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Article

Formation of Ruthenaindenes by Cyclometalation of Ruthenium(II) Diarylbutenyne Complexes

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The reaction of diarylbutenynylruthenium complexes $[Ru(\eta^3\text{-}C(C{\equiv}CC_6H_4R){=}C(R')C_6H_4R)(PMe_3)_4]^+$ (C_6H_4R = C_6H_4-4-^{t}Bu, Ph, C_6H_4-4-Me; R′ = H, Me) with dimethylmagnesium yields the cyclometalated ruthenaindene complexes $[\overline{Ru(C(C{\equiv}CC_6H_4R){=}C(R')C_6H_3R)}(PMe_3)_4]$ with ruthenium incorporated into the five-membered ring of an indene. The reaction involves the initial formation of methylruthenium complexes, which then rearrange with the elimination of methane to yield the product. The complexes $[\overline{Ru(C(C{\equiv}CC_6H_4R){=}C(R')C_6H_3R)}(PMe_3)_4]$ (C_6H_4R = C_6H_4-4-^{t}Bu, R′ = H; C_6H_4R = Ph, R′ = Me) were crystallographically characterized.

Introduction

Transition-metal butenynyl complexes have been identified as key intermediates in the metal-catalyzed head-to-head couplings of alkynes leading to *E*/*Z*-1,4-disubstituted-1-buten-3-ynes[1,2] and *E*/*Z*-1,4-disubstituted butatrienes.[3] This alkyne dimerization reaction is an attractive, atom-efficient route for the formation of enyne moieties that play an important role in medicinal and natural product chemistry and in organic synthesis.[4] We and others have been studying the formation of transition-metal butenynyl complexes with a view to better understanding the structure and chemistry of these species.[1,5−9]

Butenynyl complexes have been synthesized by reaction of transition-metal complexes with terminal alkynes,[8−13] insertion of 1,4-disubstituted buta-1,3-diynes into a transition-metal hydride bond,[14,15] coupling of coordinated acetylide units in transition-metal acetylide complexes,[16,17] and protonation of low-valent complexes bearing η^2-coordinated butadiynyl ligands.[6,15] The butenynyl ligand is known with either η^1-coordination[3,11,18] or η^3-coordination,[8,12,15,16,19] depending on the metal center.

Under acidic conditions, iron and ruthenium bisacetylides protonate at the β-carbon to form acetylide-vinylidene complexes, which may rearrange with coupling of the organic ligands to form metal butenynes (Scheme 1).[5,13,20,21]

In the metal butenynes that have been structurally characterized, the coordinated vinyl fragment preferentially adopts the stereochemistry with the metal center at one end of the double bond *trans* to the larger substituent at

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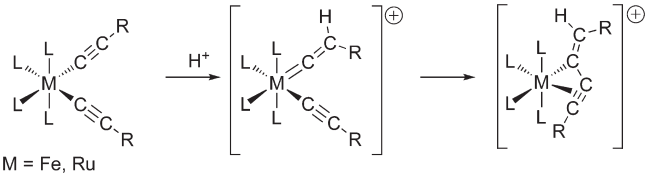
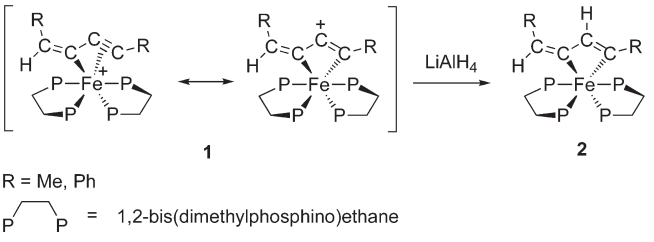
Scheme 1



Scheme 2



the other end of the double bond. The *trans* stereoisomer presumably has less steric strain than the *cis* isomer, where there would be significant crowding between the metal center and the larger substituent. In the case of $[Ru(\eta^3\text{-}C(C{\equiv}CMe){=}C(H)Me)(PMe_3)_4]^+$, the complex can be formed as a mixture of *E*- and *Z*-stereoisomers at low temperature but readily isomerizes to the more stable *Z*-isomer on warming.[20]

The structures of known ruthenium butenynes confirm a degree of electron delocalization, with the preferred η^3-bonding mode for the enyne probably best described as a hybrid between a σ-vinyl/π-alkynyl butenyne complex and an η^2-1,3-butadienyl complex.[8,12,22] We have previously reported the attack of hydride (from $LiAlH_4$) on the C2 carbon of the coordinated enyne of $[Fe(\eta^3\text{-}C(C{\equiv}CR){=}C(H)R)(dmpe)_2][PF_6]$ (**1**) (R = Me, Ph) to give a metallocyclobutene product, $[\overline{Fe{-}C{=}C(H)R)C(H){=}CR}(dmpe)_2]$ (**2**).[5] The formation of the metallocyclobutene by attack of the hydride at the butenyne ligand is not unreasonable since one canonical form of the metal butenyne imparts a partial positive charge onto C2 of the coordinated enyne (Scheme 2).[16] The ferracyclobutene products are unstable in the solid state, but have been characterized by multinuclear NMR spectroscopy.

The related η^3-allenyl/propargyl complexes display enhanced reactivity toward nucleophilic addition at the central carbon of the bound organic ligand,[23] leading to metallacyclobutene products (Scheme 3).[24] This suggests that butenyne complexes should be prone to attack by other nucleophiles, possibly allowing isolation and complete characterization of the expected metallocyclobutene products.

Scheme 3

Results and Discussion

The reaction of *cis*-$RuMe_2(PMe_3)_4$ with terminal alkynes is known[25] to furnish bis(acetylido)ruthenium(II) complexes. These complexes, when protonated with weak acids such as 2,6-lutidinium salts, give ruthenium(II) butenyne complexes, $[Ru(\eta^3\text{-}C(C{\equiv}CR){=}C(H)R)(PMe_3)_4]^+$ (**3a**−**c**) in good (50−80%) yield[20] (Scheme 4), while the use of methyl trifluoromethanesulfonate in place of acid results in the formation of the related methyl-substituted butenyne complex $[Ru(\eta^3\text{-}C(C{\equiv}CPh){=}C(Me)Ph)(PMe_3)_4]^+$ (**3d**).[20]

When $[Ru(\eta^3\text{-}C(C{\equiv}CC_6H_4{}^tBu){=}C(H)C_6H_4{}^tBu)(PMe_3)_4]BF_4$ (**3a**) reacted with dimethylmagnesium in THF solution, the major product of the reaction was identified as the *ortho*-metalated ruthenaindene $[\overline{Ru(C(C{\equiv}CC_6H_4{}^tBu){=}C(H)C_6H_3\text{-}{}^tBu)}(PMe_3)_4]$ (**4a**) (Scheme 5), and the structure of the complex was confirmed by X-ray crystallography (Figure 1, Table 1). Ruthenaindenes **4b** and **4c** were formed in an exactly analogous manner when the corresponding ruthenium butenynes **3b** and **3c** were treated with Me_2Mg. The methyl-substituted butenyne **3d** also yields a ruthenaindene, **4d**, upon reaction with Me_2Mg. Slow cooling of a saturated hexane solution of the complex gave X-ray quality crystals of **4d** (Figure 2, Table 1).

