Mono- and Bis-acetylidoruthenium(II) Complexes by Controlled Metathesis of Methylruthenium Complexes with Acetylenes

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Acetylido methyl ruthenium(II) complexes, *trans*-Ru(C≡CR)(CH_3)(dmpe)$_2$, were synthesized in a single metathesis reaction from *trans*-Ru(CH_3)$_2$(dmpe)$_2$ at ambient temperature; at elevated temperatures the reaction yields *trans*-Ru(C≡CR)$_2$(dmpe)$_2$. Addition of a second terminal acetylene to a methanol solution of *trans*-Ru(C≡CR)(CH_3)(dmpe)$_2$ results in the formation of *trans*-Ru(C≡CR)(C≡CR′)(dmpe)$_2$.

Introduction

Since the mid-1980s “rigid-rod” transition-metal σ-alkynyl complexes have come under increasing scrutiny[1,2] due to their potential applications as nonlinear optical,[3] electronic communication (“molecular wire”),[4] luminescent,[5] or liquid crystalline materials.[6] This potential is mainly due to their high stability, the possibility of extended π-electron conjugation, and the relatively rigid, linear structure of the complexes.[1]

Traditionally, transition-metal σ-alkynyl complexes have been synthesized by the reaction of metal alkynides (MC≡CR; M = Li, Na, Mg, SnR$_3$, etc.) with transition-metal halides ($L_nMX_{n'}$; X = Cl, Br, I).[1,7] When used for the synthesis of polymeric metal-alkynyl complexes, these methods often result in uncontrolled multiple condensations yielding high molecular weight material. The controlled formation of dimeric, trimeric, and oligomeric complexes would allow the properties of the material (e.g., solubility and crystal packing) to be more easily tuned. The development of methods allowing controlled polymerization is therefore highly desirable. To this end, the reaction scheme reported by Dixneuf et al.,[8] in which a dichlororuthenium phosphine complex is allowed to react with a terminal alkyne in the presence of sodium hexafluorophosphate and a base, represents a significant breakthrough. The reaction may be performed in a stepwise manner, allowing the isolation of alkynyl complexes bearing two unique acetylide moieties.

The metathesis reaction of acetylenes with transition-metal alkyl complexes to yield alkynyl complexes is well-established for rhodium(I) complexes,[9] but is also known for cobalt(I)[10] and platinum(II).[11] We have described the synthesis of acetylidoiron(II) complexes by the photochemical metathesis of methyl-iron(II) complexes[12] and now wish to report a related route to mono- and bis-acetylido complexes of ruthenium(II) involving thermal metathesis of a dialkylruthenium complex.

Results and Discussion

The previously unreported *trans*-Ru(CH_3)$_2$(dmpe)$_2$ (**1**) (dmpe = 1,2-bis(dimethylphosphino)ethane) was synthesized by a modification of the procedure reported for the synthesis of *cis*-Ru(CH_3)$_2$(dmpe)$_2$.[13] Treatment of *trans*-RuCl$_2$(dmpe)$_2$ with MeLi in benzene, followed by recrystallization of the product from pentane, gave *trans*-Ru(CH_3)$_2$(dmpe)$_2$ in moderate yield. Stereochemically, *trans*-Ru(CH_3)$_2$(dmpe)$_2$ is relatively stable at room temperature; however, irradiation with UV light for 15 min or sublimation resulted in quantitative isomerization and isolation of *cis*-Ru(CH_3)$_2$(dmpe)$_2$. Once formed, the *cis* complex shows no tendency to revert to the *trans*-isomer over time; the *cis*-isomer is clearly the thermodynamically more stable isomer, but there is a considerable activation barrier to *cis/trans* isomerization. Crystals of **1** suitable for X-ray diffraction were grown by slow evaporation of a benzene solution (Figure 1, Table 1). The asymmetric unit contains two half complex

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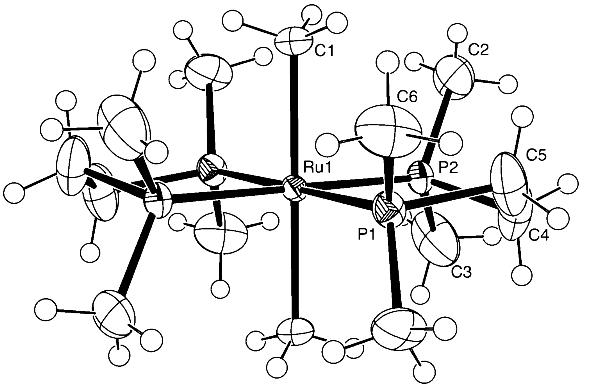


Figure 1. Molecular projection of *trans*-Ru$(CH_3)_2$(dmpe)$_2$ (**1**) with thermal ellipsoids shown at the 50% probability level. Only a single molecule of the unit cell and the major component of the disordered phosphorus atoms are shown.

