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Ti–Ru bimetallic complexes: catalysts for ring-closing metathesis

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Dedicated to Professor François Mathey on the occasion of his 60th birthday

Abstract

The reaction of the titanocene monophosphanes (**1**–**4**) with the dimer [(*p*-cymene)$RuCl_2]_2$ gives the heterobimetallic compounds (*p*-cymene)[(η^5-C_5H_5)(μ-η^5:η^1-$C_5H_4(CR_2)_nPR'_2$)$TiCl_2$]$RuCl_2$ (**5**–**8**). The structure of **8**, determined by X-ray diffraction, is reported here. A preliminary assessment of the performance of these complexes in ring-closing metathesis (RCM) revealed an excellent Ti–Ru–allenylidene pre-catalyst **12**. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Titanocene; Ruthenium; Heterobimetallic complexes; Metathesis; Allenylidenes

1. Introduction

The catalytic behavior of early–late heterobimetallic compounds remains almost unexplored [1]. However, the combination of two metal centers with different properties in the same molecule may show enhanced cooperative effect. In an attempt to examine such type of activity, we focused our attention on the synthesis and study of heterobimetallic complexes in which both metal fragments are already well known in the field of catalysis. Our goal was achieved via the reaction between the bent-titanocene phosphanes **1** and **3** with the dimer [(*p*-cymene)$RuCl_2]_2$ (Scheme 1) [2]. Herein, we report the synthesis of two new Ti–Ru bimetallic complexes (**6** and **8**) with complementary features by using the same strategy. The complex **6** contains a C1 spacer between the Cp and PPh_2 functionalities and the complex **8** has a highly basic and bulky phosphane group. Work was then focused on RCM as a representative reaction for comparing the activity of the bimetallic complexes (**5**–**8**) with the monometallic species (*p*-cymene)$RuCl_2(PCy_3)$. At this point, we should mention that the performance of ruthenium-based metathesis catalysts has recently been upgraded by the addition of a substoichiometric amount of titanium complexes [3].

2. Results and discussion

The monophosphanes **2** and **4** were prepared according to similar procedures as **1** and **3**, i.e. synthesis of the lithium [1-methyl-1-(diphenylphosphino)ethyl] or [(dicyclohexylphosphino)ethyl] cyclopentadienides by means of the fulvene [4] or the spiro[2,4]hepta-4,6-diene [5] routes, followed by treatment with $CpTiCl_3$. As expected, the $^{31}P\{^1H\}$-NMR spectrum of **2** appears as a singlet but with a very unusual chemical shift at 30.1 ppm. This value, when compared with the other phosphanes, corresponds to a downfield shift of about 50 ppm. This result, closely similar to those reported by G. Erker and co-workers [4,6] for the analogue zirconocene series, is probably due to the presence of the alkyl substituents on the spacer carbon between the Cp and PPh_2 groups. It is worth mentioning that both lithium cyclopentadienide and its cyclopentadiene derivative formed by hydrolysis show ^{31}P-chemical shifts in the 20 ppm range. This suggests that the titanium atom is not responsible for this unexpected deshielding. The ^1H-NMR spectrum shows a doublet for the methyl groups bound to the spacer carbon with phosphorus coupling of 15.3 Hz. The ^1H- and ^{31}P-

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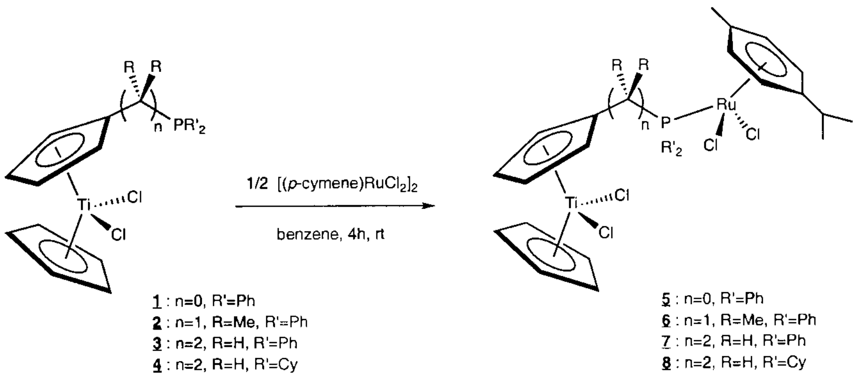


Scheme 1.

