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Ruthenium Acetate Complexes as Versatile Probes of Metal–Ligand Interactions: Insight into the Ligand Effects of Vinylidene, Carbene, Carbonyl, Nitrosyl and Isocyanide

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Reaction of *cis*-Ru(κ^2-OAc)$_2$(PPh_3)$_2$ with two-electron donor ligands L results in the formation of complexes *trans*-[Ru(κ^1-OAc)(κ^2-OAc)L(PPh_3)$_2$] (L = CO, NO^+, CN*t*Bu). Vinylidene complexes (L = C=CHR) may be prepared from the corresponding reaction with terminal alkynes HC≡CR, and species containing hydroxyvinylidene ligands (L = C=CHCR^{1}R^2{OH}) may be prepared from related reactions with propargyl alcohols HC≡CCR^{1}R^2{OH}. Treatment of *cis*-Ru(κ^2-OAc)$_2$(PPh_3)$_2$ with ω-alkynols HC≡C(CH$_2$)$_n$OH (*n* = 2–4) results in the formation of oxacyclocarbene complexes [L = CCH$_2$(CH$_2$)$_n$O]. An analysis of the spectroscopic data and the structural metrics (as determined by X-ray crystallography) of this series of complexes allows for the relative donor/acceptor properties of the ligand L to be evaluated. This comparison indicates that the vinylidene ligand behaves in a similar fashion to the isocyanide ligand.

Introduction

An understanding of metal–ligand interactions is crucial for developing structure/activity relationships in transition-metal chemistry. A popular method to probe the electronic properties of a given ligand (or series of ligands) is to study the changes in the IR spectrum of a suitable metal–carbonyl complex.[1] The sensitivity of the C–O stretching frequency to the environment of the metal ensures that this is a versatile indicator of the electronic properties of the ligand in question. One important aspect of this approach is to have a consistent metal scaffold that will allow for facile incorporation of suitable ligands and allow a direct comparison of their properties. For phosphane and *N*-heterocyclic carbene ligands a number of frameworks have been employed including [Ni(CO)$_3$L],[1,2] [MCl(CO)$_2$L] (M = Rh,[3] Ir[4]) and Ir(η^5-C$_5$H$_5$)(CO)L.[5]

We have previously demonstrated that the ruthenium bis(acetate) complex *cis*-[Ru(κ^2-OAc)$_2$(PPh_3)$_2$] (**1**), which contains mutually *cis* phosphane ligands, is a versatile precursor for the preparation of complexes containing vinylidene ligands.[6] Reaction of **1** with, for example, HC≡CPh results in the formation of vinylidene complexes under extremely mild conditions and a theoretical study demonstrated that a key step in this process was an acetate-mediated deprotonation/reprotonation of the alkyne, for which we coined the term Ligand-Assisted Proton Shuttle (LAPS) mechanism.[7] In addition, **1** is able to catalyse the addition of carboxylic acids to propargyl alcohols to give β-oxopropyl ethers.[8]

Given that **1** appears to react selectively with alkynes to give vinylidene complexes and also with CO to give the carbonyl complex *trans*-[Ru(κ^1-OAc)(κ^2-OAc)(CO)(PPh_3)$_2$] (**2**),[6,9] we anticipated that it might be able to act as a versatile precursor for complexes containing a range of σ-donor/π-acceptor ligands. Furthermore, it was anticipated that, given the presence of a considerable number of characteristic spectroscopic features in the NMR and IR spectra, complexes based on the *trans*-[Ru(κ^1-OAc)(κ^2-OAc)L(PPh_3)$_2$] framework might act as potential probes for the nature of the metal–ligand interactions.

We now report on the preparation of a series of compounds of the general type *trans*-[Ru(κ^1-OAc)(κ^2-OAc)-L(PPh_3)$_2$], where L = CO, NO^+, CN*t*Bu, vinylidene or carbene. An analysis of the structural and spectroscopic parameters of these species enables the relative electron demands of these ligands to be assessed.

Results and Discussion

Reaction of 1 with Two-Electron Donor Ligands

The reactions of **1** with two-electron donor, σ-donor/π-acceptor ligands CO, NO^+ and CN*t*Bu all proceeded in a similar fashion (Scheme 1). It has previously been reported that treatment of a CH_2Cl_2 solution of **1** with CO for ca. 20 min results in the exclusive formation of *trans*-[Ru(κ^1-

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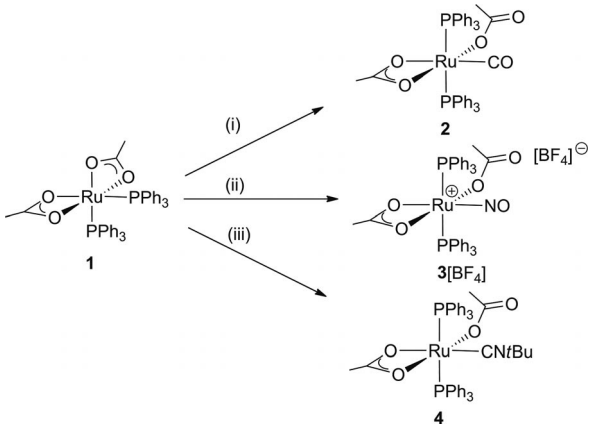
OAc)(κ^2-OAc)(CO)(PPh_3)$_2$] (**2**), although prolonged carbonylation does result in the formation of [Ru(κ^1-OAc)$_2$(CO)$_2$(PPh_3)$_2$].[6,8,9] As shown by single-crystal X-ray diffraction and NMR spectroscopy, complex **2** contains two mutually *trans* PPh_3 ligands. The κ^1- and κ^2-acetate ligands undergo rapid exchange on the NMR timescale at room temperature: the ^{1}H NMR spectrum of **2** exhibits a singlet resonance for the methyl groups of the acetate ligands. On cooling to 195 K this single peak undergoes decoalescence and separate peaks for the methyl groups of the κ^1- and κ^2-acetate are observed. All of the complexes prepared only show a single resonance for the two acetate environments at room temperature, which, in some examples, separate on cooling. An analysis of this behaviour is presented later.



Scheme 1. (i) + $CO_{(g)}$, CH_2Cl_2, 20 min, room temp.; (ii) + NO[BF_4], CH_2Cl_2, 60 min, room temp.; (iii) + CN*t*Bu, CH_2Cl_2, 30 min, room temp.

The formation of the *trans* isomer of **2** contrasts with the report by Robinson on the related complexes *cis*-[Ru(κ^1-O_2CR)(κ^2-O_2CR)(CO)(PPh_3)$_2$] (R = *p*-C_6H_4Cl or *p*-$C_6H_4NO_2$). These are prepared from the addition of the appropriate carboxylic acid to [RuH_2(CO)(PPh_3)$_3$] in boiling 2-methoxyethanol (125 °C), which contains mutually *cis*-phosphane ligands.[10] However, it should be noted that prolonged heating of a sample of **2** for 50 d at 50 °C does result in the formation of some *cis*-**2**. Notably, *cis*-**2** is characterised by a broad singlet resonance in the $^{31}P\{^1H\}$ NMR spectrum at δ_P = 47.8 ppm, which resolved into two doublets at δ_P = 45.7 and 49.0 ppm ($^2J_{PP}$ = 25.0 Hz) when cooled to 235 K.

The reaction of a CH_2Cl_2 solution of **1** with NO[BF_4] afforded *trans*-[Ru(κ^1-OAc)(κ^2-OAc)(NO)(PPh_3)$_2$][BF_4] (**3**[BF_4]), which is isoelectronic with **2**. The pertinent features in the ^{1}H NMR and $^{31}P\{^1H\}$ NMR spectra displayed by **2** are also exhibited by **3**[BF_4]. Notably a temperature-invariant singlet resonance in the $^{31}P\{^1H\}$ NMR spectrum is consistent with a change in geometry of the phosphane ligands from *cis* in **1** to *trans*. This was confirmed by a single-crystal X-ray diffraction study (Figure 1b), which demonstrated that the cation **3**$^+$ possessed an essentially identical topology to that of **2**. Although a more comprehensive discussion of the structural metrics within this class of complexes is presented later, it is important to note the presence of a linear NO ligand in **3**$^+$ and the fact that the uncoordinated oxygen atom of the κ^1-acetate exhibits a close interaction with the nitrogen atom of this ligand: O(4)–N(1) 2.773(3) Å. In the case of **2** this interaction is weaker [O(4)–C(5) 2.840(2) Å], which may simply reflect the more electrophilic nature of the nitrogen in the nitrosyl ligand.

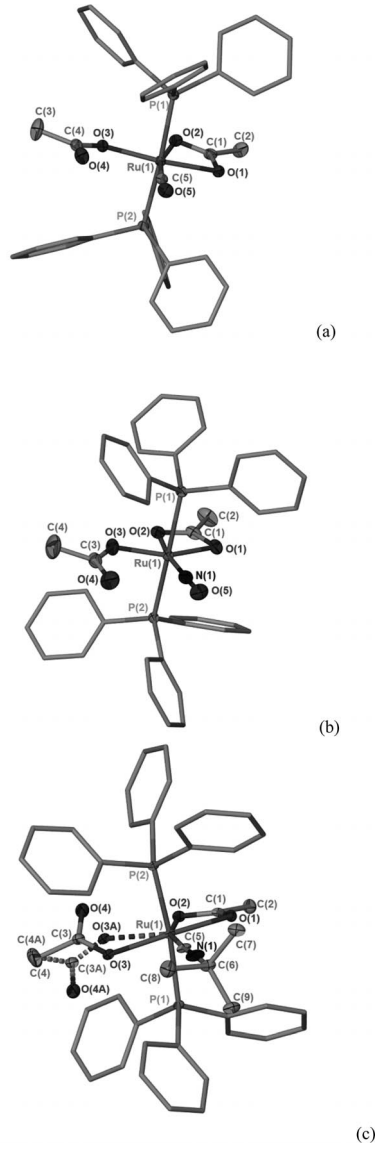


Figure 1. Molecular structures of (a) **2**, (b) cation **3**$^+$ and (c) **4**. Thermal ellipsoids where shown are at the 50% probability level, hydrogen atoms are omitted for clarity. The κ^1-acetate ligand in **4** is disordered over two sites with an 82.4(2):17.6(2) occupancy, the minor form being represented with hatched bonds.

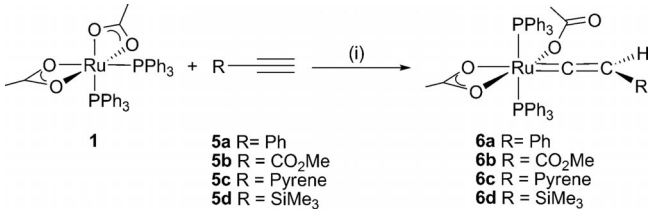
The IR spectra of **3**[BF_4] recorded as a KBr disc exhibited many of the expected features, including a band at 1865 cm^{-1} confirming the presence of an NO ligand adopting a linear geometry:[11] asymmetric and symmetric stretches for an acetate ligand coordinated in a κ^1-fashion were also observed. However no bands that could be assigned to an acetate ligand bound in κ^2-fashion could be observed.

The reaction of **1** with CN*t*Bu followed a similar pattern to that described for CO and NO^+. The formation of *trans*-[Ru(κ^1-OAc)(κ^2-OAc)(CN*t*Bu)(PPh_3)$_2$] (**4**) was observed to occur over the course of ca. 30 min (as shown by a characteristic colour change from orange to yellow). The structure of **4** was also confirmed by single-crystal X-ray diffraction (Figure 1c), which exhibited the expected *trans* disposition of the phosphane ligands and the presence of a linear CN*t*Bu ligand [Ru–C(5)–N(1) 175.6(2) °]. In contrast to **2** and **3**[BF_4] there is no close contact between the uncoordinated oxygen atom of the κ^1-bound acetate ligand and the isocyanide ligand. As this is a weak interaction, crystal packing effects cannot be discounted. However, it would also be expected that the metal-bound carbon of the isocyanide would be less electrophilic than the carbonyl carbon in **2** and the nitrogen of the NO^+ ligand in **3**$^+$. The IR spectra of **4** in both CH_2Cl_2 solution and as a KBr disc exhibit two bands in the region associated with the C≡N stretch of the isocyanide ligand. Although the appearance of two bands may be due to the occurrence of two different conformations of the complex, Fermi resonance cannot be excluded.[12]

Reaction of 1 with Terminal Alkynes

We have previously reported that the reaction of **1** with the terminal alkynes HC≡CR [R = Ph (**5a**), R = CO_2Me (**5b**)] results in the formation of vinylidene complexes *trans*-[Ru(κ^1-OAc)(κ^2-OAc)(=C=CH{R})(PPh_3)$_2$] [R = Ph (**6a**), R = CO_2Me (**6b**)].[6] The corresponding reaction of **1** with propargyl alcohols, HC≡CCR^{1}R^2(OH) [R^1 = R^2 = Ph (**7a**), R^1 = R^2 = Me (**7b**)], allow for the formation of hydroxy-substituted vinylidene complexes [Ru(κ^1-OAc)(κ^2-OAc)(=C=CHCR^{1}R^2{OH})(PPh_3)$_2$] [R^1 = R^2 = Ph (**8a**), R^1 = R^2 = Me (**8b**)]. The reaction of **1** with a number of different terminal alkynes was investigated in order to explore the scope of this reaction with regard to functional group tolerance and to investigate the potential effects of different substitution on metal–ligand interactions.[13]

The reaction of **1** with HC≡C(pyrene) (**5c**) or HC≡C$SiMe_3$ (**5d**) results in the formation of vinylidene complexes [Ru(κ^1-OAc)(κ^2-OAc)(=C=CH{pyrene})(PPh_3)$_2$] (**6c**) and [Ru(κ^1-OAc)(κ^2-OAc)(=C=C$HSiMe_3$)(PPh_3)$_2$] (**6d**), respectively (Scheme 2). The vinylidene complexes exhibited a common set of spectroscopic features including low-field triplet resonances for the α-carbon of the vinylidene ligand at ca. δ = 350 ppm ($^2J_{PC}$ ≈ 16 Hz) and the



1 **5a** R= Ph, **5b** R = CO_2Me, **5c** R = Pyrene, **5d** R = $SiMe_3$ **6a** R= Ph, **6b** R = CO_2Me, **6c** R = Pyrene, **6d** R = $SiMe_3$

Scheme 2. Reaction of **1** with **5a**–**d**. (i) CH_2Cl_2 solution, room temp.,1 h.

β-carbon at ca. δ = 110 ppm ($^3J_{PC}$ ≈ 4 Hz). Triplet resonances are observed in the ^{1}H NMR spectrum for the proton attached to the β-carbon of the vinylidene ligand. The chemical shift, however, exhibited a dependence on the nature of the functional group present.

The structure of **6c** was confirmed by single-crystal X-ray diffraction and, since our initial report, we have now obtained a satisfactory solution for a structure of complex **6b**. The molecular structures of these two compounds in the solid state are shown in Figure 2. The complexes exhibited short ruthenium–carbon and carbon–carbon bond lengths for the vinylidene ligand and demonstrated that the acetate ligands are present in both κ^2- and κ^1-coordination modes.

