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Synthesis, Characterization, and Reactivity of Neutral and Cationic Pd–C,N,N Pincer Complexes

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The *ortho*-palladation of the iminophosphane ligand 6-phenyl-2-[(2,6-diisopropylphenyl)imino]pyridine (**HL**) with $Pd(OAc)_2$ and $PdCl_2(PhCN)_2$ in benzene yields the neutral Pd–C,N,N pincer complexes $Pd(OAc)(\kappa^3\text{-C,N,N-L})$ (**1**) and $PdCl(\kappa^3\text{-C,N,N-L})$ (**2**), respectively. In the presence of $NaBAr'_4$ [$Ar' = 3,5\text{-}(CF_3)_2C_6H_3$], **2** reacts in CH_2Cl_2 with MeCN, PPh_3, or $PH[o\text{-}MeO(C_6H_4)]_2$ to give the cationic palladium(II) pincer complexes $[Pd(CH_3CN)(\kappa^3\text{-C,N,N-L})]BAr'_4$ (**3**), $[Pd(PPh_3)(\kappa^3\text{-C,N,N-L})]BAr'_4$ (**4**) and $\{Pd[PH(o\text{-}MeOC_6H_4)_2](\kappa^3\text{-C,N,N-L})\}BAr'_4$ (**5**), respectively. Complexes **1**–**5** have been characterized by multinuclear NMR and IR spectroscopy. The solid-state structures of **1** and **2** have been determined by single-crystal X-ray diffraction techniques. Both the neutral compounds **1** and **2** and the cationic derivatives **3**, **4**, and **5** were tested as catalyst precursors for the Suzuki cross-coupling of 4-bromo- and 4-chloroacetophenone with phenylboronic acid.

Introduction

Palladacycles constitute a numerous and thoroughly investigated class of organometallics commonly stabilized by four-electron (bidentate) or six-electron (tridentate) donor ligands.[1] The synthesis of palladacycles is relatively facile and the modulation of their electronic and steric properties can be achieved by varying (i) the size of the metallacyclic ring, (ii) the nature of the metallated carbon atom (aliphatic, aromatic, vinylic), (iii) the type of donor atoms (N, P, S, O) in the supporting ligand, and (iv) the nature of the co-ligands. Proper combinations of these factors determine whether dinuclear, mononuclear, neutral, or cationic compounds are formed.

Herrmann's discovery in 1995 that palladacycles can be effective catalysts for Heck coupling reactions of aryl halides has stimulated much research aimed at using these organometallics in C–C bond-forming processes.[2] The most important applications reported so far include Heck coupling, Suzuki and Stille cross-couplings, and Sonogashira reactions.[1a] Some of the most active palladacycle catalysts for Suzuki coupling reactions are reported in Scheme 1.

The C,N-palladacycles **g** and **h** reported by Milstein[3a] and Nájera,[3b] respectively, are the only really efficient phosphane-free catalysts for the Suzuki reaction of bromoarenes and chloroarenes, while the C,N- and C,O-palladacycles **b**–**f** in conjunction with either secondary bulky phosphanes[4] or N-heterocyclic carbenes[5] are very active catalytic systems for the Suzuki reaction of chloroarenes. The phosphinite P,C,P pincer complex **i** described by Bedford exhibits a good activity for bromoarenes and constitutes a successful example of the application of a terdentate palladium(II) pincer complex in a Suzuki reaction.[6] Terdentate Pd–C,N,N pincer complexes have also been used to catalyze Heck and Heck-type reactions.[7]

The ligands that have been employed so far for the synthesis of Pd–C,N,N pincer complexes are shown in Scheme 2.[8] A common structural motif to most ligands is a planar assembly of nitrogen donor atoms from either pyridine rings or imine groups, yet the combination of both moieties in the same molecule has never been tested in palladium *ortho*-metallation.

Aimed at filling this gap, we decided to study the coordination chemistry of the (imino)pyridine ligand 6-phenyl-2-[(2,6-diisopropylphenyl)imino]pyridine (**HL**) (Scheme 3) that has been successfully employed to oligomerize ethylene in conjunction with $CoCl_2$ and MAO.[9] As a result, both neutral and cationic Pd^{II}–C,N,N pincer complexes have been obtained and fully characterized. A preliminary study of the performance of these complexes in Suzuki cross-coupling reactions of 4-bromo- and 4-chloroacetophenone with phenylboronic acid has been carried out and is herein reported.

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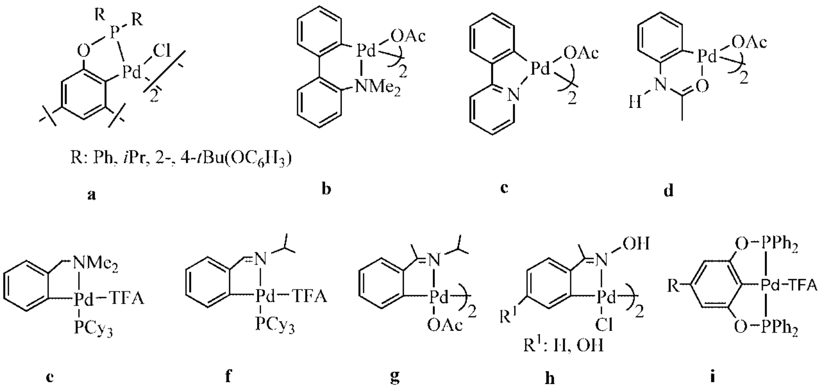
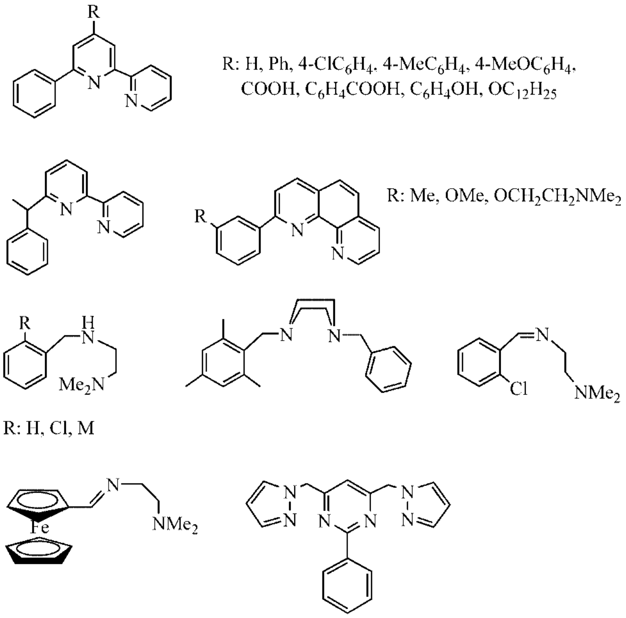
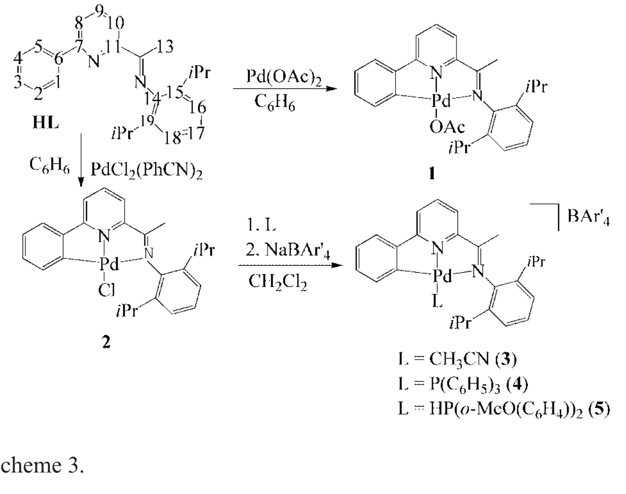


