

Hydrogen Transfer Reduction of Aldehydes with Alkali-Metal Carbonates and Iridium NHC Complexes

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Summary: Some neopentyl-substituted NHC iridium complexes catalyze the reduction of a variety of aldehydes and even enolizable aldehydes by hydrogen transfer from refluxing 2-propanol with alkali-metal carbonate bases. Imidazole and 1,2,4-triazole complexes had comparable activities. The aldehydes could also be reduced more slowly using a mild carbonate base and no iridium complex.

Aldehydes are hard to reduce^{1–6} successfully by hydrogen transfer catalysis^{7–17} from a solvent such as refluxing 2-propanol. Several reasons may apply. First, substrate decarbonylation¹⁸ (eq 1) may potentially



poison the catalyst by transfer of a carbonyl from the aldehyde to the metal. Second, the basic conditions required for the catalysis can also deprotonate any CH group α to the carbonyl, to give aldol and related products.

Traditional transition-metal catalysts for these aldehyde reduction reactions have almost always contained phosphine ligands.^{12a,19} We felt that N-heterocyclic

carbene (NHC) complexes might be a better choice because, being stronger electron donors than phosphines,^{20–22} they might disfavor attainment of the Ir(I) oxidation state normally required to give decarbonylation. Since they are extremely active catalysts,²³ we felt they might avoid slower side reactions.

The precatalyst **1**, previously found to be extremely active for transfer hydrogenation reduction of ketones, was tried for aldehydes under the strong base (KOH) conditions previously used.²³ No reduction was seen for *p*-tolualdehyde, and incomplete reduction was seen for 2-naphthaldehyde.

Compound **1** and the new iridium bis-NHC complexes **2** and **3** were prepared according to Scheme 1.^{23,24} For **3**, higher yields were obtained with $[\text{Ir}(\text{coe})_2\text{Cl}]_2$ than with the $[\text{Ir}(\text{cod})\text{Cl}]_2$ normally used, no doubt because *coe* is a better leaving group (*coe* = cyclooctene; *cod* = 1,5-cyclooctadiene).

On moving to the weaker base, K_2CO_3 , we now find that reduction can be achieved successfully (Table 1, entries 1–20).²⁵ We chose R = neopentyl for this study because it gave the best prior results for transfer hydrogenation of ketones²³ and also because the neopentyl group cannot decompose via a Hoffmann elimination.²⁶

The products were detected by ¹H NMR by comparison with authentic material. In no case was there any indication of reduction of $-\text{NO}_2$ substituents. Other types of the precatalyst were comparable: for example, the triazole-based NHC species **3** (Table 1). Precatalyst **2**, with a neopentanedyl linker, exhibited higher activity than precatalyst **1**, with a methylene linker (Table 1).

For the most volatile aldehyde starting materials, such as 2-phenylpropionaldehyde and hydrocinnamaldehyde, an internal standard, mesitylene, was added initially. The reaction and subsequent workup were performed as usual. Proton NMR experiments showed no aldehyde starting material after 1 h and alcohol as

