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Synthesis and reactivity of neutral vinylidene and σ-alkynyl complexes containing the hemilabile ligand $Ph_2PCH_2CH_2OMe$☆ Part 16. Ruthenium tris(pyrazolyl)borate complexes

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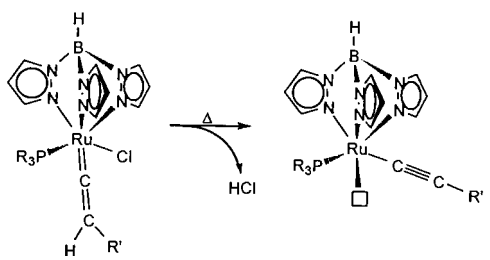
Abstract

RuTp(COD)Cl reacts readily with $Ph_2PCH_2CH_2OMe$ to give the neutral complex RuTp(κ^2(P,O)-$Ph_2PCH_2CH_2OMe$)Cl (**2**) which transforms with terminal alkynes HC≡CR (R = Ph, *n*-Bu, C_6H_9) and carbon monoxide, respectively, into the neutral vinylidene complexes RuTp(κ^1(P)-$Ph_2PCH_2CH_2OMe$)(Cl)(=C=CHR) (**3a–c**) and RuTp(κ^1(P)-$Ph_2PCH_2CH_2OMe$)(Cl)(CO) (**4**). The κ^1(P) bonding mode of the phosphinoether testifies to its hemilabile nature. Complex **3a** reacts with lithium diisopropylamide to give the neutral α-acetylide complex RuTp(κ^2(P,O)-$Ph_2PCH_2CH_2OMe$)(–C≡CPh) (**5**) which couples with stoichiometric amounts of HC≡CPh to give RuTp(κ^1(P)-$Ph_2PCH_2CH_2OMe$)(C(Ph)=CHC≡CPh) (**6**), featuring a σ,η^2-bound enynyl ligand. Treatment of **3a** with $AgCF_3SO_3$ affords the cationic vinylidene complex [RuTp(κ^2(P,O)-$Ph_2PCH_2CH_2OMe$)(=C=CHPh)]CF_3SO_3 (**7**). Complex **5** is found to catalyze the dimerization of HC≡CR (R=Ph, $SiMe_3$, *n*-Bu, *t*-Bu, C_6H_9) to give enynes. The structures of **3a**, **4**, **5** and **7** have been determined by X-ray crystallography.

Keywords: Ruthenium; Hydrido-trispyrazolylborate; Vinylidene complexes; Alkynyl complexes; Enynes; Catalysis

1. Introduction

We have shown recently [2] that highly reactive 16 electron alkynyl species can be generated in situ from vinylidene complexes of the type RuTp(PR_3)(Cl)(=C=CHR′) (Tp = hydrido trispyrazolylborate) via HCl elimination at higher temperatures (Scheme 1).



Scheme 1.

These unsaturated σ-acetylide species are able to catalytically dimerize terminal alkynes to give enynes. In order to facilitate HCl elimination we have utilized RuTp(κ^2(P,N)-$Ph_2PCH_2CH_2NMe_2$)Cl as the catalyst precursor [3]. What we expected was facile Ru–N bond cleavage with the formation of the vinylidene complex RuTp(κ^1(P)-$PPh_2CH_2CH_2NMe_2$)(Cl)(=C=CHR) followed by intramolecular deprotonation by the pendant basic $CH_2CH_2NMe_2$ moiety to afford the 16 electron σ-alkynyl complex (RuTp(κ^1(P)-$PPh_2CH_2CH_2NHMe_2$)(–C≡CR)]Cl. Phosphinoamine ligands are in fact often hemilabile promoting the formation of vinylidene complexes [4] However, the crucial step in forming the vinylidene complex RuTp(κ^1(P)-$PPh_2CH_2CH_2NMe_2$)(Cl)(=C=CHR) turned out to be the opening of the κ^2(P,N) chelate, which requires relatively high temperatures. Although this is somewhat alleviated by in-

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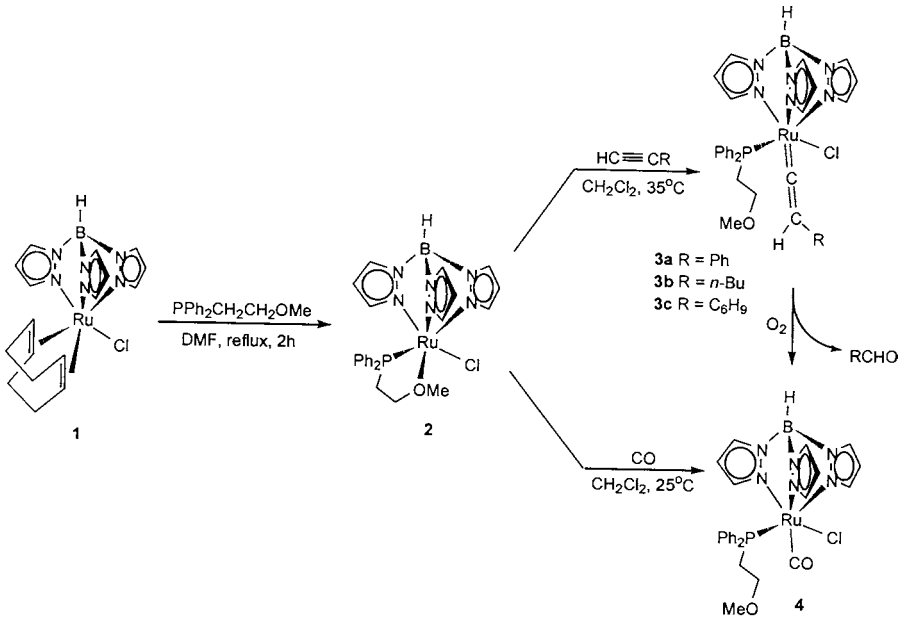


Scheme 2.

creasing the steric demand of the N-donor site, e.g. by replacing NMe_2 with NEt_2, or even N*i*-Pr_2, these species are catalytically inactive initiating instead an unusual C–C coupling [5].

In the present contribution we report on the synthesis and reactivity of some neutral RuTp vinylidene and σ-alkynyl complexes upon utilizing the phosphinoether $Ph_2PCH_2CH_2OMe$ in place of phosphinoamines. We will demonstrate that in these RuTp complexes the Ru–O bond is very much weaker than the Ru–P as well as Ru–N bonds [6]. Accordingly, Ru–O bond cleavage is already achieved at room temperature. X-ray structures of representative complexes are presented.

2. Results and discussion

2.1. Synthesis and characterization of vinylidene, alkynyl, and enynyl complexes

RuTp(COD)Cl (**1**) reacts readily in boiling dmf with the phosphinoether $Ph_2PCH_2CH_2OMe$ to give, on workup, the neutral complex RuTp(κ^2(P,O)-$Ph_2PCH_2CH_2OMe$)Cl (**2**) in 78% isolated yield as an air stable yellow solid (Scheme 2). This compound was characterized by ^{1}H-, ^{13}C{^{1}H}- and ^{31}P{^{1}H}-NMR spectroscopy as well as by elemental analysis. The κ^2(P,O) bonding fashion of the phosphinoether is revealed in the ^{1}H- and ^{13}C{^{1}H}-solution NMR spectra through three distinct sets of pyrazol-1-yl resonances in a 1:1:1 ratio. This points to three distinct pyrazol-1-yl rings differing by their *trans* ligand atoms.

