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Homoleptic Iron(II) and Cobalt(II) Bis (phosphoranimide) Complexes for Selective Hydrofunctionalization of Unsaturated Molecules

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The low-coordinate homoleptic bulky $M_2(NP^tBu_3)_4$ (M = Fe (A), Co (B)) complexes were synthesized and characterized as dimeric structures by crystallographic studies. Iron complex A can catalyze the hydroboration reaction of aldehydes and ketones. Cobalt complex B outperformed its iron counterpart in hydrogenations of several typical alkenes and alkynes under mild conditions. Poisoning experiments indicate that the Co(II)/HB(pin) catalytic system could be homogeneous.

Hydrofunctionalization of unsaturated compounds is an important area among organic transformations. Primary and secondary alcohols can be easily obtained via the hydroboration of corresponding aldehydes and ketones followed by the hydrolysis of boronate esters.¹ Hydrogenation of C-C double or triple bonds is another well-established area in fine chemical synthesis.² Complexes of precious metals such as rhodium, ruthenium, iridium, and palladium have been widely used as catalysts in hydroboration, hydrogenation, or transfer hydrogenation of polar and non-polar π -bonds.^{1a, 3} There are growing demands to find cheaper and more environmentally friendly surrogates of precious metal catalysts for organic transformations.⁴

There are growing demands to find cheaper and more environmentally friendly surrogates of precious metal catalysts for organic transformations. Base metals such as iron and cobalt are less expensive and less toxic than precious metals, and may serve as practical replacements. Other features of base metals, such as their small covalent radii and the narrow energy gaps among their *d* orbitals, make catalyst development a challenging task.⁵ Therefore; ligand design is essential for the purpose of maintaining catalytic activity. One successful approach has been the use of redox-active ligands, which can behave as a single electron sponge, making it

^{Pt} Bu ₃ " "Bu₂P=N−M [™] .M−N=PtBu₂	$M = E_{0}(\mathbf{A})$
P ^t Bu ₂	$M = Co(\mathbf{B})$

Scheme 1. Tri-t-butyl-phosphoranimidometal(II) dimers.

unnecessary for the metal centre to change oxidation state directly. $^{\rm 6}$

Phosphoranimide ligands were discovered and studied by Dehnicke and Weller around 20 years ago.⁷ Stoichiometric reactions between transition metal halide precursors and phosphoranimide ligands have been systematically studied as well. However, the catalytic reactivity is rarely studied.^{8, 9} Herein we wish to report the preparation and characterization of non-pincer homoleptic base metal complexes $M_2(\mu$ - $NP^{t}Bu_{3}_{2}(NP^{t}Bu_{3})_{2}$ (M = Fe (A), Co(B)) (Scheme 1). We also selective catalytic reactivity demonstrated in the hydrofunctionalization of unsaturated molecules. The Fe (II) complex A is an effective catalyst for the hydroboration reaction of aldehydes and ketones; the Co (II) counterpart B is a hydrogenation catalyst for alkenes and alkynes under mild conditions with the assistance of an organo borane cocatalyst.

Treatment of MCl₂ with nearly 2 eq. lithium phosphoranimide salt (^tBu₃PN)Li (C) in THF resulted in the formation of $M_2(NP^tBu_3)_4$ complexes **A** and **B** with 75% and 72% yield respectively (eq 1). Both A and B are very hydrocarbon soluble and can be crystallized from saturated pentane or hexane solutions at -35 °C. An X-ray diffraction study of A revealed the dimeric nature of iron complex. The structure contains two terminal and two bridging phosphoranimide units. The distances between bridging ligand and the metal centers are in the range of 1.998-2.006 Å (M = Fe) (Figure 1) and 1.964-1.976 Å (M = Co) (Figure 2). The terminal phosphoranimide ligands, approach closer to the metal center with M-N bond lengths of 1.856, 1.863 Å (M = Fe) and 1.811, 1.815 Å (M = Co). The intermetal distances are out of the range of bonding (Fe(1)-Fe(2) = 2.565(6) Å; Co(1)-Co(2) = 2.514(6) Å).^{10a} The geometry of both metals is planar and three-coordinate. There is no obvious peak for both complexes on

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⁺ CCDC 1525454, 1542180. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x



Figure 1. ORTEP drawing of complex $Fe_2(NP^4Bu_3)_4$ A at 50% probability ellipsoids. The hydrogen and co-crystallized solvent is omitted for clarity. Selected bond lengths (Å) and angles (): Fe(1)-N(1) 1.863(2), Fe(1)-N(2) 2.006(3), Fe(1)-N(2) 2.000(2), Fe(2)-N(2) 1.998(3), Fe(2)-N(3) 1.856(3), Fe(2)-N(3) 2.001 (3), Fe(1)-Fe(2)-N(2) 1.998(3), Fe(2)-N(3) 1.856(3), Fe(2)-N(3) 2.001 (3), Fe(1)-Fe(2)-N(2) 1.998(3), Fe(2)-N(3) 1.856(3), Fe(2)-N(3) 2.3.4(1), N(4)-Fe(1)-N(2) 133.4(1), N(4)-Fe(1)-N(2) 133.4(1), N(4)-Fe(2)-N(2) 135.8(1).



