Ruthenium titanocene and ruthenium titanium half-sandwich bimetallic complexes in catalytic cyclopropanation

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Abstract

The reaction of the phosphine functionalised titanium half-sandwich complexes **7**, **9** and **10** with the binuclear complex [(*p*-cymene)RuCl$_2$]$_2$ allowed the access to three new early-late bimetallic complexes (*p*-cymene)[(μ-η^5:η^1-C$_5$H$_4$(CH$_2$)$_n$PR$_2$)TiX$_3$]RuCl$_2$ (**11**–**13**). The structure of **11** (*n* = 0, X = Cl) has been confirmed by X-ray diffraction. The ruthenium titanium half-sandwich bimetallic complexes so formed and the ruthenium titanocene analogues **4**–**6** catalyse the addition of ethyl diazoacetate to styrene with high selectivity toward cyclopropanation versus metathesis contrary to the monometallic complexes (*p*-cymene)RuCl$_2$PR$_3$.
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Keywords: Titanium; Ruthenium; Heterobimetallic complexes; Cyclopropanation

1. Introduction

Early-late heterobimetallic complexes represent promising catalysts owing to the potential cooperative reactivity of widely different metals [1]. However, their synthesis often constitute a challenge and therefore a screening of their catalytic behaviour is not possible. To start with the design of such systems, we prepared early-late complexes which combined two well known fragments in catalysis field, a titanocene and an (arene)ruthenium moieties [2]. The bimetallic complexes **4**–**6** were obtained easily via the reaction of the titanocene phosphines **1**–**3** with the binuclear complex [(*p*-cymene)RuCl$_2$]$_2$ and have already proved to be active catalyst in ring closing metathesis [3] and in enol esters synthesis (Scheme 1) [4].

Here, we report the synthesis and the characterisation of a complementary series of ruthenium titanium half-sandwich bimetallic complexes. We feel that the titanium atom with a stronger Lewis acid character and a less crowded environment should be more able to interact with both ruthenium and substrate. Continuing our screening of catalytic reactions we focused then our work on cyclopropanation and we compared the activity of the bimetallic complexes with the monometallic species (*p*-cymene)RuCl$_2$PR$_3$.

2. Results and discussion

By using a strategy which has proved to be effective in the ruthenium titanocene bimetallic series [2,3], we first concentrate our efforts in the preparation of phosphine functionalised titanium half-sandwich complexes. The complex (η^5-C$_5$H$_4$PPh$_2$)TiCl$_3$ (**7**) was prepared according to an earlier method involving the synthesis of the trimethylsilyl cyclopentadiene derivative C$_5$H$_4$(SiMe$_3$)PPh$_2$, followed by treatment with TiCl$_4$ [5]. In order to expand our choice of ligands we attempted to replace the chloride atoms at the titanium atom in **7**

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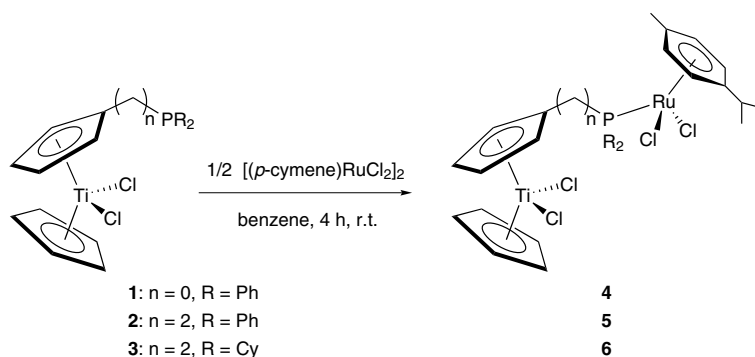
Scheme 1.

