ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 612 (2000) 36–45

Journal of Organometallic Chemistry

ortho-Metalated dirhodium(II)-catalyzed α-diazocarbonyl transformation. Diastereoselective cyclopropanation of menthyl-α-diazo-β-keto ester and C–H insertion of α-diazo ester

Pascual Lahuerta [a,*1], Inés Pereira [a], Julia Pérez-Prieto [b,*2], Mercedes Sanaú [a], Salah-Eddine Stiriba [a,d,*3], Douglass F. Taber [c,*4]

[a] *Departamento de Química Inorgánica, Facultad de Químicas, Dr Moliner 50, 46100 Burjassot, Valencia, Spain*
[b] *Departamento de Química Orgánica, Facultad de Farmacia, Vicent Andrés Estellés s/n, 46100 Burjasot, Valencia, Spain*
[c] *Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, USA*
[d] *Laboratoire de Chimie Organométallique et de Catalyse, Institut le Bel, Université Louis Pasteur, 4 rue Blaise Pascal, 67007 Strasbourg Cedex, France*

Received 19 April 2000; received in revised form 2 June 2000

Abstract

ortho-Metalated rhodium(II) compound (**1d$_1$**) containing two metalated $P(C_6H_5)_2(C_6F_5)$ and two acetates has successfully catalyzed cyclopropanation of menthyl-2-diazo-3-oxo-6-heptanoate (**4**) to form cyclopropanes **6** and **7** with significant *cis–trans* (30:70) diastereoselectivity. An enhanced performance of methyl-2-diazoundecanoate (**5**) cyclization has been achieved mediated by **2d$_1$** and **2d$_4$** catalysts, obtaining 71 and 85%, respectively, of the 1,5-C–H insertion product, *trans*-2-pentylcyclopentanecarboxylate (**8**) versus 1,2-elimination product, (*Z*)-2-undecenoate (**9**) (29 and 15%, respectively). The three possible diastereomers of catalyst (**1d**) which possess two *ortho*-metalated $P(C_6H_5)_2(C_6F_5)$ ligands in a head-to-tail configuration, with the two pentafluorophenyl groups in an *endo–endo*, *endo–exo* or *exo–exo* disposition have been separated by standard column chromatography. The X-ray structure analysis for two of these isomers **1d$_{3endo-exo}$** and **1d$_{1endo-endo}$** allows their structural assignment.

Keywords: Rhodium; *ortho*-Metalated; Diazo compounds; Carbenoid; Selectivity

1. Introduction

The rhodium(II)-mediated reactions of α-diazocarbonyl compounds onto appropriate substrates have emerged as a powerful method in organic synthesis in general and for the selective construction of carbocyclic building blocks in particular, e.g. cyclopropanes and cyclopentanes [1–3]. However, intramolecular cyclopropanation of α-diazocompounds catalyzed by Rh(II) compounds is usually moderately diastereoselective [2]. Much less information is known, however, about controlling the relative and absolute chemistry around the cyclopropane ring [3,4]. On other hand, only rhodium(II) tetracarboxylates have been investigated in catalytic C–H insertion of α-diazo ester in which a β-hydride elimination reaction occurred concomitantly [5]. In this respect, the design of a rhodium(II) complex that itself would cyclize such esters with high selectivity has not yet been achieved.

Most recently, *ortho*-metalated dirhodium(II) compounds of formula $Rh_2(OOCR)_2(PC)_2$ [PC = *ortho*-metalated phosphine, OOCR = carboxylate, head-to-tail configuration] (**1**) (Chart 1) have been studied in C–C bond formation mediated α-diazo ketone transformation, exhibiting good chemoselectivity and good to excellent regioselectivity [6–8]. These compounds offer interesting electronic and steric features, which make them very attractive for rhodiumcarbenoid catalytic purposes [9].

[1] * Corresponding author. Tel.: +34-96-3864854; fax: +34-96-3864322.
[2] * Corresponding author.
[3] * Corresponding author. E-mail: stiriba@chimie.u-strasbg.fr
[4] * Corresponding author.

0022-328X/00/$ - see front matter
PII: S0022-328X(00)00357-0

Table 1
List of ortho-metalated rhodium(II) catalysts [a]

Catalyst	R_1	R_2	R_3	R_4	R	Isomer	Ref.
1a$_1$	C_6H_5	C_6H_5	C_6H_5	C_6H_5	CH_3		[12]
1a$_2$	C_6H_5	C_6H_5	C_6H_5	C_6H_5	CF_3		[6b]
1a$_3$	C_6H_5	C_6H_5	C_6H_5	C_6H_5	C_3F_7		[6b]
1a$_4$	C_6H_5	C_6H_5	C_6H_5	C_6H_5	$C(CH_3)_3$		This work
1d$_1$ $_{exo–exo}$	C_6F_5	C_6H_5	C_6H_5	C_6F_5	CH_3	*exo–exo*	This work
1d$_1$ $_{endo–endo}$	C_6H_5	C_6F_5	C_6F_5	C_6H_5	CH_3	*endo–endo*	This work
1d$_1$ $_{endo–exo}$	C_6H_5	C_6F_5	C_6H_5	C_6F_5	CH_3	*endo–exo*	[7]
1d$_3$ $_{endo–exo}$	C_6H_5	C_6F_5	C_6H_5	C_6F_5	C_3F_7	*endo–exo*	[7]
1d$_4$ $_{endo–exo}$	C_6H_5	C_6F_5	C_6H_5	C_6F_5	$C(CH_3)_3$	*endo–exo*	This work
2a$_1$	C_6H_5	C_6H_5			CH_3		[13a]
2d$_1$	C_6H_5	C_6F_5			CH_3		[7]
2d$_4$	C_6H_5	C_6F_5			$C(CH_3)_3$		This work

[a] See (Chart 1) for catalysts structures.

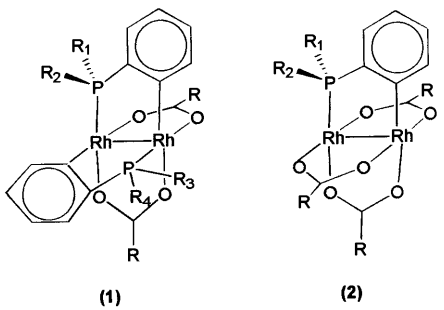


Chart 1.

We found of interest to assess the mixed carboxylate–phosphine complexes in the aforementioned cyclizations. In this report, we describe the finding that intramolecular cyclopropanation with menthyl-2-diazo-3-oxo-6-heptenoate (**4**) catalyzed by the complex **1** and **2** (Table 1) can be significantly diastereoselective and competition between the 1,5-C–H insertion and the β-elimination reaction with methyl-2-diazoundecanoate (**5**) could be highly modulated. Results are compared with those obtained with other catalysts.

2. Results

2.1. Catalytic considerations

Table 1 summarizes the structures of all the metalated rhodium(II) compounds used in this report. The catalytic reactions were performed as reported elsewhere [7].

