ChemPubSoc Europe

DOI: 10.1002/chem.201403945

CHEMISTRY
A European Journal
Communication

Hydroboration

# (*N*-Phosphinoamidinate)cobalt-Catalyzed Hydroboration: Alkene Isomerization Affords Terminal Selectivity

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**Abstract:** Herein we establish the utility of a three-coordinate (*N*-phosphinoamidinate)cobalt(amido) pre-catalyst that is capable of effecting challenging alkene isomerization/hydroboration processes at room temperature, leading to the selective terminal addition of the boron group.

Over the past thirty years, metal-catalyzed alkene hydroboration[1] has evolved into a versatile and atom-economical synthetic methodology for the assembly of alkylboronic ester synthons that in turn can be applied in a range of chemical transformations, including now-ubiquitous Suzuki–Miyaura[2,3] cross-couplings. Complexes based on the platinum-group metals, in particular rhodium and iridium, are among the most widely explored and broadly effective classes of catalysts for such transformations, offering high levels of selectivity and excellent substrate scope.[4] Notwithstanding the utility of platinum-group metals in this context, their expensive and toxic nature provides motivation for the pursuit of alternative classes of hydroboration catalysts that mimic the desirable behavior of platinum-group metals, and/or provide access to entirely new reactivity manifolds. Catalysts based on comparatively abundant first-row transition metals, including iron[5,6] and cobalt, represent attractive candidates in this regard.

Some progress has been made as of late with regard to the development of iron catalysts for alkene hydroboration. Notable achievements include the addition of pinacolborane (HBPin) to conjugated dienes,[7] terminal alkenes including unactivated olefins and styrene,[8–11] as well as cyclic aliphatic alkenes,[9] where relevant with *anti*-Markovnikov selectivity and including examples that proceed at room temperature in the absence of added solvent. The key role of ancillary ligand design in enabling such reactivity is established in these reports, with appropriately substituted tridentate bis(imino)pyridine[9] and bipyridylphosphine[8] ligands, as well as photochemically activated (NHC)Fe(CO)$_4$[10] pre-catalysts proving effective. However, a number of important substrate scope limitations have been encountered to date in iron-catalyzed hydroboration chemistry; efficient transformations involving linear internal aliphatic alkenes have proven to be a considerable challenge, with reports of such reactivity being limited to a small number of examples, whereby high conversion but poor regiochemistry is achieved.[9,10]

Despite recent progress in the development of iron-catalyzed alkene hydroborations, and the well-established efficacy of rhodium and iridium in such transformations,[1,4] reports of cobalt-catalyzed alkene hydroboration are few. At the time we initiated the studies disclosed herein, reports documenting cobalt-catalyzed alkene hydroboration reactions were limited to a pair of publications by Zaidlewicz and Meller,[12,13] in which (bisphosphine)$CoCl_2$ complexes were shown to catalyze the hydroboration of 1-octene as well as isoprene in combination with catecholborane, albeit with poor conversion and/or regioselectivity. During the preparation of this manuscript, the remarkable catalytic efficacy of (bis(imino)pyridine)CoMe[14] and (bipyridylphosphine)$CoCl_2$/$NaBHEt_3$[15] in alkene hydroboration was reported. The (bis(imino)pyridine)CoMe (1–5 mol%) system disclosed by Obligacion and Chirik[14] proved capable of catalyzing the addition of HBPin to terminal, geminal, disubstituted internal, tri- and tetrasubstituted alkenes with high activity and *anti*-Markovnikov selectivity, in neat substrate at room temperature, and with selective terminal addition of the BPin moiety. Use of the (bipyridylphosphine)$CoCl_2$/$NaBHEt_3$ catalyst system by Huang and co-workers[15] enabled the room temperature *anti*-Markovnikov hydroboration of vinylarenes and α-olefins with HBPin, at catalyst loadings as low as 0.005 mol%.

