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Dimerization of Ethylene by Palladium Complexes Containing Bidentate Trifluoroborate-Functionalized Phosphine Ligands

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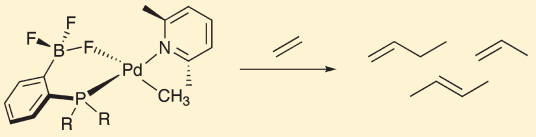
Supporting Information

ABSTRACT: As an alternative to the widely reported phosphine−sulfonate ligand system, a series of potassium aryltrifluoroborate-functionalized phosphine ligands and zwitterionic phosphonium salts were prepared and structurally characterized. The phosphine ligands formed complexes of the general formula [κ^2-(P,F)^{R}PdClMe] (where R = Ph, 2-OMe-Ph) when reacted with PdClMe(COD); however, cleavage of the chloride ligand proved problematic. Reaction of the phosphonium salts with $PdMe_2$(tmeda) yield complexes of the general type [κ-(P)^{R}PdMe(tmeda)], which react with pyridine derivatives to displace tmeda. Manipulation of the steric bulk of the pyridine ligands affords some control over the coordination mode of the fluoroborate phosphine, yielding facile access to complexes of the general type [κ^2-(P,F)^{R}PdMe(lutidine)]. Investigations into the insertion chemistry of the palladium methyl moiety with simple small molecules revealed that the release of the lutidine ligand is slow and that insertion of ethylene occurs in a very slow manner; this is attributed to the relative electron deficiency of the aryltrifluoroborate moiety as compared to sulfonate. The palladium lutidine complexes slowly dimerize ethylene to a mixture of propene and butenes.



INTRODUCTION

The development of organometallic compounds capable of the copolymerization of ethylene and polar monomers is an area of great current interest.[1] Using the lessons learned from the application of well-defined single-site olefin polymerization catalysts, the synthesis of copolymers with novel properties that could be rationally predicted and manipulated by appropriate electronic and steric tuning of a well-defined catalyst would be a significant breakthrough in the development of functionalized polymeric materials. This is especially true in the case of monomers such as acrylonitrile, where polymerization takes place via either radical[2] or anionic[3] processes.

To reach this goal, numerous challenges to the improvement of catalysts capable of mediating such a process exist. Chief among them is the unwanted binding of the polar monomer to the transition element center via the polar group, at the expense of the ethylene comonomer. While this can be mitigated to some extent by the choice of a later transition element over an earlier one, the fact remains that electrophilic complexes employed in such processes strongly bind comonomers with "hard" donor groups as ligands, forming species inert to further insertion. To circumvent such an issue requires promotion of the π-bound isomer **Ia** at the expense of the σ-bound complex **Ib** (Chart 1). One such line of investigation is the incorporation of bulky, anionic functionalities into ligand frameworks—thus making overall monoanionic complexes—which would result in the repulsion of the lone pairs of the polar monomer, thus promoting the binding of the polar monomer in the π-coordination mode.[4]

To this end, we recently reported a series of palladium(II)salicylaldiminato complexes **II**, related to a Ni-mediated ethylene/acrylate copolymerization system reported by Grubbs et al.[5] The salicylaldimine framework was functionalized with a trifluoroborate moiety in the *para* position of the aromatic ring;[6] while kinetic studies showed that the rate of insertion of acrylonitrile was indeed faster in the anionic complexes than in their neutral counterparts, the effect was limited due to the distant location of the BF_3K moiety from the site of insertion. The number of acrylonitrile insertions was also limited, due to the coordination of the nitrile functionality to the Pd center, thus forming catalytically inactive oligomeric structures consistent with the independent observations of Jordan and co-workers.[7] It proved to be synthetically difficult to move the trifluoroborate moiety into the *ortho* position of the aryl ring, and so we turned our attention to other ligand systems for which the synthesis could be readily altered to incorporate such groups. One such system was the phosphine−sulfonate ligand system **III**, first reported by Drent and co-workers[8] A wealth of information is available from studies on metal systems supported by such ligands, and their reactivities with olefins,[9] as well as numerous polar monomers such as acrylonitrile,[10] carbon monoxide,[11] mixed N/O donors,[12] acrylates,[13] vinyl acetate,[14] carboxylic acids,[15] sulfones,[16] vinyl halides,[17] polar allylic monomers[18] and ethers,[19] are well documented. The syntheses of such ligands

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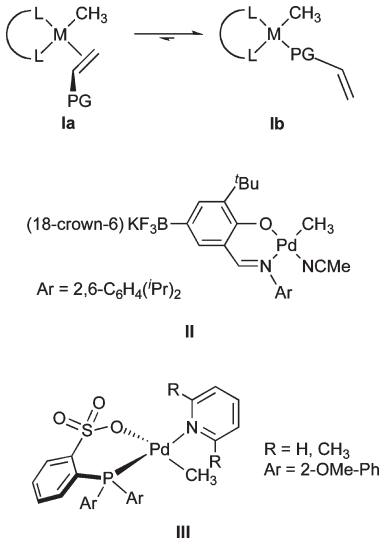
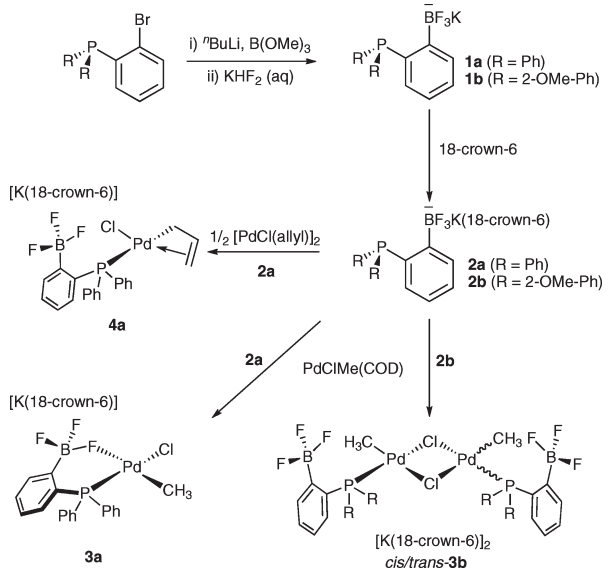
Chart 1



Scheme 1



are relatively simple and amenable to alteration, and complexation is facile.

This contribution details our findings in the replacement of the sulfonate moiety in phosphine−sulfonate ligand systems with a trifluoroborate group, and the effect such a group has on coordination chemistry and reactivity.

RESULTS AND DISCUSSION

Borate Salt Synthesis. According to established methodology,[6] treatment of Ph_2P(2-Br-Ph) with ^{n}BuLi, followed by quenching with an excess of trimethylborate and subsequent hydrolysis furnished the corresponding boronic acid in essentially quantitative yield. Immediate dissolution in methanol and treatment with three equivalents of KHF_2[20] yielded the trifluoroborate salt **1a** in good yield, as shown in Scheme 1. **1a** was characterized by its relatively poor solubility in most common solvents. In contrast, the same synthetic procedure incorporating Ar_2P(2-Br-Ph) (where Ar = 2-methoxyphenyl) yielded the slightly more soluble **1b**.

The diagnostic spectroscopic feature for **1a**/**b** was observed in their ^{31}P NMR spectra: a single resonance split into a quartet due to coupling to the fluorine atoms of the trifluoroborate moiety. The shift from δ −7.7 ppm (**1a**) to −31.0 ppm (**1b**) demonstrated the increased electron density at phosphorus in the latter due to delocalization of the methoxy lone pair onto phosphorus. The P−F coupling constant was determined to be 34 Hz in **1a** and 39 Hz in **1b**, somewhat smaller than the related Ph_2P(2-CF_3-Ph) (53 Hz).[21] Both show a characteristic, broad resonance in the ^{19}F NMR spectrum: at δ −133.3 ppm (**1a**) and −138.6 ppm (**1b**), typical of aryltrifluoroborates.[20] The ^{11}B NMR resonances were located at ca. +2.5 ppm and were consistent with four-coordinate boron.[22] Compound **1b** is significantly hygroscopic; such behavior has also been noted in related phosphine−sulfonate systems.[10b] The slightly increased solubility of **1b** allowed crystallographic characterization; the structure can be seen in Figure S1 of the Supporting Information, along with relevant bond lengths and data-processing parameters. To increase the solubility of **1a**, it was reacted with one equivalent of 18-crown-6, yielding, after recrystallization, the highly crystalline 18-crown-6 adduct **2a**. The spectroscopic properties of **2a** are largely the same as for **1a**, but the enhanced solubility of **2a** allowed structural characterization by X-ray crystallography, and the structure can be seen in Figure S2, along with selected metrical data. Ligand **2b** can be accessed similarly.

Palladium Complexes of Aryltrifluoroborates. NMR-scale reactions between ligands **2** and PdClMe(COD) saw complete displacement of the 1,5-cyclooctadiene ligand, yielding new species **3**, as shown in Scheme 1. Ligation of phosphorus was demonstrated by a shift to lower field in the ^{31}P{^{1}H} NMR spectrum (from δ −6.4 ppm to +31.1 ppm for **3a**) and confirmed by the ^{1}H NMR spectrum, in which the Pd−methyl resonance at δ 0.75 ppm was split into a doublet due to coupling to phosphorus, with a coupling constant of 2 Hz. Coordination of the fluoroborate caused an upfield shift of the ^{19}F NMR resonance, from δ −134.3 ppm to −152.9 ppm in **3a**. The coordination mode of the ligand was confirmed by X-ray crystallography; the structure of **3a** can be seen in Figure 1, with selected bond lengths and angles. The structure of the compound is the expected square-planar geometry, in which the coordination sphere of the palladium center is completed by methyl, chloride, and chelating trifluoroborate-functionalized triphenylphosphine ligands; the compound is therefore formally monoanionic. The presence of the chloride ligand demonstrated no salt metathesis with potassium had occurred, as compared to other similarly functionalized trifluoroborate ligands.[23] The potassium cation is sequestered by 18-crown-6, though it shows interactions with both the trifluoroborate moiety (K(1)−F(2) = 2.617(2) Å) and an acetone ligand (K(1)−O(7) = 2.783(3) Å). The former distance is comparable to the few crystallographically characterized examples, which lie in the range 2.60−2.94 Å.[6,24] The palladium−fluorine bond length was determined to be 2.181(2) Å, which is shorter than the two known values for Pd−F−BF_3 connectivities (2.241(2)[25] and 2.354(5) Å[26]). The trifluoroborate moiety lies *trans* to the methyl group, raising the potential of hemilabile behavior given the high *trans* influence of the methide anion.

The ligand **2b** also reacted with PdClMe(COD), as monitored by ^{1}H NMR spectroscopy, but there was no shift in the −BF_3 resonance in the ^{19}F NMR spectrum, which remained at −136 ppm,

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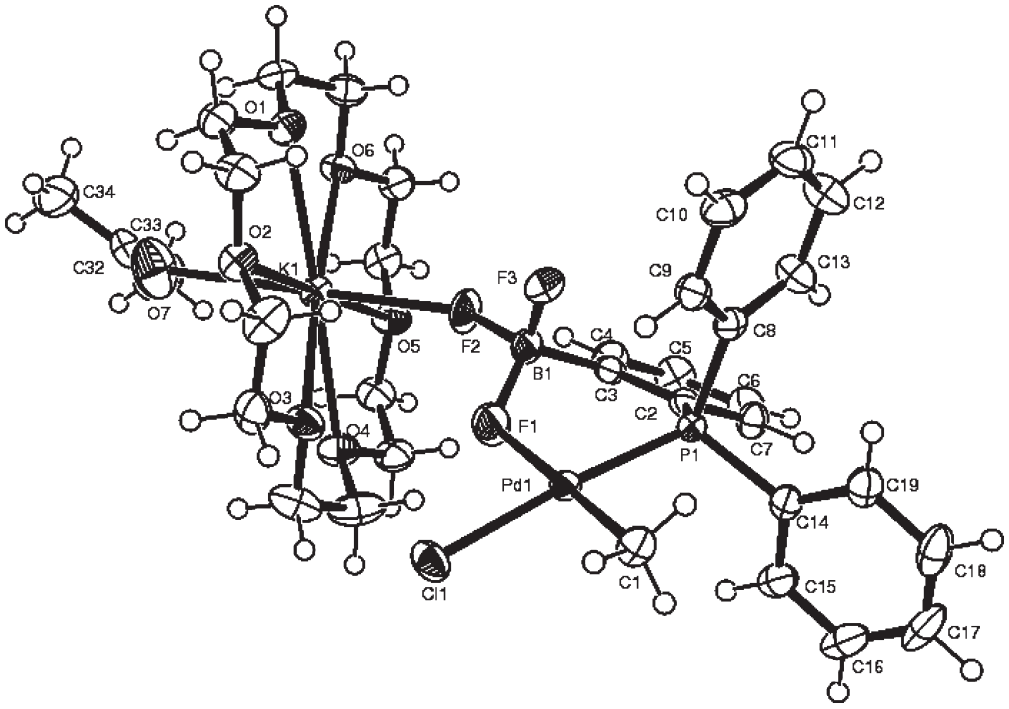


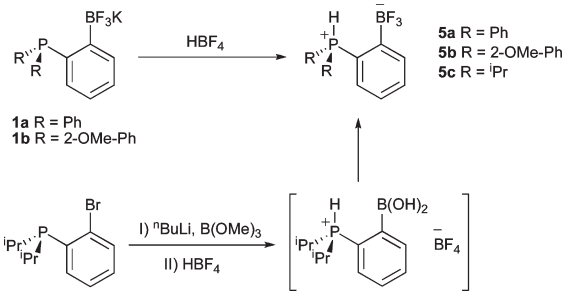
Figure 1. Molecular structure of **3a**. Displacement ellipsoids are at the 50% probability level. Acetone molecule of crystallization is omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−C(1) = 2.030(4), Pd(1)−Cl(1) = 2.3747(10), Pd(1)−P(1) = 2.2281(9), Pd(1)−F(1) = 2.181(2), B(1)−F(1) = 1.406(2), B(1)−F(2) = 1.421(2), B(1)−F(3) = 1.393(2), K(1)−F(2) = 2.617(2), K(1)−O(7) = 2.828(4), C(1)−Pd(1)−Cl(1) = 90.51(11), Cl(1)−Pd(1)−F(1) = 88.25(6) Pd(1)−F(1)−B(1) = 117.0(2), F(1)−B(1)−C(3) = 109.5(3), F(1)−Pd(1)−P(1) = 93.10(6), C(2)−P(1)−Pd(1) = 112.16(11), P(1)−Pd(1)−C(1) = 88.20(11).

indicating noncoordination. Such data implied that the compound existed as a chloride-bridged dimer; this was supported by ESI-mass spectrometry, which yielded a spectrum that included a base peak of m/z 546 (molecular weight of 1092/2− charge), plus a smaller peak at m/z 1046, corresponding to the monoanionic $[M^{2-}]$ −Cl. Presumably in this instance, the donor properties of the more electron-rich phosphine ligand are such that coordination of the weakly donating trifluoroborate moiety to Pd is unnecessary to satisfy the electronic requirements of the Pd center. Further confirmation of the dimeric nature of **3b** came from both ^{1}H and ^{13}C{^{1}H} NMR spectra, where two sets of resonances were observed (in an 84:16 ratio), for example at δ 0.30 and 1.09 ppm in the ^{1}H NMR spectrum, corresponding to *cis* and *trans* arrangements of the terminal methyl groups.

