Synthesis, characterization and electrochemistry of [Pd(PP)MeCl] compounds with 1,1′-bis(phosphino)ferrocene ligands

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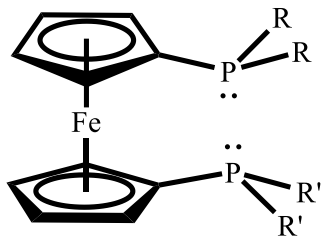
ABSTRACT

Three new [Pd(κ^2-PP)MeCl] (PP = 1,1'-bis(dicylohexylphosphino)ferrocene (dcpf), 1-diphenylphosphino-1'-ditert-butylphosphinoferrocene (dppdtbpf) or 1,1′-bis(5-methyl-2-furanylphosphino)ferrocene (dfurpf)) compounds were prepared and characterized. The X-ray crystal structure of [Pd(dppdtbpf)MeCl] was obtained which allowed for unambiguous determination of the *cis*/*trans*- relationship between the methyl and chloride ligands with respect to the different phosphine groups. The oxidative electrochemistry of the three new compounds as well as that of the reported [Pd(κ^2-PP)MeCl] (PP = 1,1'-bis(diphenylphosphino)ferrocene (dppf), or 1,1'-bis(diiso-propylphosphino)ferrocene (dippf)) and [Pd(κ^3-dtbpf)Me]Cl (dtbpf = 1,1'-bis(ditert-butylphosphino)ferrocene) was examined. The compounds with the κ^2-bis(phosphino)ferrocene ligands react with sodium tetrakis(3,5-bis(trifluoromethyl)phenylborate)

to lose a chloride ligand and the catalytic activity of these compounds was investigated for the polymerization of phenylacetylene.

1. Introduction

Bidentate phosphines with ferrocenyl backbones are a popular class of ligands used in a variety of catalytic systems [1–5]. The most well-studied of these ligands is 1,1′-bis(diphenylphosphino)ferrocene (dppf) [6,7]. Considering dppf as the basis, there are numerous ways to modify these ligands such as changing the metal center [8–10] or changing the pnictogen donor [9]. However, the most common modification to these ligands is changing the phosphine substituents (Fig. 1) which has been shown to affect the steric and electronic properties of the



R	R′	Ligand	[Pd(PP)Cl$_2$] Structure
Ph	Ph	dppf	[11]
^{i}Pr	^{i}Pr	dippf	[12]
Cy	Cy	dcpf	[13]
^{t}Bu	^{t}Bu	dtbpf	[14]
Ph	^{t}Bu	dppdtbpf	[15]
5-methyl-2-furanyl	5-methyl-2-furanyl	dfurpf	[16]
Me	Me	dmpf	[17]
Et	Et	depf	[18]

Fig. 1. 1,1′-bis(phosphino)ferrocene ligands.

ligands. Altering the steric and electronic properties of the ligands not only impacts the reactivity of the compounds, it can also impact the way in which the ligand coordinates to a metal center. The structures of all of the [Pd(PP)Cl$_2$] compounds for the ligands in Fig. 1 have been reported and the bis(phosphino)ferrocene ligands adopt the κ^2-coordination mode (Fig. 2). The reaction of [Pd(PP)Cl$_2$] (PP = dppf, dippf, dcpf, or dppdtbpf) with Na[BArF$_{24}$] (BArF$_{24}$ = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) yields a dimeric dication [Pd$_2$(PP)$_2$(μ-Cl)$_2$][BArF$_{24}$]$_2$ in which the bis(phosphino)ferrocene ligand maintains κ^2-coordination [19]. However, when [Pd(dtbpf)Cl$_2$] reacted with Na[BArF$_{24}$] the product was instead the monomeric cation

[Pd(dtbpf)Cl][$BArF_{24}$] in which the dtbpf ligand adopts the κ^3-coordination mode [19]. While many studies have examined the catalytic activity of [Pd(dppf)Cl_2] and related compounds [20,21,30,22–29], there have been relatively few reports on the closely related asymmetric [Pd(PP)MeCl] compounds.

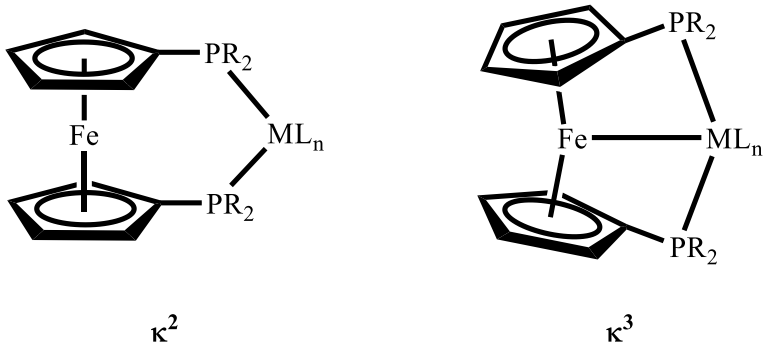


Fig. 2. Coordination modes of bis(phosphino)ferrocene ligands.

The syntheses of four [Pd(PP)MeCl] (PP = dppf [31–33], dippf [34,35], dmpf [17] or depf [35]) compounds have been reported. In these compounds the bis(phosphino)ferrocene ligand adopts the κ^2-coordination mode. The [Pd(depf)MeCl] compound is somewhat unique in that it initially formed [$Pd_2(\mu\text{-depf})_2Me_2Cl_2$] which over the course of three days dissociated to form [Pd(depf)MeCl] [35]. A related compound with dtbpf was also reported, however the compound that formed was not [Pd(dtbpf)MeCl] but rather [Pd(dtbpf)Me]Cl in which the dtbpf adopts the κ^3-coordination mode [35]. Of these compounds, only the structures of [Pd(dippf)MeCl] [34] and [Pd(dtbpf)Me][CF_3SO_3] [35] have been reported.

