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FULL PAPER

Cobalt-Catalyzed Intramolecular Hydroacylation Involving Cyclopropane Cleavage

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Dedication ((optional))

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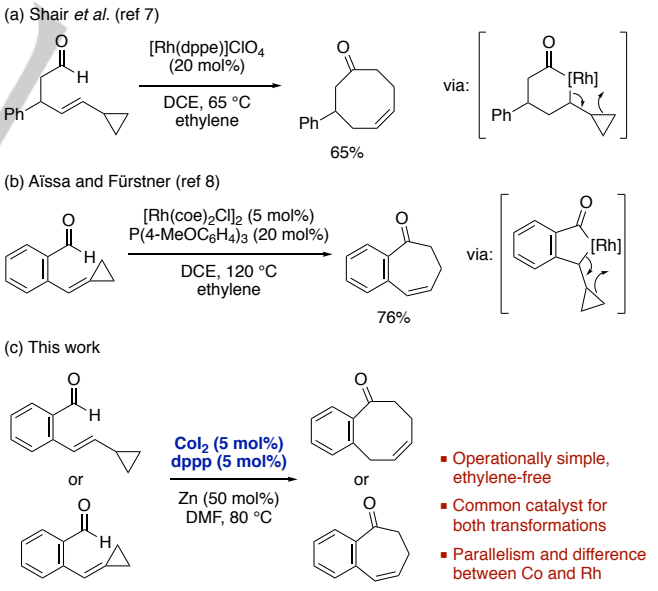
Abstract: A simple cobalt–diphosphine catalyst has been found to efficiently promote intramolecular cyclization of *ortho*-cyclopropylvinyl- and cyclopropylidenemethyl-substituted benzaldehydes into benzocyclooctadienone and benzocycloheptadienone derivatives, respectively. This ring-opening hydroacylation likely involves aldehyde C–H oxidative addition, olefin insertion, cyclopropane cleavage by β-carbon elimination, and C–C bond-forming reductive elimination, as supported by mechanistic experiments and DFT calculations.

Introduction

The transition metal-mediated, strain-driven C–C bond cleavage of small rings allows generation of organometallic intermediates that are otherwise difficult to access, and can be utilized for a variety of catalytic bond formation and skeletal rearrangement reactions.[1,2] Such small ring cleavage typically takes place through C–C bond oxidative addition or through β-carbon elimination. In this regard, rhodium represents one of the most versatile metals for small ring transformations, as it can operate in both the mechanisms of C–C bond cleavage, thus enabling a number of cycloaddition, rearrangement, and other transformations. By contrast, cobalt, the lighter congener of rhodium, has been only sporadically utilized in catalytic small ring transformations.[3-6] Herein, we report that cobalt is capable of emulating the reactivity of rhodium in intramolecular ring-opening hydroacylation of vinylcyclopropane[7] or alkylidenecyclopropane[8] that involves a β-carbon elimination process (Scheme 1a, b). Thus, an inexpensive cobalt–diphosphine catalyst promotes conversion of *ortho*-cyclopropylvinyl- or cyclopropylidenemethyl-substituted benzaldehydes into benzocyclooctadienone or benzocycloheptadienone derivatives, respectively, in good yields under operationally simple conditions (Scheme 1c). Unlike the reactions in Scheme 1a and 1b, the present catalytic system does not require ethylene atmosphere to suppress undesirable decarbonylation, while ethylene proved not to be a prerequisite for analogous rhodium-catalyzed reactions reported later.[9] Mechanistic studies have shed light on the parallelism and difference between the present cobalt catalysis and the reported rhodium catalysis.



Scheme 1. Rh- and Co-catalyzed intramolecular hydroacylation involving cyclopropane cleavage.

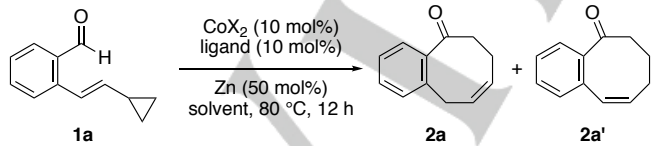
The merger of C–H and C–C cleavages in the rhodium(I)-catalyzed intramolecular hydroacylation[10] was first achieved by Shair and co-workers using cyclopropyl-substituted 4-pentenals as substrates (Scheme 1a),[7] and later by Aïssa and Fürstner

using cyclopropylidenemethyl-substituted benzaldehydes (Scheme 1b).[8,9] These eight- or seven-membered ring formations are commonly proposed to involve aldehyde C–H oxidative addition, olefin insertion into Rh–H, and β-carbon elimination of the thus-formed rhodacycles bearing an adjacent cyclopropyl ring. Meanwhile, we have demonstrated the competence of a cobalt–chiral diphosphine complex as a catalyst for enantioselective intramolecular hydroacylation of 2-alkenylbenzaldehydes,[11,12] which likely operates in the same way as typical rhodium(I) catalysts. We have also reported cobalt–diphosphine-catalyzed cycloaddition and cycloisomerization of tethered alkyne/vinylcyclopropane via cyclopropane cleavage.[3c] These backgrounds, together with our continuing interest in low-valent cobalt catalysis,[13] prompted us to investigate the potential ability of cobalt to promote cyclopropane cleavage in the course of hydroacylation.