NMR chemical shifts of the phosphane **4** are consistent with the free ligand not coordinated to a metal atom. However, it is noteworthy that its NMR characterization has been done in a nonprotic solvent like C_6D_6 and often shows slightly broadened signals.

Preliminary complexation studies have shown that the titanocene monophosphanes **1** and **3** are able to cleave the chloride bridges of the dimer [(*p*-cymene)$RuCl_2$]$_2$ to lead to the bimetallic complexes **6** and **8** [2]. Therefore, we carried out experiments by using the metalloligands **2** and **4** to obtain the targeted heterobimetallic complexes **6** and **8**. Except for the single ^{1}H resonances of the cyclopentadienyl and *p*-cymene hydrogens, which are apparently degenerate, all other ^{31}P and ^{1}H resonances are in accordance with their structural features. A single crystal of **8**, suitable for X-ray diffraction, was obtained by slow evaporation of a $CHCl_3$ solution of the compound. An ORTEP view of **8** is given in Fig. 1.

The molecular structures of the bimetallic complexes **7** and **8** with a diphenyl or a dicyclohexylphosphane group are very similar. Surprisingly, although the dicyclohexylphosphane group is known to be bulkier than its diphenyl analogue, the only structural change, observed in the arene–ruthenium moiety, consists in a slight elongation of the Ru–P bond distance (2.350(2) Å for **7** [2]) (Table 1).

Recently, it has been demonstrated that the complex (*p*-cymene)$RuCl_2(PCy_3)$ converts into an efficient metathesis catalyst upon photochemical irradiation (light emitted by neon tube) [7]. We, therefore, carried out experiments by refluxing a solution of *N*,*N*-diallyltosylamide (**10**) and a catalytic amount of the bimetallic complex **8** in CH_2Cl_2 under neon light (Scheme 2). In this reaction, only 3% of the cyclization product **11** could be detected by GC and NMR analysis of the crude mixture. Other bimetallic complexes (**5**–**7**) showed no catalytic activity under the same conditions.

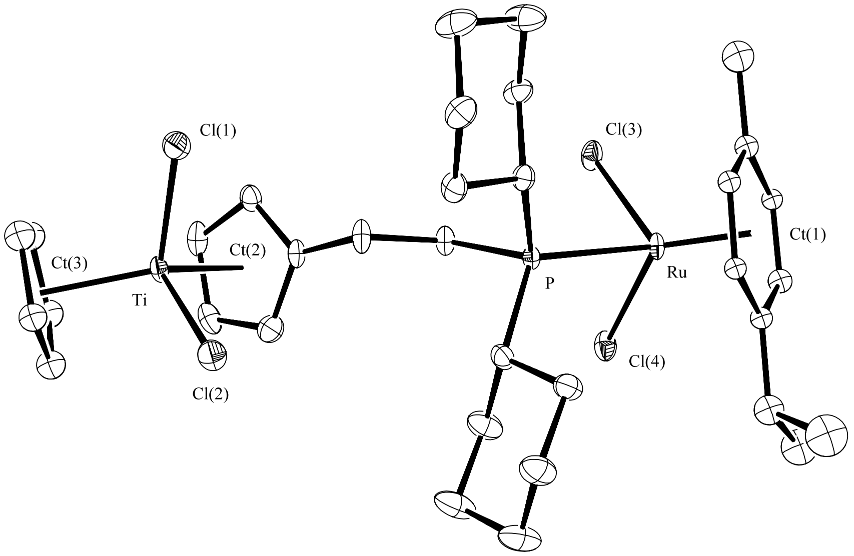
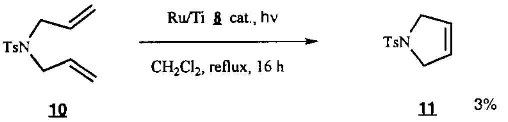


