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Functionally Altered Ruthenaindenes with Electron-Rich and Electron-Poor Substituents

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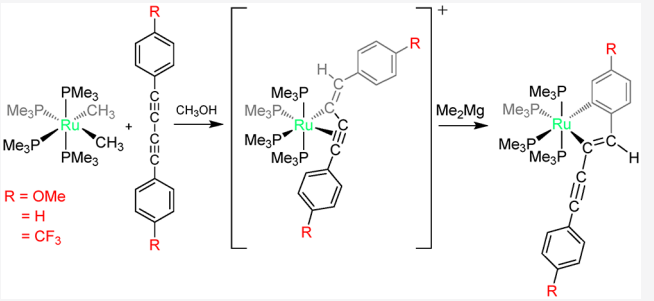
ABSTRACT: A series of ruthenaindene complexes containing electron-donating and -withdrawing groups were synthesized and characterized. The ruthenaindenes were synthesized from ruthenium butenynyl complexes which were formed by the treatment of $Me_2Ru(PMe_3)_4$ with 1,4-diaryl-1,3-butadiynes in methanol. Electrochemistry of the metal center in ruthenaindenes showed that the complexes with electron-donating groups on the aromatic ring have significantly lower oxidation potentials in comparison to complexes with electron-withdrawing groups. Even though the substitution of the aromatic ring with electron-donating/-withdrawing groups is remote from the metal center, the electronic properties of the substituents are relayed effectively to the metal center, indicating that the metal center in the ruthenaindenes is quite intimately embedded into the organic aromatic framework.



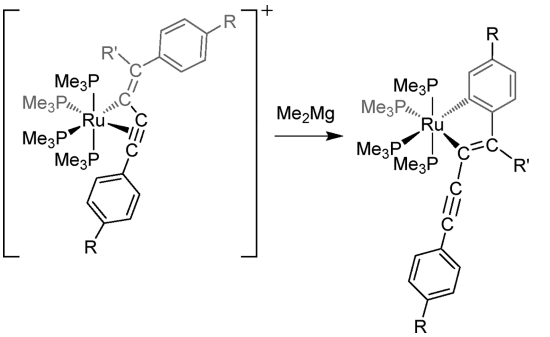
INTRODUCTION

The indene ring system has a benzene ring fused to a cyclopentene ring. Ruthenaindenes are cyclometalated ruthenium complexes where the ruthenium metal replaces one of the carbon atoms in the five-membered ring of an indene molecule. Ruthenaindenes are a subset of ruthenacyclopentadienes that have very few occurrences in the literature.[1] Despite the relative rarity of ruthenaindene-type complexes, there are examples of metalloindenes among the early transition metals such as titanium,[2] vanadium,[3] zirconium,[4] and tantalum,[5] as well as late transition metals including rhodium,[6] osmium,[7] and iridium.[8]

Our interest in ruthenaindenes stems from an earlier discovery where the treatment of ruthenium butenynyl complexes $[Ru(\eta^3\text{-}RC_6H_4C{\equiv}CC{=}CR'(C_6H_4R))(PMe_3)_4]^+$ (R = ^{t}Bu, H, Me; R′ = H, Me) with dimethylmagnesium afforded ruthenaindenes $[Ru(RC_6H_4C{\equiv}CC{=}CR'(C_6H_3R)(PMe_3)_4]$ (Scheme 1).[9] The reaction involves decoordination of the alkyne fragment, isomerization of the metal-substituted alkene, and then ortho metalation of the aromatic ring attached to the vinylic group with concomitant loss of the ortho proton.

The ruthenaindenes are remarkably stable and, as the Ru metal is σ-bonded directly to the rigid aromatic framework, better overlap of the metal orbitals with the organic framework would suggest better electronic communication across the extended metalloaromatic network. In this paper, we probe the effect of changing the electronic properties of the organic framework on the properties of the metal center through the synthesis of a series of ruthenaindenes with remote electron-donating and electron-withdrawing substituents attached to the aryl rings.

Scheme 1. Synthesis of Ruthenaindenes



RESULTS AND DISCUSSION

Synthesis of Ruthenium Butenynyl Complexes. The most direct route to metal butenynyl complexes is by reaction of a metal hydride with a 1,4-diaryl- or 1,4-dialkyl-1,3-butadiyne.[10] For example, the iron butenynyl complex $[Fe(\eta^3\text{-}PhC{\equiv}CC{=}CHPh)(dmpe)_2]^+$ has been synthesized

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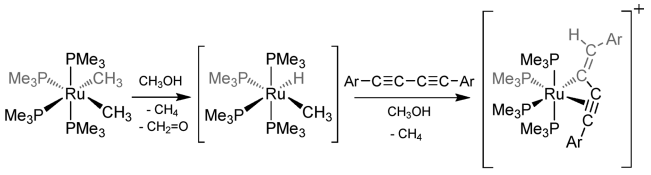
by treatment of $[FeH_2(dmpe)_2]$ with 1,4-diphenyl-1,3-butadiyne in an alcohol solution.[11]

While treatment of $[RuH_2(PMe_3)_4]$ with 1,4-bis(4-methoxyphenyl)-1,3-butadiyne does form the desired butenynyl complex **1a**, the reaction does not go to completion and hydrogenated butadiyne products were also formed in the reaction, including 4-$MeOC_6H_4CH{=}CHCH_2CH_2C_6H_4$-4-OMe.[12]

The formation of hydrogenated butadiyne products was minimized by using the dimethyl complex $[RuMe_2(PMe_3)_4]$ as the metal precursor. Treatment of $[RuMe_2(PMe_3)_4]$ with diarylbutadiynes and sodium tetraphenylborate in methanol solution afforded the butenynyl complexes **1a–c** as tetraphenylborate salts (Scheme 2). A small amount of $[RuH(PMe_3)_5]^+$ was also isolated as a byproduct.[13] While we have not investigated the mechanism of this reaction in detail, the methanol solvent plays an important role and the reaction probably proceeds by protodemethylation of the dimethyl ruthenium complex to form a methoxy methyl complex where β-hydride elimination produces "slow release" of a metal hydride in situ.[14] Reaction of the butadiyne with the metal hydride followed by a further protodemethylation reaction would give the desired butenynyl complex.

Scheme 2. Synthesis of Ruthenium Butenynes



1a: Ar = C_6H_4-4-OMe
1b: Ar = Ph
1c: Ar = C_6H_4-4-CF_3

The butenynyl complexes **1a–c** can also be synthesized as tetrafluoroborate salts by protonation of the bis(acetylide) complexes *cis*-$[Ru(C{\equiv}CAr)_2(PMe_3)_4]$ with a mild acid such as 2,6-lutidinium tetrafluoroborate (vide infra).

$^{31}P\{^1H\}$ NMR spectra of each of the butenynyl complexes **1a–c** exhibit three sharp signals: two sets of doublets of triplets integrating to 1P each, corresponding to the two inequivalent equatorial phosphines, and a triplet integrating to 2P for the two equivalent axial phosphines, similar to spectra reported for analogous complexes in the literature.[15] In addition, a phosphorus-coupled doublet is observed for the vinylic proton in the region 7.0–7.6 ppm in the ^1H NMR spectra, as previously reported for analogous butenynyl complexes.[16] ^{13}C NMR resonances of the alkene carbons Ru*C*=C and C=*C*H were assigned with the aid of 2D NMR experiments in the ranges 144–155 and 128–131 ppm, respectively. ^{13}C NMR resonances for alkyne carbons Ar*C*≡C and ArC≡*C* were found in the ranges 113–118 and 57–66 ppm, respectively.[17]

Crystals of the butenynyl complex **1c**, suitable for X-ray crystallography, were grown from an acetone solution layered with pentane, and the structure is shown in Figure 1. Ru–C and C–C bond lengths as well as the C–C–C bond angle follow trends similar to the analogous bond lengths and angles for related Ru–butenyne complexes that have previously been characterized crystallographically: $[Ru(\eta^3\text{-}PhC{\equiv}CC{=}CHPh)(PMe_2Ph)_4]^+$, $[Ru(\eta^3\text{-Me-4-}C_6H_4C{\equiv}CC{=}CH(C_6H_4\text{-4-Me}))(P(OEt)_2Ph)_4]^+$, and $[Ru(\eta^3\text{-}PhC{\equiv}CC{=}CHPh)(dppm)_2]^+$.[18]

