Phosphinidine-Palladium Complexes for the Polymerization and Oligomerization of Ethylene

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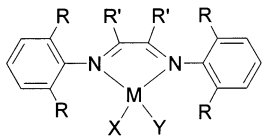
Several cationic palladium complexes containing bulky phosphinidine-imine, phosphinidine-sulfide, and imine-sulfide ligands have been prepared. These complexes catalyze the oligomerization and polymerization of ethylene with moderate to high rates (for palladium catalysts) and display higher stability compared to diimine-palladium systems.

Introduction

The development of well-defined late-transition metal catalysts for the polymerization of ethylene and α-olefins has been the subject of intense recent study.[1] Following the pioneering studies of Wilke,[2a] Keim,[2b] and Klabunde and Ittel[2c] we disclosed highly versatile Ni(II) and Pd(II)-α-diimine-based catalysts of type **1**.[3a] Hindered aryl groups on the α-diimine nitrogens block the axial coordination sites and retard chain transfer relative to propagation, resulting in high molecular weight polymer. These complexes polymerize ethylene, producing polyethylene with microstructures ranging from almost linear to hyperbranched depending on the catalyst used and reaction variables.[3b,c] Nickel catalysts are stable for hours at room temperature;[3d] however, in the case of palladium catalysts, lowering of reaction temperature to 5 °C is necessary to achieve living polymerization and prevent substantial catalyst decomposition.[3e]

Recently, cationic palladium-diphosphinidenecyclobutene complexes of type **2** were described by Ozawa, Yoshifuji, and co-workers.[4] At 60−100 °C they catalyze the conversion of ethylene to polyethylene with moderate M_w's (4000−33 000), high polydispersities (4.2−14.8), and moderate activities (up to 4500 TO/h at 70 °C). Noteworthy is the exceptional thermal stability of these complexes. Palladium-diimine catalysts deactivate at moderate rates at RT,[3e] and at 70 °C deactivation is observed within 15 min.[4] Since arylphosphinidines and arylimines possess similar structural features, we sought to incorporate the phosphinidine functionality into one arm of bidentate Pd(II) complexes in the hope of imparting greater thermal stability to these catalysts.



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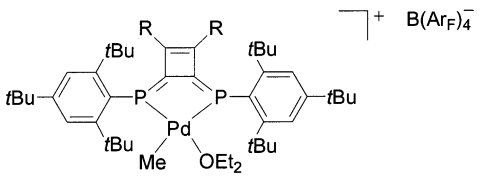

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We report here synthesis and ethylene polymerization activity of a number of cationic phosphinidine-imine, phosphinidine-sulfide, and imine-sulfide palladium complexes.

Results and Discussion

1. Pd(II) Catalysts Incorporating Phosphinidine-Imine Ligands. The most straightforward modification of the diimine system was the incorporation of both a phosphinidine and imine moiety into the catalysts. Starting phosphinidine-imine ligands were prepared taking advantage of elimination methodology developed by Bickelhaupt et al. for unstabilized phosphinidines.[5] Imines **3a**,**b** were deprotonated with LDA, followed by reaction with Mes*PCl_2 (Mes* = 2,4,6-tri-*tert*-butylphenyl). Elimination of HCl from the intermediate chlorophosphines using DBU afforded the requisite phosphinidine-imine ligands **4a**,**b** as yellow-red crystalline solids. In the case of more hindered **4a** it was necessary to use acetonitrile as solvent and elevated temperatures in the elimination step to obtain a reasonable conversion to the phosphinidine (Scheme 1).

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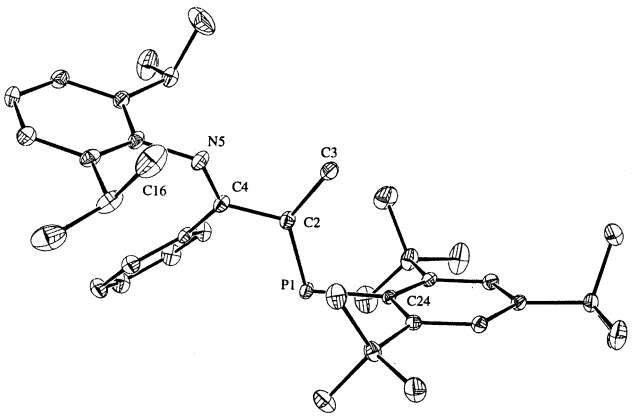
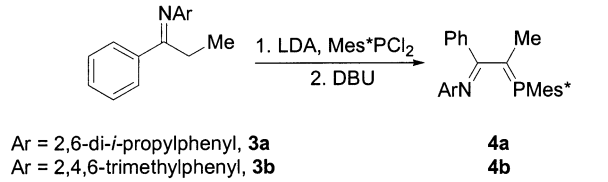


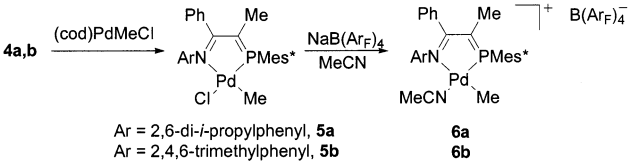
Figure 1. ORTEP view of **4a**. Selected interatomic distances (Å) and angles (deg): P(1)−C(2) = 1.684(2), P(1)−C(24) = 1.85(2), N(5)−C(4) = 1.288(3), C(4)−C(2) = 1.484(3); C(24)−P(1)−C(2) = 104.36(9), P(1)−C(2)−C(4) = 116.36(15), C(2)−C(4)−N(5) = 116.75(18).

Scheme 1



Ar = 2,6-di-*i*-propylphenyl, **3a** **4a**
Ar = 2,4,6-trimethylphenyl, **3b** **4b**

Scheme 2



Ar = 2,6-di-*i*-propylphenyl, **5a** **6a**
Ar = 2,4,6-trimethylphenyl, **5b** **6b**

An X-ray structure of the ligand **4a** was obtained to verify the geometry around the C=P and C=N bonds (Figure 1). As expected, a trans configuration of the imine and phosphinidine double bonds was observed. Bond lengths observed in **4a** are common for phosphaalkenes[6] (C(2)=P(1), 1.684(2) Å; C(24)−P(1), 1.850(2) Å). The C(24)−P(1)−C(2) angle of 104.36(9)° and C(24)−P(1)−C(2)−C(4) dihedral angle of −176.1(3)° are also typical for phosphinidines not bearing two bulky substituents on the carbon terminus of the P=C bond.[6a]

Ligands **4a**,**b** readily displace cod from (cod)PdMeCl[7] to give single isomers of the corresponding complexes **5a**,**b** in good yields. Chloride ion abstraction was effected by reaction of **5a**,**b** with $NaB(Ar_F)_4$ (Ar_F = [3,5-$(CF_3)_2C_6H_3$]) in acetonitrile/dichloromethane, affording cationic acetonitrile complexes **6a**,**b** as yellow-red powders (Scheme 2). The phosphorus chemical shifts of the complexes **5a**,**b** and **6a**,**b** show considerable shielding compared to the free ligands (δP, ppm: **4a**, +303.0 ppm; **5a**, +268.3; **6a**, +267.4 ppm). The magnitude of Me−P coupling constants suggests that phosphorus is cis to the methyl group (**6b**, *J* Me-P, ^{1}H; 2.6 Hz; ^{13}C, 2.7 Hz; similar values for **5a**,**b** and **6a**).[6b]

A single-crystal X-ray analysis confirmed the structure of **6a** and its geometrical similarity to the corresponding diimine-palladium complexes. The crystal structure shows a square planar arrangement of the ligands around the palladium center. As expected from the spectral data, the methyl group on palladium is positioned cis to the phosphorus atom, suggesting a stronger trans-influence[8] of the phosphinidine moiety. The P(1)=C(6) bond length in **6a** is slightly shortened compared to free ligand **4a** (1.660(11) vs 1.684(2) Å) and is comparable to the bond lengths in other phosphinidine-palladium complexes.[9,10] The Pd−P bond length of 2.183(3) Å is shorter than in palladium-diphosphinidenecyclobutane complexes[9a,b,d] (2.23−2.33 Å) but similar to Pd−P lengths in palladium complexes of phosphinidine-pyridines[6b] and orthopalladated phosphinidines.[10] The length of the N(14)=C(7) bond (1.287(15) Å) is in the standard range for palladium-imine complexes.[11] The five-membered chelate ring is planar within two degrees. N-Aryl and P-aryl groups lie almost perpendicular to the plane of the five-membered ring (torsion angles: C(6)−P(1)−C(15)−C(20), 88.0(11)°, C(7)−N(14)−C(33)−C(38), 96.5(15)°), efficiently blocking the axial coordination sites (Figure 2).

Complexes **6a**,**b** proved to be ethylene oligomerization catalysts and were studied at 26 °C and 400 psi ethylene. Results are summarized in Table 1. A turnover rate of 23 TO/h was observed for more hindered catalyst **6a** in a 3 h run. Decreased hindrance in **6b** gave rise to higher turnover numbers (94 TO/h) with a concurrent drop of oligomer molecular weight from 670 to 300. The catalysts are more stable than diimine-Pd complexes at RT; comparing entries 1 and 2 shows that **6a** does not significantly deactivate in a 15 h run.

