ORGANOMETALLICS

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Mapping the Elimination of Water from Hydroxyvinylidene Complexes of Ruthenium(II): Access to Allenylidene and Vinylvinylidene Complexes in a Stepwise Fashion

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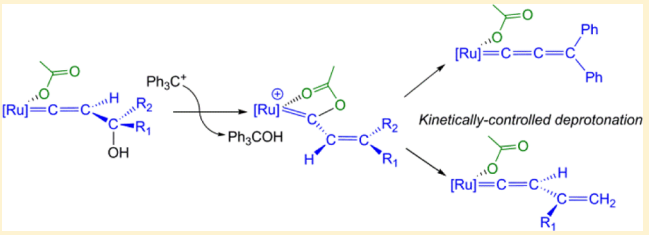
Supporting Information

ABSTRACT: Reaction of hydroxyvinylidene complexes $[Ru(\kappa^1\text{-OAc})(\kappa^2\text{-OAc})(=C=CHC\{OH\}R^1R^2)(PPh_3)_2]$ ($R^1 = R^2 = Ph$; $R^1 = R^2 = Me$; $R^1 = Ph$, $R^2 = Me$) with $[CPh_3]BF_4$ results in the formation of the cationic carbene species $[Ru(\kappa^2\text{-OAc})(OC\{Me\}OCC\{H\}=CR^1R^2)(PPh_3)_2]BF_4$. In these complexes, the κ^1-acetate ligand has changed its binding mode in order to stabilize the resulting cationic species. The carbene complexes may be deprotonated, although the outcome of the reaction depends markedly on the substituent present. In the case in which $R^1 = R^2 = Ph$, the hydrogen on the β-carbon of the organic ligand is removed to afford an allenylidene complex $[Ru(\kappa^1\text{-OAc})(\kappa^2\text{-OAc})(=C=C=CPh_2)(PPh_3)_2]$. An examination of the structural and spectroscopic parameters for the allenylidene complex indicates that the electronic influence of this ligand is very similar to the corresponding vinylidene and isonitrile analogues. In the cases where $R^1 = R^2 = Me$ and $R^1 = Me$, $R^2 = Ph$ deprotonation occurs at a methyl group to afford vinylvinylidene complexes $[Ru(\kappa^1\text{-OAc})(\kappa^2\text{-OAc})(=C=C\{H\}\text{-}CR^2=CH_2)(PPh_3)_2]$ ($R^2 = Me$, Ph). No interconversion between vinylvinylidene and allenylidene complexes was observed. The overall process is analogous to a formal E_1-type elimination in which the cationic carbene complex may be viewed as a stabilized carbocation intermediate. A DFT study provided insight into selectivity of the deprotonation step indicating that the greatest relative difference in energy between all the possible isomers of the vinylvinylidene and allenylidene complexes was *ca.* 20 kJ mol^{-1}. Interconversion between the two forms of the complex by a [1,3]-hydrogen shift appears to be unlikely due to the higher energy of the corresponding transition state; hence the selectivity in the formation of the vinylvinylidene complexes may be due the site of deprotonation being kinetically controlled. An alternative mechanism for this interconversion between vinylvinylidene and allenylidene complexes in cationic half sandwich metal complexes is proposed, which proceeds via a deprotonation/reprotonation pathway.

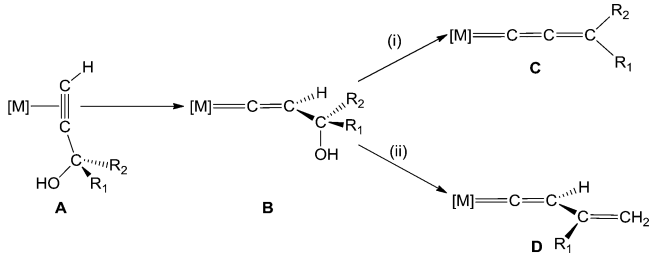


INTRODUCTION

Transition metal complexes containing unsaturated carbene ligands, such as vinylidene,[1] allenylidene,[2] and longer cumulenylidenes[2b,3] play an important role in a number of fields. For example, vinylidene complexes are key intermediates in a range of catalytic reactions of terminal alkynes which result in carbon−carbon and carbon−element bond formation in an atom-efficient manner.[1a,4] Moreover, the intermediacy of vinylidene complexes in these processes may often promote the anti-Markovnikov addition of substrates to alkynes.[4a,5] In a similar fashion, metal complexes containing allenylidene ligands also play an important catalytic role. For example, Nishibayashi has demonstrated that the thiolate-bridged ruthenium dimer $[\{RuCl(\eta^5\text{-}C_5Me_5)\}(\mu\text{-SR})]_2$ is an excellent catalyst for a range of propagyl-substitution reactions: the formation of a ruthenium-bound allenylidene ligand being a key step in this process.[6] Complexes containing allenylidene ligands have also been shown to be catalysts for alkene metathesis[7] and also the decarbonylation of propargyl alcohols.[8] In addition to their uses as intermediates in catalytic reactions, complexes containing cumulene ligands have been extensively studied for their interesting electronic and optical properties.[2a,9]

The simplest manner to generate vinylidene ligands is via the metal-promoted formal 1,2-hydrogen migration of terminal alkynes (**A** → **B**, Scheme 1),[1b,10] although more recently the formation of disubstituted vinylidene ligands from internal alkynes has been reported.[11] The formation of substituted

Scheme 1[a]



[a](i) − H_2O; (ii) − H_2O, R_1 = alkyl or aryl, R_2 = Me.

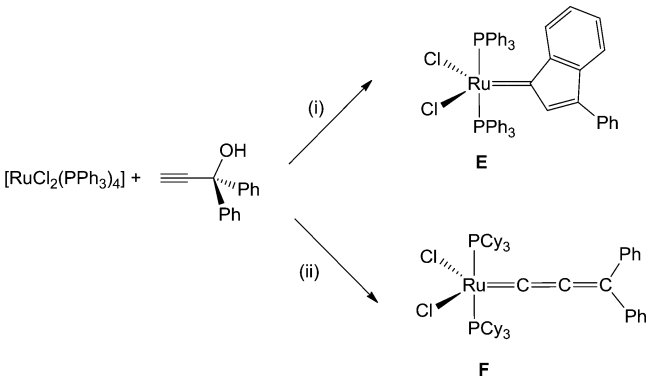
Received: September 16, 2013
Published: December 3, 2013

   dx.doi.org/10.1021/om4009247 | *Organometallics* 2013, 32, 7407−7417

vinylidene complexes has also been exploited for the formation of allenylidene complexes. In a method pioneered by Selegue,[12] the reaction of a terminal propargyl alcohol with an unsaturated metal complex results in the formation of an intermediate hydroxy-substituted vinylidene species (Scheme 1, **B**), which may then undergo dehydration (either spontaneously or upon suitable stimulus) to give the desired allenylidene complexes, **C**.[2b,3c,6l,7f,13] This is generally a robust synthetic method and may be applied to a range of metal complexes and alkynes bearing different substituents. Although there is a report of stable uncoordinated allenylidenes which may subsequently be coordinated to suitable metal complexes,[13b] the vast majority of cumulene ligands have been assembled within the coordination sphere of a metal from alkyne precursors.

Although the Selegue method does have a wide applicability, there are a number of instances in which allenylidene complexes are not obtained. In the case of propargyl alcohols which have alkyl substituents, it is possible that an alternative dehydration pathway may occur to give vinylvinylidene complexes, **D**,[14] and there are examples of this being a competitive process with both isomers being in equilibrium. An additional case in which the Selegue method fails to afford an allenylidene complex, but has important consequences for catalysis, is the reaction of $[RuCl_2(PPh_3)_4]$ with $HC{\equiv}CCPh_2(OH)$. As shown in Scheme 2, this reaction affords a ruthenium indenylidene

Scheme 2[a]



[a](i) H_2O, − $2PPh_3$, (ii) + PCy_3, − H_2O, − $2PPh_3$.

complex, **E**,[15] which has been exploited as an alkene metathesis catalyst,[7f,16] although by the addition of PCy_3 it is possible to prepare allenylidene **F**.[17]

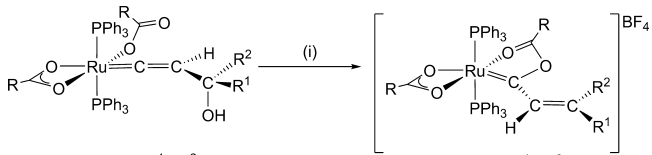
Although the Selegue method is now well established, there appears to be little mechanistic information on the fundamental processes which governs the elimination of water. We have recently demonstrated that the ruthenium acetate complex, *cis*-$[Ru(\kappa^2\text{-OAc})_2(PPh_3)_2]$, **1**, is a versatile precursor to a range of complexes containing π-acidic ligands. Reactions of **1** with CO, $[NO]BF_4$, CN^tBu, and terminal alkynes gives rise to complexes *trans*-$[Ru(\kappa^1\text{-OAc})(\kappa^2\text{-OAc})(L)(PPh_3)_2]$ (L = CO, NO^+, CN^tBu, and =C=CHR, respectively).[18] The presence of the acetate ligand plays an important role in the formation of the vinylidene complexes as it lowers the energy to the hydrogen migration step by a Ligand-Assisted Proton Shuttle (LAPS) mechanism.[10b] The reactions of **1** with propargyl alcohols does not lead to the spontaneous formation of allenylidene complexes. In this instance, long-lived metastable hydroxyvinylidene complexes were obtained. For example, the reaction of **1** with $HC{\equiv}CCPh_2(OH)$ leads to the formation of *trans*-$[Ru(\kappa^1\text{-OAc})(\kappa^2\text{-OAc})(=C=CHC\{OH\}Ph_2)(PPh_3)_2]$, **2**, which undergoes a subsequent reaction to give carbonyl complex *trans*-$[Ru(\kappa^1\text{-OAc})(\kappa^2\text{-OAc})(CO)(PPh_3)_2]$ and $H_2C{=}CPh_2$: this proved to be a general reaction for propargyl alcohols of the general form $HC{\equiv}CCR_2(OH)$.[19]

Access to long-lived hydroxy-substituted vinylidene complexes offers an opportunity to study the reactivity of such species, with a view to gaining mechanistic insight into the Selegue mechanism. In particular, we sought to gain an understanding of the different elimination pathways. In order to achieve this goal, we considered that the first step in the process would be the abstraction of the hydroxy-substituent on the vinylidene with a suitable Lewis acid, this should give rise to a cationic metal complex which would be amenable to deprotonation. We now report how the elimination of water from hydroxy-vinylidene complexes **2** may be accomplished in a stepwise fashion to provide initial access to cationic Fischer carbene complexes stabilized by an acetate ligand. On treatment with a base, these carbene complexes provided access to allenylidene and vinylvinylidene complexes.

RESULTS AND DISCUSSION

Synthesis of Cationic Carbene Complexes. Treatment of a CH_2Cl_2 solution of the hydroxy-substituted vinylidene complex $[Ru(\kappa^1\text{-OAc})(\kappa^2\text{-OAc})(=C=CHC\{OH\}Ph_2)(PPh_3)_2]$, **2a** [generated *in situ* from the reaction of **1** with $HC{\equiv}CCPh_2(OH)$], with an equimolar amount of $[CPh_3]BF_4$ resulted in an instantaneous color change from yellow to deep green. Following concentration of the solution, the carbene complex $[Ru(\kappa^2\text{-OAc})(OC\{Me\}OCC\{H\}{=}CPh_2)(PPh_3)_2]BF_4$, $[\mathbf{3a}]BF_4$, could be isolated by precipitation with pentane (Scheme 3). The resulting green powder could be crystallized

Scheme 3[a]



2a R = Me R^1= R^2 = Ph
2b R = R^1= R^2 = Me
2c R = Me R^1= Ph R^2 = Me
2a^{Bz} R = R^1= R^2 = Ph

[**3a**]BF_4 R = Me R^1= R^2 = Ph
[**3b**]BF_4 R = R^1 = R^2 = Me
[**3c**]BF_4 R = Me R^1= Ph R^2 = Me
[**3a**^{Bz}]BF_4 R = R^1= R^2 = Ph

[a](i) + $[CPh_3]BF_4$, − Ph_3COH, CH_2Cl_2, room temperature, 90 min.

by slow diffusion of diethyl ether into a CH_2Cl_2 solution of the complex. The ^1H NMR spectrum of $[\mathbf{3a}]BF_4$ exhibited two resonances for the methyl groups of the acetate ligands at δ 0.79 and δ 1.31, confirming the different coordination environments. The $^{13}C\{^1H\}$ NMR spectrum of the complex also confirmed the presence of two inequivalent acetate ligands, and importantly, a triplet resonance was observed at δ 279.8 ($^2J_{PC}$ = 9.3 Hz) for the metal-bound carbon atom. The carbon atoms in the β and γ positions of the vinyl carbene ligand were observed at δ 127.7 (s) and δ 146.9 (s), respectively. When the reaction was monitored by NMR spectroscopy, the formation of $[\mathbf{3a}]^+$ was shown to occur in a quantitative fashion, and the formation of one equivalent of Ph_3COH was observed.

