DOI: 10.1002/ejic.200900574

Reactivity of {Ru(C_5Me_5)[η^2-*P*,*O*-Ph_2PCH_2C(*t*Bu)=O](CO)}[PF_6] towards Terminal Alkynes and Unexpected Rearrangement of a Fischer-Type Carbene Ligand

Bernard Demerseman*[a] and Loïc Toupet[a]

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

The ruthenium complex {Ru(C_5Me_5)[η^2-*P*,*O*-Ph_2PCH_2C(*t*Bu)=O](CO)}[PF_6] reacts with terminal alkynes HC≡CR (R = H, *t*Bu, Ph) in methanol to afford {Ru[:C(OMe)-CH_2R](C_5Me_5)[η^1-*P*-Ph_2PCH_2C(=O)*t*Bu](CO)}[PF_6] derivatives. The similar reaction conducted in dichloromethane as solvent led to six-membered metallacyclic complexes {Ru(C_5Me_5)[η^2-*C*,*P*-:C(CH_2R)OC(*t*Bu)=CH–PPh_2](CO)}[PF_6], which, when R is an aromatic group (R = Ph, *p*-tolyl), rearrange under moderate thermal activation into {Ru(C_5Me_5)-[η^3-*C*,*C*,*P*-RCH=CH-OC(*t*Bu)=CHPPh_2](CO)}[PF_6] derivatives, according to an isomerization of a Fischer-type carbene ligand into an η^2-coordinated vinylic ether, as shown by X-ray single crystal analysis (R = *p*-tolyl).

Introduction

Ruthenium complexes RuCl(Cp)(L_2) (L = phosphane, or L_2 = diphosphane) have a remarkable ability to generate numerous stable ruthenium–vinylidene complexes.[1,2] As a preliminary step, chloride–ruthenium bond cleavage was usually achieved in methanol and allowed subsequent coordination of terminal alkynes that rearrange into vinylidene ligands. From a theoretical point of view, the mechanism of the alkyne to vinylidene rearrangement continues to stimulate interest.[3] Indeed, electron-rich precursors RuCl(Cp*)(L_2) (Cp* = pentamethylcyclopentadienyl; L = PEt_3 or L_2 = dippe) allowed hydrido acetylide ruthenium intermediates to be disclosed,[4,5] and such intermediates have been more conveniently obtained starting from coordinatively unsaturated ruthenium complexes [Ru(Cp*)(L_2)]-[BAr′$_4$] [Ar′ = 3,5-$C_6H_3(CF_3)_2$].[6] By contrast, less information is available when starting from RuX(η^5-C_5R_5)(L)(CO) complexes, which are relatively less electron rich, owing to the presence of a carbon monoxide ligand instead of a phosphane one. Complexes of the type RuCl(Cp*)(L)(CO) remain rare,[7] but the reactivity towards terminal alkynes of complexes RuX(η^5-1,2,3-$R_3C_9H_4$)-(L)(CO) (X = Br or I) featuring an indenyl-type ligand has been investigated.[8,9] In the presence of a silver salt as halide abstractor, vinylidene ruthenium derivatives were obtained at low temperature. Isomerization resulting in mixtures of η^2-alkyne and vinylidene ruthenium species easily occurred at room temperature and favoured η^2-alkyne coordination. Favourable formation of an η^2-alkyne complex already resulted from the protonation of the neutral acetylide complex Ru(C≡CPh)(Cp)(PPh_3)(CO).[10]

In contrast, complexes {Ru(Cp)(PR_3)[η^2-*P*,*O*-Ph_2-PCH_2C(*t*Bu)=O]}[PF_6] behaved as [Ru(Cp)(L_2)]$^+$ 16-electron species, owing to the hemilabile properties of the keto-phosphane ligand and allowed coordination of ethyne without requirement of halide abstractor or the presence of methanol.[11] Offering the same conveniency, the related complex {Ru(Cp*)[η^2-*P*,*O*-Ph_2PCH_2C(*t*Bu)=O](CO)}[PF_6] (**1**) bearing the more electron-donating Cp* ligand as compared to the Cp one but a less electron-donating carbon monoxide ligand as compared to a phosphane one was recently synthesized.[12]

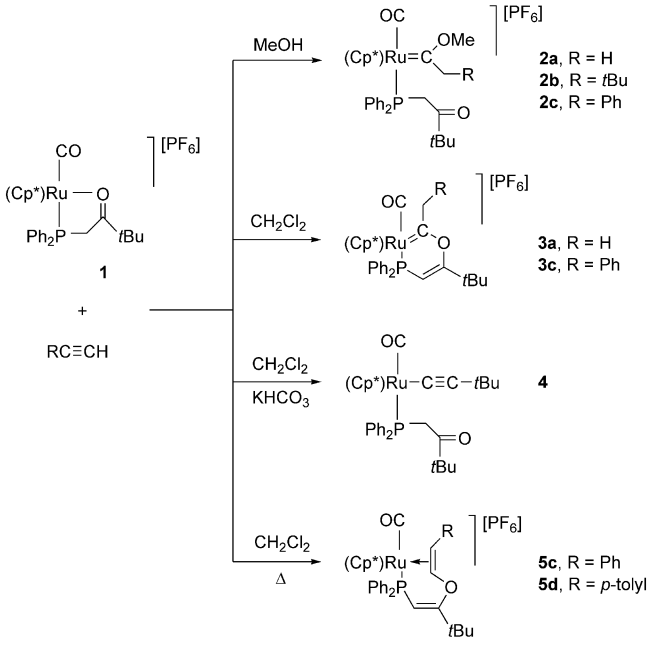
We report herein the reactivity of complex **1** towards terminal alkynes. Fischer-type carbene ligands were generated by using methanol as solvent. Six-membered metallacyclic complexes were obtained in dichloromethane and still involved similar carbene coordination. However, an unexpected easy isomerization of the carbene moiety into η^2-coordinated vinylic ether occurred subsequently.

