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Controlled Synthesis of Dinuclear Acetylide-Bridged Ruthenium Complexes

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A series of dinuclear and trinuclear, acetylide-bridged ruthenium(II) complexes was synthesized by the condensation of terminal acetylenes with methyl ruthenium complexes. Dinuclear ruthenium(II) complexes *trans,trans*-(RC≡C)Ru(dmpe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru(C≡CR′)(dmpe)$_2$ (R = R′ = Ph; R = R′ = ^{t}Bu; R = Ph, R′ = ^{t}Bu; R = ^{t}Bu, R′ = 3,5-^{t}Bu$_2$-C$_6$H$_3$) were synthesized by the reaction of *trans*-(CH$_3$)Ru(dmpe)$_2$(C≡CR) with the unsymmetrical bis(acetylido)ruthenium(II) complex *trans*-(R′C≡C)Ru(dmpe)$_2$(C≡CC$_6$H$_4$C≡CH) at ambient temperature and pressure. These complexes were fully characterized by NMR spectroscopy, and *trans,trans*-(^{t}BuC≡C)Ru(dmpe)$_2$-(μ-C≡CC$_6$H$_4$C≡C)Ru(dmpe)$_2$(C≡C^{t}Bu) was characterized crystallographically. The symmetrical trinuclear ruthenium(II) complexes *trans,trans,trans*-(RC≡C)Ru(dmpe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru-(depe)$_2$(μ-C≡CC$_6$H$_4$C≡C)-Ru(dmpe)$_2$(C≡CR) (R = Ph, ^{t}Bu, SiMe$_3$) were also prepared and characterized, and the redox behavior of a subset of the complexes was studied using cyclic voltammetry.

Introduction

"Rigid-rod" transition-metal σ-alkynyl complexes have been an active area of research in recent years[1,2] as a consequence of their potential applications as nonlinear optical,[3,4] electronic communication ("molecular wire"),[4–6]

luminescent,[7,8] or liquid crystalline materials.[9] All of these properties depend on their extended linear structures, high stability, and their π-electron configuration.[2]

Until recently, most transition-metal σ-alkynyl complexes have been synthesized either by the reaction of an alkali-metal alkynide or an alkaline-earth-metal alkynide RC≡CM (M = Li, Na, Mg, etc.) with a transition-metal halide L$_n$MX$_{n'}$ (X = Cl, Br, I) or by the reaction of a terminal alkyne with a transition-metal complex.[2,6] When these routes are applied to the synthesis of oligomeric or polymeric metal-alkynyl complexes, they usually result in an uncontrolled reaction with the formation of high molecular weight materials. Thus, the development of methods allowing controlled (step-by-step) condensation of metal centers with acetylides is highly desirable. The controlled formation of dimeric, trimeric, and oligomeric complexes also permits the properties of the materials (e.g., solubility and crystal packing) to be more easily explored and tuned.

Touchard et al.[7] have made significant progress in this regard, accessing dinuclear and trinuclear σ-alkynyl-bridged complexes in moderate yields via the formation of vinylidene intermediates, a reaction pioneered by Dixneuf and co-workers.[7,10–14] We have

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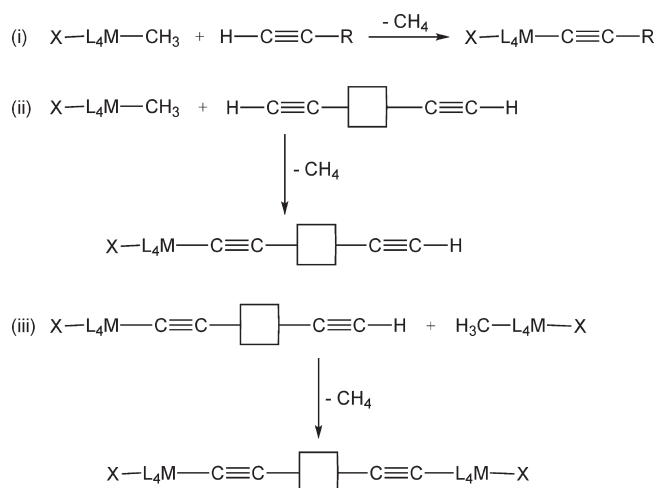
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Scheme 1

(i)   X—L$_4$M—CH$_3$ + H—C≡C—R $\xrightarrow{\text{- CH}_4}$ X—L$_4$M—C≡C—R

(ii) X—L$_4$M—CH$_3$ + H—C≡C—☐—C≡C—H

| - CH$_4$
↓

X—L$_4$M—C≡C—☐—C≡C—H

(iii) X—L$_4$M—C≡C—☐—C≡C—H + H$_3$C—L$_4$M—X

| - CH$_4$
↓

X—L$_4$M—C≡C—☐—C≡C—L$_4$M—X

been interested in the controlled stepwise synthesis of alkyne-bridged oligomers via the reaction of a terminal alkyne with a metal center and have previously described the development of a route to mono- and bis-acetylido complexes of ruthenium(II).[15] We now report the synthesis of a synthetically more elaborate ruthenium bis(acetylide) complex and the first dinuclear and trinuclear complexes prepared by this approach (Scheme 1).

Results and Discussion

Mononuclear Complexes. We have previously reported the synthesis of unsymmetrically substituted bis(acetylido)-ruthenium(II) complexes bearing two different acetylide moieties via the reaction of a methylacetylidoruthenium(II) complex with an excess of a second terminal alkyne.[15] The methylacetylidoruthenium(II) complexes *trans*-(CH$_3$)Ru(dmpe)$_2$-(C≡CPh) (**1a**), *trans*-(CH$_3$)Ru(dmpe)$_2$(C≡C^{t}Bu) (**1b**), *trans*-(CH$_3$)Ru(dmpe)$_2$(C≡CC$_6$H$_3$-3,5-(^{t}Bu)$_2$) (**1c**), and *trans*-(CH$_3$)-Ru(dmpe)$_2$(C≡CSiMe$_3$) (**1d**) were all synthesized by the reaction of the appropriate terminal alkyne with *trans*-(CH$_3$)$_2$Ru(dmpe)$_2$ under controlled conditions.[15] The complexes **1a** and **1b** have been structurally characterized previously,[15] and complex **1c** was characterized crystallographically during the course of this work; its structure is unexceptional (see Supporting Information).

Using the reaction between a methylacetylidoruthenium-(II) complex and 1,4-diethynylbenzene, bis(acetylide) complexes *trans*-(RC≡C)Ru(dmpe)$_2$(C≡CC$_6$H$_4$C≡CH) (R = Ph **2a**, R = ^{t}Bu **2b**) were prepared, and these contain a synthetically useful, free terminal alkyne moiety (Scheme 2).

Treatment of *trans*-(CH$_3$)Ru(dmpe)$_2$(C≡CPh) (**1a**) (dmpe = 1,2-bis(dimethylphosphino)ethane) with excess 1,4-diethynylbenzene in toluene, in the presence of a small quantity of methanol, furnished *trans*-(PhC≡C)Ru(dmpe)$_2$(C≡CC$_6$H$_4$C≡CH) (**2a**) in good yield. In the absence of methanol, the reaction does not proceed. While the role of methanol in this reaction is still not clear, it is possible that this more acidic solvent promotes proto-demethylation of the complex to yield methane and an intermediate ruthenium methoxide complex, where the methoxide ligand acts as a more effective leaving group that can be displaced by the terminal alkyne.

The ^{31}P{^{1}H} NMR spectrum of **2a** shows a single resonance at δ 40.3 ppm, indicative of a *trans*-substituted product.

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The chemical shift is typical of bis(acetylido)ruthenium(II) complexes with the 1,2-bis(dimethylphosphino)ethane ligand.[16,17] The ^{1}H NMR spectrum confirms the 1,4-diethynylbenzene ligand has coordinated, as the aromatic protons of the acetylide appear as two apparent doublets in a second-order AA′XX′ spin system and the intensity of the resonance corresponding to the terminal alkynyl hydrogen is reduced to a single proton. Complex **2a** is poorly soluble in most common organic solvents, with the exception of DCM, toluene, and THF, in which it displays only moderate solubility.

The analogous reaction of *trans*-(CH$_3$)Ru(dmpe)$_2$-(C≡C^{t}Bu) (**1b**) with excess 1,4-diethynylbenzene afforded the somewhat more soluble *trans*-(^{t}BuC≡C)Ru(dmpe)$_2$-(C≡CC$_6$H$_4$C≡CH) (**2b**), which was recrystallized from pentane. The ^{31}P{^{1}H} NMR spectrum again confirms a *trans* arrangement of the acetylide ligands around the ruthenium center, while the ^{1}H NMR spectrum is indicative of unsymmetrical *trans* substitution, with the phosphorus-bound methyl groups exhibiting two distinct resonances owing to the unsymmetrical substitution. The structure of the complex was established by X-ray crystallography (Figure 1, Table 1).