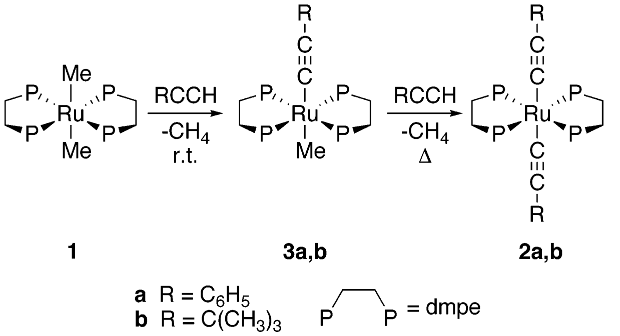
Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1, 3a, and 3b

	1	3a	3b
Ru−C(1)	2.236(3)	2.247(2)	2.2213(8)
Ru−C(2)	N/A	2.069(2)	2.0682(8)
C(2)−C(3)	N/A	1.198(2)	1.221(1)
Ru(1)−P(1)	2.286(1)	2.3048(6)	2.2881(2)
Ru(1)−P(2)	2.285(1)	2.3010(5)	2.2871(3)
Ru(1)−P(3)	N/A	2.2927(5)	2.2914(2)
Ru(1)−P(4)	N/A	2.2962(5)	2.2989(3)
C(1)−Ru(1)−C(2)	N/A	179.10(7)	178.50(4)
P(2)−Ru(1)−P(1)	84.29(4)	90.29(5)	84.28(1)
C(2)−C(3)−C(4)	N/A	177.5(2)	178.3(1)

molecules, the metal centers of which reside on symmetry inversion sites. Significant residual electron density peaks in the vicinity of the phosphorus atoms were modeled as minor occupancy phosphorus sites associated with a second orientation of the complexes; the associated carbon sites were not resolved. The Ru−CH_3 bond distances (Ru(1)−C(1), 2.236(3) Å; Ru(2)−C(8), 2.225(3) Å) are significantly longer than in *cis*-Ru$(CH_3)_2$(PNP) (PNP = $(^tBuPCH_2SiMe_2)_2N^-$) (Ru−CH_3, 2.075(2) and 2.149(3) Å),[14] reflecting the stronger *trans* influence of a methyl group in comparison to an amido nitrogen. Dimethylruthenium(II) complexes are rare in the crystallographic literature, and **1** represents, to the best of our knowledge, the first example of a structurally characterized octahedral dimethylruthenium(II) complex.

When heated, the reaction of *trans*-Ru$(CH_3)_2$(dmpe)$_2$ (**1**) with excess phenylacetylene in benzene proceeds smoothly to yield the known[15] complex *trans*-Ru$(C\equiv CPh)_2$(dmpe)$_2$ (**2a**). When monitored by $^{31}P\{^1H\}$ NMR spectroscopy, the reaction proceeded via a single intermediate, **3a**, which was the sole product when the reaction was carried out at room temperature for 24 h. In the absence of external heating, the reaction will not progress past this initial stage (Scheme 1). It is interesting to note that the *cis*-stereoisomer of Ru$(CH_3)_2$(dmpe)$_2$ failed to react under identical conditions.

Scheme 1



Pure **3a** could be obtained after removal of the solvent *in vacuo* and recrystallization from pentane. The ^1H and $^{31}P\{^1H\}$ NMR spectra of **3a** are indicative of a *trans*-substituted product, with a single resonance in the $^{31}P\{^1H\}$ NMR spectrum occurring at 43.4 ppm, slightly upfield of the resonance displayed by **1**. The ^1H NMR spectrum shows a phosphorus-coupled methyl resonance at −1.29 ppm, again slightly upfield from the corresponding resonance in **1**. The identity of complex **3a** was unequivocally assigned by X-ray crystallography as *trans*-Ru$(C\equiv CPh)(CH_3)$(dmpe)$_2$ (Figure 2, Table 1). The complex exhibits a distorted octahedral geometry, with the methyl and acetylide ligands occupying mutually *trans* positions.