Treatment of **2** with HC≡CR (R=Ph, *n*-Bu, C_6H_9) at 35°C results in the formation of the vinylidene complexes RuTp(κ^1(P)-$Ph_2PCH_2CH_2OMe$)(Cl)(=C=CHR) (**3a**–**c**) in high yields (Scheme 2). In these complexes, the $Ph_2PCH_2CH_2OMe$ ligand is coordinated in κ^1(P) fashion. This is not unexpected since the Ru–O bond in **2** is considerably weaker than the Ru–P bond. The complexes **3a**–**c** are air stable in the solid state and have again been characterized by elemental analysis and by ^{1}H-, ^{13}C{^{1}H}- and ^{31}P{^{1}H}-NMR spectroscopy. Characteristic features comprise, in the ^{13}C{^{1}H}-NMR spectrum, a marked low-field resonance in the range of 372.4–362.6 ppm (d, $J_{CP} = 19$–18 Hz) assignable to the α-carbon of the vinylidene moiety. The C_β atom displays a doublet resonance centered at 112.2, 126.7 and 106.1 ppm, with J_{CP} coupling constants of 1.7–1.4 Hz. Further, the C_β, hydrogen atom shows a doublet centered at 4.95 ($J_{CP} = 4.3$ Hz), 4.58 ($J_{CP} = 4.4$ Hz) and 4.07 ppm ($J_{CP} = 3.9$ Hz). The ^{31}P{^{1}H}-NMR resonances are observed at 27.2, 28.0 and 29.5 ppm. Finally, the ^{1}H- and ^{13}C{^{1}H}-NMR resonances of Tp and $Ph_2PCH_2CH_2OMe$ are in the expected ranges.

A structural view of **3a** is depicted in Fig. 1 with selected bond distances and angles given in Table 1. The coordination geometry of **3a** is approximately octahedral with all angles at ruthenium between 82 and 99° and 176 and 178°, There are no structural features pointing to unusual deviations or distortions. The $Ph_2PCH_2CH_2OMe$ ligand is κ^1(P) coordinated with a Ru–P bond distance of 2.34 Å. The two Ru–N(Tp) bond lengths *cis* to vinylidene are significantly shorter (Ru–N(2) = 2.10 Å, RuN(4) = 2.14 Å) than that *trans* to vinylidene (Ru–N(6) = 2.21 Å). Clearly, vinylidene is a strongly π-accepting ligand giving rise to an appreciable *trans* influence. The Ru–C(25) bond distance is 1.82 Å comparable to other neutral RuTp vinylidene com-

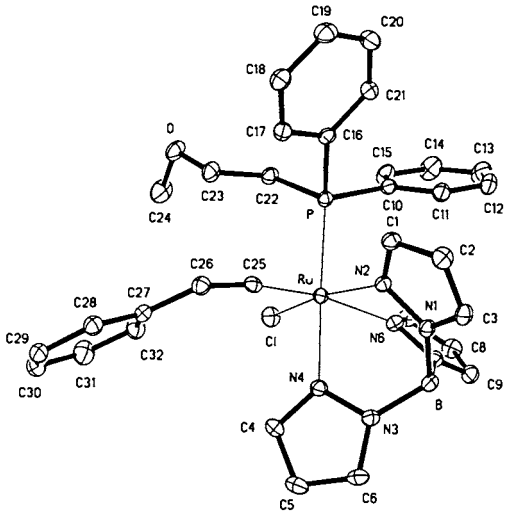


Fig. 1. Structural view of RuTp(κ¹(P)-$Ph_2PCH_2CH_2OMe$)-(=C=CHPh)Cl (**3a**) showing 20% thermal ellipsoids.

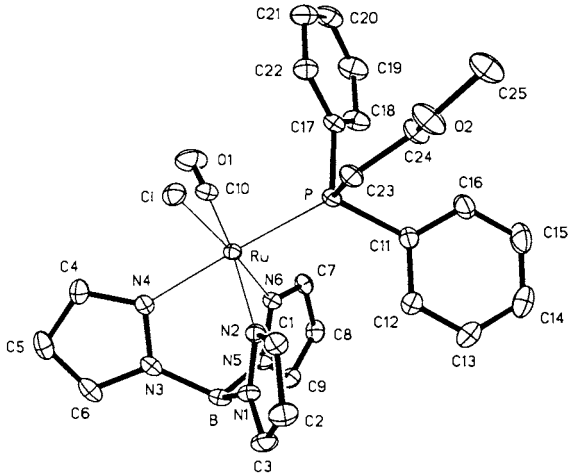


Fig. 2. Structural view of RuTp(κ¹(P)-$Ph_2PCH_2CH_2OMe$)(CO)Cl (**4**) showing 20% thermal ellipsoids.

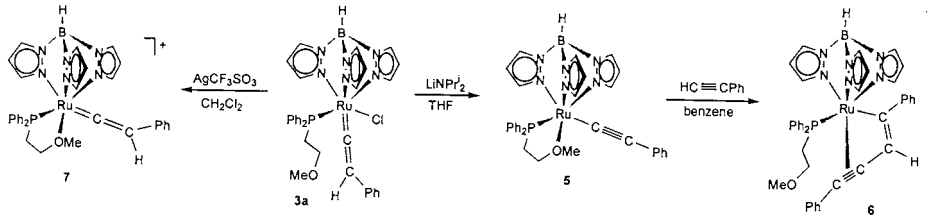
plexes but somewhat shorter than in cationic RuTp vinylidene complexes. For instance, in RuTp(PPh_3)(Cl)-(=C=CHPh) the Ru–C bond distance is 1.801(4) Å [2a], while in [RuTp($Me_2NCH_2CH_2NMe_2$)(=C=CHPh)]$^+$, [RuTp($Ph_2PCH_2CH_2NMe_2$)(=C=CHPh)]$^+$ and [RuTp-(PEt_3)$_2$(=C=CHPh)]$^+$, the Ru–C distances are 1.820 (5), 1.821(5) and 1.81(1) Å, respectively [7,8]. The Ru=C=C group is slightly bent with a Ru–C(25)–C(26) angle of 170°. The C(25)–C(26) bond distance is 1.31 Å corresponding to a bond order between two and three.

The hemilabile nature of the $Ph_2PCH_2CH_2OMe$ ligand is also revealed by the reaction of **2** with carbon monoxide. Thus, when **2** is stirred under an CO atmosphere for 1 h at ambient temperature, the Ru–O bond is cleaved to afford the neutral complex RuTp(κ¹(P)-$Ph_2PCH_2CH_2OMe$)(Cl)(CO) (**4**) in 92% isolated yield (Scheme 2). It is noteworthy that the same complex is formed by the reaction of **3a** with O_2 via an oxidative cleavage of the C=C bond as also shown in Scheme 2 [9]. The identity of **4** was proven by a combination of elemental analysis, ^{1}H-, ^{13}C{^{1}H}- and ^{31}P{^{1}H}-NMR spectroscopy. In the ^{13}C{^{1}H}-NMR spectrum, the CO ligand exhibits a characteristic low-intensity doublet centered at 203.7 ppm ($J_{CP} = 16.0$ Hz). A structural view of **4** is depicted in Fig. 2 with selected structural data reported in Table 1. The overall octahedral structure of **4** is very similar to that of **3a**. While the Ru–N(2) and Ru–N(4) distances are relatively similar (2.157(1) and 2.130(1) Å), Ru–N(6) *trans* to chloride is significantly shorter with 2.073(1) Å. The Ru–Cl and

Table 1
Selected bond distances (Å) and angles (°) for complexes **3a**, **4**, **5** and **7**·CH_2Cl_2