Results and Discussion

The present study commenced with a screening of reaction conditions for the cyclization of 2-(2-cyclopropylvinyl)benzaldehyde (**1a**; Table 1). In light of the prominent performance of diphosphine ligands in the previously developed cobalt-catalyzed hydroacylation reactions,[11] several diphosphines were screened in combination with $CoCl_2$ as the cobalt source and Zn dust as the reductant. As a result, several diphoshine ligands such as dppe, dppp, and dppb were found to promote substantial conversion of **1a** in DMF to afford the ring-opening hydroacylation product **2a** (entries 1–6). In particular, dppp caused full conversion of **1a** to afford **2a** in 68% yield, which was accompanied by its olefin regioisomer **2a'** as a minor product. The use of DMSO as the solvent led to a significant drop in the yield (entry 7), while THF and toluene completely shut down the conversion of **1a**. Notably, the cobalt precatalyst had a profound influence on the reaction outcome. While the reaction using $CoBr_2$ also produced a mixture of **2a** and **2a'** (entry 8), the use of CoI_2 resulted in a clean and exclusive formation of **2a** in 91% yield (entry 9). An equally high yield was achieved by reducing the catalyst loading to 5 mol% (entry 10). Note that no simple hydroacylation product, i.e., 2-cyclopropylindanone, was observed in these screening experiments.

Table 1. Effect of reaction conditions.[a]

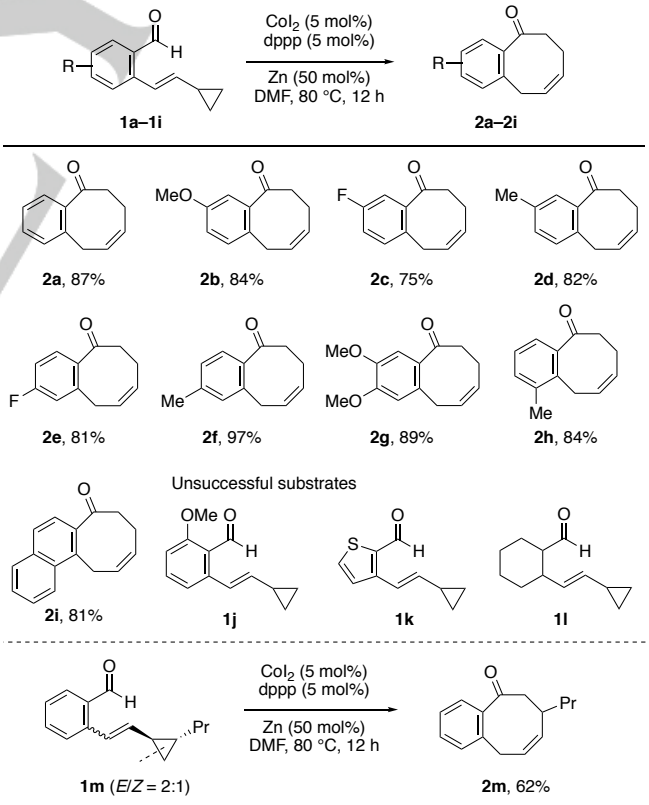


1a **2a** **2a'**

Entry	CoX_n	Ligand[b]	Solvent	Yield [%][c]	
				2a	**2a'**
1	$CoCl_2$	dppm	DMF	0	0
2	$CoCl_2$	dppe	DMF	56	0
3	$CoCl_2$	dppp	DMF	68	20
4	$CoCl_2$	dppb	DMF	30	0
5	$CoCl_2$	dppbz	DMF	23	4
6	$CoCl_2$	DPEphos	DMF	0	6
7	$CoCl_2$	dppp	DMSO	55	8
8	$CoBr_2$	dppp	DMF	40	23
9	CoI_2	dppp	DMF	91	0
10[d]	CoI_2	dppp	DMF	92	0

[a] The reaction was performed on a 0.1 mmol scale at a concentration of 0.3 M. [b] dppm = bis(diphenylphosphino)methane; dppe = 1,2-bis(diphenylphosphino)ethane; dppp = 1,3-bis(diphenylphosphino)propane; dppb = 1,4-bis(diphenylphosphino)butane; dppbz = 1,2-bis(diphenylphosphino)benzene; DPEphos = bis[(2-diphenylphosphino)phenyl] ether. [c] Determined by ^1H NMR using 1,1,2,2,-tetrachloroethane as an internal standard. [d] CoI_2 (5 mol%) and dppp (5 mol%) were used.

