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Iminophosphine palladium(II) complexes: synthesis, characterization, and application in Heck cross-coupling reaction of aryl bromides

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Palladium(II) complexes containing phosphorus and nitrogen donor atoms (iminophosphine), dichlorido{*N*-[2-(diphenylphosphino)benzylidene]-2-trifluoromethylaniline}palladium(II) 1, dichlorido{*N*-[2-(diphenylphosphino)benzylidene]-3-trifluoromethylaniline}palladium(II) 2, dichlorido{*N*-[2-(diphenylphosphino)benzylidene]-2-methylaniline}palladium(II) 3, dichlorido{*N*-[2-(diphenylphosphino)benzylidene]-3-methylaniline}palladium(II) 4 have been successfully synthesized and fully characterized by FT-IR and NMR (^{1}H, ^{31}P, ^{19}F, and ^{13}C) spectroscopy techniques. These complexes were first step tested in the reaction of bromobenzene and styrene to determine the optimal coupling reaction conditions and then successfully applied as catalysts for Heck cross-coupling reactions of activated and deactivated aryl bromides with styrene derivatives and several acrylates.

Keywords: iminophosphine; palladium; Heck cross-coupling reaction; aryl bromides

Introduction

The coupling of aryl or vinyl halides with terminal alkenes by the Heck cross-coupling reaction is a powerful tool for the preparation of substituted olefins, dienes, and precursors to conjugated polymers.[1–3] This reaction, which relates to the formation of new C—C bonds, is generally catalyzed with Pd complexes formed by tertiary phosphine ligands or PN-type ligands which are thought to stabilize the active palladium intermediates.[4–7] Heterodentate phosphine ligands bearing hard nitrogen and soft phosphorus donor atoms have emerged as an important class of ligands, and this feature provides that unique property to their metal complexes. This hemilability of complexes with a mixed donor ligands improves the catalytic activity for C—C coupling reactions, because it changes the symmetry around the palladium orbitals.[8,9] In this paper, we wish to report the synthesis and characterization of new palladium(II) complexes coordinated with hemilabile bidentate iminophosphine ligands (Scheme 1) and we used our catalysts in Heck C—C bond-forming reactions.

Experimental

General Comments

All ligands and complexes were synthesized using standard Schlenk techniques under an argon atmosphere. Unless otherwise noted, all reagents were used without further purification. Toluene and methanol were distilled and degassed prior to use.[10] All other solvents used were of analytical grade and dried over activated molecular sieves (4A). Flash column chromatography was performed on silica gel (230–400 mesh). Pd(cod)Cl_2 (cod = 1,5-cyclooctadiene)[11] and 2-(diphenylphosphino)benzaldehyde[12] were prepared according to previously reported procedures. NMR spectra were recorded in deuterated chloroform and DMSO on a Bruker NMR-400 MHz (^{1}H: 400.2 MHz; ^{31}P: 162.0 MHz; ^{13}C: 100.6 MHz; ^{19}F: 376.5 MHz) spectrometer. ^{1}H NMR and ^{13}C NMR spectra were obtained at room temperature using tetramethylsilane as a reference. ^{31}P NMR spectra of the ligands and complexes were obtained at room temperature using *o*-phosphoric acid as an internal standard. ^{19}F NMR spectra were obtained using trichlorofluoromethane as a reference. All chemical shifts (δ) are given in parts per million (ppm), and coupling constants (J) in Hertz (Hz). Infrared spectra were obtained using a PerkinElmer Spectrum 1 FT-IR spectrophotometer in the range 4000–650 cm^{-1}. Melting points were determined on a PerkinElmer Pyris 6 differential scanning calorimetry (DSC) instrument. GC analyses were performed on a PerkinElmer Clarus 500 gas chromatograph equipped with a flame ionization detector (FID) and a 30 m capillary column containing dimethyl polysiloxane stationary phase.

Synthesis of Ligands

Synthesis of $Ph_2PC_6H_4CH{=}N(2\text{-}CF_3C_6H_4)$ ***a***

A mixture of 2-(diphenylphosphino)benzaldehyde (1.0 g, 3.4 mmol) and 2-(trifluoromethyl)aniline (0.6 ml, 4.6 mmol) was dissolved in methanol (30 ml) with two drops of formic acid and stirred at reflux temperature for 2 h. The mixture was allowed to warm to room temperature, washed with saturated sodium bicarbonate aqueous solution, and dried over anhydrous sodium

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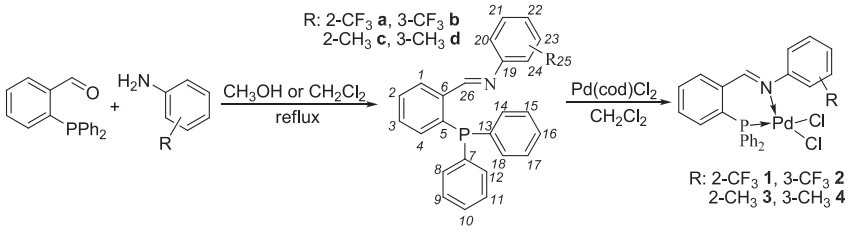


Scheme 1. Synthesis of iminophosphine ligands a-d and palladium complexes 1-4.

