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C–H functionalization by high-valent Cp*Co(III) catalysis

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Significant progress has been accomplished in directed C–H functionalization through the use of earth-abundant and inexpensive first-row transition metals. Among these base metals, Co is especially attractive in view of its versatile applications in C–H functionalization, in both low- and high-valent states. In this vein, catalytic Co(III) species can be generated from the dissociation of a Cp*Co(III) catalyst or through the oxidation of a low-valent cobalt catalyst in the presence of an oxidant. In this feature article, we will discuss the breakthroughs in Cp*Co(III)-promoted C–H functionalization. In this field, C(sp^2)–H functionalization has been extensively studied and developed. In contrast, few C(sp^3)–H functionalization reactions have been reported.

1. Introduction

The formation of a new C–C or C–X bond *via* directed C–H functionalization has been identified as an ideal synthetic approach.[1] This method is step-economic and environmentally friendly because it avoids the prefunctionalization steps of traditional reactions.[2] In recent decades, C–H bond activations have been successfully accomplished with transition metals, especially noble metals with 4d and 5d electrons.[3] Very recently, first-row 3d transition metals have drawn special attention in C–H activation reactions because of their earth-abundant and low-cost characteristics as well as their potential reactivity.[4]

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Cobalt plays important roles in biological systems, such as the active center of vitamin B12. Furthermore, cobalt is comparatively less toxic[5] and less expensive than the noble metals, and it is widely used as a catalyst in cross-coupling reactions,[6] which collectively renders it a particularly attractive alternative to noble metals in C–H activation.

Both low- and high-valent cobalt catalysts can promote C–H functionalization to form new C–C or C–X bonds. The C–H transformations catalyzed by low-valent cobalt were initiated by Nakamura, Yoshikai and Ackermann and have recently been realized under mild conditions. Several reviews have well summarized the developments in this field.[4g,4h,7] A classic ternary catalytic system consisting of a cobalt precatalyst, a phosphine ligand and a stoichiometric reducing agent has been developed and two hypothetical catalytic cycles have been proposed. Although the low-valent cobalt-catalyzed system has been studied extensively, it requires the use of a Grignard

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Shan-Yong Chen

Shan-Yong Chen was born in Sichuan, China in 1977. In 2005, he joined the Department of Chemistry at Sichuan University. He received his PhD in 2010 (with Prof. Xiao-Qi Yu). In 2013–2014, he worked as a visit scholar with Prof. Lin Pu at the University of Virginia. His current research interests focus on new synthetic methods.

reagent and has hitherto only been applied to C–C bond formation.

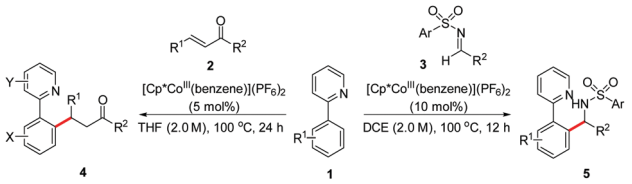
In contrast to the prevalence of low-valent cobalt catalysis, a high-valent Co(III)-catalyzed system for C–H functionalization has been developed in recent years. A major breakthrough in high-valent cobalt-catalyzed C–H activation was disclosed by Matsunaga, Kanai, and co-workers in 2013 employing a Cp*Co(III) reagent as the catalyst.[8] In 2014, Daugulis *et al.* proposed another Co(III) catalysis strategy in which a Co(II) catalyst and an oxidant were used.[9] The developed Co(III) catalysis system can avoid the use of Grignard reagents. Based on the above advantages, high-valent Co(III)-catalysis has been increasingly developed during the past four years.

In this feature article, we will discuss the breakthroughs in Cp*Co(III)-catalyzed C–H functionalization. In this field, Cp*Co(III) catalysts have demonstrated extraordinary capability for directed C–H functionalization. Moreover, in addition to imitating expensive Cp*Rh(III) catalysis, Cp*Co(III) also exhibits unique reactivities.

2. Cp*Co(III)-catalyzed C(sp^2)–H functionalization

2.1 Addition reactions

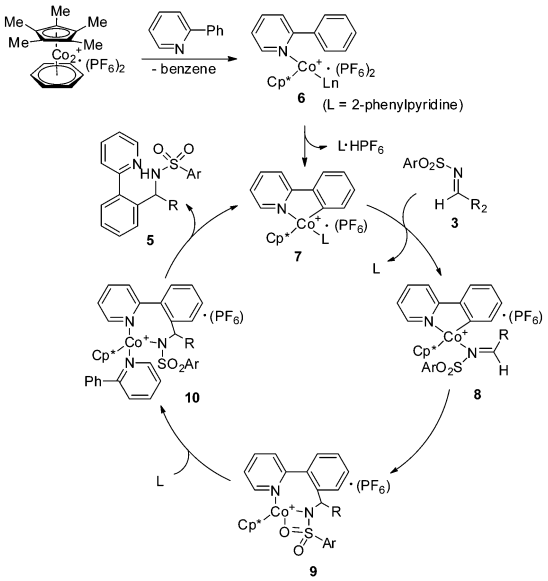
2.1.1 Addition to double bonds. Cp*Rh-catalyzed C–H activations have undergone explosive development since the late 2000s.[1e,10] A variety of directing group-assisted transformations have been carried out in both oxidative and redox-neutral manners. Encouraged by these extensive developments, a Cp*Co(III)-catalyzed addition of 2-aryl pyridines **1** to enones **2** and imines **3** has been reported by Matsunaga, Kanai, and co-workers (Scheme 1).[8] Several cationic [CpCo(III)(arene)] complexes were investigated with various Cp-type ligands, and the [Cp*Co(III)(arene)][PF6)$_2$ complex demonstrated the best balance in terms of stability and reactivity.



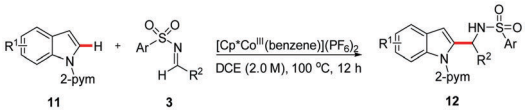
Scheme 1 Addition of 2-aryl pyridines to imines and enones.

Based on the related Rh(III) catalysis,[11] a plausible mechanism was outlined and is displayed in Scheme 2.[8] Initially, the dissociation of the coordinating benzene ring in the [Cp*Co(III)(arene)](PF$_6$)$_2$ complex upon heating and coordination with the 2-phenylpridine generated complex **6** were observed. Then, the cyclometalated intermediate **7** was formed by C–H activation, which likely occurred through an electrophilic aromatic substitution or a concerted metalation–deprotonation (CMD) mechanism. After ligand exchange with imine **3** to give **8**, intermediate **9** was generated by the insertion of the electrophile, which was followed by the coordination of another 2-phenylpridine to give **10**. Finally, product **5** was obtained by proto-demetalation, and the key intermediate **7** was regenerated.

Apart from arylpyridines **1**, the addition to imines was further explored at the C-2 position of *N*-pyrimidylindoles **11**, which are more synthetically useful (Scheme 3).[12] Notably, the reaction can be attained with as low as 0.5 mol% catalyst loading. Furthermore,



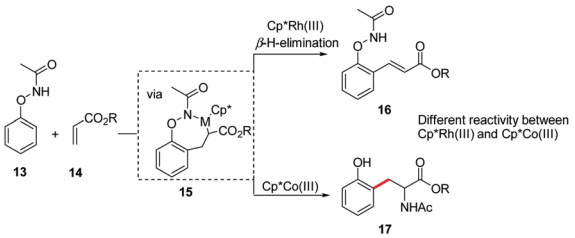
Scheme 2 Proposed catalytic cycle for the arylation of imines.



Scheme 3 Addition of indoles to imines.

Xiao-Qi Yu

Xiao-Qi Yu was born in Sichuan, China in 1965. He received his PhD from Sichuan University (SCU). In 1999, he became a full professor at SCU. He worked as a research associate in Prof. C.-M. Che's group at the University of Hong Kong during 1999–2001. From 2010 to present, he has been a Changjiang Scholars Professor and the dean of College of Chemistry, SCU. His research interests include biomedical materials chemistry (especially for non-viral gene and drug delivery vectors) and methodology of organic syntheses (green synthetic methodologies). He has published over 300 scientific papers. He has received several awards, including New Century Excellent Talent Award (2003, Ministry of Education of China), Outstanding Young Scientist Award (2003, Sichuan Province), Excellent Teacher Awards (2001 and 2004, SCU) and Distinguished Young Scholars Awarded (2007, National Science Foundation of China).



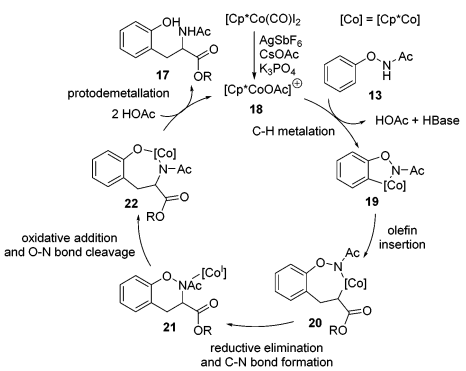
Scheme 4 Non-annulative carboamination of alkenes.

the introduction of catalytic amounts of KOAc was found to achieve a higher yield. This may be due to the formation of catalytically active Co(III) acetate species induced by anionic ligand exchange with KOAc after the initial dissociation of the benzene ligand from Cp*Co(III).[13]

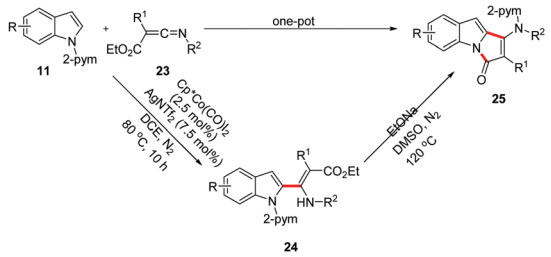
Recently, cobalt(III)-catalyzed carboamination of alkenes **14** with phenoxyacetamide **13** was also realized by the Glorius group (Scheme 4).[14] This methodology provided an efficient direct preparation of highly valuable unnatural amino acid derivatives **17**. A possible mechanism was shown in Scheme 5. Initially, a cationic Co(III) species **18** was generated upon treatment of the $CoCp^*(CO)I_2$ precursor with $AgSbF_6$, CsOAc and K_3PO_4, followed by C–H activation to afford intermediate **19** with the elimination of HOAc. The 7-membered intermediate **20** was produced following an olefin-coordination of intermediate **19**. Intermediate **20** underwent unusual reductive elimination to form the C–N bond through the concomitant generation of Co(I) species **21**. Afterwards, the desired product **17** was obtained by subsequent oxidative addition, O–N bond cleavage and protodemetallation.

