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Bimetallic complexes with ruthenium and tantalocene moieties: Synthesis and use in a catalytic cyclopropanation reaction

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Abstract

The reaction of the tantalocene dichloride monophosphines (**1**–**2**) with the binuclear complex [(*p*-cymene)$RuCl_2$]$_2$ gives the heterobimetallic compounds (*p*-cymene)[(η^5-C_5H_5)(μ-η^5:η^1-$C_5H_4(CH_2)_2PR_2$)$TaCl_2$]$RuCl_2$ (**3**–**4**). The air oxidation of these bimetallic species **3**–**4**, leads to the cationic hydroxo tantalum ruthenium derivatives **5**–**6**. The last ones are easily deprotonated by a base to afford the oxo analogues **7**–**8**. A preliminary assessment in catalytic cyclopropanation of styrene with tantalum ruthenium bimetallic complexes **3**–**8** as precatalysts revealed a cooperative effect with a subtle role of the early metal fragment.

Keywords: Tantalum; Ruthenium; Heterobimetallic complexes; Cyclopropanation

1. Introduction

The preparation and the study of "early–late" heterobimetallic complexes is a particularly active research area in organometallic chemistry [1]. Part of the increasing interest in this investigation is the hope that these species might exhibit unusual catalytic activity due to a cooperative reactivity between the electron-deficient and the electron-rich metals [2]. Convinced that a marked cooperative effect may occur rather with a joined binuclear catalysts than with a mixture of their dissociated monometallic analogues, we designed our complexes around cyclopentadienylphosphine ligands able to strongly bind both "early" and "late" fragments and to maintain them in a close proximity [3]. Previous studies in our laboratory using this linker gave rise to a straightforward access to several titanium ruthenium and titanium rhodium complexes [4]. These last ones have been obtained in sufficient amount to carry out a screening of their catalytic behavior and they have already proved to be efficient precatalysts in ring closing metathesis, in enol esters synthesis and in cyclopropanation [5]. These results prompt us to extend this family of heterobimetallic catalysts by replacing the titanium atom in the "early" fragment with a less oxophilic metal such as tantalum. Herein, we report the synthesis and the characterization of a series of new tantalum ruthenium bimetallic complexes. Work was then focused on cyclopropanation as a representative reaction in order to compare the activity of the bimetallic complexes **3**–**8** with the monometallic species (*p*-cymene)$RuCl_2PR_3$.

2. Results and discussion

Our strategy to construct the bimetallic complexes consists first in synthesizing the tantalocene dichloride phosphine compounds and then coordinating these early metal ligands to the late metal fragment. One aspect of interest of this approach is the structural flexibility of the tantalocene phosphine. Indeed the basicity and the crowding of the phosphine can be modulated by appropriate

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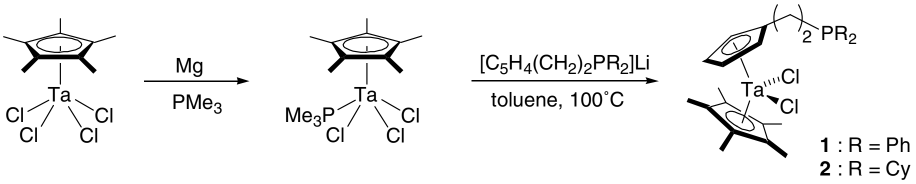
substitution. Moreover, the introduction of an alkyl spacer between the cyclopentadienyl ring and the phosphino group might prevent steric constraints on the complex and will allow greater conformational freedom of the two metal coordination spheres. Accordingly, we have decided to use (phosphinoethyl)cyclopentadienyl ligands, one with a diphenylphosphino group and another with a bulkier and more basic dicyclohexylphosphino moiety. The synthesis of the metallophosphines **1** and **2** Cp*[η^5-$C_5H_4(CH_2)_2PR_2$]$TaCl_2$ is adapted to Bercaw's method as outline in Scheme 1 [6]. The starting material Cp*$TaCl_4$ is reduced by magnesium in the presence of trimethylphosphine to afford the red intermediary Cp*$TaCl_3PMe_3$ which reacts with [$C_5H_4(CH_2)_2PR_2$]Li to lead to the desired products **1** and **2**. Complexes **1** and **2** have been isolated in good yields as green solids. They display the eight-line ESR spectra characteristic of bis(cyclopentadienyl)tantalum (IV) derivatives [7]. Although **1** and **2** are paramagnetic products, their ^{31}P NMR spectra in C_6D_6 show slightly broadened singlets at $\delta = -17.4$ ppm for **1** and at $\delta = -6.0$ ppm for **2** as expected for free metallophosphines.

