes.[35]

The *n*-propyl chain on the central nitrogen donor of PNP and the σ-phenylethynyl ligand are mutually *anti*.[36,37] Thus, **8** adopts an *anti,mer* stereochemistry similar to that found in the related complex Ru(C≡CPh){η^3-PhC_3=C(H)Ph}(Cytpp) which, however, shows a different orientation of the butenynyl moiety with respect to the L_3Ru(C≡CPh) fragment [Cyttp = $PhP\{(CH_2CH_2CH_2P(c\text{-}C_6H_{11})_2\}_2$].[38] As a consequence of the *anti* stereochemistry of **8**, the angle N−Ru−C8 [102.5(4)°] is larger than the angle N−Ru−C13 [86.5(4)°] because the *n*-propyl substituent can sterically interact with the phenyl ring of the butenynyl −C≡CPh group. This part of the enynyl fragment is weakly bound to ruthenium as shown by the long Ru−C8 and Ru−C9 separations [2.39(1) and 2.19(1) Å, respectively] as well as the short C8−C9 separation [1.23(2) Å]. Consequently, the bent-back angle of the phenyl substituent C9−C8−C1E is fairly large [154(1)°]. The amplitude of this angle is commonly taken as a relevant parameter for establishing the nature of alkyne bonding to metal centers.[39] In the case at hand, the value of the bent-back angle, which is larger than that found for simple η^2-PhC≡CPh complexes (135−140°), is consistent with a modest perturbation of the sp character of the alkynyl carbons and definitely agrees with a weak

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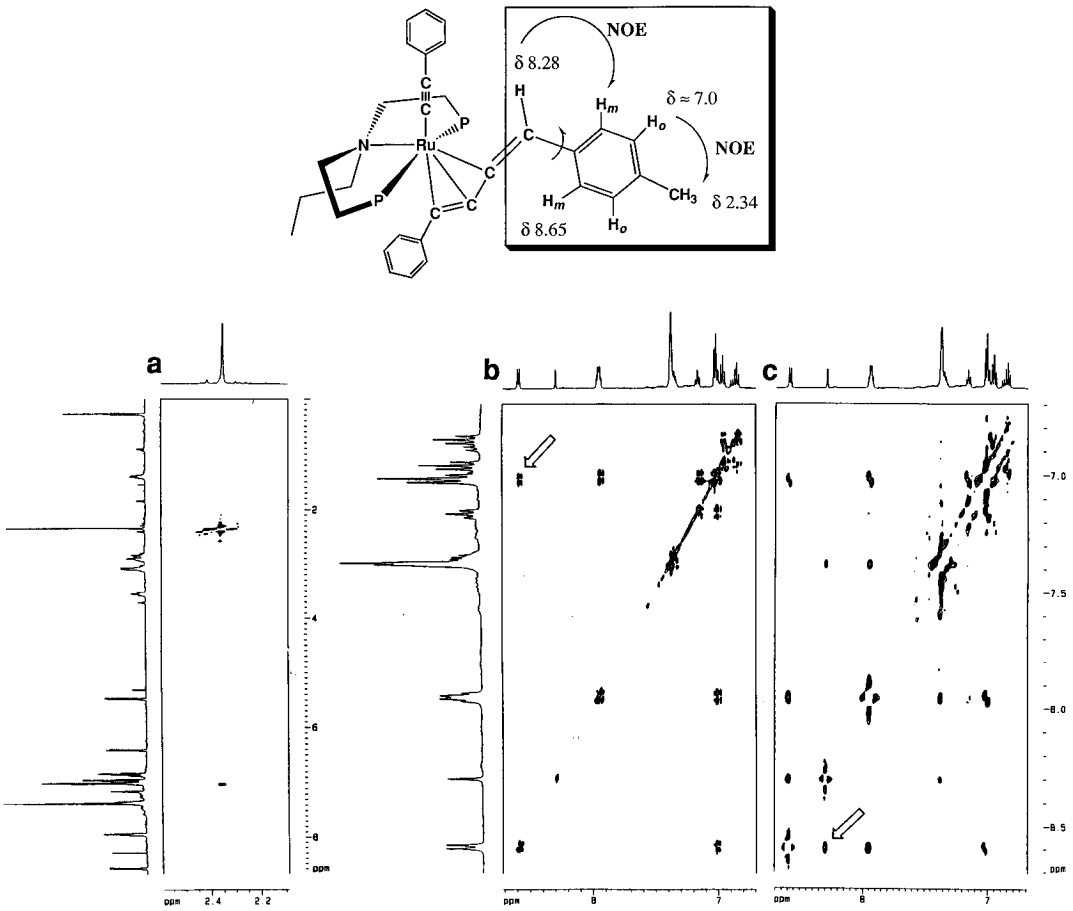
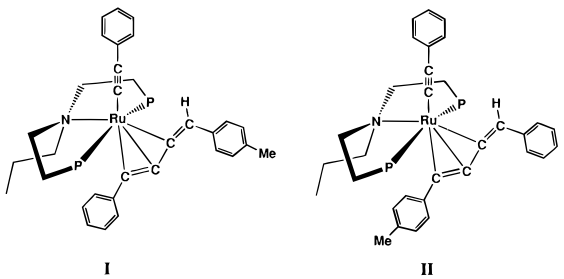