In an effort to better understand this system, ethylene insertion barriers were measured for the less hindered mesitylimine system **6b**. Cationic ethylene complex **7** was generated at −78 °C via the reaction of **5b** with $NaB(Ar_F)_4$ under excess olefin (20 equiv). Upon warming to −23 °C, migratory insertion of ethylene into the Pd−Me bond was observed with $k = 7.9 \times 10^{-5}$ s^{-1}, corresponding to $\Delta G^{\ddagger} = 19.2(1)$ kcal/mol. After the disappearance of the Pd−Me signal, insertion of ethylene into Pd−alkyl bonds was measured giving $k = 2.4 \times 10^{-4}$, $\Delta G^{\ddagger} = 18.7(1)$ kcal/mol. For comparison, typical migratory insertion barriers in (diimine)palladium (methyl)(ethylene) complexes are ca. 17 kcal/mol.[3a] Since $\Delta\Delta G^{\ddagger} = 2$ kcal corresponds to $k_2/k_1 = 30$ (25 °C),

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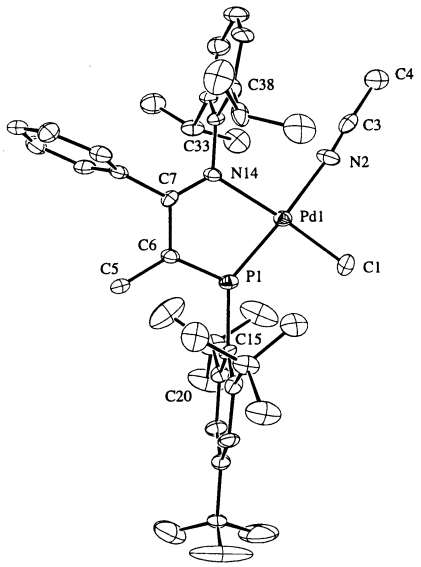


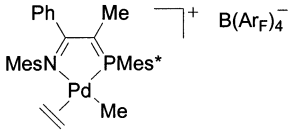
Figure 2. ORTEP view of **6a**. Selected interatomic distances (Å) and angles (deg): P(1)−Pd(1) = 2.183(3), N(14)−Pd(1) = 2.166(8), Pd(1)−C(1) = 2.052(10), Pd(1)−N(2) = 2.063(10), P(1)−C(6) = 1.660(11), P(1)−C(15) = 1.799(9), N(14)−C(7) = 1.287(15), N(2)−C(3) = 1.107(17); C(6)−P(1)−C(15) = 113.7(5), C(7)−N(14)−C(33) = 122.3(8).

Table 1. Oligomerization of Ethylene by 6a,b at 26 °C, 400 psi in CH_2Cl_2

entry	catalyst[a]	time, h	mg oligomers	TOF, h^{-1}	M_n[b]
1	**6a**	3	19	23	670
2	**6a**	15	76	18	590
3	**6b**	3	79[c]	94	300
4	**6b**	15	270[c]	65	230

[a] 0.01 mmol of catalyst in 100 mL of CH_2Cl_2 used. [b] M_n determined by ^1H NMR spectroscopy (see Experimental Section for details). [c] Butene, hexene, and octene fractions partially lost during evaporation of solvent (GC analysis).

the difference in insertion barriers accounts for the observed difference in TOF (Pd diimines: ca. 4500 TO/h;[3e] **6b**, 94 TO/h at RT).



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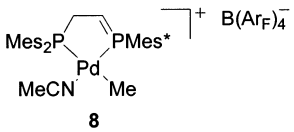

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2. Palladium(II) Catalysts Containing Phosphinidine-Sulfide Ligands. Since the oligomerizations using phosphinidine-imine palladium complexes were relatively slow, we decided to examine other chelating ligand-palladium complexes incorporating the phosphinidine moiety. The use of phosphine-phosphinidine palladium complex **8** (geometry around Pd arbitrary) was not successful (butenes were produced at 1 atm C_2H_4 in an NMR experiment). Modification of this structure was problematic due to the instability of the ligand and synthetic intermediates (high air and moisture sensitivity, low crystallinity). As a consequence, we turned to the investigation of phosphinidine-sulfide-based catalysts. Initially, two ligands possessing bulky substituents on sulfur were synthesized using phospha-Petersen methodology developed by Yoshifuji et al.[12] The reaction of the potassium salt of tri-isopropylthiophenol with bromoacetaldehyde diethyl acetal followed by acidic hydrolysis afforded tri-isopropylphenylthioacetaldehyde **9**. The aldehyde was then treated with Mes*P(Li)TBS to give a 100:8 mixture of phosphinidine isomers. Crude phosphinidine was converted into the corresponding complex **10a** by treatment with (cod)PdMeCl. Chloride abstraction with $Na(BAr_F)_4$ in the presence of acetonitrile afforded the cationic complex **11a**. In a similar way, complex **11b** was obtained starting from the known α-*tert*-butylthioacetaldehyde (Scheme 3).[13]

Table 2. Oligomerization/Polymerization of Ethylene by 11a and 14 at 26 °C, 400 psi in CH_2Cl_2

entry	catalyst[a]	time, h	g polymer	TOF, h^{-1}	M_n[b]	branching[c]
1	**11a**	3	3.6	4300	215[d]	60
2	**11a**	15	12.5	3000	180[d]	40
3	**14**	3	2.6	3100	2300	119
4	**14**	8	5.2	2300	2500[e]	119

[a] 0.01 mmol of catalyst in 100 mL of CH_2Cl_2 used. [b] M_n determined by ^1H NMR spectroscopy (see Experimental Section for details). [c] Branching determined by ^1H NMR spectroscopy (see Experimental Section for details). [d] Butene, hexene, and octene fraction partially lost during evaporation of solvent (GC analysis). [e] GPC data: M_n = 1900, M_w = 2900, PDI = 1.5.

The reactions of ethylene with cationic complexes **11a**,**b** were initially studied by NMR spectroscopy using 20 equiv of olefin and 0.01 mmol of catalyst in CD_2Cl_2. Under these conditions *tert*-butyl-substituted complex **11b** produces a mixture of internal butenes. Interestingly, the major component was *cis*-2-butene (2:1). Gratifyingly, tri-isopropylphenyl-substituted catalyst **11a** afforded ethylene oligomers in a relatively fast reaction. In 3 h under 400 psi of ethylene, 0.01 mmol of **11a** produced 3.6 g of oligomers (corresponding to 4300 TO/h) with M_n = 215. In a 15 h run, TOF dropped to 3000 h^{-1}, showing some catalyst decomposition (Table 2). Compared to diimine-Pd complexes, **11a** displays higher stability and produces lower molecular weight material.

In an effort to increase the molecular weight of the oligomer/polymer produced, catalyst **14** was designed and synthesized (Scheme 4). Geminal dimethyl groups on the chelate backbone should impart a more restricted conformation to the S-aryl group, possibly leading to more efficient blocking of the axial sites on the metal and potentially higher molecular weight material. The synthesis started with the reaction of tri-isopropylphenylsulfenyl chloride[14] with the potassium enolate of isobutyraldehyde to give the corresponding α-thioaldehyde **12**.[15] The conversion to the cationic palladium complex **14** was carried out as in the case of **11**.

Under 400 psi of ethylene, **14** produced highly branched (119 br/1000 C) polyethylene with M_n = 2300−2500, PDI = 1.5, consistent with a single-site catalyst

(12) Yoshifuji, M.; Toyota, K.; Matsuda, I.; Niitsu, T.; Inamoto, N. *Tetrahedron Lett.* **1985**, *26*, 1727.
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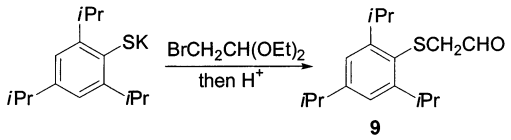
Scheme 3



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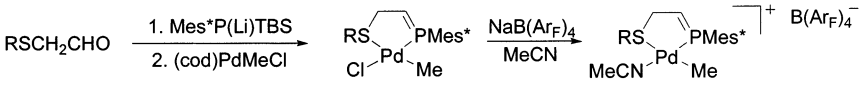


R = 2,4,6-tri-*i*-propylphenyl, **10a** — **11a**
R = *t*-butyl, **10b** — **11b**

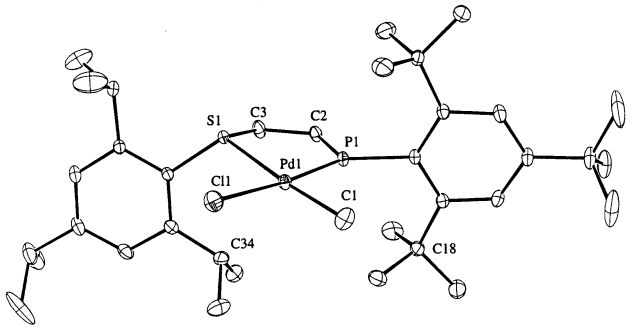
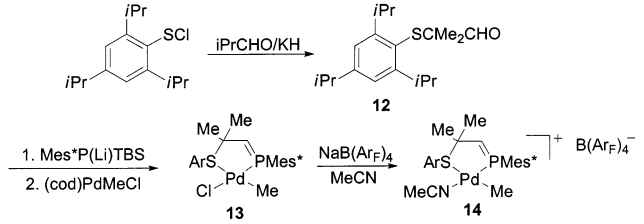


Figure 3. ORTEP view of **10a**. Selected interatomic distances (Å) and torsion angles (deg): P(1)−Pd(1) = 2.1920(7), S(1)−Pd(1) = 2.3965(7), Pd(1)−C(1) = 2.046(3), Pd(1)−Cl(1) = 2.3496(7), P(1)−C(2) = 1.652(3), S(1)−C(3) = 1.826(3), C(34)−C(18) = 5.130(4); P(1)−Pd(1)−S(1)−C(3) 13.96(15).

