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The development of phosphinoamine–Pd(II)–imidazole complexes: implications in room-temperature Suzuki–Miyaura cross-coupling reaction

Geetika Borah*, Devajani Boruah, Gayatri Sarmah, Saitanya K. Bharadwaj and Utpal Bora‡

The reaction of *N*-methylimidazole (N-MeIm) and *N*-butylimidazole (N-BuIm) with the complexes [$PdCl_2$(PPh_2py–P,N)] and [$PdCl_2$(PPh_2Etpy–P,N)] in the presence of NH_4PF_6 under N_2 at room temperature afforded four new cationic Pd(II) complexes [PdCl(PPh_2py–P,N)(N-MeIm)](PF_6) (1), [PdCl(PPh_2py–P,N)(N-BuIm)](PF_6) (2), [PdCl(PPh_2Etpy–P,N)(N-MeIm)](PF_6) (4) and [PdCl(PPh_2Etpy-P,N)(N-BuIm)](PF_6) (5) in good yields, where PPh_2py is 2-(diphenylphosphino)pyridine and PPh_2Etpy is 2-{2-(diphenylphosphino)ethyl}pyridine). The complexes were fully characterized. The catalytic activities of these complexes were investigated for Suzuki–Miyaura cross-coupling reactions at room temperature. Complex 2 exhibited excellent activity compared to other analogs. Copyright © 2013 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: palladium(II) cationic complex; imidazole; Suzuki–Miyaura cross-coupling

Introduction

The coordination chemistry of platinum group metals occupies a special position in the field of catalysis for different chemical transformations.[1–8] Among the various chemical transformations triggered by platinum group metals, palladium-catalyzed Suzuki–Miyaura reaction is vital and widely used process in chemistry as it generates various bio-active natural products, agrochemicals, pharmaceuticals, polymers, etc.[9–11] The catalytic cycle of the Suzuki–Miyaura reaction involves activation of C–X bond by Pd(0) or Pd(II) and the efficiency of the catalytic system has been achieved by changing the ligand environment around palladium.[12–14] Along with other ligand environments, significant efforts have been also made in designing novel catalytic systems of Pd(0) or Pd(II) complexes with phosphine-based ligands like tertiaryphosphines, hemilabile-type phosphines, sterically crowded biphenyl-type phosphines, and imidazole- and imidazolium-functionalized phosphines.[15–21] Although complexes containing such ligands often show excellent activity, moisture sensitivity,[22] and the requirement for high temperature and undesirable solvents such as dimethyl formamide, *N*-methylpyrrolidine and dimethoxyethane,[23] are some of the major drawbacks. Therefore the development of an eco-friendly and technologically feasible newer approach for designing highly active catalytic systems in environmentally preferred solvents for the Suzuki–Miyaura cross-coupling reaction is highly desirable.

Cheap, commercially available imidazoles are an important class of N-donor ligands with strong σ-donor ability and weak π-acceptor capability. Several air-stable Pd(II)-imidazole complexes have been developed and documented to be efficient catalysts in various cross-coupling reactions, including Suzuki–Miyaura.[24] Moreover, other N–N and P–N type ligands have also been used in the Suzuki–Miyaura reaction.[25] However, to the best of our knowledge no phosphinoamine–Pd(II)–imidazole type complexes have been synthesized and investigated for their catalytic efficiency in Suzuki–Miyaura reactions. Herein, we wish to report the synthesis and characterization of four new cationic palladium(II) complexes **1**, **2**, **4** and **5** containing both phosphinoamine and imidazole ligands. The catalytic efficiency of the synthesized complexes in Suzuki–Miyaura cross-coupling reactions is also reported here.

Experimental

General Information

$PdCl_2$, tetrabutylammonium perchlorate (TBAP) and 1,5-cyclooctadiene (COD) were purchased from Acros Chemicals. The ligands 2-(diphenylphosphino)pyridine (PPh_2py) and 2-[2-(diphenylphosphino)ethyl]pyridine)] (PPh_2Etpy) were purchased from Aldrich (USA). NH_4PF_6, *N*-methylimidazole, *N*-butylimidazole were procured from Fluka and used without further purification. The precursor complexes [$PdCl_2$(COD)][26]

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and $[PdCl_2(PPh_2py\text{-}P,N)]$[27] were synthesized according to the published procedure. Another previously reported precursor complex $[PdCl_2(PPh_2Etpy\text{-}P,N)]$ (**3**) was prepared by using $[PdCl_2(COD)]$ instead of $[PdCl_2(PhCN)_2]$.[28] The solvents used were of analytical grade and distilled and dried over 4 Å molecular sieves. All reactions were carried out under nitrogen atmosphere.

The melting points of the complexes were determined using Buchi B450 melting point apparatus. Elemental analyses were performed by Elementar Vario EL III Carlo Erba 1108. IR spectra (4000–250°cm^{-1}) were recorded in KBr on a Shimadzu Prestige-21 FT-IR spectrophotometer. UV–visible spectra were recorded in dichloromethane /acetonitrile using a 1°cm^3 quartz cell in the range 800–200 nm on Shimadzu-Graphicord UV-1700 spectrometer. The conductivity of the complexes was measured in dichloromethane–acetonitrile (10^{-2} M) by using a digital conductivity bridge, type ELICO-CM-180 at 25°C. The ^{1}H, ^{13}C and ^{31}P{^{1}H}NMR spectra were recorded in $CD_3CN/CDCl_3$ solutions operating at 400.13, 100.62 and 161.98 MHz respectively on a Bruker Advance II 400 NMR spectrometer and chemical shifts were reported relative to tetramethylsilane for ^{1}H, ^{13}C NMR spectra and 85% aqueous H_3PO_4 for ^{31}P{^{1}H}NMR spectra as standard. The ^{1}H NMR assignments were done with respect to the labeling chart (Scheme 1). The electrospray ionization (ESI) (+) mass spectra were recorded on a Waters ZQ-4000 mass spectrometer in $CH_3CN/CHCl_3$. A cyclic voltammetry study of the complexes was performed in acetonitrile solution with a CH Instrument (Model 600C) using platinum as working electrode and Ag/AgCl as the reference electrode with 0.1 M TBAP as the supporting electrolyte at different scan rates 30–200 mV s^{-1}.

