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Synthesis and structure of cobalt(II) iodide bearing a bulky *N*-heterocyclic carbene ligand, and catalytic activation of bromoalkanes

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ABSTRACT

A divalent cobalt iodine complex bearing 1,3-bis(mesityl)imidazol-2-ylidene and pyridine ligands was synthesized and its structure was determined. The cobalt center has a typical d^7-tetrahedral geometry, as expected. Catalytic application of this cobalt complex with bromoalkanes and Grignard reagents demonstrated high-yield formation of alkenes as a result of β-hydrogen elimination; in sharp contrast, the activation of alkyl halides was not successful using the larger *N*-heterocyclic carbene ligand, 1,3-bis(2,6-diisopropyl-phenyl)imidazol-2-ylidene. In the presence of styrene, Heck reaction proceeded with *trans* selectivity. The reaction of a substrate containing a bromobenzyl moiety yielded a homocoupling product.

1. Introduction

The first-row late transition metals such as iron, cobalt, nickel and copper are now the most important transition metals used as catalysts in the development of organic reactions [1], rather than the catalytically active noble metals, such as ruthenium, rhodium, and palladium [2]. The development of alternative processes for cross-coupling reactions mediated by these first-row metal catalysts has also attracted much attention [3]. Because of the difficulty of identification as a result of their paramagnetic properties, structurally defined cobalt complexes have rarely been used as catalysts [4], in comparison with their nickel and iron counterparts. Using well-defined complexes is essential to obtain information on the reaction mechanism and/or discover novel reactions. Fruitful results have been obtained in studies of cross-coupling reactions of alkyl halides catalyzed by in situ-generated cobalt species [5]. It is therefore important to develop active and useful cobalt complexes for cross-coupling reactions of alkyl halides.

Recently, *N*-heterocyclic carbenes (NHCs) have become one of the most valuable candidates designing active and stable metal catalysts [6]. Several cobalt NHC complexes have been synthesized and structurally determined [7]. However, only a few examples of catalysts for organic reactions, particularly for cross-coupling reactions, have been reported [4]. In addition, cobalt catalysts bearing bulky NHC ligands are unknown, although Oshima and Yorimitsu et al. have reported efficient cobalt-mediated activation of alkyl halides in the presence of bulky NHC ligands as cocatalysts [8]. Our previous report showed that the bulky NHC ligand, 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) coordinates to divalent cobalt halides to form unstable dinuclear cobalt(II)–IPr complexes, which were stabilized by addition of pyridine to yield monomeric cobalt(II) complexes, namely Co(IPr)X_2(Py) (**1a**: $X = \mathrm{I}$, **1b**: $X = \mathrm{Br}$, **1c**: $X = \mathrm{Cl}$) (Scheme 1) [9]. These compounds successfully catalyzed Kumada–Tamao–Corriu cross-coupling reaction of aryl halides, but were not suitable for catalytic activation of alkyl halides. We hypothesized that cobalt complex bearing less bulky NHC ligand such as 1,3-bis(mesityl)imidazol-2-ylidene (IMes) instead of IPr could perform catalytic activation of alkyl halides. Here we report the synthesis, structure, and reactivity of a new IMes–cobalt(II) diiodide, which mediates catalytic activation of alkyl halides. Interestingly, the products obtained depended on the conditions: 1-alkene or homocoupling products in the presence of a Grignard reagent, and Heck reaction products in the presence of styrene and a Grignard reagent.

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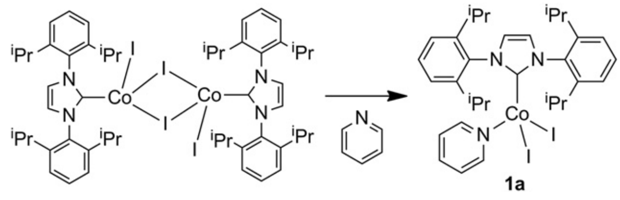


Scheme 1. Synthesis of **1a** in the previous report [9].

