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Modularly Designed Transition Metal PNP and PCP Pincer Complexes based on Aminophosphines: Synthesis and Catalytic Applications

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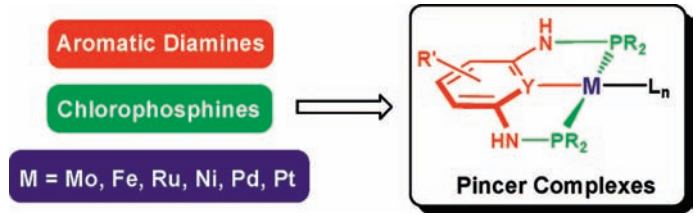

Transition metal complexes are indispensable tools for any synthetic chemist. Ideally, any metal-mediated process should be fast, clean, efficient, and selective and take place in a catalytic manner. These criteria are especially important considering that many of the transition metals employed in catalysis are rare and expensive. One of the ways of modifying and controlling the properties of transition metal complexes is the use of appropriate ligand systems, such as pincer ligands. Usually consisting of a central aromatic backbone tethered to two two-electron donor groups by different spacers, this class of tridentate ligands have found numerous applications in various areas of chemistry, including catalysis, due to their combination of stability, activity, and variability. As we focused on pincer ligands featuring phosphines as donor groups, the lack of a general method for the preparation of both neutral (PNP) and anionic (PCP) pincer ligands using similar precursor compounds as well as the difficulty of introducing chirality into the structure of pincer ligands prompted us to investigate the use of amines as spacers between the aromatic ring and the phosphines. By introduction of aminophosphine and phosphoramidite moieties into their structure, the synthesis of both PNP and PCP ligands can be achieved via condensation reactions between aromatic diamines and electrophilic chlorophosphines (or chlorophosphites). Moreover, chiral pincer complexes can be easily obtained by using building blocks obtained from the chiral pool. Thus, we have developed a modular synthetic strategy with which the steric, electronic, and stereochemical properties of the ligands can be varied systematically. With the ligands in hand, we studied their reactivity towards different transition metal precursors, such as molybdenum, ruthenium, iron, nickel, palladium, and platinum. This has resulted in the preparation of a range of new pincer complexes, including various iron complexes, as well as the first heptacoordinated molybdenum pincer complexes and several pentacoordinated nickel complexes by using a controlled ligand decomposition pathway. In addition, we have investigated the use of some of the complexes as catalysts in different C−C coupling reactions: for example, the palladium PNP and PCP pincer complexes can be employed as catalysts in the well known Suzuki−Miyaura coupling, while the iron PNP complexes catalyze the coupling of aromatic aldehydes with ethyl diazoacetate under very mild reaction conditions to give selectively 3-hydroxyacrylates, which are otherwise difficult to prepare. While this Account presents an overview of current research on the chemistry of P−N bond containing pincer ligands and complexes, we believe that further investigations will give deeper insights into the reactivity and applicability of aminophosphine-based pincer complexes.

1. Introduction

The development of well-designed ligand systems with which the properties of metal centers can be easily varied in a controlled manner is one of the most important goals in modern inorganic and organometallic chemistry. Among the many ligand systems that can be found in the chemical literature, pincer ligands[1] and their complexes

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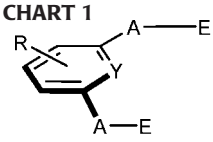
have attracted increasing interest due to their high stability, activity, and variability. The first pincer ligands and complexes were synthesized already in the late 1970s.[2] However, this area remained comparatively unexplored until in the late 1990s several applications of pincer complexes in the fields of catalysis, molecular recognition, and supramolecular chemistry were discovered, turning this area into an intensively investigated subject in organometallic chemistry. For example, pincer complexes have been used as catalysts in different transition metal mediated processes, including C−C bond forming reactions, polymerization reactions, and transfer hydrogenation and dehydrogenation reactions.[3] Moreover, pincer complexes have been employed as sensors,[4] have been used to investigate C−C, C−H and C−O bond activation processes,[5] or have been serving as building blocks for the synthesis of self-assembled supramolecular structures.[3]

Pincer ligands, named after their particular coordination mode to metal centers, are tridentate ligands usually featuring a central aromatic ring that is *ortho*,*ortho*-disubstituted with heteroatom, two electron-donor substituents (E) (Chart 1). However, anionic PNP pincer ligands in which the ligand backbone is not part of an aromatic ring have also been reported.[6] The substituents E can be connected to the central aromatic backbone by different spacers (A), such as methylene groups ($-CH_2-$), amines ($-NR-$) or oxygen atoms ($-O-$). The (un)substituted aromatic ring can be either a pyridine ring (Y = N) or a benzene ring (Y = C). Thus, both neutral and anionic pincer ligands can be obtained. As for the neutral lone pair donors E, they are typically amines (NR_2), phosphines (PR_2), phosphites ($P(OR)_2$), ethers (OR), thioethers (SR), and even N-heterocyclic carbenes (NHCs), arsines (AsR_2), and selenoethers (SeR). The donor groups need not be identical, and systems with two different donor atoms have been reported.[7] Pincer ligands coordinate to the metal center in a meridional way via the two electron-donor groups and metal−carbon (benzene-based pincer complexes) or metal−nitrogen (pyridine-based pincer complexes) σ bonds. Thus, a wide variety of different EYE pincer ligands are accessible by modifying one or more of the parameters in the general structure of the ligand, that is, the donor groups, the aromatic ring and its substitution, and the spacer groups.

The most widely utilized class of pincer ligands contains phosphines or phosphites as donor groups. However, the lack of a general method for the preparation of both PNP and PCP pincer ligands using similar precursor compounds, as well as the difficulty of introducing chirality into the structure of pincer ligands, prompted us to investigate the use of amines as spacers between the aromatic ring and the phosphines. These studies allowed us to develop a modular synthetic strategy for a range of different PNP and PCP pincer ligands in which chirality can be easily introduced by using electrophilic chlorophosphines and chlorophosphites derived from the chiral pool. The use of these ligands with several transition metal precursors has resulted in the preparation of new pincer complexes, including the first heptacoordinated molybdenum pincer complexes and several pentacoordinated nickel pincer complexes by using a controlled ligand decomposition pathway. Furthermore, some of these complexes have proven to be effective catalysts in different coupling reactions: palladium PNP and PCP pincer complexes can be used as catalysts in the Suzuki−Miyaura coupling, while iron PNP complexes catalyze the coupling of aromatic aldehydes with ethyl diazoacetate to give selectively 3-hydroxyacrylates, which are otherwise difficult to prepare.