Figure 2. ORTEP drawing of complex $Co_{1}(NP^{1}Bu_{3})_{4}$ **B** at 50% probability ellipsoids. The hydrogen and co-crystallized solvent is omitted for clarity. There are disordered atoms shown in the crystal structure. Selected bond lengths (Å) and angles (°): Co(1)-N(1) 1.964(Å), Co(1)-N(2) 1.815(5), Co(1)-N(4) 1.976(Å), Co(2)-N(4) 1.96(Å), Co(2)-N(4) 1.96(Å), Co(2)-N(4) 1.96(Å), Co(2)-N(4) 1.976(Å), Co(2)-N(4) 1.970(Å), Co(1)-N(4) 2.514 (6); N(1)-Co(1)-N(2) 1.84.1(5), N(1)-Co(1)-N(4) 89.5(4), N(1)-Co(2)-N(3) 136.1(2), N(3)-Co(2)-N(4) 133.7(2).

³¹P NMR and several broad peaks in ¹H NMR spectra due to the paramagnetic characteristics (see ESI for detail).

Inspired by the reaction of HNP^tBu₃ with pinacolborane (HBpin) to generate H₂ and pinB-NP^tBu₃ under mild conditions.¹¹ We envisioned that HBpin may undergo metathesis with A to yield a catalytically active metal hydride intermediate. To test this hypothesis, we attempted hydroboration of C=O π bonds¹² using Fe(II) complex **A**. Fortunately, the desired reduction compounds can be obtained via hydroboration followed by hydrolysis of the boronate ester (Table 1). Aldehydes and ketones were suitable to produce the corresponding primary or secondary alcohols. For the aryl aldehyde substrates, the primary alcohol can be obtained in 74-85% isolated yield. Different electron donating or withdrawing groups on the phenyl ring can be tolerated in this reaction (2a-2f, Table 1). The non-conjugated aldehyde 1g can also be reacted to form 2g in 95% yield; the α , β unsaturated aldehyde 1h could be reduced to form the alcohol 2h without forming the 1,4- reduction product. Also, alkyl substituted aldehyde 1i can form the fatty alcohol 2i in 82% yield. Several ketones were applied to generate the secondary alcohols: employing methyl, isopropyl and phenyl substituents



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Table 1. Hydroboration of aldehydes and ketones catalyzed by iron(II) complex A.^a

^aThe reaction was set up in glove box with H_2O and $O_2<0.1$ ppm; the reaction scale was 0.2 mmol for aldehydes and ketones

on the carbonyl group can afford the alcohol in 65-95% yield (**2j-2n**, Table **1**). Ketones without conjugation to a phenyl ring are also suitable substrates (**2o** and **2p**, Table 1); the cyclic aliphatic alcohol **2q** can be obtained by employing cyclic ketone **1q** as substrate.

In order to study the chemoselectivity of hydroboration employng iron catalyst **A**, competition experiments between aldehydes and ketones were conducted both inter- and intramolecularly (**Scheme 2**). Equimolar amounts of aldehyde, ketone and HBpin were mixed together with complex A as catalyst at room temperature (eqs. 1-3, Scheme 2)¹³. In all three examples, the reactions afforded the boronate esters of aldehydes with the NMR yields of 72-87% as major products regardless of the electronic effect on the phenyl ring. The intramolecular chemoselective hydroboration reactions of aldehydes and ketones were also studied with 2-formylphenyl acetate (**1r**) and 4-(2-0x0-2-phenylethoxy)benzaldehyde (**1s**) as substrates, which gave the hydroboration products of aldehydes as well with 63% (**2r**) and 80% (**2s**) isolated yields after hydrolysis.

When allyl benzene was employed as the hydroboration substrate, no desired product formed. However, the hydrogenation product **4a** can be observed from the proton NMR analysis of crude reaction mixture. Therefore, we realized that the iron (II) complex and the organo-borane compound could be hydrogenation co-catalysts. This hypothesis was tested on the hydrogenation of allyl benzene (**Table 2**). The iron complex **A** could only show 8% hydrogenation product. Published on 09 August 2017. Downloaded by University of Windsor on 09/08/2017 17:30:33

Scheme 2. Competing Hydroboration reaction between Aldehydes and ketones.