The analogous reaction of **1** with *tert*-butylacetylene afforded *trans*-Ru$(C\equiv C^tBu)(CH_3)$(dmpe)$_2$ (**3b**) when carried out at room temperature; however, in this case 8 days were required for the reaction to reach completion. If the reaction mixture was heated at reflux, *trans*-Ru$(C\equiv C^tBu)_2$(dmpe)$_2$[15] (**2b**) was the sole product, with **3b** being observable as an intermediate by $^{31}P\{^1H\}$ NMR spectroscopy. The observed differences in the reactivity of **1** with phenyl- and *tert*-butylacetylene are unlikely to be the result of differences in the steric requirements of the ligands and may involve the formation of stabilizing π interactions between the aryl substituents of the acetylene and the metal center in **1**. Alternatively, the observed difference in reactivity may be ascribed to the differences in the respective acidities of the starting acetylenes.

Crystals of **3b** suitable for X-ray analysis were grown by slow evaporation of a toluene solution. The complex is isostructural with **3a**, with some slight differences in bond lengths (Figure 2). The ruthenium−acetylide bond distances in **3a** and **3b** are identical within experimental error (2.069(2) and 2.0682(8) Å, respectively); however, the ruthenium−methyl bond is slightly elongated in **3a** (2.247(2) vs 2.2213(8) Å, respectively). The carbon−carbon triple bond of the acetylide unit is longer in **3b** than **3a** (1.221(1) and 1.198(2) Å, respectively). The metal−acetylide bond in **3a** (2.069(2) Å) is longer than the bonds observed in the bis-acetylide complex *trans*-Ru$(C\equiv CPh)_2$(dmpe)$_2$ (2.042(5) and 2.044(5) Å)[15] and significantly longer than in the analogous iron(II) complex, Fe$(C\equiv CPh)CH_3$(dmpe)$_2$ (1.923(3) Å).[12] Similarly, the metal−methyl bond in **3a** is significantly longer than in the iron complex (2.247(2) vs 2.144(3) Å).

Both **3a** and **3b** have potential as starting materials in the preparation of unsymmetrically substituted bis-acetylidoruthenium(II) complexes bearing two different acetylide moieties by a controlled exchange of the methyl group with a second acetylide. In an attempt to exploit this potential and thereby prepare *trans*-Ru$(C\equiv CPh)(C\equiv C^tBu)$(dmpe)$_2$, a benzene solution of **3a** was allowed to react with excess *tert*-butylacetylene. Under ambient conditions no reaction was observed; however, if the reaction mixture was heated or irradiated with UV light, the desired mixed acetylide product was formed but in conjunction with appreciable amounts of both *trans*-Ru$(C\equiv CPh)_2$(dmpe)$_2$ and *trans*-Ru$(C\equiv C^tBu)_2$(dmpe)$_2$.

When the reaction was performed in methanol containing a small amount of benzene to solubilize the starting materials, a single complex with *trans* geometry was formed, as evidenced

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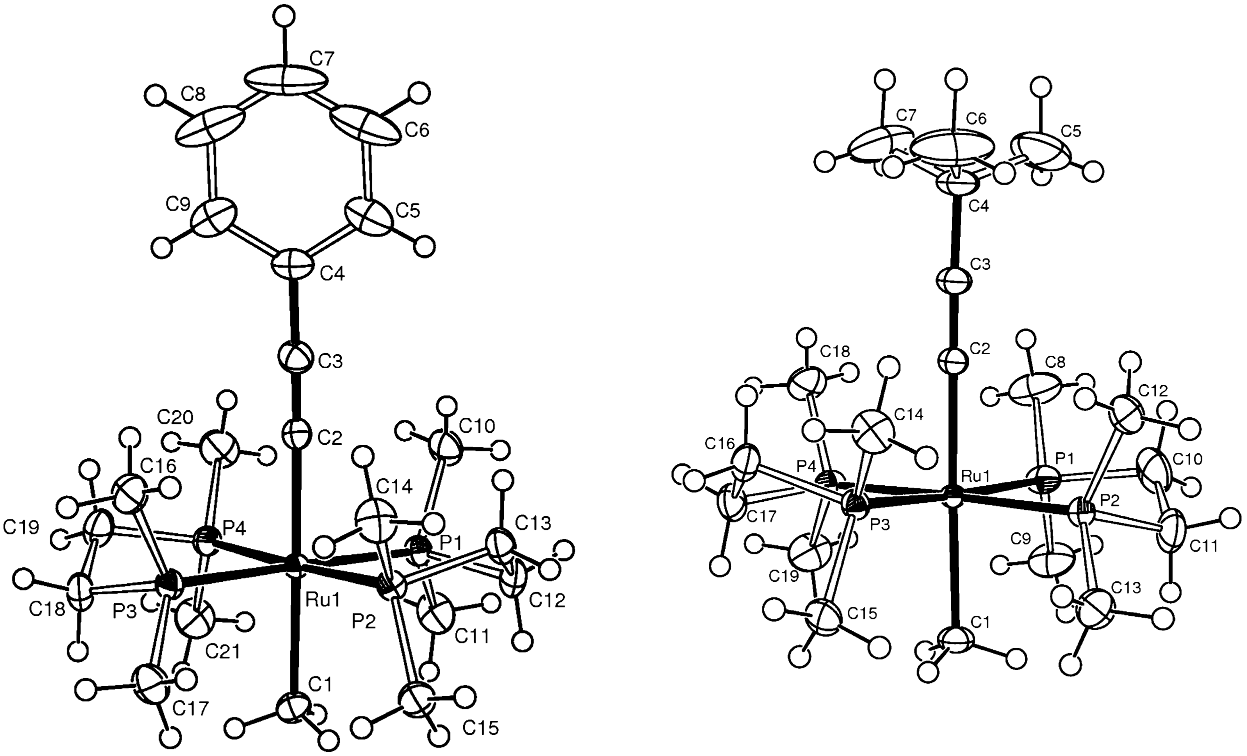
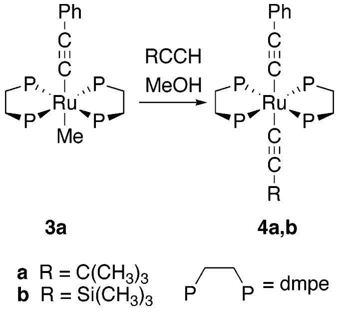