Structurally characterized monometallic ruthenaindenes are rare in the literature, with three examples previously reported.[26,27] Complex **4a** exhibits a distorted octahedral geometry, with the expected unsymmetrical coordination environment about the metal center. The $Ru{-}C_{aryl}$ bond, at 2.150(2) Å, is slightly longer than the value reported for the related complexes $[Cp^*\overline{Ru(C(Ph){=}C(R)C_6H_4)}NO]$ (R = Ph, 2.088(8) Å; R = Me, 2.093 Å),[26] but comparable to that of $[\overline{Ru(C(C(O)OCH_3){=}C(C(O)OCH_3)C_6H_4)}(CO)_2(PMe_2Ph)_2]$ (2.122 Å).[27] The remaining ruthenium−carbon bond (2.147(2) Å) is slightly longer than those in the previously reported examples (2.129(5), 2.114(7),[26] and 2.098 Å[27]). The ruthenaindene core is essentially planar, with the exocyclic aromatic ring being twisted relative to this plane by approximately 23°.

The methyl-substituted complex **4d** is isostructural with **4a**, with some minor differences in bond lengths. The $Ru{-}C_{aryl}$ bond is shorter (2.132(2) vs 2.150(2) Å), while the double bond in the five-membered metallocyclic ring is slightly elongated (1.367(3) vs 1.346(2) Å). The core bond angles are essentially identical. The exocyclic aromatic ring of **4d** is twisted relative to the ruthenaindene core by approximately 55°.

While ruthenaindenes are relatively rare in the literature, metalloindenes incorporating early transition metals are

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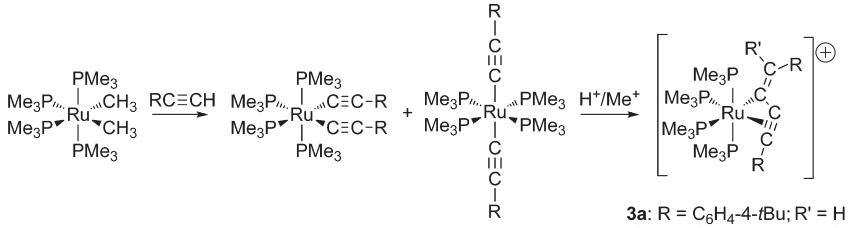
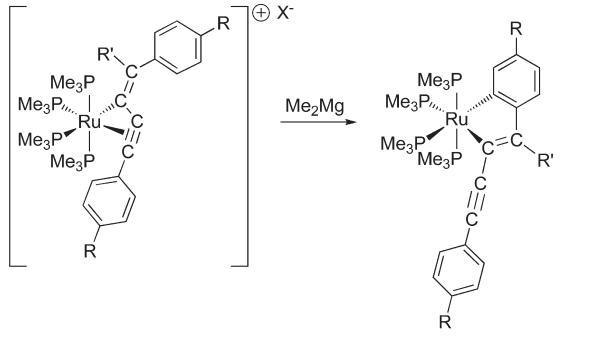
Scheme 4



3a: R = C_6H_4-4-*t*Bu; R' = H
3b: R = Ph; R' = H
3c: R = C_6H_4-4-Me; R' = H
3d: R = Ph; R' = Me

Scheme 5



3a: R = *t*Bu; R' = H
3b: R = H; R' = H
3c: R = Me; R' = H
3d: R = H; R' = Me

4a: R = *t*Bu; R' = H (55%)
4b: R = H; R' = H (64%)
4c: R = Me; R' = H (49%)
4a: R = H; R' = Me (61%)

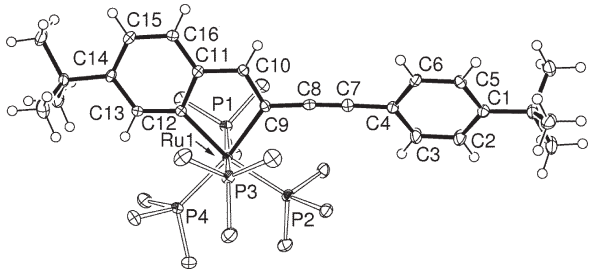


Figure 1. Molecular projection of [Ru(C(C≡CC_6H_4*t*Bu)=C(H)C_6H_3'Bu)(PMe_3)$_4$] (**4a**). Thermal ellipsoids are shown at the 50% probability level, while hydrogen atoms have an arbitrary radius of 0.1 Å. Hydrogen atoms on phosphine ligands have been omitted for clarity.

reasonably common and are typically prepared by the addition of an internal alkyne to a benzyne complex.[28] Metalloindenes of late transition metals have previously been prepared

Table 1. Selected Bond Lengths (Å) and Angles (deg) for [Ru(C(C≡CC_6H_4'Bu)=C(H)C_6H_3'Bu)(PMe_3)$_4$] (4a) and [Ru(C(C≡CPh)=C(Me)C_6H_4)(PMe_3)$_4$] (4d)

parameter	4a	4d	parameter	4a	4d
Ru(1)−C(9)	2.147(2)	2.141(2)	Ru(1)−P(2)	2.3818(5)	2.3805(7)
Ru(1)−C(12)	2.150(2)	2.132(2)	Ru(1)−P(3)	2.3308(5)	2.3131(5)
C(9)−C(10)	1.346(2)	1.367(3)	Ru(1)−P(4)	2.3575(6)	2.3596(7)
C(10)−C(11)	1.444(3)	1.457(3)	C(9)−Ru(1)−C(12)	77.86(7)	77.32(9)
C(11)−C(12)	1.427(3)	1.426(3)	P(1)−Ru(1)−P(3)	168.92(2)	170.09(2)
C(7)−C(8)	1.217(3)	1.214(3)	P(2)−Ru(1)−P(4)	99.02(2)	99.65(2)
Ru(1)−P(1)	2.3486(6)	2.3493(6)			

