Vinylidene-, Alkynyl-, and *trans*-Bis(alkynyl)ruthenium Complexes. Crystal Structure of *trans*-[Ru(NH_3)(C≡C−Ph)($Ph_2PCH_2CH_2PPh_2$)$_2$]PF_6

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A variety of vinylidene−ruthenium complexes [*trans*-Ru=C=CHR(Cl)(dppe)$_2$]PF_6 (**2**) are obtained by reaction of $RuCl_2$(dppe)$_2$ (**1**) with terminal alkynes and $NaPF_6$. On treatment with a base, complexes **2** afford the alkynyl−ruthenium derivatives *trans*-Ru−C≡C−R(Cl)-(dppe)$_2$ (**3**). *trans*-Ru(C≡CR)$_2$(dppe)$_2$ **4** are prepared under mild conditions *via* the reaction of $RuCl_2$(dppe)$_2$ with terminal alkynes HC≡C−R (R = Ph, ^{n}Bu, $SiMe_3$, $C_{10}H_{21}$, CH_2OSiMe_3, CH_2OMe) in the presence of an excess amount of $NaPF_6$ and NEt_3, whereas *trans*-Ru(C≡CH)$_2$-(dppe)$_2$ (**5**) was obtained directly from HC≡C−$SnBu_3$ and precursor **1**. In contrast, unsymmetrically substituted complexes *trans*-Ru(C≡CR^1)(C≡CR^2)(dppe)$_2$ (**6**) were built from the vinylidenes **2** in the presence of another alkyne, $NaPF_6$, and NEt_3. On protonation with $NH_4^+PF_6^-$, the bis(alkynyl) derivatives **4** lead to the release of RC≡CH and the formation of *trans*-[Ru(NH_3)(C≡CR)(dppe)$_2$]PF_6 complexes **7**. The structure of *trans*-[Ru(NH_3)-(C≡CC_6H_5)($Ph_2PCH_2CH_2PPh_2$)]PF_6 (**7a**) has been determined by X-ray diffraction.

Introduction

Carbon-rich organometallics, especially those containing σ-alkynyl−metal linkages, are attracting interest since they allow both the connection of the metal to functional groups and the electronic communication of the latter to the metal through the C≡C bond(s). σ-Alkynyl−metal derivatives associated with functional groups contain specific properties similar to those in liquid crystals[1] or for use in nonlinear optics.[2,3] They are also used to generate carbon-rich oligomers[4] or metal containing polymers[3,5] and to produce bimetallic systems with carbon bridges[6,7] and mixed-valence systems.[8] In addition alkynyl−metal complexes have

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recently been shown to give access to metallocumulenes,[9] favor selective C−C coupling,[10−12a] and promote catalytic reactions, especially *via* their corresponding vinylidene derivatives.[12,13]

These properties motivate the selective building of alkynyl−metal complexes and unsymmetrically substituted bis(alkynyl)−metal derivatives. The σ-alkynyl−metal complexes are usually made by substitution of metal halides by classical alkynyl derivatives of Li, Mg, or Cu[11,14] or more efficiently with an alkynyltin derivative and palladium catalysts.[15] The metal activation of terminal alkynes into vinylidene−metal complexes is a well-known process,[16−19] and the easy deprotonation of the latter may constitute a good method to produce (σ-alkynyl)ruthenium metal complexes.[19] Following our preliminary work,[20] we now (i) report the synthesis of new (vinylidene)ruthenium and (alkynyl)ruthenium complexes, (ii) report the selective formation of *trans*-bis(alkynyl)ruthenium derivatives, symmetrically substituted directly from $RuCl_2(Ph_2PCH_2CH_2PPh_2)_2$ ($RuCl_2(dppe)_2$; **1**) and unsymmetrically substituted from vinylidene derivatives, and (iii) show that the *trans*-$Ru(C{\equiv}CR)_2(dppe)_2$ precursors can be used for the preparation of new mixed ammonia−alkynylruthenium complexes.

Results and Discussion

Synthesis of Ruthenium−Vinylidene Complexes 2. The reaction of *cis*-$RuCl_2(dppe)_2$[21] (**1**) in dichloromethane with 2 equiv of (trimethylsilyl)acetylene, at room temperature, in the presence of 2 equiv of $NaPF_6$ afforded the yellow complex **2a** in 87% yield (Scheme 1). The structure of **2a** corresponds to the *trans*-chloro(vinylidene)ruthenium complex, as indicated in NMR by the equivalence of the four phosphorous nuclei, the low-frequency resonance as a quintet of the (Ru=C) carbon nucleus (δ = 349.9 ppm, $^2J_{PC}$ = 13 Hz), and the $=CH_2$ carbon signal as a triplet at δ = 92.4 ppm, $^1J_{CH}$ = 165 Hz). This reaction corresponds to the activation of the terminal alkyne into the vinylidene with subsequent desilylation.[22]

Complex **1** was also reacted with several terminal alkynes under the same conditions, and *trans*-chloro(vinylidene)ruthenium complexes **2b**−**e** were isolated in 77−86% yields and characterized by elemental analysis and NMR (Scheme 1). The vinylidenes **2a**−**e** are air stable and do not react with methanol, as it was observed to occur by activation of the same alkynes with $RuCl_2(PR_3)$(arene) derivatives to give the carbene complexes $[Ru{=}C(OMe)CH_2R(Cl)(PR_3)(arene)]PF_6$.[18] This is likely due to the steric hindrance of the four phenyl groups of the dppe ligands around the carbon C_1 in **2** and to the electron-donor character of the $(dppe)_2ClRu^+$ moiety, which makes the vinylidene less electrophilic than the $(arene)(PR_3)ClRu^+$ moiety despite its cationic nature.

All of these complexes **2** show a low-field quintet in the ^{13}C NMR in the range δ = 358−327 ppm (Ru=C) with *cis*-P,C coupling ($^2J_{PC} \approx$ 13 Hz) and a Ru=C=C*H* quintet in the ^1H NMR at $\delta \approx$ 3.00 ppm ($^4J_{PH}$ = 3 Hz). This proton is clearly at high field as compared to other ruthenium vinylidene derivatives.[23−25]

The activation of the alkyne into a vinylidene by complex **1** in the presence of $NaPF_6$ is expected to take place by initial formation of the 16-electron species $RuCl(dppe)_2{}^+PF_6{}^-$, which has already been characterized,[26] followed by η^2-coordination of the alkyne and an intramolecular 1,2-shift of the terminal hydrogen[27] or by C−H bond oxidative addition to the 16-electron ruthenium(II) intermediate to generate a ruthenium(IV) moiety, with subsequent migration of the (RuH) hydride to the β carbon, as observed with the more electron-rich and bulky complex $[RuCl(^iPr_2PCH_2CH_2P^iPr_2)(C_5Me_5)]$.[28]

Synthesis of Ruthenium−Acetylide Complexes 3. Complexes **2** in dichloromethane were easily deprotonated with a base such as Et_3N or DBU (1,8-diazabicyclo[5.4.0]-undec-7-ene) at room temperature. Complexes **3** were isolated after chromatography on alumina and identified as the *trans*-acetylide ruthenium(II) complexes **3a**−**e**, obtained in 64−67% yields (Scheme 1). The acetylide complexes show, in the infrared, a C≡C absorption at 1933 cm^{-1} for **3a**, 1952 cm^{-1} for **3e**, and 2094 cm^{-1} for **3b**. The *trans*-position of the chloro and acetylide ligands is indicated by the equivalence of the phosphorus nuclei in the ^{31}P NMR spectrum and the ^{13}C NMR spectrum shows one quintet for Ru−C≡ and one singlet for ≡CR carbon nuclei (Table 1).

Synthesis of Symmetrical Bis(acetylide) Ruthenium Complexes 4−5. It was not found possible or easily feasible to directly introduce two alkynyl groups on the $Ru(dppm)_2$ moiety from the complex $RuCl_2(dppm)_2$,[19] which is isoelectric to derivative **1**. However, $RuCl_2(dppm)_2$ has been shown to give *trans*-$Ru(C{\equiv}C{-}Ph)_2(dppm)_2$ on reaction with the stannyl alkyne

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(23) δ (Ru=C=C*H*)= 5.66 ppm in $[Ru{=}C{=}CHPh(Cl)(PMe_3)(C_6Me_6)]PF_6$,[18a] 5.42 ppm in $[Ru{=}C{=}CHPh(PMe_2Ph)_2C_5Me_5)]PF_6$,[24] or 5.22 in $[Ru{=}C{=}CHPh(PPh_3)_2(\eta^5\text{-}C_9H_7)]PF_6$.[25] This high-field shift is likely due to the presence of four phenyl groups neighboring the vinylidene ligand as it is found in $[Ru{=}C{=}CHPh(Cl)(dppm)_2]PF_6$ (δ = 3.05 ppm).[19]
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Scheme 1