Scheme 1.



Scheme 2.



Scheme 3.

Results and Discussion

The reaction of **HL** with $Pd(OAc)_2$ and $PdCl_2(PhCN)_2$ in refluxing benzene yields the yellow, air-stable, neutral terdentate Pd–C,N,N pincer complexes Pd(OAc)L (**1**) and PdClL (**2**) in fairly good yields (57 and 81%), respectively. Complex **2** was transformed into the monocationic Pd–C,N,N pincer compounds **3**, **4**, and **5** by scavenging the chloride ion with $NaBAr'_4$ in the presence of MeCN, PPh_3, or $PH(o\text{-}MeOC_6H_4)_2$. The synthesis of the latter compounds was readily achieved by dissolving **2** in oxygen-free dichloromethane and adding acetonitrile, PPh_3, or the new secondary monophosphane $PH(o\text{-}MeOC_6H_4)_2$ (Scheme 3).

The cationic complexes were isolated in good yields, from 60–70%, as yellow, air- and moisture-stable solids. All our attempts to isolate **3**, **4**, and **5** with chloride as the counterion were unsuccessful.

The solid-state structures of **1** and **2** have been determined by a single-crystal X-ray diffraction analysis. Crystallographic data as well as selected bond lengths and angles of both compounds are reported in Tables 1 and 2, respectively, while ORTEP illustrations are presented in Figure 1.

The asymmetric unit of **1** contains one molecule of the neutral pincer complex, while that of **2** contains one molecule of **2** together with one molecule of CH_2Cl_2 and half a molecule of toluene located on an inversion center. Both complexes exhibit a distorted square-planar coordination geometry. The metal center in **1** deviates by 0.004(6) Å in the direction of C(20) from the plane defined by the atoms C(1), N(1), and N(2). From the analogous plane, **2** deviates by 0.016(6) Å in the direction of C(23). In both structures, the Pd atom is coordinated by nitrogen atoms from pyridine and imine groups and by one carbon atom, C(1), from the 6-phenyl ring. The square-planar geometry is completed by an oxygen atom, O(1) from an acetate ligand in **1**, and by a chloride atom in **2**. The slightly longer Pd(1)–N(2) bond in **1** as compared to **2** is probably due to a significant steric interaction between the acetate unit and an isopropyl group of the ligand [shortest O···H contact distance of 2.844 Å between O(2) and H(21B)]. A longer $Pd–N_{imine}$ distance in **1** was also inferred from the IR spectrum which shows a less pronounced red shift of the C=N band in **1** (21 cm^{-1})

Table 1. Crystallographic data for **1** and **2**·CH_2Cl_2·0.5 C_7H_8.

	1	**2**·CH_2Cl_2·0.5 C_7H_8
Empirical formula	$C_{27}H_{30}N_2O_2Pd$	$C_{29.5}H_{33}Cl_3N_2Pd$
Formula mass	520.93	628.33
Temperature [K]	293(2)	293(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$P2_1/c$
a [Å]	12.050(3)	9.788(7)
b [Å]	13.909(15)	12.924(2)
c [Å]	14.530(9)	23.027(6)
β [°]	90.0	91.97(3)
V [Å^3]	2435(3)	2911(2)
Z [g m^{-3}]	4	4
$D_{calcd.}$ [g m^{-3}]	1.421	1.434
Absorption coefficient [mm^{-1}]	0.787	0.933
F(000)	1072	1284
Crystal size [mm]	$0.70 \times 0.28 \times 0.25$	$0.4 \times 0.2 \times 0.2$
θ range for data collection [°]	2.03–25.08	2.08–25.02
Limiting indices	$0 \le h \le 14$	$-11 \le h \le 11$
	$0 \le k \le 16$	$0 \le k \le 15$
	$0 \le l \le 17$	$0 \le l \le 27$
Measured reflections	2427	5087
Unique reflections	2427	5087
GOF on F^2	1.066	1.012
Data/restraints/parameters	2427/0/289	5087/8/302
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0470$, $wR_2 = 0.1226$	$R_1 = 0.0583$, $wR_2 = 0.1291$
R indices (all data)	$R_1 = 0.0555$, $wR_2 = 0.1281$	$R_1 = 0.1474$, $wR_2 = 0.1586$
Largest diff. peak/hole [e·Å^{-3}]	1.076/–1.271	0.762/–0.892

Table 2. Selected bond lengths [Å] and angles [°] for compounds **1** and **2**·CH_2Cl_2·0.5 C_7H_8.

	1	**2**·CH_2Cl_2·0.5 C_7H_8
Pd(1)–N(1)	1.954(6)	1.955(5)
Pd(1)–N(2)	2.184(6)	2.156(6)
Pd(1)–C(1)	1.957(8)	1.970(7)
Pd(1)–O(1)	2.051(6)	
Pd(1)–Cl(1)		2.295(2)
N(2)–C(12)	1.262(10)	1.286(9)
N(1)–Pd(1)–N(2)	77.7(3)	77.4(2)
N(1)–Pd(1)–C(1)	81.8(3)	81.6(3)
C(1)–Pd(1)–O(1)	98.7(3)	
N(1)–Pd(1)–O(1)	171.5(3)	
C(1)–Pd(1)–Cl(1)		97.6(2)
N(1)–Pd(1)–Cl(1)		177.9(2)