	3a [a] complex **1**	**3a** [a] complex **2**	**4**	**5**	**7**·CH_2Cl_2
Ru–N(2)	2.093(2)	2.111(3)	2.157(1)	2.164(2)	2.144(3)
Ru–N(4)	2.146(2)	2.132(3)	2.130(1)	2.025(2)	2.046(3)
Ru–N(6)	2.204(2)	2.214(3)	2.073(1)	2.138(2)	2.166(2)
Ru–P	2.330(1)	2.343(1)	2.331(1)	2.235(1)	2.307(1)
Ru–Cl	2.403(1)	2.398(1)	2.412(1)		
Ru–C(25)	1.810(3)	1.821(3)		2.004(3)	1.838(4)
Ru–C(10)			1.868(2)		
Ru–O				2.202(2)	2.156(2)
C(25)–C(26)	1.316(4)	1.310(4)		1.200(4)	1.286(5)
N(2)–Ru–N(4)	85.7(1)	86.6(1)	82.4(1)	84.2(1)	84.7(1)
N(2)–Ru–N(6)	85.1(1)	84.0(1)	88.4(1)	83.9(1)	84.4(1)
N(4)–Ru–N(6)	82.9(1)	82.5(1)	86.2(1)	89.6(1)	88.1(1)
Ru–C(25)–C(26)	170.8(2)	168.8(3)		175.1(2)	170.4(3)

[a] **3a** contains two independent Ru complexes of analogous ligand disposition but with differing orientations of vinylidene phenyl rings (*syn* and *anti* relative to Ru–Cl bond) and P-bound $C_2H_4OCH_3$ groups.



Scheme 3.

Ru–P distances are 2.412(1) and 2.331(2) Å, respectively. The Ru–C(10) distance is 1.868(2) Å.

Complex **3a** reacts with lithium diisopropylamide in THF to give the neutral alkynyl complex RuTp(κ^2(P,O)-$Ph_2PCH_2CH_2OMe$)(–C≡CPh) (**5**) in 61% isolated yield (Scheme 3). This complex is air stable in the solid state but decomposes in solution on exposure to air. Complex **5** has been characterized by ^{1}H-, ^{13}C{^{1}H}- and ^{31}P{^{1}H}-NMR spectroscopy and elemental analysis. Characteristic NMR spectroscopic features comprise, in the ^{13}C{^{1}H}-NMR spectrum resonances at 110.7 and 105.9 ppm assignable to the α- and β-carbon of the alkynyl moiety. These figures are comparable to those of other ruthenium σ-alkynyl complexes [10]. In the ^{31}P{^{1}H}-NMR the phosphorus atom of the κ^2(P,O)-coordinated phosphinoether displays a singlet at 66.6 ppm (cf. 27.2 ppm in **3a** where the $Ph_2PCH_2CH_2OMe$ ligand is κ^1(P)-coordinated). All other resonances are inconspicuous. The solid state structure of **5** has been determined by single-crystal X-ray diffraction. An ORTEP diagram is depicted in Fig. 3 with selected bond distances and angles reported in Table 1. The overall octahedral structure of **5** is very similar to those of **3a** and **4**. The two Ru–N(Tp) bond distances *trans* to the OMe moiety is significantly shorter (Ru–N(4) = 2.025(2) Å) than the one *trans* to the phosphine and alkynyl moieties (Ru–N(2) = 2.164(2), Ru–N(6) = 2.138(2) Å). The Ru–P and Ru–O bond lengths are 2.235(1) and 2.202(2) Å), respectively. The Ru–C(25) bond distance (2.004(4) Å) is in the range of other σ-alkynyl complexes [11]. The Ru–C≡C group is virtually linear (Ru–C(25)–C(26) = 175.1(2)°). The C(25)–C(26) bond distance is 1.200(4) Å corresponding to a bond order of three.

Complex **5** reacts readily with stoichiometric amounts of HC≡CPh in benzene to give the alkyne coupling product RuTp(κ^1(P)-$Ph_2PCH_2CH_2OMe$)-(–C(Ph)=CHC≡CPh) (**6**) featuring an E-1,4-enynyl ligand in 66% yield (Scheme 3). This orange complex is air stable and is very soluble in polar as well as non-polar solvents. Thus, all efforts to obtain single crystals suitable for X-ray structure analysis where unsuccessful and **6** was characterized by ^{1}H-, ^{13}C{^{1}H}- and ^{31}P{^{1}H}-NMR spectroscopy and elemental analysis. The σ-bound quaternary vinyl carbon of the enynyl ligand appears as a doublet centered at 184.1 ppm (J_{CP} = 12.2 Hz) whereas the tertiary β-vinyl carbon is observed at 135.6 ppm. Quite unusual is the high-field resonance of the two sp carbon atoms of the enynyl moiety observed at 69.3 and 70.5 ppm. This strongly suggests that the enynyl ligand is, in addition to its Ru–C single bond, also η^2-coordinated via its C≡C triple bond thus leaving the phosphino ether ligand κ^1(P) coordinated. For comparison, the vinylic and acetylenic carbon atoms of σ,η^2-bound enynyl in RuTp(P*i*-Pr_2Me)(–C(Ph)=C(Ph)–C≡CR) (R = Ph, *t*-Bu) appear at ca. 180 and 137 ppm and 60–75 ppm, respectively, while the corresponding resonances of σ-bound enynyl in RuCp*(PPh_3)(CO)(–C(Me)=CMe–C≡C*t*-Bu) are found at 166.5 and 120.0 ppm and 92.0 and 89.8 ppm [12]. Also the ^{1}H- and ^{13}C{^{1}H}-NMR resonances of the OMe functionality have a bearing on the coordination mode of the $Ph_2PCH_2CH_2OMe$ ligand. Thus, the resonances of the Me group at about 3.2 and 59 ppm for κ^1(P) coordination (in **3a**–**c** and **4**) are shifted downfield to about 3.4 and 65 ppm for the κ^1(P,O) coordination mode (in **2**, **5** and **7**). Therefore, the resonances found for **6** at 2.91 and 58.1 ppm point to κ^1(P) coordination (Scheme 3). On the other hand, a Z-ar-

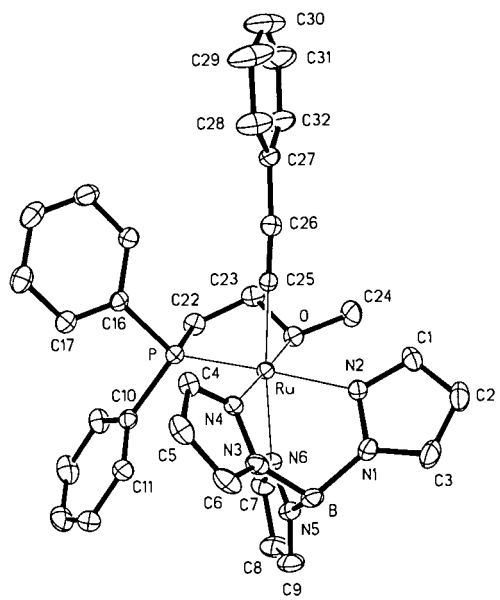


Fig. 3. Structural view of RuTp(κ^2(P,O)-$Ph_2PCH_2CH_2OMe$)-(–C≡CPh) (**5**) showing 20% thermal ellipsoids.

