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Half-sandwich ruthenium(II) complexes of aminophosphines: synthesis, structures and catalytic applications in C–C coupling reactions between styrenes and diphenyldiazomethane

Srinivasan Priya [a], Maravanji S. Balakrishna [a,*], Shaikh M. Mobin [b], Robert McDonald [c]

[a] Department of Chemistry, Indian Institute of Technology, Bombay, Mumbai 400 076, India
[b] National Single Crystal X-ray Diffraction Facility, Indian Institute of Technology, Bombay, Mumbai 400 076, India
[c] X-ray Diffraction Facility, University of Alberta, Edmonton, Canada T6G 2G2

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Abstract

The half-sandwich Ru(II) complexes of the type [CpRu($PPh_2N(H)R$)(PPh_3)Cl], [CpRu($PPh_2N(H)R)_2$Cl] (R = Ph, C_6H_{11}) and [CpRu($PPh_2N(R')PPh_2$-κP,κP)(PPh_3)]Cl (R′ = Et, ^{n}Pr, ^{i}Pr, ^{n}Bu), were synthesized and the structures of complexes [CpRu($PPh_2N(H)Ph$)(PPh_3)Cl] and [CpRu($PPh_2N(H)Ph)_2$Cl] were confirmed by single crystal X-ray diffraction studies. All ruthenium complexes were employed in the cyclopropanation reaction of styrene derivatives in the presence of diphenyldiazomethane. All complexes afford 1,1,3,3-tetraphenyl cyclobutane along with cyclopropane derivatives; complex, [CpRu($PPh_2N(^n$Bu)PPh_2-κP,κP)(PPh_3)]Cl shows better selectivity in the formation of 1,1,2-triphenylcyclopropane. In all reactions appreciable amounts of cyclopropanation products and metathesis products, 1,2-diphenylcyclopropane and 1,1-diphenylethene were obtained along with 1,1,3-triphenylpropene derivatives. The variable temperature NMR studies have suggested that the cyclopropanation reactions in the presence of ionic complex, [CpRu($PPh_2N(R')PPh_2$-κP,κP)(PPh_3)]Cl proceeds via carbene intermediate, [CpRu(=CPh_2)($PPh_2N(R')PPh_2$-κP)(PPh_3)]Cl.

Keywords: Aminophosphine; Ruthenium(II) complexes; Cyclopropanation; Crystal structures

1. Introduction

In recent years, there has been an exponential increase in the use of transition metal complexes containing phosphines in organic transformations [1,2]. Among different types of transition metal complexes known, the rhodium complexes play prominent role in terms of highest efficiency and the turnover number [3]. Ruthenium has been introduced as a cheaper alternative to the rhodium, however, the limitation associated with it is its low turnover numbers. Ruthenium complexes of phosphines are of considerable interest as they find application in classical catalytic processes such as hydrogenation [4], isomerisation [5,6], decarbonylation [7–9], reductive elimination [10], oxidative addition [11], in making and breaking C–H bonds [12], and cleavage of N–H and O–H bonds [13]. In recent years ruthenium complexes of phosphines are utilized in the catalytic cyclopropanation reactions and the popular Grubbs catalyst [14] comes under this category. The factors governing the activity and mechanism for the cyclopropanation are not known. However, the half-sandwich ruthenium complexes of the type [CpRu($PR_3)_2$X] have been proven to be effective catalysts for dimerisation of ethyldiazoacetate [15,16]. Thus, as a part of our ongoing research [17], we have examined the catalytic activity of the reactions of terminal olefins with diazo compound

* Corresponding author. Fax: +91-22-2576-7152.
E-mail address: krishna@iitb.ac.in (M.S. Balakrishna).

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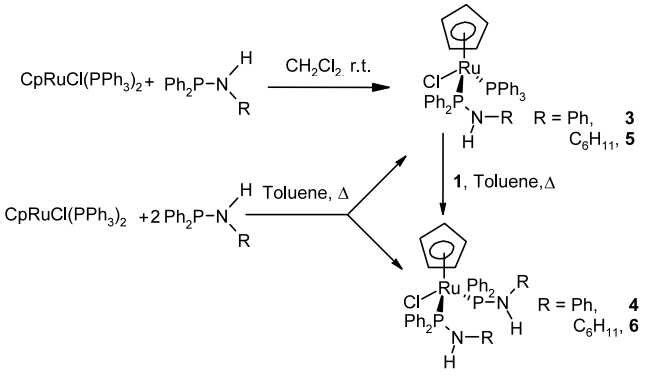
using Ru(II) complexes of aminophosphines; the preliminary results are presented. To the best of our knowledge this is the first instance where the complexes of aminophosphines are employed in this type of catalytic reaction.

