Palladium Complexes with Metallocene-Bridged Bidentate Diphosphine Ligands: Synthesis, Structure, and Catalytic Activity in Amination and Cross-Coupling Reactions

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Received October 7, 2005

The syntheses and characterization of series of new metallocene-bridged diphosphines and the structures of complexes of some of them with Pd(II) are reported. These complexes were examined as the catalysts in amination reactions of halogenoarenes and in the Suzuki reaction. The complexes based on ruthenocene (**2**) and osmocene (**3**) showed lower activities then the palladium complex with dppf in amination reactions and the same activities in the Suzuki reaction. New palladium complexes with the bidentate bulky and electron-rich ligands Fe(η^5-$C_5H_4P(o\text{-}Pr^iC_6H_4)_2)_2$ (**6**) and Fe(η^5-$C_5H_4P(o\text{-}MeOC_6H_4)_2)_2$ (**5**) showed a very high catalytic activity in amination and Suzuki coupling of aryl bromides. A complex with ligand **6** was used in the amination of 4-bromotoluene by primary and secondary amines and showed excellent activity.

Introduction

New phosphine ligands, bidentate chelate phosphine ligands in particular, have attracted constant attention because of their crucial role in defining the catalytic activity of transition-metal complexes. Relatively small changes in their electronic or spatial structure, or "bite angle" (in complexes), often produce dramatic effects on the reaction catalyzed by the corresponding complex. These effects revealed themselves most vividly in the amination reactions of aryl halides (Buchwald−Hartwig reaction), the application of bidentate phosphine ligands being of pivotal importance on the early stage of its development.[1−4] Metal-containing ligands and particularly those based on a ferrocene scaffold have played a very important role in many organic transformations catalyzed by palladium complexes.[5−10]

In this paper we report the synthesis of series of new metal-containing bidentate phosphine ligands and the structures of their complexes with Pd(II). The catalytic activity of these complexes was studied in two types of reactions: amination of aryl bromide and Suzuki−Miyaura coupling.

Results and Discussion

Synthesis of the Phosphine Ligands M(η^5-$C_5H_4PPh_2)_2$ (1, M = Fe; 2, M = Ru; 3, = Os), Fe(η^5-$C_5Me_4PPh_2)_2$ (4), Fe(η^5-$C_5H_4PR_2)_2$ (5, R = *o*-$MeOC_6H_4$; 6, R = *o*-$Pr^iC_6H_4$; 7, R = *o*-MeC_6H_4; 8, R = Et; 9, R = C_6F_5; 10, R = OEt) and Their Complexes. The metallocene-bridged diphosphines [M(η^5-$C_5H_4PPh_2)_2$] (**1**, M = Fe; **2**, M = Ru; **3**, M = Os) and [Fe(η^5-$C_5Me_4PPh_2)_2$] (**4**) and the corresponding Pd complexes were prepared according to the procedures reported earlier.[11−22]

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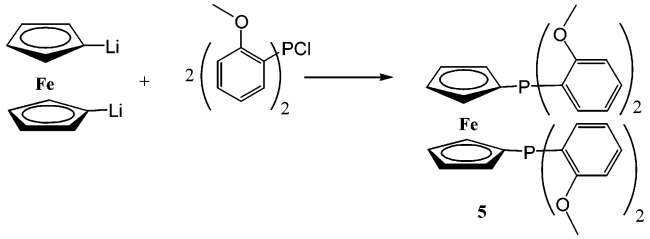
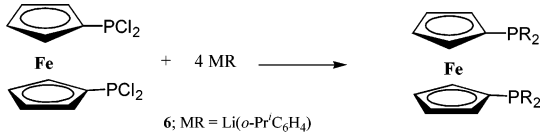
10.1021/om050869w CCC: $33.50
Publication on Web 04/20/2006

Scheme 1

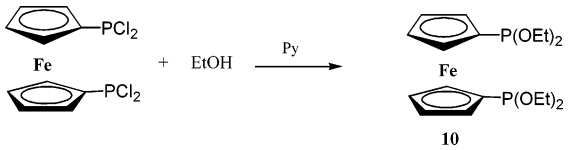


Scheme 2



6; MR = Li(*o*-Pr^{i}C$_6$H$_4$)
7; MR=Li(*o*-MeC$_6$H$_4$)
8; MR = BrMgEt
9; MR = LiC$_6$F$_5$

Scheme 3



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The synthesis of new ferrocene-based ligands was carried out by two alternative pathways. 1,1′-Bis(bis(*o*-methoxyphenyl)-phosphino)ferrocene (**5**) was obtained by the reaction of bis-(*o*-methoxyphenyl)chlorophosphine[23] with 1,1′-dilithioferrocene[4,24] (Scheme 1).

However, the same method cannot be applied for the synthesis of a ligand with *o*-isopropylphenyl substituents at the phosphorus. In a reaction with the sterically congested chlorophosphine ClP(*o*-Pr^{i}C$_6$H$_4$)$_2$, only the diphosphine monoxide (*o*-Pr^{i}C$_6$H$_4$)$_2$P−P(=O)(*o*-Pr^{i}C$_6$H$_4$)$_2$ and ferrocene were isolated, presumably due to reduction of chlorophosphine by dilithioferrocene with the formation of a P−P bond and further oxidation of one phosphorus atom (during isolation).[25] Therefore, the *o*-isopropylphenyl-substituted ligand [Fe(η^5-C$_5$H$_4$P{*o*-Pr^{i}C$_6$H$_4$}$_2$)$_2$] (**6**) was synthesized by treatment of 1,1′-bis(dichlorophosphino)-ferrocene with o-Pr^{i}C$_6$H$_4$Li in 68% yield (Scheme 2). This method was also used for the synthesis of Fe(η^5-C$_5$H$_4$PR$_2$)$_2$ (**7**, R = *o*-MeC$_6$H$_4$; **8**, R = Et; **9**, R = C$_6$F$_5$).

The ligand [Fe(η^5-C$_5$H$_4$P{OEt}$_2$)$_2$] (**10**) was obtained by treatment of 1,1′-bis(dichlorophosphino)ferrocene with ethanol and pyridine (Scheme 3).

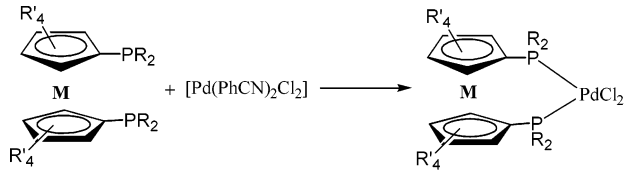
It is worth noting that the ligands **5**−**10** were synthesized in high yields and can easily be purified. All the compounds obtained were characterized by spectroscopy and by elemental analysis.

In the ^{1}H NMR spectrum of **8** the CH$_2$ groups were observed at δ 1.59 as a broadened multiplet, while for **10** two signals at δ 3.75 and 3.89 arose from the methylene groups due to diastereotopicity of the CH$_2$ protons. Chemical shifts and coupling constants for the other signals in the ^{1}H and ^{31}P{^{1}H} spectra of **8** and **10** were similar to those of related diphosphines.

In ^{31}P NMR spectra the *o*-tolyl- (**7**), *o*-anisyl- (**5**), and pentafluorophenyl-substituted (**9**) ligands were characterized by sharp signals at δ −36.0, −44.4, and −58.7, respectively. In the ^{1}H NMR spectra of **7**, **5**, and **9** the Cp rings were characterized by two signals for H$_\alpha$ and H$_\beta$. Methyl and methoxy groups for **7** and **5** were observed as singlets at δ 2.45 and 3.75, respectively. In the ^{19}F{^{1}H} NMR spectrum of **9** three signals at δ −51.8, −82.1, and −71.6 arose from *o*-F, *m*-F, and *p*-F of the pentafluorophenyl rings. This implies fast rotation of the substituted phenyl rings in **7**, **5**, and **9**. Analogous conclusions can be drawn from the ^{13}C{^{1}H} NMR spectra of **5** and **9**.

In the ^{31}P{^{1}H} NMR spectrum of the *o*-isopropylphenyl-substituted compound **6** there is one sharp singlet at δ −40.1. The Cp rings are characterized by two signals of H$_\alpha$ and H$_\beta$ protons at δ 4.07 and 4.36 in the ^{1}H NMR spectrum and by the signals at δ 71.72, 73.30, and 78.36 in the ^{13}C{^{1}H} NMR spectrum, which is evidence for a symmetric ferrocene moiety. The carbons of the phenyl rings are also characterized by one set of signals at δ 125.06, 125.11, 128.73, 133.98, 136.61, and 152.32. At the same time the signals of the isopropyl groups in the ^{1}H NMR spectrum were observed as two doublets at δ 0.92 and 1.30 for the methyls and as a broadened multiplet at δ 3.88 for the CH groups, which implied inequivalence of the isopropyl groups. Two sets of signals for the isopropyl groups were observed in the ^{13}C{^{1}H} NMR spectrum as well: δ 23.65, 23.97 (Me) and δ 30.90, 31.15 (CH). The signals of the methyl groups in the ^{1}H NMR spectrum did not collapse upon heating the sample of **6** in toluene-d_8 up to 100 °C. However, exchange between these two isopropyl groups was observed by selective saturation of one of the methyl signals in ^{1}H NMR, resulting in a simultaneous decrease of signal for the second methyl group. This exchange proceeded slowly on the NMR time scale, perhaps due to the need for concerted rotation of the bulky ortho-substituted aryl rings around C−P bonds.

Scheme 4



11; R = Ph, R' = H, M = Fe,
12; R = Ph, R' = H, M = Ru,
13; R = Ph, R' = H, M = Os,
14; R = Ph, R' = Me, M = Fe,
15; R = *o*-MeOC$_6$H$_4$, R' = H, M = Fe,
16; R = *o*-^{i}PrC$_6$H$_4$, R' = H, M = Fe,
17; R = *o*-MeC$_6$H$_4$, R' = H, M = Fe,
18; R = Et, R' = H, M = Fe,
19; R = C$_6$F$_5$, R' = H, M = Fe,
20; R = OEt, R' = H, M = Fe.

