Unsaturated Pd(0), Pd(I), and Pd(II) Complexes of a New Methoxy-Substituted Benzyl Phosphine. Aryl−X (X = Cl, I) Oxidative Addition, C−O Cleavage, and Suzuki−Miyaura Coupling of Aryl Chlorides

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The 14e$^-$ Pd(0)L_2 complex **2** was prepared by reduction of [Pd(2-methylallyl)Cl]$_2$ in the presence of the new, electron-rich, bulky methoxy benzyl phosphine (dmobp) ligand **1**. Structural characterization of this complex indicates that the methoxy groups are not coordinated to the metal center. Complex **2** undergoes oxidative addition of iodo- and chlorobenzene at room temperature to yield the monophosphine complexes LPd(Ph)X (**4**, X = I; **5**, X = Cl) in which the methoxy group is coordinated to the Pd(II) center in the solid state, as indicated by the X-ray structure of **4**. In solution there is no evidence for methoxy coordination, indicating the availability of a Pd(II) 14e$^-$ complex. The Me−O bond in **4** is longer than the corresponding bond in **2**, indicating that coordination of the methoxy group weakens the C−O bond. Reaction of complex **4** or **5** with the free ligand **1** results in nucleophilic attack and C−O cleavage, leading to the dimeric phenoxy-bridged complex **7**, which was structurally characterized. Partial reduction of [Pd(2-methylallyl)Cl]$_2$ in the presence of the ligand **1** leads to the Pd(I) dimer **3**, which can be converted to the Pd(0) complex **2** by addition of ligand **1** and a base. This complex, which bears only one phosphine for each Pd atom, is a suitable precursor to a presumed catalytically active 12e$^-$ Pd(0) catalyst. Complexes **2** and **3** catalyze the Suzuki−Miyaura cross-coupling of chlorobenzene with PhB(OH)$_2$ even at room temperature, albeit slowly, while the C−O cleaved phenoxy-bridged complex **7** is not catalytically active at 40 °C, indicating that it is not an intermediate in the catalysis. The dmobp ligand **1** is more effective in Suzuki−Miyaura coupling than an analogous benzyl ligand lacking methoxy substituents.

Introduction

Bulky trialkylphosphine ligands can promote the generation of unsaturated Pd(0) and Pd(II) intermediates and thereby enhance the catalytic activity of Pd complexes in coupling reactions.[1,2] While 14-electron three-coordinate Pd(II) complexes are proposed as intermediates in many of these reactions, such complexes are rare, and the first example of an isolated monomeric arylpalladium(II) monophosphine complex was reported only recently by Hartwig.[3] We describe here the preparation of a new, methoxy-substituted, di-*tert*-butylbenzylphosphine ligand, namely, di-*tert*-butyl(2,6-dimethoxybenzyl)phosphine (dmobp), **1**. This ligand is analogous to the previously reported di-*tert*-butyl-(2,4,6-trimethylbenzyl)phosphine (tmbp), lacking methoxy groups.[4] It was of interest to us to explore the possibility that the methoxy substituent would be involved in hemilabile coordination during catalysis, thus enhancing the stability of the active species without adversely affecting its reactivity. The dmobp ligand **1** is a monodentate analogue of the known PCP-type ligand 1,3-bis-[(di-*tert*-butylphosphanyl)methyl]-2-methoxybenzene.[5] We report on the preparation and X-ray characterization of unsaturated Pd(0), Pd(I), and Pd(II) complexes of this ligand, including a monophosphine Pd(II) complex resulting from aryl−X (X = Cl, I) oxidative addition and stabilized (in the solid state) by coordination of the methoxy moiety. Unexpectedly, this complex was observed to undergo ArO−Me activation of the ligand under mild heating. Catalysis of Suzuki−Miyaura-type coupling of chlorobenzene by the Pd(0)L_2 complex has

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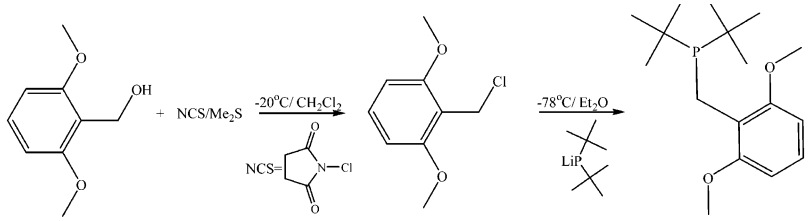
Scheme 1. Preparation of Dmobp 1



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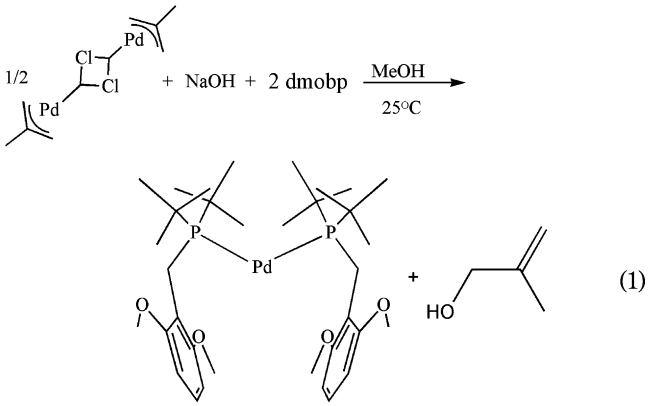
been observed to proceed even at room temperature (albeit slowly), and the possible involvement of the complexes mentioned above in the catalysis is addressed.

Results and Discussion

Ligand Synthesis. The new dmobp ligand **1** was synthesized in three steps from the commercially available 2,6-dimethoxybenzoic acid. Reduction of this compound with $LiAlH_4$ according to a literature procedure[6] yielded 2,6-dimethoxybenzyl alcohol, which was converted to 2,6-dimethoxybenzyl chloride in 92% yield by its reaction with *N*-chlorosuccinimide-dimethyl sulfide adduct (Scheme 1). Reaction of this compound with lithium di-*tert*-butyl phosphide yielded the pure ligand **1** as a colorless oil in 25% yield after purification by column chromatography.

Synthesis of a Pd(0) Complex. The Pd(0) complex **2** was prepared in analogy with a literature procedure[7] by reaction of $[(2\text{-methylallyl})PdCl]_2$ in MeOH with NaOH in the presence of ligand **1**. It precipitated as a white powder in 85% yield (eq 1). The $^{31}P\{^1H\}$ NMR spectrum of **2** exhibits a singlet at 60.89 ppm, indicating that the two phosphorus atoms are equivalent and that the complex is symmetric. The *tert*-butyl groups appear in the ^1H NMR spectrum at 1.49 ppm as a virtual triplet, indicating that the phosphines are disposed in a mutually trans arrangement.



(1)

White crystals (plates) suitable for a single-crystal X-ray diffraction study were obtained upon slow evaporation of a pentane solution of **2** under nitrogen at room temperature. The overall structural features (Figure 1, Table 1) are similar to those reported for the very few other structurally characterized 14e⁻ Pd(0) complexes.[8] Interestingly, the P−Pd−P angle (166.9°) is bent toward

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 2

Pd(1)−P(2)	2.2860(19)	O(1)−C(32)	1.387(9)
Pd(1)−P(3)	2.2965(19)	O(1)−C(37)	1.424(9)
P(2)−C(21)	1.877(7)	O(2)−C(36)	1.380(9)
P(2)−C(22)	1.903(7)	O(2)−C(38)	1.421(9)
P(2)−C(26)	1.913(7)	O(3)−C(56)	1.375(9)
P(3)−C(41)	1.868(7)	O(3)−C(57)	1.435(9)
P(3)−C(43)	1.890(7)	O(4)−C(52)	1.369(9)
P(3)−C(42)	1.896(7)	O(4)−C(58)	1.419(9)
P(2)−Pd(1)−P(3)	166.86(7)	C(56)−O(3)−C(57)	116.4(6)
C(21)−P(2)−Pd(1)	121.9(2)	C(52)−O(4)−C(58)	118.1(6)
C(22)−P(2)−Pd(1)	110.6(2)	C(33)−C(32)−O(1)	123.5(7)
C(26)−P(2)−Pd(1)	111.5(2)	O(1)−C(32)−C(31)	114.1(7)
C(41)−P(3)−Pd(1)	122.8(2)	O(2)−C(36)−C(35)	123.5(7)
C(43)−P(3)−Pd(1)	111.6(2)	O(2)−C(36)−C(31)	114.7(7)
C(42)−P(3)−Pd(1)	109.4(2)	O(4)−C(52)−C(51)	116.4(7)
C(32)−O(1)−C(37)	117.0(6)	O(4)−C(52)−C(53)	122.5(7)
C(36)−O(2)−C(38)	118.0(6)	C(55)−C(56)−O(3)	123.6(7)

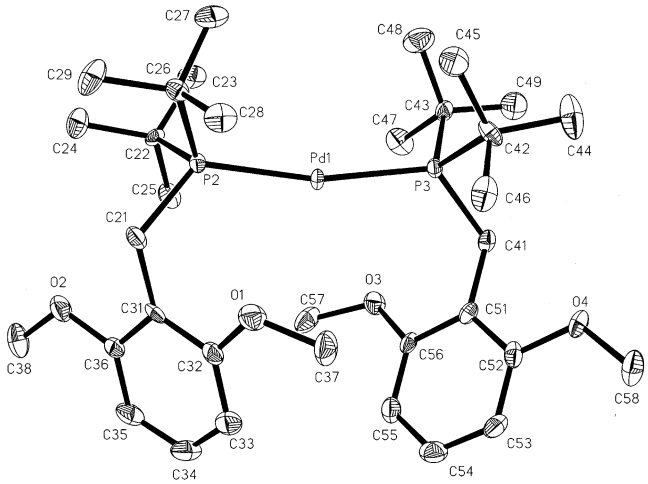


Figure 1. ORTEP drawing of a molecule of **2** (50% probability level). Hydrogen atoms are omitted for clarity.

the *tert*-butyl groups, and it is 10° smaller than the analogous angle reported for $((^tBu)_2PhP)_2Pd(0)$,[8b] indicating a large steric effect induced by the benzylic moiety.