2. Results and discussion

The reactions of aminophosphines, $Ph_2PN(H)R$ (R = Ph, **1**; C_6H_{11}, **2**) with $CpRuCl(PPh_3)_2$] afford monosubstituted [$CpRuCl(PPh_3)(PPh_2N(H)R)$] or disubstituted [$CpRuCl(PPh_2N(H)R)_2$] complexes depending upon the stoichiometry and the reaction conditions. The reactions of $Ph_2PN(H)R$ (R = Ph, **1**; C_6H_{11}, **2**) with [$CpRuCl(PPh_3)_2$] in dichloromethane in equimolar ratio at room temperature, afford [$CpRuCl(PPh_3)(PPh_2N(H)R)$] (R = Ph, **3**; C_6H_{11}, **5**) in good yield. The ^{31}P-NMR spectra of complexes **3** and **5** show two doublets at 42.9, 72.4 ppm and 42.9, 77.9 ppm, respectively. The chemical shifts at high fields are due to the PPh_3 group whereas the aminophosphines appear at lower field. The $^2J_{PRuP}$ couplings are 42.4 and 48.5 Hz for complexes **3** and **5**, respectively. The reactions of [$CpRuCl(PPh_3)_2$] with **1** and **2** in 1:2 molar ratio in toluene at 80–90 °C resulted in the formation of disubstituted complexes of the type, [$CpRuCl(PPh_2N(H)R)_2$] (R = Ph, **4**; C_6H_{11}, **6**) in ~75% yield containing trace amount of monosubstituted complex, [$CpRuCl(PPh_3)(PPh_2N(H)R)$] (R = Ph, **3**; C_6H_{11}, **5**). The ^{31}P-NMR spectra of complexes **4** and **6** show single resonances at 72.6 and 81.8 ppm, respectively. The monosubstituted complex **3** with excess of ligand **1** also affords the disubstituted complex **4** as shown in Scheme 1. The structures of complexes **3** and **4** are established by single crystal X-ray diffraction studies.

The perspective views of complexes **3** and **4** are shown in Figs. 1 and 2 respectively. Crystallographic data, selected bond distances and bond angles are given in Tables 1–3. The coordination geometry around ruthenium centres in both complexes **3** and **4** may be



Scheme 1.

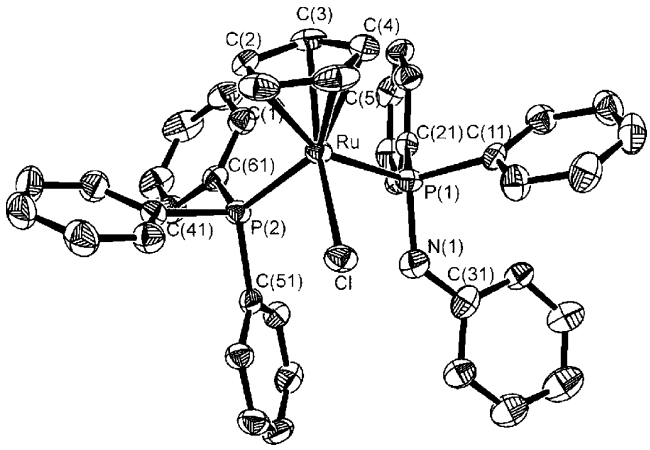


Fig. 1. Perspective view of [$CpRuCl(PPh_3)(PPh_2N(H)Ph)$] (**3**) showing 50% probability thermal ellipsoids.

described as pseudo octahedral three-legged piano stool. The P–N bond distance(s) of 1.681(3) Å in **3** and 1.688(3) and 1.700(3) Å in **4** are slightly shorter than the sum of Pauling covalent radii (1.77 Å) as expected due to the P–N multiple bonding. The Ru–P(1) and Ru–P(2) distances (2.289(2) Å and 2.309(1) Å in **3** and 2.290(1) Å and 2.302(1) Å in **4**) are comparable with those in [$CpRu(PPh_3)_2Cl$] [18] (2.337(1) and 2.225(1) Å), [$CpRu(PMe_3)_2Cl$] [18] (2.373(5) and 2.280(6) Å) and are shorter when compared to [$CpRu\{P(OMe)_3\}_2Cl$] [19] (2.234(2) and 2.199(3) Å). The C′–Ru–Cl (C′ is the centroid of the C_5H_5 ring) angle is smaller when compared to other C′–Ru–P(1) and C′–Ru–P(2) angles and the P(1)–Ru–P(2) angles are wider when compared to P–Ru–Cl angles in both **3** and **4**.

The reactions of aminobis(phosphines), $Ph_2PN(R)PPh_2$ (R = Et, ^{n}Pr, ^{i}Pr, ^{n}Bu) with equimolar quantity of [$CpRuCl(PPh_3)_2$] afford cationic complexes, [$CpRu(PPh_3)(Ph_2PN(R)PPh_2$-κP,κP)]Cl (R = Et [20], **7**; ^{n}Pr, **8**; ^{i}Pr, **9**; ^{n}Bu, **10**) in 50–60% yield (Scheme 2). The ^{31}P-NMR spectra of complexes **7**–**10** show triplets for PPh_3 around 44–45 ppm and doublets for PPh_2 in the range of 80–83 ppm with $^2J_{PRuP}$ couplings of 35 Hz. Further evidence for the formation of complexes **7**–**10** comes from the ^{1}H-NMR spectra and the microanalytical data.

2.1. Cyclopropanation of styrenes with Ph_2CN_2 using half sandwich Ru(II) catalysts

Diphenyldiazomethane on treatment with styrene gives 1,1,2-triphenyl propane under thermal or photochemical conditions by the elimination of N_2 [21]. Baratta et al. [15] have reported that the presence of a catalytic amount of [$CpRuCl(PPh_3)_2$] in the above reaction leads to a mixture of products as shown in Eq. (1) with 1,1,2-triphenyl propane as the minor product.