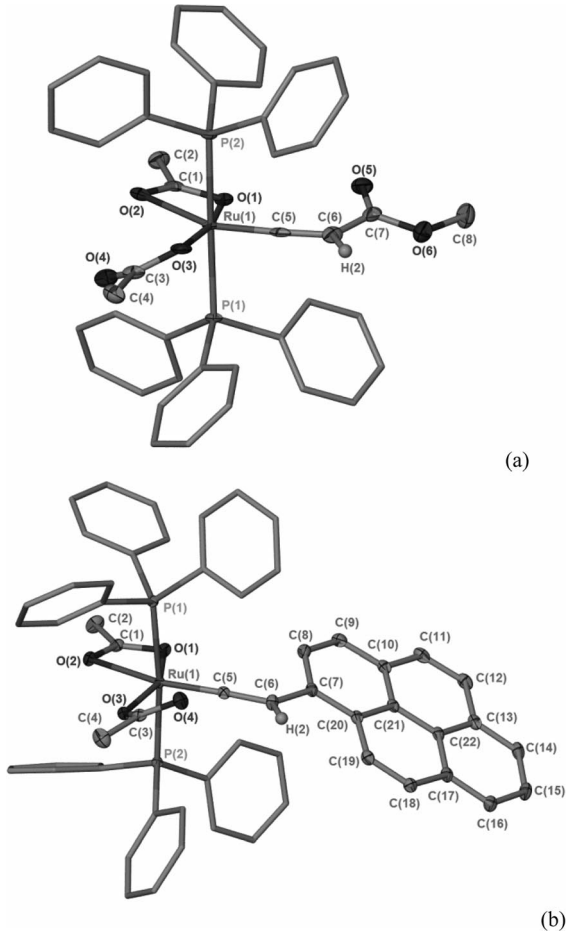
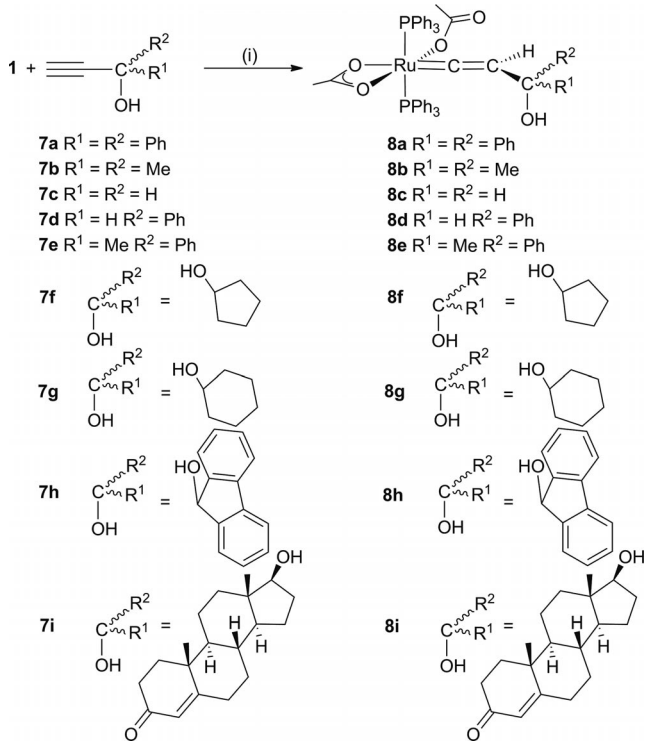


Figure 2. Molecular structures of (a) **6b** and (b) **6c**. Thermal ellipsoids where shown are at the 50% probability level, hydrogen atoms (except for those attached to the vinylidene ligand) are omitted for clarity.

The reaction of **1** with propargyl alcohols HC≡CCR^{1}R^2(OH) (**7**) resulted, in all cases, in the rapid formation of hydroxyvinylidene complexes **8**, regardless of the substituents employed (Scheme 3). This proved to be the case even when substituted steroid ethisterone (**7i**) was employed. As in the case of the simpler vinylidene complexes **6**, characteristic resonances were observed in the ^{13}C NMR and ^{1}H NMR spectra of these species. Notably low-field resonances for the α-carbon were observed again at ca. δ = 350 ppm.



Scheme 3. Reaction of **1** with **7a**–**i**. (i) CH_2Cl_2 solution, room temp.,1 h.

The structures of complex **8e** and **8f** (Figure 3a and b) were also confirmed by single-crystal X-ray diffraction. The structures of these complexes again conform to the general type showing κ^1- and κ^2-bound acetate ligands and two PPh_3 ligands in a mutually *trans* arrangement. The Ru–C and C–C bond lengths within the vinylidene ligands are typical.

In contrast to the solid structure of **8a**, which exhibits an intramolecular hydrogen bond between the OH group of the hydroxyvinylidene ligand and the uncoordinated oxygen atom of the κ^1-acetate ligand, the structure of **8e** appears to show an OH–π interaction with one of the aromatic rings of a PPh_3 ligand.

The solid-state structure of **8f** shows a further motif in which the OH group of the hydroxyvinylidene ligand is engaged in intermolecular hydrogen bonding with the uncoordinated oxygen atom of the κ^1-acetate ligand of a neighbouring molecule [intermolecular distance O(5)–H(5)···O(4) 2.802(3) Å]. Additional weaker interactions are observed between the CH_2Cl_2 of crystallisation and both the OH group of the hydroxyvinylidene [O(5)–C(48) 3.243(4) Å] and an oxygen atom of the κ^2-acetate on a second molecule of **8e** [O(2)–C(48) 3.241(4) Å]. The net result of these effects is to produce a one-dimensional polymer in the solid state, the structure of which is illustrated in Figure 3c.

The elimination of water from hydroxyvinylidene complexes to afford species containing allenylidene, $M=C=C=CR^1R^2$, ligands is a well-established reaction.[13f,14] All of the complexes with structure **8** were metastable, the ultimate products from these reactions proved to

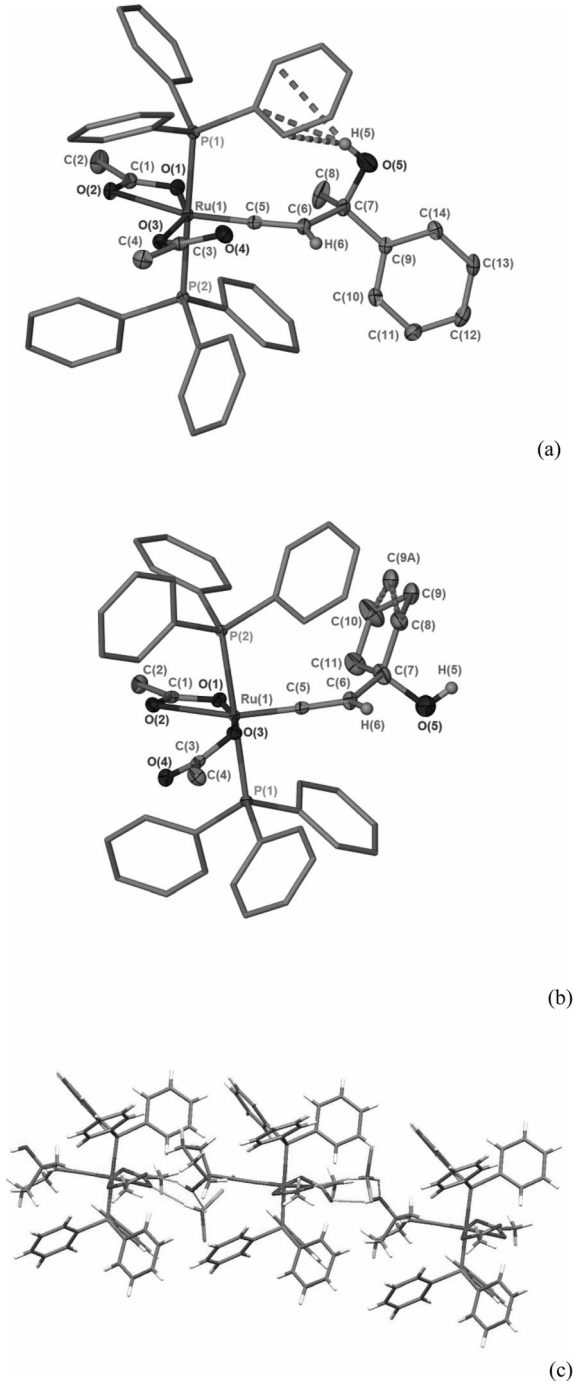
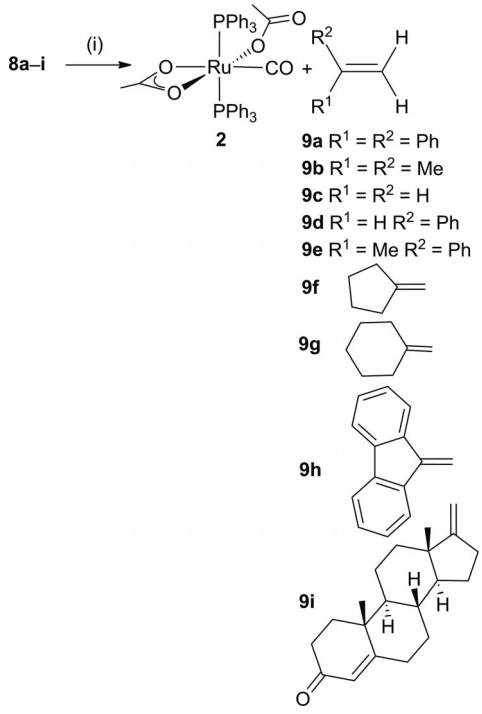


Figure 3. Molecular structures of (a) **8e** and (b) **8f**. Thermal ellipsoids where shown are at the 50% probability level, hydrogen atoms (except for those attached to the vinylidene ligand) are omitted for clarity. (c) Solid-state hydrogen bonding motif observed in **8f**.

be the carbonyl complex **2** and alkenes $H_2C=CR^1R^2$ (**9**) (Scheme 4). The stoichiometric[15] and catalytic[16] conversion of propargyl alcohols to alkenes has been reported previously and alkenes have been observed as side products in other catalytic transformations of these substrates.[17] In the case of complexes **8** the only significant difference in behaviour is in the time required for this reaction to come to completion. In the case of complex **8c**, in which the hy-

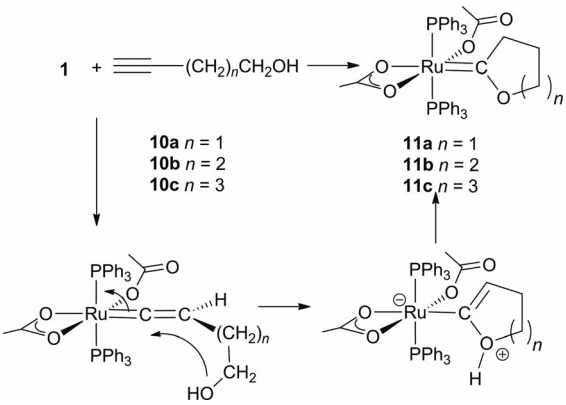
droxyvinylidene ligand only contains hydrogen substituents, the generation of **2** and ethene is complete in 48 h. In contrast to the case of ethisterone-containing **8i** this reaction required three weeks to reach completion. Indeed, the time for this reaction to achieve completion broadly correlates with the steric demands of the substituents on the vinylidene.



Scheme 4. (i) CH_2Cl_2, room temperature.

Reaction of 1 with ω-Alkynols

Given that the reaction of **1** with terminal alkynes has proven to be a selective method for the preparation of vinylidene ligands, the corresponding reactions with ω-alkynols $HC{\equiv}C(CH_2)_nOH$ [n = 2 (**10a**), n = 3 (**10b**), n = 4 (**10c**)] were investigated. In the case where n = 2 and 3 essentially identical behaviour was observed: treatment of a CD_2Cl_2 solution of **1** with the appropriate alkyne at room temperature resulted in the rapid formation of the corresponding oxacyclocarbene complexes **11a** and **11b** (Scheme 5).[18] In



Scheme 5.

contrast, the treatment of **1** with $HC{\equiv}C(CH_2)_4OH$ under identical conditions resulted in a much slower reaction: **11c** was observed to be formed over a period of 24 h, although no intermediates could be detected. As shown in Scheme 5, the generally accepted mechanism[19] for such a process involves the initial formation of a vinylidene complex with a pendant alcohol, which then undergoes nucleophilic attack at the vinylidene α-carbon.

The spectroscopic data for complexes **11a**–**c** support the assignment of these species as oxacyclocarbene complexes. For example, the $^{13}C\{^1H\}$ NMR spectra of the complexes exhibited resonances at δ = 304.7 (t, $^2J_{PC}$ = 11.8 Hz), δ = 306.8 (t, $^2J_{PC}$ = 11.7 Hz) and δ = 311.0 ppm (t, $^2J_{PC}$ = 11.8 Hz) for **11a**, **11b** and **11c**, respectively. An analysis of the chemical shift of a number of oxacyclocarbene ligands (Table 1) demonstrates that this trend of increasing chemical shift with increasing ring size appears to be present in a number of species of this type.[20]

Table 1. Comparison of carbene carbon chemical shifts in oxacyclocarbene ligands.

[M]	^{13}C NMR: δC_α [M]=C_4H_6O	^{13}C NMR: δC_α [M]=C_5H_8O	^{13}C NMR: δC_α [M]=$C_6H_{10}O$
$[Ru(OAc_2)_2(PPh_3)_2]$[a]	304.7	306.8	311.0
$[RuTp(PPh_2iPr)]Cl$[b][21]	313.2	318.3	323.7
$[RuTp(PPh_3)]Cl$[b][21]	314.4	320.2	325.0
$[Ru(Ind)(PPh_3)_2]$[c][22]	296.3	302.5	306.8
$[Ru(Ind)(PMe_2Ph)_2]$[c][22]	295.1	302.5	306.7
[Ru(Ind)(dppm)][c][22]	300.3	308.1	312.5
$[Ru(Ind)(PPh_3)(PMe_3)]$[c][22]	296.8	303.9	307.5
$[Re(triphos)(CO)_2]BF_4$[23]	293.4	303.0	310.8

[a] This work. [b] Tp = tris(pyrazolyl)borate. [c] Ind = η^5-C_9H_7; triphos = $MeC(CH_2PPh_2)_3$.

The structures of complexes **11a**–**c** were also confirmed by single-crystal X-ray diffraction: the molecular structures are presented in Figure 4. In all three cases the structure determinations demonstrated that the complexes contained two mutually *trans*-PPh_3 ligands. In the case of **11a** and **11c**, the ruthenium was also shown to be bound to a κ^1- and a κ^2-OAc ligand with the remaining coordination site being occupied by the oxacyclocarbene ligand. The structure of **11b** is somewhat different from those of the other complexes reported. It crystallised in the orthorhombic space group *Aba*2 with the asymmetric unit constituting half the complex. The acetate ligand in this complex is bound formally in a κ^1-fashion, although the distance of the uncoordinated oxygen atom O(2) to the ruthenium is somewhat shorter [2.748(2) Å] than in (for example) **11a** [2.908(4) Å], perhaps representing a weak interaction. In solution, the ^1H NMR spectrum of **11b** recorded at a low temperature demonstrated that two inequivalent OAc groups were present and the IR spectra recorded in CH_2Cl_2 solution or as a KBr disc showed the presence of both κ^1- and κ^2-coordination modes. These data led to the conclusion that the conformation of the acetate ligands observed in the X-ray diffraction experiment was not representative of the solution-state behaviour.

