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Enolate-Phosphane Ligands Providing a Tool for the Selective Substitution of Triphenylphosphane by Carbon Monoxide or Trimethylphosphane in Complex {Ru(Cp)[η^2-*P*,*O*-$Ph_2PCH_2C(t$Bu)=O](PPh$_3$)}[PF_6], and Subsequent Reactivity Towards Terminal Alkynes

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Keywords: Cyclopentadienyl ligands / Metallacycles / Phosphane ligands / Ruthenium / Vinylidene ligands

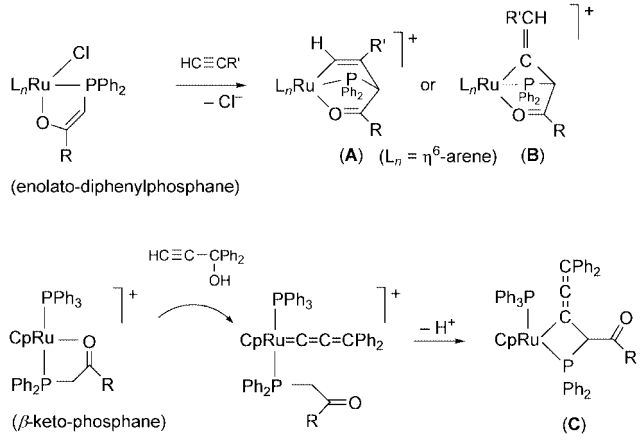
The deprotonation under basic conditions of the keto-phosphane ligand in complexes {Ru(Cp)[η^1-*P*-Ph_2PCH_2C(=O)-*t*Bu](PPh$_3$)(L)}[PF_6] (L = CO or PMe_3) that arise from the addition of L to {Ru(Cp)[η^2-*P*,*O*-$Ph_2PCH_2C(t$Bu)=O](PPh$_3$)}[PF_6] generates {Ru^+(Cp)[η^1-*P*-Ph_2PCH=C(*t*Bu)O^-](PPh$_3$)(L)} zwitterionic species, as shown by an X-ray crystal structure determination (L = CO). The removal of the triphenylphosphane ligand is subsequently achieved under thermal activation to afford the neutral derivatives Ru(Cp)[η^2-*P*,*O*-Ph_2PCH=C-(*t*Bu)O](L). A further protonation step is sufficient to complete the formation of the new complex {Ru(Cp)[η^2-*P*,*O*-$Ph_2PCH_2C(t$Bu)=O](PMe$_3$)}[PF_6], which reacts in methanol at reflux with 1,1-diphenyl-2-propyn-1-ol to afford the six-membered metallacyclic derivative {Ru(Cp)[η^2-*C*,*P*:C(CH=CPh_2)OC(*t*Bu)=CH–PPh_2](PMe$_3$)}[PF_6], as shown by an X-ray single crystal analysis. The synthesis of related η^5-indenyl ruthenium complexes and of {Ru(Cp)-(=C=CH_2)[Ph_2PCH_2C(=O)*t*Bu](PR$_3$)}[PF_6] (PR_3 = PPh_3 or PMe_3) vinylidene complexes is also reported.

Introduction

Enolato-phosphane chelates derived from β-keto-phosphanes associate an ancillary phosphorus coordinating centre with a strongly coordinating but reactive enolate moiety. Thus, the enolato function had been shown to interfere in the 1-alkyne to vinylidene rearrangement when coordination of 1-alkynes at a ruthenium centre was additionally instigated. As depicted on Scheme 1, carbon–carbon bond formation occurred and resulted in cationic metallacyclic derivatives **A** and **B**.[1–3]

On the other hand, protonation of the enolato function under acidic conditions converted the chelate into a hemilabile β-keto-phosphane one, where the oxygen atom might compare to a weakly coordinating ketone.[4–6] Taking advantage of the hemilabile property of β-keto-phosphanes in related cyclopentadienyl ruthenium complexes, the synthesis of allenylidene ruthenium derivatives had been achieved (Scheme 1).[7] A further deprotonation of the η^1-*P*-coordinated keto-phosphane still resulted in a formal carbon–carbon coupling reaction between an enolate moiety and the allenylidene ligand to afford a neutral ruthenaphosphacyclobutane derivative (**C**).

These results emphasised the nucleophilic character of the enolate moiety from functional enolato-phosphane chelate, or generated in situ under basic conditions from η^1-*P*-coordinated keto-phosphane. We wish to report now (i) an unusual η^1-*P* coordination mode of an enolate-phosphane ligand in new zwitterionic cyclopentadienyl ruthenium complexes, (ii) the reactivity of the uncoordinated anionic enolate moiety, which provides a new tool to cleanly achieve ligand-exchange reactions, and (iii) the formation of a ruthenaoxophosphacyclohexadiene ring, which may be formally summarised as an oxygen–carbon coupling reaction between an allenylidene ligand and an η^1-*P*-coordinated enol-phosphane.



Scheme 1. Carbon–carbon coupling reactions leading to ruthenacycles **A**–**C**.

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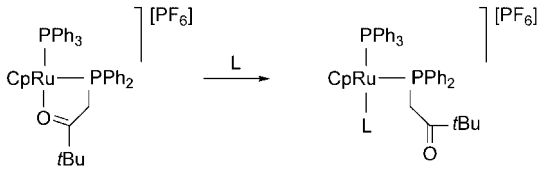
Results and Discussion

The hemilabile property of the β-keto-phosphane in the cyclopentadienyl ruthenium complex {Ru(Cp)[η²-*P*,*O*-$Ph_2PCH_2C(tBu)$=O](PPh₃)}[PF₆] (**1a**) allowed the entrance not only of 1-alkynols or carbon monoxide as reported previously,[7] but also of phosphorus ligands such as trimethylphosphane or trimethyl phosphite [Equation (1)].

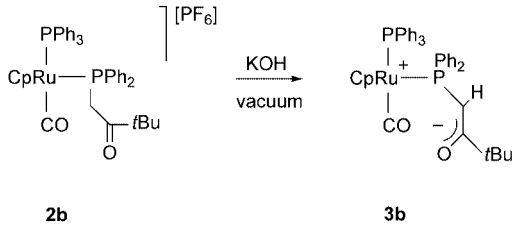


(1)

The new complexes **2c**,**d** were thus isolated as yellow solids in a nearly quantitative yield and were characterised by a combination of ^1H, $^{13}C\{^1H\}$, ^{13}C and $^{31}P\{^1H\}$ NMR, IR spectroscopy, and elemental analysis. The ^1H and $^{31}P\{^1H\}$ NMR spectra accounted for the coordination of the phosphorus ligands besides the cyclopentadienyl one while IR spectroscopy indicated the η¹-*P*-coordination mode of the keto-phosphane.[7] Attempts to achieve a similar entrance of triphenylphosphane failed. Indeed, steric congestion in the putative expected complex {Ru(Cp)[η¹-*P*-$Ph_2PCH_2C(=O)tBu$](PPh₃)₂}[PF₆] was believed to be responsible for the easy synthesis of **1a**, by reacting the keto-phosphane $Ph_2PCH_2C(=O)tBu$ with RuCl(Cp)(PPh₃)₂ and NH_4PF_6 in methanol as solvent.[7] The loss of steric constraints in complexes **2b**–**d** provided thermal stability and complexes **2b**–**d** remained unchanged when they were heated in toluene at reflux. Unfortunately, such thermal stability precluded a removal of the triphenylphosphane ligand in **2b**–**d** and thus an easy recovery of the chelate coordination mode of the keto-phosphane.

The generation of an enolate anion might be expected to enhance the reactivity of the oxygen atom from the keto-phosphane when involved as an η¹-*P*-coordinated ligand, but such a formation would require basic conditions. No reaction was detected when an excess of KOH was added to a stirred solution of **2b** in methanol. However, a subsequent complete removal of volatiles under prolonged vacuum at room temperature resulted in the formation of the new enolate-phosphane complex **3b** [Equation (2)].

Complex **3b** was isolated in 79% yield as orange crystals that were found to be stable in air and could be kept at room temperature. IR spectroscopy indicated the retention of a carbon monoxide ligand ($\tilde{\nu}$ = 1959 cm⁻¹) and the conversion of the keto-function into an enolate one ($\tilde{\nu}$ = 1489 cm⁻¹). The $^{31}P\{^1H\}$ NMR spectrum of **3b** indicated the coordination of two phosphorus atoms with a normal coupling constant value ($^2J_{PP}$ = 26.7 Hz). More noteworthy was the observation by ^1H NMR spectroscopy of a doublet at δ = 3.66 ppm exhibiting a high $^2J_{PH}$ coupling constant



(2)

value of 27.1 Hz and assigned to the PCH= proton, whereas the $^{13}C\{^1H\}$ NMR resonance of the corresponding carbon nucleus displayed usual features (δ = 60.6 ppm, $^1J_{PC}$ = 70.9 Hz). Further characterisation of **3b** was obtained from an X-ray crystal structure determination. An ORTEP drawing of **3b** is shown in Figure 1, and selected bond lengths and angles are given in the caption.