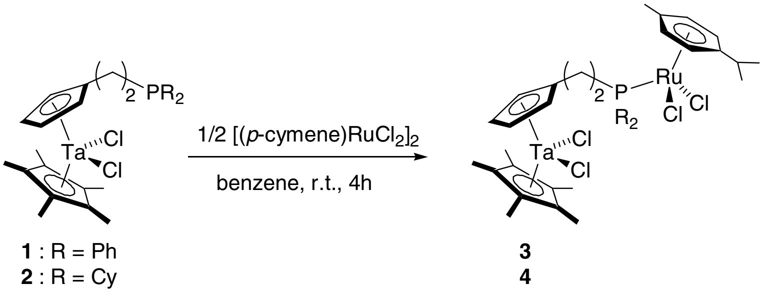
Organic phosphines can easily cleave the chloride bridges of the binuclear complex [(*p*-cymene)$RuCl_2$]$_2$ to lead to (*p*-cymene)$RuCl_2PR_3$ complexes [8]. On the basis of this result, we carried out experiments by using the metallophosphines **1** and **2** with the ruthenium binuclear complex [(*p*-cymene)$RuCl_2$]$_2$ in dichloromethane. The desired heterobimetallic complexes **3** and **4** were obtained in good yields after 4 h at room temperature (Scheme 2). The characterization of **3** and **4** are based upon elemental analysis, ESR and ^{31}P NMR spectroscopic data. The ^{31}P NMR chemical shifts of **3** and **4** at $\delta = 21.4$ and $\delta = 22.1$ ppm correspond to a downfield shift of 38.8 and 28.1 ppm, respectively, to free metalloligands (**1** and **2**). These results are indicative of the coordination of the phosphorus atoms to the ruthenium metal. Moreover, ESR spectra still exhibit the eight-line characteristic of tantalum (IV) dichloride derivatives.

Recently, we have described a new route to cationic hydroxo tantalum (V) species by air oxidation of tantalocene dichloride complexes. The hydroxo complexes can be easily deprotonated to generate the corresponding oxo derivatives [9]. In the aim to expand substantially the number of Ta–Ru bimetallic complexes, we studied the air oxidation of the Ta–Ru heterobimetallic species **3** and **4**. A THF solution of **3** and **4** was exposed to air for 12 h affording a red precipitate identified as the hydroxo bimetallic complexes **5** and **6** (Scheme 3). The ^{31}P NMR spectra of **5** and **6** exhibit singlets at $\delta = 23.8$ and $\delta = 27.9$ ppm which confirms that the phosphorus atom remains coordinated in both cases to the ruthenium metal. The ^1H NMR spectra show all the signals attempted for both metallic fragments. The cyclopentadienyl ring protons appear as four signals, which confirmed the loss of symmetry expected by the substitution of one chloride atom by a hydroxyl group on the tantalum atom. Moreover, the strong deshielding of these signals (from $\delta = 5.53$ to 7.00 ppm) is in agreement with a cationic tantalum (V) species. IR spectra exhibit a broad and strong peak from 2100 to 2900 cm^{-1} corresponding to the OH stretching band which is in accordance with our previous study [9].

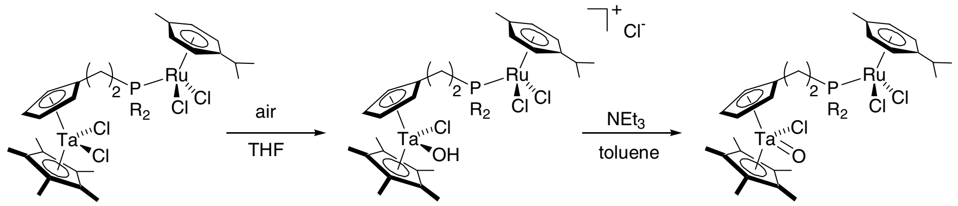
Finally, **6** has been partially characterized using single-crystal X-ray diffraction, although because of extensive disorder of the solvate molecule(s), only a partial structure refinement was possible. The electron difference density map was not sufficiently clear to successfully model a badly disordered solvent molecule and so the BYPASS procedure implemented in the PLATON program [10] was used to handle this problem. In this procedure the contribution of the solvent electron density is substracted to the structure factors. Despite the poor quality of the data, the experiment does, however, confirm the basic connectivity around the



Scheme 1.