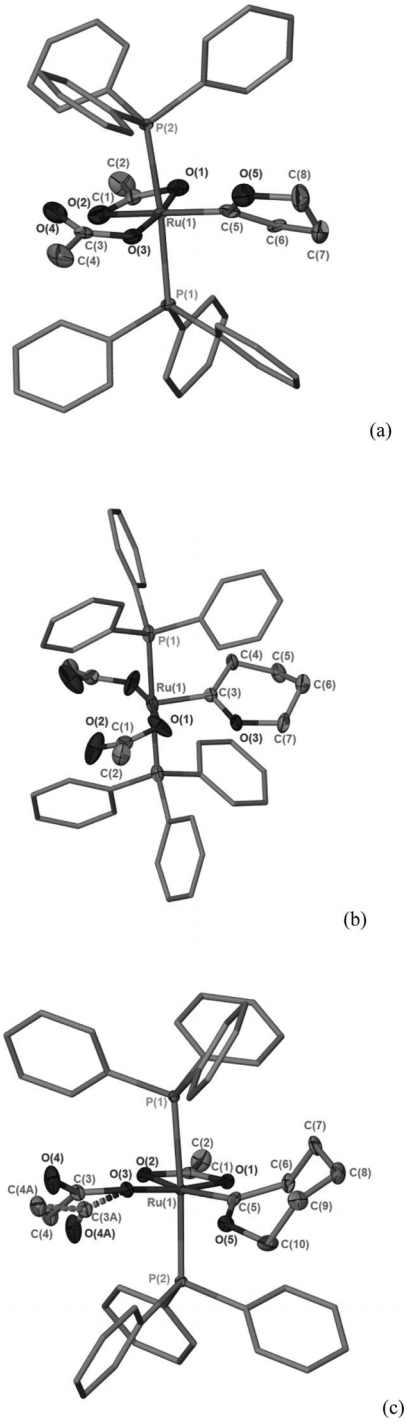


Figure 4. Molecular structures of (a) **11a**, (b) **11b** and (c) **11c**. Thermal ellipsoids where shown are at the 50% probability level, hydrogen atoms are omitted for clarity. For the structure of **11b** only confirmation of the disordered carbene ligand is shown. The κ^1-acetate ligand in **11c** is disordered over two sites with an 82.2(4):17.8(4) occupancy, the minor form being represented with hatched bonds.

The structure determinations for all three of the complexes confirm the presence of the oxacyclocarbene ligands, with Ru–C bond lengths of 1.878(6) Å (**11a**), 1.865(3) Å (**11b**) and 1.902(3) Å (**11c**). Although there are a number of structurally-characterised oxacyclocarbene ligands based on five- and six-membered rings, to the best of our knowledge only one other example of a crystallographically characterised complex containing a seven-membered ring has been reported. The complex $[Ru(=C_6H_{10}O)(\eta^5\text{-}C_9H_7)(PPh_3)_2]PF_6$ has been prepared and exhibits a Ru=C distance of 1.89(1) Å.[22]

Comparison of Structural Properties of Complexes based on the *trans*-[Ru(κ^1-OAc)(κ^2-OAc)(L)(PPh_3)$_2$] Framework

All of the complexes reported have the same core structure, which is shown, with an appropriate labelling scheme, in Figure 5. Having such a range of isostructural compounds in hand allows for the effects of the ligands L on various metal–ligand interactions to be evaluated. Key crystallographic parameters are presented in Tables 2 and 3, IR data in Table 4 and NMR spectroscopic data in Tables 5 and 6.

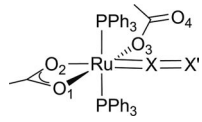


Figure 5. Labelling scheme for complexes of the general type *trans*-[Ru(κ^1-OAc)(κ^2-OAc)(L)(PPh_3)$_2$].

An examination of the geometric parameters for the *trans*-[Ru(κ^1-OAc)(κ^2-OAc)(PPh_3)$_2$] framework demonstrate that a series of systematic changes are present that may be rationalised on the basis of the different electronic demands of the ligand L. Considering, for example, the series **2**, **3**[BF_4] and **4**, it is generally accepted that the π-acceptor ability decreases in the sequence $NO^+ > CO > CNtBu$ with the ability of the ligand to act as a σ-donor exhibiting the opposite trend.[24,25] Therefore, it would be expected that the bond lengths between the ruthenium and π-donor ligands would increase for the series **3**[BF_4] < **2** < **4**, whereas π-acceptor ligands would exhibit the opposite trend. This is indeed what is observed. The O(2)–Ru bond lengths (i.e. in a position *trans* to the ligand L) increase in the sequence **3**[BF_4] [2.0744(19) Å] < **2** [2.1897(11) Å] < **4** [2.2465(16) Å], consistent with the predicted trend, as does the Ru–O(3) bond length. In contrast, the Ru–P distances for this class of compounds exhibit the opposite trend (mean bond lengths **3**[BF_4] [2.4401(1) Å] < **2** [2.3967(6) Å] < **4** [2.3536(8)Å), which, as the PPh_3 ligands are the only other π-acceptor ligands present in the coordination sphere of the metal after L, is again as expected.

Furthermore, the bite angle of the κ^2-acetate ligand [O(1)–$\hat{C}$(1)–O(2)] also shows a correlation with the type of ligand L that is present. In the case of complex **3**[BF_4], this angle is 61.55(8)° decreasing to 60.42(4)° for **2** and 59.80(6)° for **4**. Also, the O(2)–Ru–X angle increases in the series **4** [158.95(9)°] < **2** [164.49(6)°] < **3**[BF_4] [168.00(9)°]. Again they may be rationalised on the basis of both σ- and π-effects, but it is clear that the structural metrics within the *trans*-[Ru(κ^1-OAc)(κ^2-OAc)(L)(PPh_3)$_2$] framework are sensitive to the electronic properties of the ligand L.

Table 2. Summary of pertinent bond lengths [Å] for complexes reported (n.a. = not applicable). In the case of complexes with disorded acetate ligands only the major conformer is considered.

Complex	Ru–X	X–X′	Ru–O(1)	Ru–O(2)	Ru–O(3)	Ru–P(1)	Ru–P(2)
2	1.8318(17)	1.146(2)	2.1466(11)	2.1897(11)	2.0365(11)	2.4060(4)	2.3873(4)
3[BF_4]	1.739(2)	1.137(3)	2.1336(19)	2.0744(19)	1.9966(19)	2.4336(8)	2.4466(8)
4	1.882(2)	1.159(3)	2.1352(16)	2.2465(16)	2.056(2)	2.3592(6)	2.3479(6)
6a	1.786(3)	1.318(4)	2.1139(17)	2.2863(18)	2.0699(17)	2.3853(7)	2.3910(7)
6b	1.766(6)	1.296(8)	2.102(4)	2.282(4)	2.063(4)	2.3788(14)	2.3762(14)
6c	1.7863(16)	1.325(2)	2.1116(11)	2.2465(12)	2.0160(11)	2.4195(5)	2.3720(5)
8a	1.8027(15)	1.312(2)	2.1100(11)	2.2588(11)	2.0344(11)	2.4178(4)	2.3652(4)
8e	1.7959(18)	1.316(2)	2.1141(13)	2.2620(13)	2.0179(12)	2.4040(5)	2.3757(5)
8f	1.805(3)	1.297(4)	2.1119(19)	2.3259(19)	2.088(2)	2.3734(7)	2.3850(7)
11a	1.878(6)	n.a.	2.204(4)	2.355(4)	2.058(4)	2.3840(14)	2.3642(14)
11b	1.865(3)	n.a.	n.a.	n.a.	2.104(2)	2.3734(5)	n.a.
11c	1.902(3)	n.a.	2.126(2)	2.325(2)	2.086(2)	2.3891(8)	2.3591(8)

Table 3. Summary of pertinent bond angles [°] for complexes reported (n.a. = not applicable). In the case of complexes with disorded acetate ligands only the major conformer is considered.

	Ru–X–X′	O(1)–Ru–X	O(2)–Ru–X	O(3)–Ru–X
2	175.02(15)	104.71(6)	164.49(6)	99.45(6)
3[BF_4]	176.5(2)	106.75(9)	168.00(9)	102.25(10)
4	175.6(2)	99.46(9)	158.95(9)	89.13(10)
6a	176.5(2)	97.81(9)	155.65(9)	93.90(9)
6b	173.6(5)	97.5(2)	154.7(2)	94.1(2)
6c	174.72(14)	101.92(6)	161.77(6)	102.72(6)
8a	175.16(13)	101.35(6)	161.05(6)	101.59(6)
8e	178.10(16)	103.64(6)	162.68(6)	104.95(7)
8f	178.2(3)	98.99(10)	155.45(10)	92.52(10)
11a	n.a.	96.6(2)	151.5(2)	92.4(2)
11b	n.a.	95.45(7)	n.a.	n.a.
11c	n.a.	98.29(11)	157.19(11)	89.40(12)
	P(1)–Ru–P(2)	O(1)–Ru–O(2)	O(1)–Ru–O(3)	O(2)–Ru–O(3)
2	176.545(15)	60.42(4)	155.62(5)	95.71(5)
3[BF_4]	176.05(2)	61.55(8)	150.64(9)	89.64(8)
4	173.30(2)	59.80(6)	170.17(8)	111.25(7)
6a	178.89(3)	59.08(6)	168.17(7)	109.09(7)
6b	178.20(6)	58.78(14)	168.40(15)	109.67(15)
6c	174.126(15)	59.86(4)	154.87(5)	95.49(4)
8a	173.647(14)	59.79(4)	156.68(4)	97.36(4)
8e	177.844(17)	59.78(5)	151.04(5)	92.05(5)
8f	178.45(3)	58.45(7)	168.47(7)	110.09(7)
11a	173.69(5)	56.40(15)	170.95(16)	114.74(16)
11b	178.60(4)	n.a.	169.10(13)	n.a.
11c	175.91(3)	58.92(8)	170.96(9)	113.25(8)

An examination of the structural metrics of complexes **11** provided insight into the relative donor/acceptor properties of these Fischer-type carbene complexes. One would expect there to be less metal–ligand π back-donation occurring in this instance, which is consistent with the observed structural metrics. For example, the O(2)–Ru distance is 2.355(4) Å (**11a**) and 2.325(2) Å (**11c**), notably longer than those observed in complexes **2**, **3**[BF_4] and **4**. The Ru–P bonds in this series are not as short as those observed in **4**, although with the introduction of a carbene ligand steric factors cannot be ignored. The bite angles of the κ^2-acetate in **11a** and **11c** are 56.40(15)° and 58.92(8)°, respectively, with O(2)–Ru–X angles of 151.5(2)° and 157.19(11)°, respectively. The IR data for the complexes of the general type *trans*-[Ru(κ^1-OAc)(κ^2-OAc)(L)(PPh_3)$_2$] also support these changes to the binding of the κ^2-acetate ligand as the oxacyclocarbene complexes show the largest differences in frequency between the symmetric and asymmetric stretch of all of the complexes reported and have the most acute acetate bite angles. These data point to the Fischer carbene ligands being better net donor ligands to the metal than either NO^+, CO or CN*t*Bu.

The relative π-acidity of vinylidene ligands has been probed by analysis of the IR spectra in the series of compounds [Mn(η^5-C_5H_5)(CO)$_2$(=C=CHR)].[26] This study revealed that in this case the vinylidene ligand is a better π-acceptor than CO. However, in 2002 Werner reported that the CO ligand is a better π-acceptor, but poorer σ-donor ligand than the vinylidene ligand based on DFT, IR and Raman spectroscopic studies of the square-planar complex [Rh(X)(L)(P*i*Pr$_3$)$_2$] (X = halogen; L = CO, =C=CH_2).[27] An examination of the available O(2)–Ru bond lengths for the vinylidene and hydroxy-substituted vinylidene complex vary from 2.2465(12) Å for complex **6c** to 2.2863(18) Å for **6a**. For the purposes of this discussion the O(2)–Ru bond length in **8f** is not considered as O(2) appears to be involved in hydrogen bonding to the CH_2Cl_2 of crystallisation. The bite angle of the κ^2-acetate ligand [O(1)–$\hat{C}$(1)–O(2)] varies from 59.86(4)° in **6c** to 59.08(6)° in **6a** (again ignoring **8f**). Once more these values are similar to that observed in the isocyanide complex **4**, as are the differences in frequency observed between the symmetric and asymmetric stretch of the κ^2-acetate ligand in all cases. This therefore indicates that in this series of compounds[28] the vinylidene and isocyanide ligands have similar net donor/acceptor properties.

The NMR spectroscopic data for these complexes exhibit a few common features worthy of note. For example, the chemical shift of the two PPh_3 ligands within the complexes fall into a very narrow region (Table 5) from δ = 41.8 ppm for **4** to δ = 33.8 ppm for **6c**: complex **1** (in which the phosphane ligands are mutually *cis*) exhibits a resonance at δ = 63.1 ppm.

In all cases, at room temperature a singlet resonance was observed for the six protons of the two acetate ligands, demonstrating that these ligands undergo an exchange process that is rapid on the NMR timescale. In some instances, it has been possible to observe the decoalescence of the two environments upon cooling, the low-temperature limiting regime was not obtained in most cases, therefore, the ob-

Table 4. IR data [cm^{-1}] from KBr discs for complexes reported (n.a. = not applicable; n.d. = not determined).

Complex	C=C	κ^1-OCO_{sym}	κ^1-OCO_{asym}	κ^1-$\Delta\upsilon$	κ^2-OCO_{sym}	κ^2-OCO_{asym}	κ^2-$\Delta\upsilon$
2	n.a.	1368	1607	239	1466	1520	54
3[BF_4]	n.a.	1364	1636	272	n.d.	n.d.	n.d.
4	n.a	1366	1627	261	1462	1529	67
6a	1635	1360	1595	235	1459	1534	75
6b	1684	1365	1600	235	1466	1535	69
6c	1607	1366	1590	224	1462	1530	68
6d	1636	1366	1616	250	1459	1531	72
8a	1654	1378	1595	217	1465	1527	62
8b	1648	1362	1619	257	1460	1533	73
8c	1655	1372	1595	223	1457	1533	76
8d	1648	1369	1592	223	1454	1537	83
8e	1649	1361	1601	240	1458	1536	78
8f	1654	1364	1590	226	1458	1536	78
8g	1646	1366	1591	225	1458	1538	80
8h	1636	1367	1597	230	1463	1534	71
8i	1649	1374	1620	246	1456	1530	74
8j	1651	1359	1597	238	1457	1537	80
11a	n.a.	1368	1616	248	1447	1541	94
11b	n.a.	1375	1615	240	1446	1549	103
11c	n.a.	1382	1608	225	1450	1546	96

Table 5. Selected NMR spectroscopic data in CD_2Cl_2 solutions for complexes reported (n.a. = not applicable; n.d. = not determined).