Synthesis of $[PdCl(PPh_2py\text{–}P,N)(N\text{-}MeIm)](PF_6)$ (1)

To a suspension of $[PdCl_2(PPh_2py\text{–}P,N)]$ (0.13 g, 0.295 mmol) in 20 ml dichloromethane, NH_4PF_6 (0.05 g, 0.301 mmol) was added and stirred at room temperature for 2 h under N_2, resulting a wine-red mixture, to which a solution of N-MeIm (0.025 g, 0.301 mmol) in dichloromethane was added with constant stirring. The color of the solution changed sharply from wine-red to brown. The resulting mixture was stirred for 14 h at room temperature. The white precipitate of NH_4Cl was separated by filtration and the filtrate was evaporated *in vacuo*. The sticky residue was washed with petroleum ether and recrystallized from dichloromethane to yield the product as a brown solid. Yield: 80% (0.15 g); m.p. 60°C; Anal. Calcd for $C_{21}H_{20}N_3P_2ClF_6Pd$: C, 39.81%; H, 3.16%; N, 6.64%. Found: C, 39.30%; H, 3.02%; N, 6.34%; $\Lambda = 84\ \Omega^{-1}\ cm^2\ mol^{-1}$; IR (KBr, cm^{-1}): 3106 (m), 3054 (m), 2925 (m), 2867 (m), 1568 (m) $\nu_{py(C=N)}$, 843 (s) ν_{P-F}, 557 (m) δ_{P-F-P}, 536 (m), 514 (m) ν_{Pd-py}, 432 (w) ν_{Pd-P}, 355 (s) ν_{Pd-Cl}, 272 (m) ν_{Pd-Im}; UV–visible: λ_{max} (CH_2Cl_2, nm): 229, 269 and 344. ^{1}H NMR ($CDCl_3$, δ ppm): 3.50 (s, 3H, CH_3), 7.06 (s, br, 1H, H$^{5'}$), 7.40–7.48 (m, 10 H, Ph), 7.60 (s, br, 1H, H$^{4'}$), 7.88–7.79 (m, 2H, H^{3,5}), 8.15 (s, 1H, H$^{2'}$), 8.24 (m, 1H, H^4) and 8.75(d, $J = 4.0$ Hz, 1H, H^6); ^{13}C NMR ($CDCl_3$, δ ppm): 33.4 (C–CH_3), 120.10 (C^5), 120.28 (C^3), 128.68 (2C, C–Ph), 129.40 (4C, C–Ph), 129.51 (2C, C–Ph), 133.58 (4C, C–Ph), 134.24 (C^4), 139.27(C$^{4'}$), 139.31(C$^{5'}$), 141.25(C^6), 152.34(C$^{2'}$), 158.23(C^2); ^{31}P{^{1}H}NMR ($CDCl_3$, δ ppm): −9.98 (s,1P) and −175.60 (spt, PF_6^-, $J_{PF} = 712$ Hz). ESI/MS (*m/z*): 656 [M+Na]$^+$.

Synthesis of $[PdCl(PPh_2py\text{–}P,N)(N\text{-}BuIm)](PF_6)$ (2)

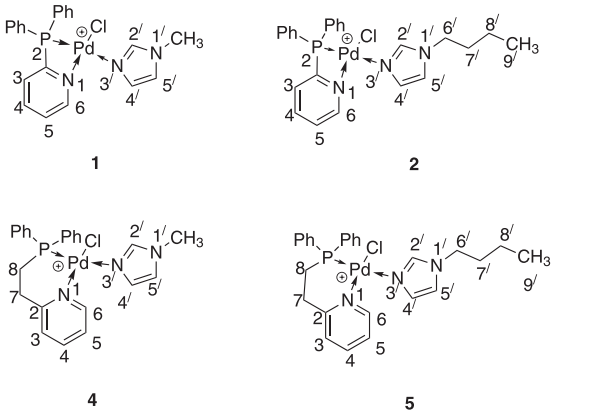
Complex **2** was prepared as described for complex **1**, using N-BuIm (0.038 g, 0.301 mmol), $[PdCl_2(PPh_2py\text{–}P,N)]$ (0.130 g, 0.295 mmol) and NH_4PF_6 (0.049 g, 0.301 mmol) to yield the product as a reddish-brown solid. Yield: 90% (0.179 g), m.p. 68° C; Anal. Calcd for $C_{24}H_{26}N_3P_2ClF_6Pd$: C, 42.60%; H, 3.85%; N, 6.21%, Found: C, 42.10%; H, 3.45%; N, 6.12%. $\Lambda = 89\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR (KBr, cm^{-1}): 3108 (m), 3054 (m), 2928 (m), 2865 (m), 1570 (m) $\nu_{py(C=N)}$, 843 (s) ν_{P-F}, 557 (m), 536 (s), 515 (m) ν_{Pd-N}, 430 (m) ν_{Pd-P}, 351 (s) ν_{Pd-Cl}, 278 (ms) ν_{Pd-Nim}; UV–visible: λ_{max} (CH_2Cl_2, nm): 228 and 270; ^{1}H NMR ($CDCl_3$, δ ppm): 0.88–0.95 (m, 5H, H$^{9',8'}$), 1.29–1.33 (m, 2H, H$^{7'}$), 3.88–3.94 (m, 2H, H$^{6'}$), 6.84 (s, br, 1H, H$^{5'}$), 7.60 (s, br, 1H, H$^{4'}$), 7.40–7.48 (m, 10H, Ph), 7.87–7.79 (m, 2H, H^{3,5}), 8.21 (s, 1H, H$^{2'}$) 8.25 (m, 1H, H^4) and 8.75(d, $J = 4.4$ Hz, 1H, H^6); ^{13}C NMR ($CDCl_3$, δ ppm): 13.47 (C$^{9'}$), 19.24 (C$^{8'}$), 32.51 (C$^{7'}$), 48.03 (C$^{6'}$), 120.23 (C^5), 120.38 (C^3), 128.13 (2C,C–Ph), 129.35 (4C, C–Ph), 129.12(2C, C–Ph), 131.98(4C, C–Ph), 132.84 (C$^{4'}$), 138.95 (C$^{5'}$), 139.21 (C^4), 140.87 (C^6), 153.04 (C$^{2'}$), 159.23 (C^2); ^{31}P{^{1}H}NMR ($CDCl_3$, δ ppm): −9.76 (s,1P) and −176.57 ppm (spt, PF_6^-, $J_{PF} = 712$ Hz); ESI/MS (*m/z*): 554 [M+Na−PF_6]$^+$.

