Polymerization and Oligomerization of Ethylene by Cationic Nickel(II) and Palladium(II) Complexes Containing Bidentate Phenacyldiarylphosphine Ligands

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A series of Ni(II) and Pd(II) catalysts have been synthesized from the P,O chelating ligands phenacyl(aryl)$_2$phosphine. The (P,O)Ni-allyl$^+$B(Ar$_f$)$_4^-$ [Ar$_f$ = 3,5-(CF$_3$)$_2$C$_6$H$_3$] complexes **6a**−**c** are active for polymerization of ethylene in the case of **6b** (aryl = 2,4,6-(CH$_3$)$_3$C$_6$H$_2$) and for dimerization of ethylene to butenes in the case of **6a** (aryl = C$_6$H$_5$) and **6c** (aryl = C$_6$H$_5$, 2,4,6-(C$_6$H$_5$)$_3$C$_6$H$_2$). These catalysts are characterized by their high initial activity but relatively short catalytic lifetime and poor thermal stability. The palladium analogues (P,O)PdMe(NCMe)$^+$B(Ar$_f$)$_4^-$ are approximately an order of magnitude less active than the Ni analogues and generate butenes and hexenes. The barriers for migratory insertion in a series of methyl ethylene complexes [(*p*-XC$_6$H$_4$)$_2$PCH$_2$C(O)(*p*-YC$_6$H$_4$)]Pd(CH$_3$)(C$_2$H$_4$)$^+$B(Ar$_f$)$_4^-$ (X,Y = H, H; −OCH$_3$, H; −CF$_3$, H; H, −OCH$_3$; H, −CF$_3$) were measured. Values of $\Delta G^{\ddagger}$ ranged from 18.2 to 20.3 kcal/mol and, relative to the unsubstituted system, decreased for X,Y = −CF$_3$ and increased for X,Y = −OCH$_3$.

Introduction

During 1995−1996 our group and the DuPont Versipol group reported a series of highly active cationic d^8 square-planar Ni(II) and Pd(II) olefin polymerization catalysts based on aryl-substituted α-diimine ligands.[1−3] The key structural feature of these systems is the incorporation of bulky substituents at the *ortho* positions of the aryl rings, which project into the axial sites and retard the rate of chain transfer, thereby generating high molecular weight polymer. These catalysts polymerize ethylene and α-olefins to a wide range of linear to highly branched polymers and have been shown to copolymerize ethylene and polar comonomers such as methyl acrylate and more recently vinyl alkoxysilanes.[4−7] These results have sparked considerable interest in developing new late metal olefin polymerization catalysts based on both cationic and neutral metal centers and incorporating a wide variety of heteroatom substituents on the supporting ligands. Recent reviews cover much of this work.[8−11]

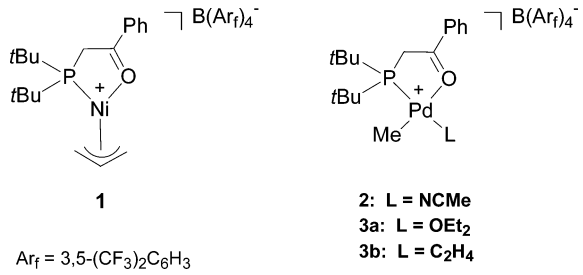

Figure 1. (P,O)Ni(II) and -Pd(II) Catalysts.

We recently reported the synthesis of Ni(II) and Pd(II) complexes based on the bidentate P,O chelating ligand phenacyldi-*tert*-butylphosphine (Figure 1).[12,13] These catalysts are cationic analogues of the well-known SHOP systems[14−16] in which B(Ar$_f$)$_4^-$ [Ar$_f$ = 3,5-(CF$_3$)$_2$-C$_6$H$_3$] serves as a bulky, noncoordinating counteranion. The Ni-allyl complex **1** is highly active (TOFs > 3 × 10^6 h^{-1}) at high temperatures and ethylene pressures for formation of linear polyethylene (M_w = 5000−12 000,

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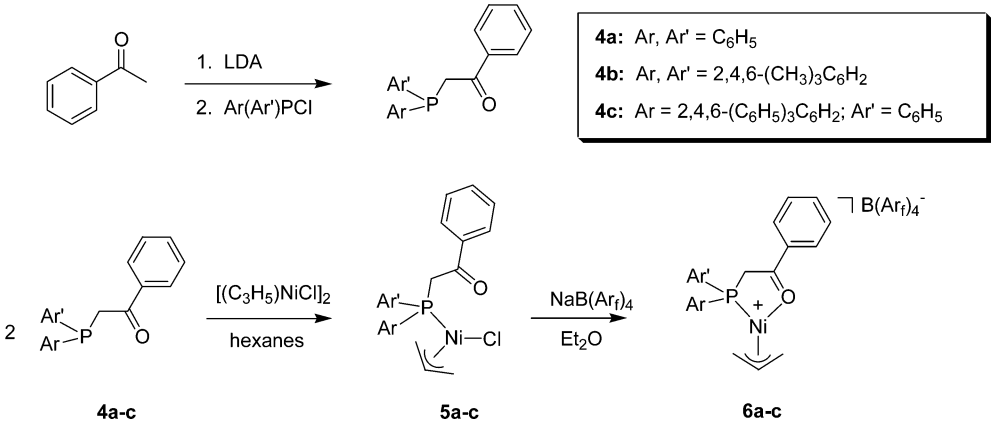
Scheme 1. Synthesis of Phenacyldiarylphosphine Ligands and Corresponding Cationic Ni-allyl Catalysts



6−8 branches/1000 carbons). In addition, catalyst **1** copolymerizes ethylene and methyl-10-undecenoate, a polar-functionalized monomer, albeit with significantly reduced yields and low comonomer incorporation. Palladium catalysts **2** and **3a** were found to oligomerize ethylene to an amorphous material (TOF = 2×10^4 h^{-1}, $M_n \approx 350$) in which the degree of branching decreases with increasing ethylene concentration. Despite its high activity, Ni-allyl catalyst **1** displays very slow rates of initiation, particularly at low temperatures and ethylene pressures. In addition, the barrier for ethylene insertion into the palladium methyl bond for complex **3b** was found to be $\Delta G^{\ddagger} = 21.4$ kcal/mol, which is over 4 kcal/mol higher in energy than the barrier observed for ethylene insertion in the palladium α-diimine systems.[17]

We report here the investigation of Ni(II) and Pd(II) catalysts similar to **1**−**3** but which incorporate (P,O) chelating ligands of the type (Ar)(Ar′)$CH_2C(O)C_6H_5$ [Ar, Ar′ = C_6H_5, C_6H_5; 2,4,6-$(CH_3)_3C_6H_2$, 2,4,6-$(CH_3)_3C_6H_2$; C_6H_5, 2,4,6-$(C_6H_5)_3C_6H_2$]. Electronic effects on insertion barriers in the palladium systems were probed by incorporating *p*-CF_3 and *p*-OCH_3 substituents in the aryl rings of both the phenacyl and $(Ar)_2P$ moieties.

Results and Discussion

Synthesis and Ethylene Polymerization Activity of (phenacyldiarylphosphine)Ni-allyl$^+$B(Ar$_f$)$_4^-$ Complexes. Phenacyldiarylphosphine ligands **4b** and **4c** were prepared using a modification of the procedure described for synthesis of the previously reported ligand phenacyldiphenylphosphine **4a** (Scheme 1).[18] Deprotonation of acetophenone with LDA to generate the lithium enolate followed by reaction with the corresponding diarylchlorophosphine[19,20] generates ligands **4a**−**c**. Ligand **4a** bears two phenyl groups on phosphorus, while **4b** contains bulkier mesityl groups. Ligand **4c** contains a phenyl group and a 2,4,6-triphenylaryl group on the phosphine moiety. Cationic Ni-allyl catalysts **6a**−**c** were prepared using the same procedure for synthesis of **1**. Reaction of $[(C_3H_5)NiCl]_2$ with 2 equiv of **4a**−**c** yields the neutral π-allyl complexes **5a**−**c**, in which the carbonyl oxygen of the ligand remains uncomplexed. Treatment of **5a**−**c** with $NaB(Ar_f)_4$ in diethyl ether generates the cationic complexes **6a**−**c** as stable yellow powders. Complexes **6a**−**c** are moderately air sensitive but stable indefinitely in the solid state and in solution under inert atmosphere.

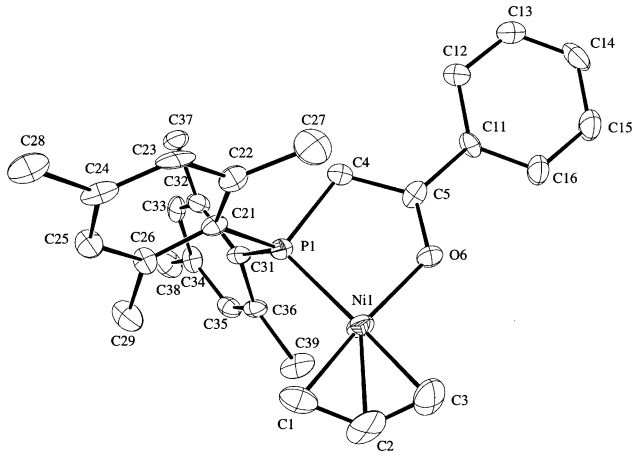


Figure 2. Thermal ellipsoid plot of **6b**. $B(Ar_f)_4^-$ counterion omitted for clarity. Selected bond distances (Å) and angles (deg): Ni(1)−P(1) = 2.169(3), Ni(1)−O(6) = 1.908(7), Ni(1)−C(1) = 1.995(11), Ni(1)−C(2) = 1.998(11), Ni(1)−C(3) = 2.024(11), C(1)−C(2) = 1.373(22), C(2)−C(3) = 1.314(24), C(27)−Ni(1) = 3.82(2), C(39)−Ni(1) = 3.13(6), P(1)−Ni(1)−O(6) = 87.95(21), C(1)−Ni(1)−C(3) = 72.94(6), C(21)−P(1)−Ni(1) = 111.7(8), C(31)−P(1)−Ni(1) = 123.9(1), C(4)−C(5)−C(11)−C(12) = 11.30, C(22)−C(21)−P(1)−C(4) = 38.79, C(36)−C(31)−P(1)−C(4) = 107.04.

X-ray quality crystals of **6b** were grown from diethyl ether/pentane at −35 °C under argon. An ORTEP diagram of complex **6b** is shown in Figure 2. The coordination geometry around Ni is distorted square planar [P(1)−Ni(1)−O(6) = 87.95(21), C(1)−Ni(1)−C(3) = 72.94(6)°] with the π-allyl group occupying two *cis* coordination sites. The phenyl ring of the ligand ketone is slightly twisted from coplanarity with C(4)−C(5)−O(6) [torsion angle C(4)−C(5)−C(11)−C(12) = 11.30°]. The tetrahedral geometry of the phosphorus atom results in projection of one of the methyl substituents of each mesityl group toward the axial sites above and

(17) The rate of insertion for ethylene into the Pd−Me bond for a typical α-diimine Pd(II) complex at −30 °C has been found to be $k_{obs} = 1.9 \times 10^{-3}$ s^{-1}, $\Delta G^{\ddagger} = 17.2$ kcal/mol. See ref 12.

(18) (a) Bouaoud, S.-H.; Bransutein, P.; Grandjean, D.; Matt, D.; Nobel, D. *Inorg. Chem.* **1986**, *25*, 3765. (b) Demerseman, B.; Guilbert, B.; Renouard, C.; Gonzalez, M.; Dixneuf, P. H.; Masi, D.; Mealli, C. *Organometallics* **1993**, *12*, 3906.

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(20) The previously unreported complex (2,4,6-triphenylaryl)chlorophenylphosphine was prepared by treatment of 2,4,6-triphenylbromobenzene with *n*-BuLi followed by reaction with dichlorophenylphosphine.

Table 1. Ethylene Polymerization with 6b at 1 atm[a]

entry	time (min)	temp (°C)	yield (g)	TON ($\times 10^{-3}$)	TOF ($\times 10^{-3}$ h^{-1})	M_n[b]	branches (/1000 C)[c]
1	15	25	0.01	0.3	1.2	810	7
2	30	25	0.17	4.1	8.2	870	8
3	45	25	0.72	17	23	850	6
4	60	25	2.17	52	53	1060	5
5	180	25	4.14	100	33	770	6
6	60	40	3.66	88	88	800	7
7	180	40	4.84	120	39	960	7
8	60	60	1.63	39	39	930	8
9	180	60	1.87	45	15	910	9
10	60	80	0.72	17	17	1130	6
11	180	80	1.08	26	9.0	850	9

[a] Polymerization conditions: 2.0 mg (1.48 μmol) of **6b**; 50 mL of toluene. [b] M_n determined by ^{1}H NMR in C_6D_5Br at 100 °C. [c] Polymer branching per 1000 carbons; determined by ^{1}H NMR in C_6D_5Br at 100 °C.

below the square plane of the molecule [C(39)−Ni(1) = 3.13(6) Å, C(27)−Ni(1) = 3.82(2) Å]. The mesityl groups orient themselves nearly perpendicular to each other in order to minimize steric interactions.