Reactions of the ligands **1**−**10** with [Pd(PhCN)$_2$Cl$_2$] lead to formation of the dichloride complexes [M(η^5-C$_5$H$_4$PPh$_2$)$_2$PdCl$_2$] (**11**, M = Fe; **12**, M = Ru; **13**, = Os), [Fe(η^5-C$_5$Me$_4$PPh$_2$)$_2$-PdCl$_2$] (**14**), and [Fe(η^5-C$_5$H$_4$PR$_2$)$_2$PdCl$_2$] (**15**, R = *o*-MeOC$_6$H$_4$; **16**, R = *o*-Pr^{i}C$_6$H$_4$; **17**, R = *o*-MeC$_6$H$_4$; **18**, R = Et; **19**, R = C$_6$F$_5$; **20**, R = OEt) in near-quantitative yields (Scheme 4).

Structural and spectral data for the complexes **11**−**14** have been published earlier.[11,22,26] Coordination of the ethyl- and ethoxy-substituted ligands **8** and **10** with PdCl$_2$ affects the signals of the diastereotopic protons of the CH$_2$ groups differently. Thus, the ethoxy groups in complex **20** were presented as a triplet at δ 1.36 and broadened multiplet at δ

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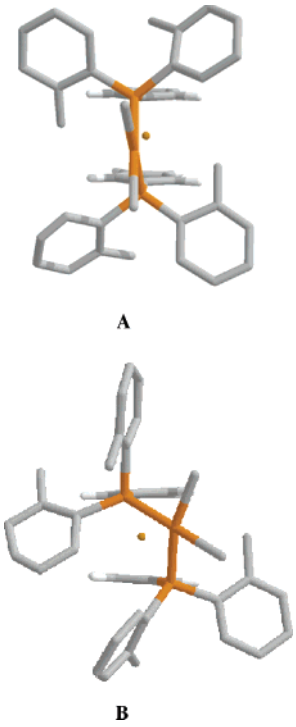
Table 1. Selected Geometrical Parameters for 13, 15, 16, and 18

	11 (M = Fe)	**12** (M = Ru)	**13** (M = Os)	**15** (M = Fe)	**16** (M = Fe)	**18** (M = Fe)
M−C_{Cp}, Å	1.994−2.055		2.129(5)−2.225(5)	2.005(6)−2.065(7)	2.018(7)−2.064(7)	2.019(4)−2.067(4)
M−X(1),[a] Å	1.629		1.811(5)	1.638(6)	1.653(7)	1.645(4)
M−X(2),[b] Å	1.632		1.800(5)	1.638(7)	1.636(7)	1.645(4)
Pd(1)−P(1), Å	2.282	2.305[f]	2.298(1)	2.2744(15)	2.292(2)	2.2742(9)
Pd(1)−P(2), Å	2.300		2.305(1)	2.2619(15)	2.318(2)	2.2727(9)
Pd(1)−Cl(1), Å	2.347	2.358[f]	2.331(1)	2.3524(15)	2.342(2)	2.3713(9)
Pd(1)−Cl(2), Å	2.349		2.351(1)	2.3609(15)	2.345(2)	2.3615(9)
P(1)−Pd(1)−P(2), deg	97.98(2)	100.02(2)	101.29(4)	100.27(5)	101.54(7)	97.74(3)
Cl(1)−Pd(1)−Cl(2), deg	89.96(4)	90.14(2)	88.19(4)	90.22(5)	88.74(7)	87.05(3)
P(1)−C(1), Å	1.804		1.804(5)	1.809(6)	1.768(7)	1.788(4)
P(1)−C(6), Å	1.796		1.796(5)	1.825(5)	1.802(7)	1.805(4)
P−C_{Ph}, Å	1.818−1.826		1.818(5)−1.826(5)	1.797(7)−1.823(7)	1.840(8)−1.856(7)	1.826(4)−1.834(4)
$\delta_{P(1)}$,[c] Å	0.019	−0.048 [f]	−0.002	0.167	0.033	0.0519
$\delta_{P(2)}$,[c] Å	0.032		−0.018	0.1824	−0.189	0.0842
Cp/Cp,[d] deg	6.2	9.2	8.9	3.1	7.1	0.58
θ,[e] deg	34.1	39.3	31.7	9.3	31.4	25.6
Pd(1)−P(1)−P(2)/ M−P(1)−P(2), deg	21.6		26.8	0.1	40.6	5.7
P(1)−Pd(1)−Cl(2)/ P(2)−Pd(1)−Cl(1), deg	6.2		2.5	1.4	20.8	5.5

[a] Centroid of the C(1)−C(5) Cp ring. [b] Centroid of the C(6)−C(7) Cp ring. [c] Deviation of the phosphorus atom from the Cp plane ring. A negative value means that P(1)/P(2) is closer to Os/Fe. [d] The dihedral angle between the two Cp rings. A positive value means that the Cp rings are inclined toward the Pd. [e] The torsion angles C(1)−X(1)−X(2)−C(6), where C(1) and C(6) are the carbon atoms bonded to the P and X is the centroid. [f] The average value according to: Nataro, C.; Campbell, A. N.; Ferguson, M. A.; Incarvito, C. D.; Rheingold, A. L. *J. Organomet. Chem.* **2003**, *673*, 47.

Chart 1



A

B

4.33 in the ^{1}H NMR spectrum and as singlets at δ 16.04 and 65.48 in the ^{13}C{^{1}H} NMR spectrum, while a doublet of triplets at δ 1.35 and two multiplets at δ 2.20 and 2.50 in the ^{1}H NMR spectrum and a singlet at δ 9.65 and a multiplet with an ABX pattern[22b] at δ 22.45 in the ^{13}C{^{1}H} NMR spectrum arose from the ethyl groups in **18**. In ^{31}P{^{1}H} NMR both complexes **18** and **20** have one singlet each at δ 42.46 and 119.96, correspondingly. Their ferrocene moieties in ^{1}H NMR spectra were observed as pairs of singlets at δ 4.50, 4.53 and at δ 4.55, 4.63 for **18** and **20**, respectively. In the ^{13}C{^{1}H} NMR spectra these moieties have signals at δ 72.71 (t), 72.39 (t), 74.95 (m) and at δ 72.63 (t), 73.62 (t), 75.05 (dd) for **18** and **20**, respectively.

In the ^{31}P{^{1}H} NMR spectra of the dichloride palladium complexes with ortho-substituted aryl groups **15**, **17**, and **19** recorded at room temperature were observed broadened signals at δ 40.15, 40.22, and 11.50, respectively. In the ^{1}H NMR spectra ferrocene moieties of **15**, **17**, and **19** were characterized by pairs of broadened signals at δ 4−5. The signals of the ortho protons of the phenyls in **15** and **17** were broad and were shifted downfield. The signal of the ortho fluorines in **19** was also broadened and appeared at δ −46.1 in the ^{19}F{^{1}H} NMR spectrum.

The NMR spectra for **15** and **17** were also recorded at low temperature. The signal of **15** in the ^{31}P{^{1}H} NMR spectrum becomes sharper upon cooling to −80 °C, although the phosphorus atoms remain equivalent. In the ^{1}H NMR spectrum of **15** at −50 °C two different MeO groups were observed, even though the signals were still rather broad. However, its ^{1}H NMR spectrum at −80 °C was well resolved and consisted of two inequivalent MeO groups at δ 3.30 and 3.87 and four Cp protons at δ 4.02, 4.08, 4.16, and 4.67; aryl protons were observed in the region δ 6.7−9.2. The appearance at lower temperatures of two different aryl substituents at one phosphorus is apparently evidence for the relatively slow rotation of the aryl rings around C−P bonds.

The ^{31}P{^{1}H} NMR spectrum of the tolyl-substituted complex **17** recorded at −50 °C showed the presence of two isomers of the symmetrical structure **A** (singlet at δ 48.83) and unsymmetrical structure **B** (two doublets at δ 33.46 and 38.46) in the ratio 2.7:1 (Chart 1). The amount of symmetric isomer increases on lowering the temperature, reaching the ratio 5.8:1 at −80 °C. The presence of ortho substituents in the aryl rings of **15**, **17**, and **19** leads to slower interconversion between symmetrical (**A**) and unsymmetrical isomers (**B**) in comparison with the case for complexes containing unsubstituted phenyls, [M(η^5-C_5H_4-PPh_2)$_2$$PdCl_2$] (**11**, M = Fe; **12**, M = Ru; **13**, = Os).[11,22,26] Thus, complexes **15** and **17** exist as a mixture of two isomers, which at room temperature are in a dynamic equilibrium.

In the ^{31}P{^{1}H} NMR spectrum of the *o*-isopropyl-substituted complex **16** two doublets at δ 38.1 and 41.0 arose, which was evidence for its unsymmetrical structure. In the ^{1}H NMR spectrum eight methyl signals (δ −0.07 to +1.74) and four CH groups (δ 1.92−3.57) were observed; these signals arose from the inequivalent isopropyl substituents. The eight broadened singlets in the region δ 4.10−5.45 were assigned to the protons of the Cp rings. Thus, according to the NMR data the structure of **16** in solution does not have any elements of symmetry.