Scheme 4



(Table 2). The observed TOF for a 3 h run was 3100 h^{-1}, for an 8 h run 2300 TO/h. Remarkably, introduction of the geminal dimethyl groups has increased the molecular weight of the polymer more than 10 times. To investigate the origin of this effect, single-crystal X-ray structures were obtained for the complexes **10a** and **13** (Figures 3 and 4).

The geometries of these complexes were thought to approximate the geometries of the active species in the polymerization reaction. The C=P bond lengths (1.659(3) Å for **13** and 1.653 Å for **10a**) are typical for phosphinidine-palladium complexes.[6a,9] The Pd−P bonds (2.2071(8) Å for **13**, 2.1920(7) Å for **10a**) are slightly longer than observed for **6a**. As expected from the small magnitude of CH_3−^{31}P coupling constants (see Experimental Section for details), the methyl group is positioned cis to phosphinidine. The palladium−sulfur bond is somewhat longer in **13** compared to **10a** (2.4277(8) vs 2.3965(7) Å). In **13**, the five-membered chelate ring is planar within 2 degrees; in **10a** it adopts an envelope conformation with the sulfur atom forming the flap of the envelope (torsion angle P(1)−Pd(1)−S(1)−C(3) = 13.96(15)°). The C(34)−C(18) distance in **10a** is 5.130(4) Å; in **13** the corresponding C(23)−C(37) distance is

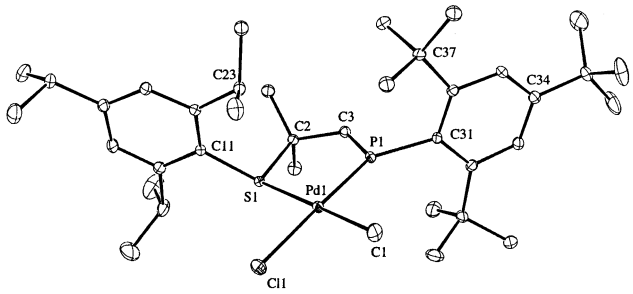


Figure 4. ORTEP view of **13**. Selected interatomic distances (Å) and angles (deg): P(1)−Pd(1) = 2.2071(8), S(1)−Pd(1) = 2.4277(8), Pd(1)−C(1) = 2.047(3), Pd(1)−Cl(1) = 2.3475(8), P(1)−C(3) = 1.659(3), S(1)−C(2) = 1.891(3), C(23)−C(37) = 4.693(4), C(11)−S(1) = 1.808(3); C(34)−C(31)−P(1) = 169.04(17).

Table 3. Comparison of Polyethylene Branching Obtained Using 14[a] and [((2,6-$Me_2C_6H_3$)N=C(Me)−C(Me)=N(2,6-$Me_2C_6H_3$))Pd(CH_2)$_3$C(O)OMe]$BArF_4$ (15)[16]

catalyst	Me[b]	Et	Pr	*n*Bu	*s*Bu	Am	higher	br/1000 C[c]
14	39.0	29.7	5.2	16.7	6.7[d]	8.8	23.6	123
% Me[e]	31.7	24.1	4.2	13.6		7.2	19.2	
15[f]	41.5	23.1	4.4	9.3	6.1[d]	4.6	31.9	114
% Me[e]	36.4	20.3	3.9	8.2		4.0	28.0	

[a] Reaction under the conditions of Table 2. [b] Number of corresponding branches per 1000 C. [c] Total number of methyl branches per 1000 C. [d] A *s*Bu branch is counted as one Me and one Et branch. [e] Percent of the methyl groups in the given branch with respect to total Me. [f] Data from ref 16, 500 psi ethylene pressure, 35 °C reaction temperature, chlorobenzene solvent.

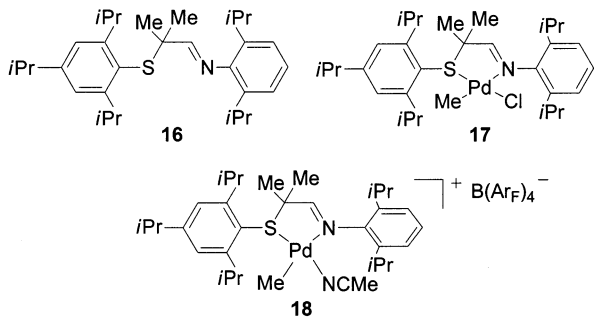
4.693(4) Å, leading to a more efficient blocking of one axial coordination site in the second case. Another interesting feature of **13** is the deformation of the P-aryl moiety, perhaps due to unfavorable steric interaction of the 2-*tert*-butyl group with the isopropyl substituent. The deformation results in a C(34)−C(31)−P(1) angle of 169.04(17)° (reflecting the bending at C(31)). Additionally in **13** the nonbonding interactions of the geminal methyl groups with the isopropyl substituent are expected to restrict the conformational mobility of the S-aryl group, leading to more efficient shielding of the lower axial coordination site on palladium.

Analysis of the nature of the branching using ^{13}C spectroscopy[16] showed that the polymer is hyperbranched, with methyl to amyl branches identified and quantified (Table 3). The distribution of branches is somewhat different from that observed for polyethylene

(16) Cotts, M. P.; Guan, Z.; McCord, E.; McLain, S. *Macromolecules* **2000**, *19*, 6945.

produced from palladium-diimine catalysts.[16] The polymer formed by **14** has somewhat fewer methyl branches (39.0/1000 C compared to 41.5/1000 C) and substantially more *n*-butyl branches (16.7 *n*Bu/1000 C compared to 9.3 *n*Bu/1000 C). The total number of branches calculated from ^{13}C spectral analysis (123/1000 C) agrees with the branching number obtained from the ^{1}H spectrum (119/1000 C).

3. Palladium(II) Catalysts Containing Imine-Sulfide Ligands. The replacement of an imine with a phosphinidine moiety in these catalysts decreased the molecular weight of ethylene polymerization products (compare **1** and **6a**,**b**). As a consequence, an interesting modification was the replacement of phosphinidine in phosphinidine-sulfide ligands with an imine functionality, leading to the structure **18**. A few imine-sulfide palladium and nickel catalysts have been described in patent literature.[17] The reaction of **12** with 2,6-diisopropylaniline afforded the corresponding imine. The complexation with palladium was more difficult than in the case of phosphinidines. Sulfide-imine ligand **16** did not displace cod from (cod)PdMeCl completely. To obtain complete conversion to **17**, azeotropic removal of cyclooctadiene from the equilibrium mixture was necessary. Conversion to **18** was carried out as in the case of phosphinidines.



16 **17** **18**

In an NMR experiment (20 equiv of ethylene, 0.01 mmol of cat., CD_2Cl_2 solvent) catalyst **18** rapidly consumed ethylene. A preparative run under 1 atm of ethylene (0.01 mmol of cat., 100 mL of CH_2Cl_2) afforded 146 mg of polyethylene ($M_n = 2800$) in 44 h. Under 400 psi ethylene, only a small amount (54 mg/3 h; 72 mg/15 h, 0.01 mmol **18**) of polyethylene with $M_n = 1800$ was obtained. Since the 400 psi experiment afforded less polyethylene than the 1 atm run, it is possible that under high pressure of ethylene the ligand is displaced from the palladium, resulting in the decomposition of the catalyst (precipitation of palladium black was observed).

Summary

Several new cationic phosphinidine-imine, phosphinidine-sulfide, and imine-sulfide palladium(II) complexes have been prepared. The complexes display moderate to high activity (for palladium complexes) in the oligomerization and polymerization of ethylene. Phosphinidine-containing catalysts are more stable under the polymerization conditions than the corresponding imine complexes; even after 15 h at RT phosphinidine-sulfide catalyst **11a** displays a turnover rate of 3000 TO/h, while for a 3 h run the TOF was determined to be 4300 h^{-1}. A new method of blocking axial sites on metal by restricting the conformational mobility of the sulfide ligand using *gem*-dimethyl substituents on the five-membered chelate ring backbone has also been developed, resulting in a 10-fold molecular weight increase of the polymer. Polyethylene obtained using phosphinidine-sulfide catalyst **14** is extremely highly branched (119 br/1000 C).

Experimental Section

General Considerations. All the operations related to catalysts or phosphines were carried out under an argon atmosphere using standard Schlenk techniques. The ^{1}H, ^{31}P, and ^{13}C spectra were recorded using Bruker 300 or 400 MHz spectrometers and referenced against residual solvent peaks (^{1}H, ^{13}C) or H_3PO_4 (^{31}P). Flash chromatography was performed using 60 Å silica gel (SAI). Room-temperature GPC measurements were performed on a Waters Alliance HPLC separations module equipped with Waters Styragel HR2, HR4, and HR5 columns in series and a Waters 2410 differential refractometer RI (refractive index) detector relative to polystyrene standards. Samples consisted of ~1 mg of polymer in 1 mL of degassed THF. Universal calibration was applied using Mark−Houwink constants for polyethylene ($k = 4.34 \times 10^{-4}$; $\alpha = 0.724$). Elemental analyses were performed by Atlantic Microlab Inc. of Norcross, GA. ^{13}C NMR analysis of polymer obtained with **14** was carried out under the conditions reported by the DuPont group.[16]

Materials. Anhydrous solvents were used in the reactions. Solvents were distilled from drying agents or passed through alumina columns under an argon or nitrogen atmosphere. NMR solvents were vacuum transferred from P_2O_5 and degassed by repeated freeze−pump−thaw cycles. The following starting materials were made using literature procedures: Mes*PCl_2,[18] Mes*PH_2,[18] (cod)PdMeCl,[7] 2,4,6-tri-isopropylthiophenol,[19] α-*tert*-butylthioacetaldehyde,[13] and 2,4,6-tri-isopropylphenylsulfenyl chloride.[14] $NaB(Ar_F)_4$ was purchased from Boulder Scientific.