The results of 1 atm ethylene polymerization studies with **6b** are shown in Table 1. Unlike catalyst **1**, complex **6b** is quite active at low temperatures and pressures and generates low molecular weight polyethylene.[21] The highest polymerization activities occur in the temperature range from 25 to 40 °C; lower polymer yields and catalyst lifetimes are observed at higher temperatures. In addition, lower calculated turnover frequencies reported for 3 h versus 1 h polymerizations at 25 and 40 °C indicate that catalyst decomposition occurs even at lower temperatures. Experiments run over 15 min intervals at 25 °C (entries 1−4) indicate that **6b** does not initiate completely at the beginning of polymerization. After 15 min only 10 mg of PE (TOF = 1.2×10^3 h^{-1}) is formed; however, at 30 and 45 min polyethylene yields increase to 170 and 720 mg, respectively, with calculated TOFs of 8.2×10^3 and 2.3×10^4 h^{-1}, suggesting that the number of active catalyst sites in solution is increasing with time. This observation was verified by NMR studies in which a large excess of ethylene was purged through a solution of **6b** in CD_2Cl_2 at 25 °C. The resulting ^{1}H NMR spectrum showed complete consumption of ethylene and formation of polyethylene with no detectable decrease in the Ni-allyl resonances. This suggests that only a very small amount of **6b** was initiated followed by rapid propagation and consumption of ethylene. Despite the observed short catalyst lifetimes and somewhat slow rate of initiation, **6b** is still significantly more active for ethylene polymerization at 1 atm ethylene pressure than the parent di-*tert*-butylphosphine-substituted Ni catalyst **1**.

Similar ethylene polymerization behavior for catalyst **6b** is observed at higher ethylene pressure. The results of polymerization of ethylene under 200 psig pressure are shown in Table 2. Catalyst **6b** is approximately an order of magnitude more active for ethylene polymerization at 200 psig (6.8×10^5 turnovers in 1 h at 25 °C vs 5.3×10^4 turnovers at 1 atm). As in the 1 atm ethylene experiments, the highest polymer yields for 200 psig ethylene polymerizations are recorded at 25 and

(21) Catalyst **1** generates only a trace amount of polyethylene under 1 atm ethylene pressure at 25 °C. See ref 20.

Table 2. 200 psig Ethylene Polymerization with 6b[a]

entry	time (h)	temp (°C)	yield (g)	TON ($\times 10^{-5}$)	TOF ($\times 10^{-5}$ h^{-1})	M_n[b]	branches (/1000 C)[c]
1	0.5	25	23.9	5.6	11	860	8
2	1	25	28.2	6.8	6.8	780	5
3	2	25	29.1	7.0	3.5	770	6
4	1	40	25.8	6.2	6.2	990	5
5	1	60	12.9	3.1	3.1	830	6

[a] Polymerization conditions: 2.0 mg (1.48 μmol) of **6b**; 200 mL of toluene. [b] M_n determined by ^{1}H NMR in C_6D_5Br at 100 °C. [c] Polymer branching per 1000 carbons; determined by ^{1}H NMR in C_6D_5Br at 100 °C.

40 °C (productivities up to 3.2×10^5 kg PE mol^{-1} h^{-1}) with a significant drop in productivity at 60 °C. Furthermore, the catalyst lifetimes at high ethylene pressure are shorter than those recorded at low pressure. At 25 °C and 1 atm ethylene pressure, turnover frequencies for **6b** decrease from 52 500 (1 h run) to 33 300 h^{-1} (3 h run; Table 1, entries 4, 5). At 25 °C and 200 psig ethylene pressure, however, the activity drops by almost half from 30 to 60 min (polymer yield increases from 23.9 to 28.2 g), indicating that the majority of active catalyst has decomposed after 1 h. The shorter catalyst lifetimes are likely due to exotherms during polymerizations. Even at very low catalyst concentrations of 7.4×10^{-6} M, polymerizations with **6b** at 200 psig ethylene pressure generate a substantial reaction exotherm (approximately 20−30 °C above starting temperature) that cannot be completely controlled by the internal cooling coils of the autoclave. Despite its short catalytic lifetime, the turnover frequencies recorded while **6b** remains active for ethylene polymerization are comparable to activities reported for well-known early metal and Ni α-diimine systems.[22]

Under either 1 atm or 200 psig ethylene pressure **6b** generates polyethylene that is isolated as a white powder. Analysis of the product by ^{1}H and ^{13}C NMR spectroscopy shows that the polymer is relatively low molecular weight with M_n values from 750 to 1130, which corresponds to an average of 26−40 ethylene units per chain.[23] The polymer chains are linear with approximately 5−9 methyl branches per 1000 carbons, which equates to about one branch on every other polymer chain.[24] In all cases the polymer end groups were greater than 95% α-olefin, implying β-hydride elimination as the predominant chain-transfer mechanism. As shown in Tables 1 and 2 the polymer molecular weight and branching do not significantly change with varying reaction time, temperature, and ethylene concentration. The polymers displayed sharp T_m values between 98 and 104 °C as measured by DSC.

Catalysts **6a** and **6c** were found to be very active at 25 °C under high ethylene pressure for dimerization of ethylene to butenes. The results of ethylene dimerization experiments are shown in Table 3. The yields of

(22) In comparison, certain Ni(II) α-diimine catalysts exhibit ethylene polymerization activities of up to 1.0×10^5 kg PE (mol Ni)$^{-1}$ h^{-1}. See ref 16.

(23) The low molecular weight of the polyethylene generated by **6b** did not allow for unambiguous polymer characterization by gel permeation chromatography.

(24) Polymer branching values were determined from ^{1}H NMR spectra (C_6D_5Br solution at 100 °C) and corrected for methyl end groups. For the formula used in this calculation see: (a) Daugulis, O.; Brookhart, M. *Organometallics* **2002**, *21*, 5926. (b) Daugulis, O.; Brookhart, M.; White, P. S. *Organometallics* **2002**, *21*, 5935.

Table 3. Dimerization of Ethylene with 6a and 6c[a]

entry	catalyst	time (min)	yield (g)[b]	TON ($\times 10^{-5}$)	TOF ($\times 10^{-5}$ h^{-1})
1	**6a**	15	12.7	3.4	13
2	**6a**	30	13.2	3.5	7.0
3	**6c**	30	20.1	5.4	11
4	**6c**	60	26.0	6.9	6.9
5	**6c**	120	28.1	7.5	3.8

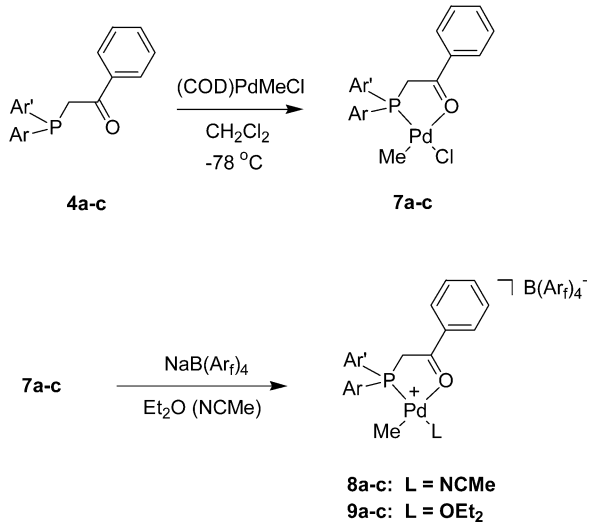
[a] Reaction conditions: 1.34 μmol of Ni catalyst; 200 psig ethylene; 105 mL of toluene; 25 °C (reaction exotherm controlled by ice bath). [b] Yield determined by mass of final reaction mixture vs mass of 105 mL of toluene (90.8 g).

oligomerization reactions were determined by subtracting the mass of the starting toluene solution from the mass of the reaction mixture following the dimerization reaction. Control experiments show the ethylene remaining in the toluene solution following the protocol used is not significant relative to the butene product. The oligomerization products for **6a** and **6c** were determined to be exclusively butenes by ^{1}H NMR and GC. Catalyst **6a** generates 85% 1- vs 2-butene, while catalyst **6c** forms α-olefin with 98% selectivity. Despite its high initial activity (TOF for 15 min experiment = 1.3×10^6 h^{-1}), catalyst **6a** is almost completely deactivated after 15 min. Catalyst **6c** displays longer catalytic lifetimes as it remains active after 1 h, although the catalyst productivity is substantially decreased. Due to the difficulty in measuring the mass of volatile butene products in hot toluene solution, oligomerization experiments were not carried out at higher temperatures, although significantly decreased catalyst lifetimes are expected as observed with catalyst **6b**.

The results of ethylene polymerization and dimerization studies show that catalysts **6a**−**c** are considerably more active at low temperatures and ethylene pressures than the parent complex **1**, but generate lower molecular weight material with shorter catalyst lifetimes. The contrasting behaviors of **6b** and **6a**,**c** show that steric bulk on aryl groups positioned both above and below the axial sites of the molecule as in **6b** is required to retard chain transfer and generate higher molecular weight polyethylene. This result is consistent with reported examples of (α-diimine)Ni and (pyridinediimine)Fe catalysts, in which decreasing the steric bulk on the imine aryl rings results in highly active olefin oligomerization catalysts.[25−28] It is conceivable that bulkier aryl groups on the ligand phosphine may generate higher molecular weight polymer. However, the competitive formation of P−O and P−P coupled products in the reaction of the diaryl phosphorus chlorides with the enolate (as determined by ^{31}P NMR) prevented the synthesis of phenacyldiarylphosphine ligands with any aryl groups larger than mesityl.[29]

Synthesis and Ethylene Polymerization Activity of (phenacyldiarylphosphine)PdMe(L)$^+$B(Ar$_f$)$_4^-$ Complexes. Cationic palladium methyl acetonitrile and

Scheme 2. Synthesis of (Phenacyldiarylphosphine)PdMe(L)$^+$B(Ar$_f$)$_4^-$ (L = NCMe, OEt$_2$)



methyl diethyl ether complexes **8a**−**c** and **9a**−**c** were prepared using an analogous procedure as described for catalysts **2** and **3** (Scheme 2).[12] The neutral palladium methyl chloride complexes **7a**−**c** were generated by treatment of (COD)PdMeCl (COD = 1,5-cyclooctadiene) with 1 equiv of the respective ligands **4a**−**c**. Slow addition of a CH_2Cl_2/ligand solution at −78 °C followed by warming to room temperature prevented the competitive formation of (bisphosphine)PdMeCl species.[30] Abstraction of chloride by NaB(Ar$_f$)$_4$ in the presence of excess acetonitrile forms the cationic palladium methyl complexes **8a**−**c**, in which an acetonitrile ligand occupies the fourth coordination site. Catalysts **8a**−**c** can be isolated as air-sensitive yellow-white powders that are stable for several hours in solution at room temperature. Complexes **9a**−**c** were generated by treatment of **7a**−**c** with NaB(Ar$_f$)$_4$ in diethyl ether solvent. The cationic methyl diethyl ether complexes **9a**−**c** are considerably less stable and decompose rapidly in solution at room temperature.

Due to the poor solution stability of the methyl diethyl ether cations **9a**−**c**, only the palladium methyl acetonitrile complexes were used for large-scale reactions with ethylene. The results of oligomerization experiments with **8a**−**c** under 200 psig ethylene pressure are shown in Table 4. As was the case with the previously reported phenacyldi-*tert*-butylphosphine-based catalysts, the Pd analogues are about an order of magnitude less active than their Ni counterparts.[12] Complexes **8a** and **8c** generate butenes, while **8b** forms a mixture of butenes and hexenes. The nature of the product from ethylene oligomerization reactions was determined by ^{1}H NMR spectroscopy and GC. In all cases the product is >90% α-olefin. Catalysts **8a**−**c** display rather short lifetimes, as the majority of the catalyst is deactivated after 1 h.

Mechanistic Studies of Ethylene Insertion into (phenacyldiarylphosphine)PdMe(η^2-C$_2$H$_4$)$^+$B-

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(26) Svejda, S. A.; Brookhart, M. *Organometallics* **1999**, *18*, 65.
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(29) P−O coupling products appear as a singlet in ^{31}P NMR spectra between 90 and 140 ppm. P−P coupled products appear as doublets from 100 to 130 and −30 to −60 ppm.