Fig. 1. An ORTEP view of compound **8** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and the chloroform solvate molecules are omitted for clarity. Only disordered fragments with s.o.f. > 0.5 are shown.

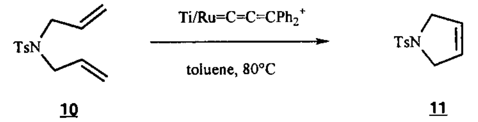
Table 1
Selected bond distances (Å) and bond angles (°) for the Ru moiety of **8**

Bond distances	
Ru–Ct(1)	1.70(1)
Ru–P	2.3869(7)
Ru–Cl(3)	2.4253(7)
Ru–Cl(4)	2.4205(7)
Bond angles	
Ct(1)–Ru–P	131.9(10)
Ct(1)–Ru–Cl(3)	122.1(9)
Ct(1)–Ru–Cl(4)	128.1(9)
P–Ru–Cl(3)	87.93(3)
P–Ru–Cl(4)	86.32(3)
Cl(3)–Ru–Cl(4)	86.19(3)



Scheme 2.

Table 2
Screening of the catalytic activity of the Ti–Ru–allenylidene complexes



Bimetallic complex	Yield (%)	Formation of the allenylidene [a]
Ti–$CH_2CH_2PCy_2$/Ru (**8**)	98	<10 min
Ti–$CH_2CH_2PPh_2$/Ru (**7**)	1 [b]	30 min
Ti–CMe_2PPh_2/Ru (**6**)	2 [b]	1.5 h
Ti–PPh_2/Ru (**5**)	1 [b]	nonobserved

Conditions: Complex Ti/Ru (0.025 mmol), AgOTf (0.026 mmol), CH_2Cl_2 (1 ml), 30 min–1 h; diphenylpropynol (0.0275 mmol), CH_2Cl_2 (1 ml), 30 min–1.5 h; *N*,*N*-diallyltosylamide (251 mg, 1 mmol), toluene (3 ml), 80 °C, 1 h.

[a] A dark-violet color characteristic of the allenylidene fragment is observed after a lapse of time.

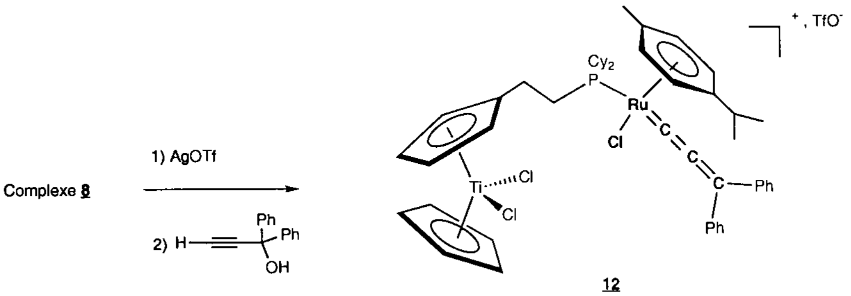
[b] Determined by ^{1}H-NMR of the crude reaction mixture.

Although in case of the monometallic complex, the precise nature of the active species is still unknown, it seems that the photochemical irradiation induces a decomplexation of the arene ligand and so liberates a 14-electron Ru^{II} entity, which triggers the catalytic process [8]. It is worth noting that both monometallic and bimetallic species show absorption maxima at 360 nm attributed to the coordinated arene; therefore, a similar dissociation should occur with the bimetallic complexes. One can then propose that both chlorides on the titanium atom work as a chelate on the ruthenium center and so inhibit the desired catalytic reaction. These results clearly show a totally different behavior between mono and bimetallic complexes.