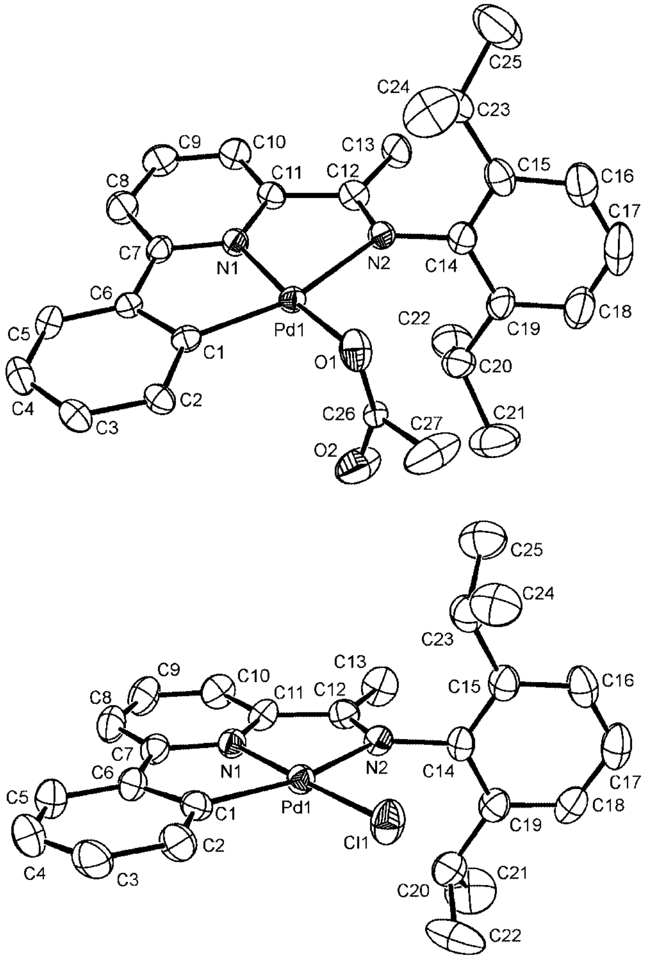


Figure 1. ORTEP representation (30% probability displacement ellipsoids) of compounds **1** (top) and **2** (bottom). Hydrogen atoms as well as solvent molecules are omitted for clarity.

as compared to **2** (30 cm^{-1}). The Pd(1)–C(1) bond lengths of either structure [1.957(8) Å in **1** and 1.970(7) Å in **2**] match well the values reported for other pincer Pd^{II} systems.[8a,8c,8d,8f,8h,8i] The two bite angles [N(1)–Pd(1)–C(1): 81.8(3)° in **1**; 81.6(3)° in **2**; N(1)–Pd(1)–N(2): 77.7(3)° in **1**; 77.4(2)° in **2**] are comparable in either structure, while the coordination angle N(1)–Pd(1)–O(1) of 171.5(3)° in **1** and the coordination angle N(1)–Pd(1)–Cl(1) of 177.9(2)° in **2** are significantly different. Indeed, **1** shows a deviation of the bonded oxygen atom O(1) by 0.292(17) Å from the plane defined by C(1), N(1), and N(2) in the direction of C(23), while **2** exhibits a deviation of Cl(1) by 0.111(16) Å from the analogous plane in the direction of C(23). In both crystal structures, the 2,6-(diisopropyl)phenyl moiety is, as expected, tilted with respect to the coordination plane, showing a dihedral angle of 76.1(5)° and 85.8(4)° in **1** and **2**, respectively, due to the pronounced steric repulsion between the coordinating acetate and an isopropyl group from the ligand.

Compounds **1**–**5** have been characterized in solution by multinuclear 1D and homo- and heteronuclear correlated 2D NMR spectroscopy.[10a] $^{13}C\{^1H\}$ NMR spectroscopy has proved to be a useful technique to elucidate the solution structure of all compounds, especially to assess the presence of a Pd–C bond involving the phenyl ring attached at the 6-position of the pyridine unit.[10b–10e] Significant ^{13}C NMR chemical shifts, namely those pertaining to the C-1, C-2,

Table 3. Selected $^{13}C\{^1H\}$ chemical shifts for HL and for compounds 1–5.

	C-1 ($^2J_{C,P}$ [Hz])	C-2 ($^3J_{C,P}$ [Hz])	C-4	C-12
HL	127.67	129.69	136.73	168.50
1	153.22	135.80	124.88	172.30
2	153.16	137.71	125.15	172.70
3	153.17	136.08	128.03	176.43
4	150.22 (4.9)	140.21 (10.5)	126.72	178.30
5	151.98 (5.4)	136.72 (10.5)	126.54	177.40

Table 4. Selected ^{1}H chemical shifts for **HL** and for compounds **1**–**5**.

	2-H (multiplicity) ([$^3J_{H,H}$, $^4J_{H,H}$, $^4J_{P,H}$ [Hz])	3-H (multiplicity) ($^3J_{H,H}$, $^4J_{H,H}$ [Hz])	4-H (multiplicity) ($^3J_{H,H}$, $^4J_{H,H}$ [Hz])	5-H (multiplicity) ($^3J_{H,H}$, $^4J_{H,H}$ [Hz])	13-H (multiplicity)
HL	7.54 (t) (7.4)	7.48 (tt) (7.2, 1.2)	7.54 (t) (7.4)	8.18 (d) (7.2, 1.4)	2.38 (s)
1	7.19 (dd) (7.5, 1.2)	7.08 (td) (7.4, 1.6)	7.02 (td) (7.5, 1.4)	7.33 (dd) (6.6, 1.5)	2.19 (s)
2	7.41 (dd) (7.4, 1.7)	7.15 (td) (7.4, 1.7)	7.11 (td) (7.4, 1.5)	7.84 (dd) (7.4, 1.6)	2.21 (s)
3	6.99 (dd) (7.6, 1.1)	7.21 (td) (7.5, 1.2)	7.13 (td) (7.6, 1.6)	7.40 (dd) (7.6, 1.5)	2.24 (s)
4	6.32 (ddd) (8.1, 0.9, 5.3)	6.52 (td) (8.1, 1.6)	6.99 (td) (7.5, 0.8)	7.43 (dd) (7.7, 1.6)	2.10 (s)
5	6.24 (ddd) (7.8, 1.0, 5.3)	6.74 (td) (7.7, 1.5)	7.06 (td) (7.4, 1.0)	7.44 (dd) (7.8, 1.5)	2.27 (s)

and C-4 carbon atoms from the phenyl ring and to the imine carbon atom C-12 are reported in Table 3, which also provides ^{13}C NMR spectroscopic data for the free ligand. In line with the literature, the signals of C-1 and C-2 are shifted down-field as compared to the free ligand, while the signal of C-4 is shifted up-field.[10e] The ^2J(C,P) coupling constants of 4.9 Hz in **4** and 5.4 Hz in **5** provide further evidence for *ortho*-palladation involving the 6-phenyl ring. The coordination of the imine nitrogen atom to the Pd^{II} center can be safely assessed on the basis of the down-field shift of the imine carbon signal of C-12.