CHART 1



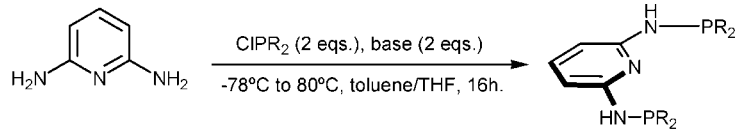
E = NR_2, PR_2, $P(OR)_2$, OR, SR, AsR_2, SeR
Y = N, C
A = CH_2, NH(R), O
R = alkyl, aryl

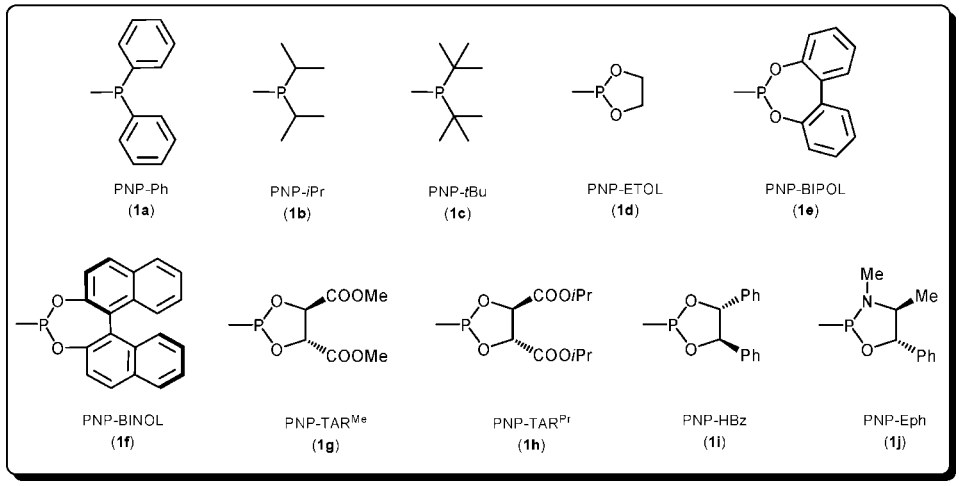
2. Ligands

Different synthetic strategies are available for the synthesis of PNP and PCP pincer ligands depending on the spacer between the central aromatic ring and the phosphines. If the spacer is a methylene group, both PNP and PCP ligands have been prepared starting, for instance, from 2,6-bis(bromomethyl)pyridine or 1,3-bis(bromomethyl)benzene upon treatment with lithium phosphides, which are typically prepared *in situ*.[2a,e] Pincers with oxygen spacers, that is, phosphinito PCP ligands, have been prepared from resorcinol and different chlorophosphines.[8] A problem arises for the synthesis of phosphinito PNP ligands, since the required 2,6-dihydroxypyridine precursor is in tautomeric equilibrium with 6-hydroxypyridin-2-one, which makes the phosphorylation of both hydroxyl groups very difficult if not impossible. Mixed PCP pincer ligands containing one oxygen spacer and a methylene or an amino spacer have also been reported.[9]

Another possibility is to use amines as spacers between the central aromatic ring and the phosphines. P−N bonds can be formed in a straightforward manner via condensation of primary and secondary amines and chlorophosphines in the presence of a base. This methodology was first reported by Haupt and co-workers[10] and has been extended by us to the synthesis of a large array of PNP[11] (**1a**−**j**) and PCP[12] (**2a**−**j**) pincer ligands with 2,6-diaminopyridine (Scheme 1) and *m*-phenylenediamine, 5-trifluoromethyl-1,3-diaminobenzene,

SCHEME 1





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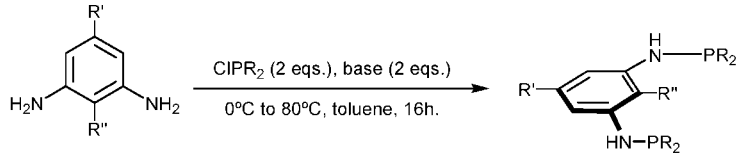
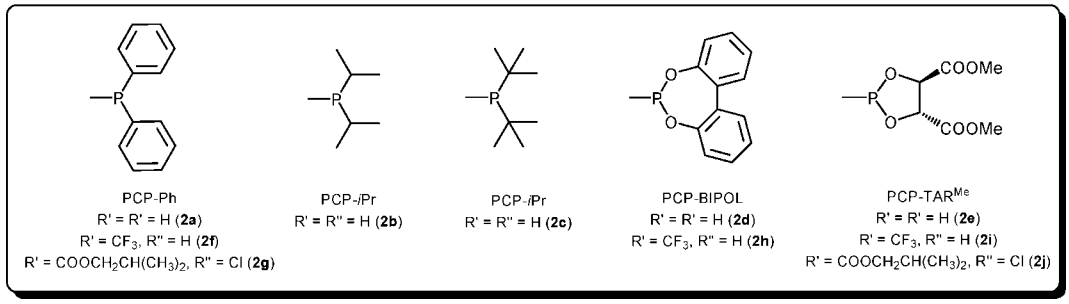


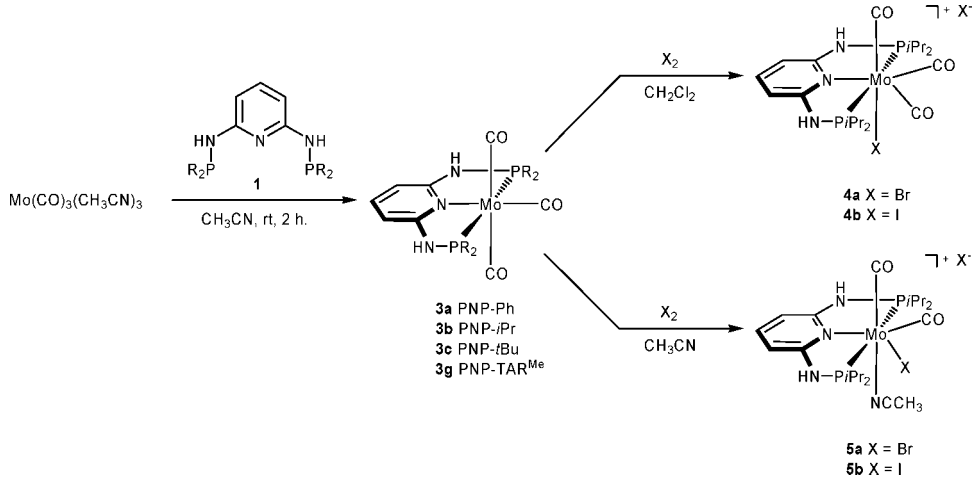


and 3,5-diamino-4-chloroisobutylbenzoate as starting materials (Scheme 2). The introduction of different substituents at the phosphines, both achiral and chiral, was achieved by using chlorophosphines derived from the reaction of diols and amino alcohols and phosphorus trichloride.

3. Metal Complexes

Molybdenum Complexes. In their original contribution, Haupt and co-workers reported the synthesis of a molybdenum tricarbonyl complex with the PNP ligand **1a**.[10] We prepared analogous complexes with the PNP ligands **1a**−**c** and **1g** to afford the tricarbonyl complexes **3a**−**d**.[11] The complexes **3a**−**d** can oxidatively add halogens. For example, **3b** reacts with Br_2 or I_2 in CH_2Cl_2 to give [Mo(PNP-*i*Pr)(CO)$_3$X]X (X = Br, I) (**4a**,**b**), while the mono(acetonitrile) complexes [Mo(PNP-*i*Pr)(CO)$_2$(CH$_3$CN)X]X (X = Br, I) (**5a**,**b**) can be obtained if the reaction is carried out in acetonitrile (Scheme 3). These are the first seven-coordinate molybdenum pincer complexes reported so far. A molecular view of **4b** is depicted in Figure 1. Heptacoordinated complexes are notorious for their fluxional behavior in solution,[13] since neither any of the idealized geometries (i.e., capped prism, capped octahedron and pentagonal bipyramide) nor less symmetrical arrangements are characterized by a markedly lower total energy.[14] Thus, interconversions between these structures are quite facile, and the $^{31}P\{^1H\}$ NMR spectra of **4** and **5** exhibit only one resonance even at −90 °C.