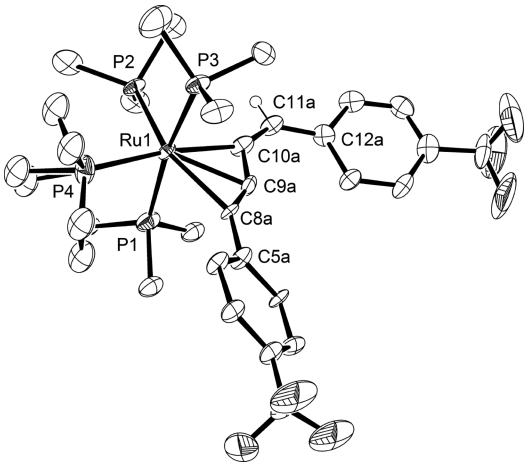
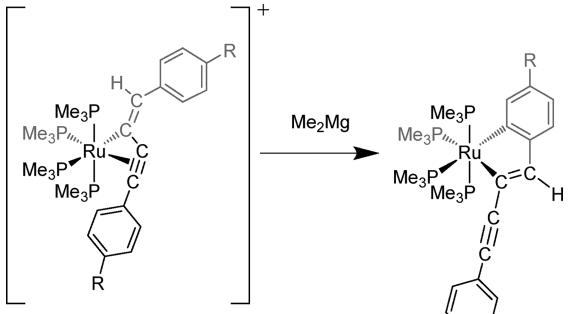


Figure 1. ORTEP plot of $[Ru(\eta^3\text{-}CF_3\text{-}4\text{-}C_6H_4C{\equiv}CC{=}CH(C_6H_4\text{-}4\text{-}CF_3))(PMe_3)_4]^+BF_4^-$ (**1c**) at 50% ellipsoid probability. Hydrogen atoms and the BF_4^- counterion have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru1–P1 2.390(4), Ru1–P2 2.302(4), Ru1–P3 2.392(4), Ru1–P4 2.384(4), Ru1–C8a 2.350(12), Ru1–C9a 2.215(14), Ru1–C10a 2.155(16), C8a–C9a 1.24(2), C9a–C10a 1.44(2), C10a–C11a 1.32(2), C9a–Ru1–C8a 31.2(5), C10a–Ru1–C8a 69.6(5), C10a–Ru1–C9a 38.3(5), C9a–C8a–C5a 142.6(13), C8a–C9a–C10a 149.0(15), C11a–C10a–C9a 135.6(15), C10a–C11a–C2a 127.7(14).

Synthesis of Ruthenaindenes. Treatment of butenynyl complexes containing BPh_4^- counterions **1a–c** (BPh_4) with halide-free dimethylmagnesium afforded the expected ruthenaindene complexes **2a–c** (Scheme 3) in moderate yields. The quality of the dimethylmagnesium reagent was crucial in this reaction, as the presence of halide impurities always afforded unwanted halide-containing byproducts. Use of other bases such as sodium amide and methyllithium did not give the desired ruthenaindenes.

Scheme 3. Synthesis of Functionalized Ruthenaindenes



1a: R = OMe
1b: R = H
1c: R = CF_3

2a: R = OMe
2b: R = H
2c: R = CF_3

The $^{31}P\{^1H\}$ NMR spectra of the ruthenaindene complexes **2a–c** exhibit a triplet integrating to 2P and two sets of doublets of triplets integrating to 1P, each being similar to those for previously reported ruthenaindene complexes.[9] The C=C*H* proton in the five-membered ring was observed as a phosphorus-coupled multiplet in the 7.5–8.3 ppm region of the ^1H NMR spectrum. The alkene and alkyne carbons appear in the 151–162 and 92–112 ppm regions of the ^{13}C NMR

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spectra, respectively. The aromatic carbon directly bonded to ruthenium appears near 184 ppm for both **2a** and **2c**, similarly to those previously reported (181−182 ppm).[9]

An X-ray crystal structure of **2a** is shown in Figure 2 and has structural parameters similar to those of the previously reported ruthenaindenes [Ru(ᵗBu-4-C_6H_4C≡CC═CH-(C_6H_3-4-ᵗBu)(PMe_3)$_4$] and [Ru(PhC≡CC═CH(C_6H_4)-(PMe_3)$_4$].[9]

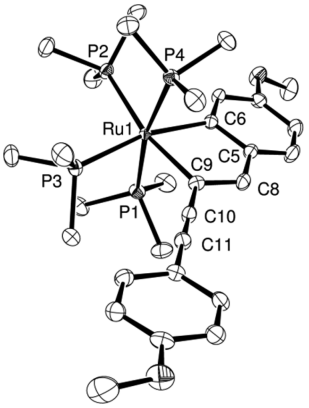


Figure 2. ORTEP plot of [Ru(MeO-4-C_6H_4C≡CC═CH(C_6H_3-4-OMe)(PMe_3)$_4$] (**2a**) at 50% ellipsoid probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru1−C6 2.135(2), Ru1−C9 2.156(3), Ru1−P4 2.3409(7), Ru1−P1 2.3531(7), Ru1−P2 2.3573(7), Ru1−P3 2.3631(7), C5−C6 1.430(3), C5−C8 1.440(4), C8−C9 1.361(4), C9−C10 1.423(4), C10−C11 1.211(4), C6−Ru1−C9 78.24(10), C6−C5−C8 115.6(2), C5−C6−Ru1 113.47(17), C9−C8−C5 118.3(2), C8−C9−C10 116.9(2), C8−C9−Ru1 114.04(19), C10−C9−Ru1 128.84(19), C9−C10−C11 177.5(3).

Synthesis of Ruthenium Butenynyl and Vinylidene Complexes from Ruthenium Bis(acetylides). We have previously reported the formation of iron and ruthenium butenynyl complexes by the coupling of the acetylide ligands in metal bis(acetylides) in the presence of an acid.[11,15] Mechanistically, it has been proposed that one of the metal-bound acetylides protonates at the β-carbon to produce a metal vinylidene and the butenyne ligand is formed by migration of the second acetylide to the α-carbon with π-coordination of the pendant C≡C.

Ru bis(arylacetylido) complexes **3a−c** were synthesized by the σ-bond metathesis reaction of [$RuMe_2(PMe_3)_4$] with a series of arylacetylenes (Scheme 4). In general, the bis-(acetylide) complexes were isolated as mixtures of cis and trans isomers, with the relative amounts of isomers varying from batch to batch. The $^{31}P\{^1H\}$ NMR spectra of the product mixture exhibited pairs of triplets for the cis isomers and singlets for the trans isomers, as previously reported for analogous complexes.[19] Using this synthetic approach, the cis isomers were generally the major isomer formed in the mixture.

Crystals of ***cis*-3c**, suitable for X-ray crystallography, were grown from a cooled solution of the complex in toluene (Figure 3). There was some orientational disorder about one

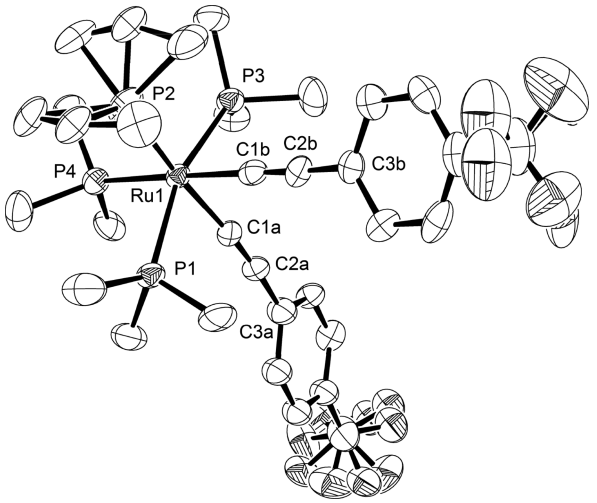


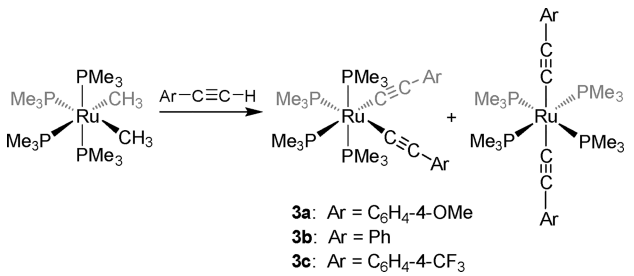
Figure 3. ORTEP plot of *cis*-[Ru(C≡CC_6H_4-4-CF_3)$_2$(PMe_3)$_4$] (**3c**) at 50% ellipsoid probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru1−P1 2.3555(18), Ru1−P2 2.3654(19), Ru1−P3 2.3511(19), Ru1−P4 2.3669(17), Ru1−C1a 2.048(6), Ru1−C1b 2.024(6), C1a−C2a 1.201(8), C1b−C2b 1.231(8), C2a-C3a 1.424(9), C2b−C3b 1.435(8), C1b−Ru1−C1a 88.6(2), C2a−C1a−Ru1 175.7(6), C1a−C2a−C3a 175.7(7), C2b−C1b−Ru1 176.8(6), C1b−C2b−C3b 175.6(7).

of the PMe_3 groups and both the CF_3 groups; however, the Ru−C and C≡C bond lengths for complex **3c** are comparable with those for the analogous cis-disposed Ru bis(acetylide) complexes [Ru(C≡CC_6H_4-4-OMe)$_2$(PMe_3)$_4$] and [Ru(C≡CPh)$_2$(P($CH_2CH_2PPh_2$)$_3$)].[19,20]

The Ru bis(arylacetylido) complexes **3a−c** were generally obtained as a mixtures of cis and trans isomers; however, there is only very slow interconversion of the isomers of **3b** at room temperature.[19] Irradiation of a cis/trans mixture of **3b** with a UV light source converts the mixture exclusively to the trans isomer.[19]