The ^{1}H NMR spectra of **1**–**5** are fully consistent with *ortho*-palladation of the 6-phenyl ring (Table 4).

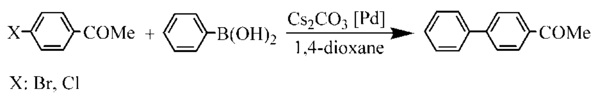
Of particular relevance to confirm the occurrence of *ortho*-metallation are the multiplicities of the resonances of the 6-phenyl ring. Indeed, the signals of 2-H and 5-H appear as a doublet of doublet and 3-H and 4-H show a triplet of doublet, while the free ligand exhibits a doublet for the *ortho* protons 1-H and 5-H, triplets for 2-H and 4-H and a triplet of triplet for the *para* proton 3-H. The small $^4J_{P,H}$ coupling constant of 5.3 Hz observed for 2-H in the ^{1}H NMR spectra of compounds **4** and **5** is consistent with the coordination of PPh_3 and HP[*o*-MeO(C_6H_4)]$_2$. The coordination of the imine nitrogen atom to the palladium atom is confirmed by an up-field shift of the methylimine resonance (13-H), as compared to the free ligand.

Compounds **1**–**5** have been tested as catalyst precursors for the Suzuki cross-coupling reaction of 4-bromo- and 4-chloroacetophenone with phenylboronic acid in the presence of Cs_2CO_3 as the basic co-reagent in 1,4-dioxane at 100 °C (Scheme 4). This catalytic protocol is rather common for Suzuki reactions leading to selective production of the unsymmetrically substituted biaryl.[1a,1b] Selected results are given in Table 5.

Table 5. Suzuki coupling of 4-bromo- and 4-chloroacetopheneone with phenylboronic acid in the presence of **1**, **2**, **3**, **4** and **5**.

Entry[a]	Complex	Substrate	[Pd] [%]	Time [h]	TON[b]
1	Pd(OAc)$_2$	Br	1.0	2	64
2	Pd(OAc)$_2$	Br	1.0	4	89
3	Pd(OAc)$_2$	Br	0.01	4	70
4	**1**	Br	1.0	2	25
5	**1**	Br	1.0	4	99
6[c]	**1**	Br	1.0	4	31
7	**2**	Br	1.0	2	83
8	**2**	Br	1.0	4	85
9	**3**	Br	1.0	2	13
10	**3**	Br	1.0	4	46
11	**4**	Br	1.0	2	100
12	**4**	Br	0.01	2	6200
13	**4**	Br	0.01	4	8900
14	**5**	Br	1.0	2	98
15	**5**	Br	0.01	2	3400
16	**5**	Br	0.01	4	9700
17	Pd(OAc)$_2$	Cl	1.0	8	0
18	**1**	Cl	1.0	8	17
19	**2**	Cl	1.0	8	2
20	**3**	Cl	1.0	8	14
21	**4**	Cl	1.0	4	17
22	**4**	Cl	1.0	8	57
23	**5**	Cl	1.0	4	61
24	**5**	Cl	1.0	8	86

[a] Catalytic conditions: 2×10^{-6} mol of Pd precatalyst, 2×10^{-4} mol of substrate, 3×10^{-4} mol of phenylboronic acid, 6×10^{-4} mol of Cs_2CO_3, *T*: 100 °C, solvent: 1,4-dioxane (15 mL). [b] TON determined by ^{1}H NMR in $CDCl_3$. [c] 1,4-Dioxane/water (14:1, v:v).



Scheme 4.

All catalytic coupling reactions were carried out under an inert gas in freshly distilled 1,4-dioxane in order to avoid the risk of imine hydrolysis, which may be responsible for the low catalytic activity observed in a water/dioxane mixture (Entry 6). Examination of withdrawn samples showed the formation of the biaryl product after only 5 min. Unlike the reaction catalyzed by Pd(OAc)$_2$, no Pd metal precipitation was observed using **1**–**5** as the catalyst precursors. In situ NMR experiments showed the absence of free phosphane ligands during the reaction catalyzed by **4** and **5**.

In line with the results reported in the literature, 4-bromoacetophenone is much more reactive than the analogous chloro derivative, due to the lower bond strength of Ar–Br as compared to Ar–Cl.[11] The coupling of 4-bromoacetophenone with phenylboronic acid is catalyzed by both the phosphane-free precursors **1**, **2**, and **3** and the phosphane-modified precursors **4** and **5**. However, the latter form much more active catalysts, which has been previously observed and attributed to the formation of coordinatively unsaturated (phosphane)Pd^0 catalysts.[1b] As a general trend, the cationic precursors originate more efficient catalysts.

In the Suzuki cross-coupling of 4-chloroacetophenone only the monophosphane-modified precursors **4** and **5** have shown a significant activity.[12] Interestingly, the catalyst modified with the secondary phosphane PH(*o*-MeOC$_6$H$_4$)$_2$ is the most active with both 4-bromo- and 4-chloroacetophenone, which is consistent with Indolese's finding that bulky secondary monophosphanes in conjunction with Pd–C,N or Pd–C,O palladacycles provide powerful systems for Suzuki and Heck reactions.[4] Indeed, most of the really efficient catalytic systems for Suzuki cross-coupling contain bulky monophosphanes,[12] hemilable P–O[13] and P–N ligands,[14] and 1,3-disubstituted imidazol-2-ylidenes.[15]

In the case of **5**, an in situ NMR study under catalytic conditions has shown the occurrence of phosphane deprotonation to give various unidentified phosphido–palladium species, which might be responsible for the high catalytic activity.

Conclusions

New Pd^{II}–C,N,N pincer complexes have been synthesized and fully characterized in both the solid state and solution. As a probe reaction to test their potential in homogeneous catalysis, these complexes have been employed as catalyst precursors for cross-coupling reactions of 4-bromo- and 4-chloroacetophenone with phenylboronic acid to give 4-acetylbiphenyl. Only the phosphane-modified complexes have shown significant activity. This activity, however, is far lower than the most active catalysts reported in the literature.