sulfate. Evaporation of the solvent gave a crude product, which was chromatographed on silica gel (4% ethyl acetate in hexane) to give the pure iminophosphine **a** as a white solid (0.96 g, 65%); m.p. 117°C. IR: 1626 cm^{-1} (ν C=N, imine). ^1H NMR (400.2 MHz, $CDCl_3$): δ (ppm) 9.06 (d, 1H, *J*=5.6 Hz, HC=N), 8.32 (m, 1H^{1}, CH), 7.63 (m, 1H^{23}, CH), 7.42–7.34 (m, 13H$^{2-18}$, CH), 7.23(m, 1H^{21}, CH), 6.95 (m, 1H^{22}, CH), 6.39 (m, 1H^{20}, CH). ^{31}P {^1H} NMR (162.0 MHz, $CDCl_3$): δ (ppm) −14.15 (s). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ (ppm) 160.26 (d, J_{PC}= 25.2 Hz, HC=N), 150.66 (C^{19}), 135.80 (d, J_{PC}= 9.1 Hz, C^{8}), 134.22 (d, J_{PC}= 20.1 Hz, C^{6}), 132.95 (d, J_{PC}=24.9 Hz, C^{7}), 131.46 (C^{2,3,10}), 128.81 (d, J_{PC}= 7.3 Hz, C^{5}), 127.97 (C^{1,21}), 127.95 (d, J_{PC}= 3.6 Hz, C^{4}), 126.14 (C^{20,22,23}), 126.11 (d, J_{PC}= 5.4 Hz, C^{9}), 124.97 (CF_3), 119.54 (C^{24}). ^{19}F NMR (376.5 MHz, $CDCl_3$): δ (ppm) −60.25 (s).

Synthesis of $Ph_2PC_6H_4CH$ N(3-$CF_3C_6H_4$) **b**

This compound was prepared as described for **a** using 2-(diphenylphosphino)benzaldehyde (1.0 g, 3.4 mmol) and 3-(trifluoromethyl)aniline (0.6 ml, 4.6 mmol), producing a white solid (0.88 g, 60%); m.p. 75°C. IR: 1625 cm^{-1} (ν C=N, imine). ^1H NMR (400.2 MHz, $CDCl_3$): δ (ppm) 9.03 (d, 1H, *J*=5.1 Hz, HC=N), 8.20 (m, 1H^{1}, CH), 7.50 (m, 1H^{21}, CH), 7.43–7.34 (m, 13H$^{2-18}$, CH), 7.05 (m, 2H^{22,24}, CH), 6.97 (m, 1H^{20}, CH). ^{31}P {^1H} NMR (162.0 MHz, $CDCl_3$): δ (ppm) −12.37 (s). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ (ppm) 160.35 (d, J_{PC}= 20.6 Hz, HC=N), 152.16 (C^{19}), 139.21 (d, J_{PC}= 20.7 Hz, C^{8}), 138.51 (d, J_{PC}= 15.9 Hz, C^{6}), 134.18 (d, J_{PC}= 20.2 Hz, C^{7}), 133.49 (C^{2,3,23}), 129.48 (C^{21}), 129.12 (C^{1}), 128.78 (d, J_{PC}= 7.4 Hz, C^{5}), 128.48 (d, J_{PC}= 3.6 Hz, C^{4,10}), 124.08 (C^{20,22}), 122.60 (CF_3), 122.33 (d, J_{PC}= 3.6 Hz, C^{9}), 117.86 (C^{24}). ^{19}F NMR (376.5 MHz, $CDCl_3$): δ (ppm) −62.57 (s).

Synthesis of $Ph_2PC_6H_4CH$ N(2-$CH_3C_6H_4$) **c**

The iminophosphine **c** has been previously reported and was prepared according to the reported method[13] using 2-(diphenylphosphino)benzaldehyde (0.55 g, 1.90 mmol) and 2-(methyl)aniline (0.21 ml, 1.91 mmol) in dry CH_2Cl_2 (25 ml), producing a light-yellow solid (0.58 g, 80%); m.p. 103°C. IR: 1625 cm^{-1} (ν C=N, imine). ^1H NMR (400.2 MHz, $CDCl_3$): δ (ppm) 8.97 (d, 1H, *J*=5.2 Hz, HC=N), 8.24 (m, 1H^{1}, CH), 7.45 (m, 1H^{23}, CH), 7.35–7.28 (m, 12H$^{2,4-18}$, CH), 7.13 (m, 1H^{21}, CH), 7.05 (m, 2H^{3,22}, CH), 6.91 (m, 1H^{20}, CH), 2.19 (s, 3H, CH_3). ^{31}P {^1H} NMR (162.0 MHz, $CDCl_3$): δ (ppm) −13.66 (s). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ (ppm) 158.31 (d, J_{PC}= 22.7 Hz, HC=N), 151.09 (C^{19}), 139.51 (d, J_{PC}= 16.9 Hz, C^{8}), 138.47 (d, J_{PC}= 19.9 Hz, C^{7}), 136.36 (d, J_{PC}= 9.7 Hz, C^{6}), 134.19 (d, J_{PC}= 19.9 Hz, C^{5}), 133.40 (C^{2,10}), 130.83 (C^{1,21}), 130.09 (C^{20,22,23}), 129.01 (d, J_{PC}= 3.5 Hz, C^{4}), 128.74 (d, J_{PC}=7.2 Hz, C^{3}), 128.35 (d, J_{PC}= 4.2 Hz, C^{9}), 117.97 (C^{24}), 17.77 (CH_3).