Synthesis of $[PdCl_2(PPh_2Etpy\text{–}P,N)]$ (3)

To a solution of $[PdCl_2(COD)]$ (0.29 g, 1.018 mmol) in 20 ml dichloromethane, a solution of PPh_2Etpy (0.296 g, 1.016 mmol) in 15 ml dichloromethane was added drop by drop. The reaction mixture was stirred under nitrogen at room temperature for 18 h, during which the color of the mixture changed from yellow-orange to pale-yellow. The volume was reduced to 2 ml and 15 ml Et_2O was added under vigorous stirring to precipitate out the product. The solid mass was separated by filtration, washed with Et_2O several times and dried in a desiccator to collect the product as a pale-yellow solid. Yield: 93% (0.444 g, 0.947 mmol). These analytical data are in accordance with those reported in the literature.[28]

Synthesis of $[PdCl(PPh_2Etpy\text{–}P,N)(N\text{-}MeIm)](PF_6)$ (4)

A solution of N-MeIm (0.020 g, 0.241 mmol) in 10 ml dichloromethane was added drop-wise to a well-stirred suspension of $[PdCl_2(PPh_2Etpy\text{–}P,N)]$ (0.11 g, 0.235 mmol) and NH_4PF_6 (0.039 g, 0.239 mmol) in dichloromethane. The resulting mixture was stirred at room temperature for 16 h under N_2. After that the yellow mixture was separated from the white precipitate of NH_4Cl by filtration. The filtrate was evaporated to dryness *in vacuo*. The sticky residue was washed with petroleum ether and recrystallized from dichloromethane to obtain the product as a pale-yellow solid. Yield: 83% (0.129 g), m.p. 128 °C; $\Lambda = 83$



Scheme 1. Numbering of H and C-atom positions in pyridyl, imidazole and alkyl group.

Ω^{-1} cm^2 mol^{-1}, Anal. Calcd for $C_{23}H_{24}N_3P_2ClF_6Pd$: C, 41.75%; H, 3.63%; N, 6.35%; Found: C, 41.43%; H, 3.33%; N, 6.12%; IR (KBr, cm^{-1}): 3106 (m), 3054 (m), 2925 (m), 2867 (m), 2780 (m), 1610 (m) $\nu_{py(C=N)}$, 841 (s) ν_{P-F}, 559 (s), 534 (m), 516 (w) ν_{Pd-N}, 449(w) ν_{Pd-P}, 355 (s) ν_{Pd-Cl}, 272 (m) ν_{Pd-Nim}; UV–visible: λ_{max} (CH_2Cl_2, nm): 230, 270 and 346; ^{1}H NMR ($CDCl_3$, δ ppm): 2.75 (s, br, 2H, H^8), 3.37 (s, 3H, CH_3), 4.26–4.29 (m, 2H, H^7), 6.45–6.48 (m, 2H, $H^{3,5}$), 6.86 (s, br, 1H, $H^{5'}$), 7.16 (s, br, 1H, $H^{4'}$), 7.38–7.42 (m, 4H, Ph), 7.71–7.76 (m, 6H, Ph), 7.84–7.87 (m, 1H, H^4), 8.42 (s, 1H, $H^{2'}$) and 9.11 (s, br, 1H, H^6); ^{13}C NMR ($CDCl_3$, δ ppm): 30.95 (C–CH_3), 33.40 (C^7), 33.42 (C^8), 120.12 (C^5) 120.18 (C^3), 129.04 (C^4), 129.10 (2C,C–Ph), 129.21 (4C,C–Ph), 129.47(2C,C–Ph), 133.14 (4C,C–Ph), 139.23 ($C^{4'}$), 139.31 ($C^{5'}$), 140.15 (C^6), 151.08 ($C^{2'}$), 158.72 (C^2); ^{31}P{^{1}H} NMR ($CDCl_3$, δ ppm): 14.38 (s), −160.85 (spt, PF_6^-, J_{PF} = 712 Hz). ESI/MS (*m/z*): 516 $[M-PF_6]^+$.

Synthesis of [PdCl(PPh$_2$Etpy–P,N)(N-BuIm)](PF$_6$) (5)

Complex **5** was synthesized following a similar procedure as that for complex **4**, using N-BuIm (0.030 g, 0.238 mmol), [$PdCl_2$(PPh$_2$Etpy–P,N)] (0.11 g, 0.235 mmol) and NH_4PF_6 (0.039 g, 0.239 mmol). During stirring, the color of the solution changed gradually from yellow to wine-red. After thorough washing with petroleum ether a blood-red sticky compound was obtained, which was recrystallized from dichloromethane. Yield: 79% (0.130 g); m.p. 68 °C. Λ = 88 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{26}H_{30}N_3P_2ClF_6Pd$: C, 44.32%; H, 4.26%; N, 5.97%; Found: C, 44.13% ; H, 4.03%; N, 5.71%; IR (KBr, cm^{-1}): 3108 (m), 3054 (m), 2928 (m), 2865 (m), 1608 (m) $\nu_{py(C=N)}$, 842 (s) ν_{P-F}, 557 (s), 532 (m), 504 (w) ν_{Pd-N}, 445 (m) ν_{Pd-P}, 376 (s) ν_{Pd-Cl}, 290 (ms) ν_{Pd-Nim}; UV–visible: λ_{max} (CH_2Cl_2, nm): 230, 268 and 321; ^{1}H NMR ($CDCl_3$, δ ppm): 0.86–0.94 (m, 5H, $H^{9',8'}$), 1.25–1.27 (m, 2H, $H^{7'}$), 2.71–2.77 (m, 2H, H^8), 3.63 (t, J = 8.0, 2H, $H^{6'}$), 4.20–4.24 (m, 2H, H^7), 6.43–6.47 (m, 2H, $H^{3,5}$), 6.50 (s, br, 1H, $H^{5'}$), 7.07 (s, br, 1H, $H^{4'}$), 7.44–7.51 (m, 4H, Ph), 7.69–7.76 (m, 6H, Ph), 7.77–7.82 (m, 1H, H^4), 8.03 (s, 1H, $H^{2'}$) and 9.00 (s, 1H, H^6); ^{13}C NMR ($CDCl_3$, δ ppm): 13.45 ($C^{9'}$–CH_3), 19.43 ($C^{8'}$–CH_2), 19.62 ($C^{7'}$–CH_2), 32.28 (C^7–CH_2), 32.68 (C^8–CH_2), 48.33 ($C^{6'}$–CH_2), 120.10 (C^5), 124.20 (C^3), 128.68 (2C,C–Ph), 129.40 (4C,C–Ph), 129.51 (2C,C–Ph), 132.18 (4C,C–Ph), 133.04 (C^4), 139.01 ($C^{4'}$), 139.51 ($C^{5'}$), 141.05 (C^6), 152.98 ($C^{2'}$), 159.83 (C^2); ^{31}P{^{1}H} NMR ($CDCl_3$, δ ppm): 14.51 (s, PPh_2), −160.79 (spt, PF_6^-, J_{PF} = 712 Hz). ESI/MS (*m/z*): 577 $[M+NH_4-PF_6]^+$.