In the X-ray of **2** as well as in NMR spectra there is no evidence of methoxy group coordination, despite the high unsaturation of the 14e⁻ Pd center and the potentially relatively stable six-membered ring that would have been formed upon coordination of a methoxy group. This is likely due to the "softness" of the Pd(0) center, which renders the "hard" oxygen atom coordination unfavorable.

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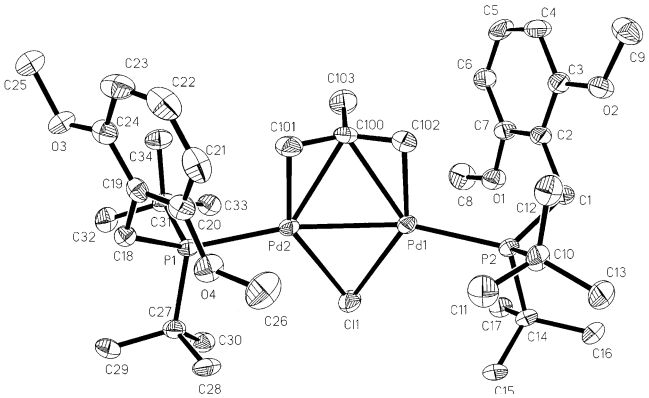
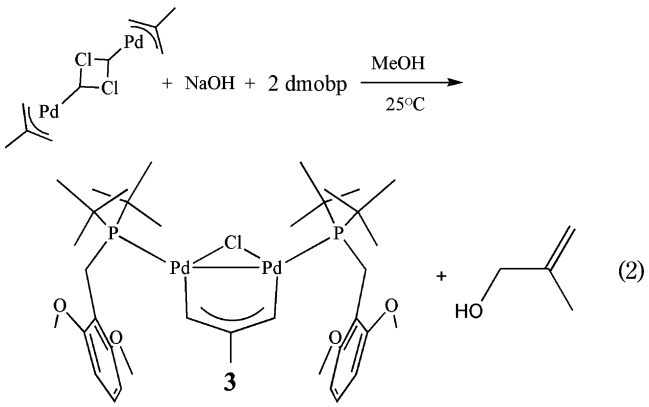


Figure 2. ORTEP drawing of a molecule of **3** (50% probability level). Hydrogen atoms are omitted for clarity.

When the preparation of complex **2** lacked sufficient excess of ligand and base, an additional signal appeared in the $^{31}P\{^1H\}$ NMR spectrum at 64.01 ppm (singlet), which could be washed away with a small amount of diethyl ether. Suspecting that this compound was a partially reduced Pd complex, we prepared and characterized the complex by reacting $[(2\text{-methylallyl})PdCl]_2$ with only 1 equiv of dmobp.

Synthesis of a Pd(I) Complex. Addition of 2 molar equiv of ligand **1** to a suspension of the dimer $[(2\text{-methylallyl})PdCl]_2$ in MeOH (i.e., ratio **1**/Pd = 1) followed immediately with 2 molar equiv of NaOH resulted, after stirring overnight at room temperature, in complex **3**, which precipitated as a green powder. Extraction with benzene and concentration under high vacuum gave complex **3** as a yellow powder in 95% yield (eq 2). The $^{31}P\{^1H\}$ NMR spectrum shows one singlet at 64.01 ppm, indicating that the two phosphorus atoms are equivalent and that the complex is symmetric. However, the ^1H NMR spectrum shows two different P-C(CH_3)$_3$ groups at 1.48 and 1.53 ppm as virtual triplets. In $^{13}C\{^1H\}$ NMR the methyl groups appear at 30.04 and 30.36 ppm as virtual triplets. The different chemical shifts indicate asymmetry in the molecule.



(2)

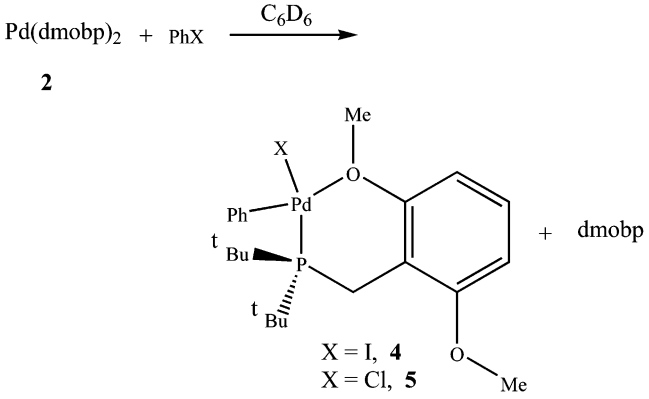
Yellow crystals were obtained upon slow evaporation of a benzene solution of **3** under nitrogen at room temperature. The overall features of the structure of **3** (Figure 2, Table 2) are similar to those observed with other Pd(I) allyl dimer complexes.[9] The angle between the allyl plane and the plane of the Pd−Pd−Cl atoms, 87.6°, is larger than the corresponding angle in other allyl- and halide-bridged Pd(I) clusters, which are in the range of 80−84°.[9a] The angle is smaller than 90° due to back-bonding interaction in the dipalladium complex involving overlap between the central carbon p orbital and the dσ−dσ and dπ−dπ orbitals of Pd_2.[9a] The larger angle might be a result of the higher steric bulk relative to other reported dimers that contained PPh_3 or P^iPr_3 as ligands.[9]

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 3

Pd(1)−C(102)	2.072(5)	C(1)−C(2)	1.510(6)
Pd(1)−P(2)	2.3122(12)	C(3)−O(2)	1.370(6)
Pd(1)−Cl(1)	2.4223(12)	C(3)−C(4)	1.399(7)
Pd(1)−Pd(2)	2.6338(5)	C(4)−C(5)	1.380(8)
Pd(2)−C(101)	2.053(5)	C(5)−C(6)	1.374(7)
Pd(2)−P(1)	2.3145(12)	C(6)−C(7)	1.401(7)
Pd(2)−Cl(1)	2.4222(12)	C(7)−O(1)	1.371(6)
P(1)−C(18)	1.870(5)	O(1)−C(8)	1.417(6)
P(1)−C(31)	1.895(4)	O(2)−C(9)	1.420(6)
P(1)−C(27)	1.903(5)	C(101)−C(100)	1.409(7)
P(2)−C(1)	1.881(4)	C(100)−C(102)	1.401(7)
P(2)−C(14)	1.898(5)	C(100)−C(103)	1.532(7)
P(2)−C(10)	1.901(5)		

C(102)−Pd(1)−P(2)	101.36(14)	Pd(2)−Cl(1)−Pd(1)	65.87(3)
C(102)−Pd(1)−Cl(1)	145.43(15)	C(2)−C(1)−P(2)	117.1(3)
P(2)−Pd(1)−Cl(1)	112.81(4)	C(7)−C(2)−C(3)	117.3(4)
C(102)−Pd(1)−Pd(2)	88.44(14)	C(7)−C(2)−C(1)	120.2(4)
P(2)−Pd(1)−Pd(2)	164.43(3)	C(3)−C(2)−C(1)	122.4(4)
Cl(1)−Pd(1)−Pd(2)	57.06(3)	O(2)−C(3)−C(4)	122.4(4)
C(101)−Pd(2)−P(1)	102.90(15)	O(2)−C(3)−C(2)	116.2(4)
C(101)−Pd(2)−Cl(1)	144.78(15)	C(4)−C(3)−C(2)	121.3(5)
P(1)−Pd(2)−Cl(1)	112.32(4)	O(1)−C(7)−C(2)	114.8(4)
C(101)−Pd(2)−Pd(1)	87.71(15)	O(1)−C(7)−C(6)	123.1(4)
P(1)−Pd(2)−Pd(1)	169.23(3)	C(2)−C(7)−C(6)	122.2(4)
Cl(1)−Pd(2)−Pd(1)	57.07(3)	C(7)−O(1)−C(8)	118.9(4)
C(1)−P(2)−C(14)	101.5(2)	C(3)−O(2)−C(9)	118.0(4)
C(1)−P(2)−C(10)	104.7(2)	C(100)−C(101)−Pd(2)	88.1(3)
C(14)−P(2)−C(10)	108.8(2)	C(102)−C(100)−C(101)	125.3(5)
C(1)−P(2)−Pd(1)	119.69(14)	C(102)−C(100)−C(103)	116.4(5)
C(14)−P(2)−Pd(1)	112.93(16)	C(101)−C(100)−C(103)	117.0(5)
C(10)−P(2)−Pd(1)	108.55(16)	C(100)−C(102)−Pd(1)	87.5(3)

Scheme 2. Reaction of 2 with Aryl Halides



Synthesis and Reactivity of Pd(II) Complexes. Oxidative Addition of Aryl Halides. The reactivity of the Pd(0) complex **2** toward oxidative addition of aryl halides was studied. Reaction with 1 equiv of iodobenzene in C_6D_6 at room temperature proceeded smoothly, quantitatively yielding complex **4** after 2 days (Scheme 2). During the follow-up of the reaction in $^{31}P\{^1H\}$ NMR, the peak corresponding to complex **2** disappeared, giving rise to two new peaks in a 1:1 ratio at 64.45 and 35.25 ppm, the latter corresponding to the free ligand **1**. After evaporation and successive washing with pentane, the

(9) (a) Review: Murahashi, T.; Kurosawa, H. *Coord. Chem. Rev.* **2002**, *231*, 207. For example: (b) Werner, H.; A Kühn, *J. Organomet. Chem.* **1979**, *179*, 439. (c) Krause, J.; Goddard, R.; Mynott, R.; Pörschke, K.-R. *Organometallics* **2001**, *20*, 1992.

oxidative addition complex (dmobp)Pd(Ph)I **4** was obtained in 60% isolated yield as a white powder. ^{1}H NMR showed a new set of aromatic peaks at 6.70, 6.83, and 7.37 ppm. ^{13}C{^{1}H} NMR exhibited three doublets at 116.29, 126.54, and 139.19 ppm, with J_{CP} = 1.2, 1.2, and 3.4 Hz, respectively. In ^{1}H NMR the *tert*-butyls appear as a doublet (J_{HP} = 13.5 Hz), indicating that only one phosphine is bound to the Pd center.

