



HAL
open science

Cp*Co(iii)-catalyzed N -alkylation of amines with secondary alcohols

Balakumar Emayavaramban, Priyanka Chakraborty, Eric Manoury, Rinaldo Poli, Basker Sundararaju

► **To cite this version:**

Balakumar Emayavaramban, Priyanka Chakraborty, Eric Manoury, Rinaldo Poli, Basker Sundararaju. Cp*Co(iii)-catalyzed N -alkylation of amines with secondary alcohols. *Organic Chemistry Frontiers*, 2019, 6 (6), pp.852-857. 10.1039/C8QO01389F . hal-02332819

HAL Id: hal-02332819

<https://hal.science/hal-02332819v1>

Submitted on 17 Nov 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Cp*Co(III)-Catalyzed N-Alkylation of Amines with Secondary Alcohols

Balakumar Emayavaramban,^{*a} Priyanka Chakraborty,^a Eric Manoury,^b Rinaldo Poli^b and Basker Sundararaju^a

Received 00th January 20xx,
Accepted 00th January 20xx

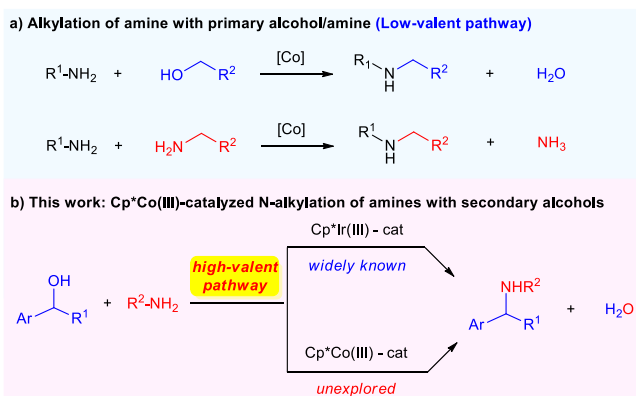
DOI: 10.1039/x0xx00000x

www.rsc.org/

The hydrogen borrowing methodology is a well-known, environmentally benign method for direct alkylation of amines and alcohols as it produces only water as side product. However, the direct alkylation of amine with secondary alcohol using first-row transition metal is very challenging. We herein report for the first time Cp*Co(III)-catalyzed direct N-alkylation of amines starting from secondary alcohols. The reaction tolerates a wide variety of functional groups, including various aryl amines and amides. Our preliminary mechanistic investigations and DFT calculations suggest that [Cp*CoI₂] is an active species, that PCy₃ stabilizes the high-valent hydride intermediate, and that the reaction indeed proceed through hydrogen auto-transfer processes.

Introduction

An efficient access to alkyl amines should have significant influence on pharmaceutical industry due to the presence of such moiety in large variety of drugs.¹ Direct alkylation of amines were generally achieved via amination of alkyl halides² and reductive amination of carbonyl compounds.³ In recent times, new catalytic transformations was emerged for instance direct amination of aryl halides,^{2b-c} hydroamination⁴ and alkylation of amines using alcohols as alkylating agent.⁵ The latter have significant impact due to sustainability, because alcohols are readily available starting materials from a variety of industrial processes,⁶ as well as from the valorization of lignocellulosic biomass.⁷ The metal-catalyzed direct alkylation of primary amines by alcohols operates through the following steps: 1) catalytic dehydrogenation of alcohols into carbonyl compounds, 2) condensation with amine to form imine/iminium ion, 3) hydrogenation of ketimine into saturated amine using the borrowed hydrogen from the first step. This external hydrogen pressure free transformation is commonly known as borrowing hydrogen methodology or hydrogen auto-transfer process.⁵ Mostly known catalysts reported earlier for such transformations are derived from noble metals.^{5,8} However, in the recent years researchers showcased that such transformations are possible using more abundant, and less toxic metals.⁹



Scheme 1: Overview of cobalt-catalyzed C-N Bond formation

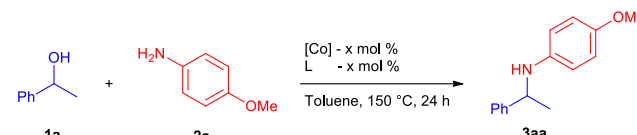
In this regard, several first-row transition metals (Fe, Co, Ni and Mn) based catalysts anchored by privileged ligands were developed for alkylation of amines in the last few years (Scheme 1a).¹⁰ However, most of these catalysts are only effective for the direct amination of primary alcohol (Scheme 1a).¹¹ Efficient catalysts for the amination of secondary alcohols based on first-row transition metals are scarce and underdeveloped.¹² In continuation of our work on high-valent cobalt chemistry for sustainable transformations,¹³ we have developed air- and moisture-stable catalysts for the challenging direct amination of secondary alcohols. This study was inspired by previous reports on the Cp*Ir(III)-catalyzed C-N bond formation directly from alcohols *via* the borrowing hydrogen methodology.¹⁴⁻¹⁹ To our surprise, the corresponding inexpensive, air-stable Cp*Co(III) had not been explored for such a green transformation until our recent report on the dehydrogenation of secondary alcohols.²⁰ In this contribution, we report the first, Cp*Co-catalyzed direct amination of secondary alcohol under hydrogen pressure free conditions (Scheme 1b).