Scheme 2.



3 : R = Ph
4 : R = Cy

5
6

7
8

Scheme 3.

metallic center (for information, the final residuals with the solvent-corrected data are: $wR_2 = 0.135$ for all data, $R_1 = 0.050$ for 6826 data with $I > 2\sigma(I)$, GOF = 0.94). An ORTEP view of **6** is shown in Fig. 1. This view shows that an oxygen atom substitutes a chlorine one on the tantalum center. The Ta–O bond's length (1.894(4) Å) is in agreement with the values of the literature for a simple bond [9,11]. Moreover the O–Ta–Cl(1) angle of 98.9(2)° in the "early" fragment corresponds to the value expected for a d^0 tantalum (V) cationic hydroxo species [9].

Treatment of **5** and **6** with NEt$_3$ in toluene for two hours gave, after evaporation of the solvent, the oxo bimetallic species **7** and **8** as red powders (Scheme 3). The ^{1}H NMR spectra exhibit four signals for the four cyclopentadienyl ring protons less deshielding than those of **5** and **6** which results from the loss of the cationic character of the tantalum atom. Finally, the IR spectra show a strong peak located at 810 cm^{-1} for **7** and 813 cm^{-1} for **8** which correspond to the Ta=O stretching band [9,12].

For more than a decade, the arene-ruthenium type precatalysts have been particularly developed for the olefin's cyclopropanation reaction [13,14]. In this context, we have been interested in comparing the catalytic activities of (p-cymene)RuCl$_2$(PR$_3$) complexes and heterobimetallic Ta–Ru complexes. Cyclopropanation experiments were performed using styrene as model substrate and ethyl diazoacetate as carbene precursor. We carried out the reaction in styrene, during four hours at 60 °C, by using a catalytic amount of the bimetallic complexes **3**–**8**. For comparative purposes, the monometallic complexes (p-cymene)RuCl$_2$(PPh$_3$) and (p-cymene)RuCl$_2$(PCy$_3$) were tested in similar conditions (see Table 1).

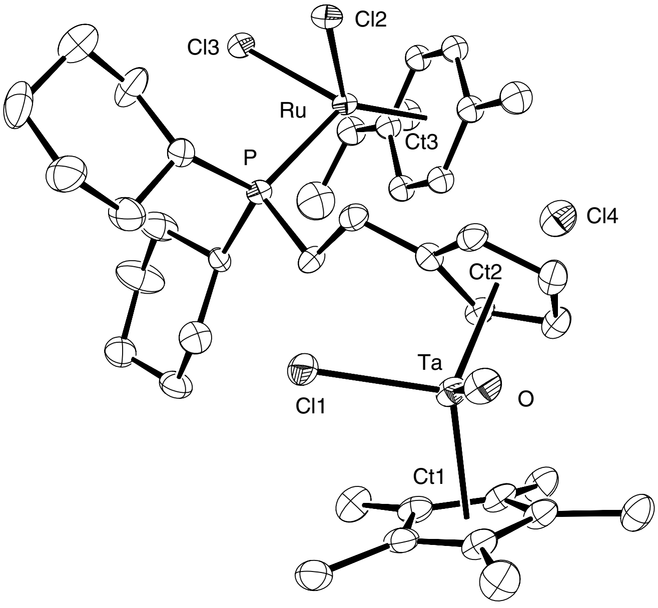
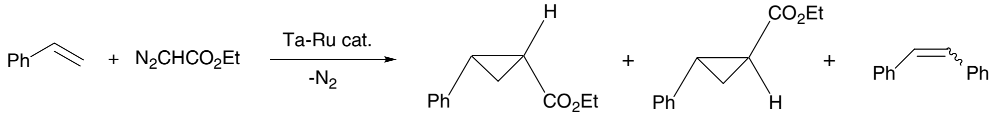


Fig. 1. ORTEP view of the bimetallic complex **6**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) for compound **6**: Ta–O = 1.894(4). O–Ta–Cl(1) = 98.9(2).