Synthesis of $Ph_2PC_6H_4CH$ N(3-$CH_3C_6H_4$) **d**

This compound was prepared as described for **c** using 2-(diphenylphosphino)benzaldehyde (1.10 g, 3.8 mmol) and 3-(methyl)aniline (0.51 ml, 3.90 mmol) in dry CH_2Cl_2 (50 ml), producing a light-yellow solid (0.79 g, 55%). m.p. 107°C. IR: 1673 cm^{-1} (ν C=N, imine). ^1H NMR (400.2 MHz, $CDCl_3$): δ (ppm) 9.03 (d, 1H, *J*=5.1 Hz, HC=N), 8.19 (m, 1H^{1}, CH), 7.47 (m, 1H^{21}, CH), 7.36–7.15 (m, 15H$^{2-18,22,24}$, CH), 6.96 (m, 1H^{20}, CH), 2.29 (s, 3H, CH_3). ^{31}P {^1H} NMR (162.0 MHz, $CDCl_3$): δ (ppm) −13.09 (s). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ (ppm) 158.68 (d, J_{PC}=21.6 Hz, HC=N), 151.76 (C^{19}), 141.18 (d, J_{PC}= 26.4 Hz, C^{8}), 139.21 (d, J_{PC}= 16.6 Hz, C^{6}), 138.82 (C^{2,23}), 136.44 (d, J_{PC}= 9.5 Hz, C^{7}), 136.12 (d, J_{PC}= 9.6 Hz, C^{5}), 134.19 (C^{21}), 133.99 (C^{1}), 129.15 (C^{20,22}), 128.89 (d, J_{PC}= 9.2 Hz, C^{4,10}), 128.77 (d, J_{PC}= 7.2 Hz, C^{9}), 128.05 (d, J_{PC}= 3.9 Hz, C^{3}), 118.07 (C^{24}), 21.39 (CH_3).

Synthesis of Complexes

*General procedure for the synthesis of the palladium(II) complexes (**1–4**)*

For each reaction, a solution of Pd(cod)Cl_2 in CH_2Cl_2 (5 ml) was added in stoichiometric proportion to a solution of an iminophosphine ligand (1.30 mmol) (**a–d**) in CH_2Cl_2 (20 ml) and then stirred at room temperature for 4 h. After completion of the reaction, the reaction mixture was concentrated *in vacuo* and diethyl ether was added to precipitate the product. The resulting light-yellow solid was filtered and then dried.

$PdCl_2$(a), ***1***. Yield 674 mg (85%). m.p. 276°C (decomposed). IR: 1619 cm^{-1} (ν C=N, imine). ^1H NMR (400.2 MHz, DMSO-d_6): δ (ppm) 8.30 (s, 1H, HC=N), 7.83 (m, 1H^{1}, CH), 7.78 (m, 1H^{23}, CH), 7.72 (m, 1H^{21}, CH), 7.67–7.49 (m, 13H$^{2-18}$, CH), 7.41 (m, 1H^{22}, CH), 7.22 (m, 1H^{20}, CH). ^{31}P {^1H} NMR (162.0 MHz, DMSO-d_6): δ (ppm) 26.68 (s). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ (ppm) 170.08 (d, J_{PC}= 11.4 Hz, HC=N), 149.59 (C^{19}), 139.13 (C^{21}), 135.58 (d, J_{PC}= 6.6 Hz, C^{8}), 133.49 (d, J_{PC}= 11.2 Hz, C^{6}), 132.14 (d, J_{PC}= 25.5 Hz, C^{7}), 128.90 (d, J_{PC}= 11.9 Hz, C^{5}), 127.26 (C^{2,10,22,23}), 125.77 (d, J_{PC}= 4.8 Hz, C^{4}), 124.44 (C^{1}), 121.68 (d, J_{PC}= 6.6 Hz, C^{3,9}), 121.53 (CF_3), 121.23 (C^{24}). ^{19}F NMR (376.5 MHz, DMSO-d_6): δ (ppm) −58.87 (s).

$PdCl_2$(b), ***2***. Yield 635mg (80%). m.p.: 275 °C (decomposed). IR: 1617 cm^{-1} (ν C=N, imine). ^1H NMR (400.2 MHz, DMSO-d_6): δ (ppm) 8.76 (s, 1H, HC=N), 8.22 (m, 1H^{1}, CH), 7.90 (m, 1H^{21}, CH), 7.74–7.61 (m, 11H$^{4-18}$, CH), 7.54(m, 4H^{2,3,22,24}, CH), 7.07 (m, 1H^{20}, CH). ^{31}P {^1H} NMR (162.0 MHz, DMSO-d_6): δ (ppm) 30.95 (s). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ (ppm) 169.49 (d, J_{PC}= 8.5 Hz, HC=N), 151.91 (C^{19}), 138.23 (C^{21}), 136.35 (d, J_{PC}= 13.8 Hz, C^{6,7}), 133.82 (d, J_{PC}= 11.0 Hz, C^{8}), 133.36 (C^{2,3}), 132.60 (C^{23}), 129.55 (C^{1}), 129.29 (d, J_{PC}=12.1 Hz, C^{5}), 127.86 (C^{20}), 125.27 (CF_3), 124.68 (C^{22}), 124.23 (d, J_{PC}= 3.6 Hz, C^{4,10}), 120.59 (C^{24}), 119.93 (d, J_{PC}= 4.5 Hz, C^{9}). ^{19}F NMR (376.5 MHz, DMSO-d_6): δ (ppm) −60.96 (s).