SCHEME 3



Iron Complexes. In contrast to other transition metals, iron pincer complexes are comparatively rare. Milstein and co-workers have prepared iron(II) pincer complexes using methylene-bridged PNP ligands,[15] while Chirik and co-workers have reported some reductive chemistry using these complexes.[16]

With the exception of the bulky PNP-*t*Bu (**1c**), the reaction of the hexaquo complex $[Fe(H_2O)_6](BF_4)_2$ with the aminophosphine and phosphoramidite PNP ligands **1a**,**b** and **1d**−**g** in acetonitrile affords the octahedral diamagnetic iron(II) complexes **6a**−**g** where the PNP ligand coordinates to the metal center in a typical meridional fashion (Scheme 4).[11] A molecular view of the chiral complex **6g** is depicted in Figure 2. Despite the fact that 6 equiv of water are released in the course of the reaction per equivalent metal precursor, no decomposition of the ligands or the complexes due to hydrolysis was observed. All three nitrile ligands in these complexes are substitutionally labile and can be displaced by bidentate and tridentate nitrogen donor chelating ligands, such as bipyridine (**7a**) or terpyridine (**7b**), or by another molecule of a PNP ligand (**7c**) (Scheme 5). The reaction of **6a** and **6b** with carbon monoxide resulted in the selective substitution of one of the nitrile ligands *cis* to the pyridine ring to give the monocarbonyl complexes **8a**,**b**. No evidence was found for the formation of iron(II) PNP dicarbonyl complexes (Scheme 6).[17] On the other hand, no reaction took place with the phosphoramidite complexes **6d**−**g**, which contain stronger π-accepting substituents at the phosphines.

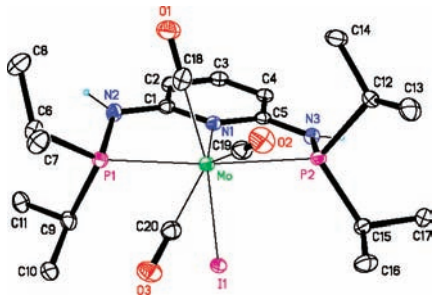
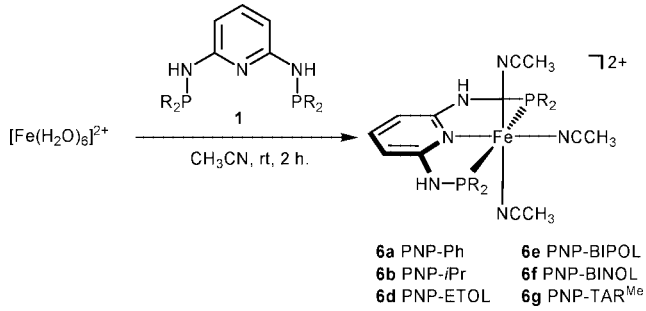


FIGURE 1. Structural view of $[Mo(PNP\text{-}iPr)(CO)_3I]^+$ (**4b**).

The attempt to obtain zero-valent iron complexes by reacting the tris(acetonitrile) complexes **6a**−**g** with NaHg (3%) was unsuccessful. Instead, the reaction of **6e** with NaHg (3%) resulted in the formation of the deprotonated monocationic complex **9** (Scheme 7).[11] Structural views of **6e** and **9** are shown in Figure 3. The same complex was obtained when **6e** was chromatographed on basic alumina. This deprotonation process is reversible, and complex **6e** can be obtained by reacting **9** with $HBF_4 \cdot Et_2O$.

SCHEME 4



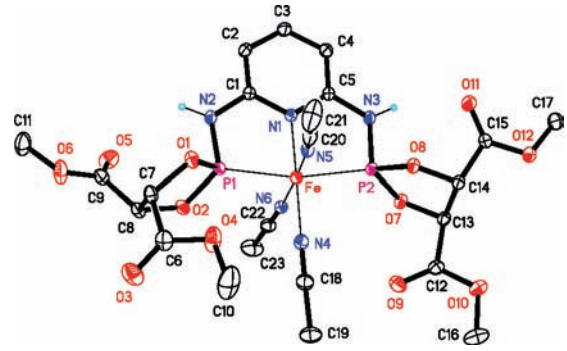
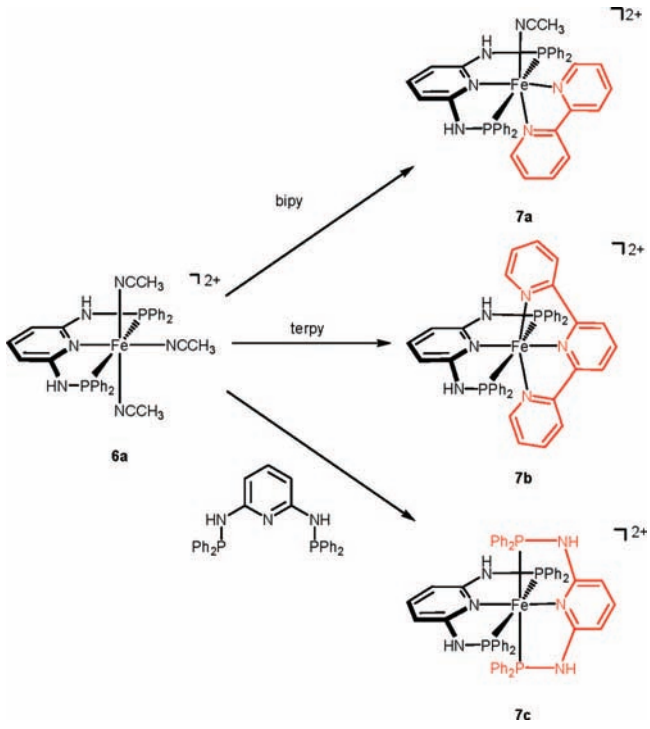


FIGURE 2. Structural view of chiral $[Fe(PNP\text{-}TAR^{Me})(CH_3CN)_3]^{2+}$ (**6g**).

SCHEME 5



The reaction of the PNP ligands **1b** and **1c** with $FeCl_2$ afforded the pentacoordinated, paramagnetic complexes **10b**,**c** (Scheme 8).[17] The synthesis of iron(II) dichloride PNP complexes was only possible when ligands with bulky substituents at the phosphines (i.e., *i*Pr and *t*Bu) were used (Figure 4). This result is in agreement with that reported by Milstein and co-workers with similar methylene-bridged PNP pincer ligands.[15] However, unlike Milstein's complexes, where only the abstraction of a chlorine atom was reported, the reaction of **10b** with 2 equiv of $AgBF_4$ in acetonitrile resulted in the formation of the tris(acetonitrile) complex **6b**.

Ruthenium Complexes. The synthesis of the octahedral ruthenium PNP complexes **11a**−**h** was achieved by reacting $RuCl_2(PPh_3)_3$ with the ligands **1a**,**b**, **1d**−**e**, and **1g**−**h** (Scheme 9).[11] Like in the case of the tris(acetonitrile) iron PNP complexes, no reaction took place when **1c** was used as the ligand, most likely due to the presence of the sterically demanding *t*Bu groups. Due to the meridional coordination mode of the PNP ligands and the rigidity of the $-NHPR_2$ substituents, the complexes **11a**−**h** form only two *mer*-stereoisomers with either a *trans*- or a *cis*-dichloro arrangement. Mixtures of them have not been observed. The chemical shifts for PPh_3 in the complexes **11a**−**h** are typical for being coordinated *trans* to neutral or anionic donor ligands. Accordingly, it is difficult to distinguish whether PPh_3 lies *cis* or *trans* to the pyridine nitrogen atom. For example, the solid structure of **11e** shows the PPh_3 ligand *cis* to the pyridine nitrogen, but in analogous ruthenium PNP[18] and NNN[19] pincer complexes both arrangements have been observed.