Complex	^{1}H NMR		^{31}P NMR	^{13}C NMR			
	δ_H [Ru]=C=C***H***	$^4J_{HP}$ [Hz]	δ_P PPh_3	δ_C [Ru]=***C***=C	$^2J_{CP}$ [Hz]	δ_C [Ru]=C=***C***	$^3J_{CP}$ [Hz]
2	n.a.	n.a.	39.1	207.4	13.2	n.a.	n.a.
3[BF_4]	n.a.	n.a.	34.7	n.a.	n.a.	n.a.	n.a.
4	n.a.	n.a.	41.8	161.9	n.d.	n.a.	n.a.
6a	5.14	3.70	34.1	355.6	16.8	112.1	4.40
6b	5.41	3.22	34.8	345.2	n.d.	104.4	3.90
6c	6.20	3.63	33.8	n.d.	n.d.	109.4	4.56
6d	3.74	3.73	35.5	337.6	15.4	94.0	3.90
8a	4.73	3.93	34.0	347.6	16.2	117.2	4.67
8b	4.32	3.87	34.1	352.0	16.3	118.4	4.78
8c	4.56	3.75	33.9	349.3	16.1	113.7	4.60
8d	4.14	3.79	34.9	345.1	16.2	112.5	4.72
8e	4.56	3.85	34.3	350.4	16.0	117.6	4.27
8f	4.38	3.84	34.3	352.0	16.3	116.3	4.63
8g	4.39	3.74	34.4	352.2	16.5	117.5	4.73
8h	4.11	3.67	35.1	345.7	16.3	106.5	4.96
8i	4.48	3.66	35.5	352.0	16.2	114.4	4.62
11a	n.a.	n.a.	35.9	304.7	11.8	n.a.	n.a.
11b	n.a.	n.a.	35.4	306.8	11.7	n.a.	n.a.
11c	n.a.	n.a.	34.2	311.0	11.8	n.a.	n.a.

Table 6. T_c, k_{coal} and $\Delta G^{\ddagger}$ values of complexes for which decoalescence is observed. Data from ^{1}H NMR spectra recorded in CD_2Cl_2 solution. Rates of exchange are minimum values and free energy of activation maximum values.

Complex	δ_v [s^{-1}]	T_c [K]	k_{coal} [s^{-1}]	$\Delta G^{\ddagger}$ [kJ mol^{-1}]
2	173.7	195	385.6	37.4
3[BF_4]	183.9	235	408.3	45.3
8a	291.3	215	646.7	40.5
8d	270.4	190	600.2	35.7
8f	175.8	195	390.2	37.4
8h	138.7	195	307.8	37.8
11a	203.0	185	451.0	35.2
11b	146.5	185	325.4	35.7

tained rates of exchange must be viewed as minimum values and the resulting free energy of activation as maximum values. The exchange parameters calculated for those complexes where decoalescence was observed are summarised in Table 6. These data show that although there is some variance in the rate of exchange (k_{coal}), the energy barrier ($\Delta G^{\ddagger}$) to this exchange for each complex is quite similar. The highest barrier is observed for the NO-containing complex **3**[BF_4], which also exhibits the shortest Ru–O(2) distance.

The NMR spectra of the four vinylidene complexes **6** show a number of similar features. The chemical shifts of the characteristic resonance for the proton attached to the vinylidene β-carbon and the metal-bound resonance are influenced by the nature of the substituent present. This varies from δ = 3.74 ppm in the case of $SiMe_3$-substituted **6d** to δ = 6.20 ppm in the case of the pyrene-containing complex **6c**: these complexes also exhibited the lowest and highest chemical shifts for the PPh_3 groups in the ^{31}P NMR

spectra, respectively. The hydroxy-substituted vinylidene complexes show far smaller differences in chemical shift for these resonances, as might be expected with the site of substitution being somewhat more remote from the metal. The vinylidene and hydroxyvinylidene complexes exhibit triplet resonances between δ = 337.4 (**6d**) and 355.6 ppm (**6a**) for the metal-bound carbon atom. The coupling constants observed between the phosphorus nuclei and these atoms are fairly uniform. The $^2J_{PC}$ values of the vinylidene (**6**) and hydroxyvinylidene (**8**) complexes are larger than the corresponding value for the carbonyl complex **2**, which is in turn larger than the $^2J_{PC}$ of the oxacyclocarbene complexes **10**. This may reflect the fact that the vinylidene ligand is more tightly bound to the ruthenium centre, as evidenced by the shorter Ru–C distances observed on structural characterisation. The resonances for the metal-bound carbon atoms of the oxacyclocarbene complexes **11** are observed at a lower chemical shift than the corresponding C_α of the vinylidene complexes. This is thought to be a result of the stronger electrophilic character of a vinylidene ligand compared to a Fischer carbene.[29]

Conclusions

Complex **1** is a versatile substrate for the preparation of complexes of the general type *trans*-[Ru(κ^1-OAc)(κ^2-OAc)(L)(PPh_3)$_2$] in which L is a σ-donor/π-acceptor ligand. This is either through a direct reaction (as in the case of CO, NO^+ or CN*t*Bu) or through a metal-mediated hydrogen-transfer reaction to form vinylidene ligands. A key feature of this reaction appears to be the change in geometry of the phosphane ligands from *cis* in **1** to mutually *trans* in the other examples. This may reflect a tendency to place the better π-acceptor ligand in the same plane as the π-donor acetate ligands.

An examination of the structural parameters and spectroscopic properties of complexes *trans*-[Ru(κ^1-OAc)(κ^2-OAc)(L)(PPh_3)$_2$] reveals a number of metrics that may reflect the relative electronic demands of the ligand L. These data indicate that the relative net donor/acceptor properties of the ligands increase in the series carbene < vinylidene ≈ CN*t*Bu < CO < NO^+.

Experimental Section

General: All experimental procedures were performed under an atmosphere of dinitrogen or argon using standard Schlenk Line and Glove Box techniques. CH_2Cl_2, pentane and hexane were purified with the aid of an Innovative Technologies anhydrous solvent engineering system. The CD_2Cl_2 solution used for the NMR experiments was dried with 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 with a Bruker AVANCE 500 (Operating Frequencies ^{1}H NMR: 500.23 MHz, ^{31}P NMR: 202.50 MHz, ^{13}C NMR: 125.77 MHz) at 298 K, except for the data for complex **11c**, which were recorded with a JEOL 400 (Operating Frequencies ^{1}H NMR: 400.13 MHz, ^{31}P NMR: 161.83 MHz, ^{13}C NMR: 100.53 MHz) at 298 K. ^{31}P NMR and ^{13}C NMR spectra were recorded with proton decoupling. The abbreviations "at" and "aq" refer to "apparent triplet" and "apparent quartet", respectively. Mass spectrometry measurements were performed with a Thermo-Electron Corp LCQ Classic (ESI), a Bruker instrument or Waters GCT Premier Acceleration TOF MS (LIFDI). IR spectra were acquired with a Thermo-Nicolet Avatar 370 FTIR spectrometer using either CsCl solution cells or as KBr discs. CHN measurements were performed using an Exeter Analytical Inc. CE-440 analyser. The proportion of CH_2Cl_2 in samples for elemental analysis was confirmed by recording a ^{1}H NMR spectrum of the material used for analysis in [D_8]toluene. Relative integration of the peak at δ_H = 4.31 (CH_2Cl_2) to that of the vinylidene proton indicated the proportion of DCM in that sample. Alkynes **5a**, **5b**, **5d**, **7a**–**g**, **7i**, **10a**–**c** and NO[BF_4] were obtained from Sigma–Aldrich, **8g** from Lancaster Synthesis and CN*t*Bu from Fluka. All were used as supplied without further purification. Compounds **1**,[6,30] **2**[6,9] and **5c**[31] were prepared as described previously.

Synthesis of [Ru(κ^1-OAc)(κ^2-OAc)(NO)(PPh_3)$_2$]BF_4 (3[BF_4]): Ru(κ^2-OAc)(PPh_3)$_2$ (0.20 g, 0.27 mmol) was dissolved in CH_2Cl_2 (15 mL) in a Schlenk tube with a stirrer bar. $NOBF_4$ (31.6 mg, 0.27 mmol, 1 equiv.) was added and the solution was allowed to stir for 1 h. After this time the solution was concentrated to approximately 5 mL and the product was precipitated by the addition of toluene (40 mL). The solution was filtered to leave a light-brown powder product that was dried in vacuo. Yield = 0.08 g (50%). ^{1}H NMR (CD_2Cl_2): δ = 0.82 (s, 6 H, OCOCH_3), 7.48 (aq, J = 6.6 Hz, 12 H, *ortho*-H of P*Ph*$_3$), 7.60 (J = 7.7 Hz, 12 H, *meta*-H of P*Ph*$_3$), 7.71 (J = 7.5 Hz, 6 H, *para*-H of P*Ph*$_3$) ppm. ^{31}P NMR (CD_2Cl_2): δ = 34.7 (*P*Ph$_3$) ppm. ^{13}C NMR (CD_2Cl_2): δ = 21.1 (s, OCO*C*H$_3$), 122.9 (t, $^1J_{CP}$ + $^3J_{CP}$ = 52.0 Hz, PPh$_3$-*C*$_1$), 129.6 (t, $^3J_{CP}$ + $^5J_{CP}$ = 10.7 Hz, PPh$_3$-*C*$_3$), 133.0 (s, PPh$_3$-*C*$_4$), 134.7 (t, $^2J_{CP}$ + $^4J_{CP}$ = 10.8 Hz, PPh$_3$-*C*$_2$) ppm, the resonance for the carbonyl carbon could not be observed, presumably because it is broadened as a result of exchange. IR (KBr): $\tilde{\nu}$ = 1364 (κ^1-OAc$_{sym}$), 1435 (P–Ph), 1483 (P–Ph), 1636 (κ^1-OAc$_{asym}$), 1865 (NO) cm^{-1}, $\Delta\nu_{(uni)}$ = 271 cm^{-1}. IR (CH_2Cl_2): $\tilde{\nu}$ = 1359 (κ^1-OAc$_{sym}$), 1438 (P–Ph), 1485 (P–Ph), 1636 (κ^1-OAc$_{asym}$), 1874 (NO) cm^{-1}, $\Delta\nu_{(uni)}$ = 277 cm^{-1}. MS (ESI): calcd. for $C_{40}H_{36}NO_5P_2Ru$ [M]$^+$ *m*/*z* = 774.1107, found *m*/*z* = 774.1094. $C_{40}H_{36}BF_4NO_5P_2Ru$ + (1.00CH_2Cl_2): calcd. C 52.08, H 4.05, N 1.48; found C 51.89, H 4.20, N 1.60.

Synthesis of [Ru(κ^1-OAc)(κ^2-OAc)(CN*t*Bu)(PPh_3)$_2$] (4): [Ru(κ^2-OAc)$_2$(PPh_3)$_2$] (0.4 g, 0.54 mmol) was dissolved in CH_2Cl_2 (25mL) in a Schlenk tube. *t*BuNC (60 μL,0.54 mmol, 1 equiv.) was added. The solution was then stirred for 30 min until the solution changed from orange-red to green. The solvent was removed in vacuo and the yellow-green residue was washed with 2 × 20 mL portions of pentane. The product was dried in vacuo. Yield = 0.15 g (35.0%). ^{1}H NMR (CD_2Cl_2): δ = 0.62 [s, 9 H, C(CH_3)$_3$] 0.65 (s, 6 H, OCOCH_3) 7.27–7.33 (m, 18 H, P*Ph*$_3$), 7.40–7.47 (m, 12 H, P*Ph*$_3$) ppm. ^{31}P NMR (CD_2Cl_2): δ = 41.8 (*P*Ph$_3$) ppm. ^{13}C NMR (CD_2Cl_2): δ = 22.5 (s, OCO*C*H$_3$), 30.2 [s, C(*C*H$_3$)$_3$], 56.9 [s, N*C*(CH$_3$)$_3$], 127.8 (t, $^3J_{CP}$ + $^5J_{CP}$ = 9.2 Hz, PPh$_3$-*C*$_3$), 129.4 (s, PPh$_3$-*C*$_4$), 132.8 (t, $^1J_{CP}$ + $^3J_{CP}$ = 44.0 Hz, PPh$_3$-*C*$_1$), 134.7 (t, $^2J_{CP}$ + $^4J_{CP}$ = 12.0 Hz, PPh$_3$-C$_2$), 161.9 (br., s Ru*C*N), 180.7 (s, RuO*C*O) ppm. IR (KBr): $\tilde{\nu}$ = 1366 (κ^1-OCO$_{sym}$), 1434 (P–Ph), 1462 (κ^2-OCO$_{sym}$), 1482 (P–Ph), 1529 (κ^2-OCO$_{assym}$), 1627 (κ^1-OCO$_{assym}$), 2067, 2105 (CN) cm^{-1}, $\Delta\nu_{(uni)}$ = 261 cm^{-1}, $\Delta\nu_{(chelate)}$ = 67 cm^{-1}. IR (CH_2Cl_2): $\tilde{\nu}$ = 1374 (κ^1-OCO$_{sym}$), 1434 (P–Ph), 1460 (κ^2-OCO$_{sym}$), 1480 (P–Ph), 1528 (κ^2-OCO$_{assym}$), 1620 (κ^1-OCO$_{assym}$), 2070, 2104 (CN), $\Delta\nu$(uni) = 246 cm^{-1}, $\Delta\nu$(chelate) = 68 cm^{-1}. MS (ESI): calcd. for [M + H]$^+$ *m*/*z* = 828.1946, found *m*/*z* = 828.1939; calcd. for $C_{45}H_{45}N_2O_2P_2Ru$ [M – OAc + MeCN]$^+$ *m*/*z* = 809.1994, found *m*/*z* = 809.1998. $C_{45}H_{45}NO_4P_2Ru$ (826.87): calcd. C 65.37, H 5.49, N 1.69; found C 64.35, H 5.19, N 1.63.