^a Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur, India – 208016.

^b Fine CNRS, LCC (Laboratoire de Chimie de Coordination), Université de Toulouse, UPS, INPT, 205 Route de Narbonne, F-31077 Toulouse Cedex 4, France.

† Footnotes relating to the title and/or authors should appear here.

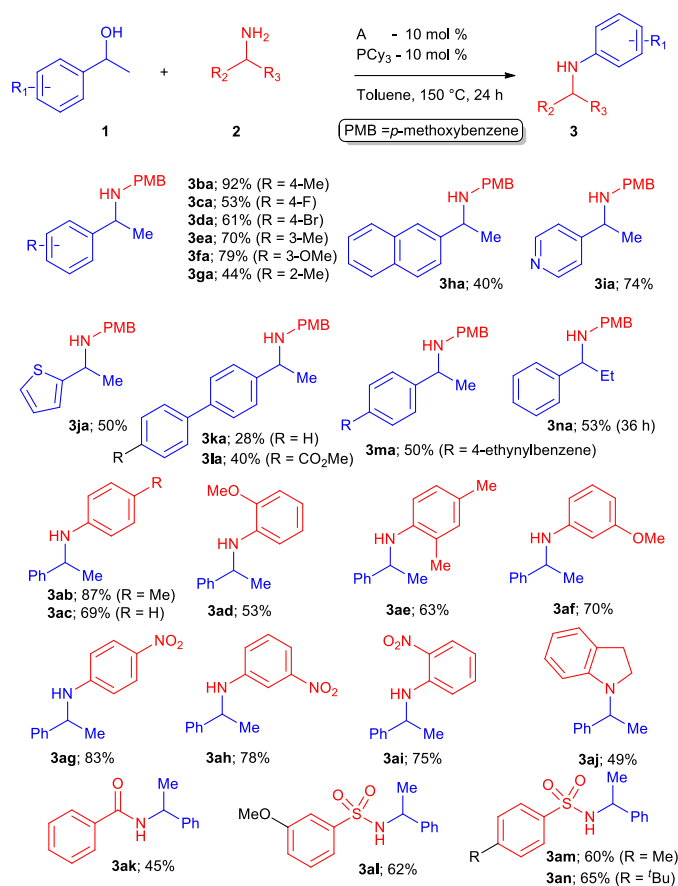
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Table 1: Optimization studies and control experiments^a


Entry	[Co] (mol %)	L (mol %)	Yield ^b
1	A (10)	-	37
2	B (10)	-	39
3	C (10)	-	n.d.
4	D (10)	-	33
5	A (10)	PPh ₃ (10)	64
6	A (10)	PCy ₃ (10)	81
7	A (10)	Dppe (10)	37
8	A (10)	2-hydroxy pyridine (10)	12
9	A (10)	8-hydroxy quinoline (10)	34
10	A (10)	PCy ₃ (10) + AgOTf (10)	47
11	A (10)	PCy ₃ (10)	65 ^c
12	A (10)	PCy ₃ (10)	10 ^d
13	A (10)	PCy ₃ (10)	65 ^e
14	A (10)	PCy ₃ (10)	21 ^f
15	A (10)	PCy ₃ (10)	51 ^g
16	-	PCy ₃ (10)	n.r.
17	B	PCy ₃ (10)	69

^[a] All reactions were carried out under an argon atmosphere unless otherwise stated using **1a/2a**/[Co]/L in 0.6/0.3/0.03/0.03 mmol in toluene (2 mL) at 150 °C for 24 h. ^[b] Isolated yield (%). ^[c] Reaction performed in α,α,α -trifluorotoluene. ^[d] Reaction performed in diglyme. ^[e] Reaction performed in *n*-dibutylether. ^[f] Reaction performed using 1 mL toluene in 0.3 M concentration. ^[g] Alcohol was used as limiting reagent (alcohol/amine ratio = 1/1.5).

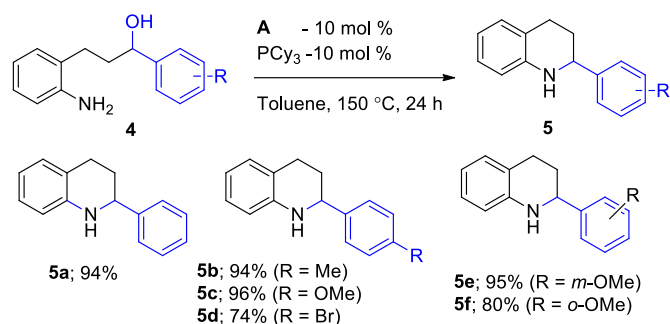
We began our investigations using *p*-anisidine as limiting amine source and 1-phenylethanol as alcohol substrate with 10 mol% of Cp*Co(CO)I₂ (**A**) in toluene at 150 °C for 24 h as shown in Table 1. The expected amine **3aa** was isolated from the crude mixture in 37% yield (entry 1, Table 1). Various reaction parameters were tested in order to further improve the efficiency of the reaction. A change of catalyst to the iodide dimer [Cp*CoI₂]**B** or to the preformed cationic complex [Cp*Co(CH₃CN)₃](SbF₆)₂ **D** did not improve the product formation (entries 2, 4). To our surprise, only traces of product were observed when the chloride bridged cobalt dimer was used as catalyst (entry 3). We also tested various mono- and bidentate ligands as additives (entries 5-9).