Experimental Section

General: All manipulations were carried out under nitrogen using Schlenk-type techniques. All the solid compounds were collected on sintered-glass frits and washed with appropriate solvents before being dried in a stream of nitrogen. PdCl$_2$(C$_6$H$_5$CN)$_2$[16] and NaB[C$_6$H$_3$(CF$_3$)$_2$]$_4$ (NaBAr′$_4$)[17] were prepared according to literature methods. The ligands (2,6-diisopropylphenyl)[1-(6-phenylpyridin-2-yl)ethylidene]amine (**HL**) and 1-(6-phenylpyridin-2-yl)ethanone were prepared as reported in the literature.[9] The solvents were distilled under nitrogen from Na (*n*-pentane, diethyl ether, benzene) or CaH$_2$ (CH$_2$Cl$_2$). All the other reagents and solvents were used as purchased from commercial suppliers. Deuterated solvents for NMR measurements were dried with molecular sieves. Elemental analyses were performed with a Carlo Erba Model 1106 elemental analyzer. Infrared spectra were recorded with an FT-IR Spectrum GX instrument. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded at 200.13, 50.32, and 81.01 MHz, respectively, with a Bruker ACP-200 spectrometer or at 400.13, 100.62, and 161.98 MHz, respectively, with a Bruker Avance DRX-400 spectrometer. Chemical shifts are reported in ppm (δ) with reference to either TMS as an internal standard [^{1}H and ^{13}C{^{1}H} NMR spectra] or 85% H$_3$PO$_4$ as an external standard [^{31}P{^{1}H} NMR spectra]. The assignment of ^{1}H and ^{13}C signals was based on 1D and 2D NMR experiments, such as ^{1}H COSY, ^{1}H NOESY, and ^{1}H-^{13}C correlations using degassed nonspinning samples. All the 2D NMR spectra were recorded with a Bruker Avance DRX-400 instrument using pulse sequences suitable for phase-sensitive representations using TPPI. The ^{1}H-^{13}C correlations were recorded using an HMQC sequence with decoupling during acquisition. GC analyses were performed with a Shimadzu GC-14A gas chromatograph equipped with a flame ionization detector and a 30 m (0.25 mm i.d., 0.25 μm film thickness) SPB-1 Supelco fused silica capillary column. GC-MS analyses were performed with a Shimadzu QP 5000 apparatus equipped with a column identical to that used for GC analysis.

Catalytic Reactions: 1,4-Dioxane (15 mL) was degassed in a round-bottomed flask by means of vacuum/nitrogen cycles. To this solvent were added 4-bromoacetophenone or 4-chloroacetophenone (2×10^{-4} mol), phenylboronic acid (36 mg, 3×10^{-4} mol), CsCO$_3$ (115 mg, 6×10^{-4} mol) and the appropriate precatalyst (2×10^{-6} mol) at room temperature under nitrogen. The resulting suspension was heated under nitrogen to 100 °C with stirring to give a clear solution. Heating was continued for the desired time. Then, the solution was cooled to room temperature and ethyl acetate (15 mL) was added. The solid products were removed from the solution by filtration and the organic layer was washed with water (three 30 mL portions) to remove CsCO$_3$. The aqueous layer was extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried with MgSO$_4$ and concentrated to yield a pale yellow solid. The yield of the product was determined by ^{1}H NMR in CDCl$_3$.

Syntheses

PH(*o*-CH$_3$OC$_6$H$_4$)$_2$: The bis(*o*-methoxyphenyl)phosphane oxide HPO(*o*-CH$_3$OC$_6$H$_4$)$_2$ was synthesized as described in the literature.[18] The subsequent reduction of the phosphane oxide was performed applying a protocol similar to that published by Vineyard.[19] HSiCl$_3$ (12.1 mL, 120.0 mmol) was added to a solution of bis(*o*-methoxyphenyl)phosphane oxide (10.48 g, 40.0 mmol) and triethylamine (16.7 mL, 120.0 mmol) in acetonitrile (250 mL) at room temperature. The reaction mixture was refluxed for 8 h. Afterwards, the solution was cooled to 0 °C and a solution of KOH (40 g) in water (150 mL) was slowly added to the reaction mixture. An off-white solid precipitated that was, however, dissolved at the end of the addition to form a clear two-phase system. The organic phase was separated and the solvent was removed under reduced pressure. The crude product was washed with degassed ethanol (30 mL) and the product was filtered off and dried in a stream of nitrogen. Yield: 7.19 g (73%). C$_{14}$H$_{14}$O$_2$P (245.1): calcd. C 68.60, H 5.71; found C 68.20; H 5.60. ^{1}H NMR (200.13 MHz, CDCl$_3$, 294 K): δ = 3.78 (s, 6 H, OCH$_3$), 5.23 (d, $^1J_{\mathrm{H,P}}$ = 229 Hz, 1 H, PH), 6.80–7.40 (m, 8 H, C$_6$H$_4$) ppm. ^{31}P{^{1}H} NMR (81.01 MHz, CDCl$_3$, 294 K): δ = –71.70 (s) ppm.

[6-C$_6$H$_4$-py-2-C(Me)=N(2,6-*i*Pr$_2$C$_6$H$_3$)]PdOAc (1): The ligand **HL** (300 mg, 0.84 mmol) and Pd(OAc)$_2$ (190 mg, 0.84 mmol) were dissolved in degassed benzene (30 mL). The resultant red solution was heated at 60 °C for 16 h. Afterwards, this solution was filtered through Celite and concentrated to 2 mL. To this solution diethyl ether (15 mL) was added to precipitate a yellow-green compound, which was filtered off and dried in a stream of nitrogen. Yield: 250 mg (57%). C$_{27}$H$_{30}$N$_2$O$_2$Pd (520.69): calcd. C 62.28, H 5.76, N 5.38; found C 62.10, H 5.55, N 5.10. ^{1}H NMR (400.13 MHz, CDCl$_3$, 294 K): δ = 1.15 [d, $^3J_{\mathrm{H,H}}$ = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.40 [d, $^3J_{\mathrm{H,H}}$ = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.75 [s, 3 H, CH$_3$CO$_2$], 2.19 [s, 3 H, 13-H], 3.17 [sept, $^3J_{\mathrm{H,H}}$ = 6.8 Hz, 2 H, C*H*(CH$_3$)$_2$], 7.02 (td, $^3J_{\mathrm{H,H}}$ = 7.5, $^4J_{\mathrm{H,H}}$ = 1.4 Hz, 1 H, 4-H), 7.08 (td, $^3J_{\mathrm{H,H}}$ = 7.4,