(30) The complex *trans*-(phenacyldiphenylphosphine)$_2$PdMeCl was independently generated by treatment of (COD)PdMeCl with 2 equiv of **4a**. This compound has been previously observed: Andrieu, J.; Braunstein, P.; Naud, F.; Adams, R. D. *J. Organomet. Chem.* **2000**, *601*, 43.

Table 4. Oligomerization of Ethylene with 8a−c[a]

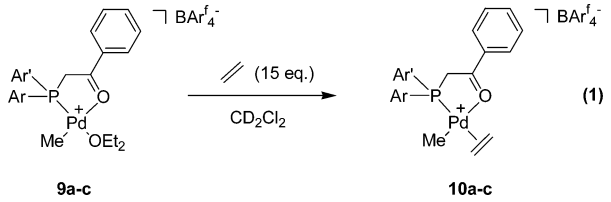
entry	catalyst	time (min)	yield (g)[b]	TON ($\times 10^{-3}$)	product[c]
1	**8a**	30	0.4	4.4	butenes
2	**8a**	60	0.5	5.6	butenes
3	**8b**	60	0.8	8.8	butenes[d]
4	**8c**	60	1.2	13	butenes

[a] Reaction conditions: 3.24 μmol of Pd catalyst; 200 psig ethylene; 105 mL of toluene; 25 °C. [b] Yield determined by mass of final reaction mixture vs mass of 105 mL of toluene (90.8 g). [c] Product determined by ^{1}H NMR and GC. [d] ^{1}H NMR suggests the presence of small quantities of higher α-olefins, presumably primarily 1-hexene.

Table 5. Ethylene Insertion Barriers for 10a−c

catalyst	temp (°C)	k_{ins} (s^{-1})	$\Delta G^{\ddagger}$ (kcal/mol)
10a	−20.0	$1.27(3) \times 10^{-4}$	19.2
10b	−20.0	$1.29(5) \times 10^{-4}$	19.2
10c	−20.0	$7.2(2) \times 10^{-5}$	19.5

$(Ar_f)_4^-$ Complexes. Treatment of palladium methyl ether complexes **9a−c** with 10−15 equiv of ethylene in CD_2Cl_2 at −78 °C cleanly generates the corresponding palladium methyl ethylene species (eq 1). These alkyl-



(1)

9a-c **10a-c**

olefin species serve as model complexes for the resting state in ethylene dimerization for these systems. The η^2-ethylene ligand appears as a broad singlet resonance at δ 5.40 in the ^{1}H NMR spectrum at −40 °C due to rapid exchange of free and bound ethylene on the NMR time scale. Sharp resonances for free diethyl ether at δ 3.41 (quartet) and 1.13 (triplet) indicate clean displacement of ether by ethylene. The kinetics of ethylene insertion into the palladium methyl bond were measured by warming the sample to −20 °C and monitoring the disappearance of the Pd-methyl resonance in the ^{1}H NMR spectrum over time. The first-order rate constants and corresponding free energies of activation for ethylene insertion into the Pd−methyl bond for **10a−c** are listed in Table 5. The insertion barriers for complexes **10a−c** are a full 2 kcal/mol lower than those previously observed for the di-*tert*-butylphosphine analogue **3**.[17] The significantly lower barrier to insertion in these systems is consistent with the observation that the phenacyldiarylphosphine catalysts display higher activities at lower reaction temperatures for ethylene polymerization and oligomerization than the analogous di-*tert*-butylphosphine complexes **1−3**. As was the case for **8a−c**, complexes **9a** and **9c** generate butenes and **9b** forms a mixture of butenes and hexenes. Since subsequent ethylene insertion and chain-transfer processes occur at approximately the same rate as ethylene insertion into the palladium−methyl bond, no palladium propyl species was observed as a reaction intermediate. After complete consumption of the Pd-methyl species a reaction mixture generated from **9b** was cooled to −90 °C; however no agostic species were observed in the ^{1}H NMR spectrum. This suggests the presence of an alkyl olefin complex, but spectra at this stage are too complex to make unambiguous assignments.

Table 6. Barriers to Ethylene Insertion for 10a and 10d−g

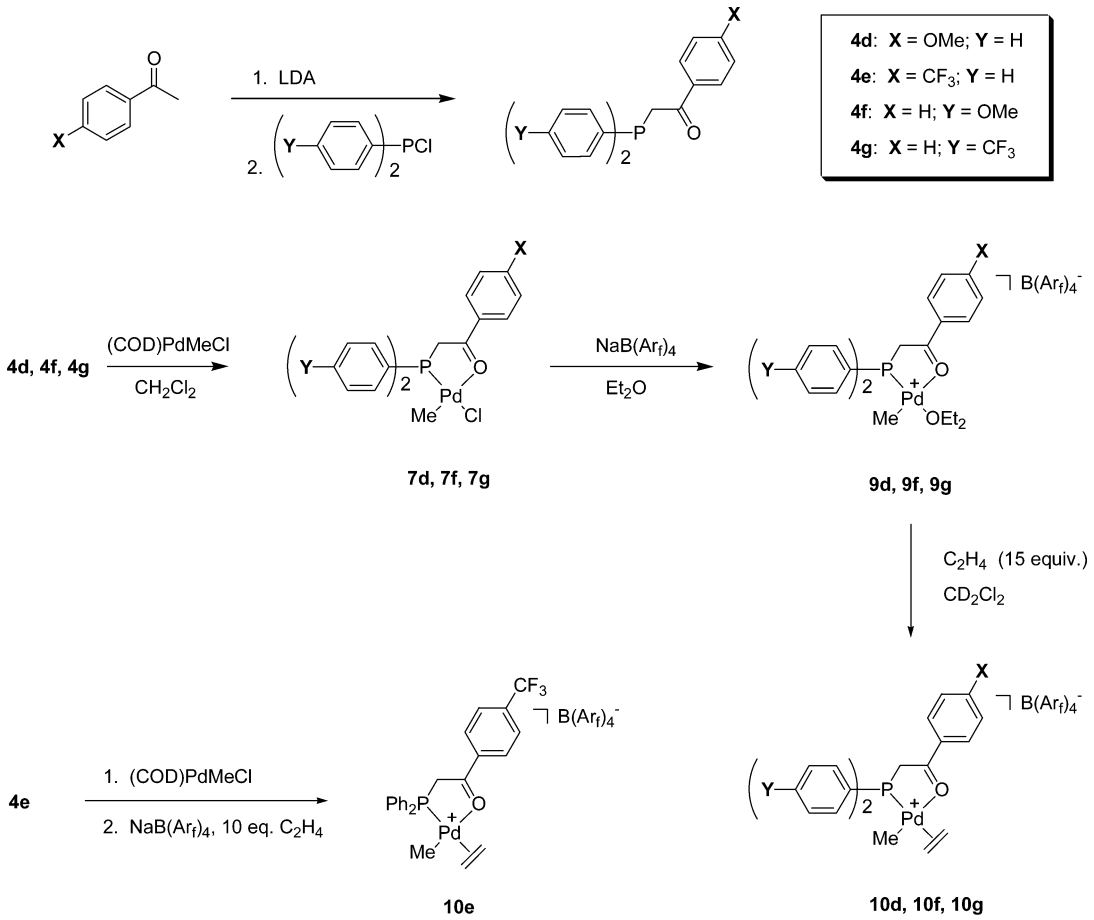
catalyst	temp (°C)	k_{ins}	$\Delta G^{\ddagger}$ (kcal/mol)
10a	−20.0	$1.27(3) \times 10^{-4}$	19.2
10d	−6.3	$1.68(9) \times 10^{-4}$	20.2
10e	−27.7	$9.6(2) \times 10^{-5}$	18.7
10f	−10.2	$6.7(1) \times 10^{-5}$	20.3
10g	−27.7	$2.9(1) \times 10^{-4}$	18.2

Electronic Effects on the Barrier to Migratory Insertion. Substitution of aryl groups for aliphatic *tert*-butyl groups on phosphorus has a significant impact on the reactivity of the corresponding cationic Ni(II) and Pd(II) catalysts, resulting in lower barriers to migratory insertion and faster catalyst initiation at low temperatures and ethylene pressures. It is unlikely that this is a result of the different steric influence of di-*tert*-butylphosphine compared to aryl phosphines since complexes **9a−c** have very different steric environments around the metal center yet very similar barriers to ethylene insertion. Thus, the observed trends in reactivity are likely due to the influence of the more electron-withdrawing aryl groups relative to the *tert*-butyl groups. Since access to palladium methyl ethylene complexes is relatively straightforward for these systems, we have investigated the electronic effects on the barrier for migratory insertion by synthesizing phenacyldiarylphosphine ligands with electron-donating and electron-withdrawing groups at the *para* position of the aryl groups of the $-PAr_2$ moiety and the $ArCO-$ moiety (Scheme 3). Ligands **4d−g** were synthesized using the same procedure as **4a−c** with the appropriate methoxy- or trifluoromethyl-substituted acetophenone and diarylchlorophosphines. Ligands **4d** and **4e** contain methoxy and trifluoromethyl groups, respectively, at the *para* positions of the phenacyl group, while ligands **4f** and **4g** bear similar substitution at the *para* positions of the diaryl substituents on phosphorus. Treatment of ligands **4d**, **4f**, and **4g** with (COD)PdMeCl generates the palladium methyl chloride complexes **7d**, **7f**, and **7g**, and subsequent chloride abstraction with $NaB(Ar_f)_4$ in diethyl ether solvent forms the cationic palladium methyl ether species **9d**, **9f**, and **9g**. The palladium methyl ethylene complex **10e** was accessed directly via reaction of $NaB(Ar_f)_4$ with the product of **4e** and (COD)PdMeCl in the presence of excess ethylene.[31]

The palladium methyl ethylene species **10d**, **10f**, and **10g** were accessed by addition of 15 equiv of ethylene to −78 °C solutions of **9d**, **9f**, and **9g** in CD_2Cl_2 (−78 °C), and the barriers for ethylene insertion into the palladium methyl bond for these complexes as well as for **10e** were determined via ^{1}H NMR spectroscopy by monitoring loss of the palladium methyl resonance over time (Table 6). The addition of an electron-donating *p*-methoxy group to the phenacyl moiety (**10d**) raises the barrier to ethylene insertion by 1.0 kcal/mol (compared to unsubstituted complex **9a**), while an electron-withdrawing trifluoromethyl group at the same position

(31) Reaction of **4e** with (COD)PdMeCl in THF yields a clear yellow solution. ^{31}P NMR indicates one product at δ 30.59 which is consistent with a κ^2-(P, O)PdMeCl complex. Upon workup, an insoluble white solid is isolated that is most likely a chloride-bridged dimeric complex. Treatment of this material with $NaBAr'_4$ in diethyl ether does not form the $(P,O)PdMe(OEt_2)^+BAr'_4{}^-$ complex but likely forms the cationic chloride-bridged dimer. Treatment of the product with $NaBAr'_4{}^-$ in the presence of excess ethylene in CD_2Cl_2 does in fact form the desired $(P,O)PdMe(\eta^2\text{-ethylene})^+BAr'_4{}^-$ complex **10e**.

Scheme 3. Synthesis of *para*-Methoxy- and *para*-Trifluoromethyl-Substituted Ligands and Corresponding Palladium Complexes



(**10e**) lowers the barrier by approximately 0.5 kcal/mol. Similarly, *p*-methoxy group substitution on the phosphine phenyl groups (**9f**) results in a 1.1 kcal/mol larger barrier, while trifluoromethyl group substitution decreases the barrier by 1.0 kcal/mol. Complexes **9d**, **9f**, **9g**, and **10e** all generate predominately 1-butene when exposed to ethylene.

There is strong evidence that, of the two possible isomers, the methyl ethylene complexes **10a**−**g** adopt the structures shown in Figure 3. This general structure is consistent with the expected ligand *trans* effects in that the better donor methyl group is *trans* to the poorer donor keto group and the weaker donor C_2H_4 is *trans* to the better donor phosphine. In addition the X-ray crystal structure in the close analogue [κ^2-(*t*-Bu)$_2$PCH$_2$-C(O)C$_6$H$_5$]PdMe(η^2-C$_2$H$_4$)$^+$B(Ar$_f$)$_4^-$, **11**, exhibits this geometry.[32] The substituent effects observed suggest that decrease in the donor ability of either the diaryl phosphine ligand or the keto group decreases the barrier to insertion, while increase in the donor ability of either group increases the insertion barrier. This observation is consistent with the general notion that increasing the electrophilicity of the metal center should decrease the insertion barrier. This trend is further reinforced by the observation that the barrier to insertion in the di-*tert*-butylphosphine complex **11** is higher than that of **10a**−**g**, and the barrier in the imine derivative **12** containing the better imine N donor atom exceeds 24 kcal/mol, although in both cases steric factors may play a role.[33,34]

These findings are somewhat unexpected in view of earlier experimental[34] and theoretical[35] results that suggest that in d^8 square-planar methyl ethylene complexes containing unsymmetrical bidentate ligands increasing the donor strength *trans* to the strong donor methyl group should lower the migration barrier, while decreasing the donor strength should raise the insertion barrier. Further study of the effects of electronically asymmetric ligands on insertion barriers is in progress.