Scheme 2: Scope of Amines. Reaction conditions: All reactions were carried out under an argon atmosphere unless otherwise stated using **1/2**/[Co]/L in 0.6/0.3/0.03/0.03 mmol in toluene (2 mL) at 150 °C for 24 h.

Among them, PCy₃ turned out to be the best ligand with 81% isolated yield of **3aa** (entry 6). Next, a system composed of the *in-situ* formed cationic complex along with PCy₃ ligand was tested, leading to a significant reduction of the **3aa** yield (entry 10). Brief screening of other solvents such as TFT (1,1,1-trifluorotoluene), diglyme and *n*-dibutylether did not provide a satisfactory amination product yield (entries 11-13). Changing the concentration or alcohol as limiting substrate did not seem to be a viable option to improve the yield (entries 14-15). A control experiment revealed that the reaction does not proceed in the absence of the cobalt catalyst (entry 16). Finally, [Cp*CoI₂]**B** along with PCy₃ was tested under standard conditions provided the corresponding product **3aa** in 69% yield, thus proving the competency of this dimer as catalyst precursor for the amination of secondary alcohols.

With the best conditions in hand, we next turned our attention to the scope of various secondary alcohols and amines as depicted in Scheme 2. The electron rich methyl substituent at the *para*-position gave a 92% yield (**3ba**), whereas the electron poor substrates 4-F- and 4-Br-phenyl-1-ethanol provided 53% and 61% yields respectively (**3ca-3da**). Substituents at the *meta*-position follow a similar trend with reasonably good yields (**3ea-3fa**). As expected, *ortho*-methyl-1-phenylethanol **1g** gave moderate yield, presumably because of steric repulsion between the substrate and the Cp* ligand. Other arene groups such as naphthyl, 4-pyridyl and 4-



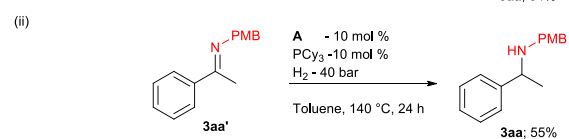
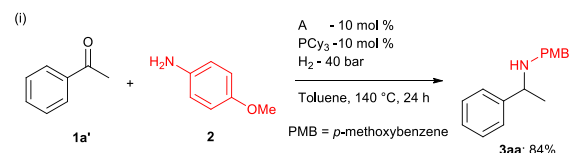
Scheme 3: Intramolecular Amination of Secondary alcohols. Reaction conditions: All reactions were carried out under an argon atmosphere unless otherwise stated using **4**/[Co]/L in 0.3/0.03/0.03 mmol in toluene (2 mL) at 150 °C for 24 h.

thiophenyl gave moderate to good yields (**3ha-3ja**). To further increase the scope, various 4-substituted phenylethanol were prepared and found amenable to amination by *p*-anisidine under the established reaction conditions (**3ka-3ma**). Next, 1-phenylpropanol was tested and the expected product **3na** was isolated in 53% yield. However, aliphatic alcohols were not aminated under these conditions. The investigation was then further extended to a broad scope of amines (**3ab-3an**). Various substituents such as Me-, MeO-, NO₂- are amenable, under the established reaction conditions, to afford the corresponding aminated products (**3ab-3ai**) in good-to-excellent yields. Even a secondary amine underwent alkylation with **1a** and afforded **3aj**, albeit in moderate yield. Less basic amines, protected with benzoyl and sulfonyl groups, equally worked well and afforded the corresponding alkylation products in good yields (**3ak-3an**). However, more basic aliphatic amine did not give any product with 1-phenylethanol, perhaps because they can strongly bind to the catalyst, thereby deactivating it.

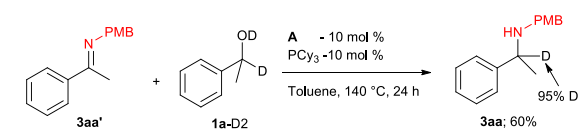
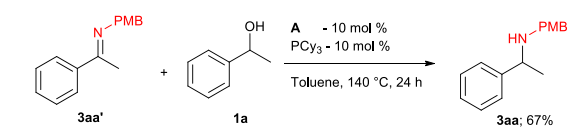
To further increase the reaction scope, the intramolecular amination of selected secondary alcohols was also examined (Scheme 3). Various 1,5-aminoalcohols efficiently underwent the intramolecular amination with excellent isolated yields of the expected 2-aryltetrahydroquinolines (**5a-5f**).

