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Cobalt-catalyzed intramolecular decarbonylative coupling of acylindoles and diarylketones through the cleavage of C–C bonds†

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We report here cobalt–*N*-heterocyclic carbene catalytic systems for the intramolecular decarbonylative coupling through the chelation-assisted C–C bond cleavage of acylindoles and diarylketones. The reaction tolerates a wide range of functional groups such as alkyl, aryl, and heteroaryl groups, giving the decarbonylative products in moderate to excellent yields. This transformation involves the cleavage of two C–C bonds and formation of a new C–C bond without the use of noble metals, thus reinforcing the potential application of decarbonylation as an effective tool for C–C bond formation.

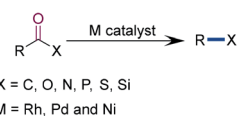
Introduction

Catalytic decarbonylation has attracted considerable attention in organic synthesis.¹ In particular, intramolecular decarbonylative coupling emerged as a more efficient and higher atom-economic strategy for the efficient formation of chemical bonds. This method allows for a common carbonyl group to serve as a “traceless handle” for chemical bond formation. In the past few decades, advances in intramolecular decarbonylative coupling, which can be used to create C–C, C–P, C–N, C–O, C–S and C–Si bonds through transition-metal catalysis, have been made (Scheme 1A).²

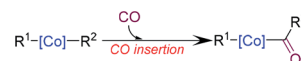
Synthesis of bi(hetero)aryls very common in the pharmaceutical, agrochemical, and materials industries.³ From the view point of step and atom economy, transition-metal-catalyzed intramolecular decarbonylative coupling of ketones would offer a distinct strategy for the synthesis of bi(hetero)aryls, which has presented many attractive features. For example, ketones can be readily prepared, are stable, and generally have low toxicity. In addition, the use of this strategy helps to reduce the amount of harmful waste products (CO is the major side product). Finally, this reaction allows carbonyl of ketones to become a “traceless handle” for the construction of the C–C bond, which will improve the flexibility of synthetic design.^{1c,k} Although highly attractive, the typical use of expensive and noble Rh complexes may hinder the development of this field.⁴ First row transition metals (iron, cobalt, nickel, and

copper) are typically inexpensive and earth-abundant; the replacement of second row transition metals as catalysts with first row transition metals would be revolutionary. Pioneering work in this field has demonstrated that nickel enables the decarbonylation of ketones.⁵ In recent years, cobalt has received considerable attention in the activation of strong σ -bonds owing to its low price, ability to access multiple oxidation states, and its extensive, yet reactive, organometallic chemistry.⁶ Co carbonyl complexes are also known to catalyze several carbonylative processes (Scheme 1B).⁷ Decarbonylation involves C(=O)–C bond oxidative addition, CO extrusion, and C–C bond forming reductive elimination, which can be regarded as the reverse process of carbonylation (Scheme 1C). The excellent

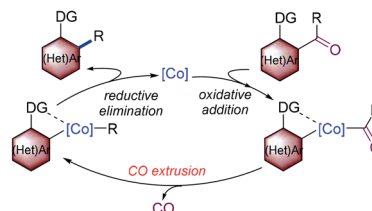
A. Intramolecular decarbonylative couplings



B. The process of Co-catalyzed carbonylation



C. The process of Co-catalyzed decarbonylation: *This work*



Scheme 1 Inspiration for Co-catalyzed decarbonylation.

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affinity of Co with a carbonyl group inspired us to explore the use of this metal as the catalyst for decarbonylation. To our knowledge, Co-catalyzed decarbonylation is challenging and remains unsolved so far.⁸ Herein, we disclose the first Co-catalyzed decarbonylation of ketones with the assistance of an N-containing directing group,⁹ in which an intramolecular decarbonylative coupling of acylindoles and diarylketones was realized with an inexpensive cobalt precatalyst.