The structure of **2b** confirms the expected *trans* octahedral geometry, with the metal center coordinated in the equatorial plane by two bidentate dmpe ligands, while the axial positions are occupied by acetylide ligands. The Ru–C bond distances (Ru(1)–C(10), 2.087(5) Å; Ru(1)–C(11), 2.106(5) Å) are slightly longer than previously reported for similar compounds (e.g., *trans*-Ru(C≡CPh)$_2$(dmpe)$_2$, 2.042(5) Å;[17] *trans*-Ru(C≡CPh)(C≡C^{t}Bu)(dmpe)$_2$, 2.056(4) and 2.074(4) Å[15]). This is coupled with a significant shortening of the C≡C bonds in the molecule (C(9)–C(10), 1.134(6) Å; C(11)–C(12), 1.172(6) Å) when compared with similar compounds (e.g., *trans*-Ru(C≡CPh)$_2$(dmpe)$_2$, 1.226(7) Å;[17] *trans*-Ru(C≡CPh)-(C≡C^{t}Bu)(dmpe)$_2$, 1.208(6) and 1.219(6) Å[15]).

Dinuclear Complexes. Both *trans*-(PhC≡C)Ru(dmpe)$_2$-(C≡CC$_6$H$_4$C≡CH) (**2a**) and *trans*-(^{t}BuC≡C)Ru(dmpe)$_2$-(C≡CC$_6$H$_4$C≡CH) (**2b**) are important starting materials for the synthesis of dinuclear acetylide-bridged ruthenium(II) complexes (Scheme 3).

Excess *trans*-(CH$_3$)Ru(dmpe)$_2$(C≡CPh) (**1a**) was added to a solution of **2a** in toluene, followed by the addition of methanol, to yield the symmetrical dinuclear acetylide-bridged ruthenium(II) complex *trans,trans*-(PhC≡C)Ru-(dmpe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru(dmpe)$_2$(C≡CPh) (**3a**). Complex **3a** was purified by successive washes with a range of organic solvents due to its relatively low solubility. All phosphorus groups are chemically equivalent, and the ^{31}P{^{1}H} NMR spectrum shows only a singlet at δ 40.3, slightly downfield from the starting unsymmetrical ruthenium(II) acetylide (**2a**). The ^{1}H NMR spectrum shows the resonances for the phosphorus-bound methyl groups are near coincident; it was not possible to record a ^{13}C NMR spectrum due to the low solubility of the complex.

The symmetrical dinuclear complex *trans,trans*-(^{t}BuC≡C)Ru(dmpe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru(dmpe)$_2$(C≡C^{t}Bu) (**3b**) was synthesized in an analogous manner. The ^{31}P{^{1}H} NMR spectrum of **3b** shows a single resonance slightly downfield from the starting unsymmetrical ruthenium(II) acetylide (**2b**).

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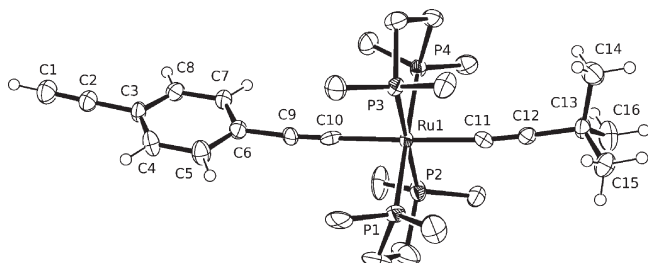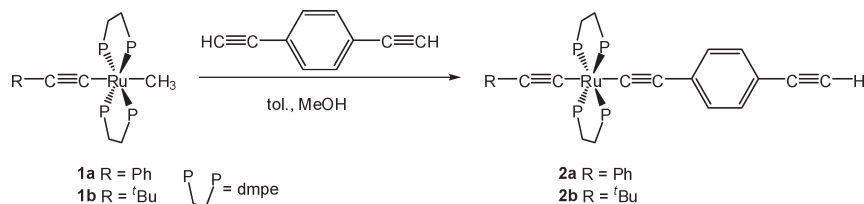
Figure 1. Molecular projection of *trans*-(*t*BuC≡C)Ru(dmpe)$_2$-(C≡CC$_6$H$_4$C≡CH) (**2b**). Thermal ellipsoids are shown at the 50% probability level; selected hydrogen atoms have been removed for clarity.

Table 1. Selected Bond Lengths and Angles for
***trans*-(*t*BuC≡C)Ru(dmpe)$_2$(C≡CC$_6$H$_4$C≡CH) (2b)**

bond length (Å)		bond angle (deg)	
Ru(1)−C(10)	2.087(5)	C(10)−Ru(1)−C(11)	178.44(17)
Ru(1)−C(11)	2.106(5)	Ru(1)−C(11)−C(12)	174.9(4)
C(9)−C(10)	1.134(6)	Ru(1)−C(10)−C(9)	178.5(4)
C(11)−C(12)	1.172(6)	C(11)−C(12)−C(13)	177.1(5)
C(1)−C(2)	1.1741	C(6)−C(9)−C(10)	175.2(5)

The aromatic protons are clearly visible as a singlet in the ^{1}H NMR spectrum, in contrast to the aromatic resonances in the starting material **2b**, which appear as a two multiplets (an AA′XX′ spin system). The *t*Bu-substituted complex **3b** is significantly more soluble than **3a**. The ^{13}C{^{1}H} NMR spectrum clearly demonstrates the C_2 symmetry of the complex, with the aryl ring displaying only two resonances: the first at δ 129.3 ppm for the protonated carbons and the second at δ 125.7 ppm for the *ipso* carbons. In addition, there are four resonances corresponding to alkynyl carbons at δ 131.1, 114.1, 108.3, and 101.8 ppm.

The unsymmetrically substituted dinuclear complexes *trans, trans*-(PhC≡C)Ru(dmpe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru(dmpe)$_2$-(C≡C*t*Bu) (**3c**) and *trans,trans*-(*t*BuC≡C)Ru(dmpe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru(dmpe)$_2$(C≡CC$_6$H$_3$-3,5-(*t*Bu)$_2$) (**3d**) were also prepared using this approach.

In **3c** and **3d**, each of the ruthenium centers has a different auxiliary acetylide group, so the set of four phosphorus nuclei surrounding each of the ruthenium atoms is different. Consequently, the ^{31}P{^{1}H} NMR spectra of complexes **3c** and **3d** appear as two distinct singlet resonances of equal intensity, corresponding to the phosphine ligands around each of the metal centers. *trans,trans*-(PhC≡C)Ru(dmpe)$_2$-(μ-C≡CC$_6$H$_4$C≡C)Ru(dmpe)$_2$(C≡C*t*Bu) (**3c**) exhibits distinct singlet resonances at δ 40.79 and 40.80 ppm in the ^{31}P{^{1}H} NMR spectrum. One phosphorus environment may be described as having aryl acetylide moieties on both faces of the metal complex, while the other environment has a metal complex with one aryl and one alkyl acetylide moiety in the two axial coordination sites.

Scheme 3
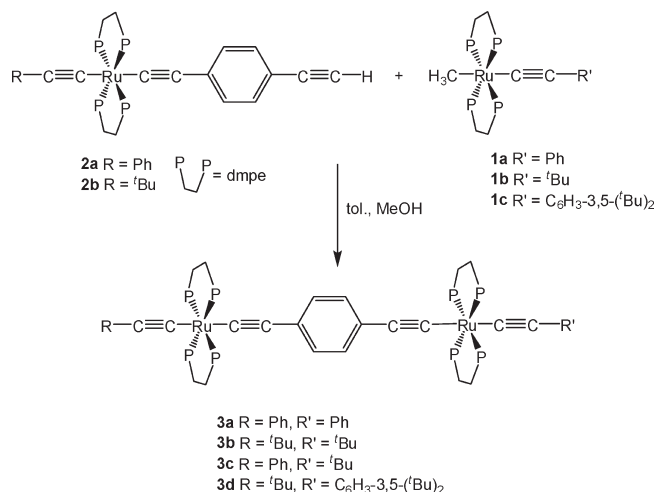
A crystal of *trans,trans*-(*t*BuC≡C)Ru(dmpe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru(dmpe)$_2$(C≡C*t*Bu) (**3b**), suitable for X-ray crystallography, was grown by slow evaporation of a solution of the complex in DCM/pentane (Figure 2, Table 2). The complex occupies a special position in the unit cell, possessing an inversion center about the center of the aromatic ring. To the best of our knowledge, this represents the first 1,4-diethynylbenzene-bridged diruthenium system to be crystallographically characterized.

There are some interesting comparisons between the bonds lengths and angles of *trans,trans*-(*t*BuC≡C)Ru-(dmpe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru(dmpe)$_2$(C≡C*t*Bu) (**3b**), *trans*-(*t*BuC≡C)Ru(dmpe)$_2$(C≡CC$_6$H$_4$C≡CH) (**2b**), and the previously reported *trans*-(*t*BuC≡C)Ru(dmpe)$_2$(C≡CPh)[15] (Table 2). The ruthenium−acetylide bond lengths of *trans,trans*-(*t*BuC≡C)Ru(dmpe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru-(dmpe)$_2$(C≡C*t*Bu) (**3b**) (2.079(6), 2.056(5) Å) are slightly shorter than those of *trans*-(*t*BuC≡C)Ru(dmpe)$_2$(C≡CC$_6$-H$_4$C≡CH) (**2b**) (2.106(5), 2.087(5) Å) and identical with *trans*-(*t*BuC≡C)Ru(dmpe)$_2$(C≡CPh) (2.074(4), 2.056(4) Å), while the C≡C distances of **3b** (1.223(8), 1.201(9) Å) are slightly longer than those of **2b** (1.172(6), 1.134(6) Å). There is a slight distortion from linearity in **2b**, in particular the C(10)−C(9)−C(6) and C(12)−C(11)−Ru(1) bond angles (175.2(5)° and 174.9(4)°, respectively), which are significantly smaller than the expected 180°. This slight distortion from linearity is evident in **3b** also, in particular the C(7)−C(8)−C(9) and C(8)−C(7)−Ru(1) bond angles (172.9(7)° and 176.1(6)°, respectively). This bending of the alkynyl core has been noted previously[18,19] in dinuclear acetylide-bridged complexes. The metal centers of **3b** are separated by ca. 12.2 Å.