Figure 2. Molecular projection of *trans*-Ru(C≡CPh)(CH$_3$)(dmpe)$_2$ (**3a**) (left) and *trans*-Ru(C≡C^{t}Bu)(CH$_3$)(dmpe)$_2$ (**3b**) (right) showing 50% displacement ellipsoids for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å.

Scheme 2



by ^{31}P{^{1}H} NMR spectroscopy (Scheme 2). Formation of the product was complete within 30 min and did not require heat or UV irradiation. While we are still studying the role of methanol in this reaction, it is possible that this more acidic solvent promotes protiodemethylation of the complex to yield methane and a ruthenium methoxide complex, with the methoxide ligand then acting as a more effective leaving group that can be displaced by the terminal acetylide.

The related unsymmetrically substituted complex *trans*-Ru(C≡CPh)(C≡CSiMe$_3$)(dmpe)$_2$ (**4b**) was prepared in an analogous fashion from **3a** and (trimethylsilyl)acetylene. The identities of these complexes were established unequivocally by X-ray diffraction studies (Figure 3, Table 2).

Complex **4a** exhibits a distorted octahedral geometry with the acetylide ligands occupying mutually *trans* positions. The phosphine ligands and the *tert*-butyl substituent are disordered, and it was necessary to restrain some phosphorus−carbon bond lengths to maintain chemical meaning within the disorder model for some of the metal ligands. Figure 3 shows only a single representation of the disordered ligands. The metal−acetylide bond distances (Ru(1)−C(8) 2.056(4) Å, Ru(1)−C(9) 2.074(4) Å) and to a lesser extent the C≡C distances (C(7)−C(8) 1.219(6) Å, C(9)−C(10) 1.208(6) Å) exhibit significant differences, likely reflecting the differing *trans* influences of the two acetylides. These metal−carbon bond distances are appreciably larger than those observed in both *trans*-Ru(C≡CPh)$_2$(dmpe)$_2$ (2.042(5)/2.044(5) Å)[15] and Ru(C≡C^{t}Bu)(CO)(PPh$_3$)(η^5-C$_5$H$_5$) (2.032(3) Å);[13] however, the C≡C bond distances of **4a** are midway between those observed for these two complexes (1.226(7)/1.221(6) and 1.197(4) Å, respectively).

Complex **4b** is isostructural with **4a** with the alkynyl units occupying mutually *trans* positions. In this case, the ruthenium−acetylide (2.064(5), 2.070(5) Å) and carbon−carbon triple bond lengths (1.215(6), 1.207(7) Å) are identical within experimental error, while a significant distortion from linearity is observed in the acetylide units, particularly in the trimethylsilyl-substituted case, which exhibits a C(9)−C(10)−Si(1) bond angle (165.6(5)°) significantly reduced from the expected 180°. Similar bending of the alkynyl core has been reported previously.[16]

In summary, we have developed a route to mono-acetylidomethyl- and bis-acetylidoruthenium complexes involving controlled thermal metathesis from a dialkylruthenium complex. The controlled nature of this reaction allows the synthesis of complexes bearing two different acetylide ligands and results in the isolation of a pure product after minimal workup. We are currently investigating the application of this synthetic approach in the stepwise synthesis of dinuclear and trinuclear acetylide-bridged ruthenium complexes.