2. Results and discussion

2.1. Synthesis and structure of cobalt(II) (IMes) diiodide (**2**)

In our previous study, IPr was added to THF solutions of cobalt(II) iodide, bromide, and chloride to form dicobalt IPr complexes $[Co(IPr)X]_2(\mu{-}X)_2$ (X = I, Br, Cl) [9]. However, the complexes sometimes decomposed to a monomeric cobalt anion $[Co(IPr)X_3]^-[IPrH]^+$, probably because of the presence of a small amount of water. Addition of pyridine to these dimers effectively stabilized them and gave monomeric neutral complexes, $Co(IPr)X_2(Py)$ (**1a**: X = I, **1b**: X = Br, **1c**: X = Cl), in good yields. Among the complexes, the iodide **1a** was the most active catalyst in the Kumada coupling of aryl halides. Based on the above experimental results, the monomeric cobalt iodide analog bearing the IMes ligand, $Co(IMes)I_2(Py)$ (**2**), was similarly synthesized by the reaction of CoI_2 with IMes in THF, followed by addition of pyridine (Scheme 2). The reaction proceeded smoothly in THF at room temperature. Direct addition of IMes and CoI_2 to pyridine also gave **2** efficiently. Dimeric species are probably generated in situ, as the corresponding IPr complexes were formed previously [9].

The product **2** was air-unstable and recrystallized under an inert-gas atmosphere from THF and *n*-hexane at −30 °C (26% yield by recrystallization). In elemental analysis of **2**, the obtained carbon, hydrogen and nitrogen contents of 44.68, 4.57 and 6.06%, respectively, agreed with the theoretical values of 44.85, 4.20 and 6.40%, respectively. The structure of **2** in solution was similar to that of **1a**, indicated by the UV–visible absorption spectroscopy. The absorption bands from 600 to 800 nm, 636, 675 and 713 nm, in Fig. 1 were assigned as the $d{-}d^*$ transition, whereas those of **1a** appeared at 644, 681 and 711 nm. The three separate bands are probably the result of spin–orbit coupling and the unsymmetric structure. The spectra suggest that **2** has the same tetrahedral d^7-geometry in solution as **1a** [9]. Moreover, these bands did not broaden at room temperature, suggesting that any equilibrium reactions, such as formation of the dimer with liberation of pyridine, could be ruled out. Compound **2** was paramagnetic and the spin-quantum number was 3/2, the same as in the case of the corresponding IPr analogs [9].

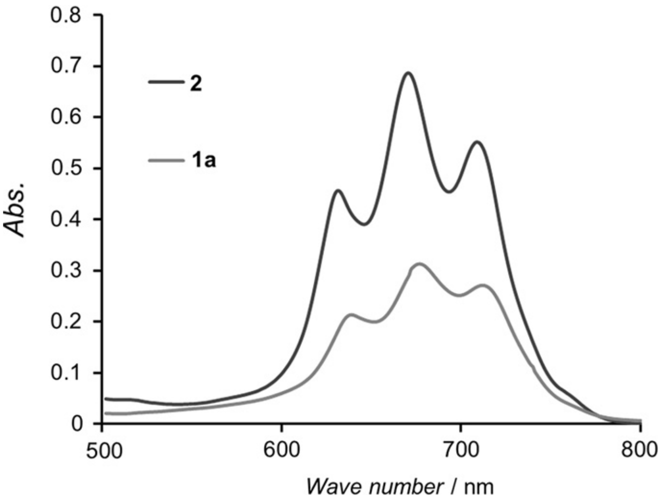
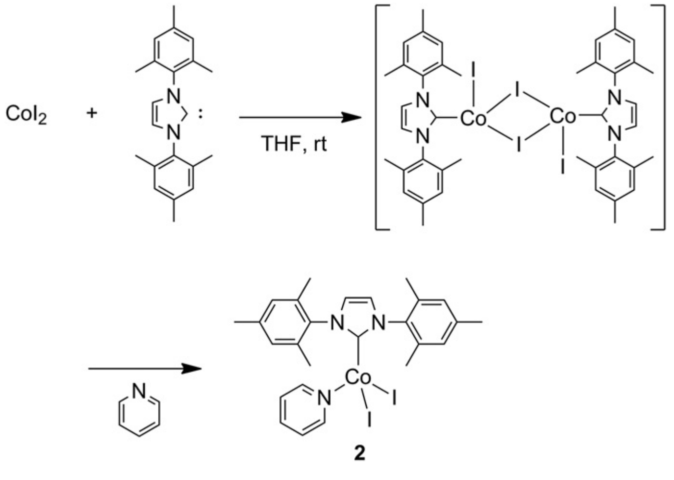