The dinuclear ruthenium(II) complexes were also characterized by high-resolution mass spectrometry (HRMS) using
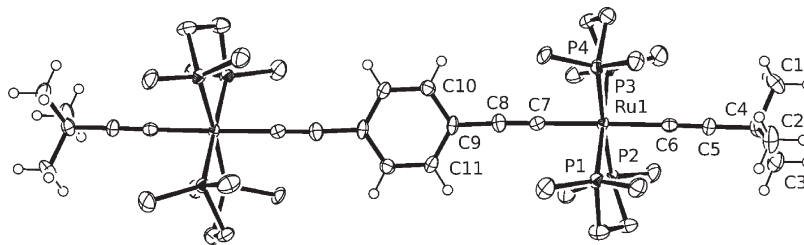
Figure 2. Molecular projection of *trans,trans*-(^{t}BuC≡C)Ru(dmpe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru(dmpe)$_2$(C≡C^{t}Bu) (**3b**). Thermal ellipsoids are shown at the 50% probability level, and selected hydrogen atoms have been removed for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for *trans*, *trans*-(^{t}BuC≡C)Ru(dmpe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru(dmpe)$_2$- (C≡C^{t}Bu) (3b) and *trans*-(^{t}BuC≡C)Ru(dmpe)$_2$(C≡CPh).[15]

	3b	*trans*-(^{t}BuC≡C)- Ru(dmpe)$_2$(C≡CPh)
Ru(1)−C(6)	2.079(6)	2.074(4)
Ru(1)−C(7)	2.056(5)	2.056(4)
C(5)−C(6)	1.223(8)	1.208(6)
C(7)−C(8)	1.201(9)	1.219(6)
C(4)−C(5)−C(6)	179.0(9)	178.8(5)
Ru(1)−C(6)−C(5)	178.5(6)	177.1(4)
C(6)−Ru(1)−C(7)	178.0(3)	178.54(16)
Ru(1)−C(7)−C(8)	176.1(6)	176.8(4)
C(7)−C(8)−C(9)	172.9(7)	175.3(4)

positive-ion electrospray ionization. The spectra clearly show the formation of the dinuclear complexes by their characteristic isotopic distribution pattern and their unique m/z values. The calculated isotope distribution pattern for *trans,trans*-(^{t}BuC≡C)Ru(dmpe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru-(dmpe)$_2$(C≡C^{t}Bu) (**3b**) (C$_{46}$H$_{86}$P$_8$Ru$_2$) correlates well with the experimental spectra (Figure 3).

The redox properties of the acetylide-bridged conjugated complexes are closely related to their ability to act as molecular wires.[7] Consequently, cyclic voltammetry traces (CVs) were obtained for *trans,trans*-(^{t}BuC≡C)Ru(dmpe)$_2$-(μ-C≡CC$_6$H$_4$C≡C)Ru(dmpe)$_2$(C≡C^{t}Bu) (**3b**) and were compared with its mononuclear precursor *trans*-(^{t}BuC≡C)Ru-(dmpe)$_2$(C≡CC$_6$H$_4$C≡CH) (**2b**) (Figure 4, Table 3). The mononuclear complex **2b** undergoes a single electron oxidation step involving the Ru^{III}/Ru^{II} couple at −0.26 V (relative
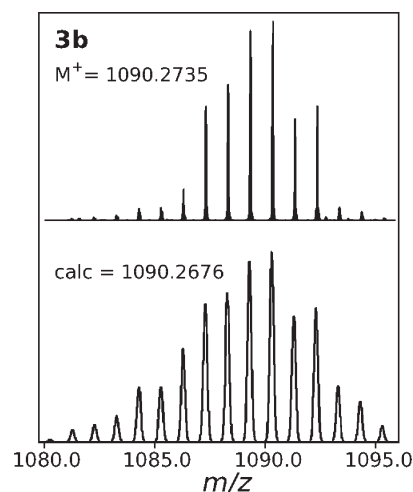

Figure 3. High-resolution mass spectrum of *trans,trans*-(^{t}BuC≡C)Ru(dmpe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru(dmpe)$_2$(C≡C^{t}Bu) (**3b**) (C$_{46}$H$_{86}$P$_8$Ru$_2$) showing both experimental (top) and simulated (bottom) spectra.

to Fc$^+$/Fc as well as an irreversible process to a second oxidized species, and this is consistent with the oxidation potentials of similar complexes Ru(C≡CPh)$_2$(dmpe)$_2$ and Ru(C≡CC$_6$H$_4$C≡CPh)$_2$(dmpe)$_2$.[19] The dinuclear complex **3b** displays two successive reversible redox processes at −0.51 and −0.22 V (in addition to an irreversible process at higher potential) originating from successive oxidation of Ru$_2^{II,II}$ to Ru$_2^{II,III}$ and then Ru$_2^{II,III}$ to Ru$_2^{III,III}$, respectively. The separation (280 mV) between the two redox couples is an indicator of electronic coupling between the metal centers, with the $\Delta E_{1/2}$ values being correlated to the comproportionation constant (K_c) (defined by the expression $K_c = \exp[\Delta E_{1/2}/25.69]$ at 298 K) and the thermodynamic stability of the Ru$_2^{II,III}$ mixed-valence complex.[20] While it is well known that other phenomena can contribute to redox potentials and consequently K_c values,[10,21] closely related complexes[10,11,14,17,20] have demonstrated these values to be directly related to the electronic coupling between metal centers and ligands. These values are consistent with those of other diruthenium systems with the 1,4-diethynylbenzene-conjugated organic bridge (Table 2).

The comproportionation constant, K_C, of 5.4×10^4 for the dinuclear complex *trans,trans*-(^{t}BuC≡C)Ru(dmpe)$_2$-(μ-C≡CC$_6$H$_4$C≡C)Ru(dmpe)$_2$(C≡C^{t}Bu) (**3b**) suggests that the electrogenerable Ru^{II}Ru^{III} monocation **3b**$^+$ belongs to the Robin−Day "Class II" (slightly delocalized) mixed-valent species,[16] indicative of some degree of electronic communication between the two metal centers.

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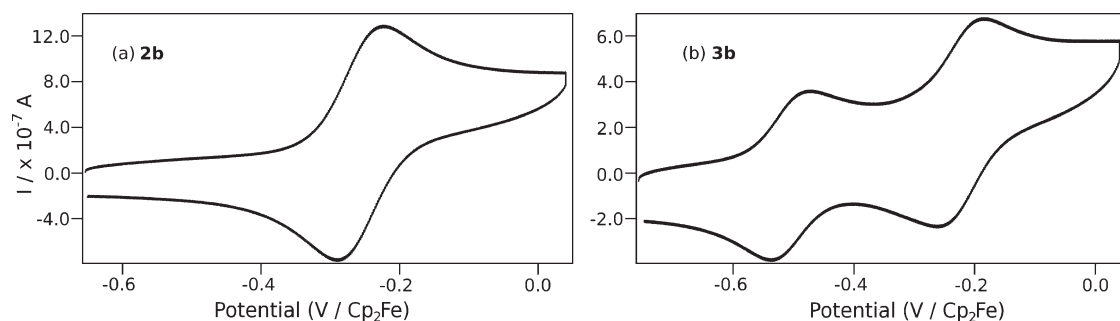
Figure 4. Cyclic voltammogram traces obtained for (a) *trans*-(*t*BuC≡C)Ru(dmpe)$_2$(C≡CC$_6$H$_4$C≡CH) (**2b**) and (b) *trans,trans*-(*t*BuC≡C)Ru(dmpe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru(dmpe)$_2$(C≡C*t*Bu) (**3b**) in CH$_2$Cl$_2$ (0.1 M Bu$_4$NPF$_6$, v = 100 mV s^{-1}).