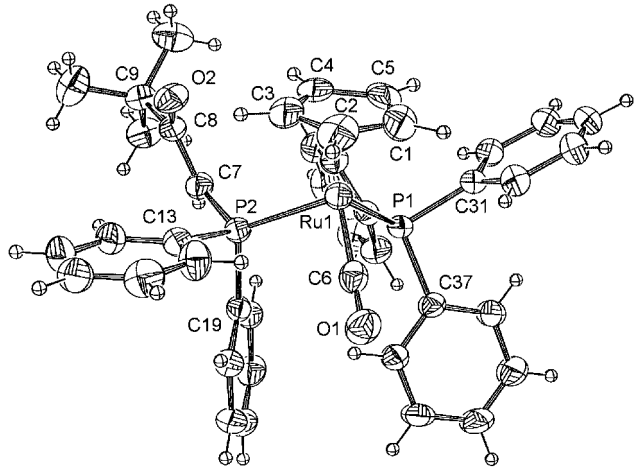
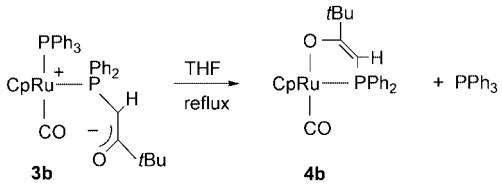


Figure 1. ORTEP drawing of **3b**·CH_2Cl_2 showing 50% probability thermal ellipsoids. The CH_2Cl_2 molecule is omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru1–C6 1.858(5), Ru1–P1 2.339(1), Ru1–P2 2.370(1), C7–C8 1.379(5), C8–C9 1.561(6), C8–O2 1.271(5), P2–C7 1.759(4); C7–C8–C9 120.1(4), C7–C8–O2 124.1(4), C8–C7–P2 123.7(3), C9–C8–O2 115.8(4), C7–P2–Ru1 120.7(1), C6–Ru1–P1 90.5(1), C6–Ru1–P2 91.3(1), P1–Ru1–P2 99.19(4).

Complex **3b** disclosed a classical piano-stool geometry involving an η⁵-cyclopentadienyl ruthenium moiety. One carbon monoxide ligand and two phosphorus atoms complete the coordination of a formal Ru^+ centre. Moreover, the two Ru–P bond lengths are close [Ru1–P1: 2.339(1), Ru1–P2: 2.370(1) Å], thus providing straightforward evidence for a normal coordination of the functionalised phosphane. The C7–C8 and C8–O2 bond lengths [1.379(5) and 1.271(5) Å, respectively] clearly indicated a marked double bond character, as expected for an anionic enolate fragment. Therefore, complex **3b** is best described as a zwitterionic compound. Remarkably, the O2 oxygen atom lies in a *cis* position relative to the P2 phosphorus atom, thus in a favourable position for a subsequent coordination of the oxygen atom.

The removal of the triphenylphosphane ligand in **3b** was achieved by heating at reflux a solution of **3b** in THF monitored by $^{31}P\{^1H\}$ NMR spectroscopy as having a new sing-

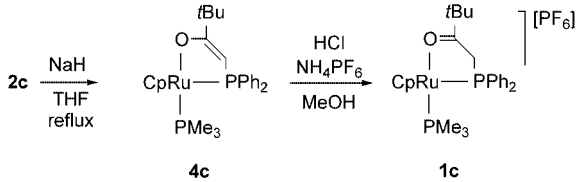
let resonance at δ = 61.4 ppm, besides a singlet resonance, as might be expected from the presence of free triphenylphosphane [Equation (3)].



3b **4b** (3)

Attempts to separate the enolato-phosphane derivative **4b** from free triphenylphosphane by generating under acidic conditions a less soluble cationic $\{Ru(Cp)[Ph_2PCH_2C(tBu)=O](CO)\}^+$ species immediately showed the additional coordination of triphenylphosphane leading to the recovery of cationic **2b**. The addition of ICH_3 to convert the free phosphane into the corresponding phosphonium salt was more successful. The neutral complex **4b** was then selectively extracted with diethyl ether and isolated as orange-yellow crystals in 72% yield. Of interest is the comparison of the ^1H and $^{13}C\{^1H\}$ NMR spectra of **4b** and **3b**, which showed in the case of **4b** the PCH= proton resonance as a doublet at δ = 4.85 ppm with a normal $^2J_{PH}$ coupling constant value of 4.1 Hz, while the corresponding $^{13}C\{^1H\}$ NMR resonance (δ = 74.0 ppm, $^1J_{PC}$ = 61.9 Hz) appeared moderately low-field shifted, relative to **3b**.

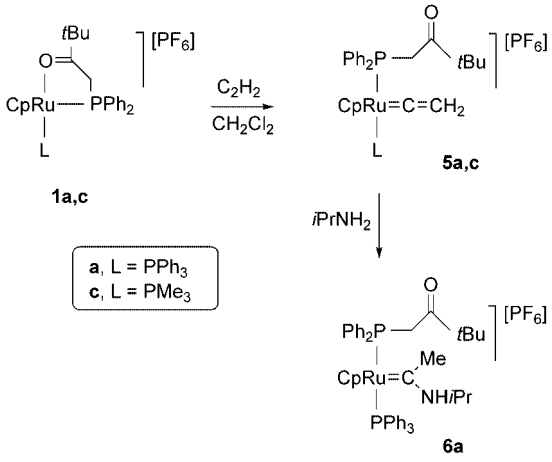
The study of the reaction between **2c** (L = PMe_3) and KOH in methanol as solvent under similar experimental conditions was disappointing, as the $^{31}P\{^1H\}$ NMR spectrum of the crude product showed a major presence of unreacted **2c**. However, a new set of resonances might indicate a partial formation of the expected zwitterionic intermediate and thus suggested that more drastic experimental conditions would allow completion of the reaction. Indeed, the enolato-diphenylphosphane complex **4c** was straightforwardly obtained when NaH was used as a base in THF at reflux [Equation (4)]. A subsequent treatment under acidic conditions (addition of anhydrous HCl and NH_4PF_6 in methanol as solvent) led to the new cationic derivative $\{Ru(Cp)[Ph_2PCH_2C(tBu)=O](PMe_3)\}[PF_6]$ (**1c**) [Equation (4)].



4c **1c** (4)

With the addition of trimethylphosphane to **1a** to generate **2c**, as a supplementary step, the whole process achieved the selective substitution of the triphenylphosphane ligand in **1a** by a trimethylphosphane one, to afford **1c** in 73% yield. NMR and IR spectroscopy, and elemental analysis accounted for the structure of the stable complexes **4c** and **1c**.

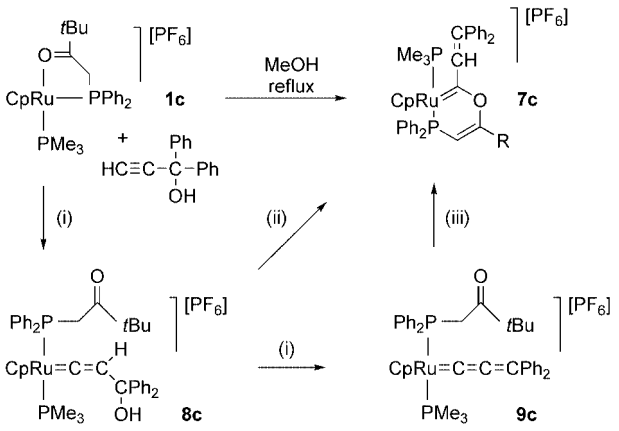
Further emphasising the usefulness of the hemilabile property of the keto-phosphane ligand to conveniently allow the entrance of an additional ligand, complexes **1a**,**c** reacted with ethyne under very mild conditions (1 atm, room temperature) to afford the new vinylidene complexes **5a**,**c** [Equation (5)].



1a,c **5a,c** **6a** (5)

Complexes **5a**,**c** were isolated as yellow-brown crystals in 93% and 92% yield, respectively, and fully characterised by ^1H, $^{13}C\{^1H\}$, ^{13}C and $^{31}P\{^1H\}$ NMR spectroscopy, and elemental analysis. Several unsubstituted vinylidene ruthenium complexes have been reported previously,[8] but the almost quantitative formation of **5a**,**c** using ethyne under mild conditions, and avoiding any formation of by-product, is noteworthy. Under the same experimental conditions, the parent complex $RuCl(Cp)(PMe_2Ph)_2$ reacted with ethyne in the presence of $TlBF_4$ to afford the η^2-ethyne complex $Ru(Cp)(\eta^2\text{-}C_2H_2)(PMe_2Ph)_2$, from which the 1-alkyne to vinylidene rearrangement needed a thermal activation to occur.[9] Similar observations were made starting from $RuCl(Cp)(PMe_3)_2$,[10] and the mechanism of the isomerisation has been fully investigated.[11] The $^{13}C\{^1H\}$ NMR spectra of **5a**,**c** showed a very low-field resonance at δ = 346.6 and 345.5 ppm, respectively, and thus unambiguously provided evidence for the presence of a vinylidene ligand. Furthermore, complexes **5a**,**c** easily added primary amines such as isopropylamine to afford amino-carbene derivatives, as emphasised by the formation of complex **6a** [Equation (5)]. Like the vinylidene ruthenium complexes **5a**,**c**, the amino-carbene derivative **6a** was a robust compound, which could be kept in air at room temperature.

