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Air Stable Iron(II) PNP Pincer Complexes as Efficient Catalysts for the Selective Alkylation of Amines with Alcohols

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Abstract: A series of well-defined iron(II) complexes of the types [Fe(PNP)Br_2] and [Fe(PNP)(CO)Br_2] with PNP pincer ligands based on triazine and pyridine backbones were prepared and fully characterized. These complexes were tested as catalysts for the alkylation of amines by alcohols. The high-spin complexes [Fe(PNP)Br_2] are catalytically inactive. The low-spin complexes [Fe(PNP)(CO)Br_2] bearing a carbonyl co-ligand efficiently and selectively convert primary alcohols and aromatic and benzylic amines selectively into mono-*N*-alkylated amines in good to excellent isolated yields. A mechanistic proposal is given.

Keywords: alcohols; amines; homogeneous catalysis; iron complexes; pincer complexes

Introduction

The choice of alcohols as substrates is highly desirable in terms of sustainability as they are readily available by a variety of industrial processes and can be obtained renewably *via* fermentation or catalytic conversion of lignocellulosic biomass.[1] Accordingly, the catalytic alkylation of amines with alcohols represents an environmentally benign and atom-economic pathway for the synthesis of substituted imines or amines that have important applications in the synthesis of dyes, fragrances, fungicides, pharmaceuticals, and agricultural chemicals.[2–4] The catalytic cycle involves three successive steps: (i) acceptorless dehydrogenation (AD) of alcohols,[5] (ii) imine formation, and (iii) *in situ* hydrogenation of imines (borrowing hydrogen methodology). Key features are that the process is hydrogen neutral and that the only stoichiometric by-product is water.

Despite the importance of such coupling reactions, homogeneous catalysts mostly employ precious metals such as ruthenium,[6] rhodium,[7] iridium,[8] and osmium,[9] while the same reaction with non-precious, earth-abundant metal catalyst[10] is much less developed. This is surprising taken the fact that base metals were found to readily oxidize alcohols *via* AD.[11,12] Kempe and co-workers described for the first time a new cobalt PNP pincer catalyst based on a triazine backbone, which was highly active for the alkylation of aromatic amines (Figure 1).[13] Hanson[14a] and Zhang[14b] reported a cobalt catalyst, stabilized by a bis(phosphino)amine (PNP) ligand (Figure 1), which is able to afford imines and/or amines depending on the reaction conditions. As far as iron catalysts are concerned the groups of Feringa and Barta,[15a] Wills,[15b] and Zhao[15c] reported the alkylation of amines with alcohols to give amines. All these iron catalysts feature functionalized cyclopentadienone or hydroxycyclopentadienyl ligands based upon Knölker's complex or derivatives thereof.[16] We have prepared the first cobalt(II) PCP pincer complexes with a 1,3-diaminobenzene backbone as well as a hydride iron(II) PNP pincer complex based on the 2,6-diamonopyridine scaffold which are also active catalysts for the alkylation of amines with alcohols to give amines.[17,18] Depending on the co-ligands, i.e., chloride *vs.* CH_2SiMe_3, the reaction with cobalt(II) works in the presence of a strong base or under base-free conditions with molecular sieve as additive. Very recently, Milstein and co-workers[19] discovered the

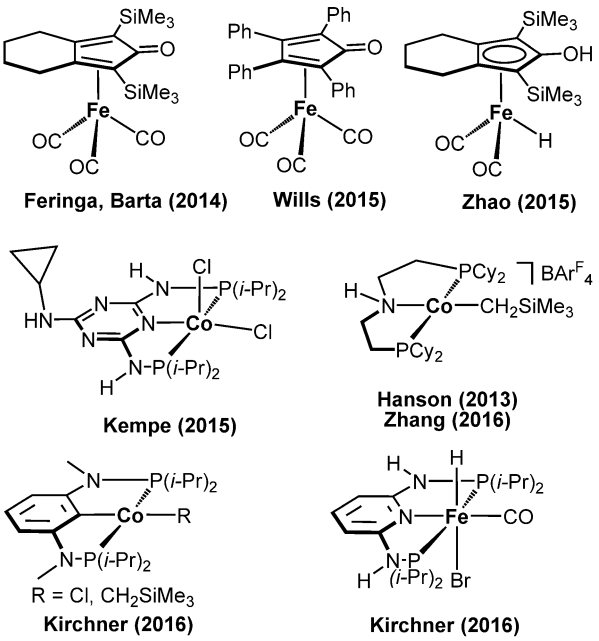


Figure 1. Efficient base metal catalysts for the alkylation of amines with alcohols.