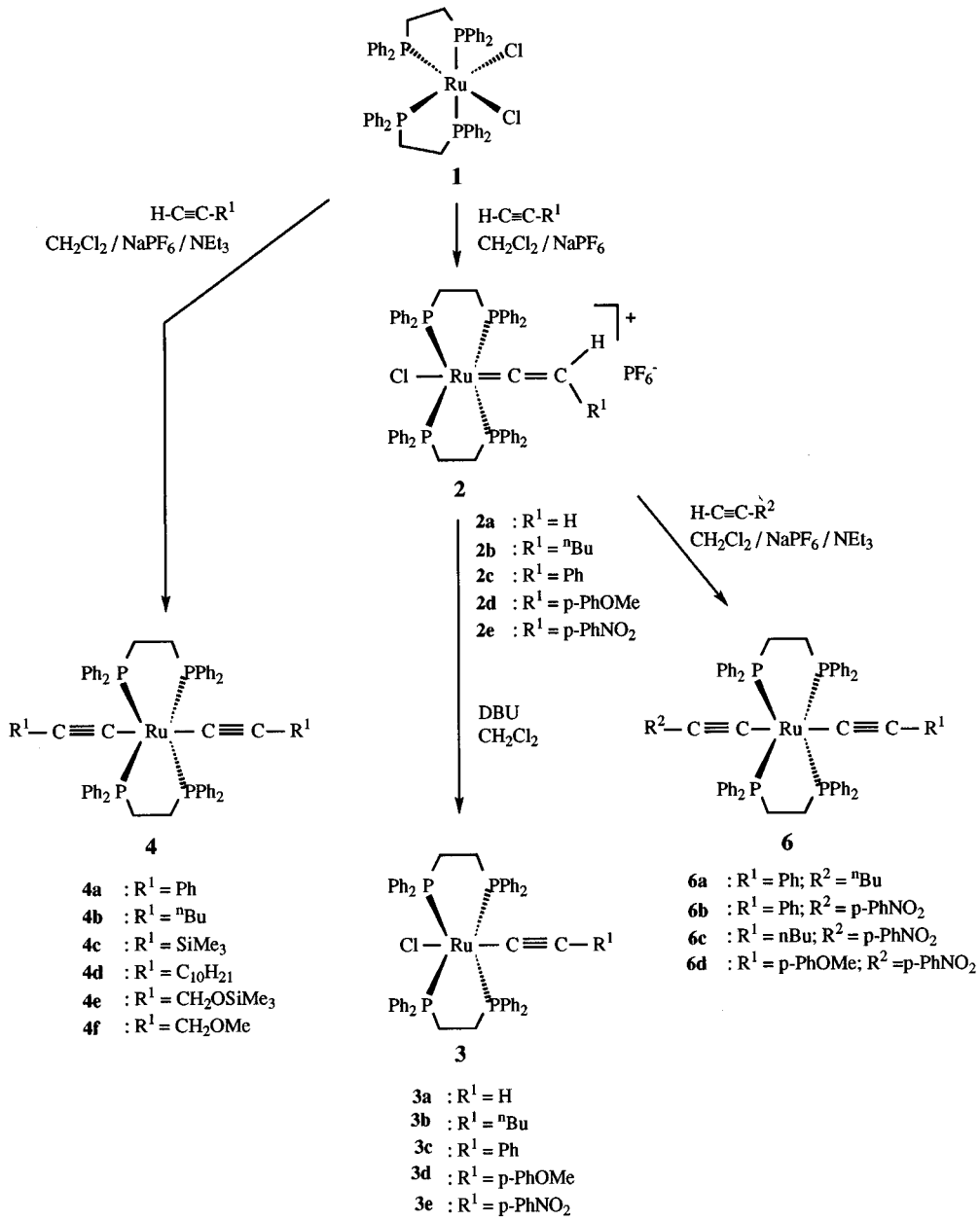

Table 1. Selected NMR Data (δ, ppm) for Compounds 3−5

		$^{13}C\{^1H\}$	
	$^{31}P\{^1H\}$	C_1	C_2
3a	49.28	131.1	100.6
3b	49.81	97.8	110.2
3c	49.44	124.4	113.6
3d	49.44	*a*	123.7
3e	48.56	*a*	129.3
4a	53.78	131.98	116.88
4b	54.36	108.1	113.1
4c	53.43	154.9	121.4
4d	55.46	108.1	113.3
4e	55.21	119.1	111.7
5	52.96	121.7	102.7

[a] C masked by phenyl carbons.

$PhC{\equiv}CSnMe_3$ in the presence of CuI,[29] whereas $Ru(C{\equiv}CPh)_2(PMe_3)_4$ was obtained directly from $RuCl_2(PMe_3)_4$ and $PhC{\equiv}CSnMe_3$ without the assistance of copper iodide.[30] It is noteworthy that other bis(acetylide) ruthenium derivatives were obtained in more drastic conditions, such as from $RuCl_2(Et_2PCH_2CH_2PEt_2)_2$, which led to a variety of *trans*-$Ru(C{\equiv}CR)_2(Et_2PCH_2CH_2PEt_2)_2$ complexes by reaction with MeONa/MeOH in the presence of alkyne $HC{\equiv}CR$.[31] From $RuCl_2(R_2PCH_2CH_2PR_2)_2$ (R = Me, Et) on reduction with sodium in isopropyl alcohol, a mixture of *cis*- and *trans*-dihydrides $Ru(H)_2(R_2PCH_2CH_2PR_2)_2$ was obtained and reacted with terminal alkynes to give the complexes *trans*-$Ru(C{\equiv}CR)_2(R_2PCH_2CH_2PR_2)_2$.[31]

The substitution of the two chlorides of complex **1** was attempted under these conditions, leading to both the formation of the monovinylidene complex **2** and its deprotonation giving **3**. Thus, complex **1** was reacted with an excess (3 equiv) of phenylacetylene, $NaPF_6$, and NEt_3 in dichloromethane at room temperature for 4 h

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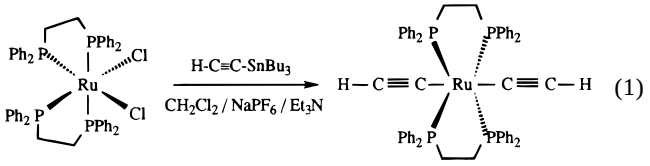
to give the yellow *trans*-bis(alkynyl)ruthenium complex **4a** in 82% yield (Scheme 1). It is noteworthy that this reaction *does not* take place in the absence of the $NaPF_6$ salt, and thus, the formation of a 16-electron ruthenium intermediate twice by displacement of the chloride ligands is an essential step in the activation process. It is likely that the alkyne on coordination is easily deprotonated either as an η^2-ligand, as observed for (η^2-alkyne)rhenium complexes,[32] or as its tautomer, the vinylidene intermediate.

Under similar conditions, a variety of terminal alkynes led to the symmetrical bis(alkynyl) derivatives **4b**−**f** (R^1 = ^{n}Bu, $SiMe_3$, $(CH_2)_9CH_3$, CH_2OSiMe_3, CH_2OMe) in 45−80% yields (Scheme 1). Their NMR data ressemble that of monoalkynyl derivatives (Table 1), except for the PCH_2CH_2P protons which are equivalent in complexes **4** and not equivalent in complexes **2** or **3**.

It should be pointed out that from (trimethylsilyl)-acetylene the bis(alkynyl) derivative **4c** was obtained without desilylation, in contrast with the formation of the vinylidene complex **2a** arising from the same alkyne. This is consistent with a more reactive (sp^2)C−Si bond in the cationic vinylidene intermediate.

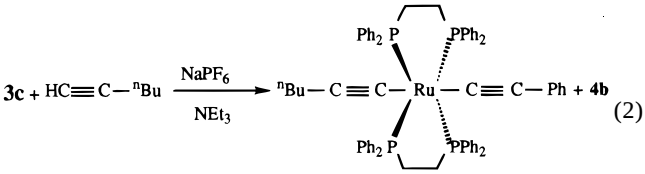
The synthesis of the unsubstituted bis(acetylide) ruthenium derivative **5** was performed according to eq 1 by activation of the stannylalkyne $HC{\equiv}CSnBu_3$ in dichloromethane with $NaPF_6$ and NEt_3, e.g., under the same conditions as the **1** → **4c** transformation, and **5** was obtained in 35% yield only (eq 1).



1 **5** (1)

Synthesis of Unsymmetrical Bis(acetylide) Ruthenium(II) Complexes 6. Several planar or octahedral *trans*-bis(alkynyl)−metal complexes have been shown to have liquid crystal properties.[1] However, in order to provide such physical properties, these organometallic molecules need to be unsymmetrically substituted and contain a lipophile chain in the *trans* position of an alkynyl chain linked to a polar group alternatively in order to create a large dipolar moment and provide nonlinear optical properties;[33] two polar groups, one electron-donating and the other electron-withdrawing, have to be linked at each end of the conjugated alkynyl chains in a linear arrangement. These properties motivate the search for synthetic methods allowing the selective introduction of two different *trans*-alkynyl groups in a metal complex.

As it is possible to introduce two identical alkynyl groups in the *trans*-position of the $Ru(dppe)_2$ unit starting from complex **1** in the presence of $NaPF_6$, the reaction of complex **3c** with an excess of $HC{\equiv}C-{}^n$Bu and $NaPF_6$ and NEt_3 was attempted in dichloromethane. A mixture of the mixed bis(alkynyl) derivative **6a** and of the symmetrical bis(alkynyl) complex **4b** was formed in the ratio **6a**:**4b** = 70:30, and **6a** was isolated by fractional crystallization in 40% yield (eq 2).



(2)

6a (70 %) + **4b** (30 %)

A more selective route was formed directly starting from the vinylidene complexes **2** by addition of a solution of 1.5 equiv of a terminal alkyne and 3 equiv of NEt_3 to a mixture of a vinylidene **2** with 1.5 equiv of $NaPF_6$ in dichloromethane at room temperature. Under these conditions, the mixed alkynylruthenium complexes **6** were formed selectively (Scheme 1).