X-ray Structures of Palladium Complexes 13, 15, 16, and 18. The crystal structures of the complexes **13**, **15**, **16**, and **18** have been determined by X-ray diffractometry (Table 1). For

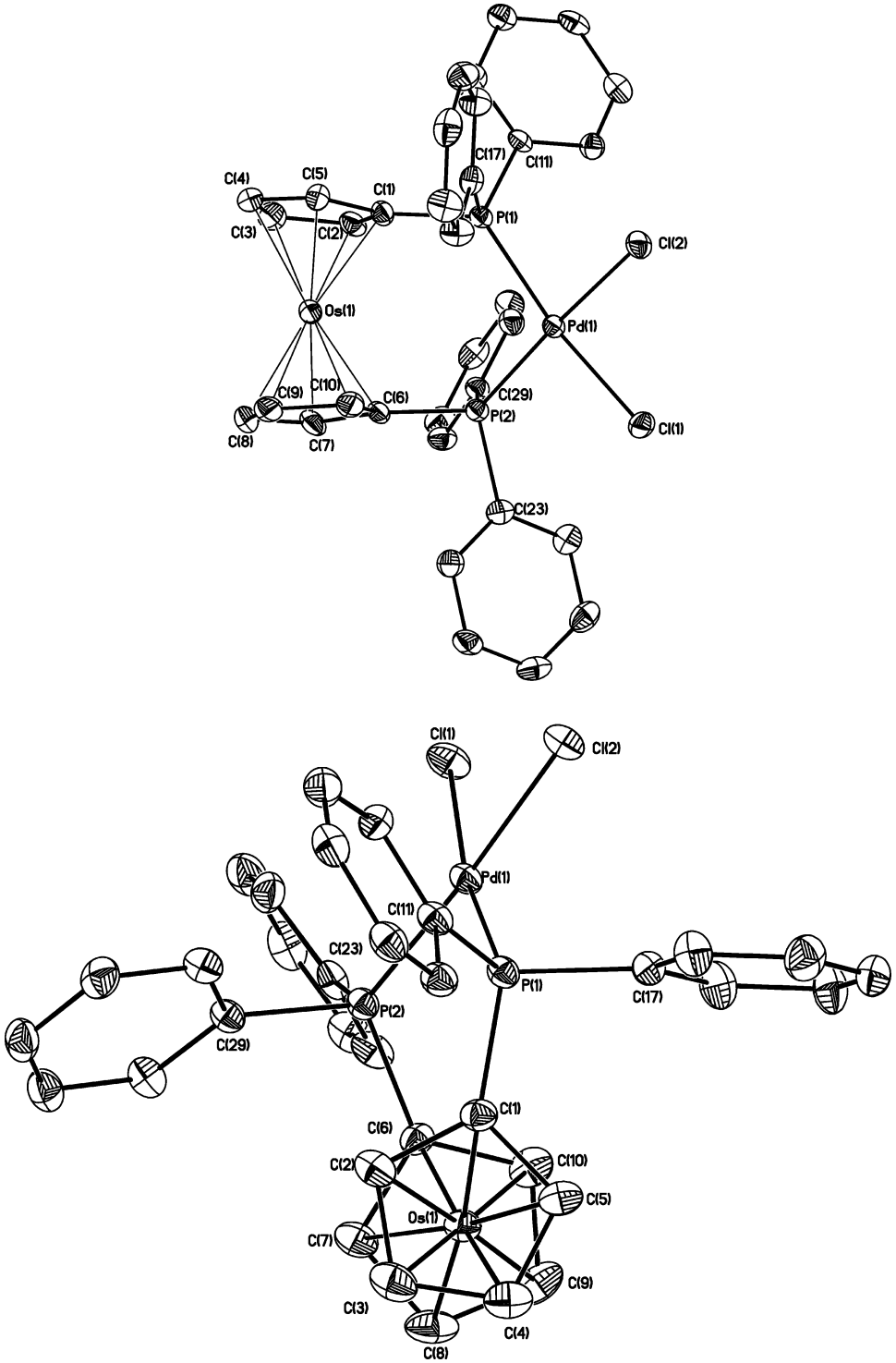


Figure 1. ORTEP drawings of **13**. Thermal ellipsoids are drawn at the 50% probability level. The bottom drawing gives a projection on the plane of the cyclopentadienyl rings.

purposes of comparison Table 1 contains structure data of complexes **11**[12,27,28] and **12**,[29] which allows us to evaluate the effect of the metal on the metallocene bridge (Figures 1−4).

Palladium in complexes **11**−**13** has nearly a square-planar configuration. The Cp rings in the metallocene moieties have staggered conformations with twist angles of 31.7−39.3° for **11**−**13**. The deviations of palladium from the plane P−M−P are 21.6 and 26.8° for **11** and **13**, respectively. Changes in the M−Cp_{center} distance going from 1.634 Å (**11**) to 1.80 Å (**12**) to 1.81 Å (**13**) results in an increase of the bite angle P−Pd−P: 97.98(2)° (**11**), 100.02(2)° (**12**), and 101.29(4)° (**13**).

Substituents at the phosphorus in **15**, **16**, and **18** define the structures of these complexes (Figures 2−4).

The structure of the sterically congested *o*-anisyl complex **15** differs significantly from that for **11**. Palladium still has a square-planar configuration (the dihedral angle Cl(1)−Pd−P(1)/

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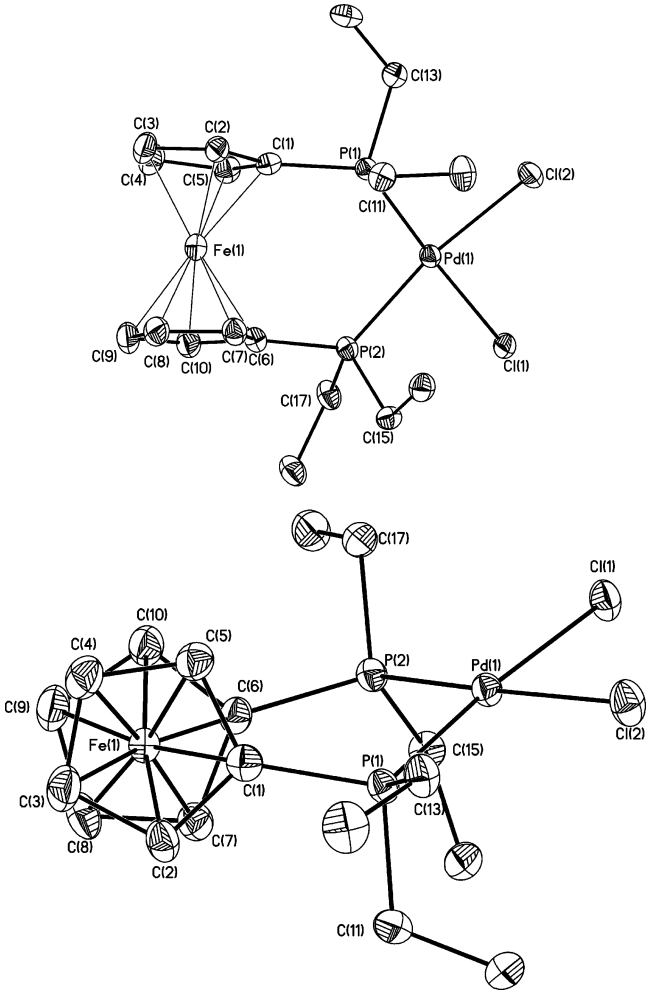


Figure 2. ORTEP drawings of **18**. Thermal ellipsoids are drawn at the 50% probability level. The bottom drawing gives a projection on the plane of the cyclopentadienyl rings.

Cl(2)−Pd−P(2) is 1.4°); it lies almost on the plane P−Fe−P (the P−Fe−P/P−Pd−P angle is 0.1°), which leads to an increase of the bite angle P−Pd−P to 100.27(5)°.

Further increase in the steric bulkiness of the aryl ortho substituent in the *o*-isopropylphenyl complex **16** results in more dramatic changes in the structure. The palladium has a configuration significantly distorted from square planar (the angle Cl(1)−Pd−P(1)/Cl(2)−Pd−P(2) is 20.8°); the palladium atom deviates from the P−Fe−P plane by 40.6°. The bite angle increases to 101.54(7)°, though the Fe−Cp_{center} distances are 1.636(7) and 1.653(7) Å, which are close to those in **11** and **15**.

The ethyl-substituted complex **18** has a structure similar to that of a complex with dppf, **11**. The palladium atom has nearly a square-planar configuration (the dihedral angle Cl(1)−Pd−P(1)/Cl(2)−Pd−P(2) is 5.5°); the palladium atom deviates from the plane P−Fe−P by −5.7°, the Cp rings are staggered (25.6°), and the bite angle P−Pd−P is 97.74(3)°.

Catalytic Properties of Pd Complexes with Ligands 1−10 in the Amination of Aryl Halides. The catalytic activity of Pd complexes with ligands **1**−**10** was studied in the amination of 4-bromotoluene by morpholine as a model reaction using 1 mol % of catalyst in dioxane (Scheme 5). The data (Table 2) allow us to compare the effect of the central metal Fe, Ru, or Os on ligands **1**−**3** and to evaluate the influence of the R group on the diphosphinoferrocene complexes **15**−**20**.