Reactivity studies of several of these compounds have also been performed. The most common type of reaction for these compounds is insertion into the Pd-Me bond. It was found that in the presence of CO, [Pd(PP)MeCl] (PP = dppe, dppp, dppb or dppf) compounds undergo a CO insertion into the Pd-Me bond [36]. The insertion reactions for the dppf, dppp and dppb compounds were faster than for the dppe analogue. In order to speed up the reaction rates of the

carbonyl insertion, $Ag[CF_3SO_3]$ was added to remove the chloride; this increased the CO insertion rate at least an order of magnitude with respect to the rate without the $Ag[CF_3SO_3]$. The dppb, dppp, and dppf compounds all exhibited similar reaction rates while the dppe compound still had a slightly slower reaction rate. Several other studies examined CO insertion reactions of these compounds in the presence of a halide abstracting agent. In the presence of CO, the use of either $Ag[CF_3SO_3]$ for [Pd(PP)MeCl] (PP = dppf or dippf) [33] or $Na[BArF_{24}]$ for [Pd(PP)MeCl] (PP = dmpf, depf or dippf) [17] was found to promote insertion into the Pd-Me bond. The k^3 compound $[Pd(dtbpf)Me][CF_3SO_3]$ was found to slowly insert CO into the Pd-CH_3 bond without the addition of a halide abstracting agent [33,37]. The insertion of xylylisocyanide into the Pd-Me bond in [Pd(PP)MeCl] (PP = dppf or dppp) was also reported [38]. Interestingly, the reaction of [Pd(PP)MeCl] (PP = dppf, dppe, dppp) with *tert*-butylisocyanide in the presence of $[Bu_3NH]_2[SnB_{11}H_{11}]$ gave an isocyanide insertion followed by coordination of the $SnB_{11}H_{11}$ to the palladium [39]. The final insertion reaction studied was of SO_2 into the Pd-Me bond which was observed with the [Pd(PP)MeCl] (PP = dppe, dppf or dippf) compounds [34].

Several stoichiometric reactions with [Pd(dppf)MeCl] have also been reported. A variety of ring-opening reactions including the ring opening of two different oxygen-bridged bicyclic compounds was accomplished using [Pd(dppf)MeCl] in the presence of either $Zn(CF_3SO_3)_2$, $Na[BArF_{24}]$, or $ZnEt_2$ [40]. Activation of [Pd(dppf)MeCl] with $Ag[BF_4]$ followed by addition of RN=CHPh (R = Ph or CH_2Ph) yielded the corresponding $[Pd(dppf)Me(imine)][BF_4]$ compounds [41]. The reaction of [Pd(dppf)MeCl] with NaS^tBu yielded $[Pd(dppf)MeS^tBu]$ which then underwent reductive elimination [42]. The reaction of [Pd(dppf)MeCl] with silica was determined to yield methane and coordinate [Pd(dppf)Cl] to the surface, but this process was less efficient for dppf than for other similar compounds that were examined [43]. Finally, the addition

of two equivalents of potassium phthalimide to [Pd(dppf)MeCl] removed the chloride and coordinate a phthalimide [44].

Limited catalytic studies of these [Pd(PP)MeCl] compounds have been reported. Several [Pd(PP)MeCl] (PP = dppp, dppb, 1,2-bis(diphenylphosphino)benzene, dppf or XantPhos) compounds were tested as catalysts for the acetylation of the peptide H_2N-LULUPhol to give an *N*-acetylated peptide and the dppf catalyst was among the best [45]. Several [Pd(PP)Me][CF_3SO_3] (PP = dtbpf, SPANphos or XantPhos) compounds were examined as catalysts for the copolymerization of CO and ethene but none of these compounds yielded the desired copolymer [37]. Finally, [Pd(PP)MeCl] (PP = dppe, dppf or dippf) compounds in the presence of Ag[CF_3SO_3] were examined as catalysts for the polymerization of phenylacetylene. Of the bidentate ligands tested, the dppf compound generated the highest reaction yield and highest average molecular weight of the polymer followed by the dippf and dppe catalysts [46].

To further examine the chemistry of [Pd(PP)MeCl] compounds with bis(phosphino)ferrocene ligands, three new compounds, PP = dcpf, dppdtbpf and dfurpf, were prepared and characterized. The X-ray crystal structure of [Pd(dppdtbpf)MeCl] was determined to determine the *cis/trans*- relationship of the methyl and chloride ligands with respect to the -PPh_2 and -P^tBu_2 groups. The oxidative electrochemistry of the [Pd(PP)MeCl] (PP = dppf, dippf, dcpf, dppdtbpf or dfurpf) compounds as well as that of the κ^3-compound [Pd(dtbpf)Me]Cl was examined. Finally, a preliminary investigation of the catalytic activity of these compounds for the polymerization of phenylacetylene was performed.

2. Experimental

2.1. General procedures

Standard Schlenk techniques under argon were employed for all reactions. Reagents were used as received unless otherwise noted. Manipulations of [Pd(COD)MeCl] were performed in an argon-filled glovebox. The [Pd(COD)MeCl], 1,1′-bis(diphenylphosphino)ferrocene ligands and ferrocene (FcH) were purchased from Strem. The FcH was sublimed prior to use. Methylene chloride, diethyl ether, di*iso*-propyl ether, acetonitrile, benzene, methanol and chloroform-*d* were purchased from Fisher. The methylene chloride, acetonitrile and diethyl ether were purified using a Solv-Tek solvent purification system [47]. Tetrabutylammonium hexafluorophosphate ($[NBu_4][PF_6]$), phenylacetylene and 1,2-dichloroethane were purchased from Aldrich. The $[NBu_4][PF_6]$ was dried at 100 °C *in vacuo* prior to use. Sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate ($Na[BArF_{24}]$) [48], [Pd(dppf)MeCl] [36], [Pd(dippf)MeCl] [33], [Pd(dtbpf)Me]Cl [33] and [Pd(dfurpf)Cl_2] [16] were prepared according to the literature procedures.

NMR spectra were obtained in $CDCl_3$ using an Avance III HD 400 FT-NMR. The ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to internal TMS while the $^{31}P\{^1H\}$ NMR spectra were referenced using external 85% H_3PO_4. Midwest Microlab performed the elemental analyses. Gel permeation chromatography (GPC) was performed using a Shimadzu LC 20-AT calibrated with PMMA standards equipped with an Agilent PolarGel-L column (eluent: acetonitrile). Flow rate was set to 1 mL/min and the samples were created by dissolving 0.01 g of sample in 1 mL of acetonitrile and allowed to dissolve into solution for 24 hours, then passed through a syringe filter before injection into the instrument.