Reaction of either the dimethyl-substituted hydroxyl-vinylidene complex, **2b**, or the related complexes bearing phenyl/methyl substituents, **2c**, with $[CPh_3]BF_4$ followed the same

dx.doi.org/10.1021/om4009247 | *Organometallics* 2013, 32, 7407−7417

course (Scheme 3) with purple ([**3b**]BF_4) and green ([**3c**]BF_4) carbene complexes being obtained, respectively. In the case of [**3c**]BF_4, only one of the two possible stereoisomers was obtained. A 2D-NOESY experiment on a CD_2Cl_2 solution of [**3c**]BF_4 exhibited NOE cross peaks between the hydrogen atom of the carbene ligand and the aromatic region which, given that no NOE peaks were observed for the methyl group, suggests that the alkene adopts the orientation shown in Scheme 3 with the hydrogen and phenyl substituents adopting a *Z* configuration. In addition, this 2D-NOSEY spectrum exhibited EXSY peaks between the two acetate resonances, suggesting that they were undergoing exchange, although this is evidently occurring on a much slower time scale than complexes containing both κ^1- and κ^2-acetate ligands where exchange is typically fast on the NMR time scale at room temperature.[18,19]

Obtaining crystals of complexes [**3**]BF_4 which gave high quality X-ray diffraction data proved to be fraught with difficulty, despite multiple attempts using a range of conditions. In many cases, crystals exhibited substantial twinning and disorder, and only the best data sets obtained are discussed. In the case of complex [**3a**]BF_4, the resulting structure determination demonstrates that the connectivity within the complex was as expected (see Supporting Information); however, the vinyl group of the carbene was disordered over two sites. It did prove possible to obtain a higher quality structure of the complex [$Ru(\kappa^2\text{-}O_2CPh)(OC\{Ph\}OCC\{H\}{=}CPh_2)(PPh_3)_2$]$BF_4$, [**3a**^{Bz}]$BF_4$ (Figure 1), which could be obtained in an identical

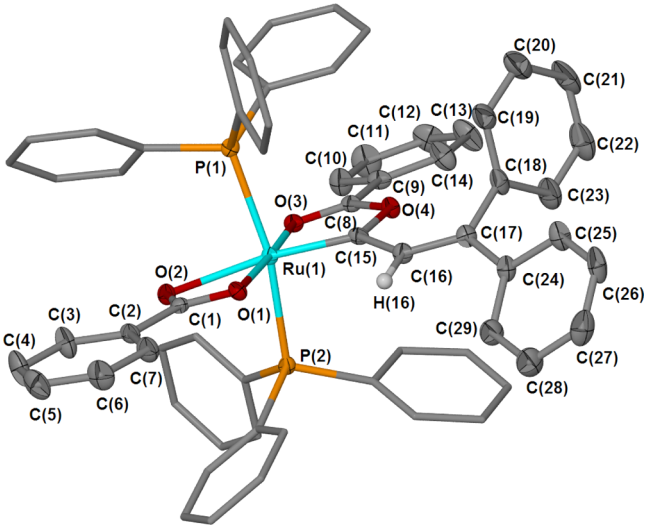
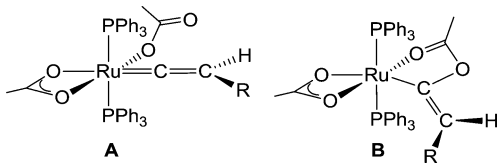


Figure 1. Solid state structure of the cation [**3a**^{Bz}]$^+$; hydrogen atoms, except for H(16), are omitted for clarity. Thermal ellipsoids, where shown, are at the 50% probability level.

fashion to [**3a**]BF_4, but using [$Ru(\kappa^1\text{-}O_2CPh)(\kappa^2\text{-}O_2CPh)(=C{=}CHC\{OH\}Ph_2)(PPh_3)_2$], **2a**^{Bz}, as the ruthenium-based precursor. In addition, a structure determination of [**3b**]BF_4 was obtained from a twinned crystal, and in this case the asymmetric unit contained two crystallographically independent ruthenium cations, (see Supporting Information).

A comparison of the structural metrics of the complexes with general structure [**3**]$^+$ (Table S2, Supporting Information) demonstrate that the structures of these compounds are distorted octahedra with the greatest deviation from an idealized geometry being imposed by the restricted bite-angle of the κ^2-acetate ligand. As suggested by the NMR spectra, the complexes also contain two mutually *trans*-triphenylphosphine ligands with the remaining two coordination sites being occupied by a bidentate ligand, which is probably best viewed as a bidentate Fischer carbene complex. The ruthenium−carbon bond lengths (1.843(4)−1.862(3) Å) are shorter than those observed in the half-sandwich Fischer carbene complexes [$Ru(\eta^5\text{-}C_5H_5)(=C\{OMe\}Et)(PPh_3)_2$]$PF_6$ (1.959(6) Å)[20] and [$Ru(\eta^5\text{-}C_5H_5)(=C\{OMe\}CH_2Ur)(PPh_3)_2$]X (Ur = uracil; X = PF_6,[21] 1.946(3) Å; X = OTf,[22] 1.9541(17) Å) but are similar in length to those observed in octahedral species such as the cyclic carbene [$Ru(\kappa^1\text{-}OAc)(\kappa^2\text{-}OAc)(=COC_3H_6)(PPh_3)_2$] (1.876(6) Å)[18] and [$RuCl_2(OC\{Me\}OCCH{=}CPh_2)(PPh_3)_2$] (1.862(5) Å).[15b] The geometry within the ester tether indicates that the bonding in the cations [**3**]$^+$ is best described as shown in Scheme 3, with the C=O distance being shorter than C−O. We have observed this type of metalloenol ester structure previously in a mechanistic study into the formation of the vinylidene complexes related to **2**; however, in this case it appears that the metalloenol ester structure **B** generally lies at higher energy than the corresponding vinylidene complexes, **A**.[10b] Presumably in the case of the cations [**3**]$^+$, the formal generation of a carbocation on removal of the OH group by $[CPh_3]^+$ results in a highly electrophilic metal-bound carbon, which is stabilized by the acetate ligand.

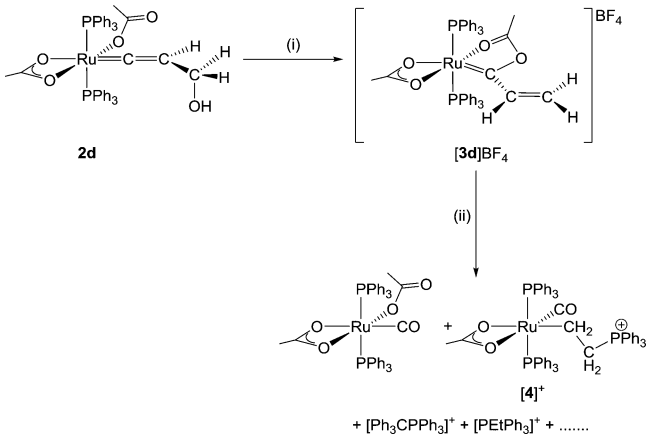


In contrast to the reactions involving **2a**−**2c**, treatment of the unsubstituted hydroxy-vinylidene complex [$Ru(\kappa^1\text{-}OAc)(\kappa^2\text{-}OAc)(=C{=}CHC\{OH\}H_2)(PPh_3)_2$], **2d**, with $[CPh_3]BF_4$ did not result in a selective reaction. Addition of $[CPh_3]BF_4$ to a CH_2Cl_2 solution of **2d** at room temperature resulted in an instantaneous color change from orange to blue. Analysis of the reaction mixture by NMR spectroscopy demonstrated that the desired cation [$Ru(\kappa^2\text{-}OAc)(OC\{Me\}OCC\{H\}{=}CH_2)(PPh_3)_2$]$BF_4$, [**3d**]$BF_4$, was not present. The ^1H and $^{31}P\{^1H\}$ NMR spectra indicated that a range of products has been formed including [$Ru(\kappa^1\text{-}OAc)(\kappa^2\text{-}OAc)(CO)(PPh_3)_2$], $[Ph_3CPPh_3]^+$, the phosphonio-ethyl complex [**4**]$^+$ (identified by X-ray crystallography, see Supporting Information), and, remarkably, $[PEtPh_3]^+$, with the relative amounts of these varying from reaction to reaction (Scheme 4).

Further attempts were made to confirm the formation of [**3d**]BF_4. An equimolar amount of $[CPh_3]BF_4$ was added to a thawing CD_2Cl_2 solution of **2d**, and after warming to room temperature, the sample was placed directly into a NMR spectrometer. Under these conditions, a series of resonances for the cation [**3d**]$^+$ could be observed. For example, in the ^1H NMR spectrum, resonances for the two geminal hydrogen atoms of the vinyl group were present at δ 6.32 (d, $^3J_{HH}$ = 11.0 Hz) and δ 6.50 (d, $^3J_{HH}$ = 17.3 Hz): both resonances exhibited a cross peak in a 2D-COSY experiments to an additional proton, which was obscured by the peaks for the PPh_3 ligands. Peaks for the two acetate groups were observed at δ 0.82 (3H) and 1.86 (3H). Although [**3d**]$^+$ was the major product formed under these conditions, additional as yet unidentified species were also detected. Complex [**3d**]$^+$ proved to be unstable and transformed to a number of number products, the dominant one in all cases

dx.doi.org/10.1021/om4009247 | *Organometallics* 2013, 32, 7407−7417

Scheme 4[a]



[a](i) + $[CPh_3]BF_4$, − Ph_3COH, thawing CD_2Cl_2, warm to room temperature, (ii) CD_2Cl_2 room temperature.

appeared to be $[PEtPh_3]^+$. Given the apparent instability of $[\mathbf{3d}]^+$, its chemistry was not pursued further.

Reactivity of Cationic Carbene Complexes. Having developed a straightforward route to the cationic carbene complexes $[\mathbf{3a}-\mathbf{3c}]^+$, the next stage of the sequential elimination of water was to perform a deprotonation. A number of different bases were screened in each case, and the one affording the most selective reactions are detailed below. The outcome of the reaction of the cations with a base depended on the nature of the substituents on the vinyl group. Reaction of $[\mathbf{3a}]BF_4$ with NaO^tBu in CH_2Cl_2 solution resulted in an instantaneous color change from green to yellow. The solvent was removed and the residue extracted with diethyl ether; concentration followed by cooling to −20 °C resulted in the formation of a red solid. Analysis of this solid (*q.v.*) indicated that the allenylidene-containing complex $[Ru(\kappa^1\text{-}OAc)(\kappa^2\text{-}OAc)(=C=C=CPh_2)(PPh_3)_2]$, **5**, was the major component of this material (Scheme 5), although small amounts of the 1,2 diphenylvinyl complex $[Ru(\kappa^2\text{-}OAc)(CH=CPh_2)(CO)(PPh_3)_2]$, **6**, were also present. Further crystallization from Et_2O afforded analytically pure **5**, albeit in a reduced yield. Complex **6** was identified on the basis of an X-ray diffraction experiment (see Supporting Information) and has presumably arisen from the formal hydrolysis of the allenylidene ligand and concomitant loss of AcOH.

The identification of **5** was secured through a combination of NMR and IR spectroscopy as well as single crystal X-ray diffraction. The $^{13}C\{^1H\}$ NMR spectrum of **5** recorded in CD_2Cl_2 exhibited characteristic resonances for the three carbons of the allenylidene ligands at δ 305.0 (t, $^2J_{PC}$ = 17.3 Hz, Ru=*C*), δ 232.8 (t, $^3J_{PC}$ = 5.50 Hz, Ru=C=*C*), and δ 147.3 (s, Ru=C=C=*C*).[23] Both the ^1H and $^{13}C\{^1H\}$ NMR spectra of **5** exhibited only a single set of resonances of the coordinated acetate ligands, indicating that these ligands were undergoing rapid κ^1/κ^2 exchange on the NMR time scale; however the presence of acetate ligands with both binding modes was confirmed by IR spectroscopy [1366 cm^{-1} (κ^1-OCO_{sym}), 1435 cm^{-1} (κ^2-OCO_{sym}), 1537 cm^{-1} (κ^2-OCO_{asym}), 1624 cm^{-1} (κ^1-OCO_{asym}), $\Delta\nu_{(uni)}$ 258 cm^{-1}, $\Delta\nu_{(chelate)}$ 78 cm^{-1}].[18,19] The IR spectrum also exhibited an intense band at 1911 cm^{-1}, again characteristic of the presence of an allenylidene ligand.[23] The corresponding reaction between $[\mathbf{3a^{Bz}}]BF_4$ with NaO^tBu or $[NMe_4]OAc$ both afforded $[Ru(\kappa^1\text{-}O_2CPh)(\kappa^2\text{-}O_2CPh)(=C=C=CPh_2)(PPh_3)_2]$, $\mathbf{5^{Bz}}$, which could be identified on the basis of $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopy. However, in the latter case, evidence for exchange of benzoate and OAc ligands was observed as were additional side products (see Supporting Information).

