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Hemilabile imino-phosphine palladium(II) complexes: synthesis, molecular structure, and evaluation in Heck reactions

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The ligands 2-(diphenylphosphino)benzyl-(2-thiophene)methylimine (*V*) and 2-(diphenylphosphino)benzyl-(2-thiophene)ethylimine (*VI*) were prepared from 2-(diphenylphosphino)benzaldehyde and thiophene amines with very good yields. An equimolar reaction of *V* and *VI* with either $PdCl_2$(cod) (cod = cyclooctadiene) or PdClMe(cod) afforded palladium(II) complexes *I*–*IV*. The molecular structure of *II* was confirmed by X-ray crystallography. The coordination geometry around the palladium atom exhibited distorted square planar geometry at the palladium centre. Complexes *I*, *II*, and *IV* were evaluated as catalysts for Heck coupling reactions of iodobenzene with methyl acrylate under mild reaction conditions; 0.1 mole % catalyst, Et_3N base, MeCN reflux for 8 h, 80 ℃; isolated yield on a 10 mmol scale with catalyst *I* (64 %), *II* (68 %), and *IV* (58 %). They all exhibited significant activities.

Keywords: imino-phosphine, palladium, Schiff-base molecular structures, Heck reaction

Introduction

The original development of new methods for the synthesis of mixed soft and hard donor P—N ligand systems is well documented in a review of pyridylphosphines (Newkome, 1993). These types of ligands have been shown to be important in metal-catalysed carbon–carbon reactions such as the Heck and Suzuki coupling (Beletskaya & Cheprakov, 2000; Scrivanti et al., 2005; Nobre & Monteiro, 2009). The phosphorus and nitrogen atoms in an imino-phosphine ligand provide a unique reaction to their metal complex due to their hemilabile property (Espinet & Soulantica, 1999; Motswainyana et al., 2011). This hemilability of the ligands affords a unique reversible protection of the coordination site, an important property of the compounds which leads to improved catalytic activities (Motswainyana et al., 2011). The use of the ligand 2-(diphenylphosphino)benzaldehyde has led to the preparation of a number of bidentate imino-phosphine ligands (Hoots et al., 1982; Garralda, 2005); their preparation is versatile because a wide range of amines and aldehydes of varying steric bulk are either available commercially or can be easily synthesised (Doherty et al., 2002; Chen & Yeh, 2011; Antonaroli & Crociani, 1998; Mogorosi et al., 2011). The present attempt to develop new ligands which would effectively promote the conversion of aryl halides into Heck products reports on the synthesis, characterisation, and test results of imino-phosphine palladium(II) complexes in standard Heck coupling reactions.

Experimental

All reactions were carried out under a nitrogen atmosphere using a dual vacuum/nitrogen line and stan-

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Table 1. Characterisation data of imino-phosphine compounds

Compound	Formula	M_r	w_i(calc.)/% w_i(found)/% C	H	N	Yield %	M.p. ℃
I	$C_{24}H_{20}Cl_2NPPdS$	562.79	51.22 50.98	3.58 3.24	2.49 2.65	86	230
II	$C_{25}H_{22}Cl_2NPPdS$	576.81	52.06 52.28	3.84 3.76	2.43 2.49	85	208
III	$C_{25}H_{23}ClNPPdS$	542.37	55.36 55.08	4.27 4.52	2.58 2.81	78	158
IV	$C_{26}H_{25}ClNPPdS$	556.40	56.13 55.98	4.53 4.45	2.52 2.32	75	142
V	$C_{24}H_{20}NPS$	385.46	74.78 75.08	5.23 5.14	3.63 3.89	92	–
VI	$C_{25}H_{22}NPS$	399.49	75.16 74.99	5.55 5.58	3.51 3.31	90	–

dard Schlenk techniques unless stated otherwise. Solvents (Sigma–Aldrich, USA) were dried and purified by heating at reflux under nitrogen in the presence of a suitable drying agent. The $PdCl_2$(cod) (cod = cyclooctadiene) and PdClMe (cod) were prepared following methods detailed in the literature (Wiedermann et al., 2006; Salo & Guan, 2003). All the reagents and starting materials were purchased from Sigma–Aldrich and were used without further purification.

The ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were recorded on a Varian (USA) XR 200 MHz spectrometer in our laboratories. The ^{31}P NMR spectra were recorded on a Varian XR200 MHz spectrometer at the University of Cape Town (South Africa). Chemical shifts are given in δ relative to internal standard (TMS). IR spectra in solution were recorded with a Perkin–Elmer (USA) Spectrum 100 Series FT-IR instrument using nujol mulls on NaCl plates. Elemental analysis was performed on Server 1112 Series (University of Cape Town) elemental analyser. The melting point of the synthesised compounds was determined in open capillaries using SMP10 melting point apparatus. Single crystal diffraction experiments were performed in the Carl Olson laboratories, Rutgers University (Newark, NJ, USA).

Synthesis of ligands

Preparation of 2-(diphenylphosphino)benzyl-(2-thiophene)methylimine (V)

2-thiophenemethylamine (116 mg, 1.028 mmol) was added drop-wise to a mixture of 2-(diphenylphosphino)benzaldehyde (293 mg, 1.009 mmol) and anhydrous magnesium sulphate (800 mg) in CH_2Cl_2 (20 mL). The reaction was stirred at ambient temperature for 18 h, resulting in a light brown mixture. The mixture was filtered, followed by evaporation of the solvent under reduced pressure to obtain a light brown oil. The yield given in Table 1 for this ligand (and for the other ligands also) is the total mass recovered from this evaporation. All of the ligands isolated by this procedure were pure, as assessed by ^{1}H NMR and ^{31}P NMR, and by elemental analyses. The ligands may be stored for extended periods of time by excluding oxygen.

Preparation of 2-(diphenylphosphino)benzyl-(2-thiophene)ethylimine (VI)

The ligand was prepared according to the procedure described for *V*. 2-(diphenylphosphino)benzaldehyde (299 mg, 1.029 mmol) and 2-thiopheneethylamine (135 mg, 1.063 mmol) were used.

Synthesis of complexes

Preparation of complex I

A solution of *V* (47 mg, 0.121 mmol) in CH_2Cl_2 (2 mL) was added drop-wise to a solution of $PdCl_2$ (cod) (36 mg, 0.126 mmol) in CH_2Cl_2 (15 mL). The reaction was stirred under reflux for 6 h, resulting in a yellow precipitate. The precipitate was filtered to afford a light yellow solid. The precipitated complex *I* (and also the precipitate for the other ligands *II*–*IV*) was the catalyst used in the experiments shown in Table 1.

Preparation of complex II

The complex was prepared according to the procedure described for *I*. $PdCl_2$(cod) (48 mg, 0.170 mmol) and *VI* (65 mg, 0.163 mmol) were used. Yellow crystals suitable for X-ray analysis were obtained when the solid was re-crystallised from a mixture of CH_2Cl_2/hexane ($\varphi_r = 1 : 6$).