$PdCl_2$(c), ***3***. Yield 586 mg (81%). m.p. 225°C (decomposed). IR: 1618 cm^{-1} (ν C=N, imine). ^1H NMR (400.2 MHz, DMSO-d_6): δ (ppm) 8.65 (s, 1H, HC=N), 8.19 (m, 1H^{1}, CH), 7.95 (m, 1H^{23}, CH), 7.80 (m, 1H^{3}, CH), 7.72–7.48, (m, 10H$^{8-18}$, CH), 7.17 (m, 3H^{2,4,22}, CH), 7.03 (m, 1H^{21}, CH), 6.91 (m, 1H^{20}, CH), 2.14 (s, 3H, CH_3). ^{31}P {^1H} NMR (162.0 MHz, DMSO-d_6): δ (ppm) 28.71 (s). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ (ppm) 168.64 (d, J_{PC}= 8.9 Hz, HC=N), 151.54 (C^{19}), 138.04 (d, J_{PC}= 8.5 Hz, C^{8}), 136.18 (d, J_{PC}= 15.6 Hz, C^{6}), 133.97 (C^{2,3}), 133.44 (d, J_{PC}= 11.0 Hz, C^{7}), 132.24 (C^{10}), 130.09 (d, J_{PC}= 16.9

Hz, C^{1}), 129.09 (d, J_{PC}= 11.7 Hz, C^{21}), 126.83 ($C^{20,22,23}$), 125.62 (C^{5}), 123.45 ($C^{4,9}$), 119.29 (C^{24}), 18.32 (CH_3).

$PdCl_2$(d), ***4***. Yield 629 mg (87%). m.p. 268°C (decomposed). IR: 1611 cm^{-1} (νC=N, imine). ^{1}H NMR (400.2 MHz, DMSO-d_6): δ (ppm) 8.64 (s, 1H, HC=N), 8.18 (m, 1H^{1}, CH), 7.95 (m, 1H^{21}, CH), 7.80 (m, 1H^{3}, CH), 7.72–7.48 (m, 10H$^{8-18}$, CH), 7.23 (m, 2H^{2,22}, CH), 7.12 (m, 2H^{4,20}, CH), 7.02 (m, 1H^{24}, CH), 2.30 (s, 3H, CH_3). ^{31}P{^{1}H} NMR (162.0 MHz, DMSO-d_6): δ (ppm) 31.23 (s). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ (ppm) 167.42 (d, J_{PC}= 9.4 Hz, HC=N), 153.57 (C^{19}), 134.73 ($C^{21,23}$), 133.75 (d, J_{PC}= 11.2 Hz, C^{8}), 133.25 (d, J_{PC}= 6.7 Hz, C^{6}), 133.08 ($C^{2,3}$), 132.49 ($C^{1,20}$), 130.53 (C^{22}), 129.15 (d, J_{PC}= 11.9 Hz, C^{7}), 128.14 (d, J_{PC}= 15.9 Hz, $C^{5,9}$), 125.11 (C^{2}), 124.52 (C^{4}), 123.30 (C^{10}), 120.58 (C^{24}), 20.78 (CH_3).

General procedure for Heck cross-coupling reaction

In a typical experiment, an oven-dried, sealed tube equipped with a magnetic stir bar was charged with aryl bromide (1.0 mmol), an olefin (1.2 mmol) and a base (1.2 mmol). The catalyst solution (0.01 mmol catalyst in 3.0 ml solvent) was then added. The reaction mixture was placed in a silicon oil bath at the desired temperature and stirred. After the required reaction time, the mixture was allowed to cool to room temperature, diluted with CH_2Cl_2, and washed with HCl aqueous solution and brine. The organic phase was separated and dried over Na_2SO_4 and the solvent evaporated. The residue was chromatographed on silica gel using an ethyl acetate/hexane (1:5) mixture as eluent. Conversion percentages were determined from the solution by GC analysis and yields were based on aryl halide.

Results and Discussion

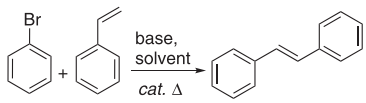
Infrared Spectroscopic Analysis

FT-IR analysis shows that important changes in the azomethine (C=N) band can be observed from FT-IR spectra of the iminophosphine ligands and their palladium(II) complexes. It was determined that C=N stretching frequencies are found in the iminophosphine ligands at 1626, 1625, 1625, and 1673 cm^{-1} for ligands **a–d**, respectively. These absorptions were shifted to lower values in the iminophosphine palladium(II) complexes, indicating the coordination of azomethine nitrogen to the palladium center. This result indicate the coordination of nitrogen atom to the metal center, because this coordination reduces the electron density on the azomethine bond, causing a downfield shift of the C=N band, which is in agreement with what was expected.[14,15]

^{1}H NMR Spectroscopic Analysis

In the ^{1}H NMR spectra of the iminophosphine ligands, the chemical shift of the proton associated with the imine appears as a characteristic doublet as a consequence of the coupling of phosphorus with corresponding azomethine protons. The peaks corresponding to the azomethine proton shifted downfield in the metal complexes. They were observed as a singlet after the ligand bound to the palladium ion via phosphorus atom.[16–19] The ^{1}H NMR spectra of the iminophosphine ligands **a–d** showed a characteristic doublet in the region of δ 9.06–8.97 ppm with a