Results and Discussion

The reaction between {Ru(Cp*)[η^2-*P*,*O*-Ph_2PCH_2C-(*t*Bu)=O](CO)}[PF_6] (**1**) and ethyne, *tert*-butylacetylene or phenylacetylene occurred at room temperature by using methanol as solvent. The reaction was monitored by the formation of a pale-yellow precipitate of the methoxy-carbene ruthenium derivatives **2a**–**c** (Scheme 1). Complexes **2a**–**c** were isolated in 71–88% yield as yellow solids and are

[a] UMR 6226 CNRS-Université de Rennes 1, Catalyse et Organométalliques, Université de Rennes 1,
35042 Rennes Cedex, France
Fax: +33-2-23236939
E-mail: bernard.demerseman@univ-rennes1.fr

stable in air. They were characterized from a combination of ^1H, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$ and ^{13}C DEPT NMR spectroscopy and elemental analysis. The observation of a ^{13}C NMR low-field resonance in the δ = 317.6–326.4 ppm range was characteristic of the presence of a carbene ligand.[13] Complexes **2a**–**c** formally arose from the addition of methanol to electrophilic {Ru(**:**C=CHR)(Cp*)[η^1-*P*-Ph_2PCH_2C(=O)*t*Bu](CO)}$^+$ vinylidene ruthenium intermediates. A similar addition of methanol was already reported to occur upon protonation of the acetylide complex Ru(C≡CPh)(Cp)(PPh_3)(CO) in the presence of methanol.[14] By contrast, the more electron-rich vinylidene ruthenium complexes [Ru(**:**C=CHR)(Cp*)(PMe_2Ph)$_2$][PF_6] were reported to be inert towards the addition of alcohols.[15]



Scheme 1. Reactivity of {Ru(Cp*)[η^2-*P,O*-Ph_2PCH_2C(*t*Bu)=O](CO)}[PF_6] (**1**) towards terminal alkynes.

The reactivity of **1** with terminal alkynes was then studied in dichloromethane as solvent. Thus, the reaction with ethyne led to a brown solution from which subsequent workup allowed isolation of pale-yellow crystals of **3a** (Scheme 1). The ^1H NMR spectrum of **3a** indicated the presence of both a methyl vinylic group and a PCH= fragment according to the observation of resonances at δ = 2.90 ppm (s, 3 H) and at δ = 6.22 ppm (d, $^2J_{P,H}$ = 5.0 Hz, 1 H), respectively, thus suggesting that the keto function from the functional phosphane added as its enol form to a vinylidene moiety. The presence of a carbene ligand in **3a** was confirmed by the observation of a ^{13}C NMR low-field resonance δ = 312.3 ppm (d, $^2J_{C,P}$ = 15.7 Hz). The similar formation of such a six-membered metallacycle was previously achieved by treating {Ru(Cp)(PMe_3)[η^2-*P,O*-Ph_2PCH_2C(*t*Bu)=O]}[PF_6] with 1,1-diphenyl-2-propyn-1-ol.[11]

Complex **3a** was moderately stable in solution and recrystallization invariably showed some decomposition. Furthermore, attempts to recrystallize **3a** in the presence of methanol resulted in complete transformation of **3a** into methoxycarbene complex **2a**.

The reaction of **1** with *tert*-butylacetylene revealed a distinct behaviour. After stirring for 3 d, a solution of **1** and a large excess of *tert*-butylacetylene in dichloromethane was evaporated to dryness. Subsequent examination of the residue by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy provided evidence for the sole presence of starting complex **1**. However, when *tert*-butylacetylene was added to a solution of **1** in CD_2Cl_2 in an NMR tube, the NMR spectra recorded after 1 d disclosed a 3:2 mixture of **1** and a distinct species. The detection of a new ^1H NMR resonance at δ = 5.35 ppm (d, $^4J_{P,H}$ = 3.5 Hz) suggested the presence of a vinylidene ruthenium complex {Ru(**:**C=CH*t*Bu)(Cp*)[Ph_2PCH_2C(=O)*t*Bu](CO)}$^+$ rather than a {Ru(η^2-HC≡C*t*Bu)(Cp*)-[Ph_2PCH_2C(=O)*t*Bu](CO)}$^+$ η^2-alkyne ruthenium one.[9] Because partial and reversible formation of the vinylidene ruthenium species precluded further characterization, $KHCO_3$ was added as a mild base to ensure irreversible deprotonation of the vinylidene ligand. The equilibrium was thus driven and the expected neutral acetylide ruthenium complex **4** was isolated as a lemon-yellow solid in 83% yield (Scheme 1). Note that a stronger base such as K_2CO_3 resulted in a less-selective reaction, affording a mixture of **4** and the previously reported enolato-phosphane complex Ru(Cp*)[η^2-*P,O*-Ph_2PCH=C(*t*Bu)O](CO).[12]

The reaction of **1** with phenylacetylene in dichloromethane afforded a crude solid as a mixture of **3c** (83%) and **5c** (17%). The presence of **5c** was minor enough to allow the characterization of **3c** by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, which both provided evidence for the formation of a six-membered metallacycle, as compared to **3a**. The nature of **3c** was further confirmed by recrystallization of the crude mixture of **3c** and **5c** in the presence of methanol, affording a mixture of the expected methoxycarbene derivative **2c** and **5c**. However, the amount of **5c** was significantly increased, as monitored by $^{31}P\{^1H\}$ NMR spectroscopy. Furthermore, $^{31}P\{^1H\}$ NMR spectroscopy revealed the sole presence of **5c** when a solution of a sample of crude **3c**/**5c** in dichloromethane was heated at reflux overnight, indicating that complete transformation of **3c** into **5c** had occurred. Indeed, **5c** was conveniently prepared according to a "one-pot" procedure by heating the solution resulting from the reaction of **1** with phenylacetylene in dichloromethane at room temperature, and subsequently isolated as thin pale-yellow needles in 62% yield. This procedure was used to straightforwardly synthesize the analogous derivative **5d** by using *p*-tolylacetylene instead of phenylacetylene. As is characteristic of **5c**, complex **5d** was stable in air and tolerated the presence of methanol in solution. Complex **5d** was isolated in 69% yield after recrystallization as pale-yellow crystals suitable for X-ray structure analysis. An ORTEP view of **5d** is shown in Figure 1 and selected bond lengths and angles are given in the caption.