2.2. Specific procedures

2.2.1. [Pd(dppdtbpf)MeCl]

The [Pd(COD)MeCl] (0.0627 g; 0.236 mmol) was added to a flask equipped with a stir bar. In a separate flask, dppdtbpf (0.121 g; 0.235 mmol) was dissolved in benzene (5 mL). The dppdtbpf solution was transferred via cannula to the flask containing the [Pd(COD)MeCl] and the reaction mixture was stirred for 1 h. The reaction mixture was then placed in a freezer overnight leading to the formation of a yellow precipitate. The solution was filtered via cannula and the resulting yellow-orange solid was washed with benzene (1 x 3 mL) and diethyl ether (2 x 3 mL) and then dried under vacuum. Collection of the yellow-orange solid gave the desired product (0.137 g; 87% yield). Crystals of this compound were grown by slow vapor diffusion of di*iso*-propyl ether into a solution of the compound in 1,2-dichloroethane. The crystals were removed from the mother liquor and placed in NVH immersion oil for shipping. ^{1}H NMR: δ (ppm) 7.83 (m, 4H, -Ph), 7.43 (m, 6H, -Ph), 4.59 (AA′BB′, 2H, H$_{\alpha}$), 4.36 (AA′BB′, 2H, H$_{\beta}$), 4.20 (AA′BB′, 2H, H$_{\alpha}$), 3.85 (AA′BB′, 2H, H$_{\beta}$), 1.53 (d, $^{3}J_{\text{H-P}}$ = 12.6 Hz, 18H, -^{t}Bu), 0.70 (dd, $^{3}J_{\text{H-P}}$ = 6.6, 4.7 Hz, 3H, -Me). ^{31}P{^{1}H} NMR: δ(ppm) 45.2 (d, $^{2}J_{\text{P-P}}$ = 27.0 Hz), 39.3 (d, $^{2}J_{\text{P-P}}$ = 27.0 Hz). ^{13}C{^{1}H} NMR: δ(ppm) 134.6 (d, $^{2}J_{\text{P-C}}$ = 13.0 Hz, DEPT +), 133.8 (d, $^{1}J_{\text{P-C}}$ = 52.6 Hz, DEPT no signal), 130.4 (d, $^{4}J_{\text{P-C}}$ = 2.5 Hz, DEPT +), 128.2 (d, $^{3}J_{\text{P-C}}$ = 11.0 Hz, DEPT +), 82.0 (dd, J = 45.6, 7.6 Hz, DEPT no signal, C$_{\text{ipso}}$), 81.6 (dd, J = 16.2, 3.8 Hz DEPT no signal, C$_{\text{ipso}}$), 76.4 (d, $^{3}J_{\text{P-C}}$ = 8.5 Hz, DEPT +, C$_{\beta}$), 73.8 (d, $^{2}J_{\text{P-C}}$ = 7.1 Hz, DEPT +, C$_{\alpha}$), 71.3 (d, $^{2}J_{\text{P-C}}$ = 4.2 Hz, DEPT +, C$_{\beta}$), 70.6 (d, $^{3}J_{\text{P-C}}$ = 5.8 Hz, DEPT +, C$_{\alpha}$), 36.9 (d, $^{1}J_{\text{P-C}}$ = 7.3 Hz, DEPT no signal, -*C*(CH$_3$)$_3$), 31.4 (d, $^{2}J_{\text{P-C}}$ = 5.4 Hz, DEPT +, -C(*C*H$_3$)$_3$), 19.8 (dd, $^{2}J_{\text{P-C}}$ = 91.0, 2.5 Hz, DEPT +, -*C*H$_3$). *Anal.* Calc. for $C_{31}H_{39}ClFeP_2Pd$: C, 55.46; H, 5.86. Found: C, 55.24; H, 5.77.

2.2.2. [Pd(dcpf)MeCl]

Using [Pd(COD)MeCl] (0.162g; 0.611 mmol) and dcpf (0.353 g; 0.610 mmol), this compound was prepared using a method analogous to that of [Pd(dppdtbpf)MeCl]. The product

was obtained as a yellow-orange solid (0.324g; 72% yield). ^{1}H NMR: δ(ppm) 4.38 (AA′BB′, 2H, Hα), 4.36 (AA′BB′, 2H, Hα), 4.33 (AA′BB′, 2H, Hβ), 4.30 (AA′BB′, 2H, Hβ), 2.43 (m, 2H, -Cy), 2.15 (m, 2H, Cy), 1.80 (m, 22H, Cy), 1.26 (m, 18H, -Cy), 0.86 (dd, $^{3}J_{H\text{-}P}$ = 7.1, 3.4 Hz, 3H, -Me). ^{31}P{^{1}H} NMR: δ(ppm) 40.4 (d, $^{2}J_{P\text{-}P}$ = 19.4 Hz), 20.9 (d, $^{2}J_{P\text{-}P}$ = 19.4 Hz). ^{13}C{^{1}H} NMR: δ(ppm) 82.5 (d, $^{1}J_{P\text{-}C}$ = 13.6 Hz, DEPT no signal, C$_{ipso}$), 82.1 (d, $^{1}J_{P\text{-}C}$ = 13.6 Hz, DEPT no signal, C$_{ipso}$), 73.4 (d, $^{2}J_{P\text{-}C}$ = 7.3 Hz, DEPT -, Cα), 73.0 (d, $^{2}J_{P\text{-}C}$ = 6.2 Hz, DEPT -, Cα), 70.9 (d, $^{3}J_{P\text{-}C}$ = 3.7 Hz, DEPT -, Cβ), 70.4 (d, $^{3}J_{P\text{-}C}$ = 5.5 Hz, DEPT -, Cβ), 35.5 (d, $^{1}J_{P\text{-}C}$ = 64.8, DEPT -, -Cy) 35.3 (d, $^{1}J_{P\text{-}C}$ = 50.9 Hz, DEPT -, -Cy), 27.7 (d, $^{2}J_{P\text{-}C}$ = 24.2 Hz, DEPT +, -Cy), 27.6 (d, $^{2}J_{P\text{-}C}$ = 24.4 Hz, DEPT +, -Cy), 27.1 (d, $^{3}J_{P\text{-}C}$ = 15.8 Hz, DEPT +, -Cy), 27.0 (d, $^{3}J_{P\text{-}C}$ = 17.6 Hz, DEPT +, -Cy), 26.2 (s, DEPT +, -Cy), 26.1 (s, DEPT +, -Cy), 7.6 (dd, $^{2}J_{P\text{-}C}$ = 98.3, 6.2 Hz, DEPT -, -Me). *Anal.* Calc. for $C_{35}H_{55}ClFeP_2Pd$: C, 57.16; H, 7.54. Found: C, 57.29; H, 7.62.