General Information Concerning Catalytic Experiments

Suzuki–Miyaura cross-coupling reactions were carried out under aerobic conditions at room temperature. The progress of the reactions was monitored by thin-layer chromatography (TLC) using aluminium-coated TLC plates (Merck) under UV light. The products were purified by column chromatographic technique using silica gel (60-120 mesh). The various products separated were characterized by melting point, ^{1}H and ^{13}C NMR and mass spectral data and compared with the authentic samples.

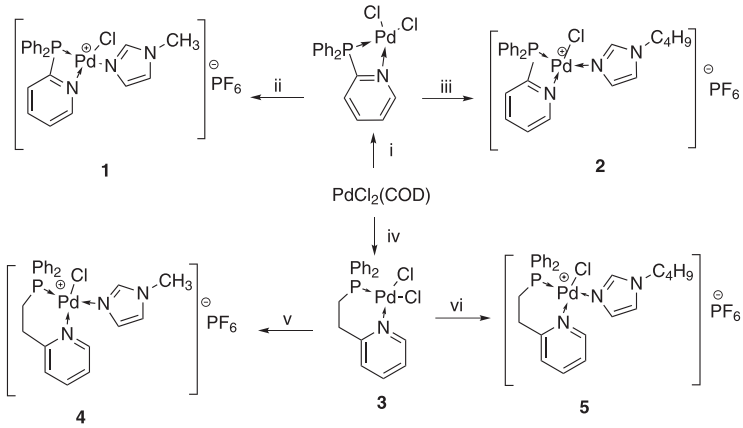
General Procedure for Suzuki–Miyaura Reactions of Aryl Halides

A 50 ml round-bottom flask was charged with a mixture of aryl halide (0.5 mmol), aryl boronic acid (0.55 mmol), base (1.5 mmol), ethanol (2 ml) and palladium complex (1.5 mol%) and the mixture was stirred at room temperature. After completion, the reaction mixture was diluted with water (20 ml) and extracted with ether (3 × 20 ml). The combined extract was washed with brine (2 × 20 ml) and dried over Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was chromatographed (silica gel–ethyl acetate-hexane, 1:9) to obtain the desired products. The products were confirmed by comparing the melting point, ^{1}H and ^{13}C NMR and mass spectral data with authentic samples (supporting information, Table S1).

Results and Discussion

Synthesis and Characterization of [PdCl(PPh$_2$py–P,N)(N-MeIm)](PF$_6$) (1)

The reaction of neutral palladium complex [$PdCl_2$(PPh$_2$py–P,N)] with N-MeIm on stirring in dichloromethane at room temperature for 14 h under N_2 led to the formation of [PdCl(PPh$_2$py–P,N)(N-MeIm)](PF$_6$)(**1**) with 80% yield (Scheme 2). The elemental analyses and ESI mass spectrum of the complex were in agreement with the proposed formulation. The mass spectrum of complex **1** demonstrated a molecular ion peak of moderate intensity at *m/z* = 656 $[M+Na]^+$. The TGA data are also in agreement with the proposed molecular formula of the complex. The TGA of the complex exhibits major weight loss 73.8% (calcd 77.6%) in the temperature range 43–338 °C, attributed to the removal of PPh_2py, N-MeIm and PF_6^- ion of the complex. The IR spectrum



Scheme 2. Synthesis of complexes **1**, **2**, **3**, **4** and **5**. Reagents and reaction conditions: (i) PPh_2py, CH_2Cl_2, 0.5 h, room temperature (r.t.), N_2; (ii) NH_4PF_6, MeIm, CH_2Cl_2, 14 h, r.t., N_2; (iii) NH_4PF_6, BuIm, CH_2Cl_2 , 14 h, r.t., N_2; (iv) PPh_2Etpy, CH_2Cl_2, 18 h, r.t., N_2; (v) NH_4PF_6, MeIm, CH_2Cl_2, 16 h, r.t., N_2; (vi) NH_4PF_6, BuIm, CH_2Cl_2, 16 h, r.t., N_2.

of **1** exhibited the characteristic peak for ν(Pd–N), ν(Pd–P) and ν(Pd–Cl) vibrations, similar to that of the precursor complex $[PdCl_2(PPh_2py–P,N)]$[27,28] with a small shift. In the far-IR region a new band at 272 cm^{-1} could be assigned to Pd–$N_{imidazole}$ stretching vibration. The UV–visible spectrum of compound **1** in dichloromethane displayed three bands at 229, 269 and 344 nm, the former two presumably due to intraligand $\pi\rightarrow\pi^*$, while the third one is due to $n\rightarrow\pi^*$[29–31] transitions with some contribution of $Cl^-\rightarrow Pd^{2+}$ charge transfer transition. Compared to the starting compound $[PdCl_2(PPh_2py–P,N)]$ (394 nm), the band for $n\rightarrow\pi^*$ transition was blue shifted, indicating a change of the ligand environment about the Pd^{2+} ion.[32,33] The $^{31}P\{^1H\}$NMR spectrum of **1** displayed a singlet at $\delta = -9.98$ ppm. Compared with the neutral parent compound $[PdCl_2(PPh_2py–P,N)]$ ($\delta = -9.15$ ppm), complex **1** shows an upfield shift of 0.83 ppm, indicating the formation of a new complex. An upfield resonance in **1** is known to be diagnostic of a four-membered chelate complex.[34,35] The N-MeIm ligand has good electron-donating ability and its coordination might increase the electron density on the metal center due to which the degree of back-donation from metal to aminophosphine ligand (dπ–pπ) increases in comparison with precursor complex.[36] The enhanced back-donation might cause an upfield shift of 0.83 ppm in **1** relative to the parent compound. The ^{31}P resonance of the PF_6^- counterion for complex **1** is observed at $\delta = -175.60$ ppm with $J_{PF} = 712$ Hz.[37] The ^1H NMR spectrum of the complex exhibits a singlet at $\delta = 8.15$ ppm due to the $H^{2'}$ (Scheme 1) proton of N-MeIm with 0.75 ppm downfield shift compared to free N-MeIm, clearly indicating coordination of the imidazole through the N(3′) atom. In addition, two singlets at $\delta = 7.06$ ppm and $\delta = 7.60$ ppm could be assigned to $H^{4'}$ and $H^{5'}$ of N-MeIm, respectively. Complex **1** in its cyclic voltammogram in acetonitrile exhibited one irreversible reductive response at -1.18 V ($\Delta E_p = 510$ mV). This feature could be assigned to the Pd(II)/Pd(0) redox couple,[38–40] since complexes of π-acceptor ligands undergo two-electron reduction with the stabilization of Pd(0).[41] Extremely high peak-to-peak separation value indicated that the redox process is quite non-Nernstian. Moreover, a reduction peak was observed at -0.80 V with no anodic response and may be assigned to PPh_2py-based reduction. During positive potential scan the oxidation at +1.52 V with no peak reversal is assumed to lead to the formation of a Pd(IV), accompanied by an increase in coordination number from 4 to 6.[40] Compared to the precursor complex $[PdCl_2(PPh_2py–P,N)]$ ($E_{pc} = -0.75$ V) the reduction was shifted to a more negative value, which may be due to the presence of electron-donating N-MeIm ligand in **1**.[38]