Fig. 1. UV–visible spectra for compounds **1a** and **2** in toluene (0.50 mM) in the area from 500 to 800 nm.



Scheme 2. In situ preparation of the monomeric complex **2**.

The structure of compound **2** was confirmed by X-ray crystallography, as shown in Fig. 2. The cobalt–carbon (C1), cobalt–nitrogen (N1), and cobalt–iodine (I1 and I2) bond distances are 2.058(8), 2.050(6), and 2.595(1) and 2.591(1) Å, respectively, which are almost the same as those of the IPr analog **1a**, 2.043(6), 2.066(3), 2.5869(7) and 2.6012(6) Å. These bond lengths are in the range of general single bond interactions. However, the C(1)–Co(1)–N(3) bond angle in the tetrahedral geometry was 111.8(3)°, that was smaller than the corresponding angle in **1a** (115.4(1)°). The other angle, C(1)–Co(1)–I(av.) was 112.0(2)°, which is also smaller than that of **1a** (115.9(1)°). The decrease of the angles in the tetrahedral geometry of **2** could be caused by the smaller methyl groups in IMes of **2** in comparison with the bulky isopropyl groups in IPr of **1a**, which could crowd the surroundings of the cobalt center. A π–π stacking interaction was found in **2** between the pyridine ring and one of the two mesityl rings; the average distance between them was 3.5 Å. This stacking interaction of the pyridine ring was not observed in **1a** because of steric hindrance caused by the two isopropyl groups in IPr. These differences are easily seen in the space-filling models of **1a** and **2** shown in Fig. 3.

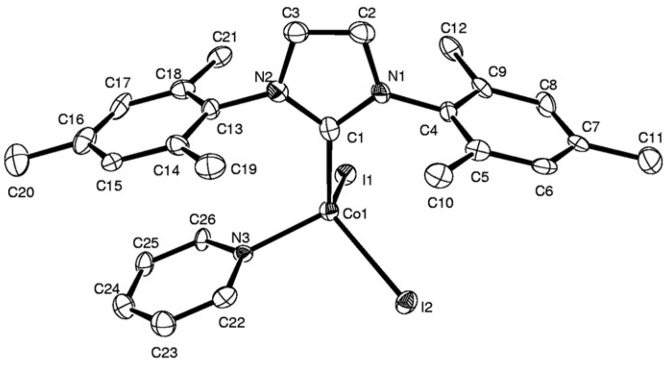


Fig. 2. ORTEP drawing of **2** (50% Probability of thermal ellipsoids). Representative bond lengths and angles are as follows: Co(1)–C(1), 2.058(8); Co(1)–N(3), 2.050(6); Co(1)–I(1), 2.595(1); Co(1)–I(2), 2.591(1) Å; C(1)–Co(1)–I(1), 105.5(2); C(1)–Co(1)–I(2), 118.5(2); C(1)–Co(1)–N(3), 111.8(3), N(3)–Co(1)–I(1), 105.9(2); N(3)–Co(1)–I(2), 103.2(2)°.