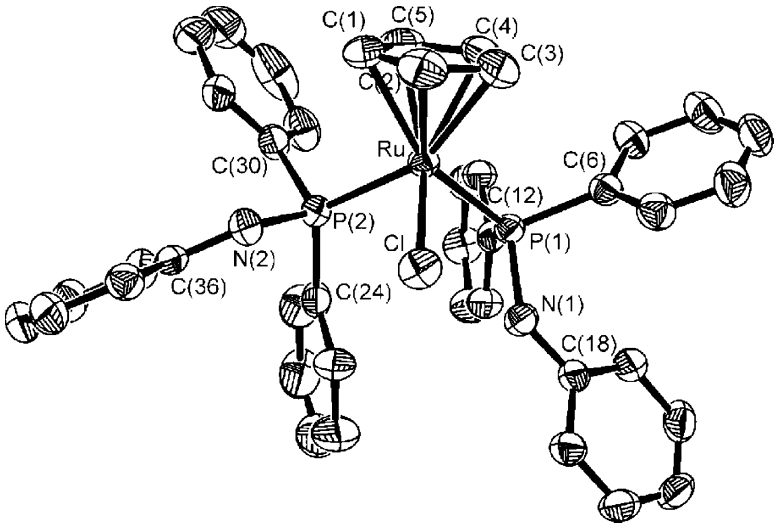
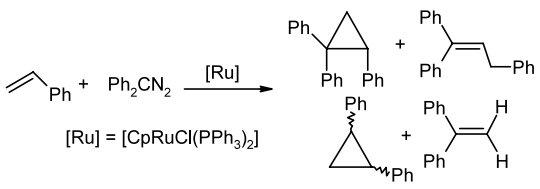


Fig. 2. Perspective view of $[CpRuCl(PPh_2N(H)Ph)_2]$ (**4**) showing 50% probability thermal ellipsoids.

Table 1
Crystallographic data for complexes **3** and **4**

	3	**4**
Empirical formula	$C_{41}H_{36}ClNP_2Ru$	$C_{41}H_{37}ClN_2P_2Ru$
Formula weight	741.17	756.19
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$ (No. 14)	$P2_1$ (No.4)
a (Å)	13.0280(10)	10.1530(6)
b (Å)	16.5916(12)	18.1520(7)
c (Å)	16.4422(12)	10.5140(11)
α (°)	–	–
β (°)	104.676(1)	113.825(6)
γ (°)	–	–
V (Å^3)	3438.1(4)	1772.6(2)
Z	4	2
D_{calc} (g cm^{-1})	1.432	1.417
μ(Mo–K$_\alpha$) [a] (mm^{-1})	0.658	0.640
Temperature (K)	193	293
R [b]	0.0377	0.0187
Rw [c]	0.0811	0.0502

[a] Graphite monochromated.
[b] $R = \Sigma|F_o - F_c|/\Sigma F_o|$.
[c] $R_w = [\Sigma w(F_o^2 - F_c^2)/\Sigma w(F_o^2)2]1/2$; $w = 1/[\sigma^2(F_o^2)+(aP)^2]$; $P = 1/3[F_o^2+2F_c^2]$.



(1)

To determine the catalytic activities of the ruthenium complexes **3**–**10**, cyclopropanation of styrene derivatives with Ph_2CN_2 was attempted. The reaction of styrene with Ph_2CN_2 in the presence of complexes **3**–**10** gave the products as shown in Scheme 3 and the yields are tabulated (Table 4). The reactions involving complexes **3**–**9** afford propene derivative **12** in 8–16% yield along with the cyclopropane product **11**, whereas complex **10** gives exclusively product **11**. The formation of product **11** occurs thermally (80 °C, 3 h), in the absence of catalyst in 55% yield [15]. Except for complex **6**, all others afford 1,1-diphenyl ethene (**13**).

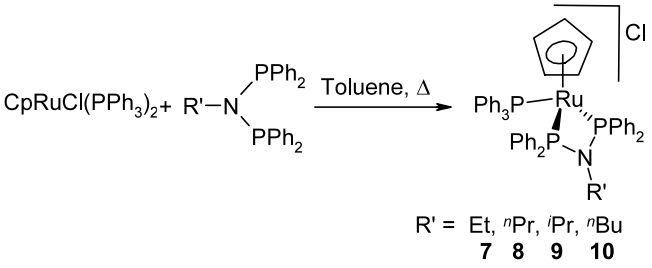
When α-methyl styrene was treated with Ph_2CN_2 in the presence of complexes **3**–**10**, the products obtained are shown in Scheme 4 and the yields of different products are tabulated (Table 5). The cyclopropane derivative **15** is obtained in 40–50% with all the complexes. Both the *cis* and *trans* cyclopropane derivatives **17a** and **17b** were obtained in 15–45% yield. Complex **6** gives only *trans*-1,2-diphenyl-1,2-dimethylcyclopropane. 1,1,3,3-Tetraphenyl cyclobutane was obtained in trace amount in all the reactions.