Experimental Section

All syntheses and manipulations involving air-sensitive compounds were carried out using standard vacuum line and Schlenk techniques under an atmosphere of dry nitrogen or argon. Diethyl ether, tetrahydrofuran, petroleum ether, toluene, and benzene were

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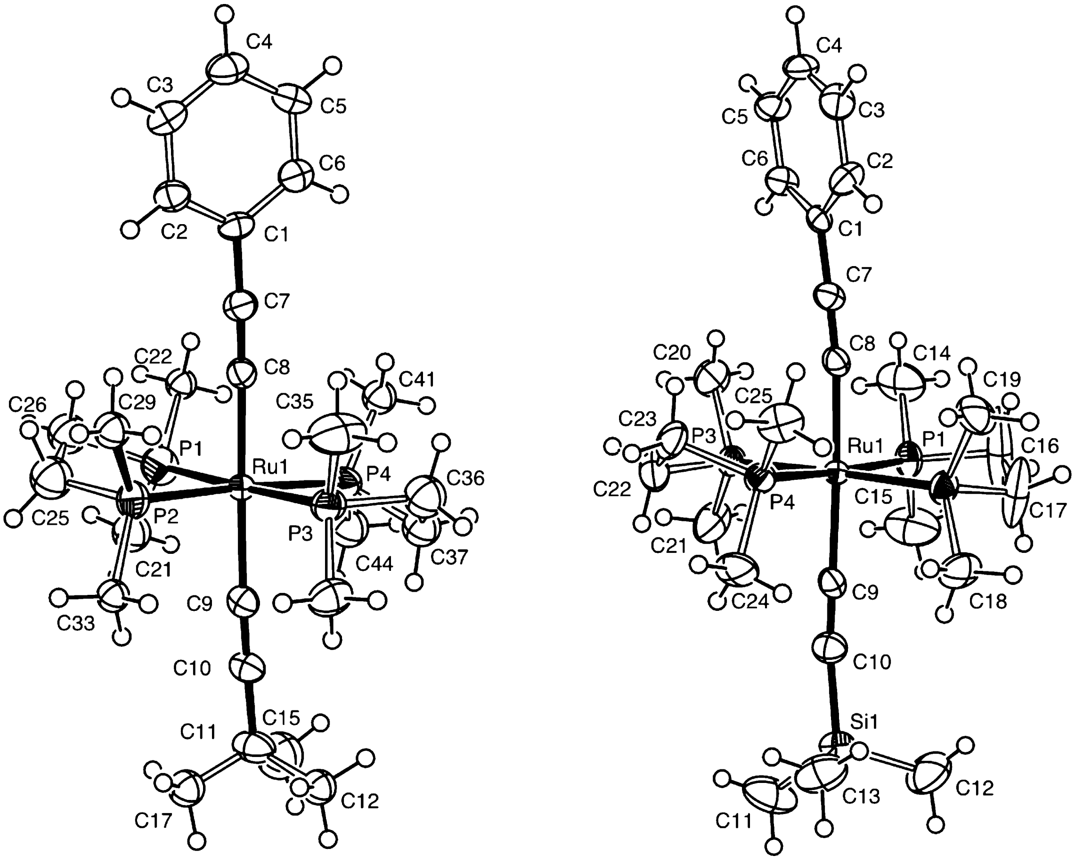

Figure 3. Molecular projection of *trans*-Ru(C≡CPh)(C≡C^{t}Bu)(dmpe)$_2$ (**4a**) (left) and *trans*-Ru(C≡CPh)(C≡CSiMe$_3$)(dmpe)$_2$ (**4b**) (right) showing 50% displacement ellipsoids for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. In the case of **4a**, only one component of the disordered atoms is shown.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 4a and 4b

	4a	4b
Ru(1)−C(8)	2.056(4)	2.064(5)
Ru(1)−C(9)	2.074(4)	2.070(5)
C(7)−C(8)	1.219(6)	1.215(6)
C(9)−C(10)	1.208(6)	1.207(7)
Ru(1)−C(8)−C(7)	176.8(4)	174.1(4)
Ru(1)−C(9)−C(10)	177.1(4)	176.8(4)
C(8)−C(7)−C(1)	175.3(4)	178.6(5)
C(9)−C(10)−X	178.8(5) (X = C(11))	165.6(5) (X = Si(1))

dried and degassed by refluxing over standard drying agents under an atmosphere of dry nitrogen and were freshly distilled prior to use. All other solvents were dried according to standard methods. THF-d_8 and benzene-d_6 were dried over sodium benzophenone ketyl and vacuum transferred into ampules prior to use.