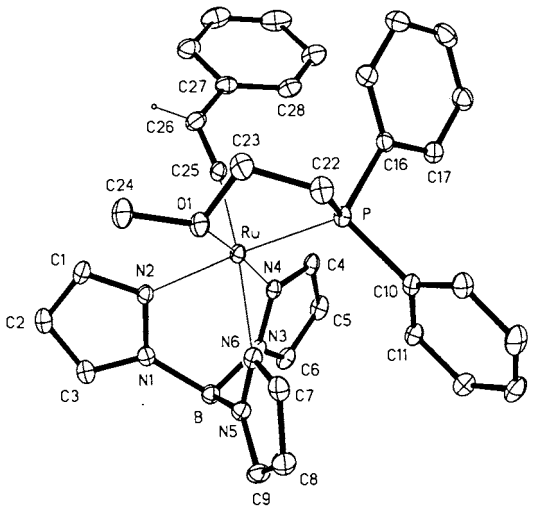
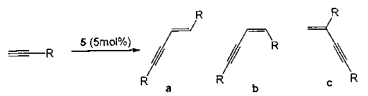


Fig. 4. Structural view of [RuTp(κ²(P,O)-$Ph_2PCH_2CH_2OMe$)-(=C=CHPh)]$CF_3SO_3 \cdot CH_2Cl_2$ (**7**·CH_2Cl_2) showing 20% thermal ellipsoids ($CF_3SO_3^-$ and CH_2Cl_2 omitted for clarity).

Table 2
Conversion and product distribution of the catalytic dimerization of terminal alkynes [a]



R	% conversion [b]	% **a**	% **b**	% **c**
Ph	88	84	4	
$SiMe_3$	98		88	12
n-Bu	97	31	23	43
t-Bu	12		99	
C_6H_9	89	73	27	

[a] Reactions were performed in boiling benzene or benzene-d_6 for 40 h.

[b] Yields are for isolated products. Product distribution has been determined by ^{1}H-NMR spectroscopy.

rangement of the enynyl moiety can be ruled out. In this case one would expect either a β-agostic interaction with the enynyl ligand or κ²(P,O) coordination of $Ph_2PCH_2CH_2OMe$ so as to avoid an unstable 16 electron situation. Neither is in keeping with the experimental findings.

Treatment of **3a** with $AgCF_3SO_3$ (one equivalent) in CH_2Cl_2 at room temperature affords, on workup, the cationic vinylidene complex [RuTp(κ²(P,O)-$Ph_2PCH_2CH_2OMe$)(=C=CHPh)]CF_3SO_3 (**7**) in 84% isolated yield (Scheme 3). The NMR spectroscopic features are similar to those of **3a**–**c**. The characteristic resonances of C_α and C_β of vinylidene are found at 377.7 (d, J_{CP} = 17.8 Hz) and 113.2 ppm (d, J_{CP} = 2.0 Hz). In the ^{1}H-NMR spectrum the C_β hydrogen atom gives rise to a doublet at 5.02 ppm (J_{HP} = 4.2 Hz). The solid state structure of **7** has been confirmed by single-crystal X-ray diffraction (Fig. 4). Selected bond distances and angles are reported in Table 3. The coordination geometry around ruthenium is slightly distorted octahedral. The Ru–N(Tp) bond distance *trans* to vinylidene is slightly longer (Ru–N(6) = 2.166(2) Å) than those in the *cis* position (Ru–N(2) = 2.144(2) Å, Ru–N(4) = 2.046(3) Å). The Ru–P and Ru–O distances are 2.307(1) and 2.156(2) Å, respectively. The Ru–C(25) bond distance (1.838(4) Å) is comparable to other cationic RuTp vinylidene complexes (see above). The Ru=C=C group is slightly bent with the Ru–C(25)–C(26) angle being 170.4(3)°. The C(25)–C(26) bond distance of 1.286(5) Å points to a bond order between two and three.

2.2. Catalytic dimerization of alkynes

Reaction of **5** with an excess of HC≡CR (R = Ph, SiMe, *n*-Bu, *t*-Bu, C_6H_9) in benzene at reflux for 40 h results in the catalytic formation of enynes (Table 2). While the degree in conversion is typically high, the selectivity varies drastically with the alkyne substituent as follows. In the case of R=Ph, the coupling reaction results in the formation of the head-to-head dimer (E)-1,4-diphenyl-l-buten-3-yne (**a**) and small amounts of the Z isomer (**b**). For R = $SiMe_3$ the regioselectivity is reversed giving no **a** but **b** instead (88%) together with the head-to-tail dimer 2,4-bis(trimethylsilyl)-l-buten-3-yne (**c**) (12%). For R = *n*-Bu the reaction is less selective giving all three isomers in a ratio of 31:23:43% (**a**:**b**:**c**) and 97% conversion. For R = *t*-Bu, only the formation of the head-to-head isomer **b** is observed with the conversion dropped to about 12%. Finally, for R = C_6H_9 the E and Z isomers of the 1,4-cyclohexenyl-l-buten-3-yne are formed in a ratio of 73:27% (**a**:**b**) with 89% conversion. It is worth noting that all of the reaction mixtures remain catalytically active. Similar results have been obtained with the complexes $RuTp(PPh_3)_2H$, $RuTp(PPh_3)(Cl)$(=C=CHPh) as well as $RuCp^*(PR_3)H_3$ (R = Me, Ph, Cy) as precatalysts [2,13] (see Scheme 4).

A possible reaction mechanism is depicted in Scheme 4 which involves the coordinatively unsaturated alkynyl complex RuTp(κ¹(P)-$Ph_2PCH_2CH_2OMe$)(–C≡CPh) formed by thermally induced Ru–O bond cleavage in RuTp(κ²(P,O)-$Ph_2PCH_2CH_2OMe$)(–C≡CPh). This proposal is in accord with other work [2b,9,13]. In this way the attack of a second alkyne molecule followed by selectivity-determining C–C coupling step becomes feasible, i.e. direct alkyne insertion (pathway A) and/or vinylidene formation with subsequent migration of the α-acetylide onto the C_α carbon of vinylidene (pathway B). The C_4 unsaturated product is eventually liberated from an intermediate σ-enynyl metal species by σ-bond metathesis with an additional alkyne molecule. It

is worth mentioning that the use of isolated **6** in an independent reaction catalyzes the coupling of HC≡CPh in a fashion nearly identical to **5** (Scheme 4).