2.2.3. [Pd(dfurpf)MeCl]

A similar procedure to that use for the synthesis of [Pd(dppdtbpf)MeCl] was employed using [Pd(COD)MeCl] (0.0976 g; 0.368 mmol) and dfurpf (0.209 g; 0.366 mmol). This gave the desired product as a yellow solid (0.223 g; 84% yield). ^{1}H NMR: δ(ppm) 7.16 (br s, 2H, -furanyl), 6.78 (t, $^{3}J_{H\text{-}H}$ = 2.9 Hz, -furanyl), 5.97 (br s, 4H, -furanyl), 4.39 (AA′BB′, 2H, Hα), 4.24 (AA′BB′, 2H, Hα), 4.16 (AA′BB′, 2H, Hβ), 4.00 (AA′BB′, 2H, Hβ), 2.25 (s, 6H, furanyl-CH_3), 2.22 (s, 6H, furanyl-CH_3), 0.97 (dd, $^{3}J_{H\text{-}P}$ = 8.3, 5.0 Hz, 3H, Pd-CH_3). ^{31}P{^{1}H} NMR: δ(ppm) -3.2 (d, $^{2}J_{P\text{-}P}$ = 36.4 Hz), -26.1 (d, $^{2}J_{P\text{-}P}$ = 36.4 Hz). ^{13}C{^{1}H} NMR: δ(ppm) 158.3 (d, $^{3}J_{P\text{-}C}$ = 5.0 Hz, DEPT no signal, furanyl), 157.7 (d, $^{3}J_{P\text{-}C}$ = 3.3 Hz, DEPT no signal, furanyl), 144.1 (d, $^{1}J_{P\text{-}C}$ = 79.2 Hz, DEPT +, furanyl), 143.3 (d, $^{1}J_{P\text{-}C}$ = 79.2 Hz, DEPT +, furanyl), 125.4 (d, $^{2}J_{P\text{-}C}$ = 22.8 Hz, DEPT +, furanyl), 124.6 (d, $^{2}J_{P\text{-}C}$ = 21.1 Hz, DEPT +, furanyl), 107.5 (d, $^{3}J_{P\text{-}C}$ = 7.9, DEPT +, furanyl) 107.3 (d, $^{3}J_{P\text{-}C}$ = 8.3 Hz, DEPT +, furanyl), 75.7 (d, $^{1}J_{P\text{-}C}$ = 59.2 Hz, DEPT no signal),

75.6 (d, $^{1}J_{P\text{-}C}$ = 58.4 Hz, DEPT no signal), 75.1 (d, $^{2}J_{P\text{-}C}$ = 13.2 Hz, DEPT +), 74.1 (d, $^{2}J_{P\text{-}C}$ = 10.8 Hz, DEPT +), 72.4 (d, $^{3}J_{P\text{-}C}$ = 8.3 Hz, DEPT +), 72.2 (d, $^{3}J_{P\text{-}C}$ = 5.8 Hz, DEPT +), 14.6 (d, $^{2}J_{P\text{-}C}$ = 100.7 Hz, DEPT +, Pd-Me), 14.1 (s, DEPT +, furanyl-*C*H_3), 14.0 (s, DEPT +, furanyl-*C*H_3). *Anal.* Calc. for $C_{31}H_{31}ClFeO_4P_2Pd$: C, 51.20; H, 4.30. Found: C, 51.36; H, 4.62.

2.2.4. Polymerization reactions

The Na[$BArF_{24}$] (~0.04 g; ~0.05 mmol) was added to a flask with a stir bar. To this was added 2.7 mL of a 3:1 (v:v) mixture of methylene chloride-acetonitrile. The mixture was stirred for ~5 min. In a separate flask, and equal molar amount of the desired palladium pre-catalyst was dissolved in 5.7 mL of the methylene chloride-acetonitrile mixture. This solution was stirred for ~ 5 min. and then the Na[$BArF_{24}$] solution was added via cannula. The flask containing the Na[$BArF_{24}$] was rinsed with an additional 3 mL of the methylene chloride-acetonitrile mixture. The yellow reaction mixture was stirred for ~ 5 min. and then filtered through a short celite pad. Phenylacetylene (~ 1.8 mmol) was added to the resulting solution and the reaction was heated to 30 °C for 24 h. During the course of the reaction, the solution turned dark red in color. The reaction mixture was cooled to room temperature and the volatiles were removed under vacuum. Methylene chloride (1 mL) was added to the residue which was stirred for ~5 min. Methanol (10 mL) was then added and the mixture was stirred for ~ 5 min. The polyphenylacetylene precipitate was collected by filtration, washed with methanol (3 x 5 mL) and dried *in vacuo*. ^{1}H NMR: δ(ppm) 6.95 (m, 8H), 6.64 (m, 5H), 5.85 (s, 2H). $^{13}C\{^{1}H\}$ NMR: δ(ppm) 142.8 (s), 139.3 (s), 131.8 (s), 127.8 (s), 127.5 (s), 126.7 (s).

2.3. Electrochemical procedures

A CH Instruments Model CHI260D potentiostat was used for all electrochemical experiments. Experiments were performed at room temperature (22 $\pm$ 1 °C) under an argon

atmosphere. Data was collected at scan rates ranging from 100 to 1000 mV/s at 100 mV/s intervals. A glassy carbon working electrode (1.0 mm) was employed for all experiments. This electrode was polished with 1.0 μm and 0.25 μm diamond paste and rinsed with methylene chloride prior to use. The counter electrode was a platinum wire and a non-aqueous Ag/AgCl electrode separated from the solution by a glass frit served as the reference electrode. Experiments were performed in methylene chloride (10 mL) with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. Analyte concentrations were 1.0 mM. At the end of each experiment, FcH was added as an internal standard giving a solution that was 0.1 mM in FcH. All reported data was background subtracted.

2.4. X-ray crystallography

A red-orange block-like crystal of [Pd(dppdtbpf)MeCl] having dimensions 0.197 x 0.279 x 0.509 mm^3 was secured to a Mitegen micromount using silicone vacuum grease. Its single crystal reflection data was collected at 293 K using a Rigaku Oxford Diffraction XtaLABminiII X-ray diffractometer equipped with a HyPix-Bantam hybrid photon counting detector and Mo $K_{\alpha 1}$ radiation (λ = 0.71073 Å). Data collection strategies to ensure completeness and desired redundancy were determined using CrysAlis^{Pro} [49]. Data processing for all samples was done using CrysAlis^{Pro} and multi-scan absorption corrections were applied using the SCALE3 ABSPACK scaling algorithm [50]. The structure was solved via intrinsic phasing methods using ShelXT [51] and refined with ShelXL [52] within the Olex2 graphical user interface [53]. Space groups were unambiguously verified by PLATON [54]. The final structural refinement included anisotropic temperature factors on all constituent non-hydrogen atoms. Hydrogen atoms were attached via the riding model at calculated positions using suitable HFIX commands.