$^{4}J_{H,H}$ = 1.6 Hz, 1 H, 3-H), 7.19 (dd, $^{3}J_{H,H}$ = 7.5, $^{4}J_{H,H}$ = 1.2 Hz, 1 H, 2-H), 7.22–7.29 (m, 3 H, 16–18-H), 7.33 (dd, $^{3}J_{H,H}$ = 6.6, $^{4}J_{H,H}$ = 1.5 Hz, 1 H, 5-H), 7.35 (dd, $^{3}J_{H,H}$ = 6.1, $^{4}J_{H,H}$ = 0.9 Hz, 1 H, 10-H), 7.73 (dd, $^{3}J_{H,H}$ = 8.4, $^{4}J_{H,H}$ = 0.9 Hz, 1 H, 8-H), 7.94 (t, $^{3}J_{H,H}$ = 7.7 Hz, 1 H, 9-H) ppm. $^{13}C\{^{1}H\}$ NMR (100.62 MHz, $CDCl_3$, 294 K): δ = 17.59 (C-13), 23.25 (CH_3CO_2), 23.72 [CH(CH_3)$_2$], 23.87 [CH(CH_3)$_2$], 28.71 [CH(CH_3)$_2$], 121.05 (C-8), 121.07 (C-10), 123.48 (C-16, C-18), 124.01 (C-5), 124.88 (C-4), 126.92 (C-17), 130.85 (C-3), 135.80 (C-2), 138.72 (C-15, C-19), 139.47 (C-9), 141.02 (C-14), 146.83 (C-6), 153.20 (C-11), 153.22 (C-1), 165.34 (C-7), 172.30 (C-12), 176.81 (CH_3COO) ppm. IR (KBr): $\tilde{\nu}$ = 1617 (C=N), 1717 (C=O) cm^{-1}.

[6-C_6H_4-py-2-C(Me)=N(2,6-*i*$Pr_2C_6H_3$)]PdCl (2): The ligand **HL** (150 mg, 0.42 mmol) and $PdCl_2(C_6H_5CN)_2$ (160 mg, 0.42 mmol) were dissolved in benzene (20 mL) at room temperature. The orange suspension was refluxed for 12 h. During this time a yellow precipitate formed. The suspension was concentrated to dryness and the yellow powder was suspended in diethyl ether and filtered off, washed several times with diethyl ether and then dried in a stream of nitrogen. Yield: 180 mg (86.1%). $C_{25}H_{27}ClN_2Pd$ (497.14): calcd. C 60.40, H 5.43, N 5.63; found C 60.62, H 5.57, N 5.70. ^{1}H NMR (400.13 MHz, $CDCl_3$, 294 K): δ = 1.16 [d, $^{3}J_{H,H}$ = 6.9 Hz, 6 H, CH(CH_3)$_2$], 1.40 [d, $^{3}J_{H,H}$ = 6.8 Hz, 6 H, CH(CH_3)$_2$], 2.21 (s, 3 H, 13-H), 3.06 [sept, $^{3}J_{H,H}$ = 7.0 Hz, 2 H, CH(CH_3)$_2$], 7.11(td, $^{3}J_{H,H}$ = 7.4, $^{4}J_{H,H}$ = 1.5 Hz, 1 H, 4-H), 7.15 (td, $^{3}J_{H,H}$ = 7.4, $^{4}J_{H,H}$ = 1.7 Hz, 1 H, 3-H), 7.23–7.30 (m, 3 H, 16–18-H), 7.41 (dd, $^{3}J_{H,H}$ = 7.4, $^{4}J_{H,H}$ = 1.7 Hz, 1 H, 2-H), 7.53 (dd, $^{3}J_{H,H}$ = 7.8, $^{4}J_{H,H}$ = 0.9 Hz, 1 H, 10-H), 7.75 (dd, $^{3}J_{H,H}$ = 8.3, $^{4}J_{H,H}$ = 0.7 Hz, 1 H, 8-H), 7.84 (dd, $^{3}J_{H,H}$ = 7.4, $^{4}J_{H,H}$ = 1.6 Hz, 1 H, 5-H), 7.99 (t, $^{3}J_{H,H}$ = 7.8 Hz, 1 H, 9-H) ppm. $^{13}C\{^{1}H\}$ NMR (100.62 MHz, $CDCl_3$, 294 K): δ = 17.40 (C-13), 23.47 [CH(CH_3)$_2$], 24.02 [CH(CH_3)$_2$], 28.74 [CH(CH_3)$_2$], 120.71 (C-8), 121.0 (C-10), 123.50 (C-16, C-18), 124.31 (C-5), 125.15 (C-4), 127.20 (C-17), 131.0 (C-3), 137.71 (C-2), 138.2 (C-15, C-19), 138.91 (C-9), 141.0 (C-14), 147.0 (C-6), 152.98 (C-11), 153.15 (C-1), 165.20 (C-7), 172.70 (C-12) ppm. IR (KBr): $\tilde{\nu}$ = 1612 (C=N) cm^{-1}.

{[6-C_6H_4-py-2-C(Me)=N(2,6-*i*$Pr_2C_6H_3$)]Pd($NCCH_3$)}BAr′$_4$ (3): Compound **2** (60 mg, 0.12 mmol) was dissolved in a mixture of dichloromethane (15 mL) and acetonitrile (1 mL). To this yellow solution NaBAr′$_4$ (115 mg, 0.13 mmol) was added. The yellow solution was stirred for 30 min. During this time NaCl precipitated, which was removed by filtration through Celite. The clear yellow solution was then concentrated to dryness. No recrystallization was needed. Yield: 120 mg (73.0%). $C_{59}H_{39}BF_{24}N_3Pd$ (1362.61): calcd. C 52.00, H 2.86, N 3.08; found C 52.10, H 2.92, N 3.15. ^{1}H NMR (400.13 MHz, $CDCl_3$, 294 K): δ = 1.19 [d, $^{3}J_{H,H}$ = 6.9 Hz, 6 H, CH(CH_3)$_2$], 1.30 [d, $^{3}J_{H,H}$ = 6.8 Hz, 6 H, CH(CH_3)$_2$], 2.00 (s, 3 H, CH_3CN), 2.24 (s, 3 H, 13-H), 2.95 [sept, $^{3}J_{H,H}$ = 6.8 Hz, 2 H, CH(CH_3)$_2$], 6.99 (dd, $^{3}J_{H,H}$ = 7.6, $^{4}J_{H,H}$ = 1.1 Hz, 1 H, 2-H), 7.13 (td, $^{3}J_{H,H}$ = 7.6, $^{4}J_{H,H}$ = 1.6 Hz, 1 H, 4-H), 7.21 (td, $^{3}J_{H,H}$ = 7.5, $^{4}J_{H,H}$ = 1.2 Hz, 1 H, 3-H), 7.28–7.35 (m, 3 H, 16–18-H), 7.40 (dd, $^{3}J_{H,H}$ = 7.6, $^{4}J_{H,H}$ = 1.5 Hz, 1 H, 5-H), 7.41 (dd, $^{3}J_{H,H}$ = 7.8, $^{4}J_{H,H}$ = 0.9 Hz, 1 H, 10-H), 7.54 [br. s, 4 H, *p*- B[$C_6H_3(CF_3)_2$]$_4$], 7.66 (dd, $^{3}J_{H,H}$ = 8.4, $^{4}J_{H,H}$ = 0.8 Hz, 1 H, 8-H), 7.73 [m, 8 H, *o*-B[$C_6H_3(CF_3)_2$]$_4$], 7.83 (t, $^{3}J_{H,H}$ = 7.9 Hz, 1 H, 9-H) ppm. $^{13}C\{^{1}H\}$ NMR (100.12 MHz, $CDCl_3$, 294 K): δ = 3.07 (CH_3CN), 17.52 (C-13), 23.35 [CH(CH_3)$_2$], 23.94 [CH(CH_3)$_2$], 28.91 [CH(CH_3)$_2$], 118.21 [*p*-$C_6H_3(CF_3)_2$], 121.19 (CH_3CN), 122.77 (C-8), 123.31 (C-10), 124.96 (C-16, C-18), 125.28 (q, $^{1}J_{C,F}$ = 272.6 Hz, CF_3), 126.70 (C-5), 128.03 (C-4), 129.01 (C-17), 129.71 (q, $^{2}J_{C,P}$ = 32.5 Hz, CCF_3), 132.96 (C-3), 135.60 [*o*-$C_6H_3(CF_3)_2$], 136.08 (C-2), 138.87 (C-15, C-19), 140.76 (C-14), 142.32 (C-9), 147.87 (C-6), 153.17 (C-1), 154.39 (C-11), 162.68 (q, $^{1}J_{C,B}$ = 49.5 Hz, *ipso*-C–B), 167.36 (C-7), 176.43 (C-12) ppm. IR (KBr): $\tilde{\nu}$ = 1609 (C=N), 2327 (C–N), 2300 (C–N) cm^{-1}.