Figure 1 clearly shows a ruthenium atom coordinated to a C_5Me_5 ring, a phosphorus atom from a diphenylalkenylphosphane, a carbon monoxide ligand and a (*Z*)-olefinic

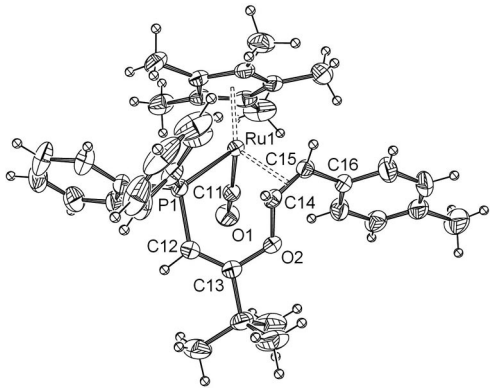
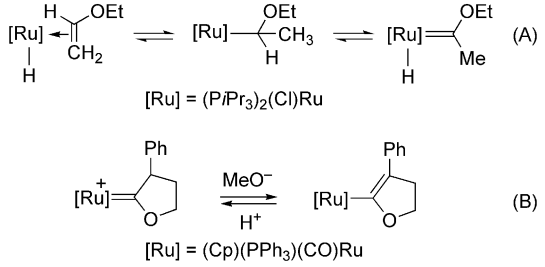


Figure 1. ORTEP drawing of the cation of **5d**. Selected bond lengths [Å] and angles [°]: Ru1–C14 2.269(2), Ru1–C15 2.255(3), C14–C15 1.383(4), O2–C14 1.390(3), C15–C16 1.489(4), Ru1–P1 2.3313(7), P1–C12 1.792(3), C12–C13 1.326(4), O2–C13 1.364(3), Ru1–C11 1.857(3), O1–C11 1.150(3); C15–Ru1–C14 35.6(1), C15–C14–Ru1 71.7(1), C14–C15–Ru1 72.7(1), C11–Ru1–C14 89.9(1), C11–Ru1–P1 88.00(8), C15–Ru1–P1 106.51(7), C14–Ru1–P1 71.49(7), C13–O2–C14 118.6(2), O1–C11–Ru1 171.9(2), C13–C12–P1 125.2(2), C12–C13–O2 123.5(2), C15–C14–O2 118.2(2), C14–C15–C16 125.3(2).

ligand formally achieving a three-membered metallacycle for which the Ru–C bond lengths are 2.255(3) and 2.269(2) Å (Ru1–C15 and Ru1–C14, respectively), and the C14–C15 bond length is 1.383(4) Å. These values compare well with those [2.285(5), 2.304(5) and 1.367(8) Å, respectively recently reported for the related complex {Ru(Cp)(PPh_3)(CO)[(*Z*)-EtCH=CHEt]}[PF_6] bearing an η^2-coordinated *cis*-3-hexene ligand.[16] The Ru1–P1 and Ru1–C11 bond lengths [2.3313(7) and 1.857(3) Å, respectively] also compare well with those reported for the latter complex [2.336(2) and 1.871(6) Å, respectively]. A short C12–C13 bond length of 1.326(4) Å in **5d** accounts for a double PCH=C(*t*Bu)O carbon–carbon bond and the coordinating arm from the chelating phosphane in **5d** may be described as a bisvinylic ether chain.

Thus, a 1,2-migration of a hydrogen atom from the CH_2Ar methylene group to the carbene carbon atom in **3** will formally account for the formation of complexes **5**. Such a transformation achieved an unexpected isomerization of a Fischer-type carbene ligand into an η^2-coordinated vinylic ether. The failure in detecting a similar isomerization starting from **3a** indicated the requirement of an aromatic CH_2Ar group.

The reverse transformation, that is, rearrangement of an η^2-coordinated vinylic ether into a carbene ligand, was previously reported by using a Ru(H)(Cl)($PiPr_3$)$_2$ 16-electron complex.[17,18] In this case, a major role was devoted to the presence of the hydrido ligand, as the proposed mechanism consisted of insertion of the vinylic ether into the ruthenium–hydrogen bond and a subsequent α-elimination step (Scheme 2, path A). The lack of a hydrido ligand in complexes **3** and **5** obviously precluded an analogous (but reverse) mechanism to account for the **3** to **5** isomerization.



Scheme 2. Generation of a carbene ligand from vinylic ether (A) [17,18] and reversible deprotonation of a Fischer-type carbene ligand (B).[10]

In contrast, a cyclic Fischer-type carbene ligand at a ruthenium centre could be deprotonated under basic conditions to generate a vinylic ruthenium complex and subsequently recovered under acidic conditions (Scheme 2, path B).[10] Thus, this carbene coordination is stable in a complex featuring cyclopentadienyl, phosphane and carbon monoxide ancillary ligands. Not surprisingly, no isomerization was detected starting from analogous complexes **2a**–**c**. Therefore, geometrical constraints arising from the metallacyclic structure of **3c**,**d** are likely responsible for the preferred olefinic coordination of the vinylic ether fragment. As previously mentioned,[18] this (η^2-olefine)metal ↔ (η^1-carbene)metal tautomerism showed some similarity to (η^2-alkyne)metal ↔ (η^1-vinylidene)metal tautomerism and thus raised the analogous mechanistic question, as direct 1,2-hydrogen shift migration and transient formation of a hydrido vinyl–ruthenium(IV) intermediate are both conceivable.