The optimized catalytic system was found to promote the ring-opening hydroacylation of a series of *ortho*-2-cyclopropylvinyl aryl aldehydes (Scheme 2). Thus, the starting materials substituted at the *meta*- or *para*-position of the formyl group smoothly underwent cyclization to afford the corresponding benzocyclooctadienone derivatives **2b**–**2i** in good to excellent yields. On the other hand, substrates bearing a substituent *ortho* to the formyl group (**1j**), a thiophene tether (**1k**), or an alkyl tether (**1l**) failed to undergo the desired cyclization. Notably, substrate **1m** bearing an alkyl substituent on the cyclopropyl ring selectively afforded one of two possible cyclooctenone products, **2m**, through cleavage of the less substituted C–C bond.



Scheme 2. Cyclization of cyclopropylvinyl-substituted benzaldehydes.

Having demonstrated the feasibility of the vinylcyclopropane-opening hydroacylation, our attention was next focused on the alkylidenecyclopropane-opening hydroacylation (Scheme 3). To

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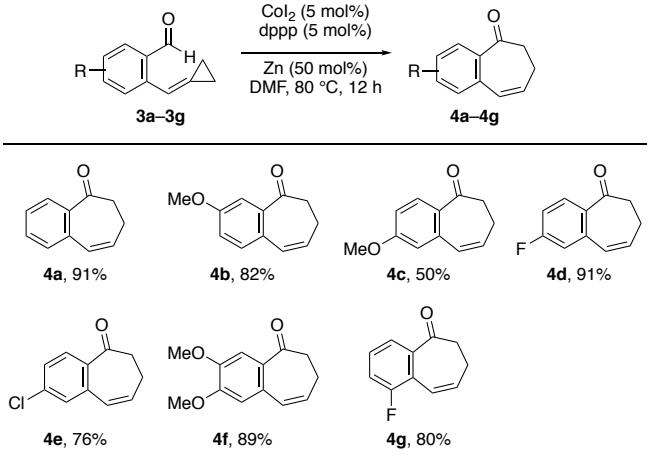
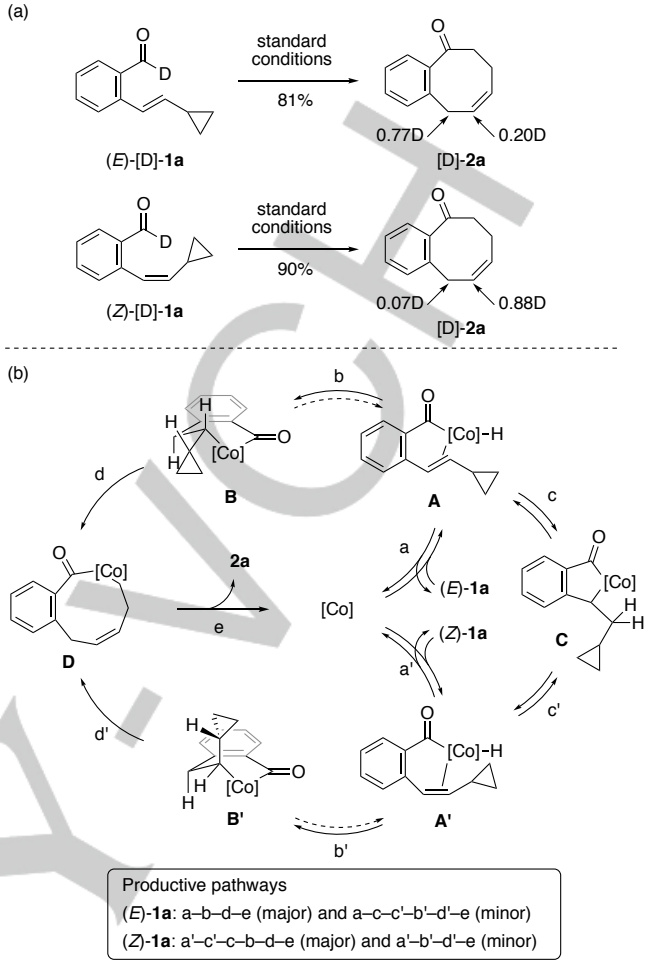
our pleasure, the transformation of (2-cyclopropylidenemethyl)benzaldehyde (**3a**) into benzocycloheptadienone **4a** was achieved in 91% yield under the identical reaction conditions as optimized for the vinylcyclopropane reaction. Likewise, a series of substituted benzocycloheptadienones **4b**–**4g** could be obtained in moderate to good yields.



Scheme 3. Cyclization of cyclopropylidenemethyl-substituted benzaldehydes.