Reaction of **2a** with $[(\eta^3\text{-allyl})PdCl]_2$ yielded the new complex **4a**, in which the ^{19}F NMR spectrum was again consistent with the binding of the phosphine borate via the phosphorus atom only; a resonance at δ −132.4 ppm in the ^{19}F NMR spectrum implied noncoordination of the trifluoroborate, and the allyl co-ligand was bound in η^3 fashion. This formulation was supported by ^{1}H NMR spectroscopy; resonances at δ 3.05, 3.17, 3.48, 4.35, and 5.62 ppm were consistent with reported data from $[(Ph_3P)PdCl(\eta^3\text{-allyl})]$,[27] as opposed to data from η^1 allyls such as $[(dppe)PdCl(\eta^1\text{-allyl})]$,[28] which display olefinic resonances at lower field due to the absence of back-bonding.

Attempts to cleave the chloride ligand from compounds **3** to yield complexes of the general formula $[\kappa^2\text{-}(P,F)^R PdMe(L)]$ with a vacant coordination site (where L = coordinating solvents such as acetonitrile, and R = Ph or 2-methoxyphenyl) were unsuccessful. Treatment with silver reagents (in an attempt to form silver chloride by salt metathesis) abstracted fluoride from the BF_3 group of the ligand. Other reagents were similarly unsuccessful; reaction of **3** with trimethylsilyl triflate[29] also removed fluoride, as demonstrated by the formation of Me_3SiF in NMR-scale reactions. Attempts to methylate the chloride ligand (to form a complex of the type $[\kappa^2\text{-}(P,F)^R PdMe_2][K(18\text{-crown-}6)]$, before treatment with protic reagents to eliminate methane) under a variety of reaction conditions were unsuccessful; either decomposition to Pd(0) was observed, or attack at fluorine in the ligand occurred, as judged by the disappearance of the fluoride signals in the ^{19}F NMR spectrum. Even mild alkylating reagents such as organocopper reagents and tetramethyltin were unsuccessful in this regard. Given the lack of success, an alternative strategy was needed to access $[\kappa^2\text{-}(P,F)^R\text{-}PdMe(L)]$.

Scheme 2



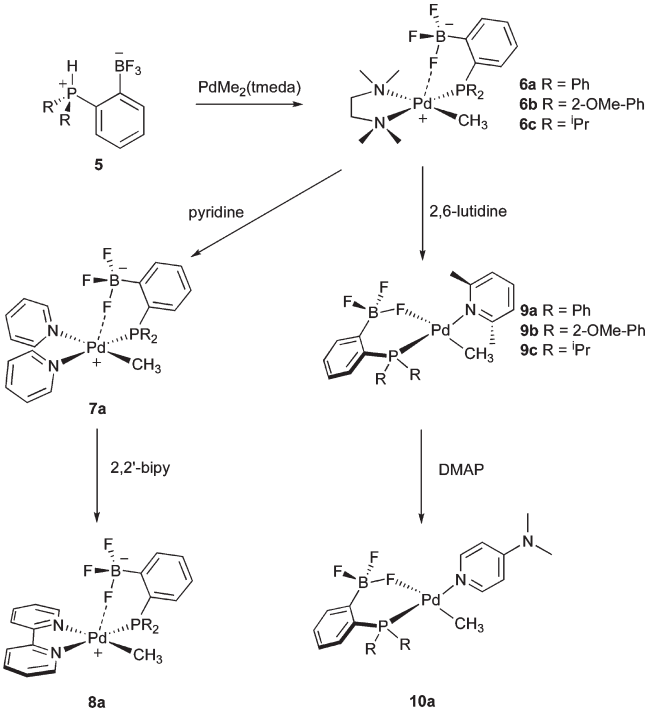
Phosphonium Salt Synthesis. It was thought that the treatment of a palladium(II) dimethyl precursor with a source of "HL" would yield the desired palladium monomethyl complexes, with

elimination of methane, in a similar fashion to that observed by the groups of Jordan[19b] and Nozaki.[10b] Such an approach necessitated the synthesis of phosphonium salts from the potassium aryltrifluoroborate salts **1**. Dissolution of **1a** and **1b** in THF, followed by treatment with one equivalent of tetrafluoroboric acid (as a 48% w/v solution in water), resulted in the precipitation of KBF_4 and production of the new compound **5**, which was separated by extraction into chlorinated solvents, as shown in Scheme 2. The principal spectroscopic feature of phosphonium salts **5** was a low-field doublet integrating to 1H in the ^{1}H NMR spectrum (centered at δ 8.85 ppm for **5a** and 8.96 ppm for **5b**), with a large, one-bond coupling to the ^{31}P nucleus of the quaternized phosphorus center (540 and 572 Hz for **5a** and **5b**, respectively). Similarly, the ^{31}P NMR spectrum displayed a single doublet resonance with identical coupling constant at δ +5.5 and −11.8 ppm, respectively. The increased electron richness of the phosphorus atom in **5b**, via incorporation of methoxyaryl groups and subsequent mesomeric effects, is demonstrated by a high-field shift of 17.3 ppm compared to its nonfunctionalized analogue. Both compounds display single broad resonances in the ^{19}F NMR spectra at ca. −137 ppm, and ^{11}B{^{1}H} NMR resonance at ca. +3 ppm. Confirmation of the formulation of **5** was achieved from diffraction-quality crystals of **5a** grown by the slow evaporation of an acetonitrile solution. The structure of **5a** can be seen in Figure S3, along with selected bond lengths and angles.

An alkyl phosphine derivative was also synthesized to further examine electronic effects of the substituent on phosphorus. In comparison to the synthesis of **5a** and **5b**, a slightly different strategy was required for the synthesis of **5c**: isolation, purification, and characterization of the analogous trifluoroborate salt "**1c**" was not possible due to apparent insolubility. As an alternative approach, the corresponding boronic acid was synthesized—according to an established procedure—as shown in Scheme 2. Subsequent *in situ* quaternization of the phosphorus center, serving to act as a protecting group, yielded the intermediate phosphonium salt, and the following fluorination reaction cleanly furnished the desired phosphonium salt **5c** in moderate yield (**5c** has been reported previously,[30] though only on a small scale). The alkyl phosphonium proton of **5c** was shifted to higher field in the ^{1}H NMR spectrum, relative to the aryl derivatives **5a** and **5b**, and was observed as a broad doublet centered at δ 6.42 ppm with a coupling constant of 472 Hz, consistent with reported literature values; $[HP^iPr_3][BF_4]$ displays a resonance at δ 5.71 ppm, with a coupling constant of 468 Hz.[31]

Complexation of Phosphonium Salts. A number of strategies for the complexation of bidentate phosphines to palladium have been reported. Most involve the treatment of the easily accessible $PdMe_2$(tmeda) with one equivalent of the phosphine ligand, in the presence of a donor ligand such as pyridine or lutidine. Such reaction conditions effect the facile displacement of the tmeda ligand, yielding complexes of the general composition [κ^2-(P,L)PdMe(pyridine)]. Accordingly, treatment of $PdMe_2$(tmeda) with one equivalent of **5a** was foreseen as a route to analogous trifluoroborate complexes, and NMR-scale reactions exhibited instant gas evolution and color change from colorless to yellow (Scheme 3). However, it became clear upon following the reaction progress by NMR spectroscopy that the reactivity was different from that previously reported; no displaced tmeda was observed by NMR spectroscopy in the new species **6**. In the case of **6a**, the NMR spectra showed a single palladium methyl resonance at δ 0.33 ppm, showing weak

Scheme 3



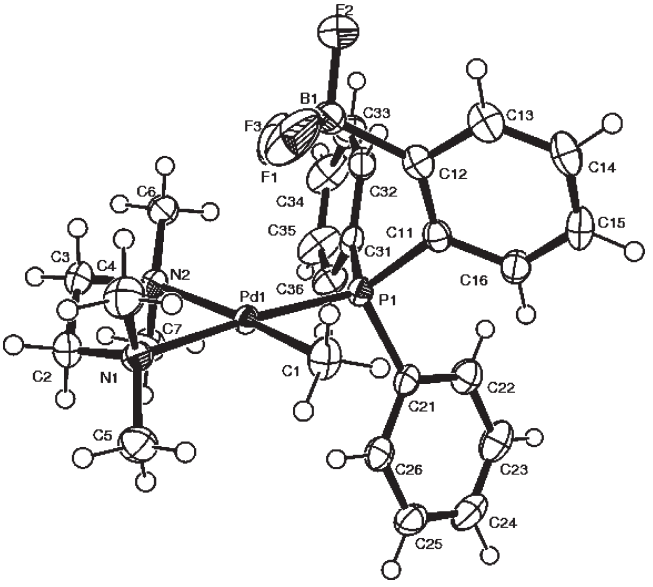


Figure 2. Molecular structure of **6a**. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): Pd(1)−C(1) = 2.049(3), Pd(1)−P(1) = 2.2407(7), Pd(1)−N(1) = 2.180(2), Pd(1)−N(2) = 2.231(2), Pd(1)−F(1) = 3.595 Pd(1)−F(3) = 3.061, N(1)−Pd(1)−N(2) = 82.10(8), N(2)−Pd(1)−P(1) = 104.60(6) N(1)−Pd(1)−C(1) = 90.56(10), C(1)−Pd(1)−P(1) 82.77(9).

coupling to the ligated phosphorus center. Resonances at δ 2.36 and 2.58 ppm—integration of 12H and 4H, respectively—confirmed the presence of tmeda, thus giving an early indication of the low donor strength of the phosphino-trifluoroborates as

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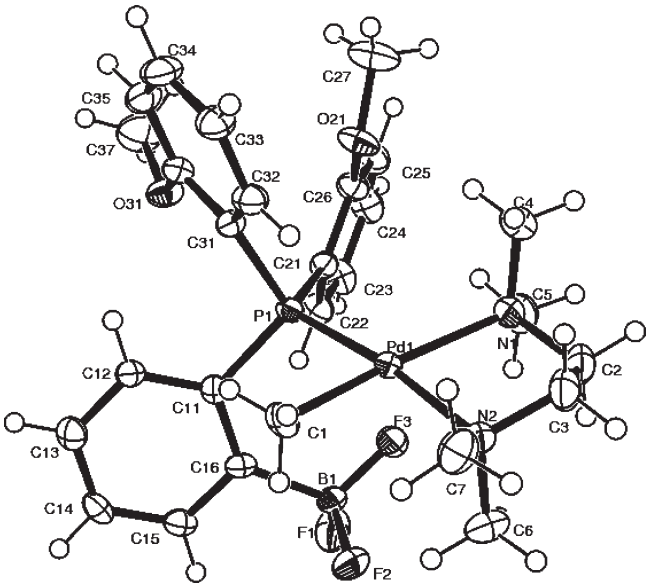

Figure 3. Molecular structure of **6b**. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): Pd(1)−C(1) = 2.041(5), Pd(1)−P(1) = 2.2718(15), Pd(1)−N(1) = 2.224(5), Pd(1)−N(2) = 2.182(2), Pd(1)−F(2) = 3.697, Pd(1)−F(3) = 2.939 N(1)−Pd(1)−P(1) = 104.08(12), N(1)−Pd(1)−N(2) = 82.07(16), N(2)−Pd(1)−C(1) = 89.98(19), C(1)−Pd(1)−P(1) = 84.11(16).

compared to the more widely known phosphino-sulfonate ligands. The spectrum was completed by multiple aryl signals at low field. The presence of nonligated aryltrifluoroborate was confirmed by ^{19}F NMR spectroscopy, in which the only observed resonance was seen at δ −133.1 ppm, inconsistent with binding to a metal center. The main feature of the $^{13}C\{^1H\}$ NMR spectrum was a doublet resonance at high field (δ 5.6 ppm) corresponding to the palladium methyl. The NMR spectra of **6c** were largely similar, appropriate resonances for differing substituents notwithstanding. Crystallographic confirmation of the structure of **6a** was obtained by X-ray diffraction on a sample grown from cooling a hot, saturated toluene solution. The structure can be seen in Figure 2, along with relevant structural data. The structure revealed the expected square-planar geometry about four-coordinate Pd(II), in which the coordination sphere was defined by a phosphine donor, a tmeda ligand, and the methyl group. The complex is formally zwitterionic in nature, with possibly a weak interaction in the solid state, as the Pd−F distance of 3.06 Å was found to be marginally less than the sum of the van der Waals radii (3.10 Å), although it did not appear to persist in solution since the ^{19}F NMR resonance did not shift significantly to high field. The Pd(1)−N(1) bond length of 2.231(2) Å is slightly longer than the analogous distance Pd(1)−N(2), as is to be expected when residing *trans* to a methyl ligand with high *trans* influence.

In comparison to **6a** and **6c**, the NMR spectra for **6b** were found to be very broad at room temperature. Integration of ^{1}H NMR spectra appeared to show a molecule consistent with the formulation of **6a** and **6c**, but experiencing an unknown dynamic exchange process. To ascertain the origin of this behavior, **6b** was also subjected to a crystallographic examination, the result of which can be seen in Figure 3, along with relevant bond lengths and angles. The investigation revealed that the solid-state structure of **6b** is essentially the same as **6a**, in that the complex is a four-coordinate Pd(II) methyl cation, displaying a weak interaction with the aryltrifluoroborate moiety. The bond lengths and angles are very similar to those of **6a**, indicating apparently little electronic perturbation of the Pd center by the incorporation of methoxy groups on the aryl rings of the phosphine.

Inspection of the structure revealed that one of the methoxy groups (O21) was proximate to the nitrogen atom of the tmeda ligand *trans* to the methyl group. To assess whether there was an exchange process underway involving displacement of tmeda and coordination of the potentially hemilabile aryloxy ligand, variable-temperature NMR studies were carried out. Cooling a $CDCl_3$ sample of **6b** resulted in a ^{1}H NMR spectrum that decoalesced at ca. 280 K and gave a sharp spectrum for a single species at 230 K, as demonstrated chiefly by a single palladium methyl signal at δ 0.06 ppm. Twelve separate resonances integrating to 1H were observed in the aromatic region, in addition to two separate resonances at δ 3.04 and 3.09 ppm, corresponding to two diastereotopic methoxy groups; the methyl groups of the tmeda ligand were also observed as four separate resonances. Correspondingly, warming the sample from 298 K resulted in sharpening of the broad spectrum into a single species displaying a ^{1}H NMR spectrum broadly similar to those obtained for **6a**/**c**. The observations inferred that the rotation of the phosphine methoxyaryl rings of **6b** was hindered relative to those of **6a**/**c**, which is unsurprising, given the potential steric clashes with the methoxy substituents.