Conclusions

The ruthenium complex {Ru(Cp*)[η^2-*P*,*O*-Ph_2PCH_2C(*t*Bu)=O](CO)}[PF_6] behaves as a 16-electron reactive species, as the hemilabile properties of the ketophosphane ligand allowed easy coordination of terminal alkynes. The straightforward formation of Fischer-type methoxycarbene derivatives observed when the reaction was conducted in methanol clearly indicated transient formation of highly electrophilic vinylidene ruthenium species. Without the presence of methanol, the keto function from the functional phosphane adds as its enol form to generate six-membered metallacycles still involving Fischer-type carbene coordination. Easy isomerization of the Fischer-type carbene into η^2-coordinated vinylic ether was promoted by the presence of a benzylic group at the carbene carbon atom and represented a rare example of such a transformation.

Experimental Section

General Considerations: The reactions were performed under an inert atmosphere of argon according to Schlenk-type techniques. Solvents were distilled after drying according to conventional methods. NMR spectra were recorded at 297 K with a DPX 200 Bruker instrument and referenced internally to the solvent peak. Elemental

analyses were performed by the "Service de Microanalyse du CNRS" Solaize, France. Complex **1** was prepared as reported previously.[12]

{Ru[:C(Me)OMe](Cp*)[$Ph_2PCH_2C(=O)t$Bu](CO)}[PF_6] (2a): A solution of **1** (1.00 g, 1.44 mmol) in methanol (20 mL) was stirred for 24 h under an atmosphere of ethyne at room temperature. The resulting slurry was evaporated under vacuum, and the residue was dissolved in dichloromethane (30 mL). The pale-yellow solution was covered with diethyl ether (140 mL) to afford pale-yellow crystals of **2a**. Yield: 0.95 g, 88%. ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 1.05 (s, 9 H, CMe_3), 1.66 (d, $^4J_{P,H}$ = 1.7 Hz, 15 H, C_5Me_5), 2.70 (d, $^4J_{P,H}$ = 0.9 Hz, 3 H, =CMe), 3.75 (dd, $^2J_{H,H}$ = 17.8 Hz, $^2J_{P,H}$ = 7.1 Hz, 1 H, PCH_2, H[a]), 3.85 (dd, $^2J_{H,H}$ = 17.8 Hz, $^2J_{P,H}$ = 8.8 Hz, 1 H, PCH_2, H[b]), 4.32 (d, $^5J_{P,H}$ = 0.8 Hz, 3 H, OMe), 7.29–7.62 (m, 10 H, Ph) ppm. ^{13}C{^{1}H} NMR (50.3 MHz, CD_2Cl_2): δ = 9.8 (s, C_5Me_5), 26.4 (s, CMe_3), 40.3 (d, ^1J = 35.1 Hz, PCH_2), 43.7 (s, Me), 45.7 (d, ^3J = 2.1 Hz, CMe_3), 65.4 (s, OMe), 101.9 (s, C_5Me_5), 129.3 (d, ^2J = 11.0 Hz, Ph, *ortho*), 129.3 (d, ^2J = 9.4 Hz, Ph, *ortho*), 129.8 (d, ^1J = 57.7 Hz, Ph, *ipso*), 131.5 (d, ^4J = 2.4 Hz, Ph, *para*), 131.9 (d, ^3J = 10.9 Hz, Ph, *meta*), 132.0 (d, ^4J = 2.1 Hz, Ph, *para*), 132.7 (d, ^1J = 48.9 Hz, Ph, *ipso*), 132.9 (d, ^3J = 11.0 Hz, Ph, *meta*), 205.0 (d, ^2J = 15.9 Hz, C≡O), 209.8 (d, ^2J = 6.1 Hz, C=O), 318.8 (d, ^2J = 12.3 Hz, Ru=C) ppm. ^{31}P{^{1}H} NMR (81.0 MHz, CD_2Cl_2): δ = 37.2 (s) ppm. $C_{32}H_{42}F_6O_3P_2Ru$ (751.69): calcd. C 51.13, H 5.63, P 8.24; found C 51.12, H 5.62, P 8.13.

{Ru[:C(CH_2tBu)OMe](Cp*)[$Ph_2PCH_2C(=O)t$Bu](CO)}[PF_6] (2b): To a solution of **1** (2.03 g, 2.93 mmol) in methanol (35 mL) was added 3,3-dimethyl-1-butyne (1.0 mL, 8.12 mmol, excess), and the mixture was stirred for 24 h at room temperature. The resulting slurry was evaporated under vacuum and the residue was dissolved in dichloromethane (30 mL). The yellow solution was covered with diethyl ether (120 mL) to afford yellow crystals of **2b**. Yield: 1.69 g, 71%. ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 1.07 (br. s, 18 H, CMe_3), 1.69 (d, $^4J_{P,H}$ = 1.7 Hz, 15 H, C_5Me_5), 2.73–2.96 and 3.73–3.77 (2 br. m, 4 H, PCH_2 and tBuCH_2), 4.49 (s, 3 H, OMe), 7.32–7.42 (m, 4 H, Ph), 7.52–7.63 (m, 6 H, Ph) ppm. ^{13}C{^{1}H} NMR (50.3 MHz, CD_2Cl_2): δ = 10.3 (s, C_5Me_5), 26.8 (s, CMe_3), 31.4 (v. br. s, CMe_3), 36.9 (v. br. s, CH_2tBu), 40.9 (d, ^1J = 34.4 Hz, PCH_2), 46.1 (d, ^3J = 1.9 Hz, CMe_3), 68.5 (s, OMe), 102.1 (br. s, C_5Me_5), 129.7 (d, ^2J = 10.4 Hz, Ph, *ortho*), 129.8 (br. d, ^2J = 10.4 Hz, Ph, *ortho*), 131.9 (part of d, Ph, *ipso*), 132.2 (d, ^4J = 2.5 Hz, Ph, *para*), 132.3 (d, ^4J = 1.9 Hz, Ph, *para*), 132.7 (d, ^3J = 12.3 Hz, Ph, *meta*), 132.9 (d, ^3J = 10.9 Hz, Ph, *meta*), 206.8 (br. s, C≡O), 210.0 (s, C=O), 326.4 (br. s, Ru=C) ppm. ^{31}P{^{1}H} NMR (81.0 MHz, CD_2Cl_2): δ = 35.34 (br. s) ppm. $C_{36}H_{50}F_6O_3P_2Ru$ (807.80): calcd. C 53.53, H 6.24, P 7.67; found C 53.54, H 6.29, P 7.25.