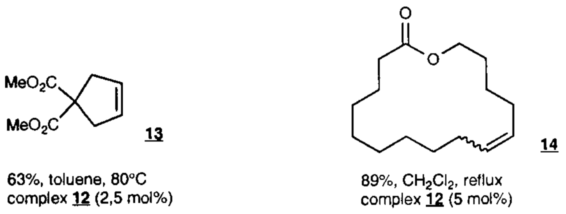
Cationic allenylidene ruthenium complexes of the type (*p*-cymene)RuCl(PR_3)(=C=C=CPh_2)$^+$TfO$^-$ prepared in situ or not, by successive addition of silver triflate and diphenylpropynol to (*p*-cymene)$RuCl_2$(PR_3), have proved to be excellent catalysts for RCM [9]. We, therefore, studied the RCM of *N*,*N*-diallyltosylamide (**10**) by using a mixture of the bimetallic complexes **5**–**8**, silver triflate and diphenylpropynol as in situ catalysts. Table 2 summarizes both the conversions in dihydropyrrole **11** and the rates of formation of the cumulene species according to the bimetallic complex used. The catalytic system obtained from **8**, allows the cyclization of *N*,*N*-diallyltosylamide (**10**) with complete conversion after 1 h at 80 °C in toluene.

This result comparable to those obtained with (*p*-cymene)RuCl(PCy_3)(=C=C=CPh_2)$^+$TfO$^-$ suggests that a similar structure is obtained with the bimetallic complex **8**. In order to check this hypothesis, we isolated the cationic Ti–Ru–allenylidene complex **12** (Scheme 3). The reaction of **8** with AgOTf in CH_2Cl_2 yields the isolable cationic 16-electron ruthenium compound. Subsequent treatment with diphenylpropynol at room temperature affords the dark-violet complex **12**. The most significant spectroscopic data for **12** is a strong IR absorption at 1964 cm^{-1} which corresponds to the asymmetric C=C=C stretch of an allene system [10].

Other bimetallic complexes (**5**–**7**) tested in similar conditions led to very low conversions (Table 2). In line with previous observations, these results can be correlated with the nature of the phosphane. Indeed, a



Scheme 3.



Scheme 4.

highly basic and bulky phosphane ligand on the ruthenium center is required for the catalytic reaction to turn over. Finally, these results highlight the tremendous influence of the spacer between both metals on the easiness of access to the allenylidene complex. Indeed, the shorter the alkyl arm, the slower the appearance of the dark-violet color of the cumulene complex. Thus, when the PPh_2 group is directly bonded to the cyclopentadienyl ring, which corresponds to the worst case, no change in the coloration of the reaction mixture has been observed. This aspect is subjected to further studies in our laboratory.

We also employed catalyst **12** in RCM of α,ω-dienes. As can be seen in Scheme 4, this catalytic system performs the cyclization of the dimethyl diallylmalonate well and gives the RCM product **13** with 63% yield [11]. In the macrocyclic series, the 16-membered cycloalkene **14** has been efficiently obtained in high dilution conditions [12].

These preliminary results which are comparable to those obtained with the monometallic species illustrate the compatibility of both metallic fragments with functional groups such as esters or sulfonamides. Current work in our laboratory is aiming at exploring the catalytic activity of the Ti–Ru–allenylidene complex **12** with other diene substrates including other functional groups (ether, amide, silyl ether, ...) as well as replacing the chloride atoms on the titanium center in order to implicate it more in the catalytic reaction. Further applications of these Ti–Ru bimetallic complexes in catalysis are also under study.