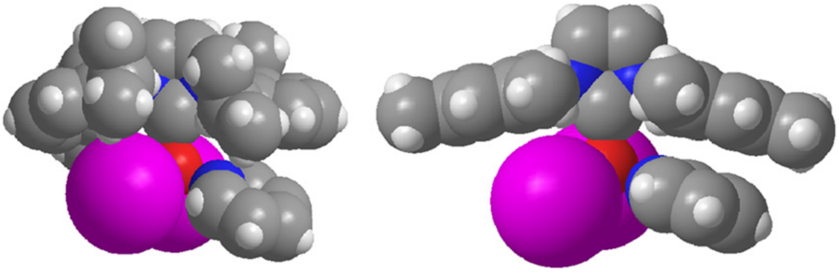


Fig. 3. Space-filling models of **1a** (left) and **2** (right) are depicted using the X-ray crystallographic results. The colors of the atoms are purple (I), red (Co), blue (N), gray (C) and white (H). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

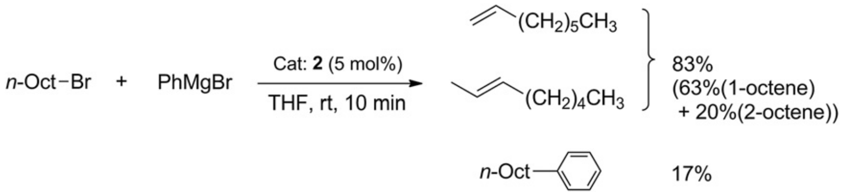
*2.2. Catalytic behavior of cobalt(II) (IMes) diiodide (**2**) with alkyl halides*

As noted in our previous report, the complex **1a** performed the catalytic activity to aryl halides with Grignard reagents but not good to alkyl halides [9]. We therefore first examined the reaction of 4-bromobiphenyl or 1-bromooctane with phenylmagnesium chloride in the presence of a catalytic amount of **2** (5 mol%). As the Kumada-coupling reaction of aryl halides was successful using **1a** as the catalyst [9], the compound **2** also mediated the coupling of 4-bromobiphenyl with phenylmagnesium chloride to form terphenyl in an 89% yield (90% yield using **1a**). However, in contrast to the case of **1a**, 1-octene and 2-octene (total 73%, containing 18% of 2-octene) generated as β-elimination and/or subsequent olefin isomerization products, after complete consumption of 1-bromooctane in only 10 min at room temperature (Scheme 3). The Kumada coupling product, *n*-octylbenzene was obtained in only a 15% yield. Oshima and Yorimitsu achieved the catalytic formation of 1-alkenes and 2-alkenes from 2-bromoalkanes mediated by $CoCl_2$ and IMes/HCl with $Me_2PhSiCH_2MgCl$, after screening of the free ligand (precursors) and Grignard reagents [10]. IMes/HCl and phenylmagnesium bromide with $CoCl_2$ did not provide sufficiently good results, with formation of only 8% and 9% of 1- and 2-alkenes, respectively, and recovery of 2-bromoalkane (25%), in sharp contrast to our result, using 1-bromoalkane with the cobalt iodide complex **2**.