Consistent with these data, the molecular structure of **5**, as determined by single crystal X-ray diffraction, demonstrates that the ruthenium is coordinated to two mutually *trans*-phosphine ligands, κ^2- and κ^1-bound acetate groups and a diphenylallenylidene ligand (Figure 2). The allenylidene ligand is orientated so

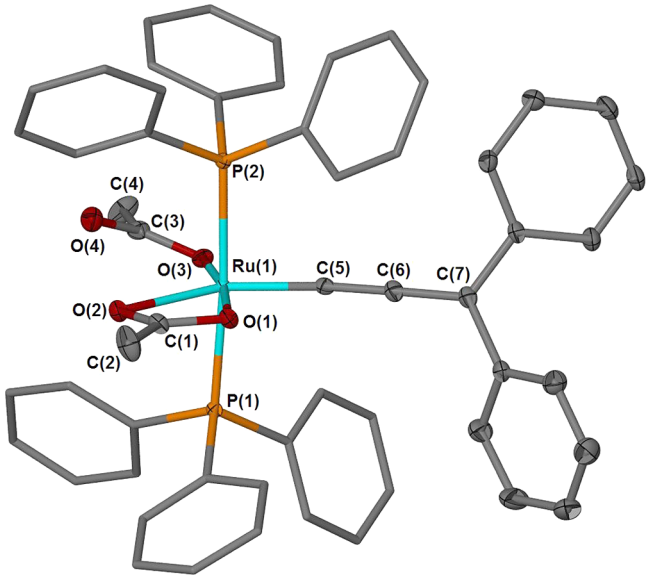
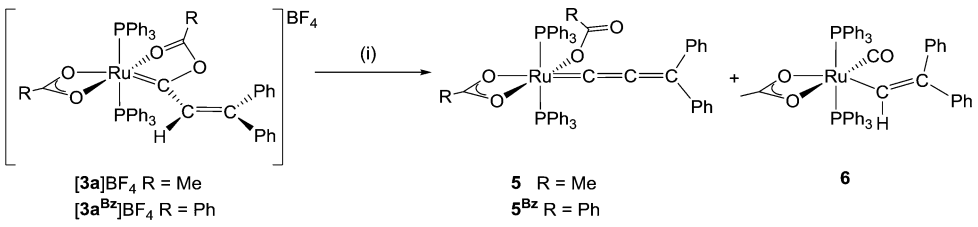


Figure 2. Molecular structure of complex **5**. Thermal ellipsoids (where shown) are at the 50% probability level. Hydrogen atoms and an Et_2O of crystallization have been omitted for clarity.

that the phenyl substituents are lying essentially parallel to the P−Ru−P axis, whereas in the corresponding vinylidene complexes the substituents lie perpendicular to this orientation. This preference is as expected and demonstrates that both vinylidene and allenylidene ligands have adopted an orientation so as to

Scheme 5[a]



[a](i) + NaO^tBu, − $NaBF_4$, − HO^tBu, CH_2Cl_2, 15 min.

dx.doi.org/10.1021/om4009247 | *Organometallics* 2013, 32, 7407−7417

Table 1. Comparison of Structure and Spectroscopic Metrics from Complexes *trans*-[Ru(κ^1-OAc)(κ^2-OAc)(L)(PPh_3)$_2$]

L	Ru−P(1)/Å	Ru−P(2)/Å	Ru−O(2)/Å	O(1)−Ru-O(2)	$\Delta\nu_{(chelate)}$/cm^{-1}
NO^+	2.4336(8)	2.4466(8)	2.0744(19)	61.55(8)	n.d.
CO	2.4060(4)	2.3873(4)	2.1897(11)	60.42(2)	54
CN^tBu	2.3592(6)	2.3479(6)	2.2465(16)	59.80(6)	67
=C=CHPh	2.3853(7)	2.3910(7)	2.2863(18)	59.08(6)	75
=C=C=CPh_2, **5**	2.3844(3)	2.3787(3)	2.2914(10)	60.12(7)	78
=CC_3H_6O	2.3840(14)	2.3642(14)	2.3575(4)	56.40(15)	94

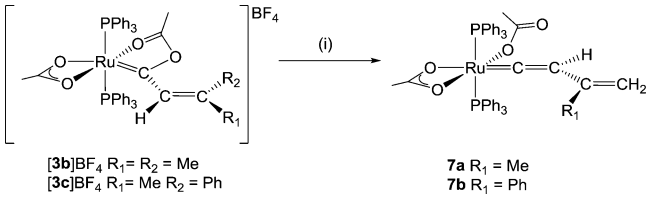
maximize π-back-donation from the d orbital, which is shared with the π-donor acetate ligands.[18] The bond lengths within the ruthenium allenylidene unit (Ru(1)−C5 1.8468(13) Å, C(5)−C(6) 1.2635(19) Å, C(6)−C(7) 1.3569(19)) are similar to the related complexes [$RuCl_2$(L)(=C=C=CPh_2)(PPh_3)] (L = EtOH, 1.836(4) Å; MeOH 1.833(6) Å, H_2O 1.848(9) Å, DMAP, 1.902(4) Å),[17] but the metal carbon bond is longer than in either [$RuCl_2$(=C=C=CPh_2)(PCy_3)$_2$] (1.794(11) Å) and [$RuCl_2$(=C=C=CPh_2)(PCy_3)(IMes)] (1.7932(13) Å), which may represent the greater basicity of the metal in the latter examples.[17]

We have recently proposed that the structural and spectroscopic metrics within complexes of the general form *trans*-[Ru(κ^1-OAc)(κ^2-OAc)(L)(PPh_3)$_2$] (L = CO, NO^+, CN^tBu, =C=CHR, =$CC_nH_{(n+2)}O$) are diagnostic of the relative σ-donor, π-acceptor characteristics of the ligands L.[18] A comparison of the data for complex **5** allowed for the effects of the allenylidene ligand on the electron density at ruthenium to be evaluated. By comparison with the key parameters shown in Table 1, it is clear that the electronic effects of the allenylidene ligand are directly comparable with those for the vinylidene example.

The reaction of the two methyl-substituted cations [**3b**]BF_4 and [**3c**]BF_4 with a base did not lead to the formation of the corresponding allenylidene derivatives (Scheme 6). In these cases, reaction with [NMe_4]OAc in CH_2Cl_2 solution led to selective deprotonation at the methyl groups of the vinyl ligand and formation of vinylvinylidene complexes [Ru(κ^1-OAc)(κ^2-OAc)(=C=C{H}-CR_1=CH_2)(PPh_3)$_2$] (**7a** R_1 = Me, **7b** R_1 = Ph). Although we have not been able to obtain crystals of either complex suitable for study by X-ray diffraction, the identity of the complexes was determined by NMR spectroscopy. In the case of **7a**, the $^{13}C\{^1H\}$ NMR spectrum exhibited resonances at δ 360.4 (t, $^2J_{PC}$ = 17.0 Hz, C_α), 117.4 (s, C_β), 137.4 (s, C_γ), and 104.6 (s, C_δ) for the four atoms of the vinylvinylidene ligand. The ^1H NMR spectrum of **7a** exhibited a triplet resonance at δ 5.21 (t, $^3J_{PH}$ = 3.8 Hz) for the proton attached to the β-carbon of the vinylidene ligand, whereas singlet resonances were observed at δ 3.75 and 3.48 for the two protons of the terminal CH_2 group. An HSQC experiment demonstrated that these protons were both connected to the carbon atom which exhibited a resonance at δ 104.6. Furthermore, a HMBC experiment demonstrated that the resonances at δ 3.75, the proton on the β-carbon of the vinylidene ligand, and the methyl group all showed long-range correlations with the resonance at δ 137.4, consistent with the proposed assignment.

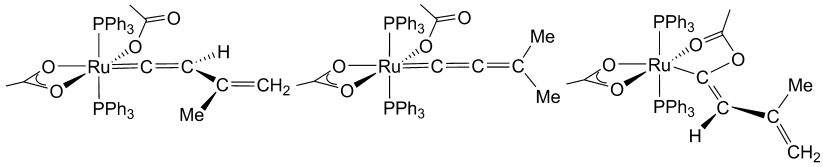
The reaction between [**3c**]BF_4 and [NMe_4]OAc appeared to undertake a similar course, and the ^1H NMR spectrum of the product, **7b**, exhibited a similar series of resonances to **7a**. Unfortunately, **7b** provided to be unstable in solution, which prohibited the acquisition of a $^{13}C\{^1H\}$ NMR spectrum, or obtaining a combustion analysis. However, a mass spectrum obtained using the LIFDI method did possess a peak at the correct m/z for the proposed molecular ion. The deprotonation step was shown to be reversible, as the addition of one equivalent of HBF_4·OEt_2 to a sample of **7b** resulted in the reformation of [**3c**]$^+$ as shown by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.

Scheme 6[a]



[a](i) + [NMe_4]OAc, − [NMe_4]BF_4, − HOAc, CH_2Cl_2, 10 min.

Theoretical Studies and Mechanistic Discussion. The highly selective deprotonation of the cationic carbene complexes [**3b**]$^+$ and [**3c**]$^+$ to give vinylvinylidene complexes contrasts with the behavior of water elimination from many half-sandwich complexes containing hydroxyvinylidene ligands.[14a] For example, allenylidene and vinylidene complexes supported by the [Ru(η^5-C_9H_7)(PPh_3)$_2$]$^+$ group are in equilibrium, and theoretical studies have shown that they may interconvert via a hydrogen migration pathway.[14a] In order to gain insight into apparent lack of isomerization exhibited by the vinylvinylidene complex **7a** to

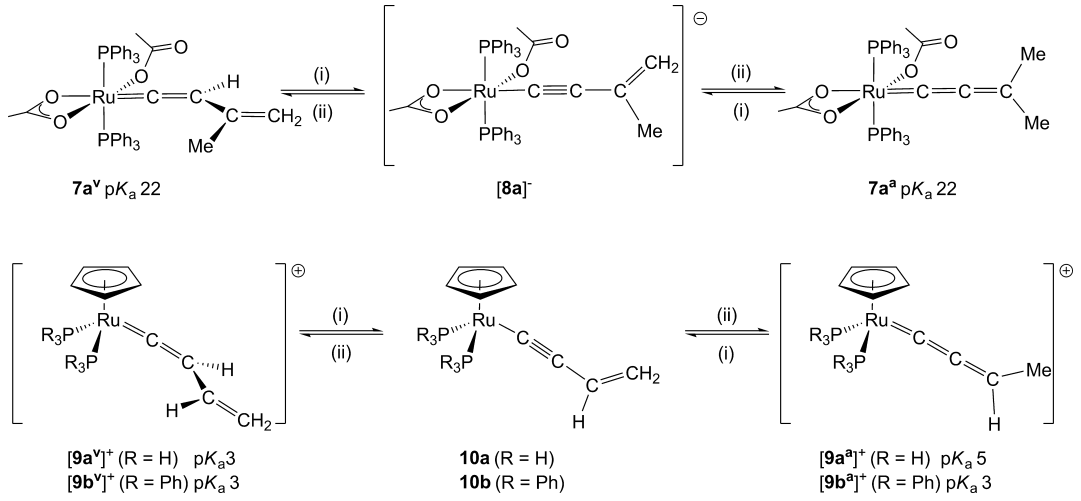


	7a^v	**7a**^{a}	**7a**^{m}
ΔG (BP86/SV(P))	0 kJ mol-1	+7 kJ mol^{-1}	+14 kJ mol^{-1}
ΔE (pbe0/def2-TZVPP)	0 kJ mol^{-1}	+20 kJ mol^{-1}	+1 kJ mol^{-1}
ΔG (pbe0/def2-TZVPP)	0 kJ mol^{-1}	+12 kJ mol^{-1}	+2 kJ mol^{-1}

Figure 3. Potential isomers of **7a** examined by DFT.

dx.doi.org/10.1021/om4009247 | *Organometallics* 2013, 32, 7407−7417

Scheme 7[a]



[a](i) − H$^+$; (ii) + H$^+$.

