

Ruthenium(II) complexes containing both arene and functionalized phosphines. Synthesis and catalytic activity for the hydrogenation of styrene and phenylacetylene

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Abstract

The $[\text{RuCl}_2(\eta^6\text{-arene})]_2$ complex reacts with PPh_2R ($\text{R} = \text{H}$, Py , CH_2Py , $\text{C}\equiv\text{CPh}$, $\text{C}\equiv\text{C}^i\text{Bu}$ and $\text{C}\equiv\text{Cp-Tol}$) ligands in CH_2Cl_2 to give neutral P-coordinated ruthenium(II) complexes $[\text{RuCl}_2(p\text{-cymene})\text{PPh}_2\text{R}]$. The structure of $[\text{RuCl}_2(p\text{-cymene})\text{PPh}_2\text{H}]$ and $[\text{RuCl}_2(p\text{-cymene})\text{PPh}_2\text{Py}]$ complexes has been established by X-ray diffraction. The neutral P-coordinated complexes $[\text{RuCl}_2(p\text{-cymene})\text{PPh}_2\text{Py}]$ and $[\text{RuCl}_2(p\text{-cymene})\text{PPh}_2\text{CH}_2\text{Py}]$ react with NaBF_4 in $\text{CH}_2\text{Cl}_2\text{--MeOH}$ mixture to give $[\text{RuCl}(\eta^6\text{-p-cymene})\text{PPh}_2\text{Py}]\text{BF}_4$ and $[\text{RuCl}(\eta^6\text{-p-cymene})\text{PPh}_2\text{CH}_2\text{Py}]\text{BF}_4$ complexes, in which PPh_2Py and $\text{PPh}_2\text{CH}_2\text{Py}$ act as bidentate ligands. The structure of $[\text{RuCl}(\eta^6\text{-p-cymene})\text{PPh}_2\text{Py}]\text{BF}_4$ was determined by X-ray diffraction. The reaction of $[\text{RuCl}_2(\eta^6\text{-arene})]_2$ with $\text{PPh}_2\text{C}\equiv\text{CPh}_2$ led to the $[\text{RuCl}_2(p\text{-cymene})]_2\text{PPh}_2\text{C}\equiv\text{CPh}_2$ complex, in which the diphosphine ligand bridges two $[\text{RuCl}_2(p\text{-cymene})]$ units. $[\text{RuCl}_2(p\text{-cymene})\text{PPh}_2\text{Py}]$ and $[\text{RuCl}(\eta^6\text{-p-cymene})\text{PPh}_2\text{Py}]\text{BF}_4$ are suitable catalyst precursors for the hydrogenation of styrene and phenylacetylene. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium; Arene; Hydrogenation; Phosphine

1. Introduction

The synthesis and applications of ruthenium(II) complexes have been studied by several authors owing to their promising roles in catalytic and stoichiometric reactions. Our group has recently reported the activity of these complexes in C–C bond formation [1], and in CO [2], CO_2 [3], CS_2 [4] and alkyne [5] insertion reactions. Arene ruthenium(II) complexes are very interesting roles as precursors for hydrogenation catalysts [6]. In particular, arene–ruthenium(II) are precursors of catalysts in asymmetric hydrogenation of α - and β -functionalized ketones [7,8]. It is well documented that $[\text{RuCl}_2(\eta^6\text{-arene})]_2$ complexes (I) are readily prepared

by dehydrogenation of cyclohexa-1,3- or cyclohexa-1,4-dienes with ruthenium(III) trichloride in ethanolic solution [9], but it has been shown recently that a $\eta^6\text{-toluene}$ ruthenium(II) compound can be obtained by refluxing dichlorotris(triphenylphosphine)ruthenium(II) in toluene [10]. This result suggests that $\eta^6\text{-arene}$ ruthenium(II) species are present in reactions with ruthenium(II) complexes performed in aromatic solvents. In addition, complexes of type (I) react with Lewis bases to give neutral $[\text{RuCl}_2(\eta^6\text{-arene})\text{L}]$ ($\text{L} = \text{Lewis base}$) complexes of type (II), which can be converted to $[\text{RuCl}_2(\eta^6\text{-arene})\text{L}]^+$ complexes of type (III) in polar solvents when L is a bidentate hemilabile ligand [11,12].

Previous studies of diphenylphosphinoalkynes have shown both $\eta^1\text{-P}$ -coordination [13] and P-coordination with $\text{C}\equiv\text{C}$ bond activation [14]. The nature of the π -effects on phosphinoalkynes was also examined in a

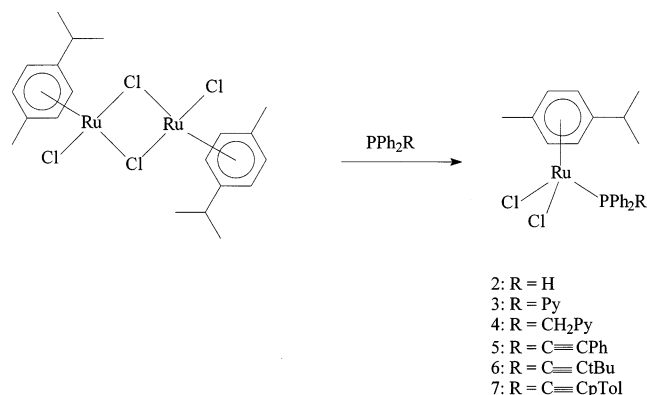
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combined experimental and theoretical study on $[\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_2\text{PPh}_2\text{C}\equiv\text{CR}]^+$ systems [15].

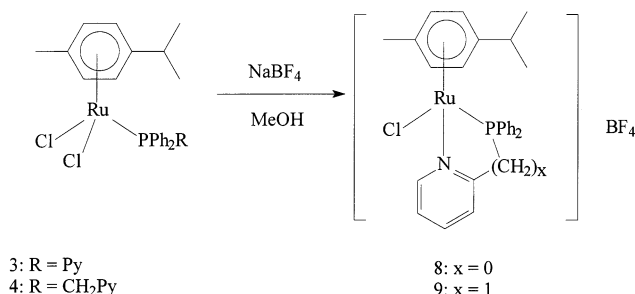
Arene Ru(II) complexes catalyze the hydrogenation of arenes and olefins. In order to extend the study of such complexes we have prepared a new set of ruthenium(II) compounds with PPh_2H , PPh_2Py , $\text{PPh}_2\text{CH}_2\text{Py}$ and $\text{PPh}_2\text{C}\equiv\text{CR}$ ($\text{R} = \text{Ph}$, $t\text{-Bu}$, $p\text{-Tol}$ and PPh_2). Some of these ligands were coordinated to arene–Ru(II) fragments in previous studies [17–20]. Our purpose here is to compare the coordinating abilities of various functionalized phosphines in arene–Ru(II) complexes and to examine the activity of certain complexes in the catalytic hydrogenation of styrene and phenylacetylene.