{Ru[:C(CH_2Ph)OMe](Cp*)[$Ph_2PCH_2C(=O)t$Bu](CO)}[PF_6] (2c): Using phenylacetylene, the procedure detailed for **2b** was appropriate to prepare **2c** in 86% yield as shiny yellow crystals that retained 1 mol of water per Ru. ^{1}H NMR (200.1 MHz, CD_2Cl_2): δ = 1.06 (s, 9 H, CMe_3), 1.56 (d, $^4J_{P,H}$ = 1.4 Hz, 15 H, C_5Me_5), 3.84 (d, $^2J_{P,H}$ = 7.7 Hz, 2 H, PCH_2), 4.08 (d, $^2J_{H,H}$ = 13.6 Hz, 1 H, CH_2Ph), 4.27 (d, $^2J_{H,H}$ = 13.7 Hz, 1 H, CH_2Ph), 4.55 (s, 3 H, OMe), 7.24–7.29 (m, 2 H, Ph), 7.39–7.64 (m, 13 H, Ph) ppm. ^{13}C{^{1}H} NMR (50.3 MHz, CD_2Cl_2): δ = 9.7 (s, C_5Me_5), 26.3 (s, CMe_3), 40.5 (d, ^1J = 34.1 Hz, PCH_2), 45.8 (s, CMe_3), 60.7 (br. s, CH_2Ph), 67.4 (s, OMe), 102.4 (s, C_5Me_5), 128.4 (s, CH_2Ph, *para*), 129.4 (d, ^2J = 10.6 Hz, PPh_2, *ortho*), 129.7 (s, CH_2Ph), 130.1 (s, CH_2Ph), 131.6 (d, ^1J = 57.8 Hz, PPh_2, *ipso*), 131.9 (d, ^4J = 2.7 Hz, PPh, *para*), 131.9 (s, CH_2Ph, *ipso*), 132.0 (d, ^4J = 2.8 Hz, PPh, *para*), 132.6 (d, ^3J = 9.8 Hz, PPh_2, *meta*), 205.5 (d, ^2J = 17.2 Hz, C≡O), 209.7 (d, ^2J = 6.1 Hz, C=O), 317.6 (d, ^2J = 12.3 Hz, Ru=C) ppm. ^{31}P{^{1}H} NMR (81.0 MHz, CD_2Cl_2): δ = 37.2 (s) ppm. $C_{38}H_{46}F_6O_3P_2Ru{\cdot}H_2O$ (845.81): calcd. C 53.96, H 5.72, P 7.32; found C 53.90, H 5.50, P 7.09.

{Ru(Cp*)[η²-*C,P*-:C(Me)OC(tBu)=CH–PPh_2](CO)}[PF_6] (3a): A solution of **1** (2.02 g, 2.91 mmol) in dichloromethane (35 mL) was stirred for 24 h under an atmosphere of ethyne at room temperature. The resulting brown solution was evaporated under vacuum, and the residue was dissolved in dichloromethane (25 mL). Diethyl ether (110 mL) was then added to obtain a solution that was kept overnight in a refrigerator to produce pale-yellow crystals of **3a**. Yield: 1.04 g, 50%. ^{1}H NMR (200.1 MHz, CD_2Cl_2): δ = 1.26 (s, 9 H, CMe_3), 1.81 (d, $^4J_{P,H}$ = 1.5 Hz, 15 H, C_5Me_5), 2.90 (s, 3 H, =CMe), 6.22 (d, $^2J_{P,H}$ = 5.0 Hz, 1 H, PCH=), 7.19–7.30 (m, 2 H, Ph), 7.62–7.64 (m, 8 H, Ph) ppm. ^{13}C{^{1}H} NMR (50.3 MHz, CD_2Cl_2): δ = 10.2 (s, C_5Me_5), 27.5 (s, CMe_3), 38.3 (d, ^3J = 5.8 Hz, CMe_3), 46.3 (s, =C*Me*), 98.4 (d, ^1J = 60.5 Hz, PCH=), 105.1 (s, C_5Me_5), 129.1 (part of d, Ph, *ipso*), 130.0 (d, ^2J = 10.9 Hz, Ph, *ortho*), 130.0 (d, ^2J = 11.0 Hz, Ph, *ortho*, likely overlapping the second part of d, Ph, *ipso*), 131.2 (d, ^3J = 11.1 Hz, Ph, *meta*), 131.2 (d, ^1J = 60.0 Hz, Ph, *ipso*), 132.4 (d, ^4J = 2.5 Hz, Ph, *para*), 132.9 (d, partially overlapped, Ph, *meta*), 133.0 (d, partially overlapped, Ph, *para*), 177.2 (s, O*C*=CH), 202.1 (d, ^2J = 15.0 Hz, C≡O), 312.3 (d, ^2J = 15.7 Hz, Ru=C) ppm. ^{31}P{^{1}H} NMR (81.0 MHz, CD_2Cl_2): δ = 37.2 (s) ppm. $C_{31}H_{38}F_6O_2P_2Ru$ (719.65): calcd. C 51.74, H 5.32, P 8.61; found C 51.63, H 5.27, P 8.60.