Interestingly, when Cp*Co(III) was replaced by Cp*Rh(III), only trace amounts of the carboamination product **17** were observed, and the oxidative Heck product **16** was the major product, indicating that β-H-elimination prevailed over the saturation of the promising $C(sp^3)$–metal center when Cp*Rh was used as a catalyst. In contrast, no saturation of the $C(sp^3)$–metal center was needed and carboamination was intrinsically preferred over β-H-elimination in Cp*Co catalysis.

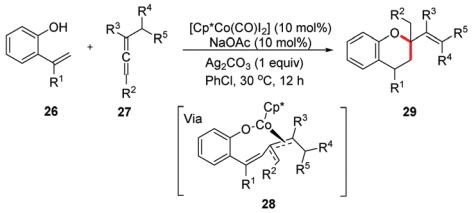
In comparison with the simple addition reactions, chemists pay more attention to tandem addition/annulation reactions. The addition of **11** to ketenimines **23** bearing cumulative double bonds and subsequent intramolecular cyclization afforded



Scheme 5 The mechanism of carboamination of alkenes.



Scheme 6 Enaminylation of indoles with ketenimines and base-promoted cyclization.

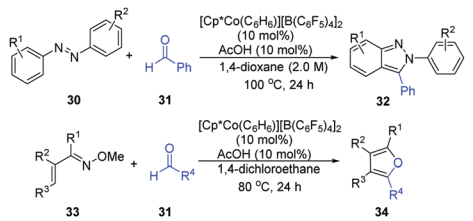


Scheme 7 Cobalt-catalyzed annulation for 2-*H*-chromenes.

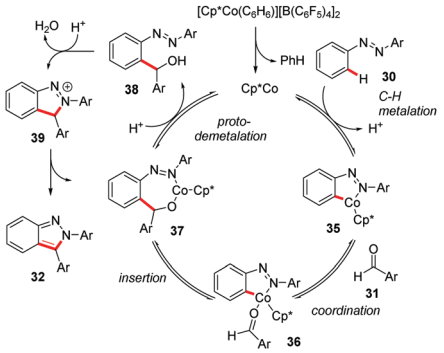
3*H*-pyrrolo[1,2-*a*]indol-3-ones **25** (Scheme 6).[15] The generation of the active cationic complex by the addition of a silver salt $AgNTf_2$ was shown to be essential. Furthermore, the utilization of allenes **27** as nucleophiles in cobalt-catalyzed C–H activation was reported by Cheng *etc.*,[16] wherein 2-vinylphenols **26** and allenes **27** underwent [5+1] annulation in the presence of 1 equiv. of Ag_2CO_3 to afford a wide range of 2-*H*-chromones **29** in high yields *via* intermediate **28** (Scheme 7).

Catalytic addition of C–H bonds to aldehydes, producing either alcohols or further annulation products, has been largely achieved by rhodium[17] or rhenium[18] catalysis. The Ellman group disclosed a cobalt-catalyzed synthesis of indazoles **32** and furans **34** by additions to aldehydes **31** followed by *in situ* cyclization and aromatization (Scheme 8).[19] Although a high yield of indazole **32** was obtained by using 5 mol% of $[Cp^*CoCl_2]_2$ as the catalyst, 25 mol% of $AgB(C_6F_5)_4$ and 20 mol% of AgOAc were also necessary in this transformation. To eliminate any use of Ag salts, a new precatalyst $[Cp^*Co(C_6H_6)][B(C_6F_5)_4]_2$ was synthesized. The use of only a catalytic amount of this catalyst and AcOH promoted this reaction well, making it both low-cost and convenient to handle.

A possible catalytic cycle mechanism was also provided (Scheme 9). Initially, the dissociation of benzene from the $[Cp^*Co(C_6H_6)][B(C_6F_5)_4]_2$ complex generated the active Cp*Co catalyst. Then, cobaltacycle **35** was produced by reversible



Scheme 8 The cobalt-catalyzed synthesis of indazoles and furans by C–H bond additions to aldehydes.

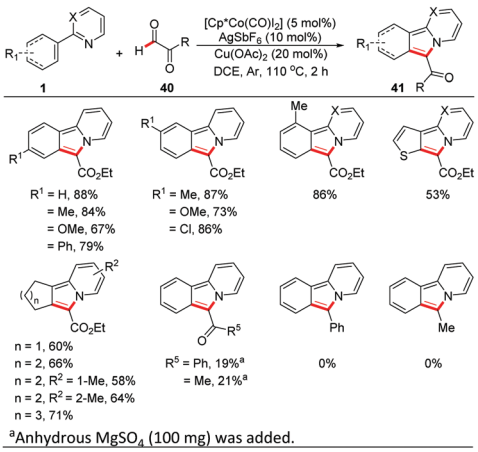


Scheme 9 A possible catalytic cycle of the cobalt-catalyzed synthesis of indazoles.

coordination and C–H metalation. The seven-membered metallacycle **37** was formed by reversible coordination with aldehyde **31** and migratory insertion, followed by the protonation of this metallacycle **37** to give the alcohol intermediate **38** and regenerate the active catalyst. Then, indazole **32** was obtained *via* intramolecular nucleophilic substitution and deprotonation of the alcohol intermediate **38**.

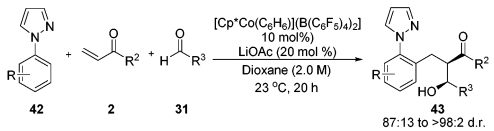
Moreover, the Zeng group disclosed a cobalt-catalyzed synthesis of indolizines **41** including benzoindolizines by C–H bond addition to aldehydes followed by *in situ* cyclization and aromatization, when 20 mol% of $Cu(OAc)_2$ was used (Scheme 10).[20] Unfortunately, aldehydes were limited to *ortho*-dicarbonyl substrates **40**, such as ethyl oxoacetate, oxo-arylacetaldehyde and oxo-alkyl-acetaldehyde. Unactivated aldehydes like benzaldehyde and acetaldehyde were not compatible in this transformation.

Significantly, a three-component $C(sp^2)H$ bond addition between alkene and polarized π-bonds with high stereoselectivity was reported by the Ellman group (Scheme 11a).[21] The reaction demonstrated excellent group tolerance to afford products **43** in good yields and high diastereoselectivity. However, the similar $[Cp^*RhCl_2]_2$ catalyst was only efficient with ethyl glyoxylate in poor diastereoselectivity.[22] Moreover, when other non-activated aldehydes **31** were employed, the three-component addition products **43** were obtained in only trace amounts, while the

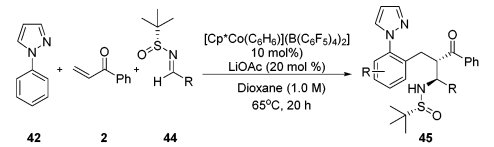


Scheme 10 Cobalt-catalyzed sythesis of indolizines.

a) Cobalt-catalyzed three-component C-H bond addition



b) Asymmetric three-component coupling with N-*tert*-butanesulfinyl imines.

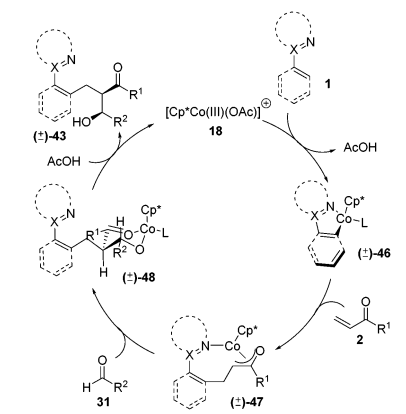


Scheme 11 Cobalt-catalyzed three-component C–H bond addition.

addition products of the $C(sp^2)$–H bond with enones **2** were achieved instead in high yields, presenting great difference between Cp*Rh(III) and Cp*Co(III) catalysis in both reactivity and stereoselectivity. Delightfully, the first cobalt-catalyzed asymmetric reaction also worked very well in this reaction system. The asymmetric three-component addition to chiral *N-tert*-butanesulfinyl imines **44** afforded the corresponding product **45** with good yield and high diastereoselectivity.

A plausible mechanism was proposed in Scheme 12. After the coordination of the directing group to the cationic Co(III) catalyst **18**, directed C–H bond metalation occurred and gave the active cobaltacycle **46**. The conjugate addition of **46** to enone **2** provided the racemic cobalt enolate **47**.[22] The diastereoselective addition of aldehyde **31** *via* a chair transition state generated cobalt alkoxide **48**. The desired alcohol **43** was generated by proto-demetalation while the cationic Co(III) catalyst **18** was regenerated. The high diastereoselectivity might be due to the generation of *Z*-Co(III) enolate **47** that was added to the aldehyde *via* a boat transition state, with expected coordination with the nitrogen in the directing group.