Table 3. Electrochemical Data for *trans*-(*t*BuC≡C)Ru(dmpe)$_2$(C≡CC$_6$H$_4$C≡CH) (2b), *trans,trans*-(*t*BuC≡C)Ru(dmpe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru(dmpe)$_2$(C≡C*t*Bu) (3b), and Similar Complexes[a,b]

complex	$E_{1/2}^{I}$ (V)	$E_{1/2}^{II}$ (V)	$\Delta E_{1/2}$ (mV)	K_{com}
trans-(*t*BuC≡C)Ru(dmpe)$_2$(C≡CC$_6$H$_4$C≡CH) (**2b**)[c]	−0.26			
trans-Ru(C≡CPh)$_2$(dmpe)$_2$[19]	−0.21			
trans-Ru(C≡CC$_6$H$_4$C≡CPh)$_2$(dmpe)$_2$[19]	−0.14			
trans,trans-(*t*BuC≡C)Ru(dmpe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru(dmpe)$_2$(C≡C*t*Bu) (**3b**)	−0.51	−0.22	280	5.4×10^4
Ru$_2$(μ-C≡CC$_6$H$_4$C≡C)(bph)$_2$(PPh$_3$)$_4$[12]	−0.520	−0.195	325	3.1×10^5
Ru$_2$(μ-C≡CC$_6$H$_4$C≡C)(phtpy)$_2$(PPh$_3$)$_4$[ClO$_4$]$_2$[12]	0.030	0.250	220	5.2×10^3
Ru$_2$(μ-C≡CC$_6$H$_4$C≡C)Cl$_2$(dppe)$_4$[13]	−0.328	0.013	341	6.0×10^5
Ru$_2$(μ-C≡CC$_6$H$_4$C≡C)Cl$_2$(dppm)$_4$[11]	−0.30	0.00	300	1.2×10^5
Ru$_2$(μ-C≡CC$_6$H$_4$C≡C)(C≡CPh)(C≡CC$_6$H$_4$NC)(dppe)$_4$[7]	−0.24	0.06	300	1.5×10^5
Ru$_2$(μ-C≡CC$_6$H$_4$C≡C)(C≡CC$_6$H$_4$NC)$_2$(dppe)$_4$[7]	−0.20	0.11	310	1.5×10^5

[a] All $E_{1/2}$ values are referenced to FeCp$_2$. $E_{1/2}^{I}$ and $E_{1/2}^{II}$ are the first and second electrode potentials of the dinuclear species. $\Delta E_{1/2}$ = $E_{1/2}^{II} - E_{1/2}^{I}$. [b] Conditions: in CH$_2Cl_2$, 0.1 M NBu$_4PF_6$, 100 mV/s scan rate, glass working electrode, Pt aux. electrode, Ag ref electrode. [c] This work.

Scheme 4

4a R = Ph; R' = C$_6$H$_4$
4b R = *t*Bu; R' = C$_6$H$_4$
4c R = SiMe$_3$; R' = C$_6$H$_4$
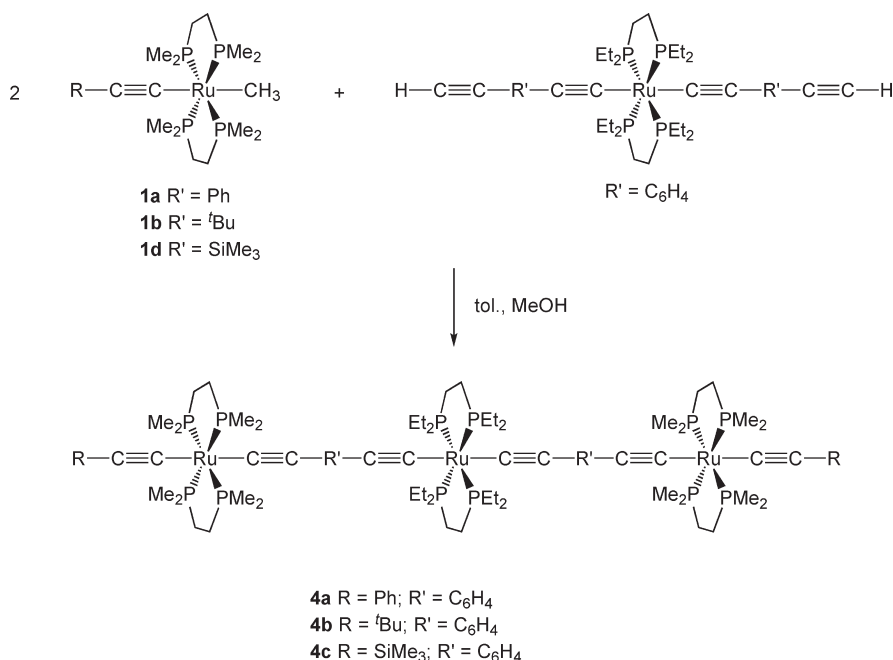
Trinuclear Complexes. The symmetrical trinuclear ruthenium(II) complexes *trans,trans,trans*-(RC≡C)Ru(dmpe)$_2$-(μ-C≡CC$_6$H$_4$C≡C)Ru(depe)$_2$(μ-C≡CC$_6$H$_4$C≡C)-Ru(dmpe)$_2$-(C≡CR) (R = Ph (**4a**), *t*Bu (**4b**), SiMe$_3$ (**4c**)) were prepared by the reaction of 2 equiv of the appropriate acetylidomethyl-ruthenium(II) complex *trans*-Ru(CH$_3$)(C≡CR)(dmpe)$_2$ (R = Ph (**1a**), *t*Bu (**1b**), SiMe$_3$ (**1d**)) with *trans*-Ru(C≡CC$_6$-H$_4$C≡CH)$_2$(depe)$_2$ in toluene and methanol (Scheme 4). The

complexes obtained were poorly soluble in most organic solvents.

trans-Ru(C≡CC$_6$H$_4$C≡CH)$_2$(depe)$_2$ was used as the central unit in the complex in preference to *trans*-Ru-(C≡CC$_6$H$_4$C≡CH)$_2$(dmpe)$_2$ to improve the solubility of the trinuclear product. Complex solubility was expected to be an issue, as the dinuclear complexes **3a**−**d** synthesized so far were relatively insoluble in many organic solvents.
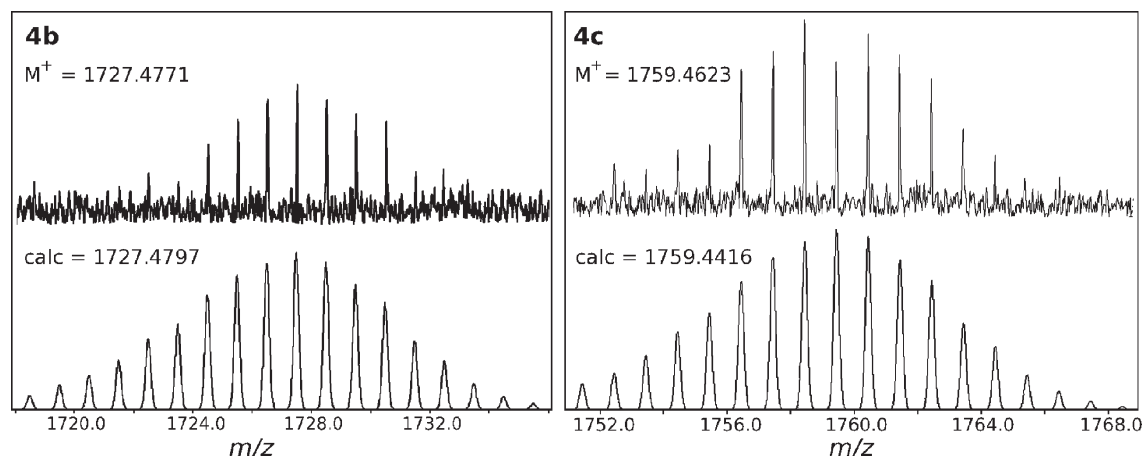
Figure 5. High-resolution mass spectrum of *trans,trans,trans*-(^{t}BuC≡C)Ru(dmpe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru(depe)$_2$(μ-C≡CC$_6$H$_4$C≡C)-Ru(dmpe)$_2$(C≡C^{t}Bu) (**4b**) (left) and *trans,trans,trans*-(SiMe$_3$C≡C)Ru(dmpe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru(depe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru-(dmpe)$_2$(C≡CSiMe$_3$) (**4c**) (right) showing both experimental (top) and calculated (bottom) spectra.

In addition, *trans*-Ru(C≡CC$_6$H$_4$C≡CH)$_2$(depe)$_2$ is readily available from the reaction of 1,4-diethynylbenzene with *trans*-RuCl$_2$(depe)$_2$.[17]

The ^{31}P{^{1}H} NMR spectra of the trinuclear ruthenium(II) complexes each displayed two singlet resonances, due to the presence of two distinct sets of phosphine ligands (each complex contains both dmpe and depe ligands). For example, *trans,trans,trans*-(PhC≡C)Ru(dmpe)$_2$(μ-C≡CC$_6$H$_4$C≡C)-Ru(depe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru(dmpe)$_2$(C≡CPh) (**4a**) exhibited singlet resonances at δ 51.48 and 39.73 ppm. The low-field and high-field resonances are typical of bis(acetylido)ruthenium-(II) complexes with depe and dmpe ligands, respectively, and the high-field resonance integrates to twice the low-field resonance.

The ^{1}H and ^{1}H{^{31}P} NMR spectra of **4a−c** were significantly more complicated than those of the dinuclear species, mainly due to the presence of two different types of phosphine ligands with overlapping resonances. In most cases, resonances were assigned using a range of 2D NMR experiments, including NOESY, ^{1}H−^{13}C HMBC and ^{1}H−^{13}C HMQC.