2. Results and discussion

The starting ruthenium(II) complex was $[\text{RuCl}_2(p\text{-cymene})]_2$ (**1**), which was prepared from the reaction of the commercially available α -phellandrene (5-isopropyl-2-methylcyclohexa-1,3-diene) with RuCl_3 [9]. The reaction of (**1**) with two equivalents of PPh_2R ($\text{R} = \text{H}$, Py , CH_2Py , $\text{C}\equiv\text{CPh}$, $\text{C}\equiv\text{C}^t\text{Bu}$ and $\text{C}\equiv\text{Cp-Tol}$) in CH_2Cl_2 led to a family of stable and neutral P-coordinated ruthenium(II) complexes $[\text{RuCl}_2(p\text{-cymene})\text{PPh}_2\text{R}]$ (**2–7**) in 53–80% yield (Scheme 1). These complexes are highly soluble in CH_2Cl_2 and slightly soluble in hexane and they can be crystallized from CH_2Cl_2 /hexane solutions. The structure of the P-coordinated complexes (**2–7**) is supported by C and H analyses, spectroscopic data (IR and ^1H -, ^{13}C - and ^{31}P -NMR spectroscopy) and the X-ray structure of complexes **2** and **3**. ^1H -NMR spectra of complexes display signals of the η^6 - p -cymene ligand together with the resonances of the hydrogens of the P-coordinated ligands. The arene signals are well resolved and show only H–H coupling, as found in previously reported mononuclear p -cymene compounds [19] and in a recent study on ketophosphines [11]. The ^1H -NMR spectrum of **3** shows the signal of the 6-hydrogen at 8.79 ppm, whereas this signal appears at 8.94



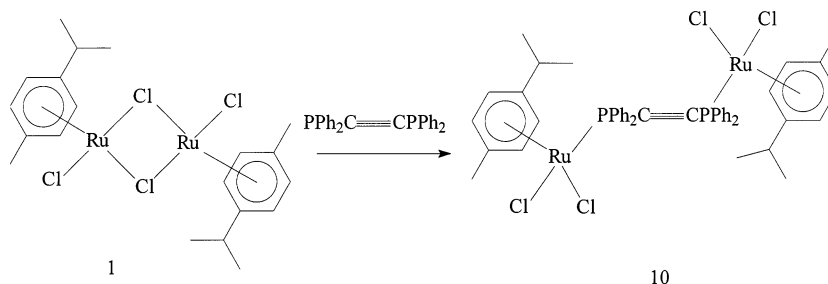
Scheme 1.



Scheme 2.

ppm in the spectrum of **4**. This complex also shows also a doublet at 4.13 ppm, which can be assigned to methylene protons PCH_2 with $^2J_{\text{PH}} = 9.6$ Hz. The ^1H -NMR spectra of diphenylphosphinoalkyne complexes **5–7** are consistent with the monodentate behaviour of these ligands. The observation of the $\nu(\text{C}\equiv\text{C})$ absorption at $2170\text{--}2180\text{ cm}^{-1}$ in the IR spectra of compounds **5–7** supports this coordination. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of complexes **2–7** display resonances that are consistent with a P-coordination of ligands. It has been suggested that the chemical shift ^{13}C -NMR differences ($\delta\text{C}_2 - \delta\text{C}_1$) of acetylenic carbons for different compounds are related to the triple bond polarization, and that the sum ($\delta\text{C}_1 + \delta\text{C}_2$) is associated with the charge changes [21]. A recent experimental and theoretical study of $[\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_2\text{PPh}_2\text{C}\equiv\text{CR}]^+$ showed that polarization of the $\text{C}\equiv\text{C}$ bond is higher than in the free ligand but lower than in $[\text{RPPH}_2\text{C}\equiv\text{CR}]^+$ phosphonium salts [15]. The ($\delta\text{C}_2 - \delta\text{C}_1$) values for complexes **5–7** are 25.35 ($\text{R} = \text{C}\equiv\text{CPh}$), 44.74 ($\text{R} = \text{C}\equiv\text{C}^t\text{Bu}$) and 29.00 ($\text{R} = \text{C}\equiv\text{Cp-Tol}$) ppm, slightly higher than those measured for the free ligands and significantly lower than found in $[\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_2\text{PPh}_2\text{C}\equiv\text{CR}]^+$ complexes [15]. This difference could be attributed to the neutral nature of complexes **5–7**, which induces a smaller contraction of molecular distances (including the P–C bond) than in iron compounds. Otherwise, the ($\delta\text{C}_2 + \delta\text{C}_1$) values are similar to those of the diphenylphosphinoalkyne ligands, which suggests that complexation has no influence on charge transfer, as found in cationic iron complexes [15]. $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra of **2–7** compounds show the phosphorus resonance as a singlet between 20 and 30 ppm in complexes **2–4** and between -2 and -8 ppm in complexes **5–7**. These values are typical of unidentate P-coordinated ligands [18,19,22,23].

The additional coordination of the pyridine nitrogen atom to ruthenium(II) was found when complexes **3** and **4** were reacted in CH_2Cl_2 with one equivalent of NaBF_4 dissolved in methanol, which afforded complexes **8** and **9** (Scheme 2). These compounds are highly soluble in CH_2Cl_2 and methanol but insoluble in hexane, and they were isolated in 85 and 62% yield,



Scheme 3.

respectively. The elemental analyses and spectroscopic data of **8** and **9** are consistent with a molecular formula $[\text{RuCl}(\eta^6\text{-}p\text{-cymene})\text{L}]\text{BF}_4$ ($\text{L} = \text{PPh}_2\text{Py}$ or $\text{PPh}_2\text{CH}_2\text{Py}$). Their ^1H -NMR spectra differ from the spectra of compounds **3** and **4**. First, the 6-hydrogen of the pyridine group has moved down field and the methyl hydrogens of the *p*-cymene ligand are highfield shifted [19], and secondly, four signals are observed for the benzene ring hydrogens, as in related compounds where the metal atom bears four different groups [24]. The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra of complexes **8** and **9** show resonances at -17.42 and 54.04 ppm, respectively, which reveal the strong effect of pyridine coordination. Two signals corresponding to benzene ring carbons of the *p*-cymene ligand are also observed in the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of compounds **8** and **9**.

The reaction of $[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})]_2$ (**1**) with one equivalent of bis(diphenylphosphino)acetylene in CH_2Cl_2 gave a new orange product **10** (Scheme 3), which is soluble in CH_2Cl_2 and partially soluble in hexane and whose C and H analyses suggest the formula $[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})]_2\text{PPh}_2\text{C}\equiv\text{CPh}_2$. The spectroscopic data are consistent with a structure in which the bis(diphenylphosphino)acetylene ligand bridges two $[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})]$ units. The ^1H - and $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra display signals of both arene and diphosphine ligands. An interesting feature in the ^{13}C -NMR spectrum is the doublet at 103.10 ppm ($J_{\text{CP}} = 76.5$ Hz) which is in agreement with a symmetrical coordination of bis(diphenylphosphino)acetylene. This hypothesis is confirmed by the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of **10**, which shows only one singlet at 10.13 ppm. On the other hand the $\nu(\text{C}\equiv\text{C})$ absorption is not observed in the IR spectrum of compound **10**. These spectroscopic data are coherent with those found in other acetylene bridged bis(diphenylphosphino)compounds [25].

3. Crystal structures of compounds **2**, **3** and **8**

Structures of compounds **2** and **3** consists of molecular units linked by van der Waals forces whereas **8** is formed by complex cations and BF_4^- anions joined by coulombic forces. Figs. 1–3 and Table 1 displays se-

lected bonds length and angles and Tables 2–4 display atomic coordinates of compounds **2**, **3** and **8**.