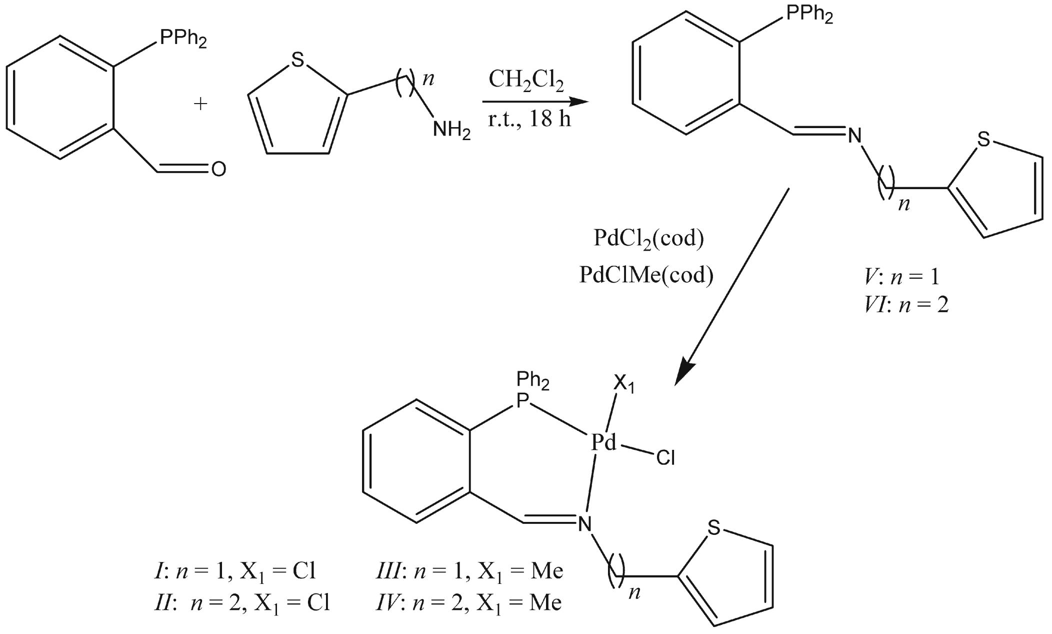

Fig. 1. Preparation of imino-phosphine palladium(II) complexes *I–IV*.

Preparation of complex III

A solution of *V* (52 mg, 0.134 mmol) in CH_2Cl_2 (2 mL) was added to a solution of PdClMe(cod) (35 mg, 0.131 mmol) in CH_2Cl_2/Et_2O (15 mL; $\varphi_r = 1 : 2$). The reaction mixture was stirred at ambient temperature for 8 h, resulting in a white precipitate. The precipitate was filtered to afford a white solid. White crystals suitable for X-ray analysis were obtained when the solid was recrystallised from a mixture of CH_2Cl_2/hexane ($\varphi_r = 1 : 3$) (Onani et al., 2010).

Preparation of complex IV

The complex was prepared according to the procedure described for *III*. The PdClMe(cod) (37 mg, 0.141 mmol) and *VI* (56 mg, 0.140 mmol) were used as starting materials. White crystals suitable for X-ray analysis were obtained when the solid was recrystallised from a mixture of CH_2Cl_2/hexane ($\varphi_r = 1 : 3$) (Motswainyana et al., 2012).

Catalytic experiments

A dry 100 mL capacity Schlenk tube equipped with a magnetic stirrer bar was charged with iodobenzene (10 mmol), methyl acrylate (11 mmol), and triethylamine (10 mL). The catalyst (0.01 mmol) was dissolved in 10 mL of CH_3CN and transferred quantitatively to the reaction vessel. The reaction mixture was heated under stirring at 80 ℃. Samples were taken at regular intervals and analysed by GC to determine the percentage conversions. The coupling product was isolated by pouring the reaction mixture into water (50 mL) and extracted with CH_2Cl_2 to give a pure product which was confirmed by ^{1}H NMR spectroscopy. Mercury drop experiments were performed in duplicate by adding two drops of elemental mercury to the reaction described above and the product (*trans*- methyl cinnamate) was also analysed by ^{1}H NMR spectroscopy (^{1}H NMR (200 MHz, $CDCl_3$), δ: 7.83 (s, 1H, HC=C), 7.56–7.51 (m, 2H, aromatic), 7.37–7.34 (m, 3H, aromatic), 6.27 (d, 1H, $J = 15.2$ Hz, C=CH), 3.63 (s, 3H, CH_3).