We then attempted the Heck reaction of an alkyl halide with styrene in the presence of **2** and a Grignard reagent. Oshima et al. achieved a similar Heck reaction of an alkyl halide using cobalt chloride bearing a bisphosphine ligand [11]. However, the reaction using cobalt–NHC complex has not been reported. As shown in Table 1, several Grignard reagents were used in the reaction. Other reducing agents, such as sodium *tert*-butoxide, resulted in no reaction. The starting 1-bromooctane was completely consumed when trimethylsilylmethylmagnesium chloride and methylmagnesium bromide were used (entries 1 and 2). However, the amounts of 1-octene (**B**) and other by-products, such as hexadecene and hexadecane, were high compared with that of the Heck reaction product 1-phenyl-1-decene (**A**). Similarly, using ethylmagnesium bromide and isopropylmagnesium chloride did not provide adequate yields of the Heck reaction product (entries 3 and 4). The alkene products **A** and **B** were not generated using a sterically hindered Grignard reagent, 2,6-dimethylphenylmagnesium bromide (entry 6), suggesting that β-elimination of the octylcobalt species or styrene coordination might be suppressed by coordination of 2,6-dimethylphenyl group after transmetallation. Phenylmagnesium chloride was the most suitable Grignard reagent for the Heck reaction (entry 5). Product **A** is a known compound, identified on the basis of the ^1H NMR spectroscopy as a *trans* form, which is generally produced in transition metal-catalyzed Heck reactions with styrene [12].

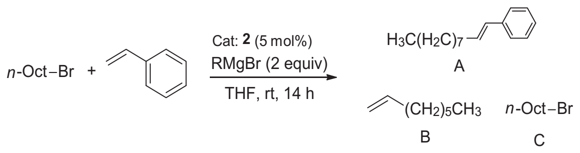
Interestingly, the ratios of 1-bromooctane and styrene were important for the predominant formation of the Heck reaction product. When similar ratios of 1-bromooctane and styrene were used, the product ratios of **A** and **B** were comparable (Table 2, entries 1 and 2). However, a higher concentration of styrene than that of 1-bromooctane resulted in predominant formation of **A** (yields up to 50%) (entries 3 and 4) [13]. As previously commented, the β-elimination process completed in several minutes at room temperature, but it took several hours in the presence of styrene. This indicates that coordination of styrene to the octylcobalt species competes with intramolecular β-elimination to form 1-octene in the catalytic cycle.

It might be possible to suppress β-elimination to achieve an efficient Heck reaction by using alkyl halides with no β-hydrogen atoms, such as benzyl halides and carbonylmethyl halides. We therefore examined the reaction of 9-bromofluorene with styrene in the presence of phenylmagnesium chloride. The Heck reaction did not proceed, but a catalytic homocoupling reaction occurred to form bifluorene quantitatively in 5 h at room temperature. In the absence of styrene, bifluorene was also formed in the same manner (Scheme 4). Several studies of metal-catalyzed reductive homocoupling reactions of benzyl halides have been reported [14]. However, most of the reactions required high reaction temperatures and/or high catalyst loadings. For example, the reaction of benzyl halides with iron powder at 80 °C in the presence of a copper chloride catalyst formed bibenzyl [14a], and benzyl chloride coupled in the presence of Pd/C and sodium formate at 120 °C [14b]. Manganese(II) chloride (10 mol%) catalyzed homocoupling of benzyl bromide with Mg at room temperature [14c]. Neither a cobalt reagent as the catalyst nor a Grignard



Scheme 3. Reaction of *n*-octyl bromide with phenylmagnesium bromide in the presence of **2**.

Table 1
Heck reaction of 1-bromooctane with styrene catalyzed by **2**.



Entry	RMg*X*	Yield (%)[a]		
		A	**B**	**C**
1	Me_3SiCH_3MgCl	30	27	0
2	MeMgBr	21	15	0
3	EtMgBr	30	22	43
4	^{i}PrMgCl	12	0	37
5	PhMgCl	46	12	16
6	2,6-Me_2PhMgBr	0	0	68

[a] The yields were determined by ^{1}H NMR spectroscopy and GC–MS spectra using a standard sample, mesitylene.

reagent as the reducing agent have been used in the previous studies. This is the first example of cobalt-catalyzed homocoupling of 9-bromofluorene using a Grignard reagent as the reducing agent to achieve efficient formation of bifluorene at ambient temperature.