by alkoxy groups. We just began by refluxing **7** in methanol [6], but it resulted in products of decomposition. This preliminary result and the weak stability of **7** prompted us to investigate a second route previously described by Rausch and co-workers [7]. Thus, the reaction of the lithium diphenylphosphino cyclopentadienide with $ClTi(O^iPr)_3$ allowed us the access to the triisopropoxy titanium half-sandwich complex (η^5-$C_5H_4PPh_2)Ti(O^iPr)_3$ (**8**). In an extension of this procedure, we conducted a reaction between the lithium [(diphenylphosphino)ethyl] or [(dicyclohexylphosphino)ethyl] cyclopentadienides with $ClTi(O^iPr)_3$ and obtained the desired complexes $[\eta^5$-$C_5H_4(CH_2)_2$-$PPh_2]Ti(O^iPr)_3$ (**9**) and $[\eta^5$-$C_5H_4(CH_2)_2PCy_2]Ti(O^iPr)_3$ (**10**) in good yields. Both ^1H NMR spectra are very similar to the spectrum of **8**. All three show doublet and heptet resonances for the three isopropoxy groups and also two pseudotriplet resonances for the protons of the cyclopentadienyl ring. The ^{31}P NMR spectra of **9** and **10** appear as singlets with chemical shifts at -18.1 and -3.6 ppm, respectively.

Once a series of phosphine functionalised titanium half-sandwich complexes with complementary steric and electronic features has been prepared, we investigated their complexation with ruthenium. Thus, the reaction of **7** with 0.5 molar equivalent of the binuclear complex $[(p$-cymene)RuCl_2]_2$ gave the targeted early-late bimetallic complex **11** (Scheme 2).

The ^{31}P NMR chemical shift of the complex **11** at 23.5 ppm corresponds to a downfield shift of 31.5 ppm relatively to the free ligand. The ^1H NMR spectrum of **11** exhibits all the signals relative to both metallic fragments. Single crystal of **11**, suitable for X-ray diffraction was obtained by layering technique. ORTEP view of **11** is reported in Fig. 1 and selected bond lengths and an-
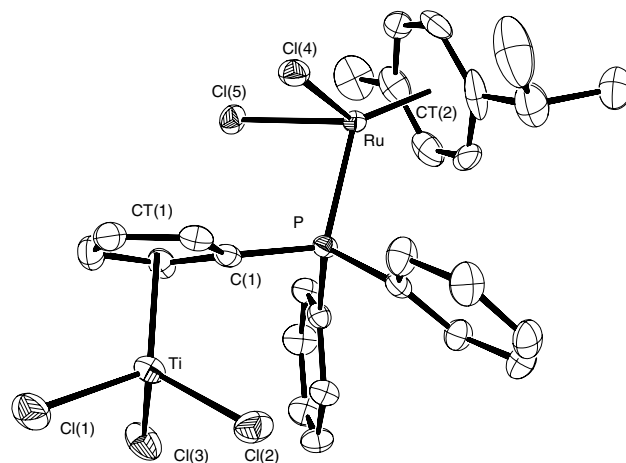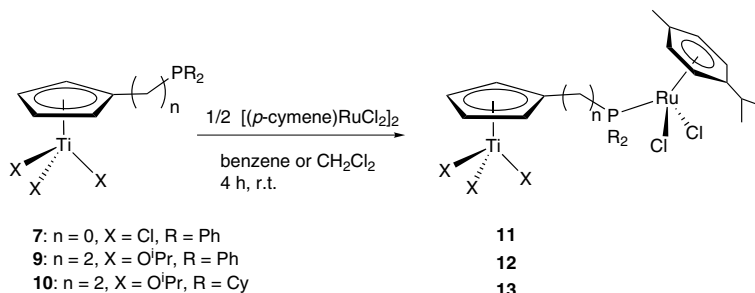

Fig. 1. ORTEP view of the compound **11** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and solvate molecules are omitted for clarity.

Scheme 2.

