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Suzuki–Miyaura, Mizoroki–Heck carbon–carbon coupling and hydrogenation reactions catalysed by Pd^{II} and Rh^{I} complexes containing cyclodiphosphazane *cis*-{^{t}BuNP(OC$_6$H$_4$OMe-*o*)}$_2$

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Abstract. The catalytic activity of the palladium complex *cis*-[PdCl$_2${(^{t}BuNP(OC$_6$H$_4$OMe-*o*))$_2$-κP}$_2$] (**2**) containing *cis*-{^{t}BuNP(OC$_6$H$_4$OMe-*o*)}$_2$ (**1**) in Suzuki–Miyaura and Mizoroki–Heck carbon–carbon cross coupling reactions is described. The compound **2** also displays very high activity in Mizoroki–Heck coupling reactions. The rhodium(I) complex [RhCl(COD){(^{t}BuNP(OC$_6$H$_4$OMe-*o*))$_2$-κP}] (**3**) acts as an excellent catalyst for the hydrogenation of several terminal olefins.

Keywords. Cyclodiphosphazane; catalysis; palladium and rhodium complexes; Suzuki–Miyaura reactions; Mizoroki–Heck reactions; hydrogenation reactions.

1. Introduction

Although a large number of phosphorus-based ligands are available, the enthusiasm to design newer ones is remarkable mainly due to the demand from the industry for economical and robust ligands that can combine with appropriate transition metals to generate universal homogeneous catalysts for more than one type of organic transformations.[1] In recent years Suzuki–Miyaura[2] and Mizoroki–Heck[3] reactions have received wide acceptance in the field of cross-coupling reactions. Catalytic reactions employed by phosphine modified palladium complexes often benefited due to the mild reaction conditions and selectivity in some cases. Consequently, bountiful phosphorus-based ligands have been developed and their catalytic usefulness has been demonstrated.[4]

The four-membered saturated P_2N_2 ring system known as cyclodiphosphazanes or diazadiphosphetidines [RNPX]$_2$ (R = ^{t}Bu, Ph, X = Cl, NR, OR, R, etc.) has attracted increased attention[5] in recent years because of its excellent synthetic utility in the design of macrocycles,[6] as ligands in coordination and organometallic chemistry and also as catalysts in ethene polymerization reactions.[7] Apart from the recent reports on the application of cyclodiphosphazanes in N–C coupling reactions and as mechanistic probes for organic reactions,[8] the catalytic ability of the transition metal complexes of cyclodiphosphazanes in coupling reactions or hydrogenation reactions is not explored regardless of their resistance towards acid and base promoted hydrolysis reactions which often tend to degrade the ligands during catalytic reactions. Recently, we have reported a series of cyclodiphosphazanes with various donor functionalities and their extensive transition metal chemistry[9] and biological studies.[10] As a part of our interest in designing new inexpensive and robust ligands and studying their coordination behaviour and catalytic applications,[11] we report here the catalytic behaviour of palladium(II) and rhodium(I) complexes[12] of cyclodiphosphazane, toward carbon–carbon coupling and hydrogenation reactions.

2. Experimental

Most of the bromo and chloro compounds, phenylboronic acid, styrene, *n*-butyl acraylate and *t*-butyl acraylate were purchased from Aldrich. Anhydrous K_3PO_4, and K_2CO_3 were purchased from SIGMA chemicals and SDFINE chemicals, respectively and used as received without further purification. Technical grade methanol, DME and DMF were used for all catalytic reactions. Gas chromatographic analyses

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were performed on a Thermo Scientific Polaris Q and focus GC equipped with a capillary column. ^{1}H NMR spectra were recorded on VRX 400 spectrometer operating at a frequency of 400 MHz. Chemical shifts are in ppm using tetramethyl silane as internal standard. Microanalysis was carried out on a Carlo Erba Model 1106 elemental analyser. Melting points of all compounds were determined on Vergo melting point apparatus and are uncorrected. Electro-spray ionization (EI) mass spectrometry experiments were carried out using Waters Q-Tof micro-YA-105. The compounds *cis*-[$PdCl_2${(^{t}BuNP(OC_6H_4OMe-*o*))$_2$-*κP*}$_2$] (**2**) and [RhCl(COD){(^{t}BuNP(OC_6H_4OMe-*o*))$_2$-*κP*}] (**3**) were prepared according to the published procedures.[12]

