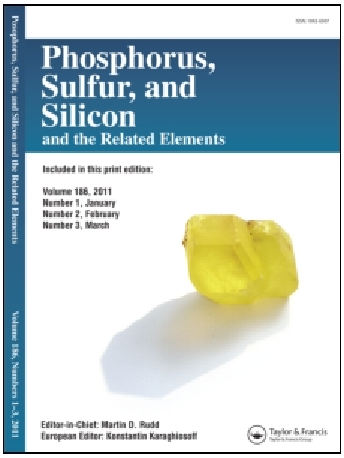

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Synthesis, Characterization and Applications of Novel Iminophosphinites

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Synthesis, Characterization and Applications of Novel Iminophosphinites

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Keywords Iminophosphinites; palladium complexes; Suzuki reaction; unsymmetrical ligands

INTRODUCTION

Ligand design plays an important role in organometallic synthesis and catalysis. The combination of a soft donor and a hard donor induces different interactions between metal centers and the unsymmetrical donors, which may lead to hemilabile properties.[1,2] Recently unsymmetrical ligands with two or more different donors such as phosphorus and nitrogen (P,N type) donors have attracted increasing attention due to their bonding versatility and catalytic applications.[3] Here, we report the synthesis, characterization and catalytic applications of two novel bidentate and potentially hemilabile iminophosphinites, and a palladium complex bearing one of the iminophosphinite ligands.

The reactions between Schiff bases, 2-(2,6- diisopropylphenylimino)methyl)phenol from salicylaldehyde and 2,6-di-isopropylaniline[4] or 2-(diphenylmethyleneamino)phenol from 2-aminophenol and benzophenone,[5] and chlorodiphenylphosphine in the presence of 4-dimethylaminopyridine (DMAP) in Et_2O afforded iminophosphinite compounds **1** and **2** (Schemes 1 and 2).[6,7] Both compounds can be

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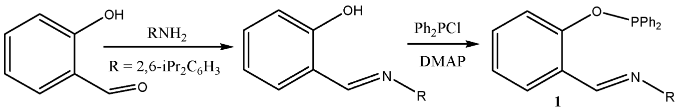
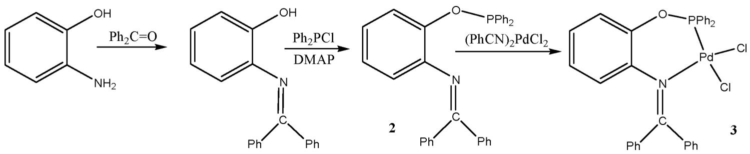


SCHEME 1

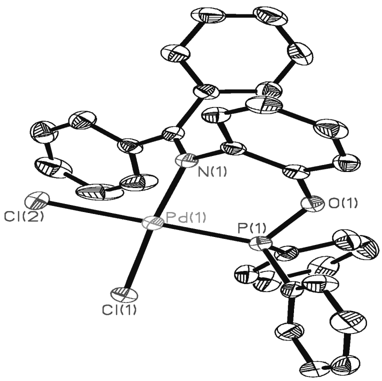


SCHEME 2

recrystallized from ether/hexane. The crystals are fairly air stable and remain unchanged in the air after several days. Reaction of iminophosphinite **2** and bis(benzonitrile)palladium chloride in CH_2Cl_2 afforded the expected palladium complex **3** (Scheme 2).[8] Single crystals of **3** were grown from CH_2Cl_2/hexane through slow evaporation. In the solid state of **3**, palladium ion adopts a slightly distorted square planar geometry, with the sum of the bond angles surrounding the Pd ion at 360.16(3)°. The IR spectra show characteristic C=N stretches at 1627 and 1638 cm^{-1} for **1** and **2** respectively. Upon coordination of **2** to palladium, the C=N stretch decreased to 1596 cm^{-1} in **3**, indicating back-bonding from the electron-rich palladium ion. The ^{31}P signal increased from 111.93 ppm in **2** to 131.55 ppm in **3** after coordination.