Crystals of complex **4** were obtained by slow evaporation of a C_6H_6/THF solution. The X-ray structure of **4** (Figure 3, Table 3) shows a square planar coordination around the Pd center, the methoxy group occupying one of the corners. Coordination of the methoxy group is not observed in solution by NMR, probably due to its hemilabile character. Another case of oxidative addition that results in an alkoxy group coordinated to the Pd (II) center was reported recently.[10] The phenyl ring is located trans to the methoxy group, and the iodide ligand is positioned trans to the phosphorus atom. This configuration is probably the thermodynamically stable one, the ligands with the high trans influence being located opposite the weak trans influence ligands. Hartwig has recently reported the monomeric, 14e$^-$ Pd(II) complexes ^{t}Bu$_2$(adamantyl)PPd(Ph)Br and ^{t}Bu$_3$-PPd(2,4-xylyl)I, formed by aryl halide oxidative addition to PdL$_2$.[3] With ^{t}Bu$_2$(adamantyl)PPd(Ph)Br, an agostic interaction between the Pd center and an adamantyl−H bond was observed, the hydrogen atom occupying one of the corners of the twisted square plane around the Pd center.

Another fact worth noting about the structure of complex **4** is the elongation of the Ar−O (O(2)−C(3) 1.395 Å) and O−Me (O(2)−C(9) 1.449 Å) bonds of the coordinated methoxy group relative to the Ar−O (O(1)−C(7) 1.372 Å) and the noncoordinated O−Me (O(1)−C(8) 1.429 Å). This elongation suggests the weakening of the C−O bond, making its activation possible. Indeed, C−O activation in our system was observed, as will be detailed later.

As expected, there is a large difference in the reactivity of iodobenzene and chlorobenzene with complex **2**. When 0.02 mmol of iodobenzene was reacted with 0.02 mmol of complex **2** in 500 μL of C_6D_6 at room temperature, ca. 88% yield was obtained after 4 h. On the other hand, reaction of 10 equiv of chlorobenzene with complex **2** under the same conditions resulted in ca. 2% yield after 4 h. Thus, the reaction of complex **2** with iodobenzene is more than 2 orders of magnitude faster than with chlorobenzene (roughly 400 times faster in case of first-order dependence in the complex and the aryl halide).

The complex (dmobp)Pd(Ph)Cl, **5**, was prepared by reaction of complex **2** with 10 equiv of chlorobenzene in C_6D_6 at 40 °C. The reaction proceeded smoothly and quantitatively yielded complex **5** after 2 days. Reaction follow-up by ^{31}P{^{1}H} NMR revealed that the peak corresponding to complex **2** disappeared, giving rise to two new peaks in a 1:1 ratio at 71.01 and 35.25 ppm, the latter corresponding to the free ligand **1**. After evaporation and successive washing with pentane the oxidative addition product, (dmobp)Pd(Ph)Cl, **5**, was obtained in 70% isolated yield as a white powder. ^{1}H NMR showed a new set of aromatic peaks at 6.80, 6.89, and 7.43 ppm. ^{13}C{^{1}H} NMR exhibited three doublets at 115.77, 126.93, and 137.91 ppm, with J_{CP} = 1.6, 1.2, and 3.2 Hz, respectively. In ^{1}H NMR the *tert*-butyls appear as a doublet with J_{HP} = 13.5 Hz, indicating that only one phosphine is bound to the Pd center.

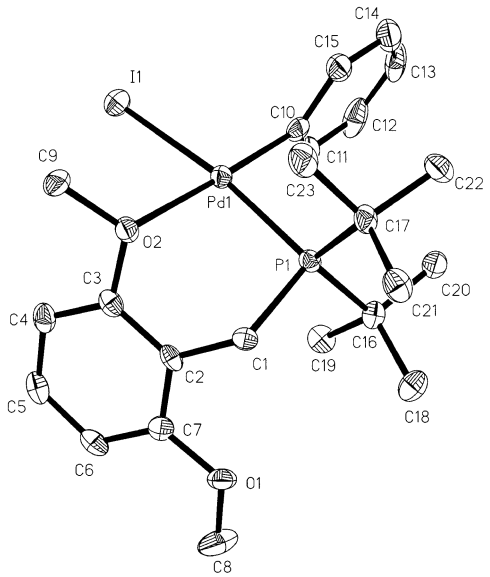


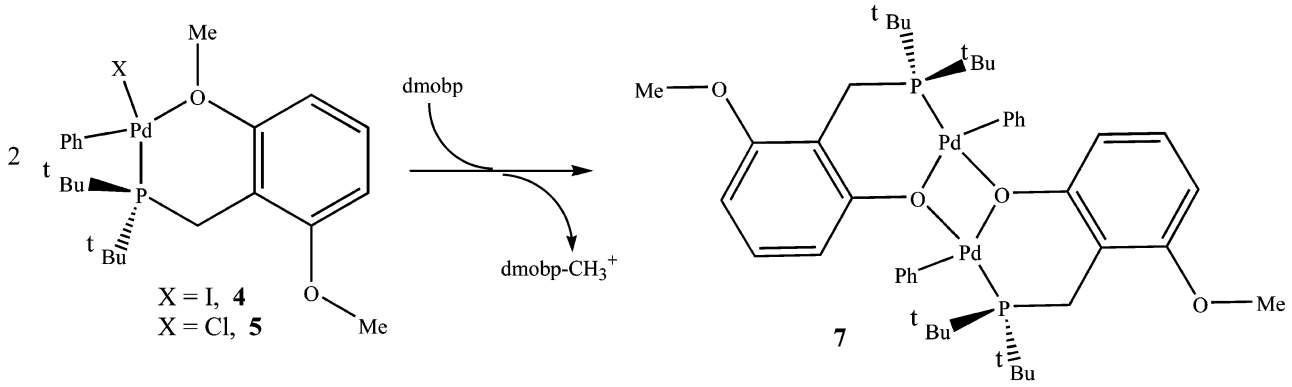
Figure 3. ORTEP drawing of a molecule of **4** (50% probability level). Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 4

I(1)−Pd(1)	2.6481(9)	P(1)−C(16)	1.888(5)
Pd(1)−C(10)	1.977(5)	O(1)−C(7)	1.372(6)
Pd(1)−O(2)	2.276(3)	O(1)−C(8)	1.429(6)
Pd(1)−P(1)	2.3172(15)	O(2)−C(3)	1.395(5)
P(1)−C(1)	1.870(4)	O(2)−C(9)	1.449(5)
P(1)−C(17)	1.882(4)		
C(10)−Pd(1)−O(2)	176.44(16)	C(9)−O(2)−Pd(1)	121.4(3)
C(10)−Pd(1)−P(1)	94.42(13)	C(2)−C(1)−P(1)	116.3(3)
O(2)−Pd(1)−P(1)	86.03(9)	C(4)−C(3)−O(2)	122.7(4)
C(10)−Pd(1)−I(1)	89.08(13)	C(2)−C(3)−O(2)	114.3(4)
O(2)−Pd(1)−I(1)	90.91(8)	O(1)−C(7)−C(6)	123.5(4)
P(1)−Pd(1)−I(1)	172.14(3)	O(1)−C(7)−C(2)	115.4(4)
C(1)−P(1)−C(17)	100.9(2)	C(11)−C(10)−Pd(1)	122.1(4)
C(1)−P(1)−C(16)	104.5(2)	C(15)−C(10)−Pd(1)	119.4(4)
C(17)−P(1)−C(16)	113.4(2)	C(18)−C(16)−P(1)	113.3(3)
C(1)−P(1)−Pd(1)	103.34(15)	C(19)−C(16)−P(1)	105.8(3)
C(17)−P(1)−Pd(1)	113.38(16)	C(20)−C(16)−P(1)	111.8(3)
C(16)−P(1)−Pd(1)	118.58(16)	C(21)−C(17)−P(1)	114.2(3)
C(7)−O(1)−C(8)	117.3(4)	C(23)−C(17)−P(1)	105.2(3)
C(3)−O(2)−C(9)	116.9(3)	C(22)−C(17)−P(1)	111.2(3)
C(3)−O(2)−Pd(1)	107.0(2)		

C−O Bond Activation of an Aromatic Methyl Ether by a Monophosphine Pd Complex. Complex **4** was stable for days at 45 °C and for at least 1.5 h at 65 °C, but when a solution of complex **4** was heated in C_6D_6 at 80 °C, it decomposed to unidentified products. However, upon prolonged heating of complex **4** or **5** in C_6D_6 at 80 °C in the presence of 1 equiv of ligand **1**, these complexes and the ligand disappeared and a white precipitate, identified as the phosphonium salt **6** (see below), appeared. ^{31}P{^{1}H} NMR of the solution exhibited in both cases a new singlet at 92.08 ppm, corresponding to complex **7** (see below) and an AX system at 70.91 and 40.23 ppm (J_{PP} = 367.1 Hz). Additional peaks were observed at 49.07 and 49.80 ppm in the thermolysis of complexes **4** and **5**, respectively. Complex **5** decomposed faster than complex **4**. Follow-up of the reaction revealed that after 20 h ca. 30% of complex **4** converted to

Scheme 3. Dealkylation of η^2-Coordinated Dmobp by a Second Dmobp Ligand



complex **7** and 17% to the peaks at 70.91 and 40.23 ppm. Under similar conditions, after 11 h ca. 42% of complex **5** converted to complex **7** and 17% to the peaks at 70.91 and 40.23 ppm. $^{31}P\{^1H\}$ NMR of complex **4** after 20 h of heating at 80 °C revealed an integration ratio of complex **7**/complex **4**/AX system of 0.6:1.0:0.6. Upon addition of ligand **1** (2.5 equiv relative to the amount of complex **4** prior to the thermolysis) at room temperature to the reaction mixture, the ratio of the peaks changed to 0.2:1.0:1.0, respectively. In other words, complex **7** diminished and the peaks of the AX system increased at its expense relative to the peak of complex **4**. It seems that the compound, which is responsible for the AX system, is the product of the reaction between ligand **1** and **7** in the presence of 1 equiv of ligand **1** (see below).