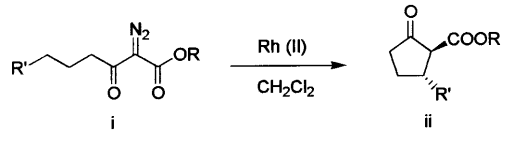
Our interest in *ortho*-metalated Rh(II) carbene-transfer reactions has centered on intramolecular cyclopropanation and C–H insertion reactions [6,7]. We had previously reported that the double-metalated complexes **1a$_1$** and **1a$_2$** were unreactive with α-diazo-β-keto esters in refluxing dichloromethane [7]. We initiated our study by examining the possibility of effecting catalytic cyclization with *t*-butyl-2-diazo-3-oxoundecanoate in the presence of **1** and **2**. Fortunately, all attempts resulted in the formation of substantial amounts of the cyclized product upon heating at 100°C[5].

2.2. Diastereoselective α-diazo-β-keto ester cyclopropanation

As asymmetric synthesis can be accomplished by the use of a chiral substrate, menthyl-2-diazo-3-oxo-6-heptenoate (**4**) was used for *face selectivity* studies in intramolecular cyclopropanation catalyzed by *ortho*-metalated Rh(II) compounds. The chiral nature of the ester group could induce stereoselection in its transformation [10]. In fact the carbene insertion reaction would give rise to diastereoisomeric bicyclic cyclopentanones (**6**) and (**7**) which could be easily separated by silica gel chromatography. Several years ago, one of us reported that copper bronze catalyzed the cyclization of **4**, leading to a 1:1 mixture of the ketones **6** and **7**, respectively (Table 2) [10b]. Using $Rh_2(OOCCH_3)_4$ we observed an equimolar mixture of both ketones.

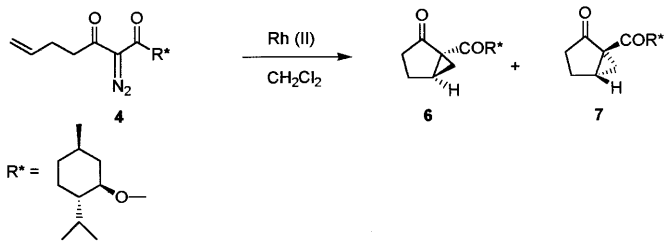
We have found again, that the double-metalated complexes **1a$_1$** and **1a$_2$** were not reactive on exposure to the α-diazo-β-keto ester **4** at room temperature, but they provided the cyclization products on heating at 100°C (sealed tube). We heretofore carried out all ex-

[5] * All the *ortho*-metalated Rh(II) complexes, structure type **1** and those of group **2**, we have investigated, induce C–H insertion of an α-diazo-β-keto ester, such as *t*-butyl-2-diazo-3-oxoundecanoate (**i**), when the reaction is performed at 100°C. Only **2d$_1$** lead to **ii** at room temperature with high yield (89%).



R = C(CH$_3$)$_3$, R' = C$_5$H$_{11}$

Table 2
Ortho-metalated rhodium(II)-catalyzed reaction of α-diazo-β-keto ester (**4**)



Entry	Catalyst [a]	Time (h)	Yield (%)	Relative ratio (%)		% De
				6	**7**	
1	Cu [b]	1	61	50	50	0
2	$Rh_2(OOCCH_3)_4$	1	56	50	50	0
3	$\mathbf{1a_1}$	1	49	50	50	0
4	$\mathbf{1d_1}_{\text{mixture}}$	2	66	35	65	30
5	$\mathbf{1d_1}_{endo-endo}$	2	74	37	63	26
6	$\mathbf{1d_1}_{endo-exo}$	2	64	40	60	20
7	$\mathbf{1a_2}$	2	54	40	60	20
8	$\mathbf{2d_1}$	1	68	43	57	14

[a] All the reactions were carried out in a sealed tube at 100°C.
[b] See Ref. [10b].

periments at this temperature (Table 2). For the ratio measurement of the cyclopropane diastereomers, ^{13}C-NMR of the reaction mixtures have been used looking at changes which occur in signals of the methine chemical shifts at 74.60 and 74.87 ppm of **6** and **7**, respectively. The error bars of our ratios were in the range of 1–3%[6]. We observed a change in the diastereoselectivity of intramolecular cyclopropanation on changing the transition metal complex used. Low yield and no diastereomeric excess were obtained when the catalyst $\mathbf{1a_1}$ was used. Increasing the electrophilicity of the ligands (catalysts $\mathbf{1a_2}$ and $\mathbf{1d_1}$) resulted in a small improvement in the selectivity (20–30%) of these catalysts. The three diastereoisomers $\mathbf{1d_1}$ (*endo–endo*, *exo–endo* and *exo–exo*) gave rise to quite similar results. The monometalated catalyst $\mathbf{2d_1}$ was less selective.

2.3. Cyclization versus elimination of an α-diazo ester

It has been reported that the type of ligand on the dirhodium(II) catalyst and the temperature play an important role in the cyclization of α-diazo esters [5c,11]. We present here the results obtained with methyl-2-diazoundecanoate (**5**) (Table 3).

Treatment of **5** with rhodium(II) tetracarboxylates parallel previously reported results with similar diazo derivatives. Rhodium(II) trifluoroacetate in dichloromethane at −78°C resulted in trace amounts of the cyclization product, methyl *trans*-2-pentylcyclopentanecarboxylate (**8**). The major product, methyl (*Z*)-2-undecenoate (**9**), was produced in 80% yield [11]. By using higher temperature or/and less electrophilic catalysts, as $Rh_2(OOC(CH_3)_3)_4$, the 1,5-C–H insertion reaction competed with the elimination reaction (Table 3).

We extended these studies to the *ortho*-metalated complexes **1**–**2** (Table 3). Surprisingly, at room temperature doubly metalated complexes, $\mathbf{1a_1}$, $\mathbf{1d_1}$ and $\mathbf{1a_2}$ led to only the β-elimination product in high yield. A less electrophilic carboxylate ligand (as pivalate) was necessary for a competitive 1,5-C–H insertion reaction, such as $\mathbf{1a_4}$ and $\mathbf{1d_4}$ to appear.

In the case of monometalated Rh(II) complexes, one actually obtains only the β-elimination product when compound $\mathbf{2a_1}$ (with triphenylphosphine and acetate as ligands) is used. Surprisingly, the cyclization product was favored using a catalyst with a less basic phosphine, $P(C_6F_5)(C_6H_5)_2$. In this regard, it should be noted that the excellent cyclization result was obtained with catalysts possessing less electrophilic carboxylates such as pivalates and the fluorinated metalated phosphine (see entry 10–12, Table 3).

[6] The ratio of both diastereomers has been followed looking at changes in ^{13}C of CH.