Protonation of the trans isomer of **3b** with lutidinium afforded pink crystals of the *trans*-vinylidene complex [Ru(═C═CH(Ph))(C≡CPh)(PMe_3)$_4$]$^+$ (**4b**) (Scheme 5 and

Scheme 4. Synthesis of Ruthenium Bis(acetylides)



Scheme 5. Protonation of *trans*-Bis(acetylide) Complexes

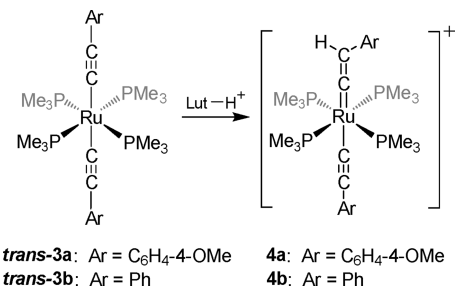


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Figure 4). The crystal structure of **4b** revealed bond lengths and angles similar to those reported for the vinylidene complex

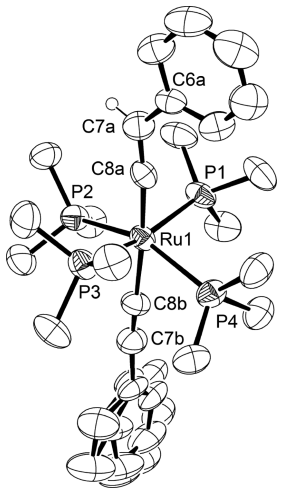


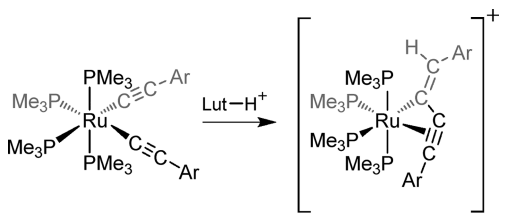
Figure 4. ORTEP plot of *trans*-[Ru(=C=CH(Ph))(C≡CPh)-$(PMe_3)_4]^+BF_4^-$ (**4b**) at 50% ellipsoid probability. Hydrogen atoms, pentane solvate (partially occupied), and the BF_4^- counterion have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru1−P1 2.3754(14), Ru1−P2 2.3655(15), Ru1−P3 2.3721(15), Ru1−P4 2.4055(16), Ru1−C8a 1.873(5), Ru1−C8b 2.083(5), C7a−C8a 1.336(8), C7b−C8b 1.197(8), C6a−C7a 1.480(8), C7a−C8a−Ru1 172.2(5), C7b−C8b−Ru1 178.2(5), C8a−C7a−C6a 127.6(6).

$[Ru(=C=CMe(Ph))(C\equiv CPh)(P(OEt)_3)_4]^+$.[21] The pentet at 5.36 ppm in the ^1H NMR spectrum and the pentet at 355.3 ppm in the ^{13}C NMR spectrum are characteristic for a vinylidene moiety, as reported in the literature for analogous Ru complexes (^1H 3.8−6.0 ppm, ^{13}C 351−380 ppm).[15,21]

Crystals of the vinylidene complex $[Ru(=C=CH(C_6H_4\text{-}4\text{-}OMe))(C\equiv CC_6H_4\text{-}4\text{-}OMe)(PMe_3)_4]^+$ (**4a**) were also isolated by treatment of the bis(acetylide) complex **3a** containing about 30% trans isomer with lutidinium tetrafluoroborate. The X-ray crystal structure including the core bond lengths and bond angles and NMR parameters are available in the Supporting Information.

The *trans*-vinylidene complexes **4a,b** are stable, and the vinylidene and acetylide groups do not rearrange and couple to form the butenynyl complexes even on heating. However, treatment of the bis(acetylide) complexes **3a−c** (as mixtures of cis and trans isomers) with a mild acid (2,6-lutidinium tetrafluoroborate) presumably protonates at the *β*-carbon to form the cationic vinylidene species, but the protonated cis isomers (not observed) rapidly rearrange with C−C coupling to give the butenynyl complexes **1a−c** (Scheme 6). The butenynyl complexes can be isolated from the product mixture by crystallization.

Scheme 6. Protonation and Rearrangement of *cis*-Bis(acetylide) Complexes



1a: Ar = C_6H_4-4-OMe
1b: Ar = Ph
1c: Ar = C_6H_4-4-CF_3

The fact that the *trans*-vinylidenes are stable suggests that it is only the isomers of the ruthenium bisacetylides with the cis stereochemistry which protonate and rearrange to form butenynyl complexes.

Electrochemistry. The cyclic voltammograms (CVs) of the ruthenium butenynyl complexes **1a−c** exhibit a single reversible one-electron process between 0.50 and 0.82 V, indicative of a Ru^{2+}/Ru^{3+} couple (Figure 5 and Table 1). The

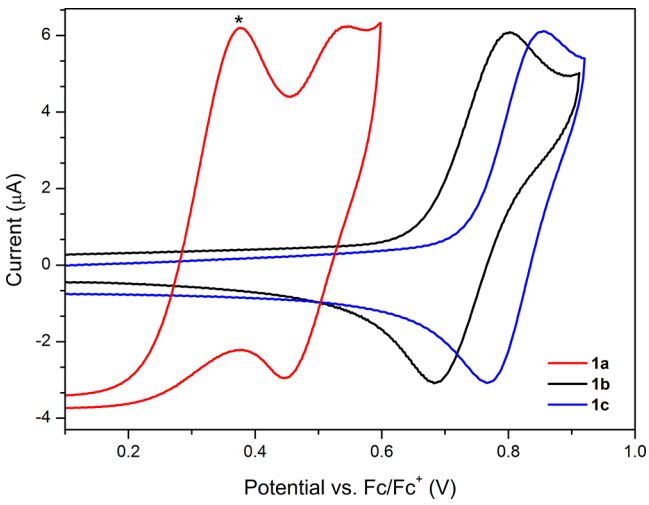


Figure 5. Cyclic voltammogram traces for butenynyl complexes $[Ru(\eta^3\text{-}R\text{-}4\text{-}C_6H_4C\equiv CC{=}CH(C_6H_4\text{-}4\text{-}R))(PMe_3)_4]^+BF_4^-$ (**1a** (R = OMe); **1b** (R = H); **1c** (R = CF_3)) acquired in 0.1 M NBu_4PF_6 in CH_2Cl_2. Scan rate: 100 mV/s. The asterisk denotes oxidation of the BPh_4^- counterion.

Table 1. Electrochemical Data for Butenynyl and Ruthenaindene Complexes

complex	−R	$E_{1/2}$/V[a]
1a	−OMe	0.50
1b	−H	0.74
1c	$-CF_3$	0.82
2a	−OMe	−0.40
2b	−H	−0.30
2c	$-CF_3$	−0.06

[a] $E_{1/2}$ potential referenced to Fc/Fc^+. Conditions for CV: in CH_2Cl_2, 0.1 M NBu_4PF_6, scan rate 100 mV/s, glassy-carbon working electrode, Pt/Ti auxiliary electrode, Ag/Ag^+ quasi-reference electrode.

trace for complex **1a** (which was isolated as its BPh_4^- salt) shows an additional irreversible process at 0.38 V, which we ascribe to oxidation of the tetraphenylborate counterion.[22]

The relatively high oxidation potential of the butenynyl complexes is consistent with the positive charge on these metal complexes and the presence of a weakly bound *π*-acetylene donor in the ligand set.

The oxidation potential for the complex where the aromatic rings bear electron-withdrawing $-CF_3$ substituents (complex **1c**) is higher than those for the other two butenynyl complexes. Conversely, the Ru^{2+} center in complex **1a**, where the aromatic rings have electron-donating − OMe

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substituents, is the most easily oxidized complex of the series of butenynyl complexes.

The CVs of the ruthenaindene complexes **2a**−**c** exhibited a reversible one-electron process ascribed to a Ru^{2+}/Ru^{3+} couple between −0.40 and −0.06 V (Figure 6 and Table 1).

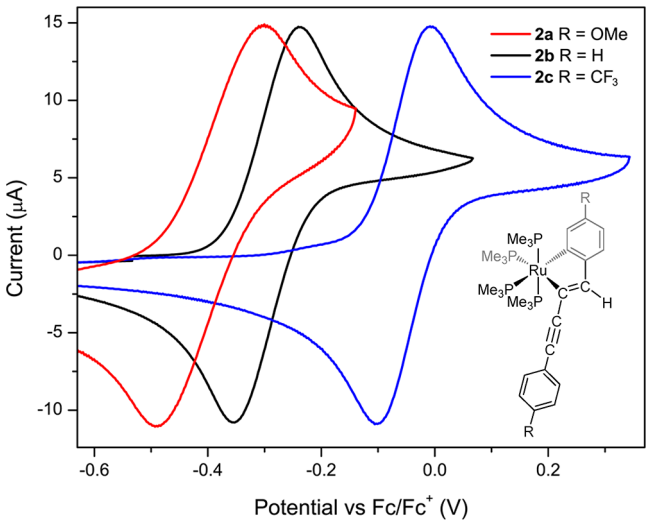

Figure 6. Cyclic voltammogram traces for ruthenaindene complexes [Ru(R-4-C_6H_4C≡CC═CH(C_6H_3-4-R)(PMe_3)$_4$] (**2a** (R = OMe); **2b** (R = H); **2c** (R = CF_3).) acquired in 0.1 M NBu_4PF_6 in CH_2Cl_2. Scan rate: 100 mV/s.