The labile keto-oxygen ligand in complexes **1a**,**c** also allowed the entrance of 1-alkynols and the synthesis of the allenylidene derivative $\{Ru(Cp)(=C=C=CPh_2)[Ph_2PCH_2C(=O)tBu](PPh_3)\}[PF_6]$ by reacting **1a** with 1,1-diphenyl-2-propyn-1-ol in methanol at reflux has already been reported.[7] By contrast, a distinct complex **7c** was selectively formed when the same alkynol was treated with **1c** under similar experimental conditions (Scheme 2).



Scheme 2. Reactivity of complex **1c** towards 1,1-diphenyl-2-propyn-1-ol: (i) in CH_2Cl_2 as solvent, (ii) in MeOH as solvent (room temperature), (iii) in CH_2Cl_2 as solvent and in the presence of aqueous K_2CO_3.

Such a formation of **7c** in methanol also occurred at room temperature but the completion of the reaction needed 10 days instead of 1 h under reflux conditions. The stable complex **7c** was isolated in 69% yield as dark-red crystals. The $^{31}P\{^1H\}$ NMR spectrum of **7c** indicated the retention of two coordinating phosphorus centres, while ^1H NMR and IR spectroscopy both indicated the transformation of the keto-phosphane into an enolate-phosphane. Furthermore, the $^{13}C\{^1H\}$ NMR spectrum of **7c** exhibited a very low-field resonance at δ = 286.1 ppm and thus suggested that a carbene ligand completed the coordination of the ruthenium centre. Finally, an X-ray crystal structure determination of **7c** showed a vinyl-carbene ligand to formally arise from an addition at the C_α position of an allenylidene ligand of the enol form of an η^1-*P*-coordinated keto-phosphane. An ORTEP drawing of **7c** is shown in Figure 2, and selected bond lengths and angles are given in the caption.

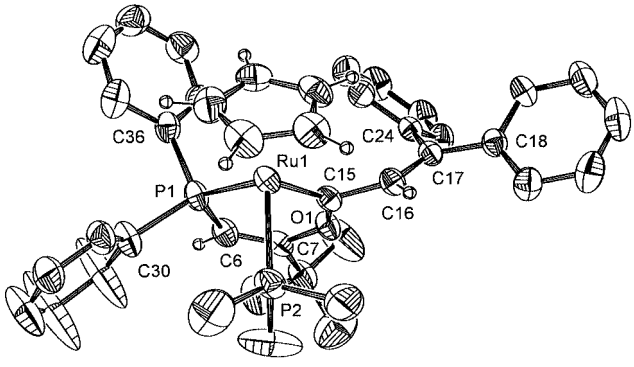


Figure 2. ORTEP drawing of **7c** showing 50% probability thermal ellipsoids. The hydrogen atoms and the PF_6 anion are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru1–C15 1.924(3), Ru1–P1 2.2497(7), Ru1–P2 2.3197(8), C6–C7 1.319(4), C7–O1 1.393(3), P1–C6 1.776(3), C15–C16 1.472(4), C16–C17 1.354(4); C6–P1–Ru1 113.2(1), C7–C6–P1 125.6(2), C6–C7–O1 125.7(3), C7–O1–C15 128.1(2), O1–C15–Ru1 134.3(2), C15–Ru1–P1 90.21(8), C15–Ru1–P2 89.62(8), P1–Ru1–P2 95.57(3), Ru1–C15–C16 119.1(2), C15–C16–C17 129.0(3).

Figure 2 displays a piano-stool geometry where a carbene and two phosphorus ligands complete the coordination of a formal cationic η^5-cyclopentadienyl ruthenium fragment. One phosphorus and the (carbene)-carbon atoms are involved in a six-membered metallacycle that is closely planar, as monitored by a sum of internal angles of 717.1°, close to 720°. Furthermore, the ruthenacycle compares with a 1,4-cyclohexadiene ring wherein the Ru1–P1–C6 and C7–O1–C15 fragments are linked through two short C6–C7 and Ru1–C15 double bonds [1.319(4) and 1.924(3) Å, respectively].

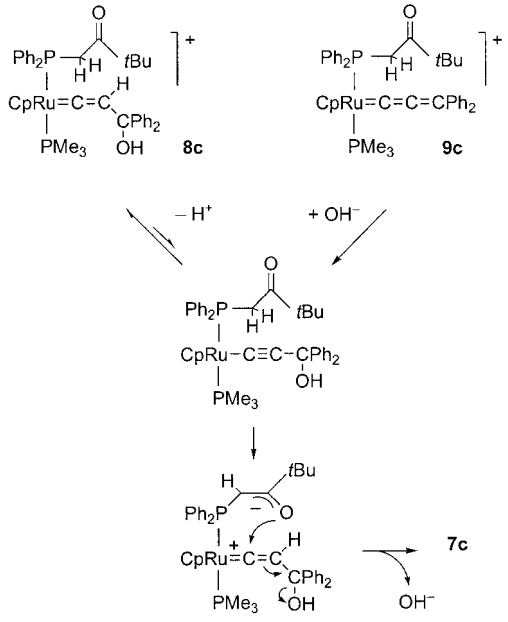
The formation of **7c** was strongly dependent on the nature of the solvent and became almost negligible when the reaction between **1c** and 1,1-diphenyl-2-propyn-1-ol was conducted in dichloromethane at room temperature. As monitored by $^{31}P\{^1H\}$ NMR spectroscopy, the complete consumption of **1c** in dichloromethane as solvent was virtually achieved after 20 h and the reaction mixture disclosed a major presence (ca. 85% as determined by ^1H NMR spectroscopy) of the hydroxy-vinylidene complex **8c** (Scheme 2). Complex **8c** then gradually disappeared, leaving the allenylidene ruthenium complex **9c** as the final product after 3 days; no further change was detected after 10 days. Complex **9c** can be rapidly synthesised by reacting **1c** and the alkynol in THF at reflux. The structure of complexes **8c** and **9c** was inferred from ^1H, $^{13}C\{^1H\}$, ^{13}C and $^{31}P\{^1H\}$ NMR spectroscopic studies. Thus, the ^1H NMR spectrum of **8c** showed two additional resonances relative to the spectrum of **9c**, at δ = 3.19 (s) and 5.25 (dd, $^4J_{PH}$ = 2.5 and 1.6 Hz) ppm, which might reasonably be assigned to the OH and Ru=C=CH protons, respectively.[12,13] The formation of the allenylidene complex $[Ru(Cp)(=C=C=CPh_2)(PMe_3)_2][PF_6]$ similarly involved a hydroxy-vinylidene intermediate when $RuCl(Cp)(PMe_3)_2$ was treated with 1,1-diphenyl-2-propyn-1-ol.[14] Moreover, several hydroxy-vinylidene complexes have been later isolated and characterised as pentamethylcyclopentadienyl ruthenium derivatives.[12,13]

The formation of the isomeric complexes **7c** and **9c**, in methanol and in dichloromethane as solvent, respectively, was intriguing. Two supplementary experiments were significantly informative. First, a mixture of **8c** and **9c** in an approximately 1:1 molar ratio was formed in dichloromethane and the solvent was evaporated under vacuum. The residue was dissolved in methanol and the solution was stirred at room temperature for 20 h. The examination of the resulting solution by $^{31}P\{^1H\}$ NMR spectroscopy surprisingly disclosed a mixture of **7c** and **9c**, indicating a conversion of **8c** into **7c** but also a passiveness of the allenylidene complex **9c** (Scheme 2). However, a very slow isomerisation of **9c** into **7c**, needing 10 days to complete, was observed to occur in methanol at ambient temperature.

In the second experiment, a small amount of a 0.07 M K_2CO_3 aqueous solution was added to a solution of **9c** in dichloromethane. On stirring, the colour of the solution rapidly (<1 h) turned from violet to red and although a deprotonation of the keto-phosphane in **9c** under such mild heterogeneous conditions was unlikely, **7c** was observed to

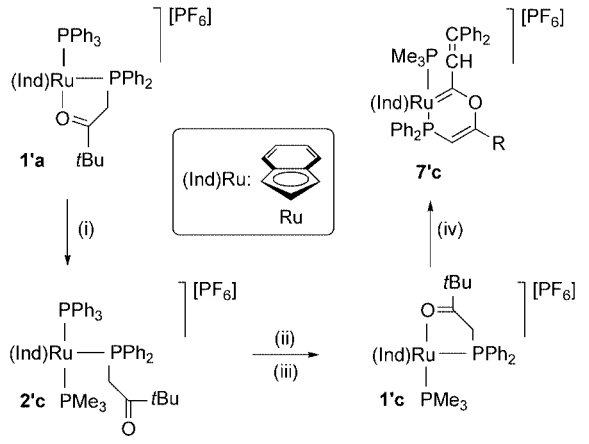
be quantitatively formed by $^{31}P\{^1H\}$ NMR spectroscopy (Scheme 2).