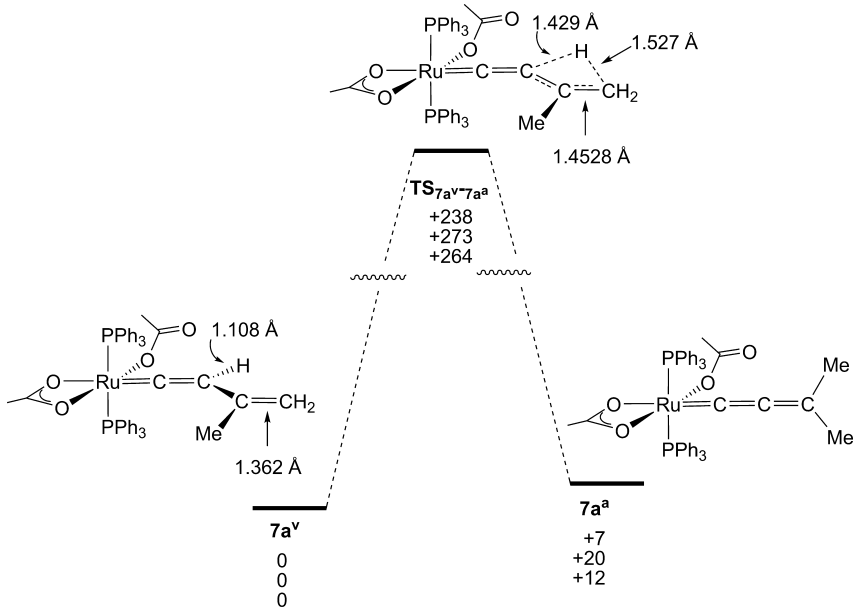


Figure 4. Potential energy surface for the interconversion between complexes **7a**^{v} and **7a**^{a} via **TS**$_{7a^{v}\text{-}7a^{a}}$. Energies relative to **7a**^{v} are given in kJ mol^{-1} for ΔG_{298} at the bp86/SVP level (top), ΔE at the pbe0/def2-TZVPP level (middle), and ΔG_{298} at the pbe0/def2-TZVPP level (bottom).

an allenylidene isomer, a theoretical study was undertaken to determine the relative energy of the vinylvinylidene **7a**^{v}, allenylidene **7a**^{a}, and metalloenol ester **7a**^{m} isomers of the complex (Figure 3). Calculations were performed with the Turbomole program; initial geometry optimizations and frequency calculations were performed at the BP86/SV(P) level and subsequent single point energies at pbe0/def2-TZVPP.[24]

For complex **7a**^{v}, a total of eight isomers were considered on the basis of the relative orientation of the κ^1-acetate ligand and the substituent on the vinylvinylidene group (see Supporting Information). The structure **7a**^{v} shown in Figure 3 was the lowest energy conformation and was the global minimum for all structures investigated at all levels of theory employed. Two isomers were considered for complex **7a**^{a} and four for **7a**^{m}. It should be noted that the relative energies of these complexes varied depending on the computational method employed. At the BP86/SV(P) level, the calculations indicate that the isomers of **7a**^{a} are consistently lower in energy than **7a**^{m}, whereas the opposite is true at the pbe0/def2-TZVPP level. Indeed, at this higher level, the isomers of **7a**^{m} are almost identical to **7a**^{v} and may interconvert via a low energy transition state (see Supporting Information). However, the experimental spectroscopic data (most notably the resonance at δ 360.4 in the $^{13}C\{^1H\}$ NMR spectra of **7a**) indicate that the vinylidene form is the dominant species in solution.

The potential to interconvert **7a**^{v} and **7a**^{a} via a 1,3-hydrogen migration pathway in a similar manner to the $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$ system was then investigated.[14a] In this case, previous calculations performed on the simplified system $[Ru(\eta^5\text{-}C_5H_5)(PH_3)_2]^+$ indicated that the vinylvinylidene [**9a**^{v}]$^+$ (Scheme 7) was *ca.* 9 kJ mol^{-1} lower in energy than the corresponding allenylidene [**9a**^{a}]$^+$, and the free energy of the transition state for the interconversion was 288 kJ mol^{-1} higher in energy than [**9a**^{v}]$^+$. In the case of the acetate-substituted complexes, transition state **TS**$_{7a^{v}\text{-}7a^{a}}$ connects **7a**^{v} and **7a**^{a} (as shown by a DRC analysis) with

dx.doi.org/10.1021/om4009247 | *Organometallics* 2013, 32, 7407−7417

a relative free energy at 298 K of +264 kJ mol^{-1} at the pbe0/def2-TZVPP level (Figure 4). In order to make an appropriate comparison with the literature data, calculations on $[Ru(\eta^5\text{-}C_5H_5)(PH_3)_2]^+$ and $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2]^+$-based vinylvinylidene and allenylidene systems were performed using the computational method used in our studies. In these cases, transition states for hydrogen migration were found at the pbe0/def2-TZVPP level with ΔG_{298} +261 kJ mol^{-1} and +256 kJ mol^{-1}, respectively, relative to the vinylvinylidene isomer.

As noted by Gimeno, the magnitude of this barrier is somewhat high for a spontaneous process at 298 K.[14a] This is further reinforced by the fact that rapid equilibrium between vinylvinylidene and allenylidene complexes occurs for the $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$ system but not in the case of $[Ru(\kappa^1\text{-}OAc)(\kappa^2\text{-}OAc)(PPh_3)_2]$, despite the barriers being similar in both cases. With this in mind, alternative explanations of the difference in behavior between the two sets of complexes were investigated.

It has been demonstrated that the acidity of vinylidene β-protons occurs over a wide range. For example, the pK_a of the vinylidene proton in $[Fe(\eta^5\text{-}C_5H_5)(=C=CHMe)(dppe)]^+$ was found to be 7.74 ± 0.05 in 2:1 THF-H_2O,[25] whereas $[Ru(\eta^5\text{-}C_5H_5)(=C=CHBu^t)(PMe_3)_2]^+$ is much less acidic (pK_a 20.2 ± 0.2 in CH_3CN).[26] In addition, pyridine has been shown to deprotonate $[Ru(\eta^5\text{-}C_5H_5)(=C=CHPh)(PPh_3)_2]^+$,[27] whereas weak bases such as $NaHCO_3$ readily convert $[Ru(\eta^5\text{-}C_5H_5)(=C=CHSMe)(PMe_3)_2]^+$ to $[Ru(\eta^5\text{-}C_5H_5)(\text{-}C{\equiv}CSMe)(PMe_3)_2]$.[28] With this in mind, an alternative mechanism for the interconversion of allenylidene and vinylvinylidene complexes was envisaged in which deprotonation of either species would afford a common alkynyl intermediate: subsequent reprotonation could then afford either compound (Scheme 7). Further support for such a proposal comes from the observation that treatment of equilibrium mixtures of cationic half sandwich vinylvinylidene and allenylidene complexes with a base results in the formation of alkynyl complexes. This process is fully reversible, regenerating the equilibrium mixture on addition of acid.[14a]

In order to determine the feasibility of this process for the two different systems, the pK_a values for the vinylvinylidene and allenylidene complexes were calculated[29] with the alkynyl intermediate being the conjugate base in each case. The resulting data indicated a marked difference between the cationic half-sandwich and neutral carboxylate-substituted species. The neutral compounds **7a**^{v} and **7a**^{a} are predicted to have a far higher pK_a in MeOH (22), and therefore deprotonation/reprotonation via alkynyl complex $[\mathbf{8a}]^-$ is predicted to be unfavorable. This is consistent with the fact that the related compound $[RuCl_2(=C=C\{H\}\text{-}CMe=CH_2)(PCy_3)]$ does not appear to be deprotonated in the presence of bases such as NEt_3 and O^{t}Bu.[14n] In contrast, cationic complexes $[\mathbf{9}]^+$ are all predicted to be far more acidic (pK_a 5 or 3). Although this analysis does not give any information about the rate of proton transfer, it does indicate that the alkynyl intermediates **10** should be readily thermodynamically accessible in the case of the cationic complexes. Therefore, this proposed mechanism does provide effective discrimination between the two systems under investigation and should be considered as a potential alternative pathway to the [1,3]-hydrogen migration pathway.

CONCLUSIONS

The ready availability of the hydroxyvinylidene complexes **2** has enabled key intermediates in the Selegue mechanism to be observed. A two-step dehydration process has been developed with the initial formation of a cationic intermediate through formal hydroxide extraction followed by deprotonation, which may be viewed as being directly analogous to the classical E_1-elimination of water from alcohols to form alkenes. Central to these observations is the inherent stability of the cationic carbene complexes. Although the related species $[RuCl_2(OC\{Me\}OCC\{H\}=CPh_2)(PPh_3)_2]$ has been prepared from the reaction of the carbyne complex $[RuCl_3(\equiv CCH=CPh_2)(PPh_3)_2]$ with acetic acid,[15b] in the current case the acetate ligand plays a key role by ensuring that there is no formal coordinative unsaturation present at any stage during the formation of $[\mathbf{3}]^+$. This is a further example of the chemical noninnocence of carboxylate ligands in the chemistry of vinylidene and related ligands,[10b] which complements their role played in C−H functionalization reactions.[30]

The experimental and theoretical data indicate that the outcome of the deprotonation of the cationic species, $[\mathbf{3}]^+$, is kinetically controlled and this factor controls the regiochemical outcome of the dehydration process. The fact that no rearrangement to the allenylidene isomer is observed either in the case of **7a** or in the related compounds $[RuCl_2(=C=CHC\{Me\}=CH_2)(PCy_3)]$[14n] may be explained on the basis of either the higher energy of the transition state for [1,3]-hydrogen migration or the high pK_a of the vinylvinylidene and allenylidene complexes.

In summary, we have shown that a Lewis acid may abstract the OH group from hydroxyvinylidene complexes and that deprotonation of the subsequently formed cations is a kinetically controlled process allowing access to allenylidene and vinylvinylidene ligands.

EXPERIMENTAL SECTION

All experimental procedures were performed under an atmosphere of dinitrogen using standard Schlenk line and glove box techniques. CH_2Cl_2 and pentane were purified with the aid of an Innovative Technologies anhydrous solvent engineering system. The Et_2O was distilled over sodium (under argon) before use. The CD_2Cl_2 used for NMR experiments was dried over CaH_2 and degassed with three freeze−pump−thaw cycles. The solvent was then vacuum transferred into NMR tubes fitted with PTFE Young's taps. NMR spectra were acquired on either a Jeol ECS400 (Operating frequencies; ^{1}H 399.78 MHz, ^{13}C 100.53 MHz, ^{19}F 376.17 MHz, ^{11}B 128.27 MHz) or a Bruker AVANCE 500 (Operating Frequencies ^{1}H 500.23 MHz, ^{31}P 202.50 MHz, ^{13}C 125.77 MHz). ^{31}P and ^{13}C spectra were recorded with proton decoupling. Assignments were completed with the aid of COSY, DEPT, NOESY, HSQC, HMBC, and ^{1}H−^{31}P HMQC experiments. Mass spectrometry measurements were performed on a either a Bruker micrOTOF MS (ESI) or a Waters GCT Premier Acceleration TOF MS (LIFDI) instrument. IR spectra were acquired on either a Mattson Research Series or Thermo-Nicolet Avatar 370 FTIR spectrometer using CsCl solution cells. Elemental analyses were performed using an Exeter Analytical Inc. CE-440 analyzer. Analysis of all of the cationic species $[\mathbf{3}]BF_4$ is reported. However, all were found to have a much lower percentage of carbon than expected. These results were found to be reproducible between batches. Single crystal X-ray diffraction was carried out on an Oxford Diffraction SuperNova diffractometer with a molybdenum source. The crystals were kept at 110.0(1) K during data collection. Using Olex2,[31] the structures were solved with either the Superflip[32] structure solution program using Charge Flipping or the XS[33] structure solution program using direct methods or the Patterson method. They were refined with the ShelXL[33] refinement package using least squares minimization. After data collection of $[\mathbf{3b}]BF_4{\cdot}CH_3COCH_3$, the crystal was found to be non-merohedrally twinned, which was modeled using CrysAlisPro to obtain an HKLF 5 formatted data set. This meant that the data coverage for the minor component and hence overall was low. The crystal of $[\mathbf{4}]BF_4$ was weakly diffracting with complete data only obtained for theta less than

dx.doi.org/10.1021/om4009247 | Organometallics 2013, 32, 7407−7417

22.5°. The BF_4 anion was modeled as disordered over two positions with all B–F and F–B–F bond lengths and angles constrained to be approximately equal. A disordered mixture of DCM and pentane was observed in the asymmetric unit; however this could not be modeled satisfactorily. The contribution of the disordered solvent to the hkl file was removed using the olex2 solvent mask function, which accounted for a volume of 334 cubic angstroms and 12 electrons.

Full details of the theoretical methods used and the different isomers of complexes **7a**^{v}, **7a**^{a}, and **7a**^{m} are presented in the Supporting Information.

cis-[Ru(κ^2-OAc)$_2$(PPh_3)$_2$][19,34] and *cis*-[Ru(κ^2-O_2CPh)$_2$(PPh_3)$_2$][35] were synthesized from [$RuCl_2$(PPh_3)$_3$],[36] as described previously. HC≡CC(OH)Ph_2, HC≡CC(OH)MePh, HC≡CCH_2OH, and [Ph_3C]BF_4 were obtained from Aldrich Chemicals and HC≡CC(OH)-Me_2 from Acros Organics; all were used as supplied. [NMe_4]OAc and NaO^{t}Bu were obtained from Aldrich Chemicals and dried by heating at 50 °C under reduced pressure for 16 h prior to use.