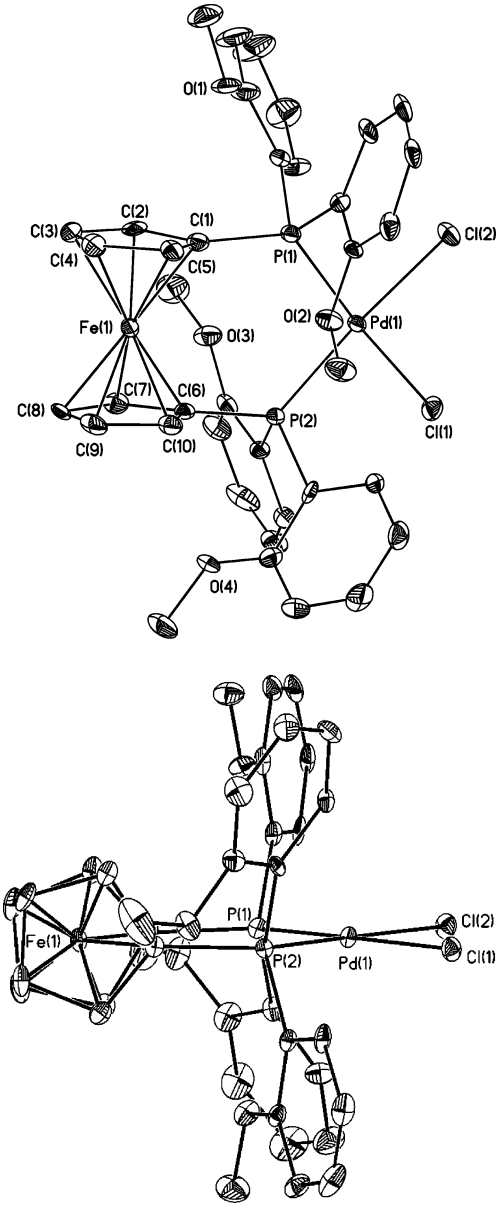


Figure 3. ORTEP drawings of **15**. Thermal ellipsoids are drawn at the 50% probability level. The bottom drawing gives a projection on the plane of the cyclopentadienyl rings.

It is thought that Pd(II) is rapidly reduced to Pd(0) in the *t*-BuONa−amine system. This is supported by the fact that the Pd(0)−BINAP complex was much less active than complexes **15** and **16**.

The comparison of activity demonstrates that the efficiency of the catalyst decreases in the triad $(\eta^5\text{-Cp}')_2M(PPh_2)_2$ when Fe is substituted by Ru, in agreement with the results reported by Hartwig,[4] or Os. Little difference was found between ligands containing Ru and Os. When Cp* (Cp* = tetramethylcyclopentadiene) was used instead of Cp (dppf analogue **4**), a significant increase in the yield was observed (63% in 20 min). Complexes having ethyl (**18**), ethoxy (**20**), and pentafluorophenyl groups (**19**) at the phosphorus atom turned out to be ineffective (entries 6, 8, and 7). As expected, the complex with ligand **7**, having *o*-tolyl groups at the phosphorus atom, showed higher activity (entry 5) than the complex with dppf (62% compared to 42%). However, complexes with phosphine ligands **5** and **6**, containing *o*-methoxyphenyl and *o*-isopropylphenyl substituents, respectively, were found to be much more active. With these complexes 100% conversion in the reaction is

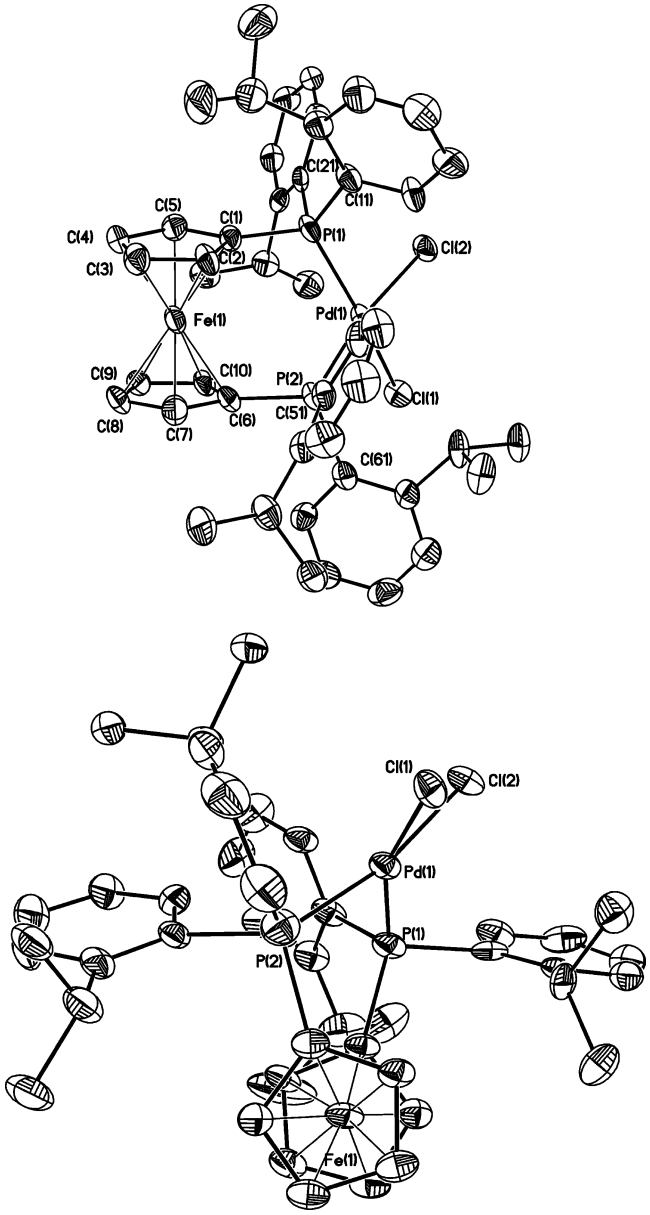
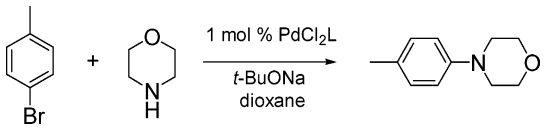


Figure 4. ORTEP drawings of **16**. Thermal ellipsoids are drawn at the 50% probability level. The bottom drawing gives a projection on the plane of the cyclopentadienyl rings.

Scheme 5



achieved in 5 min (entries 9 and 10). Moreover, the above complexes are more active than complexes with dppf and even with BINAP (entries 1 and 11). Apparently, this can be explained by steric factors, which in this case play a major role. According to Hartwig[4] the electronic influence of a methoxy group in a para position (4-anisyl) of a ferrocene-based ligand in amination reactions is insignificant. Ligands **5** and **6** showed some catalytic activity even at room temperature (entries 12 and 13), while BINAP and dppf were not active under these conditions (entries 14 and 15).

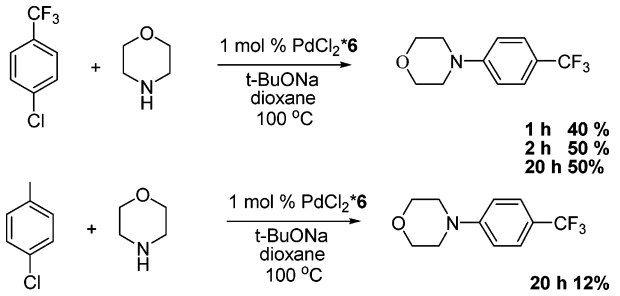
The complex with ligand **6** also allowed the amination of an activated aryl chloride with a modest yield and even of *p*-tolyl chloride, though the yield was poor (Scheme 6).

Table 2. Amination of 4-Bromotoluene with Morpholine Catalyzed by Palladium Complexes with Ligands 1−10

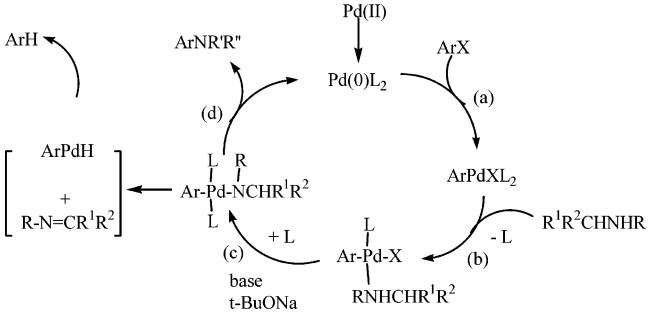
entry	ligand	reacn time	temp, °C	yield of *N*-(4-methylphenyl) morpholine,[a] %
1	**1**	20 min	100	42[b]
2	**2**	20 min	100	8
3	**3**	20 min	100	12
4	**4**	20 min	100	63[b]
5	**7**	20 min	100	62
6	**8**	20 min	100	16
7	**9**	20 min	100	13
8	**10**	20 min	100	1−2
9	**5**	5 min	100	99[b]
10	**6**	5 min	100	99[b]
11	BINAP[c]	5 min	100	59
12	**5**	20 h	20	6
13	**6**	20 h	20	18
14	**1**	20 h	20	0
15	BINAP[c]	20 h	20	0

[a] Yields determined by ^{1}H NMR with acetylferrocene as a standard relative to bromotoluene. [b] Isolated yield. [c] $Pd(dba)_2$/BINAP (1:1).

Scheme 6



Scheme 7

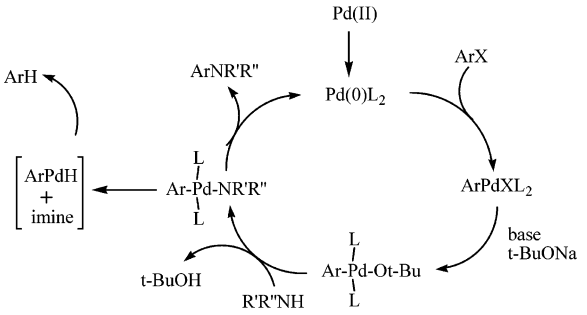


Amination reactions are more complex than any other cross-coupling reactions, leading to the formation of carbon−carbon or carbon−heteroatom bonds.[1−4] This fact is related to the different requirements for the acid−base properties of amine at different stages of the catalytic cycle: there is still much uncertainty about the nature of the catalytic cycle itself, as well as its rate-limiting step, which is presumably the reductive elimination step, unlike the case for other cross-coupling reactions.

The catalytic cycle shown in Scheme 7, which involves ligand substitution by amine, resulting in an increased N−H bond acidity in the coordinated complex, has an equally appropriate alternative (Scheme 8), in which the amide complex is formed by the nucleophilic attack of amine at the alkoxide complex.