Structure of complex **2** is made up by a Ru(II) atom η^6 -coordinated to a *p*-cymene molecule, two chlorine atoms and to a PPh_2H ligand through the P atom leading to the usual ‘three-legged piano stool’ coordination. The Ru–Cl distances ($2.416(1)$ and $2.407(1)$ Å) are slightly different, as found in related structures with bulky phosphines [26]. The Ru–C(arene) distances average $2.214(2)$ Å and the Ru–centroid (*p*-cymene ring) length is $1.707(1)$ Å. The arene ring is nearly planar and shows C–C bond distances that appear to be normal. The Cl(1)–Ru–Cl(2) of $87.53(2)^\circ$ is similar to that found in $[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})\text{PPh}_2\text{Me}]$, suggesting a similar steric hindrance [27]. However, Cl(1)–Ru–P and Cl(2)–Ru–P angles ($82.73(2)$ and $81.42(2)^\circ$, respectively) are smaller than those found in similar complexes bearing bulky phosphines [28].

The structure of complex **3** is similar to that of **2**. It consists of a Ru(II) atom η^6 -bonded to a *p*-cymene ligand, to two chlorine atoms and to a monodentate PPh_2Py molecule via the P atom. The geometry of the molecule is also a ‘three-legged piano stool’. This structure shows Ru–Cl distances ($2.392(2)$ and $2.520(2)$ Å), which are very different. This could be because the

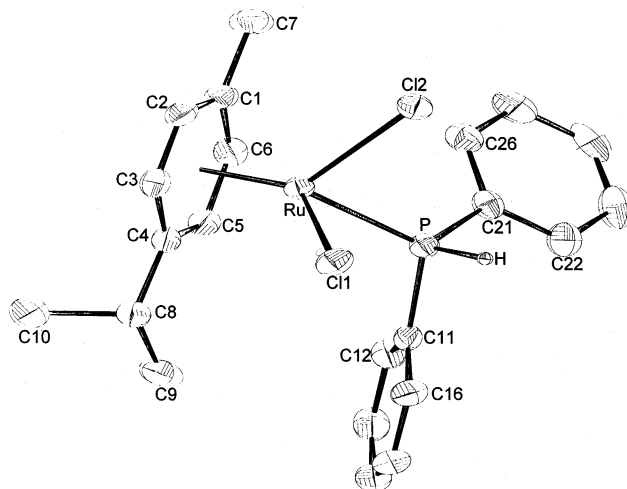


Fig. 1. Molecular structure of the complex $[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})(\text{PPh}_2\text{H})]$ (**2**).

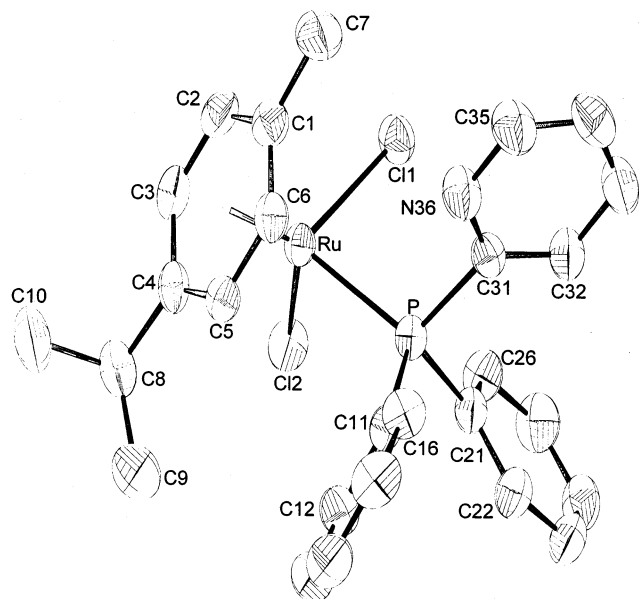


Fig. 2. Molecular structure of complex $[\text{RuCl}_2(p\text{-cymene})(\text{PPh}_2\text{Py})]$ (**3**).

2-pyridyl group is oriented through the Ru atom. The Ru–N distance of 3.645 Å is too long to be considered as a bond length [29] but the lone pair of electrons of the N could lengthen the Ru–Cl(2) bond. Otherwise, the H(6)–N distance of 2.74 Å suggests an arene–pyridine interaction. The Ru–P bond distance of 2.364(2) Å is quite similar to values reported for similar P-linked complexes [26,27]. The Ru–C(arene) bond lengths show small differences, giving a mean distance of 2.198(4) Å. The distance between Ru(II) and the centroid of the arene ring is 1.704(2) Å. The relative positions of the substituents in a projection of the

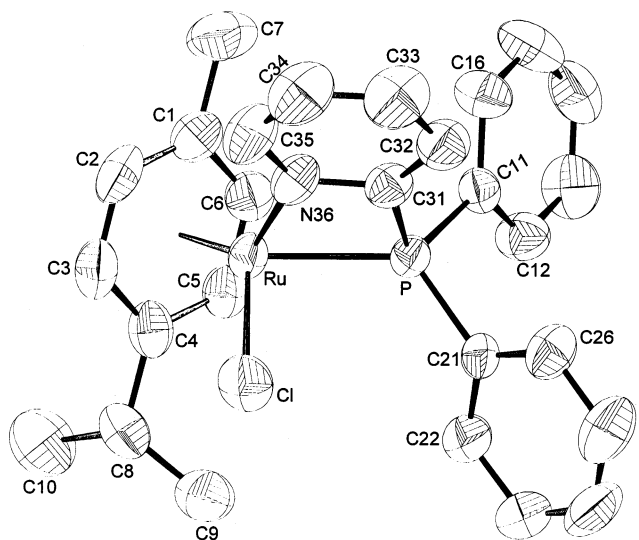


Fig. 3. Molecular structure of the cation $[\text{RuCl}(p\text{-cymene})(\text{PPh}_2\text{Py})]^+$ (**8**).

molecule along the Ru–centroid axis are alternate in complex **2**. The angle Cl(1)–Ru–Cl(2) of 92.54(6)° is larger than that found in complex **2** (87.53(2)°) and in other complexes with bulky phosphines [26]. The P–Ru–Cl(1) and P–Ru–Cl(2) angles (86.91(5) and 89.09(0)°, respectively) are also large. The C–C(arene) bond lengths show non-significant differences with those of complex **2**.

Complex **8** consists of cationic complexes $[\text{RuCl}(p\text{-cymene})(\text{PPh}_2\text{Py})]^+$ and anions BF_4^- . The complex cations contain a Ru(II) atom η^6 -coordinated to a *p*-cymene ring and bonded to a chlorine atom and a bidentate PPh_2Py ligand through N and P atoms. The Ru–Cl bond of 2.384(2) Å is shorter than that found in complexes **2** and **3**, which is consistent with the values reported for other cationic Ru(II) complexes [10]. The bidentate ligand PPh_2Py is η^2 -bonded through both pyridinic N atom (Ru–N(36) = 2.106(4) Å) and the P atom (Ru–P(1) = 2.332(1) Å). This last distance is shorter than that observed in the complex with the monocoordinated PPh_2Py ligand (**3**). The Ru–N bond is also shorter than in the Ru(II) complex $[\text{RuCl}_2(\text{CO})_2(\text{PPh}_2\text{Py})]$ [22] in spite of having a strong π acceptor CO ligand *trans* to the pyridinic N donor atom. The angles Cl–Ru–P(1) and Cl–Ru–N(36) are 87.54(6) and 83.98(12)°, respectively. The rigidity of the chelate ligand generates a narrow angle N(36)–Ru–P(1) of 67.21(13)°. The Ru–C(arene) distances average 2.208(5) Å, whereas the distance between Ru(II) and the centroid of the arene ring is 1.697(2) Å.