3. Results and discussion

The compounds [Pd(dppdtbpf)MeCl], [Pd(dcpf)MeCl] and [Pd(dfurpf)MeCl] were synthesized using a method similar to that used for the previously reported [Pd(dppf)MeCl] [36] and [Pd(dippf)MeCl] [33]. For [Pd(dcpf)MeCl] and [Pd(dfurpf)MeCl], two doublets were observed in the $^{31}P\{^{1}H\}$ NMR spectrum. This suggests that, like the dppf and dippf analogs, the dcpf and dfurpf ligands are coordinated through the two phosphorus atoms in a κ^2-mode and the chloride remains bound to the palladium. This differs from [Pd(dtbpf)Me]Cl in which the dtbpf ligand exhibits a κ^3-mode in which both phosphorus atoms are coordinated to the palladium and there was proposed to be an interaction between the iron and palladium [33,35]. In this case, the chloride is not coordinated to the palladium and both phosphorous atoms in [Pd(dtbpf)Me]Cl are equivalent. The asymmetry of the dppdtbpf ligand does not allow for the definitive assignment of the structure based solely on ^{31}P NMR data, as two doublets would be expected in the $^{31}P\{^{1}H\}$ NMR spectrum for either the κ^2- or κ^3- compounds. In addition, a dimeric form of the compound similar to that observed for 1,1′-bis(diethylphosphino)ferrocene could also result in two doublets depending on the distribution of the phosphine groups [35]. The relatively narrow range of the signals for the protons on the C_5- rings suggests that the dppdtbpf ligand is not in a κ^3-mode [33]. The presence of a NOE signal in the ^{1}H NOESY spectrum suggests that the compound is κ^2- and the -PPh_2 group is *cis*- to the methyl ligand.

Initially, crystals of [Pd(dppdtbpf)MeCl] were grown over a period of two weeks by vapor diffusion of diethyl ether into a solution of the compound in methylene chloride. The crystals were shipped in the mother liquor during which time the compound reacted with the solvent resulting in the formation of a small amount of [Pd(dppdtbpf)Cl_2]. The structure was best modeled with disordered occupancy of [Pd(dppdtbpf)Cl_2] (9%) and [Pd(dppdtbpf)MeCl] (91%). Prior to shipping there was no evidence of [Pd(dppdtbpf)Cl_2] in the $^{31}P\{^{1}H\}$ NMR spectrum of a

sample of the crystals. A second sample was prepared over the course of five days and the crystals were transferred to NVH immersion oil for shipment. While there was residual electron density near the methyl group, incorporation of a partially occupied chloride site at that position did not improve the model. The ellipsoid for the chloride in the molecule is elongated indicating possible disorder, however, modeling it as a 2-component disorder did not improve the model. Attempts at growing X-ray quality crystals by vapor diffusion of di-*iso*propylether into a solution of the compound in benzene were unsuccessful.

The X-ray crystal structure of [Pd(dppdtbpf)MeCl] confirmed that the methyl group on the palladium is *cis*- to the -PPh_2 group (Fig. 3). Select bond lengths, angles and other metrics are reported (Table 1). The palladium is slightly distorted from square planar. The bite angle (P(1)-Pd-P(2)) of 102.57(3) of the dppdtbpf ligand is similar to the bite angle reported in [Pd(dppdtbpf)Cl_2] (101.97 [55] and 101.37 [56]).

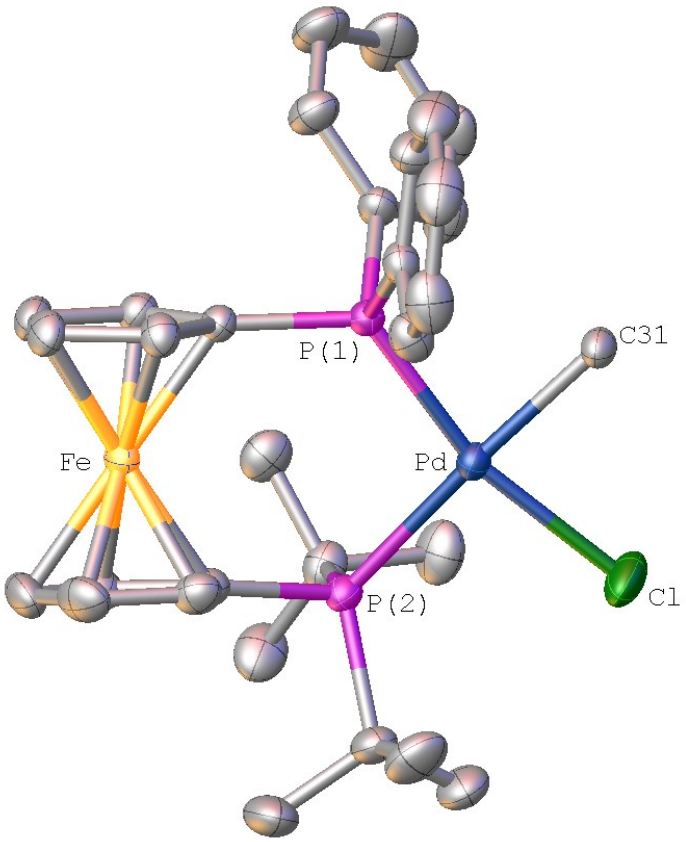


Fig 3. Structure of [Pd(dppdtbpf)MeCl]. Thermal ellipsoids are drawn at the 50% probability level and H atoms are removed for clarity.

Table 1
Select bond lengths (Å), angles (°), and structural parameters for [Pd(PP)MeCl] compounds.