Table 2
Selected bond distances (Å) and bond angles (°) for **3**

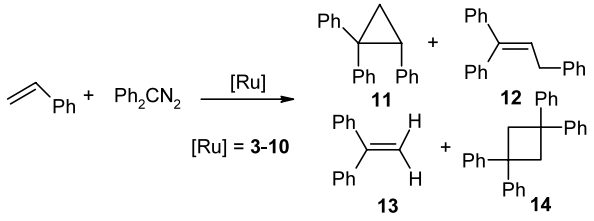
Bond distances			
Ru–Cl	2.437(1)	Ru–P(1)	2.289(1)
Ru–P(2)	2.309(1)	Ru–C(1)	2.214(3)
Ru–C(2)	2.196(3)	Ru–C(3)	2.192(3)
Ru–C(4)	2.217(3)	Ru–C(5)	2.214(3)
P(1)–N(1)	1.680(3)	P(1)–C(11)	1.838(3)
P(1)–C(21)	1.824(3)	P(2)–C(51)	1.843(3)
P(2)–C(41)	1.851(3)	P(2)–C(61)	1.829(3)
N(1)–C(31)	1.372(4)		
Bond angles			
Cl–Ru–P(1)	89.50(3)	Cl–Ru–P(2)	89.36(3)
P(1)–Ru–P(2)	96.90(3)	Ru–P(1)–C(11)	113.98(10)
Ru–P(1)–C(21)	116.25(11)	Ru–P(1)–N(1)	111.69(10)
N(1)–P(1)–C(11)	104.01(15)	C(11)–P(1)–C(21)	104.01(14)
N(1)–P(1)–C(21)	105.78(14)	Ru–P(2)–C(51)	120.98(11)
Ru–P(2)–C(41)	108.50(10)	C(41)–P(2)–C(51)	103.50(14)
Ru–P(2)–C(61)	118.00(10)	C(51)–P(2)–C(61)	100.86(14)
C(41)–P(2)–C(61)	102.74(16)	P(1)–N(1)–C(31)	131.4(2)
C′–Ru–P(1)	125.35	C′–Ru–C(1)	121.71
C′–Ru–P(2)	124.07		

Table 3
Selected bond distances (Å) and bond angles (°) for **4**

Bond distances			
Ru–Cl	2.450(1)	Ru–P(1)	2.290(1)
Ru–P(2)	2.302(1)	Ru–C(1)	2.235(4)
Ru–C(2)	2.227(4)	Ru–C(3)	2.230(5)
Ru–C(4)	2.182(4)	Ru–C(5)	2.189(3)
P(1)–N(1)	1.688(3)	P(1)–C(12)	1.830(3)
P(1)–C(6)	1.847(3)	P(2)–N(2)	1.700(3)
P(2)–C(36)	1.836(4)	P(2)–C(24)	1.838(4)
N(1)–C(18)	1.402(5)	N(2)–C(30)	1.410(4)
Bond angles			
Cl–Ru–P(1)	91.09(3)	Cl–Ru–P(2)	89.72(3)
P(1)–Ru–P(2)	97.64(3)	Ru–P(1)–N(1)	112.1(1)
Ru–P(1)–C(12)	118.9(1)	Ru–P(1)–C(6)	112.9(1)
N(1)–P(1)–C(12)	104.2(2)	N(1)–P(1)–C(6)	103.6(2)
C(12)–P(1)–C(6)	103.6(2)	Ru–P(2)–N(2)	108.4(1)
Ru–P(2)–C(36)	111.2(1)	Ru–P(2)–C(24)	123.1(1)
N(2)–P(2)–C(36)	103.3(2)	N(2)–P(2)–C(24)	102.1(2)
C(36)–P(2)–C(24)	106.8(2)	P(1)–N(1)–C(18)	133.8(3)
P(2)–N(2)–C(30)	129.4(3)	C′–Ru–P(1)	124.94
C′–Ru–P(2)	122.67	C′–Ru–C(1)	121.68



Scheme 2.



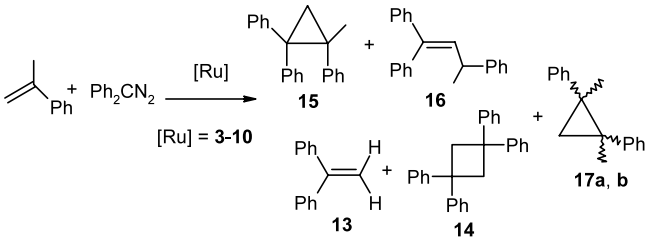
Scheme 3.

When 4-methyl styrene was treated with Ph_2CN_2 in the presence of complexes **3** and **6**, the products obtained are shown in Scheme 5 and the yields of different products are tabulated (Table 6). The cyclopropane derivative **18** was obtained as the major product. When complex **6** was used, the product **13** was not obtained as observed with other two styrenes.

All complexes **3**–**10** show different catalytic activity compared to $[CpRuCl(PPh_3)_2]$ in the reactions between styrenes and carbenes. The reaction of styrene with diazocompound in the presence of complex **10** shows very poor activity as it gives 99% cyclopropane derivative with trace amount of cyclobutane product.

Table 4
Reaction of Ph_2CN_2 with styrene catalysed by **3**–**10**

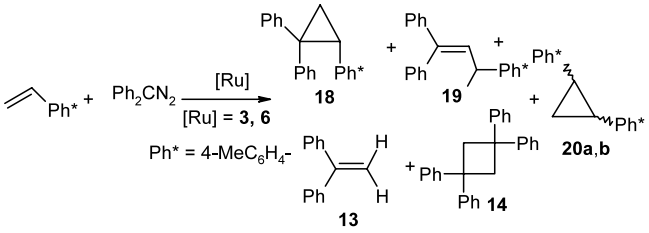
Complex	*T* (°C)	Time (h)	Yield (%)			
			11	**12**	**13**	**14**
3	55	6	74	8	–	18
4	55	6	74	13	–	13
5	60	7	71	12	–	17
6	60	7	83	–	–	17
7	75	7	72	16	–	12
8	75	7	60	14	17	9
9	75	7	59	14	18	9
10	75	7	99.9	–	–	0.1



Scheme 4.