The low solubility of the complexes hampered the acquisition of ^{13}C{^{1}H} NMR spectra, and only *trans,trans,trans*-(^{t}BuC≡C)Ru(dmpe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru(depe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru(dmpe)$_2$(C≡C^{t}Bu) (**4b**) was fully characterized by ^{13}C{^{1}H} NMR spectroscopy. The ^{13}C{^{1}H,^{31}P} NMR spectrum of **4b** shows six alkynyl resonances at δ 137.3, 131.2, 114.5, 111.7, 108.6, and 102.1 ppm, consistent with the proposed C_2 symmetry. The remaining spectral data are also consistent with the proposed product (see Experimental Section).

The trinuclear ruthenium(II) complexes were also characterized by high-resolution mass spectrometry (HRMS). The HRMS spectra clearly show the formation of the trinuclear complexes by their characteristic isotopic distribution pattern and their unique *m/z* values. The calculated isotope distribution patterns for *trans,trans,trans*-(^{t}BuC≡C)-Ru(dmpe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru(depe)$_2$(μ-C≡CC$_6$H$_4$C≡C)-Ru(dmpe)$_2$(C≡C^{t}Bu) (**4b**) and *trans,trans,trans*-(SiMe$_3$C≡C)-Ru(dmpe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru(depe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru(dmpe)$_2$(C≡CSiMe$_3$) (**4c**) correlate extremely well with the experimental spectra (Figure 5).

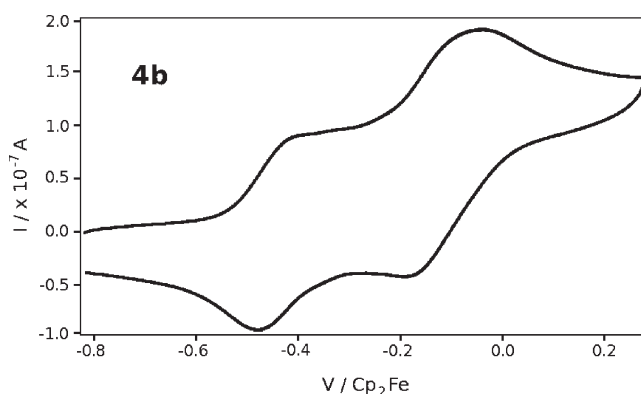Cyclic voltammograms (CVs) were obtained for *trans,trans,trans*-(^{t}BuC≡C)Ru(dmpe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru(depe)$_2$-

Figure 6. Cyclic voltammogram trace obtained for *trans,trans,trans*-(^{t}BuC≡C)Ru(dmpe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru(depe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru(dmpe)$_2$(C≡C^{t}Bu) (**4b**) in CH$_2$Cl$_2$ (0.1 M Bu$_4$NPF$_6$, v = 100 mV s^{-1}).

(μ-C≡CC$_6$H$_4$C≡C)Ru(dmpe)$_2$(C≡C^{t}Bu) (**4b**) (Figure 6). The trinuclear complex, **4b**, displays two successive oxidation processes (in addition to a higher potential irreversible process), and on the basis of peak intensities, the second oxidation can be considered to be a result of two overlapping one-electron processes. Closer inspection reveals that this second process is significantly broader (ΔE_p = 120 mV) than the second oxidation couple for the dinuclear complex **3b** (ΔE_p = 64 mV) and for the other couples measured in this work (ΔE_p ≈ 65 mV). This indicates the first oxidation at −0.48 V for **4b** is followed by two one-electron couples separated by ca. 55 mV at −0.18 and −0.13 V. The first couple is attributed to the oxidation of the central ruthenium center (Ru$_3^{II,II,II}$ to Ru$_3^{II,III,II}$). The following consecutive, merged couples are attributed to successive oxidations of the outer two ruthenium centers (i.e., Ru$_3^{II,III,II}$ to Ru$_3^{III,III,II}$, then at 55 mV higher potential Ru$_3^{III,III,II}$ to Ru$_3^{III,III,III}$), which indicates communication between these centers is significant even though they are estimated to be ~24 Å apart. Overall, these observations support an electronic communication along the trinuclear complexes in different oxidized states. These results are again consistent with those of the other reported trinuclear ruthenium(II) systems.[7,13]

In summary, we have developed a route to di- and trinuclear acetylide-bridged ruthenium(II) complexes via the unsymmetrically substituted bis(acetylido)ruthenium-(II) complexes. The controlled nature of these reactions allows the stepwise synthesis and isolation of these complexes in a high yield and purity with minimal workup. We are also currently continuing the investigation into the electrochemical and nonlinear optical properties of these series of 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. Methanol, toluene, and benzene were 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. 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) spectrometers 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. Where indicated, mass spectra were recorded by electrospray ionization (ESI) mass spectra on a Finnigan LCQ mass spectrometer or by matrix-assisted laser desorption/ionization−time-of-flight (MALDI-tof) on a Micromass TOF SPEC 2E spectrometer with a 2-amino-5-nitropyridine (ANP) matrix. Cyclic voltammetry measurements were carried out under nitrogen using a conventional three-electrode cell using a computer-controlled Pine Instrument Co. AFCBP1 bipotentiostat (as described in detail elsewhere[22]). The reported data were recorded with a 0.5 mm glassy carbon working electrode at a scan rate of 100 mV s^{-1}. Potentials are referenced to the ferrocenium−ferrocene (Fe^{III}−Fe^{II}) couple measured under identical experimental conditions (concentrations, solvent, support electrolyte, electrodes, temperature, and scan rate).

Complexes *trans*-Ru(CH$_3$)(C≡CPh)(dmpe)$_2$ (**1a**), *trans*-Ru-(CH$_3$)(C≡C^{t}Bu$_2$)(dmpe)$_2$ (**1b**), *trans*-Ru(CH$_3$)(C≡CSiMe$_3$)-(dmpe)$_2$ (**1d**), and *trans*-RuMe$_2$(dmpe)$_2$ were prepared as described previously.[15] *trans*-Ru(C≡CC$_6$H$_4$C≡CH)$_2$(depe)$_2$ was prepared according to the literature procedure.[17] Terminal alkynes were purchased from Aldrich and used as received.

trans-Ru(CH$_3$)(C≡CC$_6$H$_3$-3,5-^{t}Bu$_2$)(dmpe)$_2$ (1c). 3,5-Di-*tert*-butylphenylacetylene (0.50 g, 2.3 mmol) was added to a solution of *trans*-Ru(CH$_3$)$_2$(dmpe)$_2$ (0.40 g, 0.93 mmol) in toluene (30 mL). The solution was stirred under nitrogen at 40 °C for 120 h. The solvent was removed under reduced pressure, and the residue was recrystallized from pentane to give *trans*-Ru-(CH$_3$)(C≡CC$_6$H$_3$-3,5-^{t}Bu$_2$)(dmpe)$_2$ (**34**) was as a white crystalline solid (0.54 g, 92%). Anal. Calcd for C$_{29}$H$_{56}$P$_4$Ru: C, 55.31, H, 8.96. Found: C, 55.58, H, 8.66. MS (ESI$^+$) (%): m/z 828 [M + C≡CC$_6$H$_3$-3,5-^{t}Bu$_2$]$^+$ (15), 655 [M + MeCN − CH$_3$]$^+$ (13), 630 [M + H]$^+$ (15), 457 [M + MeCN − C≡CC$_6$H$_3$-3,5-^{t}Bu$_2$]$^+$ (25), 441 [M + MeCN − (C≡CC$_6$H$_3$-3,5-^{t}Bu$_2$)-(CH$_3$)]$^+$ (100), 401 [M − (C≡CC$_6$H$_3$-3,5-^{t}Bu$_2$)(CH$_3$)]$^+$ (30). ^{31}P{^{1}H} NMR (121.51 MHz, benzene-d$_6$): δ 43.64 (s) ppm. ^{1}H{^{31}P} NMR (300.13 MHz, benzene-d$_6$): δ 7.35 (d, $^3J_{HH}$ = 1.8 Hz, 2H, Ar*H*), 7.21 (t, $^3J_{HH}$ = 1.8 Hz, 1H, Ar*H*), 1.51 (s, 12H, PC*H$_3$*), 1.51−1.39 (m, 4H, PC*H$_2$*), 1.34 (s, 18H, C(C*H$_3$*)$_3$), 1.29−1.20 (m, 4H, PC*H$_2$*), 1.08 (s, 12H, PC*H$_3$*),

−1.29 (p, $^3J_{PH}$ = 5.7 Hz, 3H, RuC*H$_3$*) ppm. ^{13}C{^{1}H,^{31}P} (75.49 MHz, benzene-d$_6$): δ 150.4 (*C*C(CH$_3$)$_3$), 132.7 (Ar*C*), 131.7 (Ru*C*≡C), 125.3 (Ar*C*H), 117.3 (Ar*C*H), 110.8 (Ru*C*≡*C*), 35.3 (*C*(CH$_3$)$_3$), 32.3 (C(*C*H$_3$)$_3$), 31.0 (P*C*H$_2$), 17.9 (P*C*H$_2$), 13.7 (P*C*H$_3$), −23.2 (Ru*C*H$_3$) ppm. IR: ν_{max} (KBr): 2046 ν(C≡C) cm^{-1}.