It is well-known that the reduction of the C−Hal bond in aryl halides is usually the main side process competing with the amination reactions (see the catalytic cycle). To study such selectivity, we measured the ArNR′R″/ArH ratio in the reaction of 4-bromobiphenyl with morpholine (Scheme 9). Since 4-bromobiphenyl is a more reactive substrate than 4-bromotoluene, the yields were determined after 10 min (Table 3). The Pd

Scheme 8



Scheme 9

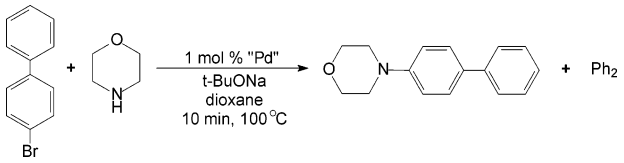


Table 3. Amination of 4-Bromobiphenyl by Morpholine Catalyzed by Palladium Complexes with 1−10

entry	ligand	yield of *N*-(4-biphenyl)-morpholine,[a] %	yield of biphenyl,[a] %	approx ratio $ArNR_1R_2/ArH$
1	**1**	48	5	10
2	**2**	18	5	4
3	**3**	24	5	5
4	**4**	60	4	15
5	**5**	98	2	49
6	**6**	97	2	48
7	**7**	57	3	14
8	**8**	22	10	2
9	**9**	12	1	12
10	**10**	11	8	<2

[a] Yield determined by LC relative to ArBr.

complex with **1** demonstrates in this reaction higher activity than do the complexes with **2** and **3** (entries 1−3), in the same way as in the reaction of 4-bromotoluene, and the amount of reduction product is noticeable (10−20% relative to amination product). For poorly effective complexes with ligands **8**−**10** the yield of the reduction product is comparable to that of the amination product. One can see that even with ligands **1** and **4** (entries 1 and 4) the yield of ArH is far from negligible. However, for the most active complexes **15** and **16**, the yield of amination product is close to quantitative (entries 5 and 6).

These results are in agreement with previous observations[4] that the $ArNR_1R_2/ArH$ ratio grows with an increase of the P−Pd−P bite angle in catalytic complexes (compare 100.27° for **15** and 101.54° for **16** with 97.74° for **18**). However, the bite angle is obviously not the only factor governing the catalytic activity, since in the Fe, Ru, Os triad an opposite trend is observed (compare 97.98° (Fe) with 100.02° (Ru) and 101.29 (Os)). Even though the structure data have not been obtained for the catalytically active Pd(0) complexes, but for their precursors, we suppose that the most important structural features, including the bite angles, are retained in the corresponding Pd(0) complexes or at least follow the same trend.

Using the complex $PdCl_2$-**6** as the best catalyst for the amination reaction, we carried out the reactions of 4-bromotoluene with different types of amines (Scheme 10). The results are presented in Table 4. All reactions are usually complete within 5−30 min. In the case of primary amines monoarylation is sometimes accompanied by diarylation.

Scheme 10

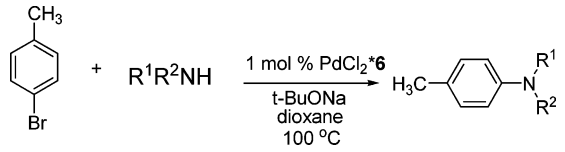
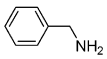
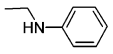
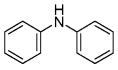
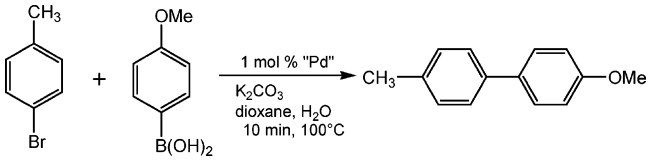


Table 4. Amination of 4-Bromotoluene by Various Amines Catalyzed by Complex 16

$CH_3(CH_2)_{10}CH_2NH_2$	30	85 (+7% diarylation)
	5	68
	30	80
	5	87 (+6% diarylation)
	5	68
	30	96
	30	99

[a] Yields determined by ^1H NMR with acetylferrocene as a standard.

Scheme 11



Thus, complexes based on ligands **5** and **6** are new, highly efficient catalysts for the amination of aryl bromides. The high activity of their complexes as well as the high selectivity displayed in amination reactions are in accord with the views that chelate ligands, especially sterically hindered ones, promote amination and hamper the process of β-hydride elimination.

Catalytic Activity of Pd Complexes with Ligands 1−10 in Suzuki−Miyaura Coupling between 4-Tolyl Bromide and (4-Methoxyphenyl)boronic Acid.[30] Though Suzuki type cross-coupling reactions do not require the presence of bidentate phosphine ligands, the latter are sometimes applied in this reaction.[31] We have shown that all complexes described above are active in the reaction of 4-bromotoluene with (4-methoxyphenyl)boronic acid and in all cases the coupling product is formed quantitatively (Scheme 11). Therefore, the relative activities of these complexes were determined by comparing the yields of the coupling product after 10 min (Table 5).

We found that, in contrast to the case for amination, the nature of the metal in the metallocene has practically no effect on the complex activity—almost equal yields (60−69% in 10 min) were obtained for all the triad **1**−**3**. The addition of eight methyl groups to the cyclopentadienyl rings of dppf (ligand **4**) leads to an increase of the complex activity (yield 84%), as was observed in the amination reaction. Though complexes **18**−**20** are less active than dppf, they are effective in Suzuki coupling and show similar activities, which shows that the Suzuki reaction is much

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(31) (a) Shen, W. *Tetrahedron Lett.* **1997**, *38*, 5575. (b) Saton, Y.; Gude, C.; Chan, K.; Firooznia, F. *Tetrahedron Lett.* **1997**, *38*, 7645. (c) Franc, C.; Denonne, F.; Cuisinier, C.; Ghosez, L. *Tetrahedron Lett.* **1999**, *40*, 4555. (d) Ali, N. M.; McKillop, A.; Mitchel, M. B.; Rebelo, R. A.; Wallbank, P. J. *Tetrahedron* **1992**, *48*, 8117.

Table 5. Suzuki Coupling of 4-Bromotoluene with 4-(Methoxyphenyl)boronic Acid Catalyzed by Palladium Complexes with Ligands 1−10[a]

ligand	yield of 4-methyl-4′-methoxybiphenyl,[b] %	ligand	yield of 4-methyl-4′-methoxybiphenyl,[b] %
1	60	**6**	100 (99)[c]
2	63	**7**	83
3	69	**8**	50
4	84	**9**	52
5	100	**10**	44

[a] Conditions: aqueous dioxane, K_2CO_3, 100 °C. [b] Yields determined by ^{1}H NMR with acetylferrocene as a standard. [c] Isolated yield.

less sensitive to the nature of the catalyst than the amination reaction. As in the amination reaction the activities of complexes with ligands **4** and **7** are equal, and both are more active than complexes with ligands **1**−**3** and **8**−**10**.

However, the highest activity was observed, as in the amination reaction, for complexes with ligands **5** and **6**. Using these complexes allows us to carry the reaction to completion in 10 min and to obtain 4-methoxy-4′-methylbiphenyl selectively in quantitative yield.

It is worth noting that the reason complexes **15** and **16** always have the highest activity in such different types of reactions is not clear. These reactions are thought to have different rate-determining steps. While in the amination reaction an increase of the bite angle would facilitate the reductive elimination,[32] which is thought to be the rate-determining step, the same increase does not favor Suzuki coupling, where oxidative addition and transmetalation are more important.

Conclusions

Palladium complexes with the bulky and electron-rich bidentate ligands Fe(η^5-C_5H_4P(*o*-Pr^iC_6H_4)$_2$)$_2$ (**6**) and Fe(η^5-C_5H_4P-(*o*-$MeOC_6H_4$)$_2$)$_2$ (**5**) showed a very high catalytic activity in amination and Suzuki coupling and allow us to perform the reaction with nonactivated aryl bromides in a very short time, with high selectivity and product yield.

Experimental Section

General Procedures. All experiments were performed under argon in solvents purified by standard methods. ^{1}H, ^{31}P{^{1}H}, ^{19}F-{^{1}H}, and ^{13}C{^{1}H} NMR spectra were recorded on Bruker AMX 400 and Varian VXR 400 spectrometers. Chemical shifts are reported in ppm (δ) with reference to TMS as an internal standard (^{1}H and ^{13}C{^{1}H} NMR spectra), and CF_3COOH for ^{19}F{^{1}H} NMR or 85% H_3PO_4 for ^{31}P{^{1}H} NMR spectra as an external standards. Microanalyses were performed at the A. N. Nesmeyanov Institute of Organoelement Compounds. The following compounds were synthesized according to published procedures: ClP(*o*-C_6H_4-OMe)$_2$,[23] Fe(η^5-$C_5H_4PCl_2$)$_2$,[33] [$PdCl_2$(PhCN)$_2$].[34]

Synthesis of Fe(η^5-C_5H_4P{*o*-C_6H_4OMe}$_2$)$_2$ (5). To a solution of ferrocene (1.02 g, 5.5 mmol) in hexane/Et_2O (30/30 mL) cooled to 0 °C was added a solution of *n*-BuLi (1.45 M, 9.1 mL, 13.0 mmol) following the addition of TMEDA (2.0 mL, 13.0 mmol). The solution was warmed to room temperature and was stirred for 20 h to afford a slurry of 1,1′-dilithioferrocene. The reaction mixture was cooled to 0 °C, and a solution of ClP(*o*-C_6H_4OMe)$_2$ (3.0 g, 12.0 mmol) in Et_2O (50 mL) was added. The solution/slurry obtained was warmed to room temperature, stirred overnight, and then refluxed for 3 h. The solvent was removed under reduced pressure. The residue was washed with hexane (2 × 20 mL) and then dissolved in hot benzene (100 mL). The resulting solution was passed through a column (8 cm × 2 cm) of silica, which then washed with benzene until the washings became colorless. The solution thus obtained was concentrated to 10 mL, affording a yellow precipitate of the product, which was filtered off, washed with benzene (5 mL) and hexane (10 mL), and dried under vacuum. Yield: 2.05 g (55%). Anal. Calcd for $C_{38}H_{36}FeO_4P_2$: C, 67.67; H, 5.38. Found: C, 67.74; H, 5.44. ^{1}H NMR ($CDCl_3$): δ 3.75 (s, 12H, O*Me*), 3.96 (s, 4H, C_5H_4), 4.39 (s, 4H, C_5H_4), 6.80−7.25 (m, 16H, *o*-C_6H_4OMe). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −44.4 (s). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 55.43 (s, OMe), 72.48 (s, β-C, C_5H_4), 73.64 (d, J = 15.3 Hz, α-C, C_5H_4), 75.55 (d, J = 6.4 Hz, *ipso*-C, C_5H_4), 109.96 (s, C_6H_4), 120.25 (s, C_6H_4), 127.02 (d, J = 11.2 Hz, *ipso-C*(P), C_6H_4), 129.65 (s, C_6H_4), 133.98 (s, C_6H_4), 160.67 (d, J = 17.3 Hz, *ipso-C*(OMe), C_6H_4).