Table 1
Selected geometrical parameters [bond lengths (Å) and bond angle (°)] for **11**

Ti–Ct(1)	2.020(5)
Ti–Cl(2)	2.2249(14)
Ti–Cl(3)	2.2264(14)
Ti–Cl(1)	2.2329(14)
Ru–Ct(2)	1.711(5)
Ru–P	2.345(1)
Ru–Cl(4)	2.413(1)
Ru–Cl(5)	2.406(1)
P–C(1)	1.823(4)
Ct(1)–Ti–Cl(1)	113.99(13)
Ct(1)–Ti–Cl(2)	115.96(13)
Ct(1)–Ti–Cl(3)	115.76(13)
Cl(1)–Ti–Cl(2)	104.64(6)
Cl(1)–Ti–Cl(3)	100.46(6)
Cl(2)–Ti–Cl(3)	104.22(6)
Ct(2)–Ru–Cl(4)	128.05(15)
Ct(2)–Ru–Cl(5)	124.71(15)
Ct(2)–Ru–P	129.66(15)
P–Ru–Cl(5)	87.04(4)
P–Ru–Cl(4)	86.25(4)
Cl(5)–Ru–Cl(4)	87.16(4)
C(1)–P–Ru	113.04(13)
C(12)–P–Ru	116.92(14)
C(1)–P–Ru–Ct(2)	179.1

gles in Table 1. The structure consists in two fragments: a half titanocene trichloride moiety and a (*p*-cymene)RuCl$_2$ moiety linked by a phosphorus atom. The geometry of the CpTiCl$_3$ fragment is typically tetrahedral with structural parameters similar to the phosphine **4** [5]. The ruthenium moiety which presents a usual three-legged piano stool structure [8] lies on the exo face of the cyclopentadiene ring in an open area.

Then we carried out the coordination of the phosphine functionalised triisopropoxy titanium half-sandwich complexes **8–10** in similar conditions. The addition of **8** to the binuclear complex [(*p*-cymene)RuCl$_2$]$_2$ did not lead to the expected bimetallic complex but gave the monometallic complex (C$_5$H$_5$PPh$_2$)RuCl$_2$(*p*-cymene). The disengagement of the cyclopendiene results probably from a too big steric hindrance at the titanium atom. On the other hand, both other complexes **9** and **10**, with an ethylene spacer between the Cp ring and the phosphorus atom, allowed us the access to the bimetallic complexes **12** and **13** in quantitative yields. The ^{31}P NMR spectra of **12** and **13** appear as singlets with chemical shifts at 24.0 and 25.7 ppm, respectively, and the ^{1}H NMR spectra show all the signals relative to each metallic fragment.

Recently, it has been demonstrated that arene ruthenium complexes catalyse the addition of ethyldiazoacetate to styrene resulting in the formation of cyclopropane [9,10]. For comparative purposes, we examined this reaction with the aid of mono- and bimetallic spe-

cies in similar conditions (Table 2). This procedure, if successful, could provide good insight of the influence of the titanocene and of the titanium half-sandwich fragments on its late metal neighbour.

All the complexes showed an acceptable level of activity. The ratios *cis/trans* are quite comparable and always in favor of the *trans* isomer. Looking at these results more in detail, it appears that the early metal fragment plays a subtle role on the reactivity of the catalyst. Indeed, while (*p*-cymene)RuCl$_2$PPh$_3$ gives a better yield than (*p*-cymene)RuCl$_2$PCy$_3$, the bimetallic complexes Ti–Cp(CH$_2$)$_2$PCy$_2$/Ru **6** and **13** are more active than Ti–Cp(CH$_2$)$_2$PPh$_2$/Ru **5** and **12**. The competitive formation of stilbene could explain the inconsistency between these two results. Indeed a turnover number of 40 for the metathesis of styrene is reached with (*p*-cymene)RuCl$_2$PCy$_3$ while (*p*-cymene)RuCl$_2$PPh$_3$ gives only 10. This result confirms the fact that bulky and basic phosphine are required for metathesis reaction to turnover [11]. So the sluggish complex (*p*-cymene)RuCl$_2$PPh$_3$ leads to better yield in cyclopropane than (*p*-cymene)RuCl$_2$PCy$_3$. A similar phenomenon with bimetallic species is not observed. Indeed, in agreement with previous observations [3], it seems that the titanium fragment inhibits metathesis reaction and so allows the Ti–Cp(CH$_2$)$_2$PCy$_2$/Ru complexes **6** and **13** to be more active than Ti–Cp(CH$_2$)$_2$PPh$_2$/Ru **5** and **12**. It is also noteworthy that the overall best result was obtained with the bimetallic complex Ti–CpPPh$_2$/Ru **7** which belongs to the titanocene series with the closest distance between both metals. We should also mention that the adjunction of a catalytic amount of Cp$_2$TiCl$_2$ or CpTiCl$_3$ to a run performed with (*p*-cymene)RuCl$_2$PCy$_3$ has almost no effect on the reactivity and the selectivity of the reaction. At last this first comparison between the ruthenium titanium half-sandwich bimetallic complexes and the ruthenium titanocene bimetallic complexes is in favour of the titanocene series.