Table 2. Catalytic reactivity comparison of iron and cobalt complexes by the hydrogenation of allylbenzene.

	2.5 mol% [M 10 mol% HE	2(N=P ⁱ Bu ₃)2 B(pin)	↓ →	+	+	+	C
3a 2 mmol	[−] 2 (1 atm)	, n, 13-15ns	3a		3aa	3ab	4a
_	Fastar		NM	R yield o	f produc	cts (%)ª	_
_	Entry	IVI	За	3aa	3ab	4a	
	1	Fe	14.5	43	4	8	
	2	Со	0	0	0	82	
	3	Co⁵	71	0	0	0	

no reaction occur without the participation of HB(pin) at room temperature.

The major products are the isomerization products **3aa** and **3ab** (entry 1, Table 2). Surprisingly, the hydrogenation process can be accomplished by using the cobalt complex **B** with 82% NMR yield without any contamination of internal alkenes (entry 2, Table 2); ¹⁴ a catalytic amount of HBpin is very essential for this reaction. There will be starting material recovered in 71% yield without the assistance of HBpin (entry 3, Table 2).

Other alkenes and alkynes were also tried under these mild hydrogenation conditions. The results are summarized in **Table 3**. The terminal alkyne **3b** and **3e** can also afford the fully hydrogenated product **4b** and **4e** with high NMR yield (**entries 2 and 5, Table 3**). The alkyl substituted terminal alkynes **3f** and **3g** can also be hydrogenated to give the saturated hydrocarbon products with 92% and 80% yield respectively (**entries 6 and 7, Table 3**); the internal alkynes were also suitable for the transformation with excellent yields (**entries 3** and **4, Table 3**). The stoichiometric reactions of complexes **A** or **B** with 2 eq. of HB(pin) (**M**/[**B**] = 1:2) were also conducted to give the ^tBu₃P=N-B(pin) as only phosphorus containing product,

which was shown on ³¹P NMR spectrum (see ESI for detail). Furthermore, in order to understand the properties of the

hydrogenation catalytic system, we studied the poisoning effect by adding different reagents to the catalytic system. (**Table 4**).¹⁵ Different equivalents of mercury cannot poison the

hydrogenation reaction of phenylacetylene, as evidenced by

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	H ₂ (1atm),	rt, 13-15 hrs	`R'''
	3a-3g	4a	-4f
Entry	Substrates 3	Products 4	NMR yields
			of 4 (%)
1	Ph		82
	3a	^{Pn—} 4a	
	Ph-===	Ph	
2	3b	4b	81
	Ph	Ph	
3	3c	4a	83
	Ph Ph	Ph	
4	3d	4c	>99
	Ph-	Ph 🔿 🧹	
5		4d	83
	3e	44	
	Cy—	Cv	
6	3f	́4е	92
7	ⁿ C ₆ H ₁₃	ⁿ C ₆ H ₁₃	80
	3g	4f	

^a The reaction scale is 0.2 mmol; NMR yield was measured using mesitylene as internal standard.

the maintenance of product yields, which implies that Co nano-particles are not formed during catalysis. (entries 1-3, Table 4). The catalytic system could also be tolerated under normal monophosphine ligand (PPh₃), even more nucleophilic phosphine ligand (PMe₃) (entries 4 and 5, Table 4); diphosphine and bipyridine ligands as poisoning additive (entries 6 and 7, Table 4). Based on the observations above, homogeneous hydrogenation under catalysis of Co(II) complex B is most likely.

Table 4. Poisoning effect of Co (II) B catalyzed hydrogenation reaction.					
	2.5 mol% [Co(N=P ⁴ Bu ₃) ₂] ₂ 10 mol% HB(oin)				



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Conclusions

Novel homoleptic three coordinate base metal complexes have been synthesized and characterized. These non-pincer dimers are effective catalysts under mild conditions for the hydrofunctionalization of π -bonds. The iron (II) complex is an effective hydroboration catalyst for aldehydes and ketones; the cobalt (II) counterpart is a hydrogenation catalyst for C-C π bonds. It's the simple and effective approach to accomplish the different type of reduction reaction by the same ligand environment. It is noteworthy that different types of reduction reactions can be accomplished by the same ligand environment. The design of new highly active Fe and Co based catalysts presents an opportunity for constructing other base metal catalyst systems.

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Entry	Poisoning reagent	Equivalent (mol %)	NMR yield of 3b (%)	NMR yield of 4b (%)	NMR yield of 4c (%)
1	Hg	20	<1	80	<1
2	Hg	50	<1	75	<1
3	Hg	100	<1	63	<1
4	PPh₃	5	<1	78	4
5	PMe ₃	5	<1	74	<1
6	dppe	5	<1	80	3
7	2,2'- bipyridine	5	<1	88	<1

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