Analysis of Polymer Molecular Weight and Branching by ^{1}H NMR Spectroscopy. The following labels are used for denoting different types of hydrogen signals in the polymer spectrum ($CDCl_3$ solvent): H1 (vinylidene end group, C═CH_2, br s, 4.7 ppm); H2 (1,2-disubstituted olefin, C*H*═C*H*, m, 5.3−5.4 ppm); H3 (trisubstituted olefin C═C*H*, m, 5.18 ppm); H4 (α-olefin, H_2C═C*H*, m, 5.85, 5.0, 4.9 ppm); H5 (alkyl methyl, alk-CH_3, m, 0.77−0.95 ppm); H6 (allylic methyl, C═C−CH_3, m, 1.6 ppm); H7 (alkyl methylene and methine, alk-C*H* and alk-CH_2, m, ca. 1.0−1.45 ppm); H8 (allylic methylene or methine, C═C−CH_2 and C═C−C*H*, m, 1.85−2.05 ppm). In the following formulas H_n's refer to integral values.

$N_{av} = (2/V)(A) + 2$, where N_{av} = average number of carbons in polymer chain, V = H1 + H2 + 2H3 + (2/3)H4, and A = (H5 + H6 + H7 + H8 − H1 − H2 − 3H3 − (1/3)H4)/2

$M_n = (N_{av})14.01$

$N_{br} = (1000/N_{av})(Y - X)$ where N_{br} = number of methyl branches per 1000 C, Y = ((H5 + H6)/3)(2/V), and X = ((H1/2) + H2 + 2H3 + (H4/3))*(2/V). The formula is not exact since the signal of the secondary homoallylic hydrogen overlaps with the signal of H6.

(17) Al-Ahmad, S. WO 01/87996 A2, 2001. Several examples of ethylene polymerization using cationic imine-sulfide Pd complexes are described in this patent. Polyethylene with M_n of 200−700 was obtained.

(18) Cowley, A. H.; Norman, N. C.; Pakulski, M. *Inorg. Synth.* **1990**, *27*, 235.
(19) Costanza, A. J.; Coleman, R. J.; Pierson, R. M.; Marvel, C. S.; King, C. *J. Polym. Sci.* **1955**, *17*, 319.

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

$B[3,5\text{-}C_6H_3(CF_3)_2]_4^-$ ($B(Ar_F)_4$). ^1H NMR (CD_2Cl_2): 7.74 (br s, 8H), 7.57 (s, 4H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 162.2 (q, J_{C-B} = 37.4 Hz), 135.2, 129.3 (q, J_{C-F} = 31.3 Hz), 125.0 (q, J_{C-F} = 272.5 Hz), 117.9.

General Polymerization Procedure. Polymerizations were carried out in a mechanically stirred 300 mL Parr reactor equipped with an electric heating mantle controlled by a thermocouple in the reaction mixture. The reactor was charged with toluene (100 mL) and heated for 1 h at 150 °C. After cooling to RT the solvent was poured out and the reactor heated under vacuum at 150 °C for 1 h. The reactor was filled with Ar, cooled to RT, pressurized to 200 psi ethylene, and vented three times. A solution of the catalyst in 100 mL of CH_2Cl_2 was added to the reactor via cannula, the reactor pressurized with ethylene to 400 psig, and the pressure maintained at this value during the polymerization. After that the reaction mixture was stirred for the appropriate time. Observed exotherms were always less than 2 °C, and the polymerizations were run at 26 °C. After venting the reaction mixture was evaporated and the distillate checked for oligomers by GC.

Propiophenone 2,6-Di-isopropylphenylimine, 3a. 2,6-Diisopropylaniline (3.8 mL, 20 mmol, Aldrich) was mixed with propiophenone (2.7 mL, 20 mmol, Aldrich) and *p*-TsOH (0.4 g, 2.1 mmol, Aldrich). The resulting mixture was heated at 205 °C for 1.5 h under a weak stream of Ar to remove formed H_2O. After cooling to RT the reaction mixture was poured into hexanes (50 mL) and filtered, and the precipitate was washed with additional hexanes (2 × 20 mL) followed by the evaporation of the filtrate and distillation of the residue. After the initial fraction of starting materials (80−110 °C/0.5 mm) the product was collected as a yellow oil, bp 110−125 °C/0.5 mm. Crystallization from methanol at −30 °C afforded the product as yellow crystals (4.3 g, 73.3%). ^1H NMR ($CDCl_3$): 7.99−7.91 (m, 2H); 7.54−7.44 (m, 3H); 7.20−7.13 (m, 2H); 7.12−7.04 (m, 1H); 2.78 (septet, 2H; J = 6.9 Hz); 2.53 (q, 2 H; J = 7.7 Hz); 1.21 (d, 6 H; J = 6.9 Hz); 1.16 (d, 6 H; J = 6.9 Hz); 0.99 (t, 3 H; J = 7.7 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 169.9, 146.6, 138.2, 136.1, 130.3, 128.7, 127.9, 123.4, 123.0, 28.4, 24.3, 23.7, 22.7, 11.4. Anal. Calcd for $C_{21}H_{27}N$: C 85.95, H 9.27, N 4.77. Found: C 86.05, H 9.32, N 4.79.

Propiophenone 2,4,6-Trimethylphenylimine, 3b. 2,4,6-Trimethylaniline (11.5 mL, 82 mmol, Aldrich) was mixed with propiophenone (10 mL, 74.5 mmol, Aldrich) and *p*-TsOH (1.4 g, 7.3 mmol, Aldrich). The resulting mixture was heated for 2 h at 200 °C under a weak stream of Ar to remove formed H_2O. After cooling to RT the reaction mixture was poured into hexanes (100 mL) and filtered, and the precipitate washed with additional hexanes (2 × 100 mL) followed by the evaporation of the filtrate. The residue was filtered through a 9 × 4.1 cm plug of silica gel in 10:1 hexanes/ether (300 mL collected). After evaporation of the solvent the unreacted starting materials were distilled off under vacuum (45−50 °C/0.4 mm). The residue was crystallized from methanol at −30 °C. Product was isolated as large orange-yellow crystals, 4.8 g (25.6%). ^1H NMR ($CDCl_3$): 8.00−7.94 (m, 2H); 7.51−7.45 (m, 3H); 6.89 (s, 2H); 2.50 (q, 2H; J = 7.7 Hz); 2.31 (s, 3H); 2.04 (s, 6H); 0.98 (t, 3H; J = 7.7 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 170.8, 146.4, 138.2, 131.9, 130.3, 128.7, 128.6, 127.7, 125.6, 23.9, 20.9, 18.2, 11.6. Anal. Calcd for $C_{18}H_{21}N$: C 86.00, H 8.42, N 5.57. Found: C 85.79, H 8.41, N 5.56.

(2,6-(*i*-Pr)$_2$C$_6$H$_3$)N=C(Ph)C(Me)=PMes*, 4a. *n*BuLi (3.3 mL of a 1.6 M solution in hexanes, 5.25 mmol, Aldrich) was added to a solution of diisopropylamine (0.77 mL, 5.5 mmol, Aldrich) in THF (5 mL) at −78 °C. The solution was stirred for 10 min at −78 °C followed by the addition of a solution of propiophenone 2,6-diisopropylphenylimine (1.47 g, 5 mmol) in THF (7 mL). The cooling bath was removed, and the reaction mixture was stirred for 3 h at RT. The solution of lithium azaenolate was added dropwise to a solution of 2,4,6-tri-*tert*-butylphenyldichlorophosphine (1.77 g, 5 mmol; contained some ArPBrCl) in THF (10 mL) at −78 °C. The reaction mixture was warmed to RT and stirred for 1 h. Assay by ^{31}P NMR showed the presence of ArP(Cl)R (+99.8 ppm). The solvent was evaporated under Ar, and dry DBU (1,8-diazabicyclo[5.4.0]-undec-7-ene, 1.5 mL, 10 mmol, Aldrich) was added, followed by dry CH_3CN (7 mL). The mixture was heated in a sealed Kontes flask at 90 °C for 3 h. Assay by ^{31}P NMR showed the presence of product and chloro (or bromo)phosphine in a 2.5:1 ratio (+304.0, +87.2 ppm) together with some unidentified decomposition products. The solvent was evaporated and the residue filtered through a 10 × 3.3 cm silica gel column in toluene, collecting the red-yellow product band. After evaporation the residue was recrystallized from CH_3CN twice at −30 °C to give product as red-yellow crystals, 0.88 g (31.0%). R_f = 0.53 (1:1 toluene/hexane). ^1H NMR (C_6D_6): 7.60 (s, 2H); 7.46−7.39 (m, 2H); 7.07−6.85 (m, 6H); 3.12 (septet, 2H; J = 6.8 Hz); 2.09 (d, 3H; J = 12.5 Hz); 1.54 (s, 18H); 1.34 (s, 9H); 1.23 (d, 6H, J = 6.8 Hz); 1.13 (d, 6H, J = 6.8 Hz). $^{13}C\{^1H, ^{31}P\}$ NMR ($CDCl_3$): 184.5; 169.0; 153.4; 150.5; 146.7; 137.7; 137.6; 135.4; 129.0; 128.6; 127.9; 127.4; 123.0; 122.4; 122.1; 38.1; 35.2; 32.7; 31.6; 28.8; 23.9; 22.0; 21.7. $^{31}P\{^1H\}$ NMR (C_6D_6): +303.0 ppm. Anal. Calcd for $C_{39}H_{54}NP$: C 82.49, H 9.59, N 2.47. Found: C 82.28, H 9.73, N 2.43.

