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Catalytic application of dinuclear palladium(II) bis(thiosemicarbazone) complex in the Mizoroki-Heck reaction

Rupesh Narayana Prabhu, Rengan Ramesh *

School of Chemistry, Bharathidasan University, Tiruchirappalli 620 024, Tamil Nadu, India

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ABSTRACT

A convenient synthesis of new square planar dinuclear palladium(II) terephthaldehyde bis(thiosemicarbazone) complex has been described. The compositions of the complex have been established by elemental analysis, spectral methods and single crystal X-ray crystallographic technique. The new complex acts as an active recyclable homogeneous catalyst for the Mizoroki-Heck reaction of electron deficient (activating) and electron rich (deactivating) aryl halides with various olefins under optimized conditions.

Carbon–carbon coupling reactions catalysed by transition metal complexes are one of the most powerful and versatile tools in synthetic organic chemistry.[1] Mizoroki and Heck independently reported the palladium(II)-mediated arylation of olefins using palladium(II) salts.[2] Several conditions have been developed since then for the palladium-catalysed Mizoroki-Heck cross-coupling reaction of aryl halides with a wide range of olefinic substrates. Unlike other C–C coupling reactions, the Mizoroki-Heck reaction has the ability to tolerate a variety of functional groups (such as unprotected amino, hydroxyl, aldehyde, ketone, carboxyl, ester, cyano or nitro groups) thus avoiding the need for protection and deprotection of functional groups during the organic transformations.[3] Phosphorous-based ligands improve the catalytic activity of the Mizoroki-Heck reaction as a result of their increasing bulkiness and electron-donating functionality.[4] The reactivity of the different aryl halides decreases in the order ArI > ArBr > ArCl because of the different strengths of the aryl-X bond (C–I < C–Br < C–Cl). For the Mizoroki-Heck coupling reaction of aryl iodides with olefins, very high turnover numbers (TON) have been reported already,[5] however, the search for efficient catalysts for the coupling of olefins with deactivated aryl bromides and ultimately, towards activated aryl chlorides is under progress.[6] A large number of reports have been published on this coupling reaction ascertaining the use of improved catalysts in order to obtain a higher TON and on the influence of various factors such as reactants, catalysts and additives on the rate of the reaction and the selectivity towards the desired products.[7]

There have been a number of reports on the scope and versatility of the Mizoroki-Heck reaction,[8] giving emphasis to air and thermally stable palladium catalysts,[9] palladium nanoparticles,[10] palladium complexes containing sterically hindered phosphines,[11] water soluble catalysts[12] and the use of molten salts as reaction media.[13] Promising approaches for the coupling reaction of aryl bromides and activated aryl chlorides have been reported by using palladium complexes as catalysts containing N-heterocyclic carbene ligands,[14] Schiff base ligands,[15] pincer ligands,[16] aniline ligands[17] as well as cyclometallated ligands containing phosphorous, nitrogen and sulfur donor atoms.[18] Immobilized and non-immobilized palladium compounds have also been employed as effective catalysts for this reaction.[19]

Thiosemicarbazones constitute an important class of Schiff base ligands containing nitrogen and sulfur donor atoms for transition metal ions exhibiting thione–thiol tautomerism in solution owing to the presence of the –NH–C=S functional group. They are versatile ligands exhibiting a wide range of coordination modes in their metal complexes and bind to the metal ion in neutral or anionic form, resulting in four- or five-membered chelate rings.[20] A careful view into the literature shows that there are several reports on the synthesis, characterization and biological applications[21] of palladium(II) thiosemicarbazone complexes, however, there are only a few reports on the use of Pd(II) thiosemicarbazone complexes as catalysts for the Mizoroki-Heck reaction.[22]

Though the Mizoroki-Heck reaction has been extensively studied using various palladium complexes, there is no report in the literature where dinuclear palladium(II) bis(thiosemicarbazone) complex was used as a catalyst for this reaction. We herein describe the synthesis and characterization of new dinuclear palladium(II)

* Corresponding author. Tel.: +91 431 240 7053; fax: +91 431 240 7045.
E-mail address: ramesh_bdu@yahoo.com (R. Ramesh).