Synthesis of Fe(η^5-C_5H_4P{*o*-$C_6H_4Pr^i$}$_2$)$_2$ (6). A solution of *o*-Li$C_6H_4Pr^i$ was prepared as follows. Lithium wire (0.70 g, 100 mmol) was placed under an argon atmosphere in a three-necked flask, upon which Et_2O (50 mL) was added. A solution of *o*-BrC_6H_4-Pr^i (10.0 g, 50.3 mmol) in Et_2O (20 mL) was added dropwise through a dropping funnel for 1 h to allow the slow reflux of ether. The mixture was stirred overnight, and the solution was decanted through a cannula to give a solution of *o*-Li$C_6H_4Pr^i$ in Et_2O (60 mL, 0.78 M, 46.8 mmol). To the solution of aryllithium obtained was added a solution of Fe(η^5-$C_5H_4PCl_2$)$_2$ (4.10 g, 10.6 mmol) in Et_2O (60 mL) dropwise at 0 °C. The mixture was warmed, stirred overnight, and then refluxed for 2 h. The resulting mixture was quenched with MeOH (2 mL), and the solvent was evaporated. The residue was dissolved in hexane (100 mL), filtered through a short bed of silica, and concentrated to 10 mL. The precipitated yellow crystals were filtered off, quickly washed with hexane (10 mL), and dried under vacuum. Yield: 5.2 g (68%). Anal. Calcd for $C_{46}H_{52}FeP_2$: C, 76.45; H, 7.25. Found: C, 76.21; H, 7.24. ^{1}H NMR ($CDCl_3$): δ 0.92 (d, 6H, J = 6.7, CH(CH_3)$_2$), 1.30 (d, 6H, J = 6.7, CH(CH_3)$_2$), 3.88 (dq, J_1 = 13.8, J_2 = 6.7 Hz, *CH*(CH$_3$)$_2$), 4.07 (s, 4H, C_5H_4), 4.36 (s, 4H, C_5H_4), 6.95−7.25 (m, 16H, *o*-C_6H_4-Pr^i). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −40.1 (s). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 23.65 (s, Me), 23.97 (s, Me), 30.90 (s, *C*H$_{Pr}$), 31.15 (s, *C*H$_{Pr}$), 71.72 (d, J = 3.5 Hz, β-C, C_5H_4), 73.30 (d, J = 13.2 Hz, α-C, C_5H_4), 78.36 (d, J = 9.1 Hz, *ipso*-C, C_5H_4), 125.09 (d, J = 4.4, C_6H_4), 125.35 (s, C_6H_4), 128.73 (s, C_6H_4), 133.98 (s, C_6H_4), 136.64 (d, J = 11.6 Hz, *ipso-C*(P), C_6H_4), 152.32 (d, J = 24.4 Hz, *ipso-C*(Pr^i), C_6H_4).

Synthesis of Fe(η^5-C_5H_4P{*o*-C_6H_4Me}$_2$)$_2$ (7). The solution of *o*-LiC_6H_4Me was prepared as follows. Lithium wire (1.54 g, 220 mmol) was placed under an argon atmosphere in a three-necked flask, whereupon Et_2O (50 mL) was added. A solution of *o*-BrC_6H_4-Me (9.4 g, 6.6 mL, 55 mmol) in Et_2O (20 mL) was added dropwise through a dropping funnel for 1 h to allow slow reflux of ether. The mixture was stirred overnight, and the solution was decanted through a cannula to give a solution of *o*-LiC_6H_4Me in Et_2O (60 mL, 0.85 M, 51.0 mmol). To the solution of aryllithium (11.8 mL, 10 mmol) obtained was added a solution of Fe(η^5-$C_5H_4PCl_2$)$_2$ (1.00 g, 2.6 mmol) in Et_2O (70 mL) dropwise at 0 °C. The mixture was warmed, stirred overnight, and then refluxed for 2 h. The resulting mixture was quenched with MeOH (2 mL), and the solvent was evaporated. The residue was dissolved in benzene (100 mL) and the solution filtered through a short bed of silica. The filtrate was evaporated, and the yellow crystals obtained were dried under vacuum. Yield: 1.09 g (69%). ^{1}H NMR ($CDCl_3$): δ 2.45 (s, 12H, Me), 4.07 (s, 4H), 4.28 (s, 4H), 7.05 (m, 16H, C_6H_4). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −36.00 (s).

Synthesis of [Fe(η^5-$C_5H_4PEt_2$)$_2$] (8). A solution of EtMgBr (1.21 M, 23.4 mL, 28.4 mmol) was added dropwise at 0 °C to a stirred

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solution of Fe(η^5-$C_5H_4PCl_2)_2$ (1.85 g, 4.77 mmol) in Et_2O (50 mL). The mixture was warmed and stirred for 3 h. The resulting mixture was quenched with degassed water (2 mL); the solvent was then removed under vacuum, and the solid was dissolved in benzene (100 mL). This solution was filtered through a short bed of silica. The solvent was evaporated, and the residue was dried under vacuum. Yield: 1.36 g (80%). ^{1}H NMR ($CDCl_3$): δ 1.06 (m, 12H, Me), 1.59 (m, 8H, CH_2), 4.18 (s, 4H, C_5H_4), 4.26 (s, 4H, C_5H_4). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −26.1 (s).

Synthesis of Fe(η^5-$C_5H_4P\{C_6F_5\}_2)_2$ (9). To a solution of pentafluorobenzene (4.30 g, 25.5 mmol) in Et_2O (60 mL) cooled to −78 °C was added a solution of *n*-BuLi (1.96 M, 13.0 mL, 25.5 mmol). The reaction mixture was stirred at this temperature for 1 h, and then a solution of Fe(η^5-$C_5H_4PCl_2)_2$ (2.47 g, 6.36 mmol) in Et_2O (40 mL) was added dropwise. The resulting solution was slowly warmed to room temperature and was stirred overnight. The mixture was quenched with MeOH (2 mL); the solvent was then removed under vacuum, and the solid was dissolved in hexane (60 mL). This solution was filtered through a glass frit, concentrated to 10 mL, and placed in a refrigerator for 3 days. The yellow precipitate was obtained, the mother liquor was decanted, and the solid was washed quickly with cold hexane (10 mL) and dried. Yield 4.6 g (79%). Anal. Calcd for $C_{34}H_8F_{20}FeP_2$: C, 44.67; H, 0.88. Found: C, 44.64; H, 0.88. ^{1}H NMR ($CDCl_3$): δ 4.29 (s, 4H, C_5H_4), 4.42 (s, 4H, C_5H_4). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −58.7 (quintet, J(P−F) = 30.5 Hz). ^{19}F{^{1}H} NMR ($CDCl_3$): δ −82.1 (br. t, 8F, J = 20 Hz, *m*-F(C_6F_5)), −71.6 (t, 4F, J = 20.5 Hz, *p*-F(C_6F_5)), −51.8 (t, 8F, J = 28 Hz, *o*-F(C_6F_5)). ^{13}C{H} NMR ($CDCl_3$): δ 68.61 (s, *ipso*-C, C_5H_4), 72.95 (d, J = 4.9 Hz, β-C, C_5H_4), 74.53 (d, J = 19.7 Hz, α-C, C_5H_4), 108.77 (m, $J_1 + J_2$ = 37.2 Hz, C_6F_5), 147.25 (d, J = 275 Hz, C_6F_5), 137.58 (dt, J_1 = 254, J_2 = 14 Hz, C_6F_5), 142.50 (dt, J_1 = 256, J_2 = 12.5 Hz, C_6F_5).

Synthesis of [Fe(η^5-$C_5H_4P\{OEt\}_2)_2$] (10). A solution of EtOH (1.24 mL, 21.6 mmol) and pyridine (1.75 mL, 21.6 mmol) in hexane (50 mL) was added dropwise at 0 °C to a solution of Fe(η^5-$C_5H_4PCl_2)_2$ (2.04 g, 5.26 mmol) in hexane (150 mL). The mixture was warmed, stirred for 1 h, filtered through a glass frit, and placed in a refrigerator for 1 day. The precipitate of pyridinium chloride was filtered off, the resulting solution was evaporated, and the residue was dried under vacuum. Yield: 1.96 g (87%). ^{1}H NMR ($CDCl_3$): δ 1.21 (t, 12H, J = 7 Hz, Me), 3.72 (m, 4H, CH_2), 3.87 (m, 4H, CH_2), 4.36 (s, 4H, C_5H_4), 4.39 (s, 4H, C_5H_4). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 157.82 (s).