Synthesis of [Ru(κ^2-OAc)(OC{Me}OCC{H}=CPh$_2$)(PPh_3)$_2$]BF_4, [3a]BF_4. *cis*-[Ru(κ^2-OAc)$_2$(PPh_3)$_2$] (250 mg, 0.34 mmol) and 1,1-diphenylprop-2-yn-1-ol (70 mg, 0.34 mmol) were dissolved in CH_2Cl_2 (20 mL) and stirred at room temperature for 90 min. Trityl carbenium tetrafluoroborate (111 mg, 0.34 mmol) was added, and the resulting solution stirred for 15 min. The CH_2Cl_2 was then reduced to *ca.* 3 mL and the product precipitated by the addition of pentane. After filtration, the solid product was then redissolved in CH_2Cl_2 (5 mL), and diethyl ether (7 mL) was added as a layer. After 2 days, the mother liquor was removed, and [Ru(κ^2-OAc)(OC{Me}OCC{H}=CPh$_2$)(PPh_3)$_2$]-[BF_4] (245 mg, 0.24 mmol, 71% yield) was obtained as green crystals.

The diphenyl moiety has been assigned as Ph_A and Ph_B, though the relative orientation of the rings is unknown. The peak for the C_4 carbon of Ph_B could not be located in the ^{13}C NMR spectrum; it is assumed that the peak is obscured under a resonance from the triphenyl phosphine.

NMR spectra CD_2Cl_2: ^{1}H δ_H 0.79 (s, 3H, COOCH_3), 1.31 (s, 3H, COOCH_3), 6.58 (m, 2H, ***Ph***$_A$-H$_2$), 7.26 (m, 2H, ***Ph***$_B$-H$_2$), 7.42 (m, 14H, ***Ph***$_B$-H$_3$, P***Ph***$_3$-H$_{2\ or\ 3}$), 7.45 (m, 1H, ***Ph***$_A$-H$_4$), 7.49 (m, 12H, P***Ph***$_3$-H$_{2\ or\ 3}$), 7.60 (m, 6H, P***Ph***$_3$-H$_4$), 7.65 (m, 1H, ***Ph***$_B$-H$_4$), 8.37 (s, 1H, Ru=C–C***H***=CPh$_2$). ^{31}P{^{1}H} δ_P 32.4 (s, ***P***Ph$_3$). ^{13}C{^{1}H} δ_C 17.7 (s, COO***C***H$_3$), 21.9 (s, COO***C***H$_3$), 127.7 (s, Ru=C-***C***H=CPh$_2$), 128.3 (s, ***Ph***$_A$-C$_3$), 128.4 (t, $^1J_{PC}$+$^3J_{PC}$ = 45.5 Hz, P***Ph***$_3$-C$_1$), 128.8 (s, ***Ph***$_A$-C$_2$), 129.6 (t, Σ*J* = 11.5 Hz, P***Ph***$_3$-C$_{2\ or\ 3}$), 129.7 (s, ***Ph***$_B$-C$_3$), 129.9 (s, ***Ph***$_A$-C$_4$), 130.1 (s, Ph$_B$-C$_2$), 131.9 (s, P***Ph***$_3$-C$_4$), 134.4 (t, Σ*J* = 10.1 Hz, P***Ph***$_3$-C$_{2\ or\ 3}$), 140.4 (s, ***Ph***$_{A/B}$-C$_1$), 141.2 (s, ***Ph***$_{A/B}$-C$_1$), 146.9 (s, Ru=CCH=***C***Ph$_2$), 183.2 (s, ***C***OOCH$_3$), 186.6 (s, ***C***OOCH$_3$), 279.8 (t, $^2J_{PC}$ = 9.3 Hz, Ru=***C***). ^{11}B{^{1}H} δ_B −2.1 (s, BF_4). ^{19}F δ_F −153.3 (s, $^{10}BF_4$), −153.4 (s, $^{11}BF_4$). IR (CH_2Cl_2): 1095 cm^{-1} (B–F), 1434 cm^{-1} (κ^2–OCO_{sym}), 1530 cm^{-1} (κ^2–OCO_{asym}), 1542 cm^{-1} ν(C=C), 1630 cm^{-1} ν(C=O), $\Delta\nu_{(chelate)}$ 96 cm^{-1}. MS (ESI): *m*/*z* 935.1998 (calculated for $C_{55}H_{47}{}^{102}RuP_2O_4$ [M]$^+$ = 935.2002, Δ = 0.4 mDa), *m*/*z* 673.1079 (calculated for $C_{37}H_{32}{}^{102}RuPO_4$ [M]$^+$ −PPh_3 = 673.1086, Δ = 0.7 mDa), *m*/*z* 613.0861 (calculated for $C_{35}H_{28}{}^{102}RuPO_2$ [M − H]$^+$ −PPh_3 −AcO = 613.0874, Δ = 1.5 mDa; MS/MS showed that the lower mass species are observed due to fragmentation in the spectrometer). Anal. for $C_{55}H_{47}BF_4O_4P_2Ru$, calcd: C, 64.65; H, 4.65. Found: C, 64.00; H, 4.67.

Synthesis of [Ru(κ^2-OAc)(OC{Me}OCC{H}=CMe$_2$)(PPh_3)$_2$]BF_4, [3b]BF_4. [Ru(κ^2-OAc)(OC{Me}OCC{H}=CMe$_2$)(PPh_3)$_2$][BF_4] (174 mg, 0.20 mmol, 58% yield) was prepared in a similar manner to [**3a**]BF_4 and was obtained as purple crystals from *cis*-[Ru(κ^2-OAc)$_2$-(PPh_3)$_2$] (250 mg, 0.34 mmol), 2-methyl-3-butyn-2-ol (32.5 μL, 0.34 mmol), and trityl carbenium tetrafluoroborate (111 mg, 0.34 mmol) in CH_2Cl_2 (20 mL).

NMR spectra CD_2Cl_2: ^{1}H δ_H 0.77 (s, 3H, COOCH_3), 1.40 (s, 3H, COOCH_3), 1.74 (s, 3H, C***Me***$_2$), 1.80 (s, 3H, C***Me***$_2$), 7.37 (m, 12H, P***Ph***$_3$-H$_{2\ or\ 3}$), 7.45 (m, 12H, P***Ph***$_3$ -H$_{2\ or\ 3}$), 7.54 (m, 6H, P***Ph***$_3$-H$_4$), 7.69 (s, 1H, Ru=C–C***H***=CMe$_2$). ^{31}P{^{1}H} δ_P 32.6 (s, PPh_3); ^{13}C{^{1}H} δ_C 18.5 (s, COOCH_3), 22.1 (s, COOCH_3), 24.1 (s, C***Me***$_2$), 30.4 (s, C***Me***$_2$), 128.3 (t, $^1J_{PC}$+$^3J_{PC}$ = 45.7 Hz, P***Ph***$_3$-C$_1$), 129.5 (t, Σ*J* = 10.2 Hz, P***Ph***$_3$-C$_{2\ or\ 3}$), 130.9 (s, Ru=C-***C***H=CMe$_2$), 131.9 (s, P***Ph***$_3$-C$_4$), 134.3 (t, Σ*J* = 11.7 Hz, P***Ph***$_3$-C$_{2\ or\ 3}$), 152.7 (s, Ru=CCH=***C***Me$_2$), 183.5 (s, ***C***OOCH$_3$), 186.4 (s, ***C***OOCH$_3$), 284.9 (t, $^2J_{PC}$ = 9.2 Hz, Ru=***C***). ^{11}B{^{1}H} δ_B −2.1 (s, BF_4). ^{19}F δ_F −153.3 (s, $^{10}BF_4$), −153.4 (s, $^{11}BF_4$). IR (CH_2Cl_2): 1096 cm^{-1} (B–F), 1435 cm^{-1} (κ^2–OCO_{sym}), 1527 cm^{-1} ν(C=C), 1631 cm^{-1} ν(C=O), 1590 cm^{-1} (κ^2–OCO_{asym}), $\Delta\nu_{(chelate)}$ 155 cm^{-1}. MS (ESI): *m*/*z* 811.1684 (calculated for $C_{45}H_{43}{}^{102}RuP_2O_4$ [M]$^+$ = 811.1687, Δ = 0.3 mDa), [M]$^+$, *m*/*z* 549.0772 (calculated for $C_{27}H_{28}{}^{102}RuPO_4$ [M]$^+$ −PPh_3 = 549.0770, Δ = 0.2 mDa). Anal. for $C_{45}H_{43}$ $RuP_2O_4BF_4$ calcd: C, 60.21; H, 4.83. Found: C, 59.53; H, 5.08.

Synthesis of [Ru(κ^2-OAc)(OC{Me}OCC{H}=CPhMe)(PPh_3)$_2$]-BF_4, [3c]BF_4. [Ru(κ^2-OAc)(OC{Me}OCC{H}=CPhMe)(PPh_3)$_2$]-[BF_4] (170 mg, 0.177 mmol, 53% yield) was prepared in a similar manner to [**3a**]BF_4 and was obtained as a dark green powder from *cis*-[Ru(κ^2-OAc)$_2$(PPh_3)$_2$] (250 mg, 0.336 mmol), 2-phenyl-3-butyn-2-ol (49 mg, 0.336 mmol), and trityl carbenium tetrafluoroborate (111 mg, 0.336 mmol) in CH_2Cl_2 (20 mL).

NMR spectra CD_2Cl_2: ^{1}H δ_H 0.86 (s, 3H, COOCH_3), 1.82 (s, 3H,CPhCH_3), 1.92 (s, 3H, COOCH_3), 7.46 (m, 12H, P***Ph***$_3$-H$_{2\ or\ 3}$), 7.52 (t, $^3J_{HH}$ = 7.6 Hz, 12H, P***Ph***$_3$H$_{2\ or\ 3}$), 7.57 (d, $^3J_{HH}$ = 7.0 Hz, 2H, ***Ph***-H$_{2\ or\ 3}$), 7.62 (m, 8H, PPh_3-H$_4$ and ***Ph***-H$_{2\ or\ 3}$), 7.67 (t, $^3J_{HH}$ = 7.0 Hz, 1H, ***Ph***-H$_4$), 8.10 (s, 1H, Ru=C–C***H***=CPh$_2$). ^{31}P{^{1}H} δ_P 32.3 (s, PPh_3). ^{13}C{^{1}H} δ_C 19.6 (s, COO***C***H$_3$), 22.9 (s, COO***C***H$_3$), 23.2 (s, CPh***C***H$_3$), 128.6 (s, Ru=C-***C***H=CPh$_2$), 129.4 (t, $^1J_{PC}$+$^3J_{PC}$ = 46.5 Hz, P***Ph***$_3$-C$_1$), 130.6 (t, Σ*J* = 10.4 Hz, P***Ph***$_3$-C$_{2\ or\ 3}$), 130.9 (s, ***Ph***), 131.5 (s, ***Ph***), 132.4 (s, ***Ph***), 133.1 (s, P***Ph***$_3$-C$_4$), 135.4 (t, Σ*J* = 12.1 Hz, P***Ph***$_3$-C$_{2\ or\ 3}$), 144.0 (s, ***Ph***-C$_1$), 148.7 (s, Ru=CCH=***C***PhMe), 184.7 (s, ***C***OOCH$_3$), 187.7 (s, ***C***OOCH$_3$), 284.3 (t, $^2J_{PC}$ = 8.6 Hz, Ru=***C***). ^{11}B{^{1}H} δ_B −2.2 (s, BF_4). ^{19}F δ_F −153.3 (s, $^{10}BF_4$), −153.4 (s, $^{11}BF_4$). IR (CH_2Cl_2): 1098 cm^{-1} (B–F), 1433 cm^{-1} (κ^2-OCO_{sym}), 1554 cm^{-1} ν(C=C), 1579 cm^{-1} (κ^2-OCO_{asym}), 1631 cm^{-1} ν(C=O), $\Delta\nu_{(chelate)}$ 146 cm^{-1}. MS (ESI): *m*/*z* 873.1830 (calculated for $C_{50}H_{45}{}^{102}RuP_2O_4$ [M]$^+$ = 873.1845, Δ = 1.5 mDa), *m*/*z* 813.1624 (calculated for $C_{48}H_{41}{}^{102}RuP_2O_2$ [M − H]$^+$ −AcO = 813.1632, Δ = 1.0 mDa), *m*/*z* 611.0912 (calculated for $C_{32}H_{30}{}^{102}RuPO_4$ [M]$^+$ −PPh_3 = 611.0929, Δ = 1.7 mDa), *m*/*z* 551.0695 (calculated for $C_{30}H_{26}{}^{102}RuPO_2$ [M − H]$^+$ −PPh_3 −AcO = 551.0717, Δ = 2.2 mDa). Anal. for $C_{50}H_{45}RuP_2O_4BF_4$ calcd: C, 62.58; H, 4.73; Found: C, 60.27; H, 4.52.