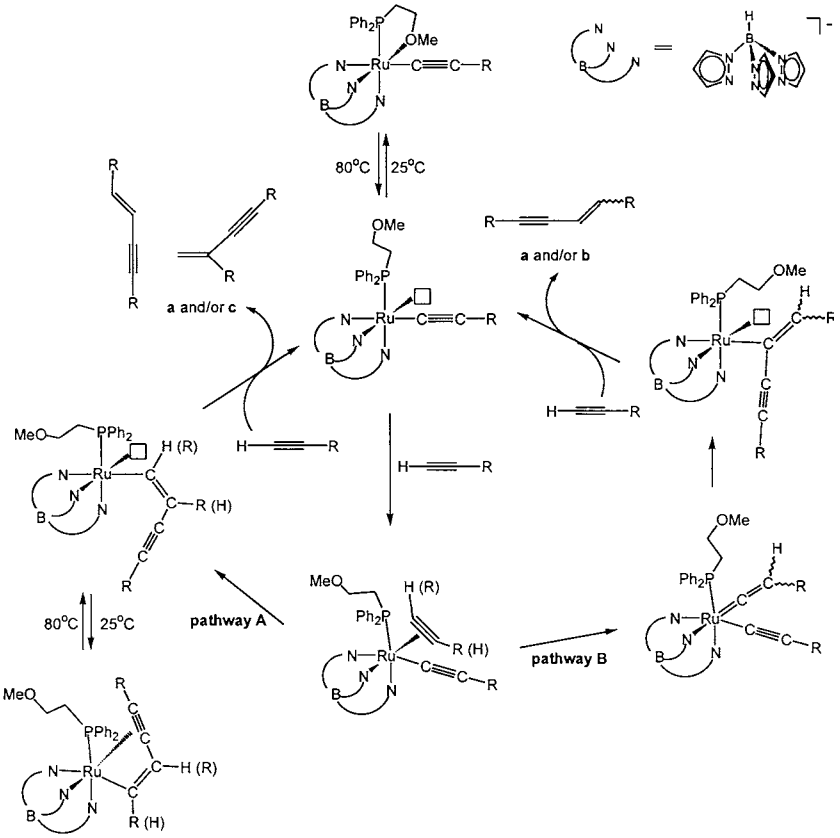
3. Experimental

3.1. General methods

All manipulations were performed under an inert atmosphere of argon by using Schlenk techniques. All chemicals were standard reagent grade and used without further purification. The solvents were purified according to standard procedures [14]. The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. RuTp(COD)Cl (**1**) [15] and $Ph_2PCH_2CH_2OMe$ [16] were prepared according to the literature. ^1H-, $^{13}C\{^1H\}$- and $^{31}P(^1H\}$-NMR spectra were recorded on a Bruker AC-250 spectrometer operating at 250.13, 62.86 and 101.26 MHz, respectively, and were referenced to $SiMe_4$, and H_3PO_4 (85%).

3.1.1. Synthesis of $RuTp(\kappa^2(P,O)\text{-}Ph_2PCH_2CH_2OMe)Cl$ (**2**)

A suspension of **1** (300 mg, 0.655 mmol) and $Ph_2PCH_2CH_2OMe$ (170 mg, 0.696 mmol) in DMF (4 ml) was heated for 2 h at reflux temperature. The solution was evaporated to dryness and upon addition of methanol (2 ml) a yellow precipitate formed, which was collected on a glass frit, washed with methanol (3×2 ml) and dried under vacuum. Yield: 300 mg (78%). $C_{24}H_{27}BClN_6OPRu$ requires: C, 48.54; H, 4.58; N, 14.15. Found: C, 48.67; H, 4.69; N, 14.01%. ^1H-NMR (δ, $CDCl_3$, 20°C): 8.45 (d, $J = 2.1$ Hz, Tp), 7.81 (d, $J = 2.1$ Hz, Tp), 7.73 (d, $J = 2.6$ Hz, Tp), 7.70 (d, $J = 2.5$ Hz, Tp), 7.59–7.52 (m, 2H, Ph), 7.37 (m, 3H, Ph), 7.29–7.23 (m, 1H, Ph), 7.10–7.04 (m, 2H, Ph), 6.98 (d, $J = 2.1$ Hz, Tp), 6.74–6.67 (m, 2H, Ph), 6.55 (d, $J = 2.1$ Hz, Tp), 6.38 (m, Tp), 6.19 (pt, $J = 2.1$ Hz, Tp), 5.82 (pt, $J = 2.5$, $J = 2.1$ Hz, Tp), 4.53 (m, 1H, PCH_2CH_2O), 3.91 (m, 1H, PCH_2CH_2O), 3.58 (s, 3H, OCH_3), 2.97 (m, 1H, PCH_2CH_2O), 2.75 (m, 1H, PCH_2CH_2O). $^{13}C\{^1H\}$-NMR (δ, $CDCl_3$, 20°C): 147.5 (d, $J = 2.4$ Hz, Tp), 144.6 (d, $J = 1.0$ Hz, Tp), 143.7 (d, $J = 2.4$ Hz, Tp), 138.0 (d, $^1J_{PC} = 40.0$ Hz, Ph^1), 136.7 (Tp), 136.2 (Tp), 135.3 (d, $J = 2.4$ Hz, Tp), 133.5 (d,



Scheme 4.

$^1J_{PC} = 42.4$ Hz, Ph), 133,40 (d, $^2J_{PC} = 10.0$ Hz, Ph), 133,38 (d, $^2J_{PC} = 9.1$ Hz, Ph), 130.1 (d, $^4J_{PC} = 1.9$ Hz, Ph), 129.5 (d, $^4J_{PC} = 2.4$ Hz, Ph), 128.6 (d, $^3J_{PC} = 9.5$ Hz, Ph), 12 8.2 (d, $^3J_{PC} = 9.1$ Hz, Ph), 106.5 (Tp), 106.2 (d, $^4J = 2.4$ Hz, Tp), 106.1 (Tp), 77.1 (d, $^2J_{PC} = 2.6$ 31 Hz, PCH_2CH_2O), 65.2 (OCH_3), 30.8 (d, $^1J_{PC} = 22.4$ Hz, PCH_2CH_2O). $^{31}P\{^1H\}$-NMR (δ, $CDCl_3$, 20°C). 65.6.

3.1.2. Synthesis of RuTp(κ¹(P)-Ph₂PCH₂CH₂OMe)-(=C=CHPh)Cl (3a)

A solution of **2** (200 mg, 0.338 mmol) in CH_2Cl_2 (3 ml) was treated with HC≡CPh (180 μl, 1.68 mmol) and stirred for 3 h at 35°C. The volume of the solution was reduced to about 0.5 ml and upon addition of Et_2O and *n*-hexane, an orange precipitate was formed, which was collected on a glass frit, washed with *n*-hexane (4 × 1 ml) and dried under vacuum. Yield: 200 mg (85%). $C_{32}H_{13}BClN_6OPRu$ requires: C, 55.23; H, 4.78; N, 12.08. Found: C, 55.30; H, 4.99; N, 11.93%. ^{1}H-NMR (δ, $CDCl_3$, 20°C): 7.80 (d, $J = 2.0$ Hz, Tp), 7.68–7.58 (m, 5H, Tp, Ph), 7.42–7.03 (m, 14H, Tp, Ph), 6.32 (d, $J = 2.3$ Hz, Tp), 6.13 (m, Tp), 5.97 (pt, $J = 2.3$, $J = 2.0$ Hz, Tp), 5.87 (pt, $J = 2.3$ Hz, Tp), 4.95 (d, $^4J_{HP} = 4.27$ Hz, 1H, Ru=C=C*H*Ph), 3.67–3.56 (m, 2H, PCH_2CH_2O), 3.47–3.20 (m, 2H, PCH_2CH_2O), 3.19 (s, 3H, OCH_3). $^{13}C\{^1H\}$-NMR (δ, $CDCl_3$, 20°C): 368.3 (d, $^2J_{CP} = 19.9$ Hz, Ru=*C*=CHPh), 145.2 (Tp), 143.9 (2C, Tp), 137.1 (Tp), 135.2 (Tp), 134.9 (d, $J = 3.1$ Hz, Tp). 133.5 (d, $^2J_{PC} = 9.1$ Hz, Ph), 133.4 (d, $^2J_{PC} = 8.4$ Hz, Ph), 133.0 (d, $^1J_{PC} = 42.0$ Hz, Ph). 131.1 (d, $^4J_{PC} = 2.3$ Hz, Ru=C=CHPh), 130.7 (d, $^4J_{PC} = 2.3$ Hz, Ph) 130.6 (d, $^4J_{PC} = 2.3$ Hz, Ph), 130.6 (d, $^1J_{PC} = 41.2$ Hz, Ph), 129.4 (2C, Ru=C=CHPh), 129.0 (d, $^3J_{PC} = 9.2$ Hz, Ph), 128.8 (d, $^3J_{PC} = 9.9$ Hz, Ph), 126.8 (2C, Ru=C=CHPh), 125.7 (Ru=C=CHPh), 112.2 (d, $^3J_{PC} = 1.5$ Hz, Ru=C=*C*HPh), 106.6 (d, $J = 3.8$ Hz, Tp), 106.5 (Tp), 106.2 (Tp), 68.8 (PCH_2CH_2O), 59.0 (OCH_3), 27.5 (d, $^1J_{PC} = 30.5$ Hz, PCH_2CH_2O). $^{31}P\{^1H\}$-NMR (δ, $CDCl_3$, 20°C): 27.7.