Coordination of the Trifluoroborate Ligand. In order to access complexes of the general formula $[\kappa^2\text{-}(P,F)^R PdMe(L)]$, it was hoped that reaction with pyridine and derivatives would result in the displacement of the tmeda ligand, binding of the trifluoroborate moiety, and coordination of one equivalent of N-donor. Dissolution of complexes **6** in acetonitrile-d_3 saw no reaction; as monitored by NMR spectroscopy, no free tmeda was observed, even after prolonged periods. Heating caused the slow deposition of Pd(0). Conversely, dissolution of **6a** in pyridine-d_5 saw complete displacement of the tmeda ligand and the formation of a single new complex, **7a**. The inclusion of two equivalents of pyridine was subsequently confirmed by a preparative-scale experiment; the structure can be seen in Figure 4. While a detailed discussion of metric parameters is not appropriate in view of the poor quality of the crystal, the data establish the connectivity in the compound and show that the coordination geometry about the Pd center is the expected square-planar arrangement. The trifluoroborate phosphine was determined to be bound via phosphorus only, with the coordination sphere completed by two pyridine ligands and a methyl ligand. Once more—as in the case of **6a** and **6b**—there is potentially a weak contact between the trifluoroborate moiety and the cationic Pd center. The Pd−N bond lengths of 2.117(9) and 2.148(9) Å are consistent with other known palladium monomethyl complexes ligated by pyridine and phosphine-sulfonates, which range between 2.051(4) and 2.108(3) Å.[9g,11b,32] Over the course of several days, slow dissociation of one equivalent of pyridine occurred, as demonstrated by a resonance slowly appearing in the ^{19}F NMR spectrum at δ −154.6 ppm (in comparison to the chemical shift of −137.2 ppm for **7a**), consistent with the binding of the trifluoroborate moiety to yield a bidentate ligand. The pyridine complex **7a** could also be readily converted to the corresponding 2,2′-bipyridine complex **8a**, although its very much poorer solubility precluded it from further study. Compound

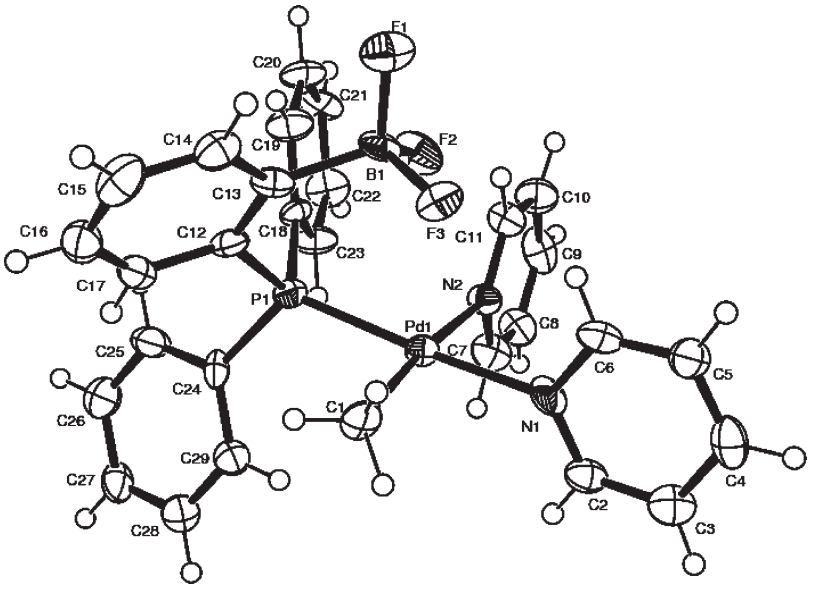

Figure 4. Molecular structure of **7a**. Displacement ellipsoids are shown at the 50% probability level.

8a could also be generated from **6a** directly by the addition of one equivalent of 2,2′-bipyridine.

Palladium Lutidine Complexes. Inspection of the structure of **7a** revealed that the two pyridine ligands experience significant steric abutment. It was postulated that replacement of pyridine with the more sterically demanding 2,6-lutidine would only allow the coordination of one equivalent of donor ligand, thus encouraging coordination of trifluoroborate. Reaction of tmeda complex **6a** with lutidine resulted in a yellow solution, which over the course of several hours saw a white precipitate develop. Filtration of the solid and characterization by ^{1}H NMR spectroscopy showed the material to be complex **6a**. Drying of the supernatant *in vacuo* yielded another species, **9a**, with spectral properties consistent with the desired formulation of $[\kappa^2$-(P,F)^{Ph}PdMe(lutidine)] (*vide infra*); however the reaction was far from clean, and some 30−35% by mass of the starting material **6a** was present. This suggests that **6a** and **9a** are in equilibrium and the free tmeda present precludes complete formation of the desired product. Thus, the synthesis was repeated in a series of iterations: dissolution, removal of all volatiles (including tmeda), and further dissolution in lutidine. After five such cycles, followed by washing with diethyl ether, an essentially quantitative yield of **9a** was obtained in high purity. The corresponding derivatives **9b** and **9c** were thus obtained similarly, though in slightly lower yields due to increased solubility.

The ^{1}H NMR spectrum of **9a** showed a single Pd methyl resonance at δ 0.49 ppm, and a singlet resonance at δ 3.17 ppm integrating to 6H, consistent with the methyl groups of ligated lutidine, in good agreement with the closely related complex $[\kappa^2$-(P,O)^{Ar}PdMe(lutidine)] at δ 3.14 ppm.[10b] Binding of the fluoroborate group was confirmed by ^{19}F NMR; resonances were observed at δ −158.1 (**9a**), −157.6 (**9b**), and −161.1 ppm (**9c**), respectively. The improved electronic donor properties of the methoxyaryl phosphine versus the diphenyl derivative were shown in a slight high-field shift in the palladium methyl resonance (δ 0.34 ppm in **9b** vs δ 0.49 ppm in **9a**). The increased electron density on the Pd center—as conferred by the more electron rich ligands **9b** and **9c**—is also shown by a high-field shift of the Pd methyl resonances in the ^{13}C{^{1}H} NMR spectrum: the methyl resonances of **9b** and **9c** (δ −3.1 and −8.9 ppm, respectively) are at lower chemical shift than **9a** (δ −2.9 ppm). Further corroboration for the coordination of the trifluoroborate group was obtained from the ^{13}C{^{1}H} NMR spectrum, in which the palladium methyl resonances were split into an apparent quartet due to coupling ($^2J_{CF}$ = 9 Hz for **9a**, 14 Hz for **9b**, and 12 Hz for **9c**) to the three fluorine atoms of trifluoroborate. This is in contrast to **3a**, which displays no F-coupling to the methyl carbon; the coupling constant of 9 Hz (for **9a**) is far larger than that observed in a the recently reported [(5,5′-^{t}Bu-bipy)PdFMe][33] ($^2J_{CF}$ = 1.3 Hz). Other such palladium methyl fluoride complexes are known,[34,35] but no ^{13}C NMR data have been reported from which to draw comparisons. The methyl carbon coupling to the phosphorus nucleus was not observed.

Crystallographic confirmation of the structure was sought; despite multiple attempts, crystals of **9a** suitable for diffraction could not be isolated. The more soluble isopropyl derivative **9c** readily yielded suitable crystals, and the structure can be seen in Figure 5, in addition to pertinent data. The structure confirmed the bidentate coordination mode of the trifluoroborate ligand; the Pd(1)−F(1) bond distance of 2.1634(17) Å was in good agreement with the 2.181(2) Å found in **3a**. The coordination of the trifluoroborate group caused a lengthening of the B(1)−F(1) bond, to 1.467(4) Å, as opposed to an average of 1.37 Å in B(1)−F(2)/B(1)−F(3). The palladium−nitrogen distance was determined to be 2.135(2) Å, corresponding very well to other crystallographically characterized Pd-lutidine complexes,[10b,14a,36] in which the average Pd−N distance was determined to be 2.133 Å.

Reactivity with Olefins. Nozaki and co-workers have recently demonstrated that analogous sulfonated phosphines of the general formula $[\kappa^2$-(P,O)PdMe(lutidine)] (where (P,O) = arylphosphinosulfonate) homopolymerize ethylene and have isolated products and model complexes consonant with multiple (i.e., >10) insertions into the Pd−methyl bond.[9e] The catalytic process is thought to be catalyzed by the presence of a small amount (ca. 10 mol % by ^{1}H NMR) of $[\kappa^2$-(P,O)^{Ar}PdMe-(C_2H_4)], where the displaced lutidine could be observed by NMR spectroscopy. Accordingly, chloroform-d_3 solutions of palladium complexes **9** were degassed via freeze−pump−thaw

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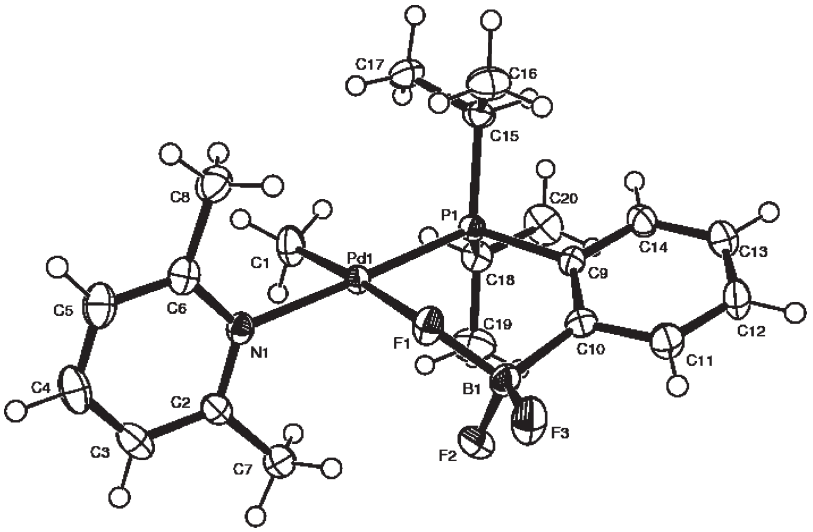


Figure 5. Molecular structure of **9c**. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): Pd(1)−C(1) = 2.010(3), Pd(1)−F(1) = 2.1634(17), Pd(1)−P(1) = 2.2510(8), Pd(1)−N(1) = 2.135(2), B(1)−F(1) = 1.467(4), B(1)−F(2) = 1.392(4), B(1)−F(3) = 1.397(4), C(1)−Pd(1)−P(1) = 91.97(10), P(1)−Pd(1)−F(1) = 91.92(5), F(1)−Pd(1)−N(1) = 90.14(8), N(1)−Pd(1)−C(1) = 85.97(11), Pd(1)−F(1)−B(1) = 117.48(7), F(1)−B(1)−C(10) = 111.5(3), B(1)−C(10)−C(9) = 127.1(3), C(10)−C(9)−P(1) = 123.9(2), C(9)−P(1)−Pd(1) = 114.48(10).

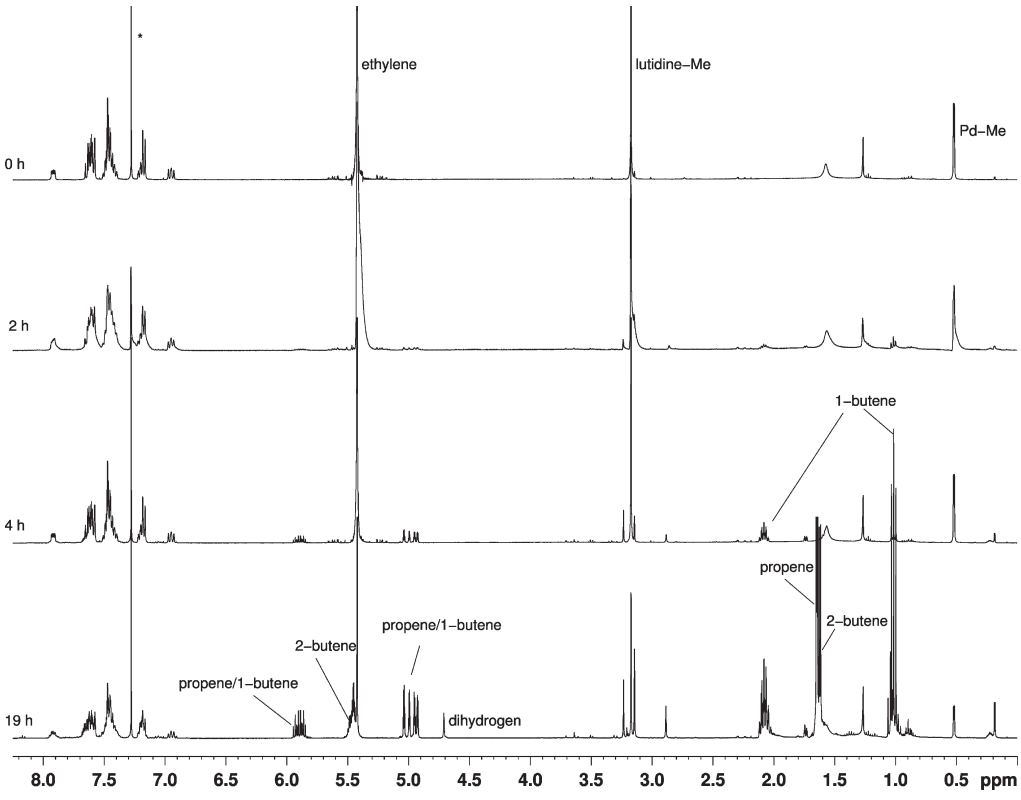
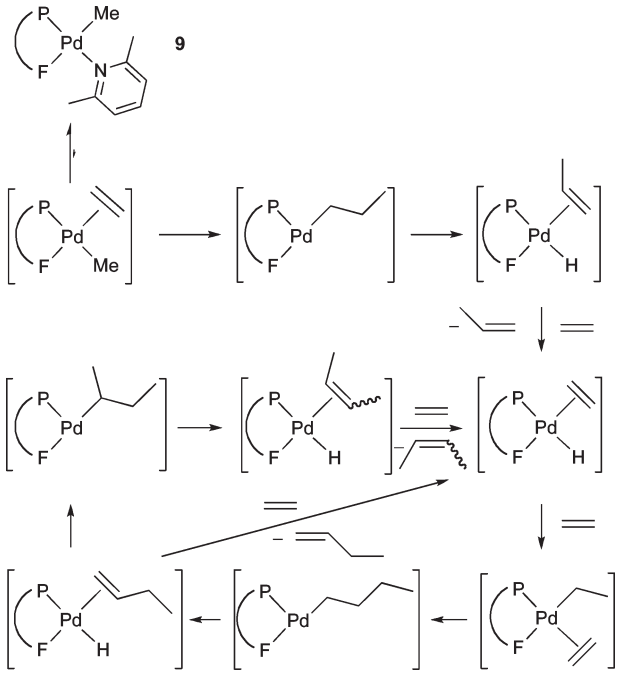


Figure 6. ^{1}H NMR spectra after treatment of **9a** with ethylene. Asterisk denotes residual protio-solvent.

cycles and exposed to one atmosphere of ethylene. No immediate color changes were observed, nor any precipitation of polymeric materials. The reaction with **9a** was immediately assayed by NMR spectroscopy, showing essentially no reaction at ambient temperature. Monitoring over the course of several hours showed the very slow formation of products exhibiting resonances in the olefinic region of the ^{1}H NMR spectrum consistent with formation of oligomers. After approximately 18 h it became clear that the ethylene was being consumed, at the expense of the formation of a mixture of propene (48% by integration of methyl group protons), 1-butene (35%), 2-butene (23%), and a small amount of dihydrogen (4%), along with concomitant disappearance of the palladium methyl resonance. ^{1}H NMR spectra at various time intervals during the reaction can

Scheme 4



be seen in Figure 6. The resonances associated with the Pd complex **9a** were identical to that of the free complex; no other significant species were observed in solution, and furthermore, no free lutidine was observed. Jordan and co-workers have reported similar observations in a related Pd system[37] where the Pd center was supported by a chelating dipyridyl ligand, and their suggested mechanism can be seen in Scheme 4, which is consistent with the observations above. Over the course of three days, the ethylene was completely consumed, with the concomitant appearance of black particulate matter and apparent degradation of the metal complex in solution.