2.1 *General procedure for the Suzuki–Miyaura coupling reaction*

In a two-necked round bottom flask the appropriate amount of catalyst and 5 mL of solvent were placed with a magnetic stir bar. After stirring for 5 min and the aryl halide (0·5 mmol), aryl boronic acid (0·75 mmol) and base (1 mmol) were added to the reaction flask. The reaction mixture was heated to the appropriate temperature for the required time (the course of reaction was monitored by GCMS analysis) and then the solvent was removed under reduced pressure. The resultant residual mixture was diluted with H_2O (8 mL) and Et_2O (8 mL), followed by extraction twice (2 × 6 mL) with Et_2O.

The combined organic fraction was dried ($MgSO_4$), filtered and the solvent was removed under reduced pressure and the residue was redissolved in 5 mL of dichloromethane. An aliquot was taken with a syringe and subjected to GCMS analysis. Yields were calculated against consumption of the aryl halides. The crude material was purified by silica column chromatography using hexane–ethylacetate as an eluent to give the desired biaryls. For experiments with low catalyst loading and comparison of other Pd^{II} sources stock solution of appropriate concentration were prepared by dissolving 1·0 mg of the palladium catalyst in appropriate amount of dichloromethane and used for each independent run.

2.2 *General procedure for the Mizoroki–Heck reaction*

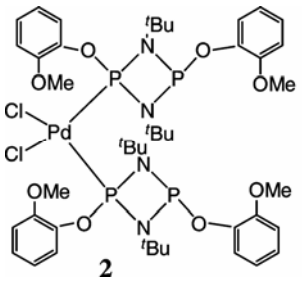
In a two-necked round bottom flask the appropriate amount of catalyst and 5 mL of solvent were placed with a magnetic stir bar. After stirring for 5 min, the terminal olefin (3 mmol) aryl halide (1 mmol) and the base (1·4 mmol) were added to the reaction flask. The reaction mixture was heated to 130 °C for the required time (the course of reaction was monitored by GC–MS analysis) under aerobic conditions and then the solvent was removed under reduced pressure. The resultant residual mixture was diluted with H_2O (8 mL) and Et_2O (8 mL), followed by extraction twice (2 × 6 mL) with Et_2O. The combined organic fraction was dried ($MgSO_4$), filtered, stripped of the solvent under vacuum and the residue was redissolved in 5 mL of dichloromethane. An aliquot was taken with a syringe and subjected to GCMS analysis. Yields were calculated against consumption of the aryl halides.

2.3 *General procedure for hydrogenation reactions*

All catalytic experiments were performed in a 50 mL stainless steel autoclave pressurized with hydrogen at required temperature. In a typical experiment, a solution of the catalyst precursor, the organic substrate (olefin) and base in 20 mL of THF was placed into the reactor and was sealed. The vessel was purged three times with hydrogen and then the autoclave was pressurized with hydrogen (required amount). The reaction mixture was stirred at a particular temperature at 500 rpm and the extent of conversion was determined by periodic GC–MS analysis.

3. Results and discussion

The cyclodiphosphazane, *cis*-[^{t}BuNP(OC_6H_4OMe-*o*)]$_2$ (**1**) containing complexes [$PdCl_2${(^{t}BuNP(OC_6H_4OMe-*o*))$_2$-*κ*P}$_2$] (**2**) and [RhCl(COD){(^{t}BuNP(OC_6H_4OMe-*o*))$_2$-*κ*P}] (**3**) were employed in Suzuki–Miyaura, and Mizoroki–Heck cross coupling and hydrogenation reactions, respectively. The