Synthesis of [Ru(κ¹-OAc)(κ²-OAc)(=C=CH{py}(PPh$_3$)$_2$)] (6c): 1-Ethynylpyrene (20.0 mg, 0.09 mmol) was dissolved in CH_2Cl_2 (7 mL) in a round-bottomed flask. This solution was then transferred by a cannula wire to a Schlenk tube containing **1** (66.7 mg, 0.09 mmol) with a stirrer bar. The mixture was stirred under N_2 for 1 h. After this time the solution was concentrated in vacuo and pentane (25 mL) was added to precipitate the product as a bright-red powder. The liquid was removed by a filter-tipped cannula and the product was washed with two further portions of pentane (10 mL) before finally drying in vacuo. Yield = 0.035 g (41%). ^{1}H NMR (CD_2Cl_2): δ = 0.95 (s, 6 H, OCOCH_3), 6.20 (t, $^4J_{HP}$ = 3.6 Hz, 1 H, [Ru]=C=C***H***), 7.27–7.33 (m, 18 H, PPh$_3$), 7.54–7.58 (m, 12 H, PPh$_3$), 7.77–7.87 (m, 3 H, pyrene), 7.91–8.00 (m, 4 H, pyrene), 8.09 (t, J = 7.6 Hz, 2 H, pyrene) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ_P = 33.8 (PPh$_3$) ppm. ^{13}C{^{1}H}NMR (CD_2Cl_2): δ = 22.0 (s, OCO*C*H$_3$), 109.4 (t, $^3J_{PC}$ = 4.56 Hz, Ru=C=CPh), 124.0, 124.2, 124.3, 124.5 (q), 124.8, 125.2, 125.2 (q), 125.3, 125.5, 125.7, 127.6, 127.9 (t, $^3J_{CP}$ + $^5J_{CP}$ = 9.24 Hz, PPh$_3$-C3), 128.1 (q), 128.7 (q), 129.4 (t, $^1J_{CP}$ + $^3J_{CP}$ = 43.1 Hz, PPh$_3$-*C*$_1$), 130.0 (s, PPh$_3$-*C*$_4$), 131.4, 131.8, 134.9 (t, $^2J_{CP}$ + $^4J_{CP}$ = 10.9 Hz, PPh$_3$-*C*$_2$), 179.8 (s, O*C*OCH$_3$) (q) ppm. IR (KBr): $\tilde{\nu}$ = 1360 (κ¹-OAc$_{sym}$), 1434 (P-Ph), 1458 (κ²-OAc$_{sym}$), 1536 (κ²-OAc$_{asym}$), 1587 (κ¹-OAc$_{asym}$), 1610 (C=C) cm^{-1}, Δν(uni) = 227 cm^{-1}, Δν(chelate) 78 cm^{-1}. IR (CH_2Cl_2): $\tilde{\nu}$ = 1366 (κ¹-OAc$_{sym}$), 1434 (P–Ph), 1462 (κ²-OAc$_{sym}$), 1530 (κ²-OAc$_{asym}$), 1590 (κ¹-OAc$_{asym}$), 1607 (C=C) cm^{-1}, Δν$_{(uni)}$ = 224 cm^{-1}, Δν$_{(chelate)}$ = 68 cm^{-1}. MS (ESI): calcd. for [M + H]$^+$ *m*/*z* = 971.1988, found *m*/*z* = 971.1968; calcd. for $C_{58}H_{46}NO_2P_2Ru$ [M – OAc + MeCN]$^+$ *m*/*z* = 952.2042, found *m*/*z* = 952.2034. $C_{58}H_{46}O_4P_2Ru$ + (0.30CH_2Cl_2): calcd. C 70.34, H 4.72; found C 69.89, H 4.82.

Synthesis of [Ru(κ¹-OAc)(κ²-OAc)(=C=CH{SiMe$_3$})(PPh$_3$)$_2$]BF$_4$ (6d): Complex **1** (200 mg, 0.27 mmol) was dissolved in CH_2Cl_2 (10 mL) and HC≡CSiMe$_3$ (38.0 μL, 0.27 mmol, 1 equiv.) was then added. The mixture was stirred for 1 h at room temperature. The solvent was evaporated and the solid was washed with three portions of pentane (10 mL). After drying in vacuo, the desired yellow product (134 mg, 59%) was obtained. ^{1}H NMR (CD_2Cl_2): δ = –0.43 (s, 9 H, Si*Me*$_3$), 0.74 (s, 6 H, OCOCH_3), 3.74 (t, $^4J_{PH}$ = 3.7 Hz, 1 H, Ru=C=C*H*SiMe$_3$) ppm. ^{31}P NMR (CD_2Cl_2): δ = 35.5 (s, *P*Ph$_3$) ppm. ^{13}C NMR (CD_2Cl_2): δ = 0.44 (Si*Me*$_3$), 22.2 (OCO*C*H$_3$), 94.0 (Ru=C=*C*), 127.9 (t, $^3J_{CP}$ + $^5J_{CP}$ = 10.2 Hz, PPh$_3$-*C*$_3$), 129.9 (s, PPh$_3$-*C*$_4$), 130.2 (t, $^1J_{CP}$ + $^3J_{CP}$ = 40.8 Hz, PPh$_3$-*C*$_1$), 135.0 (t, $^2J_{CP}$ + $^4J_{CP}$ = 11.2 Hz, PPh$_3$-*C*$_2$), 179.6 (s, O*C*OCH$_3$), 337.6 (t, $^2J_{CP}$ = 15.3 Hz, Ru=*C*=C) ppm. IR (KBr): $\tilde{\nu}$ = 1361 (κ¹-OCO$_{sym}$), 1433 (P–Ph), 1463 (κ²-OCO$_{sym}$), 1521 (κ²-OCO$_{asym}$), 1611 (κ¹-OCO$_{asym}$), 1633 (C=C) cm^{-1}, Δν$_{(uni)}$ = 250 cm^{-1}, Δν$_{(chelate)}$ = 58 cm^{-1}. IR (CH_2Cl_2): $\tilde{\nu}$ = 1366 (κ¹-OCO$_{sym}$), 1433 (P–Ph), 1459 (κ²-OCO$_{sym}$), 1531 (κ²-OCO$_{asym}$), 1617 (κ¹-OCO$_{asym}$), 1636 (C=C) cm^{-1}, Δν$_{(uni)}$ = 250 cm^{-1}, Δν$_{(chelate)}$ = 72 cm^{-1}. MS (ESI): calcd. for $C_{45}H_{46}NaO_4P_2RuSi$ [M + Na]$^+$ *m*/*z* = 866.1582, found *m*/*z* = 865.1608; calcd. for $C_{45}H_{47}O_4P_2RuSi$ [M + H]$^+$ *m*/*z* = 843.1757, found *m*/*z* = 843.1791; calcd. for $C_{45}H_{46}NO_2P_2RuSi$ [M – OAc + NCMe]$^+$ *m*/*z* = 824.1817, found *m*/*z* = 824.1828; calcd. for $C_{43}H_{43}O_2P_2RuSi$ [M – OAc]$^+$ *m*/*z* = 783.1546, found *m*/*z* = 783.1551; calcd. for $C_{27}H_{32}O_4PRuSi$ [M + H – PPh$_3$]$^+$ *m*/*z* = 581.0851, found *m*/*z* = 581.0849; calcd. for $C_{24}H_{24}O_4PRuSi$ [M + 2H – PPh$_3$ – SiMe$_3$]$^+$ *m*/*z* = 509.0456, found *m*/*z* = 509.0459. On crystallisation, small quantities of dark-red crystals of **1** were reformed in addition to the bright-yellow crystals of **5d**, which precluded an accurate elemental analysis.

General Procedure for Complexes 8 and 11: In a typical experiment, ca. 1 equiv. of the appropriate alkyne was added to a Schlenk vessel containing a solution of **1** in CH_2Cl_2. After stirring for 1 h the product was precipitated by addition of pentane or hexane. The resulting powder was isolated by filtration and washed twice more with pentane or hexane and dried in vacuo. If required, this product was recrystallised by slow diffusion of pentane or hexane into a CH_2Cl_2 solution of the complex.

Complex 8c: This complex was obtained as a yellow-orange powder from **1** (0.30 g, 0.40 mmol) and HC≡CCH$_2$OH (22.0 μL, 0.38 mmol) in CH_2Cl_2 (20 mL). Yield = 0.17 g (53%). ^{1}H NMR (CD_2Cl_2): δ = 0.85 (s, 6 H, OCOCH_3), 1.26 [t, $^3J_{HH}$ = 5.6 Hz, 1 H, (Ru)=C=CHC(O*H*)], 3.88 ($^3J_{HH}$ = 6.5 Hz, at 2 H, [Ru]=C=CHCH_2), 4.11 (apparent septet, $^4J_{HP}$ = 3.7 Hz, 1 H, [Ru]=C=C*H*), 7.40–7.51 (m, 30 H, P*Ph*$_3$) ppm. ^{31}P NMR (CD_2Cl_2): δ = 35.1 (s, *P*Ph$_3$) ppm. ^{13}C NMR (CD_2Cl_2): δ = 21.8 (s, OCO*C*H$_3$), 54.9 (s, Ru=C=CH–*C*OH), 106.5 (t, $^3J_{PC}$ = 4.96 Hz, Ru=C=*C*), 128.0 (t, $^3J_{PC}$ + $^5J_{PC}$ = 9.21 Hz, PPh$_3$-*C*$_3$), 129.8 (t, $^1J_{PC}$ + $^3J_{PC}$ = 40.3 Hz, PPh$_3$-*C*$_1$), 130.1 (s, PPh$_3$-*C*$_4$), 134.8 (t, $^2J_{PC}$ + $^4J_{PC}$ = 11.8 Hz, PPh$_3$-*C*$_2$), 179.7 (s, O*C*OCH$_3$), 345.7 (t, $^2J_{PC}$ = 16.3 Hz, Ru=*C*) ppm. IR (KBr): $\tilde{\nu}$ = 1372 (κ¹-OCO$_{sym}$), 1433 (P–Ph), 1457 (κ²-OCO$_{sym}$), 1533 (κ²-OCO$_{asym}$), 1595 (κ¹-OCO$_{asym}$), 1655 (C=C), 3337 (OH) cm^{-1}, Δν$_{(uni)}$ = 223 cm^{-1}, Δν$_{(chelate)}$ = 76 cm^{-1}. IR (CH_2Cl_2): $\tilde{\nu}$ = 1368 (κ¹-OCO$_{sym}$), 1434 (P–Ph), 1456 (κ²-OCO$_{sym}$), 1538 (κ²-OCO$_{asym}$), 1605 (κ¹-OCO$_{asym}$), 1651 (C=C), 3573 (OH) cm^{-1}, Δν$_{(uni)}$ = 237 cm^{-1}, Δν$_{(chelate)}$ = 82 cm^{-1}. MS (ESI): calcd. for $C_{43}H_{41}O_5P_2Ru$ [M + H]$^+$ *m*/*z* = 801.1473, found *m*/*z* = 801.1502. MS (LIFDI): *m*/*z* = 798 [M – 2H]$^+$. Elemental analysis could not be obtained because of rapid conversion to **2** and ethene.

Complex 8d: This complex was obtained as a pale-yellow powder from **1** (0.20 g, 0.27 mmol) and HC≡CC(OH)(Ph)(H) (32.7 μL, 0.27 mmol) in CH_2Cl_2 (15 mL). Yield = 0.16 g (70%) ^{1}H NMR (CD_2Cl_2): δ = 0.86 (s, 6 H, OCOCH_3), 2.87 [br. s, 1 H, (Ru)=C=CHCH(O*H*)Ph], 4.14 [dt, $^4J_{HP}$ = 3.8, $^3J_{HH}$ = 6.4 Hz, 1 H, (Ru)=C=C*H*CH(OH)Ph], 5.44 [d, $^3J_{HH}$ = 6.34 Hz, 1 H, (Ru)=C=CHC*H*(OH)Ph], 6.83 (d, J = 7.3 Hz, 2 H, H_2-Ph), 7.09 (J = 7.5 Hz, 2 H, H_3-Ph), 7.14 (tt, J = 7.2 Hz, J = 1.4 Hz, 1 H, H_4-Ph), 7.41 (at, J = 7.3 Hz, 12 H, H_3-P*Ph*$_3$), 7.48 (t, J = 7.2 Hz, 6 H, H_4-P*Ph*$_3$), 7.53 (m, 12 H, H_2-P*Ph*$_3$) ppm. ^{31}P NMR (CD_2Cl_2): δ = 34.9 (s, *P*Ph$_3$) ppm. ^{13}C NMR (CD_2Cl_2): δ = 21.8 (s, OCO*C*H$_3$), 67.0 (s, Ru=C=CH–*C*OH), 112.5 (t, $^3J_{PC}$ = 4.72 Hz, Ru=C=*C*), 126.3 [s, Ru=C=C–C(Ph–*C*$_3$)], 126.6 [s, Ru=C=C–C(Ph–*C*$_4$)], 127.8 [s, Ru=C=C–C(Ph–*C*$_2$)], 128.1 (t, $^3J_{PC}$ + $^5J_{PC}$ = 9.25 Hz, PPh$_3$-*C*$_3$), 129.7 (t, $^1J_{PC}$ + $^3J_{PC}$ = 42.4 Hz, PPh$_3$-*C*$_1$), 130.2 (s, PPh$_3$-*C*$_4$), 134.9 (t, $^2J_{PC}$ + $^4J_{PC}$ = 12.2 Hz, PPh$_3$-*C*$_2$), 144.9 [Ru=C=C-C(Ph-*C*$_1$)], 179.9 (s, O*C*OCH$_3$), 345.1 (t, cm$^{-12}J_{PC}$ = 16.2 Hz, Ru=*C*) ppm. IR (KBr): $\tilde{\nu}$ = 1369 (κ¹-OCO$_{sym}$), 1435 (P–Ph), 1454 (κ²-OCO$_{sym}$), 1537 (κ²-OCO$_{asym}$), 1592 (κ¹-OCO$_{asym}$), 1648 (C=C) cm^{-1}, Δν$_{(uni)}$ = 223 cm^{-1}, Δν$_{(chelate)}$ = 83 cm^{-1}; IR (CH_2Cl_2): $\tilde{\nu}$ = 1373 (κ¹-OCO$_{sym}$), 1435 (P–Ph), 1455 (κ²-OCO$_{sym}$), 1538 (κ²-OCO$_{asym}$), 1596 (κ¹-OCO$_{asym}$), 1647 (C=C) cm^{-1}, Δν$_{(uni)}$ = 223 cm^{-1}, Δν$_{(chelate)}$ = 83 cm^{-1}. MS (LIFDI): *m*/*z* = 876 [M]$^+$. $C_{49}H_{44}O_5P_2Ru$ + (1.60CH_2Cl_2): calcd. C 60.07, H 4.70; found C 60.20, H 5.00.

Complex 8e: This complex was obtained as a bright-yellow powder from the reaction of **1a** (0.15 g, 0.20 mmol) and HC≡CC(OH)(Ph)(Me) (0.03 g, 0.20 mmol) in CH_2Cl_2 (10 mL). Pentane (40 mL) was used to precipitate the product, and it was washed further with 2 × 15 mL portions of pentane. Yield = 0.12 g (67%) ^{1}H NMR (CD_2Cl_2): δ = 0.81 (s, 6 H, OCOCH_3), 1.10 [s, 3 H, HC≡CC(CH_3)], 2.79 [br. s, 1 H, (Ru)=C=CHC(O*H*)], 4.56 (t, $^4J_{HP}$ = 3.9 Hz, 1 H, [Ru]=C=C*H*), 6.96–7.10 [m, 5 H, HC≡CC(*Ph*)], 7.37–7.50 (m, 31 H, P*Ph*$_3$) ppm. ^{31}P NMR (CD_2Cl_2): δ = 34.3 (s, *P*Ph$_3$) ppm. ^{13}C NMR (CD_2Cl_2): δ = 21.8 (s, OCO*C*H$_3$), 33.6 [s, Ru=C=C–C(*C*H$_3$)], 71.1 (s, Ru=C=CH–*C*OH), 117.6 (t, $^3J_{PC}$ = 4.3 Hz, Ru=C=*C*), 124.9 [s, Ru=C=C–C(Ph–*C*$_3$)], 125.8 [s, Ru=C=C–C(Ph–*C*$_4$)], 127.7 [s, Ru=C=C–C(Ph–*C*$_2$)], 128.0

(t, $^3J_{PC}$ + $^5J_{PC}$ = 9.55 Hz, PPh_3-C_3), 129.4 (t, $^1J_{PC}$ + $^3J_{PC}$ = 43.2 Hz, PPh_3-C_1), 130.1 (s, PPh_3-C_4), 135.0 (t, $^2J_{PC}$ + $^4J_{PC}$ = 11.6 Hz, PPh_3-C_2), 150.4 (Ru=C=C-CPh-C_1), 179.6 (s, O*C*OCH$_3$), 350.4 (t, $^2J_{PC}$ = 16.0 Hz, Ru=*C*) ppm. IR (KBr): $\tilde{\nu}$ = 1361 (κ^1-OCO_{sym}), 1434 (P–Ph), 1458 (κ^2-OCO_{sym}), 1536 (κ^2-OCO_{asym}), 1601 (κ^1-OCO_{asym}), 1649 (C=C), 3366 (OH) cm^{-1}, $\Delta\nu_{(uni)}$ = 240 cm^{-1}, $\Delta\nu_{(chelate)}$ = 78 cm^{-1}. IR (CH_2Cl_2): $\tilde{\nu}$ = 1367 (κ^1-OCO_{sym}), 1434 (P–Ph), 1463 (κ^2-OCO_{sym}), 1533 (κ^2-OCO_{asym}), 1601 (κ^1-OCO_{asym}), 1652 (C=C), 3565 (OH) cm^{-1}, $\Delta\nu_{(uni)}$ = 234 cm^{-1}, $\Delta\nu_{(chelate)}$ = 70 cm^{-1}. MS (ESI): calcd. for $C_{50}H_{45}O_4P_2Ru$ [M – OH]$^+$ *m*/*z* = 873.1831, found *m*/*z* = 873.2074. $C_{50}H_{46}O_5P_2Ru$ + (0.40CH_2Cl_2) : calcd. C 65.52, H 5.11; found C 65.75, H 5.21.

