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Preliminary communication

Novel reactions of the low valent cobalt reagent generated using $CoCl_2$ and $NaBH_4/C_2H_5OH$ in the presence of carbon monoxide

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Abstract

Low valent cobalt species, prepared in situ in tetrahydrofuran (THF) by the reduction of $CoCl_2$ with $NaBH_4/C_2H_5OH$ under carbon monoxide, isomerize of alkenes, reduce alkenes, and carbonylate benzyl halides under appropriate conditions.

Anhydrous cobalt(II) halides react with alkali metal borohydrides at low temperatures (−80 °C) to give cobalt(II) borohydride, $Co(BH_4)_2$, which decomposes into black cobalt boride, B_2H_6, and H_2 on warming to room temperature [1,2]. The $CoCl_2/NaBH_4$ system has been utilized for reduction of alkenes [3–5], hydroboration of alkenes [3,4], isomerization of alkenes, and hydrodimerization of 1-alkynes in the presence of Ph_3P [6,7]. We now report some novel reactions of cobalt species generated using $NaBH_4$ in ethanol under carbon monoxide.

We found that when $NaBH_4$ (20 mmol) was added to anhydrous $CoCl_2$ (10 mmol) in THF (80 ml) through which carbon monoxide was being bubbled at 0 °C no black cobalt boride was formed. Instead, the mixture was green and presumably, the carbon monoxide ligand is able to stabilize the cobalt borohydride complex. When 1-decene (10 mmol) was injected to this green mixture and the contents were stirred for 3 h at room temperature under carbon monoxide, no 1-decene remained. Work-up of the residue obtained after oxidiation with $H_2O_2/NaOH$, gave 1-decanol in 70% yield. This indicates that the residue was an organoboron compound and that the $CoCl_2/NaBH_4/CO$ system is able to give a $>B{-}H$ species capable of hydroborating alkenes. Since our objective is to explore the modes of reaction of the cobalt species, we repeated the procedure with $NaBH_4$ in ethanol so as to prevent hydroboration. Addition of $NaBH_4$ (20 mmol) in ethanol (15 ml) to $CoCl_2$ (10 mmol) in THF (80 ml) under carbon monoxide at 0 °C gave a black mixture. 1-Decene (10 mmol) was injected and the mixture was stirred for 2 h at room temperature. After work-up, 1-decene was recovered quantitatively. However, when

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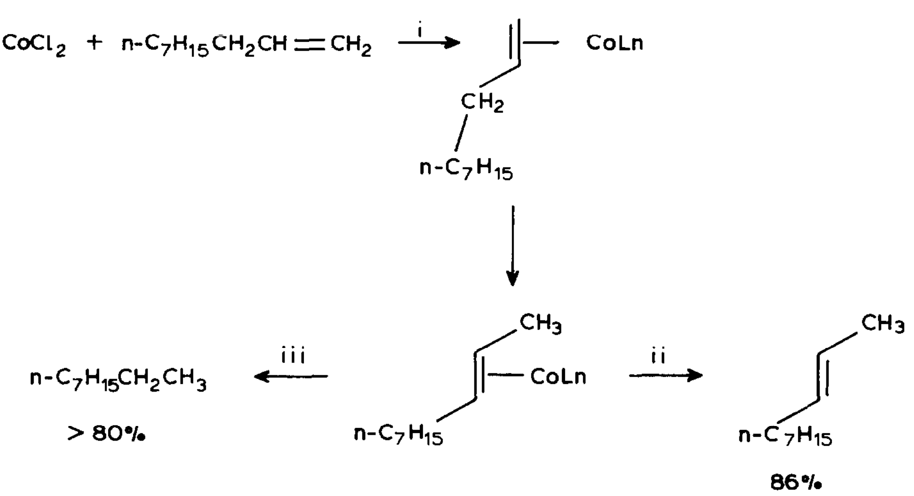
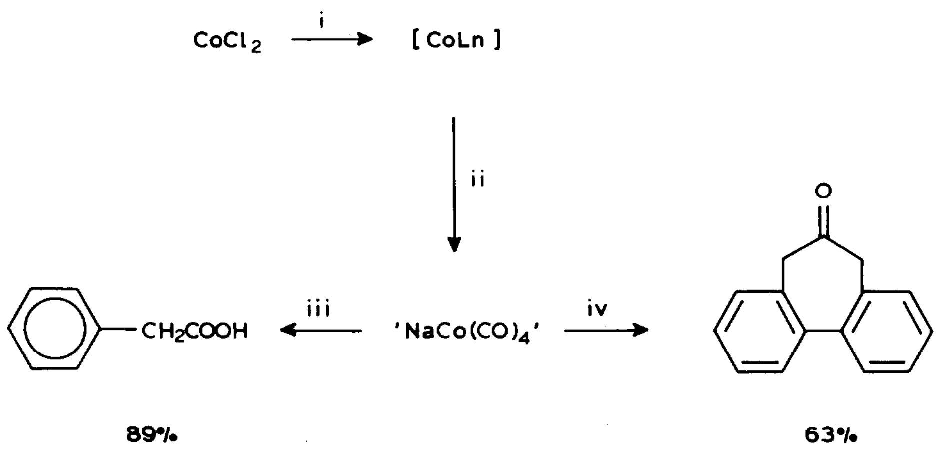


Scheme 1. Reagent conditions (i) $NaBH_4/C_2H_5OH/CO$, (ii) hexane/H_2O, (iii) C_2H_5OH, 12 h at room temperature or HCl, 2 h at room temperature.