Synthesis and Characterization of [PdCl(PPh_2py–P,N)(N-BuIm)](PF_6) (2)

Treatment of $[PdCl_2(PPh_2py-P,N)]$ with N-BuIm on stirring in dichloromethane at room temperature for 14 h under N_2 led to the formation of [PdCl(PPh_2py–P,N)(N-BuIm)](PF_6) (**2**) with 90% yield (Scheme 2). Similar to complex **1**, the elemental analyses and mass spectrum are in good agreement with the above composition. The mass spectrum of complex **2** shows a molecular ion peak at 554, which correspond to $[M+Na-PF_6]^+$ ions. TGA shows major weight loss of 75.8% (cald78.9%) in the temperature range 178–394°C, consistent with the loss of PPh_2py, BuIm and PF_6^- ion, respectively. The IR spectrum in KBr shows a new band at 278 cm^{-1}, consistent with Pd–$N_{imidazole}$ vibration. Similar to complex **1**, all other bands are observed as expected.[37] In the UV–visible spectrum, complex **2** also displays two bands at 270 nm and 228 nm for intra-ligand $\pi\rightarrow\pi^*$ and one at 342 nm with a blue shift for $n\rightarrow\pi^*$ transitions.[29–31] The $^{31}P\{^1H\}$NMR study (Fig. S1, supporting information) shows a singlet at $\delta =$ 9.76 ppm which was shifted upfield with respect to the neutral parent compound $[PdCl_2(PPh_2py–P,N)]$ ($\delta = -9.15$ ppm). The PF_6^- ion resonance for complex **2** was observed at $\delta = -176.57$ ppm with $J_{PF} = 712$ Hz.[37] The ^1H NMR spectrum of complex **2**, in addition to aromatic protons, shows a singlet at $\delta = 8.21$ ppm for $H^{2'}$ of N-BuIm (Scheme 1), which is shifted downfield compared to free ligand. The electrochemical study of complex **2** revealed one irreversible reduction at -1.39 V ($\Delta E_p = 670$ mV), similar to complex **1**, attributed to Pd(II)/Pd(0) redox couple.[38–40] The shift of this reduction to a more negative value compared to complex **1** might be due to higher electron-donating ability of N-BuIm relative to N-MeIm ligand. The oxidation at +1.32 V is assumed to lead to the formation of a Pd(IV).[40] The reduction at -0.95 V with no corresponding oxidation during anodic sweep clearly suggested a PPh_2py-based process.

Synthesis and Characterization of [PdCl(PPh_2Etpy–P,N)(N-MeIm)](PF_6) (4)

The reaction of N-MeIm with $[PdCl_2(PPh_2Etpy–P,N)]$ (**3**) in dichloromethane on stirring at room temperature for 16 h under N_2 atmosphere afforded complex **4** with 83% yield. Similar to complexes **1** and **2**, the elemental analyses and mass spectrum are consistent with the proposed composition. The IR spectrum revealed a slight shift of ν(Pd–N), ν(Pd–P) and ν(Pd–Cl) bands compared to $[PdCl_2(PPh_2Etpy–P,N)]$. A new band in the far-IR region at 272 cm^{-1} could be assigned to ν(Pd–$N_{imidazole}$). The UV–visible spectrum displays intra-ligands $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ and are shifted towards blue compared to precursor complex **3**, indicating a change in the ligand environment. The $^{31}P\{^1H\}$ NMR spectrum showed a singlet at $\delta = 14.38$ ppm, assignable to the ^{31}P nuclei of the PPh_2Etpy. The signal associated with ^{31}P nuclei of the PPh_2Etpy exhibited a significant upfield shift in complex **4** in comparison to the other reported complexes,[42,43] which might be due to an increase in electron density at the metal center on coordination of N-MeIm ligand. Enhanced electron density at the metal center increases the degree of back-donation from metal to PPh_2Etpy ligand. The signal for ^{31}P nuclei of the PF_6^- ion was detected as a septet at $\delta = -160.85$ ppm with $J_{PF} = 712$ Hz.[37] In the ^1H NMR spectrum two singlets at $\delta = 8.42$ and 3.37 ppm with downfield shift are attributed to $H^{2'}$ and N–CH_3 protons. The ^{13}C NMR spectrum shows characteristic resonances for the aromatic, aliphatic as well as imidazole carbon. TGA also supported the assigned formulation. Electrochemical study of complex **4** demonstrates an irreversible reductive event at -1.29 V ($\Delta E_p = 750$ mV), which is shifted to a more negative potential compared to starting compound $[PdCl_2(PPh_2Etpy–P,N)]$ (**3**) ($E_{pc} = -0.78$ V). This feature is consistent with Pd(II)/Pd(0) redox couple.[38–40] A ligand-based reduction was also observed at -0.83 V with no peak reversal.