Complex 8f: This complex was obtained as a bright pink-orange powder from **1** (0.25 g, 0.34 mmol) and 1-ethynylcyclopentanol (40.0 μL, 0.35 mmol) in CH_2Cl_2 (15 mL). Yield = 0.28 g (84%). ^{1}H NMR (CD_2Cl_2): δ = 0.83 (s, 6 H, OCOC*H*$_3$), 1.00 (m, 2.0 H), 1.24 (m, 4 H), 1.35 [br. s, 1.0 H, (Ru)=C=CHC(O*H*)], 1.50 (m, 2 H), 4.38 (t, $^4J_{HP}$ = 3.8 Hz, 1.0 H, [Ru]=C=C*H*), 7.39–7.51 (m, 32 H, P*Ph*$_3$) ppm. ^{31}P NMR (CD_2Cl_2): δ = 34.3 (s, *P*Ph$_3$) ppm. ^{13}C NMR (CD_2Cl_2): δ = 21.9 (s, OCO*C*H$_3$), 23.5 (*C*H$_2$), 23.6 (*C*H$_2$), 41.5 (*C*H$_2$), 42.5 (*C*H$_2$), 70.7 (s, Ru=C=CH–*C*OH), 116.3 (t, $^3J_{PC}$ = 4.63 Hz, Ru=C=*C*), 128.0 (t, $^3J_{PC}$ + $^5J_{PC}$ = 9.50 Hz, PPh_3-C_3), 129.1 (t, $^1J_{PC}$ + $^3J_{PC}$ = 42.3 Hz, PPh_3-C_1), 130.0 (s, PPh_3-C_4), 134.9 (t, $^2J_{PC}$ + $^4J_{PC}$ = 12.3 Hz, PPh_3-C_2), 179.6 (s, O*C*OCH$_3$), 352.0 (t, $^2J_{PC}$ = 16.3 Hz, Ru=*C*) ppm. IR (KBr): $\tilde{\nu}$ = 1364 (κ^1-OCO_{sym}), 1434 (P–Ph), 1458 (κ^2-OCO_{sym}), 1536.2 (κ^2-OCO_{asym}), 1590 (κ^1-OCO_{asym}), 1654 (C=C), 3370 (OH) cm^{-1}, $\Delta\nu_{(uni)}$ = 226 cm^{-1}, $\Delta\nu_{(chelate)}$ = 77 cm^{-1}; IR (CH_2Cl_2): $\tilde{\nu}$ = 1364 (κ^1-OCO_{sym}), 1431 (P–Ph), 1479 (κ^2-OCO_{sym}), 1532 (κ^2-OCO_{asym}), 1624 (κ^1-OCO_{asym}), 1656 (C=C), 3569 (OH) cm^{-1}, $\Delta\nu_{(uni)}$ = 260 cm^{-1}, $\Delta\nu_{(chelate)}$ = 53 cm^{-1}. MS (ESI): calcd. for $C_{47}H_{45}O_4P_2Ru$ [M – OH]$^+$ *m*/*z* = 837.1837, found *m*/*z* = 837.18. $C_{47}H_{46}O_5P_2Ru$ + (1.40CH_2Cl_2): calcd. C 59.76, H 5.06; found C 59.67, H 5.07.

Complex 8g: This complex was obtained as a pale-orange powder from **1** (0.50 g, 0.67 mmol) and 1-ethynylcyclohexanol (90.0 μL, 0.70 mmol) in CH_2Cl_2 (15 mL). Pentane (25 mL) was used to precipitate the product, and it was washed further with 2 × 15 mL portions of pentane. Yield = 0.25 g (43%). ^{1}H NMR (CD_2Cl_2): δ = 0.82 (s, 6 H, OCOC*H*$_3$), 0.86–1.09 (m, 6 H, C*H*$_2$), 1.17 [br. s, 1 H, (Ru)=C=CHC(O*H*)], 1.23–1.35 (m, 4 H, C*H*$_2$), 4.39 (t, $^2J_{HP}$ = 3.7 Hz, 1.0 H, [Ru]=C=C*H*), 7.40–7.51 (m, 31 H, P*Ph*$_3$) ppm. ^{31}P NMR (CD_2Cl_2): δ = 34.4 (s, *P*Ph$_3$) ppm. ^{13}C NMR (CD_2Cl_2): δ = 21.9 (s, OCO*C*H$_3$), 22.6 (***C***H$_2$), 23.2 (***C***H$_2$), 25.5 (***C***H$_2$), 39.7 (***C***H$_2$), 39.9 (***C***H$_2$), 69.6 (s, Ru=C=CH–*C*OH), 117.5 (t, $^3J_{PC}$ = 4.7 Hz, Ru=C=*C*), 128.0 (t, $^3J_{PC}$ + $^5J_{PC}$ = 9.3 Hz, PPh_3-C_3), 129.6 (t, $^1J_{PC}$ + $^3J_{PC}$ = 43.0 Hz, PPh_3-C_1), 130.1 (s, PPh_3-C_4), 135.0 (t, $^2J_{PC}$ + $^4J_{PC}$ = 11.5 Hz, PPh_3-C_2), 179.5 (s, O*C*OCH$_3$), 352.1 (t, $^2J_{PC}$ = 16.5 Hz, Ru=*C*) ppm. IR (KBr): $\tilde{\nu}$ = 1366 (κ^1-OCO_{sym}), 1434 (P–Ph), 1458 (κ^2-OCO_{sym}), 1538 (κ^2-OCO_{asym}), 1591 (κ^1-OCO_{asym}), 1646 (C=C), 3421 (OH) cm^{-1}, $\Delta\nu_{(uni)}$ = 225 cm^{-1}, $\Delta\nu_{(chelate)}$ = 80 cm^{-1}; IR (CH_2Cl_2): $\tilde{\nu}$ = 1368 (κ^1-OCO_{sym}), 1434 (P–Ph), 1461 (κ^2-OCO_{sym}), 1536 (κ^2-OCO_{asym}), 1600 (κ^1-OCO_{asym}), 1648 (C=C), 3571 (OH) cm^{-1}, $\Delta\nu_{(uni)}$ = 232 cm^{-1}, $\Delta\nu_{(chelate)}$ = 75 cm^{-1}. MS (ESI): MS (ESI): calcd. for $C_{48}H_{47}O_4P_2Ru$ [M – OH]$^+$ *m*/*z* = 851.1993, found *m*/*z* = 851.1927. $C_{48}H_{48}O_5P_2Ru$·1.20CH_2Cl_2 : calcd. C 60.93, H 5.24; found C 61.10, H 5.29.

Complex 8h: This complex was obtained as a bright-orange powder from **1** (0.20 g, 0.27 mmol) and 9-ethynyl-9-fluorenol (0.06 mg, 0.29 mmol) in CH_2Cl_2 (15 mL). Yield = 0.12 g, (48%). ^{1}H NMR (CD_2Cl_2): δ = 0.82 (s, 6 H, OCOC*H*$_3$), 2.77 [br. s, 1 H, (Ru)=C=CHC(O*H*)], 4.56 (t, $^4J_{HP}$ = 3.8 Hz, 1.0 H, [Ru]=C=C*H*), 6.63–7.26 (m, 8 H, C*H* of fluorenyl), 7.35–7.47 (m, 34 H, P*Ph*$_3$) ppm. ^{31}P NMR (CD_2Cl_2): δ = 33.9 (s, *P*Ph$_3$) ppm. ^{13}C NMR (CD_2Cl_2): δ = 21.8 (s, OCO*C*H$_3$), 77.1 (s, Ru=C=CH–*C*OH), 113.6 (t, $^3J_{PC}$ = 4.58 Hz, Ru=C=*C*), 119.3 (s, *C*H), 124.1 (s, *C*H), 127.7, (s, *C*H) 127.9 (s, *C*H) 128.0 (t, $^3J_{PC}$ + $^5J_{PC}$ = 9.2 Hz, PPh_3-C_3), 129.2 (t, $^1J_{PC}$ + $^3J_{PC}$ = 41.6 Hz, PPh_3-C_1), 130.2 (s, PPh_3-C_4), 135.0 (t, $^2J_{PC}$ + $^4J_{PC}$ = 11.5 Hz, PPh_3-C_2), 138.6 (s, *C*), 150.3, (s, *C*) 179.6 (s, O*C*OCH$_3$), 349.3 (t, $^2J_{PC}$ = 16.1 Hz, Ru=*C*) ppm. IR (KBr): $\tilde{\nu}$ = 1367 (κ^1-OCO_{sym}), 1433 (P–Ph), 1463 (κ^2-OCO_{sym}), 1534 (κ^2-OCO_{asym}), 1597 (κ^1-OCO_{asym}), 1636 (C=C), 3403 (OH) cm^{-1}, $\Delta\nu_{(uni)}$ = 230 cm^{-1}, $\Delta\nu_{(chelate)}$ = 71 cm^{-1}; IR (CH_2Cl_2): $\tilde{\nu}$ = 1367 (κ^1-OCO_{sym}), 1435 (P–Ph), 1463 (κ^2-OCO_{sym}), 1531 (κ^2-OCO_{asym}), 1606 (κ^1-OCO_{asym}), 1646 (C=C), 3554 (OH) cm^{-1}, $\Delta\nu_{(uni)}$ = 239 cm^{-1}, $\Delta\nu_{(chelate)}$ = 68 cm^{-1}. MS (ESI): calcd. for $C_{55}H_{46}NO_3P_2Ru$ [M – OAc + MeCN]$^+$ *m*/*z* = 932.1996, found *m*/*z* = 932.1995. $C_{55}H_{46}O_5P_2Ru$·1.20CH_2Cl_2: calcd. C 64.17, H 4.64; found C 64.33, H 4.66.

Complex 8i: This complex was obtained as a bright-yellow powder from **1** (0.30 g, 0.40 mmol) and ethisterone (0.16 g, 0.50 mmol) in CH_2Cl_2 (30 mL). The solvent was removed completely in vacuo before the product was washed with 3 × 30 mL portions of pentane. Yield = 0.21 g (50%). ^{1}H NMR (CD_2Cl_2): δ = 0.37–0.67 (m, 3 H, –CH–, –CH$_2$–), 0.71 (s, 3 H, CH$_3$), 0.75 (s, 6 H, OCOCH$_3$), 1.13 (s, 3 H, CH$_3$), 1.20–2.04 (m, 12 H, –CH–, –CH$_2$–), 2.16 (s, 1 H, OH), 2.19 –2.47 (m, 4 H, –CH–, –CH$_2$–), 4.48 (t, $^4J_{HP}$ = 3.7 Hz, 1 H, [Ru]=C=CH), 5.70 (br. s, 1 H, =CH–), 7.41 (*J* = 7.1 Hz, 12 H, H3-PPh$_3$), 7.45–7.51 (m, 18 H, H2-PPh$_3$ and H4-PPh$_3$) ppm. ^{31}P NMR (CD_2Cl_2): δ = 35.5 (s, PPh$_3$) ppm. ^{13}C NMR (CD_2Cl_2): δ = 13.3 (s, CH$_3$), 17.1 (s, CH$_3$), 20.5 (s, CH$_2$), 21.7 (s, OCOCH$_3$), 24.1 (s, CH$_2$), 31.5 (s, CH$_2$), 31.8 (s, CH$_2$), 32.9 (s, CH$_2$), 34.2 (s, CH$_2$), 35.8 (s, CH$_2$), 36.1 (s, C), 38.3 (s, CH), 38.7 (s, CH$_2$), 46.5 (s, C), 48.7 (s, CH), 52.4 (s, CH), 81.6 (s, Ru=C=CH–COH), 114.4 (t, $^3J_{PC}$ = 4.6 Hz, Ru=C=C), 123.5 (s, =CH–), 128.1 (t, $^3J_{PC}$ + $^5J_{PC}$ = 9.26 Hz, PPh_3–C_3), 129.4 (t, $^1J_{PC}$ + $^3J_{PC}$ = 42.4 Hz, PPh_3-C_1), 130.1 (s, PPh_3-C_4), 135.1 (t, $^2J_{PC}$ + $^4J_{PC}$ = 10.8 Hz, PPh_3-C_2), 171.8 (s, C), 179.5 (s, O*C*OCH$_3$), 199.1 (s, CO), 352.0 (t, $^2J_{PC}$ = 16.2 Hz, Ru=C) ppm. IR (KBr): $\tilde{\nu}$ = 1374 (κ^1-OCO_{sym}), 1433 (P–Ph), 1456 (κ^2-OCO_{sym}), 1530 (κ^2-OCO_{asym}), 1620 (κ^1-OCO_{asym}), 1649 (C=C), 3573 (OH) cm^{-1}, $\Delta\nu_{(uni)}$ = 246 cm^{-1}, $\Delta\nu_{(chelate)}$ = 74 cm^{-1}. IR (CH_2Cl_2): $\tilde{\nu}$ = 1372 (κ^1-OCO_{sym}), 1433 (P–Ph), 1458 (κ^2-OCO_{sym}), 1538 (κ^2-OCO_{asym}), 1616 (κ^1-OCO_{asym}), 1652 (C=C), 3564 (OH) cm^{-1}, $\Delta\nu_{(uni)}$ = 244 cm^{-1}, $\Delta\nu_{(chelate)}$ = 80 cm^{-1}. MS (ESI): calcd. for $C_{61}H_{64}NaO_6P_2Ru$ [M + Na]$^+$ *m*/*z* = 1079.3119, found *m*/*z* = 1079.3098; calcd. for $C_{61}H_{65}NO_4P_2Ru$ [M – OAc + MeCN]$^+$ *m*/*z* = 1039.3432, found *m*/*z* = 1039.3. $C_{61}H_{64}O_5P_2Ru$ + (0.10CH_2Cl_2): calcd. C 68.93, H 6.08; found C 68.59, H 6.18.