The white solid was characterized as the phosphonium salt of the ligand dmobp. It was independently prepared by reaction of dmobp with MeI and had identical spectroscopic properties. The chemical shifts in $^{31}P\{^1H\}$ NMR of the phosphonium salts dmobp(Me)I, **6**, and dmobp(Me)Cl are 49.07 and 49.86 ppm, respectively.[11]

We confirmed the C−O bond activation by the preparation, isolation, and characterization of the new Pd complex containing the demethylated ligand, [(η^2-dmobp-μ-*O*)PdPh]$_2$, complex **7**, which has a dimeric form in the solid state (Figure 4; Scheme 3). Complex **7** was prepared by reaction of complex **2** with 10 equiv of chlorobenzene in C_6D_6 at 80 °C. The reaction proceeded smoothly and quantitatively. Follow-up of the reaction by $^{31}P\{^1H\}$ NMR revealed that the concentration of complex **2** and later complex **5** and ligand **1** diminish, giving rise to a new singlet at 92.08 ppm corresponding to complex **7**, in addition to a small amount of the AX system mentioned earlier. After evaporation and successive washing with pentane, the phenoxide complex, [(η^2-dmobp-μ-*O*)PdPh]$_2$, **7**, was obtained in 61% isolated yield as a white powder and was characterized by ^1H NMR and $^{13}C\{^1H\}$ NMR. The aromatic carbon, *para* to the phenoxide oxygen, appears in the $^{13}C\{^1H\}$ NMR at 99.61 ppm. The carbon *para* to the methoxy moves from 106.78 ppm in complex **5** to 114.63 ppm. The chemical shifts of the phenyl ring carbons almost do not shift relative to the corresponding ones of complexes **4** and **5**.

The compound responsible for the AX system in the $^{31}P\{^1H\}$ NMR at 70.91 and 40.23 ppm, although not isolated, may belong to the monomer (η^2-dmobp-*O*)Pd(dmobp)Ph, which might form by bridge cleavage of the dimer **7** by dmobp. Indeed, addition of dmobp to **7** resulted in appearance of the AX system in the $^{31}P\{^1H\}$ NMR. The analogous (η^2-TMMP-*O*)Pd(TMMP)Cl was reported by Dunbar.[15f] The peak at 40.23 ppm is broad, indicating dynamic behavior of the bound monodentate dmobp. (η^2-dmobp-*O*)Pd(dmobp)Ph might be in an equilibrium with complex **7**, which did not disappear even after prolonged heating at 80 °C in the presence of more than 2 equiv of dmobp. This fact is compatible with the dynamic character of the bound dmobp.

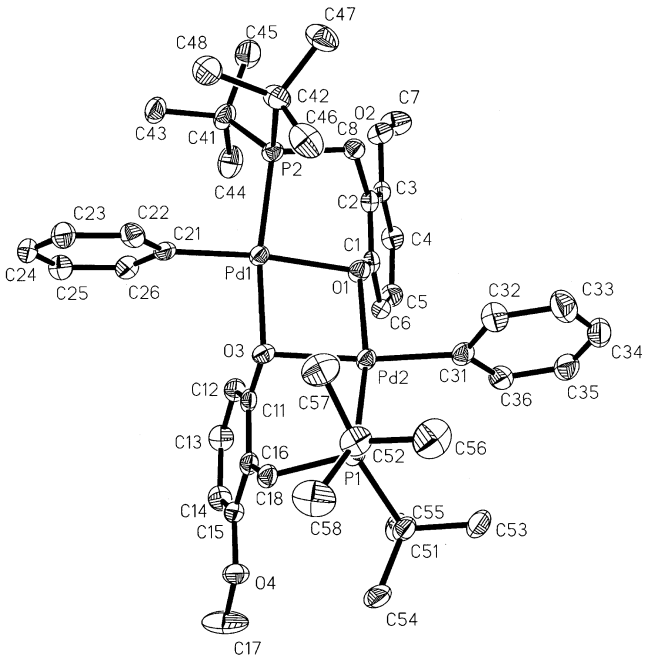


Figure 4. ORTEP drawing of complex **7** (50% probability level). Hydrogen atoms are omitted for clarity.

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(11) The dmobp(Me)Cl salt yielded single crystals that were suitable for X-ray crystallography.

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Table 4. Selected Bond Lengths (Å) and Angles (deg) for 7 (averages of values for two independent molecules)

Pd(1)−C(21)	1.954(3)	P(1)−C(51)	1.872(3)
Pd(1)−O(3)	2.097(2)	P(2)−C(8)	1.836(3)
Pd(1)−O(1)	2.119(2)	P(2)−C(41)	1.858(3)
Pd(1)−P(2)	2.2334(8)	P(2)−C(42)	1.864(3)
Pd(1)−Pd(2)	3.1615(4)	O(1)−C(1)	1.340(3)
Pd(2)−C(31)	1.952(3)	C(3)−O(2)	1.369(4)
Pd(2)−O(1)	2.099(2)	O(2)−C(7)	1.418(4)
Pd(2)−O(3)	2.117(2)	O(3)−C(11)	1.322(4)
Pd(2)−P(1)	2.2308(8)	C(15)−O(4)	1.370(4)
P(1)−C(18)	1.821(3)	O(4)−C(17)	1.405(5)
P(1)−C(52)	1.859(3)		
C(21)−Pd(1)−O(3)	93.16(11)	O(1)−Pd(2)−O(3)	80.45(8)
C(21)−Pd(1)−O(1)	173.52(11)	C(31)−Pd(2)−P(1)	96.87(9)
O(3)−Pd(1)−O(1)	80.45(8)	O(1)−Pd(2)−P(1)	169.24(6)
C(21)−Pd(1)−P(2)	96.09(9)	O(3)−Pd(2)−P(1)	89.99(6)
O(3)−Pd(1)−P(2)	169.80(7)	C(1)−O(1)−Pd(2)	126.65(19)
O(1)−Pd(1)−P(2)	90.37(6)	C(1)−O(1)−Pd(1)	108.63(19)
C(21)−Pd(1)−Pd(2)	132.91(9)	Pd(2)−O(1)−Pd(1)	97.12(9)
O(3)−Pd(1)−Pd(2)	41.62(6)	C(3)−O(2)−C(7)	117.2(3)
O(1)−Pd(1)−Pd(2)	41.20(6)	C(11)−O(3)−Pd(1)	127.25(19)
P(2)−Pd(1)−Pd(2)	128.30(3)	C(11)−O(3)−Pd(2)	106.61(18)
C(31)−Pd(2)−O(1)	92.62(11)	Pd(1)−O(3)−Pd(2)	97.23(9)
C(31)−Pd(2)−O(3)	173.06(11)		

The molecular structure of **7** was confirmed by an X-ray diffraction study of colorless single crystals obtained by slow evaporation of its benzene/pentane solution (Figure 4, Table 4). The crystal contained two independent, structurally analogous molecules in the asymmetric unit. Complex **7** exhibits a distorted square planar geometry around the Pd centers, with the sum of the four angles at the metal being equal to 360.09°. A similar geometry with almost no deviation from planarity was observed for [Pd(dppmp-μ-O)(Cl)]$_2$ (dppmp = 2-diphenylphosphino-4-methylphenoxide) and [Pd(dippmp-μ-O)(Cl)]$_2$ (dippmp = 2-diisopropylphosphino-4-methyl phenoxide).[12b] The length of the Pd(1)−O(3) bond of 2.097 Å is shorter by ca. 0.02 Å than that of Pd(1)−O(1). However, in [Pd(dppmp-μ-O)(Cl)]$_2$ and [Pd(dippmp-μ-O)(Cl)]$_2$[12b] the differences in lengths between the analogous Pd(1)−O(1) and Pd(1)−O(3) are 0.12−0.14 Å, while for both complexes the length of the bond Pd(1)−O(1), 2.022 Å, is the shorter one. The difference between these complexes and complex **7** may be explained by the significant differences in bulk and ring strain. Analogous dimeric Pd complexes with an intramolecular bridging phenoxide have been reported,[12] including an imine-based system, [Pd(3,5-dimethoxy-2-phenyliminomethylphenoxide-μ-O)(OAc)]$_2$, [12a] and the tetramer [Pd(2-diphenyl phosphanyl-4-hydroxyphenoxide-μ-*O*)(Br)]$_4$.[12c] A bulky Pd complex similar to **7** with an intermolecular bridging phenoxide, [Pd[P(ferrocenyl)(*tert*-Bu)$_2$](*o*-MeC$_6$H$_4$)(μ-O-*p*-C$_6$H$_4$OMe)]$_2$, was reported recently.[13] Its structure exhibits a distorted square planar geometry around the Pd centers with a smaller Pd−O−Pd−O torsion angle of 33.2°. Complex **7** has a Pd−O−Pd−O torsion angle of 16.4°, which can be explained by the smaller bulk and the constraint induced by the chelating character of the (dmobp-*O*) in complex **7**. The Pd(1)−Pd(2) distance in complex **7** is shorter by ca. 0.06 Å than the corresponding distances in Pd(dppmp-μ-O)(Cl)]$_2$ and [Pd(dippmp-μ-O)(Cl)]$_2$.[12b] However, it is still ca. 0.53 Å longer than the distance Pd(1)−Pd(2) of complex **3** (Table 2), corresponding to an antibonding interaction between the typical bridged Pd(II) dimers.[9a]

Phosphine complexes bearing *ortho* methoxy-arene groups[14,15] and a methoxy-substituted pincer ligand[5] were reported to undergo ArO−Me cleavage.