Reactions of dichlorobis(benzonitrile)palladium with iminophosphinite **1** at either 1:1 or 1:2 ratio afforded mixtures, as suggested by the ^{31}P NMR spectra which gave more than one phosphorus signals. This may be indicative of the lability of this type of iminophosphinte as it can only form seven-membered palladacycles if both P and N coordinate to Pd, which is not as stable as six-membered ones formed by iminophosphinite **2**. Similarly, recent studies have shown that longer bisphosphines may act as monodentate donors instead of bidentate ones, leading to lower stability in the metal complexes.[9]

The catalytic activities of compounds **1** and **2**, and complex **3** were investigated in Suzuki coupling reaction,[10] an important carbon-carbon bond formation reaction. We employed a deactivated aryl bromide, 4-bromoanisole, and phenylboronic acid in the studies [Equation (1)]. In comparative studies, we found that with 2% Pd catalyst and ligand loading, systems based on iminophosphinite **1** gave better yields (up to 99%) than those based on iminophosphinite **2** and its palladium complex **3**. These systems are generally better than those

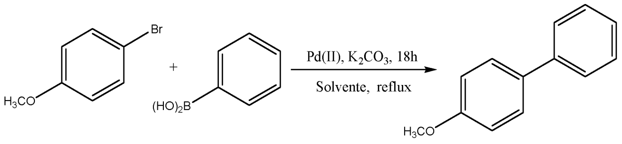


Molecular structure of **3**

SCHEME 3

based on related but monodentate ligands such as triphenylphosphine and ethyl diphenylphosphinite (Table I). The higher activity of systems base on iminophosphinite **1** may be attributed to the hemilabile property of the iminophosphinite ligand, which may facilitate aryl bromide oxidative addition. On the other hand, the stability of palladium complex bearing iminophosphinite **2** hinders palladium interaction with organic substrates which makes it less active.

In conclusion, we synthesized and characterized two novel iminophosphinite ligands and investigated their coordination to palladium metal center. In Suzuki coupling studies, the potentially hemilabile iminophosphinite **1** showed better catalytic activity than the iminophosphinite **2** under similar conditions. We are attempting to syntheisize iminophosphinites with bulky alkyl (e.g., ^{t}Bu) substituents on the phosphorus atom, which should lead to enhanced σ-donating ability and thus improved catalytic activity. Furthermore, we will attempt to make the imine moiety more labile by introducing electron-withdrawing substituents such as nitro group on the phenyl ring.[11]



(1)

SCHEME 4

TABLE I Pd(II) Catalyzed Suzuki Reactions

Entry	Ligand or Complex, 2% loading	Solvent	Yield (%)[a]
1	1	Toluene	99
2	2	Toluene	59
3	3	Toluene	74
4	1	Dioxane	54
5	2	Dioxane	33
6	3	Dioxane	62
7	PPh_3	Toluene	43
8	$EtOPPh_2$	Toluene	26

[a] Yields are calculated using single point external standard with authentic samples through GC/MS analysis.

SUPPLEMENTARY INFORMATION

CCDC 642499 contains 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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[6] Characterization of **1**: m.p. 109–111°C. IR (KBr, cm^{-1}): 2957, 1627, 1596, 1457, 1436, 1222, 1096, 885, 760, 696. ^1H NMR (CD_2Cl_2): δ 8.62 (1H, s, CH=N), 7.13–7.59 (17H, m, phenyl), 2.97 (2H, sept, CH(CH_3)$_2$), 1.13 (12H, d, CH(CH_3)$_2$). ^{13}C NMR (CD_2Cl_2): δ 158.20 (C=N), 123.36–138.07 (phenyl), 28.34 (CH(CH_3)$_2$), 23.76 (CH(CH$_3$)$_2$). $^{31}P^1H$ NMR (CD_2Cl_2): δ 107.85.

[7] Characterization of **2**: m.p. 75–76°C. IR (KBr, cm^{-1}): 3055, 1638, 1578, 1480, 1442, 1432, 1293, 1238, 1198, 891, 747, 740, 693. ^1H NMR (CD_2Cl_2): δ 6.62–7.73 (22H, m,

phenyl). ^{13}C NMR (CD_2Cl_2): δ 145.78 (C=N), 121.80–131.21 (phenyl). $^{31}P^1H$ NMR (CD_2Cl_2, ppm): δ 111.93.

[8] Characterization of **3**: m.p. 222°C (dec.). IR (KBr, cm^{-1}): 3053, 1596, 1580, 1565, 1477, 1437, 1238, 1110, 1096, 906, 771, 748, 735, 702. ^{1}H NMR (CD_2Cl_2): δ 6.82–8.12 (22H, m, phenyl). ^{13}C NMR (CD_2Cl_2): δ 149.96 (C=N), 120.99–137.76 (phenyl). $^{31}P^1H$ NMR (CD_2Cl_2): δ 131.55.

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