In comparison to **9a**, initial ^{1}H NMR spectra from the reactions of **9b**/**c** with ethylene showed slightly different behavior in that a number of minor, unidentified species (although less than 5% by integration) were observed. Larger amounts of the olefinic products were present at given times (versus **9a**) for **9b** and **9c**, as judged by NMR integration of product versus "catalyst"; as might be expected, the stronger donor ligands afford a more electron-rich metal center, and thus a more labile lutidine ligand. Also noteworthy in the case of **9b** and **9c** is that the amount of 2-butene observed in either sample was significantly suppressed early in the course of the reaction. Over the course of time, the 2-butene resonance grew in, consistent with the mechanism shown in Scheme 4;[38] however the experiments still required more than two days for the ethylene to be completely consumed. The implication of such an observation is that the Pd center was, overall, too electron deficient to allow the tightly bound lutidine ligand to labilize to the degree necessary to allow faster initiation, coordination, and insertion.

To assess whether the ligand displaced—in the absence of evidence of free lutidine—to coordinate the ethylene was actually the trifluoroborate moiety, one equivalent of 4-dimethylaminopyridine (DMAP) was added. The reaction to form the new complex **10a** was instantaneous, as monitored by various NMR spectroscopies, and showed that the bidentate ligand was still intact, best demonstrated by a ^{19}F NMR signal resonating at −152.4 ppm. Preparative-scale reactions were similarly facile. No ligated lutidine resonances were observed. The inference from this observation is that it is indeed the lutidine ligand that is displaced during the ethylene insertion and not the potentially hemilabile phosphine-borate ligand. Exposure of **10a** to ethylene under identical conditions to those described above and monitoring by ^{1}H NMR spectroscopy revealed essentially no reaction after 24 h, in comparison to the significant amount of dimerization afforded by complexes **9**. Similarly, exposure of the less sterically demanding (versus lutidine complexes **9**) **7a** to one atmosphere of ethylene also led to no reaction, doubtless due to the stronger binding of the pyridine co-ligands to the overall cationic complex.

CONCLUSIONS

Lithiation of arylphosphines, followed by quenching with a boron-containing electrophile and subsequent fluorination, yields trifluoroborate-functionalized phosphines, which form palladium chloromethyl complexes in a facile manner when reacted with PdClMe(COD). Cleavage of the Pd−Cl bond in attempts to access catalytically feasible compounds was found to be problematic under a variety of reaction conditions. To circumvent this problem, a series of zwitterionic phosphonium salts containing aryltrifluoroborate moieties have been reported and, in one instance, structurally characterized. Reaction with $PdMe_2$(tmeda) yielded zwitterionic palladium monomethyl complexes of the general formula [κ-(P)^{R}PdMe(tmeda)], which can be cleanly converted to the corresponding chelated species [κ^2-(P,F)^{R}PdMe(lutidine)] by reaction with 2,6-lutidine at ambient temperature. Such complexes have been crystallographically characterized and react slowly with ethylene at ambient temperature and pressure, yielding a mixture of butenes, propene, and hydrogen consistent with ethylene dimerization probably via a mechanism proposed by Jordan et al. for a related system.[37] In comparison to analogous sulfonated phosphine ligands and complexes, the rate of insertion is much slower and more limited in number. This is attributed to the relative electron deficiency of the trifluoroborate moiety as compared to sulfonate, resulting in an electron-deficient palladium center and more tightly bound lutidine.

EXPERIMENTAL DETAILS

General Considerations. Unless otherwise indicated, all manipulations were carried out in either an MBraun inert atmosphere glovebox or on a greaseless dual-manifold vacuum line using Teflon (Kontes) needle valves and swivel-frit-type glassware. Toluene, THF, and hexanes were dried using a Grubbs/Dow solvent purification system and stored in evacuated bombs prior to use. Dichloromethane was predried over CaH_2 before vacuum transfer into a separate evacuated bomb over CaH_2. $CDCl_3$ was purchased from Cambridge Isotopes and used as received for characterization of complexes; for ethylene experiments it was dried over CaH_2. Acetone-d_6, dimethylsulfoxide-d_6, and methanol-d_4 were purchased from Cambridge Isotopes and used as received. Potassium hydrogen fluoride, trimethylborate, tetrafluoroboric acid (as a 48% solution in water), ^{n}BuLi, pyridine, 2,2′-bipyridine, chlorobenzene, 2,6-lutidine, and DMAP were purchased from Aldrich and used as received. 18-Crown-6 was purchased from Acros Organics and used as received. Ethylene was purchased from Praxair and passed through an OxiClear gas purifier prior to use. PPh_2(2-Br-Ph),[39] PdClMe(COD),[40] and $PdMe_2$(tmeda)[41] were prepared according to literature procedures.

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$P(2\text{-OMe-Ph})_2(2\text{-Br-Ph})$[42] and $P^iPr_2(2\text{-Br-Ph})$[43] were prepared via literature procedures from $PCl_2(2\text{-Br-Ph})$,[44] which was obtained via a modified literature procedure, for which details are given. $[PdCl(\eta^3\text{-allyl})]_2$ was purchased from Strem, transferred to a glovebox freezer, and used as received. NMR spectra were obtained on Bruker AMX-300, AMX-400, and DRX-400 spectrometers. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to tetramethylsilane, $^{11}B\{^1H\}$ NMR spectra to $BF_3\cdot OEt_2$, ^{19}F NMR spectra to $CFCl_3$, and ^{31}P NMR spectra to 85% aqueous phosphoric acid. Full structural assignment was confirmed by 2-D NMR spectra where necessary. Elemental analyses and mass spectra were obtained by the Instrumentation Facility of the Department of Chemistry, University of Calgary. Quoted elemental analysis results are the average of two separate determinations.

$PPh_2(2\text{-}BF_3K\text{-Ph})$, 1a. A 250 mL round-bottomed flask was charged with $Ph_2P(2\text{-Br-Ph})$ (5.00 g, 14.7 mmol, ground and dried under high vacuum for 2 h prior to use to remove ethanol of recrystallization). THF (75 mL) was condensed in at −78 °C, and ^{n}BuLi (2.5 M in hexanes, 6.0 mL, 15.0 mmol) was added dropwise via syringe, resulting in a color change to orange. The reaction was stirred at low temperature for 2 h. Trimethylborate (8.3 mL, 73.5 mmol, 5 equiv) was added via syringe, resulting in an immediate reaction and dissipation of the reaction coloration to pale yellow. The reaction was allowed to warm to ambient temperature over the course of 30 min, before being allowed to stir overnight. Water (30 mL) was then added via syringe, resulting in the precipitation of a white solid from a pale yellow solution, which slowly redissolved with stirring. Diethyl ether (50 mL) was added, and the layers were separated. The aqueous layer was extracted with diethyl ether (2 × 50 mL). The organic phase was dried over $MgSO_4$ and the solvent removed to yield a viscous, white gum, which was dried under high vacuum to yield a white foam. [^1H NMR (300 MHz, $CDCl_3$, 298 K): δ 6.24 ppm (br s, 2H, $B(OH)_2$), 7.15−7.37 (m, 12H, aryl C-*H*), 7.75 (m, 1H, aryl C-*H*), 8.06 (m, 1H, aryl C-*H*). $^{31}P\{^1H\}$ NMR (162.00 MHz, $CDCl_3$, 298 K): δ −13.2 ppm (s, $PPh_2(2\text{-}B(OH)_2\text{-Ph})$).] The foam was dissolved in methanol (75 mL) in a 250 mL round-bottomed flask. A solution of KHF_2 (3.4 g, 44.1 mmol, 3 equiv) in water (15 mL) was added slowly, with stirring. After 1 min the solution became turbid; after ca. 5 min a white solid precipitated. The reaction was left to stir for 2 h at room temperature, before filtration under reduced pressure and washing with cold methanol and diethyl ether. The resulting white solid was dried under high vacuum before use. Yield: 2.96 g (8.0 mmol, 55%). ^1H NMR (400 MHz, $(CD_3)_2SO$, 298 K): δ 6.72 ppm (app. d of d, 1H, aryl C-*H*, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 4 Hz), 6.96 (t of d, 1H, aryl C-*H*, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.10 (m, 5H, aryl C-*H*), 7.25 (m, aryl C-H, 5H, aryl C-*H*), 7.44 (d of d, 1H, aryl C-*H*, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.53 (d of d, 1H, aryl C-*H*, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz). $^{13}C\{^1H\}$ NMR (75.5 MHz, $(CD_3)_2SO$, 298 K): δ 125.8 ppm (d, aryl C_q, $^1J_{CP}$ = 41 Hz), 127.1 (aryl *C*-H), 128.4 (d, aryl *C*-H, $^3J_{CP}$ = 5 Hz), 132.0 (d, aryl *C*-H, $^3J_{CP}$ = 5 Hz), 132.7 (aryl *C*-H), 133.5 (d, aryl *C*-H, $^2J_{CP}$ = 19 Hz), 139.0 (d, aryl *C*-H, $^2J_{CP}$ = 19 Hz), 141.4 (d, aryl *C*-H, $^3J_{CP}$ = 16 Hz). Carbon adjacent to boron not observed. $^{11}B\{^1H\}$ NMR (128.4 MHz, $(CD_3)_2SO$, 298 K): δ +2.9 ppm (br s, $C_6H_4BF_3K$). ^{19}F NMR (376.6 MHz, $(CD_3)_2SO$, 298 K): δ −133.3 ppm (br s, $C_6H_4BF_3K$). $^{31}P\{^1H\}$ NMR (162.0 MHz, $(CD_3)_2SO$, 298 K): δ −7.7 ppm (q, $PPh_2(2\text{-}BF_3K\text{-Ph})$, $^4J_{PF}$ = 34 Hz). HRMS (ESI −ve): calcd for $[M^-]$ *m*/*z* 329.09201; found 329.08897.

Improved Synthesis of $PCl_2(2\text{-Br-Ph})$. The reaction between PCl_3 and 2-bromophenyldiazonium tetrafluoroborate was carried out according to the reported methods of Talay and Rehder,[44a] and Wills et al.,[44b] as far as the overnight reaction with Al powder in acetonitrile. After the overnight reaction, all volatiles were removed *in vacuo* to yield a viscous, brown residue. Dry toluene (50 mL) was condensed in at −78 °C, and the resulting suspension left to stir vigorously for one hour. The reaction mixture was then allowed to settle and filtered to remove insoluble Al and $BF_3\cdot$NCMe, yielding an orange solution, which was concentrated *in vacuo* to yield the title compound as a yellow-orange oil. Yield: typically 50−55%. ^1H NMR spectroscopy showed the material to be essentially pure. ^{31}P NMR spectroscopy showed the title compound present in ca. 95% purity. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.41 (t of d, 1H, aryl C-*H*, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 7.56 (t of d, 1H, aryl C-*H*, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 7.62 (d of t, aryl C-*H*, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 8.11 (d of d, 1H, aryl C-*H*, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz). $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 298 K): δ +154.0 ppm (s, $PCl_2(2\text{-Br-Ph})$).

$P(2\text{-OMe-Ph})_2(2\text{-}BF_3K\text{-Ph})$, 1b. As for **1a**, using $P(2\text{-OMe-Ph})_2(2\text{-Br-Ph})$ (1.30 g, 3.2 mmol), ^{n}BuLi (1.3 mL of a 2.5 M solution in hexanes, 1 equiv), and trimethylborate (1 mL) in THF (50 mL), and then KHF_2 (0.75 g, 9.6 mmol) in water (5 mL), yielded the title compound as an off-white, crystalline solid. Yield: 1.05 g (2.3 mmol, 71%). Single crystals suitable for X-ray diffraction were grown from a saturated acetone solution. ^1H NMR (400 MHz, $(CD_3)_2CO$, 298 K): δ 3.61 ppm (s, 6H, 2 × OCH_3), 6.63 (m, 2H, aryl C-*H*), 6.79 (m, 3H, aryl C-*H*), 6.94 (m, 3H, aryl C-*H*), 7.11 (m, 1H, aryl C-*H*), 7.26 (m, 2H, aryl C-*H*), 7.71 (m, 1H, aryl C-*H*). $^{13}C\{^1H\}$ NMR (100.6 MHz, $(CD_3)_2SO$, 298 K): δ 55.9 ppm (OCH_3), 110.8, 120.8, 125.9, 126.8 (all aryl *C*-H), 128.8 (d, $^1J_{CP}$ = 20 Hz, aryl C_q), 129.4 (aryl *C*-H), 132.7 (d, aryl *C*-H, $^2J_{CP}$ = 10 Hz), 134.0 (aryl *C*-H), 138.8 (d, aryl C_q, $^2J_{CP}$ = 17 Hz), 161.1 (d, aryl C_q, $^2J_{CP}$ = 16 Hz). Carbon adjacent to boron not observed. $^{11}B\{^1H\}$ NMR (128.4 MHz, $(CD_3)_2SO$, 298 K): δ +3.6 ppm (br s, $C_6H_4BF_3K$). ^{19}F NMR (376.6 MHz, $(CD_3)_2CO$, 298 K): δ −137.0 ppm (br s, $C_6H_4BF_3K$). $^{31}P\{^1H\}$ NMR (162.0 MHz, $(CD_3)_2CO$, 298 K): δ −31.4 ppm (q, $P(2\text{-OMe-Ph})_2(2\text{-}BF_3K\text{-Ph})$, $^4J_{PF}$ = 39 Hz). Anal. Calcd for $C_{20}H_{18}BF_3KO_2P\cdot(H_2O)_{1.5}$: C, 52.77; H, 4.65. Found: C, 52.74; H, 4.27. MS (ESI −ve): *m*/*z* 389 $[M^+ - K]$.