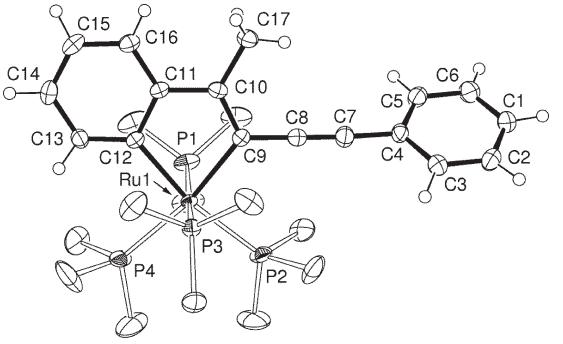
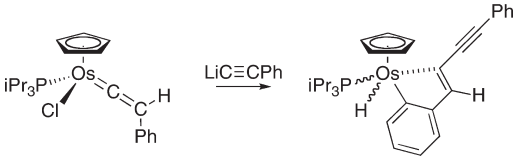


Figure 2. Molecular projection of [Ru(C(C≡CPh)=C(Me)C_6H_4)(PMe_3)$_4$] (**4d**). Thermal ellipsoids are shown at the 50% probability level, while hydrogen atoms have an arbitrary radius of 0.1 Å. Hydrogen atoms on phosphine ligands have been omitted for clarity.

Scheme 6.[30]



by elimination of triflic acid from ruthenium- or rhodium-vinyl and osmium-vinylidene complexes.[26,29] The related osmium(II) complex [(Cp)Os(C(C≡CPh)=C(H)C_6H_4)(H)(P^iPr_3)] has been reported to form from the reaction of an osmium vinylidene complex with lithium phenylacetylide (Scheme 6).[30]

Ruthenaindene **4a** exhibits three resonances in the $^{31}P\{^1H\}$ NMR spectrum in the ratio 1:2:1, consistent with an

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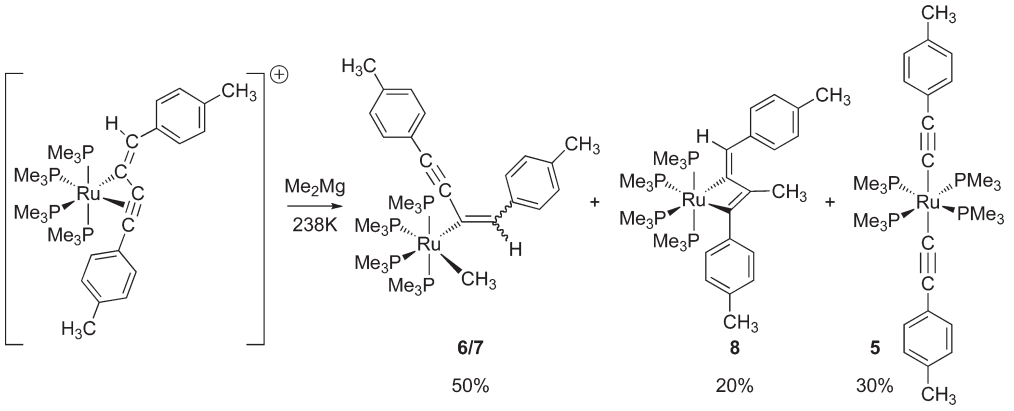
Scheme 7



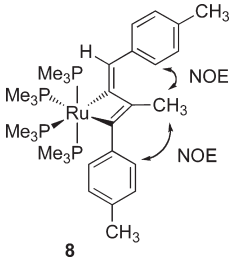
octahedral complex with two equivalent axial phosphines and two nonequivalent equatorial phosphines. One of the equatorial phosphines appears at unusually high field (δ −17.4 ppm). In addition, there is a complex phosphorus-coupled multiplet at δ 8.10 ppm in the ^{1}H NMR spectrum (C_6D_6) attributed to the proton on the five-membered metal-containing ring.

Mechanistically, the formation of ruthenaindenes from the butenyne starting materials is unexpected. Overall, the reaction involves decoordination of the π-bound acetylene of the butenyne fragment, $Z \rightarrow E$ isomerization of the metal-substituted alkene, *ortho*-metalation of the aromatic ring attached to the vinyl group of the butenyne, and loss of a proton.

Since the Me_2Mg is not incorporated into the reaction product, it could be argued that it behaves merely as a relatively strong base in this reaction. Attempts to prepare ruthenaindenes **4a**−**c** using KO^{t}Bu in place of Me_2Mg simply resulted in formation of the bis(acetylide) complexes *trans*-Ru(C≡CR)$_2$(PMe$_3$)$_4$. This reaction with KO^{t}Bu is not unprecedented since metal butenynes are known to revert to metal bisacetylides on treatment with base,[5] presumably via a process that is essentially the reverse of the reaction depicted in Scheme 1. Clearly Me_2Mg does not act merely as a base in its reaction with metal butenynes.

The reaction between [Ru(η^3-C(C≡CC$_6$H$_4$CH$_3$)=C(H)C$_6$H$_4$CH$_3$)(PMe$_3$)$_4$]BF$_4$ (**3c**) and Me_2Mg in THF-d_8 was monitored carefully by NMR spectroscopy at low temperature (238 K). At this temperature, no ruthenaindene product is formed. On addition of Me_2Mg to **3c** at 238 K, three major products are present in the reaction mixture immediately after the reagents are mixed, in a ratio of approximately 20:30:50, and these are assigned as complexes **8**, **5**, and **6/7**, respectively (Scheme 7).

The minor product, **8**, exhibits a 1-proton phosphorus-coupled vinylic resonance at δ 6.27 ppm (d, $^4J_{PH}$ = 7.0 Hz) and a 3-proton methyl resonance at δ 1.27 ppm (m) in the ^{1}H NMR spectrum. There are no alkynyl resonances associated with complex **8** in the ^{13}C{^{1}H} NMR spectrum. There are two *para*-substituted aromatic rings, and the methyl resonance at δ 1.27 exhibits an NOE to two sets of aryl protons on different aromatic rings. The ^{13}C{^{1}H} NMR spectrum exhibits resonances at low field (δ 163.5 and 146.0 ppm) corresponding to carbons of the metallocyclobutene, and these display a long-range correlation in the ^{1}H−^{13}C HMBC to the methyl resonance at δ 1.27 ppm.[31] Complex **8** is assigned as the metallocyclobutene complex, which would form by direct methylation of the butenyne **3c** at the central carbon of the bound enyne ligand.