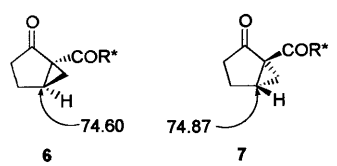
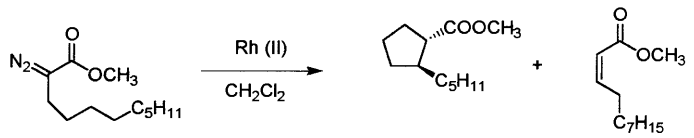


Table 3
ortho-Metalated rhodium(II)-catalyzed reactions of α-diazo ester (**5**)



5 **8** **9**

Entry	Catalyst	*T* (°C)	Yield (%)	Relative ratio (%)	
				8	**9** [a]
1	$Rh_2(OOCCF_3)_4$ [b]	−78	80	0	100
2	$Rh_2(OOCCH_3)_4$	25	93	49	51
3	$Rh_2(OOCC(CH_3)_3)_4$	25	82	69	31(2/1) [a]
5	**1a$_1$**	25	80	0	100
6	**1a$_2$**	25	96	0	100
7	**1a$_4$**	25	88	49	51(2/1) [a]
8	**1d$_1$** [c]	25	91	0	100
9	**1d$_{4endo-exo}$**	25	96	32	68(3/1) [a]
10	**2a$_1$**	25	68	0	100
11	**2d$_1$**	25	90	71	29
12	**2d$_4$**	25	99	85	15

[a] In the indicated cases the *cis*-**9** was contaminated with the *trans*-**9** (the relative ratio of both isomers appears into parentheses).
[b] See reference [11].
[c] All stereoisomers led to similar results.

2.4. Synthetic aspects of catalysts

The doubly metalated compound of formula $Rh_2(OOCCH_3)_2[(C_6H_4)P(C_6H_5)_2]_2{\cdot}2H_2O$ (**1a$_1$**), was prepared according to the synthetic method described by Cotton [12]. The monometalated compounds **2a$_1$** [13a] and **2d$_1$** [7], were prepared according to reported methods. The doubly metalated compound of formula $Rh_2(OOCCH_3)_2[(C_6H_4)P(C_6F_5)(C_6H_5)]_2{\cdot}2H_2O$ (**1d$_1$**) [7], was also prepared by published methods. However, the photochemically-assisted *ortho*-metalation to obtain **1d$_1$** isomers proved to be more efficient than the thermal process, starting from **2d$_1$** and $P(C_6H_5)_2(C_6F_5)$ in a 1:1 ratio in 3:1 chloroform–acetic acid solution by irradiation.

Three diastereoisomers can be expected for compound **1d$_1$** depending on the relative disposition of the C_6F_5 and C_6H_5 groups attached to both P atoms. These three isomers labeled, *exo–exo*, *exo–endo* and *endo–endo* are schematically depicted in Fig. 1. All the possible isomers were present in the crude reaction mixture, they have been separated by the usual technique of chromatography, the predominant one being (**1d$_{1endo-exo}$**) which was isolated in yield of ~90% [7] **1d$_{1exo-exo}$** and **1d$_{1endo-endo}$** were obtained in yields of 1.2 and 3%, respectively. They have been characterized by ^{1}H-, ^{13}C-, ^{31}P-, ^{19}F-NMR and elemental analysis.

In order to confirm this structural assignment, we carried out a crystal structure determination by X-ray diffraction methods that we report here. The best crys-

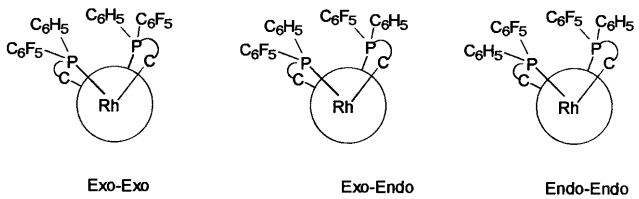


Fig. 1. The three possible configurations of diastereoisomers derived from **1d**.

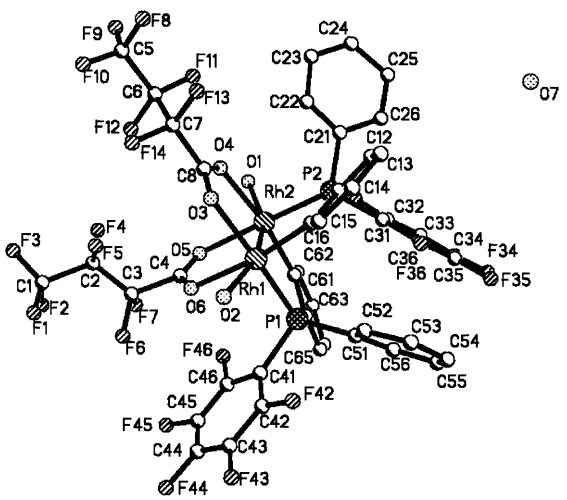


Fig. 2. Perspective view and atom labeling scheme of compound **1d$_{3endo-exo}$**. Hydrogen atoms are omitted for clarity.

Table 4
NMR data for the three ($\mathbf{1d_1}$) isomers

Isomer	$^{31}P\{^1H\}$-NMR, δ (ppm)	$^1J_{Rh-P}$ (Hz)	$^2J_{Rh-P}$ (Hz)	$^{19}F\{^1H\}$-NMR, δ (ppm)		
				ortho	*meta*	*para*
$\mathbf{1d}_{1exo-exo}$	14.4 (d)	170.8		−125.5 (br)	−161.0 (m)	−150.4 (t)
$\mathbf{1d}_{1endo-exo}$	14.5 (dd)	173.3	9.5	−126.6 (br)	−162.4 (m)	−151.2 (t)
	17.7 (dd)	175.3	7.4	−120.5 (br)	−160.9 (m)	−150.5 (t)
$\mathbf{1d}_{1endo-endo}$	19.4 (d)	175.3		−122.6 (br)	−162.5 (t)	−151.5 (t)

tal (Fig. 2) was obtained from the perfluorobutyrate derivative ($\mathbf{1d_{3}}_{endo-exo}$). The two remaining isomers, obtained in much lower yield in the crude reaction mixture, were also isolated as pure samples by chromatography. As the NMR data (Table 4) do not allow us to assign definitively the relative configuration of each of these isomers, X-ray data were collected on the best single crystal grown from the more polar of these minor isomers.

The quality of the data was not completely satisfactory, and the presence of disordered molecules of solvent in the asymmetric unit resulted in a high residual *R* value (11%). Multiple attempts to form better crystals were unsuccessful. However, the important structural features of the molecule (Fig. 3) were unambiguously established and an *endo–endo* structure was assigned for this isomer. These data proved that the order of isomer elution from the column chromatography was: *exo–exo* (minor), *endo–exo* (major) and *endo–endo* (minor).

The exchange of acetate groups with other carboxylates such as trifluoroacetates, heptafluorobutyrates and pivalates in compounds $\mathbf{1d_1}$, $\mathbf{2a_1}$ and $\mathbf{2d_1}$ using the method described by Doyle [14], afforded the rest of the products used in these studies.