trans-Ru(C≡CC$_6$H$_4$C≡CH)(C≡CPh)(dmpe)$_2$ (2a). *trans*-Ru-(CH$_3$)(C≡CPh)(dmpe)$_2$ (**1a**) (0.33 g, 0.64 mmol) was dissolved in toluene (6 mL), and excess 1,4-diethylbenzene (0.50 g, 4.0 mmol) was added. Methanol (3 mL) was added, and the reaction was left stirring at room temperature for 45 min. The solvent was removed under reduced pressure. The unsymmetrical bisacetylide *trans*-Ru(C≡CC$_6$H$_4$C≡CH)(C≡CPh)-(dmpe)$_2$ (0.361 g, 90%) was isolated as an orange powder after being washed with pentane (3 × 5 mL). Anal. Calcd for C$_{30}$H$_{42}$P$_4$Ru: C, 57.41; H, 6.75. Found: C, 56.99; H, 6.67. MS (MALDI, 4HCCA matrix): m/z 628 (8, M), 555 (73), 531 (100), 503 (40, M − C≡CC$_6$H$_4$C≡CH), 402 (55, M − C≡CC$_6$H$_4$C≡CH, − C≡CC$_6$H$_5$). HRMS: 629.135749 (calcd for M + 1 629.135324). ^{31}P{^{1}H} NMR (121.51 MHz, C$_6$D$_6$): δ 40.33 (s) ppm. ^{1}H{^{31}P} NMR (300.17 MHz, CD$_2$Cl$_2$): δ 7.09 (AA′ of AA′XX′, 2H, Ar*H*(2)), 6.95 (m, 4H, Ar*H*(2′,3′)), 6.89 (XX′ of AA′XX′, 2H, Ar*H*(3)), 6.80 (m, 1H, Ar*H*(4′)), 3.34 (s, 1H, C≡C*H*), 1.71 (s, 8H, P-C*H$_2$*), 1.58 (s, 24H, P-C*H$_3$*) ppm. ^{13}C{^{1}H,^{31}P} NMR (125.76 MHz, CD$_2$Cl$_2$): δ 137.3 (Ru*C*≡CC$_6$H$_4$), 132.7 (*Ar*(1′)), 132.2 (*Ar*(1)), 131.7 (*Ar*H(2)), 131.0 (*Ar*(3′)), 130.2 (*Ar*H(3)), 129.5 (Ru*C*≡CC$_6$H$_5$), 128.2 (*Ar*H(2′)), 123.1 (*Ar*H(4′)), 115.0 (*Ar*(4)), 110.1 and 110.5 (Ru*C*≡*C*C$_6$H$_5$, Ru*C*≡*C*C$_6$H$_4$), 84.7 (*C*≡CH), 76.4 (C≡*C*H), 30.3 (P-*C*H$_2$), 15.6 (P-*C*H$_3$), 15.6 (P-*C*H$_3$) ppm. $\nu_{C≡C}$ (KBr disk): 2049 cm^{-1}.

trans-Ru(C≡CC$_6$H$_4$C≡CH)(C≡C^{t}Bu)(dmpe)$_2$ (2b). *trans*-Ru(CH$_3$)(C≡C^{t}Bu)(dmpe)$_2$ (**1b**) (0.50 g, 1.0 mmol) was dissolved in toluene (7 mL), and excess 1,4-diethylbenzene (0.75 g, 5.9 mmol) was added. Methanol (3 mL) was added, and the reaction was left stirring at room temperature for 45 min. The solvent was removed under reduced pressure. The unsymmetrical bisacetylide *trans*-Ru(C≡CC$_6$H$_4$C≡CH)(C≡C^{t}Bu)-(dmpe)$_2$ (0.53 g, 87%) was recrystallized as an orange-red crystalline material from pentane. MS (ESI): m/z 609 (22, M + 1), 568 (25), 524 (30), 511 (100), 442 (55), 401 (20). HRMS: 609.170371 (calcd for M + 1 609.168478). ^{31}P{^{1}H} NMR (121.51 MHz, C$_6$D$_6$): δ 40.31 (s) ppm. ^{1}H{^{31}P} NMR (300.17 MHz, CD$_2$Cl$_2$): δ 7.14 (AA′ of AA′XX′, 2H, C*H*), 6.89 (XX′ of AA′XX′, 2H, C*H*), 3.06 (s, 1H, C≡C*H*), 1.64 (s, 8H, P-C*H$_2$*), 1.52 (s, 12H, P-C*H$_3$*), 1.49 (s, 12H, P-C*H$_3$*), 1.03 (s, 9H, C-(C*H$_3$*)$_3$) ppm. ^{13}C{^{1}H,^{31}P} NMR (125.76 MHz, CD$_2$Cl$_2$): δ 138.9 (Ru*C*≡CC$_6$H$_4$), 132.4 (*Ar*(1)), 131.5 (*Ar*H(3)), 129.8 (*Ar*H(2)), 114.8 (Ru*C*≡CC(CH$_3$)$_3$), 114.3 (*Ar*(4)), 109.1 (Ru*C*≡*C*C$_6$H$_4$), 102.1 (Ru*C*≡*C*C(CH$_3$)$_3$), 84.8 (*C*≡CH), 76.3 (C≡*C*H), 33.0 (*C*(CH$_3$)$_3$), 30.2 (P-*C*H$_2$), 29.3 (C(*C*H$_3$)$_3$), 15.7 (P-*C*H$_3$), 15.2 (P-*C*H$_3$) ppm. $\nu_{C≡C}$ (KBr disk): 2049, 2030 cm^{-1}. Crystals suitable for X-ray diffraction were isolated by cooling a pentane solution of the complex. Crystal data and refinement details for **2b** are given in Table 4.

trans,trans-(PhC≡C)Ru(dmpe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru(C≡CPh)-(dmpe)$_2$ (3a). *trans*-Ru(C≡CC$_6$H$_4$C≡CH)(C≡CPh)(dmpe)$_2$ (**2a**) (0.22 g, 0.35 mmol) was mixed with toluene (5 mL), and *trans*-Ru(CH$_3$)(C≡CPh)(dmpe)$_2$ (**1a**) (0.32 g, 0.62 mmol) was added. Methanol (3 mL) was added, and the reaction was left stirring at room temperature for 1 h. The solvent was removed under reduced pressure, and the light brown powder was washed with benzene (2 × 2 mL) and DCM (2 × 2 mL) to yield the symmetrically substituted dinuclear acetylide-bridged ruthenium-(II) complex *trans,trans*-(PhC≡C)Ru(dmpe)$_2$(μ-C≡CC$_6$H$_4$C≡C)-Ru(C≡CPh)(dmpe)$_2$ (0.27 g, 68%). MS (ESI): m/z 1130 (85, M + 1), 631 (10), 531 (90), 447 (75), 401 (100). HRMS: 1130.202275 (calcd for M + 1 1130.211227). ^{31}P{^{1}H} NMR (121.51 MHz, CD$_2$Cl$_2$): δ 40.60 (s) ppm. ^{1}H{^{31}P} NMR (300.13 MHz, CD$_2$Cl$_2$): δ 7.05−6.95 (m, 8H, Ar*H*), 6.85 (m, 2H, Ar*H*), 6.70 (s, 4H, Ar*H*), 1.75 − 1.62 (m, 16H, P-C*H$_2$*), 1.53 (s, 48H, P-C*H$_3$*). $\nu_{C≡C}$ (KBr disk): 2054 cm^{-1}.

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Table 4. Crystallographic and Structure Refinement Data for 2b and 3b

	2b	3b
chemical formula	$C_{28}H_{46}P_4Ru$	$C_{23}H_{43}P_4Ru$
M_r	607.60	544.52
cell syst, space group	monoclinic, $P2_1/n$	triclinic, $P\bar{1}$
temp (K)	173(2)	150(2)
a (Å)	9.6302(18)	9.0216(8)
b (Å)	12.118(2)	9.1604(7)
c (Å)	26.325(5)	17.2534(15)
α (deg)		96.199(4)
β (deg)	91.897(7)	92.234(3)
γ (deg)		104.126(4)
V (Å^3)	3070.3(9)	1371.5(2)
Z	4	2
D_x (Mg m^{-3})	1.314	1.319
μ(Mo Kα) (mm^{-1})	0.734	0.812
cryst form, color	red block	light yellow thin plate
cryst size (mm)	$0.40 \times 0.30 \times 0.25$	$0.21 \times 0.12 \times 0.02$
T_{min}	0.5559	0.8479
T_{max}	0.8379	0.9879
N, N_{ind}	22 007, 5782	35 383, 4791
N_{obs} ($I > 2\sigma(I)$)	3855	2958
R_{int}	0.0638	0.1404
θ_{max} (deg)	25.90	25.00
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.0465, 0.0897, 1.040	0.0427, 0.1048, 0.884
no. of reflns	5782	4791
no. of params	314	253
H-atom treatment	mixture of independent and constrained refinement	riding model
weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0331P)^2 + 4.9015P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1000P)^2 + 0.1591P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$	0.520, −0.594	0.484, −0.531