Summary

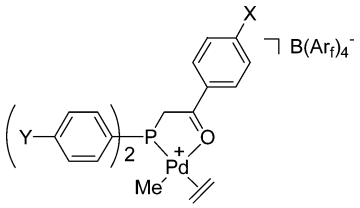
In summary, a new series of cationic Ni(II) and Pd(II) catalysts bearing bidentate phenacyldiarylphosphine ligands are reported. Ni-allyl complexes **6a**−**c** are very active catalysts for polymerization and oligomerization of ethylene. Complex **6b** generates linear polyethylene with M_n = 770−1130, while **6a** and **6c** are highly active for the dimerization of ethylene to predominantly 1-butene. These results indicate that *ortho*-substitution on both phosphine aryl substituents is required to sufficiently retard the rate of chain transfer relative to propagation to generate polymeric materials.

(32) Malinoski, J. M.; Brookhart, M. *Organometallics* **2003**, *22*, 621.

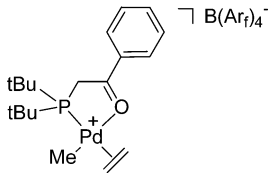
(33) The palladium methyl ethylene complex **12** was stable (no ethylene insertion) in CD_2Cl_2 solution at 25 °C for over 6 h. Assuming a minimum half-life of 24 h at this temperature, we calculate a maximum $k_{obs} = 8 \times 10^{-6}$ s^{-1} and a minimum $\Delta G^{\ddagger} = 24.5$ kcal/mol. Malinoski, J. M.; Brookhart, M. Unpublished results. For a general procedure for synthesis of complexes of the type **12** see ref 34.

(34) Daugulis, O.; Brookhart, M. *Organometallics* **2002**, *21*, 5926.

(35) Chan, M. S. W.; Deng, L.; Ziegler, T. *Organometallics* **2000**, *19*, 2741.



10a-g



11

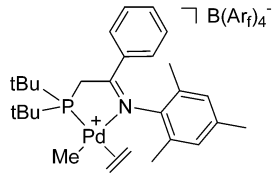


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Figure 3. (P,O)Pd methyl ethylene complexes.

Table 7. Summary of Crystal Data, Data Collection, and Structure Refinement Parameters for Complex 6b

formula	$C_{65}H_{56}O_2BF_{24}PNi$
fw	1425.60
temp (K)	173
space group	$P\bar{1}$
a (Å)	12.7745(9)
b (Å)	14.2552(11)
c (Å)	17.9429(14)
V, Å^3	3225.0(4)
Z	2
μ(Mo Kα) (Å)	0.71073
ρ_{calcd} (mg m^{-3})	1.468
cryst size (mm)	0.30 × 0.25 × 0.05
2θ range (deg)	5.00−45.00
total no. of reflns	28031
no. of unique data, $I = 3.0\sigma(I)$	4133
R_{merge}	0.047
no. of params	847
R1	0.062
wR2	0.064
goodness of fit	2.3211

Catalysts **6a**−**c** are characterized by their high activities at lower reaction temperatures but poor thermal stability and short catalyst lifetimes. Cationic palladium methyl acetonitrile complexes **8a**−**c** showed modest activity for oligomerization of ethylene to butenes and hexenes at high ethylene pressure but also displayed short catalyst lifetimes. The barrier to migratory insertion of ethylene in the palladium methyl ethylene complexes in these systems was found to be 19.2−19.5 kcal/mol, which is about 2 kcal/mol lower than that previously measured for the analogous phenacyldi-*tert*-butylphosphine complex. Electronic effects on the ethylene barrier were investigated by synthesis of ligands **4d**−**g** bearing electron-donating methoxy and electron-withdrawing trifluoromethyl groups at the *para* position of the phenacyl group and phosphine aryl groups. Measurement of the barrier for ethylene insertion in the palladium methyl ethylene complexes derived from these ligands showed that the electron-withdrawing $-CF_3$ group on either the phenacyl group or the arylphosphine substituents lowered the activation barrier by 0.5−1.0 kcal/mol, while the electron-donating $-OCH_3$ group in these positions raised the barrier to insertion by approximately 1.0 kcal/mol. These results suggest that the magnitude of the insertion barrier for these systems is governed by the overall electrophilic nature of the metal and not the donor properties of the phosphine or ketone binding sites alone.

Experimental Section

General Considerations. All manipulations of compounds were performed using standard high-vacuum or Schlenk techniques. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves. Solid organometallic compounds were transferred in an argon-filled MBraun drybox. NMR spectra were acquired with Bruker AMX300 or DRX400 spectrometers. ^{1}H and ^{13}C chemical shifts are reported in ppm downfield of TMS and were referenced to residual ^{1}H NMR signals and to the ^{13}C NMR signals of the deuterated solvents, respectively. ^{31}P NMR chemical shifts are reported relative to H_3PO_4. Coupling constant J values are reported in Hz. All spectra were acquired at room temperature unless otherwise noted.

Materials. Hexanes, diethyl ether, pentane, methylene chloride, toluene, and acetonitrile were deoxygenated and dried via passage over a column of activated alumina.[36] Tetrahydrofuran was distilled from sodium/benzophenone under nitrogen. Chloroform-*d*, methylene chloride-d_2, and bromobenzene-d_5 were purchased from Cambridge Isotope Laboratories and dried over 4 Å molecular sieves. Polymer grade ethylene was purchased from Matheson and used without further purification for both the bulk polymerizations and the NMR experiments. Diisopropylamine was distilled and stored over molecular sieves. Acetophenone, n-C_4H_9Li (1.6 M in hexanes), chlorodiphenylphosphine, dichlorophenylphosphine, 4′-methoxyacetophenone, and 4′-trifluoroacetophenone were purchased from Aldrich and used without further purification. NaB(Ar$_f$)$_4$ was purchased from Boulder Scientific Company and used without further purification. Phenacyldiphenylphosphine[18] (**4a**), dimesitylchlorophosphine,[19] 2,4,6-triphenylbromobenzene,[37] bis (4-methoxyphenyl)chlorophosphine,[37] bis[4-(trifluoromethyl)phenyl]chlorophosphine,[38] [(C_3H_5)NiCl]$_2$,[39] and (COD)PdMeCl[40] were prepared according to literature procedures.

Spectral Data for the B(Ar$_f$)$_4$ Counterion. The following ^{1}H and ^{13}C spectroscopic assignments of the BAr′$_4^-$ counterion in CD_2Cl_2 were invariant for different complexes and temperatures and are not reported in the spectroscopic data for each of the cationic complexes.

B[3,5-C$_6$H$_3$-(CF$_3$)$_2$]$_4^-$ [B(Ar$_f$)$_4$]. ^{1}H NMR (CD_2Cl_2): δ 7.74 (s, 8H, H$_o$), 7.57 (s, 4H, H$_p$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 162.2 (q, J_{CB} = 37.4 Hz, C$_{ipso}$), 135.2 (C$_o$), 129.3 (q, J_{CF} = 31.3 Hz, C$_m$), 125.0 (q, J_{CF} = 272.5 Hz, CF_3), 117.9 (C$_p$).

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(Phenacyldiphenylphosphine)Ni-allyl(Cl) (5a). To a mixture of $[(C_3H_5)NiCl]_2$ (0.075 g, 0.28 mmol) and **4a** (0.175 g, 0.58 mmol) was added 15 mL of hexanes. The resulting orange suspension was stirred for 3 h. The orange solid precipitate was isolated by filtration, washed with 10 mL of pentane, and dried under high vacuum. Yield: 0.196 g (82%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.93 (d, 2H, J = 7.2, H−Ar$_o$), 7.66 (m, 3H, H$_{Ar}$), 7.56 (m, 2H, H$_{Ar}$), 7.42 (m, 8H, H$_{Ar}$), 5.44 (m, 1H, allyl −CH−), 4.21 (d, 2H, J_{PH} = 9.3, −CH$_2$−), 3.36 (br s, 2H, allyl H$_2$C−), 2.51 (br s, 2H, allyl H$_2$C−). ^{13}C{^{1}H} NMR (100.62 MHz, CD_2Cl_2): δ 196.1 (d, J_{CP} = 2), 137.4 (d, J_{CP} = 2), 133.8, 133.6 (d, J_{CP} = 12), 132.9 (d, J_{CP} = 40), 130.7 (d, J_{CP} = 1.6), 129.0, 128.9, 128.9, 128.8, 111.3. ^{31}P{^{1}H} NMR (121.49 MHz, CD_2Cl_2): δ 17.15. Anal. Calcd for $C_{23}H_{17}ClOPNi$: C, 62.84; H, 3.90. Found: C, 62.90; H, 4.70.

(Phenacyldiphenylphosphine)Ni-allyl$^+$B(Ar$_f$)$_4^-$ (6a). To a mixture of **5a** (0.050 g, 0.11 mmol) and NaB(Ar$_f$)$_4$ (0.102 g, 0.12 mmol) at −78 °C was added 10 mL of diethyl ether. The resulting yellow suspension was warmed to room temperature and stirred for 2 h. The solution was isolated via filtration, and the solvent was removed in vacuo. The resulting yellow-orange oil was coevaporated with 2 × 5 mL of pentane, and the residual brittle foam was dried under high vacuum to form a yellow powder. Yield: 0.097 g (67%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.11 (d, 2H, J = 8.6, H−Ar$_o$), 7.87 (t, 1H, J = 7.6, H−Ar$_p$), 7.60 (m, 12H, H$_{Ar}$), 5.94 (m, 1H, allyl −CH−), 4.33 (br s, 2H, −CH$_2$−), 3.55 (br s, 2H, allyl CH$_2$−), 2.35 (br s, 2H, allyl CH$_2$−). ^{13}C{^{1}H} NMR (75.48 MHz, CD_2Cl_2): δ 212.4, 138.6, 133.0, 132.7, 132.5, 131.6, 130.3, 130.2, 130.1, 119.4, 44.8. ^{31}P{^{1}H} NMR (161.96 MHz, CD_2Cl_2): δ 28.63. Anal. Calcd for $C_{55}H_{29}BF_{24}OPNi$: C, 52.13; H, 2.31. Found: C, 52.34; H, 2.89.

(Phenacyldiphenylphosphine)PdMe(Cl) (7a). To a solution of (COD)PdMeCl (0.158 g, 0.60 mmol) in 10 mL of CH_2Cl_2 at −78 °C was added a solution of **4a** (0.181 g, 0.59 mmol) in 10 mL of CH_2Cl_2. The resulting solution was warmed to room temperature and stirred for 1 h. The solvent was removed in vacuo, and the resulting white solid residue was washed with 2 × 10 mL of pentane and dried under high vacuum. Yield: 0.162 g (59%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (m, 4H, H$_{Ar}$), 7.67 (m, 1H, H$_{Ar}$), 7.35 (m, 8H, H$_{Ar}$), 7.21 (m, 2H, H$_{Ar}$), 4.18 (d, 2H, J_{PH} = 10, −CH$_2$−), 0.60 (s, 3H, Pd−Me). ^{13}C-{^{1}H} NMR (75.48 MHz, CD_2Cl_2): δ 204.5, 134.1. 134.0, 133.5, 131.0 (d, J_{CP} = 2), 130.7, 130.0, 128,6 (d, J_{CP} = 2), 128.5, 38.8, 5.1. ^{31}P{^{1}H} NMR (161.87 MHz, $CDCl_3$): δ 31.69. Anal. Calcd for $C_{21}H_{20}ClOPPd$: C, 54.69; H, 4.37. Found: C, 55.09; H, 4.57.