Results and discussion

N-Pyrimidinyl 2-benzoyl indole **1a** was employed as the model substrate. After a careful survey of the reaction parameters (see the ESI†), we discovered that the combined use of Co₂(CO)₈, IMes·HCl, and Cs₂CO₃ in dioxane afforded 2-phenyl indole **2a** in 93% yield (Table 1, entry 1). Control experiments were carried out to understand the role of each reactant (see Table 1). In the absence of Co₂(CO)₈, the desired product was not observed (entry 2). The reaction without the ligand afforded the desired product, albeit in a lower yield (entry 3). When IMes·HCl (20 mol%) loading was reduced to IMes·HCl (10 mol%), the reaction produced 85% yield of **2a** (entry 4). Other NHC ligands also promoted this reaction but gave lower yields as compared to that obtained with IMes (entries 5–7). Phosphine ligands such as P(*n*-Bu)₃ or PCy₃ also promoted this reaction but the yields were lower (entries 8 and 9). Dioxane as the solvent

proved to be superior to toluene or *i*PrOH (entries 10 and 11). Co(II) complexes such as CoBr₂ and salen Co complexes were not reactive for this transformation (entries 12 and 13). Next, several other coordinating groups were tested (Scheme 2). Comparable results were obtained when replacing the pyrimidyl group with a pyridyl group (**1a-1**), while no product was observed when the pyrimidyl group was removed (**1a-2**) or replaced with a weakly coordinating group such as carboxamide or urea (**1a-3** and **1a-4**).

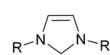
With the optimized reaction conditions in hand, we next investigated the scope of indole substrates. As shown in Table 2, electron-donating and -withdrawing substituents at the 3-, 4-, 5-, and 6-positions were compatible with the reaction conditions. Common functional groups such as aryl fluoride (**2b**), cyanide (**2c**), acetyl (**2d**), ether (**2e** and **2f**), trifluoromethyl (**2h**) and ester (**2i**) were unaffected by the reaction conditions, thus highlighting the versatility of the transformation. The reaction efficiency was unaffected when a 3-methyl group (**2k**) was introduced, thus indicating tolerance of steric hindrance. A wide variety of electron-donating (**2r**) or electron-withdrawing (**2m**, **2s** and **2t**) substituents on the benzene ring were also well tolerated. Polyaromatic ketones (**2u** and **2v**) reacted smoothly to give the corresponding decarbonylation products. The substrates could be changed from indole to pyrrole, with pyrimidine as a directing group, to furnish the desired product **2x** in moderate yield. In addition, aryl alkyl ketones were suitable for this transformation, and the corresponding 2-alkyl indoles (**2ya–2yf**) were obtained in moderate yields.¹⁰ Note that aryl alkyl ketones had failed in the Ni system. However, under the standard conditions, no products were detected when secondary alkyl aryl ketones were used (**2yg**, **2yh** and **2yi**), affording byproduct **2a-H**.

We also investigated the decarbonylation of diaryl ketones. For these substrates, ICy instead of IMes in the Co catalysis gave better yields (see the ESI†). A variety of diaryl ketones bearing a 2-pyridyl directing group also underwent decarbonylation to deliver the corresponding products in moderate to good yields. Further, a wide variety of functional groups, including ethers, trifluoromethyl, fluorides, and esters, were tolerated in the reaction. The directing group was also extended to a pyrimidine (**4m**) and a pyrazole (**4o**); however, no product was observed when the directing group was replaced with an oxime (**4p**).

A preliminary density functional theory (DFT) study was conducted to explore the reaction mechanism (Fig. 1). The geometries were optimized at the B3LYP/DZ level of theory¹¹ and the electronic energies were further improved by single-point calculations at the M06/TZ level.¹² Solvation effects in 1,4-dioxane were treated by the continuum implicit solvation model SMD.^{13a} In the simulation, we chose Co₂(CO)₄(NHC) to be the