2.5. Crystal structural aspects

2.5.1. $Rh_2(O_2CC_3F_7)_2[(C_6H_4)P(C_6H_5)(C_6F_5)]_2\cdot 2H_2O$ ($\mathbf{1d_{3}}_{endo-exo}$)

Relevant crystallographic data for $\mathbf{1d_{3}}_{endo-exo}$ are summarized in Table 5. A view of the molecule is shown in Fig. 2.

Important bond distances and angles are listed in Table 6. In the molecular structure two Rh atoms are bridged by two perfluorobutyrate groups and by two $P(C_6H_5)_2(C_6F_5)$ ligands, in a head-to-tail conformation, each one metalated in one phenyl ring. The two phosphorus atoms have different configurations, as is shown in Fig. 2. Two water molecules, occupying the axial positions, complete the slightly distorted octahedral coordination around the metals [angles in the range 84.5(5)–95.5(5)°]. The value of the Rh–Rh bond distance, 2.530(2)Å, falls within the range reported for dirhodium compounds of similar structures [12,13,15]. The bridge involving the metalated phosphine shows an 'envelope' conformation that is normal in this type of rhodium compounds [12]. The two Rh–P bond distances, Rh(1)–P(1) 2.210(6) and Rh(2)–P(2) 2.213(6) Å, are comparable to those found in other doubly metalated compounds [12,13]. The four equatorial Rh–O bond distances are within the experimental error, 2.17(12)–2.18(2) Å. The longest Rh–O bond distance corresponds to the axial water molecules, Rh(1)–O(2) 2.337(12) and Rh(2)–O(1) 2.35(2) Å, and is indicative of the high *trans* influence of the metal–metal bond. The Rh–Rh–O_{axial} angles, 163.7(4) and 160.7(6)° deviate from linearity, most likely due to steric interactions between the non-metalated phenyl rings and the axial ligands. This deviation is among the highest observed for this type of rhodium dimer [16].

The angles around the two phosphorus atoms show some significant differences, reflecting the different configurations of the two P atoms. It is remarkable that the value for the angle Rh(1)–P(1)–C(41) 107.9(7)° is considerably smaller than the average of the other three angles 118.5(6)°. This small angle can probably be traced back to a hydrogen bridge between O(2)–H···F(46).

2.5.2. $Rh_2(OOCCH_3)_2[(C_6H_4)P(C_6H_5)(C_6F_5)]_2\cdot 2H_2O$ ($\mathbf{1d_{1}}_{endo-endo}$)

Relevant crystallographic data are summarized in Table 5. Selected bond distances and angles are listed in

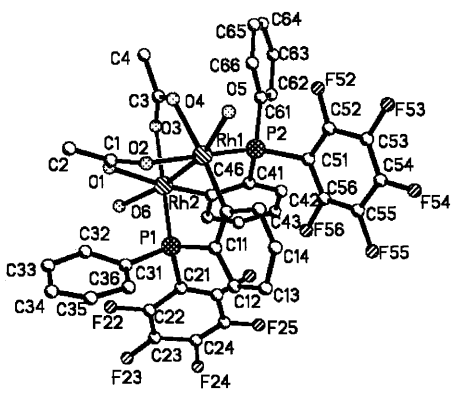


Fig. 3. Perspective view and atom labeling scheme of compound $\mathbf{1d_{1}}_{endo-endo}$. Hydrogen atoms are omitted for clarity.

Table 5
Crystallographic data and structure refinement for ($\mathbf{1d}_{\mathbf{3}endo-exo}$) and ($\mathbf{1d}_{\mathbf{1}endo-endo}$) [a]

	$\mathbf{1d}_{\mathbf{3}endo-exo}$	$\mathbf{1d}_{\mathbf{1}endo-endo}$
Formula	$C_{44}H_{22}F_{24}O_6P_2Rh_2$	$C_{40}H_{28}F_{10}O_6P_2Rh_2$
Formula weight	1370.38	1062.39
Crystal system	Triclinic	Monoclinic
Temperature (K)	568 (2)	293 (2)
Space group	$P\bar{1}$	$P2_1/c$
Unit cell dimensions		
a (Å)	12.2216(11)	13.2990(14)
b (Å)	13.9965(12)	23.625(3)
c (Å)	15.6232(14)	14.758(2)
α (°)	94.7230 (10)	90
β (°)	102.8360(10)	110.962(2)
γ (°)	90.2770(10)	90
V (Å^3)	2596.1(4)	4330.0(8)
Z	2	4
D_{calc} (mg m^{-3})	1.753	1.631
Crystal size (mm)	$0.3\times0.3\times0.6$	$0.15\times0.05\times0.05$
Absorption coefficient (mm^{-1})	0.828	0.923
F (000)	1340	2108
Index ranges	$-11\le h\le 11$, $-12\le k\le 12$, $-14\le l\le 12$	$-14\le h\le 6$, $-26\le k\le 7$, $-15\le l\le 16$
Theta range for data collection (°)	1.46–18.84	1.64–23.30
Reflections collected	3922	9533
Unique data	3309 ($R_{int}=0.0417$)	5905 ($R_{int}=0.0599$)
Absorption correction	None	SADABS
Data/restraints/parameters	3906/28/644	5905/0/578
Goodness-of-fit on F^2	1.109	0.766
Final R indices [$I>2\sigma(I)$]	$R_1=0.0968$, $wR_2=0.2427$	$R_1=0.1160$, $wR_2=0.2810$
R indices (all data)	$R_1=0.1140$, $wR_2=0.2597$	$R_1=0.2021$, $wR_2=0.3587$
Largest difference peak and hole (e Å^{-3})	1.468 and −0.900	4.569 and −1.407

[a] Both external water molecules are not considered in the molecular formula.

Table 7. The molecular structure of $\mathbf{1d}_{\mathbf{1}endo-endo}$ is closely related to that described for the $\mathbf{1d}_{\mathbf{3}endo-exo}$ isomer with the two *ortho*-metalated $P(C_6H_5)_2(C_6F_5)$ ligands in a head-to-tail arrangement. Nevertheless the perfluorobutyrate groups have been replaced by two acetate groups and the two pentafluorophenyl groups are now an *endo–endo* disposition. So the two phosphorus atoms have the same configurations as is shown in Fig. 3. The important Rh–L distances for $\mathbf{1d}_{\mathbf{3}endo-exo}$ and $\mathbf{1d}_{\mathbf{1}endo-endo}$ isomers are equal within the standard errors. The relatively high standard deviations do not allow a detailed comparative discussion of the structural features in these isomers.

These types of structures are not new, they were reported a long time ago [12,13,16] for *ortho*-metalated Rh(II) compounds with a tertiary phosphine, but we can not recall any example with a C_6F_5 group in the phosphine being used.