4. Catalytic properties of compounds **3** and **8**

Complexes **3** and **8** are catalyst precursors in the hydrogenation of styrene and phenylacetylene with molecular hydrogen in dichloromethane solution. Catalytic studies have been performed without addition of organic bases or coordinating solvents which increase the catalytic activity of Ru(II) complexes [30]. The pyridinic N of the bidentate ligand PPh_2Py can play the role of the solvent or the base in catalytic reactions. Arene Ru(II) complexes are precursors for catalysts of hydrogenation [16]. In order to complete our study of PPh_2Py containing arene Ru(II) complexes we tested the catalytic activity of neutral **3** and cationic **8** complexes.

Using milder conditions than Bennet applied with the catalyst $[\text{RuClH}(\text{C}_6\text{H}_6)(\text{PPh}_3)]$ ([16]a) (CH_2Cl_2 solvent; [complex **3**] = 5 mM; styrene/complex **3** = 200; 80°C; 20 atm H_2), we detected a 97% conversion of styrene to ethylbenzene after 80 h. Complex **3** showed no significant activity below 80°C and an increase of H_2 pressure did not improve its performance. Cationic complex **8** showed better activity than **3** (CH_2Cl_2 solvent; [complex **8**] = 5 mM; styrene/complex **8** = 200; 80°C; 30 atm H_2),

Table 1
Selected bond lengths (Å) and angles (°) for complexes (2), (3) and (8)

[RuCl ₂ (<i>p</i> -cymene)(PPh ₂ H)] (2)		[RuCl ₂ (<i>p</i> -cymene)(PPh ₂ Py)] (3)		[RuCl(<i>p</i> -cymene)(PPh ₂ Py)][BF ₄] (8)	
Bond length (Å)					
Ru–Cl(1)	2.407(1)	Ru–Cl(1)	2.520(1)	Ru–Cl	2.384(2)
Ru–Cl(2)	2.416(1)	Ru–Cl(2)	2.392(2)	Ru–P	2.332(1)
Ru–P	2.316(1)	Ru–P	2.364(2)	Ru–N(36)	2.106(4)
Ru–C(1)	2.227(2)	Ru–C(1)	2.165(4)	Ru–C(1)	2.200(6)
Ru–C(2)	2.240(2)	Ru–C(2)	2.236(4)	Ru–C(2)	2.220(6)
Ru–C(3)	2.250(2)	Ru–C(3)	2.269(4)	Ru–C(3)	2.242(5)
Ru–C(4)	2.217(2)	Ru–C(4)	2.232(3)	Ru–C(4)	2.225(5)
Ru–C(5)	2.175(2)	Ru–C(5)	2.160(3)	Ru–C(5)	2.190(4)
Ru–C(6)	2.199(2)	Ru–C(6)	2.126(4)	Ru–C6	2.172(5)
P–H	1.25(2)				
Bond angle (°)					
Cl(1)–Ru–P	82.73(2)	Cl(1)–Ru–P	86.91(5)	Cl–Ru–P	87.54(6)
Cl(2)–Ru–P	81.42(2)	Cl(2)–Ru–P	89.09(5)	Cl–Ru–N(36)	83.98(12)
Cl(1)–Ru–Cl(2)	87.53(2)	Cl(1)–Ru–Cl2	92.54(6)	P–Ru–N(36)	67.21(13)
Ru–P–H	112.05(11)				

hydrogenating styrene to ethylbenzene with 94% conversion after 24 h.

Complexes **3** and **8** are also active species for hydrogenation of phenylacetylene to styrene and ethylbenzene. Reaction conditions were: CH₂Cl₂ solvent; [complex] = 5 mM; phenylacetylene/complex = 5 mM;

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2**

Atom	x	y	z	U_{eq}
Ru	8354(1)	422(1)	3638(1)	33(1)
Cl(1)	7442(1)	–1253(1)	4156(1)	47(1)
Cl(2)	10049(1)	–785(1)	3260(1)	48(1)
P	7279(1)	–258(1)	2490(1)	36(1)
C(11)	5530(2)	–47(2)	2339(1)	38(1)
C(12)	4978(2)	875(2)	1925(1)	48(1)
C(13)	3646(3)	1043(3)	1856(2)	60(1)
C(14)	2875(3)	299(3)	2202(2)	62(1)
C(15)	3423(3)	–610(3)	2619(2)	60(1)
C(16)	4744(2)	–788(2)	2685(2)	49(1)
C(21)	7815(2)	146(2)	1574(1)	43(1)
C(22)	7172(3)	–290(2)	893(2)	58(1)
C(23)	7604(4)	–6(3)	192(2)	74(1)
C(24)	8633(4)	702(3)	169(2)	71(1)
C(25)	9274(3)	1140(3)	837(2)	67(1)
C(26)	8868(3)	854(2)	1539(2)	53(1)
C(1)	9714(2)	1892(2)	3793(2)	45(1)
C(2)	9618(2)	1409(2)	4534(1)	47(1)
C(3)	8423(2)	1254(2)	4787(1)	43(1)
C(4)	7242(2)	1563(2)	4326(1)	39(1)
C(5)	7347(2)	2049(2)	3603(1)	41(1)
C(6)	8570(2)	2226(2)	3341(1)	45(1)
C(7)	11016(2)	2037(2)	3515(1)	67(1)
C(8)	5972(2)	1393(2)	4650(1)	50(1)
C(9)	4785(3)	1565(4)	4088(2)	82(1)
C(10)	5920(3)	2193(4)	5336(2)	96(1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

phenylacetylene/complex = 200; 80°C; 20–30 atm H₂. The reaction profile of a run with complex **3** at 30 atm and 80°C is shown in Fig. 4. Hydrogenation of phenylacetylene to styrene or ethylbenzene did not occur below 80°. From the reaction profile we can deduce that:

1. phenylacetylene is hydrogenated faster than styrene,
2. phenylacetylene is hydrogenated to styrene and ethylbenzene (conversions of 89.3 and 3%, respectively after 15 h),
3. the alkyne hydrogenation is completed in 25 h and
4. after this time, styrene is hydrogenated to ethylbenzene

Reduction of unsaturated substrates to ethylbenzene is practically complete after 150 h. Cationic rhodium complexes also show strong catalytic activity in the hydrogenation of alkynes to *cis* olefins but the rate of hydrogenation is greater [31]. Using the same reaction conditions previously quoted for complex **3**, compound **8** hydrogenates phenylacetylene to styrene (85% conversion) in 80 h and to ethylbenzene (99% conversion) in 400 h. It is interesting to note that decreasing the H₂ pressure (20 atm) improves the rate of hydrogenation of phenylacetylene to styrene (90.3% conversion in 24 h) and decreases the rate of hydrogenation of styrene to ethylbenzene. In these conditions selective hydrogenation of phenylacetylene to styrene or to ethylbenzene can be accomplished.