The relatively low oxidation potential of the ruthenaindenes may be rationalized by the ability of strongly electron-donating organic ligands to stabilize the oxidized Ru^{3+} center. The oxidation potential for complex **2c**, where the aromatic rings bear the most electron-withdrawing substituents (−CF_3), is significantly higher than for the other two complexes. This suggests that substituents which make the aromatic ligand a more electron-poor donor pull electron density away from the Ru^{2+} center and make it more difficult to oxidize. Conversely, the Ru^{2+} center in complex **2a**, where the −OMe substituents are electron-donating and make the aromatic ligand a more electron rich donor, is the most easily oxidized of the complexes examined in this study. All three complexes exhibited an irreversible oxidation process at higher potentials (between 0.25 and 0.70 V).

CONCLUSIONS

In this work, we have extended our study of ruthenaindenes that are formed from the reaction of ruthenium butenynyl complexes with dimethylmagnesium. We have developed a new synthetic approach to ruthenium butenynyl complexes by the reaction of dimethylruthenium complexes with butadiynes in a protic solvent. This new route avoids the intermediacy of ruthenium bis(acetylides), which are typically formed as mixtures of cis and trans isomers, where only the cis isomer reacts to form the desired butenynyl complexes. The butadiyne precursors are readily available by the head-to-head Glaser coupling of terminal acetylenes;[23] thus, the new route provides a more general synthesis of ruthenium butenynyl complexes and ruthenaindenes.

Electrochemical analysis of the ruthenaindenes containing different substituents on the benzene ring demonstrated that, even though the substituents are remote from the ruthenium center, they have a significant influence on the oxidation potential of the metal. With an electron-donating substituent (−OMe) on the aromatic ring, the potential of the Ru^{2+}/Ru^{3+} couple (−0.40 V) is substantially lower than that for the complex with an electron-withdrawing (−CF_3) substituent (−0.06 V). Even though the substitution of the aromatic ring with electron-donating/-withdrawing groups is distant from the metal center, the electronic properties of the substituents are relayed effectively to the metal center, in line with the notion that metal center in the ruthenaindenes is quite intimately embedded into the organic aromatic framework. Electron-donor substituents that render the aromatic system more electron rich make the Ru center easier to oxidize. Conversely, electron-withdrawing substituents attached to the aromatic ring pull electron density away from the Ru center and make it more difficult to oxidize. There is obvious scope to moderate the electronic characteristics of the metal center over a significant range by tuning the substituents on the aromatic rings.

EXPERIMENTAL SECTION

General Procedures. All syntheses and manipulations involving air-sensitive compounds were carried out using standard Schlenk techniques or in nitrogen- or argon-filled glove boxes. Solvents were dried and distilled under nitrogen from sodium/benzophenone (benzene, toluene, tetrahydrofuran) or boric anhydride (acetone). Diethyl ether and pentane were dried and deoxygenated using a Pure Solv 400-4-MD (Innovative Technology) solvent purification system. Deuterated solvents were dried and distilled under vacuum from sodium/benzophenone (benzene-d_6, tetrahydrofuran-d_8) and boric anhydride (acetone-d_6). NMR spectra were recorded on Bruker Avance 400 and 600 NMR spectrometers at 298 K unless otherwise stated. ^{1}H and ^{13}C NMR spectra were referenced to residual solvent resonances, ^{31}P NMR spectra were referenced to external neat trimethyl phosphite at δ 140.85, and ^{19}F spectra were referenced to external neat hexafluorobenzene at δ −164.9. Mass spectrometric analyses were carried out at the Bioanalytical Mass Spectrometry Facility, UNSW. Microanalyses were carried out at the Campbell Microanalytical Laboratory, University of Otago, Otago, New Zealand. Crystallographic analyses were performed on a Bruker Kappa APEXII area detector diffractometer (Mo Kα radiation, λ = 0.71071 Å, T = 150 K). Crystallographic data are presented in Table S1 in the Supporting Information. Electrochemistry was performed using a Metrohm Autolab potentiostat connected to an electrochemical cell assembled in a nitrogen glovebox; the compound of interest was dissolved in dry and degassed electrolyte solution (0.1 M NBu_4PF_6 in dichloromethane). Cyclic voltammograms (CV) were recorded with a glassy-carbon working electrode, a Pt/Ti-wire auxiliary electrode, and an Ag/Ag^+ quasi-reference electrode at a scan rate of 100 mV s^{-1}. An internal ferrocene/ferrocenium ion (Fc/Fc^+) standard was added to the sample solution at the end of each set of measurements.

cis-[$RuMe_2(PMe_3)_4$],[9] [$Ru(C{\equiv}CPh)_2(PMe_3)_4$],[19] and [Ru($\eta^3$-PhC≡CC═CH(Ph))($PMe_3$)$_4$]$^+BF_4^-$[15] were prepared by literature methods. 1-Ethynyl-4-methoxybenzene was purchased commercially and used without further purification or prepared via a $Pd(PPh_3)_4$-catalyzed cross-coupling reaction of 4-bromoanisole with ethynylmagnesium bromide.[24] 1-Ethynyl-4-(trifluoromethyl)benzene[25] was prepared by the $PdCl_2(PPh_3)_2$-catalyzed Sonogashira coupling of 4-bromobenzotrifluoride with trimethylsilylacetylene and subsequent deprotection with K_2CO_3. 2,6-Lutidinium tetrafluoroborate,[26] 1,4-diaryl-1,3-butadiynes,[23] and halide-free dimethylmagnesium[27] were prepared according to literature procedures.

[Ru(η^3-MeO-4-C_6H_4C≡CC═CH(C_6H_4-4-OMe))(PMe_3)$_4$]$^+$X$^-$ (1a). *X* = BPh_4^-. [$RuMe_2(PMe_3)_4$] (0.341 g, 0.783 mmol) and 1,4-bis(4-methoxyphenyl)-1,3-butadiyne (0.205 g, 0.783 mmol) were stirred in methanol (5 mL) at room temperature overnight, and the

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resulting yellow suspension was filtered. A solution of $NaBPh_4$ (0.268 g, 0.783 mmol) in methanol (6 mL) was filtered and then added to the above filtrate to afford $[Ru(\eta^3\text{-MeO-4-}C_6H_4C{\equiv}CC{=}CH(C_6H_4\text{-4-OMe}))(PMe_3)_4]^+BPh_4^-$ (**1a BPh$_4^-$**) as a bright yellow precipitate which was collected by filtration, washed with methanol (3 mL), and then dried in vacuo (0.676 g, 0.684 mmol, 87% yield). $^{31}P\{^1H\}$ NMR (162 MHz, acetone-d_6): δ 1.55 (dt, $^2J_{PP}$ = 33 Hz, $^2J_{PP}$ = 20 Hz, 1P, P_{eq}), −8.1 (dd, $^2J_{PP}$ = 33 Hz, $^2J_{PP}$ = 30 Hz, 2P, P_{ax}), −15.4 (dt, $^2J_{PP}$ = 30 Hz, $^2J_{PP}$ = 20 Hz, 1P, P_{eq}). ^1H NMR (400 MHz, acetone-d_6): δ 7.77 (*AA′*XX′, 2H, *o*-Ar*H*(alkene)), 7.72 (*AA′*XX′, 2H, *o*-Ar*H*(alkyne)), 7.34 (m, 8H, *o*-*H*(BPh_4)), 7.08 (AA′*XX*′, 2H, *m*-Ar*H*(alkyne)), 7.03 (m, 1H, C=C*H*), 7.01 (AA′*XX*′, 2H, *m*-Ar*H*(alkene)), 6.92 (m, 8H, *m*-*H*(BPh_4)), 6.77 (m, 4H, *p*-*H*(BPh_4)), 3.87 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 1.84 (d, $^2J_{HP}$ = 8 Hz, 9H, PCH_3), 1.80 (d, $^2J_{HP}$ = 7 Hz, 9H, PCH_3), 1.19 (apparent triplet, splitting = 3 Hz), 18H, PCH_3). The product contains approximately 4% $[RuH(PMe_3)_5]^+$ [13] and was used without further purification.