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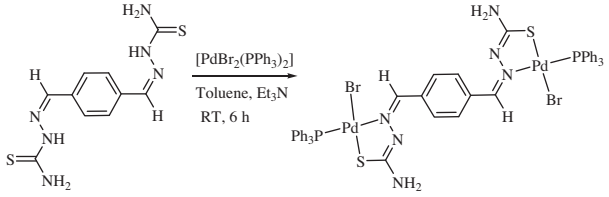
terephthaldehyde bis(thiosemicarbazone) complex incorporated with bromide and triphenylphosphine as ancillary ligands.

The terephthaldehyde bis(thiosemicarbazone) ligand (L) was prepared by the condensation of terephthaldehyde and thiosemicarbazide as reported in the literature.[23] The ligand reacts with $[PdBr_2(PPh_3)_2]$ in 1: 2 molar ratio in toluene and Et_3N for 6 h at room temperature to give the new dinuclear Pd(II) complex of the formula $[Pd_2(L)Br_2(PPh_3)_2]$ (**1**) in 81% yield (Scheme 1). The oxidation state of palladium remains unchanged during the formation of the complex. The complex is air stable in both the solid and liquid states at room temperature and is non-hygroscopic. The complex is readily soluble only in highly polar solvents such as dimethyl formamide (DMF), dimethyl sulfoxide (DMSO) or *N*-methyl-2-pyrrolidone (NMP) producing intense orange coloured solutions. The elemental analysis data of the complex (Calcd: C, 47.00; H, 3.43; N, 7.15; S, 5.46. Found: C, 47.09; H, 3.40; N, 7.19; S, 5.49) are in good agreement with the molecular structure proposed.

The FT-IR spectrum of the complex displays $\nu_{C=N}$ stretch at 1589 cm^{-1} which is at a lower frequency than that of the free ligand (1620 cm^{-1}) indicating coordination of azomethine nitrogen to Pd(II) ion. The $\nu_{C=S}$ and ν_{N-H} of the –N–NH–C=S group at 847 cm^{-1} and 3203 cm^{-1}, respectively in the free ligand disappeared in the complex suggesting enolization and subsequent coordination through the thiolate sulfur to the Pd(II) ion.[24] In the electronic spectrum of the complex, the band below 350 nm is assigned to ligand centred transitions whereas the two strong bands with absorption maxima at 390 nm and 411 nm and the weak broad band at 490 nm are assigned to a combination of charge transfer and d–d transitions.[25]

In the ^1H NMR spectrum of the complex, the aromatic protons appeared as multiplets in the region of δ 8.0–7.0 ppm. The singlet due to azomethine proton (δ 8.6 ppm) in the complex is slightly downfield compared to the free ligand (δ 8.0 ppm), suggesting deshielding upon coordination to Pd(II) ion.[26] The singlet that appeared for the N–NH–C=S proton of the free ligand at δ 11.5 ppm is absent in the complex, supporting enolization and coordination of the thiolate sulfur to the Pd(II) ion. The ^{13}C NMR of the complex shows resonances in the expected regions and the complex revealed a downfield shift of the azomethine carbon relative to the free ligands indicating coordination of the azomethine nitrogen to the metal centre. Also, the signal assigned to the thioketone carbon, which moves upfield from δ 178 ppm in the free ligand to δ 170 ppm in the complex, results from the reduced C–S bond order upon coordination.[27] The ^{31}P NMR spectra of the complex showed a singlet resonance in the region of δ 26.8 ppm in agreement with the existence of equivalent phosphorus nuclei.[28] The ^1H, ^{13}C and ^{31}P NMR spectra of the complex are given in Figure S1–S3, Supplementary data.

Single crystal of the complex, **1**, was obtained by the slow evaporation of DMSO solution of the complex at room temperature. The molecular structure of the complex has been determined by single crystal X-ray diffraction to confirm the coordination mode of the ligand and geometry of the complex. The ORTEP view of complex is shown in Figure 1. The ligand coordinates with each Pd(II) ion via the azomethine nitrogen and the thiolate sulfur forming



Scheme 1. Synthesis of dinuclear Pd(II) bis(thiosemicarbazone) complex.