To gain mechanistic insight into the present ring-opening hydroacylation, we first performed deuterium-labeling experiments on the vinylcyclopropane reaction. The reaction of (*E*)-[D]-**1a** took place with predominant deuterium transfer from the formyl group to the benzylic position of the benzocyclooctadienone product, accompanied by a minor but finite degree of deuteration of the vinylic position (Scheme 4a, top). A near opposite deuteration pattern was observed for the reaction of (*Z*)-[D]-**1a** (Scheme 4a, bottom). To explain these observations, we formulated a possible catalytic cycle shown in Scheme 4b. The most straightforward reaction pathway for (*E*)-**1a** would involve C–H oxidative addition to give an acyl(hydrido)cobalt species **A**, olefin insertion into Co–H to give a six-membered cobaltacycle **B**, β-carbon elimination to give a ring-expanded cobaltacycle **D**, and reductive elimination (path a–b–d–e), as is also the case for (*Z*)-**1a** (path a'–b'–d'–e). These pathways should result in transfer of the aldehyde hydrogen to the benzylic position of the product. Meanwhile, *E*/*Z* isomerization of the olefin moiety could take place via a common five-membered cobaltacycle **C**, which coincides with exchange of the aldehyde-derived hydrogen and the β-styryl hydrogen. Given this mechanistic model, the results of the deuterium-labeling experiments suggest that the majority of the product is formed via the *E*-isomer-derived cobaltacycle **B**, while the other cobaltacycle **B'** also contributes in part to the product formation. It is worthwhile to note that the Rh-catalyzed cyclooctenone formation (Scheme 1a) was proposed to proceed exclusively via an *E*-isomer-derived rhodacycle regardless of the *E*/*Z* stereochemistry of the starting material.[7]



Scheme 4. Deuterium-labeling experiments and proposed reaction pathways for the ring-opening hydroacylation of vinylcyclopropane.

Exploration of possible reaction pathways by DFT calculations, using $[Co(dppp)]^+$ and **1a** as the model catalyst and substrate,[14] suggested that the catalytic cycle in Scheme 4b is qualitatively reasonable, while providing more insight into the details of the critical intermediates and transition states as summarized in Figure 1 (see the Supporting Information for computational details). From the complex between $[Co(dppp)]^+$ and (*E*)-**1a** ((*E*)-**CP1**), we could locate two distinct transition states of aldehyde C–H oxidative addition, (*E*)-**TS1** and (*E*)-**TS1'**, which feature orientationally opposite approaches of the cobalt center to the formyl C–H bond, leading to the acyl(hydrido)cobalt intermediates (*E*)-**CP2** and (*E*)-**CP2'**, respectively. The relative orientation of the Co–H and C=C bonds of (*E*)-**CP2** is suited for alkene insertion ((*E*)-**TS2**) leading to the six-membered cobaltacycle *eq*-**CP3**, which bears the cyclopropyl group in the pseudo-equatorial position. Meanwhile, (*E*)-**CP2'** is connected to the five-membered cobaltacycle **CP3'** via (*E*)-**TS2'**. Likewise, the precursor complex (*Z*)-**CP1** derived from (*Z*)-**1a** also has two oxidative addition pathways leading to the distinct intermediates (*Z*)-**CP2** and (*Z*)-**CP2'**, which further undergo alkene insertion to give six-membered and five-membered cobaltacycles *ax*-**CP3** and **CP3'**, respectively. All the C–H oxidative addition processes were endergonic, while for each oxidative addition intermediate, the forward reaction (i.e., alkene insertion) required a much lower

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barrier than the reverse reaction (i.e., C–H reductive elimination). Among the four C–H oxidative addition TSs, those converging to the five-membered cobaltacycle **CP3'** (26.3–28.8 kcal mol^{-1}) were lower in energy than the others (30.5–31.2 kcal mol^{-1}), which suggested the feasibility of the interconversion between (*E*)-**CP1** and (*Z*)-**CP1**.

With the pseudo-axial orientation of the cyclopropyl group, the intermediate *ax*-**CP3** derived from (*Z*)-**1a** is ready to undergo β-carbon elimination via *ax*-**TS3** to generate the ring-expanded cobaltacycle intermediate (*Z*)-**CP4** with *cis* configuration of the newly formed C=C bond. This is followed by C–C bond forming reductive elimination via (*Z*)-**TS4** to afford the product complex (*Z*)-**PD**. On the other hand, direct β-carbon elimination from *eq*-**CP3** was found to be energetically more demanding (*eq*-**TS3**), leading to less stable intermediate (*E*)-**CP4** with *trans* configuration of the C=C bond. In fact, with the pseudo-equatorial position of the cyclopropyl ring in *eq*-**CP3**, we could not locate a β-carbon elimination TS leading to a *cis* C=C bond, presumably because such a TS requires inward orientation of the to-be olefinic hydrogens, which should cause extremely high ring strain. Because of the ring strain associated with the *trans* C=C bond, reductive elimination of (*E*)-**CP4** required a high activation energy ((*E*)-**TS4**, ΔE = 46.7 kcal mol^{-1}), and the resulting *trans*-product complex (*E*)-**PD** was less stable than the starting complex by 15.8 kcal mol^{-1}. For *eq*-**CP3** to be productive, it has to transform to *ax*-**CP3'** (mirror image of *ax*-**CP3**) by ring flipping of the cobalt-containing six-membered ring, which transposes the cyclopropyl group from the pseudo-equatorial to the pseudo-axial position. The energy of this ring-flipping TS (**TS5**; 27.8 kcal mol^{-1}) was lower than that of (*E*)-**TS1** (30.5 kcal mol^{-1}) and (*Z*)-**TS1** (31.2 kcal mol^{-1}), suggesting the feasibility of the conversion of *eq*-**CP3** to (*Z*)-**PD** without reverting back to (*E*)-**CP1** and then to (*Z*)-**CP1**. Overall, the energy diagram suggests that 1) the aldehyde C–H oxidative addition is the rate-determining step, 2) the oxidative addition from (*E*)-**CP1** is energetically preferred to that from (*Z*)-**CP1** albeit with a relatively small difference (and hence the latter may also contribute to the product formation), 3) the five-membered cobaltacycle **CP3'** is a non-productive but important intermediate connecting (*E*)-**CP1** and (*Z*)-**CP1**.