To account for the selectivity towards cyclopropanation versus metathesis, we presume that the vacant sites on the ruthenium atom resulting from the disengagement of the *p*-cymene ligand are probably partially blocked by a chelate effect of the metalloligand. Therefore, the coordination of styrene to the carbene–ruthenium complexes to form a ruthenacyclobutane is no more possible. Nevertheless, the bimetallic complexes would be able to transfer the carbene moiety onto styrene not coordinated to the ruthenium atom and so to catalyse the synthesis of cyclopropane. This bimolecular process has been recently proposed for olefin cyclopropanation catalysed by ruthenium–arene complexes containing chelating phosphine–arene ligands [9b]. The splitting of the heterobimetallic species during catalysis into monometallic ruthenium complexes containing phosphines with pendent cyclopentadienes could also explain this selectivity. Nevertheless, both ruthenium

Table 2
Addition of ethyl diazoacetate to styrene catalysed by the heterobimetallic complexes **4**–**6** and **11**–**13** or by the monometallic complexes (*p*-cymene)RuCl$_2$PR$_3$[a]
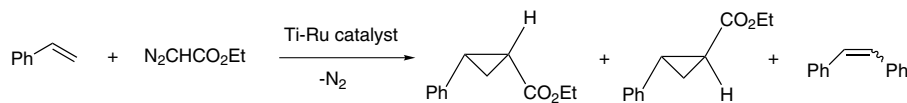
Catalyst	Cyclopropanation		Metathesis
	Yield (%)[b]	*trans/cis*[c]	TON[b]
(*p*-Cymene)RuCl$_2$PPh$_3$	57	62/38	10
(*p*-Cymene)RuCl$_2$PCy$_3$[d]	46	55/45	40
CpTiCl$_2$–CpPPh$_2$/Ru (**4**)	60	62/38	1
CpTiCl$_2$–Cp(CH$_2$)$_2$PPh$_2$/Ru (**5**)	38	65/35	0
CpTiCl$_2$–Cp(CH$_2$)$_2$PCy$_2$/Ru (**6**)	49	57/43	4
TiCl$_3$–CpPPh$_2$/Ru (**11**)	36	65/35	1
Ti(O^{i}Pr)$_3$–Cp(CH$_2$)$_2$PPh$_2$/Ru (**12**)	26	62/38	0
Ti(O^{i}Pr)$_3$–Cp(CH$_2$)$_2$PCy$_2$/Ru (**13**)	47	64/36	1

[a] Conditions: catalyst (0.01 mmol), olefin (20 mmol), ethyl diazoacetate (1 mmol) diluted with the substrate up to 1 ml, 60 °C, addition time (4 h), overall reaction time (4.25 h).
[b] Determinated by GC using *n*-decane as internal standard.
[c] Determinated by GC analysis.
[d] Demonceau and Noels [9c] have recently obtained a closely similar result.

titanocene bimetallic complexes and ruthenium titanium half-sandwich bimetallic complexes should give, after splitting, the same ruthenium complexes and so far similar catalytic results. Moreover in case of the bimetallic complexes **4** and **11**, the phosphorus atom being directly tethered to the cyclopentadienyl ring, the splitting of the bimetallic complexes could not lead to a chelating ruthenium complex.