{[6-C_6H_4-py-2-C(Me)=N(2,6-*i*$Pr_2C_6H_3$)]Pd[P(C_6H_5)]$_3$}BAr′$_4$ (4): Compound **2** (80 mg, 0.16 mmol) and PPh_3 (40 mg, 0.16 mmol) were dissolved in degassed CH_2Cl_2 (20 mL). To this yellow solution NaBAr′$_4$ (170 mg, 0.19 mmol) was added. During a reaction time of 3 h, NaCl was formed, which was removed by filtration through Celite. The clear yellow solution was then concentrated to 2 mL and *n*-hexane was added to precipitate a yellow product, which was filtered off and dried in a stream of nitrogen. Yield: 160 mg (62.7%). $C_{75}H_{54}BF_{24}N_2PPd$ (1586.78): calcd. C 56.77, H 3.40, N 1.76; found C 56.62, H 3.55, N 1.84. ^{1}H NMR (400.13 MHz, $CDCl_3$, 294 K): δ = 0.79 [d, $^{3}J_{H,H}$ = 6.8 Hz, 6 H, CH(CH_3)$_2$], 1.01 [d, $^{3}J_{H,H}$ = 6.8 Hz, 6 H, CH(CH_3)$_2$], 2.10 (s, 3 H, 13-H), 2.86 [sept, $^{3}J_{H,H}$ = 6.8 Hz, 2 H, CH(CH_3)$_2$], 6.32 (ddd, $^{3}J_{H,H}$ = 8.1, $^{3}J_{H,P}$ = 5.3, $^{4}J_{H,H}$ = 0.8 Hz, 1 H, 2-H), 6.52 (td, $^{3}J_{H,H}$ = 8.1, $^{4}J_{H,H}$ = 1.6 Hz, 1 H, 3-H), 6.88 (d, $^{3}J_{H,H}$ = 7.8 Hz, 2 H, 16-H, 18-H), 6.99 (td, $^{3}J_{H,H}$ = 7,5, $^{4}J_{H,H}$ = 0.8 Hz, 1 H, 4-H), 7.15 (t, $^{3}J_{H,H}$ = 7.8 Hz, 1 H, 17-H), 7.23 (m, 12 H, *o*+*m*-PPh_3), 7.41 (m, 3 H, *p*-PPh_3), 7.43 (dd, $^{3}J_{H,H}$ = 7.7, $^{4}J_{H,H}$ = 1.6 Hz, 1 H, 5-H), 7.52 (d, 1 H, 10-H), 7.53 {br. s, 4 H, *p*-B[$C_6H_3(CF_3)_2$]$_4$}, 7.74 {m, 8 H, *o*-B[$C_6H_3(CF_3)_2$]$_4$}, 7.88 (t, $^{3}J_{H,H}$ = 8.2 Hz, 1 H, 9-H), 7.89 (d, $^{3}J_{H,H}$ = 8.2 Hz, 1 H, 8-H) ppm. $^{13}C\{^{1}H\}$ NMR (100.62 MHz, $CDCl_3$, 294 K): δ = 18.90 (C-13), 22.71 [CH(CH_3)$_2$], 23.50 [CH(CH_3)$_2$], 28.73 [CH(CH_3)$_2$], 117.50 [*p*-$C_6H_3(CF_3)_2$], 122.10 (C-8), 122.60 (C-10), 124.20 (C-16, C-18), 124.50 (q, $^{1}J_{CF}$ = 272.6 Hz, CF_3), 125.80 (C-5), 126.72 (C-4), 128.0 (*p*-PPh_3), 128.80 (d, $^{3}J_{C,P}$ = 10.8 Hz, *m*-PPh_3), 128.80 (q, $^{2}J_{C,P}$ = 32.5 Hz, CCF_3), 128.90 (C-17), 128.90 (d, $^{1}J_{C,P}$ = 49.8 Hz, *ipso*-PPh_3), 130.90 (d, $^{4}J_{C,P}$ = 4.5 Hz, C-3), 131.50 (*o*-PPh_3), 134.80 [*o*-$C_6H_3(CF_3)_2$], 137.80 (C-15, C-19), 140.21 (d, $^{3}J_{C,P}$ = 10.5 Hz, C-2), 141.80 (C-9), 142.80 (C-14), 148.10 (C-6), 150.22 (d, $^{2}J_{C,P}$ = 4.9 Hz, C-1), 151.98 (C-11), 161.80 (q, $^{1}J_{C,B}$ = 49.5 Hz, *ipso*-CB), 164.20 (C-7), 178.30 (C-12) ppm. $^{31}P\{^{1}H\}$(161.98 MHz, $CDCl_3$, 294 K): δ = 39.2 (s) ppm. IR (KBr): $\tilde{\nu}$ = 1608 (C=N) cm^{-1}.