3. Discussion

It is remarkable to note that α-diazo-β-keto esters can react with *ortho*-metalated complexes **1** at 100°C. With this information in mind, we evaluated the change in diastereoselectivity of catalytic intramolecular cyclopropanation reaction of **4** using *ortho*-metalated Rh(II)

Table 6
Selected bond distances (Å) and angles (°) for ($\mathbf{1d}_{\mathbf{3}endo-exo}$)

Bond lengths			
Rh(1)–Rh(2)	2.530(2)	Rh(2)–O(4)	2.18(2)
Rh(1)–P(1)	2.210(6)	Rh(2)–O(5)	2.182(14)
Rh(2)–P(2)	2.213(6)	Rh(2)–O(1)	2.35(2)
Rh(2)–C(61)	2.01(2)	Rh(1)–O(6)	2.172(12)
Rh(1)–C(16)	1.98(2)	Rh(1)–O(2)	2.337(12)
Rh(1)–O(3)	2.175(13)		
Bond angles			
Rh(2)–Rh(1)–O(2)	163.7(4)	Rh(1)–Rh(2)–O(1)	160.7(6)
Rh(2)–Rh(1)–P(1)	89.71(15)	Rh(1)–Rh(2)–P(2)	89.8(2)
Rh(2)–Rh(1)–C(16)	95.4(7)	Rh(1)–Rh(2)–C(61)	95.5(6)
Rh(2)–Rh(1)–O(3)	88.0(4)	Rh(1)–Rh(2)–O(4)	84.7(4)
Rh(2)–Rh(1)–O(6)	85.9(2)	Rh(1)–Rh(2)–O(5)	87.1(4)
P(1)–Rh(1)–O(3)	176.0(4)	P(2)–Rh(2)–O(4)	96.8(4)
P(1)–Rh(1)–O(6)	92.1(3)	P(2)–Rh(2)–O(5)	177.0(4)
P(1)–Rh(1)–C(16)	97.0(6)	P(2)–Rh(2)–C(61)	92.1(6)
O(3)–Rh(1)–O(6)	84.4(5)	O(4)–Rh(2)–O(5)	83.0(6)
Rh(1)–P(1)–C(41)	107.9(7)	Rh(2)–P(2)–C(21)	118.0(7)
Rh(1)–P(1)–C(51)	120.4(8)	Rh(2)–P(2)–C(31)	117.0 (6)
C(41)–P(1)–C(51)	105.2(10)	C(21)–P(2)–C(31)	102.2(11)

Table 7
Selected bond distances (Å) and angles (°) for ($\mathbf{1d}_{\mathbf{1}endo-endo}$)

Bond lengths			
Rh(1)–Rh(2)	2.496(2)	Rh(2)–O(1)	2.168(12)
Rh(1)–P(2)	2.210(5)	Rh(2)–O(6)	2.367(13)
Rh(2)–P(1)	2.203(5)	Rh(1)–O(5)	2.31(2)
Rh(2)–C(46)	1.97(2)	Rh(2)–O(3)	2.134(13)
Rh(1)–C(16)	2.05(2)	Rh(1)–O(2)	2.112(13)
Rh(1)–O(4)	2.131(12)		
Bond angles			
Rh(2)–Rh(1)–O(4)	83.8(3)	Rh(2)–Rh(1)–O(2)	87.1(3)
Rh(1)–Rh(2)–P(1)	87.63(14)	Rh(2)–Rh(1)–P(2)	88.21(14)
Rh(1)–Rh(2)–C(46)	95.6(6)	Rh(1)–Rh(2)–C(46)	95.6(6)
Rh(1)–Rh(2)–O(6)	170.3(4)	Rh(1)–Rh(2)–O(1)	82.6(3)
Rh(1)–Rh(2)–O(1)	82.6(3)	Rh(1)–Rh(2)–O(6)	170.3(4)
P(1)–Rh(2)–O(6)	95.4(3)	P(1)–Rh(2)–O(3)	174.3(4)
P(2)–Rh(1)–O(4)	95.0(4)	P(2)–Rh(1)–O(2)	175.3(3)
P(2)–Rh(1)– O(5)	98.7(6)	C(46)–Rh(2)–O(1)	173.7(7)
O(3)–Rh(2)–O(1)	80.5(5)	O(2)–Rh(1)–O(5)	85.7(6)
Rh(2)–P(1)–C(21)	116.9(6)	Rh(2)–P(1)–C(11)	111.3(6)
Rh(2)–P(1)–C(31)	114.5(7)	Rh(1)–P(2)–C(41)	111.1(7)
C(11)–P(1)–C(31)	105.0(8)		

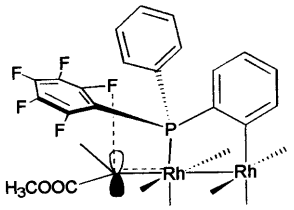


Fig. 4. Proposed Rh–carbenoid intermediate stabilization in $\mathbf{2d_1}$. The three carboxylates ligands completing the lantern structure are incompletely drawn to provide better overview.

compounds. In this respect, Taber has used only Cu dust for the same study [10b]. This prompted us to reinvestigate this reaction, and we found that the chiral auxiliary in the keto ester **4** does not provide any induction of asymmetry in its cyclization when the reaction is mediated by dirhodium tetraacetate (Table 2). Similarly, doubly-metalated $\mathbf{1a_1}$ (with acetate and triphenylphosphine as bridging ligands) also leads to an equimolar ratio of both stereoisomers **6** and **7**. Surprisingly, more acidic *ortho*-metalated complexes such as **1d** isomers that would give rise to cyclization through an early transition state provided some diastereoselectivity. One interesting feature of these *ortho*-metalated Rh(II) catalysts is that they react with bulky α-diazo-β-keto esters such as **4** and permit a preference for the occurrence of **7** over **6**. We can just point out that $Rh_2(OOCCH_3)_4$ gave **6** and **7** in equal ratio. The formation of the cyclopropanation product with significant diastereoselectivity is certainly an interesting result.

On the other hand, in the competition between β-elimination and 1,5-C–H insertion (Table 3) our results demonstrate that monometalated catalysts $\mathbf{2d_1}$ and $\mathbf{2d_4}$ with $P(C_6H_5)_2(C_6F_5)$ are substantially more selective to give cyclized product than doubly-metalated catalysts with PPh_3 and even with $P(C_6H_5)_2(C_6F_5)$. To provide some explanation to these results, we recall that this type of α-diazo ester transformation with rhodium(II) carboxylates involving a competitive reaction between elimination and 1,5-insertion has been previously reported by Taber [5a,c,d]. He postulated that [5c]; the selective occurrence of one or the other of these processes might be dominated by their respective entropy of activation. Hence, β-hydride elimination with a smaller entropy of activation might take place readily instead of carbocycle formation and more exclusively at −78°C, such an explanation appears to be in accordance with the use of very reactive catalysts such as $Rh_2(OOCCF_3)_4$.

It would seem likely that Taber's report and the present instances are fully in agreement that a less electron-withdrawing group lead to the cyclization reaction, thereby, rendering the rhodium carbenoid less electrophilic. This allows the cyclization reaction to occur when the elimination reaction is slowing. This behavior appears with doubly metalated compounds containing pivalate carboxylates $\mathbf{1a_4}$ and $\mathbf{1d_4}$.