3. Conclusion

This study provides a straightforward access to three new early-late bimetallic complexes. Preliminary assessment in catalytic cyclopropanation of styrene with ruthenium titanium half-sandwich bimetallic complexes and ruthenium titanocene bimetallic complexes as catalyst revealed a cooperative effect. In fact, the early metal fragment prevents any metathesis reaction to turn over and so focused the catalytic activity of the late metal on cyclopropanation. Further studies to rationalised the different catalytic behaviours of the mono- and bimetallic complexes are under progress.

4. Experimental

All reactions were carried out under an atmosphere of purified argon. The solvents and eluents were dried by the appropriate procedure and distilled under argon immediately before use. Standard Schlenk techniques and conventional glass vessels were employed. Elemen-tal analyses were carried out with a EA 1108 CHNS-O FISONS Instruments. ^{1}H (500 MHz) and ^{31}P{^{1}H} (202 MHz) spectra were collected on a Bruker 500 MHz Avance DRX spectrometer. Chemical shifts are relative to internal TMS (^{1}H) or external H$_3$PO$_4$ (^{31}P). The catalytic cyclopropane synthesis was monitored on a GC-17A SHIMADZU with a 007 Methyl 5% Phenyl Silicone Capillary column (30 m). The titanocene phosphines **1**, **2** and **3** and the heterobimetallic complexes **4**, **5** and **6** were synthesised as previously reported [2,3]. The cyclopentadienyl phosphine ligands Li[C$_5$H$_4$(CH$_2$)$_2$PR$_2$] [12] and the complexes (η^5-C$_5$H$_4$PPh$_2$)TiCl$_3$ **7** [5], (η^5-C$_5$H$_4$PPh$_2$)Ti(O^{i}Pr)$_3$ [7], (*p*-cymene)RuCl$_2$(PR$_3$) [13], were prepared according to the literature methods.

4.1. Complex 9

A solution of 0.5 g (1.7 mmol) of Li[C$_5$H$_4$-(CH$_2$)$_2$PPh$_2$] in 20 ml of THF was added slowly at 0 °C to an equimolar solution of ClTi(O^{i}Pr)$_3$ in 20 ml of THF. After stirring for 3 h at room temperature, the solvent was removed under vacuo. The residue was extracted with 80 ml of pentane, filtered through celite, and evaporated to dryness to afford a yellow oil (84% yield). ^{31}P{^{1}H} NMR (202 MHz, CDCl$_3$) δ −14.0 (s, PPh$_2$). ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.26 (d, *J* = 6.5 Hz, 18H, ^{i}Pr), 2.52–2.54 (m, CH$_2$, 2H), 2.96–2.98 (m, CH$_2$, 2H), 4.61 (hept, *J* = 6.5 Hz, 3H, ^{i}Pr), 6.11 (pseudo-triplet, *J* = 2.5 Hz, Cp, 2H), 6.16 (pseudotriplet, *J* = 2.5 Hz, Cp, 2H), 7.17–7.23 (m, 6H, Ph), 7.57–7.60 (m, 4H, Ph). Anal. Calc. for C$_{28}$H$_{39}$O$_3$PTi (502.45): C, 66.93; H, 7.82. Found: C, 66.71; H, 7.77%.

4.2. Complex 10

This compound was obtained following the above procedure but with $Li[C_5H_4(CH_2)_2PCy_2]$ (yellow oil, 98% yield). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6) δ −3.60 (s, PCy_2). ^1H NMR (500 MHz, C_6D_6) δ 1.27 (d, J = 6.1 Hz, 18H, ^iPr), 1.30–1.94 (m, 22H, Cy), 1.85 (m, 2H, CH_2), 3.00 (m, 2H, CH_2), 4.64 (hept, J = 6.1 Hz, 3H, ^iPr), 6.14 (pseudotriplet, J = 2.3 Hz, Cp, 2H), 6.17 (pseudotriplet, J = 2.3 Hz, Cp, 2H). Anal. Calc. for $C_{28}H_{51}O_3PTi$ (514.54): C, 65.36; H, 9.99. Found: C, 65.12; H, 10.63%.