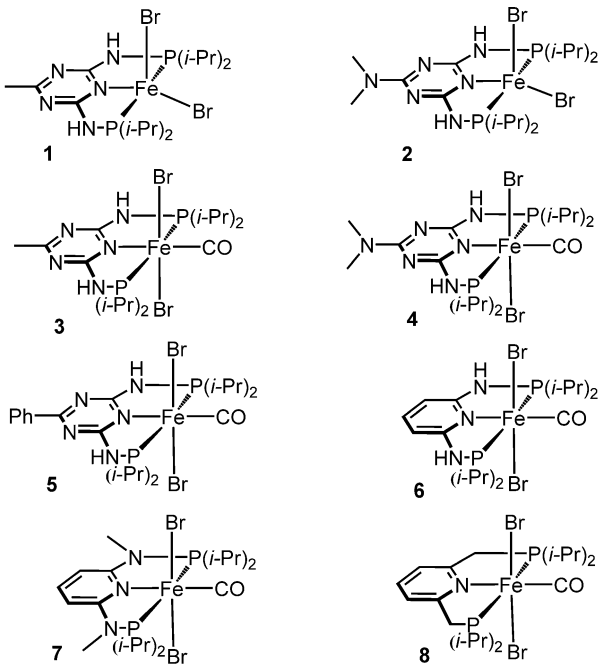


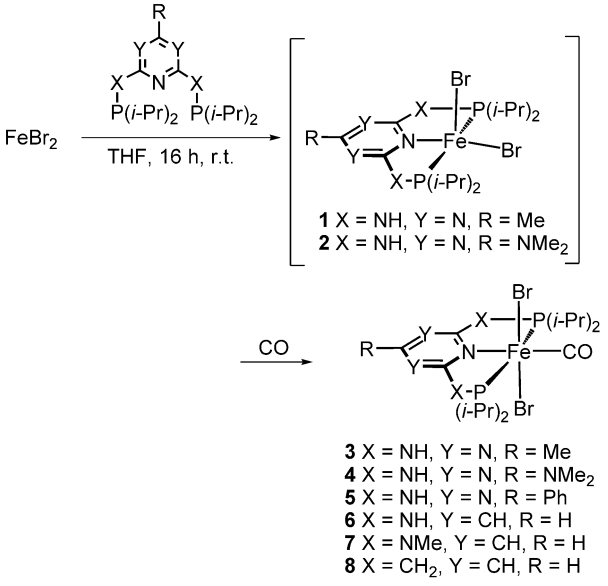
Figure 2. Iron(II) PNP pincer complexes tested as catalysts.

first manganese catalyst which is active for the dehydrogenative coupling of alcohols and amines to form selectively imines. This catalyst features a deprotonated 2,6-bis-(di-*tert*-butylphosphinomethyl)pyridine pincer ligand.

Inspired by these recent discoveries in this area, we describe here an efficient alkylation of amines with alcohols catalyzed by well-defined iron(II) complexes which are stabilized by PNP ligands featuring triazine and pyridine backbones as shown in Figure 2.

Results and Discussion

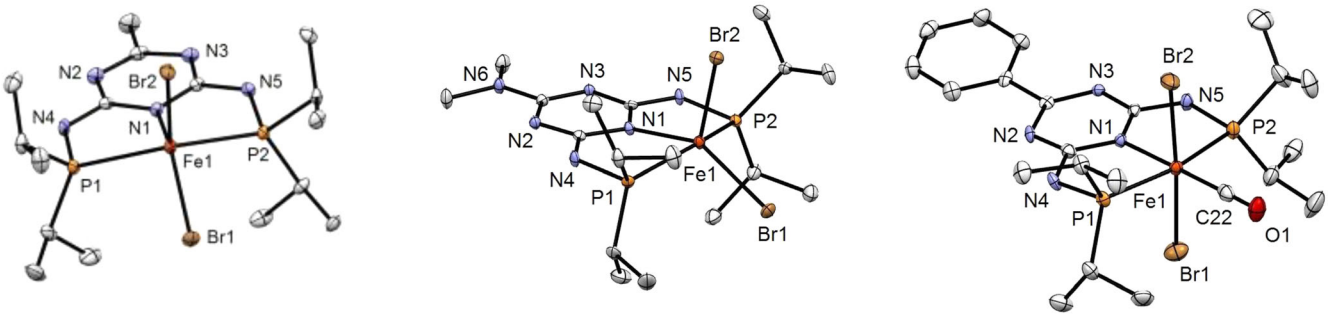
Treatment of anhydrous $FeBr_2$ with 1 equiv. of the PNP ligands Triaz^{Me}-*i*-Pr and Triaz^{NMe_2}-*i*-Pr in THF at room temperature afforded the pentacoordinated complexes [Fe(Triaz^{Me}-*i*-Pr)Br_2] (**1**) and [Fe(Triaz^{NMe_2}-*i*-Pr)Br_2] (**2**) in 90 and 93% isolated yields (Scheme 1). These complexes are paramagnetic with an effective magnetic moment of 5.1 μ_B as determined in solution (Evans method[20]) corresponding to four unpaired electrons. These types of complex do not need to be isolated, as they readily react with carbon monoxide to afford the diamagnetic octahedral mono-carbon monoxide complexes *trans*-[Fe(Triaz^{Me}-*i*-Pr)(CO)Br_2] (**3**) and *trans*-[Fe(Triaz^{NMe_2}-*i*-Pr)(CO)Br_2] (**4**). Accordingly, all mono-carbon monoxide complexes were obtained in an one-step procedure yielding directly *trans*-[Fe(Triaz^{Me}-*i*-Pr)(CO)Br_2] (**3**), *trans*-[Fe(Triaz^{NMe_2}-*i*-Pr)(CO)Br_2] (**4**) and *trans*-[Fe(Triaz^{Ph}-*i*-Pr)(CO)Br_2] (**5**) in 89–95% isolated