Synthesis of [Fe(η^5-$C_5H_4PAr_2)_2PdCl_2$] (15). General Procedure. A solution of [Pd(PhCN)$_2$Cl$_2$] (0.46 g, 1.20 mmol) in benzene (30 mL) was added to a solution of **5** (0.83 g, 1.23 mmol) in benzene (50 mL). A precipitate readily formed in a few minutes, and the mixture was stirred overnight. Red-brown crystals of **15** were filtered off, washed with benzene, and dried under vacuum. Yield: 0.98 g (96%). Anal. Calcd for $C_{38}H_{36}FeO_4P_2PdCl_2$: C, 53.58; H, 4.23. Found: C, 53.68; H, 4.26. ^{1}H NMR ($CDCl_3$): δ 3.62 (s, 12H, O*Me*), 4.12 (s, 4H, C_5H_4), 4.47 (s, 4H, C_5H_4), 7.00 (d, 4H, J = 7.8 Hz, *o*-C_6H_4OMe), 7.03 (t, 4H, J = 7.2 Hz, *o*-C_6H_4-OMe), 7.55 (t, 4H, J = 7.8 Hz, *o*-C_6H_4OMe), 8.08 (m, 4H, *o*-C_6H_4-OMe). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 40.1 (s).

Synthesis of [{Fe(η^5-$C_5H_4P\{o$-$C_6H_4Pr^i\}_2)_2$}PdCl$_2$] (16). Complex **16** was prepared analogously from **6** (0.96 g, 1.33 mmol) and [Pd(PhCN)$_2$Cl$_2$]] (0.50 g, 1.30 mmol) as brown crystals. Yield: 0.98 g (84%). Anal. Calcd for $C_{46}H_{52}FeP_2PdCl_2$: C, 61.39; H, 5.82. Found: C, 61.58; H, 5.79. ^{1}H NMR ($CDCl_3$): δ −0.07 (s, 3H, Me), 0.00 (s, 3H, Me), 0.42 (s, 3H, Me), 0.83 (s, 3H, Me), 1.18 (s, 3H, Me), 1.31 (s, 3H, Me), 1.74 (s, 6H, 2Me), 1.92 (s, 1H, *CH*(CH_3)$_2$), 2.82 (s, 1H, *CH*(CH_3)$_2$), 3.34 (s, 1H, *CH*(CH_3)$_2$), 3.57 (s, 1H, *CH*(CH_3)$_2$), 4.10 (s, 2H, C_5H_4), 4.19 (s, 1H, C_5H_4), 4.32 (s, 1H, C_5H_4), 4.57 (s, 1H, C_5H_4), 4.91 (s, 1H, C_5H_4), 5.45 (s, 2H, C_5H_4), 6.3−7.7 (br m, 14H, C_6H_4), 9.02 (br m, 1H, H$_1$(C_6H_4)), 9.59 (br m, 1H, H$_1$(C_6H_4)). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 38.1 (d, 1P, J = 47.7 Hz), 41.0 (d, 1P, J = 47.7 Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 22.75 (s, Me), 23.28 (s, Me), 24.6 (s, 5Me), 26.81 (s, Me), 30.73 (s, CH_{Pr}), 32.53 (s, CH_{Pr}), 34.68 (s, CH_{Pr}), 35.38 (s, CH_{Pr}), 70.39 (s, C_5H_4), 71.49 (s, C_5H_4), 72.22 (s, 2C, C_5H_4), 73.69 (s, C_5H_4), 75.15 (s, C_5H_4), 77.3 (s, C_5H_4), 78.37 (s, C_5H_4), 81.70 (d, *ipso*-C, C_5H_4, J = 48.3 Hz), 85.6 (d, *ipso*-C, C_5H_4, $J \approx$ 20 Hz), 130.00 (m, 18C), 140.58 (d, *ipso*-C(P), C_6H_4, J = 27 Hz), 142.22 (d, *ipso*-C(P), C_6H_4, J = 27 Hz), 150.86 (d, *ipso*-C(Pr^i), C_6H_4), 151.84 (s, *ipso*-C(Pr^i), C_6H_4), 152.89 (s, *ipso*-C(Pr^i), C_6H_4), 154.07 (s, *ipso*-C(Pr^i), C_6H_4).

Synthesis of [{Fe(η^5-$C_5H_4P\{o$-$C_6H_4Me\}_2)_2$}PdCl$_2$] (17). Similarly, complex **17** was synthesized from **7** as yellow crystals. Yield: 0.48 g (74%) Anal. Calcd for $C_{34}H_8F_{20}FeP_2PdCl_2 \cdot 0.5C_6H_6$: C, 59.56; H, 4.75. Found: C, 59.61; H, 4.60. ^{1}H NMR ($CDCl_3$): δ 1.45 (s, 6H, Me), 3.37 (s, 6H, Me), 4.10 (s, 2H, C_5H_4), 4.21 (s, 2H, C_5H_4), 4.28 (s, 2H, C_5H_4), 4.32 (C, 2H), 7.38 (m, 14H, C_6H_4), 9.12 (m, 2H, *o*-H, C_6H_4). ^{31}P{^{1}H} NMR ($CDCl_3$, −50 °C): δ 48.84 (s), 38.46 (d, J = 33.2 Hz), 33.47 (d, J = 33.2 Hz).

Synthesis of [{Fe(η^5-$C_5H_4P\{C_6F_5\}_2)_2$}PdCl$_2$] (19). Similarly, complex **19** was synthesized from **9** (0.74 g, 0.81 mmol) and [Pd(PhCN)$_2$Cl$_2$] (0.30 g, 0.78 mmol) as purple crystals. Yield: 0.73 g (86%). Anal. Calcd for $C_{34}H_8F_{20}FeP_2PdCl_2$: C, 37.41; H, 0.74. Found: C, 37.56; H, 0.71. ^{1}H NMR ($CDCl_3$): δ 4.42 (s, 4H, C_5H_4), 4.72 (s, 4H, C_5H_4). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 11.5 (br s). ^{19}F{^{1}H} NMR ($CDCl_3$): δ −81.0 (t, 8F, J = 20 Hz, *m*-F(C_6F_5)), −67.5 (t, 4F, J = 20.5 Hz, *p*-F(C_6F_5)), −46.1 (br m, 8F, *o*-F(C_6F_5)). ^{13}C{H} NMR ($CDCl_3$): δ 73.09 (s, β-C, C_5H_4), 77.21 (s, α-C, C_5H_4), 84.25 (m, *ipso*-C, C_5H_4, $J_1 + J_2$ = 67.0 Hz, C_6F_5), 106.75 (m, *ipso*-C_6F_5), 146.95 (d, *o*-C_6F_5, J = 247 Hz), 138.21 (d, *m*-C_6F_5, J = 255 Hz), 144.49 (d, *p*-C_6F_5, J = 245 Hz).

Synthesis of [Fe(η^5-$C_5H_4PEt_2)_2PdCl_2$] (18). A solution of [Pd(PhCN)$_2$Cl$_2$] (0.75 g, 1.96 mmol) in benzene (30 mL) was added to a solution of **8** (0.75 g, 2.07 mmol) in benzene (50 mL). A precipitate readily formed in a few minutes, and the mixture was stirred overnight. Red-brown crystals of **18** were filtered off, washed with benzene, and dried under vacuum. Yield: 0.94 g (89%). Anal. Calcd for $C_{18}H_{28}FeP_2PdCl_2$: C, 40.07; H, 5.23. Found: C, 38.46; H, 5.01. ^{1}H NMR ($CDCl_3$): δ 1.35 (dt, J_1 = 18.6, J_2 = 7.6 Hz, 12H, Me), 2.19 (m, 4H, 2CH_2), 2.51 (m, 4H, 2CH_2), 4.50 (s, 4H), 4.53 (s, 4H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 42.50 (s). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 9.65 (Cs, Me), 22.44 (m, CH_2, $J_1 + J_2$ = 35.0 Hz), 72.71 (t, β-C, C_5H_4, J = 3.2), 73.39 (t, α-C, C_5H_4, J = 4.4 Hz), 74.95 (m, *ipso*-C, C_5H_4, $J_1 + J_2$ = 56.8 Hz).

Synthesis of [Fe(η^5-$C_5H_4P(OEt)_2)_2PdCl_2$] (20). A solution of [Pd(PhCN)$_2$Cl$_2$] (0.65 g, 1.68 mmol) in benzene (30 mL) was added to a solution of **10** (0.71 g, 1.68 mmol) in benzene (50 mL). The mixture was stirred overnight, and the solvent was then removed under vacuum. The solid was dissolved in benzene (10 mL), and then 50 mL of Et_2O was added to give pale yellow crystals. This crystals were filtered off, washed with Et_2O, and dried under vacuum. Yield: 0.79 g (78%). Anal. Calcd for $C_{18}H_{28}FeO_4P_2PdCl_2$: C, 35.82; H, 4.68. Found: C, 35.94; H, 4.68. ^{1}H NMR ($CDCl_3$): δ 1.36 (t, 12H, J = 6.94 Hz, Me), 4.33 (m, 8H, CH_2), 4.54 (s, 4H, C_5H_4), 4.62 (s, 4H, C_5H_4). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 119.93 (s).^{13}C{^{1}H} NMR ($CDCl_3$): δ 16.10 (t, CH_3, J = 3.2 Hz), 65.50 (t, CH_2, J = 2.5 Hz), 72.63 (t, β-C, C_5H_4, J = 7.0 Hz), 73.62 (t, α-C, C_5H_4, J = 4.8 Hz), 75.05 (dd, *ipso*-C, C_5H_4, J_1 = 2.8, J_2 = 94.8 Hz).