4.3. Complex 11

A 25 ml Schlenk flask was charged under argon with **7** (0.14 g, 0.35 mmol), $[(p\text{-cymene})RuCl_2]_2$ (0.11 g, 0.17 mmol) and degassed benzene. The mixture was stirred at room temperature for 4 h during which time a brick precipitate slowly formed. The solvent was removed by filtration and the red residue was dried under vacuum (brick-red powder, 75% yield). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$) δ 23.50 (s, PPh_2). ^1H NMR (500 MHz, $CDCl_3$) δ 1.05 (d, J = 6.9 Hz, 6H, ^iPr), 1.71 (s, 3H, CH_3), 2.60 (hept, J = 6.9 Hz, 1H, ^iPr), 5.05 (d, J = 6.1 Hz, 2H, p-cymene), 5.24 (d, J = 6.1 Hz, 2H, p-cymene), 6.82 (pseudotriplet, J = 3.7 Hz, Cp, 2H), 7.14 (pseudo-triplet, J = 3.7 Hz, Cp, 2H), 7.48–7.56 (m, 6H, Ph), 8.10–8.15 (m, 4H, Ph). Anal. Calc. for $C_{27}H_{28}Cl_5PRuTi$ (709.69): C, 45.69; H, 3.98. Found: C, 45.36; H, 4.49%.

4.3.1. X-ray structure determination of the complex 11

Single-crystal X-ray diffraction study of **11**. Intensities were collected on an Enraf-Nonius KappaCCD diffractometer at 110 K using Mo Kα radiation. The structure was solved via a Patterson search program [14] and refined with full-matrix least-squares methods [15] based on $|F^2|$ with the aid of the WINGX program [16]. All non-hydrogen atoms were refined with anisotropic thermal parameters (except for one CH_2Cl_2 disordered solvate molecule). Hydrogen atoms were included with a riding model with isotropic temperature factors fixed to 1.2 times (1.5 for methyl groups) those of the corresponding parent atoms. One CH_2Cl_2 molecule is located close to a twofold axis and was isotropically refined with an occupation factor of 0.5 with restrained bond distances and angle. The essential crystallographic parameters are listed in Table 3.

Table 3
Crystal data and structure refinement for **11**

Formula	$C_{27}H_{28}PCl_5RuTi \cdot 1.5CH_2Cl_2$
Molecular weight	837.07
T (K)	110(2)
Crystal system	Monoclinic
Space group	$C2/c$
a (Å)	31.3285(4)
b (Å)	13.5589(3)
c (Å)	19.3432(3)
β (°)	126.620(1)
V (Å^3)	6594.7(2)
Z	8
$F(0\,0\,0)$	3352
D_{calc} (g/cm^3)	1.686
Diffractometer	Enraf-Nonius KappaCCD
Scan type	Mixture of ϕ rotations and ω scans
λ (Å)	0.71073
μ (mm^{-1})	1.417
Crystal size (mm^3)	$0.50 \times 0.45 \times 0.45$
$\sin(\theta)/\lambda_{max}$ (Å^{-1})	0.65
Index ranges	$-36 \leqslant h \leqslant 40, -16 \leqslant k \leqslant 17, -25 \leqslant l \leqslant 24$
Absorption correction	SCALEPACK
Number of reflections collected (RC)	19067
Number of independent reflections (IRC) (R_{int})	7494 (0.029)
IRCGT = IRC and $[I > 2\sigma(I)]$	6001
Refinement method	Full-matrix least-square on F^2
Data/restraints/parameters	7494/3/360
R for IRCGT	R_1[a] = 0.0511, wR_2[b] = 0.1247
R for IRC	R_1[b] = 0.0683, wR_2[b] = 0.1341
Goodness-of-fit (GoF)[c]	1.042
Largest difference peak and hole (e Å^{-3})	2.38 and −1.73

[a] $R_1 = \sum(\|F_o| - |F_c\|)/\sum|F_o|$.
[b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum[w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + 47.12P + (0.061P)^2]$ where $P = (\max(F_o^2, 0) + 2^*F_c^2)/3$.
[c] $GoF = [\sum w(F_o^2 - F_c^2)^2/(N_o - N_v)]^{1/2}$.