X = BF_4^-. *cis-/trans*-$[Ru(C{\equiv}CC_6H_4\text{-4-OMe})_2(PMe_3)_4]$ (**3a**; 0.303 g, 0.454 mmol) and 2,6-lutidinium tetrafluoroborate (0.088 g, 0.454 mmol) were stirred in tetrahydrofuran (6 mL) overnight under an atmosphere of nitrogen. The reaction mixture was evaporated to dryness and the residue washed with pentane (30 mL) and diethyl ether (30 mL). The crude material was recrystallized from acetone (5 mL) and pentane (5 mL) to afford $[Ru(\eta^3\text{-MeO-4-}C_6H_4C{\equiv}CC{=}CH(C_6H_4\text{-4-OMe}))(PMe_3)_4]^+BF_4^-$ (**1a BF$_4^-$**) as a bright yellow crystalline solid (0.200 g, 0.265 mmol, 58%). MS (ESI, acetonitrile): *m*/*z* 669.1883 ($[Ru(MeOC_6H_4C{\equiv}CC{=}CH(C_6H_4OMe))(PMe_3)_4]^+$, calcd for $C_{30}H_{51}O_2P_4Ru$ 669.1886), 593.1446 ($[Ru(MeOC_6H_4C{\equiv}CC{=}CH(C_6H_4OMe))(PMe_3)_3]^+$, calcd for $C_{27}H_{42}O_2P_3Ru$ 593.1441), 517.1003 ($[Ru(MeOC_6H_4C{\equiv}CC{=}CH(C_6H_4OMe))(PMe_3)_2]^+$, calcd for $C_{24}H_{33}O_2P_2Ru$ 517.0999), 441.0556 ($[Ru(MeOC_6H_4C{\equiv}CC{=}CH(C_6H_4OMe))(PMe_3)]^+$, calcd for $C_{21}H_{24}O_2PRu$ 441.0557). $^{31}P\{^1H\}$ NMR (243 MHz, acetone-d_6): δ 1.60 (dt, $^2J_{PP}$ = 33 Hz, $^2J_{PP}$ = 20 Hz, 1P, P_{eq}), −8.0 (apparent triplet, splitting = 32 Hz, 2P, P_{ax}), −15.4 (dt, $^2J_{PP}$ = 30 Hz, $^2J_{PP}$ = 20 Hz, 1P, P_{eq}). ^1H NMR (600 MHz, acetone-d_6): δ 7.77 (*AA′*XX′, 2H, *o*-Ar*H*(alkene)), 7.73 (*AA′*XX′, 2H, *o*-Ar*H*(alkyne)), 7.10 (AA′*XX*′, 2H, *m*-Ar*H*(alkyne)), 7.04 (br d, $^4J_{HP}$ = 4 Hz, 1H, C=C*H*), 7.02 (AA′*XX*′, 2H, *m*-Ar*H*(alkene)), 3.89 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 1.85 (d, $^2J_{HP}$ = 8 Hz, 9H, PCH_3), 1.81 (d, $^2J_{HP}$ = 7 Hz, 9H, PCH_3), 1.20 (apparent triplet, splitting = 3 Hz), 18H, PCH_3). $^{13}C\{^1H\}$ NMR (151 MHz, acetone-d_6): δ 160.9 (*p*-ArC(alkyne)), 159.9 (*p*-ArC(alkene)), 144.9 (m, RuC=C), 134.2 (*o*-ArC(alkyne)), 132.3 (*ipso*-ArC(alkene)), 129.5 (C=CH), 128.0 (*o*-ArC(alkene)), 121.0 (*ipso*-ArC(alkyne)), 115.7 (*m*-ArC(alkyne)), 115.2 (*m*-ArC(alkene)), 113.7 (m, ArC≡C), 57.5 (ArC≡*C*), 55.9 (OCH$_3$), 55.7 (OCH$_3$), 25.1 (d, $^1J_{CP}$ = 26 Hz, PCH$_3$), 24.0 (m, PCH$_3$), 18.4 (apparent triplet, splitting = 14 Hz, PCH$_3$). ^{19}F NMR (565 MHz, acetone-d_6): δ −149.0 (s, BF_4).

$[Ru(\eta^3\text{-PhC}{\equiv}CC{=}CH(Ph))(PMe_3)_4]^+BPh_4^-$ (1b BPh$_4$). $[RuMe_2(PMe_3)_4]$ (0.417 g, 0.958 mmol) and 1,4-diphenyl-1,3-butadiyne (0.203 g, 1.00 mmol) were stirred in methanol (6 mL) at room temperature overnight to afford a dark brown solution. A solution of $NaBPh_4$ (0.338 g, 0.988 mmol) in methanol (5 mL) was filtered and then added to the reaction mixture to afford $[Ru(\eta^3\text{-PhC}{\equiv}CC{=}CH(Ph))(PMe_3)_4]^+BPh_4^-$ (**1b BPh$_4$**) as a bright yellow precipitate, which was collected by filtration, washed with methanol (3 mL), and then dried in vacuo (0.699 g, 0.753 mmol, 79% yield). $^{31}P\{^1H\}$ NMR (243 MHz, acetone-d_6): δ 1.40 (dt, $^2J_{PP}$ = 33 Hz, $^2J_{PP}$ = 21 Hz, 1P, P_{eq}), −8.3 (apparent triplet, splitting = 32 Hz, 2P, P_{ax}), −15.8 (dt, $^2J_{PP}$ = 30 Hz, $^2J_{PP}$ = 21 Hz, 1P, P_{eq}). ^1H NMR (600 MHz, acetone-d_6): δ 7.84 (m, 2H, *o*-ArH), 7.80 (m, 2H, *o*-ArH), 7.54 (m, 2H, *m*-ArH), 7.48−7.42 (m, 3H, *p*- and *m*-ArH), 7.34 (m, 8H, *o*-H(BPh_4)), 7.28 (m, 1H, *p*-ArH), 7.16 (br d, $^4J_{HP}$ = 4 Hz, 1H, C=CH), 6.92 (m, 8H, *m*-H(BPh_4)), 6.78 (m, 4H, *p*-H(BPh_4)), 1.86 (d, $^2J_{HP}$ = 8 Hz, 9H, PCH$_3$), 1.81 (d, $^2J_{HP}$ = 7 Hz, 9H, PCH$_3$), 1.21 (apparent triplet, splitting = 3 Hz), 18H, PCH$_3$).

The product contained approximately 12% $[RuH(PMe_3)_5]^+$ [13] and was used without further purification for the synthesis of the ruthenaindene $[Ru(PhC{\equiv}C{-}C{=}CH(C_6H_4)(PMe_3)_4]$ (**2b**).

NMR data for $[RuH(PMe_3)_5]^+$ are as follows. $^{31}P\{^1H\}$ NMR (243 MHz, acetone-d_6): δ −9.1 (d, $^2J_{PP}$ = 25 Hz, 4P, P_{eq}), −22.2 (p, $^2J_{PP}$ = 27 Hz, 1P, P_{ax}). ^1H NMR (600 MHz, acetone-d_6): δ 1.62 (m, 36H, PCH_3), 1.47 (d, $^2J_{HP}$ = 6 Hz, 9H, PCH_3), −11.31 (dp, $^2J_{HP}$ = 74 Hz, $^2J_{HP}$ = 25 Hz, Ru*H*). NMR data match those reported previously.[13]

$[Ru(\eta^3\text{-}CF_3\text{-4-}C_6H_4C{\equiv}CC{=}CH(C_6H_4\text{-4-}CF_3))(PMe_3)_4]^+X^-$ (1c). *X* = BPh_4^-. $[RuMe_2(PMe_3)_4]$ (0.320 g, 0.735 mmol) and 1,4-bis(4-(trifluoromethyl)phenyl)-1,3-butadiyne (0.256 g, 0.757 mmol) were stirred in methanol (8 mL) at room temperature overnight to afford a dark red solution. A solution of $NaBPh_4$ (0.264 g, 0.771 mmol) in methanol (8 mL) was filtered and then added to the reaction mixture to afford $[Ru(\eta^3\text{-}CF_3\text{-4-}C_6H_4C{\equiv}CC{=}CH(C_6H_4\text{-4-}CF_3))(PMe_3)_4]^+BPh_4^-$ (**1c BPh$_4^-$**) as an orange precipitate, which was collected by filtration, washed with methanol (3, 10, and 5 mL), and then dried in vacuo (0.409 g, 0.384 mmol, 52% yield). $^{31}P\{^1H\}$ NMR (162 MHz, acetone-d_6): δ 0.8 (dt, $^2J_{PP}$ = 22 Hz, $^2J_{PP}$ = 33 Hz, 1P, P_{eq}), −8.8 (apparent triplet, splitting = 32 Hz, 2P, P_{ax}), −16.5 (dt, $^2J_{PP}$ = 22 Hz, $^2J_{PP}$ = 31 Hz, 1P, P_{eq}). ^1H NMR (400 MHz, acetone-d_6): δ 8.07 (AA′XX′, 2H, *o*-Ar*H*(alkene)), 8.05 (AA′XX′, 2H, *o*-Ar*H*(alkyne)), 7.86 (AA′XX′, 2H, *m*-Ar*H*(alkyne)), 7.78 (AA′XX′, 2H, *m*-Ar*H*(alkene)), 7.34 (m, 9H, C=C*H* and *o*-*H*(BPh_4)), 6.92 (m, 8H, *m*-*H*(BPh_4)), 6.78 (m, 4H *p*-*H*(BPh_4)), 1.88 (d, $^2J_{HP}$ = 9 Hz, 9H, PCH_3), 1.85 (d, $^2J_{HP}$ = 7 Hz, 9H, PCH_3), 1.21 (apparent triplet, splitting = 3 Hz, 18H, PCH_3). ^{19}F NMR (565 MHz, acetone-d_6): δ −60.2 (CF_3), −60.7 (CF_3). The product contained approximately 15% $[RuH(PMe_3)_5]^+$ [13] and was used without further purification for the synthesis of the ruthenaindene $[Ru(CF_3\text{-4-}C_6H_4C{\equiv}CC{=}CH\text{-}(C_6H_3\text{-4-}CF_3)(PMe_3)_4]$ (**2c**).