***trans,trans*-(^{t}BuC≡C)Ru(dmpe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru(C≡C^{t}Bu)(dmpe)$_2$ (3b).** *trans*-Ru(C≡CC$_6$H$_4$C≡CH)(C≡C^{t}Bu)(dmpe)$_2$ (2b) (0.19 g, 0.25 mmol) was mixed with toluene (5 mL), and *trans*-Ru(CH$_3$)(C≡C^{t}Bu)(dmpe)$_2$ (1b) (0.30 g, 0.6 mmol) was added. Methanol (4 mL) was added, and the reaction was left stirring at room temperature for 45 min. The solvent was removed under reduced pressure, and the residual brown-orange powder was washed with benzene (2 × 2 mL) and DCM (2 × 2 mL) to yield the symmetrically substituted dinuclear acetylide-bridged ruthenium(II) complex *trans,trans*-(^{t}BuC≡C)Ru(dmpe)$_2$-(μ-C≡CC$_6$H$_4$C≡C)Ru(C≡C^{t}Bu)(dmpe)$_2$ (0.11 g, 41%). The product was recrystallized by slow evaporation of a DCM/pentane solution (1:2). Anal. Calcd for C$_{46}$H$_{86}$P$_8$Ru$_2$: C, 50.73; H, 7.96. Found: C, 50.90; H, 7.93. MS (ESI): *m/z* 1090 (24, M + 1), 1048 (10), 524 (32), 511 (15), 442 (25), 402 (100), 351 (28). HRMS: 1090.273542 (calcd for M + 1 1090.267632). ^{31}P{^{1}H} NMR (121.51 MHz, CD$_2$Cl$_2$): δ 40.70 (s) ppm. ^{1}H{^{31}P} NMR (300.13 MHz, CD$_2$Cl$_2$): δ 6.64 (s, 4H, Ar*H*), 1.62−1.56 (m, 16H, P-C*H$_2$*), 1.48 (s, 24H, P-C*H$_3$*), 1.46 (s, 24H, P-C*H$_3$*), 1.00 (s, 9H, C-(C*H$_3$*)$_3$) ppm. ^{13}C{^{1}H} NMR (150.90 MHz, CD$_2$Cl$_2$): δ 131.1 (m, Ru*C*≡CC$_6$H$_4$), 129.3 (*Ar*H), 125.7 (*Ar*), 114.1 (RuC≡*C*C(CH$_3$)$_3$), 108.3 (RuC≡*C*C$_6$H$_4$), 101.8 (m, Ru*C*≡CC(CH$_3$)$_3$), 33.0 (*C*(CH$_3$)$_3$), 30.2 (P-*C*H$_2$), 29.2 (C(*C*H$_3$)$_3$), 15.7 (P-*C*H$_3$), 15.3 (P-*C*H$_3$) ppm. $\nu_{C≡C}$ (KBr disk): 2049 cm^{-1}. Crystals suitable for X-ray diffraction were isolated by slow evaporation of a DCM/pentane solution of the complex. Crystal data and refinement details for **3b** are given in Table 4.

***trans,trans*-(PhC≡C)Ru(dmpe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru(C≡C^{t}Bu)(dmpe)$_2$ (3c).** *trans*-Ru(CH$_3$)(C≡C^{t}Bu)(dmpe)$_2$ (1b) (0.15 g, 0.30 mmol) was added to a solution of *trans*-Ru(C≡CC$_6$H$_4$C≡CH)(C≡CPh)(dmpe)$_2$ (2a) (0.070 g, 0.11 mmol) in toluene (3 mL). Methanol (3 mL) was added, and the reaction mixture was stirred at room temperature for 45 min. The solvent was removed under reduced pressure, and the light brown powder was washed with pentane (4 × 2 mL) to afford the unsymmetrically substituted dinuclear acetylide-bridged ruthenium(II) complex *trans,trans*-(PhC≡C)Ru(dmpe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru(C≡C^{t}Bu)(dmpe)$_2$ (3c) (0.10 g, 82%). HRMS (ESI$^+$, MeOH): 1142.2301 (calcd for M + MeOH 1142.2661). ^{31}P{^{1}H} NMR (121.51 MHz,

DCM-*d$_2$*): δ 40.80 (s, 4P), 40.79 (s, 4P) ppm. ^{1}H{^{31}P} NMR (300.13 MHz, DCM-*d$_2$*): δ 7.01 (t, $^3J_{HH}$ = 7.3 Hz, 2H, Ar*H*), 6.96 (d, $^3J_{HH}$ = 8 Hz, 2H, Ar*H*), 6.84 (t, $^3J_{HH}$ = 7.3 Hz, 1H, Ar*H*), 6.66 (s, 4H, Ar*H*), 1.71−1.58 (m, 16H, PC*H$_2$*), 1.52−1.48 (m, 48H, PC*H$_3$*), 0.96 (s, 9H, C(C*H$_3$*)$_3$) ppm. ^{13}C{^{1}H,^{31}P} NMR (100.61 MHz, DCM-*d$_2$*): δ 132.0 (Ru*C*≡C), 131.8 (Ru*C*≡C), 131.7 (Ru*C*≡C), 131.5 (Ar*C*), 129.9 (Ar*C*H), 129.3 (2 × Ar*C*H), 129.2 (Ar*C*H), 127.7 (Ar*C*H), 122.2 (2 × Ar*C*), 114.2 (RuC≡*C*C(CH$_3$)$_3$), 109.2 (RuC≡*C*), 108.6 (RuC≡*C*), 108.3 (RuC≡*C*), 101.7 (Ru*C*≡CC(CH$_3$)$_3$), 33.0 (*C*(CH$_3$)$_3$), 30.2 (P*C*H$_2$), 29.5 (C(*C*H$_3$)$_3$), 15.6 (P*C*H$_3$), 15.3 (P*C*H$_3$) ppm. IR ν_{max} (KBr): 2055 ν(C≡C) cm^{-1}.

***trans,trans*-(^{t}BuC≡C)Ru(dmpe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru(C≡CC$_6$H$_3$-3,5-^{t}Bu$_2$)(dmpe)$_2$ (3d).** *trans*-Ru(CH$_3$)(C≡CC$_6$H$_3$-3,5-^{t}Bu$_2$)-(dmpe)$_2$ (1c) (0.080 g, 0.13 mmol) was added to a solution of *trans*-Ru(C≡CC$_6$H$_4$C≡CH)(C≡C^{t}Bu)(dmpe)$_2$ (2b) (0.050 g, 0.082 mmol) in toluene (3 mL). Methanol (3 mL) was added, and the reaction mixture was stirred at room temperature for 45 min. The solvent was removed under reduced pressure, and the light brown residue was washed with pentane (4 × 2 mL) to afford the unsymmetrically substituted dinuclear acetylide-bridged ruthenium-(II) complex *trans,trans*-(^{t}BuC≡C)Ru(dmpe)$_2$(μ-C≡CC$_6$H$_4$C≡C)-Ru(C≡CC$_6$H$_3$-3,5-^{t}Bu$_2$)(dmpe)$_2$ (3d) as a dark brown powder (0.090 g, 90%). Anal. Calcd for C$_{56}$H$_{98}$P$_8$Ru$_2$: C, 55.07; H, 8.09. Found: C, 55.19; H, 7.99. HRMS (ESI$^+$, MeOH): *m/z* 1254.3575 (calcd for M + MeOH 1254.3913). ^{31}P{^{1}H} NMR (121.51 MHz, DCM-*d$_2$*): δ 40.91 (s, 4P), 40.82 (s, 4P) ppm. ^{1}H{^{31}P} NMR (300.13 MHz, DCM-*d$_2$*): δ 6.96 (s, 1H, Ar*H*), 6.83 (s, 2H, Ar*H*), 6.67 (s, 4H, Ar*H*), 1.71−1.59 (m, 16H, PC*H$_2$*), 1.54−1.48 (m, 48H, PC*H$_3$*), 1.23 (s, 18H, C(C*H$_3$*)$_3$), 1.00 (s, 9H, C(C*H$_3$*)$_3$) ppm. ^{13}C{^{1}H, ^{31}P} NMR (150.92 MHz, DCM-*d$_2$*): δ 149.9 (Ar*C*C(CH$_3$)), 129.3 (4 × Ar*C*H), 129.0 (2 × Ru*C*≡CC$_6$H$_4$), 128.5 (Ru*C*≡CC$_6$H$_3$), 126.2 (Ar*C*), 125.9 (Ar*C*), 125.4 (Ar*C*), 124.0 (2 × Ar*C*H), 116.9 (Ar*C*H), 114.2 (RuC≡*C*C(CH$_3$)$_3$), 109.5 (RuC≡*C*), 109.2 (RuC≡*C*), 108.4 (RuC≡*C*), 101.8 (RuC≡*C*C(CH$_3$)$_3$), 34.4 (Ar*C*C(CH$_3$)$_3$), 33.0 (C≡C*C*(CH$_3$)$_3$), 31.2 (ArC*C*(CH$_3$)$_3$), 30.2 (P*C*H$_2$), 29.3 (C≡C*C*(CH$_3$)$_3$), 15.6 (P*C*H$_3$), 15.3 (P*C*H$_3$) ppm. IR ν_{max} (KBr): 2048 ν(C≡C) cm^{-1}.