On other hand, the observation that catalysts $\mathbf{2d_1}$ and $\mathbf{2d_4}$ with $P(C_6H_5)_2(C_6F_5)$ (entry 11 and 12, Table 3) are efficient for a cyclization reaction, is certainly of importance in several ways. This appears to be unexpected, since such a fluorinated phosphine will increase the electrophilicity of the rhodium–carbenoid. To explain this result, we propose the intermediate shown in (Fig. 4).

We suggest that the fluorine atom can stabilize the Rh–carbenoid, making the elimination process slower and favoring the cyclization reaction. This idea can be supported by comparison with the recognized charge distribution of hexafluorobenzene. In this case the electron charge density is contained in the plane of the carbon ring pointing toward the fluorine atoms due to their strong electronegativity [17]. However, in the case of doubly metalated compounds, the presence of a second metalated phosphine provides a more encumbered face of the Rh center and prevents the stabilization of the carbocationic intermediate. These findings reflect that the combination of both steric and electronic features is critical.

4. Conclusions

In summary, the Rh(II) compounds described herein exhibit interesting catalytic properties. Thus, *ortho*-metalated dirhodium(II) offered unprecedented high diastereocontrol when employed for cyclopropanation of **4**. Furthermore, the use of the appropriate *ortho*-metalated Rh(II) catalyst playing on the nature of the OOCR group and the metalated phosphine, e.g. steric and electronic features, lead to further improvements in the selectivity of 1,5-C–H insertion of the α-diazo ester **5**. In particular $\mathbf{2d_4}$ was found to be a suitable and efficient catalyst for the extremely sensitive cyclization of **5** since it provides mainly the cyclized product **8**. The synthesis and characterization details of the novel *ortho*-metalated Rh(II) complexes based upon $P(C_6F_5)(C_6H_5)_2$ and PPh_3 with structure types **1** and **2** have been reported. Two isomers (*endo–exo* and *endo–endo*) of **1d** have been analyzed by X-ray diffraction.

5. Experimental

5.1. General data

The general procedures and instrumentation have been described previously [7]. Photochemical reactions were carried out in a photochemical reactor equipped with a mercury vapor lamp (Osram-125). Column chro-

matography for organic compounds was performed on TLC-mech silica gel, as described elsewhere [18].

Toluene and chloroform were dried and degassed, methylene chloride was distilled from CaH_2 under argon atmosphere and filtered over K_2CO_3 immediately before use in catalytic reactions. Tetrahydrofuran (THF) was distilled from sodium–benzophenone under argon atmosphere. Acetic acid was only degassed. The preparation of $Rh_2(OOCCH_3)_4$ [19], $Rh_2(OOCCF_3)_4$ [20], $Rh_2(OOC(CH_3)_3)_4$ [21], was prepared as described in the literature. Diazo compounds **4** [10b] and **5** [11] were prepared as described. Compounds **6**, **7** [10b], **8** and **9** [12] were fully characterized as reported.

5.2. X-ray diffraction analysis

X-ray diffraction experiments were carried out on a Siemens Smart diffractometer with a CCD detector using Mo–K_α radiation. All calculations were done using SMART software for data collection [22]. The structures were solved by direct methods, and refined on F^2 with the program SHELXTL [23]. Scattering factors for neutral atoms and anomalous dispersion corrections were taken from the International Tables for X-Ray Crystallography [24]. The positions of the remaining non-hydrogen atoms were located after an alternating series of least-squares cycles and difference Fourier maps and were refined anisotropically. Hydrogen atoms were placed in geometrically generated positions and refined riding on the carbon atom to which they are attached.

Owing to the poor quality of the crystals we could not refine the structures further. This fact, together with the existence of some remaining, and also disordered, solvent water molecules made it impossible to reach lower R values.

5.3. Synthesis of $Rh_2[OOCC(CH_3)_3]_2[(C_6H_4)P(C_6H_5)_2]_2 \cdot 2HOOCC(CH_3)_3$ (**1a$_4$**)

$Rh_2(OOC(CH_3)_3)_4 \cdot 2H_2O$ (100 mg, 0.167 mmol) and $P(C_6H_5)_3$ (0.0965 g, 0.36 mmol) were reacted in 3:1 toluene–pivalic acid at reflux for 1 h. Pivalic acid was removed by distillation under vacuum and the dark-violet crude was chromatographed. Elution with 1:1 CH_2Cl_2–hexane gave a purple band which was collected and concentrated and the purple crude was redissolved in CH_2Cl_2. Addition of hexane, precipitated a purple solid (0.020 g) of $Rh_2(OOCC(CH_3)_3)_2((C_6H_4)P(C_6H_5)_2)_2 \cdot 2HOOCC(CH_3)_3$ (**1a$_4$**) at -20°C. ^{1}H-NMR ($CDCl_3$): δ 0.57 (18H, s, bridging pivalate), 1.25 (18H, s, axial pivalate), 6.49–7.78 (28H, m, aromatics), 11.43 (br, $HOOCC(CH_3)_3$). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 20.5 (d, $^1J_{Rh-P} = 171.03$ Hz). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 27.07 (s, CH_3, bridging pivalate), 27.28 (s, CH_3, axial pivalate), 38.85 (s, $C(CH_3)_3$, bridging pivalate), 38.88 (s, $C(CH_3)_3$, axial pivalate), 114.55–154.24 (m, aromatics), 167.03–167.18 (m), 178.99 (s, OCO), 182.02 (s, OCO). Anal. Calc. for $C_{56}H_{66}O_8P_2Rh_2$: C, 59.25; H, 5.86. Found: C, 59.62; H, 6.31%.

5.4. Synthesis of $Rh_2(OOCCH_3)_2[(C_6H_4)P(C_6F_5)(C_6H_5)]_2 \cdot 2H_2O$ (**1d$_{1exo-exo}$**) and (**1d$_{1endo-endo}$**)

$Rh_2(OOCCH_3)_3[(C_6H_4)P(C_6H_5)(C_6F_5)] \cdot 2H_2O$ (**2d$_1$**) (0.300 g, 0.389 mmol) and $P(C_6H_5)_2(C_6F_5)$ (0.164 g, 0.467 mmol) were dissolved in 30 ml of degassed $CHCl_3$. After stirring for 10 min, 10 ml of acetic acid were added and the mixture was irradiated for 3 h. The resulting solution was evaporated to dryness under vacuum and the residue was transferred to a chromatography column and was washed with acetone collecting a single band, which was concentrated and transferred to a new column. The column was washed with 5:1 hexane–acetone and a minor purple band was collected, concentrated and crystallized from CH_2Cl_2–ethyl acetate–hexane to give a purple solid 5 mg (1.2% yield) of $Rh_2(OOCCH_3)_3)_2((C_6H_4)P(C_6F_5)(C_6H_5))_2 \cdot 2H_2O$: (*exo–exo*) (**1d$_{1exo-exo}$**). ^{1}H-NMR ($CDCl_3$): δ 1.35 (s, 6H, bridging acetate), 6.67–7.75 (m, 18H, aromatics). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 14.4 (d, $^1J = 170.8$ Hz). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 24.0 (s, CH_3, bridging acetate), 122.0–148.0 (m, aromatics), 162.5 (m, RhC), 182.5 (s, OCO). $^{19}F\{^1H\}$-NMR ($CDCl_3$): δ -161.0 (m, 2F, *meta*), -150.4 (t, 1F, *para*), -125.5 (br, 2F, *ortho*). Anal. Calc. for $C_{40}H_{28}F_{10}O_6P_2Rh_2$: C, 45.22; H, 2.66. Found: C, 45.66; H, 2.31%.