We have demonstrated previously that our newly developed *N*-phosphinoamidine/amidinate ligands are effective in supporting first-row transition metal catalysts with applications spanning the chromium-catalyzed selective tri-/tetramerization of ethylene[16] to the iron-catalyzed hydrosilylation of aldehydes, ketones, and esters to alcohols (using **1-Fe**, Figure 1).[17]

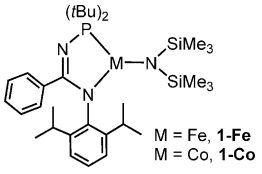


**Figure 1.** Three-coordinate (*N*-phosphinoamidinate)metal-(amido) pre-catalysts, **1-Fe** and **1-Co**.

Notably, whereas such hydrosilylations proceed under mild condi-

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*Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201403945.*


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tions (0.01–1.0 mol% **1-Fe**; room temperature), and with broadest substrate scope known for such iron-catalyzed transformations, the analogous cobalt complex **1-Co** performed poorly in this chemistry.[17] We have also successfully employed this ligand class in the preparation of 16-electron Cp*Ru(*N*-phosphinoamidinate) complexes.[18]

Encouraged by the utility of *N*-phosphinoamidines/amidinates in these diverse applications, we turned our attention to the identification of first-row transition metal derivatives that could be used to address challenges in alkene hydroboration chemistry. In particular we sought to identify catalysts of this type that are useful in promoting alkene isomerization/hydroboration processes that transform linear internal aliphatic alkenes and related substrates selectively into 1-alkylboronate products—a challenging yet useful reaction class that at the time had only proved feasible with either rhodium or iridium catalysts.[19–23] Herein we report on the successful application of the three-coordinate (*N*-phosphinoamidinate)cobalt(amido) pre-catalyst (**1-Co**) in the room-temperature addition of HBPin to linear and branched mono-substituted terminal alkenes, gem-disubstituted terminal alkenes, linear internal octenes, and cyclic alkenes with or without added solvent and with excellent *anti*-Markovnikov selectivity (where relevant); the hydroboration of selected ketones using **1-Co** is also presented. The remarkable ability of **1-Co** to promote alkene isomerization/hydroboration processes involving linear internal alkenes, leading to the selective terminal addition of the BPin group, is demonstrated.

Our initial investigations focused on the application of **1-Fe** and **1-Co** as pre-catalysts for the addition of HBPin to octene isomers over the course of one hour at room temperature in the absence of additional solvent (Figure 2). In the case of 1-octene (**2a**), quantitative formation of the anticipated 1-octylboronic ester (**3**) was achieved by use of 1 mol% (unoptimized) of either catalyst. In moving to *cis*-4-octene (**2b**), near quantitative formation of the terminal *anti*-Markovnikov hydroboration product (**3**) was again observed when using **1-Co** (1 mol%)—a transformation that corresponds to a net alkene isomerization/hydroboration process. The use of modestly higher loadings of **1-Co** (1.5%) reproducibly enabled the quantitative formation of **3**. Such transformations could also be achieved by use of **1-Fe**, although consumption of **2b** and clean formation of the terminal addition product **3** was only achieved at the 2.5 mol% catalyst loading level. Significant differences in reactivity between **1-Fe** and **1-Co** were observed when employing the more challenging substrate *trans*-4-octene (**2c**); whereas quantitative formation of **3** was again observed by use of **1-Co** (2.5 mol%), no conversion was achieved when using **1-Fe** as the pre-catalyst, even at the 5 mol% loading level. Efforts to employ lower loadings of **1-Co** in the isomerization/hydroboration of *trans*-4-octene (**2c**) by conducting reactions at 65 °C were unsuccessful, resulting in apparent catalyst decomposition with poor conversions. Notably, the use of $M\{N(SiMe_3)_2\}_2$ (M = Fe or Co)[24,25] as pre-catalysts resulted in negligible conversion of the starting materials for each of the above-mentioned reactions under analogous conditions, thereby underscoring the importance of the ancillary ligand in supporting suitably reactive pre-catalysts in this system. In keeping with these results, the hydroboration of an equimolar mixture of **2a–c** with HBPin in the presence of **1-Co** (2.5 mol%) afforded **3** cleanly over the course of one hour at room temperature under neat reaction conditions. It is worthy of mention that while synthetically useful, yet challenging, net alkene isomerization/hydroboration processes of this type catalyzed by rhodium or iridium complexes are known,[19–23] such processes promoted by cobalt complexes are limited only to a very recent publication by Obligacion and Chirik[14] that appeared while this manuscript was in preparation, who employed tridentate (bis(imino)pyridine)CoMe catalysts.