Figure 3. (a) Section of the phase-sensitive 2D-^{1}H NOESY spectrum of **9** (500.13 MHz, CD_2Cl_2, 25 °C, τ_{mix} = 800 ms) showing the negative cross peak between the methyl protons and the aromatic *ortho* protons of the *p*-tolyl group. (b) Contour plot of a section of the 2D-^{1}H COSY spectrum of **9** (500.13 MHz, CD_2Cl_2, 25 °C) showing the scalar couplings for the aromatic protons. The relevant cross peak between the protons of the *p*-tolyl group is marked. (c) Section of the phase-sensitive 2D-^{1}H NOESY spectrum of **9** (500.13 MHz, CD_2Cl_2, 25 °C, τ_{mix} = 800 ms) showing the spatial relationships between the aromatic protons. The relevant cross peak between the protons of the *p*-tolyl group and the butenynyl hydrogen atom at δ 8.28 is marked.

bonding interaction of ruthenium with the C≡CPh moiety of the butenynyl ligand.

The Ru−C and C−C bonding patterns are similar to those found for other η^3-butenynyl complexes in which some degree of electronic delocalization in the RuC_3 moiety has been suggested.[1,38]

NMR Analysis of *anti,mer*-(PNP)Ru(C≡CPh){η^3-PhC$_3$=CH(*p*-tolyl)} (9). Two different regioisomers (**I** and **II**) are possible for **9**, which differ from each other



I **II**

in the position of the *p*-tolyl group in the C_4 chain of the butenynyl ligand. The question of determining the precise structure of **9** is not of marginal importance as the position of the *p*-tolyl group is evidently related to the mechanism of formation of the butenynyl ligand which is a central point of the present work.

A complete assignment of the relevant hydrogen atoms obtained by using a combination of ^{1}H,^{1}H-2D COSY and NOESY NMR spectra unambiguously shows that the *p*-tolyl group in **9** is bound to the β-carbon atom of the vinyl moiety (structure **I**). In particular, a perusal of the 2D-COSY NMR experiment allows one to establish the sequence of the hydrogens which are spin−spin coupled, while, in the phase-sensitive NOESY spectrum, the negative correlation peaks provide information on the spatial relationships between the hydrogen atoms. In the case at hand, the decisive feature of the NOESY spectrum, which is presented in Figure 3a, consists of a strong cross-peak between the *p*-tolyl CH_3 hydrogens (δ 2.34) and the two aromatic *ortho* hydrogens at *ca.* 7.0 ppm (partially overlapping with other aromatic protons of the PPh_2 groups). These, in turn, show a clear correlation in the double-quantum filtered COSY spectrum with the 2H-multiplet at δ 8.65 due to the remaining pair of the *p*-tolyl hydrogen nuclei (Figure 3b). As expected, these protons do not exhibit further scalar couplings in the COSY spectrum but display a NOESY pattern which shows a NOE contact with the butenynyl hydrogen at 8.28 ppm (Figure 3c).

These experiments clearly indicate that there is a direct relationship between the butenynyl hydrogen and the *p*-tolyl CH_3 group *via* the four aromatic hydrogen

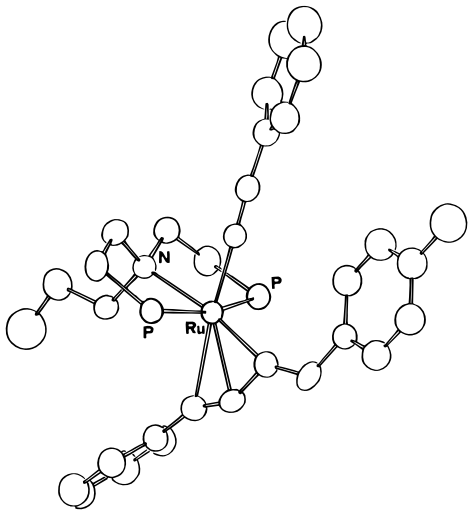


Figure 4. Drawing of the complex *mer*-(PNP)Ru(C≡CPh)-{η^3-PhC$_3$═CH(*p*-tolyl)} (**9**). All of the phenyl rings of PNP ligand are omitted for clarity.

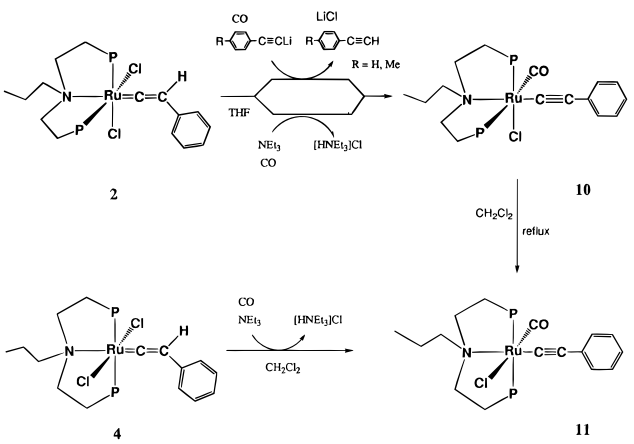
atoms of the *p*-tolyl substituent and rule out the alternative structure **II** in which there is not a geminal disposition of the *p*-tolyl group and of the butenynyl hydrogen atom.