Table 1 Evaluation of reaction conditions^a

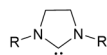
Entry	Deviations from above	Yield ^b [%]	
		2a	2a-H
1	“Standard conditions” with 1a	93	<5
2	Without Co ₂ (CO) ₈	0	0
3	Without IMes·HCl	18	0
4	IMes·HCl (10 mol%)	85	<5
5	ICy·HCl instead of IMes·HCl	68	10
6	SIPr·HCl instead of IMes·HCl	14	17
7	IPr·HCl instead of IMes·HCl	47	20
8	P(<i>n</i> -Bu) ₃ instead of IMes·HCl	72	<5
9	PCy ₃ instead of IMes·HCl	80	<5
10	Toluene instead of dioxane	86	<5
11	<i>i</i> PrOH instead of dioxane	0	70
12	CoBr ₂ instead of Co ₂ (CO) ₈	0	10
13	Salen Co(II) instead of Co ₂ (CO) ₈	0	19



IMes (R = 2,4,6-Me₃C₆H₂)

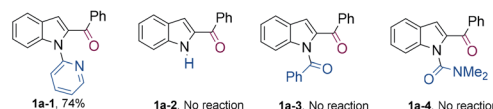
ICy (R = cyclohexyl)

IPr (R = 2,6-*i*Pr₂C₆H₃)



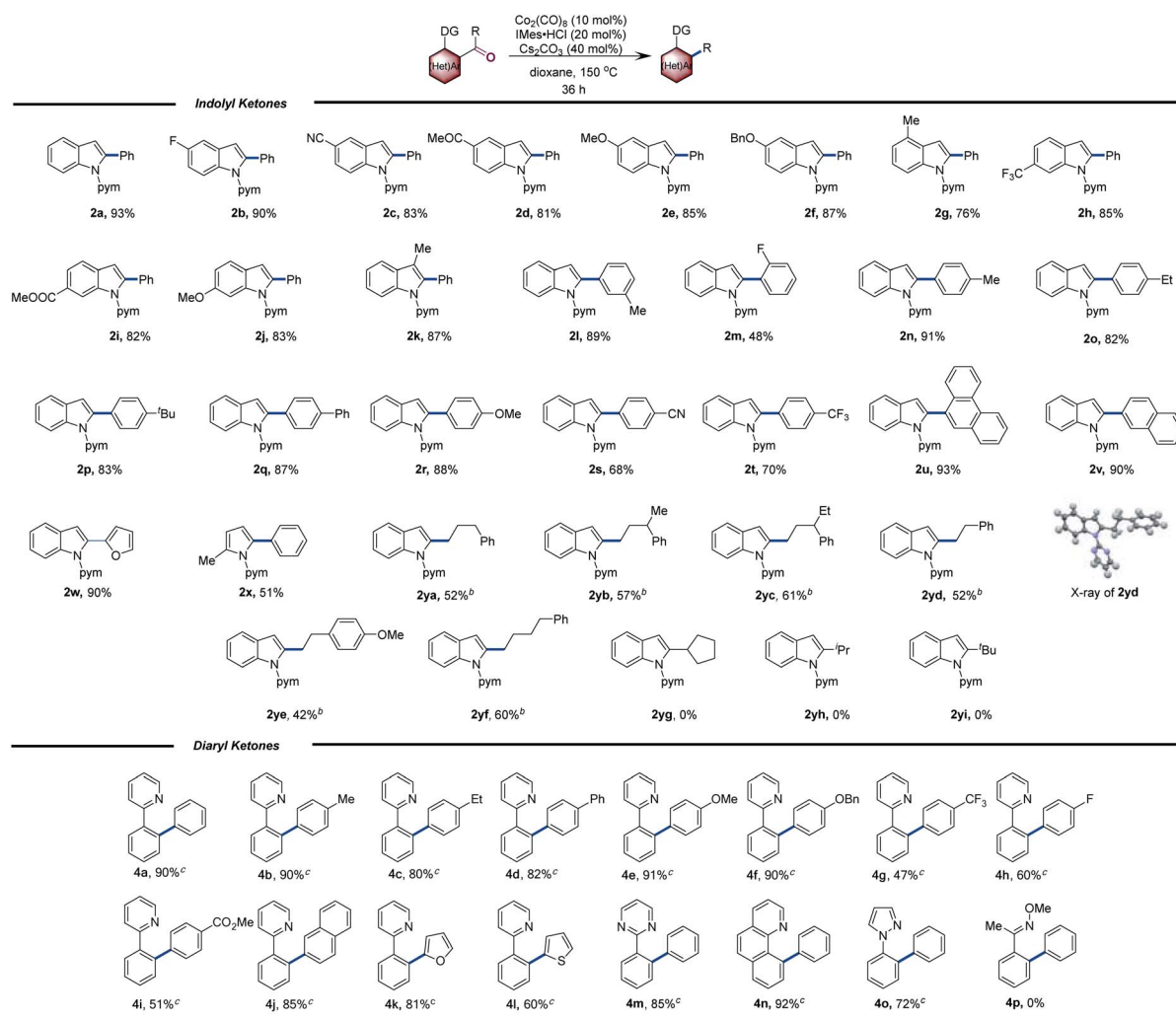
SIPr (R = 2,6-*i*Pr₂C₆H₃)