To understand the reaction mechanism various experiments were conducted as shown in Scheme 4. The reductive amination of acetophenone was conducted with *p*-anisidine using the same reaction conditions established for amination of secondary alcohol, except for the addition of hydrogen (40 bar) as reducing agent. The amination product **3aa** was isolated in 84% yield. The isolated ketimine, prepared by condensation of acetophenone and *p*-anisidine was exposed to a hydrogen pressure under similar conditions (Scheme 4a), leading to **3aa** in 55% yield. These experimental results clearly indicate that the ketone (**1a'**) and imine (**3aa'**) are probable intermediate formed *in situ* during the reaction. The transfer hydrogenation of **3aa'** with **1a-D2** under the same reaction conditions gave **3aa** in 60% yield with 95% deuterium incorporation at the α -position (Scheme 4b). The amination of (*S*)-1-phenylethanol with *p*-anisidine provided the expected amination product in 80% yield (Scheme 4c) as a racemic mixture, as expected for the oxidation (dehydrogenation) pathway. Parallel experiments using **1a** and **1a-D₂** gave a $k_{\text{H}}/k_{\text{D}}$ value of 1.74 ± 0.119 , suggesting that the alcohol

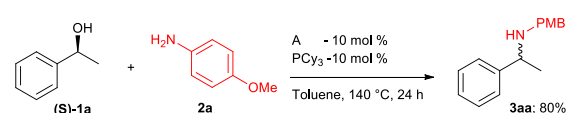
(a) Reductive amination using molecular hydrogen:



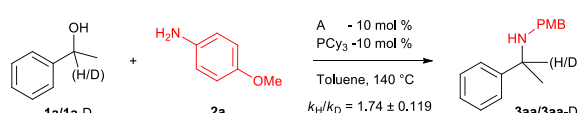
(b) Transfer hydrogenation using **1a**:



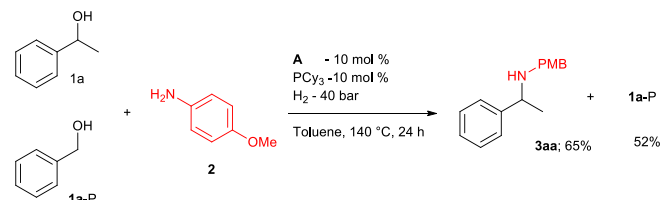
(c) Racemization of (*S*)-**1a** through borrowing hydrogen



(d) KIE experiment (parallel):

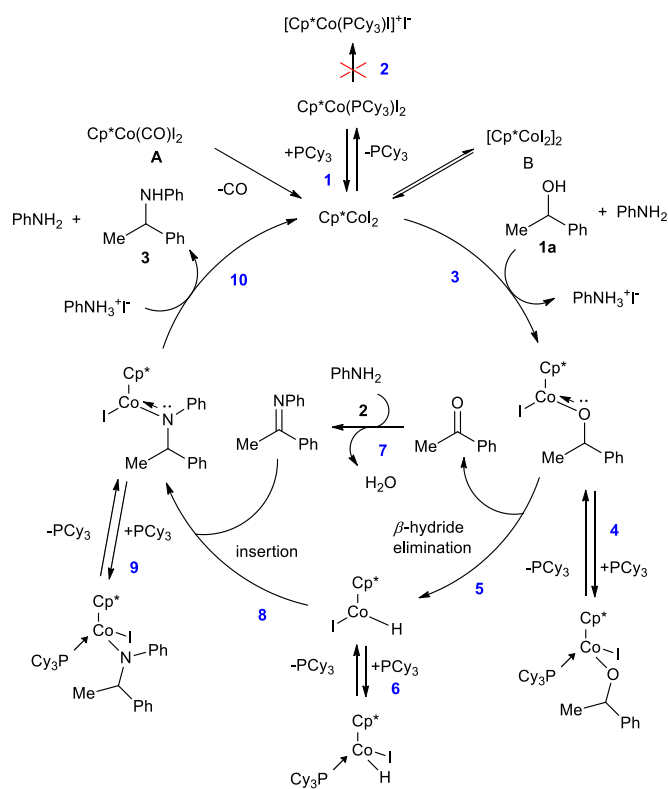


(e) Intermolecular Competitive Experiment:



Scheme 4: Mechanistic Investigations

dehydrogenation is not the rate determining step (see the SI). Finally, the intermolecular competitive experiment between a primary (**1a-P**) and a secondary (**1a**) alcohol led to the exclusive amination of the secondary alcohol, with no observed traces of the putative *N*-benzylated amine with **1a-P** (see the SI). Additional mechanistic aspects were probed by a DFT investigation on the Co-catalyzed amination of 1-phenylethanol by aniline, which focused only on the thermodynamics (no transition state calculations) and the results are summarized in Scheme 5 and Figure 1. For computational efficiency, simpler model systems with Cp in place of Cp* and PMe₃ in place of PCy₃ were used and the energies are reported as $\Delta G_{\text{toluene, 1M}}$ in kcal/mol at 150 °C unless otherwise stated (for details, see the SI). All previous computational work on the analogous Cp*Ir(III) system,²¹ as well as the above-described experimental work on the Cp*Co(III) system, is suggestive of alcohol dehydrogenation