	[Pd(dppdtbpf)MeCl]	[Pd(dippf)MeCl][a]	[Pd(PP)MeCl][b,c]
P(1)-Pd	2.2508(7)	2.3338(7)	2.2604
P(2)-Pd	2.4202(6)	2.3338(7)	2.4382
Pd-Cl	2.3775(7)	2.340(3)	2.3754
Pd-C	2.134(10)	2.051(12)	2.084
Fe-Pd	4.3567(7)	4.3211(7)	4.3001
P(1)-Pd-P(2)	102.57(3)	104.74(3)	97.92
C(31)-Pd-Cl	82.9(3)	82.7(4)	86.10
X_A-Fe-X_B[d]	177.38(1)	179.71(10)	177.33
θ[e]	4.2(4)	2.3(2)	3.4

τ^{f}	-24.2(6)	38.3(3)	30.4
$\tau_4{}^{g}$	0.16	0.17	0.08
$\tau'_4{}^{h}$	0.13	0.17	0.08
Twist angle[i]	5.1(4)	9.0(6)	1.8
$\%V_{bur}$	57.4	54.9	59.4

[a] Ref. [57].
[b] Ref. [58]. Values are averages of two crystallographically independent molecules.
[c] PP = [($C_5H_4PPh_2$)Fe(1,2-C_5H_3(CHMeNMe_2)PPh_2)].
[d] The angle formed between the centroid of each C_5 ring and the Fe center.
[e] The dihedral angle between the two C_5 rings.
[f] The torsion angle formed between C_A-X_A-X_B-C_B with C being the carbon atom bonded to the phosphorus and C being the centroid of the C_5 ring.
[g] Four-coordinate geometry index where $\tau_4 = 0.00$ is square planar and $\tau_4 = 1.00$ is tetrahedral [59].
[h] Modified four-coordinate geometry index where $\tau'_4 = 0.00$ is square planar and $\tau'_4 = 1.00$ is tetrahedral [60].
[i] The angle between the P-Pd-P plane and the Cl-Pd-C(31) plane.

In comparing the structure of [Pd(dppdtbpf)MeCl] to the structures of the closely related [Pd(dippf)MeCl] [57] and [Pd(($C_5H_4PPh_2$)Fe(1,2-C_5H_3(CHMeNMe_2)PPh_2))MeCl] [58] the metrics are fairly similar. The Fe-Pd distances are over 4 Å suggesting that there is no interaction between the metal centers. In both [Pd(dppdtbpf)MeCl] and [Pd(($C_5H_4PPh_2$)Fe(1,2-C_5H_3(CHMeNMe_2)PPh_2))MeCl] the longer P-Pd bond is *trans*- to the methyl group which has a greater *trans*- effect than the chloride. The methyl group of [Pd(($C_5H_4PPh_2$)Fe(1,2-C_5H_3(CHMeNMe_2)PPh_2))MeCl] is *cis*- to the more sterically encumbered C_5 ring, however, the -CHMeNMe_2 group is likely far enough removed that steric effects are not significant in the observed ligand arrangement.

The steric bulk of the dppdtbpf ligand was estimated by performing a percent buried volume ($\%V_{bur}$) calculation [61]. The dppdtbpf ligand was found to occupy a slightly smaller percentage of the volume around the palladium atom in this compound than in the corresponding

[Pd(dppdtbpf)Cl_2] (58.3%) [62]. A similar trend is noted in [Pd(dippf)MeCl] (54.9% - calculated as part of this work) [57] as compared to [Pd(dippf)Cl_2] (56.5%) [63]. As a methyl group is bulkier than chloride [64], it is reasonable that the bidentate phosphine occupies slightly less volume in the dichlorides. The $\%V_{bur}$ for chloride (15.9%) and methyl (16.3%) were also calculated for [Pd(dppdtbpf)MeCl] lending further support to the methyl being the bulkier substituent. In comparing the $\%V_{bur}$ values for the dppf (55.5%) and dtbpf (60.9%) in the corresponding [Pd(PP)Cl_2] compounds [63], it is clear that the -P^tBu_2 group is bulkier than the -PPh_2 group, and as such, not surprising that the bulkier methyl group is *cis*- to the less bulky -PPh_2 group. This arrangement of a -PPh_2 group being *cis*- to the methyl and a -P^tBu_2 *cis*- to the chloride has also been observed in [Pd(1-$CH_2P^tBu_2$-2-CH_2PPh_2-C_6H_4)MeCl] [65], [Pd(1-P^tBu_2-2-PPh_2-1H-imidazole)MeCl] [66], [Pd(1-PPh_2-2-P^tBu_2-1H-imidazole)MeCl] [66] and [Pd(1-$CH_2P^tBu_2$-2-PPh_2-C_6H_4)MeCl] [67].

Surprisingly, the oxidative electrochemistry of these compounds has not been reported. In fact, the oxidative electrochemistry of very few palladium compounds with methyl ligands has been reported. The complex [Pd(κ^2- N,N′-di*tert*-butyl-2,11-diaza[3.3](2,6)pyridinophane)MeCl] undergoes two one-electron oxidations resulting in a change in coordination of the pyridinophane ligand from κ^2- to κ^4-binding [68]. The dimeric [Pd_2((μ-$FcCH_2N(CH_2PPh_2)CH_2)_2)_2Me_2Cl_2$] undergoes a single reversible oxidation at 0.02 v vs. $FcH^{0/+}$ which is 0.03 V less positive than the free ligand [69]. The electrochemistry of [Pd(κ^2-(C_5H_4N=$PR_3)_2$Fe)MeCl] and [Pd(κ^3-(C_5H_4N=$PR_3)_2$Fe)Me][BPh_4] (R = Et or Ph) was examined and displayed multiple irreversible reductions and subsequent oxidations of the new species [70].

Unlike the corresponding [Pd(PP)Cl_2] species which exhibit a single reversible wave, oxidation of the [Pd(PP)MeCl] compounds displayed two waves (Fig. 4) of varying reversibility