5. Experimental section

All reactions were performed under dinitrogen using standard Schlenk techniques. IR spectra were recorded on a Perkin-Elmer model 1710-FT spectrophotometer with KBr pellets. The NMR spectra were measured on

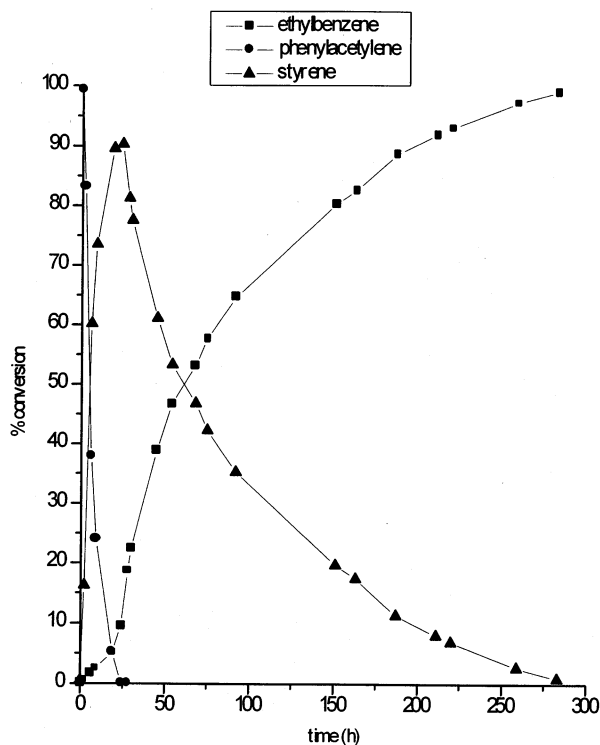


Fig. 4. The hydrogenation of phenylacetylene (CH_2Cl_2 solvent; [complex **3**] = 5 mM; phenylacetylene/complex **3** = 5 mM; phenylacetylene/complex = 200; 80°C ; 30 atm H_2).

5.2. Synthesis of $[\text{RuCl}_2(p\text{-cymene})(\text{PPh}_2\text{Py})]$ (**3**)

A 100 mg (0.16 mmol) sample of complex $[\text{RuCl}_2(p\text{-cymene})]_2$ (**1**) and 100 mg (0.38 mmol) of PPh_2Py were mixed and stirred for 10 h at r.t. in 20 ml of dichloromethane. The solvent was removed in vacuo and the residue was washed several times with hexane. Red crystals of **3** were obtained from crystallization in a dichloromethane/hexane solution (yield 150 mg, 83%). Anal. Calc. for $\text{C}_{27}\text{H}_{28}\text{Cl}_2\text{NPRu}$: C, 56.98; H, 4.92; N, 2.46. Found: C, 56.14; H, 5.10; N, 2.49%. ^1H -NMR (CDCl_3 sol.): 8.79 (m, 1H, py), 7.30 (m, 10H, Ph), 7.90, (m, 3H, py), 5.46, 5.42, 5.32, 5.30 (4m, 4H, H cym), 2.53 (sept, $J_{\text{HH}} = 6.9$ Hz; 1H, CHMe_2), 1.61 (s, 3H, Me), 0.84 (d, $J_{\text{HH}} = 6.9$ Hz; 6H, CHMe_2) ppm. $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3 sol.): 159.7 (d, $J_{\text{PC}} = 68.1$ Hz; py), 148.6 (d, $J_{\text{PC}} = 14.8$ Hz; py), 123.7 (d, $J_{\text{PC}} = 2.8$ Hz; py), 128.5–133.4 (Ph + py), 109.9 (s; CCHMe_2), 94.4 (s, CMe), 91.3 (d, $J_{\text{PC}} = 3.7$, CH cym), 85.1 (d, $J_{\text{PC}} = 3.7$, CH cym), 29.94 (s, CHMe_2), 21.5 (s, CHMe_2), 16.8 (s, CMe) ppm. $^{31}\text{P}\{^1\text{H}\}$ -NMR (CDCl_3 sol.): 20.8 (s) ppm.

5.3. Synthesis of $[\text{RuCl}_2(p\text{-cymene})(\text{PPh}_2\text{CH}_2\text{Py})]$ (**4**)

A total of 200 mg (0.33 mmol) of $[\text{RuCl}_2(p\text{-cymene})]_2$ (**1**) and 180 mg (0.65 mmol) of $\text{PPh}_2\text{CH}_2\text{Py}$ were dissolved in 20 ml of dichloromethane and stirred for 20 h at r.t. The solvent was removed in vacuo and the residue

was washed with hexane. The product of the reaction is an orange oil which can be converted to a solid under vacuum for several hours (yield 23 mg, 0.40 mmol, 62%). Anal. Calc. for $\text{C}_{28}\text{H}_{30}\text{Cl}_2\text{NPRu}$: C, 57.36; H, 5.15; N, 2.40. Found: C, 56.32; H, 5.35; N, 2.44%. ^1H -NMR (CDCl_3 sol.): 8.98 (m, 1H, py), 7.30 (m, 13H, Ph + py), 5.29, 5.27, 5.12, 5.11 (4m, 4H, H cym), 4.13 (d, $J_{\text{PH}} = 9.6$; 2H, PCH_2), 2.50 (sept, $J_{\text{HH}} = 6.9$ Hz; 1H, CHMe_2), 1.84 (s, 3H, Me), 0.85 (d, $J_{\text{HH}} = 6.9$ Hz; 6H, CHMe_2) ppm. $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3 sol.): 155.6 (d, $J_{\text{PC}} = 13.0$ Hz; py), 148.5 (d, $J_{\text{PC}} = 2.5$ Hz; py), 135.0–125.6 (Ph + py), 108.3 (s; CCHMe_2), 93.5 (s, CMe), 90.2 (d, $J_{\text{PC}} = 4.6$, CH cym), 85.5 (d, $J_{\text{PC}} = 5.5$, CH cym), 41.9 (d, $J_{\text{PC}} = 21.1$ Hz, CH_2), 29.9 (s, CHMe_2), 21.4 (s, CHMe_2), 17.3 (s, CMe) ppm. $^{31}\text{P}\{^1\text{H}\}$ -NMR (CDCl_3 sol.): 29.7 (s) ppm.

5.4. Synthesis of $[\text{RuCl}_2(p\text{-cymene})(\text{PPh}_2\text{C}\equiv\text{CR})]$ [R = Ph (**5**), ^tBu (**6**) and $p\text{-Tol}$ (**7**)]

A total of 100 mg (0.16 mmol) of $[\text{RuCl}_2(p\text{-cymene})]_2$ (**1**) were dissolved in 15 ml of methanol and an equimolar amount of the alkynylphosphine (0.16 mmol) was added. The mixture was stirred for 20 h at r.t. and the solvent was evaporated to dryness. The residue was washed several times with hexane and the corresponding products **5–7** were precipitated as red solids by adding hexane. Yields were 77 (**5**), 75 (**6**) and 60% (**7**), respectively.