Molecular structure determination

Single crystals of complex *II* suitable for X-ray crystallography were grown by slow diffusion of hexane into a CH_2Cl_2 solution of the complex at 4 ℃. X-ray diffraction data for the compound were collected on a Bruker (Germany) KAPPA APEX II DUO diffractometer using graphite-monochromated CuK_α radiation ($\chi = 0.71073$ Å). The crystal structure was resolved by direct methods using SHELX (Sheldrick, 2008) and refined by full-matrix least-squares methods based on F2 (Sheldrick, 2008) using SHELX (Sheldrick, 2008) and using the graphics interface program ORTEP-3 for Windows (Farrugia, 1999, 1997).

Results and discussion

Synthesis of ligands and metal complexes

The reaction of 2-(diphenylphosphino)benzaldehyde with an equivalent amount of thiophene amine in CH_2Cl_2 at ambient temperature afforded very good yields of ligands *V* and *VI* (Fig. 1). These com-

Table 2. Spectral data of imino-phosphine compounds

Compound	Spectral data
I	IR, $\tilde{\nu}$/cm^{-1}: 1629 (C=N), 1435 (P—Ph), 1304 (C—S—C) ^{1}H NMR (DMSO-d_6), δ: 8.79 (s, 1H, –N=CH), 7.99 (dd, 1H, J = 1.8 Hz, phenyl), 7.90–7.16 (m, aromatic and heterocycle), 7.04 (t, 1H, J = 4.8 Hz, thiophene), 6.94 (t, 1H, J = 3.0 Hz, thiophene), 5.67 (d, 2H, J = 2.8 Hz, –N=CH_2) ^{31}P NMR ($CDCl_3$), δ: 35.0
II	IR, $\tilde{\nu}$/cm^{-1}: 1628 (C=N), 1435 (P—Ph), 1306 (C—S—C) ^{1}H NMR (DMSO-d_6), δ: 8.55 (d, 1H, J = 5.2 Hz, –N=CH), 7.97–6.56 (m, 4H, aromatic and heterocycle), 4.53 (t, 2H, J = 2.8 Hz, –CH_2), 3.08 (t, 2H, J = 3.0 Hz, –N=CH_2) ^{31}P NMR ($CDCl_3$), δ: 35.1
III	IR, $\tilde{\nu}$/cm^{-1}: 1632 (C=N), 1438 (P—Ph), 1296 (C—S—C) ^{1}H NMR (DMSO-d_6), δ: 8.20 (d, 1H, J = 4.2 Hz, –N=CH), 7.44–6.90 (m, 4H aromatic and heterocycle), 5.61 (s, 2H, –N=CH_2 aliphatic), 1.53 (s, 3H, Pd—Me (CH_3)) ^{31}P NMR ($CDCl_3$), δ: 37.0
IV	IR, $\tilde{\nu}$/cm^{-1}: 1636 (C=N), 1435 (P—Ph), 1307 (C—S—C) ^{1}H NMR (DMSO-d_6), δ: 7.78 (d, 1H, J = 4.6 Hz, –N=CH), 7.50–6.14 (m, 4H, aromatic and heterocycle), 4.43 (s, 2H, –CH_2), 3.25 (s, 2H, –N=CH_2), 1.46 (s, 3H, Pd—Me (CH_3)) ^{31}P NMR ($CDCl_3$), δ: 36.1
V	IR, $\tilde{\nu}$/cm^{-1}: 1635 (C=N), 1434 (P–Ph), 1313 (C—S—C) ^{1}H NMR ($CDCl_3$), δ: 9.01 (d, 1H, J = 5.4 Hz, –CH=N), 8.07 (t, 1H, J = 2.6 Hz, phenyl), 7.58 (s, 1H, thiophene), 7.43 (s, 1H, phenyl), 7.36 (d, 1H, J = 2.0 Hz, phenyl), 7.33 (t, 1H, J = 2.2 Hz, phenyl), 6.92 (dd, 1H, J = 3.4 Hz, thiophene), 6.73 (dd, 1H, J = 3.4 Hz, thiophene), 4.84 (s, 2H, –N=CH_2) ^{13}C NMR ($CDCl_3$), δ: 161.0, 160.5 (CH imine), 141.7 (CH heterocycle), 139.4–126.7 (CH aromatic), 127.5, 125.0, 124.5, 59.0 (CH_2 aliphatic) ^{31}P NMR (161.9 Hz, $CDCl_3$), δ: –14.0
VI	IR, $\tilde{\nu}$/cm^{-1}: 1637 (C=N), 1434 (P—Ph), 1339 (C—S—C) ^{1}H NMR ($CDCl_3$), δ: 8.81 (d, 1H, J = 4.6 Hz, –CH=N-), 7.71 (t, 1H, J = 3.2 Hz, phenyl), 7.05 (d, 1H, J = 2.8 Hz, phenyl), 6.98 (d, 1H, J = 2.8 Hz, phenyl), 6.80 (d, 1H, J = 3.4 Hz, phenyl), 6.69 (dd, 1H, J = 2.2 Hz, thiophene), 6.46 (s, 1H, thiophene), 3.70 (t, 2H, J = 6.8 Hz, –N=CH_2), 2.94 (t, 2H, J = 3.0 Hz, –CH_2) ^{13}C NMR ($CDCl_3$), δ: 160.7, 160.3 (CH imine), 142.4–126.6 (CH aromatic), 139.7, 136.5, 124.9, 123.4, (CH heterocycle), 62.6, 31.3 (CH_2 aliphatic) ^{31}P NMR ($CDCl_3$), δ: –13.6