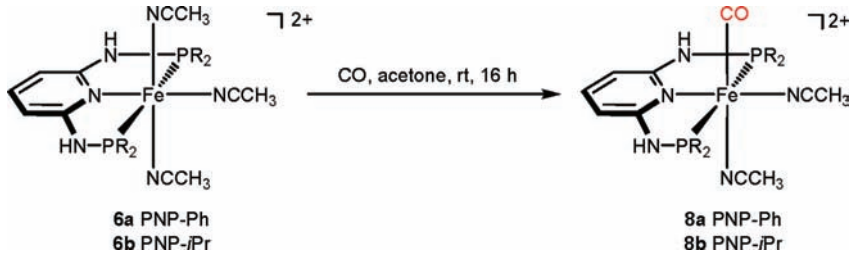
Nickel, Palladium, and Platinum Complexes. Treatment of $M(cod)X_2$ (M = Pd, X = Cl; M = Pt, X = Br) with the ligands **1a**−**h** resulted in the clean formation of the cationic, tetracoordinated, square-planar palladium and platinum complexes **12a**−**h** and **13a**−**g** (Scheme 10).[11] For solubility reasons, a counterion exchange was performed in the case of the palladium and platinum phosphoramidite complexes using KCF_3SO_3 as halide scavenger.

The palladium aminophosphine complexes **12a**−**c** are air-stable solids both in the solid state and in solution; however, a P−N bond cleavage process was observed in the case of the phosphoramidite complex **12e** when a DMF solution of **12e** was left in air at room temperature for several days. The product obtained was identified as the neutral, square-planar complex **14**, which contains an anionic phosphinito ligand and a bidentate PN ligand derived from the decomposition of the PNP ligand (Scheme 11).[20]

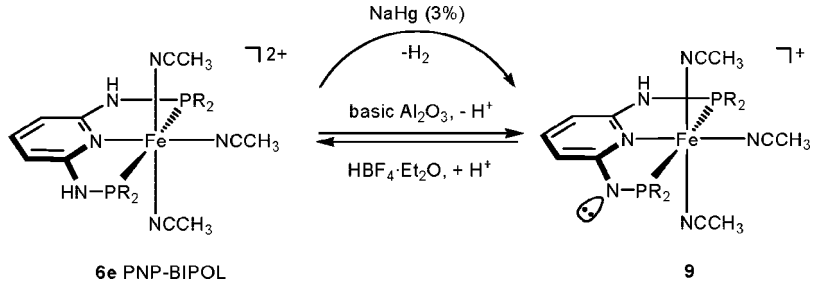
Tetracoordinated, square-planar nickel PNP complexes (**15a**−**c**) were obtained by reacting $Ni(dme)Br_2$ with the aminophosphine ligands **1a**−**c**.[11] These complexes are extremely stable and can be stored in air for several months without signs of decomposition. However, the reaction of the phosphoramidite PNP ligands **1e** and **1g**−**j** with nickel precursors resulted in the formation of the pentacoordinated, square-planar pyramidal nickel(II) complexes **16e**−**j**, featuring an intact PNP ligand and a κ^1-(P)-coordinated anionic phosphinito ligand $R_2P{=}O^-$ (Scheme 12).[20]

A plausible mechanism for the formation of the complexes **16e**−**j** is depicted in Scheme 13. This mechanism is supported by various experimental findings: In the first place, monitoring of the reaction of $Ni(dme)Br_2$ with PNP-BIPOL (**1e**) with different metal precursor to ligand ratios revealed that when a 1:1.5 ratio is used, complete consumption of both metal precursor and ligand takes place. The use of less than 1.5 equiv or of an excess of ligand leaves unreacted metal precursor and unreacted ligand in the reaction mixture, respectively. Second, 2,6-diaminpyridinium bromide was isolated as a reaction byproduct, meaning that the two P−N bonds of a PNP ligand must cleave in the course of the reaction. Since the cleavage of an aminophosphine bond is possible in the case of palladium(II) phosphoramidite complexes (Scheme 11),[20] it would be reasonable to assume that such a process might be involved (although at a much faster rate) in the formation of the complexes **16e**−**j**. Finally, ^1H and $^{31}P\{^1H\}$ NMR spectroscopy revealed the formation of a reaction intermediate (**D**, Scheme 13). In contrast to the final products **16e**−**j**, in which the phosphinito ligand is located in the basal position, in

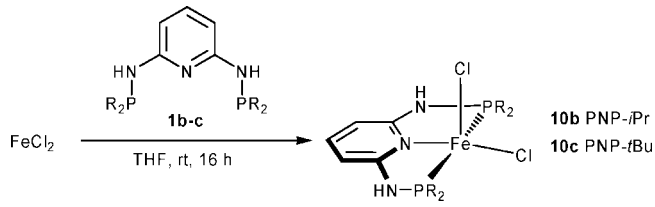
SCHEME 6



SCHEME 7



SCHEME 8



the reaction intermediate **D** this ligand is coordinated in the apical position. This intermediate isomerizes at room temperature within 16 h to give the corresponding complex **16**.

Neutral, tetracoordinated, square-planar nickel, palladium, and platinum PCP complexes were synthesized by direct metalation of the ligands **2a**−**j** with $NiCl_2 \cdot 6H_2O$, $Pd(cod)Cl_2$, and $Pt(cod)Br_2$, respectively (Scheme 14).[12] In the case of nickel, PCP complexes could only be prepared with the aminophosphine ligands **2a**−**c**. Decomposition of the ligands takes place when P−O bond containing PCP ligands are employed. With palladium and platinum, there is no limitation as to the nature of the substituent at the phosphines, but the preparation of the platinum PCP complexes requires the addition of an external base (NEt_3) to facilitate the C−H bond activation process. A similar observation has been made for the synthesis of platinum complexes with methylene-bridged PCP ligands.[21] Alternatively, palladium PCP complexes featuring a coordinated TFA ligand were obtained by the reaction of $Pd(TFA)_2$ with the ligands **2a**, **2d**, and **2e**,**f**. Due to the basic nature of the TFA anion, the temperature required for the synthesis of the complexes **19a**−**d** was lower than that necessary for the preparation of the chloride analogues **18a**−**g**. A molecular view of **19d** is depicted in Figure 5. Finally, palladium PCP complexes were also generated by oxidative addition of the C_{Ar}−Cl bond in the ligands **2c** and **2j** to $Pd_2(dba)_3$ to give the complexes **21a**,**b** (Scheme 15).