Finally, in accord with the *anti,mer* stereochemistry of **9**, the NOESY spectrum does not show any contact between the hydrogen atoms of the *n*-propyl chain and those of the *p*-tolyl ring.

A single-crystal X-ray analysis of **9** has fully confirmed the structural formulation determined in solution by NMR spectroscopy. Although details of the structure of **9** will be given elsewhere, a drawing of **9** is shown in Figure 4.[40]

Synthesis and Characterization of *fac*-(PNP)-RuCl(C≡CPh)(CO) (10) and *mer*-(PNP)RuCl(C≡CPh)(CO) (11). Treatment of **2** in THF with 1 equiv of LiC≡CPh, followed by different workups (removal of the solvent *in vacuo*, addition of either *n*-hexane or EtOH), invariably gives several Ru complexes (^{31}P NMR). A separate experiment carried out in a sealed NMR tube showed that a selective reaction between stoichiometric amounts of **2** and LiC≡CPh occurs in THF-d_8 with formation of a unique product (^{31}P NMR: singlet at 59.93 ppm) at a temperature as low as −50 °C. Above −10 °C, however, extensive decomposition already occurs which at room temperature results in the complete disappearance of the low-temperature compound and formation of several unidentified products. Since a similar sequence of events is observed by treatment of **2** in THF with 1 equiv of *n*-BuLi (particularly the selective formation of the same product at low temperature), our conclusion is that the first 1 equiv of LiC≡CPh added to **2** deprotonates the vinylidene ligand to give a σ-alkynyl ligand and also removes a chloride from Ru as LiCl. As a result, the unsaturated (PNP)-RuCl(C≡CPh) complex may form which apparently degrades at room temperature to several products by reaction with various potential reagents in the surrounding environment (HC≡CPh, solvent, water). In a successful attempt to intercept this reactive intermediate, the addition of LiC≡CPh to **2** was carried out under an atmosphere of carbon monoxide (which alone does not react with **2**): the octahedral carbonyl complex *fac*-(PNP)RuCl(C≡CPh)(CO) (**10**) was quantitatively obtained as yellow crystals (Scheme 3).

Scheme 3



In order to definitely probe that a stoichiometric amount of LiC≡CPh serves to deprotonate the vinylidene ligand, complex **2** in THF was reacted in the presence of CO with either a different acetylide (LiC≡C-*p*-tolyl) or a base of different type (NEt$_3$). In both reactions, **2** is quantitatively converted to **10** (no incorporation of the *p*-tolylacetylide unit into the complex occurs, while the conjugated acid NHEt$_3^+$, isolated as the Cl$^-$ salt, forms in the reaction with NEt$_3$).

The ^{31}P{^{1}H} NMR spectrum of **10** in CD_2Cl_2 consists of an AM spin system. On the basis of the different *trans* influence exerted by the Cl and and CO ligands on the ^{31}P chemical shifts,[20,41] the signal at 49.43 ppm can be assigned to the PPh$_2$ group *trans* to the chloride, while the upfield signal at 23.33 ppm is assigned to the phosphorus *trans* to the carbonyl ligand. The IR spectrum shows ν(C≡O) of the carbonyl ligand at 1968 cm^{-1} and ν(C≡C) of the alkynyl group at 2089 cm^{-1}. Consistent with the structure proposed in Scheme 3, the resonance of the carbonyl carbon atom in the ^{13}C{^{1}H} NMR spectrum is observed at 200.20 ppm (dd) with *cis* and *trans* ^{31}P−^{13}CO coupling constants [^2J(CP$_{trans}$) 100.6 Hz, ^2J(CP$_{cis}$) 14.9 Hz] in line with those observed for several ruthenium carbonyl complexes.[42]

On standing in CH_2Cl_2 solution, **10** slowly converts to the thermodynamic isomer *mer*-(PNP)RuCl(C≡CPh)-(CO) (**11**). At room temperature the complete isomerization of 20 mg of **1** in 0.7 mL of CD_2Cl_2 occurs in 4−5 days, while at 50 °C the isomerization is complete in 3 h.

Compounds **10** and **11** exhibit very similar spectroscopic characteristics, the only relevant differences being those directly connected with the coordination mode of the PNP ligand; *e.g.*, the ^{31}P{^{1}H} NMR of **11** consists of a singlet at 34.18 ppm suggestive of the *mer* structure. Notably, the carbonyl carbon atom signal in the ^{13}C{^{1}H} NMR spectrum of **11** falls in the same position of the analogous resonance of **10** but appears as a triplet [^2J(CP) = 12.8 Hz], which further supports the structure shown in Scheme 3.

(40) Bianchini, C.; Peruzzini, M. Unpublished results.

(41) Balimann, G.; Pregosin, P. S. *J. Magn. Reson.* **1976**, *22*, 235.