$[PPh_2(2\text{-}BF_3\text{-Ph})][K(18\text{-crown-6})]$, 2a. A 100 mL round-bottomed flask was charged with **1a** (1.75 g, 4.8 mmol) and a magnetic stir bar. Acetone (25 mL) was added. To the resulting white slurry was added dropwise a solution of 18-crown-6 (1.25 g, 4.8 mmol) in acetone (10 mL). The suspended white solid slowly dissolved on addition of the crown ether solution; the colorless solution was left to stir at ambient temperature. After a period of ca. 30 min a white solid was seen to precipitate. The solution was heated to dissolve the white solid, before being allowed to cool to ambient temperature; the title compound precipitated as a highly crystalline, colorless solid, which was isolated by filtration and dried *in vacuo*. Concentration of the supernatant and storage at low temperature yielded further crops of material. Yield: 1.73 g (2.7 mmol, 58%). Single crystals suitable for X-ray diffraction were grown by the slow cooling of a saturated acetone solution. ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ 3.59 ppm (s, 24H, OCH_2 of 18-crown-6), 6.95 (t, 1H, aryl C-*H*, $^3J_{HH}$ = 7 Hz), 7.07 (t, 1H, aryl C-*H*, $^3J_{HH}$ = 7 Hz), 7.23 (m, 7H, aryl C-*H*), 7.32−7.35 (m, 4H, aryl C-*H*), 7.87 (m, 1H, aryl C-*H*). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 298 K): δ 70.0 ppm (OCH_2 of 18-crown-6), 126.7 (d, aryl C_q, $^1J_{CP}$ = 75 Hz), 127.1 (aryl *C*-H), 127.7 (d, aryl *C*-H, $^3J_{CP}$ = 8 Hz), 127.8 (d, aryl *C*-H, $^3J_{CP}$ = 8 Hz), 132.7 (d, aryl *C*-H, $^2J_{CP}$ = 19 Hz), 133.7 (d, aryl *C*-H, $^2J_{CP}$ = 18 Hz) 138.6, 141.0 (both d, aryl *C*-H, $^3J_{CP}$ = 15 Hz). Carbon adjacent to boron not observed. $^{11}B\{^1H\}$ NMR (128.4 MHz, $CDCl_3$, 298 K): δ +2.9 ppm (br s, $C_6H_4BF_3$). ^{19}F NMR (376.6 MHz, $CDCl_3$, 298 K): δ −134.3 ppm (br s, $C_6H_4BF_3$). $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 298 K): δ −6.4 ppm (q, $PPh_2(2\text{-}BF_3\text{-Ph})$), $^4J_{PF}$ = 35 Hz). Anal. Calcd for $C_{30}H_{38}BF_3KO_6P.C_3H_6O$: C, 55.82; H, 6.25. Found: C, 55.90; H, 5.97. MS (ESI −ve): *m*/*z* 329 $[M - K(18\text{-crown-6})]$.

$[P(2\text{-OMe-Ph})_2(2\text{-}BF_3\text{-Ph})][K(18\text{-crown-6})]$, 2b. As for **2a**, using **1b** (0.300 g, 0.65 mmol) and 18-crown-6 (0.175 g, 0.65 mmol) in acetone (2 mL) yielded a highly crystalline, colorless solid. Yield: 0.427 g (0.59 mmol, 91%). ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ 2.19 ppm (s, 6H, CH_3 of acetone), 3.54 (s, 24H, OCH_2 of 18-crown-6), 3.62 (s, 6H, 2 × OCH_3), 6.77−6.84 (m, 6H, aryl C-*H*), 7.00 (t, 1H, aryl C-*H*, $^3J_{HH}$ = 7 Hz), 7.18−7.22 (m, 3H, aryl C-*H*), 7.86 (m, 1H, aryl C-*H*). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K): δ 55.8 ppm (OCH_3), 69.9

(OCH_2 of 18-crown-6), 110.7, 120.7, 125.6, 126.5, 129.2 (all aryl *C*-H), 129.4 (d, $^1J_{CP}$ = 22 Hz, aryl C_q), 132.5 (aryl *C*-H), 132.8 (d, $^3J_{CP}$ = 8 Hz, aryl *C*-H), 134.0 (aryl *C*-H), 139.9 (d, $^1J_{CP}$ = 20 Hz, aryl C_q), 162.1 (d, $^2J_{CP}$ = 17 Hz, aryl C_q). Carbon adjacent to boron not observed. $^{11}B\{^1H\}$ NMR (128.4 MHz, $(CD_3)_2SO$, 298 K): δ +2.8 ppm (br s, $C_6H_4BF_3$). ^{19}F NMR (376.6 MHz, $CDCl_3$, 298 K): δ −136.5 ppm (br s, $C_6H_4BF_3$). $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 298 K): δ − 25.5 ppm (q, *P*(2-OMe-Ph)$_2$(2-BF_3-Ph), $^4J_{PF}$ = 35 Hz). Anal. Calcd for $C_{32}H_{42}BF_3KO_8P$: C, 55.50; H, 6.11. Found: C, 55.26; H, 6.12. MS (ESI −ve): *m*/*z* 389 [M − K(18-crown-6)].

[κ^2-(P,F)^{Ph}PdClMe][K(18-crown-6)], 3a. A 50 mL round-bottomed flask was charged with PdClMe(COD) (0.20 g, 0.74 mmol) and **2a** (0.576 g, 0.74 mmol). Dichloromethane was syringed in at room temperature, and the resulting pale yellow-green solution stirred at room temperature overnight (a small amount of Pd(0) was deposited during the reaction). The reaction mixture was filtered through Celite to yield a clear, yellow solution; removal of volatiles *in vacuo* yielded the title compound as a crystalline, pale yellow solid, which was crystallized by the slow evaporation of a dichloromethane solution. Yield: 0.241 g (0.27 mmol, 36%). Single crystals suitable for X-ray diffraction were grown by the slow evaporation of an acetone solution. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.75 ppm (d, 3H, Pd-C*H*$_3$, $^3J_{PH}$ = 2 Hz), 3.56 (s, 24H, OC*H*$_2$ of 18-crown-6), 6.87 (t, 1H, aryl C-*H*, $^3J_{HH}$ = 7 Hz), 7.12 (t, 1H, aryl C-*H*, $^3J_{HH}$ = 7 Hz), 7.36−7.54 (m, 11H, aryl C-*H*), 7.73 (m, 1H, aryl C-*H*). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K): δ −2.7 ppm (Pd-*C*H$_3$), 70.0 (OCH_2 of 18-crown-6), 126.0 (d, aryl *C*-H, $^3J_{CP}$ = 8 Hz), 128.0 (d, aryl *C*-H, $^2J_{CP}$ = 12 Hz), 128.3 (d, aryl *C*-H, $^2J_{CP}$ = 12 Hz), 129.2, 129.7 (both aryl *C*-H), 132.2 (d, aryl C_q, $^1J_{CP}$ = 43 Hz), 132.4 (aryl *C*-H), 132.8 (d, aryl *C*-H, $^2J_{CP}$ = 12 Hz), 134.2 (d, aryl *C*-H, $^2J_{CP}$ = 12 Hz). Carbon adjacent to boron not observed. $^{11}B\{^1H\}$ NMR (128.4 MHz, $CDCl_3$, 298 K): δ +2.9 ppm (br s, $C_6H_4BF_3$). $^{19}F\{^1H\}$ NMR (376.6 MHz, $CDCl_3$, 298 K): δ −152.9 ppm (br s, $C_6H_4BF_3Pd$). $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 298 K): δ +31.1 ppm (s, *P*Ph_2(2-BF_3K(18-crown-6)-Ph). Anal. Calcd for $C_{31}H_{41}O_6BF_3KPPdCl\cdot(CH_2Cl_2)_{0.2}$: C, 46.47; H, 5.17. Found: C, 46.74; H, 5.33. MS (ESI −ve): *m*/*z* 484 [M − K(18-crown-6)].

[κ-(P)^{Ar}PdClMe]$_2$[K(18-crown-6)]$_2$, 3b. As for **3a**, using **2b** (0.3.00 g, 0.38 mmol) and PdClMe(COD) (0.102 g, 0.38 mmol) yielded the title compound, after crystallization from toluene, as a highly crystalline yellow solid. Yield: 0.155 g (0.082 mmol, 43%). ^1H NMR (400 MHz, $CDCl_3$, 298 K) (major isomer only): δ 1.07 ppm (d, 3H, Pd-C*H*$_3$, $^3J_{PH}$ = 2 Hz), 3.60 (s, 24H, OC*H*$_2$ of 18-crown-6), 3.80 (s, 6H, OC*H*$_3$), 6.87−6.93 (m, 4H, aryl C-*H*), 7.03 (m, 2H, aryl C-*H*), 7.31 (t, 1H, aryl C-*H*, $^3J_{HH}$ = 7 Hz), 7.36−7.42 (m, 4H, aryl C-*H*), 7.87 (m, 1H, aryl C-*H*). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K) (major isomer only): δ −3.3 ppm (Pd-*C*H$_3$), 56.2 (O*C*H$_3$), 70.0 (OCH_2 of 18-crown-6), 110.8 (aryl *C*-H), 119.4 (d, $^1J_{CP}$ = 51 Hz, aryl *C*-H), 119.8 (d, $^3J_{CP}$ = 11 Hz, aryl *C*-H), 120.9 (d, $^3J_{CP}$ = 10 Hz, aryl *C*-H), 120.9 (d, $^1J_{CP}$ = 51 Hz, aryl C_q), 125.3 (d, $^3J_{CP}$ = 10 Hz, aryl *C*-H), 128.9, 131.8 (both aryl *C*-H), 132.7 (d, $^3J_{CP}$ = 10 Hz, aryl *C*-H), 134.1 (d, $^2J_{CP}$ = 16 Hz, aryl *C*-H), 136.2 (d, $^3J_{CP}$ = 10 Hz, aryl *C*-H), 160.7 (aryl C_q). Carbon adjacent to boron not observed. $^{11}B\{^1H\}$ NMR (128.4 MHz, $CDCl_3$, 298 K): δ +3.2 ppm (br s, $C_6H_4BF_3$). ^{19}F NMR (376.6 MHz, $CDCl_3$, 298 K): δ −136.9 ppm (br s, $C_6H_4BF_3$). $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 298 K): δ +29.4 ppm (s, *P*(2-OMe-Ph)$_2$(2-BF_3-Ph)). Anal. Calcd for $C_{66}H_{90}B_2F_6K_2O_{16}P_2Pd_2Cl_2\cdot(C_7H_8)_{0.5}$: C, 47.84; H, 5.43. Found: C, 47.99; H, 5.36. MS (ESI −ve): *m*/*z* 1055 [M^{2-} − 2 K (18-crown-6) − Cl], 546 [M^{2-} − 2 K(18-crown-6)].

[κ-(P)^{Ph}PdCl(η^3-allyl)], 4a. A 50 mL round-bottomed flask was charged in the glovebox with [PdCl(η^3-allyl)]$_2$ (0.20 g, 0.55 mmol) and **2a** (0.691 g, 1.10 mmol). Dichloromethane was condensed in at −78 °C, and the reaction was slowly allowed to warm to room temperature, yielding a yellow solution. The reaction was left to stir at room temperature overnight, and all volatiles were removed *in vacuo* to yield the title compound as an off-white solid, which was crystallized from acetone. Yield: 0.845 g (1.04 mmol, 94%). ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 3.08 ppm (d, 1H, allylic C*H*$_2$, $^3J_{HH}$ = 12 Hz), 3.09 (d, 1H, allylic C*H*$_2$, $^3J_{HH}$ = 7 Hz), 3.39 (d of d, 1H, =C*H*$_2$, $^2J_{HH}$ = 14 Hz, $^3J_{HH}$ = 10 Hz), 3.47 (s, 24H, OC*H*$_2$ of 18-crown-6), 4.23 (m, 1H, =C*H*$_2$), 5.56 (m, 1H, =C-*H*), 6.48 (t, 1H, aryl C-*H*, J_{HH} = 7 Hz), 6.95 (t, 1H, aryl C-*H*, $^3J_{HH}$ = 7 Hz), 7.25 (m, 7H, aryl C-*H*), 7.68 (m, 5H, aryl C-*H*). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 298 K): δ 53.5, 62.7 ppm (both allyl *C*-H), 70.0 (OCH_2 of 18-crown-6), 74.5 (d, allyl *C*-H, $^1J_{CP}$ = 32 Hz), 117.0 (d, allyl *C*-H, $^4J_{CP}$ = 5 Hz), 125.9 (d, aryl *C*-H, $^3J_{CP}$ = 8 Hz), 127.7 (br), 128.4, 129.0 (all aryl *C*-H), 130.4 (d, aryl *C*-H, $^3J_{CP}$ = 8 Hz), 134.4 (d, aryl *C*-H, $^2J_{CP}$ = 13 Hz), 135.2 (d, aryl *C*-H, $^2J_{CP}$ = 13 Hz), 135.9 (d, aryl C_q, $^1J_{CP}$ = 37 Hz). Carbon adjacent to boron not observed. $^{11}B\{^1H\}$ NMR (128.4 MHz, $CDCl_3$, 298 K): δ +3.6 ppm (br s, $C_6H_4BF_3$). ^{19}F NMR (376.6 MHz, $CDCl_3$, 298 K): δ −132.3 ppm (br s, $C_6H_4BF_3$). $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 298 K): δ +22.5 ppm (s, *P*Ph_2(2-BF_3-Ph)) Anal. Calcd for $C_{33}H_{43}BF_3KO_6PPdCl$: C, 48.62; H, 5.32. Found: C, 48.66; H, 5.37. MS (ESI −ve): *m*/*z* 511 [M − K(18-crown-6)].

PHPh$_2$(2-BF_3-Ph), 5a. Potassium salt **1a** (3.25 g, 8.8 mmol) was slurried in THF (50 mL). HBF_4 (1.6 mL of a 48 wt % solution in water, 8.8 mmol) was added, and the white suspension left to stir at room temperature for 2 h. All volatiles were removed under reduced pressure, and the white solid was extracted with chloroform (3 × 50 mL). The solvent was removed under reduced pressure to yield the title compound as a white solid. Yield: 2.87 g (8.7 mmol, 95%). While generally pure enough for subsequent use, the compound could be recrystallized from hot acetonitrile, if necessary. Single crystals suitable for X-ray diffraction were grown by the slow evaporation of a saturated acetonitrile solution. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.21 ppm (t, 1H, aryl C-*H*, $^3J_{HH}$ = 7 Hz), 7.35 (m, 1H, aryl C-*H*), 7.57−7.67 (m, 9H, aryl C-*H*), 7.76 (m, 2H, aryl C-*H*), 8.13 (m, 1H, aryl C-*H*), 8.85 (d, 1H, *H*-PPh_2(2-BF_3−Ph), $^1J_{PH}$ = 540 Hz). $^{13}C\{^1H\}$ NMR (100.6 MHz, $(CD_3)_2SO$, 298 K): δ 125.0 ppm (d, aryl C_q, $^1J_{CP}$ = 50 Hz), 126.8 (d, aryl C_q, $^1J_{CP}$ = 51 Hz), 127.2 (d, aryl *C*-H, $^3J_{CP}$ = 9 Hz), 127.9 (d, aryl *C*-H, $^2J_{CP}$ = 19 Hz), 128.4 (aryl *C*-H), 128.7 (d, aryl *C*-H, $^4J_{CP}$ = 6 Hz), 129.7 (d, aryl *C*-H, $^3J_{CP}$ = 11 Hz), 131.6, 132.3, 133.3 (all aryl *C*-H), 133.5 (d, aryl *C*-H, $^4J_{CP}$ = 5 Hz), 133.7 (d, aryl *C*-H, $^4J_{CP}$ = 6 Hz), 134.0 (d, aryl *C*-H, $^3J_{CP}$ = 13 Hz). Carbon adjacent to boron not observed. $^{11}B\{^1H\}$ NMR (128.4 $CDCl_3$, 298 K): δ +2.4 ppm (br s, $C_6H_4BF_3$). ^{19}F NMR (376.6 MHz, $CDCl_3$, 298 K): δ −136.2 ppm (br s, $C_6H_4BF_3$). $^{31}P\{^1H\}$ NMR (162.00 MHz, $CDCl_3$, 298 K): +5.5 ppm (s, H*P*Ph_2(2-BF_3-Ph)). ^{31}P NMR (162.00 MHz, $CDCl_3$, 298 K): +5.5 ppm (d, $^1J_{PH}$ = 540 Hz, H*P*Ph_2(2-BF_3-Ph). Anal. Calcd for $C_{18}H_{15}BF_3P$: C, 65.50; H, 4.58. Found: C, 65.26; H, 4.62. MS (EI +ve): *m*/*z* 310 [M^+ − HF], 180 [M^+ − $C_6H_4BF_3$].