Thus, from complex **2c** (R^1 = Ph) complexes **6a** (R^2 = ^{n}Bu) and **6b** (R^2 = *p*-$PhNO_2$) were obtained in 47% and 45% yields. The red complexes **6c** (51%) and **6d** (47%), which contain an electron-donor or an electron-acceptor group, were made by reaction of *p*-$O_2N-C_6H_4C{\equiv}CH$ with **2b** and **2e**, respectively.

These unsymmetrically substituted complexes **6** show, in the NMR spectra, one singlet for the four equivalent ^{31}P nuclei, consistent with the *trans*-arrangement of the alkynyl groups. In the ^{13}C NMR spectra, the (Ru−C≡) carbon nuclei are nonequivalent and give a quintet of triplets for the ^{n}Bu−C≡*C*−Ru and a simple quintet for the PhC≡*C*−Ru carbon nuclei (**6a** = 107.0 ($^2J_{PC}$ = 16 Hz, $^3J_{CH}$ = 4 Hz), 133.8 ($^2J_{PC}$ = 16 Hz)).

Preparation of Ammonia−Alkynylruthenium Complexes 7. The preparation of bis(alkynyl)ruthenium complexes **4** and **6** may take place *via* the formation of a vinylidene alkynylruthenium intermediate, before deprotonation. However, mixed vinylidene−alkynyl−metal complexes are still exceptions,[10e,11] but they are likely to be formed in the head-to-head dimerization of terminal alkynes, *via* insertion of the vinylidene ligand into the σ-alkynyl carbon−ruthenium bond.[11−13] We have attempted to produce them simply by protonation of the *trans*-bis(alkynyl)ruthenium complexes **4**, but these attempts led us to discover a new route to ammonia−ruthenium complexes.

The protonation of bis(alkynyl) complexes **4a** or **4b** with strong acids, such as HCl, HBF_4, CF_3CO_2H, takes place, but the resulting intermediate rapidly decomposes. However, when **4a** was reacted with an excess of $NH_4^+PF_6^-$ in dichloromethane, an orange compound was obtained and identified as the ammonia complex **7a** (73%) (Scheme 2). Analogously, the reaction of **4b** and **4c** with NH_4PF_6 afforded the derivatives **7b** (81%) and **7c** (73%), respectively.

The infrared and NMR spectra of the complexes **7** show the presence of the alkynyl group, the equivalence of the four ^{31}P nuclei (*trans* isomer), and a resonance for the NH_3 ligand in the ^{1}H NMR spectra (δ = 0.09 (**7a**), 0.01 (**7b**), and −0.08 (**7c**)). The structure has been ascertained by an X-ray diffraction study of the derivative **7a**.

The formation of complex **7** can be understood as the protonation with the ammonium ion NH_4^+ of the β carbon of one alkynyl chain of complex **4** to produce an unstable mixed vinylidene−alkynylruthenium interme-

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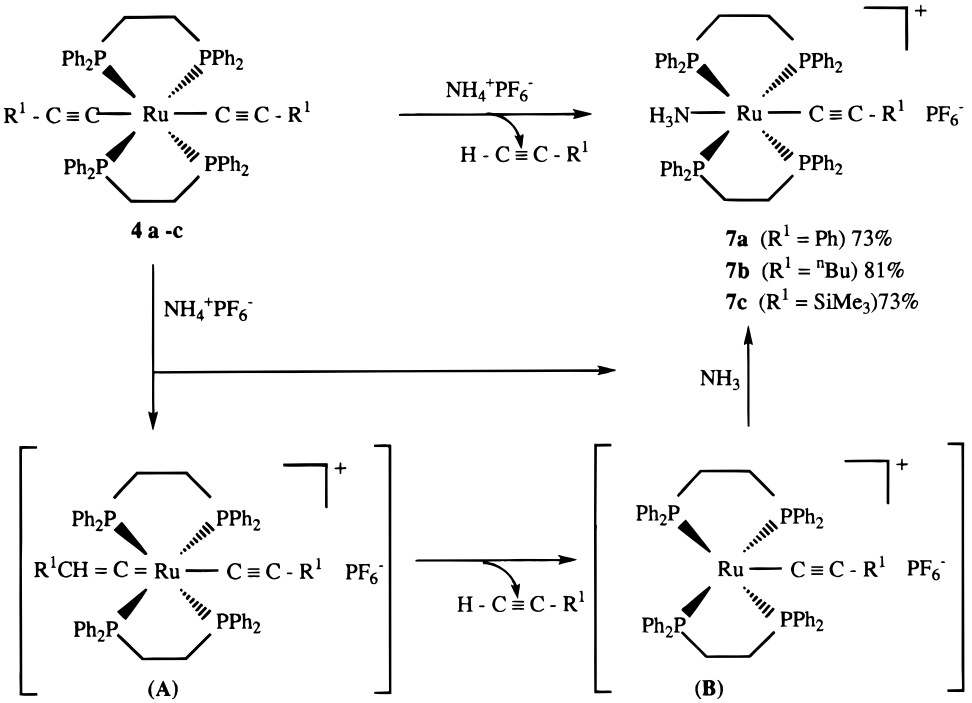
Scheme 2



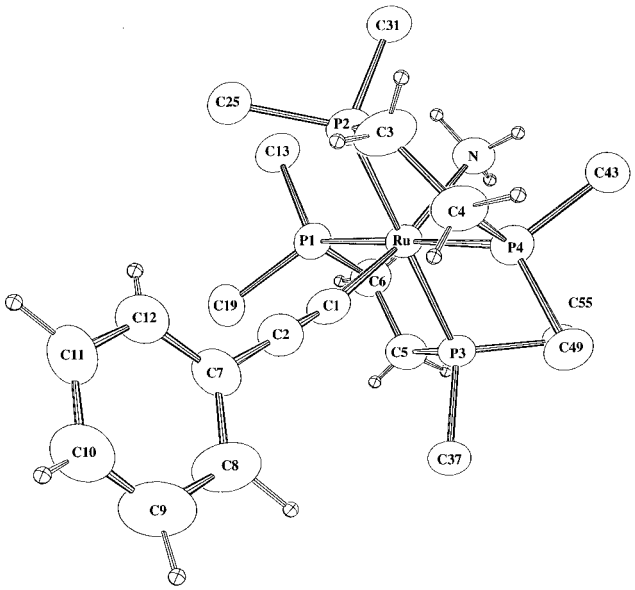


Figure 1. ORTEP diagram for *trans*-[(NH_3)Ru(C≡C−Ph)-$(dppe)_2$]PF_6 (**7a**).

diate (**A**) and ammonia. The transformation of **A** takes place with the release of the vinylidene ligand, rearranging into the terminal alkyne, and the formation of the 16-electron ruthenium intermediate **B**, eager to trap the two electrons of the free ammonia. When the latter, **B**, is generated by addition of a strong acid (HBF_4 or CF_3CO_2H), it decomposes in the absence of a coordinating ligand. Ammonia−ruthenium complexes have been recently prepared by protonation of $Ru(H)_2(PR_3)_4$ complexes with NH_4PF_6. Elimination of molecular hydrogen takes place, generating a 16-electron ruthenium intermediate which coordinates the ammonia.[34]

The molecular structure of **7a** is shown in Figure 1. Experimental crystallographic data are given in Table 2, and a selection of bond distances and angles are given in Table 3. The structural data shows a distorded octahedral coordination for the ruthenium atom. The ammonia occupies an apical position *trans* to the alkynyl group, without colinearity [C_1−Ru−N 169.1(2)°]. The metal atom is in the center of the plane formed by the four phosphorous atoms. The C_1−C_2 bond distance (1.187(7) Å) is long with respect to that in the neutral

Table 2. Experimental Crystallographic Data for 7a

formula	$RuP_4NC_{60}H_{56}PF_6$
mol wt	1161.05
cryst syst	monoclinic
space group	*Cc*
a (Å)	14.345(7)
b (Å)	22.079(3)
c (Å)	17.857(4)
β	104.00(3)
V (Å^3)	5488(2)
Z	4
ρ_{calcd} (g cm^{-3})	1.405
F(000)	2384
μ(Mo Kα) (cm^{-1})	4.81
T (K)	294
cryst size (mm)	0.30 × 0.45 × 0.55
radiation	Mo Kα
max 2θ (deg)	50
scan type	$\omega/2\theta = 1$
t_{max} (for one measure) (s)	60
variance of standards	0.1%
range of *HKL*	0−18, 0−28, −22 to 22
no. of reflns measd	6396
no. of reflns obsd ($I > \sigma(I)$)	5134 (2σ)
R_{int} (from merging equiv refl)	0.014
R (isotropic)	0.09
R (anisotropic)	0.07
Fourier difference	0.21−0.09
N(obs)/*N*(var)	5134/819
final *R*	0.033
R_w[a]	0.031
S_w	1.10
max residual e·Å^{-3}, Δ/σ	0.12, 0.74

[a] $w = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.04F_o^2)^2]^{-1/2}$.