Synthesis of [Ru(κ^1-OAc)(κ^2-OAc)(=CO{CH_2}$_3$)(PPh_3)$_2$] (11a): Complex **11a** (0.04 g, 19.0%) was obtained as a bright-yellow powder from **1** (0.20 g, 0.27 mmol) and HC≡C(CH$_2$)$_2$OH (20.0 μL, 0.26 mmol) in DCM (15 mL). After reducing the volume of the solution by half in vacuo, pentane (40 mL) was used to precipitate the product, and it was washed further with 2 × 20 mL portions of pentane. Crystals for X-ray diffraction were obtained from a CH_2Cl_2/pentane solution. ^{1}H NMR (CD_2Cl_2): δ = 0.82 (s, 6 H, OCOC*H*$_3$), 0.93 (qn, $^3J_{HH}$ = 7.5 Hz, 2 H, [Ru]=COCH$_2$C*H*$_2$CH$_2$), 2.48 (t, $^3J_{HH}$ = 7.7 Hz, 2 H, [Ru]=COC*H*$_2$CH$_2$CH$_2$), 3.90 (t, $^3J_{HH}$ = 7.3 Hz, 2 H, [Ru]=COCH$_2$CH$_2$C*H*$_2$), 7.37 (*J* = 7.2 Hz, 12 H, *H*$_3$-P*Ph*$_3$), 7.42 (t, *J* = 7.1 Hz, 6 H, *H*$_4$-P*Ph*$_3$), 7.54 (m, 12 H, 12 H, *H*$_2$-P*Ph*$_3$) ppm. ^{31}P NMR (CD_2Cl_2): δ = 35.9 (s, *P*Ph$_3$) ppm. ^{13}C NMR (CD_2Cl_2): δ = 21.9 (s, OCO*C*H$_3$), 22.6 (s, [Ru]=COCH$_2$*C*H$_2$CH$_2$), 52.8 (s, [Ru]=COCH$_2$CH$_2$*C*H$_2$), 79.2 (s, [Ru]=CO*C*H$_2$CH$_2$CH$_2$), 127.8 (t, $^3J_{PC}$ + $^5J_{PC}$ = 9.3 Hz, PPh_3-C_3), 129.4 (s, PPh_3-C_4), 132.9 (t, $^1J_{PC}$ + $^3J_{PC}$ = 39.3 Hz, PPh_3-C_1), 134.4 (t, $^2J_{PC}$ + $^4J_{PC}$ = 11.8 Hz, PPh_3-C_2), 180.0 (s, O*C*OCH$_3$), 304.7 (t,

$^2J_{PC}$ = 11.8 Hz, [Ru]=*C*) ppm. IR (KBr): $\tilde{\nu}$ = 1368 (κ^1-OCO_{sym}), 1433 (P–Ph), 1481 (κ^2-OCO_{sym}), 1541 (κ^2-OCO_{asym}), 1616 (κ^1-OCO_{asym}) cm^{-1}, $\Delta\nu_{(uni)}$ = 248 cm^{-1}, $\Delta\nu_{(chelate)}$ = 60 cm^{-1}. IR (CH_2Cl_2): $\tilde{\nu}$ = 1375 (κ^1-OCO_{sym}), 1433 (P–Ph), 1483 (κ^2-OCO_{sym}), 1540 (κ^2-OCO_{asym}), 1615 (κ^1-OCO_{asym}) cm^{-1}, $\Delta\nu_{(uni)}$ = 240 cm^{-1}, $\Delta\nu_{(chelate)}$ = 57 cm^{-1}. MS (ESI): calcd. for $C_{44}H_{42}NO_3P_2Ru$ [M – OAc + MeCN]$^+$ *m*/*z* = 796.1683, found *m*/*z* = 796.1615; MS (LIFDI): *m*/*z* = 814 [M]$^+$. $C_{44}H_{42}O_5P_2Ru$ + (0.20CH_2Cl_2): calcd. C 63.90, H 5.14; found C 63.90, H 5.14.

Synthesis of [Ru(κ^1-OAc)(κ^2-OAc)(=CO{CH_2}$_4$)(PPh_3)$_2$] (11b): Complex **11b** (0.03 g, 11.1%) was obtained as a bright-yellow powder from **1** (0.25 g, 0.33 mmol) and HC≡C(CH_2)$_3$OH (32.0 μL, 0.34 mmol) in DCM (30 mL). After reducing the volume of the solution by half in vacuo, pentane (20 mL) was used to precipitate the product, and it was washed further with 2 × 20 mL portions of pentane. Crystals for X-ray diffraction were obtained from a CD_2Cl_2/pentane solution. ^{1}H NMR (CD_2Cl_2): δ = 0.77 (qn, $^3J_{HH}$ = 6.9 Hz, 2 H, [Ru]=COCH$_2$CH$_2$C*H*$_2$CH$_2$), 0.83 (s, 6 H, OCOC*H*$_3$), 1.02 (qn, $^3J_{HH}$ = 6.1 Hz, 2 H, [Ru]=COCH$_2$C*H*$_2$CH$_2$CH$_2$), 2.61 (t, $^3J_{HH}$ = 6.9 Hz, 2 H, [Ru]=COC*H*$_2$CH$_2$CH$_2$CH$_2$), 3.85 (t, $^3J_{HH}$ = 5.8 Hz, 2 H, [Ru]=COCH$_2$CH$_2$CH$_2$C*H*$_2$), 7.38 (*J* = 7.2 Hz, 12 H, *H*$_3$-P*Ph*$_3$), 7.42 (t, *J* = 7.1 Hz, 6 H, *H*$_4$-P*Ph*$_3$), 7.56 (m, 12 H, *H*$_2$-P*Ph*$_3$) ppm. ^{31}P NMR (CD_2Cl_2): δ = 35.4 (s, *P*Ph$_3$) ppm. ^{13}C NMR (CD_2Cl_2): δ = 17.0 (s, [Ru]=COCH$_2$CH$_2$*C*H$_2$CH$_2$), 21.6 (s, OCO*C*H$_3$), 22.6 (s, [Ru]=COCH$_2$*C*H$_2$CH$_2$CH$_2$), 47.2 (s, [Ru]=COCH$_2$CH$_2$CH$_2$*C*H$_2$), 72.3 (s, [Ru]=CO*C*H$_2$CH$_2$CH$_2$CH$_2$), 127.8 (t, $^3J_{PC}$ + $^5J_{PC}$ = 9.39 Hz, PPh$_3$–*C*$_3$), 129.4 (s, PPh$_3$–*C*$_4$), 133.3 (t, $^1J_{PC}$ + $^3J_{PC}$ = 39.6 Hz, PPh$_3$–*C*$_1$), 134.5 (t, $^2J_{PC}$ + $^4J_{PC}$ = 11.3 Hz, PPh$_3$–*C*$_2$), 179.8 (s, O*C*OCH$_3$), 306.8 (t, $^2J_{PC}$ = 11.7 Hz, [Ru]=*C*) ppm. IR (KBr): $\tilde{\nu}$ = 1375 (κ^1-OCO_{sym}), 1432 (P–Ph), 1481 (κ^2-OCO_{sym}), 1549 (κ^2-OCO_{asym}), 1615 (κ^1-OCO_{asym}) cm^{-1}, $\Delta\nu_{(uni)}$ = 240 cm^{-1}, $\Delta\nu_{(chelate)}$ = 68 cm^{-1}. IR (CH_2Cl_2): $\tilde{\nu}$ = 1375 (κ^1-OCO_{sym}), 1434 (P–Ph), 1481 (κ^2-OCO_{sym}), 1545 (κ^2-OCO_{asym}), 1613 (κ^1-OCO_{asym}) cm^{-1}, $\Delta\nu_{(uni)}$ = 238 cm^{-1}, $\Delta\nu_{(chelate)}$ = 64 cm^{-1}. MS (ESI): calcd. for $C_{45}H_{44}NO_3P_2Ru$ [M – OAc + MeCN]$^+$ *m*/*z* = 810.1834, found *m*/*z* = 810.1825. $C_{45}H_{44}O_5P_2Ru$ + (1.80CH_2Cl_2): calcd. C 57.32, H 4.89; found C 57.60, H 4.90.

Synthesis of [Ru(κ^1-OAc)(κ^2-OAc)(=CO{CH_2}$_5$)(PPh_3)$_2$] (11c): Minor modifications were made to the general procedure for the preparation of **11c**. In this instance the mixture was stirred for 28 h at room temperature and the CH_2Cl_2 solvent was entirely removed in vacuo before the product was washed with pentane. Complex **11c** (0.09 g, 52.9%) was obtained as an orange powder from **1** (0.15 g, 0.19 mmol) and HC≡C(CH_2)$_4$OH (21.4 μL, 0.19 mmol) in DCM (10 mL). After removing the solvent in vacuo, the product was washed with 3 × 20 mL portions of pentane. Crystals for X-ray diffraction were obtained from a CH_2Cl_2/pentane solution. ^{1}H NMR (CD_2Cl_2): δ = 0.67 (m, 2 H, CH_2), 0.84 (s, 6 H, OCOC*H*$_3$), 0.91 (m, 2 H, CH_2), 1.16 (m, 2 H, CH_2), 2.72 (br. s, 2 H, CH_2), 3.85 (t, *J* = 4.2 Hz, 2 H, CH_2), 7.36–7.43 (m, 18 H, P*Ph*$_3$), 7.59–7.61 (m,

Table 7. Data collection and structural refinement details for single-crystal X-ray diffraction studies of compounds **3**[BF_4]·2CH_2Cl_2, **4**, **6b**·2CH_2Cl_2, **6c**·2CH_2Cl_2 and **8e**.

	3[BF_4]·2CH_2Cl_2	**4**	**6b**·2CH_2Cl_2	**6c**·2CH_2Cl_2	**8e**
Empirical formula	$C_{42}H_{40}BCl_4F_4NO_5P_2Ru$	$C_{45}H_{45}NO_4P_2Ru$	$C_{46}H_{44}Cl_4O_6P_2Ru$	$C_{60}H_{50}Cl_4O_4P_2Ru$	$C_{50}H_{46}O_5P_2Ru$
M_r [g mol^{-1}]	1030.37	826.83	997.62	1139.81	889.88
T [K]	110(2)	110(2)	110(2)	110(2)	110(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	triclinic	triclinic	triclinic
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	14.592(4)	23.2257(5)	11.1010(14)	13.5902(10),	11.6253(5)
b [Å]	20.189(6)	16.0087(3)	13.9967(17)	13.9934(10),	13.3991(6)
c [Å]	15.770(5)	10.42840(18)	15.1277(19)	16.6038(8)	15.2933(6)
α [°]	90	90	105.694(3)	98.866(5),	87.3510(10)
β [°]	100.348(6)	94.5276(18)	92.102(2)	106.633(5),	68.0190(10)
γ [°]	90	90	97.559(3)	115.860(7)	71.9900(10)
V [Å^3]	4570(2)	3865.32(13)	2236.8(5)	2576.1(3)	2094.27(15)
Z	4	4	2	2	2
ρ_{calcd} [Mg m^{-3}]	1.498	1.421	1.481	1.469	1.411
μ [mm^{-1}]	0.707	0.533	0.708	0.623	0.499
F(000)	2088	1712	1020	1168	920
Crystal size [mm]	0.24 × 0.17 × 0.06	0.13 × 0.11 × 0.07	0.14 × 0.05 × 0.04	0.24 × 0.17 × 0.13	0.11 × 0.10 × 0.04
θ range for data collection [°]	1.74 to 28.36	2.93 to 29.15	1.40 to 28.42	3.02 to 32.15	2.19 to 29.99
Index ranges	$19 \le h \le 19$	$-31 \le h \le 17$	$-14 \le h \le 14$	$-20 \le h \le 19$	$-16 \le h \le 16$
	$-26 \le k \le 26$	$-20 \le k \le 20$	$-18 \le k \le 18$	$-19 \le k \le 16$	$-18 \le k \le 18$
	$-21 \le l \le 20$	$-12 \le l \le 14$	$-20 \le l \le 20$	$-23 \le l \le 19$	$-21 \le l \le 21$
Measured reflections	46131	16216	22964	25341	23951
Unique reflections	11370	8830	11014	16076	11837
	[*R*(int) = 0.0377]	[*R*(int) = 0.0243]	[*R*(int) = 0.0706]	[*R*(int) = 0.0206]	[*R*(int) = 0.0201]
Completeness to θ	99.6 (to 28.36)	99.6 (to 26.32)	97.8 (to 28.42)	99.3 (to 30.0)	96.5 (to 30.03)
Absorption correction	semiempirical from equivalents				
Max., min. transmission	0.958, 0.748	0.963, 0.949	0.972, 0.742	0.955, 0.908	1.00, 0.851
Refinement method	full-matrix least squares on F^2				
Data/restraints/parameters	11370/33/593	8830/3/497	11014/4/533	16076/12/649	11837/0/527
GoF on F^2	1.029	1.086	1.007	1.044	1.033
Final *R* indices	R_1 = 0.0433	R_1 = 0.0385	R_1 = 0.0722	R_1 = 0.0337	R_1 = 0.0332
[$I > 2\sigma(I)$]	wR_2 = 0.1080	wR_2 = 0.0812	wR_2 = 0.1620	wR_2 = 0.0750	wR_2 = 0.0777
R indices	R_1 = 0.0625	R_1 = 0.0500	R_1 = 0.1345	R_1 = 0.0415	R_1 = 0.0449
(all data)	wR_2 = 0.1187	wR_2 = 0.0873	wR_2 = 0.1884	wR_2 = 0.0802	wR_2 = 0.0830
$\Delta\rho_{max/min}$ [e Å^{-3}]	1.317/–0.743	1.097/–0.943	1.373/–1.625	1.290/–0.944	1.094/–0.847

12 H, P*Ph*$_3$) ppm. ^{31}P NMR (CD_2Cl_2): δ = 34.2 (s, *P*Ph$_3$) ppm. ^{13}C NMR (CD_2Cl_2): δ = 20.4 (s, *C*H$_2$), 22.5 (s, OCO*C*H$_3$), 28.4 (s, *C*H$_2$), 29.2 (s, *C*H$_2$), 50.8 (s, [Ru]=C*C*H$_2$), 74.6 (s, [Ru]=CO*C*H$_2$), 127.7 (t, $^3J_{PC}$ + $^5J_{PC}$ = 9.2 Hz, PPh$_3$-*C*$_3$), 129.4 (s, PPh$_3$-*C*$_4$), 133.2 (t, $^1J_{PC}$ + $^3J_{PC}$ = 38.8 Hz, PPh$_3$-*C*$_1$), 134.5 (t, $^2J_{PC}$ + $^4J_{PC}$ = 11.5 Hz, PPh$_3$-*C*$_2$), 179.6 (s, O*C*OCH$_3$), 311.0 (t, $^2J_{PC}$ = 11.8 Hz, [Ru]=*C*) ppm. IR (KBr): $\tilde{\nu}$ = 1382 (κ^1-OCO$_{sym}$), 1433 (P–Ph), 1450 (κ^2-OCO$_{sym}$), 1546 (κ^2-OCO$_{asym}$), 1608 (κ^1-OCO$_{asym}$) cm^{-1}, $\Delta\nu_{(uni)}$ = 225 cm^{-1}, $\Delta\nu_{(chelate)}$ = 96 cm^{-1}. IR (CH_2Cl_2): $\tilde{\nu}$ = 1382 (κ^1-OCO$_{sym}$), 1433 (P–Ph), 1452 (κ^2-OCO$_{sym}$), 1548 (κ^2-OCO$_{asym}$), 1607 (κ^1-OCO$_{asym}$) cm^{-1}, $\Delta\nu_{(uni)}$ = 225 cm^{-1}, $\Delta\nu_{(chelate)}$ = 96 cm^{-1}. MS (ESI): calcd. for $C_{46}H_{47}O_5P_2Ru$ [M + H]$^+$ *m*/*z* = 843.1942, found *m*/*z* = 843.1936. $C_{46}H_{46}O_5P_2Ru$ + (0.30CH_2Cl_2): calcd. C 64.11, H 5.42; found C 64.17, H 5.50.