Table 5
Reaction of Ph_2CN_2 with α-methyl styrene catalysed by **3**–**10**

Complex	*T* (°C)	Time (h)	Yield (%)					
			15	**16**	**17a**	**17b**	**13**	**14**
3	50	6	41	10	9	14	20	6
4	50	6	48	–	27	17	–	8
5	55	6.5	49	10	13	10	10	8
6	50	7	49	14	–	29	–	8
7	75	8	45	11	11	14	11	8
8	75	8	39	15	13	15	10	8
9	75	8	45	13	19	–	17	6
10	75	8	48	13	10	6	15	8

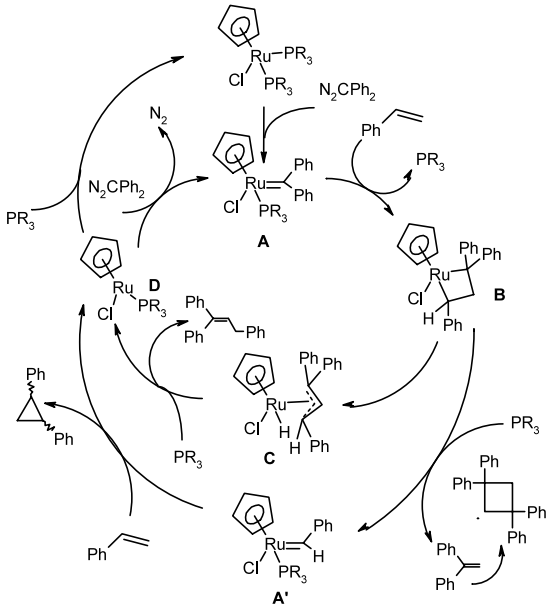


Scheme 5.

It is well known that many metal-mediated C–C bond-forming reactions using diazo compounds proceed through a carbene intermediate [22,23]. The reactions follow the mechanism proposed earlier by Werner [24] and are shown in Scheme 6, which explains the formation of all products (cyclopropane, propene and

Table 6
Reaction of Ph_2CN_2 with 4-methyl styrene catalysed by **3** and **6**

Complex	T (°C)	Time (h)	Yield (%)				
			18	**19**	**20a,b**	**13**	**14**
3	80	8	22	10	26	15	27
6	80	8	57	11	24	–	8



Scheme 6.

ethene) except for cyclobutane derivative. The product 1,1,3,3-tetraphenyl cyclobutane may be the result of dimerisation of diphenyl ethene.

The reactions of styrenes with Ph_2CN_2 in the presence of Ru(II) complexes are presumed to proceed through carbene intermediates. When disubstituted complexes (**4** and **6**) were used the possible intermediate is [CpRu(=CPh_2)Cl($PPh_2N(H)R$)] (R = Ph, C_6H_{11}). In the case of monosubstituted complexes (**3** and **5**), the carbene intermediate may be a mixture of complexes, [CpRu(=CPh_2)Cl(PPh_3)] and [CpRu(=CPh_2)Cl($PPh_2N(H)R$)] (R = Ph, C_6H_{11}). The possible intermediates involving the complexes **7**–**10** can be either [CpRu(=CPh_2)($Ph_2PN(R)PPh_2$-κP)(PPh_3)]Cl (**X**) or [CpRu(=CPh_2)($Ph_2PN(R)PPh_2$-κP,κP)]Cl (**Y**). In order to identify the carbene intermediates in the reactions involving the ionic complexes **7**–**10**, a typical reaction was carried out in an NMR tube in the presence of complex **10** and was monitored by ^{31}P-NMR spectroscopy. The ^{31}P-NMR spectroscopic features for the intermediates **X** and **Y** are different; **Y** is anticipated to give a single resonance, whereas for **X** two doublets (one for uncoordinated PPh_2 end and the other for PPh_3) and a doublet of doublet for coordinated PPh_2 are expected.

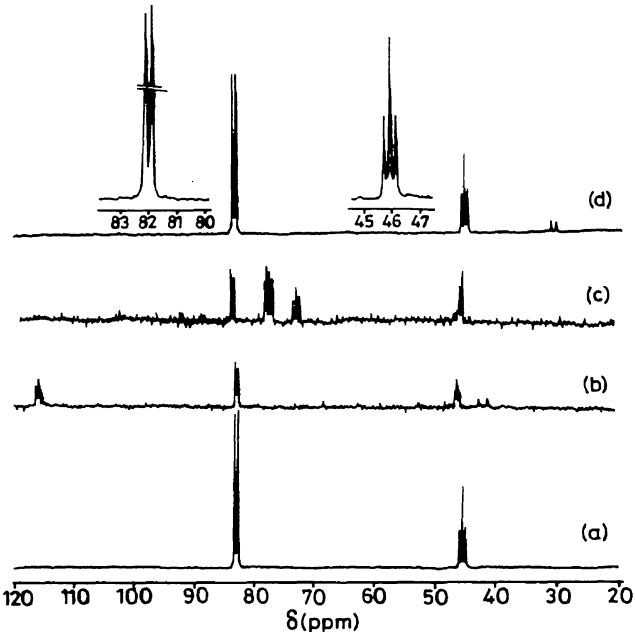
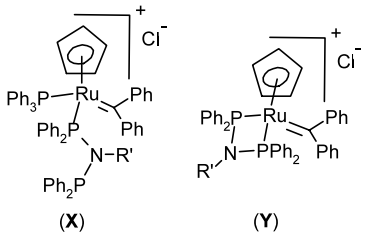


Fig. 3. Variable temperature ^{31}P-NMR (in C_6D_6) spectra of the reaction of α-methyl styrene with diphenyldiazomethane (a) complex **10** at room temperature before the reaction, (b) after 1 h at 70 °C, (c) after 3 h at 75 °C, (d) after the reaction is complete (recorded after 9 h at room temperature).