Aromatic ethers, such as anisole, undergo exclusive sp^3−sp^3 C−O cleavage upon reaction with HI or HBr at elevated temperatures to give an alkyl halide and an aromatic alcohol (eq 4).[16] Lewis acids, such as $AlCl_3$ or BF_3, are also effective. The reaction proceeds by protonation of (or Lewis acid binding to) the oxygen followed by an external nucleophilic attack of the anion on the alkyl group (S_N2 mechanism).

$$ArO{-}CH_3 + HX \rightarrow ArOH + CH_3X \qquad (4)$$

Examples of $H_3C{-}O$ bond cleavage of aryl alkyl ethers with soluble metal complexes were reported.[5,15] A Lewis acid-type interaction with a metal could promote the loss of the alkyl group by a subsequent internal interaction with a coordinated anion, as suggested by Shaw[15a,b] and Tolman,[15c,d] or by an external nucleophilic attack.[14,15e−g] $H_3C{-}OAr$ bond cleavage with late transition metal complexes and analogous ligands includes Rh(III) with (2,6-dimethoxyphenyl)diphenylphosphine,[14c] Ru(II) and Pd(II) with tris(2,6-dimethoxyphenyl)phosphine,[14a,b,d] Rh(I), Pd(II), and Pt(II) with tris(2,4,6-trimethoxyphenyl)phosphine, and TMPP[15e,f] (Scheme 4) and Ru(II) with 2-(ethoxyphenyl)diphenylphosphine.[15g]

As mentioned earlier, C−O bond cleavage proceeds via nucleophilic attack of dmobp on the methyl group of the coordinated methoxy group. This bond is activated toward the attack by coordination to Pd, as evident from the elongated C−O bond of the coordinated methoxy group in the X-ray structure of complex **4** (Table 3). Demethylation of an aromatic methoxy group by a diphosphine-chelated Pd complex was reported (Scheme 5).[5] It is likely that the electrophilic Pd(II) center formed after the oxidative addition of chloro- or iodobenzene acts as a Lewis acid and upon coordination to the methoxy group generates an electrophilic methyl group. The thermal decomposition of complex **4** in the absence of free dmobp confirms the need for an external nucleophile for clean C−O activation. An exception in this series of metal complexes is the diphosphine-chelated Rh(I) complex (Scheme 5),[5] which activates the O−aryl bond and not the O−Me bond.

Notably, there is a halide ligand effect on the rate of the thermal decomposition of complexes **4** and **5**, the chloro complex **5** decomposing faster. The two-step decomposition suggested by Shaw[15a,b] seems unlikely, because in that case the decomposion should proceed even in the absence of free ligand. It is also unlikely that the decomposition proceeds through a three-step mechanism proposed by Dunbar et al. (Scheme 4)[15e] or

(15) Jones, C. E.; Shaw, B. L.; Turtle, B. L. *J. Chem. Soc., Dalton Trans.* **1974**, 992. (b) Empsall, H. D.; Hyde, E. M.; Jones, C. E.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1974**, 1980. (c) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 1742. (d) Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7577. (e) Dunbar, K. R.; Haefner, S. C.; Ezelmeier, C.; Howard, A. *Inorg. Chem. Acta* **1995**, *240*, 527. (f) Sun, J.-S.; Uzelmeier, C. E.; Ward, D. L.; Dunbar, K. R. *Polyhedron* **1998**, *17*, 2049. (g) Rogers, C. W.; Patrick, B. O.; Rettig, S. J.; Wolf, M. O. *J. Chem. Soc., Dalton Trans.* **2001**, 1278.

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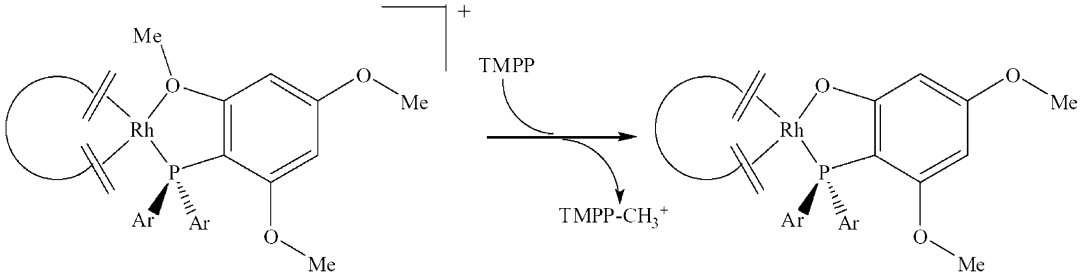
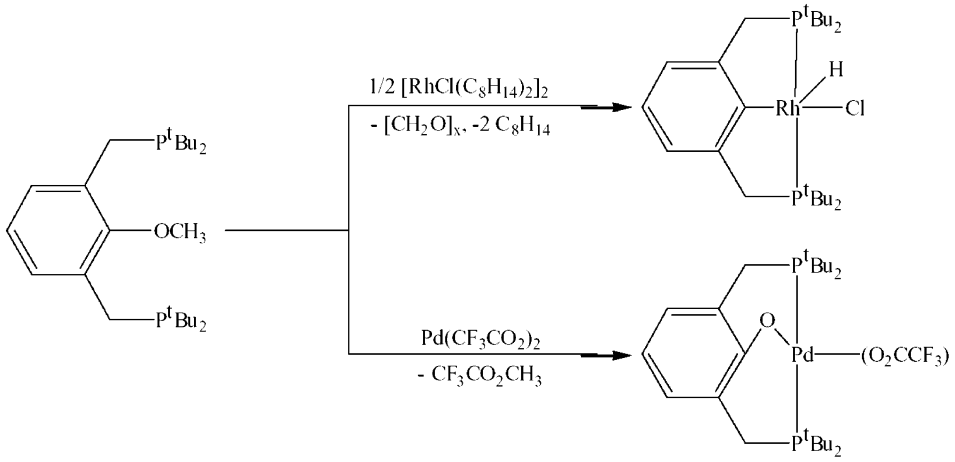
Scheme 4. Dealkylation of η^2-Coordinated TMPP by a Second TMPP Ligand



Scheme 5. C−O Activation in a Bisphosphine Chelating Ligand



Wolf et al.,[15g] involving halide dissociation followed by its nucleophilic attack on the methyl group and reaction of the product methyl halide with free phosphine. Due to the stronger bond of the chloride to the Pd atom relative to the iodide, such a mechanism is expected to result in faster decomposition of the iodo complex **4**, contrary to what we observed. The faster decomposition with the chloro complex **5** as compared with **4** might be explained by the higher electrophilicity of the Pd center when the more electronegative chloride is bound to it, facilitating nucleophilic attack on the methyl group (Scheme 3).

Catalysis with Dmobp Pd Complexes. The new Pd complexes were tested as catalysts for the Suzuki−Miyaura coupling of chlorobenzene with phenyl boronic acid. While reaction conditions were not optimized, some trends emerge. Complex **2** catalyzes this reaction even at 25 °C, although the reaction is slow (Table 5). Comparing the reactions at 40 °C, it is interesting to note that the Pd(I) complex **3** is more active than **2**, whereas the phenoxy Pd(II) complex **7** is completely inactive at this temperature. Thus, we can conclude that **7** does take part in the catalysis by **2** or **3**. This may indicate that (a) complex **7** cannot undergo reduction to Pd(0) under the reaction conditions or (b) a Pd(II)/Pd(IV) mechanism with complex **7** is impossible. The issue of Pd(II)/Pd(IV) versus Pd(0)/Pd(II) mechanisms in the catalytic activation of organic halides is of considerable current interest.[17]

We believe that complex **3** is reduced under the reaction conditions to give the active 12e$^-$ species (dmobp)Pd, which is stabilized by the dmobp ligand bulk and the hemilabile coordination of the methoxy groups. With complex **2**, an additional phosphine is present, which may retard the catalysis by competition with the substrate for free binding sites of the Pd center. Pd(0) complexes that are possible precursors to 12e$^-$ Pd(0)[9c,18,19] catalytic species were reported.