1-decene (10 mmol) was used along with $CoCl_2$ (10 mmol) in THF (80 ml), and $NaBH_4$ (20 mmol), in ethanol (15 ml) was added during 10 minutes at 0 °C with carbon monoxide bubbling through and the mixture was stirred for a further 30 minutes at room temperature and the reaction then quenched by addition of hexane (100 ml) and water (15 ml), *trans*-2-decene (> 95% pure) was isolated in 86% yield. We carried out several experiments in order to investigate this transformation. When concentrated HCl (12 *N*, 5 ml) was added before work-up and the mixture stirred for 1 h, decane was isolated in 89% yield. When the mixture was stirred for 12 h after the $NaBH_4$ addition, decane was isolated in 82% yield even without the addition of HCl. Presumably, the 1-decene complexes with the reactive cobalt species formed and is converted into a *trans*-2-decenecobalt complex which undergoes decomposition to give *trans*-2-decene or protonolysis by C_2H_5OH or HCl to give decene (Scheme 1). Protonolysis of olefin-$Fe(CO)_4$ complexes have been reported to yield the corresponding reduction products [8].

In order to find out whether the *trans*-2-decene is liberated during the course of the reaction and then reduced, we carried out an experiment involving additional of a further 10 mmol of 1-decene after the addition of $NaBH_4$ was complete and found that 10 mmol of 1-decene remained unchanged. In another run, we replaced this additional 1-decene by methyl-10-undecenoate (10 mmol) and stirred the mixture for 12 h room temperature; no 1-decene remained, decane was isolated in 80% yield and the recovered methyl-10-undecenoate showed no ^{13}C NMR signals corresponding to methyl undecanoate. These experiments show that the isomerization and the reduction products are formed from the alkene-CoLn complex (Scheme 1), and that there is no exchange of alkene with the alkenes added after the formation of the complex.

When allylbenzene was used in the place of 1-decene and the reaction was quenched with hexane and water as indicated for the isomerization of 1-decene (Scheme 1), n-propyl benzene was isolated in 84% yield. Presumably protonolysis of the alkene-CoLn complex (Scheme 1) by the ethanol is very fast in this case.



Scheme 2. Reagents and conditions: (i) $NaBH_4/C_2H_5OH$, CO, 15 min, 0 °C, (ii) 5 *N* NaOH (10 ml)/CO/room temperature 10 min. (iii) Benzyl bromide, benzyl triethylammonium bromide, CO, 50 °C, 2 h, (iv) 2,2′-bis(bromomethyl)biphenyl, benzyl triethylammonium bromide, CO, 50 °C, 2 h.

We also observed that $NaCo(CO)_4$ or its equivalent can be prepared by reducing $CoCl_2$ (10 mmol) with $NaBH_4$ (20 mmol) in ethanol (15 ml) in THF (80 ml) at 0 °C with carbon monoxide through, followed by treatment of aqueous NaOH. The formation of $NaCo(CO)_4$ or its equivalent is indicated by the carbonlylation of benzyl bromide and 2,2′-bis(bormomethyl)biphenyl in the presence of catalytic amounts of benzyl trimethylammonium bromide (Scheme 2)

It has been reported that reduction of cobalt(II) halides with NaH in the presence of sodium t-amyloxide under carbon monoxide gives $NaCo(CO)_4$ in 10% yield [9]. We previously observed [10] that the green coloured mixture obtained by the reaction of $NaBH_4$ and $CoCl_2$ in THF in the presence of carbon monoxide, on treatment with aqueous NaOH gives $NaCo(CO)_4$ or its equivalent, as indicated by the reaction with benzyl bromide to give phenyl acetic acid [11]. The present $CoCl_2/NaBH_4/C_2H_5OH/CO$ system would give similar species. However, the reactions now reported the isomerization and reductions, have not been observed with $NaCo(CO)_4$ or $Co_2(CO)_8$ [13]. The $HCo(CO)_4$ reagent is known to isomerize alkenes [14], but gives a mixture of *cis*- and *trans*-2-alkenes is formed, and also 3-alkenes and 4-alkenes in some cases. Moreover, reactions utilizing $HCo(CO)_4$ have been carried out in hydrocarbon solvents and the isomerization reaction is catalytic with respect to the cobalt reagent [14]. In our new system, even if the $HCo(CO)_4$ were formed at some stage it would not survive for long, since it is highly acidic it would react with a $H{-}B{<}$ species to give the corresponding $LnCo{-}B{<}$ complexes. Probably, in our system the alkene enters the coordination sphere of the cobalt along with CO ligands as the $CoCl_2$ is reduced with $NaBH_4/C_2H_5OH$, and then undergoes isomerization and reduction (Scheme 1).

The results indicate that the $CoCl_2/NaBH_4/C_2H_5OH/CO$ system provides easy access to the carbonylmetal complexes and the corresponding alkene complexes. The questions of the structure of the reactive species, the mechanism of the observed transformations, and the possibilities of generating other transition metal organometallic complexes under a carbon monoxide atmosphere under such simple conditions will be addressed in future studies.

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