8

The second most abundant product is the known bis(acetylide) *trans*-Ru(C≡CC$_6$H$_4$-4-Me)$_2$(PMe$_3$)$_4$ (**5**), formed by simple deprotonation and cleavage of the butenyne starting material.

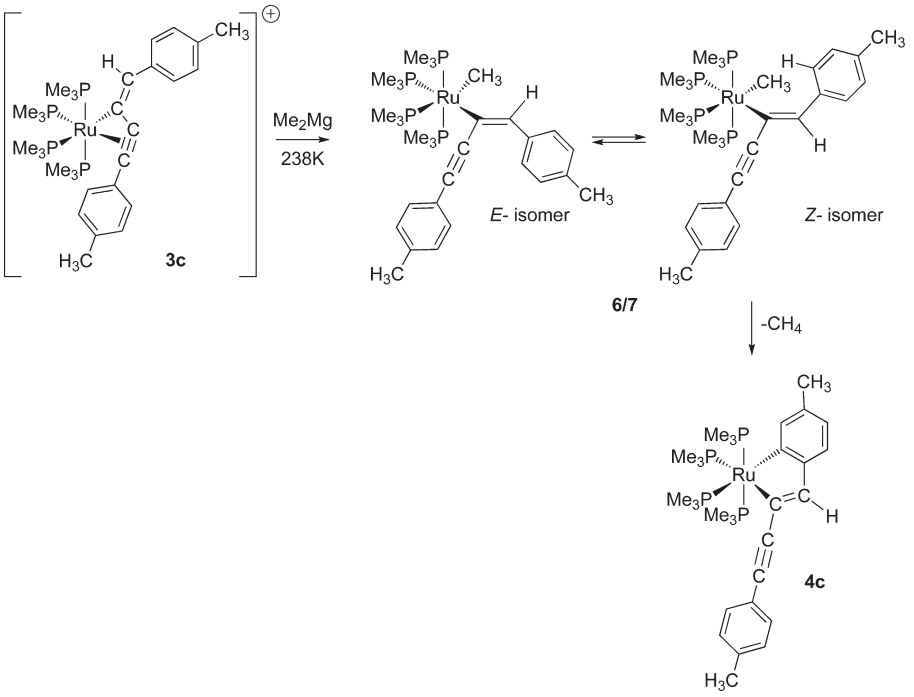
The major product of the reaction at 238 K is assigned as complex **6** (or its isomer **7**). This product contains a phosphorus-coupled doublet in the ^{1}H NMR spectrum corresponding to a vinylic proton at δ 6.62 ppm ($^4J_{PH}$ = 5.0 Hz). The spectrum also contains a broad phosphorus-coupled multiplet at δ −0.46 ppm, corresponding to a ruthenium-bound methyl group. The methyl resonance shows broadening down to at least 188 K and shows exchange (confirmed by exchange peaks in the NOESY spectrum) with another Ru-bound methyl resonance due to a minor product (<15%) in the reaction mixture (δ −1.56 ppm). The second species is probably the alternate stereoisomer of **6**; that is, if **6** is the *E*-isomer, then **7** is the *Z*-isomer or *vice versa* (Scheme 8). Complex **6** is the product that would be expected from the direct attack of the methylating agent on the cationic metal center with loss of the coordinated alkyne. At low temperature, the deprotonation of the butenyne **3c** to yield the bisacetylide **5** occurs in competition with the methylation reactions that give rise to **6/7** and **8**.

Above 248 K, the signals corresponding to **6** broaden, and this complex rapidly decomposes near room temperature to yield the ruthenaindene product **4c** together with other minor products. Free methane is also visible as a sharp singlet in the ^{1}H NMR spectrum at δ 0.20 ppm.

The cyclometalation of complex **6** to form the ruthenaindene product **4c** must occur from the *Z*-stereoisomer of **6/7**

(31) The related ferracyclobutene [Fe-C(=C(H)Ph)C(H)=CPh-(dmpe)$_2$] displays resonances at δ 141.9, 166.6, and 167.5 ppm in the ^{13}C{^{1}H} NMR spectrum corresponding to the carbon atoms of the cyclobutene core. See ref 5.

Scheme 8



(Scheme 8). We have previously reported that $[Ru(\eta^3\text{-}C(C{\equiv}CMe){=}C(H)Me)(PMe_3)_4]^+$ can be formed as a mixture of *E*- and *Z*- stereoisomers at low temperature but readily isomerizes to the more stable *Z*-isomer on warming.[20] Indeed the *E*/*Z* isomerization of vinyl-type complexes is well established in the literature and is often proposed to proceed via a carbene-type structure in which rotation around the C−C bond is possible.[26,32]

Ortho-metalation of aryl ligands resulting from methane elimination is not unprecedented; for example the reaction of $FeMe_2(PMe_3)_4$ with 1-(diphenylphosphino)naphthalene or benzyldiphenylphosphine yields metalated methyl iron complexes via selective activation of a C−H aryl bond.[33] Analogous reactions are also known for cobalt.[34]

Conclusion

The reaction of aryl-substituted butenynylruthenium compounds with Me_2Mg provides a novel synthetic route to alkynyl-substituted ruthenaindenes. The mechanism of formation involves an initial change from η^3- to η^1-binding in the butenynyl ligand, induced by attack of Me^- at the metal center to yield a methyl-η^1-butenynylruthenium complex. The double bond of the enyne isomerizes from *Z* to *E* followed by elimination of methane with metalation of an aromatic ring to yield the final product.

The reaction sequence provides a good synthetic approach to new members of this relatively rare class of organometallic compound with ruthenium embedded within a highly conjugated organic framework.

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 dried and degassed by refluxing over standard drying agents[35] 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. Acetone-d_6 was dried over 4 Å molecular sieves.