{[6-C_6H_4-py-2-C(Me)=N(2,6-*i*$Pr_2C_6H_3$)]Pd[PH(*o*-MeOC_6H_4)]$_2$}-BAr′$_4$ (5): Compound **2** (100 mg, 0.22 mmol) and PH(*o*-MeO-C_6H_4)$_2$(53 mg, 0.22 mmol) were dissolved in degassed CH_2Cl_2 (20 mL). To this yellow solution NaBAr′$_4$ (190 mg, 0.21 mmol) was added. During a reaction time of 2 h NaCl was formed, which was removed by filtration through Celite. The clear yellow solution was then concentrated to 3 mL and *n*-hexane was added to precipitate a bright yellow product, which was filtered off and dried in a stream of nitrogen. Yield: 0.16 g, (60.0%). $C_{71}H_{54}BF_{24}N_2O_2PPd$ (1570.71): calcd. C 54.29, H 3.44, N 1.78; found C 54.15, H 3.33, N 1.67. ^{1}H NMR (400.13 MHz, $CDCl_3$, 294 K): δ = 0.85 [d, $^{3}J_{H,H}$ = 6.8 Hz, 6 H, CH(CH_3)$_2$], 1.06 [d, $^{3}J_{H,H}$ = 6.8 Hz, 6 H, CH(CH_3)$_2$], 2.27 (s, 3 H, 13-H), 2.86 [sept, $^{3}J_{H,H}$ = 6.8 Hz, 2 H, CH(CH_3)$_2$], 3.66 (s, 3 H, OCH_3), 5.39 (d, $^{1}J_{P,H}$ = 381.5 Hz, 1 H, PH), 6.24 (ddd, $^{3}J_{H,H}$ = 7.8, $^{4}J_{H,H}$ = 1.0, $^{4}J_{PH}$ = 5.3 Hz, 2-H), 6.74 (td, $^{3}J_{H,H}$ = 7.7, $^{4}J_{H,H}$ = 1.5 Hz, 3-H), 6.84–6.95 (m, 6 H, *m* + *o*-Anisyl), 7.06 (td, $^{3}J_{H,H}$ = 7.4, $^{4}J_{H,H}$ = 1.0 Hz, 1 H, 4-H), 7.22 (m, 2 H, 16-H, 18-H), 7.34 (m, 1 H, 17-H), 7.44 (dd, $^{3}J_{H,H}$ = 7.8, $^{4}J_{H,H}$ = 1.5 Hz, 1 H, 5-H), 7.46 (dt, $^{3}J_{H,H}$ = 8.7, $^{4}J_{H,H}$ = 1.0, $^{5}J_{H,P}$ = 1.0 Hz, 1 H, 10-H), 7.50 (m, 2 H, *p*-Anisyl), 7.53 {m, 4 H, *p*-B[$C_6H_3(CF_3)_2$]$_4$}, 7.71 (dt, $^{3}J_{H,H}$ = 7.7, $^{4}J_{H,H}$ = 1.0, $^{5}J_{H,P}$ = 1.0 Hz, 1 H, 8-H), 7.73 {m, 8 H, *o*-B[$C_6H_3(CF_3)_2$]$_4$}, 7.81 (dd, $^{3}J_{H,H}$ = 7.7, $^{3}J_{H,H}$ = 8.4 Hz, 1 H, 9-H) ppm. $^{13}C\{^{1}H\}$ NMR (100.62 MHz, $CDCl_3$, 294 K): δ = 18.92 (C-13), 22.40 [CH(CH_3)$_2$], 23.98 [CH(CH_3)$_2$], 28.73 [CH(CH_3)$_2$], 55.70 (OCH_3), 111.35 (d, $^{2}J_{C,P}$ = 4.7 Hz, *o*-Anisyl), 111.41 (d, $^{1}J_{C,P}$ = 54.5 Hz, *ipso*-Anisyl), 117.80 {*p*-[$C_6H_3(CF_3)_2$]}, 121.64 (d, $^{3}J_{C,P}$ = 4.7 Hz, *m*-Anisyl), 121.93 (C-8), 122.29 (C-10) 124.37 (C-17), 124.50 (d, $^{1}J_{C,F}$ = 272.6 Hz, CF_3), 125.89 (C-5), 126.54 (C-4), 127.96 (C-16, C-18), 128.80 (d, $^{2}J_{\mathrm{C,F}}$ = 32.5 Hz, $C\mathrm{CF_3}$), 129.50 (q, $^{2}J_{\mathrm{C,F}}$ = 32.5 Hz, $C\mathrm{CF_3}$), 131.86 (d, $^{4}J_{\mathrm{C,P}}$ = 4.0 Hz, C-3), 134.80 $\{o\text{-}[\mathrm{C_6H_3(CF_3)_2}]\}$, 135.57 (d, $^{3}J_{\mathrm{C,P}}$ = 8.0 Hz, *m*-Anisyl), 134.24 (*p*-Anisyl), 136.72 (d, $^{3}J_{\mathrm{C,P}}$ = 10.5 Hz, C-2), 138.06 (C-15, C-19), 140.98 (C-14), 141.51 (C-9), 148.60 (C-6), 151.98 (d, $^{2}J_{\mathrm{C,P}}$ = 5.4 Hz, C-1), 152.24 (C-11), 160.82 (d, $^{2}J_{\mathrm{C,P}}$ = 3.3 Hz, C–OCH$_3$), 162.30 (q, $^{1}J_{\mathrm{C,B}}$ = 49.5 Hz, *ipso*-C–B), 164.25 (C-7), 177.40 (C-12) ppm. ^{31}P{^{1}H}(161.98 MHz, CDCl$_3$, 294 K): δ –23.34 (s) ppm. IR (KBr): $\tilde{\nu}$ = 1607 (C=N) cm^{-1}.

X-ray Crystallographic Analysis of 1 and 2: Single crystals of both compounds were obtained by slow diffusion of toluene at room temperature into a saturated CH$_2$Cl$_2$ solution of **1** and **2**, respectively. Diffraction data were collected at room temperature with an Enraf Nonius CAD4 automatic diffractometer with Mo-K_α radiation (graphite monochromator). Unit cell parameters of both structures were determined from a least-squares refinement of the setting angles of 25 carefully centered reflections. Crystal data and data collection details are given in Table 1. Lorentz polarization and absorption corrections were applied.[20a] Atomic scattering factors were taken from ref.[20b] and an anomalous dispersion correction, with a real and imaginary part, was applied.[20c] The structures were solved by direct methods and refined by full-matrix F^2 refinement. While in **1** anisotropic thermal parameters were assigned to all non-hydrogen atoms, in **2** only the disordered toluene molecule was treated isotropically. In both structures, the hydrogen atoms were introduced in their calculated positions, with thermal parameters 20% larger than those of the respective carbon atoms. All the calculations were performed with a PC using the WINGX package[20d] with SIR-97,[20e] SHELX-97,[20f] and ORTEP-3 programs.[20g] CCDC-271410 (**1**), and -271409 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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