2.1.2 Addition to triple bonds. Matsunaga, Kanai and co-workers also established an exceptional reactivity of the Cp*Co(III) catalyst in the addition to alkyne **50** (Scheme 13a).[23] A C2-selective indole alkenylation and annulation progressed smoothly with a



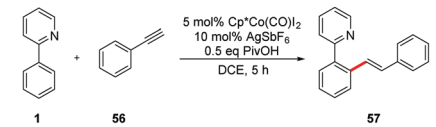
Scheme 12 The mechanism of cobalt-catalyzed three-component C–H bond addition.

catalytic amount of the $[Cp^*Co(III)(C_6H_6)](PF_6)_2$ complex and KOAc. The product selectivity could be controlled by using different directing groups and reaction conditions. However, similar Cp*Rh(III) catalysis only produced C2-alkenylated indole, indicating a clear difference between the catalytic activities of the Cp*Co(III) complex and the Cp*Rh(III) complexes.[24] The distinctive nucleophilic activity of the organocobalt species could be attributed to the more polarized properties of a Co(III)–C bond compared with that of a Rh(III)–C bond, allowing an intramolecular nucleophilic attack of the alkenyl Co(III) intermediate to the carbamoyl group. A cobalt-catalyzed site-, regio- and mono-selective alkenylation of dimethylcarbamoyl-protected pyrroles with alkynes was reported by Matsunaga and co-workers (Scheme 13b).[25] Low C5/C2 selectivity and moderate yields were found by using Cp*Rh as the catalyst.[24] The higher site-selectivity was attributed to the smaller ionic radius of Co, which would enhance the steric repulsion between the substituent (X) and the Cp* ligand.[26] The alkenylcobalt intermediate might exhibit less stability and faster proto-demetalation than the alkenylrhodium intermediate because of much less consumption of PivOH under Cp*Co(III) catalysis.

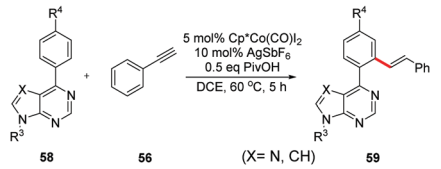
Using $Cp^*Co(CO)I_2$ as the catalyst under mild conditions, the Yu group extended the scope of the addition to 2-phenylpyridines **1** and 6-arylpurines **58** with terminal alkynes **56** in high yields (Scheme 14).[27] An outstanding functional group compatibility was observed in this strategy. Furthermore, 6-arylpurines **58** were also suitable for this alkenylation with terminal alkynes **56** under the same conditions to afford the relevant product **59** in high yields. Remarkably, the styrylation of 1-(pyrimidin-2-yl)-1*H*-indole **11** was readily established under these conditions, and this strategy was practical to design a novel mitochondria-staining dye based on an indole backbone.

N-Heterocyclic quaternary ammonium salts such as pyridoisoquinolinium, cinnolinium, isoquinolinium, and quinolizinium salts were obtained by four Cp*Co(III)-catalyzed oxidative annulation reactions (Scheme 15).[28] The silver salts AgOAc and $AgBF_4$ were necessary, which served to remove I^-, acting as oxidants to regenerate the cobalt(III) active species and acting as an anion source (BF_4^-) for the final products **60** and **61**.

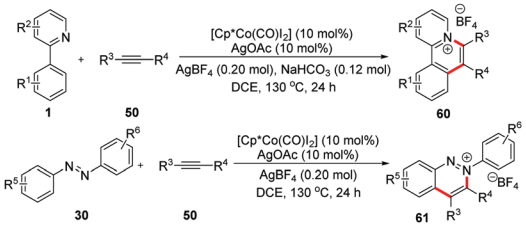
a) Alkenylation of 2-phenylpridines with terminal alkynes



b) Alkenylation of 6-arylpurines with terminal alkynes



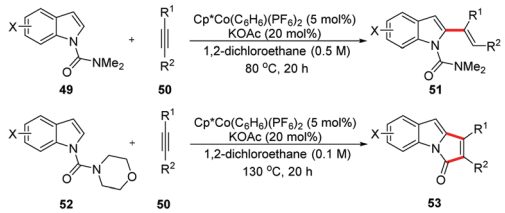
Scheme 14 Alkenylation of 2-phenylpridines and 6-arylpurines.



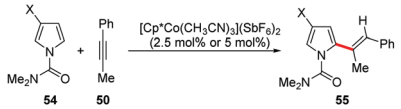
Scheme 15 Cp*Co(III)-catalyzed oxidative annulation reactions.

In 2015, the Matsunaga and Kanai, Ackermann, and Sundararaju groups reported the synthesis of isoquinolines **63** by cyclization reactions of *O*-acyl oxime derivatives **62** and alkynes **50** with a Cp*Co(III) catalyst (Scheme 16a).[26a,29] A directing group bearing an N–O bond served as an internal oxidant. In this case, the Cp*Co(III) catalyst displayed a much higher site selectivity (15 : 1 to 20 : 1) than a Cp*Rh(III) catalyst when unsymmetrical *O*-acyl oximes and terminal alkynes were adopted. Using $[Cp^*Co(CO)I_2]$, the Co(III)-catalyzed annulation of oxime **64** with different alkynes was also reported to offer multi-substituted isoquinoline derivatives **63** *via* C–H and N–OH activation without the need for ionization (Scheme 16b). No external oxidant was required in this reaction and water was the only by-product.

a) Alkenylation and annulation of indoles with alkynes.

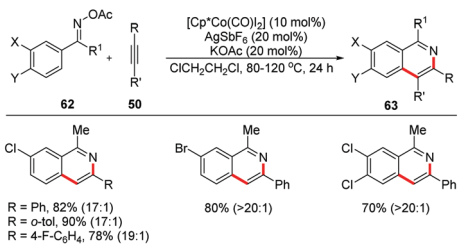


b) Alkenylation of pyrroles with alkynes.

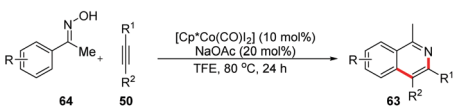


Scheme 13 Alkenylation and annulation of indoles with alkynes.

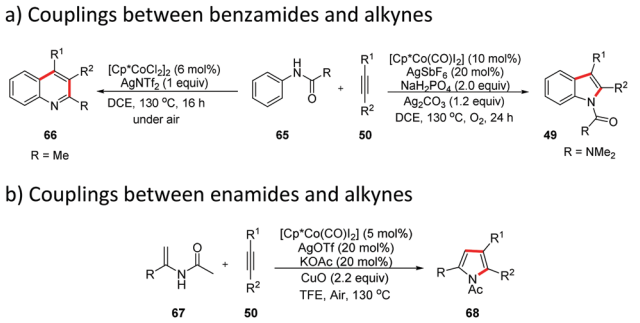
a) Synthesis of multisubstituted isoquinolines with *O*-acyl oxime



b) Synthesis of multisubstituted isoquinolines with oxime



Scheme 16 Synthesis of multisubstituted isoquinolines from alkynes.

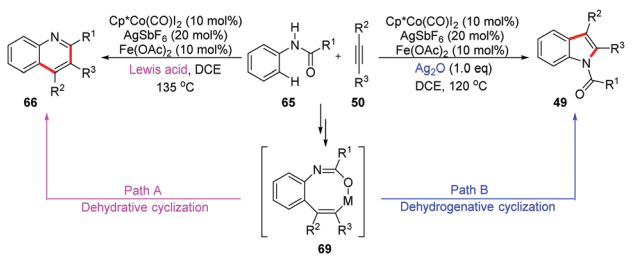


Scheme 17 Co(III)-catalyzed couplings of amides with alkynes.

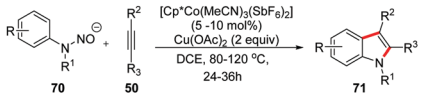
Moreover, Li and co-workers used amide NH as an electrophilic directing group to accomplish $[Cp^*CoCl_2]_2$-catalyzed redox-neutral coupling between arenes and alkynes (Scheme 17a).[30] The protocol was conducted in DCE using $[Cp^*CoCl_2]_2/AgSbF_6$ as the catalyst at 130 °C to afford quinolines **66** with water as the sole by-product. Furthermore, switching acetanilide to a less electrophilic *N*-phenylurea in the presence of $[Cp^*Co(CO)I_2]$ as the catalyst and Ag_2CO_3 as the oxidant resulted in the formation of *N*-substituted indoles **49** rather than quinolones **66** (Scheme 17a).[31] The synthesis of multi-substituted pyrroles **68** also relied on amide NH as an electrophilic directing group.[32] *N*-(1-Phenylvinyl)acetamide **67** could be transformed to the corresponding products **68** using a catalytic amount of $Cp^*Co(CO)I_2$ and CuO as the oxidant (Scheme 17b).

Similar work was reported independently by the Glorius goup (Scheme 18).[33] The cooperation of Cp*Co(III) and Lewis acid encouraged dehydrative cyclization reaction to afford quinolones **66**. $[(p\text{-Cymene})RuCl_2]_2$, $[Cp^*RhCl_2]_2$, $Pd(OAc)_2$ and $[Cp^*IrCl_2]_2$ were all inactive for this transformation to give the corresponding products quinolones **66**, demonstrating the irreplaceable catalytic efficacy of Cp*Co(III). While the Lewis acid was replaced by 1 equiv. of Ag_2O, *N*-substituted indole **49** was achieved through dehydrogenative cyclization. And the ratio of quinolones **66** and *N*-substituted indole **49** depended on the R^1 group. The results indicated that the larger R^1 group in the cobaltacycle intermediate **69** might obstruct dehydrative cyclization by suppression of the nucleophilic addition process. In addition, dehydrative cyclization could be inhibited completely by tuning the directing group thus producing *N*-substituted indole **49** only.