Synthesis of [Ru(κ^2-O_2CPh)(OC{Ph}OCC{H}=CPh$_2$)(PPh_3)$_2$]BF_4 [3a^{Bz}]BF_4. [Ru(κ^2-O_2CPh)(OC{Ph}OCC{H}=CPh$_2$)(PPh_3)$_2$][BF_4] (275 mg, 0.27 mmol, 80% yield) was prepared in a similar manner to [**3a**]BF_4 and was obtained as dark green crystals from *cis*-[Ru(κ^2-O_2CPh)$_2$(PPh_3)$_2$] (250 mg, 0.29 mmol),1,1-diphenylprop-2-yn-1-ol (60 mg, 0.29 mmol), and trityl carbenium tetrafluoroborate (95 mg, 0.29 mmol) in CH_2Cl_2 (20 mL).

The diphenyl moiety has been assigned as Ph_A and Ph_B, though the relative orientation of the rings is unknown. Some resonances in the ^{13}C NMR spectrum could not be unequivocally assigned.

NMR spectra CD_2Cl_2: ^{1}H δ_H 6.52 (br s, 2H, ***Ph***), 6.74 (m, 2H, ***Ph***$_A$-H$_2$), 7.11 (m, 2H, ***Ph***), 7.22 (m, 6H, ***Ph***$_B$-H$_2$, COO***Ph***-H$_2$ and Ph), 7.32 (m, 13H, P***Ph***$_3$-H$_{2\ or\ 3}$, ***Ph***), 7.40 (m, 8H, P***Ph***$_3$-H$_4$ and ***Ph***$_A$-H$_3$), 7.45 (m, 15H, P***Ph***$_3$-H$_{2\ or\ 3}$, ***Ph***), 7.57 (tt, 1H, COO***Ph***-H$_4$), 7.64 (tt, 1H, ***Ph***-H$_4$), 7.69 (tt, 1H, ***Ph***), 8.56 (s, 1H, Ru=C–C***H***=CPh$_2$). ^{31}P{^{1}H} δ_P 31.5 (s, PPh_3). ^{13}C{^{1}H} δ_C 123.8 (s, COO***Ph***-C$_1$), 128.9 (s, ***Ph***), 129.5 (t, $^1J_{PC}$+$^3J_{PC}$ = 46.0 Hz, P***Ph***$_3$-C$_1$), 129.5 (s, Ru=C-***C***H=CPh$_2$), 129.7 (s, COOPh−C$_2$), 130.1 (s, ***Ph***$_A$-C$_{3\ or\ 4}$), 130.3 (s, ***Ph***$_A$-C$_2$), 130.4 (s, ***Ph***), 130.5 (t, Σ*J* = 9.7 Hz, P***Ph***$_3$-C$_{2\ or\ 3}$), 130.8 (s, ***Ph***), 130.9 (s, ***Ph***), 131.3 (s, ***Ph***), 132.2 (s, COO***Ph***-C$_1$), 132.2 (s, ***Ph***), 132.7 (s, P***Ph***$_3$-C$_4$), 133.0 (s, ***Ph***), 133.7 (s, ***Ph***), 135.5 (t, Σ*J* = 11.6 Hz, P***Ph***$_3$-C$_{2\ or\ 3}$), 138.1 (s, COO***Ph***-C$_4$), 142.5 (s, ***Ph***-C$_1$), 143.1 (***Ph***-C$_1$), 147.7 (s, Ru=CCH=***C***PhMe), 179.7 (s, ***C***OOPh), 182.0 (s, ***C***OOPh), 281.1 (t, $^2J_{PC}$ = 9.6 Hz, Ru=***C***). ^{11}B δ_B −2.1 (s, BF_4). ^{19}F δ_F −153.4 (s, $^{10}BF_4$), −153.5 (s, $^{11}BF_4$). IR (CH_2Cl_2): 1095 cm^{-1} (B–F), 1434 cm^{-1} (κ^2–OCO_{sym}), 1541 cm^{-1} ν(C=C), 1575 cm^{-1} (κ^2–OCO_{asym}), 1602 cm^{-1} ν(C=O), $\Delta\nu_{(chelate)}$ 141 cm^{-1}. MS (ESI): *m*/*z* 1059.2280 (calculated for $C_{65}H_{51}{}^{102}RuP_2O_4$ [M]$^+$ = 1059.2319, Δ = 3.9 mDa), *m*/*z* 797.1371 (calculated for $C_{47}H_{36}{}^{102}RuPO_4$ [M]$^+$ −PPh_3 = 797.1402, Δ = 3.1 mDa), *m*/*z* 675.1028 (calculated for $C_{40}H_{30}{}^{102}RuPO_2$ [M − H]$^+$ −PPh_3 −AcO = 675.1032, Δ = 0.4 mDa). Anal. for $C_{65}H_{51}$ $RuP_2O_4BF_4$ calcd: C, 68.12; H, 4.49. Found: C, 66.70; H, 4.44.

dx.doi.org/10.1021/om4009247 | *Organometallics* 2013, 32, 7407–7417

Synthesis of [Ru(κ^2-OAc)(κ^1-OAc)(PPh_3)$_2$(=C=C=CPh_2)], 5. [Ru(κ^2-OAc)(OC{Me}OCC{H}=CPh_2)(PPh_3)$_2$]BF_4, [**3a**]BF_4 (100 mg, 0.1 mmol), and sodium *tert*-butoxide (19 mg, 0.15 mmol) were dissolved in CH_2Cl_2 and stirred at RT for 15 min. The CH_2Cl_2 was then removed and the residue extracted with ether. The resulting solution was then reduced slightly before being placed in the freezer overnight. This either produced a red solid of approximately 83% purity by ^{31}P NMR (20 mg, 0.020 mmol, 22% yield) or analytically pure red needle like crystals (5 mg, 0.005 mmol, 5% yield).

NMR spectra CD_2Cl_2: ^{1}H δ_H 0.91 (s, 6H, COO***C***H$_3$), 6.93 (at, 7.8 Hz, 4H, Ph-H$_2$), 7.15 (ad, 8.2 Hz, 4H, ***Ph***-H$_3$), 7.29 (at, 7.3 Hz, 12H, P***Ph***$_3$-H$_{2\ or\ 3}$), 7.33 (ad, 7.0 Hz, 6H, P***Ph***$_3$-H$_4$), 7.36 (m, 6H, ***Ph***-H$_4$), 7.52 (m, 12H, P***Ph***$_3$-H$_{2\ or\ 3}$). ^{31}P{^{1}H} δ_P 32.6 (s, PPh_3). ^{13}C{^{1}H} δ_C 23.9 (s, COO***C***H$_3$), 129.2 (s, ***Ph***-C$_4$), 129.4 (t, ΣJ = 9.6 Hz, PPh_3-C$_{2\ or\ 3}$), 129.9 (s, ***Ph***-C$_3$), 130.0 (s, ***Ph***-C$_2$), 131.4 (s, P***Ph***$_3$-C$_4$), 132.6 (t, $^1J_{PC}$+$^3J_{PC}$ = 41.4 Hz, P***Ph***$_3$-C$_1$), 136.2 (t, ΣJ = 12.1 Hz, P***Ph***$_3$-C$_{2\ or\ 3}$), 147.3 (s, Ru=C=C=***C***), 181.7 (s, ***C***OOCH$_3$), 232.8 (t, $^3J_{PC}$ = 5.50 Hz, Ru=***C***=C), 305.0 (t, $^2J_{PC}$ = 17.3 Hz, Ru=***C***). IR (CH_2Cl_2): 1366 cm^{-1} (κ^1-OCO$_{sym}$), 1435 cm^{-1} (P-Ph), 1459 cm^{-1} (κ^2-OCO$_{sym}$), 1537 cm^{-1} (κ^2-OCO$_{asym}$), 1624 cm^{-1} (κ^1-OCO$_{asym}$), 1911 cm^{-1} ν(C=C=C), $\Delta\nu_{(uni)}$ 258 cm^{-1}, $\Delta\nu_{(chelate)}$ 78 cm^{-1}. MS (ESI), *m*/*z* 957.1781 (calculated for $C_{55}H_{46}{}^{102}RuP_2O_4Na$ [M + Na]$^+$ = 957.1822, Δ = 4.1 mDa), *m*/*z* 935.1993 (calculated for $C_{55}H_{47}{}^{102}RuP_2O_4$ [M + H]$^+$ = 935.2002, Δ = 0.9 mDa). MS (LIFDI): *m*/*z* 934.13 [M]$^+$, *m*/*z* 892.14 [M + H]$^+$ −Ac. Anal. for $C_{55}H_{46}RuP_2O_4$ calcd: C, 70.73; H, 4.96. Found: C, 70.33; H, 5.00.

Spectroscopic Data for [Ru(κ^2-OAc)(CH=CPh_2)(CO)(PPh_3)$_2$], 6. Complex **6** was observed as a minor impurity in samples of **5**. In contaminated samples, the following spectroscopic data were assigned to **6**.

NMR CD_2Cl_2 ^{1}H NMR δ_H 0.47 (s, COO***C***H$_3$). ^{31}P{^{1}H} δ_P 38.1 (s, PPh_3). MS (ESI) *m*/*z* 833.1649 (calculated for $C_{51}H_{41}{}^{102}RuP_2O$ [M − H]$^+$ −AcO = 833.1684, Δ = 3.5 mDa).

Synthesis of [Ru(κ^2-OAc)(κ^1-OAc)(PPh_3)$_2$(=C=CH-C(Me)=CH_2)], 7a. [Ru(κ^2-OAc)(OC{Me}OCC{H}=C(Me)$_2$)(PPh_3)$_2$]BF_4, [**3b**]BF_4, (100 mg, 0.111 mmol) and tetramethylammonium acetate (17 mg, 0.125 mmol) were suspended in CH_2Cl_2 (10 mL). Two minutes of sonication aided dissolution, and the subsequent reaction was observed by a color change from dark purple to orange. After 10 min of stirring at room temperature, the solvent was removed and the residue extracted with diethyl ether. Removal of the solvent yielded an orange powder (18 mg, 0.022 mmol, 20% yield).

NMR CD_2Cl_2 ^{1}H δ_H 0.84 (s, 6H, COOC***H***$_3$), 1.31 (s, 3H, Ru=C=C(H)C(C***H***$_3$)CH$_2$), 3.75 (s, 1H, Ru=C=C(H)C(CH$_3$)C***H***$_2$), 3.48 (s, 1H, Ru=C=C(H)C(CH$_3$)C***H***$_2$), 5.21 (t, 3.8 Hz, 1H, Ru=C=C***H***), 7.40 (t, 7.2 Hz, 12H, P***Ph***$_3$−H$_{2\ or\ 3}$), 7.44−7.54 (m, 18H, P***Ph***$_3$−H$_{2\ or\ 3}$ and P***Ph***$_3$−H$_4$). ^{31}P{^{1}H} δ_P 33.4 (s, PPh_3). ^{13}C{^{1}H} δ_C 23.5 (s, COO***C***H$_3$), 23.7 (Ru=C=C(H)C(***C***H$_3$)CH$_2$), 104.6 (s, Ru=C=C(H)C(Me)***C***H$_2$), 117.4 (s, Ru=C=***C***H), 129.5 (t, ΣJ = 10.1 Hz, P***Ph***$_3$-C$_{2\ or\ 3}$), 131.0 (t, $^1J_{PC}$+$^3J_{PC}$ = 43.3 Hz, P***Ph***$_3$-C$_1$), 131.6 (s, P***Ph***$_3$-C$_4$), 136.4 (t, ΣJ = 10.8 Hz, P***Ph***$_3$-C$_{2\ or\ 3}$), 137.4 (s, Ru=C=C(H)***C***(CH$_3$)-CH$_2$), 181.0 (s, ***C***OOCH$_3$), 360.4 (t, $^2J_{PC}$ = 17.0 Hz, Ru=***C***). IR (CH_2Cl_2): 1367 cm^{-1} (κ^1−OCO$_{sym}$), 1434 cm^{-1} (P-Ph), 1466 cm^{-1} (κ^2-OCO$_{sym}$), 1552 cm^{-1} (κ^2-OCO$_{asym}$), 1617 cm^{-1} (κ^1-OCO$_{asym}$), 1628 cm^{-1} ν(C=C), $\Delta\nu_{(uni)}$ 250 cm^{-1}, $\Delta\nu_{(chelate)}$ 86 cm^{-1}. MS (ESI): *m*/*z* 811.1637 (calculated for $C_{45}H_{43}{}^{102}RuP_2O_4$ [M + H]$^+$ = 811.1687, Δ = 5.0 mDa). MS (LIFDI): *m*/*z* 810.19 [M]$^+$.