Scheme 1. Synthesis of pre-catalysts **1**–**8**.

yields (Scheme 1). In all cases, selectively the *trans*-dibromide complexes were obtained as indicated by only one strong ν_{CO} band in the range of 1947 to 1963 cm^{-1}. The syntheses of complexes *trans*-[Fe(PNP-*i*-Pr)(CO)Br_2] (**6**),[21] *trans*-[Fe(PNP^{Me}-*i*-Pr)(CO)Br_2] (**7**),[22] and *trans*-[Fe(PNP^{CH_2}-*i*-Pr)(CO)Br_2] (**8**)[23] were reported elsewhere.

Unlike **5**, complexes **3** and **4** were poorly soluble in all common solvents. All complexes were characterized by elemental analysis and IR spectroscopy. Com-



1 2 3

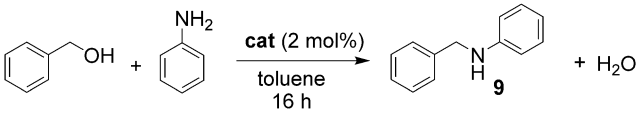
Figure 3. Structural views of [Fe(Triaz^{Me}-*i*-Pr)Br$_2$]·1THF (**1**·THF), [Fe(Triaz^{NMe_2}-*i*-Pr)Br$_2$]·THF (**2**·THF), and *trans*-[Fe(Triaz^{Ph}-*i*-Pr)(CO)Br$_2$]·2THF (**5**·2THF) and showing 50% thermal ellipsoids (H atoms and solvent molecules omitted for clarity). Selected bond lengths (Å) and bond angles (°):**1:** Fe1–N1 2.186(2), Fe1–Br1 2.5338(5), Fe1–Br2 2.4161(5), Fe1–P1 2.4790(9), Fe1–P2 2.4804(9), N1–Fe1–Br1 139.36(6), N1–Fe1–Br2 104.84(5), Br1–Fe1–Br2 115.73(2), P1–Fe1–P2 148.48(3). **2:** Fe1–Br1 2.5196(6), Fe1–Br2 2.4516(6), Fe1–P1 2.482(1), Fe1–P2 2.490(1), Fe1–N1 2.171(3), Br1–Fe1–Br2 111.51(3), P1–Fe1–P2 149.24(2). **5:** Br1–Fe1 2.4517(8), Fe1–Br2 2.4426(8), Fe1–P1 2.266(1), Fe1–P2 2.264(1), Fe1–N1 1.984(3), Fe1–C22 1.782(4), P1–Fe1–P2 165.09(4), Br1–Fe1–Br2. 175.34(3), N1–Fe1–C22 179.5(2).

plex **5** was also characterized by solution ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectroscopy, while **3** and **4** were characterized by solid state ^{13}C and ^{31}P NMR spectroscopy. In addition, the molecular structures of **1, 2** and **5** were determined by X-ray crystallography. Structural views are depicted in Figure 3 with selected bond distances and angles given in the caption.

Iron complexes **1** to **8** were screened for the alkylation of aniline (1.2 equiv.) with benzyl alcohol (1.0 equiv.) in toluene (4 mL) at 80 °C with KO-*t*-Bu (1.3 equiv.) as additive. The role of stoichiometric amounts of base is not fully understood at this stage. One role is the deprotonation of the PNP ligand, but another role may be the facilitation of the condensation reaction, i.e., the liberation of water. All reactions were performed in a closed vial. A mercury poisoning experiment supports a homogeneous catalyzed pathway. The results are summarized in Table 1. The products were analyzed by ^{1}H, ^{13}C{^{1}H} NMR, and ESI MS and identified by comparison with authentic samples reported elsewhere.[17,18] In general, isolated yields after purification by column chromatography are reported.