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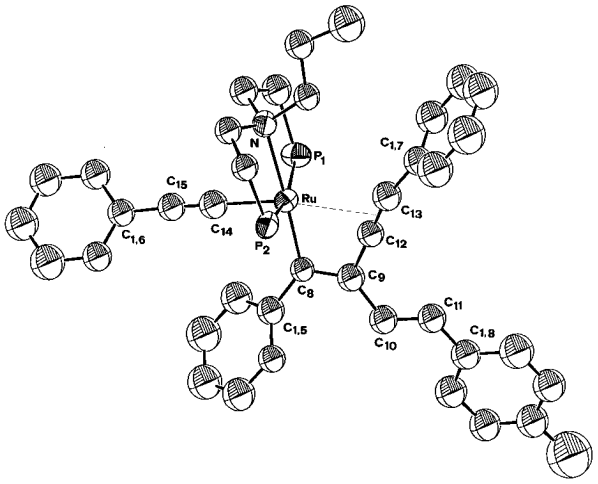

Figure 5. ORTEP drawing (30% thermal ellipsoids probability) of the complex *mer*-(PNP)Ru(C≡CPh){η^1-PhC=C-(C≡CPh)CH=CH(*p*-tolyl)}] (**13**). All of the phenyl rings of PNP ligand are omitted for clarity.

Reactions of the *mer,trans* Vinylidene Complexes with LiC≡CPh. Synthesis of the σ-Alkynyl−η^1-Hexadienynyl Complexes *mer*-(PNP)Ru(C≡CPh){η-PhC=C(C≡CPh)CH=CH(R)} (R = Ph, 12; R = *p*-tolyl, 13). Unlike the *fac,cis* isomers, the *mer,trans* vinylidene complexes **4** and **5** in THF consume 3 equiv of LiC≡CPh. From the reaction mixture, red orange crystalline complexes of the formula *mer*-(PNP)Ru(C≡CPh){η-PhC=C(C≡CPh)CH=CH(R)} (R = Ph, **12**; R = *p*-tolyl, **13**) are obtained in fairly good yield (*ca.* 60%) only if a primary alcohol (EtOH or MeOH) is subsequently added. When EtOD is employed, stereospecific incorporation of deuterium occurs in the 2-position of the butadienyl fragment of the C_6 unsaturated ligand (Scheme 2).

Both the use of 3 equiv of LiC≡CPh and the addition of alcohol are of mandatory importance for the formation of **12** and **13** in acceptable yields. In the absence of either reaction conditions, only trace amounts of **12** and **13** are formed together with several unidentified (PNP)-Ru compounds.

Given the evident complexity of the underlying chemical reactions involving the addition of 3 "C≡CPh" units and one hydrogen atom to the *mer*-(PNP)Ru=C=C(H)R fragment, a single-crystal X-ray analysis of the *p*-tolyl derivative **13** has been of paramount importance for elucidating the structure of the organyl ligands bound to Ru. An ORTEP view of **13** is shown in Figure 5, while selected bond angles and interatomic distances are collected in Table 3.

The structure consists of discrete molecules of *mer*-(PNP)Ru(C≡CPh){η-PhC=C(C≡CPh)CH=CH(*p*-tolyl)} and clathrated CH_2Cl_2 molecules; the packing is dictated by van der Waals interactions with no unusual intramolecular contacts. The Ru atom is coordinated by a *mer*-PNP ligand which shows metrical parameters and geometrical distortions similar to those of **8** [P1−Ru−P2 = 164.3(2)°]. The coordination geometry around Ru is completed by a σ-bonded phenylethynyl ligand and by an unprecedented 1-*p*-tolyl-3-(phenylethynyl)-4-phenyl-buta-1(*E*),3(*Z*)-dien-4-yl ligand which essentially uses a carbon atom *trans* to the nitrogen to bind the metal [N−Ru−C8 = 177.6(8)°; Ru−C8 = 2.04(2) Å]. However, a weak bonding interaction between the metal center and the phenylethynyl substituent on the C9 carbon atom may be envisaged [Ru−C12 = 2.48(2), Ru···C13 = 2.82(2) Å] which is probably important for the overall stability of the complex. Consistent with a very weak bonding interaction, the C12−C13 separation is 1.22(3) Å and the C9−C12−C13 sequence of carbon atoms is practically linear [179(2)°]. Also, the value of the bent-back angle of the phenyl substituent (164(2)°) is intermediate between the values exhibited by η^3-(144.6−158.6°)[1cd,38,43,44] and η^1-butenynyl complexes (173−175.6°).[1b,39,45]

In the butadiene part of the C_6 ligand there is alternation of short and long C−C bond distances.[46] Double bonds are localized between the C8−C9 [1.35-(3) Å] and C10-C11 [1.34(3) Å] carbon atoms, while the separation C9−C10 of 1.50(3) Å corresponds to a single bond. The "RuC_6" assembly is essentially planar with a maximum deviation of 0.062 Å for Ru from the plane. In the alkynyl substituent, the separation C9−C12 [1.43(3) Å] although slightly shorter than a C(sp^3)-C(sp) single bond (1.47 Å)[47] excludes a significative delocalization of the alkyne π-electrons. Finally, the bond angles and distances relative to the σ-alkynyl ligand are normal and do not deserve further comments.