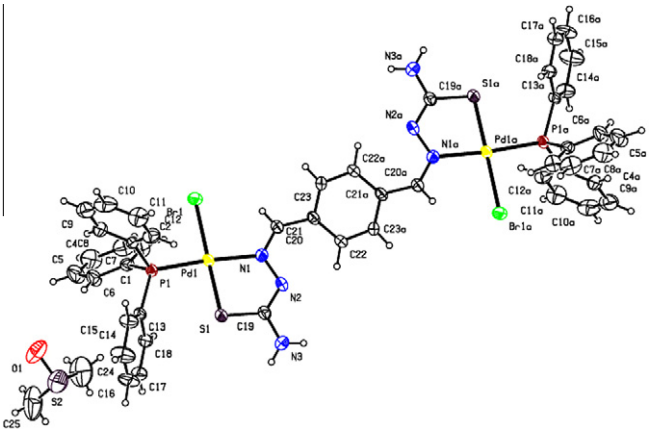


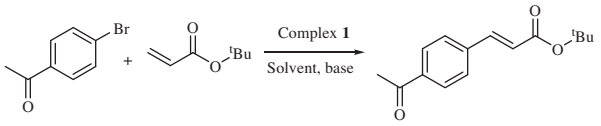
Figure 1. ORTEP diagram of **1**. DMSO with 30% probability. Selected bond lengths (Å): Pd1–N1 2.106(5), Pd1–S1 2.2326(18), Pd1–P1 2.2594(16), Pd1–Br1 2.4534(9), S1–C19 1.729(7), C19–N2 1.326(7), N1–N2 1.370(7), N1–C20 1.270(8). Selected bond angles (°): N1–Pd1–S1 83.36(15), S1–Pd1–P1 92.12(6), P1–Pd1–Br1 88.56(5), N1–Pd1–Br1 96.01(15), N1–Pd1–P1 175.10(15), S1–Pd1–Br1 178.35(5), C19–N2–N1 113.4(5), C20–N1–N2 116.2(6), N2–C19–S1 125.8(6).

one five-membered chelate ring. One PPh_3 group (trans to the azomethine nitrogen) and one bromide ion (trans to thiolate sulfur) also coordinate with the Pd(II) ion to form a BrNPS square plane. The complex is having a distorted square planar geometry as reflected in all the bond parameters around Pd(II) ion. The crystal structure also reveals the presence of one solvent molecule (DMSO) of crystallization. The planar Pd units are slightly deviated from planarity with the central phenylene moiety with a twist angle of 7.30°. The bond lengths and bond angles are in good agreement with the reported data on related Pd(II) thiosemicarbazone complexes.[29]

A careful view into the literature shows that the reaction conditions such as solvent, base and reaction temperature have a dramatic influence on the yield of the Mizoroki-Heck reaction. In order to optimize solvent, base and reaction temperature, the Mizoroki-Heck cross-coupling reaction of 4-bromoacetophenone with *t*-butyl acrylate using complex **1** as catalyst under various reaction conditions was initially examined (Table 1). A controlled experiment indicated that no cross-coupling product was observed in the absence of the catalyst or base. The extent of conversion is solvent-dependent and low conversions were observed in NMP and DMSO as solvent even at higher temperature. DMF was found to be the solvent of choice with excellent isolated yield even at a lower temperature. A variety of inorganic and organic bases were screened as the role of the base used is to neutralize and remove HBr. The reaction rates were found to be strongly dependent on the base employed. A remarkable increase in the product formation was observed in the presence of inorganic bases like K_2CO_3 or Na_2CO_3. However, K_2CO_3 being slightly more basic than Na_2CO_3 (entry 10) gave a higher conversion (entry 6). In the case of organic bases such as triethylamine, pyridine or pyrrolidine, the yield of the cross-coupled product was considerably reduced. The cross-coupling reaction proceeds even at room temperature in DMF using K_2CO_3 as base, however, the reaction was slow with a lower isolated yield even after 24 h. Thus it was concluded that K_2CO_3 as base in DMF solvent at 100 °C is the optimized condition for the coupling reaction.