When **1**, **2** and **7** were used as pre-catalyst no reaction took place (Table 1, entries 1, 4 and 7). In the case of **1** and **2** this may be due to the fact that these complexes, in contrast to all other compounds, contain no carbon monoxide co-ligand and are thus paramagnetic d^6 high-spin complexes. Alternatively, these complexes may be also unstable to dehydrogenative deprotonation without the stabilizing carbonyl co-ligand. Complex **7**, on the other hand contains an NMe linker instead of an NH linker and thus deprotonation of the ligand is blocked, a feature which turned out to be very important for these types of complexes in order to exhibit a good catalytic performance. Moreover, the pyridine-based complex **8**[23] bearing CH_2 linkers showed only modest activity (Table 1, entry 8). All other complexes showed excellent to good activities, with **4** being the best catalyst yielding selectively *N*-benzylaniline in 91% yield (entry 5). Lower catalyst loading (1 mol%) or shorter reaction times (8 and 4 h) resulted in slightly lower yields (Table 1, entries 12–14). The best solvent for

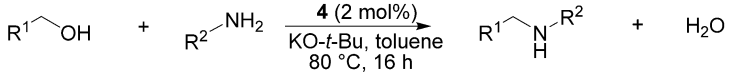
Table 1. Catalyst screening of the alkylation of aniline with benzyl alcohol.[a,b]

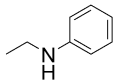
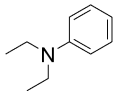
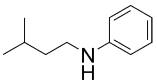
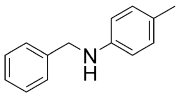
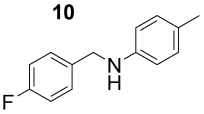
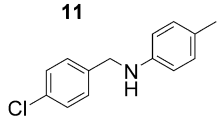
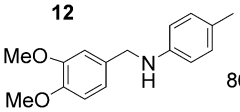
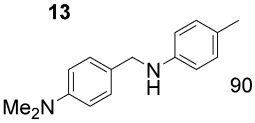
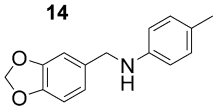
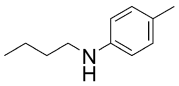
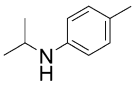
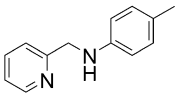
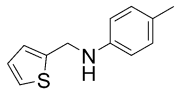
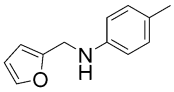
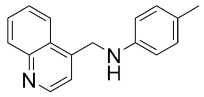
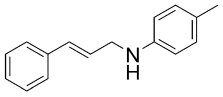
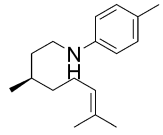
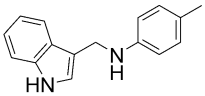
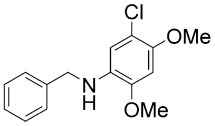
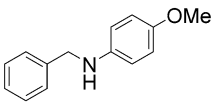
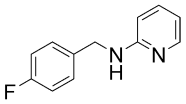
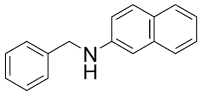
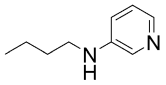
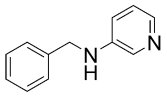
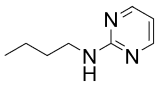
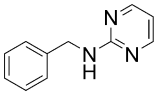
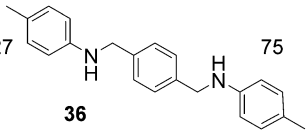
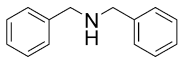
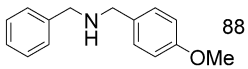
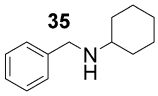


Entry	Catalyst	Solvent	Yield [%]
1	**1**	toluene	0
2	**2**	toluene	0
3	**3**	toluene	80
4	**4**	toluene	91
5	**5**	toluene	51
6	**6**	toluene	84
7	**7**	toluene	0
8	**8**	toluene	24
9	**4**	benzene	90
10	**4**	THF	34
11	**4**	dioxane	28
12[c]	**4**	toluene	79
13[d]	**4**	toluene	69
14[e]	**4**	toluene	54

[a] *Reaction conditions:* 1.0 mmol benzyl alcohol, 1.2 mmol aniline, 1.3 mmol KO-*t*-Bu, 2 mol% catalyst, 4 mL toluene, 16 h, 80 °C.
[b] Isolated yields.
[c] With 1 mol% catalyst.
[d] For 8 h.
[e] For 4 h.

Table 2. Coupling of primary alcohols and amines catalyzed by **4**.[a,b]