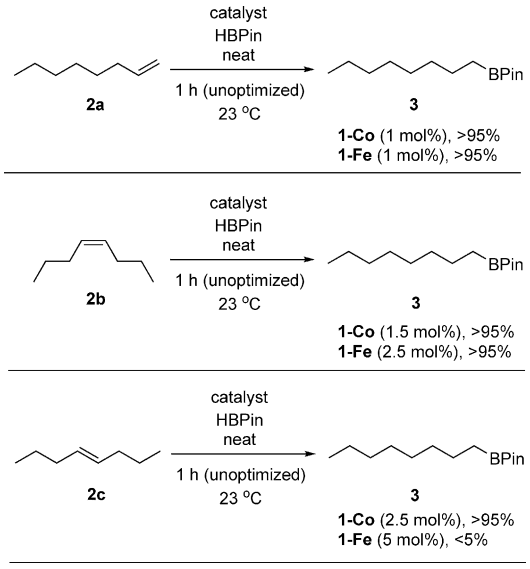


**Figure 2.** Octene isomerization/hydroboration reactions catalyzed by **1-Fe** and **1-Co** and employing HBPin (conversions given on the basis of NMR spectroscopic data).

In an effort to learn more about the progress of these alkene isomerization/hydroboration processes involving **1-Co**, we sought to monitor the fate of *trans*-4-octene (**2c**) under catalytically relevant conditions (neat, room temperature, 2.5 mol% **1-Co**). In probing the reaction by use of $^1$H NMR methods, the clean consumption of **2c** and HBPin along with the formation of **3** was observed within 20 min, in the absence of detectable intermediates or alternative octene isomers. In reducing the catalyst loading to 1 mol% **1-Co**, again only **2c**, HBPin and **3** were observed by use of $^1$H NMR methods; the reaction did not go to completion under these conditions. Similarly, reactions conducted using 2.5 mol% **1-Co** in the presence of a 2:1 mixture of **2c** and HBPin afforded cleanly a 1:1 mixture of unreacted **2c** and **3**, in the absence of detectable quantities of alternative octene isomers. Collectively, these preliminary observations suggest that **1-Co** catalyzed alkene isomerization/hydroboration chemistry employing *trans*-4-octene (**2c**; and presumably other linear aliphatic internal alkenes by analogy) proceeds via internal $L_nCo$(octyl) isomeric intermediates that are resistant to reactivity with HBpin until the $L_nCo$(*n*-octyl) isomer is accessed. Moreover, presumptive β-hydride elimination/1,2-insertion sequences that are likely to transform


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internal $L_nCo$(octyl) isomers into the terminal $L_nCo$(*n*-octyl) form that is apparently intercepted by HBPin must proceed in a manner that does not involve facile loss of alkene from putative intermediates of the type $L_nCo$(octene)(H), given the absence of alternative octene isomers observed during the course of **1-Co** catalyzed transformations involving **2c**.

Encouraged by the remarkable catalytic behavior exhibited by **1-Co**, we sought to develop a more streamlined synthetic route to this pre-catalyst (Figure 3). Our previously reported synthesis of **1-Co** involves addition of the amidine **4** to Co{N(SiMe$_3$)$_2$}$_2$, followed by recrystallization to give **1-Co** in 68% isolated yield. While apparently simple, the published preparation and subsequent isolation of Co{N(SiMe$_3$)$_2$}$_2$ from $CoCl_2$ and NaN(SiMe$_3$)$_2$ is somewhat tedious, involving recrystallization of crude Co{N(SiMe$_3$)$_2$}$_2$ (reported 53% yield), followed by sublimation;[24] using this protocol we routinely obtain pure Co{N(SiMe$_3$)$_2$}$_2$ in approximately 40% isolated yield, giving an effective yield of **1-Co** of approximately 27% starting from $CoCl_2$. We have subsequently demonstrated that **1-Co** can be prepared in a more expedient fashion by sequentially treating $CoCl_2$ with LiN(SiMe$_3$)$_2$ and **4**, thereby enabling the isolation of pure **1-Co** in 52% isolated yield following recrystallization.