These observations suggested that the coupling process leading to **7c** preliminarily required the formation of an intermediate that would arise either from **8c** in methanol or from the addition of hydroxide anion to **9c**. As depicted in Scheme 3, a plausible candidate consisted of a neutral alkynyl complex arising from a deprotonation (requiring a solvent with proton-acceptor ability such as methanol) of the vinylidene ligand in **8c**, or from the addition of hydroxide anion at the γ position of the allenylidene ligand in **9c**. A subsequent proton migration from the keto-fragment to the alkynyl ligand would subsequently lead to **7c**. Finally, the presence of a bulkier triphenylphosphane ligand in **1a** might sufficiently hinder closeness between the keto function and the alkynyl chain to preclude a similar coupling process.



Scheme 3. Rationale accounting (i) for the formation of **7c** in methanol and (ii) for the isomerisation of **9c** into **7c** catalysed by hydroxide anions.

The reactions allowing the synthesis of the trimethylphosphane derivatives **2c**, **1c** and **7c** tolerated the presence of an indenyl ligand instead of the cyclopentadienyl one. As summarised in Scheme 4, the indenyl ruthenium precursor complex {Ru(Ind)[η^2-*P*,*O*-$Ph_2PCH_2C(tBu)$=O](PPh$_3$)}[PF$_6$] (**1′a**) (Ind = η^5-C_9H_7)[7] easily added trimethylphosphane to afford **2′c**, which was isolated as orange-red crystals, in 89% yield. Treatment of **2′c** with NaH in THF under reflux and subsequent work under acidic conditions (HCl + NH_4PF_6) led to **1′c**, which was isolated as orange crystals, in 77% yield. Finally, complex **1′c** reacted with 1,1-diphenyl-2-propyn-1-ol in methanol at reflux to afford **7′c** isolated as deep-red crystals, in 71% yield. The ^1H, $^{13}C\{^1H\}$, ^{13}C and $^{31}P\{^1H\}$ NMR spectroscopic data collected for **7′c** unambiguously indicated a similar structure relative to complex **7c**.



Scheme 4. Synthesis of the new complexes **2′c**, **1′c** and **7′c**: (i) PMe_3, CH_2Cl_2, (ii) NaH, THF, reflux, (iii) HCl, NH_4PF_6, MeOH, (iv) HC≡CC(OH)Ph_2, MeOH, reflux.

Conclusions

The deprotonation of an η^1-*P*-coordinated β-keto-phosphane in cyclopentadienyl or indenyl ruthenium complexes was achieved under basic conditions and was observed to enhance the affinity of the oxygen atom to coordinate the metal centre. Subsequent removal of a triphenylphosphane ligand was facilitated and allowed the chelate coordination mode of the functionalised phosphane. Thus, using the β-keto-phosphane as a tool, the substitution of a triphenylphosphane ligand by a less sterically demanding ligand such as carbon monoxide or trimethylphosphane was achieved. Furthermore, such a synthesis offered an opportunity to compare two analogous complexes but with distinct steric constraints. The presence of the hemilabile β-keto-phosphane not only allowed an easy additional coordination of ethyne but also facilitated further rearrangement into vinylidene derivatives. The coordination of 1-alkynols similarly led to allenylidene complexes, but the presence of a reactive functionalised phosphane might interfere in the process to afford new metallacyclic complexes.

Experimental Section

General Comments: The reactions were performed under inert argon according to Schlenk-type techniques. THF, diethyl ether and dichloromethane were distilled after drying according to conventional methods. NMR spectra were recorded at 297 K with an AC 300 Bruker instrument and referenced internally to the solvent peak. IR spectra were recorded as Nujol mulls with Bruker IFS28. Elemental analyses were performed by the "Service de Microanalyse du CNRS", Vernaison, France. Complexes **1a** (as its dichloromethane adduct) and **1′a** were prepared as described previously.[7]

{Ru(Cp)[Ph_2PCH_2C(=O)*t*Bu](PPh$_3$)(CO)}[PF$_6$] (2b): In a 125 mL stainless steel vessel, a solution of **1a** (13.8 g, 14.6 mmol) in dichloromethane (70 mL) was stirred for 3 days at room temperature under carbon monoxide pressure (65 atm). The resulting solution was concentrated under vacuum (≈40 mL) before being covered with methanol (10 mL) and then diethyl ether (160 mL), to afford lemon-yellow crystals. Yield: 11.9 g, 92%. $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2): δ = 25.7 (s, CMe_3), 35.9 (d, ^1J = 29.4 Hz,

PCH_2), 45.5 (d, ^3J = 1.5 Hz, CMe_3), 90.9 (s, Cp), 129.0–135.1 (m, 5 Ph groups), 202.5 (t, $^2J \approx 17.8$ Hz, C≡O), 207.6 (d, ^2J = 8.2 Hz, C=O) ppm. ^1H and $^{31}P\{^1H\}$ NMR, and IR spectroscopic data were given elsewhere.[7]

{Ru(Cp)[Ph_2PCH_2C(=O)*t*Bu](PPh$_3$)(PMe$_3$)}[PF$_6$] (2c): A 1.0 M solution of trimethylphosphane in THF (8.0 mL, 8.0 mmol) was added to a stirred solution of **1a** (7.04 g, 7.47 mmol) in THF (40 mL). The mixture was further stirred overnight to obtain a yellow precipitate, which was collected by filtration, then washed with diethyl ether and dried under vacuum. Yield: 7.00 g, 100%. IR: $\tilde{\nu}$ = 1699 cm^{-1}, C=O. ^1H NMR (300.13 MHz, CD_2Cl_2): δ = 0.64 (s, 9 H, *t*Bu), 1.45 (d, $^2J_{PH}$ = 8.6 Hz, 9 H, PMe_3), 2.99 (dd, $^2J_{HH}$ = 16.4, $^2J_{PH}$ = 8.5 Hz, 1 H, PCH_2, H_a), 3.16 (dd, $^2J_{HH}$ = 16.4, $^2J_{PH}$ = 4.0 Hz, 1 H, PCH_2, H_b), 4.68 (s, 5 H, Cp), 6.80–7.47 (m, 25 H, Ph) ppm. $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2): δ = –10.4 (t, $^2J_{PP} \approx {}^2J_{PP'} \approx$ 38 Hz, PMe), 36.9 (t, $^2J_{PP} \approx {}^2J_{PP'} \approx$ 38 Hz), 43.9 (t, $^2J_{PP} \approx {}^2J_{PP'} \approx$ 38 Hz) ppm. $C_{44}H_{50}F_6OP_4Ru$ (933.84): calcd. C 56.59, H 5.40; found C 56.66, H 5.87.

{Ru(Cp)[Ph_2PCH_2C(=O)*t*Bu](PPh$_3$)[P(OMe)$_3$]}[PF$_6$] (2d): Trimethyl phosphite (0.80 mL, 6.78 mmol) was added to a solution of **1a** (3.00 g, 3.18 mmol) in dichloromethane (50 mL). After being stirred overnight, the solution was evaporated to dryness to leave the crude product. Recrystallisation from dichloromethane (20 mL) and diethyl ether (110 mL) afforded thin yellow needles that were collected by filtration. Yield: 3.05 g, 98%. IR: $\tilde{\nu}$ = 1703 cm^{-1}, C=O. ^1H NMR (300.13 MHz, $CDCl_3$): δ = 0.55 (s, 9 H, *t*Bu), 2.43 (dd, $^2J_{HH}$ = 16.1, $^2J_{PH}$ = 10.8 Hz, 1 H, PCH_2, H_a), 3.71 (d, $^3J_{PH}$ = 10.8 Hz, 10 H, POMe and hidden PCH_2, H_b), 4.71 (d, $^2J_{PH}$ = 0.7 Hz, 5 H, Cp), 6.92–7.61 (m, 25 H, Ph) ppm. $^{31}P\{^1H\}$ NMR (121.50 MHz, $CDCl_3$): δ = 41.9 (dd, $^2J_{PP}$ = 63 and 32 Hz, PPh), 45.9 (dd, $^2J_{PP}$ = 63 and 32 Hz, PPh), 144.3 (t, $^2J_{PP} \approx {}^2J_{PP'} \approx$ 63 Hz, POMe) ppm. $C_{44}H_{50}F_6O_4P_4Ru$ (981.84): calcd. C 53.83, H 5.13, P 12.62; found C 53.73, H 5.10, P 12.34.