^a Standard conditions: **1a** (0.1 mmol), Co₂(CO)₈ (10 mol%), IMes·HCl (20 mol%), Cs₂CO₃ (40 mol%), and dioxane (0.5 mL) at 150 °C in a sealed tube, 36 h. ^b Isolated yields.



Scheme 2 Screening of directing groups.



Table 2 Intramolecular carbonylative coupling of ketones^a

^a Reaction conditions: **1** (0.1 mmol), Co₂(CO)₈ (0.01 mmol, 10 mol%), IMes·HCl (0.02 mmol, 20 mol%), Cs₂CO₃ (0.04 mmol, 40 mol%), dioxane (0.5 mL) at 150 °C, 36 h in a sealed tube, isolated yields. ^b PCy₃ as the ligand and toluene as the solvent. ^c ICy as ligand.

catalyst as can be seen from Fig. 2 (The justifications are described in the ESI†). The dissociation of CO ligands is necessary to initiate catalysis and create coordination sites (Co₂(CO)₈ + L = Co₂(CO)₄L (CAT) + 4CO ($\Delta G = 25.2$ kcal mol⁻¹). The catalytic cycle commences upon coordination between the Co(0) complex (CAT) and substrate **1a**, giving the catalyst-substrate complex **INT1**.

Then, **INT1** undergoes oxidative addition to form **INT2A** via **TS1**, requiring an activation free energy of 18.9 kcal mol⁻¹; this step is endergonic by 12.3 kcal mol⁻¹. **INT2A** is converted to **INT2B** via the transfer of carbon monoxide. Next, **INT2B** is converted to **INT3A** via decarbonylation, requiring an activation free energy of 8.5 kcal mol⁻¹. The decarbonylation step was endergonic by 4.1 kcal mol⁻¹. **INT3A** can rearrange into intermediate **INT3B**, which then undergoes reductive elimination to form **INT4** (via **TS3**). Finally, **INT4** is converted to **INT5** with the release of CO.¹⁴ The dissociation of CO from **INT3A** or **INT3B**

was also considered but deemed unlikely as the energy barrier (**TS4**) is 2 kcal mol⁻¹ higher than that of **TS3**. The overall free energy for the reaction is -3.1 kcal mol⁻¹. Considering the activation free energy of each step, evidently, the highest energy barrier is the transition from **INT1** to **TS1** (18.9 kcal mol⁻¹). According to the energetic span approximation,^{13b,c} the rate-determining transition state (RDTS) and the rate-determining intermediate (RDI) are **TS3** and **INT1**, respectively, thus, the energetic span $\delta E = 25.2$ kcal mol⁻¹.