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Table 3. Selected Bond Distances and Angles for 7a

Bond Distances (Å)			
Ru−C_1	2.014(5)	Ru−P_1	2.401(1)
C_1−C_2	1.187(7)	Ru−P_2	2.347(1)
C_2−C_7	1.441(7)	Ru−P_3	2.385(1)
Ru−N	2.215(5)	Ru−P_4	2.347(1)
Bond Angles (deg)			
P_1-Ru−P_4	176.4(6)	C_2-C_1-Ru	168.9(5)
P_2−Ru−P_3	176.6(5)	P_2−Ru−N	90.2(1)
C_1−Ru−N	169.1(2)	C_1−Ru−P_3	98.7(1)
P_3−Ru−N	92.1(1)	C_1−Ru−P_2	78.9(1)

complex (1.162(9) Å in Cl(dppm)$_2$Ru(C≡CH))[19] but slightly shorter than that in the derivatives Ru−C≡C−Ph(dppe)(C_5H_5) (1.204(5) Å)[35] or *trans*-Ru(C≡CH)$_2$(CO)$_2$(PEt$_3$)$_2$ (1.199(2) Å).[36] The Ru−N bond distance (2.215(5) Å) is longer than (2.159(6) Å) in the cation [Ru(NH$_2$-CHMe$_2$(H)(PMe$_3$)(η^6-C_6Me_6]$^+$,[37] probably due to the *trans* influence of the alkynyl group.

Conclusion

The above methodology for the preparations of symmetrical and unsymmetrical bis(alkynyl)−metal derivatives has been used to give access to ferrocenylalkynylruthenium complexes.[40] It also motivates the search for the formation of a carbon−carbon bond by the coupling of the alkynyl ligands to give functional polyynes and suggests that bis(alkynyl)−metal or mixed ammonia−alkynyl−metal derivatives should be used for the generation of 16-electron ruthenium intermediates.

Experimental Section

General Data. All reactions were performed under an argon or nitrogen atmosphere with the use of Schlenk techniques. The solvents were deoxygenated and dried by standard methods. Infrared spectra were recorded on a Nicolet 205 FT-IR spectrometer. ^{1}H (300.13 MHz), ^{31}P (121.50 MHz), and ^{13}C (75.47 MHz) NMR spectra were recorded on a Bruker AC300P spectrometer at 297 K and referenced to TMS for ^{1}H and ^{13}C and to 86% H_3PO_4 for ^{31}P. Elemental analyses were performed by the Service National de Microanalyses du CNRS at Vernaison, France. The complex *cis*-RuCl$_2$(dppe)$_2$ (dppe = $Ph_2PCH_2CH_2PPh_2$) was prepared by the literature method.[21]

Synthesis of Vinylidenes *trans*-[(dppe)$_2$(Cl)Ru=C=CHR]PF$_6$ (2a−e). A solution of the terminal alkyne (1 mmol) in 50 mL of dichloromethane was added to *cis*-RuCl$_2$(dppe)$_2$ (**1**; 0.5 mmol, 484 mg) and $NaPF_6$ (1 mmol, 168 mg). After 12 h of stirring at room temperature, the solution was filtered through a filter-paper-tipped cannula, the solvent was removed under *vacuum*, and the precipitate was washed with diethyl ether. After dissolution in a minimum amount of dichloromethane and slow addition of hexane in order to form a biphasic system, crystals of **2** were obtained.

***trans*-[(dppe)$_2$(Cl)Ru=C=CH$_2$]PF$_6$ (2a).** From 140 μL of (trimethylsilyl)acetylene (1.0 mmol), 480 mg of yellow crystals of **2a** (87%) was isolated. Anal. Calcd for $C_{54}H_{50}ClF_6P_5Ru$: C, 58.73; H, 4.56. Found: C, 58.58; H, 4.73. IR (cm^{-1}, KBr): 1619 (s, $\nu_{C=C}$), 889 (s, ν_{PF_6}). ^{1}H NMR (300.133 MHz, CD_2Cl_2, 297 K, δ (ppm)): 7.45−7.10 (40H, Ph), 2.91, 2.80 (m, 8H, PCH_2CH_2P), 2.43 (quint, 2H, =CH$_2$, $^4J_{PH}$ = 3 Hz). ^{13}C NMR (75.47 MHz, CD_2Cl_2, 297 K, δ (ppm)): 349.9 (quint, Ru=C, $^2J_{PC}$ = 13 Hz), 135.5−126.3 (Ph), 92.4 (t, =CH$_2$, $^1J_{CH}$ = 165 Hz), 29.02 (t m, PCH_2CH_2P, $^1J_{CH}$ = 136 Hz). ^{13}C{^{1}H} NMR (δ, ppm): 349.9 (quint, Ru=C, $^2J_{PC}$ = 13 Hz), 92.4 (quint, =CH$_2$, $^3J_{PC}$ = 1.5 Hz), 29.03 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{P'C}|$ = 23 Hz). ^{31}P{^{1}H} NMR (121.50 MHz, CD_2Cl_2, 297 K, δ (ppm)): 41.47 (s, PPh_2), −143.94 (sept, PF_6, $^1J_{PF}$ = 710 Hz).

***trans*-[(dppe)$_2$(Cl)Ru=C=CH^{n}Bu]PF$_6$ (2b).** From 180 μL of 1-hexyne (1.5 mmol), 475 mg of orange crystals of **2b** (82%) was isolated. Anal. Calcd for $C_{58}H_{58}ClF_6P_5Ru$: C, 60.03; H, 5.04. Found: C, 59.80; H, 5.00. IR (cm^{-1}, KBr): 1648 (s, $\nu_{C=C}$), 838 (s, ν_{PF_6}). ^{1}H NMR (300.133 MHz, CD_2Cl_2, 297 K, δ (ppm)): 7.41−6.99 (40H, Ph), 2.84, 2.60 (m, 8H, PCH_2CH_2P), 2.15 (m, 1H, =CH), 1.37 (m, 2H, =CH−CH$_2$−), 0.80 (m, 2H, =CHCH$_2$−CH$_2$−), 0.67 (m, 5H, −CH$_2$CH$_3$). ^{13}C NMR (75.47 MHz, CD_2Cl_2, 297 K, δ (ppm)): 327.9 (quint, Ru=C, $^2J_{PC}$ = 13 Hz), 135.5−127.3 (Ph), 105.3 (d m, =CH, $^1J_{CH}$ = 151 Hz), 32.8 (t m, =CH−CH$_2$−, $^1J_{CH}$ = 124 Hz), 29.4 (t quint, PCH_2CH_2P, $^1J_{CH}$ = 132 Hz, $|^1J_{PC} + {}^3J_{P'C}|$ = 23 Hz), 22.2 (t m, =CH−CH$_2$−CH$_2$−, $^1J_{CH}$ = 127 Hz), 21.1 (t m, −CH$_2$−CH$_3$, $^1J_{CH}$ = 132 Hz), 13.8 (q m, −CH$_3$, $^1J_{CH}$ = 126 Hz). ^{13}C{^{1}H} NMR (δ, ppm): 327.94 (quint, Ru=C, $^2J_{PC}$ = 13 Hz), 105.3 (quint, =CH, $^3J_{PC}$ = 2 Hz), 32.7 (s, =CH−CH$_2$−), 29.4 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{P'C}|$ = 23 Hz), 22.17 (s, =CH−CH$_2$−CH$_2$−), 21.16 (s, −CH$_2$−CH$_3$), 13.8 (s, −CH$_3$). ^{31}P{^{1}H} NMR (121.50 MHz, CD_2Cl_2, 297 K, δ (ppm)): 42.77 (s, PPh_2), −143.93 (sept, PF_6, $^1J_{PF}$ = 709 Hz).

***trans*-[(dppe)$_2$(Cl)Ru=C=CHPh]PF$_6$ (2c).** From 110 μL of phenylacetylene (1.0 mmol), 490 mg of red crystals of **2c** (83%) was isolated. Anal. Calcd for $C_{60}H_{54}ClF_6P_5Ru$: C, 61.05; H, 4.61. Found: C, 60.77; H, 4.59. IR (cm^{-1}, KBr): 1628 (s, $\nu_{C=C}$), 837 (s, ν_{PF_6}). ^{1}H NMR (300.133 MHz, CD_2Cl_2, 297 K, δ (ppm)): 7.33−5.67 (45H, Ph), 3.04 (quint, 1H, =CH, $^4J_{PH}$ = 3 Hz), 2.87, 2.66 (m, 8H, PCH_2CH_2P). ^{13}C NMR (75.47 MHz, CD_2Cl_2, 297 K, δ (ppm)): 354.5 (d quint, Ru=C, $^2J_{PC}$ = 13 Hz, $^2J_{CH}$ = 4 Hz), 135.6−127.4 (Ph), 109.7 (d m, =CH, $^1J_{CH}$ = 150 Hz), 29.02 (t m, PCH_2CH_2P, $^1J_{CH}$ = 138 Hz). ^{13}C{^{1}H} NMR (δ, ppm): 354.5 (quint, Ru=C, $^2J_{PC}$ = 13 Hz), 109.7 (quint, =CH, $^3J_{PC}$ = 2 Hz), 29.03 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{P'C}|$ = 23 Hz). ^{31}P{^{1}H} NMR (121.50 MHz, CD_2Cl_2, 297 K, δ (ppm)): 40.15 (s, PPh_2), −143.87 (sept, PF_6, $^1J_{PF}$ = 709 Hz).