pounds are susceptible to oxidation (Antonaroli & Crociani, 1998; Shirakawa et al., 1997). The imino-phosphine palladium(II) complexes *I–IV* were prepared from equimolar reactions of *V* and *VI* with either $PdCl_2$(cod) or PdClMe(cod) under reflux for 6 h, resulting in a yellow precipitate with up to 75 % yields. Complexes *III* and *IV* are reported for the first time, at least to the best of our knowledge, while the ligands and complexes *I* and *II* have been independently prepared by another group (Mogorosi et al., 2011). All the compounds were characterised by ^{1}H NMR and ^{31}P NMR spectroscopy, IR, and elemental analyses (Tables 1 and 2).

In the IR spectra of the ligands, imine formation was confirmed by the absorption band observed at 1635 cm^{-1} and 1637 cm^{-1} for *V* and *VI*, respectively. The other absorption band observed at approximately 1434 cm^{-1} confirmed the presence of uncoordinated (P—Ph) phosphorus (Park & Hendra, 1968). The IR spectra of the ligands did not show an infrared absorption band due to (P—O) at around 1185 cm^{-1}, an indication that the ligands did not form phosphine oxide (Baldwin & Washburn, 1965). The ^{1}H NMR spectra of the ligands showed a characteristic doublet in the region δ 8.81–9.01 due to (HC=N), confirming a Schiff base condensation reaction. The doublet is a characteristic of an imine proton coupling to phosphorus (Ruelke et al., 1996). The ^{31}P NMR spectra of the ligands showed an upfield singlet at around δ –13.9 which is a characteristic of uncoordinated phosphorus (Mogorosi et al., 2011). Coordination of the ligands to the metal centre was confirmed in the IR spectra of complexes *I* and *II*, which showed an absorption band between 1625 cm^{-1} and 1628 cm^{-1} typical of coordinated imines (Nobre & Monteiro, 2009; Mogorosi et al., 2011). However, complexes *III* and *IV* did not show any significant shift in absorption frequency from their corresponding free imines, probably due to the presence of the methyl group bound to the palladium centre, which would inductively increase the electron density on the metal centre. The general pattern in the ^{1}H NMR spectra of the complexes revealed an upfield shift in the imine protons compared with their corresponding ligands, indicating coordination. In the ^{31}P NMR spectra, the complexes showed a characteristic phosphorus singlet further downfield in the region of δ 32.4–37.2, which is a typical confirmation of coordinated phosphorus (Doherty et al., 2002; Mogorosi