The Jiao group disclosed an excellent pathway to prepare *N*-substituted indoles **71** through cobalt-catalyzed cyclization of *N*-nitrosoanilines **70** with alkynes **50** (Scheme 19).[34] Importantly,



Scheme 18 Cp*Co(III)-catalyzed switchable cyclization to quinolines and indoles.



Scheme 19 The synthesis of *N*-substituted indoles with *N*-nitrosoanilines.

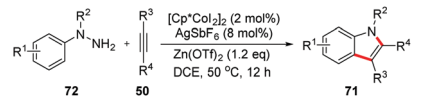
internal alkynes **50** containing an electron-deficient group, which are usually less reactive in Cp*Rh catalysis, exhibited good reactivity in this transformation.

The Zhu group developed an alternative approach to prepare *N*-substituted indoles by the cyclization of phenylhydrazines **72** with alkynes **50** by the utilization of 2 mol% of $[Cp^*CoI_2]_2$ as the catalyst, 8 mol% of $AgSbF_6$ as well as 1.2 equiv. of $Zn(OTf)_2$ as additives (Scheme 20).[35] Notably, this procedure established regioselectivity for a *meta*-substituted arylhydrazine and regioselectivity for a chain-branched terminal alkyne.

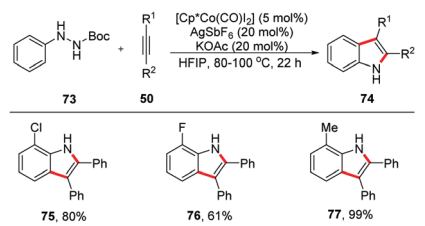
To extend the application of Cp*Co(III) catalysis, a strategy for the synthesis of unprotected indoles **74** showing a cleavage of the N–N bond was developed by the Glorius group (Scheme 21).[36] In this reaction, **75–77** could be attained with good yields under Cp*Co(III) catalysis, which had rarely been achieved in rhodium(III) catalysis.[37] Moreover, competition cross-over and decomposition studies indicated the inherent electronic properties and substitution patterns of the directing group, which prompted reactions in the related Co(III) and Rh(III) systems.

The competition experiment showed that the reactivity of *p*-chloro-Boc-phenylhydrazine is higher than that of *p*-methyl-Boc-phenylhydrazine, thus a CMD-type mechanism was suggested for the reaction displayed therein.[24,38] Furthermore, the ^{15}N isotope-labelled Boc-phenyl-hydrazine **78** gave the pure isotope-labelled indole product **79** in 77% yield (Scheme 22a). A k_H/k_D value of 2.2 for the parallel experiment and a KIE of 2.8 for the competition experiment suggested that the C–H bond activation probably determined the reaction rate (Scheme 22b).

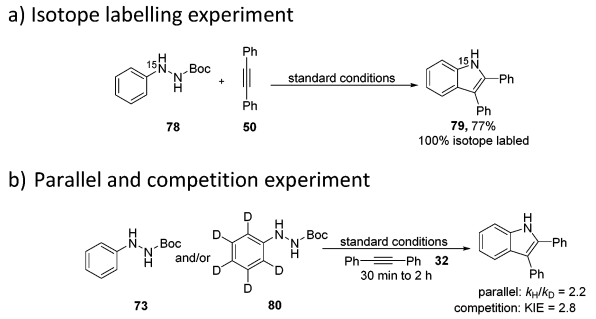
Based on previous work and preliminary mechanistic experiments, a catalytic cycle has been proposed (Scheme 23).[32] Initially, treatment of the $CoCp^*(CO)I_2$ precursor with $AgSbF_6$ and KOAc will generate a cationic Co(III) species **18**, followed by C–H metalation to afford cobaltacycle **81** *via* a CMD mechanism. A stabilization of



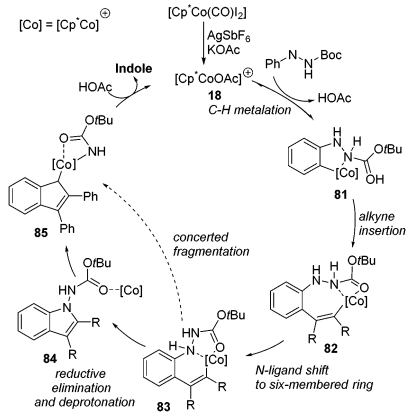
Scheme 20 The synthesis of *N*-substituted indoles with arylhydrazine.



Scheme 21 Cobalt(III)-catalyzed redox-neutral synthesis of unprotected indoles *via* N–N bond cleavage.



Scheme 22 Mechanism studies *via* N–N bond cleavage.



Scheme 23 The proposed mechanism *via* N–N bond cleavage.

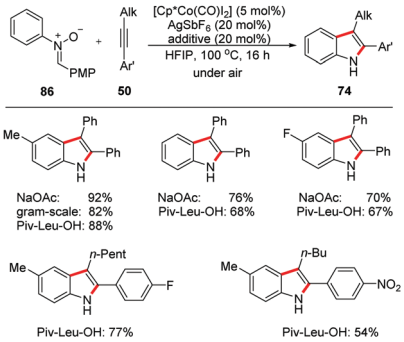
cobaltacycle **81** was probably assisted by the Boc group.[39] Then, the insertion of alkyne will occur to afford **83**, probably *via* the 7-membered intermediate **82** with the N-ligand shifted to the 6-membered ring.[26a,29] The desired product could be obtained from **83** *via* two different routes. Intermediate **84** was produced through reductive elimination, and then an oxidative addition of the N–N bond to cobalt occurred to give the species **85**. Alternatively, a concerted fragmentation of **83** could produce intermediate **85**. The targeted indole product was obtained *via* the protonation of intermediate **85**, and the active catalyst **18** was concurrently regenerated.

Another strategy to synthesize unprotected indole **74** with easily accessible nitrones **86** by cobalt-catalyzed C–H/N–O functionalization was reported by the Ackermann group (Scheme 24).[40] The robust procedure showed an excellent functional group tolerance with either NaOAc or Piv-Leu-OH as the additive. Notably, a unique regioselectivity in the annulation of unsymmetrical alkynes was realized when Piv-Leu-OH was used as the additive.

An efficient Cp*Co(III)-catalyzed protocol for the synthesis of indenones **88** has been developed by the Zhang group using benzoic esters **87** as the substrate (Scheme 25),[41] which showed good functional group tolerance. However, high temperature was necessary for this process.

2.2 Alkynylation

Alkynylindoles **90** are privileged structural motifs widely found in organic synthesis, pharmaceuticals, biochemistry, and functional

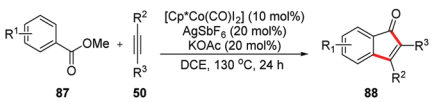


Scheme 24 The synthesis of indoles with nitrones.

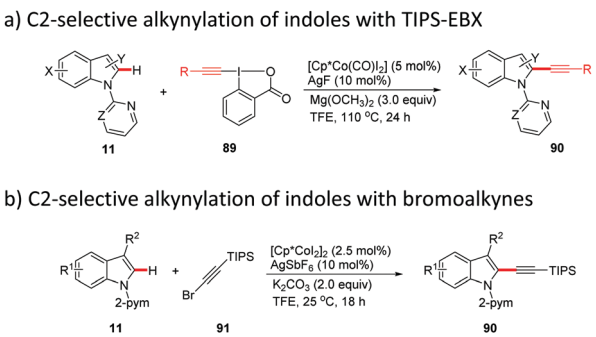
materials. However, compared with arylation, alkylation, and vinylation, the direct alkynylation of the indole nucleus continues to be scarce, especially for C2-selective alkynylation of indoles.[42] However, the Shi group reported a cobalt(III)-catalyzed C2-selective C–H alkynylation of *N*-pyrimidyl-indoles **11** with hypervalent iodine-alkyne reagents 1-[(triisopropylsilyl)-ethynyl]-1,2-benziodoxol-3(1*H*)-one (TIPS-EBX) **89** (Scheme 26a).[43] The reaction demonstrated good functional group tolerance using $Mg(OCH_3)_2$ as the additive. At the same time, the Ackermann group also reported a cobalt(III)-catalyzed C–H alkynylation of *N*-pyrimidyl-indole **11** with bromoalkynes **91** (Scheme 26b).[44] This reaction was conducted under exceedingly mild reaction conditions with $[Cp^*CoI_2]_2$ and $AgSbF_6$ as the catalysts and K_2CO_3 as the additive at room temperature. Moreover, the pyrimidyl directing group and the triisopropylsilyl group could be easily removed.

2.3 Alkenylation

Fluoroalkenes play a significant role among olefins due to their individual biological properties and application in organic chemistry.[45] Very recently, the Li group settled a cobalt-catalyzed fluoroalkenylation through C–H activation and C–F bond cleavage. And diverse (hetero)arenes **1** or **11** with gem-difluorostyrenes **92**



Scheme 25 The synthesis of indenones *via* tandem addition/annulation.

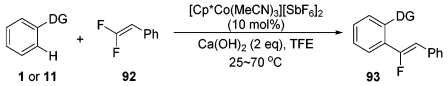


Scheme 26 Cp*Co(III)-catalyzed C2-selective alkynylation of indoles.