Nuclear magnetic resonance spectra were recorded on a Bruker DMX500 (operating at 500.13, 125.92, and 202.45 MHz for ^{1}H, ^{13}C, and ^{31}P, respectively), Bruker AVANCE DRX400 (operating at 400.13, 125.76, and 161.98 MHz for ^{1}H, ^{13}C, and ^{31}P, respectively), or Bruker DPX300 (operating at 300.13 and 121.49 MHz for ^{1}H and ^{31}P, respectively) at 300 K unless otherwise stated. ^{1}H and ^{13}C NMR spectra were referenced to residual solvent resonances, while ^{31}P NMR spectra were referenced to external H_3PO_4. Infrared spectra were recorded on a Shimadzu 8400 series FTIR. UV irradiation of metal complex was performed using an Oriel 300 W high-pressure mercury vapor lamp with the incident beam directed through a water-filled jacket to filter infrared radiation.

Terminal acetylenes were purchased from Aldrich and used as received.

***trans*-Ru(CH$_3$)$_2$(dmpe)$_2$ (1).** A solution of *trans*-RuCl$_2$(dmpe)$_2$ (4.25 g, 9.0 mmol) in benzene (150 mL) was treated with methyllithium (3.5 equiv, 32 mmol, 1.6 M solution in diethyl ether). The mixture was stirred for 48 h, the solvent was removed, and the product was extracted into pentane (3 × 50 mL). The solvent was removed, and the product, *trans*-Ru(CH$_3$)$_2$(dmpe)$_2$ (**1**) (1.54 g, 40%), was dried under vacuum to give an off-white solid. The product was recrystallized from pentane. Anal. Calcd for $C_{14}H_{38}P_4$Ru: C, 38.98; H, 8.88. Found: C, 39.04; H, 8.72. MS (ESI): *m*/*z* 431 (8%) [M − 1], 401 (100) [M − 1 − 2 × CH$_3$]. HRMS: 431.08908 (calcd for M − 1: 431.08873). ^{1}H{^{31}P} NMR (300.17 MHz, C_6D_6): δ 1.30 (s, 8H, 4 × P−C*H*$_2$), 1.17 (s, 24H, 8 × P−C*H*$_3$), −1.20 (s, 6H, Ru−C*H*$_3$). ^{31}P{^{1}H} NMR (121.51 MHz, C_6D_6): δ 46.74 (s). ^{13}C{^{1}H,^{31}P} NMR (125.76 MHz, C_6D_6): δ 31.1 (*C*H$_2$), 15.1 (*C*H$_3$), −24.0 (Ru−*C*H$_3$).

***trans*-Ru(CH$_3$)(C≡CPh)(dmpe)$_2$ (3a).** Phenylacetylene (0.5 mL, 4.5 mmol) was added to a solution of *trans*-Ru(CH$_3$)$_2$(dmpe)$_2$ (**1**) (0.20 g, 0.46 mmol) in benzene (70 mL). The solution was stirred for 24 h at room temperature. The solvent was removed under vacuum to give crude *trans*-Ru(CH$_3$)(C≡CPh)(dmpe)$_2$ (**3a**) (0.23 g, 95%) as a pale brown solid, which was recrystallized from pentane. Anal. Calcd for $C_{21}H_{40}P_4$Ru: C, 48.74; H, 7.79. Found: C, 48.75; H, 7.76. MS(ESI): *m*/*z* 519 [M + 1]$^+$ (8%), 504 [M + 1 − CH$_3$]$^+$ (35), 417 [M + 1 − CCPh]$^+$ (8), 401 [M − CH$_3$ − CCPh]$^+$ (100). HRMS: 519.118778 (calc for M + 1 519.12038). ^{1}H{^{31}P} NMR (400.13 MHz, C_6D_6): δ 7.40 (m, 2H, Ar*H*), 7.16 (m, 2H, Ar*H*), 7.01 (m, 1H, Ar*H*), 1.49 (s, 12H, 4 × P−C*H*$_3$), 1.40 (m, 4H, 2 × P−C*H*$_2$), 1.25 (m, 4H, 2 × P−C*H*$_2$), 1.07 (s, 12H, 4 × P−C*H*$_3$), −1.30 (s, 3H, Ru−C*H*$_3$). ^{31}P{^{1}H} NMR (161 MHz, C_6D_6): δ 43.5 (s). ^{13}C{^{1}H,^{31}P} NMR (100.6 MHz, C_6D_6): δ 133.9 (Ru*C*≡C), 131.8 (Ar*C*), 130.5 (Ar*C*H), 128.1 (Ar*C*H), 122.2 (Ar*C*H), 109.2 (RuC≡*C*), 30.4 (P−*C*H$_2$), 17.3 (P−*C*H$_3$), 13.0 (P−*C*H$_3$). IR: $\nu_{C\equiv C}$ (Nujol) 2044 cm^{-1}.