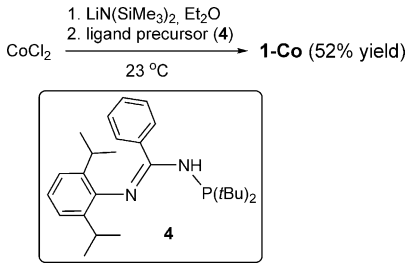


**Figure 3.** Streamlined synthesis of **1-Co**.

We then turned our attention to exploring briefly the hydroboration reactivity of **1-Co** with other olefinic or carbonyl-containing substrates. The spectroscopically determined conversions of the octenes **2a–c** and HBPin to **3** in the presence of **1-Co** (Figure 2) were authenticated on the basis of the high isolated yields obtained (Figure 4). A selection of other mono-substituted terminal alkenes with varying steric profile also underwent successful hydroboration with HBPin in the presence of **1-Co**, affording the *anti*-Markovnikov addition products **5**–**8** in high isolated yield. Similarly excellent results were obtained in the hydroboration of the gem-disubstituted terminal alkene 2-methyl-1-pentene, leading to **9**. The ability of **1-Co** to catalyze the hydroboration of cyclic alkenes was confirmed by the clean transformation of cyclooctene and cyclohexene into the cycloalkylboronate products **10** and **11** (Figure 4). While the aforementioned transformations were conducted under neat conditions, we also demonstrated that analogous reactions leading to **3** (from **2a**) and **5**–**7** could be conducted in the presence of diethyl ether at the 0.5 mol% level, affording the terminal HBPin addition products (92–97%). Further preliminary experimentation with **1-Co** in alkene hydroborations using HBPin under similar conditions revealed some important sub-

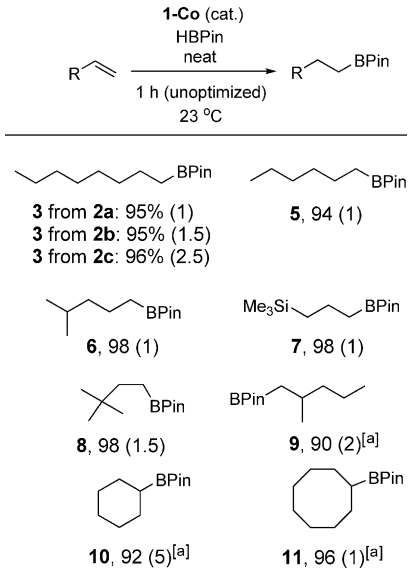


**Figure 4.** Alkene hydroboration employing **1-Co** as a pre-catalyst. Isolated yields (mol% **1-Co** stated in parentheses) of the *anti*-Markovnikov hydroboration product derived from the corresponding terminal or cyclic alkene, with the exception of hydroborations involving the internal 4-octene isomers **2b** and **2c**. [a] 1.2 equivalents of the alkene employed.

strate scope limitations, with styrenes, heteroatom-functionalized alkenes, dienes and enones affording low conversions and/or complex product mixtures. The inability of **1-Co** to catalyze the hydroboration of enones cannot be attributed to the presence of the ketone functionality alone; acetophenone, cyclohexanone, and 2-heptanone were each successfully hydroborated, affording the corresponding secondary alcohols **12**–**14** cleanly upon workup (Figure 5).

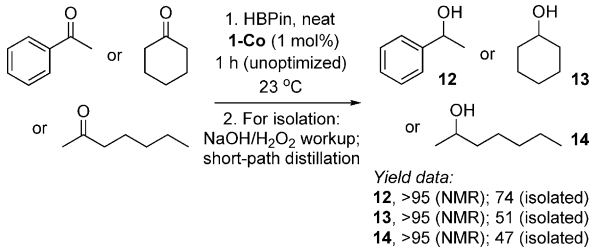


**Figure 5.** Ketone hydroboration employing **1-Co** as a pre-catalyst. The low isolated yields in the case of **13** and **14** can be attributed to losses incurred upon distillative workup.