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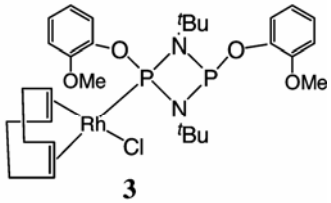
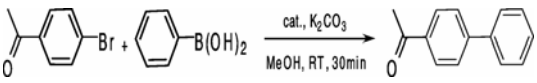


3

coupling reactions between 4-bromoacetophenone and phenylboronic acid in methanol using different catalysts were performed under very mild conditions, viz. room temperature for 30 min (table 1). The best results were obtained by using isolated palladium(II) complex **2** or by generating it *in situ* by mixing **1** and $Pd(COD)Cl_2$ (entries 1 and 2). Use of the other palladium precursors such as $Pd(OAc)_2$ along with **1** also gave satisfactory yield (entry 4). Under similar conditions, $PdCl_2$ and $Pd(SMe_2)_2Cl_2$ supported by cyclodiphosphazane **1** afforded very poor yields (entries 5 and 6). When only [$Pd(COD)Cl_2$] was used, the yield was low (entry 3), which improved to 70% (entry 2) when ligand **1** was introduced. These results suggest that **2** or its precursor mixture is very effective in promoting the Suzuki cross-coupling reactions.

Complex **2** is an active catalyst for Suzuki–Miyaura coupling reactions (table 2). A number of aryl bromides and chlorides have been successfully coupled with phenylboronic acid. We choose as a model reaction, the coupling between *p*-bromoacetophenone (0·5 mmol) and phenylboronic acid (0·75 mmol) in methanol at room temperature in the presence of K_2CO_3 (1 mmol) as a base with catalyst loading of 0·06 mol%. In general, this coupling can be satisfactorily carried out at room temperature for all bromo precursors. Specifically, **2** is an effective catalyst precursor for the coupling of activated (entries 1, 2 and 3) and deactivated (entry 4) aryl bromides. Under similar reaction conditions, both 1,3- and 1,4-dibromo benzene also afforded good yields (entries 5 and 6). The high catalytic efficiency of **2** at room temperature makes it a valuable catalyst.

Table 1. Effect of different palladium catalysts on Suzuki-Miyaura cross coupling reaction[a].



Entry	Catalyst	Yield (%)
1	2	72
2	$Pd(COD)Cl_2$/1	70
3	$Pd(COD)Cl_2$	56
4	$Pd(OAc)_2$/1	57
5	$Pd(SMe_2)_2Cl_2$/1	18
6	$PdCl_2$/1	15

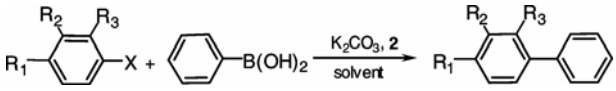
[a]Reaction conditions: Catalyst (0·01 mol%), 4-bromoacetophenone (0·5 mmol), phenylboronic acid (0·75 mmol), K_2CO_3 (1 mmol) and MeOH (5 mL). [b]Conversion to the coupled product determined by GC-MS, based on aryl bromide; average of two runs

As expected, aryl chlorides are more stubborn and their coupling with phenylboronic acid gave modest yields (table 2). Reactions with arylchlorides require higher catalyst loading. The reaction between 2-chlorobenzaldehyde and phenylboronic acid was used as test reaction at 110°C with K_2CO_3 as a base in DMF. The coupling proceeds for 20 h with catalyst loading of 1 mol% and 2 mol% giving 25% and 46% conversions respectively (entries 7 and 8). This catalyst system is able to couple activated aryl chlorides with phenylboronic acid efficiently with 4 mol% of catalyst (entries 9, 10, 11 and 12).