(Phenacyldiphenylphosphine)PdMe(NCMe)$^+$B(Ar$_f$)$_4^-$ (8a). To a mixture of **7a** (0.050 g, 0.11 mmol) and NaB(Ar$_f$)$_4$ (0.097 g, 0.110 mmol) at −78 °C were added 8 mL of diethyl ether and acetonitrile (0.20 mL, 2.82 mmol). The resulting pale yellow suspension was warmed to 0 °C and stirred for 1 h. The solution was isolated via filtration and the solvent removed in vacuo. The yellow oil residue was coevaporated with 2 × 5 mL of pentane at 0 °C, and the resulting brittle foam was dried under high vacuum to form a white-yellow solid powder. Yield: 0.061 g (42%). ^{1}H NMR (400 MHz, CD_2Cl_2, 258 K): δ 8.02 (d, 2H, J = 8.2, H−Ar$_o$) 7.75 (m, 1H, H−Ar$_p$) 7.62 (m, 8H, H$_{Ar}$), 7.51 (m, 4H, H$_{Ar}$), 4.41 (d, 2H, J_{PH} = 11.2, −CH$_2$−), 2.36 (s, 3H, Pd−NCMe), 0.84 (s, 3H, Pd−Me). ^{13}C-{^{1}H} NMR (100.62 MHz, CD_2Cl_2, 258 K): δ 197.2, 137.2, 133.4, 133.2, 132.9, 130.6, 130.0, 129.9, 129.8, 129.7, 128.7, 34.4, 3.4. ^{31}P{^{1}H} NMR (161.96 MHz, CD_2Cl_2, 258 K): δ 37.02. This compound was not sufficiently stable for elemental analysis.

(Phenacyldiphenylphosphine)PdMe(OEt$_2$)$^+$B(Ar$_f$)$_4^-$ (9a). To a mixture of **7a** (0.050 g, 0.11 mmol) and NaB(Ar$_f$)$_4$ (0.097 g, 0.110 mmol) at −78 °C was added 10 mL of diethyl ether. The resulting pale yellow suspension was warmed to 0 °C and stirred for 1 h. The solution was isolated via filtration and the solvent removed in vacuo. The yellow oil residue was coevaporated with 2 × 5 mL of pentane at 0 °C, and the resulting brittle foam was dried under high vacuum to form a pale white solid powder. Yield: 0.063 g (43%). ^{1}H NMR (300 MHz, CD_2Cl_2, 258 K): δ 7.96 (d, 2H, J = 7.5, H−Ar$_o$), 7.60 (m, 9H, H$_{Ar}$), 7.46 (m, 4H, H$_{Ar}$), 4.40 (d, 2H, J_{PH} = 11, −CH$_2$−), 3.91 (m, 4H, OC*H*$_2$CH$_3$), 1.58 (m, 6H, OCH$_2$C*H*$_3$), 0.97 (s, 3H, Pd−Me). ^{13}C{^{1}H} NMR (75.48 MHz, CD_2Cl_2, 258 K): δ 205.3, 137.6, 133.3, 130.7, 130.1, 130.0, 129.9, 126.6, 47.0 (d, J_{CP} = 37), 22.8, 16.4, −0.1. ^{31}P{^{1}H} NMR (121.49 MHz, CD_2Cl_2, 258 K): δ 37.51. This compound was not sufficiently stable for elemental analysis.

Phenacyldimesitylphosphine (4b). To a −78 °C solution of diisopropylamine (0.34 mL, 2.41 mmol) in 10 mL of THF was added *n*-C_4H_9Li (1.5 mL, 2.41 mmol, 1.6 M solution in hexanes). The LDA solution was stirred for 30 min and added via cannula to a −78 °C solution of acetophenone (0.28 mL, 2.41 mmol) in 10 mL of THF. The solution was stirred for 2 h and added via cannula to a −78 °C solution of dimesitylchlorophosphine (0.700 g, 2.30 mmol) in 20 mL of THF. The resulting yellow solution was warmed to room temperature and stirred for 2 h. The reaction mixture was concentrated to ca. 5 mL in vacuo, and 20 mL of toluene was added to fully precipitate the white solid LiCl. The solution was filtered through Celite, and the solvent was removed in vacuo to yield a yellow oil. The residue was stirred in 20 mL of pentane at 0 °C for 1 h to yield a white precipitate. The solid was isolated via filtration and washed with 10 mL of cold pentane to yield a white powder. Yield: 0.485 g (54%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, 2H, J = 7.6, Ar−H$_o$), 7.47 (t, 1H, J = 7.2, Ar−H$_p$), 7.34 (t, 2H, J = 7.6, Ar−H$_m$), 6.70 (d, 4H, J = 3, Ar$_{Mes}$), 4.12 (d, 2H, J_{PH} = 1.6, −CH$_2$−), 2.18 (s, 6H, Mes−Me$_p$), 2.16 (s, 12H, Mes−Me$_o$). ^{13}C{^{1}H} NMR (75.48 MHz, CD_2Cl_2): δ 197.4 (d, J_{CP} = 9.9), 141.9 (d, J_{CP} = 14.7), 138.3, 138.2, 133.0, 132.0 (d, J_{CP} = 24.4), 130.1 (d, J_{CP} = 3), 128.7 (d, J_{CP} = 3), 128.5, 39.4 (d, J_{CP} = 25), 22.9 (d, J_{CP} = 13.8), 20.7. ^{31}P{^{1}H} NMR (161.87 MHz, $CDCl_3$): δ −24.73. Anal. Calcd for $C_{26}H_{29}OP$: C, 80.38; H, 7.52. Found: C, 79.41; H, 7.47.

(Phenacyldimesitylphosphine)Ni-allyl(Cl) (5b). To a mixture of $[(C_3H_5)NiCl]_2$ (0.051 g, 0.19 mmol) and **4b** (0.150 g, 0.39 mmol) was added 15 mL of hexanes. The resulting orange suspension was stirred for 3 h. The orange solid precipitate was isolated by filtration, washed with 10 mL of pentane, and dried under high vacuum. Yield: 0.119 g (60%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.68 (m, 2H, Ar−H$_o$), 7.46 (t, 1H, J = 6.4, Ar−H$_p$), 7.32 (m, 2H, Ar−H$_m$), 6.79 (s, 4H, Ar−H$_m$), 5.44 (m, 1H, allyl −CH−), 4.41 (m, 2H, −CH$_2$−), 3.34 (br s, 2H, allyl CH$_2$−), 2.55 (s, 6H, Mes−Me$_p$), 2.37 (br s, 2H, allyl CH$_2$−), 2.22 (s, 12H, Mes−Me$_o$). ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2): δ 196.6, 141.6 (d, J_{CP} = 9.5), 140.0, 138.3, 133.2, 131.1, 131.0, 128.7, 128.5. 109.8, 39.7 (d, J_{CP} = 19.7), 25.2, 21.0. ^{31}P{^{1}H} NMR (161.87 MHz, CD_2Cl_2): δ −0.59. Anal. Calcd for $C_{29}H_{34}ClOPNi$: C, 66.51; H, 6.54. Found: C, 65.55; H, 6.48.

(Phenacyldimesitylphosphine)Ni-allyl$^+$B(Ar$_f$)$_4^-$ (6b). To a mixture of **5b** (0.090 g, 0.17 mmol) and NaB(Ar$_f$)$_4^-$ (0.152 g, 0.17 mmol) at −78 °C was added 10 mL of diethyl ether. The resulting yellow suspension was warmed to room temperature and stirred for 2 h. The solution was isolated via filtration, and the solvent was removed in vacuo. The resulting yellow-orange oil was coevaporated with 2 × 5 mL of pentane, and the residual brittle foam was dried under high vacuum to form a yellow powder. Yield: 0.169 g (73%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.02 (d, 2H, J = 8, Ar−H$_o$), 7.82 (t, 1H, J = 7, Ar−H$_p$), 7.58 (m, 2H, Ar−H$_m$), 6.98 (s, 4H, Ar−H$_m$), 5.86 (m, 1H, allyl −CH−), 4.81 (m, 2H, −CH$_2$−), 4.17 (m, 1H, allyl C*H*H′−), 3.70 (m, 1H, allyl CH*H*′−), 3.06 (br s, 1H, allyl −*H*H′C), 2.42 (d, 12H, J = 6, Mes−Me$_o$), 2.28 (d, 6H, J = 3.6, Mes−Me$_p$), 1.95 (d, 1H, J = 13, allyl −CH*H*′). ^{13}C{^{1}H} NMR (75.48 MHz, CD_2Cl_2): δ 204.2, 138.7, 133.2, 132.3 (d, J_{CP} = 8.4), 131.9 (d, J_{CP} = 9), 131.7, 130.4, 126.9, 123.3, 119.7, 117.4, 51.3, 48.2 (d, J_{CP} = 28.7), 24.8, 21.2. ^{31}P{^{1}H} NMR (161.87 MHz, CD_2Cl_2): δ 5.64. Anal. Calcd for $C_{61}H_{46}BF_{24}OPNi$: C, 54.23; H, 3.43. Found: C, 53.61; H, 3.45.

(Phenacyldimesitylphosphine)PdMe(Cl) (7b). To a suspension of (COD)PdMeCl (0.105 g, 0.40 mmol) in 10 mL of diethyl ether was added a solution of **4b** (0.185 g, 0.48 mmol) in 10 mL of diethyl ether. The resulting yellow solution was stirred for 2 h, during which time a white precipitate formed. The solid was isolated via filtration, washed with 2 × 10 mL of pentane, and dried under high vacuum to yield a white-yellow solid. Yield: 0.120 g (56%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.92 (d, 2H, J = 8.6, Ar−H_o), 7.67 (t, 1H, J = 9, Ar−H_p), 7.47 (t, 2H, J = 8, Ar−H_m), 6.91 (d, 4H, J = 3.6, Ar−H_m), 4.51 (d, 2H, J_{PH} = 10, −CH_2−), 2.48 (s, 12H, Mes−Me_o), 2.26 (s, 6H, Mes−Me_p), 0.86 (d, 3H, J_{PH} = 3.6, Pd−Me). ^{13}C{^{1}H} NMR (75.48 MHz, CD_2Cl_2): δ 204.7 (d, J_{CP} = 4.9), 141.5, (d, J_{CP} = 2.3), 136.1, 135.1 (d, J_{CP} = 4.9), 131.8 (d, J_{CP} = 8.5), 130.3, 129.63, 127.1, 126.4, 48.4 (d, J_{CP} = 30.5), 24.9 (d, J_{CP} = 8.7), 21.1, −1.3. ^{31}P{^{1}H} NMR (161.87 MHz, CD_2Cl_2): δ 9.32. Anal. Calcd for $C_{27}H_{32}ClOPPd$: C, 59.46; H, 5.92. Found: C, 58.32; H, 5.99.

(Phenacyldimesitylphosphine)PdMe(NCMe)$^+$B(Ar$_f$)$_4^-$ (8b). To a mixture of **7b** (0.040 g, 0.073 mmol) and NaB(Ar_f)$_4$ (0.066 g, 0.074 mmol) at −78 °C was added 10 mL of diethyl ether and acetonitrile (0.50 mL, 9.6 mmol). The resulting pale yellow suspension was warmed to 0 °C and stirred for 1 h. The solution was isolated via filtration and the solvent removed in vacuo. The yellow oil residue was coevaporated with 2 × 5 mL of pentane at 0 °C, and the resulting brittle foam was dried under high vacuum to form a white-yellow solid powder. Yield: 0.043 g (41%). ^{1}H NMR (300 MHz, CD_2Cl_2, 268 K): δ 7.93 (d, 2H, J = 7.5, Ar−H_o), 7.70 (m, 1H, Ar−H_p), 7.50 (t, 2H, Ar−H_m), 6.94 (d, 4H, J = 4, Ar−H_m), 4.55 (d, 2H, J_{PH} = 10, −CH_2−), 2.43 (s, 12H, Mes−Me_o), 2.36 (s, 3H, Pd−NCMe), 2.26 (s, 6H, Mes−Me_p), 0.76 (d, 3H, J_{PH} = 2, Pd−Me). ^{13}C{^{1}H} NMR (75.48 MHz, CD_2Cl_2, 268 K): δ 206.7, 142.5, 140.7 (d, J_{CP} = 9.6), 137.2, 133.8 (d, J_{CP} = 5.8), 132.0 (d, J_{CP} = 9.0), 130.5, 129.8, 124.7, 124.0, 49.5 (d, J_{CP} = 41), 25.0 (d, J_{CP} = 8.6), 22.8, 21.1, 3.5. ^{31}P{^{1}H} NMR (121.49 MHz, CD_2Cl_2, 268 K): δ 7.63. This compound was not sufficiently stable for elemental analysis.