After elution with 5:3 hexane–ethyl acetate a violet band was separated corresponding to the previously described **1d$_{1endo-exo}$** isomer [7]. Immediately with the same eluent a minor purple band was isolated, concentrated and crystallized from a mixture of ethyl acetate–hexane–CH_2Cl_2 to give 11.1 mg (3% yield) of $Rh_2(OOCCH_3)_2[(C_6H_4)P(C_6H_5)(C_6F_5)]_2 \cdot 2H_2O$ (**1d$_{1endo-endo}$**). ^{1}H-NMR ($CDCl_3$): δ 1.30 (s, 3H, bridging acetate), 6.80–7.84 (m, 18H aromatics). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 19.4 (d, $^1J = 175.3$ Hz). $^{13}C\{^1H\}$-NMR ($CDCl_3$): 23.2 (s, CH_3, bridging acetate), 122.0–136.8 (m, aromatics), 167.2 (m, RhC), 182.5 (s, OCO). $^{19}F\{^1H\}$-NMR ($CDCl_3$): δ -162.5 (t, 2F, *meta*), -151.5 (t, 1F, *para*), -122.6 (b, 2F, *ortho*). Anal. Calc. for $C_{40}H_{28}F_{10}O_6P_2Rh_2$: C, 45.22; H, 2.66. Found: C, 44.88; H, 3.05%.

5.5. Synthesis of $Rh_2[OOCC(CH_3)_3]_2[(C_6H_4)P(C_6H_5)(C_6F_5)]_2 \cdot 2HOOCC(CH_3)_3$ (**1d$_{4endo-exo}$**)

To 0.100 g (0.073 mmol) of $Rh_2(OOCC_3F_7)_2[(C_6H_4)P(C_6H_5)(C_6F_5)]_2 \cdot 2H_2O$ and 10 ml of pivalic acid were mixed with vigorous stirring. The solution was refluxed for 24 h. The excess pivalic acid was distilled off under vacuum, the residue was dissolved in

CH_2Cl_2–hexane and was then chromatographed on silica gel. Elution with 20:1 hexane–acetone separated a dark-green band that was collected. The solvent was evaporated and the product was crystallized from CH_2Cl_2–hexane at 0°C. Yield: 0.055 g (60%). ^{1}H-NMR ($CDCl_3$): δ 0.65 (s, 9H, bridging pivalate), 0.75 (s, 9H, bridging pivalate), (s, 18H, axial pivalate), 6.45–7.78 (m, 28H, aromatics). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 16.4 (d, $^1J_{Rh-P} = 53.02$ Hz), 17.89 (d, $^1J_{Rh-P} = 58.13$ Hz). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 26.94 (s, axial pivalate), 29.30 (s, bridging pivalate), 29.64 (s, bridging pivalate), 39.02 (s, $C(CH_3)_3$), 39.74 (s, $C(CH_3)_3$), 121.51–150.0 (m, aromatics), 161.5 (m, RhC), 186.59 (OCO), 189.22 (s, OCO), 189.836 (s, OCO). $^{19}F\{^1H\}$-NMR ($CDCl_3$): δ −124.54 (br, 2F, *ortho*), −122.91 (br, 2F, *ortho*), −152.21–(−152.49) (m, 2F, *para*), −161.69 (t, J = 18.9 Hz, 2F), −162.54 (t, J = 19.2 Hz, 2F). Anal. Calc. for $C_{56}H_{56}O_{8F10}P_2Rh_2$: C, 51.14; H, 4.29. Found: C, 51.68; H, 3.99%.

5.6. Synthesis of $Rh_2[OOCC(CH_3)_3]_3[(C_6H_4)P(C_6H_5)(C_6F_5)]\cdot 2HOOCC(CH_3)_3$ (**2d$_4$**)

To 0.100 g (0.11 mmol) of $Rh_2(OOCCF_3)_3[(C_6H_4)P(C_6H_5)(C_6F_5)]\cdot 2H_2O$ (**2d$_1$**) and 10 ml of pivalic acid were mixed with vigorous stirring. The solution was refluxed for 24 h. The excess pivalic acid was distilled off under vacuum and the residue was dissolved in CH_2Cl_2–hexane and was chromatographed on silica gel. Elution with 20:1 hexane–acetone separated a dark-blue band that was collected. The solvent was evaporated and the product was crystallized from CH_2Cl_2–hexane. Yield: 0.074 g (55%). ^{1}H-NMR ($CDCl_3$): δ 0.5 (s, *cis* bridging pivalate), 0.65 (s, *cis* bridging pivalate), 1.35 (s, *trans* bridging pivalate), 1.45 (s, axial pivalate), 6.7–7.65 (m, aromatics), 8.45 (br, $HOOCC(CH_3)_3$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 27.20 (s, $(CH_3)_3$, *trans* bridging), 28.10 (s, $(CH_3)_3$, *cis* bridging), 39.54 (s, $C(CH_3)_3$), 40.67 (s, $C(CH_3)_3$), 122.25 (d, J = 9 Hz, aromatic), 128.10 (d, J = 2.57 Hz, aromatic), 128.66 (d, J = 11 Hz, aromatic), 130.90 (s, aromatic), 132.91 (d, J = 49 Hz, aromatic), 134.9 (d, J = 12 Hz, aromatic), 139.9 (d, J = 16 Hz, aromatic), 147 (d, J = 26 Hz), 162 (m, RhC); 188,83 (s, OCO); 197.49 (s, OCO), 197.69 (s, OCO). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 14.67 (dd, ^1J = 160.1, ^2J = 5.6 Hz). $^{19}F\{^1H\}$-NMR ($CDCl_3$): δ −125.21 to −125.0 (m, 2F, *meta*), −114.02 (t, J = 20.5 Hz, 1F, para), −90.45 (d, J_{PF} = 20.1 Hz, *para*). Anal. Calc. for $C_{43}H_{56}O_{10}F_5PRh_2$: C, 51.14; H, 5.30. Found: C, 50.64; H, 5.65%.

46. Supplementary material

Experimental details for the preparation of **i** and **ii** (2 pages). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC 142825 for the compound **1d$_{3}$**$_{endo-exo}$ and CCDC 142826 for the compound **1d$_{1}$**$_{endo-endo}$. 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).

Acknowledgements

We are grateful to the Dirección General de Investigación Científica y Técnica (DGICYT) (Project PB94-0988) and the EC (Project TMR Network ERBFMRXCT 60091) for financial support. S.-E.S. is a CNRS fellow.