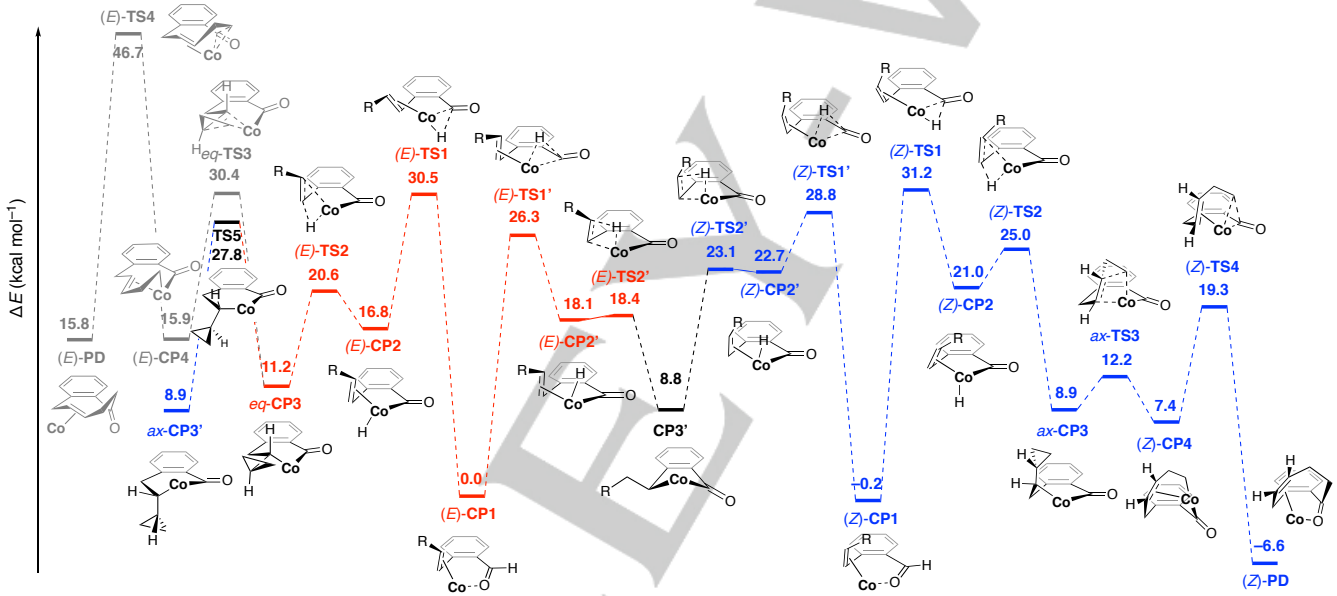
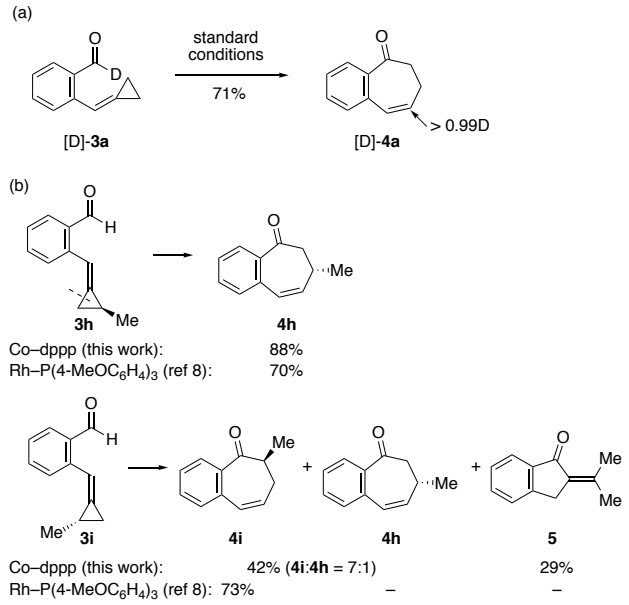