3.1.3. Synthesis of RuTp(κ¹(P)-Ph₂PCH₂CH₂OMe)-(=C=CHHex^c)Cl (3b)

This compound was prepared analogously to **3a** using **2** (200 mg, 0.338 mmol) and **1** cyclohexenylacetylene (200 μl, 1.76 mmol) as starting materials. Yield: 224 mg (95%). $C_{32}H_{37}BClN_6OPRu$ requires: C, 54.91; H, 5.33; N, 12.01. Found: C, 54.99; H, 5.48; N, 11.87%. ^{1}H-NMR (δ, $CDCl_3$, 20°C): 7.89 (d, $J = 2.1$ Hz, Tp), 7.66–7.56 (m, 5H, Tp, Ph), 7.48–7.30 (m, 4H, Tp, Ph), 7.21–7.14 (m, 5H, Tp, Ph), 6.25 (d, $J = 2.1$ Hz, Tp), 6.18 (m, Tp), 5.97 (pt, $J = 2.1$ Hz, Tp), 5.82 (pt, $J = 2.4$, $J = 2.1$ Hz, Tp), 5.25 (m, 1H, Hex^c), 4.58 (d, $^4J_{HP} = 4.4$ Hz, 1H, Ru=C=C*H*Hex^c), 3.66–3.54 (m, 2H, PCH_2CH_2O), 3.41–3.15 (m, 2H, PCH_2CH_2O), 3.28 (s, 3H, OCH_3), 2.30–2.20 (m, 2H, Hex^c), 2.02–1.95 (m, 2H, Hex^c), 1.69–1.56 (m, 4H, Hex^c). $^{13}C\{^1H\}$-NMR (δ, CDCl, 20°C): 372.4 (d, $^2J_{CP} = 19.5$ Hz, Ru=C=CHHex^c), 145.2 (Tp), 143.8 (Tp), 143.3 (Tp), 136.8 (Tp), 135.2 (Tp), 134.8 (d, $J = 3.4$ Hz, Tp), 133.5 (d, $^2J_{PC} = 9.3$ Hz, Ph), 133,3 (d, $^2J_{PC} = 8.5$ Hz, Ph), 132.9 (d, $^1J_{PC} = 44.1$ Hz, Ph), 130.8 (d, $^1J_{PC} = 39.8$ Hz, Ph), 130.5 (m, 2C, Ph), 128.9 (d, $^3J_{PC} = 9.3$ Hz, Ph), 128.7 (d, $^3J_{PC} = 9.3$ Hz, Ph), 126.7 (m, $^4J_{PC} = 1.7$ Hz, Ru=C=CHcHex^1), 117.3 (cHex^2), 114.5 (d, $^3J_{PC} = 1.5$ Hz, Ru=C=CHHex^c), 106.2 (2C, Tp), 106.1 (Tp), 68.9 (PCH_2CH_2O), 59.0 (OCH_3), 30.4 (Hex^c), 27.3 (d, $^1J_{PC} = 29.7$ Hz, PCH_2CH_2O), 26.2 (Hex^c), 23.7 (Hex^c), 23.0 (Hex^c). $^{31}P\{^1H\}$-NMR (δ, $CDCl_3$, 20°C): 28.0.

3.1.4. Synthesis of RuTp(κ¹(P)-Ph₂PCH₂CH₂OMe)-(=C=CHBu^n)Cl (3c)

This complex has been prepared analogously to **3a** using **2** (200 mg, 0.338 mmol) and *n*-hexyne (200 μl, 1.74 mmol) as starting materials. Yield: 212 mg (93%). $C_{30}H_{37}BClN_6OPRu$ requires: C, 53.31; H, 5.52, N, 12.43. Found: C, 53.47; H, 5.76; N, 12.23%. ^{1}H-NMR (δ, $CDCl_3$, 20°C): 7.82 (d, $J = 2.5$ Hz, Tp), 7.67–7.55 (m, 5H, Tp, Ph), 7.44–7.28 (m, 4H, Tp, Ph), 7.20–7.15 (m, 5H, Tp, Ph), 6.29 (d, $J = 2.5$ Hz, Tp), 6.17 (m, Tp), 5.96 (pt, $J = 2.1$ Hz, Tp), 5.80 (pt, $J = 2.5$ Hz, Tp), 4.07 (d, $^4J_{HP} = 3.9$ Hz, 1H, Ru=C=CHBu^n), 3.71–3.57 (m, 2H, PCH_2CH_2O), 3.39–3.09 (m, 2H, PCH_2CH_2O), 3.30 (s, 3H, OCH_3), 2.48 (m, 2H, Bu^n), 1.53–1.27 (m, 4H, Bu^n), 0.85 (t, 3H, Bu^n). $^{13}C\{^1H\}$-NMR (δ, $CDCl_3$, 20°C): 362.6 (d, $^2J_{CP} = 18.9$ Hz, Ru=C=CHBu^n), 145.8 (Tp), 143.8 (Tp), 143.2 (Tp), 136.8 (Tp), 135.2 (Tp), 134.7 (d, $J = 2.7$ Hz, Tp), 133.8 (d,$^1J_{PC} = 43.1$ Hz, Ph), 133.4 (d, $^2J_{PC} = 9.0$ Hz, Ph), 133.3 (d, $^2J_{PC} = 9.0$ Hz, Ph), 131.4 (d, $^1J_{PC} = 40.4$ Hz, Ph), 130.44 (d, $^4J_{PC} = 2.3$ Hz, Ph), 130.37 (d, $^4J_{PC} = 2.3$ Hz, Ph), 128.8 (d, $^3J_{PC} = 9.0$ Hz, Ph), 128.6 (d, $^9J_{PC} = 9.0$ Hz, Ph), 106.16 (Tp), 106.14 (d, $^3J_{PC} = 1.4$ Hz, Ru=C=CHBu^n), 106.1 (Tp), 105.5 (d, $^4J_{CP} = 1.8$ Hz, Tp), 69.0 (PCH_2CH_2O), 59.0 (OCH_3), 34.7 (Bu^n), 27.8 (d, $^1J_{PC} = 29.6$ Hz, PCH_2CH_2O), 22.7 (Bu^n), 18.1 (Bu^n), 14.3 (Bu^n). $^{31}P\{^1H\}$-NMR (δ, $CDCl_3$, 20°C): 29.5.