(Phenacyldimesitylphosphine)PdMe(OEt$_2$)$^+$B(Ar$_f$)$_4^-$ (9b). To a mixture of **7b** (0.040 g, 0.073 mmol) and NaB(Ar_f)$_4$ (0.066 g, 0.074 mmol) at −78 °C was added 10 mL of diethyl ether. The resulting pale yellow suspension was warmed to 0 °C and stirred for 1 h. The solution was isolated via filtration and the solvent removed in vacuo. The yellow oil residue was coevaporated with 2 × 5 mL of pentane at 0 °C, and the resulting brittle foam was dried under high vacuum to form a pale white solid powder. Yield: 0.050 g (48%). ^{1}H NMR (300 MHz, CD_2Cl_2, 258 K): δ 7.88 (d, 2H, J = 7.8, Ar−H_o), 7.68 (m, 1H, Ar−H_p), 7.41 (t, 2H, J = 7.5, Ar−H_m), 6.91 (d, 4H, J = 4, Ar−H_m), 4.58 (d, 2H, J_{PH} = 10, −CH_2−), 3.85 (q, 4H, J = 7, OCH_2CH$_3$), 2.41 (s, 12H, Mes−Me_o), 2.25 (s, 6H, Mes−Me_p), 1.47 (t, 6H, OCH$_2$CH_3), 0.85 (s, 3H, Pd−Me). ^{13}C{^{1}H} NMR (75.48 MHz, CD_2Cl_2, 258 K): δ 206.1, 142.4, 140.4 (d, J_{CP} = 9.6), 132.0 (d, J_{CP} = 9.1), 130.4, 129.8, 126.6, 123.0, 119.4, 50.2 (d, J_{CP} = 38), 34.5, 24.9 (d, J_{CP} = 8.8), 21.0, 15.9, 2.8. ^{31}P{^{1}H} NMR (121.49 MHz, CD_2Cl_2, 258 K): δ 6.91. This compound was not sufficiently stable for elemental analysis.

(2,4,6-Triphenylaryl)chlorophenylphosphine. A −78 °C solution of 2,4,6-triphenylbromobenzene (2.00 g, 5.2 mmol) and 20 mL of THF was charged with n-C_4H_9Li (3.3 mL, 5.2 mmol, 1.6 M solution in hexanes). The resulting white suspension was stirred for 1 h, then added via cannula to a −78 °C solution of dichlorophenylphosphine (0.70 mL, 5.2 mmol) in 15 mL of THF. The reaction mixture was warmed to room temperature and stirred for 2 h. The solvent was removed in vacuo, and 15 mL of toluene was added to precipitate LiCl. The suspension was filtered through Celite and the solvent removed in vacuo to yield a pale yellow oil. The residue was stirred in 15 mL of hexanes for 2 h, during which time a white precipitate formed. The solid was isolated via filtration, washed with 10 mL of pentane, and dried in vacuo to yield a white powder. Yield: 1.153 g (50%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64 (d, 2H, J = 7, Ar−H_o), 7.51 (d, 6H, J = 2.4, Ar−H_0), 7.38 (m, 8H, H_{Ar}), 7.00 (m, 4H, H_{Ar}), 6.89 (m, 2H, H_{Ar}). ^{13}C{^{1}H} NMR (75.48 MHz, $CDCl_3$): δ 151.5 (d, J_{CP} = 30), 143.3, 141.9 (d, J_{CP} = 8), 139.6, 138.6 (d, J_{CP} = 35), 136.4 (d, J_{CP} = 45), 134.3 (d, J_{CP} = 45), 130.1 (d, J_{CP} = 3), 129.2, 129.1, 128.9, 128.5, 127.9 (d, J_{CP} = 5), 127.7, 127.5, 127.3. ^{31}P{^{1}H} NMR (121.49 MHz, $CDCl_3$): δ 79.15. Anal. Calcd for $C_{30}H_{22}ClP$: C, 80.26; H, 4.94. Found: C, 80.06; H, 5.03.

Phenacyl(2,4,6-triphenylaryl)phenylphosphine (4c). To a −78 °C solution of diisopropylamine (0.31 mL, 2.23 mmol) in 10 mL of THF was added n-C_4H_9Li (1.4 mL, 2.23 mmol, 1.6 M solution in hexanes). The LDA solution was stirred for 30 min and added via cannula to a −78 °C solution of acetophenone (0.26 mL, 2.23 mmol) in 10 mL of THF. The solution was stirred for 2 h and added via cannula to a −78 °C solution of (2,4,6-triphenylaryl)chlorophenylphosphine (1.00 g, 2.23 mmol) in 20 mL of THF. The resulting yellow solution was warmed to room temperature and stirred for 2 h. The reaction mixture was concentrated to ca. 5 mL in vacuo and 20 mL of toluene was added to fully precipitate the white solid LiCl. The solution was filtered through Celite, and the solvent was removed in vacuo to yield a yellow oil. The residue was stirred in 20 mL of pentane at 0 °C for 1 h to yield a white precipitate. The solid was isolated via filtration and washed with 10 mL of cold pentane to yield a white powder. Yield: 0.584 g (49%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.65 (m, 5H, H_{Ar}), 7.53 (m, 3H, H_{Ar}), 7.42 (m, 8H, H_{Ar}), 7.17 (m, 7H, H_{Ar}), 6.97 (m, 4H, H_{Ar}), 3.13 (m, 2H, −CH_2−). ^{13}C{^{1}H} NMR (75.48 MHz, CD_2Cl_2): δ 197.6 (d, J_{CP} = 11), 150.5 (d, J_{CP} = 16), 143.1 (d, J_{CP} = 4.8), 141.2, 141.1, 139.8, 137.0, 133.1, 132.9, 130.8 (d, J_{CP} = 17), 129.9 (d, J_{CP} = 2), 129.1, 129.0 (d, J_{CP} = 2.7), 128.6 (d, J_{CP} = 3), 128.5, 128.4, 128.2, 128.1, 127.8, 127.5, 127.2 (d, J_{CP} = 4.5), 39.2 (d, J_{CP} = 22). ^{31}P{^{1}H} NMR (161.86 MHz, CD_2Cl_2): δ −20.79. Anal. Calcd for $C_{38}H_{29}BOP$: C, 85.69; H, 5.49. Found: C, 83.29; H, 5.52.

[Phenacyl(2,4,6-triphenylaryl)phenylphosphine]Ni-allyl(Cl) (5c). To a mixture of $[(C_3H_5)NiCl]_2$ (0.044 g, 0.16 mmol) and **4c** (0.091 g, 0.17 mmol) was added 15 mL of hexanes. The resulting orange suspension was stirred for 3 h. The orange solid precipitate was isolated by filtration, washed with 10 mL of pentane, and dried under high vacuum. Yield: 0.170 g (78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, 2H, J = 7.6, Ar−H_o), 7.57 (m, 5H, H_{Ar}), 7.42 (m, 10H, H_{Ar}), 7.39 (m, 6H, H_{Ar}), 6.95 (m, 4H, H_{Ar}), 5.18 (m, 1H, allyl −CH−), 3.98 (m, 2H, −CH_2−), 2.65 (m, 2H, allyl H_2C−), 1.91 (m, 2H, allyl −CH_2). ^{13}C{^{1}H} NMR (75.48 MHz, CD_2Cl_2): δ 198.0, 149.8 (d, J_{CP} = 15), 147.6, 143.8 (d, J_{CP} = 7), 142.7, 139.6, 139.2, 137.9, 132.0, 131.9, 130.9 (d, J_{CP} = 11.3), 129.7, 129.5, 128.9, 128.8, 128.3, 127.8, 111.3, 41.6 (m). ^{31}P{^{1}H} NMR (161.87 MHz, $CDCl_3$): δ 10.98. Anal. Calcd for $C_{41}H_{34}ClOPNi$: C, 73.74; H, 5.13. Found: C, 71.78; H, 5.34.

[Phenacyl(2,4,6-triphenylaryl)phenylphosphine]Ni-allyl$^+$B(Ar$_f$)$_4^-$ (6c). To a mixture of **5c** (0.085 g, 0.13 mmol) and NaB(Ar_f)$_4$ (0.113 g, 0.13 mmol) at −78 °C was added 15 mL of diethyl ether. The resulting yellow suspension was warmed to room temperature and stirred for 2 h. The solution was isolated via filtration, and the solvent was removed in vacuo. The resulting yellow-orange oil was coevaporated with 2 × 5 mL of pentane, and the residual brittle foam was dried under high vacuum to form an orange powder. Yield: 0.123 g (65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, 2H, J = 7.6, Ar−H_o), 7.76 (t, 1H, J = 7.6, Ar−H_p), 7.65 (m, 8H, H_{Ar}), 7.47 (m, 7H, H_{Ar}), 7.28 (m, 1H, Ar−H_p), 7.18 (m, 2H, H_{Ar}), 6.74 (m, 2H, H_{Ar}), 4.75 (m, 1H, allyl −CH−), 4.25 (m, 1H, allyl HH'C−), 3.49 (m, 2H, −CH_2−), 3.07 (br s, 1H, allyl HH'C−), 2.50 (br s, 1H, allyl −CHH′), 1.95 (br s, 1H, allyl −CHH'). ^{13}C{^{1}H} NMR (100.62 MHz, CD_2Cl_2): δ 210.8 (d, J_{CP} = 20), 150.6 (d, J_{CP} = 11), 145.6, 142.3 (d, J_{CP} = 5.4), 138.8, 138.6, 133.4, 131.6, 130.9, 130.7 (d, J_{CP} = 7.3), 130.4, 130.0, 129.9, 129.8, 129.7, 129.3, 129.2, 128.9, 127.8, 123.7 (d, J_{CP} = 40), 117.2, 53.3, 44.0 (d,

J_{CP} = 27). $^{31}P\{^1H\}$ NMR (161.87 MHz, $CDCl_3$): δ 16.91. Anal. Calcd for $C_{73}H_{46}BF_{24}OPNi$: C, 58.63; H, 3.10. Found: C, 58.17; H, 3.16.

[Phenacyl(2,4,6-triphenylaryl)phenylphosphine]PdMe(Cl) (7c). To a suspension of (COD)PdMeCl (0.091 g, 0.34 mmol) in 10 mL of diethyl ether was added a solution of **4c** (0.200 g, 0.37 mmol) in 10 mL of diethyl ether. The resulting yellow solution was stirred for 2 h, during which time a white precipitate formed. The solid was isolated via filtration, washed with 2 × 10 mL of pentane, and dried under high vacuum to yield a white-yellow solid. Yield: 0.173 g (74%). ^1H NMR (300 MHz, CD_2Cl_2): δ 7.77 (br s, 2H, H_{Ar}), 7.60 (m, 6H, H_{Ar}), 7.41 (m, 9H, H_{Ar}), 7.32 (m, 5H, H_{Ar}), 7.22 (m, 5H, H_{Ar}), 3.54 (m, 2H, $-CH_2-$), 0.62 (s, 3H, Pd−Me). $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2): δ 195., 149.1, 143.2, 139.4, 137.0, 134.3, 134.2, 133.5, 130.6 (d, J_{CP} = 8), 130.4, 129.5, 129.2, 128.9, 127.7, 39.9, 6.5. $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2): δ 20.20. Anal. Calcd for $C_{39}H_{32}ClOPPd$: C, 67.93; H, 4.68. Found: C, 66.27; H, 4.79.

[Phenacyl(2,4,6-triphenylaryl)phenylphosphine]PdMe(NCMe)$^+$B(Ar$_f$)$_4^-$ (8c). To a mixture of **7c** (0.025 g, 0.036 mmol) and NaB(Ar$_f$)$_4$ (0.033 g, 0.036 mmol) at −78 °C was added 8 mL of diethyl ether and acetonitrile (0.10 mL, 1.9 mmol). The resulting pale yellow suspension was warmed to 0 °C and stirred for 1 h. The solution was isolated via filtration and the solvent removed in vacuo. The yellow oil residue was coevaporated with 2 × 5 mL of pentane at 0 °C, and the resulting brittle foam was dried under high vacuum to form a white-yellow solid powder. Yield: 0.025 g (46%). ^1H NMR (300 MHz, CD_2Cl_2, 268 K): δ 7.87 (d, 2H, J = 7.2, Ar−H_o), 7.56 (m, 6H, H_{Ar}), 7.41 (m, 8H, H_{Ar}), 7.31 (t, 2H, J = 7.2, Ar−H_m), 7.13 (m, 2H, H_{Ar}), 6.90 (d, 2H, J = 6.6, Ar−H_o), 3.78 (m, 2H, $-CH_2-$), 2.10 (s, 3H, −NCMe), 0.61 (d, 3H, J_{PH} = 3, Pd−Me). $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2, 268 K): δ 194.4, 148.4 (d, J_{CP} = 11.2), 144.9, 138.4, 137.4, 137.4, 135.8 (d, J_{CP} = 3), 135.3, 132.1, 131.5 (d, J_{CP} = 2), 131.3, 131.1, 130.8, 130.7 (d, J_{CP} = 9.4), 130.3, 130.1, 129.4, 127.6, 125.4, 124.1, 119.5, 36.6 (d, J_{CP} = 30), 29.5 (d, J_{CP} = 20), 22.8, 11.1. $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 268 K): δ 20.85. This compound was not sufficiently stable for elemental analysis.