Reactions were also carried out at 130 °C with Pd(OAc)$_2$ and the ligand, generating the active Pd(0)

Table 5. Suzuki−Miyaura Reaction of Aryl Chlorides Catalyzed by Pd(0) Catalysts[a]

entry	catalyst	aryl chloride	temp (°C)	time[b] (h)	yield[c] (%)
1	**2**	PhCl	25	27	14
2	**2**	PhCl	25	92	25
3	**2**	PhCl	40	22	16
4	**2**	PhCl	40	46	31
5	**3**	PhCl	40	22	32
6	**3**	PhCl	40	46	41
7	**3**	3-chloro-toluene	40	46	43
8	**7**	PhCl	40	22	0
9	Pd(OAc)$_2$ + 2dmobp	PhCl	130	20	42
10	Pd(OAc)$_2$ + 4dmobp	PhCl	130	2	83
11	Pd(OAc)$_2$ + 2dmbp	PhCl	130	25	10
12	Pd(OAc)$_2$ + 4dmobp	3-chloro-toluene	130	2	88

[a] Typical reaction conditions: into a 25 mL round-bottom flask fitted with a condenser were added under Ar atmosphere 13 mL of *o*-xylene, 2.5 mmol of aryl chloride, 3.75 mmol of PhB(OH)$_2$, 5.5 mmol of CsF, and 0.025 mmol of catalyst. The reaction mixture was stirred at the specified temperature. Reaction times were not optimized and are given for the purpose of comparison. [b] The yield is based on the aryl chloride and was determined by GC. The rest of the product solution is unreacted aryl chloride.

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(19) Viciu, M. S.; Navarro, O.; Germaneau, R. F.; Kelly, R. A., III; Sommer, W.; Marion, N.; Stevens, E. D.; Cavallo, L.; Nolan, S. P. *Organometallics* **2004**, *23*, 1629.

catalyst in situ under the reaction conditions. Significantly higher rates were obtained, leading to an 83% yield after 2 h with the dmobp ligand, although excess ligand is required for stabilization of the complex at the elevated temperature (compare entries 9 and 10). Use of the analogous ligand, which lacks methoxy groups, di-*tert*-butyl-(2,4,6-trimethylbenzyl)phosphine (tmbp), resulted in a much lower yield (compare entries 9 and 11), perhaps a reflection of the absence of the stabilization effect of the active catalyst by the methoxy groups. Several systems for efficient Suzuki−Miyaura catalysis of aryl chlorides have been reported.[1a−c,e,18,20]

Summary

Pd(0), Pd(I), and Pd(II) complexes of the new electron-rich methoxy benzyl phosphine ligand dmobp were prepared and structurally characterized. The 14e$^-$ PdL_2 complex **2**, in which the methoxy groups are not coordinated, undergoes facile oxidative addition of iodo- and chlorobenzene to yield the monophosphine complexes LPd(Ph)X **4** (X = I) and **5** (X = Cl) in which the methoxy group is coordinated to the Pd(II) center in the solid state, although in solution there is no evidence for its coordination, probably because of its hemilabile nature, indicating the availability of a Pd(II) 14e$^-$ complex. Coordination of the methoxy group weakens the C−O bond, as observed in the X-ray structure, and results in its cleavage upon nucleophilic attack by the free ligand, leading to the dimeric phenoxy-bridged complex **7**. Partial reduction of $[Pd(2\text{-methylallyl})Cl]_2$ leads to the Pd(I) dimeric complex **3**, which can be converted to the Pd(0) complex **2** by addition of the dmobp ligand and a base. Complexes **2** and **3** catalyzed the Suzuki−Miyaura cross-coupling of chloroarenes with $PhB(OH)_2$. The Pd(I) dimer **3** is a possible precursor to a catalytically active monophosphine 12e$^-$ Pd(0) catalyst. The phenoxy-bridged complex **7**, obtained by C−O cleavage, was catalytically inactive at 40 °C, and hence it is not an intermediate in the catalysis, probably indicating that Pd(0) is essential for the Suzuki−Miyaura catalysis in this system. The effect of the dmobp ligand in Suzuki−Miyaura coupling was found to be superior to that of an analogous ligand that does not bear methoxy substituents.

Experimental Section

General Procedures. All procedures with air- and moisture-sensitive compounds were performed in a nitrogen-filled glovebox (Vacuum Atmospheres, equipped with a "Nexus One" purification system) or on a high-vacuum line using Schlenk techniques. All solvents were reagent grade or better. All nondeuterated solvents were refluxed over sodium/benzophenone ketyl and distilled under argon atmosphere. Deuterated solvents were used as received. All the solvents were degassed with argon and kept in the glovebox over 4 Å molecular sieves, except MeOH, which was kept over 3 Å molecular sieves. Commercially available reagents were used as received. $[(2\text{-methylallyl})PdCl]_2$[21] and 2,6-dimethoxybenzyl alcohol[6] were prepared according to literature procedures. NMR measurements were performed on a Bruker AVANCE APX 250 spectrometer at 250 MHz (^{1}H) and 101 MHz (^{31}P) or a Bruker AVANCE 400 spectrometer at 400 MHz (^{1}H), 162 MHz (^{31}P), 100 MHz (^{13}C) or 61 MHz (^{2}D). All spectra were recorded at 23 °C. ^{1}H NMR and $^{13}C\{^1H\}$ NMR chemical shifts are reported in ppm downfield from tetramethylsilane. ^{1}H NMR chemical shifts were referenced to the residual hydrogen signal of the deuterated solvents (7.15 ppm, benzene; 7.24 ppm, chloroform; 5.32 ppm, dichloromethane). In $^{13}C\{^1H\}$ NMR measurements the signals of C_6D_6 (128.0 ppm), $CDCl_3$ (77.0 ppm), and CD_2Cl_2 (53.8 ppm) were used as a reference. ^{31}P NMR chemical shifts are reported in ppm downfield from H_3PO_4 and referenced to an external 85% solution of phosphoric acid in D_2O. Screwcap 5 mm NMR tubes were used in the NMR follow-up experiments. Abbreviations used in the description of NMR data are as follows: b, broad; s, singlet; d, doublet; t, triplet; q, quartet, m, multiplet, v, virtual. Elemental analyses were performed by The Microanalysis Laboratory of The Hebrew University, Israel. GC analysis was performed on a HP6890 chromatograph with FID detector using capillary columns HP5 (30 m × 0.32 mm × 0.25 μm). ES-MS were preformed on a MicroMass-LSZ4000 instrument.

Synthesis of 2,6-Dimethoxybenzyl Chloride. A solution of *N*-chlorosuccinimide (6.2 g, 0.046 mmol) in 200 mL of (alumina dried HPLC grade) CH_2Cl_2 was cooled to 0 °C under argon, and 3.7 mL of Me_2S was added during a few minutes, resulting in a white precipitate. The reaction mixture was cooled to −20 °C, and a solution of 2,6-dimethoxybenzyl alcohol (7.04 g, 0.043 mmol) in 25 mL of CH_2Cl_2 was added dropwise. The solution was stirred for 2 h, allowing the temperature to reach 0 °C, during which time all the solid precipitate had redissolved, giving a clear solution. The solution was poured over cold brine and extracted twice with diethyl ether. The combined organic layers were washed twice with cold brine (neutral pH), dried over Na_2SO_4, filtered, and concentrated in a vacuum. The resulting solid was washed with cold pentane, decanted, and dried under high vacuum. Yield: 7.2 g (92.4%). ^{1}HNMR ($CDCl_3$): δ 3.99 (s, OCH_3, 6H), 4.90 (s, CH_2Ar, 2H), 6.67 (d, J_{HH} = 8.4 Hz, Ar-*H*, 2H), 7.37 (t, J_{HH} = 8.4 Hz, Ar-*H*, 1H). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 35.68 (s, CH_2Ar), 55.90 (s, 2 OCH_3), 103.68 (s, 2 *Ar*CH_2-P), 114.17 (s, *Ar*CH_2-P), 130.21 (s, *Ar*CH_2-P), 158.54 (s, 2 *Ar*CH_2-P). The compound is known, but neither preparation procedure nor spectral data are available.

Synthesis of the Dmobp Ligand 1. A solution of di-*tert*-butylphosphine (5.548 g, 38 mmol) in 50 mL of freshly distilled degassed ether was placed in a 500 mL Schlenk flask and cooled to −40 °C under argon. ^{n}BuLi in hexanes (30 mL, 1.43 M) was added dropwise, and the solution was stirred for 2−3 h, allowing the temperature to reach 0 °C. The reaction mixture was cooled to −78 °C, and a solution of 2,6-dimethoxybenzyl chloride (5.763 g, 31 mmol) in 60 mL of freshly distilled, degassed ether was added dropwise. The reaction mixture was stirred at room temperature for 48 h and decomposed with 50 mL of double distilled, degassed water. The organic layer was separated (under argon pressure) via cannula, and the aqueous layer was extracted with ether (2 × 150 mL). The combined organic layers were dried on sodium sulfate, filtered under argon pressure with a sintered cannula, and concentrated under high vacuum. The residue was introduced to a drybox and chromatographed on dry silica eluted with pentane, pentane/ether 2%, and finally pentane/ether 5%. The main fractions gave 2.1 g (25%) of pure ligand. ^{1}H NMR (C_6D_6): δ 1.26 (d, J_{PH} = 10.1 Hz, $C(CH_3)_3$, 18H), 3.05 (d, J_{HH} = 3.8 Hz, CH_2Ar, 2H), 3.43 (s, OCH_3, 6H), 6.35 (d, J_{HH} = 8.2 Hz, Ar-*H*, 2H), 7.02 (td, J_{HH} = 8.4 Hz, J_{PH} = 1.3 Hz, Ar-*H*, 1H), $^{13}C\{^1H\}$ NMR (C_6D_6): δ 16.84 (d, J_{CP} = 26.8 Hz, $ArCH_2$-P) 29.70 (d, J_{CP} = 14.2 Hz, P6 $C(CH_3)_3$), 32.23 (d, J_{CP} = 14.2 Hz, $(H_3C)_3$-*C*-P), 55.07 (s, 2 OCH_3), 104.27 (d, J_{CP} = 1.2 Hz, 2 *Ar*CH_2-P), 119.01 (d, J_{CP} = 2.2 Hz, *Ar*CH_2-P), 126.40 (d, J_{CP} = 1.9 Hz, *Ar*CH_2-P), 158.54 (d, J_{CP} = 2.8 Hz, 2 *Ar*CH_2-P). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 35.25.