3. Experimental

All manipulations were carried out under argon atmosphere using vacuum line techniques. Solvents were dried and distilled under argon before use. NMR spectra were recorded in a BRUKER AC200 (200.135 MHz for ^{1}H, 81.004 MHz for ^{31}P) spectrometer. IR spectra were obtained in a Bruker IFS 66v; abbreviations: vs (very strong). Elemental analyses were performed on a FISON EA 1108 within the laboratory. $CpTiCl_3$ [13] and the cyclopentadienyl phosphane ligands $Li[C_5H_4(CR_2)_nPR'_2]$ [4,5] were prepared according to the literature method.

*3.1. Complex **2***

A 0.71 g (2.4 mmol) sample of $Li[C_5H_4(CMe_2)PPh_2]$ in 10 ml of THF was added to 0.52 g of $CpTiCl_3$ (2.4 mmol) in 15 ml of THF. After stirring for 4 h at room temperature (r.t.), the solvent was removed in vacuo. The red residue was extracted with CH_2Cl_2, filtered through celite, and precipitated by the addition of hexane. The solution was then placed in a freezer (−20 °C) overnight. The solvent was removed by filtration and the red residue was dried under vacuum (70% yield). $^{31}P\{^{1}H\}$-NMR (81.004 MHz, $CDCl_3$): δ 30.70 (s, PPh_2). ^{1}H-NMR (200.135 MHz, $CDCl_3$): δ 1.62 (d, $J = 15.3$ Hz, 6H, CH_3), 6.46 (s, 5H, Cp), 6.32–6.66 (m, 4H, Cp′), 7.17–7.50 (m, 10H, Ph). Anal. Calc. for $C_{25}H_{25}TiCl_2P$ (475.2578): C, 63.18; H, 5.30. Found: C, 62.10; H, 5.25%. The relatively low percentage of carbon can be attributed to the presence of LiCl.

*3.2. Complex **4***

This compound was obtained by following the above procedure but with $Li[C_5H_4CH_2CH_2PCy_2]$ (80% yield). $^{31}P\{^{1}H\}$-NMR (81.004 MHz, C_6D_6): δ −7.03 (s, PCy_2). ^{1}H-NMR (200.135 MHz, C_6D_6): δ 1.08–2.05 (m, 24H, Cy + CH_2), 3.16 (pseudoquadruplet, $J = 8.5$ Hz, 2H, CH_2), 5.74 (pseudotriplet, $J = 2.6$ Hz, 2H, Cp′), 6.08 (s, 5H, Cp), 6.17 (pseudotriplet, $J = 2.6$ Hz, 2H, Cp′). Anal. Calc. for $C_{24}H_{35}TiCl_2P$ (473.3263): C, 60.90; H, 7.45. Found: C, 60.10; H, 7.30%. The relatively low percentage of carbon can be attributed to the presence of LiCl.

*3.3. Complex **6***

A 25 ml Schlenk flask was charged under argon with **2** (0.13 g, 0.28 mmol), $[(p\text{-cymene})RuCl_2]_2$ (0.086 g, 0.14 mmol) and degassed benzene. The mixture was stirred at r.t. for 4 h during which time a brick-red precipitate slowly formed. The solvent was removed by filtration and the red residue was dried under vacuum (85% yield). $^{31}P\{^{1}H\}$-NMR (81.004 MHz, $CDCl_3$): δ 25.37 (s, PPh_2). ^{1}H-NMR (200.135 MHz, $CDCl_3$): δ 1.04 (d, $J = 7.0$ Hz, 6H, isopropyl CH_3), 1.48 (s, 3H, CH_3 *p*-cymene), 1.72 (d, $J = 15.9$ Hz, 6H, CH_3), 2.50 (hept, $J = 7.0$ Hz, 1H, CH isopropyl), 4.99 (d, $J = 5.6$ Hz, 2H, =CH *p*-cymene), 5.04 (d, $J = 5.6$ Hz, 2H, =CH *p*-cymene), 6.19 (pseudotriplet, $J = 2.6$ Hz, 2H, Cp′), 6.46 (s, 5H, Cp), 6.57 (pseudotriplet, $J = 2.6$ Hz, 2H, Cp′), 7.34–7.54 (m, 6H, *m*,*p*-Ph), 7.84–7.92 (m, 4H, *o*-Ph). Anal. Calc. for $C_{35}H_{39}TiRuCl_4P$ (781.4291): C, 53.80; H, 5.03. Found: C, 54.13; H, 5.13%.