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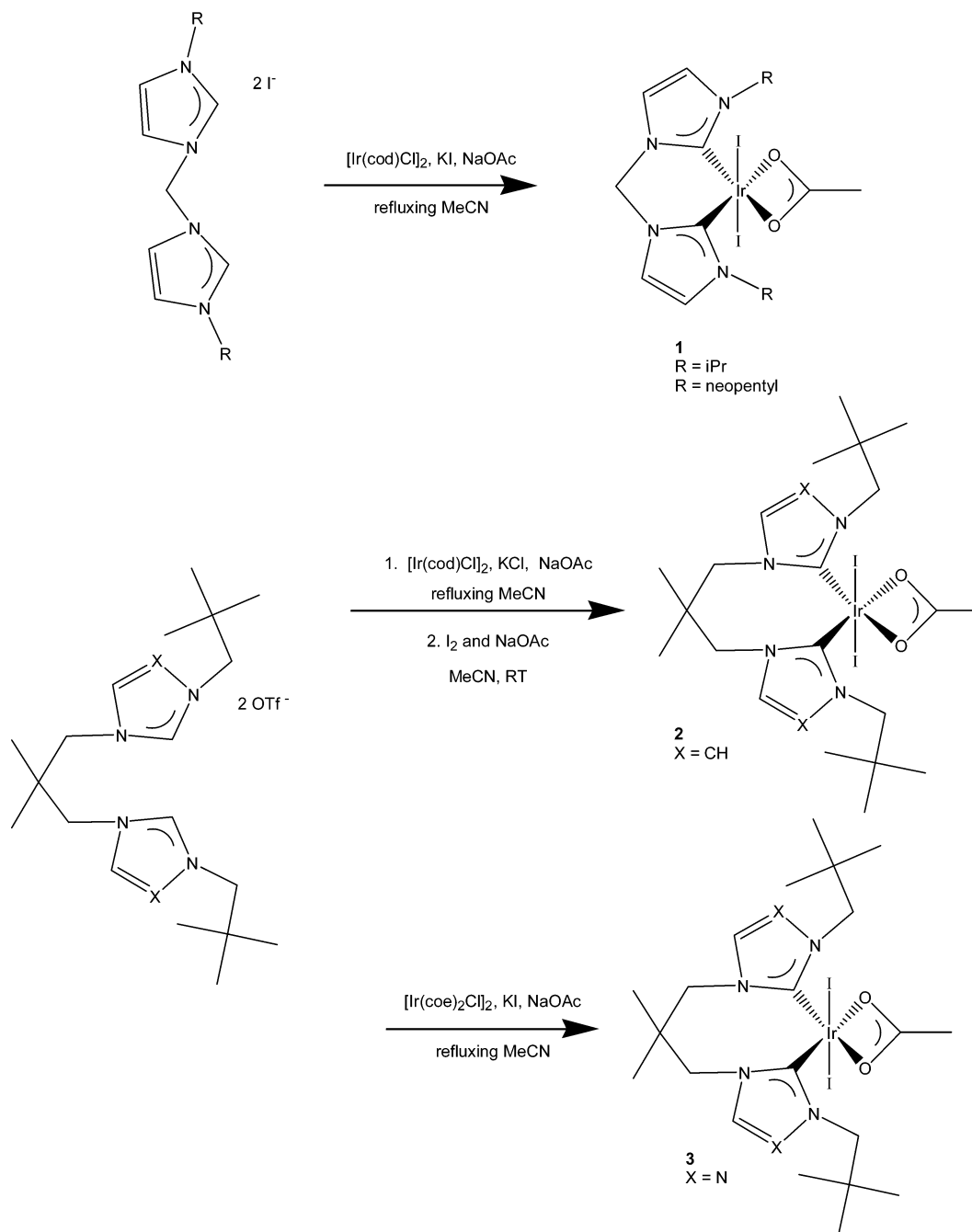
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Scheme 1. Syntheses of the Iridium Bis-NHC Complexes 1–3



the major (>95%) product. GC-MS was consistent with this result.

Both Rb_2CO_3 and Cs_2CO_3 were effective bases (Table 2, entries 7, 8, 11, 12, 15, and 16). A control experiment without metal precatalyst showed that a slower, purely organic Meerwein–Ponndorf–Verley (MPV) reaction is also possible for these bases. Complete conversion can be achieved, given sufficient time (Table 2, entries 3–5). Grinding the base to a fine powder before the reaction seems to accelerate the MPV reaction (Table 2, entry 4) but not the reaction catalyzed by **3** (Table 2, entry 14).

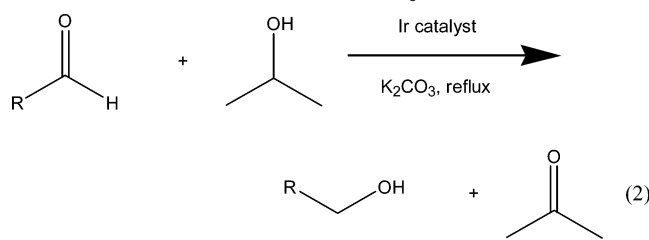
When we looked for undesired decarbonylation in the reduction of 2-naphthaldehyde using **3** as a precatalyst under the standard base conditions with KOH, we saw characteristic²⁷ Ir–CO stretching frequencies at 1991 and 2018 cm^{-1} in the IR spectrum of the residue after

reaction. With K_2CO_3 instead of KOH, these Ir–CO stretching frequencies were much weaker in intensity, implying slower decarbonylation.

Phenylacetaldehyde was chosen as an especially stringent test because of its high tendency to undergo aldol reactions. As shown in entries 10 and 11 (Table 1), this substrate was successfully reduced under these conditions with no detectable aldol products. Other enolizable aldehydes were also reduced successfully (Table 1, entries 12–16 and 19–20).