Scheme 5: Proposed Catalytic Cycle

with proton delivery to a spectator ligand (e.g. carbonato,^{21a} alkoxo or aryloxo^{21b-c}) or to an external base^{21d} to produce a key hydride intermediate followed by the mirror processes for the imine substrate, which is produced in the meantime by the non-catalyzed condensation of the ketone intermediate with the amine. A vacant coordination site is needed on the metal center to host the hydride ligand. In the present case, the similar activities of the pre-catalysts **A** and **B** (Table 1) suggests the formation of a common active species, which may be either $[\text{Cp}^*\text{CoI}_2]$ or $[\text{Cp}^*\text{CoI}(\text{PCy}_3)]^+\text{I}^-$. The presence of the 18-electron $[\text{Cp}^*\text{CoI}_2(\text{PCy}_3)]$ may also be questioned because numerous examples of $\text{Cp}^*\text{CoI}_2(\text{PR}_3)$ adducts are known in the literature.²² However, the PCy_3 adduct is not among them. The DFT calculations indicate favorable association of the small PMe_3 to $[\text{Cp}^*\text{CoI}_2]$ (-27.7 kcal/mol at 25°C, -22.9 kcal/mol at 150°C), but an unfavorable one for the bulkier PCy_3 with the bulkier $[\text{Cp}^*\text{CoI}_2]$ (+4.0 and +10.4 kcal/mol at 25 and 150°C, respectively). The role of PCy_3 is presumably the stabilization of the hydride intermediate (*vide infra*). The possible iodide dissociation to generate $[\text{Cp}^*\text{CoI}(\text{PMe}_3)]^+\text{I}^-$ is quite costly in toluene (+52.6 and +48.5 kcal/mol at 25 and 150°C and the same process on the real Cp^*/PCy_3 would undoubtedly also be unfavorable (this process is very solvent-dependent, with the cost dropping to +13.2 and +12.3 kcal/mol in MeCN and H_2O , respectively, at 25°C). Hence, the rest of the cycle was explored on the assumption that the alcohol activating species is the unsaturated $[\text{Cp}^*\text{CoI}_2]$ monomer.

The alcohol activation (reaction 3), presumably taking place *via* alcohol coordination followed by deprotonation by the

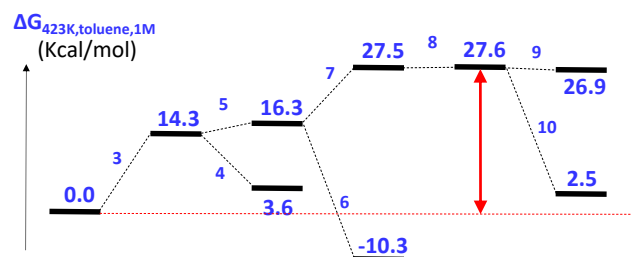


Figure 1. Calculated $\Delta G_{423\text{K}, \text{toluene}, 1\text{M}}$ changes at 150°C for the reactions illustrated in Scheme 5 using the computational model (PMe_3 and Cp used in place of PCy_3 and Cp^*).

external base, yields the 16-electron alkoxide $[\text{Cp}^*\text{CoI}(\text{OCHMePh})]$ with a cost of 14.3 kcal/mol at 150°C. The anilinium iodide product is ion-paired in toluene (dissociation to the free ions requires 35.5 kcal/mol). The alternative elimination of HI without aniline intervention would require 17.3 kcal/mol. The alkoxide complex is slightly stabilized by PMe_3 coordination (reaction 4, -10.7 kcal/mol), lower than the stabilization of $[\text{Cp}^*\text{CoI}_2]$ (-22.9 kcal/mol) because the additional π donation of the alkoxide ligand is greater than that of iodide. Therefore, the real Cp^*/PCy_3 system would undoubtedly not enjoy any stabilization by phosphine association at this stage. The next step (β -H elimination, reaction 5) is thermodynamically quite facile. The 16-electron $[\text{Cp}^*\text{CoHI}]$ intermediate is now greatly stabilized by PMe_3 coordination (reaction 6, -26.6 kcal/mol), because the vacant metal orbital can only interact with a lone pair of the residual iodide, a weak π -donor. This stabilization is greater than for $[\text{Cp}^*\text{CoI}_2]$, presumably for both steric and electronic reasons. Therefore, it appears possible that the real Cp^*/PCy_3 system could benefit from a slight stabilization of this intermediate by phosphine coordination. The imine formation (reaction 7) is endoergic by +11.2 kcal/mol, but the subsequent coordination and insertion into the Co-H bond is essentially neutral. The 16-electron $[\text{Cp}^*\text{CoI}(\text{NPhCMePh})]$ is the highest-energy intermediate of the catalytic cycle, at 27.6 kcal/mol from the starting point. This intermediate is essentially not stabilized at all by PMe_3 coordination (reaction 9, -0.7 kcal/mol), because of the strong π -donor power of the amido ligand and of steric impediments. Final protonation and product release (reaction 10) stabilize the system to yield an overall thermodynamic cost of 2.5 kcal/mol. The unsuitability of this number (the process is thermodynamically favorable) may be associated to the neglect of H-bonding (stronger homo- and hetero-interactions in the $\text{PhNHCHMePh} + \text{H}_2\text{O}$ products than in the $\text{PhCH}(\text{OH})\text{Me} + \text{PhNH}_2$ reactants, a neglect that may also affect the calculated energies of the other intermediates of the cycle. Taking the energy difference between highest and lowest points in the cycle (27.6 kcal/mol at 150°C) as a low limit of the energy span, a TOF of $\leq 180 \text{ h}^{-1}$ can be calculated from the Eyring equation, which does not appear unreasonable considering the observed catalytic activities (table 1 and schemes 1-3) and the Cp^* ligand simplification.