From a comparison of the spectroscopic and structural data, one may readily infer that **13** exhibits the same structure in both the solid state and solution (the ^{31}P-

Table 3. Selected Bond Distances (Å) and Angles (deg) for *mer*-[(PNP)Ru(C≡CPh)-{η^1-PhC=C(C≡CPh)CH=CH(*p*-tolyl)}]·CH_2Cl_2 (13·CH_2Cl_2)

Ru−P_1	2.326(7)	C_9−C_{10}	1.50(3)
Ru−P_2	2.312(7)	C_9−C_{12}	1.43(3)
Ru−N	2.30(2)	C_{10}−C_{11}	1.34(3)
Ru−C_8	2.04(2)	C_{12}−C_{13}	1.22(3)
Ru−C_{14}	2.03(2)	C_{14}−C_{15}	1.18(3)
P_1−C_1	1.85(2)	C_{11}−$C_{1,8}$	1.44(3)
P_2−C_3	1.86(2)	C_{13}−$C_{1,7}$	1.45(3)
Ru−C_{12}	2.48(2)	C_{15}−$C_{1,6}$	1.43(3)
C_8−C_9	1.35(3)	$C_{4,8}$−C_{16}	1.46(5)
C_8−C_9	1.35(3)	Ru···C_{13}	2.82(2)
P_1−Ru−P_2	164.3(2)	C_8−Ru−C_{14}	95.4(9)
P_1−Ru−N	83.0(4)	C_{12}−Ru−C_{14}	153.8(8)
P_2−Ru−N	81.4(4)	Ru−C_8−C_9	108(1)
P_1−Ru−C_8	98.2(6)	Ru−C_8−$C_{1,5}$	132(1)
P_2−Ru−C_8	97.3(6)	C_9−C_8−$C_{1,5}$	120(1)
N−Ru−C_8	177.6(8)	C_8−C_9−C_{10}	131(2)
P_1−Ru−C_{12}	95.0(6)	C_8−C_9−C_{12}	107(2)
N−Ru−C_{12}	123.6(7)	C_9−C_{10}−C_{11}	121(2)
P_1−Ru−C_{14}	89.1(7)	C_{10}−C_{11}−$C_{1,8}$	124.(2)
P_2−Ru−C_{12}	95.3(5)	C_9−C_{12}−C_{13}	179(2)
P_2−Ru−C_{14}	87.0(7)	C_{12}−C_{13}−$C_{1,7}$	164(2)
N−Ru−C_{14}	83.6(8)	C_{14}−C_{15}−C_{16}	177(2)
C_8−Ru−C_{12}	58.5(8)		

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(44) (a) Field, L. D.; George, A. V.; Hambley, T. W. *Inorg. Chem.* **1990**, *29*, 4565. (b) Hills, A.; Hughes, D. L.; Jimenez-Tenorio, M.; Leigh, G. J.; McGeary, C. A.; Rowley, A. T.; Bravo, M.; McKenna, M.-C. *J. Chem. Soc., Dalton Trans.* **1991**, 522.

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(46) A similar alternation of bonds lengths has been found in [Ru-{C(Ph)=C(Ph)C(η^6-C_6H_5)=C(Ph)CH_2CH=CH_2}{P($OMe)_3$}$_2$][BF_4]$_2$: Crocker, M.; Green, M.; Nagler, K. R.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1990**, 2571. Another example is found in [(PPh_3)$_2$(CO)-(MeO_2CC≡C)Ru(MeOOCC=CHCH=CHCO_2Me)]: Torres, M. R.; Santos, A.; Ros, J.; Solans, X. *Organometallics* **1987**, *6*, 1091.

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Table 4. Summary of Crystal Data for *fac,cis*-(PNP)RuCl$_2$(CO) (6) and *anti,mer*-(PNP)Ru(C≡CPh){η^3-PhC$_3$=CH(Ph)} (8)

	6	8
formula	$C_{32}H_{35}NCl_2OP_2Ru_1$	$C_{56}H_{51}NP_2Ru_1$
M_r	683.52	888.98
temp, K	293(2)	293(2)
cryst size, mm	0.18 × 0.22 × 0.16	0.12 × 0.32 × 0.21
cryst system	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	11.562(2)	12.914(3)
b, Å	14.888(3)	16.234(3)
c, Å	19.403(4)	21.737(4)
α, deg	90	90
β, deg	98.65(3)	92.97(3)
γ, deg	90	90
V, Å^3	3301.9 (11)	4551(2)
Z	4	4
ρ(calcd), g cm^{-3}	1.375	1.297
μ(Mo Kα), mm^{-1}	0.758	0.452
F(000)	1400	1848
radiation	graphite-monochromated Mo Kα, λ = 0.710 69 Å	graphite-monochromated Mo Kα, λ = 0.710 69 Å
scan type	$\omega-2\theta$	$\omega-2\theta$
θ range, deg	2.53−22.47	2.51−22.48
scan width, deg	0.8 + 0.35 tan θ	0.8 + 0.35 tan θ
index ranges, h, k, l	−12 to 12; 0 to 15; 0 to 20	−13 to 13; 0 to 17; 0 to 23
reflcns collcd	3165	3610
indepdt reflcns	3056 [R(int) = 0.0367]	3506 [R(int) = 0.0313]
no. of refined params	311	250
goodness-of-fit on F^2	1.146	1.075
R	0.0594 [$I > 2\sigma(I)$]	0.0538 [$I > 2\sigma(I)$]
R_w	0.1891	0.1299
largest diff peak, e Å^{-3}	1.487	0.658
largest diff hole, e Å^{-3}	−0.683	−0.445