3.1.5. Synthesis of RuTp(κ¹(P)-Ph₂PCH₂CH₂OMe)-(CO)Cl (4)

A solution of **2** (100 mg, 0.168 mmol) in CH_2Cl_2 (3 ml) was stirred under an atmosphere of CO for 1 h. The volume of the solution was then reduced to about 1 ml and upon addition of diethylether, a yellow precipitate was formed which was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 96 mg (92%). $C_{25}H_{27}BClN_6O_2PRu$ requires C, 48.29; H, 4.38; N, 13.51. Found: C, 48.42; H, 4.49; N, 13.35%. ^{1}H-NMR (δ, $CDCl_3$, 20°C): 7.98 (d, $J = 2.1$ Hz, Tp), 7.67 (d, $J = 2.4$ Hz, Tp), 7.65 (d, $J = 2.4$ Hz, Tp), 7.59–7.27 (m, 8H, Ph, Tp), 7.19–7.12 (m, 2H, Ph), 7.07–6.99 (m, 2H, Ph), 6.58 (d, $J = 2.1$ Hz, Tp), 6.20 (m, Tp), 5.95 (pt, $J = 2.1$ Hz, Tp), 5.87 (pt, $J = 2.4$ Hz,

$J = 2.1$ Hz, Tp), 3.71–3.57 (m, 2H, PCH_2CH_2O), 3.40–3.22 (m, 1H, PCH_2CH_2O), 3.23 (s, 3H, OCH_3), 3.08–2.90 (m, 1H, PCH_2CH_2O). $^{13}C\{^1H\}$-NMR (δ, $CDCl_3$, 20°C): 203.7 (d, $^2J_{CP} = 16.0$ Hz, Ru–CO), 146.1 (Tp), 143.7 (2C, Tp), 136.9 (Tp), 135.5 (Tp), 135.2 (d, $J = 2.3$ Hz, Tp), 133.6 (d, $^1J_{PC} = 44.3$ Hz, Ph), 133.3 (d, $^2J_{PC} = 9.2$ Hz, Ph), 132.5 (d, $^2J_{PC} = 9.2$ Hz, Ph), 130.7 (d, $^4J_{PC} = 2.3$ Hz, Ph), 130.6 (d, $^4J_{PC} = 2.3$ Hz, Ph), 130.3 (d, $^1J_{PC} = 40.4$ Hz, Ph), 129.2 (d, $^3J_{PC} = 9.2$ Hz, Ph), 128.7 (d, $^3J_{PC} = 9.2$ Hz, Ph), 106.7 (Tp), 106.5 (d, $J = 2.3$ Hz, Tp), 106.2 (Tp), 68.7 (PCH_2CH_2O), 59.0 (OCH_3), 28.1 (d, $^1J_{PC} = 29.0$ Hz, PCH_2CH_2O). $^{31}P\{^1H\}$-NMR (δ, $CDCl_3$, 20°C): 33.3.

3.1.6. Reaction of **3a** with O_2 in a sealed NMR tube

Solid **3a** (30 mg, 0.051 mmol) was dissolved in $CDCl_3$ saturated with dioxygen (0.5 ml) and then transferred into a 5 mm NMR tube. The reaction was followed by ^1H- and $^{31}P\{^1H\}$-NMR spectroscopy at room temperature (r.t.). After 2 days **3a** was completely decomposed to the CO complex **4** and an equal amount of benzaldehyde.

3.1.7. Synthesis of RuTp(κ^2(P,O)-$Ph_2PCH_2CH_2OMe$)-(–C≡CPh) (**5**)

To a solution of **3a** (600 mg, 0.909 mmol) in tetrahydrofuran (5 ml), lithium diisopropylamide (1.2 ml, 1.82 mmol) was added and stirred for 20 min at r.t. After removal of the solvent, the residue was dissolved in about 5 ml of CH_2Cl_2 and insoluble materials were removed by filtration. The volume of the solution was then reduced to about 1 ml and on treatment with diethyl ether, a yellow precipitate was obtained which was collected on a glass frit, washed with petroleum ether, and dried under vacuum. Yield: 366 mg (61%). $C_{32}H_{32}BN_6OPRu$ requires C, 58.28; H, 4.89; N, 12.74. Found: C, 58.26; H, 4.90; N, 12.70%. ^1H-NMR: (δ, CD_2Cl_2, 20°C): 8.35 (m, 1H, Tp), 7.73–7.61 (m, 5H), 7.33–7.19 (m, 4H), 7.11–7.01 (m, 6H), 6.93 (m, 2H), 6.77–6.71 (m, 3H), 6.31 (m, 1H, Tp), 5.91–5.84 (m, 2H, Tp), 4.39–4.19 (m, 1H, PCH_2CH_2O), 3.89–3.67 (m, 1H, PCH_2CH_2O), 3.41 (s, 3H, OCH_3), 2.85–2.47 (m, 2H, PCH_2CH_2O) $^{13}C\{^1H\}$-NMR: (δ, CD_2Cl_2, 20°C). 147.5 (d, $J = 2.4$ Hz, Tp), 143.9 (d, $J = 2.4$ Hz, Tp), 142.7 (Tp), 139.3 (d, $^1J_{PC} = 42.7$ Hz, Ph), 136.1 (2C, Tp), 135.0 (Tp), 133.4 (d, $^2J_{PC} = 9.8$ Hz, Ph), 133.0 (d, $^2J_{PC} = 9.8$ Hz, Ph), 132.8 (d, $^1J_{PC} = 44.0$ Hz, Ph), 132.3 (Ph), 131.2 (Ph), 129.8 (Ph), 129.05 (Ph), 128.3 (d, $^3J_{PC} = 8.6$ Hz, Ph), 128.0 (Ph), 127.9 (d, $^3J_{PC} = 9.8$ Hz, Ph), 123.1 (Ph), 110.7 (Ru–C≡C), 105.9 (Tp), 105.8 (Ru–C≡C), 105.7 (d, $J = 2.4$ Hz, Tp), 105.1 (Tp), 77.7 (PCH_2CH_2O), 65.3 (OCH_3), 30.8 (d, $^1J_{PC} = 23.2$ Hz, PCH_2CH_2O). $^{31}P\{^1H\}$-NMR (δ, CD_2Cl_2, 20°C): 66.50.

3.1.8. Synthesis of RuTp(κ^1(P)-$Ph_2PCH_2CH_2OMe$)-(σ,η^2-CPh=CHC≡CPh) (**6**)

To a solution of **5** (200 mg, 0.303 mmol) in benzene (5 ml), HC≡CPh (67 μl, 0.606 mmol) was added and the solution was stirred for 24 h at r.t. After removal of the solvent, the residue was dissolved in diethyl ether (5 ml) and insoluble materials were removed by filtration. The solvent was again removed under vacuum and the residue was extracted five times with petroleum ether (3 ml). After removal of the solvent analytically pure **6** was obtained as an orange powder. Yield: 120 mg (66%). $C_{40}H_{30}BN_6OPRu$ requires: C, 63.08; H, 5.03; N, 11.03. Found: C, 63.10; H, 5.07; N, 11.00%. ^1H-NMR (δ, benzene-d_6, 20°C): 7.73 (m, 2H), 7.62 (m, 1H), 7.54 (m, 1H), 7.48–6.45 (m, 23H), 5.82 (m, 1H), 5.68 (m, 1H), 5.58 (m, 1H), 3.44–2.77 (m, 4H), 2.91 (s, 3H, OCH_3). $^{13}C\{^1H\}$-NMR: (δ, benzene-d_6, 20°C): 184.1 (d, $J_{CP} = 12.2$ Hz, RuC(Ph)=C), 147.6, 146.5, 145.1, 140.2, 139.1, 139.0 (Tp), 135.6 (RuC(Ph)=C), 135.1, 135.0, 134.5, 133.9, 133.5, 133.4, 133.3, 131.9, 129.1, 128.9, 128.4, 128.1,127.8, 127.4, 126.9, 126.6, 125 7, 124.0, 122.4, 121.8 (Ph), 105.6, 105.1, 105.0 (Tp), 70.5 (C≡C), 69.3 12 (C≡C), 58.6 (PCH_2CH_2O), 58.1 (OCH_3), 28.8 (d, $^1J_{PC} = 22.4$ Hz, PCH_2CH_2O). $^{31}P\{^1H\}$ NMR (δ, benzene-d_6, 20°C): 41.34.