When the reaction was carried out in an NMR tube in the presence of complex **10** with α-methyl styrene, the triplet due to PPh_3 group became broad and then turned to a doublet, whereas the doublet due to the chelate complex deformed and appeared as a doublet of doublet at 78.2 ppm and a doublet at 72.7 ppm which were assigned to coordinated and uncoordinated phosphorus centres of $Ph_2N(R)PPh_2$. This indicates that the catalytic process involves the carbene intermediate '**X**' and not '**Y**'. An additional peak appeared at 115.9 ppm at high temperature and disappeared after 1 h which remains unidentified. After 9 h complex **10** was regenerated, as confirmed by its ^{31}P-NMR spectrum shown in Fig. 3.



3. Conclusion

The reactions of [CpRuCl(PPh_3)$_2$] with aminophosphines, $Ph_2PN(H)R$ (R = Ph, C_6H_{11}) afford monosubstituted and disubstituted ruthenium(II) complexes **3**–**6**

depending upon the reaction conditions and the stoichiometry. The ionic complexes of aminobis(phosphines) **7**–**10** were obtained in moderate yield. Complexes **3**–**10** have been found to catalyse the cyclopropanation and C–C coupling reaction of diphenyldiazomethane and terminal alkene (styrene derivatives). The catalytic activity of complexes **3**–**10** is different when compared to that of [CpRuCl(PPh_3)$_2$]. This could be due to the different substituents on phosphorus atom and this difference in reactivity gives scope for new catalytic conversions at metal centre. Formation of 1,1,3,3-tetraphenyl cyclobutane was observed for the first time in the cyclopropanation reactions. Further investigation to isolate the carbene intermediates in the catalytic cycle and to understand the mechanism to get insight into the factors governing chemo- and stereoselectivity are in progress in our laboratory.

4. Experimental

4.1. General methods

All manipulations were performed under rigorously anaerobic conditions using Schlenk techniques. Solvents were dried and distilled under the nitrogen atmosphere prior to use. The aminophosphines, RN(H)PPh_2 (R = Ph, [25] C_6H_{11} [17i]), bis(diphenylphosphino)amines, RN(PPh_2)$_2$ (R = Et, ^{n}Pr, ^{i}Pr [26], ^{n}Bu [27]), CpRuCl(PPh_3)$_2$ [28] and Ph_2CN_2 [29] were prepared according to the literature procedures, whereas styrene, α-methyl styrene and 4-methyl styrene were purchased from Aldrich and used without further purification. NMR spectra were recorded using VXR 300 and Bruker AMX 400 spectrometer and shifts were determined with reference to deuterium signal of the solvent employed. The ^{1}H-NMR chemical shifts are reported in ppm from internal Me_4Si and ^{31}P-NMR spectra are reported in ppm from external 85% H_3PO_4. Positive values indicate downfield shifts. IR spectra were recorded on a Nicolet Impact 400 FT IR instrument in KBr disk. Microanalyses were performed on a Carlo Erba model 1112 elemental analyser. Melting points were determined in capillary tubes and were not corrected. High-resolution mass spectra (HRMS) were recorded on MASPEC (msco/9849) system. GC–MS measurements were performed with HP G1800A GCD instrument.

4.2. Preparation of [CpRuCl(PPh_3)($Ph_2PN(H)Ph$)] (**3**)

A mixture of CpRuCl(PPh_3)$_2$ (0.05 g, 0.068 mmol) and $Ph_2PN(H)Ph$ (0.019 g, 0.068 mmol) in CH_2Cl_2 (7 ml) was stirred at room temperature (r.t.) for 8 h. The reaction mixture was evaporated under reduced pressure and the residue obtained was crystallized from Et_2O (5 ml) at r.t. to get orange–red crystals of **3**. Yield: 90% (0.46 g, 0.0619 mmol). M.p.: 158–161 °C (dec.). Anal. Calc. for $C_{41}H_{36}ClNP_2Ru$: C, 66.44; H, 4.89; N, 1.89. Found: C, 66.74; H, 4.68; N, 1.75%. IR (KBr disk) cm^{-1}: ν_{NH}: 3250 br m. ^{1}H-NMR ($CDCl_3$):δ 8.00–7.20 (m, *phenyl*, 30H) 5.20 (s, C_5H_5, 5H). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 42.9 (d, PPh_3), 72.4 (d, PPh_2) ($^2J_{PP}$ = 42.4 Hz).

4.3. Preparation of [CpRuCl($PPh_2N(H)Ph$)$_2$] (**4**)

To a solution of CpRuCl(PPh_3)$_2$ (0.05 g, 0.068 mmol) in toluene (6 ml) was added $Ph_2PN(H)Ph$ (0.038 g, 0.13 mmol) in toluene (7 ml). The reaction mixture was heated to 90 °C for 8 h. The reaction mixture was dried under *vacuo*, and the orange red residue obtained was washed with hot heptane (3 × 5 ml) and crystallized from CH_2Cl_2–*n*-hexane (2:1) mixture at −10 °C and was identified as **4**. Yield: 75% (0.046 g, 0.0608 mmol). M.p.: 200–202 °C (dec.). Anal. Calc. for $C_{41}H_{37}ClN_2P_2Ru$: C, 65.12; H, 4.93; N, 3.70. Found: C, 64.95; H, 4.84; N, 3.60%. IR (KBr disk) cm^{-1}: ν_{NH}: 3256 br s. ^{1}H-NMR ($CDCl_3$): δ 7.45–7.16 (m, P*Ph*, 20H), 6.85 (t, N-Ph-*m*, 4H, $^3J_{HH}$ = 7.5 Hz), 6.61 (t, N-Ph-*p*, 2H, $^3J_{HH}$ = 7.5 Hz), 6.34 (d. N-Ph-*o*, 4H, $^3J_{HH}$ = 7.8 Hz), 5.20 (s, C_5H_5, 5H). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 72.6 (s). MS (HRMS): 756.12 (*m*/*z*).