Table 3
Crystal data and structure refinement parameters for complex **8**

Empirical formula	$C_{34}H_{49}Cl_4PRuTi \cdot 3(CHCl_3)$
Formula weight	1137.58
Temperature (K)	110(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	9.9486(1)
b (Å)	15.4455(2)
c (Å)	17.3907(3)
α (°)	68.604(1)
β (°)	76.978(1)
γ (°)	77.069(1)
V (Å^3)	2394.42(6)
Z	2
D_{calc} (g cm^{-3})	1.578
Absorption coefficient (mm^{-1})	1.268
$F(000)$	1152
Crystal size (mm)	$0.20 \times 0.15 \times 0.10$
Diffractometer	Enraf–Nonius Kappa-CCD
Scan type	Mixture of ϕ rotations and ω scans
Sin(θ)/λ max (Å^{-1})	0.65
Index ranges	$-12 \leq h \leq 9$, $-19 \leq k \leq 20$, $-22 \leq l \leq 21$
Absorption correction	SCALEPACK
RC = reflections collected	15886
IRC = independent RC	10726 [$R_{int} = 0.021$]
IRCGT = IRC and [$I > 2\sigma(I)$]	9526
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	10726/18/466
R for IRCGT	R_1 [a] = 0.0438, wR_2 [b] = 0.0987
R for IRC	R_1 [a] = 0.0512, wR_2 [b] = 0.1029
Goodness-of-fit [c]	1.055
Largest difference peak and hole (e Å^{-3})	1.60 and −0.93

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$.

[b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + 7.73P + (2.63P)^2]$ where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$.

[c] Goodness-of-fit $= [\Sigma w(F_o^2 - F_c^2)^2/(N_o - N_v)]^{1/2}$.

3.4. Complex **8**

Under the above experimental conditions, 90% of **8** was isolated as a brick-red powder. $^{31}P\{^1H\}$-NMR (81.004 MHz, $CDCl_3$): δ 23.61 (s, PCy_2). ^1H-NMR (200.135 MHz, $CDCl_3$): δ 1.15–2.41 (m, 24H, Cy + CH_2), 1.28 (d, $J = 7.0$ Hz, 6H, isopropyl CH_3), 2.09 (s, 3H, CH_3 *p*-cymene), 2.72–2.98 (m, 3H, CH_2 + CH isopropyl), 5.57 (pseudosinglet, 4H, =CH *p*-cymene), 6.42 (pseudosinglet, 4H, Cp′), 6.56 (s, 5H, Cp). Anal. Calc. for $C_{34}H_{49}TiRuCl_4P$ (779.5254): C, 52.39; H, 6.34. Found: C, 52.92; H, 6.33%.