A comparison of the reactivity patterns between the mono- and the bimetallic complexes show that all the complexes catalyze the reaction with a comparable level of activity. Moreover, the ratio *cis*/*trans* are similar and always in favor of the *trans* isomer. At first sight, these results show that the ruthenium moiety is the active metal center, and that the tantalocene acts as a simple spectator atom. Looking at these results more in detail, it appears that the bimetallic complexes are more selective than the monometallic ones in the way that they do not catalyze the competitive formation of stilbene. At this point, it is worth mentioning that the adjunction of a catalytic amount of Cp*CpTaCl$_2$ to a run performed with (p-cymene)RuCl$_2$PCy$_3$ has almost no effect on the selectivity of this reaction. Therefore, it can be assumed that both metallic fragments should be tethered to exhibit a significant cooperative effect. Finally, the nature of the ligands on the tantalum atom plays also a role. Indeed, the bimetallic complexes **4**, **6** and **8** with the same dicyclohexylphosphino group mediate the cyclopropanation of styrene with ethyl diazoacetate with comparable chemo- and diastereoselectivity but with different yields, the overall best result being obtained with the cationic hydroxo tantalum ruthenium complex **6** (61% yield). To account for the selectivity towards cyclopropanation versus metathesis, we presume that this chemoselectivity occurs thanks to a multidentate ligand effect rather than to the bimetallic effect itself. In accordance with our previous study related to the titanium ruthenium bimetallic complexes in catalytic cyclopropanation, we propose that the vacant sites on the ruthenium atom, resulting from the disengagement of the p-cymene, are partially occupied by a chelate effect of the metalloligand which prevents the coordination of the styrene and so inhibits the formation of metathesis by-products.

Table 1
Addition of ethyl diazoacetate to styrene catalyzed by the heterobimetallic complexes **3**–**8** or by the monometallic complexes (*p*-cymene)RuCl$_2$PR$_3$[a]



Catalyst	Cyclopropanation[a]		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
TaCl$_2$—PPh$_2$ [Ru] **3**	44	62/38	0.4
TaCl$_2$—PCy$_2$ [Ru] **4**	51	61/39	0.8
Ta^{+}OH—PPh$_2$ [Ru] **5**	33	59/41	0.4
Ta^{+}OH—PCy$_2$ [Ru] **6**	61	62/38	0.4
Ta=O—PPh$_2$ [Ru] **7**	42	62/38	0.4
Ta=O—PCy$_2$ [Ru] **8**	41	62/38	1.2

[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] Determined by GC using *n*-decane as internal standard.

[c] Determined by GC analysis.

[d] Demonceau and Noels have recently obtained a closely similar result [13c].

3. Conclusion

We report the preparation of six new heterobimetallic complexes containing both tantalocene and ruthenium(arene) fragments. These synthesis involves first the preparation of two tantalocene dichloride phosphines followed by their coordination to the ruthenium binuclear complex [(*p*-cymene)RuCl$_2$]$_2$. Then, the air-oxidation of the tantalocene dichloride fragment within the bimetallic complexes affords the corresponding cationic hydroxo tantalum ruthenium heterobimetallic complexes. The last one can be easily deprotonated to form the oxo bimetallic complexes. All these new bimetallic complexes have been tested in catalytic cyclopropanation of styrene with ethyl diazoacetate in comparison with their monometallic ruthenium analogues ((*p*-cymene)RuCl$_2$(PPh$_3$) and (*p*-cymene)RuCl$_2$(PCy$_3$)). The results show that the active catalyst is the ruthenium and that the early metal fragment within these bimetallic systems prevents any metathesis reaction to turn over and so focuses the catalytic activity of the late metal on cyclopropanation. Further studies to rationalize the different catalytic behaviors of the bimetallic complexes are under progress.

4. Experimental

All the reactions were carried out under an atmosphere of purified argon. The solvents were dried by the appropriate procedure and distilled under argon immediately before use. Standard Schlenk techniques and conventional glass vessels were employed. Elemental analyses were carried out with a EA 1108 CHNS-O FISONS. ^{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). ESR spectra have been collected on a Bruker ESP 300 spectrometer. Infrared spectra were obtained with a Bruker IFS 66v, Perkin–Elmer 1600 FTIR instrument. The catalytic cyclopropane synthesis was monitored on a GC-17A SHIMADZU with a 007 methyl 5% phenyl silicone capillary column (30 m). The cyclopentadienyl phosphine ligands [C$_5$H$_4$(CH$_2$)$_2$PR$_2$]Li [15] and the complexes Cp*TaCl$_4$ [6], (*p*-cymene)RuCl$_2$(PR$_3$) [8], were prepared according to the literature methods.