Table 1. Effect of base, solvent and temperature on the Heck coupling of bromobenzene with styrene[a]

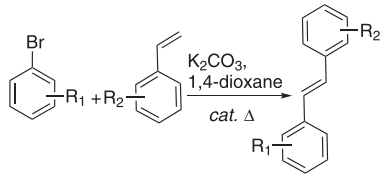


Entry	Base	Solvent	Temp. (°C)	Conversion %[b]			
				1	**2**	**3**	**4**
1	NEt_3	Toluene	140	<5	<5	10	6
2	NaOAc	Toluene	80	<5	<5	<5	<5
3	K_2CO_3	Toluene	80	<5	<5	—	—
4	NaOAc	Toluene	120	18	23	14	24
5	K_2CO_3	Toluene	120	5	7	5	<5
6	NaOAc	Toluene	140	18	13	20	33
7	K_2CO_3	Toluene	140	40	39	56	51
8	NEt_3	DMF	140	<5	<5	<5	<5
9	NaOAc	DMF	140	40	40	38	55
10	K_2CO_3	DMF	140	<5	5	<5	5
11	K_2CO_3	1,4-Dioxane	80	12	17	28	24
12	NaOAc	1,4-Dioxane	100	15	18	42	32
13	K_2CO_3	1,4-Dioxane	100	27	76	34	31
14	NaOAc	1,4-Dioxane	120	17	<5	45	43
15	K_2CO_3	1,4-Dioxane	120	33	—	47	52
16	NEt_3	1,4-Dioxane	140	10	—	15	10
17	NaOAc	1,4-Dioxane	140	56	—	68	67
18	K_2CO_3	1,4-Dioxane	140	98	—	>99	>99

[a]Conditions: Solvent (3 mL), base (1.2 mmol), bromobenzene (1.0 mmol), styrene (1.2 mmol), catalyst (0.01 mmol).
[b]Percentage conversions were determined by GC based on bromobenzene after 6 h.

coupling constant of J_{PH}=5.6–5.1 Hz due to the imine proton, confirming coupling to the phosphorus atom. The peaks for the imine protons in the complexes appear as singlets in the region of δ 8.76–8.30 ppm. This shows that the phosphine donor of the iminophosphine ligands coordinated to the palladium metal. The peaks corresponding to the methyl protons appeared at δ 2.19 and 2.29 ppm for the *ortho*-substituted, **c**, and *meta*-substituted, **d** ligand, respectively. Similarly, the singlet peaks of the *ortho*-methyl protons in **3** and *meta*-methyl protons in **4** in the palladium (II) complexes appeared at about δ 2.14 and 2.30 ppm, respectively.[20]

Table 2. Pd-catalyzed Heck coupling reactions between substituted aryl bromides and styrenes[a]



Entry	R_1	R_2	**1**[b]		**2**[c]		**3**[b]		**4**[b]	
			Time (h)	Conv. (%)[d]	Time (h)	Conv. (%)[d]	Time (h)	Conv. (%)[d]	Time (h)	Conv. (%)[d]
1	3-Cl	2-CH_3	4	100	5	43	2	99	4	99
2	3-COH	2-CH_3	4	100	5	70	4	93	4	99
3	4-COH	2-CH_3	2	100	5	81	2	100	2	99
4	2-$COCH_3$	2-CH_3	5	8	5	7	4	13	4	0
5	3- $COCH_3$	2-CH_3	4	100	5	47	4	90	4	100
6	4- $COCH_3$	2-CH_3	3	95	5	48	2	99	4	100
7	4-CH_3	2-CH_3	4	100	5	19	4	70	4	99
8	3-Cl	2-Cl	3	99	5	66	1.5	100	4	100
9	2-$COCH_3$	2-Cl	3	27	5	20	3	0	4	0
10	3-$COCH_3$	2-Cl	3	100	5	53	1.5	92	4	98
11	4-$COCH_3$	2-Cl	3	100	5	67	1.5	100	4	100
12	4-CH_3	2-Cl	3	100	5	57	1.5	99	4	97
13	3-Cl	4-Cl	3	99	5	70	1.5	97	2	100
14	2-$COCH_3$	4-Cl	4	11	5	7	1.5	<5	4	46
15	4-$COCH_3$	4-Cl	2	100	5	86	1.5	99	2	100
16	4-CH_3	4-Cl	2	100	5	35	3	91	4	100
17	3-Cl	2-Br	4	32	5	36	3	37	4	96
18	2-$COCH_3$	2-Br	4	8	5	9	1.5	6	4	8
19	3-$COCH_3$	2-Br	4	39	5	35	3	40	4	52
20	4-$COCH_3$	2-Br	4	39	5	52	3	37	4	52
21	4-CH_3	2-Br	4	35	5	26	3	28	4	28
22	3-Cl	4-Br	4	31	5	58	3	77	4	49
23	2-$COCH_3$	4-Br	4	6	5	27	3	15	4	38
24	4-$COCH_3$	4-Br	4	44	5	71	3	34	4	56
25	4-CH_3	4-Br	4	28	5	50	3	34	4	41
26	3-Cl	2-OCH_3	2	100	5	83	3	99	4	100
27	3-COH	2-OCH_3	4	94	5	96	3	97	4	95
28	4-COH	2-OCH_3	2	100	5	97	3	100	4	100
29	2-$COCH_3$	2-OCH_3	4	6	5	12	3	<5	4	16
30	3-$COCH_3$	2-OCH_3	2	100	5	79	3	88	4	100
31	4-$COCH_3$	2-OCH_3	2	100	5	96	3	100	4	100
32	4-CH_3	2-OCH_3	2	100	5	72	3	57	4	100
33	3-Cl	4-OCH_3	2	100	5	68	3	95	4	100
34	3-COH	4-OCH_3	2	71	5	93	1.5	100	4	100
35	4-COH	4-OCH_3	2	100	5	98	1.5	100	4	100
36	3-$COCH_3$	4-OCH_3	2	100	5	87	3	80	4	100
37	4-$COCH_3$	4-OCH_3	2	100	5	91	3	100	4	100
38	4-CH_3	4-OCH_3	2	100	5	56	3	35	4	100