Nuclear magnetic resonance spectra were recorded on a Bruker DMX600 (operating at 600.13, 150.92, and 242.95 MHz for ^{1}H, ^{13}C, and ^{31}P, respectively), Bruker Avance III (operating at 500.15, 125.76, and 202.46 MHz for ^{1}H, ^{13}C, and ^{31}P, respectively), Bruker Avance III 400 (operating at 400.13, 100.61, and 161.98 MHz for ^{1}H, ^{13}C, and ^{31}P, respectively), or a 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. A solution of dimethylmagnesium in THF was prepared according to the literature.[36] *cis*-$RuMe_2(PMe_3)_4$ was prepared from the reaction of *trans*-$RuCl_2(PMe_3)_4$[37] with Me_2Mg in THF; the NMR spectra were identical to that reported in the literature.[38] The butenyne complexes **3b**−**d** were prepared as described previously.[20]

$[Ru(\eta^3\text{-}C(C{\equiv}CC_6H_4{}^t\!Bu){=}C(H)C_6H_4{}^t\!Bu)(PMe_3)_4]BF_4$ (3a). A solution of *cis*-$RuMe_2(PMe_3)_4$ (0.348 g, 0.880 mmol) in THF (20 mL) was treated with 4-*tert*-butylphenylacetylene (0.7 mL, 3.88 mmol). The mixture was warmed to 40 °C for 2 h, before the volatiles were removed under reduced pressure.

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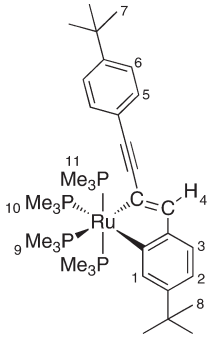
(38) Andersen, R. A.; Jones, R. A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1978**, 446–453.

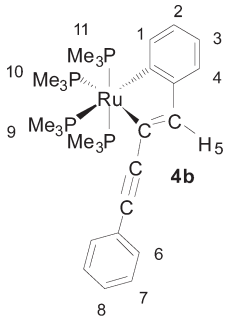
The residual sticky solid was dissolved in THF, and 2,6-lutidinium tetrafluoroborate (0.153 g, 0.785 mmol) was added and the mixture stirred at room temperature. After 80 min, the volatiles were removed under reduced pressure and the residue was washed with Et_2O (3 × 5 mL) and dried *in vacuo* to give [Ru(η^3-C(C≡C$C_6H_4{}^t$Bu)=C(H)$C_6H_4{}^t$Bu)(PMe_3)$_4$]BF_4, **3a**, as a yellow powder. Yield: 0.463 g (65%). Anal. Calcd for $C_{36}H_{63}F_4P_4RuB$: C, 53.54; H, 7.86. Found: C, 53.65; H, 7.58. $^{31}P\{^1H\}$ NMR (acetone-d_6, 242 MHz): δ 0.35 (dt, $^2J_{PP}$ = 33.2, 22.5 Hz, 1P, P_{eq}), −9.10 (apparent t, splitting = 31.9 Hz, 2P, P_{eq}), −16.35 (m, 1P, P_{ax}) ppm. ^1H NMR (acetone-d_6, 600 MHz): δ 7.78 (AA′ of AA′XX′, 2H, ArH), 7.74 (AA′ of AA′XX′, 2H, ArH), 7.59 (XX′ of AA′XX′, 2H, ArH), 7.50 (XX′ of AA′XX′, 2H, ArH), 7.11 (d, $^4J_{PH}$ = 4.4 Hz, 1H, =C(*H*)), 1.87 (d, $^2J_{PH}$ = 8.6 Hz, 9H, $P_{eq}(CH_3)_3$), 1.82 (d, $^2J_{PH}$ = 7.3 Hz, 9H, $P_{eq}(CH_3)_3$), 1.37 (s, 9H, $C(CH_3)_3$), 1.34 (s, 9H, $C(CH_3)_3$), 1.21 (apparent t, splitting = 3.0 Hz, 18H, $P_{ax}(CH_3)_3$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, acetone-d_6): δ 152.7 (*C*-$C(CH_3)_3$), 150.7 (*C*-$C(CH_3)_3$), 146.9 (m, Ru-*C*), 136.4 (d, J_{PC} = 4.6 Hz, ArC_{ipso}), 132.4 (Ar*C*H), 130.4 (=*C*H), 127.1 (Ar*C*H), 126.7 (2 × Ar*C*H), 126.3 (ArC_{ipso}), 115.1 (*C*≡CAr), 59.0 (C≡*C*Ar), 35.5 ($C(CH_3)_3$), 35.2 ($C(CH_3)_3$), 31.7 ($C(CH_3)_3$), 31.5 ($C(CH_3)_3$), 25.2 (d, J_{PC} = 25.7 Hz, $P_{eq}(CH_3)_3$), 24.0 (d, J_{PC} = 30.2 Hz, $P_{eq}(CH_3)_3$), 18.5 (apparent t, splitting = 14.0 Hz, $P_{ax}(CH_3)_3$) ppm.

[Ru(C(C≡C$C_6H_4{}^t$Bu)=C(H)$C_6H_3{}^t$Bu)(PMe_3)$_4$] (4a).