4.1. Complex **1**

Compound **1** was synthesized according to Bercaw's method reported for Cp*CpTaCl$_2$ [6] with minor modifications. Cp*TaCl$_4$ (4.58 g, 10 mmol) was reduced with magnesium (0.12 g, 5 mmol) in THF (50 mL) in the presence of PMe$_3$ (0.76 g, 10 mmol). Removal of the solvent afforded a red residue which was treated with Li[C$_5$H$_4$-(CH$_2$)$_2$PPh$_2$] (2.94 g, 10 mmol) in toluene (50 mL) at 100 °C. After 12 h of stirring, extraction and crystallization from CH$_2$Cl$_2$ afforded the green paramagnetic product **1** (green powder, 80% yield). ^{31}P{^{1}H} NMR (202 MHz, CDCl$_3$) δ −17.4 (s, PPh$_2$). The ESR spectrum in toluene showed an eight-line spectrum: $g_{\text{iso}} = 1.9293$; $A_{\text{Ta,iso}} = 113.98$ G. Anal. Calc. for C$_{29}$H$_{33}$Cl$_2$PTa (664.44): C, 52.42; H, 5.02. Found: C, 52.60; H, 5.10%.

4.2. Complex **2**

This compound was obtained following the above procedure but with Li[C$_5$H$_4$(CH$_2$)$_2$PCy$_2$] (green powder, 81% yield). ^{31}P{^{1}H} NMR (202 MHz, C$_6$D$_6$) δ −6.0 (s, PCy$_2$). The ESR spectrum in toluene showed an eight-line spectrum: $g_{iso} = 1.9285$; $A_{Ta,iso} = 120.35$ G. Anal. Calc. for $C_{29}H_{45}Cl_2PTa$ (676.56): C, 51.47; H, 6.72. Found: C, 51.10; H, 6.60%.

4.3. Complex **3**

A 25 ml Schlenk flask was charged under argon with **1** (0.23 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 this time a brick red precipitate was 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 21.4 (s, PPh_2). The ESR spectrum in toluene showed an eight-line spectrum: $g_{iso} = 1.9238$; $A_{Ta,iso} =$ 113.03 G. Anal. Calc. for $C_{39}H_{47}Cl_4PRuTa$ (970.65): C, 48.25; H, 4.89. Found: C, 48.01; H, 4.71%.

4.4. Complex **4**

This compound was obtained following the above procedure but with **2** (brick-red powder, 69% yield). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$) δ 22.1 (s, PCy_2). The ESR spectrum in toluene showed an eight-line spectrum: $g_{iso} = 1.9245$; $A_{Ta,iso} = 119.30$ G. Anal. Calc. for $C_{39}H_{59}Cl_4PRuTa$ (982.77): C, 47.66; H, 6.06. Found: C, 47.37; H, 5.90%.

4.5. Complex **5**

A 25 ml Schlenk flask was charged under argon with **3** (0.33 g, 0.35 mmol) in 30 mL of degassed THF. The mixture was stirred at room temperature under air atmosphere for 12 h during this time a brick precipitate was slowly formed. The resulting red suspension was filtered, the solid washed with 2 × 5 mL of THF and dried under vacuum to afford a red powder (40% yield). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$) δ 23.8 (s, PPh_2). ^1H NMR (500 MHz, $CDCl_3$) δ 0.87 (d, $J = 6.9$ Hz, 6H, ^{i}Pr), 1.89 (s, 3H, CH_3), 2.16 (s, 15H, Cp*), 2.54 (hept, $J = 6.9$ Hz, 1H, ^{i}Pr), 2.56–2.88 (m, 4H, CH_2), 5.09–5.15 (m, 2H, *p*-cymene), 5.29–5.31 (m, 2H, *p*-cymene), 5.53 (m, 1H, Cp), 5.75 (m, 1H, Cp), 6.63 (m, 1H, Cp), 7.00 (m, 1H, Cp), 7.50–7.54 (m, 6H, Ph), 8.07–8.10 (m, 4H, Ph). IR (KBr, cm^{-1}): ν_{Ta-OH} 2100–2900 (vs). Anal. Calc. for $C_{39}H_{48}Cl_4OPRuTa$ (987.66): C, 47.42; H, 4.91. Found: C, 47.59; H, 5.07%.