Synthesis of [Ru(κ^2-OAc)(κ^1-OAc)(PPh_3)$_2$(=C=CH-C(Ph)=CH_2)], 7b. [Ru(κ^2-OAc)(OC{Me}OCC{H}=C(Me)Ph)(PPh_3)$_2$]-BF_4, [**3c**]BF_4 (100 mg, 0.104 mmol), and tetramethylammonium acetate (15 mg, 0.114 mmol) were suspended in CH_2Cl_2 (10 mL). Two minutes of sonication aided dissolution, and the subsequent reaction was observed by a color change from dark green to orange. After 10 min of stirring at RT, the solvent was removed and the residue extracted with diethyl ether. Removal of the solvent yielded [Ru(κ^2-OAc)(κ^1-OAc)(PPh_3)$_2$(=C=CH-C(Ph)=CH_2)] as an orange powder (15 mg, 0.017 mmol, 16% yield). The compound was found to decompose in solution too fast for a ^{13}C NMR spectrum to be recorded.

NMR spectra CD_2Cl_2: ^{1}H δ_H 0.84 (s, 6H, COOC***H***$_3$), 4.70 (s, 1H, Ru=C=C(H)C(Ph)C***H***$_2$), 4.87 (s, 1H, Ru=C=C(H)C(Ph)C***H***$_2$), 5.17 (t, 3.6 Hz, 1H, Ru=C=C(***H***), 6.84−7.57 (39H, ***Ph***). ^{31}P{^{1}H} NMR δ_P 34.6 (s, PPh_3). IR (CH_2Cl_2): 1366 cm^{-1} (κ^1-OCO$_{sym}$), 1436 cm^{-1} (P-Ph), 1465 cm^{-1} (κ^2-OCO$_{sym}$), 1534 cm^{-1} (κ^2-OCO$_{asym}$), 1617 cm^{-1} (κ^1-OCO$_{asym}$), 1932 cm^{-1} ν(C=C), $\Delta\nu_{(uni)}$ 251 cm^{-1}, $\Delta\nu_{(chelate)}$ 69 cm^{-1}. MS (ESI): *m*/*z* 873.1848 (calculated for $C_{50}H_{45}{}^{102}RuP_2O_4$ [M + H]$^+$ = 873.1845, Δ = 0.3 mDa), *m*/*z* 812.1744 (calculated for $C_{48}H_{41}{}^{102}RuP_2O_2$ [M − H]$^+$ −AcO = 812.1555, Δ = 18.9 mDa). MS (LIFDI): *m*/*z* 872.20 [M]$^+$, *m*/*z* 812.06 [M − H]$^+$ −Ac.

Reaction of [Ru(κ^2-OAc)(κ^1-OAc)(=C=CH-C(Ph)=CH_2)-(PPh_3)$_2$], 7b, with HBF_4. [Ru(κ^2-OAc)(κ^1-OAc)(=C=CH-C-(Ph)=CH_2)(PPh_3)$_2$], **7b** (20 mg, 0.023 mmol), was dissolved in CD_2Cl_2 (0.5 mL) to give an orange solution. HBF_4·Et_2O (3 μL, 0.023 mmol) was added and an immediate color change to dark green observed. The major product from this reaction was [Ru(κ^2-OAc)(OC{Me}OCC{H}=CPhMe)(PPh_3)$_2$]BF_4, [**3c**]BF_4, as shown by comparison of the spectroscopic data with an authentic sample.

■ ASSOCIATED CONTENT

Supporting Information

Details of theoretical methods used, details of data collection and structural refinement for X-ray diffraction experiments in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC 961152 [**3a**]BF_4·$(CH_2Cl_2)_{1.5}$, 961153 [**3b**]BF_4·CH_3COCH_3, 961154 [**3a**^{Bz}]BF_4·CH_2Cl_2, 961155 [**4**]BF_4, 961156 [**5**]·$(Et_2O)_{0.5}$, and 961157 [**6**] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful to the EPSRC and University of York for funding (EPSRC DTA studentship to E.J.S.). This work was supported in-part by the EPSRC - 'ENERGY' grant, ref. no. EP/K031589/1. Insightful discussions with Professor Odile Eisenstein (Montpellier) and Dr. John Slattery (York) are gratefully acknowledged. We thank Miss Natalie Pridmore and Dr. Sam Hart for assistance with X-ray diffraction experiments.

■ REFERENCES

(1) (a) Bruneau, C.; Dixneuf, P. H. *Acc. Chem. Res.* **1998**, *32*, 311. (b) Lynam, J. M. *Chem.—Eur. J.* **2010**, *16*, 8238. (c) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (d) Antonova, A. B. *Coord. Chem. Rev.* **2007**, *251*, 1521.

(2) (a) Coletti, C.; Marrone, A.; Re, N. *Acc. Chem. Res.* **2011**, *45*, 139. (b) Cadierno, V.; Gimeno, J. *Chem. Rev.* **2009**, *109*, 3512. (c) Werner, H. *Chem. Commun.* **1997**, 903.

(3) (a) Ilg, K.; Werner, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 1632. (b) Re, N.; Sgamellotti, A.; Floriani, C. *Organometallics* **2000**, *19*, 1115. (c) Cadierno, V.; Gamasa, M. P.; Gimeno, J. *Eur. J. Inorg. Chem.* **2001**, 571. (d) Ilg, K.; Werner, H. *Chem.—Eur. J.* **2002**, *8*, 2812. (e) Marrone, A.; Re, N. *Organometallics* **2002**, *21*, 3562. (f) Marrone, A.; Coletti, C.; Re, N. *Organometallics* **2004**, *23*, 4952. (g) Venkatesan, K.; Blacque, O.; Fox, T.; Alfonso, M.; Schmalle, H. W.; Berke, H. *Organometallics* **2004**, *23*, 4661. (h) Cadierno, V.; Gamasa, M. P.; Gimeno, J. *Coord. Chem. Rev.* **2004**, *248*, 1627. (i) Bruce, M. I.; Ellis, B. G.; Skelton, B. W.; White, A. H.