Synthesis and Characterization of [PdCl(PPh_2Etpy–P,N)(N-BuIm)](PF_6) (5)

Complex **5** was prepared in a manner analogous to **4**, where N-BuIm reacted at 1:1 molar ratio with $[PdCl_2(PPh_2Etpy–P,N)]$ (**3**) to form [PdCl(PPh_2Etpy–P,N)(N-BuIm)](PF_6) (**5**) in good yield (79%). The elemental analyses and mass spectrum are consistent

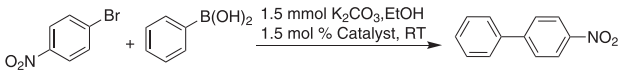
with the assigned formulation. The fragmentation pattern of the complex clearly indicates its mononuclear nature. TGA also supports the above formulation. In the far-IR region, the band at 290 cm^{-1} is attributed to ν(Pd–$N_{imidazole}$). The presence of PF_6^- ion was confirmed by the observation of ν(P–F) and δ(PFP) vibrations at 842 and 557 cm^{-1}, respectively.[37] Similar to the complexes **1**, **2** and **4**, complex **5** also demonstrated intra-ligand $\pi\rightarrow\pi^*$ (268 nm) and $n\rightarrow\pi^*$ (321 nm) transitions in its UV–visible spectrum. Compared to [$PdCl_2$(PPh_2Etpy–P,N)] (**3**) (λ_{max}, $n\rightarrow\pi^*$ = 346 nm), $n\rightarrow\pi^*$ transition was shifted towards blue due to the change of ligand environment about the Pd^{2+} ion. The $^{31}P\{^1H\}$NMR spectrum of **5** (Fig. S2, supporting information) consisted of a singlet at δ = 14.51 ppm and a septet at δ = −160.79 ppm (J_{PF} = 712 Hz), corresponding to the ^{31}P nuclei of the PPh_2Etpy and PF_6^- ion, respectively. The signal associated with ^{31}P nuclei of the PPh_2Etpy ligand also exhibited a significant upfield shift in complex **5** as in **4**, attributable to the increase of electron density at the metal center on coordination of N-Bulm ligand. The resonances for $H^{4'}$ and $H^{5'}$ protons of N-Bulm were detected as a singlet at δ = 7.07 and 6.50 ppm respectively. Moreover, the presence of characteristic peaks for the aromatic, aliphatic as well as imidazole carbon further substantiated formation of complex **5**. The electrochemical behavior of complex **5** showed similar features to the above complexes. An irreversible reductive event at −1.35 V (ΔE_p = 630 mV) could be ascribable to Pd(II)/Pd(0) redox couple.[38–40] The shift of this event to a more negative potential compared to precursor complex [$PdCl_2$(PPh_2Etpy-P,N)] (**3**) (E_{pc} = −0.78 V) and the complex **4** may be attributed to the presence of more electron-donating N-Bulm ligands. Two reductive responses at −0.42 and −0.92 V with no corresponding anodic peak may be assigned to ligand-based reduction. During anodic sweep oxidation at +1.47 V with no cathodic peak is likely to be due to the formation of Pd(IV).[40]

Suzuki–Miyaura Cross-Coupling Reactions using Complexes 1, 2, 4 and 5 as Catalyst

The effectiveness of complexes **1–5** has been studied by carrying out the model reaction of 4-bromonitrobenzene with phenylboronic acid in ethanol using K_2CO_3 under aerobic conditions at room temperature. The results are summarized in Table 1. The newly synthesized palladium complexes are found to be effective in the Suzuki–Miyaura reaction; however, significant variations in yields have been noticed. Application of complex **1** as catalyst in the coupling reaction proceeded with a good yield of desired hetero-coupling product (Table 1, entry 1), accompanied by a trace amount of homodiaryl compound as a byproduct. Formation of homodiaryl as side product in the Suzuki–Miyaura reaction is very common. The use of complex **2** afforded the desired product in improved yield within a shorter reaction time compared to **1** (Table 1, entry 2). However, the use of complexes **4** and **5** significantly reduced the yield of the product even after prolong reaction time (Table 1, entries 3 and 4). However, none of the palladium metal complex was found to be effective when aryl chloride was used as coupling partner. In order to compare the efficiency of the Pd–imidazole complexes (**1**, **2**, **4**, **5**) with complex **3**, the above coupling reaction was carried out under identical experimental conditions. But the use of complex **3** under our reaction conditions gave the desired cross-coupling product only in 40% isolated yield accompanied by a significant amount of homodiaryl compound as a by-product (Table 1, entry 5), which provides an additional advantage of Pd–imidazole complexes reported herein.

From the above study, complex **2** was found to be most effective as catalyst and therefore further studies on the Suzuki–Miyaura coupling reaction have been carried out in the presence of complex **2**. Results obtained from screening of different bases and solvents are incorporated in Table 2. Potassium carbonate has been found to be the most efficient base in ethanol (Table 2, entry 1). Besides K_2CO_3, the reaction can tolerate other inorganic bases such as Na_2CO_3, Cs_2CO_3 and $Na_3PO_4.12H_2O$, and gave almost comparable yields of the cross-coupling product (Table 2, entries 2–5). However, the yield was dramatically decreased with triethylamine (Table 2, entry 6). Moreover, complex **2** was found to show better activity in protic

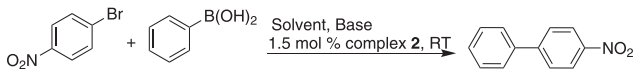
Table 1. Suzuki–Miyaura cross-coupling reactions with various catalysts[a]



Entry	Catalyst (complex)	Time	Yield (%)[b]
1	**1**	22	97
2	**2**	5	99
3	**4**	24	50
4	**5**	22	45
5	**3**	24	40

[a]0.5 mmol 4-bromonitrobenzene and 0.55 mmol arylboronic acid were used.
[b]Isolated yields.

Table 2. Studies on the effects of different bases and solvents



Entry	Solvent	Base	Time (h)	Yield (%)[a]
1	EtOH	K_2CO_3	5	99
2	EtOH	Na_2CO_3	24	90
3	EtOH	$NaHCO_3$	24	50
4	EtOH	$Na_3PO_4.12H_2O$	24	95
5	EtOH	Cs_2CO_3	24	87
6	EtOH	Et_3N	24	30
7	Water	K_2CO_3	24	Trace
8	THF	K_2CO_3	24	30
9	MeCN	K_2CO_3	24	50
10	Hexane	K_2CO_3	24	45
11	DMF	K_2CO_3	24	50
12	i-PrOH	K_2CO_3	24	85
13	i-PrOH:H_2O (1:1)	K_2CO_3	24	85
14	EtOH	—	14	—
15	EtOH	K_2CO_3	4	99
16[b]	EtOH	K_2CO_3	4	85
17[c]	EtOH	K_2CO_3	4	64

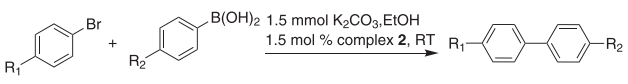
[a]Isolated yield.
[b]1 mol% catalyst was used.
[c]$PdCl_2$ (1.5 mol%) was used as catalyst.

solvents, although significant variations in yield have been noted with aprotic solvents, and both polar and non-polar (Table 2, entries 8–11) gave comparatively lower yields. The lowest yield (30%) was obtained with THF (Table 2, entry 8). The coupling reactions did not proceed in the absence of base (Table 2, entry 14). The amount of catalyst required for efficient activity has also been scrutinized and 1.5 mol% of complex **2** was found to be the optimum amount for the Suzuki–Miyaura cross-coupling reaction. The yield of the product was reduced to 85% when we used 1 mol% of the catalyst (Table 2, entry 16) under the same reaction conditions. In order to demonstrate the better catalytic efficiency of complex **2**, reaction with 1.5 mol% $PdCl_2$ was carried out under the same reaction conditions, and it was found that the yield of cross-coupling product was dramatically reduced to 64%, accompanied by the formation of a significant amount of homodiaryl compound as byproduct (Table 2, entry 17).