X = BF_4^-. *cis-/trans*-$[Ru(C{\equiv}CC_6H_4\text{-4-}CF_3)_2(PMe_3)_4]$ (**3c**; 0.327 g, 0.440 mmol) and 2,6-lutidinium tetrafluoroborate (0.105 g, 0.539 mmol) were stirred in tetrahydrofuran (10 mL) overnight under an atmosphere of nitrogen. The reaction mixture was diluted with pentane (10 mL) and filtered, and the solid was washed with pentane (10 mL) and then dried in vacuo. Recrystallization from acetone (5 mL)/pentane (10 mL) afforded $[Ru(\eta^3\text{-}CF_3\text{-4-}C_6H_4C{\equiv}CC{=}CH\text{-}(C_6H_4\text{-4-}CF_3))(PMe_3)_4]^+BF_4^-$ (**1c**) as a bright yellow-orange solid (0.240 g, 0.289 mmol, 66%). Anal. Calcd for $C_{30}H_{45}BF_{10}P_4Ru$ (831.45): C, 43.34; H, 5.46. Found: C, 43.23; H, 5.45. $^{31}P\{^1H\}$ NMR (162 MHz, acetone-d_6): δ 0.9 (dt, $^2J_{PP}$ = 22 Hz, $^2J_{PP}$ = 33 Hz, 1P, P_{eq}), −8.7 (apparent triplet, splitting = 32 Hz, 2P, P_{ax}), −16.4 (dt, $^2J_{PP}$ = 22 Hz, $^2J_{PP}$ = 31 Hz, 1P, P_{eq}). ^1H NMR (400 MHz, acetone-d_6): δ 8.09 (AA′XX′, 2H, *o*-Ar*H*(alkene)), 8.07 (AA′XX′, 2H, *o*-Ar*H*(alkyne)), 7.87 (AA′XX′, 2H, *m*-Ar*H*(alkyne)), 7.79 (AA′XX′, 2H, *m*-Ar*H*(alkene)), 7.38 (br d, $^4J_{HP}$ = 4 Hz, 1H, C=C*H*), 1.91 (d, $^2J_{HP}$ = 9 Hz, 9H, PCH_3), 1.88 (d, $^2J_{HP}$ = 7 Hz, 9H, PCH_3), 1.23 (apparent triplet, splitting = 3 Hz, 18H, PCH_3). $^{13}C\{^1H\}$ NMR (101 MHz, acetone-d_6): δ 153.2 (RuC=C), 142.1 (*ipso*-ArC(alkene)), 133.9 (*ipso*-ArC(alkyne)), 133.2 (*o*-ArC(alkyne)), 130.1 (q, $^2J_{CF}$ = 32 Hz, *p*-ArC), 129.9 (C=CH), 128.7 (q, $^2J_{CF}$ = 32 Hz, *p*-ArC), 127.4 (*o*-ArC(alkene)), 127.0 (q, $^3J_{CF}$ = 4 Hz, *m*-ArC(alkene)), 126.8 (q, $^3J_{CF}$ = 4 Hz, *m*-ArC(alkyne)), 125.6 (q, $^1J_{CF}$ = 271 Hz, CF_3), 125.2 (q, $^1J_{CF}$ = 271 Hz, CF_3), 116.9 (ArC≡C), 63.1 (ArC≡C), 25.0 (d, $^1J_{CP}$ = 27 Hz, PCH$_3$), 23.7 (d, $^1J_{CP}$ = 30 Hz, PCH$_3$), 18.3 (apparent triplet, splitting = 14 Hz, PCH$_3$). ^{19}F NMR (375 MHz, acetone-d_6): δ −60.3 (CF_3), −60.7 (CF_3), −148.9 (BF_4). Crystals of **1c BF$_4^-$** suitable for X-ray crystallography were grown from an acetone-d_6 solution layered with pentane.

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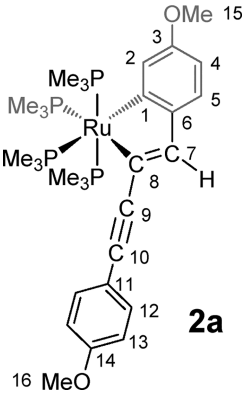
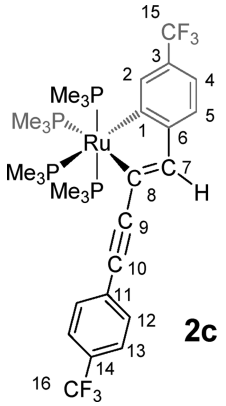
[Ru(MeO-4-$C_6H_4C{\equiv}CC{=}CH(C_6H_3$-4-OMe))$(PMe_3)_4$] (2a).



A solution of dimethylmagnesium (58 mg, 1.1 mmol) and [Ru(η^3-MeO-4-$C_6H_4C{\equiv}CC{=}CH(C_6H_4$-4-OMe))$(PMe_3)_4$]$^+$ BPh_4^- (**1a**; 0.102 g, 0.103 mmol) in tetrahydrofuran (5 mL) was stirred under an atmosphere of nitrogen overnight, in which time the solution changed from orange to yellow. The solvent was removed under reduced pressure, and the residue was extracted with benzene (3 × 3 mL). The benzene extract was filtered through diatomaceous earth and the filtrate evaporated to dryness under reduced pressure to afford a yellow gum, which was washed with pentane (3 × 3 mL) to afford a yellow solid. The yellow solid was dissolved in tetrahydrofuran (3 mL), treated with methanol (0.6 mL) to decompose excess Me_2Mg, and then evaporated to dryness. The residue was extracted with benzene (3 × 3 mL) and filtered through diatomaceous earth and the filtrate evaporated to dryness under reduced pressure to afford [Ru(MeO-4-$C_6H_4C{\equiv}CC{=}CH(C_6H_3$-4-OMe))$(PMe_3)_4$] (**2a**) as a yellow solid (38 mg, 55% yield). MS (ESI, acetonitrile): *m/z* 1359.3532 ([2 M + Na]$^+$, calcd for $C_{60}H_{100}NaO_4P_8Ru$ 1359.3507), 691.1702 ([M + Na]$^+$, calcd for $C_{30}H_{50}NaO_2P_4Ru$ 691.1705), 517.0997 ([Ru(MeO$C_6H_4C{\equiv}CC{=}CH(C_6H_3$OMe)$(PMe_3)_2$ + H]$^+$, calcd for $C_{24}H_{33}O_2P_2Ru$ 517.0999). $^{31}P\{^1H\}$ NMR (162 MHz, tetrahydrofuran-d_8): δ −7.6 (t, $^2J_{PP}$ = 28 Hz, 2P, P_{ax}), −13.0 (dt, $^2J_{PP}$ = 28 Hz, $^2J_{PP}$ = 15 Hz, 1P, P_{eq}), −17.0 (dt, $^2J_{PP}$ = 28 Hz, $^2J_{PP}$ = 15 Hz, 1P, P_{eq}). ^1H NMR (400 MHz, tetrahydrofuran-d_8): δ 7.38 (dt, $^4J_{HP}$ = 7 Hz, $^4J_{HP}$ = 3 Hz, 1H, *H7*), 7.23 (*AA′XX′*, 2H, *H12*), 7.16 (m, 1H, *H2*), 6.83 (dd, $^3J_{HH}$ = 8 Hz, $^5J_{HP}$ = 1.5 Hz, 1H, *H5*), 6.80 (*AA′XX′*, 2H, *H13*), 6.27 (dd, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz, 1H, *H4*), 3.74 (s, 3H, *H16*), 3.67 (s, 3H, *H15*), 1.58 (d, $^2J_{HP}$ = 5 Hz, 9H, PCH_3), 1.55 (d, $^2J_{HP}$ = 5 Hz, 9H, PCH_3), 1.04 (apparent triplet, splitting = 3 Hz, 18H, PCH_3). $^{13}C\{^1H\}$ NMR (101 MHz, tetrahydrofuran-d_8): δ 184.3 (*C1*), 158.7 (*C14*), 155.5 (*C3*), 154.6 (*C7*), 154.2 (*C6*), 152.4 (*C8*), 131.7 (*C12*), 127.9 (*C2*), 122.0 (*C5*), 120.8 (*C11*), 114.3 (*C13*), 107.0 (*C9*), 105.6 (*C4*), 92.8 (*C10*), 55.2 (*C16*), 54.7 (*C15*), 26.1 (PCH$_3$), 25.9 (PCH$_3$), 21.4 (PCH$_3$). Crystals of **2a** suitable for X-ray crystallography were grown from a pentane solution cooled to −20 °C.