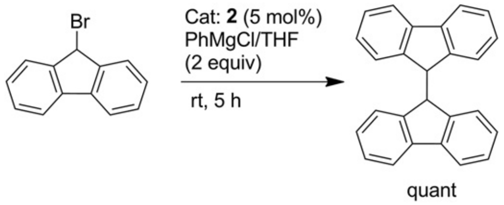
2.3. Mechanistic insights in the reactions of alkyl halides

Because cobalt complexes can have various oxidation states, it is difficult to discuss the mechanism in terms of the oxidation state of cobalt without direct detection of the intermediates. We found that the cobalt solution changed color from dark blue–green to brown, which is generally the color of a monovalent species rather than a divalent species. After quenching, the color reverted to dark blue–green. Chen et al. also proposed a monovalent cobalt species as the intermediate in the catalytic cycle of the Kumada cross-coupling reaction [4a]. Other important points are as follows: (1) styrene coordination competes with β-elimination of octylcobalt species; (2) the yield of the Kumada-coupling product, octylbenzene, was low. Detailed studies, such as detection of intermediates and kinetics, are required for further discussion. The homocoupling product was obtained from 9-bromofluorene. No other products, such as the Kumada coupling or Heck reaction product, were obtained, even in the presence of phenylmagnesium chloride and styrene. We think that generation of benzyl radicals, which are much more stable than primary alkyl radicals, from alkylcobalt species is the most probable process. Reduction of cobalt bromide species with the Grignard reagent could make the catalytic process possible. We do not have any information on why the cross-coupling reaction of the alkyl halide with the Grignard reagents is not predominant in any of these cases, in contrast to the successful Kumada coupling of aryl halides mediated by the cobalt IPr halides.

Table 2
Changing the ratios of 1-bromooctane and styrene for dominant formation of the Heck reaction product.

Entry	Oct-Br:Styrene	Yield (%)[a]		
		A	**B**	**C**
1	1.0:0.9	30	27	48
2	1.0:1.3	40	38	11
3	1.0:2.0	49	40	0
4	1.0:2.7	50	27	0

[a] The yields were determined by ^{1}H NMR spectroscopy and GC–MS spectra using a standard sample, mesitylene.



Scheme 4. Homo-coupling reaction of 9-bromofluorene.

The activation process of alkyl halides using the cobalt catalysts may be substantially different from that of aryl halides. In our hypothesis, strong electron donation from the NHC ligand to the cobalt atom might destabilize the cobalt-carbon (sp^3) bonding interaction, which would make other reactions, such as β-elimination, alkene insertion, or homolytic elimination, faster than the reductive–elimination process.

3. Conclusion

Structurally defined cobalt compounds active for catalytic organic transformations have great potential and possibilities in catalysis using first-row transition-metals. We successfully synthesized and characterized divalent cobalt–iodine complex bearing IMes and pyridine ligands. The cobalt center had a typical d^7-tetrahedral geometry, as expected. This cobalt complex performed catalytic activation of bromoalkanes to provide high yields of alkenes in the presence of PhMgCl. In the presence of styrene, a *trans*-selective Heck reaction also occurred. The reaction of 1-bromofluorene containing a bromobenzyl moiety yielded a homocoupling product efficiently under mild conditions. These results show that the catalytic performance of activation of alkyl halides of the IMes–cobalt complex is superior to that of the IPr analog. Further development of the catalyst system by increasing the range of substrates and reactions, and monitoring of the active cobalt species in the catalytic cycle are now in progress.