To evaluate the scope and limitations of the current procedure, reactions of a wide array of electronically diverse aryl bromides with different arylboronic acids were examined using complex **2** and the results are shown in Table 3. The aryl bromides with electron- withdrawing and donating substituents underwent coupling reactions with phenylboronic acid effectively to afford the desired biaryls in excellent yields (87–99%). The catalytic system is equally effective for electronically diversified arylboronic acids. Thus our present result is quite significant as the desired biaryls could be achieved at room temperature.

As far as the reaction mechanism is concerned, the actual reason for the efficiency of complex **2** is not clear. However, it was reported that dissociation of ligand in the reaction medium produces palladium(0) colloids or nanoparticles and the palladium(0) nanoparticle is the active catalytic species for the Suzuki–Miyaura reaction.[24e] With these aspects in mind, we have also investigated the nature of the catalytic species after completion of the reaction. Transmission electron microscopic images of the catalyst after reaction clearly show the formation of Pd(0) nanoparticles (Figs S1 and S2, see supporting information). We believe that the weaker Pd–imidazole bond dissociates easily in the reaction medium and forms stable palladium(0) nanoparticles which might be stabilized by imidazole. Therefore, the different catalytic activities of the complexes (**1**, **2**, **4** and **5**) might depend on the rate of ligand dissociation to produce the real catalytic species. The steric strain of complexes **1** and **2** might enhance the rate of ligand dissociation and formation of palladium nanoparticles. Moreover, the stabilization effect of the *n*-butyl side chain in complex **2** is comparatively greater than that of *n*-methyl side chain, thereby forming more stable Pd(0) nanoparticles, and hence complex **2** is more efficient for the Suzuki–Miyaura cross-coupling reaction.

Table 3. Suzuki–Miyaura cross-coupling reactions of various aryl bromides with different arylboronic acids



Entry	R^1	R^2	Time (h)	Yield (%)[a]
1	NO_2	H	5	99
2	CHO	H	8	93
3	OCH_3	H	3	88
4	CH_3	H	1	94
5	$COCH_3$	H	4	89
6	H	H	2	91
7	OCH_3	OCH_3	5	97
8	CH_3	OCH_3	3	96
9	H	OCH_3	5	90
10	H	CH_3	4	87

[a]Isolated yield.

Conclusion

In summary, four new cationic phosphinoamine–Pd(II)–imidazole complexes (**1**, **2**, **4** and **5**) have been synthesized and characterized by different physicochemical methods. The catalytic activities of all the complexes have been investigated for Suzuki–Miyaura cross-coupling reactions of aryl halides with aryl boronic acids at room temperature. Among the complexes, complex **2** exhibited highest efficacy, while **4** and **5** were found to have poor activity. A range of electronically diverse aryl bromides underwent the coupling reactions in good to excellent yields at room temperature with complex **2** as catalyst. Use of ethanol as solvent is one of the most important advantages of the present catalytic system.

Supporting Information

Supporting information may be found in the online version of this article.

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References

[1] N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457.
[2] T. E. Barder, S. D. Walker, J. R. Martinelli, S. L. Buchwald, *J. Am. Chem. Soc.* **2005**, *127*, 4685.
[3] A. Suzuki, *J. Organomet. Chem.* **1999**, *576*, 147.
[4] J. Flapper, H. Kooijman, M. Lutz, A. L. Spek, P. W. N. M. van Leeuwen, C. J. Elsevier, P. C. J. Kamer, *Organometallics* **2009**, *28*, 3272.
[5] A. M. Trzeciak, J. J. Ziólkowski, *Coord. Chem. Rev.* **2005**, *249*, 2308.
[6] M. Guo, F. Jian, R. He, *Tetrahedron Lett.* **2006**, *47*, 2033.
[7] K. Saikia, B. Deb, B. J. Borah, P. P. Sarmah, D. K. Dutta, *J. Organomet. Chem.* **2012**, *696*, 4293.
[8] M. Mondal, U. Bora, *Green Chem.* **2012**, *14*, 1873.
[9] F. A. Littke, G. C. Fu, *Angew. Chem. Int. Ed.* **2002**, *41*, 4176.
[10] a) J. Dupont, C. S. Consorti, J. Spencer, *Chem. Rev.* **2005**, *105*, 2527; b) A. V. Gaikwad, A. Holuigue, M. B. Thathagar, J. E. Elshof, G. Rothenberg, *Chem. Eur. J.* **2007**, *13*, 6908; c) J. D. Sellars, P. G. Steel, *Chem. Soc. Rev.* **2011**, *40*, 5170; d) D. V. Partyka, *Chem. Rev.* **2011**, *111*, 1529.
[11] a) A. Suzuki, *Angew. Chem. Int. Ed.* **2011**, *50*, 6722; b) A. Suzuki, Y. Yamamoto, *Chem. Lett.* **2011**, *40*, 894; c) A. Fihri, M. Bouhrara, B. Nekoueishahraki, J.-M. Basset, V. Polshettiwar, *Chem. Soc. Rev.* **2011**, *40*, 5181; d) A. Balanta, C. Godard, C. Claver, *Chem. Soc. Rev.* **2011**, *40*, 4973.