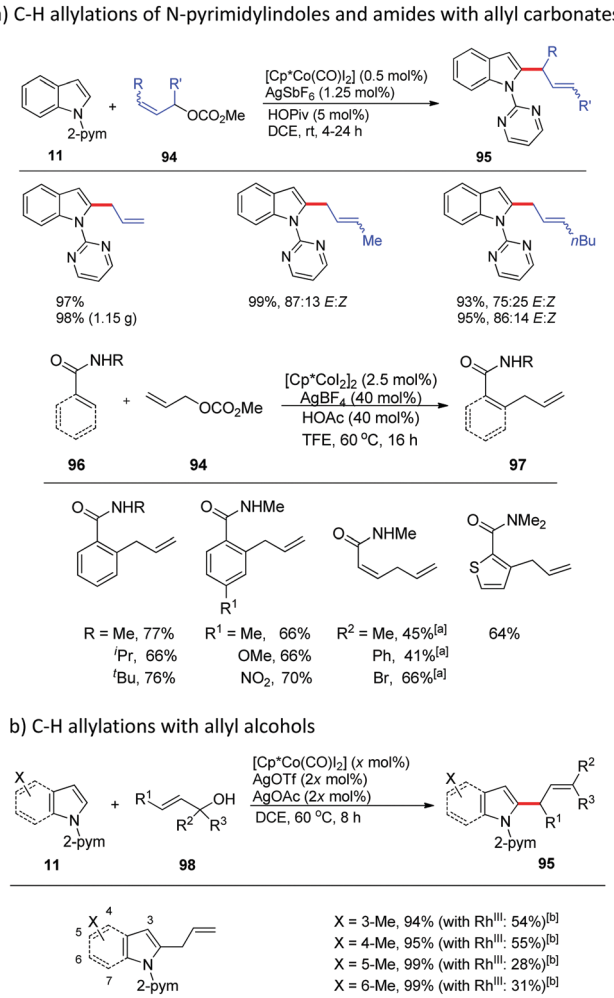
were applicable to form 1,2-diaryl-substituted monofluoroalkenes **93** in excellent *Z* selectivity (Scheme 27).[46]

2.4 Allylation

The allyl moiety is an exceptionally versatile functional group, offering a wealth of opportunities for further functionalizations. Recently, the Glorius, Ackermann, Matsunaga and Kanai and Li groups have contributed to this area.[26b,47–51] The Glorius group reported Cp*Co(III)-catalyzed direct allylations of *N*-pyrimidylindoles **11** and amides **96** with allyl carbonates **94** under mild conditions (Scheme 28a).[47] Remarkably, only 0.5 mol% of [Cp*Co(CO)I_2] and 1.25 mol% of the silver(I) salt were needed to give C-2-selective allylated indoles **95** with good (*Z*)/(*E*) selectivity, suggesting that the turnover number (TON) was as high as 2200. Furthermore,

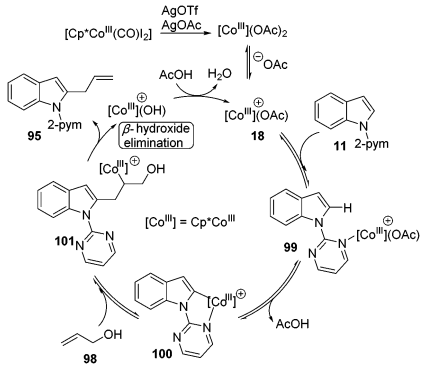


Scheme 27 Cobalt-catalyzed α-fluoroalkenylation.



[a] 110 °C. [b] Number within parentheses was obtained using [{Cp*$RhCl_2$}$_2$] (2.5 mol%) instead of [Cp*Co(CO)I_2].

Scheme 28 Cp*Co(III)-catalyzed C–H allylations.



Scheme 29 The mechanism of C–H allylations with allyl alcohols.

when aryl- and alkenylamides were used, only (*E*)-allylated products **97** were obtained.

Using allylic alcohols **98**, Matsunaga, Kanai and co-workers reported a directed C–H allylation *via* Cp*Co(III) catalysis (Scheme 28b).[48] The allylated products **95** were achieved more efficiently under Cp*Co(III) catalysis than under analogous Cp*Rh(III) catalysis, indicating the direct dehydrative C–H allylation facilitated by Cp*Co(III) with allyl alcohols **98** through a β-hydroxide elimination pathway rather than a conventional β-hydride elimination pathway. This might be due to the higher oxophilicity of cationic high-valent Cp*Co(III) complexes than that of Cp*Rh(III). This allylation was extended to 6-arylpurines **58**, benzamides **96**, and an aromatic Weinreb amide with fluorinated alcohol as the solvent.[49]

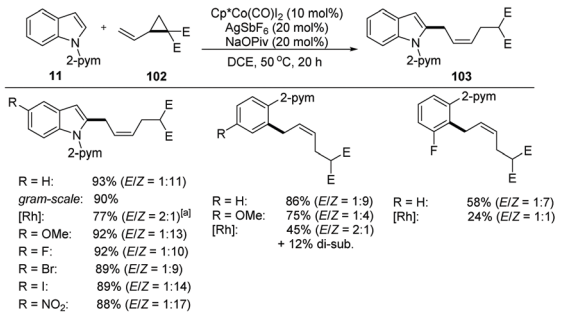
A possible mechanism was proposed (Scheme 29). The initial halide abstraction of [Cp*Co(CO)I_2] produced the active catalyst **18**. The following C–H cobaltation of this cationic cobalt species **18** resulted in the formation of intermediate **100**. A key β-hydroxide elimination followed the insertion of allyl alcohol **98**, to afford the desired product **95**. Additionally, according to density functional theory (DFT) calculations, the β-hydroxide elimination pathway was estimated to be 2.4 kcal mol^{-1}, which is more favourable than the β-hydride elimination pathway.[48]

Catalyzed C–H activations combined with the challenging C–C cleavage have been rarely reported, and always using Rh catalysis.[50] Very recently, the Ackermann group reported allylations *via* C–H/C–C activation by *Z*-selective cobalt catalysis (Scheme 30a).[26b] The allylated products **103** were formed efficiently with vinylcyclopropanes **102** at room temperature, showing unique levels of chemo- and diastereoselectivity and excellent group tolerance. Notably, this C–H/C–C functionalization demonstrated unprecedented diastereoselectivity towards thermodynamically less stable *Z* alkenes. Except for C–H/C–C activation, allylations with 2-vinyloxirane **104** *via* C–H/C–O activation under Cp*Co(III) catalysis were also reported by the Li group (Scheme 30b).[51] Allylic alcohol products **105** were obtained from these transformations. It appeared that Co-catalyzed *ortho* C–H activation, olefin insertion, and subsequent β-oxygen elimination were involved in this reaction.

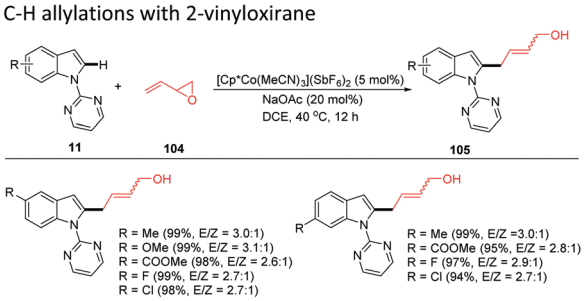
2.5 Arylation

When 7-oxabenzonorbornadienes **106** were used to replace 2-vinyloxirane **104**, the arylations could be realized *via* the same

a) C-H allylations with vinylcyclopropane

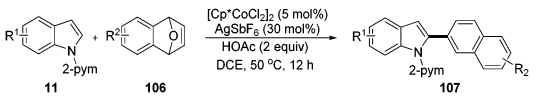


b) C-H allylations with 2-vinyloxirane



[a] $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ was used as the catalyst.

Scheme 30 C–H allylations *via* C–H/C–X activations.



Scheme 31 Dehydrative coupling with 7-oxabenzonorbornadienes.

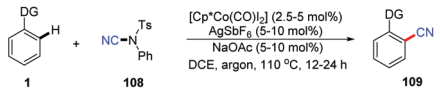
C–H/C–O activation (Scheme 31).[51] Compared with the required temperature of 130 °C for an analogous Rh(III)-catalyzed system,[52] the Cp*Co(III) system only required 50 °C, indicating the higher efficiency of the Co(III) catalyst. A dehydration step was considered after the Co-catalyzed *ortho* C–H activation, olefin insertion, and β–oxygen elimination to yield the corresponding 2-naphthylated indoles **107**.

2.6 Cyanation

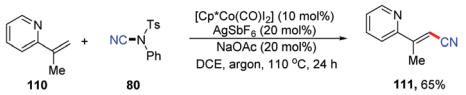
Cyano groups are important structural motifs[53] and are easily derivatized.[54] C–H cyanations had previously only been achieved with 4d transition-metal complexes of ruthenium[55] or rhodium.[56] Recently, Cp*Co(III)-catalyzed cyanations were concurrently reported by the Glorius group and the Ackermann group (Scheme 32a).[57] The readily available *N*-cyano-*N*-phenyl-*p*-toluenesulfonamides (NCTS) **108** were used as the cyanating reagents, showing an excellent functional group tolerance and remarkable site-selectivity under the optimized conditions with $Cp^*Co(CO)I_2$ as the precatalyst, along with $AgSbF_6$ and NaOAc as the additives. Additionally, 2-pyridylpropene **110** was also capable of cyanation under the same conditions, and the corresponding product **111** was gained in moderate yield (Scheme 32b).[47a]

A possible catalytic cycle was pointed out (Scheme 33).[57] The cyclometalated intermediate **112** was attained *via* a reversible

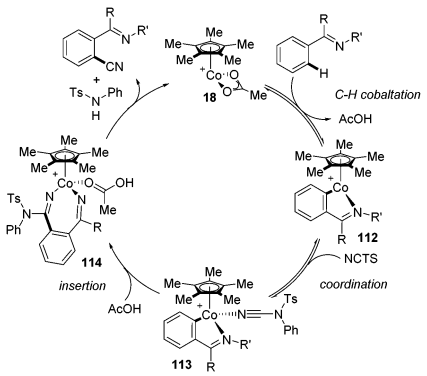
a) Cyanations of arenes



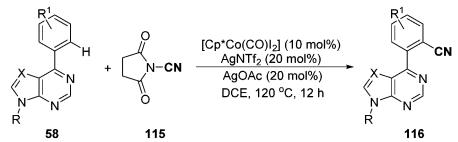
b) Cyanations of 2-pyridylpropene



Scheme 32 Cp*Co(III)-catalyzed cyanations with *N*-cyano-*N*-phenyl-*p*-toluenesulfonamides.