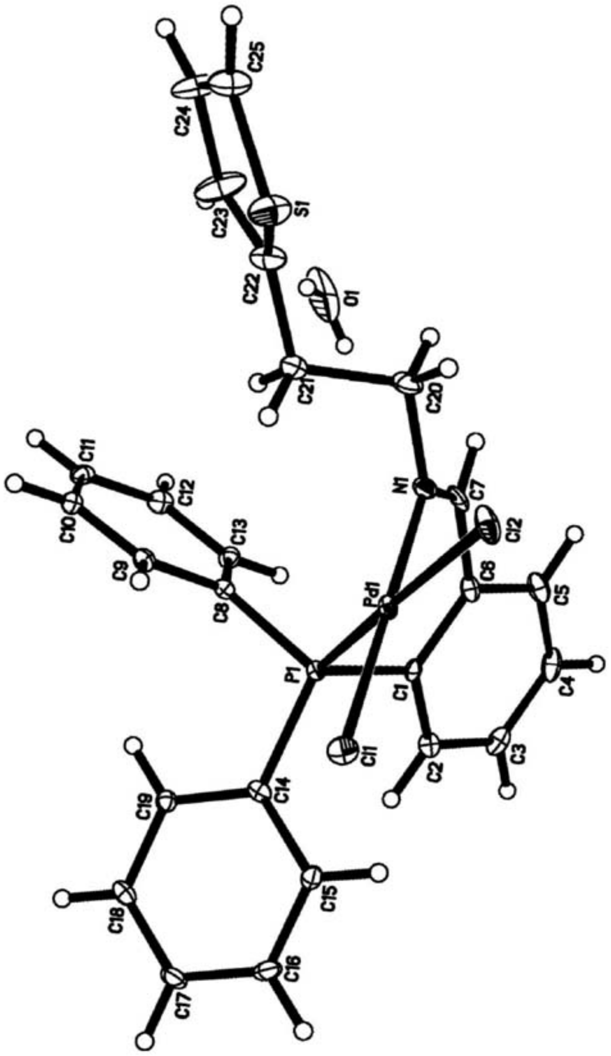

Fig. 2. X-ray crystal structure of complex *II*.

et al., 2011; Reddy et al., 2000).

Single crystal X-ray diffraction studies

The molecular structure of *II*, shown in Fig. 2, was confirmed by X-ray crystallography. The two atoms near the carbon atoms in the thiophene ring are representations of the disorder of C-23 and C-24 and are denoted as C-23A and C-24A (with their associated H atoms). The ratio of the disorder is 64 : 36(9). That means that C-23 and C-24 are there 64 % of the time (with an error of 9 %), and C-23A and C-24A are there 36 % of the time.

The crystallographic data and refinement residuals are summarised in Table 3 while selected bond lengths and bond angles are summarised in Table 4. The structure crystallises in the monoclinic space group $P2_1/n$. The ligands are tetra-coordinated via the P and N atoms and two chloride anions to the palladium atom, generating a distorted square planar coordination geometry around the metal centre. The bond angles Cl(1)—Pd(1)—Cl(2) (90.84 (6)°) and P(1)—Pd(1)—N(1) (85.68(16)°) describe the distorted square planar geometry.