[a]Conditions: aryl bromide (1.0 mmol), 1,4-dioxane (3 ml), K_2CO_3 (1.2 mmol), olefin (1.2 mmol), catalyst (0.01 mmol).
[b]140°C.
[c]100°C.
[d]Percentage conversions were determined by GC based on aryl bromide.

^{31}P NMR Spectroscopic Analysis

The ^{31}P NMR spectrum of iminophosphine ligands **a–d** showed one phosphorus singlet in the region δ −14.15 to −12.37 ppm, which is typical of unoxidized tertiary phosphines. The palladium complexes also showed a downfield singlet peak in the region δ 26.68–31.23 ppm. These chemical shifts clearly demonstrated that all iminophosphine ligands are coordinated to the palladium metal via the phosphorus donor atom.[21,22]

^{13}C NMR Spectroscopic Analysis

In ^{13}C NMR spectrum of palladium complexes we observed a shift from the ligands to the metal for the imine carbon. The signal of the imine carbon for **a–d** in the ^{13}C NMR spectrum of the free ligands each appeared as doublet resonance at δ 160.26, 160.35, 158.31, and 158.68 ppm with coupling constant J_{PC}= 25.2–20.6 Hz due to phosphorus carbon coupling, respectively. These signals have totally shifted in the ^{13}C NMR spectrum of the complexes, indicating the coordination of the azomethine nitrogen to the palladium metal.[23,24] As mentioned, the doublet signals for the imine carbon **1–4** to δ 170.08, 169.49, 168.64, and 167.42 ppm with coupling constant J_{PC}= 11.4–8.5 Hz was observed. Besides that, the singlet signals of the trifluoromethyl carbon for the **a**, **b**, **1**, and **2** compounds were observed at δ 124.08, 124.97, 121.23, and 124.68 ppm, respectively.[25] Additionally, for the methyl carbon singlet signals of the **c**, **d**, **3**, and **4** compounds were observed at δ 17.77, 21.39, 18.32, and 20.78 ppm, respectively.[26]

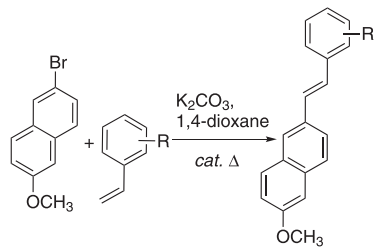
^{19}F NMR Spectroscopic Analysis

In the ^{19}F NMR spectra, fluorine singlet peaks arising from the trifluoromethyl group for compounds **a**, **b**, **1**, and **2** were observed at δ −60.25, −62.57, −58.87, and −60.96 ppm, respectively. These values are in line with previously observed results for similar compounds.[27]

Heck Coupling Reactions

The Heck coupling reaction between bromobenzene and styrene was chosen to optimize suitable reaction conditions using different bases (NEt_3, NaOAc, K_2CO_3), temperatures (80, 100, 120, 140° C), solvents (DMF, toluene, 1,4-dioxane) and 1.0 mol% of catalyst. The results are listed in Table 1. As can be seen, poor yields were obtained with NEt_3 (Table 1, entry 8), NaOAc (Table 1, entry 9), and K_2CO_3 (Table 1, entry 10) using DMF as the solvent at 140° C. Likewise, when using toluene as solvent we could not obtain a significant beneficial effect on catalyst performance with K_2CO_3 (Table 1, entries 3, 5, and 7), Et_3N (Table 1, entry 1), and NaOAc (Table 1, entries 2, 4, and 6). On the other hand, when 1,4-dioxane was used as the solvent, relatively high conversions were obtained depending on the temperature effect (Table 1, entries 13–17); however, by increasing the temperature to 140°C (Table 1, entry 18) almost complete conversions were obtained for **1**, **3**, and **4** catalysts using K_2CO_3, and no palladium black formation was observed during these reactions. Generally, for the Heck coupling reactions higher reaction temperatures (normally 110–180°C) are required unless they cause catalyst decomposition, and it is also necessary to coordinate the carbon atom of the C–Br group to Pd(0) intermediate during the catalytic cycle.[28–30] As shown in entries 15 and 18, no activity was observed for catalyst **2** at temperatures above 100°C. This can be explained by the formation of palladium black species, which was observed at reaction temperatures 120 and 140°C.[1] Therefore, all other subsequent coupling reactions activated by catalyst **2** were carried out at 100°C, different from catalysts **1**, **3**, and **4** (at 140°C), using K_2CO_3 as a base in 1,4-dioxane.