By employing the same palladium complex **2**, Mizoroki–Heck reaction was performed for a range of aryl bromides and the details are given in table 3. All the reactions were examined with K_3PO_4 as a base and N,N-dimethyl acetamide (DMA) as solvent at 130 °C. As expected, the more reactive 4-bromobenzaldehyde and 4-bromoacetophenone underwent clean coupling with styrene giving essentially quantitative yields (entries 1 and 2). The inactivated bromobenzene was coupled with styrene giving excellent yield (entry 3). Reactions involving deactivated arylbromides bearing a methoxy group afforded fewer yields with 0·1 mol% of catalyst (entry 4). On increasing the catalyst loading up to 0·5 mol%, the yield increased to 72% (entry 5). Furthermore, the activated terminal olefins such as *n*-butylacrylate and *t*-butylacrylate efficiently coupled with activated arylbromides (entries 6, 7 and 8). The data given in table 3 shows the efficiency of this new catalyst towards the Mizoroki–Heck coupling of aryl bromides and terminal olefins. This catalyst is more efficient than the Hermann's palladacycle which catalyses the reaction between bromobenzene and styrene in DMA at 140 °C giving 77% yield of the product.

Rhodium complex [$RhCl(COD)\{(^tBuNP(OC_6H_4OMe\text{-}o))_2\text{-}\kappa P\}$] (**3**) has been employed successfully in the catalytic hydrogenation of styrene, α-methyl styrene, etaconic acid and its derivative such as dimethyl etaconate (table 4). For all substrates, the hydrogenation reactions were performed at 80 °C under 4 atm of H_2 in the presence of triethylamine as a base and THF as solvent. The conversion of styrene to ethyl benzene was observed at room temperature with 0·5 mol% of catalyst loading (entry 1) and the rate of the reaction was found to be temperature dependent. At 25 °C or room temperature, the

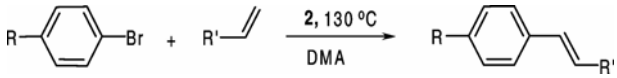
Table 2. Suzuki cross coupling of aryl halides with phenylboronic acid.[a]



Entry	Aryl halides R_1	R_2	R_3	X	Conditions [cat (mol%), time (h), temp (°C), solvent]	Yield (%)[b]	TON/TOF (h^{-1})[c]
1	OMe	H	H	Br	0·05 mol%, 4·5 h, RT, MeOH	99	1980/440
2	CN	H	H	Br	0·06 mol%, 1·5 h, RT, MeOH	99	1650/1100
3	CHO	H	H	Br	0·06 mol%, 2 h, RT, MeOH	99	1650/825
4	OMe	H	H	Br	0·06 mol%, 20 h, RT, MeOH	98	1632/816
5	H	Br	H	Br	0·06 mol%, 4·5 h, RT, MeOH	84	1400/311
6	Br	H	H	Br	0·06 mol%, 20 h, RT, MeOH	83	1384/70
7	H	H	CHO	Cl	1·0 mol%, 20 h, 110°C, DMF	25	25/1
8	H	H	CHO	Cl	2·0 mol%, 20 h, 110°C, DMF	46	23/1
9	H	H	CHO	Cl	4·0 mol%, 20 h, 110°C, DMF	77	20/1
10	NO_2	H	H	Cl	4·0 mol%, 20 h, 110°C, DMF	77	20/1
11	H	H	NO_2	Cl	4·0 mol%, 20 h, 110°C, DMF	75	19/1
12	CN	H	H	Cl	4·0 mol%, 20 h, 110°C, DMF	66	17/1

[a]Reaction conditions: Aryl halide (0·5 mmol), phenylboronic acid (0·75 mmol), K_2CO_3 (1 mmol), solvent (5 mL). [b]Conversion to the coupled product determined by GC–MS, based on aryl halide; average of two runs. [C]Defined as mol product per mol of catalyst (TON); TON per hour (TOF).

Table 3. Mizoroki–Heck coupling of aryl bromides with olefins.[a]