Synthesis of 2. A solution of dmobp (120 mg, 0.405 mmol) in 2 mL of MeOH was added to a stirred suspension of [(2-

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Table 6. Experimental Crystallographic Data for Complexes 2, 3, 4, and 7

	2	4	3	7
color, shape	colorless, plate	colorless, prism	colorless, prism	colorless, prism
empirical formula	$C_{34}H_{58}O_4P_2Pd$	$C_{23}H_{34}O_2PIPd + C_4H_8O$	$C_{38}H_{65}O_4P_2ClPd_2$	$C_{44}H_{62}O_4P_2Pd_2$
fw	699.14	678.88	869.09	929.68
radiation	Mo Kα (0.710)	Mo Kα (0.710)	Mo Kα (0.710)	Mo Kα (0.710)
cryst syst	triclinic	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
unit cell				
a/Å	10.8540(3)	10.755(2)	12.9240(3)	13.022(1)
b/Å	12.31120(3)	11.280(2)	16.4440(5)	18.466(1)
c/Å	13.7990(4)	14.160(3)	20.1180(6)	18.605(1)
α/deg	89.479(2)	67.82(3)		111.130(2)
β/deg	93.469(1)	79.31(3)	107.63(1)	89.660(2)
χ/deg	71.771(2)	62.50(3)		97.270(3)
D_{calcd}/g cm^{-3}	1.333	1.598	1.461	1.493
μ(Mo Kα)/mm^{-1}	0.659	1.833	1.063	0.988
cryst size/mm	0.1 × 0.1 × 0.05	0.1 × 0.05 × 0.05	0.05 × 0.02 × 0.02	0.05 × 0.05 x 0.03
total/unique no. of reflns	14 198, 7926	15 354, 5779	49 523, 10540	36 890,15419
R_{int}	0.052	0.052	0.087	0.045
no. of params, restraints	386, 0	306, 0	520, 0	965, 0
R1, wR2	0.0498, 0.1334	0.0302, 0.0639	0.0434, 0.0915	0.0331, 0.0759
resid density/e Å^3	2.348	0.581	1.247	0.687

methylallyl)PdCl]$_2$ (34.4 mg, 0.087 mmol) in 4 mL of MeOH under N_2, immediately followed by an addition of NaOH (8.2 mg, 0.405 mmol) in 2 mL of methanol. The solution turned clear yellow and was stirred at room temperature overnight. Pd(dmobp)$_2$ was obtained as a white precipitate. The solids were collected on a sinter no. 4 and washed with a small amount of MeOH three times. The solids left on the sinter were dissolved in benzene. After evaporation of the solvent, 100 mg (85% yield) of pure complex **2** as a white powder was obtained. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a pentane solution. ^{1}H NMR (C_6D_6): δ 1.49 (vt, J_{HP} = 5.9 Hz, C(C*H*$_3$)$_3$, 36H), 3.10 (vt, J_{HP} = 3.1 Hz, ArC*H*$_2$, 4H), 3.36 (s, OC*H*$_3$,12H), 6.34 (d, J_{HH} = 8.2 Hz, Ar*H*, 4H), 7.04 (t, J_{HH} = 8.2 Hz, 2H, Ar*H*). ^{13}C{^{1}H} NMR (C_6D_6): δ 18.44 (vt, J_{CP} = 1.6 Hz, 2 Ar*C*H$_2$-P), 31.03 (vt, J_{CP} = 3.1 Hz, 12 (H$_3$*C*)$_3$-C-P), 35.94 (vt, $^3J_{CP}$ = 3.1 Hz, 4 (H$_3$C)$_3$*C*-P), 55.26 (s, 4 O*C*H$_3$), 104.57 (bs, 2 *Ar*CH$_2$-P), 126.27 (bs, 2 *Ar*CH$_2$-P), 158.63 (bs, 4 *Ar*CH$_2$-P). ^{31}P{^{1}H} NMR (C_6D_6): δ 60.89. ES-MS 699 m/z^+, 699.2 is the calculated mass. Anal. Calcd for $C_{34}H_{58}O_4P_2Pd$: C, 58.41; H, 8.36. Found: C, 58.57; H, 8.30.

Synthesis of Complex 3. A solution of dmobp (22.2 mg, 0.072 mmol) in 2 mL of MeOH was added to a stirred suspension of [(2-methylallyl)PdCl]$_2$ (14.8 mg, 0.036 mmol) in 4 mL of MeOH under N_2, immediately followed by addition of NaOH solution (2 mL, of 0.018 M). The solution turned yellow and was stirred at room temperature overnight. (dmobp)Pd-(μ-Cl)(μ-2-methylallyl)Pd(dmobp) was obtained as a green precipitate. The methanol solution was decanted, and the solids were extracted three times with benzene. Some Pd black was left as residue. After evaporation of the solvent 31 mg (95% yield) of pure complex **3** as a yellow powder was obtained. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a benzene solution. ^{1}H NMR (C_6D_6): δ 1.1 (br s, PdCCH$_3$(C*H*$_2$)$_2$, 2H), 1.25 (vt, $J_{H,P}$ = 2.8 Hz, PdCC*H*$_3$-(CH$_2$)$_2$, 3H), 1.48 (vt, $J_{H,P}$ = 12.5 Hz, C(C*H*$_3$)$_3$, 18H), 1.53 (vt, $J_{H,P}$ = 12.3 Hz, C(C*H*$_3$)$_3$, 18H), 2.84 (vt, $J_{H,P}$ = 5.5 Hz, PdCCH$_3$-(C*H*$_2$)$_2$, 2H), 3.31 (vt, $J_{H,P}$ = 4.6 Hz, PC*H*$_2$Ar, 2H), 3.32 (vt, $J_{H,P}$ = 3.3 Hz, PC*H*$_2$Ar, 2H) 3.36 (s, OC*H*$_3$, 12H), 6.25 (d, $J_{H,H}$ = 8.15 Hz, PCH$_2$Ar-*H*, 4H), 7.01 (t, $J_{H,H}$ = 8.5 Hz, PCH$_2$Ar-*H*, 2H). ^{13}C{^{1}H} NMR (C_6D_6): δ 18.87 (vt, $J_{C,P}$ = 2.2 Hz, Ar*C*H$_2$-P), 26.08 (vt, $J_{C,P}$ = 2.3 Hz, PdC*C*H$_3$(CH$_2$)$_2$), 30.04 (vt, $J_{C,P}$ = 3.7 Hz, 6 6 C(*C*H$_3$)$_3$), 30.36 (vt, $J_{C,P}$ = 3.9 Hz, 6 6 C(*C*H$_3$)$_3$), 36.12 (vt, $J_{C,P}$ = 3.5 Hz, *C*(CH$_3$)$_3$), 36.15 (vt, $J_{C,P}$ = 3.2 Hz, *C*(CH$_3$)$_3$), 38.92 (vt, $J_{C,P}$ = 4.8 Hz, PdCCH$_3$(*C*H$_2$)$_2$), 54.73 (s, O*C*H$_3$, 4C), 103.77 (s, 4 *Ar*CH$_2$-P), 116.63 (s, 2 *Ar*CH$_2$-P), 127.08 (s, 2 *Ar*CH$_2$-P), 158.62 (d, $J_{C,P}$ = 1.5 Hz, Pd*Ph*). ^{31}P NMR {^{1}H} (C_6D_6): δ 64.01. ES-MS m/z^+ 934 (M + K$^+$), 460 (crotylPd$^+$(dmobp)). MALDI-TOF-MS: m/z^+ 934 (M + K$^+$). Anal. Calcd for $C_{38}H_{65}O_4P_2ClPd_2$: C, 50.93; H, 7.31. Found: C, 50.85; H, 7.40.

Synthesis of 4 and 5. X = I, 4. Iodobenzene (21.2 μL, 0.19 mmol) was added to a solution of 13.2 mg (0.019 mmol) of Pd-(dmobp)$_2$ in 500 μL of C_6D_6 in a screw-cap NMR tube. After 2 days at room temperature the reaction was complete. The solvent was evaporated, and the residue was washed five times with pentane and dried under high vacuum. Pure (dmobp)-Pd(Ph)I, **4** (6.8 mg, 60% yield), was obtained. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a benzene solution. ^{1}H NMR (C_6D_6): δ 1.02 (d, J_{HP} = 13.5 Hz, C(C*H*$_3$)$_3$, 18H), 2.63 (d, J_{HP} = 10.3 Hz, PhC*H*$_2$P, 2H), 3.63 (s, OC*H*$_3$, 6H), 6.46 (d, J_{HH} = 8.2 Hz, PCH$_2$Ar-*H*, 2H), 6.70 (t, J_{HH} = 7.05 Hz, PdPh-*H*, 1H), 6.83 (t, J_{HH} = 7.8 Hz, PdPh-*H*, 2H), 6.91 (td, J_{HH} = 8.34 Hz, J_{HP} = 1.6 Hz, PCH$_2$-Ar-*H*, 1H), 7.38 (ddd, J_{HH} = 8.2 Hz, J_{HH} = 1.6 Hz, J_{HP} = 1.2 Hz, PdPh-*H*, 2H). ^{13}C{^{1}H} NMR (C_6D_6): δ 14.56 (d, J_{CP} = 14.3 Hz, Ar*C*H$_2$-P), 29.16 (d, J_{CP} = 4.6 Hz, 6 C(*C*H$_3$)$_3$), 36.71 (d, J_{CP} = 9.9 Hz, *C*(CH$_3$)$_3$), 59.76 (s, 2 O*C*H$_3$), 107.58 (d, J_{CP} = 1.8 Hz, 2 *Ar*CH$_2$-P), 116.29 (d, J_{CP} = 1.2 Hz, Pd*Ph*), 123.04 (s, Pd*Ph*), 126.54 (d, J_{CP} = 1.2 Hz, Pd*Ph*), 128.53 (d, J_{CP} = 2.3 Hz, *Ar*CH$_2$-P), 129.51 (s, *Ar*CH$_2$-P), 139.19 (d, J_{CP} = 3.4 Hz, Pd*Ph*), 157.44 (d, J_{CP} = 3.7 Hz, 2 *Ar*CH$_2$-P). ^{31}P NMR {^{1}H} (C_6D_6): δ 64.45. ES-MS: m/z^+ 646 (M + K$^+$), 629 (M + Na$^+$), 479 (M$^+$ − I), m/z^- 127 (I$^-$). MALDI-TOF-MS: m/z^+ 629 (M + Na$^+$). Anal. Calcd for $C_{23}H_{34}O_2PIPd{\cdot}C_4H_8O$: C, 58.41; H, 8.36. Found: C, 58.57; H, 8.30.