***trans*-[(dppe)$_2$(Cl)Ru=C=CH(*p*-PhOMe)]PF$_6$ (2d).** From 132 mg of 4-methoxyphenylacetylene (1.0 mmol), 520 mg of green crystals of **2d** (86%) was isolated. Anal. Calcd for $C_{61}H_{56}ClF_6P_5Ru$: C, 60.53; H, 4.66. Found: C, 60.39; H, 4.54. IR (cm^{-1}, KBr): 1637 (m, $\nu_{C=C}$), 837 (s, ν_{PF_6}). ^{1}H NMR (300.133 MHz, CD_2Cl_2, 297 K, δ (ppm)): 7.40−5.66 (44H, Ph), 3.67 (s, 3H, OCH$_3$), 3.02 (quint, 1H, =CH, $^4J_{PH}$ = 3 Hz), 2.92, 2.69 (m, 8H, PCH_2CH_2P). ^{13}C NMR (75.47 MHz, CD_2Cl_2, 297 K, δ (ppm)): 357.4 (quint, Ru=C, $^2J_{PC}$ = 14 Hz), 135.6−113.2 (Ph), 109.2 (d m, =CH, $^1J_{CH}$ = 147 Hz), 55.6 (q, OCH$_3$, $^1J_{CH}$ = 145 Hz), 29.04 (t quint, PCH_2CH_2P, $^1J_{CH}$ = 133 Hz, $|^1J_{PC} + {}^3J_{P'C}|$ = 23 Hz). ^{13}C{^{1}H} NMR (δ, ppm): 357.4 (quint, Ru=C, $^2J_{PC}$ = 14 Hz), 109.2 (s large, =CH), 29.09 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{P'C}|$ = 23 Hz). ^{31}P{^{1}H} NMR (121.50 MHz, CD_2Cl_2, 297 K, δ (ppm)): 40.46 (s, PPh_2), −143.93 (sept, PF_6, $^1J_{PF}$ = 710 Hz).

***trans*-[(dppe)$_2$(Cl)Ru=C=CH(*p*-PhNO$_2$)]PF$_6$ (2e).** From 147 mg of 4-nitrophenylacetylene (1.0 mmol), 472 mg of dark red crystals of **2e** (77%) was isolated. Anal. Calcd for $C_{60}H_{53}ClF_6O_2NP_5Ru$: C, 58.81; H, 4.36. Found: C, 58.67; H, 4.27. IR (cm^{-1}, KBr): 1630 (m, $\nu_{C=C}$), 838 (s, ν_{PF_6}). ^{1}H NMR (300.133 MHz, CD_2Cl_2, 297 K, δ (ppm)): 7.38−5.62 (44H, Ph), 3.96 (quint, 1H, =CH, $^4J_{PH}$ = 2.9 Hz), 2.98, 2.81 (m, 8H, PCH_2CH_2P). ^{13}C NMR (75.47 MHz, CD_2Cl_2, 297 K, δ (ppm)): 350.7 (d quint, Ru=C, $^2J_{PC}$ = 13 Hz, $^2J_{CH}$ = 2 Hz), 135.5−123 (Ph), 109.3 (d quint, =CH, $^1J_{CH}$ = 151 Hz, $^3J_{PC}$ = 2 Hz), 29.03 (t quint, PCH_2CH_2P, $^1J_{CH}$ = 138 Hz, $|^1J_{PC} + {}^3J_{P'C}|$ = 23 Hz). ^{13}C-{^{1}H} NMR (δ, ppm): 350.7 (quint, Ru=C, $^2J_{PC}$ = 13 Hz), 109.3 (quint, =CH, $^3J_{PC}$ = 2 Hz), 29.1 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{P'C}|$ = 23 Hz). ^{31}P{^{1}H} NMR (121.50 MHz, CD_2Cl_2, 297 K, δ (ppm)): 39.94 (s, PPh_2), −143.84 (sept, PF_6, $^1J_{PF}$ = 710 Hz).

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Synthesis of Monoacetylides *trans*-[(dppe)$_2$(Cl)Ru−C≡C−R] (3a−e). A mixture of **2** (0.25 mmol) and an excess of Et_3N (1 mmol) was stirred in 20 mL of dichloromethane at room temperature. After 1 h of stirring, the solvent was removed under *vacuum*. The residue was purified by filtration through a column of neutral alumina using diethyl ether as eluent. After dissolution in a minimum amount of dichloromethane and slow addition of hexane, in order to form a biphasic system, crystals of **3** were obtained.

***trans*-[(dppe)$_2$(Cl)Ru−C≡C−H] (3a).** From 276 mg of **2a** (0.25 mmol), 20 mL of dichloromethane, and 140 μL of triethylamine (1.0 mmol), 163 mg of yellow crystals of **3a** (68%) was obtained. Anal. Calcd for $C_{54}H_{49}ClP_4Ru$: C, 67.67; H, 5.15. Found: C, 67.49; H, 5.07. IR (cm^{-1}, KBr): 1932.7 (s, $\nu_{C\equiv C}$), 3279.9 (m, $\nu_{\equiv CH}$). ^{1}H NMR (300.133 MHz, CD_2Cl_2, 297 K, δ (ppm)): 7.57−6.89 (40H, Ph), 2.67 (m, 8H, PCH_2CH_2P), 1.30 (quint, 1H, ≡C−H, $^4J_{PH} = 1.6$ Hz). ^{13}C NMR (75.47 MHz, CD_2Cl_2, 297 K, δ (ppm)): 136−125.5 (Ph), 131.1 (quint, Ru−C≡, $^2J_{PC} = 15.5$ Hz), 100.6 (d, ≡CH, $^1J_{CH} = 224$ Hz), 31.0 (t m, PCH_2CH_2P, $^1J_{CH} = 141$ Hz). ^{13}C{^{1}H} NMR (δ, ppm): 131.1 (quint, Ru−C≡, $^2J_{PC} = 15$ Hz), 100.6 (s, ≡CH), 31.0 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{P'C}| = 24$ Hz). ^{31}P{^{1}H} NMR (121.50 MHz, CD_2Cl_2, 297 K, δ (ppm)): 49.28 (s, PPh_2).

***trans*-[(dppe)$_2$(Cl)Ru−C≡C−^{n}Bu] (3b).** From 290 mg of **2b** (0.25 mmol), 20 mL of dichloromethane, and 140 μL of triethylamine (1.0 mmol), 162 mg of **3b** (64%) was isolated. Anal. Calcd for $C_{58}H_{57}ClP_4Ru$: C, 68.67; H, 5.66. Found: C, 68.17; H, 5.69. IR (cm^{-1}, KBr): 2094.3 (m, $\nu_{C\equiv C}$). ^{1}H NMR (300.133 MHz, CD_2Cl_2, 297 K, δ (ppm)): 7.37−6.90 (40H, Ph), 2.57 (m, 8H, PCH_2CH_2P), 1.83 (m, 2H, ≡C−CH_2−), 1.13 (m, 4H, −CH_2−CH_2−), 0.77 (t, 3H, CH_3, $^3J_{HH} = 7$ Hz). ^{13}C NMR (75.47 MHz, CD_2Cl_2, 297 K, δ (ppm)): 137.5−126 (Ph), 110.2 (m, ≡C−), 97.9 (m, Ru−C≡), 33.83 (m, ≡C−CH_2−), 31.24 (t m, PCH_2CH_2P, $^1J_{CH} = 134$ Hz), 23.95 (t, −CH_2−, $^1J_{CH} = 126$ Hz), 23.22 (t m, −CH_2−, $^1J_{CH} = 124$ Hz), 14.28 (q, −CH_3, $^1J_{CH} = 124$ Hz). ^{13}C{^{1}H} NMR (δ, ppm): 110.2 (s, ≡C−), 97.8 (quint, Ru−C≡, $^2J_{PC} = 16$ Hz), 33.8 (s, ≡C−CH_2−), 31.22 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{P'C}| = 24$ Hz), 23.9 (s, −CH_2−), 23.17 (s, −CH_2−), 14.27 (s, −CH_3). ^{31}P{^{1}H} NMR (121.50 MHz, CD_2Cl_2, 297 K, δ (ppm)): 49.81 (s, PPh_2).

***trans*-[(dppe)$_2$(Cl)Ru−C≡C−Ph] (3c).** From 295 mg of **2c** (0.25 mmol), 20 mL of dichloromethane, and 140 μL of triethylamine (1.0 mmol), 199 mg of **3c** (77%) was isolated. Anal. Calcd for $C_{60}H_{53}ClP_4Ru$: C, 69.62; H, 5.16. Found: C, 69.48; H, 5.11. IR (cm^{-1}, KBr): 2066.8 (s, $\nu_{C\equiv C}$). ^{1}H NMR (300.133 MHz, CD_2Cl_2, 297 K, δ (ppm)): 7.40−6.62 (45H, Ph), 2.67 (quint, 8H, PCH_2CH_2P, $|^2J_{PH} + {}^4J_{P'H}| = 8$ Hz). ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2, 297 K, δ (ppm)): 137.3−123.2 (Ph), 124.4 (quint, Ru−C≡, $^2J_{PC} = 16$ Hz), 113.6 (s, ≡C−), 31.08 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{P'C}| = 24$ Hz). ^{31}P{^{1}H} NMR (121.50 MHz, CD_2Cl_2, 297 K, δ (ppm)): 49.44 (s, PPh_2).