{Ru(Cp*)[η²-*C,P*-:C(CH_2Ph)OC(tBu)=CH–PPh_2](CO)}[PF_6] (3c): To a solution of **1** (3.01 g, 4.34 mmol) in dichloromethane (40 mL) was added phenylacetylene (1.00 mL, 9.11 mmol, excess), and this mixture was stirred for 5 d at room temperature. The resulting dark solution was evaporated to leave a sticky residue. On standing for 5 d, yellow crystals formed. Methanol (15 mL) was added, and the mixture was shaken for 5 min to obtain a crystalline yellow precipitate that was collected by filtration, then washed with diethyl ether (30 mL) and dried under vacuum. Analysis of the product by ^{1}H NMR spectroscopy disclosed a mixture of **3c** (83%) and **5c** (17%). Overall yield: 2.28 g, 66%. Data for **3c**: ^{1}H NMR (200.1 MHz, CD_2Cl_2): δ = 0.90 (s, 9 H, CMe_3), 1.86 (d, $^4J_{P,H}$ = 1.5 Hz, 15 H, C_5Me_5), 4.31 (d, $^2J_{H,H}$ = 17.0 Hz, 1 H, CH_2Ph), 4.59 (d, $^2J_{H,H}$ = 17.0 Hz, 1 H, CH_2Ph), 6.17 (d, $^2J_{P,H}$ = 5.1 Hz, 1 H, PCH=), 6.99–7.04 (m, 2 H, Ph), 7.26–7.70 (m, 13 H, Ph) ppm. ^{13}C{^{1}H} NMR (50.3 MHz, CD_2Cl_2): δ = 10.3 (s, C_5Me_5), 27.1 (s, CMe_3), 38.3 (d, ^3J = 6.9 Hz, CMe_3), 65.2 (s, CH_2Ph), 98.3 (d, ^1J = 60.4 Hz, PCH=), 105.3 (d, ^2J = 1.7 Hz, C_5Me_5), 127.8 (s, Ph, *para*), 129.1 (s, Ph, *ortho* or *meta*), 129.6 (s, Ph, *ortho* or *meta*), 130.1 (d, ^2J = 11.6 Hz, PhP, *ortho*), 130.1 (d, ^2J = 11.6 Hz, PhP, *ortho*), 130.7 (d, ^1J = 57.7 Hz, PhP, *ipso*), 131.1 (d, ^1J = 60.2 Hz, PhP, *ipso*), 131.3 (d, ^3J = 11.2 Hz, PhP, *meta*), 132.5 (d, ^4J = 2.3 Hz, PhP, *para*), 133.1 (d, ^3J = 13.5 Hz, PhP, *meta*), 133.2 (d, ^4J = 2.5 Hz, PhP, *para*), 135.2 (s, Ph, *ipso*), 177.3 (d, ^2J = 1.7 Hz, O*C*tBu), 202.1 (d, ^2J = 14.0 Hz, C≡O), 310.6 (d, ^2J = 16.0 Hz, Ru=C) ppm. ^{31}P{^{1}H} NMR (81.0 MHz, CD_2Cl_2): δ = 36.8 (s) ppm.

Ru(C≡CtBu)(Cp*)[$Ph_2PCH_2C(=O)t$Bu](CO) (4): A mixture consisting of **1** (2.00 g, 2.88 mmol), $KHCO_3$ (1.00 g, 10.0 mmol), *tert*-butylacetylene (1.20 mL, 9.74 mmol, excess) and dichloromethane (35 mL) was stirred for 3 d at room temperature. The slurry was then evaporated to dryness to afford a solid that was extracted with dichloromethane (30 mL). The solution was filtered, and the yellow filtrate was evaporated under vacuum to yield crude product **4**, which was dissolved in hexane (5 mL). A light-yellow crystalline solid was obtained upon cooling the solution in a refrigerator. Yield: 1.50 g, 83%. ^{1}H NMR (200.1 MHz, CD_2Cl_2): δ = 0.91 (s, 9 H, CMe_3), 1.37 (s, 9 H, CMe_3), 1.63 (d, $^4J_{P,H}$ = 1.8 Hz, 15 H,

C_5Me_5), 4.07 (dd, $^2J_{H,H}$ = 16.3 Hz, $^2J_{P,H}$ = 7.2 Hz, 1 H, PCH_2), 4.18 (dd, $^2J_{H,H}$ = 16.5 Hz, $^2J_{P,H}$ = 8.8 Hz, 1 H, PCH_2), 7.42–7.50 (m, 6 H, Ph), 7.77–7.97 (m, 4 H, Ph) ppm. $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2): δ = 9.9 (s, C_5Me_5), 26.0 (s, CMe_3), 29.9 (s, CMe_3), 33.5 (s, CMe_3), 40.2 (d, ^1J = 28.2 Hz, PCH_2), 45.6 (s, CMe_3), 92.6 (d, ^2J = 22.9 Hz, Ru*C*≡C), 97.2 (d, ^2J = 2.7 Hz, C_5Me_5), 116.6 (s, RuC≡*C*), 134.7 (d, ^1J = 45.1 Hz, P*Ph*, *ipso*), 134.0 (d, ^1J = 41.0 Hz, P*Ph*, *ipso*), 133.9 (d, ^2J = 10.9 Hz, PPh_2, *ortho*), 130.2 (d, ^4J = 2.6 Hz, P*Ph*, *para*), 130.1 (d, ^4J = 2.8 Hz, P*Ph*, *para*), 128.1 (d, ^3J = 9.5 Hz, P*Ph*, *meta*), 127.8 (d, ^3J = 9.7 Hz, P*Ph*, *meta*), 207.6 (d, ^2J = 19.5 Hz, C≡O), 210.4 (d, ^2J = 8.5 Hz, C=O) ppm. $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2): δ = 48.39 (s) ppm. $C_{35}H_{45}O_2PRu$ (629.79): calcd. C 66.75, H 7.20; found C 66.75, H 7.32.