PH(2-OMe-Ph)$_2$(2-BF_3-Ph), 5b. As for **5a**, using **1b** (1.05 g, 2.30 mmol) and HBF_4 (48 wt % aq) (0.37 mL, 4.2 mmol) yielded the title compound as an off-white, hygroscopic solid. Yield: 0.830 g, 2.12 mmol, 92%. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 3.81 ppm (s, 6H, 2 × OC*H*$_3$), 7.04−7.09 (m, 7H, aryl C-*H*), 7.62 (t, 1H, aryl C-*H*, $^3J_{HH}$ = 7 Hz), 7.68 (m, 2H, aryl C-*H*), 8.08 (t, 1H, aryl C-*H*, $^3J_{HH}$ = 7 Hz), 8.96 (d, 1H, *H*-P(2-OMe-Ph)$_2$(2-BF_3-Ph), $^1J_{PH}$ = 572 Hz). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K): δ 56.3 ppm (O*C*H$_3$), 106.8 (d, aryl C_q, $^1J_{CP}$ = 94 Hz), 111.7 (aryl *C*-H), 116.2 (d, aryl C_q, $^1J_{CP}$ = 93 Hz), 121.8 (d, aryl *C*-H, $^2J_{CP}$ = 13 Hz), 126.8 (d, aryl *C*-H, $^2J_{CP}$ = 14 Hz), 131.9 (d, aryl *C*-H, $^2J_{CP}$ = 15 Hz), 133.0 (d, aryl *C*-H), 134.5 (d, aryl *C*-H, $^2J_{CP}$ = 15 Hz), 136.4 (d, aryl *C*-H, $^3J_{CP}$ = 8 Hz), 161.0 (aryl C_q of $C_6H_4OCH_3$). Carbon adjacent to boron not observed. $^{11}B\{^1H\}$ NMR (128.4 MHz, $CDCl_3$, 298 K): δ +2.6 ppm (br s, $C_6H_4BF_3$). ^{19}F NMR (376.6 MHz, $CDCl_3$, 298 K): δ −138.0 ppm (br s, $C_6H_4BF_3$). ^{31}P NMR (162.0 MHz, $CDCl_3$, 298 K): δ −11.8 ppm (d, H-*P*(2-OMe-Ph)$_2$(2-BF_3-Ph), $^1J_{PH}$ = 572 Hz). $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 298 K): δ −11.8 ppm (s, H-*P*(2-OMe-Ph)$_2$(2-BF_3-Ph)), Anal. Calcd for $C_{20}H_{19}BF_3O_2P\cdot$

$(H_2O)_{0.5}$: C, 60.18; H, 5.05. Found: C, 60.54; H, 5.29. MS (EI −ve): m/z 370 [M^+ − HF], 336 [M^+ − HF − OMe].

PH^{i}Pr$_2$(2-BF$_3$-Ph), 5c. In a manner similar to the synthesis of **1a/b**, a 100 mL round-bottomed flask was charged with a solution of ^{i}Pr$_2$P(2-Br-Ph) (2.49 g, 9.2 mmol) in THF (40 mL) and cooled to −78 °C. ^{n}BuLi (3.7 mL of a 2.5 M solution in hexanes, 9.2 mmol) was added dropwise, with a concomitant color change to orange. The reaction was left to stir at low temperature for two hours, before addition of trimethylborate (4.7 mL, 46.0 mmol, 5 equiv). The reaction was allowed to warm to room temperature, yielding a yellow solution, which was left to stir at ambient temperature overnight. The reaction was quenched by the addition of water (0.5 mL, 28.0 mmol), left to stir for 30 min, and all volatiles were then removed by prolonged drying *in vacuo* to yield an off-white solid. THF (40 mL) was condensed in, and the resultant slurry treated with HBF_4 (1.9 mL of a 48% solution in water, 9.2 mmol, 1 equiv), resulting in a clear, yellow solution. All volatiles were removed after 1 h to yield a viscous, white paste. [^{1}H NMR (400 MHz, CD_3OD, 298 K): δ 1.22 ppm (d of d, 6H, CH_3 of ^{i}Pr, $^3J_{PH}$ = 19 Hz, $^3J_{HH}$ = 7 Hz), 1.42 ppm (d of d, 6H, CH_3 of ^{i}Pr, $^3J_{PH}$ = 19 Hz, $^3J_{HH}$ = 7 Hz), 3.03 (m, 1H, CH of ^{i}Pr, $^3J_{HH}$ = 7 Hz), 7.45 (m, 1H, aryl C-H), 7.62 (m, 2H, aryl C-H), 7.85 (m, 1H, aryl C-H). Boronic acid and phosphonium protons not observed due to H/D exchange.] The compound thus obtained was dissolved in methanol, and a solution of KHF_2 (2.10 g, 27.0 mmol) in water (15 mL) was added. The resulting white suspension was left to stir for one hour, whereupon all volatiles were removed, and the product was extracted in chloroform (3 × 50 mL). Removal of the solvent under reduced pressure yielded the title compound as an off-white, waxy solid. Yield: 1.22 g (4.7 mmol, 51%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.28 ppm (d of d, 6H, CH_3 of ^{i}Pr, $^3J_{PH}$ = 18 Hz, $^3J_{HH}$ = 7 Hz), 1.47 ppm (d of d, 6H, CH_3 of ^{i}Pr, $^3J_{PH}$ = 18 Hz, $^3J_{HH}$ = 7 Hz), 2.99 (m, 2H, CH of ^{i}Pr), 6.44 (d, v br, 1H, H-P^{i}Pr$_2$(2-BF$_3$-Ph), $^1J_{PH}$ = 464 Hz), 7.38 (m, 1H, aryl C-H), 7.47 (m, 1H, aryl C-H), 7.62 (m, 1H, aryl C-H), 8.01 (m, 1H, aryl C-H). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 298 K): δ 18.0 ppm (d, CH_3 of ^{i}Pr, $^2J_{CP}$ = 16 Hz), 22.2 (d, CH of ^{i}Pr, $^1J_{CP}$ = 44 Hz), 115.1 (d, aryl C_q, $^1J_{CP}$ = 78 Hz), 125.8 (d, aryl C-H, $^3J_{CP}$ = 13 Hz), 127.1 (d, aryl C-H, $^3J_{CP}$ = 13 Hz), 133.4 (aryl C-H), 134.6 (d, aryl C-H, $^2J_{CP}$ = 16 Hz). Carbon adjacent to boron not observed. ^{11}B{^{1}H} NMR (128.4 MHz, $CDCl_3$, 298 K): δ +2.6 ppm (br s, $C_6H_4BF_3$). ^{19}F NMR (376.6 MHz, $CDCl_3$, 298 K): δ −136.4 ppm (br s, $C_6H_4BF_3$). ^{31}P NMR (162.0 MHz, $CDCl_3$, 298 K): δ +30.2 ppm (br d, H-P^{i}Pr$_2$(2-BF$_3$-Ph), $^1J_{PH}$ = 550 Hz). ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$, 298 K): δ +30.2 ppm (br s, H-P^{i}Pr$_2$(2-BF$_3$-Ph)). Anal. Calcd for $C_{12}H_{19}BF_3P$: C, 55.00; H, 7.31. Found: C, 55.10; H, 7.21. MS (ESI −ve): m/z 261 [M^- − H].

[κ-(P)^{Ph}PdMe(tmeda)], 6a. A 100 mL round-bottomed flask was charged with $PdMe_2$(tmeda) (0.288 g, 1.14 mmol), **5a** (0.379 g, 1.14 mmol), and stir bar. Dichloromethane (25 mL) was condensed in at −78 °C. The flask was refilled with argon and allowed to warm to room temperature, yielding effervescence and a color change from colorless to yellow. The reaction was stirred one hour at room temperature before all volatiles were removed *in vacuo* to yield a yellow, foamy residue. Dissolution in chlorobenzene (in air) and leaving to stand yielded the title compound as a crystalline, off-white solid. Yield: 0.457 g (0.81 mmol, 71%). Further material was obtained by concentration of the supernatant. Single crystals suitable for X-ray diffraction were grown from the slow cooling of a hot toluene solution. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.32 ppm (d, 3H, Pd-CH_3, $^3J_{PH}$ = 4 Hz), 2.34 (s, 12H, 4 × NCH_3 of tmeda), 2.58 (s, 4H, 2 × NCH_2 of tmeda), 7.02 (m, 1H, aryl C-H), 7.12 (m, 1H, aryl C-H), 7.26−7.37 (m, 7H, aryl C-H), 7.66 (m, 4H, aryl C-H), 8.10 (m, 1H, aryl C-H). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 298 K): δ 5.6 ppm (d, Pd-CH_3, $^2J_{CP}$ = 9 Hz), 49.0 (NCH_3 of tmeda) 60.5 (NCH_2 of tmeda), 125.4 (d, aryl C-H, $^2J_{CP}$ = 9 Hz), 127.7 (d, aryl C-H, $^2J_{CP}$ = 9 Hz), 129.2, 129.8, 130.1, 130.2 (all aryl C-H), 130.7 (d, aryl C_q, $^1J_{CP}$ = 52 Hz), 132.1 (d, aryl C_q, $^1J_{CP}$ = 46 Hz), 135.4 (d, aryl C-H, $^2J_{CP}$ = 11 Hz), 136.7 (d, aryl C-H, $^2J_{CP}$ = 11 Hz). Carbon adjacent to boron not observed. ^{11}B{^{1}H} NMR (128.4 MHz, $CDCl_3$, 298 K): δ +3.4 ppm (br s, $C_6H_4BF_3$). ^{19}F NMR (376.6 MHz, $CDCl_3$, 298 K): δ −133.1 ppm (br s, $C_6H_4BF_3$). ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$, 298 K): δ +41.2 ppm (s, PPh$_2$(2-BF$_3$-Ph). Anal. Calcd for $C_{25}H_{33}N_2BF_3PPd$: C, 52.98; H, 5.87; N, 4.94. Found: C, 52.53; H, 5.80; N, 4.77. MS (ESI +ve): m/z 567 [M^+ + H], 547 [M^+ − F], 499 [M^+ − BF_3].

[κ-(P)^{Ar}PdMe(tmeda)], 6b. As for **6a**, using $PdMe_2$(tmeda) (0.47 g, 1.9 mmol) and **5b** (0.700 g, 1.9 mmol) yielded a hygroscopic, white solid. Yield: 0.351 g (0.60 mmol, 32%). Single crystals suitable for X-ray diffraction were grown via the slow evaporation of a chlorobenzene solution. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.20 ppm (br s, 3H, Pd-CH_3), 2.10 (br s, 4H, 2 × NCH_2 tmeda), 2.63 (br s, 12H, 4 × NCH_3 of tmeda), 3.49 (br s, 6H, OCH_3 of aryl), 6.77 (br m, 2H, aryl C-H), 6.99 (br m, 5H, aryl C-H), 7.32 (m, 3H, aryl C-H), 7.79 (br s, 1H, aryl C-H), 8.05 (br s, 1H, aryl C-H). ^{1}H NMR (400 MHz, $CDCl_3$, 230 K): δ 0.08 ppm (d, 3H, Pd-CH_3, $^3J_{PH}$ = 2 Hz), 2.01 (s, 4H, 2 × NCH_2 of tmeda), 2.55 (s, 6H, 2 × NCH_3 of tmeda), 2.67 (s, 3H, NCH_3 of tmeda), 3.02 (s, 3H, NCH_3 of tmeda), 3.05 (s, 3H, OCH_3), 3.09 (s, OCH_3), 6.60 (m, 1H, aryl C-H), 6.78 (d of d, 1H, aryl C-H, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz), 6.92 (t, 1H, aryl C-H, $^3J_{HH}$ = 7 Hz), 7.02 (m, 2H, overlapping, aryl C-H), 7.09 (t, 1H, aryl C-H, $^3J_{HH}$ = 7 Hz), 7.21 (1H, aryl C-H, $^3J_{HH}$ = 7 Hz), 7.36 (1H, aryl C-H, $^3J_{HH}$ = 7 Hz), 7.47 (1H, aryl C-H, $^3J_{HH}$ = 7 Hz), 7.71 (1H, aryl C-H, $^3J_{HH}$ = 7 Hz), 8.07 (m, 1H, aryl C-H), 8.59 (m, 1H, aryl C-H). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 298 K, all resonances broad): δ 6.0 ppm (Pd-CH_3), 49.9 (CH_3 of tmeda), 54.7 (OCH_3), 60.4 (NCH_2 of tmeda), 111.2, 120.1, 120.3, 124.8, 126.5, 128.4, 128.6, 129.8, 131.3, 134.6 (all aryl C-H), 138.5, 142.6, 160.9 (all aryl C_q). Carbon adjacent to boron not observed. ^{11}B{^{1}H} NMR (128.4 MHz, $CDCl_3$, 298 K): δ +3.0 ppm (br s, $C_6H_4BF_3$). ^{19}F NMR (376.6 MHz, $CDCl_3$, 298 K): δ −133.1 ppm (br s, $C_6H_4BF_3$). ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$, 298 K): δ +36.0 ppm (s, P(2-OMe-Ph)$_2$(2-BF$_3$-Ph)). Anal. Calcd for $C_{27}H_{37}N_2BF_3O_2PPd\cdot(H_2O)_{1.5}$: C, 49.60; H, 6.17; N, 4.66. Found: C, 49.39; H, 5.92; N, 4.28. MS (ESI −ve): m/z 543 [M^+ − CH_3 − BF_3], 495 [M^+ − tmeda − CH_3].

[κ-(P)$^{i\text{-}Pr}$PdMe(tmeda)], 6c. As for **6a**, using $PdMe_2$(tmeda) (0.500 g, 2.0 mmol) and **5c** (0.520 g, 2.0 mmol) yielded a white, crystalline solid from a dichloromethane/diethyl ether solution. Yield: 0.279 g (0.60 mmol, 30%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.54 ppm (d, 3H, Pd-CH_3, $^3J_{PH}$ = 2 Hz), 1.26 (d, 6H, 2 × CH_3 of ^{i}Pr, $^3J_{HH}$ = 7 Hz), 1.33 (d, 6H, 2 × CH_3 of ^{i}Pr, $^3J_{HH}$ = 7 Hz), 2.43 (s, 12H, 4 × NCH_3 of tmeda), 2.59 (s, 4H, 2 × NCH_2 of tmeda), 2.70 (m, 2H, 2 × CH of ^{i}Pr), 7.17 (t, 1H, aryl C-H, $^3J_{HH}$ = 7 Hz), 7.27−7.36 (m, 2H, aryl C-H), 8.02 (d of d, 1H, aryl C-H). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 298 K): δ 0.39 ppm (app. s, Pd-CH_3), 19.9, 20.4 (CH_3 of ^{i}Pr), 24.8 (d, CH of ^{i}Pr, $^1J_{CP}$ = 25 Hz), 49.4 (CH_3 of tmeda), 60.4 (CH_2 of tmeda), 124.9 (d, aryl C-H, $^1J_{CP}$ = 8 Hz), 128.6 (d, aryl C_q, $^1J_{CP}$ = 43 Hz), 128.8 (d, aryl C-H, $^1J_{CP}$ = 4 Hz), 129.5 (d, aryl C-H, $^1J_{CP}$ = 5 Hz), 136.2 (d, aryl C-H, $^1J_{CP}$ = 17 Hz). Carbon adjacent to boron not observed. ^{11}B{^{1}H} NMR (128.4 MHz, $CDCl_3$, 298 K): δ +3.1 ppm (br s, $C_6H_4BF_3$). ^{19}F NMR (376.6 MHz, $CDCl_3$, 298 K): δ −132.4 ppm (br s, $C_6H_4BF_3$). ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$, 298 K): δ +41.6 ppm (s, P^iPr$_2$(2-BF$_3$-Ph). Anal. Calcd for $C_{19}H_{37}N_2BF_3PPd\cdot(CH_2Cl_2)_{0.25}$: C, 44.47; H, 7.27; N, 5.39. Found: C, 44.49; H, 7.58; N, 5.55. MS (ESI +ve): m/z 431 [M^+ − BF_3], 415 [M^+ − BF_3 − Me].