***trans*-[(dppe)$_2$(Cl)Ru−C≡C−C$_6$H$_4$−*p*-OMe] (3d).** From 302 mg of **2d** (0.25 mmol), 20 mL of dichloromethane, and 140 μL of triethylamine (1.0 mmol), 183 mg of **3d** (69%) was isolated. Anal. Calcd for $C_{61}H_{55}ClOP_4Ru$: C, 68.83; H, 5.21. Found: C, 69.07; H, 5.19. IR (cm^{-1}, KBr): 2073 (s, $\nu_{C\equiv C}$). ^{1}H NMR (300.133 MHz, CD_2Cl_2, 297 K, δ (ppm)): 7.39−6.55 (44H, Ph), 3.74 (s, 3H, OCH_3), 2.66 (quint, 8H, PCH_2CH_2P, $|^2J_{PH} + {}^4J_{P'H}| = 8$ Hz). ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2, 297 K, δ (ppm)): 137.5−127.2 (Ph), Ru−C≡ masked by phenyl carbons, 123.7 (s, ≡C−), 55.5 (s, OCH_3), 31.08 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{P'C}| = 23$ Hz). ^{31}P{^{1}H} NMR (121.50 MHz, CD_2Cl_2, 297 K, δ (ppm)): 49.44 (s, PPh_2).

***trans*-[(dppe)$_2$(Cl)Ru−C≡C−C$_6$H$_4$−*p*-NO$_2$] (3e).** From 306 mg of **2e** (0.25 mmol), 20 mL of dichloromethane, and 140 μL of triethylamine, 172 mg of **3e** (64%) was isolated. Anal. Calcd for $C_{60}H_{52}ClO_2P_4Ru$: C, 66.76; H, 4.86. Found: C, 66.47; H, 4.77. IR (cm^{-1}, KBr): 2052 (s, $\nu_{C\equiv C}$). ^{1}H NMR (300.133 MHz, CD_2Cl_2, 297 K, δ (ppm)): 7.85−6.35 (44H, Ph), 2.62 (quint, 8H, PCH_2CH_2P, $|^2J_{PH} + {}^4J_{P'H}| = 8$ Hz). ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2, 297 K, δ (ppm)): 135−127.4 (Ph), Ru−C≡ masked by phenyl groups, 129.3 (s, ≡C−), 30.86 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{P'C}| = 23$ Hz). ^{31}P{^{1}H} NMR (121.50 MHz, CD_2Cl_2, 297 K, δ (ppm)): 48.56 (s, PPh_2).

Synthesis of Symmetrical Bis(acetylides) *trans*-[(dppe)$_2$Ru(C≡C−R^1)$_2$] (4a−f). A mixture of terminal alkyne (1.5 mmol) and triethylamine (3 mmol) in 60 mL of dichloromethane was added to **1** (0.5 mmol) and $NaPF_6$ (1.5 mmol). After 4 h of stirring at room temperature, the solution was filtered, the solvent was removed under *vacuum*, and the residue was washed with hexane. After dissolution in a minimum amount of THF, the solution was filtered through an alumina column using ether as the eluent. The solvent was removed under *vacuum*, and the resulting powder was recrystallized in a mixture of dichloromethane−hexane to obtain crystals of **4**.

***trans*-[(dppe)$_2$Ru(C≡C−Ph)$_2$] (4a).** From 484 mg of **1** (0.5 mmol), 252 mg of $NaPF_6$ (1.5 mmol), 160 μL of phenylacetylene (1.5 mmol), and 420 μL of Et_3N, 450 mg of yellow crystals of **4a** (82%) were isolated. Anal. Calcd for $C_{68}H_{58}P_4Ru$: C, 74.24; H, 5.31. Found: C, 73.97; H, 5.27. IR (cm^{-1}, KBr): 2058 (s, $\nu_{C\equiv C}$). ^{1}H NMR (300.133 MHz, CD_2Cl_2, 297 K, δ (ppm)): 7.45−6.69 (m, 50H, Ph), 2.57 (m, 8H, PCH_2CH_2P). ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2, 297 K, δ (ppm)): 137.66−123.28 (Ph), 131.98 (quint, Ru−C≡, $^2J_{PC} = 15$ Hz), 116.88 (s, Ru−C≡C), 31.87 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{P'C}| = 23$ Hz). ^{31}P{^{1}H} NMR (121.50 MHz, CD_2Cl_2, 297 K, δ (ppm)): 53.78 (s, PPh_2).

***trans*-[(dppe)$_2$Ru(C≡C−^{n}Bu)$_2$] (4b).** From 484 mg of **1** (0.5 mmol), 252 mg of $NaPF_6$ (1.5 mmol), 140 μL of 1-hexyne (1.5 mmol), and 420 μL of Et_3N, 371 mg of yellow crystals of **4b** (70%) were isolated. Anal. Calcd for $C_{64}H_{66}P_4Ru$: C, 72.43; H, 6.27. Found: C, 72.40; H, 6.11. IR (cm^{-1}, KBr): 2086 (s, $\nu_{C\equiv C}$). ^{1}H NMR (300.134 MHz, CD_2Cl_2, 297 K, δ (ppm)): 7.40−6.86 (m, 40H, Ph), 2.49 (m, 8H, PCH_2CH_2P), 1.88 (m, 4H, ≡C−CH_2), 1.21 (m, 8H, −CH_2−CH_2−), 0.82 (m, 6H, −CH_3). ^{13}C NMR (75.47 MHz, CD_2Cl_2, 297 K, δ (ppm)): 138.47−125.80 (Ph), 113.15 (m, Ru−C≡C), 108.06 (m, Ru−C), 33.03 (t, ≡CCH_2, $^1J_{CH} = 127$ Hz), 32.08 (t m, PCH_2CH_2P, $^1J_{CH} = 133$ Hz), 23.75 (t m, ≡CCH_2CH_2, $^1J_{CH} = 127$ Hz), 23.15 (t, ≡CCH_2-CH_2CH_2, $^1J_{CH} = 125$ Hz), 14.31 (q, CH_3, $^1J_{CH} = 124$ Hz). ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2, 297 K, δ (ppm)): 138.61−126.88 (Ph), 113.15 (s, Ru−C≡C), 108.06 (quint, Ru−C, $^2J_{PC} = 15$ Hz), 33.04 (s, ≡CCH_2), 32.08 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{P'C}| = 24$ Hz), 23.75 (s, ≡CCH_2CH_2), 23.16 (s, ≡CCH_2CH_2-CH_2), 14.31 (s, CH_3). ^{31}P{^{1}H} NMR (121.50 MHz, CD_2Cl_2, 297 K, δ (ppm)): 54.36 (s, PPh_2).

***trans*-[(dppe)$_2$Ru(C≡CSiMe$_3$)$_2$] (4c).** From 484 mg of **1** (0.5 mmol), 252 mg of $NaPF_6$ (1.5 mmol), 140 μL of (trimethylsilyl)acetylene (1.5 mmol), and 420 μL of Et_3N, 300 mg of yellow crystals of **4c** (55%) were isolated. Anal. Calcd for $C_{62}H_{66}P_4Si_2Ru$: C, 64.84; H, 5.79. Found: C, 65.16; H, 5.97. IR (cm^{-1}, KBr): 1985 (s, $\nu_{C\equiv C}$). ^{1}H NMR (300.134 MHz, CD_2Cl_2, 297 K, δ (ppm)): 7.46−6.89 (m, 40H, Ph), 2.61 (m, 8H, PCH_2CH_2P), −0.22 (s, 18H, $SiMe_3$). ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2, 297 K, δ (ppm)): 154.98 (quint, Ru−C, $^2J_{PC} = 15$ Hz), 137.97−127.17 (Ph), 121.43 (s, Ru−C≡C), 31.73 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{PC}| = 24$ Hz). ^{31}P{^{1}H} NMR (121.50 MHz, CD_2Cl_2, 297 K, δ (ppm)): 53.43 (s, PPh_2).

***trans*-[(dppe)$_2$Ru(C≡C−(CH$_2$)$_9$CH$_3$)$_2$] (4d).** From 484 mg of **1** (0.5 mmol), 252 mg of $NaPF_6$ (1.5 mmol), 180 μL of H−C≡C−$C_{10}H_{21}$ (1.5 mmol), and 420 μL of Et_3N, 522 mg of **4d** (85%) was isolated. Anal. Calcd for $C_{76}H_{90}P_4Ru\cdot 0.25CH_2Cl_2$: C, 73.28; H, 7.30. Found: C, 73.47; H, 7.34. IR (cm^{-1}, KBr): 2087 (s, $\nu_{C\equiv C}$). ^{1}H NMR (300.133 MHz, $CDCl_3$, 297 K, δ (ppm)): 7.48−6.92 (m, 40H, Ph), 2.56 (m, 8H, PCH_2CH_2P), 1,92 (m, 4H, C≡CCH_2−), 1.33−1.25 (m, 32H, −(CH_2)$_8$−CH_3), 0.89 (t, 6H, CH_3, $^3J_{HH} = 6.7$ Hz). ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2, 297 K, δ (ppm)): 138.76−126.95 (Ph), 113.29 (s, Ru−C≡*C*), 108.15 (quint, Ru−*C*≡C, $^2J_{PC} = 15.2$ Hz), 54.60−23.21 (−(CH_2)$_9$−CH_3), 32.13 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{P'C}| = 24.4$ Hz), 14.41 (s, CH_3). ^{31}P{^{1}H} NMR (121.50 MHz, $CDCl_3$, 297 K, δ (ppm)): 55.46 (s, PPh_2).