4.6. Complex **6**

This compound was obtained following the above procedure but with **4** (red powder, 43% yield). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$) δ 27.9 (s, PCy_2). ^1H NMR (500 MHz, $CDCl_3$) δ 1.29 (d, $J = 6.9$ Hz, 6H, ^{i}Pr), 1.30–2.04 (m, 22H, Cy), 2.09 (s, 3H, CH_3), 2.17 (s, 15H, Cp*), 2.54 (hept, $J = 6.9$ Hz, 1H, ^{i}Pr), 2.83–2.89 (m, 2H, CH_2), 3.11–3.13 (m, 2H, CH_2), 5.54–5.57 (m, 2H, *p*-cymene), 5.61–5.63 (m, 2H, *p*-cymene), 5.80 (m, 1H, Cp), 5.82 (m, 1H, Cp), 6.66 (m, 1H, Cp), 6.67 (m, 1H, Cp). IR (KBr, cm^{-1}): ν_{Ta-OH} 2100–2900 (vs). Anal. Calc. for $C_{39}H_{60}Cl_4OPRuTa$ (999.78): C, 46.85; H, 6.06. Found: C, 46.84; H, 6.18%.

4.7. Complex **7**

To a solution of **5** (0.5 g, 0.50 mmol) in 10 mL of toluene, is added an excess of triethylamine. The mixture is stirred for 2 h at room temperature. Salts are filtered through a path of celite, solvent is removed under vacuum to afford a red powder (95% yield). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$) δ 25.1 (s, PPh_2). ^1H NMR (500 MHz, $CDCl_3$) δ 0.80 (d, $J = 6.9$ Hz, 3H, ^{i}Pr), 0.84 (d, $J = 6.9$ Hz, 3H, ^{i}Pr), 1.90 (s, 3H, CH_3), 2.00 (s, 15H, Cp*), 2.44–2.48 (m, 2H, CH_2), 2.54 (hept, $J = 6.9$ Hz, 1H, ^{i}Pr), 2.80–2.84 (m, 2H, CH_2), 5.07–5.14 (m, 2H, *p*-cymene), 5.27–5.31 (m, 2H, *p*-cymene), 5.58 (m, 1H, Cp), 5.63 (m, 1H, Cp), 5.71 (m, 1H, Cp), 5.73 (m, 1H, Cp), 7.48–7.51 (m, 6H, Ph), 7.91–7.95 (m, 4H, Ph). IR (KBr, cm^{-1}): $\nu_{Ta=O}$ 810 (s). Anal. Calc. for $C_{39}H_{47}Cl_3OPRuTa$ (951.20): C, 49.24; H, 4.99. Found: C, 49.10; H, 5.02%.

4.8. Complex **8**

This compound was obtained following the above procedure but with **6** (red powder, 93% yield). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$) δ 26.0 (s, PCy_2). ^1H NMR (500 MHz, $CDCl_3$) δ 1.26 (d, $J = 6.9$ Hz, 6H, ^{i}Pr), 1.30 (d, $J = 6.9$ Hz, 6H, ^{i}Pr), 1.31–1.92 (m, 22H, Cy), 1.93 (s, 3H, CH_3), 2.06 (s, 15H, Cp*), 2.32–2.33 (m, 1H, ^{i}Pr), 2.82–2.91 (m, 4H, CH_2), 5.56–5.60 (m, 4H, *p*-cymene), 5.70 (m, 1H, Cp), 5.73 (m, 1H, Cp), 5.80 (m, 1H, Cp), 5.89 (m, 1H, Cp). IR (KBr, cm^{-1}): $\nu_{Ta=O}$ 813 (s). Anal. Calc. for $C_{39}H_{59}Cl_3OPRuTa$ (963.32): C, 48.62; H, 6.18. Found: C, 48.44; H, 6.38%.

4.9. Cyclopropanation

Cyclopropanation reactions were performed according to the procedure described by Demonceau, Noels et al. [13]. Ethyl diazoacetate (1 mmol diluted by styrene up to 1 ml) was added during a period of 4 h with 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 determinated by GC using the experimentally measured cyclopropane–decane response ratio.

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