Catalytic Amination of 4-Bromotoluene with Morpholine. 4-Bromotoluene (117 mg 0.684 mmol), morpholine (75 mg, 0.850 mmol), sodium *tert*-butoxide (81 mg, 0.850 mmol), and 1 mol % of palladium catalyst were stirred in dioxane (2.5 mL) under reflux for an appropriate time. The reaction mixture was treated with water and extracted twice with CH_2Cl_2. The organic layer was then dried over Na_2SO_4 and concentrated in vacuo. The product was purified by flash chromatography on silica gel, with a hexane/benzene/diethyl ether (6:1:1) mixture as eluent. Yield of *N*-(4-methylphenyl)-

Table 6. Crystallographic Data for Complexes 13, 15, 16, and 18

	13	15	16	18
formula	$C_{34}H_{28}Cl_2OsP_2Pd\cdot 2CH_2Cl_2$	$C_{38}H_{36}Cl_2FeO_4P_2Pd\cdot 0.25CH_2Cl_2$	$C_{46}H_{52}Cl_2FeP_2Pd\cdot 2.3CH_2Cl_2$	$C_{18}H_{28}Cl_2FeP_2Pd$
T, K	120	153	120	120
cryst syst, space group	monoclinic, $P2_1/c$	orthorhombic, $Fdd2$	monoclinic, $P2_1/n$	monoclinic, $P2_1/n$
a, Å	19.965(3)	25.320(5)	12.283(2)	10.4630(6)
b, Å	10.402(1)	45.294(9)	24.199(5)	16.7987(9)
c, Å	18.939(3)	14.530(3)	16.735(3)	11.5739(7)
α, deg				
β, deg	111.534(3)		98.051(5)	94.6840(10)
γ, deg				
V, Å^3; Z	3658.8(8); 4	16663(6); 16	4925.3(18); 4	2027.5(2); 4
M_r	1035.86	872.99	1095.30	539.49
μ, cm^{-1}	45.13	10.52	11.16	20.22
$F(000)$	2008	7080	2242	1088
d_{calcd}, g cm^{-3}	1.88	1.392	1.477	1.767
$2\theta_{max}$, deg	55	54	52	60
no. of rflns measd (R_{int})	24 780 (0.0384)	4651	23 470 (0.0888)	13 343 (0.0267)
no. of indep rflns	8763	4651	9581	5784
no. of rflns with $I > 2\sigma(I)$	7119	3330	4545	4495
no. of params	415	449	555	217
R1	0.0406	0.0439	0.0704	0.0451
wR2	0.0859	0.0833	0.1425	0.0881
GOF	1.084	0.911	1.09	1.081
max/min peak, e Å^{-3}	1.81/−1.726	0.80/−0.89	1.101/−0.896	1.75/−0.66

morpholine (for the catalyst with the ligand **6**): 121 mg (99%). Mp: 42−43 °C (lit.[35] mp 43−44 °C). ^{1}H NMR ($CDCl_3$): δ 7.07 (m, 2H, C_6H_4), 6.81 (m, 2H, C_6H_4), 3.84 (m, 4H, CH_2), 3.08 (m, 4H, CH_2), 2.26 (s, 3H, CH_3).

Catalytic Amination of 4-Bromobiphenyl with Morpholine. 4-Bromobiphenyl (100 mg 0.429 mmol), morpholine (45 mg, 0.515 mmol), sodium *tert*-butoxide (49 mg, 0.515 mmol), and 1 mol % of palladium catalyst were stirred in dioxane (2 mL) under reflux for 10 min. The yield of the amination product was determined by LC.

Catalytic Amination of 4-Chlorotoluene with Morpholine. The reaction was carried out according to the general procedure 1 using the catalyst with ligand **6**. The reaction mixture was refluxed for 20 h. *N*-(4-Methylphenyl)morpholine was obtained in 12% yield (12 mg) from 86.5 mg (0.684 mmol) of 4-chlorotoluene.

Amination of 1-Chloro-4-(trifluoromethyl)benzene with Morpholine. The reaction was carried out according to the general procedure 1 using the catalyst with ligand **6**. The reaction mixture was refluxed for 20 h. *N*-(4-(Trifluoromethyl)phenyl)morpholine was obtained in 50% yield (79 mg) from 123.5 mg (0.684 mmol) of 1-chloro-4-(trifluoromethyl)benzene. Mp: 69 °C. (lit.[36] mp 69−70 °C). ^{1}H NMR ($CDCl_3$): δ 7.05 (m, 2H, C_6H_4), 6.79 (m, 2H, C_6H_4), 3.81 (m, 4H, CH_2), 3.06 (m, 4H, CH_2).

Amination of 4-Bromotoluene by Various Amines. The reaction was carried out according to the general procedure 1, using 4-bromotoluene (117 mg 0.684 mmol), amine (0.855 mmol), sodium *tert*-butoxide (76 mg 0.855 mmol) and $PdCl_2$***6** (6 mg, 6.84 mmol). Yields of the products were determined by ^{1}H NMR.

N-Dodecyl-4-methylaniline[37] was obtained from *n*-dodecylamine and 4-bromotoluene in 85% yield. ^{1}H NMR ($CDCl_3$): δ 7.01 (m, 2H, C_6H_4), 6.52 (m, 2H, C_6H_4), 4.61 (s, 1H, NH), 3.10 (t, 2H, CH_2), 2.28 (s, 3H, CH_3), 1.62 (m, 2H, CH_2), 1.35 (m, 18H), 0.92 (m, 3H, CH_3).

N-2-(Methoxyphenyl)-4-methylaniline[38] was obtained from 2-methoxyaniline and 4-bromotoluene in 80% yield. ^{1}H NMR ($CDCl_3$): δ 7.04 (m, 2H, C_6H_4), 6.74 (m, 2H, C_6H_4), 6.80 (m, 4H, C_6H_4), 4,23 (s, 1H, NH), 3.77 (s, 3H, OCH_3), 2.26 (s, 3H, CH_3).

N-Benzyl-4-methylaniline[39] was obtained from benzylamine and 4-bromotoluene in 87% yield. ^{1}H NMR ($CDCl_3$): δ 7.33 (m, 4H, C_6H_5), 7.26 (m, 1H, C_6H_5), 7.05 (m, 2H, C_6H_4), 6.53 (m, 2H, C_6H_4), 4.29 (s, 2H, CH_2), 3.94 (s, 1H, NH), 2.26 (s, 3H, CH_3).

N-(4-Methylphenyl)-N-ethylaniline[40] was obtained from *N*-ethylaniline and 4-bromotoluene in 96% yield. ^{1}H NMR ($CDCl_3$): δ 7.14 (m, 2H, C_6H_5), 7.05 (m, 2H, C_6H_4), 6.93 (m, 2H, C_6H_5), 6.83 (m, 2H, C_6H_4), 6.78 (m, 1H, C_6H_4), 3.69 (k, 2H, CH_2, J = 7.2 Hz), 2.26 (s, 3H, CH_3), 1.16 (t, 3H, CH_3, J = 7.2 Hz).

N,N-Diphenyl-4-methylaniline[41] was obtained from *N,N*-diphenylamine and 4-bromotoluene in 99% yield. ^{1}H NMR ($CDCl_3$): δ 7.16 (m, 6H, C_6H_4, C_6H_5), 6.93 (m, 8H, C_6H_4, C_6H_5), 2.26 (s, 3H, CH_3).

Cross-Coupling of 4-Bromotoluene with 4-(Methoxyphenyl)-boronic Acid. 4-Bromotoluene (50 mg 0.292 mmol), 4-(methoxyphenyl)boronic acid (59 mg, 0.385 mmol), potassium carbonate (121 mg, 0.877 mmol), and 1 mol % of palladium catalyst were stirred in a mixture of dioxane (1.5 mL) and water (0.5 mL) under reflux for 10 min. The reaction mixture was treated with water and twice extracted with CH_2Cl_2. The organic layer was then dried over Na_2SO_4 and concentrated in vacuo. The product was purified by flash chromatography on silica gel, with a hexane/benzene (6:1:1) mixture as eluent. Yield of 4-methoxy-4-methylbiphenyl (for the complex **16**): 52 mg (99%). Mp: 127−128 °C (lit.[42] mp 127−128 °C). ^{1}H NMR ($CDCl_3$): δ 7.48 (m, 2H, C_6H_4), 7.42 (m, 2H, C_6H_4), 7.20 (m, 2H, C_6H_4), 6.94 (m, 2H, C_6H_4), 3.81 (s, 3H, OCH_3), 2.36 (s, 3H, CH_3).

X-ray Structure Determination. X-ray diffraction experiments for **13**, **16**, and **18** were carried out with a Bruker SMART 1000 CCD area detector, using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å, ω scans with a 0.3° step in ω and 10 s per frame exposure) at 110 K. The data collection for **15** was performed on a Syntex $P2_1$ diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å, $\theta/2\theta$ scans) at 153 K. Reflection intensities were integrated using SAINT software[43] and the semiempirical method SADABS.[44] The structures were solved by direct methods and refined by full-matrix least squares against F^2 in an anisotropic approximation for non-hydrogen atoms. All hydrogen atoms were placed in geometrically calculated positions and included in final refinements using the "riding" model with the U_{iso}(H) parameters equal to 1.2[U_{eq}(C_i)] or 1.5[U_{eq}(C_{ii})], where U(C_i) and U(C_{ii}) are respectively the equivalent thermal parameters

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of the methyne and methylene carbon atoms to which corresponding H atoms are bonded. Crystal data and structure refinement parameters for **13**, **15**, **16**, and **18** are given in Table 6. All calculations were performed on an IBM PC/AT computer using SHELXTL software.[45]

Acknowledgment. Thanks are due to a CNR-RAS bilateral agreement, to the Russian Foundation for Basic Research (Grant 03-03-32471), and to the Science Support Foundation of the Russian Federation for financial support.

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Supporting Information Available: CIF files giving crystallographic data for compounds **13**, **15**, **16**, and **18**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050869W