[Phenacyl(2,4,6-triphenylaryl)phenylphosphine]PdMe(OEt$_2$)$^+$B(Ar$_f$)$_4^-$ (9c). To a mixture of **7c** (0.100 g, 0.145 mmol) and NaB(Ar$_f$)$_4$ (0.128 g, 0.145 mmol) at −78 °C was added 15 mL of diethyl ether. The resulting pale yellow suspension was warmed to 0 °C and stirred for 1 h. The solution was isolated via filtration and the solvent removed in vacuo. The yellow oil residue was coevaporated with 2 × 5 mL of pentane at 0 °C, and the resulting brittle foam was dried under high vacuum to form a yellow-white solid powder. Yield: 0.108 g (47%). ^1H NMR (300 MHz, CD_2Cl_2, 258 K): δ 7.85 (s, 2H, Ar−H_o), 7.63 (m, 4H, H_{Ar}), 7.44 (m, 8H, H_{Ar}), 7.26 (m, 4H, H_{Ar}), 7.08 (s, 2H, H_{Ar}), 6.95 (s, 2H, H_{Ar}), 3.98 (m, 2H, $-CH_2-$), 3.48 (q, 4H, J = 7, $-OCH_2CH_3$), 1.15 (t, 6H, J = 7, $-OCH_2CH_3$), 0.63 (s, 3H, Pd−Me). $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2, 258 K): δ 197.5, 149.0 (d, J_{CP} = 10), 144.6, 138.8, 138.4, 135.9, 131.4, 131.0, 130.8, 130.7, 130.3, 130.1, 128.9 (d, J_{CP} = 2), 127.5, 126.9, 67.9, 41.0, 15.3, 14.3. $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 258 K): δ 24.55. This compound was not sufficiently stable for elemental analysis.

***(para*-Methoxy)phenacyldiphenylphosphine (4d).** To a −78 °C solution of diisopropylamine (0.94 mL, 6.66 mmol) in 10 mL of THF was added *n*-C_4H_9Li (4.2 mL, 6.66 mmol, 1.6 M solution in hexanes). The LDA solution was stirred for 30 min and added via cannula to a −78 °C solution of 4′-methoxyacetophenone (1.00 g, 6.66 mmol) in 10 mL of THF. The solution was stirred for 2 h and added via cannula to a −78 °C solution of chlorodiphenylphosphine (1.2 mL, 6.66 mmol) in 20 mL of THF. The resulting yellow solution was warmed to room temperature and stirred for 2 h. The reaction mixture was concentrated to ca. 5 mL in vacuo, and 20 mL of toluene was added to fully precipitate the white solid LiCl. The solution was filtered through Celite, and the solvent was removed in vacuo to yield a yellow oil. The residue was stirred in 20 mL of pentane at 0 °C for 1 h to yield a white precipitate. The solid was isolated via filtration and washed with 10 mL of cold pentane to yield a white powder. Yield: 1.045 g (46%). ^1H NMR (300 MHz, CD_2Cl_2): δ 7.92 (d, 2H, J = 8.7, Ar−H_o), 7.44 (m, 4H, H_{Ar}), 7.35 (m, 6H, H_{Ar}), 6.92 (d, 2H, J = 9, Ar−H_p), 3.86 (s, 3H, −OMe), 3.76 (s, 2H, $-CH_2-$). $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2): δ 195.8 (d, J_{CP} = 8.5), 164.2, 138.4 (d, J_{CP} = 15), 133.3 (d, J_{CP} = 20), 131.5 (d, J_{CP} = 2), 130.4, 129.4, 129.0 (d, J_{CP} = 6.5), 114.2, 56.1, 40.6 (d, J_{CP} = 20). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2): δ −17.48. Anal. Calcd for $C_{21}H_{20}O_2P$: C, 75.21; H, 6.01. Found: C, 75.25; H, 5.74.

[(*para*-Methoxy)phenacyldiphenylphosphine]PdMe(Cl) (7d). To a solution of (COD)PdMeCl (0.158 g, 0.60 mmol) in 10 mL of CH_2Cl_2 at −78 °C was added a solution of **4d** (0.200 g, 0.59 mmol) in 10 mL of CH_2Cl_2. The resulting solution was warmed to room temperature and stirred for 1 h. The solvent was removed in vacuo, and the resulting white solid residue was washed with 2 × 10 mL of pentane and dried under high vacuum. Yield: 0.198 g (67%). ^1H NMR (400 MHz, CD_2Cl_2): δ 7.75 (m, 6H, H_{Ar}), 7.41 (m, 6H, H_{Ar}), 6.76 (d, 2H, J = 8.8, Ar−H_o), 4.11 (d, 2H, J_{PH} = 10.4, $-CH_2-$), 3.77 (s, 3H, −OMe), 0.54 (s, 3H, Pd−Me). $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2): δ 193.1, 164.3, 134.5 (d, J_{CP} = 11.8), 131.4, 131.3, 131.0, 130.5, 128.8 (d, J_{CP} = 10.9), 114.1, 56.0, 39.0, 5.4. $^{31}P\{^1H\}$ NMR (161.87 MHz, CD_2Cl_2): δ 30.77. Anal. Calcd for $C_{22}H_{23}ClO_2PPd$: C, 53.68; H, 4.71. Found: C, 54.40; H, 4.70.

[(*para*-Methoxy)phenacyldiphenylphosphine]PdMe(OEt$_2$)$^+$B(Ar$_f$)$_4^-$ (9d). To a mixture of **7d** (0.050 g, 0.102 mmol) and NaB(Ar$_f$)$_4$ (0.092 g, 0.104 mmol) at −78 °C was added 10 mL of diethyl ether. The resulting pale yellow suspension was warmed to 0 °C and stirred for 1 h. The solution was isolated via filtration and the solvent removed in vacuo. The yellow oil residue was coevaporated with 2 × 5 mL of pentane at 0 °C, and the resulting brittle foam was dried under high vacuum to form a yellow-white solid powder. Yield: 0.067 g (47%). ^1H NMR (300 MHz, CD_2Cl_2, 258 K): δ 7.96 (d, 2H, J = 8.7, Ar−H_o), 7.57 (m, 10H, H_{Ar}), 6.92 (m, 2H, Ar−H_p), 4.36 (d, 2H, J_{PH} = 11.4, $-CH_2-$), 3.86 (s, 3H, −OMe), 3.80 (m, 4H, $-OCH_2CH_3$), 1.52 (m, 6H, $-OCH_2CH_3$), 0.83 (s, 3H, Pd−Me). $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2, 258 K): δ 202.5, 167.1, 133.7, 133.3, 133.1, 130.0 (d, J_{CP} = 12), 127.3, 126.2 (d, J_{CP} = 5.4), 115.1, 70.5, 56.4, 46.8 (d, J_{CP} = 35.5), 16.3, −0.5. $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 258 K): δ 38.04. This compound was not sufficiently stable for elemental analysis.

***(para*-Trifluoromethyl)phenacyldiphenylphosphine (4e).** To a −78 °C solution of diisopropylamine (1.5 mL, 10.6 mmol) in 10 mL of THF was added *n*-C_4H_9Li (6.7 mL, 10.6 mmol, 1.6 M solution in hexanes). The LDA solution was stirred for 30 min and added via cannula to a −78 °C solution of 4′-trifluoromethylacetophenone (2.00 g, 10.6 mmol) in 10 mL of THF. The solution was stirred for 2 h and added via cannula to a −78 °C solution of chlorodiphenylphosphine (1.91 mL, 10.6 mmol) in 20 mL of THF. The resulting yellow solution was warmed to room temperature and stirred for 2 h. The reaction mixture was concentrated to ca. 5 mL in vacuo, and 20 mL of toluene was added to fully precipitate the white solid LiCl. The solution was filtered through Celite, and the solvent was removed in vacuo to yield a yellow oil. The residue was stirred in 20 mL of pentane at 0 °C for 1 h to yield a white precipitate. The solid was isolated via filtration and washed with 10 mL of cold pentane to yield a white powder. Yield: 1.800 g (46%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, 2H, J = 8.4, Ar−H_o), 7.65 (d, 2H, J = 8.4, Ar−H_o), 7.43 (m, 5H, H_{Ar}), 7.33 (m, 5H, H_{Ar}), 3.79 (s, 2H, $-CH_2-$). $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2): δ 196.7 (d, J_{CP} = 8.4), 140.2, 137.8, 137.6, 133.2 (d, J_{CP} = 20), 132.3 (q, J_{CF} = 312), 129.7, 129.5 (d, J_{CP} = 2), 129.2 (d, J_{CP} = 6.8), 126.1 (q, J_{CF} = 4), 41.2 (d, J_{CP} = 22). $^{31}P\{^1H\}$ NMR (161.87 MHz, $CDCl_3$): δ −15.16. Anal. Calcd for $C_{21}H_{16}F_3OP$: C, 67.75; H, 4.33. Found: C, 67.55; H, 4.39.

[(*para*-Trifluoromethyl)phenacyldiphenylphosphine]-PdMe(η^2-C_2H_4)$^+$B(Ar$_f$)$_4^-$ (10e). To a solution of (COD)-PdMeCl (0.053 g, 0.20 mmol) in 10 mL of THF at −78 °C was added a solution of **4e** (0.075 g, 0.20 mmol) in 10 mL of THF. The resulting solution was warmed to room temperature and stirred for 1 h. $^{31}P\{^1H\}$ NMR of the crude reaction mixture shows a single resonance at δ 30.59 ppm. The solvent was removed in vacuo, and the resulting white solid residue was washed with 2 × 10 mL of pentane and dried under high vacuum. Yield: 0.053 g (50%). Product not soluble for ^1H, ^{13}C NMR analysis. $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2): δ 30.59 (in THF solution). Anal. Calcd for $C_{22}H_{19}ClF_3OPPd$: C, 49.93; H, 3.62. Found: C, 50.18; H, 3.73. An NMR tube was charged with white solid product (4.0 mg, 7.6 μmol) and NaB(Ar$_f$)$_4$ (6.7 mg, 7.6 μmol) under argon. The NMR tube was fitted with a rubber septum, cooled to −78 °C, and charged with ethylene (1.0 mL, 40.6 μmol) and 0.8 mL of dry CD_2Cl_2. The resulting pale yellow solution (very little NaCl precipitate) was used for NMR characterization and ethylene insertion kinetics studies. ^1H NMR (300 MHz, CD_2Cl_2, 243 K): δ 8.14 (d, 2H, J = 7.8, Ar−H$_o$), 7.81 (d, 2H, J = 7.5, Ar−H$_m$), 7.62 (m, 4H, H$_{Ar}$), 7.56 (m, 6H, H$_{Ar}$), 5.41 (br s, Pd-[η^2-C_2H_4]), 4.51 (d, 2H, J_{PH} = 12, −CH$_2$−), 0.94 (s, 3H, Pd−Me). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 243 K): δ 29.28. This compound was not sufficiently stable for elemental analysis.

[Phenacylbis(*para*-methoxyphenyl)phosphine]PdMe-(Cl) (7f). To a −78 °C solution of diisopropylamine (0.59 mL, 4.2 mmol) in 10 mL of THF was added *n*-C_4H_9Li (2.6 mL, 4.2 mmol, 1.6 M solution in hexanes). The LDA solution was stirred for 30 min and added via cannula to a −78 °C solution of acetophenone (0.49 mL, 4.2 mmol) in 10 mL of THF. The solution was stirred for 2 h and added via cannula to a −78 °C solution of bis(4-methoxyphenyl)chlorophosphine (1.14 g, 4.2 mmol) in 20 mL of THF. The resulting yellow solution was warmed to room temperature and stirred for 2 h. $^{31}P\{^1H\}$ NMR of the crude reaction mixture displays the major resonance (>85% of phosphorus-containing products) at δ −18.41 ppm. The reaction mixture was concentrated to ca. 5 mL in vacuo, and 20 mL of toluene was added to fully precipitate the white solid LiCl. The solution was filtered through Celite, and the solvent was removed in vacuo to yield 1.36 g of crude yellow oil **4f**. $^{31}P\{^1H\}$ NMR (161.87 MHz, CD_2Cl_2): δ −18.41 (major peak). The product was dissolved in 10 mL of CH_2Cl_2 and added via cannula to a −78 °C solution of (COD)PdMeCl (0.084 g, 0.32 mmol) in 10 mL of CH_2Cl_2. The resulting solution was warmed to room temperature and stirred for 1 h. $^{31}P\{^1H\}$ NMR of the crude reaction mixture shows a single resonance at δ 28.65 ppm. The solvent was removed in vacuo, and the resulting white solid residue was washed with 2 × 10 mL of pentane and dried under high vacuum. Yield: 0.105 g (63%). ^1H NMR (400 MHz, CD_2Cl_2): δ 7.67 (m, 6H, H$_{Ar}$), 7.46 (m, 1H, H$_{Ar}$), 7.28 (m, 2H, H$_{Ar}$), 6.89 (m, 4H, H$_{Ar}$), 4.12 (d, 2H, J_{PH} = 12, −CH$_2$−), 3.81 (s, 6H, −OMe), 0.53 (s, 3H, Pd−Me). $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2): δ 195.1 (d, J_{CP} = 5), 162.2, 137.7, 136.1 (d, J_{CP} = 13.4), 133.7, 129.0, 128.9, 121.4 (d, J_{CP} = 56), 114.4 (d, J_{CP} = 12), 55.9, 39.7 (d, J_{CP} = 30), 5.5. $^{31}P\{^1H\}$ NMR (161.87 MHz, CD_2Cl_2): δ 28.64. Anal. Calcd for C23H26ClO$_3$PPd: C, 52.79; H, 5.01. Found: C, 52.95; H, 4.85.