Conclusions

We have demonstrated the first, high-valent cobalt-catalyzed direct N-alkylation of amines with secondary alcohols. Variety amines including benzamides and sulfonamides were amenable for alkylation. Intramolecular amination of secondary alcohols led to 2-arylsubstituted tetrahydroquinoline in excellent yields. Preliminary mechanistic investigation reveals that the reaction indeed proceeds through borrowing hydrogen strategy. The DFT study further validates the action of $[\text{Cp}^*\text{CoI}_2]$ and a competent species to catalyze the amination of secondary alcohols by the borrowing hydrogen methodology and points to the possible role of PCy_3 as a stabilizer of the unsaturated hydride intermediate, possibly protecting this complex against unwanted decomposition. On the other hand, this phosphine additive does not favorably bind to $[\text{Cp}^*\text{CoI}_2]$ (no ground state stabilization) thus maintaining a relatively small energy span for the catalytic cycle.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

Financial Support provided by CEFIPRA (IF-5805-1) to carry out this work is gratefully acknowledged. BE, PC thanks to IITK for their fellowship. PK Kelkar Young Faculty Award to BS is gratefully acknowledged. This work was granted access to the HPC resources of IDRIS under the allocation 2016-086343 made by GENCI (Grand Equipement National de Calcul Intensif) and to the resources of the CICT (Centre Interuniversitaire de Calcul de Toulouse, project CALMIP).