References

[1] For leading references to Rh(II)-catalyzed cyclization of diazo compounds see: (a) M.P. Doyle, M.A. McKervey, T. Ye, Modern Catalytic Methods for Organic Synthesis with Diazo Compounds, Wiley, New York, 1998. (b) T. Ye, M.A. McKervey, Chem. Rev. 74 (1994) 1091. (c) A. Padwa, K.E. Krumpe, Tetrahedron 48 (1992) 5385. (d) M.A. McKervey, M.P. Doyle, J. Chem. Soc. Chem. Commun. (1997) 983. (e) J. Adams, D.M. Spero, Tetrahedron 47 (1991) 1765. (f) W.D. Wulf, in: B.M. Trost, I. Fleming, (Eds.), Comprehensive Organic Synthesis, vol. 5, Pergamon, New York, 1990. (g) E.J. Corey, A. Guzman-Perez, Angew. Chem. Int. Ed. Engl. 37 (1998) 388.

[2] For Rh-mediated intramolecular C–H insertion to form cyclopentanes see: (a) D.F. Taber, in: G. Helmchen, R.W. Hoffman, J. Mulzer, E. Schaumann (Eds.), Methods of Organic Chemistry, Thieme–Verlag, Stuttgart, 1995, p. 1127. (b) D.F. Taber, in: B.M. Trost, I. Fleming, (Eds.), Comprehensive Organic Synthesis, vol. 3, Pergamon, New York, 1991 (Chapter 4.2). (c) M.P. Doyle, in: L.S. Hegedus (Ed.), Comprehensive Organometallic Chemistry II, vol. 12, Pergamon, New York, 1995, (Chapter 5.2). (d) M.P. Doyle, in: W.R. Moser, D.W. Slocum (Eds.), Homogenous Transition Metal Catalysts in Organic Synthesis, ACS Advanced Chemistry Series 230, American Chemical Society, Washington, DC, 1992, (Chapter 30). (e) D.F. Taber, S.-E. Stiriba, Chem. Eur. J. 4 (1998) 990. (f) P. Wang, J. Adams, J. Am. Chem. Soc. 116 (1994) 3296 and references cited therein. (g) D.F. Taber, R.E. Ruckle, J. Am. Chem. Soc. 108 (1986) 7686. (h) D.F. Taber, K.K. You, A.L. Rheingold, J. Am. Chem. Soc. 118 (1996) 547 and references cited therein. (i) S. Hashimoto, N. Watanabe, S. Ikegami, Tetrahedron Lett. 31 (1990) 5173.

[3] S.D. Burke, P.A. Grieco, Org. React. (N.Y.) 26 (1979) 361.

[4] New insight on both relative and absolute stereochemistry of cyclopropanation see: H.M.L. Davies, N.J.S. Huby Jr, W.R. Cantrell, J.L. Olive, J. Am. Chem. Soc. 115 (1993) 9468.

[5] For references on β-elimination versus 1,5-C–H insertion reactions see: (a) D.F. Taber, M.J. Hennessy, J.P. Louey, J. Org. Chem. 57 (1992) 436. (b) E. Galeazzi, A. Gazman, A. Pinedo, A. Saldana, D. Torre, J.M. Muchowski, Can. J. Chem. 61 (1983) 454. (c) D.F. Taber, S.C. Malcolm, J. Org. Chem. 63 (1998) 3717.

[6] (a) F. Estevan, P. Lahuerta, J. Pérez-Prieto, S.-E. Stiriba, M.A. Ubeda, Synlett (1995) 1121. (b) F. Estevan, P. Lahuerta, J. Pérez-Prieto, M. Sanaú, S.-E. Stiriba, M.A. Ubeda, Organometallics 16 (1997) 880.
[7] F. Estevan, P. Lahuerta, J. Pérez-Prieto, I. Pereira, S.-E. Stiriba, Organometallics 17 (1998) 3442.
[8] P. Lahuerta, J. Pérez-Prieto, S.-E. Stiriba, M.A. Ubeda, Tetrahedron Lett. 40 (1999) 1751.
[9] For highly readable reports on ligands effect on metal–carbenoid selectivity, see: (a) A. Padwa, D.J. Austin, Angew. Chem. Int. Ed. Engl. 33 (1994) 1797. (b) M.C. Pirrung, A.T. Morehead Jr., J. Am. Chem. Soc. 116 (1994) 8991. (c) M.P. Doyle, D.C. Forbes, Chem. Rev. 98 (1998) 911.
[10] (a) D.F. Taber, J.C. Amedio Jr., K. Raman, J. Org. Chem. 53 (1988) 2984. (b) D.F. Taber, S.A. Saleh, R.W. Korsmeyer, J. Org. Chem. 45 (1980) 4699.
[11] D.F. Taber, H.R. Jason, S.K. Pack, J.M. Geremina, J. Org. Chem. 61 (1996) 2908.
[12] A.R. Chakravarty, F.A. Cotton, D.A. Tocher, J.H. Tocher, Organometallics 4 (1985) 8.
[13] (a) P. Lahuerta, J. Payá, M.A. Pellinghelli, A. Tiripicchio, Inorg. Chem. 31 (1992) 1224. (b) P. Lahuerta, J. Payá, X. Solans, M.A. Ubeda, Inorg. Chem. 31 (1992) 385.
[14] M.P. Doyle, W.R. Winchester, J.A.A. Hoorn, V. Lynch, S.H. Simonsen, R. Ghosh, J. Am. Chem. Soc. 115 (1993) 9968.
[15] P. Lahuerta, M.A. Ubeda, J. Payá, S. García-Granda, F. Gómez-Beltrán, A. Anillo, Inorg. Chim. Acta 205 (1993) 91.
[16] F.A. Cotton, R.A. Walton, Multiple Bonds Between Metals Atoms, 2nd edition, Oxford University Press, Oxford, 1993, p. 452.
[17] (a) J.H. Williams, Acc. Chem. Res. 26 (1993) 593. (b) J.P. Gallivan, D.A. Dougherty, Org. Lett. 1 (1999) 103.
[18] D.F. Taber, J. Org. Chem. 47 (1982) 1351.
[19] G.A. Rampel, P. Legzdins, H. Smith, G. Wilkinson, Inorg. Synth. 13 (1972) 90.
[20] S.A. Johnson, H.R. Hunt, H.M. Neumann, Inorg. Chem. 2 (1963) 960.
[21] F.A. Cotton, T.R. Felthouse, Inorg. Chem. 19 (1980) 323.
[22] Siemens Data Collection and Procedure, Software for the SMART System, Siemens Analytical X-Ray Instruments Inc., WI, USA, 1995.
[23] SHELXTL, Version. 5.05, AXS Siemens, 1996.
[24] D.T. Cromer, J.T. Waber, International Tables for X-Ray Crystallography, vol. IV, Kynoch Press, Birmingham, 1974, pp. 72, 149, (Tables 2.2B and 2.3.1).