[Phenacylbis(*para*-methoxyphenyl)phosphine]PdMe-(OEt$_2$)$^+$B(Ar$_f$)$_4^-$ (9f). To a mixture of **7f** (0.030 g, 0.057 mmol) and NaB(Ar$_f$)$_4$ (0.052 g, 0.058 mmol) at −78 °C was added 10 mL of diethyl ether. The resulting pale yellow suspension was warmed to 0 °C and stirred for 1 h. The solution was isolated via filtration and the solvent removed in vacuo. The yellow oil residue was coevaporated with 2 × 5 mL of pentane at 0 °C, and the resulting brittle foam was dried under high vacuum to form a yellow-white solid powder. Yield: 0.035 g (43%). ^1H NMR (300 MHz, CD_2Cl_2, 258 K): δ 7.98 (m, 2H, Ar−H$_o$), 7.75 (t, 1H, J = 7.8, Ar−H$_p$), 7.50 (m, 6H, H$_{Ar}$), 7.00 (d, 4H, J = 7.2, Ar−H$_o$), 4.38 (d, 2H, J_{PH} = 10.8, −CH$_2$−), 3.87 (q, 4H, J = 7, −OCH_2CH$_3$), 3.81 (s, 6H, −OMe), 1.56 (t, 6H, J = 7, −OCH$_2$CH_3), 0.79 (s, 3H, Pd−Me). $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2, 258 K): δ 205.7, 137.4, 135.1, 134.9, 130.7, 130.2, 129.8, 115.5 (d, J_{CP} = 13.3), 70.3, 56.0, 47.9 (d, J_{CP} = 30), 22.8, 14.3 (d, J_{CP} = 10), −0.2. $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 258 K): δ 36.17. This compound was not sufficiently stable for elemental analysis.

Phenacylbis(*para*-trifluoromethylphenyl)phosphine (4g). To a −78 °C solution of diisopropylamine (0.78 mL, 5.53 mmol) in 10 mL of THF was added *n*-C_4H_9Li (3.4 mL, 5.59 mmol, 1.6 M solution in hexanes). The LDA solution was stirred for 30 min and added via cannula to a −78 °C solution of acetophenone (0.65 mL, 5.53 mmol) in 10 mL of THF. The solution was stirred for 2 h and added via cannula to a −78 °C solution of bis[4-(trifluoromethyl)phenyl]chlorophosphine (1.972 g, 5.53 mmol) in 20 mL of THF. The resulting yellow solution was warmed to room temperature and stirred for 2 h. The reaction mixture was concentrated to ca. 5 mL in vacuo, and 20 mL of toluene was added to fully precipitate the white solid LiCl. The solution was filtered through Celite, and the solvent was removed in vacuo to yield a yellow oil. The residue was stirred in 20 mL of pentane at 0 °C for 1 h to yield a white precipitate. The solid was isolated via filtration and washed with 10 mL of cold pentane to yield a white powder. Yield: 0.886 g (36%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.93 (m, 2H, H$_{Ar}$), 7.59 (m, 9H, H$_{Ar}$), 7.46 (m, 2H, H$_{Ar}$), 3.85 (s, 2H, −CH$_2$−). $^{13}C-\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2): δ 196.8 (d, J_{CP} = 8), 142.7 (d, J_{CP} = 17.8), 137.1, 134.1, 133.7 (d, J_{CP} = 15), 131.5 (d, J_{CP} = 32), 129.2, 129.1 (d, J_{CP} = 2), 125.9, 124.6 (q, J_{CF} = 273), 40.2 (d, J_{CP} = 18.8). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): δ −18.68. Anal. Calcd for $C_{22}H_{15}F_6OP$: C, 60.01; H, 3.43. Found: C, 59.72; H, 3.47.

[Phenacylbis(*para*-trifluoromethylphenyl)phosphine]-PdMe(Cl) (7g). To a solution of (COD)PdMeCl (0.090 g, 0.34 mmol) in 10 mL of CH_2Cl_2 at −78 °C was added a solution of **4g** (0.150 g, 0.34 mmol) in 10 mL of CH_2Cl_2. The resulting solution was warmed to room temperature and stirred for 1 h. The solvent was removed in vacuo, and the resulting white solid residue was washed with 2 × 10 mL of pentane and dried under high vacuum. Yield: 0.095 g (47%). ^1H NMR (300 MHz, CD_2Cl_2): δ 7.88 (m, 4H, H$_{Ar}$), 7.75 (d, 2H, J = 13, Ar−H$_o$), 7.67 (d, 4H, J = 7.2, Ar−H$_o$), 7.51 (m, 1H, Ar−H$_p$), 7.34 (m, 2H, Ar−H$_m$), 4.19 (d, 2H, J_{PH} = 10, −CH$_2$−), 0.58 (d, 3H, J_{PH} = 3, Pd−Me). $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2): δ 194.3 (d, J_{CP} = 4.5), 137.1 (d, J_{CP} = 3), 135.4, 134.8 (d, J_{CP} = 12.5), 134.3, 133.2 (q, J_{CF} = 33), 129.2, 128.9, 125.9, 122.4, 39.1 (d, J_{CP} = 30.5), 5.9. $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2): δ 29.92. Anal. Calcd for $C_{23}H_{18}ClF_6OPPd$: C, 46.26; H, 3.04. Found: C, 45.96; H, 3.00.

[Phenacylbis(*para*-trifluoromethylphenyl)phosphine]-PdMe(OEt$_2$)$^+$B(Ar$_f$)$_4^-$ (9g). To a mixture of **7g** (0.150 g, 0.251 mmol) and NaB(Ar$_f$)$_4$ (0.222 g, 0.251 mmol) at −78 °C was added 15 mL of diethyl ether. The resulting pale yellow suspension was warmed to 0 °C and stirred for 1 h. The solution was isolated via filtration and the solvent removed in vacuo. The yellow oil residue was coevaporated with 2 × 5 mL of pentane at 0 °C, and the resulting brittle foam was dried under high vacuum to form a yellow-white solid powder. Yield: 0.218 g (58%). ^1H NMR (300 MHz, CD_2Cl_2, 258 K): δ 8.01 (d, 2H, J = 7.5, Ar−H$_o$), 7.86 (m, 5H, H$_{Ar}$), 7.76 (m, 4H, H$_{Ar}$), 7.50 (m, 2H, H$_{Ar}$), 4.52 (d, 2H, J_{PH} = 11.4, −CH$_2$−), 3.78 (m, 4H, −OCH_2CH$_3$), 1.44 (m, 6H, −OCH$_2$CH_3), 0.85 (s, 3H, Pd−Me). $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2, 258 K): δ 204.9, 138.1, 133.8 (d, J_{CP} = 13.4), 133.1 (d, J_{CP} = 5.7), 131.2, 130.9, 130.0, 127.2 (m), 125.3, 121.6, 69.6, 46.7 (d, J_{CP} = 34.6), 16.1, 1.0. $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 258 K): δ 37.54. This compound was not sufficiently stable for elemental analysis.

Procedure for 1 atm Ethylene Polymerizations with 6b. Complex **6b** (2.0 mg, 1.48 μmol) was added to a Schlenk flask under argon. The flask was back-filled three times with 1 atm ethylene, charged with 50 mL of toluene, and placed in an oil bath at the appropriate reaction temperature. The

reaction solution was vigorously stirred under 1 atm ethylene for the desired reaction time. The polymerization was quenched by addition of 10 mL of acetone, and the reaction mixture was poured into 300 mL of stirring methanol to precipitate the polymer. The product was isolated via filtration, washed with acetone, and dried overnight in a vacuum oven at 80 °C.

Procedure for 200 psig Ethylene Polymerizations with 6b. A 1000 mL Parr autoclave was heated under vacuum at 100 °C for 4 h, cooled to room temperature, and back-filled with ethylene. The reaction solvent (190 mL of toluene) was added, and the reactor was warmed to the desired reaction temperature under 200 psig ethylene pressure. The reactor was vented, and a solution of **6b** (2.0 mg, 1.48 μmol) in 10 mL of toluene was added via cannula under argon pressure. The reactor was pressurized to 200 psig ethylene and stirred for the desired reaction time. The polymerization was quenched by venting the autoclave followed by addition of acetone. The reaction mixture was poured into a stirring solution of 750 mL of methanol and ca. 5 mL of HCl to precipitate the polymer. The polymer product was isolated by filtration, washed with acetone, and dried in vacuo.

Procedure for 200 psig Ethylene Oligomerization with 6a and 6c. A 300 mL Parr autoclave was heated under vacuum at 100 °C for 4 h, cooled to room temperature, and back-filled with ethylene. The reaction solvent (95 mL of toluene) was added, and the reactor was pressurized under 200 psig ethylene. The reactor was vented, and a solution of 1.34 μmol of catalyst and 10 mL of toluene was added via cannula under argon pressure. The reactor was pressurized to 200 psig ethylene and stirred at 25 °C for the desired reaction time. The reaction temperature was maintained using an external ice bath to control the reaction exotherm. The reactor was vented to ambient pressure, and the contents were poured into a pre-tared 500 mL flask and weighed. This procedure was performed as quickly as possible to minimize the potential evolution of butene products; however, we cannot rule out a small loss of volatile products during workup. The reaction yield was determined from the final mass of reaction mixture versus the control mass of 105 mL of toluene after ethylene pressurization and decompression (see below). An aliquot (approximately 0.5 mL) of the reaction mixture was transferred to a NMR tube containing 1 mL of CD_2Cl_2 and promptly sealed. The products were analyzed by ^{1}H NMR spectroscopy and GC. The 1-butene was identified by ^{1}H NMR resonances at δ 5.78 (=CHR), 4.95 ($=CH_2$), 2.0 ($-CH_2-$), and 1.0 ($-CH_3$). Resonances for the 2-butenes appear at δ 5.55 (=CHR) and 1.95−1.85 ($-CH_3$). To determine the mass of the control reaction solution (reaction mixture with no catalyst or butene product), 105 mL of toluene was added to the autoclave and stirred under 200 psig ethylene at 25 °C for 30 min. The reactor was vented to ambient pressure, and the contents were quickly poured into a 500 mL flask and weighed. Mass of control reaction mixture = 90.8 g.

Procedure for 200 psig Ethylene Oligomerization with 8a−c. The same procedure and product analysis were followed as described above using 3.24 μmol of catalysts **8a**−**c** and 105 mL of toluene.

^{1}H NMR Analysis for Polyethylene Olefinic End Groups. The olefinic end groups were determined from ^{1}H NMR spectra. α-Olefin: δ 5.85 (m, 1H, H_2C=C*H*−), δ 5.0−4.9 (m, 2H, *H*$_2$C=CH−). Internal olefin: δ 5.39 (m, 2H, *trans* isomer), δ 5.34 (m, 2H, *cis* isomer). Vinylidene: δ 4.7 (br s, 2H). Trisubstituted olefin: δ 5.18 (m or br t, 1H).

Procedure for in Situ Generation of (P,O)PdMe(η^2-C_2H_4) Complexes (10a−d, 10f,g) for Measurement of Ethylene Insertion Kinetics. The appropriate (P,O)PdMe(O-Et$_2$)$^+$B(Ar$_f$)$_4^-$ complex **9a**−**d** and **9f**,**g** (3.0 μmol) was added to an NMR tube under argon. The tube was sealed with a septum, cooled to −78 °C, and charged with 0.8 mL of CD_2Cl_2 and 1.0 mL (40.6 μmol) of ethylene. The kinetics of ethylene insertion were measured via ^{1}H NMR by monitoring the loss of the palladium methyl resonance. See above for preparation of **9e**.

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Supporting Information Available: X-ray crystallographic data for **6b** and kinetics plots for ethylene migratory insertion in selected complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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