***trans*-[(dppe)$_2$Ru(C≡CCH$_2$OSiMe$_3$)$_2$] (4e).** From 484 mg of **1** (0.5 mmol), 252 mg of $NaPF_6$ (1.5 mmol), 160 μL of

H−C≡C−CH_2OSiMe_3 (1.5 mmol), and 420 μL of Et_3N, 392 mg of **4e** (68%) was isolated. Anal. Calcd for $C_{64}H_{70}RuP_4O_2Si_2$: C, 66.71; H, 6.12. Found: C, 66.87; H, 6.30. IR (cm^{-1}, KBr): 2087 (s, $\nu_{C\equiv C}$). ^1H NMR (300.133 MHz, $CDCl_3$, 297 K, δ (ppm)): 7.47−6.91 (m, 40H, Ph), 3.95 (s, 4H, CH_2OSiMe$_3$), 2,59 (m, 8H, PCH_2CH_2P), 0.05 (s, 18H, $OSiMe_3$). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K, δ (ppm)): 138.21−127.05 (Ph), 119.12 (quint, Ru−*C*≡C, $^2J_{PC}$ = 15.2 Hz), 111.75 (s, Ru−C≡*C*), 54.73 (s, *C*H_2OSiMe$_3$), 31.96 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{P'C}|$ = 24.4 Hz), −0,13 (s, $OSiMe_3$). $^{31}P\{^1H\}$ NMR (121.50 MHz, $CDCl_3$, 297 K, δ (ppm)): 55.21 (s, PPh_2).

***trans*-[(dppe)$_2$Ru(C≡CCH$_2$OMe)$_2$] (4f).** From 484 mg of **1** (0.5 mmol), 252 mg of $NaPF_6$ (1.5 mmol), 160 μL of H−C≡C−CH_2OMe (1.5 mmol), and 420 μL of Et_3N, 233 mg of **4f** (45%) was isolated. Anal. Calcd for $C_{60}H_{58}RuP_4O_2$: C, 69.48; H, 5.64. Found: C, 69.14; H, 5.55. IR (cm^{-1}, KBr): 2075 (s, $\nu_{C\equiv C}$). ^1H NMR (300.133 MHz, $CDCl_3$, 297 K, δ (ppm)): 7.45−6.95 (m, 40H, Ph), 3.78 (quint large, 4H, CH_2, $^5J_{PC}$ = 1.3 Hz), 3.1 (s, 6H, OCH_3), 2.57 (m, 8H, PCH_2CH_2P). $^{31}P\{^1H\}$ NMR (121.50 MHz, $CDCl_3$, 297 K, δ (ppm)): 54.80 (s, PPh_2).

***trans*-[(dppe)$_2$Ru(C≡CH)$_2$] (5).** From 484 mg of **1** (0.5 mmol), 252 mg of $NaPF_6$ (1.5 mmol), 170 μL of H−C≡C−$SnBu_3$ (1.5 mmol), and 420 μL of Et_3N, 166 mg of **5** (35%) was isolated. Anal. Calcd for $C_{56}H_{50}P_4Ru$: C, 70.95; H, 5.21. Found: C, 71.17; H, 5.32. IR (cm^{-1}, KBr): 1917 (s, $\nu_{C\equiv C}$). ^1H NMR (300.134 MHz, CD_2Cl_2, 297 K, δ (ppm)): 7.51−6.64 (m, 40H, Ph), 2.65 (m, 8H, PCH_2CH_2P), 1.42 (quint, 2H, ≡CH, $^4J_{PH}$ = 2 Hz). ^{13}C NMR (75.47 MHz, CD_2Cl_2, 297 K, δ (ppm)): 137.80−125.85 (Ph), 121.74 (quint, Ru−C, $^2J_{PC}$ = 15 Hz), 102.72 (d, Ru−C≡CH, $^1J_{CH}$ = 219 Hz), 31.77 (t m, PCH_2CH_2P, $^1J_{CH}$ = 129 Hz). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K, δ (ppm)): 137.95−126.93 (Ph), 121.74 (quint, Ru−C, $^2J_{PC}$ = 15 Hz), 102.72 (s, Ru−C≡C), 31.78 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{P'C}|$ = 24 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K, δ (ppm)): 52.96 (s, PPh_2).

Synthesis of Mixed Bis(acetylides) *trans*-[(dppe)$_2$Ru(C≡C−R^1)(C≡CR^2)] (6a−d) from Vinylidenes 2. A solution of the terminal alkyne (0.75 mmol) and triethylamine (1.5 mmol) in 50 mL of dichloromethane was transferred into a Schlenk tube containing 0.5 mmol of vinylidene **2** and 0.75 mmol of $NaPF_6$. After 12 h of stirring at room temperature, the solution was filtered through a filter-paper-tipped cannula and the solvent removed under *vacuum*. The residue was purified by column chromatography (neutral alumina) using diethyl ether as the solvent. The crude product was recrystallized in a dichloromethane−hexane mixture to give crystals of **6**.

***trans*-[(dppe)$_2$Ru(C≡C−Ph)(C≡C^{n}Bu)] (6a).** From 590 mg of **2c** (0.5 mmol), 126 mg of $NaPF_6$ (0.75 mmol), 105 μL of 1-hexyne, and 210 μL of Et_3N in 50 mL of dichloromethane, 254 mg of yellow crystals of **6a** (47%) were isolated. Anal. Calcd for $C_{66}H_{62}P_4Ru$: C, 73.39; H, 5.79. Found: C, 73.59; H, 5.83. IR (cm^{-1}, KBr): 2061 (s, $\nu_{C\equiv C}$). ^1H NMR (300.133 MHz, CD_2Cl_2, 297 K, δ (ppm)): 7.51−6.73 (m, 45H, Ph), 2.58 (quint, 8H, PCH_2CH_2P, $|^2J_{PH} + {}^4J_{P'H}|$ = 8 Hz), 1.95 (m, 2H, ≡C−CH_2), 1.29 (m, 4H, −CH_2−CH_2−), 0.88 (t, −CH_3, $^3J_{HH}$ = 7 Hz). ^{13}C NMR (75.47 MHz, CD_2Cl_2, 297 K, δ (ppm)): 138.6−121.8 (Ph), 133.8 (quint, Ru−*C*≡C−Ph, $^2J_{PC}$ = 15 Hz), 116.8 (s, Ru−C≡*C*−Ph), 114.5 (m, Ru−C≡*C*−^{n}Bu), 106.9 (t quint, Ru−*C*≡C−^{n}Bu, $^2J_{PC}$ = 15 Hz, $^3J_{CH}$ = 4 Hz), 32.9 (t m, ≡C−*C*H_2−, $^1J_{CH}$ = 127 Hz), 32.0 (t m, PCH_2CH_2P, $^1J_{CH}$ = 135 Hz), 23.7 (t m, −CH_2−CH_2, 126 Hz), 23.1 (t m, −CH_2−CH_2, $^1J_{CH}$ = 121 Hz), 14.3 (q, −CH_3, $^1J_{CH}$ = 124 Hz). $^{13}C\{^1H\}$ NMR (δ, ppm): 133.8 (quint, Ru−*C*≡C−Ph, $^2J_{PC}$ = 15 Hz), 116.8 (s, Ru−C≡*C*−Ph), 114.5 (s, Ru−C≡*C*−^{n}Bu), 106.94 (quint, Ru−*C*≡C−^{n}Bu, $^2J_{PC}$ = 15 Hz), 32.95 (s, ≡C−*C*H_2−) 32.03 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{P'C}|$ = 24 Hz), 23.76 (s, −*C*H_2−CH_2−), 23.19 (s, −CH_2−*C*H_2−), 14.32 (s, −*C*H_3). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K, δ (ppm)): 54.08 (s, PPh_2).

***trans*-[(dppe)$_2$Ru(C≡C−Ph)(C≡C−C$_6$H$_4$−*p*-NO$_2$)] (6b).** From 590 mg of **2c** (0.5 mmol), 126 mg of $NaPF_6$ (0.75 mmol), 110 mg of H−C≡C−*p*-$PhNO_2$ (0.75 mmol), and 210 μL of Et_3N, 258 mg of **6b** (45%) of red crystals were obtained. Anal. Calcd for $C_{68}H_{57}NO_2P_4Ru$: C, 71.25; H, 5.02. Found: C, 70.77; H, 4.99. IR (cm^{-1}, KBr): 2052 (s, $\nu_{C\equiv C}$). ^1H NMR (300.133 MHz, CD_2Cl_2, 297 K, δ (ppm)): 7.96−6.52 (49H, Ph), 2.61 (m, 8H, PCH_2CH_2P). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K, δ (ppm)): 154.73 (quint, Ru−C≡, $^2J_{PC}$ = 15 Hz), 142.95−123.68 (Ph), 119.11 (s, Ru−C≡*C*), 118.63 (s, Ru−C≡*C*), 31.76 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{P'C}|$ = 24 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, $CDCl_3$, 297 K, δ (ppm)): 54.02 (s, PPh_2).