It is preferred to use small amounts of catalyst and still achieve high conversions in the Mizoroki-Heck cross-coupling reactions. Also, it has been reported that low palladium catalyst loading is required in some cases because the palladium black formation at high catalyst loading inhibits the catalytic reaction.[30] In order to ascertain the efficiency of the catalyst, different catalyst: substrate

Table 1
Optimization of reaction conditions[a]

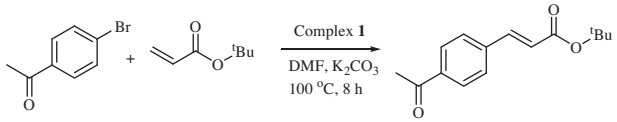


Entry	Solvent	Base	Temp (°C)	Yield[b] (%)	TON[c]
1	NMP	K_2CO_3	145	73	730
2	NMP	K_2CO_3	100	53	530
3	DMSO	K_2CO_3	145	43	430
4	DMSO	K_2CO_3	100	32	320
5	DMF	K_2CO_3	145	>99	990
6	DMF	K_2CO_3	100	>99	990
7	DMF	K_2CO_3	25[d]	38	380
8	DMF	K_2CO_3	100[e]	—	—
9	DMF	—	100	—	—
10	DMF	Na_2CO_3	100	96	960
11	DMF	CH_3COOK	100	32	320
12	DMF	CH_3COONa	100	29	290
13	DMF	Et_3N	100	<15	<150
14	DMF	Pyridine	100	<15	<150
15	DMF	Pyrrolidine	100	<15	<150

[a] Reaction conditions: 4-bromoacetophenone (5 mmol), *t*-butyl acrylate (10 mmol), base (6 mmol), complex **1** (0.1 mol %), solvent (3 mL) for 8 h under N_2 atmosphere.
[b] Isolated yield after column chromatography based on 4-bromoacetophenone (average of two runs).
[c] TON = Turnover number = ratio of moles of product formed to moles of catalyst used.
[d] Reaction carried out for 24 h.
[e] Reaction carried out in the absence of catalyst.

ratios were tested in the cross-coupling reaction of 4-bromoacetophenone with *t*-butyl acrylate in the presence of complex **1** as catalyst and the results are summarized in Table 2. The reaction proceeds with quantitative yield of the cross-coupled product when 1.0 or 0.1 mol % of the catalyst is used (entries 1 and 2). Even when 0.01 mol % of the catalyst is used (entry 3), excellent isolated yield of the cross-coupled product is obtained. Further, it was observed that even under very low catalyst loading of 0.001 or 0.0001 mol % (entries 4 and 5), the reaction proceeds smoothly accompanied by a drop in isolated yields. Interestingly these reactions can be conducted with an ultra-low catalyst loading of 0.00001 mol % (entry 6) with high turnover numbers (TON). Since the isolated yields are good with appreciable TON when 0.01 mol % of catalyst is used, it was concluded that this catalyst: substrate ratio is the best suitable for the coupling reaction.

Table 2
Effect of catalyst loading[a]



Entry	Catalyst (mol %)	Yield[b] (%)	TON[c]
1	1.0	>99	99
2	0.1	>99	990
3	0.01	94	9400
4	0.001	72	72,000
5	0.0001	49	490,000
6	0.00001	11	11,00,000

[a] Reaction conditions: 4-bromoacetophenone (5 mmol), *t*-butyl acrylate (10 mmol), K_2CO_3 (6 mmol), DMF (3 mL) at 100 °C for 8 h under N_2 atmosphere.
[b] Isolated yield after column chromatography based on 4-bromoacetophenone (average of two runs).
[c] TON = Turnover number = ratio of moles of product formed to moles of catalyst used.

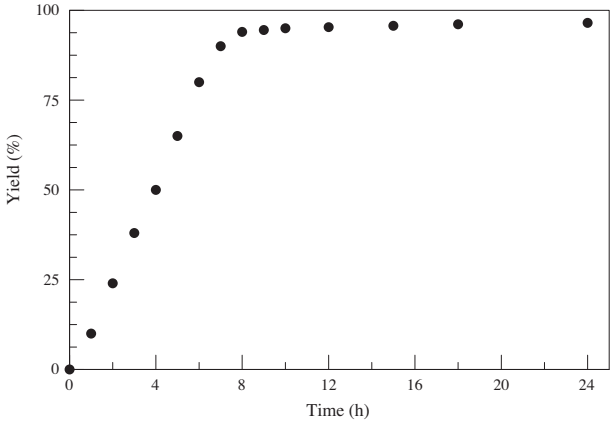


Figure 2. Influence of reaction time on isolated yield.