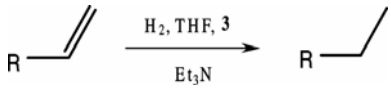


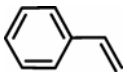
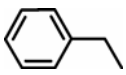
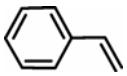
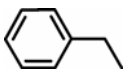
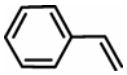
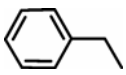
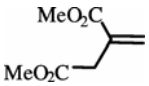
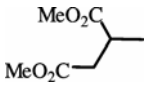
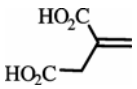
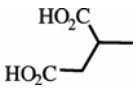
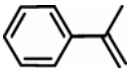
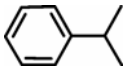
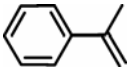
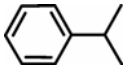
Entry	Aryl bromides (R)	Alkene (R′)	Conditions [cat(mol%), time(h)]	Yield (%)[b]	TON, TOF(h^{-1})
1	CHO	Ph	0·1 mol%, 20 h	100	1000/50
2	$COCH_3$	Ph	0·1 mol%, 20 h	100	1000/50
3	H	Ph	0·1 mol%, 5 h	100	1000/50
4	OMe	Ph	0·1 mol%, 20 h	32	320/16
5	OMe	Ph	0·5 mol%, 20 h	72	720/36
6	$COCH_3$	^{t}BuOC(O)	0·1 mol%, 20 h	100	1000/50
7	$COCH_3$	^{t}BuOC(O)	0·1 mol%, 20 h	100	1000/50
8	$COCH_3$	^{t}BuOC(O)	0·1 mol%, 20 h	100	1000/50

[a]Reaction conditions: Aryl bromide (1 mmol), olefin (1·2 mmol), K_3PO_4 (1·4 mmol), solvent (5 mL). [b]Conversion to the coupled product determined by GC–MS, based on aryl bromide; average of two runs

styrene hydrogenation shows 100% conversion in 20 h (entry 1) and on increasing the temperature to 80 °C, the quantitative conversion takes place within 30 min (entry 2). When the catalyst loading was reduced to 0·1 mol%, the conversion of styrene to ethyl benzene takes 5 h for completion (entry 3). Interestingly, dimethyl etaconate and etaconic acid were hydrogenated efficiently with 0·1 mol% of catalyst giving 100% and 98% yields at 80 °C, respectively (entries 4 and 5). However, the hydrogenation of α-methyl styrene at 80 °C is slow with 40% conversion even after 20 h (entry 6). When the

Table 4. Catalytic olefin hydrogenation reaction.[a]



Entry	Olefin	Product	Conditions [cat (mol %), temp (°C), time (h)]	Yield (%)[b]	TON, TOF (h^{-1})
1			0·5 mol%, RT, 20 h	100	200/10
2			0·5 mol%, 80°C, 0.5 h	100	200/400
3			0·1 mol%, 80°C, 5 h	100	1000/200
4			0·1 mol%, 80°C, 5 h	100	1000/200
5			0·1 mol%, 80°C, 5 h	98	980/196
6			0·1 mol%, 80°C, 20 h	40	400/20
7			0·5 mol%, 80°C, 2 h	100	200/100

[a]Reaction conditions: The molar ratio of substrate to base (Et_3N) was 20 : 1. p(H_2) = 4 atm, solvent (20 mL).
[b]The hydrogenation products determined by GC–MS analysis based on conversion of olefin; average of two runs

catalyst loading was increased to 0·5 mol%, it showed quantitative conversion after 2 h (entry 7). The homogeneous nature of the catalysis was checked by the classical mercury test.[13] The catalyst was found to be considerably more efficient in terms of conversion under mild conditions.

In summary, the use of cyclodiphosphazane based catalysts in the homogeneous catalysis is encouraging because of their high efficiency. The use of palladium complex **2** demonstrated that the higher yields can be achieved under mild conditions in Suzuki–Miyaura coupling reactions for both activated and unactivated aryl bromides. The palladium complex **2** and the rhodium complex **3** were also proved as effective catalysts for Mizoroki–Heck and hydrogenation reactions, respectively. The palladium catalyst was found to be thermally robust for Suzuki–Miyaura coupling of aryl chlorides and Mizoroki–Heck reactions. Because of the versatile catalytic ability of cyclodiphosphazane derivatives, the new catalytic system provides an opportunity to design a catalyst that can promote in one-pot, more than one type of organic transformation. The closer investigation of the mechanism and other catalytic studies with this system are underway in our laboratory.

Acknowledgements

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