[12] M. Kranenburg, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Eur. J. Inorg. Chem.* **1998**, 155.
[13] R. Martin, S. L. Buchwald, *Acc. Chem. Res.* **2008**, *41*, 1461.
[14] P. Bhattacharyya, J. D. Woollins, *Polyhedron* **1995**, *14*, 3367.
[15] T. Schareina, R. Kepme, *Angew. Chem. Int. Ed.* **2002**, 41,1521.
[16] S. Urgaonkar, M. Nagarajan, J. G. Verkade, *Tetrahedron Lett.* **2002**, *43*, 8921.
[17] C. Sarmah, M. Borah, P. Das, *Appl. Organometal. Chem.* **2011**, *25*, 552.
[18] N. Biricik, F. Durap, C. Kayan, B. Gumgum, N. Gurbuz, I. Ozdemir, W. H. Ang, Z. Fei, R. Scopelliti, *J. Organomet. Chem.* **2008**, *693*, 2693.
[19] G. A. Molander, B. Canturk, *Angew. Chem. Int. Ed.* **2009**, *48*, 9240.
[20] a) M. Borah, P. K. Bhattacharyya, P. Das, *Appl. Organometal. Chem.* **2012**, *26*, 130; (b) B. Milde, D. Schaarschmidt, T. Rüffer, H. Lang, *Dalton Trans.* **2012**, *41*, 5377.
[21] a) A. Kumar, M. Agarwal, A. K. Singh, R. J. Butcher, *Inorg. Chim. Acta* **2009**, *362*, 3208; b) A. Kumar, M. Agarwal, A. K. Singh, *J. Organomet. Chem.* **2008**, *693*, 3533; c) F. Saleem, G. K. Rao, P. Singh, A. K. Singh, *Organometallics* **2013**, *32*, 387; d) H. M. Lee, P. L. Chiu, J. Y. Zeng, *Inorg. Chim. Acta* **2004**, *357*, 4313; e) G. Roymahapatra, S. Giri, A. A. Danopoulos, P. K. Chattaraj, A. Mahapatra, V. Bertolasi, J. Dinda, *Inorg. Chim. Acta* **2012**, *383*, 83; f) D.-H. Lee, J.-H. Kim, B.-H. Jun, H. Kang, J. Park, Y.-S. Lee, *Org. Lett.*, **2008**, *8*, 1609; g) P. Das, U. Bora, A. Tairai, C. Sharma, *Tetrahedron Lett.* **2010**, *51*, 1479.
[22] a) M.-H. Hsu, C.-M. Hsu, J.-C. Wang, C. H. Sun, *Tetrahedron* **2008**, *64*, 4268; b) J.-H. Li, W.-J. Liu, *Org. Lett.* **2004**, *6*, 2809; c) J.-H. Li, W.-J. Liu, Y.-X. J. Xie, *Org. Chem.* **2005**, *70*, 5409.
[23] K. Alfonsi, J. Colberg, P. J. Dunn, T. Fevig, S. Jennings, T. A. Johnson, H. P. Kleine, C. Knight, M. A. Nagy, D. A. Perry, M. Stefaniak, *Green Chem.* **2008**, *10*, 31.
[24] a) C. J. Mathews, P. J. Smith, T. Welton, *J. Mol. Catal. A: Chem.* **2004**, *214*, 27; b) C. J. Mathews, P. J. Smith, T. Welton, *J. Mol. Catal. A: Chem.* **2003**, *206*, 77; c) C. Zhang, J. Huang, M. L. Trudell, S. P. Nolan, *J. Org. Chem.* **1999**, *64*, 3804; d) G. A. Grasa, M. S. Viciu, J. Huang, C. Zhang, M. L. Trudell, S. P. Nolan, *Organometallics* **2002**, *21*, 2866; e) M. Trivedi, G. Singh, R. Nagarajan, N. P. Rath, *Inorg. Chim. Acta* **2013**, *394*, 107.
[25] a) C.-M. Weng, F.-E Hong, *Dalton Trans.* **2011**, *40*, 6458; b) M.-A. Gunawan, C. Qiao, I. Abrunhosa-Thomas, B. Puget, J.-P. Roblin, D. Prim, Y. Troin, *Tetrahedron Lett.* **2010**, *51*, 5392; c) D.-H. Lee, M.-J. Jin, *Org. Lett.* **2011**, *13*, 252; d) A. Mukherjee, A. Sarkar, *Tetrahedron Lett.* **2004**, *45*, 9525; e) D. N. Korolev, N. A. Bumagin, *Tetrahedron Lett.* **2005**, *46*, 5751; f) C. M. So, C. P. Lau, F. Y. Kwong, *Org. Lett.* **2007**, *9*, 2795.
[26] D. Drew, J. R. Doyle, *Inorg. Synth.* **1972**, *XIII*, 47.
[27] C. G. Arena, E. Rotondo, F. Faraone, *Organometallics* **1991**, *10*, 3877.
[28] V. E. Uhlig, S. Keiser, *Z. anorg. allg. Chemie* **1974**, *406*, 1.
[29] N. M. F. Carvalho, A. Horn Jr., A. J. Bortoluzzi, V. Drago, O. A. C. Antunes, *Inorg. Chim. Acta* **2006**, *359*, 90.
[30] P. Das, P. P. Sarmah, M. Borah, A. K. Phukan, *Inorg. Chim. Acta* **2009**, *362*, 5001.
[31] K. Wajda-Hermanowicz, Z. Ciunik, A. Kochel, *Inorg. Chem.* **2006**, *45*, 3369.
[32] Y. Xie, C.-L. Lee, Y. Yang, S. J. Rettig, B. R. James, *Can. J. Chem.* **1992**, *70*, 751.
[33] D. Sutton, Electronic Spectra of Transition Metal Complexes, McGraw-Hill, London, **1968**.
[34] P. E. Garrou, *Chem. Rev.* **1981**, *81*, 229.
[35] S. Hietkamp, D. J. Stufkens, K. Vrieze, *J. Organomet. Chem.* **1979**, *169*, 107.
[36] P. Govindaswamy, P. J. Carroll, Y. A. Mozharivskyj, M. R. Kollipara, *J. Chem. Sci.* **2006**, *118*, 319.
[37] V. Díez, G. Espino, F. A. Jalón, B. R. Manzano, M. Pérez-Manrique, *J. Organomet. Chem.* **2007**, *692*, 1482.
[38] M. Keleş, O. Altan, O. Serindağ, *Heteroatom Chem.* **2008**, *19*, 113.
[39] K. Ding, D. L. Miller, V. G. Young Jr., C. C. Lu, *Inorg. Chem.* **2011**, *50*, 2545.
[40] A. J. Downard, A. M. Bond, A. J. Clayton, L. R. Hanton, D. A. McMorran, *Inorg. Chem.* **1996**, *35*, 7684.
[41] J. G. Gilbert, A. W. Addison, R. J. Butcher, *Inorg. Chim. Acta* **2000**, *308*, 22.
[42] H.-H. Wang, A. L. Casalnuovo, B. J. Johnson, A. M. Mueting, L. H. Pignolet, *Inorg. Chem.* **1988**, *27*, 325.
[43] P. Kumar, M. Yadav, A. K. Singh, D. S. Pandey, *Eur. J. Inorg. Chem.* **2010**, 704.