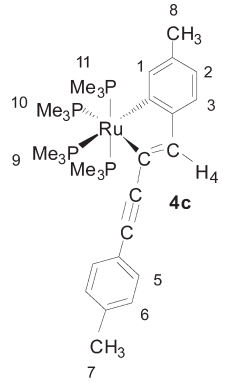
A solution of [Ru(η^3-C(C≡C$C_6H_4{}^t$Bu)=C(H)$C_6H_4{}^t$Bu)-(PMe_3)$_4$]BF_4, **3a** (0.0743 g, 0.0920 mmol), in THF (10 mL) was treated with Me_2Mg (0.68 mL, 0.15 M solution in THF, 0.10 mmol), and the mixture stirred at room temperature overnight. The volatiles were removed under reduced pressure, and the residue was extracted with hexane (3 × 5 mL). The combined hexane extracts were filtered through Celite and concentrated under reduced pressure. [Ru(C(C≡CC_6H_4tBu)=C(H)C_6H_3tBu)-(PMe_3)$_4$], **4a**, was obtained as an orange solid. Yield: 0.0366 g (55%). Crystals suitable for X-ray diffraction were obtained by slow evaporation of a hexane solution of the product. Anal. Calcd for $C_{36}H_{62}P_4Ru$: C, 60.07; H, 8.68. Found: C, 59.96; H, 8.53. $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6): δ −5.38 (apparent t, splitting = 27.8 Hz, 2P, P_{ax}), −10.73 (dt, $^2J_{PP}$ = 30.0, 15.0 Hz, 1P, P_{eq}), −15.35 (dt, $^2J_{PP}$ = 26.7, 15.1 Hz, 1P, P_{eq}) ppm. ^1H NMR (500 MHz, C_6D_6): δ 8.10 (m, 1H, =C*H*), 7.69 (br d, J_{PH} = 5.0 Hz, 1H, H1), 7.62 (AA′ of AA′XX′, 2H, H5), 7.38 (dd, $^3J_{HH}$ = 7.7 Hz, J_{HP} = 1.3 Hz, 1H, H3), 7.28 (XX′ of AA′XX′, 2H, H6), 7.12 (br d, $^3J_{HH}$ = 7.7 Hz, 1H, H2), 1.51 (s, 9H, H8), 1.45 (d, $^2J_{PH}$ = 5.4 Hz, 9H, H10), 1.30 (d, $^2J_{PH}$ = 5.1 Hz, 9H, H9), 1.22 (s, 9H, H7), 0.96 (apparent t, splitting = 2.8 Hz, 18H, H11) ppm. Selected $^1H\{^{31}P\}$ NMR (500 MHz, C_6D_6): δ 8.10 (s, 1H, H4), 7.69 (d, $^4J_{HH}$ = 1.7 Hz, 1H, H1), 7.62 (AA′ of AA′XX′, 2H, H5), 7.38 (dd, $^3J_{HH}$ = 7.7 Hz, 1H, H3), 7.28 (XX′ of AA′XX′, 2H, H6), 7.12 (dd, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, H2) ppm. $^{13}C\{^1H,^{31}P\}$ NMR (125 MHz, THF-d_8): δ 181.3 (C_α of C_6H_3), 158.3 (Ru-*C*-C≡C), 156.4 (=*C*H), 155.8 ($C_{ipso}C_6H_3$), 149.2 ($C_{C6H4}C(CH_3)_3$), 143.7 ($C_{C6H3}C(CH_3)_3$), 139.5 (C1), 130.8 (C5), 125.9 (C6), 125.8 ($C_{ipso}C_6H_4$), 121.8 (C3), 118.0 (C2), 108.3 (*C*≡C−C_6H_4), 94.2 (C≡*C*-C_6H_4), 35.3 ($C(CH_3)_3$), 35.0 ($C(CH_3)_3$), 32.6 (C8), 31.8 (C7), 26.5 (C9), 25.3 (C10), 21.8 (C11) ppm.

[Ru(C(C≡CPh)=C(H)C_6H_4)(PMe_3)$_4$] (4b).



A solution of [Ru(η^3-C(C≡CPh)=C(H)Ph)(PMe_3)$_4$]BF_4, **3b** (0.0518 g, 0.0745 mmol), in THF (20 mL) was treated with Me_2Mg (1 mL, 0.15 M in THF, 0.15 mmol). The mixture was stirred at room temperature for 1 h before the volatiles were removed under reduced pressure. The residue was extracted with benzene (20 mL) and the extract filtered through Celite to give a clear yellow filtrate. The filter-cake was washed with additional benzene (2 × 5 mL) and the combined filtrate concentrated under reduced pressure to give [Ru(C(C≡CPh)=C(H)C_6H_4)-(PMe_3)$_4$], **4b**, as a yellow solid. Yield: 0.0291 g (64%). Anal. Calcd for $C_{28}H_{46}P_4Ru$: C, 55.35; H, 7.63. Found: C, 55.26; H, 7.83. $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6): δ −6.80 (apparent t, splitting = 28.5 Hz, 2P, P_{ax}), −12.42 (dt, $^2J_{PP}$ = 28.6, 15.1 Hz, 1P, P_{eq}), −16.48 (dt, $^2J_{PP}$ = 28.6, 15.4 Hz, 1P, P_{eq}) ppm. ^1H NMR (600 MHz, C_6D_6): δ 8.10 (m, 1H, =C*H*), 7.70 (m, 1H, H1), 7.61 (m, 2H, H6), 7.46 (d, $^3J_{HH}$ = 7.2 Hz, 1H, H4), 7.21 (m, 1H, H3), 7.17 (m, 2H, H7), 7.05 (m, 1H, H2), 7.03 (m, 1H, H8), 1.38 (d, $^2J_{PH}$ = 5.5 Hz, 9H, H10), 1.22 (d, $^2J_{PH}$ = 5.2 Hz, 9H, H9), 0.96 (apparent t, splitting = 2.7 Hz, 18H, H11) ppm. Selected $^1H\{^{31}P\}$ NMR (600 MHz, C_6D_6): δ 8.10 (s, 1H, =C*H*), 7.70 (d, $^3J_{HH}$ = 7.5 Hz, 1H, H1), 7.61 (d, $^3J_{HH}$ = 7.6 Hz, 2H, H6), 7.46 (d, $^3J_{HH}$ = 7.2 Hz, 1H, H4), 7.21 (m, 1H, H3), 7.17 (m, 2H, H7), 7.05 (m, 1H, H2), 7.03 (m, 1H, H8) ppm. $^{13}C\{^1H,^{31}P\}$ NMR (151 MHz, C_6D_6): δ 181.9 (C_α of C_6H_4), 160.8 ($C_{ipso}C_6H_4$), 156.9 (=*C*H), 156.7 (Ru−C), 141.7 (C1), 131.1 (C6), 129.0 (C7), 126.4 ($C_{ipso}C_6H_5$), 126.3 (C8), 123.1 (C4), 122.7 (C2), 122.0 (C3), 109.0 (*C*≡C-Ph), 94.6 (C≡*C*-Ph), 26.1 (C9), 25.5 (C10), 21.7 (C11) ppm.

[Ru(C(C≡CC_6H_4Me)=CH)C_6H_3Me)(PMe_3)$_4$] (4c).