4. Catalytic Applications

Iron(II) Catalyzed Coupling of Aromatic Aldehydes and Ethyl Diazoacetate. Aromatic aldehydes are known to react with ethyl diazoacetate (EDA) in the presence of Lewis acids such as BF_3, $ZnCl_2$, $AlCl_3$, $GeCl_2$, and $SnCl_4$ to give 3-oxo-arylpropanoic acids (β-ketoesters), but 3-hydroxy-2-arylacrylic acid

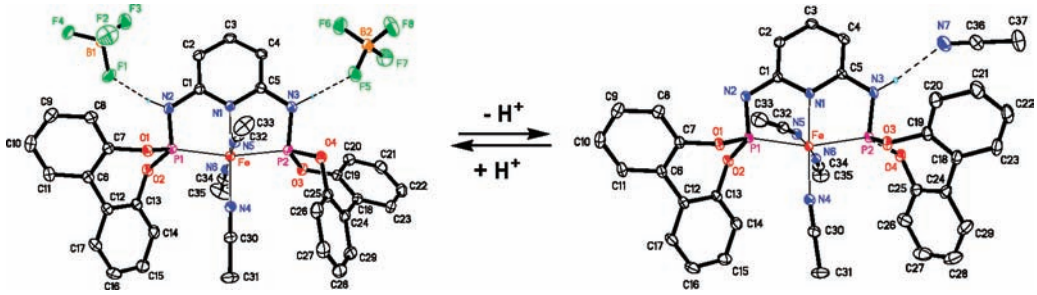
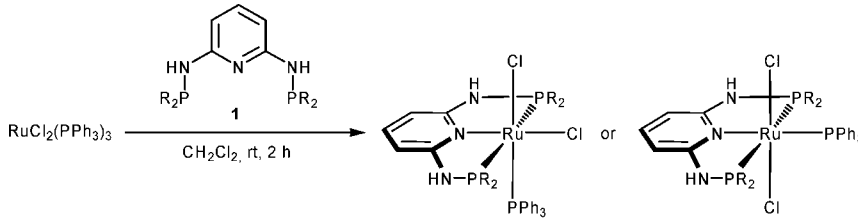


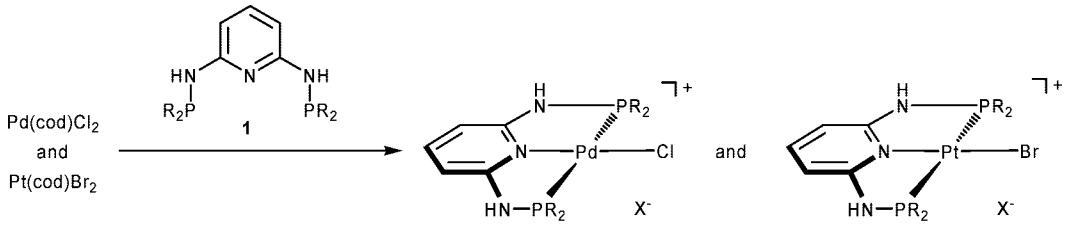
FIGURE 3. Structural views of the diprotonated and mono-deprotonated complexes $[Fe(PNP\text{-}BIPOL)(CH_3CN)_3]^{2+}$ (**6e**) and $[Fe(PNP\text{-}BIPOL)(CH_3CN)_3]^{+}$ (**9**).

SCHEME 9



11a PNP-Ph
11b PNP-*i*Pr
11d PNP-ETOL
11e PNP-BIPOL
11g PNP-TAR^{Me}
11h PNP-TAR^{Pr}

SCHEME 10

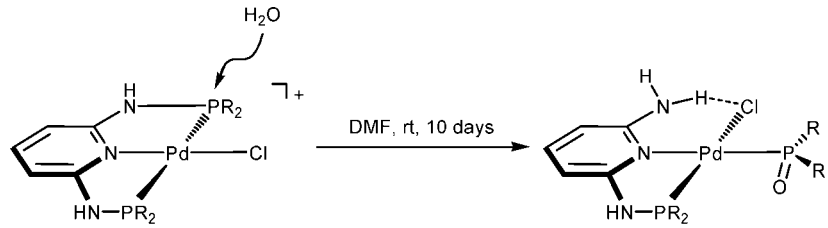


X = Cl, Br; CH_2Cl_2, rt, 2 h
X = CF_3SO_3; CH_3CN, KCF_3SO_3, rt, 2 h

12a PNP-Ph, X = Cl
12b PNP-*i*Pr, X = Cl
12c PNP-*t*Bu, X = Cl
12d PNP-ETOL, X = CF_3SO_3
12e PNP-BIPOL, X = CF_3SO_3
12f PNP-BINOL, X = CF_3SO_3
12g PNP-TAR^{Me}, X = CF_3SO_3
12h PNP-TAR^{Pr}, X = CF_3SO_3

13a PNP-Ph, X = Br
13b PNP-*i*Pr, X = Br
13c PNP-*t*Bu, X =Br
13e PNP-BIPOL, X = CF_3SO_3
13g PNP-TAR^{Me}, X = CF_3SO_3

SCHEME 11



12e **14**

ethyl esters (3-hydroxyacrylates) are usually obtained as a byproduct of this reaction (Scheme 16).[22] Hossain and co-workers have found that the cyclopentadienyl dicarbonyl Lewis acid $[FeCp(CO)_2(THF)]BF_4$ is an active catalyst for the coupling of aromatic aldehydes with EDA to give mainly 3-hydroxyacrylates,[23] and similar results have been reported by the same authors using the Brönsted acid $HBF_4 \cdot Et_2O$ as catalyst.[24] In these cases, however, the slow addition of EDA over a period of 6−7 h at low temperature is required, and substantial amounts of β-ketoesters are typically formed. Similar results were also described by Kanemasa et al. by using $ZnCl_2$ in the presence of chlorotrimethylsilane as catalyst.[25] We found out that the iron(II) PNP complexes described above are also effective catalysts for the coupling of aromatic aldehydes with EDA to give 3-hydroxyacrylates as the main products and β-ketoesters only in trace amounts.[17] The most effective catalyst was found to be **8b**, featuring a PNP ligand with *i*Pr substituents at the phosphines and one carbonyl and two acetonitrile groups as coligands. The tris(acetonitrile) complexes **6a**−**c** were all less efficient, most likely because the