[Ru(PhC≡CC═CH(C_6H_4))$(PMe_3)_4$] (2b). [Ru(η^3-PhC≡CC═CH(Ph))$(PMe_3)_4$]$^+$$BPh_4^-$ (**1b**; 0.142 g, 0.153 mmol) and Me_2Mg (0.042 g, 0.77 mmol) were stirred in tetrahydrofuran (5 mL) under an atmosphere of nitrogen overnight. The yellow-orange suspension was treated with methanol (0.2 mL) to decompose excess Me_2Mg and then evaporated to dryness under reduced pressure. The residue was extracted with benzene (3 × 3 mL) and filtered through diatomaceous earth, and the filtrate was evaporated to dryness under reduced pressure. The residue was washed with pentane (1 and 3 mL) to afford [Ru(PhC≡CC═CH(C_6H_4))$(PMe_3)_4$] (**2b**) as a yellow solid (0.044 g, 47% yield). NMR data matched those reported previously.[9]

[Ru(CF_3-4-$C_6H_4C{\equiv}CC{=}CH(C_6H_3$-4-$CF_3$))$(PMe_3)_4$] (2c).



A solution of dimethylmagnesium (24 mg, 0.44 mmol) and [Ru(η^3-CF_3-4-$C_6H_4C{\equiv}CC{=}C(H)(C_6H_4$-4-$CF_3$))$(PMe_3)_4$]$^+$$BPh_4^-$ (**1c**; 0.159 g, 0.149 mmol) in tetrahydrofuran (5 mL) was stirred under an atmosphere of nitrogen overnight. The dark red suspension was treated with methanol (approximately 150 μL) to decompose excess Me_2Mg. The solvent was removed under reduced pressure and the residue extracted with benzene (3 × 3 mL, 1 mL) and then filtered through diatomaceous earth. The orange filtrate was evaporated to dryness under reduced pressure to afford [Ru(CF_3-4-$C_6H_4C{\equiv}CC{=}CH(C_6H_3$-4-$CF_3$))$(PMe_3)_4$] (**2c**) as an orange solid (23 mg, 21% yield). Anal. Calcd for $C_{30}H_{44}F_6P_4Ru$ (743.64): C, 48.46; H, 5.96. Found: C, 48.46; H, 5.96. MS (ESI, acetonitrile): *m/z* 744.1336 (M$^+$, calcd for $C_{30}H_{44}F_6P_4Ru$ 744.1344), 709.1158 ([M − PMe_3 + CH_3CN]$^+$, calcd for $C_{29}H_{38}F_6NP_3Ru$ 709.1165), 668.0896 ([M − PMe_3]$^+$, calcd for $C_{27}H_{35}F_6P_3Ru$ 668.0899). $^{31}P\{^1H\}$ NMR (243 MHz, tetrahydrofuran-d_8): δ −8.4 (t, $^2J_{PP}$ = 30 Hz, 2P, P_{ax}), −13.4 (dt, $^2J_{PP}$ = 29 Hz, $^2J_{PP}$ = 16 Hz, 1P, P_{eq}), −17.7 (dt, $^2J_{PP}$ = 29 Hz, $^2J_{PP}$ = 16 Hz, 1P, P_{eq}). ^1H NMR (600 MHz, tetrahydrofuran-d_8): δ 7.83 (br d, $^4J_{HP}$ = 4 Hz, 1H, *H2*), 7.58 (m, 3H, *H7* and *H13*), 7.48 (m, 1H, *H12*), 7.02 (m, 1H, *H5*), 6.99 (m, 1H, *H4*), 1.60 (d, $^2J_{HP}$ = 6 Hz, 9H, PCH_3), 1.57 (d, $^2J_{HP}$ = 5 Hz, 9H, PCH_3), 1.02 (apparent triplet, splitting = 3 Hz, 18H, PCH_3). $^{13}C\{^1H\}$ NMR (151 MHz, tetrahydrofuran-d_8): δ 184.0 (*C1*), 164.1 (*C6*), 162.8 (*C8*), 155.8 (*C7*), 137.5 (*C2*), 131.9 (*C11*), 131.0 (*C12*), 127.9 (q, $^2J_{CF}$ = 32 Hz, *C14*), 127.0 (q, $^1J_{CF}$ = 271 Hz, *C15*), 125.8 (q, $^3J_{CF}$ = 4 Hz, *C13*), 125.4 (q, $^1J_{CF}$ = 272 Hz, *C16*), 122.9 (*C3*), 121.2 (*C5*), 118.1 (q, $^3J_{CF}$ = 4 Hz, *C4*), 111.1 (*C9*), 94.9 (*C10*), 25.3 (PCH$_3$), 24.9 (PCH$_3$), 21.1 (PCH$_3$). ^{19}F NMR (565 MHz, tetrahydrofuran-d_8): −60.0 (CF_3), −61.3 (CF_3).

***cis-/trans*-[Ru(C≡CC_6H_4-4-OMe)$_2$$(PMe_3)_4$] (3a).** *cis*-[Ru$Me_2(PMe_3)_4$] (0.317 g, 0.728 mmol) and 1-ethynyl-4-methoxybenzene (0.205 g, 1.55 mmol) were stirred in tetrahydrofuran (10 mL) overnight under an atmosphere of nitrogen. The reaction was incomplete; therefore, an additional amount of 1-ethynyl-4-methoxybenzene (0.024 g, 0.18 mmol) was added and the mixture was stirred overnight. The solvent was removed under reduced pressure and the residue washed with pentane (2 × 20 mL) and then dried in vacuo to afford *cis-/trans*-[Ru(C≡CC_6H_4-4-OMe)$_2$$(PMe_3)_4$] (**3a**) as an off-white solid (0.355 g, 0.532 mmol, 73%). The product contained 91% cis and 9% trans isomers. MS (ESI, acetonitrile): *m/z* 669.1888 ([M + H]$^+$, calcd for $C_{30}H_{51}O_2P_4Ru$ 669.1886), 593.1446 ([M − PMe_3 + H]$^+$, calcd for $C_{27}H_{42}O_2P_3Ru$ 593.1441), 517.1003 ([M − 2PMe_3 + H]$^+$, calcd for $C_{24}H_{33}O_2P_2Ru$ 517.0999), 441.0557 ([M − 3PMe_3 + H]$^+$, calcd for $C_{21}H_{24}O_2PRu$ 441.0557). $^{31}P\{^1H\}$ NMR (162 MHz, tetrahydrofuran-d_8): δ −4.0 (s, trans isomer), −8.6 (t, $^2J_{PP}$ = 29 Hz, cis isomer), −12.2 (t, $^2J_{PP}$ = 29 Hz, cis isomer). ^1H NMR (400 MHz, tetrahydrofuran-d_8): δ 7.04 (*AA′XX′*, 4H, *o*-ArH), 6.63 (*AA′XX′*, 4H, *m*-ArH), 3.67 (s, 6H, OCH$_3$), 1.59 (apparent triplet, splitting = 3 Hz, 18H, PCH$_3$), 1.43 (m, 18H, PCH$_3$). $^{13}C\{^1H\}$ NMR (101 MHz, tetrahydrofuran-d_8): δ 156.8 (*p*-ArC), 131.4 (*o*-ArC), 125.7 (m, RuC≡C), 125.0 (*ipso*-ArC), 113.8 (*m*-ArC), 107.2 (m, RuC≡C), 55.1 (OCH$_3$), 23.1 (m, PCH$_3$), 21.4 (m, PCH$_3$).