5.4.1. Complex **5**

Anal. Calc. for $\text{C}_{30}\text{H}_{29}\text{Cl}_2\text{PRu}$ (CH_2Cl_2): C, 55.96; H, 4.61. Found: C, 57.26; H, 4.46%. ^1H -NMR (CDCl_3 sol.): 7.64 (m, 15H, Ph), 5.23, 5.30 (2m, 4H, H cym), 2.90 (sept, $J_{\text{HH}} = 6.9$ Hz; 1H, CHMe_2), 1.95 (s, 3H, Me), 1.14 (d, $J_{\text{HH}} = 6.9$ Hz; 6H, CHMe_2) ppm. $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3 sol.): 132.0–128.5 (Ph), 109.5 (CCHMe_2), 108.9 (d, $J_{\text{PC}} = 11.1$ Hz; CPh), 96.0 (s, CMe), 90.3 (d, $J_{\text{PC}} = 5.5$ Hz; CH cym), 86.6 (d, $J_{\text{PC}} = 5.5$, CH cym), 83.5 (d, $J_{\text{PC}} = 88.8$ Hz; PPh_2C), 30.3 (s, CHMe_2), 22.0 (s, CHMe_2), 17.5 (s, CMe) ppm. $^{31}\text{P}\{^1\text{H}\}$ -NMR (CDCl_3 sol.): –5.8 (s) ppm. IR (KBr): $\nu(\text{C}\equiv\text{C})$ 2169 cm^{-1} .

5.4.2. Complex **6**

Anal. Calc. for $\text{C}_{28}\text{H}_{33}\text{Cl}_2\text{PRu}$: C, 58.36; H, 6.26. Found: C, 58.38; H, 6.50%. ^1H -NMR (CDCl_3 sol.): 7.30 (m, 10H, Ph), 5.11, 5.20 (2m, 4H, H cym), 2.78 (sept, $J_{\text{HH}} = 6.9$ Hz; 1H, CHMe_2), 1.80 (s, 3H, Me), 1.32 (s, 9H, ^tBu), 1.07 (d, $J_{\text{HH}} = 6.9$ Hz; 6H, CHMe_2) ppm. $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3 sol.): 133.0–128.6 (Ph), 119.5 (d, $J_{\text{PC}} = 9.0$ Hz; C^tBu), 109.3 (CCHMe_2), 95.5 (s, CMe), 90.4 (d, $J_{\text{PC}} = 3.6$ Hz; CH cym), 86.6 (d, $J_{\text{PC}} = 6.2$, CH cym), 74.7 (d, $J_{\text{PC}} = 101.6$ Hz; PPh_2C), 30.2 (s, CHMe_2), 22.0 (s, CHMe_2), 17.4 (s, CMe) ppm. $^{31}\text{P}\{^1\text{H}\}$ -NMR (CDCl_3 sol.): –7.5 (s) ppm. IR (KBr): $\nu(\text{C}\equiv\text{C})$ 2181 cm^{-1} .

5.4.3. Complex 7

Anal. Calc. for $C_{21}H_{31}Cl_2PRu$: C, 61.40; H, 5.09. Found: C, 60.40; H, 5.12%. 1H -NMR ($CDCl_3$ sol.): 7.54 (m, 10H, Ph), 7.43 (d, $J_{HH} = 8.0$ Hz; 2H, Tol), 7.13 (d, $J_{HH} = 8.0$ Hz; 2H, Tol), 5.16, 5.24 (2m, 4H, H cym), 2.83 (sept, $J_{HH} = 6.9$ Hz; 1H, $CHMe_2$), 2.31 (s, 3H, Tol), 1.87 (s, 3H, Me), 1.07 (d, $J_{HH} = 6.9$ Hz; 6H, $CHMe_2$) ppm. $^{13}C\{^1H\}$ -NMR ($CDCl_3$ sol.): 133.0–128.5 (Ph), 117.5 (d, $J_{PC} = 3.7$ Hz; Cp -Tol), 109.2 ($CCHMe_2$), 95.7 (s, CMe), 90.1 (s, CH cym), 86.3 (d, $J_{PC} = 5.5$, CH cym), 88.6 (d, $J_{PC} = 91.6$ Hz; PPh_2C), 30.0 (s, $CCHMe_2$), 21.3 (s, Tol), 21.6 (s, $CHMe_2$), 17.2 (s, CMe) ppm. $^{31}P\{^1H\}$ -NMR ($CDCl_3$ sol.): -2.3 (s) ppm. IR (KBr): $\nu(C\equiv C)$ 2168 cm^{-1} .

5.5. Synthesis of $[RuCl(p\text{-cymene})(PPh_2Py)][BF_4]$ (8)

A solution of 25 mg (0.22 mmol) of $NaBF_4$ in 10 ml of methanol was added to a solution of 130 mg (0.23 mmol) of compound 3 in 10 ml of dichloromethane. The mixture was stirred for 10 h at r.t. The solvent was removed in vacuo, the residue was dissolved in 5 ml of dichloromethane and filtered off and methanol was added. Cooling to $-20^\circ C$ induced the formation of 120 mg (85% yield) of compound 8. Anal. Calc. for $C_{27}H_{28}BClF_4NPRu$: C, 52.25; H, 4.57; N, 2.26. Found: C, 52.34; H, 4.78; N, 2.37%. 1H -NMR ($CDCl_3$ sol.): 8.79 (m, 1H, py), 7.30 (m, 10H, Ph), 7.90, (m, 3H, py), 5.46, 5.42, 5.32, 5.30 (4m, 4H, H cym), 2.53 (sept, $J_{HH} = 6.9$ Hz; 1H, $CHMe_2$), 1.61 (s, 3H, Me), 0.84 (d, $J_{HH} = 6.9$ Hz; 6H, $CHMe_2$) ppm. $^{13}C\{^1H\}$ -NMR ($CDCl_3$ sol.): 154.9 (d, $J_{PC} = 16.5$ Hz; py), 139.0–128.6 (Ph + py), 111.0 (d, $J_{PC} = 3.7$ Hz; $CCHMe_2$), 101.9 (s, CMe), 84.8 (d, $J_{PC} = 1.8$ Hz; CH cym), 85.8 (d, $J_{PC} = 1.8$ Hz; CH cym), 88.1 (d, $J_{PC} = 4.6$ Hz; CH cym), 88.2 (d, $J_{PC} = 4.6$ Hz; CH cym), 28.9 (s, $CHMe_2$), 22.3 (d, $J_{PC} = 7.3$ Hz; $CHMe_2$), 22.6 (d, $J_{PC} = 7.3$ Hz; $CHMe_2$), 18.3 (s, CMe) ppm. $^{31}P\{^1H\}$ -NMR ($CDCl_3$ sol.): -17.4 (s) ppm.