The heptane extract was evaporated to dryness and Et_2O (3 ml) was added, which gave orange–red crystals of **3**. Yield: 20% (0.011 g, 0.014 mmol).

Complex, CpRuCl($PPh_2N(H)Ph$)$_2$ (**4**) can also be prepared from CpRuCl(PPh_3)($PPh_2N(H)Ph$) (**3**). A mixture of **3** (0.030 g, 0.04 mmol) and $Ph_2PN(H)Ph$ (0.013 g, 0.048 mmol) in toluene (10 ml) was heated to 80 °C for 6 h. The reaction mixture was evaporated to dryness and the residue obtained was washed with hot heptane (3 × 5 ml) and re-dissolved in CH_2Cl_2–*n*-hexane (2:1) mixture and cooled to −10 °C to give orange–red crystals of **4**. Yield: 50% (0.015 g, 0.020 mmol).

4.4. Preparation of [CpRuCl($PPh_2N(H)C_6H_{11}$)(PPh_3)] (**5**)

A mixture of CpRuCl(PPh_3)$_2$ (0.05 g, 0.068 mmol) and $PPh_2N(H)C_6H_{11}$ (0.019 g, 0.068 mmol) in CH_2Cl_2 (7 ml) was stirred at r.t. for 8 h. The solvent was evaporated under reduced pressure and the residue obtained was crystallized from Et_2O (5 ml) at r.t. to give orange–red crystalline solid identified as the product, **5**. Yield, 83% (0.043 g, 0.057 mmol). M.p.: 158–161 °C (dec.). Anal. Calc. for $C_{41}H_{42}ClNP_2Ru$: C, 65.90; H, 5.66; N, 1.87%. Found: C, 66.14; H, 5.49; N, 1.78%. IR (KBr disk) cm^{-1}: ν_{NH}: 3250 br m. ^{1}H-NMR ($CDCl_3$):δ 7.98–7.02 (m, *phenyl*, 25H), 4.14 (s, C_5H_5,

5H), 3.87 (m, N*H*, 1H), 2.56–0.77 (m, C_6H_{11}, 11H). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 42.9 (d, *P*Ph_3, 1P), 77.9 (d, *P*Ph_2, 1P) ($^2J_{PP} = 48.5$ Hz). MS (HRMS): 747.11 (*m*/*z*).

4.5. Preparation of [CpRuCl(PPh$_2$N(H)C$_6$H$_{11}$)$_2$] (6)

A mixture of $CpRuCl(PPh_3)_2$ (0.05 g, 0.068 mmol) and $Ph_2PN(H)C_6H_{11}$ (0.049 g, 0.172 mmol) in toluene (12 ml) was heated to 95 °C for 12 h. The solution was evaporated to dryness under reduced pressure and the residue obtained was washed with *n*-hexane (5 × 3 ml). The orange–red residue was crystallized from CH_2Cl_2–*n*-hexane (2:1) mixture at −10 °C and was identified as **6**. Yield: 69% (0.047 g, 0.047 mmol). M.p.: 180–182 °C (dec.). Anal. Calc. for $C_{41}H_{49}ClN_2P_2Ru$: C, 64.10; H, 6.43; N, 3.65. Found: C, 63.74; H, 6.41; N, 3.76%. IR (KBr disk) cm^{-1}: ν_{NH}: 3318 s. ^{1}H-NMR (CD_2Cl_2):δ 7.98–7.04 (m, *phenyl*, 20H), 4.12 (s, C_5H_5, 5H), 2.90–0.44 (m, C_6H_{11}, 22H). $^{31}P\{^1H\}$-NMR (CD_2Cl_2): δ 81.8 (s). MS (HRMS): 768.21 (*m*/*z*).

The *n*-hexane filtrate was evaporated under reduced pressure and Et_2O (5 ml) was added and cooled to 0 °C to result in orange–red crystals of **5**. Yield: 39% (0.02 g, 0.027 mmol).

4.6. Preparation of [CpRu(PPh$_2$N(R)PPh$_2$)(PPh$_3$)]Cl (R = Et, 7; ^{n}Pr, 8; ^{i}Pr, 9; ^{n}Bu, 10)

To a stirring solution of $CpRuCl(PPh_3)_2$ (0.050 g, 0.069 mmol) in toluene (5 ml) was added a solution of $PPh_2N(R)PPh_2$ (R = Et, ^{n}Pr, ^{i}Pr, ^{n}Bu) (0.069 mmol) also in toluene (5 ml) and the reaction mixture was heated to 100–105 °C for 10 h (12 h when R = ^{i}Pr). The yellow solid precipitated out was filtered and washed with Et_2O (3 × 5 ml) and crystallized from CH_2Cl_2–*n*-hexane (2:1) mixture to give analytically pure products, **7**–**10**.