Detection of {Ru(:C=CH*t*Bu)(Cp*)[Ph_2PCH_2C(=O)*t*Bu](CO)}-[PF_6]: A solution of **1** (0.05 g, 0.07 mmol) and 3,3-dimethyl-1-butyne (0.20 mL, 1.62 mmol, large excess) in CD_2Cl_2 (0.50 mL) was kept at room temperature for 24 h and then examined by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum showed a new resonance at δ = 38.6 ppm besides a major resonance located at δ = 66.5 ppm, as expected for the presence of unreacted **1**. The ^1H NMR spectrum confirmed a 3:2 mixture of **1** and a new species, for which the observed distinct resonances suggest a vinylidene ruthenium complex. ^1H NMR (200 MHz, CD_2Cl_2): δ = 1.01 (s, 9 H, CMe_3), 1.29 (s, 9 H, CMe_3), 1.75 (d, $^4J_{P,H}$ = 1.7 Hz, 15 H, C_5Me_5), 3.98 (d, $^2J_{P,H}$ = 9.3 Hz, 2 H, PCH_2), 5.35 (d, $^4J_{P,H}$ = 3.5 Hz, 1 H, =C*H*tBu) ppm.

{Ru(Cp*)[η³-*C*,*C*,*P*-(Ph)CH=C(H)-O-C(*t*Bu)=CH–PPh_2](CO)}-[PF_6] (5c): To a solution of **1** (3.00 g, 4.32 mmol) in dichloromethane (40 mL) was added phenylacetylene (0.60 mL, 5.46 mmol, excess), and the mixture was stirred for 3 d at room temperature. The brown solution was then heated at reflux for 24 h and then evaporated under vacuum. The residue (which disclosed a single resonance at δ = 41.8 ppm by $^{31}P\{^1H\}$ NMR spectroscopy) was dissolved in dichloromethane (30 mL), and the solution was covered with methanol (10 mL) then diethyl ether (110 mL) to afford thin pale-yellow needles of **5c**. Yield: 2.13 g, 62%. ^1H NMR (200.1 MHz, CD_2Cl_2): δ = 1.20 (s, 9 H, *t*Bu), 1.55 (d, $^4J_{P,H}$ = 1.8 Hz, 15 H, C_5Me_5), 3.76 (d, $^3J_{H,H}$ = 5.3 Hz, 1 H, =C*H*Ph), 5.56 (dd, $^3J_{P,H}$ = 21.7 Hz, $^3J_{H,H}$ = 5.4 Hz, 1 H, OCH=), 5.79 (d, $^2J_{P,H}$ = 5.1 Hz, 1 H, PCH=), 7.21–7.32 (m, 2 H, Ph), 7.44–7.69 (m, 13 H, Ph) ppm. $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2): δ = 9.6 (s, C_5Me_5), 28.1 (s, CMe_3), 38.0 (d, ^3J = 6.6 Hz, CMe_3), 63.0 (s, *C*HPh), 92.1 (d, ^2J = 10.4 Hz, O*C*H=CH), 94.3 (d, ^1J = 61.8 Hz, PCH=), 103.1 (s, C_5Me_5), 127.6–134.8 (m, Ph), 180.2 (s, O*C*tBu), 200.1 (d, ^2J = 16.6 Hz, C≡O) ppm. $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2): δ = 41.8 (s) ppm. $C_{37}H_{42}F_6O_2P_2Ru$ (795.75): calcd. C 55.85, H 5.32, P 7.78; found C 55.58, H 5.31, P 7.82.

{Ru(Cp*)[η³-*C*,*C*,*P*-(*p*-MeC_6H_4)CH=C(H)-O-C(*t*Bu)=CH–PPh_2]-(CO)}[PF_6] (5d): To a solution of **1** (2.00 g, 2.88 mmol) in dichloromethane (35 mL) was added *p*-tolylacetylene (0.60 mL, 4.73 mmol, excess), and the mixture was stirred for 24 h at room temperature. The brown solution was then heated at reflux for 24 h and then evaporated under vacuum. The residue was dissolved in dichloromethane (25 mL), and the solution was covered with methanol (10 mL) then diethyl ether (110 mL) to afford large pale-yellow needles of **5d**. Yield: 1.58 g, 69%. ^1H NMR (200.1 MHz, CD_2Cl_2): δ = 1.20 (s, 9 H, *t*Bu), 1.54 (d, $^4J_{P,H}$ = 1.8 Hz, 15 H, C_5Me_5), 2.43 (s, 3 H, Me), 3.72 (d, $^3J_{H,H}$ = 5.3 Hz, 1 H, =C*H*C_6H_4Me), 5.50 (dd, $^3J_{P,H}$ = 21.7 Hz, $^3J_{H,H}$ = 5.4 Hz, 1 H, OCH=), 5.78 (d, $^2J_{P,H}$ = 5.1 Hz, 1 H, PCH=), 7.20–7.30 (m, 4 H, Ph and C_6H_4), 7.46 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, C_6H_4), 7.61–7.69 (m, 8 H, Ph) ppm. $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2): δ = 9.6 (s, C_5Me_5), 21.4 (s, MeC_6H_4), 28.1 (s, CMe_3), 38.0 (d, ^3J = 7.8 Hz, CMe_3), 63.5 (s, =*C*HC_6H_4), 91.6 (d, ^2J = 10.1 Hz, O*C*H=CH), 94.1 (d, ^1J = 61.8 Hz, PCH=), 102.9 (s, C_5Me_5), 128.2 (d, ^1J = 56.4 Hz, P*Ph*, *ipso*), 129.3 (s,C_6H_4), 129.8 (d, ^2J = 11.1 Hz, P*Ph*, *ortho*), 130.3 (d, ^2J = 10.8 Hz, P*Ph*, *ortho*), 131.1 (s,C_6H_4), 131.5 (s,C_6H_4, *C*Me), 131.8 (d, ^3J = 9.5 Hz, P*Ph*, *meta*), 132.1 (d, ^4J = 2.4 Hz, P*Ph*, *para*), 132.8 (d, ^4J = 2.5 Hz, P*Ph*, *para*), 133.9 (d, ^1J = 54.8 Hz, P*Ph*, *ipso*), 134.1 (d, ^3J = 10.8 Hz, P*Ph*, *meta*), 139.1 (s,C_6H_4, *C*CH=), 180.1 (s, O*C*tBu), 200.1 (d, ^2J = 16.4 Hz, C≡O) ppm. $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2): δ = 41.8 (s) ppm. $C_{38}H_{44}F_6O_2P_2Ru$ (809.78): calcd. C 56.36, H 5.48, P 7.65; found C 56.12, H 5.44, P 7.67.