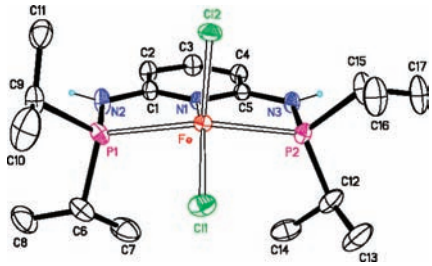
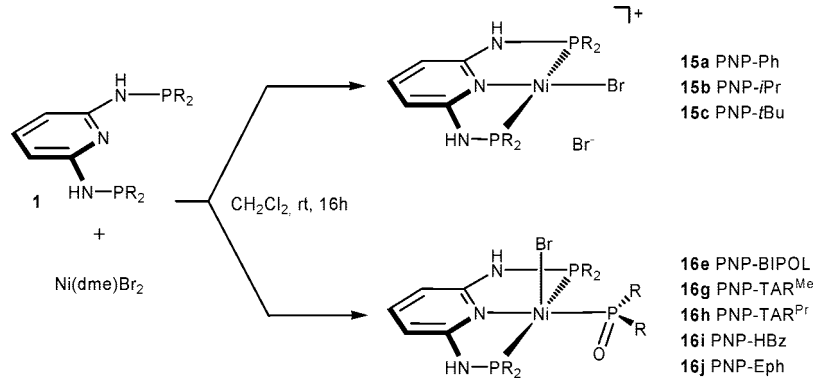
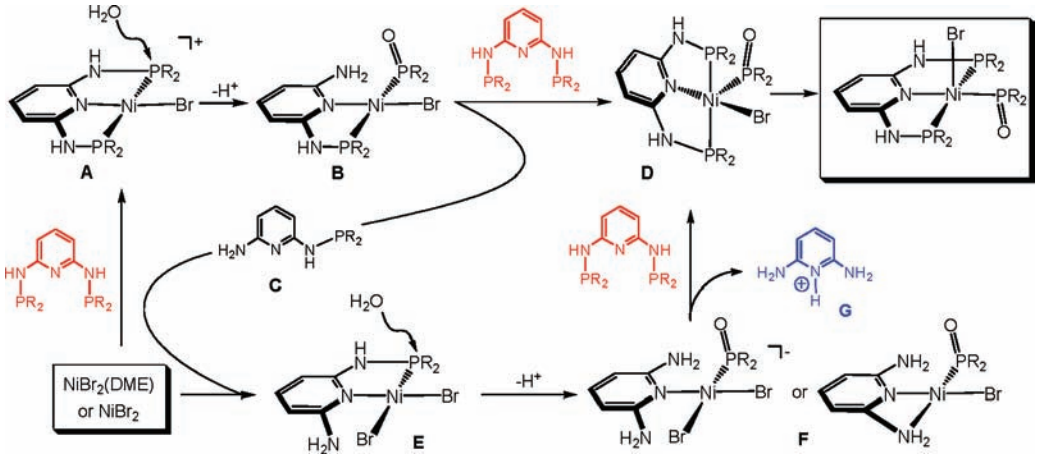


FIGURE 4. Structural view of $[Fe(PNP\text{-}iPr)Cl_2$ (**10b**).

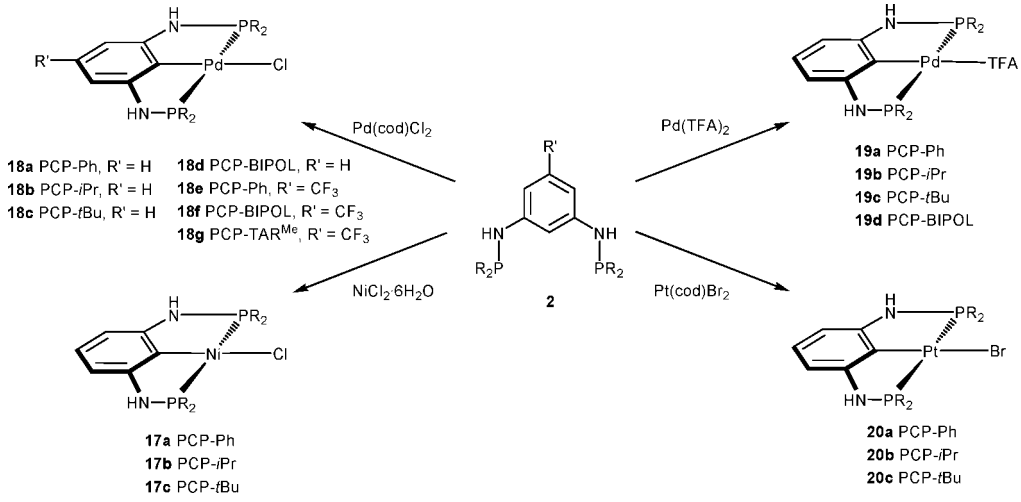
SCHEME 12



SCHEME 13



SCHEME 14



presence of a carbonyl group in **8b** renders the iron center more Lewis acidic. Likewise, the dichloro complexes **10a**,**b**, both in the presence and in the absence of $AgSbF_6$ as halide scavenger, turned out to be rather ineffective catalysts presumably due to decomposition of the complexes. Using **8b** as the catalyst, the coupling of *p*-anisaldehyde with EDA gave 84% isolated yield of the 3-hydroxyacrylate and <3% of the β-ketoester. For comparison, with $[FeCp(CO)_2(THF)]BF_4$ as catalyst, a 60:40 mixture of 3-hydroxyacrylate and β-ketoester was obtained.

In contrast to what has been frequently observed for Lewis-acid-catalyzed transformations,[26] the nature of the counte-

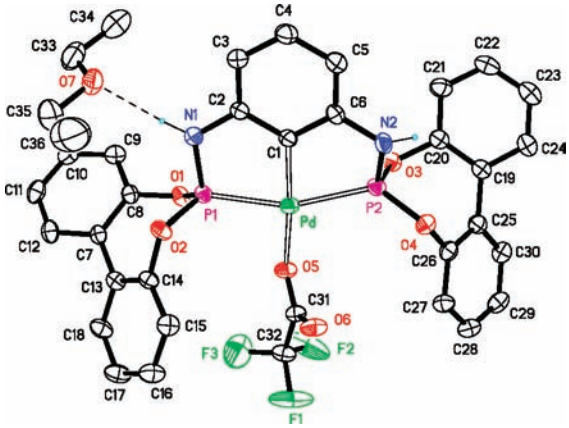
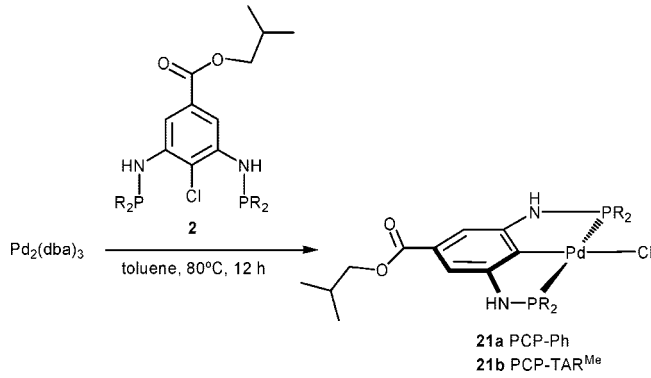
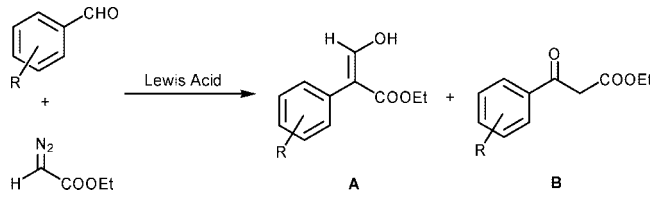


FIGURE 5. Structural view of Pd(PCP-BIPOL)(TFA) (**19d**).

SCHEME 15



SCHEME 16



rion does not seem to have any effect on the reaction. The coupling of *p*-anisaldehyde with EDA using **8b** as the catalyst led to similar yields and reaction rates with both the weakly coordinating counterion BF_4 and the noncoordinating anion tetrakis(3,5-difluoromethylphenyl)borate (BArF).