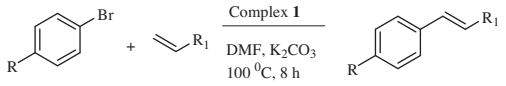
The progress of the formation of 4-acetyl-trans-cinnamic acid *tert*-butyl ester from the cross-coupling reaction of 4-bromoacetophenone and *t*-butyl acrylate as a function of time using complex **1** as catalyst is displayed in Figure 2. The reaction conditions were similar to that given in Table 2, where 0.01 mol % of the complex **1** is used. The results indicate that the formation of the cross-coupled product increased initially with the progress of the reaction time, reached a maximum and then remained unchanged. Reasonably good isolated yield for the formation of the cross-coupled product was observed at the optimum reaction time of 8 h (94%) whereas over a period 15 h the maximum isolated yield (~96%) was achieved.

Using the above optimized conditions, the Mizoroki-Heck cross-coupling reaction of activated, non- and deactivated aryl bromides with a variety of vinylic substrates (*t*-butyl acrylate, methyl acrylate, styrene, 4-methyl styrene and 4-chloro styrene) was carried out with complex **1** as catalyst using DMF/K_2CO_3 at 100 °C (Table 3). Only trans products were obtained selectively in all the cases. In general, for a particular aryl bromide, the cross-coupled products were obtained in excellent isolated yield with *t*-butyl acrylate (entries 1–6) or methyl acrylate (entries 7–12) as the vinylic substrate. The corresponding reactions with styrene as the olefinic partner gave slightly lower yield (entries 13–18). Electron donating substituent (4-methyl) on styrene gave slightly lower yield (entries 19–24) when compared to that of styrene, whereas electron withdrawing substituent (4-chloro) on styrene gave slightly higher yield (entries 25–30) as that compared with styrene. It was also observed that for a particular olefin, activated electron deficient aryl bromides (such as 1-bromo-4-nitro benzene or 4-bromo acetophenone) could effectively couple with the olefins providing the corresponding products in excellent yield after 8 h. The non-activated electron neutral substrate (bromo benzene) and deactivated electron rich substrates (such as 4-bromo toluene, 4-bromo anisole and 4-bromo phenol) gave moderate amount of products when coupling with the olefins. All these indicated that the electronic effect of substituents on the aryl bromides had great influence on the reaction and the electron withdrawing substituents were more favourable for cross coupling.

The Mizoroki-Heck cross-coupling reaction of an activated aryl chloride, 4-chloroacetophenone, with various olefinic substrates was also investigated using complex **1** as the catalyst and K_2CO_3 as base in DMF at 100 °C (Table 4). It was observed that complex **1** acts as an active catalyst for the cross-coupling reaction of 4-chloroacetophenone with various olefins. However, compared to the bromo analogue, the cross-coupling reaction of the chloro derivative is sluggish even at higher catalyst loading and longer reaction time.

The recycling of the catalyst is one of the important aspects for practical applications. The Mizoroki-Heck cross-coupling of

Table 3
Mizoroki-Heck reaction of aryl bromides with olefins[a]

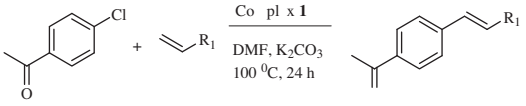


Entry	–R	–R$_1$	Yield[b] (%)	TON[c]	TOF[d]
1	–NO_2	–COO^{t}Bu	97	9700	1213
2	–$COCH_3$	–COO^{t}Bu	94	9400	1175
3	–H	–COO^{t}Bu	89	8900	1113
4	–CH_3	–COO^{t}Bu	83	8300	1038
5	–OCH_3	–COO^{t}Bu	79	7900	988
6	–OH	–COO^{t}Bu	75	7500	938
7	–NO_2	–$COOCH_3$	98	9800	1225
8	–$COCH_3$	–$COOCH_3$	96	9600	1200
9	–H	–$COOCH_3$	91	9100	1138
10	–CH_3	–$COOCH_3$	86	8600	1075
11	–OCH_3	–$COOCH_3$	81	8100	1013
12	–OH	–$COOCH_3$	77	7700	963
13	–NO_2	–C_6H_5	87	8700	1088
14	–$COCH_3$	–C_6H_5	82	8200	1025
15	–H	–C_6H_5	78	7800	975
16	–CH_3	–C_6H_5	74	7400	925
17	–OCH_3	–C_6H_5	68	6800	850
18	–OH	–C_6H_5	64	6400	800
19	–NO_2	–C_6H_4-4-CH_3	84	8400	1050
20	–$COCH_3$	–C_6H_4-4-CH_3	79	7900	988
21	–H	–C_6H_4-4-CH_3	73	7300	913
22	–CH_3	–C_6H_4-4-CH_3	69	6900	863
23	–OCH_3	–C_6H_4-4-CH_3	64	6400	800
24	–OH	–C_6H_4-4-CH_3	60	6000	750
25	–NO_2	–C_6H_4-4-Cl	91	9100	1138
26	–$COCH_3$	–C_6H_4-4-Cl	88	8800	1100
27	–H	–C_6H_4-4-Cl	82	8200	1025
28	–CH_3	–C_6H_4-4-Cl	78	7800	975
29	–OCH_3	–C_6H_4-4-Cl	74	7400	925
30	–OH	–C_6H_4-4-Cl	70	7000	875