***trans*-Ru(CH$_3$)(C≡C^{t}Bu)(dmpe)$_2$ (3b).** *tert*-Butylacetylene (2.0 mL, 16.2 mmol) was added to a solution of *trans*-Ru(CH$_3$)$_2$-

Table 3. Crystal Data and Refinement Details for 1, 3a, 3b, 4a, and 4b

	1	**3a**	**3b**	**4a**	**4b**
empirical formula	$C_{14}H_{38}P_4Ru$	$C_{21}H_{40}P_4Ru$	$C_{19}H_{44}P_4Ru$	$C_{26}H_{46}P_4Ru$	$C_{25}H_{46}SiP_4Ru$
M	431.39	517.48	497.49	583.58	599.66
temp (K)	150(2)	150(2)	150(2)	173(2)	173(2)
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/c$ (#14)	$P2_1/n$ (#14)	$P\bar{1}$ (#2)	$P2_1/c$	$C2/c$
unit cell dimensions					
a (Å)	12.825(3)	9.091(2)	9.4092(3)	18.807(4)	39.173(12)
b (Å)	12.607(3)	8.867(2)	9.6418(3)	10.809(2)	10.478(3)
c (Å)	13.035(4)	31.194(6)	15.5081(5)	15.165(3)	15.255(5)
α *(deg)*	90	90	79.873(2)	90	90
β *(deg)*	93.952(4)	95.538(3)	79.755(2)	102.438(4)	100.810(7)
γ *(deg)*	90	90	70.210(2)	90	90
V (Å^3)	2103(1)	2502.7(9)	1292.53(7)	3010(1)	6151(3)
Z	4	4	2	4	8
ρ(calc) (g cm^{-3})	1.363	1.373	1.278	1.288	1.295
μ(Mo Kα) (mm^{-1})	1.040	0.886	0.855	0.745	0.768
N	20 479	23 810	44 221	19 390	16 973
N_{ind}	5058	5936	13 885	6634	6745
N_{obs} ($I > 2\sigma(I)$)	4495	5203	11 857	4438	4564
$R_1(F)^a$	0.0449	0.0248	0.0220	0.0471	0.0588
$wR_2(F^2)^b$	0.1237	0.0626	0.0552	0.1025	0.1249

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ for $F_o > 2\sigma(F_o)$. [b] $wR_2 = (\sum w(F_o^2 - F_c^2)^2/\sum(wF_c^2)^2)^{1/2}$ all reflections $w = 1/[\sigma^2(F_o^2) + (0.04P)^2 + 5.0P]$ where $P = (F_o^2 + 2F_c^2)/3$.

$(dmpe)_2$ (**1**) (0.70 g, 1.41 mmol) in benzene (50 mL). The solution was stirred at room temperature for 7 days. The solvent was removed under vacuum, and the crude product, *trans*-$Ru(CH_3)(C{\equiv}C^tBu)(dmpe)_2$ (**3b**) (0.73 g, 90%), was obtained as a beige solid. The product was recrystallized from cold pentane. MS(ESI): m/z 499 $[M + 1]^+$ (4%), 483 $[M + 1 - CH_3]^+$ (10), 417 $[M + 1 - CC^tBu]^+$ (7), 401 $[M - CH_3 - CC^tBu]^+$ (100). HRMS: 499.152120 (calcd for M + 1 499.151538). $^1H\{^{31}P\}$ NMR (400.13 MHz, C_6D_6): δ 1.51 (s, 12H, 4 × P−CH_3), 1.46 (m, 4H, 2 × P−CH_2), 1.36 (s, 9H, C−(CH_3)$_3$), 1.27 (m, 4H, 2 × P−CH_2), 1.11 (s, 12H, 4 × P−CH_3), −1.30 (s, 3H, Ru−CH_3). $^{31}P\{^1H\}$ NMR (161 MHz, C_6D_6): δ 43.4 (s). $^{13}C\{^1H,^{31}P\}$ NMR (75.47 MHz, C_6D_6): δ 113.5 (Ru*C*≡C), 105.0 (RuC≡*C*), 34.0 (C−(*C*H$_3$)$_3$), 30.6 (P−CH$_2$), 30.0 (*C*−(CH$_3$)$_3$), 17.1 (P−*C*H$_3$), 13.3 (P−*C*H$_3$), −23.9 (Ru−*C*H$_3$). IR: $\nu_{C\equiv C}$ (Nujol) 2067 cm^{-1}.