3.4.1. Crystal structure determination of complex **8**

A red crystal of **8** (0.20 × 0.15 × 0.10 mm) suitable for an X-ray analysis was obtained from a slow evaporation of a $CHCl_3$ solution of **8**. The crystal was mounted on an Enraf–Nonius Kappa-CCD using Mo–K_α radiation under a cold nitrogen flux (110 K) and 15886 reflections (10726 unique) were collected up to $\sin(\theta)/\lambda = 0.65$ Å^{-1}. Absorption corrections were applied to the data during integration by the SCALEPACK [14] algorithm. The structure was solved via a Patterson search program [15] and refined (space group $P\bar{1}$) with full-matrix least-squares methods [15] based on $|F^2|$. During refinement, one cyclopentadienyl ring, the *p*-cymene ligand and one $CHCl_3$ solvate were found to be disordered. The former two occupy two positions while the solvate molecule is disordered over three positions. The occupation factors converged to $m_1 = 0.623$ and $m'_1 = 1 - m_1$ for the Cp rings (restrained to regular pentagons, AFIX 59), to $m_2 = 0.571$ and $m'_2 = 1 - m_2$ for the *p*-cymene and to the three independent values $m_3 = 0.425$, $m'_3 = 0.425$ and $m''_3 = 0.144$ (leading to $\Sigma m = 0.994$) for the $CHCl_3$ molecule. Furthermore, the C–Cl distances and Cl–C–Cl angles in the disordered $CHCl_3$ molecule were restrained (DFIX card). The atoms belonging to the disordered groups were left isotropic during the refinement while other atoms were anisotropically refined. Hydrogen atoms were included in their calculated positions and refined with a riding model. Crystal data and final agreement indices are reported in Table 3.

3.5. Complex **12**

A 0.03 g (0.17 mmol) sample of silver triflate was added to a solution of **8** (0.091 g, 0.17 mmol) in CH_2Cl_2 (5 ml). The mixture was stirred for 3 h at r.t. The solution was filtered, evaporated to dryness and washed with 5 ml of ether. The residue was dissolved in CH_2Cl_2 (5 ml) and 1,1-diphenylpropynol (0.029 g, 0.2 mmol) was added. After stirring for 1 h, the solvent was evaporated and the crude product washed with 5 ml of ether to afford the dark-violet powder **12** (85% yield). $^{31}P\{^1H\}$-NMR (81.004 MHz, $CDCl_3$): δ 49.54 (s, PCy_2). ^1H-NMR (200.135 MHz, $CDCl_3$): δ 1.05–2.50 (m, 24H, Cy + CH_2), 1.25 (d, $J = 7.0$ Hz, 3H, isopropyl CH_3), 1.27 (d, $J = 7.0$ Hz, 3H, isopropyl CH_3), 2.30 (s, 3H, CH_3 *p*-cymene), 2.60–3.10 (m, 3H, CH_2 + CH isopropyl), 5.92–6.00 (m, 1H, Cp′), 6.10 (d, $J = 6.0$ Hz, 1H, =CH *p*-cymene), 6.47–6.83 (m, 6H, =CH *p*-cymene + Cp′), 6.55 (s, 5H, Cp), 7.47 (pseudotriplet, $J = 7.4$ Hz, 4H, *o*-Ph), 7.76 (triplet, $J = 7.4$ Hz, 2H, *p*-Ph), 7.88 (d, $J = 7.4$ Hz, 4H, *m*-Ph). IR (KBr): 1964, cm^{-1}.

3.6. General procedure for the RCM of N,N-diallyltosylamide (**10**) promoted by the in situ Ti–Ru–allenylidene complex **12**

A 0.0067 g (0.026 mmol) sample of silver triflate was added to a solution of **8** (0.0195 g, 0.025 mmol) in CH_2Cl_2 (1 ml). The mixture was stirred for 1 h at r.t.;

then 1,1-diphenylprop-2-yn-1-ol (0.0057 g, 0.027 mmol) was added and the solution stirred for 30 min more at r.t. The solution was then evaporated to dryness and a deep-violet solid was thus obtained. To this solid, were added toluene (5 ml) and *N*,*N*-diallyltosylamide (**10**) (0.251 g, 1 mmol). The mixture was heated to 80 °C for 1 h. After evaporation of the solvent, *N*-tosyl-2,5-dihydropyrrole (**11**) was purified by flash chromatography on silica gel using diethyl ether–pentane (1:4) as eluent and obtained as a white solid for which analytical data are in full agreement with those reported in the literature [9b].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 166284 for compound **8**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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