[κ-(P)^{Ph}PdMe(py)$_2$], 7a. A 25 mL round-bottomed flask was charged with **6a** (0.52 g, 0.91 mmol) and dissolved in pyridine. The reaction was stirred for two hours at ambient temperature before all volatiles were removed *in vacuo*. The residue was washed with diethyl ether and dried to yield the title compound as a yellow foam, which was crystallized from dichloromethane. Yield: 0.360 g (0.59 mmol, 65%). Single crystals suitable for X-ray diffraction were grown by the diffusion of diethyl ether vapor into a chlorobenzene solution. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.71 ppm (d, 3H, Pd-CH_3, $^3J_{PH}$ = 2 Hz), 6.91 (t, 1H, aryl C-H, $^3J_{HH}$ = 7 Hz), 7.15 (t, H, aryl C-H, $^3J_{HH}$ = 7 Hz),

7.33−7.46 (m, 11H, aryl C-*H*), 7.54 (m, 4H, aryl C-*H*), 7.74 (br s, 2H, aryl C-*H*), 7.99 (m, 1H, aryl C-*H*), 8.64 (br s, 4H, aryl C-*H*). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K): δ 1.5 ppm (Pd-CH_3), 124.9 (aryl *C*-H), 126.0 (d, aryl *C*-H, $^3J_{CP}$ = 8 Hz), 127.8 (d, aryl *C*-H, $^3J_{CP}$ = 10 Hz), 129.5, 129.8 (both aryl *C*-H), 130.2 (d, aryl C_q, $^1J_{CP}$ = 51 Hz), 131.6 (d, aryl *C*-H, $^3J_{CP}$ = 8 Hz), 132.7 (d, aryl C_q, $^1J_{CP}$ = 49 Hz), 134.6 (d, aryl *C*-H, $^2J_{CP}$ = 17 Hz), 135.0 (d, aryl *C*-H, $^2J_{CP}$ = 11 Hz), 137.3, 150.4 (both aryl *C*-H). Carbon adjacent to boron not observed. $^{11}B\{^1H\}$ NMR (128.4 MHz, $CDCl_3$, 298 K): δ +3.1 ppm (br s, $C_6H_4BF_3$). ^{19}F NMR (376.6 MHz, $CDCl_3$, 298 K): δ −137.2 ppm (br s, $C_6H_4BF_3$). $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 298 K): δ +21.0 ppm (s, PPh_2(2-BF_3-Ph). Anal. Calcd for $C_{29}H_{27}N_2BF_3PPd\cdot(CH_2Cl_2)_{0.5}$: C, 56.05; H, 4.41; N, 4.48. Found: C, 56.37; H, 4.51; N, 4.51. MS (ESI +ve): *m*/*z* 499 [M^+ − py].

[κ-(P)^{Ph}PdMe(bipy)], 8a. A solution of 2,2′-bipyridine (0.055 g, 0.32 mmol) in dichloromethane (2 mL) was added, with stirring, to a solution of **6a** (0.200 g, 0.32 mmol) in dichloromethane (10 mL). The reaction was left to stir overnight; the resultant white precipitate was isolated by filtration. Yield: 0.131 g (0.22 mmol, 62%). ^1H NMR (300 MHz, $(CD_3)_2SO$, 298 K): δ 0.73 ppm (s, 3H, Pd-CH_3), 7.00 (t, 1H, aryl C-*H*, $^3J_{HH}$ = 7 Hz), 7.13 (t, 1H, aryl C-*H*, $^3J_{HH}$ = 7 Hz), 7.25−7.49 (m, 13H, aryl C-*H*), 7.69 (br s, 1H, aryl C-*H*), 8.05 (v br s, 2H, aryl C-*H*), 8.19 (t, 2H, aryl C-*H*, $^3J_{HH}$ = 7 Hz), 8.60 (d, 2H, aryl C-*H*, $^3J_{HH}$ = 7 Hz). The compound is too poorly soluble to obtain satisfactory ^{13}C NMR spectra. $^{11}B\{^1H\}$ NMR (128.4 MHz, $(CD_3)_2SO$, 298 K): δ +3.4 ppm (br s, $C_6H_4BF_3$). ^{19}F NMR (376.6 MHz, $(CD_3)_2SO$, 298 K): δ −130.3 ppm (br s, $C_6H_4BF_3$). $^{31}P\{^1H\}$ NMR (162.0 MHz, $(CD_3)_2SO$, 298 K): δ +40.3 ppm (s, PPh_2(2-BF_3-Ph)). HRMS (ESI +ve): calcd for [M^+] *m*/*z* 629.07430; found 629.07404.

[κ^2-(P,F)^{Ph}PdMe(lutidine)], 9a. A 50 mL round-bottomed flask was charged with **6a** (0.300 g, 0.51 mmol) and a stir bar. 2,6-Lutidine (10 mL) was added via syringe, and the off-white slurry left to stir for 20−30 min. All volatiles were removed *in vacuo*, and the process was repeated four times. The crude compound was washed with diethyl ether (2 × 50 mL) and dried *in vacuo* to yield the title compound as an off-white solid in essentially quantitative yield. Yield: 0.271 g (0.48 mmol, 94%). ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.52 ppm (d, 3H, Pd-CH_3, $^3J_{PH}$ = 3 Hz), 3.17 (s, 6H, 2 × CH_3 of lutidine), 6.95 (m, 1H, aryl C-*H*), 7.16−7.21 (m, 3H, aryl C-*H*), 7.42−7.48 (m, 7H, aryl C-*H*), 7.57−7.63 (m, 5H, aryl C-*H*), 7.91 (m, 1H, aryl C-*H*). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K): δ −2.9 ppm (q, Pd-CH_3, $^2J_{CF}$ = 9 Hz), 26.4 (CH_3 of lutidine), 122.6 (d, aryl *C*-H, $^2J_{CP}$ = 3 Hz), 126.9 (d, aryl *C*-H, $^2J_{CP}$ = 8 Hz), 128.5 (d, aryl *C*-H, $^2J_{CP}$ = 11 Hz), 130.0 (aryl *C*-H), 130.4 (d, aryl *C*-H, $^2J_{CP}$ = 3 Hz), 130.8, 131.3 (both aryl *C*-H), 132.6 (d, aryl *C*-H, $^2J_{CP}$ = 5 Hz), 133.4 (d, aryl C_q, $^2J_{CP}$ = 14 Hz), 134.0 (d, aryl *C*-H, $^2J_{CP}$ = 12 Hz), 138.8 (aryl *C*-H), 158.9 (C_q of lutidine). Carbon adjacent to boron not observed. $^{11}B\{^1H\}$ NMR (128.4 MHz, $CDCl_3$, 298 K): δ +3.1 ppm (br s, $C_6H_4BF_3$). ^{19}F NMR (376.6 MHz, $CDCl_3$, 298 K): δ −158.0 ppm (br s, $C_6H_4BF_3$Pd). $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 298 K): δ +29.0 ppm (s, PPh_2(2-BF_3-Ph)). Anal. Calcd for $C_{26}H_{26}NBF_3PPd$: C, 56.00; H, 4.70; N, 2.51. Found: C, 55.90; H, 4.68; N, 2.48. MS (ESI +ve): *m*/*z* 499 [M^+ − 3F].

[κ^2-(P,F)^{Ar}PdMe(lutidine)], 9b. As for **9a**, using **6b** (0.25 g, 0.40 mmol) and 2,6-lutidine (5 × 10 mL) yielded the title compound from dichloromethane as an off-white solid. Yield: 0.194 g (0.32 mmol, 79%). ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.34 ppm (d, 3H, Pd-CH_3, $^3J_{PH}$ = 3 Hz), 3.16 (s, 6H, 2 × CH_3 of lutidine), 3.67 (s, 6H, 2 × OCH_3), 6.92−7.13 (m, 8H, aryl C-*H*, overlapping), 7.33 (t, 1H, aryl C-*H*, $^3J_{HH}$ = 7 Hz), 7.40−7.52 (m, 4H, aryl C-*H*, overlapping), 7.59 (t, 1H, aryl C-*H*, $^3J_{HH}$ = 7 Hz), 7.82 (m, 1H, aryl C-*H*). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K): δ −3.1 ppm (q, Pd-CH_3, $^2J_{CF}$ = 14 Hz), 26.2 (CH_3 of lutidine), 55.1 (OCH_3), 110.7 (aryl *C*-H), 117.6 (d, aryl C_q, $^1J_{CP}$ = 53 Hz), 120.6 (d, aryl *C*-H, $^3J_{CP}$ = 11 Hz), 122.4 (aryl *C*-H), 125.6 (d, aryl *C*-H, $^3J_{CP}$ = 11 Hz), 129.0 (d, aryl *C*-H, $^4J_{CP}$ = 3 Hz), 130.2 (d, aryl C_q, $^1J_{CP}$ = 52 Hz), 132.0 (d, aryl *C*-H, $^4J_{CP}$ = 3 Hz), 132.3 (d, aryl *C*-H, $^2J_{CP}$ = 19 Hz), 132.5 (aryl *C*-H), 132.9 (d, aryl *C*-H, $^2J_{CP}$ = 17 Hz), 136.7 (d, aryl *C*-H, $^3J_{CP}$ = 11 Hz), 138.3 (aryl *C*-H), 159.1, 160.5 (both aryl C_q). Carbon adjacent to boron not observed. $^{11}B\{^1H\}$ NMR (128.4 MHz, $CDCl_3$, 298 K): δ +4.0 ppm (br s, $C_6H_4BF_3$). ^{19}F NMR (376.6 MHz, $CDCl_3$, 298 K): δ −157.6 ppm (br s, $C_6H_4BF_3$Pd). $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 298 K): δ +20.9 ppm (s, P(2-OMe-Ph)$_2$(2-BF_3-Ph). Anal. Calcd for $C_{28}H_{30}NBF_3O_2PPd\cdot(CH_2Cl_2)_{0.25}$: C, 53.10; H, 4.83; N, 2.19. Found: C, 52.99; H, 4.86; N 2.25. MS (ESI +ve): *m*/*z* 598 [M^+ − F], 491 [M^+ − CH_3 − lutidine].

[κ^2-(P,F)$^{i\text{-}Pr}$PdMe(lutidine)], 9c. As for **9a**, using **6c** (0.200 g, 0.40 mmol) and 2,6-lutidine (5 × 10 mL) yielded the title compound as an off-white solid. Yield: 0.154 g (0.31 mmol, 76%). Single crystals suitable for X-ray diffraction were grown by the diffusion of diethyl ether vapor into a chlorobenzene solution. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.62 ppm (d, 3H, Pd-CH_3, $^3J_{PH}$ = 2 Hz), 1.27 (d of d, 6H, 2 × CH_3 of ^{i}Pr, $^3J_{PH}$ = 16 Hz, $^3J_{HH}$ = 7 Hz), 1.32 (d of d, 6H, 2 × CH_3 of ^{i}Pr, $^3J_{PH}$ = 16 Hz, $^3J_{HH}$ = 7 Hz), 2.52 (m, 2H, 2 × C*H* of ^{i}Pr, overlapping), 3.19 (s, 6H, 2 × CH_3 of lutidine), 7.16 (d, 2H, aryl C-*H*, $^3J_{HH}$ = 7 Hz), 7.24 (d, 1H, aryl C-*H*, $^3J_{HH}$ = 7 Hz), 7.41 (t, 1H, aryl C-*H*, $^3J_{HH}$ = 7 Hz), 7.49 (t, 1H, aryl C-*H*, $^3J_{HH}$ = 7 Hz), 7.61 (t, 1H, aryl C-*H*, $^3J_{HH}$ = 7 Hz), 7.92 (d, 1H, aryl C-*H*, $^3J_{HH}$ = 7 Hz). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K): δ −8.9 ppm (q, Pd-CH_3, $^2J_{CP}$ = 12 Hz), 18.4, 19.2 (both CH_3 of ^{i}Pr), 25.5 (d, *C*H of ^{i}Pr, $^1J_{CP}$ = 27 Hz), 26.0 (CH_3 of lutidine), 122.8 (aryl *C*-H), (d, aryl *C*-H, $^3J_{CP}$ = 6 Hz), 127.1, (d, aryl C_q, $^1J_{CP}$ = 40 Hz), 129.7, 130.7 (both aryl *C*-H), 133.5 (d, aryl *C*-H, $^2J_{CP}$ = 17 Hz), 138.6 (aryl *C*-H), 159.0 (C_q of lutidine). Carbon adjacent to boron not observed. $^{11}B\{^1H\}$ NMR (128.4 MHz, $CDCl_3$, 298 K): δ +3.1 ppm (br s, $C_6H_4BF_3$). ^{19}F NMR (376.6 MHz, $CDCl_3$, 298 K): δ −161.2 ppm (br s, $C_6H_4BF_3$Pd). $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 298 K): δ +37.2 ppm (s, P^iPr_2(2-BF_3-Ph)). Anal. Calcd for $C_{20}H_{30}NBF_3PPd$: C, 49.06; H, 6.18; N, 2.86. Found: C, 48.90; H, 6.26; N, 2.84. MS (ESI +ve): *m*/*z* 502 [M^+ + Na], 489 [M^+], 405 [M^+ − lutidine + Na].