Table 5. Summary of Crystal Data for *mer*-(PNP)Ru(C≡CPh)-{η^1-PhC=C(C≡CPh)C(H)=CH(*p*-tolyl)}·CH$_2$Cl$_2$ (13·CH$_2$Cl$_2$)

formula	$C_{65}H_{62}P_2NCl_2Ru$
M_r	1090.15
temp, K	293(2)
cryst size, mm	0.28 × 0.30 × 0.27
cryst system	monoclinic
space group	$P2_1/n$ (No. 14)
a, Å	13.890(4)
b, Å	18.255(7)
c, Å	21.857(9)
b, deg	97.52(2)
V, Å^3	5494.44
Z	4
ρ(calcd), g cm^{-3}	1.32
μ(Cu Kα), mm^{-1}	4.136
radiation	graphite-monochromated Cu Kα, λ = 1.54 18 Å
scan type	$\omega-2\theta$
2θ range, deg	5−100
scan width, deg	0.9 + 0.15 tan θ
scan speed, deg min^{-1}	0.02−0.1
reflcs collcd	6080
unique data [$I > 3\sigma(I)$]	1824
refined params	231
R	0.070 [$I > 3\sigma(I)$]
R_w	0.073

{^{1}H} NMR spectrum shows a singlet at *ca.* 31 ppm). The presence of the 1-*p*-tolyl-3-(phenylethynyl)-4-phenylbuta-1(*E*),3(*Z*)-dien-4-yl ligand is confirmed by the ^{1}H NMR spectrum. This contains a doublet (1H) at 6.14 ppm which is not coupled to the phosphorus nuclei but is scalarly connected (^{1}H,^{1}H-2D COSY NMR experiment) to a signal at *ca.* 7.1 ppm [J(HH) = 15.7 Hz] buried under the crowded aromatic hydrogen resonances. Finally, ^{1}H,^{13}C-2D HMQC and DEPT NMR experiments disclose the positions of all the carbon atoms of the two organyl ligands bound to Ru (see Experimental Section).

The perphenylated compound **12** exhibits ^{1}H and ^{13}C-{^{1}H} NMR spectra which are practically coincident with those of **13** (the only difference being the resonances due to the methyl substituent of the tolyl group in **13**), and thus, the two compounds are assigned the same structure.

Stoichiometrically, **12** and **13** differ from **8** and **9** for containing one more "HC≡CR" unit (R = Ph, *p*-tolyl). In an attempt to convert **8** and **9** to **12** and **13**, the former compounds were dissolved in THF and then treated with excesses of either HC≡CR or LiC≡CR (with or without EtOH) at different temperatures. In no case, was a transformation of the starting compounds observed leading to the conclusion that **8** and **9** are not intermediates to **12** and **13**.

The reaction of the vinylidene precursor **4** with 1 equiv of LiC≡CPh in the presence of CO is not technically feasible due to the very poor solubility of the complex in the solvents in which lithium acetylide can safely be handled. However, treatment of **4** in CH_2Cl_2 with a slight excess of NEt_3 in the presence of CO gives the carbonyl **11** and [$HNEt_3$]Cl suggesting that, like the enynyl complexes **8** and **9**, also the formation of the dienynyl complexes **12** and **13** initially proceeds *via* deprotonation of the vinylidene group and removal of one chloride ligand by the first 1 equiv of LiC≡CPh.

Discussion

Schemes 4 and 5 summarize our mechanistic interpretation for the formation of the present enynyl and dienynyl Ru(II) complexes, respectively.