3.1.9. Synthesis of [RuTp(κ^2(P,O)-$Ph_2PCH_2CH_2OMe$)-(=C=CHPh)]CF_3SO_3 (**7**)

A solution of **3a** (300 mg, 0.43 mmol) in CH_2Cl_2 (5 ml) was treated with $AgCF_3SO_3$ (111 mg, 0.43 mmol) and stirred at r.t. for 24 h. After removal of AgCl, the volume of the solution was reduced to about 1 ml. Upon treatment with diethyl ether and petroleum ether an orange precipitate was obtained which was collected on a glass frit, washed with petroleum ether and dried under vacuum. Yield: 231 mg (66%). $C_{12}H_{33}BF_3N_6OPSRu$ requires: C, 48.19; H, 4.17; N, 10.54. Found: C, 48.21; H, 4.19; N, 10.50%. ^1H-NMR: (δ, CD_2Cl_2, 20°C): 7.93–615 (m, 24H, Ph, Tp), 5.02 (d, 1H, $^4J_{HP} = 4.3$ Hz, 1H, Ru=C=CHPh), 4.52–4.32 (m, 1H, PCH_2CH_2O), 3.77–3.31 (m, 1H, PCH_2CH_2O), 3.47 (s, –OCH_3), 3.23–2.88 (m, 2H, PCH_2CH_2O). $^{13}C\{^1H\}$-NMR: (δ, CD_2Cl_2, 20°C): 377.7 (d, $^2J_{CP} = 17.8$ Hz, Ru=C=CHPh), 146.5 (d, $J = 1.4$ Hz, Tp), 144.1 (d, $J = 1.7$ Hz, Tp), 143.7 (d, $J = 1.4$ Hz, Tp), 138.7 2 (Tp), 137.2 (Tp), 136.6 (d, $J = 3$ Hz, Tp), 133.6 (d, $^1J_{PC} = 42.0$ Hz, Ph), 133.3 (d, $^2J_{PC} = 9.9$ Hz, Ph), 132.3 (d, $^4J_{PC} = 2.3$ Hz, Ph), 132.2 (Ru=C=CHPh), 131.9 (d, $^2J_{PC} = 9.2$ Hz, Ph), 131.6 (d, $^4J_{PC} = 3$ Hz, Ph), 129.7 (d, $^1J_{PC} = 42.0$ Hz, Ph), 129.6 (Ru=C=CHPh), 129.4 (d, $^3J_{PC} = 9.2$ Hz, Ph), 129.2 (d, $^3J_{PC} = 9.2$ Hz, Ph), 127.9 (Ru=C=CHPh), 127.2 (Ru=C=CHPh), 127.1 (Ru=C=CHPh), 126.8 (Ru=C=CHPh), 113.2 (d, $^3J_{PC} = 2.0$ Hz, Ru=C=CHPh), 107.9 (Tp), 107.3 (d, $J = 3$ Hz, Tp), 107.2 (Tp), 81, 41 (PCH_2CH_2O), 67.9 (OCH_3), 29.0 (d, $^1J_{PC} = 29.8$ Hz, PCH_2CH_2O). $P\{^1H\}$-NMR (δ, CD_2Cl_2, 20°C): 49.61.

Table 3
Crystallographic data for **3a**, **4**, **5** and **7**·CH_2Cl_2

	3a	**4**	**5**	**7**·CH_2Cl_2
Empirical formula	$C_{32}H_{33}BClN_6OPRu$	$C_{32}H_{27}BClN_6O_2PRu$	$C_{32}H_{32}BN_6OPRu$	$C_{34}H_{35}BCl_2F_3N_6O_4PRuS$
Formula weight	695.94	621.83	659.49	894.49
Crystal size (mm)	$0.32\times0.22\times0.10$	$0.44\times0.16\times0.12$	$0.76\times0.32\times0.12$	$0.60\times0.14\times0.06$
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
a (Å)	25.438(9)	7.925(3)	9.464(2)	9.638(4)
b (Å)	12.732(6)	21.345(8)	13.798(3)	13.772(5)
c (Å)	19.370(8)	16.613(5)	24.075(4)	16.102(6)
α (°)				68.95(2)
β (°)	92.24(1)	100.42(2)	96.00(1)	77.40(2)
γ (°)				74.62(2)
V (Å^3)	6269(5)	2764(2)	3127(1)	1905(1)
Z	8	4	4	2
D_{calc} (g cm^{-3})	1.475	1.494	1.401	1.559
Temperature (K)	297(2)	298(2)	299(2)	223(2)
$F(000)$	2848	1264	1352	908
μ (mm^{-1}) (Mo–K_α)	0.673	0.756	0.588	0.710
Absorption correction	Multi scan	Multi scan	Empirical	Multi scan
θ_{max} (°)	25	30	25	25
Index ranges	$-30\le h\le30$	$-11\le h\le11$	$-11\le h\le11$	$-11\le h\le11$
	$-15\le k\le15$	$-29\le k\le30$	$0\le k\le16$	$-16\le k\le16$
	$-23\le l\le23$	$-23\le l\le23$	$0\le l\le28$	$-19\le l\le19$
Reflections measured	63 924	40 280	5496	24 320
Unique reflections	10 982	7994	5496	6577
Reflections $I>2\sigma(I)$	8143	6659	4462	5750
Parameters	770	332	380	479
R_1 ($I>2\sigma(I)$) [a]	0.030	0.026	0.030	0.045
R_1 (all data)	0.053	0.037	0.045	0.052
wR_2 (all data)	0.077	0.062	0.066	0.120
Difference Fourier peaks min/max (e Å^{-3})	−0.46/0.70	−0.41/0.28	−0.29/0.27	−1.02/0.85

[a] $R_1=\Sigma\big||F_o|-|F_c|\big|/\Sigma|F_o|$, $wR_2=[\Sigma(w(F_o^2-F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$.

3.1.10. Catalytic dimerization of terminal alkynes

In a typical procedure, alkynes (0.3 M) were added to a suspension of complex **5** as pre-catalyst (5 mol%) in benzene (5 ml) using Schlenk techniques. The sealed Schlenk tube was heated in an oil bath (80°C) for 40 h. After that time the reaction mixture was evaporated to dryness under vacuum and the coupling product was extracted with *n*-hexane. The solvent was again removed under vacuum affording an isomeric mixture of butynes. The product distribution was determined by ^{1}H-NMR spectroscopy. Alternatively, the same procedure was performed in a sealed NMR tube in benzene-d_6 at 80°C for 40 h. The course of reaction was continuously monitored by ^{1}H-NMR spectroscopy.

*3.2. X-ray structure determination for **3a**, **4**, **5** and **7**·CH_2Cl_2*

Crystals of **3a**, **4**, **5** and **7**·CH_2Cl_2 were obtained by diffusion of Et_2O into CH_2Cl_2 solutions. Crystal data and experimental details are given in Table 3. X-ray data for **3a**, **4** and **7**·CH_2Cl_2 were collected on a Siemens Smart CCD area detector diffractometer (graphite monochromated Mo K_α radiation, $\lambda=$ 0.71073 Å, a nominal crystal-to-detector distance of 4.45 cm, 0.30° ω-scan frames). For **5** X-ray data were collected on a Philips PW 1100 four-circle diffractometer using graphite-monochromated Mo–K_α radiation and the $\theta-2\theta$ scan technique. Corrections for Lorentz and polarization effects, for crystal decay, and for absorption were applied (program SADABS [17]). All structures were solved by direct methods using the program SHELXS97 [18]. Structure refinement on F^2 was carried out with program SHELXL97 [19]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded.

4. Supplementary material

Crystallographic data (excluding structure factors) for the crystal structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 147401–147404. Copies of the data can be obtained, free of charge, from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK

(fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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