Scheme 33 The mechanism of cyanation with *N*-cyano-*N*-phenyl-*p*-toluenesulfonamides.



Scheme 34 Cyanations with *N*-cyanosuccinimides.

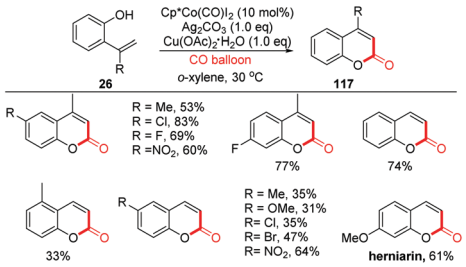
C–H cobaltation. The key intermediates **113** and **114** were produced subsequently *via* coordination and insertion of NCTS **108**. The desired product **109** was achieved from β-elimination of intermediate **114**, and the catalytically active cobalt(III) catalyst **18** was meanwhile regenerated by proto-demetalation.

N-Cyanosuccinimide **115** can also be used as an electrophilic cyanating agent (Scheme 34), which was reported by the Chang group.[58] *N*-Cyanosuccinimide **115** is easy to prepare, bench stable, and gives succinimide as a readily removable by-product. Notably, this protocol is applicable to the cyanation of 6-arylpurines **58**.

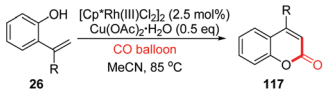
2.7 Carbonylation

Cp*Co(III)-catalyzed cyclocarbonylations of 2-alkenylphenols **26** with CO to attain coumarin derivatives **117** have been developed by the Wang group (Scheme 35a).[59] Coumarin derivatives **117** have been identified with a variety of biological and pharmacological activities, Cp*Co(III)-catalyzed cyclocarbonylations provided an atom- and step-economic approach for the preparation of coumarin derivatives **117**, and this process worked under mild conditions

a) Cp*Co(III)-catalyzed cyclocarbonylations of 2-alkenylphenols



b) Cp*Rh(III)-catalyzed cyclocarbonylations of 2-alkenylphenols



Scheme 35 Cyclocarbonylations of 2-alkenylphenols for the synthesis of coumarin derivatives.

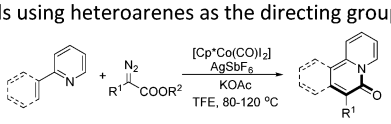
with a good functional group tolerance. Similarly, the Cp*Rh(III) salt can also be consumed in this reaction (Scheme 35b).[60] A relatively higher temperature was required in Cp*Rh (III) catalysis; however, a larger amount of catalyst loading and oxidants were needed in Cp*Co(III) catalysis.

2.8 Carbenoid insertion

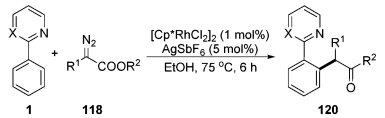
The Glorius group described the first cobalt-catalyzed C–H functionalization with diazo compounds **118** through the carbenoid insertion pathway (Scheme 36a).[61] 2-Phenylpyridine **1** stirred with $Cp^*Co(CO)I_2$, $AgSbF_6$, KOAc and diazo ester **118** in TFE would offer structurally diverse conjugated polycyclic hydrocarbons **119**. And catalyst loading could be as low as 1 mol%. Conversely, the similar Cp*Rh(III)-catalyzed system furnished distinctive product **120** (Scheme 36b).[62]

According to the distinction in reactivity between the Cp*Co(III) and Cp*Rh(III) complexes, it was believed that the Co species worked not only as a transition metal but also as a Lewis acid catalyst.[61] And a probable catalytic cycle was suggested (Scheme 37). The metal–carbene intermediate **121** might be formed by dediazonization after cobaltacycle **112** reacted with the diazo compound **118**. The cobaltacyclic intermediate **122** was obtained through migratory insertion followed by proton-demetalation. Subsequently, Co(III)

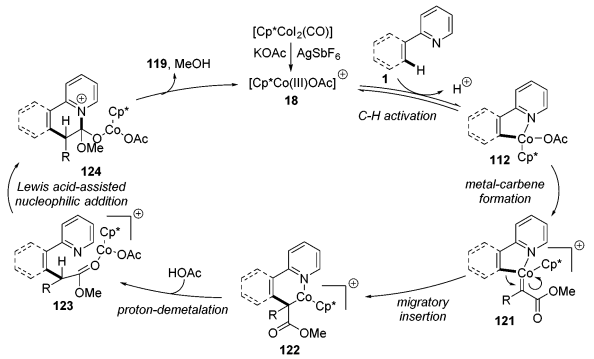
a) Cp*Co(III)-catalyzed C-H functionalizations with diazo compounds using heteroarenes as the directing group.



b) Cp*Rh(III)-catalyzed C-H functionalizations with diazo compounds using heteroarenes as the directing group

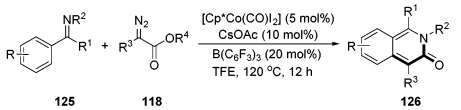


Scheme 36 C–H functionalizations with diazo compounds using heteroarenes as the directing group.

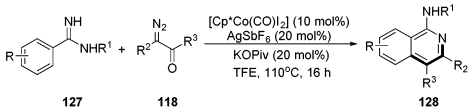


Scheme 37 The proposed pathway of Cp*Co(III)-catalyzed C–H functionalizations with diazo compounds using heteroarenes as the directing group.

a) C-H activations of imines with diazo compounds



b) C-H activations of amidines with diazo compounds



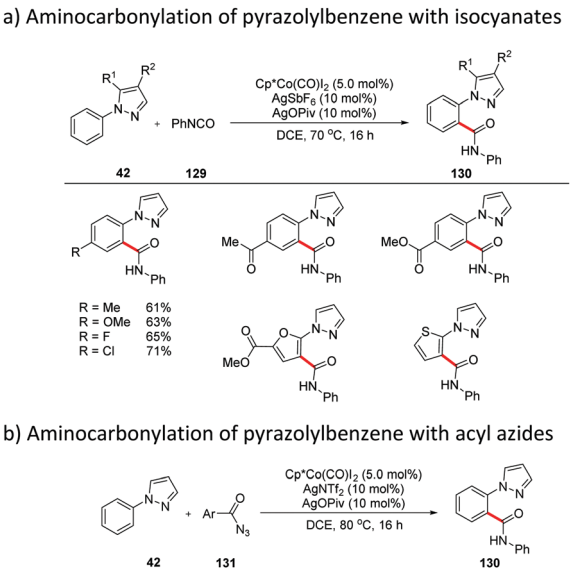
Scheme 38 The synthesis of isoquinoline derivatives through carbenoid insertion mechanism.

species functioned as a Lewis acid and assisted subsequently nucleophilic addition. The desired product **119** was attained by aromatization of the corresponding intermediate **124** and the active species **18** was regenerated.

Afterwards, the Glorius group developed a new Cp*Co(III)/$B(C_6F_5)_3$ cooperative catalytic system for C–H activation with diazo compounds **118**. Hereinto, an unusual imine performed as the auxiliary to prepare highly substituted isoquinolin-3-ones **126** (Scheme 38a).[63] The addition of catalytic amounts of $B(C_6F_5)_3$ was considered to act as follows: (1) assisting the generation of active cationic Cp*Co(III) **18** and stabilizing this Co(III) species **18**;[64] (2) accelerating the C–H activation and carbene insertion steps. Then 1-aminoisoquinolines **128** were also gained by employing amidines **127** as the substrate (Scheme 38b).[65]

2.9 Aminocarbonylation

The scope of substrates was further extended to isocyanates **129**, which worked as the electrophiles that provided expedient access to the aminocarbonylation of pyrazolylbenzene **42** under mild reaction conditions (Scheme 39a).[66] The reaction showed an excellent functional group tolerance and remarkable site-selectivity under the optimized conditions with $Cp^*Co(CO)I_2$ as the precatalyst and $AgSbF_6$ and AgOPiv as the additives. Meanwhile, a similar work with $[Cp^*Co(C_6H_6)][PF_6]_2$ as the catalyst in the absence of silver salts was reported independently by the Ellman group.[67] Additionally, acyl azides **131** were found to be capable of aminocarbonylation under cobalt catalysis (Scheme 39b)[66] because



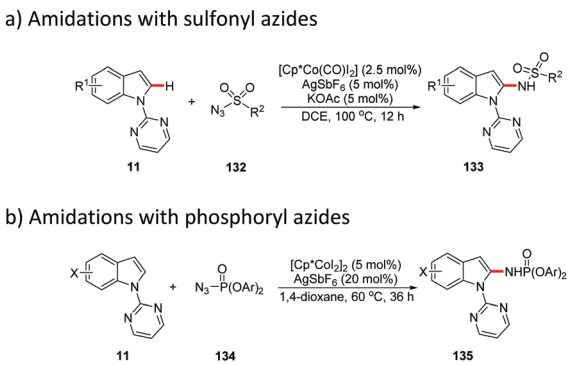
Scheme 39 Aminocarbonylation of pyrazolylbenzene.

isocyanates **129** could be generated *in situ* from the corresponding acyl azides **121**[68,69] through a Curtius[70] rearrangement.