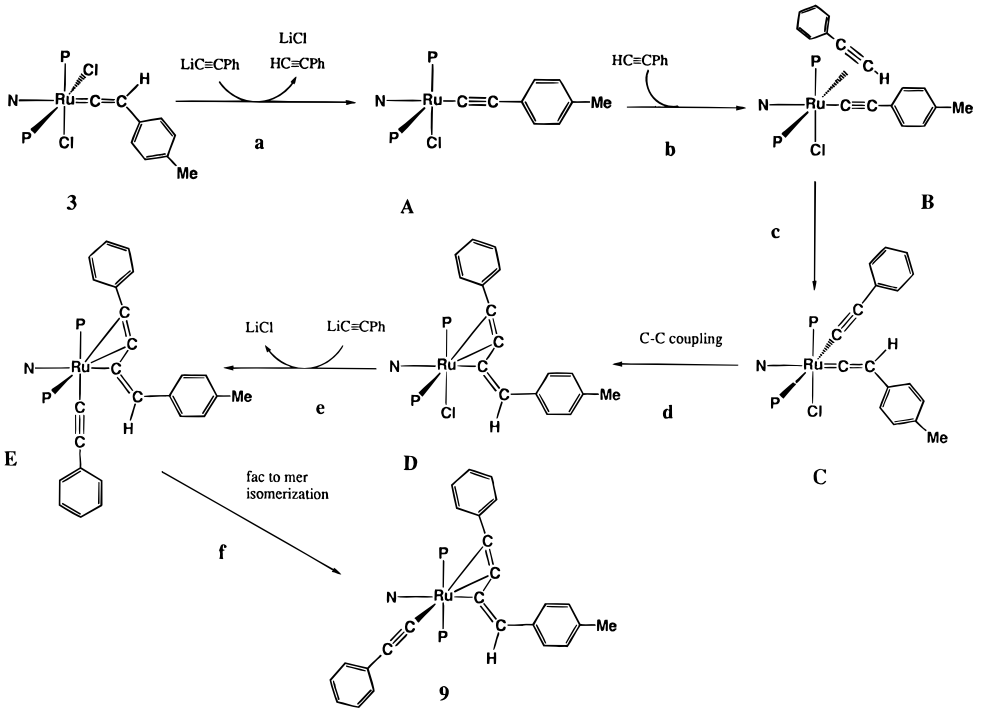
The stepwise mechanism proposed for the formation of the butenynyl complex **9** (Scheme 4) is quite similar to many others previously reported.[1] However, the position of the *p*-tolyl substituent in the final product provides some interesting mechanistic information.

We have demonstrated that the first 1 equiv of LiC≡CPh serves to deprotonate the starting vinylidene ligand. As a result, 1 equiv of HC≡CPh and a free coordination site at Ru are simultaneously generated (step **a**). The HC≡CPh molecule, generated *in situ*, can thus readily interact with the metal center.

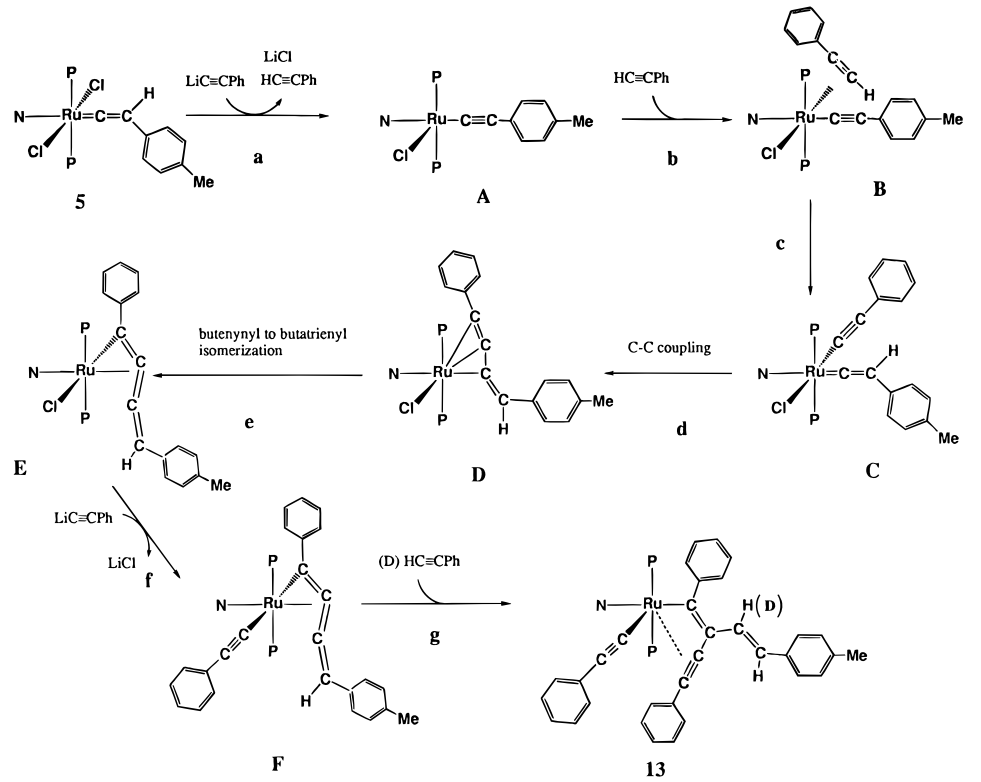
Since the *p*-tolyl group in the final product is regioselectively incorporated into the vinyl portion of the C_4 ligand, the interaction between the 1-alkyne and the ruthenium center (step **b**) must necessarily result in a proton transfer from the 1-alkyne to the β-carbon atom of the alkynyl ligand. *Cis* σ-phenylethynyl and *p*-tolylvinylidene ligands are consequently formed (step **c**), and from their coupling (vinylidene migratory insertion) (step **e**),[1a,b] the *E*-butenynyl ligand is finally assembled (step **d**).