Ru$^+$(Cp)[η^1-*P*-Ph_2PCH=C(*t*Bu)O$^-$](PPh$_3$)(CO)·CH_2Cl_2 (3b): A mixture consisting of a sample of **2b** (3.00 g, 3.39 mmol), KOH (0.31 g, 5.54 mmol) and methanol (50 mL) was stirred for 3 days at room temperature. The resulting pale-yellow slurry was evaporated under vacuum until an orange colour was observed, and the residue was extracted with dichloromethane (20 mL). The solution was filtered and the orange filtrate was covered with diethyl ether (100 mL). The subsequent diffusion of solvents was conducted at –20 °C to avoid decomposition, and afforded large orange crystals, which were washed with hexane (20 mL). Yield: 2.20 g, 79%. IR: $\tilde{\nu}$ = 1489 cm^{-1}, C=CO; 1959 cm^{-1}, C≡O. ^1H NMR (300.13 MHz, CD_2Cl_2): δ = 1.10 (s, 9 H, *t*Bu), 3.66 (d, $^2J_{PH}$ = 27.1 Hz, 1 H, PCH=), 4.98 (s, 5 H, Cp), 7.00–7.65 (m, 25 H, Ph) ppm. $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2): δ = 29.6 (s, CMe_3), 40.7 (d, ^3J = 10.7 Hz, CMe_3), 60.6 (d, ^1J = 70.9 Hz, PCH=), 90.4 (s, Cp), 127.8 (d, ^2J = 9.9 Hz, PPh, *ortho*), 127.8 (d, ^2J = 10.8 Hz, PPh, *ortho*), 128.1 (d, ^4J = 2.7 Hz, PPh, *para*), 128.5 (d, ^2J = 9.9 Hz, PPh_3, *ortho*), 128.7 (d, ^4J = 2.7 Hz, PPh, *para*), 130.6 (d, ^4J = 1.8 Hz, PPh_3, *para*), 131.7 (d, ^3J = 9.0 Hz, PPh, *meta*), 132.6 (d, ^3J = 10.8 Hz, PPh, *meta*), 134.0 (d, ^3J = 10.8 Hz, PPh_3, *meta*), 135.3 (d, ^1J = 48.5 Hz, PPh_3, *ipso*), 140.8 (d, ^1J = 53.0 Hz, PPh, *ipso*), 141.7 (d, ^1J = 50.3 Hz, PPh, *ipso*), 191.9 (s, =CO), 205.6 (dd, ^2J = 19.3 and 15.7 Hz, C≡O) ppm. ^{13}C NMR (75.47 MHz, CD_2Cl_2, selected values): δ = 60.6 (dd, $^1J_{HC}$ = 158, $^1J_{PC}$ = 70.5 Hz, PCH=) ppm. $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2): δ = 19.5 (d, $^2J_{PP}$ = 27 Hz), 47.9 (d, $^2J_{PP}$ = 27 Hz). $C_{42}H_{40}O_2P_2Ru$·CH_2Cl_2 (824.73): calcd. C 62.62, H 5.13, Cl 8.60, P 7.51; found C 62.36, H 5.10, Cl 7.36, P 7.51.

Ru$^+$(Cp)[η^1-*P*-Ph_2PCH=C(*t*Bu)O$^-$](PPh$_3$)(PMe$_3$): A similar treatment of **2c** with KOH in methanol was attempted, but examination of the crude product after evaporation of the resulting dichloromethane solution by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy disclosed resonances corresponding to unreacted **2c** as well as a new set of resonances arising from the presence of the assumed zwitterionic complex. ^1H NMR (300.13 MHz, $CDCl_3$, available values): δ = 1.01 (s, 9 H, *t*Bu), 1.44 (d, $^2J_{PH}$ = 8.6 Hz, 9 H, PMe_3), 4.35 (s, 5 H, Cp) ppm. $^{31}P\{^1H\}$ NMR (121.50 MHz, $CDCl_3$, the additional presence of **2c** is omitted): δ = –5.3 (t, $^2J_{PP} \approx {}^2J_{PP'} \approx$ 42 Hz, PMe), 18.7 (dd, $^2J_{PP}$ = 42 and 35 Hz), 46.8 (dd, $^2J_{PP}$ = 42 and 35 Hz) ppm.

Ru(Cp)[η^2-*P*,*O*-Ph_2PCH=C(*t*Bu)O](CO) (4b): Crude **3b** was obtained from evaporation of the dichloromethane solution as described above starting from **2b** (13.0 g, 14.7 mmol), and then dissolved in THF (70 mL). The solution was heated at reflux for 20 h and then evaporated. Dichloromethane (60 mL) then methyl iodide (2.0 mL, 32.1 mmol, an excess) were added and this mixture was stirred overnight, then evaporated. The residue was extracted with diethyl ether (100 mL). The solution was filtered and the filtrate was evaporated to leave crude **4b**. Yield: 5.03 g, 72%. Heptane (60 mL) was added to a solution of crude **4b** in dichloromethane (30 mL) and this solution was slowly concentrated under vacuum to yield pure **4b** as a crystalline yellow powder. Orange-yellow crystals were also obtained by recrystallisation from hot hexane. IR: $\tilde{\nu}$ = 1494 cm^{-1}, C=CO; 1940 cm^{-1}, C≡O. ^1H NMR (300.13 MHz, C_6D_6): δ = 1.40 (s, 9 H, *t*Bu), 4.45 (s, 5 H, Cp), 4.85 (d, $^2J_{PH}$ = 4.1 Hz, 1 H, PCH=), 6.99–7.79 (m, 10 H, Ph) ppm. $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2): δ = 29.8 (s, CMe_3), 39.3 (d, ^3J = 12.1 Hz, CMe_3), 74.0 (d, ^1J = 61.9 Hz, PCH=), 84.5 (d, ^2J = 1.6 Hz, Cp), 128.6 (d, ^2J = 10.5 Hz, PPh, *ortho*), 128.6 (d, ^2J = 10.8 Hz, PPh, *ortho*), 129.2 (d, ^4J = 2.6 Hz, PPh, *para*), 130.3 (d, ^4J = 2.5 Hz, PPh, *para*), 130.7 (d, ^3J = 11.3 Hz, PPh, *meta*), 133.3 (d, ^3J = 10.8 Hz, PPh, *meta*), 136.9 (d, ^1J = 62.0 Hz, PPh, *ipso*), 143.4 (d, ^1J = 46.8 Hz, PPh, *ipso*), 202.7 (d, ^2J = 15.5 Hz, =CO), 203.6 (d, ^2J = 18.9 Hz, C≡O) ppm. $^{31}P\{^1H\}$ NMR (121.50 MHz, C_6D_6): δ = 61.4 (s) ppm. $C_{24}H_{25}O_2PRu$ (477.51): calcd. C 60.37, H 5.28; found C 60.54, H 5.28.

Ru(Cp)[η^2-*P*,*O*-Ph_2PCH=C(*t*Bu)O](PMe$_3$) (4): The slow concentration under vacuum of a solution of crude **4c** in methanol, the preparation of which is detailed below (see synthesis of **1c**), allowed the formation of orange crystals of analytical purity. IR: $\tilde{\nu}$ = 1492 cm^{-1}, C=CO. ^1H NMR (300.13 MHz, C_6D_6): δ = 0.91 (d, $^2J_{PH}$ = 9.0 Hz, 9 H, PMe_3), 1.42 (s, 9 H, *t*Bu), 4.21 (s, 5 H, Cp), 4.95 (d, $^2J_{PH}$ = 1.3 Hz, 1 H, PCH=), 6.98–7.74 (m, 10 H, Ph) ppm. $^{31}P\{^1H\}$ NMR (121.50 MHz, C_6D_6): δ = 6.8 (d, $^2J_{PP}$ = 42 Hz, PMe), 64.8 (d, $^2J_{PP}$ = 42 Hz, PPh) ppm. $C_{26}H_{34}OP_2Ru$ (525.58): calcd. C 59.42, H 6.52, P 11.79; found C 59.72, H 6.71, P 12.12.

{Ru(Cp)[Ph_2PCH_2C(*t*Bu)=O](PMe$_3$)}[PF$_6$] (1): A mixture consisting of a sample of **2c** (6.13 g, 6.56 mmol), an excess of NaH (0.89 g, 37.1 mmol) and THF (80 mL) was heated at reflux for 20 h. The resulting mixture was filtered and the orange-yellow filtrate was evaporated to dryness to leave crude **4c** as a solid. The solid was dissolved in hot methanol (50 mL) to obtain an orange solution that was filtered. NH_4PF_6 (1.34 g, 8.22 mmol) and a 6 M solution of HCl in diethyl ether (2.0 mL, 12.0 mmol) were added to the filtrate, and the mixture was further stirred for 10 min. The resulting yellow precipitate was collected by filtration and washed with diethyl ether (50 mL), and then extracted with dichloromethane (60 mL). The solution was filtered and the filtrate was covered with methanol (20 mL) then diethyl ether (160 mL) to afford yellow crystals. Yield: 3.20 g, 73%. IR: $\tilde{\nu}$ = 1603 cm^{-1}, C=O. ^1H NMR (300.13 MHz, CD_2Cl_2): δ = 1.16 (d, $^2J_{PH}$ = 9.1 Hz, 9 H, PMe_3), 1.26 (s, 9 H, *t*Bu), 3.32 (dd, $^2J_{HH}$ = 19.3, $^2J_{PH}$ = 7.2 Hz, 1 H, PCH_2,

H_a), 4.23 (dd, $^2J_{HH}$ = 19.3, $^2J_{PH}$ = 10.7 Hz, 1 H, PCH_2, H_b), 4.55 (s, 5 H, Cp), 6.87–7.64 (m, 10 H, Ph) ppm. $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2): δ = 2.3 (d, $^2J_{PP}$ = 39 Hz, PMe), 67.3 (d, $^2J_{PP}$ = 39 Hz, PPh) ppm. $C_{26}H_{35}F_6OP_3Ru$ (671.55): calcd. C 46.50, H 5.25, P 13.84; found C 46.18, H 5.28, P 13.84.