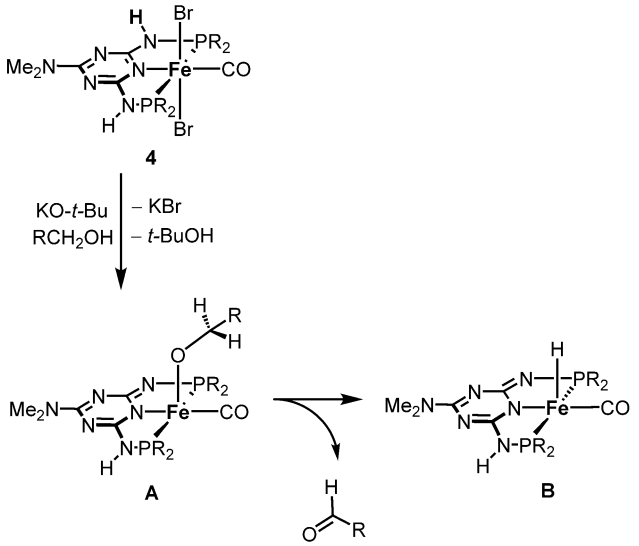
Entry	Product	Yield [%]	Entry	Product	Yield [%]	Entry	Product	Yield [%]	Entry	Product	Yield [%]
1	 **10**	88	2	 **11**	4	3	 **12**	63	4	 **13**	93
5	 **14**	82	6	 **15**	71	7	 **16**	86	8	 **17**	90
9	 **18**	85	10	 **19**	87	11	 **20**	0	12	 **21**	34
13	 **22**	81	14	 **23**	87	15	 **24**	82	16	 **25**	91
17	 **26**	88	18	 **27**	73	19	 **28**	74	20	 **29**	87
21	 **30**	21	22	 **31**	90	23	 **32**	71	24	 **33**	74
25	 **34**	62	26	 **35**	76	27	 **36**	75	28	 **37**	81
29	 **38**	88	77	 **39**	62						

[a] *Reaction conditions:* 1.0 mmol alcohol, 1.2 mmol amine, 1.3 mmol KO-*t*-Bu, 2 mol% catalyst, 4 mL toluene, 80 °C, 16 h.
[b] Isolated yields.
[c] With 4 mol% catalyst.

these reactions was toluene, while in THF or dioxane much lower yields were achieved (Table 1, entries 10 and 11).

Having established **4** as the most efficient catalyst in this series, this methodology was applied to other substrates including substituted benzyl alcohols or furfuryl aclohol, aliphatic alcohols such as *R*-citronellol, EtOH, and *n*-BuOH as well as aromatic amines. These results are shown in Table 2. In most cases the resulting mono-*N*-alkylated amines were isolated in good to excellent yields. Exceptions are the reactions of 2-propanol and 2-pyridinemethanol with *p*-toluidine (Table 2, entries 11 and 21) where no and only 17% product yield, respectively, could be isolated. It has to be noted that, in general, dialkylated amines were not formed. This has been tested with EtOH (2.2 mmol), KO-*t*-Bu (2.6 mmol) and aniline (1.0 mmol) affording only 7% of the dialkylated aniline (Table 2, entry 2). The major product is the monoalkylated amine **10** (Table 2, entry 1).

The actual catalyst is presumably formed upon reaction of pre-catalyst **4** with the strong base KO-*t*-Bu



Scheme 2. Proposal for the formation of catalyst **B** (R = *i*-Pr).

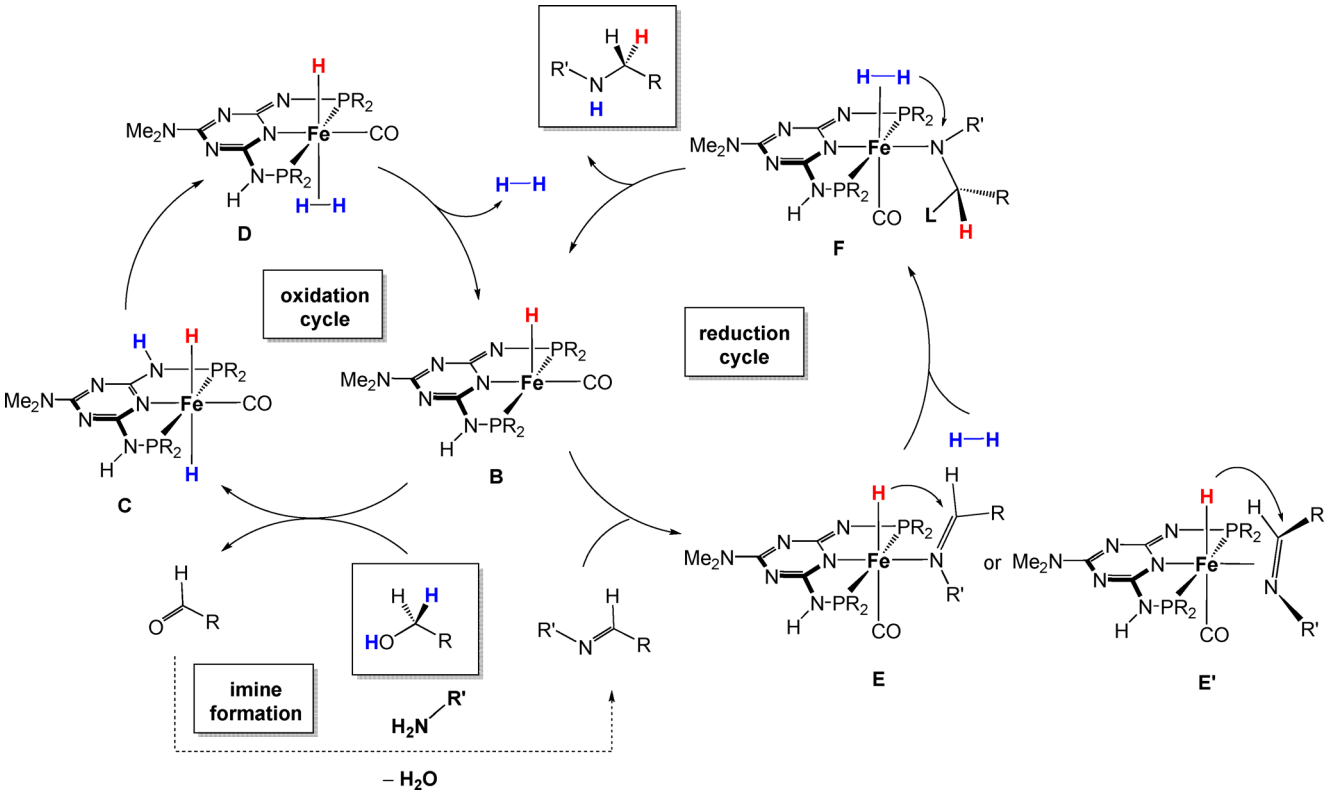
in the presence of a primary alcohol (Scheme 2). Deprotonation of both the triazine ligand and the alcohol affords initially the alkoxide complex **A** which undergoes β-elimination to yield the hydride complex **B** thereby releasing aldehyde.