4. Experimental section

4.1. General considerations

All experiments were carried out under an inert gas atmosphere using standard Schlenk techniques and glove box (MBraun UniLab) unless otherwise noted. THF, toluene, hexane, benzene-d_6 were distilled from benzophenone ketyl and stored under a nitrogen atmosphere. Organic reagents used for coupling reactions were distilled just before use. Other reagents were used as received. *N*-Heterocyclic carbene (IMes) was prepared according to the published methods [15]. Column chromatography of organic products was carried out using silica gel (Kanto Kagaku, silica gel 60 N (spherical, neutral)). The ^{1}H NMR spectra were taken with a VARIAN Mercury Y plus 400 MHz spectrometer at room temperature. Chemical shifts (δ) were recorded in ppm from the solvent signal. The magnetic properties of the materials were investigated using a Quantum Design MPMS-5S superconducting quantum interference device (SQUID) magnetometer. The UV–visible spectra were taken with a JASCO V-550 spectrometer in toluene using a quartz cell (1.0 cm). The elemental analysis was carried out with YANACO CHN Corder MT-5, AUTO-SAMPLER, using thin aluminum foil, where the samples were held in a glove box. GC–MS spectra were recorded on a JEOL JMS-GCmateII (EI-MS), equipped with Agilent 6890 N gas chromatography.

*4.2. Synthesis of **2***

Anhydrous cobalt(II) iodide (62.5 mg, 0.20 mmol) was dissolved in THF (1.0 mL). Then, IPr (609 mg, 0.20 mmol) and pyridine (16 μL, 0.20 mmol) was added. After addition of 2 mL of THF, the solution was stirred for 2 h. The solvent was removed under reduced pressure. The residual solid was dissolved in small amount of toluene, filtered through celite, and added to a tube, where *n*-hexane was added slowly onto the solution. Dark-green crystals of **2** were obtained during cooling the tube at −30 °C (36 mg, 26%). Anal. Calcd for $C_{26}H_{29}N_3CoI_2$: C, 44.85; H, 4.20; N, 6.40. Found: C, 44.68; H, 4.57; N, 6.06.

*4.3. Reaction of alkyl halide with Grignard reagent in the presence of **2***

In a typical example, 1-bromooctane (0.173 mL, 1.0 mmol) and **2** (34.8 mg, 0.05 mmol) were dissolved in THF (2.0 mL). After stirring for 5 min, phenylmagnesium chloride in THF (1.50 mL, 1.0 M) was added to the solution at −30 °C. After the appropriate reaction time, water (20 mL) was added. The organic layer was extracted with dichloromethane and dried over magnesium sulfate. The volatiles were evaporated under reduced pressure. From the residual oil, 1-phenyloctane was purified with silica gel column chromatography eluting with hexane (colorless oil; 28 mg, 15%). The volatile products, the mixture of 1-octene and 2-octene, were determined by GC–MS and ^{1}H NMR spectra using a standard compound, mesitylene (bp: 166 °C at 760 mmHg).

*4.4. Reaction of alkyl halide with Grignard reagent and styrene in the presence of **2***

In a typical example, 1-bromooctane (52.0 μL, 0.30 mmol), styrene (22.0 μL, 0.20 mmol) and mesitylene (14 μL, 0.10 mmol) was added. After dissolved in ether (0.50 mL), **2** (7.0 mg, 0.01 mmol) and phenylmagnesium chloride THF solution (0.25 mL, 1.0 M) were added to the solution. After stirring at room temperature for the appropriate reaction time, the crude mixture was filtered through short alumina to remove cobalt and magnesium species. The product in the solution was analyzed by means of GC–MS and ^{1}H NMR spectra to determine the yields using mesitylene as a standard compound.

*4.5. Single crystal X-ray diffraction study of **2***

A single crystal of **2** suitable for a X-ray diffraction study was grown at −30 °C from the toluene/hexane solution. The data at 123 K was collected on a Rigaku Saturn CCD diffractometer, using graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71070$ Å). Data reductions of the measured reflections were carried out using the software package, CrystalStructure. The structures were solved by direct methods and refined by full-matrix least-squares fitting based on F^2 using the program SHELXL 97-2 PC version [16]. All non-hydrogen atoms were refined with anisotropic displacement parameters. All H atoms were located at ideal positions and were included in the refinement, but were restricted to ride on the atom to which they were bonded.

Acknowledgments

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Appendix A. Supplementary material

CCDC-887524 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2012.12.025.

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