5.6. Synthesis of $[RuCl(p\text{-cymene})(PPh_2CH_2Py)][BF_4]$ (9)

Following the same procedure and using 150 mg (0.23 mmol) of $[RuCl_2(p\text{-cymene})(PPh_2CH_2Py)]$ (4), yellow crystals of compound 9 were obtained (yield 115 mg, 70%). Anal. Calc. for $C_{28}H_{30}BClF_4NPRu$: C, 52.97; H, 4.73; N, 2.21. Found: C, 52.85; H, 4.75; N, 1.97%. 1H -NMR ($CDCl_3$ sol.): 9.39 (m, 1H, py), 7.40 (m, 13H, Ph + py), 5.66, 5.70, 5.78, 5.82 (4m, 4H, H cym), 4.10 (d, $J_{PH} = 12.4$ Hz; 2H, PCH_2), 2.63 (sept, $J_{HH} = 6.9$ Hz; 1H, $CHMe_2$), 1.58 (s, 1H, Me), 0.88 (d, $J_{HH} = 6.9$ Hz; 6H, $CHMe_2$) ppm. $^{13}C\{^1H\}$ -NMR ($CDCl_3$ sol.): 161.9 (d, $J_{PC} = 2.6$ Hz; py), 158.8 (s, py), 140.4–124.5 (Ph + py), 113.8 (s; $CCHMe_2$), 103.8 (s, CMe), 92.1 (d, $J_{PC} = 3.4$, CH cym), 90.9 (d, $J_{PC} = 3.4$, CH cym), 88.1

(d, $J_{PC} = 1.0$, CH cym), 87.4 (d, $J_{PC} = 1.4$, CH cym), 41.9 (d, $J_{PC} = 21.1$ Hz; CH_2), 30.7 (s, $CHMe_2$), 21.9 (s, $CHMe_2$), 22.2 (s, $CHMe_2$), 17.7 (s, CMe) ppm. $^{31}P\{^1H\}$ -NMR ($CDCl_3$ sol.): 54.0 (s) ppm.

5.7. Synthesis of $[RuCl_2(p\text{-cymene})(PPh_2C\equiv CPh_2)]$ (10)

A 100 mg (0.16 mmol) sample of $[RuCl_2(p\text{-cymene})]_2$ (1) was mixed with 64 mg (0.16 mmol) of $PPh_2C\equiv CPh_2$ in 15 ml of dichloromethane. The mixture was stirred for 20 h at r.t. and the solvent was evaporated to dryness in vacuo. The residue was washed several times with hexane and the resulting solid was crystallized in a dichloromethane–hexane mixture. Compound 10 was obtained as a red solid (yield 96 mg, 60%). Anal. Calc. for $C_{46}H_{28}Cl_2PRu$ (2 CH_2Cl_2): C, 48.98; H, 4.42. Found: C, 48.87; H, 4.37%. 1H -NMR ($CDCl_3$ sol.): 7.61 (m, 20H, Ph), 5.31 (m, 8H, H cym), 2.43 (sept, $J_{HH} = 6.9$ Hz; 2H, $CHMe_2$), 1.70 (s, 6H, Me), 0.94 (d, $J_{HH} = 6.9$ Hz; 12H, $CHMe_2$) ppm. $^{13}C\{^1H\}$ -NMR ($CDCl_3$ sol.): 133.5–128.3 (Ph), 109.9 ($CCHMe_2$), 103.1 (d, $J_{PC} = 76.5$ Hz; PPh_2C), 98.6 (s, CMe), 89.1 (d, $J_{PC} = 4.8$ Hz; CH cym), 87.0 (d, $J_{PC} = 3.5$, CH cym), 30.2 (s, $CHMe_2$), 21.8 (s, $CHMe_2$), 17.4 (s, CMe) ppm. $^{31}P\{^1H\}$ -NMR ($CDCl_3$ sol.): 10.1 (s) ppm. IR (KBr): $\nu(C\equiv C)$ not observed.

5.8. Catalytic hydrogenation reactions

All catalytic experiments were performed in a 100 ml home-built stainless steel autoclave equipped with gas and liquid inlets, heating device and magnetic stirrer. In a typical experiment, a solution of the catalyst precursor 3 or 8 (0.1 mmol) and the organic substrate (styrene or phenylacetylene) (20 mmol) in 20 ml of dichloromethane was placed into the reactor under nitrogen and the autoclave was pressurized with H_2 .

5.9. X-ray structure determination and refinement of complexes 2, 3 and 8

5.9.1. Crystal data

Crystals of 2, 3 or 8 suitable for X-ray diffraction analysis were obtained by recrystallization in dichloromethane–hexane mixtures at $-20^\circ C$.

Compound 2: $C_{22}H_{25}Cl_2PRu$; $M = 492.36$. Monoclinic; $a = 10.394(1)$, $b = 11.741(3)$, $c = 17.472(2)$ Å, $\beta = 97.02(1)^\circ$; $V = 2116.2(6)$ Å³ (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, $\lambda = 0.71069$ Å), space group $P2_1/c$ (no. 14), $Z = 4$; $D_{calc.} = 1.545$ g cm^{-3} . Red, air-stable crystals, $\mu(Mo-K\alpha) = 10.7$ cm^{-1} .

Compound 3: $C_{27}H_{28}Cl_2NPRu$, $M = 569.44$. Triclinic, $a = 10.514(1)$, $b = 10.940(2)$, $c = 13.301(2)$ Å, $\alpha = 66.80(1)$, $\beta = 88.87(1)$, $\gamma = 66.82(1)^\circ$, $V = 1276.0(4)$

$\text{\AA}^3$ (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, $\lambda = 0.71069 \text{ \AA}$), space group $P\bar{1}$ (no. 2), $Z = 2$, $D_{\text{calc.}} = 1.482 \text{ g cm}^{-3}$. Red, air-stable crystals, $\mu(\text{Mo-K}\alpha) = 9.0 \text{ cm}^{-1}$.

Compound 8: $\text{C}_{27}\text{H}_{28}\text{BClF}_4\text{NPRu}$, $M = 620.80$. Monoclinic, $a = 9.227(3)$, $b = 14.082(1)$, $c = 10.788(1) \text{ \AA}$, $\beta = 106.59(1)^\circ$, $V = 1343.4(5) \text{ \AA}^3$ (by least-squares refinement on diffractometer angles for 25 automatically centred reflections $\lambda = 0.71069 \text{ \AA}$), space group $P2_1$ (no. 4), $Z = 2$, $D_{\text{calc.}} = 1.535 \text{ g cm}^{-3}$. Orange, air-stable crystals, $\mu = 7.9 \text{ cm}^{-1}$.

5.9.2. Data collection and processing

Data collected on a CAD4 diffractometer, $\omega - 2\theta$ mode with ω scan width $= 0.80 + 0.35 \tan \theta$, ω scan speed $1.3\text{--}5.5^\circ$, graphite monochromated $\text{Mo-K}\alpha$ radiation. Reflection ranges for the data collection were $1 < \theta < 25^\circ$.

Complex 2: $-12 \leq h \leq 12$, $0 \leq k \leq 13$, $0 \leq l \leq 20$. A total of 3713 unique reflections (Lp and empirical absorption correction from Ψ -scan [35], min and max transmission $= 0.926$ and 0.998 , respectively), 3311 with $I > 2\sigma(I)$.

Complex 3: $-12 \leq h \leq 12$, $-11 \leq k \leq 12$, $0 \leq l \leq 15$. A total of 4303 unique reflections (Lp and empirical absorption correction from Ψ -scan [35], min and max transmission $= 0.938$ and 1.000 , respectively), 3719 with $I > 2\sigma(I)$.

Complex 8: $-10 \leq h \leq 10$, $0 \leq k \leq 16$, $0 \leq l \leq 12$. A total of 2454 unique reflections (Lp and empirical absorption correction from Ψ -scan [35], min and max transmission $= 0.956$ and 0.997 , respectively), 2390 with $I > 2\sigma(I)$.