{Ru(Cp)(=C=CH$_2$)[Ph$_2$PCH$_2$C(=O)*t*Bu](PPh$_3$)}[PF$_6$]·1/6CH$_2$Cl$_2$ (5a): A solution of **1a** (3.90 g, 4.14 mmol) in dichloromethane (40 mL) was stirred for 2 days under ethyne. The resulting solution was then covered with diethyl ether (120 mL) to afford orange-brown crystals. Yield: 3.45 g, 93%. IR: $\tilde{\nu}$ = 1632 cm^{-1}, =C=CH$_2$; 1703 cm^{-1}, C=O. ^1H NMR (300.13 MHz, CD_2Cl_2): δ = 0.60 (s, 9 H, *t*Bu), 2.04 (dd, $^2J_{HH}$ = 17.6, $^2J_{PH}$ = 11.5 Hz, 1 H, PCH_2, H_a), 3.76 (dd, $^2J_{HH}$ = 17.2, $^2J_{PH}$ = 2.4 Hz, 1 H, PCH_2, H_b), 4.33 (dd, $^4J_{PH}$ = 3.1 and 1.7 Hz, 2 H, =CH_2), 5.06 (s, 5 H, Cp), 6.98–7.76 (m, 25 H, Ph) ppm. $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2): δ = 25.8 (s, C*Me*$_3$), 32.5 (d, ^1J = 29.7 Hz, PCH_2), 45.8 (d, ^3J = 1.8 Hz, *C*Me$_3$), 94.9 (s, Cp), 97.5 (s, =CH_2), 128.7–134.9 (m, Ph resonances), 207.4 (d, ^2J = 9.9 Hz, C=O), 346.6 (t, $^2J \approx$ 15.7 Hz, Ru=C) ppm. ^{13}C NMR (75.47 MHz, CD_2Cl_2, selected values): δ = 97.5 (t, $^1J_{HC}$ = 165 Hz, =CH_2) ppm. $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2): δ = 38.8 (d, $^2J_{PP}$ = 27 Hz), 45.7 (d, $^2J_{PP}$ = 27 Hz) ppm. $C_{43}H_{43}F_6OP_3Ru$·1/6CH_2Cl_2 (897.95): calcd. C 57.74, H 4.86, Cl 1.32, P 10.35; found C 57.44, H 4.87, Cl 1.13, P 10.06.

{Ru(Cp)(=C=CH$_2$)[Ph$_2$PCH$_2$C(=O)*t*Bu](PMe$_3$)}[PF$_6$] (5c): A solution of **1c** (2.07 g, 3.08 mmol) in dichloromethane (60 mL) was stirred for 2 days under ethyne. The resulting solution was then covered with diethyl ether (130 mL) to afford yellow-brown crystals. Yield: 1.97 g, 92%. IR: $\tilde{\nu}$ = 1630 cm^{-1}, =C=CH$_2$; 1706 cm^{-1}, C=O. ^1H NMR (300.13 MHz, CD_2Cl_2): δ = 1.00 (s, 9 H, *t*Bu), 1.22 (d, $^2J_{PH}$ = 10.5 Hz, 9 H, PMe_3), 3.80 (dd, $^2J_{HH}$ = 17.6, $^2J_{PH}$ = 9.7 Hz, 1 H, PCH_2, H_a), 4.02 (dd, $^4J_{PH}$ = 2.7 and 2.0 Hz, 2 H, =CH_2), 4.07 (dd, $^2J_{HH}$ = 17.6, $^2J_{PH}$ = 5.8 Hz, 1 H, PCH_2, H_b), 5.35 (s, 5 H, Cp), 7.26–7.52 (m, 10 H, Ph) ppm. $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2): δ = 21.2 (d, ^1J = 35.9 Hz, PMe_3), 26.4 (s, C*Me*$_3$), 39.9 (d, ^1J = 33.1 Hz, PCH_2), 46.1 (d, ^3J = 2.5 Hz, *C*Me$_3$), 92.8 (s, Cp), 95.1 (s, =CH_2), 129.1 (d, ^2J = 10.8 Hz, PPh, *ortho*), 129.4 (d, ^2J = 10.8 Hz, PPh, *ortho*), 131.5 (d, ^4J = 2.7 Hz, PPh, *para*), 131.7 (d, ^4J = 2.7 Hz, PPh, *para*), 132.6 (d, ^3J = 10.8 Hz, PPh, *meta*), 132.9 (d, ^3J = 10.8 Hz, PPh, *meta*), 133.9 (dd, ^1J = 51.2, ^3J = 1.8 Hz, PPh, *ipso*), 135.4 (d, ^1J = 50.3 Hz, PPh, *ipso*), 209.0 (d, ^2J = 6.9 Hz, C=O), 345.5 (t, $^2J \approx$ 15.3 Hz, Ru=C) ppm. ^{13}C NMR (75.47 MHz, CD_2Cl_2, selected values): δ = 95.1 (t, $^1J_{HC}$ = 164 Hz, =CH_2) ppm. $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2): δ = 7.4 (d, $^2J_{PP}$ = 31 Hz, PMe), 38.0 (d, $^2J_{PP}$ = 31 Hz, PPh) ppm. $C_{28}H_{37}F_6OP_3Ru$ (697.58): calcd. C 48.21, H 5.35, P 13.32; found C 48.00, H 5.46, P 13.08.

{Ru(Cp)(=CMeNH*i*Pr)[Ph$_2$PCH$_2$C(=O)*t*Bu](PPh$_3$)}[PF$_6$] (6a): Isopropylamine (1.00 mL, 11.7 mmol) was added to a solution of **5a** (3.02 g, 3.36 mmol) in dichloromethane (40 mL) and the mixture was stirred for 20 h. The resulting green solution was evaporated under vacuum. The residue was dissolved in dichloromethane (30 mL) and the solution was covered with diethyl ether (140 mL) to afford yellow crystals. Yield: 2.85 g, 90%. ^1H NMR (300.13 MHz, CD_2Cl_2): δ = 0.80 (s, 9 H, *t*Bu), 1.10 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, CH*Me*), 1.13 (d, $^3J_{HH}$ = 6.5 Hz, 3 H, CH*Me*), 2.36 (s, 3 H, RuCMe), 2.53 (dd, $^2J_{HH}$ = 17.9, $^2J_{PH}$ = 4.4 Hz, 1 H, PCH_2, H_a), 3.64 (dd, $^2J_{HH}$ = 17.9, $^2J_{PH}$ = 12.3 Hz, 1 H, PCH_2, H_b), 4.15 (m, 1 H, C*H*Me$_2$), 4.46 (s, 5 H, Cp), 6.69–7.48 (m, 25 H, Ph), 10.4 (broad s, 1 H, NH) ppm. $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2): δ = 21.3 (s, CH*Me*), 21.6 (s, CH*Me*), 26.7 (s, C*Me*$_3$), 38.0 (s, RuC*Me*), 42.3 (d, ^1J = 17.5 Hz, PCH_2), 45.4 (s, *C*Me$_3$), 51.6 (s, *C*HMe$_2$), 88.0 (s, Cp), 128.5–145.8 (m, Ph), 215.0 (d, ^2J = 4.5 Hz, C=O), 247.3 (dd, ^2J = 16.2 and 11.7 Hz, Ru=C) ppm. $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2): δ = 33.9 (d, $^2J_{PP}$ = 34 Hz), 51.2 (d, $^2J_{PP}$ = 34 Hz) ppm. $C_{46}H_{52}F_6NOP_3Ru$ (942.91): calcd. C 58.60, H 5.56, N 1.49, P 9.85; found C 58.41, H 5.58, N 1.64, P 9.42.