In conclusion, the results presented herein establish the utility of the easily prepared, three-coordinate (*N*-phosphinoamidinate)cobalt(amido) pre-catalyst (**1-Co**) in challenging room-temperature alkene hydroboration reactions that can be conducted in the presence or absence of added solvent. The efficient *anti*-Markovnikov addition of HBPin to linear and branched mono-substituted terminal alkenes, gem-disubstituted terminal alkenes, and linear internal octenes is reported, as is the hydroboration of cyclic alkenes and ketones. Particularly significant is the observation that **1-Co** promotes alkene isomerization/hydroboration processes involving both


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*cis*- and *trans*-4-octene, leading to the selective terminal addition of the BPin group. Such alkene isomerization/hydroboration chemistry underscores how appropriately ligated cobalt complexes can provide access to challenging and synthetically useful reactivity manifolds that are normally reserved for the platinum-group metals.

## Experimental Section

**General considerations**: Unless otherwise noted, all experiments were conducted under nitrogen in an MBraun glovebox or using standard Schlenk techniques. Dry, deoxygenated solvents were used unless otherwise indicated. Pentane was deoxygenated and dried by sparging with nitrogen and subsequent passage through a double-column solvent purification system purchased from MBraun Inc. with one column packed with activated alumina and one column packed with activated Q5. Diethyl ether and tetrahydrofuran were dried over Na/benzophenone and distilled under nitrogen. $CDCl_3$ (Cambridge Isotopes) was used as received. All alkenes were degassed via three repeated freeze–pump–thaw cycles and were stored over activated 4 Å molecular sieves for a minimum of 12 h prior to use. Pinacolborane (HBPin, Alfa) was used as received and stored under nitrogen. $^1H$ and $^{13}C$ NMR characterization data were collected at 300 K on a Bruker AV-300 spectrometer operating at 300.1 and 75.5 MHz (respectively) with chemical shifts reported in parts per million downfield of $SiMe_4$. $^{11}B$ NMR characterization data were collected at 300 K on a Bruker AV-300 spectrometer operating at 96.3 MHz with chemical shifts reported in parts per million downfield of $BF_3{\cdot}OEt_2$. The *N*-phosphinoamidine **4**[17] was prepared according to literature procedures.

**General procedure for determination of conversion in catalytic hydroboration (GP1)**: In a nitrogen atmosphere glovebox, an oven-dried screw-capped vial containing a stirbar was charged with pinacolborane (145 μL, 1 mmol) and the alkene (1 or 1.2 mmol) or carbonyl compound (1 mmol). Either **1-Co** or **1-Fe** (1–5 mol%) was then added as a solid and the vial was sealed with a cap containing a PTFE septum and stirred in the glovebox for 1 h. After 1 h the vial was removed from the glovebox and the catalyst mixture was deactivated by exposure to air. The contents of the vial were extracted with $CDCl_3$ and filtered through silica into a NMR tube. The $^1H$ and/or $^{11}B$ NMR spectra were analyzed to monitor the progress of the reaction. If no pinacolborane or alkene/carbonyl compound was found to be present in the sample, the reaction was determined to have achieved full conversion. For 4-octene isomers, the $^{13}C$ DEPT-Q NMR spectrum was also analyzed to aid in determining if an isomerization process involving the starting alkene had occurred.

**General procedure for determination of NMR yield in carbonyl hydroboration (GP2)**: In a nitrogen atmosphere glovebox, an oven-dried screw-capped vial containing a stirbar was charged with pinacolborane (145 μL, 1 mmol) and the carbonyl substrate (1 mmol). **1-Co** (1 mol%) was then added as a solid, followed by the addition of a stock solution of $Cp_2Fe$ (internal standard) in $C_6D_6$ (250 μL of 0.4 M solution, 0.1 mmol) and the vial was sealed with a cap containing a PTFE septum and stirred in the glovebox for 1 h. After 1 h an aliquot of the reaction mixture was analyzed by use of $^1H$ NMR spectroscopy. Comparison of the integrals of the methine peaks of the hydroboration products and the $Cp_2Fe$ signal was used to obtain the NMR yield.