MesN=C(Ph)C(Me)=PMes*, 4b. *n*BuLi (2.3 mL of a 1.6 M solution in hexanes, 3.7 mmol, Aldrich) was added to a solution of diisopropylamine (0.54 mL, 3.85 mmol, Aldrich) in THF (10 mL) at −78 °C. The solution was stirred for 10 min at −78 °C followed by the addition of a solution of propiophenone 2,4,6-trimethylphenylimine (0.88 g, 3.51 mmol) in THF (15 mL). The cooling bath was removed, and the reaction mixture was stirred for 3 h at RT. The solution of lithium azaenolate was added dropwise to a solution of 2,4,6-tri-*tert*-butylphenyldichlorophosphine (1.24 g, 3.57 mmol; contained some ArPBrCl) in THF (10 mL) at −78 °C. The reaction mixture was warmed to RT and stirred for 1 h. Assay by ^{31}P NMR showed the presence of ArP(Cl)R (+90.3 ppm). Dry DBU (1.1 mL, 7.36 mmol, Aldrich) was added. After 2 h, assay by ^{31}P NMR showed no reaction. The solvent was evaporated under vacuum, and dry CH_2Cl_2 (10 mL) and dry CH_3CN (10 mL) were added. The mixture was stirred at RT for 15 h 30 min. Assay by ^{31}P NMR (crude reaction mixture) showed the presence of product isomers in a 100:4 ratio (+306.7; +279.3 ppm). The solvent was evaporated and the residue filtered through a 16 × 3.3 cm silica gel plug in CH_2Cl_2, collecting 100 mL. After evaporation the residue was recrystallized from dry CH_3CN at −30 °C to give product as yellow crystals, 1.04 g (57.0%). ^1H NMR ($CDCl_3$): 7.46 (s, 2H); 7.28−7.12 (m, 5H); 6.64 (s, 2H); 2.13 (s, 3H); 1.96 (s, 6H); 1.70 (d, 3H; J = 12.4 Hz); 1.47 (s, 18H); 1.36 (s, 9H). $^{13}C\{^1H, ^{31}P\}$ NMR ($CDCl_3$): 183.9; 170.7; 153.3; 150.6; 146.6; 138.4; 137.6; 131.5; 128.6; 128.4; 128.3; 127.4; 125.1; 122.1; 38.1; 35.2; 32.7; 31.6; 21.6; 20.9; 18.6. $^{31}P\{^1H\}$ NMR ($CDCl_3$): +307.0 ppm. Anal. Calcd for $C_{36}H_{48}NP$: C 82.24, H 9.20, N 2.66. Found: C 82.11, H 9.32, N 2.67.

[(2,6-(*i*-Pr)$_2$C$_6$H$_3$)N=C(Ph)C(Me)=PMes*]PdMeCl, 5a. (Cod)PdMeCl (0.047 g, 0.176 mmol) was mixed with **4a** (0.10 g, 0.176 mmol) and CH_2Cl_2 (3 mL). The yellowish solution was stirred for 14 h at RT. After evaporation the residue was triturated with hexanes (3 mL). The hexanes were evaporated, and the residue was dried under vacuum to give **5a** as a reddish solid (0.109 g, 85.4%). ^1H NMR ($CDCl_3$): 7.62 (d, 2H; J = 3.3 Hz); 7.22−7.14 (m, 3H); 7.09−6.94 (m 3H); 6.92−6.83 (m, 2H); 3.00 (septet, 2H; J = 6.8 Hz); 1.69 (d, 18H; J = 0.7 Hz); 1.47 (d, 6H; J = 6.8 Hz); 1.36 (s, 9H); 1.26 (Pd-Me; d, 3H;

J = 4.2 Hz); 1.18 (d, 3H; J = 26.0 Hz); 1.00 (d, 6H; J = 6.8 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): +268.3 ppm. Anal. Calcd for $C_{40}H_{57}ClNPPd$: C 66.29, H 7.93, N 1.93. Found: C 66.20, H 8.01, N 1.91.

[MesN=C(Ph)C(Me)=PMes*]PdMeCl, 5b. The synthesis was performed as in the case of **5a**, using **4b** (0.200 g, 0.38 mmol) and (cod)PdMeCl (0.101 g, 0.38 mmol) in CH_2Cl_2 (5 mL). The product was isolated as a reddish solid (0.23 g, 88.7%). ^1H NMR (CD_2Cl_2): 7.65 (d, 2H; J = 3.3 Hz); 7.27−7.17 (m, 3H); 6.99−6.90 (m, 2H); 6.69 (s, 2H); 2.19 (s, 6H); 2.18 (s, 3H); 1.69 (d, 18H; J = 1.1 Hz); 1.37 (s, 9H); 1.12 (Pd-Me; d, 3H; J = 4.4 Hz); 1.11 (d, 3H; J = 26.3 Hz). $^{13}C\{^1H\}$ (CD_2Cl_2) 176.8 (d, J_{C-P} = 11.1 Hz); 163.5 (d, J_{C-P} = 45.8 Hz); 157.0; 155.4 (d, J_{C-P} = 2.4 Hz); 144.8 (d, J_{C-P} = 3.3 Hz); 135.6 (d, J_{C-P} = 10.9 Hz); 134.8; 129.6; 129.5 (d, J_{C-P} = 4.1 Hz); 128.6; 128.1; 126.3; 124.4 (d, J_{C-P} = 8.0 Hz); 121.0 (d, J_{C-P} = 3.5 Hz); 39.4; 35.9; 33.7 (d, J_{C-P} = 1.4 Hz); 31.1; 22.1 (d, J_{C-P} = 11.7 Hz); 21.1; 19.4; 2.0 (Pd-Me; d, J_{C-P} = 2.9 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): +267.3 ppm. Anal. Calcd for $C_{37}H_{51}ClNPPd$: C 65.09, H 7.53, N 2.05. Found: C 64.96, H 7.53, N 2.08.

[((2,6-(*i*-Pr)$_2$C$_6$H$_3$)N=C(Ph)C(Me)=PMes*)Pd(NCMe)Me]$^+$B(Ar$_F$)$_4^-$, 6a. To the mixture of **5a** (prepared from 0.176 mmol of **4a**, 0.176 mmol of (cod)PdMeCl) and $NaB(Ar_F)_4$ (0.156 g, 0.176 mmol) were added dry acetonitrile (1 mL) and CH_2Cl_2 (3 mL). The mixture was stirred for 1 h at RT, cannula filtered to remove NaCl, evaporated, and coevaporated with hexanes (3 mL). The product was obtained as a reddish solid (0.270 g, 96.3%). X-ray quality crystals were obtained by crystallization from warm toluene. ^1H NMR (CD_2Cl_2): 7.70 (d, 2H; J = 4.0 Hz); 7.36−7.28 (m, 3H); 7.18−7.08 (m, 3H); 6.98−6.93 (m, 2H); 2.94 (septet, 2H; J = 6.8 Hz); 1.75 (s, 3H); 1.67 (d, 18 H; J = 1.3 Hz); 1.4 (d, 6H; J = 6.8 Hz); 1.37 (s, 9H); 1.36 (d, 3H; J = 29.3 Hz); 1.09 (d, 6H; J = 6.8 Hz); 1.03 (Pd-Me; d, 3H; J = 2.6 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): +267.4 ppm. Anal. Calcd for $C_{74}H_{72}BF_{24}N_2PPd$: C 55.77, H 4.55, N 1.76. Found: C 55.48, H 4.42, N 1.73.

[(MesN=C(Ph)C(Me)=PMes*)Pd(NCMe)Me]$^+$B(Ar$_F$)$_4^-$, 6b. The synthesis was performed as in the case of **6a**, using **4b** (0.100 g, 0.19 mmol), (cod)PdMeCl (0.050 g, 0.19 mmol), and $NaB(Ar_F)_4$ (0.169 g, 0.19 mmol). Product was obtained as a reddish powder, 0.292 g (100%). ^1H NMR (CD_2Cl_2): 7.69 (d, 2H; J = 3.9 Hz); 7.37−7.23 (m, 3H); 7.00−6.94 (m, 2H); 6.80 (s, 2H); 2.22 (s, 6H); 2.19 (s, 3H); 1.74 (s, 3H); 1.66 (d, 18H; J = 1.3 Hz); 1.37 (s, 9H); 1.30 (d, 3H; J = 29.4 Hz); 1.02 (Pd-Me; d, 3H; J = 2.6 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 177.8 (d, J_{C-P} = 8.0 Hz); 167.5 (d, J_{C-P} = 54.4 Hz); 157.5 (d, J_{C-P} = 1.8 Hz); 157.1 (d, J_{C-P} = 2.9 Hz); 143.9 (d, J_{C-P} = 3.7 Hz); 136.6; 133.6 (d, J_{C-P} = 10.7 Hz); 130.9; 129.2; 129.1 (d, J_{C-P} = 2.4 Hz); 126.4; 125.1 (d, J_{C-P} = 9.3 Hz); 120.5; 117.5 (d, J_{C-P} = 15.3 Hz); 39.5 (d, J_{C-P} = 1.7 Hz); 36.0; 33.9; 31.2; 22.6 (d, J_{C-P} = 11.3 Hz); 20.9; 19.0; 3.8 (Pd-Me; d, J_{C-P} = 2.7 Hz); 2.0. One aromatic carbon is unaccounted for. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): +266.0 ppm. Anal. Calcd for $C_{71}H_{66}BF_{24}N_2PPd$: C 54.96, H 4.29, N 1.80. Found: C 55.32, H 4.63, N 1.78.