As recently shown by Kempe[24] and by us,[25] triazine-based PNP pincer complexes are indeed readily deprotonated in the presence of strong bases.

A tentative, simplified catalytic cycle with **B** as key species is depicted in Scheme 3. Intermediate **B** can participate in two catalytic reactions performing both alcohol dehydrogenation (oxidation cycle) and imine hydrogenation (reduction cycle) *via* an insertion mechanism. A related oxidation cycle was recently described for a related manganese(I) PNP complex based on DFT calculations.[18] In the reduction cycle coordination of dihydrogen (**F**) and subsequent protonation of the imine *N*-atom with formation of the amine and regeneration of the hydride **B** is essential. A similar insertion mechanism with complexes of the type **B** as catalyst was recently proposed for the hydrogenation of ketones and aldehydes by an iron(II) PNP pincer complex.[26a] It has to be noted that an outer sphere hydrogenation of imines, as proven recently for the chemoselective hydrogenation of aldehydes,[26b] cannot be fully excluded but appears to be less likely in this particular case.

Conclusions

We have prepared and fully characterized a series of well-defined iron(II) complexes of the types



Scheme 3. Tentative catalytic cycle with **B** as catalyst (R = *i*-Pr).

[Fe(PNP)Br_2] and [Fe(PNP)(CO)Br_2] with PNP pincer ligands based on triazine and pyridine backbones. While complexes with carbon monoxide as co-ligand, which are diamagnetic d^6 low-spin systems, are catalytically active, paramagnetic d^6 high-spin complexes [Fe(PNP)Br_2] are completely inactive. We have described here an example of an efficient alkylation of amines with alcohols catalyzed by well-defined iron(II) complexes which are stabilized by a PNP ligand based on the 4,6-diaminotriazine scaffold. The precatalyst is easily prepared from commercially available reagents in a two-step procedure in high yields. These alkylation reactions are environmentally benign processes and implement inexpensive, earth-abundant non-precious metal catalysts and are based on the acceptorless alcohol dehydrogenation concept. A range of substituted benzyl alcohols including heterocyclic systems such as furfuryl alcohol and aliphatic alcohols (*R*-citronellol, EtOH, *n*-BuOH) and aromatic amines were efficiently converted into mono-*N*-alkylated amines in good to excellent isolated yields. A mechanistic proposal is presented with a deprotonated hydride iron(II) complex as key intermediate.

Experimental Section

General

All manipulations were performed under an inert atmosphere of argon by using Schlenk techniques or in an MBraun inert-gas glovebox. The solvents were purified according to standard procedures.[27] The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. The ligands *N*,*N*′-bis(diisopropylphosphino)-2,4-diamino-6-methyltriazine (Triaz^{Me}-*i*-Pr),[22] *N*,*N*′-bis(diisopropylphosphino)-2,4-diamino-6-phenyltriazine (Triaz^{Ph}-*i*-Pr),[28] *N*,*N*′-bis(diisopropylphosphino)-*N*″-dimethyl-2,4,6-triaminotriazine (Triaz^{NMe_2}-*i*-Pr),[28] and the complexes *trans*-[Fe(PNP-*i*-Pr)(CO)Br_2] (**6**),[21] *trans*-[Fe(PNP^{Me}-*i*-Pr)(CO)Br_2] (**7**),[22] and *trans*-[Fe(PNP^{CH_2}-*i*-Pr)(CO)Br_2] (**8**)[23] were prepared according to literature procedures. All substrates are known compounds and were used as obtained from commercial sources. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on Bruker AVANCE-250 and AVANCE-400 spectrometers. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced internally to residual protio-solvent, and solvent resonances, respectively, and are reported relative to tetramethylsilane ($\sigma = 0$ ppm). ^{31}P{^{1}H} NMR spectra were referenced externally to H_3PO_4 (85%) ($\sigma = 0$ ppm). Room-temperature solution magnetic moments were determined by ^{1}H NMR spectroscopy using the method of Evans (CD_3OD/CH_3OH).[20]