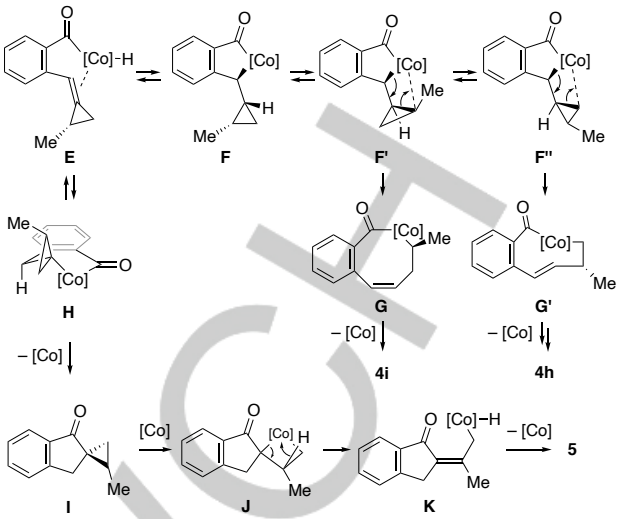
Figure 1. Energy diagram of ring-opening hydroacylation of **1a** with [Co(dppp)]$^+$. The symbols **Co** and R in the structural formula refer to the cationic Co(dppp) moiety and the cyclopropyl group, respectively.

The cycloheptadienone formation from [D]-**3a** took place with a clean transfer of the aldehyde deuterium to the newly formed vinylic position (Scheme 5a), as expected from the mechanism of the rhodium-catalyzed variant (*cf.* Scheme 1b).[8] The cobalt catalyst also operated in the same way as the rhodium catalyst in the reaction of the substrate **3h** bearing a methyl group at the cyclopropyl carbon distal from the benzene ring (Scheme 5b). The C–C bond *cis* to the C–aryl bond was exclusively cleaved to give **4h** as the sole product. By contrast, the cobalt catalyst was found to work differently from the rhodium catalyst on the substrate **3i** bearing a methyl group at the cyclopropyl carbon proximal to the benzene ring (Scheme 5c). Thus, the cobalt-catalyzed reaction of **3i** resulted in a 7:1 mixture of cycloheptenone isomers **4i** and **4h** along with a substantial amount of 2-methyleneindanone derivative **5**, while the rhodium catalyst converted **3i** exclusively to **4i**.



Scheme 5. Deuterium-labeling experiment and effect of cyclopropane substituent on the ring-opening hydroacylation of alkylidenecyclopropane.

The reaction of **3i** under the cobalt catalysis may be rationalized by key steps and intermediates outlined in Scheme 6. Upon C–H oxidative addition, olefin insertion into Co–H in an *exo*-fashion leads to the five-membered cobaltacycle intermediate **F**. As discussed for the rhodium catalysis,[8] rotation of the *exo* C–C bond allows β-carbon elimination from the conformer **F'** to form eight-membered cobaltacycle **G**, while ensuring the *cis* geometry of the newly formed C=C bond. Reductive elimination of **G** then affords the major cycloheptenone product **4i**. Alternatively, β-carbon elimination may also take place from another conformer **F''**, although the resulting cobaltacycle **G'** would suffer ring strain due to the *trans* geometry of the C=C bond. The intermediate **G'** is considered to give rise to the minor cycloheptenone **4h**. While the detailed mechanism of *trans*-to-*cis* olefin isomerization remains unclear, the conversion of **G'** to **4h** might involve a CO extrusion/reinsertion process as suggested by Aïssa for a related Rh-catalyzed reaction of alkylidenecyclobutane.[9c] In addition to these pathways, olefin insertion would also take place in an *endo*-fashion, and reductive elimination of the resulting six-membered cobaltacycle **H** would afford a spirocyclic indanone **I**. Subsequently, **I** would be rearranged to **5** via C–C oxidative addition of the cyclopropane moiety,[15] β-hydride elimination of the cobaltacyclobutane **J**, and reductive elimination of the allyl(hydrido)cobalt species **K**. We speculate that steric repulsion caused by the methyl group slows the β-carbon elimination from **F'**, which, in turn, renders the pathways to the byproducts **4h** and **5** feasible. The different behaviors of the cobalt and rhodium catalysts on **3i** might be ascribed to the shorter ionic radius of cobalt, which would increase the steric repulsion in **F'**.



Scheme 6. Proposed reaction pathways of **3i** under cobalt catalysis.