4.4. Complex 12

A 25 ml Schlenk flask was charged under argon with **9** (0.5 g, 1 mmol), [(*p*-cymene)RuCl$_2$]$_2$ (0.3 g, 0.5 mmol) and dichloromethane. After stirring for 4 h at room temperature, the solvent was removed in vacuo and the crude residue washed by 2 × 5 ml of pentane to afford a red powder (100% yield). ^{31}P{^{1}H} NMR (202 MHz, CDCl$_3$) δ 24.00 (s, PPh$_2$). ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.90 (d, *J* = 6.9 Hz, 6H, ^{i}Pr), 1.20 (d, *J* = 6.1 Hz, 18H, ^{i}Pr), 1.84 (s, 3H, CH$_3$), 2.70 (m, 2H, CH$_2$), 2.76 (hept, *J* = 6.9 Hz, 1H, ^{i}Pr), 3.55 (m, 2H, CH$_2$), 4.56 (hept, *J* = 6.1 Hz, 3H, ^{i}Pr), 5.04 (d, *J* = 6.0 Hz, 2H, *p*-cymene), 5.11 (d, *J* = 6.0 Hz, 2H, *p*-cymene), 6.00 (pseudotriplet, *J* = 2.4 Hz, Cp, 2H), 6.02 (pseudotriplet, *J* = 2.4 Hz, Cp, 2H), 7.23–7.27 (m, Ph, 6H), 8.07–8.10 (m, Ph, 4H). Anal. Calc. for C$_{38}$H$_{53}$Cl$_2$O$_3$PRuTi (808.64): C, 56.44; H, 6.61. Found: C, 56.40; H, 6.29%.

4.5. Complex 13

This compound was obtained following the above procedure but with **10** (red powder, 100% yield). ^{31}P{^{1}H} NMR (202 MHz, CDCl$_3$) δ 25.70 (s, PPh$_2$). ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.10 (d, *J* = 6.1 Hz, 18H, ^{i}Pr), 1.25 (d, *J* = 6.9 Hz, 6H, ^{i}Pr), 1.39–2.16 (m, 22H, Cy), 2.07 (s, 3H, CH$_3$), 2.30 (m, 2H, CH$_2$), 2.71 (m, 2H, CH$_2$), 2.82 (hept, *J* = 6.9 Hz, 1H, ^{i}Pr), 4.49 (hept, *J* = 6.1 Hz, 3H, ^{i}Pr), 5.52–5.56 (m, 4H, *p*-cymene), 6.00 (pseudotriplet, *J* = 2.7 Hz, Cp, 2H), 6.06 (pseudotriplet, *J* = 2.7 Hz, Cp, 2H). Anal. Calc. for C$_{38}$H$_{65}$Cl$_2$O$_3$PRuTi (820.74): C, 55.61; H, 7.98. Found: C, 55.59; H, 7.83%.

4.6. Cyclopropanations

Cyclopropanation reactions were performed according to the procedure described by Demonceau and co-workers [9]. Ethyl diazoacetate (1 mmol diluted by styrene up to 1ml) was added over the period of 4 h with the aid of a syringe pump to a solution of styrene (20 mmol) containing the catalyst (0.01 mmol) and 1 mmol of decane (internal standard). The reaction was stirred at 60 °C during an overall time of 4.25 h. Product yields were determined by GC using the experimentally measured cyclopropane–decane response ratio.

5. Supplementary material

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 237979. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223336033 or e-mail: deposit@ccdc.cam.ac.uk).

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