The solid state NMR spectra were measured at room temperature with a Bruker AVANCE 300 spectrometer using a 4 mm MAS broadband probe head. The rotor spinning speed for all performed experiments was 11 kHz. The ^{13}C NMR spectra were measured with ramped-CP/MAS experiments at a resonance frequency of 75.40 MHz. The ^{31}P NMR spectra were measured with high power decoupled (HPDEC) experiments at a resonance frequency of 121.38 MHz and the spectra were referenced externally against phosphoric acid (^{31}P: 0 ppm).

All mass spectrometric measurements were performed on an Esquire 3000^{plus} 3D-quadrupole ion trap mass spectrometer (Bruker Daltonics, Bremen, Germany) in positive-ion mode by means of electrospray ionization (ESI). Mass calibration was done with a commercial mixture of perfluorinated trialkyltriazines (ES Tuning Mix, Agilent Technologies, Santa Clara, CA, USA). All analytes were dissolved in $CH_3CN/H_2O/HCOOH$ "hypergrade for LC-MS Lichrosolv" quality (Merck, Darmstadt, Germany) to form a concentration of roughly 1 mg mL^{-1} in order to suppress dehydrogenations of several analytes. Direct infusion experiments were carried out using a Cole Parmer model 74900 syringe pump (Cole Parmer Instruments, Vernon Hills, IL, USA) at a flow rate of 2 μL min^{-1}. Full scan and MS/MS (low energy CID)-scans were measured in the range m/z 100–1100 with the target mass set to m/z 1000. Further experimental conditions include: drying gas temperature: 200 °C; capillary voltage: −4 kV; skimmer voltage: 40 V; octapole and lens voltages: according to the target mass set. Mass spectra were averaged during data acquisition time of 1 to 2 min and one analytical scan consisted of five successive micro scans resulting in 50 and 100 analytical scans, respectively, for the final full scan mass spectrum.

Syntheses

[Fe(Triaz^{Me}-*i*-Pr)Br_2] (1): A suspension of anhydrous $FeBr_2$ (1.15 g, 5.3 mmol) and Triaz^{Me}-*i*-Pr (2.0 g, 5.6 mmol) in THF (10 mL) was stirred for 16 h at room temperature. The volume of the solvent was then reduced to about 3 mL and the formed solid was collected on a glass frit, then washed with *n*-pentane (3 × 7 mL) and dried under vacuum; yield: 2.74 g (90%); pale yellow solid. Anal. calcd. for $C_{16}H_{33}Br_2FeN_5P_2$ (573.08): C 33.53, H 5.80, N 12.22; found: C 33.40, H 5.90, N 12.30; $\mu_{eff} = 5.1$ μ_B (CD_3OD/CH_3OH).

[Fe(Triaz^{NMe_2}-*i*-Pr)Br_2] (2): This complex was prepared analogously to **1** with $FeBr_2$ (1.06 g, 4.9 mmol) and Triaz^{NMe_2}-*i*-Pr (2.0 g, 5.2 mmol) as starting materials; yield: 2.72 g (92%); white solid. Anal. calcd. for $C_{17}H_{36}Br_2FeN_5P_2$ (602.12): C 33.91, H 6.03, N 13.96; found: C 33.90, H 6.03, N 13.95; $\mu_{eff} = 5.1$ μ_B (CD_3OD/CH_3OH).

***trans*-[Fe(Triaz^{Me}-*i*-Pr)(CO)Br_2] (3):** A suspension of anhydrous $FeBr_2$ (1.15 g, 5.3 mmol) and Triaz^{Me}-*i*-Pr (2.0 g, 5.6 mmol) in THF (10 mL) was stirred for 30 min at room temperature. Afterwards CO was bubbled into the clear solution for 5 min and then stirred for additional 16 h. The solvent was then reduced to about 3 mL, the formed solid was collected on a glass frit, then washed with *n*-pentane (3 × 7 mL) and dried under vacuum; yield: 2.97 g (93%); red solid. IR (ATR): $\nu = 3166$ (m, NH), 1947 cm^{-1} (m, CO); anal. calcd. for $C_{17}H_{33}Br_2FeN_5OP_2$ (601.09): C 33.97, H 5.53, N 11.65; found: C 34.16, H 5.61, N, 11.58; solid-state NMR: ^{13}C-CP/MAS (20 °C): $\delta = 217.2$ (CO), 164.3 (C_{Triaz}), 158.5 (C_{Triaz}), 54.8 (d, $J = 51.7$ Hz, CH), 28.4 (CH_3), 12.2 (d, $J = 10.5$ Hz, CH_3); ^{31}P HPDEC NMR (20 °C): $\delta = 121.00$.