Table 3. Crystallographic data and refinement for *II*

Crystallographic data/dimension	Value
Empirical formula	$C_{25}H_{22}Cl_2NPPdS$ – H_2O
M_r	594.78
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions/Å	
a	9.8933(3)
b	18.8451(5)
c	13.4998(4)
β/°	94.892(2)
V/Å^3	2507.74(13)
Z	4
Dcal/(Mg m^{-3})	1.575
F(000)	1200
Crystal size/mm	0.14 × 0.07 × 0.06
Final R indices (R1)	$R1 = 0.053$, $wR2 = 0.157$
Theta range for data collection/°	4.0 to 71.4
Goodness-of-fit on F2	1.05
Largest diff. peak and hole/(e Å^{-3})	3.14 and –0.92

The Pd(1)—C1(1) bond length of 2.2885(16) Å is in good agreement with the average Pd—Cl bond distance of 2.298(15) Å for known palladium complexes (Allen, 2002). A detectable *trans* influence is taking place in the compound since the Pd(1)—C1(2) bond length of 2.3643(16) Å is significantly longer than the average value, which reflects the stronger *trans*-influence of the diphenylphosphino group compared to an amine (Doherty et al., 2002). We previously reported on the molecular structures of *III* and *IV* depicting the geometry of these compounds. (Onani et al., 2010; Motswainyana et al., 2012). The average bond lengths Pd(1)—N(1) of 2.058(6) Å and Pd(1)—P(1) of 2.2179(16) Å compare well with the literature values (Reddy et al., 2000).

Heck coupling reactions

Complexes *I*, *II*, and *IV* were screened towards the standard Heck coupling reaction of iodobenzene with methyl acrylate (Fig. 3) using CH_3CN as a solvent, Et_3N as base, and a temperature of 80 ℃. Highly polar solvents in Heck reactions are necessary for high reaction rates, and polar solvents such as dimethylacetamide (DMA), *N*-methylpyrrolidinone (NMP), or dimethylformamide (DMF) at high temperatures have supported high activities (Scrivanti et al., 2005; Ojwach et al., 2007; Pelagatti et al., 2005). However, reactions involving CH_3CN as a solvent have yielded equally good results (Smith & Mapolie, 2004). The mole ratio Pd/PhI/alkene/Et_3N

Table 4. Selected bond lengths and bond angles for complex *II*

Type of bond	Bond length/Å	Type of bond	Bond angle/°
Pd(1)—N(1)	2.058(6)	N(1)—Pd(1)—P(1)	85.68(16)
Pd(1)—P(1)	2.2179(16)	N(1)-Pd(1)-Cl(1)	179.52(17)
Pd(1)—Cl(1)	2.2885(16)	P(1)—Pd(1)—Cl(1)	93.84(6)
Pd(1)—Cl(2)	2.3643(16)	N(1)—Pd(1)—Cl(2)	89.64(16)
		P(1)—Pd(1)—Cl(2)	174.17(6)
		Cl(1)—P(1)—Cl(2)	90.84(6)

Table 5. Heck coupling reactions[a] of iodobenzene with methyl acrylate catalysed with complexes *I*, *II*, and *IV*

Entry	Complex no.	Time	Amount of catalyst	Conversion[b]	Yield	TON[b]	TOF[b]	Selectivity[c]
		h	mole %	%				%
1	*I*	8	0.10	79	64	790	99	80
2	*I*	24	0.10	84	69	840	35	83
3	*II*	8	0.10	83	68	830	104	83
4	*II*	24	0.10	90	75	900	38	85
5[d]	*II*	24	0.10	88	75	880	37	85
6	*II*	24	0.05	69	52	690	29	80
7	*II*	24	0.01	62	40	620	26	80
8	*IV*	8	0.10	72	58	720	90	80
9	*IV*	24	0.10	76	60	760	32	82

a) Reaction conditions: PhI (10 mmol), methyl acrylate (11 mmol), Et_3N (10 mmol), 80 °C, CH_3CN (10 mL); *b*) determined by GC; *c*) percentage of *E*-diastereomer; *d*) mercury drop test; TON – turnover number; TOF – turnover frequency. Internal standard; mesitylene.