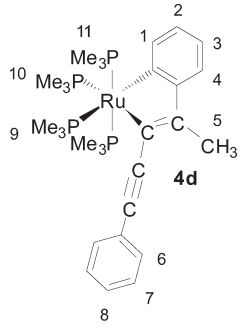
A solution of [Ru(η^3-C(C≡CC_6H_4-4-Me)=C(H)C_6H_4-4-Me)-(PMe_3)$_4$]BF_4 (0.1152 g, 0.159 mmol) in THF (20 mL) was treated with Me_2Mg (2.5 mL, 0.15 M in THF, 0.38 mmol). The mixture was stirred at room temperature for 1 h before the volatiles were removed under reduced pressure. The residue was

Table 2. Crystallographic and Structure Refinement Data for 4a and 4d

	4a	4d
chemical formula	$C_{36}H_{62}P_4Ru$	$C_{29}H_{48}P_4Ru$
M_r	719.81	621.62
cell syst, space group	orthorhombic, $P2_12_12_1$	monoclinic, $P2(1)/n$
temp (K)	100(2)	150(2)
a (Å)	9.9351(8)	18.2619(7)
b (Å)	11.5379(11)	9.7641(4)
c (Å)	32.773(3) Å	19.3009(7)
β (deg)		116.9080(10)
V (Å^3)	3756.8(6)	3069.0(2)
Z	4	4
D_x (Mg m^{-3})	1.273	1.345
μ(Mo Kα) (mm^{-1})	0.61	0.74
cryst form, color	Yellow Block	Yellow Plates
cryst size (mm)	0.6 × 0.5 × 0.25	0.38 × 0.17 × 0.13
T_{min}	0.786	0.767
T_{max}	0.862	0.910
N, N_{ind}	108 552, 10 809	22 796, 5381
N_{obs} ($I > 2\sigma(I)$)	9942	5058
R_{int}	0.069	0.047
θ_{max} (deg)	30.8°	25.0
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.030, 0.057, 1.03	0.027, 0.111, 0.94
no. of reflns	10 809	5381
no. of params	388	355
H-atom treatment	constrained refinement	mixture of independent and constrained refinement
weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0206P)^2 + 1.0017P]$ where $P = (F_o^2 + 2F_c^2)/3$	calculated $w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 0.7602P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.002	0.003
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.48, −0.45	0.62, −0.78

extracted with benzene (20 mL) and the extract filtered through Celite to give a clear yellow filtrate. The filter-cake was washed with additional benzene (2 × 5 mL) and the combined filtrate concentrated under reduced pressure to give **4c** as a yellow solid. Yield: 0.051 g (49%). Anal. Calcd for $C_{30}H_{50}P_4Ru$: C, 56.68; H, 7.93. Found: C, 56.48; H, 7.99. $^{31}P\{^1H\}$ NMR (121 MHz, THF-d_8): δ −7.79 (apparent t, splitting = 28.7 Hz, 2P, P_{ax}), −13.50 (dt, $^2J_{PP}$ = 28.7, 15.0 Hz, 1P, P_{eq}), −17.61 (dt, $^2J_{PP}$ = 28.0, 15.0 Hz, 1P, P_{eq}) ppm. ^1H NMR (500 MHz, C_6D_6): δ 8.10 (m, 1H, =C*H*), 7.54 (AA′ of AA′XX′, 2H, H5), 7.53 (br d, J_{PH} = 4.4 Hz, 1H, H1), 7.37 (dd, $^3J_{HH}$ = 7.4 Hz, J_{HP} = 1.0 Hz, 1H, H3), 7.01 (XX′ of AA′XX′, 2H, H6), 6.97 (br d, $^3J_{HH}$ = 7.4 Hz, 1H, H2), 2.49 (s, 3H, H7), 2.10 (s, 9H, H8), 1.41 (d, $^2J_{PH}$ = 5.4 Hz, 9H, H10), 1.27 (d, $^2J_{PH}$ = 5.1 Hz, 9H, H9), 0.96 (apparent t, splitting = 2.8 Hz, 18H, H11) ppm. Selected $^1H\{^{31}P\}$ NMR (500 MHz, C_6D_6): δ 7.45 (s, 1H, =CH), 7.43 (d, $^4J_{HH}$ = 1.2 Hz, 1H, H1) ppm. $^{13}C\{^1H,^{31}P\}$ NMR (125 MHz, C_6D_6): δ 181.9 (Ru-*C*$_\alpha$ of C_6H_3), 158.2 (*C*$_{ipso}C_6H_3$), 156.4 (=*C*H), 154.9 (Ru−C), 143.0 (C1), 135.7 (*C*$_{C6H4}CH_3$), 131.0 (C5), 130.4 (*C*$_{C6H3}CH_3$), 129.6 (C6), 126.0 (*C*$_{ipso}C_6H_4$), 122.8 (C3), 122.4 (C2), 108.4 (*C*≡C-Ar), 94.2 (C≡*C*-Ar), 26.1 (C9), 25.4 (C10), 22.9 (C7), 21.7 (C11), 21.6 (C8) ppm.

[Ru(C(C≡CPh)=C(Me)C$_6$H$_4$)(PMe$_3$)$_4$] (4d).



A solution of [Ru(η^3-C(C≡CPh)=C(Me)Ph)(PMe$_3$)$_4$]OTf (0.2685 g, 0.348 mmol) in THF (20 mL) was treated with Me_2Mg (2.0 mL, 0.15 M in THF, 0.30 mmol). The mixture was stirred at room temperature for 1 h before the volatiles were removed under reduced pressure. The residue was extracted with benzene (20 mL) and the extract filtered through Celite to give a clear yellow filtrate. The filter-cake was washed with additional benzene (2 × 5 mL) and the combined filtrate concentrated under reduced pressure to give **4d** as a yellow solid. Yield: 0.133 g (61%). Slow cooling a saturated hexane solution of the complex grew crystals of X-ray quality. Anal. Calcd for $C_{29}H_{48}P_4Ru$: C, 56.03; H, 7.78. Found: C, 56.17; H, 7.83. $^{31}P\{^1H\}$ NMR (THF-d_8): δ −5.4 (dd, $^2J_{PP}$ = 27.6, 28.9 Hz, 2P, $P_{ax}(CH_3)_3$), −13.5 (dt, $^2J_{PP}$ = 28.9, 12.9 Hz, 1P, $P_{eq}(CH_3)_3$), −16.7 (dt, $^2J_{PP}$ = 27.6, 12.9 Hz, 1P, $P_{eq}(CH_3)_3$) ppm. ^1H NMR (THF-d_8): δ 7.57 (m, 1H, H1), 7.32 (m, 2H, H6), 7.23 (m, 2H, H7), 7.11 (m, 1H, H8), 6.91 (m, 1H, H4), 6.75 (m, 1H, H3), 6.59 (m, 1H, H2), 2.28 (apparent t, splitting = 2.6 Hz, 3H, H5), 1.59 (d, $^2J_{PH}$ = 5.5 Hz, 9H, H10), 1.54 (d, $^2J_{PH}$ = 5.1 Hz, 9H, H9), 0.96 (apparent t, splitting = 2.7 Hz, 18H, H11) ppm. $^{13}C\{^1H,^{31}P\}$ NMR (THF-d_8): δ 182.8 (Ru-*C*$_\alpha$ of C_6H_4), 160.8 (*C*$_{ipso}C_6H_4$), 157.1 (*C*-CH_3), 151.5 (Ru-*C*), 142.3 (C1), 130.8 (C6), 129.0 (C7), 128.9 (*C*$_{ipso}C_6H_5$), 126.3 (C8), 122.8 (C2), 121.5 (C4), 121.1 (C3), 107.5 (*C*≡C-Ph), 100.2 (C≡*C*-Ph), 26.3 (C9), 25.7 (C10), 21.6 (C11), 18.4 (C5) ppm.