Conclusion

In summary, we have reported cobalt-catalyzed cyclization of cyclopropylvinyl- and cyclopropylidenemethyl-substituted benzaldehydes, which demonstrate the competence of a simple cobalt–diphosphine catalyst as an alternative to rhodium catalysts to promote ring-opening hydroacylation via β-carbon elimination. The mechanistic study has supported the parallelism between the cobalt and rhodium catalysts, but also highlighted the different behaviour of the cobalt catalyst. In light of the breadth of synthetic transformations involving rhodium-mediated small ring cleavage,[16] the present finding would hold promise for further development of small ring transformations catalyzed by cost-effective cobalt complexes.

Experimental Section

General Procedure for Ring-Opening Hydroacylation: In an argon-filled glove box, a 4-mL vial equipped with a magnetic stir bar was charged sequentially with CoI_2 (4.7 mg, 0.015 mmol), dppp (6.2 mg, 0.015 mmol), zinc powder (9.8 mg, 0.15 mmol), and 2-(2-cyclopropylvinyl)benzaldehyde or 2-(cyclopropylidenemethyl)benzaldehyde derivative (0.30 mmol), followed by the addition of DMF (0.9 mL). The vial was closed and removed from the glove box, and the mixture was stirred at 80 °C for 12 h. Upon cooling to room temperature, the reaction mixture was diluted with ethyl acetate (3 mL) and filtered through a pad of silica gel with additional ethyl acetate (10 mL) as an eluent. The organic solution was concentrated under reduced pressure, and the residue was purified by flash chromatography on silica gel to afford the desired product.

Acknowledgements

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Keywords: cobalt • C–H activation • hydroacylation • C–C bond cleavage • cyclopropanes

[1] a) G. Fumagalli, S. Stanton, J. F. Bower, *Chem. Rev.* **2017**, *117*, 9404-9432; b) M. Murakami, N. Ishida, *J. Am. Chem. Soc.* **2016**, *138*, 13759-13769; c) L. Souillart, N. Cramer, *Chem. Rev.* **2015**, *115*, 9410-9464; d) I. Marek, A. Masarwa, P. O. Delaye, M. Leibeling, *Angew. Chem. Int. Ed.* **2015**, *54*, 414-429; e) K. Ruhland, *Eur. J. Org. Chem.* **2012**, 2683-2706; f) M. Murakami, T. Matsuda, *Chem. Commun.* **2011**, *47*, 1100-1105; g) C.-H. Jun, *Chem. Soc. Rev.* **2004**, *33*, 610-618; h) Y.-J. Park, J.-W. Park, C.-H. Jun, *Acc. Chem. Res.* **2008**, *41*, 222-234; i) T. Kondo, *Eur. J. Org. Chem.* **2016**, 1232-1242.

[2] a) "C-C Bond Activation"*: Topics in Current Chemistry, Vol. 346* (Ed.: G. Dong), Springer, Berlin, **2014**; b) *Cleavage of Carbon-Carbon Single Bonds by Transition Metals* (Eds.: M. Murakami, N. Chatani), Wiley-VCH, Weinheim, **2016**.

[3] For the cleavage of vinylcyclopropanes, see: a) T. Kurahashi, A. de Meijere, *Synlett* **2005**, 2619-2622; b) D. Zell, Q. Q. Bu, M. Feldt, L. Ackermann, *Angew. Chem. Int. Ed.* **2016**, *55*, 7408-7412; c) C. Wu, N. Yoshikai, *Angew. Chem. Int. Ed.* **2018**, *57*, 6558-6562.

[4] For the cleavage of alkylidenecyclopropane, see: a) T. Kurahashi, A. de Meijere, *Angew. Chem. Int. Ed.* **2005**, *44*, 7881-7884; b) M. Li, F. Y. Kwong, *Angew. Chem. Int. Ed.* **2018**, *57*, 6512-6516.

[5] For the cleavage of benzocyclobutenones, see: Z. Zhu, X. Li, S. Chen, P.-H. Chen, B. A. Billett, Z. Huang, G. Dong, *ACS Catal.* **2018**, *8*, 845-849.

[6] For stoichiometric C–C cleavages, see: a) L. S. Liebeskind, J. P. Leeds, S. L. Baysdon, S. Iyer, *J. Am. Chem. Soc.* **1984**, *106*, 6451-6453; b) M. A. Huffman, L. S. Liebeskind, *J. Am. Chem. Soc.* **1990**, *112*, 8617-8618; c) C. Perthuisot, B. L. Edelbach, D. L. Zubris, W. D. Jones, *Organometallics* **1997**, *16*, 2016-2023; d) J. Foerstner, A. Kakoschke, R. Wartchow, H. Butenschön, *Organometallics* **2000**, *19*, 2108-2113.

[7] A. D. Aloise, M. E. Layton, M. D. Shair, *J. Am. Chem. Soc.* **2000**, *122*, 12610-12611.

[8] C. Aïssa, A. Fürstner, *J. Am. Chem. Soc.* **2007**, *129*, 14836-14837.