Generation of [(MesN=C(Ph)C(Me)=PMes*)Pd(ethylene)Me]$^+$B(Ar$_F$)$_4^-$, 7. Measurement of Ethylene Insertion Barrier. Solid **5b** (0.0068 g, 0.01 mmol) was mixed with $NaB(Ar_F)_4$ (0.012 g, 0.014 mmol) in a Teflon-lined screw-cap NMR tube. After cooling to −78 °C ethylene (1 mL, 0.045 mmol) was added, followed by CD_2Cl_2 (0.7 mL) and more ethylene (4 mL, 0.18 mmol). The NMR tube was placed in an NMR probe at 250 K, and the disappearance of the methyl peak (0.95 ppm) of the formed methyl ethylene complex was observed vs time, affording $k = 7.9 \times 10^{-5}$ s^{-1}, corresponding to $\Delta G^{\ddagger}$ = 19.2(1) kcal/mol. After the disappearance of the methyl peak, additional ethylene (5 mL, 0.22 mmol) was added and the disappearance of the ethylene peak was measured with respect to time, affording $k = 2.4 \times 10^{-4}$ s^{-1}, $\Delta G^{\ddagger}$ = 18.7(1) kcal/mol. The error was derived from the error in the rate constant, which in turn was obtained by the least-squares fit of the kinetic data.

Spectral Data for 7. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 233 K): +255.6 ppm. ^1H NMR (CD_2Cl_2, 243 K): 7.65 (d, 2H; J = 3.7 Hz); 7.35−7.21 (m, 3H); 6.94−6.87 (m, 2H); 6.80 (s, 2H); 2.17 (s, 3H); 2.15 (s, 6H); 1.60 (s, 18H); 1.35 (d, 3H; J = 29.0 Hz); 1.32 (s, 9H); 0.95 (Pd−Me; d, 3H; J = 3.7 Hz). Complexed ethylene exchanges with excess free ethylene fast even at 193 K, resulting in coalescence of NMR signals (5.37 ppm at 243 K and 22 equiv of ethylene).

(2,4,6-Tri-isopropylphenylthio)acetaldehyde, 9. To a solution of 2,4,6-tri-isopropylthiophenol (8.0 g, 33.9 mmol) in THF (130 mL) was added KHMDS (74.5 mL of a 0.5 M toluene solution, 37.3 mmol, Aldrich) at 0 °C and the resulting mixture stirred for 30 min at 0 °C. Bromoacetaldehyde diethylacetal (5.6 mL, 37.3 mmol, Aldrich) was added dropwise to the solution of the potassium thiolate at 0 °C. The ice bath was removed and the reaction mixture stirred for 4 h at RT. After that, it was poured into H_2O (300 mL) and extracted with diethyl ether (3 × 200 mL). Extracts were then dried ($MgSO_4$), filtered, and evaporated (aspirator). The crude reaction mixture was refluxed with 2% aqueous HCl (60 mL) and acetone (100 mL) for 2 h. The reaction mixture was poured into saturated aqueous sodium bicarbonate solution and extracted with diethyl ether (2 × 200 mL), and the extracts were dried ($MgSO_4$), filtered, and evaporated. Distillation of the product gave a clear liquid, bp 108−113 °C/0.5 mm, 5.79 g (61.4%). The compound slowly decomposes at RT and needs to be stored in the freezer. ^1H NMR (C_6D_6): 9.57 (t, 1H; J = 3.4 Hz); 7.00 (s, 2H); 3.96 (septet, 2H; J = 7.0 Hz); 2.81 (d, 2H; J = 3.4 Hz); 2.70 (septet, 1H; J = 7.0 Hz); 1.21 (d, 12H; J = 7.0 Hz); 1.13 (d, 6H; J = 7.0 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 193.3; 154.0; 151.1; 127.2; 122.8; 47.5; 35.0; 32.3; 24.9; 24.4. Anal. Calcd for $C_{17}H_{26}OS$: C 73.32, H 9.41. Found: C 73.38, H 9.50.

Mes*P(Li)TBS.[6b] *n*BuLi (2.6 mL of a 1.6 M solution in hexanes, 4.2 mmol, Aldrich) was added to a solution of 2,4,6-tri-*tert*-butylphenylphosphine (1.11 g, 4 mmol) in THF (30 mL) at −78 °C. The yellow suspension was stirred at −78 °C for 10 min, warmed to RT, and stirred for additional 15 min. A dark red solution was formed. Next, a solution of TBSCl (*tert*-butyldimethylsilyl chloride, 0.63 g, 4.2 mmol, Aldrich) in THF (10 mL) was added to ArPHLi over 10 min at 0 °C. The resulting yellowish solution was stirred at 0 °C for 20 min, warmed to RT, and stirred for 30 min. Assay by ^{31}P NMR showed clean formation of ArPHTBS (−135.5 ppm). After cooling to −78 °C additional *n*BuLi (2.6 mL of a 1.6 M solution in hexanes, 4.2 mmol, Aldrich) was added, and the solution was immediately warmed to RT to give a reddish solution of ArP(Li)TBS that was used in the phosphinidine synthesis.

[(2,4,6-(*i*-Pr)$_3$C$_6$H$_2$)SCH$_2$CH=PMes*]PdMeCl, 10a. A solution of (2,4,6-tri-isopropylphenylthio)acetaldehyde (0.835 g, 3.0 mmol) in THF (10 mL) was dropwise added to a solution of ArP(TBS)Li prepared as above (3.15 mmol scale) at −78 °C. The reaction color changed from red to yellow at the end of the reaction. After stirring for 30 min at −78 °C the reaction was warmed to RT and stirred for 1 h. TMSCl (0.3 mL) was then added to quench TBSOLi. Assay by ^{31}P NMR showed the presence of phosphinidine isomers in the ratio of 100:8 (+262.5; +254.1 ppm). The solution was evaporated, CH_2Cl_2 (10 mL) was added followed by (cod)PdMeCl (0.670 g, 2.53 mmol), and the reaction mixture was stirred for 12 h at RT. The solution was evaporated and the residue purified by flash chromatography on silica gel (7.5 × 3.7 cm). Initially cod, $ArPH_2$, and a minor phosphinidine diastereomer were eluted with hexanes (300 mL). After that, a dark red impurity was eluted with toluene (475 mL). Then, product was eluted with CH_2Cl_2 (400 mL). Fractions containing **10a** were evaporated and crystallized from acetonitrile (50 mL) at −30 °C. Product was obtained as a light yellow, somewhat light sensitive solid, 0.60 g (28.7%). ^1H NMR (CD_2Cl_2): 7.61 (d, 2H; J = 3.5 Hz); 7.37 (dt, 1H; J = 19.8, 4.2 Hz); 7.14 (s, 2H); 3.96 (septet, 2H; J = 6.8 Hz); 3.56 (dd, 2H; J = 40.4; 4.2 Hz); 2.94 (septet, 1H: J = 6.9 Hz); 1.67 (s, 18H); 1.39 (d, 6H; J = 6.8 Hz); 1.36 (s, 9H);

1.31 (d, 6H; J = 6.8 Hz); 1.29 (d, 6H; J = 6.9 Hz); 1.15 (Pd-Me; d, 3H; J = 4.1 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): +237.6 ppm. Anal. Calcd for $C_{36}H_{58}ClPPdS$: C 62.14, H 8.40. Found: C 62.17, H 8.45.

[((2,4,6-(*i*-Pr)$_3$C$_6$H$_2$)SCH$_2$CH=PMes*)Pd(NCMe)Me]$^+$B(Ar$_F$)$_4^-$, 11a. To the mixture of **10a** (0.129 g, 0.186 mmol) and $NaB(Ar_F)_4$ (0.165 g, 0.186 mmol) were added dry acetonitrile (1 mL) and CH_2Cl_2 (3 mL). The mixture was stirred for 17 h at RT, cannula filtered to remove NaCl, evaporated, and coevaporated with hexanes (3 mL). The product was obtained as a reddish solid (0.250 g, 85.9%). ^1H NMR (CD_2Cl_2): 7.65 (d, 2H; J = 4.2 Hz); 7.48 (dt, 1H; J = 19.4, 4.2 Hz); 7.19 (s, 2H); 3.88 (septet, 2H; J = 6.8 Hz); 3.76 (dd, 2H; J = 42.4; 4.2 Hz); 2.95 (septet, 1H; J = 6.9 Hz); 2.00 (s, 3H); 1.64 (s, 18H); 1.36 (s, 9H); 1.33 (br d, 12H; J = 6.8 Hz); 1.26 (d, 6H; J = 6.9 Hz), 1.19 (Pd-Me; d, 3H; J = 2.4 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): +231.0 ppm. Anal. Calcd for $C_{70}H_{74}BF_{24}NPPdS$: C 53.70, H 4.76, N 0.89. Found: C 53.88, H 4.88, N 0.80.