Notes and references

- (a) G. Guillena, D. J. Ramón and M. Yus, *Chem. Rev.* 2010, **110**, 1611-1641; (b) J. L. McGuire, *Pharmaceuticals: Classes, Therapeutic Agents, Areas of Application*. Wiley-VCH, 2000, Vol. **1-4**.
- (a) R. N. Salvatore, C. H. Yoon and K. W. Jung, *Tetrahedron* 2001, **57**, 7785-7811; (b) J. F. Hartwig, *Synlett*, 2006, 1283; (c) S. L. Buchwald, C. Mauger, G. Mignani and U. Scholz, *Adv. Synth. Catal.* 2006, **348**, 23-39; (d) O. Navarro, N. Marion, J. Mei and S. P. Nolan, *Chem. Eur. J.* 2006, **12**, 5142-5148; (e) X. Li, E. A. Mintz, X. R. Bu, O. Zehnder, C. Bosshard and P. Gunter, *Tetrahedron*, 2000, **56**, 5785-5791.
- (a) T. Senthamarai, K. Murugesan, J. Schneidewind, N. V. Kalevaru, W. Baumann, H. Neumann, P. C. J. Kamer, M. Beller, R. V. Jagadeesh, *Nat. Commun.* 2018, **9**, 4123; (b) G. K. M. Verzijl, C. Schuster, T. Dax, A. H. M. De vries, L. Lefort, *Org. Process. Res. Dev.* 2018, **22**, 1817-1822. (c) X. Tan, S. Gao, W. Zeng, S. Xin, Q. Yin and X. Zhang, *J. Am. Chem. Soc.* 2018, **140**, 2024-2027; (d) R. V. Jagadeesh, K. Murugesan, A. S. Alshammari, H. Neumann, M.-M. Pohl, J. Radnik, and M. Beller, *Science*, 2017, **358**, 326-332; (e) S. Zhou, S. Fleischer, H. Jiao, K. Junge and M. Beller, *Adv. Synth. Catal.* 2014, **356**, 3451-3455; (g) A. Pagnoux-Ozherelyeva, N. Pannetier, M. D. Mbaye, S. Gaillard and J. -L. Renaud, *Angew. Chem. Int. Ed.* 2012, **51**, 4976-4980; (g) S. Werkmeister, K. Junge and M. Beller, *Green Chem.* 2012, **14**, 2371-2374; (h) C. Li, B. Villa-Marcos and J. Xiao, *J. Am. Chem. Soc.* 2009, **131**, 6967-6969; (i) V. I. Tararav and A. Borner, *Synlett* 2005, 203-211; (j) K. N. Gusak, Z. V. Ignatovich and E. V. Koroleva, *Russ. Chem. Rev.* 2015, **84**, 288-309.
- (a) T. E. Müller, K. C. Hultsch, M. Yus, F. Foubelo and M. Tada, *Chem. Rev.* 2008, **108**, 3795-3892; (b) L. Huang, M. Arndt, K. Gooßen, H. Heydt and L. J. Gooßen, *Chem. Rev.* 2015, **115**, 2596-2697.
- (a) G. E. Debereiner and R. H. Crabtree, *Chem. Rev.* 2010, **110**, 681-703; (b) G. Guillena, D. J. Ramón and M. Yus, *Chem. Rev.* 2010, **110**, 1611-1641; (c) A. J. A. Watson and J. M. J. Williams, *Science*, 2010, **329**, 635-636; (d) S. Bähn, S. Imm, L. Neubert, M. Zhang, H. Neumann and M. Beller, *ChemCatChem*, 2011, **3**, 1853-1864; (e) C. Gunanathan and D. Milstein, *Science*, 2013, **341**, 1229712; (f) Q. Yang, Q. Wang and Z. Yu, *Chem. Soc. Rev.* 2015, **44**, 2305-2329; (g) A. Corma, J. Navas and M. J. Sabater, *Chem. Rev.* 2018, **118**, 1410-1459.
- J. Leonard, A. J. Blacker, S. P. Mardsen, M. F. Jones, K. R. Mulholland and R. A. Newton, *Org. Process. Res. Dev.* 2015, **19**, 1400-1410.
- T. P. Vispute, H. Zhang, A. Sanna, R. Xiao, and G. W. Huber, *Science* 2010, **330**, 1222-1227.
- (a) R. Grigg, T. R. B. Mitchell, S. Sutthivaiyakit and N. Tongpenyai, *J. Chem. Soc., Chem. Commun.*, 1981, 611-612; (b) Y. Watanabe, Y. Tsuji and Y. Ohsugi, *Tetrahedron Lett.*, 1981, **22**, 2667-2670.
- P. Chirik and R. Morris, *Acc. Chem. Res.* 2015, **48**, 2495.
- (a) B. G. Reed-Berendt, K. Polidano and L. C. Morrill, *Org. Biomol. Chem.* 2018, DOI: 10.1039/c8ob01895b; (b) F. Kallmeier and R. Kempe, *Angew. Chem. Int. Ed.* 2018, **57**, 46-60; (c) M. Garbe, K. Junge and M. Beller, *Eur. J. Org. Chem.* 2017, **30**, 4344-4362; (d) B. Maji and M. Barman, *Synthesis*, 2017, **49**, 3377-3393; (e) A. Mukherjee and D. Milstein, *ACS Catal.* 2018, DOI: 10.1021/acscatal.8b02869
- (a) S. Elangovan, J. Neuman, J. B. Sortais, K. Junge, C. Darcel and M. Beller, *Nat. Commun.* 2016, **7**, 12641; (b) J. Neumann, S. Elangovan, A. Spannenberg, K. Junge and M. Beller, *Chem. Eur. J.* 2017, **23**, 5410-5413; (c) A. Bruneau-Voisine, D. Wang, V. Dorcet, T. Roisnel, C. Darcel and J. -B. Sortais, *J. Catal.* 2017, **347**, 57-62; (d) S. Rösler, M. Ertl, T. Irrgang and R. Kempe, *Angew. Chem. Int. Ed.* 2015, **54**, 15046-15050; (e) G. Zhang, Z. Yin and S. Zheng, *Org. Lett.* 2016, **18**, 300-303; (f) Z. Yin, H. Zeng, J. Wu, S. Zheng and G. Zhang, *ACS Catal.* 2016, **6**, 6546-6550; (g) M. Mastalir, G. Tomsu, E. Pittenauer, G. Allmaier and K. Kirchner, *Org. Lett.* 2016, **18**, 3462-3465; (h) S. Midya, A. Mondal, A. Begum and E. Balaraman, *Synthesis*, 2017, **49**, 3957-3961; (i) M. Bala, P. K. Verma, U. Sharma, N. Kumar and B. Singh, *Green Chem.* 2013, **15**, 1687-1693; (j) T. Tan, B. L. Feringa and K. Barta, *Nat. Commun.* 2014, **5**, 5602; (k) B. Emayavaramban, M. Roy and B. Sundararaju, *Chem. Eur. J.* 2016, **22**, 3952-3955; (l) B. Emayavaramban, M. Sen and B. Sundararaju, *Org. Lett.* 2017, **19**, 6-9; (m) A. J. Rawlings, L. J. Diorazio and M. Wills, *Org. Lett.* 2015, **17**, 1086-1089; (n) M. Mastalir, B. Stöger, E. Pittenauer, M. Puchberger, G. Allmaier and K. Kirchner, *Adv. Synth. Catal.* 2016, **358**, 3824-3831; (o) M. Vellakaran, K. Singh and D. Banerjee, *ACS Catal.* 2017, **7**, 8152-8158; (p) K. Singh, M. Vellakaran and D. Banerjee, *Green Chem.* 2018, **20**, 2250-2256; (q) A. Afanasenko, S. Elangovan, M. C. A. Stuart, G. Bonura, F. Frusteric and K. Barta, *Catal. Sci. Technol.* 2018, DOI: 10.1039/c8cy01200h.
- (a) H.-J. Pan, T. Wei Ng and Y. Zhao, *Chem. Commun.* 2015, **51**, 11907-11910; (b) P. Yang, C. Zhang, Y. Ma, C. Zhang, A. Li, B. Tang and J. S. Zhou, *Angew. Chem. Int. Ed.* 2017, **56**, 14702-14706; (c) O. S. Nayal, M. S. Thakur, M. Kumar, N. Kumar and S. K. Maurya, *Adv. Synth. Catal.* 2018, **360**, 730-737; also see, A. Tillack, D. Hollmann, D. Michalik, M. Beller, *Tetrahedron Letters*, 2006, **47**, 8881-8885.
- (a) T. Yoshino and S. Matsunaga, *Adv. Synth. Catal.* 2017, **359**, 1245; (b) R. Mandal and B. Sundararaju, *Org. Lett.* 2017, **9**, 2544-2547; (c) M. Sen, P. Dahiya, R. Premkumar and B.