***trans*-[(dppe)$_2$Ru(C≡C−^{n}Bu)(C≡C−C$_6$H$_4$−*p*-NO$_2$)] (6c).** From 580 mg of **2b** (0.5 mmol), 126 mg of $NaPF_6$ (0.75 mmol), 110 mg of H−C≡C−*p*-$PhNO_2$ (0.75 mmol), and 210 μL of Et_3N, 287 mg of red crystals **6c** (51%) were obtained. Anal. Calcd for $C_{66}H_{61}NO_2P_4Ru$: C, 70.45; H, 5.46. Found: C, 70.21; H, 5.23. IR (cm^{-1}, KBr): 2050 (s, $\nu_{C\equiv C}$). ^1H NMR (300.133 MHz, CD_2Cl_2, 297 K, δ (ppm)): 7.87−6.46 (44H, Ph), 2.53 (m, 8H, PCH_2CH_2P), 2.00 (m, 2H, ≡C−CH_2), 1.22 (m, 4H, −CH_2CH_2), 0.83 (m, 3H, −CH_3). ^{13}C NMR (75.47 MHz, CD_2Cl_2, 297 K, δ (ppm)): 157.44 (quint, Ru−C≡, $^2J_{PC}$ = 14 Hz), 142.20−122.24 (Ph), 118.55 (t, Ru−*C*≡C−CH_2, $^2J_{CH}$ = 4 Hz), 104.75 (quint, Ru−*C*≡C−^{n}Bu, $^2J_{PC}$ = 16 Hz), 32.43 (t m, ≡C−CH_2, $^1J_{CH}$ = 124 Hz), 31.49 (t m, PCH_2CH_2P, $^1J_{CH}$ = 134 Hz), 22.69 (t m, −CH_2−, $^1J_{CH}$ = 125 Hz), 15.32 (q m, CH_3, $^1J_{CH}$ = 126 Hz, $^3J_{CH}$ = 3 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K, δ (ppm)): 53.57 (s, PPh_2).

***trans*-[(dppe)$_2$Ru(C≡C−C$_6$H$_4$−*p*-NO$_2$)(C≡C−C$_6$H$_4$−*p*-OMe)] (6d).** From 610 mg of [(dppe)$_2$Ru(Cl)=C=CH−*p*-$PhNO_2$)]PF_6 (**2e**; 0.5 mmol), 126 mg of $NaPF_6$ (0.75 mmol), 100 mg of H−C≡C−*p*-PhOMe (0.75 mmol), and 210 μL of Et_3N, 276 mg of red crystals of **6d** (47%) were obtained. Anal. Calcd for $C_{69}H_{59}NO_3P_4Ru$: C, 70.52; H, 5.06. Found: C, 70.69; H, 4.97. IR (cm^{-1}, KBr): 2050 (s, $\nu_{C\equiv C}$). ^1H NMR (300.133 MHz, CD_2Cl_2, 297 K, δ (ppm)): 7.94−6.54 (48H, Ph), 3.76 (s, 3H, OCH_3), 2.61 (m, 8H, PCH_2CH_2P). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K, δ (ppm)): 53.40 (s, PPh_2).

Synthesis of *trans*-[(NH$_3$)(dppe)$_2$Ru−C≡C−R^1]PF$_6$ (7a−c). A suspension in 50 mL of dichloromethane of 0.5 mmol of bis(acetylide) complex **4** and 2.5 mmol of NH_4PF_6 was stirred for 12 h at room temperature. The solution was filtered, and after evaporation of the solvent, the residue was dissolved in a minimum amount of dichloromethane. After slow addition of hexane, in order to form a biphasic system, crystals of complex **7** were obtained.

***trans*-[(dppe)$_2$Ru(NH$_3$)(C≡C−Ph)]PF$_6$ (7a).** From 550 mg of **4a** (0.5 mmol) and 407 mg of NH_4PF_6 (2.5 mmol), 424 mg of **7a** was isolated (73%). Anal. Calcd for $C_{60}H_{56}F_6NP_5Ru$: C, 62.07; H, 4.86; N, 1.21. Found: C, 61.89; H, 4.91; N, 1.15. IR (cm^{-1}, KBr): 2078 (s, $\nu_{C\equiv C}$), 836 (s, PF_6). ^1H NMR (300.133 MHz, CD_2Cl_2, 297 K, δ (ppm)): 8.07−6.38 (44H, Ph), 2.58 (m, 8H, PCH_2CH_2P), 0.09 (s large, 3H, NH_3). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K, δ (ppm)): 136.25−124.96 (Ph), 117.84 (s, Ru−C≡*C*−), 114.98 (quint, Ru−*C*≡, $^2J_{PC}$ = 16 Hz), 30.59 (quint, PCH_2CH_2P), $|^1J_{PC} + {}^3J_{P'C}|$ = 23 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K, δ (ppm)): 53.24 (s, PPh_2), −143.9 (sept, PF_6, $^1J_{PF}$ = 710 Hz).

***trans*-[(dppe)$_2$Ru(NH$_3$)(C≡C−^{n}Bu)]PF$_6$ (7b).** From 530 mg of **4b** (0.5 mmol) and 407 mg of NH_4PF_6 (2.5 mmol), 462 mg of yellow crystals of **7b** were isolated (81%). Anal. Calcd for $C_{58}H_{60}F_6NP_5Ru$: C, 61.05; H, 5.30. Found: C, 60.77; H, 5.17. IR (cm^{-1}, KBr): 2094 (s, $\nu_{C\equiv C}$), 837 (s, PF_6). ^1H NMR (300.133 MHz, CD_2Cl_2, 297 K, δ (ppm)): 8.09−6.41 (40H, Ph), 2.59 (quint, 8H, PCH_2CH_2P, $|^2J_{PH} + {}^4J_{P'H}|$ = 7 Hz), 2.38 (m, 2H, ≡C−CH_2−), 1.39 (m, 4H, CH_2−CH_2−), 0.89 (t, −CH_3, $^3J_{HH}$ = 7 Hz), 0.01 (s large, 3H, NH_3). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K, δ (ppm)): 136.64−128.18 (Ph), 116.23 (s, Ru−C≡*C*−), 91.04 (quint, Ru−*C*≡C, $^2J_{PC}$ = 16 Hz), 32.72 (s, ≡C−CH_2−), 30.59 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{P'C}|$ = 23 Hz), 23.31, 23.15 (s, −CH_2−CH_2−), 14.18 (s, CH_3). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K, δ (ppm)): 53.30 (s, PPh_2), −143.96 (sept, PF_6, $^1J_{PF}$ = 718 Hz).

***trans*-[(dppe)$_2$Ru(NH$_3$)(C≡C−SiMe$_3$)]PF$_6$ (7c).** From 574 mg of **4c** (0.5 mmol) and 407 mg of NH_4PF_6 (2.5 mmol),

422 mg of **7c** was isolated (73%). Anal. Calcd for $C_{57}H_{60}F_6NP_5RuSi$: C, 59.17; H, 5.23. Found: C, 58.87; H, 5.07. IR (cm^{-1}, KBr): 1996 (s, $\nu_{C\equiv C}$), 836 (s, PF_6). ^1H NMR (300.133 MHz, CD_2Cl_2, 297 K, δ (ppm)): 8.17−6.31 (40H, Ph), 2.58 (m, 8H, PCH_2CH_2P), 0.01(s, 9H, $SiMe_3$), −0.08 (s large, 3H, NH_3). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K, δ (ppm)): 136.33−128.17 (Ph), 139.75 (quint, Ru−*C*≡, $^2J_{PC} = 15$ Hz), 125.38 (s, Ru−C≡*C*−), 30.48 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{P'C}| = 23$ Hz), 0.01 (s, $SiMe_3$). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K, δ (ppm)): 53.36 (s, PPh_2), −143.9 (sept, PF_6, $^1J_{PF} = 713$ Hz).

Crystal Structure Analysis of 7a. The sample (0.30 × 0.45 × 0.55 mm) was studied on an automatic diffractometer (CAD_4 Enraf-Nonius) with graphite-monochromated Mo Kα radiation. The cell parameters were obtained by fitting a set of 25 high-θ reflections. The data collection ($2\theta_{max} = 54°$, scan $\omega/20 = 1$, $t_{max} = 60$ s, range *hkl*: *h*, 0.18, *k*, 0.28, *l* −22 to 22; intensity controls without appreciable decay (0.1%)) gave 6396 reflections from which 5134 were independent ($R_{int} = 0.014$) with $I > 2\sigma(I)$.

After Lorentz and polarization corrections, the structure was solved with direct methods which reveal the Ru and P atoms. The remaining non-hydrogen atoms of the structure were found after successive scale factor refinements and Fourier differences. After isotropic ($R = 0.090$) then anisotropic refinement ($R = 0.07$), many hydrogen atoms (in particular hydrogen atoms of nitrogen) were found with a Fourier difference (between 0.21 and 0.09 e $Å^{-3}$). The whole structure was refined by full-matrix least-square techniques (use of *F* magnitude; *x*, *y*, *z* β_{ij} for Ru, P, F, N, and C atoms and *x*, *y*, *z* for H atoms; 819 variables and 5134 observations; $w = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.04F_o^2)^2]^{-1/2}$), with $R = 0.033$, $R_w = 0.031$, and $S_w = 1.1$ (residual $\Delta\rho \leq 0.12$ e $Å^{-3}$). Atomic scattering factors were obtained from ref 38. All of the calculations were performed on a Digital Micro VAX 3100 computer with the MolEN package (Enraf-Nonius, 1990).[39]

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Supporting Information Available: Tables of bond lengths and angles, torsion angles, positional parameters, and displacement parameters and ORTEP diagram for **7a** (23 pages). Ordering information is given on any current masthead page.

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