[κ^2-(P,F)^{Ph}PdMe(DMAP)], 10a. A 10 mL round-bottomed flask was charged with a solution of **9a** (0.100 g, 0.18 mmol) in dichloromethane (2 mL). A solution of DMAP (0.022 g, 0.18 mmol) in dichloromethane (0.5 mL) was added. The reaction was left to stir for 30 min before all volatiles were removed *in vacuo*. The title compound was obtained as a crystalline, white solid via the diffusion of diethyl ether vapor into a chlorobenzene solution. Yield: 0.045 g (0.08 mmol, 44%). ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.71 ppm (d, 3H, Pd-CH_3, $^3J_{PH}$ = 3 Hz), 3.07 (s, 6H, N(CH_3)$_2$ of DMAP), 6.46 (d, 2H, aryl C-*H* of DMAP, $^3J_{HH}$ = 7 Hz), 6.91 (t, 1H, aryl C-*H*, $^3J_{HH}$ = 7 Hz), 7.18 (t, 1H, aryl C-*H*, $^3J_{HH}$ = 7 Hz), 7.38 (m, 7H, aryl C-*H*), 7.56 (m, 4H, aryl C-*H*), 7.91 (m, 1H, aryl C-*H*), 8.23 (d, 2H, aryl C-*H* of DMAP, $^3J_{HH}$ = 7 Hz). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K): δ 0.52 ppm (Pd-CH_3), 39.1 (N(CH_3)$_2$ of DMAP), 107.0, 126.4 (both aryl *C*-H), 126.7 (d, aryl *C*-H, $^2J_{CP}$ = 11 Hz), 128.3 (d, aryl *C*-H, $^2J_{CP}$ = 11 Hz, and aryl *C*-H, overlapping), 129.7, 130.2 (both aryl *C*-H), 131.9 (d, aryl *C*-H, $^3J_{CP}$ = 9 Hz), 132.5 (aryl *C*-H), 134.1 (d, aryl *C*-H, $^2J_{CP}$ = 11 Hz), 134.4, 148.9 (both aryl C_q). Carbon adjacent to boron not observed. $^{11}B\{^1H\}$ NMR (128.4 MHz, $CDCl_3$, 298 K): δ +3.4 ppm (br s, $C_6H_4BF_3$). ^{19}F NMR (376.6 MHz, $CDCl_3$, 298 K): δ −152.4 ppm (br s, $C_6H_4BF_3$Pd). $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 298 K): δ +36.7 ppm (s, PPh_2 (2-BF_3-Ph)). Anal. Calcd for $C_{26}H_{27}N_2BF_3PPd$: C, 54.53; H, 4.75; N, 4.89. Found: C, 54.75; H, 4.82; N, 4.83. MS (ESI +ve): *m*/*z* 576 [M^+], 457 [M^+ − DMAP].

Ethylene Reactions. A J. Young NMR tube was charged with **7a**, **9a**/**b**/**c**, or **10a** (2.5 mg), and $CDCl_3$ (0.4 mL) was added by vacuum transfer. A blank ^1H NMR spectrum was recorded to assess complex purity. The sample was then degassed via repeated freeze−pump−thaw cycles at −78 °C. Ethylene was introduced from a vacuum line at one atmosphere pressure, and the NMR tube sealed. The reaction was monitored at regular (ca. 2 h) intervals to assess the course of the

reaction. Product distribution was determined by ^{1}H NMR integration of the terminal methyl group.

X-ray Crystallography. Single crystals of **1b**, **2a**, **3a**, **5a**, **6a**, **6b**, **7a**, and **9c** were grown as described in the relevant experimental section. Diffraction data for **1b**, **2a**, **3a**, **5a**, **6b**, **7a**, and **9c** were collected on a Bruker P4/RA/SMART 1000 CCD diffractometer using Mo Kα radiation at −100 °C. Data for **6a** were collected on a Bruker PLATFORM/SMART 1000 CCD diffractometer using graphite-monochromated Mo Kα radiation at −100 °C. All data were corrected for absorption using SADABS,[45] and the structures solved in SHELXS97[46] and refined using full-matrix least-squares on F^2 using SHELXL97.[46]

■ ASSOCIATED CONTENT

Supporting Information. Structural diagrams, selected bond lengths and angles, and crystallographic data/processing parameters for all structures. Crystallographic information files for **1b**, **2a**, **3a**, **5a**, **6a**, **6b**, **7a**, and **9c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) (a) Ito, S.; Nozaki, K. *Chem. Rec.* **2010**, *10*, 315. (b) Nakamura, A.; Ito, S.; Nozaki, K. *Chem. Rev.* **2009**, *109*, 5215. (c) Chen, E. Y. X. *Dalton Trans.* **2009**, 8784. (d) Chen, E. Y. X. *Chem. Rev.* **2009**, *109*, 5157. (e) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169. (f) Boffa, L. S.; Novak, B. M. *Chem. Rev.* **2000**, *100*, 1479.

(2) (a) Barboiu, B.; Percec, V. *Macromolecules* **2001**, *34*, 8626. (b) Matyjaszewski, K.; Jo, S. M.; Paik, H. J.; Shipp, D. A. *Macromolecules* **1999**, *32*, 6431. (c) Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. *J. Am. Chem. Soc.* **1999**, *121*, 3904. (d) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559.

(3) (a) Ono, H.; Hisatani, K.; Kamide, K. *Polym. J.* **1993**, *25*, 245. (b) Kamide, K.; Ono, H.; Hisatani, K. *Polym. J.* **1992**, *24*, 917. (c) Kuran, W.; Borycki, J. *J. Polym. Sci. Polym. Chem.* **1981**, *19*, 1251.

(4) Szabo, M. J.; Galea, N. M.; Michalak, A.; Yang, S.-Y.; Groux, L. F.; Piers, W. E.; Ziegler, T. *Organometallics* **2005**, *24*, 2147.

(5) Younkin, T. R.; Conner, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460.

(6) Groux, L. F.; Weiss, T.; Reddy, D. N.; Chase, P. A.; Piers, W. E.; Ziegler, T.; Parvez, M.; Benet-Buchholz, J. *J. Am. Chem. Soc.* **2005**, *127*, 1854.

(7) (a) Wu, F.; Jordan, R. F. *Organometallics* **2006**, *25*, 5631. (b) Wu, F.; Foley, S. R.; Burns, C. T.; Jordan, R. F. *J. Am. Chem. Soc.* **2005**, *127*, 1841.

(8) (a) Drent, E.; van Dijk, R.; van Ginkel, R.; van Oort, B.; Pugh, R. I. *Chem. Commun.* **2002**, 744. (b) Drent, E.; van Dijk, R.; van Ginkel, R.; van Oort, B.; Pugh, R. I. *Chem. Commun.* **2002**, 964.(c) Drent, E.; Sjardijn, W.; Suykerbuyk, J.; Wanninger, K.(Shell) PCT Int. Appl., WO2000006615(A1), 2000.

(9) (a) Shen, Z. L.; Jordan, R. F. *J. Am. Chem. Soc.* **2010**, *132*, 52. (b) Piche, L.; Daigle, J. C.; Poli, R.; Claverie, J. P. *Eur. J. Inorg. Chem.* **2010**, 4595. (c) Noda, S.; Kochi, T.; Nozaki, K. *Organometallics* **2009**, *28*, 656. (d) Zhang, D.; Guironnet, D.; Gottker-Schnetmann, I.; Mecking, S. *Organometallics* **2009**, *28*, 4072. (e) Noda, S.; Nakamura, A.; Kochi, T.; Chung, L. W.; Morokuma, K.; Nozaki, K. *J. Am. Chem. Soc.* **2009**, *131*, 14088. (f) Liu, S.; Borkar, S.; Newsham, D.; Yennawar, H.; Sen, A. *Organometallics* **2007**, *26*, 210. (g) Vela, J.; Lief, G. R.; Shen, Z. L.; Jordan, R. F. *Organometallics* **2007**, *26*, 6624.

(10) (a) Nozaki, K.; Kusumoto, S.; Node, S.; Kochi, T.; Chung, L. W.; Morokuma, K. *J. Am. Chem. Soc.* **2010**, *132*, 16030. (b) Kochi, T.; Noda, S.; Yoshimura, K.; Nozaki, K. *J. Am. Chem. Soc.* **2007**, *129*, 8948.

(11) (a) Luo, R.; Newsham, D. K.; Sen, A. *Organometallics* **2009**, *28*, 6994. (b) Newsham, D. K.; Borkar, S.; Sen, A.; Conner, D. M.; Goodall, B. L. *Organometallics* **2007**, *26*, 3636. (c) Haras, A.; Michalak, A.; Rieger, B.; Ziegler, T. *Organometallics* **2006**, *25*, 946. (d) Hearley, A. K.; Nowack, R. A. J.; Rieger, B. *Organometallics* **2005**, *24*, 2755.

(12) Skupov, K. M.; Piche, L.; Claverie, J. P. *Macromolecules* **2008**, *41*, 2309.

(13) (a) Kageyama, T.; Ito, S.; Nozaki, K. *Chem. Asian J.* **2011**, *6*, 690. (b) Runzi, T.; Guironnet, D.; Gottker-Schnetmann, I.; Mecking, S. *J. Am. Chem. Soc.* **2010**, *132*, 16623. (c) Kryuchkov, V. A.; Daigle, J. C.; Skupov, K. M.; Claverie, J. P.; Winnik, F. M. *J. Am. Chem. Soc.* **2010**, *132*, 15573. (d) Guironnet, D.; Caporaso, L.; Neuwald, B.; Gottker-Schnetmann, I.; Cavallo, L.; Mecking, S. *J. Am. Chem. Soc.* **2010**, *132*, 4418. (e) Skupov, K. M.; Hobbs, J.; Marella, P.; Conner, D.; Golisz, S.; Goodall, B. L.; Claverie, J. P. *Macromolecules* **2009**, *42*, 6953. (f) Guironnet, D.; Roesle, P.; Runzi, T.; Gottker-Schnetmann, I.; Mecking, S. *J. Am. Chem. Soc.* **2009**, *131*, 422. (g) Nakamura, A.; Munakata, K.; Kochi, T.; Nozaki, K. *J. Am. Chem. Soc.* **2008**, *130*, 8128. (h) Skupov, K. M.; Marella, P. R.; Simard, M.; Yap, G. P. A.; Allen, N.; Conner, D.; Goodall, B. L.; Claverie, J. P. *Macromol. Rapid Commun.* **2007**, *28*, 2033. (i) Kochi, T.; Yoshimura, K.; Nozaki, K. *Dalton Trans.* **2006**, 25.

(14) (a) Ito, S.; Munakata, K.; Nakamura, A.; Nozaki, K. *J. Am. Chem. Soc.* **2009**, *131*, 14606. (b) Kochi, T.; Nakamura, A.; Ida, H.; Nozaki, K. *J. Am. Chem. Soc.* **2007**, *129*, 7770.

(15) Runzi, T.; Frohlich, D.; Mecking, S. *J. Am. Chem. Soc.* **2010**, *132*, 17690.

(16) Bouilhac, C.; Runzi, T.; Mecking, S. *Macromolecules* **2010**, *43*, 3589.

(17) (a) Shen, Z. L.; Jordan, R. F. *Macromolecules* **2010**, *43*, 8706. (b) Weng, W.; Shen, Z.; Jordan, R. F. *J. Am. Chem. Soc.* **2007**, *129*, 15450.

(18) Ito, S.; Kanazawa, M.; Munakata, K.; Kuroda, J.; Okumura, K.; Nozaki, K. *J. Am. Chem. Soc.* **2011**, *133*, 1232.

(19) (a) Chen, C. L.; Luo, S. J.; Jordan, R. F. *J. Am. Chem. Soc.* **2008**, *130*, 12892. (b) Luo, S.; Vela, J.; Lief, G. R.; Jordan, R. F. *J. Am. Chem. Soc.* **2007**, *129*, 8946.

(20) Vedejs, E.; Chapman, R. W.; Fields, S. C.; Lin, S.; Schrimpf, M. R. *J. Org. Chem.* **1995**, *60*, 3020.

(21) (a) Brune, H. A.; Falck, M.; Hemmer, R.; Schmidtberg, G.; Alt, H. G. *Chem Ber.* **1984**, *117*, 2791. (b) Ankianiec, B. C.; Young, G. B. *Polyhedron* **1991**, *10*, 1411.

(22) Hermanek, S. *Chem. Rev.* **1992**, *92*, 325.

(23) Gott, A. L.; Piers, W. E.; McDonald, R.; Parvez, M. *Inorg. Chim. Acta* **2011**, *369*, 180.

(24) (a) Chase, P. A.; Henderson, L. D.; Piers, W. E.; Parvez, M.; Clegg, W.; Elsegood, M. R. J. *Organometallics* **2006**, *25*, 349. (b) Hudnall, T. W.; Bondi, J. F.; Gabbai, F. P. *Main Group Chem.* **2006**, *5*, 319.

(25) Chernyshova, E. S.; Goddard, R.; Porschke, K.-R. *Organometallics* **2007**, *26*, 3236.

(26) Rheingold, A. L.; Wu, G. Z.; Heck, R. F. *Inorg. Chim. Acta* **1987**, *131*, 147.

(27) (a) Powell, J.; Shaw, B. L. *J. Chem. Soc. A* **1967**, 1839. (b) Fantasia, S.; Nolan, S. P. *Chem.—Eur. J.* **2008**, *14*, 6987.

(28) Kurosawa, H.; Urabe, A.; Miki, K.; Kasai, N. *Organometallics* **1986**, *5*, 2002.

(29) Weng, W.; Chen, C. H.; Foxman, B. M.; Ozerov, O. V. *Organometallics* **2007**, *26*, 3315.

(30) Moebs-Sanchez, S.; Saffon, N.; Bouhadir, G.; Maron, L.; Bourissou, D. *Dalton Trans.* **2010**, *39*, 4417.

(31) Sola, E.; Navarro, J.; Lopez, J. A.; Lahoz, F. J.; Oro, L. A.; Werner, H. *Organometallics* **1999**, *18*, 3534.
(32) Liang, H.; Liu, J. Y.; Li, X. F.; Li, Y. S. *Polyhedron* **2004**, *23*, 1619.
(33) Ball, N. D.; Kampf, J. W.; Sanford, M. S. *Dalton Trans.* **2010**, *39*, 632.
(34) (a) Pilon, M. C.; Grushin, V. V. *Organometallics* **1998**, *17*, 1774. (b) Fraser, S. L.; Antipin, M. Y.; Khroustalyov, V. N.; Grushin, V. V. *J. Am. Chem. Soc.* **1997**, *119*, 4769.
(35) (a) Canty, A. J.; Traill, P. R.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1992**, *433*, 213. (b) Canty, A. J.; Traill, P. R.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1991**, *402*, C33.
(36) Nagai, Y.; Kochi, T.; Nozaki, K. *Organometallics* **2009**, *28*, 6131.
(37) Burns, C. T.; Jordan, R. F. *Organometallics* **2007**, *26*, 6726.
(38) (a) Rix, F. C.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **1996**, *118*, 4746. (b) Rix, F. C.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 1137.
(39) Pugin, B.; Feng, X.; Spindler, F. PCT Int. Appl. WO2008000815 A1, 2008.
(40) Ladipo, F. T.; Anderson, G. K. *Organometallics* **1994**, *13*, 303.
(41) De Graaf, W.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; Van Koten, G. *Organometallics* **1989**, *8*, 2907.
(42) Reisinger, C. M.; Nowack, R. J.; Volkmer, D.; Rieger, B. *Dalton Trans.* **2007**, 272.
(43) Korshin, E. E.; Leitus, G.; Shimon, L. J. W.; Konstantinovski, L.; Milstein, D. *Inorg. Chem.* **2008**, *47*, 7177.
(44) (a) Talay, R.; Rehder, D. *Z. Naturforsch. B* **1981**, *36*, 451. (b) Xu, Y. J.; Alcock, N. W.; Clarkson, G. J.; Docherty, G.; Woodward, G.; Wills, M. *Org. Lett.* **2004**, *6*, 4105.
(45) Sheldrick, G. M. *SADABS, Program for Area Detector Absorption Correction*; Institute for Inorganic Chemistry, University of Gottingen: Germany, 1996.
(46) Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112.