- Sundararaju, *Org. Lett.* 2017, **19**, 3699-3702; (d) M. Sen, R. Mandal, A. Das, D. Kalsi and B. Sundararaju, *Chem. Eur. J.* 2017, **23**, 17454-17457; (e) M. Sen, N. Rajesh, B. Emayavaramban, J. Richard Premkumar and B. Sundararaju, *Chem. Eur. J.* 2018, **24**, 342-346; (f) R. Mandal, B. Emayavaramban and B. Sundararaju, *Org. Lett.* 2018, **20**, 2835-2838; (g) D. Kalsi, S. Dutta, N. Barsu, M. Rueping and B. Sundararaju, *ACS Catal.* 2018, **8**, 8115-8120; (h) B. Emayavaramban, P. Chakraborty, B. Sundararaju, *ChemSusChem*, 2018, DOI: 10.1002/cssc.201802144
- 14 S. Pan and T. Shibata, *ACS Catal.* 2013, **3**, 704-712.
- 15 (a) K. Fujita, K. Yamamoto and R. Yamaguchi, *Org. Lett.* 2002, **4**, 2691-2694; (b) R. Kawahara, K.-I. Fujita and R. Yamaguchi, *J. Am. Chem. Soc.* 2010, **132**, 15108-15111; (c) R. Kawahara, K.-I. Fujita and R. Yamaguchi, *J. Am. Chem. Soc.* 2012, **134**, 3643-3646.
- 16 A. Prades, R. Corberán, M. Poyatos and E. Peris, *Chem. Eur. J.* 2008, **14**, 11474-11479.
- 17 D. Gnanamgari, E. L. O. N. Sauer, D. Schley, C. Butler, C. D. Incarvito and R. H. Crabtree, *Organometallics* 2009, **28**, 321-325.
- 18 K. Yuan, F. Jiang, Z. Sahli, M. Achard, T. Roisnel and C. Bruneau, *Angew. Chem. Int. Ed.* 2012, **51**, 8876-8880.
- 19 P. Qu, C. Sun, J. Ma and F. Li, *Adv. Synth. Catal.* 2014, **356**, 447-459.
- 20 (a) M. K. Gangwar, P. Dahiya, B. Emayavaramban and B. Sundararaju, *Chem. Asian. J.* 2018, **13**, 2445-2448; also see (b) Y. M. Badiei, W.-H. Wang, J. F. Hull, D. J. Szalda, J. T. Mukerman, Y. Himeda, E. Fujita, *Inorg. Chem.* 2013, **52**, 12576-12586.
- 21 (a) D. Balcells, A. Nova, E. Clot, D. Gnanamgari, R. H. Crabtree, O. Eisenstein, *Organometallics* 2008, **27**, 2529-2535; (b) H. Li, G. Lu, J. Jiang, F. Huang, Z.-X. Wang, *Organometallics* **2011**, **30**, 2349-2363; (c) A. Bartoszewicz, G. G. Miera, R. Marcos, P.-O. Norrby, *ACS Catal.* **2015**, **5**, 3704-3716; (d) D.-D. Zhang, X.-K. Chen, H.-L. Liu, X.-R. Huang, *RSC Adv.*, **2016**, **6**, 87362-67372.
- 22 (a) M. L. H. Green and R. B. A. Pardy, *J. Chem. Soc., Dalton Trans.* 1979, (1972-1979), 355-360; (b) J. Okuda and K. H. Zimmermann, *Chem. Ber.* 1990, **123**, 1641-1648; (c) H. Werner, L. Scheller, *Polyhedron*, 2012, **34**, 13-23.

TOC