5.9.3. Structure analysis and refinement

Direct methods (SHELXS-86 program [36]) and full-matrix least-squares refinement on F^2 for all reflections (SHELXL-93 program [37]) were applied. Non-H atoms were refined anisotropically. In compound **3**, *p*-cymene distances were not sensible when its coordinates were refined freely, probably due to structural disorder not resolved. The same problem was observed for a phenyl-P ring. So, benzene rings were refined as rigid bodies and restraints were applied to *p*-cymene geometry. In compound **8**, some restraints were also applied to benzene geometries. Hydrogen atoms were placed in calculated positions with isotropic temperature factor fixed at 1.5 (methylic hydrogens) or 1.2 (the rest) times U_{eq} for the corresponding carbon atoms. The weighting scheme was $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

Complex 2: $a = 0.0344$, $b = 0.8742$. Final $R(F)$ and $R_w(F^2)$ values were 0.021 and 0.061, respectively, for reflections with $I > 2\sigma(I)$.

Complex 3: $a = 0.0629$, $b = 2.75$. Final $R(F)$ and $R_w(F^2)$ values were 0.043 and 0.120, respectively, for reflections with $I > 2\sigma(I)$.

Complex 8: $a = 0.0623$, $b = 0.3336$. Final $R(F)$ and $R_w(F^2)$ values were 0.029 and 0.081, respectively, for reflections with $I > 2(I)$.

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References

- [1] M.R. Torres, A. Santos, J. Ros, X. Solans, *Organometallics* 6 (1987) 1091.
- [2] H. Lomhrari, J. Ros, M.R. Torres, A. Santos, A.M. Echavarren, *J. Organomet. Chem.* 411 (1991) 255.
- [3] H. Lomhrari, J. Ros, R. Yáñez, M.R. Torres, *J. Organomet. Chem.* 408 (1991) 233.
- [4] M.R. Torres, A. Perales, J. Ros, *Organometallics* 7 (1988) 1223.
- [5] M.R. Torres, A. Vegas, A. Santos, J. Ros, *J. Organomet. Chem.* 326 (1987) 413.
- [6] (a) W.E. Silverthorn, *Adv. Organomet. Chem.* 13 (1975) 48. (b) H. Le Bozec, D. Touchard, P.H. Dixneuf, *Adv. Organomet. Chem.* 29 (1989) 163.
- [7] (a) K. Haak, S. Hashiguchi, A. Fujii, Y. Ikariya, R. Noyori, *Angew. Chem. Int. Ed. Engl.* 36 (1997) 285. (b) S. Hashiguchi, A. Fujii, K. Haak, K. Matsumura, T. Ikariya, R. Noyori, *Angew. Chem. Int. Ed. Engl.* 36 (1997) 288.
- [8] K. Kashima, K. Kusano, N. Sato, et al., *J. Org. Chem.* 59 (1994) 3064.
- [9] M.A. Bennett, G.B. Robertson, A.K. Smith, *J. Organomet. Chem.* 43 (1972) C41.
- [10] J.R. Polam, L.C. Porter, *Inorg. Chim. Acta* 205 (1993) 119.
- [11] B. Demerseman, R. Le Lagadeec, B. Guilbert, C. Renouard, P. Crochet, P.H. Dixneuf, *Organometallics* 13 (1994) 2269.
- [12] D. Drommi, C.G. Arena, F. Nicolo, G. Bruno, F. Faraone, *J. Organomet. Chem.* 485 (1995) 115.
- [13] E. Louattani, J. Suades, R. Mathieu, *J. Organomet. Chem.* 421 (1991) 335.
- [14] D. Montlló, J. Suades, F. Dahan, R. Mathieu, *Organometallics* 9 (1990) 2933.
- [15] E. Louattani, A. Lledós, J. Suades, A. Alvarez-Larena, J.F. Piniella, *Organometallics* 14 (1995) 1053.
- [16] (a) M.A. Bennett, T. Huang, A.K. Smith, T.W. Turney, *J. Chem. Soc. Chem. Commun.* (1978) 582. (b) R. Iwata, I. Ogata, *Tetrahedron* 29 (1973) 2753.
- [17] R. Regragui, P.H. Dixneuf, *Organometallics* 3 (1984) 1020.
- [18] D. Drommi, C.G. Arena, F. Nicolo, G. Bruno, F. Faraone, *J. Organomet. Chem.* 485 (1995) 115.
- [19] H. Yang, N. Luga, R. Mathieu, *An. Quim.* 93 (1997) 28.
- [20] D.F. Jones, P.H. Dixneuf, A. Benoit, J. Le Marouille, *J. Chem. Soc. Chem. Commun.* (1982) 1217.
- [21] D. Rosenberg, W. Drenth, *Tetrahedron* 29 (1973) 2753.
- [22] M.M. Olmstead, A. Maisonnat, J.P. Farr, A.L. Balch, *Inorg. Chem.* 20 (1981) 3877.
- [23] C.G. Arena, E. Rotondo, F. Faraone, M. Lanfranchi, A. Tiripicchio, *Organometallics* 10 (1991) 3877.
- [24] J.A. Cabeza, P. Maitlis, *J. Chem. Soc. Dalton Trans.* (1985) 573.

- [25] E. Louattani, J. Suades, K. Urtiaga, M.I. Arriortua, X. Solans, *Organometallics* 15 (1996) 468.
- [26] P. Pertici, E. Pitzalis, F. Marchetti, C. Rosini, O. Salvadori, M.A. Bennet, *J. Organomet. Chem.* 466 (1994) 221.
- [27] M.A. Bennett, G.B. Robertson, A.K. Smith, *J. Organomet. Chem.* 43 (1972) C41.
- [28] Y. Yamamoto, R. Sato, F. Matsuo, C. Sudoh, T. Igoshi, *Inorg. Chem.* 35 (1996) 2329.
- [29] van der Waals radii taken from: J.E. Huheey, E.A. Keiter, R. Keiter, *Inorganic Chemistry*, 4th Ed., Harper Collins, p. 292.
- [30] T. Ohkuma, H. Ooka, S. Hashiguchi, R. Noyori, *J. Am. Chem. Soc.* 117 (1995) 2675.
- [31] R.R. Schrock, J.A. Osborn, *J. Am. Chem. Soc.* 98 (1976) 2143.
- [32] G.R. Newkome, D.C. Hager, *J. Org. Chem.* 43 (1978) 947.
- [33] M. Alvarez, N. Lugan, R. Mathieu, *J. Chem. Soc. Dalton Trans.* (1994) 2755.
- [34] A.J. Carty, N-K. Hota, T.W. Ng, H.A. Patel, T.J. O'Connor, *Can. J. Chem.* 49 (1971) 2706.
- [35] A.C.T. North, P.C. Philips, F.S. Mathews, *Acta Crystallogr. Sect. A* 24 (1968) 351.
- [36] G.M. Sheldrick, *Acta Crystallogr. Sect. A* 46 (1990) 467.
- [37] G.M. Sheldrick, SHELXL-93, Program for the refinement of crystal structures from diffraction data, Institut für Anorg. Chem., Göttingen, Germany, 1993.