[a] Reaction conditions: aryl bromide (5 mmol), olefin (10 mmol), K_2CO_3 (6 mmol), complex **1** (0.01 mol %), DMF (3 mL) at 100 °C for 8 h under N_2 atmosphere.
[b] Isolated yield after column chromatography based on aryl bromide (average of two runs).
[c] TON = Turnover number = ratio of moles of product formed to moles of catalyst used.
[d] TOF = Turnover frequency = TON per hour.

4-bromoacetophenone with *t*-butyl acrylate was selected to demonstrate the feasibility of recycling usage with complex **1** as the catalyst using DMF/K_2CO_3 at 100 °C for 8 h in each run. The recyclability of the complex was investigated for six cycles. The catalyst can be used three times without detectable loss of activity (isolated yield). After that, a gradual loss of activity was observed for the next three cycles with the isolated yields of ~85%, ~77% and ~65% for the fourth, fifth and sixth cycles. Though mononuclear Pd(II) thiosemicarbazone complexes have been used as effective catalysts for the Mizoroki-Heck reaction,[22] a direct comparison of the mononuclear complexes with the dinuclear palladium(II) bis(thiosemicarbazone) complex is difficult due to the difference in the reaction conditions such as solvents, base, temperature, reaction time and catalyst loading. The dinuclear Pd(II) bis(thiosemicarbazone) complex can be synthesized conveniently from inexpensive starting materials and obtained with satisfactory yield making it a very promising catalyst. Further, a key advantage of the ligand and complex over some others is that the reactions can typically be performed in standard laboratory glassware without dry-box technique.

Table 4
Mizoroki-Heck reaction of 4-chloroacetophenone with olefins[a]



Entry	–R$_1$	Yield[b] (%)	TON[c]	TOF[d]
1	–COO^{t}Bu	44	440	18.3
2	–$COOCH_3$	46	460	19.2
3	–C_6H_5	35	350	14.6
4	–C_6H_4-4-CH_3	30	300	12.5
5	–C_6H_4-4-Cl	38	380	15.6

[a] Reaction conditions: 4-chloroacetophenone (5 mmol), olefin (10 mmol), K_2CO_3 (6 mmol), complex **1** (0.1 mol %), DMF (3 mL) at 100 °C for 24 h under N_2 atmosphere.
[b] Isolated yield after column chromatography based on 4-chloroacetophenone (average of two runs).
[c] TON = Turnover number = ratio of moles of product formed to moles of catalyst used.
[d] TOF = Turnover frequency = TON per hour.

In conclusion, dinuclear Pd(II) complex bearing terephthaldehyde bis(thiosemicarbazone) ligand has been synthesized and characterized. The single crystal X-ray evidenced the N and S coordination mode of the ligand and a distorted square planar geometry around each Pd(II) ion. The new Pd(II) complex was found to be highly efficient homogeneous catalyst for the Mizoroki-Heck reaction of aryl bromides with various olefinic substrates with large turnover numbers in relatively short times. The complex also acts as an active catalyst for the Mizoroki-Heck cross-coupling reaction of activated aryl chloride with various olefins.

Acknowledgments

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Supplementary data

Supplementary data (Crystallographic data for the structural analysis have been deposited with Cambridge crystallographic center, CCDC No. 870247. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union roads, Cambridge CB2 1EZ, UK (email: deposit@ccdc.cam.ac.uk). The summary of the data collection and refinement parameters for the complex; Experimental procedures; ^{1}H, ^{13}C and ^{31}P NMR spectra of the complex; ^{1}H NMR data for all the Mizoroki-Heck coupling products.) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.08.120.

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