***t*-BuSCH$_2$CH=PMes*.** A solution of (*tert*-butylthio)acetaldehyde (0.32 g, 2.4 mmol) in THF (7 mL) was added dropwise to a solution of 2,4,6-tri-*tert*-butylphenylP(TBS)Li prepared from 2,4,6-tri-*tert*-butylphenylphosphine (2 mmol) at −78 °C. The reaction color changed from red to yellow at the end of the reaction. After stirring for 30 min at −78 °C the reaction was warmed to RT. Assay by ^{31}P NMR showed the presence of phosphinidine isomers in the ratio of 100:11 (+258.9; +252.8 ppm). TMSCl (0.3 mL) was added to quench TBSOLi, the solution was evaporated, and the residue was purified by flash chromatography on silica gel (14.5 × 3.3 cm) in 15:1 hexane/toluene followed by 10:1. Fractions containing the major isomer were evaporated to give colorless oil that slowly crystallized. After recrystallization from dry acetonitrile at −30 °C colorless crystals (0.303 g, 38.6%) were obtained. Major diastereomer (trans) R_f = 0.16 (15:1 hexane/toluene). Minor diastereomer (cis) R_f = 0.25. The ligand is somewhat sensitive to water. ^1H NMR (major diastereomer, CD_2Cl_2): 7.39 (d, 2H; J = 0.9 Hz); 7.28 (dt, 2H; J = 24.7, 9.2 Hz); 3.67 (dd, 2H; J = 20.9, 9.2 Hz); 1.49 (s, 18H); 1.31 (s, 9H); 1.30 (s, 9H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): +258.0 ppm. Anal. Calcd for $C_{24}H_{41}PS$: C 73.41, H 10.51. Found: C 73.40, H 10.69.

[*t*-BuSCH$_2$CH=PMes*]PdMeCl, 10b. The synthesis was performed as in the case of **5a**, using *t*-BuSCH$_2$CH=PMes* (0.05 g, 0.127 mmol) and (cod)PdMeCl (0.034 g, 0.127 mmol). Product was obtained as an off-white solid, 0.058 g (83.1%). ^1H NMR ($CDCl_3$): 7.54 (d, 2H; J = 3.4 Hz); 7.45 (dt, 1H; J = 19.0, 4.2 Hz), 3.29 (dd, 2H; J = 40.0, 4.2 Hz); 1.62 (s, 9H); 1.58 (s, 18H); 1.33 (s, 9H); 1.23 (Pd-Me; d, 3H; J = 3.7 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): +236.9 ppm. Anal. Calcd for $C_{25}H_{44}ClPPdS$: C 54.64, H 8.07. Found: C 54.88, H 8.10.

[(*t*-BuSCH$_2$CH=PMes*)Pd(NCMe)Me]$^+$B(Ar$_F$)$_4^-$, 11b. The synthesis was performed as in the case of **6a**, using *t*-BuSCH$_2$CH=PMes* (0.100 g, 0.255 mmol), (cod)PdMeCl (0.068 g, 0.255 mmol), and $NaB(Ar_F)_4$ (0.226 g, 0.255 mmol). Product was obtained as a reddish foam, 0.290 g (86.7%). ^1H NMR (CD_2Cl_2): 7.62 (d, 2H; J = 4.1 Hz); 7.59 (dt, 1H; J = 18.3, 4.2 Hz); 3.44 (dd, J = 42.1, 4.2 Hz); 2.37 (s, 3H); 1.56 (d, 18H; J = 0.9 Hz); 1.54 (s, 9H); 1.34 (s, 9H); 1.14 (Pd-Me; d, 3H; J = 2.3 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): +229.3 ppm. Anal. Calcd for $C_{59}H_{59}BF_{24}NPPdS$: C 49.96, H 4.19, N 0.99. Found: C 50.28, H 4.23, N 0.99.

2-Methyl-2-(2,4,6-tri-isopropylphenylthio)propanal, 12. To a suspension of KH (383 mg, 9.5 mmol, Aldrich; washed with hexanes to remove oil and dried in a vacuum) in THF (10 mL) was added dropwise isobutyric aldehyde (0.79 mL, 8.7 mmol, Aldrich) in THF (3 mL). The suspension was stirred for 25 min at RT under Ar (evolution of H_2!). A solution of 2,4,6-tri-isopropylphenylsulfenyl chloride (2.35 g, 8.7 mmol) in THF (10 mL) was then added in one portion. The color immediately changed from red to yellow. The solution was stirred at RT for 10 min, and water (20 mL) was added to the reaction mixture under Ar (caution: H_2 evolution!). The solution was extracted with diethyl ether (2 × 30 mL), and the extracts were dried ($MgSO_4$), filtered, and evaporated. The residue was purified by flash chromatography on silica gel (13 × 4.3 cm) in 1:5 toluene/hexane followed by 1:4. Fractions containing the product were evaporated to give a light yellow oil that slowly crystallized, m = 2.034 g (68.5%). R_f = 0.33 (1:3 toluene/hexane). ^1H NMR ($CDCl_3$): 9.34 (s, 1H); 7.00 (s, 2H); 3.85 (septet, 2H; J = 6.9 Hz); 2.86 (septet, 1H; J = 6.9 Hz); 1.29 (s, 6H); 1.24 (d, 6H; J = 6.9 Hz); 1.18 (unresolved br d, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 333 K): 195.8; 155.2; 151.1; 123.7; 122.1; 55.7; 34.5; 32.3; 24.5; 24.0; 21.7. Anal. Calcd for $C_{19}H_{30}OS$: C 74.45, H 9.87. Found: C 74.52, H 9.98.

[(2,4,6-(*i*-Pr)$_3$C$_6$H$_2$)SCMe$_2$CH=PMes*]PdMeCl, 13. A solution of 2-methyl-2-(2,4,6-tri-isopropylphenylthio)propanal (0.307 g, 1.0 mmol) in THF (5 mL) was added dropwise to a solution of ArP(TBS)Li prepared from 2,4,6-tri-*tert*-butylphenylphosphine (1.05 mmol) at −78 °C. The reaction color changed from red to light yellow at the end of the reaction. After stirring for 30 min at −78 °C the reaction was warmed to RT. Assay by ^{31}P NMR showed the presence of phosphinidine (+249.5 ppm). TMSCl (0.2 mL) was added to quench TBSOLi, the solution was evaporated, and the residue was coevaporated with hexanes (10 mL). A solution of (cod)PdMeCl (0.265 g, 1.0 mmol) in CH_2Cl_2 (5 mL) was added to the crude phosphinidine and the mixture stirred at RT for 10 h. The color gradually changed from colorless to red-brown. After evaporation, the residue was dissolved in hexanes and purified on a 4 × 2.3 cm silica gel column, eluting first with hexanes (80 mL) to remove cod and $ArPH_2$, then with CH_2Cl_2 (60 mL) to obtain the product. After evaporation the residue was triturated with hexanes (−30 °C) to give 0.63 g (87.1%) of **13** as yellow crystals. X-ray quality crystals were obtained by crystallization from acetonitrile at −30 °C. ^1H NMR ($CDCl_3$): 7.54 (d, 2H; J = 3.4 Hz); 7.18 (d, J = 18.9 Hz); 7.05 (s, 2H); 4.09 (septet, 2H; J = 6.8 Hz); 2.86 (septet, 1H; J = 6.9 Hz); 1.66 (s, 18H); 1.39 (d, 6H; J = 6.8 Hz); 1.32 (s, 15H; accidental overlap of *t*-Bu and *gem*-dimethyl); 1.29 (d, 6H; J = 6.8 Hz); 1.24 (Pd-Me; d, 3H; J = 4.7 Hz); 1.23 (d, 6H; J = 6.9 Hz). $^{13}C\{^1H\}$ ($CDCl_3$) 173.3 (d, J_{C-P} = 55.3 Hz); 156.0 (d, J_{C-P} = 3.2 Hz); 154.1; 153.7 (d, J_{C-P} = 2.6 Hz); 152.0; 123.9 (d, J_{C-P} = 8.9 Hz); 123.6 (d, J_{C-P} = 8.7 Hz); 123.0; 122.5 (d, J_{C-P} = 2.5 Hz); 58.0 (d, J_{C-P} = 7.1 Hz); 39.4 (d, J_{C-P} = 1.3 Hz); 35.5; 34.4; 34.2 (d, J_{C-P} = 2.3 Hz); 32.6; 31.3; 29.9 (d, J_{C-P} = 16.0 Hz); 26.5; 24.0; 23.6; 10.8 (Pd-Me; d, J_{C-P} = 5.7 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): +219.1 ppm. Anal. Calcd for $C_{38}H_{62}ClPPdS$: C 63.05, H 8.63. Found: C 62.94, H 8.64.