General Procedure for Monitoring the Degradation of Complexes 8a–i to Alkenes 9 by NMR Spectroscopy: Complex **1** (ca. 20 mg) was added to an NMR tube fitted with a Young's Tap and dissolved in approximately 0.5 mL CD_2Cl_2. The appropriate alkyne (1 equiv.) was then added to the sample to generate **8** in situ. NMR spectra were recorded soon after addition, and were re-recorded over a number of days until the conversion was judged to have gone to completion, although in some cases a trace amount of **8** remained. The alkenes **9a**, **9b**, **9c**, **9d**,[32] **9e**,[33] **9f**,[32] **9g**,[32] **9h**[34] and **9i**[35] were identified by comparison to literature data.

Details of X-ray Diffraction Experiments: Structural characterisation for complexes **3**[BF_4], **6b**, **8e**, **8f**, **11a** and **11b** was conducted using a Bruker Smart Apex diffractometer with Mo-K_α radiation (λ = 0.71073 Å) with a SMART CCD camera. Diffractometer control, data collection and initial unit cell determination were performed using the SMART program.[36] Frame integration and unit-cell refinement software were carried out with the program Saint+.[37] Absorption corrections were applied by SADABS (v 2.03, Sheldrick).[38] Structures were solved by direct methods using SHELXS-97, and refined by full-matrix least-squares using SHELX-97.[39] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using a riding model and included in the refinement at calculated positions.

Diffraction data for complexes **4**, **11c** and **6c**, were collected at 110 K on an Oxford Diffraction SuperNova diffractometer with Mo-K_α radiation (λ = 0.71073 Å) using an EOS CCD camera. The crystal was cooled with an Oxford Instruments Cryojet. Diffractometer control, data collection, initial unit cell determination, frame integration and unit-cell refinement were carried out with the program Crysalis.[40] Face-indexed absorption corrections were applied using spherical harmonics, implemented by the SCALE3 ABSPACK scaling algorithm.[41] OLEX2[42] was used for overall structure solution, refinement and preparation of computer graphics and publication data. Within OLEX2, the algorithms used for

Table 8. Data collection and structural refinement details for single-crystal X-ray diffraction studies of compounds **8f**·2CH_2Cl_2, **11a**·2CH_2Cl_2, **11b**·2CH_2Cl_2 and **11c**.

	8f·CH_2Cl_2	**11a**·2CH_2Cl_2	**11b**·2CH_2Cl_2	**11c**
Empirical formula	$C_{48}H_{48}Cl_2O_5P_2Ru$	$C_{46}H_{46}O_5P_2Cl_4Ru$	$C_{47}H_{48}Cl_4O_5P_2Ru$	$C_{46}H_{46}O_5P_2Ru$
M_r [g mol^{-1}]	938.77	983.64	997.66	841.84
T [K]	110(2)	110(2)	110(2)	110(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$Aba2$	$P2_1/c$
a [Å]	14.2578(11)	14.328(2)	18.2165(18)	23.3069(7)
b [Å]	20.5627(15)	21.311(3)	16.3759(16)	15.8366(3)
c [Å]	15.1557(11)	15.088(2)	15.0598(15)	10.6439(2)
α [°]	90	90	90	90
β [°]	104.8250(10)	105.083(3)	90	92.537(2)
γ [°]	90	90	90	90
V [Å^3]	4295.4(6)	4448.4(12)	4492.5(8)	3924.85(15)
Z	4	4	4	4
ρ_{calcd} [Mg m^{-3}]	1.452	1.469	1.475	1.425
μ [mm^{-1}]	0.611	0.710	0.704	0.528
F(000)	1936	2016	2048	1744
Crystal size [mm]	0.14 × 0.08 × 0.03	0.21 × 0.06 × 0.03	0.31 × 0.25 × 0.10	0.23 × 0.17 × 0.08
θ range for data collection [°]	2.48 to 28.24	1.69 to 25.03	2.15 to 28.31	3.11 to 30.04
Index ranges	$-19 \le h \le 19$	$-17 \le h \le 17$	$-24 \le h \le 24$	$-32 \le h \le 28$
	$-27 \le k \le 27$	$-25 \le k \le 25$	$-21 \le k \le 21$	$-20 \le k \le 20$
	$-19 \le l \le 20$	$-17 \le l \le 17$	$-20 \le l \le 20$	$-6 \le l \le 14$
Measured reflections	43320	34027	22618	16799
Unique reflections	10665	7825	5538	9876
	[R(int) = 0.0441]	[R(int) = 0.0891]	[R(int) = 0.0168]	[R(int) = 0.0367]
Completeness to θ	99.9 (to 28.24)	99.8 (to 25.00)	99.9 (to 28.31)	99.4 (to 27.45)
Absorption correction	semiempirical from equivalents			
Max., min. transmission	1.00, 0.611	1.00, 0.84	0.932, 0.799	1.00, 0.730
Refinement method	full-matrix least squares on F^2			
Data/restraints/parameters	10665/6/538	7825/1/529	5538/4/317	9876/3/500
GoF on F^2	1.016	1.011	1.055	1.043
Final R indices	R_1 = 0.0435	R_1 = 0.0566	R_1 = 0.0293	R_1 = 0.0481
[$I > 2\sigma(I)$]	wR_2 = 0.1022	wR_2 = 0.1217	wR_2 = 0.0693	wR_2 = 0.0989
R indices	R_1 = 0.0732	R_1 = 0.1045	R_1 = 0.0309	R_1 = 0.0739
(all data)	wR_2 = 0.1178	wR_2 = 0.1431	wR_2 = 0.0705	wR_2 = 0.1054
$\Delta\rho_{max/min}$ [e Å^{-3}]	2.094/–0.670	1.279/–0.772	0.423/–1.230	1.139/–1.818

structure solution were either "direct methods" or "Patterson map". Refinement was by full-matrix least-squares using the SHELXL-97[39] algorithm within OLEX2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using a riding model and included in the refinement at calculated positions, except for the O–H hydrogen atom in **8f**, which was found by a difference map.

Details of data collection and structure refinement are presented in Tables 7 and 8. CCDC-842583 (**3**[BF_4]·2CH_2Cl_2), -842584 (**4**), -842585 (**6b**·2CH_2Cl_2), -842586 (**6c**·2CH_2Cl_2), -842587 (**8e**), -842588 (**8f**·2CH_2Cl_2), -842589 (**11a**·2CH_2Cl_2), -842590 (**11b**·2CH_2Cl_2) and -842591 (**11c**) 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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[1] C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313.
[2] L. Perrin, E. Clot, O. Eisenstein, J. Loch, R. H. Crabtree, *Inorg. Chem.* **2001**, *40*, 5806.
[3] C. Köcher, W. A. Herrmann, *J. Organomet. Chem.* **1997**, *532*, 261.
[4] a) A. R. Chianese, X. Li, M. C. Janzen, J. W. Faller, R. H. Crabtree, *Organometallics* **2003**, *22*, 1663; b) R. A. Kelly, H. Clavier, S. Giudice, N. M. Scott, E. D. Stevens, J. Bordner, I. Samardjiev, C. D. Hoff, L. Cavallo, S. P. Nolan, *Organometallics* **2008**, *27*, 202.
[5] a) D. G. Gusev, *Organometallics* **2009**, *28*, 763; b) D. G. Gusev, *Organometallics* **2009**, *28*, 6548.
[6] J. M. Lynam, C. E. Welby, A. C. Whitwood, *Organometallics* **2009**, *28*, 1320.
[7] D. G. Johnson, J. M. Lynam, J. M. Slattery, C. E. Welby, *Dalton Trans.* **2010**, *39*, 10432.
[8] N. P. Hiett, J. M. Lynam, C. E. Welby, A. C. Whitwood, *J. Organomet. Chem.* **2011**, *696*, 378.
[9] A. Spencer, G. Wilkinson, *J. Chem. Soc., Dalton Trans.* **1974**, 786.
[10] S. D. Robinson, M. F. Uttley, *J. Chem. Soc., Dalton Trans.* **1973**, 1912.
[11] G. B. Richter-Addo, P. Legzdins, *Metal Nitrosyls*, Oxford University Press, **1992**.
[12] a) D. A. Morgenstern, G. M. Ferrence, J. Washington, J. I. Henderson, L. Rosenhein, J. D. Heise, P. E. Fanwick, C. P. Kubiak, *J. Am. Chem. Soc.* **1996**, *118*, 2198; b) I. S. Zavarine, C. P. Kubiak, T. Yamaguchi, K. Ota, T. Matsui, T. Ito, *Inorg. Chem.* **2000**, *39*, 2696.
[13] For general reviews of transition-metal vinylidene chemistry see; a) M. I. Bruce, *Chem. Rev.* **1991**, *91*, 197; b) H. Werner, *J. Organomet. Chem.* **1994**, *475*, 45; c) M. C. Puerta, P. Valerga, *Coord. Chem. Rev.* **1999**, *193–195*, 977; d) . Y. Wakatsuki, *J. Organomet. Chem.* **2004**, *689*, 4092; e) A. B. Antonova, *Coord. Chem. Rev.* **2007**, *251*, 1521; f) C. Bruneau, P. H. Dixneuf, *Metal Vinylidenes and Allenylidenes in Catalysis: From Reactivity to Applications in Synthesis*, **2008**, Wiley–VCH, Weinheim, Germany; g) J. M. Lynam, *Chem. Eur. J.* **2010**, *16*, 8238.
[14] a) J. P. Selegue, *Organometallics* **1982**, *1*, 217; b) D. Touchard, P. H. Dixneuf, *Coord. Chem. Rev.* **1998**, *178*, 409; c) M. I. Bruce, *Chem. Rev.* **1998**, *98*, 2797; d) V. Cadierno, M. P. Gamasa, J. Gimeno, *Eur. J. Inorg. Chem.* **2001**, 571; e) S. Rigaut, D. Touchard, P. H. Dixneuf, *Coord. Chem. Rev.* **2004**, *248*, 1585; f) J. P. Selegue, *Coord. Chem. Rev.* **2004**, 248, 1543; g) V. Cadierno, J. Gimeno, *Chem. Rev.* **2009**, *109*, 3512.
[15] a) E. Bustelo, P. H. Dixneuf, *Adv. Synth. Catal.* **2005**, *347*, 393; b) E. Bustelo, P. H. Dixneuf, *Adv. Synth. Catal.* **2007**, *349*, 933.
[16] S. Datta, C. L. Chang, K.-L. Yeh, R. S. Liu, *J. Am. Chem. Soc.* **2003**, *125*, 9294.
[17] V. Cadierno, J. Francos, J. Gimeno, *Green Chem.* **2010**, *12*, 135.
[18] B. Weyershausen, K. H. Dötz, *Eur. J. Inorg. Chem.* **1999**, 1057.
[19] a) M. I. Bruce, A. G. Swincer, B. J. Thomson, R. C. Wallis, *Aust. J. Chem.* **1980**, *33*, 2605; b) K. H. Dötz, W. Sturm, *Organometallics* **1987**, *6*, 1424.
[20] R. W. Grime, M. Helliwell, Z. I. Hussain, H. N. Lancashire, C. R. Mason, J. J. W. McDouall, C. M. Mydlowski, M. W. Whiteley, *Organometallics* **2008**, *27*, 857.
[21] S. Pavlik, K. Mereiter, M. Puchberger, K. Kirchner, *J. Organomet. Chem.* **2005**, *690*, 5497.
[22] M. P. Gamasa, J. Gimeno, B. M. Martín-Vaca, R. Isea, A. Vegas, *J. Organomet. Chem.* **2002**, *651*, 22.
[23] C. Bianchini, A. Marchi, N. Mantovani, L. Marvelli, D. Masi, M. Peruzzini, R. Rossi, *Eur. J. Inorg. Chem.* **1998**, 211.
[24] B. J. Coe, S. J. Glenwright, *Coord. Chem. Rev.* **2000**, *203*, 5.
[25] See for example M. Mitoraj, A. Michalak, *Organometallics* **2007**, *26*, 6576.
[26] A. B. Antonova, N. E. Kolobova, P. V. Petrovsky, B. V. Lokshin, N. S. Obezyuk, *J. Organomet. Chem.* **1977**, *137*, 55.
[27] D. Moigno, B. Callejas-Gasper, J. Gil-Rubio, H. Werner, W. Kiefer, *J. Organomet. Chem.* **2002**, *661*, 181.
[28] The nature of the metal fragment will also influence the nature of the interaction with the ligand, this effect is more noticeable for π back-bonding. See G. Frenking, K. Wichmann, N. Fröchlich, J. Grobe, W. Golla, D. Le Van, B. Krebs, M. Läge, *Organometallics* **2002**, *21*, 2921 and references therein.[24]
[29] For a relationship between the electrophilicity of Fischer carbene complexes and the chemical shift see W.-Q. Zhang, A. C. Whitwood, I. J. S. Fairlamb, J. M. Lynam, *Inorg. Chem.* **2010**, *49*, 8941.
[30] R. W. Mitchell, A. Spencer, G. Wilkinson, *J. Chem. Soc., Dalton Trans.* **1973**, 846.
[31] W. Wu, W. Wu, S. Ji, H. Guo, J. Zhao, *Eur. J. Inorg. Chem.* **2010**, 4470.
[32] Data compared to that found for the appropriate compound at http://www.sigmaaldrich.com/.
[33] S. K. Pondey, A. E. Greene, J.-F. Poisson, *J. Org. Chem.* **2007**, *72*, 7769.
[34] B. P. Cho, *Tetrahedron Lett.* **1995**, *36*, 2403.
[35] a) B. S. Macdonald, P. J. Sykes, P. M. Adhikary, R. A. Harkness, *Steroids* **1971**, *18:6*, 753; b) J. F. Templeton, C. J. C. Jackson, *Steroids* **1983**, *41*, 485.
[36] *SMART, Control Software*, Bruker SMART Apex X-ray Diffractometer. v5.625, Bruker-AXS GMBH, Karlsruhe, Germany.
[37] *SAINT+, Integrion Software*, Bruker SMART detectors. v6.45, Bruker-AXS GMBH, Karlsruhe, Germany.
[38] G. M. Sheldrick, *SADABS, Program for Absorption Correction. v2.10*, Bruker AXS Inc., Madison, Wisconsin, USA, **2007**.
[39] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112.
[40] *CrysAlisPro Version 1.171.34.40*, Oxford Diffraction Ltd.
[41] Empirical absorption correction using spherical harmonics, implemented by the SCALE3 ABSPACK scaling algorithm within the *CrysAlisPro Version 1.171.34.40* software, Oxford Diffraction Ltd.
[42] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339.

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