[9] a) D. Crépin, J. Dawick, C. Aïssa, *Angew. Chem. Int. Ed.* **2010**, *49*, 620-623; b) D. Crépin, C. Tugny, J. H. Murray, C. Aïssa, *Chem. Commun.* **2011**, *47*, 10957-10959; c) Aïssa, C.; Crépin, D.; Tetlow, D. J.; Ho, K. Y. T. *Org. Lett.* **2013**, *15*, 1322-1325.

[10] For reviews on transition metal-catalyzed hydroacylation, see: a) A. Ghosh, K. F. Johnson, K. L. Vickerman, J. A. Walker, L. M. Stanley, *Org. Chem. Front.* **2016**, *3*, 639-644; b) S. K. Murphy, V. M. Dong, *Chem. Commun.* **2014**, *50*, 13645-13649; c) J. C. Leung, M. J. Krische, *Chem. Sci.* **2012**, *3*, 2202-2209; d) M. C. Willis, *Chem. Rev.* **2010**, *110*, 725-748.

[11] a) J. Yang, N. Yoshikai, *J. Am. Chem. Soc.* **2014**, *136*, 16748-16751; b) J. Yang, A. Rérat, Y. J. Lim, C. Gosmini, N. Yoshikai, *Angew. Chem. Int. Ed.* **2017**, *56*, 2449-2453.

[12] For other examples of cobalt–diphosphine-catalyzed hydroacylation, see: a) Q. A. Chen, D. K. Kim, V. M. Dong, *J. Am. Chem. Soc.* **2014**, *136*, 3772-3775; b) J. Yang, Y. W. Seto, N. Yoshikai, *ACS Catal.* **2015**, *5*, 3054-3057; c) J. Yang, N. Yoshikai, *Angew. Chem. Int. Ed.* **2016**, *55*, 2870-2874; d) D. K. Kim, J. Riedel, R. S. Kim, V. M. Dong, *J. Am. Chem. Soc.* **2017**, *139*, 10208-10211.

[13] a) K. Gao, N. Yoshikai, *Acc. Chem. Res.* **2014**, *47*, 1208-1219; b) P. Gandeepan, C.-H. Cheng, *Acc. Chem. Res.* **2015**, *48*, 1194-1206; c) M. Moselage, J. Li, L. Ackermann, *ACS Catal.* **2016**, *6*, 498-525; d) P. Rose, G. Hilt, *Synthesis* **2016**, *48*, 463-492.

[14] Q. Meng, F. Wang, *J. Mol. Model.* **2016**, *22*, 60.

[15] To our knowledge, there is no precedence of the C-C oxidative addition of cyclopropane to cobalt without neigboring group assistance. For the oxidative addition of vinylcyclopropane and cyclopropene, see refs 3a and 6d, respectively.

[16] For examples of Rh-catalyzed reactions involving cleavage of vinylcyclopropanes or alkylidenecyclopropanes, see: a) S. Simaan, I. Marek, *J. Am. Chem. Soc.* **2010**, *132*, 4066-4067; b) P. A. Wender, R. T. Stemmler, L. E. Sirois, *J. Am. Chem. Soc.* **2010**, *132*, 2532-2533; c) M. Lin, F. Li, L. Jiao, Z.-X. Yu, *J. Am. Chem. Soc.* **2011**, *133*, 1690-1693; d) P. A. Evans, P. A. Inglesby, *J. Am. Chem. Soc.* **2012**, *134*, 3635-3638; e) M. Lin, G.-Y. Kang, Y.-A. Guo, Z.-X. Yu, *J. Am. Chem. Soc.* **2012**, *134*, 398-405; f) S. Mazumder, D. J. Shang, D. E. Negru, M. H. Baik, P. A. Evans, *J. Am. Chem. Soc.* **2012**, *134*, 20569-20572; g) P. A. Wender, D. N. Fournogerakis, M. S. Jeffreys, R. V. Quiroz, F. Inagaki, M. Pfaffenbach, *Nat. Chem.* **2014**, *6*, 448-452; h) P. A. Evans, D. E. Negru, D. J. Shang, *Angew. Chem. Int. Ed.* **2015**, *54*, 4768-4772; i) R. N. Straker, Q. Peng, A. Mekareeya, R. S. Paton, E. A. Anderson, *Nat. Commun.* **2016**, *7*, 10109.

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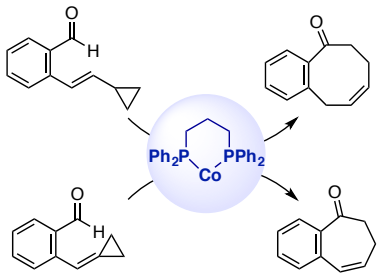

A simple cobalt–diphosphine catalyst efficiently promotes intramolecular ring-opening hydroacylation of vinylcyclopropane and alkylidenecyclopropane to afford eight- and seven-membered carbocyclic products. The reaction likely proceeds via C–H oxidative addition, olefin insertion, β-carbon elimination, and C–C reductive elimination as key steps, as supported by mechanistic experiments and DFT calculations.

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