***trans,trans,trans*-(PhC≡C)Ru(dmpe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru-(depe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru(C≡CPh)(dmpe)$_2$ (4a).** *trans*-Ru-(CH$_3$)(C≡CPh)(dmpe)$_2$ (**1a**) (0.30 g, 0.58 mmol) was added to a solution of *trans*-Ru(C≡CC$_6$H$_4$C≡CH)$_2$(depe)$_2$ (0.10 g, 0.13 mmol) in toluene (4 mL). Methanol (3 mL) was added, and the reaction mixture was left stirring at room temperature for 1 h. The solvent was removed under reduced pressure, and the dark brown powder was washed with benzene (2 × 2 mL) and DCM (2 × 2 mL) to afford the symmetrically substituted trinuclear acetylide-bridged ruthenium(II) complex *trans,trans,trans*-(PhC≡C)Ru(dmpe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru(depe)$_2$-(μ-C≡CC$_6$H$_4$C≡C)Ru(C≡CPh)(dmpe)$_2$ (**4a**) as a dark brown-orange powder (0.21 g, 90%). MS (ESI$^+$) (%): *m/z* 1266 [M − 1 − Ru(dmpe)$_2$(C≡CPh)]$^+$ (30), 1097 (20), 667 (95), 639 (100). ^{31}P{^{1}H} NMR (121.51 MHz, DCM-d_2): δ 51.48 (s, 4P, *P*Et$_2$), 39.73 (s, 8P, *P*Me$_2$) ppm. ^{1}H{^{31}P} NMR (600.13 MHz, DCM-d_2): δ 7.16 (AA′ of AA′XX′, 4H, Ar*H*), 7.00 (m, 4H, Ar*H*), 6.91 (m, 4H, Ar*H*), 6.89 (XX′ of AA′XX′, 4H, Ar*H*), 6.84 (m, 2H, Ar*H*), 2.24 (m, 8H, PC*H*HCH$_3$), 1.89 (m, 8H, PCH*H*CH$_3$), 1.71 (m, 24H, PC*H*$_2$), 1.54 (s, 24H, PC*H*$_3$), 1.46 (s, 24H, PC*H*$_3$), 1.17 (m, 24H, PCH$_2$C*H*$_3$) ppm. ^{13}C{^{1}H,^{31}P} NMR (150.92 MHz, DCM-d_2): 131.4 (Ar*C*H), 129.5 (Ar*C*H), 129.1 (Ar*C*H), 127.4 (Ar*C*H), 121.9 (Ar*C*H), 29.1 (PC*H*$_2$ of dmpe), 21.2 (PC*H*$_2$ of depe), 20.2 (PCH$_2$C*H*$_3$), 14.4 (PC*H*$_3$), 12.7 (PC*H*$_3$), 8.6 (PCH$_2$C*H*$_3$) ppm. Remaining resonances not observed. IR ν_{max} (KBr): 2061, 2055, 2049 ν(C≡C) cm^{-1}.

***trans,trans,trans*-(^{t}BuC≡C)Ru(dmpe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru-(depe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru(C≡C^{t}Bu)(dmpe)$_2$ (4b).** *trans*-Ru-(CH$_3$)(C≡C^{t}Bu)(dmpe)$_2$ (**1b**) (0.24 g, 0.48 mmol) was added to a solution of *trans*-Ru(C≡CC$_6$H$_4$C≡CH)$_2$(depe)$_2$ (0.15 g, 0.20 mmol) in toluene (5 mL). Methanol (4 mL) was added, and the reaction mixture was left stirring at room temperature for 1 h. The solvent was removed under reduced pressure. The dark brown-orange powder was washed with benzene (2 × 2 mL) and DCM (2 × 2 mL) to afford the symmetrically substituted trinuclear acetylide-bridged ruthenium(II) complex *trans,trans,trans*-(^{t}BuC≡C)Ru(dmpe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru(depe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru(C≡C^{t}Bu)(dmpe)$_2$ (**4b**) as a light brown-orange powder (0.29 g, 84%). HRMS (ESI$^+$, MeOH): 1727.4771 (calcd for M$^+$ 1727.4797). ^{31}P{^{1}H} NMR (121.51 MHz, DCM-d_2): δ 51.76 (s, 4P, *P*Et$_2$), 39.59 (s, 8P, *P*Me$_2$) ppm. ^{1}H{^{31}P} NMR (600.13 MHz, DCM-d_2): δ 6.64 (m, 8H, Ar*H*), 2.23 (m, 8H, PC*H*HCH$_3$), 1.85 (m, 8H, PCH*H*CH$_3$), 1.68 (m, 16H, PC*H*$_2$), 1.60 (m, 8H, PC*H*$_2$), 1.52−42 (m, 48H, PC*H*$_3$), 1.15 (s, 24H, PCH$_2$C*H*$_3$), 0.99 (s, 18H, C(C*H*$_3$)$_3$) ppm. ^{13}C{^{1}H,^{31}P} NMR (150.92 MHz, DCM-d_2): δ 137.3 (Ru(depe)$_2$*C*≡CC$_6$H$_4$), 131.2 (Ru(dmpe)$_2$*C*≡CC$_6$H$_4$), 129.6 (Ar*C*H), 126.2 (Ar*C*), 126.0 (Ar*C*), 114.5 (Ru*C*≡CC(CH$_3$)$_3$), 111.7 (Ru(depe)$_2$C≡*C*C$_6$H$_4$), 108.6 (Ru(dmpe)$_2$C≡*C*C$_6$H$_4$), 102.1 (RuC≡*C*C(CH$_3$)$_3$), 33.3 (*C*(CH$_3$)$_3$), 30.6 (PC*H*$_2$ of dmpe), 29.6 (C(*C*H$_3$)$_3$), 21.9 (PC*H*$_2$ of depe), 20.8 (PCH$_2$*C*H$_3$), 16.0 (PC*H*$_3$), 15.6 (PC*H*$_3$), 9.2 (PCH$_2$*C*H$_3$) ppm. IR ν_{max} (KBr): 2080, 2047 ν(C≡C) cm^{-1}.

***trans,trans,trans*-(SiMe$_3$C≡C)Ru(dmpe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru-(depe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru(C≡CSiMe$_3$)(dmpe)$_2$ (4c).** *trans*-Ru-(CH$_3$)(C≡CSiMe$_3$)(dmpe)$_2$ (**1d**) (0.20 g, 0.39 mmol) was added to a solution of *trans*-Ru(C≡CC$_6$H$_4$C≡CH)$_2$(depe)$_2$ (0.10 g, 0.13 mmol) in toluene (5 mL). Methanol (4 mL) was added, and the reaction mixture was left stirring at room temperature for 1 h. The solvent was removed under reduced pressure. The brown-orange powder was washed with benzene (2 × 2 mL) and DCM (2 × 2 mL) to afford the symmetrically substituted trinuclear acetylide-bridged ruthenium(II) complex *trans,trans,trans*-(SiMe$_3$C≡C)Ru(dmpe)$_2$-(μ-C≡CC$_6$H$_4$C≡C)Ru(depe)$_2$(μ-C≡CC$_6$H$_4$C≡C)Ru(C≡CSiMe$_3$)-(dmpe)$_2$ (**4c**) as a light brown powder (0.20 g, 88%). HRMS (ESI$^+$, MeOH): 1759.4362 (calcd for M$^+$ 1759.4416). ^{31}P{^{1}H} NMR (121.51 MHz, DCM-d_2): δ 51.51 (s, 4P, *P*Et$_2$), 39.91 (s, 8P, *P*Me$_2$) ppm. ^{1}H{^{31}P} NMR (600.13 MHz, DCM-d_2): δ 6.66 (m, 8H, Ar*H*), 2.23 (m, 8H, PC*H*HCH$_3$), 1.86 (m, 8H, PCH*H*CH$_3$), 1.68 (m, 16H, PC*H*$_2$), 1.62 (m, 8H, PC*H*$_2$), 1.50 (s, 24H, PC*H*$_3$), 1.47 (s, 24H, PC*H*$_3$), 1.15 (s, 24H, PCH$_2$C*H*$_3$), 0.07 (s, 18H, Si(C*H*$_3$)$_3$) ppm. ^{13}C{^{1}H,^{31}P} NMR (150.92 MHz, DCM-d_2): δ 129.4 (Ar*C*H), 129.3 (Ar*C*H), 125.6 (Ar*C*), 125.5 (Ar*C*), 111.5 (Ru(depe)$_2$C≡*C*C$_6$H$_4$), 109.3 (Ru(dmpe)$_2$C≡*C*C$_6$H$_4$), 30.2 (PC*H*$_2$ of dmpe), 21.6 (PC*H*$_2$ of depe), 20.5 (PCH$_2$*C*H$_3$), 15.6 (PC*H*$_3$), 15.3 (PC*H*$_3$), 8.9 (PCH$_2$*C*H$_3$), 1.7 (Si(*C*H$_3$)$_3$) ppm. Remaining resonances not observed. IR ν_{max} (KBr): 2048, 1989 ν(C≡C) cm^{-1}.

Supporting Information Available: Crystallographic files (.cif) of **1c**, **2b**, and **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.