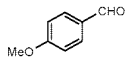
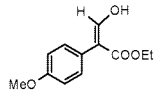
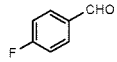
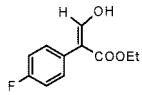
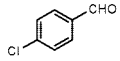
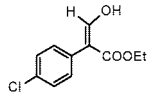
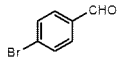
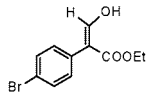
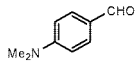
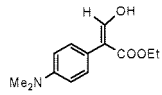
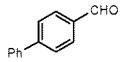
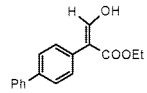
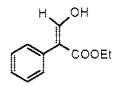
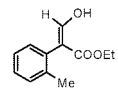
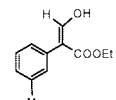
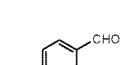
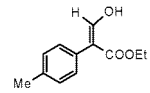
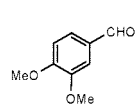
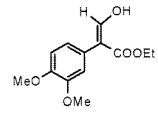
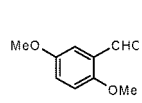
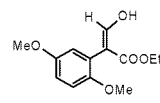
Complex **8b** can be used as catalyst in the coupling of different aromatic aldehydes with EDA (Table 1). No slow addition of EDA at low temperature was required; both the aldehyde and EDA were added together in a 1:1 ratio to a CH_3NO_2 solution of the catalyst at room temperature, and the reaction was stirred for 16 h. In all cases, 3-hydroxyacrylates were formed selectively; the formation of β-ketoesters was <3%, while the formation of epoxides was not observed in any of these reactions. This is in contrast to the results reported by Hossain and co-workers using $[FeCp(CO)_2(THF)]BF_4$ as the catalyst, where mixtures of 3-hydroxyacrylates and β-ketoesters were obtained. For instance, the reaction of benzaldehyde with EDA with 10 mol % $[FeCp(CO)_2(THF)]BF_4$ as the catalyst affords a mixture of 3-hydroxy-2-phenylacrylic acid ethyl ester and 3-oxo-3-phenylpropionic acid ethyl ester in 58% and 25% yields.[23] The same reaction performed with **8b** yields almost exclusively 3-hydroxy-2-phenylacrylic acid ethyl ester in 91% yield. With the exception of *p*-dimethylaminobenzaldehyde, the isolated yields of 3-hydroxyacrylates are in the range between 74% and 91%. When the reaction was carried out in the absence of catalyst, no product was formed and only starting materials were recovered from the reaction mixture.

A mechanistic proposal for the coupling or aromatic aldehydes with EDA catalyzed by *cis*-$[Fe(PNP\text{-}i\text{Pr})(CO)(CH_3CN)_2]^{2+}$, which is similar to the one suggested by Hossain et al.,[23] is depicted in Scheme 17. Since CO exhibits a much stronger *trans* effect (and *trans* influence) than pyridine, the CH_3CN ligand *trans* to CO in **8b** is more labile than the one *trans* to the pyridine ring of the PNP ligand. This may account for the higher reactivity of **8b** compared with **6b**. Accordingly, the substitution of this ligand by an aldehyde molecule (which is present in a large excess in the reaction mixture under catalytic conditions) may afford $[Fe(PNP\text{-}i\text{Pr})(CO)(CH_3CN)(\kappa^1(O)\text{-aldehyde}]^{2+}$ (**A**). The nucleophilic attack of EDA to the coordinated aldehyde yields intermediate **B**. In the course of this step, the new C−C bond is formed. **B** is a high-energy intermediate liberating readily N_2 to give complex **C**. Preferential migration of the aryl substituent (Ar) leads eventually to intermediate **D** featuring a κ^1(O)-coordinated aldehyde ester ligand. After liberation of the ester aldehyde by incoming aldehyde substrates, this molecule rapidly tautomerizes to yield the thermodynamically more stable respective 3-hydoxyacrylates, and compound **B** is regenerated.

In principle, an alternative pathway could proceed via the formation of the epoxide ethyl-3-arylglycidate from complex **B** with subsequent rearrangement (epoxide opening) to the corresponding enol ester, since it is known that transition metal complexes are able to convert epoxides to ketones and aldehydes. If this mechanism was possible, complex **8b** should be able to form 3-hydroxy-2-phenylacrylic acid ethyl ester from ethyl-3-phenylglycidate. However, when the epoxide was stirred with 10 mol % **8b** in CH_3NO_2 for 16 h, no reaction was observed. Thus, this alternative mechanism was dismissed.

A mechanism where in the initial step both aldehyde and EDA are coordinated, as proposed by Kanemasa et al.,[25] seems to be less likely but cannot be completely ruled out at

TABLE 1. Yields of 3-Hydroxyacrylates from the Reactions of Aromatic Aldehydes with EDA Catalyzed by [Fe(PNP-*i*Pr)(CO)$(CH_3CN)_2](BF_4)_2$ (8b)[a,b]

entry	aldehyde	3-hydroxyacrylate	%
1			84
2			88
3			86
4			86
5			58
6			83
7			91
8			78
9			89
10			84
11			74
12			80

[a] Reaction conditions: 1 equiv of aldehyde, 1 equiv of EDA, 10 mol % catalyst; CH_3NO_2 as the solvent, rt, reaction time 16 h. Yields represent isolated yields (average of at least three experiments). [b] The yield of β-ketoester is <3%.

this stage. Likewise, the intermediacy of carbenes may have been taken into account. In this context, it has to be mentioned that **8b** does not react with EDA in the absence of aldehydes.

Palladium(II)-Catalyzed Suzuki Coupling. Palladium pincer complexes mediate a number of catalytic reactions, mostly C−C bond-forming reactions. Examples include the coupling of aryl halides with boronic acids (Suzuki reaction)[8] and olefins (Heck reaction),[27] the hydroamination of olefins,[28] the stannation and silation of allyl, allenyl, and propargyl substrates,[29] and the aldol condensation of isocyanoacetates with aldehydes.[30] The most effective catalysts in palladium-mediated coupling reactions are pincer complexes of the PCP type; PNP, SCS, and NCN pincer complexes show much lower activities. On the basis of these findings, we were interested in investigating the catalytic activity of the palladium PNP and PCP complexes **12**, **18**, and **19** in the Suzuki coupling of aryl and alkyl bromides with phenylboronic acid.

The palladium PNP complexes **12a**−**c** are able to catalyze the Suzuki coupling of phenylboronic acid with aryl and alkyl bromides.[11] The coupling reaction of 4-bromotoluene with phenylboronic acid catalyzed by **12a**−**c** proceeded smoothly to give 4-methylbiphenyl in 91%, 90%, and 60% isolated yields, respectively. This reactivity trend suggests that both the stronger donating ability and the steric demand of the PR_2 substituents make the PNP ligands more electron-rich and render catalyst **12c** less active. Thus, only **12a** was utilized as catalyst. The coupling of 4-bromoacetophenone with phenylboronic acid proceeds with 97% isolated yield with a catalyst loading of 0.05 mol %, while the electronically deactivated and thus more challenging substrate 4-bromoanisole can be efficiently coupled with 87% isolated yield with a catalyst loading of 0.05 mol %. Even the sterically demanding 2,6-dimethylbromobenzene and 1-bromo-2-ethylbenzene gave acceptable yields, namely, 78% and 83%. Attempts to couple 2-bromopyridine and 1-bromododecane, the latter bearing β-hydrogen atoms, were also successful, resulting in reasonable yields. However, if the catalyst loading is lowered below 0.05 mol %, the yields drop significantly. Moreover, palladium black is visible in the reaction vessel upon completion of the reaction, indicating the presence of some kind of catalyst decomposition pathway. This observation is in agreement with results reported recently suggesting that pincer complexes are mere precatalysts, generating some form of metallic palladium(0) species, which is the real catalyst.[31]