Table 3. Heck coupling of 2-bromo-6-methoxynaphthalene with substituted styrenes[a]



Entry	R	1		2		3		4	
		Time (h)	Conv. (%)[d]	Time (h)	Conv. (%)[d]	Time (h)	Conv. (%)[d]	Time (h)	Conv. (%)[d]
1	3-CH_3	3	100	5	20	1.5	98	4	87
2	2-Cl	3	100	5	33	1.5	75	4	100
3	3-Cl	3	100	5	35	3	100	4	100
4	2-OCH_3	2	100	5	48	3	63	4	100
5	3-OCH_3	2	100	5	39	3	63	4	100
6	4-OCH_3	2	100	5	58	3	11	4	100

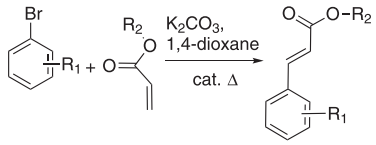
[a]Conditions: 2-Bromo-6-methoxynaphthalene (1.0 mmol), 1,4-dioxane (3 ml), K_2CO_3 (1.2 mmol), olefin (1.2 mmol), catalyst (0.01 mmol).
[b]140°C.
[c]100°C.
[d]Percentage conversions were determined by GC based on 2-bromo-6-methoxynaphthalene.

After the optimal reaction parameters were determined, the catalytic activity for complexes with substituted aryl bromides and styrene derivatives was investigated under those conditions for the Heck coupling reaction. The data in Table 2 show the results obtained from the coupling of aryl bromides and styrene derivatives.

As shown in Table 2, activated aryl bromides such as 3-bromobenzaldehyde, 4-bromobenzaldehyde, 3-bromoacetophenone, and 4-bromoacetophenone gave complete conversions when using catalyst **1** (Table 2, entries 2, 3, 5, 10, 11, 15, 28, 30, 31, and 35–37). Similarly, very high conversions (>80%) were obtained for the same aryl bromides in the presence of complex **3** or **4** (Table 2, entries 2, 3, 5, 6, 10, 11, 15, 16, 26-28, 30, 31, and 34–37). In comparison, catalyst **2** showed generally poor conversion (35–71%), palladium black being observed during the reactions (Table 2, entries 2, 5, 6, 10, 11, 19, 20, and 24). Despite the formation of palladium black during the coupling reaction of 4-bromobenzaldehyde with 4-methoxystyrene and 2-methoxystyrene, almost complete conversions, 98%, and 97% after 5 h were achieved (Table 2, entries 28 and 35). The formation of palladium black was due to the palladium precipitating out, leading to death of the catalyst. Presumably not all of the palladium had precipitated out within the 5 h time frame, leaving sufficient catalyst in solution to catalyze the reaction.

Ortho-substituted aryl bromides such as 2-bromoacetophenone produced lower conversions (Table 2, entries 4, 9, 18, and 29). These results indicate that, as expected, steric hindrance of the aryl bromides is an important factor in the rate of reaction.[31] Despite this, reasonable conversions were observed for the reaction of 2-bromoacetophenone with 4-chlorostyrene and 4-bromostyrene in the presence of catalyst **4** (Table 2, entries 14 and 23). Generally, in Heck coupling reactions, deactivated aryl bromides bearing electron-donating substituents on the aryl bromide make the oxidative addition step of the catalytic cycle more difficult than those with electron-withdrawing substituents (activated). In spite of this general trend, catalysts **1**, **3**, and **4** gave excellent conversions (>95%) for electronically deactivated aryl bromides such as 1-bromo-3-chlorobenzene (Table 2, entries 1, 8, 13, 26, and 33) and 4-bromotoluene (Table 2, entries 7, 12, 16, and 32). Catalyst **2** was less active toward these deactivated aryl bromides, giving moderate conversions (Table 2, entries 1, 7, 8, 12, 13, 16, 17, 21, 22, 25, 26, 32, and 33).

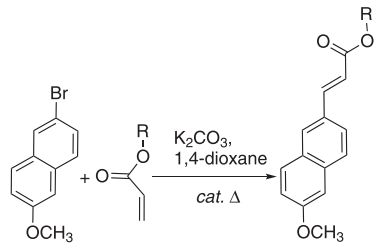
Table 4. Heck coupling reactions between substituted aryl bromides and acrylates[a]



Entry	R_1	R_2	**1**[b]		**2**[c]		**3**[b]		**4**[b]	
			Time (h)	Conv. (%)[d]	Time (h)	Conv. (%)[d]	Time (h)	Conv. (%)[d]	Time (h)	Conv. (%)[d]
1	3-Cl	Methyl	5	92	5	0	5	62	4	100
2	3-COH	Methyl	5	61	5	20	5	59	4	88
3	4-COH	Methyl	4	96	5	11	5	100	4	100
4	2-$COCH_3$	Methyl	5	8	5	12	5	<5	4	20
5	3-$COCH_3$	Methyl	5	99	5	20	5	98	4	93
6	4-$COCH_3$	Methyl	4	91	5	54	5	100	4	100
7	4-CH_3	Methyl	5	54	5	55	5	85	4	95
8	3-Cl	Ethyl	5	91	5	<5	5	85	4	100
9	3-COH	Ethyl	5	63	5	41	5	74	4	100
10	4-COH	Ethyl	5	97	5	80	5	100	4	100
11	2-$COCH_3$	Ethyl	5	7	5	16	5	5	4	29
12	3-$COCH_3$	Ethyl	3	100	5	16	5	98	4	100
13	4-$COCH_3$	Ethyl	3	100	5	61	5	100	4	100
14	4-CH_3	Ethyl	5	85	5	52	5	100	4	100
15	3-Cl	Butyl	5	82	5	9	5	67	4	100
16	3-COH	Butyl	3	100	5	46	5	100	4	96
17	4-COH	Butyl	3	100	5	87	5	100	4	100
18	2-$COCH_3$	Butyl	5	<5	5	20	5	31	4	25
19	3-$COCH_3$	Butyl	5	85	5	29	5	100	4	100
20	4-$COCH_3$	Butyl	5	100	5	59	5	100	4	100
21	4-CH_3	Butyl	5	94	5	66	5	100	4	97