[(2,4,6-(*i*-Pr)$_3$C$_6$H$_2$)SMe$_2$CH=PMes*)Pd(NCMe)Me]$^+$B(Ar$_F$)$_4^-$, 14. The synthesis was performed as in the case of **6a**, using **13** (0.160 g, 0.22 mmol) and $NaB(Ar_F)_4$ (0.200 g, 0.22 mmol). Product was obtained as a reddish foam, 0.320 g (91.3%). ^1H NMR (CD_2Cl_2): 7.66 (d, 2H; J = 4.2 Hz); 7.33 (d, 1H; J = 18.5 Hz); 7.23 (s, 2H); 4.01 (septet, 2H; J = 6.8 Hz); 2.96 (septet, 1H; J = 6.9 Hz); 2.04 (s, 3H); 1.68 (d, 18H; J = 0.8 Hz); 1.44 (d, 6H; J = 2.2 Hz); 1.38 (d, 6H; J = 6.8 Hz); 1.37 (s, 9H); 1.31 (d, 6H; J = 6.8 Hz); 1.28 (d, 6H; J = 6.9 Hz); 1.19 (Pd-Me; d, 3H; J = 2.6 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): +210.0 ppm (s). $^{13}C\{^1H\}$ (CD_2Cl_2): 176.9 (d, J_{C-P} = 62.9 Hz); 156.8 (d, J_{C-P} = 3.8 Hz); 156.0 (d, J_{C-P} = 3.1 Hz); 154.5; 154.3; 124.8 (d, J_{C-P} = 10.0 Hz); 124.2; 121.5 (d, J_{C-P} = 2.0 Hz); 121.0 (d, J_{C-P} = 20.3 Hz); 120.0; 60.1 (d, J_{C-P} = 3.3 Hz); 39.9 (d, J_{C-P} = 1.7 Hz); 36.0; 34.9; 34.5 (d, J_{C-P} = 1.7 Hz); 33.3; 31.2; 29.8 (d, J_{C-P} = 16.5 Hz); 26.6; 23.9; 23.6; 12.2 (Pd-Me; d, J_{C-P} = 5.6 Hz), 3.1. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): +210.0 ppm. Anal. Calcd for $C_{72}H_{77}BF_{24}NPPdS$: C 54.29, H 4.87, N 0.88. Found: C 54.52, H 4.92, N 0.85.

(2,4,6-(*i*-Pr)$_3$C$_6$H$_2$)SCMe$_2$CH=N(2,6-(*i*-Pr)$_2$C$_6$H$_3$), 16. To a solution of 2-methyl-2-(2,4,6-tri-isopropylphenylthio)propanal (0.556 g, 2.0 mmol) in methanol (4 mL) was added formic acid (4 drops) and 2,6-diisopropylaniline (0.76 mL, 4.0 mmol, Aldrich). The reaction was stirred for 20 h at RT. TLC assay showed that reaction was completed at that time. After

Table 4. Crystallographic Data Collection Parameters for 4a, 6a, 10a, and 13

	4a	6a	10a	13
formula	$C_{39}H_{54}NP$	$C_{74}H_{72}F_{24}N_2BPdP*1/3H_2O$	$C_{38}H_{61}PdSClPN$	$C_{40}H_{65}SClPdPN$
mol wt	567.83	1599.53	736.78	764.84
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a, Å	15.2092(5)	13.7601(8)	13.1700(4)	11.9591(5)
b, Å	9.6929(3)	14.3900(8)	26.5085(9)	15.8500(7)
c, Å	24.5249(8)	21.0682(12)	11.5411(4)	23.3435(10)
α, deg		107.898(1)		
β, deg	99.420(1)	100.978(1)	99.848(1)	104.795(1)
γ, deg		92.510(1)		
V, Å^3	3566.74(20)	3873.7(4)	3969.82(23)	4278.1(3)
Z	4	2	4	4
dens calcd, Mg/m^3	1.057	1.371	1.233	1.188
F(000)	1240.95	1630.24	1558.08	1622.11
cryst dimens, mm	0.30 × 0.30 × 0.25	0.30 × 0.30 × 0.15	0.25 × 0.20 × 0.10	0.20 × 0.20 × 0.20
temp, °C			-100	
radiation (*λ*, Å)			0.71073	
2*θ* range, deg	5.00−60.00	5.00−50.00	5.00−60.00	5.00−50.00
μ, mm^{-1}	0.1	0.36	0.65	0.61
total no. of reflns	41835	31618	56392	36040
total no. unique reflns	6330	12659	11600	7572
no. of obsd data ($I>2.5\sigma(I)$)	5169	5914	8620	6236
no. of refined params	587	933	389	407
R_F, %	0.053	0.068	0.044	0.038
R_W, %	0.057	0.075	0.054	0.050
GOF	2.4486	2.345	1.9720	1.9215

evaporating solvent, the residue was purified by flash chromatography on silica gel (12 × 3.3 cm) in 1:1 hexane/toluene. Fractions containing the product were evaporated to give product as a yellowish oil (0.822 g, 88.3%). R_f = 0.44 (1:2 toluene/hexane). ^{1}H NMR ($CDCl_3$): 7.74 (s, 1H); 7.34−7.10 (m, 3H); 7.09 (s, 2H); 4.09 (septet, 2H; *J* = 6.9 Hz); 3.00 (septet, 2H; *J* = 6.9 Hz); 2.94 (septet, 1H; *J* = 6.9 Hz); 1.52 (s, 6H); 1.31 (d, 6H; *J* = 6.9 Hz); 1.24 (unresolved br d, 12H); 1.22 (d, 12H; *J* = 6.9 Hz). ^{13}C{^{1}H} ($CDCl_3$, 238 K): 168.5, 154.8, 150.5, 147.8, 137.6, 124.8, 124.1, 122.9, 121.9, 52.2, 34.3, 32.3, 27.7, 25.9, 25.8, 24.1, 23.6, 22.9. Anal. Calcd for $C_{31}H_{47}NS$: C 79.93, H 10.17, N 3.01. Found: C 79.78, H 10.22, N 2.98.

[(2,4,6-(*i*-Pr)$_3$C$_6$H$_2$)SCMe$_2$CH=N(2,6-(*i*-Pr)$_2$C$_6$H$_3$)]PdMeCl, 17. Imine **16** (0.200 g, 0.43 mmol) was mixed with (cod)PdMeCl (0.114 g, 0.43 mmol) and benzonitrile (5 mL). The reaction mixture was stirred at RT for 1 h followed by evaporation of benzonitrile at 0.2 mm/RT overnight. The residue was coevaporated with toluene (2 × 5 mL), dissolved in CH_2Cl_2 (5 mL), and filtered through Celite. After evaporation and trituration with hexanes a yellowish solid was obtained (0.237 g, 88.5%), as a ca. 7:1 isomer mixture (ratio of Me peaks at 0.57 (major) and 0.79 ppm (minor)). The configuration at the palladium center was verified by X-ray crystallography; however, it was not possible to fully refine the structure due to twinning of the crystals. Major isomer ^{1}H NMR ($CDCl_3$): 7.55 (s, 1H); 7.25−7.08 (m, 5H); 4.38 (septet, 2H; *J* = 6.8 Hz); 3.16 (septet, 2H; *J* = 6.8 Hz); 2.93 (septet, 1H; *J* = 6.9 Hz); 1.55 (s, 6H); 1.44 (d, 6H; *J* = 6.8 Hz); 1.37 (d, 12H; *J* = 6.8 Hz); 1.28 (d, 6H; *J* = 6.9 Hz); 1.15 (d, 6H; *J* = 6.8 Hz), 0.57 (s, 3H). Major isomer ^{13}C{^{1}H} ($CDCl_3$): 175.4, 154.2, 153.2, 144.5, 139.4, 127.1, 123.7, 123.4, 119.8, 62.9, 34.4, 32.6, 28.3, 26.6, 25.7, 25.0, 24.0, 23.9, 23.5, −6.2. Anal. Calcd for $C_{32}H_{50}ClNPdS$: C 61.72, H 8.09, N 2.25. Found: C 61.86, H 8.12, N 2.31.

[((2,4,6-(*i*-Pr)^{3}C$_6$H$_2$)SCMe$_2$CH=N(2,6-(*i*-Pr)$_2$C$_6$H$_3$))Pd(NCMe)Me]$^+$B(Ar$_F$)$_4^-$, 18. The synthesis was performed as in the case of **6a**, using **17** (0.08 g, 0.128 mmol) and NaB(Ar$_F$)$_4$ (0.114 g, 0.128 mmol). Product was obtained as a yellowish powder, 0.180 g (96.9%). The configuration at the palladium center was assigned by analogy with **17**. ^{1}H NMR (CD_2Cl_2): 7.71 (s, 1H); 7.34−7.25 (m, 3H); 7.24 (s, 2H); 4.18 (septet, 2H; *J* = 6.8 Hz); 3.05 (septet, 2H; *J* = 6.8 Hz); 2.96 (septet, 1H; *J* = 6.9 Hz); 1.73 (s, 3H); 1.60 (s, 6H); 1.41 (d, 6H; *J* = 6.8 Hz); 1.39 (d, 6H; *J* = 6.8 Hz); 1.34 (d, 6H; *J* = 6.8 Hz); 1.28 (d, 6H; *J* = 6.9 Hz); 1.19 (d, 6H; *J* = 6.8 Hz); 0.56 (s, 3H). ^{13}C{^{1}H} (CD_2Cl_2): 177.9; 155.3; 154.3; 143.3; 139.5; 128.6; 124.8; 124.5; 120.1; 67.5; 34.9; 33.5; 28.8; 26.5; 25.5; 25.1; 24.0; 23.8; 23.3; 2.1; −2.9. One aromatic carbon is unaccounted for. Anal. Calcd for $C_{66}H_{65}BF_{24}N_2PdS$: C 53.14, H 4.39, N 1.89. Found: C 53.42, H 4.43, N 1.82.

X-ray Crystal Structures. Diffraction data were collected on a Bruker SMART diffractometer using the *ω*-scan mode. Refinement was carried out with the full-matrix least-squares method based on *F* (NCRVAX) with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were inserted in calculated positions and refined riding with the corresponding atom. Complete details of X-ray data collection are given below in Table 4. For **4a**, $I > 3.0\sigma(I)$.

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Supporting Information Available: X-ray crystallography data for **4a**, **6a**, **10a**, and **13** and graphs for the determination of rates of migratory insertion. This material is available free of charge via the Internet at http://pubs.acs.org.

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