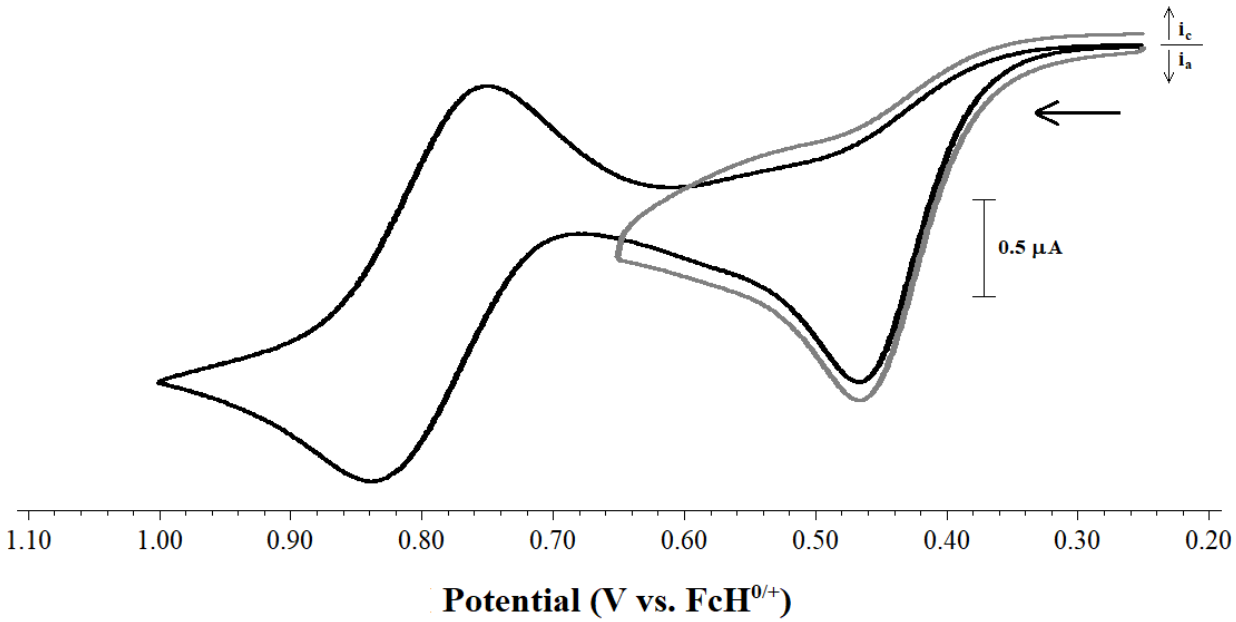


Fig 4. Cyclic voltammogram of 1.0 mM [Pd(dppf)MeCl] in CH_2Cl_2 with 0.1 M [NBu_4][PF_6] at 100mV/s. The gray trace shows a scan where the switching potential was less positive than the second wave.

(Table 2). The initial wave for the [Pd(dppf)MeCl] and [Pd(dfurpf)MeCl] compounds is irreversible. For [Pd(dippf)MeCl], [Pd(dcpf)MeCl] and [Pd(dppdtbpf)MeCl] the initial wave showed increased reversibility at higher scan rates (Fig. 5). The data suggests that oxidation of

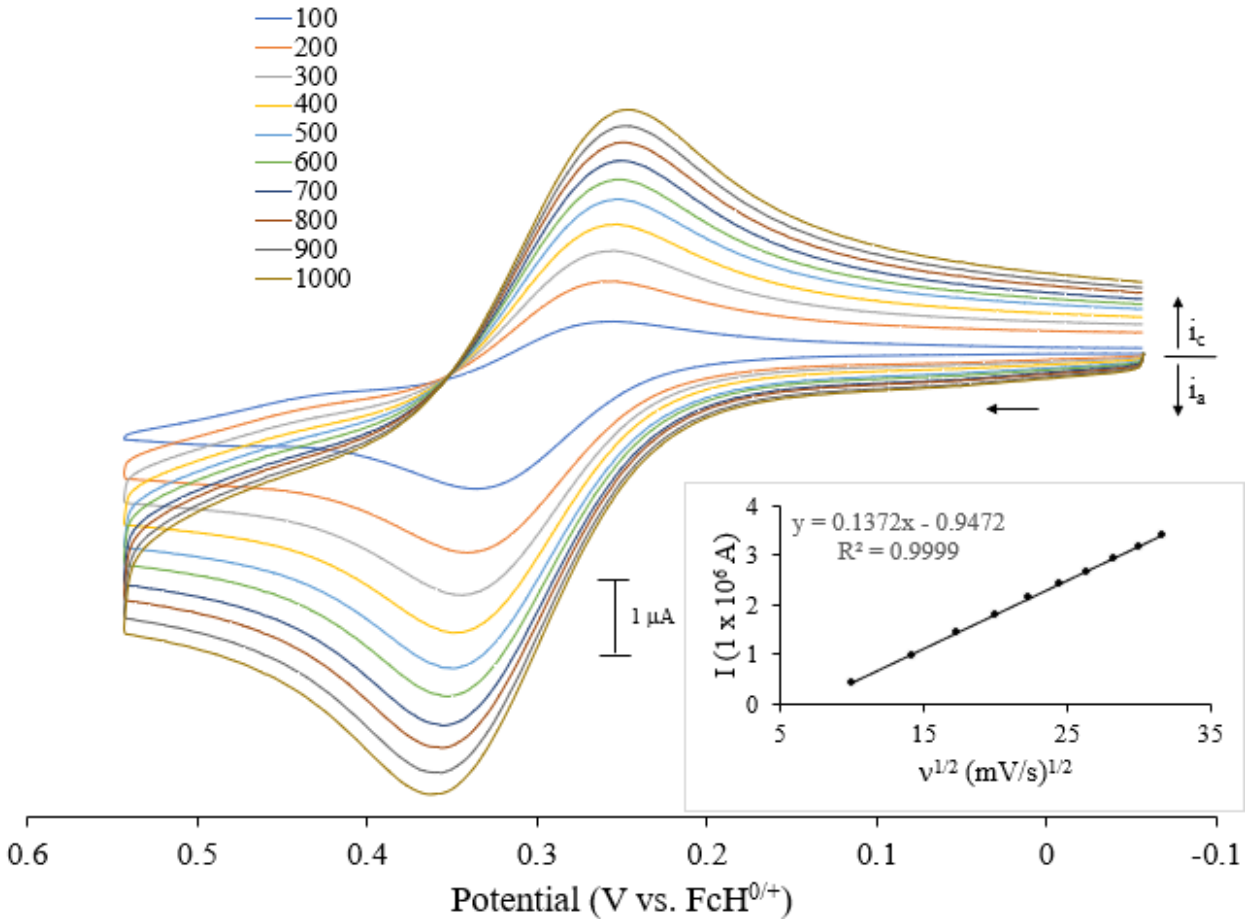


Fig 5. Cyclic voltammograms of [Pd(dcpf)MeCl] in CH_2Cl_2 at different scan rates (mV/s). The inset is a plot of peak current (I in µA) vs. the square root of the scan rate ($\nu^{1/2}$ in $(mV/s)^{1/2}$).

the compounds follows an EC mechanism in which oxidation is followed by a fast-chemical reaction. Simulations of EC mechanisms for the cyclic voltammograms for [Pd(dippf)MeCl], [Pd(dcpf)MeCl] and [Pd(dppdtbpf)MeCl] were performed using DigiSim[71] and were in good agreement with the experimental data. The simulations suggest that the rate of the follow-up reaction is fastest for [Pd(dippf)MeCl]. There appears to be a general trend that the bulkier the ferrocenylphosphine ligand, the slower the follow-up reaction. For the even less bulky ligands, dppf and dfurpf, the oxidation is totally irreversible indicating that the follow-up reaction after oxidation is very fast indeed.