J. Organomet. Chem. **2005**, *690*, 1772. (j) Dede, M.; Drexler, M.; Fischer, H. *Organometallics* **2007**, *26*, 4294.
(4) (a) Bruneau, C.; Dixneuf, P. H. *Angew. Chem., Int. Ed.* **2006**, *45*, 2176. (b) Trost, B. M.; Frederiksen, M. U.; Rudd, M. T. *Angew. Chem., Int. Ed.* **2005**, *44*, 6630. (c) Trost, B. M.; McClory, A. *Chem.—Asian J.* **2008**, *3*, 164.
(5) (a) Tokunaga, M.; Wakatsuki, Y. *Angew. Chem., Int. Ed.* **1998**, *37*, 2867. (b) Grotjahn, D. B.; Incarvito, C. D.; Rheingold, A. L. *Angew. Chem., Int. Ed.* **2001**, *40*, 3884. (c) Suzuki, T.; Tokunaga, M.; Wakatsuki, Y. *Org. Lett.* **2001**, *3*, 735.
(6) (a) Nishibayashi, Y.; Uemura, S. *Curr. Org. Chem.* **2006**, *10*, 135. (b) Fukamizu, K.; Miyake, Y.; Nishibayashi, Y. *J. Am. Chem. Soc.* **2008**, *130*, 10498. (c) Kanao, K.; Matsuzawa, H.; Miyake, Y.; Nishibayashi, Y. *Synthesis—Stuttgart* **2008**, 3869. (d) Miyake, Y.; Endo, S.; Nomaguchi, Y.; Yuki, M.; Nishibayashi, Y. *Organometallics* **2008**, *27*, 4017. (e) Yada, Y.; Miyake, Y.; Nishibayashi, Y. *Organometallics* **2008**, *27*, 3614. (f) Kanao, K.; Miyake, Y.; Nishibayashi, Y. *Organometallics* **2009**, *28*, 2920. (g) Nishibayashi, Y.; Miyake, Y.; Uemura, S. *J. Syn. Org. Chem. Jpn.* **2009**, *67*, 437. (h) Sakata, K.; Miyake, Y.; Nishibayashi, Y. *Chem.—Asian J.* **2009**, *4*, 81. (i) Tanabe, Y.; Kanao, K.; Miyake, Y.; Nishibayashi, Y. *Organometallics* **2009**, *28*, 1138. (j) Yamauchi, Y.; Miyake, Y.; Nishibayashi, Y. *Organometallics* **2009**, *28*, 48. (k) Kanao, K.; Miyake, Y.; Nishibayashi, Y. *Organometallics* **2010**, *29*, 2126. (l) Kanao, K.; Tanabe, Y.; Miyake, Y.; Nishibayashi, Y. *Organometallics* **2010**, *29*, 2381. (m) Yuki, M.; Miyake, Y.; Nishibayashi, Y. *Organometallics* **2010**, *29*, 5994. (n) Miyazaki, T.; Tanabe, Y.; Yuki, M.; Miyake, Y.; Nishibayashi, Y. *Organometallics* **2011**, *30*, 3194. (o) Ikeda, M.; Miyake, Y.; Nishibayashi, Y. *Chem.—Eur. J.* **2012**, *18*, 3321. (p) Motoyama, K.; Ikeda, M.; Miyake, Y.; Nishibayashi, Y. *Organometallics* **2012**, *31*, 3426. (q) Nishibayashi, Y. *Synthesis—Stuttgart* **2012**, *44*, 489. (r) Miyake, Y.; Endo, S.; Moriyama, T.; Sakata, K.; Nishibayashi, Y. *Angew. Chem. Int. Ed.* **2013**, *52*, 1758.
(7) (a) Lozano-Vila, A. M.; Monsaert, S.; Bajek, A.; Verpoort, F. *Chem. Rev.* **2010**, *110*, 4865. (b) Furstner, A.; Picquet, M.; Bruneau, C.; Dixneuf, P. H. *Chem. Commun.* **1998**, 1315. (c) Furstner, A.; Liebl, M.; Lehmann, C. W.; Picquet, M.; Kunz, R.; Bruneau, C.; Touchard, D.; Dixneuf, P. H. *Chem.—Eur. J.* **2000**, *6*, 1847. (d) Dragutan, I.; Dragutan, V. *Platinum Met. Rev.* **2006**, *50*, 81. (e) Sauvage, X.; Borguet, Y.; Zaragoza, G.; Demonceau, A.; Delaude, L. *Adv. Synth. Catal.* **2009**, *351*, 441. (f) Antonucci, A.; Bassetti, M.; Bruneau, C.; Dixneuf, P. H.; Pasquini, C. *Organometallics* **2010**, *29*, 4524. (g) Delaude, L.; Demonceau, A. *Dalton Trans.* **2012**, *41*, 9257.
(8) (a) Datta, S.; Chang, C. L.; Yeh, K. L.; Liu, R. S. *J. Am. Chem. Soc.* **2003**, *125*, 9294. (b) Bustelo, E.; Dixneuf, P. H. *Adv. Synth. Catal.* **2005**, *347*, 393. (c) Bustelo, E.; Dixneuf, P. H. *Adv. Synth. Catal.* **2007**, *349*, 933.
(9) (a) Roth, G.; Fischer, H.; Meyer-Friedrichsen, T.; Heck, J.; Houbrechts, S.; Persoons, A. *Organometallics* **1998**, *17*, 1511. (b) Szesni, N.; Drexler, M.; Maurer, J.; Winter, R. F.; de Montigny, F.; Lapinte, C.; Steffens, S.; Heck, J.; Weibert, B.; Fischer, H. *Organometallics* **2006**, *25*, 5774. (c) Venkatesan, K.; Blacque, O.; Berke, H. *Organometallics* **2006**, *25*, 5190. (d) Morrall, J. P.; Dalton, G. T.; Humphrey, M. G.; Samoc, M. In *Advances in Organometallic Chemistry*; West, R., Hill, A. F., Fink, M. J., Eds.; Academic Press: New York, 2008; Vol. *55*, p 61. (e) Kessler, F.; Curchod, B. F. E.; Tavernelli, I.; Rothlisberger, U.; Scopelliti, R.; Di Censo, D.; Graetzel, M.; Nazeeruddin, M. K.; Baranoff, E. *Angew. Chem., Int. Ed.* **2012**, *51*, 8030.
(10) (a) Cowley, M. J.; Lynam, J. M.; Slattery, J. M. *Dalton Trans.* **2008**, 4552. (b) Johnson, D. G.; Lynam, J. M.; Slattery, J. M.; Welby, C. E. *Dalton Trans.* **2010**, *39*, 10432.
(11) (a) Ikeda, Y.; Yamaguchi, T.; Kanao, K.; Kimura, K.; Kamimura, S.; Mutoh, Y.; Tanabe, Y.; Ishii, Y. *J. Am. Chem. Soc.* **2008**, *130*, 16856. (b) Mutoh, Y.; Ikeda, Y.; Kimura, Y.; Ishii, Y. *Chem. Lett.* **2009**, *38*, 534. (c) Mutoh, Y.; Imai, K.; Kimura, Y.; Ikeda, Y.; Ishii, Y. *Organometallics* **2010**, *30*, 204. (d) Mutoh, Y.; Kimura, Y.; Ikeda, Y.; Tsuchida, N.; Takano, K.; Ishii, Y. *Organometallics* **2012**, *31*, 5150. (e) Otsuka, M.; Tsuchida, N.; Ikeda, Y.; Kimura, Y.; Mutoh, Y.; Ishii, Y.; Takano, K. *J. Am. Chem. Soc.* **2012**, *134*, 17746. (f) Kanao, K.; Ikeda, Y.; Kimura, K.; Kamimura, S.; Tanabe, Y.; Mutoh, Y.; Iwasaki, M.; Ishii, Y. *Organometallics* **2013**, *32*, 527.
(12) Selegue, J. P. *Organometallics* **1982**, *1*, 217.
(13) (a) Grime, R. W.; Helliwell, M.; Hussain, Z. I.; Lancashire, H. N.; Mason, C. R.; McDouall, J. J. W.; Mydlowski, C. M.; Whiteley, M. W. *Organometallics* **2008**, *27*, 857. (b) Asay, M.; Donnadieu, B.; Schoeller, W. W.; Bertrand, G. *Angew. Chem. Int. Ed.* **2009**, *48*, 4796. (c) Byrne, L. T.; Koutsantonis, G. A.; Sanford, V.; Selegue, J. P.; Schauer, P. A.; Iyer, R. S. *Organometallics* **2010**, *29*, 1199. (d) Chen, C.-C.; Cheng, P.-C.; Huang, S.-L.; Lin, Y.-C.; Liu, Y.-H. *Chem.—Asian J.* **2011**, *6*, 3122. (e) Costin, S.; Widaman, A. K.; Rath, N. P.; Bauer, E. B. *Eur. J. Inorg. Chem.* **2011**, 1269. (f) Hyder, I.; Jimenez-Tenorio, M.; Carmen Puerta, M.; Valerga, P. *Organometallics* **2011**, *30*, 723. (g) Koutsantonis, G. A.; Schauer, P. A.; Skelton, B. W. *Organometallics* **2011**, *30*, 2680. (h) Coletti, C.; Gonsalvi, L.; Guerriero, A.; Marvelli, L.; Peruzzini, M.; Reginato, G.; Re, N. *Organometallics* **2012**, *31*, 57. (i) Lichtenheldt, M.; Kress, S.; Blechert, S. *Molecules* **2012**, *17*, 5177. (j) Pino-Chamorro, J. A.; Bustelo, E.; Puerta, M. C.; Valerga, P. *Organometallics* **2009**, *28*, 1546.
(14) (a) Cadierno, V.; Conejero, S.; Gamasa, M. P.; Gimeno, J.; Rodríguez, M. A. *Organometallics* **2001**, *21*, 203. (b) Selegue, J. P.; Young, B. A.; Logan, S. L. *Organometallics* **1991**, *10*, 1972. (c) Rappert, T.; Nurnberg, O.; Mahr, N.; Wolf, J.; Werner, H. *Organometallics* **1992**, *11*, 4156. (d) Matsuzaka, H.; Koizumi, H.; Takagi, Y.; Nishio, M.; Hidai, M. *J. Am. Chem. Soc.* **1993**, *115*, 10396. (e) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; GonzalezCueva, M.; Lastra, E.; Borge, J.; GarciaGranda, S.; PerezCarreno, E. *Organometallics* **1996**, *15*, 2137. (f) Esteruelas, M. A.; Gomez, A. V.; Lopez, A. M.; Oro, L. A. *Organometallics* **1996**, *15*, 878. (g) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Borge, J.; GarciaGranda, S. *Organometallics* **1997**, *16*, 3178. (h) Jia, G. C.; Lau, C. P. *J. Organomet. Chem.* **1998**, *565*, 37. (i) Bustelo, E.; Tenorio, M. J.; Puerta, M. C.; Valerga, P. *Organometallics* **1999**, *18*, 4563. (j) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Lastra, E. *J. Chem. Soc., Dalton Trans.* **1999**, 3235. (k) Bustelo, E.; Jimenez-Tenorio, M.; Puerta, M. C.; Valerga, P. *Eur. J. Inorg. Chem.* **2001**, 2391. (l) Ghebreyessus, K. Y.; Nelson, J. H. *Inorg. Chem. Commun.* **2003**, *6*, 1044. (m) Pavlik, S.; Mereiter, K.; Puchberger, M.; Kirchner, K. *J. Organomet. Chem.* **2005**, *690*, 5497. (n) Hudson, D. M.; Valente, E. J.; Schachner, J.; Limbach, M.; Mueller, K.; Schanz, H.-J. *ChemCatChem.* **2011**, *3*, 297.
(15) (a) Fürstner, A.; Guth, O.; Düffels, A.; Seidel, G.; Liebl, M.; Gabor, B.; Mynott, R. *Chem.—Eur. J.* **2001**, *7*, 4811. (b) Shaffer, E. A.; Chen, C.-L.; Beatty, A. M.; Valente, E. J.; Schanz, H.-J. *J. Organomet. Chem.* **2007**, *692*, 5221.
(16) (a) Jafarpour, L.; Schanz, H. J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 5416. (b) Clavier, H.; Nolan, S. P. *Chem.—Eur. J.* **2007**, *13*, 8029. (c) Boeda, F.; Bantreil, X.; Clavier, H.; Nolan, S. P. *Adv. Synth. Catal.* **2008**, *350*, 2959. (d) Boeda, F.; Clavier, H.; Nolan, S. P. *Chem. Commun.* **2008**, 2726. (e) de Fremont, P.; Clavier, H.; Montembault, V.; Fontaine, L.; Nolan, S. P. *J. Mol. Catal. A: Chem.* **2008**, *283*, 108. (f) Clavier, H.; Urbina-Blanco, C. A.; Nolan, S. P. *Organometallics* **2009**, *28*, 2848. (g) Broggi, J.; Urbina-Blanco, C. A.; Clavier, H.; Leitgeb, A.; Slugovc, C.; Slawin, A. M. Z.; Nolan, S. P. *Chem.—Eur. J.* **2010**, *16*, 9215. (h) Clavier, H.; Broggi, J.; Nolan, S. P. *Eur. J. Org. Chem.* **2010**, 937. (i) Urbina-Blanco, C. A.; Bantreil, X.; Clavier, H.; Slawin, A. M. Z.; Nolan, S. P. *Beilstein J. Org. Chem.* **2010**, *6*, 1120. (j) Urbina-Blanco, C. A.; Leitgeb, A.; Slugovc, C.; Bantreil, X.; Clavier, H.; Slawin, A. M. Z.; Nolan, S. P. *Chem.—Eur. J.* **2011**, *17*, 5045. (k) Urbina-Blanco, C. A.; Manzini, S.; Gomes, J. P.; Doppiu, A.; Nolan, S. P. *Chem. Commun.* **2011**, *47*, 5022. (l) Ablialimov, O.; Kedziorek, M.; Torborg, C.; Malinska, M.; Wozniak, K.; Grela, K. *Organometallics* **2012**, *31*, 7316. (m) Bantreil, X.; Poater, A.; Urbina-Blanco, C. A.; Bidal, Y. D.; Falivene, L.; Randall, R. A. M.; Cavallo, L.; Slawin, A. M. Z.; Cazin, C. S. J. *Organometallics* **2012**, *31*, 7415. (n) Manzini, S.; Blanco, C. A. U.; Slawin, A. M. Z.; Nolan, S. P. *Organometallics* **2012**, *31*, 6514. (o) van Lierop, B. J.; Reckling, A. M.; Lummiss, J. A. M.; Fogg, D. E. *ChemCatChem.* **2012**, *4*, 2020. (p) Borguet, Y.; Zaragoza, G.; Demonceau, A.; Delaude, L. *Dalton Trans.* **2013**, *42*, 7287. (q) Poater, A.; Falivene, L.; Urbina-Blanco, C. A.; Manzini, S.; Nolan, S. P.; Cavallo, L. *Dalton Trans.* **2013**, *42*, 7433. (r) Torborg, C.; Szczepaniak, G.; Zielinski, A.; Malinska, M.; Wozniak, K.; Grela, K. *Chem. Commun.*

2013, *49*, 3188. (s) Urbina-Blanco, C. A.; Poater, A.; Lebl, T.; Manzini, S.; Slawin, A. M. Z.; Cavallo, L.; Nolan, S. P. *J. Am. Chem. Soc.* **2013**, *135*, 7073.
(17) Schanz, H.-J.; Jafarpour, L.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 5187.
(18) Welby, C. E.; Eschemann, T. O.; Unsworth, C. A.; Smith, E. J.; Thatcher, R. J.; Whitwood, A. C.; Lynam, J. M. *Eur. J. Inorg. Chem.* **2012**, 1493.
(19) Lynam, J. M.; Welby, C. E.; Whitwood, A. C. *Organometallics* **2009**, *28*, 1320.
(20) Bruce, M. I.; Humphrey, M. G.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem.* **1986**, *314*, 213.
(21) Hamidov, H.; Jeffery, J. C.; Lynam, J. M. *Chem. Commun.* **2004**, 1364.
(22) Cowley, M. J.; Lynam, J. M.; Moneypenny, R. S.; Whitwood, A. C.; Wilson, A. J. *Dalton Trans.* **2009**, 9529.
(23) Bruce, M. I. *Chem. Rev.* **1998**, *98*, 2797.
(24) (a) Weigend, F. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057. (b) Eichkorn, K.; Weigend, F.; Treutler, O.; Ahlrichs, R. *Them. Chem. Acc.* **1997**, *97*, 119. (c) Deglmann, P.; Furche, F.; Ahlrichs, R. *Chem. Phys. Lett.* **2002**, *362*, 511. (d) Arnim, M. v.; Ahlrichs, R. *J. Chem. Phys.* **1999**, *111*, 9183. (e) Treutler, O.; Ahlrichs, R. *J. Chem. Phys.* **1995**, *102*, 346. (f) Eichkorn, K.; Treutler, O.; Ohm, H.; Haser, M.; Ahlrichs, R. *Chem. Phys. Lett.* **1995**, *240*, 283. (g) Eichkorn, K.; Treutler, O.; Oehm, H.; Haeser, M.; Ahlrichs, R. *Chem. Phys. Lett.* **1995**, *240*, 283. (h) Ahlrichs, R.; Bar, M.; Haser, M.; Horn, H.; Kolmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165. (i) Koga, T.; Kobayashi, H. *J. Chem. Phys.* **1985**, *82*, 1437. (j) Pulay, P. *Chem. Phys. Lett.* **1980**, *23*, 393. (k) Császár, P.; Pulay, P. *J. Mol. Struct.* **1984**, *114*, 31. (l) Csaszar, P.; Pulay, P. *J. Mol. Struct.* **1984**, *114*, 31.
(25) Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7763.
(26) Bullock, R. M. *J. Am. Chem. Soc.* **1987**, *109*, 8087.
(27) Johnson, D. G.; Lynam, J. M.; Mistry, N. S.; Slattery, J. M.; Thatcher, R. J.; Whitwood, A. C. *J. Am. Chem. Soc.* **2013**, *135*, 2222.
(28) Miller, D. C.; Angelici, R. J. *Organometallics* **1991**, *10*, 79.
(29) (a) Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P.; Ortuño, M. A.; Ujaque, G.; Lledós, A. *Inorg. Chem.* **2013**, *52*, 8919. (b) Alongi, K. S.; Shields, G. C. In *Annual Reports in Computational Chemistry*; Wheeler, R. A., Ed.; Elsevier Science: New York, 2010; Vol. *6*, p 113. (c) Liptak, M. D.; Gross, K. C.; Seybold, P. G.; Feldgus, S.; Shields, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 6421. (d) Liptak, M. D.; Shields, G. C. *J. Am. Chem. Soc.* **2001**, *123*, 7314.
(30) (a) Davies, D. L.; Donald, S. M. A.; Macgregor, S. A. *J. Am. Chem. Soc.* **2005**, *127*, 13754. (b) Garcia-Cuadrado, D.; de Mendoza, P.; Braga, A. A. C.; Maseras, F.; Echavarren, A. M. *J. Am. Chem. Soc.* **2007**, *129*, 6880. (c) Gorelsky, S. I.; Lapointe, D.; Fagnou, K. *J. Am. Chem. Soc.* **2008**, *130*, 10848. (d) Ackermann, L. *Chem. Rev.* **2011**, *111*, 1315. (e) Ackermann, L. *Acc. Chem. Res.* **2013**, DOI: 10.1021/ar3002798.
(31) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42*, 339.
(32) Palatinus, L.; Chapuis, G. *J. Appl. Crystallogr.* **2007**, *40*, 786.
(33) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112.
(34) Mitchell, R. W.; Spencer, A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 846.
(35) Hiett, N. P.; Lynam, J. M.; Welby, C. E.; Whitwood, A. C. *J. Organomet. Chem.* **2011**, *696*, 378.
(36) Hallman, P. S.; Stephenson, T. A.; Wilkinson, G. *Inorg. Synth.* **1970**, *12*, 237.