Finally, the utility of this reaction was demonstrated for a variety of valuable target motifs (Scheme 3A). The *N*-pyrimidyl directing group could be smoothly removed from **2a** to obtain the corresponding *N*-H indole **5a** in 82% yield. In the presence of IBr, **5a** reacted with acetophenone to give the corresponding carbazole derivative **6a**.¹⁵ Such scaffolds are prevalent in natural products and drug candidates with intriguing bioactivities,¹⁶ thus highlighting the synthetic applicability of the present



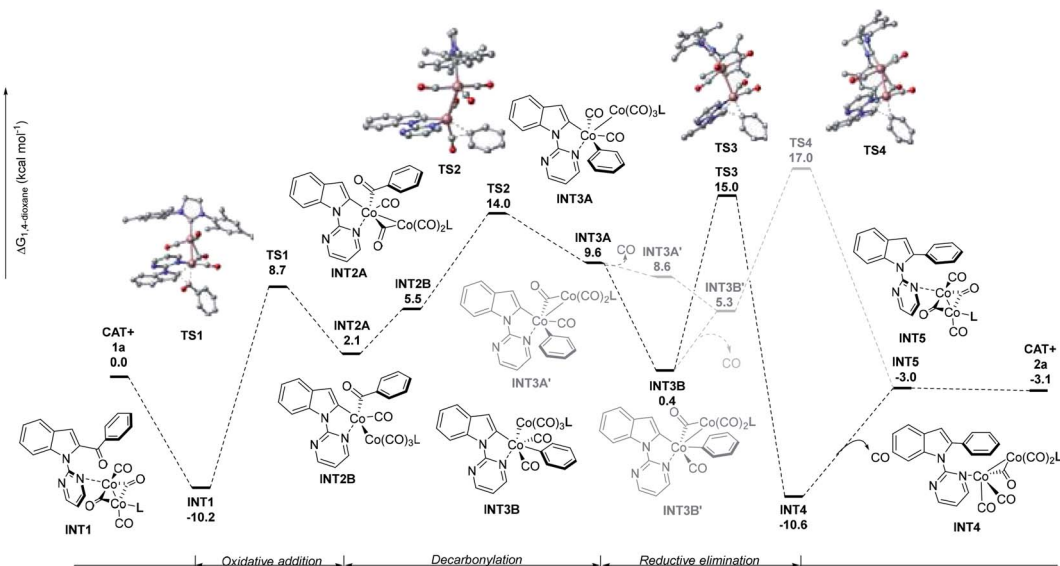
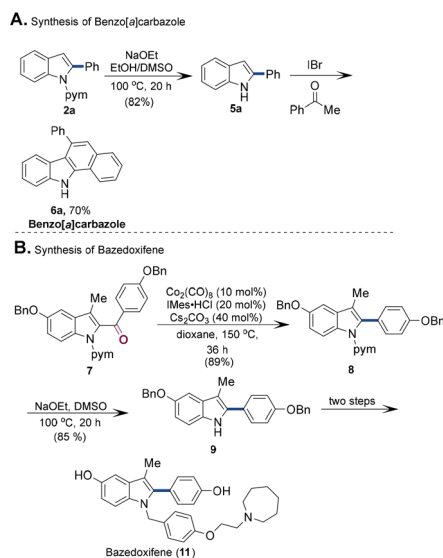


Fig. 1 Density functional theory (DFT) calculated pathways for the intramolecular decarbonylative coupling.



Scheme 3 Synthetic utility.

method. The protocol was additionally applied to the synthesis of bazedoxifene, a third-generation selective estrogen receptor modulator (SERM).¹⁷ As shown in Scheme 3B, the synthesis was initiated by the conversion of ketones **7** to **8** under standard conditions. The removal of the directing group from **8** gave indole derivative **9**. The conversion of **9** to bazedoxifene has been reported.^{17c}

Conclusions

In summary, we have discovered a simple Co system that can catalyze the decarbonylation of ketones *via* the cleavage of two C–C bonds. This work showcases the unique ability of the Co catalyst to trigger C–C bond disconnections, and further

reinforces the potential of using decarbonylation as a tool for chemical bond formation and cleavage. However, this coupling reaction is still associated with significant drawbacks such as the requirement of high temperatures and directing groups. The use of directing groups aids the decarbonylation, but it complicates the whole synthesis and limits the application of this strategy in synthesis.¹⁸ Studies aimed at expanding this decarbonylative strategy to simple ketones without directing groups are ongoing in our laboratories.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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