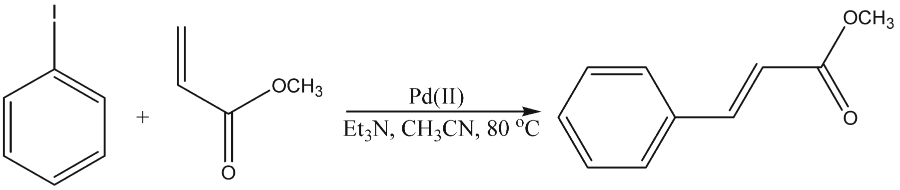

Fig. 3. Heck coupling reaction of iodobenzene with methyl acrylate.

(1 : 1000 : 1100 : 1000) was maintained in all the catalytic experiments. A summary of the catalytic results is given in Table 5. Aryl iodides are the preferred substrates in Heck reactions because of their lower C—X bond strength compared to the aryl bromides and chlorides (Grushin & Alper, 1994). The bond strength makes the aryl iodides more susceptible to oxidative addition to the catalytic species, a step viewed as an initiation stage for a Heck reaction (Scrivanti et al., 2005). Historically, phosphine complexes have been extensively used as catalysts in Heck coupling reactions despite their air sensitivity, because they provide thermally robust catalysts (Pelagatti et al., 2005).

The complexes successfully catalysed the arylation of methyl acrylate, giving good yields after 24 h (Table 5, Entries 2 and 4 and 9). Complex *II* was observed to be the most active, giving a 68 % yield after 8 h, and eventually achieving 75 % after 24 h. The major coupling product was observed to be *trans*-methyl cinnamate, as confirmed by ^{1}H NMR spectroscopy. There was a good selectivity of up to 85 % towards the formation of *trans*-methyl cinnamate. Although the reactions were performed under mild reaction conditions in acetonitrile, high substrate conversions and yields were achieved, which could be explained only by the hemilability of the imino-phosphine ligands (Motswainyana et al., 2011). The influence of the thiophene ring in the catalytic activity of the complexes was noted (Table 5, Entries 2 and 4). Higher conversions and yields were obtained with catalyst *II*, possibly due to the presence of the thermo-flexible ethylene linker of the thiophene imine which imparts a hemilabile property (Jeffrey & Rauchfuss, 1979; Marson et al., 2009). The effect of catalyst concentration on the performance of the catalysts was also investigated using catalyst *II* (Table 5, Entries 6 and 7). The catalytic results showed that smaller amounts of the catalyst were capable of effectively catalysing the arylation of methyl acrylate at 80 °C (Cui & Zhang, 2005). At a low catalyst loading of 0.01 mole %, catalyst *II* was still active and returned a yield of 40 %. Mercury drop experiments showed no significant difference in conversion between the experiments with or without mercury (Table 5, Entry 5), thereby excluding the formation of Pd(0) which could influence the catalytic results. Structurally, the prepared complexes could show a potential in the activation of more challenging substrates such as bromo- and chloroarenes. Chloroarenes are the most inexpensive in the group. Unfortunately, the high C—Cl bond strength compared with C—Br and C—I bonds precludes oxidative addition, a first step in catalytic coupling reactions. This makes the coupling of such substrates far more challenging. Hence, there is currently much interest in the synthesis of catalysts that are able to activate aryl chloride substrates at ever lower catalyst loading (Herrmann et al., 1995; Ahrens et al., 2006). A change in the catalytic reaction media to non-aqueous ionic liquids instead of common organic solvents is reported to provide superior Heck vinylation of chloroarenes, opening an avenue for further investigations of these compounds (Böhm & Herrmann, 2000).

Conclusions

In conclusion, imino-phosphine ligands and complexes were successfully synthesised and characterised by various spectroscopic techniques. Evaluation of the activity of complexes *I*, *II*, and *IV* towards Heck coupling of iodobenzene with methyl acrylate was carried out under mild reaction conditions and low catalyst loading. The conversion results showed the complexes to be active, with good selectivity towards the formation of *trans*-methyl cinnamate. The higher activities of the complexes suggest that the imino-phosphine ligands are hemilabile.

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Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 874818 for compound *II*. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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