***trans*-Ru(C≡CPh)(C≡C^{t}Bu)(dmpe)$_2$ (4a).** *trans*-$Ru(CH_3)(C{\equiv}CPh)(dmpe)_2$ (**3a**) (0.11 g, 0.21 mmol) was dissolved in benzene (3 mL), and excess *tert*-butylacetylene (1.5 mL, 12.1 mmol) was added. Methanol (3 mL) was added, and the reaction was stirred at room temperature for 45 min. The volatile components were removed under reduced pressure, to give crude *trans*-$Ru(C{\equiv}CPh)(C{\equiv}C^tBu)(dmpe)_2$ (0.12 g, 95%), which was recrystallized from cold pentane. Anal. Calcd for $C_{26}H_{46}P_4Ru$: C, 53.51; H, 7.95. Found: C, 53.32; H, 8.00. MS (ESI): m/z 583.9 $[M + 1]^+$ (5%), 538.9 (8), 530.9 (11), 511.0 (42), 502.9 $[M - CC^tBu]^+$ (100), 483.0 $[M - CCPh]^+$ (71), 400.9 $[M - CC^tBu - CCPh]^+$ (12). $^1H\{^{31}P\}$ NMR (300.17 MHz, C_6D_6): δ 7.34 (d, 2H, Ar*H*), 7.13 (t, 2H, Ar*H*), 6.94 (t, 1H, Ar*H*), 1.46−1.41 (br m, 32H, 8 × P−CH_3 + 4 × P−CH_2), 1.31 (s, 9H, C−(CH_3)$_3$). $^{31}P\{^1H\}$ NMR (121.51 MHz, C_6D_6): δ 40.45 (s). $^{13}C\{^1H,^{31}P\}$ NMR (125.76 MHz, C_6D_6): δ 132.3 (Ar*C*), 131.0 (Ru*C*≡CPh), 130.7, 128.3, 122.7 (Ar*C*H), 114.8 (Ru*C*≡C^{t}Bu), 109.1 (RuC≡*C*Ph), 102.3 (RuC≡*C*^{t}Bu), 33.7 (C−(*C*H$_3$)$_3$), 30.4 (P−*C*H$_2$), 29.8 (*C*−(CH$_3$)$_3$), 16.0 (P−*C*H$_3$), 15.6 (P−*C*H$_3$). IR: $\nu_{C\equiv C}$ (Nujol) 2054 cm^{-1}.

***trans*-Ru(C≡CPh)(C≡CSiMe$_3$)(dmpe)$_2$ (4b).** *trans*-$Ru(CH_3)(C{\equiv}CPh)(dmpe)_2$ (**3a**) (0.80 g, 1.54 mmol) was dissolved in benzene (3 mL), and trimethylsilylacetylene (2.0 mL, 14.15 mmol) was added. Methanol (3 mL) was added, and the reaction was left stirring at room temperature for 45 min. The solvent and excess acetylene were removed under reduced pressure. *trans*-$Ru(C{\equiv}CPh)(C{\equiv}CSiMe_3)(dmpe)_2$ (0.86 g, 93%) was recrystallized from cold pentane. Anal. Calcd for $C_{25}H_{46}SiP_4Ru$: C, 50.07; H, 7.73. Found: C, 50.24; H, 7.80. $^{31}P\{^1H\}$ NMR (121.51 MHz, C_6D_6): δ 39.67 (s). $^1H\{^{31}P\}$ NMR (300.17 MHz, C_6D_6): δ 7.34 (d, 2H, C*H*), 7.13 (t, 2H, C*H*), 6.94 (t, 1H, C*H*), 1.43 (s, 12H, P−CH_3), 1.38 (s, 12H, P−CH_3), 1.41 (s, 8H, P−CH_2), 0.29 (s, 9H, Si−CH_3). $^{13}C\{^1H,^{31}P\}$ NMR (125.76 MHz, THF-d_8): δ 156.6 (Ru−*C*≡CSiMe$_3$), 132.6 (ipso-*C*), 131.0 (Ar*C*H), 130.5 (Ru−*C*≡CPh), 128.3 (Ar*C*H), 123.0 (Ar*C*H), 111.1 (C≡*C*SiMe$_3$), 110.1 (C≡*C*Ph), 31.02 (P*C*H$_2$), 16.14 (P*C*H$_3$), 15.79 (P*C*H$_3$), 2.41 (Si(*C*H$_3$)$_3$). IR: $\nu_{C\equiv C}$ (KBr) 2063, 1989 cm^{-1}. MS (ESI): m/z 599.7 $[M - 1]^+$ (22%), 528.9 $[M - SiMe_3]^+$ (100), 502.9 $[M - CCSiMe_3]^+$ (10), 400.9 $[M - CCSiMe_3 - CCPh]^+$ (25).

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Supporting Information Available: A CIF file giving crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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