The palladium PCP complexes, on the other hand, are much more effective catalysts than their PNP analogues in the Suzuki coupling of aryl and alkyl bromides with phenylbo-

SCHEME 17

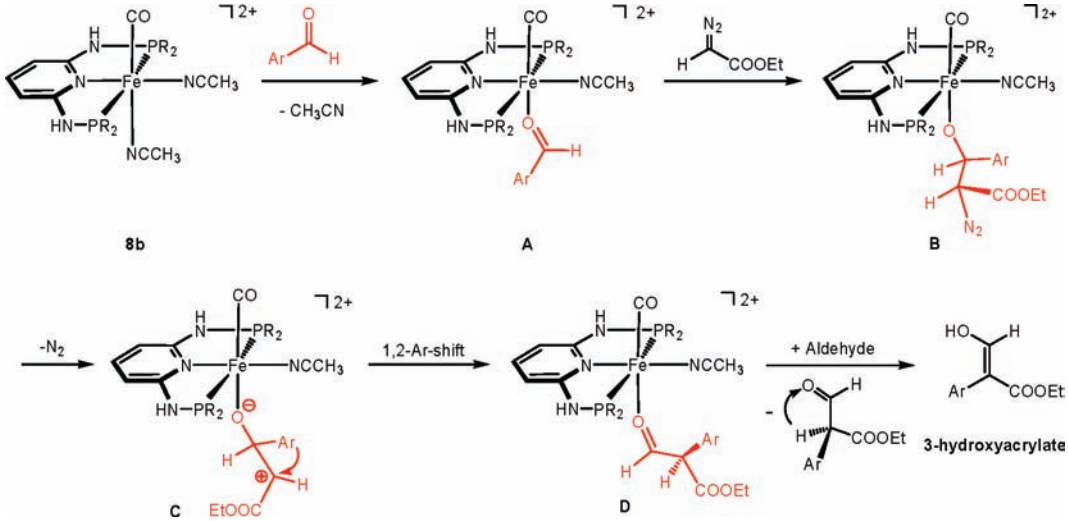


TABLE 2. Yields of the Suzuki–Miyaura Cross-Coupling of Aryl Bromides with Phenyl Boronic Acid Catalyzed by 18a, 18d, 19a, and 19d[a]

entry	R	catalyst (mol %)	yield (%)	TON
1	4-bromoacetophenone	**18a** (0.01)	>99	9.9×10^5
2	4-bromoacetophenone	**18a** (0.0001)	>99	9.9×10^5
3	4-bromoacetophenone	**18a** (0.00001)	97	9.7×10^6
4	4-bromoanisole	**18a** (0.01)	94	9900
5	4-bromoanisole	**18a** (0.001)	77	7.7×10^4
6	4-bromoanisole	**18a** (0.0001)	18	1.8×10^5
7	4-bromotoluene	**18a** (0.01)	>99	9900
8	4-bromotoluene	**18a** (0.001)	72	7.2×10^4
9	4-bromotoluene	**18a** (0.0001)	44	4.4×10^5
10	4-bromonitrobenzene	**18a** (0.01)	81	8100
11	2-ethylbromobenzene	**18a** (0.01)	65	6500
12	2-bromopyridine	**18a** (0.01)	68	6800
13	1-bromododecane	**18a** (0.01)	74	7400
14	4-bromoacetophenone	**18d** (0.01)	>99	9900
15	4-bromoanisole	**18d** (0.01)	>99	9900
16	4-bromoacetophenone	**19a** (0.01)	>99	9900
17	4-bromoacetophenone	**19a** (0.001)	15	1.5×10^4
18	4-bromotoluene	**19a** (0.01)	70	7000
19	4-bromoanisole	**19a** (0.1)	88	880
20	4-bromoacetophenone	**19d** (0.01)	>99	9900
21	4-bromoacetophenone	**19d** (0.001)	36	3600

[a] Reaction conditions: 1.0 mmol of bromide, 1.5 mmol of $PhB(OH)_2$, 2.0 mmol of K_2CO_3, 5 mL of toluene, 110 °C; reaction time is 16 h; yields represent isolated yields (average of at least three experiments) of compounds estimated to be ≥95% pure as judged by ^1H NMR.

ronic acid (Table 2).[12] In general, the chloro complexes **18a**–**f** are better catalysts than the respective TFA complexes **19a**–**d**. Much lower catalyst loadings can be reached; for example, the reaction of 4-bromoacetophenone with phenylboronic acid and **18a** as catalyst proceeds with 97% isolated yield even with 0.00001 mol % catalyst (TON = 9.7×10^6), while the electronically deactivated and thus more challenging substrate 4-bromoanisole can still be coupled in 18% yield with a catalyst loading of 0.0001 mol % (TON = 1.8×10^5). This results in turnover frequencies (TOFs) as high as 600 000 h^{-1} (170 s^{-1}), which are among the highest reported for palladium pincer complexes in the Suzuki reaction. Contrary to what was observed for the palladium PNP complexes, no palladium black is visible in the reaction vessel after the reaction is complete, which may be attributed to the higher stability of the PCP complexes due to the presence of the stronger Pd–C bonds. Moreover, the catalyst remains active after the reaction is complete, and upon addition of more substrates, the reaction is resumed, leading to the coupling product in the same yields and at the same reaction rates. The coupling of heterocyclic and alkyl bromides with phenylboronic acid is also possible, and reasonable yields were obtained using 0.01 mol % **18a** as the catalyst.

5. Conclusions

In sum, we have shown that new achiral and chiral PNP and PCP ligands are easily prepared from commercially available and inexpensive 2,6-diaminopyridine, 1,3-diaminobenzene, and related precursors, which can be varied in modular fashion by choosing the appropriate monochlorophosphine or -phosphite R_2PCl. These, in turn, are easily accessible in high yields from a large array of both achiral and chiral diols and PCl_3. This methodology contrasts the generally arduous synthetic procedures required for the preparation of 1,3-bis(phosphino)benzenes. In conjunction with transition metal fragments such as $Mo(CO)_3$, $FeCl_2$, $[Fe(CH_3CN)_3]^{2+}$, and MX (M = Ni, Pd, Pt; X = Cl, Br, CF_3COO) stable PNP complexes are formed. Also PCP complexes are readily formed with the MX fragment (M = Ni, Pd, Pt; X = Cl, Br, CF_3COO). Some of these compounds are catalytically active in C–C bond-forming reactions such as in the case of iron and palladium complexes.

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BIOGRAPHICAL INFORMATION

David Benito-Garagorri was born in Bilbao (Spain) in 1980, where he received his M.Sc. in 2003 from the University of the Basque Country. He completed his Ph.D. in 2007 at the Vienna University of Technology under the supervision of Professor Karl Kirchner working on aminophosphine-based pincer ligands and complexes and is currently a research associate in the same group.

Karl Kirchner was born in Wr. Neustadt, Austria, in 1960. He obtained his diploma (1984) and his doctoral degree (1987) from the Vienna University of Technology working with Prof. Roland Schmid. After a two-year postdoctoral stay at Washington State University (1988−1990) with Prof. John P. Hunt and an additional postdoctoral year with Prof. Henry Taube at Stanford University, he returned to the Vienna University of Technology where he is presently an associate Professor of Chemistry. His research interests are in the fields of coordination chemistry, organometallic chemistry, and homogeneous catalysis.

FOOTNOTES

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