Notably, the structure of the butenynyl ligand excludes that the HC≡CPh molecule tautomerizes to vinylidene at step **b**. In this case, in fact, one would have found the *p*-tolyl substituent on the alkynyl moiety of the C_4 ligand, which is not observed. A hydrogen transfer thus occurs from an activated HC≡CPh molecule (probably *via* π-coordination) to the C_β of the alkynyl ligand (step **c**). After the C−C bond-forming

Scheme 4



Scheme 5



step, the chloride ligand in intermediate **D** can be replaced by a phenylethynyl group provided by the second 1 equiv of added LiC≡CPh, to give the *fac*-(η^3-butenynyl)alkynyl complex **E**. Finally, the latter complex converts to the thermodynamically more stable *mer* isomer **9** (in this case, the isomerization should be favored not only by steric interaction but also by the great *trans* influence of the organyl ligands).[18]

The reaction with the second 1 equiv of LiC≡CPh necessarily occurs after formation of the *p*-tolylvinylidene ligand and not before as there is selective formation of **9**. In fact, should the interaction with the HC≡CPh molecule generated *in situ* follow the metathesis reaction of compound **A** with LiC≡CPh, a mixture of different butenynyl ligands would form (having the *p*-tolyl substituent on either the vinyl or alkynyl moiety as a consequence of random protonation of the phenylethynyl and *p*-tolylethynyl ligands by HC≡CPh).

In the initial stages (steps **a**−**d**), the suggested mechanism for the formation of the 1-*p*-tolyl-3-(phenyl-

ethynyl)-4-phenyl-buta-1(*E*),3(*Z*)-dien-4-yl complex **13** is quite similar to that proposed for **9**, the only difference being the geometry of the PNP ligand in the starting vinylidene complex **5** as well as in the following intermediates.

Just the *mer* geometry of the PNP ligand in intermediate **D** may be the factor that controls the subsequent reactivity leading to incorporation of a third "HC≡CPh" moiety into the final product.

Apparently, intermediate **D** does not react with LiC≡CPh. In this case, in fact, complex **9** would form which is fully stable in the presence of either LiC≡CPh, HC≡CPh, or alcohols. Thus, it is suggested that intermediate **D** undergoes a faster reaction than the metathesis with LiC≡CPh. The structure of the dienynyl ligand in the final product **13** (particularly the positions of the *p*-tolyl and deuterium labels) suggests that **D** rapidly rearranges to the butatrienyl- isomer **E**. Indeed, butatrienyl and butenynylmetal complexes are known to rearrange into each other *via* a 1,3-metal shift.[1b] In the few cases where the isomerization to the less thermodynamically stable butatrienyl isomers has been observed, steric factors have been invoked to account for the transformation. In particular, it has been proposed that bulky substituents in the 1,4-positions of the C_4 unsaturated ligands favor the butenynyl to butatrienyl conversion at ruthenium(II).

On the basis of molecular modeling studies, Wakatsuki and co-workers have suggested that a severe steric repulsion between the tertiary phosphine ligands and the alkynyl moiety of the butenynyl group promotes the conversion of the butenynyl complex $Ru(CO)(PPh_3)_2(C{\equiv}C^tBu)(^tBuC{\equiv}CC{=}CH^tBu)$ to the butatrienyl isomer $Ru(CO)(PPh_3)_2(C{\equiv}C^tBu)(^tBuC{=}C{=}C{=}CH^tBu)$.[1b,2] A similar steric interaction (between the aromatic rings of the butenynyl ligand and of the mutually *trans* PPh_2 groups, *mer* structure) may be the driving force for the conversion of the butenynyl intermediate **D** to the butatrienyl isomer **E**. In this eventuality, the formation of the dienynyl complex **13** can be rationalized in terms of the well-known capability of cumulene and cumulenyl metal complexes to add various substrates (primary amines, water, alcohols).[48] In the case at hand, a regio- and stereoselective *trans* addition of HC≡CPh across the $C_\beta-C_\gamma$ double bond would account for the formation of the 1-*p*-tolyl-3-(phenylethynyl)-4-phenyl-buta-1(*E*),3(*Z*)-dien-4-yl ligand in **13**. The HC≡CPh molecule consumed in this step is evidently generated *in situ* by addition of ethanol to the reaction mixture which still contains 1 equiv of unreacted LiC≡CPh. In the absence of ethanol, several unidentified products are formed which may be consistent with the formation of a very reactive butatrienylmetal complex.

Unlike dimerization to enynyl compounds (precursors to disubstituted butenynes), metal-assisted trimerization of 1-alkynes to dienynyl species (precursors to trisubstituted hexadienynes) is a rare reaction.[49] In particular, very few ruthenium complexes, generally polynuclear species, have been reported to promote the trimerization of either 1-alkynes or acetylide residues.[50]

The major thermodynamic stability of the butenynyl complexes vs the butatrienyl isomers may explain why the oligomerization of 1-alkynes stops at the stage of formation of the first C−C bond for those metals like ruthenium that readily promote the tautomerization of 1-alkynes to vinylidenes. On the other hand, the use of coligands with large steric hindrance, favoring the formation of butatrienyl ligands, may provide access to Ru complexes capable of promoting the linear trimerization of 1-alkynes.

Acknowledgment. Thanks are due to Mr. Dante Masi for technical assistance in the X-ray structure determinations. Thanks are also expressed to the EC for financial support (Contract No. ERBCHRXCT930147).

Supporting Information Available: Tables of final positional parameters and isotropic and anisotropic displacement parameters for all atoms and bond lengths and angles for **6**, **8**, and **13**·CH_2Cl_2 (16 pages). Ordering information is given on any current masthead page.

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