X = Cl, 5. Chlorobenzene (36.5 μL, 0.36 mmol) was added to a solution of 25 mg (0.036 mmol) of Pd(dmobp)$_2$ in 500 μL of C_6D_6 in screw-cap NMR tube. After 2 days at 40 °C the reaction was complete, the solvent was evaporated, and the residue was washed five times with pentane and dried under high vacuum. Pure (dmobp)Pd(Ph)Cl, **5** (13 mg, 70% yield), was obtained. ^{1}H NMR (C_6D_6): δ 1.03 (d, J_{HP} = 13.5 Hz, C(C*H*$_3$)$_3$, 18H), 2.66 (d, J_{HP} = 10.5 Hz, PhC*H*$_2$P, 2H), 3.64 (s, OC*H*$_3$, 6H), 6.42 (d, J_{HH} = 8.4 Hz, PCH$_2$Ar-*H*, 2H), 6.80 (t, J_{HH} = 7.05 Hz, PdPh-*H*, 1H), 6.89 (t, J_{HH} = 7.74 Hz, PdPh-*H*, 2H), 6.93 (td, J_{HH} = 8.3 Hz, J_{HP} = 1.6 Hz, PCH$_2$Ar-*H*, 1H), 7.43 (ddd, J_{HH} = 8.3 Hz, J_{HH} = 2.2 Hz, J_{HP} = 1.2 Hz, PdPh-*H*, 2H). ^{13}C NMR {^{1}H} (C_6D_6): δ 15.05 (d, J_{CP} = 15.6 Hz, Ar*C*H$_2$-P), 29.21 (d, J_{CP} = 4.1 Hz, C(*C*H$_3$)$_3$), 36.40 (d, J_{CP} = 13.6 Hz, *C*(CH$_3$)$_3$), 58.19 (s, 2 O*C*H$_3$), 106.78 (d, J_{CP} = 1.6 Hz, 2 *Ar*CH$_2$-P), 115.77 (d, J_{CP} = 1.6 Hz, Pd*Ph*), 123.35 (s, Pd*Ph*), 126.93 (d, J_{CP} = 1.2 Hz, Pd*Ph*), 128.48 (d, J_{CP} = 2.1 Hz, *Ar*CH$_2$-P), 129.53 (s, *Ar*CH$_2$-P), 137.91 (d, J_{CP} = 3.2 Hz, Pd*Ph*), 157.40 (d, J_{CP} = 3.7 Hz, 2 *Ar*CH$_2$-P). ^{31}P NMR {^{1}H} (C_6D_6): δ 71.01. ES-MS: m/z^+ 479 (M$^+$ − Cl). Anal. Calcd for $C_{23}H_{34}O_2PClPd$: C, 53.60; H, 6.65. Found: C, 53.95; H, 6.43

Synthesis of Dmobp(Me)I, 6. A 100 μL sample of a 0.017 M solution of MeI in C_6D_6 was added to 500 μL of a solution containing 5 mg (0.017 mmol) of dmobp in C_6D_6. A precipitate of microcrystals formed immediately upon the addition of MeI. After 2 days at room temperature, the reaction was complete. The solvent was decanted, and the solids were dried under high vacuum. The phosphonium salt (7 mg, 95%) was obtained. ^{1}H NMR ($CDCl_3$): δ 1.53 (d, J_{HP} = 15.1 Hz, C(C*H*$_3$)$_3$, 18H), 1.98 (d, J_{HP} = 11.9 Hz, PC*H*$_3$, 3H), 3.60 (d, J_{HP} = 12.6 Hz, PC*H*$_2$Ar, 2H), 3.92 (s, OC*H*$_3$, 6H), 6.63 (d, J_{HP} = 8.53 Hz, PCH$_2$-Ar-*H*, 2H), 7.35 (dt, J_{HH} = 8.4 Hz, J_{HP} = 1.9 Hz, P-CH$_2$Ar-*H*, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 1.81 (d, J_{CP} = 46.5 Hz, P-*C*H$_3$), 12.80 (d, J_{CP} = 42.8 Hz, ArH$_2$*C*-P), 27.29 (bs, 6 C(*C*H$_3$)$_3$), 36.12 (d, J_{CP} = 36.4 Hz, *C*(CH$_3$)$_3$), 55.85 (s, 2 OC*H*$_3$), 104.22 (s, *Ar*CH$_2$-P), 130.6 (s, 2 *Ar*CH$_2$-P), 127.08 (s, 2 *Ar*CH$_2$-P), 157.6 (d, J_{CP} = 2.8 Hz, Pd*Ph*). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 49.07. ES-MS: m/z^+ 311 ($M^+ - I$).

Synthesis of [(η^2-dmobp-μ-*O*)PdPh]$_2$, 7. A 36.5 μL (0.36 mmol) sample of chlorobenzene was added to a solution of 25 mg (0.036 mmol) of Pd(dmobp)$_2$ in 500 μL of C_6D_6 in a screw-cap NMR tube. After 14 h at 80 °C the reaction was complete and colorless crystals of dmobp(Me)Cl precipitated in the bottom of the tube. The solvent was evaporated, and the residue was washed six times with pentane and dried under high vacuum. A total of 10 mg (61% yield) of (η^2-dmobp-*O*)-PdPh was obtained. ^{1}H NMR (C_6D_6): δ 1.25 (d, J_{HP} = 13.6 Hz, C(C*H*$_3$)$_3$, 18H), 2.68 (d, J_{HP} = 10. 7 Hz, PhC*H*$_2$P, 2H), 3.36 (s, OC*H*$_3$, 3H), 6.10 (d, J_{HP} = 8.3 Hz, PCH$_2$Ar-*H*, 1H), 6.72 (tt, J_{HH} = 7.2 Hz, J_{HH} = 1.4 Hz, PdPh-*H*, 1H), 6.90 (t, J_{HH} = 7.5 Hz, PdPh-*H*, 2H), 7.08 (td, J_{HH} = 8.2 Hz, J_{HH} = 1.6 Hz, PCH$_2$-Ar-*H*, 1H), 7.46 (d, J_{HH} = 8.0 Hz, PdPh-*H*, 1H), 7.75 (ddd, J_{HH} = 8.1 Hz, J_{HH} = 2.2 Hz, J_{HH} = 1.2 Hz, PCH$_2$Ar-*H*, 1H). ^{13}C NMR {^{1}H} (C_6D_6): δ 14.78 (d, J_{CP} = 21.1 Hz, P*C*H$_2$Ar), 29.63 (d, J_{CP} = 3.7 Hz, 6 C(*C*H$_3$)$_3$), 36.71 (d, J_{CP} = 15.9 Hz, *C*(CH$_3$)$_3$), 56.0 (s, OCH$_3$), 99.61 (s, *Ar*CH$_2$−P), 114.63 (d, J_{CP} = 2.1 Hz, Pd*Ph*), 115.29 (d, J_{CP} = 2.5 Hz, Pd*Ph*), 123.39 (s, Pd*Ph*), 126.58 (d, J_{CP} = 1.2 Hz, Pd*Ph*), 126.96 (d, J_{CP} = 1.6 Hz, *Ar*CH$_2$-P), 137.94 (d, J_{CP} = 2.5 Hz, Pd*Ph*), 144.24 (s, *Ar*CH$_2$-P), 157.07 (d, J_{CP} = 4.1 Hz, *Ar*CH$_2$-P), 163.82 (d, J_{CP} = 2.3 Hz, *Ar*CH$_2$-P). ^{31}P{^{1}H} NMR (C_6D_6): δ 92.01. ES-MS: m/z^+ 465 (M^+).

X-ray Structure Determination and Refinement of Complexes 2, 3, 4, and 7. Colorless, platelike crystals were mounted in a nylon loop and flash frozen in a cold nitrogen stream (120 K) on a Nonius Kappa CCD with Mo Kα radiation (λ = 0.71071 Å). Accurate unit cell dimensions were obtained from 20° of data. The data were processed with the Denzo-Scalepack package. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares (SHELXL-97). Idealized hydrogen atoms were placed and refined in the riding mode. Crystal data are given in Table 6.

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Supporting Information Available: NMR spectra of compounds **6** and **7**; tables of X-ray crystalographic data for complexes **2**, **3**, **4**, and **7** and the corresponding CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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