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***cis*-/*trans*-[Ru(C≡CC$_6$H$_4$-4-CF$_3$)$_2$(PMe$_3$)$_4$] (3c).** *cis*-[Ru-Me$_2$(PMe$_3$)$_4$] (0.300 g, 0.689 mmol) and 1-ethynyl-4-(trifluoromethyl)benzene (0.508 g, 2.99 mmol) were stirred in tetrahydrofuran (5 mL) at 40 °C for 2 h under nitrogen. The reaction mixture was evaporated to dryness under reduced pressure and then washed with pentane (10 mL). The residue was extracted with benzene (15 mL) and filtered through a pad of diatomaceous earth, and the filtrate was evaporated to dryness under reduced pressure to afford *cis*-/*trans*-[Ru(C≡CC$_6$H$_4$-4-CF$_3$)$_2$(PMe$_3$)$_4$] (**3c**) as a pale orange solid (0.133 g, 0.179 mmol, 26%). The product contained 96% cis and 4% trans isomers. Anal. Calcd for $C_{30}H_{44}F_6P_4Ru$ (743.64): C, 48.46; H, 5.96. Found: C, 47.93; H, 6.36. $^{31}P\{^1H\}$ NMR (162 MHz, benzene-d_6): δ −5.2 (s, trans isomer), −10.0 (t, $^2J_{PP}$ = 29 Hz, cis isomer), −13.7 (t, $^2J_{PP}$ = 29 Hz, cis isomer). ^1H NMR (400 MHz, benzene-d_6): δ 7.39 (*AA′XX′*, 4H, *m*-Ar*H*), 7.32 (*AA′XX′*, 4H, *o*-Ar*H*), 1.41 (apparent triplet, splitting = 3 Hz, 18H, PCH_3), 1.06 (m, 18H, PCH_3). $^{13}C\{^1H\}$ NMR (101 MHz, benzene-d_6): δ 136.3 (m, Ru*C*), 134.9 (*ipso*-Ar*C*), 130.7 (*o*-Ar*C*), 125.9 (q, $^1J_{CF}$ = 271 Hz, *C*F$_3$), 125.3 (q, $^3J_{CF}$ = 4 Hz, *m*-Ar*C*), 125.0 (q, $^2J_{CF}$ = 32 Hz, *C*CF$_3$), 108.4 (RuC≡*C*), 22.6 (PCH$_3$), 21.1 (P*C*H$_3$). ^{19}F NMR (376 MHz, benzene-d_6): δ −60.0 (s, C*F*$_3$). Crystals of ***cis*-3c** suitable for X-ray crystallography were grown from a toluene solution cooled to −20 °C.

***trans*-[Ru(=C=CH(C$_6$H$_4$-4-OMe))(C≡CC$_6$H$_4$-4-OMe)-(PMe$_3$)$_4$]$^+$BF$_4^-$ (4a).** 2,6-Lutidinium tetrafluoroborate (0.118 g, 0.605 mmol) was added to a solution of *cis*-/*trans*-[Ru(C≡CC$_6$H$_4$-4-OMe)$_2$(PMe$_3$)$_4$] (**3a**; 0.379 g, 0.568 mmol, 30% trans isomer) in tetrahydrofuran (2 mL) overnight under an atmosphere of nitrogen to form a dark orange solution. Pentane (5 mL) was added, and the total volume of the reaction mixture was reduced to 2 mL under reduced pressure. The orange solid that formed was collected by filtration, washed with pentane, and dried in vacuo. Recrystallization from acetone (5 mL) and pentane (10 mL) afforded *trans*-[Ru(=C=CH(C$_6$H$_4$-4-OMe))(C≡CC$_6$H$_4$-4-OMe)(PMe$_3$)$_4$]$^+$BF$_4^-$ (**4a**) as a purple-red crystalline solid (17 mg, 23 μmol, 4% yield). MS (ESI, acetonitrile): *m*/*z* 669.1889 ([Ru(=C=CHC$_6$H$_4$OMe)(C≡CC$_6$H$_4$OMe)(PMe$_3$)$_4$]$^+$, calcd for $C_{30}H_{51}O_2P_4Ru$ 669.1886), 593.1449 ([Ru(=C=CHC$_6$H$_4$OMe)(C≡CC$_6$H$_4$OMe)(PMe$_3$)$_3$]$^+$, calcd for $C_{27}H_{42}O_2P_3Ru$ 593.1441), 517.1007 ([Ru(=C=CHC$_6$H$_4$OMe)(C≡CC$_6$H$_4$OMe)(PMe$_3$)$_2$]$^+$, calcd for $C_{24}H_{33}O_2P_2Ru$ 517.0999), 441.0563 ([Ru(=C=CHC$_6$H$_4$OMe)-(C≡CC$_6$H$_4$OMe)(PMe$_3$)]$^+$, calcd for $C_{21}H_{24}O_2PRu$ 441.0557), 385.0428 ([Ru(C≡CC$_6$H$_4$OMe)(PMe$_3$)$_2$]$^+$, calcd for $C_{15}H_{25}OP_2Ru$ 385.0424). $^{31}P\{^1H\}$ NMR (162 MHz, acetone-d_6): δ −9.4 (br s). ^1H NMR (400 MHz, acetone-d_6): δ 7.24 (*AA′XX′*, 2H, *o*-*H* (acetylide)), 7.13 (*AA′XX′*, 2H, *o*-*H* (vinylidene)), 6.90 (*AA′XX′*, 2H, *m*-*H* (vinylidene)), 6.85 (*AA′XX′*, 2H, *m*-*H* (acetylide)), 5.29 (s, =C*H*), 3.77 (s, 6H, 2 × OCH_3), 1.79 (s, 36H, PCH_3). $^{13}C\{^1H\}$ NMR (101 MHz, acetone-d_6): δ 357.7 (m, Ru=*C*), 159.21 (*p*-*C*), 159.16 (*p*-*C*), 132.4 (*o*-*C* (acetylide)), 127.8 (*o*-*C* (vinylidene)), 121.4 (*ipso*-*C*), 121.3 (*ipso*-*C*), 119.8 (RuC≡*C*), 115.7 (*m*-*C* (vinylidene)), 114.9 (*m*-*C* (acetylide)), 112.9 (=CH), 111.7 (p, $^2J_{CP}$ = 23 Hz, RuC≡C), 55.7 (2 × OCH$_3$), 19.7 (br, PCH$_3$). ^{19}F NMR (565 MHz, acetone-d_6): δ −149.0 (B*F*$_4$). Magenta crystals of **4a** suitable for X-ray crystallography were grown from a solution in acetone-d_6 layered with pentane.

***trans*-[Ru(=C=CH(Ph))(C≡CPh)(PMe$_3$)$_4$]$^+$BF$_4^-$ (4b).** *trans*-[Ru(C≡CPh)$_2$(PMe$_3$)$_4$] (**3b**; 0.306 g, 0.504 mmol) and 2,6-lutidinium tetrafluoroborate (0.16 g, 0.82 mmol) were stirred in tetrahydrofuran (20 mL) for 3 days under an atmosphere of nitrogen to form a vivid pink solution. The solvent was removed under reduced pressure, and the crude solid was recrystallized from acetone/pentane to afford *trans*-[Ru(=C=CH(Ph))(C≡CPh)(PMe$_3$)$_4$]$^+$BF$_4^-$ (**4b**) as a pink crystalline solid (0.249 g, 0.358 mmol, 71%). Anal. Calcd for $C_{28}H_{47}BF_4P_4Ru$ (695.45): C, 48.36; H, 6.81. Found: C, 47.89; H, 7.26. $^{31}P\{^1H\}$ NMR (243 MHz, acetone-d_6): δ −9.5 (br s). ^1H NMR (600 MHz, acetone-d_6): δ 7.31 (m, 2H, *m*-*H* (vinylidene)), 7.30 (m, 2H, *o*-*H* (acetylide)), 7.28 (m, 2H, *m*-*H* (acetylide)), 7.20 (m, 2H, *o*-*H* (vinylidene)), 7.19 (m, 1H, *p*-*H* (acetylide)), 7.11 (m, 1H, *p*-*H* (vinylidene)), 5.36 (p, $^3J_{HP}$ = 1 Hz, = C*H*), 1.82 (br, 36H, PCH_3). $^{13}C\{^1H\}$ NMR (151 MHz, acetone-d_6): δ 355.3 (p, $^2J_{CP}$ = 14 Hz, Ru=*C*), 131.0 (*o*-*C* (acetylide)), 130.4 (*ipso*-*C* (vinylidene)), 130.0 (*m*-*C* (vinylidene)), 129.3 (*m*-*C* (acetylide)), 128.6 (*ipso*-*C* (acetylide)), 126.6 (*p*-*C* (vinylidene and acetylide)), 126.6 (*o*-*C* (vinylidene)), 120.0 (RuC≡*C*), 114.9 (p, $^2J_{CP}$ = 23 Hz, RuC≡C), 113.4 (=*C*H), 19.7 (br, PCH$_3$). ^{19}F NMR (376 MHz, acetone-d_6): δ −148.9 (B*F*$_4$). Pink crystals of **4b** suitable for X-ray crystallography were grown from a solution in acetone which was vapor infused with pentane.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.9b00788.

NMR data for all new compounds, crystallographic data for the complexes [Ru(η^3-CF$_3$-4-C$_6$H$_4$C≡CC=CH-(C$_6$H$_4$-4-CF$_3$))(PMe$_3$)$_4$]$^+$BF$_4^-$ (**1c**), [Ru(MeO-4-C$_6$H$_4$C≡CC=CH(C$_6$H$_3$-4-OMe))(PMe$_3$)$_4$] (**2a**), *cis*-[Ru(C≡CC$_6$H$_4$-4-CF$_3$)$_2$(PMe$_3$)$_4$] (**3c**), [Ru(=C=CH(C$_6$H$_4$-4-OMe))(C≡CC$_6$H$_4$-4-OMe)(PMe$_3$)$_4$]$^+$ (**4a**), and *trans*-[Ru(=C=CH(Ph))(C≡CPh)-(PMe$_3$)$_4$]$^+$BF$_4^-$ (**4b**) (PDF)

Accession Codes

CCDC 1966218−1966222 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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