{Ru(Cp)[η^2-*C*,*P*-:C(CH=CPh$_2$)OC(*t*Bu)=CH–PPh$_2$](PMe$_3$)}[PF$_6$] (7c): A solution of **1c** (1.52 g, 2.26 mmol) and 1,1-diphenyl-2-propyn-1-ol (0.60 g, 2.88 mmol) in methanol (30 mL) was heated at reflux for 1 h. The resulting dark-red mixture was evaporated under vacuum and the residue was dissolved in dichloromethane (35 mL). The solution was filtered and the filtrate was covered with methanol (15 mL), then diethyl ether (130 mL) to afford dark-red crystals. Yield: 1.34 g, 69%. IR: $\tilde{\nu}$ = 1556 cm^{-1}, C=CO; 1611 cm^{-1}, C=CPh_2. ^1H NMR (300.13 MHz, CD_2Cl_2): δ = 0.84 (s, 9 H, *t*Bu), 1.19 (d, $^2J_{PH}$ = 10.1 Hz, 9 H, PMe_3), 5.24 (s, 5 H, Cp), 5.83 (d, $^2J_{PH}$ = 0.8 Hz, 1 H, PCH=), 6.87 (s, 1 H, C*H*=CPh_2), 7.08–7.62 (m, 20 H, Ph) ppm. $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2): δ = 21.5 (d, ^1J = 34.6 Hz, PMe_3), 27.6 (s, C*Me*$_3$), 39.0 (d, ^3J = 7.1 Hz, *C*Me$_3$), 85.9 (d, ^1J = 55.0 Hz, PCH=), 93.4 (s, Cp), 129.1–133.1 (m, set of Ph resonances), 138.4 (s, *C*Ph_2), 140.2 and 142.1 (2 s, C*Ph*$_2$, *ipso*), 142.2 (dd, ^1J = 53.9, ^3J = 2.7 Hz, PPh, *ipso*), 142.3 (s, *C*HCPh_2), 178.3 (d, ^2J = 4.5 Hz, O*Ct*Bu), 286.1 (dd, ^2J = 15.7 and 13.9 Hz, Ru=C) ppm. ^{13}C NMR (75.47 MHz, CD_2Cl_2, selected values): δ = 85.9 (dd, $^1J_{HC}$ = 160, $^1J_{PC}$ = 55.0 Hz, PCH=), 138.4 (d, $^2J_{HC}$ = 2.7 Hz, *C*Ph_2), 142.3 (d, $^1J_{HC}$ = 160 Hz, *C*HCPh_2) ppm. $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2): δ = 5.9 (d, $^2J_{PP}$ = 36 Hz, PMe), 35.5 (d, $^2J_{PP}$ = 36 Hz, PPh) ppm. $C_{41}H_{47}F_6OP_3Ru$ (863.81): calcd. C 57.01, H 5.48, P 10.76; found C 56.88, H 5.37, P 10.37.

{Ru(Cp)[=C=CHC(OH)Ph$_2$][Ph$_2$PCH$_2$C(=O)*t*Bu](PMe$_3$)}[PF$_6$] (8c): An equimolar mixture of **1c** and 1,1-diphenyl-2-propyn-1-ol was dissolved in CD_2Cl_2 in an NMR tube and the solution was kept at room temperature. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded after 20 h and showed **8c** to be the major compound (≈85%). ^1H NMR (300.13 MHz, CD_2Cl_2, the presence of residual **1c** and of **9c** is omitted): δ = 0.93 (s, 9 H, *t*Bu), 1.10 (d, $^2J_{PH}$ = 10.6 Hz, 9 H, PMe_3), 3.19 (s, 1 H, OH), 3.81 (dd, $^2J_{HH}$ = 17.8, $^2J_{PH}$ = 9.1 Hz, 1 H, PCH_2, H_a), 4.21 (dd, $^2J_{HH}$ = 17.8, $^2J_{PH}$ = 6.1 Hz, 1 H, PCH_2, H_b), 5.25 (dd, $^4J_{PH}$ = 2.5 and 1.6 Hz, 1 H, =CH), 5.35 (s, 5 H, Cp), 7.26–7.61 (m, 20 H, Ph) ppm. $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2): δ = 8.9 (d, $^2J_{PP}$ = 33 Hz, PMe), 38.4 (d, $^2J_{PP}$ = 33 Hz, PPh) ppm. The conversion of **8c** into **9c** was almost complete after 75 h.

{Ru(Cp)(=C=C=CPh$_2$)[Ph$_2$PCH$_2$C(=O)*t*Bu](PMe$_3$)}[PF$_6$] (9c): A solution of **1c** (2.51 g, 3.74 mmol) and 1,1-diphenyl-2-propyn-1-ol (1.15 g, 5.52 mmol) in THF (40 mL) was heated at reflux for 2 h. The resulting solution was evaporated under vacuum and the residue was washed with diethyl ether to obtain a violet powder. Recrystallisation from dichloromethane (40 mL) and diethyl ether (130 mL) afforded a dark-green crystalline powder, but an obvious minor presence of orange crystals (presumably **7c**) precluded elemental analysis. Yield: 2.68 g, ≈83%. ^1H NMR (300.13 MHz, CD_2Cl_2): δ = 0.74 (s, 9 H, *t*Bu), 1.25 (d, $^2J_{PH}$ = 10.3 Hz, 9 H, PMe_3), 3.65 (dd, $^2J_{HH}$ = 17.6, $^2J_{PH}$ = 9.7 Hz, 1 H, PCH_2, H_a), 3.96 (dd, $^2J_{HH}$ = 17.6, $^2J_{PH}$ = 4.4 Hz, 1 H, PCH_2, H_b), 5.37 (s, 5 H, Cp), 7.22–7.81 (m, 20 H, Ph) ppm. $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2): δ = 22.1 (d, ^1J = 34.5 Hz, PMe_3), 26.1 (s, C*Me*$_3$), 40.7 (d, ^1J = 30.9 Hz, PCH_2), 45.6 (d, ^3J = 1.7 Hz, *C*Me$_3$), 92.1 (s, Cp), 128.9 (d, ^2J = 10.8 Hz, PPh, *ortho*), 129.2 (d, ^2J = 10.8 Hz, PPh, *ortho*), 129.7 (s, =C*Ph*$_2$, *ortho*), 130.7 (s, =C*Ph*$_2$, *meta*), 131.1 (d, ^4J = 2.7 Hz, PPh, *para*), 131.5 (d, ^4J = 2.7 Hz, PPh, *para*), ≈132.3 and 132.2 (d, PPh, *meta*, and s, =C*Ph*$_2$, *para*), 132.9 (d, ^3J = 9.9 Hz, PPh, *meta*), 134.1 (dd, ^1J = 49.4, ^3J = 1.8 Hz, PPh, *ipso*), 136.1 (d, ^1J = 47.6 Hz, PPh, *ipso*), 144.3 (s, =C*Ph*$_2$, *ipso*), 158.4 (t, $^4J \approx$

0.9 Hz, =*C*Ph$_2$), 208.8 (dd, ^3J = 2.7 and 1.3 Hz, Ru=C=*C*), 208.9 (d, ^2J = 7.2 Hz, C=O), 293.2 (dd, ^2J = 18.4 and 16.6 Hz, Ru=C) ppm. ^{31}P{^{1}H} NMR (121.50 MHz, CD_2Cl_2): δ = 9.6 (d, $^2J_{PP}$ = 36 Hz, PMe), 41.2 (d, $^2J_{PP}$ = 36 Hz, PPh).

Isomerisation of 9c into 7c: A solution of a sample of **9c** in methanol was stirred at room temperature and the isomerisation of **9c** into **7c** was monitored by ^{31}P{^{1}H} NMR spectroscopy. Completion of the reaction was reached after 15 days. A 0.07 M aqueous solution of K_2CO_3 (2.0 mL, 0.14 mmol) was added to a solution of **9c** (1.80 g, 2.08 mmol) in dichloromethane (40 mL) and the mixture was stirred for 1 h. Examination of the resulting orange-red solution by ^{31}P{^{1}H} NMR spectroscopy showed the isomerisation of **9c** into **7c** to be complete.

{Ru(Ind)[Ph$_2$PCH$_2$C(=O)*t*Bu](PPh$_3$)(PMe$_3$)}[PF$_6$] (2′c): A 1.0 M solution of trimethylphosphane in THF (8.0 mL, 8.0 mmol) was added to a solution of {Ru(Ind)[Ph$_2$PCH$_2$C(*t*Bu)=O](PPh$_3$)}[PF$_6$] (**1′a**) (6.00 g, 6.61 mmol) in dichloromethane (50 mL). The mixture was stirred overnight and then evaporated to dryness to leave the crude product that was recrystallised from dichloromethane (35 mL) and diethyl ether (140 mL) to afford orange-red crystals. Yield: 5.78 g, 89%. IR: $\tilde{\nu}$ = 1705 cm^{-1}, C=O. ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ = 0.63 (s, 9 H, *t*Bu), 1.46 (d, $^2J_{PH}$ = 8.5 Hz, 9 H, PMe$_3$), 3.11 (m, 2 H, PCH$_2$), 4.51 (s, broad, 1 H, Ind), 5.44 (s, broad, 1 H, Ind), 5.57 (m, 1 H, Ind), 6.80–7.45 (m, 29 H, Ph and Ind) ppm. ^{31}P{^{1}H} NMR (121.50 MHz, CD_2Cl_2): δ = –10.5. (t, $^2J_{PP} \approx {}^2J_{PP'} \approx$ 33 Hz, PMe), 42.8 (t, $^2J_{PP} \approx {}^2J_{PP'} \approx$ 33 Hz), 45.0 (t, $^2J_{PP} \approx {}^2J_{PP'} \approx$ 33 Hz) ppm. $C_{48}H_{52}F_6OP_4Ru$ (983.90): calcd. C 58.60, H 5.33, P 12.59; found C 58.51, H 5.34, P 12.64.