***trans*-[Fe(Triaz^{NMe_2}-*i*-Pr)(CO)Br_2] (4):** This complex was prepared analogously to **3** with $FeBr_2$ (1.06 g, 49 mmol) and Triaz^{NMe_2}-*i*-Pr (2 g, 5.2 mmol) as starting materials; yield: 2.94 g (95%); blue solid. IR (ATR): $\nu = 3251$ (m, NH),

1958 cm^{-1} (m, CO); anal. calcd. for $C_{18}H_{36}Br_2FeN_5OP_2$ (630.13): C 34.31, H 5.76, N 13.34; found: C 34.42, H 5.80, N 13.28; ^{13}C-CP/MAS (20 °C): $\delta = 219.9$ (CO), 168.9 (C_{Triaz}), 165.4 (C_{Triaz}), 62.3 (CH_3), 20.0 (CH), 13.6 (CH_3); ^{31}P HPDEC NMR (20 °C): $\delta = 123.6$.

***trans*-[Fe(Triaz^{Ph}-*i*-Pr)(CO)Br$_2$] (5):** This complex was prepared analogously to **3** with $FeBr_2$ (0.97 g, 4.5 mmol) and Triaz^{Ph}-*i*Pr (2.0 g, 4.7 mmol) as starting materials; yield: 2.67 g (89%); green solid. IR (ATR): $\nu = 3257$ (m, NH), 1963 cm^{-1} (CO); anal. calcd. for $C_{22}H_{35}Br_2FeN_5OP_2$ (663.16): C 39.85, H 5.32, N 10.56; found: C 39.95, H 5.27, N 10.60; ^{1}H NMR (THF-d_8, 20 °C): $\delta = 8.76$ (s, 2H, NH), 8.32 (d, $J = 7.5$ Hz, 2H, PhH), 7.43 (t, $J = 7.2$ Hz, 1H, PhH), 7.36 (d, $J = 7.4$ Hz, 2H, PhH), 3.19–3.14 (m, 4H, CH), 1.48 (q, $J = 6.9$ Hz, 12H, CH_3), 1.32 (q, $J = 7.2$ Hz, 12H, CH_3); ^{13}C{^{1}H} NMR (THF-d_8, 20 °C): $\delta = 226.0$ (t, $J = 21.6$ Hz, CO), 172.8 (t, $J = 12.7$ Hz, C_{Triaz}), 171.9 (C_{Triaz}), 136.6 (Ph), 132.5 (PhH), 129.0 (PhH), 128.6 (PhH), 27.6 (t, $J = 10.0$ Hz, CH), 19.0 (t, $J = 27.7$ Hz, CH_3), 18.0 (t, $J = 59.7$ Hz, CH_3); ^{31}P{^{1}H} NMR (THF-d_8, 20 °C): $\delta = 120.4$.

General Procedure for the Alkylation of Amines

Alcohol (1.0 mmol), aniline (1.2 mmol) and KO-*t*-Bu (1.3 mmol) were mixed in toluene (4 mL) and the catalyst (0.02 mmol, 2 mol%) was added under inert conditions. After stirring for 16 h at 80 °C the mixture was quenched with water (*ca.* 2 mL), the organic layer was dried with $MgSO_4$ and purified *via* silica column chromatography (eluted with toluene and Et_2O). The products were analyzed by ^{1}H, ^{13}C{^{1}H} NMR, and ESI-MS and identified by comparison with authentic samples reported elsewhere.[17] In general, isolated are reported.

Crystal Structure Determination

X-ray diffraction data of [Fe(Triaz^{Me}-*i*-Pr)Br$_2$]·THF (**1**·THF), [Fe(Triaz^{NMe_2}-*i*-Pr)Br$_2$]·THF (**2**·THF), and [Fe(Triaz^{Ph}-*i*-Pr)(CO)Br$_2$]·2THF (**5**·2THF) were collected at 100 K in a dry stream of nitrogen on a Bruker Kappa APEX II diffractometer system using graphite-monochromatized Mo-*K*α radiation ($\lambda = 0.71073$ Å) and fine sliced φ- and ω-scans.[29] The diffraction spots of **5**·2THF were attributed to two triclinic domains related by two-fold rotation about [100]. Data were reduced to intensity values with SAINT (in the case of **5**·2THF with overlap information) and an absorption correction was applied with the multi-scan approach implemented in SADABS or TWINABS.[30] The structures were solved by charge flipping using SUPERFLIP[31] and refined against *F* with JANA2006.[32] Although **1**·THF possessed orthorhombic metrics, the structure is monoclinic and was refined as a twin by pseudo-merohedry. **5**·2THF was refined as a twin with partially overlapping reflections. Non-hydrogen atoms and the C atoms of a disordered THF molecule in **5**·2THF were refined anisotropically. The H atoms connected to C atoms were placed in calculated positions and thereafter refined as riding on the parent atoms. The amine Hs were located in difference Fourier maps. The N–H distances were restrained to 0.870(1) Å and the C–C distances of the disordered THF molecule in **5**·2THF to 1.500(1) Å.

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