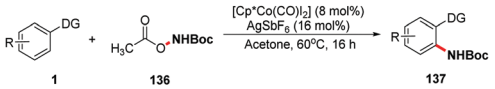
2.10 C–N cross-couplings

C–H amination/amidation reactions with azides catalyzed by Rh, Ru, and Ir have been previously reported.[71,72] However, Matsunaga, Kanai and co-workers demonstrated the Cp*Co(CO)I_2-catalyzed C-2 selective C–H amidation of *N*-pyrimidylindole **11** with sulfonyl azides **132** (Scheme 40a).[73] Additionally, Matsunaga and Kanai extended this protocol to phosphoryl azides **134** to afford phosporamidated indoles **135** (Scheme 40b).[74] Cp*Co(CO)I_2 was found to be unreactive for this reaction, but the dimeric $[Cp^*CoI_2]_2$ adapted with $AgSbF_6$ was shown to be ideal. The Cp*Co(III) catalysis was not only suitable for azides but also applicable to carbamates.

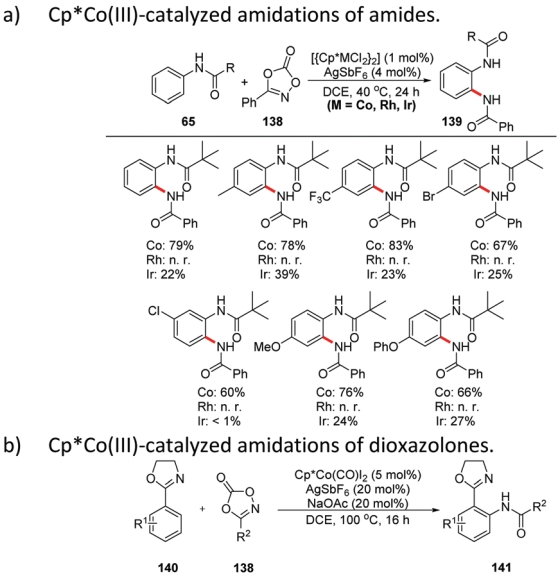
Chang and co-workers demonstrated the Co(III)-catalyzed C–H amidation of arenes **1** using acetoxycarbamates **136** as nitrogen sources (Scheme 41).[75] This transformation proceeded without external oxidants or bases and showed excellent functional group compatibility. Remarkably, 6-arylpurines **58** bearing sensitive functional groups also transformed very well.



Scheme 40 Cp*Co(III)-catalyzed C–H amidations.



Scheme 41 Co(III)-catalyzed amidations with acetoxycarbamates.

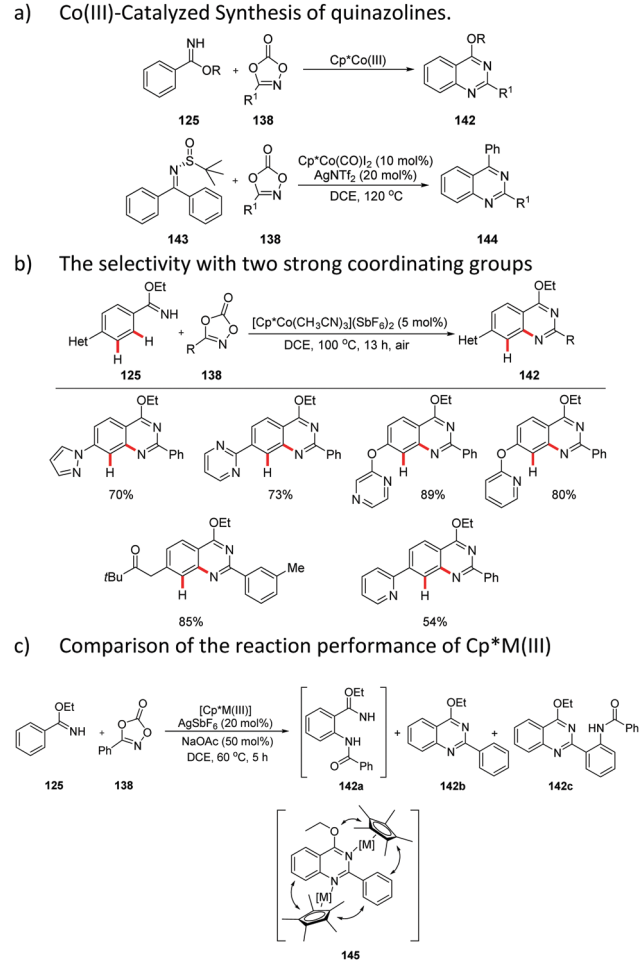


Scheme 42 Cp*Co(III)-catalyzed amidations with dioxazolones.

In 2015, the Chang group described a cobalt-catalyzed amidation with dioxazolones **138** as the amidating reagents (Scheme 42a).[76] The catalytic activity of Group 9 [Cp*M(III)] complexes for this amidation was carefully compared. Either $[\{Cp^*RhCl_2\}_2]$ or $[\{Cp^*IrCl_2\}_2]$ was examined as the catalyst, and the results showed that these catalysts displayed much less reactivity than that of $[\{Cp^*CoCl_2\}_2]$ under otherwise identical conditions. This result suggested that Cp*Co(III) catalysis not only emulates the similar Group 9 transition-metals, but also exhibited their unique reactivity, which could be advantageous over rhodium or iridium salt in certain C–H functionalizations.

Oxazolines **140** widely exist in useful compounds[77] and are easily transformed into a variety of valuable structures.[78] Thus, the Ackermann group reported an oxazolinyl-assisted C–H amidation by cobalt(III) catalysis (Scheme 42b).[79] This amidation of oxazolines **140** with dioxazolones **138** showed good group tolerance and can be extended to synthesize amidated indoles and pyrroles.

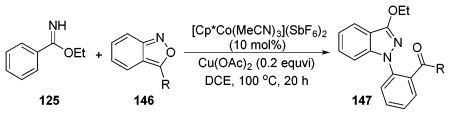
When readily cleavable benzimidates **125** or *N*-sulfinylimines **143** were employed as the directing groups, the amidated product underwent further intramolecular cyclization to give quinzolines (Scheme 43a).[80] In Ackermann's system, 5 mol% of $[Cp^*Co(CH_3CN)_3](SbF_6)_2$ was optimized as the catalyst, and any other additives were not required.[80a] Expressively, the transformation exposed extremely excellent regioselectivity even with another strong coordinating N-heterocyclic group in the same molecule (Scheme 43b). The competition experiments revealed the potencies of different auxiliaries in cobalt(III)-catalyzed C–H functionalization: imidate ≥ pyridine ≈ pyrazole > oxazoline > pyrimidine.



Scheme 43 Cp*Co(III)-catalyzed tandem C–H amidation and cyclization.

In Glorius' report, the performance of different Group 9 triads [Cp*M(III)] for producing quinazoline **142** was examined (Scheme 43c).[80c] Cp*Co(III) demonstrated the highest yield (98%) and formation rate of **142b**, while Cp*Rh(III) and Cp*Ir(III) only led to 55% and 39% yields of **142b**. By adding an extra Lewis acid $Sc(OTf)_3$ (20 mol%)], the yield of the amidation/cyclization product **142b** would be increased to 78% in Cp*Ir(III) catalysis, suggesting the highest reactivity of Cp*Co(III) due to the most Lewis acidic properties in this case. Furthermore, Cp*Rh(III) and Cp*Ir(III) would cause further amidation of **142b** to afford by-product **142c**, but this process was not available to Cp*Co(III). These results implied that Cp*Co(III) is more sensitive to steric hindrance than Cp*Rh(III) and Cp*Ir(III),[26a] as cobalt has the smallest ionic radius of among the Group 9 metals. Therefore, Cp*Co(III) exhibits higher steric repulsion between the Cp*–ligand and the substituent groups in the pyrimidine-core of **145**.

A Cp*Co(III)/Cu(II) cooperative system was developed for the coupling of imidates **125** with anthranils **146** to form 1*H*-indazoles **147** while anthranils **146** also worked as an organic oxidant (Scheme 44).[81] It suggested that the amination of imidates **125** was induced firstly by Co(III), followed by Cu-induced N–N coupling.



Scheme 44 Cp*Co(III)/Cu(II)-catalyzed C–N/N–N coupling.