{Ru(Ind)[Ph$_2$PCH$_2$C(*t*Bu)=O](PMe$_3$)}[PF$_6$] (1′c): A mixture consisting of a sample of **2′c** (3.00 g, 3.05 mmol), an excess of NaH (0.78 g, 32.5 mmol) and THF (60 mL) was heated at reflux for 20 h. The resulting mixture was filtered and the dark-orange filtrate was evaporated to dryness. Methanol (50 mL) was added to the residue and this mixture was stirred to obtain a red-orange slurry. NH_4PF_6 (0.60 g, 3.68 mmol) and then a 6 M solution of HCl in diethyl ether (2.0 mL, 12 mmol) were added to the slurry. The mixture was stirred for 10 min and the resulting orange precipitate was collected by filtration and washed with diethyl ether (50 mL). The solid was extracted with dichloromethane (25 mL), the solution was filtered and the filtrate was covered with methanol (10 mL) then diethyl ether (120 mL) to afford orange crystals. Yield: 1.70 g, 77%. IR: $\tilde{\nu}$ = 1607 cm^{-1}, C=O. ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ = 0.94 (d, $^2J_{PH}$ = 9.0 Hz, 9 H, PMe$_3$), 1.19 (s, 9 H, *t*Bu), 3.34 (dd, $^2J_{HH}$ = 19.4, $^2J_{PH}$ = 7.6 Hz, 1 H, PCH$_2$, H$_a$), 4.10 (dd, $^2J_{HH}$ = 19.4, $^2J_{PH}$ = 10.9 Hz, 1 H, PCH$_2$, H$_b$), 4.28 (m, 1 H, Ind), 4.61 (m, 1 H, Ind), 4.73 (m, 1 H, Ind), 6.82–7.62 (m, 14 H, Ph and Ind) ppm. ^{31}P{^{1}H} NMR (121.50 MHz, CD_2Cl_2): δ = 0.9 (d, $^2J_{PP}$ = 38 Hz, PMe), 75.2 (d, $^2J_{PP}$ = 38 Hz, PPh) ppm. $C_{30}H_{37}F_6OP_3Ru$ (721.61): calcd. C 49.93, H 5.17, P 12.88; found C 50.20, H 5.20, P 12.84.

{Ru(Ind)[η^2-*C*,*P*-:C(CH=CPh$_2$)OC(*t*Bu)=CH–PPh$_2$](PMe$_3$)}[PF$_6$] (7′c): Starting from **1′c** instead of **1c**, the procedure detailed for the synthesis of **7c** was used and similarly yielded **7′c** as dark-purple crystals (71%). ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ = 0.70 (s, 9 H, *t*Bu), 1.11 (d, $^2J_{PH}$ = 10.0 Hz, 9 H, PMe$_3$), 4.46 (d, $^2J_{PH}$ = 1.6 Hz, 1 H, PCH=), 4.57 (m, 1 H, Ind), 5.68 (m, 1 H, Ind), 5.72 (s, 1 H, C*H*=CPh$_2$), 5.90 (m, 1 H, Ind), 6.29–7.61 (m, 24 H, Ph and Ind) ppm. ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2): δ = 20.1 (d, ^1J = 34.1 Hz, PMe$_3$), 27.4 (s, C*Me*$_3$), 38.8 (d, ^3J = 7.1 Hz, *C*Me$_3$), 80.0 (s, Ind), 85.1 (d, ^1J = 58.5 Hz, PCH=), 87.0 (s, Ind), 96.7 (s, Ind), 109.4 (d, ^2J = 6.3 Hz, Ind), 120.2 (s, Ind), 120.7–133.3 (m, set of Ph and Ind resonances), 137.9 (d, ^4J = 2.7 Hz, *C*HCPh$_2$), 139.3 (s,

Table 1. Crystallographic data for complexes **3b**·CH_2Cl_2 and **7c**.

Complex	**3b**·CH_2Cl_2	**7c**
Empirical formula	$C_{43}H_{42}Cl_2O_2P_2Ru$	$C_{41}H_{45}F_6OP_3Ru$
Molecular weight [g mol^{-1}]	824.68	861.75
Crystal size [mm]	0.48 × 0.35 × 0.32	0.45 × 0.35 × 0.35
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
a [Å]	10.7595(1)	11.8729(1)
b [Å]	28.0871(3)	25.8064(2)
c [Å]	13.6725(2)	13.2105(1)
β [°]	109.5282(5)	96.4906(3)
V [Å^3]	3894.19(8)	4021.71(6)
Z	4	4
Density [g cm^{-3}]	1.407	1.423
Temperature [K]	293(2)	293(2)
F(000)	1696	1768
Mo-K_α radiation, λ [Å]	0.71073	0.71073
Absorption coefficient [mm^{-1}]	0.658	0.568
θ range [°]	1.74–27.48	2.70–27.48
Index ranges	$0 < h < 13$	$0 < h < 15$
	$0 < k < 36$	$0 < k < 33$
	$-17 < l < 16$	$-17 < l < 17$
Reflections collected	33970	54682
Independent reflections	8841 (R_{int} = 0.033)	9180 (R_{int} = 0.035)
Reflections $I > 2\sigma(I)$	6496	7134
Data/restraints/parameters	8841/0/447	9180/0/470
Goodness-of-fit on F^2	1.014	1.019
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0593	R_1 = 0.0437
	wR_2 = 0.1581	wR_2 = 0.1140
R indices (all data)	R_1 = 0.0851	R_1 = 0.0614
	wR_2 = 0.1769	wR_2 = 0.1250
Largest diff. peak/hole [e Å^{-3}]	1.786 and –1.618	0.869 and –0.840

$w = 1/[\sigma^2(F_o^2) + (0.0949P)^2 + 5.7242P]$ (**3b**), $1/[\sigma^2(F_o^2) + (0.0680P)^2 + 2.4890P]$ (**7c**), where $P = (F_o^2 + 2F_c^2)/3$

CPh_2), 140.2 and 140.6 (2 s, C*Ph*$_2$, *ipso*), 141.8 (dd, ^1J = 55.7, ^3J = 2.7 Hz, PPh, *ipso*), 178.1 (d, ^2J = 3.6 Hz, O*C*tBu), 285.4 (dd, ^2J = 16.2 and 12.6 Hz, Ru=C) ppm. ^{13}C NMR (75.47 MHz, CD_2Cl_2, selected values): δ = 85.1 (dd, $^1J_{HC}$ = 160, $^1J_{PC}$ = 58.5 Hz, PCH=), 137.9 (d, $^1J_{HC}$ = 160 Hz, *C*HCPh$_2$), 139.3 (d, $^2J_{HC}$ = 2.7 Hz, *C*Ph$_2$) ppm. ^{31}P{^{1}H} NMR (121.50 MHz, CD_2Cl_2): δ = 1.6 (d, $^2J_{PP}$ = 31 Hz, PMe), 42.5 (d, $^2J_{PP}$ = 31 Hz, PPh) ppm. $C_{45}H_{49}F_6OP_3Ru$ (913.87): calcd. C 59.14, H 5.40, P 10.17; found C 58.29, H 5.17, Cl 0.73, P 10.34. The presence of chlorine indicated a slight retention of dichloromethane, which is likely responsible for the low carbon value.

X-ray Crystallography: Selected crystals of **3b**·CH_2Cl_2 and **7c** were studied with a NONIUS Kappa CCD diffractometer with graphite monochromator. Crystallographic data are given in Table 1. The cell parameters were obtained with Denzo and Scalepack,[15] and data collection with NONIUS KappaCCD Software.[16] Data reduction was carried out with Denzo and Scalepack.[15] The structures were solved with SIR-97, which revealed the non-hydrogen atoms.[17] After anisotropic refinement, many hydrogen atoms may be found with Fourier difference calculations. The whole structures were refined with SHELXL97 by full-matrix least-squares methods on F^2 (x, y, z, β_{ij} for Ru, P, Cl, O and C atoms; x, y, z in riding mode for H atoms).[18] ORTEP views were prepared with PLATON98.[19] Thermal ellipsoids for some atoms in the C30 ring in **7c** might suggest a disorder problem. Calculations to split these atoms in two positions to improve the structural model were unsuccessful, probably because this defect is not symmetrical relative to the phenyl ring axis.

CCDC-291347 (for **3b**) and -291348 (for **7c**) 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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