Table 2

Electrochemical data for PP ligands, [Pd(PP)MeCl] and [Pd(PP)Cl_2] compounds. Potentials are in V vs. $FcH^{0/+}$ and irr represents an irreversible oxidation and quasi a quasireversible oxidation.

			[Pd(PP)MeCl]					
PP	**Ligand**	**Ref.**	**E_p (ox1)**	**E_p (ox2)**	**[Pd(PP)Cl_2]**	**Ref.**	**%V_{bur}**	**Ref.**
dppf	0.23	[72]	0.47 (irr)	0.79 (quasi)	0.57	[73]	55.5	[63]
dippf	0.05	[74]	0.32 (quasi)	0.45 (quasi)	0.43	[74]	56.5	[63]
dcpf	0.02	[13]	0.29 (quasi)	0.44 (irr)	0.47	[13]	57.5	[63]
dtbpf	0.06	[75]	0.56 (irr)	0.68 (quasi)	0.47 (0.94)	[75]/[19]	60.9	[63]
dppdtbpf	0.11	[73]	0.34 (quasi)	1.15 (irr)	0.51	[73]	58.3	[62]
dfurpf	0.15	[76]	0.43 (irr)	0.74 (quasi)	0.55		53.7	[77]

The potentials at which the first wave in the oxidation of the [Pd(PP)MeCl] compound occurs follows the same general trend as that of the free phosphines; the potential is most positive for dppf and dfurpf and least positive for the alkyl phosphines. The apparent exception to this is the dtbpf compound which undergoes oxidation at the most positive potential. However, the compound does not actually occur as [Pd(κ^2-dtbpf)MeCl] but rather as [Pd(κ^3-dtbpf)Me]Cl in which there is a weak, non-covalent interaction between the two metal atoms [33,35]. As the overall compound is a cation, it is not surprising that the potential at which oxidation occurs is more positive than that of the [Pd(PP)MeCl] compounds.

The oxidation of these compounds occurs approximately 0.1 V less positive than that of the corresponding [Pd(PP)Cl_2]. This is consistent with a methyl ligand being more electron donating than a chloride [78]. Again, as the dtbpf compound actually exists as [Pd(κ^3-dtbpf)Me]Cl [33,35] a more appropriate comparison for the electrochemical data is [Pd(κ^3-dtbpf)Cl][$BArF_{24}$] [19]. The potential at which oxidation of [Pd(κ^3-dtbpf)Me]$^+$ occurs is 0.38 V positive that of [Pd(κ^3-dtbpf)Cl]$^+$. The oxidation of the iron center is likely more sensitive to methyl as compared to the chloride as these ligands are *trans*- to the interaction between the iron and palladium centers.

Several reports have found greater reactivity for [Pd(PP)MeCl] (PP = dppe or dppf) compounds when dppf is the ligand [36,46]. One example was in the polymerization of

phenylacetylene in which the catalytic activity of [Pd(PP)MeCl] (PP = dppe, dppf or dippf) compounds was examined using a mixture of methylene chloride and acetonitrile as the solvent and silver triflate to abstract the chloride [46]. Under those conditions, the catalyst ranking was dppf > dippf > dppe in terms of both yield and average molecular weight of the polymer, but in terms of the narrowest polydispersity the order was dppe > dppf > dippf.

To further examine the effect of changing the substituents on bis(phosphino)ferrocene ligands, the catalytic activity of [Pd(PP)MeCl] (PP = dppf, dippf, dcpf, dppdtbpf or dfurpf) and [Pd(κ^3-dtbpf)Me]Cl for the polymerization of phenylacetylene was investigated. The optimal solvent conditions from that previous report Li were employed in this study [46]. One modification was made to those conditions at that was the use of Na[$BArF_{24}$] in place of silver triflate for the halide abstraction. Previous work in this laboratory has found Na[$BArF_{24}$] to be an effective reagent for abstracting chlorides in these types of systems [10,19].

The ^{1}H NMR spectra of the material obtained from these reactions indicated the formation of polyphenylacetylene. For almost all of the catalytic systems, the isolated yield of this material was > 75%. The two exceptions were [Pd(dppdtbpf)MeCl] which gave a 24% yield and [Pd(dtbpf)Me]Cl which gave < 5% of the product. Preliminary GPC data on these materials suggests that in terms of M_w the phosphines are ranked dtbpf > dfurpf > dcpf > dppf > dippf > dppdtbpf. However, the low M_w and high polydispersity suggest that the isolated material is a complex mixture of oligomers suggesting that these compounds and activation by the addition of Na[$BArF_{24}$] lead to very poor quality of polymer.

4. Conclusion

The preparation and subsequent characterization of [Pd(PP)MeCl] (PP = dcpf, dppdtbpf or dfurpf) indicated that the dcpf and dfurpf ligands are coordinated through the two phosphorus

atoms in a κ^2-coordination mode. The asymmetry of the dppdtbpf ligand did not allow for the definitive assignment of the structure based solely on NMR data but the presence of a NOE signal in the ^{1}H NOESY spectrum suggested that the compound was κ^2- and the -PPh_2 group was *cis*- to the methyl ligand. The X-ray crystal structure of [Pd(dppdtbpf)MeCl] confirmed this arrangement. Unlike the oxidative electrochemistry of the related [Pd(PP)Cl_2] compounds, oxidation of the [Pd(PP)MeCl] and [Pd(dtbpf)Me]Cl compounds in CH_2Cl_2 was complex and displayed multiple waves. With the exceptions of [Pd(dcpf)MeCl] and [Pd(dppdtbpf)MeCl] the initial oxidative waves of these compounds was irreversible. For [Pd(dcpf)MeCl] and [Pd(dppdtbpf)MeCl], the wave showed increased reversibility at higher scan rates suggesting that oxidation of the compounds followed an EC mechanism in which oxidation is followed by a fast-chemical reaction. The ^{1}H NMR spectra of the material obtained from the polymerization reactions indicated the formation of polyphenylacetylene. Unfortunately, the low M_w and high polydispersity suggested that the isolated material was a mixture of oligomers which indicated Na[$BArF_{24}$] was a poor halide abstracting agent.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

CCDC 2024871 and 2024872 contains the supplementary crystallographic data for [Pd(dppdtbpf)MeCl]. These data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data (including NMR data for [Pd(dppdtbpf)MeCl], [Pd(dcpf)MeCl] and [Pd(dfurpf)MeCl] and cyclic voltammograms for all [Pd(PP)MeCl] compounds can be found, in the online version, at .

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