4.7. [CpRu(PPh$_2$N(Et)PPh$_2$)(PPh$_3$)]Cl (7)

Yield: 52% (0.035 g, 0.039 mmol). M.p.: 214–218 °C (dec.). Anal. Calc. for $C_{49}H_{45}ClNP_3Ru$: C, 67.08; H, 5.17; N, 1.60. Found: C, 67.12; H, 5.21; N, 1.56%. ^{1}H-NMR ($CDCl_3$): δ 7.51–6.84 (m, *phenyl*, 35H), 4.58 (s, C_5H_5, 5H), 3.43 (m, CH_2, 2H), 1.05 (t, CH_3, 3H, $^3J_{HH}$ = 7.16 Hz). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 44.1 (t, *P*Ph_3, 1P), 82.7 (d, *P*Ph_2, 2P), ($^2J_{PP} = 34.6$ Hz).

4.8. [CpRu(PPh$_2$N(^{n}Pr)PPh$_2$)(PPh$_3$)]Cl (8)

Yield: 61% (0.038 g, 0.042 mmol). M.p.: 232–235 °C (dec.). Anal. Calc. for $C_{50}H_{47}ClNP_3Ru$: C, 67.37; H, 5.31; N, 1.57. Found: C, 67.04; H, 5.22; N, 1.56%. ^{1}H-NMR ($CDCl_3$): δ 7.55–6.84 (m, *phenyl*, 35H), 4.60 (s, C_5H_5, 5H), 3.19 (m, CH_2, 2H), 1.45 (m, CH_2, 2H), 0.67 (t, CH_3, 3H, $^3J_{HH} = 6.96$ Hz). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 44.6 (t, *P*Ph_3, 1P), 82.7 (d, *P*Ph_2, 2P) ($^2J_{PP} = 34.7$ Hz).

4.9. [CpRu(PPh$_2$N(^{i}Pr)PPh$_2$)(PPh$_3$)]Cl (9)

Yield: 65% (0.040 g, 0.045 mmol). M.p.: 212–213 °C (dec.). Anal. Calc. for $C_{50}H_{47}ClNP_3Ru\cdot 0.5CH_2Cl_2$: C, 64.96; H, 5.18; N, 1.49%. Found: C, 65.04; H, 5.15; N, 1.33%. ^{1}H-NMR ($CDCl_3$): δ 7.59–6.97 (m, *phenyl*, 35H), 4.36 (s, C_5H_5, 5H), 4.07 (septet, CH, 1H, $^3J_{HH} = 6.96$ Hz), 0.92 (d, CH_3, 6H, $^3J_{HH} = 6.96$ Hz). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 45.8 (t, *P*Ph_3, 1P), 80.8 (d, *P*Ph_2, 2P) ($^2J_{PP} = 36.3$ Hz).

4.10. [CpRu(PPh$_2$N(^{n}Bu)PPh$_2$)(PPh$_3$)]Cl (10)

Yield: 46% (0.029 g, 0.032 mmol). M.p.: 218–221 °C (dec.). Anal. Calc. for $C_{51}H_{49}ClNP_3Ru$: C, 67.65; H, 5.45; N, 1.56%. Found: C, 67.61; H, 5.46; N, 1.55%. ^{1}H-NMR ($CDCl_3$): δ 7.54–6.85 (m, *phenyl*, 35H), 4.58 (s, C_5H_5, 5H), 3.24 (m, CH_2, 2H), 1.34 (m, CH_2, 2H), 1.04 (sextet, CH_2, 2H, $^3J_{HH} = 7.28$ Hz), 0.68 (t, CH_3, 3H, $^3J_{HH} = 7.28$ Hz). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 44.1 (t, *P*Ph_3, 1P), 82.0 (d, *P*Ph_2, 2P) ($^2J_{PP} = 34.8$ Hz).

4.11. Catalytic cyclopropanation of alkenes with diphenyldiazomethane

All experimental details are given in Tables 4–6. In a typical procedure, 0.005 mmol of the complex (**3**–**10**) was dissolved in corresponding alkene (1 ml). A mixture of Ph_2CN_2 (1 mmol) and alkene (2 ml) was added to the catalyst and heated to an appropriate temperature. Then the reaction mixture was stirred for an appropriate time and the crude oil was chromatographed on a column of silica gel and eluted with *n*-hexane and CH_2Cl_2 to separate cyclopropane, propene and cyclobutane derivatives, which are detected in the reaction mixtures by GC–MS and also identified by ^{1}H-NMR spectroscopic data. Yields given in Tables 4–6 are calculated based on GC–MS.

4.12. X-ray crystallography

Crystals of compounds **3** and **4** obtained as described above were mounted on Pyrex filaments with epoxy resin. Bruker P4/Ra/SMART 1000 CCD diffractometer (for compound **3**) and Nonius MACH3 diffractometer (for compound **4**) were used for the unit cell determination and intensity data collection. The initially obtained unit cell parameters were refined by accurately centring randomly selected 25 reflections in the θ ranges (7.48–12.42°) for compound **4**. Periodic monitoring of check reflections showed stability of the intensity data. Details of the crystal and data collection are given in Table 1. The data were corrected by SADABS correction method

and the structure was solved by direct methods (SHELXS 93) and the calculations were performed with the SHELXL 93 [30,31] program for compound **3**, whereas for compound **4**, the data correction was done by psi scan method and the structure was solved by direct methods (SHELXS 97) and refined using SHELXL 97 software [32]. The non-hydrogen atoms were refined with anisotropic thermal parameters. All the hydrogen atoms were geometrically fixed and allowed to refine using riding model.

5. Supplementary material

Full details of data collection and structure refinement have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 217068 and 217069 for compounds **3** and **4**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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