[a]Conditions: aryl bromide (1.0 mmol), 1,4-dioxane (3 ml), K_2CO_3 (1.2 mmol), acrylate (1.2 mmol), catalyst (0.01 mmol).
[b]140°C.
[c]100°C.
[d]Percentage conversions were determined by GC based on aryl bromide.

Table 5. Heck coupling of 2-bromo-6-methoxynaphthalene with substituted acrylates[a]



Entry	R	**1**[b]		**2**[c]		**3**[b]		**4**[b]	
		Time (h)	Conv. (%)[d]	Time (h)	Conv. (%)[d]	Time (h)	Conv. (%)[d]	Time (h)	Conv. (%)[d]
1	Methyl	5	86	5	64	5	68	4	92
2	Ethyl	3	100	5	66	5	95	4	100
3	Butyl	5	95	5	57	5	100	4	98

[a]Conditions: 2-bromo-6-methoxynaphthalene (1.0 mmol), 1,4-dioxane (3 ml), K_2CO_3 (1.2 mmol), acrylate (1.2 mmol), catalyst (0.01 mmol).
[b]140°C.
[c]100°C.
[d]Percentage conversions were determined by GC based on 2-bromo-6-methoxynaphthalene.

The data in Table 3 show the results obtained from the coupling of 2-bromo-6-methoxynaphthalene with substituted styrenes under the previously determined optimal reaction conditions. Despite the presence of an electron-donating substituent in the other ring, 2-bromo-6-methoxynaphthalene gave complete conversion with substituted styrenes for the **1**- and **4**-catalyzed Heck coupling reactions (Table 3, entries 2–6). The **3**-catalyzed reaction between 2-bromo-6-methoxynaphthalene and 3-chlorostyrene also gave complete conversion (Table 3, entry 3). Moderate conversions (20–58%) were obtained when catalyst **2** was used for the coupling reaction of 2-bromo-6-methoxynaphthalene with styrene derivatives.

All the complexes were evaluated for Heck coupling with activated and deactivated aryl bromides and a variety of acrylates. It was observed that catalyst **4** was a very effective catalyst for the coupling of activated aryl bromides such as 3-bromo, 4-bromobenzaldehyde and 3-bromo, 4-bromoacetophenone in relatively short time frames of 4 h, showing conversion rates of 88–100%. When complex **1** or **3** was used as catalyst for these coupling reactions, high conversions (59–100%) were also observed, but in the presence of complex **2** only moderate conversions were obtained after 5 h (Table 4, entries 2, 3, 5, 6, 9, 10, 12, 13, 16, 17, 19, and 20). Additionally, the use of complex **2** as a catalyst led to no conversion in the reaction between 1-bromo-3-chlorobenzene and methyl acrylate (Table 4, entry 1). It is noteworthy that complex **4** gave complete conversion for 1-bromo-3-chlorobenzene, which was deactivated by the —*Cl* group (Table 4, entries 1, 8, and 15). It also gave almost complete conversion for the other deactivated aryl bromide (4-bromotoluene; Table 4, entries 7, 14, and 21). As expected, for each catalyst, the rate of the coupling reaction was limited in reactions with sterically hindered aryl bromides, as shown in entries 4, 11, and 18.

All the complexes were also evaluated for in the Heck coupling reaction of 2-bromo-6-methoxynaphthalene with acrylate derivatives. As shown in Table 5, very high conversions were obtained in the presence of catalysts **1**, **3**, and **4** (Table 5, entries 1, 2, and 3). The use of catalyst **2** actually slowed the rate of this reaction. Good conversions were obtained in cases where ethyl- and butyl-substituted acrylates were used (Table 5, entries 2 and 3). In the case of methyl acrylate, only moderate conversions were obtained (Table 5, entry 1).

Conclusions

In this research, several iminophosphine ligands and palladium(II) complexes were prepared and characterized by FT-IR, ^{1}H NMR, ^{31}P NMR, ^{13}C NMR, and ^{19}F NMR spectroscopy. The palladium(II) complexes were tested as catalysts for the Heck cross-coupling reaction of bromobenzene with styrene. Under the determined optimal reaction conditions, all complexes were evaluated in the Heck coupling reaction with activated and deactivated aryl bromides and a variety of styrene derivative and several acrylates. The results show that complexes **1**, **3**, and **4** were active, giving high conversions for the coupling reactions. The higher activities of these complexes suggest that the iminophosphine ligands are hemilabile. Complex **2** generally gave low catalytic activities compared to the other catalysts, due to the formation of palladium black.

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