Crystal Data for 5d: $C_{38}H_{44}F_6O_2P_2Ru$, M = 809.74, crystal size 0.33 × 0.25 × 0.25 mm, triclinic, space group $P\bar{1}$, Z = 2, a = 8.8280(4) Å, b = 11.6433(5) Å, c = 19.3792(8) Å, α = 74.290(4)°, β = 84.265(4)°, γ = 83.764(4)°, U = 1901.0(1) Å^3, $D_{calcd.}$ = 1.415 g cm^{-3}, T = 295(2) K, $F(000)$ = 832, Mo-K_α radiation (λ = 0.71073 Å), μ = 0.557 mm^{-1}, 13868 reflections measured in the range 2.79 ≤ θ ≤ 27.00°, 7976 unique (R_{int} = 0.02%), which were used in all calculations. The structure was refined by using full-matrix least-squares on F^2 to R_1 = 0.036, wR_2 = 0.103, S = 0.960, for 6787 reflections (>2σ) and 449 refined parameters, R_1(all data) = 0.044, wR_2(all data) = 0.106, goodness-of-fit on F^2 = 1.080. The samples were studied with an Oxford Diffraction Xcalibur Saphir 3 diffractometer with graphite monochromator. The data collection ($2\theta_{max}$ = 54°, omega scan frames via 1.0° ω rotation and 5 s per frame, index ranges –11 < h < 6, –14 < k < 14, –24 < l < 24) gave 13868 reflections. Data reduction was carried out with CrysAlis RED[19] and led to 7976 independent reflections, from which 6787 had I > 2σ(I). The structure was solved with SIR-97, which revealed the non-hydrogen atoms.[20] After anisotropic refinement, many hydrogen atoms may be found with Fourier difference calculations. The whole structure was refined with SHELXL97 by full-matrix least-squares methods on F^2 [x, y, z, β_{ij} for Ru, P, F, C and O atoms; x, y, z in riding mode for H atoms]; w = 1/[σ^2(F_o^2) + (0.0690P)^2 + 0.3554P], where P = (F_o^2 + 2F_c^2)/3 with the resulting R = 0.044, wR = 0.106 and S = 0.960; minimum and maximum final electron density: –0.565 and 0.703 e Å^{-3}.[21] ORTEP views were prepared with PLATON98.[22] CCDC-612929 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[1] M. I. Bruce, *Chem. Rev.* **1991**, *91*, 197–257.
[2] M. C. Puerta, P. Valerga, *Coord. Chem. Rev.* **1999**, *193–195*, 977–1025.
[3] F. De Angelis, A. Sgamellotti, N. Re, *Dalton Trans.* **2004**, 3225–3230.
[4] I. de Los Rios, M. Jiménez-Tenorio, M. C. Puerta, P. Valerga, *J. Am. Chem. Soc.* **1997**, *119*, 6529–6538.
[5] E. Bustelo, J. J. Carbó, A. Lledós, K. Mereiter, M. C. Puerta, P. Valerga, *J. Am. Chem. Soc.* **2003**, *125*, 3311–3321.
[6] H. Aneetha, M. Jiménez-Tenorio, M. C. Puerta, P. Valerga, K. Mereiter, *Organometallics* **2003**, *22*, 2001–2013.
[7] M. Jiménez-Tenorio, M. D. Palacios, M. C. Puerta, P. Valerga, *Organometallics* **2004**, *23*, 504–510, and references therein.
[8] M. P. Gamasa, J. Gimeno, C. González-Bernardo, J. Borge, S. García-Granda, *Organometallics* **1997**, *16*, 2483–2485.
[9] V. Cadierno, M. P. Gamasa, J. Gimeno, C. González-Bernardo, E. Pérez-Carreño, S. García-Granda, *Organometallics* **2001**, *20*, 5177–5188.
[10] P. Nombel, N. Lugan, R. Mathieu, *J. Organomet. Chem.* **1995**, *503*, C22–C25, and references therein.

[11] B. Demerseman, L. Toupet, *Eur. J. Inorg. Chem.* **2006**, 1573–1581.
[12] B. Demerseman, J.-L. Renaud, L. Toupet, C. Hubert, C. Bruneau, *Eur. J. Inorg. Chem.* **2006**, 1371–1380.
[13] P. T. Czech, X.-Q. Ye, R. F. Fenske, *Organometallics* **1990**, *9*, 2016–2022.
[14] M. I. Bruce, A. G. Swincer, *Aust. J. Chem.* **1980**, *33*, 1471–1483.
[15] R. Le Lagadec, E. Roman, L. Toupet, U. Müller, P. H. Dixneuf, *Organometallics* **1994**, *13*, 5030–5039.
[16] K. M. McWilliams, A. Ellern, R. J. Angelici, *Organometallics* **2007**, *26*, 1665–1673.
[17] J. N. Coalter III, G. J. Spivak, H. Gérard, E. Clot, E. R. Davidson, O. Eisenstein, K. G. Caulton, *J. Am. Chem. Soc.* **1998**, *120*, 9388–9839.
[18] J. N. Coalter III, J. C. Bollinger, J. C. Huffman, U. Werner-Zwanziger, K. G. Caulton, E. R. Davidson, H. Gérard, E. Clot, O. Eisenstein, *New J. Chem.* **2000**, *24*, 9–26.
[19] Oxford Diffraction Ltd., Abingdon, Oxfordshire, UK, **2004**.
[20] *SIR-97: A New Tool for Crystal Structure Determination and Refinement*: A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1998**, *31*, 74–77.
[21] G. M. Sheldrick, *SHELXL97: Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.
[22] A. L. Spek, *PLATON: A Multipurpose Crystallographic Tool*, University of Utrecht, The Netherlands, **1998**.

Received: June 23, 2009
Published Online: August 24, 2009