A valid comparison of our findings to those previously published cannot be made, since our reaction conditions were different. Joo and co-workers were able to reduce citronellal catalytically using a water-soluble ruthenium

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Table 1. Reduction of Aldehyde Substrates^a

entry	cat.	R	time	yield (%)	TOF (TON h ⁻¹)
1	1^b	<i>p</i> -Me-C ₆ H ₄	5 h	98	200
2	2	<i>p</i> -Me-C ₆ H ₄	45 min	98	1300
3	3	<i>p</i> -Me-C ₆ H ₄	90 min	89	590
4	1^b	<i>p</i> -MeO-C ₆ H ₄	6 h	83	140
5	2	<i>p</i> -MeO-C ₆ H ₄	3 h	72	240
6	3	<i>p</i> -MeO-C ₆ H ₄	3 h	35	120
7	1^b	<i>p</i> -NO ₂ -C ₆ H ₄	3 h	79	260
8	2	<i>p</i> -NO ₂ -C ₆ H ₄	1 h	98	1000
9	3	<i>p</i> -NO ₂ -C ₆ H ₄	45 min	98	1300
10	2	PhCH ₂	1 h	98	1000
11	3	PhCH ₂	1 h	98	1000
12	1^b	PhCHMe	11 h	98	91
13	2	PhCHMe	0.5 h	95	2000
14	3	PhCHMe	1 h	98	1000
15	2	PhCH ₂ CH ₂	1 h	98	1000
16	3	PhCH ₂ CH ₂	1 h	98	1000
17	2	2-naphthyl	20 min	98	3000
18	3	2-naphthyl	1 h	95	1000
19	2	Me ₂ C=CH(CH ₂) ₂ CHMeCH ₂	1.5 h	98	670
20	3	Me ₂ C=CH(CH ₂) ₂ CHMeCH ₂	1.5 h	98	670

^a Transfer hydrogenation of aldehydes, reaction conditions: S:C:base = 1000:1:500, with 0.2 M substrate in 10 mL of 2-propanol at reflux temperature. Product yields were determined by ¹H NMR. ^b Iridium(III) compound with R = neopentyl. These R groups were used for all experiments.

phosphine complex under aqueous conditions in 4 h with 90% yield of alcohol.³ In addition, Kaneda and co-workers were able to catalytically reduce citronellal to the alcohol with 100% yield using a polymer-bound rhodium carbonyl cluster in 4 h.¹³ **2** and **3** can reduce this substrate in 90 min.

After **3** was incubated for 15 min in refluxing 2-propanol and then K₂CO₃ and 2-phenylpropionaldehyde were added, 98% of the substrate was reduced after 1 h, just as is the case without incubation. Incubation of **3** as above but in the presence of K₂CO₃ gave a catalyst with a reduced activity for transfer hydrogenation:

Table 2. Effect of Different Bases on the Transfer Hydrogenation of 2-Naphthaldehyde^a

entry	base	catalyst	yield (%)	time	TOF (TON h ⁻¹)
1	none	1^b	0	1.25 h	
2	K ₂ CO ₃	none	6	6 h	
3	Cs ₂ CO ₃	none	98	2 h	
4	Cs ₂ CO ₃ ^c	none	98	90 min	
5	Rb ₂ CO ₃	none	98	9 h	
6	K ₂ CO ₃	1^b	98	1.5 h	670
7	Cs ₂ CO ₃	1^b	98	1.5 h	670
8	Rb ₂ CO ₃	1^b	97	30 min	2000
9	KOH ^d	1^b	30	1 h	300
10	K ₂ CO ₃	2	98	20 min	3000
11	Cs ₂ CO ₃	2	95	30 min	2000
12	Rb ₂ CO ₃	2	98	30 min	2000
13	K ₂ CO ₃	3	95	1 h	1000
14	Cs ₂ CO ₃ ^c	3	97	45 min	1300
15	Cs ₂ CO ₃	3	98	45 min	1300
16	Rb ₂ CO ₃	3	84	1.5 h	560

^a Transfer hydrogenation of aldehydes, reaction conditions: S:C:base = 1000:1:500, with 0.2 M substrate in 10 mL of 2-propanol at reflux temperature. Product yields were determined by ¹H NMR. ^b Iridium(III) compound with R = neopentyl, which was used for all studies. ^c Ground Cs₂CO₃. ^d S:C:base = 1000:1:5.

tion: only 24% of 2-phenylpropionaldehyde was subsequently reduced after 1 h. This suggests that, in the absence of substrate, the catalytically active species gradually decomposes under the basic conditions utilized.

In summary, we have developed precatalysts that can reduce aldehydes, including enolizable aldehydes, with alkali-metal carbonates via transfer hydrogenation using 2-propanol as the solvent. The triazole-based NHC precatalyst generally exhibited catalytic activity comparable to that of the imidazole-based precatalyst.

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Supporting Information Available: Text giving experimental procedures, spectroscopic information for compounds **2** and **3**, and the typical procedure for transfer hydrogenation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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