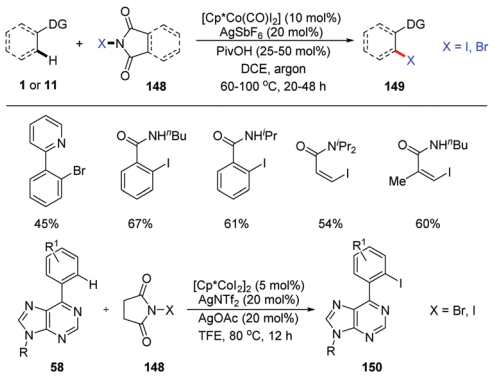
2.11 Halogenation

N-Iodosuccinimide (NIS), *N*-bromosuccinimide (NBS) and *N*-bromophthalimide (NBP) **102** containing N-based leaving groups are regarded as electrophiles to replace NCTS **80** and *N*-cyanosuccinimide **87** (Scheme 45).[47a,82] The Glorius group[36] discovered that **6** or **45** underwent selective mono-iodination with NIS or NBP to give **102** in good yield under reaction conditions similar to those of the cyanation with NCTS **80**. Pivalic acid was found to be a more efficient additive for iodination than sodium acetate. The acid might activate NIS through protonation, increasing its electrophilicity, or generate a highly reactive Co catalyst with a vacant site for coordination.[83] More recently, the Pawar group found that 6-arylpurines **38** could be halogenated by NIS and NBS with $[Cp^*CoI_2]_2$ as the catalyst and $AgNTf_2$/AgOAc as the additives.[82] Iodinated 6-arylpurines can also be facilely transformed into arylated, sulfenylated and alkoxylated 6-arylpurines.[84]

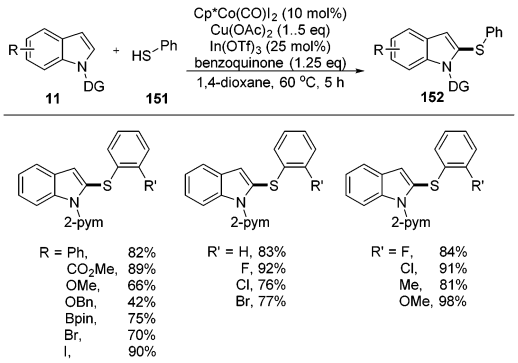
2.12 Sulphuration

Thioether is a significant motif in both bioactive compounds and organic materials.[85] Therefore, an important cobalt-catalyzed C–H thiolation was forwarded by Glorius and co-workers through dehydrogenative cross-coupling (Scheme 46).[86] The reaction was conducted with $Cp^*Co(CO)I_2$ as the catalyst, $Cu(OAc)_2$ and benzoquinone as a co-oxidant system,[87] and $In(OTf)_3$ as an additive in 1,4-dioxane at 60 °C. $In(OTf)_3$ was not only considered to be a halide abstractor but also was thought to aid the coordination chemistry of thiolates by the formation of polynuclear complexes with copper. In the absence of $Cp^*Co(CO)I_2$, thiolation would occur at both the C2- and C3-positions of indole **11**,[88] suggesting a significant function of $Cp^*Co(CO)I_2$.

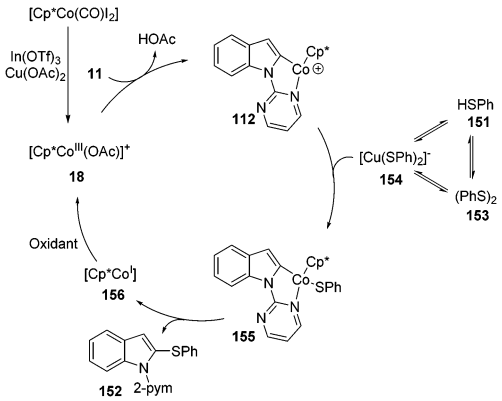
The general Cp*Co(III)-catalysis has proceeded through the addition/insertion mechanism with unsaturated reaction partners. However, a new pattern of cobalt catalysis for the formation of C–heteroatom bonds was pointed out. One plausible mechanism



Scheme 45 C–H halogenation.



Scheme 46 C–H sulphuration.

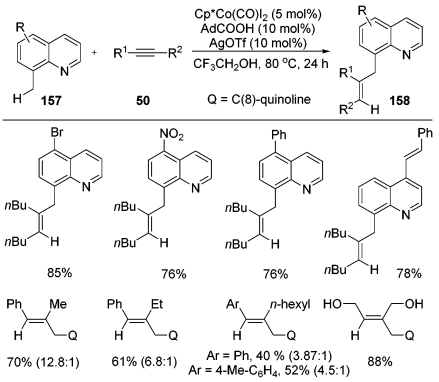


Scheme 47 The proposed mechanism of C–H sulphuration.

was that the initial halide abstraction of $[Cp^*Co(CO)I_2]$ and acetate exchange produced the active catalyst **18** with the aid of $In(OTf)_3$ and $Cu(OAc)_2$ (Scheme 47). The cyclometalated intermediate **112** was attained *via* a C–H cobaltation. PhSH **151** was shown to be converted into an active thiolating agent, which was much more reactive than disulphide **153** and PhSCu. The cobalt thiolate **155** was afforded with anionic Cu(I) complexes such as $[Cu(SPh)_2]^-$ **154**.[89] The corresponding product **152** and a cobalt(I) species **156** were obtained by reductive elimination. In addition, the active catalyst **18** would be regenerated by the oxidation of $Cu(OAc)_2$ or benzoquinone. Alternate mechanisms include nucleophilic attack of **112** to an electrophilic Cu(II) or Cu(III) thiol species or transmetalation of the indole from **112** onto a copper species. The product was achieved with subsequent reductive elimination at the copper centre. Additionally, species **18**, **112**, and **155** were all detected in ESI MS.

3. C(sp^3)–H functionalizations

Compared to Cp*Co(III)-catalyzed C(sp^2)–H functionalizations, the functionalization of C(sp^3)–H bonds catalyzed by cobalt is in its infancy. Theoretically, the challenging functionalization of C(sp^3)–H bonds is possible if the poor reactivity of C(sp^3)–H can be overcome.[90] Very recently, the Sundararaju group reported a Cp*Co(III)-catalyzed alkenylation of 8-methylquinoline **157** with

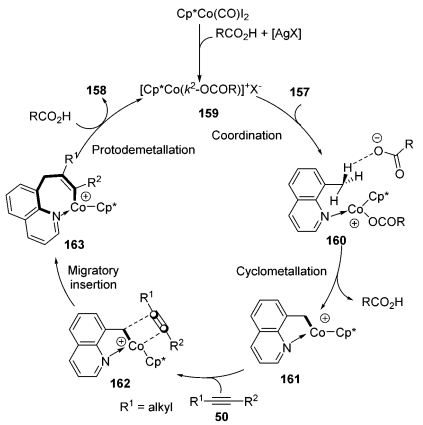


Scheme 48 The alkenylations of 8-methylquinolines.

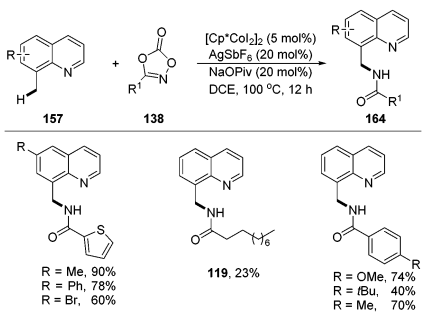
alkynes **50** (Scheme 48).[91] In contrast to Rh(III) catalysis,[92] a substoichiometric amount of copper(II) acetate was unnecessary, but the presence of carboxylate acid was imperative. The *cis*-addition products were afforded in high regioselectivity and stereoselectivity, and a variety of sensitive functional groups were retained. The results also showed that the reactivity of aryl alkynes was much lower than that of alkyl alkynes.

Based on the above reports on Cp*Co(III)-catalyzed C(sp^2)–H bond activation, a possible pathway of alkenylation of 8-methylquinoline was described (Scheme 49). The active catalyst Co(III) complex **159** was produced by halide abstraction with Ag salt and ligand exchange with carboxylate acid. The cationic Co(III) species coordinated to the N-atom in 8-methylquinoline to afford intermediate **160**, followed by external-carboxylate-assisted cyclometalation.[93] This hypothesis was supported by DFT calculations. The cationic intermediate **161** underwent coordination with alkyne **50** in a preorganized orientation, which led to a 7-membered cobalto-alkenyl intermediate **163** after migratory insertion. The desired product **158** was acquired *via* subsequent protodemetalation.

Encouraged by the success of the alkenylation of 8-methylquinoline **157**, the Sundararaju group reported a Cp*Co(III)-catalyzed C(sp^3)–H bond amidation of 8-methylquinoline **157**



Scheme 49 The proposed catalytic cycle of the alkenylation of 8-methylquinoline.



Scheme 50 C(sp^3)–H bond amidation of 8-methylquinoline.

with various oxazolones **138** (Scheme 50).[94] Unlike alkenylation, sodium carboxylate was used herein. The reaction showed good selectivity and group tolerance; especially the alkyl amidated product **164** was also achieved with a lower yield.

4. Conclusion and outlook

During the past few years, the development of cobalt-catalyzed, environmentally friendly and step-economical functionalizations has been thriving. In contrast to low-valent Co catalysis, the use of a Grignard reagent can be avoided in high-valent Co catalysis. In this period, Cp*Co(III) catalysts have exposed their remarkable capability for directed C–H functionalizations. Cp*Co(III) catalysis not only emulates the similar but more expensive Cp*Rh(III) catalysis but also exhibits unique reactivities because of the higher nucleophilicity of organometallic cobalt(III) species, as well as their Lewis-acidic properties. Although a large quantity of Cp*Co(III)-catalyzed functionalizations have been established, new challenges and opportunities have emerged along with these studies. First, enantioselective C–H functionalization is a significant challenge for further developments. Learning from other transition-metal-catalyzed asymmetric reactions,[95] three fundamental strategies are suggested in this case: (1) the use of suitable enabling chiral cyclopentadienyl (Cp^x) ligands;[95b] (2) the introduction of an appropriate chiral ligand;[95a] and (3) the utilization of a chiral cross-coupling partner.[21] Second, even though there are several examples of C(sp^3)–H functionalization of activated (benzylic) systems, the challenge remains to discover suitable conditions for the activation of unreactive C(sp^3)–H bonds. At this point, an efficient directing group is one of the key factors. Finally, while general Cp*Co(III)-catalysis proceeds through an addition/insertion mechanism with unsaturated reaction partners, new reaction modes and mechanisms should be further elucidated. Considering the maintainable nature of C–H functionalizations, inexpensive and nontoxic Cp*Co(III) catalysis is expected to achieve further exciting breakthroughs.

Acknowledgements

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