**General procedure for isolation of alkene hydroboration products (solvent free) (GP3)**: In a nitrogen atmosphere glovebox, an oven-dried screw-capped vial containing a stirbar was charged with pinacolborane (145 μL, 1 mmol) and the alkene substrate (1 or 1.2 mmol). Either **1-Co** or **1-Fe** (1–5 mol%) was then added as a solid and the vial was sealed with a cap containing a PTFE septum and stirred in the glovebox for 1 h. After 1 h the vial was removed from the glovebox and the catalyst mixture was deactivated by exposure to air. The contents were extracted with $Et_2O$ (3×2 mL) and the ether extracts were subsequently filtered through silica. The eluent was collected and concentrated under reduced pressure to furnish the hydroboration product. The $^1H$ and $^{13}C$ NMR spectra of the isolated material were analyzed to determine the purity of the sample.

**General procedure for isolation of alkene hydroboration products (with solvent) (GP4)**: In a nitrogen atmosphere glovebox, an oven-dried screw-capped vial containing a stirbar was charged with pinacolborane (145 μL, 1 mmol) and the alkene substrate (1 mmol). Either **1-Co** or **1-Fe** (0.5 mol%) was then added as a stock solution (2 mM) in $Et_2O$ (250 μL) and the vial was sealed with a cap containing a PTFE septum and stirred in the glovebox for 1 h. After 1 h the vial was removed from the glovebox and the catalyst mixture was deactivated by exposure to air. The contents were extracted with $Et_2O$ (3×2 mL) and filtered through silica. The eluent was collected and concentrated under reduced pressure to furnish the hydroboration product. The $^1H$ and $^{13}C$ NMR spectra were analyzed to determine product purity.

**General procedure for isolation of alcohols (ketone hydroboration products) (GP5)**: In a nitrogen atmosphere glovebox, an oven-dried screw-capped vial containing a stirbar was charged with pinacolborane (290 μL, 2 mmol) and the ketone substrate (2 mmol). **1-Co** (0.013 g, 1 mol%) was then added as a solid and the vial was sealed with a cap containing a PTFE septum and stirred in the glovebox for 1 h. After 1 h, the vial was removed from the glovebox and the contents were diluted with approximately 10 mL THF. The contents were then hydrolyzed by the addition NaOH (1.0 M in $H_2O$, 2.0 mL, 2 mmol) and $H_2O_2$ (30% in $H_2O$, 1.13 mL, 10 mmol).[7] The organic layer was extracted with $Et_2O$ (3× 5 mL), washed with $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residues obtained were purified by short path distillation under reduced pressure to furnish the alcohol product. The $^1H$ and $^{13}C$ NMR spectra were then analyzed to determine product purity.

**Alternative synthesis of 1-Co**: A solution of $LiN(SiMe_3)_2$ (0.788 g, 4.71 mmol) in $Et_2O$ (10 mL) was added via pipette over 2 min to a magnetically stirred slurry of $CoCl_2$ (0.306 g, 2.36 mmol) in $Et_2O$ (5 mL). A color change from pale blue to deep blue green was observed over the course of 5 min. The reaction mixture was magnetically stirred for a total of 3 h, over which time the formation of a white precipitate was observed. Subsequently, **4** (1.00 g, 2.36 mmol) was added to the reaction mixture as a solid and a color change from deep blue green to deep red was observed over the course of 2 min. After stirring for an additional 2 h the reaction mixture was filtered through Celite, the eluent was collected, and the $Et_2O$ was removed under reduced pressure. The deep red residue was then extracted with pentane (10 mL) and filtered through Celite. The filtrate was then concentrated under reduced pressure to a volume of about 3 mL, and the solution was placed in the freezer at −35 °C for 18 h. After 18 h the brown supernatant solution was decanted and the red solid crystalline precipitate was washed with cold (−35 °C) pentane (2×0.5 mL). The remaining red solid crystalline material (**1-Co**) was dried under reduced pressure (0.786 g, 52%). Spectral data for **1-Co** were in close agreement to previously reported values.[17]


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## Acknowledgements

We thank Chevron Phillips Chemical Company for supporting this research and for permission to publish. Profs. Mark Stradiotto and Laura Turculet are also grateful to NSERC of Canada and Dalhousie University for their support of this work. Dr. Michael Lumsden (NMR-3, Dalhousie) is thanked for on-going technical assistance in the acquisition of NMR data.

**Keywords:** alkene isomerization · cobalt · hydroboration · ketones · *N*-phosphinoamidinate

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Received: June 12, 2014
Published online on September 3, 2014


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