Low-Temperature NMR Studies. [Ru(η^3-C(C≡CC$_6$H$_4$-4-Me)=C(H)C$_6$H$_4$-4-Me)(PMe$_3$)$_4$]BF$_4$ (0.0292 g, 0.0372. mmol) and dimethylmagnesium (0.0048 g, 0.0887 mmol) were placed in an NMR tube fitted with a concentric Teflon valve. THF-d_8 was vacuum transferred into the tube, which was then placed into an NMR probe that had been cooled to 238 K. Signals attributable to **5**, **6**/**7**, and **8** were immediately apparent. Complex **5**, *trans*-Ru(C≡CC$_6$H$_4$-4-Me)$_2$(PMe$_3$)$_4$, has been previously reported[25] and was identified on the basis of its $^{31}P\{^1H\}$ NMR spectrum. Selected NMR data for **6**, assigned as *E*- or *Z*-[Ru(Me)(η^1-C(C≡CC$_6$H$_4$-4-Me)=C(H)C$_6$H$_4$-4-Me)(PMe$_3$)$_4$]: $^{31}P\{^1H\}$ NMR: δ −3.02 (dd, $^3J_{PP}$ = 22.2, 29.8 Hz, 2P, P_{ax}), −6.91 (dt, $^3J_{PP}$ = 17.1, 29.8 Hz, 1P, P_{eq}), −13.2 (dt, $^3J_{PP}$ = 17.1, 22.2 Hz, 1P, P_{eq}) ppm. ^1H NMR: δ 6.62 (d, $^4J_{PH}$ = 5.0 Hz, =C*H*), 1.33 (m, $P_{ax}(CH_3)_3$), 1.36 (d, $^2J_{PH}$ = 5.6 Hz, $P_{eq}(CH_3)_3$), 1.48 (d, $^2J_{PH}$ = 5.4 Hz, $P_{eq}(CH_3)_3$), −0.46 (m, Ru-CH_3) ppm. $^{13}C\{^1H,^{31}P\}$ NMR: δ 144.6 (=*C*H), 138.7, 126.9, 106.9, 24.1 ($P_{eq}(CH_3)_3$), 20.9 ($P_{ax}(CH_3)_3$), 22.8 ($P_{eq}(CH_3)_3$), −3.81 (Ru-*C*H_3) ppm. Selected NMR data for **8**, assigned as [Ru-C(=C(H)C$_6$H$_4$Me)C(H)=CC$_6$-

$H_4Me(PMe_3)_4$]: $^{31}P\{^1H\}$ NMR: δ 0.47 (dd, $^3J_{PP}$ = 20.8, 30.3 Hz, 2P, P_{ax}), −9.59 (dt, $^3J_{PP}$ = 12.8, 30.3 Hz, 1P, P_{eq}), −12.5 (dt, $^3J_{PP}$ = 12.8, 20.8 Hz, 1P, P_{eq}) ppm. ^1H NMR: δ 6.27 (d, $^4J_{PH}$ = 7.0 Hz, =C*H*), 1.46 (m, $P_{ax}(CH_3)_3$), 1.41 (d, $^2J_{PH}$ = 5.1 Hz, $P_{eq}(CH_3)_3$), 1.27 (t, J_{PH} = 4.0 Hz, C-CH_3), 1.12 (d, $^2J_{PH}$ = 4.5 Hz, $P_{eq}(CH_3)_3$) ppm. $^{13}C\{^1H,^{31}P\}$ NMR: δ 163.3 (Ru-*C*), 145.9 (*C*-CH_3), 124.7 (=*C*H), 25.1 ($P_{eq}(CH_3)_3$), 23.8 ($P_{eq}(CH_3)_3$), 21.0 ($P_{ax}(CH_3)_3$), 19.7 (C-*C*H_3) ppm. Upon warming to room temperature, signals attributed to **6** gradually diminished, while resonances attributed to **4c** increased.

X-ray Crystallography. A suitable single crystal of **4a** was selected under the polarizing microscope (Prior Scientific, Zoommaster) and was mounted on a glass fiber with the use of a dot of silicon grease. Intensities were measured on a Bruker Nonius X8 Apex-II diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and operating at a low temperature of 100(2) K with an Oxford Cryostream system. Upon collecting intensities, an average redundancy of >11 was obtained for the resolution range of inf−0.60 Å with a 10 s exposure time over a range of omega and phi scans. The data integration and reduction with the multi-scan absorption correction method was carried out using the APEX2 suite of software.[39] The structure was solved with direct methods and full-matrix least-squares refinements by using the SHELXTL-97 program package[40] to the final *R* value of 0.0304 (*wR* 0.0548) for 10 809 reflections. Hydrogen atoms were placed at calculated positions, and all non-hydrogen atoms were refined anisotropically. Cystallographic data for the structure of **4a** are summarized in Table 2.

A suitable single crystal of **4d** was selected under the polarizing microscope (Leica M165Z) and was glued to a glass fiber with a dot of silicon paste that fixed the crystal firmly upon freezing at the temperature of data collection (150 K). The intensities were measured on a Bruker kappa APEX-II CCD diffractometer with low temperature at the crystal maintained using an Oxford Cryostream 700 system. Upon obtaining an initial refinement of unit cell parameters, the data collection strategy achieved a redundancy of at least 4 throughout the resolution range (inf−0.80 Å) at 10 s exposure time per frame making use of the kappa offsets on the four-circle goniometer geometry. The data integration and reduction with the multi-scan absorption correction method was carried out using the APEX2 suite of software.[39] The structure was solved by direct methods using SHELXS-97[40] and was refined by the full-matrix least-squares refinement program SHELXL[40] to the final *R* value of 0.027 (*wR* 0.111) for 5381 reflections. Crystallographic data for the structure of **4d** are summarized in Table 2.

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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.

(39) *APEX2*; Bruker Bruker Analytical X-ray Instruments Inc.: Madison, WI, 2007.
(40) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.